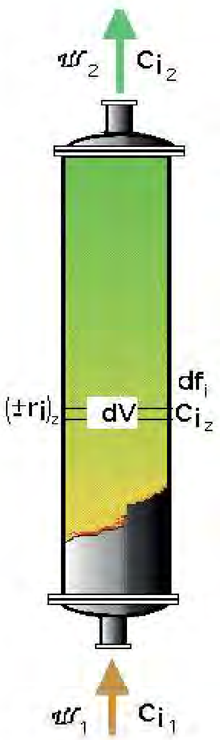
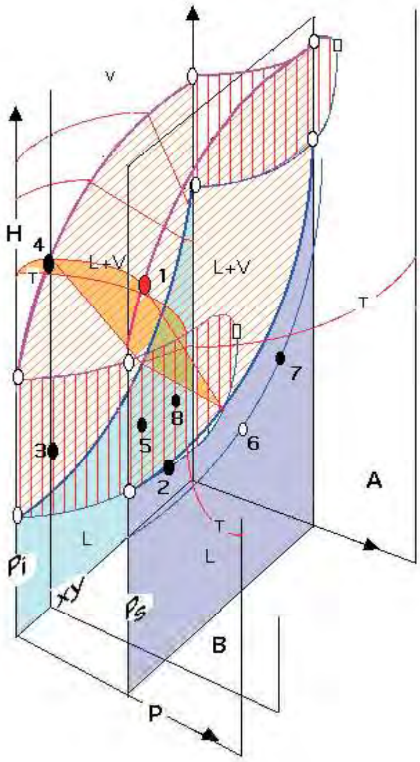
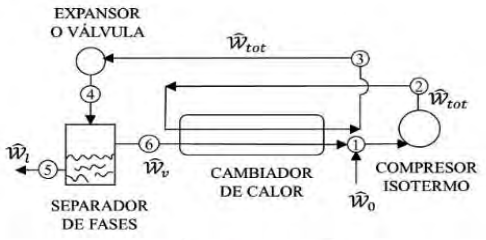
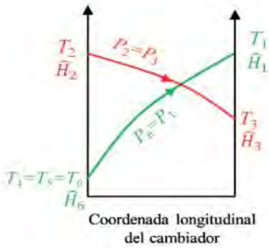
PROBLEMS OF THERMODYNAMICS APPLIED TO CHEMICAL ENGINEERING

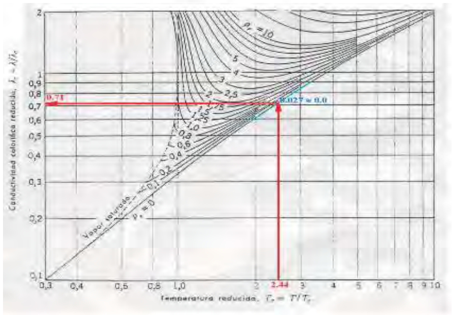
Julio L. Bueno de las Heras - Octavio Suárez Iglesias
María Matos González - Consuelo Pizarro García











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INTRODUCTION

JUSTIFICATION, STRUCTURE AND FORMAL ASPECTS

OBJECTIVES

The first edition of the book "**Termodinámica para Ingeniería Química"** (Thermodynamics for Chemical Engineering) was written in Spanish by Julio L. Bueno de las Heras and published in 2016. It was later revised and expanded (2018).

This theoretical text was then completed with another book of problems, entitled "**Problemas de Termodinámica para Ingeniería Química**" (Thermodynamic Problems for Chemical Engineering) published in 2021, co-authored with Octavio Suárez Iglesias, María Matos and Consuelo Pizarro, actually researchers and teachers. It compiled more than a hundred of original problems from among those taught over the years in Thermodynamic practical classes (Chemical Engineering Degree, IChemE accredited,University of Oviedo).

The purpose of this English version is to reach those who, beyond Asturias and Spain, are interested in this fundamental subject in a world in which English has replaced Latin as universal language.

STRUCTURE

SERIES 0: REFERENCE PROBLEMS (THEORY). 21 problems

SERIES 1: UNITS, QUANTITIES, MEASURES. 11 problems.

SERIES 2: STATE AND EQUILIBRIUM: EXPERIMENTS AND MODELS. 24 problems.

SERIES 3: TRANSPORT PROPERTIES. 2 problems.

SERIES 4: FLOW AND STORAGE OPERATIONS. 26 problems.

SERIES 5: HEAT TRANSFER OPERATIONS. 8 problems

SERIES 6: THERMOMECHANICAL OPERATIONS. 26 problems.

SERIES 7: MIXING AND SEPARATION OPERATIONS. 18 problems.

Series 0 is a summary of the 2016-2018 book, where the theoretical elements, necessary to solve all of the following series, are very briefly introduced as reference problems.

The purpose of **Series 1, 2 and 3** is the presentation of the criteria for definition, use, measurement, estimation, correlation, representation and integration of kinetic and equilibrium properties in scenarios where performing the analysis and preliminary calculations of any chemical engineering process.

The objective of **Series 4, 5 and 6** is the handling of thermodynamic diagrams by means of processes and operations in monocomponent systems (or stable mixtures assimilable to them). Particular interest is devoted to storage of liquids, vapors and gases since it illustrates multiple state variations. Heat exchangers allow the extension of the study to systems that interact without mass exchange. Finally, thermal engines connect operations and processes by introducing concepts related to coordination between stages, optimization of conditions and interpretation of efficiency and performance.

Similarly, the purpose of **Series 7** is the handling of elementary processes and operations with multicomponent systems: absorption, extraction, distillation, humidification and evaporation. This last one is frequently classified as heat transfer but, being limited to diluted regions, it can be only linked to the evaporation of the solvent, without thermal and energetic distortions.

FORMAL ASPECTS

With a couple of exceptions, each problem in **Series 1 to 7** is autonomous so it can be studied without considering the other problems of these series. This criterion implies that, seen as a whole, reiterations or common places can be perceived in statements, expressions, formulations or figures.

Except for the data of other authors duly referenced, all the content of this monograph is original and totally or partially contrasted in exams, practical classes and group tutorials. However, the authors thank in advance any suggestion or criticism, as well as the detection of any error.

We use two graphic resources: qualitative figures (illustrative, simple and informal), and thermodynamic diagrams (where calculations related to lines of operation are carried out). These diagrams, in their original format, are compiled and referenced in the corresponding appendices, with the authorization of the concerned publishers. In some cases, the original publishers have disappeared and the copyright owners are not known, so we submit to the academic practice of expressly citing the original work whose data has been taken by us. To these creators of science our memory and our sincere thanks.

SERIES 0

REFERENCE PROBLEMS

Although the theoretical knowledge necessary to solve these problems can be acquired or activated through any of the most reliable thermodynamic texts, some of which are summarized in the concise bibliography of the present book, the authors are allowed to forward the kind interested readers to the theoretical text of Julio L. Bueno (currently only in the Spanish language version), most appropriate to the purpose of the work as a whole.

0.1. Units of measurement and physical quantities:
a) Dimensional analysis.
b) Unit conversion.

Section a. A thermodynamic magnitude is a measurable property of a thermodynamic system, and it is represented by a numerical value or *quantity* ($\mathbb{x}$) followed by the verbal descriptor of a given *unit* ($\mathbb{u}$).

In the field of thermodynamics there are *basic units* (of mass, length, temperature and time) and *derived units* (from the basic ones: velocity, force, energy…). Dimensions of the derived units can be expressed from the dimensions of the basic units as a potential monomial term

$$(M)^{\omega_M}(L)^{\omega_L}(T)^{\omega_T}(t)^{\omega_t}$$

called *dimension analysis* or *equation of dimensions*, where M is the mass, L the length, T the temperature, t the time and ω_M, ω_L, ω_T and ω_t real numbers.

Section b. Magnitudes depend on the *system of units* chosen (for example, in the *International System* the length is expressed in meters, while in the *English System* in feet). The change of units between a system 1 and another system 2 will be given by

$$\mathbb{u}_1 = \left(\frac{\mathbb{x}_2}{\mathbb{x}_1}\right) \cdot \mathbb{u}_2 = \mathbb{ky}_{21} \cdot \mathbb{u}_2$$

($\mathbb{ky}_{21}$, *dimensionless conversion factor* of the quantity when changed from units $\mathbb{u}_1$ to units $\mathbb{u}_2$)

$$\mathbb{u}_2 = \left(\frac{\mathbb{x}_1}{\mathbb{x}_2}\right) \cdot \mathbb{u}_1 = \mathbb{ky}_{12} \cdot \mathbb{u}_1$$

($\mathbb{ky}_{12}$, *dimensionless conversion factor* of the quantity when changed from units $\mathbb{u}_2$ to units $\mathbb{u}_1$)

and textbooks usually contain conversion tables of the type

		$\mathbb{u}_2$		$\mathbb{u}_4$		
	1					
$\mathbb{u}_2$		1		$\mathbb{ky}_{42}$		
			1			
$\mathbb{u}_4$		$\mathbb{ky}_{24}$		1		
					1	
						1

When dealing with numerical coefficients of formulas or equations, it can be interesting the conversion of them to employ quantities in other units. Then

$$\mathbb{x}_1 = \left(\frac{\mathbb{u}_2}{\mathbb{u}_1}\right) \cdot \mathbb{x}_2 = \mathbb{K}\mathbb{y}_{21} \cdot \mathbb{x}_2$$

($\mathbb{K}\mathbb{y}_{21}$, *dimensionless conversion factor* from the quantity $\mathbb{x}_1$ in units $\mathbb{u}_1$ to the quantity $\mathbb{x}_2$ in units $\mathbb{u}_2$)

$$\mathbb{x}_2 = \left(\frac{\mathbb{u}_1}{\mathbb{u}_2}\right) \cdot \mathbb{x}_1 = \mathbb{K}\mathbb{y}_{12} \cdot \mathbb{x}_1$$

($\mathbb{K}\mathbb{y}_{12}$, *dimensionless conversion factor* from the quantity $\mathbb{x}_2$ in units $\mathbb{u}_2$ to the quantity $\mathbb{x}_1$ in units $\mathbb{u}_1$)

Obviously

$$\mathbb{K}\mathbb{y}_{21} = \frac{1}{\mathbb{k}\mathbb{y}_{21}} = \mathbb{k}\mathbb{y}_{12}$$

0.2. Thermodynamic systems:

a) Definition.
b) State of a system. Equilibrium.
c) Types of systems.
d) Thermodynamic variables.
e) State change. Process.
f) Types of processes.

Section a. A *system* is a limited and well defined region of the space which is object of the study. The *surroundings* are the matter not included in the system. According to the requirements of the level of description appropriate to each analysis, the thermodynamic system consist of -or can be considered integrated by- several systems, called *subsystems.*

Section b. A system is defined by *thermodynamic magnitudes*. The instantaneous state of a system is defined by the values of a finite number of thermodynamic magnitudes (*properties*) which characterize it. As it can be seen below (reference problem 0.5, section a.) once any property of interest is well defined, nature establishes the number of independent properties required to determine the state of a system based on its characteristics (number of components and phases).

Equilibrium occurs when the values of all the thermodynamic magnitudes of the system remain unchanged in time.

Section c. A system can be defined as *isolated* (it does not exchange matter or energy with the surroundings), *closed* (it only exchanges energy) or *open* (it exchanges both matter and energy).

A system can be defined as *monocomponent* (only one pure substance) or *multicomponent* (two, three, four… mixed substances). It can be *monophasic* (consit of a single phase: liquid, solid or vapor) or *multiphasic* (consist of several phases).

Section d. *State thermodynamic* properties (or variables) are those magnitudes describing a system in a given moment or in equilibrium: *pressure* (P), *temperature* (T), *volume* (V), *internal energy* (U), *enthalpy* (H), *Helmholtz free energy* (F), *Gibbs free energy* (G) and *entropy* (S). They are defined or related by the following equations

$$H = U + PV$$

$$F = U - TS$$

$$G = H - TS$$

Extensive variables are those that depend on the amount of substance present in the system (U, H, F, G, V…). *Intensive* ones are of two types:

- *field* properties: those that do not depend on the amount of substance (e.g. temperature and pressure).
- *specific* variables: extensive variables referred to the unit of mass (divided by the mass of the system $\widehat{U}, \widehat{H}, \hat{F}, \hat{G}, \hat{V}$ … or by the number of moles of the sytem $\widetilde{U}, \widetilde{H}, \tilde{F}, \tilde{G}, \tilde{V}$…).

The number of moles is the quotient between the mass (M) and the molecular weight ($\mathfrak{W}$). Mass and molar densities can be employed instead of mass and molar volumes ($\hat{\rho} = 1/\hat{V}$; $\tilde{\rho} = 1/\tilde{V}$).

Section e. A system undergoes a state change when at least one state variable changes. A process is the change (evolution) between two states.

Section f. Several processes are named taking into account the variable that remains constant during them: *isothermal* (no temperature variation), *isobaric* (no pressure variation), *isochoric* (no volumen variation), *isentropic* (no entropy variation), *adiabatic* (no heat exchange with the surroundings), etc.

A *reversible* process is integrated by a continuous sequence of equilibrium states (it is an idealization, since the concept of equilibrium prevents change) and can be experienced by the system in any of its directions. An *irreversible* process is a process that is not reversible, and represents a change with energy degradation.

An *isentropic* process is a particular case of the *adiabatic* process when it is also *reversible.*

Any other kind of process (spontaneous, induced, controlled or intermediate situations between them) can be included in what are known as *polytropic processes.*

.

0.3. Fundamental thermodynamic relations:

a) **Heat and entropy.**
b) **Basic equations.**
c) **Types of work.**
d) **Comments.**

Section a. In a closed system in thermal equilibrium, the amount of heat exchanged by the system in a reversible process is related to the *entropy* by the conventional definition of this property

$$\mathrm{d}Q = T\mathrm{d}S$$

Section b. According to definitions and elementary relations, the variations of the energetical properties introduced in the section d of problem 0.2 may be described by the equations

$$\begin{aligned}
\mathrm{d}U &= \mathrm{d}Q - P\mathrm{d}V = T\mathrm{d}S - P\mathrm{d}V \\
\mathrm{d}H &= \mathrm{d}Q + V\mathrm{d}P = T\mathrm{d}S + V\mathrm{d}P \\
\mathrm{d}F &= -P\mathrm{d}V - S\mathrm{d}T \\
\mathrm{d}G &= V\mathrm{d}P - S\mathrm{d}T
\end{aligned}$$

Section c. The *expansion-compression work* ($W^{\text{e-c}}$) and the *flow work* (W^{fl}) are defined as

$$\mathrm{d}W^{\text{e-c}} = -P\mathrm{d}V$$

$$\mathrm{d}W^{\text{fl}} = V\mathrm{d}P$$

Section d. Notice that, unlike temperature and pressure, U, H, F, G and W cannot be absolutely determined but only their changes (ΔU, ΔH, ΔF, ΔG, ΔW) unless a reference state is conventionally selected for them.

0.4. State variables and process variables:

a) Definition.
b) Maxwell relations.
c) Other relations.
d) Specific heat capacities.

Section a. By definition, a *state variable* depends only on the state of the system, and not on the way whereby the system reached that state ($T, P, U, H, G, F\ldots$). *Process variables* are those which depend on the type of transformation that a system undergoes from its initial state to the final one (Q, W...).

If the mathematical function Z(X, Y) represents a state variable, it will satisfy the following four conditions:

$$\mathrm{dZ} = \left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}} \mathrm{dX} + \left(\frac{\partial \mathrm{Z}}{\partial \mathrm{Y}}\right)_{\mathrm{X}} \mathrm{dY}$$

$$\frac{\partial}{\partial \mathrm{Y}}\left[\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}}\right]_{\mathrm{X}} = \frac{\partial}{\partial \mathrm{X}}\left[\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{Y}}\right)_{\mathrm{X}}\right]_{\mathrm{Y}}$$

$$\left(\frac{\partial \mathrm{X}}{\partial \mathrm{Y}}\right)_{\mathrm{Z}} \left(\frac{\partial \mathrm{Y}}{\partial \mathrm{Z}}\right)_{\mathrm{X}} \left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}} = -1$$

$$\left(\frac{\partial \mathrm{X}}{\partial \mathrm{Y}}\right)_{\mathrm{Z}} = \frac{1}{\left(\frac{\partial \mathrm{Y}}{\partial \mathrm{X}}\right)_{\mathrm{Z}}}$$

Section b. From the second condition and the fundamental thermodynamic relations it is found that

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

Section c. When the first condition is compared with the fundamental thermodynamic relations of the previous problem, several ratios of practical interest can be obtained, e.g.

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad V = \left(\frac{\partial H}{\partial P}\right)_S$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad T = \left(\frac{\partial H}{\partial S}\right)_P$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_S \qquad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

Section d. If the differential variation of specific enthalpy and specific internal energy are written as

$$\mathrm{d}\widehat{H} = \left(\frac{\partial \widehat{H}}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial \widehat{H}}{\partial P}\right)_T \mathrm{d}P$$

$$\mathrm{d}\widehat{U} = \left(\frac{\partial \widehat{U}}{\partial T}\right)_{\widehat{V}} \mathrm{d}T + \left(\frac{\partial \widehat{U}}{\partial \widehat{V}}\right)_T \mathrm{d}\widehat{V}$$

the *specific heat capacities* at constant pressure and volume will be

$$\hat{C}_P = \left(\frac{\partial \widehat{H}}{\partial T}\right)_P$$

$$\hat{C}_V = \left(\frac{\partial \widehat{U}}{\partial T}\right)_{\widehat{V}}$$

Additionally, they can be defined on a mole basis

$$\tilde{C}_P = \left(\frac{\partial \widetilde{H}}{\partial T}\right)_P$$

$$\tilde{C}_V = \left(\frac{\partial \widetilde{U}}{\partial T}\right)_{\widetilde{V}}$$

0.5. Monocomponent systems (but not necessarily monophasic):

a) Phase rule.
b) Thermodynamic diagrams. Operation line.
c) Interesting data from these diagrams.
d) Property balances in the biphasic zone.

Section a. Not all the variables of a system in thermodynamic equilibrium are independent (i.e. the modification of some of them leads to changes in others). The *Phase Rule* (that, due to its entity and interest, could be considered as a principle, although it does not reach such a rank since it can be derived from predefined thermodynamic laws and relationships, as J.W. Gibbs did) describes the algebraic relations that exist between the number of degrees of freedom (thermodynamic independent variables) in a system in equilibrium, the number of phases in equilibrium, and the number of chemical components in the system as

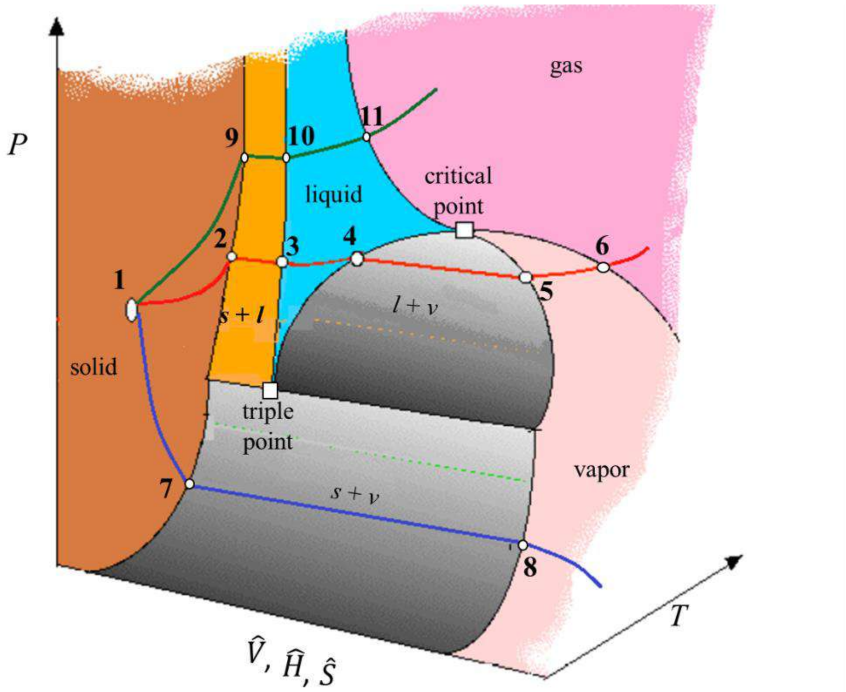
$$\begin{bmatrix}\text{Number of degrees of freedom}\\ \text{or independent variables}\end{bmatrix} = \begin{bmatrix}\text{Number of}\\ \text{components}\end{bmatrix} - \begin{bmatrix}\text{Number}\\ \text{of phases}\end{bmatrix} + 2$$

For example, a pure solid substance requires two independent variables to define its thermodynamic state, such as temperature and pressure. If both variables are increased, a point will be reached when the solid will begin to melt, creating a liquid. At that moment, the number of phases will be two, being temperature and pressure no longer independent: the variation of one will imply the variation of the other. When all the solid has been melted, there will be a single phase again (liquid) and either temperature or pressure could be increased independently again, up to the point of vaporization, where everything will repeat itself.

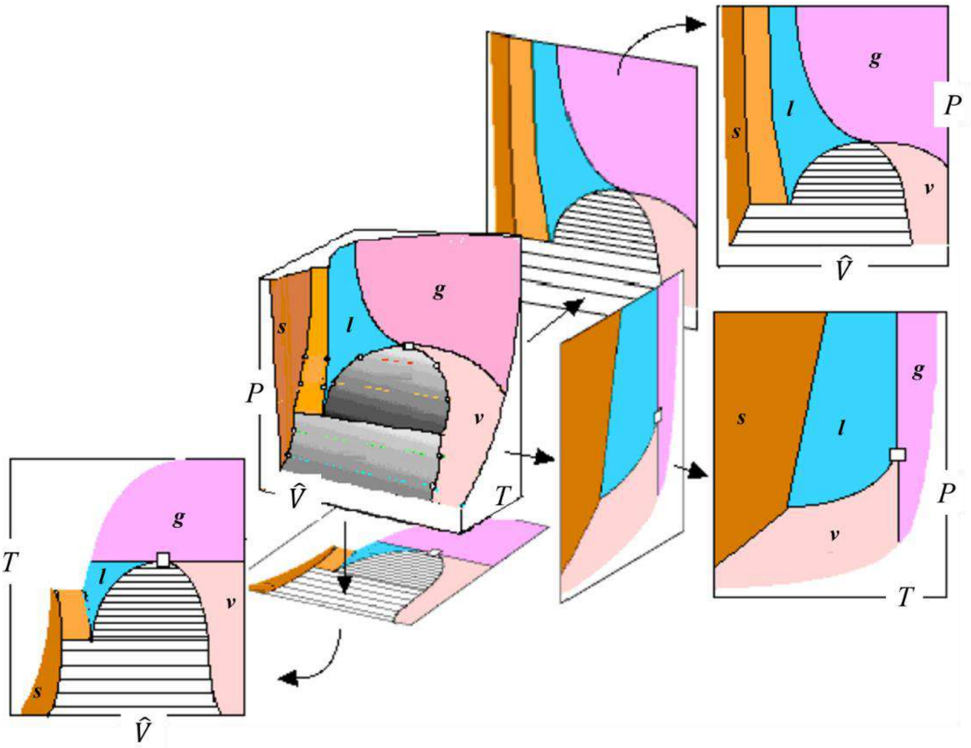
Section b. In principle, the aforesaid process could be represented on a multidimensional surface *PVTHFGU*, but since human beings, by the moment, are only able to see in three dimensions, three-dimensional diagrams *PVT*, *PHT*, *PST*… are chosen as scenarios to represent processes and take the first steps in their analysis, quantitative evaluation and optimal design.

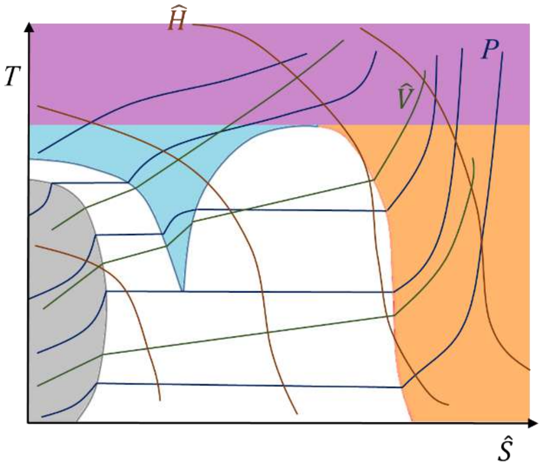
The following figure represents the process described in section a. This representation is called an *operation line.* 1 is the initial solid, 2 is the moment when melting begins, 3 is the moment when all the solid becomes liquid, 4 is the point where vaporization begins, 5 the point in which vaporization ends and 6 the point where the vapor becomes gas. A gas is a vapor that is above its temperature at the *critical point* (T_c), a concept that will be explained in section c.

Temperature and/or pressure could also have been modified to pass solid 1 through 7 and 8, causing sublimation (direct conversion of solid into vapor without melting), or through 9, 10 and 11, where there is no vaporization and the liquid becomes gas without phase change.



However, since three-dimensional diagrams are not easy to handle in chemical engineering, two-dimensional projections are often used (with other properties in isolines).





Section c.

- The *critical point* is the end point of the liquid-vapor coexistence zone. The temperature, pressure and specific volume at this point are called *critical temperature* (T_c), *critical pressure* (P_c) and *critical volume* ($\hat{V}_c$), respectively.

- The *triple point* is the point where liquid, vapor and solid coexist at a temperature (T_t) and a pressure (P_t).

- The liquid in equilibrium with the vapor between the triple point and the critical point is called *"saturated liquid"*. Vapor in equilibrium with this liquid is "*saturated vapor*".

- The *enthalpy of vaporization* ($\Delta\widetilde{H}_{vap}$) is the difference between the enthalpy of the saturated vapor and that of saturated liquid at a given vapor pressure. Far from the critical point, it is approximately constant.

- The *enthalpy of condensation* is the difference between the enthalpy of saturated liquid and the enthalpy of saturated vapor at a given vapor pressure (i.e., -$\Delta\widetilde{H}_{vap}$).

- The *vapor pressure* is the pressure at which equilibrium is reached between the liquid and vapor phases of a substance at each temperature $P(T)$ between the triple point and the critical point, and is usually represented by theoretical equations such as that of Clapeyron

  $$\ln P_v = -\frac{\Delta\widetilde{H}_{vap}}{RT} + cte$$

  where *cte* is a generic empirical constant specific to each substance. This is the basis for other more efficient semi-empirical equations, such as that of Antoine.

- The *normal boiling temperature* T_b is that at which the vapor pressure becomes 1 atm.

Section d. As advance of the mass and energy balances of reference problem 0.13 of this series, if a total mass M_{tot} is located in the liquid-vapor biphasic zone, it will split into a mass of saturated vapor (M_v) and a mass of saturated liquid (M_l) in equilibrium, for which it will be satisfied

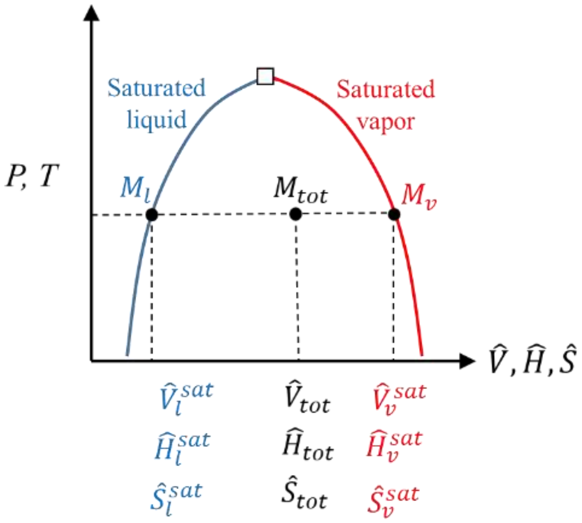
$$M_{tot} = M_l + M_v$$

$$M_{tot}\hat{V}_{tot} = M_l\hat{V}_l^{sat} + M_v\hat{V}_v^{sat}$$

$$M_{tot}\hat{H}_{tot} = M_l\hat{H}_l^{sat} + M_v\hat{H}_v^{sat}$$

$$M_{tot}\hat{S}_{tot} = M_l\hat{S}_l^{sat} + M_v\hat{S}_v^{sat}$$

$$\vdots$$



The same will happen in the solid-liquid and solid-vapor biphasic regions.

0.6. State models:
a) Definition.
b) The Ideal Gas model.
c) The equation of Van der Waals and others.

Section a. *State models* are *PVT* relations that allow the calculation of more complex thermodynamic properties (U, H, S, F) through exact mathematical integrals or derivatives.

Section b. The simplest model is that of the *ideal gas*, which was the result of several investigations over time:

- Law of Robert Boyle and Edme Mariotte (1657): At a constant temperature, the volume of a gaseous mass is inversely proportional to the pressure.
- Law of Jacques Charles (1787) and Louis Gay Lussac (1803): Gases subjected to isobaric heating undergo a volume increase proportional to the initial one.
- Law of Amadeo Avogadro (1811) and Jean Perrin (1909): The volume of a gas is proportional to the number of atoms or molecules but independent of the nature of that gas.
- Law of James Joule and William Thompson (1840): The internal energy of gases is only function of temperature (and the enthalpy as well).
- First Law of Benoit Clapeyron (1843) which establishes the equation

  $$PV = nRT \quad \text{or} \quad P\tilde{V} = RT$$

  being R the so called *universal gas constant*

  $$R = 0.082 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol-g}}$$

The ideal gas model represents a limit behaviour: it does not condense or solidify, so it has no biphasic zones, no critical point or triple point. Its particles are points (no volume) and do not interact with each other at all. Additionally, the ideal gas satitisfies the Mayer's relation

$$\tilde{C}_P - \tilde{C}_V = R$$

which can also be written as

$$\tilde{C}_P \left(\frac{\gamma - 1}{\gamma} \right) = R$$

where $\gamma = \tilde{C}_P / \tilde{C}_V$

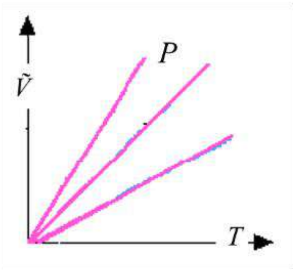
Section c. A better model, closer to experimental reality, is the *van der Waals gas*. Unlike the previous one, it contains two specific parameters for each substance: a and b. They consider the attractive *interactions* and the *volume* of the concerned molecules, respectively.

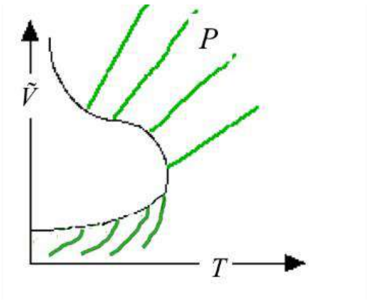
$$\left(P+\frac{a}{\tilde{V}^2}\right)\left(\tilde{V}-b\right)=RT$$

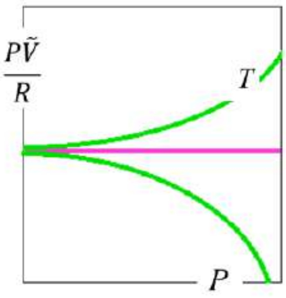
This equation qualitatively reproduces the behaviour of the liquid, vapor and gas, as well as the liquid-vapor biphasic zone up to the critical point, although the quantitative results are not very good.

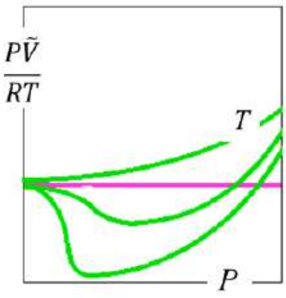
To obtain good results, complex empirical equations P= f(T, V), derived from this one, are usually employed. All of them contain numerous substance-dependent parameters.

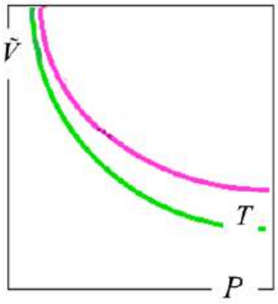
Finally, it has to be said that at low pressures or high molar volumes, both the Van der Waals model and the complex empirical formulas (green lines) tend to the ideal gas behaviour (purple lines).











In any case these equations are not valid for solids.

0.7. Transport phenomena:
a) Laws of Newton, Fourier and Fick (simple version).
b) Boundary layer. Transport coefficient.
c) Estimation of kinetic properties at low density.

Section a. The laws of Newton, Fourier and Fick display the general form

$$\begin{bmatrix}\text{Property}\\ \text{flow}\\ \text{density}\end{bmatrix} = \text{constant}\cdot\begin{bmatrix}\text{Property}\\ \text{concentration}\\ \text{gradient}\end{bmatrix}$$

According to Newton, the *momentum flow density* (or *shear stress*) in the direction of the X coordinate axis perpendicular to the Y axis (τ_{XY}), is proportional to the *velocity gradient* through the *viscosity* η

$$\frac{1}{A}\cdot\frac{\mathrm{d}(M\mathrm{v}_\mathrm{X})}{\mathrm{d}t} = \tau_{\mathrm{XY}} = -\eta\frac{\mathrm{dv}_\mathrm{X}}{\mathrm{dY}}$$

In the case of *heat flow* per unit area, $\mathbb{q}$, Fourier states that

$$\frac{1}{A}\cdot\frac{\mathrm{d}Q}{\mathrm{d}t} = \mathbb{q} = -\lambda\frac{\mathrm{d}T}{\mathrm{dY}}$$

where λ is *thermal conductivity* of the fluid

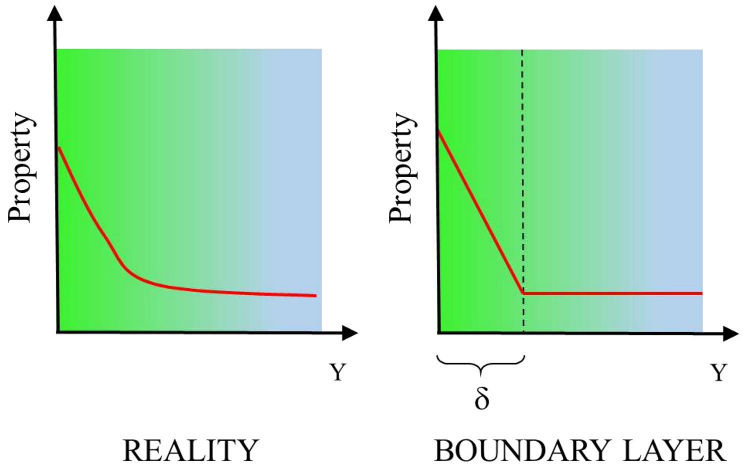
Finally, *Fick's law* is applied to the *mass flow* of a component i through a fluid in which there is a concentration gradient of this component i

$$\frac{1}{A}\cdot\frac{\mathrm{d}M_i}{\mathrm{d}t} = J_i = -D_i\frac{\mathrm{d}c_i}{\mathrm{dY}}$$

and D_i is the *diffusivity* or *diffusion coefficient* of i in the mixture.

Viscosity, thermal conductivity and diffusivity are usually known as *transport kinetic properties*.

Section b. Although the transport of momentum, heat or mass takes place in the whole space, it can be assumed that it only happens significantly and exclusively by molecular mechanism in a narrow layer of thickness δ, the *boundary layer* model.



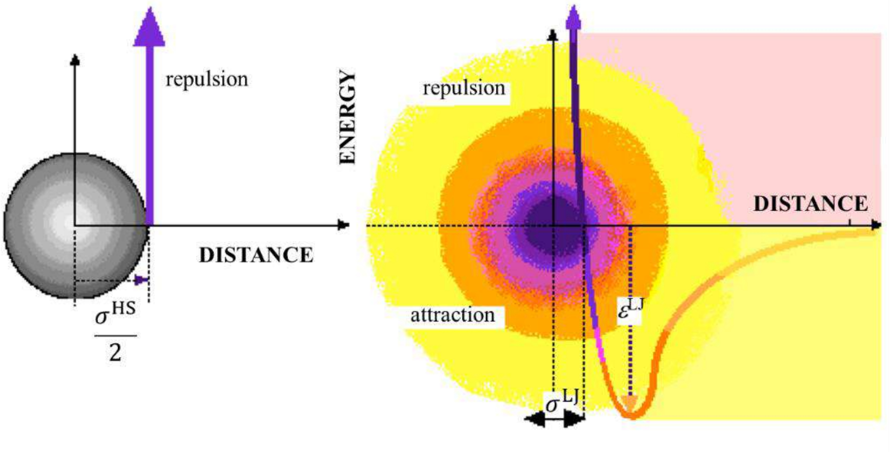
The property gradient can then be expressed as a function of δ and the property flux density as a function of a more complex *transfer coefficient* (k) in the form

$$\tau_{XY} = -\eta \frac{\mathrm{dv_X}}{\mathrm{dY}} \approx -\eta \frac{\Delta \mathrm{v_X}}{\Delta \mathrm{Y}} \approx -\eta \frac{\Delta \mathrm{v_X}}{\delta_{\mathrm{v}}} = \mathrm{k_v} \Delta \mathrm{v_X}$$

$$\mathbb{q} = -\lambda \frac{\mathrm{d}T}{\mathrm{dY}} \approx -\lambda \frac{\Delta T}{\Delta \mathrm{Y}} \approx -\lambda \frac{\Delta T}{\delta_T} = \mathrm{k}_T \Delta T$$

$$J_i = -D_i \frac{\mathrm{d}c_i}{\mathrm{dY}} \approx -D_i \frac{\Delta c_i}{\Delta \mathrm{Y}} \approx -D_i \frac{\Delta c_i}{\delta_M} = \mathrm{k}_M \Delta c_i$$

Section c. At low density the kinetic properties can be determined by intermolecular potentials.



The *hard-sphere potential* (HS) model is based on the assumption that there are no other forces than steric repulsions (existing only in the space occupied by the mass) and on an infinite cohesion that leads to invariability of shape and volume. Its main parameter is the *diameter of the sphere* (σ^{HS}). In the *Lennard-Jones potential* (LJ) model there are both attractive and repulsive forces (functions of the distance to the mass and forces center), and its main parameters are the minimum value of the potential ($\varepsilon^{\mathrm{LJ}}$) and the distance at which this potential becomes zero (σ^{LJ}).

The resulting estimation equations for transport properties of gases and vapors at low density are

$$\eta = \frac{5}{16\sigma^2\Omega_\eta}\sqrt{\frac{mkT}{\pi}} \quad ; \quad \lambda = \frac{75k}{64\sigma^2\Omega_\lambda}\sqrt{\frac{kT}{m\pi}} \quad ; \quad D_{AB} = \frac{3}{8\tilde{\rho}N_{av}\sigma_{AB}^2\Omega_D}\sqrt{\frac{kT}{\pi m_{AB}}}$$

where k is the *Boltzman constant* (quotient between the universal gas constant and the Avogadro number, N_{av}), $\tilde{\rho}N_{av}$ is the *number density* (number of particles per unit volume), Ω is the symbol of the *collision integrals* and *AB* indicates that we are dealing with mean *mixture parameters*, defined as

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \quad ; \quad \frac{2}{m_{AB}} = \frac{1}{m_A} + \frac{1}{m_B}$$

For the hard sphere, $\sigma = \sigma^{\mathrm{HS}}$ and $\Omega_\eta = \Omega_\lambda = \Omega_D = 1$. For the Lennard-Jones fluids $\sigma = \sigma^{\mathrm{LJ}}$ and the collision integrals are complex functions of $kT/\varepsilon^{\mathrm{LJ}}$ (viscosity and thermal conductivity) or of $kT/\varepsilon_{AB}^{\mathrm{LJ}}$ (binary diffusivity). $\varepsilon_{AB}^{\mathrm{LJ}}$ is calculated by the geometric mean of individual values $\varepsilon_A^{\mathrm{LJ}}$ and $\varepsilon_B^{\mathrm{LJ}}$.

0.8. Corresponding States Principle:

- **a) Compressibility factor.**
- **b) Other thermodynamic properties.**
- **c) The reference ideal state.**
- **d) Further corrections.**
- **e) Example of calculations.**
- **f) Kinetic properties.**

Section a. The *Corresponding States Principle* is based in the subliminal phenomenological analogy unveiled by the following correction to the ideal gas equation

$$\frac{P\tilde{V}}{RT} = z$$

where z is the *compressibility factor*, an empirical parameter evidenced as a generalized function of reduced variables $z=\mathrm{f}(T_r,P_r)$, that takes the same value for any substance in a homologous or corresponding state T_r, P_r.

The *reduction criterion* is the critical point for each substance: $T_r= T/T_c$ and $P_r= P/P_c$.

Section b. The previous equation of state allows the calculation, estimation and mathematical or graphical correlation *(generalized charts)* of the departures between ideal and real values of each of the thermodynamic properties, the enthalpy, the internal energy, the entropy, the molar heat capacity

$$\frac{\tilde{H}^* - \tilde{H}}{T_c} \quad \text{vs. } P_r\text{, with } T_r \text{ in isolines}$$

$$\frac{\tilde{U}^* - \tilde{U}}{T_c} \quad \text{vs. } P_r\text{, with } T_r \text{ in isolines}$$

$$\tilde{S}^* - \tilde{S} \quad \text{vs. } P_r\text{, with } T_r \text{ in isolines}$$

$$\tilde{C}_P - \tilde{C}_P^* \quad \text{vs. } P_r\text{, with } T_r \text{ in isolines}$$

and the fugacity f

$$\frac{f}{P} = \exp\left(\frac{\tilde{G} - \tilde{G}^*}{RT}\right) \quad \text{vs. } P_r\text{, with } T_r \text{ in isolines}$$

Section c. The properties of the previous section are estimated as departures from the ideal gas behaviour (*). These properties of the substances considered as ideal gases are usually calculated from $\tilde{C}_P^*$, which is given by empirical equations in the form

$$\tilde{C}_P^* = \xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4$$

and having in mind the reference problems 0.3 and 0.4 and the Mayer's relation

$$\Delta H^* = \int C_p^* \mathrm{d}T$$

$$\Delta U^* = \int C_V^* \mathrm{d}T = \int \left(C_p^* - R\right)\mathrm{d}T$$

$$\Delta S^* = \int C_P^* \frac{dT}{T} + \int R \frac{dP}{P}$$

Section d. It would be expected that the compressibility factor would serve for any compound. However, substances whose compressibility factor at the critical point is not of 0.27 (value slightly different from that theoretical estimated but accepted as quasi-universal due to its wide frequency) deviate from the generalized behavior, and need additional *correction functions* ψ (dependent on reduced temperature and reduced pressure as well), being different if z_c>0.27 or z_c <0.27.

$$(z)_{z_c \neq 0.27} = (z)_{z_c = 0.27} + [z_c - 0.27]\Psi_z$$

$$\left(\frac{\widetilde{H}^* - \widetilde{H}}{T_c}\right)_{z_c \neq 0.27} = \left(\frac{\widetilde{H}^* - \widetilde{H}}{T_c}\right)_{z_c = 0.27} + [z_c - 0.27]\Psi_H$$

$$\left(\frac{\widetilde{U}^* - \widetilde{U}}{T_c}\right)_{z_c \neq 0.27} = \left(\frac{\widetilde{U}^* - \widetilde{U}}{T_c}\right)_{z_c = 0.27} + [z_c - 0.27]\Psi_U$$

$$\left(\tilde{S}^* - \tilde{S}\right)_{z_c \neq 0.27} = \left(\tilde{S}^* - \tilde{S}\right)_{z_c = 0.27} + [z_c - 0.27]\Psi_S$$

and so on.

Section e. As previously referred in section d of reference problem 0.3, the variation of enthalpy, entropy, internal energy and Gibbs free energy can be calculated only between two states 1 and 2. Hence

$$\Delta\widetilde{H}_{21} = \left(\widetilde{H}_2 - \widetilde{H}_1\right) = \left(\widetilde{H}_2^* - \widetilde{H}_1^*\right) + \left(\widetilde{H}_1^* - \widetilde{H}_1\right)_{T_1,P_1} - \left(\widetilde{H}_2^* - \widetilde{H}_2\right)_{T_2,P_2}$$

$$\Delta\tilde{S}_{21} = \left(\tilde{S}_2 - \tilde{S}_1\right) = \left(\tilde{S}_2^* - \tilde{S}_1^*\right) + \left(\tilde{S}_1^* - \tilde{S}_1\right)_{T_1,P_1} - \left(\tilde{S}_2^* - \tilde{S}_2\right)_{T_2,P_2}$$

$$\Delta\widetilde{U}_{21} = \left(\widetilde{U}_2 - \widetilde{U}_1\right) = \left(\widetilde{U}_2^* - U_1^*\right) + \left(\widetilde{U}_1^* - \widetilde{U}_1\right)_{T_1,P_1} - \left(\widetilde{U}_2^* - \widetilde{U}_2\right)_{T_2,P_2}$$

$$\Delta\tilde{G}_{21} = \left(\tilde{G}_2 - \tilde{G}_1\right) = \left(\tilde{G}_2^* - G_1^*\right) + \left(\tilde{G}_1^* - \tilde{G}_1\right)_{T_1,P_1} - \left(\tilde{G}_2^* - \tilde{G}_2\right)_{T_2,P_2}$$

The heat capacity is an exception, because in any state

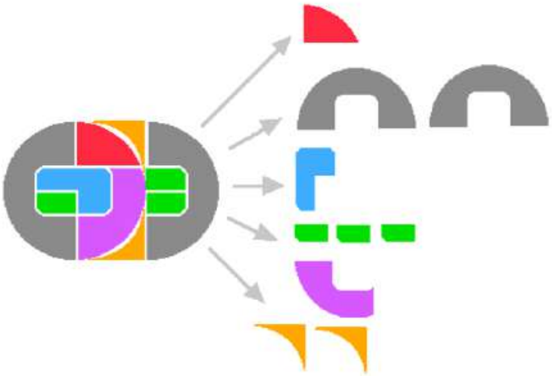
$$\tilde{C}_P = \left(\tilde{C}_P - \tilde{C}_P^*\right) + \tilde{C}_P^*$$

Section f. By employing the viscosity at the critical point (η_c) and the heat conductivity at the critical point (λ_c), *generalized charts* of $\eta_r = \eta / \eta_c$ vs. T_r with P_r in isolines and of $\lambda_r = \lambda / \lambda_c$ vs. T_r with P_r in isolines have been drawn. For diffusivity, this type of representation has not been successful.

0.9. Estimation of critical properties by group-contribution methods:

a) Fundamentals.
b) Equations of Lydersen.

Section a. *Group-contribution models* consider molecules formed by summable fragments or “groups” (like a puzzle), because the number of molecules is almost infinite, but the number of groups is limited.



In principle, it can be assumed that these functional groups and the resulting molecular configuration will have a palpable importance in the properties of the compounds of which they are part.

Section b. The empirical equations of Lydersen are

$$\frac{T_b}{T_c} = 0.567 + \Sigma\Delta_T - (\Sigma\Delta_T)^2$$

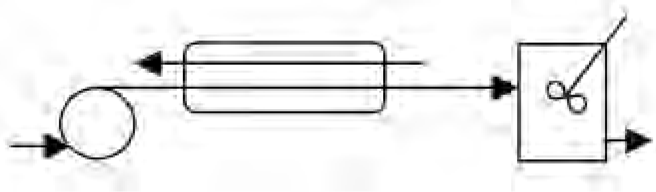
$$P_c = \frac{\mathfrak{M}}{(0.34 + \Sigma\Delta_P)^2}$$

$$\tilde{V}_c = 40 + \Sigma\Delta_V$$

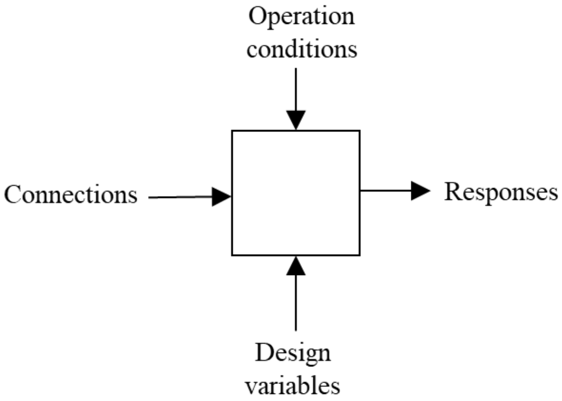
Parameters Δ_T, Δ_P and Δ_V are the contributions due to the several groups involved in a certain molecule.

0.10. Flowchart and information flow diagram.

A *flowchart* is a simple representation of a process, with circles, squares, arrows and other symbols, previously agreed upon or governed by different types and levels of regulations and normalization. The lines represent mass flows and the arrows the respective directions of the currents. For example, if a process consists of pumping, heat exchanging and chemical reaction



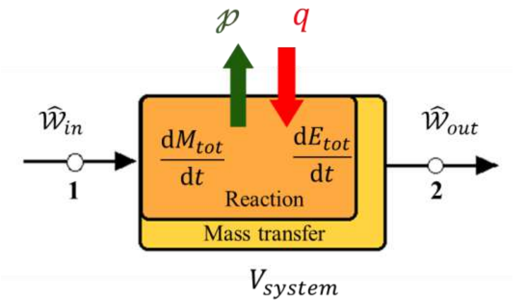
On the other hand, the *information flow diagram* displays a square (which represents the phenomenological/mathematical model of the process unit concerned) and different interaction modes with the surroundings: *connections* (explicit context of the process, conditions, demands and objectives), *design variables* (design options to consume degrees of freedom in the design or operation), *operation conditions* (implicit properties and other accessible information-experimental or bibliographical-necessary to sufficiently characterize the process) and *responses* (dimensions, conditions and other searchable parameters).



Depending on the degree of detail and the level of description, this type of logical representation can be made both for processes and for each of the operations or differentiable functional elements that are integrated into the processes. In this latter case, the flow diagram is made up of a network of duly interconnected diagrams, where, for calculation or optimization purposes, the different paths or routes of reciprocal interaction between the different units considered can be identified.

0.11. Inventory for conditions and operation:
a) Mass balance.
b) Energy balance.

Section a. The total mass balance for the system



will be formulated as

$$\begin{bmatrix}\text{Total rate}\\ \text{of entry of}\\ \text{mass into}\\ \text{the system}\end{bmatrix}-\begin{bmatrix}\text{Total rate}\\ \text{of exit of}\\ \text{mass from}\\ \text{the system}\end{bmatrix}=\begin{bmatrix}\text{Mass variation}\\ \text{in the system}\\ \text{over time}\end{bmatrix}$$

$$\hat{\mathcal{W}}_{in}-\hat{\mathcal{W}}_{out}=\frac{dM_{tot}}{dt}$$

where $\hat{\mathcal{W}}_{in}$ is the mass flow rate which enters the system and $\hat{\mathcal{W}}_{out}$ the mass flow rate that leaves it.

The mass balance to a compound i is defined as

$$\begin{bmatrix}\text{Rate of}\\ \text{entry of } i\\ \text{into the}\\ \text{system}\end{bmatrix}-\begin{bmatrix}\text{Rate of}\\ \text{exit of } i\\ \text{from the}\\ \text{system}\end{bmatrix}+\begin{bmatrix}\text{Rate of generation}\\ \text{(or loss) of } i\\ \text{because chemical}\\ \text{reaction or mass}\\ \text{transfer with the}\\ \text{surroundings}\end{bmatrix}=\begin{bmatrix}\text{Variation}\\ \text{of } i \text{ in the}\\ \text{system}\\ \text{over time}\end{bmatrix}$$

Section b. For the total energy balance to the system we get

$$\begin{bmatrix}\text{Flow of } U, PV,\\ E_{kin}, E_{rad} \text{ and } E_{pot}\\ \text{which enters}\\ \text{the sytem}\end{bmatrix}-\begin{bmatrix}\text{Flow of } U, PV,\\ E_{kin}, E_{rad} \text{ and } E_{pot}\\ \text{which leaves}\\ \text{the sytem}\end{bmatrix}+\begin{bmatrix}\text{Energy production}\\ \text{(or loss) because}\\ \text{chemical reaction,}\\ \text{heat transfer with}\\ \text{the surroundings,}\\ \text{friction, mechanical}\\ \text{work, radiation ...}\end{bmatrix}=\begin{bmatrix}\text{Energy}\\ \text{variation}\\ \text{in the system}\\ \text{over time}\end{bmatrix}$$

$$\hat{\mathcal{W}}_{in}\left(\hat{H}+\hat{E}_{kin}+\hat{E}_{rad}+\hat{E}_{pot}\right)_{in}-\hat{\mathcal{W}}_{out}\left(\hat{H}+\hat{E}_{kin}+\hat{E}_{rad}+\hat{E}_{pot}\right)_{out}+q+\wp+\cdots=\frac{\mathrm{d}E_{tot}}{\mathrm{d}t}$$

being $\hat{H}=\hat{U}+P\hat{V}$, $\hat{E}_{kin}$ the specific kinetic energy, $\hat{E}_{rad}$ the specific energy due to radiation, $\hat{E}_{pot}$ the specific potential energy, q the heat flow and $\wp$ the mechanical power. Other contributions to the energy (friction, chemical reaction…) are represented by the ellipses.

When there is no variation of the total energy and the total mass over time, the system reaches the stationary state ($\mathrm{d}M_{tot}/\mathrm{d}t=\mathrm{d}E_{tot}/\mathrm{d}t=0$), where $\hat{\mathcal{W}}_{in}=\hat{\mathcal{W}}_{out}$ and

$$\Delta\left(\hat{H}+\hat{E}_{kin}+\hat{E}_{rad}+\hat{E}_{pot}\right)_{12}+\Delta\hat{Q}+\Delta\hat{W}+\text{other terms}=0$$

0.12. The heat exchanger:
a) Fundamentals.
b) Example of energy balance.
c) Design equation.

Section a. The *heat exchanger* is a simple example of a *basic (unit) transfer operation,* in which the process objectives in a leading thermodynamic system (needed to gain or lose heat energy) are achieved through the action of other subordinate thermodynamic system (respectively heat giver or receiver).

In a heat exchanger a hot stream I gives heat to a cold stream II. The device can operate in two hydrodynamic conditions: *parallel flow* or in *counterflow*.

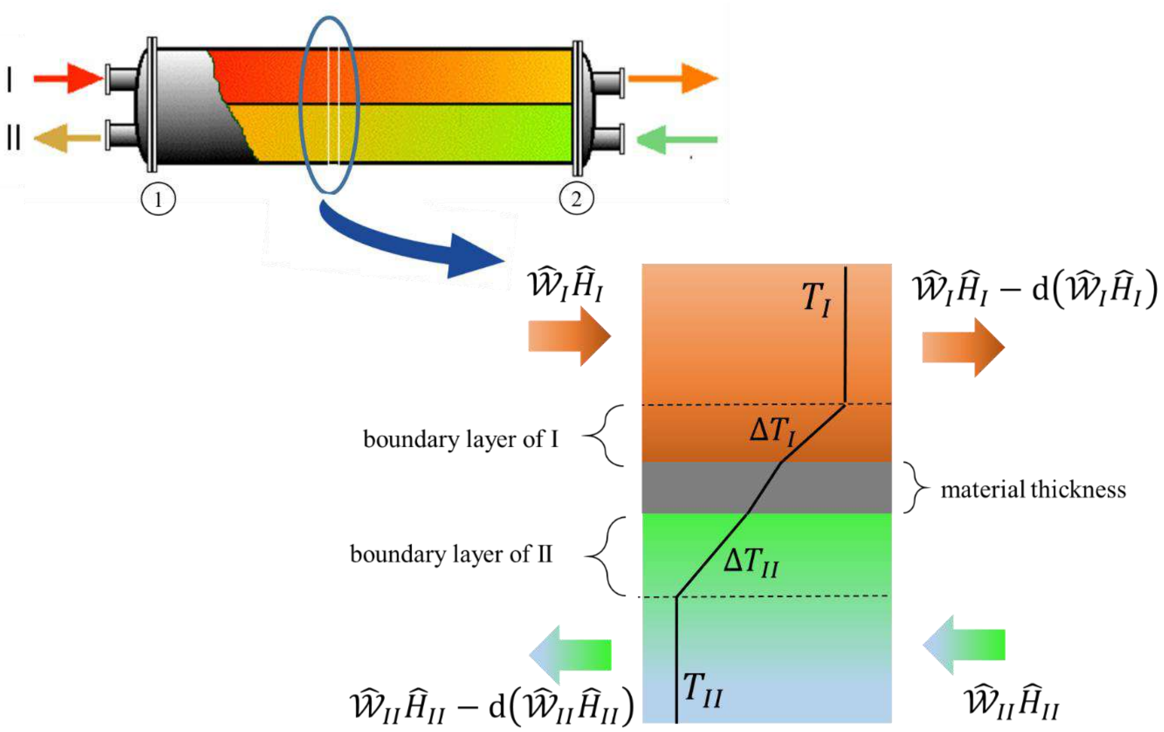
$$\begin{bmatrix}\text{heat flow given}\\ \text{by phase I}\end{bmatrix} = \begin{bmatrix}\text{heat flow gained}\\ \text{by phase II}\end{bmatrix}$$

$$-q_I = q_{II}$$

$$-\hat{\mathcal{W}}_I \Delta\hat{Q}_I = \hat{\mathcal{W}}_{II} \Delta\hat{Q}_{II}$$

$$q = \mathrm{k}_T A \Delta T \quad ; \quad \Delta\hat{Q} = \int T \mathrm{d}\hat{S}$$

Section b. The following calculations are applied to a counterflow device, but are very similar in the parallel flow case.



In a typical heat exchanger (operating in stationary state) points 1 and 2 are placed at the same height (so there is no change of the potential energy), there is no radiation or mechanical work. Furthermore it is isobaric and there is no velocity variation between 1 and 2 (ΔP is usually associated with $\Delta\hat{E}_{kin}$). Therefore, the energy balance to the stream I in a differential element of the apparatus is

$$\begin{bmatrix}\text{Enthalpy}\\\text{flow which}\\\text{enters}\end{bmatrix} - \begin{bmatrix}\text{Enthalpy}\\\text{flow which}\\\text{leaves}\end{bmatrix} + \begin{bmatrix}\text{Energy lost}\\\text{by heat}\\\text{transfer}\end{bmatrix} = \begin{bmatrix}\text{Energy}\\\text{variation}\\\text{over time}\end{bmatrix}$$

$$\widehat{\mathcal{W}}_I\hat{H}_I \quad - \quad \left[\widehat{\mathcal{W}}_I\hat{H}_I - \mathrm{d}\left(\widehat{\mathcal{W}}_I\hat{H}_I\right)\right] \quad - \quad \mathrm{k}_{T(I)}\mathrm{d}A\Delta T_I \quad = \quad 0$$

$$\mathrm{d}q = \mathrm{d}\left(\widehat{\mathcal{W}}_I\hat{H}_I\right) = -\,\mathrm{k}_{T(I)}\mathrm{d}A\Delta T_I$$

$$\widehat{\mathcal{W}}_I\;\hat{C}_{PI}\mathrm{d}T_I = -\,\mathrm{k}_{T(I)}\mathrm{d}A\Delta T_I$$

Energy balance to the stream II

$$\begin{bmatrix}\text{Enthalpy}\\\text{flow which}\\\text{enters}\end{bmatrix} - \begin{bmatrix}\text{Enthalpy}\\\text{flow which}\\\text{leaves}\end{bmatrix} + \begin{bmatrix}\text{Energy}\\\text{gained by}\\\text{heat transfer}\end{bmatrix} = \begin{bmatrix}\text{Energy}\\\text{variation}\\\text{over time}\end{bmatrix}$$

$$\widehat{\mathcal{W}}_{II}\hat{H}_{II} \quad - \quad \left[\widehat{\mathcal{W}}_{II}\hat{H}_{II} + \mathrm{d}\left(\widehat{\mathcal{W}}_{II}\hat{H}_{II}\right)\right] \quad + \quad \mathrm{k}_{T(II)}\mathrm{d}A\Delta T_{II} \quad = \quad 0$$

$$\mathrm{d}q = \mathrm{d}\left(\widehat{\mathcal{W}}_{II}\hat{H}_{II}\right) = \mathrm{k}_{T(II)}\mathrm{d}A\Delta T_{II}$$

$$\widehat{\mathcal{W}}_{II}\;\hat{C}_{PII}\mathrm{d}T_{II} = \mathrm{k}_{T(II)}\mathrm{d}A\Delta T_{II}$$

Section c. The integrated forms of the previous equations imply the introduction of a *global heat transfer coefficient* k_T (which not only includes the heat transfer resistance in the two phases, but also that of the exchanger material) and a functional dependence of the inolved distribution of temperature (in this case the *logarithmic mean temperature potential* $\langle\Delta T\rangle_{ln}$ in the form

$$A = \frac{q}{\mathrm{k}_T\langle\Delta T\rangle_{ln}} = \frac{q}{\mathrm{k}_T\left\{\dfrac{\Delta T_1 - \Delta T_2}{\ln\left(\dfrac{\Delta T_1}{\Delta T_2}\right)}\right\}}$$

In the particular case that $\Delta T_1 = \Delta T_1 = \Delta T$

$$A = \frac{q}{\mathrm{k}_T\Delta T}$$

0.13. Thermodynamic cycles:

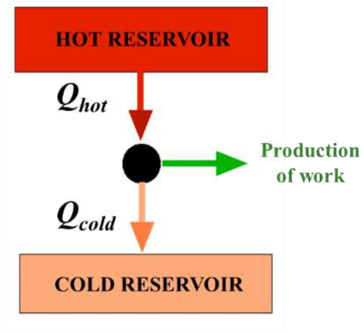
a) Definition.
b) Heat engines, refrigerators and heat pumps.
c) The Carnot cycle.
d) Yield, coefficient of performance, efficiency.
e) Cycles for creating and separating phases.

Section a. A *cycle* is a series of thermodynamic operations in which the conditions of the concerned thermodynamic system at the end of the last operation coincide with those of the feeding of the first one, i.e., the thermodynamic system goes through the same situations over and over again.

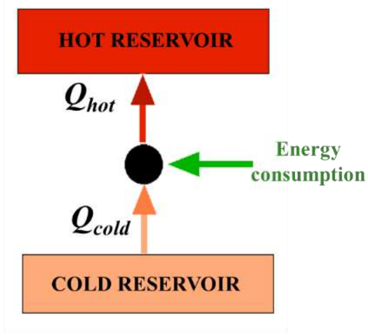
Regardless of other specific phenomenological circumstances -frequently the inaccessibility of certain changes to a single operation-, the common reason for all cyclic processes is to save resources (energy and mass) through internal interactions, allowing an approximation to the continuous regime through an efficient repetitive coupling between complementary continuous or discontinuous operations.

Section b. *Heat engine* is a cyclic machine that absorbs *heat* ($Q_{hot}> 0$) from a hot reservoir (boiler or combustion chamber), gives *heat* ($Q_{cold} < 0$) to a cold reservoir (condenser) and generates *mechanical energy* (work, $W <0$).

Refrigerator and *heat pump* are devices that absorb heat ($Q_{cold} >0$) from a cold reservoir (*evaporator*), receive energy in the form of work ($W>0$) from their surroundings and give heat ($Q_{hot} <0$) to a hot reservoir (*condenser*).



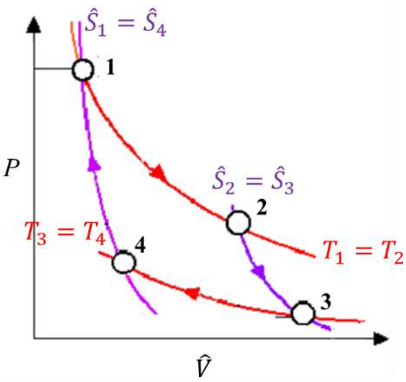
HEAT ENGINE

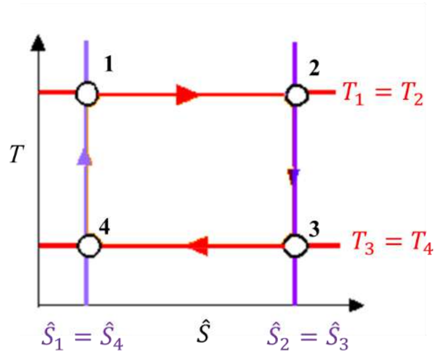


REFRIGERATOR AND HEAT PUMP

If the graphical representation of an operation in any scenario (thermodynamic diagram) gives rise to a very frequently monofunctional continuous line (see section b of reference problem 0.5), the representation of a cycle is substantiated in the closed composition of as many differentiated lines as operations are involved.

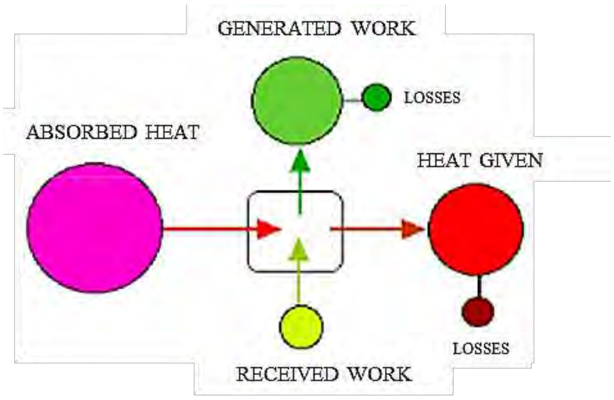
Section c. The Carnot cycle is the best known cycle.





It consists of heating with isothermal expansion, followed by isentropic expansion, isothermal cooling and subsequent isentropic compression to the initial conditions. In clockwise direction it is a thermal engyine and in counterclockwise direction it is a heat pump.

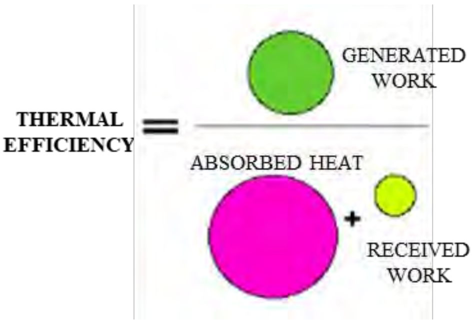
Section d. Let the following figure pseudoquantitatively represent the energy balance of a cycle



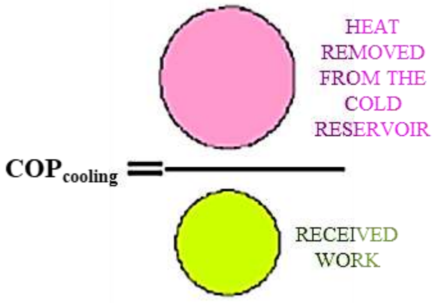
so that

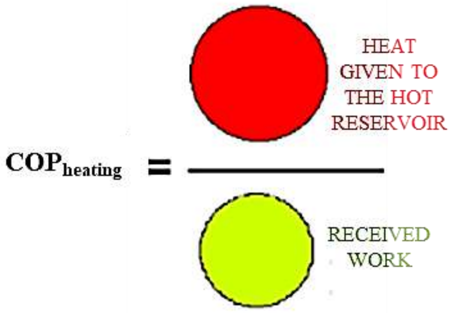
$$\Delta Q_{absorbed} + \Delta W_{received} = \Delta W_{generated} + \Delta W_{losses} + \Delta Q_{given} + \Delta Q_{losses}$$

In a heat engine, the yield is calculated by the thermal efficiency

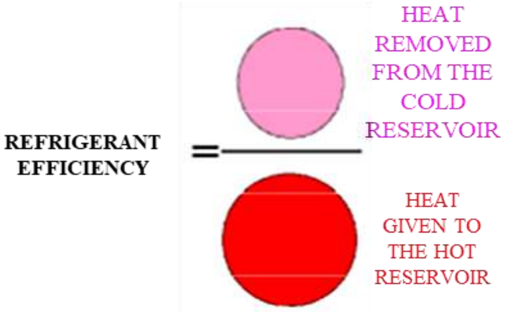


However, in refrigerators and heat pumps the *coefficient of performance* (COP) is employed. There are two COPs: one for cooling and one for heating.





Additionally, for refrigerators



Section e. There are cycles which do not produce work or remove heat, but create and separate phases. This is the case of the *condensation-sublimation* ones (e.g. to generate dry ice) and of the *gas liquefaction* ones (Linde or Claude). The latter cycles consist of isothermal gas compression, isobaric heating, expansion and phase separation (with the recirculation of the non-condensed gas to the feed, after passing through the isobaric heat exchanger). Claude employs an *isentropic expansion* and Linde uses an *isenthalpic expansion*.

0.14. Composition of mixtures:

a) Molarity.
b) Molality.
c) Mass or molar fractions.
d) Mass or molar ratios.
e) Comments.

Section a. *Molarity* of a substance i in a mixture is the number of moles of i referred to (divided by) the total volume of the mixture

$$\tilde{\mathbb{M}}_i = \frac{n_i}{V_{tot}}$$

Section b. *Molality* is the number of moles of a component i referred to (divided by) the mass of solvent

$$\mathbb{m}_i = \frac{n_i}{M_{sol}}$$

Section c. *Mass* or *molar fractions* are the quantity of every component referred to the mass of the whole mixture (the quotient between the amount of i and the amount of all the k substances present in a multicomponent mixture):

$$\tilde{x}_i = \frac{n_i}{n_{tot}} \quad ; \quad n_{tot} = \sum_{j=1}^{k} n_j \quad \text{molar fraction}$$

$$\hat{x}_i = \frac{M_i}{M_{tot}} \quad ; \quad M_{tot} = \sum_{j=1}^{k} M_j \quad \text{mass fraction}$$

Section d. *Mass* or *molar ratios* are the quotient between the amount of i and the amount of the other substances present in a multicomponent mixture (but excluding i)

$$\tilde{X}_i = \frac{n_i}{n_{part}} \quad ; \quad n_{part} = \sum_{\substack{j=1 \\ j\neq i}}^{k} n_i \quad \text{molar ratio}$$

$$\hat{X}_i = \frac{M_i}{M_{part}} \quad ; \quad M_{part} = \sum_{\substack{j=1 \\ j\neq i}}^{k} M_j \quad \text{mass ratio}$$

Section e. Molar or mass *fractions* are related with molar or mass *ratios* by

$$X_i = \frac{x_i}{1 - x_i} \qquad x_i = \frac{X_i}{1 + X_i}$$

In biphasic mixtures, letters x and X are commonly used for the liquid phase (or the heaviest one when dealing with two condensed phases) and letters y and Y for the gas (or the lightest phase).

0.15. Chemical potential.

The extension of the fundamental thermodynamic relations of reference problem 0.3 to multicomponent mixtures of k components generates the following equations

$$\mathrm{d}U = -P\mathrm{d}V + T\mathrm{d}S + \sum_{i=1}^{k} \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_{j\neq i}} \mathrm{d}n_i$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P + \sum_{i=1}^{k} \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}} \mathrm{d}n_i$$

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \sum_{i=1}^{k} \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_{j\neq i}} \mathrm{d}n_i$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} \mathrm{d}n_i$$

In principle, any of the terms

$$\left(\frac{\partial \mathrm{Z}}{\partial n_i}\right)_{\mathrm{X},\mathrm{Y},n_{j\neq i}}$$

can define the contribution of each component to the properties of the mixture and is called the *chemical potential* (μ_i). However, the preferred one is that containing the Gibbs free energy because the constancy of temperature and pressure, a quality of those conventionally designated as *partial properties* that allows *field properties* to be used as referents of state and phase equilibrium.

0.16. Ideal mixtures:
a) Definition.
b) Pseudocritical properties of ideal mixtures.

Section a. The *ideal mixture* is a mixture model in which the volume, internal energy and enthalpy of the mixture is equal to the sum of those of the separate pure components.

$$V_m = \sum_{i=1}^{k} n_i\,\tilde{V}_i$$

$$U_m = \sum_{i=1}^{k} n_i\,\tilde{U}_i$$

$$H_m = \sum_{i=1}^{k} n_i\,\tilde{H}_i$$

Section b. The *pseudocritical properties* of these mixtures will be defined as algebraic means

$$T_{cm} = \sum_{i=1}^{k} \tilde{x}_i\,T_{ci}$$

$$P_{cm} = \sum_{i=1}^{k} \tilde{x}_i\,P_{ci}$$

and, for binary mixtures

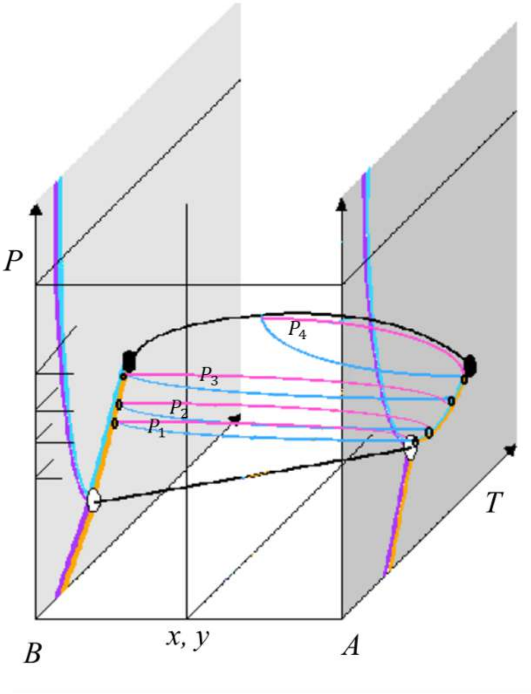
$$T_{cAB} = \tilde{x}_A T_{cA} + \tilde{x}_B T_{cB}$$

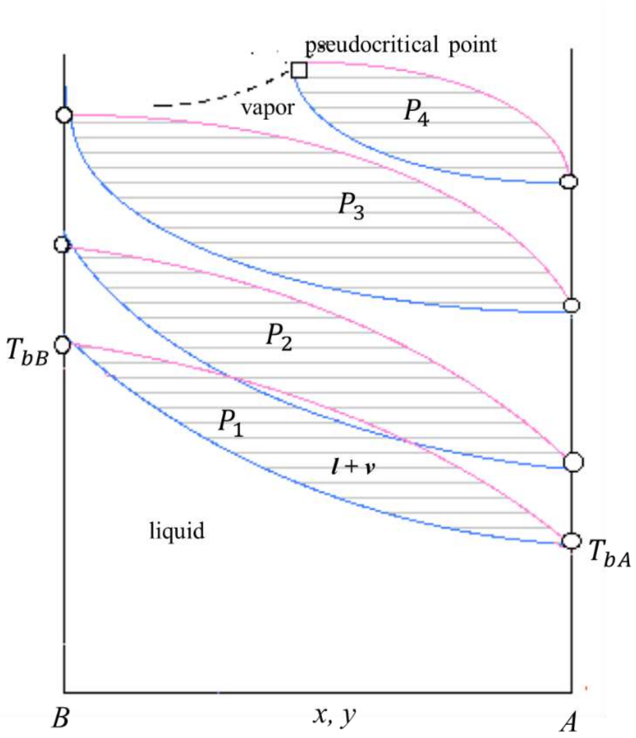
$$P_{cAB} = \tilde{x}_A P_{cA} + \tilde{x}_B P_{cB}$$

0.17. Binary mixtures in liquid-vapor equilibrium:

a) Generalities.
b) Ideal mixture.
c) Henry's law.

Section a. The mixing of two substances A and B in the liquid-vapor coexistence zone will generate diagrams such as





Section b. In the case of an ideal mixture, there will be additivity of the partial pressures in the vapor phase

$$P_A + P_B = \tilde{y}_A P_{tot} + \tilde{y}_B P_{tot} = P_{tot}$$

and additivity of vapor pressures in the liquid one

$$\tilde{x}_A P_{vA} + \tilde{x}_B P_{vB} = P_{tot}$$

Section c. By combining the equations of the previous section, it has been observed that $\tilde{y}_A$ is directly proportional to $\tilde{x}_A$, which provides the basis of the Henry's law

$$\tilde{x}_A P_{vA} = \tilde{y}_A P_{tot}$$

$$P_A = \mathcal{H}\tilde{x}_A \quad \rightarrow \quad \tilde{y}_A P_{tot} = \mathcal{H}\tilde{x}_A$$

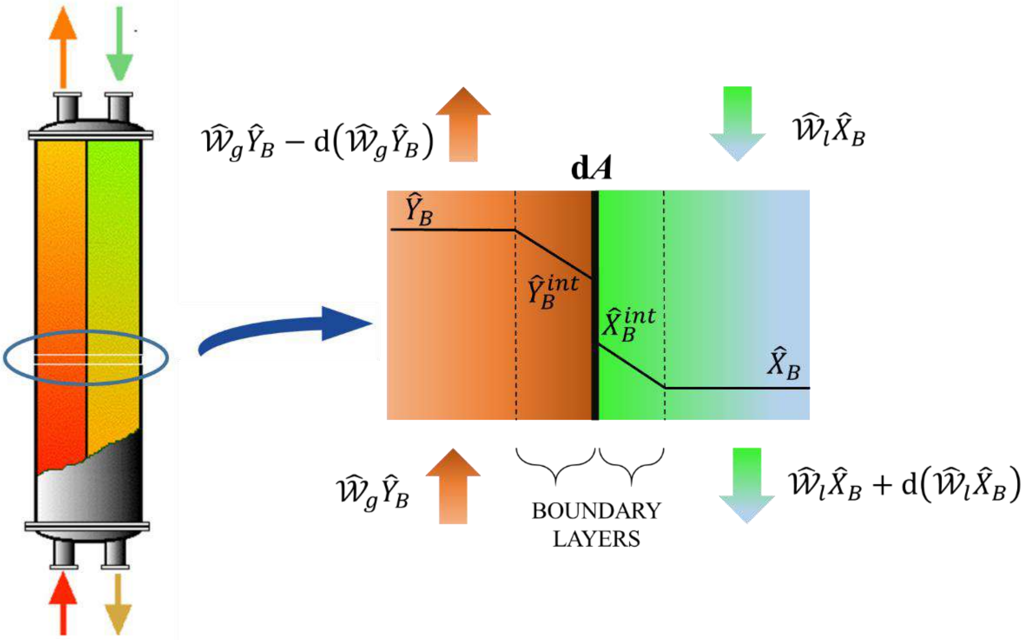
0.18. Absortion: example of mass balance.

Analogously to what was said in section a of reference problem 0.12, the *absorber* is a simple example of a *basic (unit) transfer operation,* in which the process objectives in a leading thermodynamic system (needed to be enriched or released in a certain solute) are achieved through the action of other subordinate thermodynamic system (respectively mass giver or receiver of such component).

Thus**,** to remove a substance *B* from a gas by absorbing it with a liquid, the two streams have to be put into contact in an absorber. The mass balance to *B* in a differential element of the apparatus will be

$$\begin{bmatrix}\text{flow of}\\ B\text{ that}\\ \text{enters}\end{bmatrix} - \begin{bmatrix}\text{flow of}\\ B\text{ that}\\ \text{leaves}\end{bmatrix} + \begin{bmatrix}\text{flow of } B\\ \text{because}\\ \text{mass}\\ \text{transfer}\end{bmatrix} = \begin{bmatrix}\text{Accumulation}\\ \text{of } B\end{bmatrix}$$

In absorption processes, mass and mole ratios are frequently used as composition descriptors instead of mass and mole fractions. Thus, let $\hat{W}_g$ be the inert gas flow rate (mass per unit time of all the gaseous substances except *B*) and $\hat{W}_l$ be the inert liquid flow rate (mass per unit time of all the liquid substances except *B*)



For the gaseous stream

$$\hat{W}_g\hat{Y}_B \quad - \quad \left[\hat{W}_g\hat{Y}_B - \mathrm{d}(\hat{W}_g\hat{Y}_B)\right] \quad + \quad \mathrm{k}_g \mathrm{d}A\left(\hat{Y}_B - \hat{Y}_B^{int}\right) \quad = \quad 0$$

$$\mathrm{d}\left(\hat{W}_g\hat{Y}_B\right) = -\mathrm{k}_{M(g)}\mathrm{d}A\left(\hat{Y}_B - \hat{Y}_B^{int}\right)$$

for the liquid stream

$$\hat{\mathcal{W}}_l\hat{X}_B \quad - \quad \left[\hat{\mathcal{W}}_l\hat{X}_B + \mathrm{d}\left(\hat{\mathcal{W}}_l\hat{X}_B\right)\right] \quad + \quad \mathrm{k}_l\mathrm{d}A\left(\hat{X}_B^{int} - \hat{X}_B\right) \quad = \quad 0$$

$$\mathrm{d}\left(\hat{\mathcal{W}}_l\hat{X}_B\right) = \mathrm{k}_{M(l)}\mathrm{d}A\left(\hat{X}_B^{int} - \hat{X}_B\right)$$

and the total mass balance indicates that

$$\begin{bmatrix} B \text{ gained by} \\ \text{the liquid} \\ \text{stream} \end{bmatrix} = \begin{bmatrix} B \text{ lost by} \\ \text{the gaseous} \\ \text{stream} \end{bmatrix}$$

$$-\mathrm{d}\left(\hat{\mathcal{W}}_l\hat{X}_B\right) = \mathrm{d}\left(\hat{\mathcal{W}}_g\hat{Y}_B\right)$$

$$\mathrm{k}_{M(g)}\mathrm{d}A\left(\hat{Y}_B - \hat{Y}_B^{int}\right) = \mathrm{k}_{M(l)}\mathrm{d}A\left(\hat{X}_B^{int} - \hat{X}_B\right)$$

and the concentrations at the interface $\hat{Y}_B^{int}$ and $\hat{X}_B^{int}$ are related by laws such as that of Henry

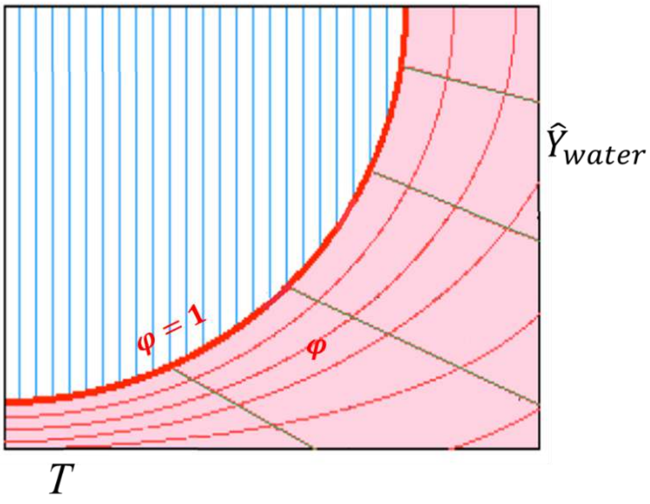
$$\hat{y}_B^{int} = \mathcal{H}\hat{x}_B^{int}$$

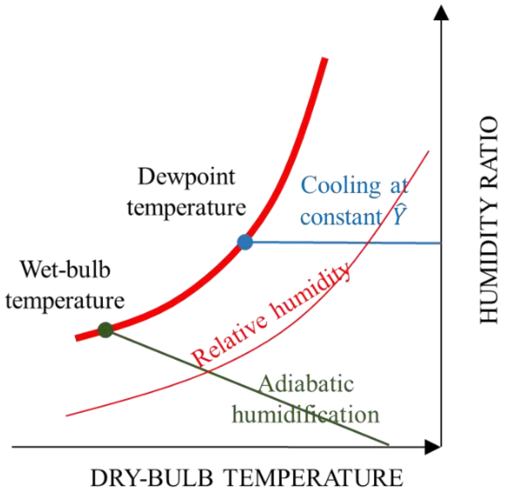
$$\frac{\hat{Y}_B^{int}}{1 + \hat{Y}_B^{int}} = \mathcal{H}\frac{\hat{X}_B^{int}}{1 + \hat{X}_B^{int}} \quad \xrightarrow{at\ low\ concentrations} \quad \hat{Y}_B^{int} \approx \mathcal{H}\hat{X}_B^{int}$$

$\mathrm{k}_{M(g)}$ y $\mathrm{k}_{M(l)}$ are the mass transfer coefficients in the gaseous and liquid parts of the boundary layer, respectively.

0.19. Humidification and dehumidification:
a) Psychrometric chart.
b) Relative humidity.
c) Humidity ratio and dewpoint temperature.
d) Specific volume of the moist air.
e) Specific heat capacity and enthalpy of the moist air.
f) Adiabatic humidification lines and wet-bulb temperature.

Section a. *Humidification* and *dehumidification* are particular cases of the non-isothermal absorption and desorption operations that, due to their importance (with the omnipresent and vital air/water system), their differentiated objectives, their operational peculiarities and the originality of the concepts derived from their singular thermodynamic formulation, have deserved special consideration**.** The *psychrometric chart* is a particular case of the *T-xy* diagrams (reference problem 0.17) for the mixture water+air at atmospheric pressure: it only displays the part corresponding to high concentrations of air. The ambient air temperature *T* is usually called "*dry-bulb temperature.*"





Section b. The isolines of *relative humidity* (*φ*) in the subsaturation zone represent the relation between the real vapor pressure of water in the moist air, P_{water}, and that which would correspond to the pure solvent at the same dry-bulb temperature, $P_{v(water)}$. When *φ*=1 the air is saturated with water.

$$\varphi = \frac{P_{water}}{P_{v(water)}}$$

Section c. Mass ratios of water in dry air are called "*humidity ratios*"

$$\tilde{Y}_{water} = \frac{n_{water}}{n_{air}} = \frac{\tilde{y}_{water}}{1-\tilde{y}_{water}} = \frac{P_{water}}{P_{tot}-P_{water}} = \frac{\varphi P_{v(water)}}{P_{tot}-\varphi P_{v(water)}}$$

$$\hat{Y}_{water} = \frac{\mathfrak{M}_{water}}{\mathfrak{W}_{air}}\tilde{Y}_{water}$$

The *dewpoint temperature* is the temperature at which a mass of moist air becomes saturated without changing the humidity ratio.

Section d. The *specific volume ratio* of the mixture per mass unit of dry air is

$$\hat{V} = \left(\frac{1}{\mathfrak{W}_{air}} + \frac{\hat{Y}_{water}}{\mathfrak{M}_{\mathrm{water}}}\right)\frac{RT}{P_{tot}}$$

and per mole unit of dry air

$$\tilde{V} = \mathfrak{W}_{air}\hat{V}$$

Section e. The *specific heat capacity* and *enthalpy* of moist air per mass unit of dry air are

$$\hat{C}_P = \hat{C}_{P_{dry\,air}} + \hat{Y}_{water}\hat{C}_{P_{steam}}$$

$$\widehat{H} = \widehat{H}_{dry\,air} + \hat{Y}_{water}\widehat{H}_{steam}$$

The *reference states* (where $\widehat{H}$=0) usually chosen are: for dry air, gas at atmospheric pressure and 0ºC; and for steam, liquid at atmospheric pressure and 0ºC. Furthermore, since the steam below 1 atm can be considered and ideal gas, specific heat capacities and enthalpies coincide with those of the *saturated vapor line* (in an ideal gas, $\widehat{H}$ does not depend on the pressure).

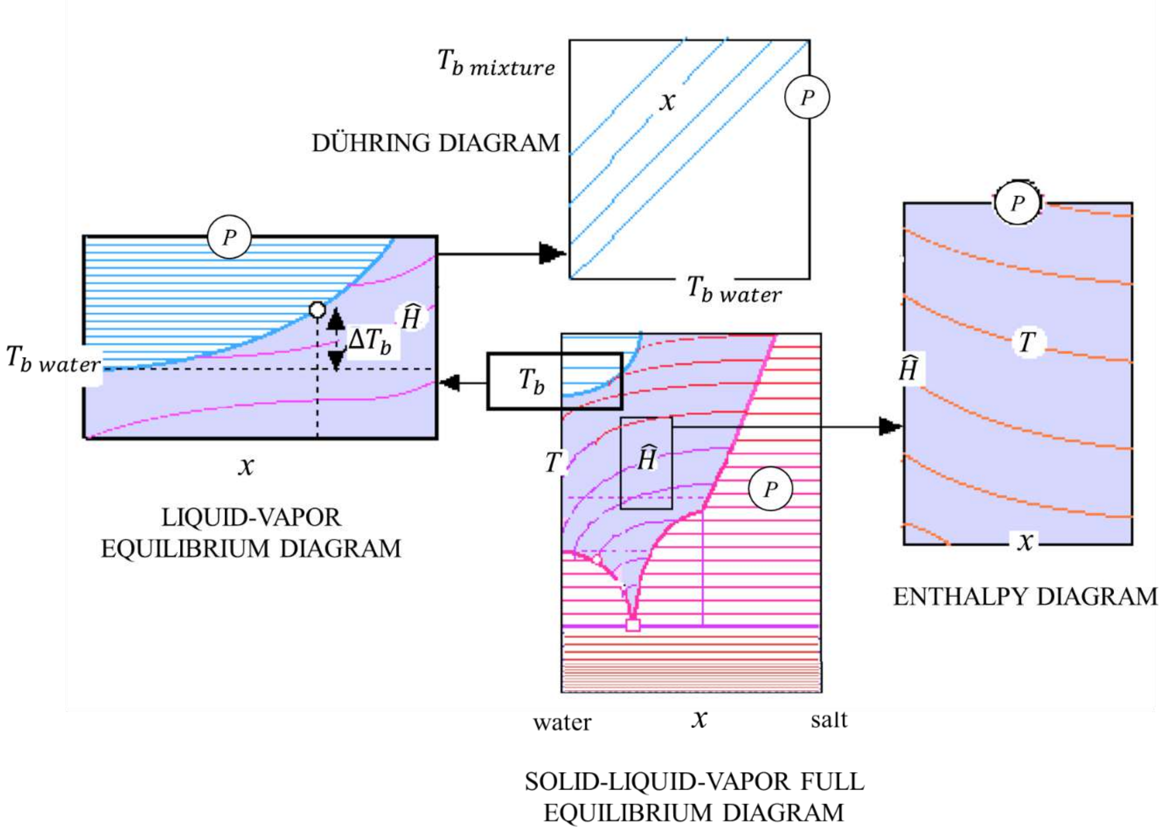
Section f. The *adiabatic humidification* lines describe the cooling of moist air in presence of a mass of water, which evaporates by taking the heat from the moist air itself. The lowest temperature that can be reached in the process (at saturation) is the "*wet-bulb temperature*" (T^{sat}).

$$\frac{\hat{Y}^{sat}-\hat{Y}}{T-T^{sat}} = \frac{\Delta\widehat{H}_{vap\,water}}{\hat{C}_{P_{moist\,air}}} \approx \text{constant}$$

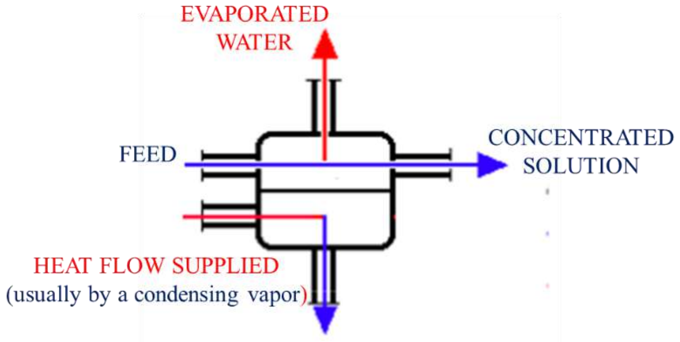
0.20. Evaporation:
a) Fundamentals.
b) Mass and Energy balance.

Section a. Evaporation is a unit operation of separation under thermodynamic conditions such that one of the components is a dissolved solid, which can be concentrated (even by insolubilization in the form of a precipitate or crystallized) by evaporation of another majoritary component in a liquid phase. In practice, either of the two components (the solute or the solvent) can be the target of separation (for example, in the desalination of seawater).

Since the process is not necessarily close to solid-liquid equilibrium, it can be studied from a purely enthalpic approach.



Section b. Balances will be



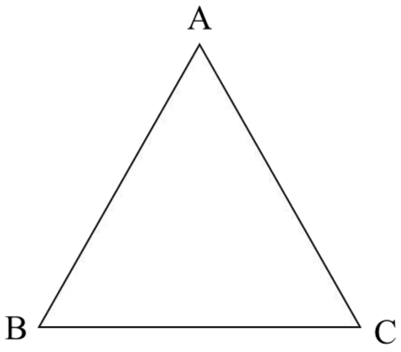
$$\begin{bmatrix}\text{Feed}\\\text{flow rate}\end{bmatrix}\times\begin{bmatrix}\text{solute content}\\\text{in the feed}\end{bmatrix}=\begin{bmatrix}\text{concentrated solution}\\\text{flow rate}\end{bmatrix}\times\begin{bmatrix}\text{solute content in the}\\\text{concentrated solution}\end{bmatrix}$$

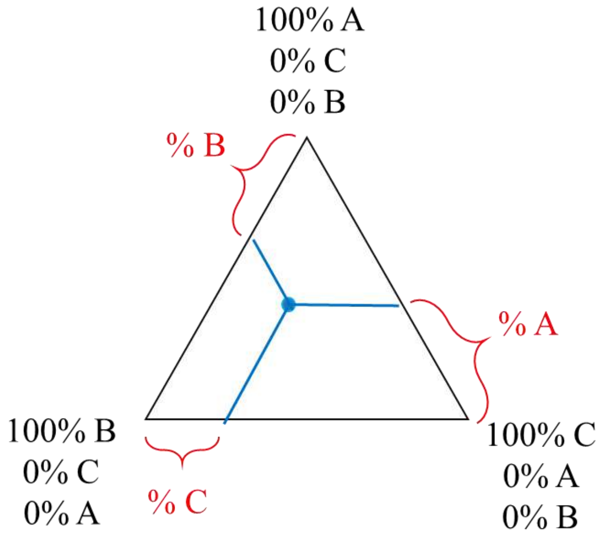
$$\begin{bmatrix}\text{heat flow}\\\text{supplied}\end{bmatrix}+\begin{bmatrix}\text{energy flow}\\\text{of the feed}\end{bmatrix}=\begin{bmatrix}\text{energy flow}\\\text{of the}\\\text{concentrated}\\\text{solution}\end{bmatrix}+\begin{bmatrix}\text{energy}\\\text{flow of the}\\\text{evaporated}\\\text{water}\end{bmatrix}$$

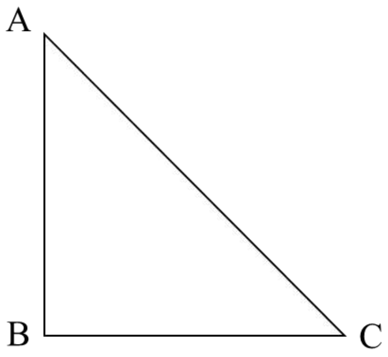
The enthalpies of the feed and of the concentrated solution will be determined by diagrams $\hat{H}$ vs. $\hat{x}$ (with T in isolines), where $\hat{x}$ is the mass fraction of solute. The enthalpies of the evaporated water will be calculated with tables and graphs for pure water. However, in both cases the ebulloscopic increase must be taken into account (using Dühring diagrams if necessary).

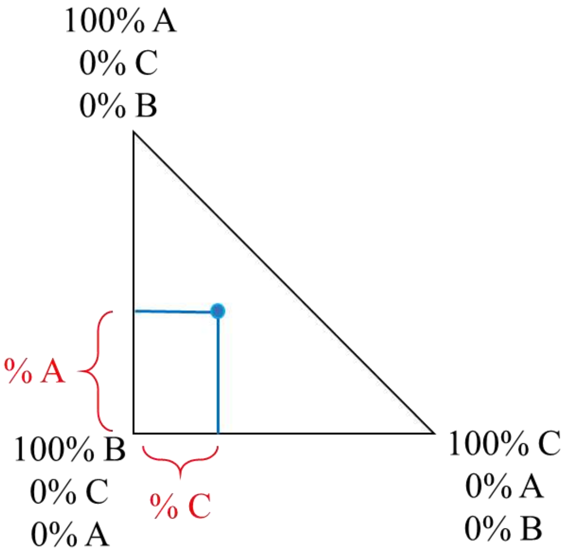
0.21. Ternary equilibria:
a) Ternary diagrams.
b) Extraction fundamentals.

Section a. *Triangular diagrams* are used for representing these equilibria. Conventionally the sides represent binary mixtures of the components located at the adjacent vertices, while the inner area represents ternary mixtures.

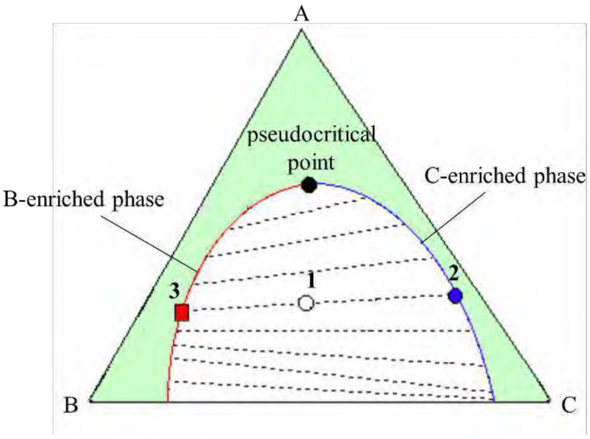






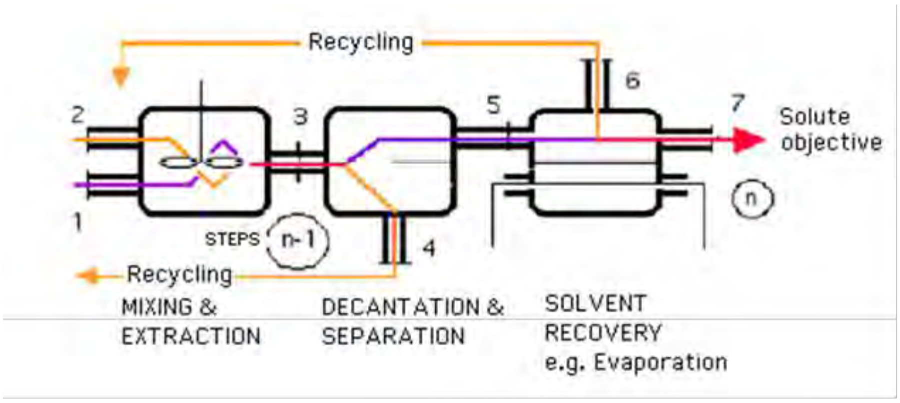


The following figure represents a frequent case: total miscibility of the binary mixtures AB and AC and partial immiscibility of the mixture BC.



A point 1 in the region of partial immiscibility represents a metastable situation that leads to the splitting of the mixture into two liquid phases (2 and 3) whose compositions correspond to points located on the equilibrium line. These points are joined by "tie lines" which allow the mass balance. Tie lines converge to a point called "pseudocritical point."

Section b. Liquid-Liquid extraction or Liquid-Solid leaching are often isothermal mass transfer operations in which a valuable (or on the contrary, unwanted) component is separated from an initial mixture with other substances (either in the liquid phase or in the solid phase) by selective dissolution in an added liquid component. The operation is complemented by one or more other suitable operations to recover all or part of the extracting agent and to concentrate or eliminate the target component. As in any other basic operation, the actual process is brought to the desired efficiency through a succession of complete mixing steps or through continuous contact.



SERIES 1

UNITS, QUANTITIES, MEASURES

1.1. Perform the dimensional analysis of the following thermodynamic properties:

a) **Heat.**
b) **Entropy.**
c) **Heat capacity.**
d) **Specific heat capacity.**
e) **Chemical potential.**
f) **Viscosity.**
g) **Diffusivity.**
h) **Thermal conductivity.**

Question a. Heat is an energy form exchanged by a system with other concrete systems or with abstract surroundings. It is a transit property since it is considered heat only when it flows. It becomes internal energy when absorbed by the matter.

$$\text{heat} = \text{energy} = Q\ [=] ML^2t^{-2}$$

Question b. Entropy is mathematically defined as the relation (quotient) between the heat exchanged in a reversible process and the absolute temperature at which this transit occurs (section a of reference problem 0.3). Thus, a differential heat change (at an instantaneous temperature) is written as

$$\mathrm{d}S = \frac{\partial Q}{T} \quad \rightarrow \quad \Delta S = \frac{\Delta\text{heat}}{T}\ [=] \frac{ML^2t^{-2}}{T} = ML^2T^{-1}t^{-2}$$

Question c. The heat capacity of a substance (*C*) is defined as the ratio (quotient) between the heat exchanged by an amount of this substance and the temperature variation caused by this exchange in the substance. Its units are cal/ºC, J/K, BTU/ºF...

$$C = \frac{\Delta\text{heat(energy)}}{\Delta\text{temperature}} = \frac{\Delta Q}{\Delta T}\ [=] \frac{ML^2t^{-2}}{T} = ML^2T^{-1}t^{-2}$$

Question d. Specific heat capacity is the heat capacity per unit system (mass or moles). Consequently, it is expressed in cal/(ºC·mol), J/(K·mol)... The best known due to their practical utility are the specific heat capacities at constant pressure or at constant volume (section d of reference problem 0.4)

$$\left.\begin{aligned} \hat{C} &= \frac{\Delta\text{heat}}{\text{mass}\cdot\Delta\text{temperature}} \\ \tilde{C} &= \frac{\Delta\text{heat}}{\text{moles}\cdot\Delta\text{temperature}} \end{aligned}\right\} = \frac{\Delta Q}{M\cdot\Delta T}\ [=] \frac{ML^2t^{-2}}{MT} = L^2T^{-1}t^{-2}$$

Question e. The chemical potential of a substance i in a multicomponent mixture is defined (in molar units) as the derivative of the Gibbs free energy of this system with respect to the amount of the substance i holding T, P and the number of moles of other substances $n_{j\neq i}$ constant (reference problem 0.15)

$$\mu_i = \tilde{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} \rightarrow \mu_i = \frac{\Delta\text{energy}}{\Delta\text{moles}} [=] \frac{ML^2t^{-2}}{M} = L^2t^{-2}$$

Question f. In the Newton's law (section a of reference problem 0.7), viscosity (η) is the coefficient of proportionality between the shear stress (force per unit area) applied in a plane (τ_{XY}) and the velocity gradient perpendicular to this plane ($\mathrm{dv_X}/\mathrm{dY}$)

$$\tau_{\mathrm{XY}} = -\eta\frac{\mathrm{dv_X}}{\mathrm{dY}} \quad\rightarrow\quad \eta = -\frac{\tau_{\mathrm{XY}}}{\left(\frac{\mathrm{dv_X}}{\mathrm{dY}}\right)} [=] \frac{\left(\frac{\mathbb{F}}{A}\right)}{\left(\frac{\mathrm{v}}{L}\right)} [=] \frac{MLt^{-1}L^{-2}}{Lt^{-1}L^{-1}} = \frac{ML^{-1}t^{-2}}{t^{-1}} = ML^{-1}t^{-1}$$

Sometimes the gradient is that of the momentum ($\rho\mathrm{v_X}$), thereby defining a new viscosity called kinematic one ($\upsilon = \eta/\rho$)

$$\tau_{\mathrm{XY}} = -\frac{\eta}{\rho}\frac{\mathrm{d}(\rho\mathrm{v_X})}{\mathrm{dY}} = -\upsilon\frac{\mathrm{d}(\rho\mathrm{v_X})}{\mathrm{dY}} \qquad\rightarrow\qquad \upsilon = \frac{\eta}{\rho}[=]\frac{ML^{-1}t^{-1}}{ML^{-3}} = L^2t^{-1}$$

Question g. In the Fick's law (section a of reference problem 0.7), diffusivity of a substance i (D_i) is the coefficient of proportionality between the mass flow density (J_i) and the concentration gradient of this substance ($\mathrm{d}c_i/\mathrm{dY}$) in the transfer direction

$$J_i = -D_i\frac{\mathrm{d}c_i}{\mathrm{dY}} \quad\rightarrow\quad D_i = -\frac{J_i}{\left(\frac{\mathrm{d}c_i}{\mathrm{dY}}\right)} [=] \frac{\left(\frac{M_i}{At}\right)}{\left(\frac{c_i}{L}\right)} [=] \frac{ML^{-2}t^{-1}}{ML^{-3}L^{-1}} = \frac{ML^{-2}t^{-1}}{ML^{-4}} = L^2t^{-1}$$

Question h. In the Fourier's law (section a of reference problem 0.7), thermal conductivity (λ) is the coefficient of proportionality between the heat flow density ($\mathbb{q}$) and the thermal gradient ($\mathrm{d}T/\mathrm{dY}$) in the transfer direction

$$\mathbb{q} = -\lambda\frac{\mathrm{d}T}{\mathrm{dY}} \quad\rightarrow\quad \lambda = -\frac{\mathbb{q}}{\left(\frac{\mathrm{d}T}{\mathrm{dY}}\right)} [=] \frac{\left(\frac{Q}{At}\right)}{\left(\frac{T}{L}\right)} [=] \frac{ML^2t^{-2}L^{-2}t^{-1}}{TL^{-1}} = \frac{Mt^{-3}}{TL^{-1}} = MLT^{-1}t^{-3}$$

1.2. Make a double-entry table showing the relations between the following ways of expressing the composition of binary mixtures: mole fraction, mass fraction, molarity, mass concentration and molality.

For the sake of simplicity, it is assumed that all properties in this problem are expressed in units of the International System.

The binary mixture consists of solute A and solvent B, and the mole (or molar) fractions and mass fractions satisfy that

$$\tilde{x}_A + \tilde{x}_B = 1 \qquad \rightarrow\ \tilde{x}_A = 1 - \tilde{x}_B$$

$$\hat{x}_A + \hat{x}_B = 1 \qquad \rightarrow\ \hat{x}_A = 1 - \hat{x}_B$$

and the mass density will be

$$\hat{\rho}_{AB} = \frac{M_A + M_B}{V}$$

The mass concentration of substance A in the binary mixture is equal to the mass of A divided by the total volume occupied by the mixture, V

$$\hat{c}_A = \frac{M_A}{V}$$

Thus, the mass fraction and the mass concentration will be related through the density

$$\frac{\hat{c}_A}{\hat{\rho}_{AB}} = \left(\frac{M_A}{V}\right)\left(\frac{V}{M_A + M_B}\right) = \frac{M_A}{M_A + M_B} = \hat{x}_A \qquad [1]$$

Furthermore, in reference problem 0.14 the molarity of a substance A in a binary mixture is defined as the number of moles of A divided by the total volume of the mixture

$$\tilde{\mathbb{M}}_A = \tilde{c}_A = \frac{n_A}{V}$$

and since the number of moles of A is the quotient between its mass and its molecular weight, it is easily deduced that the molarity is equal to the mass concentration of A divided by the molecular weight of A

$$\frac{\hat{c}_A}{\mathfrak{W}_A} = \frac{1}{\mathfrak{W}_A}\left(\frac{M_A}{V}\right) = \frac{n_A}{V} = \tilde{\mathbb{M}}_A \qquad [2]$$

$$\frac{\hat{\rho}_{AB}\hat{x}_A}{\mathfrak{W}_A} = \frac{1}{\mathfrak{W}_A}\left(\frac{M_A + M_B}{V}\right)\left(\frac{M_A}{M_A + M_B}\right) = \frac{1}{\mathfrak{W}_A}\left(\frac{M_A}{V}\right) = \frac{n_A}{V} = \tilde{\mathbb{M}}_A \qquad [3]$$

and the molar and mass fractions will be related to each other by

$$\tilde{x}_A = \frac{n_A}{n_A + n_B} = \frac{\frac{M_A}{\mathfrak{W}_A}}{\frac{M_A}{\mathfrak{W}_A} + \frac{M_B}{\mathfrak{W}_B}} = \frac{\frac{\hat{x}_A M_{tot}}{\mathfrak{W}_A}}{\frac{\hat{x}_A M_{tot}}{\mathfrak{W}_A} + \frac{\hat{x}_B M_{tot}}{\mathfrak{W}_B}} = \frac{\hat{x}_A}{\hat{x}_A + \frac{\mathfrak{W}_A}{\mathfrak{W}_B}(1 - \hat{x}_A)} =$$

$$= \frac{\mathfrak{W}_B \hat{x}_A}{\mathfrak{W}_B \hat{x}_A + \mathfrak{W}_A (1 - \hat{x}_A)} = \frac{\mathfrak{W}_B \hat{x}_A}{\mathfrak{W}_A + \hat{x}_A (\mathfrak{W}_B - \mathfrak{W}_A)} \qquad [4]$$

$$\hat{x}_A = \frac{M_A}{M_A + M_B} = \frac{n_A \mathfrak{W}_A}{n_A \mathfrak{W}_A + n_B \mathfrak{W}_B} = \frac{\tilde{x}_A n \mathfrak{W}_A}{\tilde{x}_A n \mathfrak{W}_A + \tilde{x}_B n \mathfrak{W}_B} =$$

$$= \frac{\tilde{x}_A \mathfrak{W}_A}{\tilde{x}_A \mathfrak{W}_A + (1 - \hat{x}_A) \mathfrak{W}_B} = \frac{\tilde{x}_A \mathfrak{W}_A}{\mathfrak{W}_B + \tilde{x}_A (\mathfrak{W}_A - \mathfrak{W}_B)} \qquad [5]$$

The mole fraction is expressed as a function of the mass concentration by introducing [1] in [4]

$$\tilde{x}_A = \frac{\mathfrak{W}_B \hat{x}_A}{\mathfrak{W}_A + \hat{x}_A (\mathfrak{W}_B - \mathfrak{W}_A)} = \frac{\mathfrak{W}_B \frac{\hat{c}_A}{\hat{\rho}_{AB}}}{\mathfrak{W}_A + \frac{\hat{c}_A}{\hat{\rho}_{AB}} (\mathfrak{W}_B - \mathfrak{W}_A)} = \frac{\mathfrak{W}_B \hat{c}_A}{\mathfrak{W}_A \hat{\rho}_{AB} + \hat{c}_A (\mathfrak{W}_B - \mathfrak{W}_A)} \qquad [6]$$

If [2] is combined with [6], the mole fraction is expressed as a function of molarity

$$\tilde{x}_A = \frac{\mathfrak{W}_B \hat{c}_A}{\mathfrak{W}_A \hat{\rho}_{AB} + \hat{c}_A (\mathfrak{W}_B - \mathfrak{W}_A)} = \frac{\mathfrak{W}_B \widetilde{\mathbb{M}}_A \mathfrak{W}_A}{\mathfrak{W}_A \hat{\rho}_{AB} + \widetilde{\mathbb{M}}_A \mathfrak{W}_A (\mathfrak{W}_B - \mathfrak{W}_A)} = \frac{\mathfrak{W}_B \widetilde{\mathbb{M}}_A}{\hat{\rho}_{AB} + \widetilde{\mathbb{M}}_A (\mathfrak{W}_B - \mathfrak{W}_A)}$$

and by introducing [5] in [3], molarity becomes a function of the mole fraction

$$\widetilde{\mathbb{M}}_A = \frac{\hat{\rho}_{AB} \hat{x}_A}{\mathfrak{W}_A} = \frac{\hat{\rho}_{AB}}{\mathfrak{W}_A} \frac{\tilde{x}_A \mathfrak{W}_A}{\mathfrak{W}_B + \tilde{x}_A (\mathfrak{W}_A - \mathfrak{W}_B)} = \frac{\tilde{x}_A \hat{\rho}_{AB}}{\mathfrak{W}_B + \tilde{x}_A (\mathfrak{W}_A - \mathfrak{W}_B)} \qquad [7]$$

And this last expression [7] together with [2] shows the mass concentration as a function of the mole fraction

$$\hat{c}_A = \widetilde{\mathbb{M}}_A \mathfrak{W}_A = \frac{\tilde{x}_A \hat{\rho}_{AB} \mathfrak{W}_A}{\mathfrak{W}_B + \tilde{x}_A (\mathfrak{W}_A - \mathfrak{W}_B)}$$

On the other hand, molality is the number of moles of A divided by the mass of solvent (section b of reference problem 0.14), which implies that it will be function of the molar or mass fractions as follows

$$\mathbb{m}_A = \frac{n_A}{M_B} = \frac{n_A}{n_B \mathfrak{W}_B} = \frac{\tilde{x}_A n}{\tilde{x}_B n \mathfrak{W}_B} = \frac{\tilde{x}_A}{(1 - \tilde{x}_A)\mathfrak{W}_B}$$

$$\mathbb{m}_A = \frac{n_A}{M_B} = \frac{M_A/\mathfrak{W}_A}{M_B} = \frac{1}{\mathfrak{W}_A}\frac{\hat{x}_A M_{tot}}{\hat{x}_B M_{tot}} = \frac{\hat{x}_A}{\mathfrak{W}_A(1 - \hat{x}_A)}$$

Notice that these expressions are similar to those of the molar and mass ratios (moles or mass of A divided by the moles or masses of all substances that are not A), except for the presence of the molecular weight. If the equation that includes the mass fractions is combined with [1] or [2]

$$\mathbb{m}_A = \frac{\hat{x}_A}{\mathfrak{W}_A(1 - \hat{x}_A)} = \frac{\frac{\hat{c}_A}{\hat{\rho}_{AB}}}{\mathfrak{W}_A\left(1 - \frac{\hat{c}_A}{\hat{\rho}_{AB}}\right)} = \frac{\hat{c}_A}{\mathfrak{W}_A \hat{\rho}_{AB}\left(\frac{\hat{\rho}_{AB}}{\hat{\rho}_{AB}} - \frac{\hat{c}_A}{\hat{\rho}_{AB}}\right)} = \frac{\hat{c}_A}{\mathfrak{W}_A(\hat{\rho}_{AB} - \hat{c}_A)}$$

$$\mathbb{m}_A = \frac{\hat{x}_A}{\mathfrak{W}_A(1 - \hat{x}_A)} = \frac{\frac{\mathfrak{W}_A \widetilde{\mathbb{M}}_A}{\hat{\rho}_{AB}}}{\mathfrak{W}_A\left(1 - \frac{\mathfrak{W}_A \widetilde{\mathbb{M}}_A}{\hat{\rho}_{AB}}\right)} = \frac{\mathfrak{W}_A \widetilde{\mathbb{M}}_A}{\mathfrak{W}_A \hat{\rho}_{AB}\left(\frac{\hat{\rho}_{AB}}{\hat{\rho}_{AB}} - \frac{\mathfrak{W}_A \widetilde{\mathbb{M}}_A}{\hat{\rho}_{AB}}\right)} = \frac{\widetilde{\mathbb{M}}_A}{\left(\hat{\rho}_{AB} - \mathfrak{W}_A \widetilde{\mathbb{M}}_A\right)}$$

Mass or molar fractions are expressed as a function of molality by means of their definition

$$\tilde{x}_A = \frac{n_A}{n_A + n_B} = \frac{n_A}{n_A + \frac{M_B}{\mathfrak{W}_B}} = \frac{1}{1 + \frac{M_B}{\mathfrak{W}_B n_A}} = \frac{1}{1 + \frac{1}{\mathfrak{W}_B \mathbb{m}_A}} = \frac{\mathfrak{W}_B \mathbb{m}_A}{\mathfrak{W}_B \mathbb{m}_A + 1}$$

$$\hat{x}_A = \frac{M_A}{M_A + M_B} = \frac{n_A \mathfrak{W}_A}{n_A \mathfrak{W}_A + M_B} = \frac{\mathfrak{W}_A}{\mathfrak{W}_A + \frac{M_B}{n_A}} = \frac{\mathfrak{W}_A}{\mathfrak{W}_A + \frac{1}{\mathbb{m}_A}} = \frac{\mathbb{m}_A \mathfrak{W}_A}{\mathbb{m}_A \mathfrak{W}_A + 1}$$

Finally, by combining the last formula with [1] and [3], molarity becomes a function of molality

$$\widetilde{\mathbb{M}}_A = \frac{\hat{\rho}_{AB} \mathbb{m}_A}{\mathfrak{W}_A \mathbb{m}_A + 1}$$

And all these relations are summarized in the following table

	Mole fraction	Mass fraction	Mass concentration	Molarity	Molality
Mole fraction	$\tilde{x}_A$	$\frac{\mathfrak{W}_B\hat{x}_A}{\mathfrak{W}_A+\hat{x}_A(\mathfrak{W}_B-\mathfrak{W}_A)}$	$\frac{\mathfrak{W}_B\hat{c}_A}{\mathfrak{W}_A\hat{\rho}_{AB}+\hat{c}_A(\mathfrak{W}_B-\mathfrak{W}_A)}$	$\frac{\mathfrak{W}_B\widetilde{\mathbb{M}}_A}{\hat{\rho}_{AB}+\widetilde{\mathbb{M}}_A(\mathfrak{W}_B-\mathfrak{W}_A)}$	$\frac{\mathfrak{W}_B\mathbb{m}_A}{\mathfrak{W}_B\mathbb{m}_A+1}$
Mass fraction	$\frac{\tilde{x}_A\mathfrak{W}_A}{\mathfrak{W}_B+\tilde{x}_A(\mathfrak{W}_A-\mathfrak{W}_B)}$	$\hat{x}_A$	$\frac{\hat{c}_A}{\hat{\rho}_{AB}}$	$\frac{\mathfrak{W}_A\widetilde{\mathbb{M}}_A}{\hat{\rho}_{AB}}$	$\frac{\mathbb{m}_A\mathfrak{W}_A}{\mathbb{m}_A\mathfrak{W}_A+1}$
Mass concentration	$\frac{\tilde{x}_A\hat{\rho}_{AB}\mathfrak{W}_A}{\mathfrak{W}_B+\tilde{x}_A(\mathfrak{W}_A-\mathfrak{W}_B)}$	$\hat{x}_A\hat{\rho}_{AB}$	$\hat{c}_A$	$\widetilde{\mathbb{M}}_A\mathfrak{W}_A$	$\frac{\hat{\rho}_{AB}\mathbb{m}_A\mathfrak{W}_A}{\mathbb{m}_A\mathfrak{W}_A+1}$
Molarity	$\frac{\tilde{x}_A\hat{\rho}_{AB}}{\mathfrak{W}_B+\tilde{x}_A(\mathfrak{W}_A-\mathfrak{W}_B)}$	$\frac{\hat{\rho}_{AB}\hat{x}_A}{\mathfrak{W}_A}$	$\frac{\hat{c}_A}{\mathfrak{W}_A}$	$\widetilde{\mathbb{M}}_A$	$\frac{\hat{\rho}_{AB}\mathbb{m}_A}{\mathfrak{W}_A\mathbb{m}_A+1}$
Molality	$\frac{\tilde{x}_A}{(1-\tilde{x}_A)\mathfrak{W}_B}$	$\frac{\hat{x}_A}{\mathfrak{W}_A(1-\hat{x}_A)}$	$\frac{\hat{c}_A}{\mathfrak{W}_A(\hat{\rho}_{AB}-\hat{c}_A)}$	$\frac{\widetilde{\mathbb{M}}_A}{(\hat{\rho}_{AB}-\mathfrak{W}_A\widetilde{\mathbb{M}}_A)}$	$\mathbb{m}_A$

1.3. Explain the conversion of temperatures and thermometric readings between the Fahrenheit, Celsius, Rankine, and Rèamur scales.

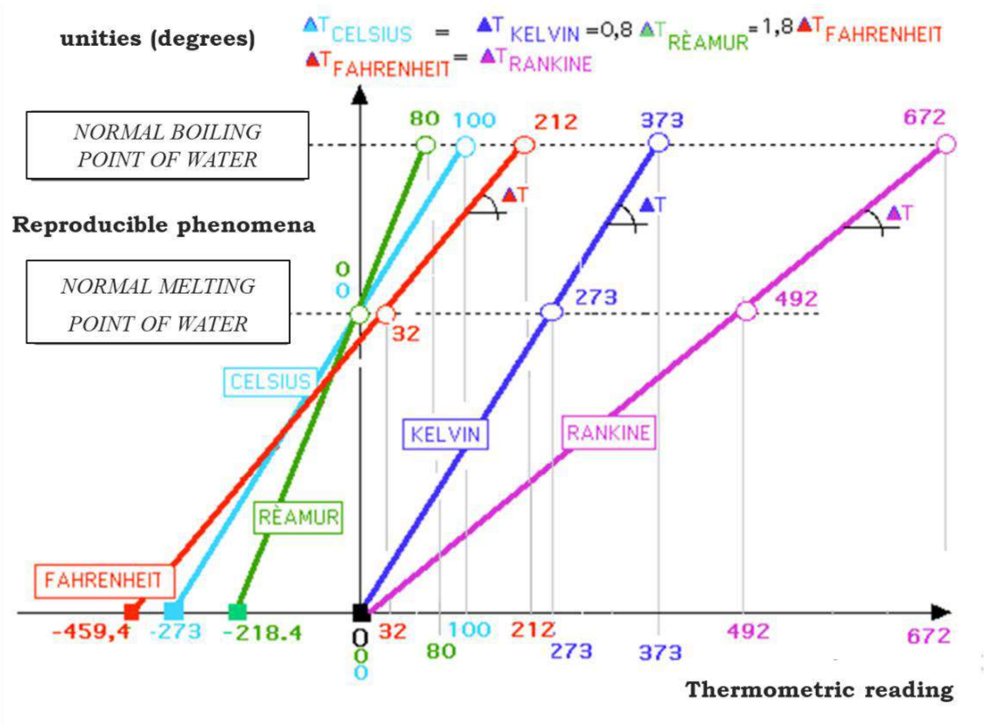
The temperature read on each scale is related to the thermometric magnitude by the following linear equation

$$\begin{bmatrix}\text{Thermometric}\\ \text{magnitude}\end{bmatrix} = \begin{bmatrix}\text{Temperature}\\ \text{interval}\\ \text{(degree)}\end{bmatrix} \cdot \begin{bmatrix}\text{Temperature}\\ \text{reading on}\\ \text{each scale}\end{bmatrix} + [\text{Intercept}]$$

$$\Theta \qquad = \qquad \alpha \qquad \cdot \qquad T \qquad + \qquad \beta$$

where for each scale the normal boiling and melting points of water and the absolute zero are defined as

	°C	°K	°Re	°F	°R
Absolute zero	-273	0	-218.4	-459.4	0
Melting point of water	0	273	0	32	492
Boiling point of water	100	373	80	212	672



Therefore, in the Celsius scale

$$\Theta_0^{°C} = \beta^{°C}$$
$$\Theta_{100}^{°C} = 100\alpha^{°C} + \beta^{°C}$$

in the Rèamur one

$$\begin{aligned}\Theta_0^{\circ\mathrm{Re}} &= \beta^{\circ\mathrm{Re}} \\ \Theta_{80}^{\circ\mathrm{Re}} &= 80\alpha^{\circ\mathrm{Re}} + \beta^{\circ\mathrm{Re}}\end{aligned}$$

in the Farenheit one

$$\begin{aligned}\Theta_0^{\circ\mathrm{F}} &= \beta^{\circ\mathrm{F}} \\ \Theta_{212}^{\circ\mathrm{F}} &= 212\alpha^{\circ\mathrm{F}} + \beta^{\circ\mathrm{F}}\end{aligned}$$

in the Kelvin one

$$\begin{aligned}\Theta_0^{\mathrm{K}} &= \beta^{\mathrm{K}} = 0 \\ \Theta_{273}^{\mathrm{K}} &= 273\alpha^{\mathrm{K}}\end{aligned}$$

and in the Rankine one

$$\begin{aligned}\Theta_0^{\circ\mathrm{R}} &= \beta^{\circ\mathrm{R}} = 0 \\ \Theta_{492}^{\circ\mathrm{R}} &= 492\alpha^{\circ\mathrm{R}}\end{aligned}$$

The thermometric magnitude must be the same in any reference condition (generally those of easily and reliably reproducible phenomena such as the boiling and melting point of water at atmospheric pressure), but its measurement will generate different temperatures according to the scales employed. Relations between these scales will be given by

Celsius and Kelvin

$$\left.\begin{aligned}100\alpha^{℃} + \beta^{℃} &= 373\alpha^{\mathrm{K}} + 0 \\ 0\alpha^{℃} + \beta^{℃} &= 273\alpha^{\mathrm{K}} + 0\end{aligned}\right\} 100\alpha^{℃} + 273\alpha^{\mathrm{K}} = 373\alpha^{\mathrm{K}} \quad \rightarrow \quad \alpha^{℃} = \alpha^{\mathrm{K}}$$

$$\begin{aligned}\alpha^{℃}T^{℃} + \quad \beta^{℃} \quad &= \alpha^{\mathrm{K}}T^{\mathrm{K}} + \beta^{\mathrm{K}} \\ \alpha^{\mathrm{K}}T^{℃} + \ 273\alpha^{\mathrm{K}} &= \alpha^{\mathrm{K}}T^{\mathrm{K}} + 0 \qquad \rightarrow \quad T^{℃} = T^{\mathrm{K}} - 273\end{aligned}$$

Celsius and Réamur

$$\left.\begin{aligned}100\alpha^{℃} + \beta^{℃} &= 80\alpha^{\circ\mathrm{Re}} + \beta^{\circ\mathrm{Re}} \\ 0\alpha^{℃} + \beta^{℃} &= 0\alpha^{\circ\mathrm{Re}} + \beta^{\circ\mathrm{Re}}\end{aligned}\right\} 100\alpha^{℃} = 80\alpha^{\circ\mathrm{Re}} \quad \rightarrow \quad \alpha^{℃} = 0.8\alpha^{\circ\mathrm{Re}}$$

$$\begin{aligned}\alpha^{℃} \cdot \ T^{℃} + \quad \beta^{℃} \quad &= \alpha^{\circ\mathrm{Re}}T^{\circ\mathrm{Re}} + \beta^{\circ\mathrm{Re}} \\ 0.8\alpha^{\circ\mathrm{R}}T^{℃} + \quad \beta^{\circ\mathrm{Re}} \quad &= \alpha^{\circ\mathrm{Re}}T^{\circ\mathrm{Re}} + \beta^{\circ\mathrm{Re}} \quad \rightarrow \quad T^{℃} = \frac{T^{\circ\mathrm{Re}}}{0.8}\end{aligned}$$

Celsius and Farenheit

$$\left.\begin{aligned}100\alpha^{\circ\mathrm{C}}+\beta^{\circ\mathrm{C}}&=212\alpha^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}}\\0\alpha^{\circ\mathrm{C}}+\beta^{\circ\mathrm{C}}&=32\alpha^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}}\end{aligned}\right\}100\alpha^{\circ\mathrm{C}}+32\alpha^{\circ\mathrm{F}}=212\alpha^{\circ\mathrm{F}}\quad\rightarrow\ \alpha^{\circ\mathrm{C}}=1.8\alpha^{\circ\mathrm{F}}$$

$$\alpha^{\circ\mathrm{C}}\cdot T^{\circ\mathrm{C}}+\qquad\beta^{\circ\mathrm{C}}\qquad=\alpha^{\circ\mathrm{F}}T^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}}$$

$$1.8\alpha^{\circ\mathrm{F}}T^{\circ\mathrm{C}}+\ (32\alpha^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}})=\alpha^{\circ\mathrm{F}}T^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}}\quad\rightarrow\quad T^{\circ\mathrm{C}}=\frac{T^{\circ\mathrm{F}}-32}{1.8}$$

Celsius and Rankine

$$\left.\begin{aligned}100\alpha^{\circ\mathrm{C}}+\beta^{\circ\mathrm{C}}&=672\alpha^{\circ\mathrm{R}}+0\\0\alpha^{\circ\mathrm{C}}+\beta^{\circ\mathrm{C}}&=492\alpha^{\circ\mathrm{R}}+0\end{aligned}\right\}100\alpha^{\circ\mathrm{C}}+492\alpha^{\circ R}=672\alpha^{\circ\mathrm{R}}\quad\rightarrow\ \alpha^{\circ\mathrm{C}}=1.8\alpha^{\circ\mathrm{R}}$$

$$\alpha^{\circ\mathrm{C}}\cdot T^{\circ\mathrm{C}}+\quad\beta^{\circ\mathrm{C}}\quad=\alpha^{\circ\mathrm{R}}T^{\circ\mathrm{R}}+\beta^{\circ\mathrm{R}}$$

$$1.8\alpha^{\circ\mathrm{R}}T^{\circ\mathrm{C}}+\ 492\alpha^{\circ\mathrm{R}}=\alpha^{\circ\mathrm{R}}T^{\circ\mathrm{R}}+0\quad\rightarrow\quad T^{\circ\mathrm{C}}=\frac{T^{\circ\mathrm{R}}-492}{1.8}$$

Kelvin and Réamur

$$\left.\begin{aligned}373\alpha^{\mathrm{K}}+0&=80\alpha^{\circ\mathrm{Re}}+\beta^{\circ\mathrm{Re}}\\273\alpha^{\mathrm{K}}+0&=0\alpha^{\circ\mathrm{Re}}+\beta^{\circ\mathrm{Re}}\end{aligned}\right\}373\alpha^{\mathrm{K}}=80\alpha^{\circ\mathrm{Re}}+273\alpha^{\mathrm{K}}\quad\rightarrow\ \alpha^{\mathrm{K}}=0.8\alpha^{\circ\mathrm{Re}}$$

$$\alpha^{\mathrm{K}}\quad\cdot\ T^{\mathrm{K}}+\beta^{\mathrm{K}}=\alpha^{\circ\mathrm{Re}}T^{\circ\mathrm{Re}}+\quad\beta^{\circ\mathrm{Re}}$$

$$0.8\alpha^{\circ\mathrm{Re}}T^{\mathrm{K}}\ +\ 0\quad=\alpha^{\circ\mathrm{Re}}T^{\circ\mathrm{Re}}+273\alpha^{\mathrm{K}}\quad\rightarrow\quad T^{\mathrm{K}}=\frac{T^{\circ\mathrm{Re}}+273}{0.8}$$

Kelvin and Farenheit

$$\left.\begin{aligned}373\alpha^{\mathrm{K}}+0&=212\alpha^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}}\\273\alpha^{\mathrm{K}}+0&=32\alpha^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}}\end{aligned}\right\}(373-273)\alpha^{\mathrm{K}}=(212-32)\alpha^{\circ\mathrm{F}}\quad\rightarrow\ \alpha^{\mathrm{K}}=1.8\alpha^{\circ\mathrm{F}}$$

$$\alpha^{\mathrm{K}}\quad\cdot\ T^{\mathrm{K}}+\beta^{\mathrm{K}}=\alpha^{\circ\mathrm{F}}T^{\circ\mathrm{F}}+\qquad\beta^{\circ\mathrm{F}}$$

$$1.8\alpha^{\circ\mathrm{F}}T^{\mathrm{K}}\quad+\ 0\quad=\alpha^{\circ\mathrm{F}}T^{\circ\mathrm{F}}\ +(1.8\cdot273-32)\alpha^{\mathrm{K}}\quad\rightarrow\quad T^{\mathrm{K}}=\frac{T^{\circ\mathrm{F}}-32}{1.8}+273$$

Kelvin and Rankine

$$\left.\begin{aligned}373\alpha^{\mathrm{K}}+0&=672\alpha^{\circ\mathrm{R}}+0\\273\alpha^{\mathrm{K}}+0&=492\alpha^{\circ\mathrm{R}}+0\end{aligned}\right\}\ \rightarrow\ \alpha^{\mathrm{K}}=1.8\alpha^{\circ\mathrm{R}}$$

$$\alpha^{\mathrm{K}}\ \cdot\ T^{\mathrm{K}}+\beta^{\mathrm{K}}=\alpha^{\circ\mathrm{R}}T^{\circ\mathrm{R}}+\ \beta^{\circ\mathrm{R}}$$

$$1.8\alpha^{\circ\mathrm{F}}T^{\mathrm{K}}\ +\ 0\ =\alpha^{\circ\mathrm{R}}T^{\circ\mathrm{R}}\ +\ \ 0\quad\rightarrow\quad T^{\mathrm{K}}=\frac{T^{\circ\mathrm{R}}}{1.8}$$

Réamur and Farenheit

$$\left.\begin{array}{r}80\alpha^{\circ\mathrm{Re}}+\beta^{\circ\mathrm{Re}}=212\alpha^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}}\\ 0\alpha^{\circ\mathrm{Re}}+\beta^{\circ\mathrm{Re}}=32\alpha^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}}\end{array}\right\} 80\alpha^{\circ\mathrm{Re}}+32\alpha^{\circ\mathrm{F}}=212\alpha^{\circ\mathrm{F}} \;\rightarrow\; \alpha^{\circ\mathrm{Re}}=2.25\alpha^{\circ\mathrm{F}}$$

$$\begin{array}{l}\alpha^{\circ\mathrm{Re}}\cdot T^{\circ\mathrm{Re}}+\beta^{\circ\mathrm{Re}}=\alpha^{\circ\mathrm{F}}T^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}}\\ 2.25\alpha^{\circ\mathrm{F}}T^{\circ\mathrm{Re}}+(32\alpha^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}})=\alpha^{\circ\mathrm{F}}T^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}} \;\rightarrow\; T^{\circ\mathrm{Re}}=\dfrac{T^{\circ\mathrm{F}}-32}{2.25}\end{array}$$

Réamur and Rankine

$$\left.\begin{array}{r}80\alpha^{\circ\mathrm{Re}}+\beta^{\circ\mathrm{Re}}=672\alpha^{\circ\mathrm{R}}+0\\ 0\alpha^{\circ\mathrm{Re}}+\beta^{\circ\mathrm{Re}}=492\alpha^{\circ\mathrm{R}}+0\end{array}\right\} 80\alpha^{\circ\mathrm{Re}}+492\alpha^{\circ\mathrm{R}}=672\alpha^{\circ\mathrm{R}} \;\rightarrow\; \alpha^{\circ\mathrm{Re}}=2.25\alpha^{\circ\mathrm{R}}$$

$$\begin{array}{l}\alpha^{\circ\mathrm{Re}}\cdot T^{\circ\mathrm{Re}}+\beta^{\circ\mathrm{Re}}=\alpha^{\circ\mathrm{R}}T^{\circ\mathrm{R}}+\beta^{\circ\mathrm{R}}\\ 2.25\alpha^{\circ\mathrm{R}}T^{\circ\mathrm{Re}}+492\alpha^{\circ\mathrm{R}}=\alpha^{\circ\mathrm{R}}T^{\circ\mathrm{R}}+0 \;\rightarrow\; T^{\circ\mathrm{Re}}=\dfrac{T^{\circ\mathrm{R}}-492}{2.25}\end{array}$$

Farenheit and Rankine

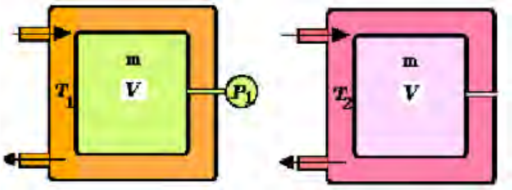
$$\left.\begin{array}{r}212\alpha^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}}=672\alpha^{\circ\mathrm{R}}+0\\ 32\alpha^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}}=492\alpha^{\circ\mathrm{R}}+0\end{array}\right\} (212-32)\alpha^{\circ\mathrm{F}}=(672-492)\alpha^{\circ\mathrm{R}} \;\rightarrow\; \alpha^{\circ\mathrm{F}}=\alpha^{\circ\mathrm{R}}$$

$$\begin{array}{l}\alpha^{\circ\mathrm{F}}T^{\circ\mathrm{F}}+\beta^{\circ\mathrm{F}}=\alpha^{\circ\mathrm{R}}T^{\circ\mathrm{R}}+\beta^{\circ\mathrm{R}}\\ \alpha^{\circ\mathrm{R}}T^{\circ\mathrm{F}}+(492-32)\alpha^{\circ\mathrm{R}}=\alpha^{\circ\mathrm{R}}T^{\circ\mathrm{R}}+0 \;\rightarrow\; T^{\circ\mathrm{F}}=T^{\circ\mathrm{R}}+460\end{array}$$

(The interested reader is suggested to make a double-entry table with these relations.)

1.4. Two gas thermometers consist of containers of invariable volume (both identical), one filled with an ideal gas and the other with a Van der Waals gas. Both are calibrated by taking the triple point (T_t, P_t) and the normal boiling point (T_b, P_b) of an unspecified substance. When will they give the same reading?

They are constant-volume gas thermometers: they measure the pressure variation as a function of temperature.



For the Van der Waals gas (section c of reference problem 0.6)

$$P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

in the triple point of the unspecified substance

$$P_t = \frac{nRT_t}{V-nb} - \frac{an^2}{V^2}$$

and in the normal boiling point

$$P_b = \frac{nRT_b}{V-nb} - \frac{an^2}{V^2}$$

Since the volume is constant, $nR/(V - nb)$ and an^2/V^2 will be constant too, and pressure will become a linear function of temperature. By solving the system of equations, we find that

$$\frac{nR}{V-nb} = \frac{P_t - P_b}{T_t - T_b} \quad ; \quad \frac{an^2}{V^2} = \frac{P_bT_t - P_tT_b}{T_t - T_b}$$

and the relation between pressure and temperature will be

$$P = \left(\frac{P_t - P_b}{T_t - T_b}\right) T^{VdW} - \left(\frac{P_bT_t - P_tT_b}{T_t - T_b}\right)$$

For the ideal gas (section b of reference problem 0.6)

$$P = \frac{nRT}{V}$$

by introducing the boiling and triple points, and rearranging the terms

$$\left.\begin{aligned} P_t &= \frac{nRT_t}{V} \\ P_b &= \frac{nRT_b}{V} \end{aligned}\right\} P_t - P_b = \frac{nR}{V}(T_t - T_b) \qquad \rightarrow \frac{nR}{V} = \frac{P_t - P_b}{T_t - T_b}$$

nR/V is constant, and the equation of a straight line without intercept emerges

$$P = \left(\frac{P_t - P_b}{T_t - T_b}\right) T^{id}$$

Finally, the relation between the two thermometrical readings at the same pressure is

$$\left(\frac{P_t - P_b}{T_t - T_b}\right) T^{id} = \left(\frac{P_t - P_b}{T_t - T_b}\right) T^{VdW} - \left(\frac{P_b T_t - P_t T_b}{T_t - T_b}\right)$$

$$T^{id} = T^{VdW} - \left(\frac{P_b T_t - P_t T_b}{P_t - P_b}\right)$$

showing that the two readings will be the same only when the intercept becomes zero, i.e., when the unspecified substance used in the calibration satisfies that

$$P_b T_t = P_t T_b$$

1.5. The thermal conductivity of steel is λ =39 kcal/(h·m·°C). Express it in

a) BTU/(h·ft·°F).

b) Units of the International System.

c) Units of the cegesimal system.

Question a. By applying one of the equations given in reference problem 0.1

$$\mathbb{x}_1\mathbb{u}_1 = \mathbb{x}_2\mathbb{u}_2$$

and comparing it with the datum of the statement of the problem

$$\underbrace{39}_{\mathbb{x}_1}\underbrace{\frac{\mathrm{kcal}}{\mathrm{h\cdot m\cdot {}^{\circ}C}}}_{\mathbb{u}_1} = \mathbb{x}_2\underbrace{\frac{\mathrm{BTU}}{\mathrm{h\cdot ft\cdot {}^{\circ}F}}}_{\mathbb{u}_2}$$

the solution is to identify the dimensionless factor $\mathbb{ky}_{12}$. This is not found in tables of appendix I, but can be calculated from the other conversion factors tabulated there.

$$1\ \mathrm{kcal} = \mathbb{x}_3\ \mathrm{BTU} \xrightarrow{tables} \mathbb{ky}_{\mathrm{BTU-kcal}} = 3.97 \rightarrow \mathrm{kcal} = 3.97\ \mathrm{BTU}$$

$$1\ \mathrm{m} = \mathbb{x}_4\ \mathrm{ft} \xrightarrow{tables} \mathbb{ky}_{\mathrm{ft-m}} = 3.28 \rightarrow \mathrm{m} = 3.97\ \mathrm{ft}$$

$$1\ {}^{\circ}\mathrm{C} = \mathbb{x}_5\ {}^{\circ}\mathrm{F} \xrightarrow{tables} \mathbb{ky}_{{}^{\circ}\mathrm{F}-{}^{\circ}\mathrm{C}} = 1.8 \rightarrow {}^{\circ}\mathrm{C} = 1.8\ {}^{\circ}\mathrm{F}$$

With these data we evaluate $\mathbb{ky}_{\frac{\mathrm{kcal}}{\mathrm{hm^{\circ}C}}-\frac{\mathrm{BTU}}{\mathrm{hft^{\circ}F}}}$ and get $\mathbb{x}_2$

$$39\ \frac{(3.97\ \mathrm{BTU})}{\mathrm{h}\cdot(3.97\ \mathrm{ft})\cdot(1.8^{\circ}\mathrm{F})} = 39 \times \underbrace{0.672}_{\mathbb{ky}_{12}}\ \frac{\mathrm{BTU}}{\mathrm{h\cdot ft.{}^{\circ}F}} = \underbrace{26.22}_{\mathbb{x}_2}\frac{\mathrm{BTU}}{\mathrm{h\cdot ft.{}^{\circ}F}}$$

Question b. For units of the International System

$$\underbrace{39}_{\mathbb{x}_1}\underbrace{\frac{\mathrm{kcal}}{\mathrm{h\cdot m\cdot {}^{\circ}C}}}_{\mathbb{u}_1} = \mathbb{x}_6\underbrace{\frac{\mathrm{J}}{\mathrm{s\cdot m\cdot K}}}_{\mathbb{u}_6}$$

and by employing appendix I or well-known data

$$1\ \mathrm{kcal} = \mathbb{x}_7\ \mathrm{J} \xrightarrow{tables} \mathbb{ky}_{\mathrm{J-kcal}} = 4180 \rightarrow \mathrm{kcal} = 4180\ \mathrm{J}$$

$$1\ \mathrm{h} = \mathbb{x}_8\ \mathrm{s} \xrightarrow{known} \mathbb{ky}_{\mathrm{s-h}} = 3600 \rightarrow \mathrm{h} = 3600\ \mathrm{s}$$

$$1\ {}^\circ\mathrm{C} = \mathbb{x}_9\ \mathrm{K} \xrightarrow{tables} \mathbb{ky}_{\mathrm{K-{}^\circ C}} = 1.0 \ \rightarrow {}^\circ\mathrm{C} = \mathrm{K}$$

from which we get the value of $\mathbb{ky}_{\frac{\mathrm{kcal}}{\mathrm{hm^\circ C}}-\frac{\mathrm{J}}{\mathrm{smK}}}$ that allows the finding of $\mathbb{x}_6$

$$39\ \frac{(4180\ \mathrm{J})}{(3600\ \mathrm{s})\cdot\mathrm{m}\cdot(\mathrm{K})} = 39\times\underbrace{1.16}_{\mathbb{ky}_{16}}\ \frac{\mathrm{J}}{\mathrm{s\cdot m\cdot K}} = \underbrace{45.24}_{\mathbb{x}_6}\frac{\mathrm{J}}{\mathrm{s\cdot m\cdot K}}$$

Question c. With regards to the units of the cegesimal system

$$\underbrace{39}_{\mathbb{x}_1}\ \underbrace{\frac{\mathrm{kcal}}{\mathrm{h\cdot m\cdot {}^\circ C}}}_{\mathbb{u}_1} = \mathbb{x}_{10}\ \underbrace{\frac{\mathrm{erg}}{\mathrm{s\cdot cm\cdot {}^\circ C}}}_{\mathbb{u}_{10}}$$

$$1\ \mathrm{kcal} = \mathbb{x}_{11}\ \mathrm{erg} \ \xrightarrow{tables} \ \mathbb{ky}_{\mathrm{erg-kcal}} = 1000 \ \rightarrow \mathrm{kcal} = 4.18\cdot 10^{10}\ \mathrm{erg}$$

$$1\ \mathrm{h} = \mathbb{x}_8\ \mathrm{s} \xrightarrow{known} \mathbb{ky}_{\mathrm{s-h}} = 3600 \ \rightarrow \mathrm{h} = 3600\ \mathrm{s}$$

$$1\ \mathrm{m} = \mathbb{x}_{12}\ \mathrm{cm} \xrightarrow{known} \mathbb{ky}_{\mathrm{m-cm}} = 100 \ \rightarrow \mathrm{m} = 100\ \mathrm{cm}$$

being 1.16·10^5 the value of $\mathbb{ky}_{\frac{\mathrm{kcal}}{\mathrm{hm^\circ C}}-\frac{\mathrm{erg}}{\mathrm{scm^\circ C}}}$

$$39\ \frac{\mathrm{kcal}}{\mathrm{h{\cdot}m{\cdot}{}^\circ C}} = 39\frac{(4.18\cdot 10^{10}\ \mathrm{erg})}{(3600\ \mathrm{s})(100\ \mathrm{cm}){}^\circ\mathrm{C}} = 39\times\underbrace{1.16\cdot 10^5}_{\mathbb{ky}_{110}}\ \frac{\mathrm{erg}}{\mathrm{s{\cdot}cm{\cdot}{}^\circ C}} = \underbrace{45.24\cdot 10^5}_{\mathbb{x}_{10}}\frac{\mathrm{erg}}{\mathrm{s{\cdot}cm{\cdot}{}^\circ C}}$$

1.6. The thermal conductivity of water is λ =0.506 kcal/(h·m·°C). Express it in

a) BTU/(h·ft·°F).
b) Units of the International System.
c) Units of the cegesimal system.

Question a. The comparison of one equation of reference problem 0.1

$$\mathbb{x}_1\mathbb{u}_1 = \mathbb{x}_2\mathbb{u}_2$$

with the datum given by the statement of the problem

$$\underbrace{0.506}_{\mathbb{x}_1}\ \underbrace{\frac{\text{kcal}}{\text{h}\cdot\text{m}\cdot{}^\circ\text{C}}}_{\mathbb{u}_1} = \mathbb{x}_2\ \underbrace{\frac{\text{BTU}}{\text{h}\cdot\text{ft}\cdot{}^\circ\text{F}}}_{\mathbb{u}_2}$$

leads to the identification of the dimensionless factor $\mathbb{ky}_{12}$, which is not in tables of appendix I, but can be evaluated from the other conversion factors tabulated there

$$1\ \text{kcal} = 3.97\ \text{BTU}$$

$$1\ \text{m} = 3.28\ \text{ft}$$

$$1\ {}^\circ\text{C} = 1.8\ {}^\circ\text{F}$$

so that

$$0.506\ \frac{\text{kcal}}{\text{h}\cdot\text{m}\cdot{}^\circ\text{C}}\times\frac{3.97\ \text{BTU}}{1\ \text{kcal}}\times\frac{1\ \text{m}}{3.28\ \text{ft}}\times\frac{1{}^\circ\text{C}}{1.8{}^\circ\text{F}} = 0.506\times\underbrace{0.672}_{\mathbb{ky}_{12}}\ \frac{\text{BTU}}{\text{h}\cdot\text{ft.}{}^\circ\text{F}} = \underbrace{0.34}_{\mathbb{x}_2}\frac{\text{BTU}}{\text{h}\cdot\text{ft.}{}^\circ\text{F}}$$

Question b. For units of the International System

$$\underbrace{0.506}_{\mathbb{x}_1}\ \underbrace{\frac{\text{kcal}}{\text{h}\cdot\text{m}\cdot{}^\circ\text{C}}}_{\mathbb{u}_1} = \mathbb{x}_3\ \underbrace{\frac{\text{BTU}}{\text{h}\cdot\text{ft}\cdot{}^\circ\text{F}}}_{\mathbb{u}_3}$$

From appendix I or from well-known data

$$1\ \text{kcal} = 4180\ \text{J}$$

$$1\ \text{h} = 3600\ \text{s}$$

$$1\ {}^\circ\text{C} = 1\ \text{K}$$

and we will get

$$0.506\ \frac{\text{kcal}}{\text{h}\cdot\text{m}\cdot{}^\circ\text{C}}\times\frac{4180\ \text{J}}{1\ \text{kcal}}\times\frac{1\ \text{h}}{3600\ \text{s}}\times\frac{1{}^\circ\text{C}}{1\text{K}} = 0.506\times\underbrace{1.16}_{\mathbb{ky}_{13}}\ \frac{\text{J}}{\text{s}\cdot\text{m}\cdot\text{K}} = \underbrace{0.587}_{\mathbb{x}_3}\frac{\text{J}}{\text{s}\cdot\text{m}\cdot\text{K}}$$

Question c. For the cegesimal system

$$\underbrace{0.506}_{\mathbb{x}_1}\ \underbrace{\frac{\mathrm{kcal}}{\mathrm{h\cdot m\cdot {}^\circ C}}}_{\mathbb{u}_1} = \mathbb{x}_4\ \underbrace{\frac{\mathrm{erg}}{\mathrm{s\cdot cm\cdot {}^\circ C}}}_{\mathbb{u}_4}$$

$$1\ \mathrm{kcal} = 4.18\cdot 10^{10}\ \mathrm{erg}$$

$$1\ \mathrm{h} = 3600\ \mathrm{s}$$

$$1\ \mathrm{m} = 100\ \mathrm{cm}$$

being the conversion

$$0.506\ \frac{\mathrm{kcal}}{\mathrm{h\cdot m\cdot {}^\circ C}}\times\frac{4.18\cdot 10^{10}\mathrm{erg}}{1\ \mathrm{kcal}}\times\frac{1\ \mathrm{h}}{3600\ \mathrm{s}}\times\frac{1\ \mathrm{m}}{100\ \mathrm{cm}} =$$

$$= 0.506\times\underbrace{1.16\cdot 10^5}_{\mathbb{ky}_{14}}\ \frac{\mathrm{erg}}{\mathrm{s\cdot cm\cdot {}^\circ C}} = \underbrace{58.75\cdot 10^3}_{\mathbb{x}_4}\frac{\mathrm{erg}}{\mathrm{s\cdot cm\cdot {}^\circ C}}$$

1.7. The specific heat capacity of a substance that behaves as ideal gas can be calculated by the following empirical equation

$$\boldsymbol{\tilde{C}_P^* = 0.01508 + 1.88 \cdot 10^{-5}T - 5.445 \cdot 10^{-9}T^2}$$

where $\tilde{C}_P^*$ is expressed in BTU/(°F· mol-g) and T in °F. Convert this equation to use temperatures expressed in K and to obtain specific heat capacities in J/(K·mol-g).

In principle, and according to reference problem 0.1, two procedures could be applied:

a) Conversion of the units of C_P^* and T
b) Conversion of the the units of the coefficients 0.01508, $1.88 \cdot 10^{-5}$ and $-5.445 \cdot 10^{-9}$

Procedure a. From tables of appendix I it is found that

$$1 \text{ BTU} = 1050 \text{ J}$$

$$T(°\text{F}) = 1.8T(\text{K}) - 460$$

$$1\ °\text{C} = \frac{1}{1.8}\ \text{K}$$

Therefore

$$\tilde{C}_P^* \frac{\text{J}}{\text{K} \cdot \text{mol-g}} \times \frac{1 \text{ BTU}}{1050 \text{ J}} \times \frac{1 \text{ K}}{1.8 °\text{F}} = 5.29 \cdot 10^{-4} \tilde{C}_P^*$$

and in the general equation

$$5.29 \cdot 10^{-4} \tilde{C}_P^* = 0.01508 + 1.88 \cdot 10^{-5}[1.8T - 460] - 5.445 \cdot 10^{-9}[1.8T - 460]^2$$

$$\tilde{C}_P^* = \frac{0.01508 + 1.88 \cdot 10^{-5}[1.8T - 460] - 5.445 \cdot 10^{-9}[1.8T - 460]^2}{5.29 \cdot 10^{-4}}$$

$$\begin{aligned}\tilde{C}_P^* &= 28.507 + 0.0355[1.8T - 460] - 1.029 \cdot 10^{-5}[1.8T - 460]^2 = \\ &= 28.507 + 0.0639T - 16.33 - 1.029 \cdot 10^{-5}[3.24T^2 + 2.11 \cdot 10^5 - 1.65 \cdot 10^3 T] = \\ &= 28.507 + 0.0639T - 16.33 - 3.334 \cdot 10^{-5}T^2 - 2.1712 + 0.01698T = \\ &= 10.006 + 0.0809T - 3.334 \cdot 10^{-5}T^2\end{aligned}$$

Procedure b. This second procedure should not be used when thermometric readings and temperature intervals simultaneously appear, because it causes errors due to the origin of the scales: the specific heat capacity would be different from that calculated in the first procedure, which is the correct one.

$$0.01508\ \frac{\text{BTU}}{\text{°F}\cdot\text{mol-g}} \qquad 1.88\cdot 10^{-5}\,\frac{\text{BTU}}{(\text{°F})^2\cdot\text{mol-g}} \qquad -5.445\cdot 10^{-9}\,\frac{\text{BTU}}{(\text{°F})^3\cdot\text{mol-g}}$$

$$0.01508\ \frac{\text{BTU}}{\text{°F}\cdot\text{mol-g}}\times\frac{1050\ \text{J}}{1\ \text{BTU}}\times\frac{1.8\text{°F}}{1\text{K}} = 28.5\,\frac{\text{J}}{\text{K}\cdot\text{mol-g}}$$

$$1.88\cdot 10^{-5}\,\frac{\text{BTU}}{(\text{°F})^2\cdot\text{mol-g}}\times\frac{1050\ \text{J}}{1\ \text{BTU}}\times\left(\frac{1.8\text{°F}}{1\text{K}}\right)^2 = 0.064\,\frac{\text{J}}{\text{K}^2\cdot\text{mol-g}}$$

$$-5.445\cdot 10^{-9}\,\frac{\text{BTU}}{(\text{°F})^3\cdot\text{mol-g}}\times\frac{1050\ \text{J}}{1\ \text{BTU}}\times\left(\frac{1.8\text{°F}}{1\text{K}}\right)^3 = -3.334\cdot 10^{-5}\,\frac{\text{J}}{\text{K}^3\cdot\text{mol-g}}$$

$$\tilde{C}_P^* = 28.5 + 0.064T - 3.334\cdot 10^{-5}T^2$$

1.8. In a pilot plant where gas absorption is studied, the following empirical equation was obtained

$$\mathbf{k}_{M(g)}\mathbf{a} = \mathbf{0.010}\left(\hat{J}_g\right)^{\mathbf{0.8}}$$

where the mass transfer coefficient $k_{M(g)}$ is measured in mol-lb/(h·ft³·atm), the specific area a in ft²/ft³ and the mass flow density of the gas phase $\hat{J}_g$ in lb/(h·ft²). Transform this expression to use mol-kg/(h·cm³·atm), cm²/cm³ and kg/(h·cm²), respectively.

According to reference problem 0.1, two procedures could be applied:
a) Conversion of the the units of the coefficient 0.010
b) Conversion of the units of k_g, a and $\hat{J}_g$

Procedure a. From the dimensional analysis, it follows that:

$$\frac{\text{mol-lb}}{\text{h}\cdot\text{ft}^3\cdot\text{atm}}\cdot\frac{\text{ft}^2}{\text{ft}^3}[=]\,0.01\left(\frac{\text{lb}}{\text{h}\cdot\text{ft}^2}\right)^{0.8} \quad\rightarrow\quad 0.01[=]\frac{\text{mol-lb}}{\text{h}\cdot\text{ft}^3\cdot\text{atm}}\cdot\frac{\text{ft}^2}{\text{ft}^3}\left(\frac{\text{h}\cdot\text{ft}^2}{\text{lb}}\right)^{0.8}$$

$$0.01\,[=]\frac{\text{mol-lb}\cdot\text{h}^{0.8}\cdot\text{ft}^{1.6}}{\text{h}\cdot\text{ft}^4\cdot\text{atm}\cdot\text{lb}^{0.8}}=\frac{\text{mol-lb}}{\text{h}^{0.2}\cdot\text{ft}^{2.4}\cdot\text{atm}\cdot\text{lb}^{0.8}}$$

and by applying the conversion factors of appendix I or those which are well-known

$$1\ \text{lb} = 0.454\ \text{kg} \quad\rightarrow\quad 1\ \text{mol-lb} = 0.454\ \text{mol-kg}$$

$$1\ \text{ft} = 0.3048\ \text{m}$$

$$1\ \text{m} = 100\ \text{cm}$$

$$0.01\frac{\text{mol-lb}}{\text{h}^{0.2}\cdot\text{ft}^{2.4}\cdot\text{atm}\cdot\text{lb}^{0.8}}\times\frac{0.454\ \text{mol-kg}}{1\ \text{mol-lb}}\times\left(\frac{1\ \text{ft}}{0.3048\ \text{m}}\right)^{2.4}\times$$

$$\times\left(\frac{1\text{m}}{100\ \text{cm}}\right)^{2.4}\times\left(\frac{1\ \text{lb}}{0.454\ \text{kg}}\right)^{0.8} = 2.39\cdot 10^{-6}\frac{\text{mol-kg}}{\text{h}^{0.2}\cdot\text{cm}^{2.4}\cdot\text{atm}\cdot\text{kg}^{0.8}}$$

and this figure, without further transformations, can be directly introduced in the formula as a new dimensional coefficient

$$\text{k}_{M(g)}\text{a} = 2.39\cdot 10^{-6}\left(\hat{J}_g\right)^{0.8}$$

Procedure b. By employing the same data from appendix I as in the previous procedure, it is obtained

$$\mathrm{k}_{M(g)}\,\frac{\text{mol-kg}}{\mathrm{h}\cdot\mathrm{cm}^3\cdot\mathrm{atm}}\times\frac{1\ \text{mol-lb}}{0.454\ \text{mol-kg}}\times\left(\frac{100\ \mathrm{cm}}{1\ \mathrm{m}}\right)^3\times\left(\frac{0.3048\ \mathrm{m}}{1\ \mathrm{ft}}\right)^3=62.37\cdot 10^3\mathrm{k}_g$$

$$\mathrm{a}\,\frac{\mathrm{cm}^2}{\mathrm{cm}^3}=\mathrm{a}\frac{1}{\mathrm{cm}}\times\frac{100\ \mathrm{cm}}{1\ \mathrm{m}}\times\frac{0.3048\ \mathrm{m}}{1\ \mathrm{ft}}=30.48\mathrm{a}$$

$$\hat{J}_g\,\frac{\mathrm{kg}}{\mathrm{h}\cdot\mathrm{cm}^2}\times\frac{1\ \mathrm{lb}}{0.454\ \mathrm{kg}}\times\left(\frac{100\ \mathrm{cm}}{1\ \mathrm{m}}\right)^2\times\left(\frac{0.3048\ \mathrm{m}}{1\ \mathrm{ft}}\right)^2=2.046\cdot 10^3\hat{J}_g$$

and rearranging them in the general expression

$$\left(62.37\cdot 10^3\mathrm{k}_{M(g)}\right)(30.48\mathrm{a})=0.01\left(2.046\cdot 10^3\hat{J}_g\right)^{0.8}$$

$$\mathrm{k}_{M(g)}\mathrm{a}=\frac{0.01(2.046\cdot 10^3)^{0.8}}{(62.37\cdot 10^5)(30.48)}\left(\hat{J}_g\right)^{0.8}=2.37\cdot 10^{-6}\left(\hat{J}_g\right)^{0.8}$$

which slightly differs from the previous result only because of the numerical rounding.

1.9. Experience suggests that the normal boiling temperature of a substance and its critical temperature are related. The Norwegian scientist A. Lydersen proposed in his Ph.D. thesis (1956) the following empirical equation, valid for many organic substances

$$\boldsymbol{\frac{T_b}{T_c} = 0.567 + \Sigma\Delta_T - (\Sigma\Delta_T)^2}$$

where T is the temperature, expressed in K and Δ_T, the so-called "critical property increments" due to functional groups (dimensionless empirical parameters tabulated by the author). Transform the equation to use °C and °F.

As can be seen, the numerical coefficients to the right of the equal sign are dimensionless, therefore, it will only be necessary to convert the temperature units.

A table of appendix I remind us that T(°C)=T(K) – 273, so T(K)=T(°C)+273 and

$$\frac{T_b(°\mathrm{C}) + 273}{T_c(°\mathrm{C}) + 273} = 0.567 + \Sigma\Delta_T - \Sigma(\Delta_T)^2$$

Additionally, in this appendix is written that

$$T(\mathrm{K}) = \frac{T(°\mathrm{F}) - 32}{1.8} + 273 = \frac{T(°\mathrm{F}) - 32 + 491.4}{1.8} = \frac{T(°\mathrm{F}) + 459.4}{1.8}$$

Hence

$$\frac{T_b(°\mathrm{F}) + 459.4}{T_c(°\mathrm{F}) + 459.4} = 0.567 + \Sigma\Delta_T - \Sigma(\Delta_T)^2$$

1.10. In a liquid-vapor equilibrium at low concentrations, Henry's law linearly relates the composition of a component i in the vapor phase to its composition in the liquid phase. When the vapor composition is expressed as partial pressure and the liquid composition as molar fraction, we get

$$P_i = \mathcal{H}_i \tilde{x}_i$$

where $\mathcal{H}_i$ is the Henry's constant. For SO_2 in aqueous solution, $\mathcal{H}_i$= 0.3125 atm. Express this law as:

a) Pressure (in mm Hg) vs. mole fraction.

b) Mole fraction vs. mole fraction when the total pressure is 1 atm.

c) Pressure (in mm Hg) vs. mass concentration (g/L) when the total pressure is 1 atm and the solution is diluted ($\hat{c}_{\mathrm{SO_2}}$< 1g/L). Take the density of the liquid mixture as 1000 g/L.

d) Mole ratio vs. mole ratio when the total pressure is 1 atm and the solution is diluted ($\tilde{Y}_{\mathrm{SO_2}} \ll 1$; $\tilde{X}_{\mathrm{SO_2}} \ll 1$).

Question a. From appendix I we have that 1 atm= 0.76 m Hg and taking into account that 1 m=1000 mm

$$0.3125 \text{ atm} \times \frac{0.76 \text{ m Hg}}{1 \text{ atm}} \times \frac{1000 \text{ mm Hg}}{1 \text{ m Hg}} = 237.5 \text{ mm Hg}$$

Therefore

$$P_{\mathrm{SO_2}} = 237.5\tilde{x}_{\mathrm{SO_2}}$$

Question b. Since the mole fraction of sulphur dioxide in the gas is related to the total pressure by

$$\tilde{y}_{\mathrm{SO_2}} = \frac{P_{\mathrm{SO_2}}}{P}$$

it follows that

$$P_{\mathrm{SO_2}} = (1 \text{ atm})\, \tilde{y}_{\mathrm{SO_2}}$$

and so

$$\tilde{y}_{\mathrm{SO_2}} = 0.3125\tilde{x}_{\mathrm{SO_2}}$$

Question c. Having in mind that the mole fraction of SO_2 is related with its mass fraction by

$$\tilde{x}_{\mathrm{SO_2}} = \frac{n_{\mathrm{SO_2}}}{n_{\mathrm{SO_2}} + n_{\mathrm{H_2O}}} = \frac{\dfrac{M_{\mathrm{SO_2}}}{\mathfrak{W}_{\mathrm{SO_2}}}}{\dfrac{M_{\mathrm{SO_2}}}{\mathfrak{W}_{\mathrm{SO_2}}} + \dfrac{M_{\mathrm{H_2O}}}{\mathfrak{W}_{\mathrm{H_2O}}}} = \frac{\dfrac{\hat{x}_{\mathrm{SO_2}} M_{tot}}{\mathfrak{W}_{\mathrm{SO_2}}}}{\dfrac{\hat{x}_{\mathrm{SO_2}} M_{tot}}{\mathfrak{W}_{\mathrm{SO_2}}} + \dfrac{\hat{x}_{\mathrm{H_2O}} M_{tot}}{\mathfrak{W}_{\mathrm{H_2O}}}} = \frac{\hat{x}_{\mathrm{SO_2}}}{\hat{x}_{\mathrm{SO_2}} + \dfrac{\mathfrak{W}_{\mathrm{SO_2}}}{\mathfrak{W}_{\mathrm{H_2O}}}\left(1 - \hat{x}_{\mathrm{SO_2}}\right)} =$$

$$= \frac{\mathfrak{W}_{\mathrm{H_2O}} \hat{x}_{\mathrm{SO_2}}}{\mathfrak{W}_{\mathrm{H_2O}} \hat{x}_{\mathrm{SO_2}} + \mathfrak{W}_{\mathrm{SO_2}}\left(1 - \hat{x}_{\mathrm{SO_2}}\right)} = \frac{\mathfrak{W}_{\mathrm{H_2O}} \hat{x}_{\mathrm{SO_2}}}{\mathfrak{W}_{\mathrm{SO_2}} + \hat{x}_{\mathrm{SO_2}}\left(\mathfrak{W}_{\mathrm{H_2O}} - \mathfrak{W}_{\mathrm{SO_2}}\right)}$$

and since the mass fraction is related to the mass concentration and solution density through

$$\hat{x}_{SO_2} = \frac{M_{SO_2}}{M_{SO_2} + M_{H_2O}} = \left(\frac{M_{SO_2}}{V}\right)\left(\frac{V}{M_{SO_2} + M_{H_2O}}\right) = \frac{\hat{c}_{SO_2}}{\hat{\rho}}$$

it results

$$\tilde{x}_{SO_2} = \frac{\mathfrak{W}_{H_2O}\hat{c}_{SO_2}}{\mathfrak{W}_{SO_2}\hat{\rho} + \hat{c}_{SO_2}\left(\mathfrak{W}_{H_2O} - \mathfrak{W}_{SO_2}\right)}$$

By taking from appendix II the molecular masses of water and sulfur dioxide (18.015 and 64.07 g/mol-g, respectively) and combining this expression with that of question **a**

$$P_{SO_2} = 237.5\frac{\mathfrak{W}_{H_2O}\hat{c}_{SO_2}}{\mathfrak{W}_{SO_2}\hat{\rho} + \hat{c}_{SO_2}\left(\mathfrak{W}_{H_2O} - \mathfrak{W}_{SO_2}\right)} =$$

$$= 237.5\frac{18.015\hat{c}_{SO_2}}{64.07 \cdot 1000 + \hat{c}_{SO_2}(18.015 - 64.07)} = 237.5\frac{18.015\hat{c}_{SO_2}}{64070 - 46.055\hat{c}_{SO_2}}$$

and by knowing that the solution is diluted, $64070 \gg 46.055\hat{c}_{SO_2}$, it is obtained that

$$P_{SO_2} \approx 237.5\frac{18.015\hat{c}_{SO_2}}{64070} = 0.067\hat{c}_{SO_2}$$

Question d. Reference problem 0.14 indicates that the molar fractions are related to the mole ratios by

$$\tilde{x}_i = \frac{\tilde{X}_i}{1 + \tilde{X}_i} \qquad \tilde{y}_i = \frac{\tilde{Y}_i}{1 + \tilde{Y}_i}$$

and if they are introduced in the equation of question **b**

$$\frac{\tilde{Y}_{SO_2}}{1 + \tilde{Y}_{SO_2}} = 0.3125\frac{\tilde{X}_{SO_2}}{1 + \tilde{X}_{SO_2}}$$

and $\tilde{Y}_{SO_2} \ll 1$; $\tilde{X}_{SO_2} \ll 1$, then

$$\tilde{Y}_{SO_2} \approx 0.3125\tilde{X}_{SO_2}$$

1.11. The definition of the normal atmosphere corresponds to the pressure exerted by a column of mercury 760 mm high when the gravitational acceleration is that at the earth's surface. Confirm that 1 atm = 29.92 in Hg = 14.696 $\mathbf{lb_f/in^2}$. Take the density of mercury as 13600 $\mathbf{kg/m^3}$.

The first calculation is a simple unit conversion. Taking from appendix I that 1 m = 39.37 in, and remembering that 1 m = 1000 mm

$$760\text{ mm}\times\frac{1\text{ m}}{1000\text{ mm}}\times\frac{39.37\text{ in}}{1\text{ m}}=29.92\text{ in}$$

From the definition of pressure

$$P=\frac{\text{force}}{\text{area}}=\frac{\text{mass}\times\text{acceleration}}{\text{area}}$$

By taking the column as a cylindrical object and assuming that the acceleration is the gravitational one

$$P=\frac{\text{density}\times\text{column volume}\times\text{acceleration}}{\text{area}}=\text{density}\times\text{column length}\times\text{acceleration}$$

By substituting the data

$$P=\left(13600\ \frac{\text{kg}}{\text{m}^3}\right)\left(760\text{ mm Hg}\times\frac{1\text{ m}}{1000\text{ mm}}\right)\left(9.80665\ \frac{\text{m}}{\text{s}^2}\right)=101361\frac{\text{kg}}{\text{m}\cdot\text{s}^2}$$

and converting kg/m to pounds per inch with the factors from tables in appendix I

$$101361\frac{\text{kg}}{\text{m}\cdot\text{s}^2}\times\frac{2.2\text{ lb}}{1\text{ kg}}\times\frac{1\text{ m}}{39.37\text{ in}}=5664\ \frac{\text{lb}}{\text{in}\cdot\text{s}^2}$$

Finally, having in mind that a mass-force is the product of the mass and the acceleration of gravity (which will have to be converted into in/s^2 with the factors of appendix I)

$$g=9.80665\frac{\text{m}}{\text{s}^2}\times\frac{39.37\text{ in}}{1\text{ m}}=386.088\frac{\text{in}}{\text{s}^2}$$

$$P=\frac{5664\frac{\text{lb}}{\text{in}\cdot\text{s}^2}}{386.088\frac{\text{in}}{\text{s}^2}}=14.67\frac{\text{lb}_\text{f}}{\text{in}^2}$$

value very close to that in the statement of the problem, 14.696.

SERIES 2

STATE AND EQUILIBRIUM: EXPERIMENTS AND MODELS

2.1. Let Z be a thermodynamic function defined for a single-component system in a single phase as a function of two other state properties, X and Y. Indicate whether it is a state property or a process property when:

a) $\mathbf{dZ = XY^2(dX + dY)}$.

b) $\mathbf{dZ = XY^2dX + YX^2dY}$.

c) $\mathrm{Z} = \frac{R\mathrm{X}}{\mathrm{Y}}$, where R is a constant.

d) Graphically interpretate the dependence among these properties.

Question a. Section a of reference problem 0.4 indicates the mathematical relations that must exist between the state variables

$$\mathrm{dZ} = \left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}} \mathrm{dX} + \left(\frac{\partial \mathrm{Z}}{\partial \mathrm{Y}}\right)_{\mathrm{X}} \mathrm{dY} \qquad [1]$$

$$\frac{\partial}{\partial \mathrm{Y}}\left[\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}}\right]_{\mathrm{X}} = \frac{\partial}{\partial \mathrm{X}}\left[\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{Y}}\right)_{\mathrm{X}}\right]_{\mathrm{Y}} \qquad [2]$$

$$\left(\frac{\partial \mathrm{X}}{\partial \mathrm{Y}}\right)_{\mathrm{Z}} \left(\frac{\partial \mathrm{Y}}{\partial \mathrm{Z}}\right)_{\mathrm{X}} \left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}} = -1 \qquad [3]$$

$$\left(\frac{\partial \mathrm{X}}{\partial \mathrm{Y}}\right)_{\mathrm{Z}} = \frac{1}{\left(\frac{\partial \mathrm{Y}}{\partial \mathrm{X}}\right)_{\mathrm{Z}}} \qquad [4]$$

Since the expression given in the statement of the problem can be written as

$$\mathrm{dZ} = \mathrm{XY^2dX} + \mathrm{XY^2dY}$$

the comparison with equation [1] leads to that

$$\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}} = \mathrm{XY^2} \qquad \left(\frac{\partial \mathrm{Z}}{\partial \mathrm{Y}}\right)_{\mathrm{X}} = \mathrm{XY^2}$$

and by applying relation [2], which is the most direct one, we obtain

$$\frac{\partial}{\partial \mathrm{Y}}\left[\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}}\right]_{\mathrm{X}} = 2\mathrm{XY} \qquad \frac{\partial}{\partial \mathrm{X}}\left[\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{Y}}\right)_{\mathrm{X}}\right]_{\mathrm{Y}} = \mathrm{Y^2}$$

Due to the fact that $2\mathrm{XY} \neq \mathrm{Y}^2$ we conclude that Z is a process property.

Question b. By proceeding as in the previous question

$$\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}} = \mathrm{XY^2} \qquad \left(\frac{\partial \mathrm{Z}}{\partial \mathrm{Y}}\right)_{\mathrm{X}} = \mathrm{YX^2}$$

$$\frac{\partial}{\partial \mathrm{Y}}\left[\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}}\right]_{\mathrm{X}} = 2\mathrm{XY} \qquad \frac{\partial}{\partial \mathrm{X}}\left[\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{Y}}\right)_{\mathrm{X}}\right]_{\mathrm{Y}} = 2\mathrm{XY}$$

The symmetry of the second derivatives indicate that Z is a state property.

Question c. In this third case, the function is given in an integral way, so it will have to be differentiated. Thus, the two members of equation [1] will be

$$\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}} = \frac{R}{\mathrm{Y}} \qquad \left(\frac{\partial \mathrm{Z}}{\partial \mathrm{Y}}\right)_{\mathrm{X}} = -\frac{R\mathrm{X}}{\mathrm{Y}^2}$$

after applying relation [2] the symmetry of the second derivatives is observed

$$\frac{\partial}{\partial \mathrm{Y}}\left[\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}}\right]_{\mathrm{X}} = \frac{\partial}{\partial \mathrm{Y}}\left[\frac{R}{\mathrm{Y}}\right]_{\mathrm{X}} = -\frac{R}{\mathrm{Y}^2}$$

$$\frac{\partial}{\partial \mathrm{X}}\left[\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{Y}}\right)_{\mathrm{X}}\right]_{\mathrm{Y}} = \frac{\partial}{\partial \mathrm{X}}\left[-\frac{R\mathrm{X}}{\mathrm{Y}^2}\right]_{\mathrm{Y}} = -\frac{R}{\mathrm{Y}^2}$$

Equations [4] and [5] are satisfied as well, indicating that this is another property of state

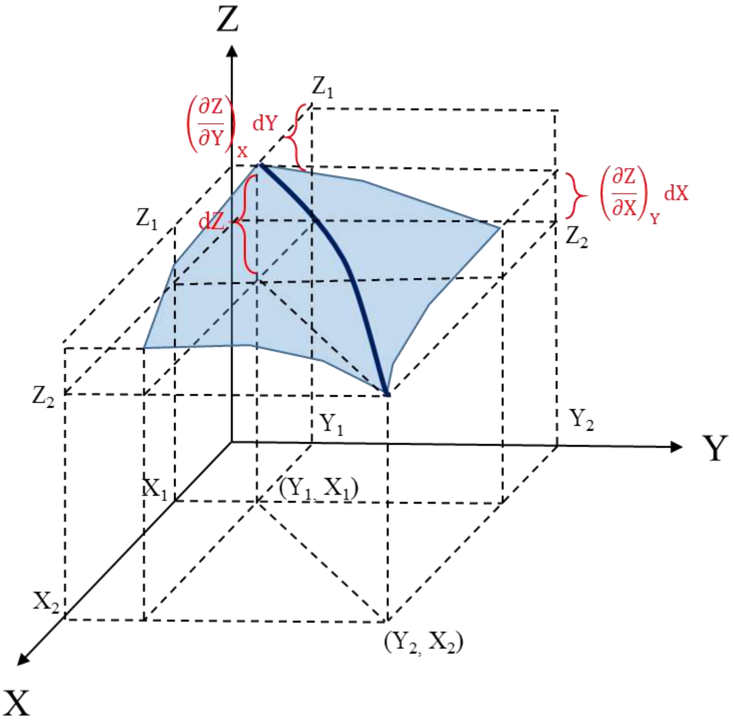
$$\left(\frac{\partial \mathrm{X}}{\partial \mathrm{Y}}\right)_{\mathrm{Z}} = \frac{\mathrm{Z}}{R} \qquad \left(\frac{\partial \mathrm{Y}}{\partial \mathrm{X}}\right)_{\mathrm{Z}} = \frac{R}{\mathrm{Z}}$$

$$\left(\frac{\partial \mathrm{X}}{\partial \mathrm{Y}}\right)_{\mathrm{Z}}\left(\frac{\partial \mathrm{Y}}{\partial \mathrm{Z}}\right)_{\mathrm{X}}\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}} = \frac{\left(\frac{\partial \mathrm{X}}{\partial \mathrm{Y}}\right)_{\mathrm{Z}}\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}}}{\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{Y}}\right)_{\mathrm{X}}} = \frac{\left(\frac{\mathrm{Z}}{R}\right)\left(\frac{R}{\mathrm{Y}}\right)}{\left(-\frac{R\mathrm{X}}{\mathrm{Y}^2}\right)} = -\frac{\mathrm{YZ}}{R\mathrm{X}} = -1$$

Notice that the function is identical to the equation of state of the ideal gas if Z= $\tilde{V}$, X=T and Y=P.

$$\mathrm{Z} = \frac{R\mathrm{X}}{\mathrm{Y}} \quad \rightarrow \quad \tilde{V} = \frac{RT}{P}$$

Question d. The graphical interpretation is summarized in the figure below. If Z is a function which takes the value Z_1 at point Y_1, X_1 and takes the value Z_2 at point Y_2, X_2 (in such a way that $\mathrm{X}_2 = \mathrm{X}_1+d\mathrm{X}$, $\mathrm{Y}_2 = \mathrm{Y}_1+d\mathrm{Y}$, $\mathrm{Z}_2 = \mathrm{Z}_1+d\mathrm{Z}$) the total spatial variation of this function is equal to the sum of variations in the ZX plane and in the ZY one.



This means that the value of Z_2 at point X_2, Y_2 is independent of the way the system got to that point. For example, take Z= $\tilde{V}$, X=T and Y=P: the obtained volume will be the same if instead of going directly from T_1, P_1 to T_2, P_2, the system first goes from T_1, P_1 to T_2, P_1 and then from T_2, P_1 to T_2, P_2.

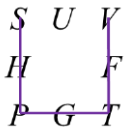
When dealing with a process function, this is not the case. If Z is the work (defined as a force applied along a displacement), and X and Y longitude and latitude, respectively, it can be seen that the work done by directly carrying an object from point Y_1, X_1 to point Y_2, X_2 is not the same as the result of carrying it first from Y_1, X_1 to Y_2, X_1 and later from Y_2, X_1 to Y_2, X_2 (although the force is the same, the length is greater in the path Y_1, X_1–Y_2, X_1–Y_2, X_2 than in Y_1, X_1–Y_2, X_2).

2.2. Describe mnemonic rules to remember the Maxwell relations and other thermodynamic equations.

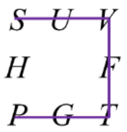
The thermodynamic square, Guggenheim scheme or Born square is configured as

$$\begin{array}{ccc} S & U & V \\ H & & F \\ P & G & T \end{array}$$

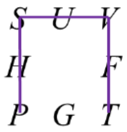
The corners represent the variables (*V, T, P* y *S*) while the sides represent the thermodynamic potentials (*U, F, G, H*). A good mnemonic to draw it in clockwise direction (starting from the Gibbs free energy) is the sentence "*Good Physicists Have Studied Under Very Fine Teachers*." Maxwell's relations are found by placing oneself at a corner of the square, drawing a ⊔ shape and rotating that shape from corner to corner



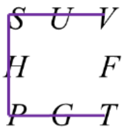
$$-\left(\frac{\partial \tilde{S}}{\partial P}\right)_T = \left(\frac{\partial \tilde{V}}{\partial T}\right)_P$$



$$\left(\frac{\partial P}{\partial T}\right)_{\tilde{V}} = \left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)_T$$



$$\left(\frac{\partial T}{\partial \tilde{V}}\right)_{\tilde{S}} = -\left(\frac{\partial P}{\partial \tilde{S}}\right)_{\tilde{V}}$$

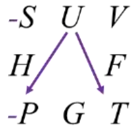


$$\left(\frac{\partial \tilde{V}}{\partial \tilde{S}}\right)_P = \left(\frac{\partial T}{\partial P}\right)_{\tilde{S}}$$

The negative sign is introduced when *P* is differentiated with respect to *S* or *S* differentiated with respect to *P*.

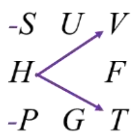
Furthermore, the square is useful to obtain the equations of reference problem 0.3 by taking into account that:

- The non differentiated variables are placed in the opposite corner of each potential.
- In the opposite corner of each non differentiated variable, it is found the variable which (in its differential form) multiplies it.
- If the non differentiated variable is placed at the left of the square (*S* or *P*) it requires a negative sign.



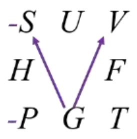
$$\mathrm{d}\tilde{U} = -P[\text{differential}] + T[\text{differential}]$$

$$\mathrm{d}\tilde{U} = -P\mathrm{d}\tilde{V} + T\mathrm{d}\tilde{S}$$



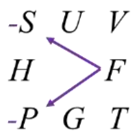
$$\mathrm{d}\tilde{H} = T[\text{differential}] + \tilde{V}[\text{differential}]$$

$$\mathrm{d}\tilde{H} = T\mathrm{d}\tilde{S} + \tilde{V}\mathrm{d}P$$

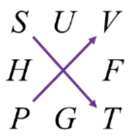


$$\mathrm{d}\tilde{G} = -\tilde{S}[\text{differential}] + \tilde{V}[\text{differential}]$$

$$\mathrm{d}\tilde{G} = -\tilde{S}\mathrm{d}T + \tilde{V}\mathrm{d}P$$

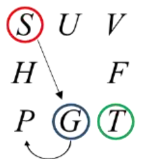


$$\mathrm{d}\tilde{F} = -\tilde{S}[\text{differential}] - P[\text{differential}]$$

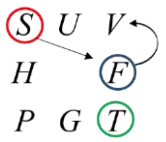


$$\mathrm{d}\tilde{F} = -\tilde{S}\mathrm{d}T - P\mathrm{d}\tilde{V}$$

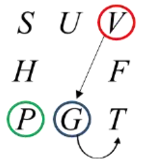
The eight relations deduced from these four equations can be obtained through the square by remembering (at least graphically) the tongue twister "*the variable of interest is equal to the derivative of the potential of the opposite side with respect to the variable that is in the opposite corner of the variable of interest, keeping constant the second variable that is on the corner adjacent to the potential* ".



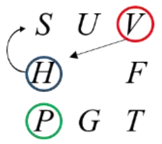
$$\tilde{S} = -\left(\frac{\partial \tilde{G}}{\partial T}\right)_P$$



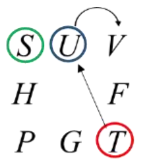
$$\tilde{S} = -\left(\frac{\partial \tilde{F}}{\partial T}\right)_{\tilde{V}}$$



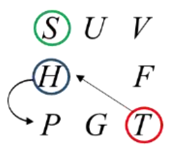
$$\tilde{V} = \left(\frac{\partial \tilde{G}}{\partial P}\right)_T$$



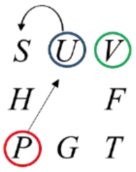
$$\tilde{V} = \left(\frac{\partial \tilde{H}}{\partial P}\right)_{\tilde{S}}$$



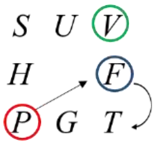
$$T = \left(\frac{\partial \tilde{U}}{\partial \tilde{S}}\right)_{\tilde{V}}$$



$$T = \left(\frac{\partial \tilde{H}}{\partial \tilde{S}}\right)_P$$



$$P = -\left(\frac{\partial \tilde{U}}{\partial \tilde{V}}\right)_{\tilde{S}}$$



$$P = -\left(\frac{\partial \tilde{F}}{\partial \tilde{V}}\right)_{T}$$

On the other hand, for expressions of the type

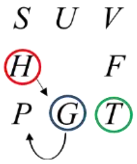
$$\tilde{H} = \tilde{G} + T\tilde{S} \qquad \tilde{H} = \tilde{U} + P\tilde{V}$$

$$\tilde{G} = \tilde{F} + P\tilde{V} \qquad \tilde{G} = \tilde{H} + T\tilde{S}$$

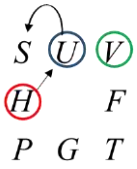
$$\tilde{F} = \tilde{U} - T\tilde{S} \qquad \tilde{F} = \tilde{G} - P\tilde{V}$$

$$\tilde{U} = \tilde{H} - P\tilde{V} \qquad \tilde{U} = \tilde{F} + T\tilde{S}$$

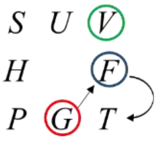
"*the potential of interest is a function of one of the potentials of the adjacent sides, multiplied by and differentiated with respect to the variable of the opposite corner of the potential of interest, keeping constant the variable of the corner between the two potentials involved.*"



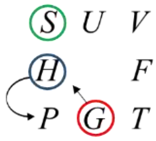
$$\tilde{H} = \tilde{G} - T\left(\frac{\partial \tilde{G}}{\partial T}\right)_{P}$$



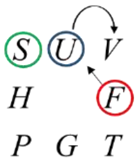
$$\tilde{H} = \tilde{U} - \tilde{V}\left(\frac{\partial \tilde{U}}{\partial \tilde{V}}\right)_{\tilde{S}}$$



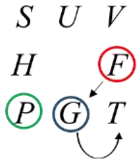
$$\tilde{G} = \tilde{F} - \tilde{V}\left(\frac{\partial \tilde{F}}{\partial \tilde{V}}\right)_{T}$$



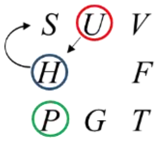
$$\tilde{G} = \tilde{H} - \tilde{S}\left(\frac{\partial \tilde{H}}{\partial \tilde{S}}\right)_{P}$$



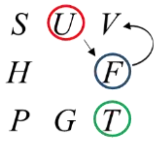
$$\tilde{F} = \tilde{U} - \tilde{S}\left(\frac{\partial \tilde{U}}{\partial \tilde{S}}\right)_{\tilde{V}}$$



$$\tilde{F} = \tilde{G} - P\left(\frac{\partial \tilde{G}}{\partial P}\right)_{T}$$



$$\tilde{U} = \tilde{H} - P\left(\frac{\partial \tilde{H}}{\partial P}\right)_{\tilde{S}}$$



$$\tilde{U} = \tilde{F} - T\left(\frac{\partial \tilde{F}}{\partial T}\right)_{\tilde{V}}$$

And regarding the relations with three terms (deduced from the preceding ones)

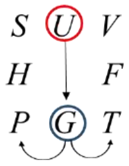
$$\tilde{U} = \tilde{G} + T\tilde{S} - P\tilde{V}$$

$$\tilde{G} = \tilde{U} - T\tilde{S} + P\tilde{V}$$

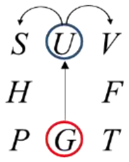
$$\tilde{F} = \tilde{H} - T\tilde{S} - P\tilde{V}$$

$$\tilde{H} = \tilde{F} + P\tilde{V} + T\tilde{S}$$

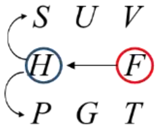
“The potential of interest is a function of the potential of the side parallel to it. This second potential is differentiated with respect to the variable in one of its closest corners, keeping the variable in the other closest corner constant. "



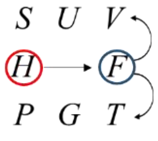
$$\tilde{U} = \tilde{G} - T\left(\frac{\partial \tilde{G}}{\partial T}\right)_{P} - P\left(\frac{\partial \tilde{G}}{\partial P}\right)_{T}$$



$$\tilde{G} = \tilde{U} - \tilde{S}\left(\frac{\partial \tilde{U}}{\partial \tilde{S}}\right)_{\tilde{V}} - \tilde{V}\left(\frac{\partial \tilde{U}}{\partial \tilde{V}}\right)_{\tilde{S}}$$



$$\tilde{F} = \tilde{H} - \tilde{S}\left(\frac{\partial \tilde{H}}{\partial \tilde{S}}\right)_{P} - P\left(\frac{\partial \tilde{H}}{\partial P}\right)_{\tilde{S}}$$



$$\tilde{H} = \tilde{F} - \tilde{V}\left(\frac{\partial \tilde{U}}{\partial \tilde{V}}\right)_{T} - T\left(\frac{\partial \tilde{F}}{\partial T}\right)_{\tilde{V}}$$

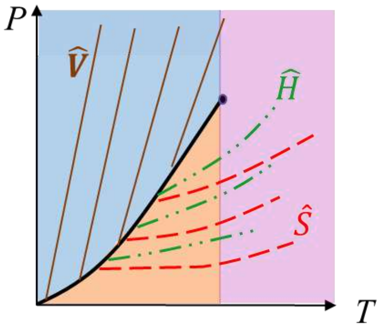
Finally, it has to be said that mnemonic rules –a mere trick for immediacy– become more artificial and unnecessary when the concepts (and the handling of them) are clear.

2.3. Qualitatively draw the following equilibrium diagrams of pure substances in the liquid-vapor-gas zone:

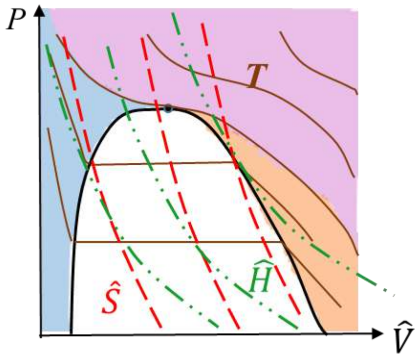
a) Pressure vs. Temperature (isolines of volume, enthalpy and entropy).
b) Pressure vs. Volume (isolines of temperature, enthalpy and entropy).
c) Enthalpy vs. Entropy, a.k.a. Mollier (isolines of temperature and pressure).

Let the colors be blue for liquid, orange for vapor, and violet for gas.

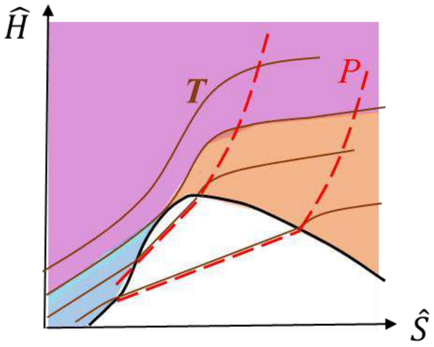
Question a.



Question b.



Question c.



2.4. According to the so called *phase rule*, three independent thermodynamic properties are necessarily linked by an equation of state in a monocomponent system. If $H(P,T)$, the enthalpy should remain unchanged in transitions at constant pressure and temperature. Why then is there a latent heat of phase change $\Delta H \neq 0$ at constant P and T?

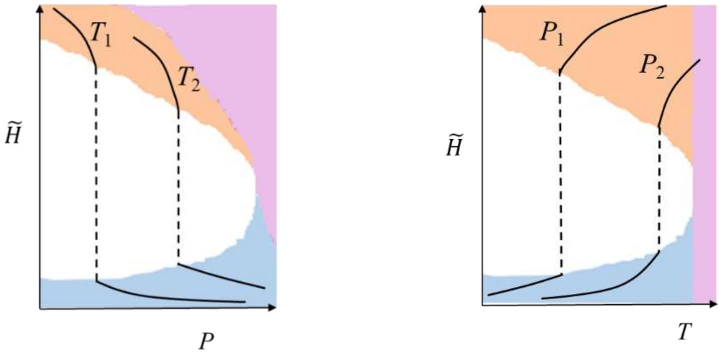
For an equation of state that relates three properties, Z= f(X, Y),

$$\mathrm{dZ} = \left(\frac{\partial \mathrm{Z}}{\partial \mathrm{X}}\right)_{\mathrm{Y}} \mathrm{dX} + \left(\frac{\partial \mathrm{Z}}{\partial \mathrm{Y}}\right)_{\mathrm{X}} \mathrm{dY}$$

which satisfies that dZ=0 when dX=0 and dY=0. However, if $\mathrm{Z}=\widetilde{H}$, X=P and Y=T

$$\mathrm{d}\widetilde{H} = \left(\frac{\partial \widetilde{H}}{\partial P}\right)_{T} \mathrm{d}P + \left(\frac{\partial \widetilde{H}}{\partial T}\right)_{P} \mathrm{d}T$$

the following curves appear in liquid-vapor transitions (although dP =dT =0)



There are two values of $\widetilde{H}$ for the same value of P and T, which implies that both $(\partial\widetilde{H}/\partial T)_P$ and $(\partial\widetilde{H}/\partial P)_T$ are infinite; thus

$$\left(\frac{\partial \widetilde{H}}{\partial T}\right)_{P} = \infty \quad \rightarrow \quad \left(\frac{\partial \widetilde{H}}{\partial T}\right)_{P} \mathrm{d}T = \infty \cdot 0$$

$$\left(\frac{\partial \widetilde{H}}{\partial P}\right)_{T} = \infty \quad \rightarrow \quad \left(\frac{\partial \widetilde{H}}{\partial P}\right)_{T} \mathrm{d}P = \infty \cdot 0$$

The product ∞·0 is an indeterminacy, so the result does not necessarily have to be zero as in other regions of the thermodynamic diagram. This indeterminacy justifies an infinite number of latent heats of state change as a function of P and T within the region of liquid-vapor transitions.

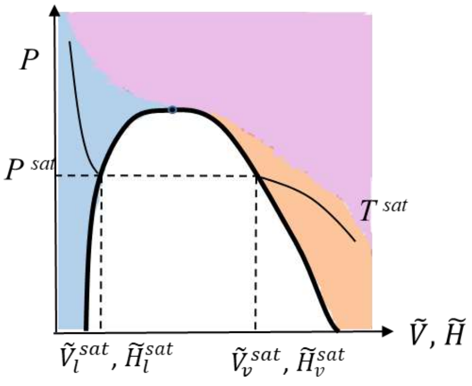
Similarly, $\Delta H \neq 0$ in the solid-liquid and solid-vapor transition regions.

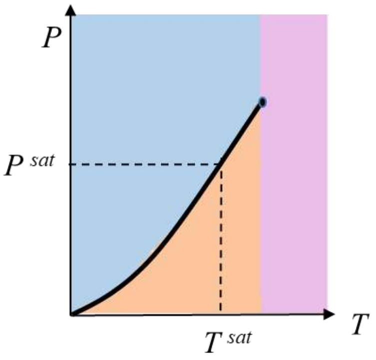
2.5. For the equilibrium line of vaporization-condensation in the *PT* diagram:

- **a) Theoretically deduce the Clapeyron equation.**
- **b) Estimate the vapor pressure of SO_2 at 373.2 K if its normal boiling temperature is 283.21 K and assuming that a Clapeyron-type equation is applicable up to the very critical point (430.7 K and 76.69 atm).**

Question a. The Clapeyron equation (section c of reference problem 0.5) can be obtained from the following Maxwell relation

$$\left(\frac{\partial P}{\partial T}\right)_{\tilde{V}} = \left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)_T$$





During phase changes in single-component systems, dP=dT=0; thus

$$\mathrm{d}\tilde{S} = \left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)_T \mathrm{d}\tilde{V} + \left(\frac{\partial \tilde{S}}{\partial T}\right)_{\tilde{V}} \mathrm{d}T \quad \xrightarrow{\mathrm{d}T=0} \quad \left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)_T = \frac{\mathrm{d}\tilde{S}}{\mathrm{d}\tilde{V}}$$

$$\mathrm{d}\tilde{H} = T\mathrm{d}\tilde{S} + \tilde{V}\mathrm{d}P \quad \xrightarrow{\mathrm{d}P=0} \quad \mathrm{d}\tilde{S} = \frac{\mathrm{d}\tilde{H}}{T}$$

and therefore

$$\left(\frac{\partial P}{\partial T}\right)_{\tilde{V}} = \frac{\mathrm{d}S}{\mathrm{d}\tilde{V}} = \frac{\mathrm{d}\tilde{H}}{T\mathrm{d}\tilde{V}}$$

The approximation of the differential elements by finite increments, and the fact that far from the critical point the molar volume of saturated vapor ($\tilde{V}_v^{sat}$) is much higher than that of saturated liquid ($\tilde{V}_l^{sat}$) lead to

$$\frac{\mathrm{d}\tilde{H}}{T\mathrm{d}\tilde{V}} \approx \frac{\left(\tilde{H}_v^{sat} - \tilde{H}_l^{sat}\right)}{T\left(\tilde{V}_v^{sat} - \tilde{V}_l^{sat}\right)} = \frac{\Delta\tilde{H}_{vap}}{T\left(\tilde{V}_v^{sat} - \tilde{V}_l^{sat}\right)} \xrightarrow{\tilde{V}_v^{sat} \gg \tilde{V}_l^{sat}} \frac{\Delta\tilde{H}_{vap}}{T\tilde{V}_v^{sat}}$$

being $\Delta\widetilde{H}_{vap}$ the latent heat of vaporization. If the ideal gas model is taken

$$\left(\frac{\partial P}{\partial T}\right)_{\widetilde{V}} = \frac{\Delta\widetilde{H}_{vap}}{T\left(\frac{RT}{P}\right)}$$

expression where the partial derivative of pressure with respect to temperature is volume independent, so it can be approximated by the total derivative and

$$\frac{\mathrm{d}P}{P} = \frac{\Delta\widetilde{H}_{vap}}{R}\frac{\mathrm{d}T}{T^2} \quad \rightarrow \quad \ln P = -\frac{\Delta\widetilde{H}_{vap}}{RT} + cte$$

Notice some conceptual juggling in this classical treatment (so cited in numerous textbooks) because the combination of a state change with an equation of state referred to the ideality.

Question b. If the equation is applicable up to the critical point, and its value is known at another point, a system of two linear equations with two unknowns can be proposed.

Since the normal boiling temperature is that at 1 atm,

$$\left.\begin{aligned} \ln(76.69\text{ atm}) &= -\frac{\Delta\widetilde{H}_{vap}}{R(430.7\text{ K})} + cte \\ \ln(1\text{ atm}) &= -\frac{\Delta\widetilde{H}_{vap}}{R(283.21\text{ K})} + cte \end{aligned}\right\} \; -\frac{\Delta\widetilde{H}_{vap}}{R} = -3589.11\text{ K} \quad ; \quad cte = 12.674$$

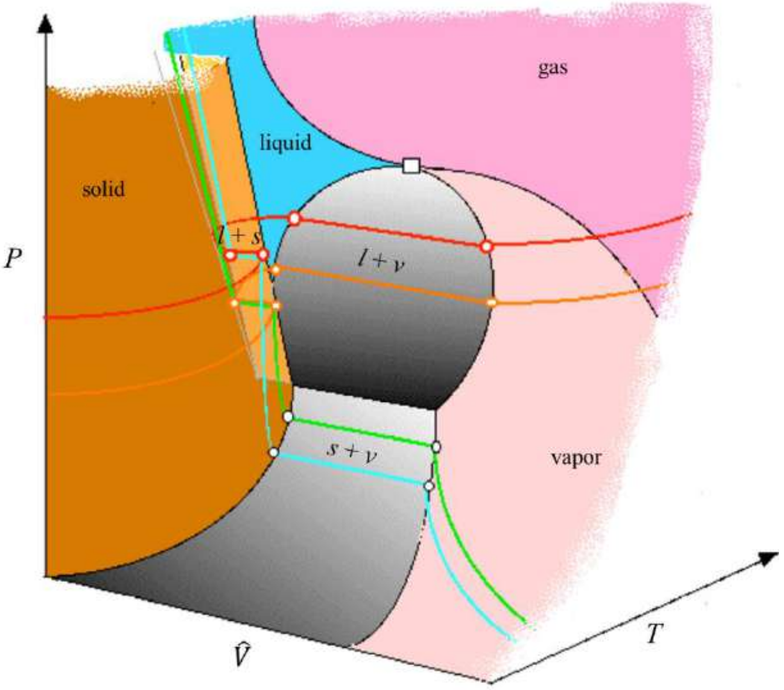
and by substituting these constants at 373.2 K

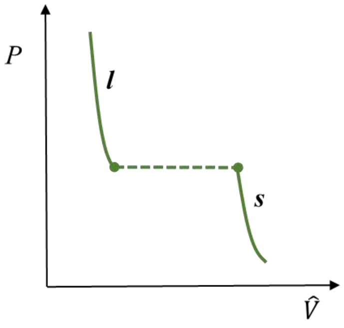
$$\ln P = -\frac{3589.11}{(373.2\text{ K})} + 12.674 = 3.057 \quad \rightarrow P = \exp(3.057) = 21.26\text{ atm}$$

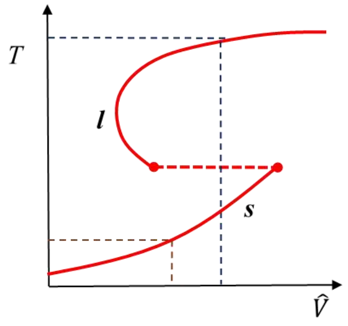
When compared with the experimental value (27.34 atm, interpolated from Perry et al. 1997), the calculated value is a 22% lower.

2.6. The adventure/fiction film “*Voyage to the bottom of the sea*” of Irvin Allen (1961) starts with a submarine surrounded by ice blocks sinking into the sea... Is it possible?

The *PVT* diagram of water differs from that of reference problem 0.5 (section b).







Along isotherms, the specific volume of the solid is always higher than that of the liquid, but along isobars this is not always true.

If ice and liquid water are not in equilibrium, and the liquid is hotter than the solid, the specific volume of the liquid can be higher than that of ice, leading to the sinking.

2.7. Demonstrate that the Joule-Thomson conditions and the Clapeyron model are redundant in the case of an ideal gas.

The Joule-Thomson conditions imply that both the internal energy and enthalpy of the ideal gas are functions of the temperature alone.

For the enthalpy

$$\tilde{H} = \tilde{G} + T\tilde{S}$$

and the derivatives with respect to pressure (at constant temperature) will be

$$\left(\frac{\partial \tilde{H}}{\partial P}\right)_T = \left(\frac{\partial \tilde{G}}{\partial P}\right)_T + T\left(\frac{\partial \tilde{S}}{\partial P}\right)_T + \tilde{S}\left(\frac{\partial T}{\partial P}\right)_T$$

Since temperature remains unchanged, the last term is zero. If the following Maxwell relations are taken into account

$$\left(\frac{\partial \tilde{G}}{\partial P}\right)_T = \tilde{V} \qquad\qquad \left(\frac{\partial \tilde{S}}{\partial P}\right)_T = -\left(\frac{\partial \tilde{V}}{\partial T}\right)_P$$

it can be found that

$$\left(\frac{\partial \tilde{H}}{\partial P}\right)_T = \tilde{V} - T\left(\frac{\partial \tilde{V}}{\partial T}\right)_P$$

For the ideal gas of Clapeyron

$$\tilde{V} = \frac{RT}{P}$$

$$\left(\frac{\partial \tilde{V}}{\partial T}\right)_P = \frac{R}{P}$$

$$\left(\frac{\partial \tilde{H}}{\partial P}\right)_T = \tilde{V} - T\left(\frac{R}{P}\right) = \tilde{V} - \tilde{V} = 0$$

In the case of internal energy, the procedure is analogous

$$\tilde{U} = \tilde{F} + T\tilde{S} = \tilde{H} - P\tilde{V}$$

$$\left(\frac{\partial \tilde{U}}{\partial P}\right)_T = \left(\frac{\partial \tilde{H}}{\partial P}\right)_T - P\left(\frac{\partial \tilde{V}}{\partial P}\right)_T - \tilde{V}\left(\frac{\partial P}{\partial P}\right)_T$$

$$\left(\frac{\partial \tilde{U}}{\partial P}\right)_T = \left(\frac{\partial \tilde{H}}{\partial P}\right)_T + P\left(\frac{\partial \tilde{V}}{\partial P}\right)_T + \tilde{V}$$

$$\left(\frac{\partial \tilde{U}}{\partial P}\right)_T = 0 + P\left(-\frac{RT}{P^2}\right) + \tilde{V} = -\frac{RT}{P} + \tilde{V} = -\tilde{V} + \tilde{V} = 0$$

Therefore they are two interpretations of the ideal behavior that only differ in the nature of the variables used as descriptors.

2.8. Theoretically deduce the equation for isentropic transformations of the ideal gas and qualitatively represent it in a *PV*(*T*,*S*) diagram.

In an isentropic process, $\mathrm{d}\tilde{S} = 0$. By taking $\tilde{S}(T, P)$ and $\tilde{S}(T, \tilde{V})$ it can be written

$$\mathrm{d}\tilde{S} = \left(\frac{\partial \tilde{S}}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial \tilde{S}}{\partial P}\right)_T \mathrm{d}P = 0$$

$$\mathrm{d}\tilde{S} = \left(\frac{\partial \tilde{S}}{\partial T}\right)_{\tilde{V}} \mathrm{d}T + \left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)_T \mathrm{d}\tilde{V} = 0$$

If the derivative with respect to temperature is expressed as a function of other variables, then

$$\left(\frac{\partial \tilde{S}}{\partial T}\right)_P = \left(\frac{\partial \tilde{S}}{\partial \tilde{H}}\right)_P \left(\frac{\partial \tilde{H}}{\partial T}\right)_P$$

$$\left(\frac{\partial \tilde{S}}{\partial T}\right)_{\tilde{V}} = \left(\frac{\partial \tilde{S}}{\partial \tilde{U}}\right)_{\tilde{V}} \left(\frac{\partial \tilde{U}}{\partial T}\right)_{\tilde{V}}$$

Notice that, according to reference problem 0.4

$$\left(\frac{\partial \tilde{U}}{\partial \tilde{S}}\right)_{\tilde{V}} = T \qquad \left(\frac{\partial \tilde{S}}{\partial P}\right)_T = -\left(\frac{\partial \tilde{V}}{\partial T}\right)_P \qquad \left(\frac{\partial \tilde{H}}{\partial T}\right)_P = \tilde{C}_P$$

$$\left(\frac{\partial \tilde{H}}{\partial \tilde{S}}\right)_P = T \qquad \left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\tilde{V}} \qquad \left(\frac{\partial \tilde{U}}{\partial T}\right)_{\tilde{V}} = \tilde{C}_V$$

and therefore

$$\mathrm{d}\tilde{S} = \frac{\tilde{C}_P}{T}\mathrm{d}T - \left(\frac{\partial \tilde{V}}{\partial T}\right)_P \mathrm{d}P = 0$$

$$\mathrm{d}\tilde{S} = \frac{\tilde{C}_V}{T}\mathrm{d}T + \left(\frac{\partial P}{\partial T}\right)_{\tilde{V}} \mathrm{d}\tilde{V} = 0$$

When the ideal gas model is assumed, $P\tilde{V} = RT$, and

$$\left(\frac{\partial \tilde{V}}{\partial T}\right)_P = \frac{R}{P}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\tilde{V}} = \frac{R}{\tilde{V}}$$

$$\mathrm{d}\tilde{S} = \tilde{C}_P \frac{\mathrm{d}T}{T} - R\frac{\mathrm{d}P}{P} = 0$$

$$\mathrm{d}\tilde{S} = \tilde{C}_V \frac{\mathrm{d}T}{T} - R\frac{\mathrm{d}\tilde{V}}{\tilde{V}} = 0$$

If $\tilde{C}_P$ and $\tilde{C}_V$ are temperature independent, the integration of both equations between an initial state $\tilde{S}_1$, P_1, T_1, $\tilde{V}_1$ and a final state $\tilde{S}_2$, P_2, T_2 y $\tilde{V}_2$ will give

$$\Delta\tilde{S} = \tilde{S}_2 - \tilde{S}_1 = \tilde{C}_P \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right) = 0 \qquad \rightarrow \quad \tilde{C}_P \ln\left(\frac{T_2}{T_1}\right) = R\ln\left(\frac{P_2}{P_1}\right)$$

$$\Delta\tilde{S} = \tilde{S}_2 - \tilde{S}_1 = \tilde{C}_V \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{\tilde{V}_2}{\tilde{V}_1}\right) = 0 \qquad \rightarrow \quad \tilde{C}_V \ln\left(\frac{T_2}{T_1}\right) = -R\ln\left(\frac{\tilde{V}_2}{\tilde{V}_1}\right)$$

from where it follows that

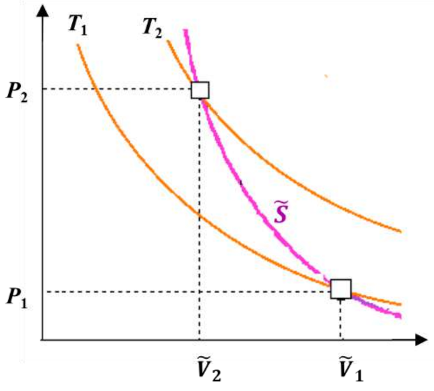
$$\ln\left(\frac{T_2}{T_1}\right) = \frac{R}{\tilde{C}_P}\ln\left(\frac{P_2}{P_1}\right) = -\frac{R}{\tilde{C}_V}\ln\left(\frac{\tilde{V}_2}{\tilde{V}_1}\right)$$

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\tilde{C}_P}{\tilde{C}_V}\ln\left(\frac{\tilde{V}_2}{\tilde{V}_1}\right)$$

$$\frac{P_2}{P_1} = \left(\frac{\tilde{V}_2}{\tilde{V}_1}\right)^{-\tilde{C}_P/\tilde{C}_V} = \left(\frac{\tilde{V}_2}{\tilde{V}_1}\right)^{-\gamma} = \left(\frac{\tilde{V}_1}{\tilde{V}_2}\right)^{\gamma}$$

$$P_1\tilde{V}_1^{\gamma} = P_2\tilde{V}_2^{\gamma}$$

and the requested representation will be



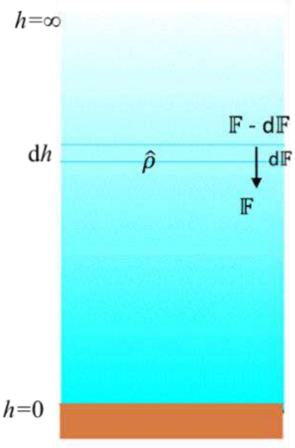
2.9. By applying the ideal gas model to the air of the atmosphere, determine:

a) The variation of pressure with altitude at a constant temperature.

b) The variation of temperature and pressure with altitude if the atmosphere is isentropic.

Question a. According to the law of universal gravitation, the force $\mathrm{d}\mathbb{F}$ that will act on a piece of atmosphere of height $\mathrm{d}h$ and area A, will be

$$\mathrm{d}\mathbb{F} = -\mathrm{d}M \cdot \mathrm{g} = -\hat{\rho} \cdot \mathrm{d}V \cdot \mathrm{g} = -\hat{\rho} \cdot A \cdot \mathrm{d}h \cdot \mathrm{g}$$



From the definition of pressure

$$\mathrm{d}P = \frac{\mathrm{d}\mathbb{F}}{A} = \frac{-\hat{\rho} \cdot A \cdot \mathrm{d}h \cdot \mathrm{g}}{A} = -\hat{\rho} \cdot \mathrm{d}h \cdot \mathrm{g}$$

and by assuming that air behaves like an ideal gas

$$\mathrm{d}P = -\frac{P\mathfrak{M}}{RT} \cdot \mathrm{d}h \cdot \mathrm{g} \qquad [1]$$

The integration of [1] between h=0 (ground level, where P=P_0) and a generic height h where the pressure is P, will give

$$\int_{P_0}^{P} \frac{\mathrm{d}P}{P} = -\frac{\mathfrak{M}\mathrm{g}}{RT} \int_0^h \mathrm{d}h$$

$$[\ln P]_{P_0}^{P} = -\frac{\mathfrak{M}\mathrm{g}}{RT}[h]_0^h \qquad \rightarrow \qquad \ln\left(\frac{P}{P_0}\right) = -\frac{\mathfrak{M}\mathrm{g}h}{RT}$$

$$P = P_0 e^{-\frac{\mathfrak{M}\mathrm{g}h}{RT}} \qquad [2]$$

which is the barometric formula.

Question b. In an isentropic system (section c of reference problem 0.8)

$$\mathrm{d}\tilde{S} = \tilde{C}_P \frac{\mathrm{d}T}{T} - R\frac{\mathrm{d}P}{P} = 0$$

but due to the fact that the Mayer's relation is

$$\tilde{C}_P = \frac{\gamma R}{(\gamma - 1)}$$

the expression can be written as

$$\frac{\gamma}{(\gamma-1)}\frac{\mathrm{d}T}{T} = \frac{\mathrm{d}P}{P}$$

By introducing equation [1]

$$\frac{\gamma}{(\gamma-1)}\frac{\mathrm{d}T}{T} = -\frac{\mathfrak{M}\mathfrak{g}}{RT}\mathrm{d}h \qquad \rightarrow \qquad \mathrm{d}T = -\frac{(\gamma-1)\mathfrak{M}\mathfrak{g}}{\gamma R}\mathrm{d}h$$

and integrating between 0 and h

$$\int_{T_0}^{T}\mathrm{d}T = -\frac{(\gamma-1)\mathfrak{M}\mathfrak{g}}{\gamma R}\int_0^h \mathrm{d}h \qquad \rightarrow \qquad T - T_0 = -\frac{(\gamma-1)\mathfrak{M}\mathfrak{g}}{\gamma R}h \qquad [3]$$

If [3] is introduced in [1] and the integration is performed again

$$\mathrm{d}P = -\frac{P\mathfrak{M}\mathfrak{g}}{R\left\{T_0 - \frac{(\gamma-1)\mathfrak{M}\mathfrak{g}}{\gamma R}h\right\}}\mathrm{d}h \qquad \rightarrow \qquad \frac{\mathrm{d}P}{P} = -\frac{P\mathfrak{M}\mathfrak{g}}{RT_0\left\{1 - \frac{(\gamma-1)\mathfrak{M}\mathfrak{g}}{\gamma RT_0}h\right\}}\mathrm{d}h$$

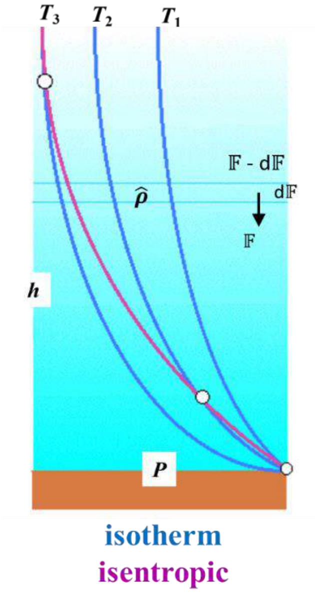
$$\int_{P_0}^{P}\frac{\mathrm{d}P}{P} = -\frac{\mathfrak{M}\mathfrak{g}}{RT_0}\int_0^h \frac{\mathrm{d}h}{\left\{1 - \frac{(\gamma-1)\mathfrak{M}\mathfrak{g}}{\gamma RT_0}h\right\}}$$

$$[\ln P]_{P_0}^{P} = \frac{\gamma}{(\gamma-1)}\left[\ln\left\{1 - \frac{(\gamma-1)\mathfrak{M}\mathfrak{g}}{\gamma RT_0}h\right\}\right]_0^h$$

$$\ln\left(\frac{P}{P_0}\right) = \frac{\gamma}{(\gamma-1)}\ln\left\{1 - \frac{(\gamma-1)\mathfrak{M}\mathfrak{g}}{\gamma RT_0}h\right\}$$

$$\left(\frac{P}{P_0}\right) = \left[1 - \frac{(\gamma - 1)\mathfrak{M}\mathbb{g}}{\gamma R T_0} h\right]^{\frac{\gamma}{(\gamma-1)}} \qquad [4]$$

Equations [3] and [4] are the requested ones.



2.10. Calculate the volume of a mixture of 0.25 mol-g of nitrogen and 0.75 mol-g of hydrogen at 400 bar and 50°C, assuming ideal gas and ideal mixture.

According to section a of reference problem 0.16, the volume of an ideal mixture is the sum of the volumes of its compounds

$$V_{tot} = V_{\mathrm{N_2}} + V_{\mathrm{H_2}} = \frac{n_{\mathrm{N_2}} RT}{P} + \frac{n_{\mathrm{H_2}} RT}{P} = \left(n_{\mathrm{N_2}} + n_{\mathrm{H_2}}\right)\frac{RT}{P}$$

By converting the units of temperature and pressure, and introducing the data in the equation

$$T(\mathrm{K}) = 50\mathrm{°C} + 273 = 323\ \mathrm{K}$$

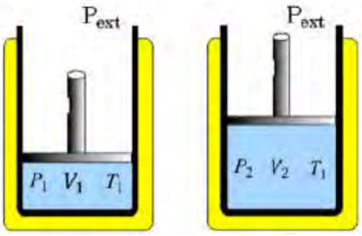
$$400\ \mathrm{bar}\ \times \frac{0.987\ \mathrm{atm}}{1\ \mathrm{bar}} = 394.8\ \mathrm{atm}$$

$$V_{tot} = \frac{(0.25\ \text{mol-g}\ \mathrm{N_2} + 0.75\ \text{mol-g}\ \mathrm{H_2})\left(0.082\,\frac{\mathrm{atm}\cdot\mathrm{L}}{\mathrm{K}\cdot\text{mol-g}}\right)(323\ \mathrm{K})}{394.8\ \mathrm{atm}} = 0.0671\ \mathrm{L}$$

2.11. Propose an example showing that in a series of thermodynamic changes from a state 1 to a state 2, the operating cost can be different, although the rest of the changes in the state properties are the same.

Thermodynamically speaking, the operating cost is associated with the work done and the heat communicated. Since neither work nor heat are state functions, this cost will depend on the path from the initial situation (point 1) to a final situation (point 2).

Simple example: Calculation of the work in the expansion of a gas from conditions P_1, T_1 and V_1 to other conditions P_2, T_1 and V_2.



By assuming that the pressure is transmitted instantaneously, one way would be to isobarically expand the system from V_1 to V_2 (at the initial pressure P_1) and then decompress it to P_2. As a consequence of the expansion, the gas will reach a temperature T_2 and the work done would be

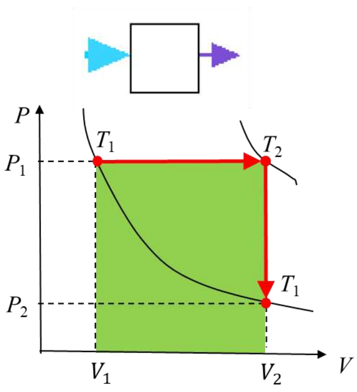
$$\mathrm{d}W^{\text{e-c}} = -P_1\mathrm{d}V \quad \rightarrow \int_{W_1}^{W_2} \mathrm{d}W^{\text{e-c}} = -\int_{V_1}^{V_2} P_1\mathrm{d}V \quad \rightarrow \Delta W^{\text{e-c}} = P_1(V_1 - V_2)$$

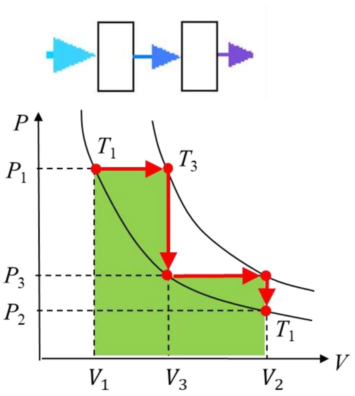
Another way would be to perform the process in two stages: expanding the gas from V_1 to an intermediate volume V_3 (at a constant P_1), decompressing to an intermediate pressure P_3, expanding it again to volume V_2 and finally decompressing to pressure P_1. Work will be now

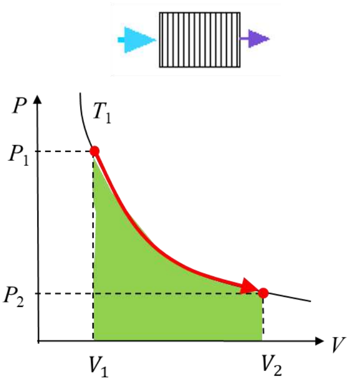
$$\int_{W_1}^{W_2} \mathrm{d}W^{\text{e-c}} = -\int_{V_1}^{V_3} P_1\mathrm{d}V - \int_{V_3}^{V_2} P_3\mathrm{d}V \quad \rightarrow \Delta W^{\text{e-c}} = P_1(V_1 - V_3) + P_3(V_3 - V_2)$$

The number of stages could be increased to infinity, when an equation of state is needed to relate P and V. If the ideal gas model is used

$$\Delta W^{\text{e-c}} = -\int_{V_1}^{V_2} P\mathrm{d}V = -\int_{V_1}^{V_2} \frac{nRT}{V}\mathrm{d}V = -nRT[\ln V]_{V_1}^{V_2} = nRT\ln\left(\frac{V_1}{V_2}\right)$$







As can be seen, in none of the cases the work done (areas under the curves) is the same (the interested readeres are suggested to calculate the heat transfer which is also implied in these operations).

2.12. Two moles of an ideal gas at 300 K and 2 atm are within a cylindrical chamber with adiabatic walls:

a) **If the pressure suddenly increases a 20% by means of a frictionless piston, determine the changes in the temperature and the internal energy of the gas. Take $\tilde{C}_P = 5R/2$.**

b) **The problem seems overdefined. What datum is unnecessary?**

c) **How does the analyzed situation differ from the real one? Describe it qualitatively.**

Question a. The process is isentropic because adiabaticity and reversibility. Hence, for an ideal gas (section c of reference problem 0.8)

$$\mathrm{d}\tilde{S} = \tilde{C}_P \frac{\mathrm{d}T}{T} - R\frac{\mathrm{d}P}{P} = 0$$

By taking the specific heat capacity of 5R/2 and integrating between states 1 and 2

$$\Delta\tilde{S} = \int_{T_1}^{T_2} \frac{5R}{2}\frac{\mathrm{d}T}{T} - \int_{P_1}^{P_2} R\frac{\mathrm{d}P}{P} = \frac{5}{2}R[\ln T]_{T_1}^{T_2} - R[\ln P]_{P_1}^{P_2} = \frac{5}{2}R\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right) = 0$$

from which we obtain

$$\frac{5}{2}\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{P_2}{P_1}\right) \quad \rightarrow \quad \left(\frac{T_2}{T_1}\right)^{\frac{5}{2}} = \left(\frac{P_2}{P_1}\right)$$

and taking into account that T_1=300 K and that P_2=1.2P_1 (a 20% higher)

$$\left(\frac{T_2}{300\ \mathrm{K}}\right)^{\frac{5}{2}} = \left(\frac{1.2P_1}{P_1}\right) \quad \rightarrow \quad T_2 = (300\ \mathrm{K})(1.2)^{\frac{2}{5}} = 322.696\ \mathrm{K}$$

On the other hand, the internal energy of the system can be evaluated from the specific heat capacity at constant volume (section d of reference problem 0.4) and the Mayer's relation (section b of reference problem 0.6)

$$\mathrm{d}U = n\tilde{C}_V\mathrm{d}T$$

$$\tilde{C}_P - \tilde{C}_V = R \qquad \rightarrow \ \tilde{C}_V = \tilde{C}_P - R = \frac{5}{2}R - R = \frac{3}{2}R$$

or from the expansion-compression work (reference problem 0.3) and the well-known equation $P_1V_1^\gamma = P_2V_2^\gamma$

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \qquad \xrightarrow{\mathrm{d}S=0} \qquad \mathrm{d}U = -P\mathrm{d}V = \mathrm{d}W^{\text{e-c}}$$

$$\Delta W^{\text{e-c}} = -\int_1^2 P\mathrm{d}V = -\int_1^2 P_1\left(\frac{V_1}{V}\right)^{\gamma}\mathrm{d}V = -\frac{P_1V_1^{\gamma}}{1-\gamma}\left[V_2^{1-\gamma}-V_1^{1-\gamma}\right] = \frac{P_1V_1}{\gamma-1}\left[\left(\frac{V_2}{V_1}\right)^{1-\gamma}-1\right]$$

$$\Delta U = \frac{P_1V_1}{\gamma-1}\left[\left(\frac{P_1}{P_2}\right)^{\frac{1-\gamma}{\gamma}}-1\right] = \frac{nRT_1}{\gamma-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}-1\right]$$

In the first case,

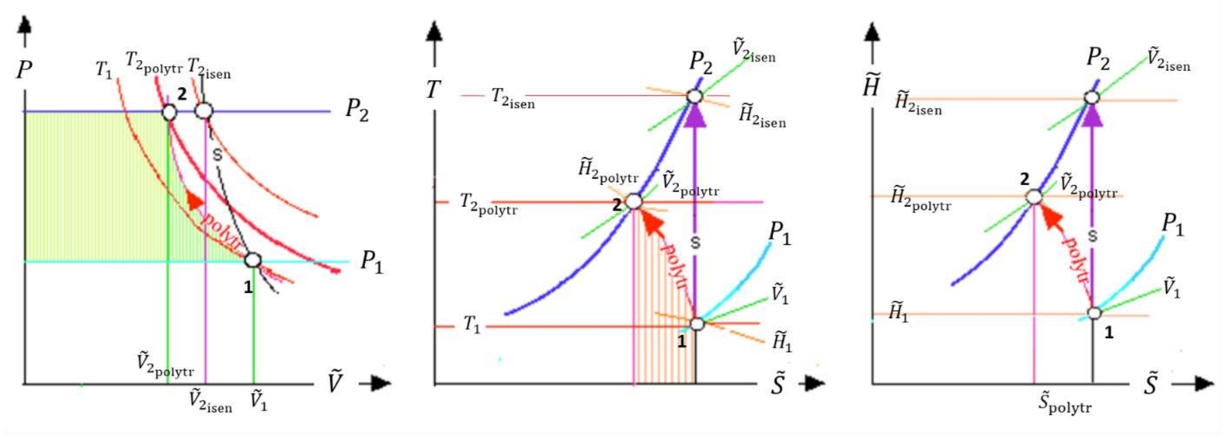
$$\Delta U = n\frac{3}{2}R(T_2-T_1) = (2\ \text{mol-g})\frac{3}{2}\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(322.696\ \text{K}-300\ \text{K}) = 5.583\ \text{atm·L}$$

and in the second one, with $\gamma=\tilde{C}_P/\tilde{C}_V=5/3$

$$\Delta U = \frac{(2\ \text{mol-g})\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(300\ \text{K})}{\frac{5}{3}-1}\left[1.2^{\frac{2}{5}}-1\right] = 5.583\ \text{atm·L}$$

Question b. As shown in the previous question, the pressure (2 atm) has not been employed in calculations. It is only required to determine the volumes in the initial and final states.

Question c. In real situations, it is very difficult to follow a strictly isentropic route, since there are heat exchanges and friction that cause an entropy increase. $T\mathrm{d}S\neq0$ and then we have a polytropic transformation, in which γ is replaced by an empirical coefficient that takes values different from 5/3.



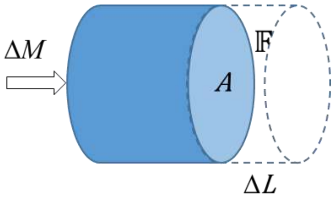
2.13. A substance in the gaseous phase is subjected to an expansion of 1 liter at atmospheric pressure:

a) Analyze the phenomenon.

b) Calculate the work done in ergs, joules and calories.

c) Qualitatively represent the operation line in *PT*(*V*), *PV*(*T*), *PH*(*T*) and *TS*(*P*) diagrams.

Question a. There are two possible types of work: that due to convective expansion and that due to thermal expansion.



Injection of a mass ΔM in an open system generates the first case. From the definition of work (product of force and displacement, equivalent to the product of pressure and volume)

$$\Delta W_{tot} = \mathbb{F} \cdot \Delta L = P \cdot A \cdot \Delta L = P \cdot \Delta V = (1\ \mathrm{atm})(1\ \mathrm{L}) = 1\ \mathrm{atm} \cdot \mathrm{L}$$

Theoretically, this injection of mass would not cause a temperature rising (isothermal system) but in real processes friction can occur, which would increase the temperature of the system. Thus, it would be necessary to apply more work than the calculated one.

Temperature increase in a closed system generates the second case. A reversible isobaric expansion requires heating. For an ideal gas $PV = nRT$ and

$$\Delta W^{\text{e-c}} = -\int_{V_1}^{V_2} P \mathrm{d}V = -P_1 \cdot [V]_{V_1}^{V_2} = P_1(V_1 - V_2) = -P \cdot \Delta V = -(1\ \mathrm{atm})(1\ \mathrm{L})$$

The absolute value of this result is numerically equal to that of the first case. The temperature change ΔT that causes the expansion will be directly proportional to the volume variation and inversely proportional to the number of moles of the system (datum not specified in the statement of the problem).

$$P_1(V_1 - V_2) = nR(T_1 - T_2) = -nR\Delta T \qquad \rightarrow \qquad \Delta T = \frac{P_1(V_2 - V_1)}{nR}$$

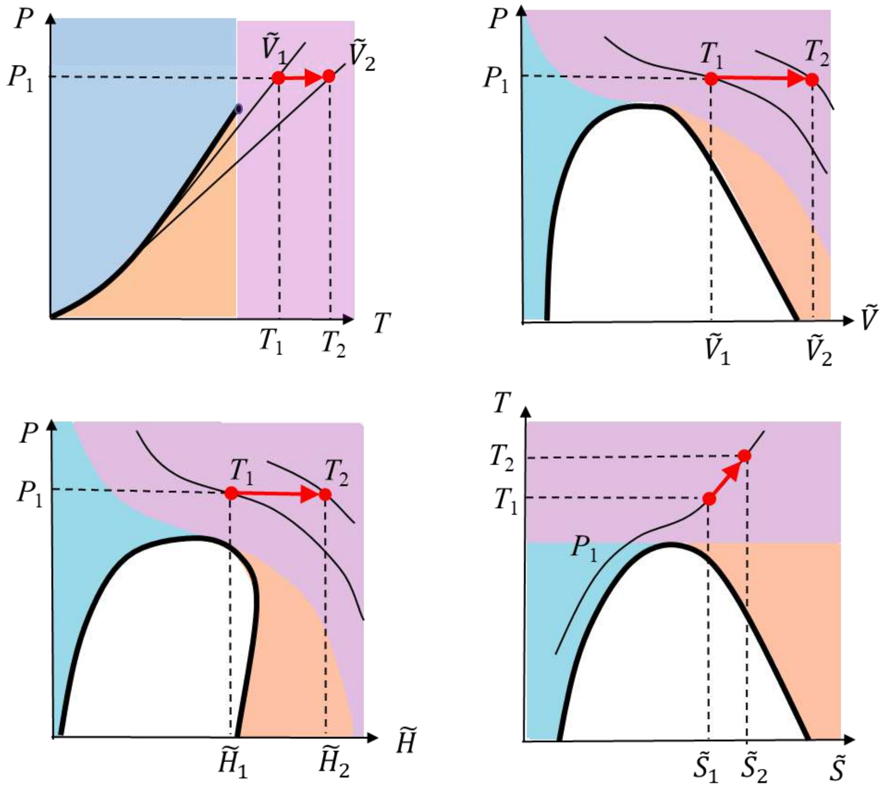
Question b. Unit conversion of the work through the factors of appendix I gives

$$1\ \mathrm{atm} \cdot \mathrm{L} \times \frac{1.01 \cdot 10^9\ \mathrm{erg}}{1\ \mathrm{atm} \cdot \mathrm{L}} = 1.01 \cdot 10^9\ \mathrm{erg}$$

$$1\ \mathrm{atm} \cdot \mathrm{L} \times \frac{101\ \mathrm{J}}{1\ \mathrm{atm} \cdot \mathrm{L}} = 101\ \mathrm{J}$$

$$1\ \text{atm}\cdot\text{L}\times\frac{0.0242\ \text{kcal}}{1\ \text{atm}\cdot\text{L}}\times\frac{1000\ \text{cal}}{1\ \text{kcal}}=24.2\ \text{cal}$$

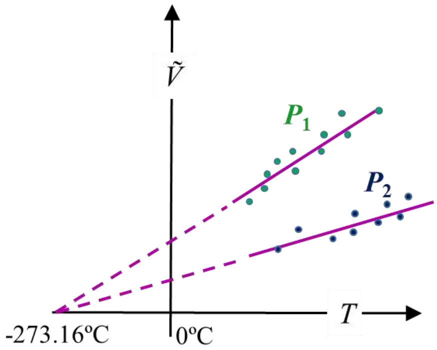
Question c. The graphical representation of the second case will be



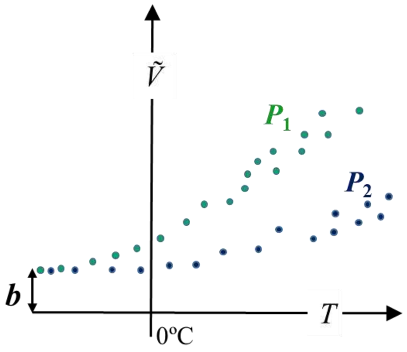
where it is seen that the volume increase not only leads to a temperature variation, but also to enthalpy and entropy changes.

2.14. When the molar volume of a gas is represented versus the temperature (at a constant pressure) data that can be fitted to a straight line are obtained. If the lines at several pressures are extrapolated they all converge to a temperature point of -273.16ºC. What does this mean?

Extrapolation indicates that the ideal gas would be fully compressible and would reach a zero molar volume at that very low temperature, which could therefore be considered an accessible limit (the absolute zero).



However, a discrepancy is observed in real cases that would allow the characterization of the condensed gas volume (roughly predictable by the Van der Waals equation) through the *b* dimensional parameter.



2.15. Compare the volumes predicted by the ideal gas and the Van der Waals equations for 1 mol-g of nitrogen at 400 atm and 0ºC if

$$\boldsymbol{a = 1.35 \cdot 10^6 \frac{\text{atm} \cdot \text{cm}^6}{\text{mol-g}^2} \qquad b = 38.64 \ \frac{\text{cm}^3}{\text{mol-g}}}$$

For the ideal gas

$$V = \frac{nRT}{P} = \frac{(1 \text{ mol-g})\left(0.082 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol-g}}\right)(273.2 \text{ K})}{400 \text{ atm}} = 0.056 \text{ L}$$

For the Van der Waals gas

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

By converting the units of the constants and introducing them in the previous expression, it is found

$$a = 1.35 \cdot 10^6 \frac{\text{atm} \cdot \text{cm}^6}{\text{mol-g}^2} \times \left(\frac{1 \text{ dm}}{10 \text{ cm}}\right)^6 \times \left(\frac{1 \text{ L}}{1 \text{ dm}^3}\right)^2 = 1.35 \frac{\text{atm} \cdot \text{L}^2}{\text{mol-g}^2}$$

$$b = 38.64 \ \frac{\text{cm}^3}{\text{mol-g}} \times \left(\frac{1 \text{ dm}}{10 \text{ cm}}\right)^3 \times \frac{1 \text{ L}}{1 \text{ dm}^3} = 0.03864 \frac{\text{L}}{\text{mol-g}}$$

$$400 \text{ atm} = \frac{(1 \text{ mol-g})\left(0.082 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol-g}}\right)(273.2 \text{ K})}{V - (1 \text{ mol-g})\left(0.03864 \frac{\text{L}}{\text{mol-g}}\right)} - \frac{\left(1.35 \frac{\text{atm} \cdot \text{L}^2}{\text{mol-g}^2}\right)(1 \text{ mol-g})^2}{V^2}$$

$$400 \text{ atm} = \frac{22.4 \text{ atm} \cdot \text{L}}{V - 0.03864 \text{ L}} - \frac{1.35 \text{ atm} \cdot \text{L}^2}{V^2} \qquad [1]$$

In this equation the value of V has to be determined by trial and error approach.

- In the first place, it can be assumed that the nitrogen is close to those conditions of the ideal gas, so the molar volume will be very large and

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad \overset{V \gg}{\longrightarrow} \quad P(V - nb) \approx nRT \quad \rightarrow V = \frac{nRT}{P} + nb$$

$$V = \frac{(1 \text{ mol-g})\left(0.082 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol-g}}\right)(273.2 \text{ K})}{400 \text{ atm}} + (1 \text{ mol-g})\left(0.03864 \frac{\text{L}}{\text{mol-g}}\right) = 0.095 \text{ L}$$

Value that has to be introduced in the general equation [1] to know the goodness of the approximation

$$\frac{22.4\ \mathrm{atm\cdot L}}{0.095\ \mathrm{L}-0.03864\ \mathrm{L}}-\frac{1.35\ \mathrm{atm\cdot L^2}}{(0.095\ \mathrm{L})^2}=247.86\ \mathrm{atm}$$

This pressure is very low, far from the 400 atm given by the statment of the problem. Thus, the actual volume will be lower than 0.095 L.

- By assuming that V=0.070 L

$$\frac{22.4\ \mathrm{atm\cdot L}}{0.070\ \mathrm{L}-0.03864\ \mathrm{L}}-\frac{1.35\ \mathrm{atm\cdot L^2}}{(0.070\ \mathrm{L})^2}=438.77\ \mathrm{atm}$$

Contrary to the previous case, the calculated pressure is much higher than 400 atm, so the actual volume will be higher.

- If V=0.075 L

$$\frac{22.4\ \mathrm{atm\cdot L}}{0.075\ \mathrm{L}-0.03864\ \mathrm{L}}-\frac{1.35\ \mathrm{atm\cdot L^2}}{(0.075\ \mathrm{L})^2}=376.06\ \mathrm{atm}$$

A result closer to 400 atm, although still lower. It indicates that the actual volume should be sligthly lower than 0.075 L.

- If V=0.0729 L

$$\frac{22.4\ \mathrm{atm\cdot L}}{0.0729\ \mathrm{L}-0.03864\ \mathrm{L}}-\frac{1.35\ \mathrm{atm\cdot L^2}}{(0.0729\ \mathrm{L})^2}=399.8\ \mathrm{atm}$$

The calculated pressure is almost the same than 400 atm, and therefore 0.0729 L will be taken as the sought volume.

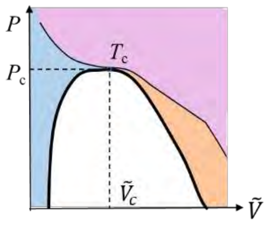
Notice that the volume given by Van der Waals is 30% higher than that estimated by the ideal gas model.

2.16. Justify the generalization of the *Corresponding States Principle* from the Van der Waals state model.

In this equation of state

$$\left(P+\frac{a}{\tilde{V}^2}\right)\left(\tilde{V}-b\right)=RT \qquad \rightarrow \qquad P=\frac{RT}{\left(\tilde{V}-b\right)}-\frac{a}{\tilde{V}^2} \qquad [1]$$

it is assumed that there is an inflection point in the $P(\tilde{V})$ curve at the critical point; i.e., its first and second derivatives are equal to zero at T_c and P_c



$$\left(\frac{\partial P}{\partial \tilde{V}}\right)_{T_c}=0 \qquad \left(\frac{\partial^2 P}{\partial \tilde{V}^2}\right)_{T_c}=0$$

By applying these conditions to [1]

$$\left(\frac{\partial P}{\partial \tilde{V}}\right)_T=-\frac{RT}{\left(\tilde{V}-b\right)^2}+\frac{2a}{\tilde{V}^3} \quad \rightarrow \quad -\frac{RT_c}{\left(\tilde{V}_c-b\right)^2}+\frac{2a}{\tilde{V}_c^3}=0 \quad \rightarrow \quad \frac{RT_c}{\left(\tilde{V}_c-b\right)^2}=\frac{2a}{\tilde{V}_c^3} \qquad [2]$$

$$\left(\frac{\partial^2 P}{\partial \tilde{V}^2}\right)_T=\frac{2RT}{\left(\tilde{V}-b\right)^3}-\frac{6a}{\tilde{V}^4}=0 \quad \rightarrow \quad \frac{2RT_c}{\left(\tilde{V}_c-b\right)^3}-\frac{6a}{\tilde{V}_c^4}=0 \quad \rightarrow \quad \frac{2RT_c}{\left(\tilde{V}_c-b\right)^3}=\frac{6a}{\tilde{V}_c^4} \qquad [3]$$

If a is obtained from [2] and introduced in [3], then

$$\frac{\tilde{V}_c^3RT_c}{2\left(\tilde{V}_c-b\right)^2}=a \qquad [4]$$

$$\frac{2RT_c}{\left(\tilde{V}_c-b\right)^3}=\frac{6a}{\tilde{V}_c^4}=\frac{6}{\tilde{V}_c^4}\frac{\tilde{V}_c^3RT_c}{2\left(\tilde{V}_c-b\right)^2} \quad \rightarrow \quad \frac{2RT_c}{\left(\tilde{V}_c-b\right)^3}=\frac{3}{\tilde{V}_c}\frac{RT_c}{\left(\tilde{V}_c-b\right)^2}$$

and therefore

$$\frac{2RT_c}{\left(\tilde{V}_c-b\right)^3}=\frac{6a}{\tilde{V}_c^4}=\frac{6}{\tilde{V}_c^4}\frac{\tilde{V}_c^3RT_c}{2\left(\tilde{V}_c-b\right)^2} \quad \rightarrow \quad \frac{2\tilde{V}_c}{3}=\tilde{V}_c-b \quad \rightarrow \quad b=\frac{\tilde{V}_c}{3} \qquad [5]$$

If this value of b is substituted in [4]

$$a = \frac{\tilde{V}_c^3 R T_c}{2\left(\tilde{V}_c - \frac{\tilde{V}_c}{3}\right)^2} = \frac{\tilde{V}_c^3 R T_c}{2\left(\frac{2\tilde{V}_c}{3}\right)^2} = \frac{9}{8} R T_c \tilde{V}_c \qquad [6]$$

When the constants given by expression [5] and [6] are introduced in [1], the Van der Waals equation becomes

$$\left(P + \frac{9}{8}\frac{R T_c \tilde{V}_c}{\tilde{V}^2}\right)\left(\tilde{V} - \frac{\tilde{V}_c}{3}\right) = RT \qquad [7]$$

whose value in the critical point will be

$$\left(P_c + \frac{9}{8}\frac{R T_c \tilde{V}_c}{\tilde{V}_c^2}\right)\left(\tilde{V}_c - \frac{\tilde{V}_c}{3}\right) = R T_c \;\rightarrow\; P_c \tilde{V}_c \left(1 + \frac{9}{8}\frac{R T_c \tilde{V}_c}{P_c \tilde{V}_c^2}\right)\left(1 - \frac{1}{3}\right) = R T_c$$

$$z_c \left(1 + \frac{9}{8 z_c}\right)\left(1 - \frac{1}{3}\right) = 1 \quad \rightarrow \quad z_c + \frac{9}{8} = \frac{3}{2} \quad \rightarrow \quad z_c = \frac{3}{8} \qquad [8]$$

On the other hand, the Corresponding States Principle is based on employing reduced coordinates $P_r = P/P_c$, $T_r = T/T_c$ and $V_r = V/V_c$

$$\left[P_c P_r + \frac{9}{8}\frac{R T_c \tilde{V}_c}{\left(\tilde{V}_c \tilde{V}_r\right)^2}\right]\left(\tilde{V}_c \tilde{V}_r - \frac{\tilde{V}_c}{3}\right) = R T_c T_r \;\rightarrow\; P_c \tilde{V}_c \left[P_r + \frac{9}{8}\frac{R T_c \tilde{V}_c}{P_c \tilde{V}_c^2 \tilde{V}_r^2}\right]\left(\tilde{V}_r - \frac{1}{3}\right) = R T_c T_r$$

$$\frac{P_c \tilde{V}_c}{R T_c}\left[P_r + \frac{9}{8}\frac{R T_c}{P_c \tilde{V}_c \tilde{V}_r^2}\right]\left(\tilde{V}_r - \frac{1}{3}\right) = T_r \;\rightarrow\; z_c \left[P_r + \frac{9}{8}\frac{1}{z_c \tilde{V}_r^2}\right]\left(\tilde{V}_r - \frac{1}{3}\right) = T_r$$

After introducing the critical compressibility factor of [8], it can be seen that the obtained equation does not depend on any substance-specific constant

$$\frac{3}{8}\left[P_r + \frac{9}{8}\frac{8}{3\tilde{V}_r^2}\right]\left(\tilde{V}_r - \frac{1}{3}\right) = T_r \quad \rightarrow \quad \left[P_r + \frac{3}{\tilde{V}_r^2}\right]\left(\tilde{V}_r - \frac{1}{3}\right) = \frac{8}{3} T_r$$

2.17. By means of the Lydersen method, evaluate the critical properties of *n*-propanol (normal boiling point of 370 K and molecular weight of 60.096 g/mol-g) and of fluorobenzene (normal boiling point of 358.1 K and molecular weight of 96.104 g/mol-g).

According to reference problem 0.9

$$\frac{T_b}{T_c} = 0.567 + \Sigma\Delta_T - (\Sigma\Delta_T)^2$$

$$P_c = \frac{\mathfrak{M}}{(0.34 + \Sigma\Delta_P)^2}$$

$$\tilde{V}_c = 40 + \Sigma\Delta_V$$

where the normal boiling point and the critical temperature, T_b and T_c, are expressed in K, P_c in atmospheres, $\mathfrak{M}$ in g/mol-g and $\tilde{V}_c$ in cm^3/mol-g. The increments Δ_T, Δ_P and Δ_V are dimensionless and are tabulated in appendix III.

For *n*-propanol

CH_3-CH_2-CH_2-OH

the increments for each group will be

group	Number	Δ_T	Δ_P	Δ_V
-CH_3	1	0.020	0.227	55
-CH_2	2	0.020	0.227	55
-OH	1	0.082	0.06	18

and so

$$\Sigma\Delta_T = 0.020+2(0.020)+0.082 = 0.142$$

$$\Sigma\Delta_P = 0.227+2(0.227)+0.06 =0.741$$

$$\Sigma\Delta_V = 55+2(55)+18 =183$$

obtaining

$$T_c = \frac{T_b}{0.567 + (0.142) - (0.142)^2} = \frac{370\ \text{K}}{0.689} = 537.13\ \text{K}$$

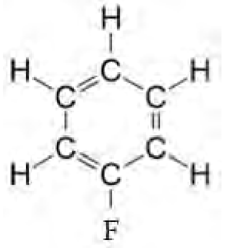
$$P_c = \frac{\mathfrak{M}}{(0.34 + 0.741)^2} = \frac{60.096\ \text{g/mol-g}}{1.168} = 51.45\ \text{atm}$$

$$\tilde{V}_c = 40 + 183 = 223\ \frac{\text{cm}^3}{\text{mol-g}}$$

$$z_c = \frac{P_c \tilde{V}_c}{RT_c} = \frac{(51.45\ \text{atm})\left(223\ \frac{\text{cm}^3}{\text{mol-g}} \times \left(\frac{1\ \text{dm}}{10\ \text{cm}}\right)^3 \times \frac{1\ \text{L}}{1\ \text{dm}^3}\right)}{\left(0.082 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol-g}}\right)(537.13\ \text{K})} = 0.26$$

Appendix II shows that T_c=536.78 K, P_c=51.08 atm, $\tilde{V}_c$=219 cm^3/mol-g and z_c=0.254 for this substance, which are very close to the calculated values.

For fluorobenzene



Group	Number	Δ_T	Δ_P	Δ_V
-CH= (ring)	5	0.011	0.154	37
-C= (ring)	1	0.011	0.154	36
-F	1	0.018	0.224	18

and operating as in the previous case

$$\Sigma\Delta_T = 5(0.011) + 0.011 + 0.018 = 0.084$$
$$\Sigma\Delta_P = 5(0.154) + 0.154 + 0.224 = 1.148$$
$$\Sigma\Delta_V = 5(37) + 36 + 18 = 239$$

$$T_c = \frac{T_b}{0.567 + (0.084) - (0.084)^2} = \frac{358.1\ \text{K}}{0.6439} = 556.1\ \text{K}$$

$$P_c = \frac{\mathfrak{M}}{(0.34 + 1.148)^2} = \frac{96.104\ \text{g/mol-g}}{2.214} = 43.40\ \text{atm}$$

$$\tilde{V}_c = 40 + 239 = 279\ \frac{\text{cm}^3}{\text{mol-g}}$$

$$z_c = \frac{P_c \tilde{V}_c}{RT_c} = \frac{(43.40\ \text{atm})\left[279\ \dfrac{\text{cm}^3}{\text{mol-g}} \times \left(\dfrac{1\ \text{dm}}{10\ \text{cm}}\right)^3 \times \dfrac{1\ \text{L}}{1\ \text{dm}^3}\right]}{\left(0.082\,\dfrac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(556.1\ \text{K})} = 0.2655$$

From tables of Perry et al. (1997), the actual values are T_c=560.09 K, P_c=4.543 MPa (44.84 atm) and $\tilde{\rho}_c = 3.72$ mol/L ($\tilde{V}_c$ =268.81 cm^3/mol)

$$z_c = \frac{P_c}{\tilde{\rho}_c RT_c} = \frac{(44.84\ \text{atm})}{\left[3.72\ \dfrac{\text{mol-g}}{\text{L}}\right]\left(0.082\,\dfrac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(560.09\ \text{K})} = 0.2624$$

2.18. Calculate the pressure of 1 mol-g of CO_2 at 40°C which occupies a volume of 0.381 L according to:

a) The ideal gas model.
b) The Van der Waals equation of state (*a*= 360 atm·L²/mol-g², *b*=4.28·10⁻² L/mol-g).
c) The generalized charts of the Corresponding States Principle.

Question a. For the ideal gas

$$P = R\frac{T}{\tilde{V}}$$

where T is the absolute temperature in K and $\tilde{V}$ the molar volume. Taking into account the unit conversion tables of appendix I and the definition of molar volume

$$T(\text{K}) = T(°\text{C}) + 273 = 40 + 273 = 313\ \text{K}$$

$$\tilde{V} = \frac{V}{n} = \frac{0.381\ \text{L}}{1\ \text{mol-g}} = 0.381\ \frac{\text{L}}{\text{mol-g}}$$

Therefore

$$P = \left(0.082\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)\frac{(313\ \text{K})}{\left(0.381\frac{\text{L}}{\text{mol-g}}\right)} = 0.082\frac{313}{0.381}\ \text{atm} = 67.36\ \text{atm}$$

Question b. According to the equation of Van der Waals

$$\left(P + \frac{a}{\tilde{V}^2}\right)\left(\tilde{V} - b\right) = RT$$

and introducing in it the values of the constants a and b given in the statement of the problem, and the absolute temperature and the molar volume calculated in the previous question

$$\left[P + \frac{\left(360\frac{\text{atm}\cdot\text{L}^2}{\text{mol-g}^2}\right)}{\left(0.381\frac{\text{L}}{\text{mol-g}}\right)^2}\right]\left[0.381\frac{\text{L}}{\text{mol-g}} - 0.043\frac{\text{L}}{\text{mol-g}}\right] = \left(0.082\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(313\ \text{K})$$

$$P = \frac{0.082\cdot 313}{0.381 - 0.043}\ \text{atm} - \frac{360}{0.381^2}\ \text{atm} = 75.93 - 24.8 = 51.13\ \text{atm}$$

Question c. According to the Corresponding States Principle (reference problem 0.8), the equation of the ideal gas is corrected by means of a function called compressibility (z) in the form

$$P\tilde{V} = zRT$$

$$\left.\begin{array}{lll} z = \mathrm{f}(T_r, P_r) & \text{if} & z_c = 0.27 \\ z = \mathrm{f}(T_r, P_r, z_c) & \text{if} & z_c \neq 0.27 \end{array}\right\}$$

where $\mathrm{f}(T_r , P_r)$ is given by figure IV.1 of this book's appendix IV, and $\mathrm{f}(T_r , P_r, z_c)$ is expressed as $\mathrm{f}(T_r , P_r)+[z_c-0.27]\Psi_z$, being Ψ_z functions of reduced temperature and pressure as well (see figure IV.2). In the case of carbon dioxide (appendix II)

$$P_c = 72.9 \text{ atm}$$
$$T_c = 304.2 \text{ K}$$
$$z_c = 0.274$$

Since the critical compressibility factor is very close to 0.27, the correction function Ψ_z will be neglected.

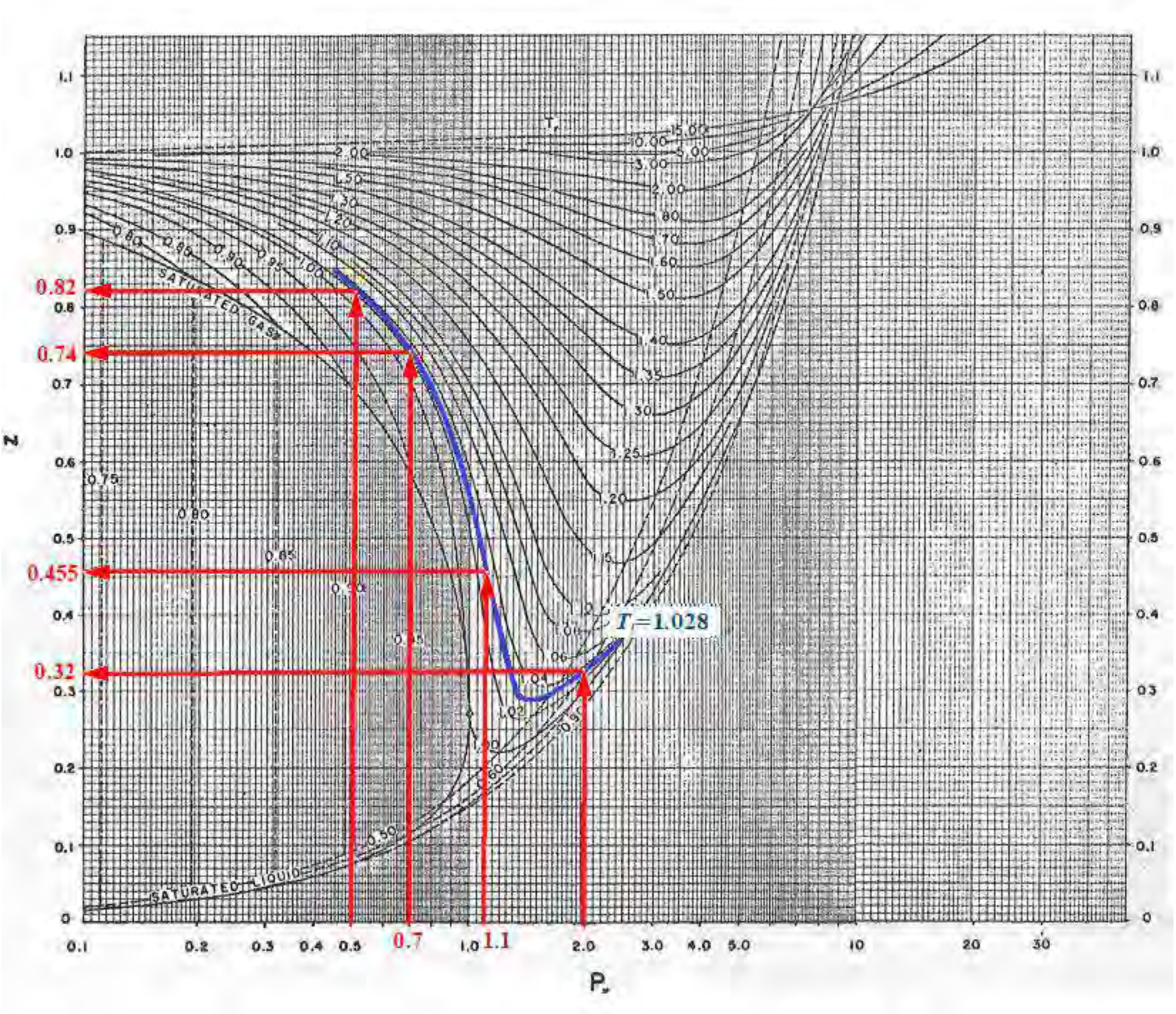
On the other hand, Figure IV.1 is an explicit function of T_r and P_r, and since pressure is not known, a trial and error procedure will be required. It will consist of assuming values of P, obtaining the corresponding value of z in the figure and checking if that value of z satisfies that

$$P_r = \frac{P}{P_c} = \frac{zRT}{P_c\tilde{V}} = \frac{z}{(72.9 \text{ atm})}\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)\frac{(313 \text{ K})}{\left(0.381\,\dfrac{\text{L}}{\text{mol-g}}\right)} = 0.924z \qquad [1]$$

Additionally, reduced temperature is constant and equal to

$$T_r = \frac{T}{T_c} = \frac{313 \text{ K}}{304.2 \text{ K}} = 1.028$$

Assumed P_r	Assumed P (atm)	z read in the graph at assumed P_r	P_r obtained from [1] with the read z	Notes
2.0	145.8	0.32	0.2957	Assumed P_r must be lower
1.1	80.19	0.455	0.434	Assumed P_r must be lower
0.5	36.45	0.82	0.757	Assumed P_r must be higher
0.7	51.03	0.74	0.688	P_r is roughly the correct value

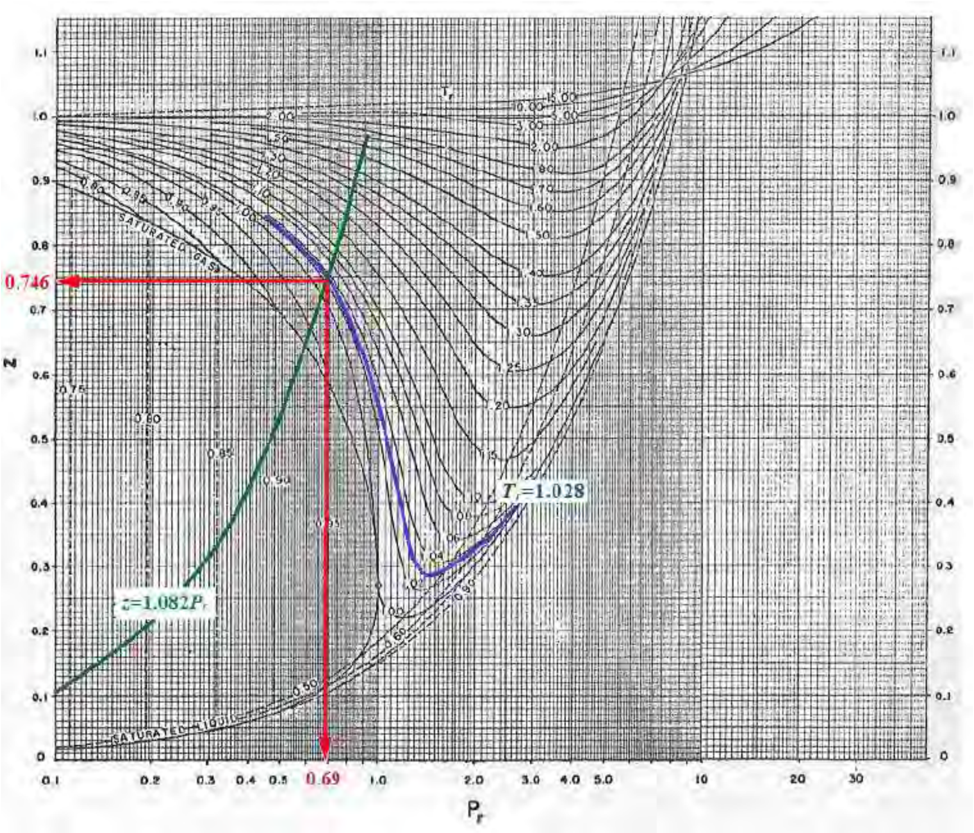


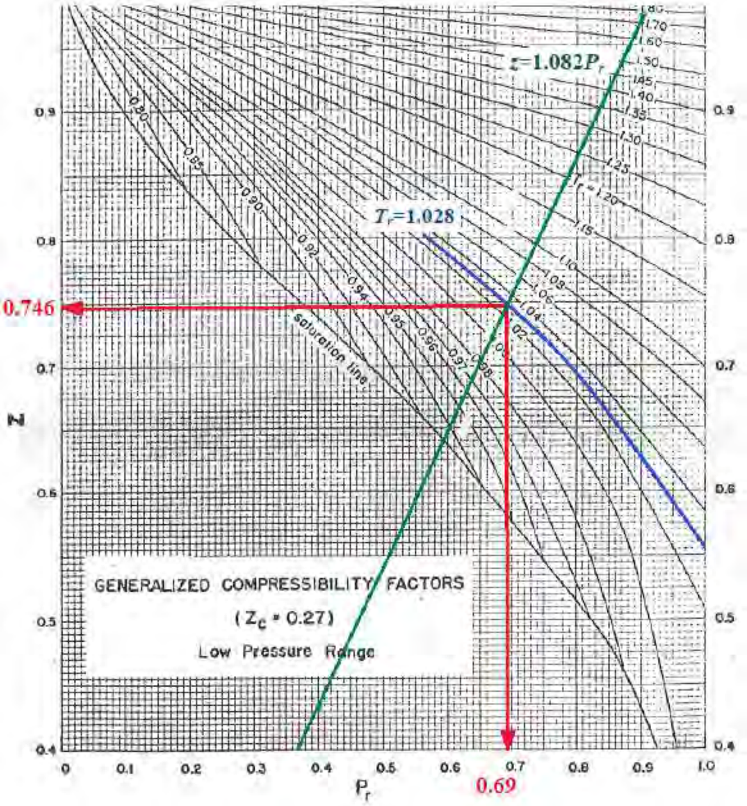
A modification of this graphical procedure is to represent the line $z=P_r/0.924=1.082P_r$ in figure IV.1 and to obtain the desired reduced pressure at the intersection of this line with the isotherm $T_r=1.028$.

P_r	z
0.1	0.1082
0.2	0.2164
0.3	0.3246
0.4	0.4328
0.5	0.5410
0.6	0.6492
0.7	0.7574
0.8	0.8656
0.9	0.9738
1.0	1.0820

The crossing occurs at P_r=0.69, so $P= 0.69P_c$= 50.30 atm.

Finally, it has to be pointed out that when a logarithmic scale is employed for P_r (abscissa axis), the line resembles a curve. When a linear scale is used for the reduced pressure, as in Figure IV.3 (enlargement of IV.1 in the low-density zone), the line z= 1.082P_r appears as such.





2.19. How much added heat is needed to raise the temperature of 1 mol-g of oxygen from 27ºC to 127ºC at 87 atm?

- **a) Calculate it by means of a specific *PH*(T,V,S) diagram for O$_2$.**
- **b) Calculate it by employing the generalized graphs of the Corresponding States Principle and assuming that its behavior does not differ from that of z_c=0.27.**
- **c) Redo the problem if the heating occurs at 1 atm.**

In general

$$\Delta Q_{21} = \int_{T_1}^{T_2} T\mathrm{d}S$$

but if pressure remains constant (dP=0), according to the equations of reference problem 0.3

$$\mathrm{d}H = \mathrm{d}Q + \mathrm{d}W^{\mathrm{fl}} = T\mathrm{d}S + V\mathrm{d}P$$

$\mathrm{d}H = \mathrm{d}Q$ and the heat exchanged can be calculated as

$$\Delta Q_{21} = \Delta H_{21} = n\Delta\widetilde{H}_{21}$$

Question a. In appendix V of this book, figure V.1 shows the dependence of the oxygen enthalpy (ordinate axis) with pressure (abscissa axis) at different temperatures, volumes and entropies (isolines). In order to use it, the quantities involved have to be expressed in the corresponding units, following the conversion factors of appendix I

$$87\ \mathrm{atm} \times \frac{2120\ \mathrm{lb_f/ft^2}}{1\ \mathrm{atm}} \times \left(\frac{1\ \mathrm{ft}}{12\ \mathrm{in}}\right)^2 = 1280.83\ \frac{\mathrm{lb_f}}{\mathrm{in^2}}$$

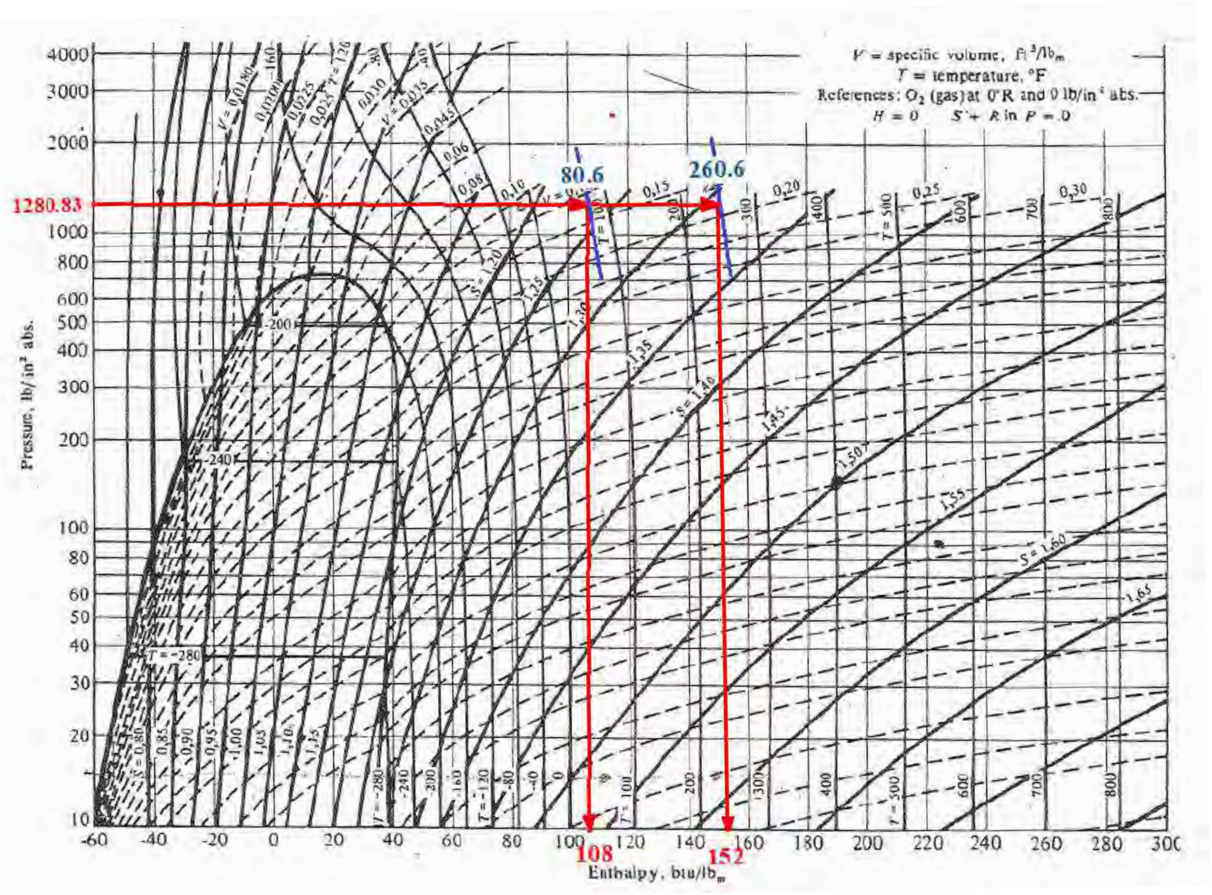
$$T_1(°\mathrm{F}) = 1.8(27°\mathrm{C}) + 32 = 80.6°\mathrm{F}$$

$$T_2(°\mathrm{F}) = 1.8(127°\mathrm{C}) + 32 = 260.6°\mathrm{F}$$

and it can be read in the graph that

$$\widehat{H}_1 = 108\ \mathrm{BTU/lb}$$

$$\widehat{H}_2 = 152\ \mathrm{BTU/lb}$$



Therefore

$$\Delta\hat{H}_{21} = \hat{H}_2 - \hat{H}_1 = 152 - 108 = 44\ \frac{\text{BTU}}{\text{lb}}$$

$$44\ \frac{\text{BTU}}{\text{lb}} \times \frac{0.252\ \text{kcal}}{1\ \text{BTU}} \times \frac{1000\ \text{cal}}{1\ \text{kcal}} \times \frac{1\ \text{lb}}{0.454\ \text{kg}} \times \frac{1\ \text{kg}}{1000\ \text{g}} \times \frac{32\ \text{g O}_2}{1\ \text{mol-g O}_2} = 781.53\ \frac{\text{cal}}{\text{mol-g}}$$

and the heat for 1 mol-g will be of 781.53 cal.

Question b. According to the *Corresponding States Principle* (section e of reference problem 0.8), the enthalpy change between a state 1 and a state 2 is

$$(\tilde{H}_2 - \tilde{H}_1) = \underbrace{(\tilde{H}_2^* - \tilde{H}_1^*)}_{\text{ideal part}} + \underbrace{(\tilde{H}_1^* - \tilde{H}_1)_{T_1,P_1} - (\tilde{H}_2^* - \tilde{H}_2)_{T_2,P_2}}_{\text{real part}} \qquad [1]$$

where the ideal part can be calculated using the specific heat capacities of the fluid when considered ideal

$$\tilde{H}_2^* - \tilde{H}_1^* = \int_{T_1}^{T_2} \tilde{C}_P^* \mathrm{d}T$$

and the departure from the ideal behavior (real contribution) has to be read from generalized graphs, such as figure IV.4 of appendix IV, in which $\left(\widetilde{H}^{*}-\widetilde{H}\right)/T_c$ is expressed as a function of T_r and P_r.

With regards to the ideal part, the specific heat capacity of the oxygen (as ideal gas) will be that of appendix II

$$\widetilde{C}_P^{*} = \xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4$$

$$\frac{\xi_0}{R} = 3.630 \qquad \frac{\xi_1}{R} = -1.794\cdot 10^{-3}\,\frac{1}{\mathrm{K}} \qquad \frac{\xi_2}{R} = 0.658\cdot 10^{-5}\,\frac{1}{\mathrm{K}^2}$$

$$\frac{\xi_3}{R} = -0.601\cdot 10^{-8}\,\frac{1}{\mathrm{K}^3} \qquad \frac{\xi_4}{R} = 0.179\cdot 10^{-11}\,\frac{1}{\mathrm{K}^4}$$

so

$$\widetilde{H}_2^{*} - \widetilde{H}_1^{*} = \int_{T_1}^{T_2} (\xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4)\,\mathrm{d}T$$

$$\begin{aligned}\widetilde{H}_2^{*} - \widetilde{H}_1^{*} &= \left[\xi_0 T + \frac{1}{2}\xi_1 T + \frac{1}{3}\xi_2 T^3 + \frac{1}{4}\xi_3 T^4 + \frac{1}{5}\xi_4 T^5\right]_{T_1}^{T_2} = \\ &= \xi_0(T_2 - T_1) + \frac{\xi_1}{2}(T_2^2 - T_1^2) + \frac{\xi_2}{3}(T_2^3 - T_1^3) + \frac{\xi_3}{4}(T_2^4 - T_1^4) + \frac{\xi_4}{5}(T_2^5 - T_1^5)\end{aligned}$$

By converting °C to K

$$T_1(\mathrm{K}) = 27^{\circ}\mathrm{C} + 273 = 300\ \mathrm{K}$$

$$T_2(\mathrm{K}) = 127^{\circ}\mathrm{C} + 273 = 400\ \mathrm{K}$$

and introducing the temperatures in the formula, it gives that

$$\begin{aligned}\widetilde{H}_2^{*} - \widetilde{H}_1^{*} = 1.9872\ \Big\{&3.630(400-300) - \frac{1.794\cdot 10^{-3}}{2}(400^2 - 300^2) + \\ &+ \frac{0.658\cdot 10^{-5}}{3}(400^3 - 300^3) - \frac{0.601\cdot 10^{-8}}{4}(400^4 - 300^4) + \\ &+ \frac{0.179\cdot 10^{-11}}{5}(400^5 - 300^5)\Big\} = 711.15\ \frac{\mathrm{cal}}{\mathrm{mol\text{-}g}}\end{aligned}$$

With regards to the real part, and by taking the critical properties of O_2 from appendix II (T_c=154.4 K, P_c=49.7 atm)

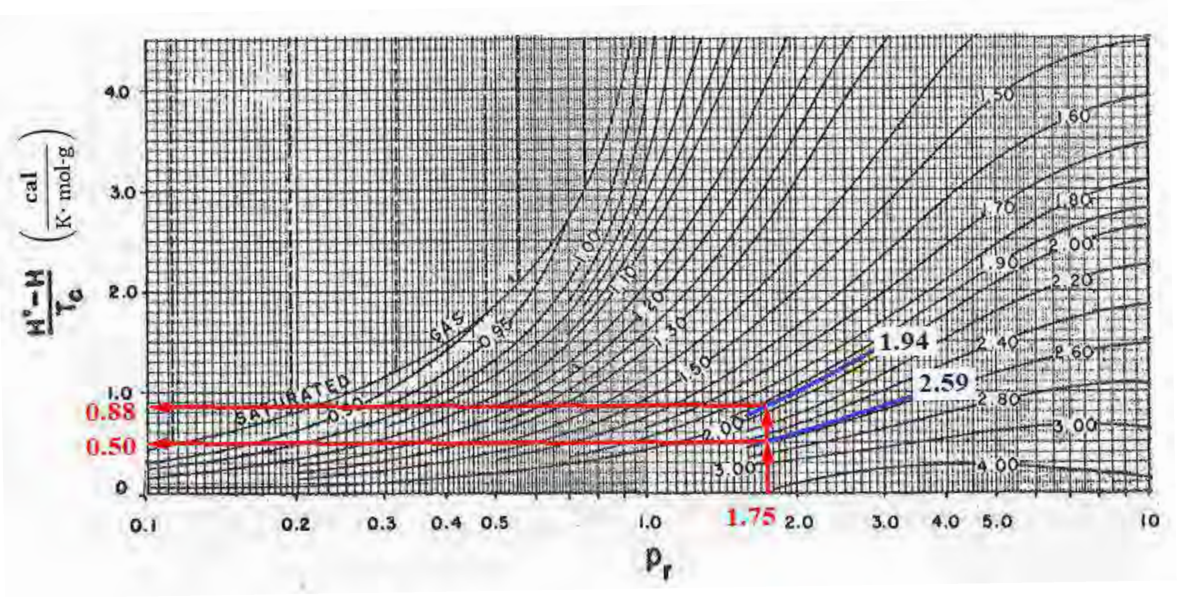
$$T_{r1} = \frac{300\ \mathrm{K}}{154.4\ \mathrm{K}} = 1.94\ ;\ P_{r1} = \frac{87\ \mathrm{atm}}{49.7\ \mathrm{atm}} = 1.75$$

$$\left(\frac{\tilde{H}_1^* - \tilde{H}_1}{T_c}\right)_{T_{r1},P_{r1}} = 0.88\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}}$$
$$\Downarrow$$
$$\left(\tilde{H}_1^* - \tilde{H}_1\right)_{T_1,P_1} = \left(0.88\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)(154.4\text{ K}) = 135.87\,\frac{\text{cal}}{\text{mol-g}}$$

and

$$T_{r2} = \frac{400\text{ K}}{154.4\text{ K}} = 2.59\ ;\ P_{r2} = \frac{87\text{ atm}}{49.7\text{ atm}} = 1.75$$

$$\left(\frac{\tilde{H}_2^* - \tilde{H}_2}{T_c}\right)_{T_{r2},P_{r2}} = 0.50\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}}$$
$$\Downarrow$$
$$\left(\tilde{H}_2^* - \tilde{H}_2\right)_{T_2,P_2} = \left(0.50\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}}\right)(154.4\text{ K}) = 77.2\,\frac{\text{cal}}{\text{mol-g}}$$



being the final result

$$\left(\tilde{H}_2 - \tilde{H}_1\right) = 711.15\,\frac{\text{cal}}{\text{mol-g}} + 135.87\,\frac{\text{cal}}{\text{mol-g}} - 77.2\,\frac{\text{cal}}{\text{mol-g}} = 769.82\,\frac{\text{cal}}{\text{mol-g}}$$

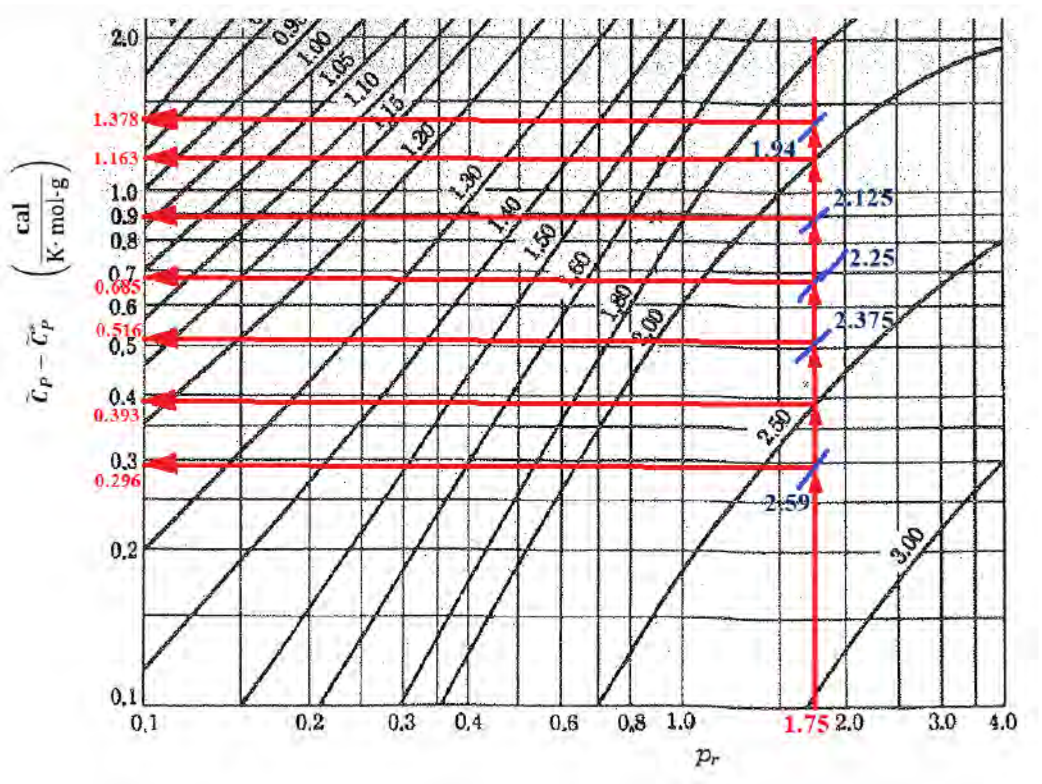
which is only 2% lower than that calculated in the previous question, despite the fact that z_c=0.292 for oxygen (see appendix II).

The Corresponding States Principle could also have been applied if, instead of equation [1], this other one would have been written

$$\Delta\tilde{H}_{21} = \int_{T_1}^{T_2} \tilde{C}_P \mathrm{d}T = \int_{T_1}^{T_2} \left[\left(\tilde{C}_P - \tilde{C}_P^*\right) + \tilde{C}_P^*\right]\mathrm{d}T = \int_{T_1}^{T_2} \left(\tilde{C}_P - \tilde{C}_P^*\right)\mathrm{d}T + \int_{T_1}^{T_2} \tilde{C}_P^* \mathrm{d}T \qquad [2]$$

where $\left(\tilde{C}_P - \tilde{C}_P^*\right)$ is taken from generalized diagram IV.6 (appendix IV), and the integration has to be performed numerically (for example, through the 'trapezoidal rule').

P_r	T_r	T (K)	$\tilde{C}_P - \tilde{C}_P^* \left(\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}}\right)$	$[T_i - T_{i-1}]\left\{\frac{\left(\tilde{C}_P - \tilde{C}_P^*\right)_i + \left(\tilde{C}_P - \tilde{C}_P^*\right)_{i-1}}{2}\right\}$
1.75	1.94	300.2	1.378	
1.75	2.00	308.8	1.163	10.92
1.75	2.125	328.1	0.900	19.91
1.75	2.25	347.4	0.685	15.30
1.75	2.375	366.7	0.516	11.59
1.75	2.50	386	0.393	8.77
1.75	2.59	400.2	0.296	4.89



The sum of all áreas is of 71.4 cal/mol-g. By applying equation [2]

$$\Delta\widetilde{H}_{21} = 711.15\ \frac{\text{cal}}{\text{mol-g}} + 71.4\ \frac{\text{cal}}{\text{mol-g}} = 782.55\ \frac{\text{cal}}{\text{mol-g}}$$

Question c. In figure V.1, enthalpies should be read at

$$1\text{ atm} \times \frac{2120\ \text{lb}_\text{f}/\text{ft}^2}{1\text{ atm}} \times \left(\frac{1\text{ ft}}{12\text{ in}}\right)^2 = 14.72\ \frac{\text{lb}_\text{f}}{\text{in}^2}$$

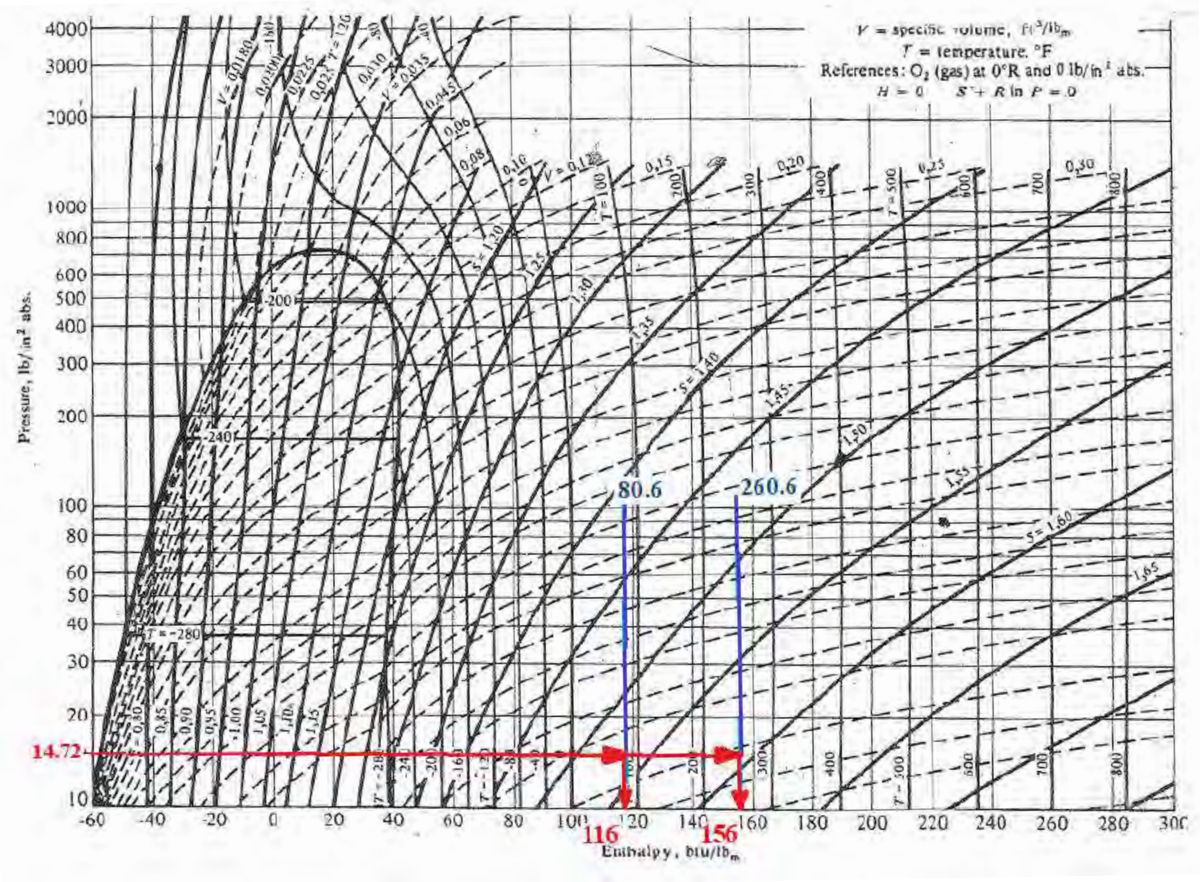
being

$$\hat{H}_1 = 116\ \frac{\text{BTU}}{\text{lb}} \qquad \text{and} \qquad \hat{H}_2 = 156\ \frac{\text{BTU}}{\text{lb}}$$

$$\Delta\hat{H}_{21} = \hat{H}_2 - \hat{H}_1 = 156\ \frac{\text{BTU}}{\text{lb}} - 116\ \frac{\text{BTU}}{\text{lb}} = 40\ \frac{\text{BTU}}{\text{lb}}$$

$$40\ \frac{\text{BTU}}{\text{lb}} \times \frac{0.252\ \text{kcal}}{1\ \text{BTU}} \times \frac{1000\ \text{cal}}{1\ \text{kcal}} \times \frac{1\ \text{lb}}{0.454\ \text{kg}} \times \frac{1\ \text{kg}}{1000\ \text{g}} \times \frac{32\ \text{g}\ O_2}{1\ \text{mol-g}\ O_2} = 710.5\ \frac{\text{cal}}{\text{mol-g}}$$

Therefore, the heat for 1 mol-g is of 710.5 cal.



Regarding the Corresponding States Principle, the ideal part of [1] is only temperature dependent, and so does not change. The terms $\left(\tilde{H}_2^* - \tilde{H}_2\right)_{T_2,P_2}$ and $\left(\tilde{H}_1^* - \tilde{H}_1\right)_{T_1,P_1}$ have to be calculated from the generalized diagram, but not from IV.4, whose lower limit is P_r=0.1, but from IV.5, where they are very low (even difficult to read)

$$T_{r1} = \frac{300\ \text{K}}{154.4\ \text{K}} = 1.94\ ;\ P_{r1} = \frac{1\ \text{atm}}{49.7\ \text{atm}} = 0.02$$

$$\left(\frac{\widetilde{H}_1^* - \widetilde{H}_1}{T_c}\right)_{T_{r1},P_{r1}} = 0.025\,\frac{\text{cal}}{\text{K·mol-g}}$$

$$\Downarrow$$

$$\left(\widetilde{H}_1^* - \widetilde{H}_1\right)_{T_1,P_1} = \left(0.025\,\frac{\text{cal}}{\text{K·mol-g}}\right)(154.4\ \text{K}) = 3.86\ \frac{\text{cal}}{\text{mol-g}}$$

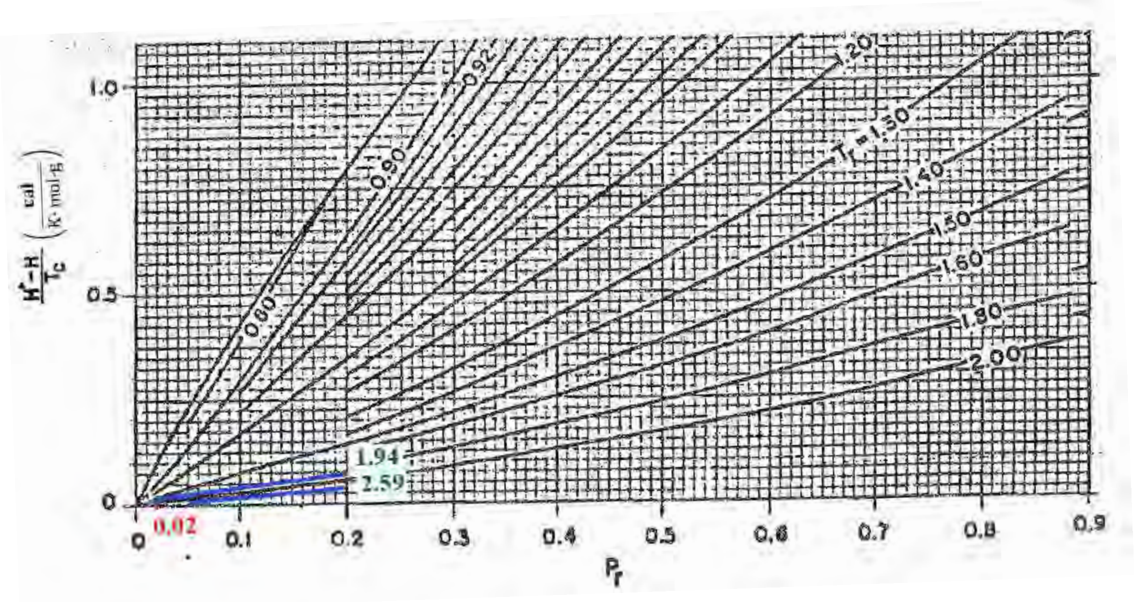
and

$$T_{r2} = \frac{400\ \text{K}}{154.4\ \text{K}} = 2.59\ ;\ P_{r2} = \frac{87\ \text{atm}}{49.7\ \text{atm}} = 0.02$$

$$\left(\frac{\widetilde{H}_2^* - \widetilde{H}_2}{T_c}\right)_{T_{r2},P_{r2}} = 0.01\,\frac{\text{cal}}{\text{K· mol-g}}$$

$$\Downarrow$$

$$\left(\widetilde{H}_2^* - \widetilde{H}_2\right)_{T_2,P_2} = \left(0.01\,\frac{\text{cal}}{\text{K· mol-g}}\right)(154.4\ \text{K}) = 1.544\ \frac{\text{cal}}{\text{mol-g}}$$



and the total enthalpy change is almost the same as that of the ideal part, i.e., at 1 atm the oxygen becomes an ideal gas.

$$\Delta\widehat{H}_{21} = 711.15\ \frac{\text{cal}}{\text{mol-g}} + 3.86\ \frac{\text{cal}}{\text{mol-g}} - 1.544\ \frac{\text{cal}}{\text{mol-g}} = 713.466\ \frac{\text{cal}}{\text{mol-g}}$$

Finally, notice that it is impossible to solve the problem by applying the graphical integration of [2] since in figure IV.6, the lower limit is P_r=0.1, and the specific heat capacity departures between 1.95<T_r<2.60 fall well below 0.1, which is the minimum value of the abscissa axis.

2.20. Estimate the enthalpy of vaporization of carbon dioxide at 20ºC and that as a gas at 90ºC and 100 bar (taking the critical point as the reference state):

a) By using the Corresponding States Principle with z_c=0.27.
b) By using a specific *PH*(*T, S, ρ*) diagram for CO_2.
c) By using a specific *TS*(*P,V,H*) diagram for CO_2.

Question a. The application of the Corresponding States Principle to the enthalpy change between two states 1 and 2 is based on the expression (section e of reference problem 0.8)

$$\left(\tilde{H}_2-\tilde{H}_1\right)=\underbrace{\left(\tilde{H}_2^*-\tilde{H}_1^*\right)}_{\text{ideal part}}+\underbrace{\left(\tilde{H}_1^*-\tilde{H}_1\right)_{T_1,P_1}-\left(\tilde{H}_2^*-\tilde{H}_2\right)_{T_2,P_2}}_{\text{real part}} \qquad [1]$$

In this case, the selection of a reference state does not alter the final result, since it can be shown that if 1 is the critical point and 2 is the saturated liquid or the saturated vapor

$$\left(\tilde{H}_l^{sat}-\tilde{H}_c\right)=\left(\tilde{H}_l^*-\tilde{H}_c^*\right)+\left(\tilde{H}_c^*-\tilde{H}_c\right)_{T_c,P_c}-\left(\tilde{H}_l^*-\tilde{H}_l^{sat}\right)_{T_2,P_2}$$

$$\left(\tilde{H}_v^{sat}-\tilde{H}_c\right)=\left(\tilde{H}_v^*-\tilde{H}_c^*\right)+\left(\tilde{H}_c^*-\tilde{H}_c\right)_{T_c,P_c}-\left(\tilde{H}_v^*-\tilde{H}_v^{sat}\right)_{T_2,P_2}$$

By subtracting one expression from another, and taking into account that the ideal part vanishes (because it is only a function of temperature, which remain constant)

$$\left(\tilde{H}_v^{sat}-\tilde{H}_l^{sat}\right)=\left(\tilde{H}^*-\tilde{H}\right)_l^{sat}-\left(\tilde{H}^*-\tilde{H}\right)_v^{sat}$$

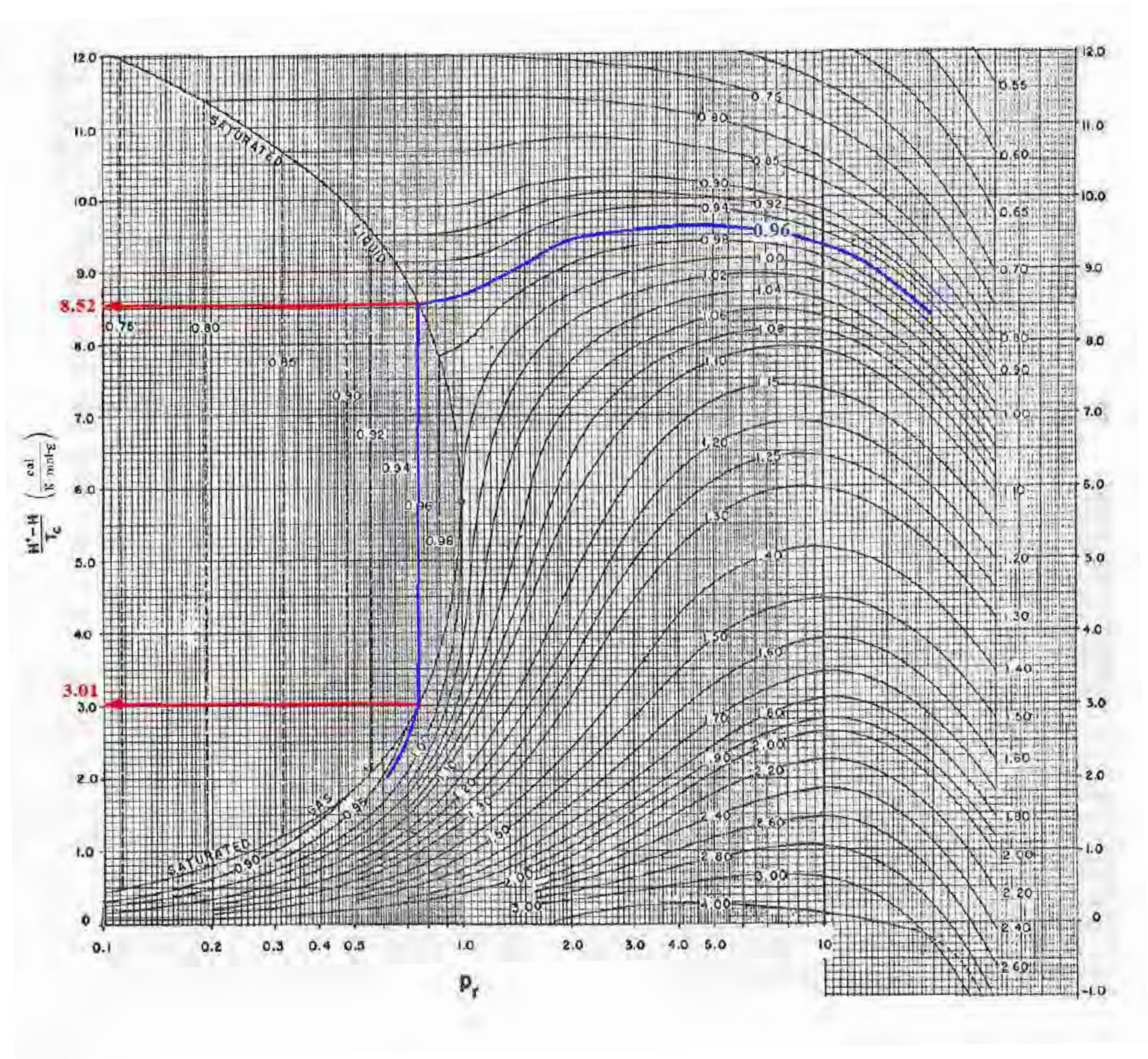
Thus, with 304.2 K as the critical temperature of carbon dioxide (appendix II) and the generalized figure IV.4 of appendix IV

$$T(K)=20℃+273=293\text{ K} \quad\rightarrow\quad T_r=\frac{293}{304.2}=0.96$$

$$\left(\frac{\tilde{H}^*-\tilde{H}}{T_c}\right)_l^{sat}=8.52\frac{\text{cal}}{\text{K· mol-g}}$$

$$\left(\frac{\tilde{H}^*-\tilde{H}}{T_c}\right)_v^{sat}=3.01\frac{\text{cal}}{\text{K· mol-g}}$$

$$\left(\tilde{H}_v^{sat}-\tilde{H}_l^{sat}\right)=\left(8.52\frac{\text{cal}}{\text{K· mol-g}}-3.01\frac{\text{cal}}{\text{K· mol-g}}\right)(304.2\text{ K})=1676.14\ \frac{\text{cal}}{\text{mol-g}}$$



To calculate the enthalpy at 90ºC and 100 bar, the ideal part will be estimated with the specific heat capacities of appendix II, employing $T_2=T_c$.

$$\widetilde{H}_2^* - \widetilde{H}_1^* = \int_{T_1}^{T_2} \tilde{C}_P^* \mathrm{d}T$$

$$\tilde{C}_P^* = \xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4$$

where

$$\frac{\xi_0}{R} = 3.259 \qquad \frac{\xi_1}{R} = 1.356 \cdot 10^{-3}\,\frac{1}{\mathrm{K}} \qquad \frac{\xi_2}{R} = 1.502 \cdot 10^{-5}\,\frac{1}{\mathrm{K}^2}$$

$$\frac{\xi_3}{R} = -2.374 \cdot 10^{-8}\,\frac{1}{\mathrm{K}^3} \qquad \frac{\xi_4}{R} = 1.056 \cdot 10^{-11}\,\frac{1}{\mathrm{K}^4}$$

Therefore

$$\widetilde{H}_2^* - \widetilde{H}_1^* = \int_{T_1}^{T_2} (\xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4)\mathrm{d}T$$

$$\widetilde{H}_2^* - \widetilde{H}_1^* = \left[\xi_0 T + \frac{1}{2}\xi_1 T + \frac{1}{3}\xi_2 T^3 + \frac{1}{4}\xi_3 T^4 + \frac{1}{5}\xi_4 T^5\right]_{T_1}^{T_2} =$$
$$= \xi_0(T_2 - T_1) + \frac{\xi_1}{2}(T_2^2 - T_1^2) + \frac{\xi_2}{3}(T_2^3 - T_1^3) + \frac{\xi_3}{4}(T_2^4 - T_1^4) + \frac{\xi_4}{5}(T_2^5 - T_1^5)$$

$$\widetilde{H}_2^* - \widetilde{H}_1^* = 1.9872 \left\{3.259(363 - 304.2) + \frac{1.356 \cdot 10^{-3}}{2}(363^2 - 304.2^2) + \right.$$
$$+ \frac{1.502 \cdot 10^{-5}}{3}(363^3 - 304.2^3) - \frac{2.374 \cdot 10^{-8}}{4}(363^4 - 304.2^4) +$$
$$\left. + \frac{1.056 \cdot 10^{-11}}{5}(363^5 - 304.2^5)\right\} = 541.22 \ \frac{\text{cal}}{\text{mol-g}}$$

Regarding the real part, and having in mind that the critical properties of carbon dioxide are T_c=304.2 K and P_c=72.9 atm (=73.63 bar)

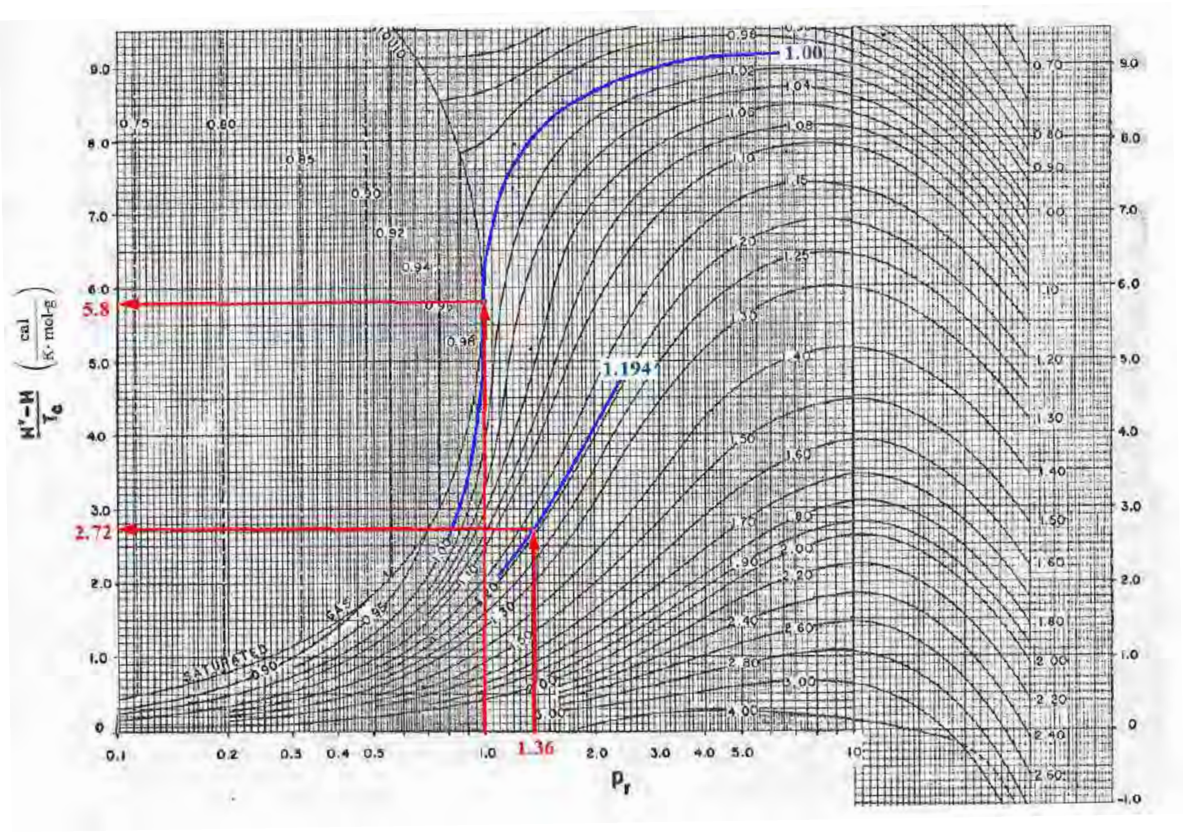
$$T_{r1} = 1.0 \ ; \quad P_{r1} = 1$$

$$\left(\frac{\widetilde{H}_1^* - \widetilde{H}_1}{T_c}\right)_{T_{r1},P_{r1}} = 5.8 \frac{\text{cal}}{\text{K}\cdot \text{mol-g}}$$
$$\Downarrow$$
$$\left(\widetilde{H}_1^* - \widetilde{H}_1\right)_{T_1,P_1} = \left(5.8 \frac{\text{cal}}{\text{K}\cdot \text{mol-g}}\right)(304.2 \text{ K}) = 1764.4 \ \frac{\text{cal}}{\text{mol-g}}$$

and

$$T_{r2} = \frac{363 \text{ K}}{304.2 \text{ K}} = 1.194 \ ; \ P_{r2} = \frac{100 \text{ bar}}{73.63 \text{ bar}} = 1.36$$

$$\left(\frac{\widetilde{H}_2^* - \widetilde{H}_2}{T_c}\right)_{T_{r2},P_{r2}} = 2.72 \frac{\text{cal}}{\text{K}\cdot \text{mol-g}}$$
$$\Downarrow$$
$$\left(\widetilde{H}_2^* - \widetilde{H}_2\right)_{T_2,P_2} = \left(2.72 \frac{\text{cal}}{\text{K}\cdot \text{mol-g}}\right)(304.2 \text{ K}) = 827.42 \ \frac{\text{cal}}{\text{mol-g}}$$



Finally, by applying equation [1]

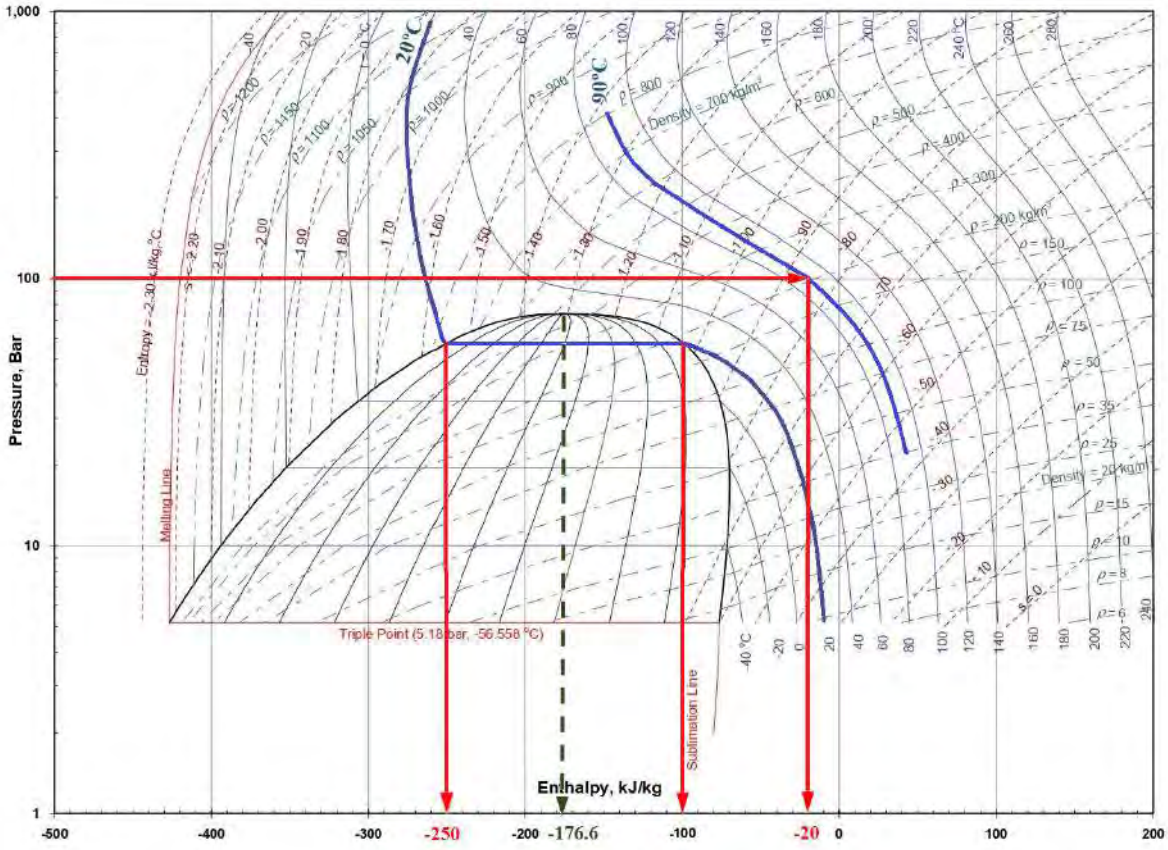
$$541.22\ \frac{\text{cal}}{\text{mol-g}} + 1764.4\ \frac{\text{cal}}{\text{mol-g}} - 827.42\ \frac{\text{cal}}{\text{mol-g}} = 1478.2\ \frac{\text{cal}}{\text{mol-g}}$$

Question b. Figure V.2 is a specific $PH(T, S, \rho)$ diagram for carbon dioxide, where enthalpy is in kJ/kg, pressure in bar and temperature in ºC. At 20ºC the saturated liquid enthalpy is of -250 kJ/kg while the saturated vapor enthalpy is of -100 kJ/kg. As in the previous question the enthalpy of vaporization does not depend on the reference state (because it is a substraction) and will be

$$\Delta\hat{H}_{vap} = \left(-100\frac{\text{kJ}}{\text{kg}}\right) - \left(-250\frac{\text{kJ}}{\text{kg}}\right) = 150\frac{\text{kJ}}{\text{kg}}$$

$$150\frac{\text{kJ}}{\text{kg}} \times \frac{1\ \text{kg}}{1000\ \text{g}} \times \frac{44.01\ \text{g}}{1\ \text{mol-g}} \times \frac{0.239\ \text{kcal}}{1\ \text{kJ}} \times \frac{1000\ \text{cal}}{1\ \text{kcal}} = 1577.76\ \frac{\text{cal}}{\text{mol-g}}$$

value that is 5.86% lower than that calculated through the Corresponding States Principle.



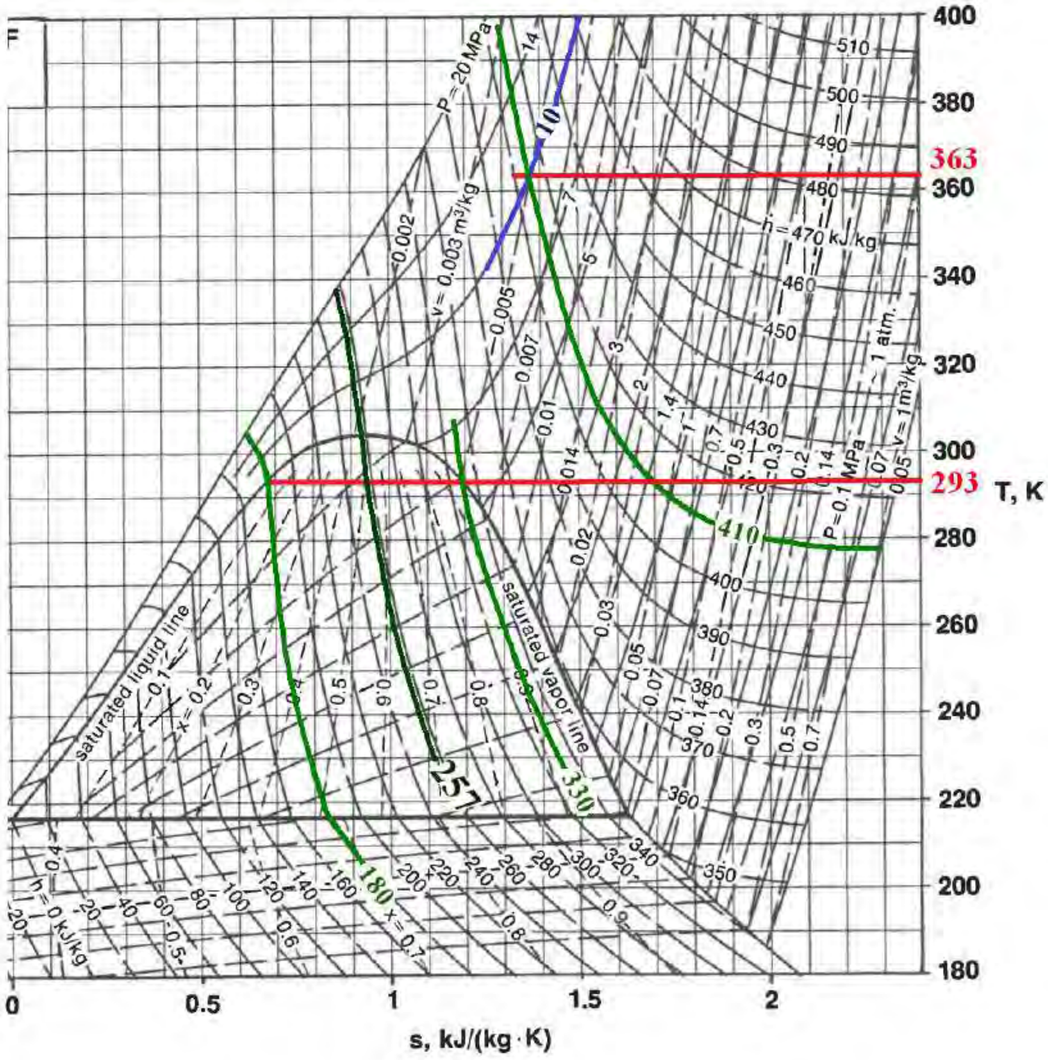
On the other hand, at the point where the 90ºC isotherm crosses the 100 bar isobar we read an enthalpy of -20 kJ/kg, but to refer this value to the critical point, the enthalpy at the máximum of the biphasic zone (-176.6 kJ/kg) has to be subtracted from -20 kJ/kg.

$$\hat{H} = \left(-20\frac{\text{kJ}}{\text{kg}}\right) - \left(-176.6\frac{\text{kJ}}{\text{kg}}\right) = 156.6\ \frac{\text{kJ}}{\text{kg}}$$

$$156.6\frac{\text{kJ}}{\text{kg}} \times \frac{1\text{ kg}}{1000\text{ g}} \times \frac{44.01\text{ g}}{1\text{ mol-g}} \times \frac{0.239\text{ kcal}}{1\text{ kJ}} \times \frac{1000\text{ cal}}{1\text{ kcal}} = 1647.18\ \ \frac{\text{cal}}{\text{mol-g}}$$

result which is a 6.7% higher than that of question **a**.

Question c. Figure V.3 of appendix V is a specific $TS(P,V,H)$ diagram for this substance.



The enthalpy of the saturated liquid is 180 kJ/kg, while that of the saturated vapor is 330 kJ/kg, so

$$\Delta \widehat{H}_{vap} = 330\ \frac{\text{kJ}}{\text{kg}} - 180\ \frac{\text{kJ}}{\text{kg}} = 150\ \frac{\text{kJ}}{\text{kg}}$$

value which coincides with that of the *PH* diagram. Regarding the enthalpy at 363 K and 10 MPa, the interpolation gives 410 kJ/kg. By also taking the isenthalpic line that passes through the critical point (approximately 257 kJ/kg)

$$\widehat{H} = 410\ \frac{\text{kJ}}{\text{kg}} - 257\ \frac{\text{kJ}}{\text{kg}} = 153\ \frac{\text{kJ}}{\text{kg}}$$

$$153\ \frac{\text{kJ}}{\text{kg}} \times \frac{1\ \text{kg}}{1000\ \text{g}} \times \frac{44.01\ \text{g}}{1\ \text{mol-g}} \times \frac{0.239\ \text{kcal}}{1\ \text{kJ}} \times \frac{1000\ \text{cal}}{1\ \text{kcal}} = 1609.31\ \frac{\text{cal}}{\text{mol-g}}$$

2.21. Assume that carbon dioxide is at its critical pressure and 90ºC. By taking the ideal gas at 0ºC and 1 bar as a reference state, calculate through the Corresponding States Principle:

a) The specific enthalpy, in kJ/kg.
b) The specific entropy, in kJ/(kg.K).
c) The specific heat capacity, in kJ/(kg.K).

Section e of reference problem 0.8 says that the property change (enthalpy or entropy) between two states 1 and 2 is given by

$$(\widetilde{H}_2 - \widetilde{H}_1) = \underbrace{(\widetilde{H}_2^* - \widetilde{H}_1^*)}_{\text{ideal part}} + \underbrace{(\widetilde{H}_1^* - \widetilde{H}_1)_{T_1,P_1} - (\widetilde{H}_2^* - \widetilde{H}_2)_{T_2,P_2}}_{\text{real part}} \qquad [1]$$

$$(\tilde{S}_2 - \tilde{S}_1) = \underbrace{(\tilde{S}_2^* - \tilde{S}_1^*)}_{\text{ideal part}} + \underbrace{(\tilde{S}_1^* - \tilde{S}_1)_{T_1,P_1} - (\tilde{S}_2^* - \tilde{S}_2)_{T_2,P_2}}_{\text{real part}} \qquad [2]$$

while for the specific heat capacity

$$\tilde{C}_{P2} = \underbrace{\tilde{C}_{P2}^*}_{\substack{\text{ideal}\\ \text{part}}} + \underbrace{(\tilde{C}_{P2} - \tilde{C}_{P2}^*)_{T_2,P_2}}_{\text{real part}} \qquad [3]$$

Being the ideal part estimated through the specific heat capacities of the substance (as if it was ideal)

$$\tilde{C}_P^* = \xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4$$

$$\widetilde{H}_2^* - \widetilde{H}_1^* = \int_{T_1}^{T_2} \tilde{C}_P^* \mathrm{d}T \qquad [4]$$

$$\tilde{S}_2^* - \tilde{S}_1^* = \int_{T_1}^{T_2} \tilde{C}_P^* \frac{\mathrm{d}T}{T} - \int_{P_1}^{P_2} R \frac{\mathrm{d}P}{P} \qquad [5]$$

For carbon dioxide, appendix II provides the polynomial constants

$$\frac{\xi_0}{R} = 3.259 \qquad \frac{\xi_1}{R} = 1.356 \cdot 10^{-3} \frac{1}{\mathrm{K}} \qquad \frac{\xi_2}{R} = 1.502 \cdot 10^{-5} \frac{1}{\mathrm{K}^2}$$

$$\frac{\xi_3}{R} = -2.374 \cdot 10^{-8} \frac{1}{\mathrm{K}^3} \qquad \frac{\xi_4}{R} = 1.056 \cdot 10^{-11} \frac{1}{\mathrm{K}^4}$$

and the critical properties as well: T_c=304.2 K y P_c=72.9 atm (=73.63 bar).

On the other hand, the reference state implies that T_1=273 K and P_1= 1 bar; thus, $\widetilde{H}_1^* = \widetilde{H}_1 = 0$ and $\tilde{S}_1^* = \tilde{S}_1 = 0$. Therefore the first term of the real part of both equations [1] and [2] vanishes.

The second terms of the real parts have to be calculated by the generalized charts of appendix IV in the conditions

$$T(\mathrm{K}) = 90℃ + 273 = 363\ \mathrm{K} \quad \rightarrow \quad T_{r2} = \frac{363\ \mathrm{K}}{304.2\ \mathrm{K}} = 1.194$$

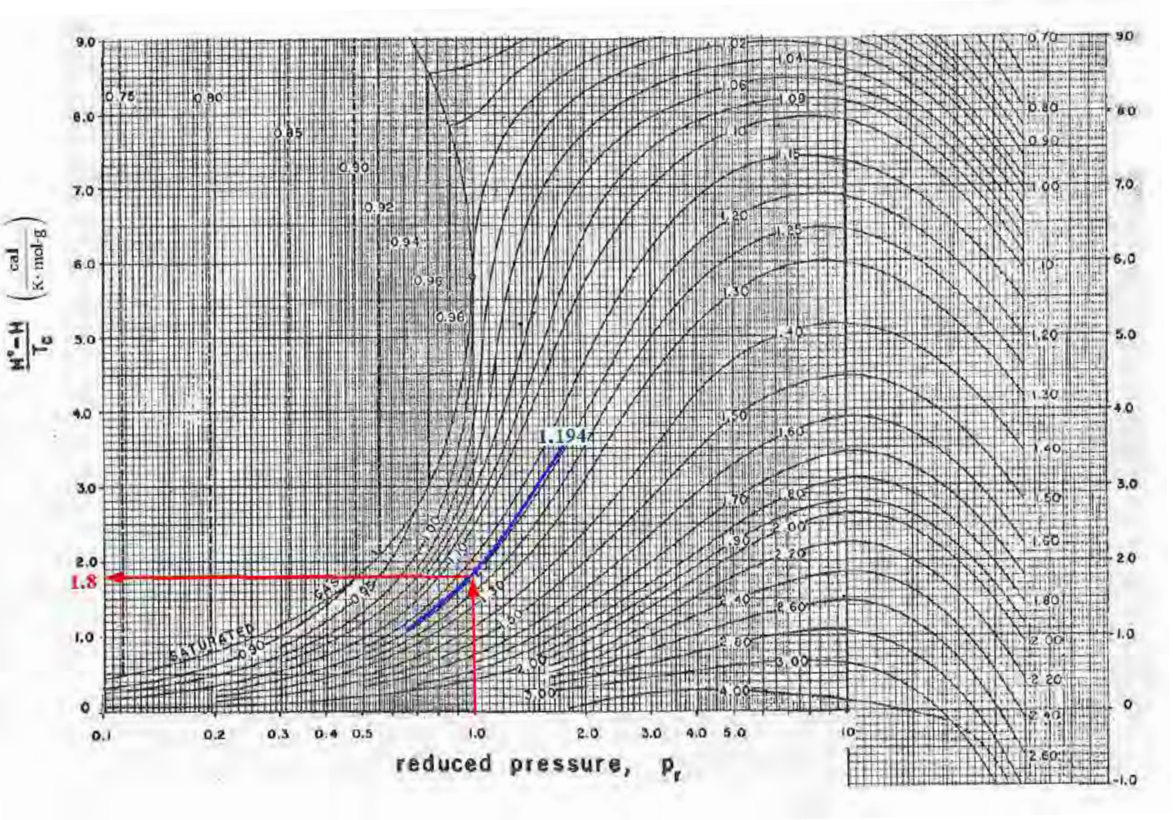
$$P = P_c \quad \rightarrow \quad P_{r2} = 1.0$$

Question a. Figure IV.4 represents the enthalpy departure as a function of the reduced pressure and temperature

$$\left(\frac{\widetilde{H}_2^* - \widetilde{H}_2}{T_c}\right)_{T_{r2},P_{r2}} = 1.8\,\frac{\mathrm{cal}}{\mathrm{K\cdot\ mol\text{-}g}}$$

$$\Downarrow$$

$$\left(\widetilde{H}_2^* - \widetilde{H}_2\right)_{T_2,P_2} = \left(1.8\,\frac{\mathrm{cal}}{\mathrm{K\cdot\ mol\text{-}g}}\right)(304.2\ \mathrm{K}) = 547.56\ \frac{\mathrm{cal}}{\mathrm{mol\text{-}g}}$$



And the ideal part will be

$$\widetilde{H}_2^* - \widetilde{H}_1^* = \int_{T_1}^{T_2} (\xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4)\mathrm{d}T$$

$$\widetilde{H}_2^* - \widetilde{H}_1^* = \left[\xi_0 T + \frac{1}{2}\xi_1 T + \frac{1}{3}\xi_2 T^3 + \frac{1}{4}\xi_3 T^4 + \frac{1}{5}\xi_4 T^5\right]_{T_1}^{T_2}$$

$$= \xi_0(T_2 - T_1) + \frac{\xi_1}{2}(T_2^2 - T_1^2) + \frac{\xi_2}{3}(T_2^3 - T_1^3) + \frac{\xi_3}{4}(T_2^4 - T_1^4) + \frac{\xi_4}{5}(T_2^5 - T_1^5)$$

$$\widetilde{H}_2^* - \widetilde{H}_1^* = 1.9872\left\{3.259(363-273) + \frac{1.356\cdot 10^{-3}}{2}(363^2-273^2) + \right.$$
$$+\frac{1.502\cdot 10^{-5}}{3}(363^3-273^3) - \frac{2.374\cdot 10^{-8}}{4}(363^4-273^4) +$$
$$\left. +\frac{1.056\cdot 10^{-11}}{5}(363^5-273^5)\right\} = 814.27\ \frac{\text{cal}}{\text{mol-g}}$$

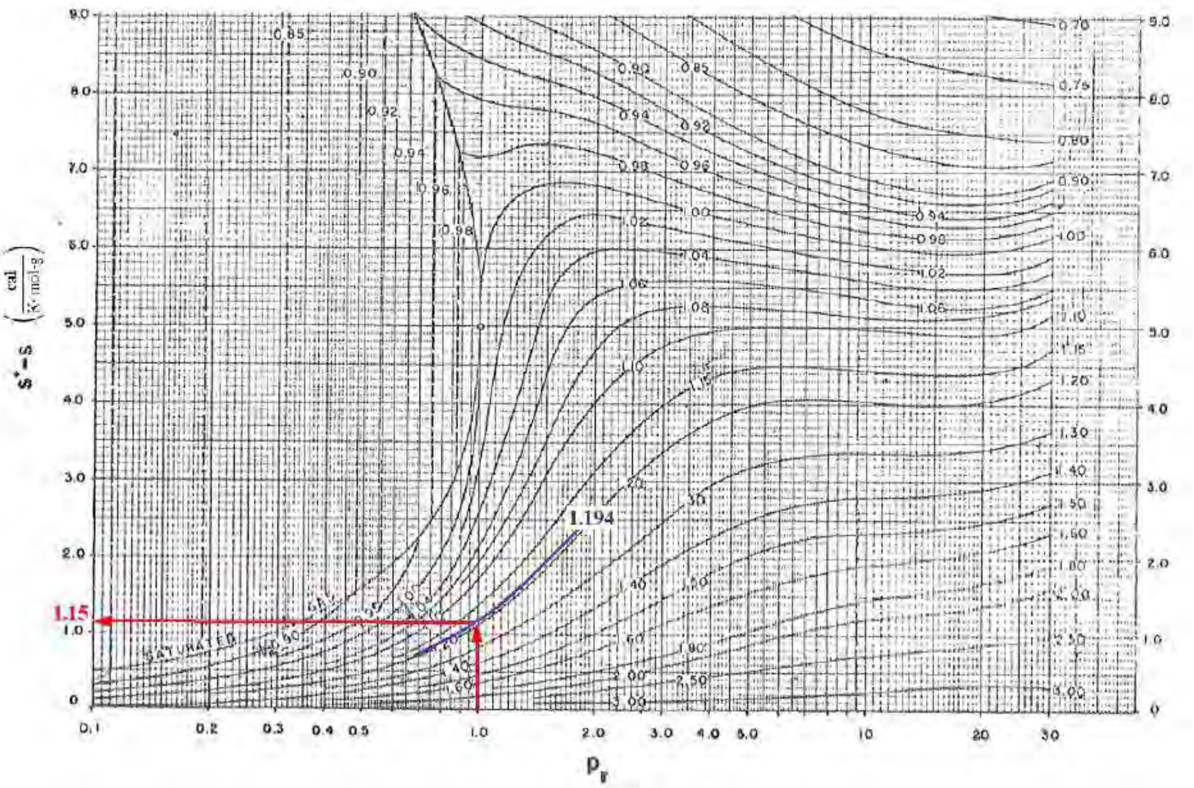
Equation [1] becomes

$$\widetilde{H}_2 = 814.27\ \frac{\text{cal}}{\text{mol-g}} - 547.5\ \frac{\text{cal}}{\text{mol-g}} = 266.77\frac{\text{cal}}{\text{mol-g}}$$

which expressed in kJ/kg

$$266.77\frac{\text{cal}}{\text{mol-g}}\times\frac{4.18\text{ J}}{1\text{ cal}}\times\frac{1\text{ mol-g}}{44.01\text{ g}}\times\frac{1\text{ kJ}}{1000\text{ J}}\times\frac{1000\text{ g}}{1\text{ kg}} = 25.34\frac{\text{kJ}}{\text{kg}}$$

Question b. The entropy departure is read in figure IV.7



$$\left(\tilde{S}_2^* - \tilde{S}_2\right)_{T_2,P_2} = 1.15\ \frac{\text{cal}}{\text{K·mol-g}}$$

and if R is taken as 1.9872 cal/(K·mol-g), the ideal part will be

$$\tilde{S}_2^* - \tilde{S}_1^* = \int_{T_1}^{T_2}(\xi_0+\xi_1 T+\xi_2 T^2+\xi_3 T^3+\xi_4 T^4)\frac{\mathrm{d}T}{T} - R\int_{P_1}^{P_2}\frac{\mathrm{d}P}{P}$$

$$\tilde{S}_2^* - \tilde{S}_1^* = \left[\xi_0 \ln T + \xi_1 T + \frac{1}{2}\xi_2 T^2 + \frac{1}{3}\xi_3 T^3 + \frac{1}{4}\xi_4 T^4\right]_{T_1}^{T_2} - R[\ln P]_{P_1}^{P_2} =$$

$$= \xi_0 \ln\frac{T_2}{T_1} + \xi_1(T_2 - T_1) + \frac{\xi_2}{2}(T_2^2 - T_1^2) + \frac{\xi_3}{3}(T_2^3 - T_1^3) + \frac{\xi_4}{4}(T_2^4 - T_1^4) - R\ln\frac{P_2}{P_1}$$

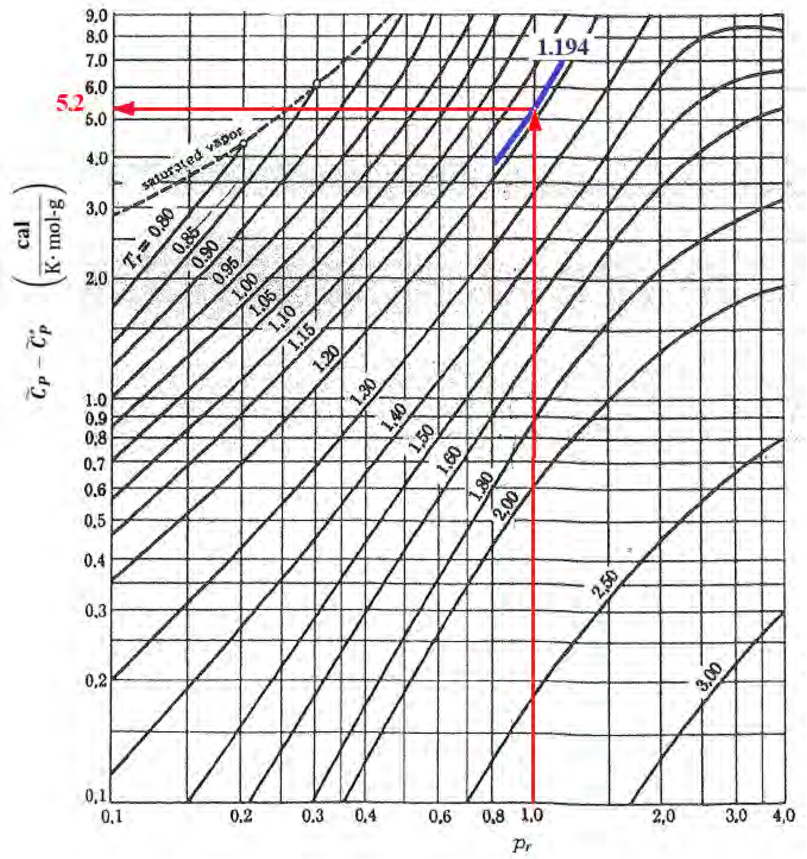
$$\tilde{S}_2^* - \tilde{S}_1^* = 1.9872\left\{3.259\ln\left(\frac{363}{273}\right) + 1.356\cdot 10^{-3}(363-273) + \right.$$
$$+\frac{1.502\cdot 10^{-5}}{2}(363^2 - 273^2) - \frac{2.374\cdot 10^{-8}}{3}(363^3 - 273^3) +$$
$$\left. + \frac{1.056\cdot 10^{-11}}{4}(363^4 - 273^4)\right\} - 1.9872\ln\left(\frac{73.9}{1}\right) = -5.98\ \frac{\text{cal}}{\text{mol-g}}$$

After introducing these values in equation [2] it is found that

$$\tilde{S}_2 = -5.98\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}} - 1.15\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}} = -7.13\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$-7.13\frac{\text{cal}}{\text{K}\cdot\text{mol-g}} \times \frac{4.18\ \text{J}}{1\ \text{cal}} \times \frac{1\ \text{mol-g}}{44.01\ \text{g}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} \times \frac{1000\ \text{g}}{1\ \text{kg}} = -0.677\frac{\text{kJ}}{\text{K}\cdot\text{kg}}$$

Question c. The specific heat capacity departure is estimated through figure IV.6



$$\left(\tilde{C}_{P_2}-\tilde{C}^*_{P_2}\right)_{T_2,P_2}=5.2\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

and the ideal part only requires the evaluation of the quartic polynomial at T_2

$$\tilde{C}^*_{P_2}=1.9872\,\{3.259+1.356\cdot10^{-3}(363)+1.502\cdot10^{-5}(363^2)-$$
$$-2.374\cdot10^{-8}(363^3)\ +1.056\cdot10^{-11}(363^4)\}=9.49\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

Then, according to equation [3], the specific heat capacity of CO_2 at its critical pressure and at 90ºC is

$$\tilde{C}_{P_2}=9.49\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}}+5.2\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}}=14.69\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$14.69\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\times\frac{4.18\text{ J}}{1\text{ cal}}\times\frac{1\text{ mol-g}}{44.01\text{ g}}\times\frac{1\text{ kJ}}{1000\text{ J}}\times\frac{1000\text{ g}}{1\text{ kg}}=1.395\frac{\text{kJ}}{\text{K}\cdot\text{kg}}$$

2.22. Suggest a procedure to draw the *H* vs. *T* diagram of a substance from the generalized chart of enthalpy departure. Take the critical compressibility as 0.27 and indicate what specific data of the substance would be needed.

According to the Corresponding States Principle (reference problem 0.8), the enthalpy change between two states 1 and 2 are

$$\left(\tilde{H}_2-\tilde{H}_1\right)=\underbrace{\left(\tilde{H}_2^*-\tilde{H}_1^*\right)}_{\text{ideal part}}+\underbrace{\left(\tilde{H}_1^*-\tilde{H}_1\right)_{T_1,P_1}-\left(\tilde{H}_2^*-\tilde{H}_2\right)_{T_2,P_2}}_{\text{real part}}$$

In order to draw the diagram, four properties are needed: the critical temperature (T_c), the critical pressure (P_c), the specific heat capacities of the substance when it behaves as ideal gas ($\tilde{C}_P^*$) and a reference state T_1, P_1 where $\tilde{H}_1=0$ (the critical point, the ideal gas at normal boiling temperature, the ideal gas at 0ºC and 1 atm…). Then

$$\tilde{H}_2=\underbrace{\left(\tilde{H}_2^*-H_1^*\right)}_{\int_{T_1}^{T_2}\tilde{C}_P^*\mathrm{d}T}+\underbrace{\left(\tilde{H}_1^*-\tilde{H}_1\right)_{T_1,P_1}}_{\substack{\text{This term only}\\ \text{depends on}\\ \text{temperature}}}-\left(\tilde{H}_2^*-\tilde{H}_2\right)_{T_2,P_2}$$

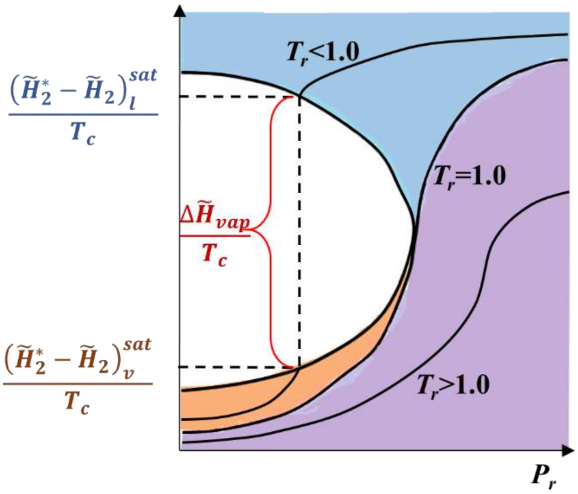
Due to the fact that the abscissa axis correspond to P_r and the isolines to T_r in the generalized enthalpy departure chart (figure IV.4 of appendix IV), the easiest way to construct the *H* vs. *T* diagram will not be to choose a reduced pressure and evaluate $\tilde{H}_2$ for several reduced temperatures (since the first term in the equation is temperature-dependent and this would imply calculating it as many times as reduced temperatures), but rather select a T_{r2} value, calculate $\tilde{H}_2^*-\tilde{H}_1^*$ with the specific heat capacity, vary P_{r2} from 0.1 to 30 (limits of figure IV.4) and read $\left(\tilde{H}_2^*-\tilde{H}_2\right)_{T_2,P_2}$ in the chart. Then choose another T_{r2} and repeat the calculations and readings for the same P_{r2} values.

When T_{r2}<1.0 some data will lay in the biphasic zone, i.e., for several pairs of T_{r2},P_{r2} there will be a value $\left(\tilde{H}_2^*-\tilde{H}_2\right)_{T_2,P_2}$ for the saturated liquid and another one for the saturated vapor, and

$$\tilde{H}_l^{sat}=\left(\tilde{H}_2^*-H_1^*\right)+\left(\tilde{H}_1^*-\tilde{H}_1\right)_{T_1,P_1}-\left(\tilde{H}_2^*-\tilde{H}_2\right)_l^{sat}$$
$$\tilde{H}_v^{sat}=\left(\tilde{H}_2^*-H_1^*\right)+\left(\tilde{H}_1^*-\tilde{H}_1\right)_{T_1,P_1}-\left(\tilde{H}_2^*-\tilde{H}_2\right)_v^{sat}$$

$$\tilde{H}_v^{sat}-\tilde{H}_l^{sat}=\Delta\tilde{H}_{vap}=-\left(\tilde{H}_2^*-\tilde{H}_2\right)_v^{sat}+\left(\tilde{H}_2^*-\tilde{H}_2\right)_l^{sat}$$

The enthalpy of vaporization ($\Delta\tilde{H}_{vap}$) could be added as fifth property: since the enthalpy departures of the saturated vapor are lower than those of the saturated liquid (and not easily readable), it is best to choose T_{r2}, read $\left(\tilde{H}_2^*-\tilde{H}_2\right)_l^{sat}$, evaluate the enthalpy of vaporization through empirical equations and estimate the term $\left(\widetilde{H}_2^* - \widetilde{H}_2\right)_v^{sat}$ by subtracting $\Delta\widetilde{H}_{vap}$ from the enthalpy departure of the saturated liquid.



Finally, realize that if the reference state is that of the ideal gas at the same temperature as the working one (T_2), then $\widetilde{H}_1^* = \widetilde{H}_1 = 0$ and $\left(\widetilde{H}_1^* - \widetilde{H}_1\right)_{T_1,P_1}$ vanishes.

2.23. Estimate the specific heat capacity departures of a mixture of 40% methane and 60% ethane (in moles) at 323.2 K and 40 atm by assuming that z_c=0.27 and:

- **a) Linear combination of the departures of each substance.**
- **b) Linear combination of the critical properties of each substance**

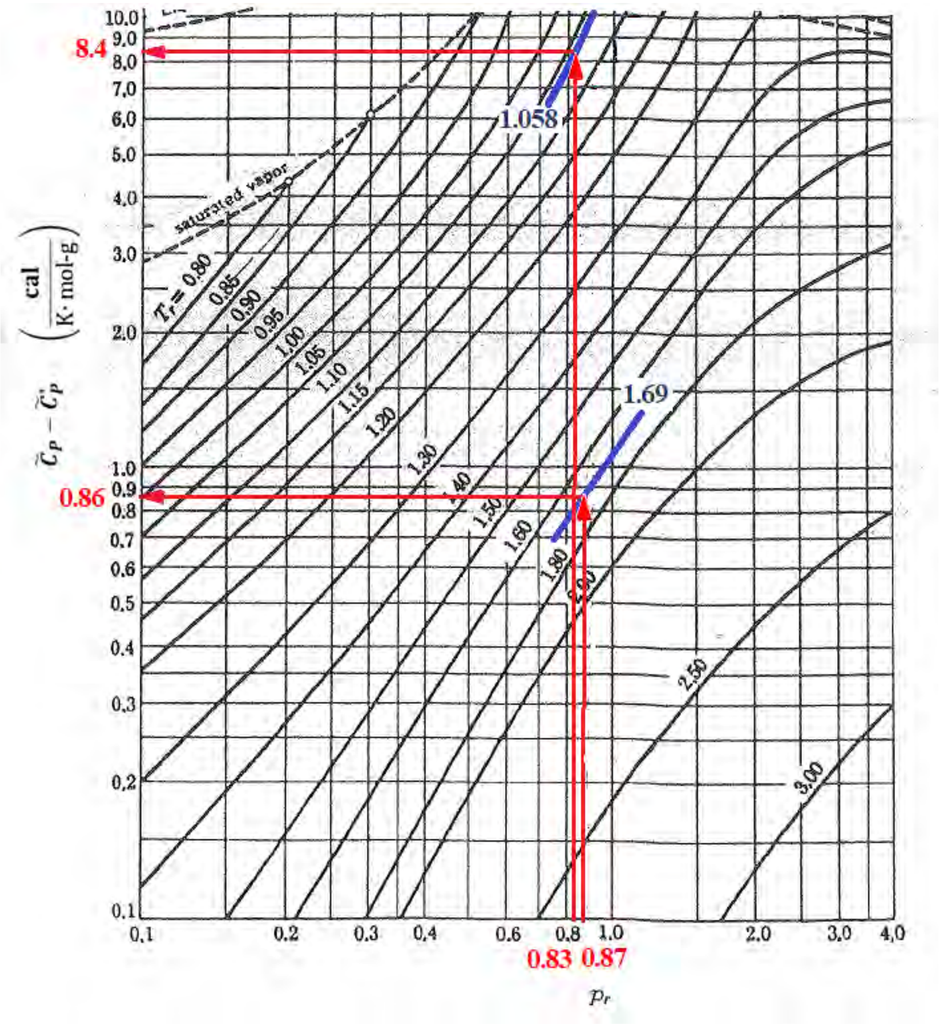
Question a. In the first case, the total departure is

$$y_A\left(\tilde{C}_P^* - \tilde{C}_P\right)_{T_{rA},P_{rA}} + y_B\left(\tilde{C}_P^* - \tilde{C}_P\right)_{T_{rB},P_{rB}}$$

being

$$T_{rA} = \frac{T}{T_{cA}} \;\; ; \;\; P_{rA} = \frac{P}{P_{cA}} \qquad\qquad T_{rB} = \frac{T}{T_{cB}} \;\; ; \;\; P_{rB} = \frac{P}{P_{cB}}$$

By taking the critical properties of methane (190.7 K, 45.8 atm) and of ethane (305.4 K, 48.2 atm) from appendix II and the generalized chart from appendix IV (figure IV.6)



$$T_{rA} = \frac{323.2\ \text{K}}{190.7\ \text{K}} = 1.69 \quad ; \quad P_{rA} = \frac{40\ \text{atm}}{45.8\ \text{atm}} = 0.87$$

$$\left(\tilde{C}_P^* - \tilde{C}_P\right)_{T_{rA},P_{rA}} = 0.86 \frac{\text{cal}}{\text{K}\cdot\ \text{mol-g}}$$

$$T_{rB} = \frac{323.2\ \text{K}}{305.4\ \text{K}} = 1.058 \quad ; \quad P_{rB} = \frac{40\ \text{atm}}{48.2\ \text{atm}} = 0.83$$

$$\left(\tilde{C}_P^* - \tilde{C}_P\right)_{T_{rA},P_{rA}} = 8.4 \frac{\text{cal}}{\text{K}\cdot\ \text{mol-g}}$$

Thus, the total departure becomes

$$0.4\left(0.86 \frac{\text{cal}}{\text{K}\cdot\ \text{mol-g}}\right) + 0.6\left(8.4 \frac{\text{cal}}{\text{K}\cdot\ \text{mol-g}}\right) = 5.38 \frac{\text{cal}}{\text{K}\cdot\ \text{mol-g}}$$

Question b. In the second case

$$\left(\tilde{C}_P^* - \tilde{C}_P\right)_{T_{rAB},P_{rAB}}$$

being

$$T_{rAB} = \frac{T}{T_{cAB}} \quad ; \quad P_{rAB} = \frac{P}{P_{cAB}}$$

$$T_{cAB} = y_A T_{cA} + y_B T_{cB}$$

$$P_{cAB} = y_A P_{cA} + y_B P_{cB}$$

hence

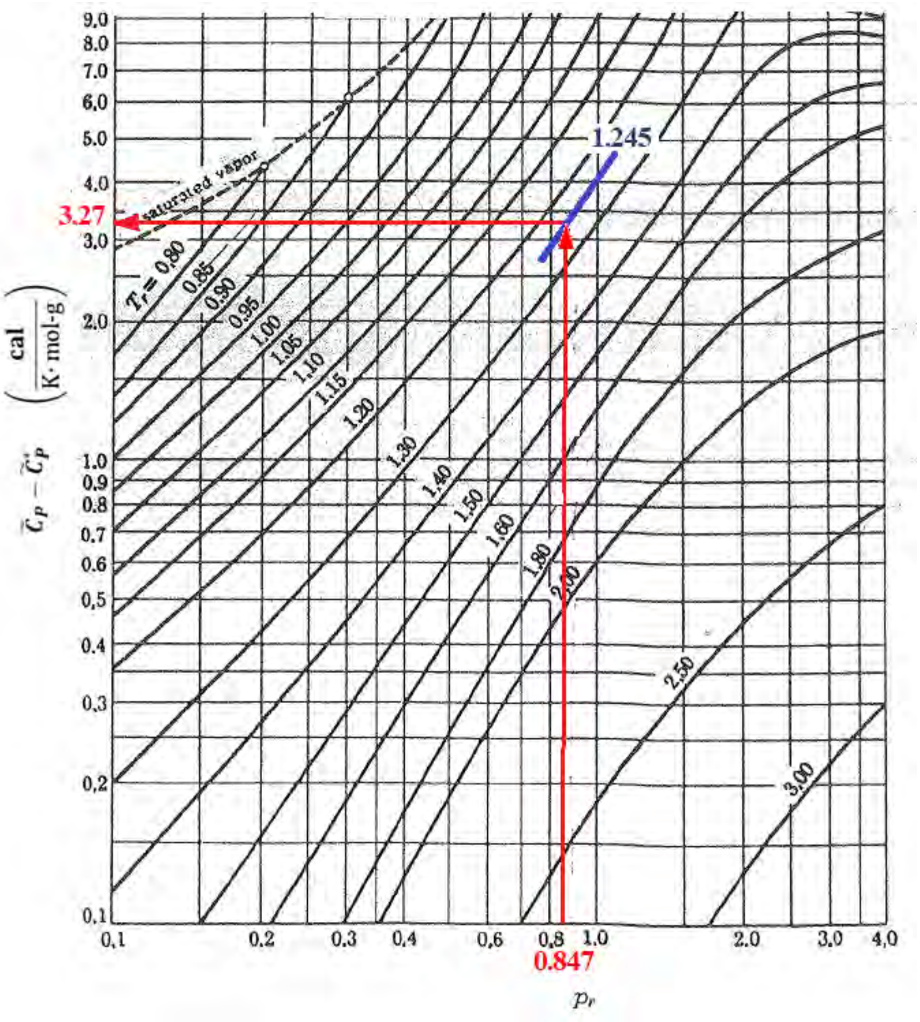
$$T_{cAB} = 0.4(190.7\ \text{K}) + 0.6(305.4\ \text{K}) = 259.52\ \text{K}$$

$$T_{rAB} = \frac{323.2\ \text{K}}{259.52\ \text{K}} = 1.245$$

$$P_{cAB} = 0.4(45.8\ \text{atm}) + 0.6(48.2\ \text{atm}) = 47.24\ \text{atm}$$

$$P_{rAB} = \frac{40\ \text{atm}}{47.24\ \text{atm}} = 0.847$$

By reading in figure IV.6



$$\left(\tilde{C}_P^* - \tilde{C}_P\right)_{T_{rAB},P_{rAB}} = 3.27\,\frac{\text{cal}}{\text{K· mol-g}}$$

Both results do not match.

In this particular context –and in the absence of experimental data– it is risky to guess which of the two procedures would be preferable. In principle, the physical-chemical reasons behind each approximation to the mixture properties should be justified.

2.24. A cylinder chamber with a piston contains 1 m³ of methane at 170 K and 2.8 atm, which is compressed adiabatically and reversibly until reaching a volume of 100 L. By assuming that z_c=0.27:

a) Calculate the number of moles of methane through the Corresponding States Principle.

b) Estimate the entropy departure from the ideal gas in the initial state through the Corresponding States Principle.

c) Estimate the temperature and pressure of the substance after the compression in the case of ideal behavior.

d) Compare them with those calculated through the Corresponding States Principle.

e) Determine the internal energy change through the Corresponding States Principle.

f) Estimate T and P after the compression, and ΔU by using a methane specific $PH(T,V,S)$ diagram.

g) Qualitatively represent the process in PT, PV, TH diagrams.

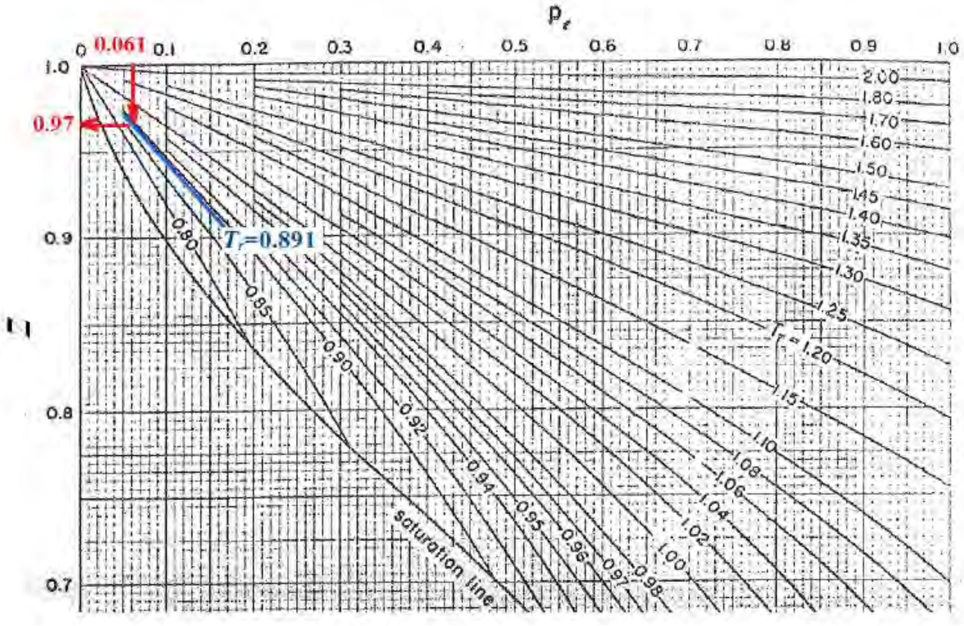
Question a. The number of moles in the initial state 1 is

$$n_1 = \frac{P_1 V_1}{z_1 R T_1}$$

where the compressibility factor z will be calculated by means of the generalized chart $z(T_r, P_r)$ of the Corresponding States Principle for z_c=0.27 (figure IV.1 of appendix IV). In appendix II,we find that T_c=190.7 K and P_c= 45.8 atm for methane, so at 170 K and 2.8 atm

$$T_{r1} = \frac{170\ K}{190.7\ K} = 0.891 \quad ; \quad P_{r1} = \frac{2.8\ \text{atm}}{45.8\ \text{atm}} = 0.061$$

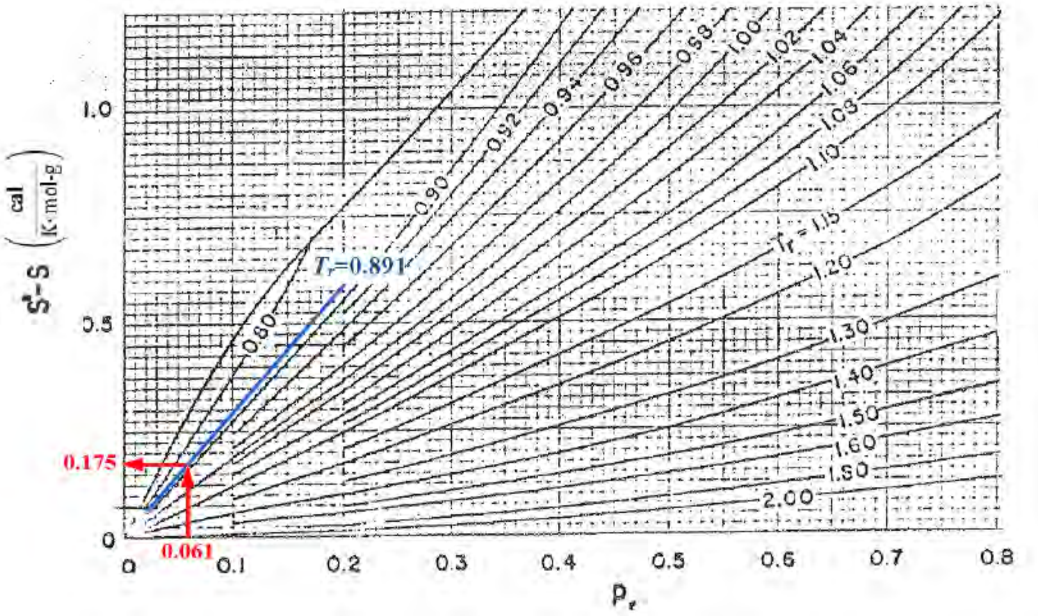
But, due to the low value of the reduced pressure, we will employ figure IV.3 of appendix IV because it is an enlargement of the low-density region of figure IV.1



from where z_1=0.97, so

$$n_1 = \frac{(2.8\ \text{atm})(1000\ \text{L})}{(0.97)\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(170\ \text{K})} = 207\ \text{mol-g}$$

Question b. Because the very low reduced pressure, the entropy departure will be read in generalized figure IV.8 ($0 \le P_r \le 1$) and not in figure IV.7 ($0.1 \le P_r \le 30$) of appendix IV



It shows that under the reduced conditions of the previous question

$$\left(\tilde{S}_1^* - \tilde{S}_1\right)_{T_1,P_1} = 0.175\ \text{cal/(K·mol-g)}$$

Question c. When a process is adiabatic, ΔQ=0. If it is also reversible, $\Delta Q=\Delta S/T$ and it will be isentropic (ΔS=0). By taking into account that the number of moles does not vary during compression, the specific entropy change between states 1 and 2 for an ideal gas is

$$\Delta\tilde{S}^* = \tilde{S}_2^* - \tilde{S}_1^* = \int_{T_1}^{T_2} \tilde{C}_P^* \frac{\mathrm{d}T}{T} - \int_{P_1}^{P_2} R\frac{\mathrm{d}P}{P} = \int_{T_1}^{T_2} \tilde{C}_P^* \frac{\mathrm{d}T}{T} - R[\ln P]_{P_1}^{P_2} = 0$$

$$\int_{T_1}^{T_2} \tilde{C}_P^* \frac{\mathrm{d}T}{T} = R\ln\frac{P_2}{P_1} = R\ln\frac{\left(\frac{n_2RT_2}{V_2}\right)}{\left(\frac{n_1RT_1}{V_1}\right)} = R\ln\left(\frac{T_2V_1}{T_1V_2}\right) = R\ln\frac{T_2}{T_1} - R\ln\frac{V_2}{V_1}$$

The specific heat capacity of methane as an ideal gas is given in appendix II as

$$\tilde{C}_P^* = \xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4$$

$$\frac{\xi_0}{R} = 4.568 \qquad \frac{\xi_1}{R} = -8.975 \cdot 10^{-3}\frac{1}{\mathrm{K}} \qquad \frac{\xi_2}{R} = 3.631 \cdot 10^{-5}\frac{1}{\mathrm{K}^2}$$

$$\frac{\xi_3}{R} = -3.407 \cdot 10^{-8}\frac{1}{\mathrm{K}^3} \qquad \frac{\xi_4}{R} = 1.091 \cdot 10^{-11}\frac{1}{\mathrm{K}^4}$$

and therefore

$$\int_{T_1}^{T_2} (\xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4)\frac{\mathrm{d}T}{T} = R\ln\frac{T_2}{T_1} - R\ln\frac{V_2}{V_1}$$

$$\left[\xi_0 \ln T + \xi_1 T + \frac{1}{2}\xi_2 T^2 + \frac{1}{3}\xi_3 T^3 + \frac{1}{4}\xi_4 T^4\right]_{T_1}^{T_2} = R\ln\frac{T_2}{T_1} - R\ln\frac{V_2}{V_1}$$

$$\xi_0 \ln\frac{T_2}{T_1} + \xi_1(T_2 - T_1) + \frac{\xi_2}{2}(T_2^2 - T_1^2) + \frac{\xi_3}{3}(T_2^3 - T_1^3) + \frac{\xi_4}{4}(T_2^4 - T_1^4) = R\ln\frac{T_2}{T_1} - R\ln\frac{V_2}{V_1}$$

$$(\xi_0 - R)\ln\frac{T_2}{T_1} + \xi_1(T_2 - T_1) + \frac{\xi_2}{2}(T_2^2 - T_1^2) + \frac{\xi_3}{3}(T_2^3 - T_1^3) + \frac{\xi_4}{4}(T_2^4 - T_1^4) + R\ln\frac{V_2}{V_1} = 0$$

$$(4.568 - 1)R\ln\left(\frac{T_2}{170}\right) - 8.975 \cdot 10^{-3}R(T_2 - 170) + \frac{3.631 \cdot 10^{-5}}{2}R(T_2^2 - 170^2) -$$
$$- \frac{3.407 \cdot 10^{-8}}{3}R(T_2^3 - 170^3) + \frac{1.091 \cdot 10^{-11}}{4}R(T_2^4 - 170^4) + R\ln\left(\frac{100}{1000}\right) = 0 \qquad [1]$$

After introducing the universal gas constant R=1.9872 cal/(K·mol-g), a trial and error procedure has to be used to determine the value of T_2 which satistifies [1]

Assumed T_2 (K)	Value of [1]	Comments
180	-4.24208173	Temperature is higher than 180 K
200	-3.62349847	Temperature is higher than 200 K
300	-1.12180923	Temperature is higher than 300 K
400	0.919709326	Temperature is lower than 400 K
350	-0.06889759	Temperature is higher than 350 K
360	0.133015066	Temperature is lower than 360 K
353	-0.00807036	Temperature is higher than 353 K
354	0.012156196	Temperature is lower than 354 K
353.3	-0.00199984	Temperature is higher than 353.3 K
353.5	0.00204596	Temperature is lower than 353.5 K
353.4	$2.31841 \cdot 10^{-5}$	It can be considered as the sought temperature

and the pressure of the ideal gas at this temperature of 353.4 K will be

$$P_2 = \frac{n_2 R T_2}{V_2} = \frac{(207\ \text{mol-g})\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(353.4\ \text{K})}{(100\ \text{L})} = 59.98\ \text{atm}$$

The well-known equation $P_1\tilde{V}_1^{\gamma} = P_2\tilde{V}_2^{\gamma}$ cannot be employed because it is deduced for temperature-independent specific heat capacities.

Question d. According to section e of reference problem 0.8, the entropy change between two states 1 and 2 can be calculated by

$$\left(\tilde{S}_2 - \tilde{S}_1\right) = \underbrace{\left(\tilde{S}_2^* - \tilde{S}_1^*\right)}_{\text{ideal part}} + \underbrace{\left(\tilde{S}_1^* - \tilde{S}_1\right)_{T_1,P_1} - \left(\tilde{S}_2^* - \tilde{S}_2\right)_{T_2,P_2}}_{\text{real part}} \qquad [2]$$

being $\left(\tilde{S}_2 - \tilde{S}_1\right) = 0$ because the process is isentropic.

Since neither T_2 nor P_2 are known, they have to be determined by trial and error routine as follows:

- A value of T_2 is assumed.
- The ideal part of equation [2] is calculated as

$$\begin{aligned}\left(\tilde{S}_2^* - S_1^*\right) = {} & (4.568-1)R\ln\left(\frac{T_2}{170}\right) - 8.975\cdot 10^{-3}R(T_2-170) + \\ & + \frac{3.631\cdot 10^{-5}}{2}R(T_2^2-170^2) - \frac{3.407\cdot 10^{-8}}{3}R(T_2^3-170^3) + \\ & + \frac{1.091\cdot 10^{-11}}{4}R(T_2^4-170^4) + R\ln\left(\frac{100}{1000}\right)\end{aligned}$$

- P_2 is obtained from the generalized chart of the compressibility factor (figure IV.1 of appendix IV) by means of a graphical procedure.
- Entropy departure at T_2 and P_2 is obtained from figure IV.7.
- Since the entropy departure in state 1 was calculated in question **b**, $\left(\tilde{S}_2^* - \tilde{S}_2\right)_{T_2,P_2}$, $\left(\tilde{S}_1^* - \tilde{S}_1\right)_{T_1,P_1}$ and $\left(\tilde{S}_2^* - S_1^*\right)$ are introduced in equation [2] and it is observed if it takes a zero value. If not, a new value of T_2 has to be selected.

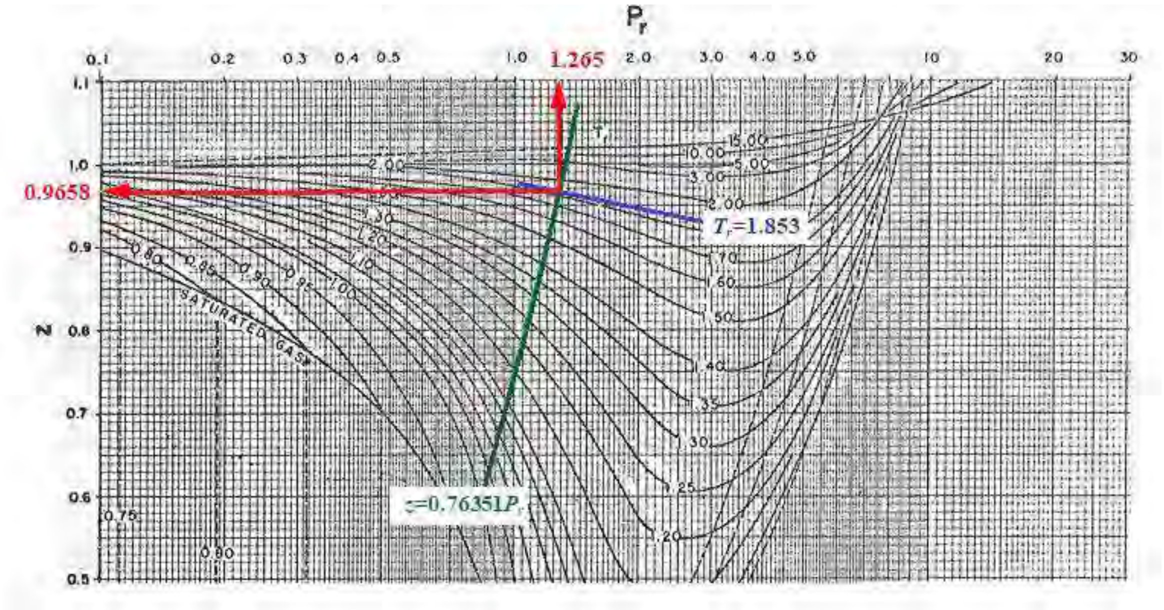
Starting of the calculation with T_2= 353.4 K, that of the ideal gas (T_{r2}=353.4/190.7=1.853). In figure IV.1, the search for P_{r2} will imply the finding of the compressibility factor that, at T_r=1.853, intersects with the line

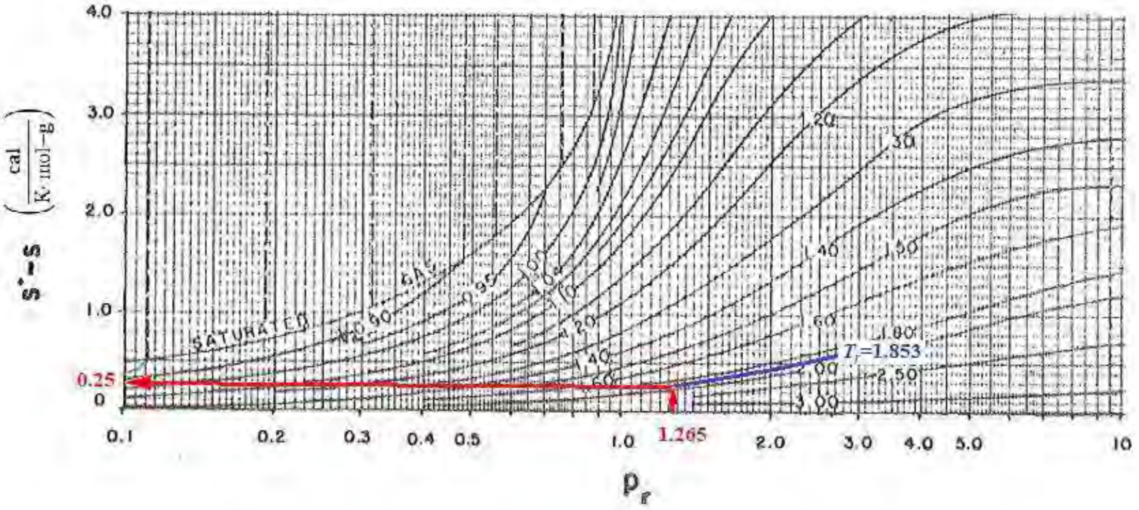
$$z_2 = \frac{P_c V_2}{n_2 R T_2} P_{r2} = \frac{(45.8\text{ atm})(100\text{ L})}{(207\text{ mol-g})\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(353.4\text{ K})} P_{r2} = 0.76351 P_{r2}$$

By giving values and representing

Assumed P_{r2}	Calculated z_2
0.8	0.610808
1.0	0.763510
1.1	0.839861
1.2	0.916212
1.3	0.992563
1.4	1.068914

the results are P_{r2}=1.265 and z_2=0.9658. Going with these reduced conditions to the graph IV.7, the entropy departure is of 0.25 cal/(K·mol-g)





Now, equation [2] will give

$$2.31841 \cdot 10^{-5} \frac{\text{cal}}{\text{K} \cdot \text{mol-g}} + 0.175 \frac{\text{cal}}{\text{K} \cdot \text{mol-g}} - 0.25 \frac{\text{cal}}{\text{K} \cdot \text{mol-g}} = -0.075 \frac{\text{cal}}{\text{K} \cdot \text{mol-g}}$$

value that is not zero or small enough.

The trial and error method continues with a higher temperature, for example, T_2= 360 K (T_{r2}=1.8877). The ideal term of equation [2] will be

$$\begin{aligned}(\tilde{S}_2^* - S_1^*) = (4.568 - 1)R \ln\left(\frac{360}{170}\right) - 8.975 \cdot 10^{-3} R(360 - 170) + \\ + \frac{3.631 \cdot 10^{-5}}{2} R(360^2 - 170^2) - \frac{3.407 \cdot 10^{-8}}{3} R(360^3 - 170^3) + \\ + \frac{1.091 \cdot 10^{-11}}{4} R(360^4 - 170^4) + R \ln\left(\frac{100}{1000}\right) = 0.133 \frac{\text{cal}}{\text{K} \cdot \text{mol-g}}\end{aligned}$$

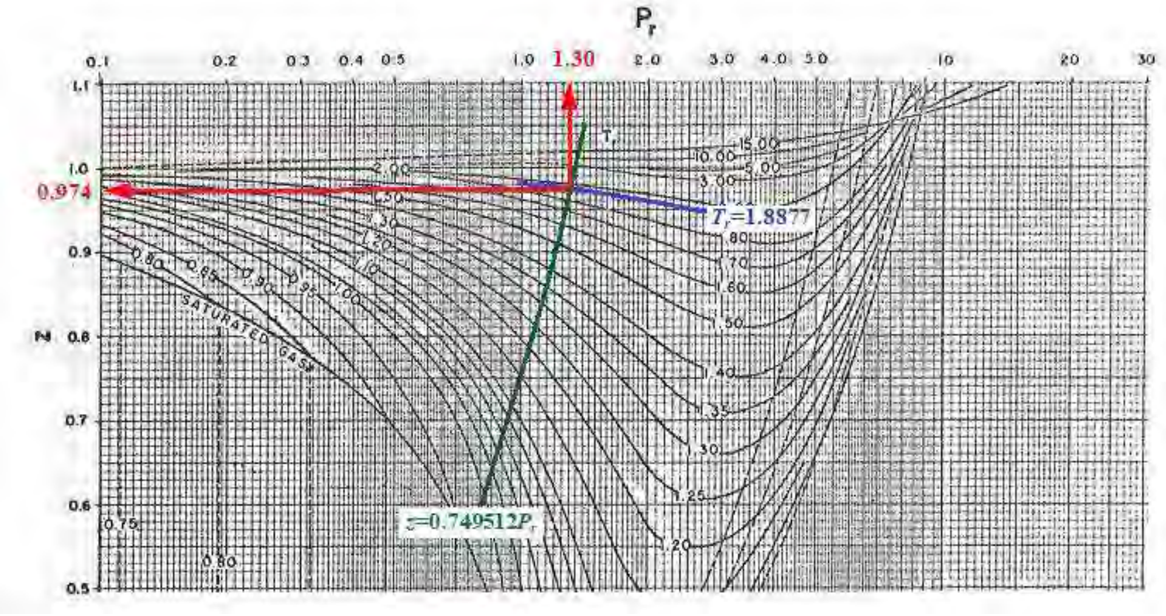
In figure IV.1 the compressibility factor is sought

$$z_2 = \frac{P_c V_2}{n_2 R T_2} P_{r2} = \frac{(45.8 \text{ atm})(100 \text{ L})}{(207 \text{ mol-g})\left(0.082 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol-g}}\right)(360 \text{ K})} P_{r2} = 0.74951233 P_{r2}$$

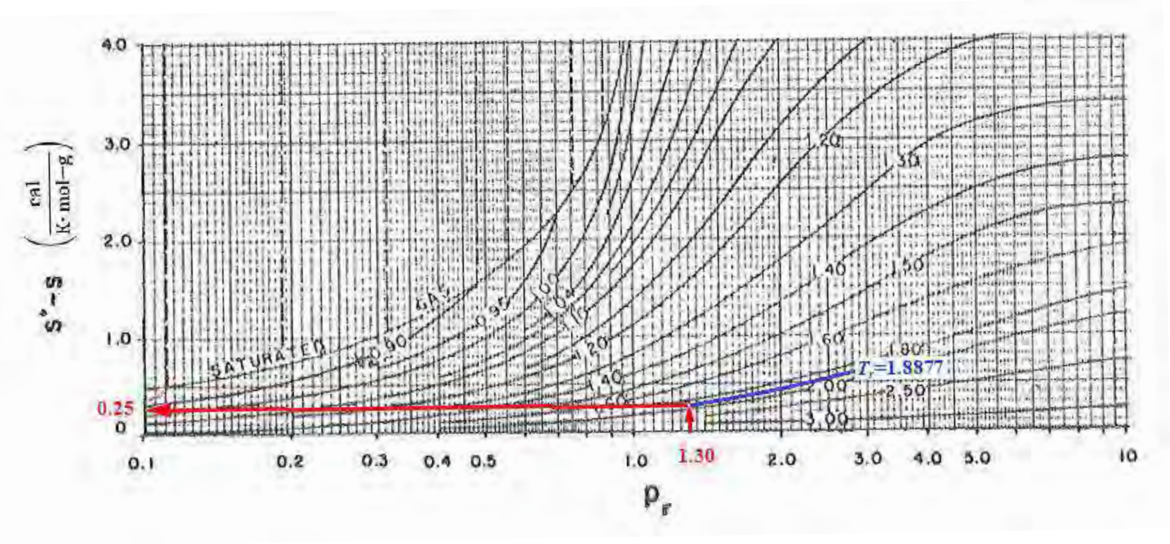
by plotting the line

Assumed P_{r2}	Calculated z_2
0.8	0.59960986
1.0	0.74951233
1.2	0.89941479
1.4	1.04931726

and the results are P_{r2}=1.3 and z_2=0.974



In figure IV.7, this reduced pressure gives an entropy departure of 0.25 cal/(K·mol-g).



Thus, according to equation [2], the ideal contribution will take a value of

$$0.133\ \frac{\text{cal}}{\text{K}\cdot\text{ mol-g}} + 0.175\ \frac{\text{cal}}{\text{K}\cdot\text{ mol-g}} - 0.25\ \frac{\text{cal}}{\text{K}\cdot\text{ mol-g}} = 0.058\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}}$$

which is not zero either. However, the sum is now positive, while in the previous try was negative: this indicates that the sought temperature lies between 353.4 and 360 K.

Furthermore, notice that $\left(\tilde{S}_2^* - \tilde{S}_2\right)_{T_2,P_2}$remains constant between these temperatures, which implies that T_2 can be found directly in equation [2] when written in the form

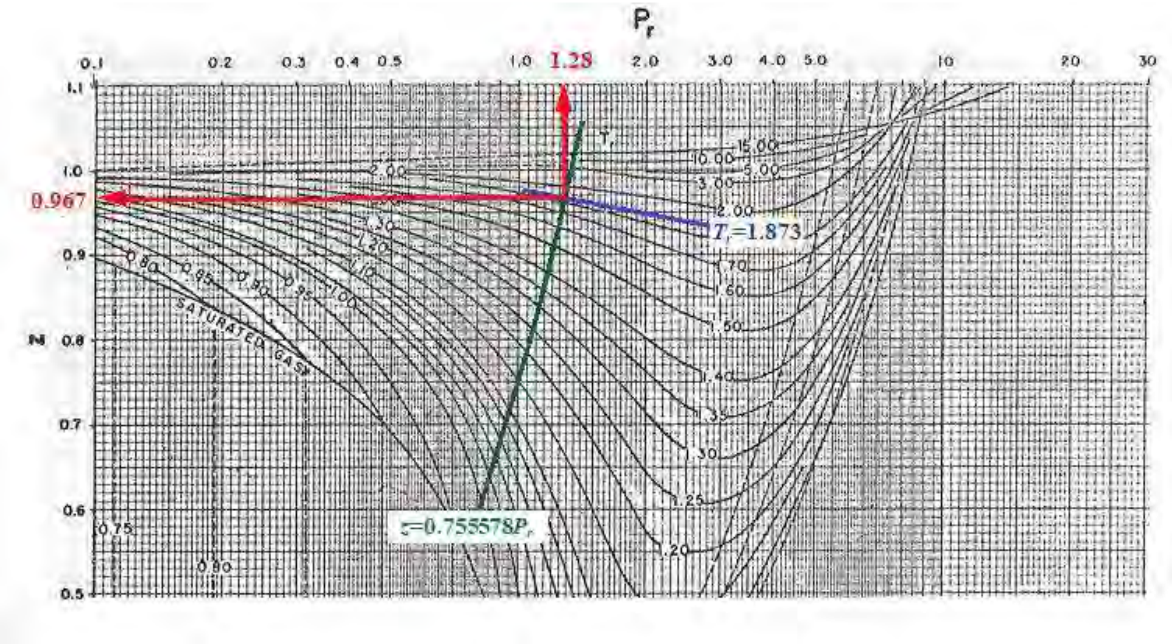
$$\begin{aligned}\left(\tilde{S}_2 - \tilde{S}_1\right) = (4.568 - 1)R\ln\left(\frac{T_2}{170}\right) - 8.975\cdot 10^{-3}R(T_2 - 170) +\\ + \frac{3.631\cdot 10^{-5}}{2}R(T_2^2 - 170^2) - \frac{3.407\cdot 10^{-8}}{3}R(T_2^3 - 170^3) +\\ + \frac{1.091\cdot 10^{-11}}{4}R(T_2^4 - 170^4) + R\ln\left(\frac{100}{1000}\right) + 0.175 - 0.25 = 0\end{aligned}$$

The result is T_2= 357.11 K (T_r=1.8726). The corresponding pressure will be found in the generalized chart of the compressibility factor where the isotherm T_r =357.11/ 190.7= 1.8726 intersects with the isoline

$$z_2 = \frac{P_cV_2}{n_2RT_2}P_{r2} = \frac{(45.8\text{ atm})(100\text{ L})}{(207\text{ mol-g})\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(357.11\text{ K})}P_{r2} = 0.755578P_{r2}$$

that takes the values

Assumed P_{r2}	Calculated z_2
0.8	0.604462
1.0	0.755578
1.2	0.906694
1.4	1.057809



The requested datum is P_r=1.28, i.e., P_2=1.28(45.8 atm) =58.624 atm. This pressure is only slightly lower than that of the ideal gas.

Question e. The internal energy is calculated with a formula analogous to [2]

$$\left(\tilde{U}_2 - \tilde{U}_1\right) = \left(\tilde{U}_2^* - U_1^*\right) + \left(\tilde{U}_1^* - \tilde{U}_1\right)_{T_1,P_1} - \left(\tilde{U}_2^* - \tilde{U}_2\right)_{T_2,P_2} \qquad [3]$$

The ideal part (or contribution of a supposed ideal behavior) will be

$$\tilde{U}_2^* - \tilde{U}_1^* = \int_{T_1}^{T_2} \tilde{C}_V^* \mathrm{d}T = \int_{T_1}^{T_2} \left(\tilde{C}_P^* - R\right) \mathrm{d}T$$

$$\tilde{U}_2^* - \tilde{U}_1^* = \int_{T_1}^{T_2} (\xi_0 - R + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4) \mathrm{d}T$$

$$\tilde{U}_2^* - \tilde{U}_1^* = \left[(\xi_0 - R)T + \frac{1}{2}\xi_1 T^2 + \frac{1}{3}\xi_2 T^3 + \frac{1}{4}\xi_3 T^4 + \frac{1}{5}\xi_4 T^5\right]_{T_1}^{T_2} =$$

$$= (\xi_0 - R)(T_2 - T_1) + \frac{\xi_1}{2}(T_2^2 - T_1^2) + \frac{\xi_2}{3}(T_2^3 - T_1^3) + \frac{\xi_3}{4}(T_2^4 - T_1^4) + \frac{\xi_4}{5}(T_2^5 - T_1^5)$$

$$\left(\widetilde{U}_2^* - U_1^*\right) = (4.568 - 1)R(357.11 - 170) - \frac{8.975 \cdot 10^{-3}}{2} R(357.11^2 - 170^2) + \\ + \frac{3.631 \cdot 10^{-5}}{3} R(357.11^3 - 170^3) - \frac{3.407 \cdot 10^{-8}}{4} R(357.11^4 - 170^4) + \\ + \frac{1.091 \cdot 10^{-11}}{5} R(357.11^5 - 170^5) = 1187.77 \frac{\text{cal}}{\text{mol-g}}$$

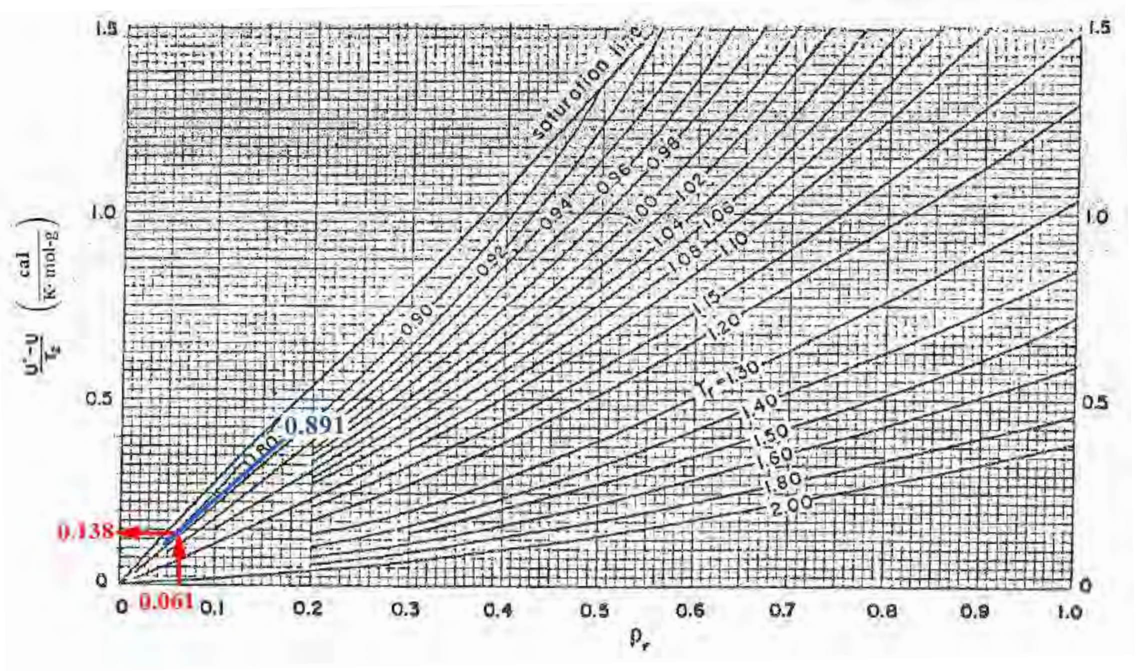
while the real part (or contribution of the departure) will be estimated by the generalized figures IV.10 (state 1, low reduced pressure) and IV.9 (state 2, high reduced pressure) of appendix IV.

$$T_{r1} = 0.891 \quad ; \quad P_{r1} = 0.061$$

$$\left(\frac{\widetilde{U}_1^* - \widetilde{U}_1}{T_c}\right)_{T_{r1},P_{r1}} = 0.138 \frac{\text{cal}}{\text{K} \cdot \text{mol-g}}$$

$$\Downarrow$$

$$\left(\widetilde{U}_1^* - \widetilde{U}_1\right)_{T_1,P_1} = \left(0.138 \frac{\text{cal}}{\text{K} \cdot \text{mol-g}}\right)(190.7\ \text{K}) = 26.32\ \text{mol-g}$$

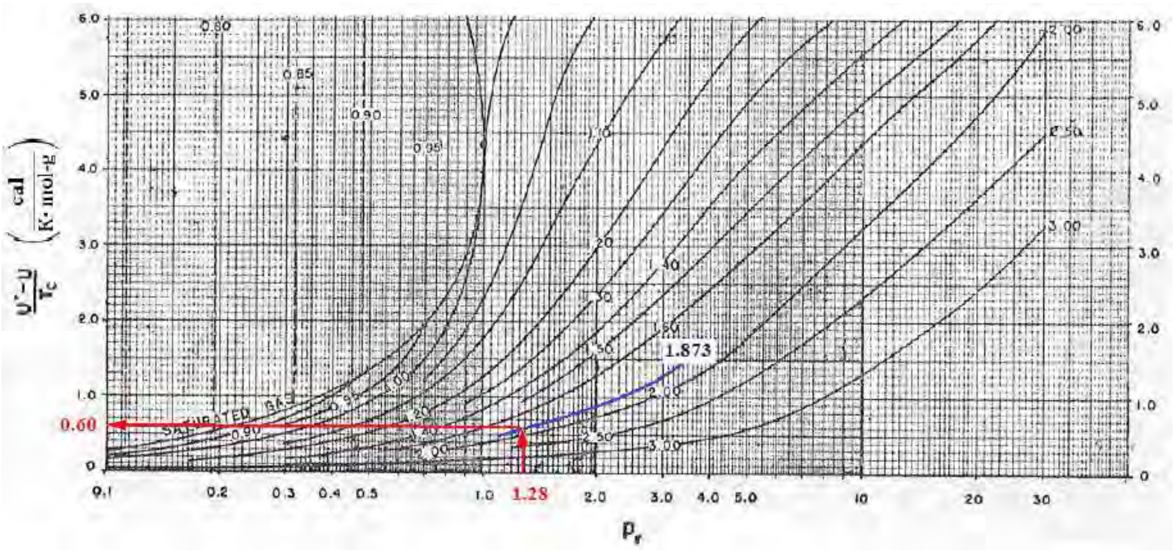


$$T_{r2} = 1.873 \quad ; \quad P_{r2} = 1.28$$

$$\left(\frac{\widetilde{U}_2^* - \widetilde{U}_2}{T_c}\right)_{T_{r2},P_{r2}} = 0.60 \frac{\text{cal}}{\text{K} \cdot \text{mol-g}}$$

$$\Downarrow$$

$$\left(\widetilde{U}_2^* - \widetilde{U}_2\right)_{T_2,P_2} = \left(0.60 \frac{\text{cal}}{\text{K} \cdot \text{mol-g}}\right)(190.7\ \text{K}) = 114.42\ \frac{\text{cal}}{\text{mol-g}}$$

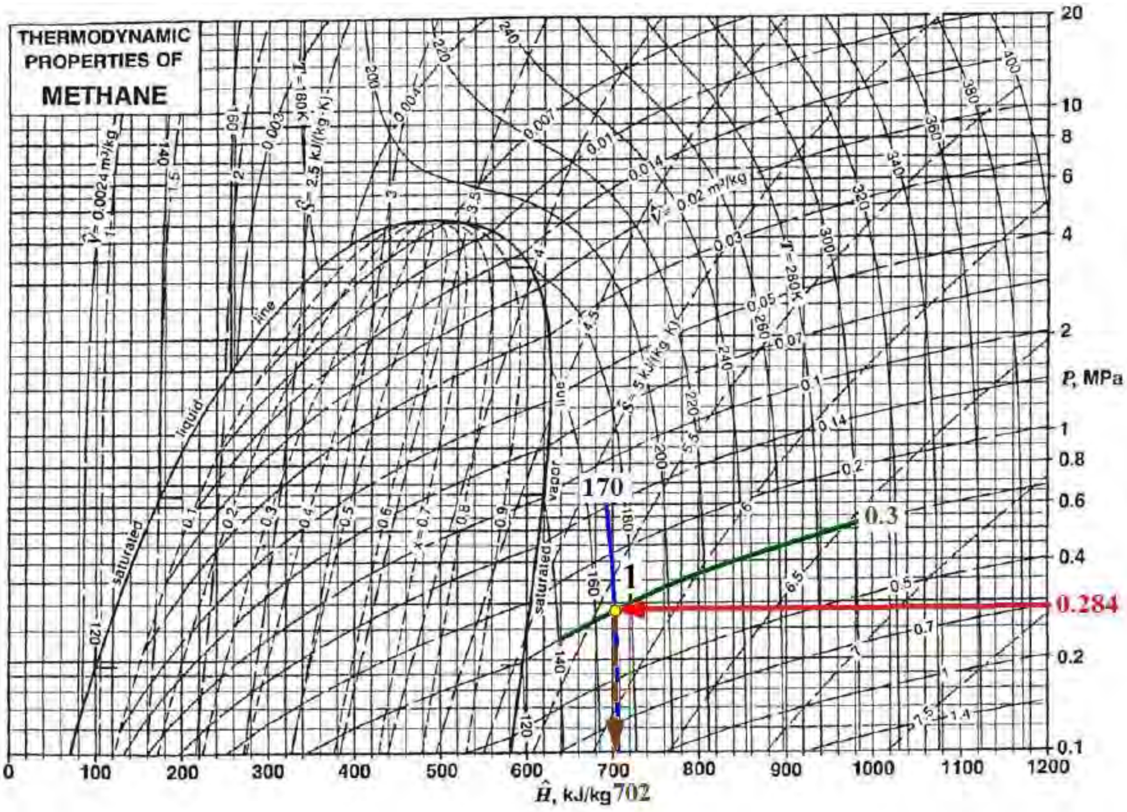


and introducing the terms in equation [3]

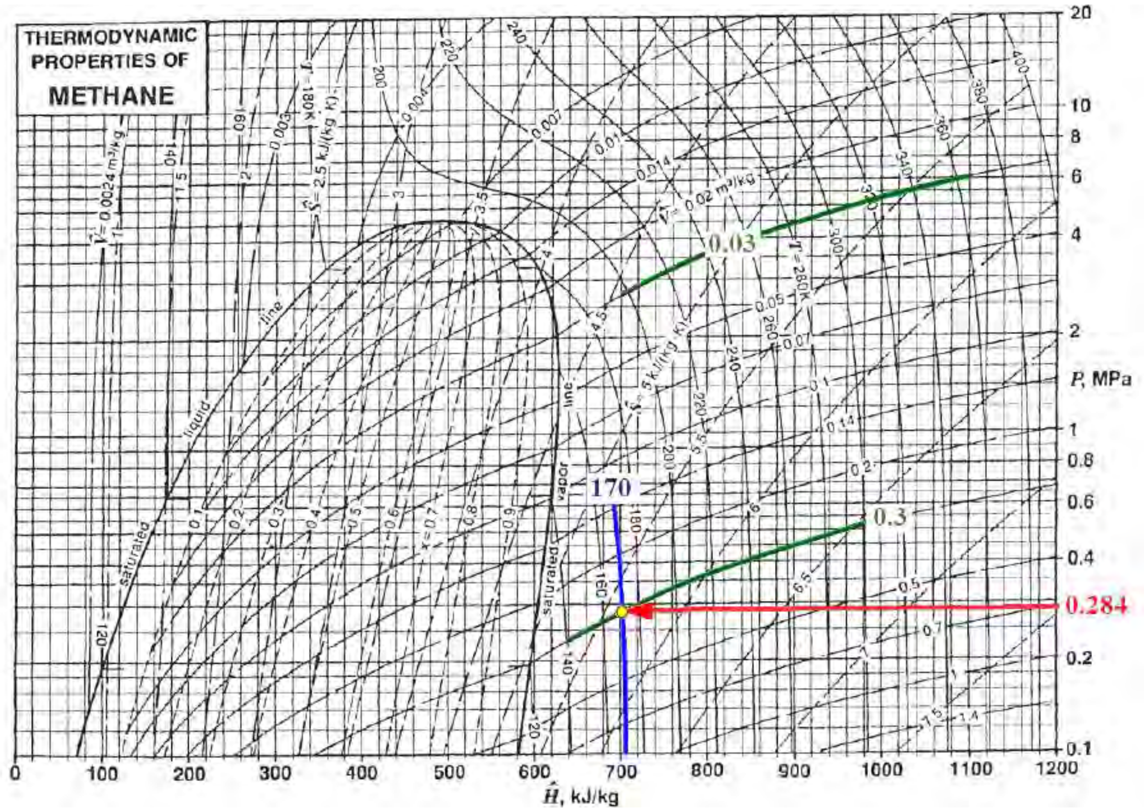
$$1187.77\ \frac{\text{cal}}{\text{mol-g}} + 26.32\ \frac{\text{cal}}{\text{mol-g}} - 114.42\ \frac{\text{cal}}{\text{mol-g}} = 1099.67\frac{\text{cal}}{\text{mol-g}}$$

Question f. Figure V.4 of appendix V is a methane-specific *PH*(*T,V,S*) diagram. In order to place the state 1 in it, pressure has to be converted to MPa

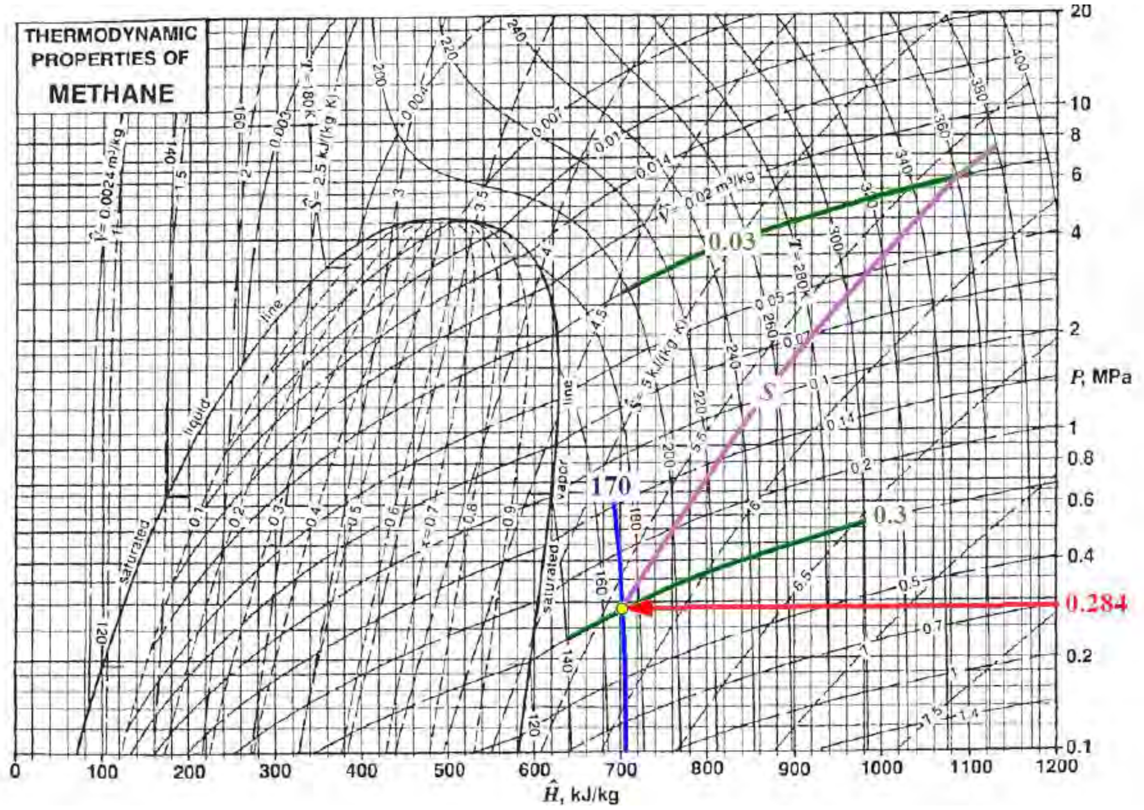
$$2.8\text{ atm} \times \frac{1.013\text{ bar}}{1\text{ atm}} \times \frac{0.1\text{ MPa}}{1\text{ bar}} = 0.284\text{ MPa}$$



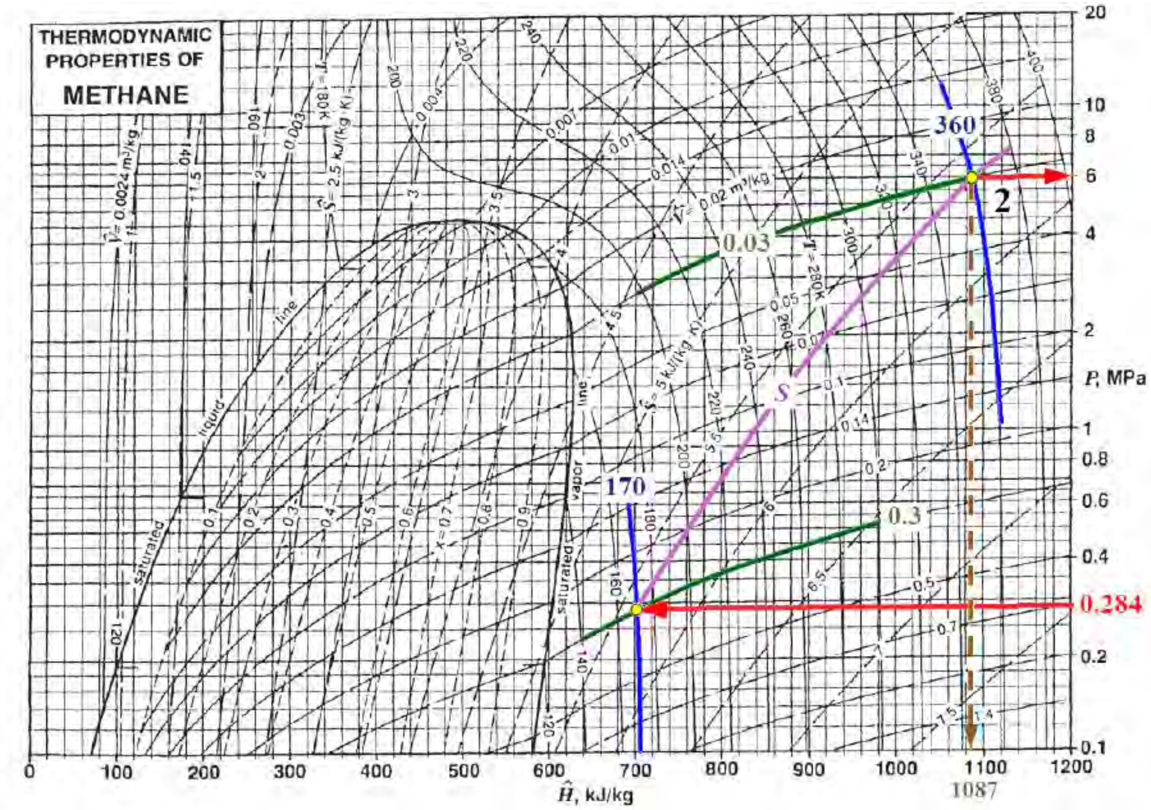
In this state, $\hat{H}_1$= 702 kJ/kg and $\hat{V}_1$= 0.3 m^3/kg. Since the statement of the problem says that the final volume is one tenth of the initial one, the 0.03 m^3/kg isochore has to be found.



Then, the isentropic line which passes through 170 K and 0.284 MPa is plotted.



The point where this isentropic crosses with the 0.03 m^3/kg isochore is point 2. By reading in the graph, temperature, pressure and enthalpy in this state are 360 K, 6 MPa and 1087 kJ/kg, respectively.



Regarding internal energy, it can be calculated from its definition (section d of reference problem 0.2) as

$$\hat{U} = \hat{H} - P\hat{V}$$

$$\hat{U}_2 - \hat{U}_1 = \hat{H}_2 - \hat{H}_1 - \left(P_2\hat{V}_2 - P_1\hat{V}_1\right)$$

where

$$P_2\hat{V}_2 - P_1\hat{V}_1 = (6000\text{ kPa})\left(0.03\frac{\text{m}^3}{\text{kg}}\right) - (284\text{ kPa})\left(0.3\frac{\text{m}^3}{\text{kg}}\right) = 94.8\frac{\text{kJ}}{\text{kg}}$$

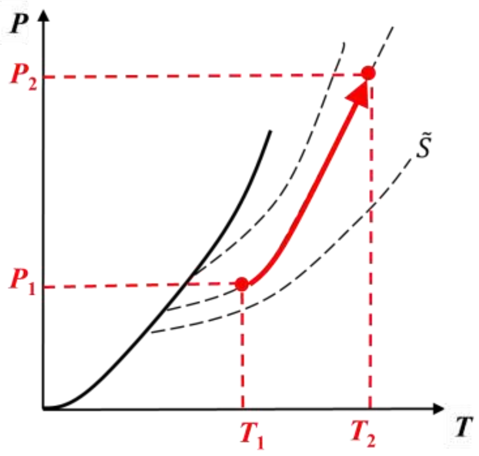
and so

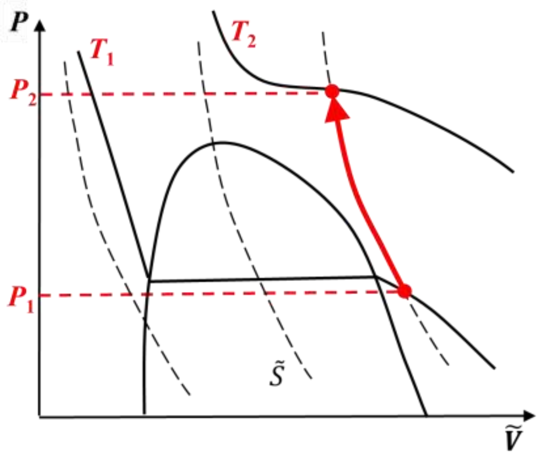
$$\hat{U}_2 - \hat{U}_1 = 1087\ \frac{\text{kJ}}{\text{kg}} - 702\ \frac{\text{kJ}}{\text{kg}} - 94.8\ \frac{\text{kJ}}{\text{kg}} = 290.2\ \frac{\text{kJ}}{\text{kg}}$$

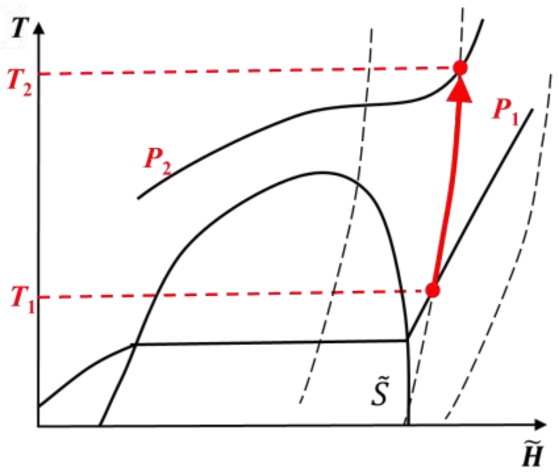
$$\Delta\tilde{U} = 290.2\ \frac{\text{kJ}}{\text{kg}} \times \frac{1\text{ kg}}{1000\text{ g}} \times \frac{16.04\text{ g}}{1\text{ mol-g}} \times \frac{0.239\text{ kcal}}{1\text{ kJ}} \times \frac{1000\text{ cal}}{1\text{ kcal}} = 1112.5\ \frac{\text{cal}}{\text{mol-g}}$$

Taking into account that z_c=0.29 for CH_4 and the errors due to graphical reading and operating, the closeness of these results with those of preceding questions can be considered satisfactory.

Question g. *PT*, *PV* and *TH* diagrams.







SERIES 3

TRANSPORT PROPERTIES

3.1. By using generalized charts based on the of Corresponding States Principle, estimate:

a) The viscosity of carbon dioxide at 75ºC and 50 bar knowing that it is of 0.0143 cp at atmospheric pressure and 20ºC.

b) The viscosity of nitrogen at 80ºC and 1 atm.

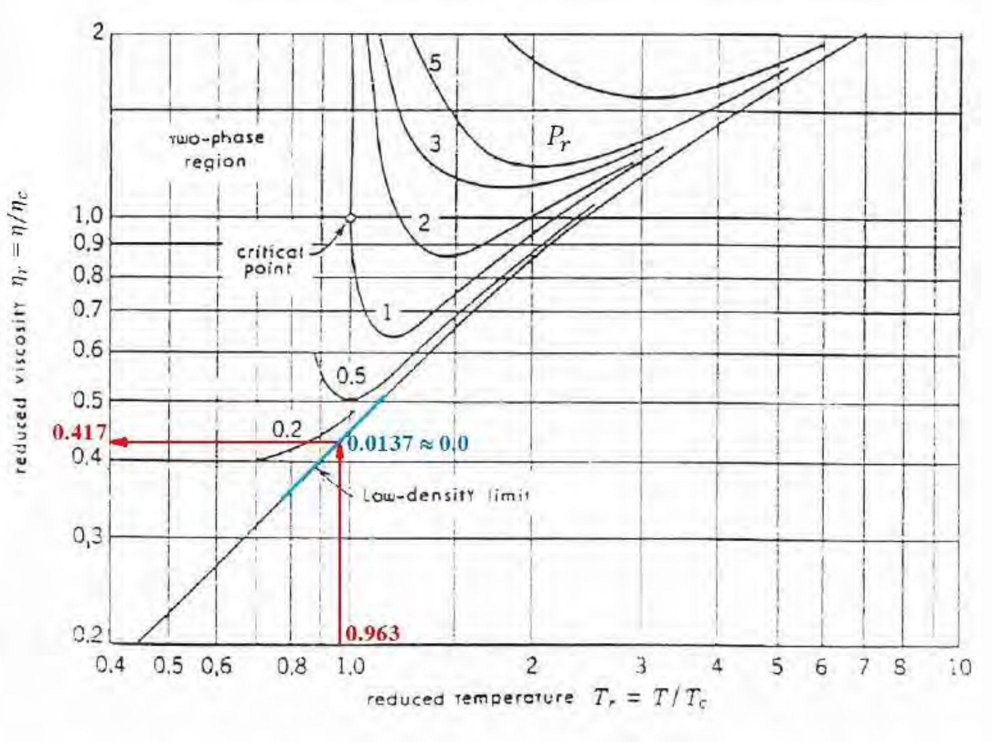
c) The thermal conductivity of air at 323.2 K and 1 atm.

Question a. Appendix II indicates that the critical temperature and pressure of CO_2 are 304.2 K and 72.9 atm, so

$$T_1(\mathrm{K}) = 20\text{°C} + 273 = 293\ \mathrm{K} \qquad \rightarrow \qquad T_{r1} = \frac{T_1}{T_c} = \frac{293\ \mathrm{K}}{304.2\ \mathrm{K}} = 0.963$$

$$P_{r1} = \frac{P_1}{P_c} = \frac{1\ \mathrm{atm}}{72.9\ \mathrm{atm}} = 0.0137$$

Visual inspection of the diagram IV.11 of the appendix IV of this book (generalized chart of reduced viscosity) reveals that such a low reduced pressure can be considered practically at the low-density limit, where the value η_{r1}=0.417 is read for T_r=0.963.



From this it follows that the critical viscosity takes a value of

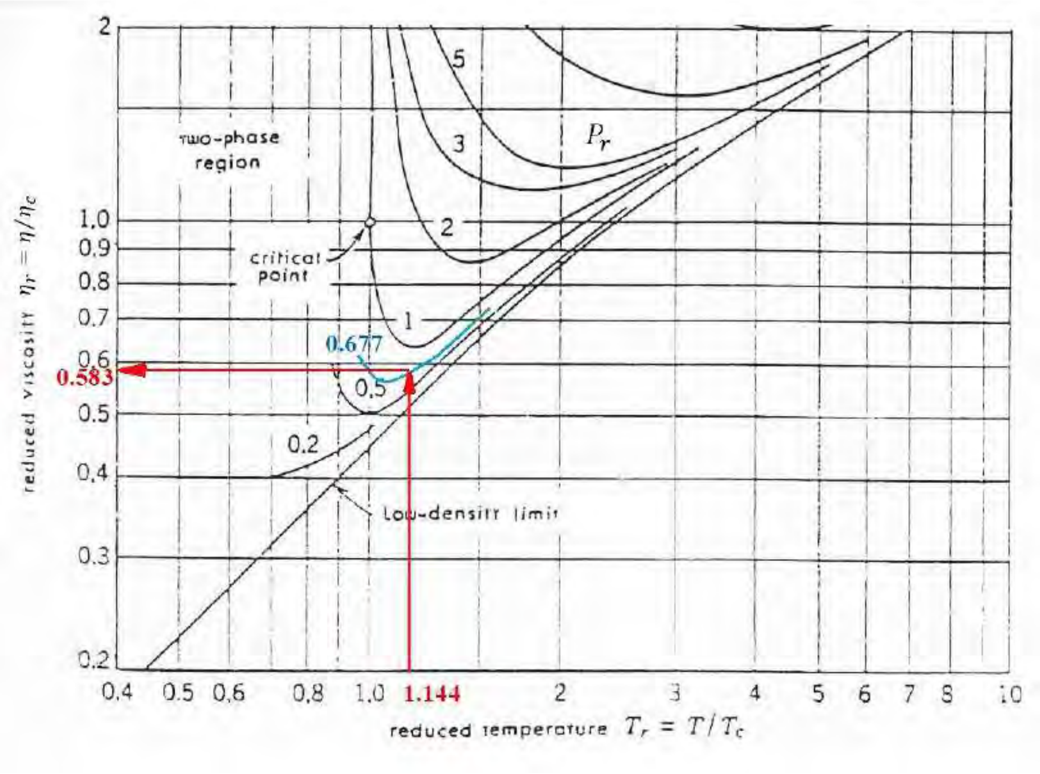
$$\eta_{r1} = \frac{\eta_1}{\eta_c} = \frac{0.0143\ \mathrm{cp}}{\eta_c} = 0.417 \qquad \rightarrow \qquad \eta_c = \frac{0.0143\ \mathrm{cp}}{0.417} = \ 0.0343\ \mathrm{cp}$$

In the second point

$$T_2(\mathrm{K}) = 75°\mathrm{C} + 273 = 348\ \mathrm{K} \qquad \rightarrow T_{r2} = \frac{T_2}{T_c} = \frac{348\ \mathrm{K}}{304.2\ \mathrm{K}} = 1.144$$

$$50\ \mathrm{bar} \times \frac{0.987\ \mathrm{atm}}{1\ \mathrm{bar}} = 49.35\ \mathrm{atm} \qquad \rightarrow \quad P_{r2} = \frac{P_2}{P_c} = \frac{49.35\ \mathrm{atm}}{72.9\ \mathrm{atm}} = 0.677$$

and from the same figure of appendix IV, η_{r2}=0.583.



By employing the critical viscosity previously calculated, the viscosity under these second conditions will be

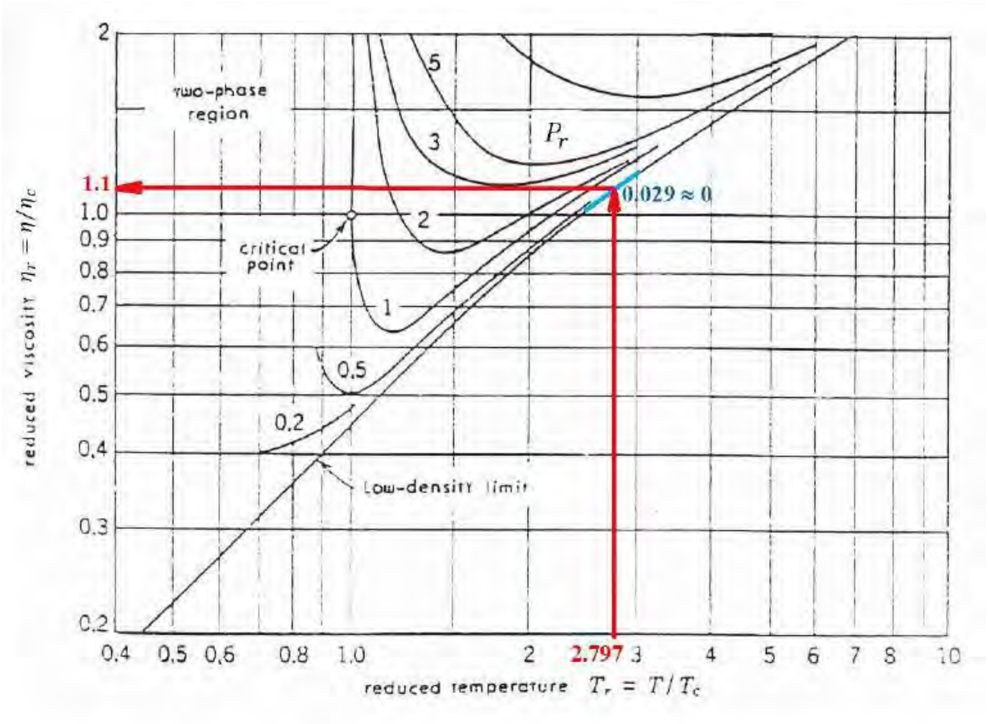
$$\eta_2 = \eta_c \eta_{r2} = (0.583)(0.0343\ \mathrm{cp}) = 0.020\ \mathrm{cp}$$

Question b. The table of appendix II says that the critical properties of nitrogen are T_c=126.2 K, P_c=33.5 atm and η_c=180·10^{-4} cp. Therefore

$$T(\mathrm{K}) = 80 + 273 = 353\ \mathrm{K} \qquad \rightarrow \quad T_r = \frac{353\ \mathrm{K}}{126.2\ \mathrm{K}} = 2.797$$

$$P_r = \frac{1 \text{ atm}}{33.5 \text{ atm}} = 0.029$$

As in the previous question, this reduced pressure practically can be considered in the low-density limit of figure IV.11, where, at T_r=2.797, the reduced viscosity is of 1.1



and

$$\eta = \eta_c \eta_r = (1.1)(180 \cdot 10^{-4} \text{ cp}) = \ 0.0198 \text{ cp}$$

Question c. Air is a mixture of 78.03% N_2, 20.99% O_2 and 0.98% Ar. The table of appendix II says that:

- the critical properties of nitrogen are T_c=126.2 K, P_c=33.5 atm and λ_c=86.8·10^{-6} cal/(cm·s·K)
- those of argon T_c=151.0 K, P_c=48.0 atm and λ_c=71.0·10^{-6} cal/(cm·s·K)
- those of oxygen, T_c=154.4 K, P_c=49.7 atm and λ_c=105.3·10^{-6} cal/(cm·s·K)

By applying the extension of the Corresponding States Principle to stable ideal mixtures (section b of reference problem 0.16) it is obtained

$$P_c = \sum_i y_i\, P_{ci} = 0.7803(33.5\text{ atm})+0.098(48\text{ atm})+0.2099(49.7\text{ atm}) = 37.01\text{ atm}$$

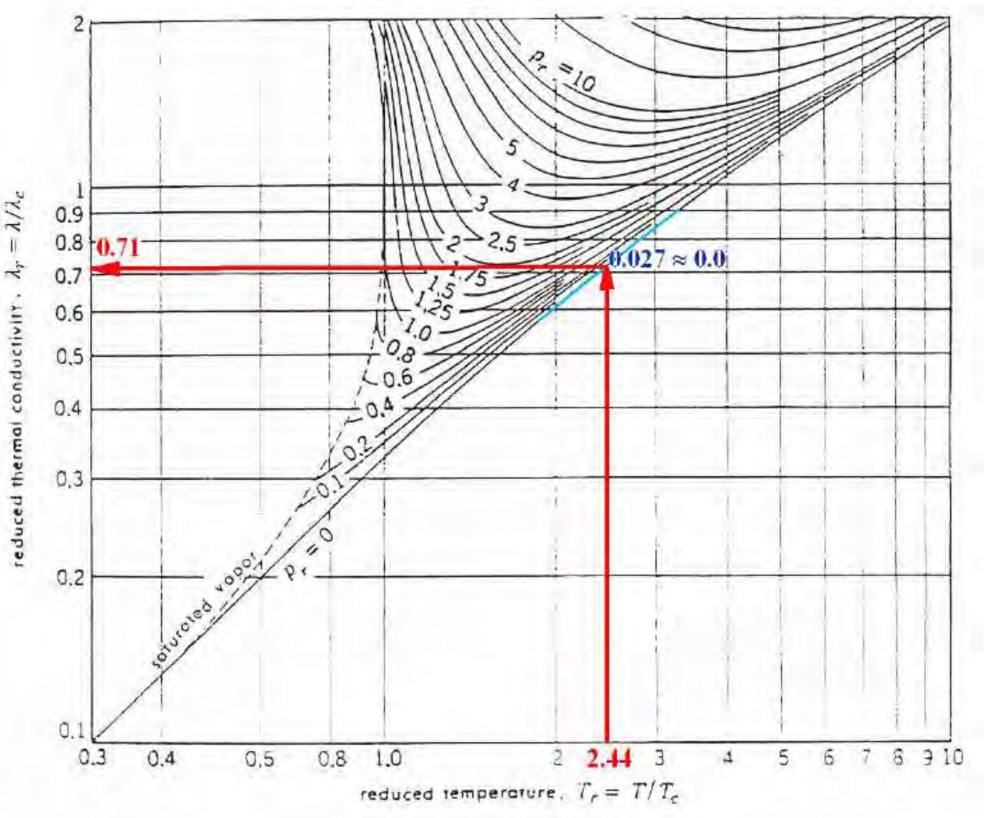
$$T_c = \sum_i y_i\, T_{ci} = 0.7803(126.2\text{ K}) + 0.098(151\text{ K}) + 0.2099(154.4\text{ K}) = 132.36\text{ K}$$

$$\lambda_c = \sum_i y_i\, \lambda_{ci} = 0.7803\left(86.8{\cdot}10^{-6}\frac{\text{cal}}{\text{cm}\cdot\text{s}\cdot\text{K}}\right) + 0.098\left(71\cdot 10^{-6}\frac{\text{cal}}{\text{cm}\cdot\text{s}\cdot\text{K}}\right) +$$
$$+0.2099\left(105.3\cdot 10^{-6}\frac{\text{cal}}{\text{cm}\cdot\text{s}\cdot\text{K}}\right) = 90.53\cdot 10^{-6}\frac{\text{cal}}{\text{cm}\cdot\text{s}\cdot\text{K}}$$

Reduced temperature and pressure will be

$$T_r = \frac{323.2\text{ K}}{132.36\text{ K}} = 2.44 \qquad ; \qquad P_r = \frac{1\text{ atm}}{37.01\text{ atm}} = 0.027$$

In figure IV.12 of appendix IV (generalized chart of the reduced thermal conductivity) this reduced pressure practically corresponds to the low-density limit, and λ_r=0.71.



being the thermal conductivity

$$\lambda = \lambda_c \lambda_r = (0.71)\left(90.53 \cdot 10^{-6} \frac{\mathrm{cal}}{\mathrm{cm} \cdot \mathrm{s} \cdot \mathrm{K}}\right) = \ 64.27 \cdot 10^{-6} \frac{\mathrm{cal}}{\mathrm{cm} \cdot \mathrm{s} \cdot \mathrm{K}}$$

3.2. By means of the equations derived from the Lennard-Jones potential, calculate:

a) The viscosity of nitrogen at 80ºC and 1 atm. Compare it with question b) of the previous problem.

b) The heat conductivity of air at 323.2 K and 1 atm. Compare it with question c) of the previous problem.

c) The diffusivity of ethanol in air at 298.2 K and 1 atm.

In section c of reference problem 0.7 it is found that

$$\eta^{\mathrm{LJ}} = \frac{5}{16(\sigma^{\mathrm{LJ}})^2\Omega_\eta}\sqrt{\frac{mkT}{\pi}} \qquad [1]$$

$$\lambda^{\mathrm{LJ}} = \frac{75k}{64(\sigma^{\mathrm{LJ}})^2\Omega_\lambda}\sqrt{\frac{kT}{m\pi}} \qquad [2]$$

$$D_{AB}^{\mathrm{LJ}} = \frac{3}{8\tilde{\rho}N_{av}\left(\sigma_{AB}^{\mathrm{LJ}}\right)^2\Omega_D}\sqrt{\frac{kT}{\pi m_{AB}}} \qquad [3]$$

where the Ω functions can be calculated in the range $0.3\leq kT/\varepsilon^{\mathrm{LJ}} \leq 100$ through the empirical equations of Neufeld (Poling et al., 2001)

$$\Omega_\eta = \Omega_\lambda = \frac{1.16145}{\left(\frac{kT}{\varepsilon^{\mathrm{LJ}}}\right)^{0.14874}} + 0.52487\exp\left(-0.77320\frac{kT}{\varepsilon^{\mathrm{LJ}}}\right) + 2.161778\exp\left(-2.43787\frac{kT}{\varepsilon^{\mathrm{LJ}}}\right) \qquad [4]$$

$$\Omega_D = 1.06036\left(\frac{\varepsilon_{AB}^{\mathrm{LJ}}}{kT}\right)^{0.15601} + 0.19300\exp\left(-0.47635\frac{kT}{\varepsilon_{AB}^{\mathrm{LJ}}}\right) + $$
$$+1.03587\exp\left(-1.52996\frac{kT}{\varepsilon_{AB}^{\mathrm{LJ}}}\right) + 1.76474\exp\left(-3.89411\frac{kT}{\varepsilon_{AB}^{\mathrm{LJ}}}\right) \qquad [5]$$

being

$$\sigma_{AB}^{\mathrm{LJ}} = \frac{\sigma_A^{\mathrm{LJ}} + \sigma_B^{\mathrm{LJ}}}{2} \quad ; \quad \frac{\varepsilon_{AB}^{\mathrm{LJ}}}{k} = \sqrt{\frac{\varepsilon_A^{\mathrm{LJ}}}{k}\cdot\frac{\varepsilon_B^{\mathrm{LJ}}}{k}} \quad ; \quad m_{AB} = \frac{2}{\frac{1}{m_A}+\frac{1}{m_B}} \qquad [6]$$

The fitting of actual values of transport properties to equations [1 – 3] allows the determination of parameters σ^{LJ} and $\varepsilon^{\mathrm{LJ}}$. Some are tabulated in appendix II. But when there are no available data, Hirschfelder et al (1964) suggested the following formulae

$$\sigma^{\mathrm{LJ}} = 1.17\tilde{V}_b^{1/3};\quad \sigma^{\mathrm{LJ}} = 0.841\tilde{V}_c^{1/3}\ ;\ \sigma^{\mathrm{LJ}} = 2.44\left(\frac{T_c}{P_c}\right)^{1/3}\ ;\ \sigma^{\mathrm{LJ}} = 0.1866\tilde{V}_c^{1/3}z_c^{-6/5} \qquad [7]$$

$$\frac{\varepsilon^{\mathrm{LJ}}}{k} = 1.15T_b \quad ; \quad \frac{\varepsilon^{\mathrm{LJ}}}{k} = 0.77T_c\ ; \quad \frac{\varepsilon^{\mathrm{LJ}}}{k} = 65.3T_cz_c^{18/5} \qquad [8]$$

where $\tilde{V}_b$ and $\tilde{V}_c$ are expressed in cm^3/mol-g, T_b, T_c and $\varepsilon^{\mathrm{LJ}}/k$ in K, P_c in atmospheres and σ^{LJ} in angstrom (1 Å= 10^{-10} m).

Question a. Appendix II gives a value of $\varepsilon^{\mathrm{LJ}}$/k= 91.5 K for nitrogen; thus

$$T(\mathrm{K}) = 80 + 273 = 353\ \mathrm{K} \quad \rightarrow \quad \frac{kT}{\varepsilon^{\mathrm{LJ}}} = \frac{353\ \mathrm{K}}{91.5\ \mathrm{K}} = 3.86$$

and in equation [4]

$$\Omega_\eta = \frac{1.16145}{(3.86)^{0.14874}} + 0.52487\exp\{-0.77320(3.86)\} + 2.161778\exp\{-2.43787(3.86)\} = 0.977$$

Appendix II also indicates that $\sigma^{\mathrm{LJ}}=3.681\cdot10^{-10}$ m and that $\mathfrak{M}$=28.02 g/mol-g, so in equation [1]

$$m = 28.02\frac{\mathrm{g}}{\mathrm{mol\text{-}g}} \times \frac{1\ \mathrm{mol\text{-}g}}{6.022\cdot10^{23}\mathrm{particles}} \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}} = 4.653\cdot10^{-26}\frac{\mathrm{kg}}{\mathrm{particle}}$$

$$\eta^{\mathrm{LJ}} = \frac{5\sqrt{(4.653\cdot10^{-26}\mathrm{kg})\left(1.38\cdot10^{-23}\frac{\mathrm{J}}{\mathrm{K}}\right)353.2\ \mathrm{K}}}{16(3.681\cdot10^{-10}\ \mathrm{m})^2(0.977)(3.1415)^{0.5}} = 200.6\cdot10^{-7}\frac{\mathrm{kg}}{\mathrm{m\cdot s}}$$

value which converted to centipoises is only slightly higher than that estimated in question **b** of the previous problem.

$$200.6\cdot10^{-7}\frac{\mathrm{kg}}{\mathrm{m\cdot s}} \times \frac{1000\ \mathrm{g}}{1\ \mathrm{kg}} \times \frac{1\ \mathrm{m}}{100\ \mathrm{cm}} = 200.6\cdot10^{-6}\frac{\mathrm{g}}{\mathrm{cm\cdot s}}\ [=]\ \mathrm{poise}$$

$$200.6\cdot10^{-6}\frac{\mathrm{g}}{\mathrm{cm\cdot s}} = 0.02006\ \mathrm{cp}$$

Question b. Appendix II gives a value of $\varepsilon^{\mathrm{LJ}}$/k= 97.0 K for air; thus

$$\frac{kT}{\varepsilon^{\mathrm{LJ}}}=\frac{323.2\ \mathrm{K}}{97\ \mathrm{K}}=3.33$$

and in equation [4]

$$\Omega_\lambda=\frac{1.16145}{(3.33)^{0.14874}}+0.52487\exp\{-0.77320(3.33)\}+2.161778\exp\{-2.43787(3.33)\}=1.011$$

The molecular mass of 28.97 g/mol-g in this appendix II is the average of an ideal mixture of 78% N_2 and 21% O_2. However, to follow the rigorous line of the previous problem, it would be necessary to consider a mixture of 78.03% N_2, 20.99% O_2 and 0.98% Ar. By calculating the total molecular weight as a linear combination of the particular ones (28.02 g/mol-g N_2, 39.994 g/mol-g Ar and 32 g/mol-g O_2) it is obtained

$$\mathfrak{W}=\sum_i y_i\,\mathfrak{M}_i=0.7803\left(28.02\frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)+0.098\left(39.994\frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)+0.2099\left(32\frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)=32.5\frac{\mathrm{g}}{\mathrm{mol\text{-}g}}$$

$$m=32.5\frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\times\frac{1\ \mathrm{mol\text{-}g}}{6.022\cdot10^{23}\mathrm{particles}}\times\frac{1\ \mathrm{kg}}{1000\ \mathrm{g}}=5.322\cdot10^{-26}\frac{\mathrm{kg}}{\mathrm{particle}}$$

Appendix II also gives σ^{LJ}=3.617·10^{-10} m. Hence, equation [2] becomes

$$\lambda^{\mathrm{LJ}}=\frac{75\left(1.38\cdot10^{-23}\frac{\mathrm{J}}{\mathrm{K}}\right)\sqrt{\left(1.38\cdot10^{-23}\frac{\mathrm{J}}{\mathrm{K}}\right)323.2\ \mathrm{K}}}{64(3.617\cdot10^{-10}\ \mathrm{m})^2(1.011)\sqrt{3.1415(5.322\cdot10^{-26}\mathrm{kg})}}=1.997\cdot10^{-2}\frac{\mathrm{J}}{\mathrm{m\cdot s\cdot K}}$$

which converted in cal/(cm·s·K) is considerably lower than that calculated with the generalized chart.

$$1.997\cdot10^{-2}\frac{\mathrm{J}}{\mathrm{m\cdot s\cdot K}}\times\frac{0.24\ \mathrm{cal}}{1\ \mathrm{J}}\times\frac{1\ \mathrm{m}}{100\ \mathrm{cm}}=47.9\cdot10^{-6}\frac{\mathrm{cal}}{\mathrm{cm\cdot s\cdot K}}$$

Question c. From the previous question, $\mathfrak{W}_A$ = 32.5 g/mol-g, σ_A^{LJ}=3.617·10^{-10} m and $\varepsilon_A^{\mathrm{LJ}}/k$= 97.0 K for air.

For ethanol, $\mathfrak{M}_B = 46.069$ g/mol-g, but the other parameters have to be calculated with some of the equations [7] and [8]. For example, if the critical properties tabulated in appendix II are chosen ($\tilde{V}_c$= 167 cm^3/mol-g and T_c=513.92 K)

$$\sigma_B^{\mathrm{LJ}} = 0.841\tilde{V}_{cB}^{1/3} = 0.841(167)^{1/3} = 4.631\ \text{Å}$$

$$\frac{\varepsilon_B^{\mathrm{LJ}}}{k} = 0.77T_{cB} = 0.77(513.92) = 395.72\ \mathrm{K}$$

Mixing parameters according to equation [6] will be

$$\sigma_{AB}^{\mathrm{LJ}} = \frac{3.617\ \text{Å} + 4.63\ \text{Å}}{2} = 4.124\ \text{Å}$$

$$\frac{\varepsilon_{AB}^{\mathrm{LJ}}}{k} = \sqrt{(97.0\ \mathrm{K})(395.72\ \mathrm{K})} = 195.92\ \mathrm{K}$$

$$\mathfrak{M}_{AB} = \frac{2}{\frac{\text{mol-g}}{32.5\ \mathrm{g}} + \frac{\text{mol-g}}{46.069\ \mathrm{g}}} = 38.11\frac{\mathrm{g}}{\text{mol-g}}$$

$$m_{AB} = 38.11\frac{\mathrm{g}}{\text{mol-g}} \times \frac{1\ \text{mol-g}}{6.022\cdot 10^{23}\text{partícula}} \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}} = 6.328\cdot 10^{-26}\frac{\mathrm{kg}}{\text{partícula}}$$

and in equation [5]

$$\frac{kT}{\varepsilon_{AB}^{\mathrm{LJ}}} = \frac{298.2\ \mathrm{K}}{195.92\ \mathrm{K}} = 1.522$$

$$\Omega_D = 1.06036\left(\frac{1}{1.522}\right)^{0.15601} + 0.19300\exp\{-0.47635(1.522)\} +$$
$$+1.03587\exp\{-1.52996(1.522)\} + 1.76474\exp\{-3.89411(1.522)\} = 1.192$$

By assuming the ideal gas behaviour at 1 atm

$$\tilde{\rho} = \frac{P}{RT} = \frac{1\ \mathrm{atm}}{\left(0.082\frac{\mathrm{atm}\cdot\mathrm{L}}{\mathrm{K}\cdot\text{mol-g}}\right)298.2\ \mathrm{K}} = 0.041\ \frac{\text{mol-g}}{\mathrm{L}} = 41\frac{\text{mol-g}}{\mathrm{m}^3}$$

$$\tilde{\rho}N_{av} = 41\frac{\text{mol-g}}{\mathrm{m}^3} \times \frac{6.022\cdot 10^{23}\text{particles}}{1\ \text{mol-g}} = 2.47\cdot 10^{25}\frac{\text{particles}}{\mathrm{m}^3}$$

and introducing the data in equation [3]

$$D_{AB}^{\mathrm{LJ}}=\frac{3\sqrt{\dfrac{\left(1.38\cdot10^{-23}\,\dfrac{\mathrm{J}}{\mathrm{K}}\right)298.2\ \mathrm{K}}{3.1415(6.328\cdot10^{-26}\ \mathrm{kg})}}}{8\left(2.47\cdot10^{25}\,\dfrac{\mathrm{particles}}{\mathrm{m}^3}\right)(4.124\cdot10^{-10}\ \mathrm{m})^2(1.192)}=1.077\cdot10^{-5}\,\frac{\mathrm{m}^2}{\mathrm{s}}$$

SERIES 4

FLOW AND STORAGE OPERATIONS

4.1. Saturated steam at 5 bar passes through an isentropic conduction, reaching a pressure of 0.1 bar at the end. Estimate the final velocity assuming that its initial velocity was practically zero and that all the points of the conduction are placed at the same height.

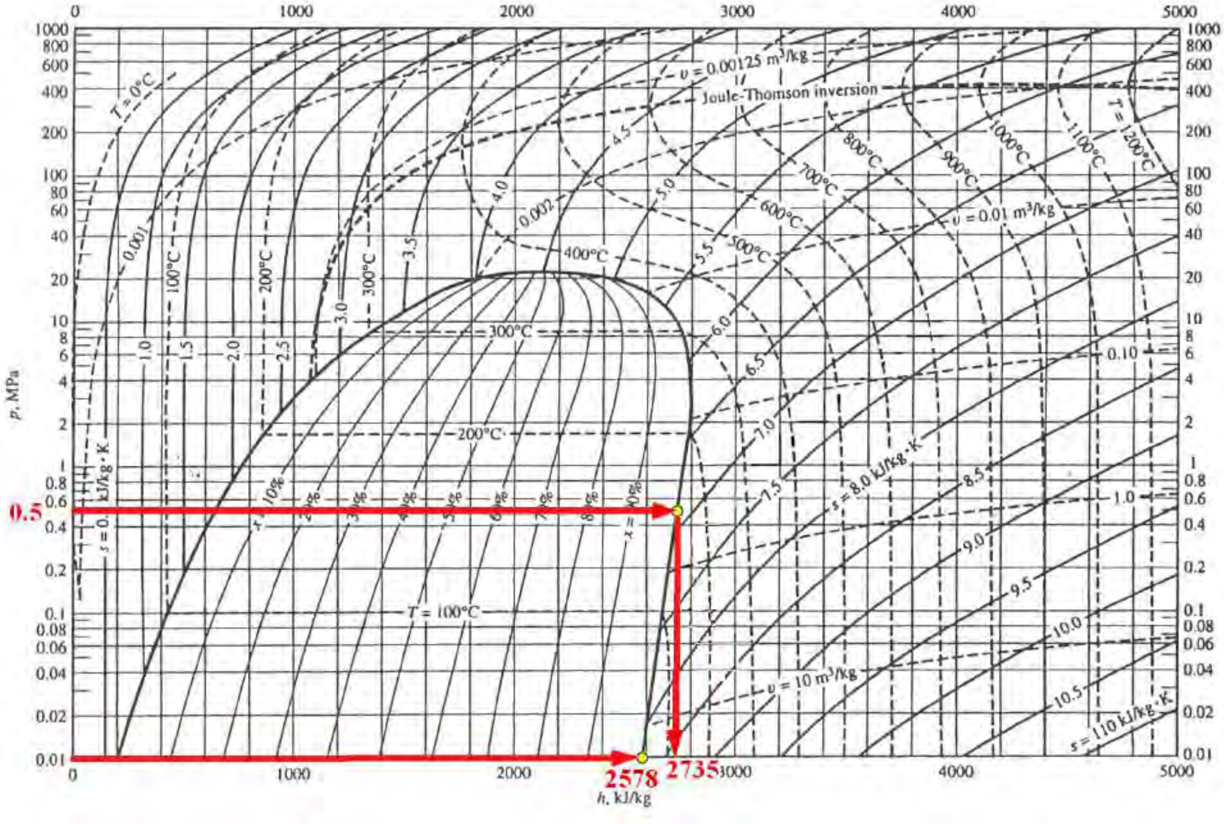
With stationary state ($dE/dt=0$; $\widehat{W}_{in} = \widehat{W}_{out}$), points at the same height (no change of potential energy), no production of work or heat and no radiation, the energy balance of reference problem 0.11 becomes

$$\left[\hat{H}_1 + \left(\hat{E}_{kin}\right)_1\right] - \left[\hat{H}_2 + \left(\hat{E}_{kin}\right)_2\right] = 0$$

$$\Delta\hat{H}_{12} + \Delta\left(\hat{E}_{kin}\right)_{12} = \Delta\hat{H}_{12} + \frac{1}{2}\left(v_1^2 - v_2^2\right) = 0$$

$$\frac{1}{2}\left[v_2^2 - v_1^2\right] = \left(\hat{H}_1 - \hat{H}_2\right)$$

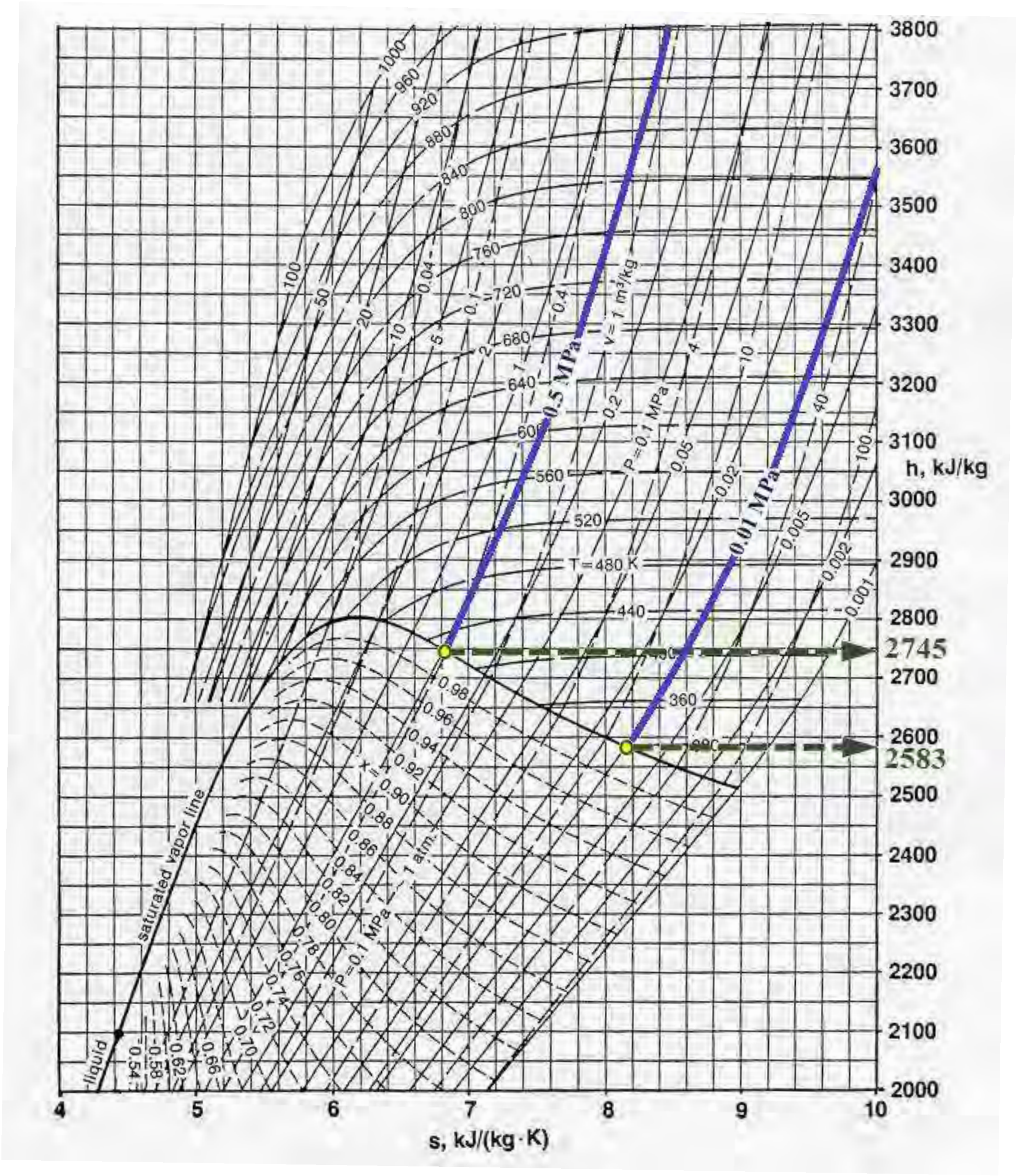
Saturated steam enthalpies at 5 and 0.1 bar (0.5 and 0.01 MPa) have to be estimated by means of a *PH* diagram, like that of figure V.5 of appendix V, in which it is read that $\hat{H} = 2735$ kJ/kg at 0.5 MPa and $\hat{H} = 2578$ kJ/kg at 0.01 MPa.



Then, applying the formula, and knowing that $v_1=0$

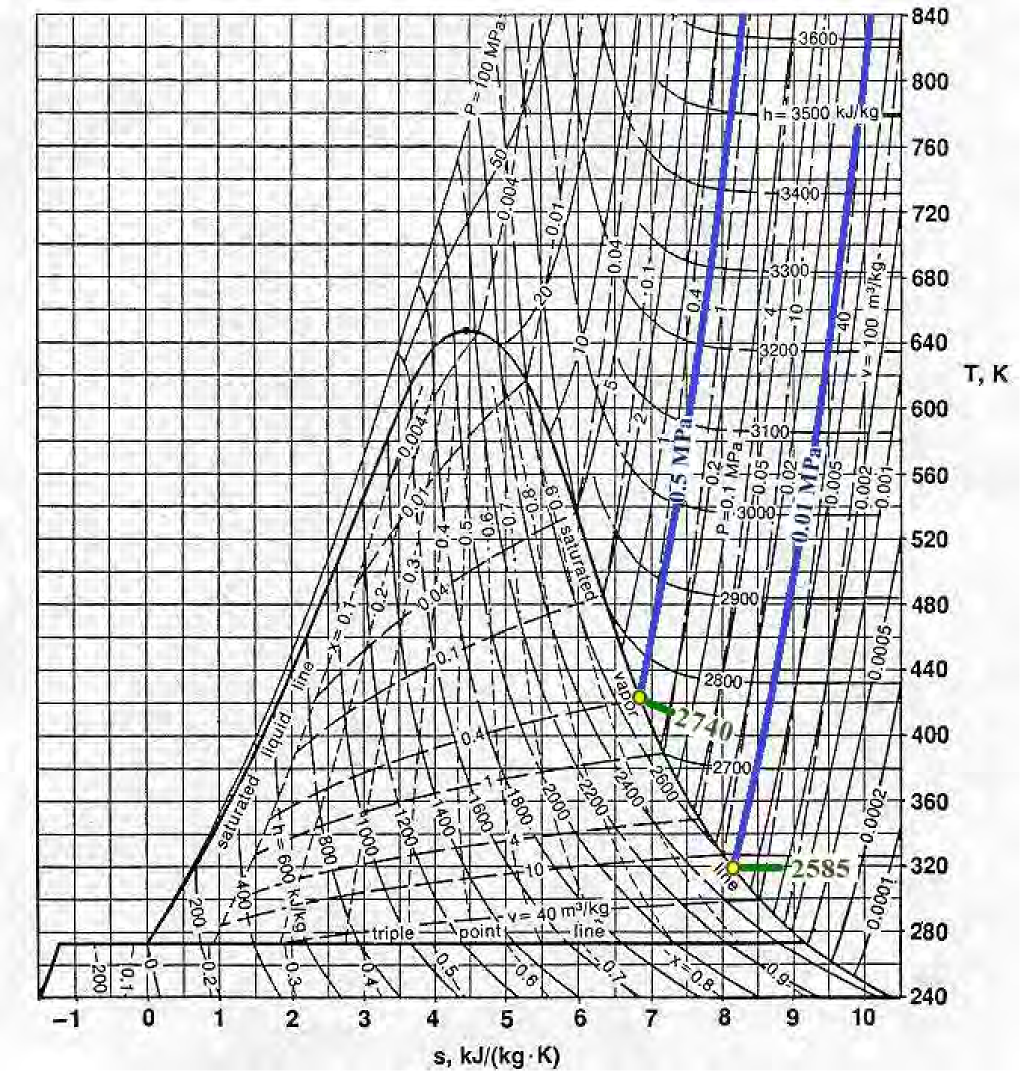
$$\frac{1}{2}\left[v_2^2 - 0^2\right] = \left(2735\frac{\text{kJ}}{\text{kg}} - 2578\frac{\text{kJ}}{\text{kg}}\right) \times \frac{1000\ \text{J}}{1\ \text{kJ}} \quad \rightarrow \quad v_2 = 560.36\ \text{m/s}$$

They can also be read from a figure like V.6 (*HS* or Mollier diagrams), where $\widehat{H} = 2745$ kJ/kg for 0.5 MPa and $\widehat{H} = 2583$ kJ/kg for 0.01 MPa



$$\frac{1}{2}[v_2^2 - 0^2] = \left(2745\frac{kJ}{kg} - 2583\frac{kJ}{kg}\right) \times \frac{1000\ J}{1\ kJ} \quad \rightarrow \quad v_2 = 569.21\ m/s$$

or from a *TS* diagram for water (figure V.7), where there is some difficulty in reading the magnitudes ($\widehat{H} \approx 2740$ kJ/kg at 0.5 MPa and $\widehat{H} \approx 2585$ kJ/kg at 0.01 MPa) because they are represented in isolines and not in the coordinate axes.



$$\frac{1}{2}[\mathrm{v}_2^2 - 0^2] = \left(2740\frac{\mathrm{kJ}}{\mathrm{kg}} - 2585\frac{\mathrm{kJ}}{\mathrm{kg}}\right) \times \frac{1000\ \mathrm{J}}{1\ \mathrm{kJ}} \quad \rightarrow \quad \mathrm{v}_2 = 556.78\ \mathrm{m/s}$$

Finally, they can be interpolated from tables such as VI.1 of appendix VI, from which it is obtained $\widehat{H}_v^{sat}$ = 2747 kJ/kg for 5 bar and $\widehat{H}_v^{sat}$ =2585 kJ/kg for 0.1 bar.

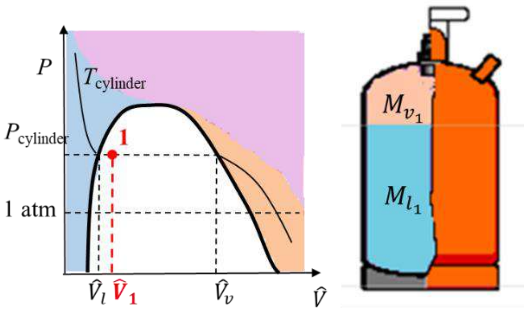
$$\frac{1}{2}[\mathrm{v}_2^2 - 0^2] = \left(2747\frac{\mathrm{kJ}}{\mathrm{kg}} - 2585\frac{\mathrm{kJ}}{\mathrm{kg}}\right) \times \frac{1000\ \mathrm{J}}{1\ \mathrm{kJ}} \quad \rightarrow \quad \mathrm{v}_2 = 569.21\ \mathrm{m/s}$$

4.2. Graphically represent in a *PV(T)* diagram the state evolution of a mass of low molecular weight hydrocarbon in a cylinder-type container as a function of its consumption, until its exhaustion.

If the cylinder is initially charged with a hydrocarbon mass M_1 at a pressure $P_{\text{cylinder}} > P_{\text{atm}}$, a vapor and a liquid phase co-existing under equilibrium will be generated, in which the apparent specific volume of the load is

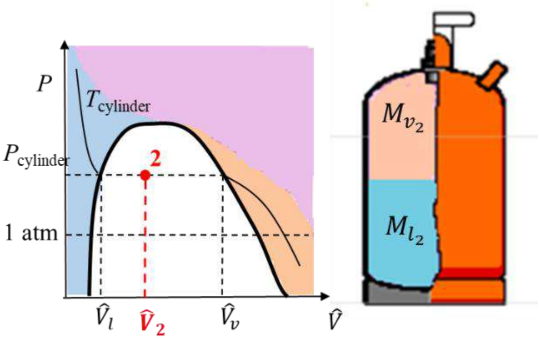
$$\hat{V}_1 = \frac{V_{tot}}{M_1} = \frac{V_{l_1} + V_{v_1}}{M_{l_1} + M_{v_1}} = \frac{M_{l_1}\hat{V}_l + M_{v_1}\hat{V}_v}{M_{l_1} + M_{v_1}}$$

being V_{tot} the total volume of the cylinder.

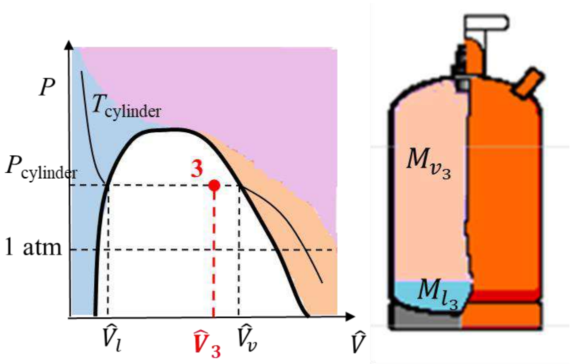


As the cylinder empties, the mass of liquid hydrocarbon decreases, so the value of $\hat{V}$ shifts towards the point of saturated vapor. This emptying will be isothermal if the discharge flow rate of the content is small enough to allow the energy input from the environment to compensate the latent heat requirements due to internal vaporization. Then

$$\hat{V}_2 = \frac{V_{tot}}{M_2} = \frac{V_{l_2} + V_{v_2}}{M_{l_2} + M_{v_2}} = \frac{M_{l_2}\hat{V}_l + M_{v_2}\hat{V}_v}{M_{l_2} + M_{v_2}}$$



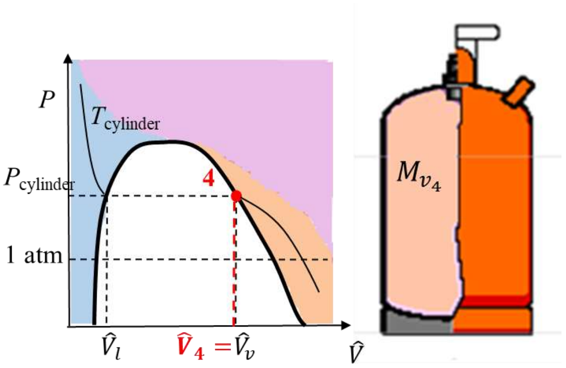
$$\hat{V}_3 = \frac{V_{tot}}{M_3} = \frac{V_{l_3} + V_{v_3}}{M_{l_3} + M_{v_3}} = \frac{M_{l_3}\hat{V}_l + M_{v_3}\hat{V}_v}{M_{l_3} + M_{v_3}}$$



and when all the liquid hydrocarbon has been consumed

$$\hat{V}_4 = \hat{V}_v = \frac{V_{tot}}{M_{v_4}}$$

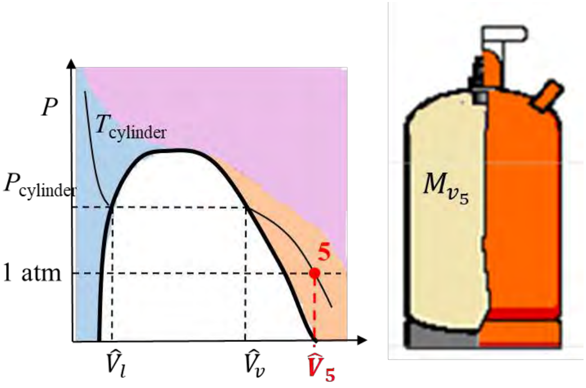
At that moment, hydrocarbon vapor begins to be used. Since there are no longer two phases, the phase rule indicates that, under isothermal conditions, the pressure will decrease.



At point 5, when reaching a pressure equal to that of the outside (the atmospheric one), the pressure flow will stop when the following molar volume is reached

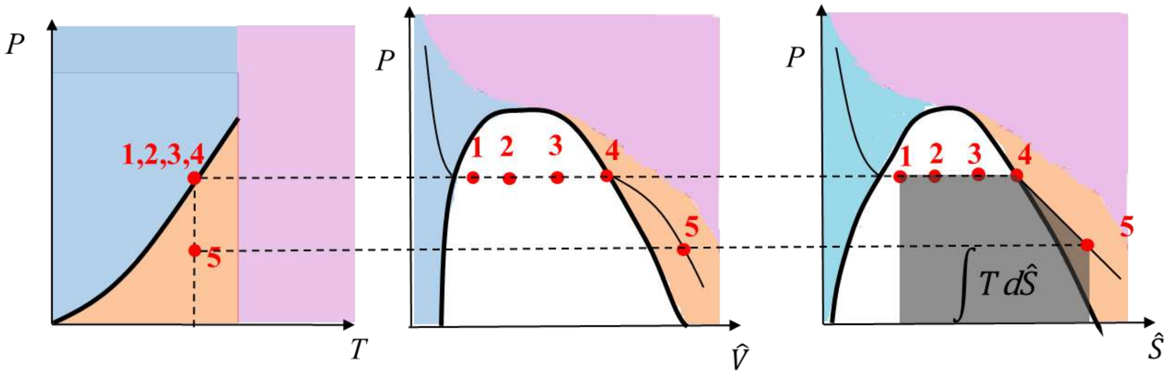
$$\hat{V}_5 = \hat{V}_{1\,\text{atm}} = \frac{V_{tot}}{M_{v_5}}$$

which allows estimating the amount of hydrocarbon that remains in the “empty” cylinder.

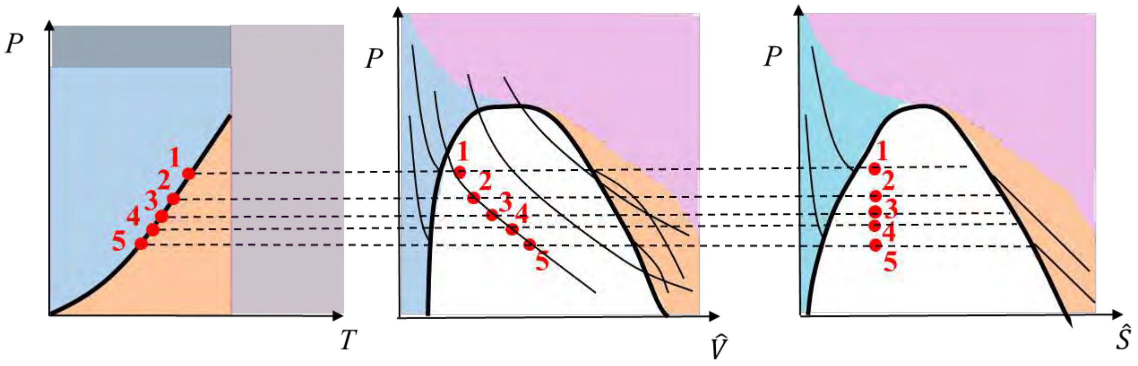


From that moment on, if the valve remains open, the system and the environment will stabilize by bidirectional isobaric molecular diffusion (hydrocarbon towards the outside and air towards the inside).

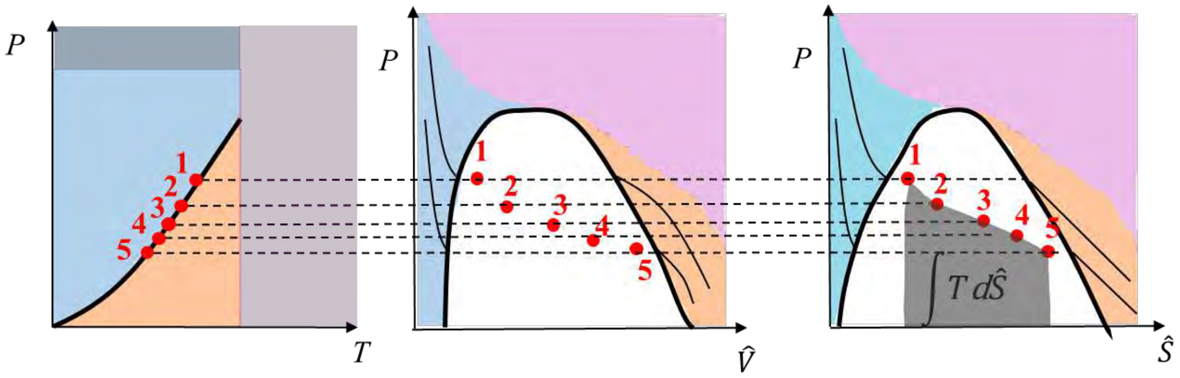
In other diagrams whose abscissa is the pressure (for example, the *PT* and *PS* ones), the transposition of these data would give



If the cylinder was adiabatically isolated, the heat required to vaporize the liquid will be obtained from the sensible heat supplied by the progressive cooling of the system itself. In this case, the evolution would be practically isentropic (except for the energy loss due to friction in the cylinder valve) and there would still be two phases when the atmospheric pressure was reached.



In most cases, the operating line will run between the isotherm and the isentropic ones, giving rise to a polytropic or isenthalpic process (the fuel is cooled, but it also receives heat from the outside). There could still be two phases to P_{atm}, but the amount of liquid that is not used would be less than in the isentropic case.



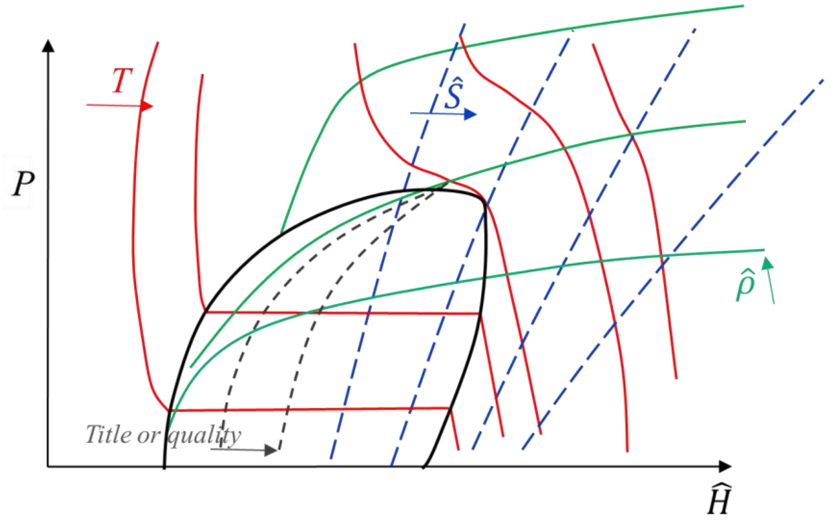
4.3. Propane is a fuel frequently used in the domestic sphere, and its storage and transport under conditions that pose certain risks are also frequent. To study these eventualities, test devices are usually employed. Their main element is a cell in which volumes, pressures and temperatures can be controlled. A typical essay may be as follows:

1) **0.010 kg of hydrocarbon is confined in a volume of 1 L at -43ºC. From these conditions several independent experiments are carried out.**
2) **Isobaric heating to 60ºC.**
3) **Isochoric heating to the same temperature.**
4) **Adiabatic and reversible compression to the same temperature.**
5) **Isothermal compression to a pressure double of the initial one.**

Therefore:

- a) **Make a qualitative $PH(T,\rho,S)$ diagram of propane, identify the isolines corresponding to the concerned properties and indicate the pattern of each one.**
- b) **Represent the initial state of the hydrocarbon with the help of a specific PH diagram of propane, and determine its conditions.**
- c) **Represent quantitatively the chamber evolution on a specific PH diagram for propane, and indicate the state and conditions of the 0.01 kg of hydrocarbon at the end of each experiment. Calculate the heat exchanged and/or the expansion-compression work in all of them.**
- d) **Subsequently, under the same initial conditions (volume, temperature and pressure), more hydrocarbon is injected into the tank (reaching a density ten times higher than the initial one) and the same experiments are repeated. Indicate the final pressure.**
- e) **Qualitatively represent the evolution of the chamber in tests 2) 3) and 4) on PT, $PV(T)$, $TS(P)$ and $z(P_r, T_r)$ diagrams.**

Question a.

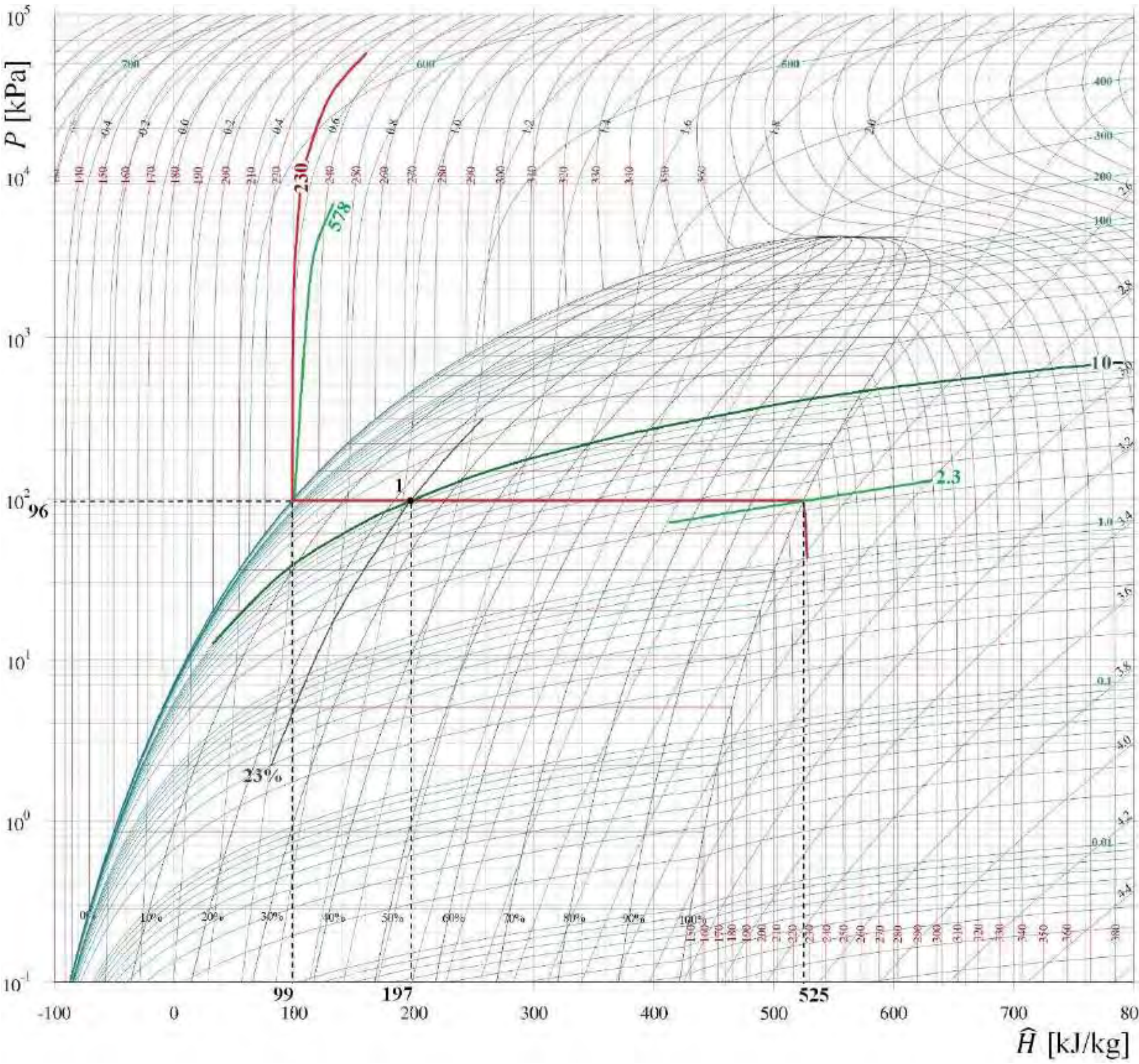


In the diagram above, the red lines represent the temperature (isotherms), with increasing values towards the right of the figure. The blue lines represent entropy (isentropics), also with increasing values to the right. The green lines are the isochores (loci of constant density), with increasing values upward and to the left. Finally, within the biphasic region, the dark gray lines of “title” or “quality” appear, indicating the percentage of vapor present: this percentage increases as one advances towards the right of the figure (the interested reader can verify and justify all the patterns indicated here).

Question b. A real diagram has to be employed: for example, figure V.8 of this book’s appendix V. To locate point 1, the initial temperature must be converted to degrees Kelvin, and the density calculated in kg/m^3

$$T_1(\mathrm{K}) = -43℃ + 273 = 230\ \mathrm{K}$$

$$\hat{\rho}_1 = \frac{M_1}{V_1} = \frac{0.01\ \mathrm{kg}}{1\ \mathrm{L}} \times \frac{1000\ \mathrm{L}}{1\ \mathrm{m}^3} = 10\ \frac{\mathrm{kg}}{\mathrm{m}^3}$$



It is observed that point 1 is located in the biphasic zone, with an approximate vapor quality or title of 23% (0.23×10 g = 2.3 g) at a pressure of 96 kPa and a total enthalpy of 197 kJ/kg. The amounts of vapor and liquid have to be determined by means of mass and volume balances, in the form

$$M_{tot} = M_{l_1} + M_{v_1} \tag{1}$$

$$\frac{M_{tot}}{\hat{\rho}_{tot}} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} + \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} \tag{2}$$

being $\hat{\rho}_{tot} = \hat{\rho}_1$, $M_{tot} = M_1$ and $\hat{\rho}_{l_1}^{sat}$ and $\hat{\rho}_{v_1}^{sat}$ the saturated liquid and vapor densities (which by interpolation in figure V.8 are 578 kg/m^3 and 2.3 kg/m^3, respectively). By combining [1] and [2] and introducing the data, it is obtained

$$M_{v_1} = M_{tot}\frac{\left(\frac{1}{\hat{\rho}_{tot}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_1}^{sat}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)} = (10\text{ g})\frac{\left(\frac{1}{10} - \frac{1}{578}\right)}{\left(\frac{1}{2.3} - \frac{1}{578}\right)} = 2.27\text{ g}$$

$$M_{l_1} = M_{tot} - M_{v_1} = 10 - 2.27 = 7.73\text{ g}$$

masses occupying the following volumes

$$V_{v_1} = \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} = \frac{2.27\text{ g}}{2.3\ \frac{\text{g}}{\text{L}}} = 0.987\text{ L}$$

$$V_{l_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} = \frac{7.73\text{ g}}{578\ \frac{\text{g}}{\text{L}}} = 0.013\text{ L}$$

The amount of vapor can also be confirmed by the mass balance (equation [1]) and the enthalpy balance

$$M_{tot}\hat{H}_{tot} = M_{l_1}\hat{H}_{l_1}^{sat} + M_{v_1}\hat{H}_{v_1}^{sat} \tag{3}$$

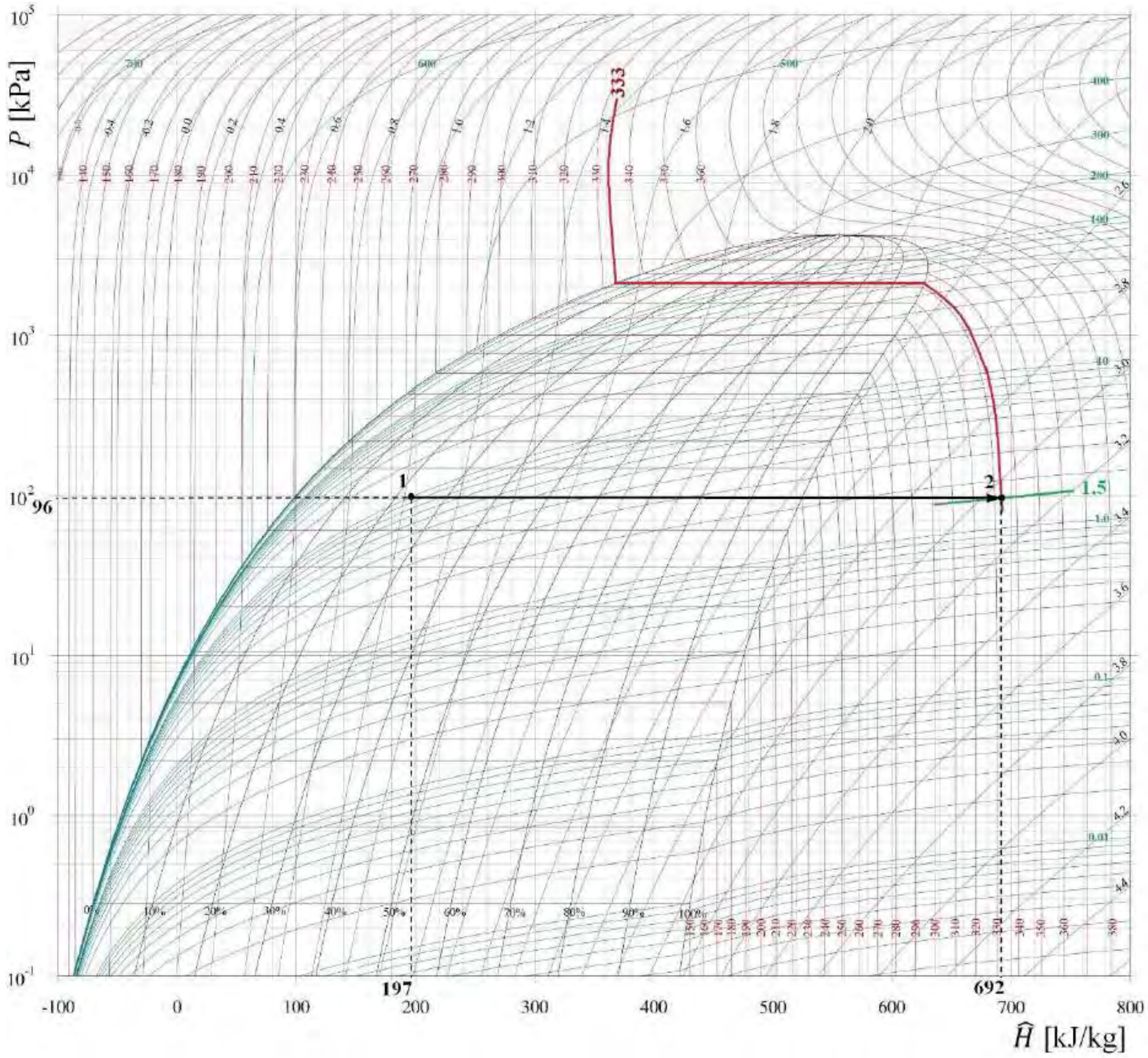
where $\hat{H}_{tot} = \hat{H}_1$. By combining [1] and [3] and reading from the diagram that the enthalpy of the saturated liquid is 99 kJ/kg and that of the saturated vapor is 525 kJ/kg

$$M_{v_1} = M_{tot}\frac{\left(\hat{H}_{tot} - \hat{H}_{l_1}^{sat}\right)}{\left(\hat{H}_{v_1}^{sat} - \hat{H}_{l_1}^{sat}\right)} = (10\text{ g})\frac{(197 - 99)}{(525 - 99)} = 2.3\text{ g}$$

a value which is not exactly the same as the one previously found from the densities because the errors inherent in the interpolation and reading of graphics, although the error is acceptable for this type of calculations because it is less than 2%.

Question c. To locate point 2 in diagram V.8, the 96 kPa isobar is extended to its intersection with the 60ºC isotherm

$$T_2(\mathrm{K}) = 60^{\circ}\mathrm{C} + 273 = 333\ \mathrm{K}$$



Propane is now all in the superheated vapor state, with an approximate density $\hat{\rho}_2$=1.5 kg/m^3 and a specific enthalpy $\hat{H}_2$=692 kJ/kg. The heat produced in the transition from state 1 to state 2 will be calculated using the general expression

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \Delta\hat{Q}_{21} = \int_1^2 T\mathrm{d}\hat{S}$$

but according to sections b and c of reference problem 0.3

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}} = \mathrm{d}\hat{Q} + \hat{V}\mathrm{d}P$$

and since the process is isobaric (P does not change), there will be no flow work and the heat produced will coincide with the enthalpy change ($\mathrm{d}\hat{H} = \mathrm{d}\hat{Q}$), which avoids the numerical integration.

$$\Delta\hat{Q}_{21}=\Delta\hat{H}_{21}=\hat{H}_2-\hat{H}_1=692\ \frac{\text{kJ}}{\text{kg}}-197\frac{\text{kJ}}{\text{kg}}=495\frac{\text{kJ}}{\text{kg}}$$

a value that, for the totality of the mass, will be

$$\Delta Q_{21}=M_{tot}\Delta\hat{Q}_{21}=(0.01\ \text{kg})\left(495\frac{\text{kJ}}{\text{kg}}\right)=4.95\ \text{kJ}$$

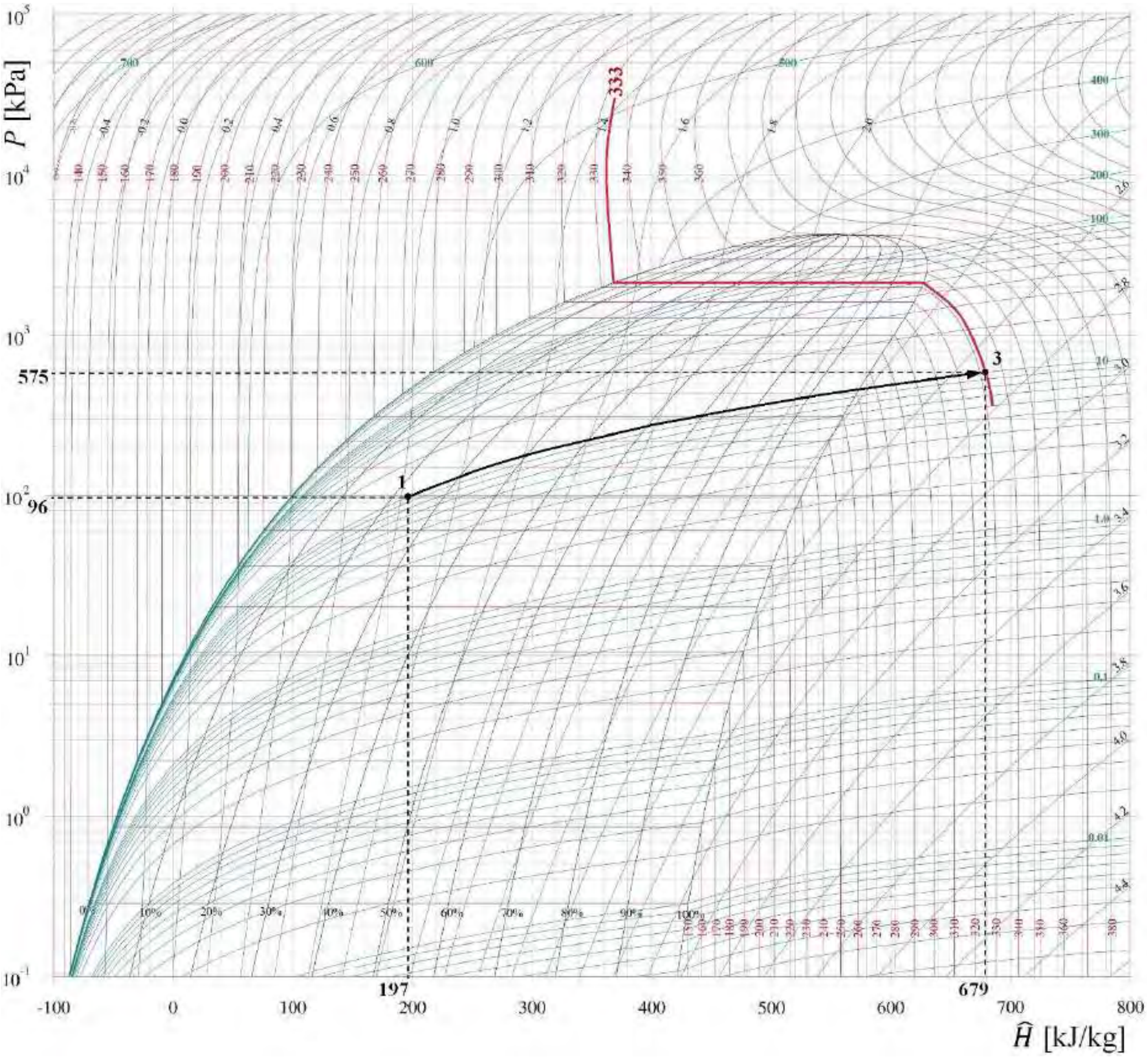
Regarding the expansion-compression work

$$\text{d}\hat{W}^{\text{e-c}}=-P\text{d}\hat{V}\quad\xrightarrow{P\ constant}\quad\Delta\hat{W}^{\text{e-c}}=-P\Delta\hat{V}$$

$$\Delta\hat{W}_{21}^{\text{e-c}}=-P_1\left(\frac{1}{\hat{\rho}_2}-\frac{1}{\hat{\rho}_1}\right)=-(96\ \text{kPa})\left(\frac{1}{1.5\ \text{kg/m}^3}-\frac{1}{10\ \text{kg/m}^3}\right)=-54.4\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta W_{21}^{\text{e-c}}=M_{tot}\Delta\hat{W}_{21}^{\text{e-c}}=(0.01\ \text{kg})\left(-54.4\ \frac{\text{kJ}}{\text{kg}}\right)=-0.544\ \text{kJ}$$

Graphically, point 3 will be identified by following the 10 kg/m^3 isochore until its intersection with T_3, which in this case is equal to T_2= 333 K.



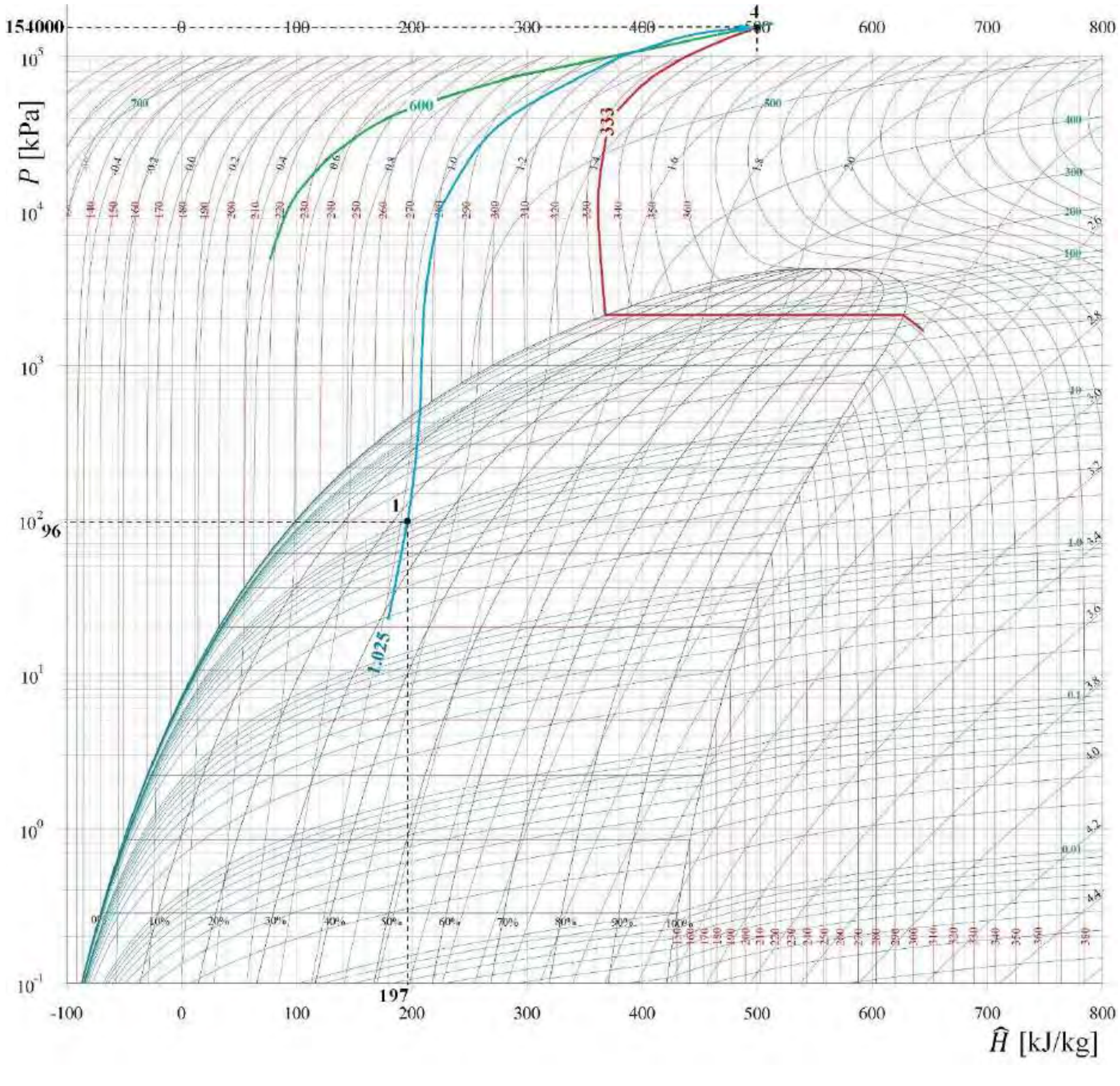
At that point, propane is at the state of superheated vapor at P_3= 575 kPa, with a specific enthalpy $\widehat{H}_3$=679 kJ/kg. Since $\hat{\rho}_1$=$\hat{\rho}_3$, there will be no expansion-compression work, and the heat can be calculated as

$$\Delta\widehat{Q}=\Delta\widehat{H}-\widehat{V}\Delta P$$

$$\Delta\widehat{Q}_{31}=\left(\widehat{H}_3-\widehat{H}_1\right)-\frac{(P_3-P_1)}{\hat{\rho}_1}=\left(679\,\frac{\text{kJ}}{\text{kg}}-197\,\frac{\text{kJ}}{\text{kg}}\right)-\frac{(575\text{ kPa}-96\text{ kPa})}{10\text{ kg/m}^3}=434.1\,\frac{\text{kJ}}{\text{kg}}$$

$$\Delta Q_{31}=M_{tot}\Delta\widehat{Q}_{31}=(0.01\text{ kg})\left(434.1\,\frac{\text{kJ}}{\text{kg}}\right)=4.341\text{ kJ}$$

The fourth experiment is adiabatic (ΔQ=0) and reversible (ΔQ=$\Delta S/T$); thus, it is isentropic (ΔS=0). Point 4 will be located at the intersection between the isentropic line that passes through 1 ($\hat{S}_1$ =1.025 kJ/kg·K) and the isotherm T_4, which is also equal to T_2= 333 K. The hydrocarbon is now a subcooled liquid at P_4=154000 kPa with an approximate density $\hat{\rho}_4$ =600 kg/m^3 and a specific enthalpy $\widehat{H}_4$= 500 kJ/kg.



The expansion-compression work should be calculated by

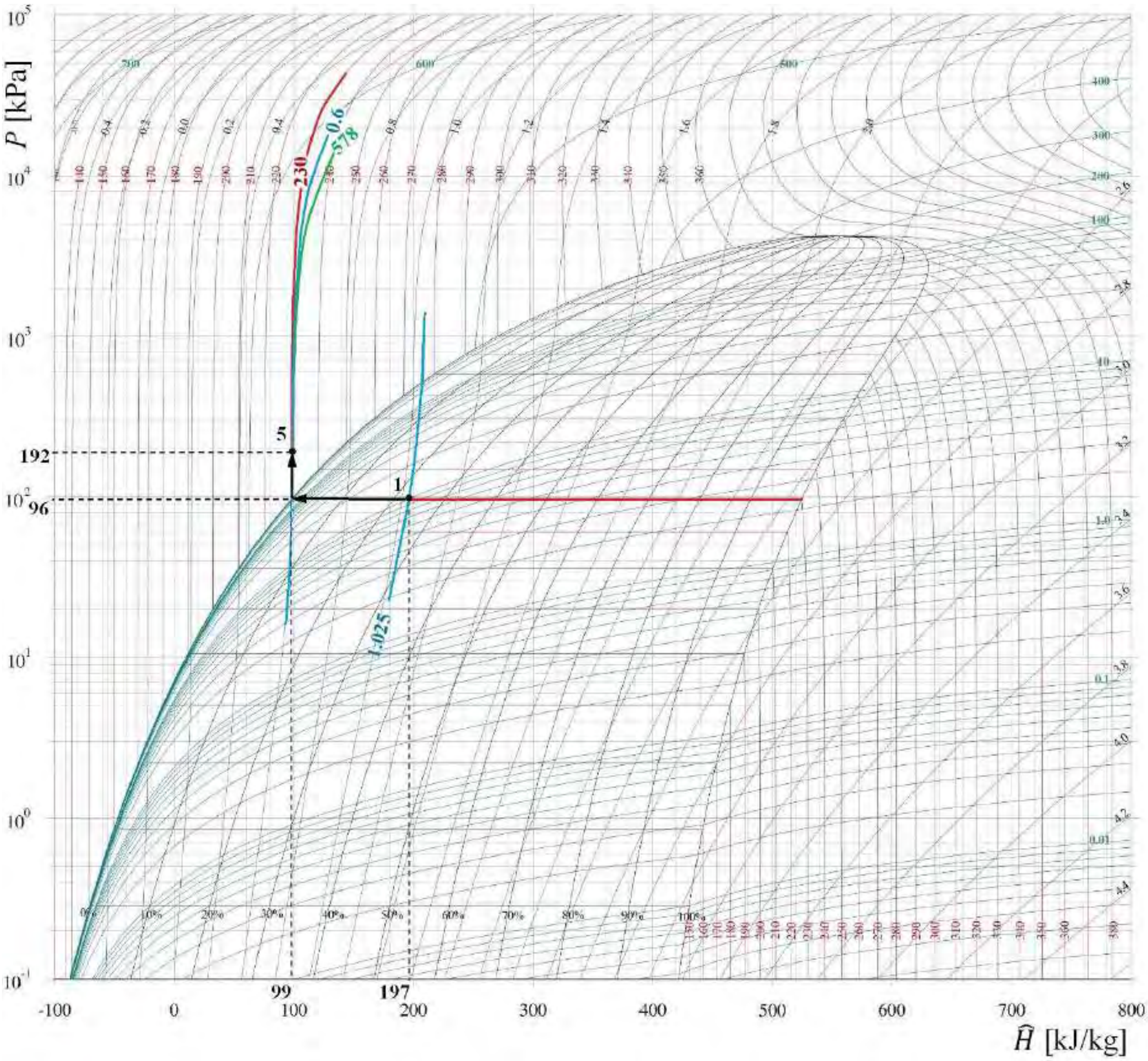
$$\mathrm{d}\widehat{W}^{\text{e-c}} = -P\mathrm{d}\widehat{V} \quad \rightarrow \quad \Delta\widehat{W}_{41}^{\text{e-c}} = -\int_{1}^{4} P\mathrm{d}\widehat{V}$$

but since the heat produced is zero ($\mathrm{d}\widehat{Q} = T\mathrm{d}\hat{S}$), the expansion-compression work will coincide with the internal energy change and numerical integration will be unnecessary

$$\mathrm{d}\widehat{U} = \mathrm{d}\widehat{Q} - P\mathrm{d}\widehat{V} \quad \xrightarrow{\mathrm{d}\widehat{Q}=0} \quad \Delta\widehat{W}^{\text{e-c}} = \Delta\widehat{U} = \Delta\left(\widehat{H} - P\widehat{V}\right)$$

$$\Delta\widehat{W}_{41}^{\text{e-c}} = \Delta\left(\widehat{H} - P\widehat{V}\right)_{41} = \left(\widehat{H}_4 - \frac{P_4}{\hat{\rho}_4}\right) - \left(\widehat{H}_1 - \frac{P_1}{\hat{\rho}_1}\right) =$$
$$= \left(500\ \frac{\text{kJ}}{\text{kg}} - \frac{154000\ \text{kPa}}{600\ \text{kg/m}^3}\right) - \left(197\ \frac{\text{kJ}}{\text{kg}} - \frac{96\ \text{kPa}}{10\ \text{kg/m}^3}\right) = 55.93\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta W_{41}^{\text{e-c}} = M_{tot}\Delta\widehat{W}_{41}^{\text{e-c}} = (0.01\ \text{kg})\left(55.93\ \frac{\text{kJ}}{\text{kg}}\right) = 0.5593\ \text{Kj}$$



Finally, point 5 will be found graphically by intersection between the 230 K isotherm and the 192 kPa isobar (double of 96 kPa). At that point, propane is a subcooled liquid, with a density $\hat{\rho}_5$ =578 kg/m^3, specific enthalpy $\widehat{H}_5$= 99 kJ/kg and specific entropy $\hat{S}_5$=0.6 kJ/kg·K. The heat resulting from the transit from 1 to 5 is

$$\Delta\hat{Q}_{51} = \int_1^5 T\mathrm{d}\hat{S}$$

but since the temperature remains constant, the integral is significantly simplified

$$\Delta\hat{Q}_{51}=T_5\Delta\hat{S}_{51} = (230\ \mathrm{K})\left(0.6\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 1.025\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = -97.75\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta Q_{51} = M_{tot}\Delta\hat{Q}_{51} = (0.01\ \mathrm{kg})\left(-97.75\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -0.9775\ \mathrm{kJ}$$

And with regards to the expansion-compression work, it can also be calculated without integration, because

$$\mathrm{d}\widehat{U} = \mathrm{d}\hat{Q} - P\mathrm{d}\widehat{V} \quad \rightarrow \ \mathrm{d}\widehat{W}^{\text{e-c}} = \mathrm{d}\widehat{U} - \mathrm{d}\hat{Q} = \mathrm{d}\widehat{H} - \mathrm{d}\big(P\widehat{V}\big) - \mathrm{d}\hat{Q}$$

$$\begin{aligned}\Delta\widehat{W}^{\text{e-c}}_{51}&=\Delta\big(\widehat{H} - P\widehat{V}\big)_{51} - \Delta\hat{Q}_{51} = \left(\widehat{H}_5 - \frac{P_5}{\hat{\rho}_5}\right) - \left(\widehat{H}_1 - \frac{P_1}{\hat{\rho}_1}\right) - \Delta\hat{Q}_{51} = \\ &= \left(99\ \frac{\mathrm{kJ}}{\mathrm{kg}} - \frac{192\ \mathrm{kPa}}{578\ \mathrm{kg/m^3}}\right) - \left(197\ \frac{\mathrm{kJ}}{\mathrm{kg}} - \frac{96\ \mathrm{kPa}}{10\ \mathrm{kg/m^3}}\right) + 97.75\ \frac{\mathrm{kJ}}{\mathrm{kg}} = 9.018\ \frac{\mathrm{kJ}}{\mathrm{kg}}\end{aligned}$$

$$\Delta W^{\text{e-c}}_{51} = M_{tot}\Delta\widehat{W}^{\text{e-c}}_{51} = (0.01\ \mathrm{kg})\left(9.018\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 0.0902\ \mathrm{kJ}$$

Question d. The density increases 10 times (100 kg/m^3) under isobaric, isochoric and isothermal conditions because the amount of hydrocarbon has increased ten times (0.1 kg).

Point 1' will be found at the intersection between the 230 K isotherm and the 100 kg/m^3 isochore, and it reveals a mixture of liquid and saturated vapor mostly consisting of liquid (the title or quality line is very close to zero).

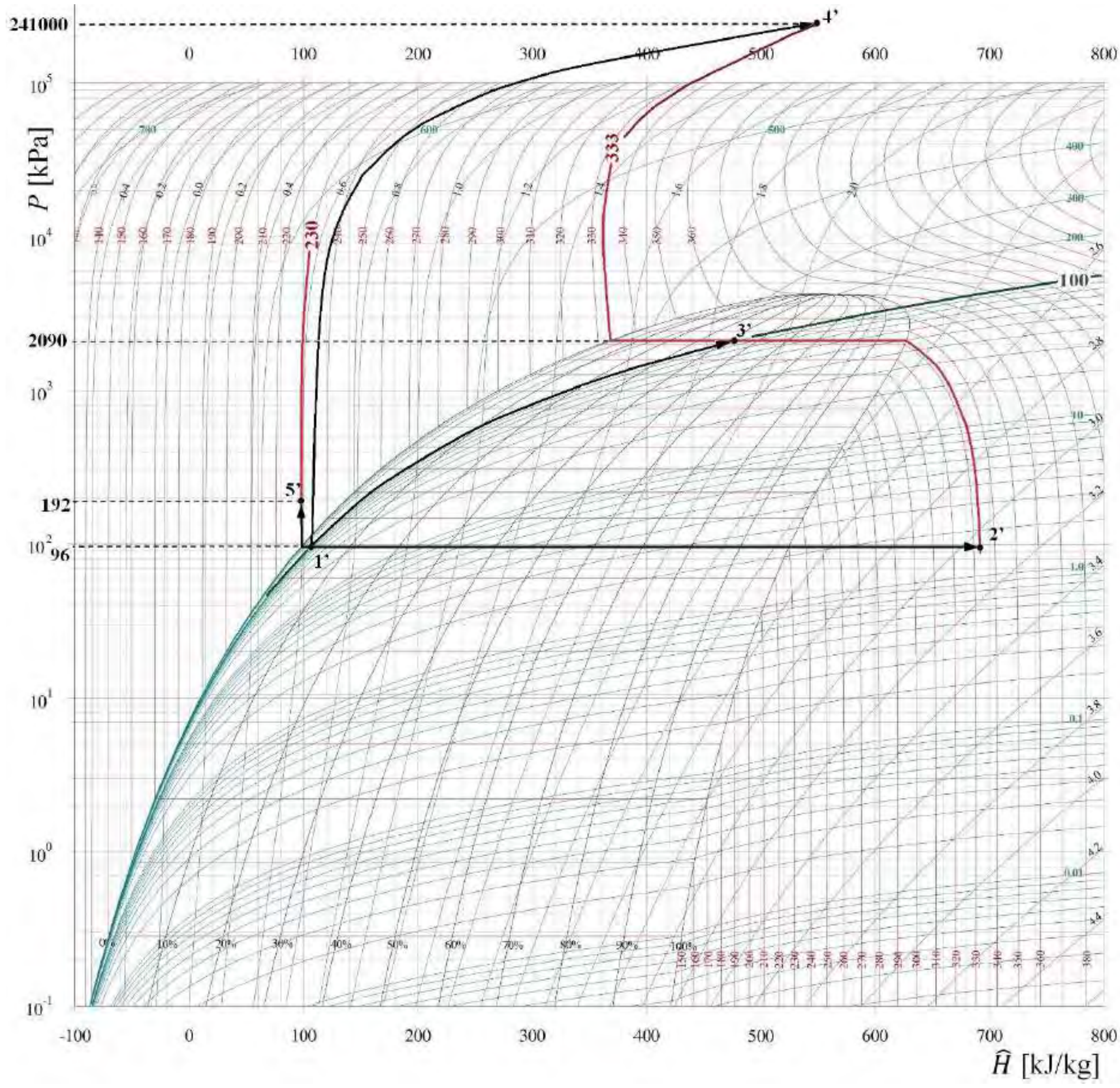
Operating as explained in the previous question, the corresponding pressures are

$$P_{1'}=P_{2'}=96\ \mathrm{kPa}$$

$$P_{3'}=2090\ \mathrm{kPa}$$

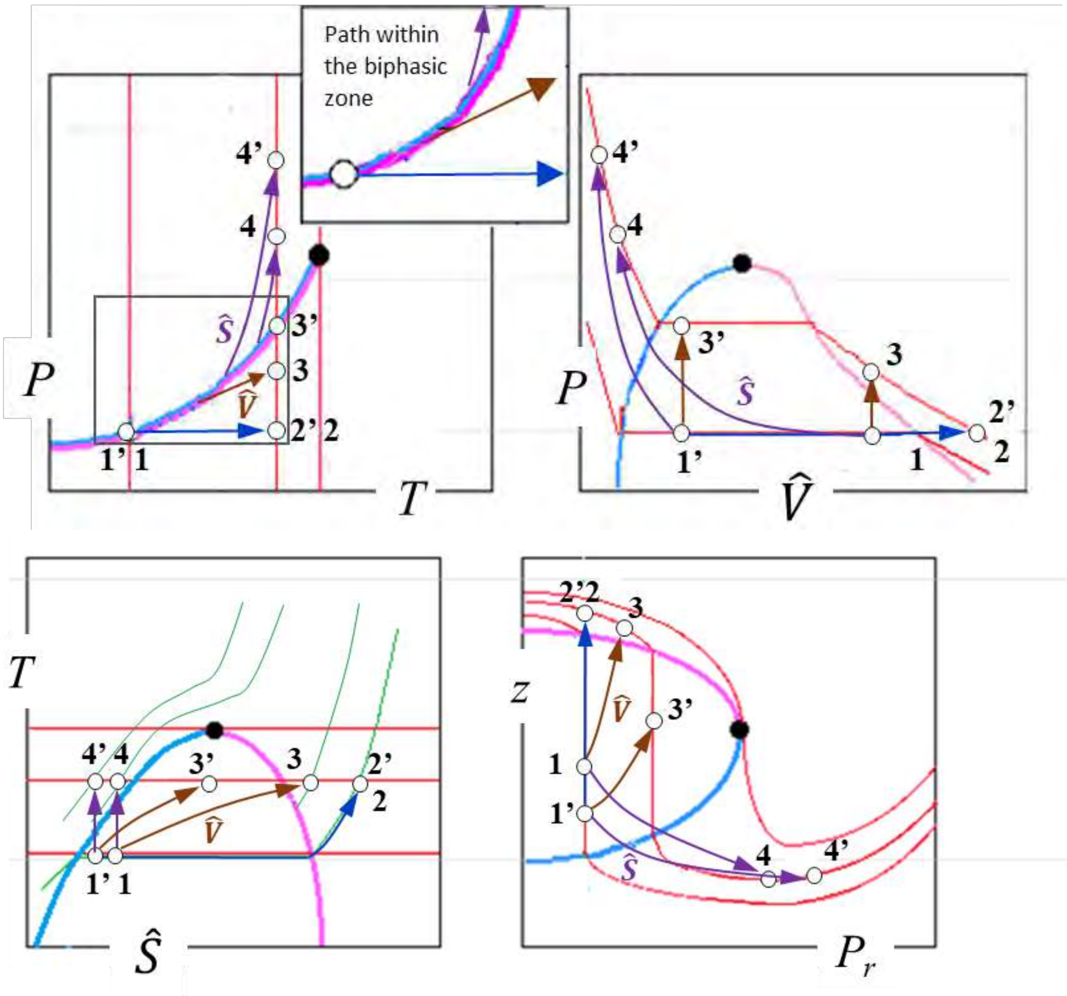
$$P_{4'}=241000\ \mathrm{kPa}$$

$P_{5'}$=192 kPa



Question e. Qualitative representations are shown in the next page.

As a curiosity, note that in the *PT* diagrams the passage from point 1 to 4 and from 1' to 4' initially follows a path within the biphasic región before reaching the corresponding isentropic line. This type of diagrams does not discern the state of phases in equilibrium. The transit from 1 to 3 also shows the same route before following the isochore.


Path within
the biphasic
zone
P
T
4'
4
3'
3
2'
2
1'
1
$\hat{S}$
$\hat{V}$
P
$\hat{V}$
T
$\hat{S}$
z
P_r
2'2

4.4. Certain tests about propane behavior are carried out in a controlled cylindrical tank of variable volume and thermostatted walls. During one of the tests, the hydrocarbon is subjected to the following physical transformations:

1) **An initial volume of 10 L is confined at 100 kPa and 20°C.**
2) **The volume is isobarically heated to 200°C.**
3) **Subsequently, it is isothermally compressed to the same pressure that would have been reached by a reversible adiabatic compression from the initial conditions.**
4) **Finally, it is cooled isochorely to the initial temperature.**

By knowing this:

a) **Qualitatively indicate the evolution of the chamber, graphically represent the successive conditions of the experiment on a *PH*(*T*,*ρ*,*S*) diagram and qualitatively depict them on *PT*, *PV*, *z*(P_r,T_r) and *TS* diagrams.**
b) **Prepare a table where densities, volumes, pressures, enthalpies and entropies in each stage were indicated.**
c) **Calculate the heat exchanged, the flow work and the expansion-compression work in the different stages, and those involved in the return to the initial conditions.**
d) **Calculate the heat exchanged, the flow work and the expansion-compression work if the aforementioned reversible adiabatic compression had been performed.**
e) **If the phases split at some point of the process, calculate the proportion of each one and the volumes occupied by them.**

Question a. Figure V.8 of this book's appendix V is necessary. Point 1 will be the intersection between the 100 kPa isobar and the isotherm

$$T_1(\text{K}) = 20°\text{C} + 273 = 293\ \text{K}$$

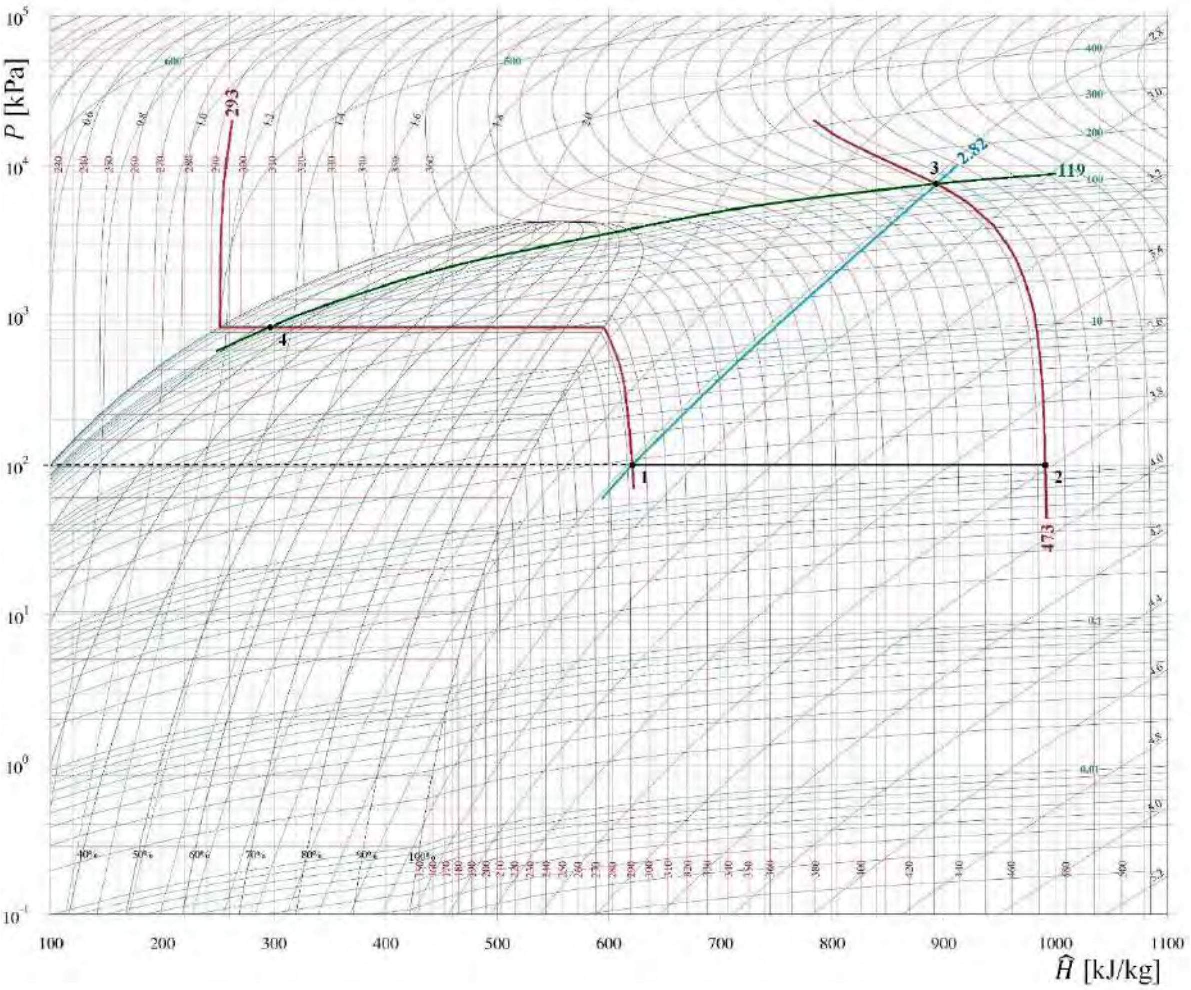
which corresponds to the superheated steam zone. Point 2 will be graphically located where the same isobar intersects the isotherm

$$T_2(\text{K}) = 200°\text{C} + 273 = 473\ \text{K}$$

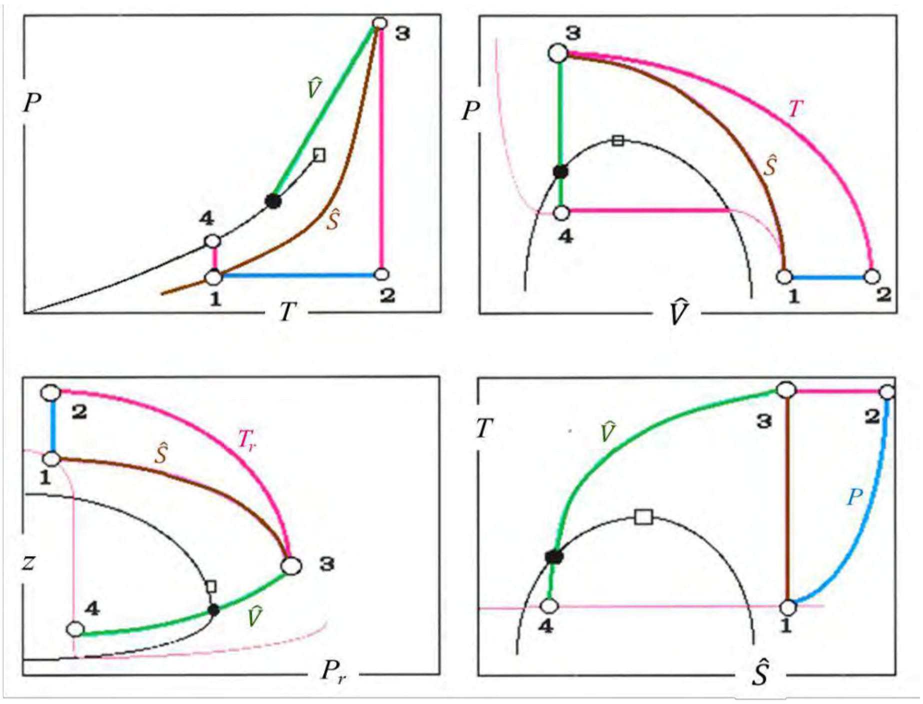
which is above the critical temperature of propane, being a gas or a supercritical fluid.

Point 3 is at the intersection of the T_2 isotherm with the isentropic line that passes through 1 (2.82 kJ/kg·K), and like point 2, it is a gas.

Point 4 is the crossing point of the T_1 isotherm with the isochore that passes through point 3 (119 kg/m^3), and designates a biphasic mixture of saturated liquid and vapor below the critical temperature.



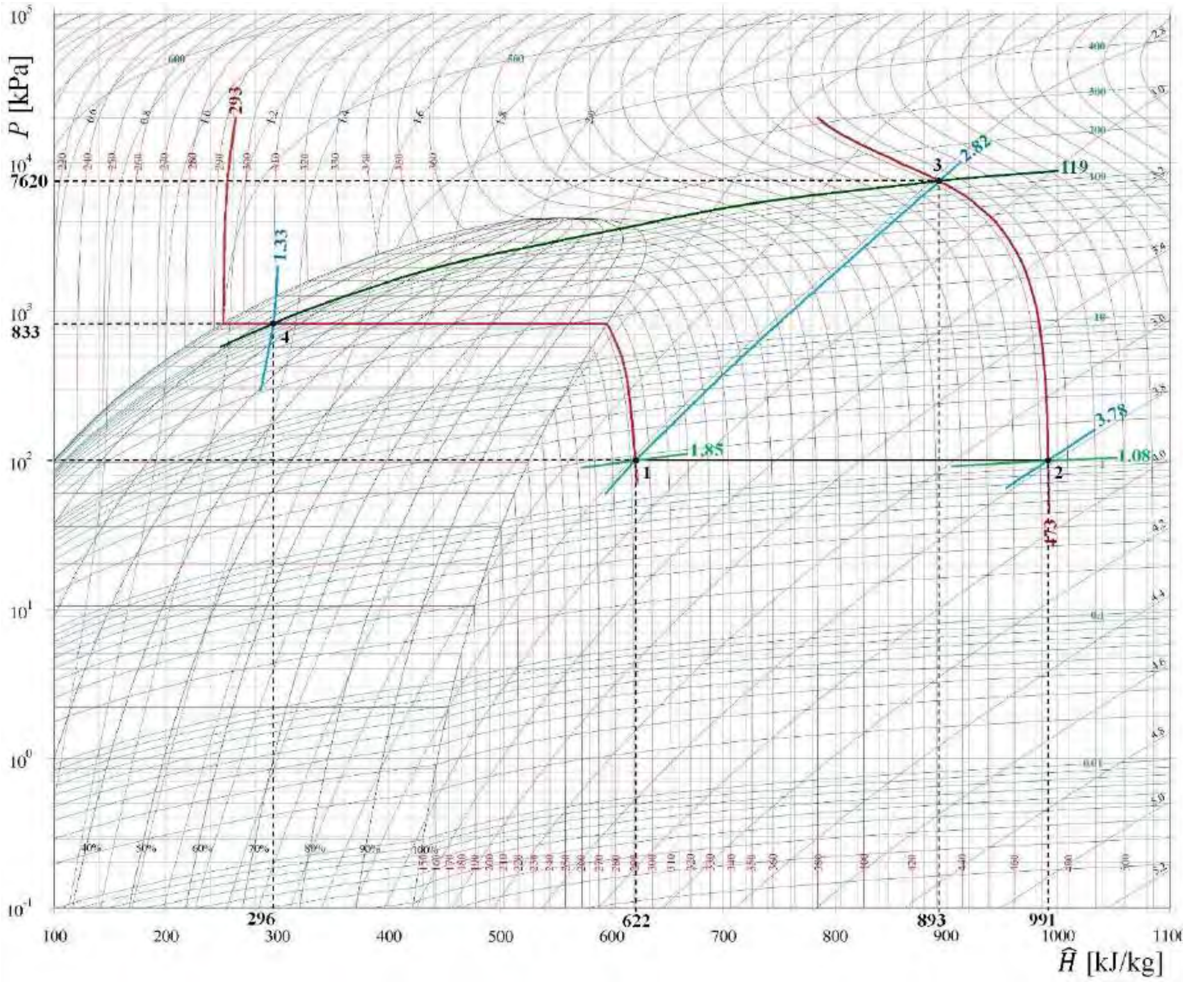
On the other hand, the qualitative representation of the process on *PT*, *PV*, $z(T_r, P_r)$ and *TS* diagrams will be



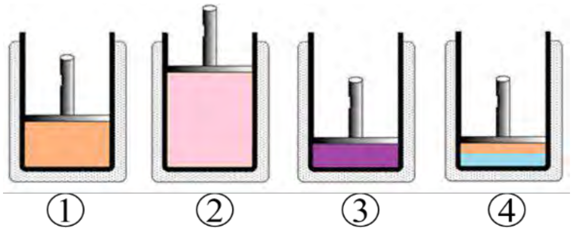
Question b. When the points 1- 4 are placed in the figure, the requested data can be simply read or interpolated. The only calculation that must be carried out is that of the volume, which requires determining the mass of the tank. By knowing that in point 1 (density of 1.85 kg/m^3= 1.85 g/L) the initial volume was of 10 L

$$M_1 = M_{tot} = \hat{\rho}_1 V_1 = \left(1.85\ \frac{\mathrm{g}}{\mathrm{L}}\right)(10\ \mathrm{L}) = 18.5\ \mathrm{g}$$

and since this mass remains constant, the volume at each point will logically be the quotient between M_{tot} and the density.



Point	T (K)	P (kPa)	$\hat{\rho}$ (g/L)	V(L)	$\hat{H}$ (kJ/kg)	$\hat{S}$ (kJ/kg·K)
1	293	100	1.85	10	622	2.82
2	473	100	1.08	17.13	991	3.78
3	473	7620	119	0.155	893	2.82
4	293	833	119	0.155	296	1.33



Question c. Heat and works involved in each stage are given by the expressions

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \Delta\hat{Q} = \int T\mathrm{d}\hat{S}$$

$$\mathrm{d}\widehat{W}^{\mathrm{fl}} = \hat{V}\mathrm{d}P \quad \rightarrow \quad \Delta\widehat{W}^{\mathrm{fl}} = \int \hat{V}\mathrm{d}P$$

$$\mathrm{d}\widehat{W}^{\mathrm{e\text{-}c}} = -P\mathrm{d}\hat{V} \quad \rightarrow \quad \Delta\widehat{W}^{\mathrm{e\text{-}c}} = -\int P\mathrm{d}\hat{V}$$

which, in principle, should be numerically solved, unless some simplification is possible because process conditions.

<u>Transit from 1 to 2</u>: As it is an isobaric step (dP=0), there will be no flow work, and according to sections b and c of reference problem 0.3 the exchanged heat will be equal to the difference of enthalpies

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\widehat{W}^{\mathrm{fl}} = \mathrm{d}\hat{Q} + \hat{V}\mathrm{d}P \quad \xrightarrow{P\ constant} \mathrm{d}\hat{H} = \mathrm{d}\hat{Q} \quad \rightarrow \ \Delta\hat{H} = \Delta\hat{Q}$$

$$\Delta\hat{Q}_{21} = \Delta\hat{H}_{21} = \hat{H}_2 - \hat{H}_1 = 991\,\frac{\mathrm{kJ}}{\mathrm{kg}} - 622\,\frac{\mathrm{kJ}}{\mathrm{kg}} = 369\,\frac{\mathrm{kJ}}{\mathrm{kg}}$$

specific value which, extended to the entire mass involved

$$\Delta Q_{21} = M_{tot}\Delta\hat{Q}_{21} = (0.0185\ \mathrm{kg})\left(369\,\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 6.83\ \mathrm{kJ}$$

Moreover, if P is constant

$$\Delta\widehat{W}_{21}^{\mathrm{e\text{-}c}} = -\int_1^2 P\mathrm{d}\hat{V} = -P_1\left(\hat{V}_2 - \hat{V}_1\right)$$

$$\Delta\widehat{W}_{21}^{\mathrm{e\text{-}c}} = -P_1\left(\frac{1}{\hat{\rho}_2} - \frac{1}{\hat{\rho}_1}\right) = -(100\ \mathrm{kPa})\left(\frac{1}{1.08\ \mathrm{kg/m^3}} - \frac{1}{1.85\ \mathrm{kg/m^3}}\right) = -38.54\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta W_{21}^{\mathrm{e\text{-}c}} = M_{tot}\widehat{W}_{21}^{\mathrm{e\text{-}c}} = (0.0185\ \mathrm{kg})\left(-38.54\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -0.713\ \mathrm{kJ}$$

Transit from 2 to 3: Isothermal step, so T_2=T_3 and

$$\Delta\hat{Q}_{32} = \int_2^3 T\mathrm{d}\hat{S} \;=\; T_2(\hat{S}_3 - \hat{S}_2) = (473\ \mathrm{K})\left(2.82\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 3.78\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = -454.08\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta Q_{32} = M_{tot}\Delta\hat{Q}_{32} = (0.0185\ \mathrm{kg})\left(-454.08\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -8.4\ \mathrm{kJ}$$

By knowing that $\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}}$

$$\Delta\hat{W}^{\mathrm{fl}}_{32} = \Delta\hat{H}_{32} - \;\Delta\hat{Q}_{32} = \left(893\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 991\frac{\mathrm{kJ}}{\mathrm{kg}}\right) - \left(-454.08\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 356.08\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta W^{\mathrm{fl}}_{32} = M_{tot}\Delta\hat{W}^{\mathrm{fl}}_{32} = (0.0185\ \mathrm{kg})\left(356.08\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 6.59\ \mathrm{kJ}$$

Finally, according to another equation of reference problem 0.3

$$\mathrm{d}\hat{U} = \mathrm{d}\hat{Q}+\mathrm{d}\hat{W}^{\text{e-c}} \quad \rightarrow \quad \Delta\hat{W}^{\text{e-c}} = \;\Delta\hat{U} - \Delta\hat{Q} = \Delta\big(\hat{H} - P\hat{V}\big) - \Delta\hat{Q}$$

$$\Delta\hat{U}_{32} = \left(\hat{H}_3 - \frac{P_3}{\hat{\rho}_3}\right) - \left(\hat{H}_2 - \frac{P_2}{\hat{\rho}_2}\right) =$$

$$= \left(893\frac{\mathrm{kJ}}{\mathrm{kg}} - \frac{7620\ \mathrm{kPa}}{119\ \mathrm{kg/m^3}}\right) - \left(991\frac{\mathrm{kJ}}{\mathrm{kg}} - \frac{100\ \mathrm{kPa}}{1.08\ \mathrm{kg/m^3}}\right) = -69.44\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta\hat{W}^{\text{e-c}}_{32} = \Delta\hat{U}_{32} - \Delta\hat{Q}_{32} = -69.44\ \frac{\mathrm{kJ}}{\mathrm{kg}} - \left(-454.08\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 384.64\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta W^{\text{e-c}}_{32} = M_{tot}\Delta\hat{W}^{\text{e-c}}_{32} = (0.0185\ \mathrm{kg})\left(384.64\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 7.116\ \mathrm{kJ}$$

Transit from 3 to 4: Since $\hat{\rho}_3$=$\hat{\rho}_4$, there will be no expansión work, and the integral corresponding to the flow work is simplified

$$\Delta\hat{W}^{\mathrm{fl}}_{43} = \int_3^4 \hat{V}\mathrm{d}P = \frac{(P_4 - P_3)}{\hat{\rho}_3} = \frac{(833\ \mathrm{kPa} - 7620\ \mathrm{kPa})}{119\ \mathrm{kg/m^3}} = -57.03\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta W^{\mathrm{fl}}_{43} = M_{tot}\Delta\hat{W}^{\mathrm{fl}}_{43} = (0.0185\ \mathrm{kg})\left(-57.03\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -1.055\ \mathrm{kJ}$$

and since $\mathrm{d}\hat{Q} = \mathrm{d}\hat{H} - \mathrm{d}\hat{W}^{\mathrm{fl}}$

$$\Delta\hat{Q}_{43} = (\hat{H}_4 - \hat{H}_3) - \Delta\hat{W}_{43}^{\mathrm{fl}} = \left(296\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 893\frac{\mathrm{kJ}}{\mathrm{kg}}\right) - \left(-57.03\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -539.97\frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta Q_{43} = M_{tot}\Delta\hat{Q}_{43} = (0.0185\ \mathrm{kg})\left(-539.97\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -9.99\ \mathrm{kJ}$$

<u>Cycle closure</u>: It is an analogous case to the transit from 2 to 3, hence

$$\Delta\hat{Q}_{14} = T_4(\hat{S}_1 - \hat{S}_4) = (293\ \mathrm{K})\left(2.82\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 1.33\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = 436.57\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta Q_{14} = M_{tot}\Delta\hat{Q}_{14} = (0.0185\ \mathrm{kg})\left(436.57\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 8.077\ \mathrm{kJ}$$

$$\Delta\hat{W}_{14}^{\mathrm{fl}} = \Delta\hat{H}_{14} - \Delta\hat{Q}_{14} = \left(622\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 296\frac{\mathrm{kJ}}{\mathrm{kg}}\right) - \left(436.57\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -110.57\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta W_{14}^{\mathrm{fl}} = M_{tot}\Delta\hat{W}_{14}^{\mathrm{fl}} = (0.0185\ \mathrm{kg})\left(-110.57\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -2.05\ \mathrm{kJ}$$

$$\begin{aligned}\Delta\hat{U}_{14} &= \left(\hat{H}_1 - \frac{P_1}{\hat{\rho}_1}\right) - \left(\hat{H}_4 - \frac{P_4}{\hat{\rho}_4}\right) = \\ &= \left(622\frac{\mathrm{kJ}}{\mathrm{kg}} - \frac{100\ \mathrm{kPa}}{1.85\ \mathrm{kg/m^3}}\right) - \left(296\frac{\mathrm{kJ}}{\mathrm{kg}} - \frac{833\ \mathrm{kPa}}{119\ \mathrm{kg/m^3}}\right) = 278.95\ \frac{\mathrm{kJ}}{\mathrm{kg}}\end{aligned}$$

$$\Delta\hat{W}_{14}^{\mathrm{e\text{-}c}} = \Delta\hat{U}_{14} - \Delta\hat{Q}_{14} = 278.95\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 436.57\ \frac{\mathrm{kJ}}{\mathrm{kg}} = -157.62\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta W_{14}^{\mathrm{e\text{-}c}} = M_{tot}\Delta\hat{W}_{14}^{\mathrm{e\text{-}c}} = (0.0185\ \mathrm{kg})\left(-157.62\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -2.916\ \mathrm{kJ}$$

Question d. In an adiabatic and reversible process, $\mathrm{d}\hat{Q} = 0$ and there is no change of entropy. Furthermore, $\mathrm{d}\hat{H} = \mathrm{d}\hat{W}^{\mathrm{fl}}$ and $\mathrm{d}\hat{W}^{\mathrm{e\text{-}c}} = \mathrm{d}\hat{U} = \mathrm{d}(\hat{H} - P\hat{V})$

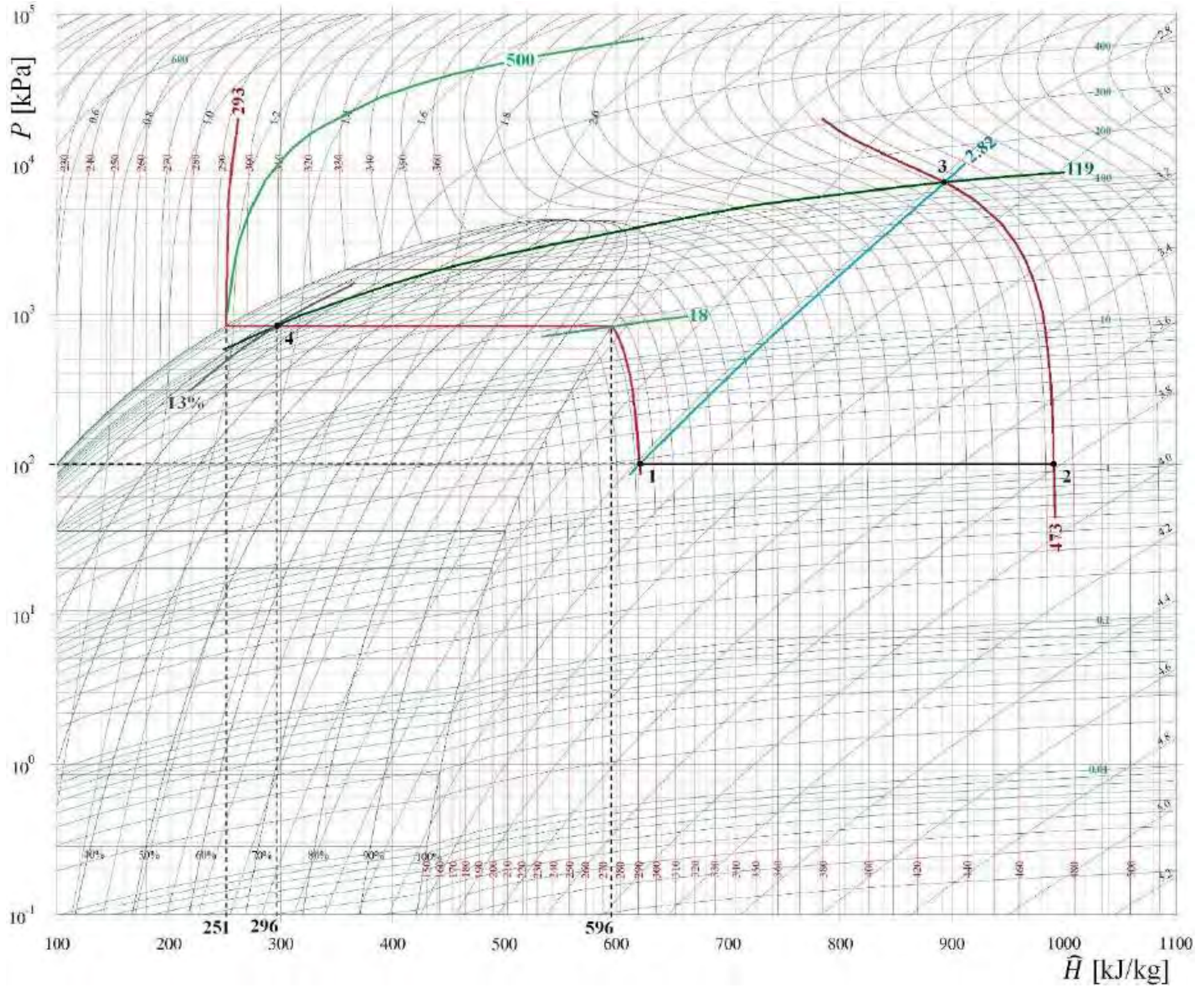
$$\Delta\hat{W}_{31}^{\mathrm{fl}} = \Delta\hat{H}_{31} = \left(893\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 622\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 271\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta W_{31}^{\mathrm{fl}} = M_{tot}\Delta\hat{W}_{31}^{\mathrm{fl}} = (0.0185\ \mathrm{kg})\left(271\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 5.014\ \mathrm{kJ}$$

$$\Delta\widehat{W}_{31}^{\text{e-c}}=\Delta\widehat{U}_{31}=\left(\widehat{H}_3-\frac{P_3}{\hat{\rho}_3}\right)-\left(\widehat{H}_1-\frac{P_1}{\hat{\rho}_1}\right)=$$
$$=\left(893\,\frac{\text{kJ}}{\text{kg}}-\frac{7620\text{ kPa}}{119\text{ kg/m}^3}\right)-\left(622\,\frac{\text{kJ}}{\text{kg}}-\frac{100\text{ kPa}}{1.85\text{ kg/m}^3}\right)=261.02\,\frac{\text{kJ}}{\text{kg}}$$

$$\Delta W_{31}^{\text{e-c}}=M_{tot}\Delta\widehat{W}_{31}^{\text{e-c}}=(0.0185\text{ kg})\left(261.02\,\frac{\text{kJ}}{\text{kg}}\right)=4.83\text{ kJ}$$

Question e. As mentioned above, point 4 corresponds to a biphasic zone. The interpolation of the title or quality line is 13% (13% of the feed is vapor, i.e., 0.13×18.5 g = 2.405 g). Saturated vapor will have a density $\hat{\rho}_{v_4}^{sat}$ = 18 kg/m^3 and saturated liquid a density $\hat{\rho}_{l_4}^{sat}$ =500 kg/m^3.



Mass and volume balance will be

$$M_{tot}=M_{l_4}+M_{v_4}$$

$$\frac{M_{tot}}{\hat{\rho}_4} = \frac{M_{l_4}}{\hat{\rho}_{l_4}^{sat}} + \frac{M_{v_4}}{\hat{\rho}_{v_4}^{sat}}$$

and their combination gives

$$M_{v_4} = M_{tot} \frac{\left(\frac{1}{\hat{\rho}_4} - \frac{1}{\hat{\rho}_{l_4}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_4}^{sat}} - \frac{1}{\hat{\rho}_{l_4}^{sat}}\right)} = (18.5\ \text{g}) \frac{\left(\frac{1}{119} - \frac{1}{500}\right)}{\left(\frac{1}{18} - \frac{1}{500}\right)} = 2.21\ \text{g}$$

$$M_{l_4} = M_{tot} - M_{v_4} = 18.5 - 2.21 = 16.29\ \text{g}$$

so that the volumes occupied by the masses will be

$$V_{l_4} = \frac{M_{l_4}}{\hat{\rho}_{l_4}^{sat}} = \frac{16.29\ \text{g}}{500\ \frac{\text{g}}{\text{L}}} = 0.0326\ \text{L}$$

$$V_{v_4} = \frac{M_{v_4}}{\hat{\rho}_{v_4}^{sat}} = \frac{2.21\ \text{g}}{18\ \frac{\text{g}}{\text{L}}} = 41.5\ \text{L}$$

Additionally, the value of M_{v_4} can be verified by combining the mass balance with the enthalpy balance

$$M_{tot}\hat{H}_4 = M_l \hat{H}_{l_4}^{sat} + M_v \hat{H}_{v_4}^{sat}$$

and since it is read in figure V.8 that the enthalpy of the saturated liquid is 251 kJ/kg and that of the saturated vapor is 596 kJ/kg

$$M_{v_4} = M_{tot} \frac{\left(\hat{H}_4 - \hat{H}_{l_4}^{sat}\right)}{\left(\hat{H}_{v_4}^{sat} - \hat{H}_{l_4}^{sat}\right)} = (18.5\ \text{g}) \frac{(296 - 251)}{(596 - 251)} = 2.41\ \text{g}$$

(There are differences due to errors of interpolation and graphical reading, but they are not higher than 9%)

4.5. A 50 m^3 storage tank contains 5000 kg of propane and, with the exception of the incident indicated in question e, operates isothermally at an ambient temperature of 20ºC. Using a *PH*(T,ρ,S) diagram specific to the substance, determine:

a) The state of the hydrocarbon in the reservoir under the conditions described.

b) The state of the hydrocarbon at maximum load capacity under the same conditions.

c) The hydrocarbon mass when the liquid is exhausted after an isothermal emptying.

d) The mass which remains in the tank when the isothermal discharge of the hydrocarbon ceases of being spontaneous, as well as the heat employed to go from the initial state to this, and from the initial state to the depletion of the liquid.

e) The expected pressure if the tank temperature increases to 50ºC from the initial conditions, from the conditions in which the liquid has been exhausted and from those when the spontaneous discharge ceases. In the three cases the tank does not explode.

Compare the results obtained in all question from propane specific data with those calculated from the Corresponding States Principle by means of generalized diagrams.

Question a. Point 1 will be located on the *PH* diagram of propane (figure V.8 in appendix V) where the isotherm

$$T_1(\mathrm{K}) = 20℃ + 273 = 293\ \mathrm{K}$$

intersects the isochore

$$\hat{\rho}_1 = \hat{\rho}_{tot} = \frac{M_1}{V_1} = \frac{M_{tot}}{V_{tot}} = \frac{5000\ \mathrm{kg}}{50\ \mathrm{m}^3} = 100\ \frac{\mathrm{kg}}{\mathrm{m}^3}$$

This intersection corresponds to the biphasic zone. It is a liquid + vapor mixture, at a pressure of 833 kPa and with an approximate title or quality of 15% (15% of the feed is vapor, i.e., 0.15×5000 kg =750 kg). Saturated vapor will have a density $\hat{\rho}_{v_1}^{sat}$=18 kg/m^3 and saturated liquid a density $\hat{\rho}_{l_1}^{sat}$=500 kg/m^3.

With these data, and the combination of the mass balance (the mass of liquid and vapor is 5000 kg) and the volume one (the volume occupied by the liquid plus the volume occupied by the vapor equals 50 m^3), the corresponding masses of vapour and liquid can be obtained

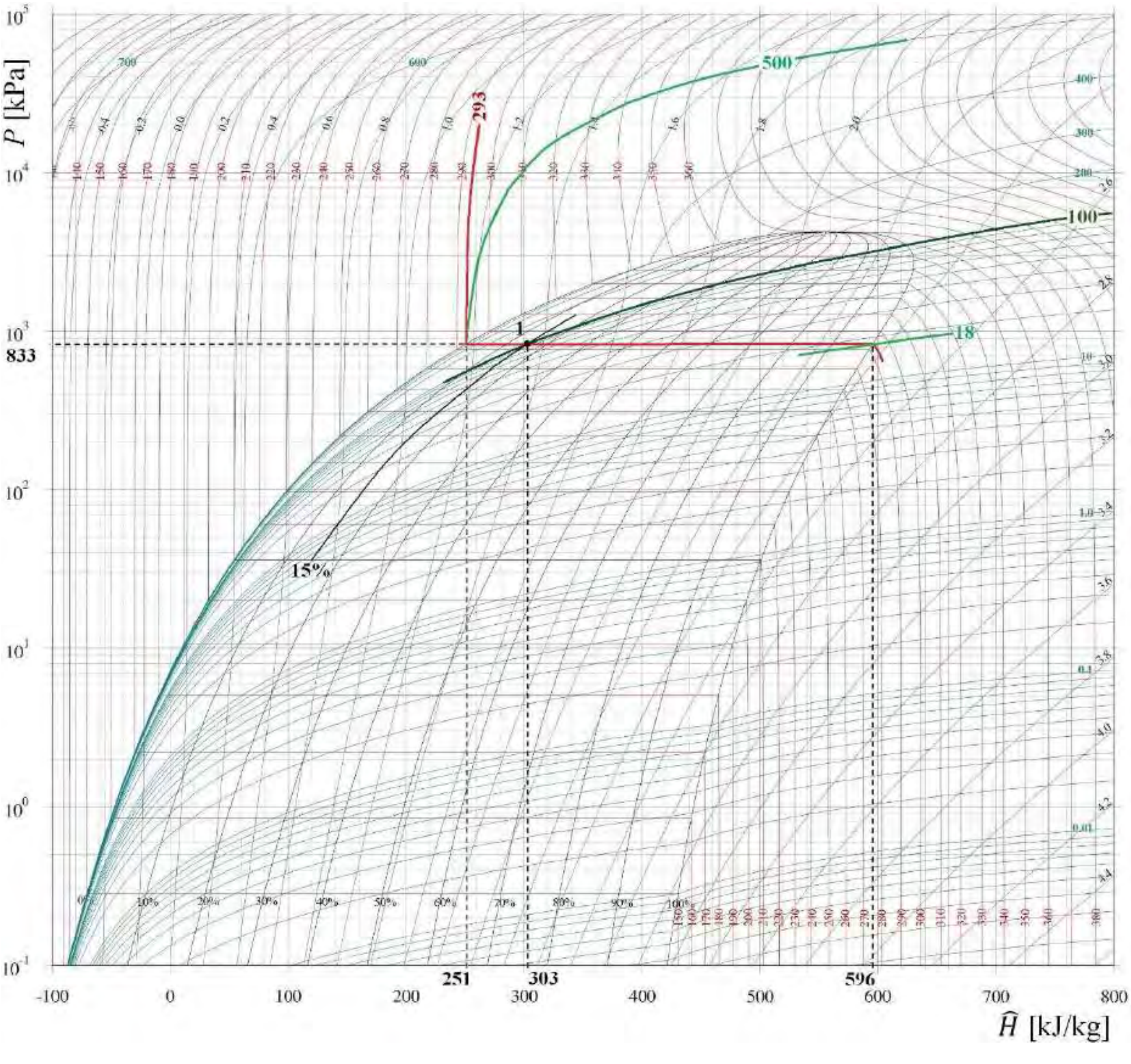
$$M_{tot} = M_{l_1} + M_{v_1}$$

$$\frac{M_{tot}}{\hat{\rho}_{tot}} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} + \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}}$$

so that

$$M_{v_1} = M_{tot}\frac{\left(\dfrac{1}{\hat{\rho}_{tot}} - \dfrac{1}{\hat{\rho}_{l_1}^{sat}}\right)}{\left(\dfrac{1}{\hat{\rho}_{v_1}^{sat}} - \dfrac{1}{\hat{\rho}_{l_1}^{sat}}\right)} = (5000\ \text{kg})\frac{\left(\dfrac{1}{100} - \dfrac{1}{500}\right)}{\left(\dfrac{1}{18} - \dfrac{1}{500}\right)} = 746.9\ \text{kg}$$

$$M_{l_1} = M_{tot} - M_{v_1} = 5000 - 746.9 = 4253.1\ \text{kg}$$



and the volumes occupied by these masses will be

$$V_{l_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} = \frac{4253.1\ \text{kg}}{500\ \dfrac{\text{kg}}{\text{m}^3}} = 8.5\ \text{m}^3$$

$$V_{v_1} = \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} = \frac{746.9\ \text{kg}}{18\ \dfrac{\text{kg}}{\text{m}^3}} = 41.5\ \text{m}^3$$

Furthermore, the value of M_{v_1} can be checked by combining the mass balance with the enthalpy one

$$M_{tot}\widehat{H}_{tot} = M_{l_1}\widehat{H}_{l_1}^{sat} + M_{v_1}\widehat{H}_{v_1}^{sat}$$

and since it is read in figure V.8 that the total enthalpy of the mixture is 303 kJ/kg, that the enthalpy of the saturated liquid is 251 kJ/kg and that the enthalpy of saturated vapor is 596 kJ/kg, it is obtained

$$M_{v_1} = M_{tot}\frac{\left(\widehat{H}_{tot} - \widehat{H}_{l_1}^{sat}\right)}{\left(\widehat{H}_{v_1}^{sat} - \widehat{H}_{l_1}^{sat}\right)} = (5000\text{ kg})\frac{(303 - 251)}{(596 - 251)} = 753.6\text{ kg}$$

value which is very close to the 746.9 kg previously found.

Question b. The maximum load capacity is the mass when the entire content of the tank is in the form of saturated liquid at 20ºC and 833 kPa (density of 500 kg/m^3)

$$V_{tot}\hat{\rho}_{l_1}^{sat} = (50\text{ m}^3)\left(500\ \frac{\text{kg}}{\text{m}^3}\right) = 25000\text{ kg}$$

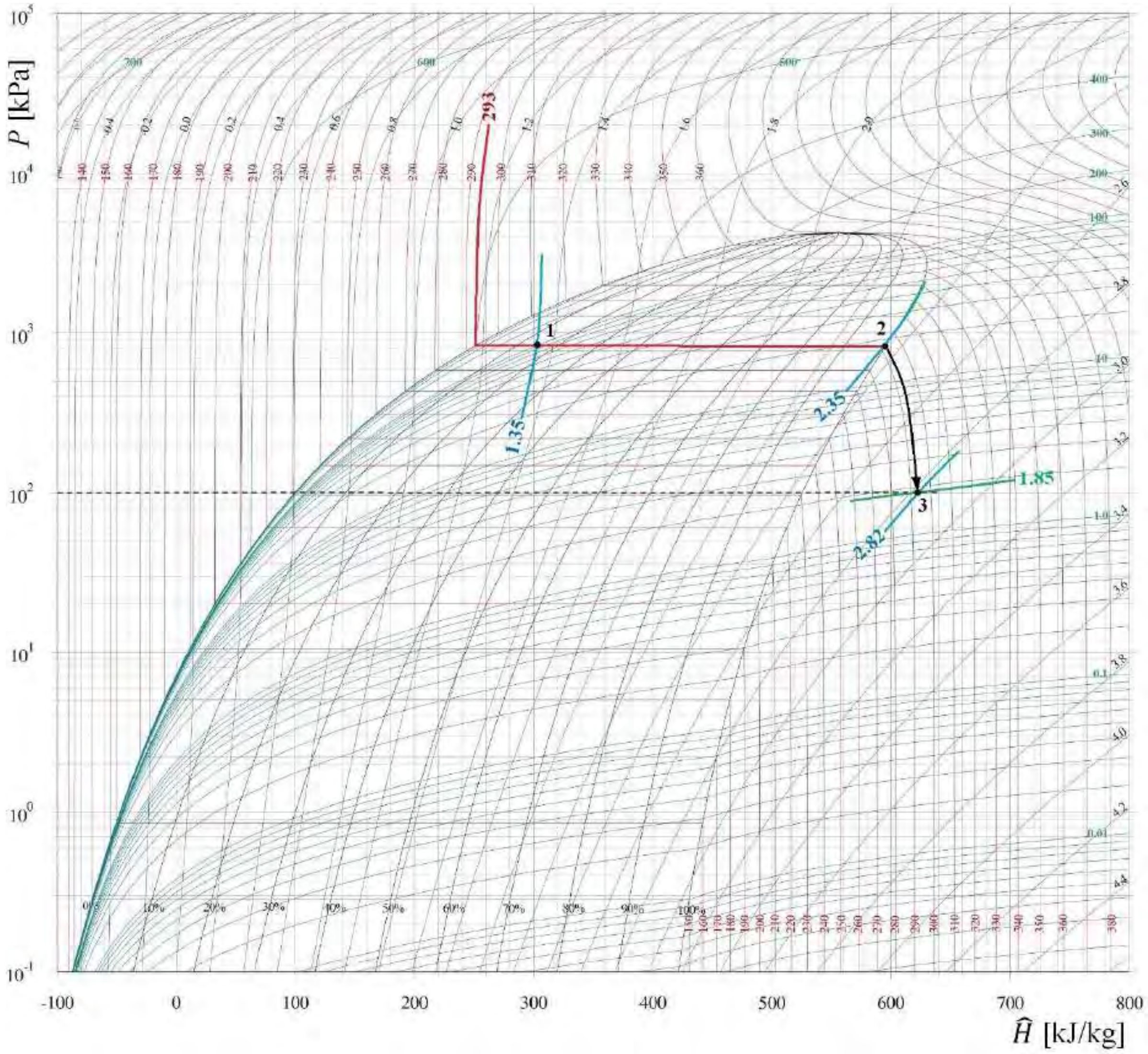
Question c. When the liquid propane is exhausted at 20ºC and 833 kPa, only saturated vapor will remain (density of 18 kg/m^3), which will occupy the total volume of the tank. Its mass will be

$$M_2 = V_{tot}\hat{\rho}_2 = V_{tot}\hat{\rho}_{v_1}^{sat} = (50\text{ m}^3)\left(18\ \frac{\text{kg}}{\text{m}^3}\right) = 900\text{ kg}$$

Question d. In the case of an isothermal discharge, it will cease when the vapor reaches a pressure equal to that of the external environment (P_3=1 atm ≈ 100 kPa).

At that moment, the density of the vapor will be $\hat{\rho}_3$ =1.85 kg/m^3 and the remaining mass at 293 K

$$M_3 = V_{tot}\hat{\rho}_3 = (50\text{ m}^3)\left(1.85\ \frac{\text{kg}}{\text{m}^3}\right) = 92.5\text{ kg}$$



On the other hand, the heat for the transit from the initial state (1) to the depletion of the liquid (2) will consist of two terms/causes: the passage of the fuel that remains inside the tank (M_2) from conditions 1 to conditions 2 and the transit of all the mass consumed ($M_1 - M_2$) from conditions 1 to unknown final conditions, which would have to be defined. If, for simplicity, it is assumed that the propane extracted from the tank has been used in the vapor phase at atmospheric pressure and 20ºC (point 3), then

$$\Delta Q = (M_1 - M_2)\int_1^3 T\mathrm{d}\hat{S} + M_2\int_1^2 T\mathrm{d}\hat{S}$$

$$\Delta Q = (M_1 - M_2)T_1\left(\hat{S}_3 - \hat{S}_1\right) + M_2 T_1\left(\hat{S}_2 - \hat{S}_1\right)$$

$$\Delta Q = (5000\ \mathrm{kg} - 900\ \mathrm{kg})(293\ \mathrm{K})\left(2.82\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 1.35\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) +$$

$$+(900\ \mathrm{kg})(293\ \mathrm{K})\left(2.35\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 1.35\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = 2029611\ \mathrm{kJ}$$

Similarly, the heat exchanged from point 1 to point 3 is due to two causes: the fuel remaining inside the tank (M_3) goes from conditions 1 to conditions 3, and the fuel consumed ($M_1 - M_3$) also goes from conditions 1 to 3

$$\Delta Q = M_3 \int_1^3 T\mathrm{d}\hat{S} + (M_1 - M_3) \int_1^3 T\mathrm{d}\hat{S}$$

and since T_1=T_3, the integration is simplified

$$\Delta Q = M_3 T_1\left(\hat{S}_3 - \hat{S}_1\right) + (M_1 - M_3) T_1\left(\hat{S}_3 - \hat{S}_1\right) = M_1 T_1\left(\hat{S}_3 - \hat{S}_1\right)$$

Reading the specific entropies from the diagram, it is obtained

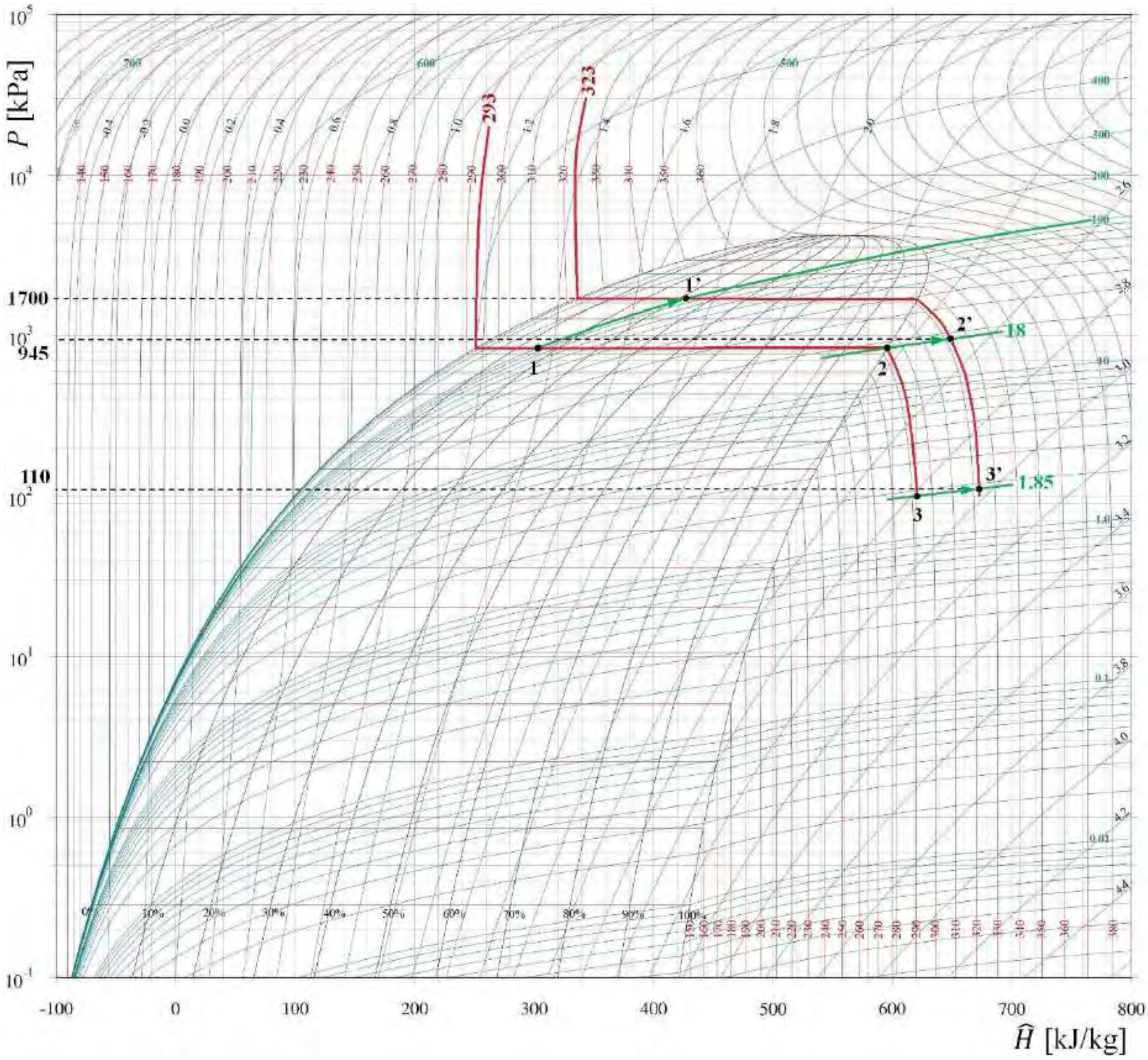
$$\Delta Q = (5000\ \mathrm{kg})(293\ \mathrm{K})\left(2.82\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 1.35\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = 2153550\ \mathrm{kJ}$$

Question e. The statement of the problem now says that the temperature increases from 293 K to

$$T(\mathrm{K}) = 50°\mathrm{C} + 273 = 323\ \mathrm{K}$$

Since the tank does not explode, it will be a constant volume/density heating, and it will follow the corresponding isochores:

- The 100 kg/m^3 one for the feed (point 1), which will intersect the 323 K isotherm at a point 1' whose pressure will be 1700 kPa.
- The 18 kg/m^3 one for the depletion of the liquid (point 2), which will intersect at point 2' (pressure of 945 kPa).
- The 1.85 kg/m^3 one for the end of spontaneous discharge (point 3), whose intersection with 323 K will take place at point 3' (pressure of 110 kPa).



Regarding the **application of the Corresponding States Principle**, it should be recalled once again that it is based on the fact that the compressibility factor z of the equation of state

$$\frac{P}{\tilde{\rho}} = zRT$$

is a generalized function of the reduced temperature and pressure (when z_c=0.27), and it is correlated in the way that is given by figure IV.1 of this book's appendix IV.

By taking from appendix II the critical properties (P_c=370 K, T_c=42 atm, z_c=0.276) and the molecular mass (44.09 g/mol-g) of propane, it results

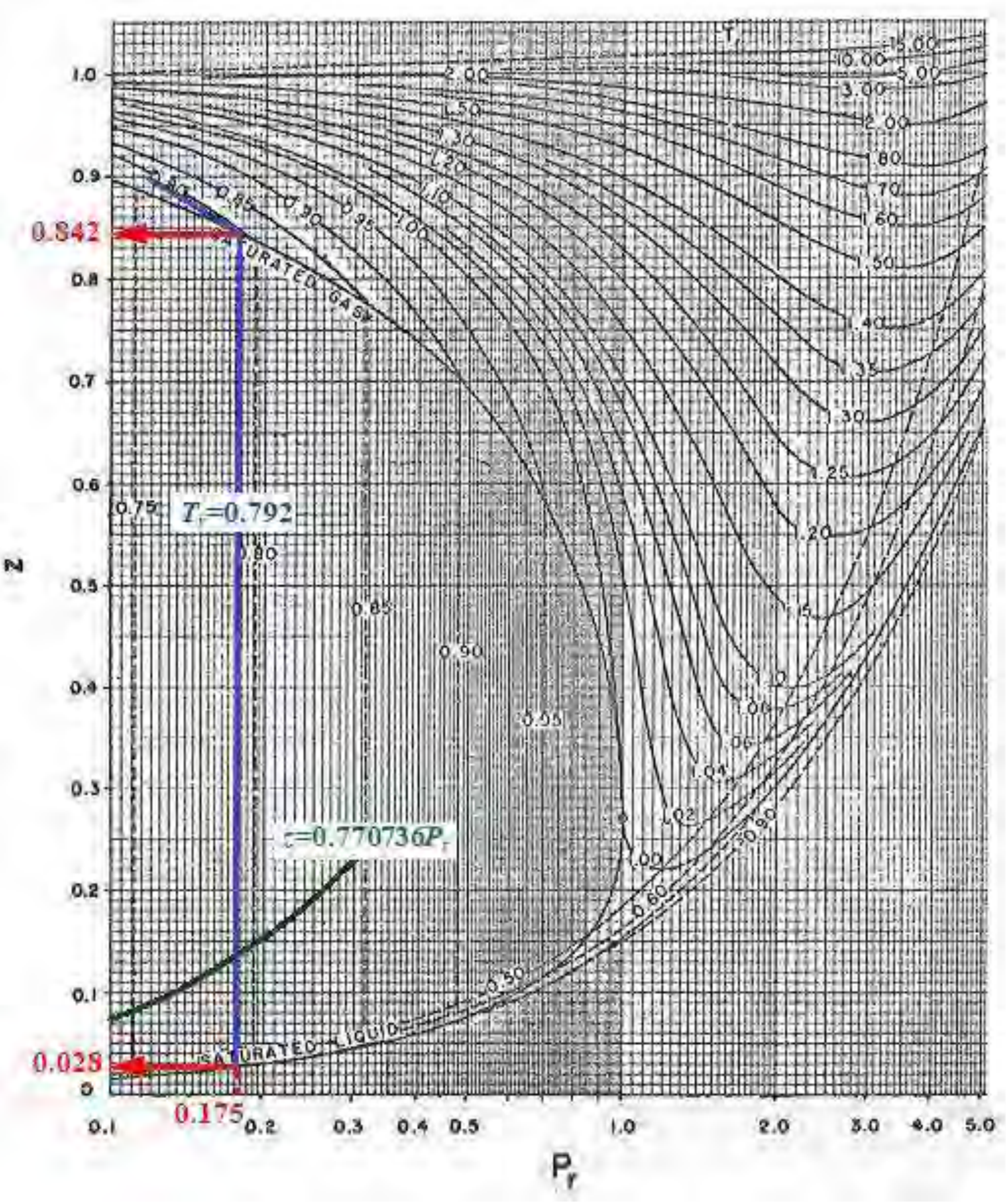
$$T_{r1} = \frac{T_1}{T_c} = \frac{293\ \text{K}}{370\ \text{K}} = 0.792$$

$$\tilde{\rho}_1 = 100\ \frac{\text{kg}}{\text{m}^3} \times \frac{1\text{m}^3}{1000\ \text{L}} \times \frac{1000\ \text{g}}{1\ \text{kg}} \times \frac{1\ \text{mol-g}}{44.09\ \text{g}} = 2.2681\ \frac{\text{mol-g}}{\text{L}}$$

However, figure IV.1 is an explicit function of T_r and P_r, and since P is not known, its graphical determination will be necessary by drawing the auxiliary line

$$z_1 = \frac{P_1}{RT_1\tilde{\rho}_1} = \frac{P_cP_{r1}}{RT_1\tilde{\rho}_1} = \frac{(42\ \text{atm})P_{r1}}{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(293\ \text{K})\left(2.2681\ \frac{\text{mol-g}}{\text{L}}\right)} = 0.770736P_{r1}$$

which is a curve on a semi-logarithmic scale (and a straight line in a diagram in linear coordinates). It has to be plotted point by point until intersecting with the T_{r1}=0.792 isotherm in the figure.



P_{r1}	z_1
0.1	0.0770736
0.11	0.08478096
0.12	0.09248832
0.13	0.10019568
0.14	0.10790304
0.15	0.1156104
0.16	0.12331776
0.175	0.1348788
0.19	0.14643984
0.2	0.1541472
0.3	0.2312208

and it is observed that the intersection takes place in the biphasic zone, being the reduced pressure equal to 0.175, so

$$P_1 = P_{r1}P_c = (0.175)(42\text{ atm}) = 7.35\text{ atm} \quad \rightarrow 7.35\text{ atm}\times\frac{1.013\text{ bar}}{1\text{ atm}}\times\frac{100\text{ kPa}}{1\text{ bar}} = 744.56\text{ kPa}$$

a value that is 10.6% less than the 833 kPa found in the *PH* diagram.

From the figure it can also be obtained the compressibility factors for the saturated liquid ($z_{l_1}^{sat}$=0.028) and for the saturated vapor ($z_{v_1}^{sat}$=0.842), which allow the estimation of the liquid and vapor densities, respectively

$$\hat{\rho}_{l_1}^{sat} = \frac{P_1\mathfrak{W}}{z_{l_1}^{sat}RT_1} = \frac{(7.35\text{ atm})\left(44.09\ \frac{\text{g}}{\text{mol-g}}\right)}{(0.028)\left(0.082\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(293\text{ K})} = 481.7\ \frac{\text{g}}{\text{L}} = 481.7\ \frac{\text{kg}}{\text{m}^3}$$

$$\hat{\rho}_{v_1}^{sat} = \frac{P_1\mathfrak{W}}{z_{v_1}^{sat}RT_1} = \frac{(7.35\text{ atm})\left(44.09\ \frac{\text{g}}{\text{mol-g}}\right)}{(0.842)\left(0.082\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(293\text{ K})} = 16.02\ \frac{\text{g}}{\text{L}} = 16.02\ \frac{\text{kg}}{\text{m}^3}$$

By applying the same equations as in question **a**

$$M_{v_1} = M_{tot}\frac{\left(\frac{1}{\hat{\rho}_{tot}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_1}^{sat}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)} = (5000\text{ kg})\frac{\left(\frac{1}{100} - \frac{1}{481.7}\right)}{\left(\frac{1}{16.02} - \frac{1}{481.7}\right)} = 656.55\text{ kg}$$

$$M_{l_1} = M_{tot} - M_{v_1} = 5000 - 656.55 = 4343.45\text{ kg}$$

$$V_{l_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} = \frac{4343.45\ \text{kg}}{481.7\ \dfrac{\text{kg}}{\text{m}^3}} = 9.02\ \text{m}^3$$

$$V_{v_1} = \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} = \frac{656.55\ \text{kg}}{16.02\ \dfrac{\text{kg}}{\text{m}^3}} = 40.98\ \text{m}^3$$

Notice that although the calculated densities are 4 - 11% lower than the experimental ones and that the mass of the vapor is almost 100 kg lower than that of question **a**, the volume occupied by the liquid is only 6% higher and that occupied by the vapor is 1.3% lower.

If the new density of the liquid at 20ºC and 744.56 kPa (481.7 kg/m^3) is employed to evaluate the maximum load capacity, it turns out to be 3.7% lower than that of question **b**

$$V_{tot}\hat{\rho}_{l_1}^{sat} = (50\ \text{m}^3)\left(481.7\ \frac{\text{kg}}{\text{m}^3}\right) = 24085\ \text{kg}$$

while with the new density of the saturated vapor (16.02 kg/m^3) the mass of hydrocarbon when the liquid is exhausted will be 11% lower than that of question **c**

$$M_2 = V_{tot}\hat{\rho}_2 = V_{tot}\hat{\rho}_{v_1}^{sat} = (50\ \text{m}^3)\left(16.02\ \frac{\text{kg}}{\text{m}^3}\right) = 801\ \text{kg}$$

In question **d**, the density of the vapor at atmospheric pressure will be determined from the compressibility factor under the conditions

$$P_{r3} = \frac{P_3}{P_c} = \frac{1\ \text{atm}}{42\ \text{atm}} = 0.0238$$

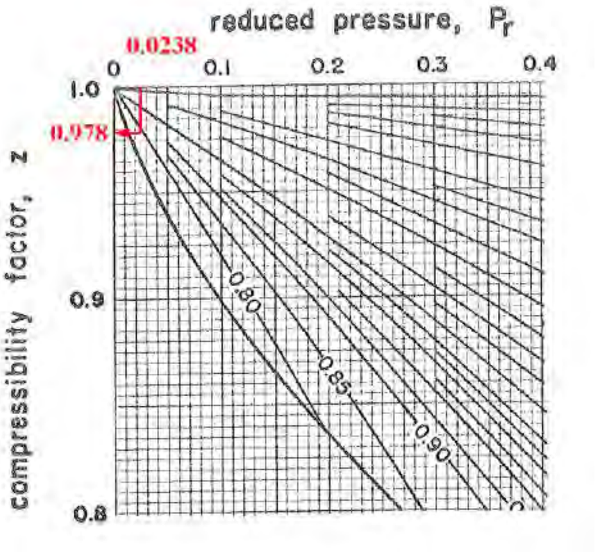
$$T_{r3} = T_{r1} = \frac{T_1}{T_c} = \frac{293\ \text{K}}{370\ \text{K}} = 0.792$$

which, in figure IV.3 is approximately z_3= 0.978 (the exact value cannot be read because the lowest isotherm in this diagram is T_r=0.8, but it can be assumed that the 0.792 isotherm is not far from it), so

$$\hat{\rho}_3 = \frac{P_3\mathfrak{W}}{z_3RT_3} = \frac{(1\ \text{atm})\left(44.09\ \dfrac{\text{g}}{\text{mol-g}}\right)}{(0.978)\left(0.082\dfrac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(293\ \text{K})} = 1.88\ \frac{\text{g}}{\text{L}} = 1.88\ \frac{\text{kg}}{\text{m}^3}$$

$$M_3 = V_{tot}\hat{\rho}_3 = (50\ \text{m}^3)\left(1.88\ \frac{\text{kg}}{\text{m}^3}\right) = 94\ \text{kg}$$

mass that is 1.6% higher than the 92.5 kg found with figure V.8.



After this, the heats concerned in question **d** require the quantification of two entropy departures, which according to section e of reference problem 0.8 will be

$$\begin{aligned}(\tilde{S}_2-\tilde{S}_1)&=\underbrace{(\tilde{S}_2^*-\tilde{S}_1^*)}_{\text{ideal part}}+\underbrace{(\tilde{S}_1^*-\tilde{S}_1)_{T_1,P_1}-(\tilde{S}_2^*-\tilde{S}_2)_{T_2,P_2}}_{\text{real part}}\\(\tilde{S}_3-\tilde{S}_1)&=\underbrace{(\tilde{S}_3^*-\tilde{S}_1^*)}_{\text{ideal part}}+\underbrace{(\tilde{S}_1^*-\tilde{S}_1)_{T_1,P_1}-(\tilde{S}_3^*-\tilde{S}_3)_{T_3,P_3}}_{\text{real part}}\end{aligned}\tag*{[1]}$$

where the so-called "ideal terms or ideal contributions" are given by

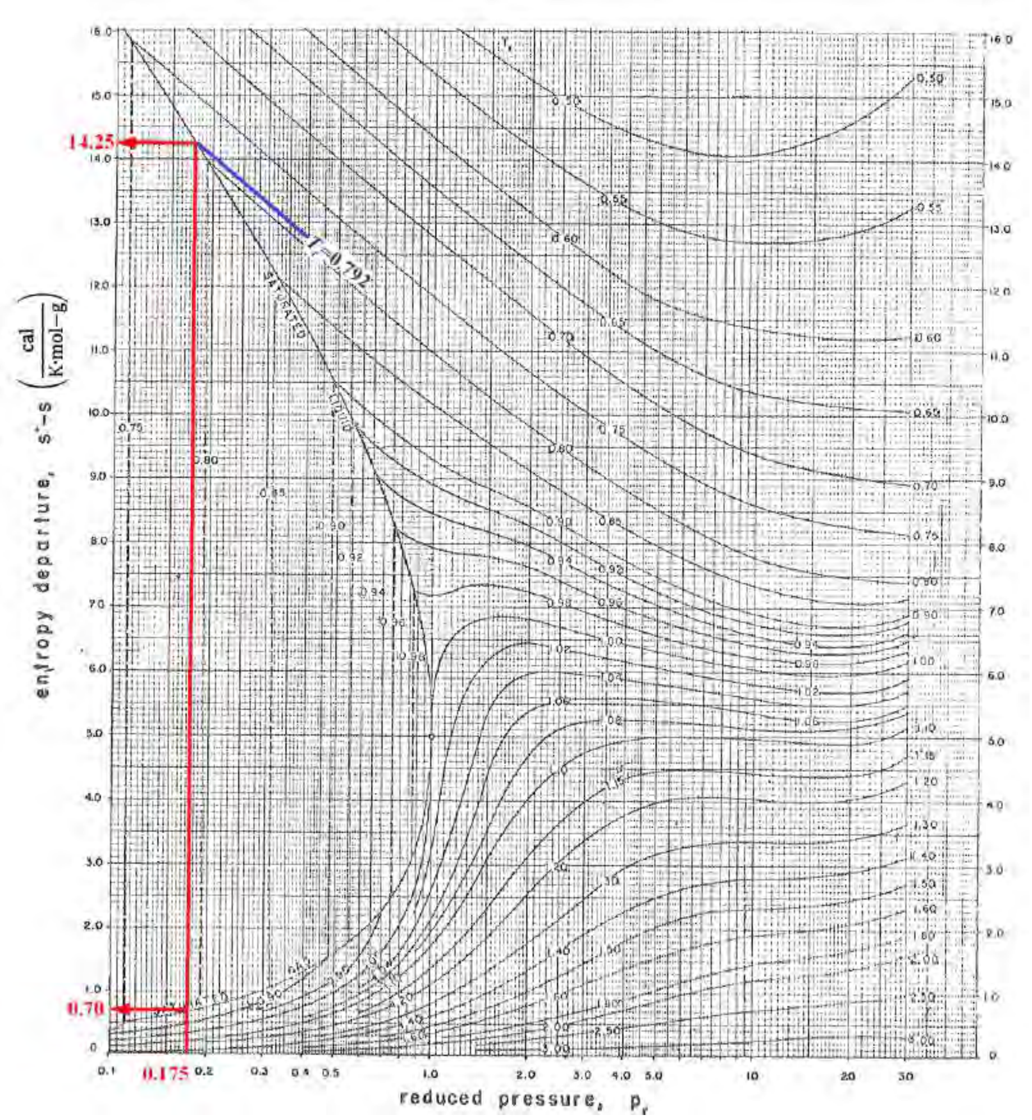
$$\begin{aligned}\tilde{S}_2^*-\tilde{S}_1^*&=\int_{T_1}^{T_2}\tilde{C}_P^*\frac{\mathrm{d}T}{T}-\int_{P_1}^{P_2}R\frac{\mathrm{d}P}{P}\xrightarrow{T_2=T_1\quad P_2=P_1}\tilde{S}_2^*-\tilde{S}_1^*=0\\\tilde{S}_3^*-\tilde{S}_1^*&=\int_{T_1}^{T_3}\tilde{C}_P^*\frac{\mathrm{d}T}{T}-\int_{P_1}^{P_3}R\frac{\mathrm{d}P}{P}\xrightarrow{T_3=T_1}\tilde{S}_3^*-\tilde{S}_1^*=-R\ln\left(\frac{P_3}{P_1}\right)\end{aligned}\tag*{[2]}$$

and the "real terms or real contributions" are read in the generalized figures IV.7 and IV.8 of appendix IV. In the first one, it can be seen that at T_{r1}=0.792 and P_{r1}=0.175 there are two values of entropy departure: one for the saturated liquid and other for the saturated vapor. Therefore, the value at point "1" has to be estimated by means of the entropy balance (with the masses of liquid and vapor)

$$(\tilde{S}_1^*-\tilde{S}_1)_l^{sat}=14.25\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\quad;\quad(\tilde{S}_1^*-\tilde{S}_1)_v^{sat}=0.70\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$(\tilde{S}_1^*-\tilde{S}_1)_{T_1,P_1}=\frac{M_{v_1}}{M_{tot}}(\tilde{S}_1^*-\tilde{S}_1)_v^{sat}+\frac{M_{l_1}}{M_{tot}}(\tilde{S}_1^*-\tilde{S}_1)_l^{sat}$$

$$\left(\tilde{S}_1^* - \tilde{S}_1\right)_{T_1,P_1} = \frac{656.55}{5000}\left(0.7\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)+\frac{4343.45}{5000}\left(14.25\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)=12.47\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$



Since point 2 coincides with the saturated vapor

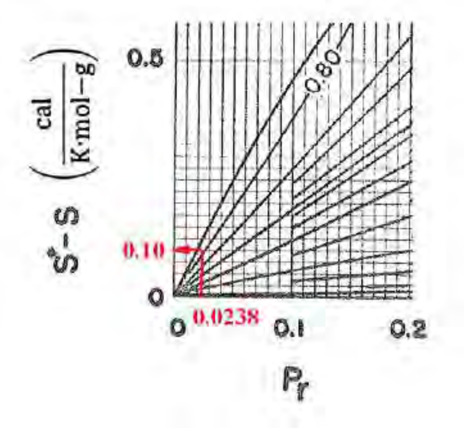
$$\left(\tilde{S}_2^* - \tilde{S}_2\right)_{T_2,P_2} = \left(\tilde{S}_1^* - \tilde{S}_1\right)_v^{sat} = 0.70\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

the combination of equations [1] and [2] generates

$$\left(\tilde{S}_2 - \tilde{S}_1\right) = 0\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}} + 12.47\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}} - 0.70\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}} = 11.77\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

For its part (and approximately, as in the reading of z_3), in point 3 (T_r=0.792, P_r=0.0238)

$$\left(\tilde{S}_3^* - \tilde{S}_3\right)_{T_3,P_3} = 0.10\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}}$$



with the result that equations [2] and [1] give

$$\tilde{S}_3^* - \tilde{S}_1^* = -\left(1.9872\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}}\right)\,\ln\left[\frac{1\text{ atm}}{7.35\text{ atm}}\right] = 3.964\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}}$$

$$\left(\tilde{S}_3 - \tilde{S}_1\right) = 3.964\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}} + 12.47\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}} - 0.10\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}} = 16.334\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}}$$

By converting the units of these differences into kJ/(kg·K) through the conversion factors of appendix I and the molecular weight of propane, it is obtained

$$\hat{S}_2 - \hat{S}_1 = 11.77\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}} \times \frac{1\text{ mol-g}}{44.09\text{ g}} \times \frac{1000\text{ g}}{1\text{ kg}} \times \frac{1\text{ kcal}}{1000\text{ cal}} \times \frac{4180\text{ J}}{1\text{ kcal}} \times \frac{1\text{ kJ}}{1000\text{ J}} = 1.115\,\frac{\text{kJ}}{\text{kg}\cdot\text{K}}$$

$$\hat{S}_3 - \hat{S}_1 = 16.334\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}} \times \frac{1\text{ mol-g}}{44.09\text{ g}} \times \frac{1000\text{ g}}{1\text{ kg}} \times \frac{1\text{ kcal}}{1000\text{ cal}} \times \frac{4180\text{ J}}{1\text{ kcal}} \times \frac{1\text{ kJ}}{1000\text{ J}} = 1.548\,\frac{\text{kJ}}{\text{kg}\cdot\text{K}}$$

being the heat necessary to the step from 1 to 3 a 5.3% higher than that evaluated with the *PH* diagram

$$\Delta Q = M_1 T_1\left(\hat{S}_3 - \hat{S}_1\right) = (5000\text{ kg})(293\text{ K})\left(1.548\,\frac{\text{kJ}}{\text{kg}\cdot\text{K}}\right) = 2267820\text{ kJ}$$

and the required one for the transit between 1 and 2 is 6.7% higher

$$\Delta Q = (M_1 - M_2)T_1\left(\hat{S}_3 - \hat{S}_1\right) + M_2 T_1\left(\hat{S}_2 - \hat{S}_1\right) =$$

$$=(5000\text{ kg}-801\text{ kg})(293\text{ K})\left(1.548\ \frac{\text{kJ}}{\text{kg·K}}\right)+(801\text{ kg})(293\text{ K})\left(1.115\frac{\text{kJ}}{\text{kg·K}}\right)=2166198\text{ kJ}$$

Finally, pressures at the new temperature

$$T_{r3'}=T_{r2'}=T_{r1'}=\frac{323\text{ K}}{370\text{ K}}=0.873$$

have to be found in a similar way to that employed in the resolution of question **a**, i.e., by means of the intersection of this isotherm with the lines

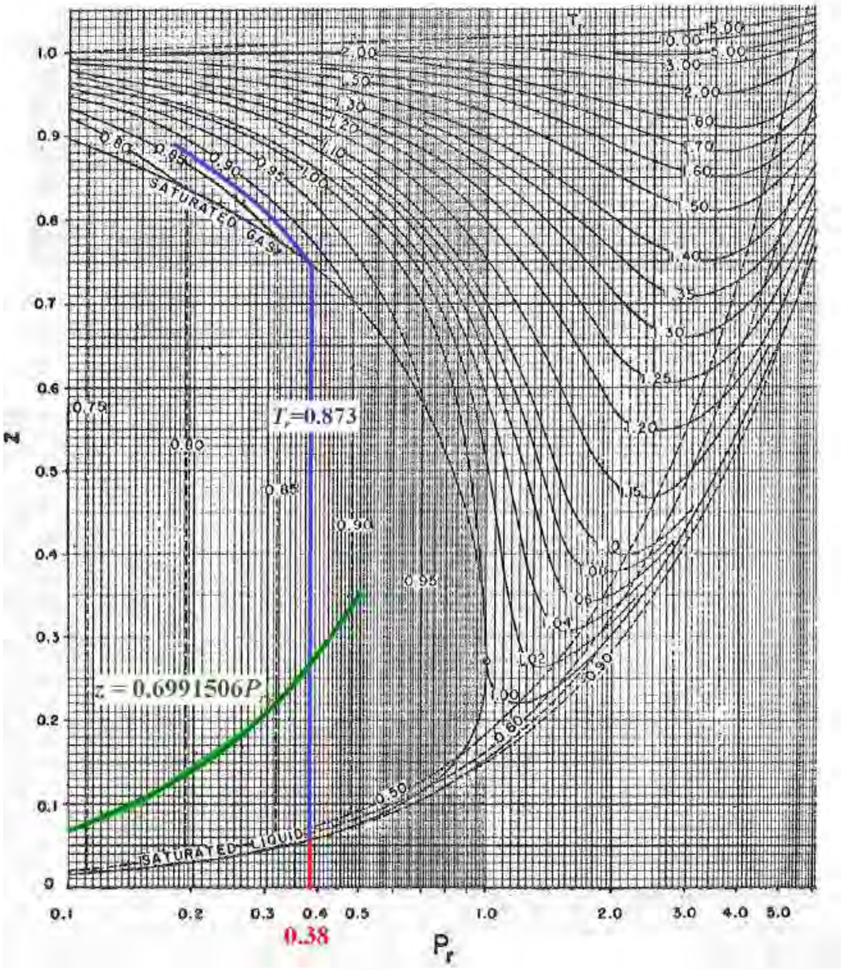
$$z_{1'}=\frac{P_{1'}}{RT_{1'}\tilde{\rho}_1}=\frac{P_cP_{r1'}}{RT_{1'}\tilde{\rho}_1}=\frac{(42\text{ atm})P_{r1'}}{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(323\text{ K})\left(2.2681\ \frac{\text{mol-g}}{\text{L}}\right)}=0.6991506P_{r1'}$$

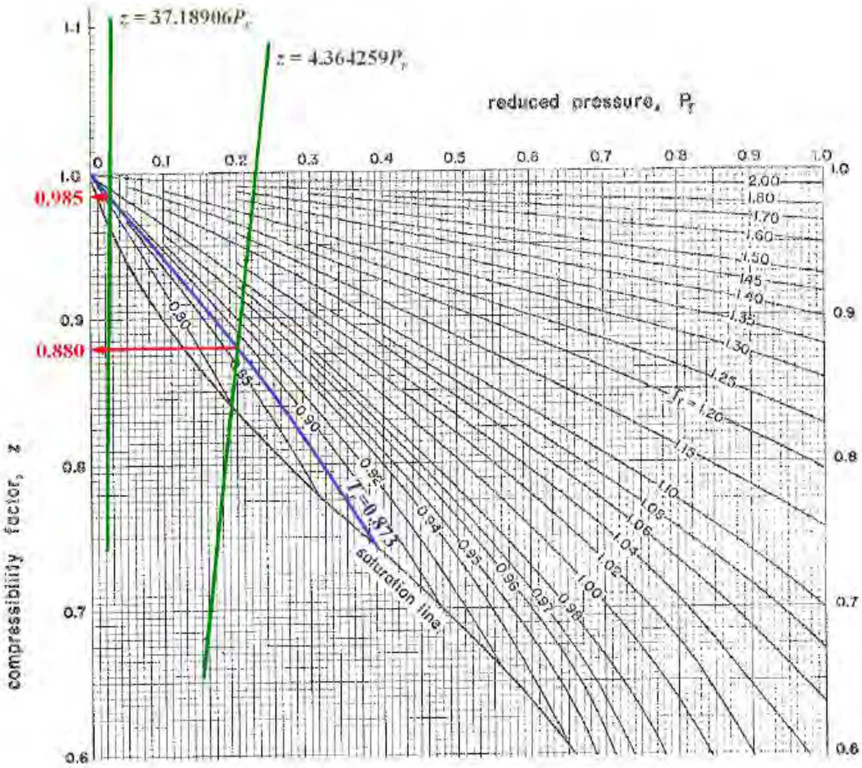
$$z_{2'}=\frac{P_{2'}}{RT_{1'}\tilde{\rho}_2}=\frac{P_cP_{r2'}\mathfrak{M}}{RT_{1'}\hat{\rho}_{v_1}^{sat}}=\frac{(42\text{ atm})P_{r2'}\left(44.09\ \frac{\text{g}}{\text{mol-g}}\right)}{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(323\text{ K})\left(16.02\ \frac{\text{g}}{\text{L}}\right)}=4.364259P_{r2'}$$

$$z_{3'}=\frac{P_{3'}}{RT_{1'}\tilde{\rho}_3}=\frac{P_cP_{r3'}\mathfrak{M}}{RT_{1'}\hat{\rho}_3}=\frac{(42\text{ atm})P_{r3'}\left(44.09\ \frac{\text{g}}{\text{mol-g}}\right)}{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(323\text{ K})\left(1.88\ \frac{\text{g}}{\text{L}}\right)}=37.18906P_{r3'}$$

By testing values and drawing the corresponding lines on generalized figures IV.1 and IV.3

P_r	$z_{1'}$	$z_{2'}$	$z_{3'}$
0.02	0.0139830	0.0872851	0.743781
0.03	0.0209745	0.1309277	1.115671
0.01	0.0069915	0.0436425	0.371890
0.1	0.0699150	0.4364259	3.718906
0.15	0.1048725	0.6546388	5.578359
0.2	0.1398301	0.8728518	7.437812
0.25	0.1747876	1.0910647	9.297265
0.3	0.2097451	1.3092777	11.15671
0.4	0.2796602	1.7457036	14.87562
0.5	0.3495753	2.1821295	18.59453


z
P_r
0.38
T_r=0.873
$z = 0.6991506P_r$
SATURATED GAS
SATURATED LIQUID
T_r
0.1
0.2
0.3
0.4
0.5
1.0
2.0
3.0
4.0
5.0


$z = 37.18906P_r$
$z = 4.364259P_r$
reduced pressure, P_r
compressibility factor, z
0.985
0.880
T_r=0.873
T_r = 1.20
saturation line

it is obtained that $z_{1'}$ intersects with T_r=0.873 in the biphasic zone, so its reduced pressure $P_{r1'}$ will be that of saturation at this reduced temperature (0.38)

$$P_{1'} = P_{r1'}P_c = (0.38)(42\ \text{atm})\times\frac{1.013\ \text{bar}}{1\ \text{atm}}\times\frac{100\ \text{kPa}}{1\ \text{bar}} = 1616.75\ \text{kPa}$$

while $z_{2'}$ and $z_{3'}$ intersect with T_r=0.873 in the values

$$z_{2'} = 0.88 \ \rightarrow\ P_{r2'} = \frac{0.88}{4.364259} = 0.2012$$

$$z_{3'} = 0.985 \ \rightarrow\ P_{r3'} = \frac{0.985}{37.18906} = 0.0265$$

which correspond to the pressures

$$P_{2'} = P_{r2'}P_c = (0.2012)(42\ \text{atm})\times\frac{1.013\ \text{bar}}{1\ \text{atm}}\times\frac{100\ \text{kPa}}{1\ \text{bar}} = 856\ \text{kPa}$$

$$P_{3'} = P_{r3'}P_c = (0.0265)(42\ \text{atm})\times\frac{1.013\ \text{bar}}{1\ \text{atm}}\times\frac{100\ \text{kPa}}{1\ \text{bar}} = 112.75\ \text{kPa}$$

being $P_{1'}$ a 4.9% lower than that evaluated by means of the $PH(T,\rho, S)$ diagram, $P_{2'}$ a 9.4% lower and $P_{3'}$ a 2.5% higher.

4.6. A domestic propane cylinder initially contains 11 kg of this hydrocarbon in a 35-liter safety container. It is doubted whether to install the cylinder outside or inside a single-family home in Trasmonte (Asturias), where, due to global warming, outside temperatures will reach 30ºC below zero in the month of August. Inside, they are usually kept constant at 25ºC because the occupants are a bit nesh.

By employing a specific *PH* diagram for propane:

a) Compare the conditions of the propane in the cylinder (pressure and amounts of liquid and vapor) in both locations –inside and outside the house under isothermal conditions– at the time of installation.

b) Compare these conditions when half of its content has been isothermally consumed, when the liquid phase is depleted, and when the cylinder is replaced because no fuel comes out (users are as nesh as they are thrifty).

c) Determine the conditions of the propane inside the cylinder (pressure and amounts of liquid and vapor) in the initial conditions and at half load if a small accidental fire (due to abuse of the heating) increases the temperature in the surroundings of the cylinder to 120ºC.

d) The heat taken from the environment and required by the isothermal evacuation of half the load due to normal use if the ambient temperature is 25ºC.

Additionally, qualitatively represent the described changes in *PT*(*V*), *PV*(*T,S,H*) and *TS*(*P,H,V*) diagrams.

Question a. Let point 1 represent the initial conditions of the cylinder on the outside, and point 1' represent them on the inside. These states will be graphically located in figure V.8 of this book's appendix V by the intersection of the isochore

$$\hat{\rho}_1 = \hat{\rho}_{1'} = \hat{\rho}_{tot} = \frac{M_{tot}}{V_{cylinder}} = \frac{11\ \text{kg}}{35\ \text{L}} = 0.314\ \frac{\text{kg}}{\text{L}} \quad \rightarrow \quad 0.314\ \frac{\text{kg}}{\text{L}} \times \frac{1000\ \text{L}}{1\ \text{m}^3} = 314\ \frac{\text{kg}}{\text{m}^3}$$

with the isotherms

$$T_1(\text{K}) = -30\text{°C} + 273 = 243\ \text{K}$$

$$T_{1'}(\text{K}) = 25\text{°C} + 273 = 298\ \text{K}$$

In both cases, they are biphasic mixtures of saturated liquid and saturated vapor, and there is more liquid than vapor (especially on the outside). The pressure at 1 is 168 kPa and at 1' is 959 kPa. It is difficult to read the title or quality lines in point 1, but in 1' it can be accepted that there is a 2.4% of vapor (0.024×11 kg = 0.264 kg)

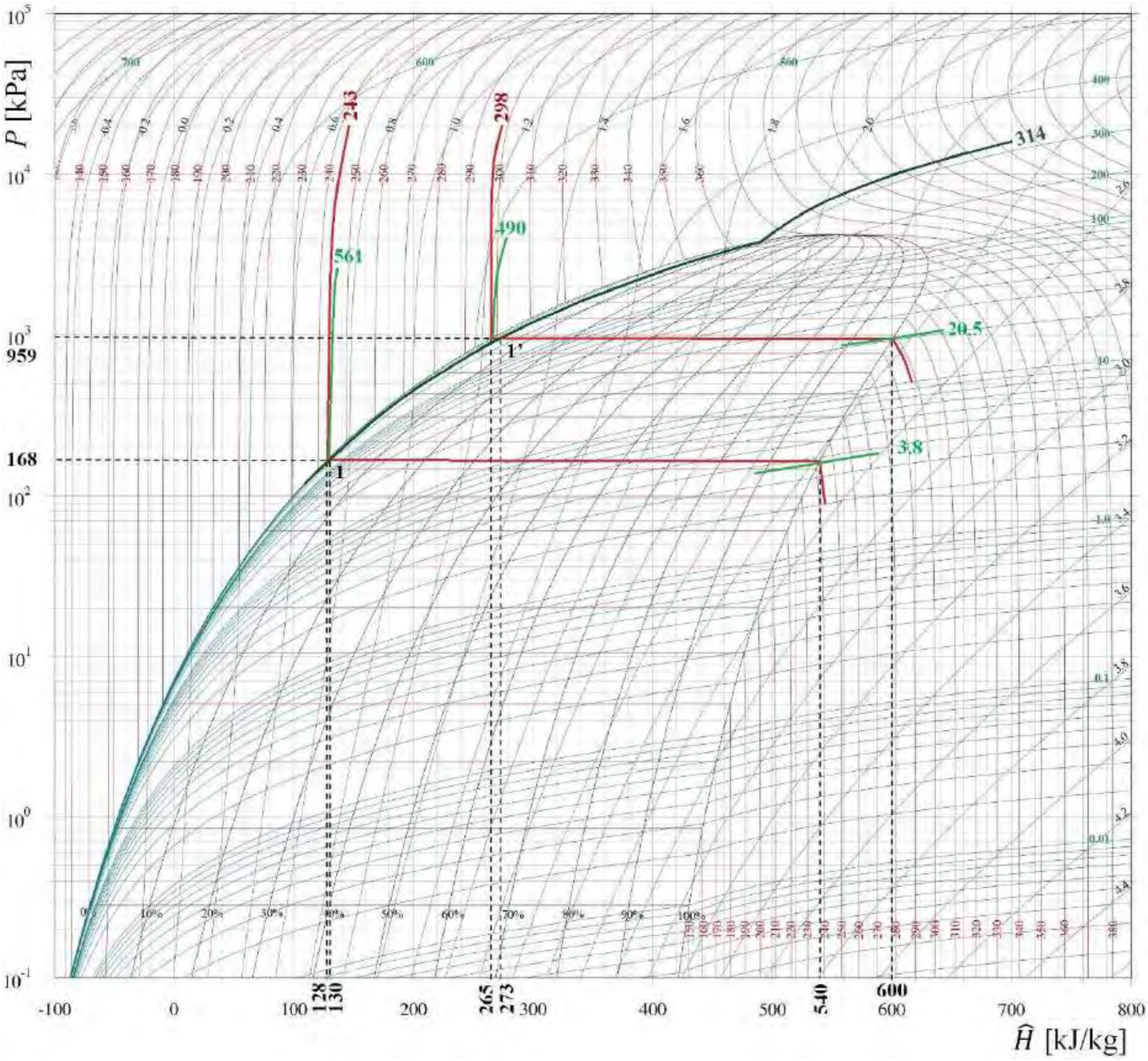
On the other hand, the masses of vapor and liquid, as well as the volumes they occupy, are determined by means of mass and volume balances

$$M_{tot} = M_l + M_v \qquad [1]$$

$$\frac{M_{tot}}{\hat{\rho}_{tot}} = \frac{M_l}{\hat{\rho}_l^{sat}} + \frac{M_v}{\hat{\rho}_v^{sat}} \quad [2]$$

whose combination generates

$$M_v = M_{tot} \frac{\left(\frac{1}{\hat{\rho}_{tot}} - \frac{1}{\hat{\rho}_l^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_v^{sat}} - \frac{1}{\hat{\rho}_l^{sat}}\right)} \quad [3]$$



At -30ºC, the saturated liquid density is $\hat{\rho}_{l_1}^{sat}$=561 kg/m^3 and that of the saturated vapor $\hat{\rho}_{v_1}^{sat}$=3.8 kg/m^3, so

$$M_{v_1} = (11\ \text{kg}) \frac{\left(\frac{1}{314} - \frac{1}{561}\right)}{\left(\frac{1}{3.8} - \frac{1}{561}\right)} = 0.059\ \text{kg}$$

$$M_{l_1} = M_{tot} - M_{v_1} = 11 - 0.059 = 10.941\ \text{kg}$$

and the volumes occupied by these masses will be

$$V_{l_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} = \frac{10.941\ \mathrm{kg}}{561\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.0195\ \mathrm{m}^3$$

$$V_{v_1} = \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} = \frac{0.059\ \mathrm{kg}}{3.8\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.0155\ \mathrm{m}^3$$

At 25ºC the saturated liquid density is $\hat{\rho}_{l_{1'}}^{sat}$= 490 kg/m^3 and that of the vapor $\hat{\rho}_{v_{1'}}^{sat}$= 20.5 kg/m^3

$$M_{v_{1'}} = (11\ \mathrm{kg}) \frac{\left(\frac{1}{314} - \frac{1}{490}\right)}{\left(\frac{1}{20.5} - \frac{1}{490}\right)} = 0.269\ \mathrm{kg}$$

$$M_{l_{1'}} = M_{tot} - M_{v_{1'}} = 11 - 0.269 = 10.731\ \mathrm{kg}$$

$$V_{l_{1'}} = \frac{M_{l_{1'}}}{\hat{\rho}_{l_{1'}}^{sat}} = \frac{10.731\ \mathrm{kg}}{490\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.0219\ \mathrm{m}^3$$

$$V_{v_{1'}} = \frac{M_{v_{1'}}}{\hat{\rho}_{v_{1'}}^{sat}} = \frac{0.269\ \mathrm{kg}}{20.5\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.0131\ \mathrm{m}^3$$

The amounts of liquid and vapor can be checked if the mass balance [1] is combined with the enthalpy balance [4]

$$M_{tot}\hat{H}_{tot} = M_l \hat{H}_l^{sat} + M_v \hat{H}_v^{sat} \qquad [4]$$

with the result that

$$M_v = M_{tot} \frac{\left(\hat{H}_{tot} - \hat{H}_l^{sat}\right)}{\left(\hat{H}_v^{sat} - \hat{H}_l^{sat}\right)}$$

At point 1, the enthalpy of the biphasic mixture is $\hat{H}_{tot_1}$=130 kJ/kg, that of the saturated liquid is $\hat{H}_{l_1}^{sat}$=128 kJ/kg and that of the saturated vapor $\hat{H}_{v_1}^{sat}$=540 kJ/kg; thus

$$M_{v_1} = (11\ \mathrm{kg}) \frac{(130 - 128)}{(540 - 128)} = 0.0534\ \mathrm{kg}$$

while in point 1', $\hat{H}_{tot_{1'}}$=273 kJ/kg, $\hat{H}_{l_{1'}}^{sat}$=265 kJ/kg and $\hat{H}_{v_{1'}}^{sat}$=600 kJ/kg

$$M_{v_{1'}} = (11\ \mathrm{kg}) \frac{(273 - 265)}{(600 - 265)} = 0.263\ \mathrm{kg}$$

Question b. When the mass is reduced to the half (M_{tot}=5.5 kg) the state of the cylinder on the outside will go to a point 2, while, if it is located inside, it will go to a point 2’, where

$$\hat{\rho}_2 = \hat{\rho}_{2'} = \hat{\rho}_{tot} = \frac{M_{tot}}{V_{cylinder}} = \frac{5.5\ \mathrm{kg}}{35\ \mathrm{L}} = 0.157\ \frac{\mathrm{kg}}{\mathrm{L}} \quad \rightarrow \quad 0.157\ \frac{\mathrm{kg}}{\mathrm{L}} \times \frac{1000\ \mathrm{L}}{1\ \mathrm{m}^3} = 157\ \frac{\mathrm{kg}}{\mathrm{m}^3}$$

It is observed that at these points there still are biphasic mixtures, that $\hat{\rho}_{l_1}^{sat}$=$\hat{\rho}_{l_2}^{sat}$=561 kg/m^3, $\hat{\rho}_{v_1}^{sat}$ = $\hat{\rho}_{v_2}^{sat}$= 3.8 kg/m^3, $\hat{\rho}_{l_{1'}}^{sat}$ = $\hat{\rho}_{l_{2'}}^{sat}$=490 kg/m^3 and that $\hat{\rho}_{v_{1'}}^{sat}$ = $\hat{\rho}_{v_{2'}}^{sat}$ =20.5 kg/m^3. Applying equations [1-3]

$$\left.\begin{aligned}
M_{v_2} &= (5.5\ \mathrm{kg})\frac{\left(\frac{1}{157}-\frac{1}{561}\right)}{\left(\frac{1}{3.8}-\frac{1}{561}\right)} = 0.0965\ \mathrm{kg} \\
M_{l_2} &= M_{tot} - M_{v_2} = 5.5 - 0.0965 = 5.4035\ \mathrm{kg} \\
V_{l_2} &= \frac{M_{l_2}}{\hat{\rho}_{l_2}^{sat}} = \frac{5.4035\ \mathrm{kg}}{561\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.0096\ \mathrm{m}^3 \\
V_{v_2} &= \frac{M_{v_2}}{\hat{\rho}_{v_2}^{sat}} = \frac{0.0965\ \mathrm{kg}}{3.8\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.0254\ \mathrm{m}^3
\end{aligned}\right\}\ \text{outside}$$

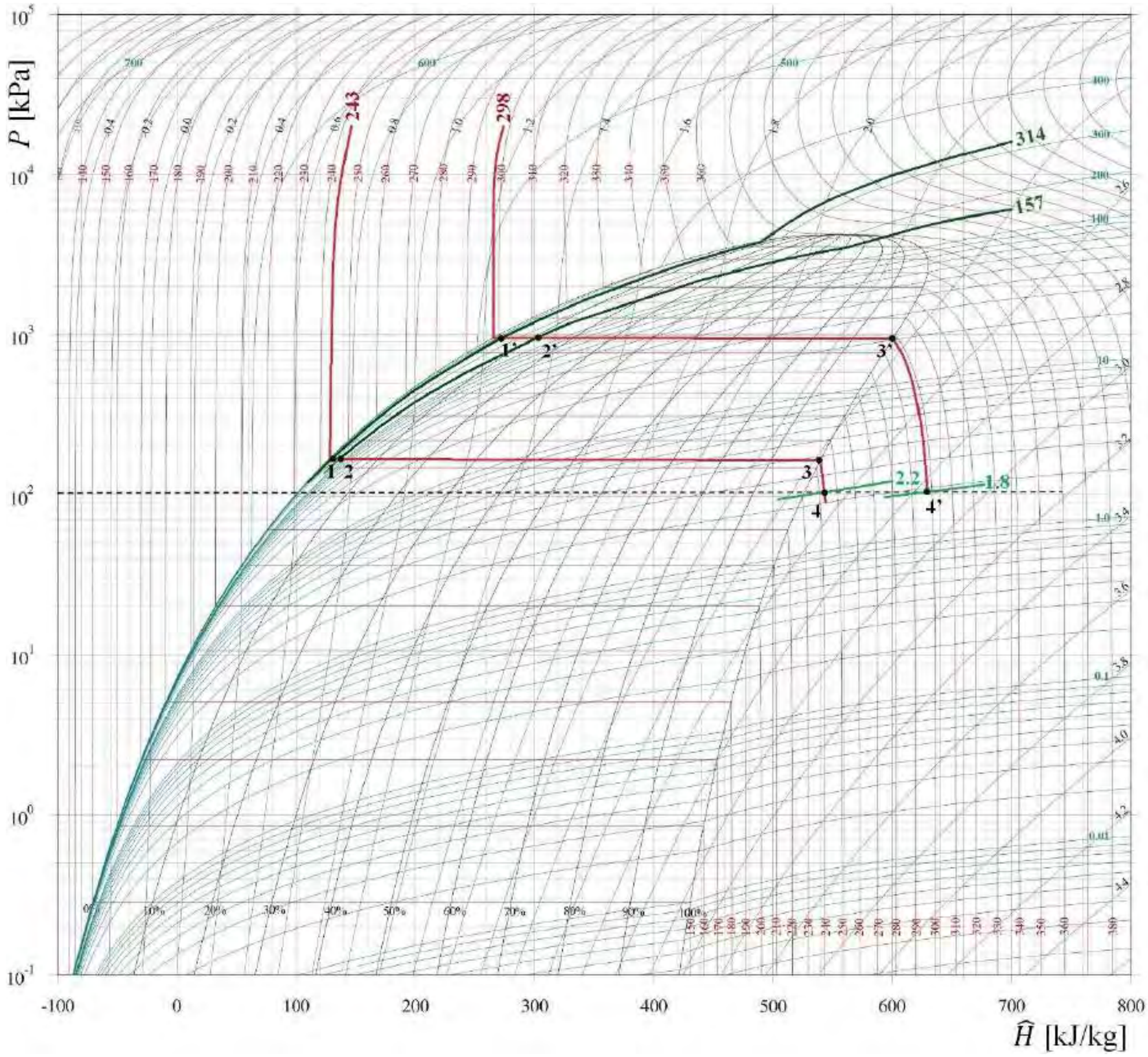
$$\left.\begin{aligned}
M_{v_{2'}} &= (5.5\ \mathrm{kg})\frac{\left(\frac{1}{157}-\frac{1}{490}\right)}{\left(\frac{1}{20.5}-\frac{1}{490}\right)} = 0.5093\ \mathrm{kg} \\
M_{l_{2'}} &= M_{tot} - M_{v_{2'}} = 5.5 - 0.5093 = 4.9907\ \mathrm{kg} \\
V_{l_{2'}} &= \frac{M_{l_{2'}}}{\hat{\rho}_{l_{2'}}^{sat}} = \frac{4.9907\ \mathrm{kg}}{490\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.0102\ \mathrm{m}^3 \\
V_{v_{2'}} &= \frac{M_{v_{2'}}}{\hat{\rho}_{v_{2'}}^{sat}} = \frac{0.5093\ \mathrm{kg}}{20.5\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.0248\ \mathrm{m}^3
\end{aligned}\right\}\ \text{inside}$$

Later, when the liquid is exhausted, the state of the cylinder will go to points 3 and 3’, where there is only saturated vapor of density $\hat{\rho}_{v_1}^{sat}$ = $\hat{\rho}_{v_2}^{sat}$ = $\hat{\rho}_{v_3}^{sat}$ =3.8 kg/m^3 at -30ºC and $\hat{\rho}_{v_{1'}}^{sat}$ = $\hat{\rho}_{v_{2'}}^{sat}$ = $\hat{\rho}_{v_{3'}}^{sat}$ =20.5 kg/m^3 at 25ºC. Therefore, their masses will be

$$M_3 = M_{v_3} = V_{tot}\hat{\rho}_{v_3}^{sat} = (0.035\ \mathrm{m}^3)\left(3.8\ \frac{\mathrm{kg}}{\mathrm{m}^3}\right) = 0.133\ \mathrm{kg}$$

$$M_{3'} = M_{v_{3'}} = V_{tot}\hat{\rho}_{v_{3'}}^{sat} = (0.035\ \text{m}^3)\left(20.5\ \frac{\text{kg}}{\text{m}^3}\right) = 0.7175\ \text{kg}$$

Finally, no fuel will come out spontaneously when the cylinder reaches the points 4 or 4’, which are at the same pressure than the ambient one (1 atm ≈ 100 kPa). Then, the vapor density outside will be 2.2 kg/m^3, and that inside of 1.8 kg/m^3, the same ones than those determined by the ideal gas equation



$$\hat{\rho}_{v_4} = \frac{\mathfrak{M}P_4}{RT_1} = \frac{\left(44.09\,\frac{\text{g}}{\text{mol-g}}\right)(1\ \text{atm})}{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(243\ \text{K})} = 2.21\,\frac{\text{g}}{\text{L}} = 2.21\,\frac{\text{kg}}{\text{m}^3}$$

$$\hat{\rho}_{v_{4'}} = \frac{\mathfrak{M}P_{4'}}{RT_{1'}} = \frac{\left(44.09\,\frac{\text{g}}{\text{mol-g}}\right)(1\ \text{atm})}{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(298\ \text{K})} = 1.8\,\frac{\text{g}}{\text{L}} = 1.8\,\frac{\text{kg}}{\text{m}^3}$$

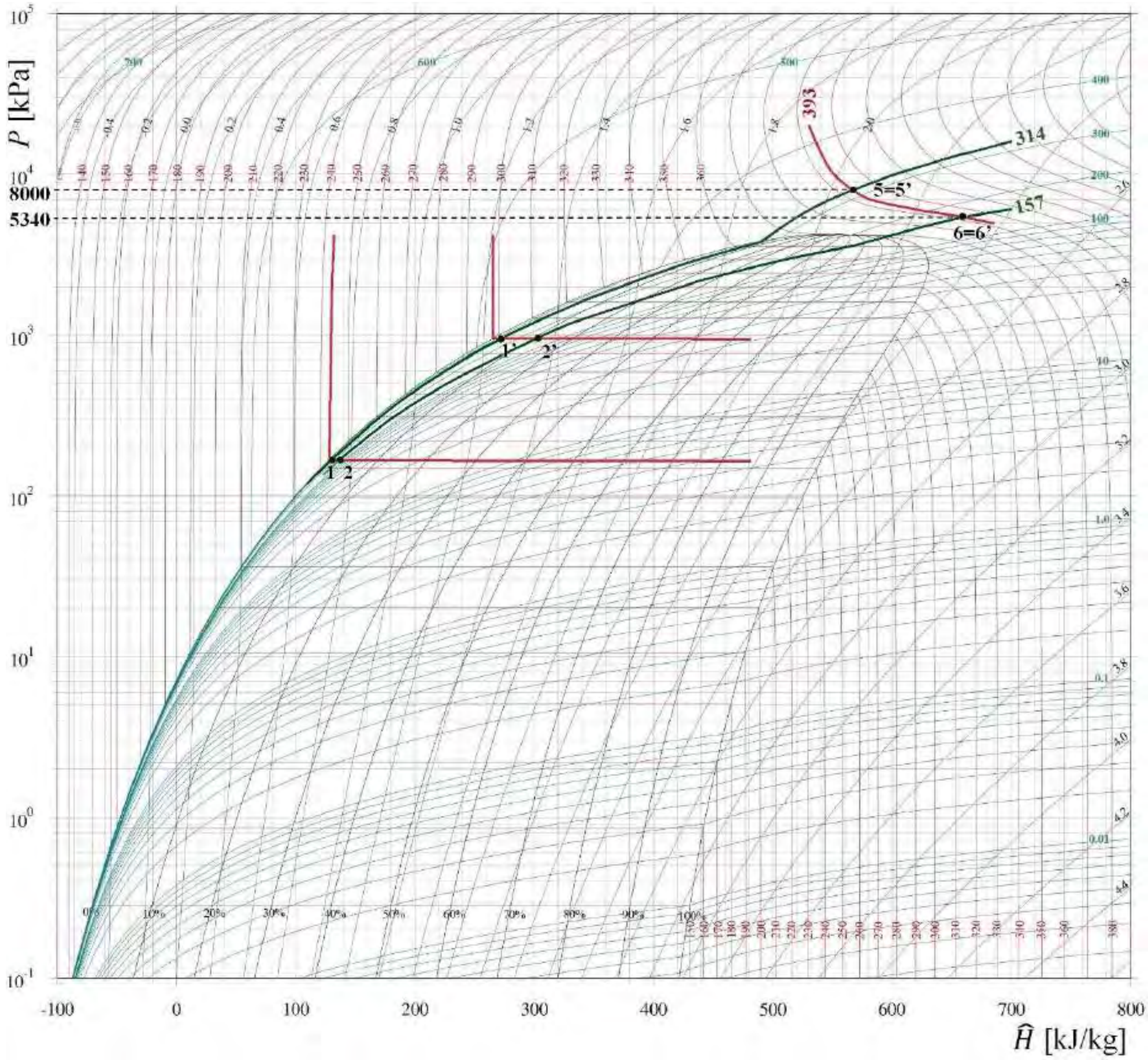
and the remaining masses of vapor in the cylinder are calculated as

$$M_4 = M_{v_4} = V_{tot}\hat{\rho}_{v_4} = (0.035\ \mathrm{m}^3)\left(2.21\ \frac{\mathrm{kg}}{\mathrm{m}^3}\right) = 0.07735\ \mathrm{kg}$$

$$M_{4'} = M_{v_{4'}} = V_{tot}\hat{\rho}_{v_{4'}} = (0.035\ \mathrm{m}^3)\left(1.8\ \frac{\mathrm{kg}}{\mathrm{m}^3}\right) = 0.063\ \mathrm{kg}$$

Question c. Given that in the initial conditions the density in the cylinder was of 314 kg/m^3, the new state will be found at the intersection of this isochore with the isotherm

$$T(\mathrm{K}) = 120℃ + 273 = 393\ \mathrm{K}$$



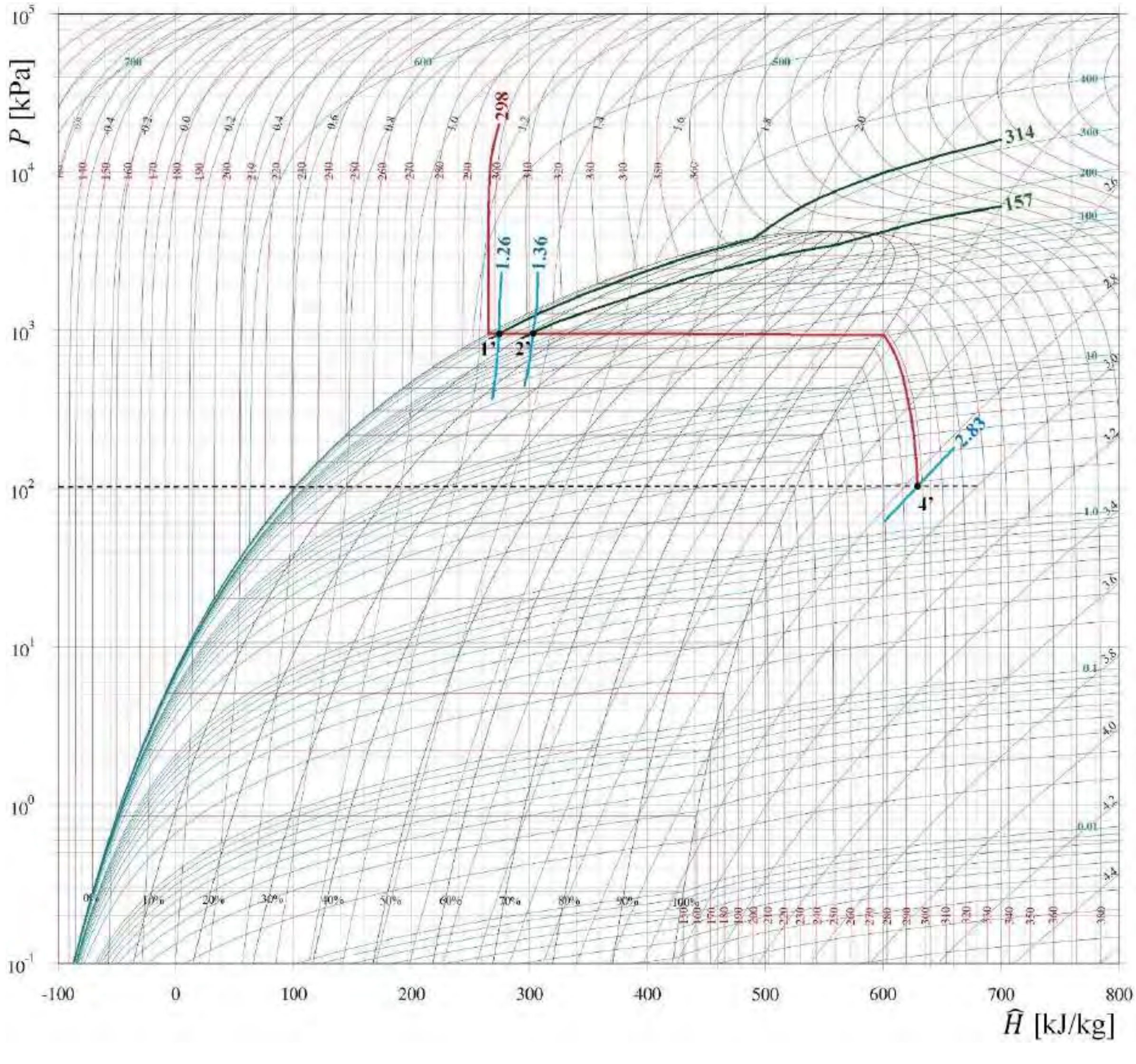
and it is observed that it is a supercritical fluid (gas) at 8000 kPa.

On the other hand, when the cylinder is at half load, its density will be of 157 kg/m^3, and graphically, its intersection with the 393 K isotherm will occur at 5340 kPa, also in the thermodynamic region corresponding to gases or supercritical fluids.

Question d. The heat taken up to the moment in which the cylinder is at half load (isothermal process) will be due to two causes: the transit of half of the load (5.5 kg) from point 1' to point 2' and the transit of the other half of the load (5.5 kg) from point 1' to consumption conditions, which are not specified in the statement of the problem and have to be supposed. For simplicity, it will be assumed that propane is employed as vapor at 1 atm and 25ºC (conditions at 4'); thus, $T_{1'}=T_{2'}=T_{4'}$ and

$$\Delta Q=\frac{M_{1'}}{2}\int_{1'}^{2'} T\mathrm{d}\hat{S}\ +\frac{M_{1'}}{2}\int_{1'}^{4'} T\mathrm{d}\hat{S}$$

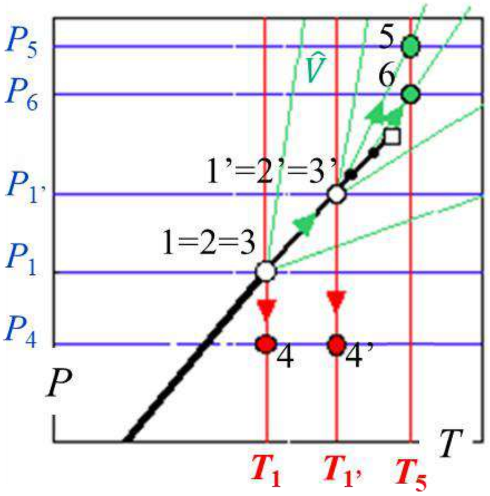
$$\Delta Q=\frac{M_{1'}}{2}T_{1'}\left(\hat{S}_{2'}-\hat{S}_{1'}\right)+\frac{M_{1'}}{2}T_{1'}\left(\hat{S}_{4'}-\hat{S}_{1'}\right)$$

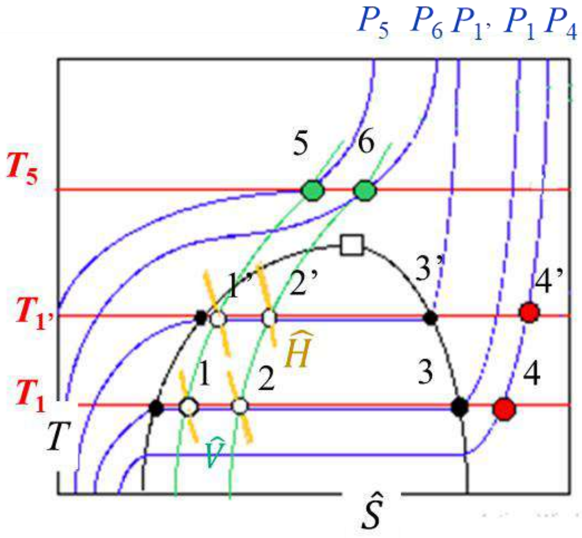


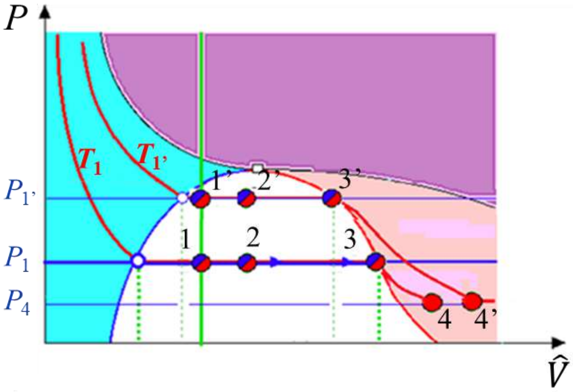
$$\Delta Q= \ (5.5\ \mathrm{kg})(298\ \mathrm{K})\left(1.36\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}-1.26\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right)+$$

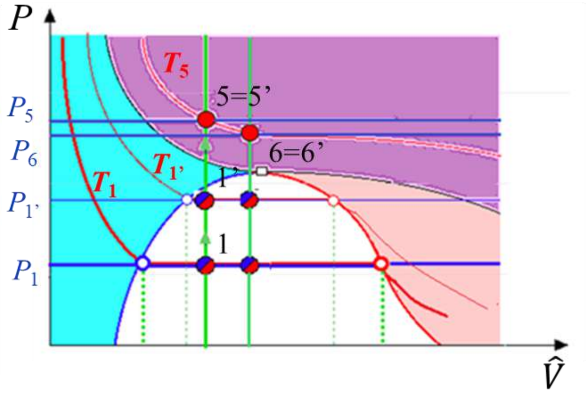
$$+(5.5\ \mathrm{kg})(298\ \mathrm{K})\left(2.83\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}-1.26\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right)=2737.13\ \mathrm{kJ}$$

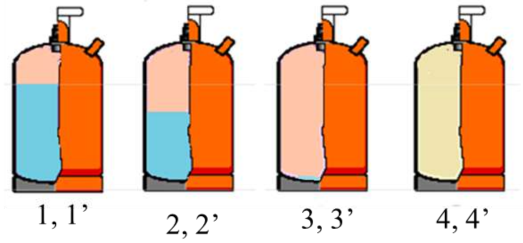
Regarding the **qualitative graphic representations**

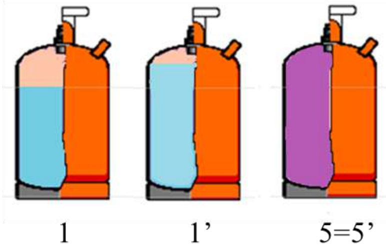












4.7. A 100 m^3 cryogenic tank contains 1 ton of propane at -50ºC. In the context of a deterministic safety study, it is desired to evaluate the effect of a refrigeration system failure at the aforementioned conditions, which would lead to a temperature of 30ºC. By using a specific $PH(T,\rho,S)$ diagram for this hydrocarbon:

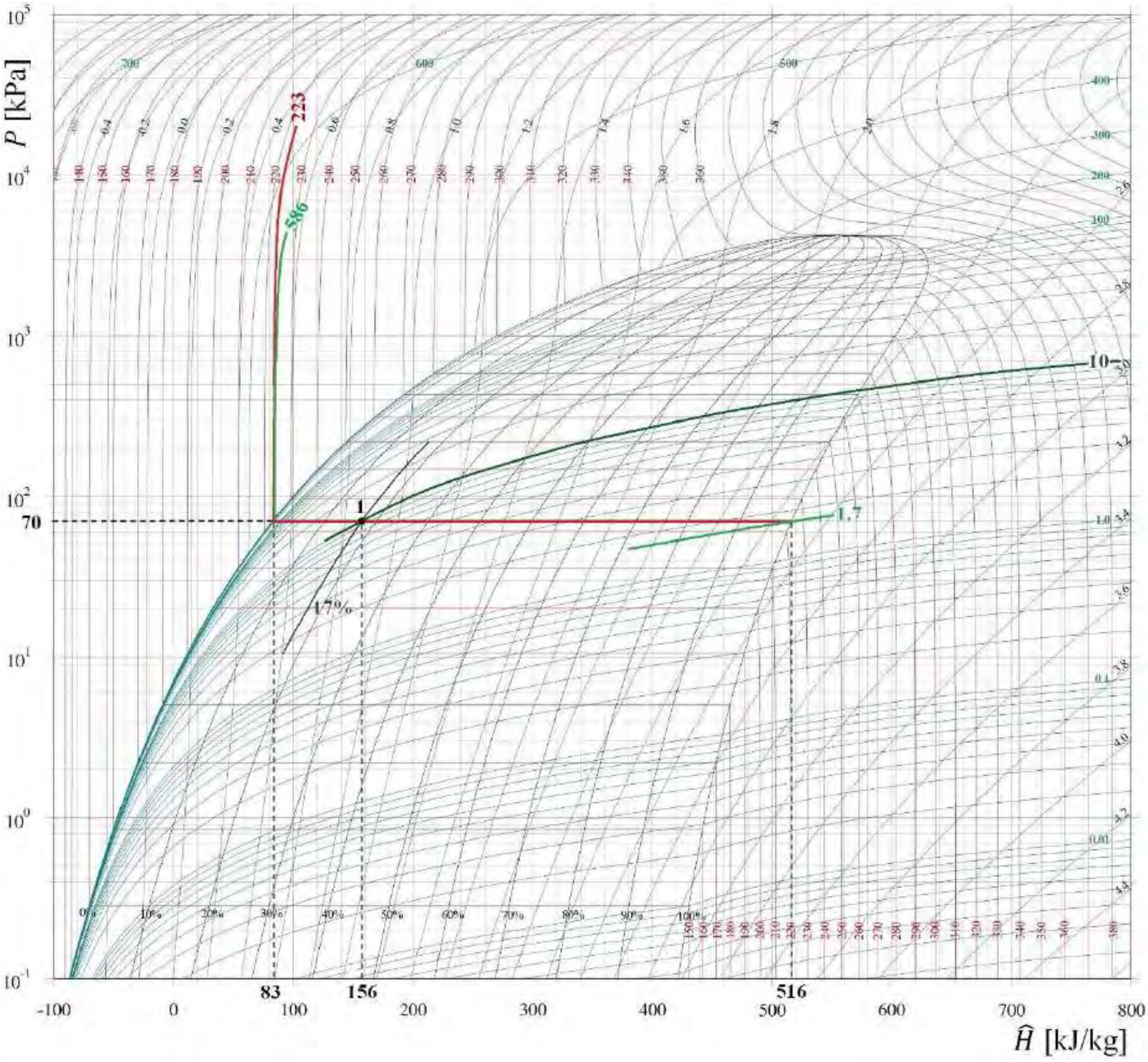
a) Describe the thermodynamic state in the tank under normal conditions.

b) Under the described incident conditions.

c) Calculate the heat that would have to be removed from the tank to return to the initial conditions.

Qualitatively represent the phenomenon in $PT(V)$, $PV(T,S,H)$ and $PS(T,H,V)$ diagrams and in the generalized one $z(P_r,T_r)$.

Question a. By resorting to figure V.8 of this book's appendix V



point 1 (initial conditions) will correspond to the intersection of the isochore

$$\hat{\rho}_1 = \hat{\rho}_{tot} = \frac{M_{tot}}{V_{tank}} = \frac{1000\ \text{kg}}{100\ \text{m}^3} = 10\ \frac{\text{kg}}{\text{m}^3}$$

with the isotherm

$$T_1(\text{K}) = -50^{\circ}\text{C} + 273 = 223\ \text{K}$$

At this point, it is observed that there is a mixture of liquid and vapor at 70 kPa with an approximate quality of 17% (17% of the feed is vapor, that is to say, 0.17×1000 kg =170 kg). It can also be obtained by combining the mass and volume balances

$$M_{tot} = M_l + M_v$$

$$\frac{M_{tot}}{\hat{\rho}_{tot}} = \frac{M_l}{\hat{\rho}_l^{sat}} + \frac{M_v}{\hat{\rho}_v^{sat}}$$

obtaining

$$M_v = M_{tot}\frac{\left(\frac{1}{\hat{\rho}_{tot}} - \frac{1}{\hat{\rho}_l^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_v^{sat}} - \frac{1}{\hat{\rho}_l^{sat}}\right)}$$

The diagram shows that the saturated liquid density is of 586 kg/m^3 and that of the saturated vapor is of 1.7 kg/m^3, so

$$M_v = (1000\ \text{kg})\frac{\left(\frac{1}{10} - \frac{1}{586}\right)}{\left(\frac{1}{1.7} - \frac{1}{586}\right)} = 167.59\ \text{kg}$$

$$M_l = M_{tot} - M_v = 1000 - 167.59 = 832.41\ \text{kg}$$

Masses which occupy the volumes

$$V_l = \frac{M_l}{\hat{\rho}_l^{sat}} = \frac{832.41\ \text{kg}}{586\ \frac{\text{kg}}{\text{m}^3}} = 1.42\ \text{m}^3$$

$$V_v = \frac{M_v}{\hat{\rho}_v^{sat}} = \frac{167.59\ \text{kg}}{1.7\ \frac{\text{kg}}{\text{m}^3}} = 98.58\ \text{m}^3$$

The calculation can be approximately checked by combining the enthalpy balance ($M_{tot}\hat{H}_{tot} = M_l\hat{H}_l^{sat} + M_v\hat{H}_v^{sat}$) with the mass balance, after reading from the graph that the specific enthalpy of the mixture is 156 kJ/kg, that of the saturated liquid is 83 kJ/kg and that of the saturated vapor 516 kJ/kg

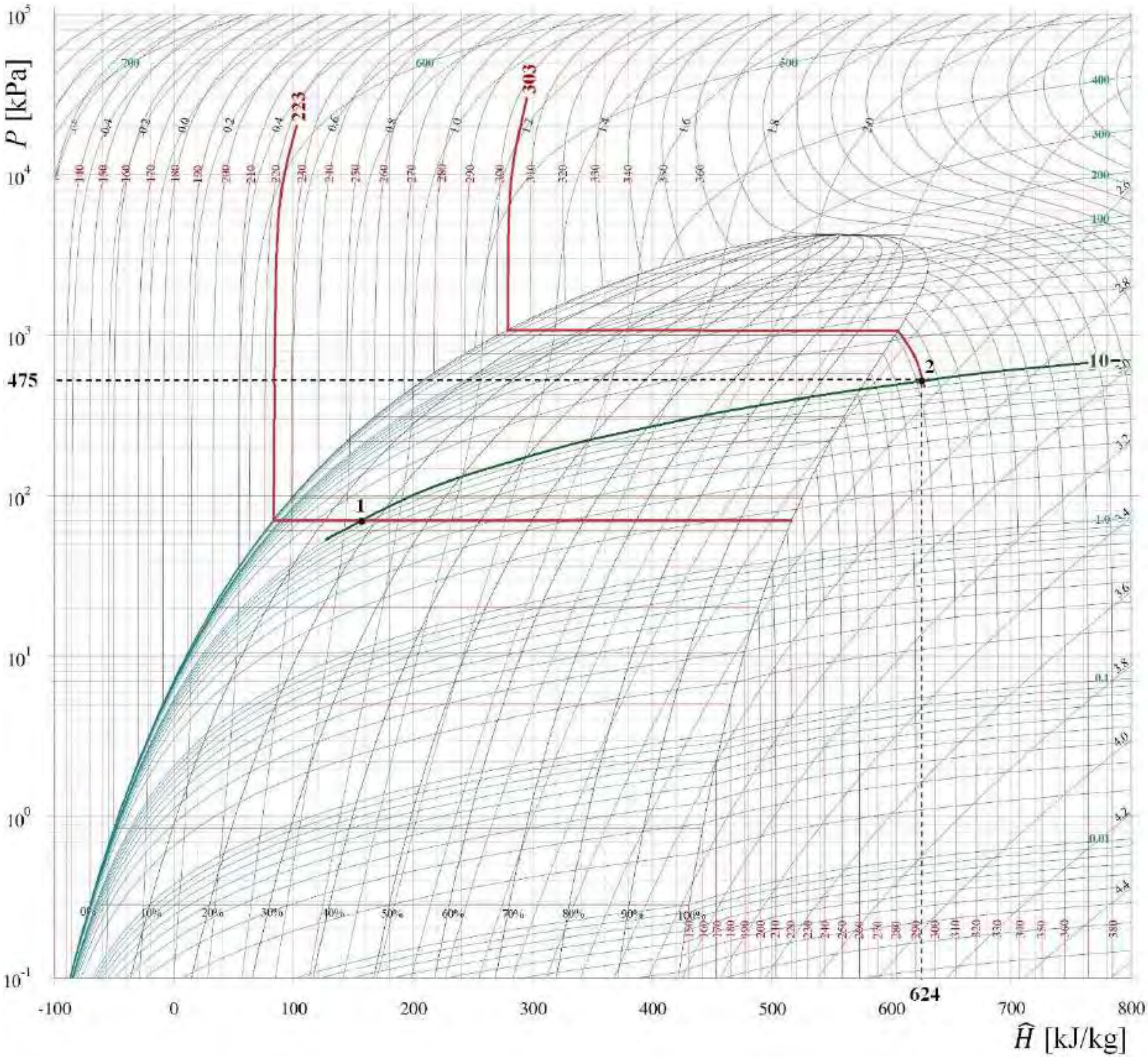
$$M_v = M_{tot}\frac{\left(\hat{H}_{tot} - \hat{H}_l^{sat}\right)}{\left(\hat{H}_v^{sat} - \hat{H}_l^{sat}\right)} = (1000\ \text{kg})\frac{(156-83)}{(516-83)} = 168.6\ \text{k}$$

value very close to that previously obtained.

Question b. Since the mass of propane and the volume of the tank do not change, the new state 2 of the system will be found by the intersection of the 10 kg/m^3 isochore with the isotherm

$$T_2(\mathrm{K}) = 30\text{°C} + 273 = 303\ \mathrm{K}$$

Intersection corresponding to the single-phase region of superheated vapor (the temperature is below the critical one) and to a pressure of 475 kPa.



Question c. The heat to be removed will coincide, in absolute value, with that gained by the fluid during heating

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \Delta\hat{Q}_{21} = \int_1^2 T\mathrm{d}\hat{S}$$

integral that should be solved numerically, taking values of temperature and entropy along the isochore. However, in this case (constant density) this calculation can be avoided, since according to section b of reference problem 0.3

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \hat{V}\mathrm{d}P \quad \xrightarrow{\hat{V}\ constant} \quad \Delta\hat{H} = \Delta\hat{Q} + \hat{V}\Delta P$$

and therefore

$$\Delta\hat{Q}_{21}=\Delta\hat{H}_{21} - \hat{V}\Delta P_{21} = \left(\hat{H}_2 - \hat{H}_1\right) - \frac{(P_2 - P_1)}{\hat{\rho}_{tot}}$$

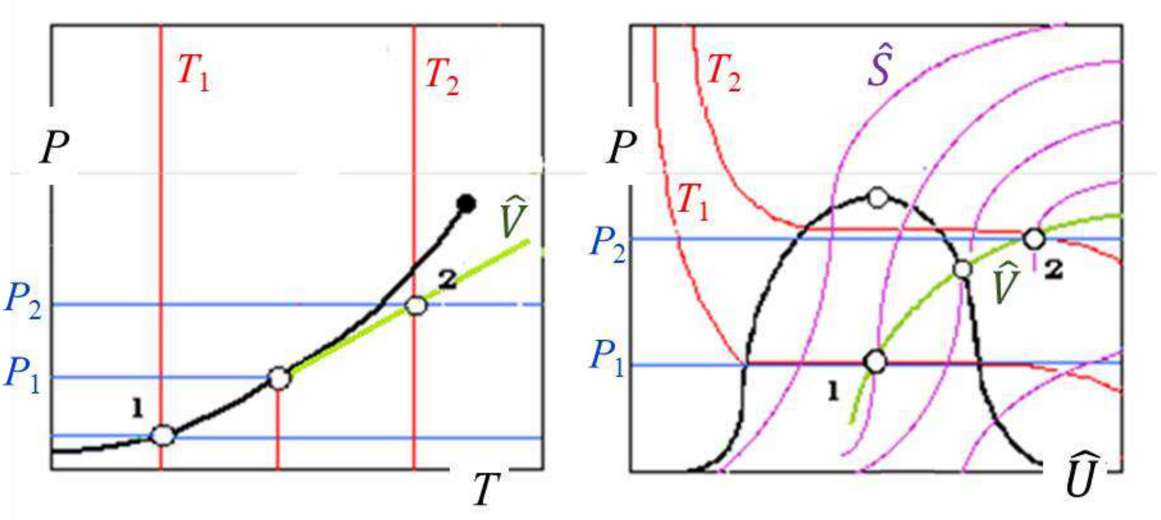
By introducing the data read in the figure, it is obtained

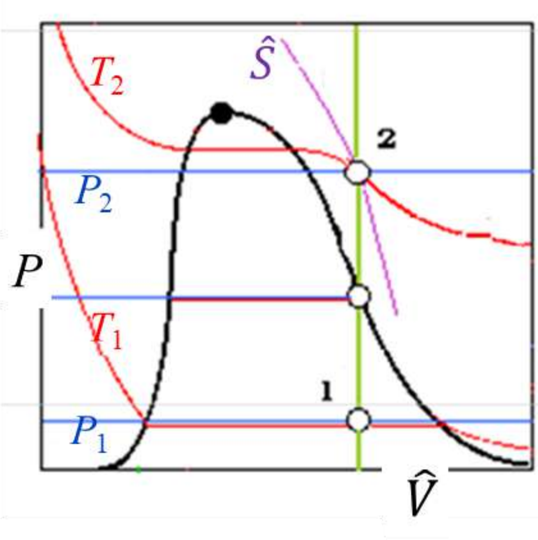
$$\Delta\hat{Q}_{21} = \left(624\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 156\frac{\mathrm{kJ}}{\mathrm{kg}}\right) - \frac{(475\ \mathrm{kPa} - 70\ \mathrm{kPa})}{\left(10\ \frac{\mathrm{kg}}{\mathrm{m}^3}\right)} = 427.5\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

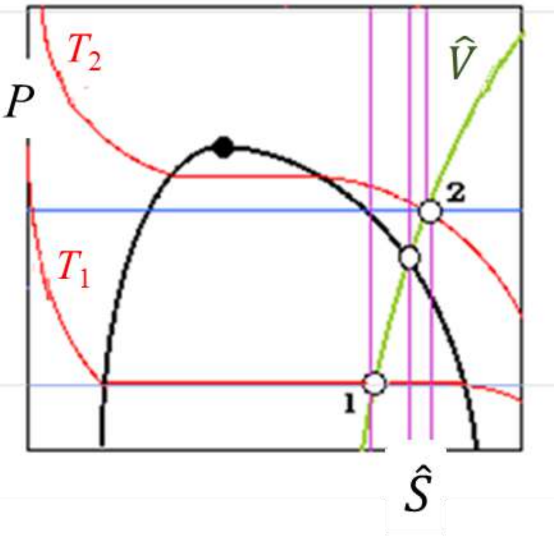
a value which extended to the whole mass gives a total heat of

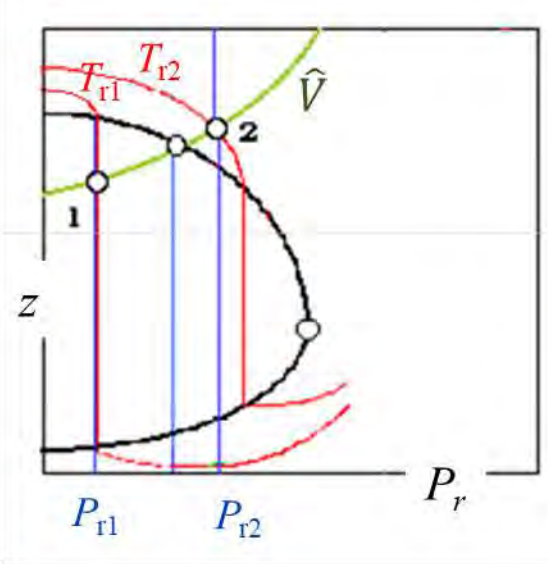
$$\Delta Q_{21} = M_{tot}\Delta\hat{Q}_{21} = 1000\ \mathrm{kg}\left(427.5\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 4.275 \cdot 10^6\ \mathrm{kJ}$$

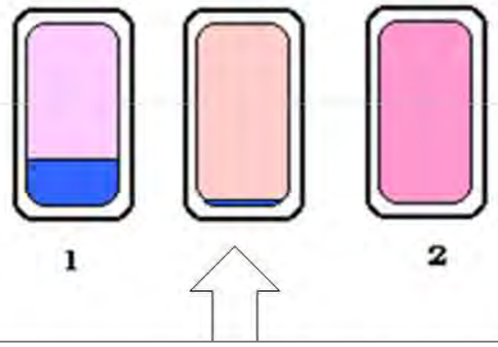
Finally, the **qualitative graphic representations** are











Strictly speaking, crossing the equilibrium line (saturated vapor) means the exhaustion of the liquid phase by the evaporation of a differential (mathematical) element assimilable to the last liquid drop.

4.8. A spherical tank with an internal volume of 1000 m^3 contains butane, which is initially kept at 27ºC and 25 atm. The temperature could increase up to 150ºC due to accidental external causes.

a) Determine the inner and outer diameter and the mass of the spherical tank shell if the wall thickness is 2 cm and the material density is of 6 g/cm^3.

b) Calculate the pressure supported by the tank in the final situation using a specific diagram *PH*(*T*,*ρ*,*S*) of butane.

c) Calculate the pressure exerted on its support base if the total surface area of this base is of 100 m^2.

d) Estimate the heat absorbed by the butane to uniformly reach the final temperature.

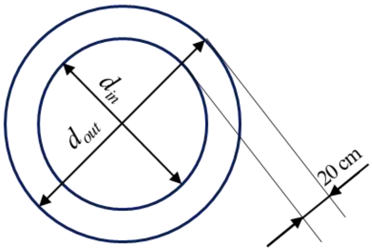
e) Qualitatively represent the evolution of the fuel in *PT*, *PV*(*T*), *PU*(*T*) and *z*(*T$_r$*,*P$_r$*) diagrams.

f) Solve the problem by employing the Corresponding States Principle and its generalized charts.

Question a. By geometric considerations, the inner diameter of the tank is

$$\frac{\pi}{6}d_{in}^3 = V_{tank} \quad \rightarrow \quad d_{in} = \sqrt[3]{\frac{6V_{tank}}{\pi}} = \sqrt[3]{\frac{6(1000\ \mathrm{m}^3)}{\pi}} = 12.4\ \mathrm{m}$$

and obviously the outer diameter will be the inner one plus twice the thickness: 12.4 m + 2(0.02 m) = 12.44 m



With these data, the volumen of the spherical shell is

$$V_{shell} = \frac{\pi}{6}(d_{out}^3 - d_{in}^3) = \frac{\pi}{6}[(12.44\ \mathrm{m})^3 - (12.4\ \mathrm{m})^3] = 9.692\ \mathrm{m}^3$$

and combining this volume with the material density (converted into kg/m^3 with the factors of appendix I), the mass of the shell is obtained

$$6\ \frac{\mathrm{g}}{\mathrm{cm}^3} \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}} \times \left(\frac{100\ \mathrm{cm}}{1\ \mathrm{m}}\right)^3 = 6000\ \frac{\mathrm{kg}}{\mathrm{m}^3}$$

$$M_{shell} = V_{shell}(\hat{\rho}_{material}) = 9.692\ \mathrm{m}^3 \left(6000\ \frac{\mathrm{kg}}{\mathrm{m}^3}\right) = 58152\ \mathrm{kg}$$

Question b. Figure V.9 of appendix V is a specific *PH* diagram for butane. In it, the normal state of the deposit (1) is located by the intersection of the isotherm

$$T_1(\mathrm{K}) = 27°\mathrm{C} + 273 = 300\ \mathrm{K}$$

with the isobar

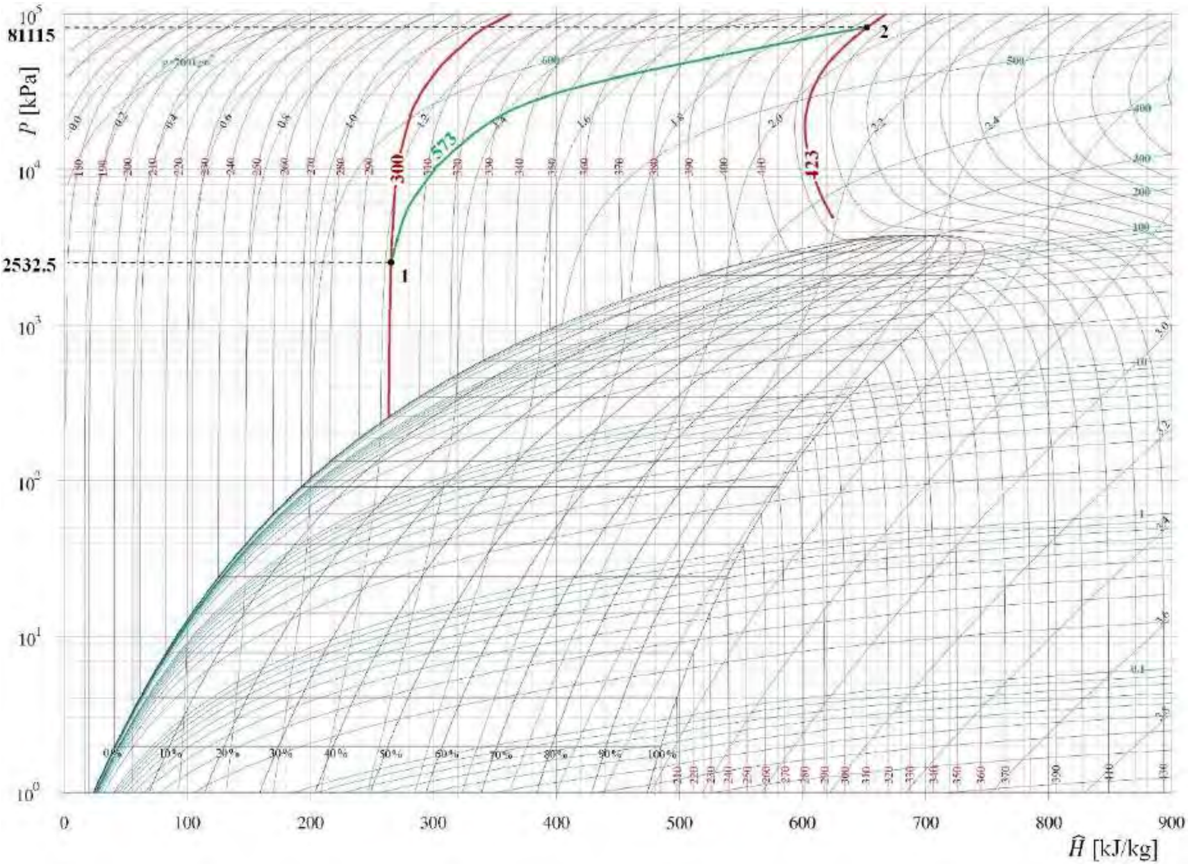
$$P_1 = 25\ \mathrm{atm} \times \frac{1.013\ \mathrm{bar}}{1\ \mathrm{atm}} \times \frac{100\ \mathrm{kPa}}{1\ \mathrm{bar}} = 2532.5\ \mathrm{kPa}$$

Using this datum, the density is determined by graphic interpolation (573 kg/m^3). Since it is not stated that the deposit undergoes morphological changes, this density will remain constant ($\hat{\rho}_1 = \hat{\rho}_2 = \hat{\rho}_{butane}$), and the intersection of the isochore with the isotherm

$$T_2(\mathrm{K}) = 150°\mathrm{C} + 273 = 423\ \mathrm{K}$$

will allow the graphical determination of the new state 2, and the reading of the new pressure, which is 81115 kPa, i.e.

$$811.15\ \mathrm{bar} \times \frac{0.987\ \mathrm{atm}}{1\ \mathrm{bar}} = 800.6\ \mathrm{atm}$$



Question c. With the density of the previous question, the butane mass can now be calculated as

$$M_{butane} = V_{tank}(\hat{\rho}_{butane}) = 1000\ \mathrm{m}^3 \left(573\ \frac{\mathrm{kg}}{\mathrm{m}^3}\right) = 573000\ \mathrm{kg}$$

and the pressure exerted on the 100 m^2 support base will be

$$P = \frac{(M_{butane} + M_{shell})\mathbb{g}}{100\ \mathrm{m}^2} = \frac{(573000\ \mathrm{kg}+58152\ \mathrm{kg})\left(9.80665\frac{\mathrm{m}}{\mathrm{s}^2}\right)}{100\ \mathrm{m}^2} = 61895\ \mathrm{Pa}$$

Question d. The heat absorbed will be given by

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \Delta\hat{Q}_{21} = \int_1^2 T\mathrm{d}\hat{S}$$

an expression that requires numerical integration. However, when density remains constant, one of the fundamental thermodynamic relations says that

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \hat{V}\mathrm{d}P \quad \xrightarrow{\hat{V}\ constant} \quad \Delta\hat{H} = \Delta\hat{Q} + \hat{V}\Delta P$$

hence

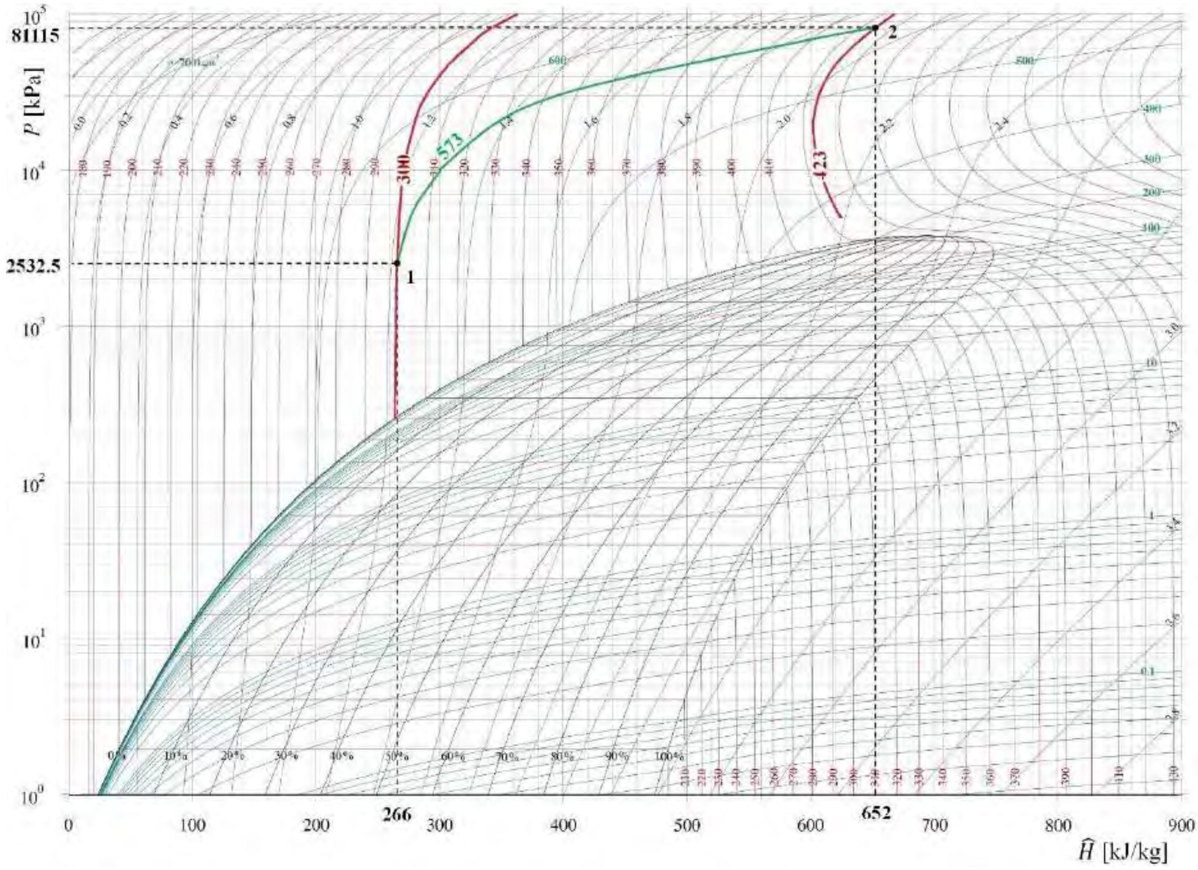
$$\Delta\hat{Q}_{21} = \Delta\hat{H}_{21} - \hat{V}\Delta P_{21} = \left(\hat{H}_2 - \hat{H}_1\right) - \frac{(P_2 - P_1)}{\hat{\rho}_{butane}} = \Delta\hat{U}_{21}$$

These enthalpies can also be read in figure V.9, being 652 kJ/kg at point 2 and 266 kJ/kg at point 1, which leads to

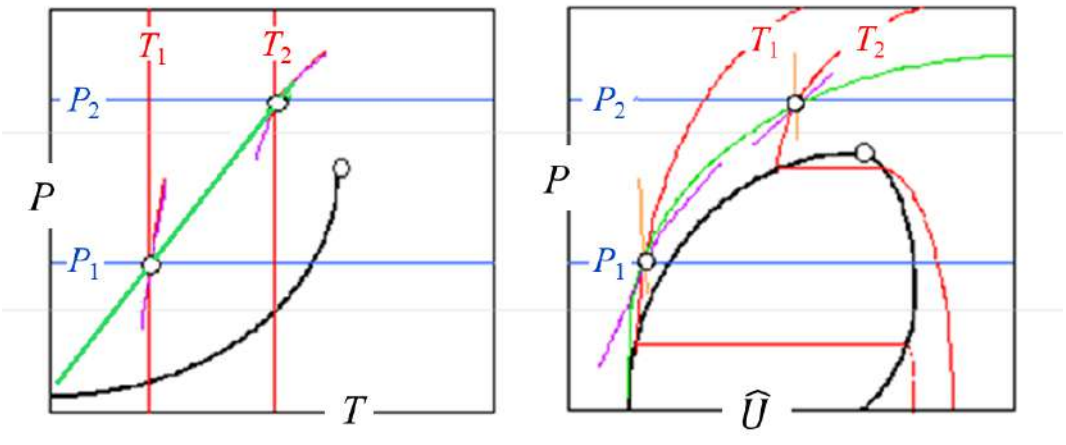
$$\Delta\hat{Q}_{21} = \left(652\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 266\frac{\mathrm{kJ}}{\mathrm{kg}}\right) - \frac{(81115\ \mathrm{kPa} - 2532.5\ \mathrm{kPa})}{\left(573\ \frac{\mathrm{kg}}{\mathrm{m}^3}\right)} = 248.86\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

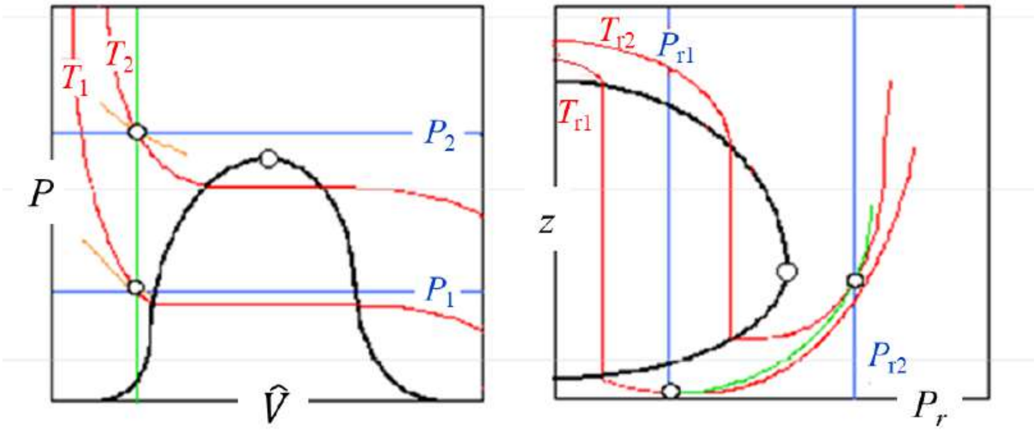
value that, extended to the whole mass, turns out to be

$$\Delta Q_{21} = M_{butane}\Delta\hat{Q}_{21} = 573000\ \mathrm{kg}\left(248.86\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 142.6 \cdot 10^6\ \mathrm{kJ}$$



Question e. The qualitative representations in the proposed diagrams are





Question f. According to the Corresponding States Principle (sections a and d of the reference problem 0.8)

$$P\tilde{V} = zRT$$

$$\left.\begin{array}{ll} z = \mathrm{f}(T_r, P_r) & \text{if} \quad z_c = 0.27 \\ z = \mathrm{f}(T_r, P_r, z_c) & \text{if} \quad z_c \neq 0.27 \end{array}\right\}$$

where $\mathrm{f}(T_r , P_r)$ is given by figure IV.1 of this book's appendix IV, and $\mathrm{f}(T_r , P_r, z_c)$ is expressed as $(z)_{z_c=0.27}+[z_c-0.27]\Psi_z$, being Ψ_z correction functions dependent on reduced temperature and pressure as well. For butane (appendix II)

$$P_c = 37.5 \text{ atm}$$
$$T_c = 425.2 \text{ K}$$

$$z_c=0.274$$

Since the critical compressibility is very close to 0.27, the Ψ_z corrections will be not taken into account.

The procedure to follow could be:

- Estimate the reduced temperature and pressure at point 1

$$T_{r1} = \frac{T_1}{T_c} = \frac{300 \text{ K}}{425.2 \text{ K}} = 0.7055 \qquad ; \qquad P_{r1} = \frac{P_1}{P_c} = \frac{25 \text{ atm}}{37.5 \text{ atm}} = 0.6667$$

- Obtain z_1 from figure IV.1 and calculate the molar volume as z_1RT_1/P_1

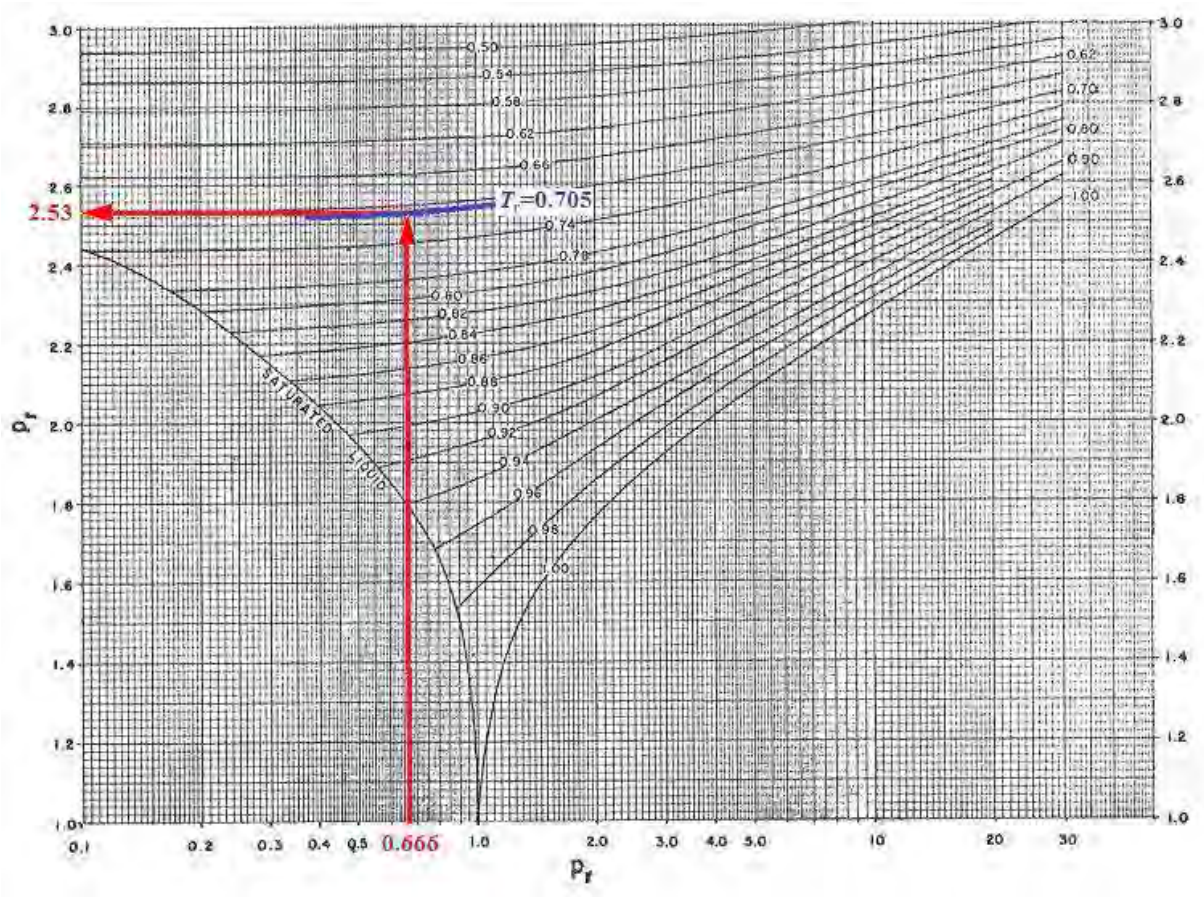
- Since the molar volume does not change during the process, $\tilde{V}_2 = \tilde{V}_1$. The reduced pressure at point 2 and its compressibility will be related by

$$z_2 = \frac{P_c\tilde{V}_2}{RT_2}P_{r2}$$

- Represent this line in figure IV.1 and find the point where it intersects the isotherm

$$T_{r2} = \frac{T_1}{T_c} = \frac{423\ \text{K}}{425.2\ \text{K}} = 0.9948$$

However, there is a major drawback: Figure IV.1 does not display reduced temperatures below 0.75. It is necessary to resort to another figure in this book's appendix IV, the IV.13 one, which covers the range 0.3≤ T_r ≤1.0. It is not a representation of compressibility factors, but of reduced densities (ρ_r=ρV_c).



As can be seen, for T_{r1}=0.7055 and P_{r1}=0.666, ρ_{r1}=2.53, which expressed as mass density will be

$$\hat{\rho}_1 = \frac{2.53}{\left(255\ \frac{\text{cm}^3}{\text{mol-g}}\right)\times\left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^3\times\frac{1\ \text{mol-g}}{58.12\ \text{g}}\times\frac{1000\ \text{g}}{1\ \text{kg}}} = 576.6\ \frac{\text{kg}}{\text{m}^3}$$

value very close to that obtained with the *PH* diagram of butane. The hydrocarbon mass is now

$$M_{butane} = V_{tank}(\hat{\rho}_{butane}) = 1000\ \text{m}^3\left(576.6\ \frac{\text{kg}}{\text{m}^3}\right) = 576600\ \text{kg}$$

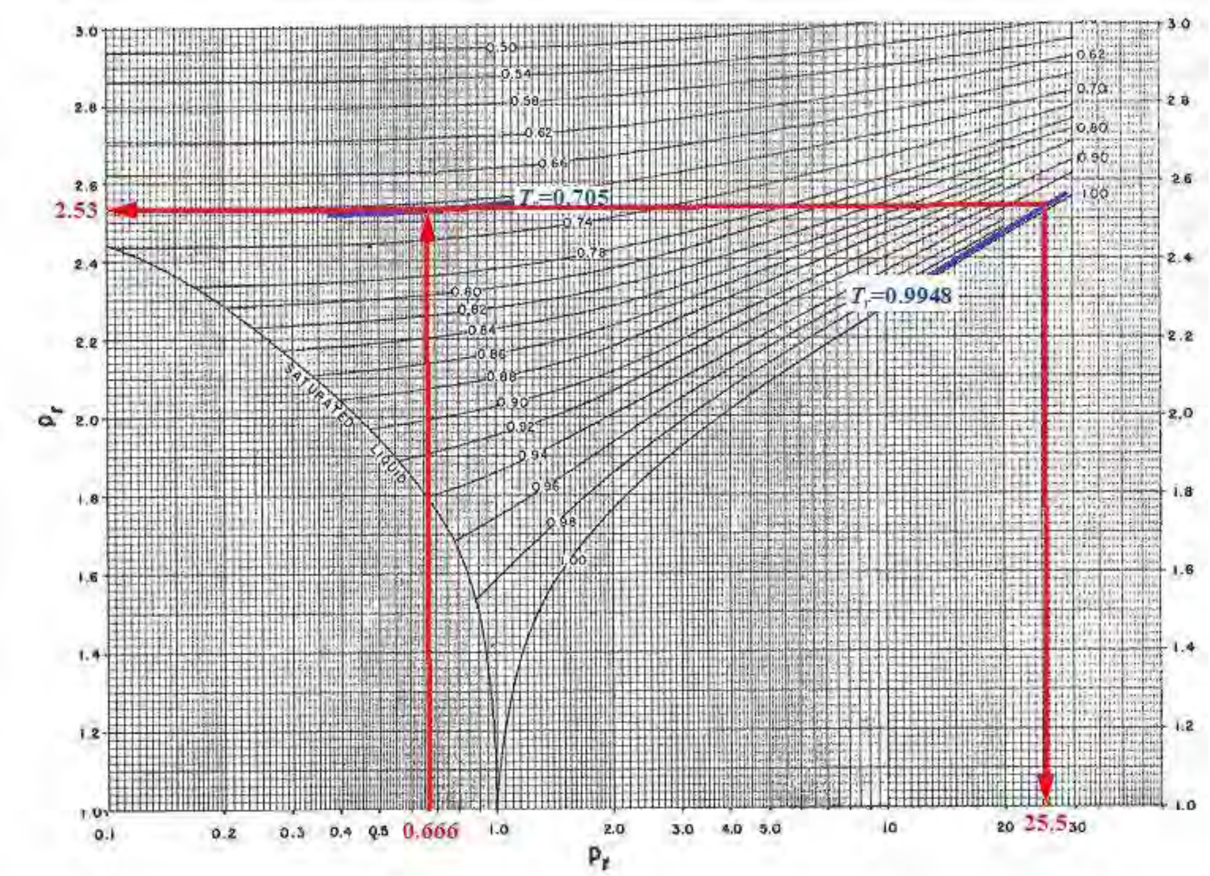
and the pressure supported by the base

$$P = \frac{(M_{butane} + M_{shell})g}{100\ \text{m}^2} = \frac{(576600\ \text{kg}+58152\ \text{kg})\left(9.80665\,\frac{\text{m}}{\text{s}^2}\right)}{100\ \text{m}^2} = 62248\ \text{Pa}$$

On the other hand, since the volume of the tank remains constant, the pressure reached will be graphically determined by drawing a straight line from ρ_{r1}=ρ_{r2}=2.53 to the point where it intersects the T_{r2}=0.9948 isotherm. The obtained value is P_{r2}=25.5, and therefore

$$P_2 = P_{r2}P_c = 25.5\ (37.5\ \text{atm}) = 956.25\ \text{atm}$$

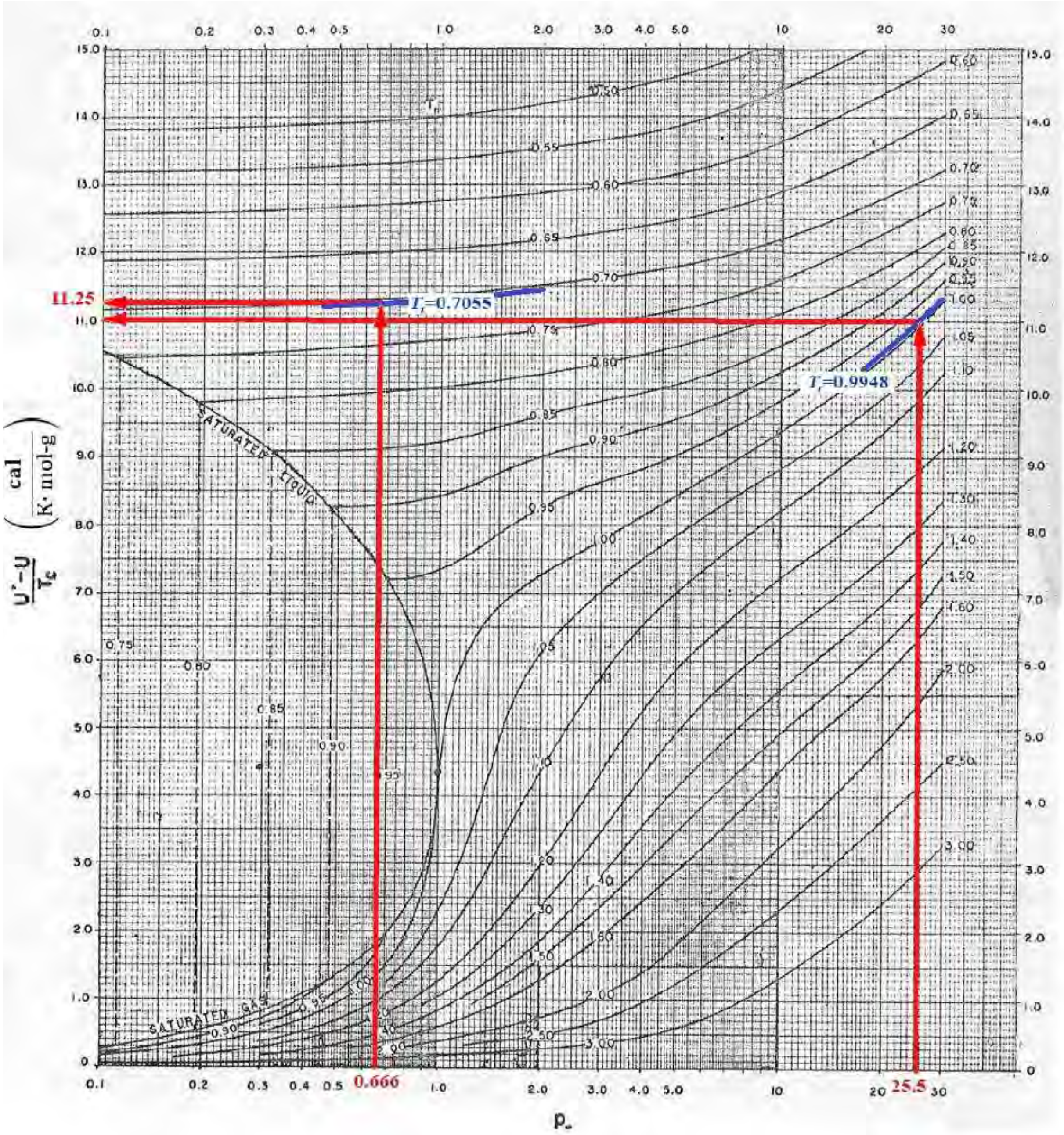
Pressure that is a 16% higher than that obtained with the *PH* diagram of butane.



Finally, in question **d**, it was found that $\Delta\hat{Q}_{21}$=$\Delta\hat{U}_{21}$. According to the Corresponding States Principle (section e of reference problem 0.8), the variation of internal energy between a state 1 and a state 2 will be given by

$$\left(\tilde{U}_2 - \tilde{U}_1\right) = \underbrace{\left(\tilde{U}_2^* - U_1^*\right)}_{\text{ideal part}} + \underbrace{\left(\tilde{U}_1^* - \tilde{U}_1\right)_{T_1,P_1} - \left(\tilde{U}_2^* - \tilde{U}_2\right)_{T_2,P_2}}_{\text{real part}} \qquad [1]$$

where the real part is estimated through the generalized correlation of figure IV.9 (appendix IV).



$$T_{r1} = 0.7055 \ ; \ P_{r1} = 0.6667$$

$$\left(\frac{\tilde{U}_1^* - \tilde{U}_1}{T_c}\right)_{T_{r1},P_{r1}} = 11.25 \frac{\text{cal}}{\text{K}\cdot \text{mol-g}}$$

$$\Downarrow$$

$$\left(\tilde{U}_1^* - \tilde{U}_1\right)_{T_1,P_1} = \left(11.25 \frac{\text{cal}}{\text{K}\cdot \text{mol-g}}\right)(425.2\ \text{K}) = 4783.5\ \frac{\text{cal}}{\text{mol-g}}$$

$$T_{r2} = 0.9948 \;;\; P_{r2} = 25.5$$

$$\left(\frac{\widetilde{U}_2^* - \widetilde{U}_2}{T_c}\right)_{T_{r2},P_{r2}} = 11\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}}$$

$$\Downarrow$$

$$\left(\widetilde{U}_2^* - \widetilde{U}_2\right)_{T_2,P_2} = \left(11\,\frac{\text{cal}}{\text{K}\cdot\text{ mol-g}}\right)(425.2\text{ K}) = 4677.2\ \frac{\text{cal}}{\text{mol-g}}$$

and the ideal part from the specific heat capacity at constant pressure of butane, considered as an ideal gas

$$\widetilde{U}_2^* - \widetilde{U}_1^* = \int_{T_1}^{T_2} \tilde{C}_V^* \mathrm{d}T = \int_{T_1}^{T_2} \left(\tilde{C}_P^* - R\right)\mathrm{d}T$$

Specific heat capacity that in appendix II is expressed by the empirical equation

$$\tilde{C}_P^* = \xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4$$

being

$$\frac{\xi_0}{R} = 5.547 \qquad \frac{\xi_1}{R} = 5.536\cdot 10^{-3}\,\frac{1}{\text{K}} \qquad \frac{\xi_2}{R} = 8.057\cdot 10^{-5}\,\frac{1}{\text{K}^2}$$

$$\frac{\xi_3}{R} = -10.571\cdot 10^{-8}\,\frac{1}{\text{K}^3} \qquad \frac{\xi_4}{R} = 4.134\cdot 10^{-11}\,\frac{1}{\text{K}^4}$$

and therefore

$$\widetilde{U}_2^* - \widetilde{U}_1^* = \int_{T_1}^{T_2} (\xi_0 - R + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4)\mathrm{d}T$$

$$\widetilde{U}_2^* - \widetilde{U}_1^* = \left[(\xi_0 - R)T + \frac{1}{2}\xi_1 T^2 + \frac{1}{3}\xi_2 T^3 + \frac{1}{4}\xi_3 T^4 + \frac{1}{5}\xi_4 T^5\right]_{T_1}^{T_2} =$$

$$= (\xi_0 - R)(T_2 - T_1) + \frac{\xi_1}{2}(T_2^2 - T_1^2) + \frac{\xi_2}{3}(T_2^3 - T_1^3) + \frac{\xi_3}{4}(T_2^4 - T_1^4) + \frac{\xi_4}{5}(T_2^5 - T_1^5)$$

By taking R=1.9872 cal/(mol-g·K), this difference becomes

$$\left(\widetilde{U}_2^* - U_1^*\right) = (5.547 - 1)R(423 - 300) + \frac{5.536\cdot 10^{-3}}{2}R(423^2 - 300^2) +$$

$$+\frac{8.057\cdot 10^{-5}}{3}R(423^3 - 300^3) - \frac{10.571\cdot 10^{-8}}{4}R(423^4 - 300^4) +$$

$$+\frac{4.134\cdot 10^{-11}}{5}R(423^5 - 300^5) = 3125.58\,\frac{\text{cal}}{\text{mol-g}}$$

and applying the equation [1]

$$3125.58\ \frac{\text{cal}}{\text{mol-g}} + 4783.5\ \frac{\text{cal}}{\text{mol-g}} - 4677.2\ \frac{\text{cal}}{\text{mol-g}} = 3231.88\frac{\text{cal}}{\text{mol-g}}$$

and by unit conversion

$$3231.88\frac{\text{cal}}{\text{mol-g}}\times\frac{1\ \text{kcal}}{1000\ \text{cal}}\times\frac{4180\ \text{J}}{1\ \text{kcal}}\times\frac{1\ \text{mol}-\text{g}}{58.12\ \text{g}}\times\frac{1000\ \text{g}}{1\ \text{kg}}\times\frac{1\ \text{kJ}}{1000\ \text{J}} = 232.44\ \frac{\text{kJ}}{\text{kg}}$$

Energy that, despite the pressure discrepancy, is only slightly lower than the 248.86 kJ/kg calculated with the *PH* diagram

$$\Delta Q_{21} = M_{butane}\Delta\widehat{U}_{21} = 576600\ \text{kg}\ \left(232.44\ \frac{\text{kJ}}{\text{kg}}\right) = 134.02\cdot 10^{6}\ \text{kJ}$$

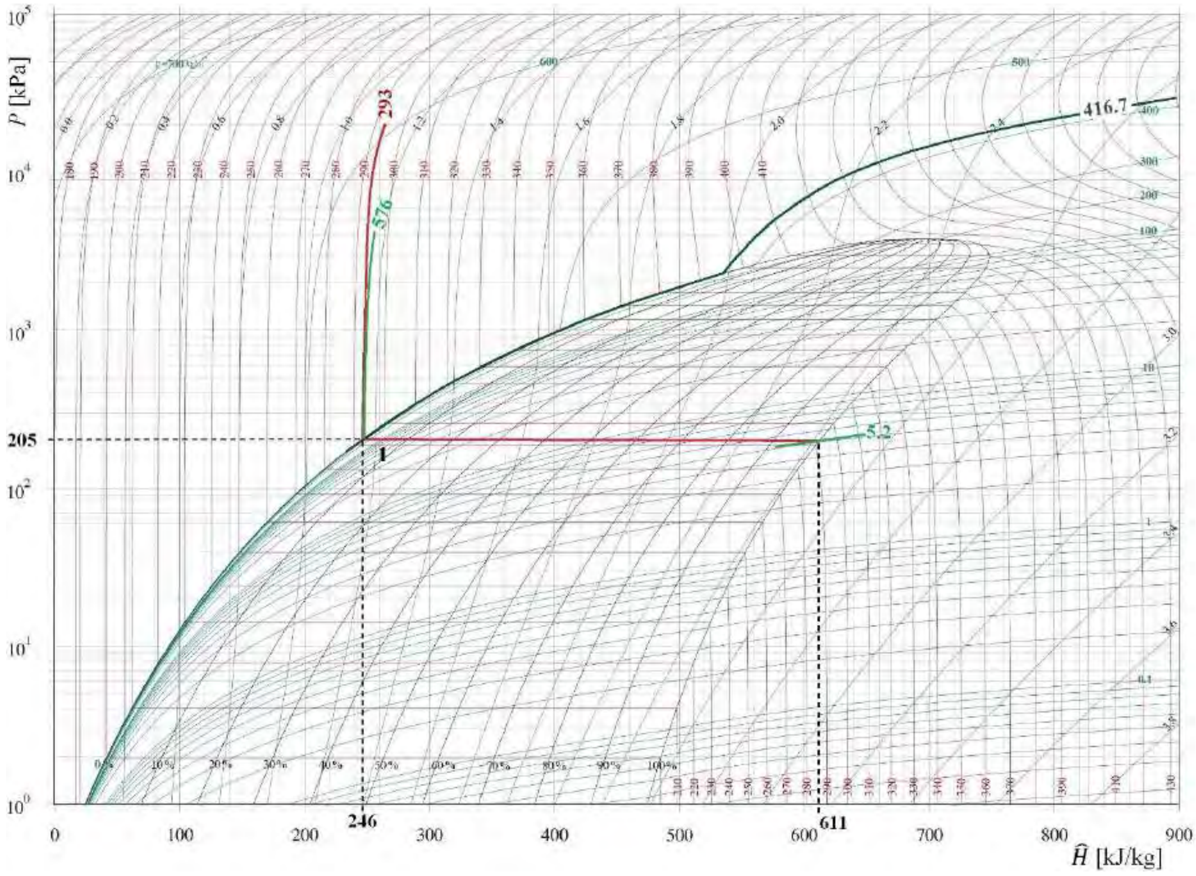
4.9. A 6 L cylinder contains 2.5 kg of butane at 20°C, which is isothermally consumed in a burner at a controlled flow rate of 10 g/min. By employing a hydrocarbon specific *PH*(*T*,*ρ*,*S*) diagram, calculate:

- **a) The initial conditions of the cylinder content.**
- **b) Conditions after 3 hours of use.**
- **c) The time required to consume the liquid phase and the amount of butane that is useless for consumption at that moment.**
- **d) The conditions when the isothermal discharge of the hydrocarbon ceases of being spontaneous.**

Repeat the calculations by employing the generalized charts of the Corresponding States Principle. Take into account that the vapor pressure for butane (in mm Hg) is

$$\log P_v = 6.8303 - \frac{945.9}{240 + T(^{\circ}\mathrm{C})}$$

Question a. It is necessary to resort to figure V.9 of this book's appendix V. To locate the corresponding point in it, the initial temperature should be converted to Kelvin degrees, and the density calculated in kg/m^3



$$T_1(\mathrm{K}) = 20^{\circ}\mathrm{C} + 273 = 293\ \mathrm{K}$$

$$\hat{\rho}_1 = \frac{M_1}{V_{cylinder}} = \frac{2.5\ \mathrm{kg}}{6\ \mathrm{L}} = 0.4167\ \frac{\mathrm{kg}}{\mathrm{L}} \quad \rightarrow \quad 0.4167\ \frac{\mathrm{kg}}{\mathrm{L}} \times \frac{1000\ \mathrm{L}}{1\ \mathrm{m}^3} = 416.7\ \frac{\mathrm{kg}}{\mathrm{m}^3}$$

It is observed that the point is placed in the biphasic zone (practically in the saturated liquid line), it has a pressure P_1=205 kPa and it is impossible to accurately read the title or quality and the enthalpy of the mixture. However, the amounts of liquid and vapor can be calculated by means of mass and volume balances, in the form

$$M_1 = M_{l_1} + M_{v_1} \qquad [1]$$

$$\frac{M_1}{\hat{\rho}_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} + \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} \qquad [2]$$

where $\hat{\rho}_{l_1}^{sat}$ and $\hat{\rho}_{v_1}^{sat}$ are the densities of the saturated liquid and vapor, and by interpolation in figure V.9 they result to be 576 kg/m^3 and 5.2 kg/m^3, respectively. After combining [1] and [2] and introducing the data, it is found that

$$M_{v_1} = M_1 \frac{\left(\frac{1}{\hat{\rho}_1} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_1}^{sat}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)} = (2500\ \mathrm{g}) \frac{\left(\frac{1}{416.7} - \frac{1}{576}\right)}{\left(\frac{1}{5.2} - \frac{1}{576}\right)} = 8.71\ \mathrm{g}$$

$$M_{l_1} = M_1 - M_{v_1} = 2500 - 8.71 = 2491.29\ \mathrm{g}$$

and the corresponding volumes are

$$V_{l_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} = \frac{2491.29\ \mathrm{g}}{576\ \frac{\mathrm{g}}{\mathrm{L}}} = 4.325\ \mathrm{L}$$

$$V_{v_1} = \frac{M_v}{\hat{\rho}_{v_1}^{sat}} = \frac{8.71\ \mathrm{g}}{5.2\ \frac{\mathrm{g}}{\mathrm{L}}} = 1.672\ \mathrm{L}$$

Question b. After 3 h of use (180 min) the consumed mass will be

$$10\ \frac{\mathrm{g}}{\mathrm{min}} (180\ \mathrm{min}) = 1800\ \mathrm{g}$$

Thus, the remaining hydrocarbon amount is M_2= 2500 – 1800= 700 g. Since the volume of the cylinder does not change, the density of the system is now

$$\hat{\rho}_2 = \frac{M_2}{V_{cylinder}} = \frac{700\ \mathrm{g}}{6\ \mathrm{L}} = 116.66\ \frac{\mathrm{g}}{\mathrm{L}} = 116.66\ \frac{\mathrm{kg}}{\mathrm{m}^3}$$

which is placed in the biphasic zone as well (T_2=T_1, P_2=P_1, $\hat{\rho}_{l_2}^{sat} = \hat{\rho}_{l_1}^{sat}$, $\hat{\rho}_{v_2}^{sat} = \hat{\rho}_{v_1}^{sat}$).

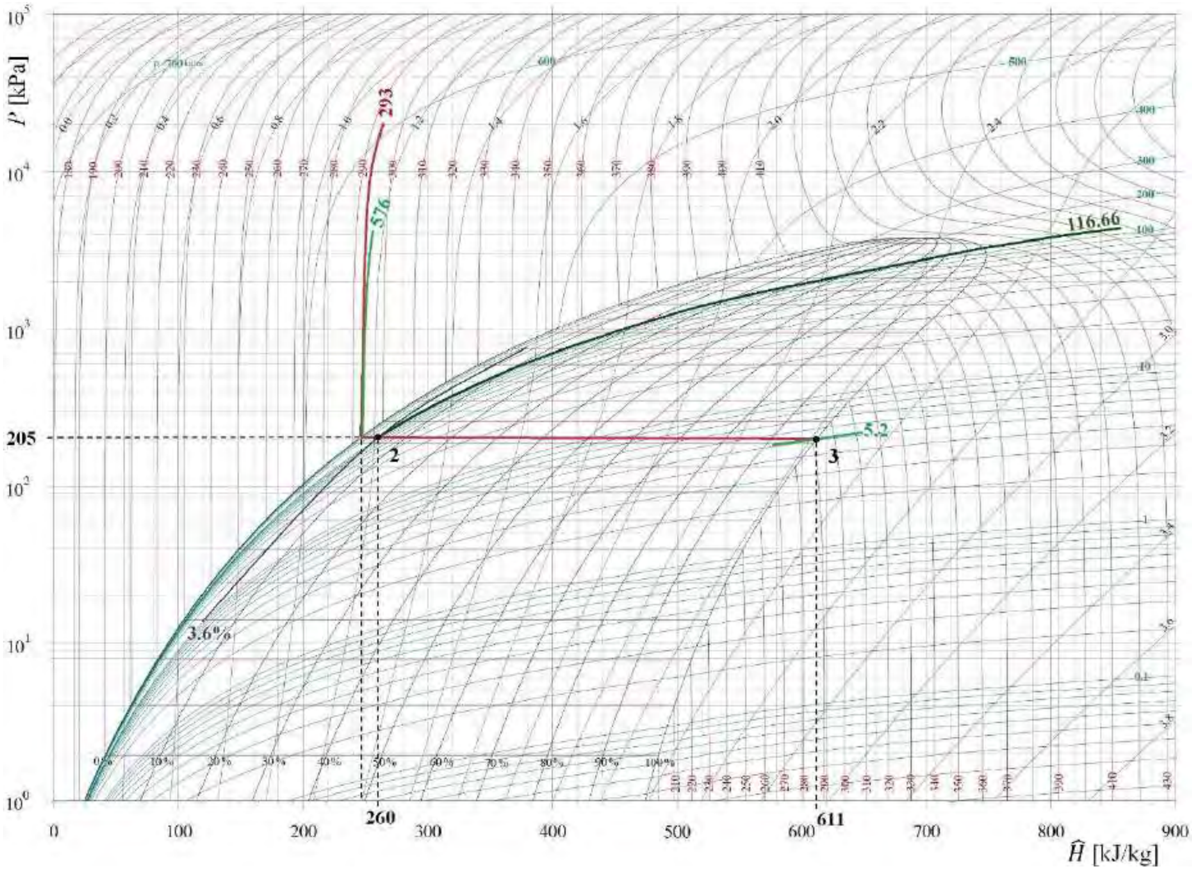
By combining [1] and [2] again

$$M_{v_2} = M_2 \frac{\left(\frac{1}{\hat{\rho}_2} - \frac{1}{\hat{\rho}^{sat}_{l_1}}\right)}{\left(\frac{1}{\hat{\rho}^{sat}_{v_1}} - \frac{1}{\hat{\rho}^{sat}_{l_1}}\right)} = (700\ \text{g}) \frac{\left(\frac{1}{116.66} - \frac{1}{576}\right)}{\left(\frac{1}{5.2} - \frac{1}{576}\right)} = 25.11\ \text{g}$$

$$M_{l_2} = M_2 - M_{v_2} = 700 - 25.11 = 674.89\ \text{g}$$

$$V_{l_2} = \frac{M_{l_2}}{\hat{\rho}^{sat}_{l_1}} = \frac{674.89\ \text{g}}{576\ \frac{\text{g}}{\text{L}}} = 1.17\ \text{L}$$

$$V_{v_2} = \frac{M_{v_2}}{\hat{\rho}^{sat}_{v_1}} = \frac{25.11\ \text{g}}{5.2\ \frac{\text{g}}{\text{L}}} = 4.83\ \text{L}$$



However, in this case, the quality or title is readable (3.6%) and the amount of vapor can be checked by combining the mass balance [1] with the enthalpy one ($M_2\hat{H}_2 = M_{l_2}\hat{H}^{sat}_{l_2} + M_{v_2}\hat{H}^{sat}_{v_2}$) since the total specific enthalpy of the liquid + vapor mixture can also be read, being 260 kJ /kg. Taking into account this value, and those of the saturated liquid ($\hat{H}^{sat}_{l_2} = \hat{H}^{sat}_{l_1} = 246$ kJ/kg) and of the saturated vapor ($\hat{H}^{sat}_{v_2} = \hat{H}^{sat}_{v_1} = 611$ kJ/kg)

$$M_{v_2} = M_2 \frac{\left(\hat{H}_2 - \hat{H}^{sat}_{l_1}\right)}{\left(\hat{H}^{sat}_{v_1} - \hat{H}^{sat}_{l_1}\right)} = (700\ \text{g}) \frac{(260 - 246)}{(611 - 246)} = 26.85\ \text{g}$$

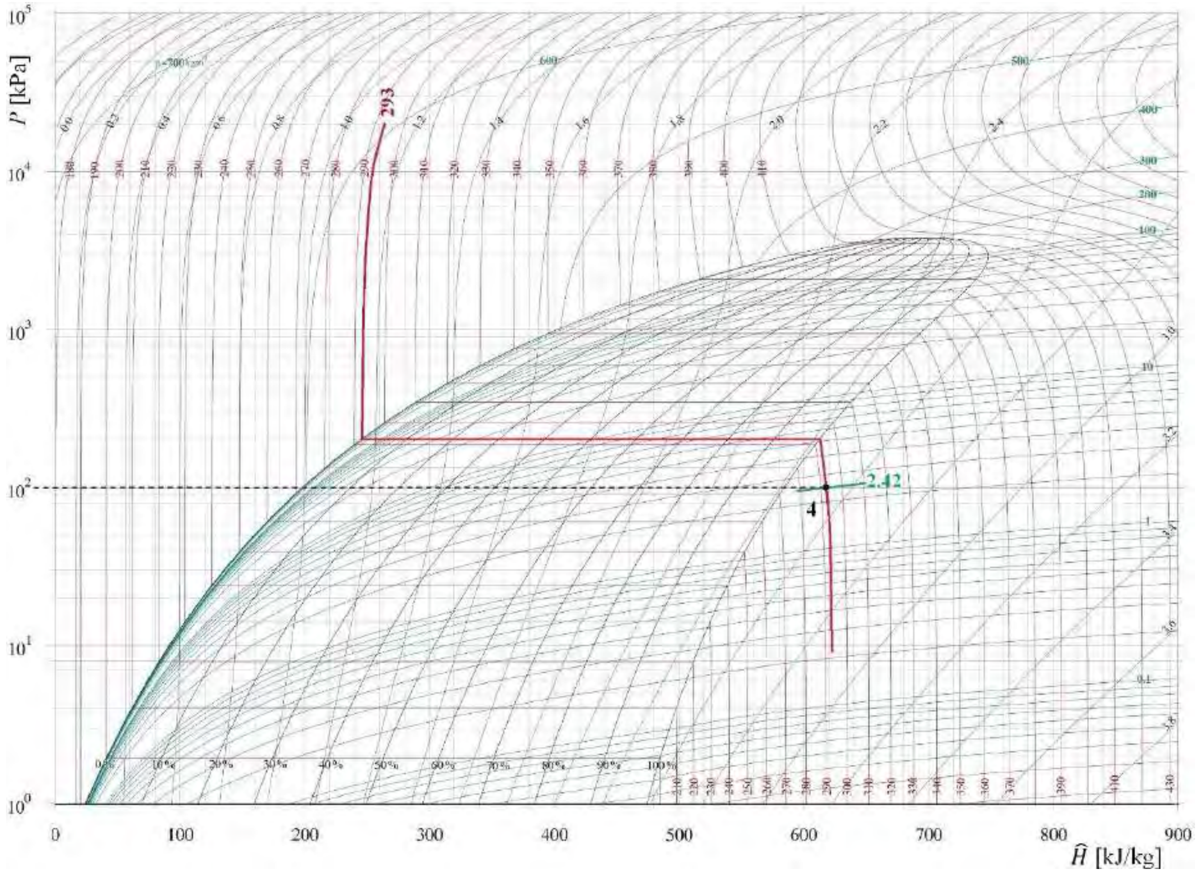
Question c. When the liquid phase is exhausted (point 3), the entire volume of the cylinder (6 L) will be occupied by saturated vapor, so

$$M_3 = M_{v_3} = V_{cylinder}\hat{\rho}_{v_1}^{sat} = (6\ \mathrm{L})\left(5.2\ \frac{\mathrm{g}}{\mathrm{L}}\right) = 31.2\ \mathrm{g}$$

The consumed amount has been 2500 – 31.2= 2468.8 g, which, referred to the flow, allows to obtain by simple division the minimum theoretical emptying time

$$t = \frac{2468.8\ \mathrm{g}}{10\ \mathrm{g/min}} = 246.88\ \mathrm{min} \ \rightarrow \quad 246.88\ \mathrm{min} \times \frac{1\ \mathrm{h}}{60\ \mathrm{min}} = 4.11\ \mathrm{h}$$

Question d. The spontaneous discharge of the cylinder will cease when it reaches a pressure around that outside, 100 kPa (≈1 atm).



At that moment, the density of the vapor in the cylinder is approximately $\hat{\rho}_4$ =2.42 kg/m^3 (read from the diagram) and

$$M_4 = M_{v_4} = V_{cylinder}\hat{\rho}_4 = (6\ \mathrm{L})\left(2.42\ \frac{\mathrm{g}}{\mathrm{L}}\right) = 14.52\ \mathrm{g}$$

Regarding the **Corresponding States Principle**, figure IV.1 of this book's appendix IV could be used without corrections, since the critical compressibility of butane (appendix II) is only 1.6% higher than 0.27.

The reduced variables would be

$$T_{r1} = \frac{T_1}{T_c} = \frac{293\ \text{K}}{425.2\ \text{K}} = 0.689$$

and

$$P_v = 10^{\left(6.8303 - \frac{945.9}{240+20℃}\right)} = 1556.76\ \text{mm Hg}$$

$$1556.76\ \text{mm Hg} \times \frac{1\ \text{m Hg}}{1000\ \text{mm Hg}} \times \frac{1.32\ \text{atm}}{1\ \text{m Hg}} = 2.055\ \text{atm}$$

$$P_{rv} = \frac{P_v}{P_c} = \frac{2.055\ \text{atm}}{37.5\ \text{atm}} = 0.0548$$

Since $T_{r1}<1$, $P_{rv}<1$ and the density in the cylinder at the begining of the operation ($\hat{\rho}_1$=416.7 kg/m^3) is higher than the critical density

$$\hat{\rho}_c = \frac{\mathfrak{M}}{\tilde{V}_c} = \frac{\left(58.12 \frac{\text{g}}{\text{mol-g}} \times \frac{1\ \text{kg}}{1000\ \text{g}}\right)}{255\ \frac{\text{cm}^3}{\text{mol-g}} \times \left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^3} = 227.92\ \frac{\text{kg}}{\text{m}^3}$$

Butane will be a liquid+vapor mixture or a pure liquid. It will be a mixture if the value of 416.7 kg/m^3 is lower than the saturated liquid density at that temperature. This density could be calculated using the Corresponding States Principle as

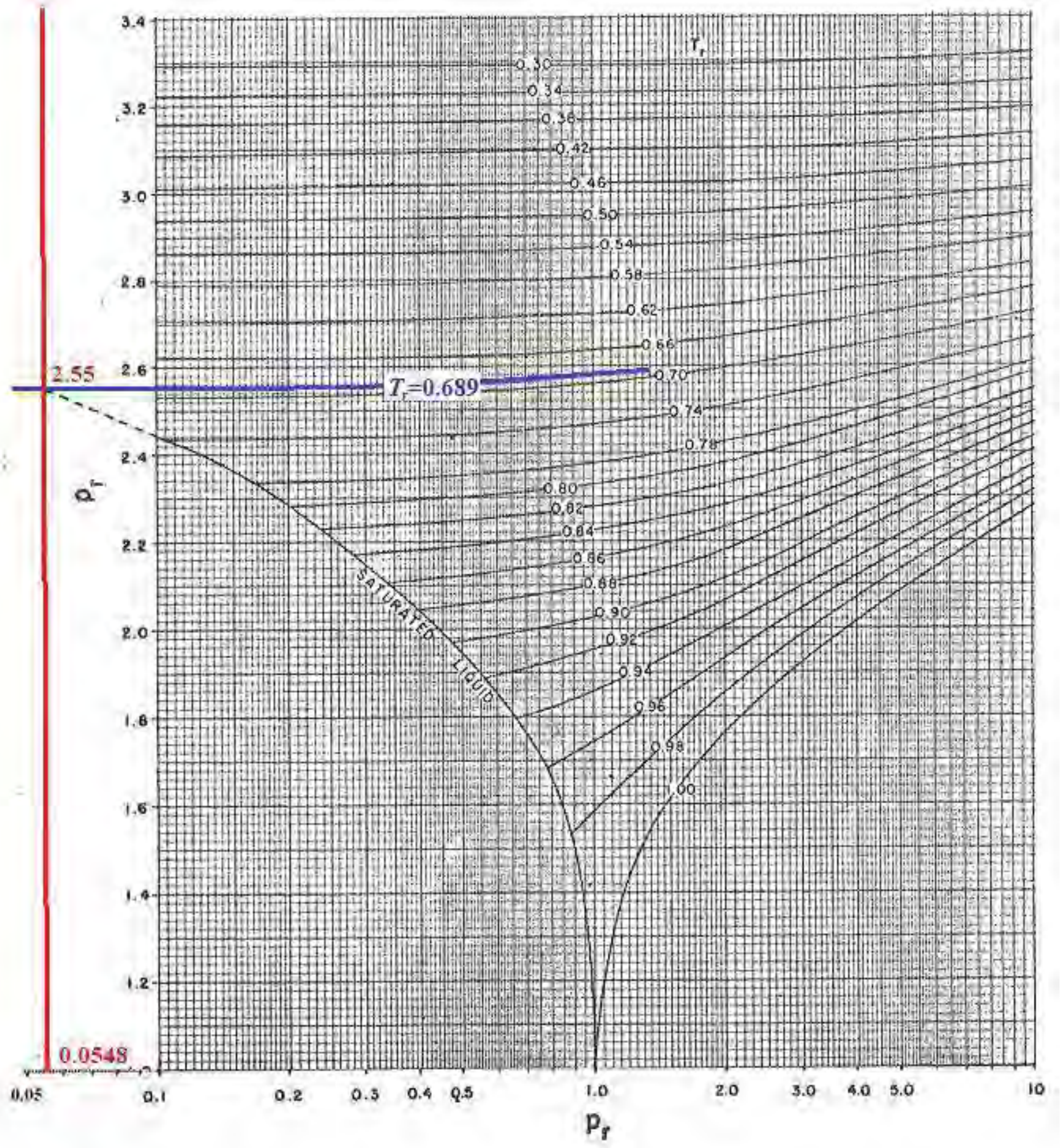
$$\hat{\rho}_{l_1}^{sat} = \frac{\mathfrak{M} P_v}{z_{l_1}^{sat} R T_1}$$

Unfortunately, figure IV.1 of appendix IV is only valid for reduced pressures higher than 0.1, there are only two isotherms (0.5 and 0.6), and they are very close one to another, so no reliable extrapolation seems possible. On the other hand, figure IV.3 of this appendix, which covers reduced pressures up to 0, is only valid for gases and vapors.

Therefore, it has to resort to figure IV.13 (ρ_r vs. P_r, with T_r in isolines) which, although it is also limited by pressure, allows a reasonable extrapolation: the isotherms for P_r <0.2 are practically straight lines parallel to the abscissa axis

$$\rho_{r1} = 2.55 \quad \rightarrow \quad \hat{\rho}_{l_1}^{sat} = 2.55\left(227.92\ \frac{\text{kg}}{\text{m}^3}\right) = 581.2\ \frac{\text{kg}}{\text{m}^3}$$

and being this density higher than $\hat{\rho}_1$=416.7 kg/m^3, it is clear that inside the cylinder there is a mixture of saturated liquid and vapor at P_1=P_v.



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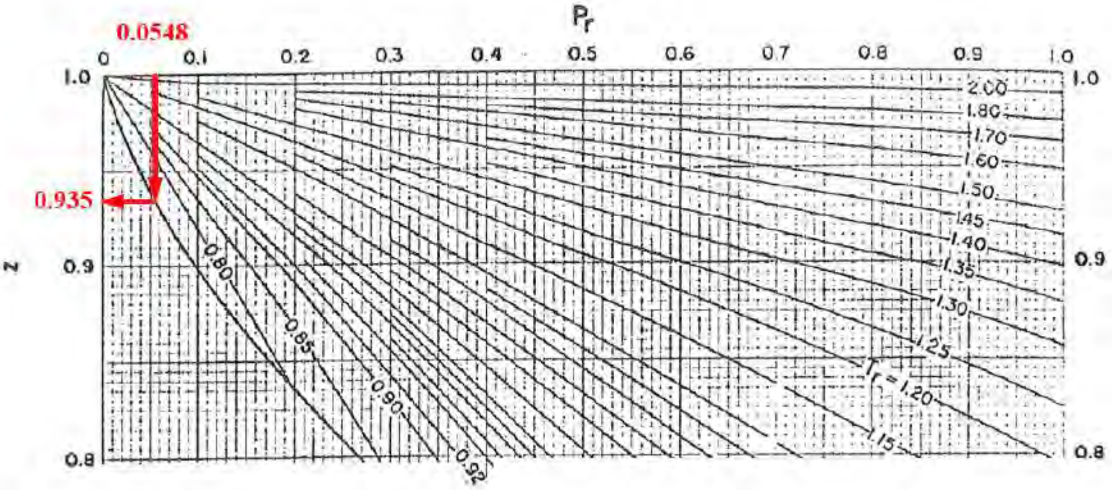
In order to apply the formula that results from combining equations [1] and [2] it is necessary to find the saturated vapor density, which can be determined by figure IV.3 of appendix IV.



$$\hat{\rho}_{v_1}^{sat} = \frac{\mathfrak{W}P_1}{z_{v_1}^{sat}RT_1} = \frac{\left(58.12\,\frac{\text{g}}{\text{mol-g}}\times\frac{1\text{ kg}}{1000\text{ g}}\right)(2.055\text{ atm})}{(0.935)\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\times\frac{1\text{ m}^3}{1000\text{ L}}\right)(293\text{ K})} = 5.32\,\frac{\text{kg}}{\text{m}^3}$$

Hence

$$M_{v_1} = M_1\frac{\left(\frac{1}{\hat{\rho}_1}-\frac{1}{\hat{\rho}_{l_1}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_1}^{sat}}-\frac{1}{\hat{\rho}_{l_1}^{sat}}\right)} = (2500\text{ g})\frac{\left(\frac{1}{416.7}-\frac{1}{581.2}\right)}{\left(\frac{1}{5.32}-\frac{1}{581.2}\right)} = 9.12\text{ g}$$

$$M_{l_1} = M_1 - M_{v_1} = 2500 - 9.12 = 2490.88\text{ g}$$

$$V_{l_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} = \frac{2490.88\text{ g}}{581.2\,\frac{\text{g}}{\text{L}}} = 4.286\text{ L}$$

$$V_{v_1} = \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} = \frac{9.12\text{ g}}{5.32\,\frac{\text{g}}{\text{L}}} = 1.714\text{ L}$$

On the other hand, in question **b** of the problem, it can be calculated that the average density of the hydrocarbon in the cylinder after 180 minutes was $\hat{\rho}_2 =$ 116.66 kg/m^3 (an amount still between the 581.2 kg/m^3 of the saturated liquid and the 5.3 kg/m^3 of the saturated vapor); thus, there is still a two-phase mixture and the pressure has not changed

$$M_{v_2} = M_2\frac{\left(\frac{1}{\hat{\rho}_2}-\frac{1}{\hat{\rho}_{l_1}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_1}^{sat}}-\frac{1}{\hat{\rho}_{l_1}^{sat}}\right)} = (700\text{ g})\frac{\left(\frac{1}{116.66}-\frac{1}{581.2}\right)}{\left(\frac{1}{5.32}-\frac{1}{581.2}\right)} = 25.75\text{ g}$$

$$M_{l_2} = M_2 - M_{v_2} = 700 - 25.75 = 674.25\text{ g}$$

$$V_{l_2} = \frac{M_{l_2}}{\hat{\rho}_{l_1}^{sat}} = \frac{697.45\text{ g}}{581.2\,\frac{\text{g}}{\text{L}}} = 1.16\text{ L}$$

$$V_{v_2} = \frac{M_{v_2}}{\hat{\rho}_{v_1}^{sat}} = \frac{25.75\text{ g}}{5.32\,\frac{\text{g}}{\text{L}}} = 4.84\text{ L}$$

Later, when the liquid phase is depleted, the saturated vapor will totally occupy the 6 liters of the cylinder, so

$$M_3 = V_{cylinder}\hat{\rho}_{v_1}^{sat} = (6\text{ L})\left(5.32\,\frac{\text{g}}{\text{L}}\right) = 31.92\text{ g}$$

and 2500 – 31.92= 2468.08 g will have been burned, a value that divided by the flow allows to find the time it took for the liquid to be consumed

$$t = \frac{2468.08\ \mathrm{g}}{10\ \mathrm{g/min}} = 246.808\ \mathrm{min}\ \rightarrow\ \ 246.808\ \mathrm{min} \times \frac{1\ \mathrm{h}}{60\ \mathrm{min}} = 4.11\ \mathrm{h}$$

Finally, the cylinder will be exhausted when pressure close to the atmospheric one is reached inside. At that time, it can be assumed that the vapor that remains in its interior behaves like an ideal gas, with z_v=1.0

$$\hat{\rho}_4 = \frac{\mathfrak{M} P_4}{z_{v_4} R T_4} = \frac{\left(58.12\,\frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)(1\ \mathrm{atm})}{(1.0)\left(0.082\,\frac{\mathrm{atm \cdot L}}{\mathrm{K \cdot mol\text{-}g}}\right)(293\ \mathrm{K})} = 2.42\,\frac{\mathrm{g}}{\mathrm{L}}$$

and this vapor will be filling the entire cylinder

$$M_4 = V_{cylinder}\hat{\rho}_4 = (6\ \mathrm{L})\left(2.42\ \frac{\mathrm{g}}{\mathrm{L}}\right) = 14.52\ \mathrm{g}$$

Notice that the density calculated by the ideal gas equation is the same as that read from the hydrocarbon *PH* diagram.

4.10. A 35-liter experimental vessel contains 11 kg of butane. Determine the conditions (pressure and amounts of liquid and vapor) of the hydrocarbon in the following situations:

- **a) Initially, at 243 K and 298 K.**
- **b) At the same two temperatures, but after an isothermal emptying of half of its content, when the liquid is exhausted, and when the emptying is no longer spontaneous.**
- **c) Repeat these estimations at 393 K.**
- **d) Estimate the heat taken from the environment in the case of isothermal evacuation of half the load at 298 K.**
- **e) Compare this problem with another one in this series and think about whether a different setting favors its understanding.**

Question a. Let point 1 represent the initial conditions of the vessel at 243 K, and point 1' represent them at 298 K. These states will be graphically located in figure V.9 of this book's appendix V by means of the intersection of the isochore

$$\hat{\rho}_1 = \hat{\rho}_{1'} = \hat{\rho}_{tot} = \frac{M_{tot}}{V_{vessel}} = \frac{3.5\ \mathrm{kg}}{35\ \mathrm{L}} = 0.1\ \frac{\mathrm{kg}}{\mathrm{L}} \quad \rightarrow \quad 0.1\ \frac{\mathrm{kg}}{\mathrm{L}} \times \frac{1000\ \mathrm{L}}{1\ \mathrm{m}^3} = 100\ \frac{\mathrm{kg}}{\mathrm{m}^3}$$

with the corresponding isotherms.

In both cases, they are biphasic mixtures of saturated liquid and saturated vapor. The pressure at 1 is of 27.6 kPa and at 1' is of 240 kPa. It is difficult to read the title or quality lines in point 1, but in 1' there is about 5% of vapor (0.05×3.5 kg = 0.175 kg).

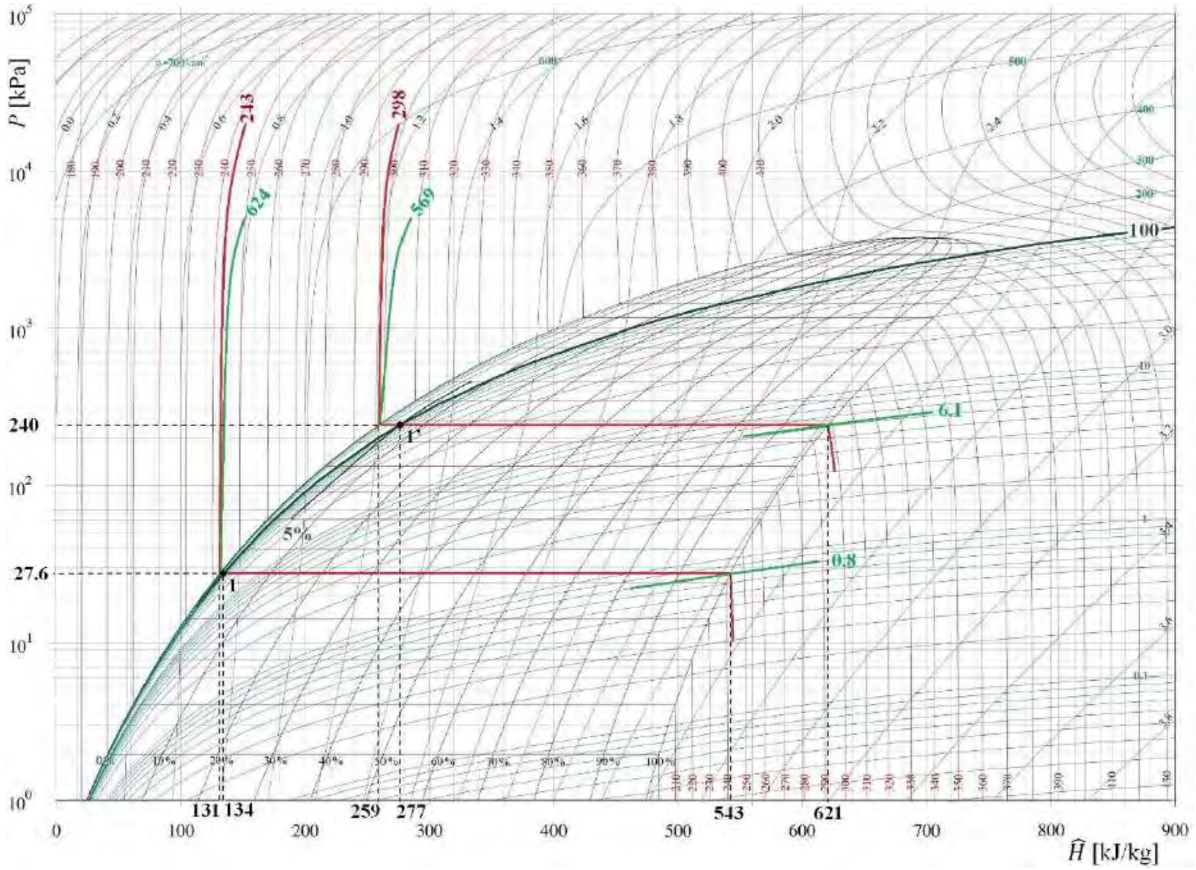
On the other hand, the masses of vapor and liquid, as well as the volumes they occupy, are determined by means of mass and volume balances

$$M_{tot} = M_l + M_v \qquad [1]$$

$$\frac{M_{tot}}{\hat{\rho}_{tot}} = \frac{M_l}{\hat{\rho}_l^{sat}} + \frac{M_v}{\hat{\rho}_v^{sat}} \qquad [2]$$

which combination generates

$$M_v = M_{tot} \frac{\left(\frac{1}{\hat{\rho}_{tot}} - \frac{1}{\hat{\rho}_l^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_v^{sat}} - \frac{1}{\hat{\rho}_l^{sat}}\right)} \qquad [3]$$



At 243 K, the saturated liquid density is $\hat{\rho}_{l_1}$=624 kg/m^3 and that of the saturated vapor $\hat{\rho}_{v_1}$=0.8 kg/m^3; thus

$$M_{v_1} = (3.5\text{ kg})\frac{\left(\frac{1}{100}-\frac{1}{624}\right)}{\left(\frac{1}{0.8}-\frac{1}{624}\right)} = 0.0235\text{ kg}$$

$$M_{l_1} = M_{tot} - M_{v_1} = 3.5 - 0.0235 = 3.4765\text{ kg}$$

and the volumes occupied by these masses will be

$$V_{l_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} = \frac{3.4765\text{ kg}}{624\ \frac{\text{kg}}{\text{m}^3}} = 0.0056\text{ m}^3$$

$$V_{v_1} = \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} = \frac{0.0235\text{ kg}}{0.8\ \frac{\text{kg}}{\text{m}^3}} = 0.0294\text{ m}^3$$

At 298 K the saturated liquid density is $\hat{\rho}_{l_{1'}}^{sat}$= 569 kg/m^3 and that of the vapor $\hat{\rho}_{v_{1'}}^{sat}$ =6.1 kg/m^3

$$M_{v_{1'}} = (3.5\ \text{kg})\frac{\left(\frac{1}{100}-\frac{1}{569}\right)}{\left(\frac{1}{6.1}-\frac{1}{569}\right)} = 0.178\ \text{kg}$$

$$M_{l_{1'}} = M_{tot} - M_{v_{1'}} = 3.5 - 0.178 = 3.322\ \text{kg}$$

$$V_{l_{1'}} = \frac{M_{l_{1'}}}{\hat{\rho}^{sat}_{l_{1'}}} = \frac{3.322\ \text{kg}}{569\ \frac{\text{kg}}{\text{m}^3}} = 0.0058\ \text{m}^3$$

$$V_{v_{1'}} = \frac{M_{v_{1'}}}{\hat{\rho}^{sat}_{v_{1'}}} = \frac{0.178\ \text{kg}}{6.1\ \frac{\text{kg}}{\text{m}^3}} = 0.0292\ \text{m}^3$$

The amounts of liquid and vapor can be checked if the mass balance [1] is combined with the enthalpy balance [4]

$$M_{tot}\hat{H}_{tot} = M_l\hat{H}^{sat}_l + M_v\hat{H}^{sat}_v \qquad [4]$$

with the result that

$$M_v = M_{tot}\frac{\left(\hat{H}_{tot} - \hat{H}^{sat}_l\right)}{\left(\hat{H}^{sat}_v - \hat{H}^{sat}_l\right)} \qquad [5]$$

At point 1, the enthalpy of the biphasic mixture is $\hat{H}_{tot_1}$=134 kJ/kg, that of the saturated liquid is $\hat{H}^{sat}_{l_1}$=131 kJ/kg and that of the saturated vapor $\hat{H}^{sat}_{v_1}$=543 kJ/kg, so

$$M_{v_1} = (3.5\ \text{kg})\frac{(134-131)}{(543-131)} = 0.0255\ \text{kg}$$

while in point 1', $\hat{H}_{tot_{1'}}$=277 kJ/kg, $\hat{H}^{sat}_{l_{1'}}$=259 kJ/kg and $\hat{H}^{sat}_{v_{1'}}$=621 kJ/kg

$$M_{v_{1'}} = (3.5\ \text{kg})\frac{(277-259)}{(621-259)} = 0.174\ \text{kg}$$

Question b. When the mass is reduced to the half (M_{tot}=1.75 kg) the state of the vessel at 243 K will go to a point 2, while, if at 298 K, it will go to a point 2', in which

$$\hat{\rho}_2 = \hat{\rho}_{2'} = \hat{\rho}_{tot} = \frac{M_{tot}}{V_{bombona}} = \frac{1.75\ \text{kg}}{35\ \text{L}} = 0.05\ \frac{\text{kg}}{\text{L}} \quad \rightarrow \quad 0.05\ \frac{\text{kg}}{\text{L}} \times \frac{1000\ \text{L}}{1\ \text{m}^3} = 50\ \frac{\text{kg}}{\text{m}^3}$$

It is observed that at these points there still are biphasic mixtures, that $\hat{\rho}_{l_1}^{sat}=\hat{\rho}_{l_2}^{sat}=624$ kg/m^3, $\hat{\rho}_{v_1}^{sat}=\hat{\rho}_{v_2}^{sat}=0.8$ kg/m^3, $\hat{\rho}_{l_{1'}}^{sat}=\hat{\rho}_{l_{2'}}^{sat}=569$ kg/m^3 and that $\hat{\rho}_{v_{1'}}^{sat}=\hat{\rho}_{v_{2'}}^{sat}$ =6.1 kg/m^3. By applying equations [1-3]

$$\left.\begin{aligned}
M_{v_2} &= (1.75\text{ kg})\frac{\left(\frac{1}{50}-\frac{1}{624}\right)}{\left(\frac{1}{0.8}-\frac{1}{624}\right)} = 0.0258\text{ kg}\\
M_{l_2} &= M_{tot}-M_{v_2} = 1.75-0.0258 = 1.7242\text{ kg}\\
V_{l_2} &= \frac{M_{l_2}}{\hat{\rho}_{l_2}^{sat}} = \frac{1.7242\text{ kg}}{624\ \frac{\text{kg}}{\text{m}^3}} = 0.00275\text{ m}^3\\
V_{v_2} &= \frac{M_{v_2}}{\hat{\rho}_{v_2}^{sat}} = \frac{0.0258\text{ kg}}{0.8\ \frac{\text{kg}}{\text{m}^3}} = 0.03225\text{ m}^3
\end{aligned}\right\}\text{at 243 K}$$

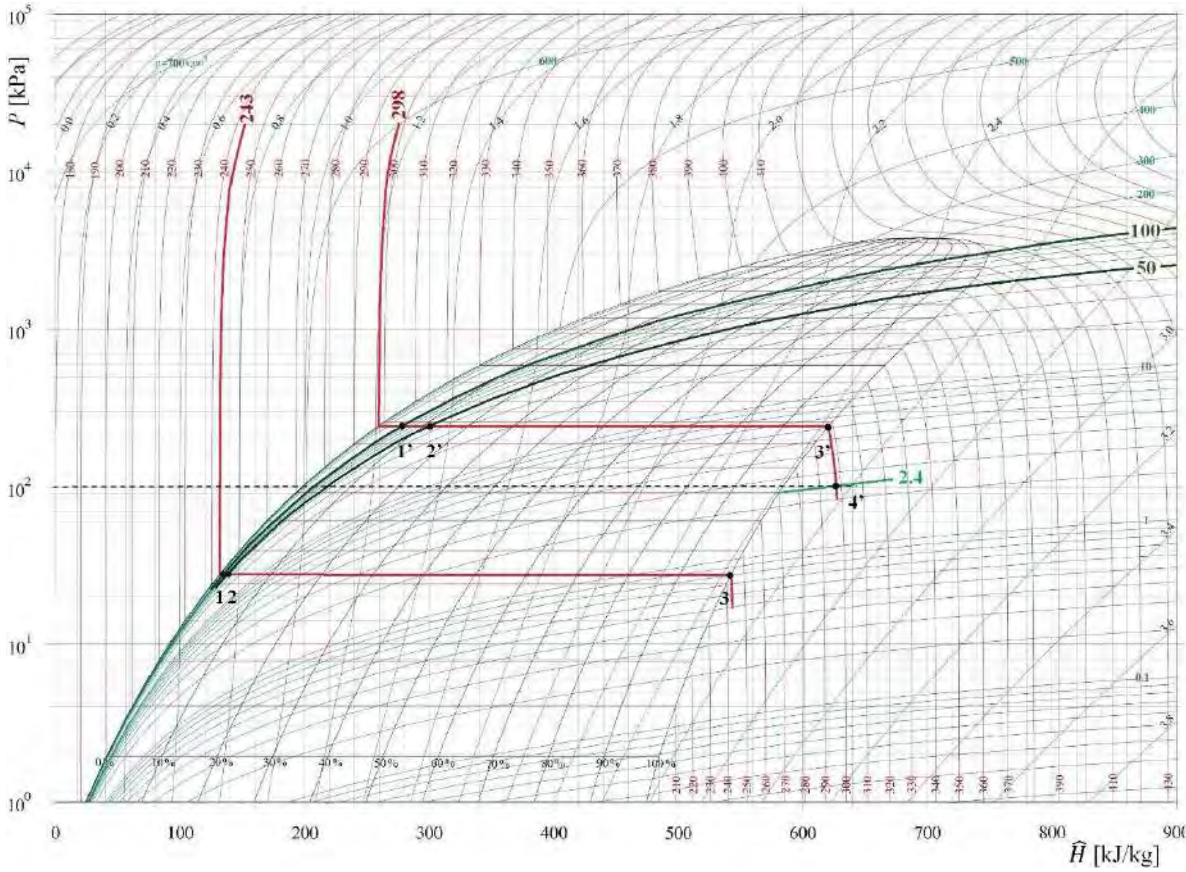
$$\left.\begin{aligned}
M_{v_{2'}} &= (1.75\text{ kg})\frac{\left(\frac{1}{50}-\frac{1}{569}\right)}{\left(\frac{1}{6.1}-\frac{1}{569}\right)} = 0.197\text{ kg}\\
M_{l_{2'}} &= M_{tot}-M_{v_{2'}} = 1.75-0.197 = 1.553\text{ kg}\\
V_{l_{2'}} &= \frac{M_{l_{2'}}}{\hat{\rho}_{l_{2'}}^{sat}} = \frac{1.553\text{ kg}}{569\ \frac{\text{kg}}{\text{m}^3}} = 0.0027\text{ m}^3\\
V_{v_{2'}} &= \frac{M_{v_{2'}}}{\hat{\rho}_{v_{2'}}^{sat}} = \frac{0.197\text{ kg}}{6.1\ \frac{\text{kg}}{\text{m}^3}} = 0.0323\text{ m}^3
\end{aligned}\right\}\text{at 298 K}$$

Later, when the liquid is exhausted, the state of the system will graphically go to points 3 and 3’, where there is only saturated vapor of density $\hat{\rho}_{v_1}^{sat}=\hat{\rho}_{v_2}^{sat}=\hat{\rho}_{v_3}^{sat}=0.8$ kg/m^3 at 243 K and $\hat{\rho}_{v_{1'}}^{sat}=\hat{\rho}_{v_{2'}}^{sat}=\hat{\rho}_{v_{3'}}^{sat}=6.1$ kg/m^3 at 298 K . Hence, their masses will be

$$M_3 = M_{v_3} = V_{tot}\hat{\rho}_{v_3}^{sat} = (0.035\text{ m}^3)\left(0.8\ \frac{\text{kg}}{\text{m}^3}\right) = 0.028\text{ kg}$$

$$M_{3'} = M_{v_{3'}} = V_{tot}\hat{\rho}_{v_{3'}}^{sat} = (0.035\text{ m}^3)\left(6.1\ \frac{\text{kg}}{\text{m}^3}\right) = 0.2135\text{ kg}$$

Finally, no fuel will come out spontaneously when the vessel reaches the same pressure as that of the environment (1 atm ≈ 100 kPa). At 298 K this corresponds to point 4’, but at 243 K there is no crossing between the 100 kPa isobar and the 243 K isotherm in the superheated steam zone, since the pressure of the latter (27.6 kPa) has been always below 100 kPa (indicating that the butane cannot leave the experimental vessel).



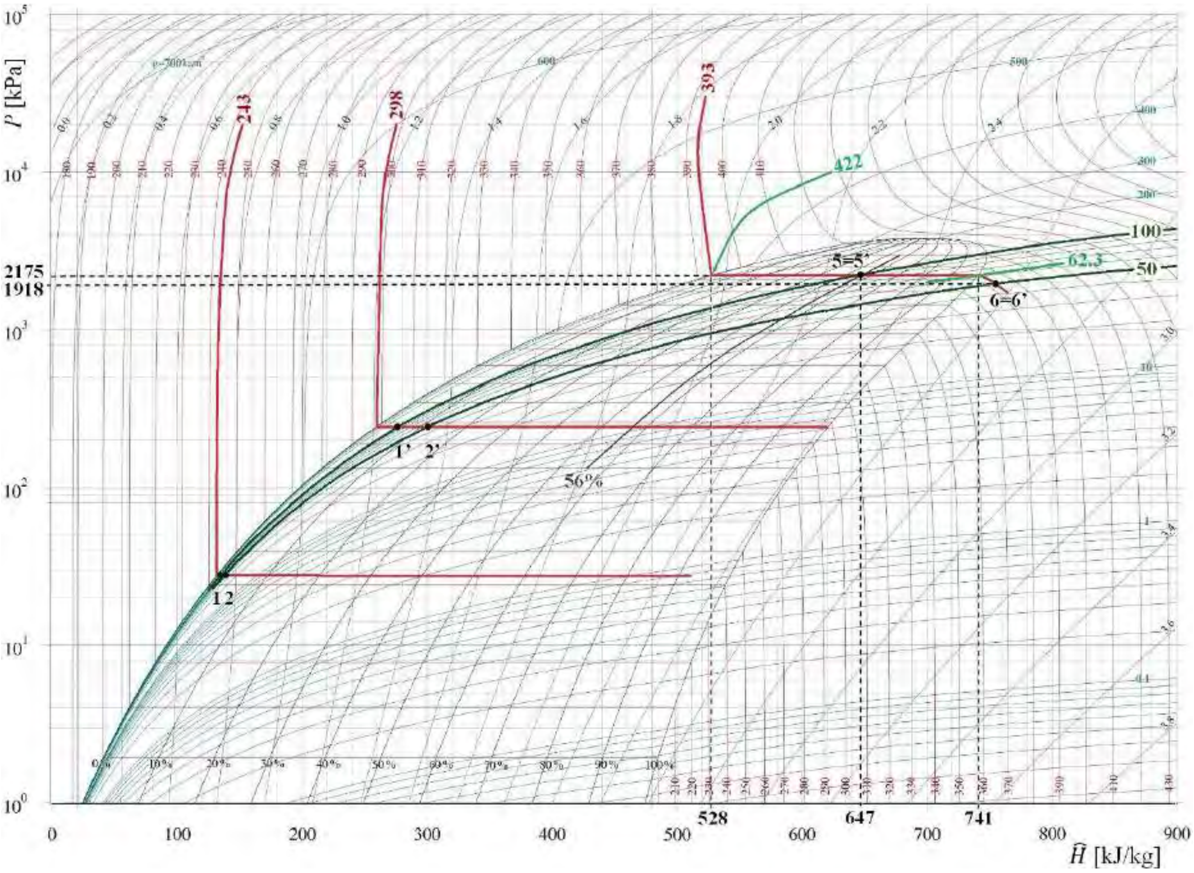
On the other hand, and within the error due to the graphical interpolation, the density read at point 4’ in the diagram is the same as that estimated by the ideal gas equation

$$\hat{\rho}_{v_{4'}} = \frac{\mathfrak{M} P_{4'}}{R T_{1'}} = \frac{\left(58.12\,\dfrac{\text{g}}{\text{mol-g}}\right)(1\text{ atm})}{\left(0.082\,\dfrac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(298\text{ K})} = 2.38\,\frac{\text{g}}{\text{L}} = 2.38\,\frac{\text{kg}}{\text{m}^3}$$

and the mass of vapor that remains in the vessel at 298 K will be

$$M_{4'} = M_{v_{4'}} = V_{tot}\hat{\rho}_{v_{4'}} = (0.035\text{ m}^3)\left(2.38\,\frac{\text{kg}}{\text{m}^3}\right) = 0.0833\text{ kg}$$

Question c. Given that in the initial conditions the density in the vessel was of 100 kg/m^3, the new state 5=5' will be found at the intersection of this isochore with the T=393 K isotherm



and it can be observed that it is a biphasic mixture at 2175 kPa, with a total specific enthalpy of 647 kJ/kg and an approximate title of 56% (0.56×3.5 kg = 1.96 kg). The saturated liquid will have a density of 422 kg/m^3 and an enthalpy of 528 kJ/kg, while in the saturated vapor, they will be 62.3 kg/m^3 and 741 kJ/kg. By applying equations [1-3]

$$M_{v_5} = (3.5\ \mathrm{kg})\frac{\left(\frac{1}{100} - \frac{1}{422}\right)}{\left(\frac{1}{62.3} - \frac{1}{422}\right)} = 1.952\ \mathrm{kg}$$

$$M_{l_5} = M_{tot} - M_{v_5} = 3.5 - 1.952 = 1.548\ \mathrm{kg}$$

$$V_{l_5} = \frac{M_{l_5}}{\hat{\rho}_{l_5}^{sat}} = \frac{1.548\ \mathrm{kg}}{422\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.00367\ \mathrm{m}^3$$

$$V_{v_5} = \frac{M_{v_5}}{\hat{\rho}_{v_5}^{sat}} = \frac{1.952\ \mathrm{kg}}{62.3\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.03133\ \mathrm{m}^3$$

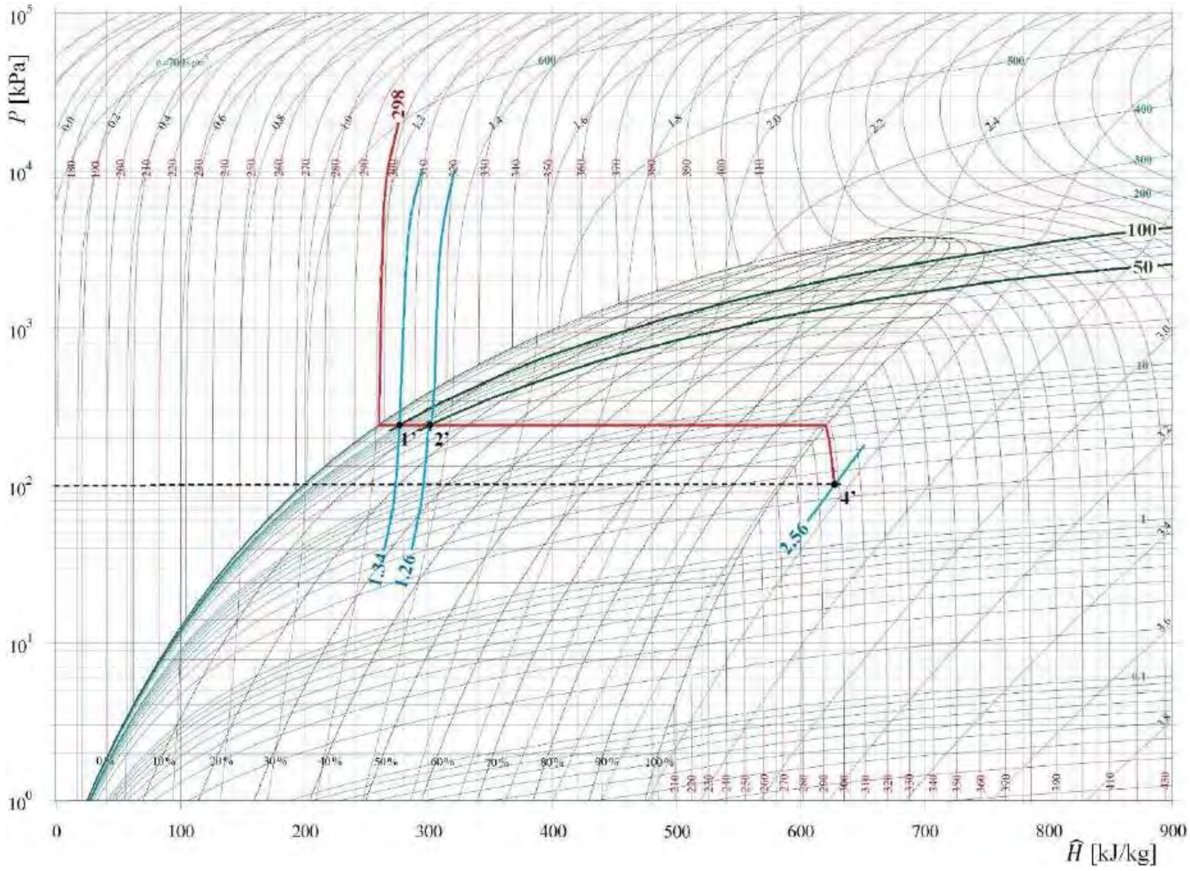
and checking with [5]

$$M_{v_5} = (3.5\ \text{kg})\frac{(647-528)}{(741-528)} = 1.955\ \text{kg}$$

On the other hand, when the cylinder is at half load, its density will be of 50 kg/m^3, and graphically, its intersection with the 393 K isotherm will occur at 1918 kPa, but in the thermodynamic zone corresponding to superheated vapors (6=6').

Question d. The heat taken up to the moment in which the experimental vessel is at half load (isothermal process) will be due to two causes: the transit of half of the load (1.75 kg) from point 1' to point 2' and the transit of the other half of the load (1.75 kg) from point 1' to consumption conditions, which are not specified in the statement of the problem and have to be supposed. For simplicity, it is assumed that butane is employed as vapor at 1 atm and 298 K (conditions at 4'); thus

$$\Delta Q = \frac{M_{1'}}{2}\int_{1'}^{2'} T\mathrm{d}\hat{S} + \frac{M_{1'}}{2}\int_{1'}^{4'} T\mathrm{d}\hat{S}$$



and since $T_{1'}=T_{2'}=T_{4'}$

$$\Delta Q = \frac{M_{1'}}{2} T_{1'}\left(\hat{S}_{2'} - \hat{S}_{1'}\right) + \frac{M_{1'}}{2} T_{1'}\left(\hat{S}_{4'} - \hat{S}_{1'}\right)$$

$$\begin{aligned}\Delta Q = \; & (1.75\ \text{kg})(298\ \text{K})\left(1.26\ \frac{\text{kJ}}{\text{kg}\cdot\text{K}} - 1.34 \frac{\text{kJ}}{\text{kg}\cdot\text{K}}\right) + \\ & +(1.75\ \text{kg})(298\ \text{K})\left(2.56\ \frac{\text{kJ}}{\text{kg}\cdot\text{K}} - 1.34 \frac{\text{kJ}}{\text{kg}\cdot\text{K}}\right) = 594.51\ \text{kJ}\end{aligned}$$

Question e. It refers to problem 4.6, where the conditions are the same as these in this problem. In 4.6 it was a propane cylinder in Trasmonte (Asturias) but here is an experimental vessel containing butane. The reader can answer the question in the depth of his heart.

4.11. The cooling system of a 100 m³ cryogenic tank containing 30000 kg of butane at 70°C suffers a breakdown, and the temperature rises to 120°C.

- **a) Quantitatively represent the phenomenon in a hydrocarbon specific *PH* diagram, and calculate the proportions of liquid and vapor at both moments, as well as the pressures and enthalpies.**
- **b) Determine the proportions and pressures by means of the Corresponding States Principle, using the generalized chart $\rho_r(T_r,P_r)$ for the liquid and $z(T_r,P_r)$ for the vapor.**
- **c) Calculate the amount of heat that has to be removed from the tank to return to the initial conditions, both with a butane specific *PH* diagram and with a generalized chart of the Corresponding States Principle.**
- **d) Qualitatively represent the phenomenon in *PT*, *PV*(*T*), *TS*(*P*) and $z(T_r,P_r)$ diagrams.**

Question a. Since neither the tank volume nor the butane mass varied during the breakdown, the location of the initial and final states on a substance specific *PH* diagram (figure V.9 of appendix V) will be found respectively at the intersections of the isochore

$$\hat{\rho}_1 = \frac{M_1}{V_1} = \hat{\rho}_2 = \frac{M_2}{V_2} = \frac{M_{tot}}{V_{tank}} = \frac{30000 \text{ kg}}{100 \text{ m}^3} = 300 \ \frac{\text{kg}}{\text{m}^3}$$

with the isotherms

$$T_1(\text{K}) = 70°\text{C} + 273 = 343 \text{ K}$$

$$T_2(\text{K}) = 120°\text{C} + 273 = 393 \text{ K}$$

When this is represented, the pressures at point 1 (P_1=800 kPa) and at point 2 (P_2=2175 kPa) can be read directly, as well as the specific enthalpies $\hat{H}_1$ =385 kJ/kg and $\hat{H}_2$ =543 kJ/kg. The title or quality lines can also be interpolated, although the position of the points does not allow doing it clearly: for 1, the proportion of vapor is between 3 - 4%, and for point 2, between 7 - 8% (they have not been drawn to avoid confusion with the isochore).

A more precise solution can be found by combining the mass balance ($M_{tot} = M_l + M_v$) and the volume balance ($M_{tot}/\hat{\rho}_1 = M_l/\hat{\rho}_l^{sat} + M_v/\hat{\rho}_v^{sat}$), a thing that additionally allows determining the volume occupied by each phase. Thus, after interpolating the saturated liquid and vapor densities at the lower temperature ($\hat{\rho}_{l_1}^{sat}$=513 kg/m³, $\hat{\rho}_{v_1}^{sat}$=20 kg/m³), it is obtained

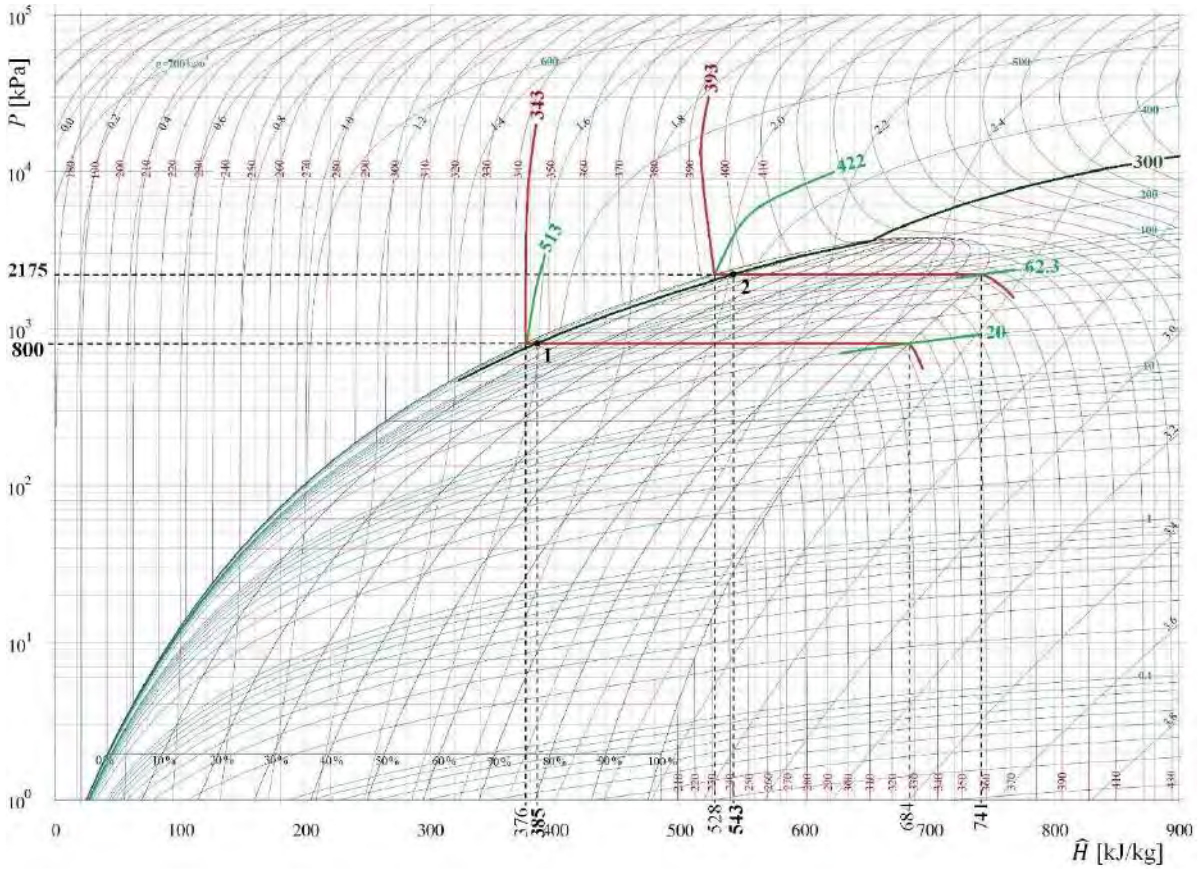
$$\frac{M_{v_1}}{M_{tot}} = \frac{\left(\frac{1}{\hat{\rho}_1} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_1}^{sat}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)} = \frac{\left(\frac{1}{300} - \frac{1}{513}\right)}{\left(\frac{1}{20} - \frac{1}{513}\right)} = 0.0288$$

$$M_{v_1} = 0.0288 M_{tot} = 0.0288(30000 \text{ kg}) = 864 \text{ kg}$$

$$M_{l_1} = M_{tot} - M_{v_1} = 30000 - 864 = 29136\ \text{kg}$$

$$V_{l_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} = \frac{29136\ \text{kg}}{513\ \dfrac{\text{kg}}{\text{m}^3}} = 56.80\ \text{m}^3$$

$$V_{v_1} = \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} = \frac{864\ \text{kg}}{20\ \dfrac{\text{kg}}{\text{m}^3}} = 43.20\ \text{m}^3$$



And after reading them at the higher temperature ($\hat{\rho}_{l_2}^{sat}$=422 kg/m^3, $\hat{\rho}_{v_2}^{sat}$=62.3 kg/m^3)

$$\frac{M_{v_2}}{M_{tot}} = \frac{\left(\dfrac{1}{\hat{\rho}_2} - \dfrac{1}{\hat{\rho}_{l_2}^{sat}}\right)}{\left(\dfrac{1}{\hat{\rho}_{v_2}^{sat}} - \dfrac{1}{\hat{\rho}_{l_2}^{sat}}\right)} = \frac{\left(\dfrac{1}{300} - \dfrac{1}{422}\right)}{\left(\dfrac{1}{62.3} - \dfrac{1}{422}\right)} = 0.0704$$

$$M_{v_2} = 0.0704 M_{tot} = 0.0704(30000\ \text{kg}) = 2112\ \text{kg}$$

$$M_{l_2} = M_{tot} - M_{v_2} = 30000 - 2112 = 27888\ \text{kg}$$

$$V_{l_2} = \frac{M_{l_2}}{\hat{\rho}_{l_2}^{sat}} = \frac{27888\ \text{kg}}{422\ \dfrac{\text{kg}}{\text{m}^3}} = 66.09\ \text{m}^3$$

$$V_{v_2} = \frac{M_{v_2}}{\hat{\rho}_{v_2}^{sat}} = \frac{2112\ \text{kg}}{62.3\ \dfrac{\text{kg}}{\text{m}^3}} = 33.90\ \text{m}^3$$

The saturated vapor proportion can also be estimated by combining the mass balance with the enthalpy balance, which at 343 K gives ($\hat{H}_{l_1}^{sat}$ =376 kJ/kg, $\hat{H}_{v_1}^{sat}$ =684 kJ/kg)

$$\frac{M_{v_1}}{M_{tot}} = \frac{\left(\hat{H}_1 - \hat{H}_{l_1}^{sat}\right)}{\left(\hat{H}_{v_1}^{sat} - \hat{H}_{l_1}^{sat}\right)} = \frac{(385 - 376)}{(684 - 376)} = 0.0292$$

and at 393 K ($\hat{H}_{l_2}^{sat}$ =528 kJ/kg, $\hat{H}_{v_2}^{sat}$ =741 kJ/kg)

$$\frac{M_{v_2}}{M_{tot}} = \frac{\left(\hat{H}_2 - \hat{H}_{l_2}^{sat}\right)}{\left(\hat{H}_{v_2}^{sat} - \hat{H}_{l_2}^{sat}\right)} = \frac{(543 - 528)}{(741 - 528)} = 0.0704$$

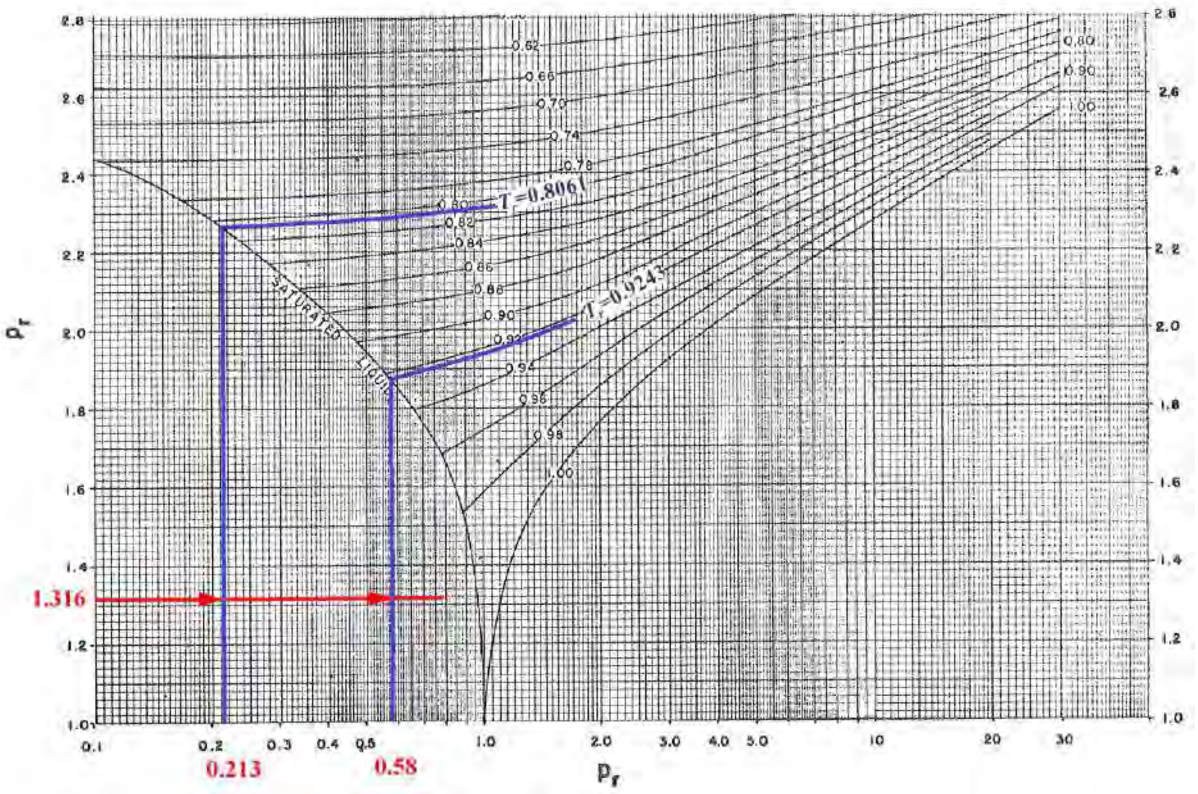
Question b. The statement of the problem proposes the use of a figure such as IV.13 of appendix IV, which is a generalized graph of reduced density as a function of reduced temperature and reduced pressure. Taking the critical properties of butane from appendix II (T_c=425.2 K, P_c=37.5 atm, $\tilde{V}_c$=255 cm^3/mol-g), its molar mass (58.12 g/mol-g) and neglecting the corrections due to $z_c \neq 0.27$ (since its critical compressibility is only 1.48% higher, i.e., z_c=0.274), the beginning and end of the phenomenon will be determined graphically by the intersection of the isochore

$$\rho_{r1} = \hat{\rho}_1 \hat{V}_c = \left(300\ \frac{\text{kg}}{\text{m}^3}\right) \times \left(255\ \frac{\text{cm}^3}{\text{mol-g}}\right) \times \left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^3 \times \frac{1\ \text{mol-g}}{58.12\ \text{g}} \times \frac{1000\ \text{g}}{1\ \text{kg}} = 1.316$$

with the isotherms

$$T_{r1} = \frac{T_1}{T_c} = \frac{343\ \text{K}}{425.2\ \text{K}} = 0.8061$$

$$T_{r2} = \frac{T_1}{T_c} = \frac{393\ \text{K}}{425.2\ \text{K}} = 0.9243$$



These intersections take place within the biphasic zone, giving the reduced pressures P_{r1}=0.213 and P_{r2}=0.58; thus

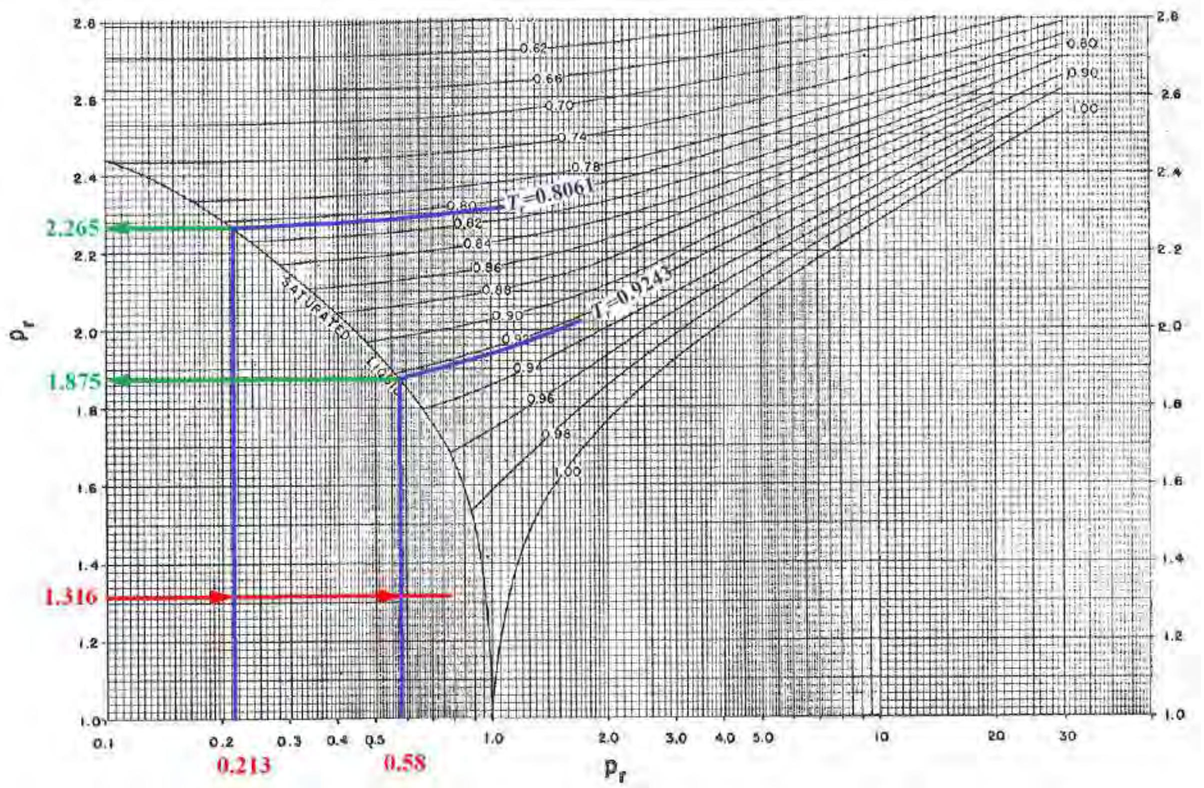
$$P_1 = P_{r1}P_c = 0.213\ (37.5\ \text{atm}) = 7.9875\ \text{atm}\ \rightarrow\ 7.9875\ \text{atm}\times\frac{101.3\ \text{kPa}}{1\ \text{atm}}=809.1\ \text{bar}$$

$$P_2 = P_{r2}P_c = 0.58\ (37.5\ \text{atm}) = 21.75\ \text{atm}\ \rightarrow\ 21.75\ \text{atm}\times\frac{101.3\ \text{kPa}}{1\ \text{atm}}=2203.3\ \text{bar}$$

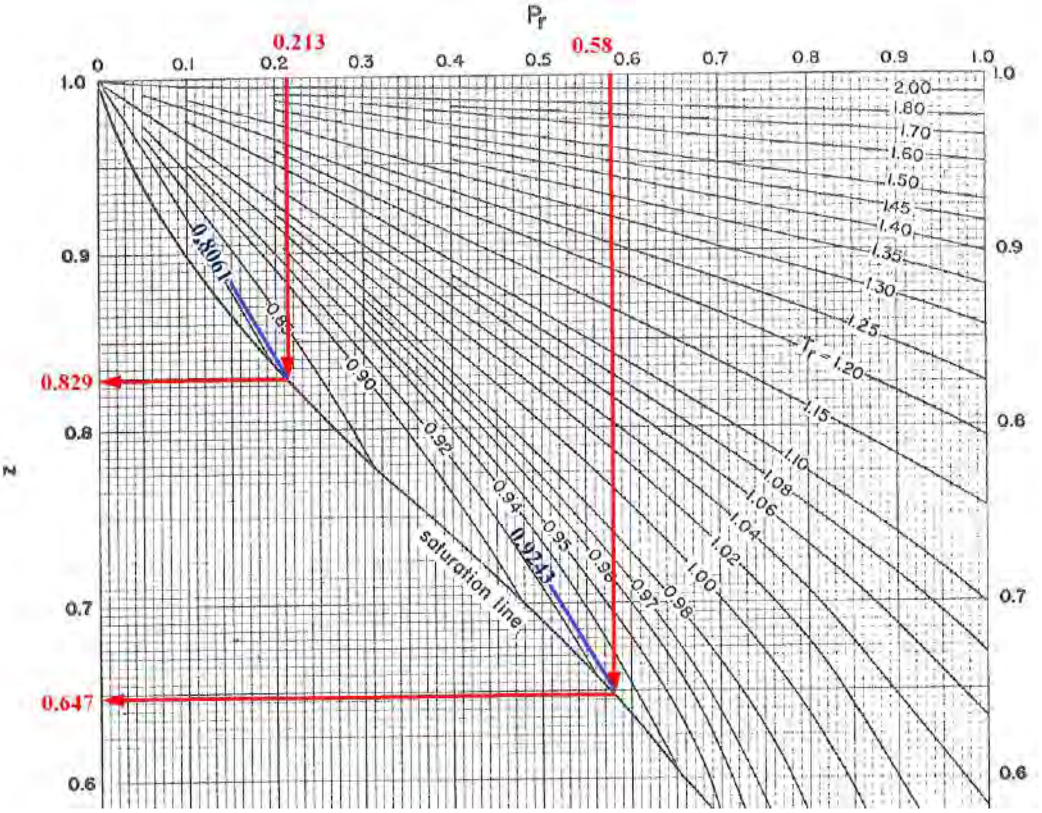
But, in addition, figure IV.13 provides the reduced densities of the saturated liquid at the two temperatures ($\hat{\rho}_{rl_1}^{sat}$ =2.265 and $\hat{\rho}_{rl_1}^{sat}$ =1.875), which are necessary for the estimation of saturated liquid and vapor amounts

$$\hat{\rho}_{l_1}^{sat} = \frac{2.265}{\left(255\ \frac{\text{cm}^3}{\text{mol-g}}\right)\times\left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^3\times\frac{1\ \text{mol-g}}{58.12\ \text{g}}\times\frac{1000\ \text{g}}{1\ \text{kg}}} = 516.24\ \frac{\text{kg}}{\text{m}^3}$$

$$\hat{\rho}_{l_2}^{sat} = \frac{1.875}{\left(255\ \frac{\text{cm}^3}{\text{mol-g}}\right)\times\left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^3\times\frac{1\ \text{mol-g}}{58.12\ \text{g}}\times\frac{1000\ \text{g}}{1\ \text{kg}}} = 427.35\ \frac{\text{kg}}{\text{m}^3}$$



On the other hand, and following the statement of the problem, figure IV.3 of appendix IV is employed for the saturated vapor densities. In it, the vapor compressibility factor is given as a function of the reduced temperature and pressure.



At T_{r1}=0.8061 and P_{r1}=0.213 it is found that $z_{v_1}^{sat}$=0.829, and at T_{r2}=0.9243 and P_{r2}=0.58, $z_{v_2}^{sat}$=0.647, so

$$\hat{\rho}_{v_1}^{sat} = \frac{P_1\mathfrak{W}}{z_{v_1}^{sat}RT_1} = \frac{(7.9875\ \text{atm})\left(58.12\ \frac{\text{g}}{\text{mol-g}}\right)}{(0.829)\left(0.082\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(343\ \text{K})} = 19.91\ \frac{\text{g}}{\text{L}} = 19.91\ \frac{\text{kg}}{\text{m}^3}$$

$$\hat{\rho}_{v_2}^{sat} = \frac{P_2\mathfrak{W}}{z_{v_2}^{sat}RT_2} = \frac{(21.75\ \text{atm})\left(58.12\ \frac{\text{g}}{\text{mol-g}}\right)}{(0.647)\left(0.082\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(393\ \text{K})} = 60.63\ \frac{\text{g}}{\text{L}} = 60.63\ \frac{\text{kg}}{\text{m}^3}$$

Finally, by operating as in question **a** with the combination of mass and volume balances, it is found, for the lower temperature, that

$$\frac{M_{v_1}}{M_{tot}} = \frac{\left(\frac{1}{\hat{\rho}_1} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_1}^{sat}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)} = \frac{\left(\frac{1}{300} - \frac{1}{516.24}\right)}{\left(\frac{1}{19.91} - \frac{1}{516.24}\right)} = 0.0289$$

$$M_{v_1} = 0.0289M_{tot} = 0.0289(30000\ \text{kg}) = 867\ \text{kg}$$

$$M_{l_1} = M_{tot} - M_{v_1} = 30000 - 867 = 29133\ \text{kg}$$

$$V_{l_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} = \frac{29133\ \text{kg}}{516.24\ \frac{\text{kg}}{\text{m}^3}} = 56.43\ \text{m}^3$$

$$V_{v_1} = \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} = \frac{867\ \text{kg}}{19.91\ \frac{\text{kg}}{\text{m}^3}} = 43.55\ \text{m}^3$$

and for the higher temperature

$$\frac{M_{v_2}}{M_{tot}} = \frac{\left(\frac{1}{\hat{\rho}_2} - \frac{1}{\hat{\rho}_{l_2}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_2}^{sat}} - \frac{1}{\hat{\rho}_{l_2}^{sat}}\right)} = \frac{\left(\frac{1}{300} - \frac{1}{427.35}\right)}{\left(\frac{1}{60.63} - \frac{1}{427.35}\right)} = 0.0702$$

$$M_{v_2} = 0.0702M_{tot} = 0.0702(30000\ \text{kg}) = 2106\ \text{kg}$$

$$M_{l_2} = M_{tot} - M_{v_2} = 30000 - 2106 = 27894\ \text{kg}$$

$$V_{l_2} = \frac{M_{l_2}}{\hat{\rho}_{l_2}^{sat}} = \frac{27894\ \mathrm{kg}}{427.35\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 65.27\ \mathrm{m}^3$$

$$V_{v_2} = \frac{M_{v_2}}{\hat{\rho}_{v_2}^{sat}} = \frac{2106\ \mathrm{kg}}{60.63\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 34.73\ \mathrm{m}^3$$

Question c. The heat produced in the transition from state 1 to state 2 is evaluated by the expression

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \Delta\hat{Q}_{21} = \int_1^2 T\mathrm{d}\hat{S}$$

but according to one of the equations of reference problem 0.3

$$\mathrm{d}\hat{U} = \mathrm{d}\hat{Q} - P\mathrm{d}\hat{V}$$

if the specific volume remains constant ($\mathrm{d}\hat{V}$=0), there is no expansion-compression work and

$$\Delta\hat{Q}_{21}=\Delta\hat{U}_{21} = \hat{U}_2 - \hat{U}_1 = \left(\hat{H}_2 - \frac{P_2}{\hat{\rho}_1}\right) - \left(\hat{H}_1 - \frac{P_1}{\hat{\rho}_1}\right) = \hat{H}_2 - \hat{H}_1 - \frac{(P_2 - P_1)}{\hat{\rho}_1}$$

Compiling the data from question **a**, and introducing them into the formula, it is obtained

$$\Delta\hat{Q}_{21}=\left(543\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 385\frac{\mathrm{kJ}}{\mathrm{kg}}\right) - \frac{(2175\ \mathrm{kPa} - 800\ \mathrm{kPa})}{300\ \mathrm{kg/m}^3} = 153.42\frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta Q_{21} = M_{tot}\Delta\hat{Q}_{21} = (30000\ \mathrm{kg})\left(153.42\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 4602600\ \mathrm{kJ}$$

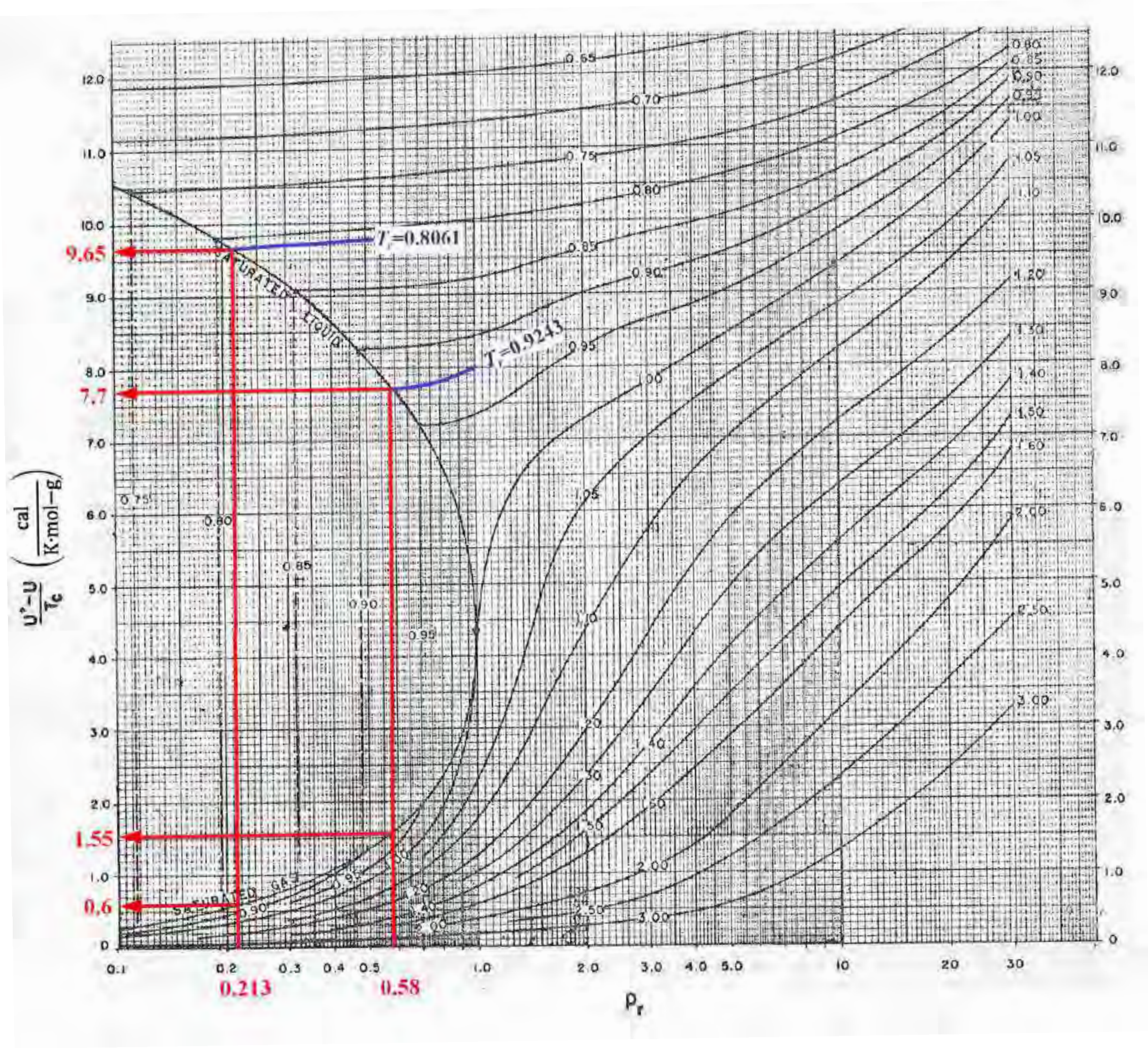
To perform the calculation by the Corresponding States Principle, it must be taken into account that the variation of internal energy between the state 1 and the state 2 will be given by the equation (section e of reference problem 0.8)

$$\left(\widetilde{U}_2 - \widetilde{U}_1\right) = \underbrace{\left(\widetilde{U}_2^* - \widetilde{U}_1^*\right)}_{\text{ideal part}} + \underbrace{\left(\widetilde{U}_1^* - \widetilde{U}_1\right)_{T_1,P_1} - \left(\widetilde{U}_2^* - \widetilde{U}_2\right)_{T_2,P_2}}_{\text{real part}} \qquad [1]$$

where the real part is estimated by the generalized figure IV.9 of appendix IV, and the ideal part by the specific heat capacity at constant pressure of butane, considered as an ideal gas

$$\widetilde{U}_2^* - \widetilde{U}_1^* = \int_{T_1}^{T_2} \tilde{C}_V^* \mathrm{d}T = \int_{T_1}^{T_2} \left(\tilde{C}_P^* - R\right) \mathrm{d}T$$

Furthermore, when resorting to figure IV.9, it is observed that at T_{r1}=0.8061 and P_{r1}=0.213 there are two values of internal energy departure: one for the saturated liquid and other for the saturated vapor, so the value in 1 must be estimated by using the internal energy balance and the vapor fraction of 2.89% from question **b**.



$$\left(\frac{\widetilde{U}_1^* - \widetilde{U}_1}{T_c}\right)_l^{sat} = 9.65 \frac{\text{cal}}{\text{K· mol-g}} \quad ; \quad \left(\frac{\widetilde{U}_1^* - \widetilde{U}_1}{T_c}\right)_v^{sat} = 0.6 \frac{\text{cal}}{\text{K· mol-g}}$$

$$\left(\frac{\widetilde{U}_1^* - \widetilde{U}_1}{T_c}\right)_{T_{r1},P_{r1}} = \frac{M_{v_1}}{M_{tot}} \left(\frac{\widetilde{U}_1^* - \widetilde{U}_1}{T_c}\right)_v^{sat} + \left(1 - \frac{M_{v_1}}{M_{tot}}\right) \left(\frac{\widetilde{U}_1^* - \widetilde{U}_1}{T_c}\right)_l^{sat}$$

$$\left(\frac{\widetilde{U}_1^* - \widetilde{U}_1}{T_c}\right)_{T_{r1},P_{r1}} = 0.0289\left(0.6\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)+(1-0.0289)\left(9.65\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)=9.388\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$\left(\widetilde{U}_1^* - \widetilde{U}_1\right)_{T_1,P_1} = \left(9.388\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)(425.2\text{ K}) = 3991.78\,\frac{\text{cal}}{\text{mol-g}}$$

And the same happens at T_{r2}=0.9243 and P_{r2}=0.58, with a vapor fraction of 7.02%

$$\left(\frac{\widetilde{U}_2^* - \widetilde{U}_2}{T_c}\right)_l^{sat} = 7.7\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}} \quad ; \quad \left(\frac{\widetilde{U}_2^* - \widetilde{U}_2}{T_c}\right)_v^{sat} = 1.55\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$\left(\frac{\widetilde{U}_2^* - \widetilde{U}_2}{T_c}\right)_{T_{r2},P_{r2}} = 0.0702\left(1.55\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)+(1-0.0702)\left(7.7\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)=7.268\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$\left(\widetilde{U}_2^* - \widetilde{U}_2\right)_{T_2,P_2} = \left(7.268\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)(425.2\text{ K}) = 3090.35\,\frac{\text{cal}}{\text{mol-g}}$$

Regarding the ideal part, the heat capacity of butane as an ideal gas is taken from appendix II

$$\tilde{C}_P^* = \xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4$$

where

$$\frac{\xi_0}{R} = 5.547 \qquad \frac{\xi_1}{R} = 5.536\cdot 10^{-3}\,\frac{1}{\text{K}} \qquad \frac{\xi_2}{R} = 8.057\cdot 10^{-5}\,\frac{1}{\text{K}^2}$$

$$\frac{\xi_3}{R} = -10.571\cdot 10^{-8}\,\frac{1}{\text{K}^3} \qquad \frac{\xi_4}{R} = 4.134\cdot 10^{-11}\,\frac{1}{\text{K}^4}$$

Hence

$$\widetilde{U}_2^* - \widetilde{U}_1^* = \int_{T_1}^{T_2}(\xi_0 - R + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4)\mathrm{d}T$$

$$\widetilde{U}_2^* - \widetilde{U}_1^* = \left[(\xi_0 - R)T + \frac{1}{2}\xi_1 T^2 + \frac{1}{3}\xi_2 T^3 + \frac{1}{4}\xi_3 T^4 + \frac{1}{5}\xi_4 T^5\right]_{T_1}^{T_2} =$$
$$= (\xi_0 - R)(T_2 - T_1) + \frac{\xi_1}{2}(T_2^2 - T_1^2) + \frac{\xi_2}{3}(T_2^3 - T_1^3) + \frac{\xi_3}{4}(T_2^4 - T_1^4) + \frac{\xi_4}{5}(T_2^5 - T_1^5)$$

By taking R=1.9872 cal/(mol-g·K), this difference is

$$\left(\tilde{U}_2^* - U_1^*\right) = (5.547-1)R(393-343) + \frac{5.536\cdot 10^{-3}}{2}R(393^2-343^2) + \\ + \frac{8.057\cdot 10^{-5}}{3}R(393^3-343^3) - \frac{10.571\cdot 10^{-8}}{4}R(393^4-343^4) + \\ + \frac{4.134\cdot 10^{-11}}{5}R(393^5-343^5) = 1290.17\frac{\text{cal}}{\text{mol-g}}$$

and equation [1] gives

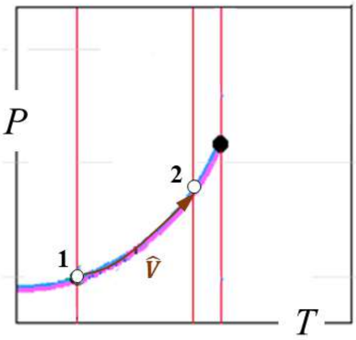
$$\left(\tilde{U}_2 - \tilde{U}_1\right) = 1290.17\ \frac{\text{cal}}{\text{mol-g}} + 3991.78\ \frac{\text{cal}}{\text{mol-g}} - 3090.35\ \frac{\text{cal}}{\text{mol-g}} = 2191.6\frac{\text{cal}}{\text{mol-g}}$$

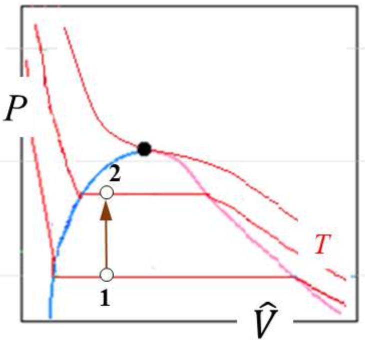
After converting the units and multiplying this internal energy by the total mass, a result very close to that of the specific diagram is obtained

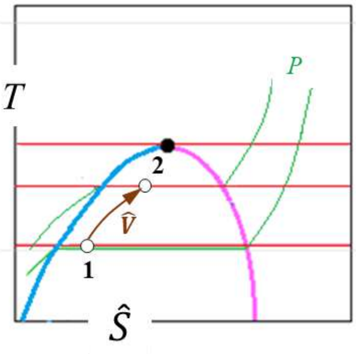
$$2191.6\frac{\text{cal}}{\text{mol-g}} \times \frac{1\ \text{kcal}}{1000\ \text{cal}} \times \frac{4180\ \text{J}}{1\ \text{kcal}} \times \frac{1\ \text{mol-g}}{58.12\ \text{g}} \times \frac{1000\ \text{g}}{1\ \text{kg}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = 157.62\ \frac{\text{kJ}}{\text{kg}}$$

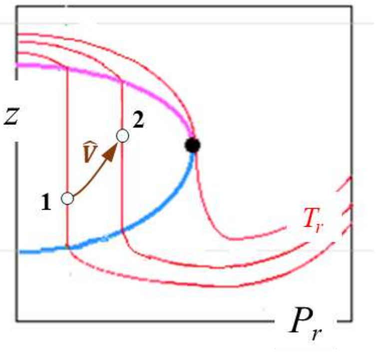
$$\Delta Q_{21} = M_{tot}\Delta\hat{U}_{21} = (30000\ \text{kg})\left(157.62\frac{\text{kJ}}{\text{kg}}\right) = 4728600\ \text{kJ}$$

Question d. The qualitative representation of the phenomenon in the *PT*, *PV*, *TS* and $z(T_r, P_r)$ diagrams will be









4.12. Propylene is a dangerous chemical substance since, in addition to being highly combustible, it can lead to mechanical explosions because heating during transport (if tanks are overloaded). To study these eventualities, a simulator is used, being its main element a controlled cylindrical tank (chamber) of variable volume and thermostatted walls.

1) **330 g of the hydrocarbon are confined in a volume of 9.9 L at 290 K. From these conditions several independent experiments are carried out.**
2) **Isobaric heating to 330 K.**
3) **Isochoric heating to the same temperature.**
4) **Adiabatic and reversible compression to the same temperature.**

Hence:

a) **Represent the initial state of the hydrocarbon on a propylene specific *PH* (*T, V, S*) diagram, and determine its conditions.**
b) **Quantitatively represent the chamber evolution on a propylene specific *PH* diagram, and indicate the state and conditions of the 330 g of hydrocarbon at the end of each experiment. Calculate the heat exchanged and/or the expansion-compression work done as well.**
c) **Subsequently, more hydrocarbon is injected into the tank (under the same initial conditions of volume, temperature and pressure), reaching a mass of 707 g. Then, the aforementioned experiments are repeated. Indicate the final conditions and the heat and/or expansión-compression work in each case.**
d) **Qualitatively represent the evolution of the chamber in *PT(S,V)*, *PV*(*T, S*), *TS*(*P,V*) and *z*(P_r, T_r) diagrams.**

Question a. It is necessary to employ the figure V.10 of this book's appendix V. The conditions of point 1 will be graphically located where the T_1=290 K isotherm intersects the isochore

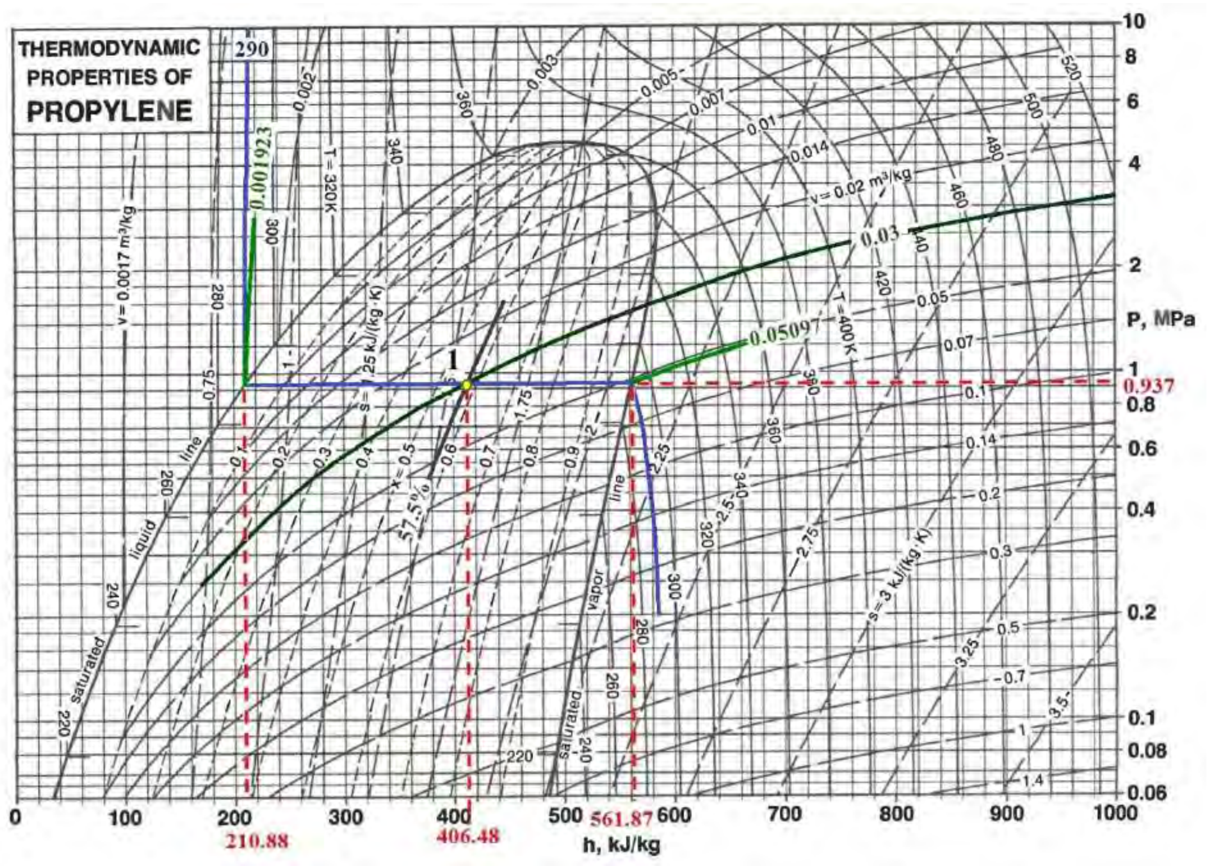
$$\hat{V}_1 = \frac{V_1}{M_1} = \frac{9.9\ \mathrm{L}}{330\ \mathrm{g}} \times \frac{1\ \mathrm{m^3}}{1000\ \mathrm{L}} \times \frac{1000\ \mathrm{g}}{1\ \mathrm{kg}} = 0.03\ \frac{\mathrm{m^3}}{\mathrm{kg}}$$

It is seen that this point falls in the biphasic zone, with an approximate title or quality of 57.5% (0.575×330 g = 189.75 g of vapor) at a pressure of 0.937 MPa and with a total enthalpy of 406.48 kJ/kg. The amounts of saturated vapor and liquid have to be determined by mass and volume balances, in the form

$$M_{tot} = M_{l_1} + M_{v_1} \quad [1]$$

$$M_{tot}\hat{V}_{tot} = M_{l_1}\hat{V}_{l_1}^{sat} + M_{v_1}\hat{V}_{v_1}^{sat} \quad [2]$$

where $\hat{V}_{tot} = \hat{V}_1$, $M_{tot} = M_1$ and $\hat{V}_l^{sat}$and $\hat{V}_v^{sat}$are the specific volumes of saturated liquid and vapor, which took values of 0.001923 kg/m^3 and 0.05097 kg/m^3, respectively (by interpolation in figure V.10).



Combining [1] and [2] and introducing the data, it is obtained that

$$M_{v_1} = M_{tot}\frac{\left(\hat{V}_{tot} - \hat{V}_{l_1}^{sat}\right)}{\left(\hat{V}_{v_1}^{sat} - \hat{V}_{l_1}^{sat}\right)} = (330\ \mathrm{g})\frac{(0.03 - 0.001923)}{(0.05097 - 0.001923)} = 188.91\ \mathrm{g}$$

$$M_{l_1} = M_{tot} - M_{v_1} = 330 - 188.91 = 141.09\ \mathrm{g}$$

masses that occupy the following volumes

$$V_{v_1} = M_{v_1}\hat{V}_{v_1}^{sat} = (188.91\ \mathrm{g})\left(0.05097\ \frac{\mathrm{L}}{\mathrm{g}}\right) = 9.63\ \mathrm{L}$$

$$V_{l_1} = M_{l_1}\hat{V}_{l_1}^{sat} = (141.09\ \mathrm{g})\left(0.001923\ \frac{\mathrm{L}}{\mathrm{g}}\right) = 0.27\ \mathrm{L}$$

The amount of saturated vapor also can be checked by means of the mass balance (equation [1]) and the enthalpy one

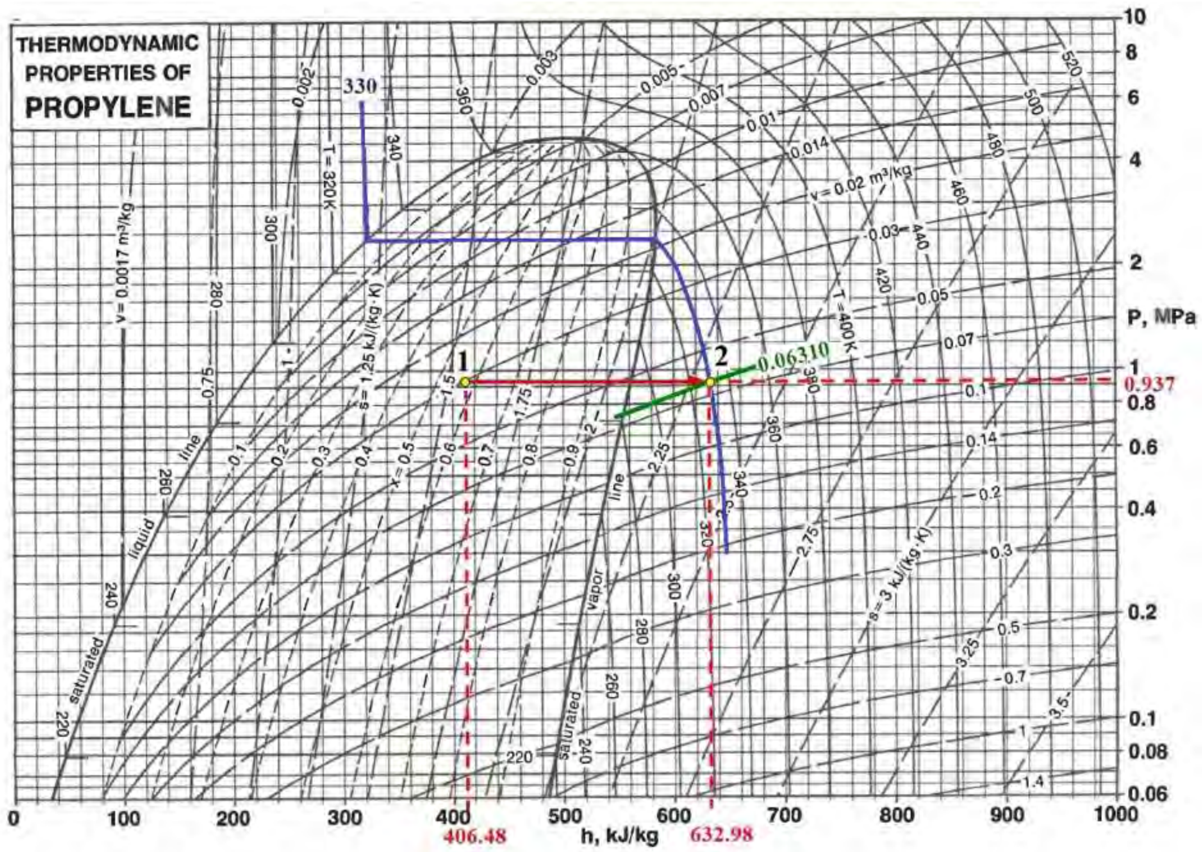
$$M_{tot}\hat{H}_{tot} = M_{l_1}\hat{H}_{l_1}^{sat} + M_{v_1}\hat{H}_{v_1}^{sat} \qquad [3]$$

where $\hat{H}_{tot} = \hat{H}_1$. Combining [1] and [3] and reading in the figure that the saturated liquid enthalpy is 210.88 kJ/kg and that of the saturated vapor 561.87 kJ/kg

$$M_{v_1} = M_{tot}\frac{\left(\hat{H}_{tot} - \hat{H}_{l_1}^{sat}\right)}{\left(\hat{H}_{v_1}^{sat} - \hat{H}_{l_1}^{sat}\right)} = (330\ \text{g})\frac{(406.48 - 210.88)}{(561.87 - 210.88)} = 183.9\ \text{g}$$

(value that is not exactly the same as the previously found from the densities because the errors associated with the interpolation and reading in graphs).

Question b. To locate point 2 in diagram V.10, the 0.937 MPa (937 kPa) isobar is drawn to where it intersects the T_2=330 K isotherm. All the propylene is now in a state of superheated vapor, with an approximate specific volume $\hat{V}_2$=0.06310 kg/m^3 and a specific enthalpy $\hat{H}_2$=632.98 kJ/kg.



On the other hand, the heat produced in the transit from states 1 to 2 will be calculated by means of the expression

$$\text{d}\hat{Q} = T\text{d}\hat{S} \quad \rightarrow \Delta\hat{Q}_{21} = \int_1^2 T\text{d}\hat{S}$$

but according to equations of reference problem 0.3

$$\text{d}\hat{H} = \text{d}\hat{Q} + \text{d}\hat{W}^{\text{fl}} = \text{d}\hat{Q} + \hat{V}\text{d}P$$

and since the process is isobaric (P does not change), there will be no flow work and the heat produced will coincide with the enthalpy change ($\mathrm{d}\widehat{H} = \mathrm{d}\widehat{Q}$), avoiding the numerical integration

$$\Delta\widehat{Q}_{21}=\Delta\widehat{H}_{21} = \widehat{H}_2 - \widehat{H}_1 = 632.98\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 406.48\frac{\mathrm{kJ}}{\mathrm{kg}} = 226.5\frac{\mathrm{kJ}}{\mathrm{kg}}$$

value that, extended to the entire mass, will give

$$\Delta Q_{21} = M_{tot}\Delta\widehat{Q}_{21} = (0.33\ \mathrm{kg})\left(226.5\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 74.745\ \mathrm{kJ}$$

Regarding the expansion-compression work

$$\mathrm{d}\widehat{W}^{\text{e-c}} = -P\mathrm{d}\widehat{V} \quad \xrightarrow{P\ constant} \quad \Delta\widehat{W}^{\text{e-c}} = -P\Delta\widehat{V}$$

$$\Delta\widehat{W}_{21}^{\text{e-c}} = -P_1\left(\widehat{V}_2 - \widehat{V}_1\right) = -(937\ \mathrm{kPa})\left(0.06310\ \frac{\mathrm{m}^3}{\mathrm{kg}} - 0.03\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right) = -31.015\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta W_{21}^{\text{e-c}} = M_{tot}\Delta\widehat{W}_{21}^{\text{e-c}} = (0.33\ \mathrm{kg})\left(-31.015\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -10.235\ \mathrm{kJ}$$

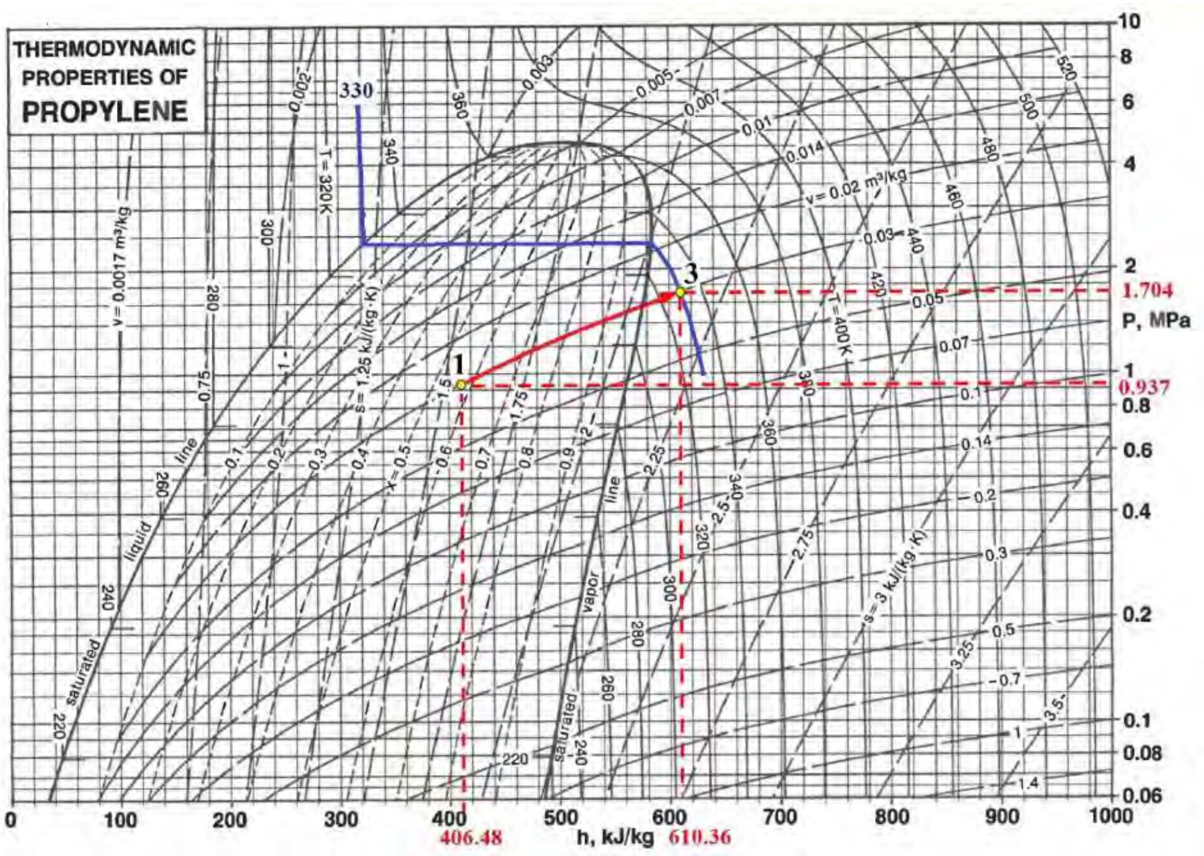
Point 3 will be found graphically following the $\widehat{V}_3 = \widehat{V}_1 = 0.03\ \mathrm{m}^3/\mathrm{kg}$ isochore until it intersects the T_3 isotherm (which in this case is equal to T_2= 330 K). At that point, propane is a superheated vapor at P_3= 1.704 MPa (1704 kPa) and with a specific enthalpy $\widehat{H}_3$=610.36 kJ/kg.

Since $\widehat{V}_1$=$\widehat{V}_3$, there will be no expansion-compression work, and the heat will be calculated as

$$\Delta\widehat{Q}=\Delta\widehat{H} - \widehat{V}\Delta P$$

$$\begin{aligned}\Delta\widehat{Q}_{31}&=\left(\widehat{H}_3 - \widehat{H}_1\right) - \widehat{V}_1(P_3 - P_1) = \\ &= \left(610.36\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 406.48\frac{\mathrm{kJ}}{\mathrm{kg}}\right) - \left(0.03\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right)(1704\ \mathrm{kPa} - 937\ \mathrm{kPa}) = 180.87\frac{\mathrm{kJ}}{\mathrm{kg}}\end{aligned}$$

$$\Delta Q_{31} = M_{tot}\Delta\widehat{Q}_{31} = (0.33\ \mathrm{kg})\left(180.87\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 59.687\ \mathrm{kJ}$$



The fourth experiment is adiabatic and reversible, so it is isentropic (ΔS=0). Point 4 will be located at the intersection between the isentropic line that passes through 1 ($\hat{S}_1$ =1.549 kJ/kg·K) and the isotherm T_4, which is also equal to T_2= 330 K. The hydrocarbon is now a mixture of liquid and vapor, at P_4=2.371 MPa (2371 kPa), with a specific volume $\hat{V}_4$ =0.00909 m^3/kg and a specific enthalpy $\widehat{H}_4$= 434.11 kJ/kg. Operating as in the first question of the problem, the combination of the mass and volume balances (when the specific volumes of the saturated vapor and the saturated liquid have been interpolated) will give

$$M_{v_4} = M_{tot}\frac{\left(\hat{V}_4 - \hat{V}_{l_4}^{sat}\right)}{\left(\hat{V}_{v_4}^{sat} - \hat{V}_{l_4}^{sat}\right)} = (330\ \mathrm{g})\frac{(0.00909 - 0.002255)}{(0.01854 - 0.002255)} = 138.50\ \mathrm{g}$$

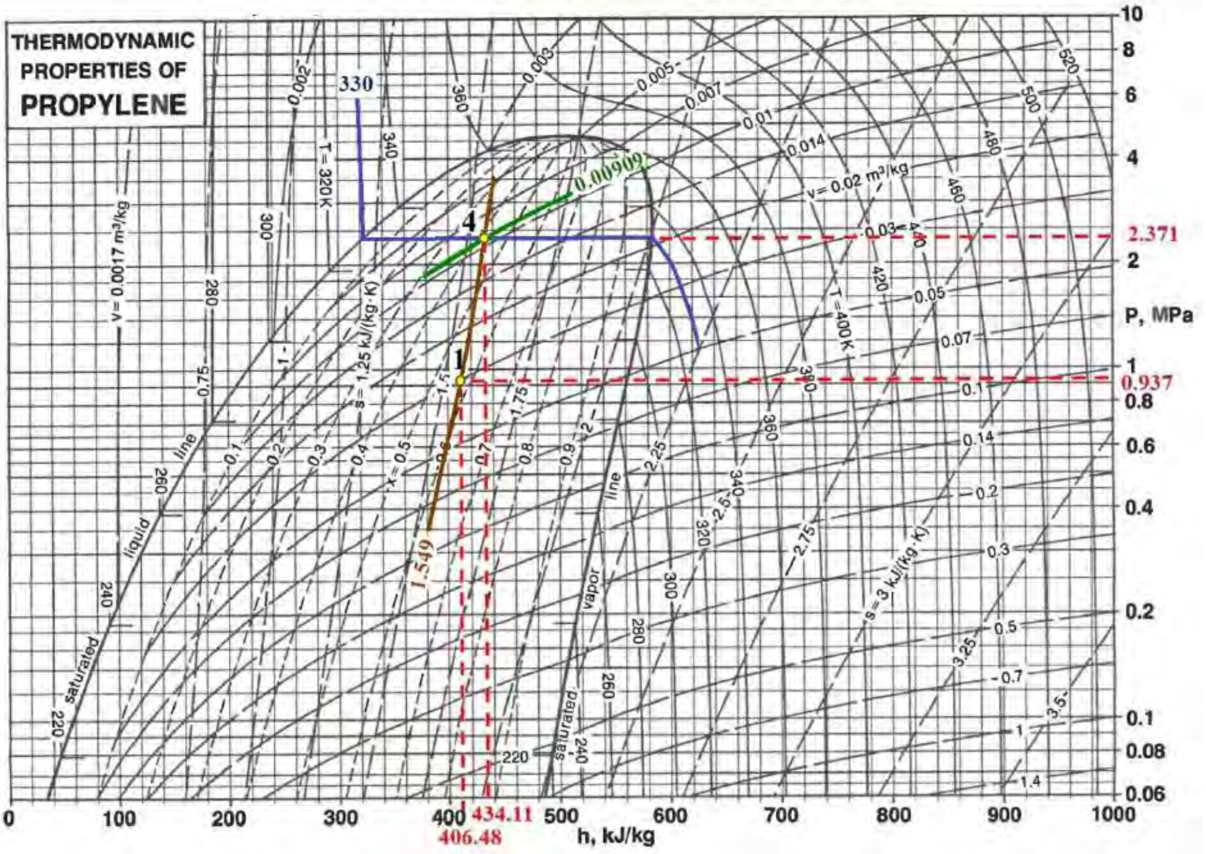
$$M_{l_4} = M_{tot} - M_{v_4} = 330 - 138.50 = 191.5\ \mathrm{g}$$

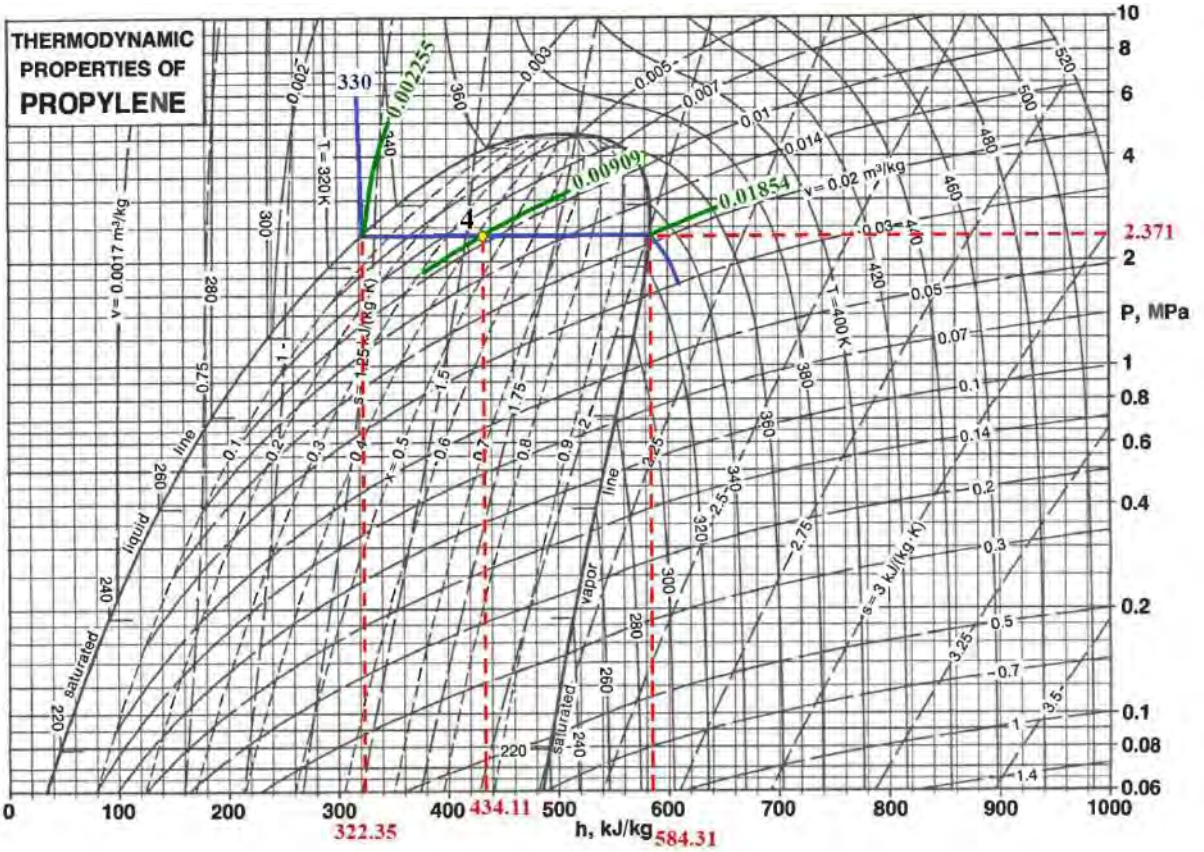
$$V_{v_4} = M_{v_4}\hat{V}_{v_4}^{sat} = (140.78\ \mathrm{g})\left(0.01854\ \frac{\mathrm{L}}{\mathrm{g}}\right) = 2.61\ \mathrm{L}$$

$$V_{l_4} = M_{l_4}\hat{V}_{l_4}^{sat} = (191.5\ \mathrm{g})\left(0.002255\ \frac{\mathrm{L}}{\mathrm{g}}\right) = 0.432\ \mathrm{L}$$

while in the enthalpy balance

$$M_{v_4} = M_{tot}\frac{\left(\widehat{H}_4 - \widehat{H}_{l_4}^{sat}\right)}{\left(\widehat{H}_{v_4}^{sat} - \widehat{H}_{l_4}^{sat}\right)} = (330\ \mathrm{g})\frac{(434.11 - 322.35)}{(584.31 - 322.35)} = 140.78\ \mathrm{g}$$


THERMODYNAMIC PROPERTIES OF PROPYLENE
330
4
1
0.00909
1.549
2.371
0.937
P, MPa
h, kJ/kg
406.48
434.11
saturated liquid line
saturated vapor line
v = 0.0017 m³/kg
v = 0.02 m³/kg
s = 1.25 kJ/(kg·K)
s = 3 kJ/(kg·K)
T = 320 K
T = 400 K
x = 0.5
0
100
200
300
400
500
600
700
800
900
1000
10
8
6
4
2
1
0.8
0.6
0.4
0.2
0.1
0.08
0.06


THERMODYNAMIC PROPERTIES OF PROPYLENE
330
4
0.002255
0.00909
0.01854
2.371
P, MPa
h, kJ/kg
322.35
434.11
584.31
saturated liquid line
saturated vapor line
v = 0.0017 m³/kg
v = 0.02 m³/kg
s = 1.25 kJ/(kg·K)
s = 3 kJ/(kg·K)
T = 320 K
T = 400 K
x = 0.5
0
100
200
300
400
500
600
700
800
900
1000
10
8
6
4
2
1
0.8
0.6
0.4
0.2
0.1
0.08
0.06

For its part, the expansion-compression work should be calculated by

$$\mathrm{d}\widehat{W}^{\text{e-c}} = -P\mathrm{d}\hat{V} \quad \rightarrow \quad \Delta\widehat{W}_{41}^{\text{e-c}} = -\int_1^4 P\mathrm{d}\hat{V}$$

but since the heat produced is zero ($\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S}$), the expansion-compression work will coincide with the change in internal energy and the numerical integration will not be necessary

$$\mathrm{d}\widehat{U} = \mathrm{d}\hat{Q} - P\mathrm{d}\hat{V} \xrightarrow{\mathrm{d}\hat{Q}=0} \Delta\widehat{W}^{\text{e-c}} = \Delta\widehat{U} = \Delta\big(\widehat{H} - P\hat{V}\big)$$

$$\Delta\widehat{W}_{41}^{\text{e-c}}=\big(\widehat{H}_4 - P_4\hat{V}_4\big) - \big(\widehat{H}_1 - P_1\hat{V}_1\big) = \left[434.11\ \frac{\text{kJ}}{\text{kg}} - \left(0.00909\ \frac{\text{m}^3}{\text{kg}}\right)(2371\ \text{kPa})\right] -$$

$$-\left[406.48\ \frac{\text{kJ}}{\text{kg}} - \left(0.03\ \frac{\text{m}^3}{\text{kg}}\right)(937\ \text{kPa})\right] = 34.188\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta W_{41}^{\text{e-c}} = M_{tot}\Delta\widehat{W}_{41}^{\text{e-c}} = (0.33\ \text{kg})\left(34.188\ \frac{\text{kJ}}{\text{kg}}\right) = 11.282\ \text{kJ}$$

Question c. When the mass is modified to 707 g, point 1’ will result from the crossing of the T_1=290 K isotherm with the isochore

$$\hat{V}_{1'} = \hat{V}_{tot'} = \frac{V_1}{M_{1'}} = \frac{V_1}{M_{tot'}} = \frac{9.9\ \text{L}}{707\ \text{g}} \times \frac{1\ \text{m}^3}{1000\ \text{L}} \times \frac{1000\ \text{g}}{1\ \text{kg}} = 0.014\ \frac{\text{m}^3}{\text{kg}}$$

which, as in question **a**, is in the biphasic zone (pressure P_1= $P_{1'}$ = 0.937 MPa, enthalpy $\widehat{H}_{tot'} = \widehat{H}_{1'}$ =295.83 kJ/kg), with an amount of vapor that can be estimated from the title or quality lines

24.7% → 0.247×707 g = 174.63 g

from the enthalpy balance combined with the mass one

$$M_{v_{1'}} = M_{tot'}\frac{\big(\widehat{H}_{tot'} - \widehat{H}_{l_1}^{sat}\big)}{\big(\widehat{H}_{v_1}^{sat} - \widehat{H}_{l_1}^{sat}\big)} = (707\ \text{g})\frac{(295.83 - 210.88)}{(561.87 - 210.88)} = 171.11\ \text{g}$$

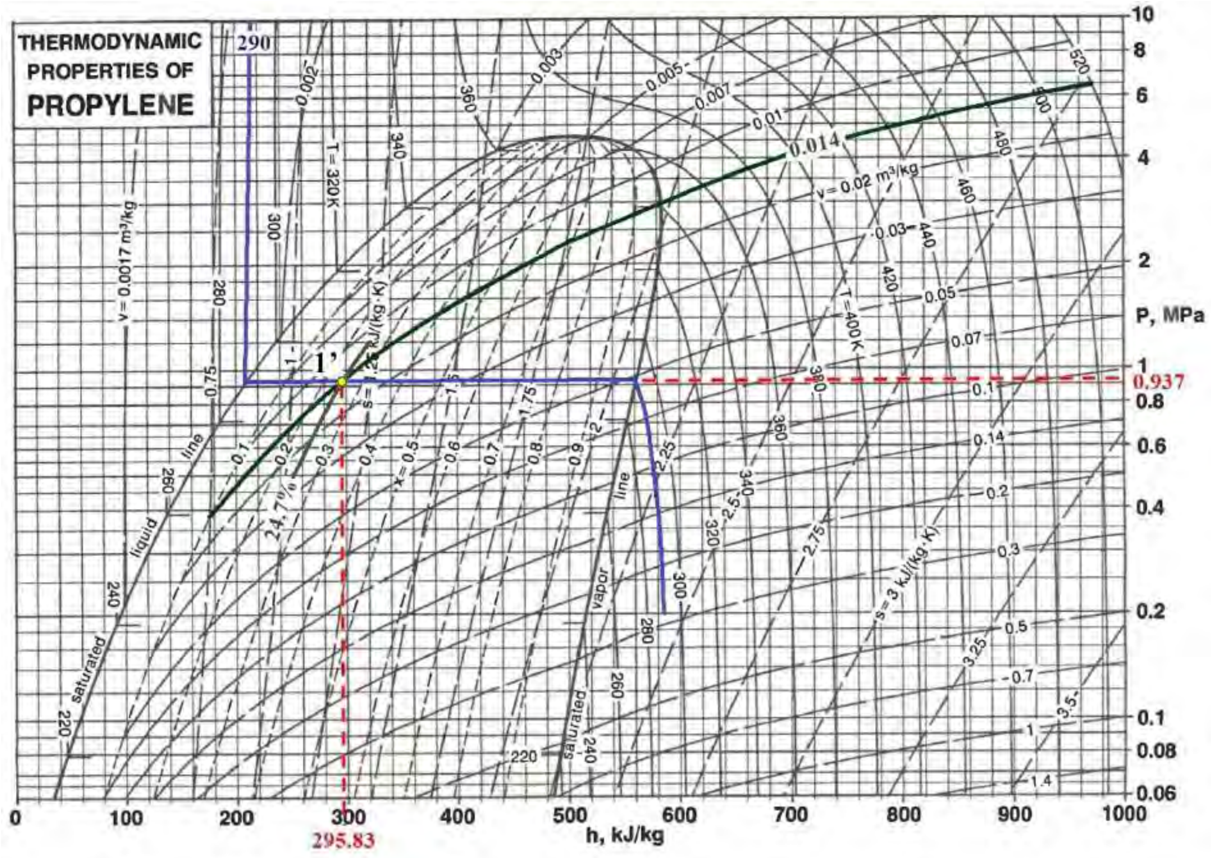
or from the volume and mass balances (which also allows calculating the volumes ocuppied by each phase)

$$M_{v_{1'}} = M_{tot'}\frac{\big(\hat{V}_{tot'} - \hat{V}_{l_1}^{sat}\big)}{\big(\hat{V}_{v_1}^{sat} - \hat{V}_{l_1}^{sat}\big)} = (707\ \text{g})\frac{(0.014 - 0.001923)}{(0.05097 - 0.001923)} = 174.09\ \text{g}$$

$$M_{l_{1'}} = M_{tot'} - M_{v_{1'}} = 707 - 174.09 = 532.91 \text{ g}$$

$$V_{v_{1'}} = M_{v_{1'}} \hat{V}_{v_1}^{sat} = (174.09 \text{ g})\left(0.05097 \ \frac{\text{L}}{\text{g}}\right) = 8.873 \text{ L}$$

$$V_{l_{1'}} = M_{l_{1'}} \hat{V}_{l_1}^{sat} = (532.91 \text{ g})\left(0.001923 \ \frac{\text{L}}{\text{g}}\right) = 1.025 \text{ L}$$



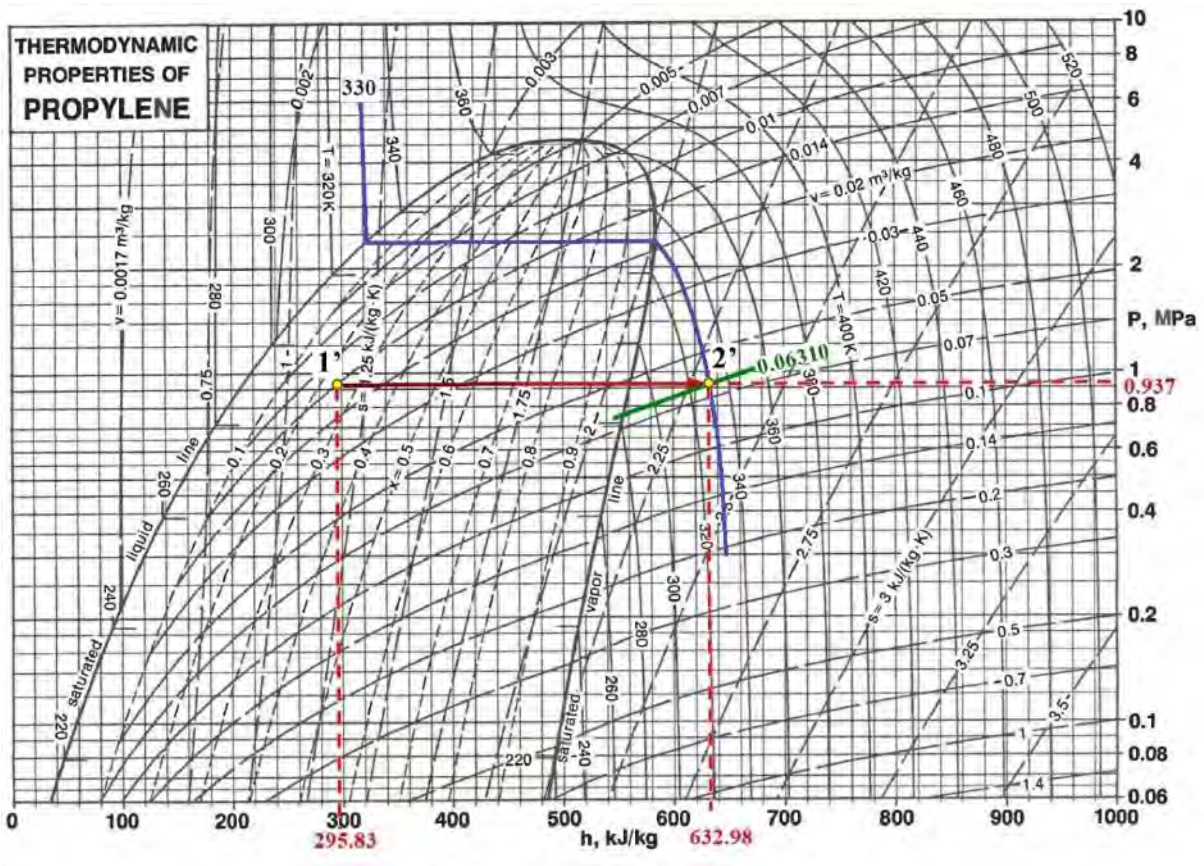
After the transit from conditions of point 1' to point 2', there is superheated vapor under the same conditions as in question **b**. The change will not generate flow work (isobaric process) and the heat and the expansion-compression work will be

$$\Delta\hat{Q}_{2'1'} = \Delta\hat{H}_{2'1'} = \hat{H}_{2'} - \hat{H}_{1'} = 632.98 \ \frac{\text{kJ}}{\text{kg}} - 295.83 \frac{\text{kJ}}{\text{kg}} = 337.15 \frac{\text{kJ}}{\text{kg}}$$

$$\Delta Q_{2'1'} = M_{tot'} \Delta\hat{Q}_{2'1'} = (0.707 \text{ kg})\left(337.15 \frac{\text{kJ}}{\text{kg}}\right) = 238.365 \text{ kJ}$$

$$\Delta\hat{W}_{2'1'}^{\text{e-c}} = -P_1\left(\hat{V}_{2'} - \hat{V}_{1'}\right) = -(937 \text{ kPa})\left(0.06310 \ \frac{\text{m}^3}{\text{kg}} - 0.014 \ \frac{\text{m}^3}{\text{kg}}\right) = -46.007 \ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta W_{2'1'}^{\text{e-c}} = M_{tot'} \Delta\hat{W}_{2'1'}^{\text{e-c}} = (0.707 \text{ kg})\left(-46.007 \ \frac{\text{kJ}}{\text{kg}}\right) = -32.527 \text{ kJ}$$



When passing to point 3' conditions, a mixture of saturated liquid and vapor is obtained (total specific enthalpy $\hat{H}_{3'}$ =508.33 kJ/kg and the same pressure, liquid and vapor densities and specific enthalpies as those of point 4 in the previous question), which is located approximately on the title line of 70% (0.70×707 g = 494.9 g of vapor), a value that can be improved by combining the enthalpy and mass balances

$$M_{v_{3'}} = M_{tot'}\frac{\left(\hat{H}_{3'} - \hat{H}_{l_{3'}}^{sat}\right)}{\left(\hat{H}_{v_{3'}}^{sat} - \hat{H}_{l_{3'}}^{sat}\right)} = (707\ \text{g})\frac{(508.33 - 322.35)}{(584.31 - 322.35)} = 501.9\ \text{g}$$

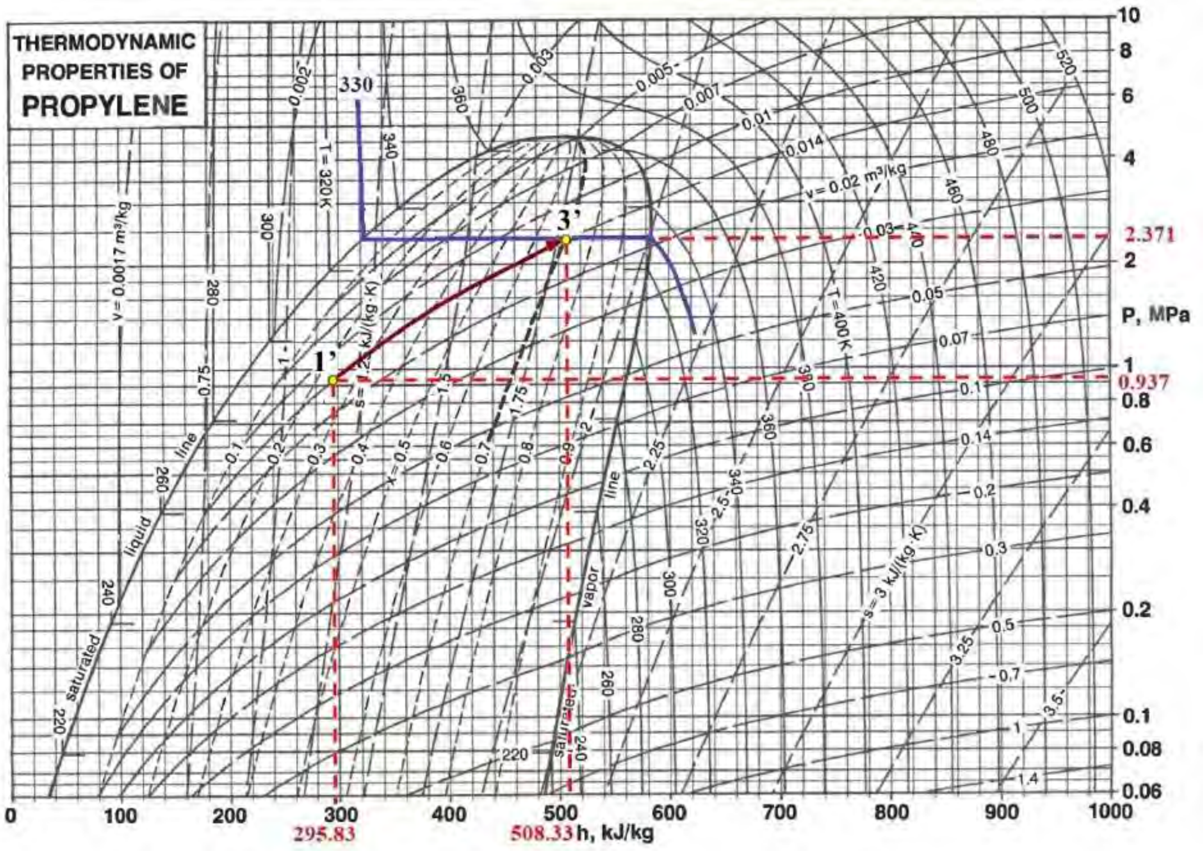
or the volume and mass balances

$$M_{v_{3'}} = M_{tot'}\frac{\left(\hat{V}_{1'} - \hat{V}_{l_{3'}}^{sat}\right)}{\left(\hat{V}_{v_{3'}}^{sat} - \hat{V}_{l_{3'}}^{sat}\right)} = (707\ \text{g})\frac{(0.014 - 0.002255)}{(0.01854 - 0.002255)} = 509.9\ \text{g}$$

$$M_{l_{3'}} = M_{tot'} - M_{v_{3'}} = 707 - 509.9 = 197.1\ \text{g}$$

$$V_{v_{3'}} = M_{v_{3'}}\hat{V}_{v_{3'}}^{sat} = (509.9\ \text{g})\left(0.01854\ \frac{\text{L}}{\text{g}}\right) = 9.453\ \text{L}$$

$$V_{l_{3'}} = M_{l_{3'}}\hat{V}_{l_{3'}}^{sat} = (197.1\ \text{g})\left(0.002255\ \frac{\text{L}}{\text{g}}\right) = 0.444\ \text{L}$$



And, since there is no expansion-compression work, the heat of the step from 1' to 3' will be calculated as in question **b**

$$\Delta\hat{Q}_{3'1'}=\left(\hat{H}_{3'}-\hat{H}_{1'}\right)-\hat{V}_{1'}(P_{3'}-P_{1'})=$$

$$=\left(508.33\ \frac{\text{kJ}}{\text{kg}}-295.83\frac{\text{kJ}}{\text{kg}}\right)-\left(0.014\ \frac{\text{m}^3}{\text{kg}}\right)(2371\ \text{kPa}-937\ \text{kPa})=192.42\frac{\text{kJ}}{\text{kg}}$$

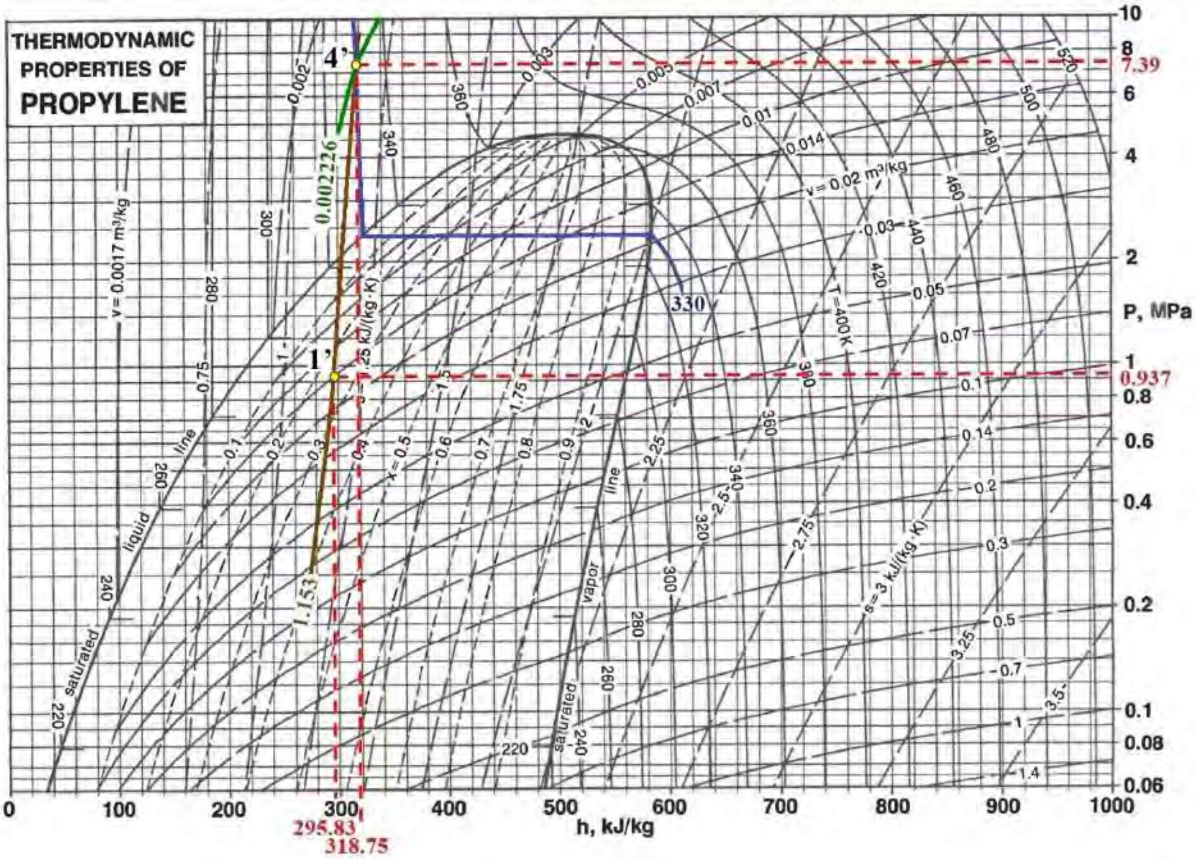
$$\Delta Q_{3'1'}=M_{tot'}\Delta\hat{Q}_{3'1'}=(0.707\ \text{kg})\left(192.42\frac{\text{kJ}}{\text{kg}}\right)=136.04\ \text{kJ}$$

Finally, point 4' will be found in the crossing of the isentropic line that passes through point 1' (1.153 kJ/kg·K) with the isotherm $T_{4'}=T_{3'}=330$ K. It is a compressed liquid, with $\hat{V}_{4'}=0.002226\ \text{m}^3/\text{kg}$, $P_{4'}=7.39$ MPa and $\hat{H}_{4'}=318.75$ kJ/kg, and reaching it will not cause heat exchange (as in question **b**). The expansion-compression work between 1' and 4' will be

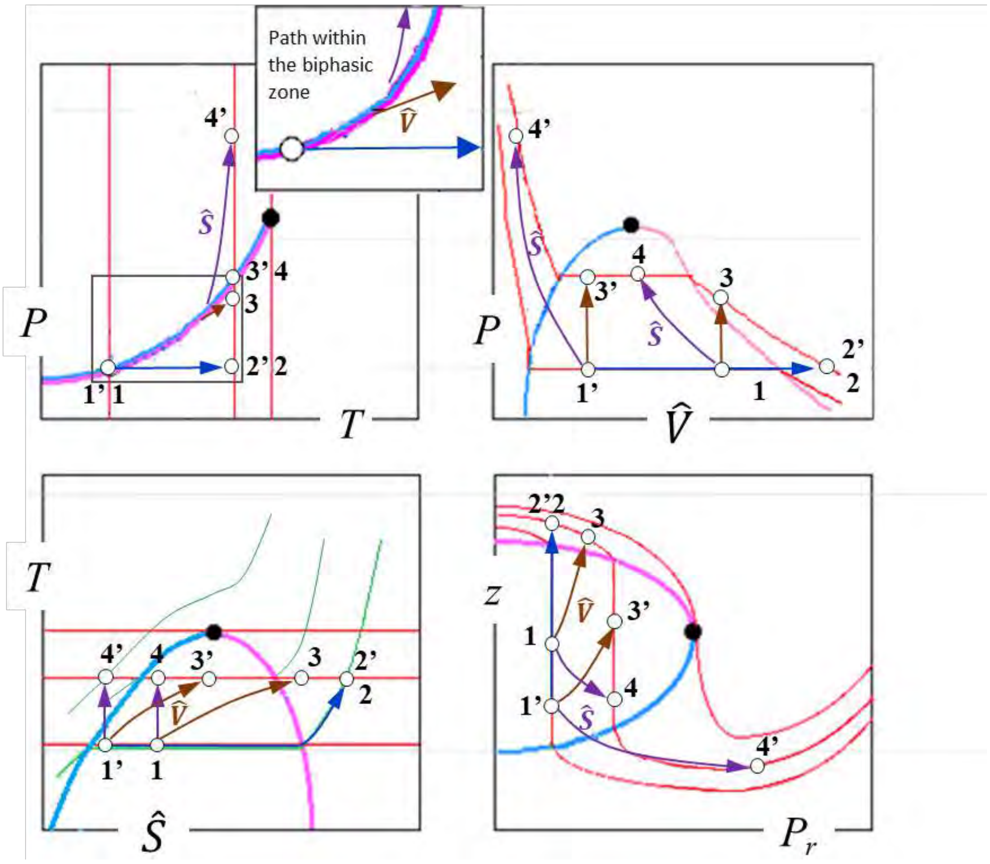
$$\Delta\widehat{W}^{\text{e-c}}_{4'1'}=\left(\hat{H}_{4'}-P_{4'}\hat{V}_{4'}\right)-\left(\hat{H}_{1'}-P_{1'}\hat{V}_{1'}\right)=\left[318.75\ \frac{\text{kJ}}{\text{kg}}-\left(0.002226\ \frac{\text{m}^3}{\text{kg}}\right)(7390\ \text{kPa})\right]-$$

$$-\left[295.83\ \frac{\text{kJ}}{\text{kg}}-\left(0.014\ \frac{\text{m}^3}{\text{kg}}\right)(937\ \text{kPa})\right]=19.59\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta W^{\text{e-c}}_{4'1'}=M_{tot'}\Delta\widehat{W}^{\text{e-c}}_{4'1'}=(0.707\ \text{kg})\left(19.59\ \frac{\text{kJ}}{\text{kg}}\right)=13.85\ \text{kJ}$$



Question d. Below are the qualitative representations required



4.13. Knowledge, skill and competence in a professional field are not just words of exams or educational experts, but required qualities and matter of civil and criminal liability when damages are caused by ignorant or irresponsible behavior at work.

Due to not knowing the profession, not obeying the rules and not establishing rigorous protocols, a 45 m^3 tanker for the transport of liquefied propylene ($\mathfrak{M}$ =42.1 g/mol-g) with a design capacity of 15000 kg was filled with 23000 kg on the morning of July 11, 1978, being the thermometer reading of 15°C. Several hours later, and after a strong insolation, the tanker burst due to overpressure, initiating a BLEVE (boiling liquid expanding vapor explosion) that took away, in minutes, the lives and physical integrity of hundreds of vacationers at the Los Alfaques campsite. Calculate:

- **a) Pressure and phase distribution at initial conditions of both correct filling and overload.**
- **b) Enthalpy in both cases.**
- **c) The internal temperature and pressure (assumed to be uniform) when the load becomes fully liquid.**
- **d) The temperature at which the safety pressure of the tanker would be reached (60 bar).**
- **e) Internal pressure and enthalpy under overload conditions when the temperature of 40°C is uniformly reached.**
- **f) The heat absorbed by the overload to reach 40°C.**
- **g) The energy of the mechanical explosion prior to the chemical explosion, evaluated from the expansion work. Suppose that the released propylene suddenly reached the ambient conditions of that fateful day (40°C and 1 atm) when the tanker broke.**
- **h) Represent the described phenomenon on a qualitative *PV*(*T*) diagram.**

Question a. In principle, the intersection of the isotherm

$$T_1(\mathrm{K}) = 15^\circ\mathrm{C} + 273 = 288\ \mathrm{K}$$

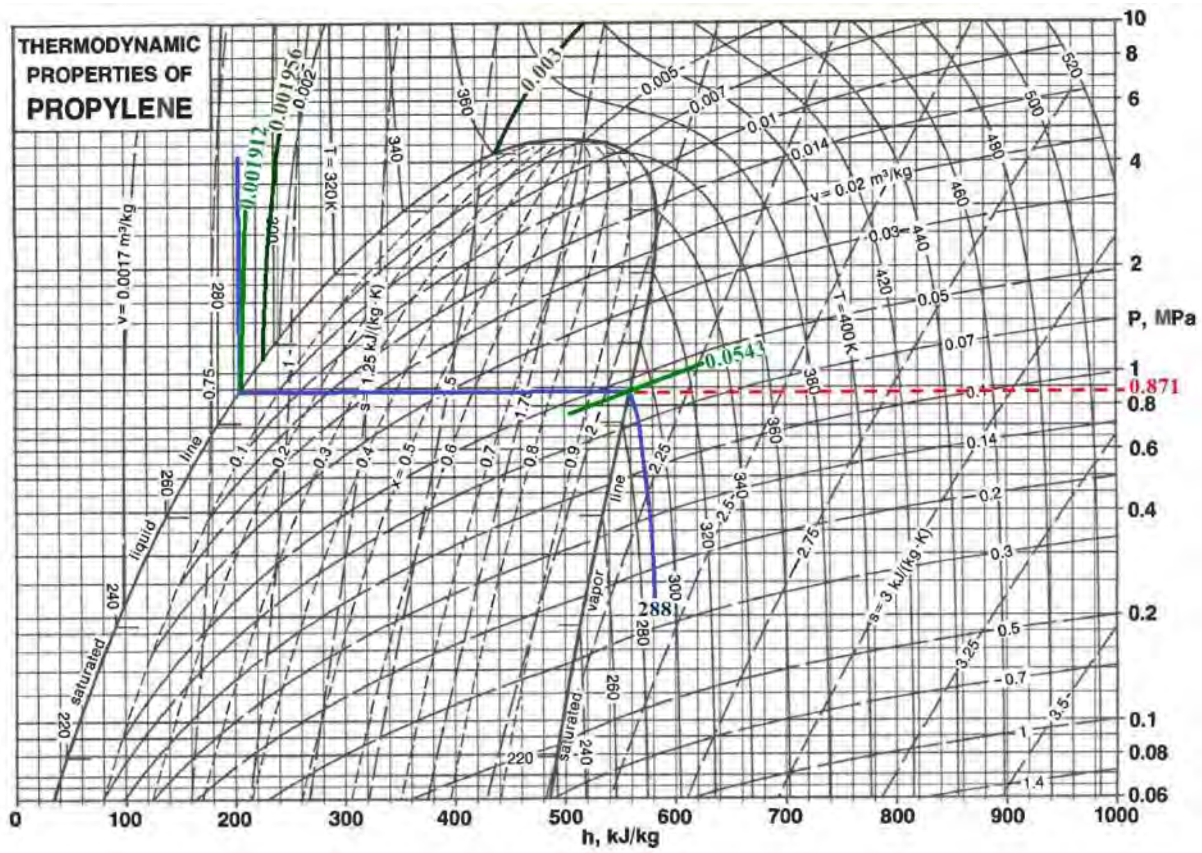
with the isochore

$$\hat{V}_1 = \frac{V_1}{M_1} = \frac{V_{tanker}}{M_{tot}} = \frac{45\ \mathrm{m}^3}{15000\ \mathrm{kg}} = 0.003\ \frac{\mathrm{m}^3}{\mathrm{kg}}$$

allows the graphical calculation of the correct filling conditions, while the intersection of the same isotherm with the isochore

$$\hat{V}_{1'} = \frac{V_1}{M_{1'}} = \frac{V_{tanker}}{M_{tot'}} = \frac{45\ \mathrm{m}^3}{23000\ \mathrm{kg}} = 0.001956\ \frac{\mathrm{m}^3}{\mathrm{kg}}$$

allows the calculation of the overload conditions.



However, in figure V.10 of this book's appendix V (*PH* diagram of propylene), isochores lower than 0.007 m^3/kg are not plotted in the biphasic zone, although visual inspection indicates that both intersections will give mixtures of saturated liquid and vapor, at 0.871 MPa, and specific volumes $\hat{V}_{l_1}^{sat} = \hat{V}_{l_{1'}}^{sat} = 0.001912$ m^3/kg and $\hat{V}_{v_1}^{sat} = \hat{V}_{v_{1'}}^{sat}$ =0.0543 m^3/kg. Thus, combining the mass and volume balances for the correct loading

$$M_{v_1} = M_{tot}\frac{\left(\hat{V}_1 - \hat{V}_{l_1}^{sat}\right)}{\left(\hat{V}_{v_1}^{sat} - \hat{V}_{l_1}^{sat}\right)} = (15000\ \text{kg})\frac{(0.003 - 0.001912)}{(0.0543 - 0.001912)} = 311.52\ \text{kg}$$

$$M_{l_1} = M_{tot} - M_{v_1} = 15000 - 311.52 = 14688.48\ \text{kg}$$

$$V_{v_1} = M_{v_1}\hat{V}_{v_1}^{sat} = (311.52\ \text{kg})\left(0.0543\ \frac{\text{m}^3}{\text{kg}}\right) = 16.916\ \text{m}^3$$

$$V_{l_1} = M_{l_1}\hat{V}_{l_1}^{sat} = (14688.48\ \text{kg})\left(0.001912\ \frac{\text{m}^3}{\text{kg}}\right) = 28.08\ \text{m}^3$$

and for overloading

$$M_{v_{1'}} = M_{tot'}\frac{\left(\hat{V}_{1'} - \hat{V}_{l_{1'}}^{sat}\right)}{\left(\hat{V}_{v_{1'}}^{sat} - \hat{V}_{l_{1'}}^{sat}\right)} = (23000\ \text{kg})\frac{(0.001956 - 0.001912)}{(0.0543 - 0.001912)} = 19.32\ \text{kg}$$

$$M_{l_{1'}} = M_{tot'} - M_{v_{1'}} = 23000 - 19.32 = 22980.68\ \text{kg}$$

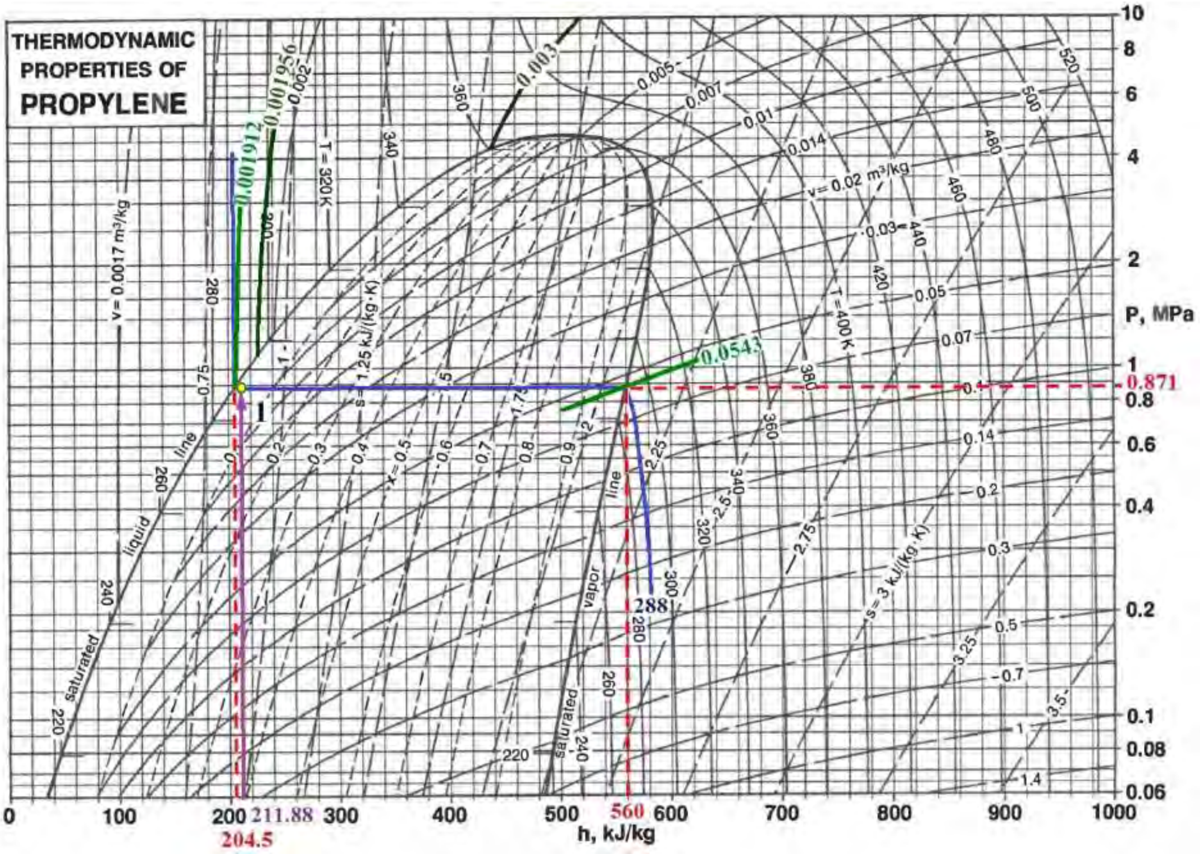
$$V_{v_{1'}} = M_{v_{1'}}\hat{V}_{v_{1'}}^{sat} = (19.32\ \text{kg})\left(0.0543\ \frac{\text{m}^3}{\text{kg}}\right) = 1.05\ \text{m}^3$$

$$V_{l_{1'}} = M_{l_{1'}}\hat{V}_{l_{1'}}^{sat} = (22980.68\ \text{kg})\left(0.001912\ \frac{\text{m}^3}{\text{kg}}\right) = 43.94\ \text{m}^3$$

Question b. Since the isochores $\hat{V}_1$ and $\hat{V}_{1'}$ are not drawn in the biphasic zone, the enthalpies of the biphasic mixtures ($\hat{H}_1$ and $\hat{H}_{1'}$) cannot be directly read in the point where these specific volumes intersect the T_1 isotherm, but have to be calculated by means of the enthalpy balance, which said that

$$M_{tot}\hat{H}_1 = M_{l_1}\hat{H}_{l_1}^{sat} + M_{v_1}\hat{H}_{v_1}^{sat} \quad \rightarrow \quad \hat{H}_1 = \frac{M_{l_1}}{M_{tot}}\hat{H}_{l_1}^{sat} + \frac{M_{v_1}}{M_{tot}}\hat{H}_{v_1}^{sat}$$

$$M_{tot'}\hat{H}_{1'} = M_{l_{1'}}\hat{H}_{l_{1'}}^{sat} + M_{v_{1'}}\hat{H}_{v_{1'}}^{sat} \quad \rightarrow \quad \hat{H}_{1'} = \frac{M_{l_{1'}}}{M_{tot'}}\hat{H}_{l_{1'}}^{sat} + \frac{M_{v_1}}{M_{tot}}\hat{H}_{v_{1'}}^{sat}$$



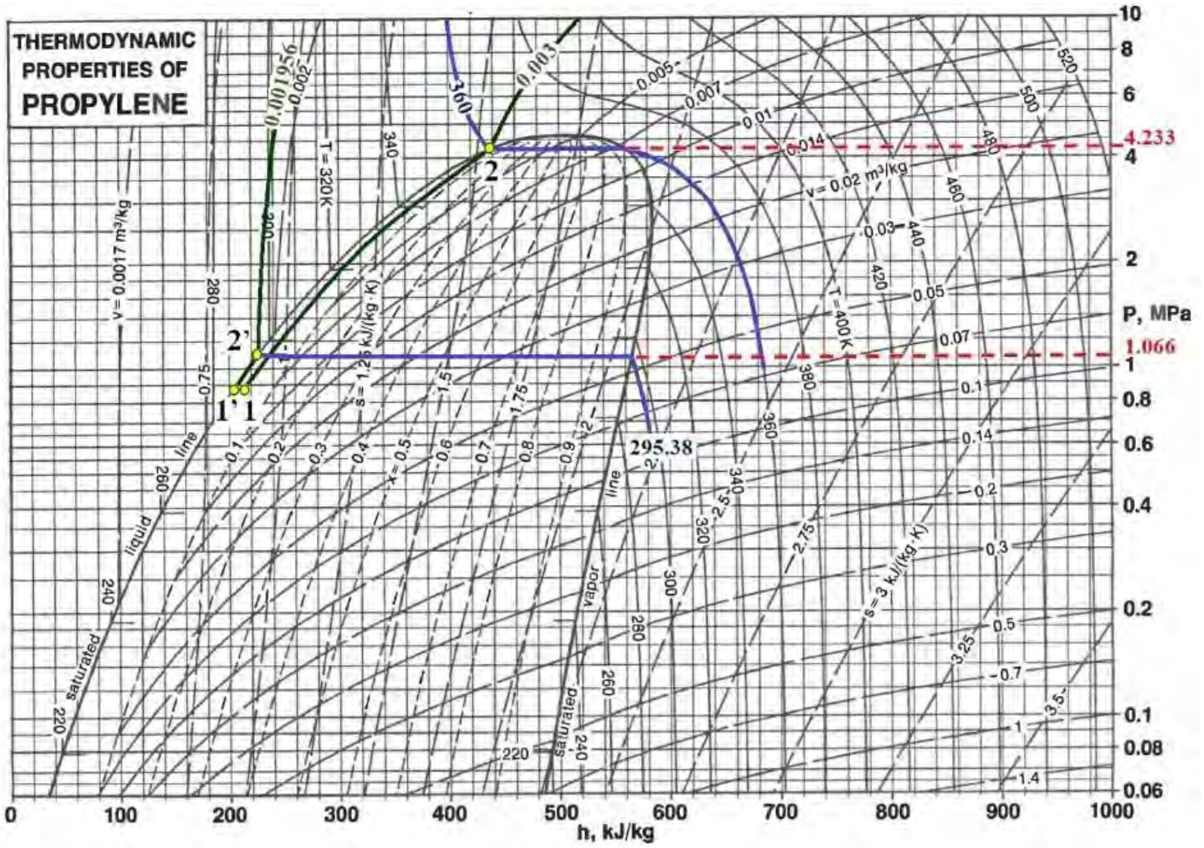
Taking into account that $\hat{H}_{l_1}^{sat} = \hat{H}_{l_{1'}}^{sat} = 204.5$ kJ/kg and $\hat{H}_{v_1}^{sat} = \hat{H}_{v_{1'}}^{sat}$ =560 kJ/kg

$$\hat{H}_1 = \left(\frac{14688.48\ \text{kg}}{15000\ \text{kg}}\right)\left(204.5\ \frac{\text{kJ}}{\text{kg}}\right) + \left(\frac{311.52\ \text{kg}}{15000\ \text{kg}}\right)\left(560\ \frac{\text{kJ}}{\text{kg}}\right) = 211.88\ \frac{\text{kJ}}{\text{kg}}$$

$$\hat{H}_{1'} = \left(\frac{22980.68\ \text{kg}}{23000\ \text{kg}}\right)\left(204.5\ \frac{\text{kJ}}{\text{kg}}\right) + \left(\frac{19.32\ \text{kg}}{23000\ \text{kg}}\right)\left(560\ \frac{\text{kJ}}{\text{kg}}\right) = 204.80\ \frac{\text{kJ}}{\text{kg}}$$

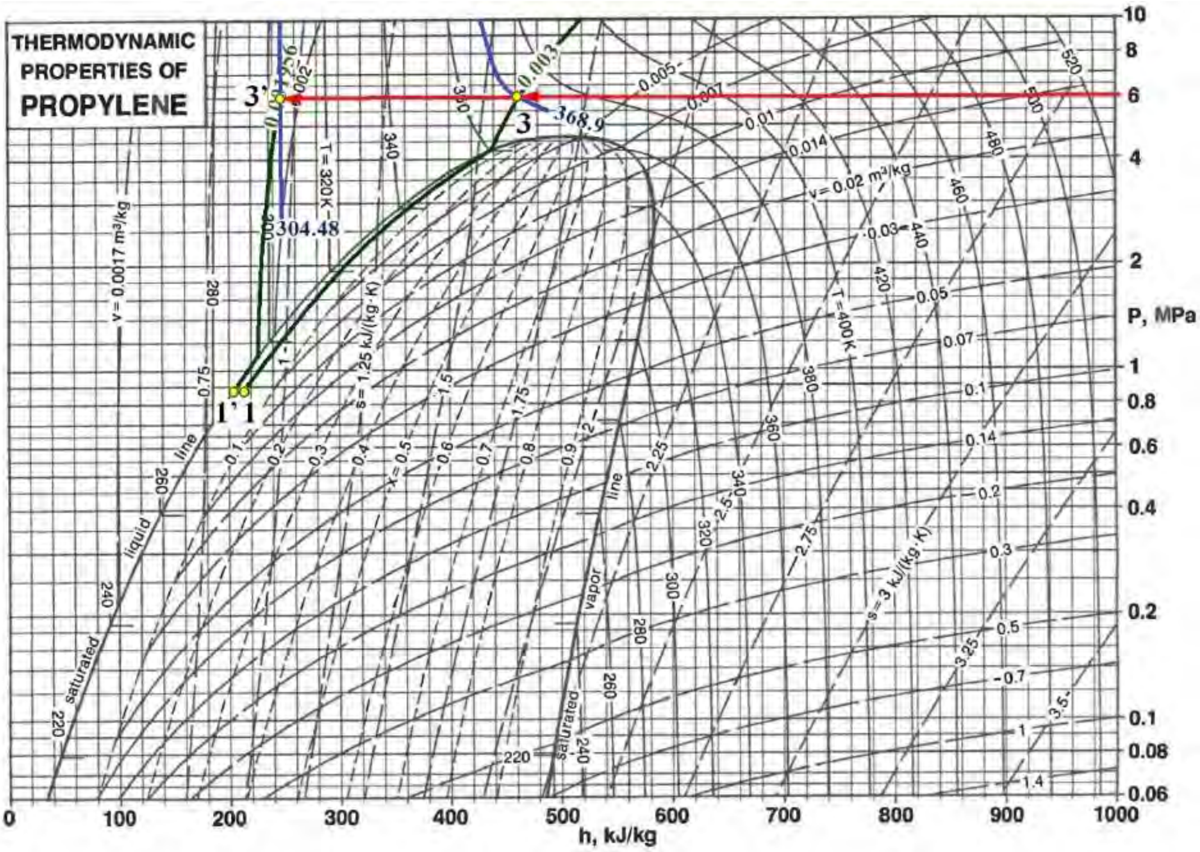
being difficult to clearly locate point 1' in the *PH* diagram because it is very close to the saturated liquid line.

Question c. When the 0.003 m^3/kg isochore (normal loading) intersects the saturated liquid line, a temperature T_2=360 K and a pressure P_2= 4.233 MPa are obtained. However, the 0.001956 m^3/kg isochore (overloading) crosses this line at a much lower temperature and pressure, $T_{2'}$=295.38 K and $P_{2'}$= 1.066 MPa.



Question d. Since the tanker volume remain constant, the solution of this question will be the isotherms that pass through the points where the 6 MPa isobar intersects the isochores 0.003 m^3/kg and 0.01956 m^3/kg.

For the correct loading, the temperature is T_3=368.9 K (95.9ºC), but for overloading, $T_{3'}$=304.48 (31.48ºC).

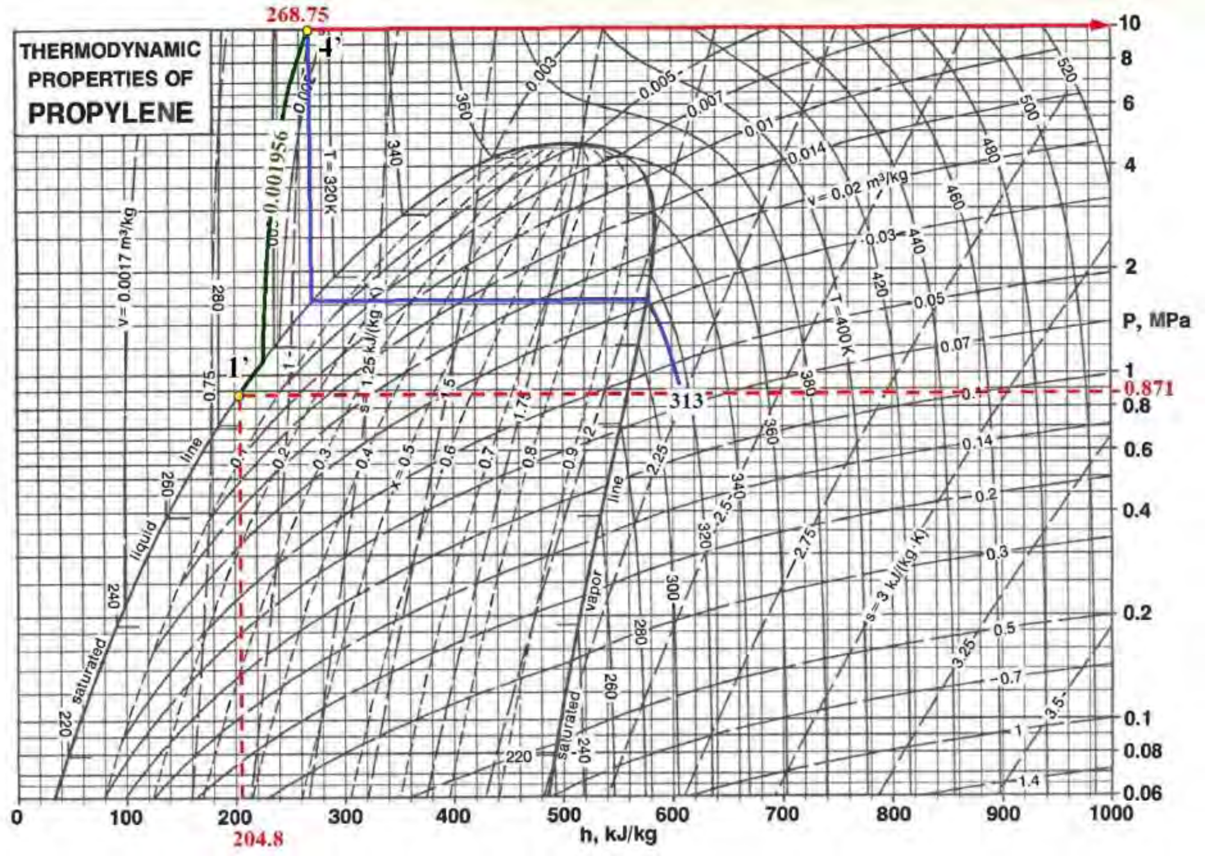


It is practically impossible to reach the first temperature under conditions of ordinary road transport (mere solar irradiation), but the second one is easily achievable by driving through warm areas on a sunny summer day.

Question e. When the isochore $\hat{V}_{1'}$=0.01956 m^3/kg crosses with the isotherm

$$T_{4'}(\mathrm{K}) = 40^{\circ}\mathrm{C} + 273 = 313\ \mathrm{K}$$

the pressure is of 10 MPa and the enthalpy of the compressed liquid takes a value of 268.75 kJ/kg



Question f. The interchanged heat in the transit from state 1’ to state 4’ should be calculated by employing the general expression

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \Delta\hat{Q}_{4'1'} = \int_{1'}^{4'} T\mathrm{d}\hat{S}$$

but according to one of the fundamental thermodynamic relations

$$\mathrm{d}\hat{U} = \mathrm{d}\hat{Q} - P\mathrm{d}\hat{V}$$

Therefore, if the specific volume remains constant ($\mathrm{d}\hat{V}$=0), there is no expansion-compression work and

$$\Delta\hat{Q}_{4'1'}=\Delta\hat{U}_{4'1'} = \hat{U}_{4'} - \hat{U}_{1'} = \left(\hat{H}_{4'} - P_{4'}\hat{V}_{4'}\right) - \left(\hat{H}_{1'} - P_{1'}\hat{V}_{1'}\right) = \hat{H}_{4'} - \hat{H}_{1'} - \hat{V}_{1'}(P_{4'} - P_{1'})$$

$$\Delta\hat{Q}_{21}=\left(268.75\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 204.8\frac{\mathrm{kJ}}{\mathrm{kg}}\right) - \left(0.001956\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right)(10000\ \mathrm{kPa} - 871\ \mathrm{kPa}) = 46.09\frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta Q_{21} = M_{tot}\Delta\hat{Q}_{21} = (23000\ \mathrm{kg})\left(46.09\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 1060070\ \mathrm{kJ}$$

Question g. The expansion-compression work evaluated in the final conditions is

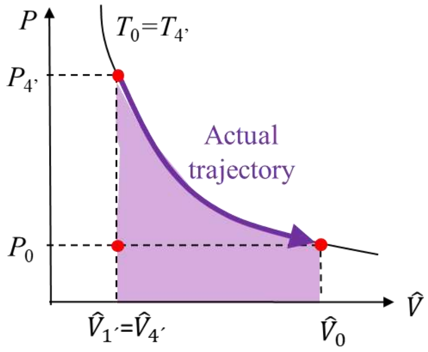
$$\mathrm{d}\widehat{W}^{\text{e-c}} = -P_0\mathrm{d}\hat{V} \quad \rightarrow \quad \int_{W_{4'}}^{W_0} \mathrm{d}\widehat{W}^{\text{e-c}} = -\int_{V_{4'}}^{V_0} P_0\mathrm{d}\hat{V} \quad \rightarrow \quad \Delta\widehat{W}^{\text{e-c}} = P_0\left(\hat{V}_{4'} - \hat{V}_0\right)$$

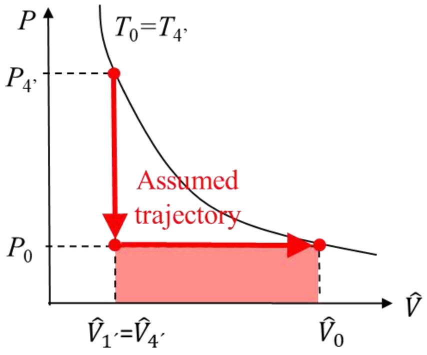
where the subscript 0 indicates atmospheric pressure (P_0=1 atm=1.013 bar= 101.3 kPa) and 40ºC (T_0=313 K), so

$$\hat{V}_0 = \frac{RT_0}{\mathfrak{M}P_0} = \frac{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(313\text{ K})}{(42.1\text{ g/mol-g})(1\text{ atm})} = 0.6096\,\frac{\text{L}}{\text{g}} = 0.6096\,\frac{\text{m}^3}{\text{kg}}$$

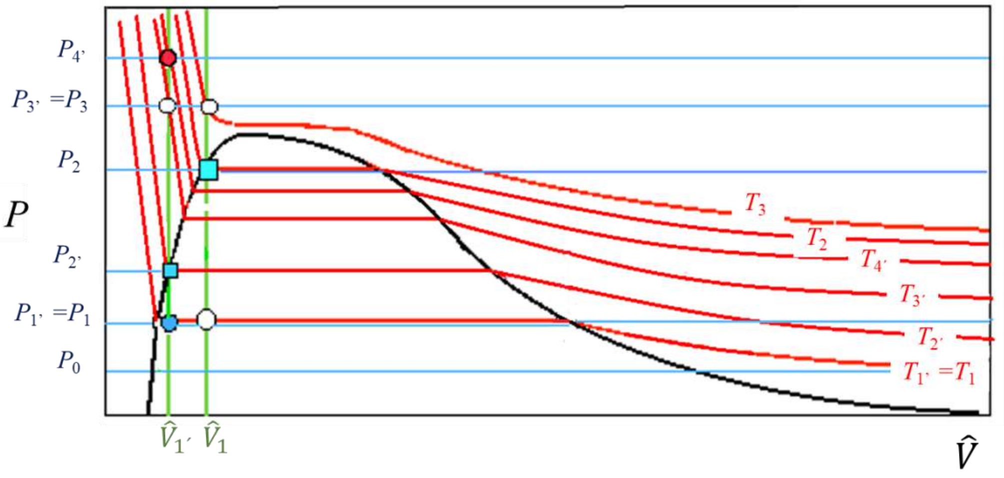
$$\Delta\widehat{W}^{\text{e-c}} = (101.3\text{ kPa})\left(0.001956\,\frac{\text{m}^3}{\text{kg}} - 0.6096\,\frac{\text{m}^3}{\text{kg}}\right) = -61.55\,\frac{\text{kJ}}{\text{kg}}$$

$$\Delta W^{\text{e-c}} = M_{tot'}\Delta\widehat{W}^{\text{e-c}} = (23000\text{ kg})\left(-61.55\,\frac{\text{kJ}}{\text{kg}}\right) = -1415650\text{ kJ}$$





Question h. The requested representation is



4.14. It is desired to transport ammonia in a 20 m^3 tanker. The maximum pressure (within safety specifications) is of 20 kg$_f$/cm^2. By means of an ammonia specific *PV*(*T*) diagram:

a) Deduce the maximum amount of ammonia that can be transported if the tanker stands a maximum temperature of 80ºC (with an oversized safety margin).

b) Pressure and state of the aforesaid amount of ammonia if loading is carried out at 20ºC.

c) What pressure would be reached if the temperature accidentally increases to 100ºC?

d) Solve questions a) and c) using the generalized graphs of the Corresponding States Principle, assuming that z$_c$=0.27.

e) Solve questions a), b) and c) using an ammonia specific *PH*(*T,V,S*) diagram.

A *PV*(*T*) diagram for NH_3 is the figure V.11 of this book's appendix V. Its volumes are expressed in ft^3/lb, its pressures in lb$_f$/in^2 and its temperatures in ºF, so unit conversion will be necessary

$$T_1(\text{°F}) = 1.8(80\text{°C}) + 32 = 176\text{°F}$$

$$T_2(\text{°F}) = 1.8(20\text{°C}) + 32 = 68\text{°F}$$

$$T_3(\text{°F}) = 1.8(100\text{°C}) + 32 = 212\text{°F}$$

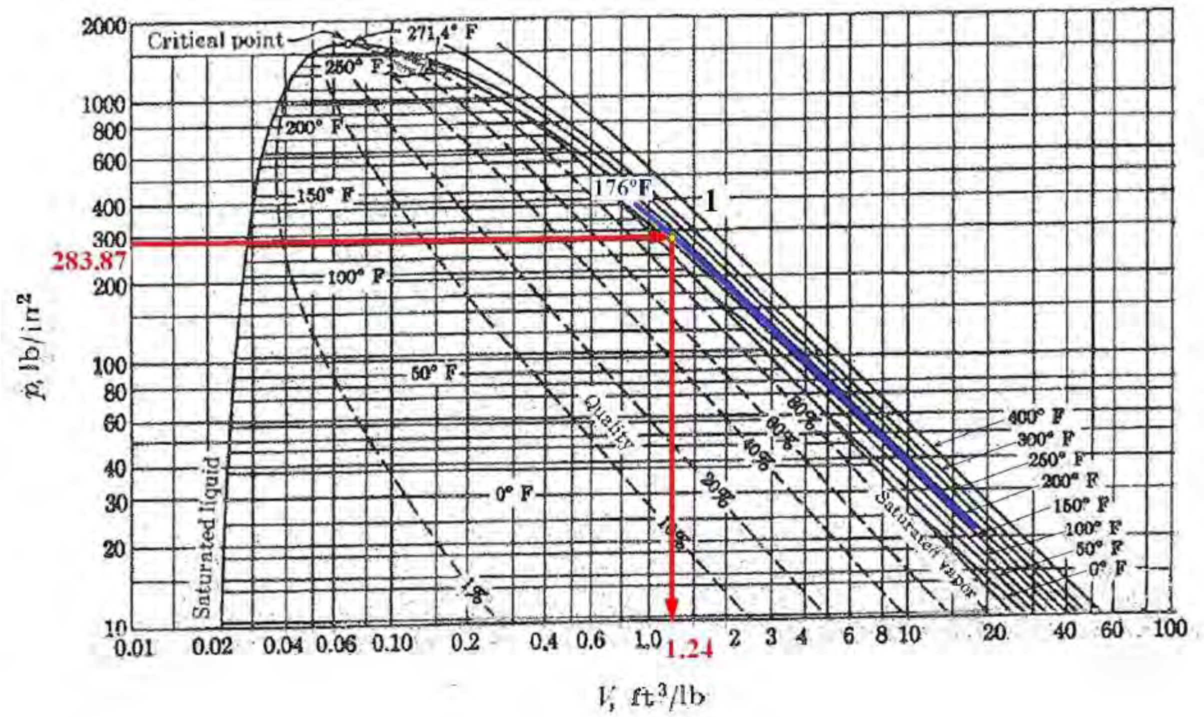
$$P_{max} = 20\ \frac{\text{kg}_\text{f}}{\text{cm}^2} \times \frac{2.2\ \text{lb}_\text{f}}{1\ \text{kg}_\text{f}} \times \left(\frac{100\ \text{cm}}{1\ \text{m}} \times \frac{1\ \text{m}}{39.37\ \text{in}}\right)^2 = 283.87\ \frac{\text{lb}_\text{f}}{\text{in}^2}$$

Question a. The load has to be calculated under the worst conditions, i.e., at maximum pressure and 176ºF. Placing these data on the diagram, it can be directly seen that the corresponding specific volume is of 1.24 ft^3/lb

$$\hat{V}_1 = 1.24\ \frac{\text{ft}^3}{\text{lb}} \times \frac{1\ \text{lb}}{0.454\ \text{kg}} \times \frac{0.028\ \text{m}^3}{1\ \text{ft}^3} = 0.0765\ \frac{\text{m}^3}{\text{kg}}$$

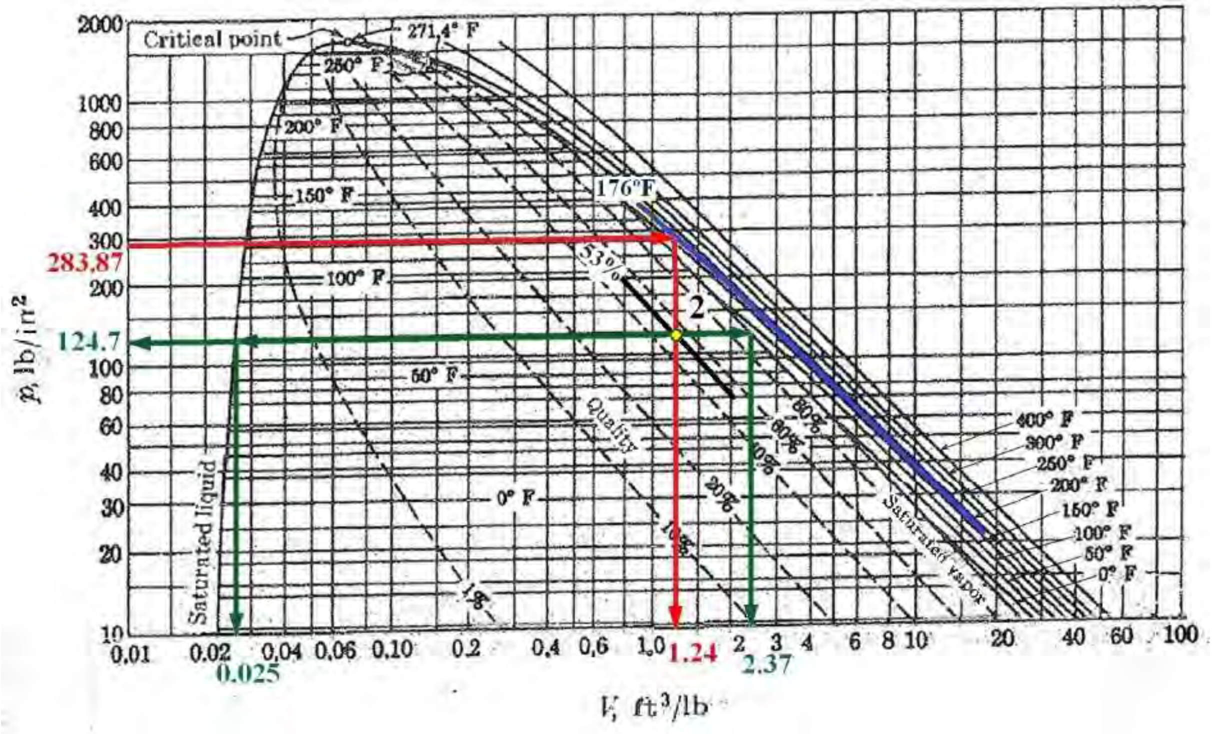
and therefore, the ammonia mass will be

$$M_{tot} = \frac{V_{tanker}}{\hat{V}_1} = \frac{20\ \text{m}^3}{0.0765\ \text{m}^3/\text{kg}} = 261.43\ \text{kg}$$



Question b. When the temperature decreases to 68ºF, the load becomes a biphasic mixture, at a pressure

$$P_2 = 124.7\ \frac{\text{lb}_\text{f}}{\text{in}^2} \times \left(\frac{12\ \text{in}}{1\ \text{ft}}\right)^2 \times \frac{0.000479\ \text{bar}}{1\ \text{lb}_\text{f}/\text{ft}^2} = 8.60\ \text{bar}$$



whose specific volumes of saturated liquid ($\hat{V}_{l_2}^{sat}$) and saturated vapor ($\hat{V}_{v_2}^{sat}$) are

$$\hat{V}_{l_2}^{sat} = 0.025\ \frac{\text{ft}^3}{\text{lb}} \times \frac{1\ \text{lb}}{0.454\ \text{kg}} \times \frac{0.028\ \text{m}^3}{1\ \text{ft}^3} = 0.0015\ \frac{\text{m}^3}{\text{kg}}$$

$$\hat{V}_{v_2}^{sat} = 2.37\ \frac{\text{ft}^3}{\text{lb}} \times \frac{1\ \text{lb}}{0.454\ \text{kg}} \times \frac{0.028\ \text{m}^3}{1\ \text{ft}^3} = 0.1462\ \frac{\text{m}^3}{\text{kg}}$$

By combining the mass balance

$$M_{tot} = M_{l_2} + M_{v_2}$$

with the volume one

$$M_{tot}\hat{V}_{tot} = M_{l_2}\hat{V}_{l_2}^{sat} + M_{v_2}\hat{V}_{v_2}^{sat}$$

it is found that

$$M_{v_2} = M_{tot}\frac{\left(\hat{V}_{tot} - \hat{V}_{l_2}^{sat}\right)}{\left(\hat{V}_{v_2}^{sat} - \hat{V}_{l_2}^{sat}\right)} = (261.43\ \text{kg})\frac{(0.0765 - 0.0015)}{(0.1462 - 0.0015)} = 135.5\ \text{kg}$$

$$M_{l_2} = M_{tot} - M_{v_2} = 261.43 - 135.5 = 125.93\ \text{kg}$$

masses that occupy the following volumes in the tanker

$$V_{l_2} = M_{l_2}\hat{V}_{l_2}^{sat} = (125.93\ \text{kg})\left(0.0015\ \frac{\text{m}^3}{\text{kg}}\right) = 0.19\ \text{m}^3$$

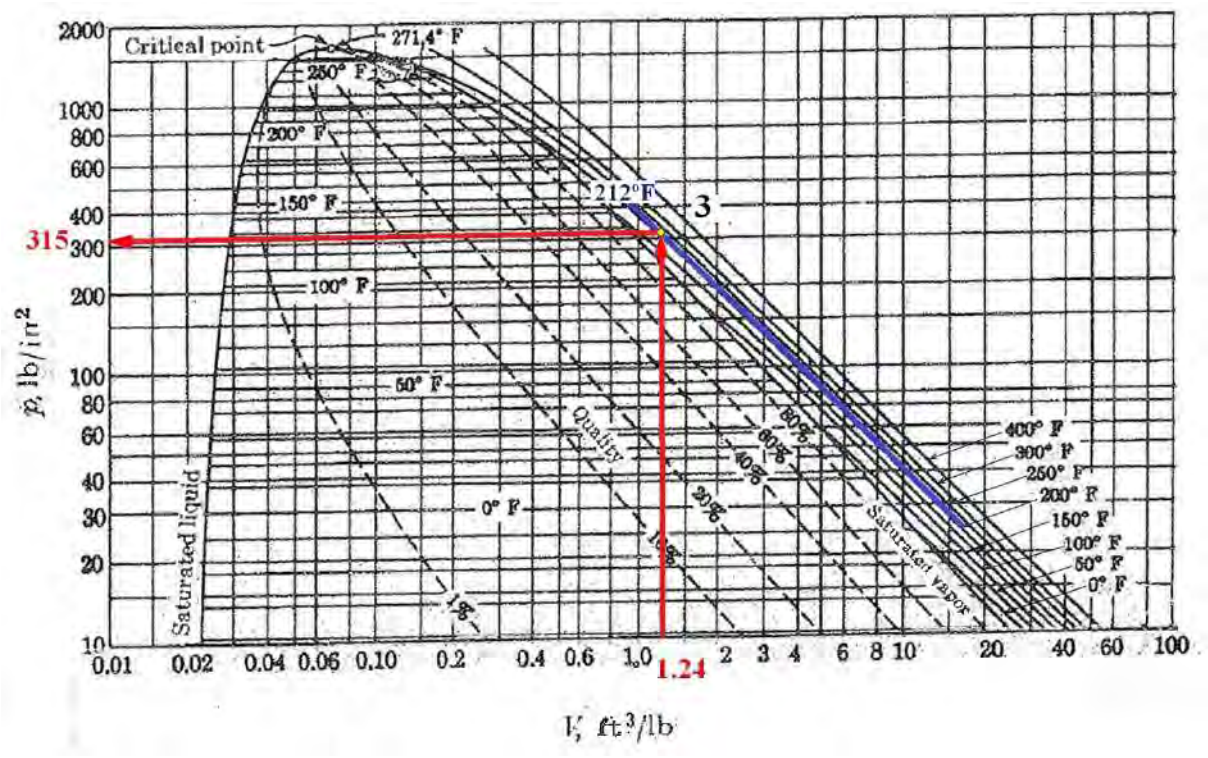
$$V_{v_2} = M_{v_2}\hat{V}_{v_2}^{sat} = (135.5\ \text{kg})\left(0.1462\ \frac{\text{m}^3}{\text{kg}}\right) = 19.81\ \text{m}^3$$

Notice that the M_{v2} value is very close to the mass calculated with the line of title or quality which passes through the point: 53% (0.53×261.43 kg=138.55 kg).

Question c. If the temperature reaches 212ºF, the total specific volume does not change, so the state of the system will be represented by the intersection of the 1.24 ft^3/lb isochore with the T_3= 212ºF isotherm. At this point the whole load is in the form of superheated vapor, at a pressure

$$P_3 = 315\ \frac{\text{lb}_\text{f}}{\text{in}^2} \times \left(\frac{12\ \text{in}}{1\ \text{ft}}\right)^2 \times \frac{0.000479\ \text{bar}}{1\ \text{lb}_\text{f}/\text{ft}^2} = 21.73\ \text{bar}$$

which is higher than P_{max}, and therefore, the tanker runs the risk of exploding.



Question d. To solve the problem by means of the Corresponding States Principle, figures IV.1 and IV.3 of appendix IV will be used. Since these figures employ coordinates reduced with respect to the critical properties, these critical parameters have to be taken from appendix II (405.4 K y 112.07 atm).

$$T_{r1} = \frac{T_2}{T_c} = \frac{80°\text{C} + 273}{405.2\ \text{K}} = \frac{353\ \text{K}}{405.2\ \text{K}} = 0.8712$$

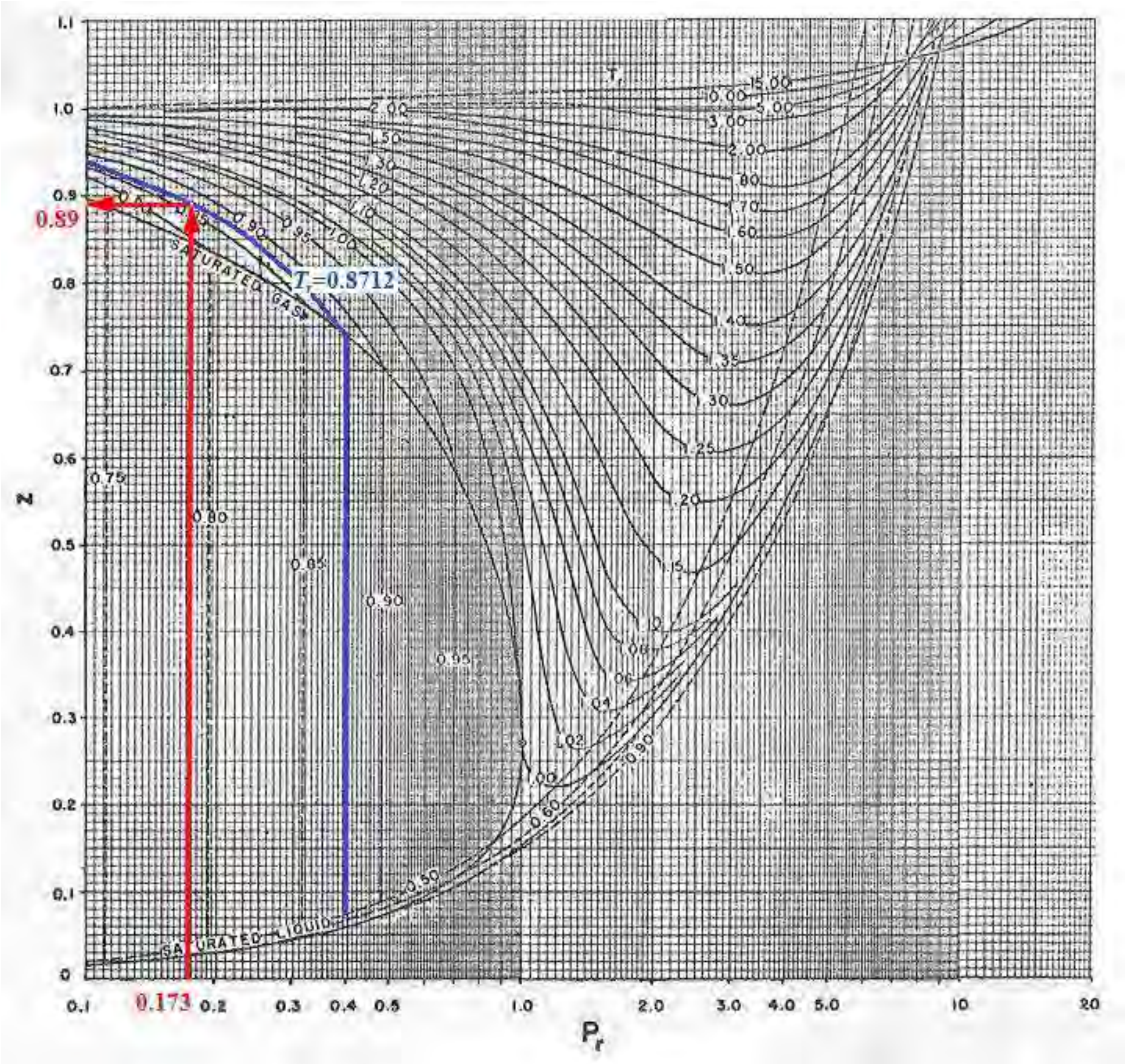
$$P_{r_{max}} = \frac{P_{max}}{P_c} = \frac{\left(20\ \dfrac{\text{kg}_\text{f}}{\text{cm}^2} \times \dfrac{0.968\ \text{atm}}{1\ \text{kg}_\text{f}/\text{cm}^2}\right)}{112.07\ \text{atm}} = \frac{19.36\ \text{atm}}{112.07\ \text{atm}} = 0.173$$

$$T_{r3} = \frac{T_3}{T_c} = \frac{100°\text{C} + 273}{405.2\ \text{K}} = \frac{373\ \text{K}}{405.2\ \text{K}} = 0.9205$$

The $z(T_r,P_r)$ chart shows that the 0.173 isobar only intersects the 0.8712 isotherm in a point that belongs to the superheated vapor zone, which corresponds to $z = 0.89$. Therefore, the solution to question **a** will be

$$\hat{V}_{tot} = \frac{zRT}{\mathfrak{M}P} = \frac{(0.89)\left(0.082\dfrac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(353\ \text{K})}{\left(17.031\dfrac{\text{g}}{\text{mol-g}}\right)(19.36\ \text{atm})} = 0.078\frac{\text{L}}{\text{g}} = 0.078\frac{\text{m}^3}{\text{kg}}$$

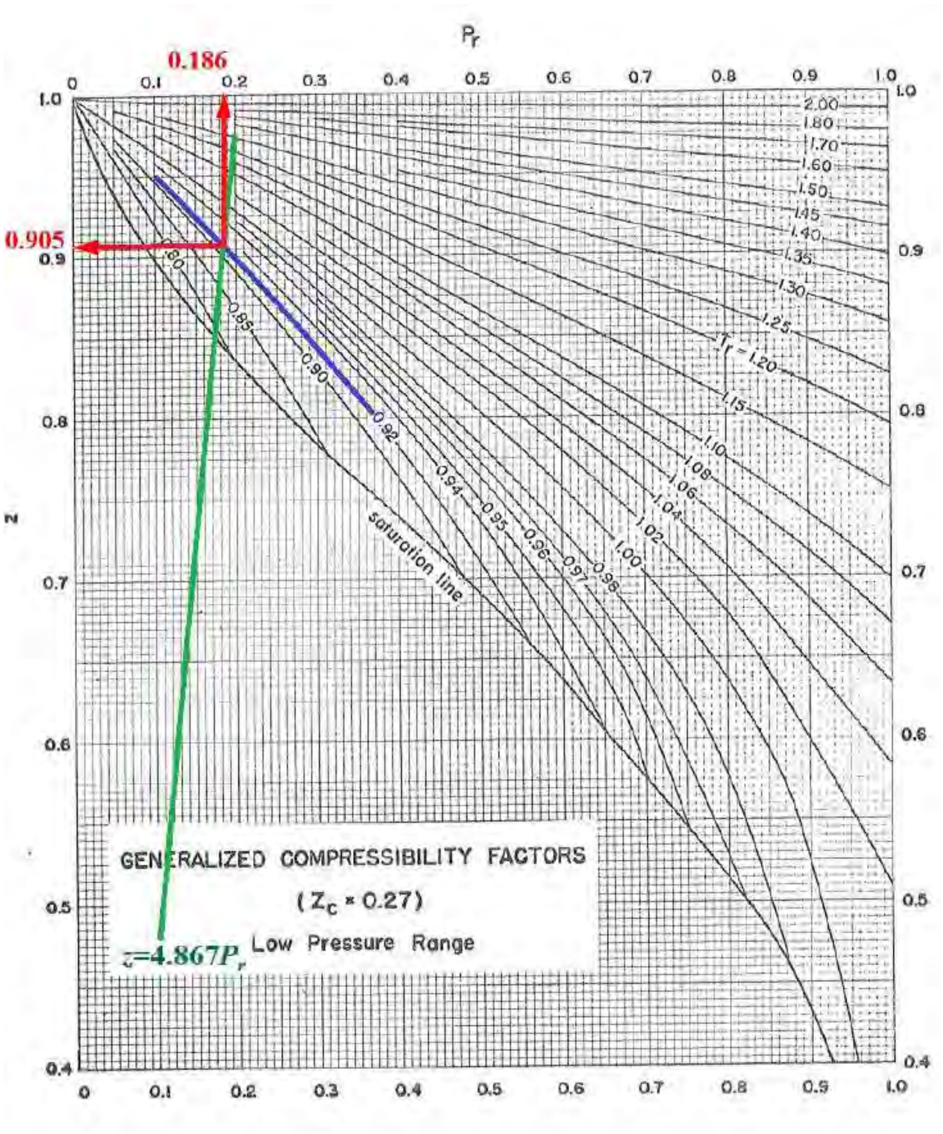
$$M_{tot} = \frac{V_{tanker}}{\hat{V}_{tot}} = \frac{20\ \mathrm{m}^3}{0.078\ \mathrm{m}^3/\mathrm{kg}} = 256.41\ \mathrm{kg}$$



Regarding the solution of question **c**, it must be taken into account that figures IV.1 and IV.3 are explicit functions of T_r and P_r, and since P is unknown, a numerical calculation has to be performed, by finding the point where the T_r=0.9205 isotherm intersects with the casuistic line

$$z = \frac{P_c \mathfrak{W} \hat{V}_{tot}}{RT} = \frac{(112.07\ \mathrm{atm})\left(17.031\,\frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)\left(0.078\,\frac{\mathrm{L}}{\mathrm{g}}\right)}{\left(0.082\,\frac{\mathrm{atm}\cdot\mathrm{L}}{\mathrm{K}\cdot\mathrm{mol\text{-}g}}\right)(373\ \mathrm{K})} P_r = 4.867 P_r$$

Assumed P_r	Calculated z
0.1	0.4867
0.15	0.73005
0.19	0.92473
0.18	0.87606
0.20	0.9734



After giving trial values to the function, it is found that the intersection occurs at P_r=0.186 and z=0.905262, so

$$P = P_r P_c = 0.186\ (112.07\ \text{atm}) = 20.845\ \text{atm}$$

$$20.845\ \text{atm} \times \frac{1.013\ \text{bar}}{1\ \text{atm}} = 21.12\ \text{bar}$$

This value is practically the same as that previously calculated, despite the fact that it is not easy to read in figure V.11 of appendix V and that z_c=0.244 for NH_3 (appendix II).

Question e. A PH diagram for NH_3 is figure V.12 of the present book's appendix V. Its temperatures are given in K and its pressures in MPa, so

$$T_1(\mathrm{K}) = 80°\mathrm{C} + 273 = 353\ \mathrm{K}$$

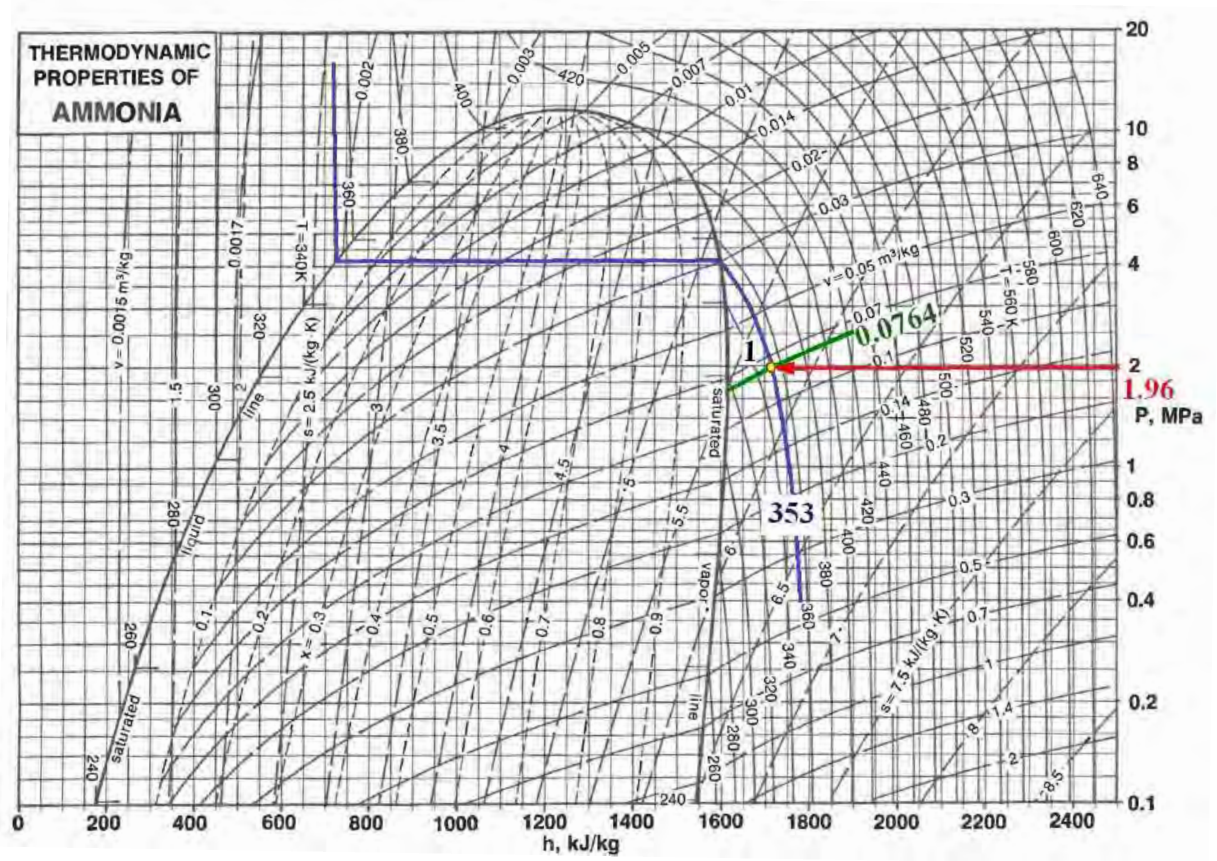
$$T_2(\mathrm{K}) = 20°\mathrm{C} + 273 = 293\ \mathrm{K}$$

$$T_3(\mathrm{K}) = 100°\mathrm{C} + 273 = 373\ \mathrm{K}$$

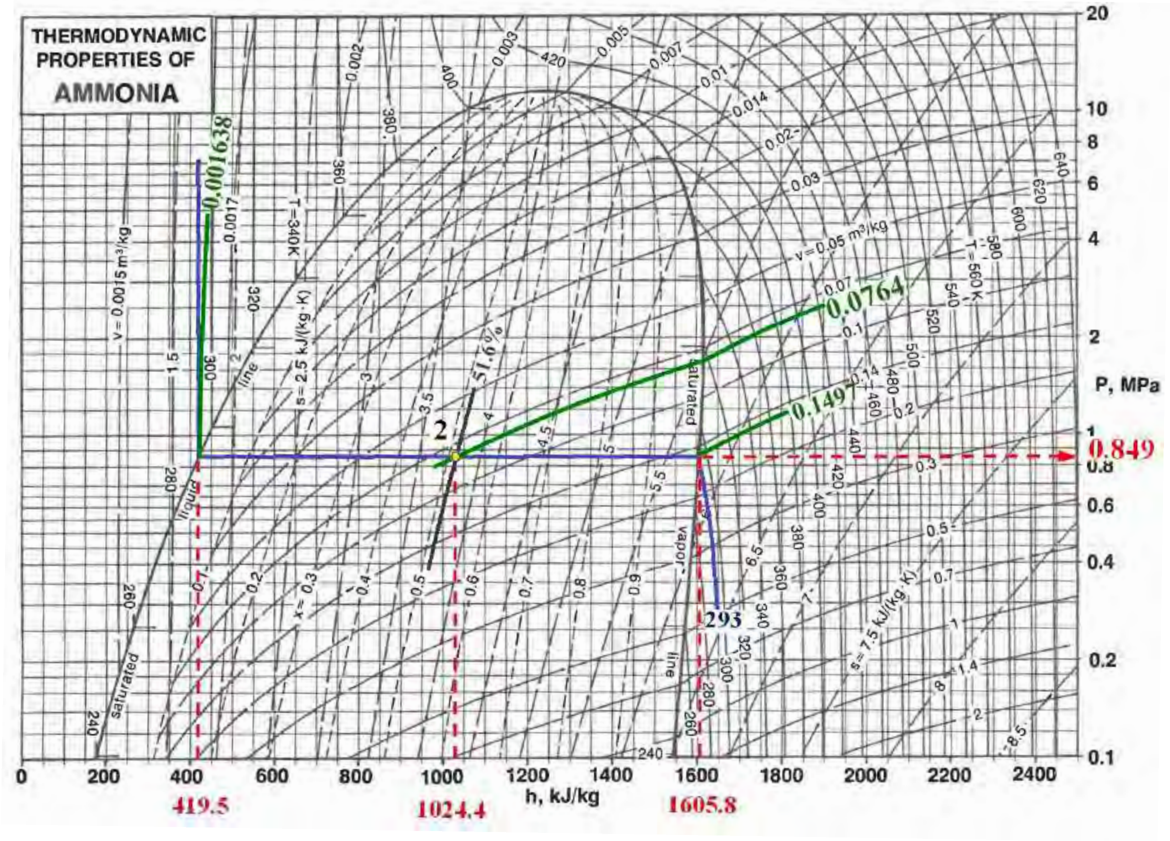
$$P_{max} = 20\ \frac{\mathrm{kg_f}}{\mathrm{cm}^2} \times \frac{0.981\ \mathrm{bar}}{1\ \mathrm{kg_f/cm^2}} \times \frac{1\ \mathrm{MPa}}{10\ \mathrm{bar}} = 1.96\ \mathrm{MPa}$$

The point where the maximum pressure crosses with the 353 K isotherm indicates a specific volume $\hat{V}_1$ =0.0764 m^3/kg, which allows the calculation of the maximum amount of ammonia as

$$M_{tot} = \frac{V_{tanker}}{\hat{V}_1} = \frac{20\ \mathrm{m}^3}{0.0764\ \mathrm{m}^3/\mathrm{kg}} = 261.78\ \mathrm{kg}$$



When the temperature drops to 293 K, the intersection of the 0.0764 m^3/kg isochore with the T_2 isotherm takes place in the biphasic zone, at a pressure of 0.849 MPa (8.49 bar, very close to the 8.60 bar of question **b**) and with a total enthalpy $\hat{H}_{tot} = \hat{H}_2 = 1024.4$ kJ/kg.



The amount of vapor can be estimated from the title or quality lines

51.6% → 0.516×261.78 kg= 135.08 kg of vapor

or from the combination of the mass and enthalpy balances

$$M_{v_2} = M_{tot}\frac{\left(\hat{H}_2 - \hat{H}_{l_2}^{sat}\right)}{\left(\hat{H}_{v_2}^{sat} - \hat{H}_{l_2}^{sat}\right)} = (261.78\text{ kg})\frac{(1024.4 - 419.5)}{(1605.8 - 419.5)} = 132.18\text{ kg}$$

or from the mass and volume balances (a thing that additionally allows determining the volume occupied by each phase)

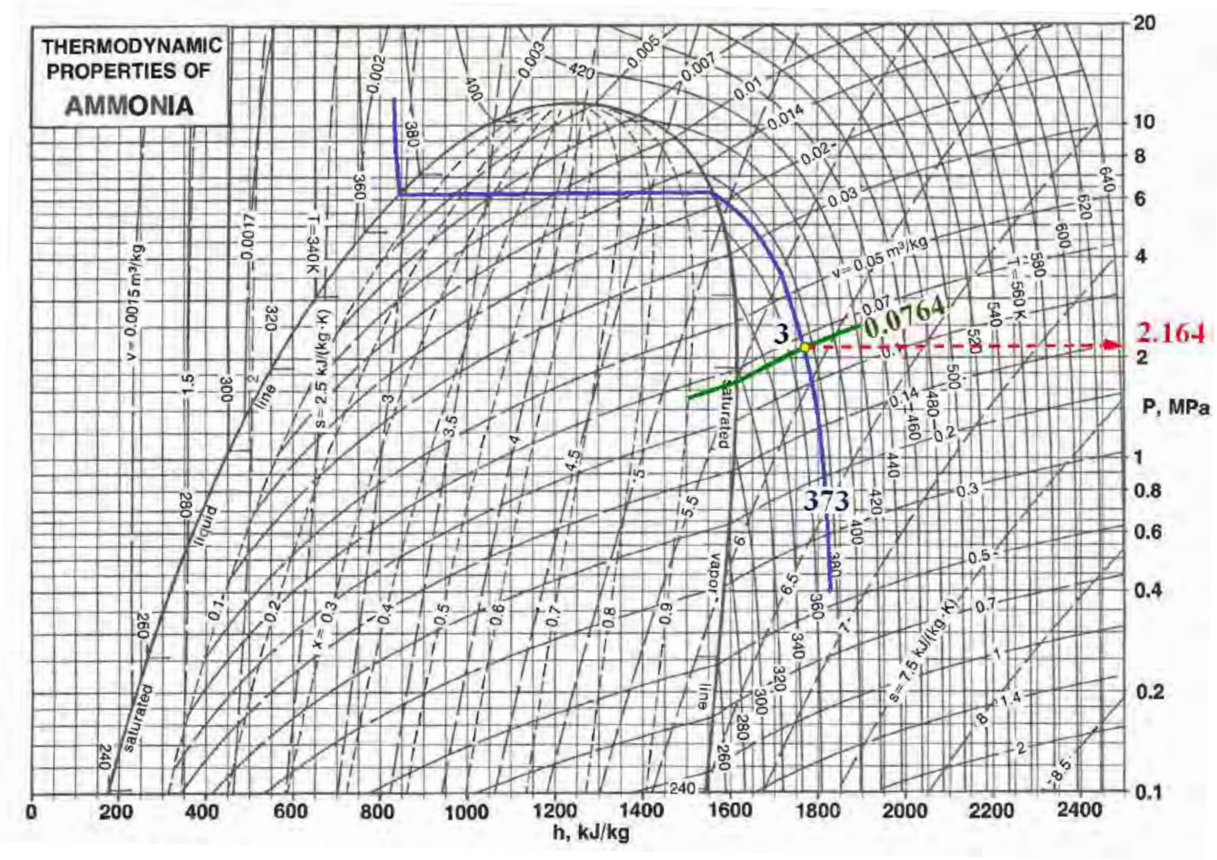
$$M_{v_2} = M_{tot}\frac{\left(\hat{V}_{tot} - \hat{V}_{l_2}^{sat}\right)}{\left(\hat{V}_{v_2}^{sat} - \hat{V}_{l_2}^{sat}\right)} = (261.78\text{ kg})\frac{(0.0764 - 0.001638)}{(0.1497 - 0.001638)} = 132.18\text{ kg}$$

$$M_{l_2} = M_{tot} - M_{v_2} = 261.78 - 132.18 = 129.60\text{ kg}$$

$$V_{v_2} = M_{v_2}\hat{V}_{v_2}^{sat} = (132.18\text{ kg})\left(0.1497\ \frac{\text{m}^3}{\text{kg}}\right) = 19.787\text{ m}^3$$

$$V_{l_2} = M_{l_2}\hat{V}_{l_2}^{sat} = (129.60\ \text{kg})\left(0.001638\ \frac{\text{m}^3}{\text{kg}}\right) = 0.212\ \text{m}^3$$

Finally, when the temperature is raised to T_3= 373 K keeping the specific volume constant, a superheated steam is obtained. It has a pressure of 2.164 MPa (21.64 bar).

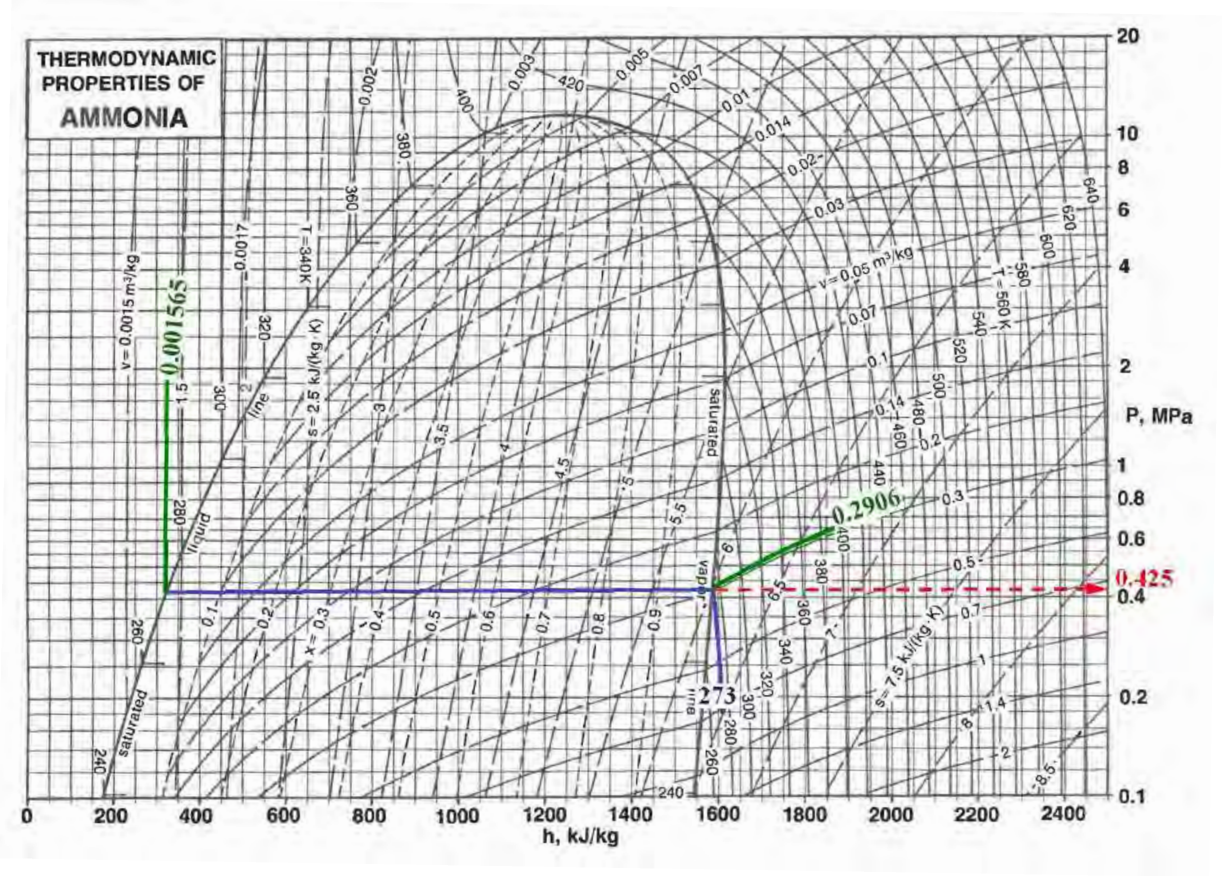


4.15. A spherical tank with an inner diameter of 20 m contains ammonia under isothermal conditions at 0ºC, the liquid occupying half the available volume. By using an ammonia specific *PH*(*T,V,S*) diagram, estimate:

- **a) The inside pressure and the masses of liquid and vapor.**
- **b) The enthalpy of the biphasic mixture at 0ºC.**
- **c) The pressure that could be reached by accidental heating to 67ºC, as well as the masses of liquid and vapor in such a state, and the volumes they occupy under these conditions.**
- **d) Enthalpy at 67ºC.**
- **e) The heat absorbed in this heating.**
- **f) What would happen if a safety valve bleeds all the liquid when a pressure of 12 bar is reached inside the tank?**
- **g) What if in addition to purging all the liquid, the valve purges part of the vapor?**

Solve questions a), c), f) and g) by means of a *PV*(*T*) diagram.

Question a. By going to figure V.12 of appendix V, it can be seen that the T_1=0ºC (273 K) isotherm in the biphasic zone corresponds to a pressure of 0.425 MPa, and that the saturated liquid and the vapor have specific volumes of 0.001565 m^3/kg and 0.2906 m^3/kg, respectively.



By knowing that the total volume of the tank is

$$V_{tank} = \frac{\pi}{6} d_{in}^3 = \frac{\pi}{6}(20\ \mathrm{m})^3 = 4188.7\ \mathrm{m}^3$$

and that the volume occupied by each phase is the half of the available one

$$V_{v_1} = V_{l_1} = \frac{1}{2} V_{tank} = \frac{1}{2}(4188.7\ \mathrm{m}^3) = 2094.35\ \mathrm{m}^3$$

it is found that

$$M_{v_1} = \frac{V_{v_1}}{\hat{V}_{v_1}} = \frac{2094.35\ \mathrm{m}^3}{\left(0.2906\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right)} = 7207\ \mathrm{kg}$$

$$M_{l_1} = \frac{V_{l_1}}{\hat{V}_{l_1}} = \frac{2094.35\ \mathrm{m}^3}{\left(0.001565\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right)} = 1338243\ \mathrm{kg}$$

On the other hand, the total mass is determined as the addition of the masses of each phase

$$M_{tot} = M_{v_1} + M_{l_1} = 7207\ \mathrm{kg} + 1338243\ \mathrm{kg} = 1345450\ \mathrm{kg}$$

and the specific volume as

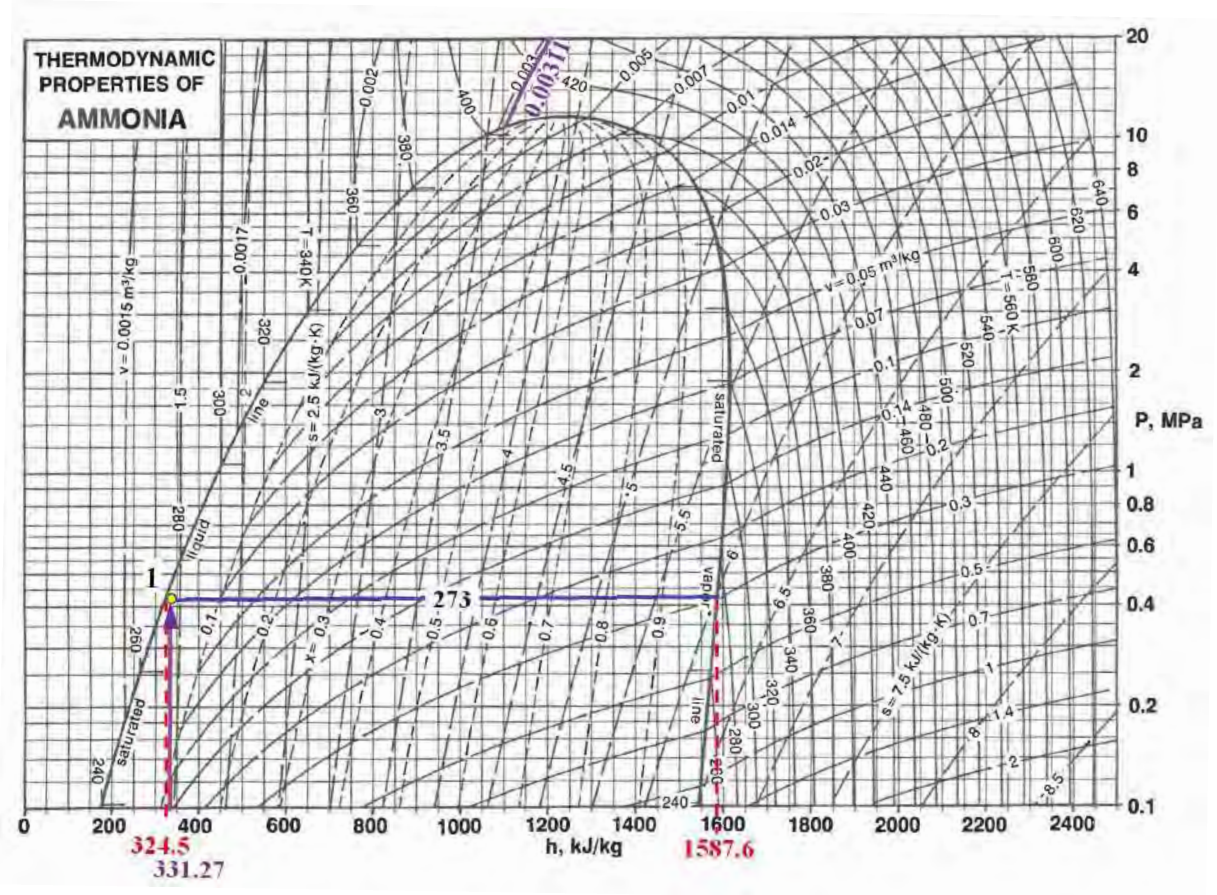
$$\hat{V}_1 = \frac{V_{tank}}{M_{tot}} = \frac{4188.7\ \mathrm{m}^3}{1345450\ \mathrm{kg}} = 0.003113\ \frac{\mathrm{m}^3}{\mathrm{kg}}$$

Question b. In principle, the enthalpy of the biphasic mixture ($\hat{H}_1$) could be graphycally read at the intersection of the $\hat{V}_1$ =0.003113 m^3/kg isochore with the T_1=273 K isotherm. Unfortunately, in figure V.12 the isochores lower than 0.005 m^3/kg are not plotted in the biphasic zone (and even those which are drawn do not fully cover it). However, the enthalpy balance also allows the calculation of this enthalpy, since

$$M_{tot}\hat{H}_1 = M_{l_1}\hat{H}_{l_1} + M_{v_1}\hat{H}_{v_1} \quad \rightarrow \quad \hat{H}_1 = \frac{M_{l_1}}{M_{tot}}\hat{H}_{l_1} + \frac{M_{v_1}}{M_{tot}}\hat{H}_{v_1}$$

Therefore, by reading the specific enthalpies of the saturated liquid and vapor, and combining them with the results of the previous question

$$\hat{H}_1 = \left(\frac{1338243\ \mathrm{kg}}{1345450\ \mathrm{kg}}\right)\left(324.5\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) + \left(\frac{7207\ \mathrm{kg}}{1345450\ \mathrm{kg}}\right)\left(1587.6\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 331.27\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$



Question c. Neither volume nor mass change, so the new point 2 will be the intersection of the $\hat{V}_1 = \hat{V}_2$ =0.003113 m^3/kg isochore with the isotherm

$$T_2(\text{K}) = 67°\text{C} + 273 = 340 \text{ K}$$

This intersection cannot be rigorously drawn on the *PH* diagram, because only two points are known (point 1 and the intersection of $\hat{V}_1 = \hat{V}_2$ with the saturated liquid curve), and it is obvious that the isochore is not a straight line. However, visual inspection shows that the intersection will also occur inside the biphasic zone (P_2=3.08 MPa), and therefore it is not necessary to know the exact position of point 2 to evaluate the masses of each phase and the volumes they occupy. Interpolating the specific volumes of the liquid and the saturated vapor, and combining the mass ($M_{tot} = M_{l_2} + M_{v_2}$) and volume ($M_{tot} = M_{l_2}\hat{V}_{l_2}^{sat} + M_{v_2}\hat{V}_{v_2}^{sat}$) balances

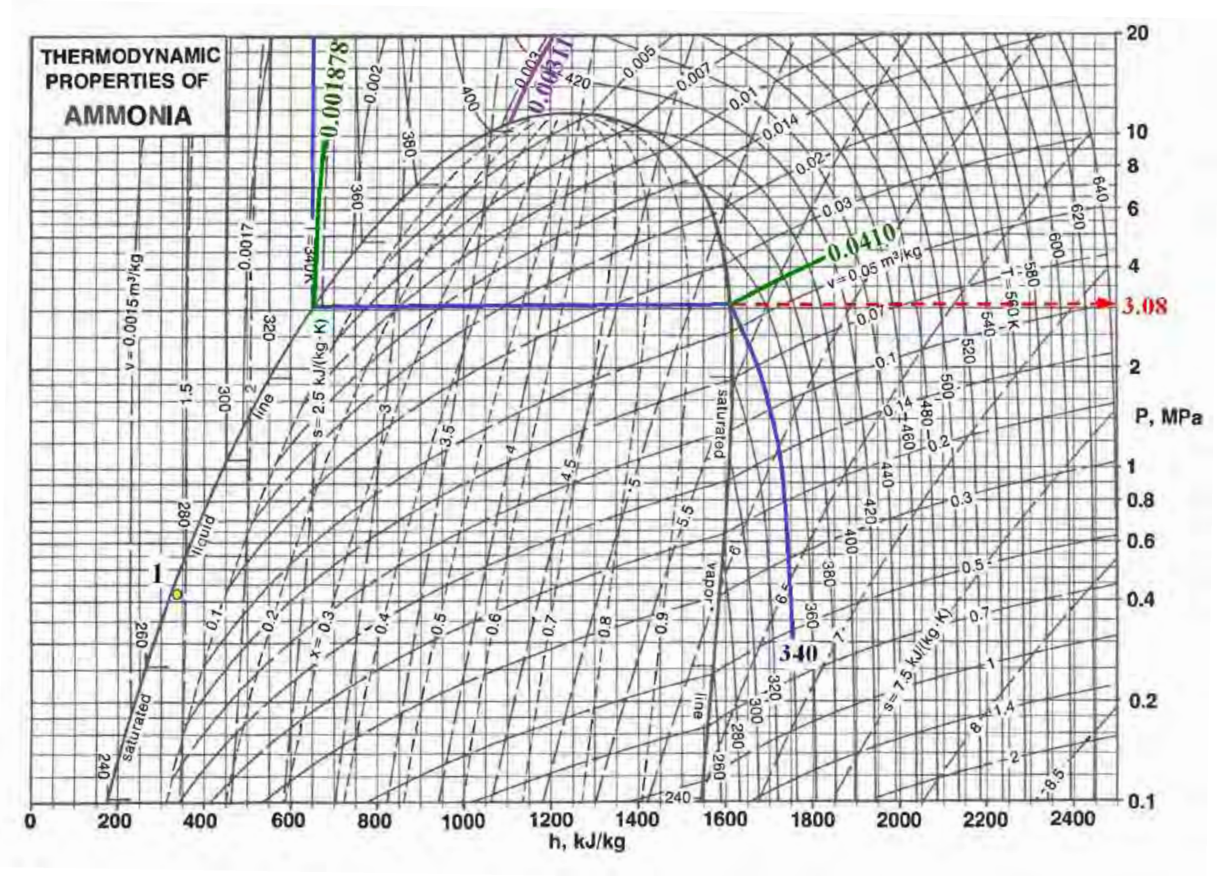
$$M_{v_2} = M_{tot}\frac{\left(\hat{V}_2 - \hat{V}_{l_2}^{sat}\right)}{\left(\hat{V}_{v_2}^{sat} - \hat{V}_{l_2}^{sat}\right)} = (1345450 \text{ kg})\frac{(0.003113 - 0.001878)}{(0.0410 - 0.001878)}\hat{V}_2 = 42373 \text{ kg}$$

$$M_{l_2} = M_{tot} - M_{v_2} = 1345450 \text{ kg} - 42373 \text{ kg} = 1302977 \text{ kg}$$

masses whose volumes are

$$V_{l_2} = M_{l_2}\hat{V}_{l_2}^{sat} = (1302977\ \mathrm{kg})\left(0.001878\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right) = 2447\ \mathrm{m}^3$$

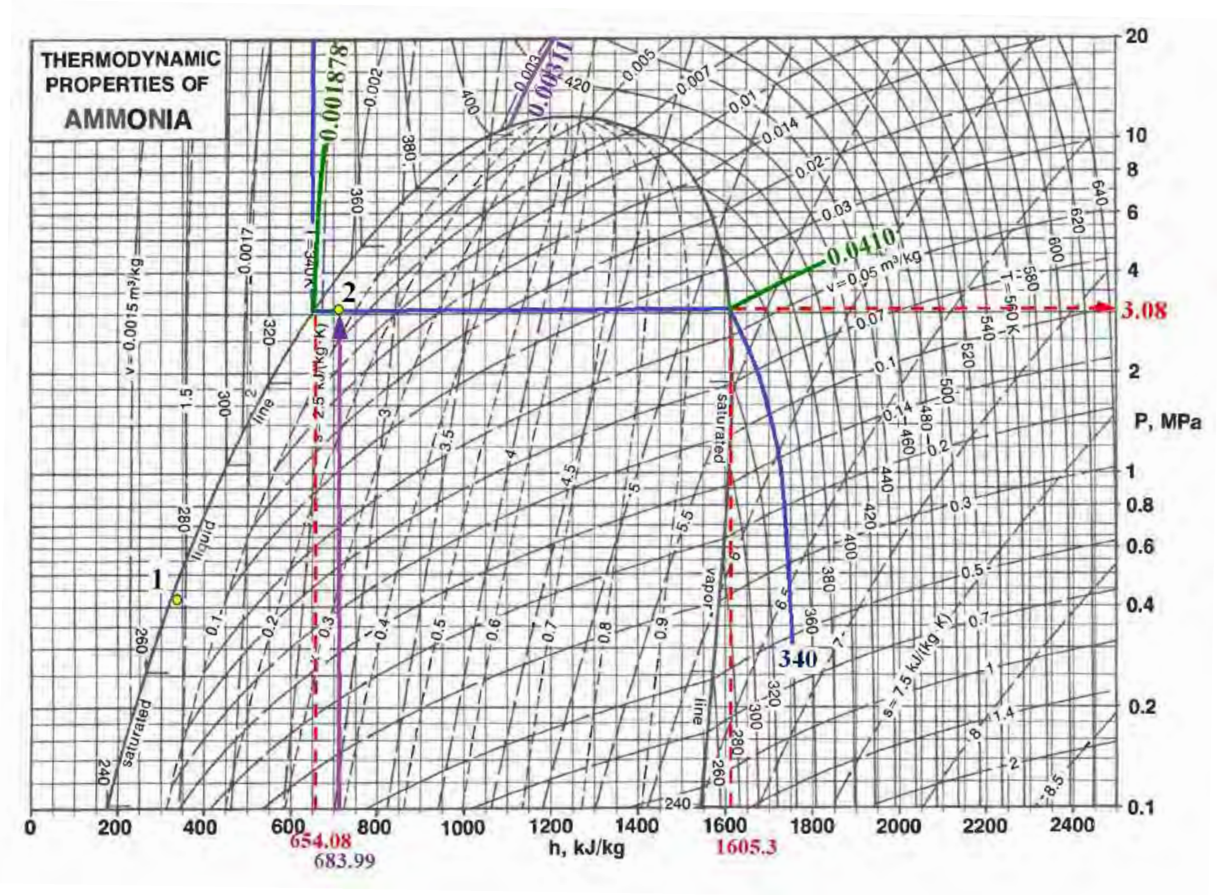
$$V_{v_2} = M_{v_2}\hat{V}_{v_2}^{sat} = (42373\ \mathrm{kg})\left(0.0410\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right) = 1741.4\ \mathrm{m}^3$$



Question d. Operating in the same way as in question **b**, with the new phase distribution and the enthalpies of the saturated liquid and vapor at 340 K

$$\hat{H}_2 = \frac{M_{l_2}}{M_{tot}}\hat{H}_{l_2} + \frac{M_{v_2}}{M_{tot}}\hat{H}_{v_2}$$

$$\hat{H}_2 = \left(\frac{1302977\ \mathrm{kg}}{1345450\ \mathrm{kg}}\right)\left(654.08\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) + \left(\frac{42373\ \mathrm{kg}}{1345450\ \mathrm{kg}}\right)\left(1605.30\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 683.99\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$



Question e. The heat exchanged between points 1 and 2 will be

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \; \Delta\hat{Q}_{21} = \int_1^2 T\mathrm{d}\hat{S}$$

but according to reference problem 0.3

$$\mathrm{d}\hat{U} = \mathrm{d}\hat{Q} - P\mathrm{d}\hat{V}$$

If the specific volume remains constant ($\mathrm{d}\hat{V}$=0) there is no expansion-compression work and

$$\Delta\hat{Q}_{21}=\Delta\hat{U}_{21} = \hat{U}_2 - \hat{U}_1 = \left(\hat{H}_2 - \hat{V}_2P_2\right) - \left(\hat{H}_1 - \hat{V}_1P_1\right) = \hat{H}_2 - \hat{H}_1 - \hat{V}_1(P_2 - P_1)$$

By compiling the values of the preceding questions

$$\Delta\hat{Q}_{21}=\left(683.99\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 331.27\frac{\mathrm{kJ}}{\mathrm{kg}}\right) - \left(0.003113\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right)(3080\ \mathrm{kPa} - 425\ \mathrm{kPa}) = 344.45\frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta Q_{21} = M_{tot}\Delta\hat{Q}_{21} = (1345450\ \mathrm{kg})\left(344.45\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 463440253\ \mathrm{kJ}$$

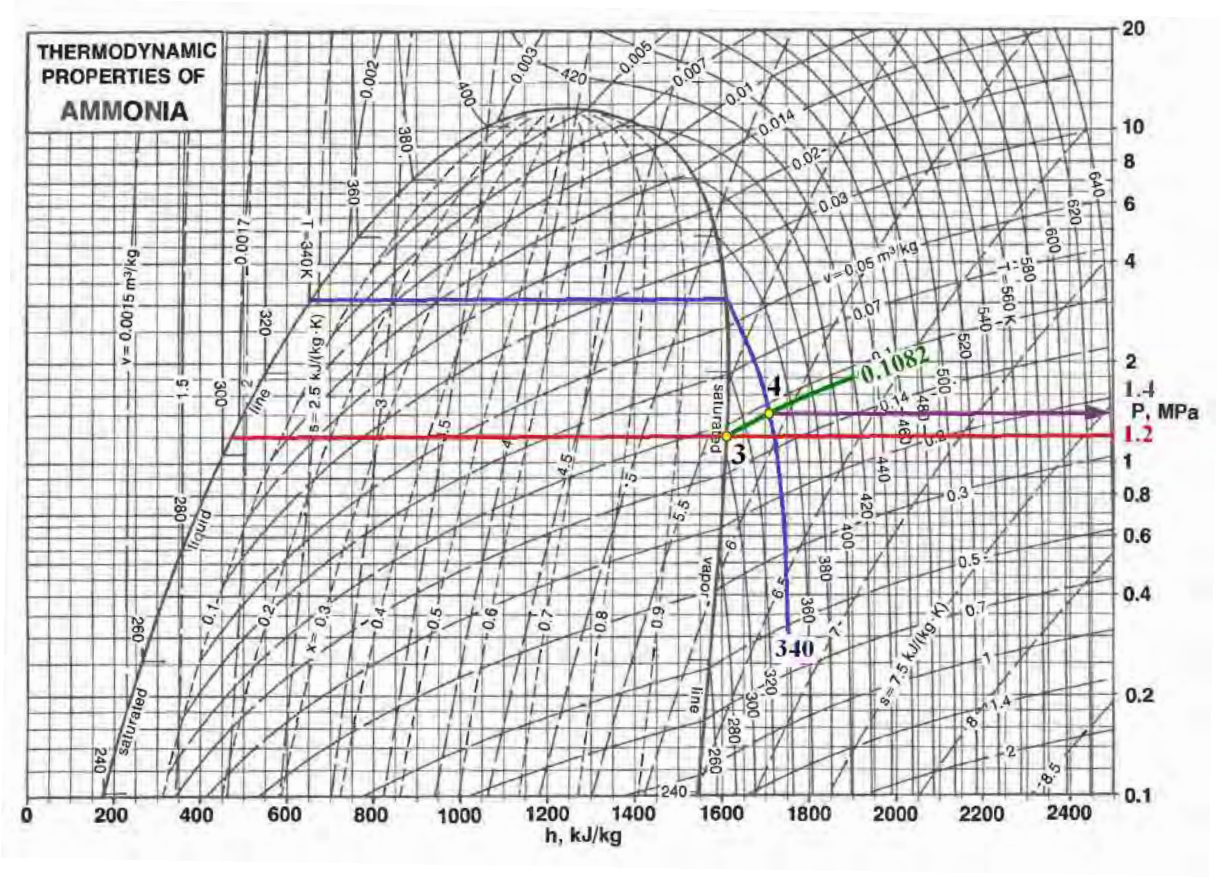
Question f. If all the liquid is purged, there will be only saturated vapor occupying the whole tank (4188.7 m^3). The specific volume of this vapor is found at the intersection of the isochore P_3= 12 bar (1.2 MPa) with the saturated vapor line (approximately 0.1082 kg/m^3), and the remaining mass will be

$$M_{v_3} = \frac{V_{tank}}{\hat{V}_{v_3}} = \frac{4188.7\ \mathrm{m}^3}{\left(0.1082\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right)} = 38712.57\ \mathrm{kg}$$

and the amount of ammonia purged will be

$$M_{purged} = M_{tot} - M_{v_3} = 1345450\ \mathrm{kg} - 38712.57\ \mathrm{kg} = 1306737.43\ \mathrm{kg}$$

But since the intersection occurs at a temperature lower than T_2, the isochoric heating of this vapor will continue until reaching 340 K, and then there will be a pressure P_4=1.4 MPa.

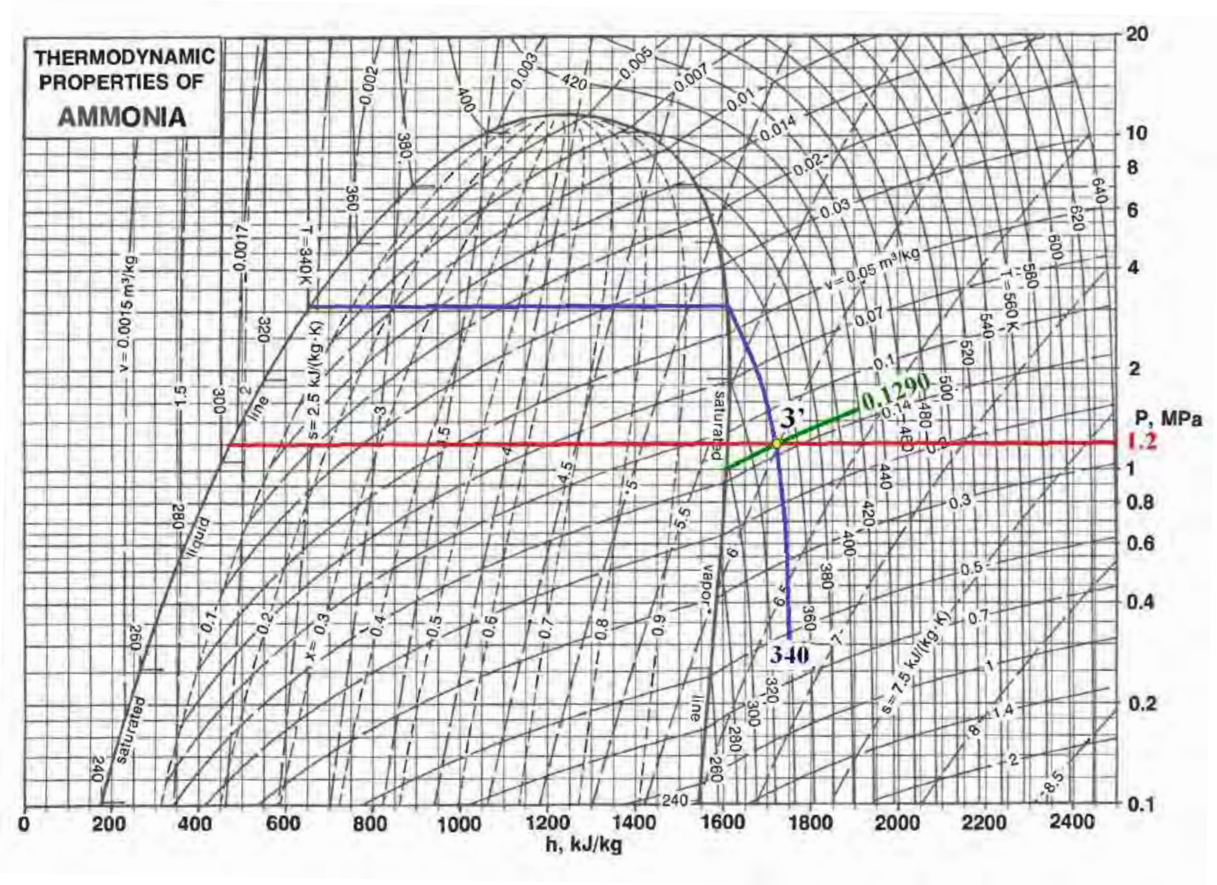


Question g. If the valve can purge steam, then the saturated vapor that remains occupying the whole tank will have a specific volume corresponding to the intersection of the P_3 isochore with the T_2 isotherm (0.1290 m^3/kg), being the remaining mass

$$M_{v_{3'}} = \frac{V_{tank}}{\hat{V}_{v_{3'}}} = \frac{4188.7\ \text{m}^3}{\left(0.1290\ \frac{\text{m}^3}{\text{kg}}\right)} = 32470.54\ \text{kg}$$

and the purged one

$$M_{purged'} = M_{tot} - M_{v_{3'}} = 1345450\ \text{kg} - 32470.54\ \text{kg} = 1312979.46\ \text{kg}$$



In order to solve the problem with figure V.11 of appendix V (***PV* diagram of ammonia**), it is necessary to convert the units of the temperatures and the volume of the tank to those used there

$$T_1(°\text{F}) = 1.8(0°\text{C}) + 32 = 32°\text{F}$$

$$T_2(°\text{F}) = 1.8(67°\text{C}) + 32 = 152.6°\text{F}$$

$$V_{tank} = 4188.7\ \text{m}^3 \times \frac{35.3\ \text{ft}^3}{1\ \text{m}^3} = 147861.11\ \text{ft}^3$$

Later, by knowing that

$$V_{v_1} = V_{l_1} = \frac{1}{2} V_{tank} = \frac{1}{2}(147861.11\ \text{ft}^3) = 73930.55\ \text{ft}^3$$

and interpolating the properties of the biphasic mixture of saturated liquid and vapor at 32ºF

$$P_1 = 60\ \frac{\text{lb}_\text{f}}{\text{in}^2} \times \left(\frac{12\ \text{in}}{1\ \text{ft}}\right)^2 \times \frac{0.000479\ \text{bar}}{1\ \text{lb}_\text{f}/\text{ft}^2} \times \frac{1\ \text{MPa}}{10\ \text{bar}} = 0.414\ \text{MPa}$$

$$\hat{V}_{v_1}^{sat} = 5\ \frac{\text{ft}^3}{\text{lb}} \times \frac{1\ \text{lb}}{0.454\ \text{kg}} \times \frac{0.028\ \text{m}^3}{1\ \text{ft}^3} = 0.30837\ \frac{\text{m}^3}{\text{kg}}$$

$$\hat{V}_{l_1}^{sat} = 0.024\ \frac{\text{ft}^3}{\text{lb}} \times \frac{1\ \text{lb}}{0.454\ \text{kg}} \times \frac{0.028\ \text{m}^3}{1\ \text{ft}^3} = 0.00148\ \frac{\text{m}^3}{\text{kg}}$$

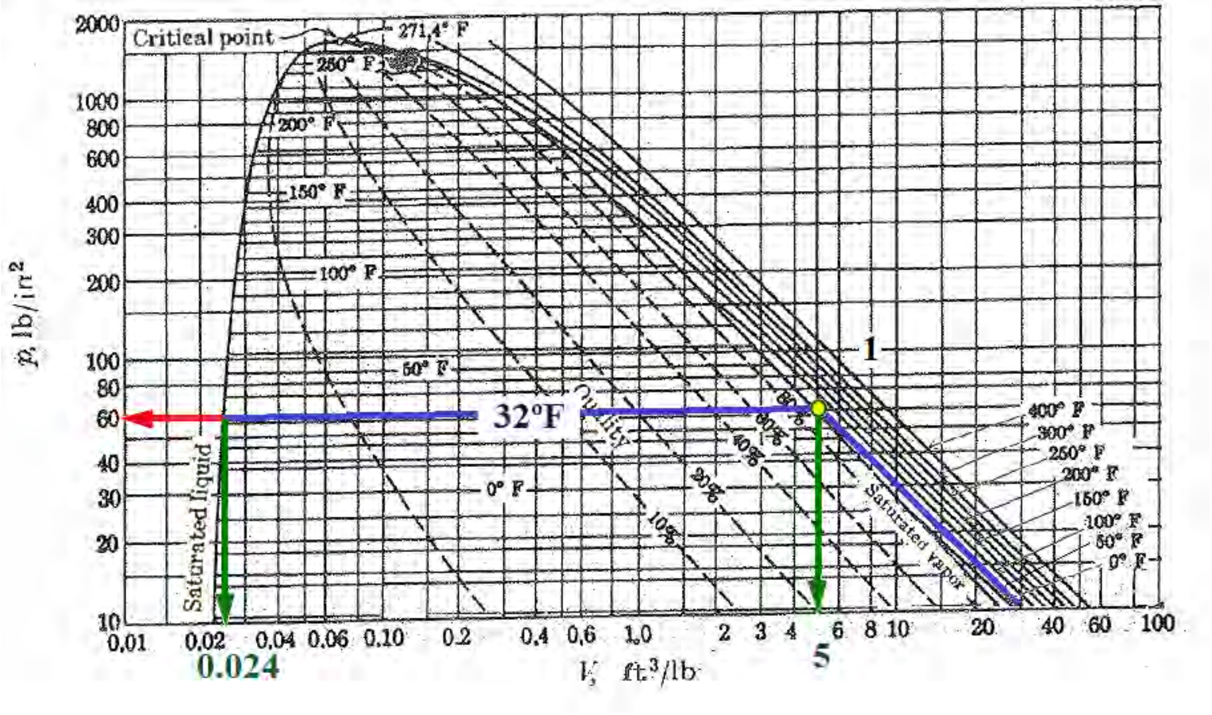
it is obtained that

$$M_{v_1} = \frac{V_{v_1}}{\hat{V}_{v_1}} = \frac{73930.55\ \text{ft}^3}{\left(5\ \frac{\text{ft}^3}{\text{lb}}\right)} = 14786.11\ \text{lb}$$

$$M_{l_1} = \frac{V_{l_1}}{\hat{V}_{l_1}} = \frac{73930.55\ \text{ft}^3}{\left(0.024\ \frac{\text{ft}^3}{\text{lb}}\right)} = 3080439.58\ \text{lb}$$

$$M_{tot} = M_{v_1} + M_{l_1} = 14786.11\ \text{lb} + 3080439.58\ \text{lb} = 3095225.69\ \text{lb}$$

$$\hat{V}_1 = \frac{V_{tank}}{M_{tot}} = \frac{147861.11\ \text{ft}^3}{3095225.69\ \text{lb}} = 0.04777\ \frac{\text{ft}^3}{\text{lb}}$$



By placing this value of $\hat{V}_1$ on the PV diagram and looking for the graphical intersection of the isochore with the 152.6ºF isotherm, it is obtained point 2. The pressure and the specific volumes of the saturated phases in the new state are

$$P_2 = 452.3\ \frac{\mathrm{lb_f}}{\mathrm{in}^2} \times \left(\frac{12\ \mathrm{in}}{1\ \mathrm{ft}}\right)^2 \times \frac{0.000479\ \mathrm{bar}}{1\ \mathrm{lb_f/ft^2}} \times \frac{1\ \mathrm{MPa}}{10\ \mathrm{bar}} = 3.12\ \mathrm{MPa}$$

$$\hat{V}_{v_2}^{sat} = 0.67098\ \frac{\mathrm{ft}^3}{\mathrm{lb}} \times \frac{1\ \mathrm{lb}}{0.454\ \mathrm{kg}} \times \frac{0.028\ \mathrm{m}^3}{1\ \mathrm{ft}^3} = 0.04138\ \frac{\mathrm{m}^3}{\mathrm{kg}}$$

$$\hat{V}_{l_2}^{sat} = 0.03021\ \frac{\mathrm{ft}^3}{\mathrm{lb}} \times \frac{1\ \mathrm{lb}}{0.454\ \mathrm{kg}} \times \frac{0.028\ \mathrm{m}^3}{1\ \mathrm{ft}^3} = 0.001863\ \frac{\mathrm{m}^3}{\mathrm{kg}}$$

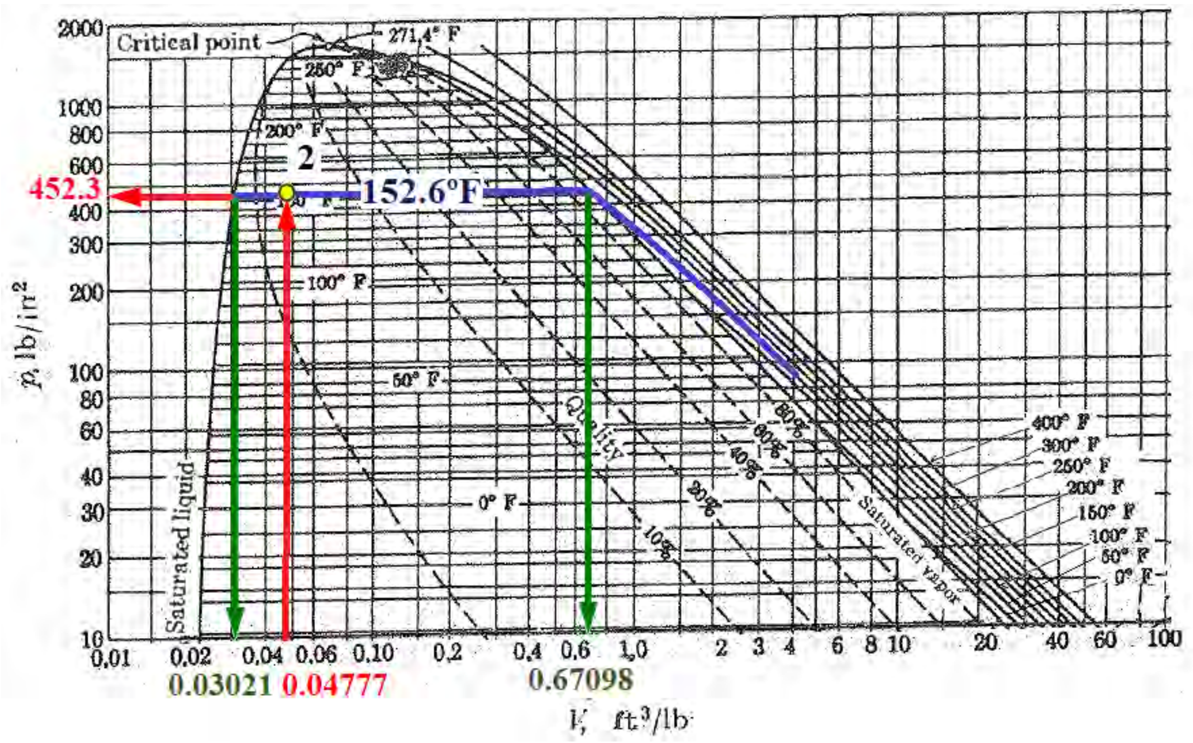
By operating as in question **c**

$$M_{v_2} = M_{tot}\frac{\left(\hat{V}_2 - \hat{V}_{l_2}^{sat}\right)}{\left(\hat{V}_{v_2}^{sat} - \hat{V}_{l_2}^{sat}\right)} = (3095225.69\ \mathrm{lb})\frac{(0.04777 - 0.03021)}{(0.67098 - 0.03021)} = 84823.20\ \mathrm{lb}$$

$$M_{l_2} = M_{tot} - M_{v_2} = 3095225.69\ \mathrm{lb} - 84823.20\ \mathrm{lb} = 3010402.49\ \mathrm{lb}$$

$$V_{l_2} = M_{l_2}\hat{V}_{l_2}^{sat} = (3010402.49\ \mathrm{lb})\left(0.03021\ \frac{\mathrm{ft}^3}{\mathrm{lb}}\right) \times \frac{0.028\ \mathrm{m}^3}{1\ \mathrm{ft}^3} = 2546.44\ \mathrm{m}^3$$

$$V_{v_2} = M_{v_2}\hat{V}_{v_2}^{sat} = (84823.20\ \mathrm{lb})\left(0.67098\ \frac{\mathrm{ft}^3}{\mathrm{lb}}\right) \times \frac{0.028\ \mathrm{m}^3}{1\ \mathrm{ft}^3} = 1593.61\ \mathrm{m}^3$$



Finally, when the valve bleeds all the liquid at

$$P_3 = 12\ \text{bar} \times \frac{2090\ \text{lb}_\text{f}/\text{ft}^2}{1\ \text{bar}} \times \left(\frac{1\ \text{ft}}{12\ \text{in}}\right)^2 = 174.17\ \frac{\text{lb}_\text{f}}{\text{in}^2}$$

only saturated vapor remains, being its specific volume

$$\hat{V}_{v_3} = 1.6818\ \frac{\text{ft}^3}{\text{lb}} \times \frac{1\ \text{lb}}{0.454\ \text{kg}} \times \frac{0.028\ \text{m}^3}{1\ \text{ft}^3} = 0.10372\ \frac{\text{m}^3}{\text{kg}}$$

and the amount of vapor

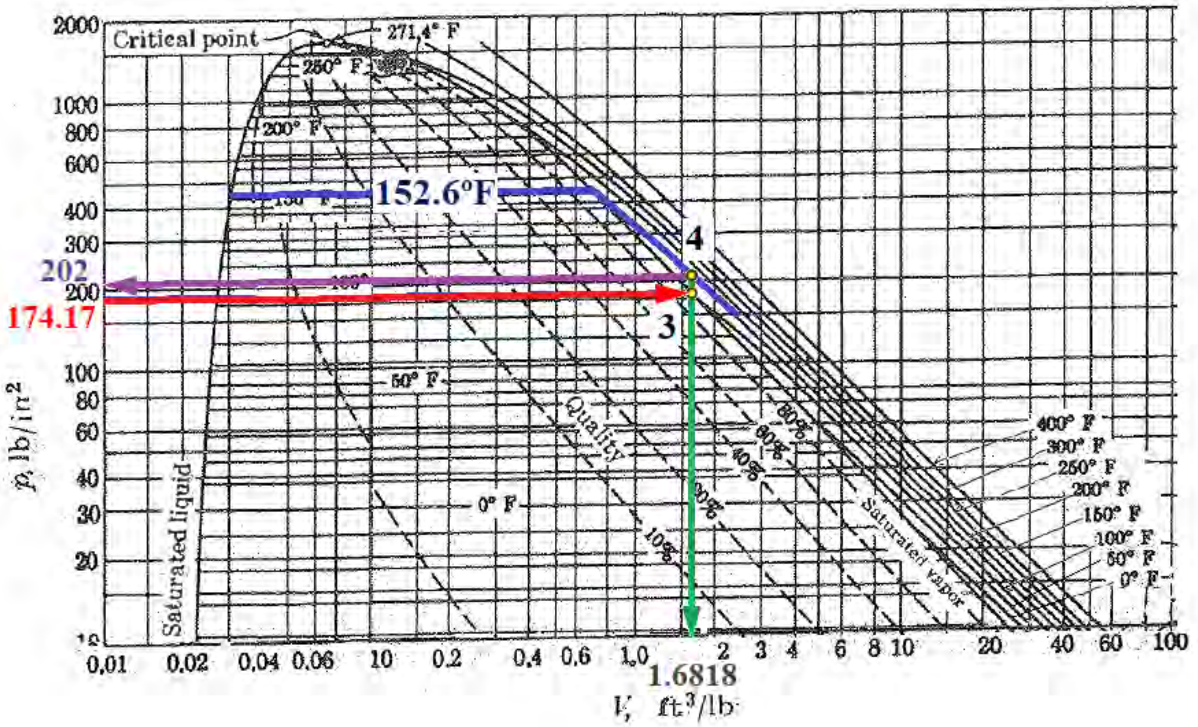
$$M_{v_3} = \frac{V_{tank}}{\hat{V}_{v_3}} = \frac{147861.11\ \text{ft}^3}{\left(1.6818\ \frac{\text{ft}^3}{\text{lb}}\right)} = 87918.37\ \text{lb}$$

Thus, the purged mass is

$$M_{purged} = M_{tot} - M_{v_3} = (3095225.69\ \text{lb} - 87918.37\ \text{lb}) \times \frac{0.454\ \text{kg}}{1\ \text{lb}} = 1365317.52\ \text{kg}$$

The isochoric heating of this vapor will continue until reaching the T_2 isotherm, and then there will be a pressure of 202 psia

$$202\ \frac{\text{lb}_\text{f}}{\text{in}^2} \times \left(\frac{12\ \text{in}}{1\ \text{ft}}\right)^2 \times \frac{0.000479\ \text{bar}}{1\ \text{lb}_\text{f}/\text{ft}^2} \times \frac{1\ \text{MPa}}{10\ \text{bar}} = 1.39\ \text{MPa}$$



On the contrary, if the valve also purges steam, the specific volume of the vapor in its final state will be

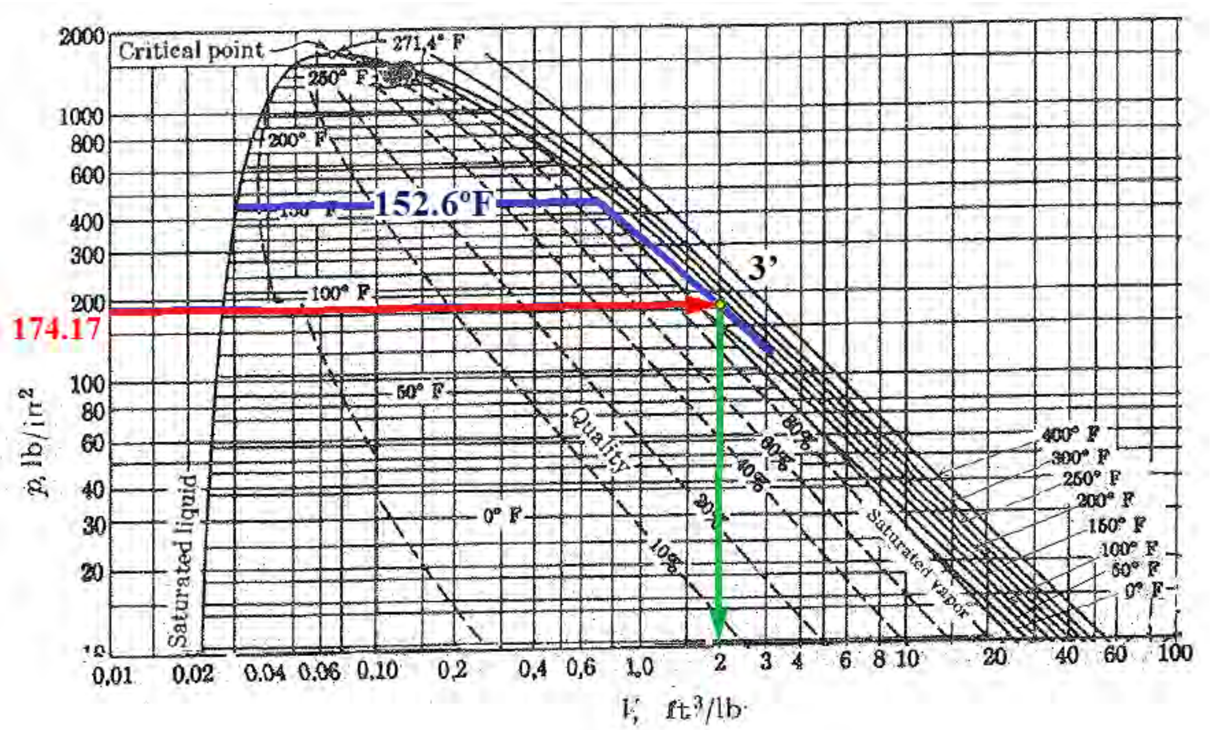
$$\hat{V}_{v_{3'}} = 2\ \frac{\text{ft}^3}{\text{lb}} \times \frac{1\ \text{lb}}{0.454\ \text{kg}} \times \frac{0.028\ \text{m}^3}{1\ \text{ft}^3} = 0.12335\ \frac{\text{m}^3}{\text{kg}}$$

the remaining mass

$$M_{v_{3'}} = \frac{V_{tank}}{\hat{V}_{v_{3'}}} = \frac{147861.11\ \text{ft}^3}{\left(2\ \frac{\text{ft}^3}{\text{lb}}\right)} = 73930.555\ \text{lb}$$

and the purged one

$$M_{purged'} = M_{tot} - M_{v_{3'}} = (3095225.69\ \text{lb} - 73930.555\ \text{lb}) \times \frac{0.454\ \text{kg}}{1\ \text{lb}} = 1371667.99\ \text{kg}$$



4.16. The analysis of data supplied by several sensors after an accident in a chemical industry revealed the following event: a 100 m^3 methane storage tank, kept at 27ºC and 25 atm, increased its temperature (because proximity to a burning area) to 381.4 K without exploding. By means of a hydrocarbon specific *PH* (*T*,*S*,*V*) diagram, calculate:

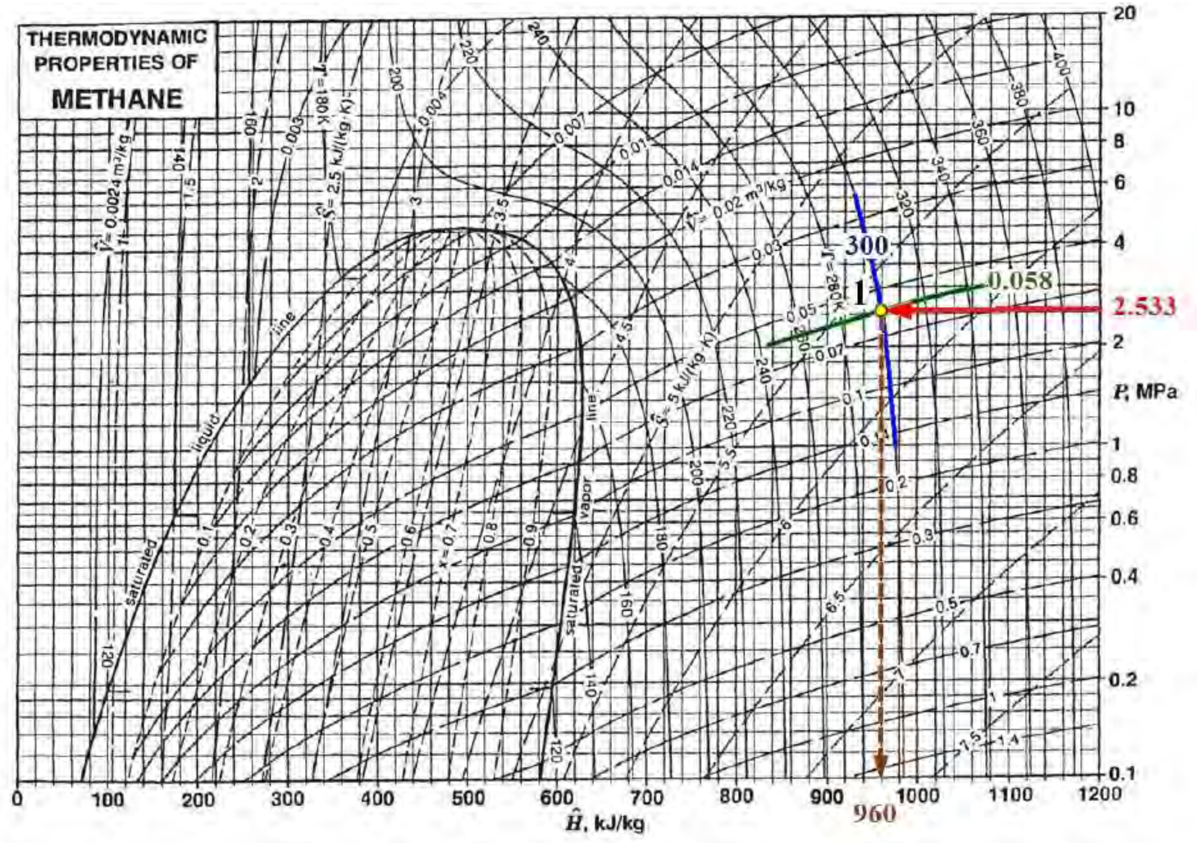
- **a) Number of moles of hydrocarbon in the initial state.**
- **b) The pressure in the final state.**
- **c) The heat absorbed by the methane during the incident.**

Also solve the problem through the Corresponding States Principle, assuming that z_c=0.27 and qualitatively represent the evolution of the phenomenon in *PT*, *PV*(*T*) and *PU*(*T*) diagrams.

Question a. Figure V.4 of Appendix V is a diagram of the type requested. To use it, units of temperature and pressure in the statement of the problem have to be converted through the factors of appendix I

$$T_1(K) = 27℃ + 273 = 300\ K$$

$$P_1 = 25\ \text{atm} \times \frac{1.013\ \text{bar}}{1\ \text{atm}} \times \frac{0.1\ \text{MPa}}{1\ \text{bar}} = 2.533\ \text{MPa}$$

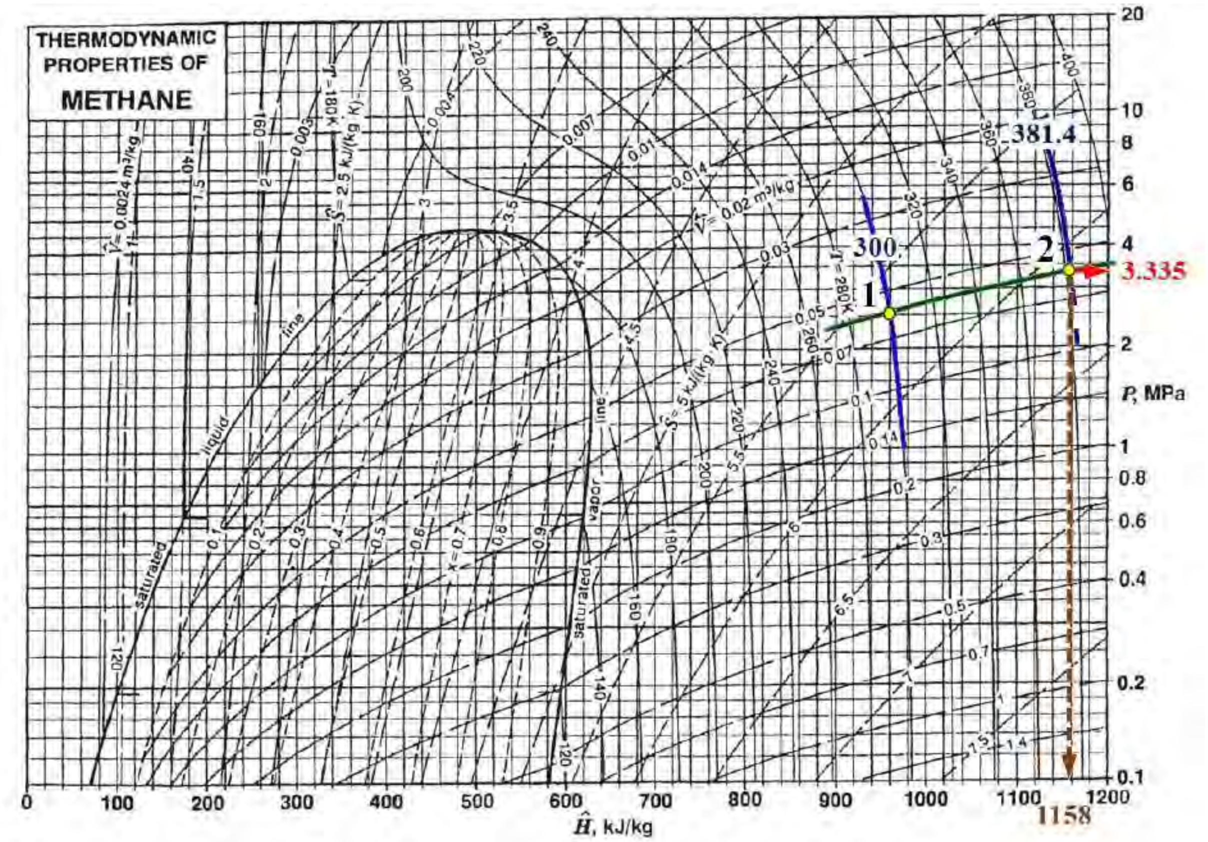


When placing the point corresponding to the initial conditions, it is read that $\widehat{H}_1$ = 960 kJ/kg and $\widehat{V}_1$ = 0.058 m^3/kg = 0.058 L/g. With this datum, the number of moles of methane can be calculated as follows

$$\widehat{V}_1 = 0.058 \frac{\text{m}^3}{\text{kg}} \times \frac{1000\ \text{L}}{1\ \text{m}^3} \times \frac{1\ \text{kg}}{1000\ \text{g}} \times \frac{16.04\ \text{g}}{1\ \text{mol-g}} = 0.9303 \frac{\text{L}}{\text{mol-g}}$$

$$n = \frac{100000\ \text{L}}{0.9303\ \frac{\text{L}}{\text{mol-g}}} = 107492.21\ \text{mol-g}$$

Question b. Since the tank did not explode, it followed the 0.058 m^3/kg isochore until crossing with the isotherm T_2= 381.4 K. A state is then reached where $\hat{H}_2$ =1158 kJ/kg and P_2= 3.335 MPa.



Question c. According to section b of reference problem 0.3

$$\mathrm{d}\hat{U} = \mathrm{d}\hat{Q} - P\mathrm{d}\hat{V}$$

if the specific volume remains constant (d$\hat{V}$=0), then

$$\Delta\hat{Q}_{21}=\Delta\hat{U}_{21} = \hat{U}_2 - \hat{U}_1 = \left(\hat{H}_2 - \frac{P_2}{\hat{\rho}_1}\right) - \left(\hat{H}_1 - \frac{P_1}{\hat{\rho}_1}\right) = \left(\hat{H}_2 - \hat{H}_1\right) - (P_2 - P_1)\hat{V}_1$$

Compiling all the data from questions **a** and **b**

$$\hat{H}_2 - \hat{H}_1 = \left(1158\ \frac{\text{kJ}}{\text{kg}} - 960\frac{\text{kJ}}{\text{kg}}\right) = 198\ \frac{\text{kJ}}{\text{kg}}$$

$$(P_2 - P_1)\hat{V}_1 = (3335\ \text{kPa} - 2533\ \text{kPa})\left(0.058\,\frac{\text{m}^3}{\text{kg}}\right) = 46.516\,\frac{\text{kJ}}{\text{kg}}$$

$$\hat{U}_2 - \hat{U}_1 = 198 - 46.516 = 151.484\ \frac{\text{kJ}}{\text{kg}}$$

$$151.484\ \frac{\text{kJ}}{\text{kg}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} \times \frac{1\ \text{kg}}{1000\ \text{g}} \times \frac{0.239\ \text{cal}}{1\ \text{J}} \times \frac{16.04\ \text{g}}{1\ \text{mol-g}} = 580.723\ \frac{\text{cal}}{\text{mol-g}}$$

and the total heat absorbed by the methane during the process is

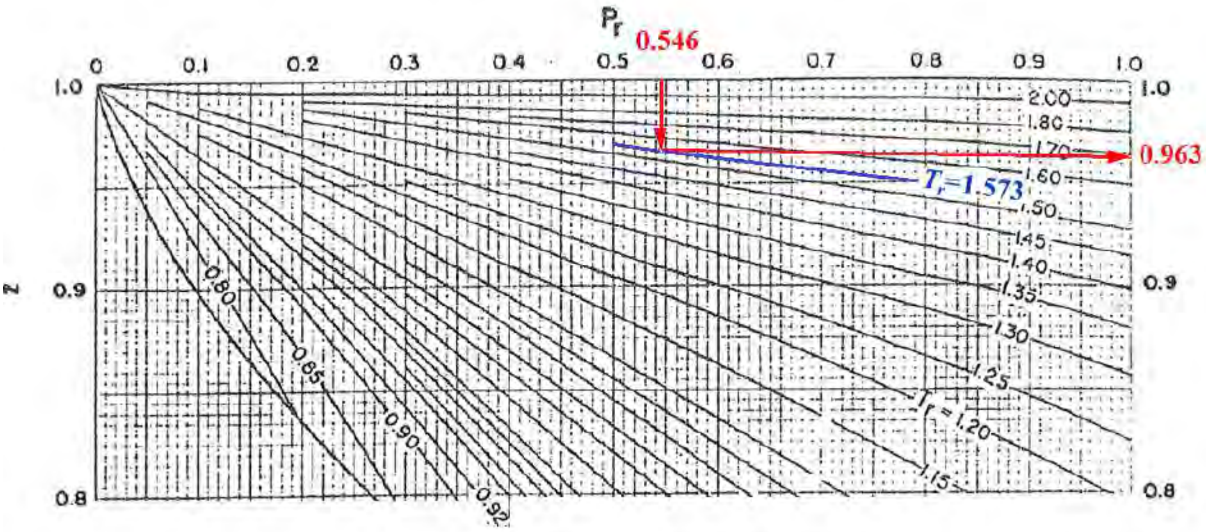
$$\Delta Q_{21} = n\Delta\hat{U}_{21} = (107492.21\ \text{mol-g})\left(580.723\ \frac{\text{cal}}{\text{mol-g}}\right) = 62.42 \cdot 10^6\ \text{cal}$$

With regard to the application of the **Corresponding States Principle**, the number of moles in the initial state 1 has to be calculated as

$$n_1 = \frac{P_1 V_1}{z_1 R T_1}$$

where the compressibility factor z_1 is estimated by a generalized chart that is a function of both the reduced temperature and the reduced pressure. From appendix II it is otained T_c=190.7 K and P_c= 45.8 atm, and therefore at 300 K and 25 atm

$$T_{r1} = \frac{300\ \text{K}}{190.7\ \text{K}} = 1.573 \quad ;\ P_{r1} = \frac{25\ \text{atm}}{45.8\ \text{atm}} = 0.546$$



Since the temperature is higher than the critical one, there will be no mixture of liquid and vapor, but a single gas phase. Furthermore, due to the low reduced pressure, it is better to employ the figure IV.3 of appendix IV than the figure IV.1, where it can be read that z_1=0.963. Thus

$$n_1 = \frac{(25\ \text{atm})(100000\ \text{L})}{(0.963)\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(300\ \text{K})} = 105530\ \text{mol-g}$$

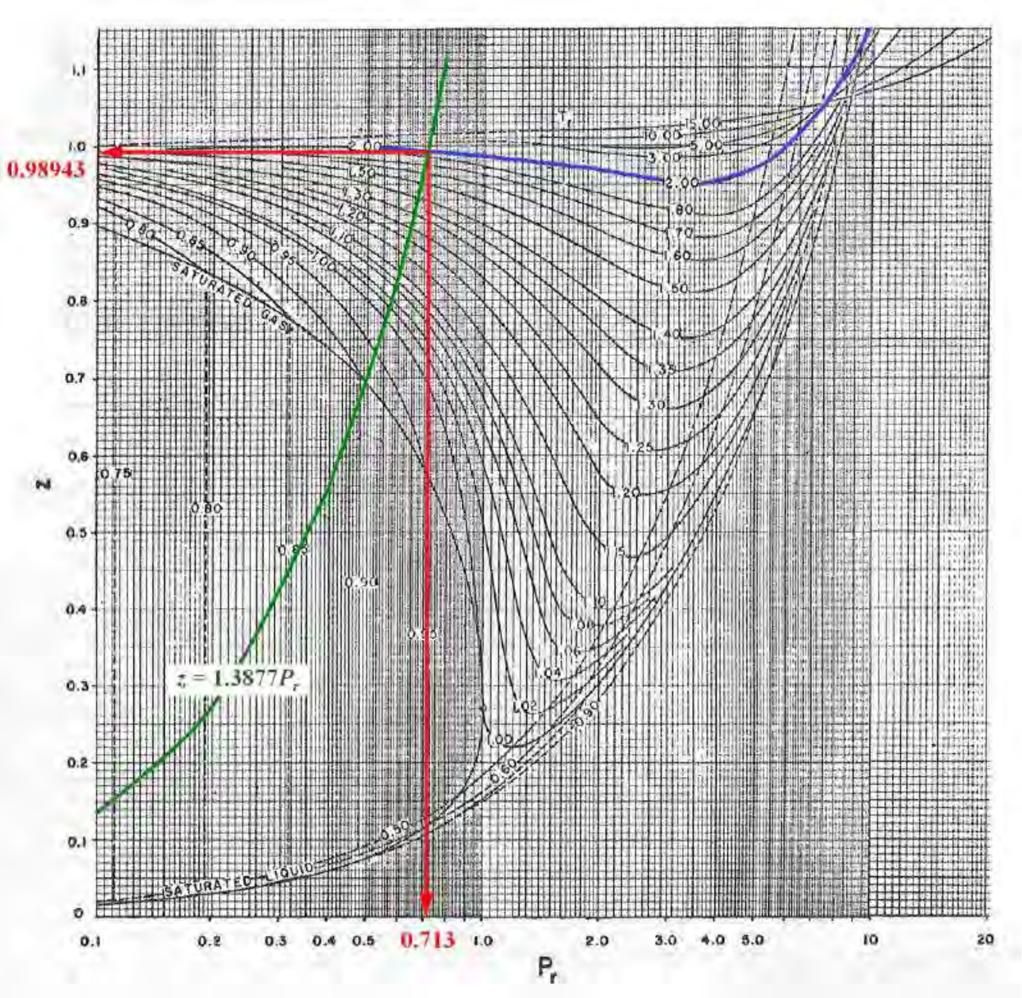
The final pressure (when 381.4 K is reached) will be calculated by the intersection of the isotherm

$$T_{r2} = \frac{381.4\ \text{K}}{190.7\ \text{K}} = 2.0$$

with the casuistic line

$$z_2 = \frac{P_c V_1}{n_1 R T_2} P_{r2} = \frac{(45.8\ \text{atm})(100000\ \text{L})}{(105530\ \text{mol-g})\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(381.4\ \text{K})} P_{r2} = 1.3877 P_{r2}$$

in figure IV.1, because this is an explicit function of T_r and P_r, and P_2 is unknown.



Assumed P_{r2}	Calculated z_2
0.1	0.13877
0.2	0.27754
0.4	0.55508
0.6	0.83262
0.8	1.11016

Results are P_{r2}=0.713 and z_2=0.98943. Thus, the reached pressure is

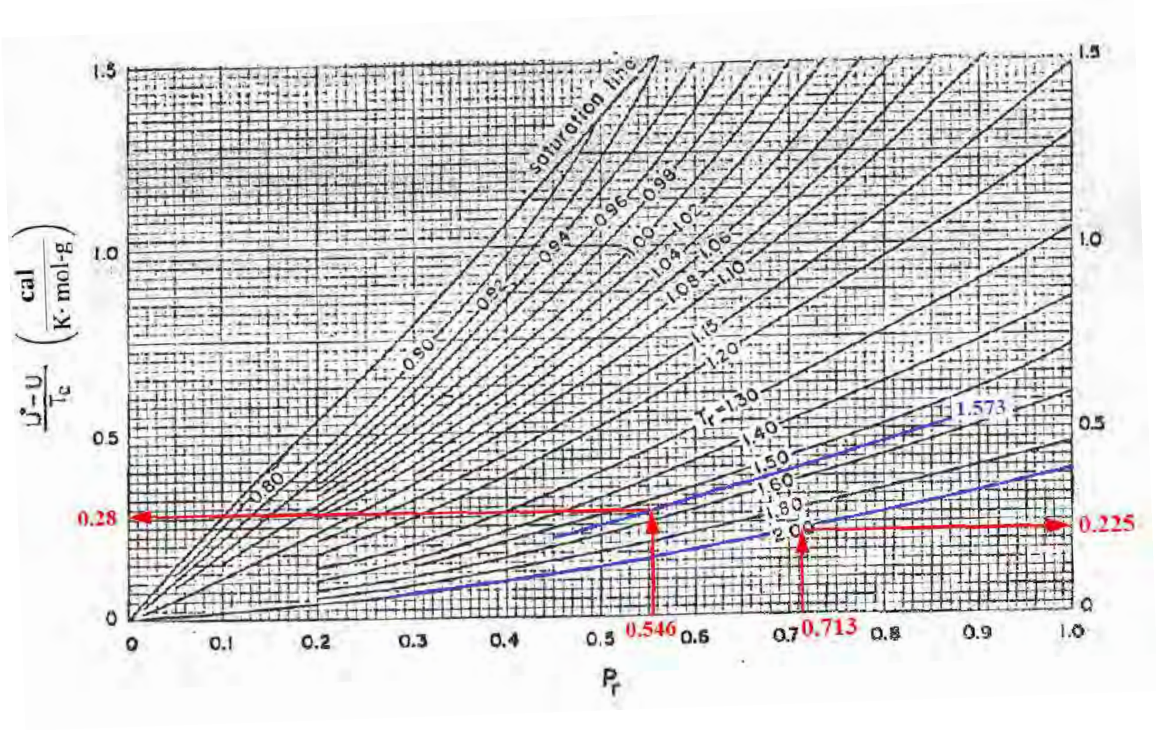
$$P_2 = P_{r2} P_c = 0.713\ (45.8\ \text{atm}) = 32.6554\ \text{atm}$$

$$32.655\ \text{atm} \times \frac{1.013\ \text{bar}}{1\ \text{atm}} \times \frac{0.1\ \text{MPa}}{1\ \text{bar}} = 3.308\ \text{MPa}$$

Finally, in question **c** it was pointed out that $\Delta\hat{Q}_{21}$=$\Delta\hat{U}_{21}$. According to the Corresponding States Principle, the variation of internal energy between a state 1 and a state 2 will be given by the equation

$$\left(\tilde{U}_2 - \tilde{U}_1\right) = \underbrace{\left(\tilde{U}_2^* - U_1^*\right)}_{\text{ideal part}} + \underbrace{\left(\tilde{U}_1^* - \tilde{U}_1\right)_{T_1,P_1} - \left(\tilde{U}_2^* - \tilde{U}_2\right)_{T_2,P_2}}_{\text{real part}} \qquad [1]$$

where the real part is estimated by the generalized figure IV.10 of appendix IV



$$T_{r1} = 1.573\,;\ P_{r1} = 0.546$$

$$\left(\frac{\widetilde{U}_1^* - \widetilde{U}_1}{T_c}\right)_{T_{r1},P_{r1}} = 0.28\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$\Downarrow$$

$$\left(\widetilde{U}_1^* - \widetilde{U}_1\right)_{T_1,P_1} = \left(0.28\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)(190.7\text{ K}) = 53.39\,\frac{\text{cal}}{\text{mol-g}}$$

$$T_{r2} = 2.0\ ;\ P_{r2} = 0.713$$

$$\left(\frac{\widetilde{U}_2^* - \widetilde{U}_2}{T_c}\right)_{T_{r2},P_{r2}} = 0.225\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$\Downarrow$$

$$\left(\widetilde{U}_2^* - \widetilde{U}_2\right)_{T_2,P_2} = \left(0.225\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)(190.7\text{ K}) = 42.908\ \frac{\text{cal}}{\text{mol-g}}$$

and the ideal part from the specific heat capacity at constant pressure of butane, considered as an ideal gas

$$\widetilde{U}_2^* - \widetilde{U}_1^* = \int_{T_1}^{T_2} \tilde{C}_V^* \mathrm{d}T = \int_{T_1}^{T_2} \left(\tilde{C}_P^* - R\right)\mathrm{d}T$$

Heat capacity which, in appendix II is given by

$$\tilde{C}_P^* = \xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4$$

$$\frac{\xi_0}{R} = 4.568 \qquad \frac{\xi_1}{R} = -8.975\cdot 10^{-3}\,\frac{1}{\text{K}} \qquad \frac{\xi_2}{R} = 3.631\cdot 10^{-5}\,\frac{1}{\text{K}^2}$$

$$\frac{\xi_3}{R} = -3.407\cdot 10^{-8}\,\frac{1}{\text{K}^3} \qquad \frac{\xi_4}{R} = 1.091\cdot 10^{-11}\,\frac{1}{\text{K}^4}$$

Therefore

$$\widetilde{U}_2^* - \widetilde{U}_1^* = \int_{T_1}^{T_2} (\xi_0 - R + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4)\mathrm{d}T$$

$$\widetilde{U}_2^* - \widetilde{U}_1^* = \left[(\xi_0 - R)T + \frac{1}{2}\xi_1 T^2 + \frac{1}{3}\xi_2 T^3 + \frac{1}{4}\xi_3 T^4 + \frac{1}{5}\xi_4 T^5\right]_{T_1}^{T_2} =$$

$$= (\xi_0 - R)(T_2 - T_1) + \frac{\xi_1}{2}(T_2^2 - T_1^2) + \frac{\xi_2}{3}(T_2^3 - T_1^3) + \frac{\xi_3}{4}(T_2^4 - T_1^4) + \frac{\xi_4}{5}(T_2^5 - T_1^5)$$

By taking R=1.9872 cal/mol-g·K

$$\left(\tilde{U}_2^* - U_1^*\right) = (4.568 - 1)R(381.4 - 300) - \frac{8.975 \cdot 10^{-3}}{2} R(381.4^2 - 300^2) + \\ + \frac{3.631 \cdot 10^{-5}}{3} R(381.4^3 - 300^3) - \frac{3.407 \cdot 10^{-8}}{4} R(381.4^4 - 300^4) + \\ + \frac{1.091 \cdot 10^{-11}}{5} R(381.4^5 - 300^5) = 570.94 \frac{\text{cal}}{\text{mol-g}}$$

and applying equation [1]

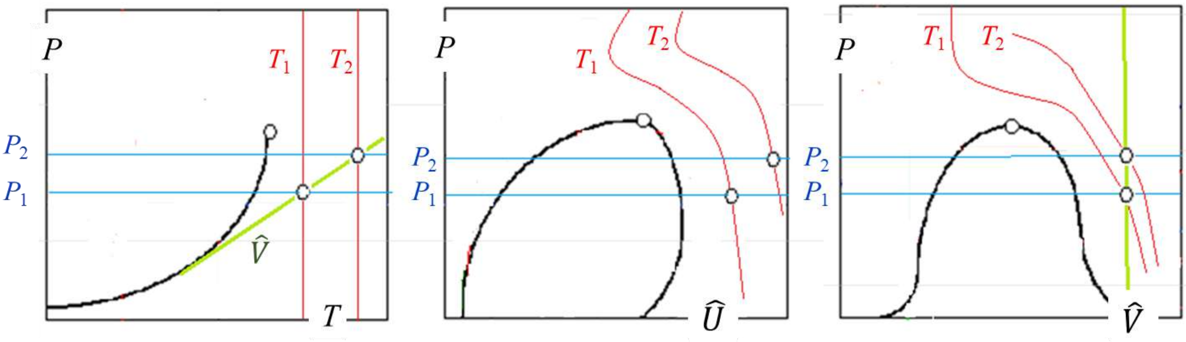
$$570.94 \ \frac{\text{cal}}{\text{mol-g}} + 53.39 \ \frac{\text{cal}}{\text{mol-g}} - 42.908 \ \frac{\text{cal}}{\text{mol-g}} = 581.422 \frac{\text{cal}}{\text{mol-g}}$$

being the total heat exchanged

$$\Delta Q_{21} = n\Delta\hat{U}_{21} = (105530 \text{ mol-g}) \left(581.422 \ \frac{\text{cal}}{\text{mol-g}}\right) = 61.36 \cdot 10^6 \text{ cal}$$

Results very close to those obtained with the *PH* diagram of methane, despite the fact that its critical compressibility factor is of 0.290.

The qualitatively graphical representation will be



4.17. A 40 m^3 storage tank, closed and thermally insulated by jacketed walls, contains 5000 kg of crude oil at 400ºC. By accident, 50 kg of cooling water at 15ºC enters the tank:

a) Calculate the pressure before the water entered.

b) Estimate the volume and mass of oil in the liquid and vapor phases before the water entered.

c) Determine the pressure and temperature in the tank after the water entered by means of a quick approximation.

d) Determine the pressure and the temperature in the tank after the water entered by means of an energy balance.

Indicate the assumptions and simplifications performed. For the liquid oil, take a density of 700 kg/m^3, a pressure-independent specific heat capacity of 2.51 kJ/(kg·K) and a vapor pressure given by

$$\mathbf{\log P_v(\text{mm Hg}) = 2.8 + \frac{52.5}{249.75 + T(\text{°C})}}$$

By the sake of simplycity, oil will be denoted as A and water as B, 1 will be the state before the mixing and 2 the state after it.

Question a. Since the interior of the tank is initially at 400ºC, the pressure will be

$$P_{A_1} = 10^{\left(2.8+\frac{52.5}{249.75+400℃}\right)} = 759.98 \text{ mm Hg}$$

which is roughly the atmospheric one (760 mm Hg).

Question b. In a first approximation, it is assumed that almost the entire oil mass is liquid

$$V_l = \frac{M_l}{\hat{\rho}_l} \approx \frac{M_A}{\hat{\rho}_l} = \frac{5000 \text{ kg}}{700 \text{ kg/m}^3} = 7.14 \text{ m}^3$$

and the volume of the oil in the vapor phase is determined from the volume of the tank

$$V_v = V_{tank} - V_l = 40 - 7.14 = 32.86 \text{ m}^3$$

At such low pressure and at high temperature, and in the absence of other data (T_c, P_c, etc), the vapor is considered an ideal gas, being easy to quantify the number of moles in this phase

$$T_{A_1}(\text{K}) = 273 + 400\text{ºC} = 673 \text{ K}$$

$$32.86 \text{ m}^3 \times \frac{1000 \text{ L}}{1 \text{ m}^3} = 32860 \text{ L}$$

$$n_{v_{A1}} = \frac{PV_v}{RT_{A_1}} = \frac{(1\text{ atm})(32860\text{ L})}{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(673\text{ K})} = 595.44\text{ mol-g}$$

Normally, this vapor will be enriched in light hydrocarbons (methane, ethane, propane...) and therefore its molar mass will be quite low. Even assuming a value similar to that of decane (146 g/mol-g)

$$M_{v_{A1}} = n_{v_{A1}}\mathfrak{W}_A = 595.44\text{ mol-g} \times \frac{146\text{ g}}{1\text{ mol-g}} \times \frac{1\text{ kg}}{1000\text{ g}} = 86.93\text{ kg}$$

86.93<<5000 kg, being acceptable the assumption that almost all the oil mass was initially as liquid.

Question c. Since the water mass (50 kg) is much lower than that of oil (5000 kg), it is expected that all the liquid water that enters will evaporate and become superheated vapor, taking latent and sensible heat from the oil.

In addition, it can be assumed that the heat taken by the water does not cause an appreciable decrease in the interior temperature ($T_{B_2} = T_{A_2} = T_2 = T_{A_1} =$ 400ºC), which will generate a vapor pressure of

$$P_2 = \left(n_{v_{A1}}\right)\frac{RT_2}{V_v} + \left(n_{v_B}\right)\frac{z_B RT_2}{V_v}$$

where

$$n_{v_B} = \frac{50000\text{ g}}{18.015\text{ g/mol-g}} = 2775.46\text{ mol-g}$$

By assuminging that $z_B \approx 1.0$, then

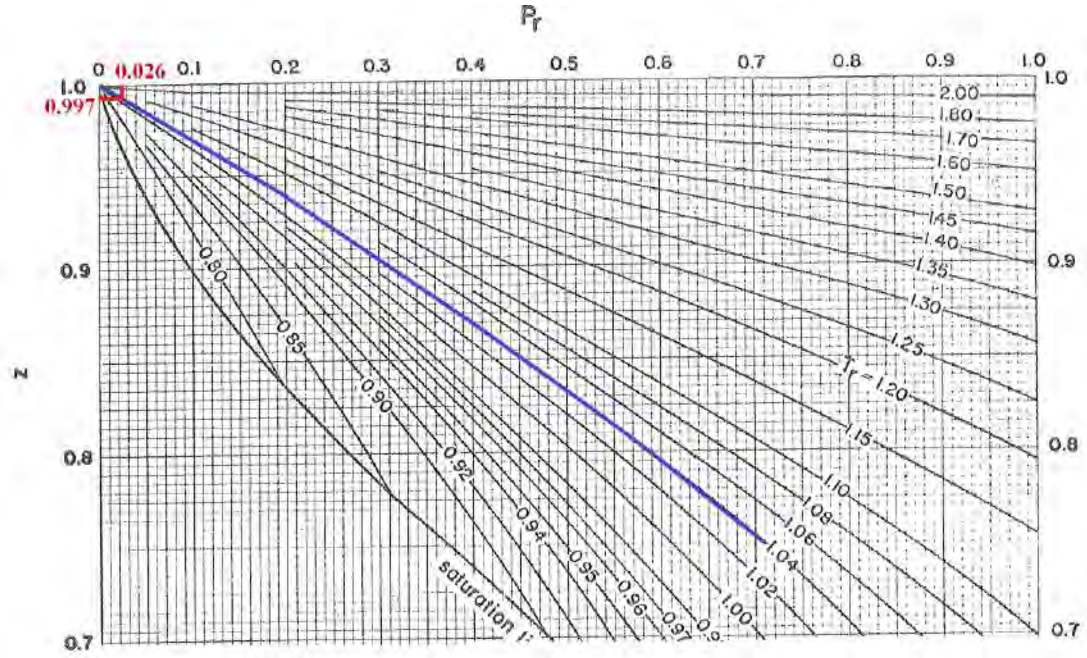
$$P_2 = \frac{(595.44\text{ mol-g} + 2775.46\text{ mol-g})\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(673\text{ K})}{(32860\text{ L})} = 5.66\text{ atm}$$

And the hypothesis that water behaves as an ideal gas is reasonable, since figure IV.3 of appendix IV displays that, under the reduced conditions

$$T_{r2} = \frac{T_2}{T_{cB}} = \frac{673\text{ K}}{647.1\text{ K}} = 1.04$$

$$P_{r2} = \frac{P_2}{P_{cB}} = \frac{5.66\text{ atm}}{217.8\text{ atm}} = 0.026$$

and in the absence of the correction functions Ψ_z (figure IV.2 does not cover reduced pressures lower than 0.1), it can be accepted that the compressibility factor is of 0.997.



Question d. According to the energy balance

$$\left[\begin{array}{c}\text{Sensible heat}\\ \text{lost by oil}\\ \text{from 400°C}\\ \text{(673 K)}\\ \text{to the final}\\ \text{conditions}\end{array}\right] = \left[\begin{array}{c}\text{Sensible heat}\\ \text{gained by}\\ \text{liquid water}\\ \text{from 15°C}\\ \text{(288 K) to}\\ \text{boiling at 100°C}\\ \text{(373 K) and 1 atm}\end{array}\right] + \left[\begin{array}{c}\text{Latent heat}\\ \text{of vaporization}\\ \text{gained by}\\ \text{liquid water}\\ \text{at 100°C}\\ \text{(373 K) and 1 atm}\end{array}\right] + \left[\begin{array}{c}\text{Sensible heat}\\ \text{gained by}\\ \text{water vapor}\\ \text{from 100°C}\\ \text{(373 K) and 1 atm}\\ \text{to the final}\\ \text{conditions}\end{array}\right]$$

$$M_A\hat{C}_{P_A}\Delta T_{Al} \;=\; M_B\hat{C}_{P_{lB}}\Delta T_{Bl} \;+\; M_B\Delta\hat{H}_{vap(373\text{ K})} \;+\; M_B\left[\hat{H}_{(T_2,P_2)} - \hat{H}^{sat}_{v(373\text{ K})}\right] \qquad [1]$$

The first term is easily evaluated with the data in the statement of the problem

$$M_A\hat{C}_{P_A}\Delta T_{Al} = (5000\text{ kg})\left(2.51\ \frac{\text{kJ}}{\text{kg·K}}\right)(673\text{ K} - T_2) = 12550(673 - T_2)\text{ kJ} \qquad [2]$$

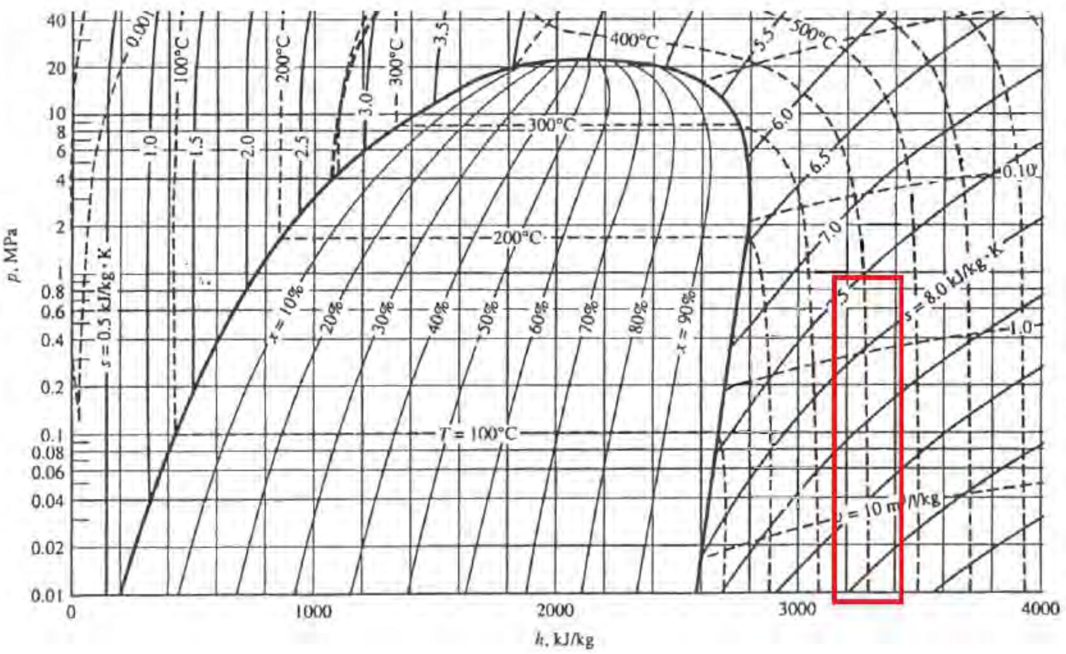
while the second and third ones are calculated with the help of table VI.1 of appendix VI: the latent heat of vaporization at 100ºC as the difference between the enthalpies of saturated vapor and liquid at that temperature ($\hat{H}_v^{sat} - \hat{H}_l^{sat} = 2676 - 419.1 = 2256.9$ kJ/kg) and $\hat{C}_{P_{lB}}$ as the average of the specific heats of the saturated liquid between 0 and 100ºC (approximately 4.19 kJ/kg·K)

$$M_B \hat{C}_{P_{lB}} \Delta T_{Bl} = (50\text{ kg})\left(4.19\,\frac{\text{kJ}}{\text{kg}\cdot\text{K}}\right)(373\text{ K} - 288\text{ K}) = 17807.5\text{ kJ} \qquad [3]$$

$$M_B \Delta \hat{H}_{vap(373\text{ K})} = (50\text{ kg})\left(2256.9\,\frac{\text{kJ}}{\text{kg}}\right) = 112845\text{ kJ} \qquad [4]$$

On the other hand, figure V.5 of appendix V shows that the enthalpy of water vapor around 400ºC is practically independent of the pressure below 1 MPa (10 bar). By assuming that this pressure is not reached, the fourth term of the energy balance can be replaced by the enthalpy change of water as an ideal gas

$$\hat{H}_{(T_2,P_2)} - \hat{H}^{sat}_{v(373\text{ K})} \approx \int_{373}^{T_2} \hat{C}^{*}_{P_B}\,\mathrm{d}T$$



According to appendix II

$$\tilde{C}^{*}_{P} = \xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4$$

$$\frac{\xi_0}{R} = 4.395 \qquad \frac{\xi_1}{R} = -4.186.\cdot 10^{-3}\,\frac{1}{\text{K}} \qquad \frac{\xi_2}{R} = 1.405\cdot 10^{-5}\,\frac{1}{\text{K}^2}$$

$$\frac{\xi_3}{R} = -1.564\cdot 10^{-8}\,\frac{1}{\text{K}^3} \qquad \frac{\xi_4}{R} = 0.632\cdot 10^{-11}\,\frac{1}{\text{K}^4}$$

and therefore

$$\begin{aligned}\int_{373}^{T_2} \hat{C}^*_{P_B}\mathrm{d}T &= \int_{373}^{T_2} (\xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4)\mathrm{d}T = \\ &= \left[\xi_0 T + \frac{1}{2}\xi_1 T + \frac{1}{3}\xi_2 T^3 + \frac{1}{4}\xi_3 T^4 + \frac{1}{5}\xi_4 T^5\right]_{373}^{T_2} = \xi_0(T_2 - 373) + \\ &+ \frac{\xi_1}{2}(T_2^2 - 373^2) + \frac{\xi_2}{3}(T_2^3 - 373^3) + \frac{\xi_3}{4}(T_2^4 - 373^4) + \frac{\xi_4}{5}(T_2^5 - 373^5)\end{aligned}$$

By taking the universal gas constant in suitable units to express the specific heat capacity in mass units

$$8.314\,\frac{\mathrm{J}}{\mathrm{K}\cdot\text{mol-g}} \times \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}} \times \frac{1\ \text{mol-g}}{18.015\ \mathrm{g}} \times \frac{1000\ \mathrm{g}}{1\ \mathrm{kg}} = 0.4615\,\frac{\mathrm{kJ}}{\mathrm{K}\cdot\mathrm{kg}}$$

the whole fourth term is given by

$$\begin{aligned}M_B \int_{373}^{T_2} \hat{C}^*_{P_B}\mathrm{d}T = (50\ \mathrm{kg})\left(0.4615\,\frac{\mathrm{kJ}}{\mathrm{K}\cdot\mathrm{kg}}\right) \{4.395(T_2 - 373) - \\ - \frac{4.186\cdot 10^{-3}}{2}(T_2^2 - 373^2) + \frac{1.405\cdot 10^{-5}}{3}(T_2^3 - 373^3) \\ - \frac{1.564\cdot 10^{-8}}{4}(T_2^4 - 373^4) + \frac{0.632\cdot 10^{-11}}{5}(T_2^5 - 373^5)\Big\}\end{aligned} \qquad [5]$$

Placing equations [2-5] in formula [1] and choosing T_2 by trial and error, it results an approximate value of 660.33 K (387.33 ºC), not far from 400 ºC. The pressure would be

$$P_2 = \frac{(594.24\ \text{mol-g} + 2775.46\ \text{mol-g})\left(0.082\,\frac{\mathrm{atm}\cdot\mathrm{L}}{\mathrm{K}\cdot\text{mol-g}}\right)(660.33\ \mathrm{K})}{(32860\ \mathrm{L})} = 5.55\ \mathrm{atm}$$

a number close to that of the previous question at 400ºC.

4.18. A substance of molecular mass 72 g/mol-g and critical properties T_c=325 K, P_c=10 atm and z_c=0.27 is introduced into a cylindrical bottle 30 cm in diameter and 42.5 cm high at 293 K and 20 atm. If it is insulated from the outside by a glass wool layer and connected to a total-consumption burner, the flame is extinguished after a few minutes (despite still containing fuel). If the insulation is removed, the bottle works for a little longer, and only if the flow is very low the non-insulated bottle can operate for hours until complete exhaustion of its loading.

a) Evaluate, through the Corresponding States Principle, the density of the fuel when it is loaded into the bottle.

b) What is the mass of the substance before starting its consumption?

c) Why the cylinder does not consume all its load when it is insulated by glass wool?

d) Suppose that the emptying of the non-insulated bottle takes place in such a way that the enthalpy departure from the ideal gas remains constant. Quantitatively indicate the conditions inside the cylinder at the moment the substance flow stops. Would they be the same if what remained constant was the entropy departure?

Question a. Given that z_c=0.27, Figure IV.1 of this book's Appendix IV is used to calculate the function $z(T_r,P_r)$ for

$$\hat{\rho} = \frac{P\mathfrak{M}}{zRT}$$

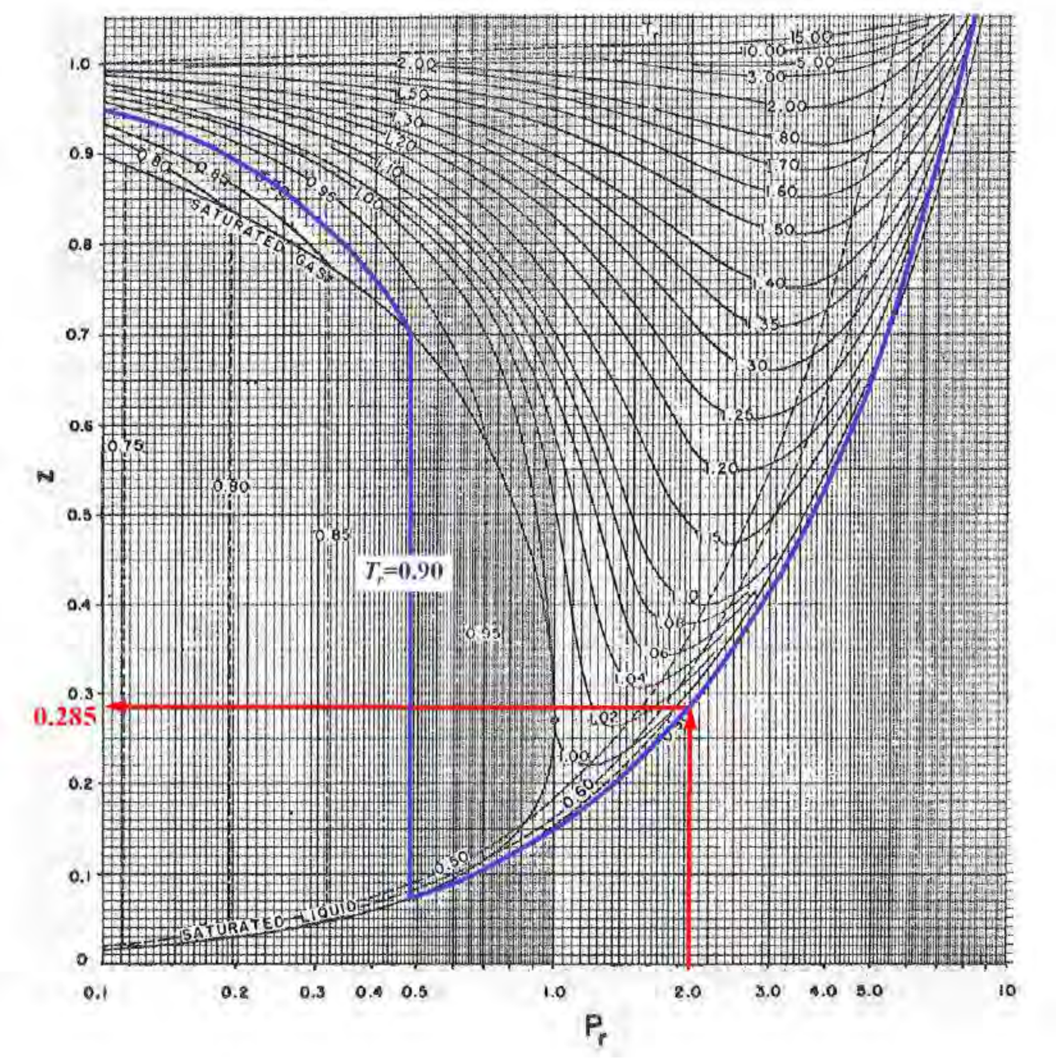
By employing the critical properties

$$T_{r1} = \frac{T_1}{T_c} = \frac{293\ \mathrm{K}}{325\ \mathrm{K}} = 0.9015\ \approx 0.90$$

$$P_{r1} = \frac{P_1}{P_c} = \frac{20\ \mathrm{atm}}{10\ \mathrm{atm}} = 2.0$$

and locating the point on the generalized chart, it is seen that it is a compressed liquid, whose compressibility factor is z=0.285. Thus

$$\hat{\rho}_1 = \frac{P_1\mathfrak{M}}{z_1RT_1} = \frac{(20\ \mathrm{atm})\left(72\ \frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)}{(0.285)\left(0.082\frac{\mathrm{atm}\cdot\mathrm{L}}{\mathrm{K}\cdot\mathrm{mol\text{-}g}}\right)(293\ \mathrm{K})} = 210.3\ \frac{\mathrm{g}}{\mathrm{L}}$$



Question b. The fuel mass before its consumption will be

$$M_1 = \hat{\rho}_1 V_{bottle}$$

where the bottle volume is that of a cylinder with 30 cm in diameter and 42.5 cm high

$$V_{bottle} = \frac{\pi}{4} d^2 h = \frac{\pi}{4} (30 \text{ cm})^2 (42.5 \text{ cm}) = 30041 \text{ cm}^3$$

$$30041 \text{ cm}^3 \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 30.041 \text{ L}$$

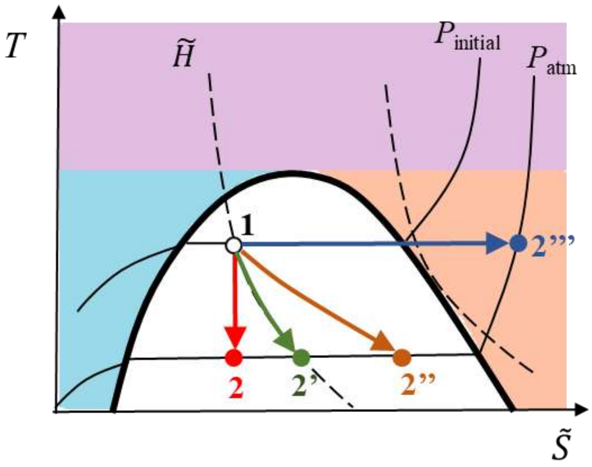
so

$$M_1 = \left(210.3 \ \frac{\text{g}}{\text{L}}\right) (30.041 \text{ L}) = 6317.62 \text{ g} = 6.318 \text{ kg}$$

Question c. The bottle content is not exhausted when insulated by glass wool because it generates an adiabatic (isentropic) emptying. The latent heat required to vaporize the liquid will not be taken from the environment, but from the sensible heat of the fuel itself, causing a fast decrease of temperature (and pressure, because the phase rule). As can be seen in the following figure (red line) the end point (2) remains in the biphasic zone, indicating that there still is liquid fuel in the bottle.

If the glass wool is removed, there will be heat exchange with the medium and the emptying will tend to be isenthalpic (green line) or polytropic (orange line), slower than the adiabatic one. The end points (2’ and 2”) remain in the biphasic zone, but they are more at the right than in the adiabatic process, showing more liquid fuel consumption.

Finally, when the flow is very small, the energy input from the environment will have the sufficient speed to provide the latent heat requirements for internal vaporization and the emptying will be isothermal (blue line). The end point (2’”) is located in the superheated vapor zone, indicating a full consumption of the liquid fuel.



Question d. The emptying concludes when a pressure of 1 atm (ambient pressure) is reached, so

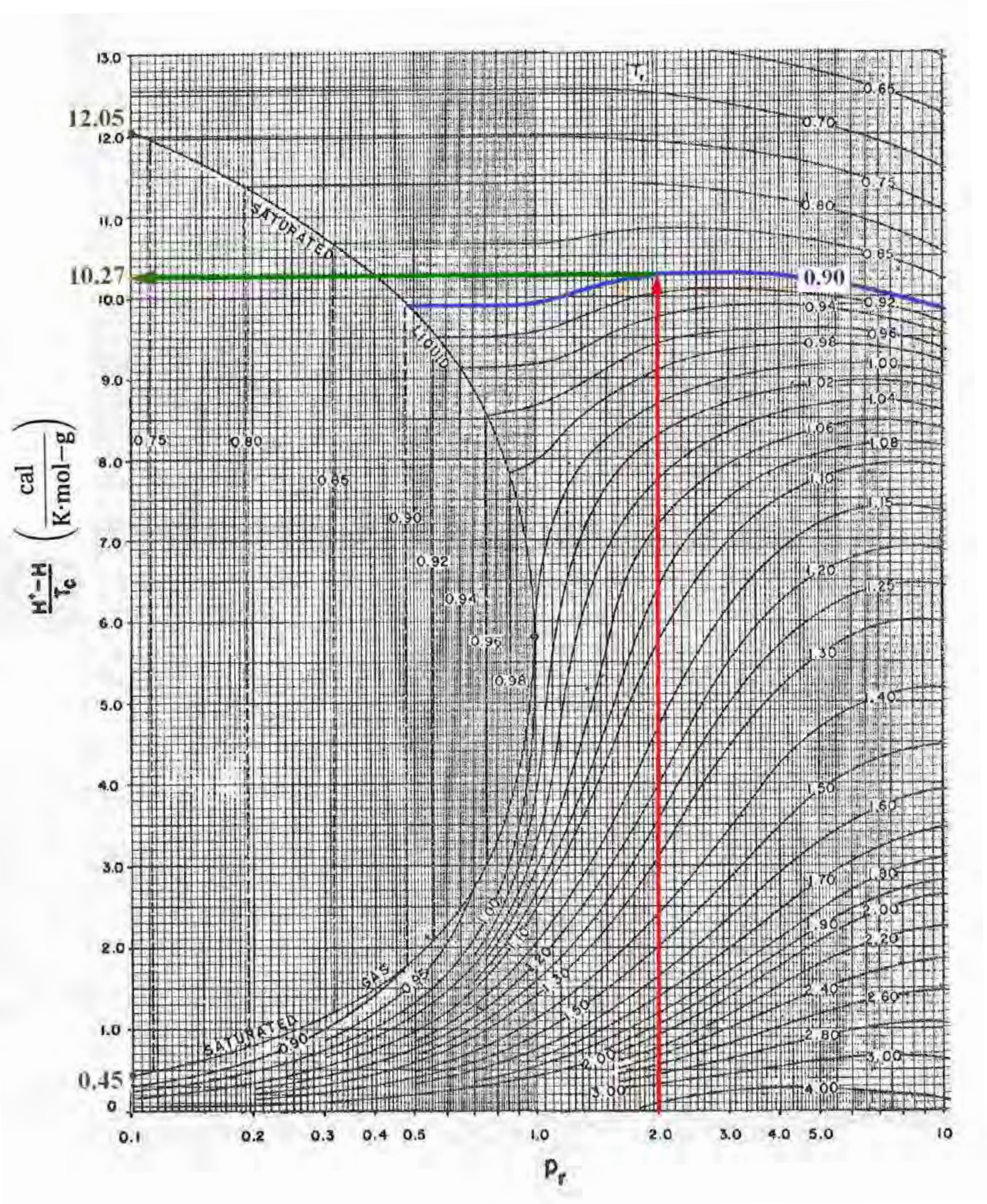
$$P_{r2} = \frac{P_2}{P_c} = \frac{1\ \text{atm}}{10\ \text{atm}} = 0.1$$

If enthalpy departure from the ideal gas does not vary from point 1 to point 2, then the process can be represented in Figure IV.4 of appendix IV by the green line, and

$$\left(\frac{\tilde{H}_1^* - \tilde{H}_1}{T_c}\right) = \left(\frac{\tilde{H}_2^* - \tilde{H}_2}{T_c}\right)_{tot} = 10.27\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$\left(\frac{\widetilde{H}_2^* - \widetilde{H}_2}{T_c}\right)_l^{sat} = 12.05\ \frac{\text{cal}}{\text{K}\cdot\ \text{mol-g}}$$

$$\left(\frac{\widetilde{H}_2^* - \widetilde{H}_2}{T_c}\right)_v^{sat} = 0.45\ \frac{\text{cal}}{\text{K}\cdot\ \text{mol-g}}$$



and the conditions inside the cylinder will be obtained from the enthalpy balance at point 2

$$n_{tot}\widetilde{H}_{tot} = n_l\widetilde{H}_l^{sat} + n_v\widetilde{H}_v^{sat}$$

Since the temperature is constant, $\widetilde{H}_2^*$ will also be constant, and it can be deducted from both sides. Taking into account that, according to the mole balance

$$n_{tot} = n_l + n_v$$

it is obtained

$$n_{tot}\widetilde{H}_{tot} - n_{tot}\widetilde{H}_2^* = n_l\widetilde{H}_l^{sat} + n_v\widetilde{H}_v^{sat} - n_{tot}\widetilde{H}_2^* = n_l\widetilde{H}_l^{sat} + n_v\widetilde{H}_v^{sat} - (n_l + n_v)\widetilde{H}_2^*$$

$$n_{tot}\left(\widetilde{H}_{tot} - \widetilde{H}_2^*\right) = n_l\left(\widetilde{H}_l^{sat} - \widetilde{H}_2^*\right) + n_v\left(\widetilde{H}_v^{sat} - \widetilde{H}_2^*\right)$$

Thus, multiplying by -1 both terms, and dividing by T_c

$$n_{tot}\left(\frac{\widetilde{H}_2^* - \widetilde{H}_{tot}}{T_c}\right) = n_l\left(\frac{\widetilde{H}_2^* - \widetilde{H}_l^{sat}}{T_c}\right) + n_v\left(\frac{\widetilde{H}_2^* - \widetilde{H}_v^{sat}}{T_c}\right)$$

adapting the notation

$$n_{tot}\left(\frac{\widetilde{H}_2^* - \widetilde{H}_2}{T_c}\right)_{tot} = n_l\left(\frac{\widetilde{H}_2^* - \widetilde{H}_2}{T_c}\right)_l^{sat} + n_v\left(\frac{\widetilde{H}_2^* - \widetilde{H}_2}{T_c}\right)_v^{sat}$$

and combining the expression again with the mole balance

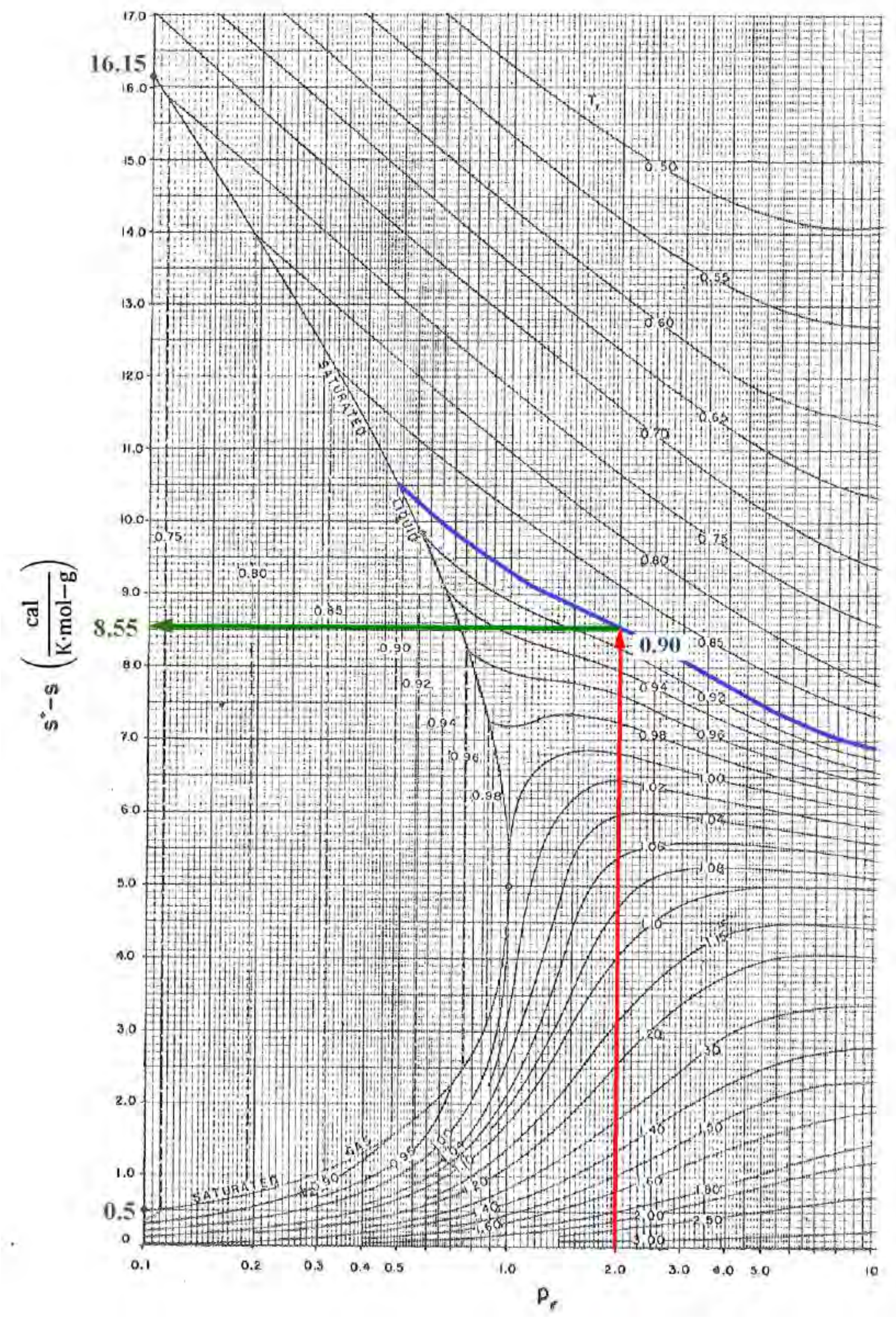
$$\frac{n_v}{n_{tot}} = \frac{\left(\frac{\widetilde{H}_2^* - \widetilde{H}_2}{T_c}\right)_{tot} - \left(\frac{\widetilde{H}_2^* - \widetilde{H}_2}{T_c}\right)_l^{sat}}{\left(\frac{\widetilde{H}_2^* - \widetilde{H}_2}{T_c}\right)_v^{sat} - \left(\frac{\widetilde{H}_2^* - \widetilde{H}_2}{T_c}\right)_l^{sat}} = \frac{10.27 - 12.05}{0.45 - 12.05} = 0.15$$

After emptying under these conditions, there will be 15% vapor and 85% liquid. If the entropy departure does not change, figure IV.7 of appendix IV has to be employed

$$\left(\tilde{S}_1^* - \tilde{S}_1\right) = \left(\tilde{S}_2^* - \tilde{S}_2\right)_{tot} = 8.55\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$\left(\tilde{S}_2^* - \tilde{S}_2\right)_l^{sat} = 16.15\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$\left(\tilde{S}_2^* - \tilde{S}_2\right)_v^{sat} = 0.5\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$



By applying the entropy balance

$$n_{tot}\tilde{S}_{tot} = n_l\tilde{S}_l^{sat} + n_v\tilde{S}_v^{sat}$$

and operating in a similar way to that of the enthalpy departure

$$\frac{n_v}{n_{tot}} = \frac{\left(\tilde{S}_2^* - \tilde{S}_2\right)_{tot} - \left(\tilde{S}_2^* - \tilde{S}_2\right)_l^{sat}}{\left(\tilde{S}_2^* - \tilde{S}_2\right)_v^{sat} - \left(\tilde{S}_2^* - \tilde{S}_2\right)_l^{sat}} = \frac{8.55 - 16.15}{0.5 - 16.15} = 0.486$$

48.6% vapor and 51.4% of liquid are now obtained. Results are not the same, and it was expected because, by combining equations of reference problems 0.2 and 0.8

$$\left(\tilde{G}^* - \tilde{G}\right) = \left(\widetilde{H}^* - \widetilde{H}\right) - T\left(\tilde{S}^* - \tilde{S}\right)$$

$$\left(\tilde{S}^* - \tilde{S}\right) = \left(\frac{\widetilde{H}^* - \widetilde{H}}{T}\right) - \left(\frac{\tilde{G}^* - \tilde{G}}{T}\right) = \frac{T_c}{T_c}\left(\frac{\widetilde{H}^* - \widetilde{H}}{T}\right) - R\left(\frac{\tilde{G}^* - \tilde{G}}{RT}\right)$$

it is found

$$\left(\tilde{S}^* - \tilde{S}\right) = \frac{1}{T_r}\left(\frac{\widetilde{H}^* - \widetilde{H}}{T_c}\right) + R\ln\left(\frac{f}{P}\right)$$

If $\Delta\left(\tilde{S}^* - \tilde{S}\right) = 0$, then

$$\Delta\left[\frac{1}{T_r}\left(\frac{\widetilde{H}^* - \widetilde{H}}{T_c}\right) + R\ln\left(\frac{f}{P}\right)\right] = 0$$

and it will be due to

$$\Delta\left[\frac{1}{T_r}\left(\frac{\widetilde{H}^* - \widetilde{H}}{T_c}\right)\right] = 0 \qquad \text{and} \qquad \Delta\left[R\ln\left(\frac{f}{P}\right)\right] = 0$$

in the desired case, or to

$$\Delta\left[\frac{1}{T_r}\left(\frac{\widetilde{H}^* - \widetilde{H}}{T_c}\right)\right] = -\Delta\left[R\ln\left(\frac{f}{P}\right)\right]$$

which is what presumably occurs under the conditions established here. Since nothing assures that $(f/P)_1 = (f/P)_2$ in any process, nothing assures that $\Delta\left(\widetilde{H}^* - H\right) = 0$ if the entropy departure remains unchanged in this process.

4.19. Chemical products are transported in spherical tanks (inner diameter of 4 m) charged at 10ºC and designed to bear a maximum pressure of 100 bar. An accident can increase the temperature to 100ºC. Calculate the maximum load at this high temperature and at 10ºC as well.

- **a) If CO_2 is transported, use specific *PH* and *TS* diagrams for it.**
- **b) If O_2, use a specific *PH* diagram for it.**
- **c) If both substances are transported, use the generalized charts of the Corresponding States Principle without considering the corrections for $z_c \neq 0.27$ in any case.**

Question a. The máximum load will be

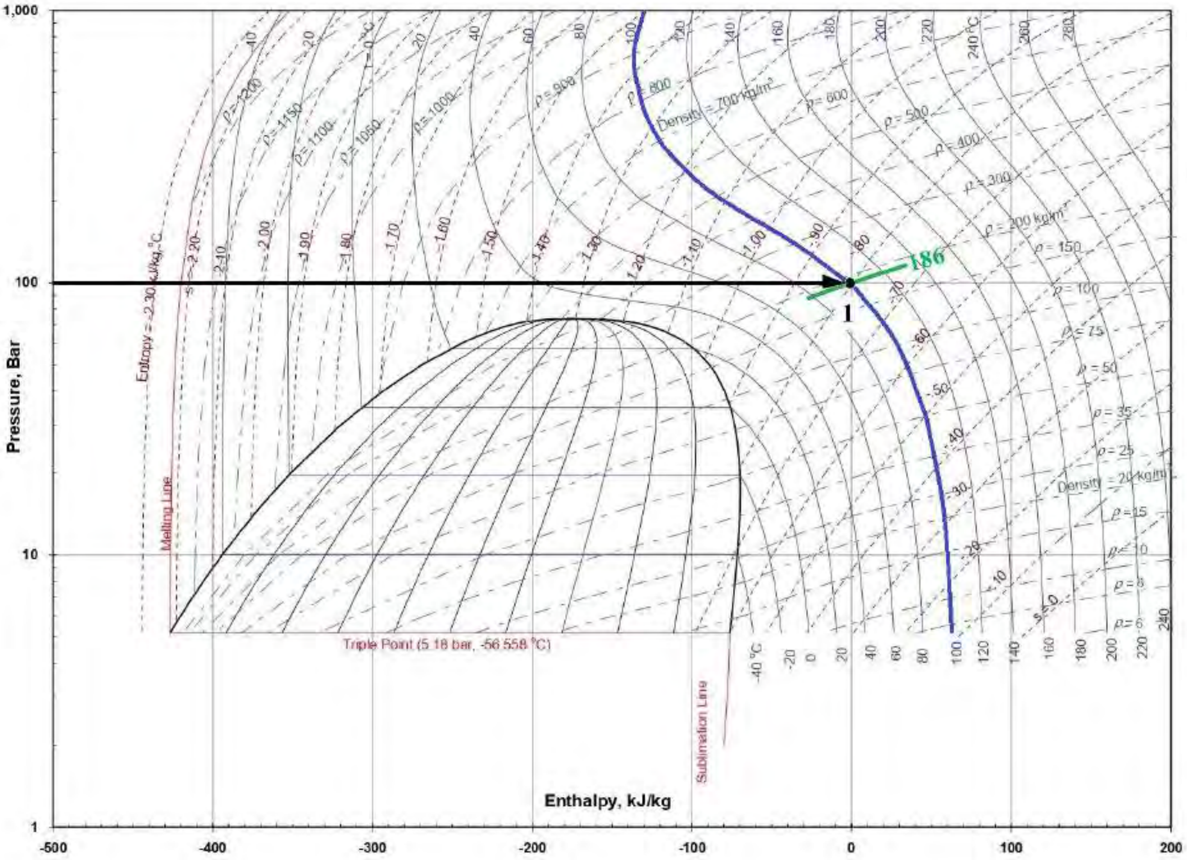
$$M_{tot} = \hat{\rho}_1 V_{tank}$$

where the volume of the spherical tank is estimated by the inner diameter given in the statement of the problem

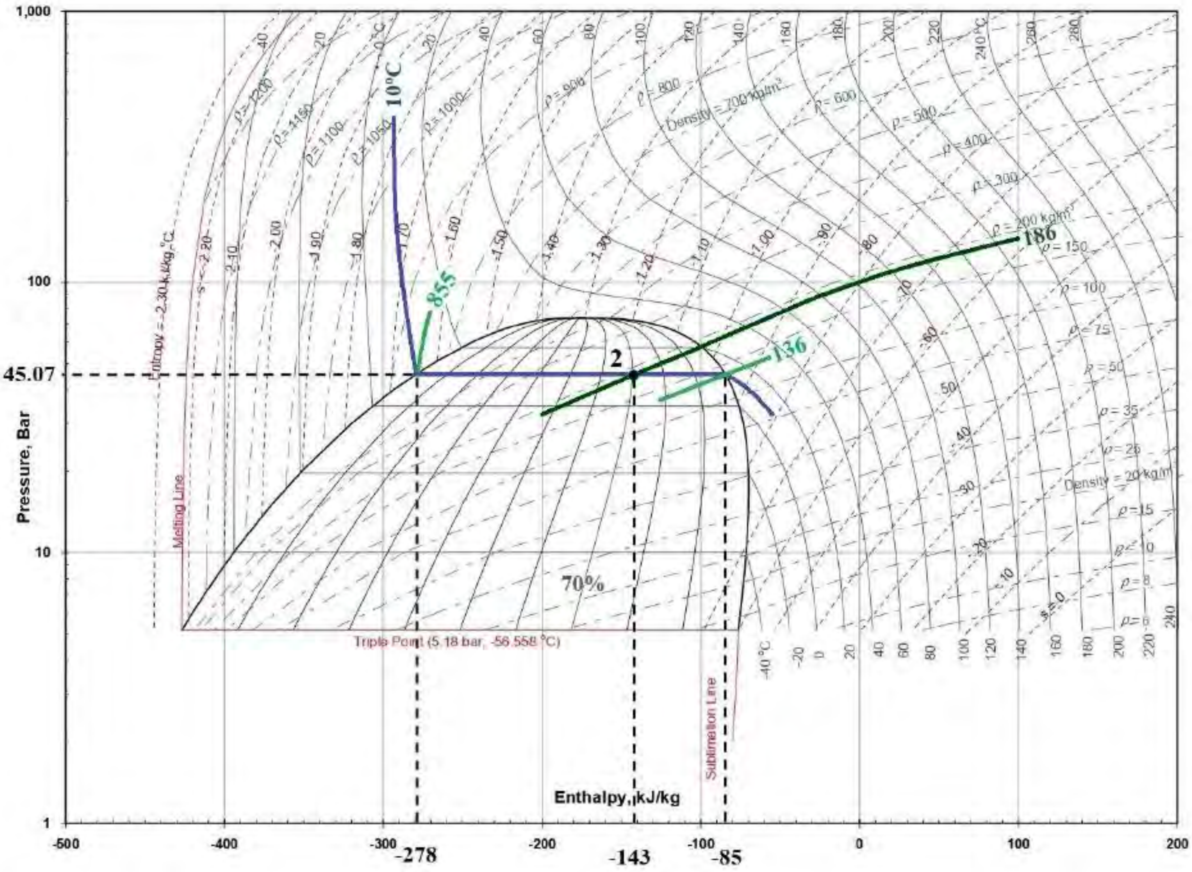
$$V_{tank} = \frac{\pi}{6} d_{in}^3 = \frac{\pi}{6} (4 \text{ m})^3 = 33.51 \text{ m}^3$$

and the density by means of figure V.2 of appendix V (specific *PH* diagram for CO_2): the intersection of the isotherm T_1=100ºC and the isobar P_1=100 bar gives point 1, whose density is $\hat{\rho}_1 = 186 \text{ kg/m}^3$. Hence

$$M_{tot} = \left(186 \ \frac{\text{kg}}{\text{m}^3}\right) (33.51 \text{ m}^3) = 6232.86 \text{ kg}$$



The state of this mass at the other temperature is determined graphically by the intersection of the isochore $\hat{\rho}_1 = \hat{\rho}_2 = 186$ kg/m^3 (since the volume of the tank does not change) with the isotherm T_2= 10ºC, being placed in the biphasic zone, at a pressure P_2= 45.07 bar, a saturated liquid density of 855 kg/m^3 and a saturated vapor density of 186 kg/m^3.



The amount of vapor can be estimated by combining the mass balance ($M_{tot} = M_{l_2} + M_{v_2}$) with the volume one ($M_{tot}/\hat{\rho}_2 = M_{l_2}/\hat{\rho}_{l_2}^{sat} + M_{v_2}/\hat{\rho}_{v_2}^{sat}$) in the form

$$M_{v_2} = M_{tot}\frac{\left(\frac{1}{\hat{\rho}_2} - \frac{1}{\hat{\rho}_{l_2}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_2}^{sat}} - \frac{1}{\hat{\rho}_{l_2}^{sat}}\right)} = (6232.86\ \text{kg})\frac{\left(\frac{1}{186} - \frac{1}{855}\right)}{\left(\frac{1}{136} - \frac{1}{855}\right)} = 4240.44\ \text{kg}$$

$$M_{l_2} = M_{tot} - M_{v_2} = 6232.86 - 4240.44 = 1992.42\ \text{kg}$$

$$V_{l_2} = \frac{M_{l_2}}{\hat{\rho}_{l_2}^{sat}} = \frac{1992.42\ \text{kg}}{855\ \frac{\text{kg}}{\text{m}^3}} = 2.33\ \text{m}^3$$

$$V_{v_2} = \frac{M_{v_2}}{\hat{\rho}_{v_2}^{sat}} = \frac{4240.44 \text{ kg}}{136 \ \frac{\text{kg}}{\text{m}^3}} = 31.18 \text{ m}^3$$

and can be checked either by a title line (which in this case is of 70%, giving $M_v = 0.7M_{tot}= 0.7\times6232.86$ kg = 4363.002 kg) or by combining the mass balance ($M_{tot} = M_{l_2} + M_{v_2}$) with the enthalpy one ($M_{tot}\hat{H}_2 = M_l\hat{H}_{l_2}^{sat} + M_v\hat{H}_{v_2}^{sat}$) after reading the enthalpies of the saturated phases in figure V.2

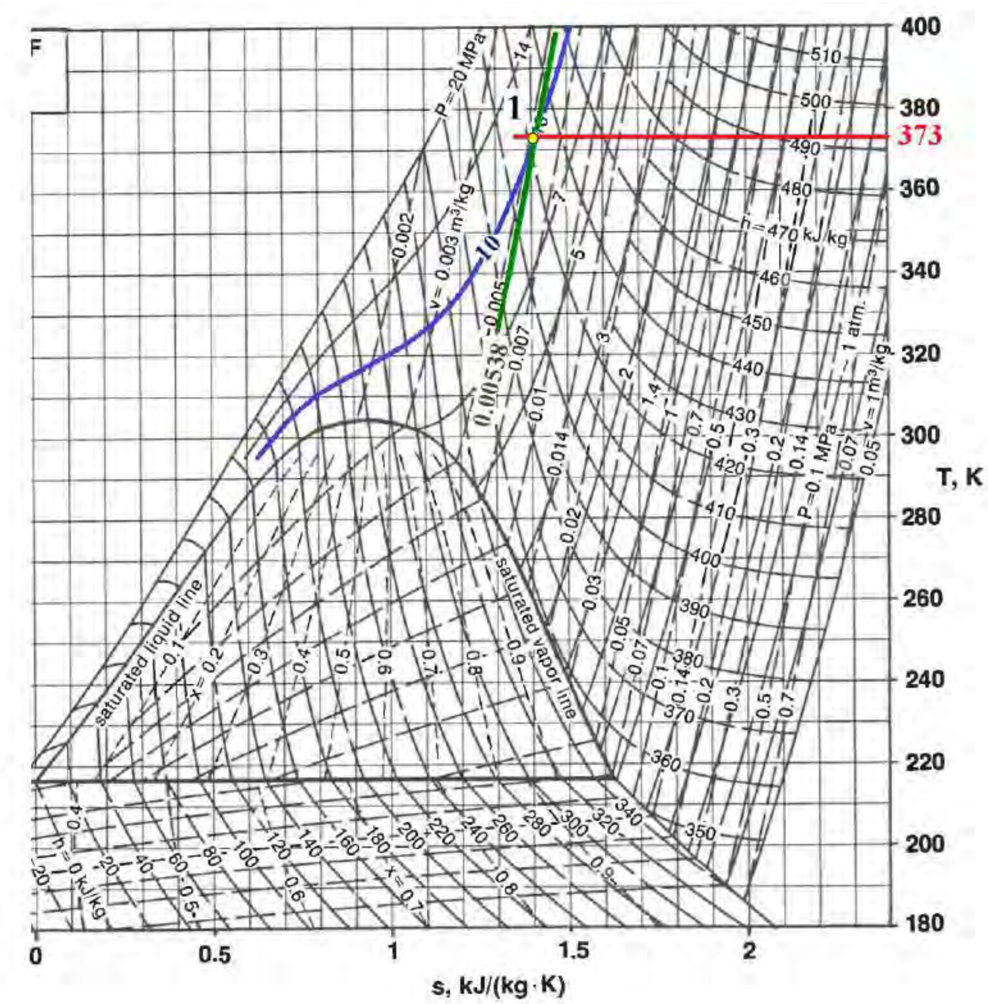
$$M_{v_2} = M_{tot}\frac{\left(\hat{H}_2 - \hat{H}_{l_2}^{sat}\right)}{\left(\hat{H}_{v_2}^{sat} - \hat{H}_{l_2}^{sat}\right)} = (6232.86 \text{ kg})\frac{(-143+278)}{(-85+279)} = 4359.77 \text{ kg}$$

Regarding the specific *TS* diagram for CO₂ (figure V.3 of appendix V), the crossing of the isotherm

$$T_1(\text{K}) = 100°\text{C} + 273 = 373 \text{ K}$$

with the isobar

$$100 \text{ bar}\times\frac{1 \text{ MPa}}{10 \text{ bar}}=10 \text{ MPa}$$



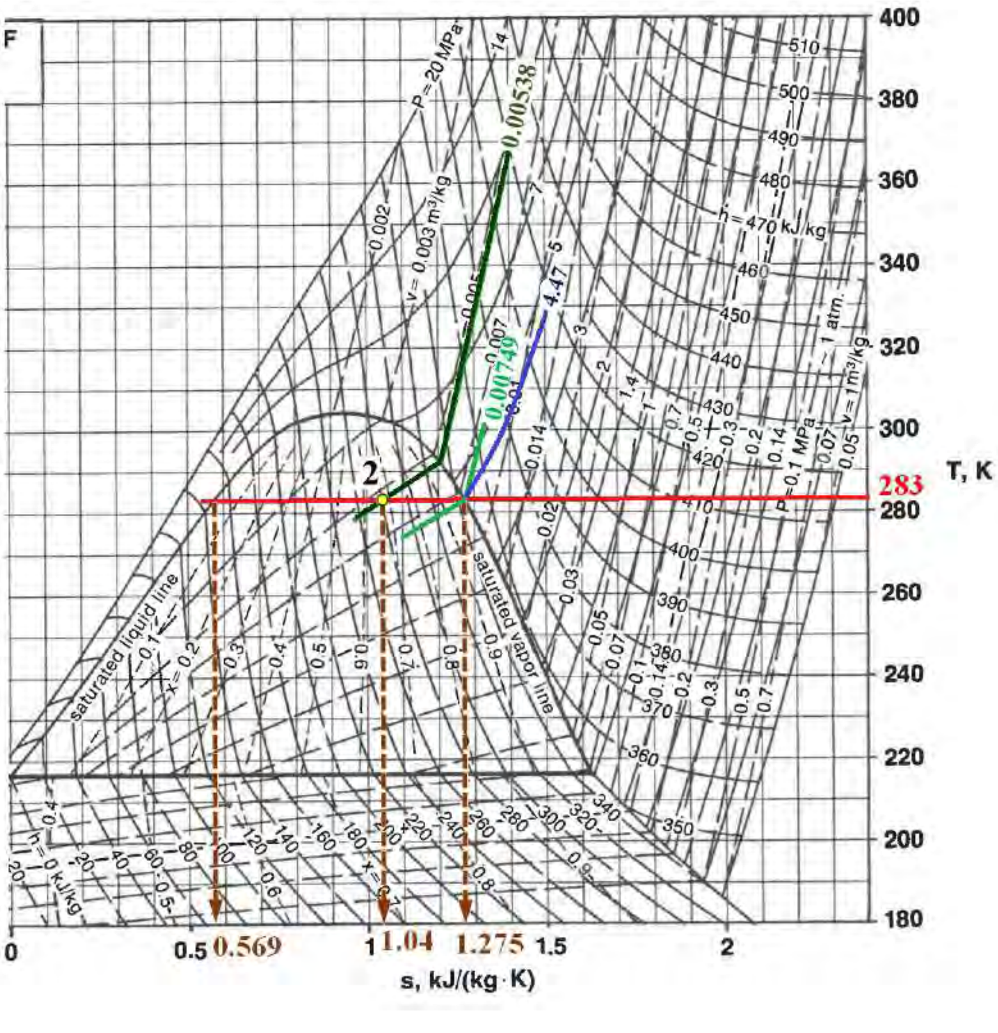
is located approximately on the isochore $\hat{V}_1 = 0.00538\ \mathrm{m^3/kg}$; thus

$$M_{tot} = \frac{V_{tank}}{\hat{V}_1} = \frac{33.51\ \mathrm{m}^3}{(0.00538\ \mathrm{m}^3/\mathrm{kg})} = 6228.62\ \mathrm{kg}$$

By graphically following this isochore, it is seen that it coincides (crosses) with the isotherm

$$T_2(\mathrm{K}) = 10℃ + 273 = 283\ \mathrm{K}$$

in the biphasic zone ($P_2 \approx 4.47$ MPa).



Unfortunately, as usually happens in this type of graphical correlations, isochores are only drawn for $\hat{V} \geq 0.002\ \mathrm{m^3/kg}$, so the mass and volume balances cannot be combined. However, the mass balance can be combined with that of entropy, obtaining a formulation similar to that found for enthalpies

$$M_{v_2} = M_{tot}\frac{\left(\hat{S}_2 - \hat{S}_{l_2}^{sat}\right)}{\left(\hat{S}_{v_2}^{sat} - \hat{S}_{l_2}^{sat}\right)} = (6228.62\ \mathrm{kg})\frac{(1.04 - 0.569)}{(1.275 - 0.569)} = 4155.35\ \mathrm{kg}$$

$$M_{l_2} = M_{tot} - M_{v_2} = 6228.62 - 4155.35 = 2073.27 \text{ kg}$$

being the volume occupied by the vapor

$$V_{v_2} = \hat{V}_{v_2}^{sat}\, M_{v_2} = \left(0.00749\ \frac{\text{m}^3}{\text{kg}}\right)(4155.35 \text{ kg}) = 31.12 \text{ m}^3$$

and that occupied by the liquid

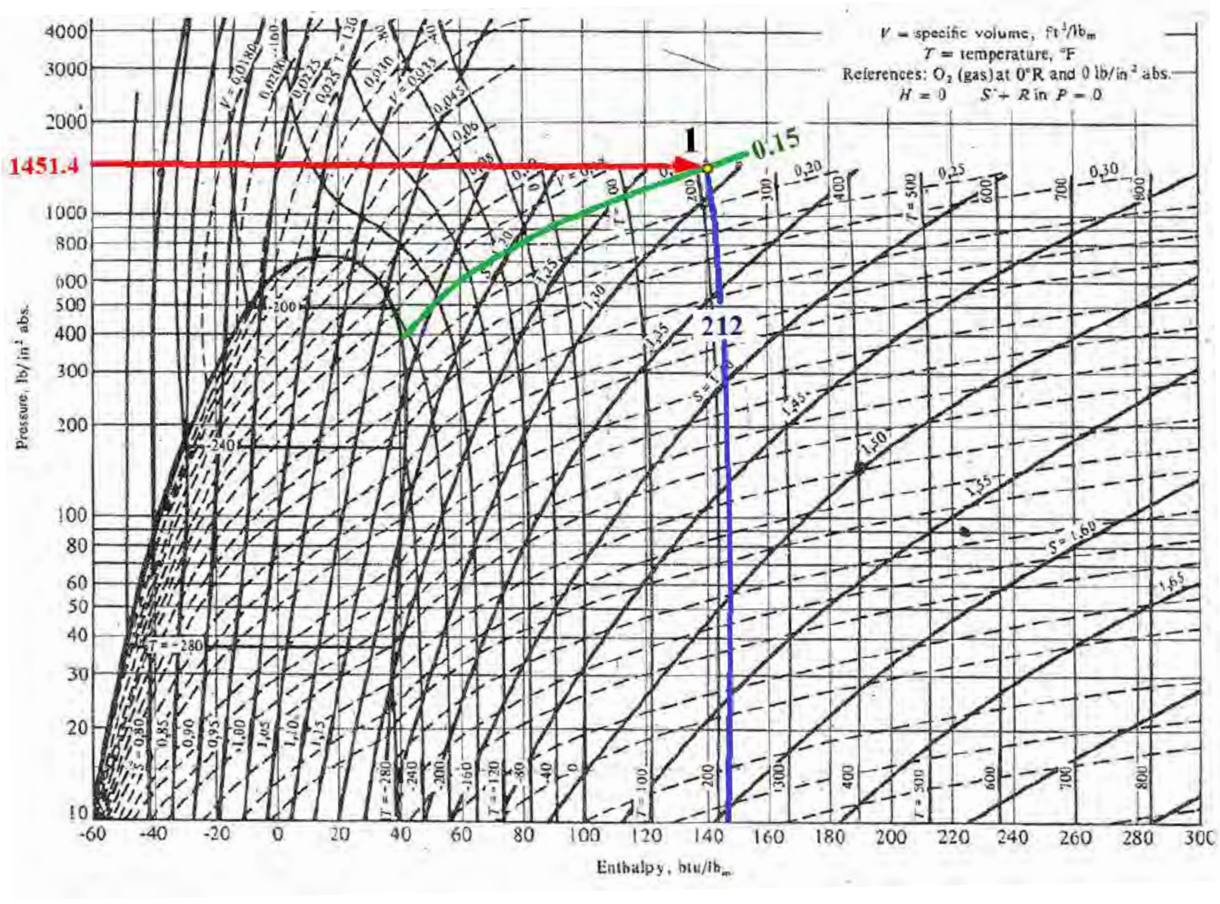
$$V_{l_2} = V_{tank} - V_{v_2} = 33.51 \text{ m}^3 - 31.12 \text{ m}^3 = 2.39 \text{ m}^3$$

Question b. In appendix V, figure V.1 shows the dependence of the enthalpy of oxygen with pressure at various temperatures. In order to use it, conversion of units has to be performed through the factors of appendix I

$$P_1 = 100 \text{ bar} \times \frac{2090 \text{ lb}_\text{f}/\text{ft}^2}{1 \text{ bar}} \times \left(\frac{1 \text{ ft}}{12 \text{ in}}\right)^2 = 1451.4\ \frac{\text{lb}_\text{f}}{\text{in}^2}$$

$$T_1(°\text{F}) = 1.8(100°\text{C}) + 32 = 212°\text{F}$$

$$T_2(°\text{F}) = 1.8(10°\text{C}) + 32 = 50°\text{F}$$



By drawing both isolines, it is observed that the crossing between P_1 and T_1 took place on the 0.15 ft^3/lb isochore

$$\hat{V}_1 = 0.15\frac{\text{ft}^3}{\text{lb}} \times \frac{28.31\text{ L}}{1\text{ ft}^3} \times \frac{1\text{ lb}}{0.454\text{ kg}} \times \frac{1\text{ m}^3}{1000\text{ L}} = 0.0093535\ \frac{\text{m}^3}{\text{kg}}$$

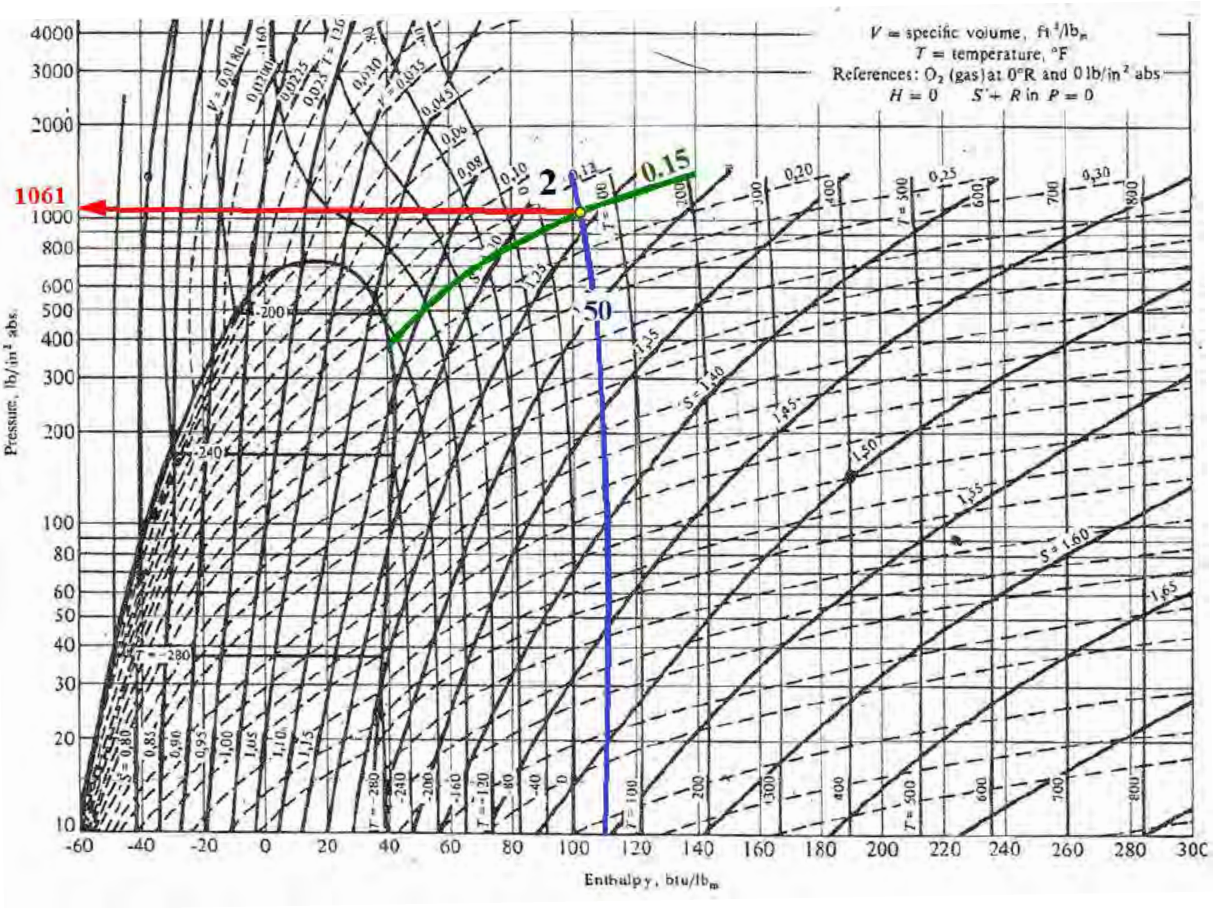
so, the load will be

$$M_{tot} = \frac{V_{tank}}{\hat{V}_1} = \frac{33.51\text{ m}^3}{(0.0093535\text{ m}^3/\text{kg})} = 3582.62\text{ kg}$$

and by prolonging this isochore and looking for the point where it intersects with the T_2 isotherm, a pressure of 1061 lb$_f$/in^2 is found, in the gas region of the diagram.

$$P_2 = 1061\ \frac{\text{lb}_\text{f}}{\text{in}^2} \times \left(\frac{12\text{ in}}{1\text{ ft}}\right)^2 \frac{0.000479\text{ bar}}{1\text{ lb}_\text{f}/\text{ft}^2} = 73.18\text{ bar}$$

At both temperatures, oxygen is in the state of a supercritical fluid.



Question c. To apply the Corresponding States Principle, figure IV.1 of appendix IV will be employed, where the compressibility factor z is a function of the reduced temperature and the reduced pressure. Taking from appendix II the critical properties of carbon dioxide (T_c=304.2 K and P_c=72.9 atm) and its molar mass (44.01 g/mol-g), and converting the units with the factors of appendix I

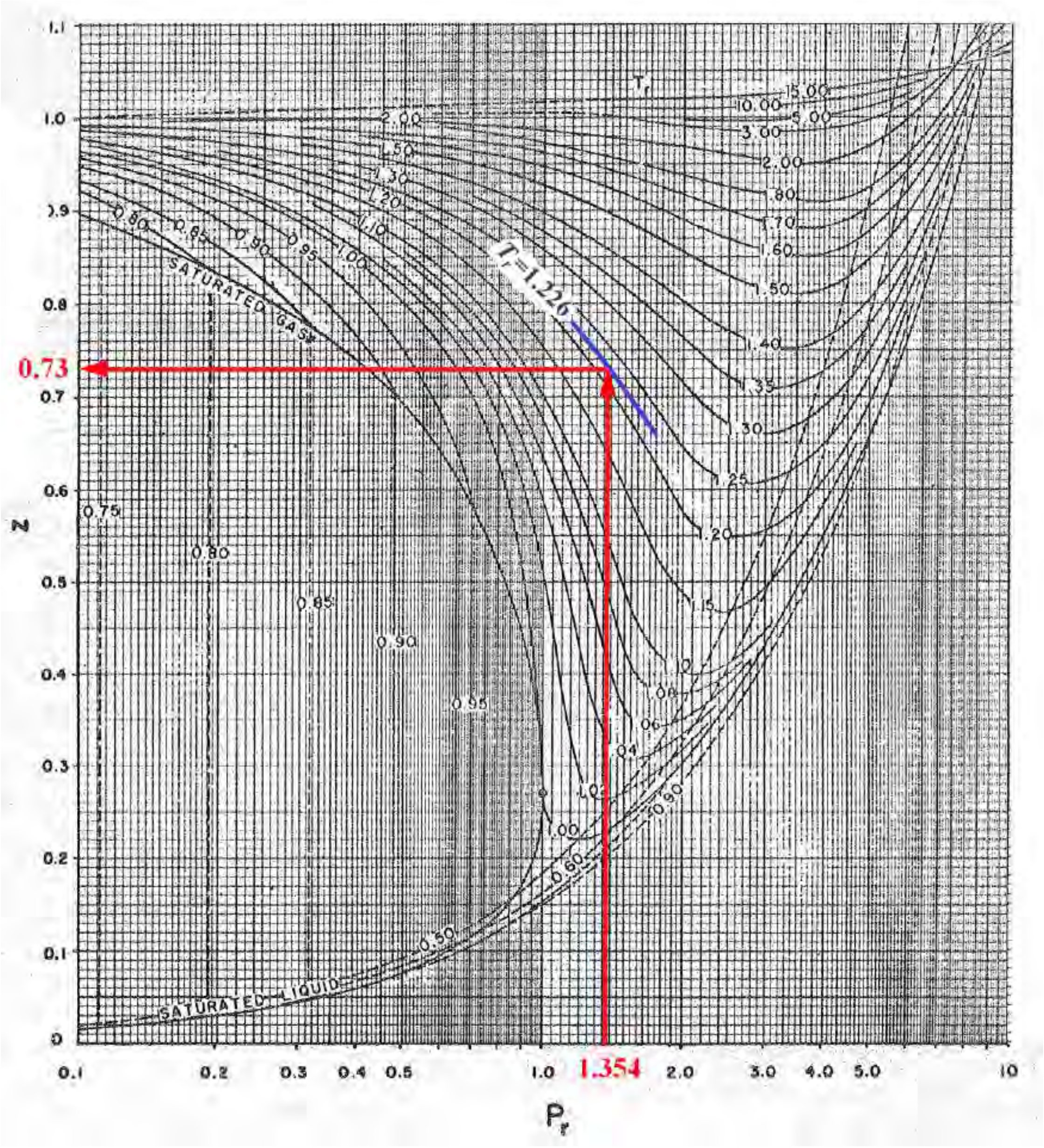
$$T_1(\mathrm{K}) = 100\,^\circ\mathrm{C} + 273 = 373\ \mathrm{K}$$

$$P_1 = 100\ \mathrm{bar} \times \frac{0.987\ \mathrm{atm}}{1\ \mathrm{bar}} = 98.7\ \mathrm{atm}$$

it is obtained that

$$T_{r1} = \frac{373\ \mathrm{K}}{304.2\ \mathrm{K}} = 1.226 \quad ; \quad P_{r1} = \frac{98.7\ \mathrm{atm}}{72.9\ \mathrm{atm}} = 1.354$$

conditions which placed in the generalized chart, give a z_1=0.73



$$\hat{\rho}_1 = \frac{P_1\mathfrak{M}}{z_1RT_1} = \frac{(98.7\ \text{atm})\left(44.01\ \frac{\text{g}}{\text{mol-g}}\right)}{(0.73)\left(0.082\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(373\ \text{K})} = 194.55\ \frac{\text{g}}{\text{L}} = 194.55\frac{\text{kg}}{\text{m}^3}$$

and the maximum load is

$$M_{tot} = \hat{\rho}_1 V_{tank} = \left(194.55\ \frac{\text{kg}}{\text{m}^3}\right)(33.51\ \text{m}^3) = 6519.37\ \text{kg}$$

This density will remain constant ($\hat{\rho}_1 = \hat{\rho}_2 = \hat{\rho}$), but due to the fact that there are no isochores in figure IV.1, point 2 has to be determined by graphically finding the point where the isotherm

$$T_{r2} = \frac{283\ \text{K}}{304.2\ \text{K}} = 0.93$$

intersects the line

$$z_2 = \frac{P_2}{RT_2\tilde{\rho}} = \frac{P_cP_{r2}\mathfrak{M}}{RT_2\hat{\rho}} = \frac{(72.9\ \text{atm})\left(44.01\ \frac{\text{g}}{\text{mol-g}}\right)P_{r2}}{\left(0.082\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(283\ \text{K})\left(194.55\ \frac{\text{g}}{\text{L}}\right)} = 0.71064P_{r2}$$

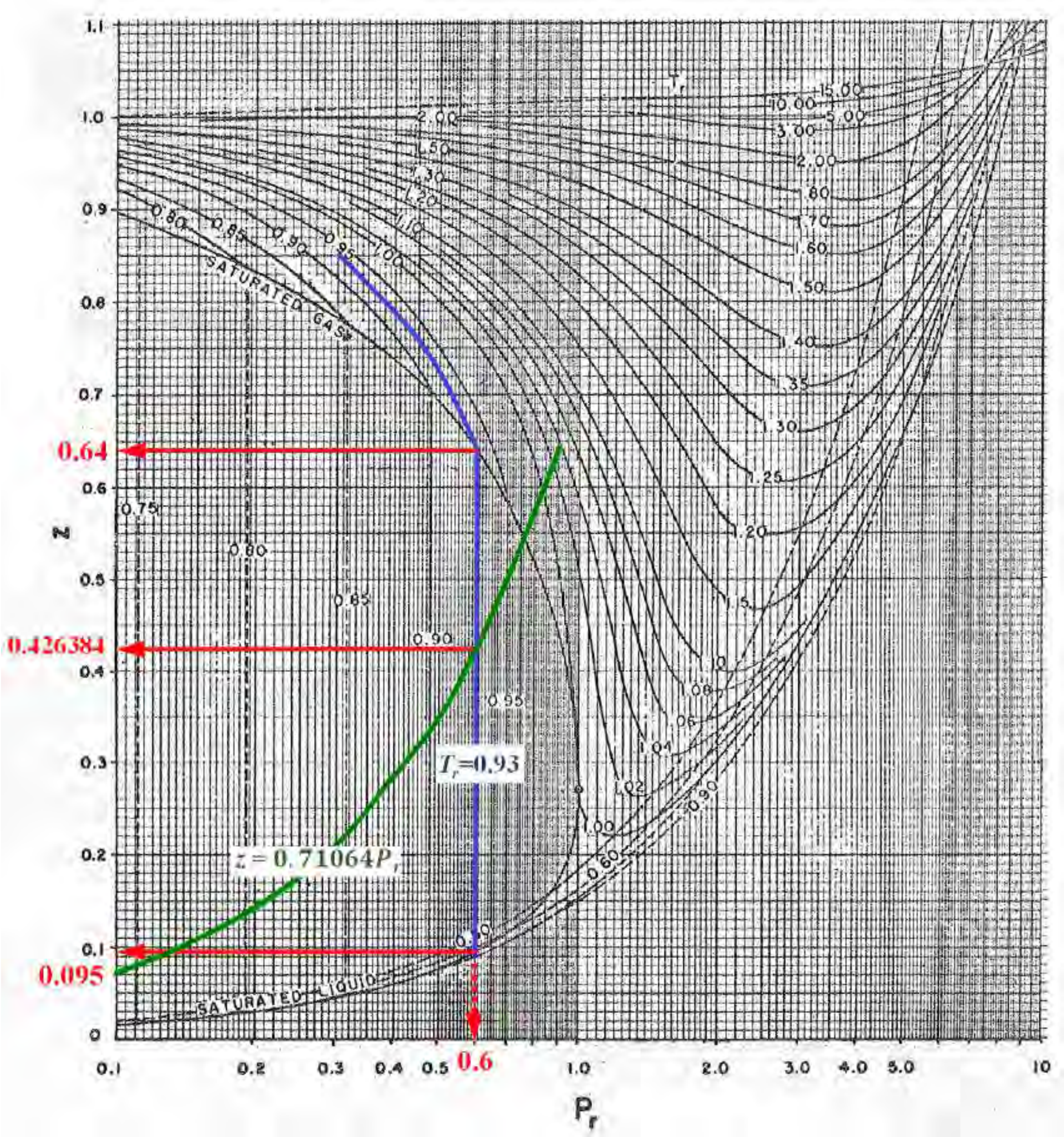
Assumed P_{r2}	Calculated z_2
0.1	0.071064
0.2	0.142128
0.3	0.213192
0.4	0.284256
0.5	0.355320
0.6	0.426384
0.7	0.497448
0.8	0.568512
0.9	0.639576
1.0	0.710640

which results to be in the biphasic zone, with P_{r2}= 0.6, $z_{l_2}^{sat} = 0.095$ and $z_{v_2}^{sat} = 0.64$; thus

$$P_2 = 0.6(72.9\ \text{atm}) = 43.74\ \text{atm}$$

$$\hat{\rho}_{l_2}^{sat} = \frac{P_2\mathfrak{M}}{z_{l_2}^{sat}RT_2} = \frac{(43.74\ \text{atm})\left(44.01\ \frac{\text{g}}{\text{mol-g}}\right)}{(0.095)\left(0.082\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(283\ \text{K})} = 873.18\ \frac{\text{g}}{\text{L}} = 873.18\ \frac{\text{kg}}{\text{m}^3}$$

$$\hat{\rho}_{v_2}^{sat} = \frac{P_2 \mathfrak{M}}{z_{v_2}^{sat} R T_2} = \frac{(43.74\ \mathrm{atm})\left(44.01\ \dfrac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)}{(0.64)\left(0.082\,\dfrac{\mathrm{atm\cdot L}}{\mathrm{K\cdot mol\text{-}g}}\right)(283\ \mathrm{K})} = 129.61\ \frac{\mathrm{g}}{\mathrm{L}} = 129.61\ \frac{\mathrm{kg}}{\mathrm{m^3}}$$



$$M_{v_2} = M_{tot}\frac{\left(\dfrac{1}{\hat{\rho}_2} - \dfrac{1}{\hat{\rho}_{l_2}^{sat}}\right)}{\left(\dfrac{1}{\hat{\rho}_{v_2}^{sat}} - \dfrac{1}{\hat{\rho}_{l_2}^{sat}}\right)} = (6519.37\ \mathrm{kg})\frac{\left(\dfrac{1}{194.55} - \dfrac{1}{873.18}\right)}{\left(\dfrac{1}{129.61} - \dfrac{1}{873.18}\right)} = 3964.13\ \mathrm{kg}$$

$$M_{l_2} = M_{tot} - M_{v_2} = 6519.37 - 3964.13 = 2555.24\ \mathrm{kg}$$

$$V_{l_2} = \frac{M_{l_2}}{\hat{\rho}_{l_2}^{sat}} = \frac{2555.24\ \mathrm{kg}}{873.18\ \dfrac{\mathrm{kg}}{\mathrm{m^3}}} = 2.93\ \mathrm{m^3}$$

$$V_{v_2} = \frac{M_{v_2}}{\hat{\rho}_{v_2}^{sat}} = \frac{3964.13\ kg}{129.61\ \dfrac{\mathrm{kg}}{\mathrm{m}^3}} = 30.58\ \mathrm{m}^3$$

With regards to oxygen, and since according to appendix II, its critical properties are T_c=154.4 K, P_c=49.7 atm and its molar mass 32 g/mol-g

$$T_{r1} = \frac{373\ \mathrm{K}}{154.4\ \mathrm{K}} = 2.416 \quad ; \quad P_{r1} = \frac{98.7\ \mathrm{atm}}{49.7\ \mathrm{atm}} = 1.986$$

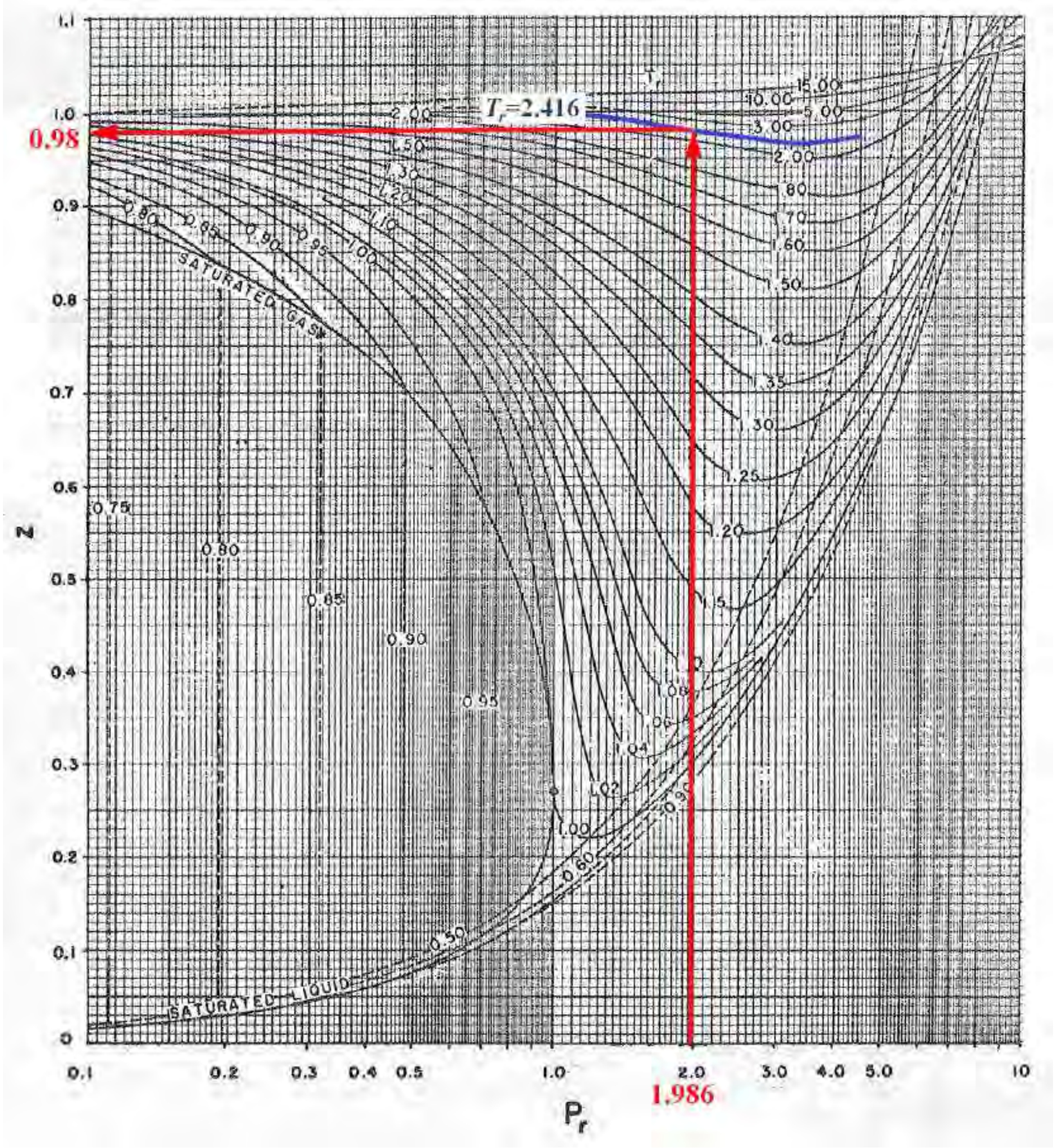


Figure IV.1 indicates a compressibility factor of 0.98; thus

$$\hat{\rho}_1 = \frac{P_1 \mathfrak{M}}{z_1 R T_1} = \frac{(98.7\ \mathrm{atm})\left(32\ \dfrac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)}{(0.98)\left(0.082\dfrac{\mathrm{atm}\cdot\mathrm{L}}{\mathrm{K}\cdot\mathrm{mol\text{-}g}}\right)(373\ \mathrm{K})} = 105.37\ \frac{\mathrm{g}}{\mathrm{L}} = 105.37\frac{\mathrm{kg}}{\mathrm{m}^3}$$

and whith this density, the mass in point 1 is

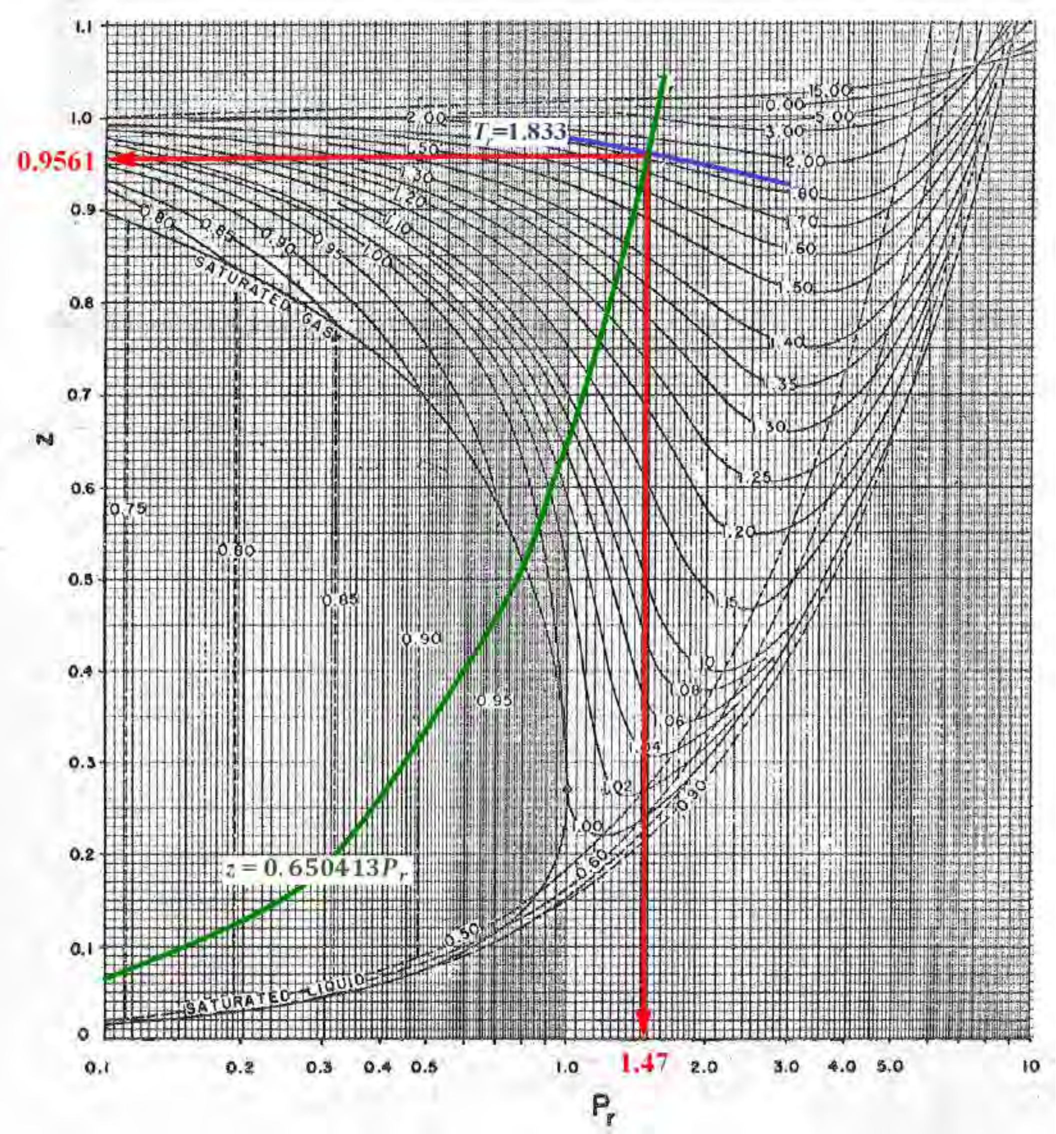
$$M_{tot} = \hat{\rho}_1 V_{tank} = \left(105.37\ \frac{\text{kg}}{\text{m}^3}\right)(33.51\ \text{m}^3) = 3530.95\ \text{kg}$$

On the other hand, point 2 will be the intersection of the isotherm

$$T_{r2} = \frac{283\ \text{K}}{154.4\ \text{K}} = 1.833$$

with the line

$$z_2 = \frac{P_2}{RT_2\tilde{\rho}} = \frac{P_c P_{r2}\mathfrak{M}}{RT_2\hat{\rho}} = \frac{(49.7\ \text{atm})\left(32\ \frac{\text{g}}{\text{mol-g}}\right)P_{r2}}{\left(0.082\ \frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(283\ \text{K})\left(105.37\ \frac{\text{g}}{\text{L}}\right)} = 0.650413P_{r2}$$



Assumed P_{r2}	Calculated z_2
0.1	0.0650413
0.2	0.1300826
0.3	0.1951239
0.4	0.2601652
0.5	0.3252065
0.7	0.4552891
1.0	0.6504130
1.5	0.9756195
1.6	1.0406608

which in this case belongs to the single-phase zone of gases or supercritical fluids, with P_{r2}=1.47 and z_2=0.9561

$$P_2 = 1.47(49.7\text{ atm}) = 73.059\text{ atm}$$

4.20. Water chlorination is generally carried out by injecting a saturated aqueous solution of molecular chlorine into the stream to be treated. This solution is obtained after evaporating and dissolving liquid chlorine from the supply tanks, which are generally connected in battery.

One of these tanks (volume of 800 L) contains 400 kg of Cl_2. By using the following equilibrium data from the Perry's handbook (1997):

T (ºC)	P (bar)	$\hat{V}_l^{sat}$ (m³/kg)	$\hat{V}_v^{sat}$ (m³/kg)	$\hat{H}_l^{sat}$ (kJ/kg)	$\hat{H}_v^{sat}$ (kJ/kg)	$\hat{S}_l^{sat}$ (kJ/kg·K)	$\hat{S}_v^{sat}$ (kJ/kg·K)
-50	0.475	0.000623	0.5448	221.5	518.2	1.7650	3.0946
-40	0.773	0.000634	0.3481	231.0	522.2	1.8074	3.0562
-30	1.203	0.000645	0.2314	240.6	526.1	1.8480	3.0223
-20	1.802	0.000656	0.1593	250.3	529.9	1.8869	2.9921
-10	2.608	0.000668	0.1134	260.0	533.9	1.9243	2.9649
0	3.664	0.000681	0.0829	269.7	537.4	1.9604	2.9402
10	5.014	0.000695	0.0619	279.4	540.5	1.9953	2.9177
20	6.702	0.00071	0.0471	289.2	543.3	2.0291	2.8924
30	8.774	0.000726	0.0364	299.0	545.7	2.0622	2.8777
40	11.27	0.000744	0.0286	308.8	548.0	2.0946	2.8593
50	14.25	0.000763	0.02276	318.6	549.8	2.1264	2.8417
60	17.76	0.000784	0.01827	329.1	551.2	2.1578	2.8245
70	21.85	0.000808	0.01481	340.0	552.1	2.1892	2.8074
80	26.65	0.000834	0.01202	351.4	552.5	2.2207	2.7900
90	32.17	0.000865	0.00972	364.1	552.4	2.2528	2.7714
100	38.44	0.000901	0.00789	377.8	551.0	2.2860	2.7502

a) Estimate the state of the load at 20ºC.

b) Estimate the state of the load in a warehouse without air conditioning in winter at -10ºC and in summer at 40ºC.

c) Determine the enthalpy change when going from 20ºC to -10ºC, and that of going from 20ºC to 40ºC.

d) Determine the entropy change when going from 20ºC to -10ºC, and that of going from 20ºC to 40ºC.

e) Determine the heat exchanged when going from 20ºC to -10ºC, and that of going from 20ºC to 40ºC.

f) Estimate the state of the load at 20ºC when 50% of the chlorine has been consumed and at the time of replacing the tank. Why are they connected in battery?

g) In the case of isothermal emptying, suppose that the tank is utilized until no Cl_2 comes out spontaneously. What would be the amount of chlorine that remains inside and therefore cannot be used?

h) Qualitatively represent the processes of the preceding questions in $PT(V)$, $TS(P,V)$, $PU(T,V)$ and $PV(T)$ diagrams.

Question a. Let point 1 represent a new tank at 20ºC. The specific volume will be

$$\hat{V}_1 = \frac{V_{tank}}{M_1} = \frac{800\ \mathrm{L}}{400\ \mathrm{kg}} \times \frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}} = 0.002\ \frac{\mathrm{m}^3}{\mathrm{kg}}$$

The table provided by the the statement of the problem shows that this value is higher than 0.00071 m^3/kg (saturated liquid at 20ºC), but lower than 0.0471 m^3/kg (saturated vapor at 20ºC), which indicates that the load will be a mixture of saturated liquid and vapor at the equilibrium pressure (P_1=6.702 bar = 670.2 kPa). The amount of each phase will be determined by combining the mass balance ($M_1 = M_{l_1} + M_{v_1}$) with the volume one ($M_1\hat{V}_1 = M_{l_1}\hat{V}_{l_1}^{sat} + M_{v_1}\hat{V}_{v_1}^{sat}$) in the form

$$\frac{M_{v_1}}{M_1} = \frac{\left(\hat{V}_1 - \hat{V}_{l_1}^{sat}\right)}{\left(\hat{V}_{v_1}^{sat} - \hat{V}_{l_1}^{sat}\right)} = \frac{(0.002 - 0.00071)}{(0.0471 - 0.00071)} = 0.0278$$

$$M_{v_1} = 0.0278M_1 = 0.0278(400\ \mathrm{kg}) = 11.12\ \mathrm{kg}$$

$$M_{l_1} = M_1 - M_{v_1} = 400 - 11.12 = 388.88\ \mathrm{kg}$$

Phases which, additionally, occupy the following volumes

$$V_{v_1} = M_{v_1}\hat{V}_{v_1}^{sat} = (11.12\ \mathrm{kg})\left(0.0471\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right) = 0.524\ \mathrm{m}^3$$

$$V_{l_1} = M_{l_1}\hat{V}_{l_1}^{sat} = (388.88\ \mathrm{kg})\left(0.00071\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right) = 0.276\ \mathrm{m}^3$$

Question b. Operating as in the previous question, it is observed that the specific volume of chlorine in the tank (which does not change, $\hat{V}_1 = \hat{V}_2 = \hat{V}_3$, since neither the mass nor the volume of the tank change at both T_2= -10ºC and T_3= 40ºC) is higher than that of the saturated liquid but lower than that of the saturated vapor. Thus, at -10ºC the biphasic mixture will be at a pressure P_2=2.608 bar= 260.8 kPa, being its mass distribution

$$\frac{M_{v_2}}{M_1} = \frac{\left(\hat{V}_1 - \hat{V}_{l_2}^{sat}\right)}{\left(\hat{V}_{v_2}^{sat} - \hat{V}_{l_2}^{sat}\right)} = \frac{(0.002 - 0.000668)}{(0.1134 - 0.000668)} = 0.0118$$

$$M_{v_2} = 0.0118M_1 = 0.0118(400\ \mathrm{kg}) = 4.72\ \mathrm{kg}$$

$$M_{l_2} = M_1 - M_{v_2} = 400 - 4.72 = 395.28\ \mathrm{kg}$$

and the volumes

$$V_{v_2} = M_{v_2}\hat{V}_{v_2}^{sat} = (4.72\ \mathrm{kg})\left(0.1134\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right) = 0.535\ \mathrm{m}^3$$
$$V_{l_2} = M_{l_2}\hat{V}_{l_2}^{sat} = (395.28\ \mathrm{kg})\left(0.000668\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right) = 0.264\ \mathrm{m}^3$$

whereas at 40ºC, P_3=11.27 bar (1127 kPa), the distribution will be

$$\frac{M_{v_3}}{M_1} = \frac{\left(\hat{V}_1 - \hat{V}_{l_3}^{sat}\right)}{\left(\hat{V}_{v_3}^{sat} - \hat{V}_{l_3}^{sat}\right)} = \frac{(0.002 - 0.000744)}{(0.0286 - 0.000744)} = 0.0451$$

$$M_{v_3} = 0.0451 M_1 = 0.0451(400\ \mathrm{kg}) = 18.04\ \mathrm{kg}$$

$$M_{l_3} = M_1 - M_{v_3} = 400 - 18.04 = 381.96\ \mathrm{kg}$$

$$V_{v_3} = M_{v_3}\hat{V}_{v_3}^{sat} = (18.04\ \mathrm{kg})\left(0.0286\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right) = 0.516\ \mathrm{m}^3$$

$$V_{l_3} = M_{l_3}\hat{V}_{l_3}^{sat} = (381.96\ \mathrm{kg})\left(0.000744\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right) = 0.284\ \mathrm{m}^3$$

Question c. Due to the fact that at the state conditions represented by points 1, 2 and 3 the system is in the form of biphasic mixtures, the enthalpies in these points will have to be estimated according to the total enthalpy balances, with $\hat{H}_{l_1}^{sat}$ =289.2 kJ/kg , $\hat{H}_{l_2}^{sat}$ =260.0 kJ/kg and $\hat{H}_{l_3}^{sat}$ =308.8 kJ/kg for the saturated liquid and $\hat{H}_{v_1}^{sat}$ =543.3 kJ/kg , $\hat{H}_{v_2}^{sat}$ =533.9 kJ/kg and $\hat{H}_{v_3}^{sat}$ =548.0 kJ/kg for the saturated vapor

$$\hat{H}_1 = \frac{M_{l_1}}{M_1}\hat{H}_{l_1}^{sat} + \frac{M_{v_1}}{M_1}\hat{H}_{v_1}^{sat} \quad ; \quad \hat{H}_2 = \frac{M_{l_2}}{M_1}\hat{H}_{l_2}^{sat} + \frac{M_{v_2}}{M_1}\hat{H}_{v_2}^{sat} \quad ; \quad \hat{H}_3 = \frac{M_{l_3}}{M_1}\hat{H}_{l_3}^{sat} + \frac{M_{v_3}}{M_1}\hat{H}_{v_3}^{sat}$$

$$\hat{H}_1 = (1 - 0.0278)\left(289.2\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) + 0.0278\left(543.3\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 296.26\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$
$$\hat{H}_2 = (1 - 0.0118)\left(260.0\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) + 0.0118\left(533.9\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 263.23\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$
$$\hat{H}_3 = (1 - 0.0451)\left(308.8\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) + 0.0451\left(548.0\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 318.59\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

being the changes

$$\Delta\hat{H}_{21} = \hat{H}_2 - \hat{H}_1 = 263.23 - 296.26 = -33.03\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$
$$\Delta\hat{H}_{31} = \hat{H}_3 - \hat{H}_1 = 318.59 - 296.26 = 22.33\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

Question d. Operating as in the previous question, but with $\hat{S}_{l_1}^{sat}$ =2.0291 kJ/(kg·K) , $\hat{S}_{l_2}^{sat}$ =1.9243 kJ/(kg·K) and $\hat{S}_{l_3}^{sat}$ =2.0946 kJ/(kg·K) for the saturated liquid and $\hat{S}_{v_1}^{sat}$ =2.8924 kJ/(kg·K), $\hat{S}_{v_2}^{sat}$ = 2.9649 kJ/(kg·K) and $\hat{S}_{v_3}^{sat}$ = 2.8593 kJ/(kg·K) for the saturated vapor

$$\hat{S}_1 = (1 - 0.0278)\left(2.0291\ \frac{\text{kJ}}{\text{kg·K}}\right) + 0.0278\left(2.8924\ \frac{\text{kJ}}{\text{kg·K}}\right) = 2.0531\ \frac{\text{kJ}}{\text{kg·K}}$$
$$\hat{S}_2 = (1 - 0.0118)\left(1.9243\ \frac{\text{kJ}}{\text{kg·K}}\right) + 0.0118\left(2.9649\ \frac{\text{kJ}}{\text{kg·K}}\right) = 1.9366\ \frac{\text{kJ}}{\text{kg·K}}$$
$$\hat{S}_3 = (1 - 0.0451)\left(2.0946\ \frac{\text{kJ}}{\text{kg·K}}\right) + 0.0451\left(2.8593\ \frac{\text{kJ}}{\text{kg·K}}\right) = 2.1291\ \frac{\text{kJ}}{\text{kg·K}}$$

$$\Delta\hat{S}_{21} = \hat{S}_2 - \hat{S}_1 = 1.9366 - 2.0531 = -0.1165\ \frac{\text{kJ}}{\text{kg·K}}$$

$$\Delta\hat{S}_{31} = \hat{S}_3 - \hat{S}_1 = 2.1291 - 2.0531 = 0.076\ \frac{\text{kJ}}{\text{kg·K}}$$

Question e. The heat exchanged between points 1-2 and 1-3 is determined by the expression

$$\text{d}\hat{Q} = T\text{d}\hat{S} \qquad \rightarrow \qquad \Delta\hat{Q}_{21} = \int_1^2 T\text{d}\hat{S} \quad ; \quad \Delta\hat{Q}_{31} = \int_1^3 T\text{d}\hat{S}$$

which, strictly speaking, would require numerical integration. In first approximation, by using the trapezoidal rule

$$\Delta\hat{Q}_{21} = \left(\frac{T_2 + T_1}{2}\right)\left(\hat{S}_2 - \hat{S}_1\right) = \frac{[(-10 + 273)\text{K} + (20 + 273)\text{K}]}{2}\left(-0.1165\ \frac{\text{kJ}}{\text{kg·K}}\right) = -32.387\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\hat{Q}_{31} = \left(\frac{T_3 + T_1}{2}\right)\left(\hat{S}_3 - \hat{S}_1\right) = \frac{[(40 + 273)\text{K} + (20 + 273)\text{K}]}{2}\left(0.076\ \frac{\text{kJ}}{\text{kg·K}}\right) = 23.028\ \frac{\text{kJ}}{\text{kg}}$$

However, according to one of the fundamental thermodynamic relations it is obtained

$$\text{d}\hat{U} = \text{d}\hat{Q} - P\text{d}\hat{V}$$

since the specific volume remains constant ($\text{d}\hat{V}$=0) there is no expansion-compression work and

$$\Delta\hat{Q}_{21}=\Delta\hat{U}_{21} = \hat{U}_2 - \hat{U}_1 = \left(\hat{H}_2 - \hat{V}_1P_2\right) - \left(\hat{H}_1 - \hat{V}_1P_1\right) = \hat{H}_2 - \hat{H}_1 - \hat{V}_1(P_2 - P_1)$$

$$\Delta\hat{Q}_{31}=\Delta\hat{U}_{31} = \hat{U}_3 - \hat{U}_1 = \left(\hat{H}_3 - \hat{V}_1P_3\right) - \left(\hat{H}_1 - \hat{V}_1P_1\right) = \hat{H}_3 - \hat{H}_1 - \hat{V}_1(P_3 - P_1)$$

being the heat analytically calculated as

$$\Delta\hat{Q}_{21} = \left(-33.03\ \frac{\text{kJ}}{\text{kg}}\right) - \left(0.002\ \frac{\text{m}^3}{\text{kg}}\right)(260.8\ \text{kPa} - 670.2\ \text{kPa}) = -32.21\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\hat{Q}_{31} = \left(22.33\ \frac{\text{kJ}}{\text{kg}}\right) - \left(0.002\ \frac{\text{m}^3}{\text{kg}}\right)(1127\ \text{kPa} - 670.2\ \text{kPa}) = 21.42\ \frac{\text{kJ}}{\text{kg}}$$

Question f. Let point 4 be the one in which the mass is the half of that of point 1, M_4=0.5M_1

$$\hat{V}_4 = \frac{V_{tank}}{M_4} = \frac{800\ \text{L}}{200\ \text{kg}} \times \frac{1\ \text{m}^3}{1000\ \text{L}} = 0.004\ \frac{\text{m}^3}{\text{kg}}$$

In the table provided by the statement of the problem, it is still observed that this specific volume is intermediate between that of the saturated liquid and that of the saturated vapor ($\hat{V}_{l_1}^{sat} = \hat{V}_{l_4}^{sat}$; $\hat{V}_{v_1}^{sat} = \hat{V}_{v_4}^{sat}$), so

$$\frac{M_{v_4}}{M_4} = \frac{\left(\hat{V}_4 - \hat{V}_{l_1}^{sat}\right)}{\left(\hat{V}_{v_1}^{sat} - \hat{V}_{l_1}^{sat}\right)} = \frac{(0.004 - 0.00071)}{(0.0471 - 0.00071)} = 0.0709$$

$$M_{v_4} = 0.0709 M_4 = 0.0709(200\ \text{kg}) = 14.18\ \text{kg}$$

$$M_{l_4} = M_4 - M_{v_4} = 200 - 14.18 = 185.82\ \text{kg}$$

$$V_{v_4} = M_{v_4}\hat{V}_{v_1}^{sat} = (14.18\ \text{kg})\left(0.0471\ \frac{\text{m}^3}{\text{kg}}\right) = 0.668\ \text{m}^3$$

$$V_{l_4} = M_{l_4}\hat{V}_{l_1}^{sat} = (185.82\ \text{kg})\left(0.00071\ \frac{\text{m}^3}{\text{kg}}\right) = 0.132\ \text{m}^3$$

and the pressure will remain at 6.702 bar. If compared with point 1, volume and mass of the saturated vapor have increased despite decreasing the total chlorine content. When all the liquid is consumed (point 5), only saturated vapor will remain occupying the tank, with a mass

$$M_5 = M_{v_5} = \frac{V_{tank}}{\hat{V}_{v_5}} = \frac{V_{tank}}{\hat{V}_{v_1}} = \frac{800\ \text{L}}{\left(0.0471\ \frac{\text{m}^3}{\text{kg}}\right)} \times \frac{1\ \text{m}^3}{1000\ \text{L}} = 16.98\ \text{kg}$$

being the moment to replace the cylinder. The tanks are connected in battery to assure continuity of supply while the exhausted cylinder is replenished.

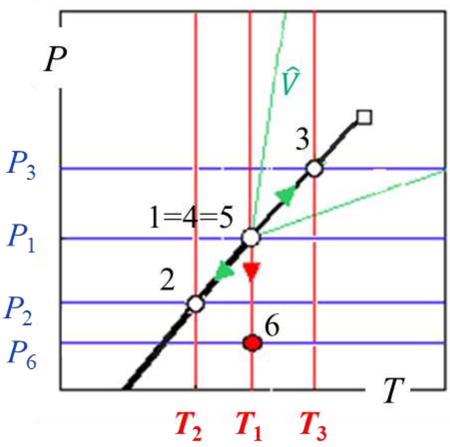
Question g. An isothermal emptying at 20ºC (=293 K) will cease of being spontaneous when the pressure in the tank decreases from 6.702 bar to the atmospheric pressure (P_6=1 atm=1.013 bar). Then, only chlorine vapor will remain inside, being its specific volume estimated by the ideal gas law. By taking the molecular weight from appendix II of the present book

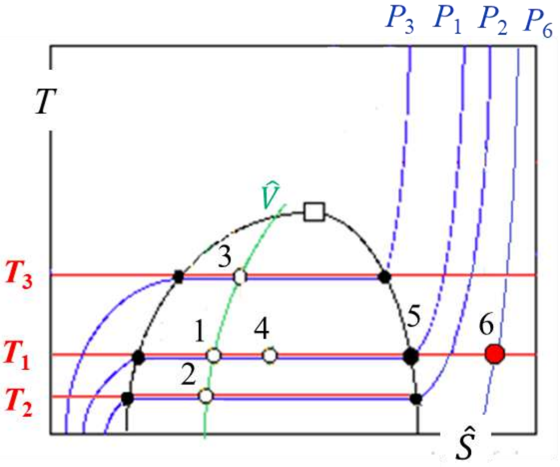
$$\hat{V}_6 = \frac{RT_1}{\mathfrak{M}P_6} = \frac{\left(0.082\,\frac{\mathrm{atm\cdot L}}{\mathrm{K\cdot mol\text{-}g}}\right)(293\ \mathrm{K})}{\left(70.91\,\frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)(1\ \mathrm{atm})} = 0.3388\,\frac{\mathrm{L}}{\mathrm{g}} = 0.3388\ \frac{\mathrm{m^3}}{\mathrm{kg}}$$

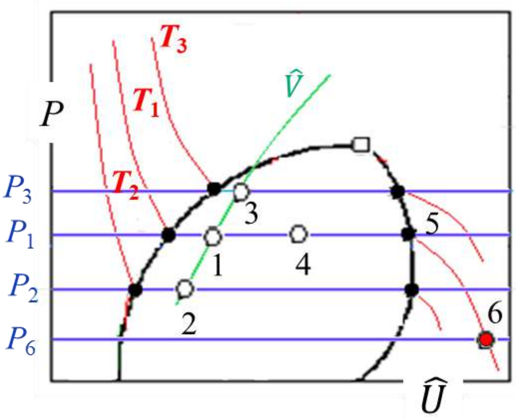
and the amount of Cl_2 that cannot be used will be found as in question **f**

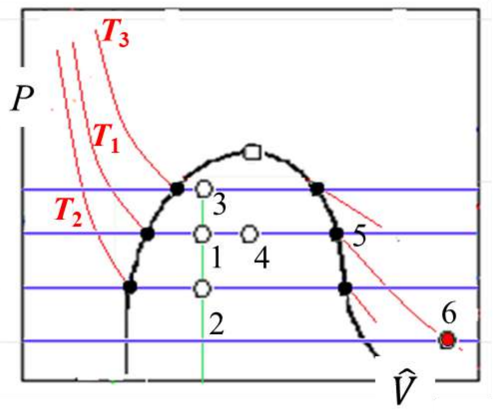
$$M_6 = \frac{V_{tank}}{\hat{V}_6} = \frac{800\ \mathrm{L}}{\left(0.3388\ \frac{\mathrm{m^3}}{\mathrm{kg}}\right)} \times \frac{1\ \mathrm{m^3}}{1000\ \mathrm{L}} = 2.361\ \mathrm{kg}$$

Question h. The required representations are displayed below









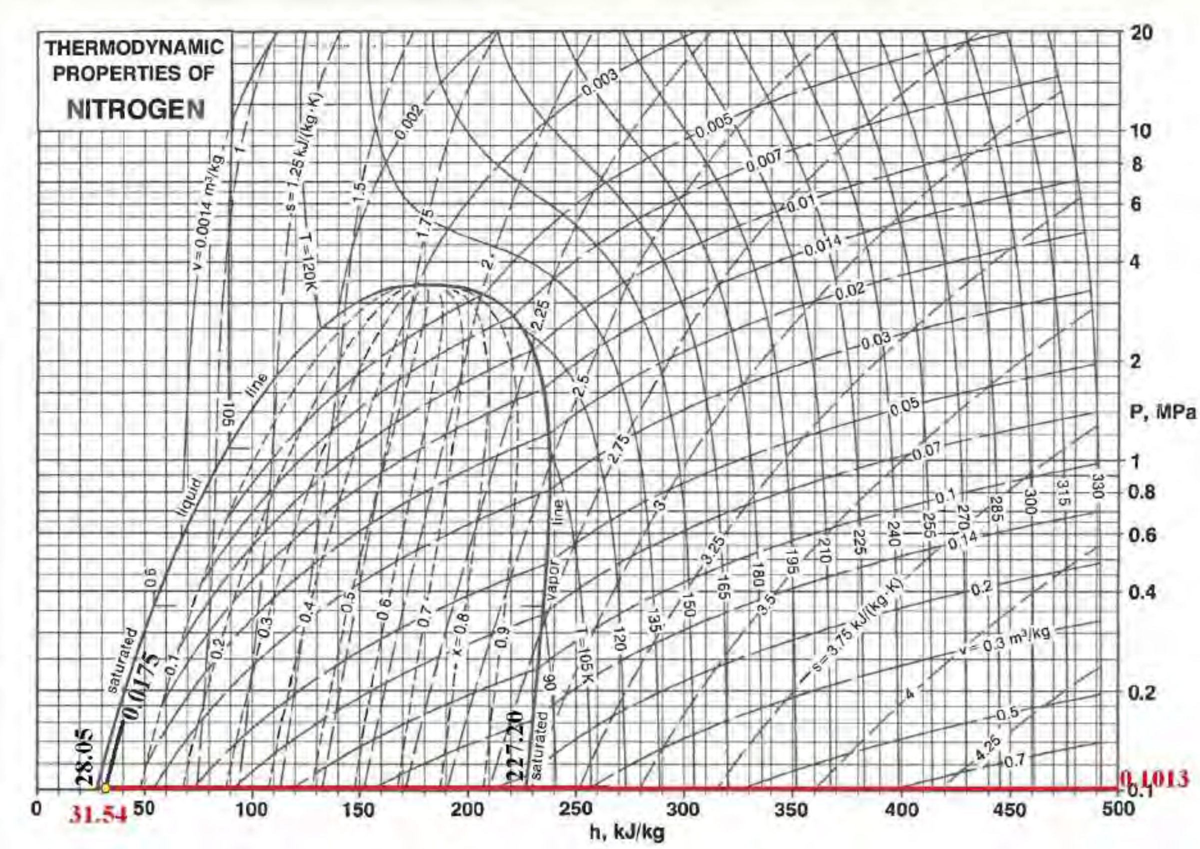
4.21. 20 kg of molecular nitrogen are contained in a 100 L cryogenic storage Dewar which, for practical reasons, is thermally insulated and open to the atmosphere. Most of the N_2 is liquid, and only 1.75% of the mass is vapor (in equilibrium with this liquid).

a) Locate the initial situation in a *PH*(*T*,*V*,*S*) diagram.

b) Draw on the same diagram the evolution experienced by the load if heat exchange with the environment is allowed (until reaching the room temperature, 20°C), whether the vessel is hermetically closed or if it remains open. Estimate the energy that would be subtracted from the environment in both cases.

c) Explain the operation of the cryogenic storage Dewars. Why do clouds and white spots appear around mouths and parts in contact with air?

Question a. Figure V.13 is a *PH*(*T*,*V*,*S*) diagram of nitrogen



The location of point 1 (saturation at 1 atm) in the diagram can be done in three ways:

- By finding the intersection of the quality line of 1.75% with the isobar

$$P_1 = 1\ \text{atm} \times \frac{0.1013\ \text{MPa}}{1\ \text{atm}} = 0.1013\ \text{MPa}$$

- By findind the intersection of the isobar P_1=0.1013 MPa with the isochore

$$\hat{V}_1 = \frac{V_{dewar}}{M_1} = \frac{100\ \text{L}}{20\ \text{kg}} \times \frac{1\ \text{m}^3}{1000\ \text{L}} = 0.005\ \frac{\text{m}^3}{\text{kg}}$$

- By calculating its enthalpy at 0.1013 MPa from the enthalpies of the saturated liquid and vapor through the enthalpy balance

$$M_{tot}\hat{H}_1 = M_{l_1}\hat{H}_{l_1}^{sat} + M_{v_1}\hat{H}_{v_1}^{sat} \quad \rightarrow \quad \hat{H}_1 = \frac{M_{l_1}}{M_{tot}}\hat{H}_{l_1}^{sat} + \frac{M_{v_1}}{M_{tot}}\hat{H}_{v_1}^{sat}$$

Since the 0.005 m^3/kg isochore does not reach low pressures, only the first and the third options are feasible. By reading in the figure the values of the enthalpies of the liquid and the saturated vapor, it is obtained

$$\hat{H}_1 = \left(\frac{19.65\ \text{kg}}{20\ \text{kg}}\right)\left(28.05\ \frac{\text{kJ}}{\text{kg}}\right) + \left(\frac{0.35\ \text{kg}}{20\ \text{kg}}\right)\left(227.20\ \frac{\text{kJ}}{\text{kg}}\right) = 31.54\ \frac{\text{kJ}}{\text{kg}}$$

Question b. If the dewar is not closed when the temperature increases, nitrogen will begin to evaporate at atmospheric pressure until reaching 293 K, i.e., the horizontal straight line (isobar) between 1 and 2 will be followed. In the end, all the substance will be gas and a part of it will have left the vessel. By assuming the ideal behavior (the isochores in the figure do not reach that temperature), the amount of N_2 that remains in the Dewar flask is

$$M_2 = \frac{V_{dewar}}{\hat{V}_2} = V_{dewar}\frac{P_2\mathfrak{M}_{\text{N}_2}}{RT_2} = (100\ \text{L})\frac{(1\ \text{atm})\left(28.02\frac{\text{g}}{\text{mol-g}}\right)}{\left(0.082\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(293\ \text{K})} = 116.62\ \text{g}$$

On the contrary, if the dewar is closed, the specific volume will remain constant (M_1=M_2), and the operation line will be the 0.005 m^3/kg isochore until intersecting the 293 K isotherm at point 2’, where the pressure is of 18 MPa.

In both cases, the heat substracted from the environment is calculated by

$$\Delta Q = M_1\Delta\hat{Q} = M_1\int_1^{2\text{ or }2'} T\text{d}\hat{S}$$

because when the dewar is not closed, the nitrogen that comes out and the one that remains inside maintain the same specific heat to evaporate or to increase its temperature.

This integral could be solved numerically, but if equations of reference problem 0.3 are taken into account, when pressure and volumen are constant

$$\text{d}\hat{H} = \text{d}\hat{Q} + \text{d}\hat{W}^{\text{fl}} = T\text{d}\hat{S} + \hat{V}\text{d}P \quad \xrightarrow{\text{d}P=0} \quad \Delta\hat{H} = \Delta\hat{Q}$$

$$\text{d}\hat{U} = \text{d}\hat{Q} + \text{d}\hat{W}^{\text{e-c}} = T\text{d}\hat{S} - P\text{d}\hat{V} \quad \xrightarrow{\text{d}\hat{V}=0} \quad \Delta\hat{Q} = \Delta\hat{U} = \Delta\left(\hat{H} - P\hat{V}\right)$$

it follows that

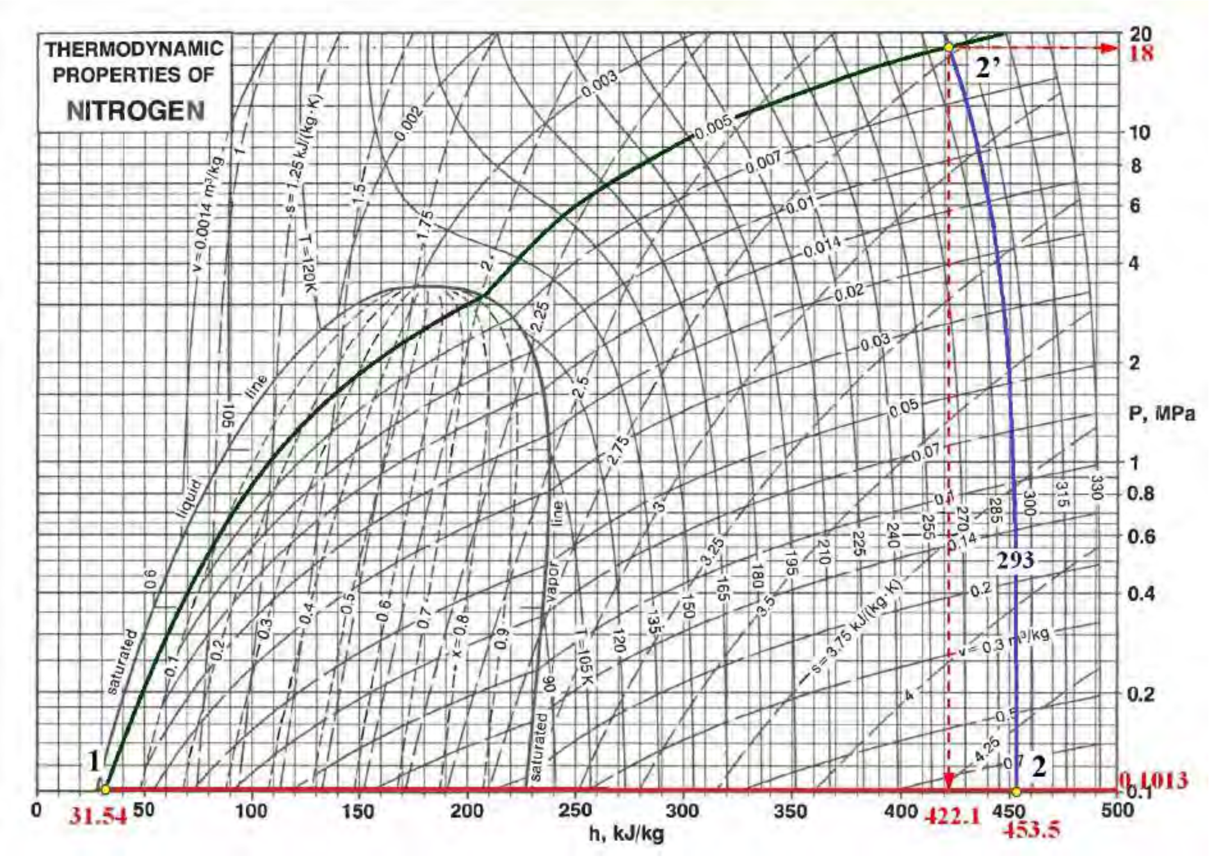
$$\Delta Q_{21} = M_1\Delta\hat{Q}_{21} = M_1\left(\hat{H}_2 - \hat{H}_1\right)$$

$$\Delta Q_{2'1} = M_1 \Delta \hat{Q}_{2'1} = M_1\left\{\left(\hat{H}_{2'} - \hat{H}_1\right) - \hat{V}_1\left(P_{2'} - P_1\right)\right\}$$

and by reading the necessary enthalpies in the figure

$$\Delta Q_{21} = (20\ \mathrm{kg})\left(453.5\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 31.54\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 8439.2\ \mathrm{kJ}$$

$$\Delta Q_{2'1}{=}(20\ \mathrm{kg})\left\{\left(422.1\frac{\mathrm{kJ}}{\mathrm{kg}} - 31.54\frac{\mathrm{kJ}}{\mathrm{kg}}\right) - \left(0.005\frac{\mathrm{m}^3}{\mathrm{kg}}\right)(18000\ \mathrm{kPa} - 100\ \mathrm{kPa})\right\}{=}6021.2\ \mathrm{kJ}$$



Question c. Because their low temperature, liquefied gases under isobaric conditions are in very unstable thermodynamic conditions, having a strong tendency to heat exchange with the environment in order to allow their evaporation and heating towards equilibrium. This evaporation implies a significant loss of condensed phase.

The cryogenic storage Dewar has two functions:

- Due to its double wall with vacuum chamber, it reduces thermal conductivity with the environment.
- Due to its narrow mouth, it reduces the free surface of contact with the surrounding atmosphere, minimizing the mass and heat transfer. This mouth, however, allows convective escapes of vapor to avoid overpressures.

White spots and clouds are the result of condensation of water vapor from the surrounding air due to the strong cooling caused by the exit of the liquefied gas and its mixing with the environment.

4.22. A transport vessel has ten spherical tanks with an inner diameter of 20 m for transporting commercial carbon dioxide loaded at 10ºC. During the journey, the load may heat up, so the loading is carried out by allowing a vapor chamber equivalent to a quarter of the tank volume. For the sake of safety, the tanks have bleed valves which open when the internal pressure reaches 64 kg$_f$/cm^2. By utilizing a specific *PH*(*T*,ρ,*S*) diagram:

a) Estimate the load transported in each tank.

b) Evaluate the temperature which can be reached by the load without bleeding, as well as the proportions of liquid and vapor at that moment.

c) Suppose that an accident increases the temperature to 40ºC, what pressure would be reached? How much CO$_2$ would have to be purged to avoid mechanical explosion of the tanks at that temperature?

d) In the accident of the previous question, calculate economic losses. Take the CO$_2$ price as 3 $/kg.

e) Qualitatively represent the accidental overheating of the tanks on *PT* and *PV*(*T*) diagrams.

Question a. Each tank will have a volume of

$$V_{tank} = \frac{\pi}{6} d_{in}^3 = \frac{\pi}{6} (20 \text{ m})^3 = 4188.7 \text{ m}^3$$

and the volume occupied by the vapor phase will be a quarter of it

$$V_{v_1} = \frac{1}{4} V_{tank} = \frac{1}{4} (4188.7 \text{ m}^3) = 1047.18 \text{ m}^3$$

being obvious that the volume of the liquid phase is

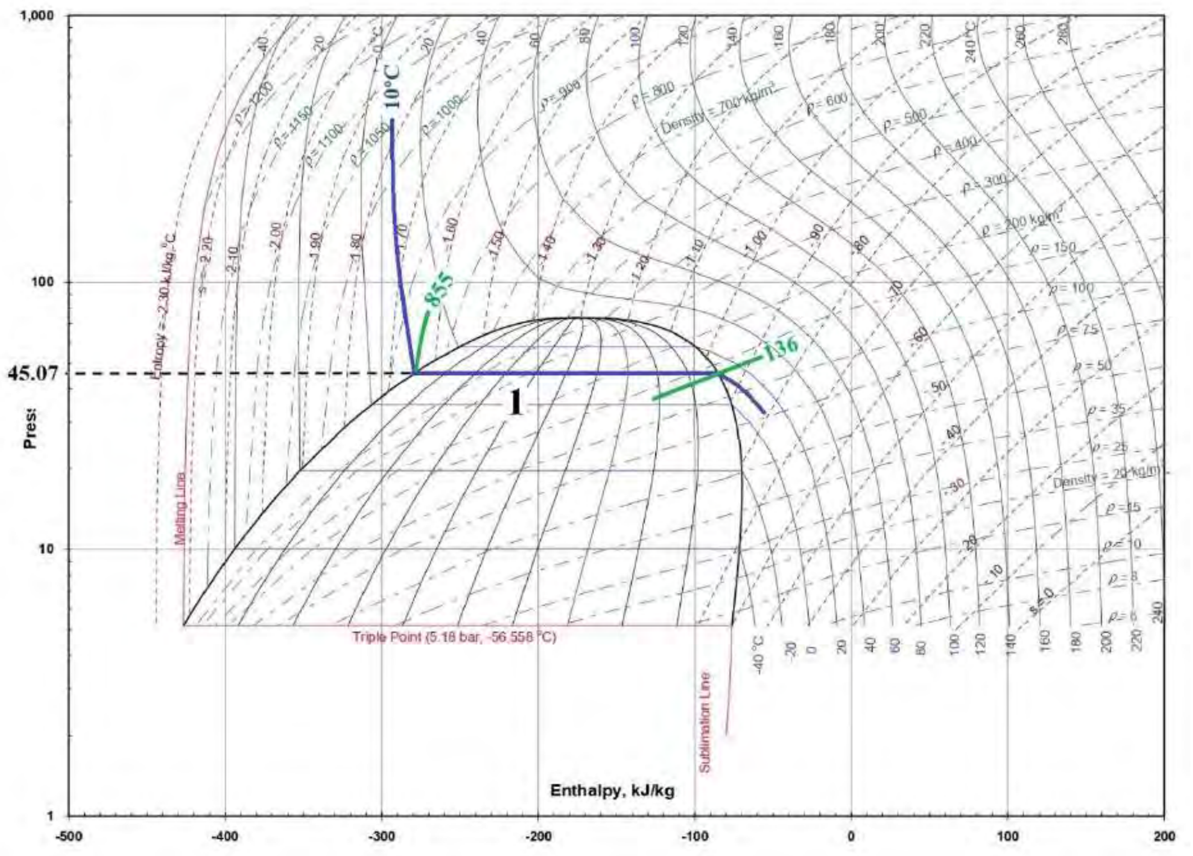
$$V_{l_1} = V_{tank} - V_{v_1} = 4188.7 - 1047.18 = 3141.52 \text{ m}^3$$

In figure V.2 of appendix V, at a temperature of 10ºC, it can be read that the pressure of the biphasic mixtures is P_1=45.07 bar. The density of the saturated liquid and that of the saturated vapor can be interpolated from this diagram (being 855 kg/m^3 and 136 kg/m^3, respectively) so that the liquid and vapor masses in each tank after the initial load will be

$$M_{l_1} = \hat{\rho}_{l_1}^{sat} V_{l_1} = \left(855 \frac{\text{kg}}{\text{m}^3}\right) (3141.52 \text{ m}^3) = 2685999.6 \text{ kg}$$

$$M_{v_1} = \hat{\rho}_{v_1}^{sat} V_{v_1} = \left(136 \frac{\text{kg}}{\text{m}^3}\right) (1047.18 \text{ m}^3) = 142416.48 \text{ kg}$$

and the total load per tank is the sum: 2828416.08 kg, that is to say, approximately 2828 tons.



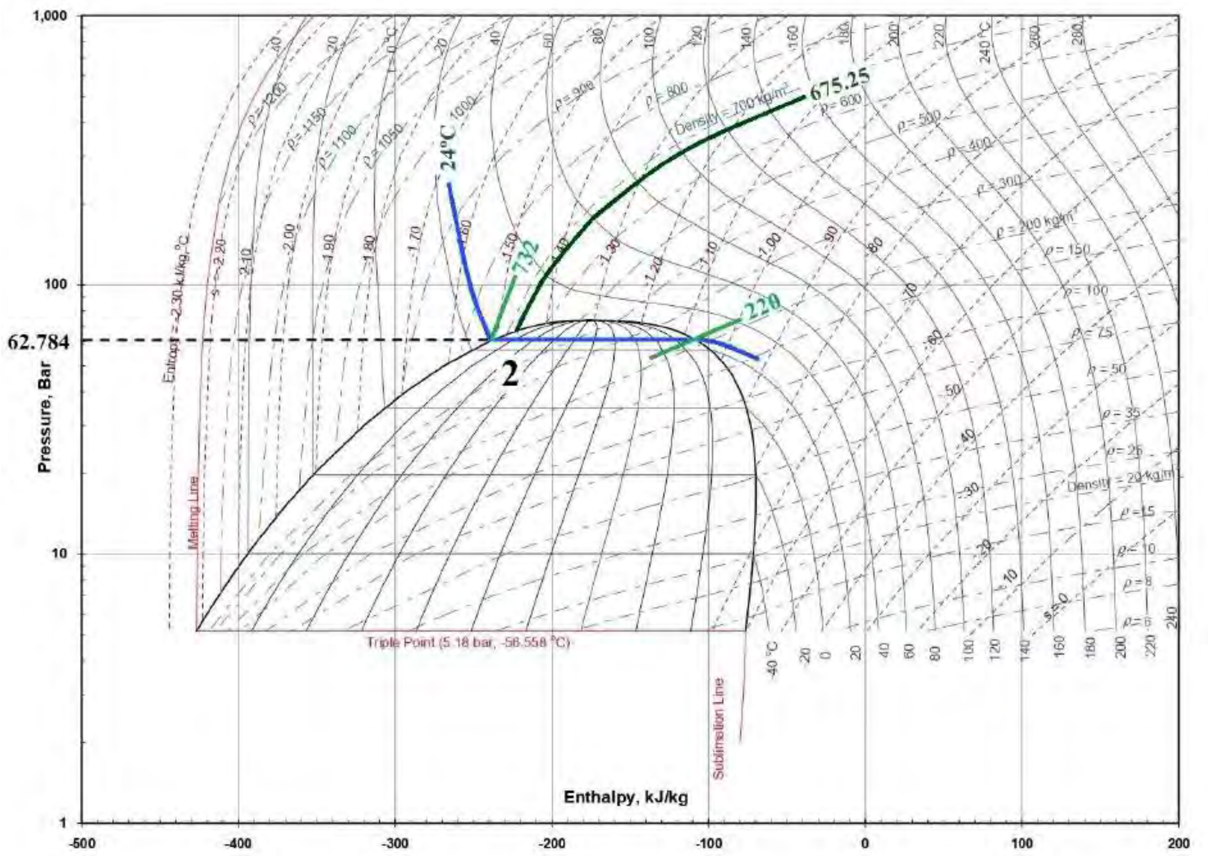
Question b. Neither the volume of the tank nor the total mass of CO_2 vary, so the conditions will be determined by the coincidence of the isochore

$$\hat{\rho}_1 = \hat{\rho}_2 = \frac{M_{tot}}{V_{tank}} = \frac{2828416.08\ \text{kg}}{4188.7\ \text{m}^3} = 675.25\ \frac{\text{kg}}{\text{m}^3}$$

with the isobar (graphical intersection)

$$P_2 = 64\frac{\text{kg}_\text{f}}{\text{cm}^2}\times\frac{0.981\ \text{bar}}{1\ \text{kg}_\text{f}/\text{cm}^2} = 62.784\ \text{bar}$$

Unfortunately, isochores higher than 400 kg/m^3 do not enter the biphasic zone of the figure, but a simple visual inspection indicates that the intersection corresponds to a mixture of liquid and vapor at T_2=24ºC, with $\hat{\rho}_{v_2}^{sat}$=732 kg/m^3 and $\hat{\rho}_{l_2}^{sat}$=220 kg/m^3.



Mass and volume balances in that point will be

$$M_{tot} = M_{l_2} + M_{v_2}$$

$$\frac{M_{tot}}{\hat{\rho}_2} = \frac{M_{l_2}}{\hat{\rho}_{l_2}^{sat}} + \frac{M_{v_2}}{\hat{\rho}_{v_2}^{sat}}$$

and the combination of both will give

$$M_{v_2} = M_{tot}\frac{\left(\frac{1}{\hat{\rho}_2} - \frac{1}{\hat{\rho}_{l_2}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_2}^{sat}} - \frac{1}{\hat{\rho}_{l_2}^{sat}}\right)} = (2828416.08\ \text{kg})\frac{\left(\frac{1}{675.25} - \frac{1}{732}\right)}{\left(\frac{1}{220} - \frac{1}{732}\right)} = 102140.34\ \text{kg}$$

$$M_{l_2} = M_{tot} - M_{v_2} = 2828416.08 - 102140.34 = 2726275.74\ \text{kg}$$

masses which occupy the following volumes

$$V_{v_2} = \frac{M_{v_2}}{\hat{\rho}_{v_2}^{sat}} = \frac{102140.34\ \text{kg}}{220\ \frac{\text{kg}}{\text{m}^3}} = 464.28\ \text{m}^3$$

$$V_{l_2} = \frac{M_{l_2}}{\hat{\rho}_{l_2}^{sat}} = \frac{2726275.74\ \text{kg}}{732\ \frac{\text{kg}}{\text{m}^3}} = 3724.42\ \text{m}^3$$

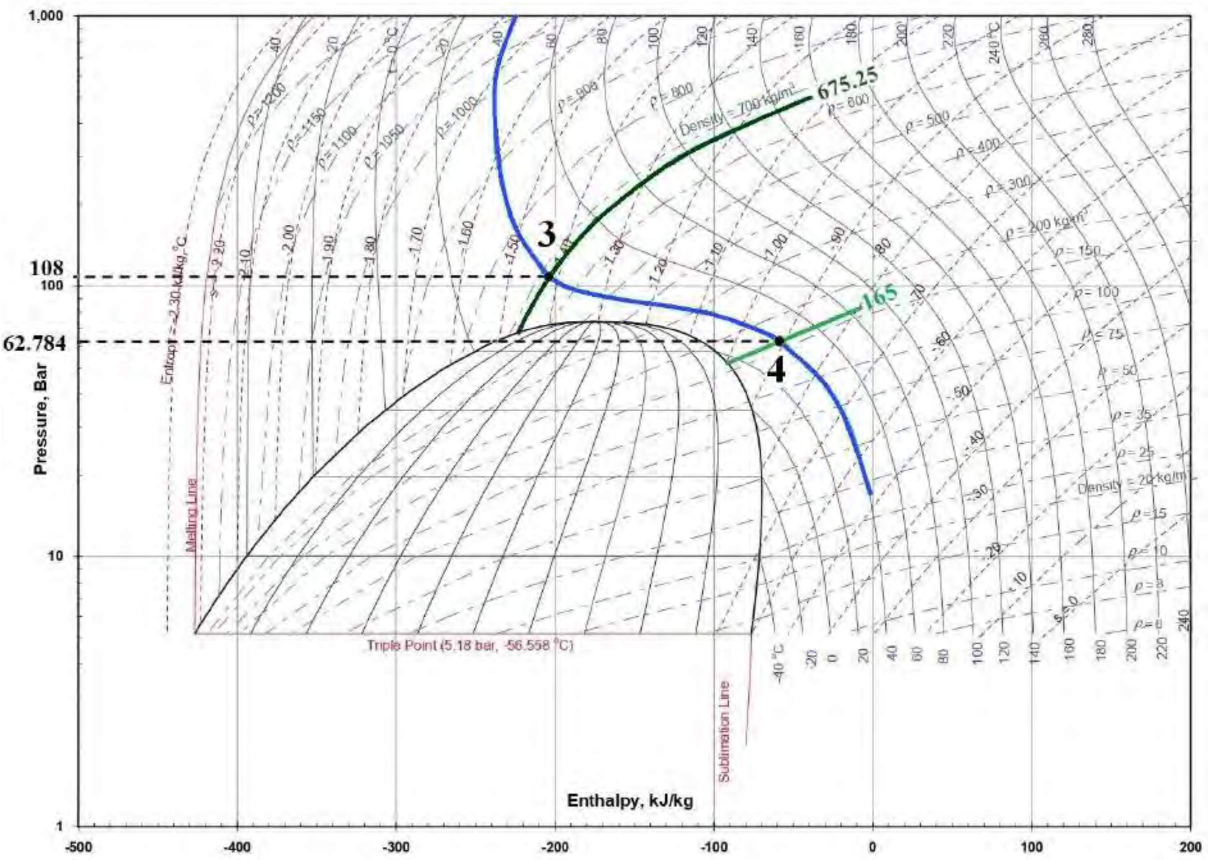
Now more vapor has condensed: both its mass and the volume it occupies are lower than in question **a**.

Question c. The crossing point between the 675.25 kg/m^3 isochore and the 40ºC isotherm indicates the pressure P_3=108 bar. In order to maintain the pressure of 62.784 bar, the density should be that of the intersection of this isobar with the 40ºC isotherm, $\hat{\rho}_4 = 165$ kg/m^3. From this density and the tank volume, the remaining mass in each tank will be

$$M_{remains} = M_4 = \hat{\rho}_4 V_{tank} = \left(165\ \frac{\text{kg}}{\text{m}^3}\right)(4188.7\ \text{m}^3) = 691135.5\ \text{kg}$$

and the purged mass

$$M_{purged} = M_{tot} - M_4 = 2828416.08 - 691135.5 = 2137280.58\ \text{kg}$$

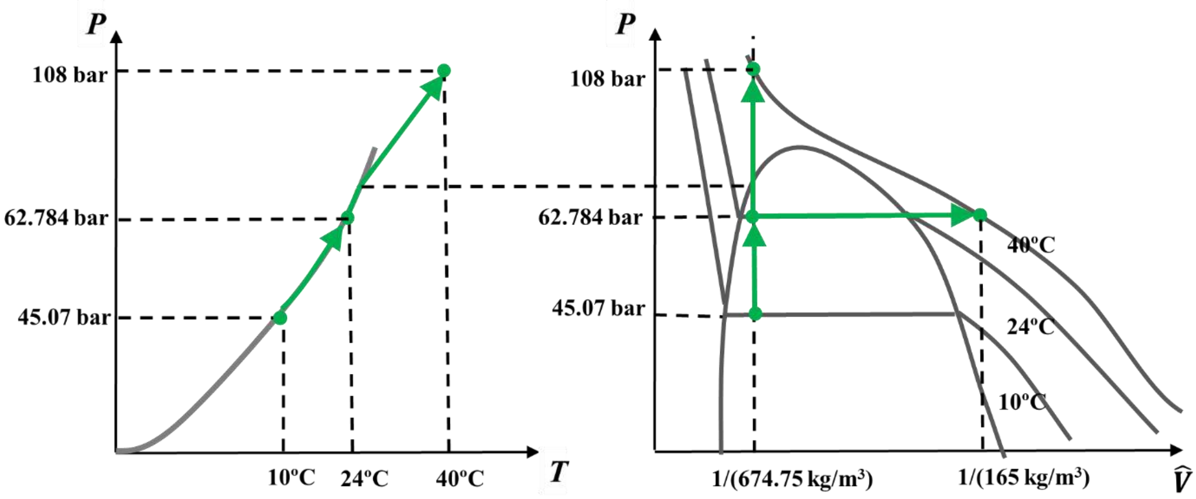


Question d. The economic loss due to one tank is

$$2137280.58\ \text{kg} \times \frac{3\ \$}{1\ \text{kg}} = 6.4 \cdot 10^6\ \$$$

and the losses of the ten tanks will obviously be 64·10^6 $.

Question e. The qualitative representations are



4.23. Liquefied carbon dioxide is commercially distributed in pressurized cylinders with or without siphon tube, depending on whether it is desired to obtain liquid or vapor. One of these cylinders is a bottle with an outer diameter of 25 cm and 1.54 m height, made of steel (relative density of 8), with a total weight of 240 kg, containing 35 kg of this substance. Its cost (without including the cylinder rental) is of 500 €.

a) Determine the useful volume of the cylinder.

b) Calculate, by means of a *PH*(*T*,*ρ*,*S*) diagram, the conditions of the tank content in thermal equilibrium with an environment at 20°C, and the money lost when the cylinder is returned to refill if only the liquid phase can be used in the laboratory.

c) Calculate by means of a *TS*(*P*,*V*,*H*) diagram the amount of CO_2 that remains in the cylinder when it is isothermally emptied, and describe what would happen if the bottle is isenthalpically emptied from the liquid phase (presence of siphon tube) or from the vapor phase (absence of siphon tube).

Question a. The useful volume will be equal to that of the cylinder (determined by the outer diameter) minus the volume that the material shell occupies.

$$V_{useful} = V_{cylinder} - V_{shell}$$

where

$$V_{cylinder} = \frac{\pi}{4} d_{out}^2 h = \frac{\pi}{4}\left(25\ \text{cm} \times \frac{1\ \text{m}}{100\ \text{cm}}\right)^2 (1.54\ \text{m}) = 0.0756\ \text{m}^3$$

$$V_{shell} = \frac{M_{material}}{\hat{\rho}_{material}} = \frac{M_{tot} - M_{CO_2}}{\rho_{relative} \times \hat{\rho}_{water}} = \frac{240\ \text{kg} - 35\ \text{kg}}{8(1000\ \text{kg/m}^3)} = 0.0256\ \text{m}^3$$

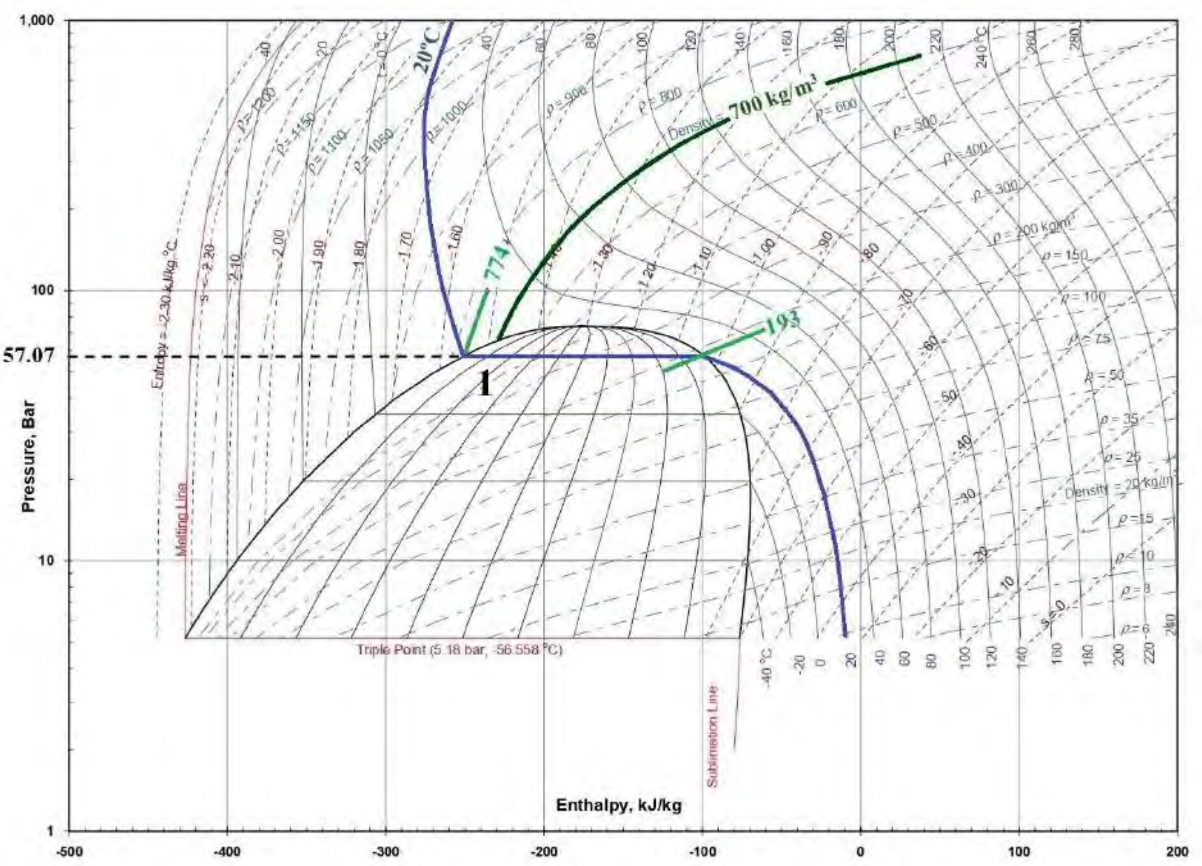
and therefore

$$V_{useful} = 0.0756\ \text{m}^3 - 0.0256\ \text{m}^3 = 0.050\ \text{m}^3$$

Question b. Conditions inside a fully loaded cylinder (1) will be found in the *PH* diagram (figure V.2 of appendix V) where the isochore

$$\hat{\rho}_1 = \frac{M_{CO_2 in\ 1}}{V_{útil}} = \frac{35\ \text{kg}}{0.050\ \text{m}^3} = 700\ \frac{\text{kg}}{\text{m}^3}$$

crosses with the isotherm T_1=20°C. In figure V.2 there are no isochores within the biphasic region for densities higher than 400 kg/m^3, which makes impossible a fast solution of the question. Nonetheless, it seems that point 1 is going to be placed in the biphasic region, which allows the direct reading of the pressure P_1 (57.07 bar), the density of the saturated liquid (774 kg/m^3) and that of the saturated vapor (193 kg/m^3) at T_1.



With these densities, and by combining the mass balance [1] and the volume one [2]

$$M_{\mathrm{CO_2}\,in\,1} = M_l + M_v \qquad [1]$$

$$\frac{M_{\mathrm{CO_2}\,in\,1}}{\hat{\rho}_1} = \frac{M_l}{\hat{\rho}_{l_1}^{sat}} + \frac{M_v}{\hat{\rho}_{v_1}^{sat}} \qquad [2]$$

it is obtained

$$M_v = M_{\mathrm{CO_2}\,in\,1}\frac{\left(\frac{1}{\hat{\rho}_1} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_1}^{sat}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)} = (35\ \mathrm{kg})\frac{\left(\frac{1}{700} - \frac{1}{774}\right)}{\left(\frac{1}{193} - \frac{1}{774}\right)} = 1.229\ \mathrm{kg}$$

$$M_l = M_{\mathrm{CO_2}\,in\,1} - M_v = 35 - 1.229 = 33.771\ \mathrm{kg}$$

$$V_v = \frac{M_v}{\hat{\rho}_{v_1}^{sat}} = \frac{1.229\ \mathrm{kg}}{193\ \frac{\mathrm{kg}}{\mathrm{m^3}}} = 0.0064\ \mathrm{m^3}$$

$$V_l = \frac{M_l}{\hat{\rho}_{l_1}^{sat}} = \frac{33.771\ \mathrm{kg}}{774\ \frac{\mathrm{kg}}{\mathrm{m^3}}} = 0.0436\ \mathrm{m^3}$$

When the liquid phase is exhausted, the entire useful volume of the cylinder (50 L) will be occupied by saturated vapor under the same initial conditions of temperature and pressure so that

$$M_v = V_{useful}\hat{\rho}_{v_1}^{sat} = (0.050\ \mathrm{m}^3)\left(193\ \frac{\mathrm{kg}}{\mathrm{m}^3}\right) = 9.65\ \mathrm{kg}$$

and since 35 kg of CO_2 have cost 500 euros, the money lost will be

$$\text{Losses} = 9.65\ \mathrm{kg} \times \frac{500\ €}{35\ \mathrm{kg}} = 137.86\ €$$

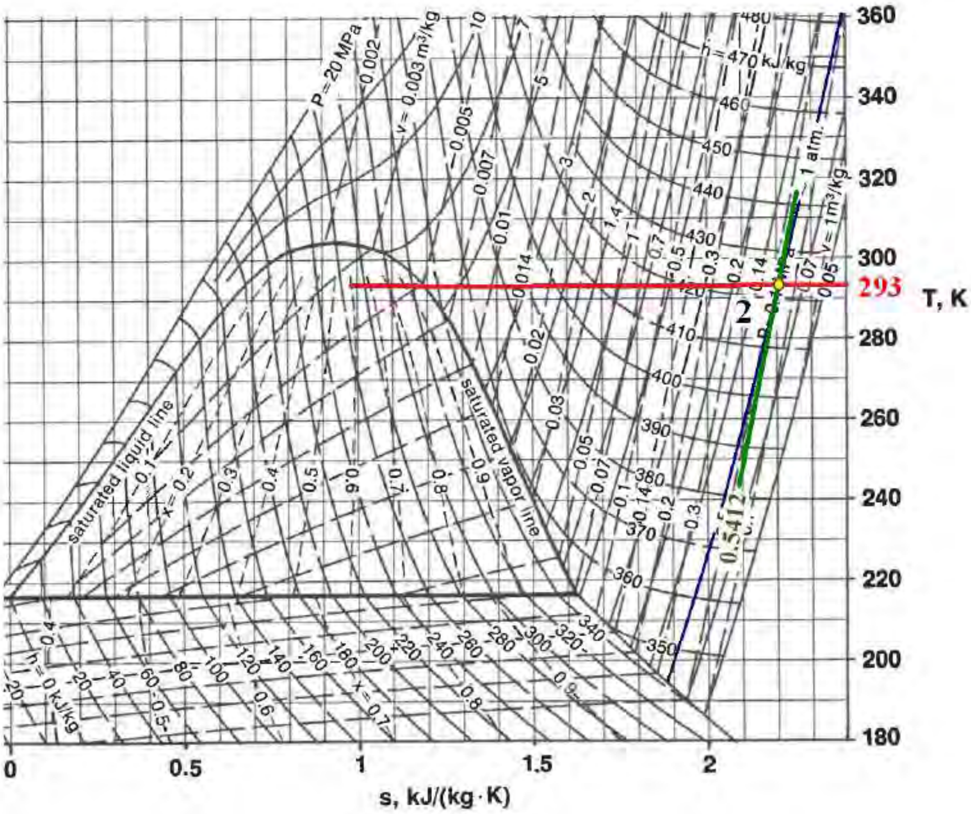
Question c. The vapor mass that remains in a cylinder after a total isothermal emptying can be calculated as

$$M_{v_2} = \frac{V_{useful}}{\hat{V}_{v_2}}$$

where $\hat{V}_{v_2}$ is the specific volume of the vapor at the point in which the isotherm

$$T_2(\mathrm{K}) = T_1(\mathrm{K}) = 20°\mathrm{C} + 273 = 293\ \mathrm{K}$$

intersects the isobar corresponding to the ambient pressure ($P_2 \approx 0.1$ MPa). In figure V.3 of this book's appendix V (*TS* diagram for CO_2) this specific volume is approximately of 0.5412 m^3/kg.

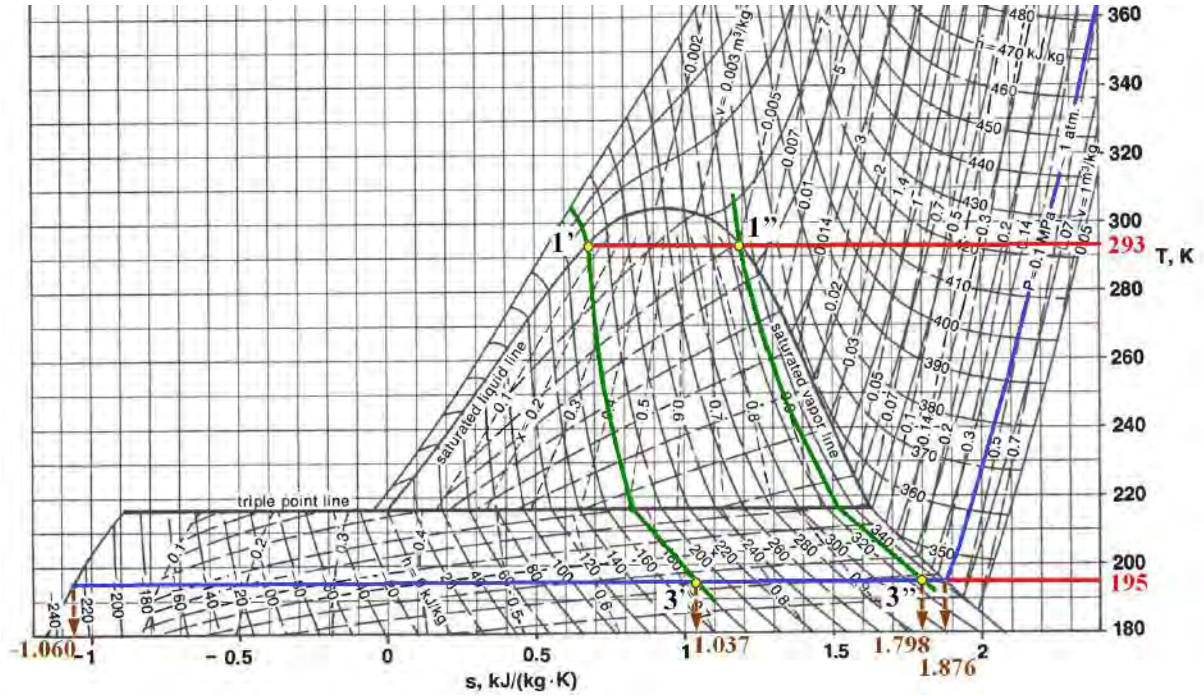


$$M_{v_2} = \frac{V_{useful}}{\hat{V}_{v_2}} = \frac{0.050\ \text{m}^3}{\left(0.5412\ \frac{\text{m}^3}{\text{kg}}\right)} = 0.0924\ \text{kg}$$

specific volume that, within the graphical reading error, coincides with that calculated employing the ideal gas law

$$\hat{V}_{v_2} = \frac{RT_2}{\mathfrak{W}P_2} = \frac{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(293\ \text{K})}{\left(44.01\,\frac{\text{g}}{\text{mol-g}}\right)(1\ \text{atm})} = 0.5459\,\frac{\text{L}}{\text{g}} = 0.5459\ \frac{\text{m}^3}{\text{kg}}$$

Regarding the isenthalpic emptying of cylinder containing CO₂, it has to be pointed out that, since its triple point is at a pressure higher than 1 atm, both the emptying from the liquid phase (presence of siphon tube) and from the vapor phase (absence of siphon tube) will generate a biphasic mixture of solid (dry ice or carbon dioxide snow) and vapor.



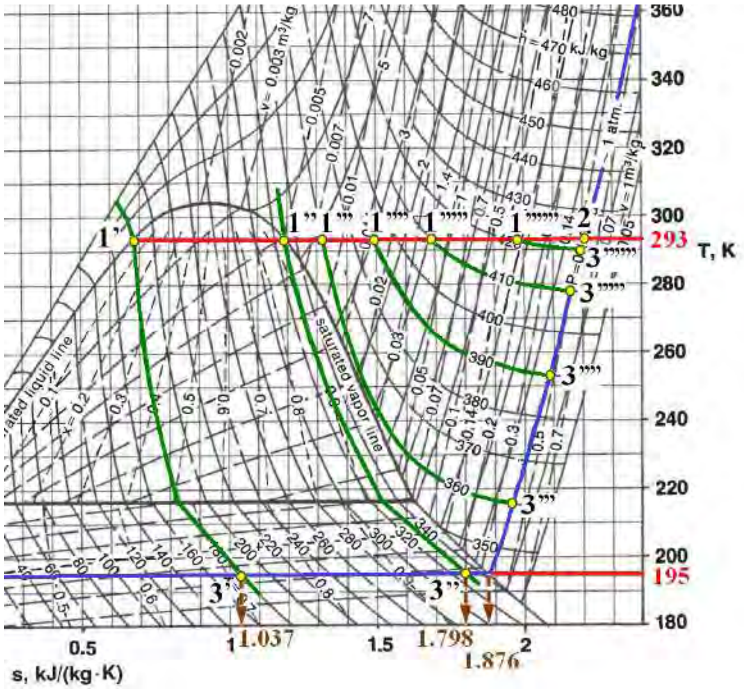
In the case of **emptying from the vapor phase**, the isenthalpic line that passes through the intersection of the 293 K isotherm with the saturated vapor line (point 1”) will be followed graphically as operating line until that isenthalpic crosses the 0.1 MPa isobar (point 3”). If the evacuation is so slow that the liquid takes from the environment the necessary heat for compensating the evaporation and there are no energy losses due to friction, there will isothermicity inside the cylinder (the mixture of liquid and vapor remains as a balance between 1’ and 1’ in progressively evolving proportions until only 1” remains, i.e., the liquid is exhausted).

Similarly, when **emptying from the liquid phase**, the process will follow the isenthalpic line from 1’ to 3’. If this evacuation is also slow (which is less likely than if the cylinder was emptied from the vapor phase), there will be isothermicity inside the bottle and a mixture of liquid and vapor, but when the liquid is exhausted, vapor will begin to come out and the system will jump abruptly from route 1’– 3’ to 1”– 3”.

Furthermore, if the emptying is sudden (flash), the vapor that comes out has the conditions at points 3’ or 3” (temperature of 195 K or -78ºC) depending on the phase from which the cylinder is emptied. And by combining the balances of entropy and mass, the proportions of solid would be

$$\frac{M_{s_{3'}}}{M_{v_{3'}}+M_{s_{3'}}}=\frac{\left(\hat{S}^{sat}_{v_{3'}}-\hat{S}_{3'}\right)}{\left(\hat{S}^{sat}_{v_{3'}}-\hat{S}^{sat}_{s_{3'}}\right)}=\frac{[1.876-1.037]}{[1.876-(-1.060)]}=0.2858$$

$$\frac{M_{s_{3''}}}{M_{v_{3''}}+M_{s_{3''}}}=\frac{\left(\hat{S}^{sat}_{v_{3''}}-\hat{S}_{3''}\right)}{\left(\hat{S}^{sat}_{v_{3''}}-\hat{S}^{sat}_{s_{3''}}\right)}=\frac{[1.876-1.798]}{[1.876-(-1.060)]}=0.0266$$



Beyond 1”– 3”, if the isothermicity is maintained in the cylinder (receiving enough heat from the environment to compensate the alteration due to the mass loss through the nozzle) the vapor inside could follow the path 1’”, 1””... until reaching 2, while the vapor that exits the cylinder would follow the path 3’”, 3””... until reaching 2, as shown in the figure to the left of this paragraph.

On the other hand, when the isothermal assumption cannot be maintained, the liquid + vapor mixture inside the cylinder will likely cool, following a polytropic line until leaving the biphasic zone... and what comes out of the nozzle will have different characteristics of pressure, temperature and liquid/vapor or solid/vapor proportions at each moment.

4.24. Carbon dioxide is a substance relatively cheap, chemically inert and with a technologically accessible critical point, which makes it suitable for certain applications such as supercritical chromatography. A chromatograph of this type utilizes CO_2 as a carrier fluid, taking it as a saturated liquid from commercially available cylinders, and then subjecting it to a series of transformations (isentropic compression followed by isobaric heating) before operation.

These cylinders are usually supplied with a useful volume of 2 ft^3, a net CO_2 load of 80 lb and a price of 425 pounds.

- **a) Calculate the masses of liquid and vapor phases in the cylinder at half load, assuming a thermal equilibrium with a laboratory environment at 68°F. Calculate the volume occupied by each phase as well.**
- **b) Evaluate the previous masses and volumes when the cylinder was just supplied.**
- **c) Estimate the amount of money that is theoretically lost (because unusable vapor) when the cylinders are returned to the manufacturer for refilling.**
- **d) Indicate a procedure to ensure that what enters the chromatograph is liquid and not vapor.**
- **e) Determine the pressures that would be reached in the cylinder if, at half load, accidental heatings increase the temperature to 40°C or to 80°C.**
- **f) Qualitatively indicate on a *PV*(*T*) diagram what would happen if the operator did not realize that the liquid had been exhausted and the chromatograph, programmed to work at 120 bar, was being fed with vapor.**

Firstly, units are converted through the factors of appendix I

$$M_{initial} = 80\ \text{lb} \times \frac{0.454\ \text{kg}}{1\ \text{lb}} = 36.32\ \text{kg}$$

$$V_{useful} = 2\ \text{ft}^3 \times \frac{0.028\ \text{m}^3}{1\ \text{ft}^3} = 0.056\ \text{m}^3$$

$$T_1(°\text{C}) = \frac{68°\text{F} - 32}{1.8} = 20°\text{C}$$

$$T_1(\text{K}) = 20°\text{C} + 273 = 293\ \text{K}$$

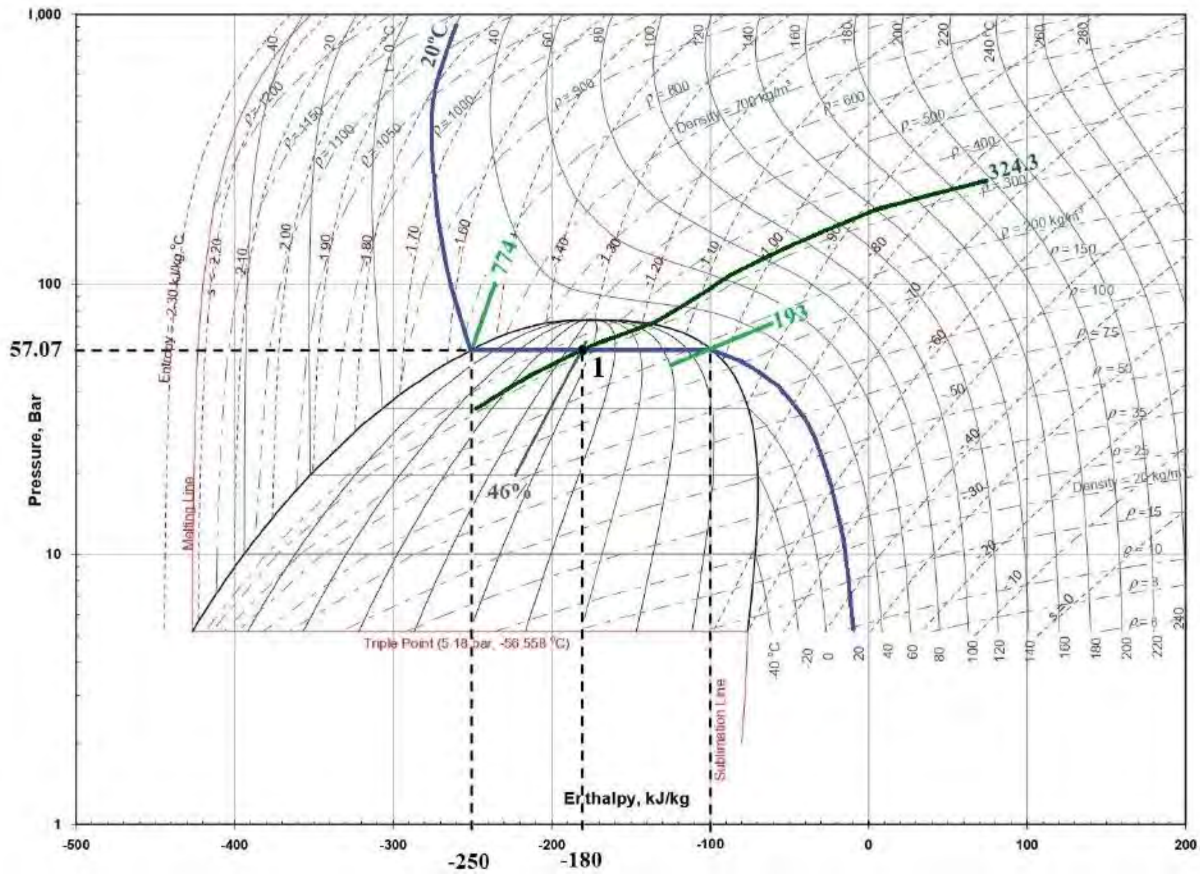
$$T_2(\text{K}) = 40°\text{C} + 273 = 313\ \text{K}$$

$$T_3(\text{K}) = 80°\text{C} + 273 = 353\ \text{K}$$

Question a. At half load, there will be 18.16 kg, so the mass density is

$$\hat{\rho}_{half} = \frac{M_{half}}{V_{useful}} = \frac{18.16\ \text{kg}}{0.056\ \text{m}^3} = 324.3\ \frac{\text{kg}}{\text{m}^3}$$

and in figure V.2 of appendix V it is observed that the intersection of this isochore with the T_1=20ºC isotherm occurs in the biphasic zone, at a pressure P_1= 57.07 bar and on an approximate quality line of 46% (0.46×18.16 kg= 8.35 kg vapor).



This last value can be further improved by the densities of the saturated liquid (774 kg/m^3), the saturated vapor (193 kg/m^3) and the combination of the volume balance ($M_{half}/\hat{\rho}_{half} = M_l/\hat{\rho}_l^{sat} + M_v/\hat{\rho}_v^{sat}$) with the mass one ($M_{half} = M_l + M_v$), which give

$$M_{v_1} = M_{half} \frac{\left(\frac{1}{\hat{\rho}_{half}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_1}^{sat}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)} = (18.16\ \text{kg}) \frac{\left(\frac{1}{324.3} - \frac{1}{774}\right)}{\left(\frac{1}{193} - \frac{1}{774}\right)} = 8.365\ \text{kg}$$

$$M_{l_1} = M_{half} - M_{v_1} = 18.16 - 8.365 = 9.795\ \text{kg}$$

or by combining the enthalpy balance ($M_{half}\hat{H}_{half} = M_l\hat{H}_l + M_v\hat{H}_v$) and the mass one, when the corresponding enthalpies have been read in the diagram

$$M_{v_1} = M_{half}\frac{\left(\hat{H}_{half} - \hat{H}_{l_1}^{sat}\right)}{\left(\hat{H}_{v_1}^{sat} - \hat{H}_{l_1}^{sat}\right)} = (18.16\ \text{kg})\frac{[-180-(-250)]}{[-100-(-250)]} = 8.47\ \text{kg}$$

$$M_{l_1} = M_{half} - M_{v_1} = 18.16 - 8.47 = 9.69\ \text{kg}$$

Values may slightly differ depending on the difficulty for reading and interpolating graphical data. Therefore, to determine the volumes that the vapor and liquid amounts occupy, it seems convenient to employ those evaluated by means of the mass and volume balances

$$V_{v_1} = \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} = \frac{8.365\ \text{kg}}{193\ \frac{\text{kg}}{\text{m}^3}} = 0.0433\ \text{m}^3$$

$$V_{l_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} = \frac{9.795\ \text{kg}}{774\ \frac{\text{kg}}{\text{m}^3}} = 0.0127\ \text{m}^3$$

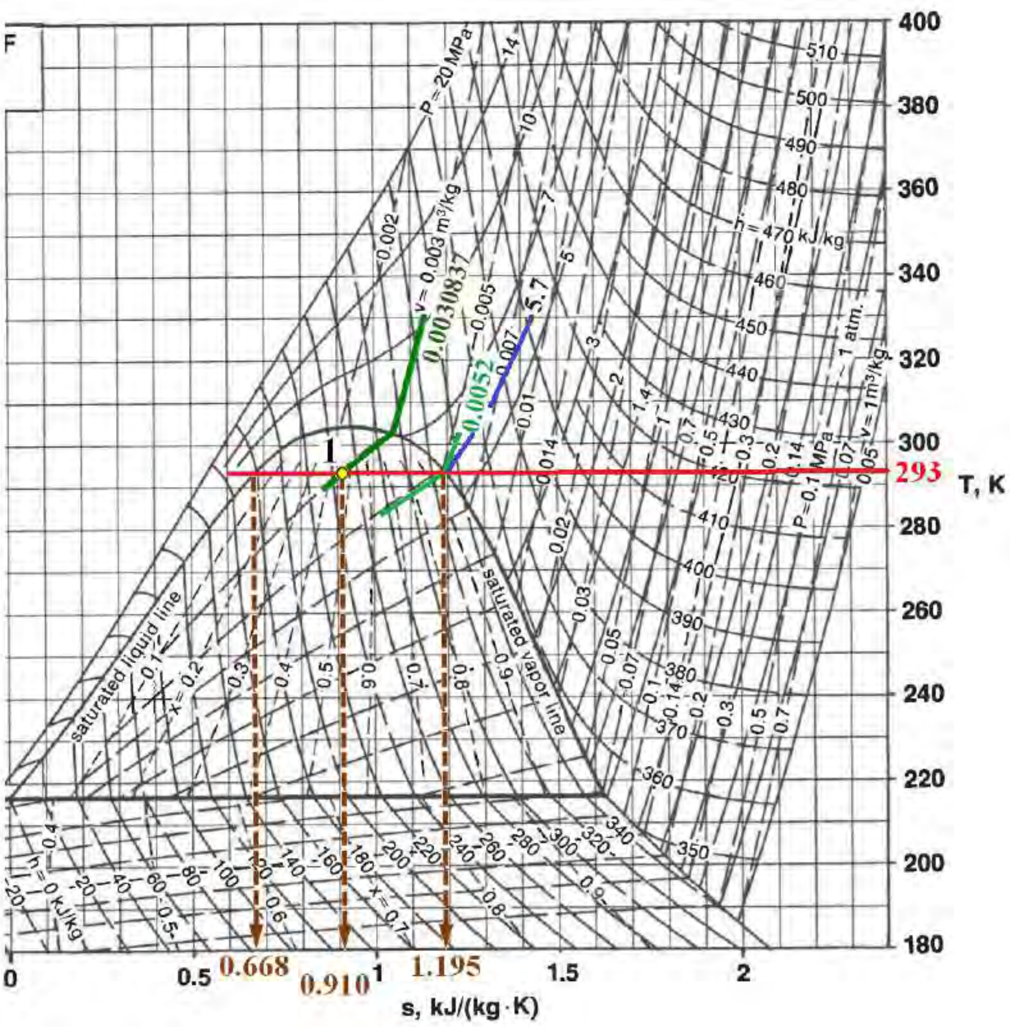
On the other hand, this question of the problem can also be solved through figure V.3 of appendix V,

$$\hat{V}_{half} = \frac{V_{useful}}{M_{half}} = \frac{0.056\ \text{m}^3}{18.16\ \text{kg}} = 0.0030837\ \frac{\text{m}^3}{\text{kg}}$$

The main difference is that isochores do not appear for specific volumes lower than 0.002 m^3/kg; thus, it is only feasible to interpolate the volume of saturated vapor (0.0052 m^3/kg). The amounts of vapor and liquid have to be estimated by combining the entropy balance ($M_{half}\hat{S}_{half} = M_l\hat{S}_l + M_v\hat{S}_v$) and that of mass, which gives a result formally analogous to the combination of the enthalpy and mass balances

$$M_{v_1} = M_{half}\frac{\left(\hat{S}_{half} - \hat{S}_{l_1}^{sat}\right)}{\left(\hat{S}_{v_1}^{sat} - \hat{S}_{l_1}^{sat}\right)} = (18.16\ \text{kg})\frac{(0.910-0.668)}{(1.195-0.668)} = 8.339\ \text{kg}$$

$$M_{l_1} = M_{half} - M_{v_1} = 18.16 - 8.339 = 9.821\ \text{kg}$$



After finding the corresponding masses, from the specific volume

$$V_{v_1} = \hat{V}_{v_1}^{sat} M_{v_1} = \left(0.0052\ \frac{\text{m}^3}{\text{kg}}\right)(8.339\ \text{kg}) = 0.04336\ \text{m}^3$$

and the volume of the saturated liquid is directly calculated from the volume balance

$$V_{l_1} = V_{cylinder} - V_{v_1} = 0.056\ \text{m}^3 - 0.04336\ \text{m}^3 = 0.01264\ \text{m}^3$$

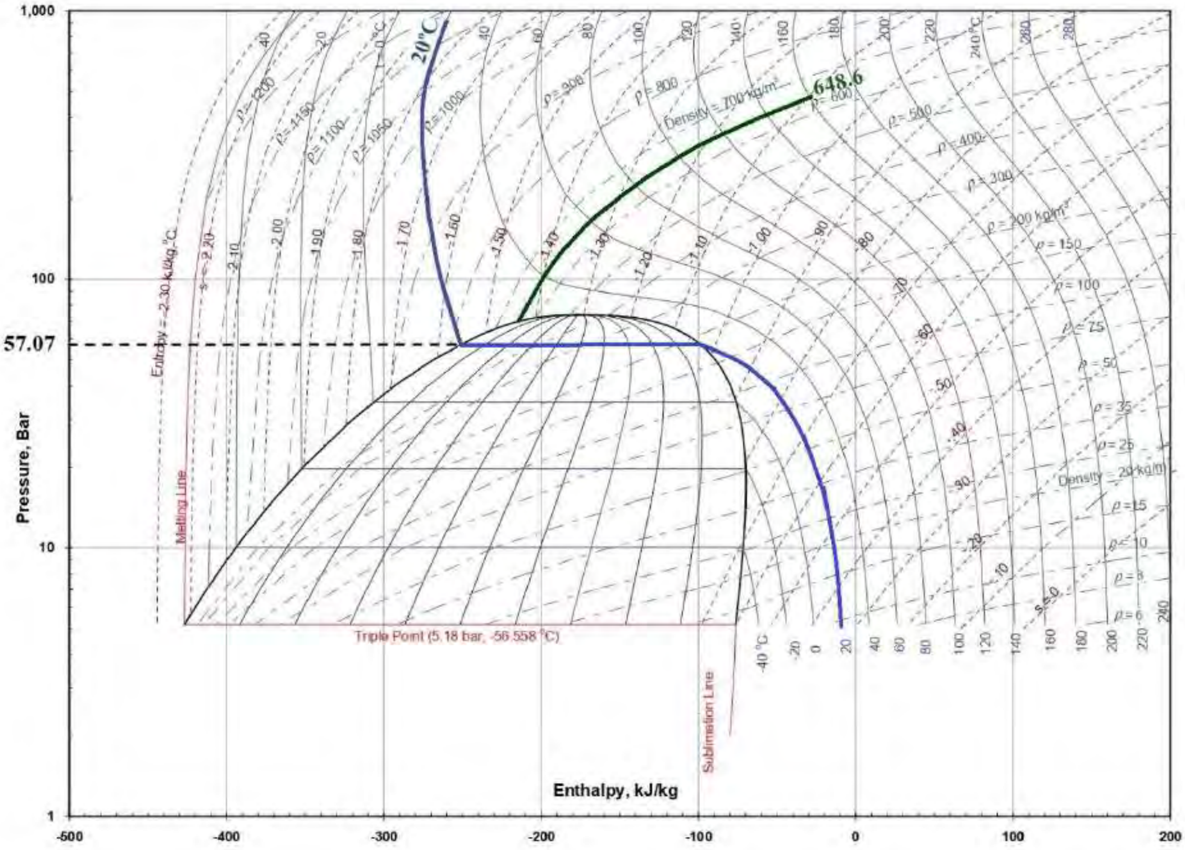
By interpolating the isobar that passes through the intersection of T_1= 293 K with the saturated vapor line, it is obtained a pressure P_2= 5.7 MPa.

Question b. When the cylinder was just supplied

$$\hat{\rho}_{tot} = \frac{M_{tot}}{V_{useful}} = \frac{36.32\ \text{kg}}{0.056\ \text{m}^3} = 648.6\ \frac{\text{kg}}{\text{m}^3}$$

$$\hat{V}_{tot} = \frac{V_{useful}}{M_{tot}} = \frac{0.056\ \mathrm{m}^3}{36.32\ \mathrm{kg\ kg}} = 0.0015419\ \frac{\mathrm{m}^3}{\mathrm{kg}}$$

This question cannot be solved with figure V.3 because, as noted above, it does not contain isochores for specific volumes lower than 0.002 m^3/kg (and only below 0.003 m^3/kg do they enter the biphasic zone). However, it cannot be completely solved with figure V.2 either, since the isochores corresponding to densities higher than 400 kg/m^3 are not drawn in the biphasic zone. Fortunately, visual inspection indicates that the crossing between the 648.6 kg/m^3 isochore and the 20ºC isotherm occurs in this biphasic region, generating a mixture of saturated liquid and saturated vapor with the same densities as in question **a**.



$$M_{v_1} = M_{tot}\frac{\left(\frac{1}{\hat{\rho}_{tot}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_1}^{sat}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)} = (36.32\ \mathrm{kg})\frac{\left(\frac{1}{648.6} - \frac{1}{774}\right)}{\left(\frac{1}{193} - \frac{1}{774}\right)} = 2.333\ \mathrm{kg}$$

$$M_{l_1} = M_{tot} - M_{v_1} = 36.32 - 2.333 = 33.987\ \mathrm{kg}$$

$$V_{v_1} = \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} = \frac{2.333\ \mathrm{kg}}{193\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.0121\ \mathrm{m}^3$$

$$V_{l_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} = \frac{33.987\ \mathrm{kg}}{774\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.0439\ \mathrm{m}^3$$

Question c. When the liquid phase is exhausted, the entire useful volume of the cylinder will be occupied by saturated gas, so

$$M_v = V_{useful}\hat{\rho}_{v_1}^{sat} = \frac{V_{useful}}{\hat{V}_{v_1}^{sat}}$$

and since 36.32 kg of CO_2 have cost 425 pounds, the monetary losses will be

$$\mathrm{Losses} = M_v\ (\mathrm{kg}) \times \frac{425}{36.32\ \mathrm{kg}}$$

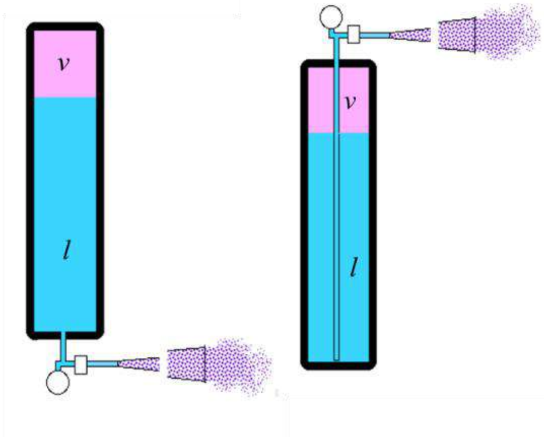
By employing the saturated vapor density of figure V.2

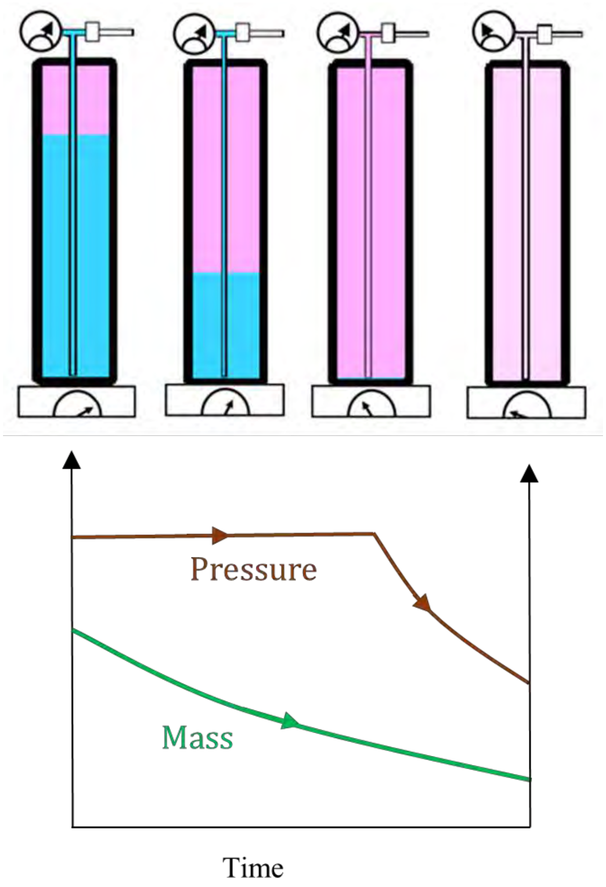
$$\mathrm{Losses} = (0.056\ \mathrm{m}^3)\left(193\ \frac{\mathrm{kg}}{\mathrm{m}^3}\right) \times \frac{425\ £}{36.32\ \mathrm{kg}} = 126.47\ £$$

By employing the specific volume of figure V.3

$$\mathrm{Losses} = \frac{0.056\ \mathrm{m}^3}{\left(0.0052\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right)} \times \frac{425\ £}{36.32\ \mathrm{kg}} = 126.02\ £$$

Question d. If the cylinder does not have a siphon tube, it must be inverted to extract the liquid carbon dioxide, whereas if it have a siphon tube, the inversion will not be necessary.





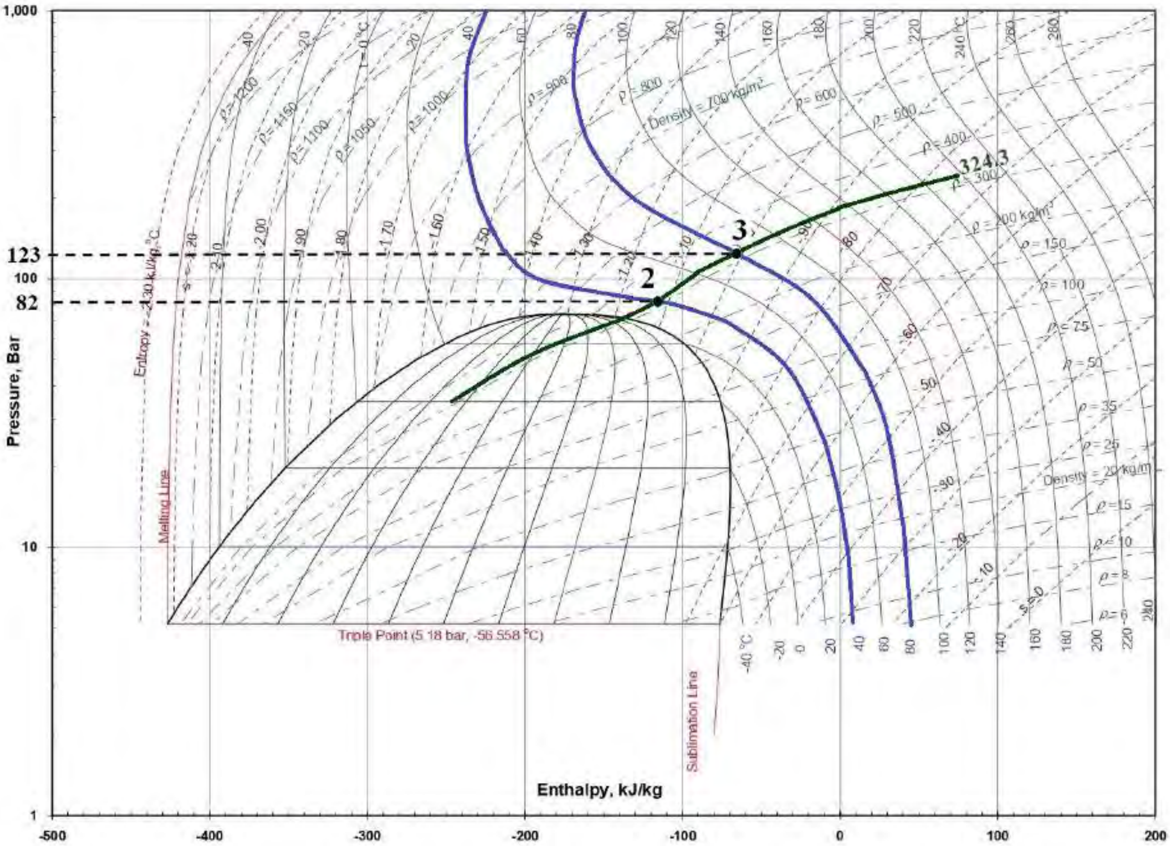
Due to the fact that the pressure does not vary as long as there is a mixture of liquid and vapor inside the cylinder, a first thought is to place a pressure gauge in the cylinder to determine the moment of its replacement. However, this does not allow to know how much liquid phase remains, and therefore does not assure a time margin to replace the cylinder (to avoid alterations in the flow and the pressure of the chromatograph). It is then recommended to employ a weighing scale, and when the mass approaches

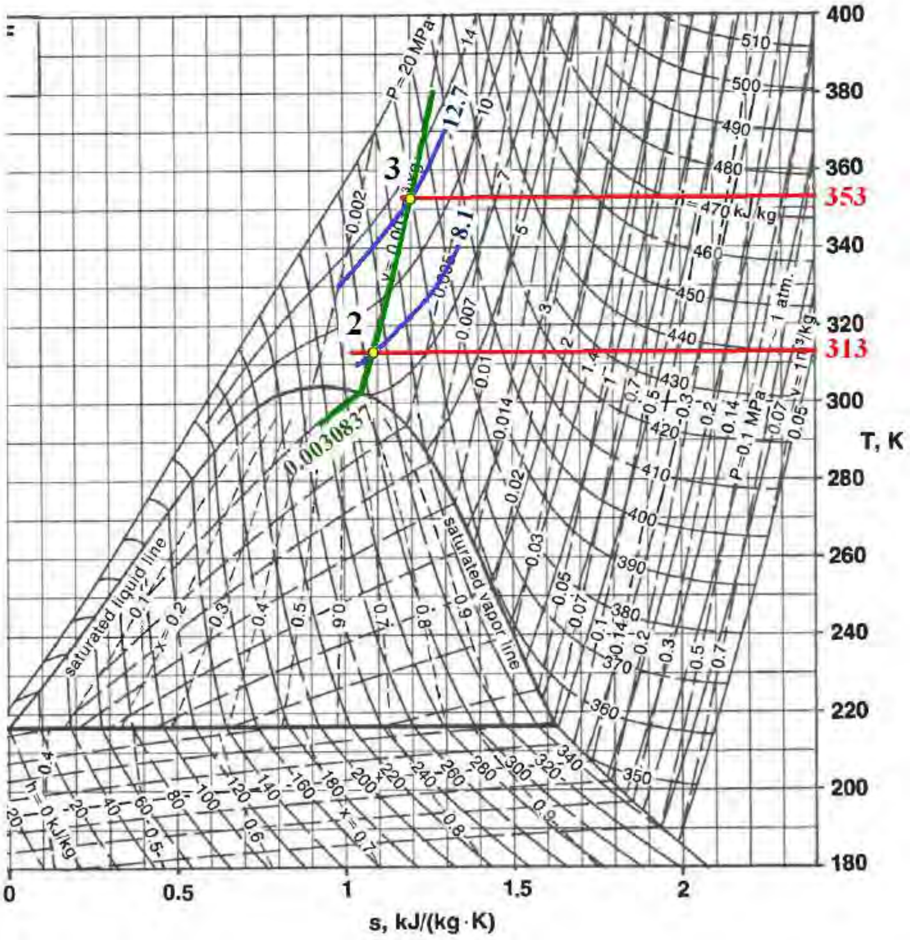
$$M_v = V_{useful}\hat{\rho}_{v_1}^{sat} = \frac{V_{useful}}{\hat{V}_{v_1}^{sat}}$$

to prepare a new cylinder in reserve.

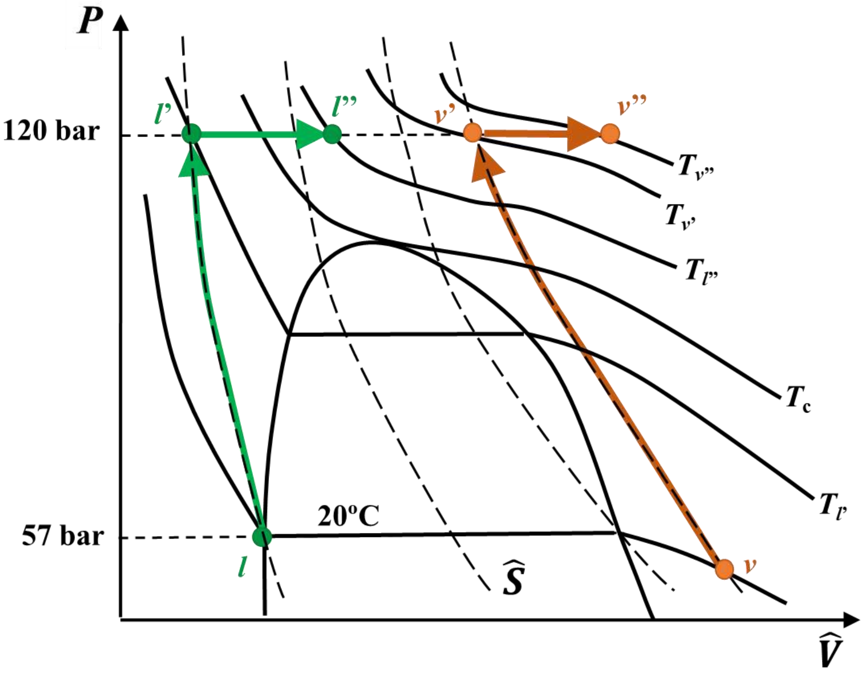
Question e. Since the mass and the volume of the system are the same as in question **a**, heating will occur at a constant specific density/volume. The requested pressures will be those where the 324.3 kg/m^3 isochore intersects the isotherms T_2= 40ºC and T_3= 80ºC (Figure V.2) or where the 0.0030837 m^3/kg isochore crosses the isotherms T_2= 313 K and T_3= 353 K (Figure V.3).

In the *PH* diagram, results are 82 bar at 40ºC and 123 bar at 80ºC. In the *TS*, 8.1 MPa at 313 K and 12.7 MPa at 353 K.


1,000
123
100
82
10
1
Pressure, Bar
Enthalpy, kJ/kg
-500
-400
-300
-200
-100
0
100
200
3
2
324.3
Triple Point (5.18 bar, -56.558 °C)
Melting Line
Sublimation Line
Entropy = 2.30 kJ/kg °C
Density = 700 kg/m³
Density = 20 kg/m³


400
380
360
353
340
320
313
300
280
260
240
220
200
180
T, K
0
0.5
1
1.5
2
s, kJ/(kg·K)
3
2
12.7
8.1
0.0030837
P = 20 MPa
P = 0.1 MPa
1 atm.
470 kJ/kg
saturated liquid line
saturated vapor line
h = 0 kJ/kg

Question f. When the chromatograph works with liquid from the cylinder (*l*), isentropically compresses it to 120 bar (*l*') and then isobarically heats it (*l*"). When the chromatograph works with vapor (*v*), the properties of this vapor compressed to 120 bar (*v*') and subsequently heated (*v*") are very different from those of the liquid (see, for example, the specific volume). Furthermore, as the pressure varies continuously (from 57 bar to the atmospheric one), the position of points *v*, *v*' and *v*" will not stop changing.



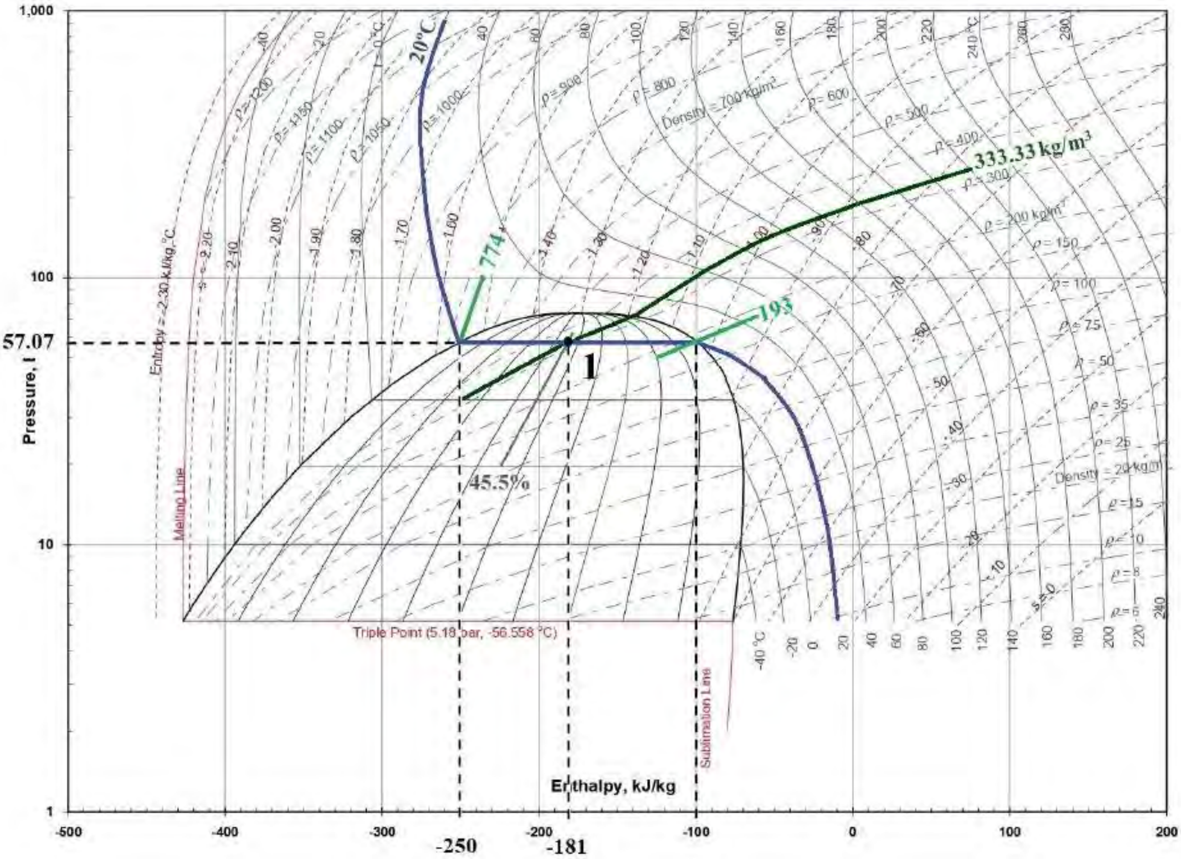
4.25. Liquefied carbon dioxide is commercially distributed in cylinders with devices that allow the discharge from the liquid phase or from the vapor one. A cylinder has a useful volume of 150 liters and contains 50 kg of this substance. Calculate:

- **a) Conditions and proportions of the content inside it (assuming thermal equilibrium with the laboratory environment at 20ºC).**
- **b) Maximum and minimum amount of CO_2 that could be in the cylinder at 20ºC for the same reading of the pressure gauge.**
- **c) Conditions and proportions if an accident increases temperature to 50ºC.**
- **d) Mass in the cylinder if the pressure at 20ºC cannot be exceeded in the aforementioned accident.**

Question a. Let point 1 indicate the initial conditions of the cylinder

$$\hat{\rho}_1 = \frac{M_1}{V_{useful}} = \frac{50\ \text{kg}}{0.15\ \text{m}^3} = 333.33\ \frac{\text{kg}}{\text{m}^3}$$

In figure V.2 of this book's appendix V, it can be seen that the intersection of this isochore with the isotherm T_1=20ºC occurs in the biphasic zone so that the CO_2 state is a mixture of saturated liquid ($\hat{\rho}_l^{sat} = 774$ kg/m^3, $\hat{H}_l$ =-250 kJ/kg) and saturated vapor ($\hat{\rho}_v^{sat} = 193$ kg/m^3, $\hat{H}_v$ =-100 kJ/kg) at 57.07 bar and with an approximate title or quality of 45.5% (0.455×50 kg=22.75 kg).



The amount of vapor (and of liquid) can also be calculated by combining the enthalpy balance ($M_1\widehat{H}_1 = M_l\widehat{H}_l + M_v\widehat{H}_v$) with the mass one ($M_1 = M_l + M_v$). After reading the global enthaly of the biphasic mixture (-181 kJ/kg)

$$M_{v_1} = M_1 \frac{\left(\widehat{H}_1 - \widehat{H}_{l_1}^{sat}\right)}{\left(\widehat{H}_{v_1}^{sat} - \widehat{H}_{l_1}^{sat}\right)} = (50\ \mathrm{kg}) \frac{[-181 - (-250)]}{[-100 - (-250)]} = 23\ \mathrm{kg}$$

$$M_{l_1} = M_1 - M_{v_1} = 50 - 23 = 27\ \mathrm{kg}$$

or by the combination of the volume balance ($M_1/\hat{\rho}_1 = M_v/\hat{\rho}_l^{sat} + M_v/\hat{\rho}_v^{sat}$) with the mass one

$$M_{v_1} = M_1 \frac{\left(\frac{1}{\hat{\rho}_1} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)}{\left(\frac{1}{\hat{\rho}_{v_1}^{sat}} - \frac{1}{\hat{\rho}_{l_1}^{sat}}\right)} = (50\ \mathrm{kg}) \frac{\left(\frac{1}{333.33} - \frac{1}{774}\right)}{\left(\frac{1}{193} - \frac{1}{774}\right)} = 21.958\ \mathrm{kg}$$

$$M_{l_1} = M_1 - M_{v_1} = 50 - 21.958 = 28.042\ \mathrm{kg}$$

and in this last case, the volumes occupied by each phase are

$$V_{l_1} = \frac{M_{l_1}}{\hat{\rho}_{l_1}^{sat}} = \frac{28.042\ \mathrm{kg}}{774\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.0362\ \mathrm{m}^3$$

$$V_{v_1} = \frac{M_{v_1}}{\hat{\rho}_{v_1}^{sat}} = \frac{21.958\ \mathrm{kg}}{193\ \frac{\mathrm{kg}}{\mathrm{m}^3}} = 0.1138\ \mathrm{m}^3$$

In addition to figure V.2, figure V.3 can be employed to solve this question. In it, the intersection of the isochore

$$\hat{V}_1 = \frac{0.15\ \mathrm{m}^3}{50\ \mathrm{kg}} = 0.003\ \frac{\mathrm{m}^3}{\mathrm{kg}}$$

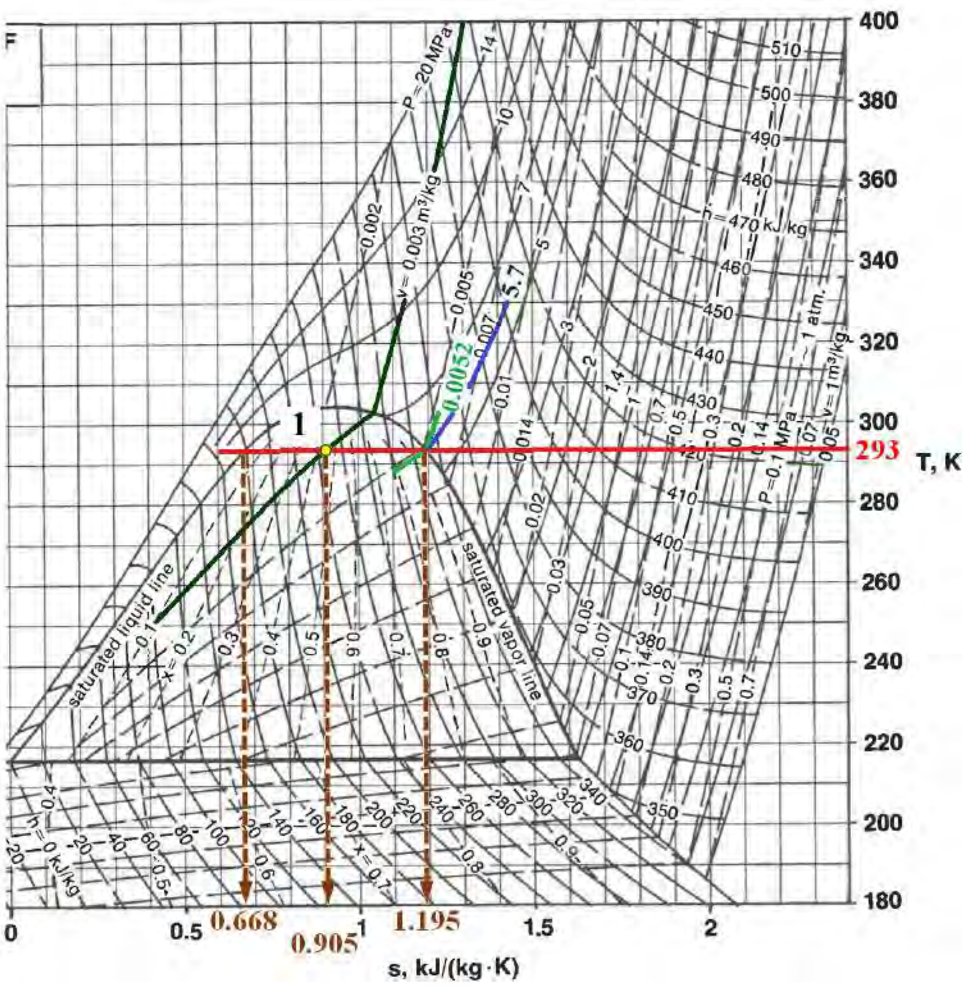
with the isotherm

$$T_1(\mathrm{K}) = 20℃ + 273 = 293\ \mathrm{K}$$

allows calculating the amounts of vapor and liquid by combining the mass balance with the entropy one ($M_1\hat{S}_1 = M_l\hat{S}_l + M_v\hat{S}_v$), since there are not isochores for specific volumes lower than 0.002 m^3/kg, and therefore the combination of mass and volume balances cannot be applied.

$$M_{v_1} = M_1 \frac{\left(\hat{S}_1 - \hat{S}_{l_1}^{sat}\right)}{\left(\hat{S}_{v_1}^{sat} - \hat{S}_{l_1}^{sat}\right)} = (50\ \mathrm{kg}) \frac{(0.905 - 0.668)}{(1.195 - 0.668)} = 22.486\ \mathrm{kg}$$

$$M_{l_1} = M_1 - M_{v_1} = 50 - 22.486 = 27.514\ \mathrm{kg}$$



However, it is feasible interpolating the saturated vapor specific volume (0.0052 m^3/kg), multiplying it by the vapor mass to find the volume occupied by this phase and then subtracting it from the total volume to evaluate the volume occupied by the liquid mass.

$$V_{v_1} = \hat{V}_{v_1}^{sat} M_{v_1} = \left(0.0052 \ \frac{\mathrm{m}^3}{\mathrm{kg}}\right)(22.486 \ \mathrm{kg}) = 0.117 \ \mathrm{m}^3$$

And the saturated liquid volume is obtained from the volume balance

$$V_{l_1} = V_{useful} - V_{v_1} = 0.15 \ \mathrm{m}^3 - 0.117 \ \mathrm{m}^3 = 0.033 \ \mathrm{m}^3$$

If V_{l_1} is divided by M_{l_1} the specific volume of the liquid (0.0012 m^3/kg) is obtained.

Question b. The maximum amount of carbon dioxide at 20ºC will be reached when the entire volume of the cylinder is filled with liquid, so

$$M_{max} = \hat{\rho}_{l_1}^{sat} V_{useful} = \frac{V_{useful}}{\hat{V}_{l_1}^{sat}}$$

and the minimum quantity at 20ºC when only vapor occupies the entire useful volume

$$M_{min} = \hat{\rho}_{v_1}^{sat} V_{useful} = \frac{V_{useful}}{\hat{V}_{v_1}^{sat}}$$

By taking data from figure V.2

$$M_{max} = \left(774\ \frac{\mathrm{kg}}{\mathrm{m^3}}\right)(0.15\ \mathrm{m^3}) = 116.1\ \mathrm{kg}$$

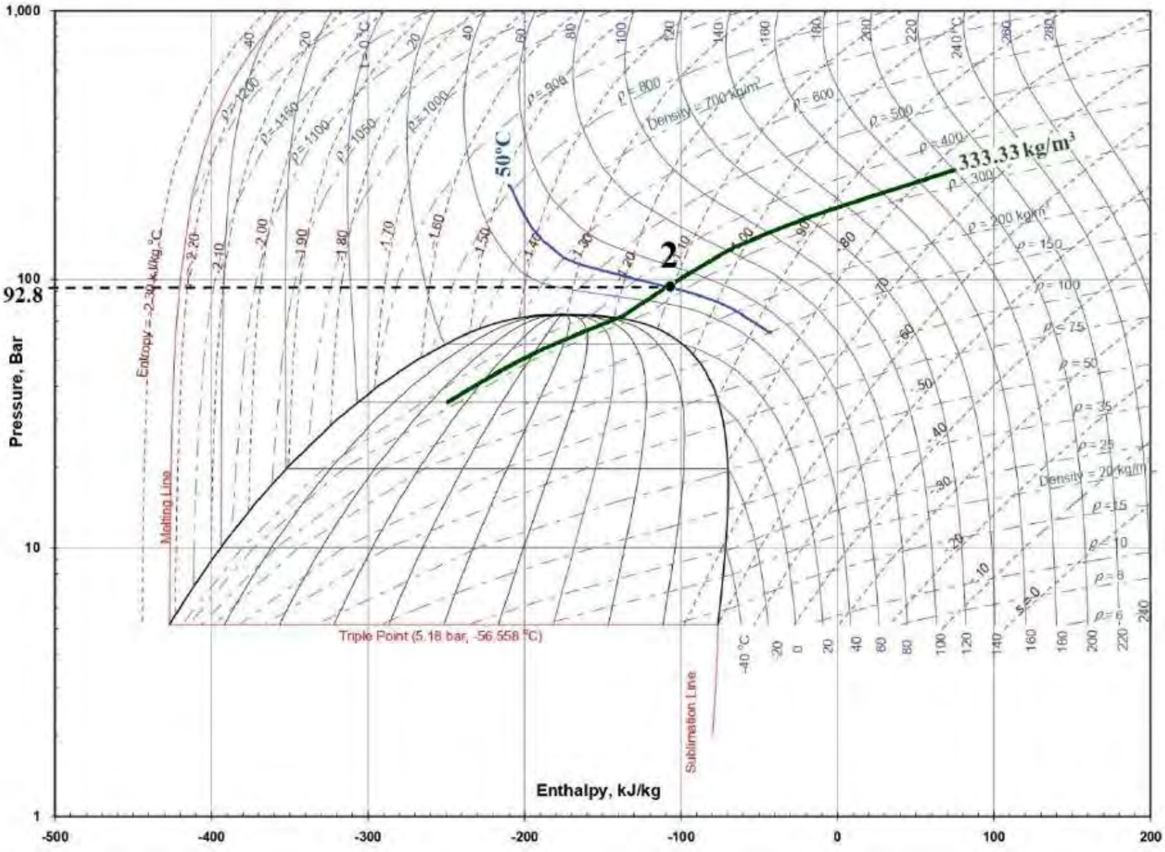
$$M_{min} = \left(193\ \frac{\mathrm{kg}}{\mathrm{m^3}}\right)(0.15\ \mathrm{m^3}) = 28.95\ \mathrm{kg}$$

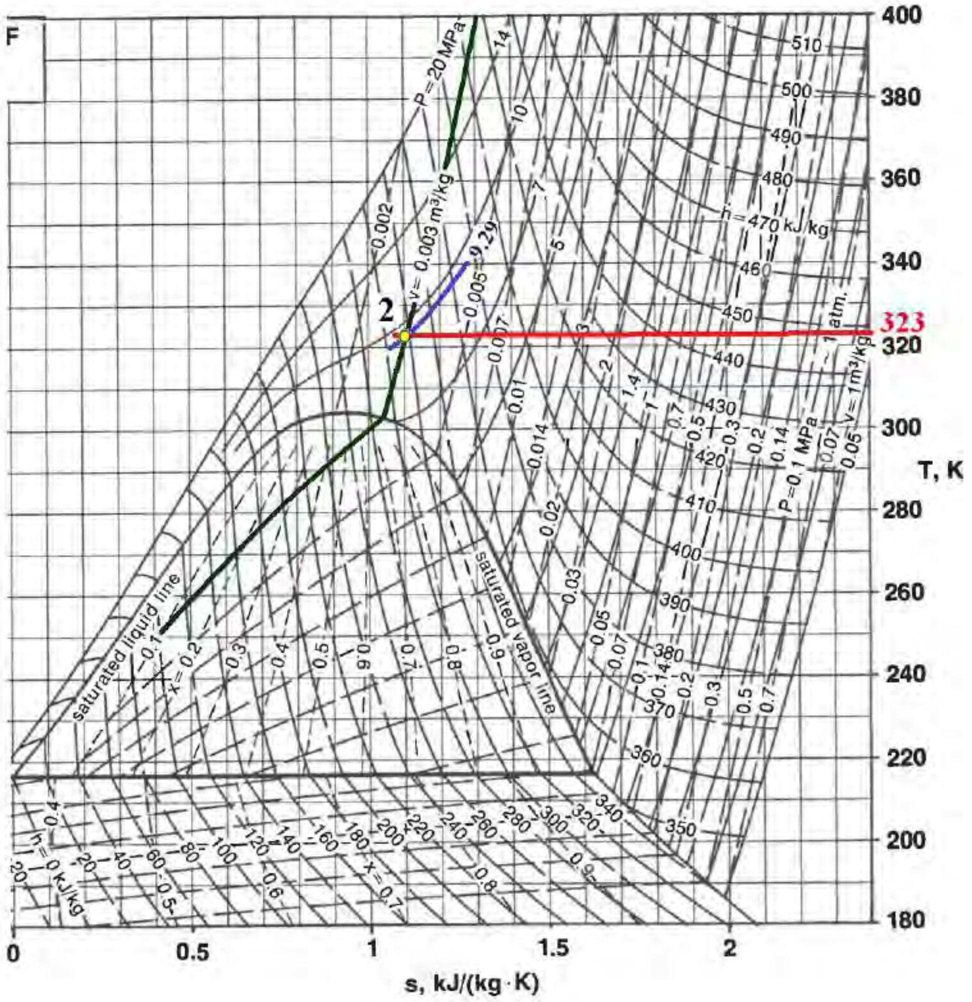
and those from figure V.3

$$M_{max} = \frac{0.15\ \mathrm{m^3}}{\left(0.0012\ \frac{\mathrm{m^3}}{\mathrm{kg}}\right)} = 125\ \mathrm{kg}$$

$$M_{min} = \frac{0.15\ \mathrm{m^3}}{\left(0.0052\ \frac{\mathrm{m^3}}{\mathrm{kg}}\right)} = 28.85\ \mathrm{kg}$$

Question c. After accidental heating to 50ºC (323 K), CO_2 is a gas or supercritical fluid at a pressure P_2=92.8 bar (*PH* diagram) or P_2=9.29 MPa (*TS* diagram).





Question d. If in figure V.2 the pressure cannot exceed 57.07 bar, the intersection of this isobar with the 50ºC isotherm will give the density at point 3, which is of 128 kg/m^3.

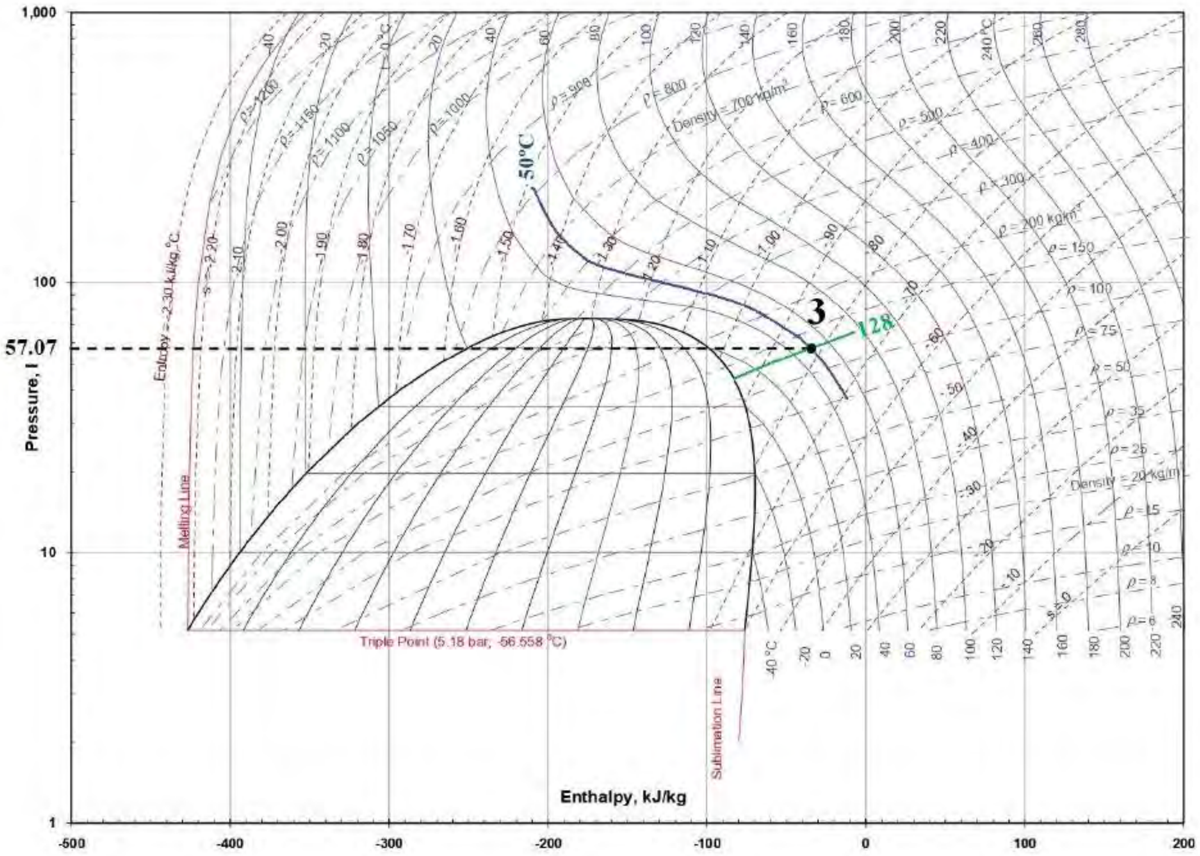
And the mass

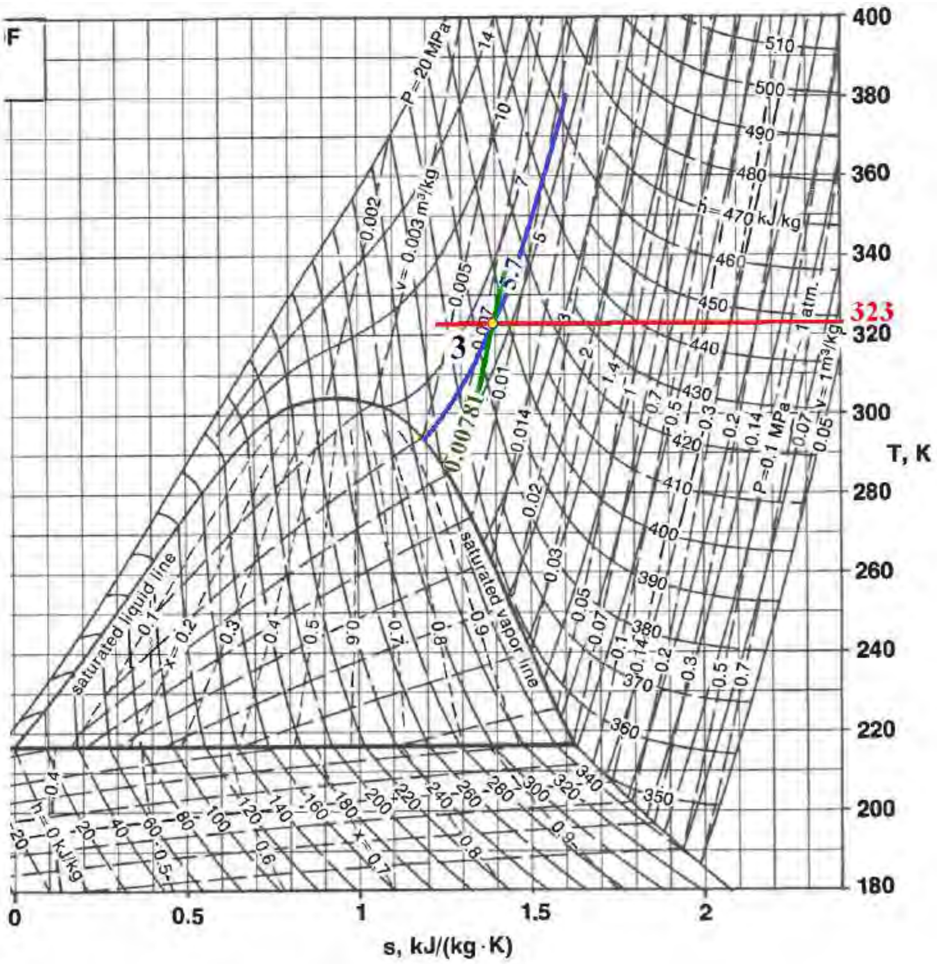
$$M_3 = \hat{\rho}_3 V_{useful} = \left(128\ \frac{\text{kg}}{\text{m}^3}\right)(0.15\ \text{m}^3) = 19.2\ \text{kg}$$

By operating in an analogous way in figure V.3 with the pressure of 5.7 MPa, the specific volume found is of 0.00781 m^3/kg; thus

$$M_3 = \frac{V_{useful}}{\hat{V}_3} = \frac{0.15\ \text{m}^3}{\left(0.00781\ \frac{\text{m}^3}{\text{kg}}\right)} = 19.21\ \text{kg}$$

And in both cases, the whole content at 20ºC will be a superheated vapor.


Pressure, I
Enthalpy, kJ/kg
57.07
50°C
3
128
Triple Point (5.18 bar, -56.558 °C)
Melting Line
Sublimation Line
Entropy = -2.30 kJ/kg °C
Density = 700 kg/m³
Density = 20 kg/m³
ρ=200 kg/m³
1,000
100
10
1
-500
-400
-300
-200
-100
0
100
200


F
T, K
s, kJ/(kg·K)
P = 20 MPa
P = 0.1 MPa
1 atm.
v = 0.003 m³/kg
v = 1 m³/kg
h = 470 kJ/kg
h = 0 kJ/kg
saturated liquid line
saturated vapor line
x = 0.2
x = 0.7
3
5.7
0.00781
323
400
380
360
340
320
300
280
260
240
220
200
180
0
0.5
1
1.5
2

4.26. A tank of 3 m^3 useful volume contains 1000 kg of CO_2 at 293 K and will experience different forms of emptying up to 1 atm. Calculate:

- **a) The heat exchanged, the flow work and the remaining mass when the emptying is carried out isothermally from the liquid phase until all the saturated liquid is consumed inside the tank.**
- **b) The heat exchanged, the flow work and the remaining mass when the emptying is carried out isothermally from the vapor phase until all the saturated liquid is consumed inside the tank.**
- **c) The heat exchanged, the flow work and the remaining mass when the emptying is carried out isoenthalpically from the liquid phase until all the saturated liquid is consumed inside the tank (which remains isothermal).**
- **d) The heat exchanged, the flow work and the remaining mass when the emptying is carried out isoenthalpically from the vapor phase, until all the saturated liquid is consumed inside the tank (which remains isothermal).**
- **e) The heat exchanged, the flow work and the remaining mass when the whole system expands isoenthalpically up to 1 atm.**
- **f) The masses of vapor, liquid and solid CO_2 in the stream that leaves the tank in questions c), d) and e), assuming that the isenthalpic emptyings are "flash".**
- **g) The heat exchanged, the flow work and the remaining mass when the whole system cools polytropically at a rate of 1 K/25 kg$_{out}$.**

Qualitatively describe the process when the emptying is performed isoenthalpically from the liquid phase, and the interior of the tank is polytropically cooled as in question g). Do the same when the emptying is performed isoenthalpically from the vapor phase, and the interior of the tank is cooled in the same way.

Question a. In figure V.3 of this book's appendix V, the initial conditions (point 1) are determined by the intersection of the isotherm T_1= 273 K with the isochore

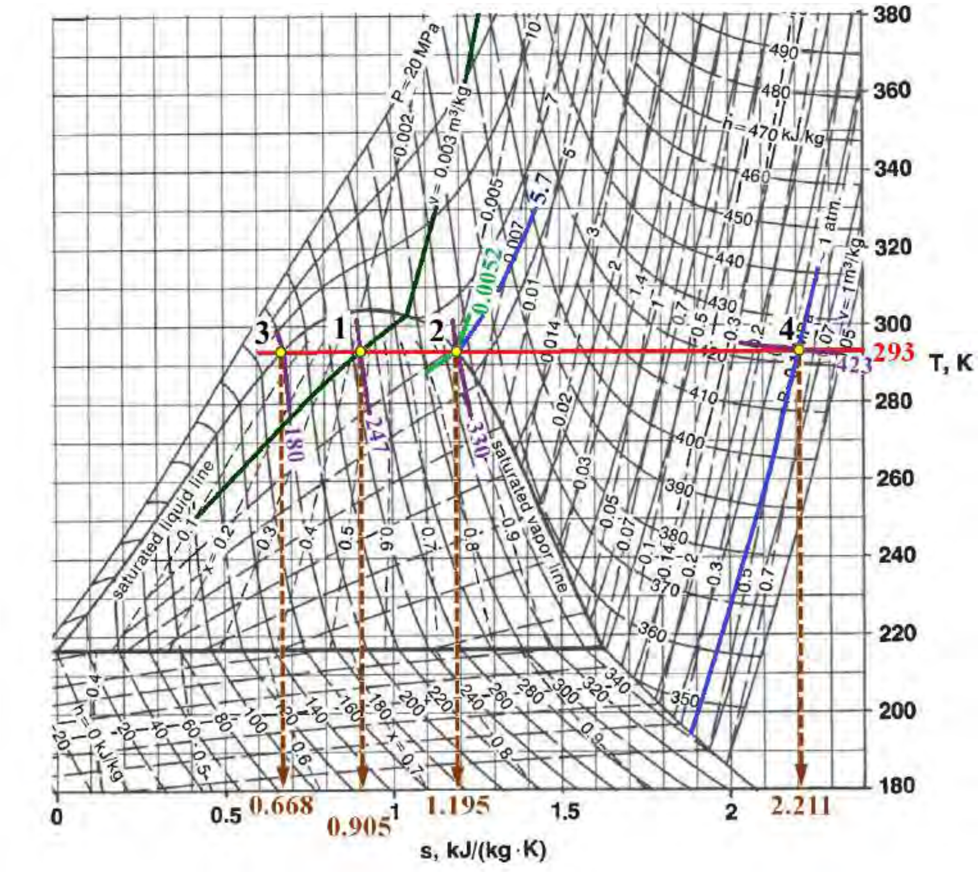
$$\hat{V}_1 = \frac{V_{useful}}{M_{tot}} = \frac{3\ \mathrm{m}^3}{1000\ \mathrm{kg}} = 0.003\ \frac{\mathrm{m}^3}{\mathrm{kg}}$$

which correspond to a biphasic mixture of saturated liquid and vapor, whose properties are those of points 3 and 2, respectively, at a pressure (interpolated from the isobars) of 5.7 MPa. In the case of an isothermal emptying of the tank, when the last drop of liquid is consumed, the whole system will be at point 2, and the useful volume will be occupied by saturated steam (whose specific volume, read in the diagram, is of 0.0052 m^3/kg). Thus, the remaining mass (M_2) will be

$$M_2 = M_{v_2} = \frac{V_{useful}}{\hat{V}_{v_2}} = \frac{3\ \mathrm{m}^3}{\left(0.0052\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right)} = 576.92\ \mathrm{kg}$$

having been consumed

$$M_{consumed} = M_{tot} - M_2 = M_1 - M_2 = 1000\ \mathrm{kg} - 576.92\ \mathrm{kg} = 423.08\ \mathrm{kg}$$



The heat exchanged during the emptying from the liquid phase will be the sum of three terms (graphically summarized as three successive lines): the evolution of the remaining mass M_2 from the conditions in point 1 to those of point 2 (saturated vapor), the travel of the consumed mass M_{tot}–M_2 from 1 to 3 (saturated liquid) and the passage of this amount M_{tot}–M_2 from 3 to 4 (intersection between the 1 atm isobar and the 273 K isotherm)

$$\Delta Q = M_2 \int_1^2 T\mathrm{d}\hat{S} + (M_{tot} - M_2) \int_1^3 T\mathrm{d}\hat{S} + (M_{tot} - M_2) \int_3^4 T\mathrm{d}\hat{S} =$$

$$= M_2 \int_1^2 T\mathrm{d}\hat{S} + (M_{tot} - M_2) \int_1^4 T\mathrm{d}\hat{S}$$

and due to the fact that $T_1 = T_2 = T_3 = T_4$, integration becomes simpler

$$\Delta Q = M_2 T_1 (\hat{S}_2 - \hat{S}_1) + (M_{tot} - M_2) T_1 (\hat{S}_4 - \hat{S}_1)$$

By reading data in the TS diagram, it is obtained that $\hat{S}_1$=0.905 kJ/(kg·K), $\hat{S}_2$=1.195 kJ/(kg·K) and $\hat{S}_4$=2.211 kJ/(kg·K), so

$$\Delta Q = (576.92\ \mathrm{kg})(293\ \mathrm{K}) \left(1.195\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 0.905 \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) +$$

$$+(423.08\ \mathrm{kg})(293\ \mathrm{K}) \left(2.211\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 0.905 \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = 210915.84\ \mathrm{kJ}$$

With regard to the flow work, this is defined as

$$\mathrm{d}\widehat{W}^{\mathrm{fl}} = \hat{V}\mathrm{d}P \quad \rightarrow \ \Delta\widehat{W}^{\mathrm{fl}} = \int \hat{V}\mathrm{d}P$$

and in this system

$$\Delta\widehat{W}^{\mathrm{fl}} = M_2 \int_1^2 \hat{V}\mathrm{d}P \ + (M_{tot} - M_2) \int_1^4 \hat{V}\mathrm{d}P \qquad [1]$$

which implies a complex numerical integration. However, according to equations of reference problem 0.3

$$\mathrm{d}\widehat{H} = \mathrm{d}\widehat{Q} + \mathrm{d}\widehat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P$$

hence

$$\Delta\widehat{W}^{\mathrm{fl}} = \Delta\widehat{H} - \Delta\widehat{Q} = \Delta\widehat{H} - \int T\mathrm{d}\hat{S}$$

being equation [1] converted in

$$\Delta W^{\mathrm{fl}} = M_2 \left[\Delta\widehat{H}_{21} - \int_1^2 T\mathrm{d}\hat{S} \ \right] + (M_{tot} - M_2)\left[\Delta\widehat{H}_{41} - \int_1^4 T\mathrm{d}\hat{S}\right]$$

Rearranging the terms of this expression it is obtained

$$\Delta W^{\mathrm{fl}} = M_2\Delta\widehat{H}_{21} + (M_{tot} - M_2)\Delta\widehat{H}_{41} - \left[M_2 \int_1^2 T\mathrm{d}\hat{S} \ + (M_{tot} - M_2)\int_1^4 T\mathrm{d}\hat{S}\right]$$

$$\Delta W^{\mathrm{fl}} = \Delta H - \Delta Q \qquad [2]$$

where ΔQ has been previously evaluated and ΔH (global enthalpy variation) is estimated as

$$\Delta H = M_2\big(\widehat{H}_2 - \widehat{H}_1\big) + (M_{tot} - M_2)\big(\widehat{H}_4 - \widehat{H}_1\big)$$

and from the data read or interpolated in figure V.3

$$\Delta H = (576.92\ \mathrm{kg})\left(330\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 247\frac{\mathrm{kJ}}{\mathrm{kg}}\right) + (423.08\ \mathrm{kg})\left(423\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 247\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 122346.44\ \mathrm{kJ}$$

After finding this value, equation [2] gives

$$\Delta W^{\mathrm{fl}} = 122346.44\ \mathrm{kJ} - 210915.84\ \mathrm{kJ} = -88569.4\ \mathrm{kJ}$$

Question b. The remaining and the consumed masses when emptying from the vapor phase will be the same as in question **a**. The heat exchanged will consist of two graphical terms: the transformation of M_{tot} from the conditions of point 1 to conditions of point 2 and the passage of M_{tot}–M_2 from 2 to 4

$$\Delta Q = M_{tot}\int_1^2 T\mathrm{d}\hat{S} + (M_{tot} - M_2)\int_2^4 T\mathrm{d}\hat{S}$$

being the integration very easy because $T_1 = T_2 = T_3 = T_4$

$$\Delta Q = M_{tot}T_1(\hat{S}_2 - \hat{S}_1) + (M_{tot} - M_2)T_1(\hat{S}_4 - \hat{S}_2)$$

$$\Delta Q = (1000\text{ kg})(293\text{ K})\left(1.195\ \frac{\text{kJ}}{\text{kg·K}} - 0.905\frac{\text{kJ}}{\text{kg·K}}\right) + \\ +(423.08\text{ kg})(293\text{ K})\left(2.211\ \frac{\text{kJ}}{\text{kg·K}} - 1.195\frac{\text{kJ}}{\text{kg·K}}\right) = 210915.84\text{ kJ}$$

Result which is exactly the same as in question **a**, showing that in an isothermal emptying, it does not matter (in energy terms) to operate from the liquid zone or from the vapor one.

On the other hand, the flow work also coincides with that of the previous question (-88569.4 kJ), since the global variation of enthalpy

$$\Delta H = M_{tot}(\hat{H}_2 - \hat{H}_1) + (M_{tot} - M_2)(\hat{H}_4 - \hat{H}_2)$$

is numerically equal

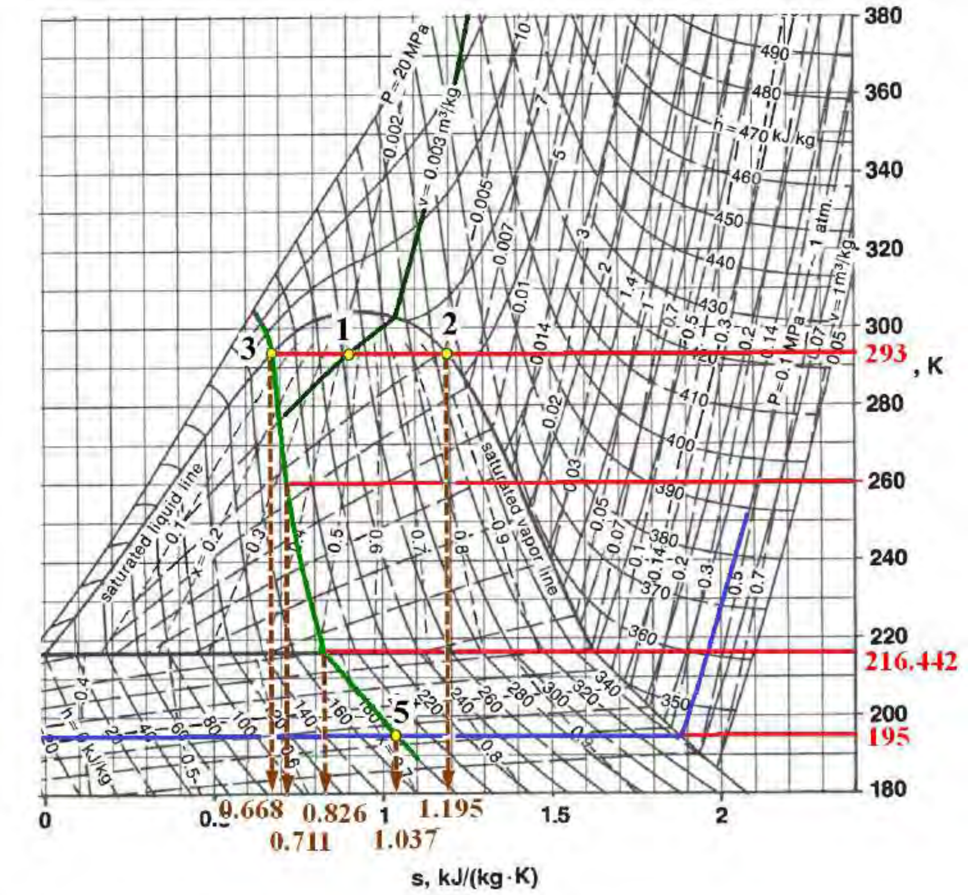
$$\Delta H = (1000\text{ kg})\left(330\ \frac{\text{kJ}}{\text{kg}} - 247\frac{\text{kJ}}{\text{kg}}\right) + (423.08\text{ kg})\left(423\ \frac{\text{kJ}}{\text{kg}} - 330\frac{\text{kJ}}{\text{kg}}\right) = 122346.44\text{ kJ}$$

Question c. When the emptying is carried out isoenthalpically from the liquid phase and the interior of the tank is kept isothermal at 293 K (and therefore also isobaric at 5.7 MPa) until exhausting the liquid, the remaining and consumed masses are the same as in questions **a** and **b**. The heat exchanged will consist of three terms: passage of the remaining mass M_2 from 1 to 2, transit of the consumed mass M_{tot}–M_2 from 1 to 3 and passage of M_{tot}–M_2 from 3 to 5 (graphically: intersection of the isenthalpic that passes through 3 with the isobar of 1 atm)

$$\Delta Q = M_2\int_1^2 T\mathrm{d}\hat{S} + (M_{tot} - M_2)\int_1^3 T\mathrm{d}\hat{S} + (M_{tot} - M_2)\int_3^5 T\mathrm{d}\hat{S}$$

Notice the similarity with question **a**. The main difference is that only $T_1 = T_2 = T_3$, while $T_3 \neq T_5$.

$$\Delta Q = M_2T_1(\hat{S}_2 - \hat{S}_1) + (M_{tot} - M_2)T_1(\hat{S}_3 - \hat{S}_1) + (M_{tot} - M_2)\int_3^5 T\mathrm{d}\hat{S}$$



Thus, the last integral cannot be solved analytically, and numerical methods are required, such as the trapezoidal rule. To do this, some pairs of values (T, S) have to be determined in figure V.3 along the isenthalpic line that passes through 3 and 5

T (K)	$\hat{S}$ (kJ/kg·K)	$[\hat{S}_i - \hat{S}_{i-1}]\left(\frac{T_i + T_{i-1}}{2}\right)$
293	0.668	
260	0.711	11.8895
216.442	0.826	27.3954
195	1.037	43.4071
	Sum=	82.692 kJ/kg

so that

$$\Delta Q = (576.92\text{ kg})(293\text{ K})\left(1.195\,\frac{\text{kJ}}{\text{kg·K}} - 0.905\,\frac{\text{kJ}}{\text{kg·K}}\right) +$$

$$+(423.08\text{ kg})(293\text{ K})\left(0.668\,\frac{\text{kJ}}{\text{kg·K}} - 0.905\,\frac{\text{kJ}}{\text{kg·K}}\right) +$$

$$+(423.08\text{ kg})\left(82.692\,\frac{\text{kJ}}{\text{kg}}\right) = 54627.125\text{ kJ}$$

Finally, by combining this value with the enthalpy change

$$\Delta H = M_2\left(\hat{H}_2 - \hat{H}_1\right) + (M_{tot} - M_2)\left(\hat{H}_3 - \hat{H}_1\right) + (M_{tot} - M_2)\left(\hat{H}_5 - \hat{H}_3\right)$$

$$\Delta H = (576.92\text{ kg})\left(330\ \frac{\text{kJ}}{\text{kg}} - 247\frac{\text{kJ}}{\text{kg}}\right) + \\ +(423.08\text{ kg})\left(180\ \frac{\text{kJ}}{\text{kg}} - 247\frac{\text{kJ}}{\text{kg}}\right) + (423.08\text{ kg})\left(180\ \frac{\text{kJ}}{\text{kg}} - 180\ \frac{\text{kJ}}{\text{kg}}\right) = 19538\text{ kJ}$$

and according to equation [2] the flow work will be

$$\Delta W^{\text{fl}} = 19538\text{ kJ} - 54627.125\text{ kJ} = -35089.125\text{ kJ}$$

Question d. The remaining and consumed masses in the emptying from the vapor phase will be the same as in question **c**. The heat exchanged will consist of two terms: the change of M_{tot} from conditions in 1 to conditions in 2 and the change of M_{tot}–M_2 from 2 to 6 (graphically: intersection of the isenthalpic that passes through 2 with the isobar of 1 atm)

$$\Delta Q = M_{tot}\int_1^2 T\text{d}\hat{S}\ + (M_{tot} - M_2)\int_2^6 T\text{d}\hat{S}$$

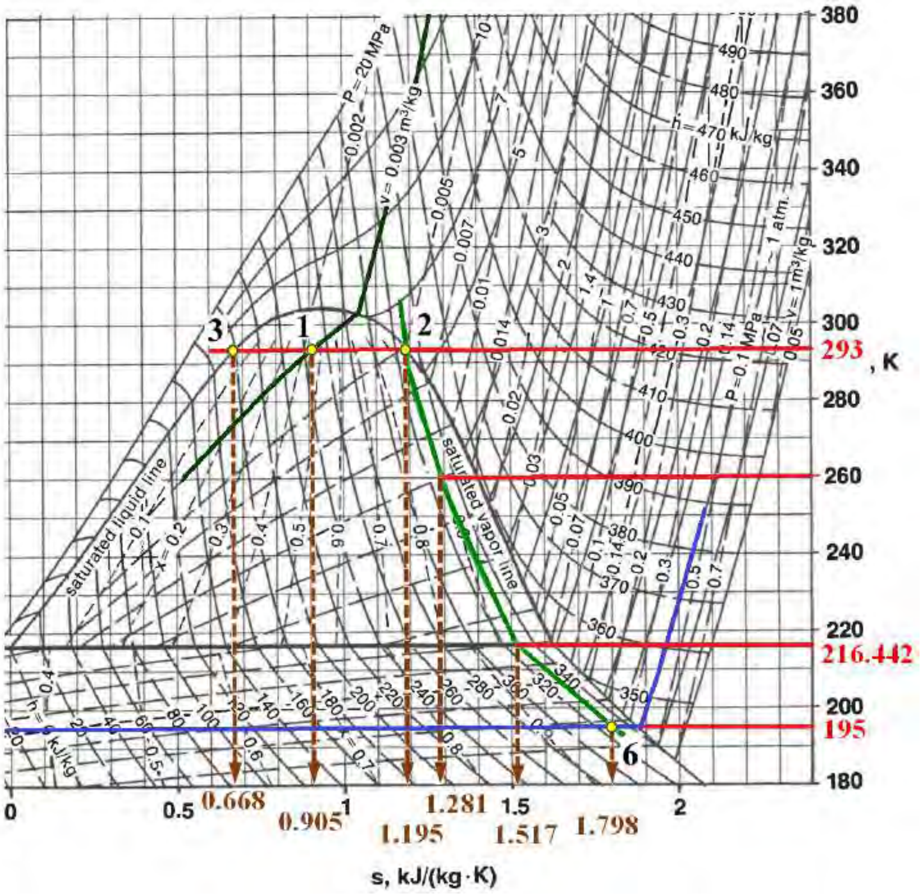
Notice the similarity with question **b**. The main difference is that only $T_1 = T_2$, while $T_2 \neq T_6$

$$\Delta Q = M_{tot}T_1\left(\hat{S}_2 - \hat{S}_1\right) + (M_{tot} - M_2)\int_2^6 T\text{d}\hat{S}$$

so the integral between 2 and 6 will have to be solved numerically, as in question **c**

T (K)	$\hat{S}$ (kJ/kg·K)	$\left[\hat{S}_i - \hat{S}_{i-1}\right]\left(\frac{T_i + T_{i-1}}{2}\right)$
293	1.195	
260	1.281	23.779
216.442	1.517	56.220
195	1.798	7.808
	Sum=	137.807 kJ/kg

$$\Delta Q = (1000\text{ kg})(293\text{ K})\left(1.195\ \frac{\text{kJ}}{\text{kg·K}} - 0.905\frac{\text{kJ}}{\text{kg·K}}\right) + \\ +(423.08\text{ kg})\left(137.807\ \frac{\text{kJ}}{\text{kg}}\right) = 143273.39\text{ kJ}$$



On the other hand, the global enthalpy variation will be

$$\Delta H = M_{tot}\left(\hat{H}_2 - \hat{H}_1\right) + \left(M_{tot} - M_2\right)\left(\hat{H}_6 - \hat{H}_2\right)$$

$$\Delta H = (1000\ \mathrm{kg})\left(330\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 247\frac{\mathrm{kJ}}{\mathrm{kg}}\right) + (423.08\ \mathrm{kg})\left(330\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 330\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 83000\ \mathrm{kJ}$$

and the flow work

$$\Delta W^{\mathrm{fl}} = 83000\ \mathrm{kJ} - 143273.39\ \mathrm{kJ} = -60273.39\ \mathrm{kJ}$$

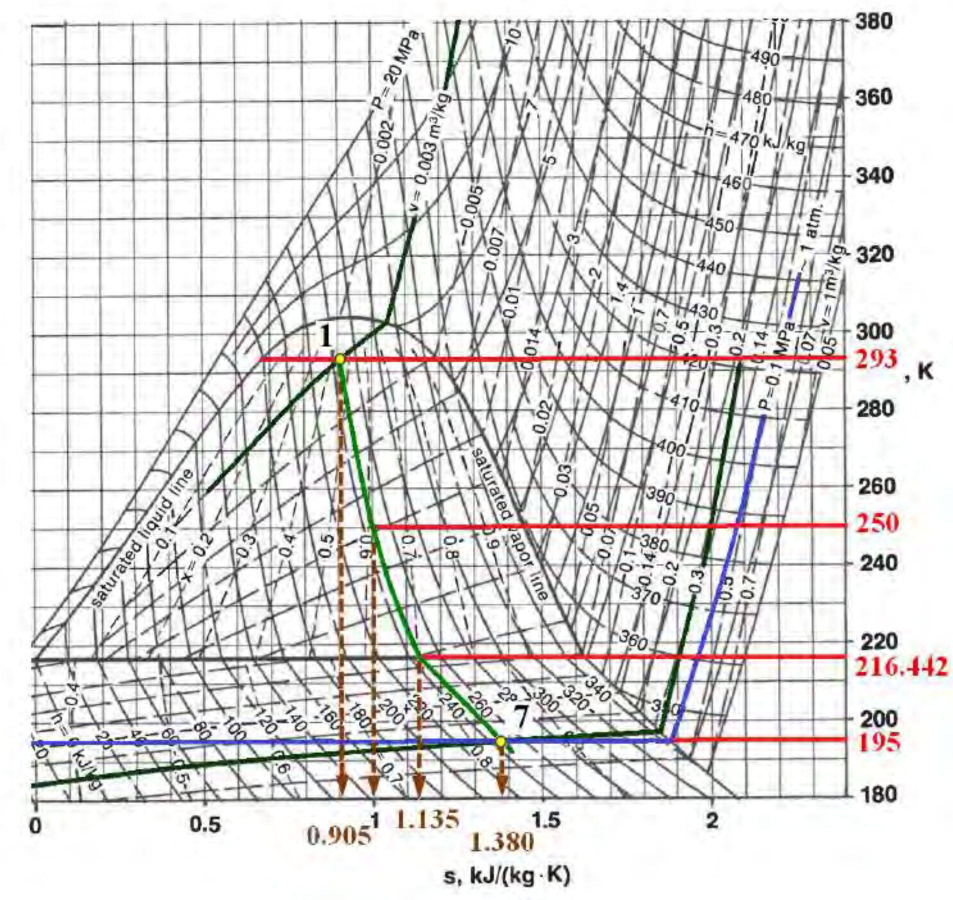
It has to be pointed out that, unlike in questions **a** and **b**, neither the heat exchanged nor the enthalpy variation nor the flow work of the isenthalpic emptying from the liquid side coincide with those from the vapor side.

Question e. In the case of both isenthalpic emptying and expansión of the CO_2 inside, the heat exchanged will be that due to transporting the entire mass from point 1 to point 7 (intersection between the isenthalpic that passes through the point 1 with the isobar of 1 atm)

$$\Delta Q = M_{tot}\int_1^7 T \mathrm{d}\hat{S}$$

Numerical integration has to be employed to solve the integral, by giving some values between T_1, $\hat{S}_1$ and T_7, $\hat{S}_7$ along the isenthalpic line

T (K)	$\hat{S}$ (kJ/kg·K)	$[\hat{S}_i - \hat{S}_{i-1}]\left(\frac{T_i + T_{i-1}}{2}\right)$
293	0.905	
260	1.135	63.595
216.442	1.380	58.364
195	1.876	102.038
	Sum=	223.997 kJ/kg



so

$$\Delta Q = (1000\ \mathrm{kg})\left(223.997\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 223997\ \mathrm{kJ}$$

and since in the whole system there has been no enthalpy change (ΔH=0) the flow work will be

$$\Delta W^{\mathrm{fl}} = \Delta H - \Delta Q = 0 - 223997\ \mathrm{kJ}\ = -223997\ \mathrm{kJ}$$

With regards to the remaining mass, it will be different from that of questions **a**–**d**, since the CO_2 inside the deposit does not remain at 273 K and 5.7 MPa, but evolves until reaching point 7, where the specific volume is approximately of 0.3 m^3/kg; thus

$$M_7 = \frac{V_{useful}}{\hat{V}_7} = \frac{3\ \mathrm{m}^3}{\left(0.3\ \frac{\mathrm{m}^3}{\mathrm{kg}}\right)} = 10\ \mathrm{kg}$$

having been consumed

$$M_{tot} - M_7 = 1000\ \mathrm{kg} - 10\ \mathrm{kg} = 990\ \mathrm{kg}$$

Question f. As seen in question **c**–**e**, these mixtures only include solid and vapor. The amounts in each case will be obtained from the combination of the mass and entropy balances

$$M_{consumed} = M_s + M_v$$

$$M_{consumed}\hat{S} = M_s\hat{S}_s^{sat} + M_v\hat{S}_v^{sat}$$

from where

$$M_s = M_{consumed}\frac{\left(\hat{S}_v^{sat} - \hat{S}\right)}{\left(\hat{S}_v^{sat} - \hat{S}_s^{sat}\right)}$$

$$M_v = M_{consumed} - M_s$$

When isenthalpically emptying from the liquid phase (question **c**)

$$M_{s_5} = (M_{tot} - M_2)\frac{\left(\hat{S}_v^{sat} - \hat{S}_5\right)}{\left(\hat{S}_v^{sat} - \hat{S}_s^{sat}\right)} = (423.08\ \mathrm{kg})\frac{[1.876 - 1.037]}{[1.876 - (-1.060)]} = 120.90\ \mathrm{kg}$$

$$M_{v_5} = (M_{tot} - M_2) - M_{s_5} = 423.08\ \mathrm{kg} - 120.90\ \mathrm{kg} = 302.18\ \mathrm{kg}$$

When isenthalpically emptying from the vapor phase (question **d**)

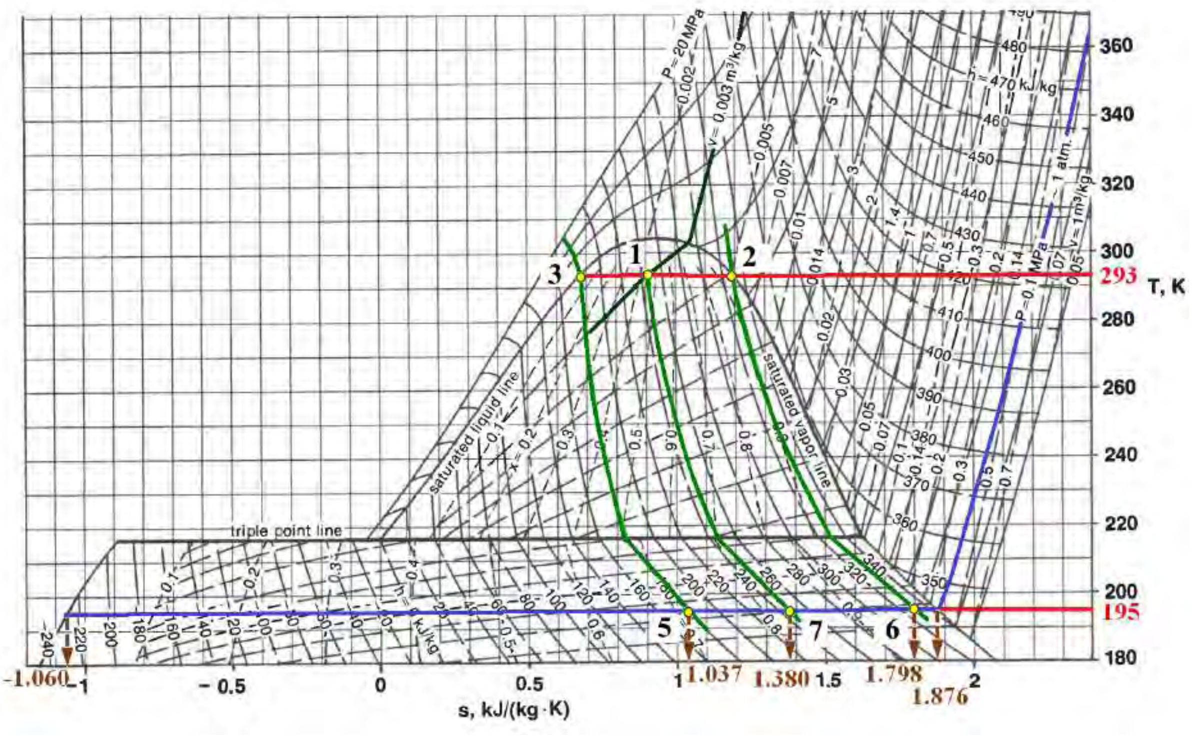
$$M_{s_6} = (M_{tot} - M_2)\frac{\left(\hat{S}_v^{sat} - \hat{S}_6\right)}{\left(\hat{S}_v^{sat} - \hat{S}_s^{sat}\right)} = (423.08\ \mathrm{kg})\frac{[1.876 - 1.798]}{[1.876 - (-1.060)]} = 11.24\ \mathrm{kg}$$

$$M_{v_6} = (M_{tot} - M_2) - M_{s_6} = 423.08\ \mathrm{kg} - 11.24\ \mathrm{kg} = 411.84\ \mathrm{kg}$$

When the whole system evolves isenthalpically (question **e**)

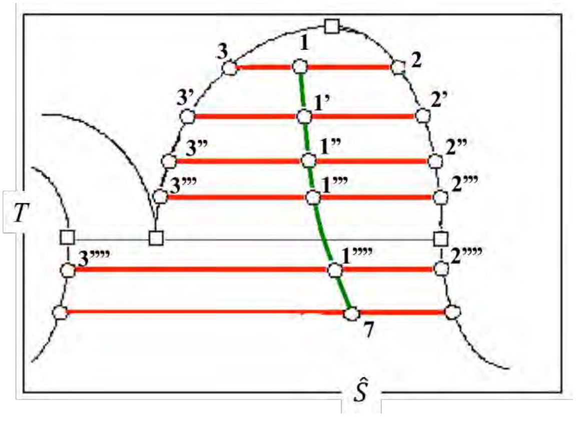
$$M_{s_7} = (M_{tot} - M_7)\frac{\left(\hat{S}_v^{sat} - \hat{S}_7\right)}{\left(\hat{S}_v^{sat} - \hat{S}_s^{sat}\right)} = (990\text{ kg})\frac{[1.876 - 1.380]}{[1.876 - (-1.060)]} = 167.24\text{ kg}$$

$$M_{v_7} = (M_{tot} - M_7) - M_{s_7} = 990\text{ kg} - 167.24\text{ kg} = 822.76\text{ kg}$$



NOTE: The interested reader is suggested to reflect on the difficulty of performing the emptying of question **e**. If the process was not an emptying and if it was carried out in a variable volume tank, an adequate control of the temperature (and thus of the vapor pressure) would allow the liquid + vapor mixture inside (or solid + vapor below the triple point) to follow the isenthalpic line from point 1 to 1', then to 1" and so on until reaching point 7, where the volume reached would be

$$V_{useful} = M_{tot}\hat{V}_7 = (1000\text{ kg})\left(0.3\ \frac{\text{m}^3}{\text{kg}}\right) = 300\text{ m}^3$$



However, if at point 1 the exact proportions of liquid and vapor that allows the system to pass to point 1' are extracted, and the extraction is repeated to allow the transit to point 1" and so on (extracting solid instead of liquid below the triple point), neither the heat exchanged will be $M_{tot}\int_1^7 T\mathrm{d}\hat{S}$ because the mass continuously varies, nor the evacuated mass will be in the same conditions as the remaining mass, but it will be a mixture of liquid, vapor and solid whose characteristics would be the average of all the extracted portions.

Question g. The following equation gives the equation of the polytropic line

$$\frac{\Delta T}{M_{out}} = \frac{293\ \mathrm{K} - T(\mathrm{K})}{1000\ \mathrm{kg} - M_{in}(\mathrm{kg})} = \frac{1\ \mathrm{K}}{25\ \mathrm{kg}} \qquad [3]$$

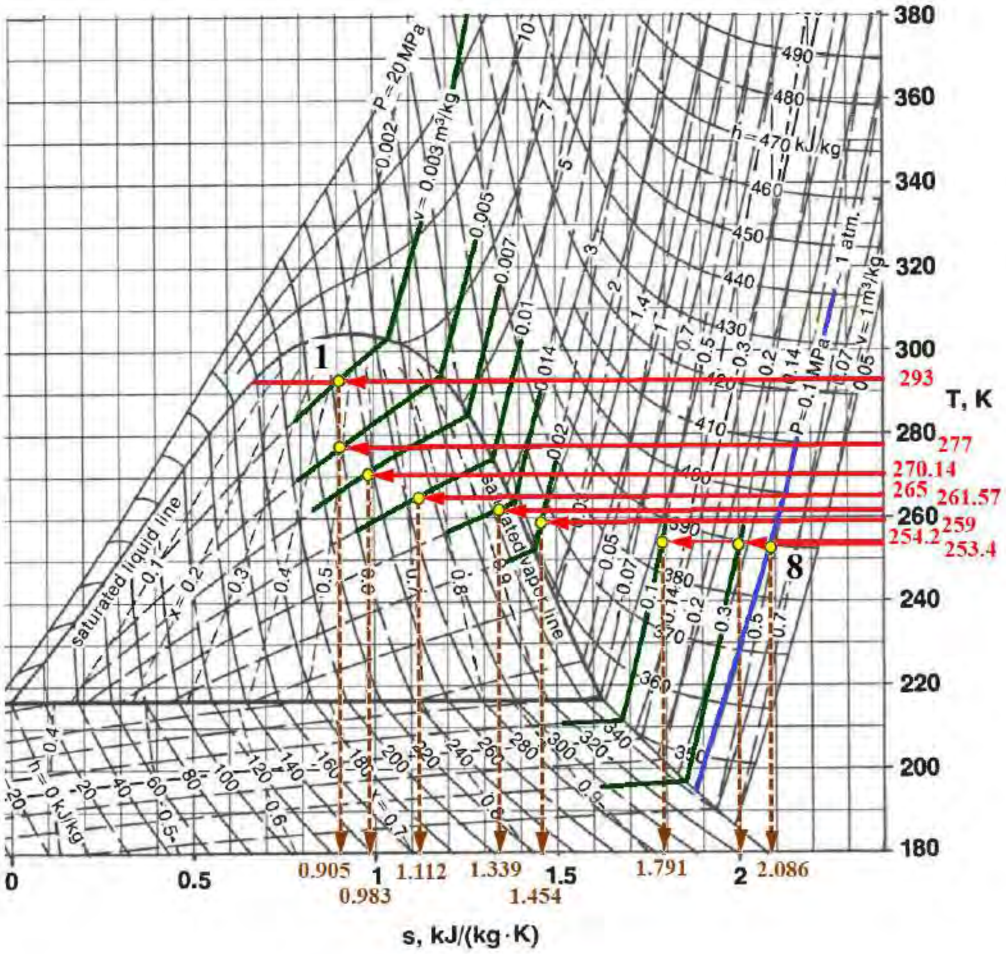
where the mass out of the tank in each moment (M_{out}) is equal to the initial mass minus the mass that remains in this tank in each moment (M_{in}), being at the end of the process $M_{out} = M_{consumed}$ and $M_{in} = M_{remaining}$. In order to draw the operation line on the $TS(V,P,H)$ diagram, it can be proceeded in several ways, but since the temperature is represented on the abscissa axis and the specific volume on isolines, the best thing to do is:

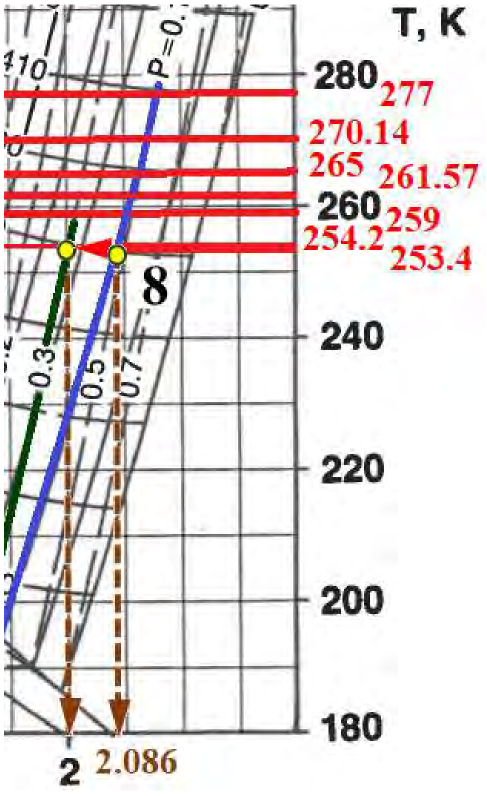
- Take the value of $\hat{V}$ from an existing isochore
- Calculate M_{in} (in kg) as $V_{useful}/\hat{V}$
- Determine M_{out} (in kg) as $1000 - M_{in}$
- Evaluate ΔT (in K) as $M_{out}/25$
- Calculate T (in K) as $293 - \Delta T$

obtaining the table

$\hat{V}$	M_{in} (kg)	M_{out} (kg)	ΔT (K)	T (K)
0.003	1000	0	0	293
0.005	600	400	16	277
0.007	428.571429	571.428571	22.8571429	270.142857
0.01	300	700	28	265
0.014	214.285714	785.714286	31.4285714	261.571429
0.02	150	850	34	259
0.03	100	900	36	257
0.05	60	940	37.6	255.4
0.07	42.8571429	957.142857	38.2857143	254.714286
0.1	30	970	38.8	254.2
0.2	15	985	39.4	253.6
0.3	10	990	39.6	253.4
0.5	6	994	39.76	253.24

Graphically, the intersection of the calculated isotherm with the corresponding isochore allows the location of these points in figure V.3, as well as to determine the specific entropy of each state.





Unfortunately, large changes in specific volume imply small changes in temperature at the end of the process, so it is difficult to find the intersection between the polytropic line and the isobar of 1.01 MPa ≈ 1 atm. It seems that it occurs on an isochore lower than 0.5 m^3/kg, but not much lower. Thus, in a somewhat arbitrary way, a value of 0.48 m^3/kg will be taken, which will give a remaining mass of

$$M_8 = \frac{V_{useful}}{\hat{V}_8} = \frac{3\ \text{m}^3}{\left(0.48\ \frac{\text{m}^3}{\text{kg}}\right)} = 6.25\ \text{kg}$$

and a consumed mass and a temperature of

$$M_{tot} - M_8 = 1000\ \text{kg} - 6.25\ \text{kg} = 993.75\ \text{kg}$$

$$T_8 = 293 - \frac{1000 - 993.75}{25} = 253.25\ \text{K}$$

On the other hand, the heat exchanged by the whole system is estimated by the expression

$$\Delta Q = M_{tot}\int_1^8 T\mathrm{d}\hat{S}$$

where the integral has to be numerically calculated by the trapezoidal rule, as in preceding questions.

$T\,(K)$	$\hat{S}$ (kJ/kg·K)	$[\hat{S}_i - \hat{S}_{i-1}]\left(\frac{T_i + T_{i-1}}{2}\right)$
293	0.905	
277	0.905	0
270.14	0.983	21.338
265	1.112	34.516
261.57	1.339	59.767
259	1.454	29.933
254.2	1.791	86.474
253.4	2	53.044
253.25	2.086	21.786
	Sum=	306.858 kJ/kg

so that

$$\Delta Q = (1000\text{ kg})\left(306.858\ \frac{\text{kJ}}{\text{kg}}\right) = 306858\text{ kJ}$$

and since the global enthalpy change can be evaluated as

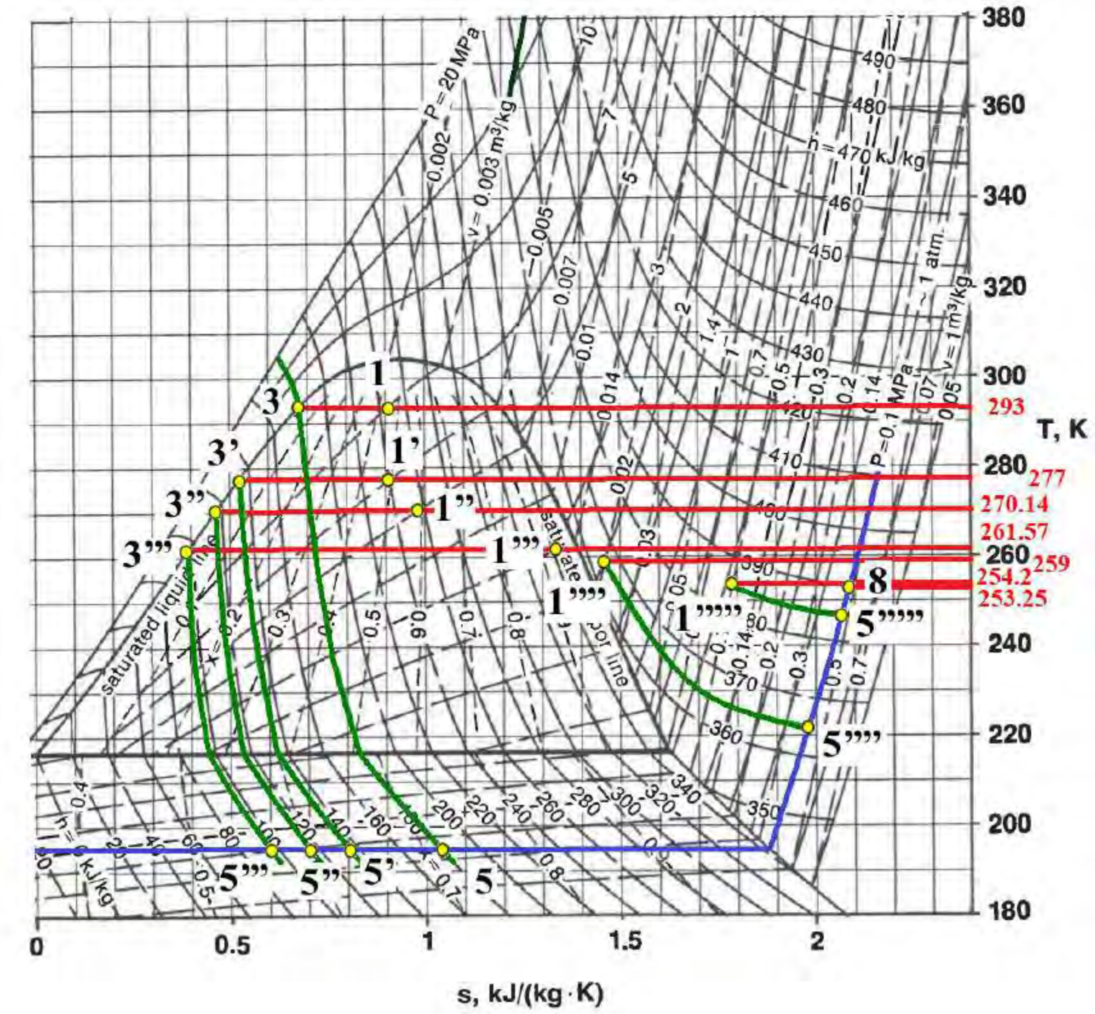
$$\Delta H = M_{tot}(\hat{H}_8 - \hat{H}_1)$$

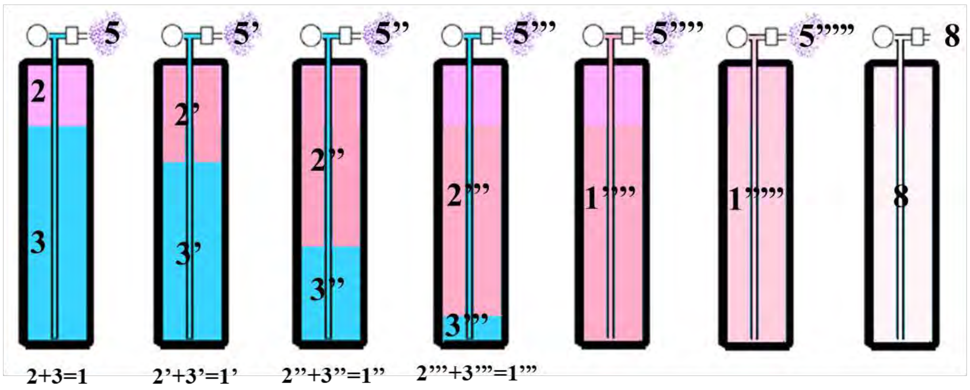
$$\Delta H = (1000\text{ kg})\left(390\ \frac{\text{kJ}}{\text{kg·K}} - 247\frac{\text{kJ}}{\text{kg·K}}\right) = 143000\text{ kJ}$$

the flow work is

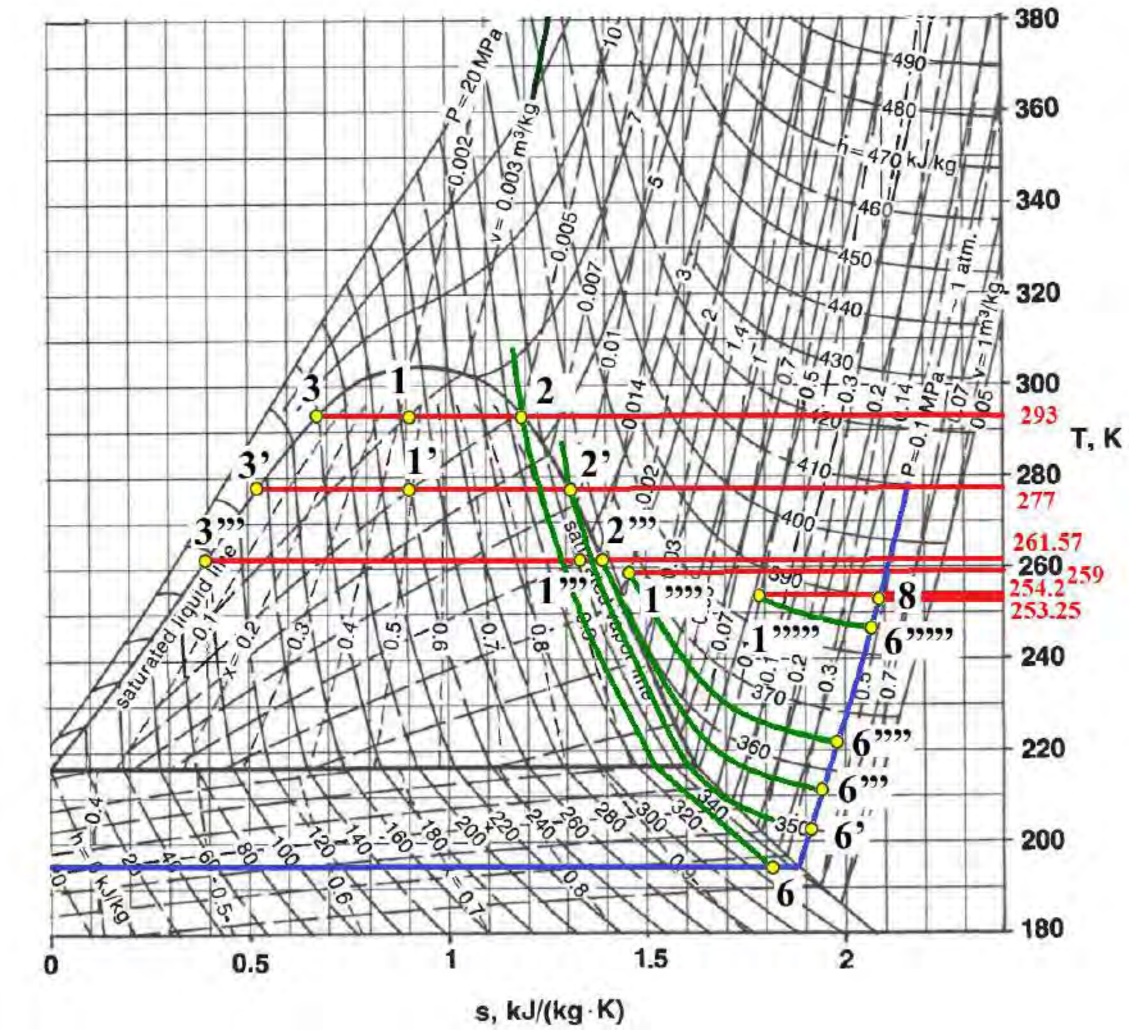
$$\Delta W^{\text{fl}} = 143000\text{ kJ} - 306858\text{ kJ} = -163858\text{ kJ}$$

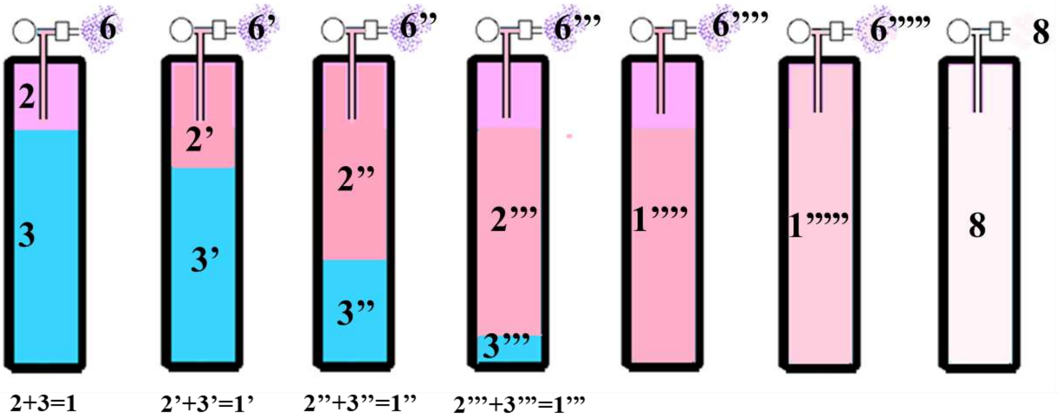
When the emptying is carried out isenthalpically from the liquid phase but the interior of the tank follows an evolution described by equation [3], the saturated liquid conditions will no longer be constant (as in question **c**) but will change. As the content of the tank goes from 1 to 1’, and then to 1”, the saturated liquid will go from 3 to 3’, and then to 3”, respectively, and the extracted mixture of vapor + solid will also be changing (from 5 to 5’, then to 5”). At a temperature between 261.57 K and 259 K, the last drop of liquid will disappear, and since then, vapor will come out in conditions 5””, 5””’ until ending in conditions of 8. For the sake of clarity, no points corresponding to saturated vapor (2, 2’, 2” and 2’”) have been included in the *TS* diagram.





When the emptying is carried out isoenthalpically from the vapor phase, vapor conditions inside the tank will not be constant either (as in question **d**) but will vary: at the beginning it will be saturated vapor (points 2, 2', 2''') in equilibrium with liquid, but from a temperature between 261.57 and 259 K all the content will be superheated vapor (points 1'''', 1''''' and 8), and the stream that comes out will evolve from a mixture of vapor + solid enriched in vapor (point 6) to superheated vapor only (points 6', 6''', 6'''', 6''''' and 8). For the sake of clarity, points 1'', 2'' and 6'' have been omitted in the *TS* diagram.


P = 20 MPa
v = 0.003 m³/kg
h = 470 kJ/kg
490
480
460
450
440
430
420
410
400
390
370
360
350
1 atm.
v = 1 m³/kg
P = 0.1 MPa
saturated liquid line
saturated vapour line
3
1
2
3'
1'
2'
3'''
2'''
1'''
1''''
1'''''
8
6'''''
6''''
6'''
6'
6
293
277
261.57
259
254.2
253.25
380
360
340
320
300
280
260
240
220
200
180
T, K
0
0.5
1
1.5
2
s, kJ/(kg · K)


6
6'
6''
6'''
6''''
6'''''
8
2
3
2'
3'
2''
3''
2'''
3'''
1''''
1'''''
8
2+3=1
2'+3'=1'
2''+3''=1''
2'''+3'''=1'''

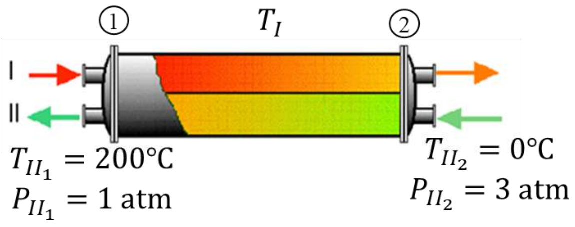
SERIES 5

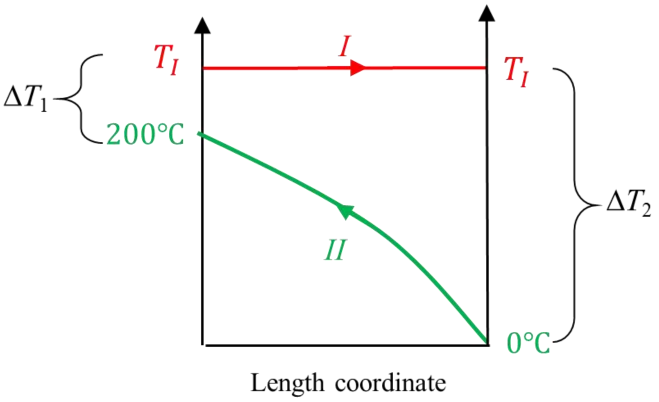
HEAT TRANSFER OPERATIONS

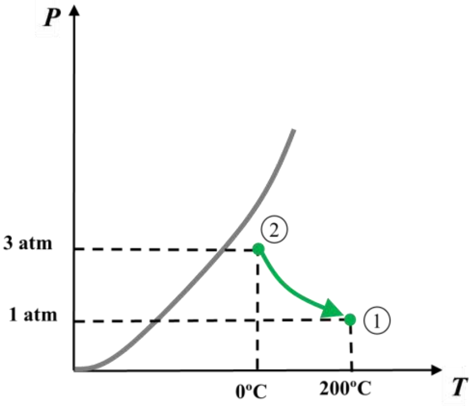
5.1. A CO_2 stream with a mass flow rate of 10 kg/h, initially at 0°C and 3 atm of pressure, is introduced into a jacketed pipe of 25 cm in diameter and 5 m in length, leaving it at 200°C and 1 atm. Condensing steam at 40 atm in counterflow is used as an energy source. The given heat covers several energy demands, such as the increase in the CO_2 internal and kinetic energies and the simultaneous variation in pressure and volume (ΔPV). Assuming that carbon dioxide behaves like an ideal gas circulating with a constant velocity across any cross-section of the pipe perpendicular to its axis:

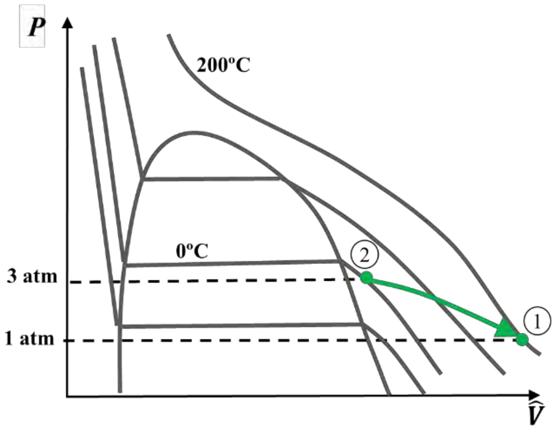
- **a) Qualitatively represent the process in the diagrams T vs. *length coordinate within the pipe*, PT, $PV(T)$, $HP(T)$ and $HT(P)$.**
- **b) Calculate the variation of enthalpy, internal energy and entropy experienced by a kilogram of circulating fluid.**
- **c) Determine the kinetic energy variation of carbon dioxide, compare it with the enthalpic term and evaluate the exchanged heat flow rate.**
- **d) Calculate the mass flow rate of condensing steam.**
- **e) Calculate the overall heat transfer coefficient that would maintain the stationary regime of the process under the established conditions.**

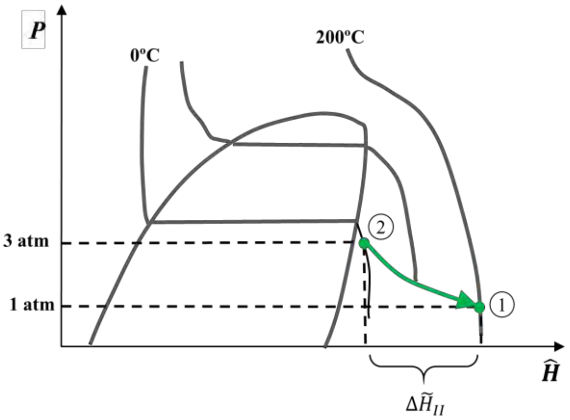
Question a. Let phase I be the steam stream and phase II the carbon dioxide stream. The representation of the operation according to conventional criteria, will be

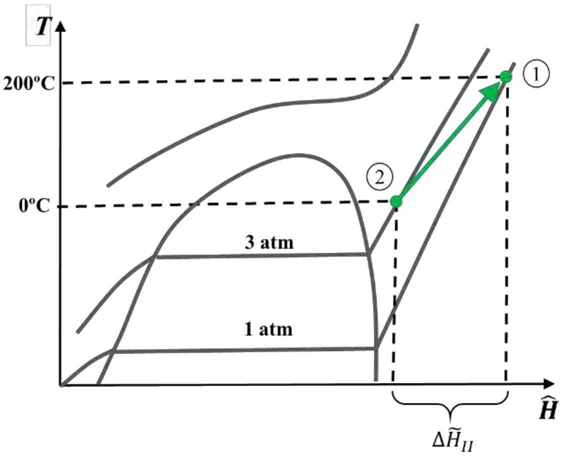












Question b. For carbon dioxide, the variation of enthalpy, internal energy and entropy per unit mass can be calculated from the specific heat capacity at constant pressure ($\tilde{C}_P^*$) because its behavior can be considered as an ideal gas, using the expression given in appendix II

$$T_{II_2}(\mathrm{K}) = 0 + 273 = 273\ \mathrm{K}$$

$$T_{II_1}(\mathrm{K}) = 200 + 273 = 473\ \mathrm{K}$$

$$\tilde{C}_P^* = R\{3.259 + 1.356 \cdot 10^{-3}T + 1.502 \cdot 10^{-5}T^2 - 2.374 \cdot 10^{-8}T^3 + 1.056 \cdot 10^{-11}T^4\}$$

$$\Delta\tilde{H}_{II} = \tilde{H}_{II_1} - \tilde{H}_{II_2} = \int_{T_{II_2}}^{T_{II_1}} \tilde{C}_P^* \mathrm{d}T = \int_{T_{II_2}}^{T_{II_1}} (\xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4)\mathrm{d}T$$

$$\Delta\tilde{H}_{II} = \left[\xi_0 T + \frac{1}{2}\xi_1 T + \frac{1}{3}\xi_2 T^3 + \frac{1}{4}\xi_3 T^4 + \frac{1}{5}\xi_4 T^5\right]_{T_{II_2}}^{T_{II_1}} =$$

$$= \xi_0\left(T_{II_1} - T_{II_2}\right) + \frac{\xi_1}{2}\left(T_{II_1}^2 - T_{II_2}^2\right) + \frac{\xi_2}{3}\left(T_{II_1}^3 - T_{II_2}^3\right) + \frac{\xi_3}{4}\left(T_{II_1}^4 - T_{II_2}^4\right) + \frac{\xi_4}{5}\left(T_{II_1}^5 - T_{II_2}^5\right)$$

$$\begin{aligned}\Delta\widetilde{H}_{II} = 1.9872\ \Bigg\{&3.259(473-273)+\frac{1.356\cdot10^{-3}}{2}(473^2-273^2)+\\&+\frac{1.502\cdot10^{-5}}{3}(473^3-273^3)-\frac{2.374\cdot10^{-8}}{4}(473^4-273^4)+\\&+\frac{1.056\cdot10^{-11}}{5}(473^5-273^5)\Bigg\}=1914.88\ \frac{\text{cal}}{\text{mol-g}}\end{aligned}$$

$$\Delta\widetilde{U}_{II}=\widetilde{U}_{II_1}-\widetilde{U}_{II_2}=\int_{T_{II_2}}^{T_{II_1}}\tilde{C}_V^*\mathrm{d}T=\int_{T_{II_2}}^{T_{II_1}}\left(\tilde{C}_P^*-R\right)\mathrm{d}T$$

$$\Delta\widetilde{U}_{II}=\int_{T_{II_2}}^{T_{II_1}}\tilde{C}_P^*\mathrm{d}T-\int_{T_{II_2}}^{T_{II_1}}R\mathrm{d}T=\Delta\widetilde{H}_{II}-R\left(T_{II_1}-T_{II_2}\right)$$

$$\Delta\widetilde{U}_{II}=1914.88\frac{\text{cal}}{\text{mol-g}}-\left(1.9872\frac{\text{cal}}{\text{mol-g}\cdot\text{K}}\right)(473\ \text{K}-273\ \text{K})=1517.44\ \frac{\text{cal}}{\text{mol-g}}$$

$$\Delta\tilde{S}_{II}=\tilde{S}_{II_1}-\tilde{S}_{II_2}=\int_{T_{II_2}}^{T_{II_1}}\tilde{C}_P^*\frac{\mathrm{d}T}{T}-\int_{P_{II_2}}^{P_{II_1}}R\frac{\mathrm{d}P}{P}=\int_{T_{II_2}}^{T_{II_1}}\tilde{C}_P^*\frac{\mathrm{d}T}{T}-R[\ln P]_{P_{II_2}}^{P_{II_1}}=$$

$$=\int_{T_{II_2}}^{T_{II_1}}\tilde{C}_P^*\frac{\mathrm{d}T}{T}-R\ln\frac{P_{II_1}}{P_{II_2}}=\int_{T_{II_2}}^{T_{II_1}}(\xi_0+\xi_1T+\xi_2T^2+\xi_3T^3+\xi_4T^4)\frac{\mathrm{d}T}{T}-R\ln\frac{P_{II_1}}{P_{II_2}}=$$

$$=\left[\xi_0\ln T+\xi_1T+\frac{1}{2}\xi_2T^2+\frac{1}{3}\xi_3T^3+\frac{1}{4}\xi_4T^4\right]_{T_{II_2}}^{T_{II_1}}-R\ln\frac{P_{II_1}}{P_{II_2}}=$$

$$=\xi_0\ln\frac{T_{II_1}}{T_{II_2}}+\xi_1\left(T_{II_1}-T_{II_2}\right)+\frac{\xi_2}{2}\left(T_{II_1}^2-T_{II_2}^2\right)+\frac{\xi_3}{3}\left(T_{II_1}^3-T_{II_2}^3\right)+\frac{\xi_4}{4}\left(T_{II_1}^4-T_{II_2}^4\right)-R\ln\frac{P_{II_1}}{P_{II_2}}$$

$$\begin{aligned}\Delta\tilde{S}_I=1.9872\ \Bigg\{&3.259\ln\left(\frac{473}{273}\right)+1.356\cdot10^{-3}(473-273)+\\&+\frac{1.502\cdot10^{-5}}{2}(473^2-273^2)-\frac{2.374\cdot10^{-8}}{3}(473^3-273^3)+\\&+\frac{1.056\cdot10^{-11}}{4}(473^4-273^4)\Bigg\}-1.9872\ln\left(\frac{1}{3}\right)=7.397\ \frac{\text{cal}}{\text{mol-g}\cdot\text{K}}\end{aligned}$$

Question c. The variation in kinetic energy per unit mass between point 2 and point 1 will be given by

$$\Delta\left(\hat{E}_{kin}\right)_{II} = \left(\hat{E}_{kin}\right)_{II_1} - \left(\hat{E}_{kin}\right)_{II_2} = \frac{1}{2}\left(\mathrm{v}_{II_1}^2 - \mathrm{v}_{II_2}^2\right)$$

Velocity can be calculated from the mass flow rate of carbon dioxide, its molecular weight and the cross-section of the tube as

$$\mathrm{v}_{II} = \frac{\hat{\mathcal{W}}_{II}\hat{V}_{II}}{A} = \frac{\hat{\mathcal{W}}_{II}\tilde{V}_{II}}{\mathfrak{M}_{II}A} = \frac{\hat{\mathcal{W}}_{II}RT_{II}}{\mathfrak{M}_{II}AP_{II}}$$

thus, at the tube entrance

$$\mathrm{v}_{II_2} = \frac{\left(10000\ \frac{\mathrm{g}}{\mathrm{h}}\right)\left(0.082\frac{\mathrm{atm\cdot L}}{\mathrm{K\cdot mol\text{-}g}} \times \frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}}\right)(273\ \mathrm{K})}{\left(44.01\ \frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)\left\{\frac{\pi}{4}(0.25\ \mathrm{m})^2\right\}(3\ \mathrm{atm})} = 34.54\ \frac{\mathrm{m}}{\mathrm{h}}$$

$$\mathrm{v}_{II_2} = 34.54\ \frac{\mathrm{m}}{\mathrm{h}} \times \frac{1\ \mathrm{h}}{3600\ \mathrm{s}} = 0.00959\ \frac{\mathrm{m}}{\mathrm{s}}$$

and at the tube exit

$$\mathrm{v}_{II_1} = \frac{\left(10000\ \frac{\mathrm{g}}{\mathrm{h}}\right)\left(0.082\frac{\mathrm{atm\cdot L}}{\mathrm{K\cdot mol\text{-}g}} \times \frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}}\right)(473\ \mathrm{K})}{\left(44.01\ \frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)\left\{\frac{\pi}{4}(0.25\ \mathrm{m})^2\right\}(1\ \mathrm{atm})} = 179.54\ \frac{\mathrm{m}}{\mathrm{h}}$$

$$\mathrm{v}_{II_1} = 179.54\ \frac{\mathrm{m}}{\mathrm{h}} \times \frac{1\ \mathrm{h}}{3600\ \mathrm{s}} = 0.04987\ \frac{\mathrm{m}}{\mathrm{s}}$$

being the result

$$\Delta\left(\hat{E}_{kin}\right)_{II} = \frac{1}{2}\left[\left(0.04987\ \frac{\mathrm{m}}{\mathrm{s}}\right)^2 - \left(0.00959\ \frac{\mathrm{m}}{\mathrm{s}}\right)^2\right] = 0.0011975\frac{\mathrm{J}}{\mathrm{kg}}$$

and in cal/mol-g

$$0.0011975\frac{\mathrm{J}}{\mathrm{kg}} \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}} \times \frac{44.01\ \mathrm{g}}{1\ \mathrm{mol\text{-}g}} \times \frac{0.000239\ \mathrm{kcal}}{1\ \mathrm{J}} \times \frac{1000\ \mathrm{cal}}{1\ \mathrm{kcal}} = 1.259\cdot 10^{-5}\frac{\mathrm{cal}}{\mathrm{mol\text{-}g}}$$

a value that is several orders of magnitude lower than the enthalpic term, $\Delta\widetilde{H}_{II}$=1914.88 cal/mol-g.

On the other hand, the heat flow can be estimated by the integral

$$q = \widehat{\mathcal{W}}_{II}\Delta\hat{Q}_{II} = \frac{\widehat{\mathcal{W}}_{II}}{\mathfrak{W}_{II}}\int_{T_{II_2}}^{T_{II_1}} T\mathrm{d}\tilde{S}_{II}$$

and in a first approximation it can be solved by the trapezoidal rule, giving

$$\Delta\tilde{Q}_{II} = \left(\frac{473\mathrm{K} + 273\mathrm{K}}{2}\right)\left(7.397\,\frac{\mathrm{cal}}{\mathrm{mol\text{-}g}\cdot\mathrm{K}}\right) = 2759.08\,\frac{\mathrm{cal}}{\mathrm{mol\text{-}g}}$$

$$q \approx \frac{\widehat{\mathcal{W}}_{II}}{\mathfrak{W}_{II}}\Delta\tilde{Q}_{II} = \frac{\left(10000\,\frac{\mathrm{g}}{\mathrm{h}}\right)}{\left(44.01\,\frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)}\left(2759.08\,\frac{\mathrm{cal}}{\mathrm{mol\text{-}g}}\right) = 626921\,\frac{\mathrm{cal}}{\mathrm{h}}$$

Question d. Section a of reference problem 0.12 indicates that

$$\begin{bmatrix}\text{heat flow given}\\ \text{by phase I}\end{bmatrix} = \begin{bmatrix}\text{heat flow gained}\\ \text{by phase II}\end{bmatrix} = q$$

$$-\widehat{\mathcal{W}}_{I}\Delta\hat{Q}_{I} = \widehat{\mathcal{W}}_{II}\Delta\hat{Q}_{II} = q$$

and since the steam side remains at constant pressure (which, according to one of the fundamental thermodynamic relations implies that $\mathrm{d}\hat{H} = \mathrm{d}\hat{Q}$) and by taking the results of the previous question for carbon dioxide, the balance becomes

$$-\widehat{\mathcal{W}}_{I}\Delta\hat{H}_{I} = \widehat{\mathcal{W}}_{II}\Delta\hat{Q}_{II} = 626921\,\frac{\mathrm{cal}}{\mathrm{h}}$$

Due to the fact that we are dealing with condensing vapor, the enthalpy difference of phase I will coincide with the latent heat of condensation (and $-\Delta\hat{H}_I = \Delta\hat{H}_{vap}$). Interpolating from table VI.1 of appendix VI, for a water vapor pressure of 40 atm (40.52 bar) a temperature of 251.5°C is obtained, a saturated liquid enthalpy of $\hat{H}_l^{sat} = 1092$ kJ/kg and a saturated vapor enthalpy of $\hat{H}_v^{sat} = 2800\ \mathrm{kJ/kg}$, so

$$\Delta\hat{H}_{vap} = \hat{H}_v^{sat} - \hat{H}_l^{sat} = 2800\,\frac{\mathrm{kJ}}{\mathrm{kg}} - 1092\,\frac{\mathrm{kJ}}{\mathrm{kg}} = 1708\,\frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$1708\,\frac{\mathrm{kJ}}{\mathrm{kg}} \times \frac{1000\ \mathrm{J}}{1\ \mathrm{kJ}} \times \frac{0.000239\ \mathrm{kcal}}{1\ \mathrm{J}} \times \frac{1000\ \mathrm{cal}}{1\ \mathrm{kcal}} = 408212\,\frac{\mathrm{cal}}{\mathrm{kg}}$$

and the balance will give

$$\widehat{\mathcal{W}}_{I} = \frac{q}{\Delta\hat{H}_{vap}} = \frac{\left(626921\,\frac{\mathrm{cal}}{\mathrm{h}}\right)}{\left(408212\,\frac{\mathrm{cal}}{\mathrm{kg}}\right)} = 1.536\,\frac{\mathrm{kg}}{\mathrm{h}}$$

Question e. According to section c of reference problem 0.12, the overall heat transfer coefficient is defined as

$$\mathrm{k}_T = \frac{q}{A\langle\Delta T\rangle_{ln}} = \frac{q}{A\left\{\dfrac{\Delta T_1 - \Delta T_2}{\ln\left(\dfrac{\Delta T_1}{\Delta T_2}\right)}\right\}}$$

where A is the pipe area (πdL), $\Delta T_2 = 251.5 - 0 = 251.5$ºC and $\Delta T_1 = 251.5 - 200 = 51.5$ºC. Hence

$$\mathrm{k}_T = \frac{\left(626921\ \dfrac{\mathrm{cal}}{\mathrm{h}}\right)}{3.1415(0.25\ \mathrm{m})(5\ \mathrm{m})\left\{\dfrac{51.5\mathrm{°C} - 251.5\mathrm{°C}}{\ln\left(\dfrac{51.5\mathrm{°C}}{251.5\mathrm{°C}}\right)}\right\}} = 1265.9\ \frac{\mathrm{cal}}{\mathrm{h}\cdot\mathrm{m}^2\cdot\mathrm{°C}}$$

5.2. A water stream needs to be heated from 40 to 80°C in an isobaric heat exchanger. The flow rate is 500 kg/min and it has a constant heat capacity of 1 cal/(g·°C). The hot stream is a thermostatic oil, with a specific heat capacity of 0.72 cal/(g·°C), whose temperature decreases from 150 to 100°C. The exchanger has an average heat transfer coefficient of 500 kcal/(h·m^2·K) and a variable surface (through an ingenious system that employs modules of 1 m^2 transfer area). Calculate the required oil flow, graphically represent the process in diagrams T_{oil} vs. T_{water} and T vs. *apparatus length coordinate* (operating both in parallel flow and counterflow) and demonstrate which is the most efficient way.

According to reference problem 0.12

$$\begin{bmatrix}\text{heat flow given}\\ \text{by the phase I}\end{bmatrix}=\begin{bmatrix}\text{heat flow gained}\\ \text{by the phase II}\end{bmatrix}$$

$$\widehat{\mathcal{W}}_I\Delta\hat{Q}_I=-\widehat{\mathcal{W}}_{II}\Delta\hat{Q}_{II}=q$$

Let phase I be oil and phase II be water. Since the pressure in the streams does not vary, $\mathrm{d}\hat{H}=\mathrm{d}\hat{Q}$ and then

$$\widehat{\mathcal{W}}_I\Delta\hat{H}_I=-\widehat{\mathcal{W}}_{II}\Delta\hat{H}_{II}=q$$

and if the specific heat capacities are temperature independent

$$\widehat{\mathcal{W}}_I\langle\hat{C}_P\rangle_I\Delta T_I=-\widehat{\mathcal{W}}_{II}\langle\hat{C}_P\rangle_{II}\Delta T_{II}=q$$

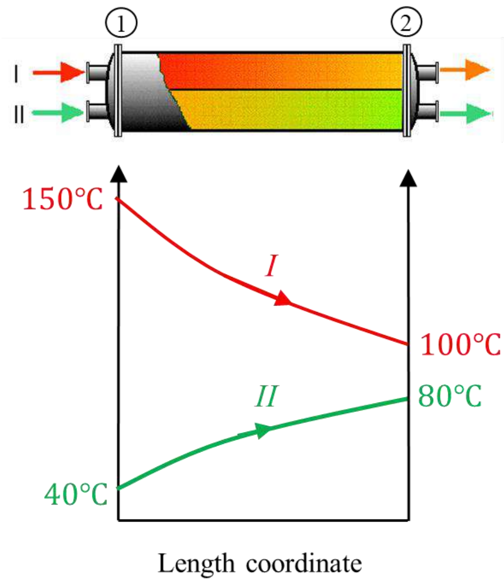
Hence

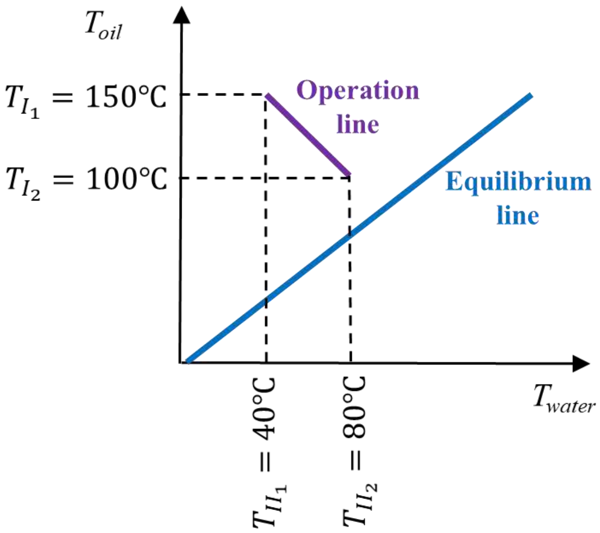
$$\widehat{\mathcal{W}}_I\left(0.72\ \frac{\mathrm{cal}}{\mathrm{g°C}}\right)(100°\mathrm{C}-150°\mathrm{C})=-\left(500\ \frac{\mathrm{kg}}{\mathrm{min}}\right)\left(1\ \frac{\mathrm{cal}}{\mathrm{g°C}}\right)(80°\mathrm{C}-40°\mathrm{C})=20000\ \frac{\mathrm{cal}}{\mathrm{min}}$$

and

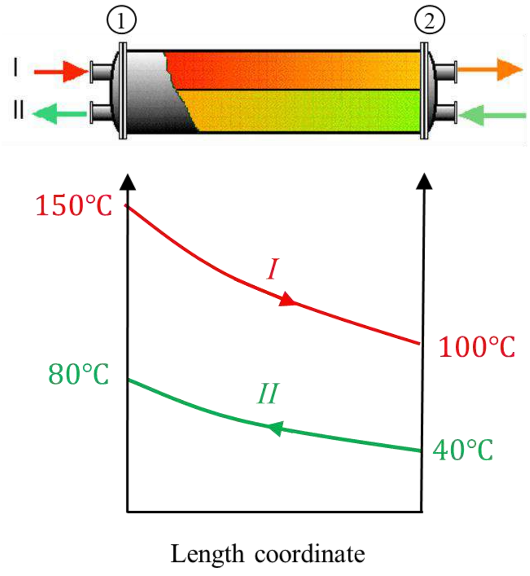
$$\widehat{\mathcal{W}}_I=-\frac{\left(500\ \frac{\mathrm{kg}}{\mathrm{min}}\right)\left(1\ \frac{\mathrm{cal}}{\mathrm{g°C}}\right)(80°\mathrm{C}-40°\mathrm{C})}{\left(0.72\ \frac{\mathrm{cal}}{\mathrm{g°C}}\right)(100°\mathrm{C}-150°\mathrm{C})}=555.55\ \frac{\mathrm{kg}}{\mathrm{min}}$$

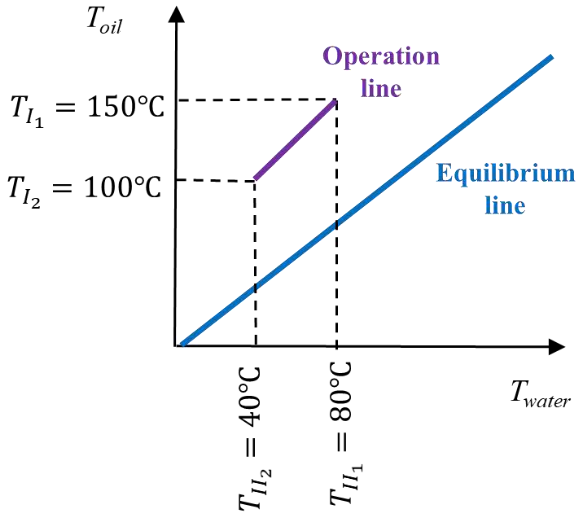
Regarding the graphical representation of the process for parallel flow in different scenarios





and for counterflow conditions





On the other hand, the efficiency of the two modes of operation can be compared by calculating the area required for heat transfer. In section c of reference problem 0.12 it is said that

$$A = \frac{q}{\mathrm{k}_T \langle \Delta T \rangle_{ln}} = \frac{q}{\mathrm{k}_T \left\{ \dfrac{\Delta T_1 - \Delta T_2}{\ln \left(\dfrac{\Delta T_1}{\Delta T_2} \right)} \right\}}$$

formula in which k_T is the heat transfer coefficient, whose units should be converted through factors of appendix I

$$\mathrm{k}_T = 500\ \frac{\mathrm{kcal}}{\mathrm{h}\cdot\mathrm{m}^2\cdot\mathrm{K}}\times\frac{1000\ \mathrm{cal}}{1\ \mathrm{kcal}}\times\frac{1\ \mathrm{h}}{60\ \mathrm{min}}\times\frac{1\ \mathrm{K}}{1\mathrm{°C}} = 8333.33\frac{\mathrm{cal}}{\mathrm{min}\cdot\mathrm{m}^2\cdot\mathrm{°C}}$$

For parallel flow, ΔT_1=150–40= 110ºC and ΔT_2=100–80= 20ºC

$$\langle\Delta T\rangle_{ln} = \frac{110-20}{\ln\left(\frac{110}{20}\right)} = 52.79\mathrm{°C}$$

$$A = \frac{\left(20000\ \frac{\mathrm{cal}}{\mathrm{min}}\right)}{\left(8333.33\frac{\mathrm{cal}}{\mathrm{min}\cdot\mathrm{m}^2\cdot\mathrm{°C}}\right)(52.79\mathrm{°C})} = 0.045\ \mathrm{m}^2$$

For counterflow, ΔT_1=150–80= 70ºC and ΔT_2=100–40= 60ºC

$$\langle\Delta T\rangle_{ln} = \frac{70-60}{\ln\left(\frac{70}{60}\right)} = 64.87\mathrm{°C}$$

$$A = \frac{\left(20000\ \frac{\mathrm{cal}}{\mathrm{min}}\right)}{\left(8333.33\frac{\mathrm{cal}}{\mathrm{min}\cdot\mathrm{m}^2\cdot\mathrm{°C}}\right)(64.87\mathrm{°C})} = 0.037\ \mathrm{m}^2$$

The area required to operate in parallel flow is higher than that in counterflow, so it can be concluded that the second way is better.

5.3. It is necessary to solidify 1000 kg/h of liquid tin at its melting temperature (231°C) by means of liquid naphthalene at its boiling point (218°C). Calculate the amount of hydrocarbon required and the contact area for the process if the heat transfer coefficient is of 1000 kcal/(m²·min·°C). Take the latent enthalpy of fusion of tin as 14.49 kcal/kg and the enthalpy of vaporization of naphthalene as 75.49 kcal/kg.

Since the statement of the problem does not inform about changes in temperature or pressure, it will be assumed that the only heats transferred are the latent ones

$$\begin{bmatrix}\text{heat flow given}\\ \text{by phase I}\end{bmatrix}=\begin{bmatrix}\text{heat flow gained}\\ \text{by phase II}\end{bmatrix}$$

$$\hat{\mathcal{W}}_I\Delta\hat{Q}_I=-\hat{\mathcal{W}}_{II}\Delta\hat{Q}_{II}=q$$

According to the fundamental thermodynamic relation $\mathrm{d}\hat{H}=\mathrm{d}\hat{Q}+\hat{V}\mathrm{d}P$. If the phases are isobaric ($\mathrm{d}P$=0), the heat transferred will be equal to the enthalpy change

$$\hat{\mathcal{W}}_I\Delta\hat{H}_I=-\hat{\mathcal{W}}_{II}\Delta\hat{H}_{II}=q$$

and then

$$\left(1000\ \frac{\text{kg}}{\text{h}}\right)\left(14.49\ \frac{\text{kcal}}{\text{kg}}\right)=\hat{\mathcal{W}}_{II}\left(75.49\ \frac{\text{kcal}}{\text{kg}}\right)=14490\ \frac{\text{kcal}}{\text{h}}$$

$$\hat{\mathcal{W}}_{II}=\frac{14490}{75.49}=192\ \frac{\text{kg}}{\text{h}}$$

The process is thermodynamically possible because phase I (tin) that has to lose heat is at a higher temperature than phase II (naphthalene), being the thermal potential of ΔT= 231–218= 13°C.

Regarding the contact surface, section c of reference problem 0.12 points out that

$$A=\frac{q}{\mathrm{k}_T\Delta T}$$

where all the data are known, but the units of the heat transfer coefficient supplied by the statement of the problem have to be converted to

$$1000\ \frac{\text{kcal}}{\text{min}\cdot\text{m}^2\cdot{}^\circ\text{C}}\times\frac{60\ \text{min}}{1\ \text{h}}=60000\frac{\text{kcal}}{\text{h}\cdot\text{m}^2\cdot{}^\circ\text{C}}$$

and therefore

$$A=\frac{\left(14490\ \frac{\text{kcal}}{\text{h}}\right)}{\left(60000\frac{\text{kcal}}{\text{h}\cdot\text{m}^2\cdot{}^\circ\text{C}}\right)(13^\circ\text{C})}=0.0186\ \text{m}^2$$

5.4. A heat exchanger uses superheated water vapor at 15 atm and 350ºC, which expands to 1.5 atm under reversible adiabatic conditions. Determine the state of the water after this process and the energy balance of the operation, neglecting the difference between the kinetic and potential energies of the fluid at the inlet and at the outlet:

a) By means of a Mollier diagram.
b) By means of a *PH*(*T*) diagram.
c) By means of a *TS*(*P*,*H*) diagram.
d) If the term due to kinetic energy change was not negligible, indicate what data would be needed to calculate it and qualitatively describe the calculation.

According to section b of reference problem 0.11, and since the mass flow rate of the stream does not change, the energy balance for water can be written as

$$\Delta\left(\tilde{U} + P\tilde{V} + \tilde{E}_{kin} + \tilde{E}_{pot} + \tilde{E}_{rad} + \tilde{E}_{other}\right)_{12} = \Delta\left(\tilde{H} + \tilde{E}_{kin} + \tilde{E}_{pot} + \tilde{E}_{rad} + \tilde{E}_{other}\right)_{12} = 0$$

if the differences of potential and kinetic energies between the inlet and outlet of the apparatus are negligible, and if the terms due to chemical reactions, friction, radiation, heat transfer and mechanical work… are included into the $\Delta\tilde{E}_{other}$ term, the balance will be reduced to the enthalpy difference between the final and initial states.

$$\Delta\left(\hat{E}_{other}\right)_{12} = -\Delta\hat{H}_{12} = \Delta\hat{H}_{21}$$

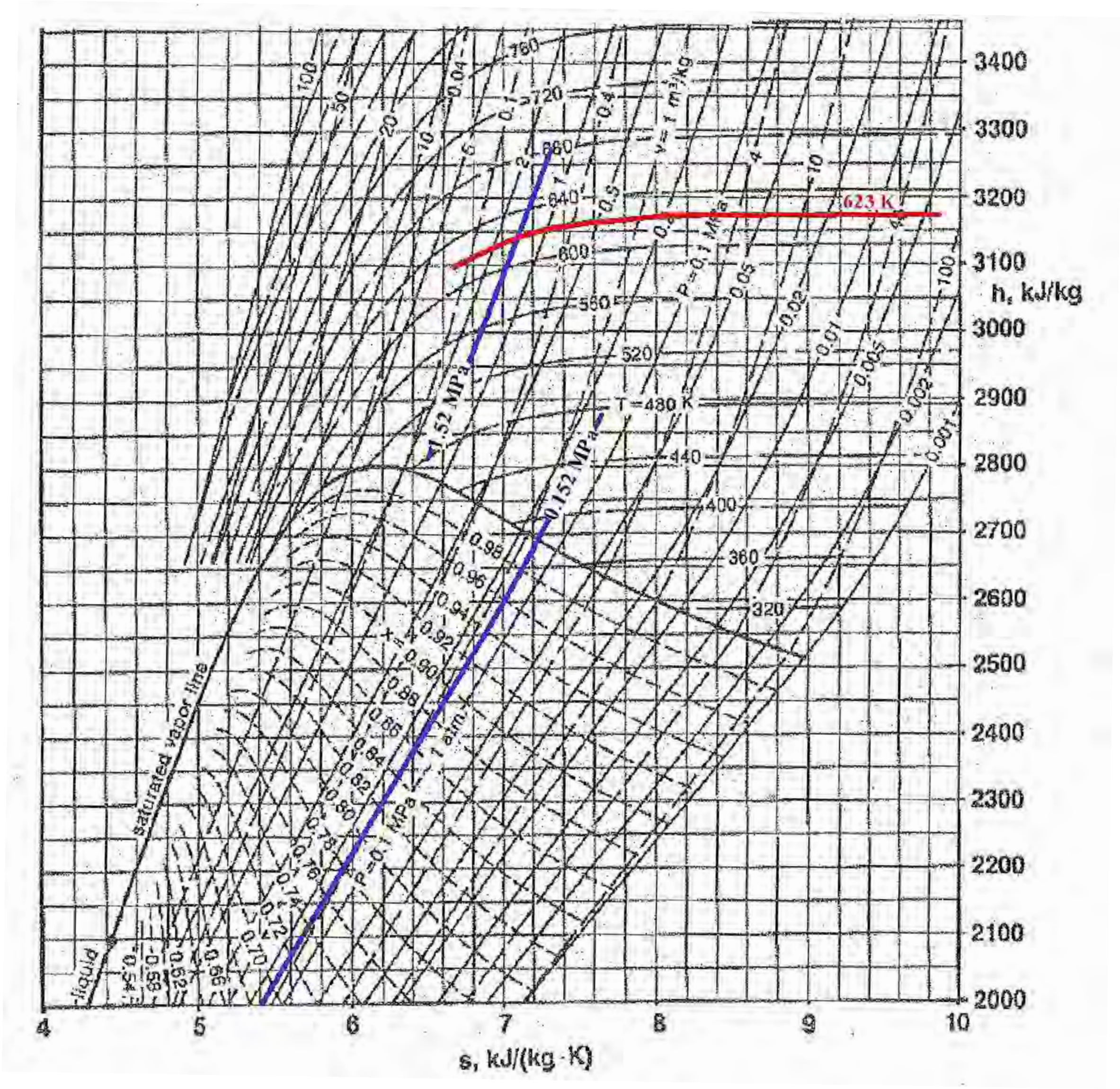
Question a. The Mollier diagram used here is the figure V.6 of appendix V, where pressures are expressed in MPa and temperature in K, so data of the statement of the problem have to be converted to these units by means of the conversion factors of appendix I

$$T_1(\text{K}) = 350\text{°C} + 273 = 623\ \text{K}$$

$$P_1 = 15\ \text{atm}\times\frac{1.013\ \text{bar}}{1\ \text{atm}}\times\frac{0.1\ \text{MPa}}{1\ \text{bar}} = 1.52\ \text{MPa}$$

$$P_2 = 1.5\ \text{atm}\times\frac{1.013\ \text{bar}}{1\ \text{atm}}\times\frac{0.1\ \text{MPa}}{1\ \text{bar}} = 0.152\ \text{MPa}$$

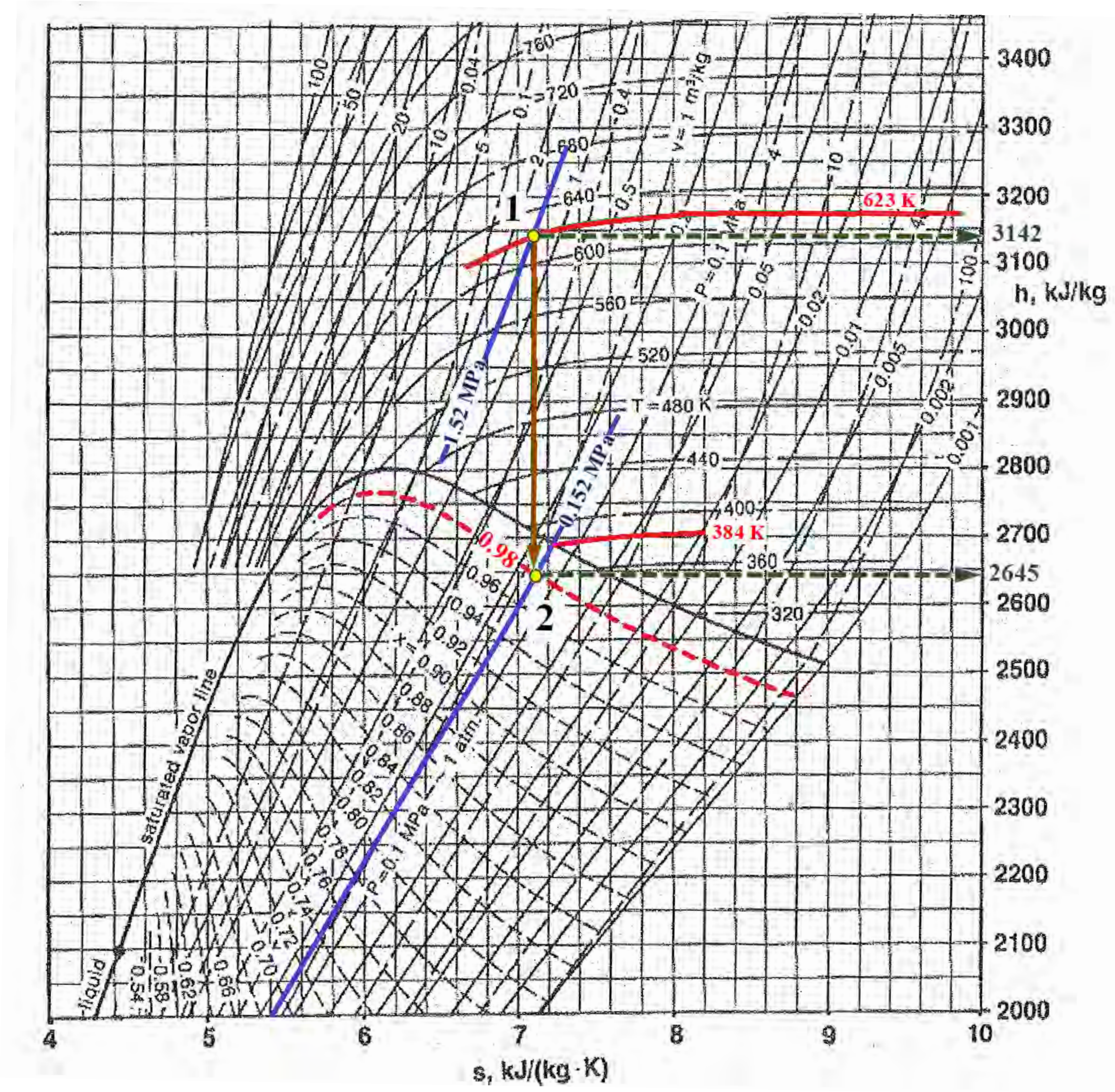
The isolines corresponding to these conditions are then obtained by graphical interpolation.



If the process is adiabatic, ΔQ=0. If it is also reversible, ΔQ=$\Delta S/T$, and therefore it will be isentropic (ΔS=0), from which it follows that the intersection between the isentropic line (in this case the operation line) that passes through the feed point (1) with the 0.152 MPa isobar will indicate the final conditions (2).

In this problem, as can be seen in the figure, the intersection takes place in the biphasic zone (mixture of saturated liquid and saturated vapor). The total enthalpy change is $\Delta\hat{H}_{21} = 2645$ kJ/kg – 3142 kJ/kg = –497 kJ/kg and the temperature of point 2 is that of saturated water at 0.152 MPa (384 K).

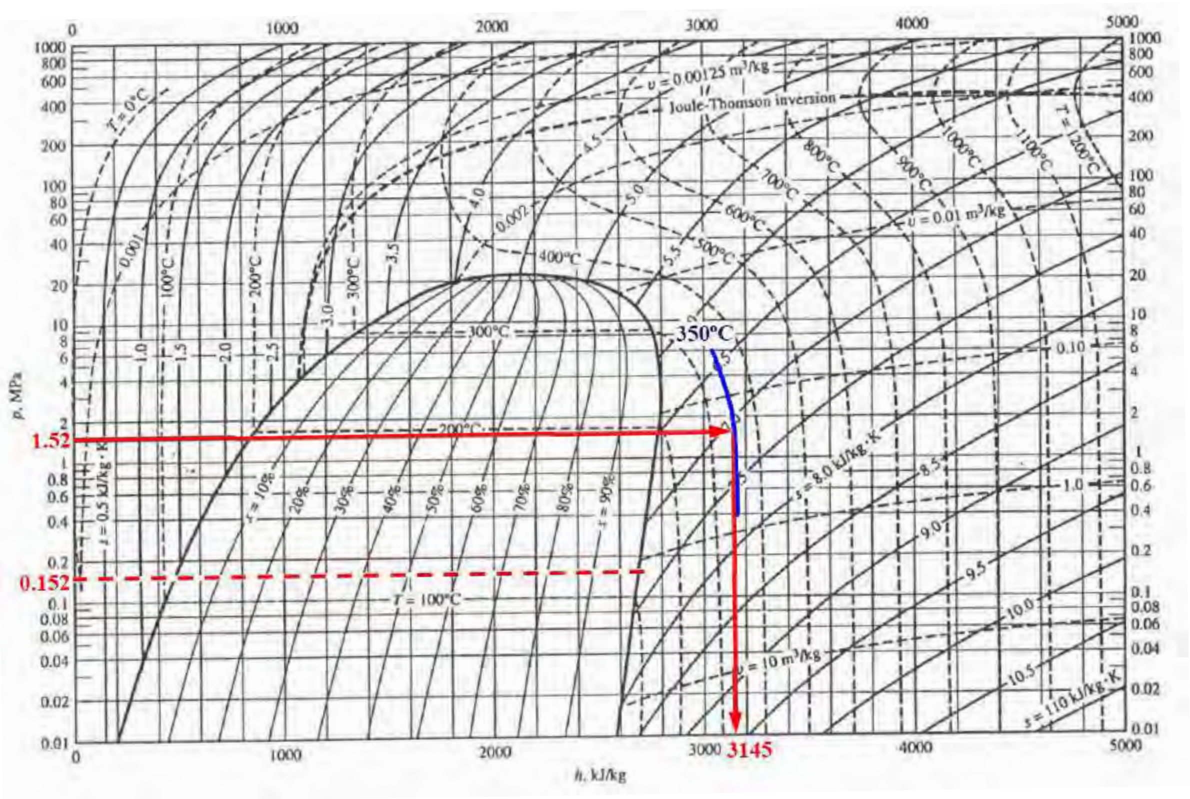
The amounts of saturated liquid and vapor could be calculated by combining the mass balance with that of enthalpy or that of entropy, but this diagram does not allow the reading of the enthalpies/ entropies in the saturated liquid at pressures far from the critical point. Fortunately, lines of title or quality are available (from 0.54 to 0.98), which indicate the proportion of vapor in the mixture. In this case, the liquid-vapor mixture contains 98% vapor.

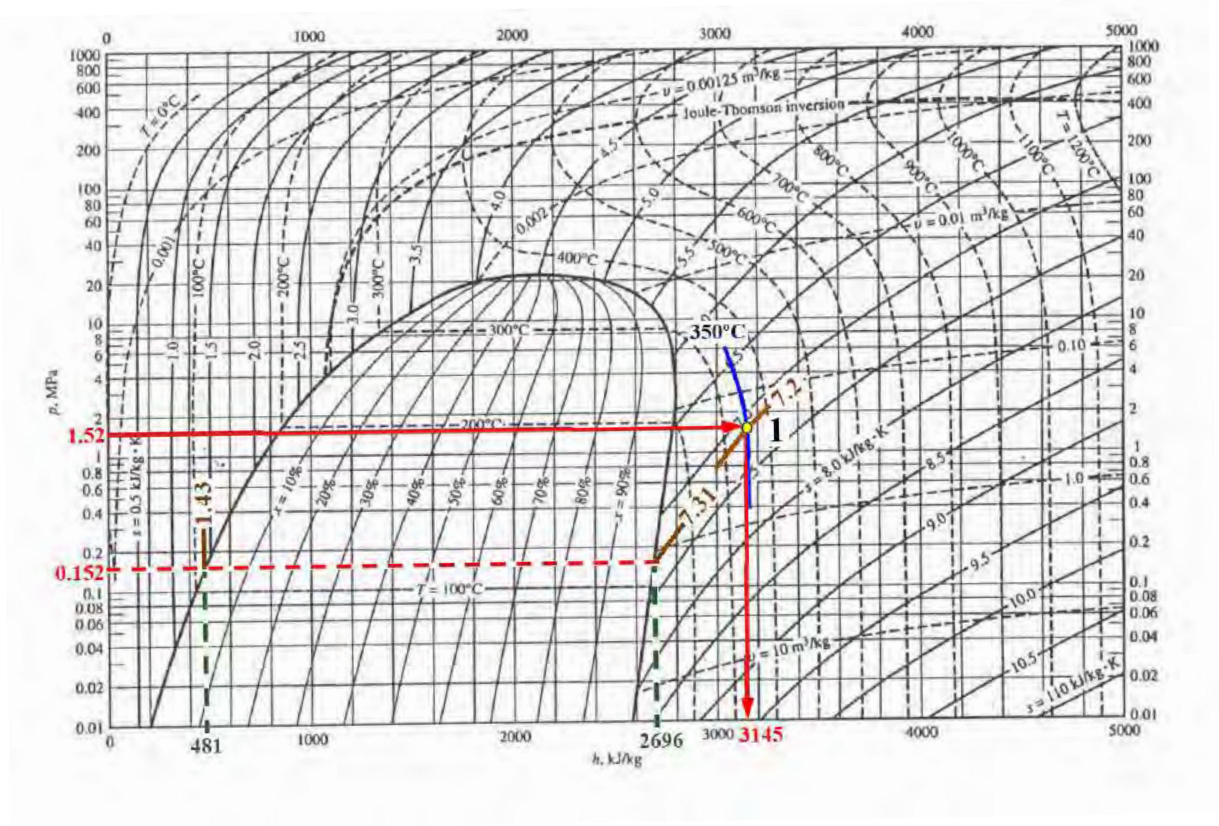


Question b. The *PH* diagram of water is the figure V.5 of appendix V. In it, the pressures are in MPa, as in the previous question.

The solution will be the crossing of the isentropic line that passes through 1.52 MPa and 350ºC (≈7.2 kJ/kg·K) with the 0.152 bar isobar, which falls in the biphasic zone. Although in the diagram the isentropic lines do not enter this zone, the location of point 2 can be found by the combination of the mass and entropy balances, after interpolating the specific entropies of the saturated liquid and vapor ($\hat{S}_{l_2}^{sat}$=1.43 kJ/kg·K, $\hat{S}_{v_2}^{sat}$ =7.31 kJ/kg·K).

$$\frac{M_{v_2}}{M_{tot}} = \frac{\left(\hat{S}_2 - \hat{S}_{l_2}^{sat}\right)}{\left(\hat{S}_{v_2}^{sat} - \hat{S}_{l_2}^{sat}\right)} = \frac{(7.2 - 1.43)}{(7.31 - 1.43)} = 0.981$$



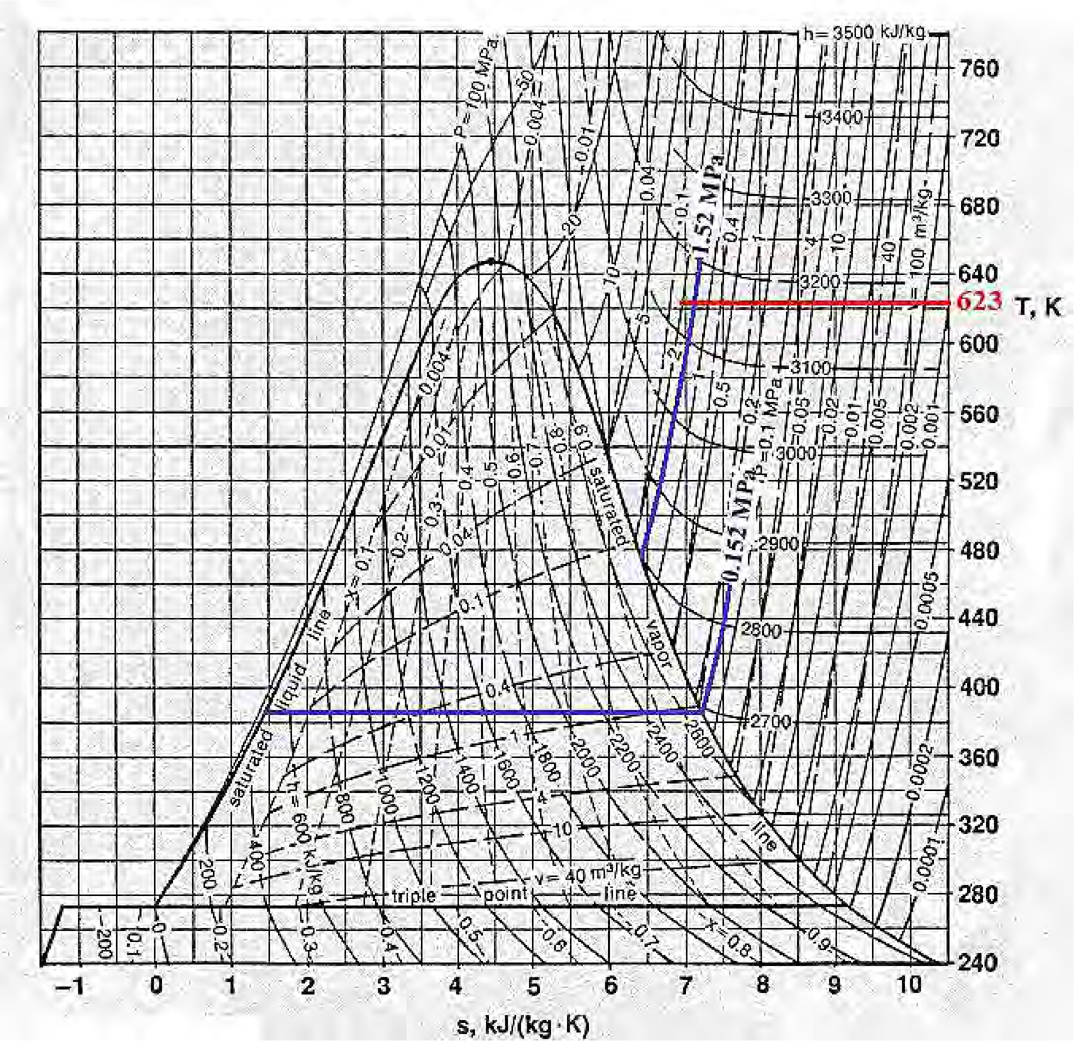


The quality line of 98.1% could be drawn between those of 90% and 100%, and then the enthalpy $\widehat{H}_2$ could be read, but it is not necessary, because by interpolating the enthalpies of the saturated liquid and vapor (481 and 2696 kJ/kg respectively) and combining the mass and enthalpy balances it can be obtained

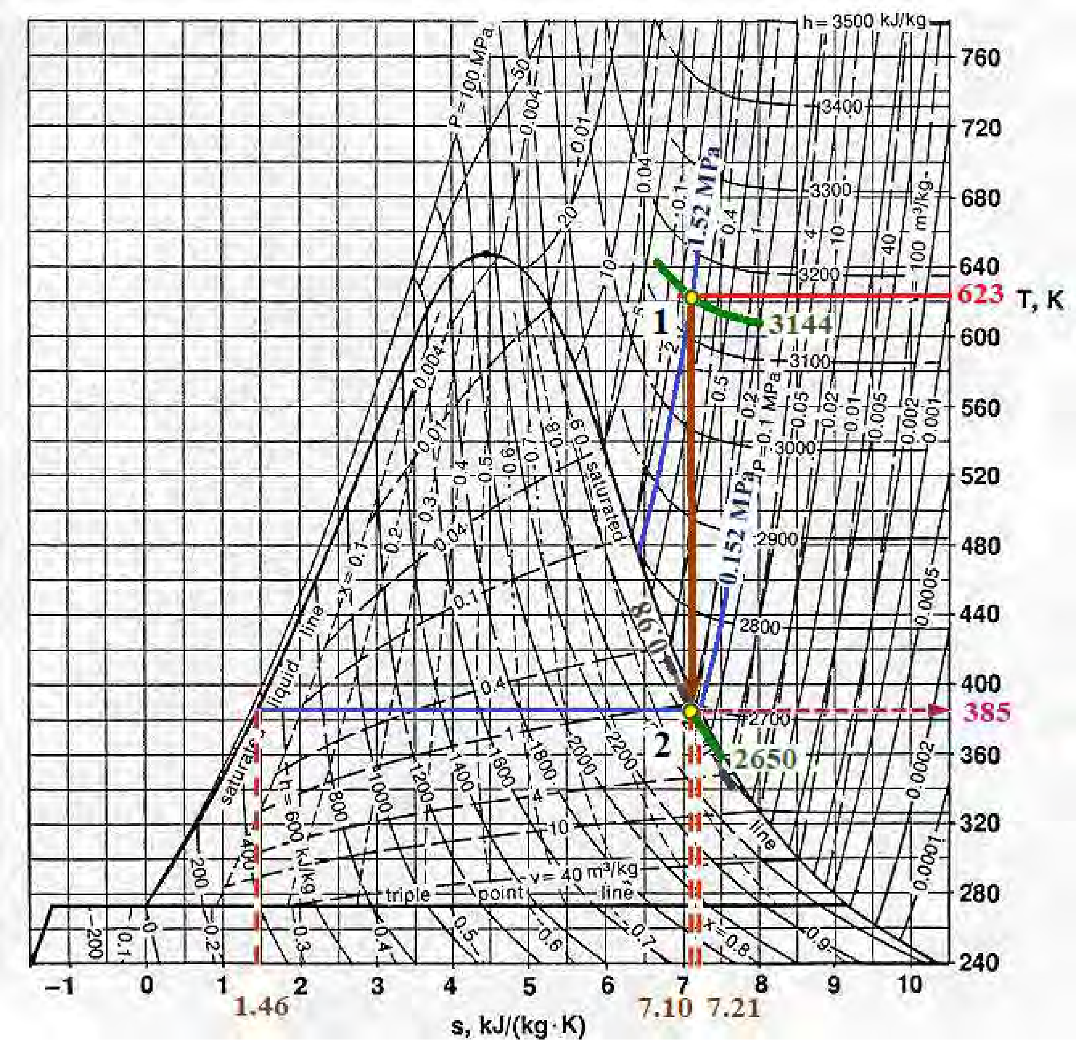
$$\widehat{H}_2=\frac{M_{v_2}}{M_{tot}}\widehat{H}_{v_2}^{sat}+\frac{M_{l_2}}{M_{tot}}\widehat{H}_{l_2}^{sat}=0.981\left(2696\ \frac{\text{kJ}}{\text{kg}}\right)+(1-0.981)\left(481\ \frac{\text{kJ}}{\text{kg}}\right)=2654\ \frac{\text{kJ}}{\text{kg}}$$

The enthalpy change will be $\Delta\widehat{H}_{21}$ = 2654 kJ/kg –3145 kJ/kg= –491 kJ/kg (the same as in the previous section if the error due to the graphical reading is considered) and the temperature is slightly higher than 100ºC (approximately of 110ºC).

Question c. In the *TS* diagram (figure V.7 of appendix V) the intersection of the isentropic line that passes through 623 K and 1.52 MPa with the isobar of 0.152 MPa



indicates a temperature of 385 K.



Enthalpy reading is not as direct as in questions **a** and **b**, because this property in this type of diagrams is represented in isolines, and interpolation is difficult (particularly within the biphasic zone).

$$\hat{H}_1 = 3144\ \frac{\text{kJ}}{\text{kg}} \qquad ; \qquad \hat{H}_2 \approx 2650\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\hat{H}_{21} = 2650\ \frac{\text{kJ}}{\text{kg}} - 3144\ \frac{\text{kJ}}{\text{kg}} = -494\ \frac{\text{kJ}}{\text{kg}}$$

Regarding the proportion of vapor, the interpolation of the title line also indicates a value of 98%. The combination of the mass balance with the entropy one (and not with that of enthalpy, because the reading of $\hat{S}$ is direct and simpler) confirms the result

$$\frac{M_v}{M_{tot}} = \frac{\hat{S}_{tot} - \hat{S}_{l_2}^{sat}}{\hat{S}_{v_2}^{sat} - \hat{S}_{l_2}^{sat}} = \frac{7.10 - 1.46}{7.21 - 1.46} = 0.981$$

Question d. The change in kinetic energy per unit mass between state 1 and state 2 will be given by

$$\Delta\hat{E}_{kin} = \frac{1}{2}(\mathrm{v}_2^2 - \mathrm{v}_1^2)$$

Since the mean velocity is related to the mass flow rate by the formula

$$\mathrm{v} = \frac{\hat{\mathcal{W}}\hat{V}}{A}$$

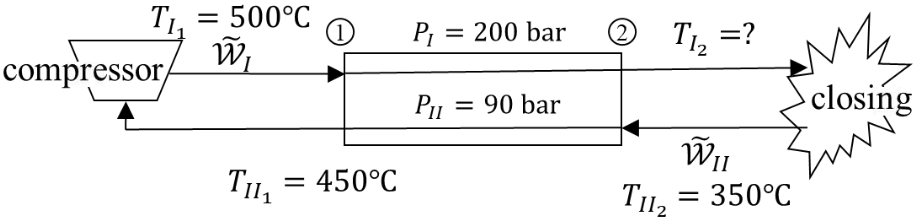
if we assume that the cross-section of the heat exchanger pipes does not vary, it can be obtained

$$\Delta\hat{E}_{kin} = \frac{1}{2}\left(\frac{\hat{\mathcal{W}}}{A}\right)^2 \left(\hat{V}_2^2 - \hat{V}_1^2\right)$$

The isochores of the HS and TS diagrams show that $0.1 < \hat{V}_1 < 0.4$ m^3/kg and $1 < \hat{V}_2 < 4$ m^3/kg, while those of the PH diagram indicates that $0.1 < \hat{V}_1 < 1$ m^3/kg and $\hat{V}_2 > 1$ m^3/kg, which implies that the kinetic term is positive. The kinetic energy of the system increases, but in a very small proportion compared with the enthalpy change.

5.5. A steam stream at 350°C and 90 bar, with a flow rate of 0.27 kg/s, circulates through a heat exchanger under practically isobaric conditions until reaching 450°C. Then, it feeds a compressor, which leaves at 500°C and 200 bar, and it is recycled in counterflow as the heating fluid of the aforementioned isobaric exchanger, which has no heat losses. The circuit is closed by means of a suitable thermomechanical operation. Estimate the mechanical work and power in each operation (if present) using a Mollier diagram, a *PH*(*T*) diagram and a *TS*(*P,H*) one.

An approximate representation of the process is



Sections b and c of reference problem 0.3 indicate that the flow work and the heat in the compressor are related by the expression

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P$$

To close the circuit it seems feasible some kind of expansion which will follow the same formula. Furthermore, in the case of an isobaric heat exchanger ($\mathrm{d}P$=0), it follows that $\mathrm{d}\hat{H} = \mathrm{d}\hat{Q}$.

In order to use the Mollier diagram (Figure V.6 of appendix V), pressures must be expressed in MPa and temperatures in K

$$T_{I_1}(\mathrm{K}) = 500°\mathrm{C} + 273 = 773\ \mathrm{K}$$

$$T_{II_1}(\mathrm{K}) = 450°\mathrm{C} + 273 = 723\ \mathrm{K}$$

$$T_{II_2}(\mathrm{K}) = 350°\mathrm{C} + 273 = 623\ \mathrm{K}$$

$$P_I = 200\ \mathrm{bar} \times \frac{0.1\ \mathrm{MPa}}{1\ \mathrm{bar}} = 20\ \mathrm{MPa}$$

$$P_{II} = 90\ \mathrm{bar} \times \frac{0.1\ \mathrm{MPa}}{1\ \mathrm{bar}} = 9\ \mathrm{MPa}$$

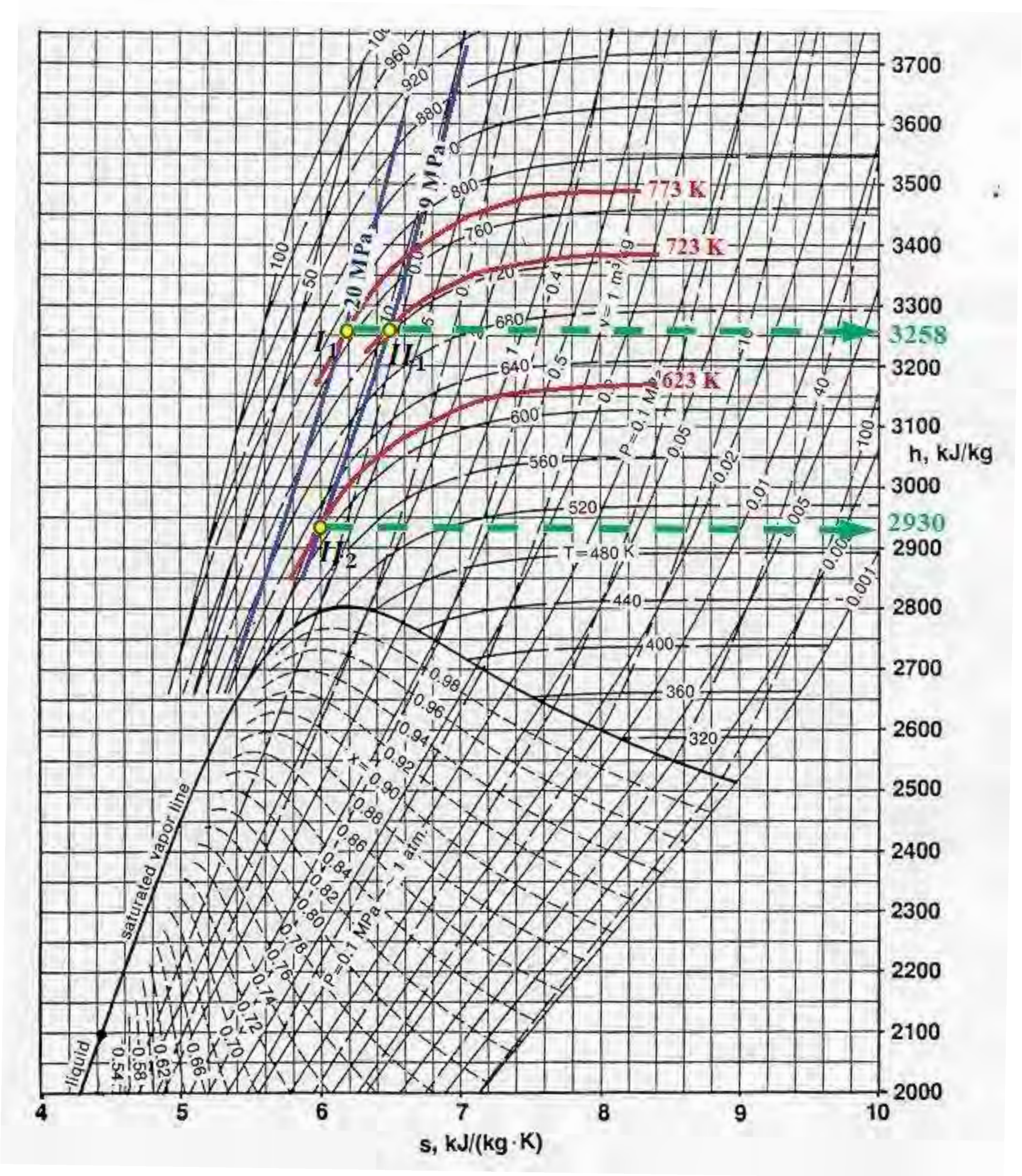
After that, the lines corresponding to these values are graphically interpolated, the enthalpies are read in the diagram and a balance is proposed to find the missing temperature

$$\begin{bmatrix}\text{heat flow given}\\ \text{by phase I}\end{bmatrix} = \begin{bmatrix}\text{heat flow gained}\\ \text{by phase II}\end{bmatrix}$$

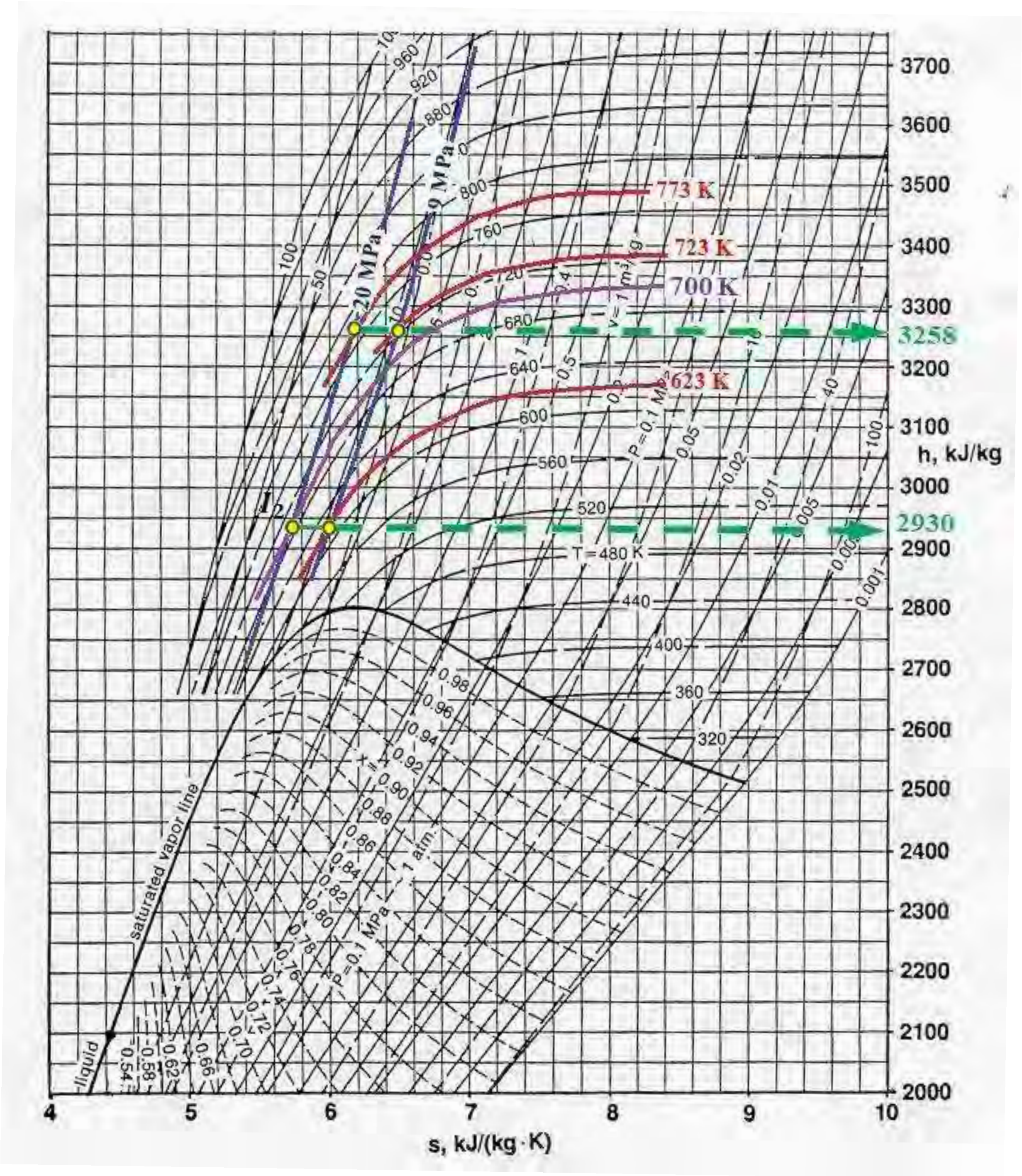
$$\widehat{\mathcal{W}}_I \Delta \hat{Q}_I = -\widehat{\mathcal{W}}_{II} \Delta \hat{Q}_{II} \quad \xrightarrow{\mathrm{d}P=0} \quad \widehat{\mathcal{W}}_I \Delta \hat{H}_I = -\widehat{\mathcal{W}}_{II} \Delta \hat{H}_{II}$$

$$\widehat{\mathcal{W}}_I\left(\hat{H}_{I_1} - \hat{H}_{I_2}\right) = \widehat{\mathcal{W}}_{II}\left(\hat{H}_{II_1} - \hat{H}_{II_2}\right)$$

from where $\hat{H}_{I_2}$ is calculated. The isotherm that intersects with the 20 MPa isobar in this enthalpy will be T_{I_2}.



However, since $\widehat{W}_I = \widehat{W}_{II}$ and the diagram shows that (by chance) $\widehat{H}_{I_1} = \widehat{H}_{II_1}$ =3258 kJ/kg, it can be easily concluded that $\widehat{H}_{I_2} = \widehat{H}_{II_2}$ = 2930 kJ/kg. The sought isotherm is approximately of 700 K (427ºC).



But the important thing to solve the problem is that $\widehat{H}_{I_1} = \widehat{H}_{II_1}$ (isenthalpic compression), i.e.

$$\mathrm{d}\widehat{W}^{\mathrm{fl}} = -T\mathrm{d}\hat{S} \qquad \rightarrow \qquad \Delta\widehat{W}_1^{\mathrm{fl}} = -\int_{II_1}^{I_1} T\mathrm{d}\hat{S}$$

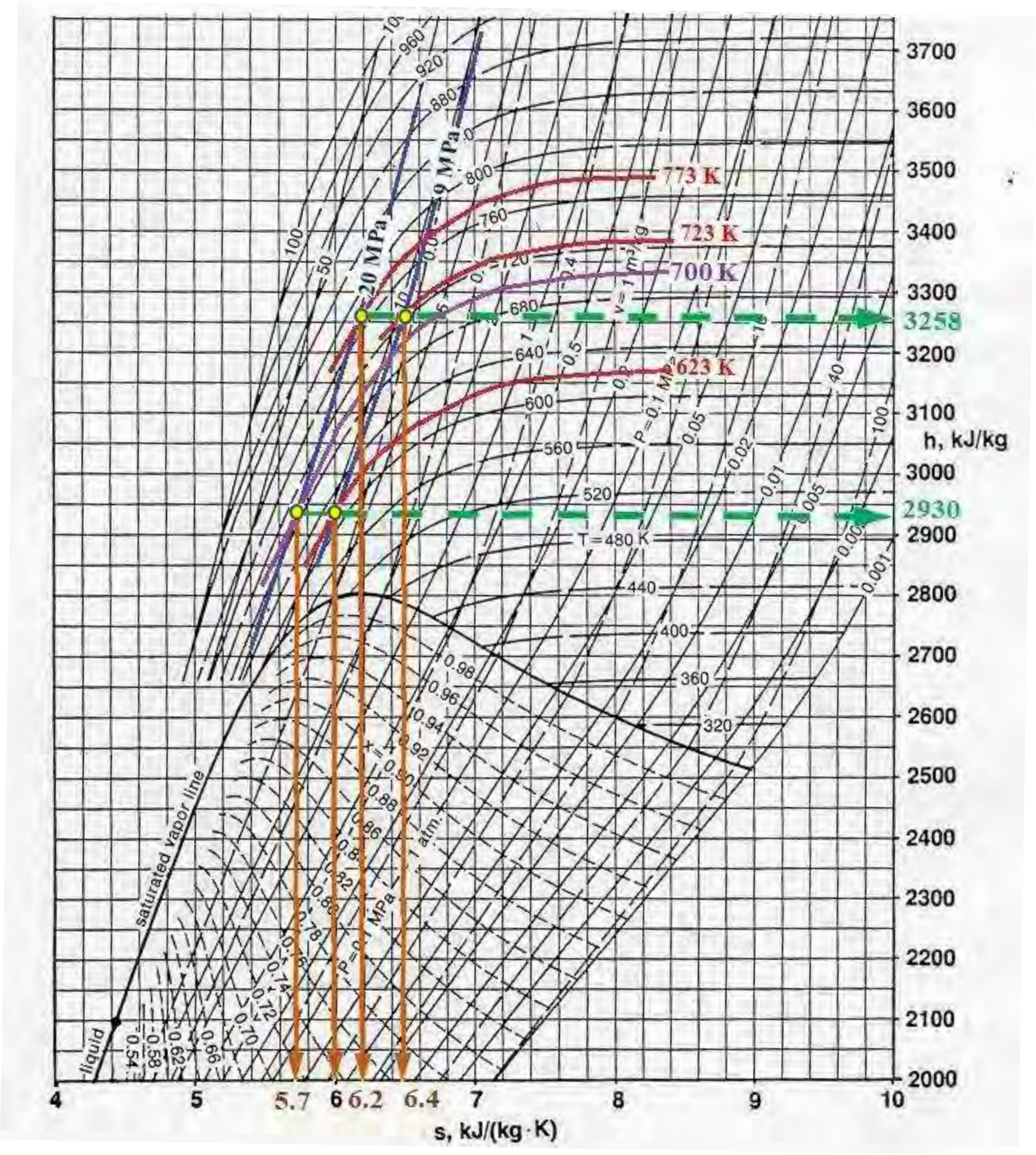
and due to the fact that $\widehat{H}_{I_2} = \widehat{H}_{II_2}$, the final expansion will be isenthalpic as well

$$\Delta\widehat{W}_2^{\text{fl}} = -\int_{I_2}^{II_2} T\mathrm{d}\hat{S}$$

The integrals have to be estimated by numerical methods, such as the trapezoidal rule, which in its simplest version establishes

$$\Delta\widehat{W}_1^{\text{fl}} = -\left(\frac{T_{I_1} + T_{II_1}}{2}\right)\left(\hat{S}_{I_1} - \hat{S}_{II_1}\right)$$

$$\Delta\widehat{W}_2^{\text{fl}} = -\left(\frac{T_{II_2} + T_{I_2}}{2}\right)\left(\hat{S}_{II_2} - \hat{S}_{I_2}\right)$$



By reading the entropies from the Mollier diagram

$$\hat{S}_{I_1} = 6.2\ \mathrm{kJ/(kg\cdot K)}$$
$$\hat{S}_{I_2} = 5.7\ \mathrm{kJ/(kg\cdot K)}$$
$$\hat{S}_{II_1} = 6.4\ \mathrm{kJ/(kg\cdot K)}$$
$$\hat{S}_{II_2} = 6.0\ \mathrm{kJ/(kg\cdot K)}$$

and performing the calculations for the involved works and powers

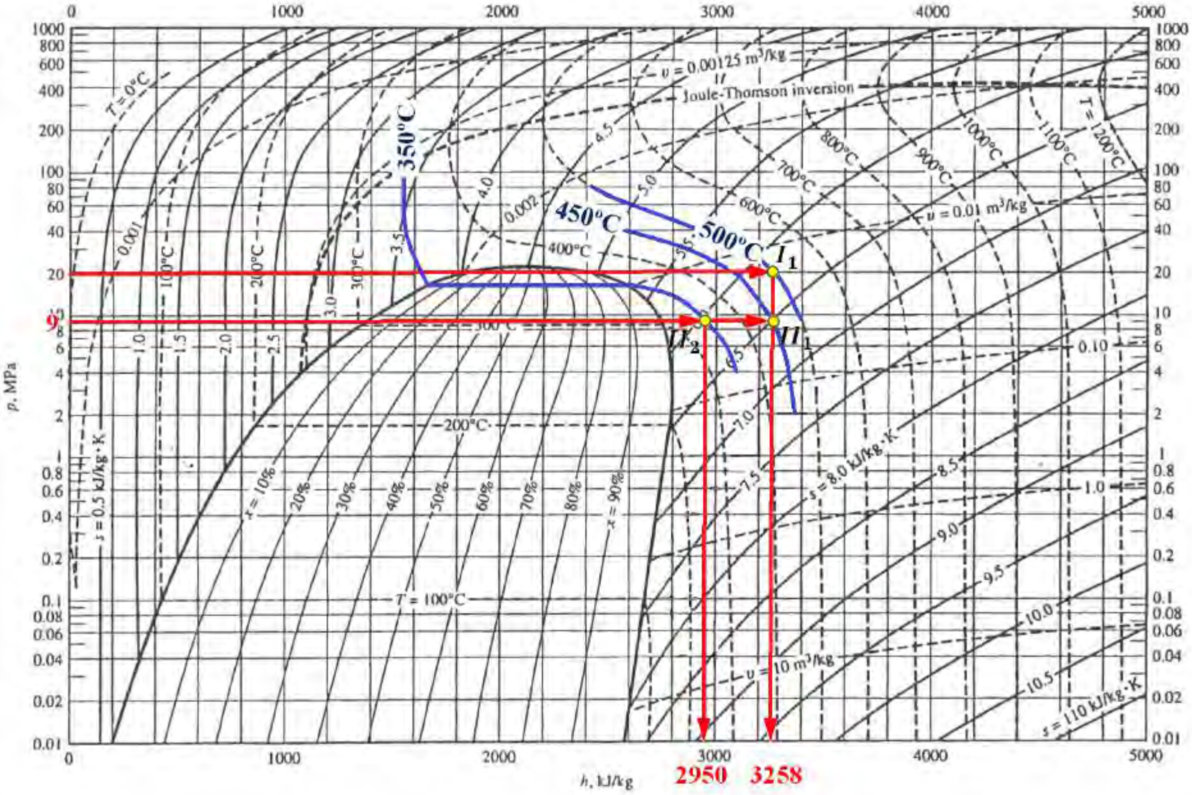
$$\Delta\widehat{W}_1^{\mathrm{fl}} = -\left(\frac{773\ \mathrm{K} + 723\ \mathrm{K}}{2}\right)\left(6.2\ \frac{\mathrm{kJ}}{\mathrm{kg\cdot K}} - 6.4\ \frac{\mathrm{kJ}}{\mathrm{kg\cdot K}}\right) = 149.6\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\mathscr{p}_1 = \widehat{\mathcal{W}}\Delta\widehat{W}_1^{\mathrm{fl}} = \left(0.27\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(149.6\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 40.39\ \mathrm{kW}$$

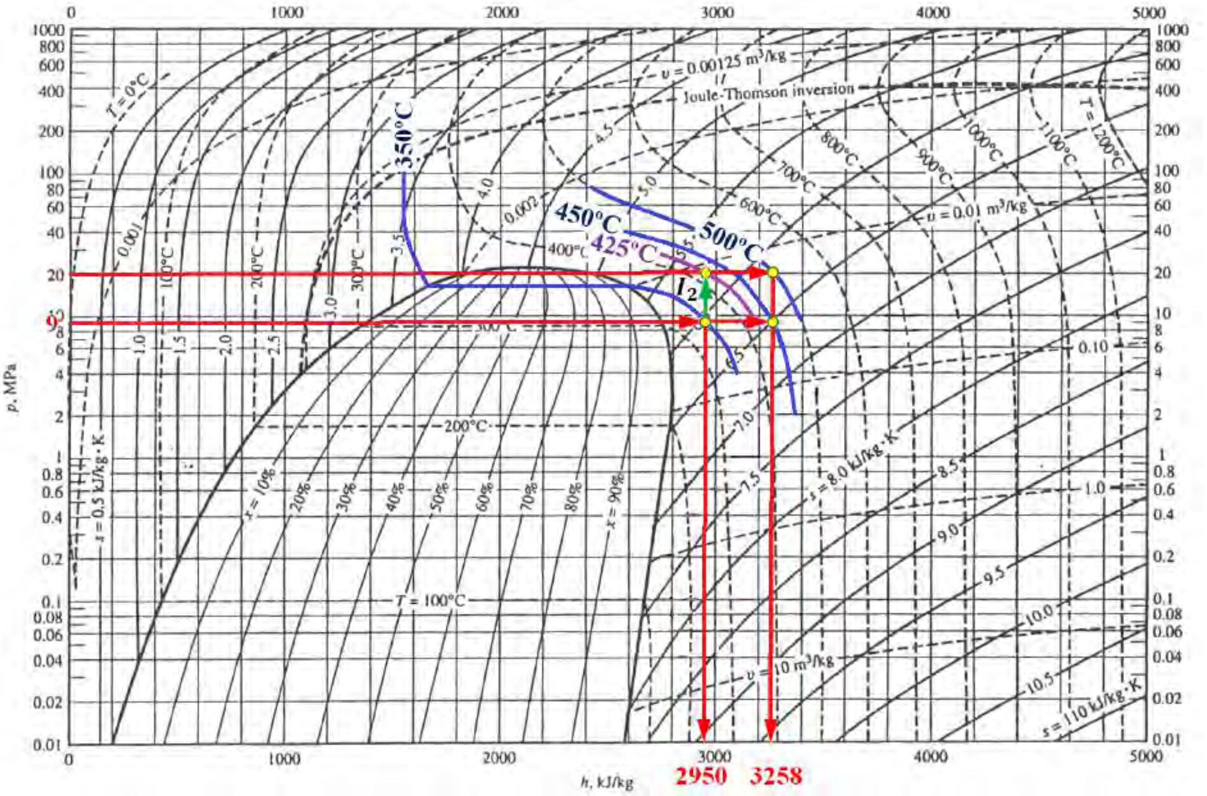
$$\Delta\widehat{W}_2^{\mathrm{fl}} = -\left(\frac{623\ \mathrm{K} + 700\ \mathrm{K}}{2}\right)\left(6.0\ \frac{\mathrm{kJ}}{\mathrm{kg\cdot K}} - 5.7\ \frac{\mathrm{kJ}}{\mathrm{kg\cdot K}}\right) = -198.45\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\mathscr{p}_2 = \widehat{\mathcal{W}}\Delta\widehat{W}_2^{\mathrm{fl}} = \left(0.27\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(-198.15\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -53.58\ \mathrm{kW}$$

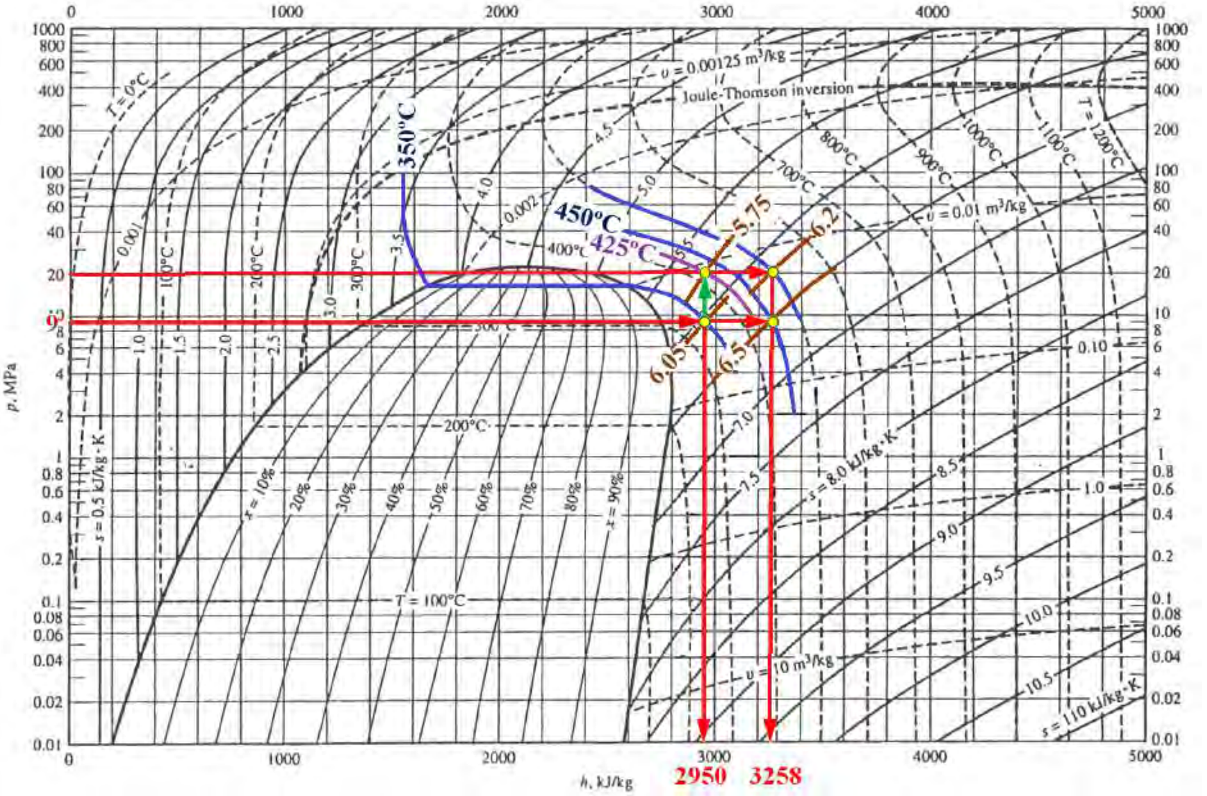
In the case of the *PH* diagram (figure V.5 of this book's appendix V) the procedure is analogous to that in the Mollier one: the streams are located by intersection of the pressure with the temperature lines, the enthalpies are directly read and it is also seen that $\widehat{H}_{I_1} = \widehat{H}_{II_1} = 3258$ kJ/kg, which implies that $\widehat{H}_{I_2} = \widehat{H}_{II_2}$.



The temperature is between 400 and 450, around 425ºC (698 K).



Regarding the reading of the isentropic lines, their values are



$$\hat{S}_{I_1} = 6.2\ \mathrm{kJ/(kg\cdot K)}$$
$$\hat{S}_{I_2} = 5.75\ \mathrm{kJ/(kg\cdot K)}$$
$$\hat{S}_{II_1} = 6.5\ \mathrm{kJ/(kg\cdot K)}$$
$$\hat{S}_{II_2} = 6.05\ \mathrm{kJ/(kg\cdot K)}$$

and the flow works and powers in the compressor and in the expansion device will give

$$\Delta\widehat{W}_1^{\mathrm{fl}} = -\left(\frac{773\ \mathrm{K} + 723\ \mathrm{K}}{2}\right)\left(6.2\ \frac{\mathrm{kJ}}{\mathrm{kg\cdot K}} - 6.5\ \frac{\mathrm{kJ}}{\mathrm{kg\cdot K}}\right) = 224.4\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\wp_1 = \widehat{\mathcal{W}}\Delta\widehat{W}_1^{\mathrm{fl}} = \left(0.27\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(224.4\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 60.59\ \mathrm{kW}$$

$$\Delta\widehat{W}_2^{\mathrm{fl}} = -\left(\frac{623\ \mathrm{K} + 698\ \mathrm{K}}{2}\right)\left(6.05\ \frac{\mathrm{kJ}}{\mathrm{kg\cdot K}} - 5.75\ \frac{\mathrm{kJ}}{\mathrm{kg\cdot K}}\right) = -198.15\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\wp_2 = \widehat{\mathcal{W}}\Delta\widehat{W}_2^{\mathrm{fl}} = \left(0.27\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(-198.15\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -53.5\ \mathrm{kW}$$

Finally, in figure V.7 of appendix V (*TS* diagram of water) the location of the points allows to determine that the enthalpies are 3235 kJ/kg and 2942 kJ/kg. By extrapolating the isenthalpic line corresponding to the second value, it intersects the 20 MPa isobar at a temperature of 700 K, as in the Mollier diagram. The entropies will be

$$\hat{S}_{I_1} = 6.12\ \mathrm{kJ/(kg\cdot K)}$$
$$\hat{S}_{I_2} = 5.72\ \mathrm{kJ/(kg\cdot K)}$$
$$\hat{S}_{II_1} = 6.50\ \mathrm{kJ/(kg\cdot K)}$$
$$\hat{S}_{II_2} = 6.0\ \mathrm{kJ/(kg\cdot K)}$$

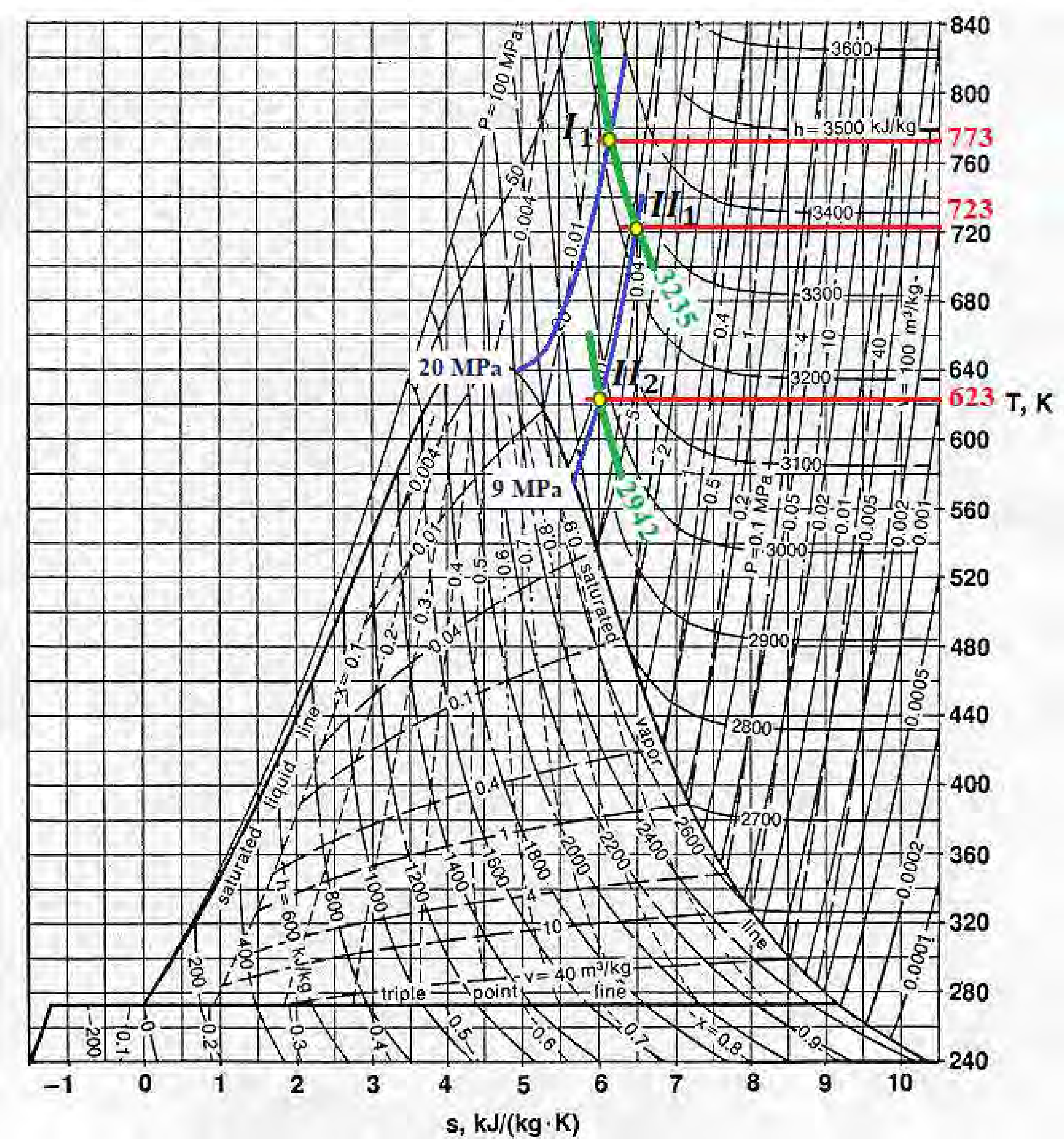
and the works and powers of the two stages

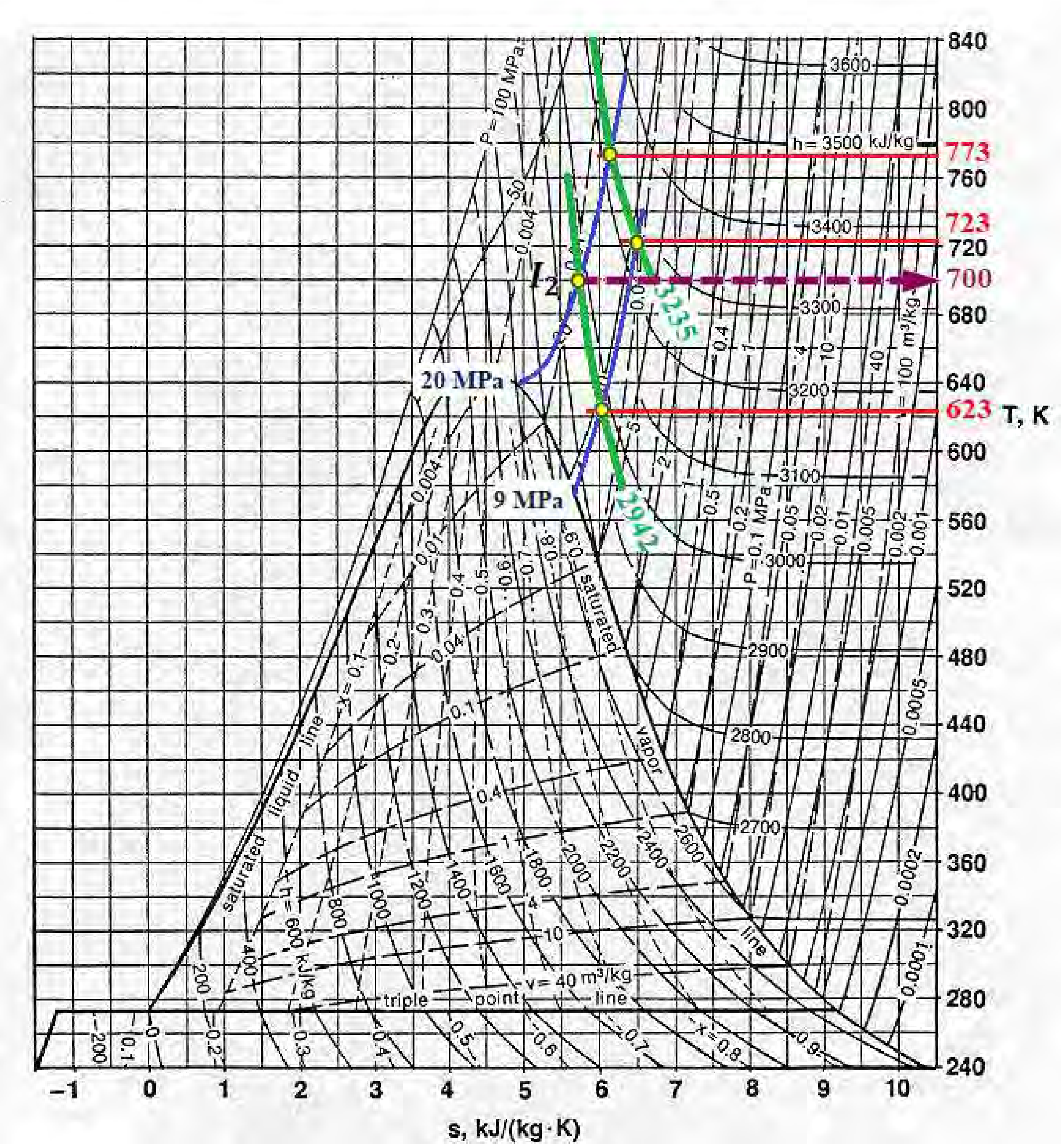
$$\Delta\widehat{W}_1^{\mathrm{fl}} = -\left(\frac{773\ \mathrm{K} + 723\ \mathrm{K}}{2}\right)\left(6.12\ \frac{\mathrm{kJ}}{\mathrm{kg\cdot K}} - 6.50\ \frac{\mathrm{kJ}}{\mathrm{kg\cdot K}}\right) = 284.24\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

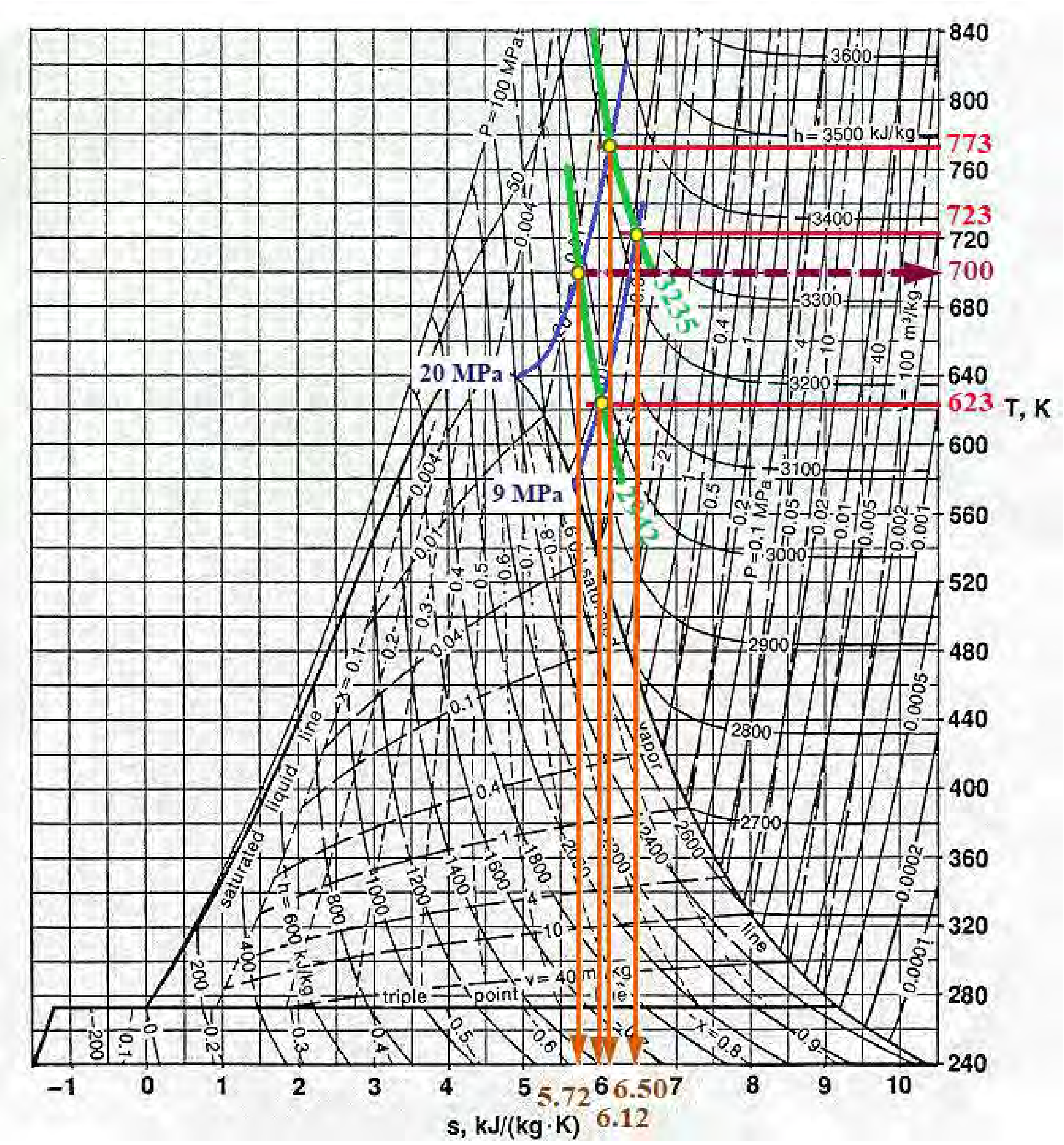
$$\wp_1 = \widehat{\mathcal{W}}\Delta\widehat{W}_1^{\mathrm{fl}} = \left(0.27\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(284.24\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 76.74\ \mathrm{kW}$$

$$\Delta\widehat{W}_2^{\mathrm{fl}} = -\left(\frac{623\ \mathrm{K} + 700\ \mathrm{K}}{2}\right)\left(6.0\ \frac{\mathrm{kJ}}{\mathrm{kg\cdot K}} - 5.72\ \frac{\mathrm{kJ}}{\mathrm{kg\cdot K}}\right) = -185.22\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\wp_2 = \widehat{\mathcal{W}}\Delta\widehat{W}_2^{\mathrm{fl}} = \left(0.27\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(-185.22\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -50.01\ \mathrm{kW}$$


I1
II1
II2
3235
2942
20 MPa
9 MPa
773
723
623
T, K
840
800
760
720
680
640
600
560
520
480
440
400
360
320
280
240
s, kJ/(kg·K)
−1
0
1
2
3
4
5
6
7
8
9
10
P = 100 MPa
50
h = 3500 kJ/kg
3600
3400
3300
3200
3100
3000
2900
2800
2700
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
h = 600 kJ/kg
400
200
0
−200
v = 100 m³/kg
40
10
4
1
0.4
0.1
0.04
0.01
0.004
0.2
P = 0.1 MPa
0.05
0.02
0.005
0.002
0.001
0.0005
0.0002
0.0001
v = 40 m³/kg
line
x = 0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
saturated liquid line
saturated vapor line
triple point line
0.1
0.2
0.3
0.4
0.5
0.6
0.7
x = 0.8
0.9

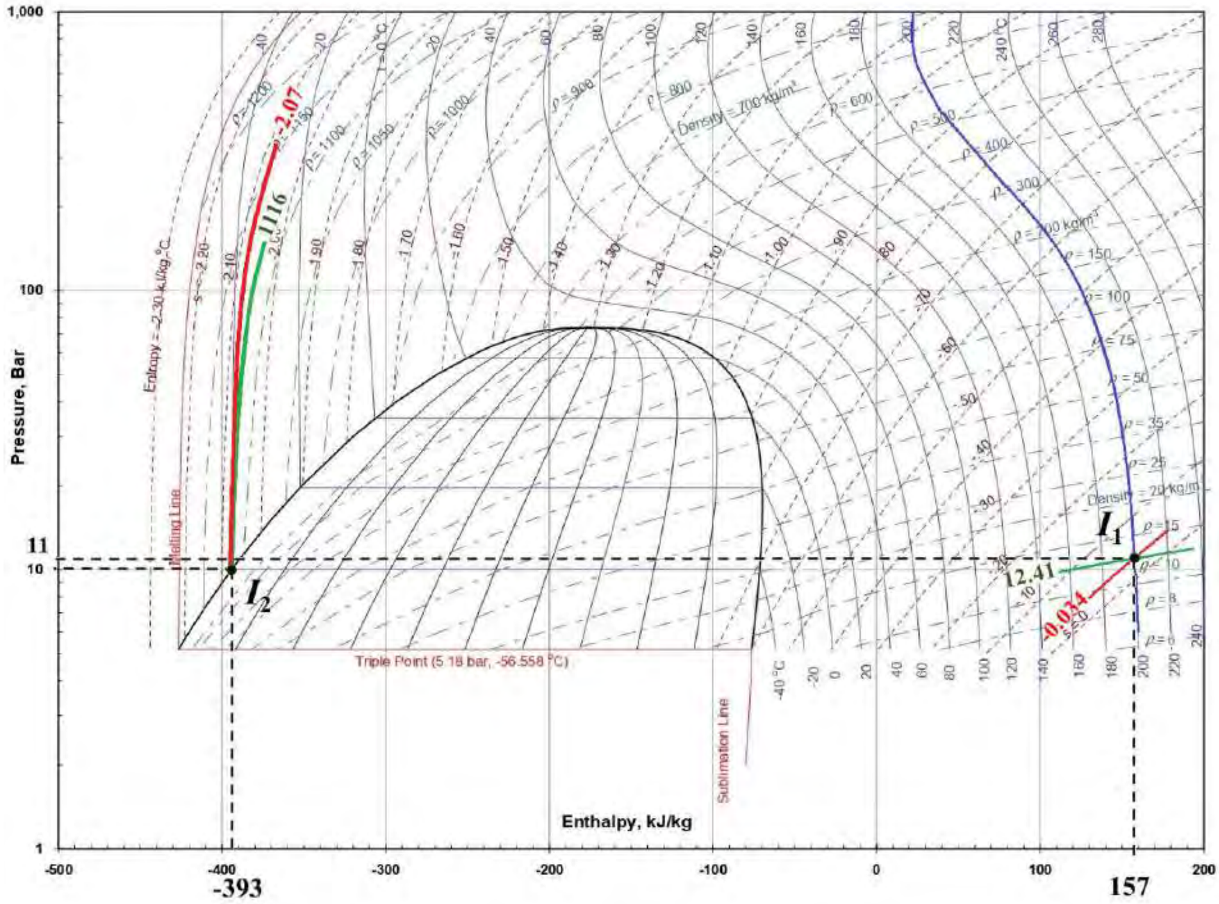

840
800
773
760
723
720
700
680
640
623
T, K
600
560
520
480
440
400
360
320
280
240
−1
0
1
2
3
4
5
6
7
8
9
10
s, kJ/(kg·K)
3600
h = 3500 kJ/kg
3400
3300
3200
3100
3000
2900
2800
2700
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
h = 600 kJ/kg
400
200
−200
P = 100 MPa
50
20 MPa
9 MPa
P = 0.1 MPa
3235
2942
I_2
v = 40 m³/kg
= 100 m³/kg
saturated liquid line
saturated vapor line
triple point line
x = 0.1
x = 0.8
0.9

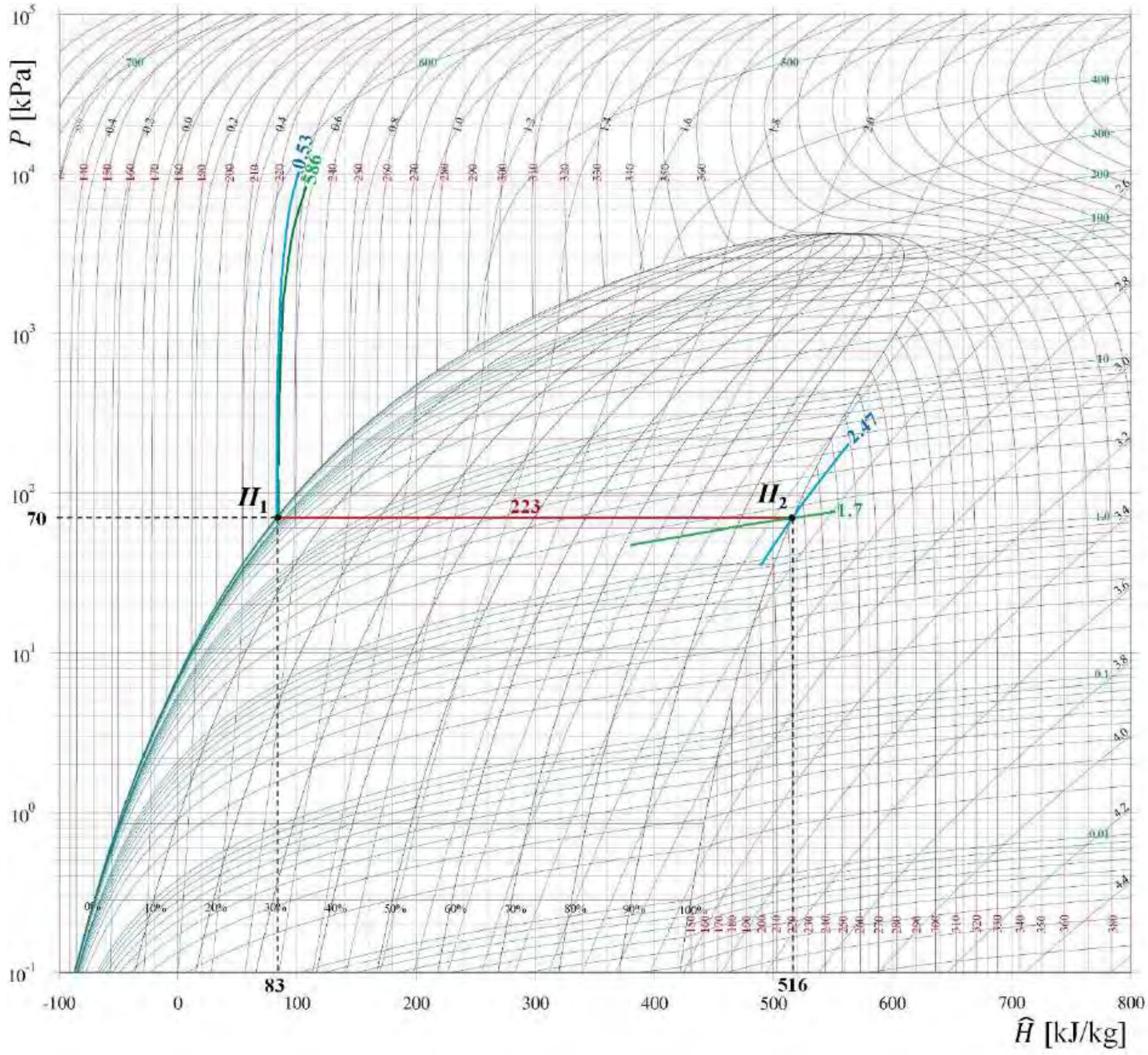

840
800
773
760
723
720
700
680
640
623
T, K
600
560
520
480
440
400
360
320
280
240
h = 3500 kJ/kg
3600
3400
3300
3200
3100
3000
2900
2800
2700
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
h = 600 kJ/kg
400
200
P = 100 MPa
50
20 MPa
9 MPa
P = 0.1 MPa
3235
2912
saturated liquid line
saturated vapor line
triple point line
v = 40 m³/kg
100 m³/kg
x = 0.1
x = 0.8
-1
0
1
2
3
4
5
5.72
6
6.12
6.507
7
8
9
10
s, kJ/(kg·K)

5.6. A 100 kg/h stream of CO_2 vapor at 11 bar and 200ºC is converted into saturated liquid at 10 bar by means of a parallel flow heat exchanger, where *n*-propane at 0.7 bar is employed as isobaric refrigerant (entering as saturated liquid and leaving the device as saturated vapor).

- **a) Calculate the changes in internal energy, enthalpy and entropy of both phases using *PH*(*T*,*S*,ρ) diagrams.**
- **b) Qualitatively represent the process in diagrams *T* vs. *apparatus length coordinate*, T_{CO2} vs. $T_{propane}$, *PT*, *PV*(*T*) and *TH*(*P*).**
- **c) Calculate the refrigerant flow rate.**
- **d) Calculate the heat transfer coefficient in the heat exchanger if it consists of two concentric tubes 10 m long and 1 and 2 inches in diameter, respectively. Its external wall is completely insulated.**

Question a. Let I be the phase that loses heat (carbon dioxide) and II the phase that gains it (propane). By using figures V.2 and V.8 of appendix V and placing in them the initial and final states described by the statement of the problem, it is seen that CO_2 leaves the apparatus at a temperature of -40ºC and that the working temperature for propane is of 323 K (-50ºC).





Apart from this, for carbon dioxide

$$\Delta\hat{H}_I = \hat{H}_{I_2} - \hat{H}_{I_1} = -393\ \frac{\text{kJ}}{\text{kg}} - 157\ \frac{\text{kJ}}{\text{kg}} = -550\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\hat{S}_I = \hat{S}_{I_2} - \hat{S}_{I_1} = -2.07\ \frac{\text{kJ}}{\text{kg·K}} - \left(-0.034\ \frac{\text{kJ}}{\text{kg·K}}\right) = -2.036\ \frac{\text{kJ}}{\text{kg·K}}$$

$$\Delta\hat{U}_I = \hat{U}_{I_2} - \hat{U}_{I_1} = \left(\hat{H}_{I_2} - \frac{P_{I_2}}{\hat{\rho}_{I_2}}\right) - \left(\hat{H}_{I_1} - \frac{P_{I_1}}{\hat{\rho}_{I_1}}\right) =$$
$$= \left(-393\ \frac{\text{kJ}}{\text{kg}} - \frac{1000\ \text{kPa}}{1116\ \text{kg/m}^3}\right) - \left(157\ \frac{\text{kJ}}{\text{kg}} - \frac{1100\ \text{kPa}}{12.41\ \text{kg/m}^3}\right) = -462.25\ \frac{\text{kJ}}{\text{kg}}$$

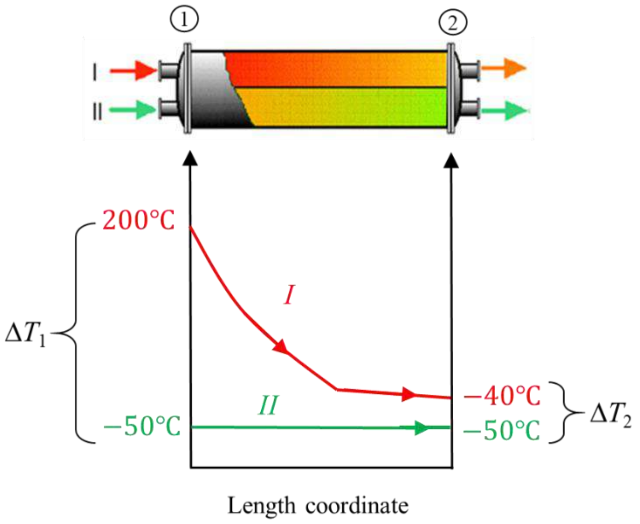
and for the hydrocarbon

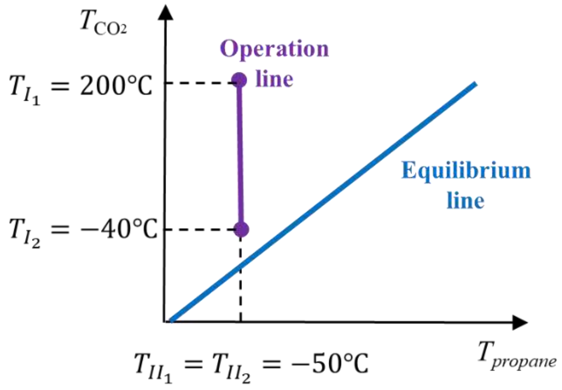
$$\Delta\hat{H}_{II} = \hat{H}_{II_2} - \hat{H}_{II_1} = 516\ \frac{\text{kJ}}{\text{kg}} - 83\ \frac{\text{kJ}}{\text{kg}} = 433\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\hat{S}_{II} = \hat{S}_{II_2} - \hat{S}_{II_1} = 2.47\ \frac{\text{kJ}}{\text{kg·K}} - 0.53\ \frac{\text{kJ}}{\text{kg·K}} = 1.94\ \frac{\text{kJ}}{\text{kg·K}}$$

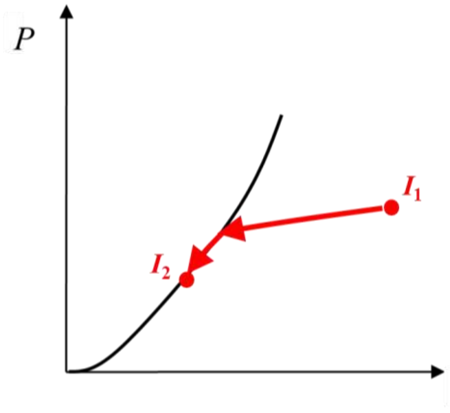
$$\Delta\hat{U}_{II} = \hat{U}_{II_2} - \hat{U}_{II_1} = \left(\hat{H}_{II_2} - \frac{P_{II_2}}{\hat{\rho}_{II_2}}\right) - \left(\hat{H}_{II_1} - \frac{P_{II_1}}{\hat{\rho}_{II_1}}\right) =$$
$$= \left(516\ \frac{\text{kJ}}{\text{kg}} - \frac{70\ \text{kPa}}{1.7\ \text{kg/m}^3}\right) - \left(83\ \frac{\text{kJ}}{\text{kg}} - \frac{70\ \text{kPa}}{586\ \text{kg/m}^3}\right) = 391.94\ \frac{\text{kJ}}{\text{kg}}$$

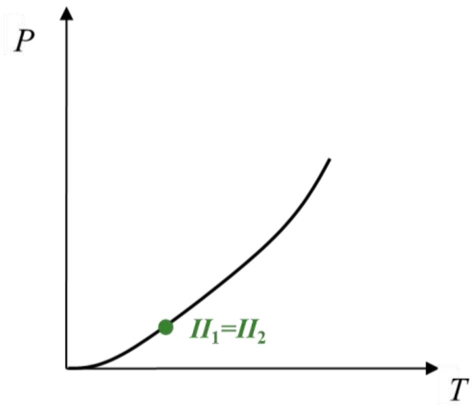
Question b. The required representations will be the following ones

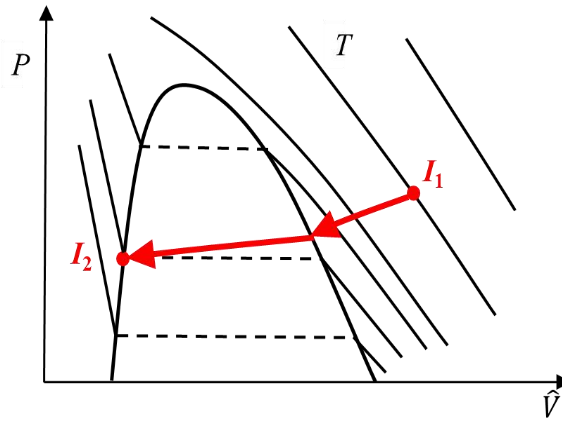


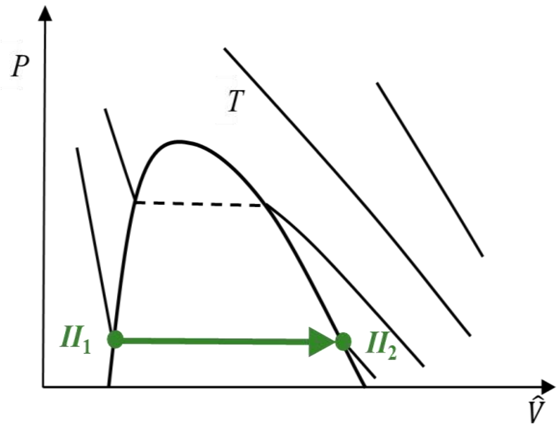


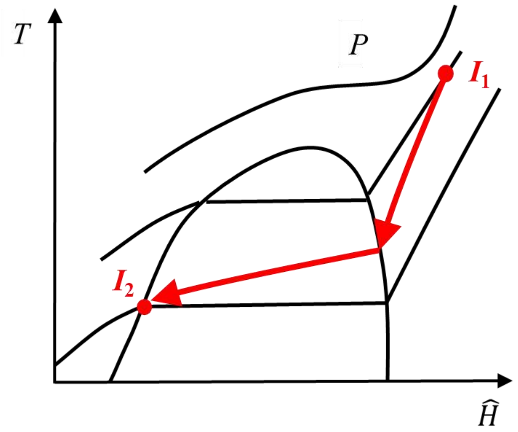
To rigorously employ the *PT*, *PV* and *TH* diagrams, the actual progression of CO_2 temperature and pressure should be known, but it is not the case. An isobar would be good for an ideal case, but with friction and phase changes it is unsuitable. Therefore, it has been drawn a progressive deviation of the isobar with a marked change of its slope (which does not have to be constant if the properties evolve with temperature) when passing from the monophasic to the biphasic zone. Other ways are also possible.

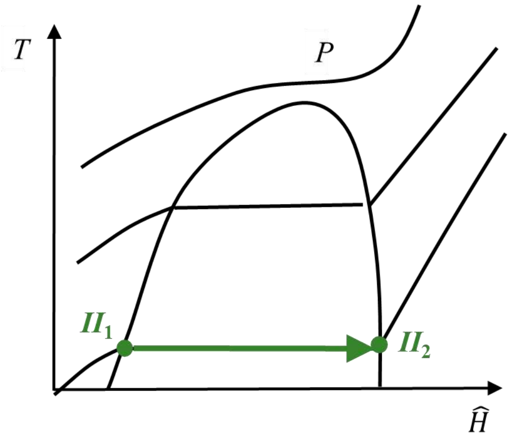












Question c. The heat exchange in the apparatus is given by

$$\begin{bmatrix}\text{heat flow given}\\ \text{by the phase I}\end{bmatrix} = q = \begin{bmatrix}\text{heat flow gained}\\ \text{by the phase II}\end{bmatrix}$$

$$\widehat{\mathcal{W}}_I \Delta\hat{Q}_I = q = -\widehat{\mathcal{W}}_{II} \Delta\hat{Q}_{II}$$

$$\widehat{\mathcal{W}}_I \int_{I_1}^{I_2} T\mathrm{d}\hat{S} = q = -\widehat{\mathcal{W}}_{II} \int_{II_1}^{II_2} T\mathrm{d}\hat{S}$$

but in the case of phase II, the integral can be evaluated by a simple difference of enthalpies, since the pressure of the hydrocarbon does not change when it evaporates

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \hat{V}\mathrm{d}P = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \quad \xrightarrow{\mathrm{d}P=0} \quad \mathrm{d}\hat{H} = \mathrm{d}\hat{Q}$$

$$\int_{II_1}^{II_2} T\mathrm{d}\hat{S} = \left(\hat{H}_{II_2} - \hat{H}_{II_1}\right) = 433\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

However, the integral of phase I cannot be estimated in this way, because a pressure drop of 10%. If the trapezoidal rule is used for its quantification

$$\int_{I_1}^{I_2} T\mathrm{d}\hat{S} = \left(\frac{T_{II_2}+T_{I_2}}{2}\right)\left(\hat{S}_{II_2}-\hat{S}_{I_2}\right) = \left(\frac{T_{II_2}+T_{I_2}}{2}\right)\Delta\hat{S}_I$$

and converting the temperature units to Kelvin

$$T_{II_2} = -40℃ + 273 = 233\ \mathrm{K}$$

$$T_{II_1} = 200℃ + 273 = 473\ \mathrm{K}$$

$$\int_{I_1}^{I_2} T\mathrm{d}\hat{S} = \left(\frac{233\ \mathrm{K} + 473\ \mathrm{K}}{2}\right)\left(-2.036\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = -718.71\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

By introducing these data in the balance

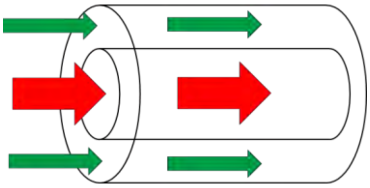
$$\left(10\ \frac{\mathrm{kg}}{\mathrm{h}}\right)\left(-718.71\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -7187.1\ \frac{\mathrm{kJ}}{\mathrm{h}} = -\widehat{\mathcal{W}}_{II}\left(433\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right)$$

$$\widehat{\mathcal{W}}_{II} = 16.6\ \frac{\mathrm{kg}}{\mathrm{h}}$$

Question d. With the provided data, the heat transfer coefficient in the exchanger can be estimated from the expression

$$\mathrm{k}_T = \frac{q}{A\langle\Delta T\rangle_{ln}} = \frac{q}{A\left\{\dfrac{\Delta T_1 - \Delta T_2}{\ln\left(\dfrac{\Delta T_1}{\Delta T_2}\right)}\right\}}$$

where ΔT_1=200–(-50)= 250ºC and ΔT_2=-40–(-50)= 10ºC are the temperature gradients at both ends of the apparatus (see figure T vs. *length coordinate*), and the area A is that of the cylinder with a smaller diameter (1 in= 0.0254 m), since the heat exchange between the fluids (one circulating externally and the other circulating internally) only occurs through it.



$$A = \pi dL = \pi(0.0254\ \mathrm{m})(10\ \mathrm{m}) = 0.798\ \mathrm{m}^2$$

$$\mathrm{k}_T = \frac{\left(7187.1\ \frac{\mathrm{kJ}}{\mathrm{h}}\right)}{(0.798\ \mathrm{m}^2)\left\{\frac{250°\mathrm{C} - 10°\mathrm{C}}{\ln\left(\frac{250°\mathrm{C}}{10°\mathrm{C}}\right)}\right\}} = 120.79\ \frac{\mathrm{kJ}}{\mathrm{h}\cdot\mathrm{m}^2\cdot°\mathrm{C}}$$

5.7. A water stream of 1000 kg/h is cooled from its boiling temperature at 2 bar to 20°C in an isobaric heat exchanger by means of another water stream with the same flow rate at 1.013 bar, introduced into the exchanger at 10°C. Assuming a constant heat capacity of 1 kcal/(kg·°C) for liquid water, indicate:

- **a) If the operation is stoichiometrically possible, and if so, the outlet temperature of the cooling water.**
- **b) If the operation is thermodynamically possible and under what operating conditions.**
- **c) If it is technologically possible and the approximate area of the apparatus when the material and the contact conditions provide an average heat transfer coefficient of 10 cal/s·cm^2·K.**

Question a. For a heat exchanger (section a of reference problem 0.12)

$$\begin{bmatrix}\text{heat flow given}\\ \text{by the phase I}\end{bmatrix}=\begin{bmatrix}\text{heat flow gained}\\ \text{by the phase II}\end{bmatrix}$$

$$\widehat{\mathcal{W}}_I \Delta \hat{Q}_I = -\widehat{\mathcal{W}}_{II} \Delta \hat{Q}_{II} = q$$

But the fundamental thermodynamic relation $\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \hat{V}\mathrm{d}P$ says that in an isobaric process (dP=0) the heat transferred will be equal to the enthalpy change

$$\widehat{\mathcal{W}}_I \Delta \hat{H}_I = -\widehat{\mathcal{W}}_{II} \Delta \hat{H}_{II} = q$$

Additionally, if specific heat capacities are constant

$$\widehat{\mathcal{W}}_I \langle \hat{C}_P \rangle_I \left(T_{I_{in}} - T_{I_{out}}\right) = -\widehat{\mathcal{W}}_{II} \langle \hat{C}_P \rangle_{II} \left(T_{II_{in}} - T_{II_{out}}\right) = q$$

After a small interpolation in table VI.1 of this book’s appendix VI, it can be observed that the water vapor pressure is of 2 bar at 120°C, so

$$\left(1000\ \frac{\mathrm{kg}}{\mathrm{h}}\right)\left(1\ \frac{\mathrm{cal}}{\mathrm{g°C}}\right)(120°\mathrm{C} - 20°\mathrm{C}) = -\left(1000\ \frac{\mathrm{kg}}{\mathrm{h}}\right)\left(1\ \frac{\mathrm{cal}}{\mathrm{g°C}}\right)(10°\mathrm{C} - T_{IIout}) = 10^8\ \frac{\mathrm{cal}}{\mathrm{h}}$$

from where

$$T_{II_{out}} = 120°\mathrm{C} - 20°\mathrm{C} + 10°\mathrm{C} = 110°\mathrm{C}$$

Therefore the operation is stoichiometrically possible, but it is not real, because at 1.013 bar (1 atm) the temperature of 110°C is above the boiling temperature of water (100°C).

Question b. Thermodynamically speaking, a part of the phase II flow ($\widehat{\mathcal{W}}_{IIv}$) will vaporize at a certain distance from the inlet, but since the pressure is set at 1.103 bar, the vapor will not be heated above 100ºC.

$$\widehat{\mathcal{W}}_I \langle \hat{C}_P \rangle_I \Delta T_I = -\widehat{\mathcal{W}}_{II} \langle \hat{C}_P \rangle_{II} \Delta T_{II} - \widehat{\mathcal{W}}_{IIv} \Delta \hat{H}_{vap}$$

The vaporization heat of water at 100ºC can be calculated with table VI.1 of appendix VI, subtracting the saturated liquid enthalpy (419.1 kJ/kg) from the saturated vapor one (2676 kJ/kg), which gives $\Delta\hat{H}_{vap}$=2676 – 419.1=2256.9 kJ/kg. After unit conversion

$$2256.9\ \frac{\text{kJ}}{\text{kg}} = 2256.9\ \frac{\text{J}}{\text{g}} \times \frac{0.000239\ \text{kcal}}{1\ \text{J}} \times \frac{1000\ \text{J}}{1\ \text{kcal}} = 539.4\ \frac{\text{cal}}{\text{g}}$$

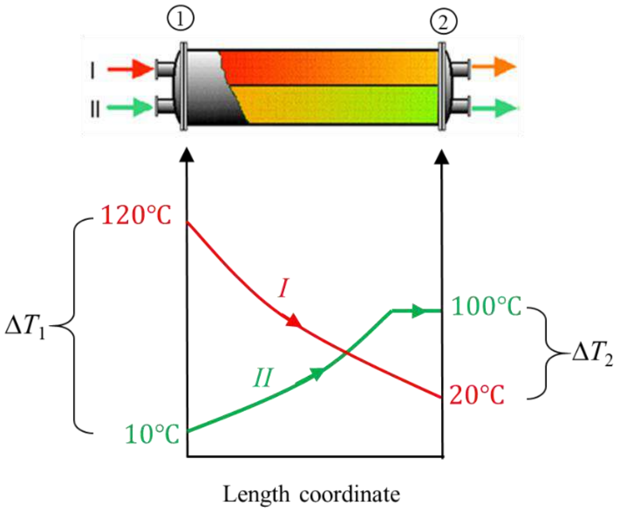
the energy balance will be

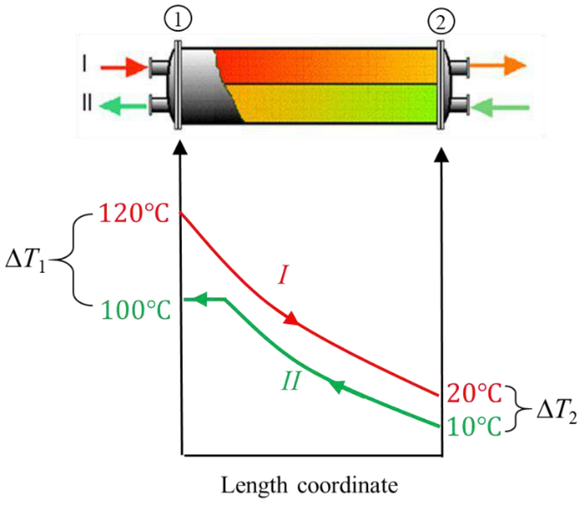
$$\left(10^6\ \frac{\text{g}}{\text{h}}\right)\left(1\ \frac{\text{cal}}{\text{g°C}}\right)(120\text{°C} - 20\text{°C}) = -\left(10^6\ \frac{\text{g}}{\text{h}}\right)\left(1\ \frac{\text{cal}}{\text{g°C}}\right)(10\text{°C} - 100\text{°C}) - \widehat{\mathcal{W}}_{IIv}\left(539.4\ \frac{\text{cal}}{\text{g}}\right)$$

so that

$$\widehat{\mathcal{W}}_{IIv} = 18539\ \frac{\text{g}}{\text{h}} = 18.539\ \frac{\text{kg}}{\text{h}}$$

Question c. From a technological point of view, the operation is only possible in counterflow because, as shown in the attached figures, thermodynamic equilibrium would be prematurely reached in parallel flow (intersection between the temperature lines of I and II).





On the other hand, the apparatus transmision area will be calculated as

$$A = \frac{q}{\mathrm{k}_T \langle \Delta T \rangle_{ln}} = \frac{q}{k_T \left\{ \dfrac{\Delta T_1 - \Delta T_2}{\ln\left(\dfrac{\Delta T_1}{\Delta T_2}\right)} \right\}}$$

where k_T is the heat transfer coefficient

$$10\ \frac{\mathrm{cal}}{\mathrm{s \cdot cm^2 \cdot K}} \times \frac{3600\ \mathrm{s}}{1\ \mathrm{h}} \times \frac{1\ \mathrm{K}}{1\mathrm{°C}} = 36000 \frac{\mathrm{cal}}{\mathrm{s \cdot cm^2 \cdot °C}}$$

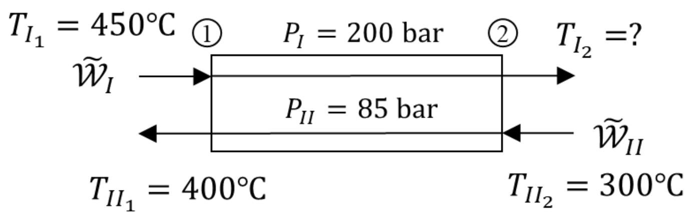
and ΔT_1=120–100= 20ºC and ΔT_2=20–10= 10ºC the temperature gradients in both ends of the device. Thus

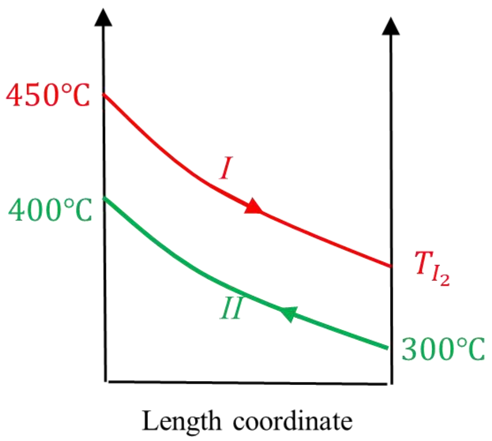
$$A = \frac{\left(10^8\ \dfrac{\mathrm{cal}}{\mathrm{h}}\right)}{\left(36000 \dfrac{\mathrm{cal}}{\mathrm{s \cdot cm^2 \cdot °C}}\right) \left\{ \dfrac{20\mathrm{°C} - 10\mathrm{°C}}{\ln\left(\dfrac{20\mathrm{°C}}{10\mathrm{°C}}\right)} \right\}} = 192.63\ \mathrm{cm^2}$$

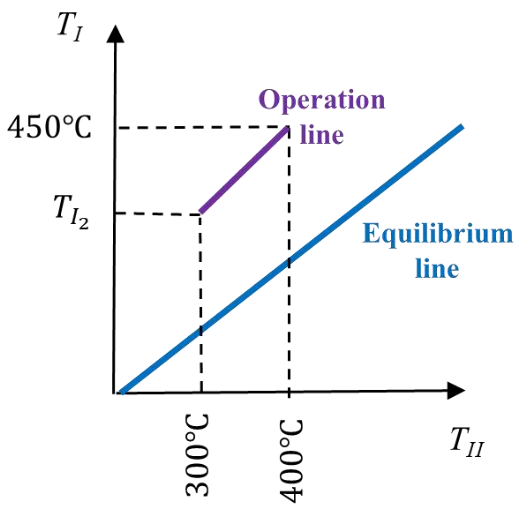
5.8. The temperature of a 10000 L/h steam stream at 300°C and 85 bar is isobarically increased to 400°C in a heat exchanger. The heating fluid is another steam stream with the same molar flow rate, introduced at 450°C and 200 bar in counterflow mode.

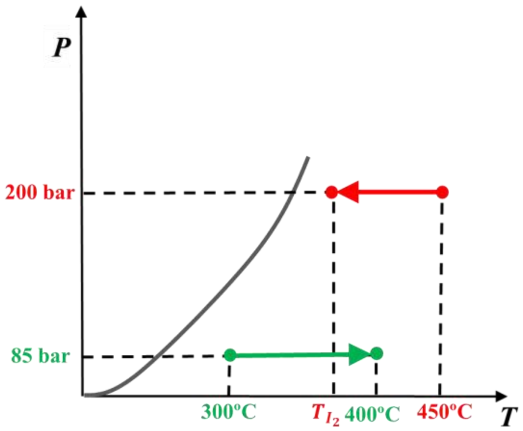
- **a) Qualitatively represent the process through flowchart, *T* vs. *apparatus length coordinate*, $T_{\text{fluid that gives heat}}$ vs. $T_{\text{fluid that gains heat}}$, *PT*, *PV(T)*, *z(P,T)*, *PH(T)*, *TS(P)*, *TH(P)* and *HS(P,T)*.**
- **a) By means of compressibility factors from the Corresponding States Principle (and assuming that z_c=0.27) calculate the molar flow of the stream at 300°C and 85 bar, its volumetric flow when leaving the exchanger and the volumetric flow of the fluid which enters at 450°C and 200 bar.**
- **b) By means of average heat capacities from the Corresponding States Principle (and assuming that z_c=0.27) calculate the temperature at which the heating fluid leaves the exchanger.**
- **c) By means of enthalpies from the Corresponding States Principle (and assuming that z_c=0.27) calculate the temperature at which the heating fluid leaves the exchanger.**
- **d) Calculate the temperature at which the heating fluid leaves the exchanger using a Mollier diagram.**
- **e) Calculate the temperature at which the heating fluid leaves the exchanger using specific *PH* and *TS* diagrams.**

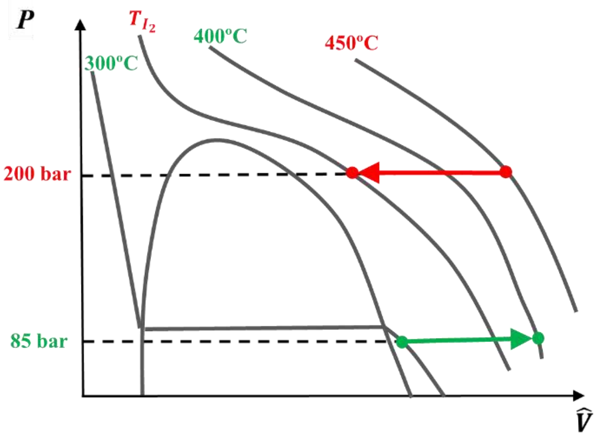
Question a. Conventional representations will be

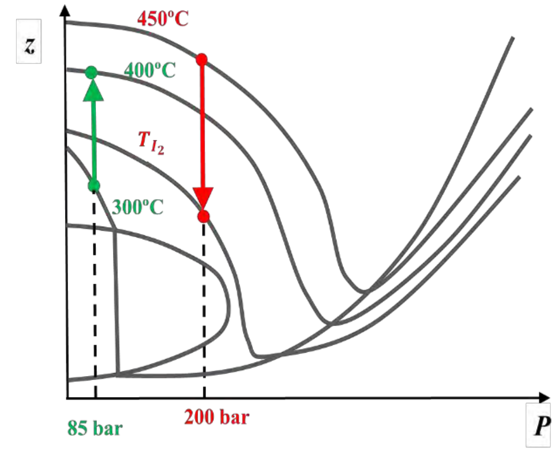


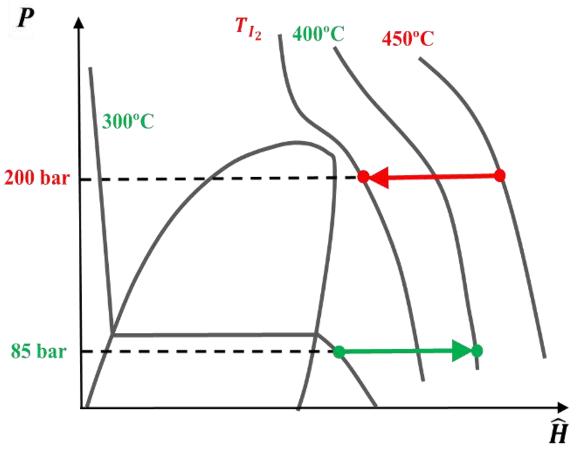


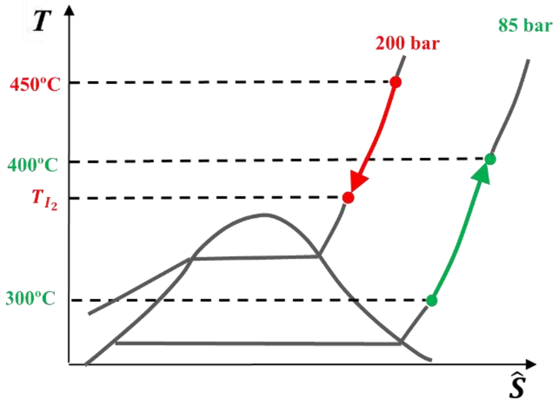


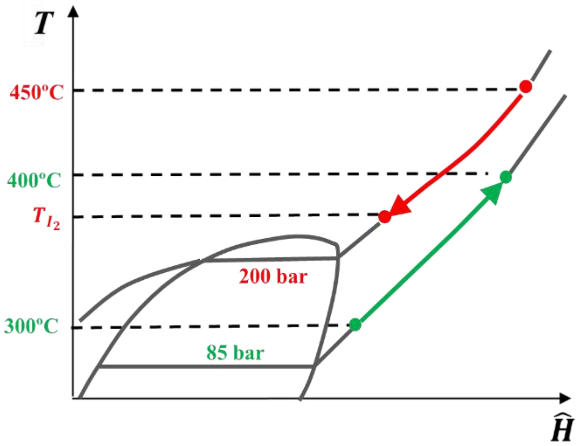

P
200 bar
85 bar
300°C
T_{I_2}
400°C
450°C
T

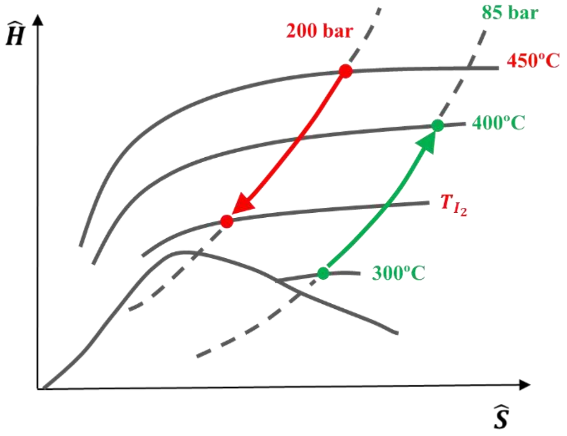

P
T_{I_2}
300°C
400°C
450°C
200 bar
85 bar
$\hat{V}$


z
450°C
400°C
T_{I_2}
300°C
85 bar
200 bar
P


P
T_{I_2}
400°C
450°C
300°C
200 bar
85 bar
$\hat{H}$


T
85 bar
200 bar
450°C
400°C
T_{I_2}
300°C
$\hat{S}$


T
450°C
400°C
T_{I_2}
200 bar
300°C
85 bar
$\hat{H}$


$\hat{H}$
200 bar
85 bar
450°C
400°C
T_{I_2}
300°C
$\hat{S}$

Question b. According to the Corresponding States Principle

$$P\tilde{V} = zRT$$

where the well-known compressibility factor z is a generalized function of the reduced temperature and pressure, given by figure IV.1 of this book's appendix IV, so the molar and volumetric flows will be related by the equation

$$\tilde{\mathcal{W}} = \frac{\breve{\mathcal{W}}}{\tilde{V}} = \breve{\mathcal{W}}\frac{P}{zRT} \qquad [1]$$

By taking the critical constants of water from appendix II, and converting the pressure in bars with factors from appendix I

$$P_c = 217.81 \text{ atm}$$
$$T_c = 647.14 \text{ K}$$

it can be obtained that

$$P_{II_2} = 85 \text{ bar} \times \frac{0.987 \text{ atm}}{1 \text{ bar}} = 83.895 \text{ atm} \quad \rightarrow \quad P_{rII_2} = \frac{83.895 \text{ atm}}{217.81 \text{ atm}} = 0.385$$

$$T_{II_2}(\text{K}) = 300℃ + 273 = 573 \text{ K} \quad \rightarrow \quad T_{rII_2} = \frac{573 \text{ K}}{647.14 \text{ K}} = 0.885$$

and in the other stablished conditions

$$P_{I_1} = 200 \text{ bar} \times \frac{0.987 \text{ atm}}{1 \text{ bar}} = 197.4 \text{ atm} \quad \rightarrow \quad P_{rI_1} = \frac{197.4 \text{ atm}}{217.81 \text{ atm}} = 0.906$$

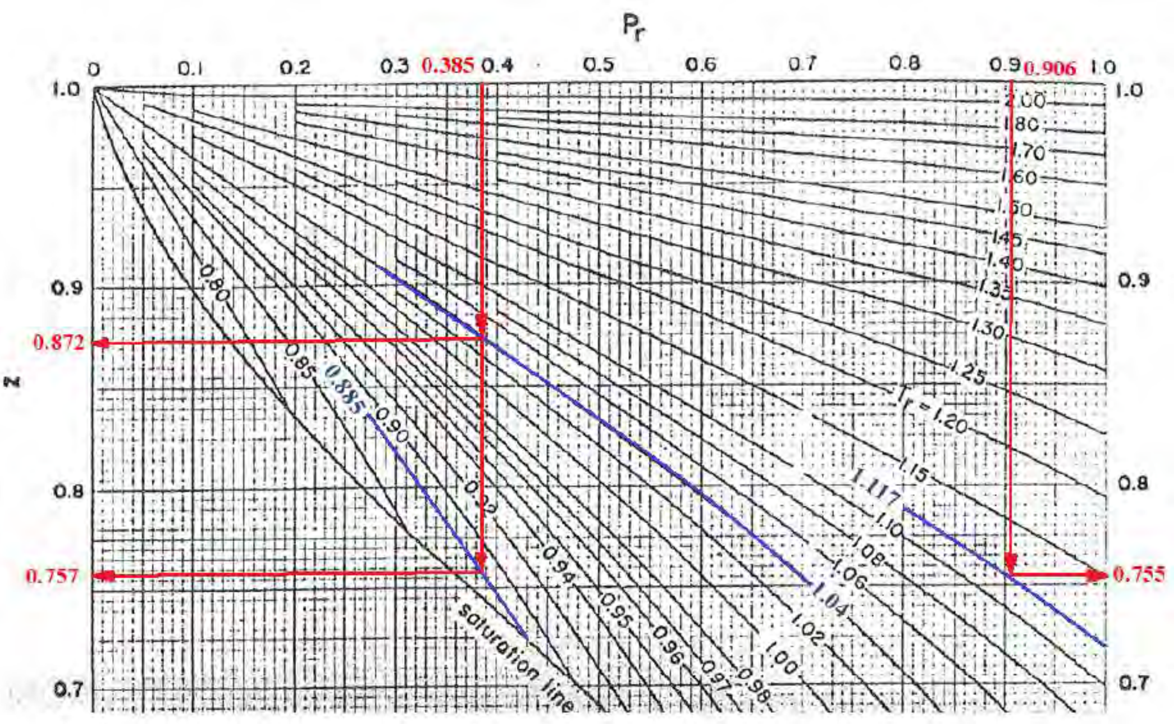
$$T_{I_1}(\text{K}) = 450℃ + 273 = 723 \text{ K} \quad \rightarrow \quad T_{rI_1} = \frac{723 \text{ K}}{647.14 \text{ K}} = 1.117$$

$$P_{II_1} = 85 \text{ bar} \times \frac{0.987 \text{ atm}}{1 \text{ bar}} = 83.895 \text{ atm} \quad \rightarrow \quad P_{rII_1} = \frac{83.895 \text{ atm}}{217.81 \text{ atm}} = 0.385$$

$$T_{II_1}(\text{K}) = 400℃ + 273 = 673 \text{ K} \quad \rightarrow \quad T_{rII_1} = \frac{673 \text{ K}}{647.14 \text{ K}} = 1.04$$

Since the reduced pressure is always lower than 1, figure IV.3 can be used instead of figure IV.1, because it is an enlargement of the second one in the low-density region, and allows a better visualization of the graphical procedure.

$$z_{II_2} = 0.757$$
$$z_{I_1} = 0.755$$
$$z_{II_1} = 0.872$$



Thus, by applying expression [1], the molar flow rate of stream II when entering (point 2) will be

$$\tilde{\mathcal{W}}_{II_2} = \left(10000\ \frac{\text{L}}{\text{h}}\right) \frac{83.895\ \text{atm}}{0.757\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(573\ \text{K})} = 23587\,\frac{\text{mol-g}}{\text{h}}$$

and its volumetric flow rate when leaving the exchanger (point 1)

$$\breve{\mathcal{W}}_{II_1} = \left(23587\,\frac{\text{mol-g}}{\text{h}}\right) \frac{0.872\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(673\ \text{K})}{83.895\ \text{atm}} = 13529.5\ \frac{\text{L}}{\text{h}}$$

On the other hand, the molar flow rate of stream I is the same as that of stram II, so its volumetric flow at point 1 has to be

$$\breve{\mathcal{W}}_{I_1} = \left(23587\,\frac{\text{mol-g}}{\text{h}}\right) \frac{0.755\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(723\ \text{K})}{197.4\ \text{atm}} = 5348.4\ \frac{\text{L}}{\text{h}}$$

Question c. Application of the energy balance to the system produces

$$\begin{bmatrix}\text{heat flow given}\\ \text{by the phase I}\end{bmatrix} = \begin{bmatrix}\text{heat flow gained}\\ \text{by the phase II}\end{bmatrix}$$

$$\hat{\mathcal{W}}_I \Delta\hat{Q}_I = -\hat{\mathcal{W}}_{II} \Delta\hat{Q}_{II}$$

but the fundamental thermodynamic relation $\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \hat{V}\mathrm{d}P$ indicates that if the stream is isobaric (dP=0) the heat transferred will be equal to the enthalpy change, so

$$\hat{\mathcal{W}}_I \Delta\hat{H}_I = -\hat{\mathcal{W}}_{II} \Delta\hat{H}_{II}$$

which, in terms of heat capacities, is expressed as

$$\tilde{\mathcal{W}}_I \tilde{C}_{PI}\left(T_{I_1} - T_{I_2}\right) = \tilde{\mathcal{W}}_{II} \tilde{C}_{PII}\left(T_{II_1} - T_{II_2}\right)$$

and although the specific heats vary with temperature, if average values are used between the inlet and outlet of the exchanger, it follows that

$$\tilde{\mathcal{W}}_I \frac{\left(\tilde{C}_{PI_1} + \tilde{C}_{PI_2}\right)}{2}\left(T_{I_1} - T_{I_2}\right) = \tilde{\mathcal{W}}_{II} \frac{\left(\tilde{C}_{PII_1} + \tilde{C}_{PII_2}\right)}{2}\left(T_{II_1} - T_{II_2}\right) \quad [2]$$

In this way, section e of reference problem 0.8 says that the specific heat capacity can be written as

$$\tilde{C}_P = \underbrace{\tilde{C}_P^*}_{\substack{\text{ideal}\\ \text{part}}} + \underbrace{\left(\tilde{C}_P^* - \tilde{C}_P\right)_{T,P}}_{\text{real part}} \quad [3]$$

Being the real part estimated from the heat capacity of generalized chart IV.6 (appendix IV) and the ideal part from the specific heat capacity of the substance, supposed to be an ideal gas (appendix II)

$$\tilde{C}_P^* = \xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4 \quad [4]$$

$$\frac{\xi_0}{R} = 4.395 \qquad \frac{\xi_1}{R} = -4.186 \cdot 10^{-3}\,\frac{1}{\mathrm{K}} \qquad \frac{\xi_2}{R} = 1.405 \cdot 10^{-5}\,\frac{1}{\mathrm{K}^2}$$

$$\frac{\xi_3}{R} = -1.564 \cdot 10^{-8}\,\frac{1}{\mathrm{K}^3} \qquad \frac{\xi_4}{R} = 0.632 \cdot 10^{-11}\,\frac{1}{\mathrm{K}^4}$$

Therefore, for the stream II at point 2 (T=573 K, T_r=0.885, P_r=0.385)

$$\left(\tilde{C}_P^* - \tilde{C}_P\right)_{II_2} = 7\ \frac{\mathrm{cal}}{\mathrm{K}\cdot\ \mathrm{mol\text{-}g}}$$

$$\tilde{C}_{PII_2}^* = 1.9872\{4.395 - 4.186 \cdot 10^{-3}(573) + 1.405 \cdot 10^{-5}(573^2) - \\ -1.564 \cdot 10^{-8}(573^3) + 0.632 \cdot 10^{-11}(573^4)\} = 8.64\ \frac{\mathrm{cal}}{\mathrm{K}\cdot\ \mathrm{mol\text{-}g}}$$

$$\tilde{C}_{PII_2} = \tilde{C}_{PII_2}^* + \left(\tilde{C}_P^* - \tilde{C}_P\right)_{II_2} = 8.64 + 7 = 15.64\,\frac{\mathrm{cal}}{\mathrm{K}\cdot\ \mathrm{mol\text{-}g}}$$

for the stream I at point 1 (T=723 K, T_r=1.117, P_r=0.906)

$$\left(\tilde{C}_P^* - \tilde{C}_P\right)_{I_1} = 7\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$\begin{aligned}\tilde{C}^*_{PI_1} &= 1.9872\{4.395 - 4.186\cdot 10^{-3}(723) + 1.405\cdot 10^{-5}(723^2) - \\ &\quad -1.564\cdot 10^{-8}(723^3) + 0.632\cdot 10^{-11}(723^4)\} = 9.00\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\end{aligned}$$

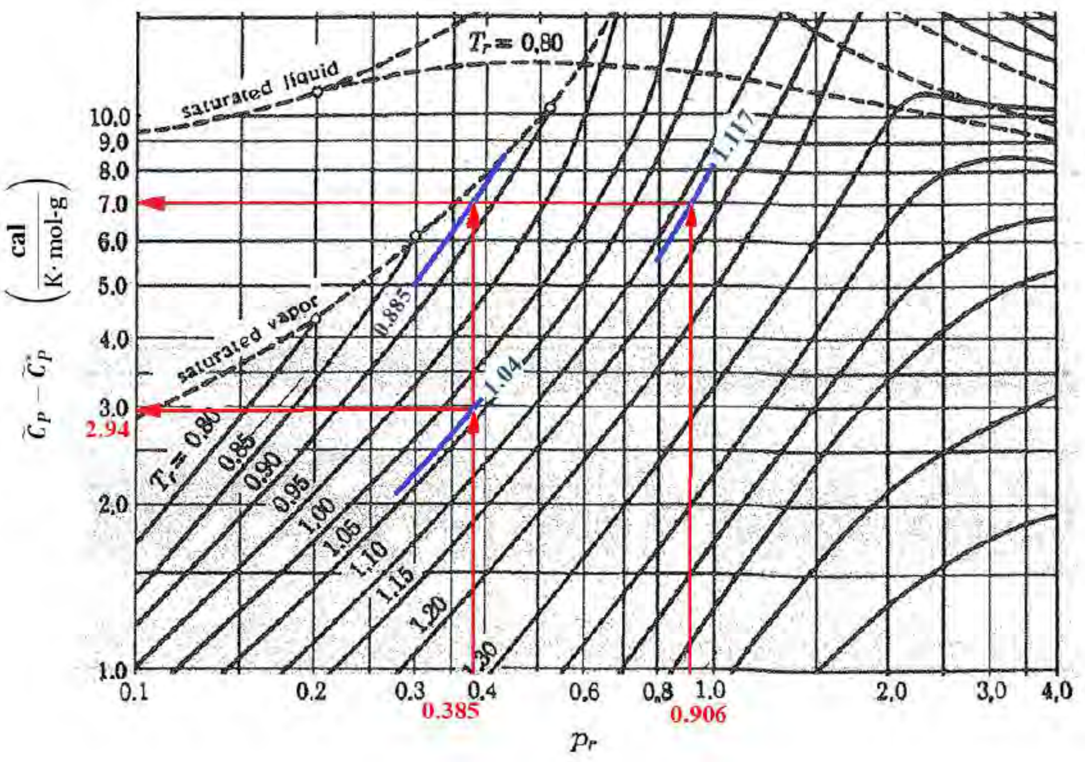
$$\tilde{C}_{PI_1} = \tilde{C}^*_{PI_1} + \left(\tilde{C}_P^* - \tilde{C}_P\right)_{I_1} = 9.00 + 7 = 16\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

for stream II at point 1 (T=673 K, T_r=1.04, P_r=0.385)

$$\left(\tilde{C}_P^* - \tilde{C}_P\right)_{II_1} = 2.94\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

$$\begin{aligned}\tilde{C}^*_{PII_1} &= 1.9872\{4.395 - 4.186\cdot 10^{-3}(673) + 1.405\cdot 10^{-5}(673^2) - \\ &\quad -1.564\cdot 10^{-8}(673^3) + 0.632\cdot 10^{-11}(673^4)\} = 8.88\ \frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\end{aligned}$$

$$\tilde{C}_{PII_1} = \tilde{C}^*_{PII_1} + \left(\tilde{C}_P^* - \tilde{C}_P\right)_{II_1} = 8.88 + 2.94 = 11.82\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$

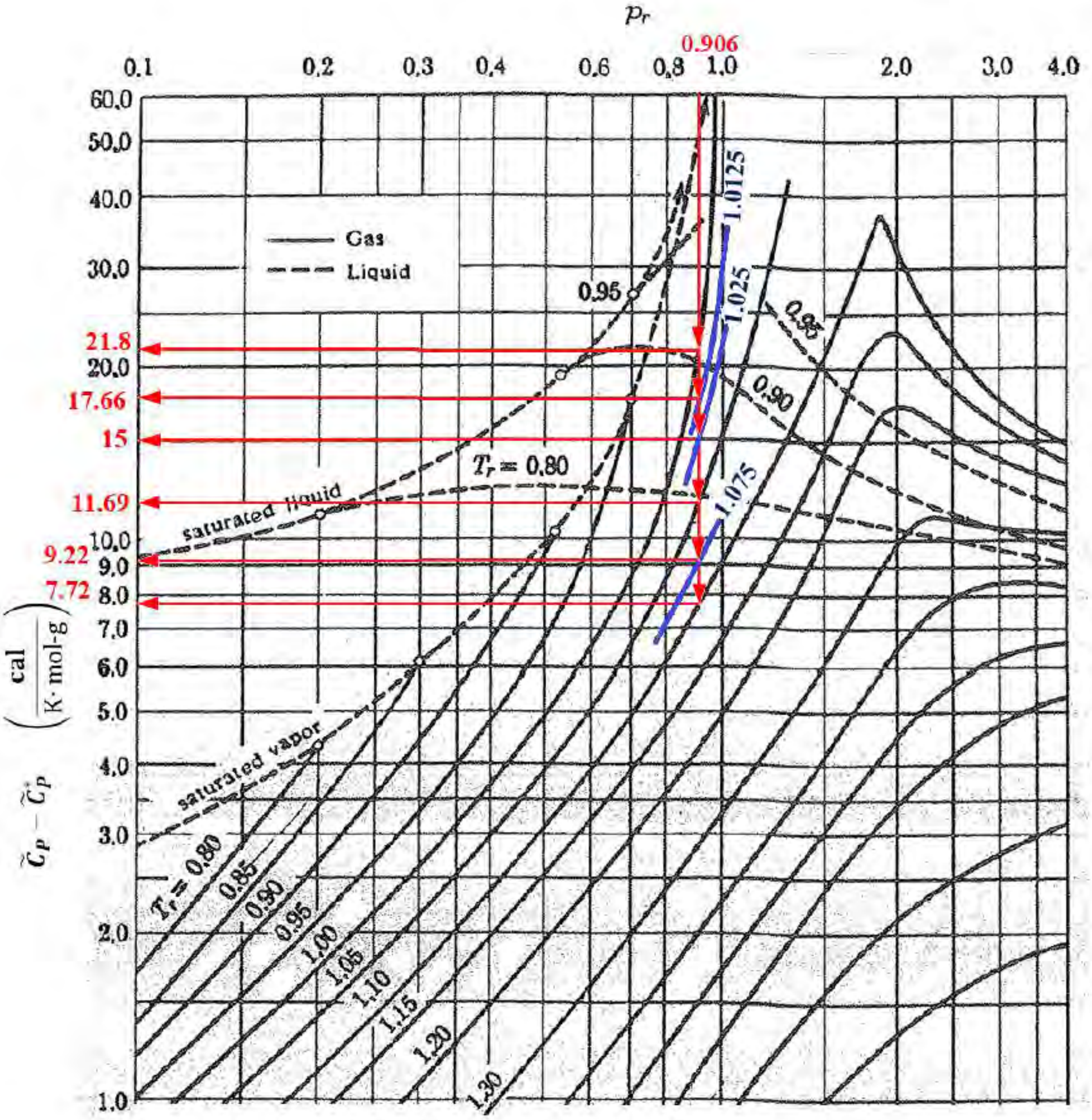


By introducing these data in equation [2], together with the molar flow rates from the previous question, the balance becomes

$$23587\frac{\left(16+\tilde{C}_{PI_2}\right)}{2}\left(723-T_{I_2}\right)=23587\frac{(11.82+15.64)}{2}(573-673)$$

$$\tilde{C}_{PI_2}=\frac{2746}{\left(723-T_{I_2}\right)}-16 \qquad [5]$$

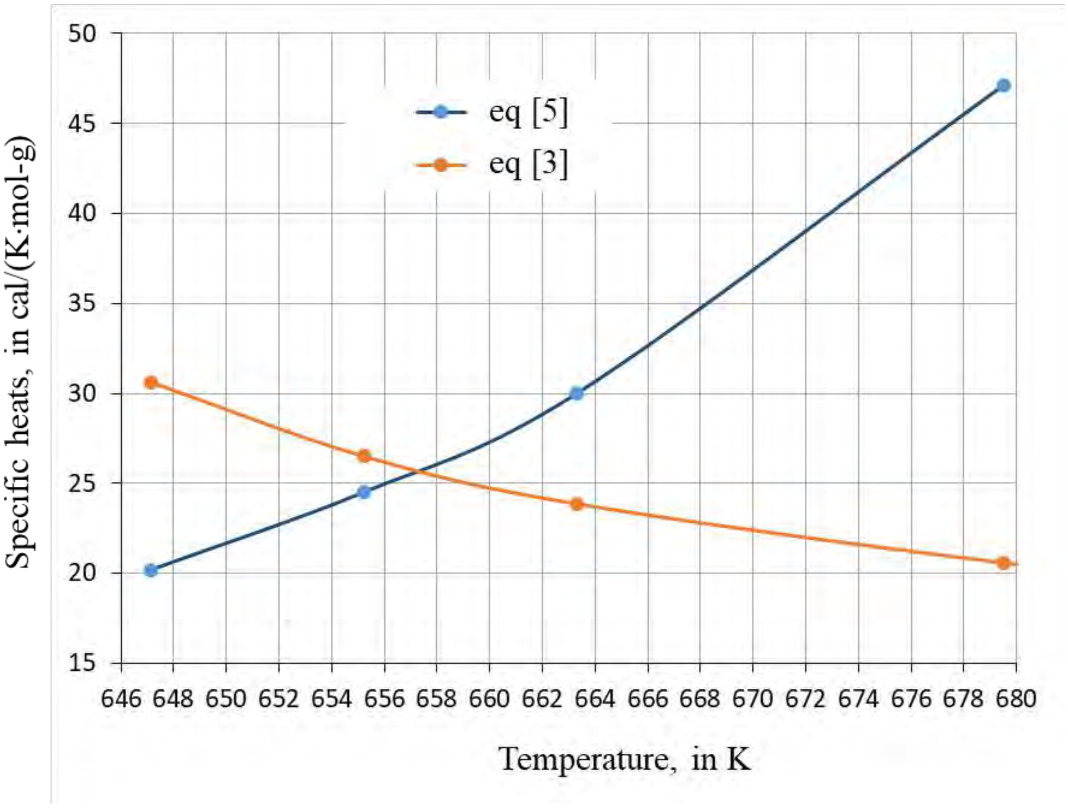
Due to the fact that $\tilde{C}_{PI_2}$ depends on T_{I_2}, the calculation of the stream I temperature at point 2 will be an iterative process in which a reduced temperature has to be assumed, then the real part of equation [3] has to be calculated with the generalized diagram IV.6 and the ideal part with expression [4] and the sum of both parts has to be compared with the heat capacity that results from introducing the assumed temperature in equation [5].



T_{rI_2}	$\left(\tilde{C}_P^* - \tilde{C}_P\right)_{I_2}$	T_{I_2}(K)	$\tilde{C}^*_{PI_2}$ eq.[4]	$\tilde{C}_{PI_2}$ eq.[3]	$\tilde{C}_{PI_2}$ eq.[5]
1.0	21.80	647.14	8.82281	30.6228	20.1982
1.0125	17.66	655.229	8.84204	26.5020	24.5189
1.025	15.00	663.318	8.86118	23.8611	30.0109
1.05	11.69	679.497	8.89914	20.5891	47.1220
1.075	9.22	695.675	8.93678	18.1567	84.4958
1.1	7.72	711.854	8.974168	16.6941	230.3664

All the specific heats in cal/(K·mol-g)

The table displays that the temperature must be higher than 655.2 K and lower than 663.31 K. Unfortunately, diagram IV.6 does not allow reading with precision in the desired zone, and to refine the search it will be necessary to represent the calculated specific heats, finding that the intersección between the two curves is approximately 657.2 K (384.2 ºC).



Question d. By using enthalpies, the energy balance will be

$$\widetilde{W}_I \widetilde{H}_{I_1} - \widetilde{W}_I \widetilde{H}_{I_2} = \widetilde{W}_{II} \widetilde{H}_{II_1} - \widetilde{W}_{II} \widetilde{H}_{II_2}$$

$$\widetilde{W}_I \left(\widetilde{H}_{I_1} - \widetilde{H}_{I_2}\right) = \widetilde{W}_{II} \left(\widetilde{H}_{II_1} - \widetilde{H}_{II_2}\right)$$

Section e of reference problem 0.8 says that the enthalpy difference between two states 1 and 2 is given by

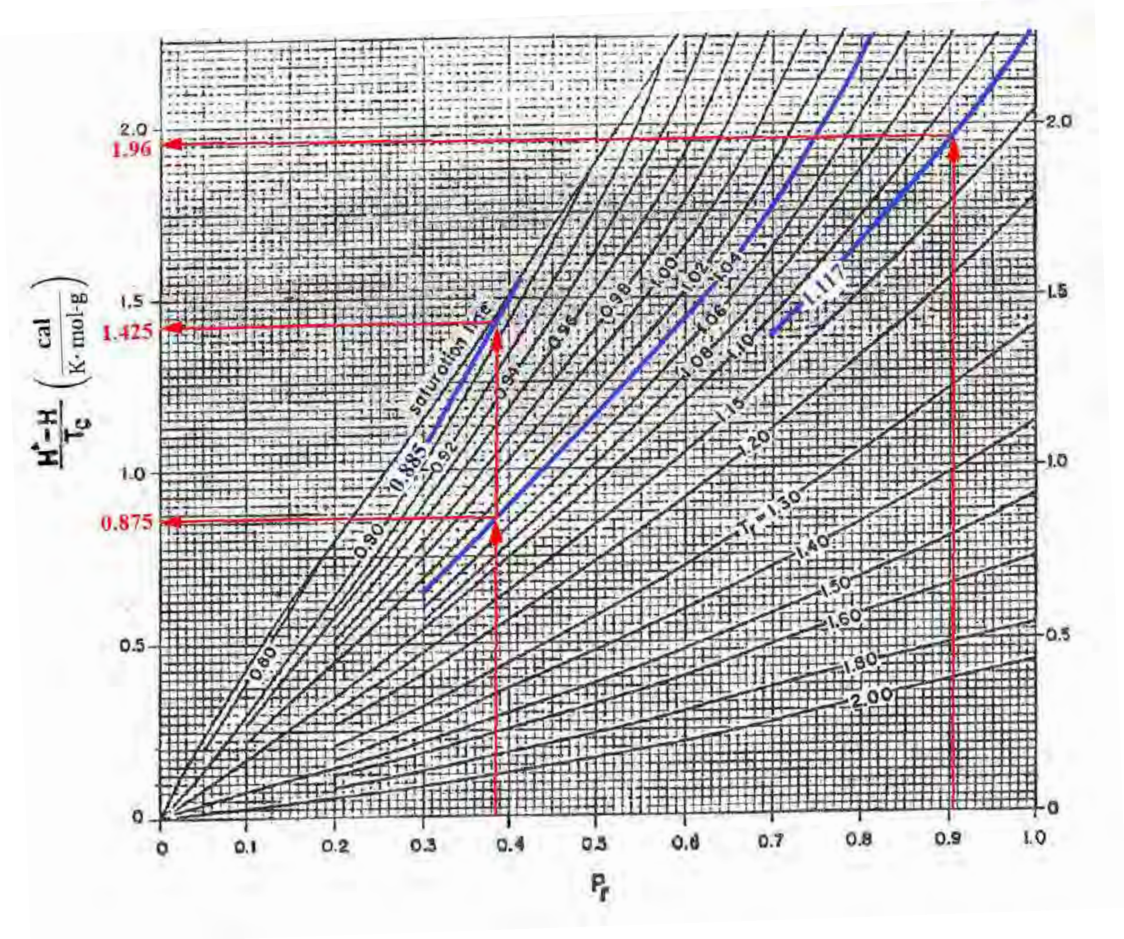
$$(\tilde{H}_2 - \tilde{H}_1) = \underbrace{(\tilde{H}_2^* - \tilde{H}_1^*)}_{\text{ideal part}} + \underbrace{(\tilde{H}_1^* - \tilde{H}_1)_{T_1,P_1} - (\tilde{H}_2^* - \tilde{H}_2)_{T_2,P_2}}_{\text{real part}} \qquad [6]$$

estimating the real part of the enthalpy by means of the generalized diagram IV.5 of appendix IV (which is an extension of IV.4 in the low-density zone) and the ideal part by means of the specific heat of the substance assumed to be an ideal gas as

$$\tilde{H}_2^* - \tilde{H}_1^* = \int_{T_1}^{T_2} \tilde{C}_P^* \mathrm{d}T = \int_{T_1}^{T_2} (\xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4) \mathrm{d}T =$$

$$= \left[\xi_0 T + \frac{1}{2}\xi_1 T + \frac{1}{3}\xi_2 T^3 + \frac{1}{4}\xi_3 T^4 + \frac{1}{5}\xi_4 T^5\right]_{T_1}^{T_2} =$$

$$= \xi_0 (T_2 - T_1) + \frac{\xi_1}{2}(T_2^2 - T_1^2) + \frac{\xi_2}{3}(T_2^3 - T_1^3) + \frac{\xi_3}{4}(T_2^4 - T_1^4) + \frac{\xi_4}{5}(T_2^5 - T_1^5)$$



Therefore, for stream II at point 2 (T=573 K, T_r=0.885, P_r=0.385)

$$\left(\frac{\widetilde{H}_{II_2}^{*}-\widetilde{H}_{II_2}}{T_c}\right)_{T_r,P_r}=1.425\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$
$$\Downarrow$$
$$\widetilde{H}_{II_2}^{*}-\widetilde{H}_{II_2}=\left(1.425\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)(647.14\ \text{K})=922.17\ \frac{\text{cal}}{\text{mol-g}}$$

and at point 1 (T=673 K, T_r=1.04, P_r=0.385)

$$\left(\frac{\widetilde{H}_{II_1}^{*}-\widetilde{H}_{II_1}}{T_c}\right)_{T_r,P_r}=0.875\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$
$$\Downarrow$$
$$\widetilde{H}_{II_1}^{*}-\widetilde{H}_{II_1}=\left(0.875\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)(647.14\ \text{K})=566.25\ \frac{\text{cal}}{\text{mol-g}}$$

The ideal contribution is

$$\widetilde{H}_{II_1}^{*}-\widetilde{H}_{II_2}^{*}=1.9872\left\{4.395(673-573)-\frac{4.186\cdot10^{-3}}{2}(673^2-573^2)+\right.$$
$$+\frac{1.405\cdot10^{-5}}{3}(673^3-573^3)-\frac{1.564\cdot10^{-8}}{4}(673^4-573^4)+$$
$$\left.+\frac{0.632\cdot10^{-11}}{5}(673^5-573^5)\right\}=876.39\ \frac{\text{cal}}{\text{mol-g}}$$

and by applying equation [6]

$$\widetilde{H}_{II_1}-\widetilde{H}_{II_2}=876.39+922.17-566.25=1139.05\,\frac{\text{cal}}{\text{mol-g}}$$

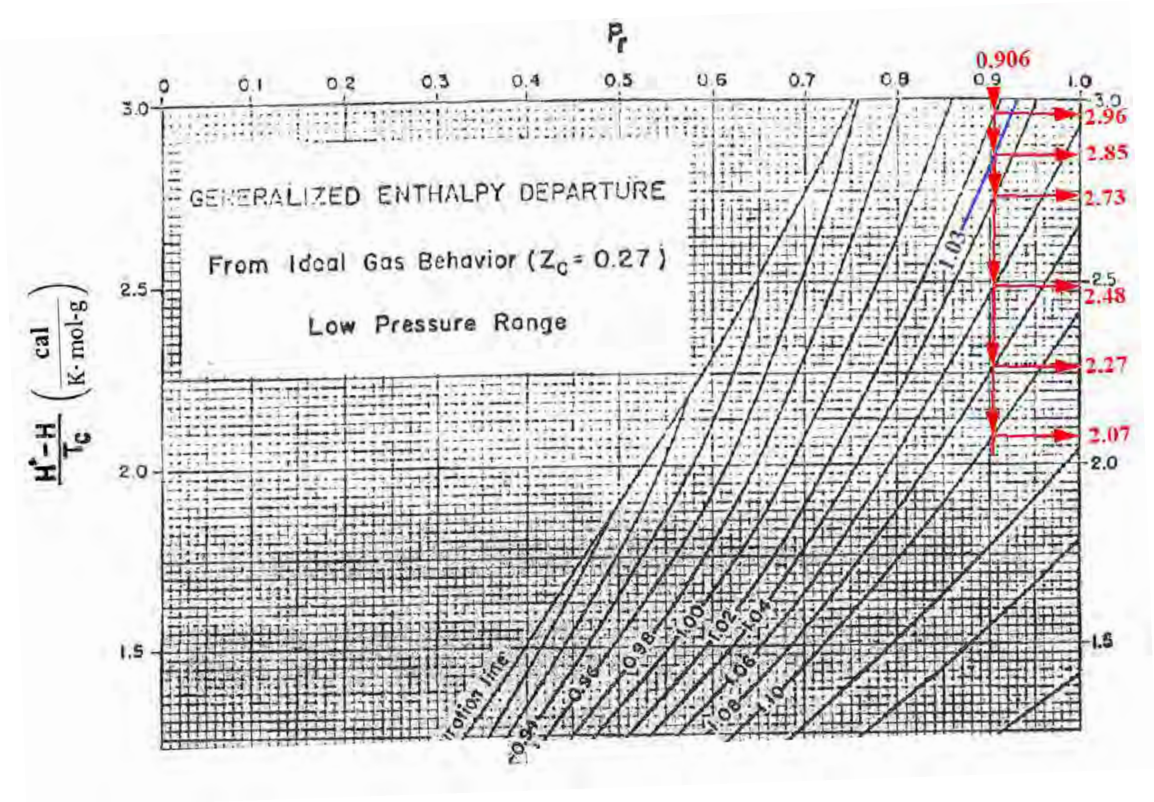
The pressure at points 1 and 2 for stream I (P_r=0.906) is known, but the temperature is only given at point 1 T=723 K, T_r=1.117), so

$$\left(\frac{\widetilde{H}_{I_1}^{*}-\widetilde{H}_{I_1}}{T_c}\right)_{T_r,P_r}=1.96\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}$$
$$\Downarrow$$
$$\widetilde{H}_{I_1}^{*}-\widetilde{H}_{I_1}=\left(1.96\,\frac{\text{cal}}{\text{K}\cdot\text{mol-g}}\right)(647.14\ \text{K})=1268.4\ \frac{\text{cal}}{\text{mol-g}}$$

As in the previous question, the value of T_{I_2} has to be obtained by trial and error: suppose a temperature, read the corresponding $\left(\widetilde{H}_{I_2}^{*}-\widetilde{H}_{I_2}\right)/T_c$ from generalized chart IV.5 and combine it with

$$\tilde{H}^*_{I_1} - \tilde{H}^*_{I_2} = 1.9872 \left\{ 4.395(723 - T) - \frac{4.186 \cdot 10^{-3}}{2}(723^2 - T^2) + \frac{1.405 \cdot 10^{-5}}{3}(723^3 - T^3) - \right. \\ \left. - \frac{1.564 \cdot 10^{-8}}{4}(723^4 - T^4) + \frac{0.632 \cdot 10^{-11}}{5}(723^5 - T^5) \right\}$$

in equation [6]. If the total enthalpy change is not equal to 1139.05 cal/mol-g (those gained by stream II, since its molar flow rate is the same than that of stream I), select another trial temperature.

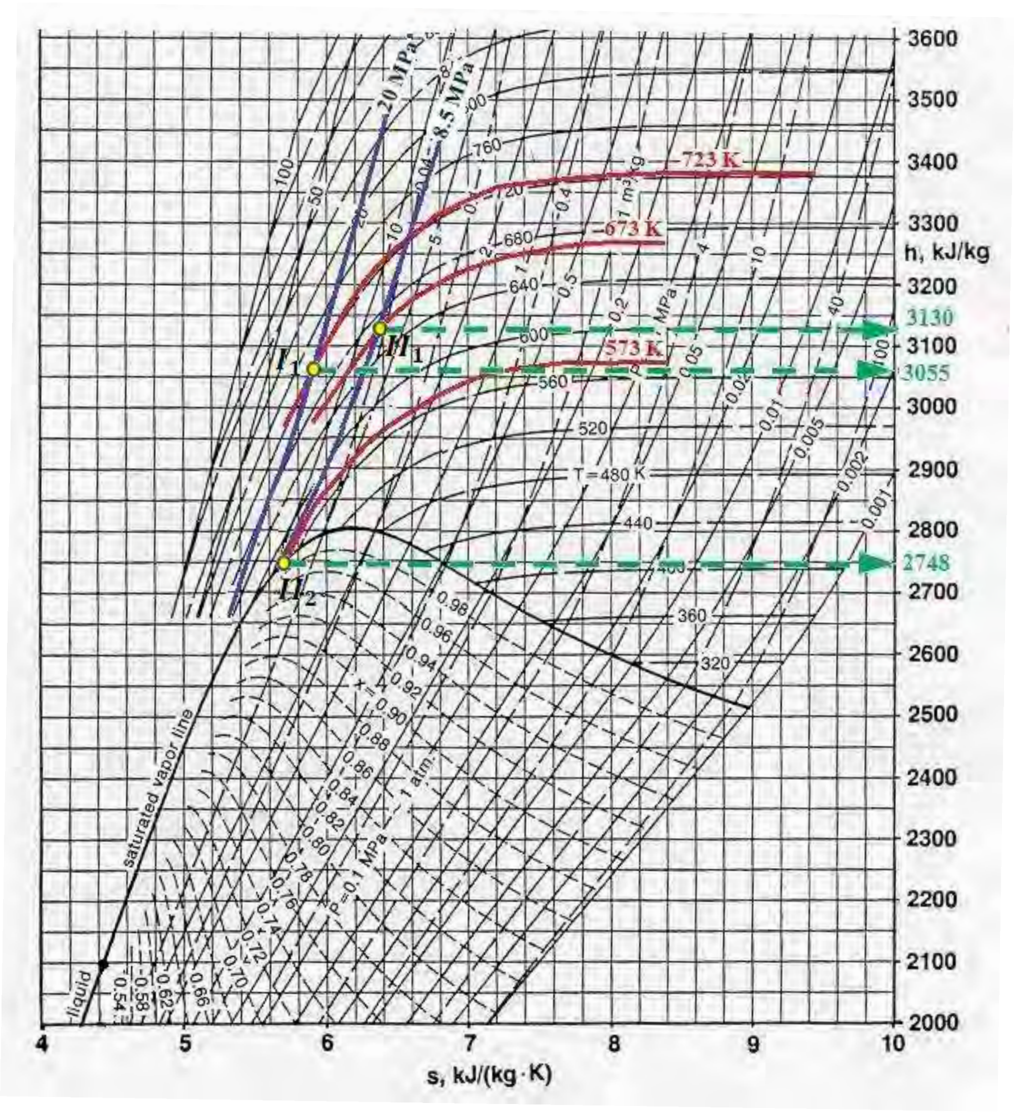


T_{rI_2}	$\left(\frac{\tilde{H}^*_{I_2} - \tilde{H}_{I_2}}{T_c}\right)_{T_r,P_r}$	$\tilde{H}^*_{I_2} - \tilde{H}_{I_2}$	T_{I_2}(K)	$\tilde{H}^*_{I_1} - \tilde{H}^*_{I_2}$	$\tilde{H}_{I_1} - \tilde{H}_{I_2}$ eq.[6]
1.1	2.07	1339.58	711.85	100.169	171.348
1.08	2.27	1469.01	698.91	216.126	416.734
1.06	2.48	1604.91	685.97	331.696	668.203
1.04	2.73	1766.69	673.03	446.876	945.168
1.02	2.96	1915.53	660.08	561.663	1208.79
1.03	2.85	1844.35	666.55	504.319	1080.27

All the enthalpies in cal/mol-g

The balance closes approximately at T_r=1.025, i.e., at 390 ºC.

Question e. The Mollier diagram for water is figure V.6 of appendix V. Only the 20 MPa (200 bar) isoline is directly displayed on it, so those of 85 bar (8.5 MPa), 723 K, 573 K and 673 K should be interpolated.

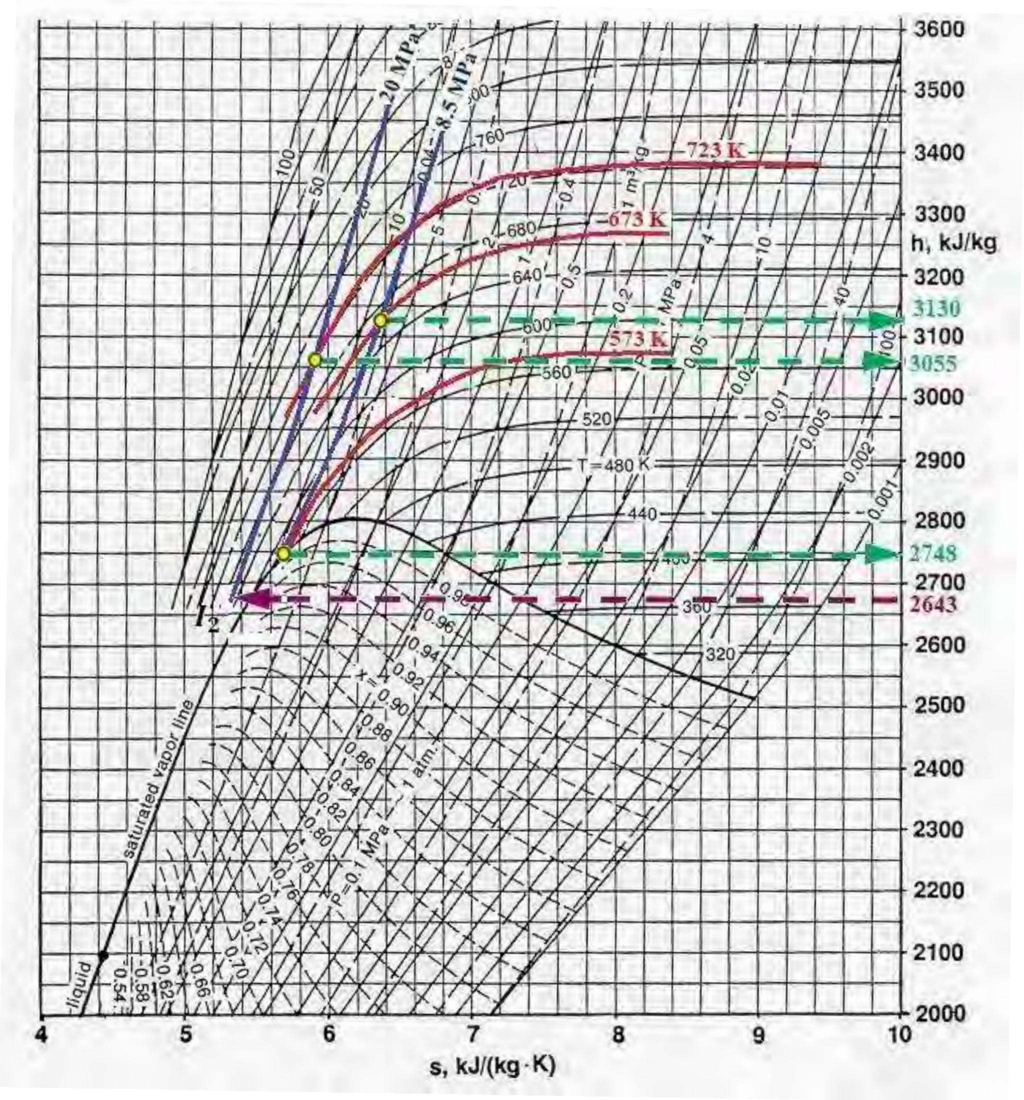


After interpolation, the point where the 573 K isotherm intersects the 8.5 MPa isobar will provide the value of $\widehat{H}_{II_2}$, while the intersection of 673 K with 8.5 MPa will indicate the value of $\widetilde{H}_{II_1}$. Similarly, the crossing of the 723 K isotherm with the 20 MPa isobar will provide $\widetilde{H}_{I_1}$. By knowing that the molar/mass flows are equal, the energy balance gives

$$\left(\widehat{H}_{I_1} - \widehat{H}_{I_2}\right) = \left(\widehat{H}_{II_1} - \widehat{H}_{II_2}\right)$$

$$3055 - \widehat{H}_{I_2} = 3130 - 2748 \quad \rightarrow \widetilde{H}_{I_2} = 2673\,\frac{\text{kJ}}{\text{kg}}$$

The drawing of the 2673 kJ/kg isenthalpic (straight line) will cross the 20 MPa isobar on an isotherm, which is the sought temperature.

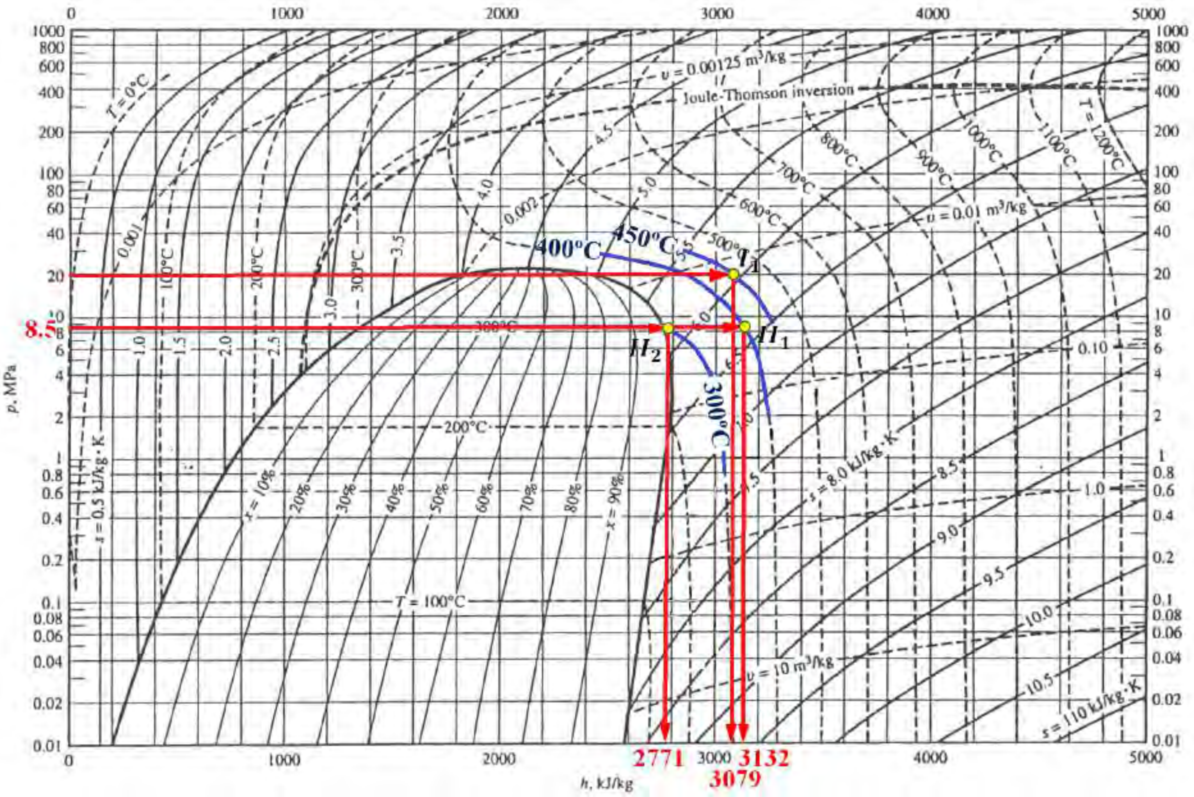


The intersection occurs between 640 and 680 K, around 660 K (probably a lower value) but the region of the diagram does not allow an improvement of the reading.

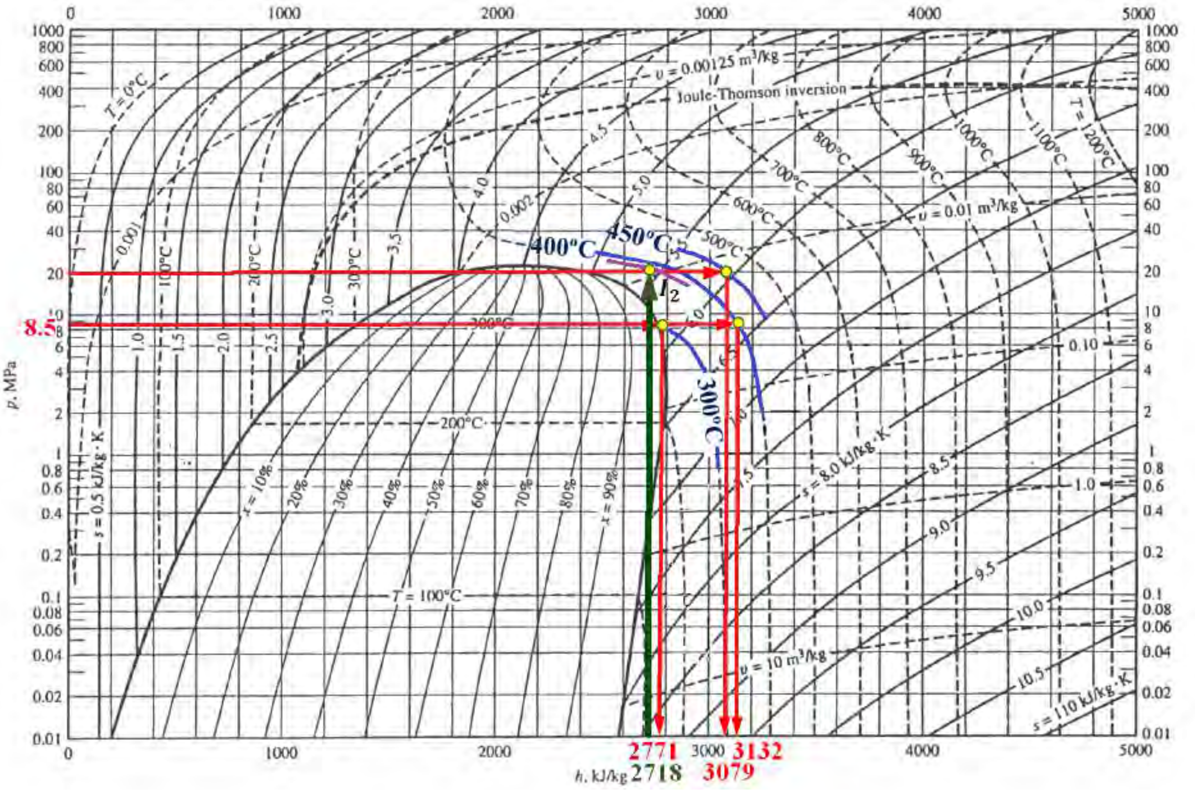
Question f. By taking figure V.5 from appendix V and proceeding in the same way as in the previous section, it can be obtained

$$\left(\hat{H}_{I_1} - \hat{H}_{I_2}\right) = \left(\hat{H}_{II_1} - \hat{H}_{II_2}\right)$$

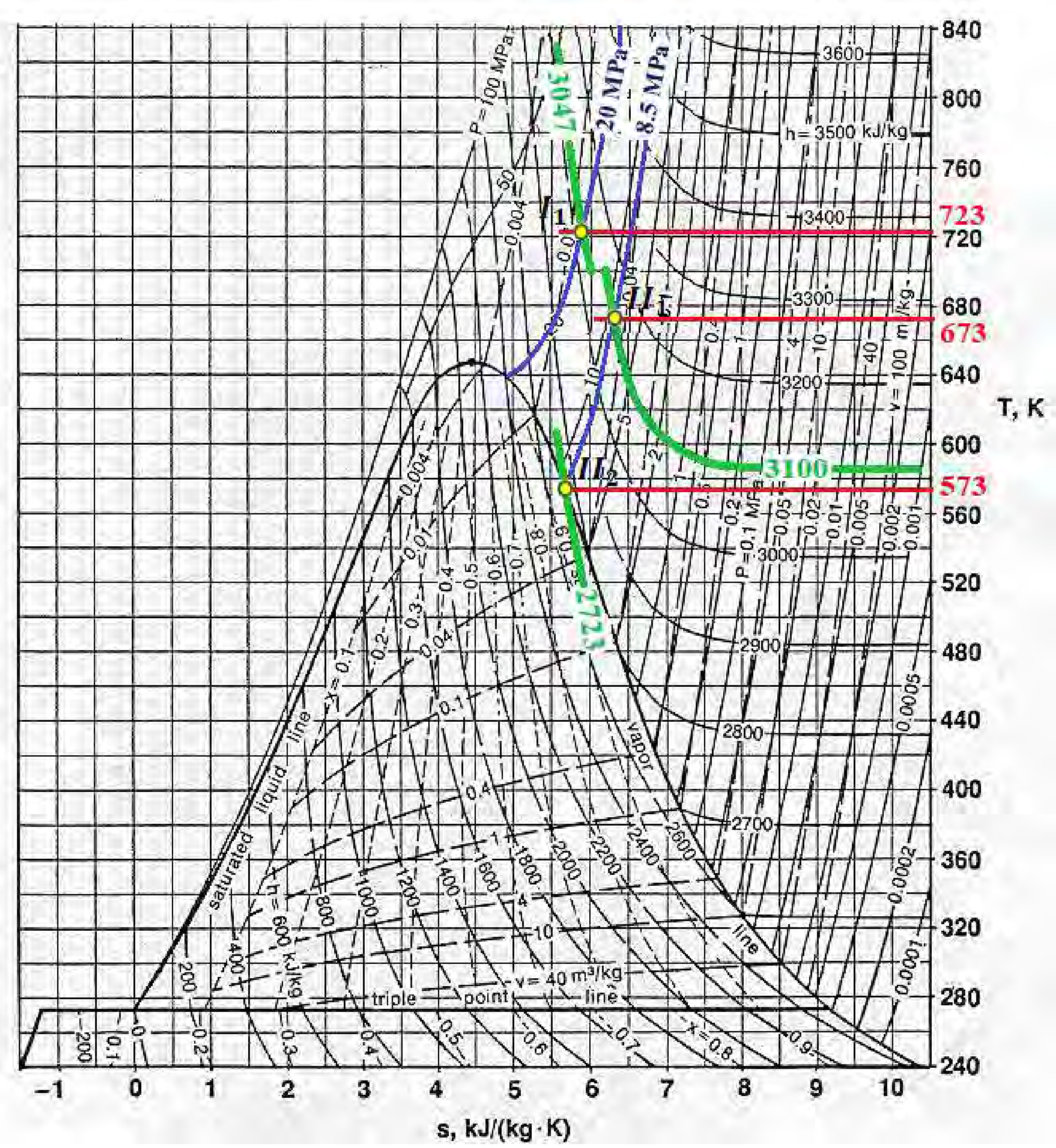
$$3079 - \hat{H}_{I_2} = 3132 - 2771 \quad \rightarrow \hat{H}_{I_2} = 2718\,\frac{\text{kJ}}{\text{kg}}$$



By placing the 2718 kJ/kg isenthalpic in the figure, and looking for its crossing with the 200 bar isoline, it is found that the temperature is approximately of 390ºC. The reading is difficult because the shape of the isotherms, but not so difficult as in the Mollier diagram.



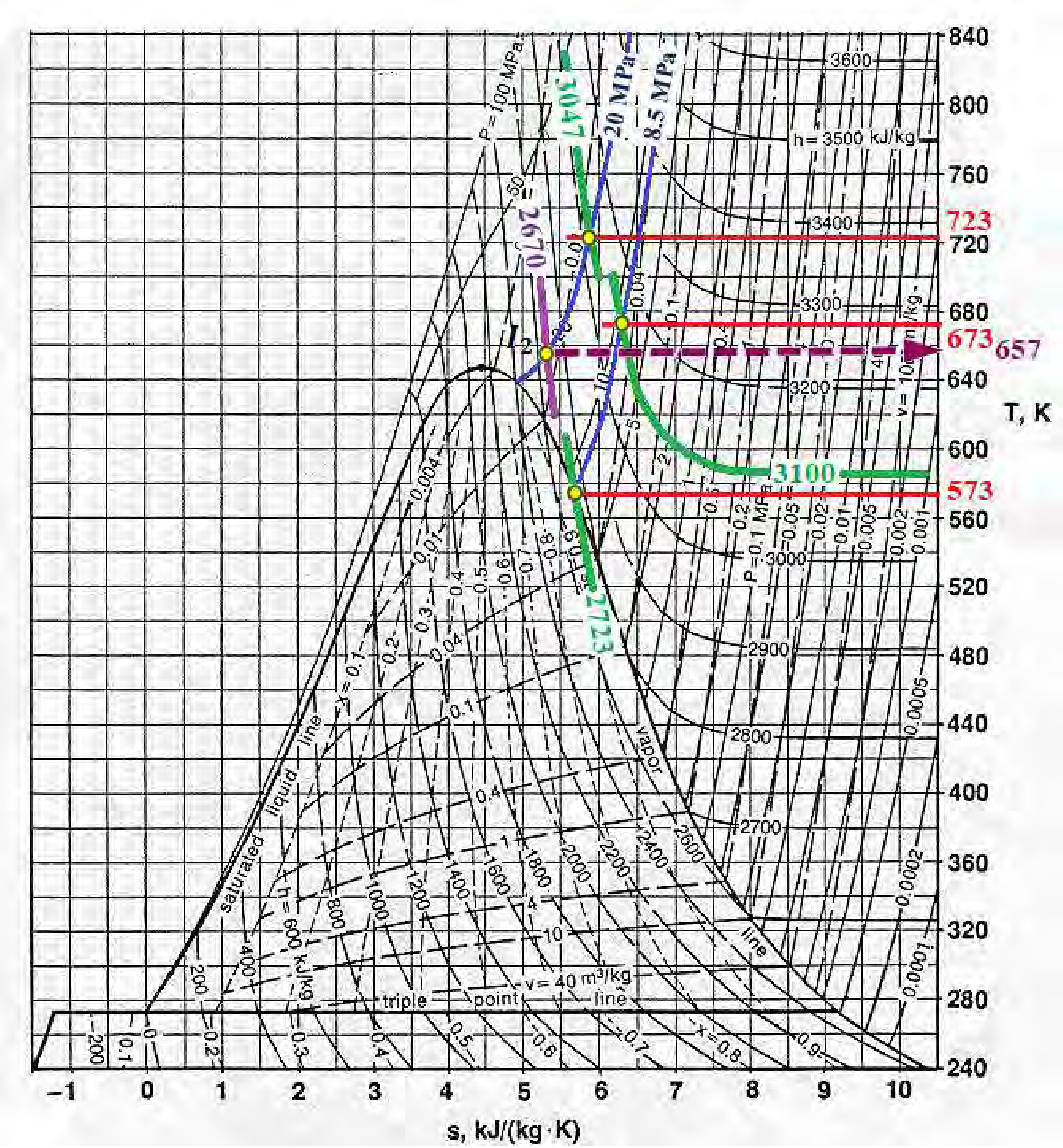
With regards to figure V.7 of the same appendix



$$\left(\hat{H}_{I_1} - \hat{H}_{I_2}\right) = \left(\hat{H}_{II_1} - \hat{H}_{II_2}\right)$$

$$3047 - \hat{H}_{I_2} = 3100 - 2723 \quad \rightarrow \hat{H}_{I_2} = 2670\,\frac{\text{kJ}}{\text{kg}}$$

The intersection of the 2670 kJ/kg isenthalpic with the 20 MPa isobar indicates a temperature of 657 K (384°C).


T, K
s, kJ/(kg·K)
840
800
760
720
680
640
600
560
520
480
440
400
360
320
280
240
-1
0
1
2
3
4
5
6
7
8
9
10
723
673
657
573
3047
20 MPa
8.5 MPa
2670
3100
2723
I2
P = 100 MPa
50
h = 3500 kJ/kg
3600
3400
3300
3200
3000
2900
2800
2700
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
h = 600 kJ/kg
400
200
-200
P = 0.1 MPa
v = 40 m³/kg
v = 100 m³/kg
x = 0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
saturated liquid line
saturated vapor line
triple point line

SERIES 6

THERMOMECHANICAL OPERATIONS

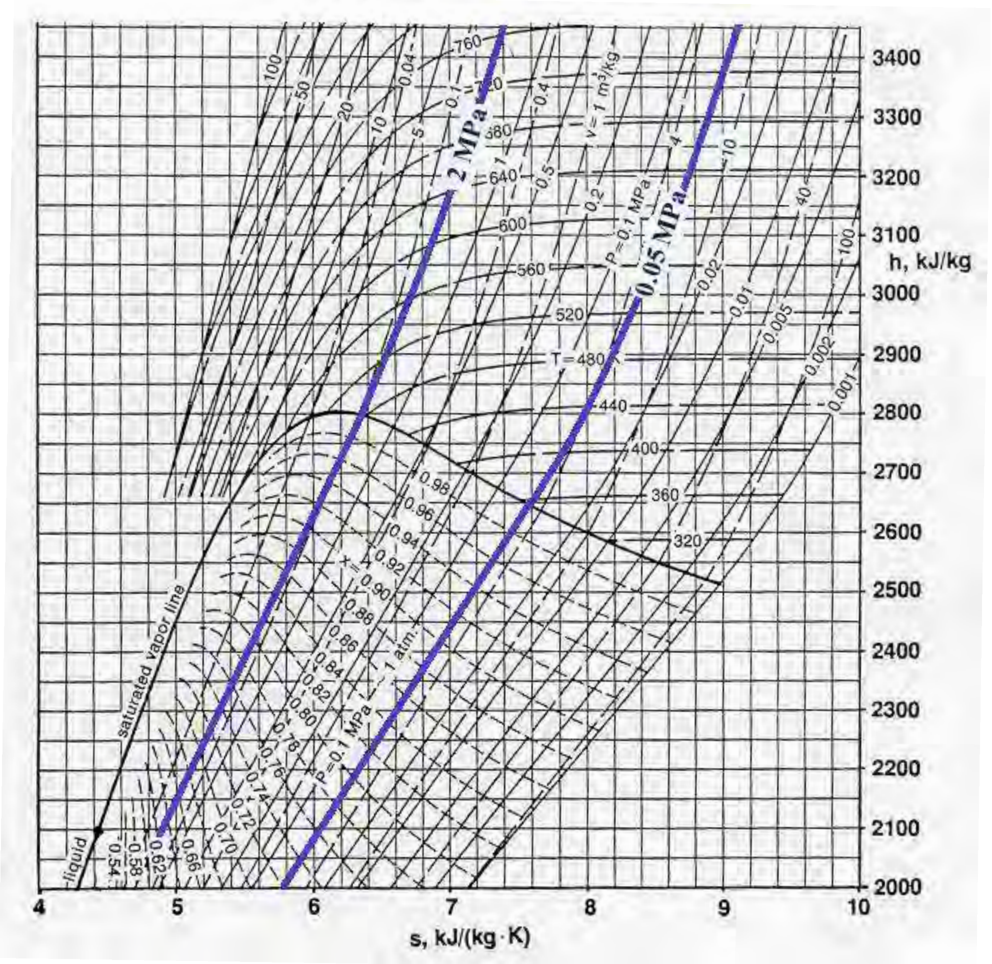
6.1. A boiler produces saturated steam at 20 bar. This vapor moves an isentropic turbine (which generates electricity) and after that, it is sent to a condenser at 0.5 bar. Calculate the liquid fraction after the expansion in the turbine and the work done (per mass unit) by means of:
a) A Mollier diagram.
b) A *TS*(*P*,*V*,*H*) diagram.
c) A *PH*(*T*,*S*,*V*) diagram.
d) Saturated water tables.

Figures V.5 (*PH* diagram), V.6 (Mollier diagram) and V.7 (*TS* diagram) of this book's appendix V and table VI.1 of appendix VI (saturated water tables), are available for this problem. In figures the pressures are expressed in MPa; thus, using the conversion factors in appendix I

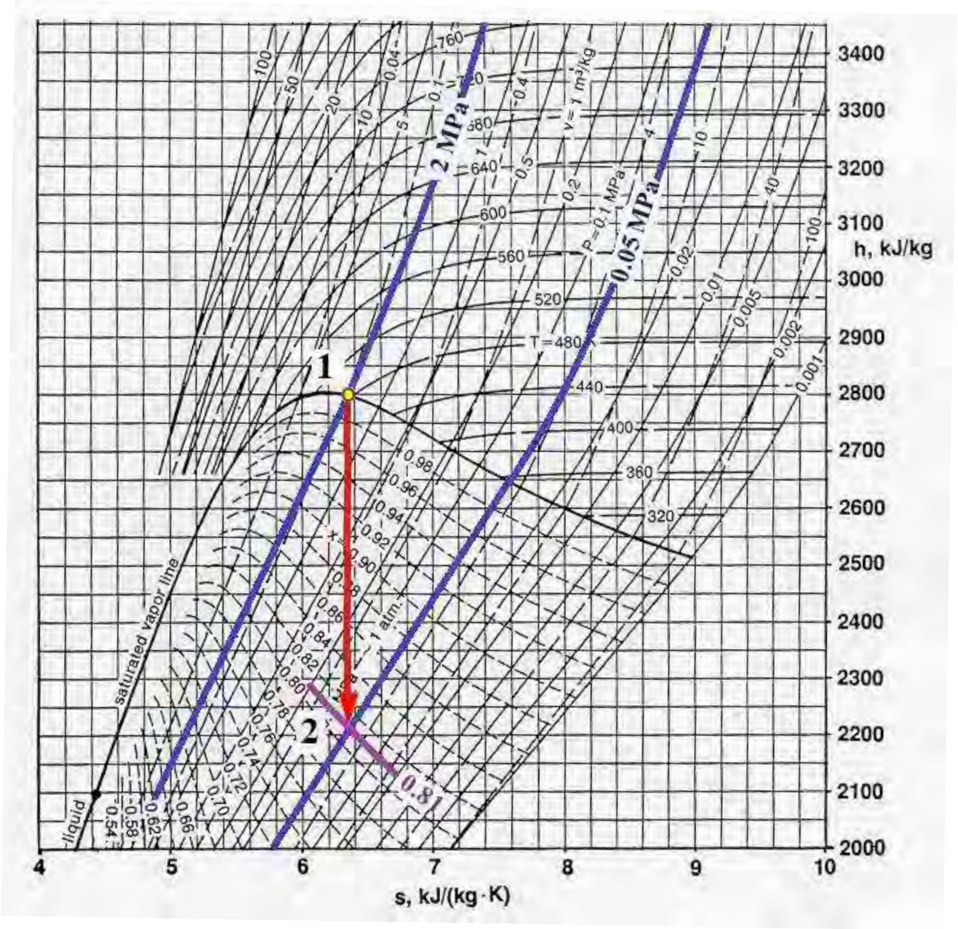
$$P_1 = 20\ \text{bar} \times \frac{100\ \text{kPa}}{1\ \text{bar}} \times \frac{1\ \text{MPa}}{1000\ \text{kPa}} = 2\ \text{MPa}$$

$$P_2 = 0.5\ \text{bar}\ \frac{100\ \text{kPa}}{1\ \text{bar}} \times \frac{1\ \text{MPa}}{1000\ \text{kPa}} = 0.05\ \text{MPa}$$

Question a. Operation lines: First, the two isobars are represented on the diagram.



Then, the intersection between the isentropic that passes through P_1 at the saturation point and the P_2 isobar is found. The title or quality line in this point indicates a vapor mass fraction of 81%, and therefore, a 19% of liquid (condensed vapor).



Regarding the work produced in the turbine

$$\mathrm{d}\widehat{W}^{\mathrm{fl}} = \widehat{V}\mathrm{d}P \quad \rightarrow \Delta\widehat{W}^{\mathrm{fl}}_{21} = \int_1^2 \widehat{V}\mathrm{d}P$$

which implies a numerical integration by selecting several pressures along the isentropic, determining the corresponding values of the specific volume and applying the trapezoidal rule or the Simpson's rule. However, according to equations of reference problem 0.3

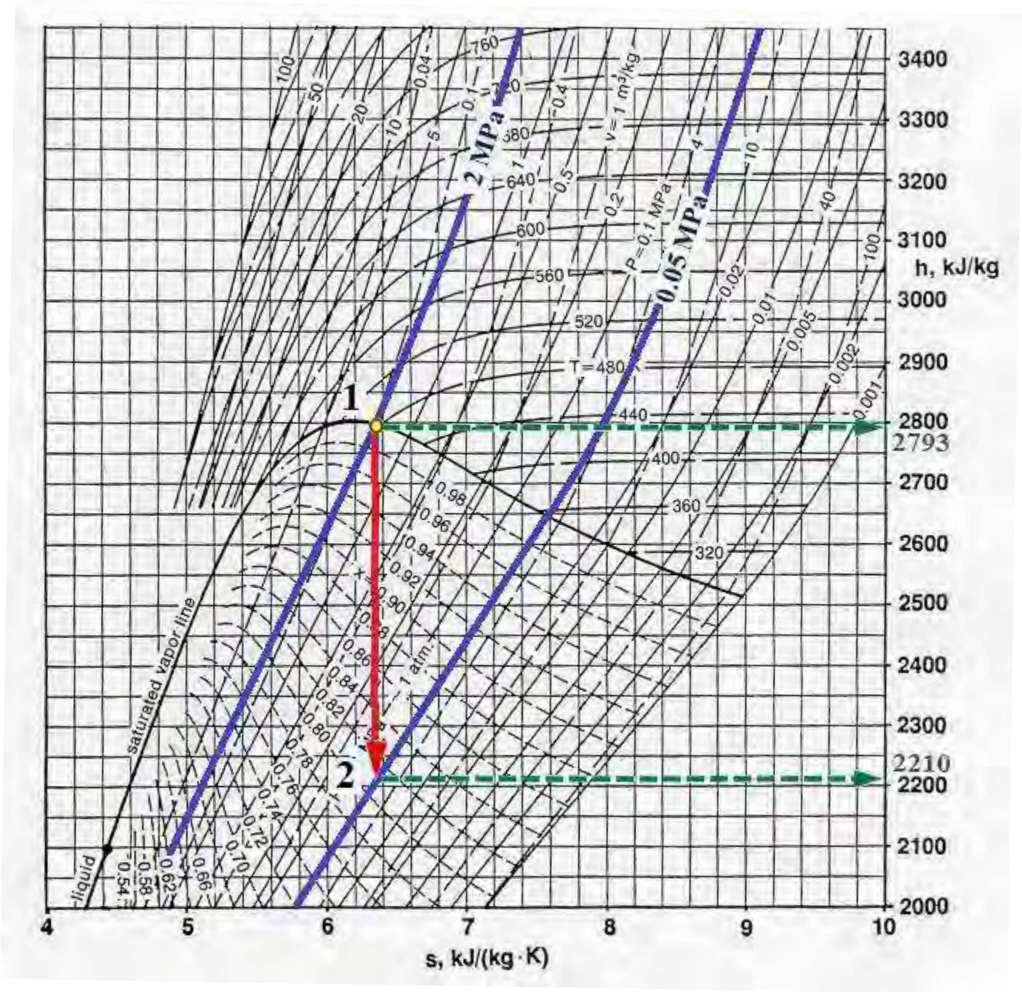
$$\mathrm{d}\widehat{H} = \mathrm{d}\widehat{Q} + \mathrm{d}\widehat{W}^{\mathrm{fl}} = T\mathrm{d}\widehat{S} + \widehat{V}\mathrm{d}P$$

If entropy remains unchanged, $\mathrm{d}\widehat{S} = 0$

$$\mathrm{d}\widehat{H} = \mathrm{d}\widehat{W}^{\mathrm{fl}} \quad \rightarrow \quad \Delta\widehat{W}^{\mathrm{fl}}_{21} = \Delta\widehat{H}_{21} = \widehat{H}_2 - \widehat{H}_1$$

being the calculations greatly simplified.

$$\Delta \widehat{W}_{21}^{\mathrm{fl}} = 2210\,\frac{\mathrm{kJ}}{\mathrm{kg}} - 2793\,\frac{\mathrm{kJ}}{\mathrm{kg}} = -583\,\frac{\mathrm{kJ}}{\mathrm{kg}}$$



Question b. By operating in the same way as in the previous question, the title or quality line of the *TS* diagram indicates 80%, but this value can be refined using the mass and entropy balances at point 2

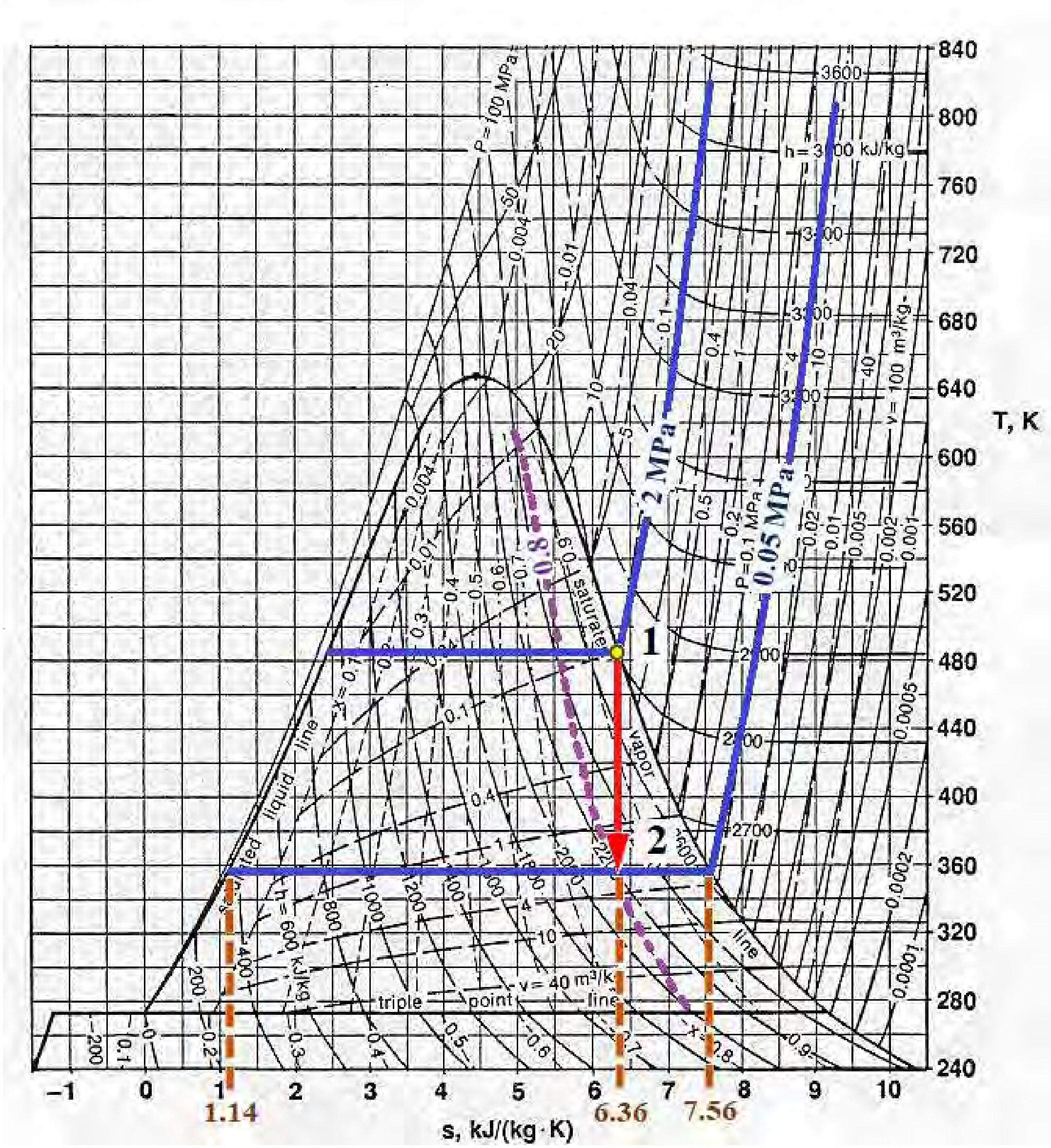
$$M_{tot} = M_{l_2} + M_{v_2}$$

$$M_{tot}\hat{S}_2 = M_{l_2}\hat{S}_{l_2}^{sat} + M_{v_2}\hat{S}_{v_2}^{sat}$$

whose combination generates

$$\frac{M_{v_2}}{M_{tot}} = \frac{\left(\hat{S}_2 - \hat{S}_{l_2}^{sat}\right)}{\left(\hat{S}_{v_2}^{sat} - \hat{S}_{l_2}^{sat}\right)} = \frac{(6.36 - 1.14)}{(7.56 - 1.14)} = 0.813$$

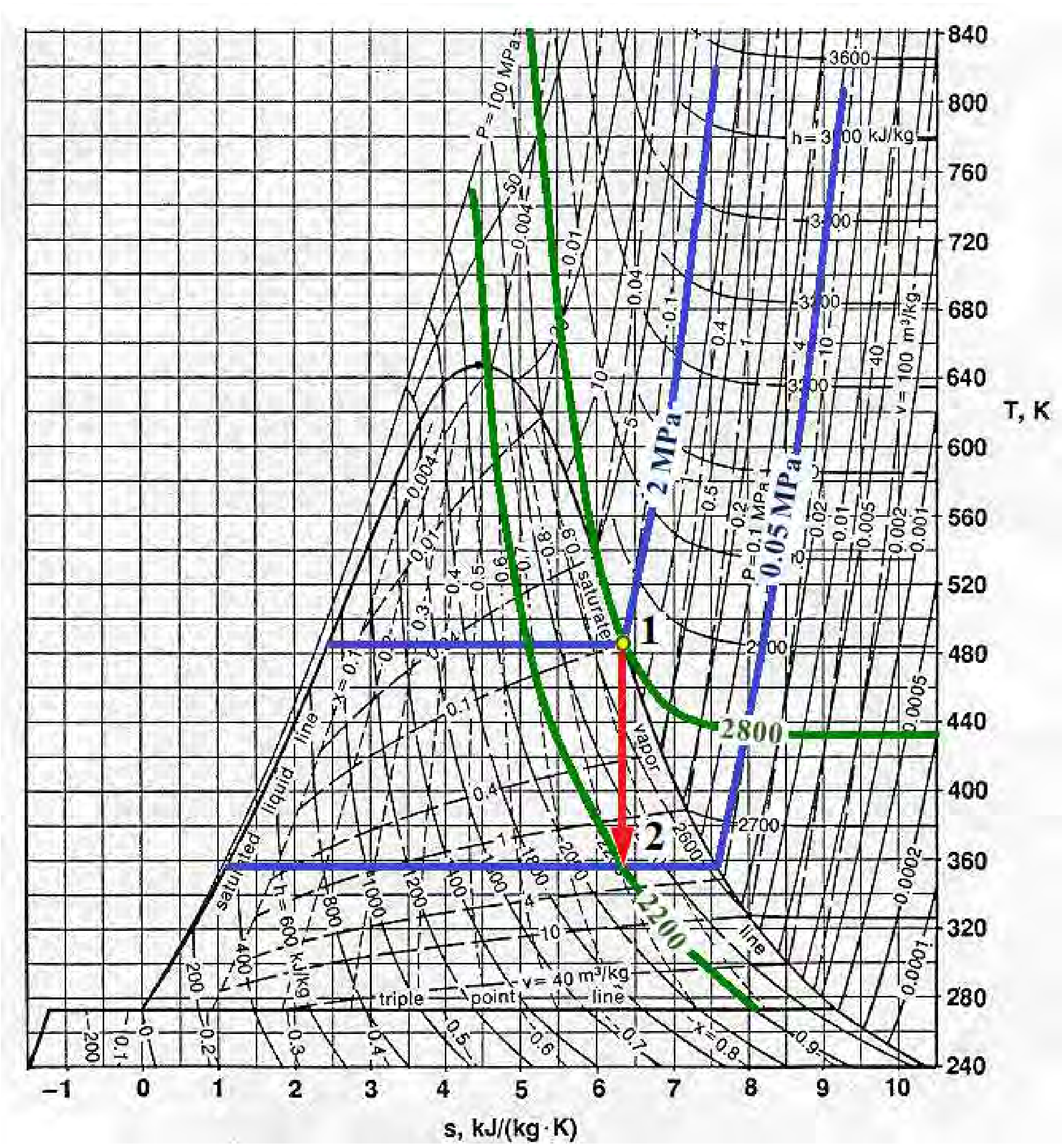
and it allows to affirm that a mass fraction of 18.7% condenses.



The work in the turbine will be

$$\Delta \widehat{W}^{\mathrm{fl}}_{21} = \widehat{H}_2 - \widehat{H}_1 = 2200\,\frac{\mathrm{kJ}}{\mathrm{kg}} - 2800\,\frac{\mathrm{kJ}}{\mathrm{kg}} = -600\,\frac{\mathrm{kJ}}{\mathrm{kg}}$$

a less precise value than that of the previous question because the enthalpies are not read in the coordinate axes but in isolines of peculiar shape.

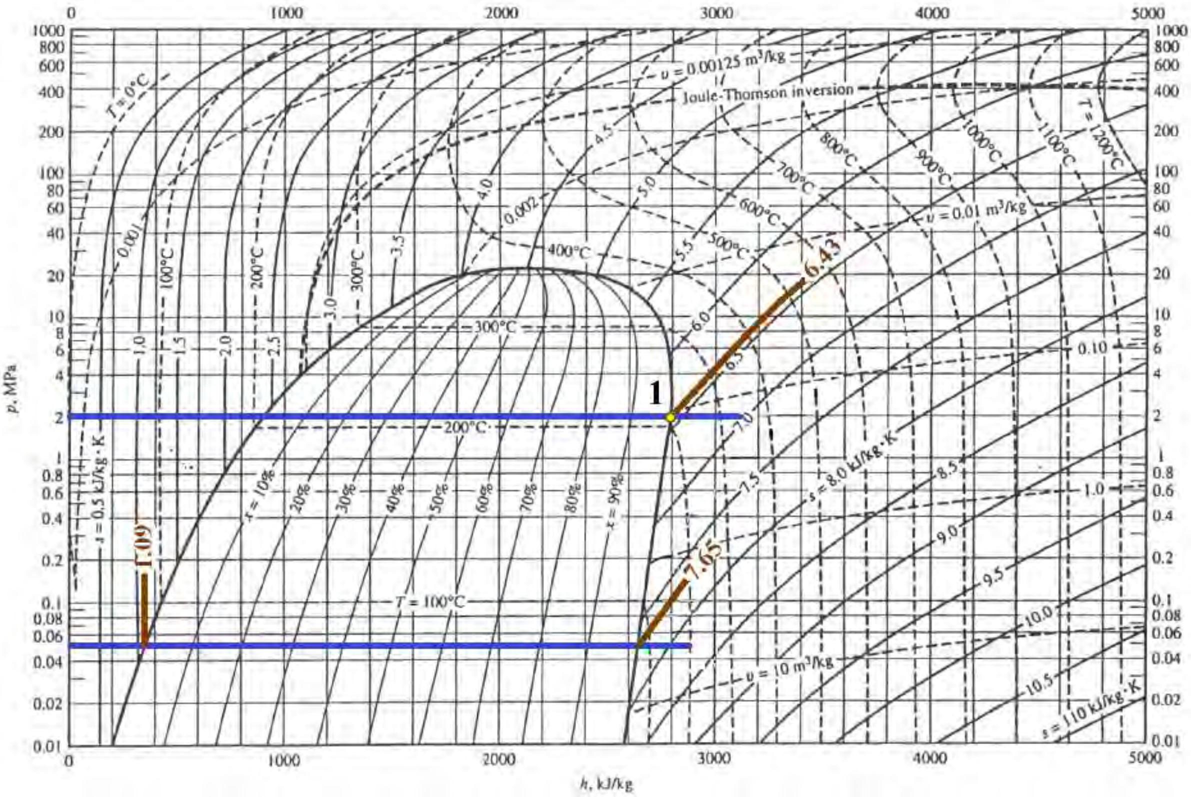


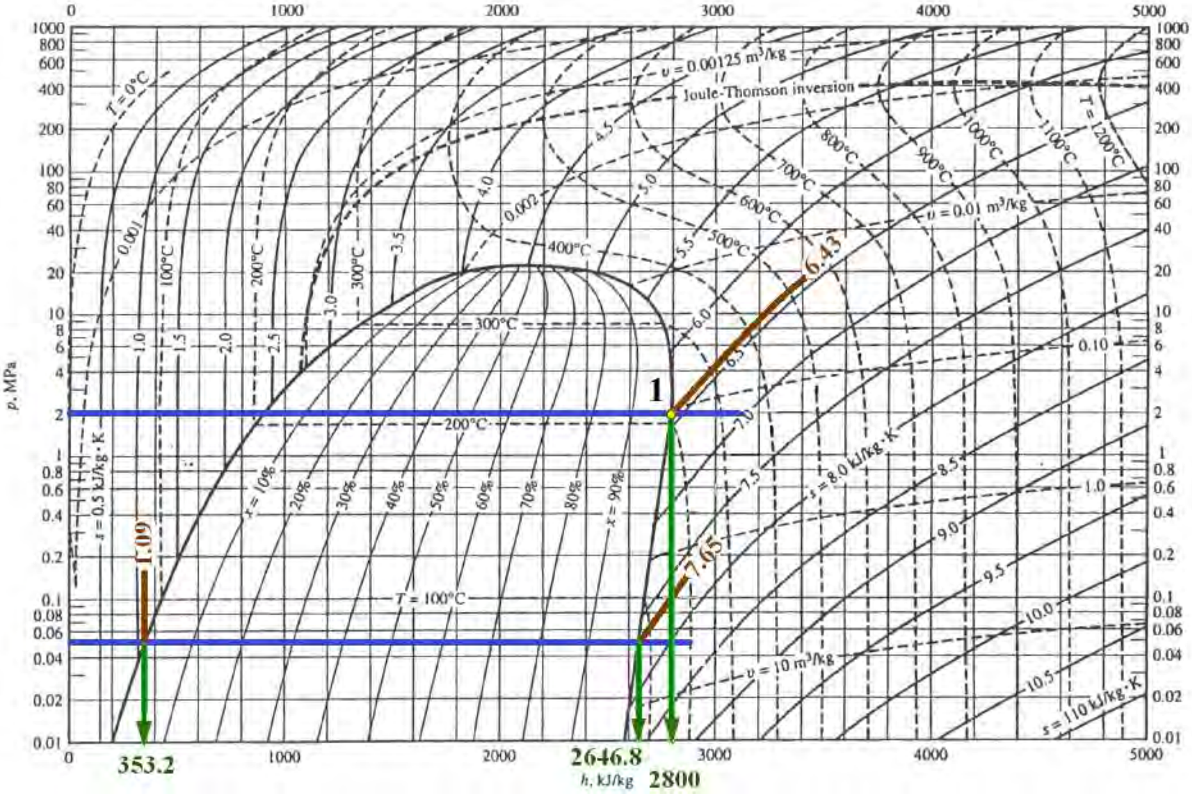
Question c. Isentropic lines are not drawn in the biphasic zone of figure V.5, but knowing that $\hat{S}_2 = \hat{S}_1$ =6.43 kJ/kg·K and that point 2 is a mixture of liquid and vapor, the combination of the mass and entropy balances will allow the calculation of the vapor fraction in this point 2 (after interpolating the specific entropies of the saturated phases, $\hat{S}_{l_2}^{sat}$=1.09 kJ/kg·K, $\hat{S}_{v_2}^{sat}$ =7.65 kJ/kg·K) as

$$\frac{M_{v_2}}{M_{tot}} = \frac{\left(\hat{S}_2 - \hat{S}_{l_2}^{sat}\right)}{\left(\hat{S}_{v_2}^{sat} - \hat{S}_{l_2}^{sat}\right)} = \frac{(6.43 - 1.09)}{(7.65 - 1.09)} = 0.814$$

The title or quality line of 81.4% could be drawn and the enthalpy $\widehat{H}_2$ read at its intersection with P_2=0.05 MPa, but it is not necessary, because by combining the mass and enthalpy balances and interpolating the enthalpies of the saturated liquid and vapor (353.2 and 2646.8 kJ/kg, respectively) it can be obtained

$$\widehat{H}_2 = \frac{M_{v_2}}{M_{tot}}\widehat{H}_{v_2}^{sat} + \frac{M_{l_2}}{M_{tot}}\widehat{H}_{l_2}^{sat} = 0.814\left(2646.8\ \frac{\text{kJ}}{\text{kg}}\right)+(1-0.814)\left(353.2\ \frac{\text{kJ}}{\text{kg}}\right)=2220.19\ \frac{\text{kJ}}{\text{kg}}$$





After reading the value of $\widehat{H}_1$, the flow work will be

$$\Delta \widehat{W}_{21}^{\text{fl}} = \widehat{H}_2 - \widehat{H}_1 = 2200.19\ \frac{\text{kJ}}{\text{kg}} - 2800\frac{\text{kJ}}{\text{kg}} = -599.82\frac{\text{kJ}}{\text{kg}}$$

Question d. When dealing with table VI.1 of appendix VI, the procedure is similar to that of question **c**:

- Saturated vapor entropy at 20 bar ($\hat{S}_1$ =6.34 kJ/kg·K) is interpolated.
- Entropies of saturated liquid and vapor at 0.5 bar ($\hat{S}_{l_2}^{sat}$=1.09 kJ/kg·K and $\hat{S}_{v_2}^{sat}$= 7.6 kJ/kg·K) are interpolated as well.
- By knowing that $\hat{S}_2 = \hat{S}_1$ and that point 2 lies on the biphasic zone, the vapor mass fraction in this point is obtained by combining the mass and entropy balances.

$$\frac{M_{v_2}}{M_{tot}} = \frac{\left(\hat{S}_2 - \hat{S}_{l_2}^{sat}\right)}{\left(\hat{S}_{v_2}^{sat} - \hat{S}_{l_2}^{sat}\right)} = \frac{(6.34 - 1.09)}{(7.6 - 1.09)} = 0.806$$

- Enthalpies of saturated liquid and vapor at 0.5 bar ($\widehat{H}_{l_2}^{sat}$ =342 kJ/kg and $\widehat{H}_{v_2}^{sat}$ =2646 kJ/kg) are read, and $\widehat{H}_2$ is calculated by combining the mass and enthalpy balances and employing the previously found vapor mass fraction.

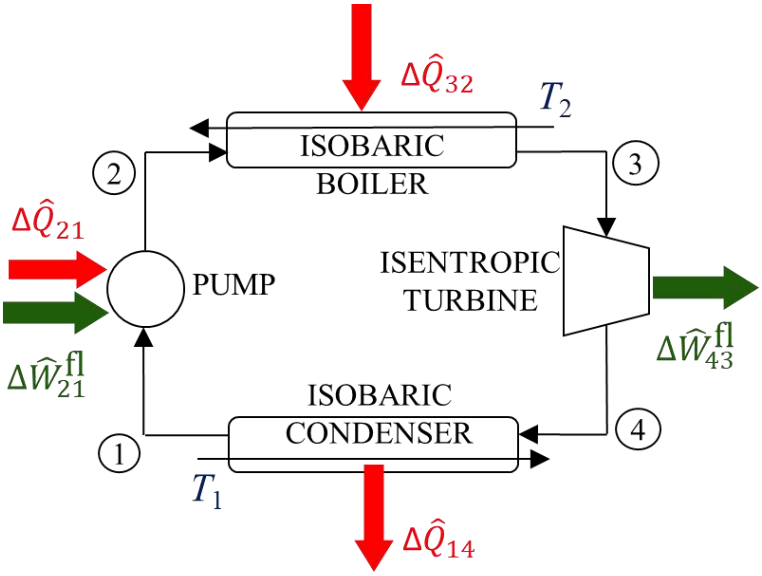
$$\widehat{H}_2 = 0.806\left(2646\ \frac{\text{kJ}}{\text{kg}}\right)+(1-0.806)\left(342\ \frac{\text{kJ}}{\text{kg}}\right)=2199\ \frac{\text{kJ}}{\text{kg}}$$

- Enthalpy of saturated vapor at 20 bar ($\widehat{H}_1 = \widehat{H}_{v_1}^{sat}$ =2797 kJ/kg) is read, and the flow work is determined as

$$\Delta \widehat{W}_{21}^{\text{fl}} = \widehat{H}_2 - \widehat{H}_1 = 2199\ \frac{\text{kJ}}{\text{kg}} - 2797\frac{\text{kJ}}{\text{kg}} = -598\frac{\text{kJ}}{\text{kg}}$$

6.2. A 500 MW thermal power station that works according to the Carnot cycle employs saturated liquid water at 100ºC and 1 bar. This liquid is pumped and compressed (in liquid-vapor equilibrium) to 300ºC, then isobarically heated at that temperature to full vaporization and after that, superheated to 750 ºC. The steam expands isentropically (in a turbine) to saturation at the initial pressure, and then, it is condensed to the starting conditions. By using the appropriate graphs, calculate:

- **a) Pressure, entropy, enthalpy and specific volume at significant points.**
- **b) The heat communicated in the pump before the boiler (in kJ/kg).**
- **c) The work generated in the turbine (in kJ/kg).**
- **d) The heat transferred to the refrigerant in the condenser (in kJ/kg).**
- **e) The heat communicated in the boiler (in kJ/kg).**
- **f) The flow of circulating water (thermal fluid).**
- **g) The global energy balance.**
- **h) The efficiency of the cycle.**



Figures V.5 (*PH* diagram), V.6 (Mollier diagram) and V.7 (*TS* diagram) of this book's appendix V are available for this problem. In two of them, the temperatures are expressed in K, so by means of the well-known conversion factors of appendix I

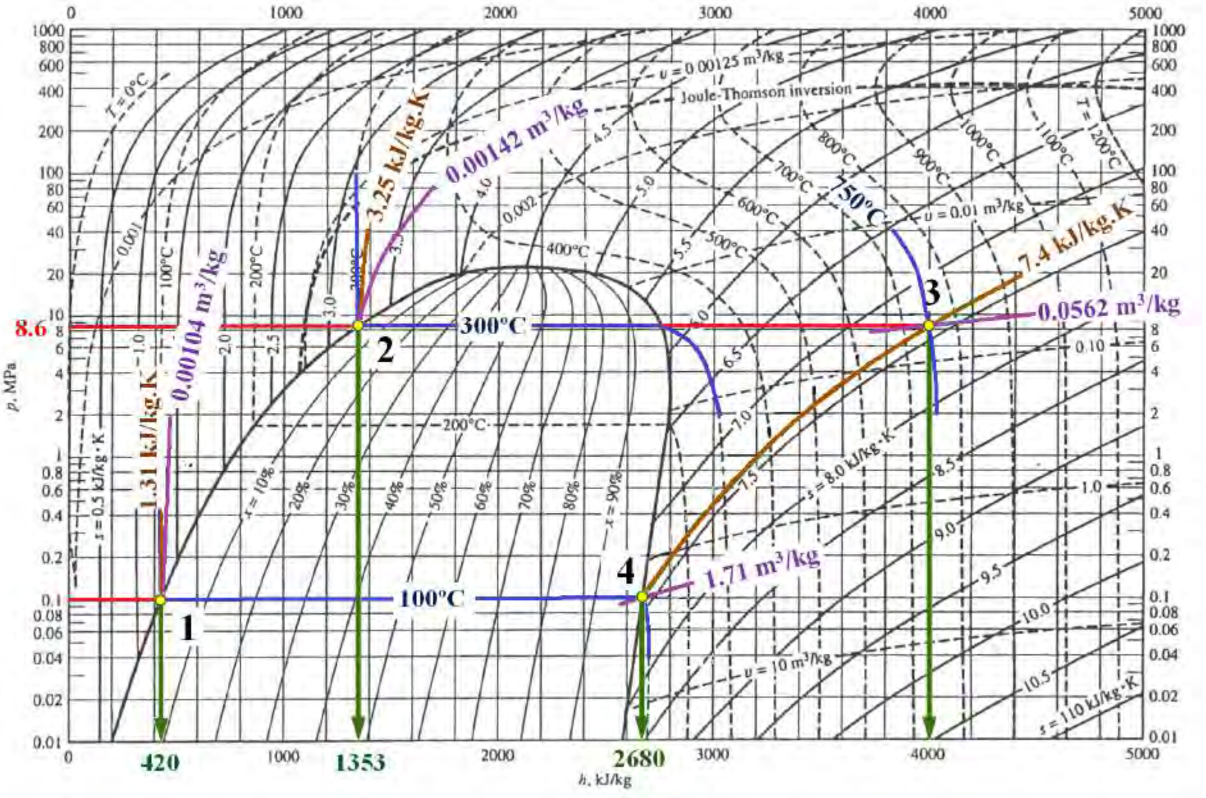
$$T_1(\text{K}) = 100\text{°C} + 273 = 373\text{ K}$$

$$T_2(\text{K}) = 750\text{°C} + 273 = 1023\text{ K}$$

Since both the Mollier diagram and the *TS* one do not show temperatures beyond 1000 K, the graphical calculations will only be carried out with figure V.5. Additionally, the Mollier diagram does not allow the reading of entropies or enthalpies for liquid water far from the critical point.

Question a. The interpolation of isochores and isentropics and the reading of the enthalpies on the abscissa axis give the following auxiliary table

Point	T (ºC)	T (K)	P (MPa)	P (kPa)	$\hat{V}$ (m^3/kg)	$\hat{H}$ (kJ/kg)	$\hat{S}$ (kJ/kg·K)
1	100	373	0.1	100	0.00104	420	1.31
2	300	573	8.6	8600	0.00142	1353	3.25
3	300	573	8.6	8600	0.0562	4000	7.4
4	100	373	0.1	100	1.71	2680	7.4



Question b. The heat communicated in the pump corresponds to the step from 1 to 2

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \Delta\hat{Q}_{21} = \int_1^2 T\mathrm{d}\hat{S}$$

which has to be evaluated numerically, and in a first approximation, it can be done by means of the trapezoidal rule with only two points

$$\Delta\hat{Q}_{21} = \left(\frac{T_2 + T_1}{2}\right)\left(\hat{S}_2 - \hat{S}_1\right) = \left(\frac{573\ \mathrm{K} + 373\ \mathrm{K}}{2}\right)\left(3.25\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 1.31\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = 917.62\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

Question c. The work generated in the turbine corresponds to the step from 3 to 4

$$\mathrm{d}\hat{W}^{\mathrm{fl}} = \hat{V}\mathrm{d}P \quad \rightarrow \Delta\hat{W}^{\mathrm{fl}}_{43} = \int_3^4 \hat{V}\mathrm{d}P$$

but fundamental thermodynamic relations indicate that

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \qquad [1]$$

and if the entropy does not vary ($\mathrm{d}\hat{S} = 0$; $\mathrm{d}\hat{Q} = 0$), the flow work can be determined by the difference of enthalpies between the initial and final states, avoiding the numerical integration

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{W}^{\mathrm{fl}} \quad \rightarrow \quad \Delta\hat{W}^{\mathrm{fl}}_{43} = \Delta\hat{H}_{43} = \hat{H}_4 - \hat{H}_3$$

$$\Delta\hat{W}^{\mathrm{fl}}_{43} = 2680\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 4000\frac{\mathrm{kJ}}{\mathrm{kg}} = -1320\frac{\mathrm{kJ}}{\mathrm{kg}}$$

Question d. The heat transferred to the refrigerant in the condenser corresponds to the to passage from point 4 to point 1

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \Delta\hat{Q}_{14} = \int_4^1 T\mathrm{d}\hat{S}$$

but since this step occurs along an isobar, dP=0 in equation [1], there will be no flow work, and no numerical integration is needed because

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} \quad \rightarrow \quad \Delta\hat{Q}_{14}{=}\Delta\hat{H}_{14} = \hat{H}_1 - \hat{H}_4 = 420\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 2680\frac{\mathrm{kJ}}{\mathrm{kg}} = -2260\frac{\mathrm{kJ}}{\mathrm{kg}}$$

However, the step is also isothermal (T_1=T_4), so

$$\int_4^1 T\mathrm{d}\hat{S} = T_1\int_4^1 \mathrm{d}\hat{S} = T_1(\hat{S}_1 - \hat{S}_4) = (373\ \mathrm{K})\left(1.31\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}\ K}} - 7.4\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}\ K}}\right) = -2271.57\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

a value that is less reliable than the previous one due to the difficulty of interpolating with precision the entropies at the points of interest.

Question e. Heat between points 2 and 3 will be

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \Delta\hat{Q}_{32} = \int_2^3 T\mathrm{d}\hat{S}$$

and as in question **d**, it represents an isobaric process. Therefore

$$\Delta\hat{Q}_{32}=\Delta\hat{H}_{32}=\hat{H}_3-\hat{H}_2=4000\ \frac{\mathrm{kJ}}{\mathrm{kg}}-1353\frac{\mathrm{kJ}}{\mathrm{kg}}=2647\frac{\mathrm{kJ}}{\mathrm{kg}}$$

Question f. The required flow rate of the thermal fluid will be calculated from the power given by the statment of the problem (500 MW= 500·10^3 kW) and from the absolute value of the work in the turbine as

$$\text{Flow rate}=\frac{\text{Power of the station}}{|\text{Work in the turbine}|}=\frac{500\cdot 10^3\ \mathrm{kW}}{\left|-1320\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right|}=378.78\ \frac{\mathrm{kg}}{\mathrm{s}}$$

Question g. According to section d of reference problem 0.13, the energy balance to this system is summarized in

$$\left|\begin{matrix}\text{Sum of heat and work}\\ \text{with positive sign}\end{matrix}\right|=\left|\begin{matrix}\text{Sum of heat and work}\\ \text{with negative sign}\end{matrix}\right| \qquad [2]$$

However, in the previous questions, all the terms required to complete the sum have not been calculated because the pump is not isobaric and it is associated with a flow work

$$\Delta\hat{W}_{21}^{\mathrm{fl}}=\int_1^2\hat{V}\mathrm{d}P$$

Numerical integral that, according to the trapezoidal rule with only two points, gives

$$\Delta\hat{W}_{21}^{\mathrm{fl}}=\left(\frac{\hat{V}_2+\hat{V}_1}{2}\right)(P_2-P_1)=\left(\frac{0.00142\ \frac{\mathrm{m}^3}{\mathrm{kg}}+0.00104\frac{\mathrm{m}^3}{\mathrm{kg}}}{2}\right)(8600\ \mathrm{kPa}-100\ \mathrm{kPa})=10.455\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

Therefore, equation [2] becomes

$$\left|\Delta\hat{Q}_{32}+\Delta\hat{W}_{21}^{\mathrm{fl}}+\Delta\hat{Q}_{21}\right|=\left|\Delta\hat{W}_{43}^{\mathrm{fl}}+\Delta\hat{Q}_{14}\right|$$

$$\left|2647\frac{\mathrm{kJ}}{\mathrm{kg}}+917.62\frac{\mathrm{kJ}}{\mathrm{kg}}+10.455\frac{\mathrm{kJ}}{\mathrm{kg}}\right|=\left|-1320\frac{\mathrm{kJ}}{\mathrm{kg}}-2260\frac{\mathrm{kJ}}{\mathrm{kg}}\right|$$

$$\left|3575\frac{\mathrm{kJ}}{\mathrm{kg}}\right|\approx\left|-3580\frac{\mathrm{kJ}}{\mathrm{kg}}\right|$$

This result indicates that the evaluation of the numerical integrals by taking only two points has been quite correct in the present case. This could also have been verified with equation [1], since

$$\Delta\widehat{H}_{21} = \Delta\widehat{Q}_{21} + \Delta\widehat{W}_{21}^{\mathrm{fl}}$$

$$\Delta\widehat{H}_{21} = 1353\,\frac{\mathrm{kJ}}{\mathrm{kg}} - 420\,\frac{\mathrm{kJ}}{\mathrm{kg}} = 933\,\frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta\widehat{Q}_{21} + \Delta\widehat{W}_{21}^{\mathrm{fl}} = 917.62\,\frac{\mathrm{kJ}}{\mathrm{kg}} + 10.455\,\frac{\mathrm{kJ}}{\mathrm{kg}} = 928.075\,\frac{\mathrm{kJ}}{\mathrm{kg}}$$

Question h. Section d of reference problem 0.13 says that the cycle efficiency is

$$\text{Efficiency (\%)} = \frac{|\text{Work in the turbine}|}{\left|\begin{matrix}\text{Sum of heat and work}\\ \text{with positive sign}\end{matrix}\right|} \times 100 = \frac{|\text{Work in the turbine}|}{\left|\begin{matrix}\text{Sum of heat and work}\\ \text{with negative sign}\end{matrix}\right|} \times 100$$

and by introducing the numerical values

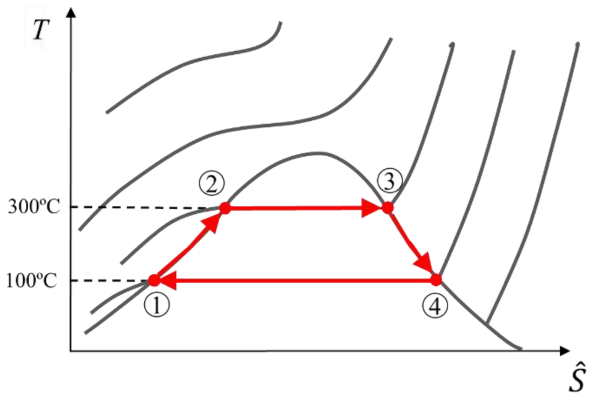
$$\frac{\left|-1320\,\frac{\mathrm{kJ}}{\mathrm{kg}}\right|}{\left|3575\,\frac{\mathrm{kJ}}{\mathrm{kg}}\right|} \times 100 \approx \frac{\left|-1320\,\frac{\mathrm{kJ}}{\mathrm{kg}}\right|}{\left|-3580\,\frac{\mathrm{kJ}}{\mathrm{kg}}\right|} \times 100$$

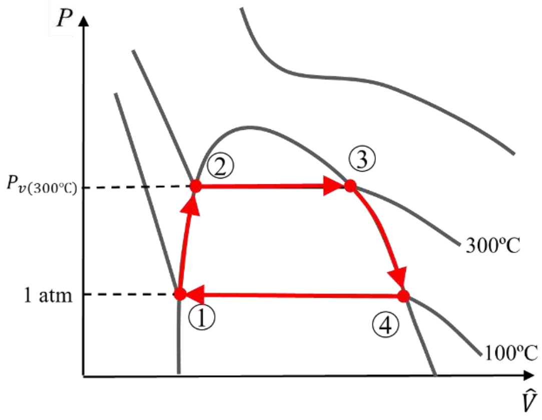
$$36.92\% \approx 36.87\%$$

6.3. A thermal power station operates according to the following modified Carnot cycle: saturated liquid water at 100ºC and 1 atm (1) is compressed in liquid-vapor equilibrium to 300ºC (2), then heated in a boiler until it all becomes saturated vapor at the same temperature (3). The saturated steam expands in a turbine to the initial pressure of 1 atm without letting be saturated vapor (4). This low pressure steam is condensed in an isobaric refrigeration system to obtain the saturated liquid of the beginning (1).

a) Qualitatively represent the cycle in *TS* and *PV*(*T*) diagrams.
b) Identify the properties *P*, *V*, *T*, *S* at the points located between the different operations of the cycle.
c) Calculate the heat transferred in the boiler (in kJ/kg).
d) Calculate the work produced in the turbine (in kJ/kg).
e) Calculate the steam flow rate that circulates if a theoretical power of 250 MW want to be achieved.
f) Calculate the heat transferred in the condenser to the refrigerant (in kJ/kg).
g) Determine the energy consumed by the compressor (in kJ/kg).
h) Carry out a total energy balance.
i) Estimate the efficiency of the cycle.
j) Why do actual Carnot cycles work in the biphasic zone and not in the monophasic one?

Question a. The qualitative representations will be





As can be seen, since the four points of interest are saturated liquid or saturated vapor, it seems that the best way to solve the questions of the problem is by employing table VI.1 of appendix VI, which allows better readings and interpolations than *TS*(*P*,*V*,*H*) and *PH*(*T*,*V*,*S*) diagrams of appendix V.

Question b. By reading in table VI.1 the values of volume, enthalpy and entropy at 100ºC and 1 atm (1.0133 bar) and interpolating the pressure, volume, enthalpy and entropy at 300ºC, the following table is obtained

Point	T (ºC)	T (K)	P (bar)	$\hat{V}$ (m^3/kg)	$\hat{H}$ (kJ/kg)	$\hat{S}$ (kJ/kg·K)
1	100	373	1.0133	0.001044	419.1	1.307
2	300	573	86.05	0.001403	1346	3.255
3	300	573	86.05	0.0217	2750	5.708
4	100	373	1.0133	1.679	2676	7.356

Question c. The heat transferred in the boiler will correspond to the passage from 2 to 3

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \Delta\hat{Q}_{32} = \int_2^3 T\mathrm{d}\hat{S}$$

but due to the fact that the passage is isothermal

$$\Delta\hat{Q}_{32} = T_2 \int_2^3 \mathrm{d}\hat{S} = T_2\left(\hat{S}_3 - \hat{S}_2\right) = (573\ \mathrm{K})\left(5.708\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}\ K}} - 3.255\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}\ K}}\right) = 1405.57\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

This heat can also be evaluated from equations of reference problem 0.3

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \tag{1}$$

Since the step is isobaric (dP=0) no energy will procude flow work and

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} \qquad \rightarrow \qquad \Delta\hat{Q}_{32} = \Delta\hat{H}_{32} = \hat{H}_3 - \hat{H}_2 = 2750\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 1346\frac{\mathrm{kJ}}{\mathrm{kg}} = 1404\frac{\mathrm{kJ}}{\mathrm{kg}}$$

a value that does not exactly coincide with the previous one due to the small rounding errors and of interpolation at 300ºC, but which is well within the precision expected in this type of calculations.

Question d. The work produced in the turbine correspond to the passage from 3 to 4

$$\mathrm{d}\hat{W}^{\mathrm{fl}} = \hat{V}\mathrm{d}P \quad \rightarrow \Delta\hat{W}_{43}^{\mathrm{fl}} = \int_3^4 \hat{V}\mathrm{d}P$$

The process is not isothermal, so a simplification based in equation [1] cannot be applied. The integral has to be numerically solved (for example, by the trapezoidal rule) taking from table VI.1 pressures and specific volumes of the vapor between 300ºC and 100ºC.

T (ºC)	P (bar)	P (kPa)	$\hat{V}_v$ (m^3/kg)	$[P_i - P_{i-1}]\left(\frac{\hat{V}_i + \hat{V}_{i-1}}{2}\right)$ P in kPa
300	86.05	8605	0.0217	
296.85	82.16	8216	0.0228	-8.65525
286.85	71.08	7108	0.0269	-27.5338
276.85	61.19	6119	0.0317	-28.9777
266.85	52.38	5238	0.0375	-30.4826
256.85	44.58	4458	0.0445	-31.98
246.85	37.7	3770	0.0525	-33.368
236.85	31.66	3166	0.0631	-34.9112
226.85	26.4	2640	0.0766	-36.7411
216.85	21.83	2183	0.0922	-38.5708
206.85	17.9	1790	0.111	-39.9288
196.85	14.55	1455	0.136	-41.3725
186.85	11.71	1171	0.167	-43.026
176.85	9.319	931.9	0.208	-44.83125
166.85	7.333	733.3	0.261	-46.5717
156.85	5.699	569.9	0.331	-48.3664
146.85	4.37	437	0.425	-50.2362
136.85	3.302	330.2	0.553	-52.2252
126.85	2.455	245.5	0.731	-54.3774
116.85	1.794	179.4	0.98	-56.54855
111.85	1.5233	152.33	1.142	-28.72127
106.85	1.2869	128.69	1.337	-29.30178
101.85	1.0815	108.15	1.574	-29.89597
100	1.0133	101.33	1.679	-11.09273
			Sum=	-847.7162 kPa·m^3/kg

Thus, the flow work per mass unit is of -847.72 kJ/kg.

Question e. The power (250 MW= 250·10^3 kW) corresponds to the turbine, so

$$\text{Flow rate}=\frac{\text{Power}}{|\text{Work in the turbine}|}=\frac{250\cdot 10^3\ \text{kW}}{\left|-847.72\ \frac{\text{kJ}}{\text{kg}}\right|}=294.91\ \frac{\text{kg}}{\text{s}}$$

Question f. This question is solved in a way analogous to that of question **c** because the heat transferred to the refrigerant corresponds to the step from 4 to 1, which is both isothermal and isobaric

$$\Delta\hat{Q}_{14}=T_4\int_4^1 \text{d}\hat{S}=T_4\left(\hat{S}_1-\hat{S}_4\right)=(373\ \text{K})\left(1.307\ \frac{\text{kJ}}{\text{kg}\cdot\text{K}}-7.356\ \frac{\text{kJ}}{\text{kg}\cdot\text{K}}\right)=-2256.28\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\hat{Q}_{14} = \Delta\hat{H}_{14} = \hat{H}_1 - \hat{H}_4 = 419.1\ \frac{\text{kJ}}{\text{kg}} - 2676\,\frac{\text{kJ}}{\text{kg}} = -2256.9\,\frac{\text{kJ}}{\text{kg}}$$

Question g. The compressor operates in a way similar to that of the turbine and it requires a numerical integration as well, but it is necessary to use the specific volume of saturated liquid instead of that of the saturated vapor.

$$\mathrm{d}\hat{W}^{\text{fl}} = \hat{V}\mathrm{d}P \quad \rightarrow \ \Delta\hat{W}_{21}^{\text{fl}} = \int_1^2 \hat{V}\mathrm{d}P$$

T (ºC)	P (bar)	P (kPa)	$\hat{V}_l$ (m^3/kg)	$[P_i - P_{i-1}]\left(\frac{\hat{V}_i + \hat{V}_{i-1}}{2}\right)$ P in kPa
100	1.0133	101.33	0.001044	
101.85	1.0815	108.15	0.001045	0.00712349
106.85	1.2869	128.69	0.001049	0.02150538
111.85	1.5233	152.33	0.001053	0.02484564
116.85	1.794	179.4	0.001058	0.028572385
126.85	2.455	245.5	0.001067	0.07023125
136.85	3.302	330.2	0.001077	0.0907984
146.85	4.37	437	0.001088	0.115611
156.85	5.699	569.9	0.001099	0.14532615
166.85	7.333	733.3	0.00111	0.1804753
176.85	9.319	931.9	0.001123	0.2217369
186.85	11.71	1171	0.001137	0.270183
196.85	14.55	1455	0.001152	0.325038
206.85	17.9	1790	0.001167	0.3884325
216.85	21.83	2183	0.001184	0.4619715
226.85	26.4	2640	0.001203	0.5454295
236.85	31.66	3166	0.001222	0.637775
246.85	37.7	3770	0.001244	0.744732
256.85	44.58	4458	0.001268	0.864128
266.85	52.38	5238	0.001294	0.99918
276.85	61.19	6119	0.001323	1.1527885
286.85	71.08	7108	0.001355	1.324271
296.85	82.16	8216	0.001392	1.521838
300	86.05	8605	0.001403	0.5436275
			Sum=	10.6856204 kPa·m^3/kg

The work or consumed energy is of 10.69 kJ/kg.

Question h. According to section d of reference problem 0.13, the energy balance to this cycle is

$$\left|\begin{array}{c}\text{Sum of heat and work}\\ \text{with positive sign}\end{array}\right| = \left|\begin{array}{c}\text{Sum of heat and work}\\ \text{with negative sign}\end{array}\right|$$

However, in the previous questions the terms required to complete the sum have not been all calculated, since the turbine and the compressor are not isoentropic and are associated with heat exchanges

$$\Delta\hat{Q}_{43} = \int_3^4 T\mathrm{d}\hat{S} \qquad ; \qquad \Delta\hat{Q}_{21} = \int_1^2 T\mathrm{d}\hat{S}$$

integrals that have to be numerically solved by taking entropies from table VI.1 between 300 and 100ºC.

<u>For the turbine</u>

T (ºC)	P (bar)	T (K)	$\hat{S}_v$ (kJ/kg)	$[\hat{S}_i - \hat{S}_{i-1}]\left(\frac{T_i + T_{i-1}}{2}\right)$ T in K
300	86.05	573	5.708	
296.85	82.16	569.85	5.733	14.285625
286.85	71.08	559.85	5.808	42.36375
276.85	61.19	549.85	5.882	41.0589
266.85	52.38	539.85	5.953	38.68435
256.85	44.58	529.85	6.023	37.4395
246.85	37.7	519.85	6.093	36.7395
236.85	31.66	509.85	6.163	36.0395
226.85	26.4	499.85	6.233	35.3395
216.85	21.83	489.85	6.312	39.09315
206.85	17.9	479.85	6.377	31.51525
196.85	14.55	469.85	6.451	35.1389
186.85	11.71	459.85	6.528	35.79345
176.85	9.319	449.85	6.607	35.93315
166.85	7.333	439.85	6.689	36.4777
156.85	5.699	429.85	6.775	37.3971
146.85	4.37	419.85	6.865	38.2365
136.85	3.302	409.85	6.959	38.9959
126.85	2.455	399.85	7.058	40.08015
116.85	1.794	389.85	7.163	41.45925
111.85	1.5233	384.85	7.218	21.30425
106.85	1.2869	379.85	7.275	21.79395
101.85	1.0815	374.85	7.333	21.8863
100	1.0133	373	7.356	8.600275
			Sum=	765.6559 kJ/kg

For the compressor

T (ºC)	P (bar)	T (K)	$\hat{S}_l$ (m^3/kg)	$[\hat{S}_i - \hat{S}_{i-1}]\left(\frac{T_i + T_{i-1}}{2}\right)$ T in K
100	1.0133	373	1.307	
101.85	1.0815	374.85	1.328	7.852425
106.85	1.2869	379.85	1.384	21.1316
111.85	1.5233	384.85	1.439	21.02925
116.85	1.794	389.85	1.494	21.30425
126.85	2.455	399.85	1.605	43.82835
136.85	3.302	409.85	1.708	41.69955
146.85	4.37	419.85	1.81	42.3147
156.85	5.699	429.85	1.911	42.90985
166.85	7.333	439.85	2.011	43.485
176.85	9.319	449.85	2.109	43.5953
186.85	11.71	459.85	2.205	43.6656
196.85	14.55	469.85	2.301	44.6256
206.85	17.9	479.85	2.395	44.6359
216.85	21.83	489.85	2.479	40.7274
226.85	26.4	499.85	2.581	50.4747
236.85	31.66	509.85	2.673	46.4462
246.85	37.7	519.85	2.765	47.3662
256.85	44.58	529.85	2.856	47.76135
266.85	52.38	539.85	2.948	49.2062
276.85	61.19	549.85	3.039	49.58135
286.85	71.08	559.85	3.132	51.60105
296.85	82.16	569.85	3.225	52.53105
300	86.05	573	3.255	17.14275
			Sum=	914.915625 kJ/kg

Therefore

$$\left|\Delta\hat{Q}_{32} + \Delta\widehat{W}_{21}^{\mathrm{fl}} + \Delta\hat{Q}_{43} + \Delta\hat{Q}_{21}\right| = \left|\Delta\widehat{W}_{43}^{\mathrm{fl}} + \Delta\hat{Q}_{14}\right|$$

$$\left|1405.57\frac{\mathrm{kJ}}{\mathrm{kg}} + 10.69\frac{\mathrm{kJ}}{\mathrm{kg}} + 765.66\frac{\mathrm{kJ}}{\mathrm{kg}} + 914.92\frac{\mathrm{kJ}}{\mathrm{kg}}\right| = \left|-847.72\frac{\mathrm{kJ}}{\mathrm{kg}} - 2256.28\frac{\mathrm{kJ}}{\mathrm{kg}}\right|$$

$$\left|3096.84\frac{\mathrm{kJ}}{\mathrm{kg}}\right| \approx \left|-3104\frac{\mathrm{kJ}}{\mathrm{kg}}\right|$$

On the other hand, note that the goodness of the numerical integrations can be checked with equation [1], since

$$\Delta\widehat{H}_{43} = \Delta\widehat{Q}_{43} + \Delta\widehat{W}_{43}^{\mathrm{fl}}$$

$$\Delta\widehat{H}_{21} = \Delta\widehat{Q}_{21} + \Delta\widehat{W}_{21}^{\mathrm{fl}}$$

$$\Delta\widehat{H}_{43} = 2676\frac{\mathrm{kJ}}{\mathrm{kg}} - 2750\frac{\mathrm{kJ}}{\mathrm{kg}} = -74\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta\widehat{Q}_{43} + \Delta\widehat{W}_{43}^{\mathrm{fl}} = 765.66\frac{\mathrm{kJ}}{\mathrm{kg}} - 847.72\frac{\mathrm{kJ}}{\mathrm{kg}} = -82.06\frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta\widehat{H}_{21} = 1346\frac{\mathrm{kJ}}{\mathrm{kg}} - 419.1\frac{\mathrm{kJ}}{\mathrm{kg}} = 926.9\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta\widehat{Q}_{21} + \Delta\widehat{W}_{21}^{\mathrm{fl}} = 914.92\frac{\mathrm{kJ}}{\mathrm{kg}} + 10.69\frac{\mathrm{kJ}}{\mathrm{kg}} = 925.61\frac{\mathrm{kJ}}{\mathrm{kg}}$$

from where it is concluded that the application of the trapezoidal rule to the turbine is not as good as to the compressor.

Question i. The same section d of reference problem 0.13 indicates that the cycle efficiency is

$$\text{Efficiency (\%)} = \frac{|\text{Work in the turbine}|}{\left|\begin{matrix}\text{Sum of heat and work}\\ \text{with positive sign}\end{matrix}\right|} \times 100 = \frac{|\text{Work in the turbine}|}{\left|\begin{matrix}\text{Sum of heat and work}\\ \text{with negative sign}\end{matrix}\right|} \times 100$$

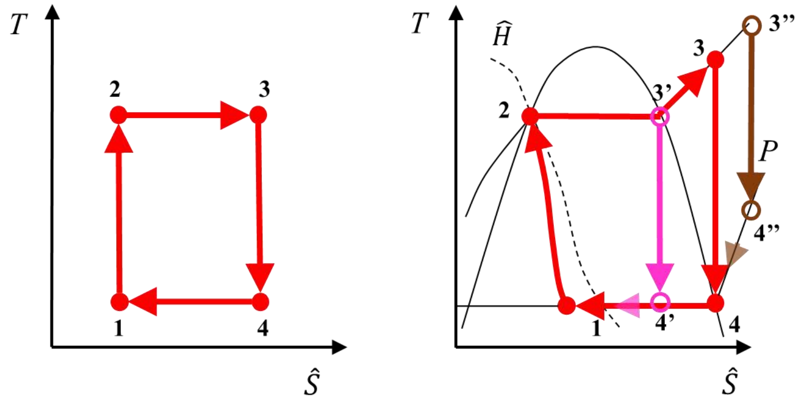
and by introducing the numerical values

$$\frac{\left|-847.72\frac{\mathrm{kJ}}{\mathrm{kg}}\right|}{\left|1405.57\frac{\mathrm{kJ}}{\mathrm{kg}} + 10.69\frac{\mathrm{kJ}}{\mathrm{kg}} + 765.66\frac{\mathrm{kJ}}{\mathrm{kg}} + 914.92\frac{\mathrm{kJ}}{\mathrm{kg}}\right|}\times 100 \approx \frac{\left|-847.72\frac{\mathrm{kJ}}{\mathrm{kg}}\right|}{\left|-847.72\frac{\mathrm{kJ}}{\mathrm{kg}} - 2256.28\frac{\mathrm{kJ}}{\mathrm{kg}}\right|}\times 100$$

$$27.37\% \approx 27.31\%$$

Question j. A theoretical cycle and an actual one are shown below. The theoretical cycle combines isothermal and isentropic transformations to obtain the maximum efficiency (i.e., maximun conversion of power into heat), but it would require a very difficult control to be experimentally feasible in the monophasic region.

For example, isothermal conditions are not natural or spontaneous, unlike isenthalpic (expansion of the system by flowing through a nozzle) and isochoric ones (confination of the system in a closed tank). However in the liquid-vapor coexistence zone, isothermality is achieved under isobaric conditions (which are also easily reachable).



THEORETICAL CYCLE ACTUAL CYCLE

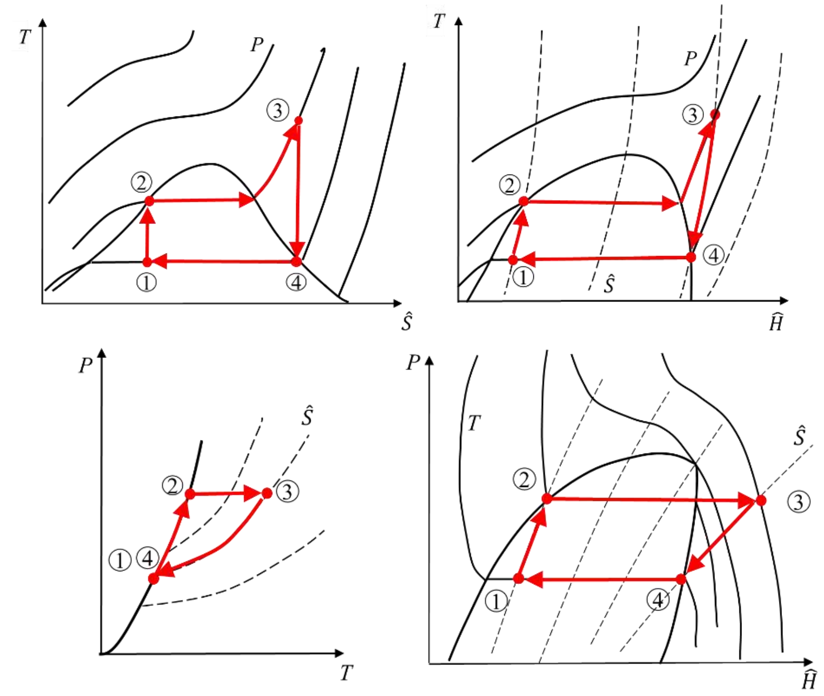
On the other hand, the presence of two phases generates some complications in turbines and compressors, so in these devices is convenient to leave the biphasic zone (4’), going to saturated vapor (4) or to superheated vapor (4”). The lack of adiabaticity and the inevitable friction will cause that lines 3’-4’, 3-4 and 3”-4” slant to the right.

The isentropic operation between 2 and 1 is also difficult to perform. Friction makes the expansion tend towards the isenthalpic line.

6.4. A design of a small thermal power station of 15 MW based on the Carnot cycle needs to be tested using water as thermal fluid. This fluid leaves an isentropic turbine as saturated vapor at 373 K and 0.1 MPa, being then partially condensed in an isobaric refrigeration system. After that, the liquid-vapor mixture is isentropically compressed to a pressure *P*, where only saturated liquid exists. Then, the liquid passes through an isobaric boiler and becomes superheated steam at 700 K, which enters the turbine.

- **a) Qualitatively represent the cycle in diagrams $TS(P)$, $TH(P,S)$, $PT(S)$ and $PH(T,S)$.**
- **b) Graphically evaluate the pressure *P*.**
- **c) Indicate the specific enthalpies and entropies at the different points of the cycle.**
- **d) Graphically calculate the work in the turbine (in kJ/kg).**
- **e) Calculate the water flow rate in the process.**
- **f) Graphically calculate the heat exchanged in the boiler (in kJ/kg), and its flow (in kW).**
- **g) Graphically calculate the heat removed in the condenser (in kJ/kg), and its flow (in kW).**
- **h) Graphically calculate the work in the compressor (in kJ/kg) and the power (in kW).**
- **i) Perform a total energy balance.**
- **j) Determine the efficiency of the process.**

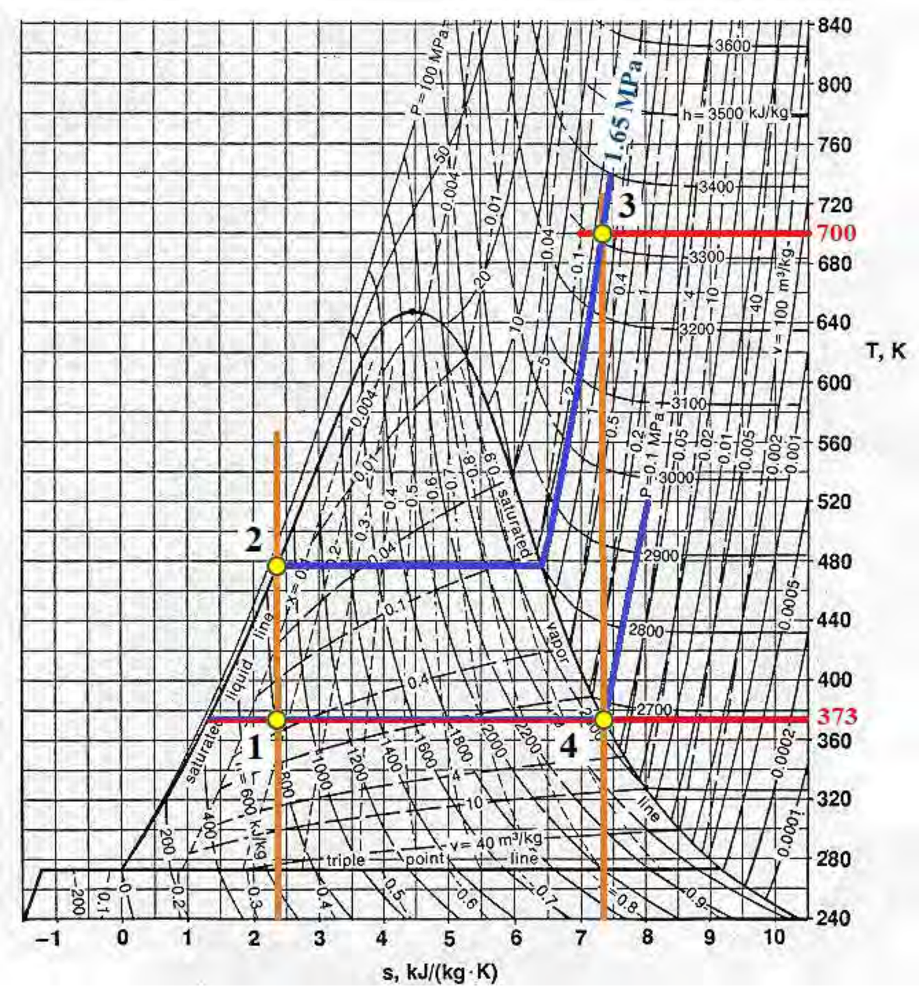
Question a. Let 1 be the stream that enters the compressor, 2 be the stream that enters the boiler, 3 be the fluid that enters the turbine and 4 be the water before condensation. The representation of the process (operation lines) in the four diagrams will be



The graphical calculations could be done with figures V.5 (*PH*), V.6 (Mollier) and V.7 (*TS*) of appendix V. However, the presence of saturated liquid rules out the use of V.6 because it does not cover this zone.

For the sake of clarity, questions **b – j** will be solved first with figure V.7 and second with V.5 (where isentropic lines are not represented within the biphasic zone and interpolation is required).

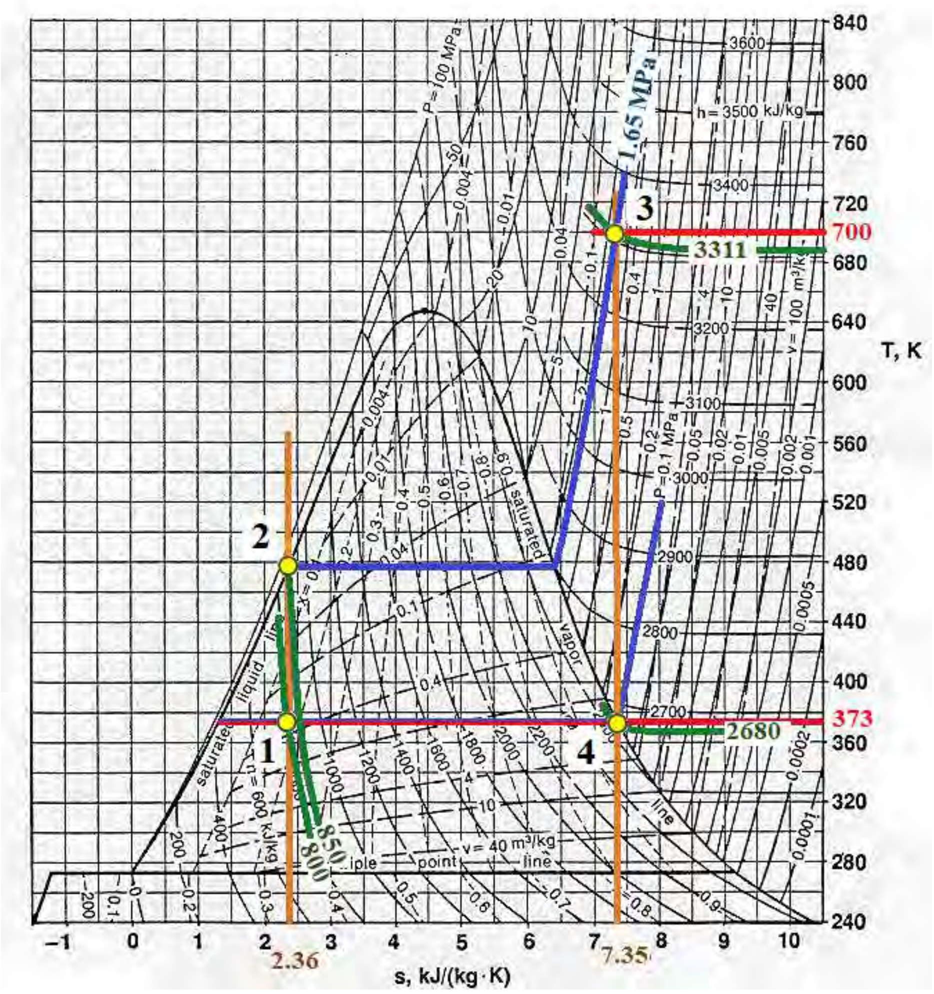
Question b. Points 3 and 4 are placed in figure V.7 by following the statement of the problem. Then, looking for the point where the 700 K isotherm intersects the isentropic that joins 3 and 4: the isobar that passes through this intersection will indicate the pressure P (1.65 MPa) and will allow the determination of points 1 and 2.



Question c. By reading the values of the specific entropies on the ordinate axis and interpolating the corresponding isenthalpic lines

$$\hat{S}_1 = \hat{S}_2 = 2.36\ \frac{\text{kJ}}{\text{kg·K}} \qquad ; \qquad \hat{S}_3 = \hat{S}_4 = 7.35\ \frac{\text{kJ}}{\text{kg·K}}$$

$$\hat{H}_1 = 800\ \frac{\text{kJ}}{\text{kg}} \quad ; \quad \hat{H}_2 = 850\ \frac{\text{kJ}}{\text{kg}} \quad ; \quad \hat{H}_3 = 3311\ \frac{\text{kJ}}{\text{kg}} \quad ; \quad \hat{H}_4 = 2680\ \frac{\text{kJ}}{\text{kg}}$$



Question d. The work on the turbine is the passage from point 3 to point 4, and will be given by

$$\mathrm{d}\hat{W}^{\text{fl}} = \hat{V}\mathrm{d}P \quad \rightarrow \Delta\hat{W}^{\text{fl}}_{43} = \int_3^4 \hat{V}\mathrm{d}P$$

However, the fundamental thermodynamic relations state that

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\text{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \qquad [1]$$

and if the entropy remains unchanged ($\mathrm{d}\hat{S} = 0$; $\mathrm{d}\hat{Q} = 0$), the flow work can be determined by the enthalpy difference between the final and initial states, avoiding the numerical integration.

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{W}^{\text{fl}} \quad \rightarrow \quad \Delta\hat{W}^{\text{fl}}_{43} = \Delta\hat{H}_{43} = \hat{H}_4 - \hat{H}_3$$

$$\Delta\hat{W}^{\text{fl}}_{43} = 2680\ \frac{\text{kJ}}{\text{kg}} - 3311\frac{\text{kJ}}{\text{kg}} = -631\frac{\text{kJ}}{\text{kg}}$$

Question e. The flow rate is the quotient between the station power (15 MW= $15{\cdot}10^3$ kW) and the absolute value of the work in the turbine

$$\text{Flow rate}=\widehat{\mathcal{W}}=\frac{\text{Power in the station}}{|\text{Work in the turbine}|}=\frac{15\cdot 10^3\ \text{kW}}{\left|-631\ \frac{\text{kJ}}{\text{kg}}\right|}=23.77\ \frac{\text{kg}}{\text{s}}$$

Question f. The heat exchanged in the boiler (from 2 to 3) will be

$$\mathrm{d}\hat{Q}=T\mathrm{d}\hat{S}\quad\rightarrow\ \Delta\hat{Q}_{32}=\int_2^3 T\mathrm{d}\hat{S}$$

but since the process takes place through an isobar, dP=0 in equation [1] and there will be no flow work. No numerical integration is required, because

$$\mathrm{d}\hat{H}=\mathrm{d}\hat{Q}\quad\rightarrow\ \Delta\hat{Q}_{32}=\Delta\hat{H}_{32}=\hat{H}_3-\hat{H}_2=3311\ \frac{\text{kJ}}{\text{kg}}-850\frac{\text{kJ}}{\text{kg}}=2461\frac{\text{kJ}}{\text{kg}}$$

and the extensión of this heat change to the full water stream will give the heat flow

$$q_{32}=\widehat{\mathcal{W}}\Delta\hat{Q}_{32}=\left(23.77\ \frac{\text{kg}}{\text{s}}\right)\left(2461\frac{\text{kJ}}{\text{kg}}\right)=58498\ \text{kW}$$

Question g. As in question **f**, the condenser (passage from 4 to 1) operates isobarically; thus

$$\Delta\hat{Q}_{14}=\Delta\hat{H}_{14}=\hat{H}_1-\hat{H}_4=800\ \frac{\text{kJ}}{\text{kg}}-2680\frac{\text{kJ}}{\text{kg}}=-1880\frac{\text{kJ}}{\text{kg}}$$

$$q_{14}=\widehat{\mathcal{W}}\Delta\hat{Q}_{14}=\left(23.77\ \frac{\text{kg}}{\text{s}}\right)\left(-1880\frac{\text{kJ}}{\text{kg}}\right)=-44687.6\ \text{kW}$$

but the process is also isothermal (T_1=T_4), so

$$\Delta\hat{Q}_{14}=\int_4^1 T\mathrm{d}\hat{S}=T_4\int_4^1\mathrm{d}\hat{S}=T_4\left(\hat{S}_1-\hat{S}_4\right)$$

$$\Delta\hat{Q}_{14}=(373\ \text{K})\left(2.36\ \frac{\text{kJ}}{\text{kg}\cdot\text{K}}-7.35\ \frac{\text{kJ}}{\text{kg}\cdot\text{K}}\right)=-1861.3\ \frac{\text{kJ}}{\text{kg}}$$

$$q_{14}=\widehat{\mathcal{W}}\Delta\hat{Q}_{14}=\left(23.77\ \frac{\text{kg}}{\text{s}}\right)\left(-1861.3\frac{\text{kJ}}{\text{kg}}\right)=-44243.1\ \text{kW}$$

Numerical results that are slightly lower than the preceding ones because the inevitable errors associated with graphical reading and interpolation.

Question h. As in question **d**, the compressor works isentropically (from 1 to 2), so

$$\Delta\widehat{W}_{21}^{\mathrm{fl}}=\Delta\widehat{H}_{21}=\widehat{H}_2-\widehat{H}_1=850\ \frac{\mathrm{kJ}}{\mathrm{kg}}-800\frac{\mathrm{kJ}}{\mathrm{kg}}=50\frac{\mathrm{kJ}}{\mathrm{kg}}$$

and the power

$$\wp_{21}=\widehat{\mathcal{W}}\Delta\widehat{W}_{21}^{\mathrm{fl}}=\left(23.77\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(50\frac{\mathrm{kJ}}{\mathrm{kg}}\right)=1188.5\ \mathrm{kW}$$

Question i. According to reference problem 0.13, the energy balance is

$$\left|\begin{matrix}\text{Sum of heat and work}\\ \text{with positive sign}\end{matrix}\right|=\left|\begin{matrix}\text{Sum of heat and work}\\ \text{with negative sign}\end{matrix}\right|$$

and all the involved terms have been evaluated in the previous questions

$$\left|\Delta\hat{Q}_{32}+\Delta\widehat{W}_{21}^{\mathrm{fl}}\right|=\left|\Delta\widehat{W}_{43}^{\mathrm{fl}}+\Delta\hat{Q}_{14}\right|$$

$$\left|2461\frac{\mathrm{kJ}}{\mathrm{kg}}+50\frac{\mathrm{kJ}}{\mathrm{kg}}\right|=\left|-631\frac{\mathrm{kJ}}{\mathrm{kg}}-1880\frac{\mathrm{kJ}}{\mathrm{kg}}\right|$$

$$\left|2511\frac{\mathrm{kJ}}{\mathrm{kg}}\right|=\left|-2511\frac{\mathrm{kJ}}{\mathrm{kg}}\right|$$

Question j. Reference problem 0.13 also says that

$$\text{Efficiency (\%)}=\frac{|\text{Work in the turbine}|}{\left|\begin{matrix}\text{Sum of heat and work}\\ \text{with positive sign}\end{matrix}\right|}\times 100=\frac{|\text{Work in the turbine}|}{\left|\begin{matrix}\text{Sum of heat and work}\\ \text{with negative sign}\end{matrix}\right|}\times 100$$

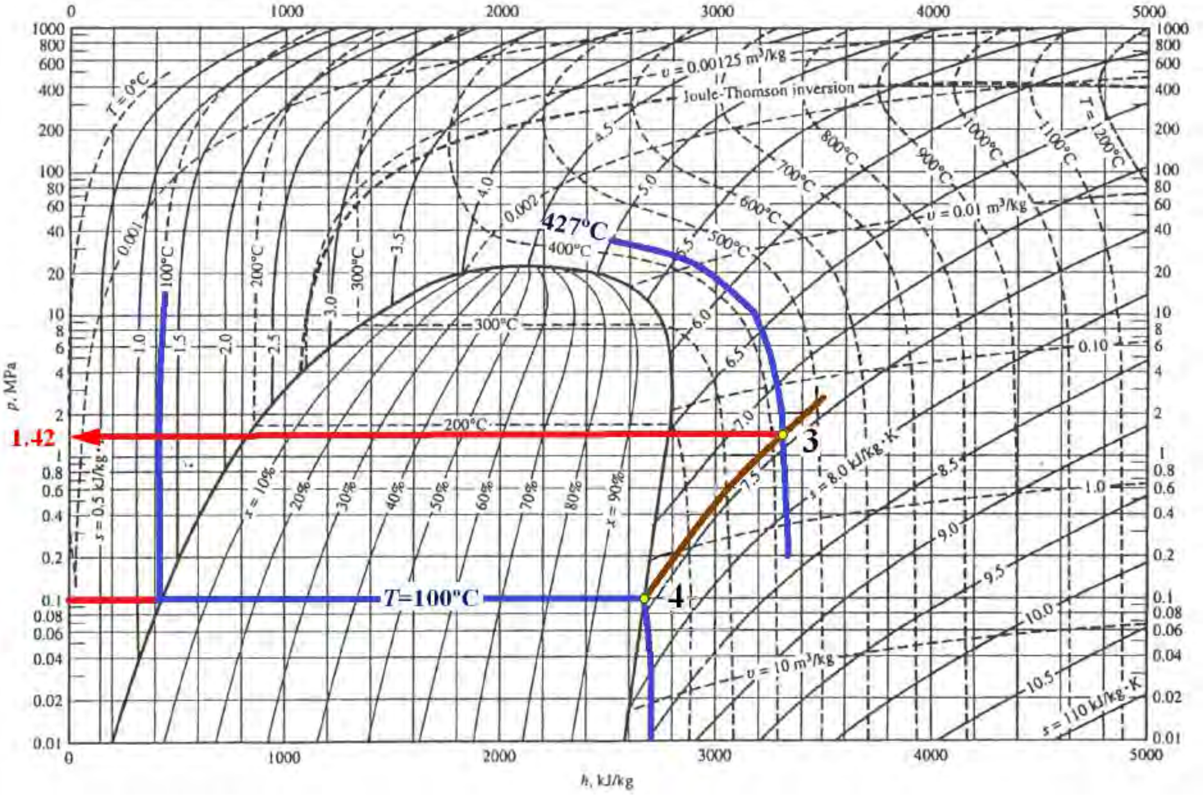
$$\frac{\left|\Delta\widehat{W}_{43}^{\mathrm{fl}}\right|}{\left|\Delta\hat{Q}_{32}+\Delta\widehat{W}_{21}^{\mathrm{fl}}\right|}\times 100=\frac{\left|\Delta\widehat{W}_{43}^{\mathrm{fl}}\right|}{\left|\Delta\widehat{W}_{43}^{\mathrm{fl}}+\Delta\hat{Q}_{14}\right|}\times 100=\frac{\left|-631\frac{\mathrm{kJ}}{\mathrm{kg}}\right|}{\left|2511\frac{\mathrm{kJ}}{\mathrm{kg}}\right|}\times 100=25.13\%$$

To **redo questions b – j of the problem with figure V.5**, the temperature units have to be changed first through the conversion factors of appendix I.

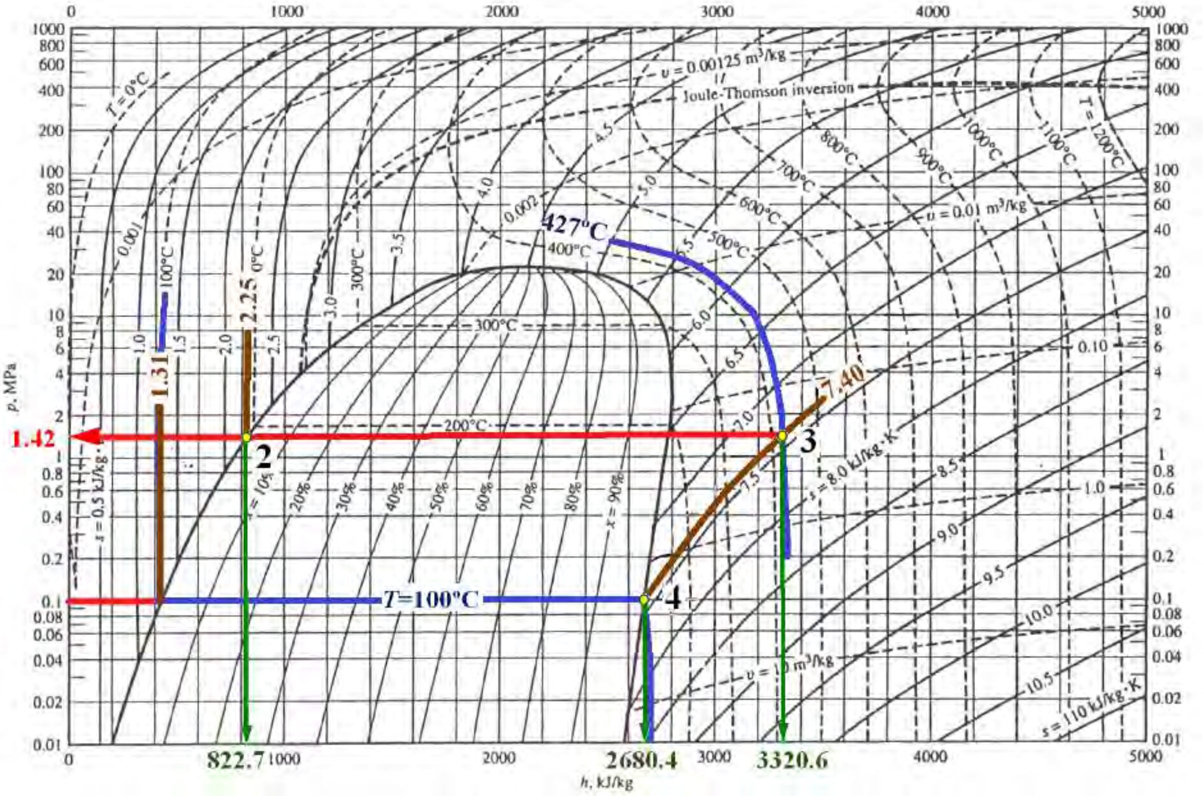
$$T_3(^\circ\mathrm{C})=373\ \mathrm{K}-273=100^\circ\mathrm{C}$$

$$T_4(^\circ\mathrm{C})=700\ \mathrm{K}-273=427^\circ\mathrm{C}$$

b'. With these temperatures and by knowing that point 3 is saturated vapor, and that the isentropic line that passes through it also passes through 4, a pressure of P=1.42 MPa (slightly lower than that found with figure V.7) is determined.



c'. From figure V.5



enthalpies and entropies are

$$\hat{S}_2 = 2.25\ \frac{\text{kJ}}{\text{kg}\cdot\text{K}} \quad ; \quad \hat{S}_3 = \hat{S}_4 = 7.40\ \frac{\text{kJ}}{\text{kg}\cdot\text{K}}$$

$$\hat{H}_2 = 822.7\ \frac{\text{kJ}}{\text{kg}} \quad ; \quad \hat{H}_3 = 3320.6\ \frac{\text{kJ}}{\text{kg}} \quad ; \quad \hat{H}_4 = 2680.4\ \frac{\text{kJ}}{\text{kg}}$$

In order to determine the enthalpy at 1 it is necessary to locate this point in the figure. Having in mind that it is a mixture of liquid and vapor, the combination of the mass balance

$$M_{tot} = M_{l_1} + M_{v_1}$$

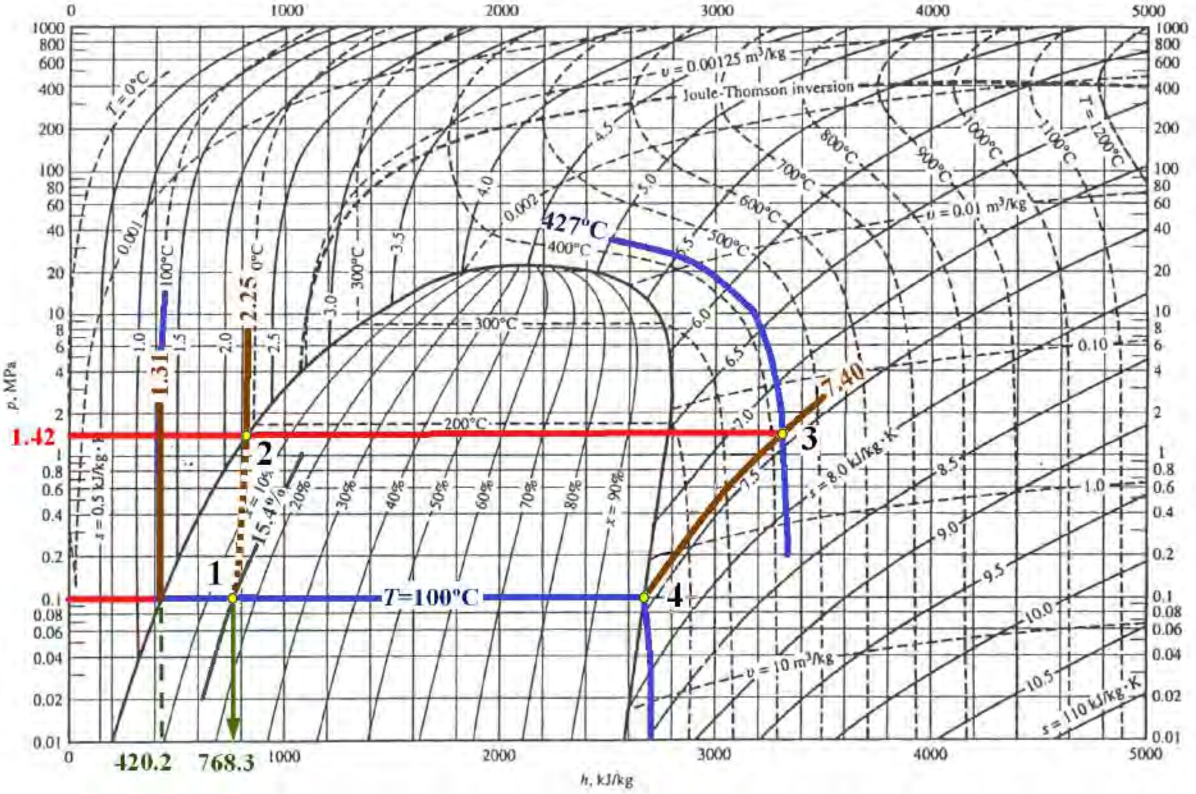
with the entropy one

$$M_{tot}\hat{S}_1 = M_{l_1}\hat{S}_{l_1}^{sat} + M_{v_1}\hat{S}_{v_1}^{sat}$$

allows the calculation of the mass vapor fraction in it when the specific entropy of the saturated liquid at 100ºC is interpolated ($\hat{S}_{l_1}^{sat}$=1.31 kJ/kg·K), since $\hat{S}_1 = \hat{S}_2$ and $\hat{S}_{v_1}^{sat} = \hat{S}_{v_4}^{sat} = \hat{S}_4$

$$\frac{M_{v_1}}{M_{tot}} = \frac{\left(\hat{S}_1 - \hat{S}_{l_1}^{sat}\right)}{\left(\hat{S}_{v_1}^{sat} - \hat{S}_{l_1}^{sat}\right)} = \frac{(2.25 - 1.31)}{(7.40 - 1.31)} = 0.154$$

And by graphically finding the intersection between the 15.4% title line with the 100ºC isotherm, it is found that $\hat{H}_1$ =768.3 kJ/kg.



Finally, it has to be pointed out that this enthalpy can be calculated from the combination of the mass and enthalpy balances at saturation at 100ºC as well

$$M_{tot}\widehat{H}_1 = M_l\widehat{H}_l^{sat} + M_{v_1}\widehat{H}_{v_1}^{sat} \quad \rightarrow \quad \widehat{H}_1 = \left(1 - \frac{M_{v_1}}{M_{tot}}\right)\widehat{H}_l^{sat} + \frac{M_{v_1}}{M_{tot}}\widehat{H}_{v_1}^{sat}$$

$$\widehat{H}_1 = (1 - 0.154)\left(420.2\ \frac{\text{kJ}}{\text{kg}}\right) + 0.154\left(2680.4\ \frac{\text{kJ}}{\text{kg}}\right) = 768.27\ \frac{\text{kJ}}{\text{kg}}$$

d’. With data from the preceding question, the work from 3 to 4 is

$$\Delta\widehat{W}_{43}^{\text{fl}} = 2680.4\ \frac{\text{kJ}}{\text{kg}} - 3320.6\frac{\text{kJ}}{\text{kg}} = -640.2\frac{\text{kJ}}{\text{kg}}$$

e’. The flow rate of water

$$\widehat{\mathcal{W}} = \frac{\text{Power in the station}}{|\text{Work in the turbine}|} = \frac{15 \cdot 10^3\ \text{kW}}{\left|-640.2\ \frac{\text{kJ}}{\text{kg}}\right|} = 23.43\ \frac{\text{kg}}{\text{s}}$$

f ’. The heat in the boiler

$$\Delta\widehat{Q}_{32} = \Delta\widehat{H}_{32} = \widehat{H}_3 - \widehat{H}_2 = 3320.6\ \frac{\text{kJ}}{\text{kg}} - 822.7\frac{\text{kJ}}{\text{kg}} = 2497.9\frac{\text{kJ}}{\text{kg}}$$

$$q_{32} = \widehat{\mathcal{W}}\Delta\widehat{Q}_{32} = \left(23.43\ \frac{\text{kg}}{\text{s}}\right)\left(2497.9\frac{\text{kJ}}{\text{kg}}\right) = 58525.8\ \text{kW}$$

g’. The heat in the condenser

$$\Delta\widehat{Q}_{14} = \Delta\widehat{H}_{14} = \widehat{H}_1 - \widehat{H}_4 = 768.3\ \frac{\text{kJ}}{\text{kg}} - 2680.4\frac{\text{kJ}}{\text{kg}} = -1912.1\frac{\text{kJ}}{\text{kg}}$$

$$q_{14} = \widehat{\mathcal{W}}\Delta\widehat{Q}_{14} = \left(23.43\ \frac{\text{kg}}{\text{s}}\right)\left(-1912.1\frac{\text{kJ}}{\text{kg}}\right) = -44800.5\ \text{kW}$$

h’. The work and power in the compressor

$$\Delta\widehat{W}_{21}^{\text{fl}} = \Delta\widehat{H}_{21} = \widehat{H}_2 - \widehat{H}_1 = 822.7\ \frac{\text{kJ}}{\text{kg}} - 768.3\frac{\text{kJ}}{\text{kg}} = 54.9\frac{\text{kJ}}{\text{kg}}$$

$$\wp_{21} = \widehat{\mathcal{W}}\Delta\widehat{W}_{21}^{\text{fl}} = \left(23.43\ \frac{\text{kg}}{\text{s}}\right)\left(54.9\frac{\text{kJ}}{\text{kg}}\right) = 1274.6\ \text{kW}$$

i’. The energy balance

$$\left|\Delta\hat{Q}_{32}+\Delta\widehat{W}_{21}^{\mathrm{fl}}\right|=\left|\Delta\widehat{W}_{43}^{\mathrm{fl}}+\Delta\hat{Q}_{14}\right|$$

$$\left|2497\,\frac{\mathrm{kJ}}{\mathrm{kg}}+54.9\,\frac{\mathrm{kJ}}{\mathrm{kg}}\right|=\left|-640.2\,\frac{\mathrm{kJ}}{\mathrm{kg}}-1912.1\,\frac{\mathrm{kJ}}{\mathrm{kg}}\right|$$

$$\left|2551.9\,\frac{\mathrm{kJ}}{\mathrm{kg}}\right|\approx\left|-2552.1\,\frac{\mathrm{kJ}}{\mathrm{kg}}\right|$$

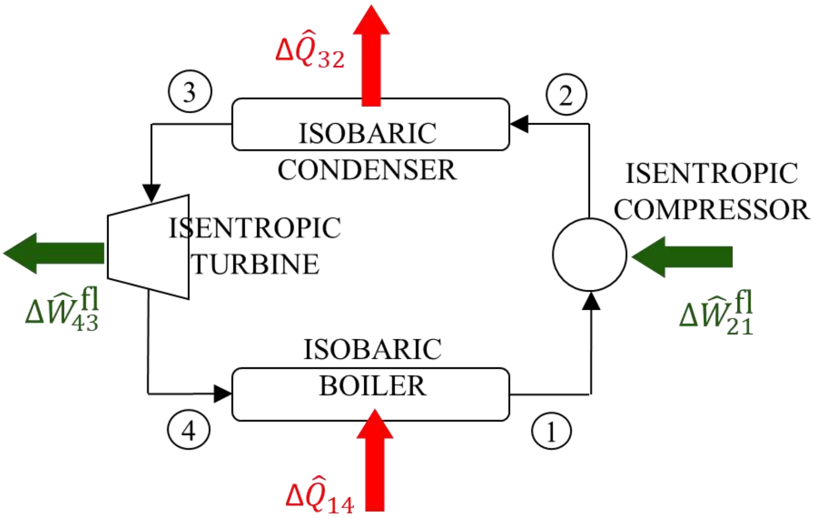
j’. The efficiency of the cycle

$$\frac{\left|\Delta\widehat{W}_{43}\right|}{\left|\Delta\hat{Q}_{32}+\Delta\widehat{W}_{21}^{\mathrm{fl}}\right|}\times 100=\frac{\left|-640.2\,\frac{\mathrm{kJ}}{\mathrm{kg}}\right|}{\left|2552\,\frac{\mathrm{kJ}}{\mathrm{kg}}\right|}\times 100=25.09\%$$

6.5. A biphasic mixture of liquid and vapor water at 380 K (1) is isentropically compressed until obtaining only saturated steam at 500 K (2). This steam passes through an isobaric condenser, where it is completely converted into a saturated liquid (3), and expands in an isentropic turbine, after which a biphasic water mixture is obtained (4) that finally passes through an isobaric boiler to return to the initial point. If the power consumed in the compressor is of 100 MW:

- **a) Draw a flowchart, indicating how to calculate the heats and/or works involved in each stage.**
- **b) Evaluate the specific enthalpies and entropies of the thermal fluid at the key points of the cycle.**
- **c) Estimate the heats and/or works mentioned in question a (in kJ/kg).**
- **d) Calculate the required water flow rate.**
- **e) Carry out a total energy balance.**
- **f) Determine the efficiency of the process.**

Question a. The flowchart will be



Heat exchange and work flow can happen in any stage. They are defined by the general expressions

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \quad \Delta\hat{Q} = \int T\mathrm{d}\hat{S}$$

$$\mathrm{d}\hat{W}^{\text{fl}} = \hat{V}\mathrm{d}P \quad \rightarrow \Delta\hat{W}^{\text{fl}} = \int \hat{V}\mathrm{d}P$$

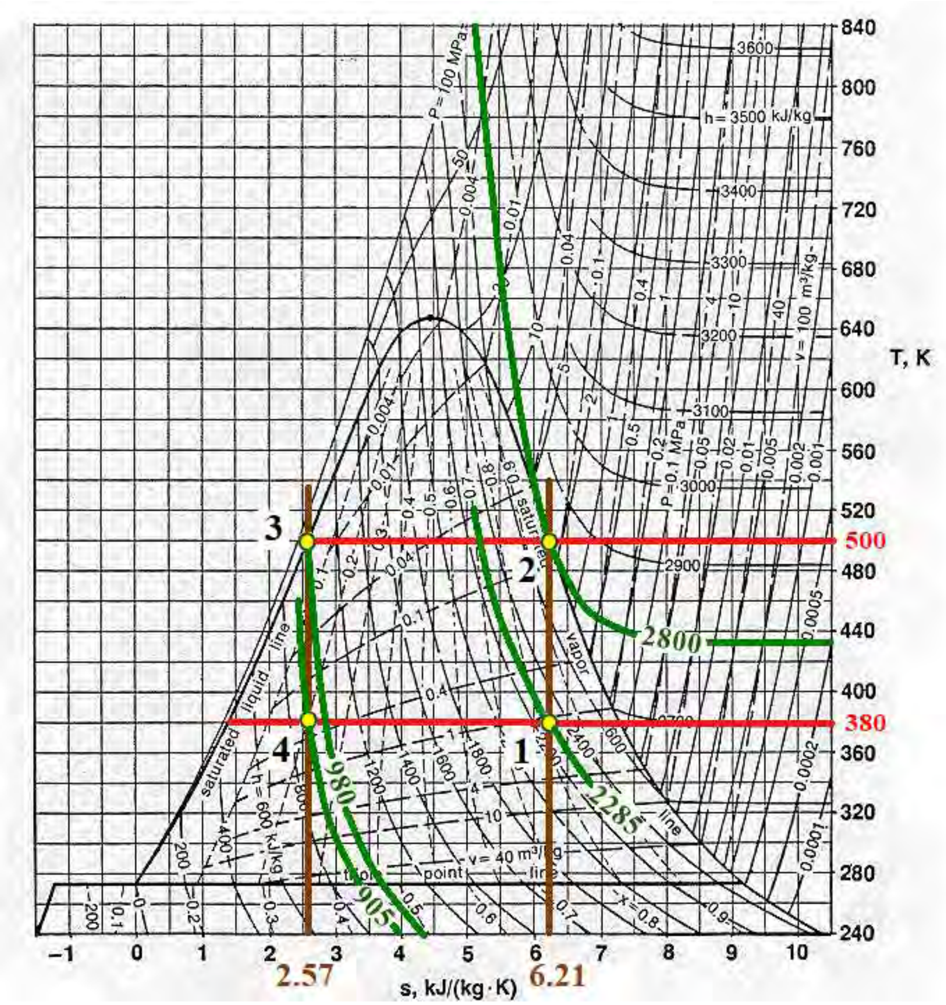
However, in the condenser and in the boiler there will only be heat transfer because they are isobaric (dP=0) and therefore d$\hat{W}^{\text{fl}}$=0; and in the compressor and in the turbine there will only be flow work because they are isentropic (d$\hat{S}$=0), so d$\hat{Q}$=0. By taking into account the equations of reference problem 0.3

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\text{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \quad \begin{cases} \mathrm{d}\hat{H} = \mathrm{d}\hat{Q} \quad \rightarrow \Delta\hat{Q} = \Delta\hat{H} \quad \text{if } \mathrm{d}\hat{W}^{\text{fl}} = 0 \\ \mathrm{d}\hat{H} = \mathrm{d}\hat{W}^{\text{fl}} \quad \rightarrow \Delta\hat{W}^{\text{fl}} = \Delta\hat{H} \quad \text{if } \mathrm{d}\hat{Q} = 0 \end{cases}$$

which avoid the numerical integration.

Figures V.5 (*PH*), V.6 (Mollier) and V.7 (*TS*) of appendix V and table VI.1 (saturated water properties) of appendix VI could be used for graphical calculations. However, working with saturated liquid rules out the use of V.6, because it does not cover this zone.

Question b. The *TS* diagram allows the direct drawing of the process described by the statement of the problem. Then, the entropies of the characteristic points can be directly read on the abscissa axis ($\hat{S}_1 = \hat{S}_2$ =6.21 kJ/kg·K; $\hat{S}_3 = \hat{S}_4$ =2.57 kJ/kg·K), but the corresponding enthalpies have to be interpolated ($\widehat{H}_1$ =2285 kJ/kg; $\widehat{H}_2$ =2800 kJ/kg; $\widehat{H}_3$ =980 kJ/kg; $\widehat{H}_4$ =905 kJ/kg).



On the contrary, the *PH* diagram does not allow the direct representation of the cycle, because the isentropic lines are not plotted in the biphasic zone. Therefore, two interpolation stages have to be performed: when the isotherms

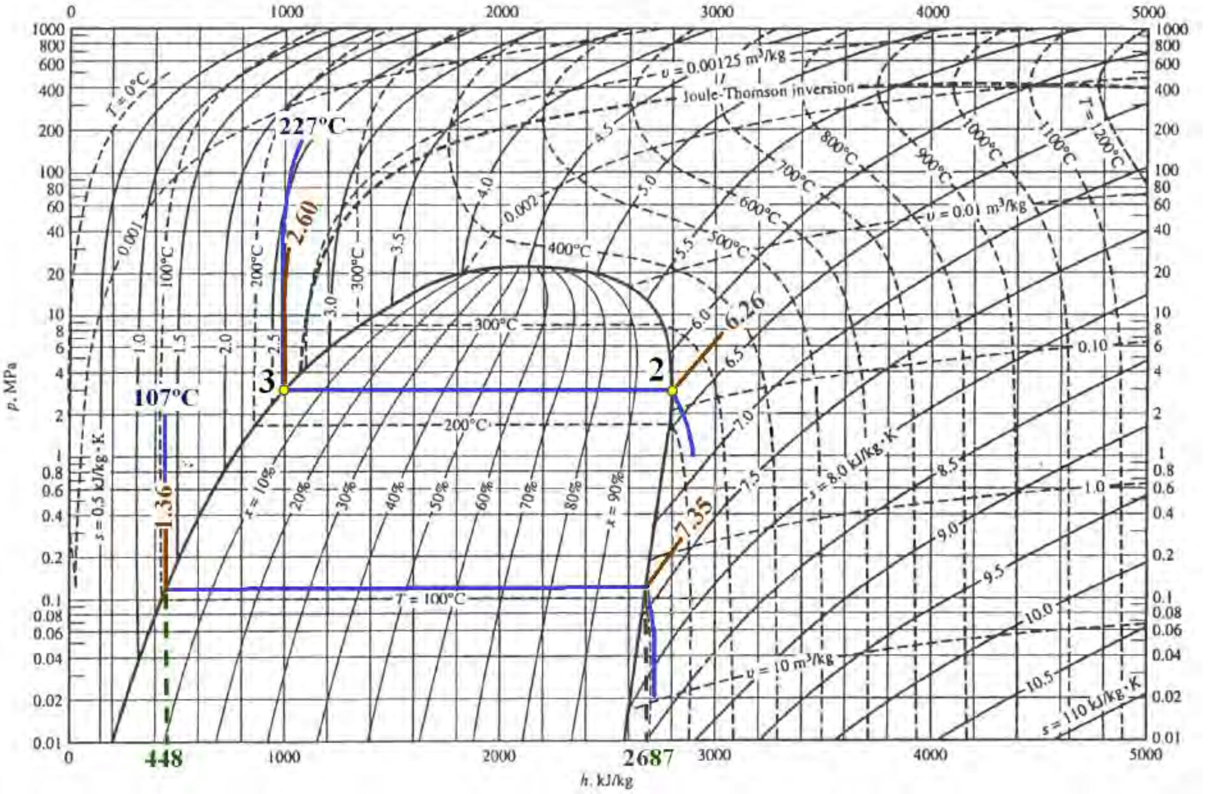
$$T_2(°\mathrm{C}) = T_3(°\mathrm{C}) = 500\ \mathrm{K} - 273 = 227°\mathrm{C}$$

$$T_1(°\mathrm{C}) = T_4(°\mathrm{C}) = 380\ \mathrm{K} - 273 = 107°\mathrm{C}$$

are drawn, and points 2 and 3 have been found, their corresponding entropies ($\hat{S}_2$ =6.26 kJ/kg·K and $\hat{S}_3$ =2.60 kJ/kg·K) are obtained. By knowing that $\hat{S}_1 = \hat{S}_2$ and $\hat{S}_3 = \hat{S}_4$, that points 1 and 4 are mixtures of saturated liquid and vapor at 107ºC, and by interpolating the entropies of these saturated phases ($\hat{S}_{v_1}^{sat} = \hat{S}_{v_4}^{sat} =$ 7.35 kJ/kg·K; $\hat{S}_{l_1}^{sat} = \hat{S}_{l_4}^{sat}$ =1.36 kJ/kg·K), the mass vapor fractions in 1 and 4 can be evaluated through combination of the mass and entropy balances

$$\frac{M_{v_1}}{M_{tot}} = \frac{\left(\hat{S}_1 - \hat{S}_{l_1}^{sat}\right)}{\left(\hat{S}_{v_1}^{sat} - \hat{S}_{l_1}^{sat}\right)} = \frac{(6.26 - 1.36)}{(7.35 - 1.36)} = 0.818$$

$$\frac{M_{v_4}}{M_{tot}} = \frac{\left(\hat{S}_4 - \hat{S}_{l_4}^{sat}\right)}{\left(\hat{S}_{v_4}^{sat} - \hat{S}_{l_4}^{sat}\right)} = \frac{(2.60 - 1.36)}{(7.35 - 1.36)} = 0.207$$

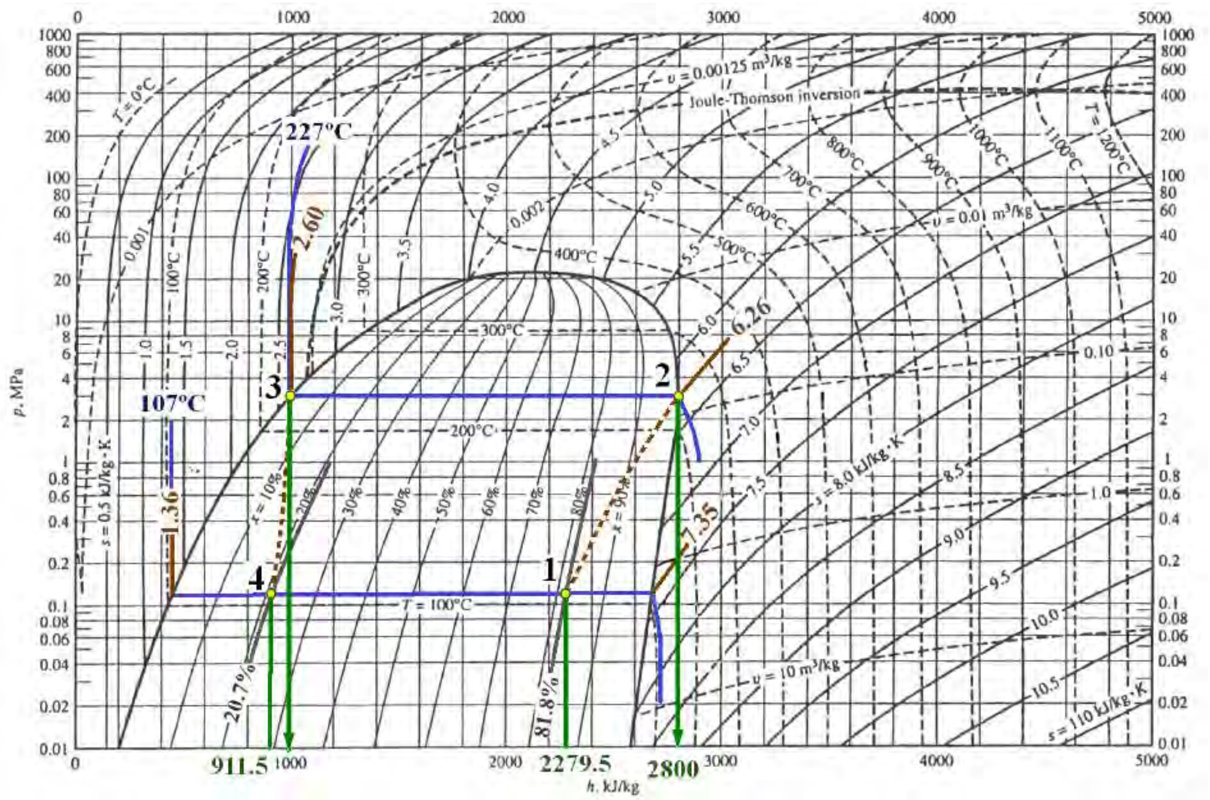


Enthalpies in 1 and 4 can be determined through two methods: graphically by the intersection of the 81.8% and 20.7% title lines with the 107ºC isotherm, or by the combination of the mass and enthalpy balances in the form

$$\widehat{H}_1 = \frac{M_{v_1}}{M_{tot}}\widehat{H}_{v_1}^{sat} + \frac{M_{l_1}}{M_{tot}}\widehat{H}_{l_1}^{sat} = 0.818\left(2687\ \frac{\text{kJ}}{\text{kg}}\right)+(1-0.818)\left(448\ \frac{\text{kJ}}{\text{kg}}\right)=2279.5\ \frac{\text{kJ}}{\text{kg}}$$

$$\widehat{H}_4 = \frac{M_{v_4}}{M_{tot}}\widehat{H}_{v_4}^{sat} + \frac{M_{l_4}}{M_{tot}}\widehat{H}_{l_4}^{sat} = 0.207\left(2687\ \frac{\text{kJ}}{\text{kg}}\right)+(1-0.207)\left(448\ \frac{\text{kJ}}{\text{kg}}\right)=911.5\ \frac{\text{kJ}}{\text{kg}}$$

The estimation of the other two enthalpies required to solve the problem may be read on the abscissa axis and are $\widehat{H}_2$ =2800 kJ/kg and $\widehat{H}_3$ =1000 kJ/kg.



Finally, the obtention of data from table VI.1 is similar to that carried out in the *PH* diagram:

- Entropies and enthalpies of the saturated phases at 227ºC are determined by interpolation ($\hat{S}_2 = \hat{S}_{v_2}^{sat}$=6.23 kJ/kg·K; $\hat{S}_3 = \hat{S}_{l_3}^{sat}$=2.59 kJ/kg·K; $\widehat{H}_2 = \widehat{H}_{v_2}^{sat}$=2801 kJ/kg; $\widehat{H}_3 = \widehat{H}_{l_3}^{sat}$=976 kJ/kg).

- Entropies of the saturated phases at 107ºC are determined by interpolation ($\hat{S}_{l_1}^{sat}$=$\hat{S}_{l_4}^{sat}$=1.39 kJ/kg·K and $\hat{S}_{v_1}^{sat}$ = $\hat{S}_{v_4}^{sat}$ = 7.27 kJ/kg·K).

- Having in mind that $\hat{S}_1 = \hat{S}_2$ and $\hat{S}_3 = \hat{S}_4$ and that points 1 and 4 are mixtures of saturated liquid and vapor at 107ºC, the mass and entropy balances are combined to obtain the vapor mass fraction in those points.

$$\frac{M_{v_1}}{M_{tot}} = \frac{\left(\hat{S}_1 - \hat{S}_{l_1}^{sat}\right)}{\left(\hat{S}_{v_1}^{sat} - \hat{S}_{l_1}^{sat}\right)} = \frac{(6.23 - 1.39)}{(7.27 - 1.39)} = 0.8231$$

$$\frac{M_{v_4}}{M_{tot}} = \frac{\left(\hat{S}_4 - \hat{S}_{l_4}^{sat}\right)}{\left(\hat{S}_{v_4}^{sat} - \hat{S}_{l_4}^{sat}\right)} = \frac{(2.59 - 1.39)}{(7.27 - 1.39)} = 0.2041$$

- Enthalpies of saturated phases at 107ºC are read ($\hat{H}_{l_1}^{sat}$=$\hat{H}_{l_4}^{sat}$=449 kJ/kg; $\hat{H}_{v_1}^{sat}$ = $\hat{H}_{v_4}^{sat}$ =2688 kJ/kg) and the combination of the mass and enthalpy balances with the vapor mass fractions allows the estimation of $\hat{H}_1$ and $\hat{H}_4$

$$\hat{H}_1 = 0.8231\left(2688\ \frac{\text{kJ}}{\text{kg}}\right)+(1-0.8231)\left(449\ \frac{\text{kJ}}{\text{kg}}\right)=2291.92\ \frac{\text{kJ}}{\text{kg}}$$

$$\hat{H}_4 = 0.2041\left(2688\ \frac{\text{kJ}}{\text{kg}}\right)+(1-0.2041)\left(449\ \frac{\text{kJ}}{\text{kg}}\right)=905.98\ \frac{\text{kJ}}{\text{kg}}$$

To avoid being repetitive, the calculations in the following sections will only be made with these last data.

Question c. The work in the compressor (transit from 1 to 2)

$$\Delta\hat{W}_{21}=\Delta\hat{H}_{21} = \hat{H}_2 - \hat{H}_1 = 2801\ \frac{\text{kJ}}{\text{kg}} - 2291.92\frac{\text{kJ}}{\text{kg}} = 509.08\frac{\text{kJ}}{\text{kg}}$$

The heat in the condenser (transit from 2 to 3)

$$\Delta\hat{Q}_{32}=\Delta\hat{H}_{32} = \hat{H}_3 - \hat{H}_2 = 976\ \frac{\text{kJ}}{\text{kg}} - 2801\frac{\text{kJ}}{\text{kg}} = -1825\ \frac{\text{kJ}}{\text{kg}}$$

The work in the turbine (transit from 3 to 4)

$$\Delta\hat{W}_{43}=\Delta\hat{H}_{43} = \hat{H}_4 - \hat{H}_3 = 905.98\ \frac{\text{kJ}}{\text{kg}} - 976\frac{\text{kJ}}{\text{kg}} = -70.02\frac{\text{kJ}}{\text{kg}}$$

The heat in the boiler (transit from 4 to 1)

$$\Delta\hat{Q}_{14}=\Delta\hat{H}_{14} = \hat{H}_1 - \hat{H}_4 = 2291.92\ \frac{\text{kJ}}{\text{kg}} - 905.98\ \frac{\text{kJ}}{\text{kg}} = 1385.94\ \frac{\text{kJ}}{\text{kg}}$$

As a curiosity, notice that the condenser and the boiler are also isothermal, so the integrals of question **a** can be simplified to

$$\Delta\hat{Q}_{32} = \int_2^3 T\mathrm{d}\hat{S} = T_2(\hat{S}_3 - \hat{S}_2) = (500\ \text{K})\left(2.59\ \frac{\text{kJ}}{\text{kg·K}} - 6.23\ \frac{\text{kJ}}{\text{kg·K}}\right) = -1820\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\hat{Q}_{14} = \int_4^1 T\mathrm{d}\hat{S} = T_4(\hat{S}_1 - \hat{S}_4) = (380\ \text{K})\left(6.23\ \frac{\text{kJ}}{\text{kg·K}} - 2.59\ \frac{\text{kJ}}{\text{kg·K}}\right) = 1383.2\ \frac{\text{kJ}}{\text{kg}}$$

values that are very close but not equal to those calculated using the enthalpy difference, because the small errors of interpolating data in the table.

Question d. The water flow rate can be determined in the compressor, since its power and its specific flow work are known

$$\hat{\mathcal{W}} = \frac{\text{Power in the compressor}}{|\text{wok in the compressor}|} = \frac{100 \cdot 10^3 \text{ kW}}{\left|509.08 \ \frac{\text{kJ}}{\text{kg}}\right|} = 196.43 \ \frac{\text{kg}}{\text{s}}$$

Question e. According to reference problem 0.13

$$\left|\begin{matrix}\text{Sum of heat and work} \\ \text{contributions with positive sign}\end{matrix}\right| = \left|\begin{matrix}\text{Sum of heat and work} \\ \text{contributions with negative sign}\end{matrix}\right|$$

and therefore

$$\left|\Delta\widehat{W}_{21} + \Delta\hat{Q}_{14}\right| = \left|\Delta\widehat{W}_{43} + \Delta\hat{Q}_{32}\right|$$

$$\left|509.08\frac{\text{kJ}}{\text{kg}} + 1385.94\frac{\text{kJ}}{\text{kg}}\right| = \left|-70.02\frac{\text{kJ}}{\text{kg}} - 1825\frac{\text{kJ}}{\text{kg}}\right|$$

$$\left|1895.02\frac{\text{kJ}}{\text{kg}}\right| = \left|-1895.02\frac{\text{kJ}}{\text{kg}}\right|$$

Question f. With regards to the efficiency, it may be defined as

$$\text{Efficiency (\%)} = \frac{|\text{Work in the turbine}|}{\left|\begin{matrix}\text{Sum of heat and work} \\ \text{with positive sign}\end{matrix}\right|} \times 100 = \frac{\left|-70.02\frac{\text{kJ}}{\text{kg}}\right|}{\left|1895.02\frac{\text{kJ}}{\text{kg}}\right|} \times 100 = 3.69\%$$

6.6. Alarmed by the news about the intentions of the Big Bad Wolf, and unable of maintaining a proper intercultural dialogue, the Three Little Pigs decided to spend the winter in the brick house of the practical brother. To obtain energy and heat, they want to employ a thermal power station, using the straw and the sticks of the previously destroyed houses as ecological fuel.

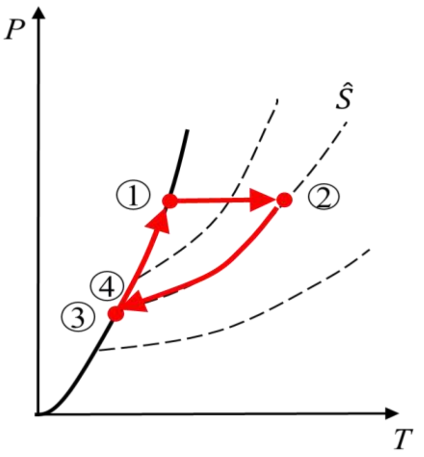
The biomass boiler produces superheated steam at 1 MPa and an unknown temperature, which enters the isentropic turbine. This temperature is fitted to reach a saturated vapor stream at 0.1 MPa after driving the turbine. Then, this low-pressure steam circulates through the home's heating system, fully condensing at the same temperature. Finally, it is compressed to the superheated conditions in order to enter the boiler and close the cycle.

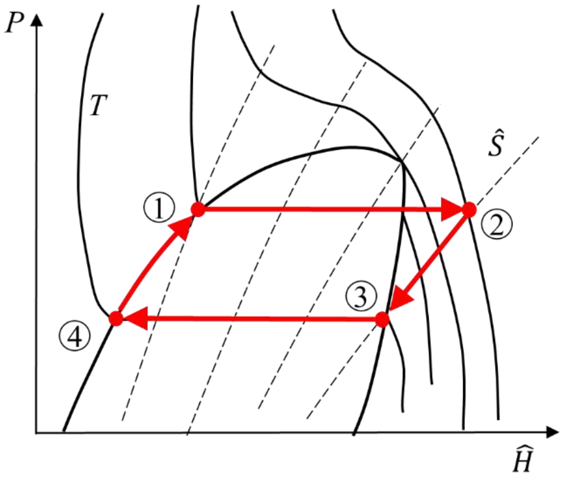
Additionally, the operation line of the compression coincides with the saturated liquid line. The biomass flow rate is of 10 kg/h, and its calorific value of 3000 kcal/kg. Since several human eyes see more than two pig eyes, the Practical Pig asks us for help with a preliminary study:

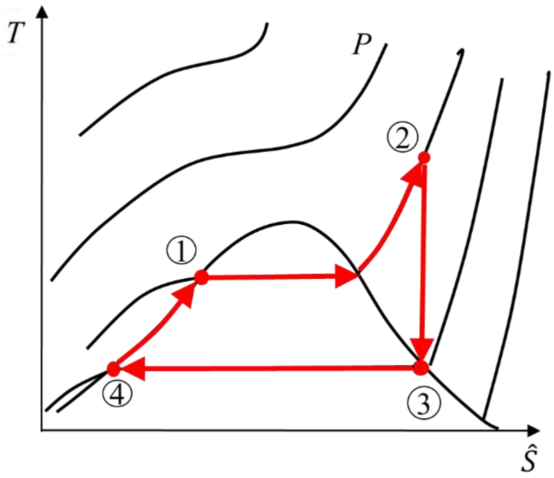
a) **Qualitatively represent the process in *PT*(*S*), *PH*(*T, S*), *TS*(*P*), *TH(P, S)*, *HS(T,P)* and *PV(T,S)* diagrams.**
a) **Represent the flowchart and indicate how to calculate the heats and flow works in each stage.**
b) **Indicate the operating temperature of the boiler.**
c) **Calculate the flow of thermal fluid (water) to be used in the cycle, taking into account the requirements of the boiler.**
d) **Evaluate the theoretical power (in kW) in the turbine.**
e) **Determine the heat flow (in kW) in the condenser.**
f) **Find the power in the compression.**
g) **Estimate the efficiency of the system.**

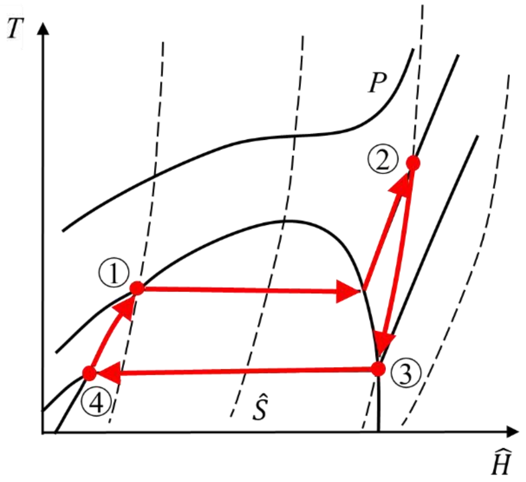
Question a. According to the statement of the problem, the biomass boiler works at a pressure of 10 bar (1 MPa), which indicates that it is isobaric; the turbine is isentropic and the steam leaves it saturated at 1 bar (0.1 MPa). This vapor condenses in the home's heating system at its saturation temperature (so the condensation is both isobaric and isothermal) and the condensate is compressed from 1 bar to 10 bar along the saturated liquid line.

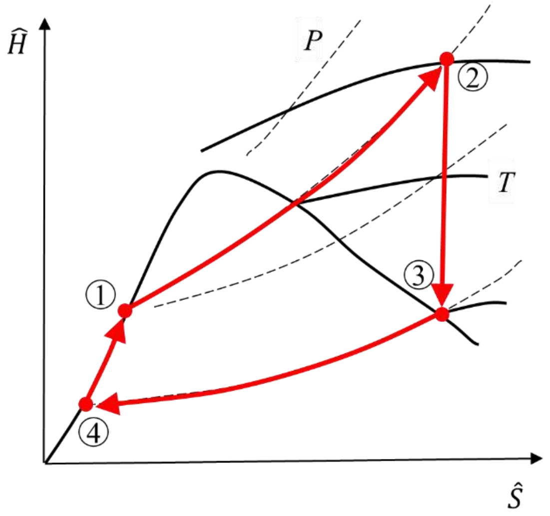
Let 1 be the stream after the compressor, 2 be the stream after the boiler, 3 be the water that leaves the turbine and 4 the fluid that exits the condenser. The six qualitative representations required will be

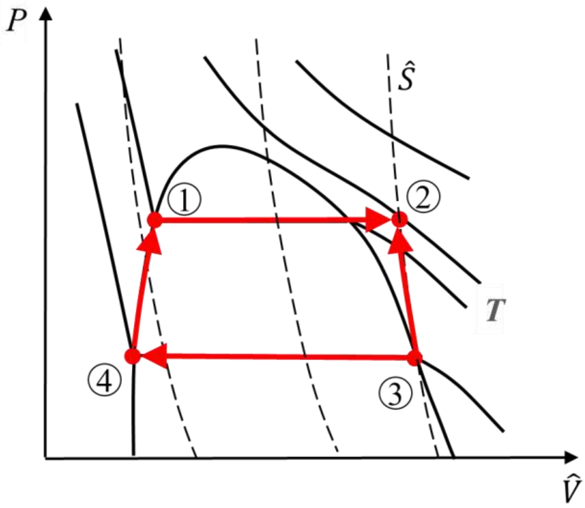




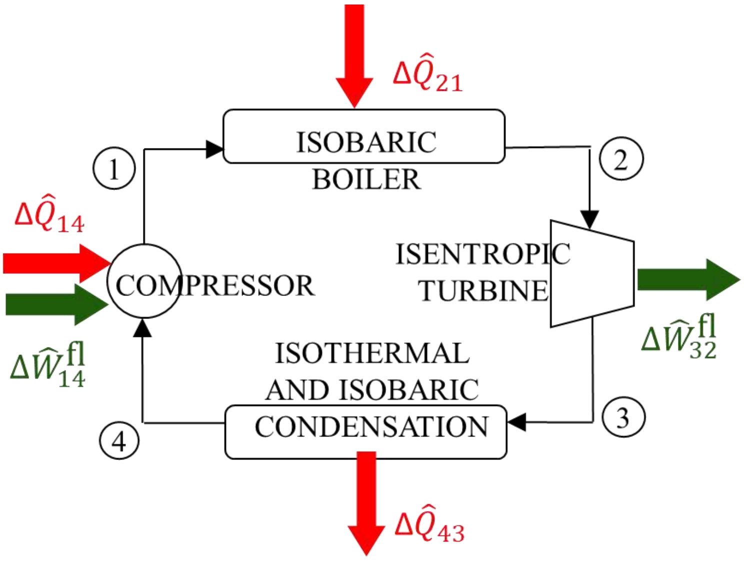








Question b. The flowchart is



where the heat and the work involved in each stage are given by the expressions (sections a and c of reference problem 0.3)

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \Delta\hat{Q} = \int T\mathrm{d}\hat{S}$$

$$\mathrm{d}\hat{W}^{\text{fl}} = \hat{V}\mathrm{d}P \quad \rightarrow \quad \Delta\hat{W}^{\text{fl}} = \int \hat{V}\mathrm{d}P$$

which can be simplified in several cases.

<u>Operation from 1 to 2</u>: Since the boiler is isobaric (dP=0), there will be no flow work, and the heat exchanged will be equal to the difference of enthalpies

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\text{fl}} = \mathrm{d}\hat{Q} + \hat{V}\mathrm{d}P \quad \xrightarrow{P\ constant} \mathrm{d}\hat{H} = \mathrm{d}\hat{Q} \quad \rightarrow \quad \Delta\hat{H}_{21} = \Delta\hat{Q}_{21}$$

<u>Operation from 3 to 4</u>: The condensation is isobaric as in the step from 1 to 2, so there will be no flow work and

$$\Delta\hat{H}_{43} = \Delta\hat{Q}_{43}$$

but it is isothermal as well, so T_3=T_4 and the integral becomes

$$\Delta\hat{Q}_{43} = \int_3^4 T\mathrm{d}\hat{S} \ = \ T_3\left(\hat{S}_4 - \hat{S}_3\right)$$

<u>Operation from 2 to 3</u>: The turbine is isentropic ($\mathrm{d}\hat{S} = 0$); thus, no heat will be exchanged whith the surroundings and the flow work will be equal to the enthalpy difference

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\text{fl}} = T\mathrm{d}\hat{S} + \mathrm{d}\hat{W}^{\text{fl}} \quad \xrightarrow{S\ constant} \mathrm{d}\hat{H} = \mathrm{d}\hat{W}^{\text{fl}} \quad \rightarrow \quad \Delta\hat{H}_{32} = \Delta\hat{W}^{\text{fl}}_{32}$$

<u>Operation from 4 to 1:</u> During compression along the saturation line, the temperature, pressure, enthalpy and entropy change, being imposible to apply any of the previous simplifications. Integrals have to be numerically evaluated, for example, through the trapezoidal rule. In a first approximation, only two points can be used

$$\Delta \widehat{W}_{14}^{\mathrm{fl}} = \int_4^1 \hat{V}\,\mathrm{d}P = \left(\frac{\hat{V}_1 + \hat{V}_4}{2}\right)(P_1 - P_4)$$

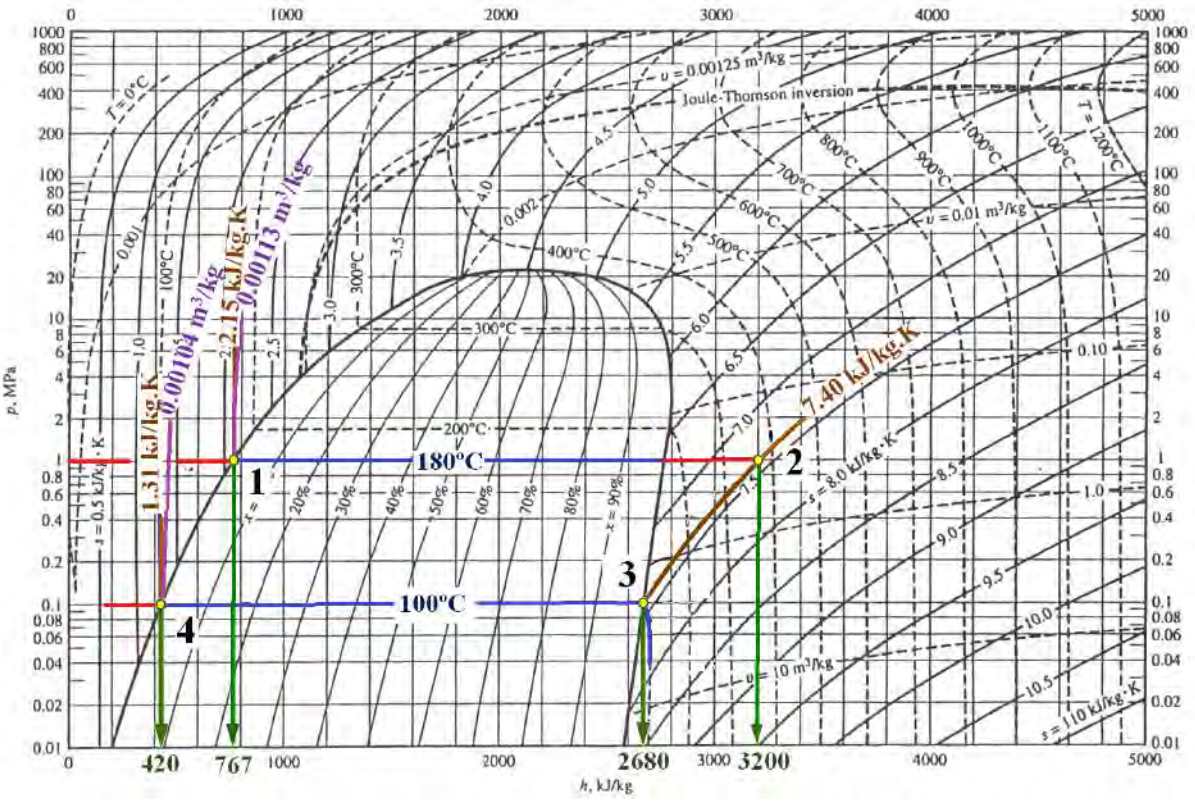
$$\Delta \hat{Q}_{14} = \int_4^1 T\,\mathrm{d}\hat{S} = \left(\frac{T_1 + T_4}{2}\right)\left(\hat{S}_1 - \hat{S}_4\right)$$

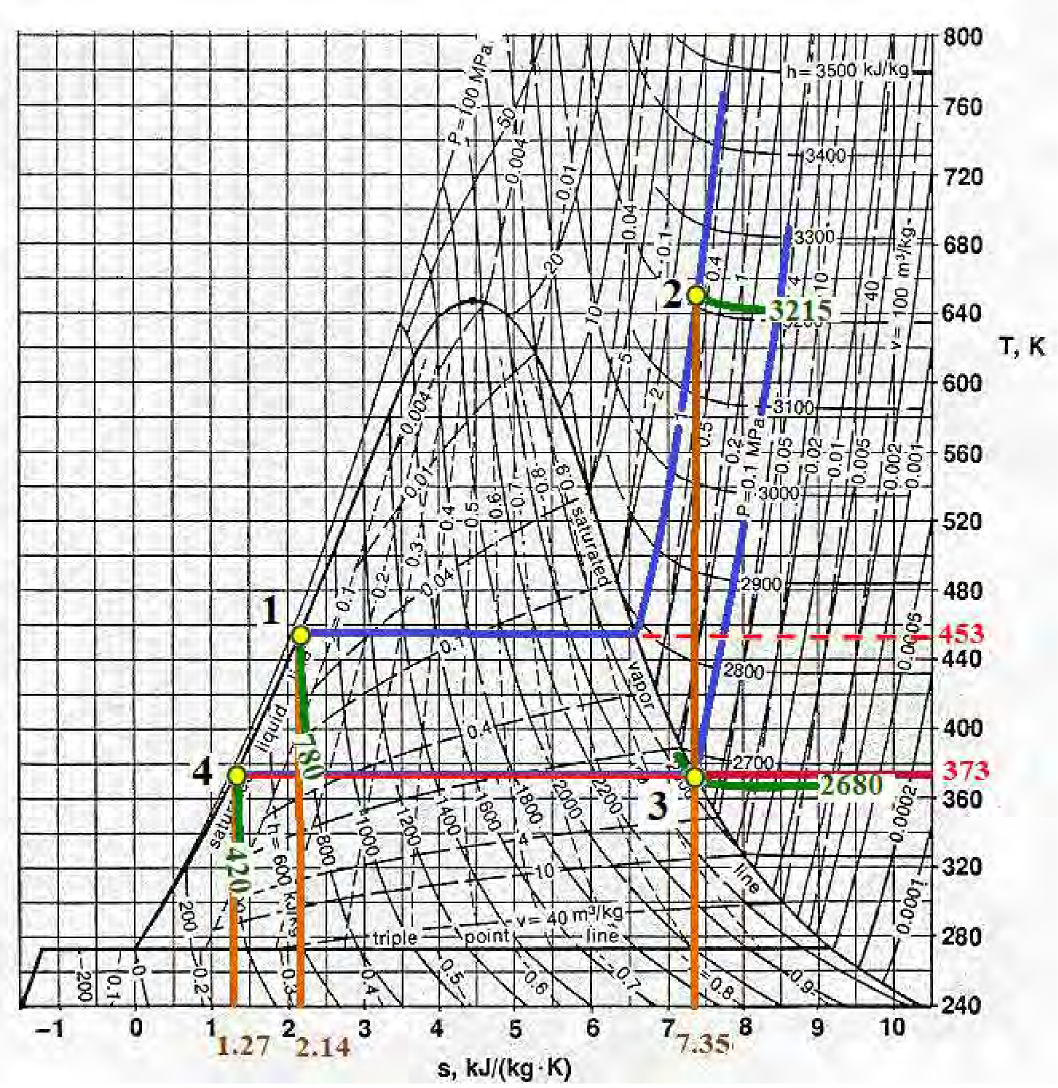
Both parameters satisfy that

$$\Delta \widehat{H}_{14} = \Delta \hat{Q}_{14} + \Delta \widehat{W}_{14}^{\mathrm{fl}}$$

Question c. The temperature at which the boiler operates will be found by taking data of the problem to the appropriate diagram. It could be the *PH* one (figure V.5 of appendix V) or the *TS* one (figure V.7), but not the Mollier diagram (figure V.6), because it does not cover the saturated liquid zone.

When placing 1, 2, 3 and 4, it can be observed that the temperature is of 180ºC or 453 K. From the *PH* and *TS* graphs the enthalpies, entropies and volumes necessary to solve the problem are also obtained.





Fort he sake of simplicity, questions **d–h** will be solved first with data from figure V.5 and then with data from V.7.

Question d. 10 kg/h of biomass with a calorific value of 3000 kcal/kg are available, so

$$q_{21} = \left(10\ \frac{\mathrm{kg}}{\mathrm{h}}\right)\left(3000\ \frac{\mathrm{kcal}}{\mathrm{kg}}\right) = 30000\ \frac{\mathrm{kcal}}{\mathrm{h}}$$

$$q_{21} = 30000\ \frac{\mathrm{kcal}}{\mathrm{h}} \times \frac{4180\ \mathrm{J}}{1\ \mathrm{kcal}} \times \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}} \times \frac{1\ \mathrm{h}}{3600\ \mathrm{s}} = 34.83\ \frac{\mathrm{kJ}}{\mathrm{s}}$$

but in the boiler

$$\Delta\hat{Q}_{21} = \Delta\hat{H}_{21} = \left(\hat{H}_2 - \hat{H}_1\right) = \left(3200\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 767\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 2433\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$q_{21} = \widehat{W}\Delta\hat{Q}_{21}$$

from where

$$\widehat{\mathcal{W}} = \frac{q_{21}}{\Delta\hat{Q}_{21}} = \frac{\left(34.83\ \frac{\mathrm{kJ}}{\mathrm{s}}\right)}{\left(2433\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right)} = 0.0143\ \frac{\mathrm{kg}}{\mathrm{s}}$$

Question e. In the turbine, the flow work is

$$\Delta\widehat{W}_{32}^{\mathrm{fl}} = \Delta\widehat{H}_{32} = \left(\widehat{H}_3 - \widehat{H}_2\right) = \left(2680\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 3200\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -520\frac{\mathrm{kJ}}{\mathrm{kg}}$$

and the power

$$\wp_{32} = \widehat{\mathcal{W}}\Delta\widehat{W}_{32}^{\mathrm{fl}} = \left(0.0143\ \ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(-520\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -7.436\ \mathrm{kW}$$

Question f. During condensation, the heat per unit mass and the heat flow will be given by

$$\Delta\hat{Q}_{43} = \Delta\widehat{H}_{43} = \left(\widehat{H}_4 - \widehat{H}_3\right) = \left(420\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 2680\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -2260\frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$q_{43} = \widehat{\mathcal{W}}\Delta\hat{Q}_{43} = \left(0.0143\ \ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(-2260\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -32.32\ \mathrm{kW}$$

or by

$$\Delta\hat{Q}_{43} = T_3\left(\hat{S}_4 - \hat{S}_3\right) = (373\ \mathrm{K})\left(1.31\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 7.40\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = -2271.57\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$q_{43} = \left(0.0143\ \ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(-2271.57\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -32.48\ \mathrm{kW}$$

coinciding within the graphical reading error.

Question g. According to question **b**, and having in mind that 1 MPa= 1000 kPa, the flow work in the compressor will be

$$\Delta\widehat{W}_{14}^{\mathrm{fl}} = \int_4^1 \hat{V}\mathrm{d}P = \left(\frac{0.00113\ \frac{\mathrm{m}^3}{\mathrm{kg}} + 0.00104\frac{\mathrm{m}^3}{\mathrm{kg}}}{2}\right)(1000\ \mathrm{kPa} - 100\ \mathrm{kPa}) = 0.9765\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

and the power

$$\wp_{14} = \widehat{W}\Delta\widehat{W}_{14}^{\mathrm{fl}} = \left(0.0143\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(0.9765\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 0.014\ \mathrm{kW}$$

But in this device there is also another energy contribution, as indicated in the same question **b**.

$$\Delta\hat{Q}_{14} = \int_4^1 T\mathrm{d}\hat{S}\ = \left(\frac{453\ \mathrm{K} + 373\ \mathrm{K}}{2}\right)\left(2.15\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 1.31\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = 346.92\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$q_{14} = \widehat{W}\Delta\hat{Q}_{14} = \left(0.0143\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(346.92\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 4.961\ \mathrm{kW}$$

Notice that $\Delta\widehat{H}_{14} = \Delta\hat{Q}_{14} + \Delta\widehat{W}_{14}^{\mathrm{fl}}$ and that in this case, the sum of the values calculated with the trapezoidal rule does not differ too much from the enthalpy difference.

$$\Delta\widehat{H}_{14} = \left(\widehat{H}_1 - \widehat{H}_4\right) = \left(767\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 420\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 347\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\Delta\hat{Q}_{14} + \Delta\widehat{W}_{14}^{\mathrm{fl}} = 346.92\ \frac{\mathrm{kJ}}{\mathrm{kg}} + 0.9765\ \frac{\mathrm{kJ}}{\mathrm{kg}} = 347.8965\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

Question h. In reference problem 0.13, the efficiency of a cycle is

$$\text{Efficiency (\%)} = \frac{|\text{Work in the turbine}|}{\left|\begin{array}{c}\text{Sum of heat and work}\\ \text{with positive sign}\end{array}\right|} \times 100 = \frac{|\text{Work in the turbine}|}{\left|\begin{array}{c}\text{Sum of heat and work}\\ \text{with negative sign}\end{array}\right|} \times 100$$

By substituting the terms, it can be obtained

$$\frac{\left|\Delta\widehat{W}_{32}\right|}{\left|\Delta\hat{Q}_{21} + \Delta\widehat{W}_{14} + \Delta\hat{Q}_{14}\right|} \times 100 = \frac{\left|\Delta\widehat{W}_{32}\right|}{\left|\Delta\widehat{W}_{32} + \Delta\hat{Q}_{43}\right|} \times 100$$

$$\frac{\left|-520\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right|}{\left|2433\ \frac{\mathrm{kJ}}{\mathrm{kg}} + 0.9765\frac{\mathrm{kJ}}{\mathrm{kg}} + 346.92\frac{\mathrm{kJ}}{\mathrm{kg}}\right|} \times 100 \approx \frac{\left|-520\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right|}{\left|\text{-}520\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 2260\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right|} \times 100$$

$$\frac{\left|-520\frac{\mathrm{kJ}}{\mathrm{kg}}\right|}{\left|2780.8965\frac{\mathrm{kJ}}{\mathrm{kg}}\right|} \times 100 \approx \frac{\left|-520\frac{\mathrm{kJ}}{\mathrm{kg}}\right|}{\left|\text{-}2780\frac{\mathrm{kJ}}{\mathrm{kg}}\right|} \times 100$$

$$18.699\% \approx 18.705\%$$

When the Practical Pig insists that the **calculations be redone** with data of Figure V.7, the results of the different questions are

d'. The flow rate of water in the boiler

$$\Delta\hat{Q}_{21} = \Delta\hat{H}_{21} = \left(\hat{H}_2 - \hat{H}_1\right) = \left(3215\ \frac{\text{kJ}}{\text{kg}} - 780\frac{\text{kJ}}{\text{kg}}\right) = 2435\ \frac{\text{kJ}}{\text{kg}}$$

$$\hat{\mathcal{W}} = \frac{q_{21}}{\Delta\hat{H}_{21}} = \frac{\left(34.83\ \frac{\text{kJ}}{\text{s}}\right)}{\left(2435\ \frac{\text{kJ}}{\text{kg}}\right)} = 0.0143\ \frac{\text{kg}}{\text{s}}$$

e'. The power in the turbine

$$\Delta\hat{W}^{\text{fl}}_{32} = \Delta\hat{H}_{32} = \left(\hat{H}_3 - \hat{H}_2\right) = \left(2680\ \frac{\text{kJ}}{\text{kg}} - 3215\frac{\text{kJ}}{\text{kg}}\right) = -535\frac{\text{kJ}}{\text{kg}}$$

$$\wp_{32} = \hat{\mathcal{W}}\Delta\hat{W}^{\text{fl}}_{32} = \left(0.0143\ \frac{\text{kg}}{\text{s}}\right)\left(-535\frac{\text{kJ}}{\text{kg}}\right) = -7.651\ \text{kW}$$

f'. The heat flow in the condenser (two ways)

$$\Delta\hat{Q}_{43} = \Delta\hat{H}_{43} = \left(\hat{H}_4 - \hat{H}_3\right) = \left(420\ \frac{\text{kJ}}{\text{kg}} - 2680\frac{\text{kJ}}{\text{kg}}\right) = -2260\frac{\text{kJ}}{\text{kg}}$$

$$q_{43} = \hat{\mathcal{W}}\Delta\hat{Q}_{43} = \left(0.0143\ \frac{\text{kg}}{\text{s}}\right)\left(-2260\frac{\text{kJ}}{\text{kg}}\right) = -32.32\ \text{kW}$$

$$\Delta\hat{Q}_{43} = T_3\left(\hat{S}_4 - \hat{S}_3\right) = (373\ \text{K})\left(1.27\ \frac{\text{kJ}}{\text{kg·K}} - 7.35\ \frac{\text{kJ}}{\text{kg·K}}\right) = -2267.84\ \frac{\text{kJ}}{\text{kg}}$$

$$q_{43} = \hat{\mathcal{W}}\Delta\hat{Q}_{43} = \left(0.0143\ \frac{\text{kg}}{\text{s}}\right)\left(-2267.84\frac{\text{kJ}}{\text{kg}}\right) = -32.43\ \text{kW}$$

g'. Isochores are not drawn in the saturated liquid zone of the *TS* diagram, so the flow work cannot be directly evaluated. It should be found from enthalpies and heat as

$$\Delta\hat{W}^{\text{fl}}_{14} = \Delta\hat{H}_{14} - \Delta\hat{Q}_{14}$$

$$\Delta\hat{H}_{14} = \left(780\ \frac{\text{kJ}}{\text{kg}} - 420\frac{\text{kJ}}{\text{kg}}\right) = 360\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\hat{Q}_{14} = \int_4^1 T\text{d}\hat{S}\ = \left(\frac{453\ \text{K} + 373\ \text{K}}{2}\right)\left(2.14\ \frac{\text{kJ}}{\text{kg·K}} - 1.27\ \frac{\text{kJ}}{\text{kg·K}}\right) = 359.31\ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\hat{W}_{14}^{\text{fl}} = 360\ \frac{\text{kJ}}{\text{kg}} -\ 359.31\ \frac{\text{kJ}}{\text{kg}} = 0.69\ \frac{\text{kJ}}{\text{kg}}$$

and therefore

$$\wp_{14} = \hat{\mathcal{W}}\Delta\hat{W}_{14}^{\text{fl}} = \left(0.0143\ \frac{\text{kg}}{\text{s}}\right)\left(0.69\ \frac{\text{kJ}}{\text{kg}}\right) = 0.00987\ \text{kW}$$

$$q_{14} = \hat{\mathcal{W}}\Delta\hat{Q}_{14} = \left(0.0143\ \frac{\text{kg}}{\text{s}}\right)\left(359.31\ \frac{\text{kJ}}{\text{kg}}\right) = 5.138\ \text{kW}$$

Notice that due to the interpolation errors in enthalpies and to the low value of the flow work, this could have been negative: for example, if 779 kJ/kg had been read instead of 780 kJ/kg, $\Delta\hat{W}_{14}^{\text{fl}}$ would have been equal to -0.31 kJ/kg.

h'. The efficiency of the system

$$\text{Efficiency (\%)} = \frac{\left|\Delta\hat{W}_{32}\right|}{\left|\Delta\hat{Q}_{21} + \Delta\hat{W}_{14} + \Delta\hat{Q}_{14}\right|} \times 100 = \frac{\left|\Delta\hat{W}_{32}\right|}{\left|\Delta\hat{W}_{32} + \Delta\hat{Q}_{43}\right|} \times 100$$

$$\frac{\left|-535\frac{\text{kJ}}{\text{kg}}\right|}{\left|2435\frac{\text{kJ}}{\text{kg}} + 0.69\frac{\text{kJ}}{\text{kg}} + 359.31\ \frac{\text{kJ}}{\text{kg}}\right|} \times 100 = \frac{\left|-535\frac{\text{kJ}}{\text{kg}}\right|}{\left|-535\frac{\text{kJ}}{\text{kg}} - 2260\frac{\text{kJ}}{\text{kg}}\right|} \times 100$$

$$\frac{\left|-535\frac{\text{kJ}}{\text{kg}}\right|}{\left|2795\frac{\text{kJ}}{\text{kg}}\right|} \times 100 = \frac{\left|-535\frac{\text{kJ}}{\text{kg}}\right|}{\left|-2795\frac{\text{kJ}}{\text{kg}}\right|} \times 100 = 19.14\%$$

NOTE: If the interested reader wants to refine question **g** further, he can employs table VI.1 of appendix VI, where there are enough numerical data between 100ºC and 186.85ºC to perform the integration using the composite trapezoidal rule. It will only be required to interpolate the values of the vapor pressure, $\hat{S}_l$, $\hat{V}_l$ and $\hat{H}_l$ at 180ºC (10.07 bar, 2.139 kJ/kg·K, 0.001127 m^3/kg and 763.15 kJ/kg, respectively)

T (°C)	P (bar)	T (K)	$\hat{S}_l$ (m^3/kg)	$[\hat{S}_i - \hat{S}_{i-1}]\left(\frac{T_i + T_{i-1}}{2}\right)$ T in K
100	1.0133	373	1.307	
101.85	1.0815	374.85	1.328	7.852425
106.85	1.2869	379.85	1.384	21.1316
111.85	1.5233	384.85	1.439	21.02925
116.85	1.794	389.85	1.494	21.30425
126.85	2.455	399.85	1.605	43.82835
136.85	3.302	409.85	1.708	41.69955
146.85	4.37	419.85	1.81	42.3147
156.85	5.699	429.85	1.911	42.90985
166.85	7.333	439.85	2.011	43.485
176.85	9.319	449.85	2.109	43.5953
180	10.07	453	2.139	13.54275
			Sum=	342.693025 kJ/kg

T (°C)	P (bar)	P (kPa)	$\hat{V}_l$ (m^3/kg)	$[P_i - P_{i-1}]\left(\frac{\hat{V}_i + \hat{V}_{i-1}}{2}\right)$ P in kPa
100	1.0133	101.33	0.001044	
101.85	1.0815	108.15	0.001045	0.00712349
106.85	1.2869	128.69	0.001049	0.02150538
111.85	1.5233	152.33	0.001053	0.02484564
116.85	1.794	179.4	0.001058	0.028572385
126.85	2.455	245.5	0.001067	0.07023125
136.85	3.302	330.2	0.001077	0.0907984
146.85	4.37	437	0.001088	0.115611
156.85	5.699	569.9	0.001099	0.14532615
166.85	7.333	733.3	0.00111	0.1804753
176.85	9.319	931.9	0.001123	0.2217369
180	10.07	1007	0.001127	0.0844875
			Sum=	0.9907134 kJ/kg

quantities which are more similar to those found with figure V.5 than to those with figure V.7. Furthermore, the integration error is small, since the sum of heat and work

$$\Delta\hat{Q}_{14} + \Delta\hat{W}_{14}^{\mathrm{fl}} = 342.693\ \frac{\mathrm{kJ}}{\mathrm{kg}} + 0.990\ \frac{\mathrm{kJ}}{\mathrm{kg}} = 343.683\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

is very close to the difference of enthalpies at 180°C and at 100°C

$$\Delta\hat{H}_{14} = \left(\hat{H}_1 - \hat{H}_4\right) = \left(763.15\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 419.1\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 344.05\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

6.7. In the film "Lawrence of Arabia" (1962), after the successive victories over the Turks by the rebel troops led by E.T. Lawrence, the temperature in the conference room during the conflictive session of the Arab Council (in Damascus) became noticeably hot. For this reason, the hero (advised by Sheikh Auda Abu Tayi) has to design on the fly a cooling system to maintain a politically correct temperature. After the initial estimation, he discoveres that 10^7 kJ/h have to be removed.

Due to the fact that Colonel Lawrence has forgotten part of the Thermology that he studied years ago at Iesus College, Oxford, it is necessary to help him through WhatsApp Time Tunnel 3.0 with wormhole option on 3D screen. To shorten the calculations before the Howeitat and other tribes reach their critical point, the evaporator temperature is set at 0°C, and that of the condenser set to ten degrees higher than the one outside (around 40°C because the euphoria of victory). Both devices are isobaric.

The rest of the system consists of reversible adiabatic compression of saturated vapor (the compressor can be connected to one of the few electrical generators that have not been destroyed), and an isenthalpic expansion of liquid (in a German valve, since the Kaiser was allied of the Turks). Taking into account that during World War I nobody was worried about the ozone layer, it is recommended to use a commercial liquid-vapor Freon 12 mixture.

The data to supply to Colonel Lawrence are:

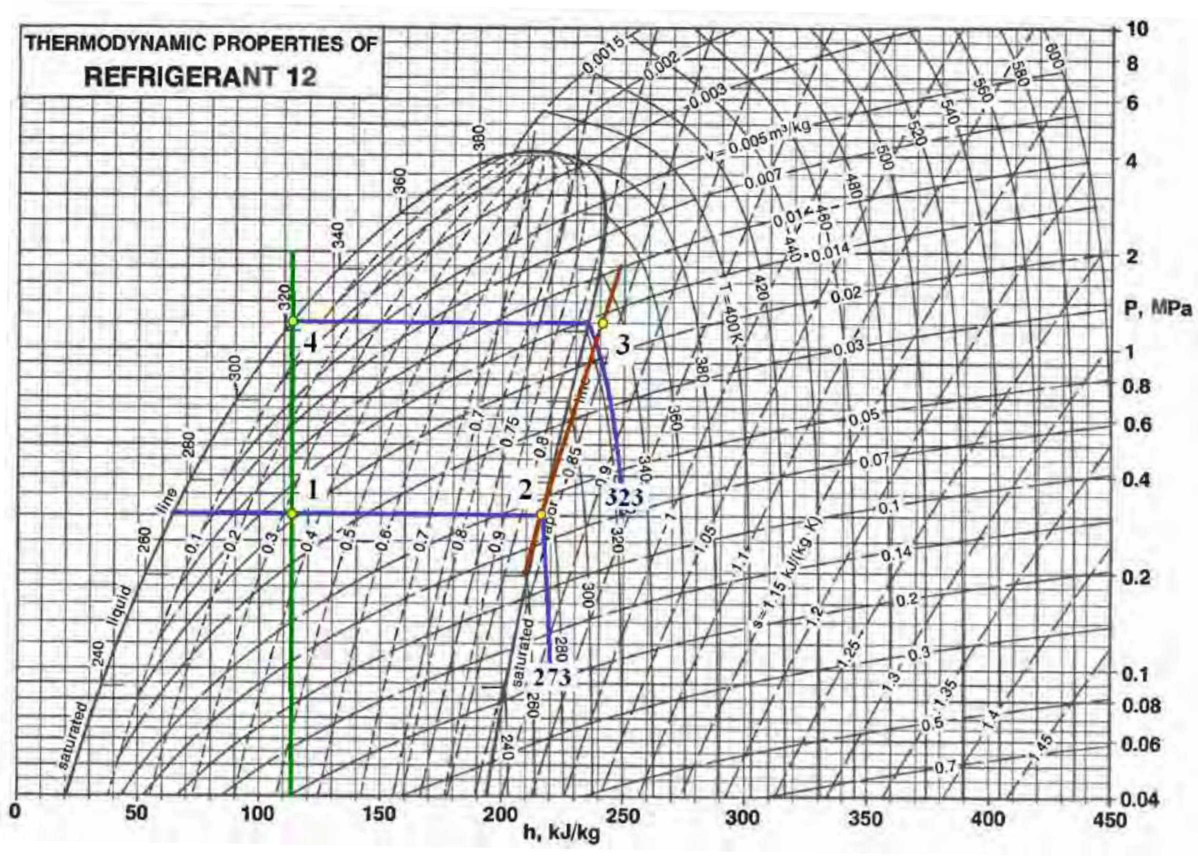
a) Quantitative representation on a *PH*(*S,T,V*) diagram.
b) Pressures and enthalpies at key points in the cycle.
c) Flowchart and information flow diagram.
d) Operation lines on *PT*(*S*), *PV*(*T,H,S*), *TS*(*P,H*) and *HS*(*P,T*) diagrams, indicating the graphical calculation of heat and power in the most suitable ones.
e) Flow rate of thermal fluid (in kg/s).
f) Heat exhanged in the condenser (in kW).
g) Power consumed by the compressor.
h) The coefficient of performance.

Question a. Figure V.14 of appendix V is a $PH(S,T,V)$ diagram of Freon 12, also known as "refrigerant 12". Let be "1" the vapor-liquid mixture of Freon 12 at 0ºC, "2" be the saturated Freon 12 vapor after isobaric evaporation, "3" be the compressed vapor and "4" be the saturated liquid after isobaric condensation at 50ºC (ten degrees above the 40ºC outside). By knowing that the transit from 1 to 2 is isenthalpic and taking into account the conversion factors of appendix I for temperature

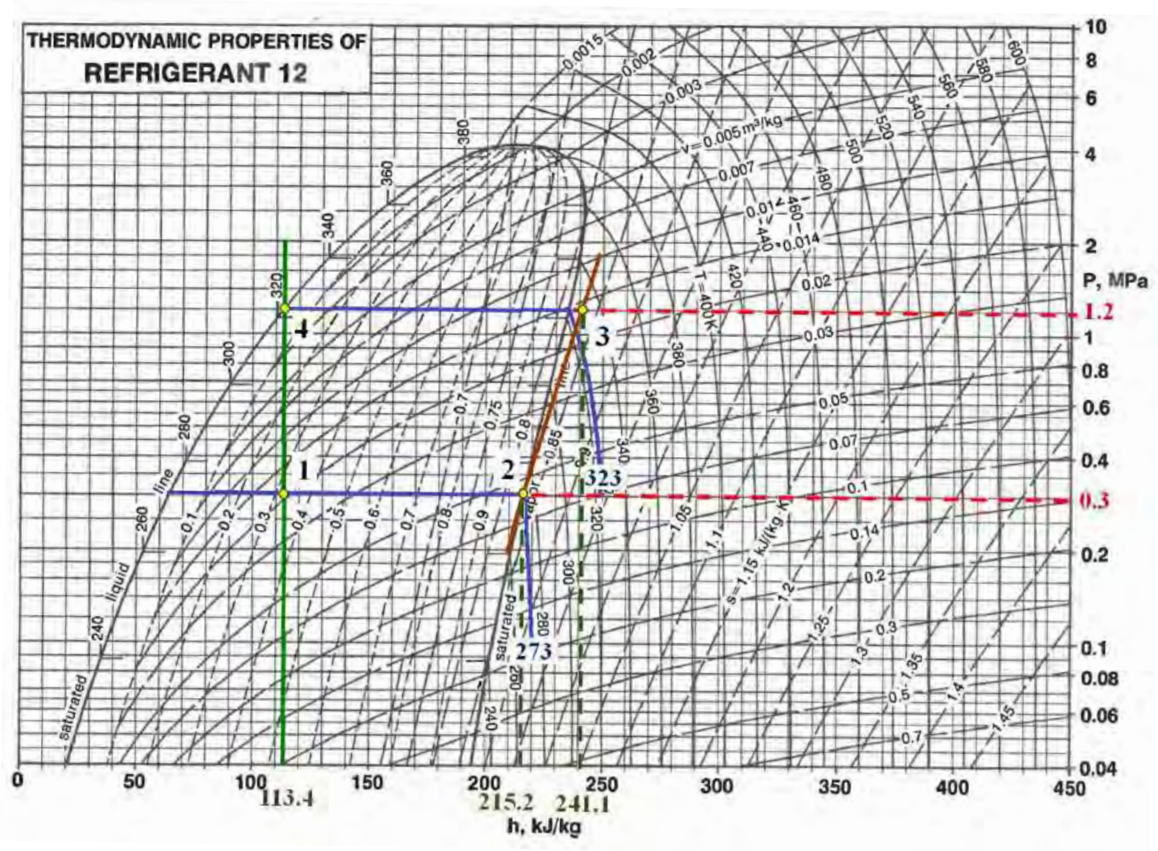
$$T_1(\mathrm{K}) = T_2(\mathrm{K}) = 0°\mathrm{C} + 273 = 273\ \mathrm{K}$$

$$T_4(\mathrm{K}) = 50°\mathrm{C} + 273 = 323\ \mathrm{K}$$

the representation of the cycle will be



Question b. By reading pressures and enthalpies in figure V.14

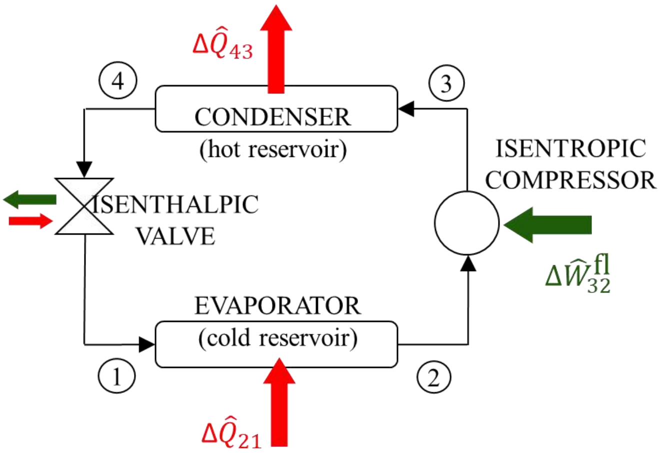


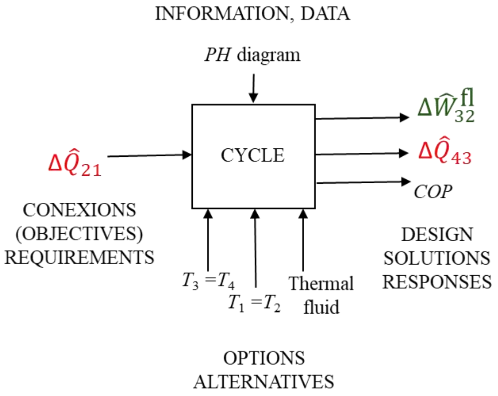
getting the following values

$$P_1 = P_2 = 0.3\ \text{MPa} \quad ; \quad P_3 = P_4 = 1.2\ \text{MPa}$$

$$\hat{H}_1 = 215.2\ \frac{\text{kJ}}{\text{kg}} \quad ; \quad \hat{H}_2 = 241.1\ \frac{\text{kJ}}{\text{kg}} \quad ; \quad \hat{H}_4 = \hat{H}_1 = 113.4\ \frac{\text{kJ}}{\text{kg}}$$

Question c. The flowchart and the information flow diagram will be





There can be exchange of heat and mechanical energy (in the form of flow work) in any of the components of the cycle. They are defined by the expressions

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} \quad \rightarrow \quad \Delta\hat{Q} = \int T\mathrm{d}\hat{S}$$

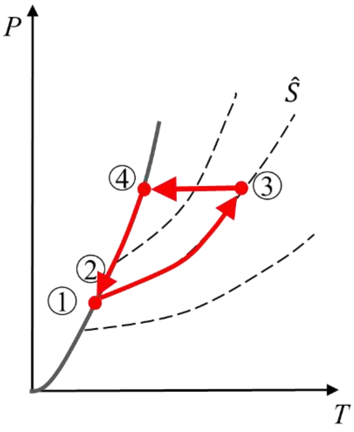
$$\mathrm{d}\hat{W}^{\text{fl}} = \hat{V}\mathrm{d}P \quad \rightarrow \Delta\hat{W}^{\text{fl}} = \int \hat{V}\mathrm{d}P$$

However, in the condenser and in the evaporator there will only be heat transfer, since they are isobaric ($\mathrm{d}P$=0) and so $\mathrm{d}\hat{W}^{\text{fl}}$=0; and in the compressor there will only be flow work, since it is adiabatic and reversible (i.e., isentropic, $\mathrm{d}\hat{S}$=0), so $\mathrm{d}\hat{Q}$=0. These particularities facilitate calculations because, according to reference problem 0.3

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\text{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \quad \begin{cases} \mathrm{d}\hat{H} = \mathrm{d}\hat{Q} & \rightarrow \ \Delta\hat{Q} = \Delta\hat{H} \quad \text{if}\ \mathrm{d}\hat{W}^{\text{fl}} = 0 \\ \mathrm{d}\hat{H} = \mathrm{d}\hat{W}^{\text{fl}} & \rightarrow \ \Delta\hat{W}^{\text{fl}} = \Delta\hat{H} \quad \text{if}\ \mathrm{d}\hat{Q} = 0 \end{cases}$$

and the numerical integration becomes unnecessary.

Question d. Below are shown the operating lines in the requested diagrams. Work and heat are represented as shaded areas in the *PV* and in the *TS* ones.


P
T
$\hat{S}$
①
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③
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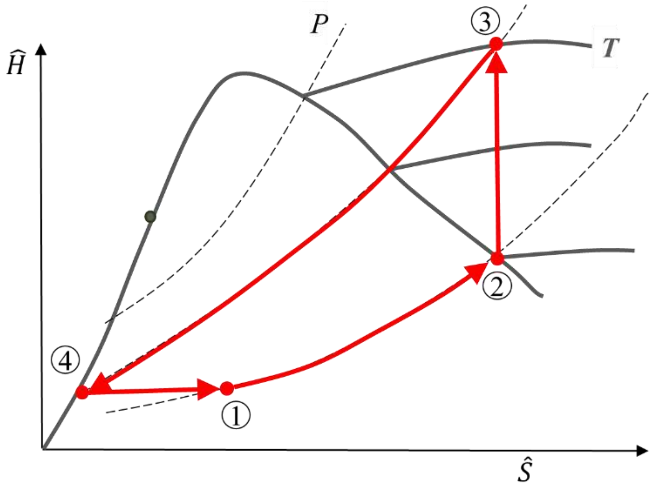
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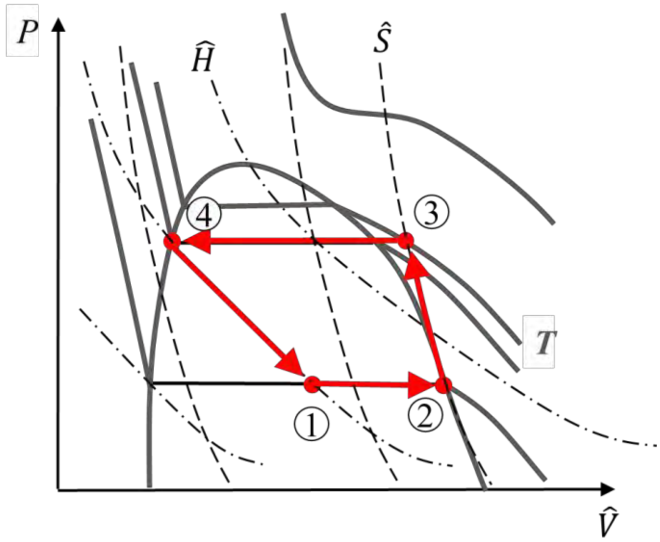
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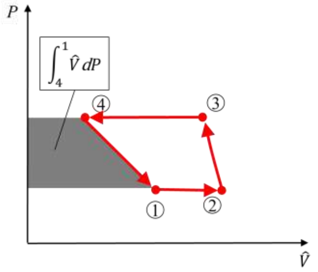
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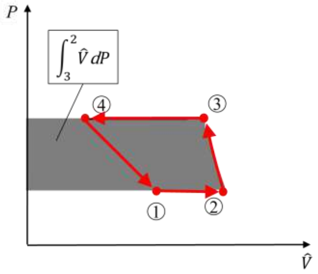
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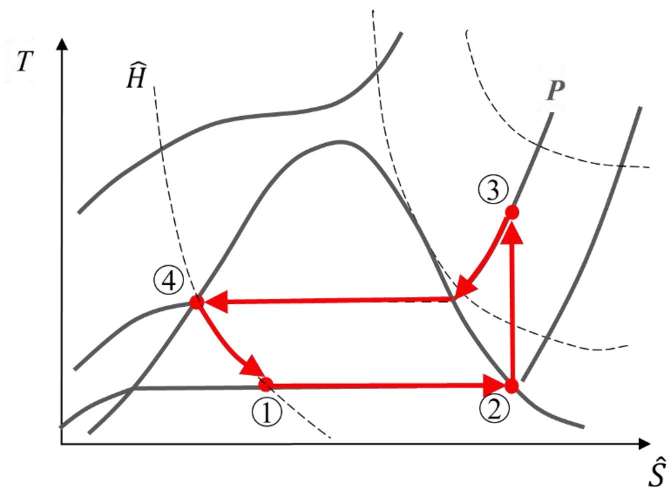
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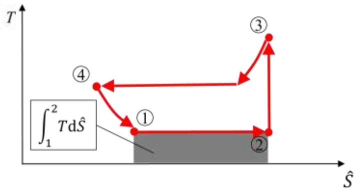
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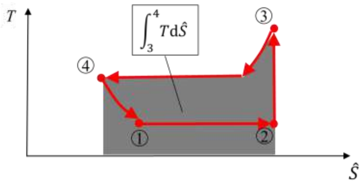
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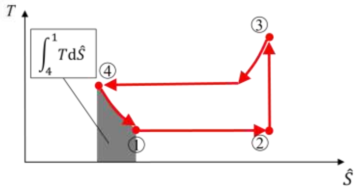
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Question e. The thermal fluid flow rate has to be estimated through

$$\widehat{\mathcal{W}} = \frac{q}{\Delta\hat{Q}}$$

where q is the heat flow removed in the device that produces cold (10^7 kJ/h), i.e., in the isobaric evaporator (step from 1 to 2), which cools the environment taking the heat necessary for the total evaporation of Freon 12. By recalling the simplifications of question **c**

$$\widehat{\mathcal{W}} = \frac{q_{21}}{\Delta\hat{Q}_{21}} = \frac{q_{21}}{\Delta\hat{H}_{21}} = \frac{10^7\ \frac{\text{kJ}}{\text{h}}}{\left(215.2\ \frac{\text{kJ}}{\text{kg}} - 113.4\ \frac{\text{kJ}}{\text{kg}}\right)} = 98231.8\ \frac{\text{kg}}{\text{h}}$$

value which converted to kg/s becomes

$$98231.8\ \frac{\text{kg}}{\text{h}} \times \frac{1\ \text{h}}{3600\ \text{s}} = 27.287\ \frac{\text{kg}}{\text{s}}$$

Question f. The heat transfer in the condenser corresponds to the transit from 3 to 4, which coincides with the enthalpy change between these points because the isobaricity

$$\Delta\hat{Q}_{43} = \Delta\hat{H}_{43} = 113.4\ \frac{\text{kJ}}{\text{kg}} - 241.1\ \frac{\text{kJ}}{\text{kg}} = -127.7\ \frac{\text{kJ}}{\text{kg}}$$

and the heat flow is

$$q_{43} = \widehat{\mathcal{W}}\Delta\hat{Q}_{43} = \left(27.287\ \frac{\text{kg}}{\text{s}}\right)\left(-127.7\ \frac{\text{kJ}}{\text{kg}}\right) = -3484.55\ \frac{\text{kJ}}{\text{s}} = -3484.55\ \text{kW}$$

Question g. In the adiabatic compressor (step from 2 to 3), the flow work will be equal to the difference of enthalpy between the two states

$$\Delta\widehat{W}_{32}^{\text{fl}} = \Delta\hat{H}_{32} = 241.1\ \frac{\text{kJ}}{\text{kg}} - 215.2\ \frac{\text{kJ}}{\text{kg}} = 25.9\ \frac{\text{kJ}}{\text{kg}}$$

and by referring this specific value to the corresponding flow

$$\wp_{32} = \widehat{\mathcal{W}}\Delta\widehat{W}_{32}^{\text{fl}} = \left(27.287\ \frac{\text{kg}}{\text{s}}\right)\left(25.9\ \frac{\text{kJ}}{\text{kg}}\right) = 706.73\ \text{kW}$$

Question h. The COP$_{\text{cooling}}$ will be (reference problem 0.13)

$$\text{COP}_{\text{cooling}} = \left|\frac{\text{Heat in the condenser}}{\text{Work in the compressor}}\right| = \left|\frac{q_{21}}{\wp_{32}}\right| = \left|\frac{10^7\ \frac{\text{kJ}}{\text{h}} \times \frac{1\ \text{h}}{3600\ \text{s}}}{706.73\ \text{kW}}\right| = 3.93$$

6.8. A heat pump that supplies 12540 kJ/h uses Freon 12® as thermal fluid. The cycle consists of two isobaric exchangers, an isentropic compressor and an isenthalpic expander. The saturated freon vapor leaves the evaporator located in the cold reservoir at saturation conditions at -20°C (1), is compressed (2) and becomes fully saturated liquid at 60°C after passing through the condenser located in the hot reservoir (3). It then expands in a valve, reaching the pressure of the evaporator (4) and closing the cycle.

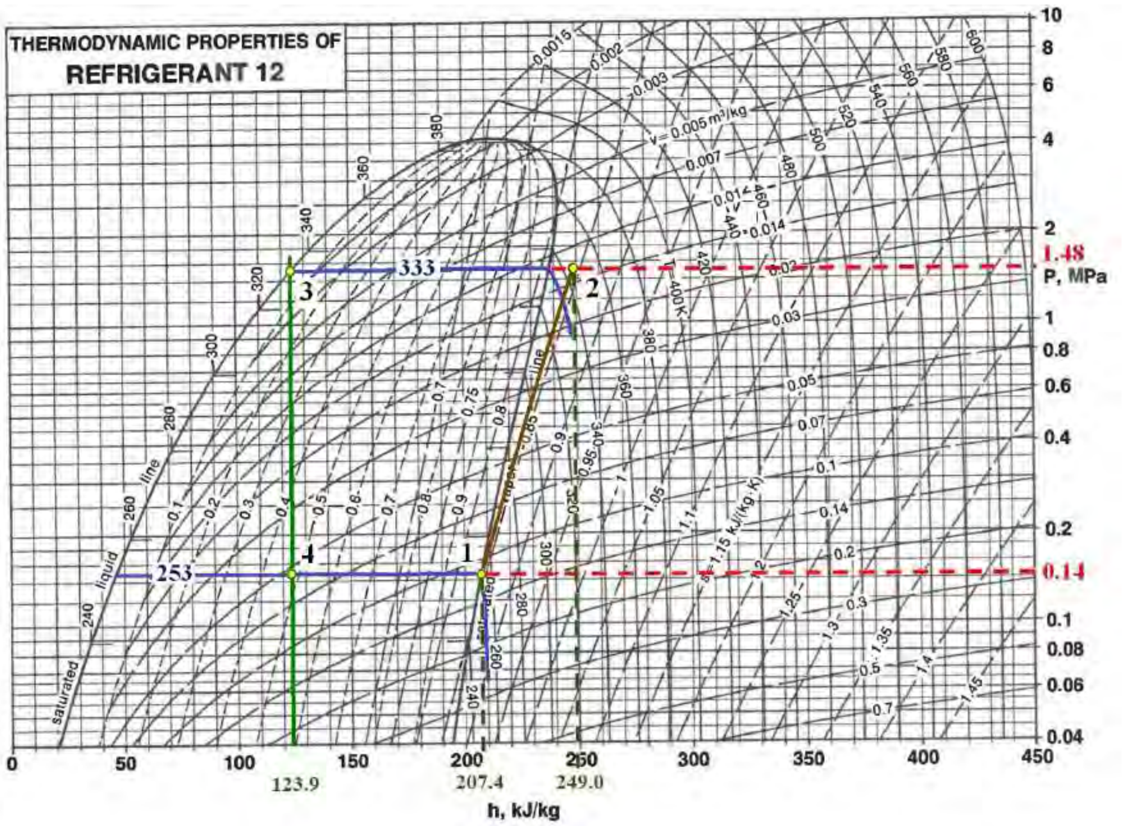
a) Represent the process in a specific *PH*(*V*,*T*,*S*) diagram for Freon 12, indicating the pressures and enthalpies at the key points.
b) Evaluate the freon flow rate which satisfies the design conditions (in kg/s).
c) Determine the heat flow in the evaporator (in kW).
d) Calculate the power of the compressor (in kW).

Question a. Taking into account the data provided by the statement of the problem and the unit conversion factors in appendix I

$$T_1(\mathrm{K}) = T_4(\mathrm{K}) = -20°\mathrm{C} + 273 = 253\ \mathrm{K}$$

$$T_3(\mathrm{K}) = 60°\mathrm{C} + 273 = 333\ \mathrm{K}$$

the representation of the process on a specific *PH* (*V*,*T*,*S*) diagram for Freon 12 (figure V.14 of this book's appendix V) will be



where it can be read that P_1=P_4= 0.14 MPa, P_2=P_3=1.48 MPa, $\hat{H}_1$ =207.4 kJ/kg, $\hat{H}_2$ =249.0 kJ/kg and $\hat{H}_3 = \hat{H}_4$ =123.9 kJ/kg.

Question b. In a heat pump, the flow of thermal fluid has to be estimated by means of the expression

$$\hat{\mathcal{W}} = \frac{q}{\Delta\hat{Q}}$$

where q is the heat per unit time in the device that produces heat (12540 kJ/h), i.e., in the isobaric condenser (step from 2 to 3), which heats the environment by providing the heat released by Freon 12 when condensing (therefore 12540 kJ/h must have a negative sign).

On the other hand, the denominator of the previous equation (heat per unit mass in the condenser) should be estimated using the numerical integral

$$\Delta\hat{Q}_{32} = \int_2^3 T\mathrm{d}\hat{S}$$

but it is an isobaric process (dP=0), so

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \quad \xrightarrow{P\ constant} \quad \mathrm{d}\hat{H} = \mathrm{d}\hat{Q} \quad \rightarrow \quad \Delta\hat{Q} = \Delta\hat{H}$$

and

$$\hat{\mathcal{W}} = \frac{q_{32}}{\Delta\hat{Q}_{32}} = \frac{q_{32}}{\Delta\hat{H}_{32}} = \frac{-12540\ \frac{\mathrm{kJ}}{\mathrm{h}}}{\left(123.9\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 249.0\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right)} = 100.24\ \frac{\mathrm{kg}}{\mathrm{h}}$$

which converted to kg/s

$$100.24\ \frac{\mathrm{kg}}{\mathrm{h}} \times \frac{1\ \mathrm{h}}{3600\ \mathrm{s}} = 0.0278\ \frac{\mathrm{kg}}{\mathrm{s}}$$

Question c. The evaporation corresponds to the passage from point 4 to point 1, and since the apparatus is isobaric, the same simplification of the previous question can be applied

$$\Delta\hat{Q}_{14} = \Delta\hat{H}_{14} = 207.4\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 123.9\ \frac{\mathrm{kJ}}{\mathrm{kg}} = 83.5\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$q_{14} = \hat{\mathcal{W}}\Delta\hat{Q}_{14} = \left(0.0278\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(83.5\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 2.32\ \frac{\mathrm{kJ}}{\mathrm{s}} = 2.32\ \mathrm{kW}$$

Question d. The power in the compressor (step from 2 to 3) will be the product of the Freon flow rate and the flow work in the apparatus. This work should be calculated using the numerical integral

$$\Delta\widehat{W}_{32}^{\mathrm{fl}} = \int_2^3 \hat{V}\mathrm{d}P$$

but the process is isentropic ($\mathrm{d}\hat{S} = 0$), so

$$\mathrm{d}\widehat{H} = \mathrm{d}\widehat{Q} + \mathrm{d}\widehat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \xrightarrow{\hat{S}\ constant} \mathrm{d}\widehat{H} = \mathrm{d}\widehat{W}^{\mathrm{fl}} \quad \rightarrow \quad \Delta\widehat{W}^{\mathrm{fl}} = \Delta\widehat{H}$$

and

$$\Delta\widehat{W}_{32}^{\mathrm{fl}} = \widehat{H}_3 - \widehat{H}_2 = 249.0\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 207.4\ \frac{\mathrm{kJ}}{\mathrm{kg}} = 41.6\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\mathcal{P}_{32} = \widehat{\mathcal{W}}\Delta\widehat{W}_{32}^{\mathrm{fl}} = \left(0.0278\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(41.6\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 1.156\ \mathrm{kW}$$

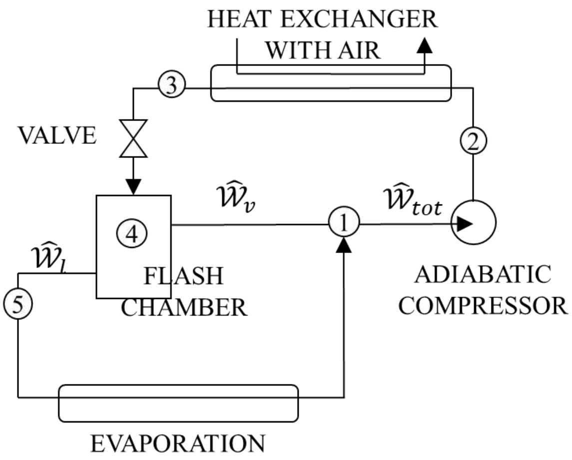
6.9. A heat engine which operates according to two flow patterns is desired to be built.

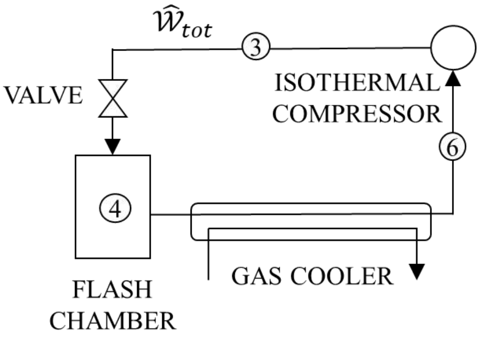
In the first one, saturated ethane vapor at 0.2 MPa is adiabatically and reversibly compressed to 9 MPa and then cooled to 310 K in a heat exchanger ventilated by ambient air. After that, the fluid suffers an isenthalpic depressurization in a valve and enters a flash chamber, where it splits into two saturated phases. The obtained liquid fraction is used as a refrigerant in another heat exchanger where it fully evaporates under practically isobaric conditions. Then, it is mixed with the vapor fraction that leaves the flash chamber, and the resulting stream becomes the feed of the initial compressor. The total circulating flow is 1 kg/s.

In the second pattern, the whole liquid-vapor mixture obtained in the flash chamber passes through a heat exchanger where exhaust gases from an adjacent machine are cooled, reaching 310 K and 0.2 MPa at the exit. Then, it is isothermally compressed to 9 MPa, suffers the isenthalpic depressurization in a valve and enters the flash chamber (analogously to the first pattern). The total circulating flow is of 1 kg/s as well.

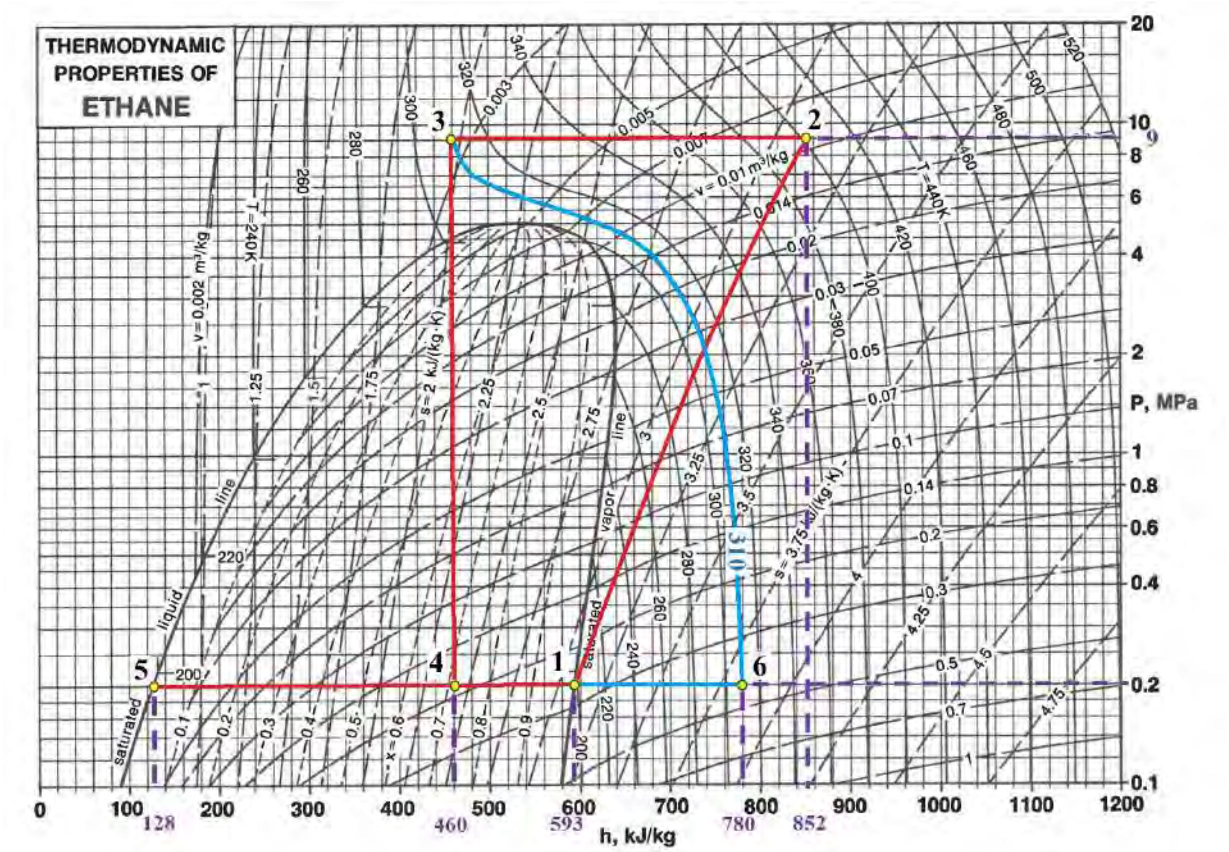
- **a) Draw the flowchart for both patterns.**
- **b) Quantitatively represent on a specific *PH*(*T,V,S*) diagram of ethane the two patterns, and read from it the enthalpies in the significant points.**
- **c) Qualitatively represent the two patterns in *PT*(*S,H*), *PV*(*H,S,T*), *TS*(*P,H*) and *TH*(*P,S*) diagrams.**
- **d) Calculate the heat flow and power in the valve for the two patterns.**
- **e) Calculate the liquid and vapor flow rates produced in the flash chamber for the two patterns.**
- **f) Calculate the power and heat flow in the adiabatic compression of the first pattern.**
- **g) Calculate the heat flow and power in the heat exchanger ventilated by air of the first pattern.**
- **h) Calculate the flow rate and power in the heat exchanger where the liquid fraction of the first pattern evaporates.**
- **i) Calculate the heat flow and power in the heat exchanger of the second pattern.**
- **j) Calculate the heat flow and power in the compressor of the second pattern.**
- **k) Compare this last power with that which would be obtained if ethane could always be considered an ideal gas.**

Question a. Let $\widehat{W}_{tot} = 1$ kg/s be the total circulating flow in both patterns, and $\widehat{W}_l$ and $\widehat{W}_v$ be the flow rates of saturated liquid and saturated vapor obtained in the flash chamber. In the first pattern there will be four significant points: 1) where the liquid fraction evaporated mixes with the vapor fraction of the flash chamber, 2) the exit of the adiabatic compressor, 3) the exit of the heat exchanger ventilated by air, 4) the fluid after isenthalpic expansion and 5) the exit of the liquid fraction after the flash separation. On the contrary, in the second pattern there will only be three significant points: 4) the exit of the flash chamber, 6) the exit of the gas cooler and 3) the exit of the isothermal compressor.





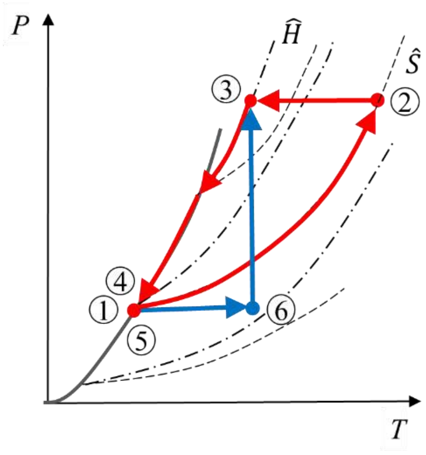
Question b. Figure V.15 of appendix V is a *PH*(*T*,*V*,*S*) diagram of ethane. With the data of the statement of the problem, all the points of the first pattern (united by red lines) and of the second one (united by blue lines) can be placed without calculations. Notice that if the compression is adiabatic and reversible, it will be isentropic.

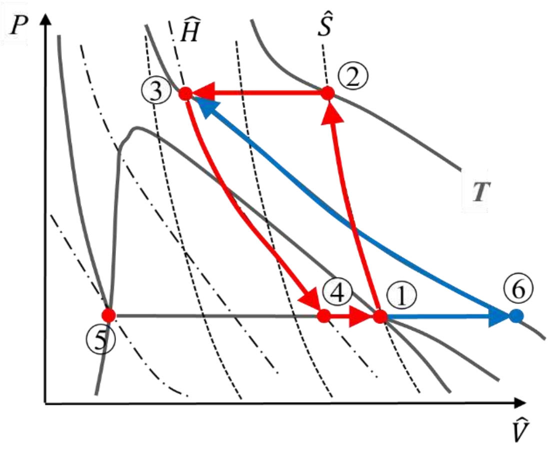


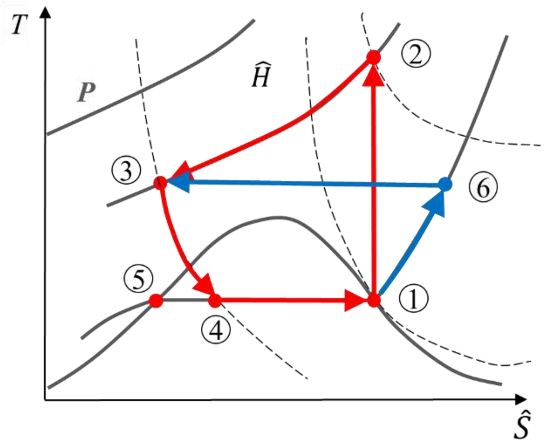
The specific enthalpies of the six significant points are compiled in the following table

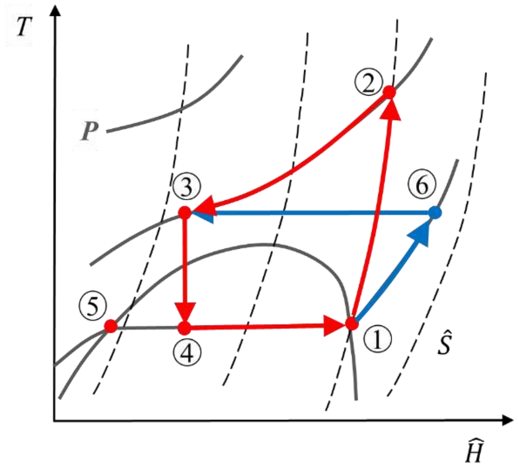
Point	P(MPa)	$\hat{H}$ (kJ/kg)
1	0.2	593
2	9	852
3	9	460
4	0.2	460
5	0.2	128
6	0.2	780

Question c. The requested representations in the four qualitative diagrams are attached below.









Question d. The heat flow and the power in the valve (transition from point 3 to point 4) are determined by the basic formulas

$$q_{43} = \hat{\mathcal{W}}_{tot}\Delta\hat{Q}_{43} = \hat{\mathcal{W}}_{tot}\int_3^4 T\mathrm{d}\hat{S} \quad ; \quad \mathcal{p}_{43} = \hat{\mathcal{W}}_{tot}\Delta\hat{W}_{43}^{\mathrm{fl}} = \hat{\mathcal{W}}_{tot}\int_3^4 \hat{V}\mathrm{d}P$$

However, fundamental thermodynamic relations indicate that

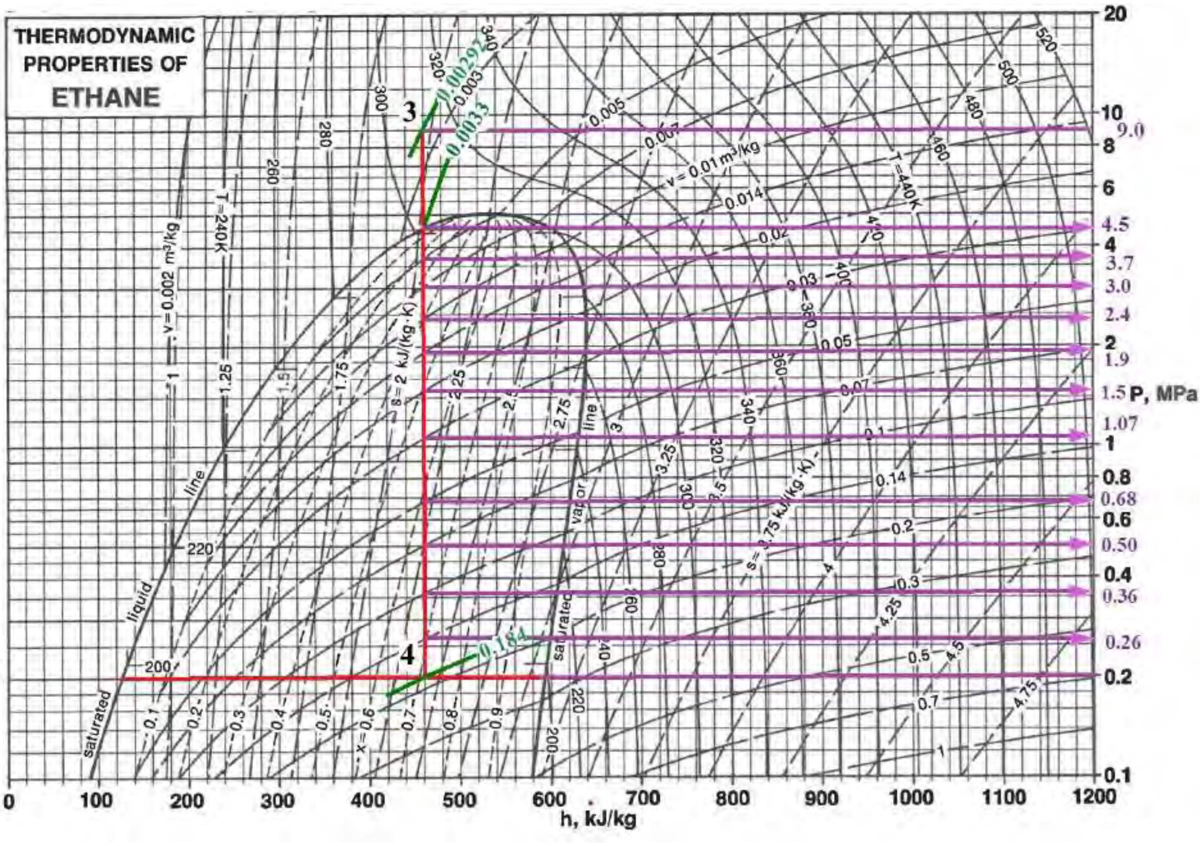
$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \tag{1}$$

Therefore, if the operation is isenthalpic, it will be satisfied that

$$\mathrm{d}\hat{H} = 0 = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \quad \rightarrow \quad \mathrm{d}\hat{Q} = -\mathrm{d}\hat{W}^{\mathrm{fl}}$$

$$\Delta\hat{Q}_{43} = -\Delta\hat{W}^{\mathrm{fl}}_{43} \qquad \rightarrow \qquad \int_3^4 T\mathrm{d}\hat{S} = -\int_3^4 \hat{V}\mathrm{d}P$$

One of the integrals has be estimated numerically (with the trapezoidal rule, for example). Due to the fact that figure V.15 has the pressure in one of the coordinate axes, it seems that the best option is to evaluate the flow work by giving values to the specific volume (preferably those of the isochores to avoid interpolations) and reading the corresponding pressure (in the intersection between the isoenthalpic line and the isochore).



$\hat{V}$ (m^3/kg)	P (MPa)	$[P_i - P_{i-1}]\left(\frac{\hat{V}_i + \hat{V}_{i-1}}{2}\right)$
0.00292	9	
0.0033	4.5	-0.013995
0.005	3.7	-0.00332
0.007	3	-0.0042
0.01	2.4	-0.0051
0.014	1.9	-0.006
0.02	1.5	-0.0068
0.03	1.07	-0.01075
0.05	0.68	-0.0156
0.07	0.5	-0.0108
0.1	0.36	-0.0119
0.14	0.26	-0.012
0.184	0.2	-0.00972
	Sum=	-0.110185

The integration gives -0.1102 MPa·m^3/kg or, what is the same, -110.2 kJ/kg; thus

$$\mathscr{p}_{43} = \left(1\ \frac{\text{kg}}{\text{s}}\right)\left(-110.2\ \frac{\text{kJ}}{\text{kg}}\right) = -110.2\ \frac{\text{kJ}}{\text{s}}$$

$$q_{43} = \left(1\ \frac{\text{kg}}{\text{s}}\right)\left(110.2\ \frac{\text{kJ}}{\text{kg}}\right) = -110.2\ \frac{\text{kJ}}{\text{s}}$$

Question e. The flow rates of liquid and vapor can be obtained by combining the mass balance to the flash chamber

$$\widehat{\mathcal{W}}_{tot} = \widehat{\mathcal{W}}_l + \widehat{\mathcal{W}}_v$$

with the enthalpy balance to that chamber

$$\widehat{\mathcal{W}}_{tot}\hat{H}_4 = \widehat{\mathcal{W}}_l\hat{H}_5 + \widehat{\mathcal{W}}_v\hat{H}_1$$

with the result that

$$\widehat{\mathcal{W}}_l = \frac{\hat{H}_4 - \hat{H}_1}{\hat{H}_5 - \hat{H}_1}\widehat{\mathcal{W}}_{tot} = \frac{460 - 593}{128 - 593}\left(1\ \frac{\text{kg}}{\text{s}}\right) = 0.286\ \frac{\text{kg}}{\text{s}}$$

$$\widehat{\mathcal{W}}_v = \widehat{\mathcal{W}}_{tot} - \widehat{\mathcal{W}}_l = 1\ \frac{\text{kg}}{\text{s}} - 0.286\ \frac{\text{kg}}{\text{s}} = 0.714\ \frac{\text{kg}}{\text{s}}$$

Question f. As in question **d**, the transit from point 1 to point 2 implies changes in heat and work

$$q_{21} = \mathcal{W}_{tot}\Delta\hat{Q}_{21} = \mathcal{W}_{tot}\int_1^2 T\mathrm{d}\hat{S} \qquad ; \qquad \wp_{21} = \mathcal{W}_{tot}\Delta\widehat{W}_{21}^{\mathrm{fl}} = \mathcal{W}_{tot}\int_1^2 \hat{V}\mathrm{d}P$$

but if the compressor is adiabatic, there will be no heat transfer ($\mathrm{d}\hat{Q}$=0) and $\Delta\hat{Q}_{21}$ and q_{21} become zero, so equation [1] gives

$$\mathrm{d}\widehat{W}^{\mathrm{fl}} = \mathrm{d}\widehat{H}$$

thus

$$\wp_{21} = \mathcal{W}_{tot}\Delta\widehat{W}_{21}^{\mathrm{fl}} = \mathcal{W}_{tot}\int_1^2 \mathrm{d}\widehat{H} = \mathcal{W}_{tot}\Delta\widehat{H}_{21} = \mathcal{W}_{tot}\left(\widehat{H}_2 - \widehat{H}_1\right)$$

$$\wp_{21} = \left(1\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(852\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 593\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 259\ \frac{\mathrm{kJ}}{\mathrm{s}}$$

Question g. In the passage from point 2 to 3

$$q_{32} = \mathcal{W}_{tot}\Delta\hat{Q}_{32} = \mathcal{W}_{tot}\int_2^3 T\mathrm{d}\hat{S} \qquad ; \qquad \wp_{32} = \mathcal{W}_{tot}\Delta\widehat{W}_{32}^{\mathrm{fl}} = \mathcal{W}_{tot}\int_2^3 \hat{V}\mathrm{d}P$$

However, if the heat exchanger is isobaric ($\mathrm{d}P$=0) there will be no flow work ($\mathrm{d}\widehat{W}^{\mathrm{fl}} = \hat{V}\mathrm{d}P$) or power, and equation [1] becomes

$$\mathrm{d}\widehat{H} = \mathrm{d}\hat{Q}$$

$$q_{32} = \mathcal{W}_{tot}\Delta\hat{Q}_{32} = \mathcal{W}_{tot}\int_2^3 \mathrm{d}\widehat{H} = \mathcal{W}_{tot}\Delta\widehat{H}_{32} = \mathcal{W}_{tot}\left(\widehat{H}_3 - \widehat{H}_2\right)$$

$$q_{32} = \left(1\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(460\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 852\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -392\ \frac{\mathrm{kJ}}{\mathrm{s}}$$

Question h. Since the heat exchanger is isobaric, this case is the same as in question **g**

$$q_{15} = \mathcal{W}_l\Delta\hat{Q}_{15} = \mathcal{W}_l\Delta\widehat{H}_{15} = \left(0.286\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(593\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 128\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 132.99\ \frac{\mathrm{kJ}}{\mathrm{s}}$$

Notice that the specific heat is multiplied by the liquid flow rate, not by the total one.

Question i. In this case the exchanger is also isobaric, and the transit from point 4 to point 6 will be as in questions **g** and **h**: zero power and heat flow calculable through the enthalpy difference

$$q_{64} = \hat{\mathcal{W}}_{tot}\Delta\hat{Q}_{64} = \hat{\mathcal{W}}_{tot}\left(\hat{H}_6 - \hat{H}_4\right) = \left(1\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(780\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 460\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 320\ \frac{\mathrm{kJ}}{\mathrm{s}}$$

Question j. In the isothermal compressor (transition from point 6 to point 3), the integral which determines the heat flow is simplified because T is constant and

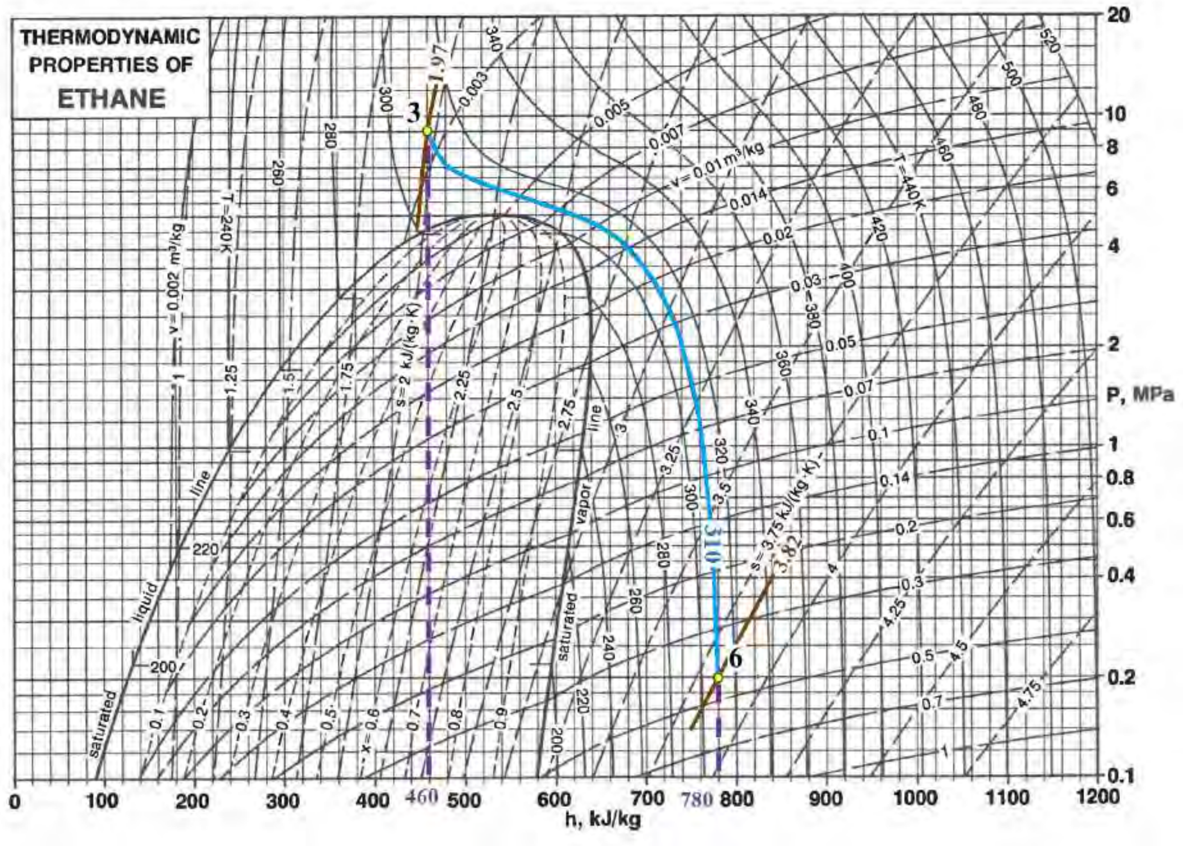
$$q_{36} = \hat{\mathcal{W}}_{tot}\Delta\hat{Q}_{36} = \hat{\mathcal{W}}_{tot}\int_6^3 T\mathrm{d}\hat{S} = \hat{\mathcal{W}}_{tot}T_6\int_6^3 \mathrm{d}\hat{S} = \hat{\mathcal{W}}_{tot}T_6\left(\hat{S}_3 - \hat{S}_6\right)$$

and the power can be calculated through equation [1] as

$$\mathrm{d}\hat{W}^{\mathrm{fl}} = \mathrm{d}\hat{H} - \mathrm{d}\hat{Q} = \mathrm{d}\hat{H} - T\mathrm{d}\hat{S}$$

$$\Delta\hat{W}^{\mathrm{fl}}_{36} = \int_6^3\left(\mathrm{d}\hat{H} - T\mathrm{d}\hat{S}\right) = \Delta\hat{H}_{36} - T_6\left(\hat{S}_3 - \hat{S}_6\right)$$

$$\wp_{36} = \hat{\mathcal{W}}_{tot}\Delta\hat{W}^{\mathrm{fl}}_{36} = \hat{\mathcal{W}}_{tot}\Delta\hat{H}_{36} - \hat{\mathcal{W}}_{tot}T_6\left(\hat{S}_3 - \hat{S}_6\right) = \hat{\mathcal{W}}_{tot}\Delta\hat{H}_{36} - q_{36}$$



After reading in figure V.15 the values of the needed entropies ($\hat{S}_3$ =1.97 kJ/kg·K and $\hat{S}_6$ =3.82 kJ/kg·K) it is found that

$$q_{36} = \left(1\ \frac{\mathrm{kg}}{\mathrm{s}}\right)(310\ \mathrm{K})\left(1.97\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 3.82\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = -573.5\ \frac{\mathrm{kJ}}{\mathrm{s}}$$

$$\wp_{36} = \left(1\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(460\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 780\frac{\mathrm{kJ}}{\mathrm{kg}}\right) - \left(-573.5\ \frac{\mathrm{kJ}}{\mathrm{s}}\right) = 253.5\ \frac{\mathrm{kJ}}{\mathrm{s}}$$

Question k. If ethane behaves as an ideal gas between points 6 and 3

$$\Delta\widehat{W}_{36}^{\mathrm{fl}} = \int_6^3 \hat{V}\mathrm{d}P = \int_6^3 \left(\frac{RT}{\mathfrak{M}_{ethane}P}\right)\mathrm{d}P = \frac{RT_6}{\mathfrak{M}_{ethane}}[\ln P]_6^3 = \frac{RT_6}{\mathfrak{M}_{ethane}}\ln\left(\frac{P_3}{P_6}\right)$$

By taking the molecular mass from the table of appendix II

$$\Delta\widehat{W}_{36}^{\mathrm{fl}} = \frac{\left(0.082\frac{\mathrm{atm\cdot L}}{\mathrm{K\cdot mol\text{-}g}}\right)(310\ \mathrm{K})}{\left(30.07\frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)}\ln\left(\frac{9\ \mathrm{MPa}}{0.2\ \mathrm{MPa}}\right) = 3.22\ \frac{\mathrm{atm\cdot L}}{\mathrm{g}}$$

and employing the conversion factors of appendix I

$$3.22\ \frac{\mathrm{atm\cdot L}}{\mathrm{g}} \times \frac{101\ \mathrm{J}}{1\ \mathrm{atm\cdot L}} \times \frac{1000\ \mathrm{g}}{1\ \mathrm{kg}} \times \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}} = 325.22\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\wp_{36} = \left(1\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(325.22\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 325.22\ \frac{\mathrm{kJ}}{\mathrm{s}}$$

This value is considerably higher than that calculated in the previous question.

6.10. A refrigerator can freeze 100 L of water from ambient conditions (20ºC and 1 atm) to 0ºC within 8 hours. The thermal fluid is ammonia, the temperature in the evaporator inside the refrigeration chamber is of -5ºC and that in the condenser outside the device is of 57ºC (both operating under isobaric conditions).

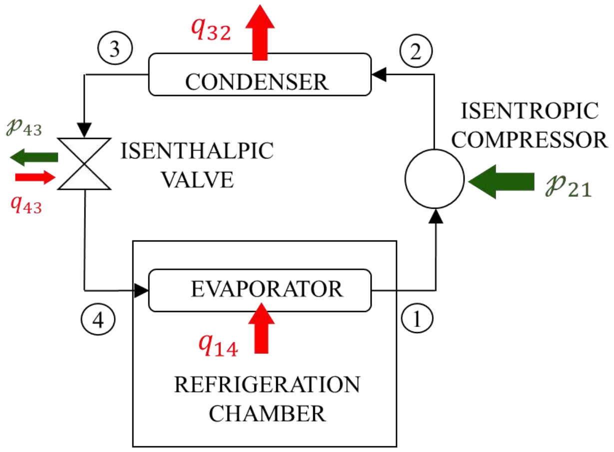
As is known, a compressor and an expander are required. The chosen compressor operates under isentropic conditions: the stream that leaves the evaporator (a two-phase mixture of 95% by mass of vapor ammonia and 5% by mass of liquid ammonia) passes through it and reaches the conditions to enter the condenser. The fluid that leaves this condenser is a liquid subcooled to 25ºC, and is expanded to the pressure of the evaporator in an isenthalpic valve. After that, it evaporates and becomes the aforesaid two-phase mixture.

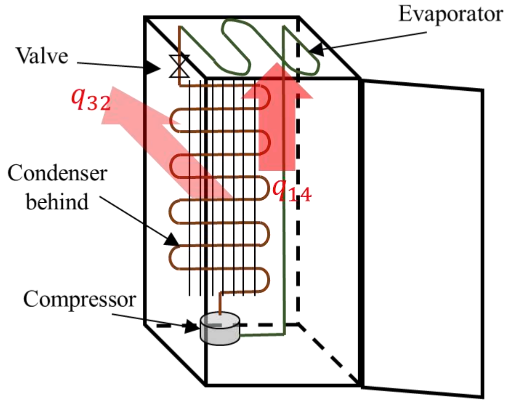
- **a) Represent a flowchart of the process, a diagram of the refrigerator (indicating the approximate location of its parts) and the evolution of H_2O and NH_3 temperatures with time.**
- **b) Qualitatively represent the thermodynamic path followed by the water in a *TH*(*P*) diagram and calculate the amount of heat to be removed.**
- **c) Express the heat flow to be removed in kJ/s.**
- **d) Quantitatively represent the thermodynamic path followed by ammonia in a *PH*(*T,S,V*) diagram and estimate the specific enthalpies and entropies at the main points of the cycle.**
- **e) Calculate the ammonia flow rate.**
- **f) Evaluate the heat flow released to the environment.**
- **g) Calculate the power requirement in the compressor.**
- **h) Determine the heat flow and power in the isenthalpic valve.**
- **i) Estimate the efficiency of the refrigerant.**
- **j) Qualitatively represent the ammonia cycle in *PT*(*S,H*), *PV*(*T,S,H*) and *TS*(*P,H*) diagrams, and indicate the works and heats in the last two.**
- **k) To improve the process efficiency, should the temperature of the fluid that enters the isenthalpic valve be increased or decreased?**

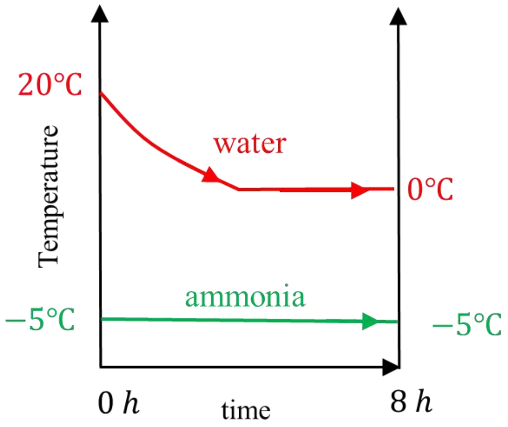
Data: density of water 1000 kg/m³, $\langle \widehat{C}_P \rangle$ of liquid water, 1 kcal/kgºC, solidification enthalpy of water, -80 kcal/kg.

Question a. Let "1" be the conditions of the thermal fluid at the exit of the evaporator, "2" be the conditions after compression, "3" be the state after leaving the condenser, and "4" be the stream after the isenthalpic expansion. A refrigerator is a reverse heat engine that consumes a mechanical power in the compressor ($\wp_{21}$) to absorb a heat flow from the refrigeration chamber by evaporation (q_{14}) and expel it by condensation to the surroundings of the refrigerator (along with other contributions, in the form of q_{32}). The condenser is usually placed behind the refrigerator, while the evaporator is on the top.

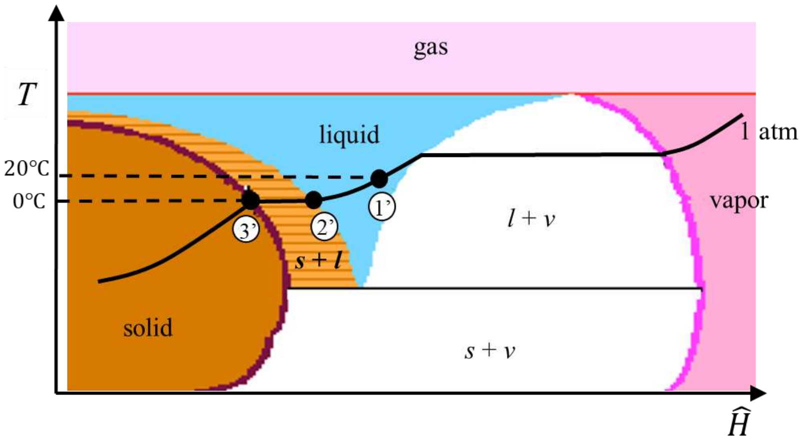
In this problem the absorption of heat in the chamber will cause the temperature to drop from 20ºC to 0ºC within 18 h, while the thermal fluid will remain at -5ºC.







Question b. Liquid water will initially be at 20ºC and 1 atm (point 1') and as time passes, temperature will decrease until 0ºC and 1 atm (point 2'). Then it will begin to solidify at that temperature. Finally, all the water will be ice at 0ºC and 1 atm (point 3').



The heat per unit mass given between 1' and 3' will be

$$\Delta\hat{Q}_{3'1'} = \int_{1'}^{3'} T\mathrm{d}\hat{S} = \begin{bmatrix}\text{heat per unit}\\ \text{mass from}\\ 20°\text{C to }0°\text{C}\end{bmatrix} + \begin{bmatrix}\text{solidification}\\ \text{heat per unit}\\ \text{mass at }0°\text{C}\end{bmatrix}$$

Fundamental thermodynamic relations of reference problem 0.3 indicate that these heats per unit mass will be equal to the specific enthalpies

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \qquad [1]$$

$$\text{if } \mathrm{d}P = 0 \quad \rightarrow \ \mathrm{d}\hat{H} = \mathrm{d}\hat{Q} \quad \rightarrow \quad \Delta\hat{H} = \Delta\hat{Q}$$

so by using the given $\hat{C}_P$ for water and the solidification enthalpy

$$\Delta\hat{Q}_{3'1'} = \Delta\hat{H}_{2'1'} + \Delta\hat{H}_{sol} = \int_{1'}^{2'} \hat{C}_P\mathrm{d}T + \Delta\hat{H}_{sol} = \langle\hat{C}_P\rangle(T_{2'} - T_{1'}) + \Delta\hat{H}_{sol}$$

$$\Delta\hat{Q}_{3'1'} = \left(1\ \frac{\text{kcal}}{\text{kg°C}}\right)(0°\text{C} - 20°\text{C}) - 80\ \frac{\text{kcal}}{\text{kg}} = -100\ \frac{\text{kcal}}{\text{kg}}$$

and the total heat involved in the cooling will be

$$\Delta Q_{3'1'} = M_{water}\Delta\hat{Q}_{3'1'} = \hat{\rho}_{water}V_{water}\Delta\hat{Q}_{3'1'}$$

$$\Delta Q_{3'1'} = \left(1000\ \frac{\text{kg}}{\text{m}^3}\right)(0.1\ \text{m}^3)\left(-100\ \frac{\text{kcal}}{\text{kg}}\right) = -10000\ \text{kcal}$$

Question c. Heat flow is determined by dividing the total heat by the time required for freezing. With the conversion factors from appendix I

$$\Delta Q_{3'1'} = -10000\ \text{kcal} \times \frac{4180\ \text{J}}{1\ \text{kcal}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = \text{-41800 kJ}$$

and the flow itself

$$q_{3'1'} = \frac{\Delta Q_{3'1'}}{\Delta t} = \frac{-41800\ \text{kJ}}{8\ \text{h}} \times \frac{1\ \text{h}}{3600\ \text{s}} = -\ 1.45\ \frac{\text{kJ}}{\text{s}}$$

This heat flow, although with the opposite sign, will be equal to that absorbed by NH_3 in the evaporator, i.e.

$$q_{3'1'} = -q_{14}$$

Question d. Figure V.12 of appendix V will be employed for this representation. In it, temperatures are expressed in K.

$$T_1(\mathrm{K}) = T_4(\mathrm{K}) = -5^\circ\mathrm{C} + 273 = 268\ \mathrm{K}$$

$$T_{condens}(\mathrm{K}) = 57^\circ\mathrm{C} + 273 = 330\ \mathrm{K}$$

$$T_3(\mathrm{K}) = 25^\circ\mathrm{C} + 273 = 298\ \mathrm{K}$$

The location of points 1 – 4 of the flow chart is done in four steps:

- Firstly, the 95% title line is interpolated, and its intersection with T_1=268 K will give point 1. It is also feasible to calculate the specific enthalpy at point 1 by combining the mass and enthalpy balances in it

  $$M_{tot} = M_{v_1} + M_{l_1}$$

  $$M_{tot}\hat{H}_1 = M_{v_1}\hat{H}^{sat}_{v_{268}} + M_{l_1}\hat{H}^{sat}_{l_{268}}$$

  After reading in the diagram the enthalpies of the saturated liquid ($\hat{H}^{sat}_{l_{268}}$) and the saturated vapor ($\hat{H}^{sat}_{v_{268}}$)

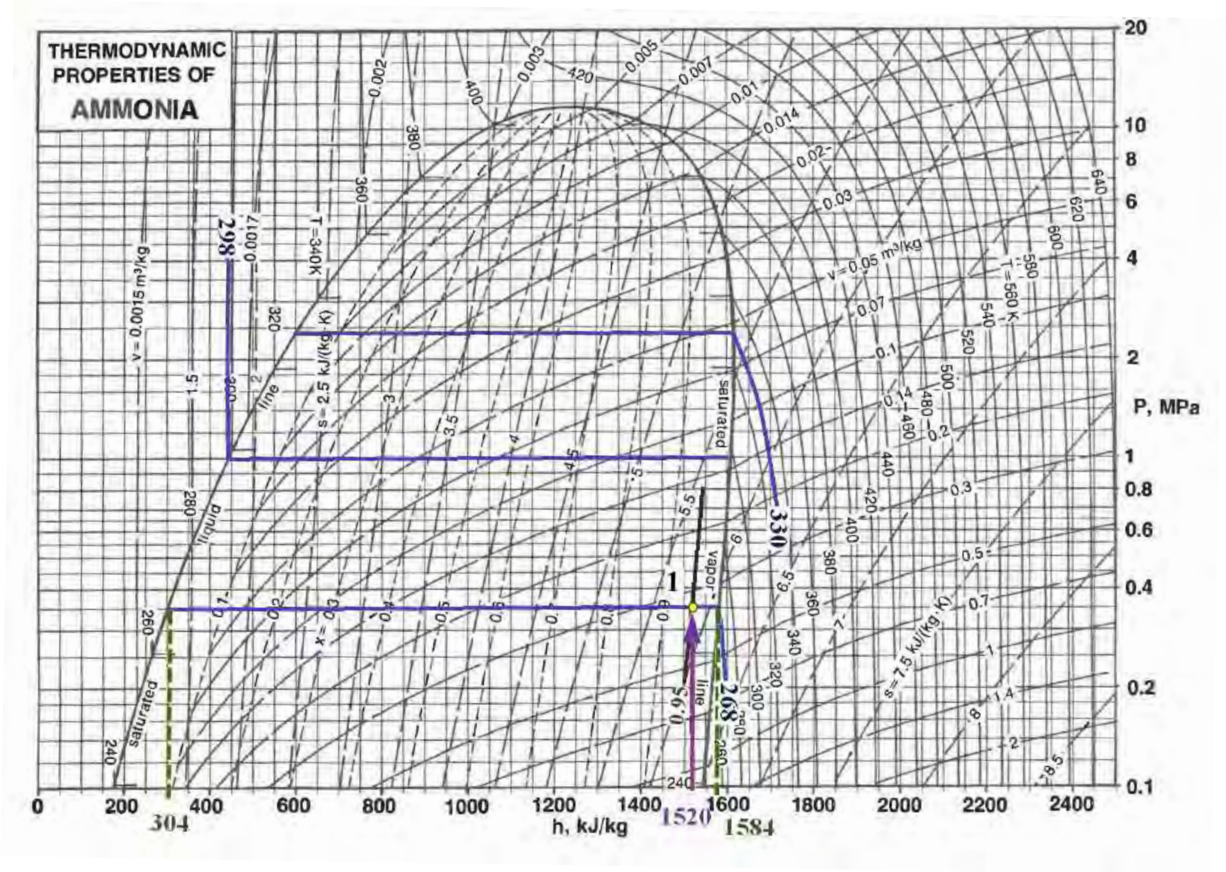
  $$\hat{H}_1 = \frac{M_{v_1}}{M_{tot}}\hat{H}^{sat}_{v_{268}} + \frac{M_{l_1}}{M_{tot}}\hat{H}^{sat}_{l_{268}} = 0.95\left(1584\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right)+0.05\left(304\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right)=1520\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

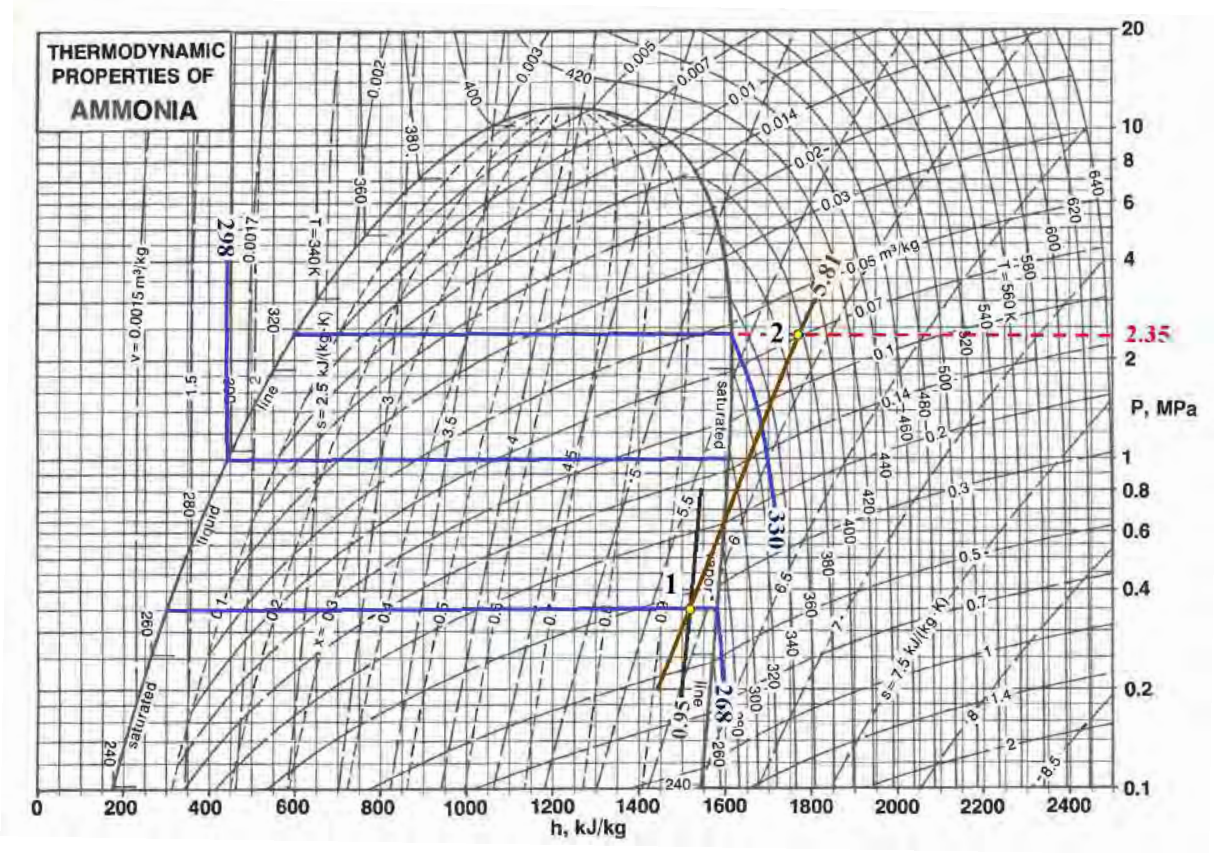
  the intersection between the isoenthalpic $\hat{H}_1$ =1520 kJ/kg and the isotherm T_1=268 K indicates point 1.

- The isentropic line that passes through 1 (5.81 kJ/kg·K) is then plotted. Its intersection with the vapor pressure corresponding to $T_{condens}$=330 K will give point 2.

- The intersection of the isobar corresponding to the vapor pressure at 330 K (2.35 MPa) with the isotherm T_3= 298 K will give point 3.

- The isenthalpic line which passes through 3 and intersects the isotherm T_1=268 will provide the location of point 4.


THERMODYNAMIC PROPERTIES OF AMMONIA
P, MPa
h, kJ/kg
v = 0.0015 m³/kg
T = 340 K
s = 2.5 kJ/(kg·K)
v = 0.05 m³/kg
T = 560 K
s = 7.5 kJ/(kg·K)
saturated liquid line
saturated vapor line
x = 0.3
298
330
268
0.95
1
304
1520
1584
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
0.1
0.2
0.4
0.6
0.8
1
2
4
6
8
10
20


THERMODYNAMIC PROPERTIES OF AMMONIA
P, MPa
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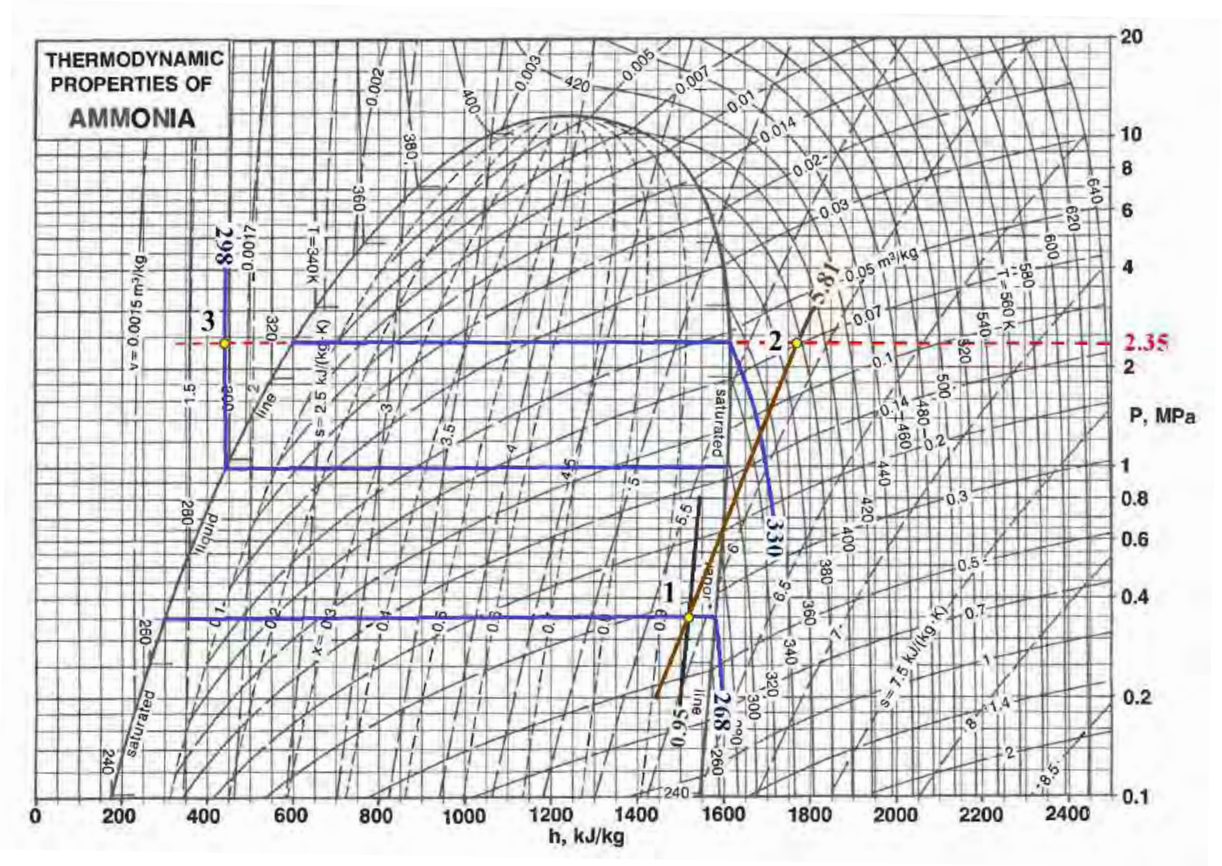
T = 340 K
s = 2.5 kJ/(kg·K)
v = 0.05 m³/kg
T = 560 K
s = 7.5 kJ/(kg·K)
saturated liquid line
saturated vapor line
x = 0.3
298
330
268
0.95
1
2
5.81
2.35
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
0.1
0.2
0.4
0.6
0.8
1
2
4
6
8
10
20


THERMODYNAMIC PROPERTIES OF AMMONIA
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2
3
298
330
268
0.95
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P, MPa
h, kJ/kg
T=340K
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s = 7.5 kJ/(kg·K)
v = 0.0015 m³/kg
0.05 m³/kg
T = 560 K
saturated liquid
saturated vapor line
x = 0.3
0.1
0.2
0.4
0.6
0.8
1
2
4
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0
200
400
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1200
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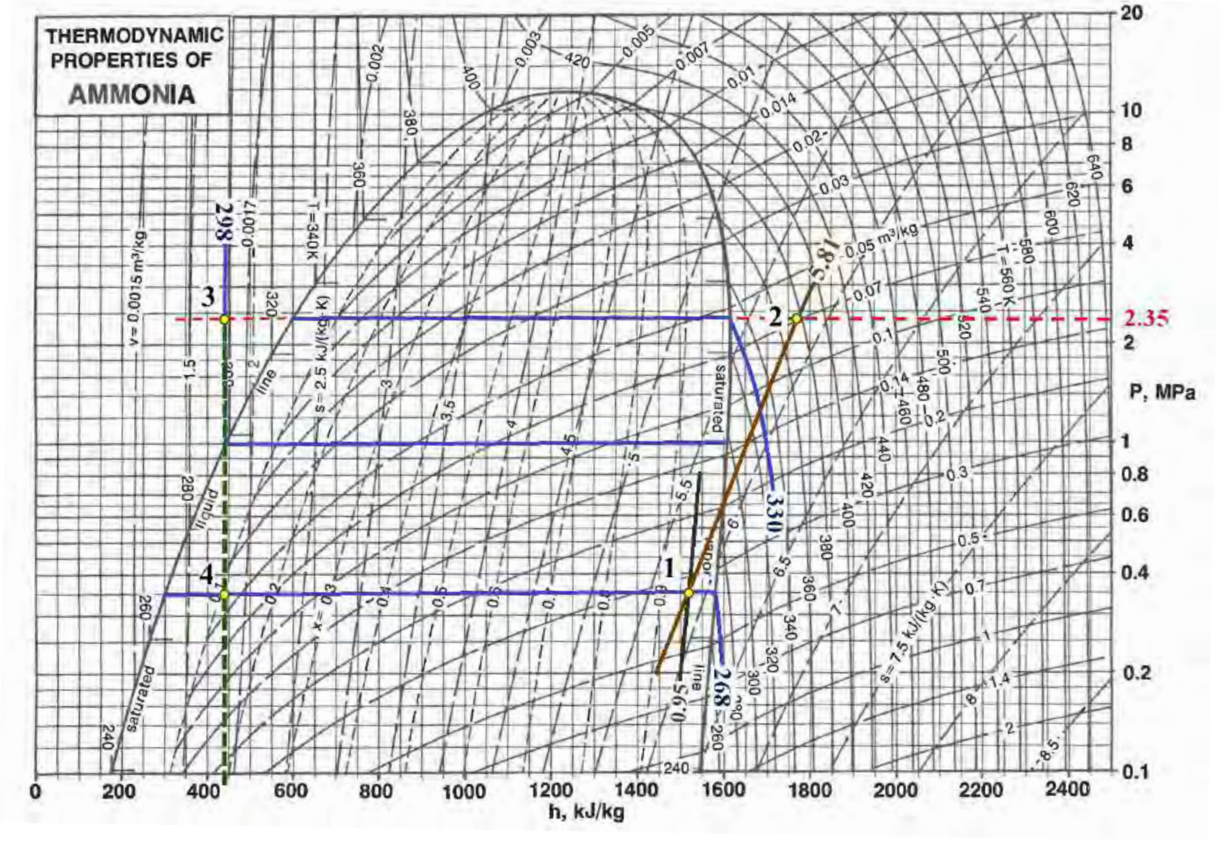
1600
1800
2000
2200
2400


THERMODYNAMIC PROPERTIES OF AMMONIA
1
2
3
4
298
330
268
0.95
5.81
2.35
P, MPa
h, kJ/kg
T=340K
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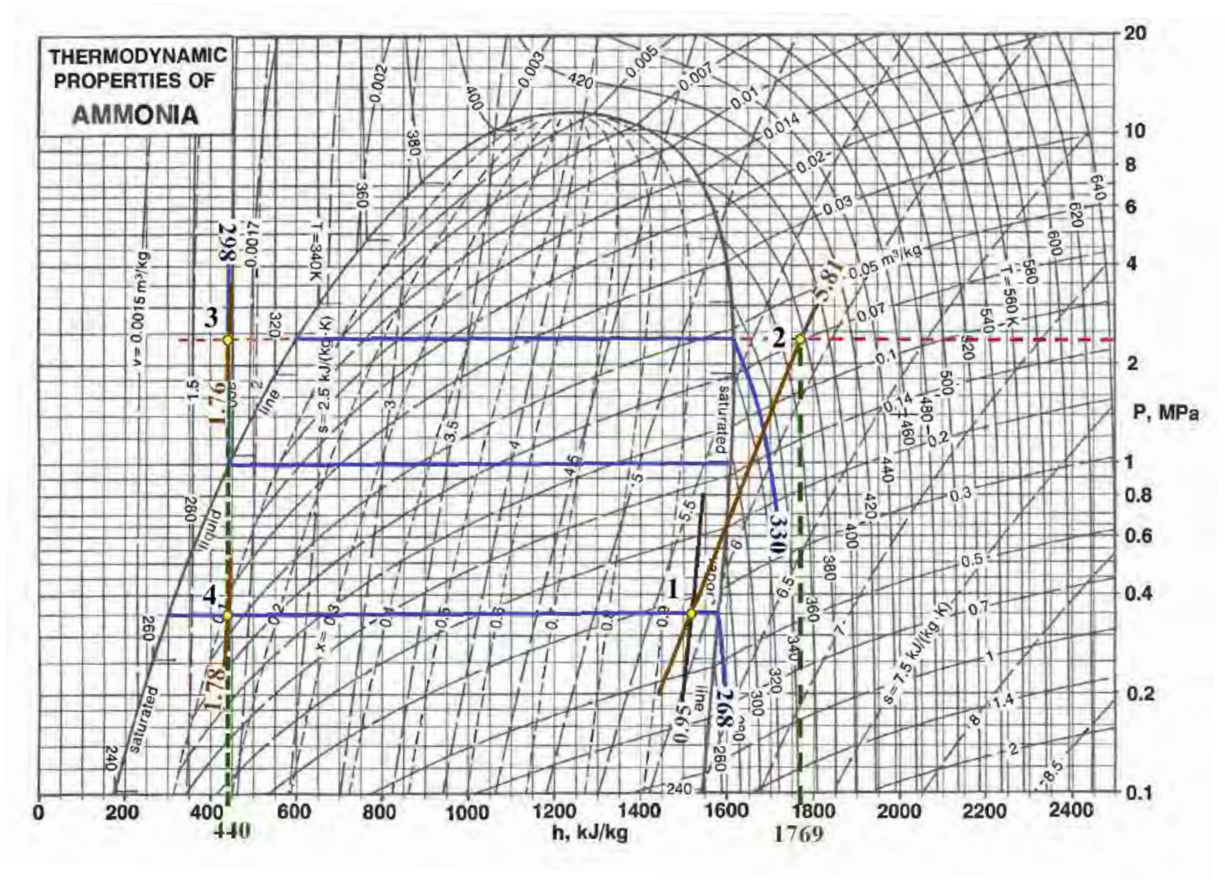
s = 7.5 kJ/(kg·K)
v = 0.0015 m³/kg
0.05 m³/kg
T = 560 K
saturated liquid
saturated vapor line
x = 0.3
0.1
0.2
0.4
0.6
0.8
1
2
4
6
8
10
20
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400

The other concerned enthalpies (apart from $\widehat{H}_1$ =1520 kJ/kg) will be $\widehat{H}_2$ = 1769 kJ/kg and $\widehat{H}_3 = \widehat{H}_4$ =440 kJ/kg, while the entropies will be $\hat{S}_3$ = 1.76 kJ/kg·K, $\hat{S}_4$ = 1.78 kJ/kg·K and $\hat{S}_1 = \hat{S}_2$ =5.81 kJ/kg·K (already obtained before).



Question e. As indicated in question **c**, $q_{3'1'} = -q_{14}$, being

$$q_{14} = \widehat{\mathcal{W}}\Delta\hat{Q}_{14} = \widehat{\mathcal{W}}\int_4^1 T\mathrm{d}\hat{S}$$

but due to the fact that the statement of the problem says that the evaporation is isobaric, the simplification of question **b** can be applied here as well, and $\Delta\hat{Q} = \Delta\widehat{H}$

$$\Delta\hat{Q}_{14} = \Delta\widehat{H}_{14} = \widehat{H}_1 - \widehat{H}_4 = 1520\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 440\ \frac{\mathrm{kJ}}{\mathrm{kg}} = 1080\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\widehat{\mathcal{W}} = \frac{q_{14}}{\Delta\hat{Q}_{14}} = \frac{1.45\ \frac{\mathrm{kJ}}{\mathrm{s}}}{\left(1080\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right)} = 1.34\cdot 10^{-3}\ \frac{\mathrm{kg}}{\mathrm{s}}$$

Additionally, notice that the isobaricity in the biphasic zone implies isothermality (T_1=T_4), so

$$\Delta\hat{Q}_{14} = T_1 \int_4^1 \mathrm{d}\hat{S} = T_1(\hat{S}_1 - \hat{S}_4) = (268\ \mathrm{K})\left(5.81 \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 1.78 \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = 1080.04\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}$$

which would lead to the same ammonia flow rate.

Question f. The condenser (transit from 2 to 3) is also isobaric. Thus, the heat flow can be calculated as in the previous question

$$q_{32} = \widehat{W}\Delta\hat{Q}_{32} = \widehat{W}\int_2^3 T\mathrm{d}\hat{S} = \widehat{W}\Delta\widehat{H}_{32}$$

$$q_{32} = \left(1.34 \cdot 10^{-3}\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(440\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 1769\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -1.78\ \frac{\mathrm{kJ}}{\mathrm{s}} = -1.78\ \mathrm{kW}$$

Question g. According to equation [1], the power of the compressor

$$\wp_{21} = \widehat{W}\Delta\widehat{W}_{21}^{\mathrm{fl}} = \widehat{W}\int_1^2 \hat{V}\mathrm{d}P$$

can be determined without numerical integration, because the device is isentropic ($\mathrm{d}\hat{S} = 0$) and

$$\mathrm{d}\widehat{H} = \mathrm{d}\widehat{W}^{\mathrm{fl}} \quad \rightarrow \quad \Delta\widehat{W}_{21}^{\mathrm{fl}} = \Delta\widehat{H}_{21}$$

Hence

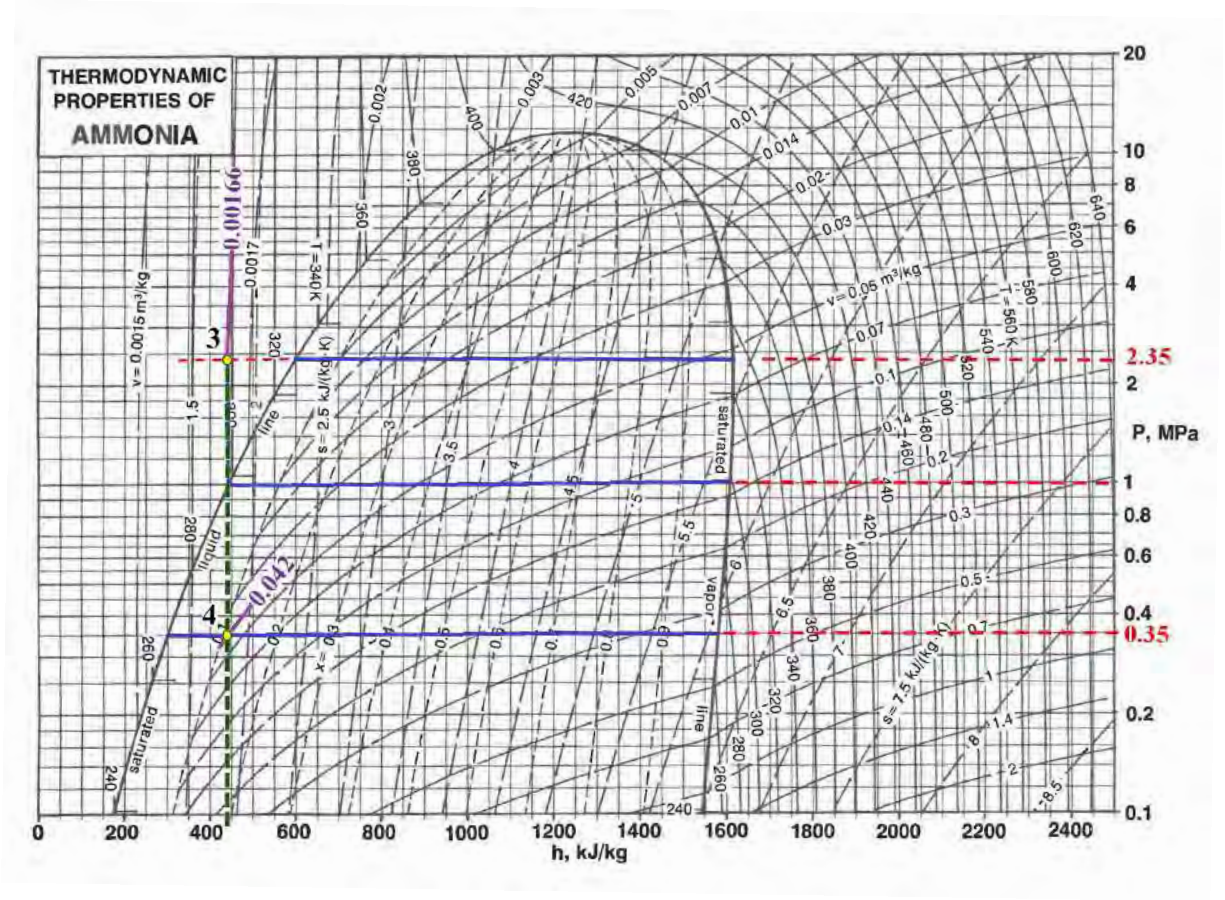
$$\wp_{21} = \left(1.34 \cdot 10^{-3}\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(1769\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 1520\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 0.33366\ \mathrm{kW}$$

Question h. According to equation [1], in an isenthalpic process

$$\mathrm{d}\widehat{H} = 0 = \mathrm{d}\hat{Q} + \mathrm{d}\widehat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P$$

$$T\mathrm{d}\hat{S} = -\hat{V}\mathrm{d}P \qquad \rightarrow \quad \Delta\hat{Q}_{43} = \int_3^4 T\mathrm{d}\hat{S} = -\int_3^4 \hat{V}\mathrm{d}P = -\Delta\widehat{W}_{43}^{\mathrm{fl}}$$

One of the integrals has to be estimated numerically (with the trapezoidal rule, for example). Since figure V.12 displays the pressure in one of the coordinate axes, it seems that the best option is to evaluate the flow work by giving values to the specific volume and reading the corresponding pressure along the isenthalpic (unfortunately, few data can be read becuse there are not very much isochores that intersect with this isenthalpic line).



$\hat{V}$ (m³/kg)	P (MPa)	$[P_i - P_{i-1}]\left(\frac{\hat{V}_i + \hat{V}_{i-1}}{2}\right)$
0.00166	2.35	
0.00166	1.0	-0.002241
0.042	0.35	-0.014189
	Sum=	-0.016430

The integration gives -0.01643 MPa·m³/kg, i.e., -16.43 kJ/kg; thus

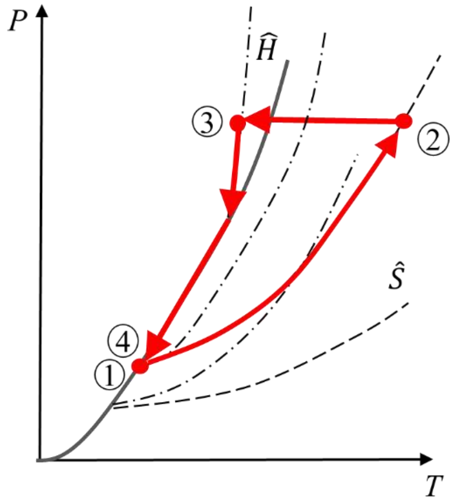
$$\wp_{43} = \left(1.34 \cdot 10^{-3}\ \frac{\text{kg}}{\text{s}}\right)\left(-16.43\ \frac{\text{kJ}}{\text{kg}}\right) = -0.022\ \frac{\text{kJ}}{\text{s}}$$

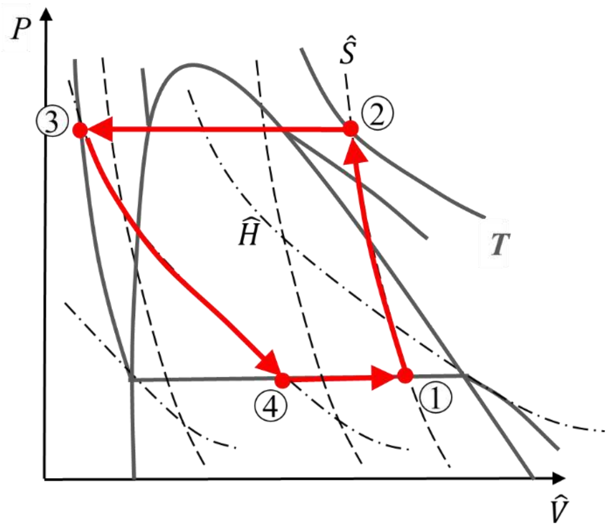
$$q_{43} = \left(1.34 \cdot 10^{-3}\ \frac{\text{kg}}{\text{s}}\right)\left(16.43\,\frac{\text{kJ}}{\text{kg}}\right) = 0.022\ \frac{\text{kJ}}{\text{s}}$$

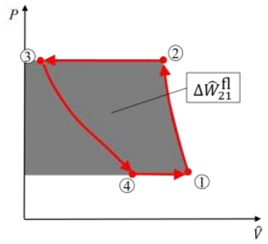
Question i. According to section d of reference problem 0.13, this efficiency will be equal to the absolute value of the quotient between the heat removed from the cold reservoir and the heat given tho the hot reservoir

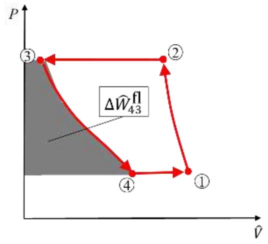
$$\text{refrigerant efficiency} = \left|\frac{q_{14}}{q_{32}}\right| = \left|\frac{1.45\ \mathrm{kJ/s}}{-1.78\ \mathrm{kJ/s}}\right| = 0.815$$

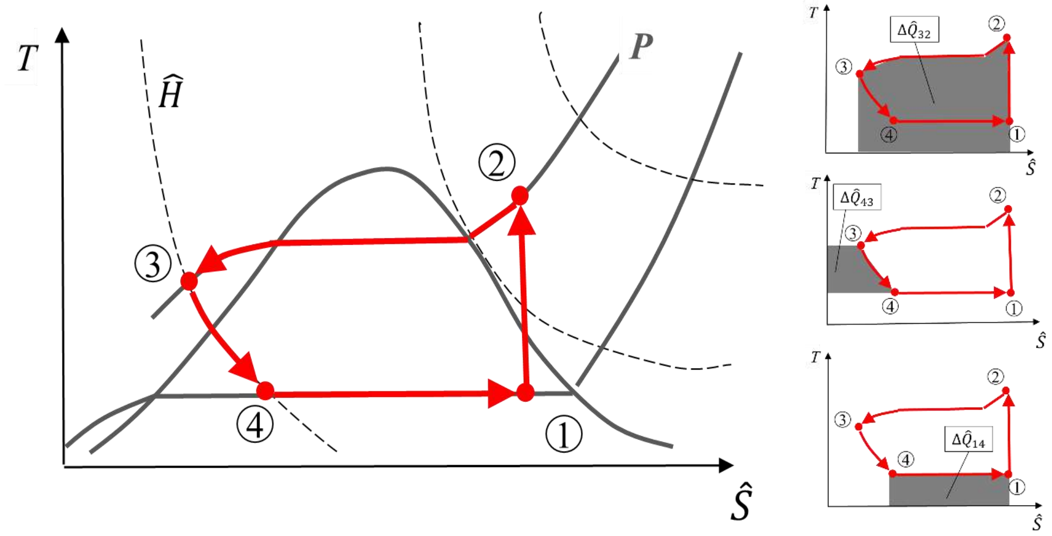
Question j. The representations in the *PT*(*S*,*H*), *PV*(*T*,*S*,*H*) and *TS*(*P*,*H*) diagrams indicating the areas which correspond to the works and heats will be











Question k. To increase efficiency, the heat given to the surroundings has to be closer to the value of the heat actually removed from the chamber. To do this, T_3 must be decreased, thereby reducing the enthalpy of 3 and 4. For example, if T_3 drops to 280 K, $\hat{H}_3 = \hat{H}_4 \approx 352$ kJ/kg and

$$\text{Refrigerant efficiency} = \left|\frac{q_{14}}{q_{32}}\right| = \left|\frac{\hat{H}_1 - \hat{H}_4}{\hat{H}_3 - \hat{H}_2}\right| = \left|\frac{1520 - 352}{352 - 1769}\right| = 0.824$$

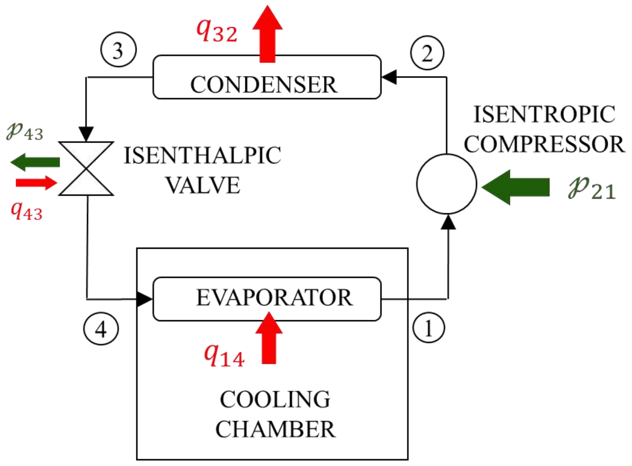
6.11. An amount of 25 kg of water at 15°C (and 1 atm) located in a cubic-shaped tank is cooled by an experimental freezer to -20°C in two hours. Propane is the thermal fluid and a potential of 10°C is maintained both in the evaporator inside the refrigeration chamber and in the condenser in contact with the surroundings. Both heat exchangers are isobaric.

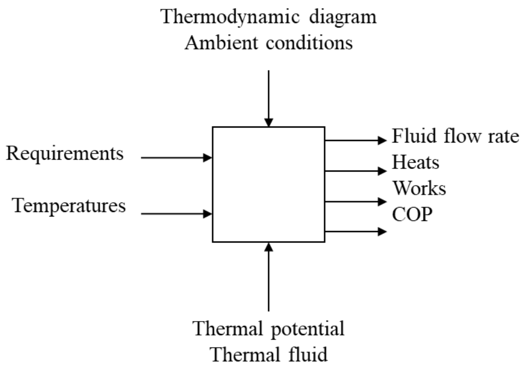
The freezer operates according to a reverse Carnot cycle, using an isentropic compressor after full evaporation and an isenthalpic expander after full condensation.

- **a) Represent the flowchart and the information flow diagram of the cycle.**
- **b) Qualitatively represent the thermodynamic path of the water in the cooling chamber in a *TH*(*P*) diagram and calculate the amount of heat to be removed.**
- **c) Determine the heat flow to be removed (in kJ/s).**
- **d) Estimate the heat transfer coefficient defined for the water tank surface.**
- **e) Quantitatively represent the thermodynamic path of propane in a *PH*(*T*,*S*,ρ) diagram and estimate the specific enthalpies and entropies at the main points of the cycle.**
- **f) Quantify the circulating flow of propane.**
- **g) Calculate the heat flow released to the surroundings.**
- **h) Evaluate the power of the compressor.**
- **i) Calculate the COP of the freezer.**

Data: density of water, 1000 kg/m³; $\langle \hat{C}_P \rangle$ of liquid water, 1 kcal/kg°C; $\langle \hat{C}_P \rangle$ of ice, 0.5 kcal/kg°C; solidification enthalpy of water, -80 kcal/kg.

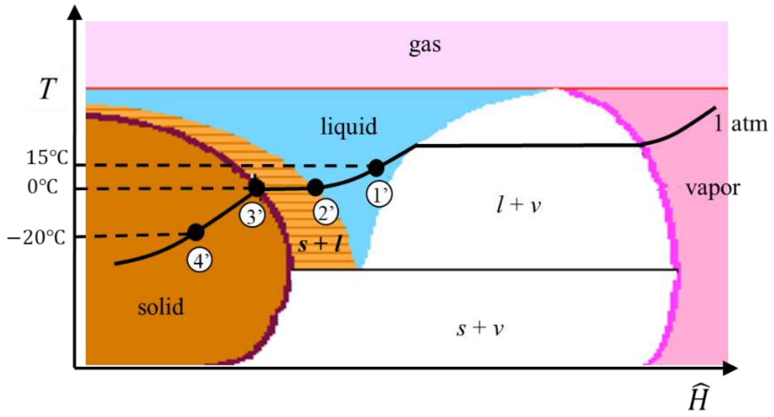
Question a. By calling “1” to the conditions of the propane at the exit of the evaporator, “2” to the conditions after compression, “3” to its state after passing through the condenser and “4” to the fluid after the isenthalpic expansion, the flowchart and the information flow diagram will be





Question b. Liquid water will initially be at 15ºC and 1 atm (point 1') and as time passes, temperature will isobarically decrease until reaching 0ºC (point 2'). Then it will begin to solidify at that temperature. When all the liquid becomes ice at 0ºC and 1 atm (point 3'), the solid temperature will start to decrease. Finally, the ice will be at -20°C and 1 atm (point 4'). The heat per unit mass of water and ice between 1' and 4' will be

$$\Delta\hat{Q}_{4'1'} = \int_{1'}^{4'} T\mathrm{d}\hat{S} = \begin{bmatrix}\text{heat per unit}\\ \text{mass of water}\\ \text{from 15°C to 0°C}\end{bmatrix} + \begin{bmatrix}\text{solidification}\\ \text{heat per unit}\\ \text{mass at 0°C}\end{bmatrix} + \begin{bmatrix}\text{heat per unit}\\ \text{mass of ice from}\\ \text{0°C to} -20\text{°C}\end{bmatrix}$$



However, since the cooling occurs at constant pressure, equations of reference problem 0.3 indicate that these heats per unit mass will be equal to the specific enthalpies

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \qquad [1]$$

$$\text{if } \mathrm{d}P = 0 \quad \rightarrow \mathrm{d}\hat{H} = \mathrm{d}\hat{Q} \quad \rightarrow \quad \Delta\hat{H} = \Delta\hat{Q}$$

Hence, if taking from the statement of the problem the specific heat capacities of liquid water and of ice and the enthalpy of solidification

$$\Delta\hat{Q}_{4'1'} = \Delta\hat{H}_{2'1'} + \Delta\hat{H}_{sol} + \Delta\hat{H}_{4'3'} = \int_{1'}^{2'} \hat{C}_{P_{water}}\mathrm{d}T + \Delta\hat{H}_{sol} + \int_{3'}^{4'} \hat{C}_{P_{ice}}\mathrm{d}T$$

$$\Delta\hat{Q}_{4'1'} = \langle\hat{C}_{P_{water}}\rangle(T_{2'} - T_{1'}) + \Delta\hat{H}_{sol} + \langle\hat{C}_{P_{ice}}\rangle(T_{3'} - T_{2'})$$

$$\Delta\hat{Q}_{4'1'} = \left(1\,\frac{\text{kcal}}{\text{kg°C}}\right)(0\text{°C} - 15\text{°C}) - 80\,\frac{\text{kcal}}{\text{kg}} + \left(0.5\,\frac{\text{kcal}}{\text{kg°C}}\right)(-20\text{°C} - 0\text{°C}) = -105\,\frac{\text{kcal}}{\text{kg}}$$

the total heat involved in the cooling will be

$$\Delta Q_{4'1'} = M_{water}\Delta\hat{Q}_{4'1'} = (25\text{ kg})\left(-105\,\frac{\text{kcal}}{\text{kg}}\right) = -2625\text{ kcal}$$

Question c. The quotient between the total heat and the freezing time gives the heat flow, which has to be expressed in kJ/kg.

$$\Delta Q_{4'1'} = -2625\ \text{kcal} \times \frac{4180\ \text{J}}{1\ \text{kcal}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = -\ 10972.5\ \text{kJ}$$

$$q_{4'1'} = \frac{\Delta Q_{4'1'}}{\Delta t} = \frac{-10972.5\ \text{kJ}}{2\ \text{h}} \times \frac{1\ \text{h}}{3600\ \text{s}} = -\ 1.52\ \frac{\text{kJ}}{\text{s}}$$

This heat flow (although with the opposite sign) will be the same as the one that the propane must absorb in the evaporator

$$q_{4'1'} = -q_{14}$$

Question d. According to section c of reference problem 0.12, the heat transfer coefficient is defined by

$$\text{k}_T = \frac{q}{\Delta T A} \qquad [2]$$

being ΔT the gradient or potential (10ºC, datum from the statement of the problem) and A the area of the cube where the water is contained, A=6L^2. The edge length of the cube is determined from its volume (and from the mass and the density of water) as

$$V = L^3 = \frac{M_{water}}{\hat{\rho}_{water}} = \frac{25\ \text{kg}}{1000\ \text{kg/m}^3} = 0.025\ \text{m}^3 \quad \rightarrow \quad L = \sqrt[3]{0.025\ \text{m}^3} = 0.2924\ \text{m}$$

Therefore, equation [2] gives

$$\text{k}_T = \frac{1.52\ \text{kJ/s}}{(10\text{°C})[6(0.2924\ \text{m})^2]} = 0.296\ \frac{\text{kJ}}{\text{s}\cdot\text{m}^2\cdot\text{°C}}$$

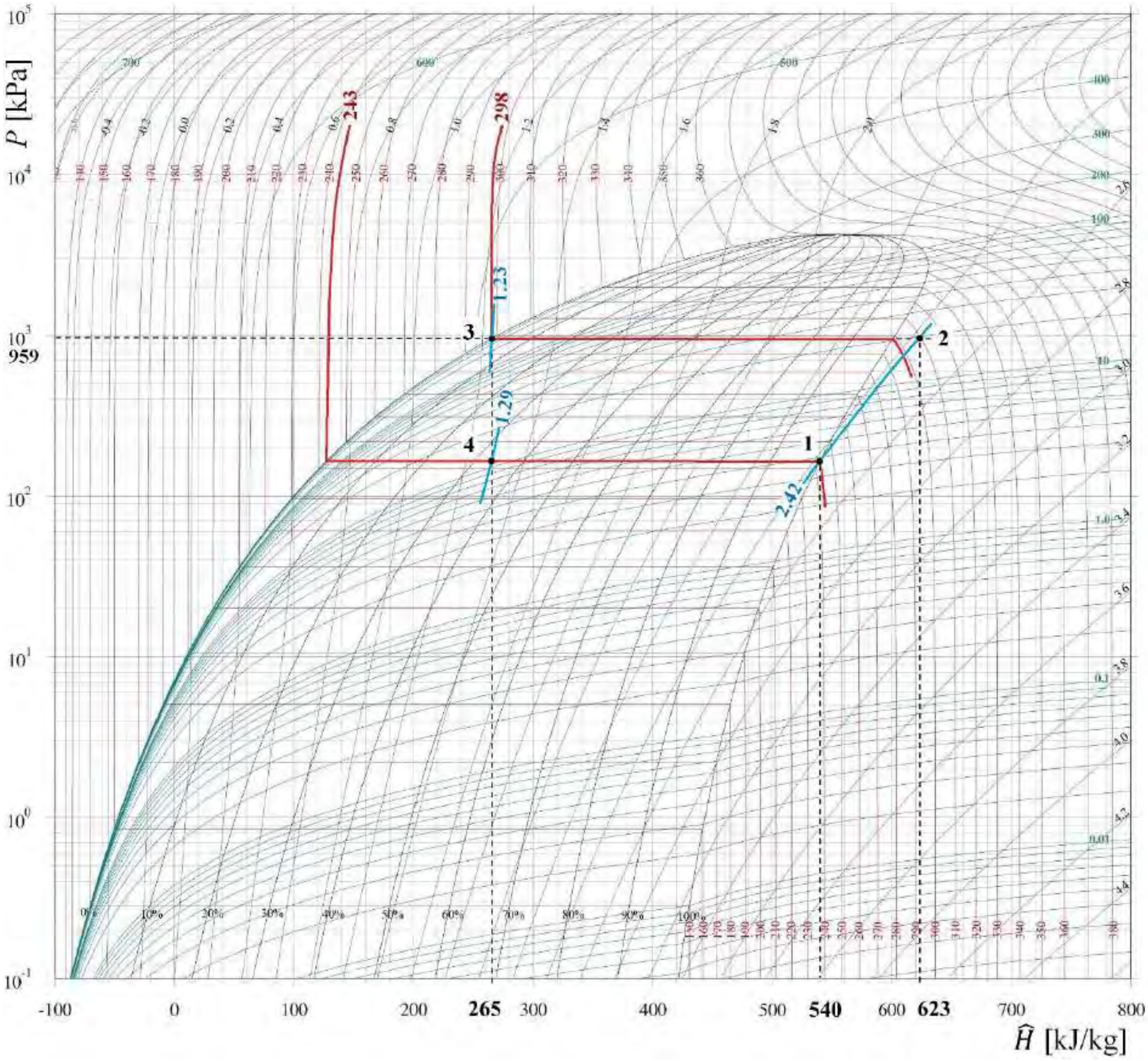
Question e. Due to the fact that the potential is of 10ºC, the evaporator should work at -20-10=-30ºC and the condenser at 15+10= 25ºC. Figure V.8 of appendix V will be employed for the requested representation after converting temperature units to K.

$$T_1(\text{K}) = T_4(\text{K}) = -30\text{°C} + 273 = 243\ \text{K}$$

$$T_3(\text{K}) = 25\text{°C} + 273 = 298\ \text{K}$$

Since the evaporation and the condensation are total, point 1 will be saturated vapor at 243 K and point 3, saturated liquid at 298 K. Point 4 will be placed by plotting the isenthalpic line that passes through 3 (vertical line) and looking for its intersection with the 243 K isotherm. Point 2 will be placed by interpolating the isentropic that passes through 1 and looking for its intersection with the vapor pressure at 298 K (959 kPa).

When the points are located, the corresponding enthalpies can be graphycally read, being $\widehat{H}_1$ =540 kJ/kg, $\widehat{H}_2$ = 623 kJ/kg and $\widehat{H}_3 = \widehat{H}_4$ =265 kJ/kg, while the entropies take values of $\hat{S}_1 = \hat{S}_2$ =2.42 kJ/kg·K, $\hat{S}_3$ = 1.23 kJ/kg·K and $\hat{S}_4$ = 1.29 kJ/kg·K.



Question f. As referred in question **c**, $q_{4'1'} = -q_{14}$, being

$$q_{14} = \widehat{W}\Delta\hat{Q}_{14} = \widehat{W}\int_4^1 T\mathrm{d}\hat{S}$$

but the evaporation is isobaric and the simplification of question **b** ($\Delta\hat{Q} = \Delta\widehat{H}$) will also be applied here

$$\Delta\hat{Q}_{14} = \Delta\hat{H}_{14} = \hat{H}_1 - \hat{H}_4 = 540\ \frac{\text{kJ}}{\text{kg}} - 265\ \frac{\text{kJ}}{\text{kg}} = 275\ \frac{\text{kJ}}{\text{kg}}$$

$$\hat{\mathcal{W}} = \frac{q_{14}}{\Delta\hat{Q}_{14}} = \frac{1.52\ \frac{\text{kJ}}{\text{s}}}{\left(275\ \frac{\text{kJ}}{\text{kg}}\right)} = 5.53 \cdot 10^{-3}\ \frac{\text{kg}}{\text{s}}$$

On the other hand, the evaporation is isothermal as well (because it happens within the biphasic zone), so

$$\Delta\hat{Q}_{14} = T_1 \int_4^1 \mathrm{d}\hat{S} = T_1\left(\hat{S}_1 - \hat{S}_4\right) = (243\ \text{K})\left(2.42\frac{\text{kJ}}{\text{kg·K}} - 1.29\frac{\text{kJ}}{\text{kg·K}}\right) = 274.59\ \frac{\text{kJ}}{\text{kg·K}}$$

a value that would have led to a propane flow rate of $5.54 \cdot 10^{-3}$ kg/s, the error being due to the inaccuracy inherent to the reading of data in graphs.

Question g. The heat flow in the condenser (step from 2 to 3) is also isobaric, and as in the previous question

$$q_{32} = \hat{\mathcal{W}}\Delta\hat{Q}_{32} = \hat{\mathcal{W}} \int_2^3 T\mathrm{d}\hat{S} = \hat{\mathcal{W}}\Delta\hat{H}_{32}$$

$$q_{32} = \left(5.53 \cdot 10^{-3}\ \frac{\text{kg}}{\text{s}}\right)\left(265\ \frac{\text{kJ}}{\text{kg}} - 623\ \frac{\text{kJ}}{\text{kg}}\right) = -1.98\ \frac{\text{kJ}}{\text{s}}$$

Question h. According to equation [1], the power in the compressor

$$\wp_{21} = \hat{\mathcal{W}}\Delta\hat{W}_{21}^{\text{fl}} = \hat{\mathcal{W}} \int_1^2 \hat{V}\mathrm{d}P$$

can be calculated without numerical integration, because it is isentropic ($\mathrm{d}\hat{S} = 0$) and so

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{W}^{\text{fl}} \quad \rightarrow \quad \Delta\hat{W}_{21}^{\text{fl}} = \Delta\hat{H}_{21}$$

$$\wp_{21} = \left(5.53 \cdot 10^{-3}\ \frac{\text{kg}}{\text{s}}\right)\left(623\ \frac{\text{kJ}}{\text{kg}} - 540\ \frac{\text{kJ}}{\text{kg}}\right) = 0.459\ \frac{\text{kJ}}{\text{s}}$$

Question i. Section d of reference problem 0.13 says that the $\text{COP}_{\text{cooling}}$ is the absolute value of the quotient between the heat released to the surroundings (in the condenser) and the power consumed (in the compressor), i.e.

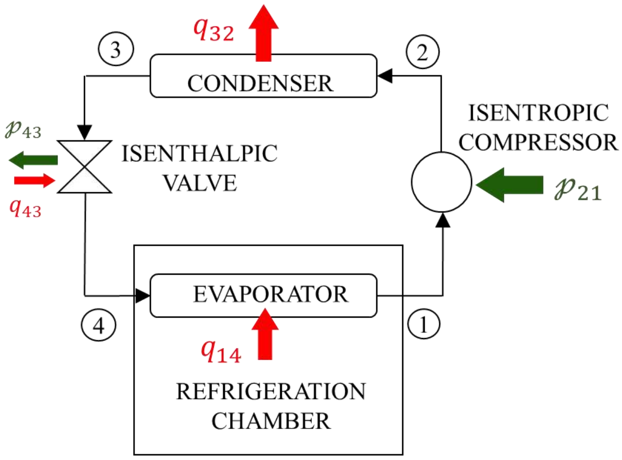
$$\text{COP}_{\text{cooling}} = \left|\frac{q_{32}}{\wp_{21}}\right| = \left|\frac{-1.98\ \text{kJ/s}}{0.459\ \text{kJ/s}}\right| = 4.31$$

6.12. It is necessary to freeze at -20°C in 4 hours four little pigs of 50 kg each by employing CO_2 as thermal fluid. The heat related to meat freezing is a 70% of the heat related to freeze the same mass of water at the same conditions. The meat is initially at 15°C and the thermal potential is of 10°C between the carbon dioxide and the meat in the freezing chamber and between CO_2 and the surroundings of the refrigerator (whose temperature is of 15°C). The cycle consists of an isenthalpic valve, an isobaric evaporator, an isentropic compressor and an isobaric condenser. On the other hand, all the thermal fluid leaves the evaporator as saturated vapor and leaves the condenser as saturated liquid.

a) Draw the flowchart of the cycle.
b) Calculate the amount of heat to remove to freeze the meat (in kcal).
c) Determine the heat flow to be removed (in kJ/s).
d) A fan must be installed when the heat transfer coefficient is higher than 10 kcal/(m^2·°C·min). If the heat transfer surface is that of the sphere with the same volume as that of the four little pigs, will the fan be required?
e) Quantitatively represent the thermodynamic path of carbon dioxide in a $TS(P,H,V)$ diagram and estimate the specific enthalpies and entropies at the main points of the cycle.
f) Quantify the circulating flow rate of propane.
g) Calculate the heat flow in the condenser.
h) Evaluate the power of the compressor.
i) Repeat questions e), f), g), h), i) with a $PH(T,S,\rho)$ diagram of carbon dioxide.

Data: density of water and of meat, 1000 kg/m³; $\langle \hat{C}_P \rangle$ of liquid water, 1 kcal/kg°C; $\langle \hat{C}_P \rangle$ of ice, 0.5 kcal/kg°C; solidification enthalpy of water, -80 kcal/kg.

Question a. By calling “1” to CO_2 after evaporation, “2” to the fluid after compression, “3” to the exit of the condenser and “4” to the stream that leaves the isenthalpic valve, the flowchart of the cycle is

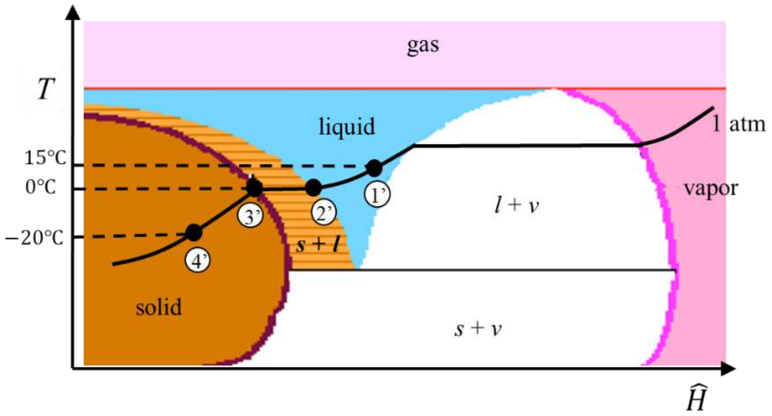


Question b. The statement of the problem says that the heat related to freezing the meat is a 70% of the heat related to freezing the same mass of water, so for freezing the four little pigs

$$\Delta Q_{meat} = 4\left(0.7 M_{water} \Delta \hat{Q}_{water}\right) \qquad [1]$$

As times goes by, liquid water at 15ºC and 1 atm (point 1') becomes saturated liquid at 0ºC and 1 atm (point 2'), saturated ice at the same temperature and pressure (point 3') and ice at -20ºC and 1 atm (point 4'). The heat per unit mass given by the water and the ice between 1' and 4' ($\Delta\hat{Q}_{4'1'} = \Delta\hat{Q}_{water}$) will be

$$\Delta\hat{Q}_{4'1'} = \int_{1'}^{4'} T\mathrm{d}\hat{S} = \begin{bmatrix}\text{heat per unit}\\ \text{mass of water}\\ \text{from 15°C to 0°C}\end{bmatrix} + \begin{bmatrix}\text{solidification}\\ \text{heat per unit}\\ \text{mass at 0°C}\end{bmatrix} + \begin{bmatrix}\text{heat per unit}\\ \text{mass of ice from}\\ \text{0°C to} - \text{20°C}\end{bmatrix}$$



But according to reference problem 0.3

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \qquad [2]$$

if the cooling takes place at constant pressure (dP=0)

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} \quad \rightarrow \quad \Delta\hat{H} = \Delta\hat{Q}$$

thus, by using the solidification enthalpy and the specific heat capacities of the statement of the problem

$$\Delta\hat{Q}_{4'1'} = \Delta\hat{H}_{2'1'} + \Delta\hat{H}_{sol} + \Delta\hat{H}_{4'3'} = \int_{1'}^{2'} \hat{C}_{P_{water}} \mathrm{d}T + \Delta\hat{H}_{sol} + \int_{3'}^{4'} \hat{C}_{P_{ice}} \mathrm{d}T$$

$$\Delta\hat{Q}_{4'1'} = \langle\hat{C}_{P_{water}}\rangle(T_{2'} - T_{1'}) + \Delta\hat{H}_{sol} + \langle\hat{C}_{P_{ice}}\rangle(T_{3'} - T_{2'})$$

$$\Delta\hat{Q}_{4'1'} = \left(1\ \frac{\text{kcal}}{\text{kg°C}}\right)(0°\text{C} - 15°\text{C}) - 80\ \frac{\text{kcal}}{\text{kg}} + \left(0.5\ \frac{\text{kcal}}{\text{kg°C}}\right)(-20°\text{C} - 0°\text{C}) = -105\ \frac{\text{kcal}}{\text{kg}}$$

and by introducing this value and the other from the statement in equation [1]

$$\Delta Q_{meat} = 4(0.7)(50\ \mathrm{kg})\left(-105\ \frac{\mathrm{kcal}}{\mathrm{kg}}\right) = -14700\ \mathrm{kcal}$$

Question c. By converting the heat of the previous question to kJ, and dividing it between the freezing time

$$\Delta Q_{meat} = -14700\ \mathrm{kcal} \times \frac{4180\ \mathrm{J}}{1\ \mathrm{kcal}} \times \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}} = -\ 61446\ \mathrm{kJ}$$

$$q_{meat} = \frac{\Delta Q_{meat}}{\Delta t} = \frac{-61446\ \mathrm{kJ}}{4\ \mathrm{h}} \times \frac{1\ \mathrm{h}}{3600\ \mathrm{s}} = -\ 4.26\ \frac{\mathrm{kJ}}{\mathrm{s}}$$

This flow, although with the opposite sign, will be the same as that which CO_2 must absorb in the evaporator, i.e.

$$q_{meat} = -q_{14}$$

Question d. According to section c of reference problem 0.12, the heat transfer coefficient is calculated as

$$\mathrm{k}_T = \frac{q}{\Delta TA}$$

where ΔT is the gradient or potential (10ºC, datum from the statement of the problem) and A the area of the sphere with the same volume as the four little pigs (not the area of four spheres) $A=\pi d^2$. The diameter of the sphere is determined from the total volume of the meat as

$$V = \frac{\pi}{6} d^3 = \frac{M_{meat}}{\hat{\rho}_{meat}} = \frac{4(50\ \mathrm{kg})}{1000\ \mathrm{kg/m^3}} = 0.2\ \mathrm{m^3} \quad \rightarrow \quad d = \sqrt[3]{\frac{6}{\pi}(0.2\ \mathrm{m^3})} = 0.7256\ \mathrm{m}$$

and so

$$\mathrm{k}_T = \frac{14700\ \mathrm{kcal/s}}{(10\mathrm{°C})[\pi(0.7256\ \mathrm{m})^2](4\ \mathrm{h})} \times \frac{1\ \mathrm{h}}{60\ \mathrm{min}} = 3.7\ \frac{\mathrm{kcal}}{\mathrm{min \cdot m^2 \cdot °C}}$$

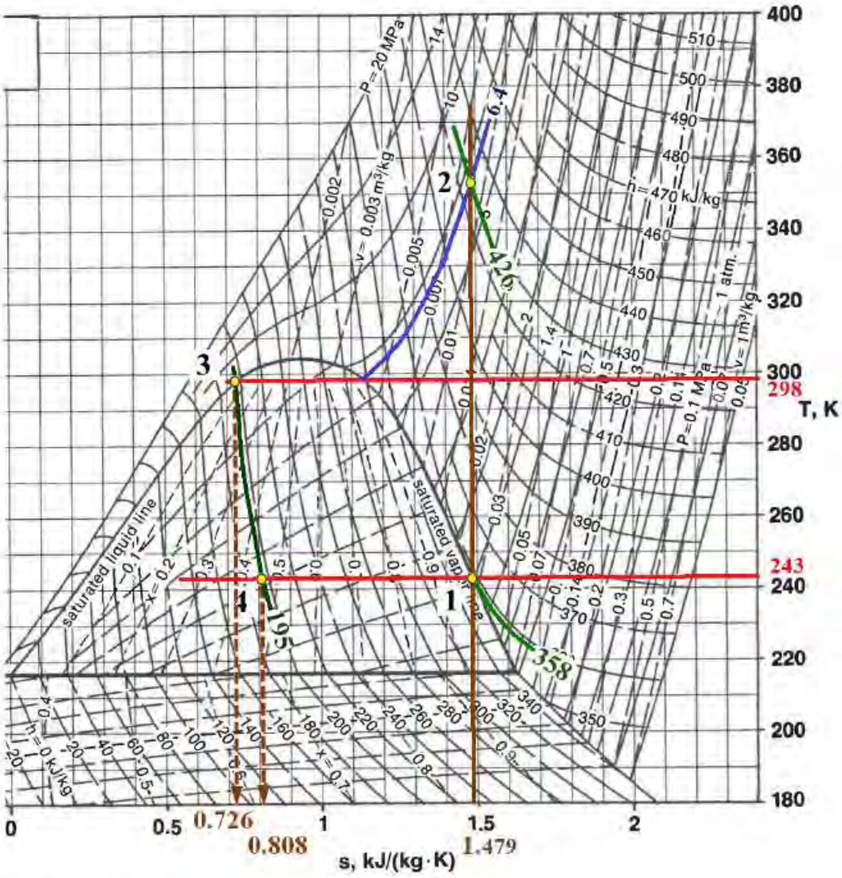
This value being lower than 10 kcal/($\mathrm{m^2 \cdot °C \cdot min}$), no fan is needed.

Question e. Since the potential is of 10ºC, the evaporator must work at a temperature of -20-10= -30ºC and the condenser at 15+10= 25ºC. Figure V.3 of appendix V (a *TS* diagram of CO_2) will be used for the representation after converting the temperature units to K.

$$T_1(\mathrm{K}) = T_4(\mathrm{K}) = -30\mathrm{°C} + 273 = 243\ \mathrm{K}$$

$$T_3(\mathrm{K}) = 25\mathrm{°C} + 273 = 298\ \mathrm{K}$$

The cycle works with total evaporation and total condensation, so point 1 will be saturated vapor at 243 K and point 3 saturated liquid at 298 K. Point 4 will be found by interpolating the isenthalpic that passes through 3 and looking for its intersection with the 243 K isotherm. Point 2 will be placed by drawing a vertical line (isentropic) through 1 and looking for the intersection of this line with the vapor pressure at 298 K (which is the same that corresponds to saturated vapor at 3, approximately 6.4 MPa).



After that, the enthalpies are seen to be $\hat{H}_1$ =358 kJ/kg, $\hat{H}_2 = 426$ kJ/kg and $\hat{H}_3 = \hat{H}_4$ =195 kJ/kg, while the entropies $\hat{S}_1 = \hat{S}_2$ =1.479 kJ/kg·K, $\hat{S}_3 = 0.726$ kJ/kg·K and $\hat{S}_4 = 0.808$ kJ/kg·K.

Question f. As said in question **c**, $q_{meat} = -q_{14}$

$$q_{14} = \widehat{\mathcal{W}}\Delta\hat{Q}_{14} = \widehat{\mathcal{W}}\int_4^1 T\,\mathrm{d}\hat{S}$$

The evaporation is isobaric, and $\Delta\hat{Q} = \Delta\hat{H}$ as in question **b**, so no numerical integration has to be performed.

$$\Delta\hat{Q}_{14} = \Delta\hat{H}_{14} = \hat{H}_1 - \hat{H}_4 = 358\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 195\ \frac{\mathrm{kJ}}{\mathrm{kg}} = 163\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

and the flow rate of CO_2 is

$$\hat{\mathcal{W}} = \frac{-q_{meat}}{\Delta\hat{Q}_{14}} = \frac{4.26\ \frac{\mathrm{kJ}}{\mathrm{s}}}{\left(163\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right)} = 26.13 \cdot 10^{-3}\ \frac{\mathrm{kg}}{\mathrm{s}}$$

On the other hand, the evaporation is isothermal as well (because it takes place within the biphasic zone). Therefore

$$\Delta\hat{Q}_{14} = T_1 \int_4^1 \mathrm{d}\hat{S} = T_1\left(\hat{S}_1 - \hat{S}_4\right) = (243\ \mathrm{K})\left(1.479\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 0.808\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = 163.053\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}$$

and the calculated flow rate would be practically the same.

Question g. The condenser (step from 2 to 3) is isobaric and the simplification of the previous section can be also applied

$$q_{32} = \hat{\mathcal{W}}\Delta\hat{Q}_{32} = \hat{\mathcal{W}} \int_2^3 T\mathrm{d}\hat{S}\ = \hat{\mathcal{W}}\Delta\hat{H}_{32}$$

$$q_{32} = \left(26.13 \cdot 10^{-3}\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(195\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 426\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -6.04\ \frac{\mathrm{kJ}}{\mathrm{s}} = -6.04\ \mathrm{kW}$$

Question h. The power in the compressor is given by definition as

$$\wp_{21} = \hat{\mathcal{W}}\Delta\hat{W}_{21}^{\mathrm{fl}} = \hat{\mathcal{W}} \int_1^2 \hat{V}\mathrm{d}P$$

but according to equation [2], if the apparatus is isentropic ($\mathrm{d}\hat{S} = 0$)

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{W}^{\mathrm{fl}} \quad \rightarrow \quad \Delta\hat{W}_{21}^{\mathrm{fl}} = \Delta\hat{H}_{21}$$

and

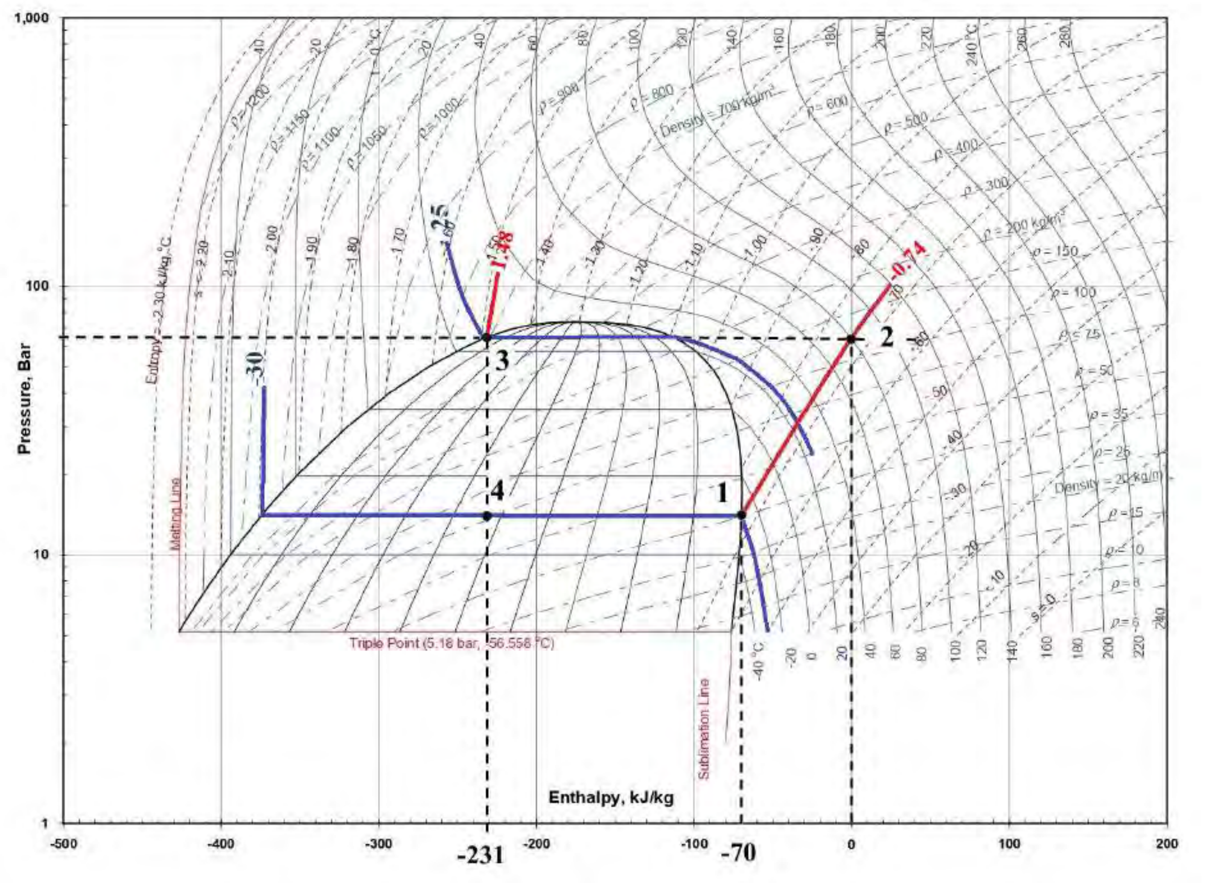
$$\wp_{21} = \left(26.13 \cdot 10^{-3}\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(426\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 358\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 1.78\ \frac{\mathrm{kJ}}{\mathrm{s}} = 1.78\ \mathrm{kW}$$

Question i. Figure V.2 of appendix V is a $PH(T, S, \rho)$ of CO_2. Temperatures are expressed in ºC. Point 1 corresponds to saturated vapor at -30ºC while point 3 corresponds to saturated liquid at 25ºC. Point 4 is located by drawing the isenthalpic that passes through 3 (vertical line) and looking for its intersection with the -30ºC isotherm. Point 2 is found graphically by interpolating the isentropic that passes through 1 and looking for the intersection of this line with the vapor pressure corresponding to 25ºC. The enthalpies read in the diagram take the values $\hat{H}_1$ =-70 kJ/kg, $\hat{H}_2 = 0$ kJ/kg and $\hat{H}_3 = \hat{H}_4$ =-231 kJ/kg, and the requested parameters are

$$\hat{\mathcal{W}} = \frac{-q_{meat}}{\Delta\hat{H}_{14}} = \frac{4.26\ \frac{\text{kJ}}{\text{s}}}{\left[-70\ \frac{\text{kJ}}{\text{kg}} - \left(-231\ \frac{\text{kJ}}{\text{kg}}\right)\right]} = 26.46\cdot 10^{-3}\ \frac{\text{kg}}{\text{s}}$$

$$q_{32} = \hat{\mathcal{W}}\Delta\hat{H}_{32} = \left(26.46\cdot 10^{-3}\ \frac{\text{kg}}{\text{s}}\right)\left(-231\ \frac{\text{kJ}}{\text{kg}} - 0\ \frac{\text{kJ}}{\text{kg}}\right) = -6.11\ \frac{\text{kJ}}{\text{s}} = -6.11\ \text{kW}$$

$$\wp_{21} = \hat{\mathcal{W}}\Delta\hat{H}_{21} = \left(26.46\cdot 10^{-3}\ \frac{\text{kg}}{\text{s}}\right)\left[0\ \frac{\text{kJ}}{\text{kg}} - \left(-70\ \frac{\text{kJ}}{\text{kg}}\right)\right] = 1.85\ \text{kW}$$



results that are very close to those calculated in the preceding questions.

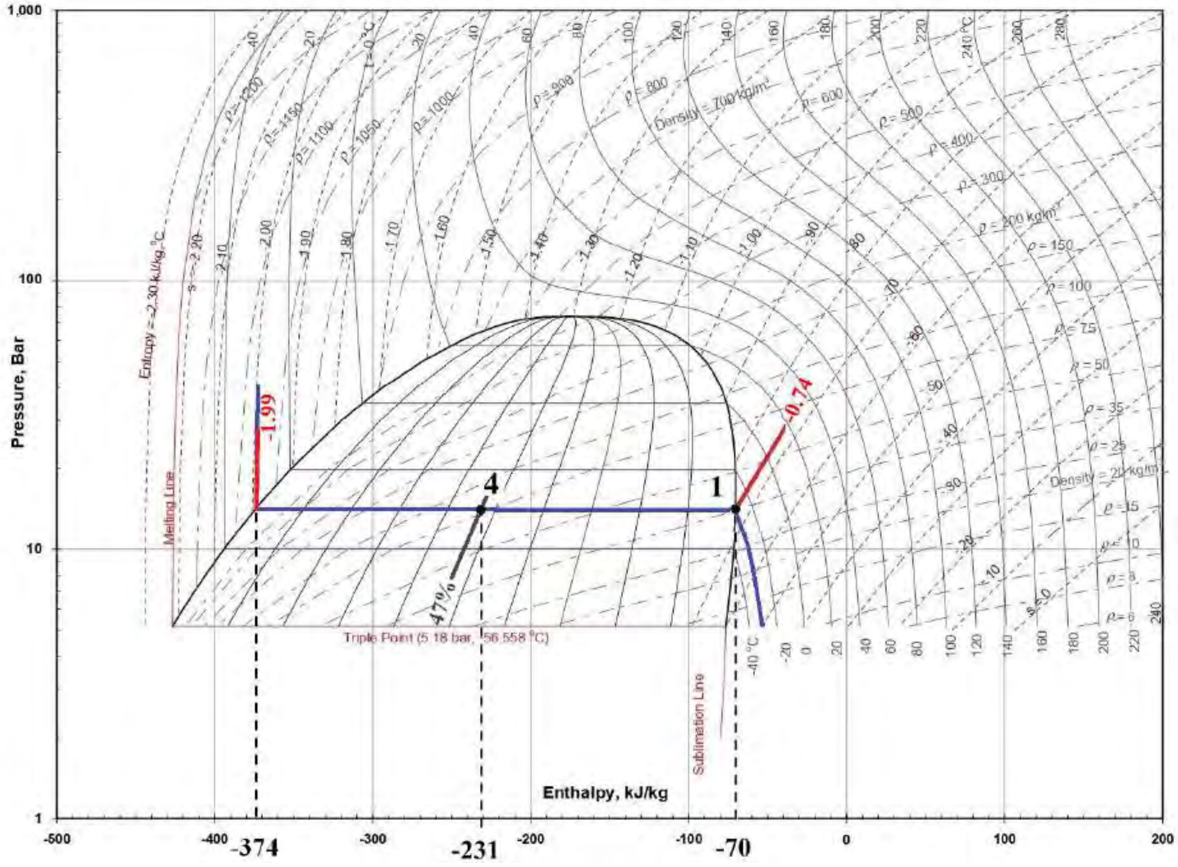
Regarding the entropies, $\hat{S}_1 = \hat{S}_2$ =-0.74 kJ/kg·K and $\hat{S}_3 = 1.48$ kJ/kg·K, but that of point 4 cannot be directly read because in this figure the isentropic lines do not enter the biphasic zone. However, it can be determined by combining the mass and entropy balances at that point.

$$\hat{S}_4 = \frac{M_{v_4}}{M_{tot}}\hat{S}_{v_4}^{sat} + \frac{M_{l_4}}{M_{tot}}\hat{S}_{l_4}^{sat} = \frac{M_{v_4}}{M_{tot}}\hat{S}_{v_4}^{sat} + \left(1 - \frac{M_{v_4}}{M_{tot}}\right)\hat{S}_{l_4}^{sat}$$

The vapor fraction (M_{v_4}/M_{tot}) can be evaluated by interpolating the title or quality lines (≈47%) or by combining the mass and enthalpy balances in the form

$$\frac{M_{v_4}}{M_{tot}} = \frac{\left(\hat{H}_4 - \hat{H}_l^{sat}\right)}{\left(\hat{H}_v^{sat} - \hat{H}_l^{sat}\right)} = \frac{(-231 + 374)}{(-70 + 374)} = 0.4704$$

$$\hat{S}_4 = 0.4704\left(-0.74\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) + (1 - 0.4704)\left(-1.99\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = -\,1.402\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$



and, from here

$$\Delta\hat{Q}_{14} = T_1\left(\hat{S}_1 - \hat{S}_4\right) = (243\ \mathrm{K})\left[-0.74\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - \left(-1.402\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right)\right] = 160.866\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}$$

$$\hat{\mathcal{W}} = \frac{-q_{meat}}{\Delta\hat{Q}_{14}} = \frac{4.26\ \frac{\mathrm{kJ}}{\mathrm{s}}}{\left(160.866\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right)} = 26.48 \cdot 10^{-3}\ \frac{\mathrm{kg}}{\mathrm{s}}$$

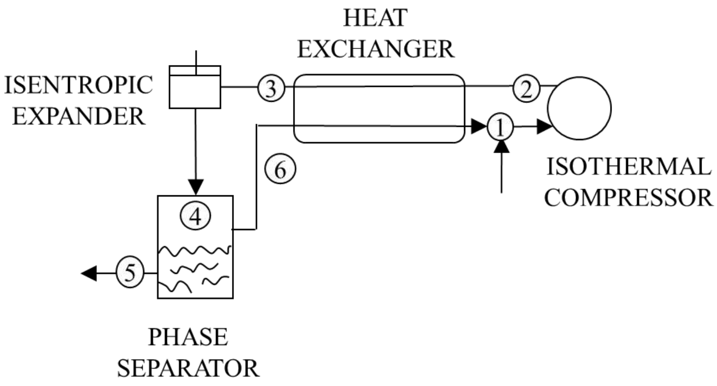
6.13. Draw the flowchart and represent in the $PH(T,S)$, $PV(T,S,H)$, $TS(P,H)$, $TH(P,S)$ and $PT(H,S)$ diagrams:

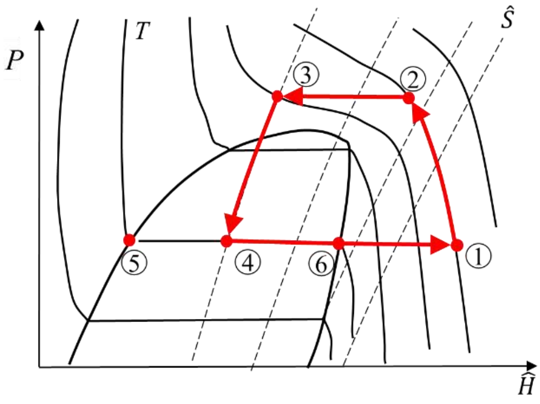
a) The Claude process.

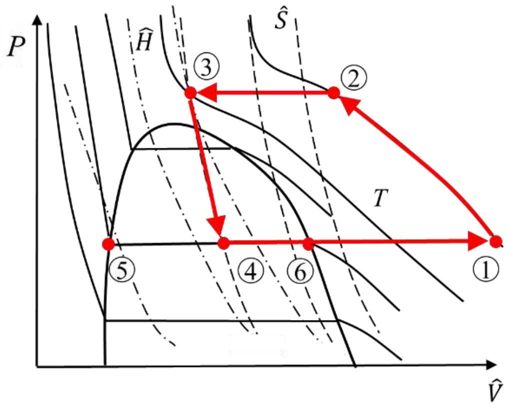
b) The Linde process.

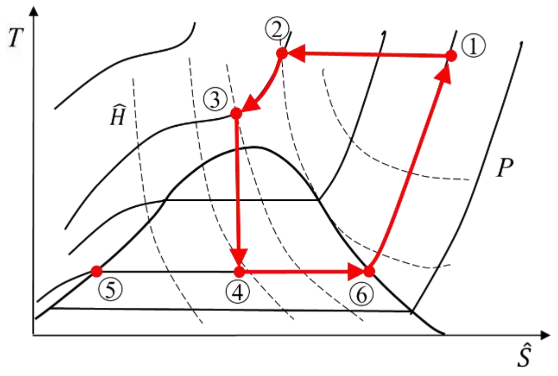
c) An acyclic vapor liquefaction process that begins with a reversible adiabatic compression, includes a phase change in the heat exchanger and ends with isenthalpic expansion in a valve, reaching a pressure similar to that of the feed but at a different temperature. Add information flow diagrams for the different operations.

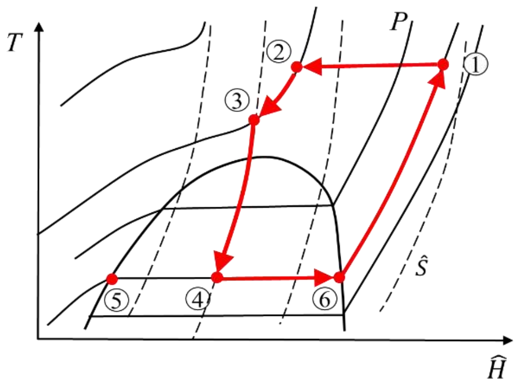
Question a. In section e of reference problem 0.13 it is said that the Claude process consists of isothermal compression of the feed (from 1 to 2), isobaric heating to a point 3, adiabatic and reversible expansion (isentropic) to the biphasic zone 4 and separation of phases (5 and 6). The vapor phase (6) can be passed through the isobaric heat exchanger (to save energy) and added to the feed in order to replace the liquid withdrawn in 5.

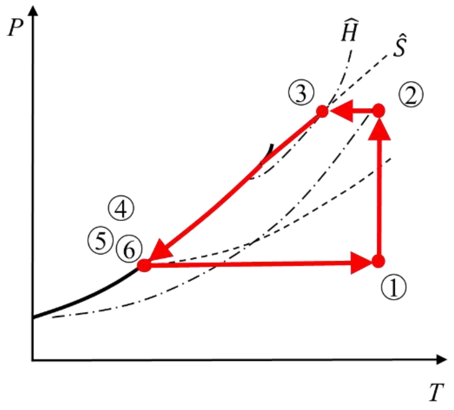




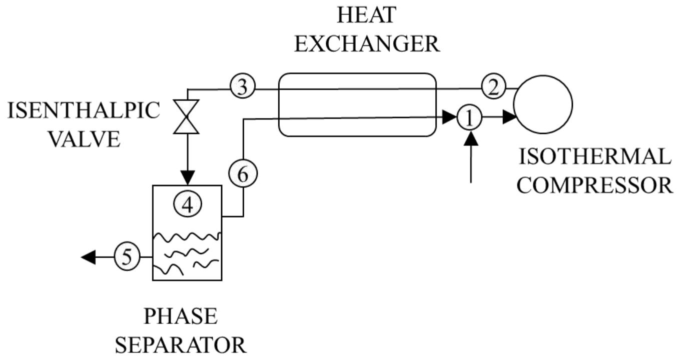




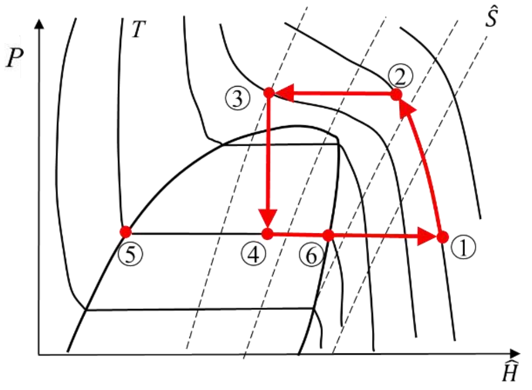


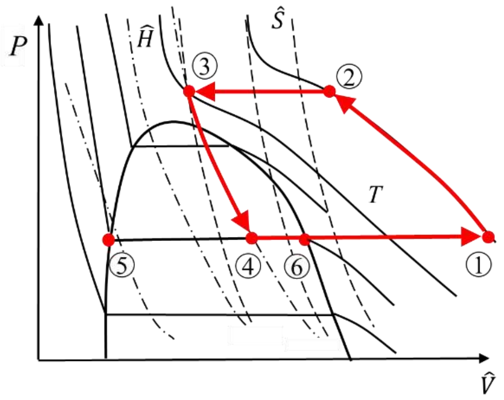


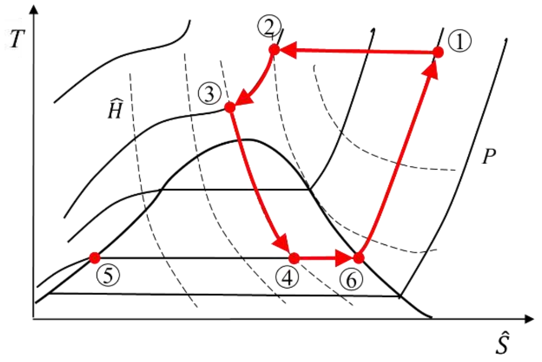
Question b. The Linde process is similar to that of Claude, but instead of reversible adiabatic expansion from 3 to the biphasic zone 4, it uses isenthalpic expansion through a low –in the best case, zero– friction valve. Its flowchart will be

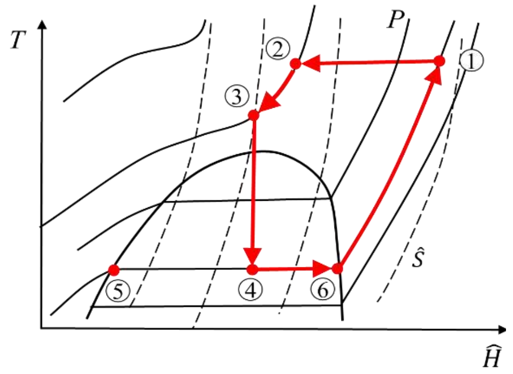


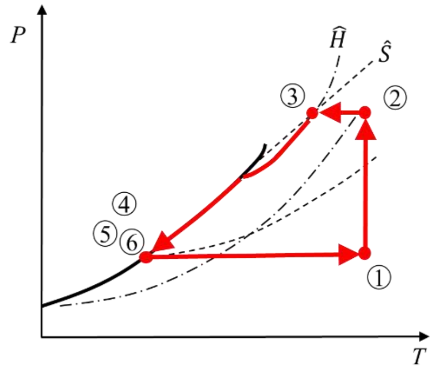
and the representantions in the qualitative *PH*(*T*,*S*), *PV*(*T*,*S*,*H*), *TS*(*P*,*H*), *TH*(*P*,*S*) and *PT*(*H*,*S*) diagrams are



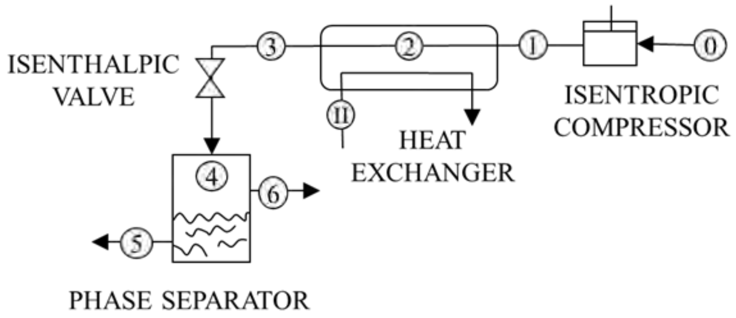


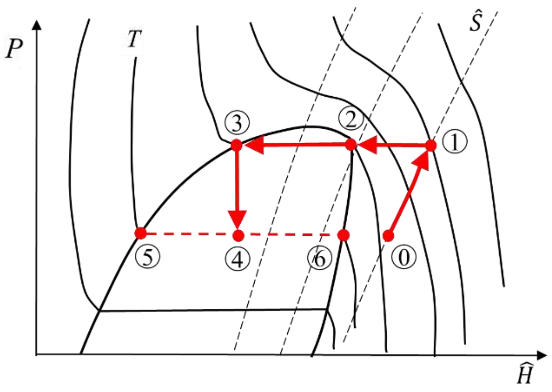


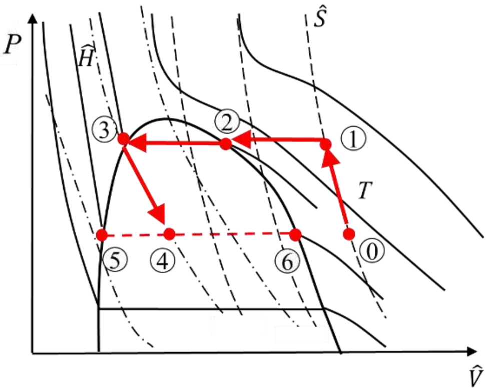


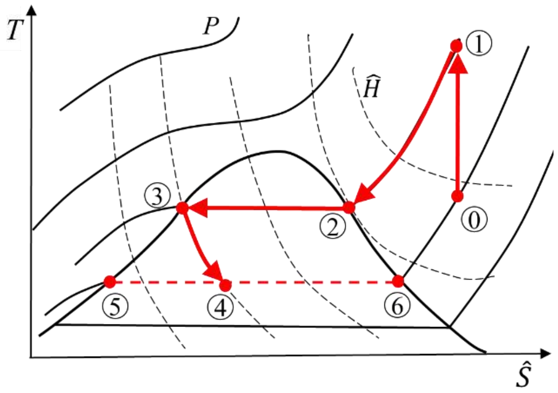


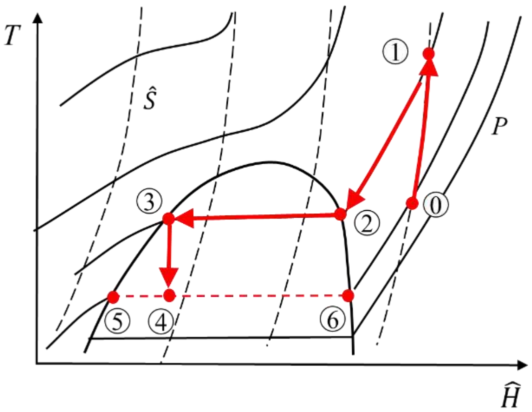
Question c. In the acyclic process suggested, a feed at 0 suffered an adiabatic and reversible compression (isentropic) to 1, a phase change within the heat exchanger (2), enters the valve in 3 and exits it at a pressure similar to that of the feed but at a different temperature.

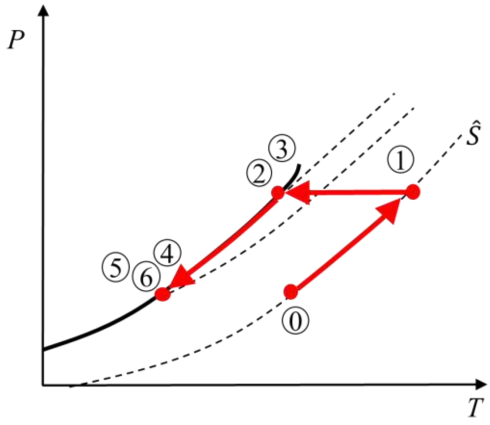




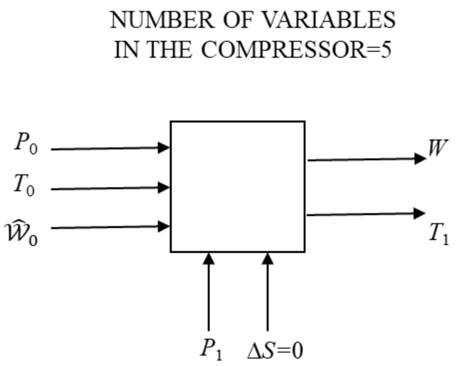








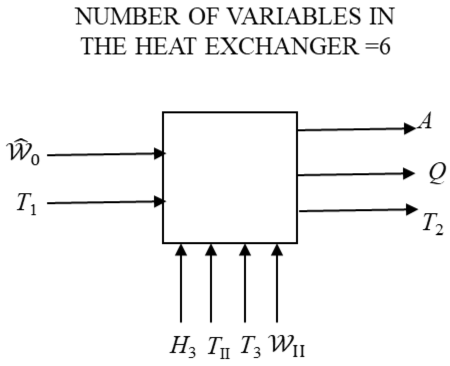
And the information flow diagrams for the several operations are

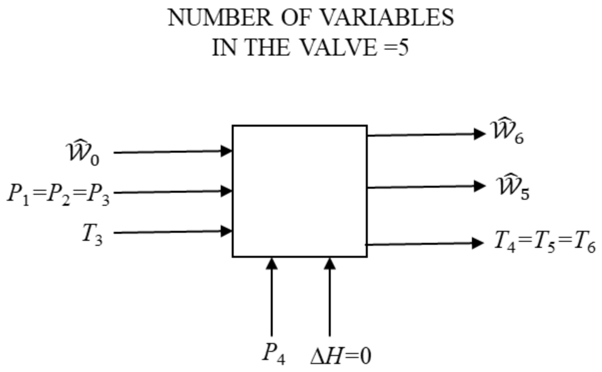


Mass balance $\hat{W}_0 = \hat{W}_1$

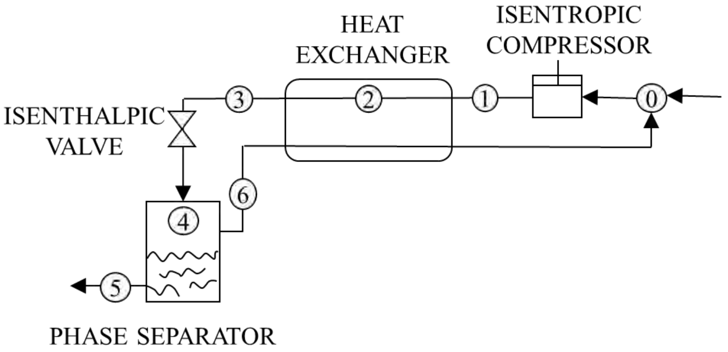
Energy balance $\left(-W_{21}^{\text{fl}}\right) = H_2 - H_1$

Pressure change $\left(\frac{\hat{W}_0}{\hat{\rho}_0}\right)^{\gamma} P_0 = \left(\frac{\hat{W}_1}{\hat{\rho}_1}\right)^{\gamma} P_1$





If the process was cyclic



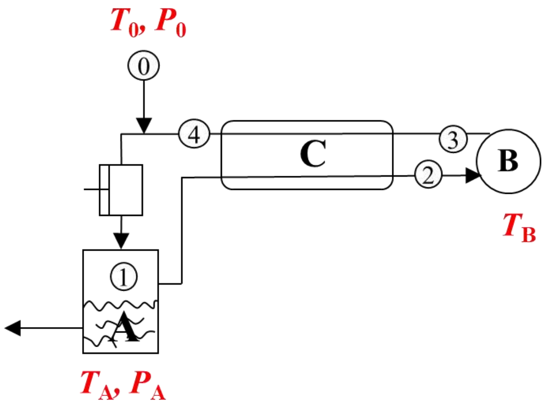
$$\widehat{\mathcal{W}}_{\mathrm{II}} = \widehat{\mathcal{W}}_6$$

$$T_{\mathrm{II}} = T_4$$

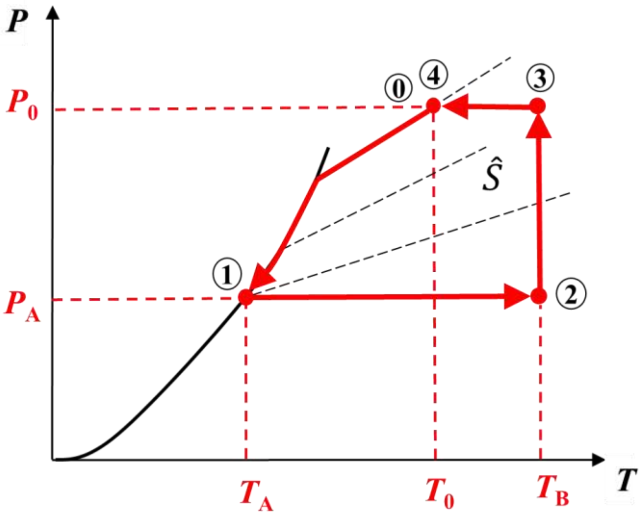
6.14. Draw the flowchart and represent in *PT*(*S*), *PV*(*S*) and Mollier diagrams the following thermodynamic cycle whose stages were:

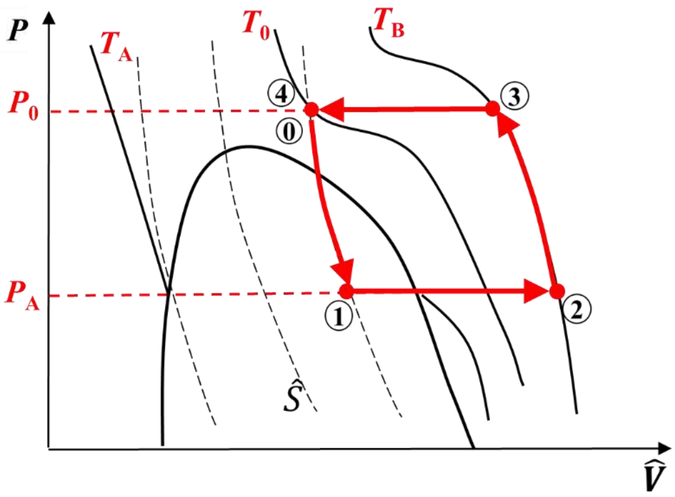
- **Liquefaction by decompression of a gas in a chamber A without friction or heat losses.**
- **Removal of the liquid from the chamber and heating of the vapor in an isobaric exchanger C (up to a temperature above the critical one).**
- **Isothermal compression of the heated vapor by means of a pump B to the feed pressure (which is above the critical one).**
- **Cooling of the compressed stream to the temperature of the feed in the heat exchanger C.**
- **Mixing of the feed and the cooled compressed stream.**
- **Decompression in chamber A.**

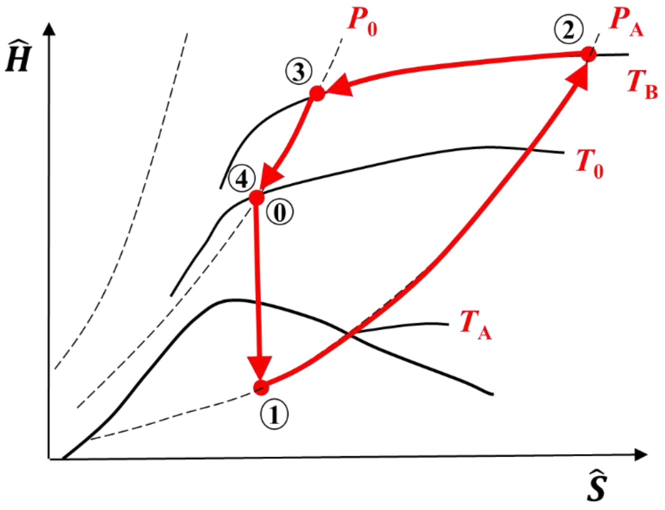
Let “1” be the conditions inside the chamber A after an isentropic decompresion (i.e. without friction or heat losses), “2” be the vapor heated in the heat exchanger C, “3” the heated vapor after isothermal compression in the pump B and “4” be the same stream after cooling in the heat exchanger C (and before its mixture with the feed 0). The flowchart will be



and the other suggested diagrams




P
T_A
T_0
T_B
P_0
④
⓪
③
P_A
①
②
$\hat{S}$
$\hat{V}$

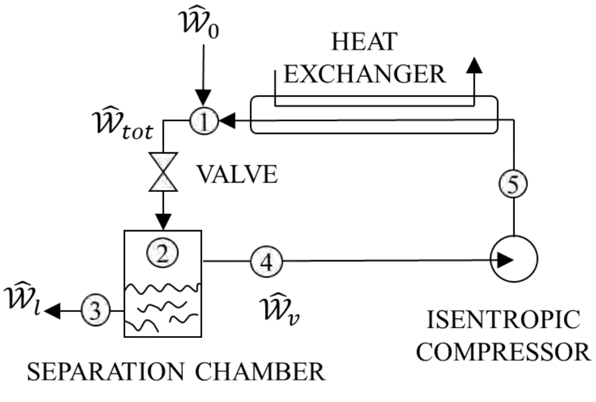

$\hat{H}$
P_0
②
P_A
③
T_B
T_0
④
⓪
T_A
①
$\hat{S}$

6.15. A stream of ethane at 25ºC and 100 bar is employed to produce 2000 kg/h of liquid hydrocarbon at 5 bar by means of a modified Linde cycle. It consists of several basic operations: an expansion valve (isenthalpic) and a separation chamber (for the two phases produced, which are in equilibrium). The liquid is removed and the vapor passes through an adiabatic and reversible compressor that takes it to the pre-expansion pressure. Next, an isobaric heat exchanger adjusts the temperature to the pre-expansion one.

To maintain the process in a steady state, a feed flow is added where its conditions are the same as those of the circulating fluid: between the heat exchanger and the valve.

- **a) Represent the flowchart of the process.**
- **b) Quantitatively represent the cycle in a $HP(T,V,S)$ diagram and read in it the specific enthalpies corresponding to the different points as well as the temperature at which the ethane leaves the compressor.**
- **c) Calculate the flow rates through each point of the circuit.**
- **d) Calculate the power (in kilowatts) required in the compressor.**
- **e) Calculate the heat flow in the heat exchanger.**
- **f) Qualitatively represent the cycle in PT, $PV(T,S,H)$, $TS(P,H)$, $z(P_r,T_r)$ and $HS(T,P)$ diagrams**
- **g) If the vapor phase has to be recycled, why is the process not adjusted to only obtain liquid phase?**
- **h) If the compressor was not adiabatic (causing a 10% increase in the entropy of the fluid) and the heat exchanger was not isobaric (causing a 5% pressure drop) determine the temperature and the pressure of the ethane that leaves the compressor. Qualitatively represent in diagrams P vs. *Length coordinate of the basic operations* and T vs. *Length coordinate* this case and that of the preceding sections (adiabatic compressor and isobaric exchanger).**

Question a. The flowchart of the process is



where point “1” represents the place in which the mass flow of the feed ($\widehat{W}_0$) is mixed with the stream that leaves the heat exchanger, point “2” represent this mixture (flow rate $\widehat{W}_{tot}$) after the isenthalpic expansion and points “3” and “4” are the flows of saturated liquid ($\widehat{W}_l$) and saturated vapor ($\widehat{W}_v$) respectively. This mass flow of vapor is isentropically compressed to point “5” before entering the heat exchanger.

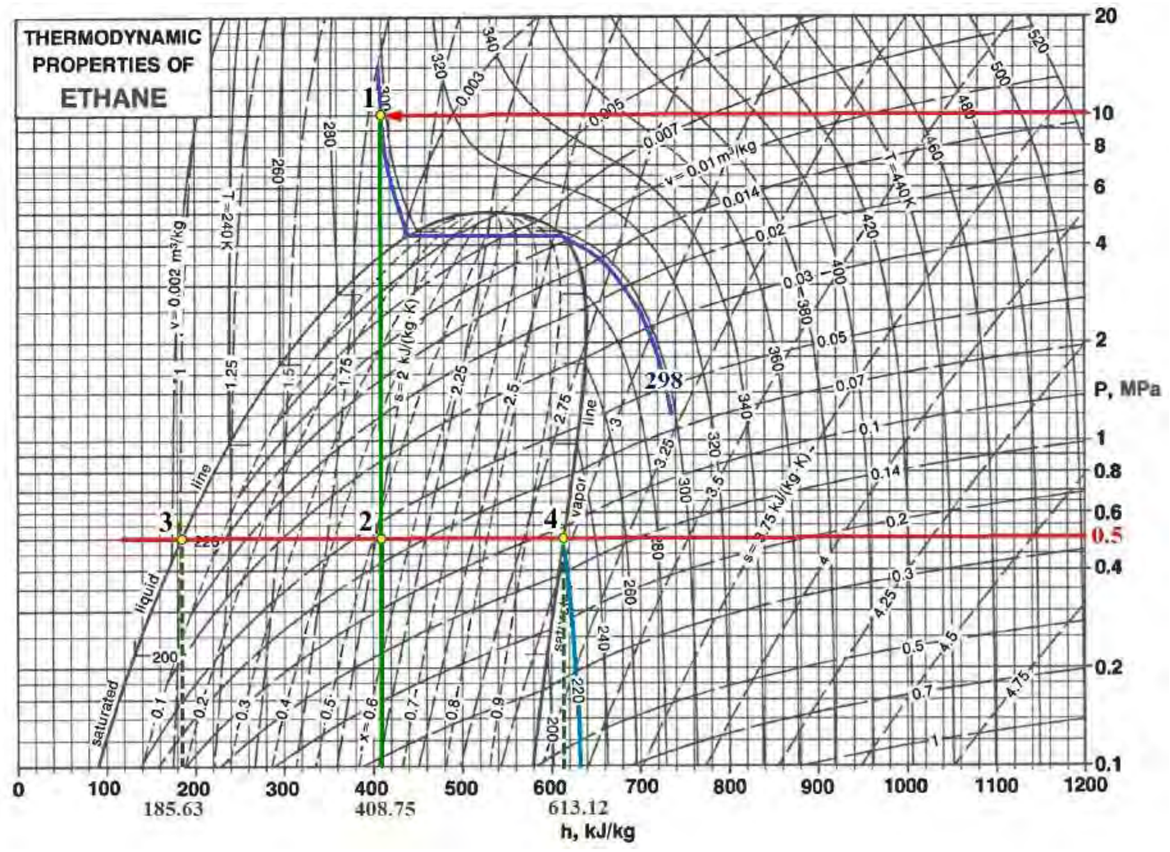
Question b. Figure V.15 of appendix V is a quantitative $PH(S,T,V)$ diagram of ethane. To use it, temperatures have to be converted to K and pressures to MPa by means of the factors of appendix I

$$T_1(\mathrm{K}) = 25\mathrm{^\circ C} + 273 = 298\ \mathrm{K}$$

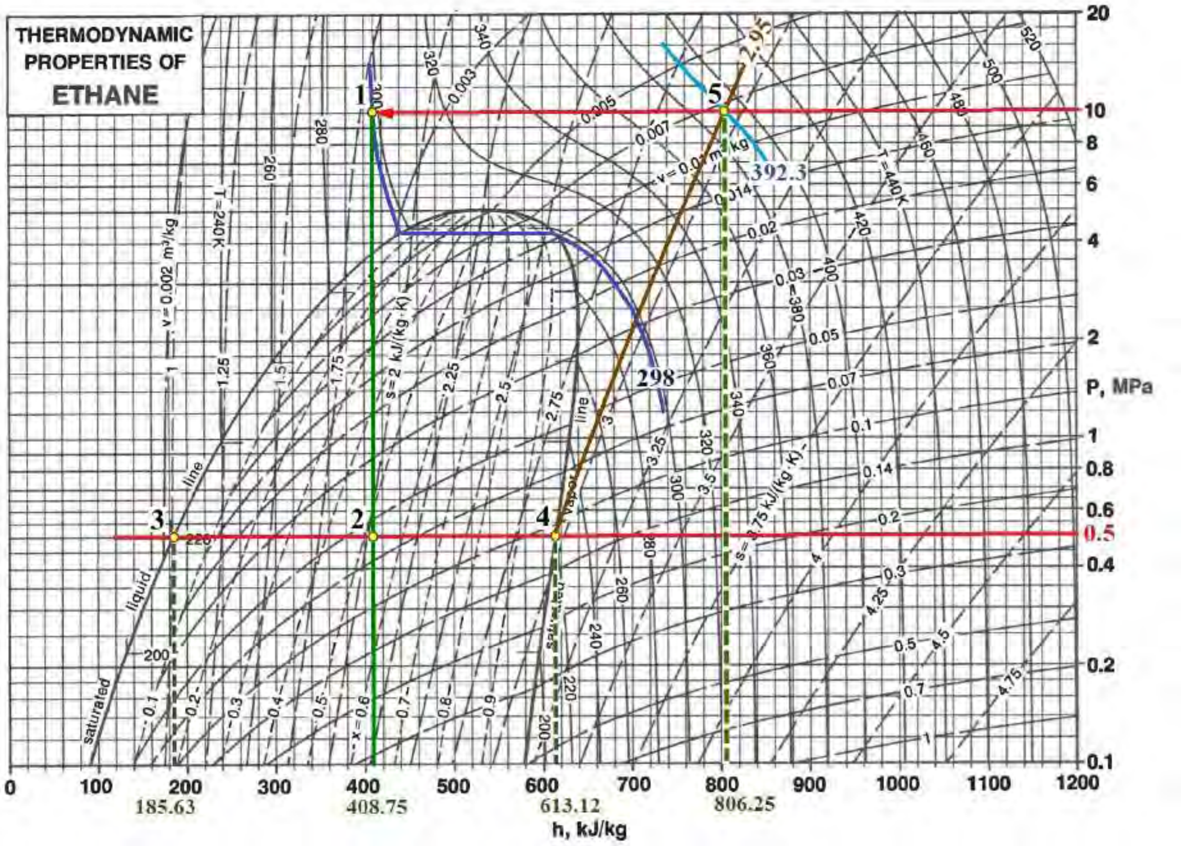
$$P_1 = 100\ \mathrm{bar} \times \frac{0.1\ \mathrm{MPa}}{1\ \mathrm{bar}} = 10\ \mathrm{MPa}$$

$$P_2 = 5\ \mathrm{bar} \times \frac{0.1\ \mathrm{MPa}}{1\ \mathrm{bar}} = 0.5\ \mathrm{MPa}$$

By interpolating the isotherm of 298 K and taking into account that the step from 1 to 2 is isenthalpic (both points have the same enthalpy), that the pressure of the liquid is of 0.5 MPa and that the liquid and the vapor are in equilibrium, it is possible to locate in the diagram the points 1 – 4 and to read the corresponding enthalpies: $\widehat{H}_1 = \widehat{H}_2 = 408.75$ kJ/kg, $\widehat{H}_3 = 185.63$ kJ/kg and $\widehat{H}_4 = 613.12$ kJ/kg. The temperature of the saturated liquid and vapor at 0.5 MPa is of 220 K.



On the other hand, the location of point 5 (ethane leaving the adiabatic compressor) will require interpolating the isentropic line that passes through 4 (approximately 2.95 kJ/kg·K) and finding the intersection of that isentropic with the P_1 isobar. The isotherm that passes through this intersection will be the temperature of the stream that leaves the compressor and enters the heat exchanger.



These operations lead to $\hat{H}_5$ =806.25 kJ/kg and T_5=392.3 K.

Question c. Since the feed flow must compensate the flow of withdrawn liquid, the global mass balance to the entire system gives

$$\hat{\mathcal{W}}_0 = \hat{\mathcal{W}}_l = 2000\ \frac{\text{kg}}{\text{h}}$$

and according to the mass balance to the separation chamber

$$\hat{\mathcal{W}}_{tot} = \hat{\mathcal{W}}_l + \hat{\mathcal{W}}_v$$

If both are combined with the enthalpy balances to the valve and to the chamber

$$\hat{\mathcal{W}}_{tot}\hat{H}_1 = \hat{\mathcal{W}}_{tot}\hat{H}_2 = \hat{\mathcal{W}}_l\hat{H}_3 + \hat{\mathcal{W}}_v\hat{H}_4$$

it can be obtained that

$$\hat{\mathcal{W}}_{tot} = \frac{(\hat{H}_3 - \hat{H}_4)}{(\hat{H}_1 - \hat{H}_4)}\hat{\mathcal{W}}_l = \frac{(185.63 - 613.12)}{(408.75 - 613.12)}\left[2000\ \frac{\text{kg}}{\text{h}}\right] = 4183.5\ \frac{\text{kg}}{\text{h}}$$

$$\hat{\mathcal{W}}_v = \hat{\mathcal{W}}_{tot} - \hat{\mathcal{W}}_l = 4183.5\ \frac{\text{kg}}{\text{h}} - 2000\ \frac{\text{kg}}{\text{h}} = 2183.5\ \frac{\text{kg}}{\text{h}}$$

Question d. The work in the compressor (transit from point 4 to point 5) is given by the integral

$$\mathrm{d}\widehat{W}^{\mathrm{fl}} = \widehat{V}\mathrm{d}P \quad \rightarrow \ \Delta\widehat{W}^{\mathrm{fl}}_{54} = \int_4^5 \widehat{V}\mathrm{d}P$$

However, equations of reference problem 0.3 indicate that

$$\mathrm{d}\widehat{H} = \mathrm{d}\widehat{Q} + \mathrm{d}\widehat{W}^{\mathrm{fl}} = T\mathrm{d}\widehat{S} + \widehat{V}\mathrm{d}P \qquad [1]$$

and if the compressor is adiabatic and reversible, $\mathrm{d}\widehat{Q} = T\mathrm{d}\widehat{S} = 0$, so

$$\mathrm{d}\widehat{W}^{\mathrm{fl}} = \mathrm{d}\widehat{H} \quad \rightarrow \ \Delta\widehat{W}^{\mathrm{fl}}_{54} = \int_4^5 \mathrm{d}\widehat{H} = \Delta\widehat{H}_{54}$$

$$\Delta\widehat{W}^{\mathrm{fl}}_{54} = \widehat{H}_5 - \widehat{H}_4 = \left(806.25\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 613.12\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 193.13\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

Therefore, the power will be

$$\wp_{54} = \widehat{\mathcal{W}}_v \Delta\widehat{W}^{\mathrm{fl}}_{54} = \left(2183.5\ \frac{\mathrm{kg}}{\mathrm{h}}\right)\left(193.13\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 421.7 \cdot 10^3\ \frac{\mathrm{kJ}}{\mathrm{h}}$$

and by employing the conversion factors of appendix I

$$\wp_{54} = 421.7 \cdot 10^3\ \frac{\mathrm{kJ}}{\mathrm{h}} \times \frac{1000\ \mathrm{J}}{1\ \mathrm{kJ}} \times \frac{2.78 \cdot 10^{-7}\ \mathrm{kW{\cdot}h}}{1\ \mathrm{J}} = 117.23\ \mathrm{kW}$$

Question e. The heat exchanged when passing from point 5 to 1 will be

$$\Delta\widehat{Q}_{15} = \int_5^1 T\mathrm{d}\widehat{S}$$

but if the heat exchanger is isobaric ($\mathrm{d}P$=0) there will be no flow work ($\mathrm{d}\widehat{W}^{\mathrm{fl}}=\widehat{V}\mathrm{d}P = 0$) and according to equation [1] the heat per unit mass could be calculated as

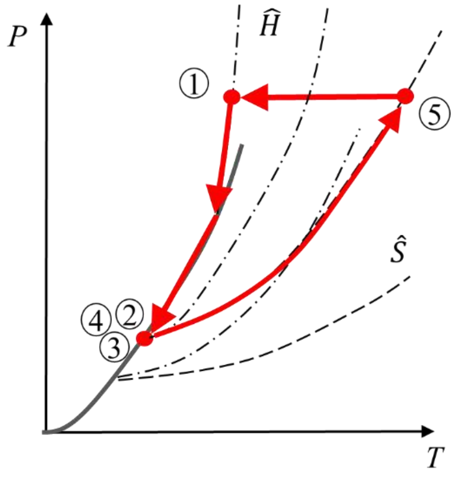
$$\mathrm{d}\widehat{H} = \mathrm{d}\widehat{Q} \ \ \rightarrow \ \Delta\widehat{Q}_{15} = \int_5^1 \mathrm{d}\widehat{H} = \Delta\widehat{H}_{15}$$

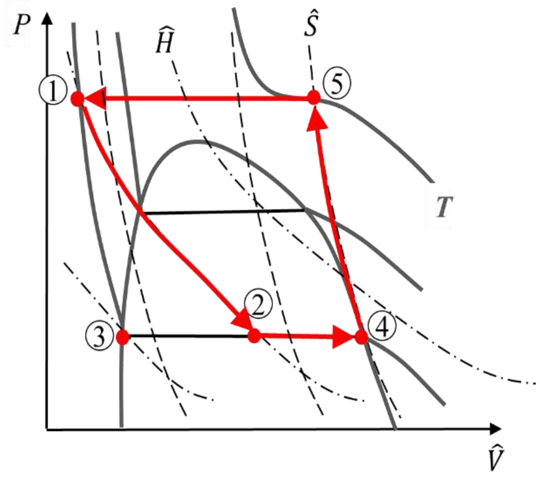
$$\Delta\widehat{Q}_{15} = \widehat{H}_1 - \widehat{H}_5 = 408.75\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 806.25\frac{\mathrm{kJ}}{\mathrm{kg}} = -397.5\frac{\mathrm{kJ}}{\mathrm{kg}}$$

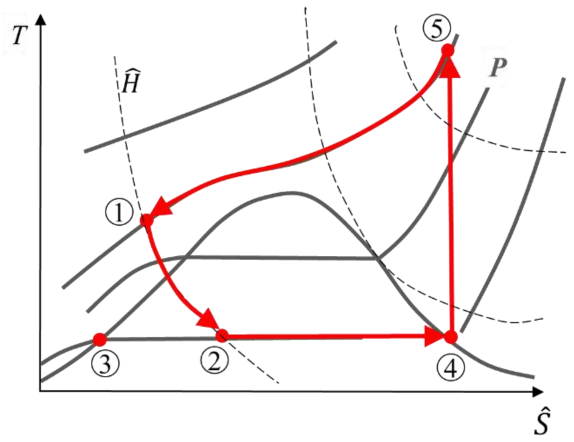
and the heat flow is the product

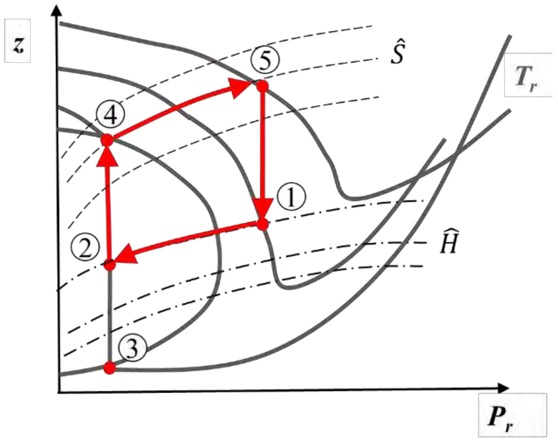
$$q_{15} = \widehat{\mathcal{W}}_v \Delta\widehat{Q}_{15} = \left(2183.5\ \frac{\mathrm{kg}}{\mathrm{h}}\right)\left(-397.5\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -868 \cdot 10^3\ \frac{\mathrm{kJ}}{\mathrm{h}}$$

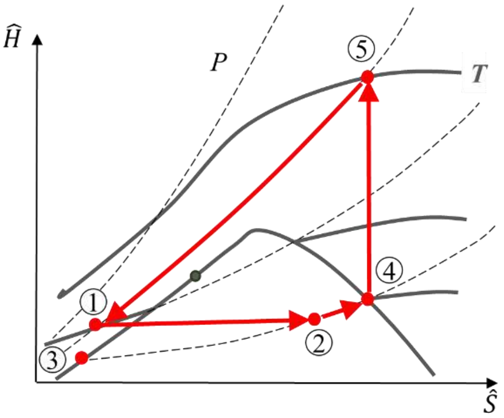
Question f. Having in mind that $P_1=P_2>P_c$ and that $T_5>T_c>T_1$, the qualitative representations are



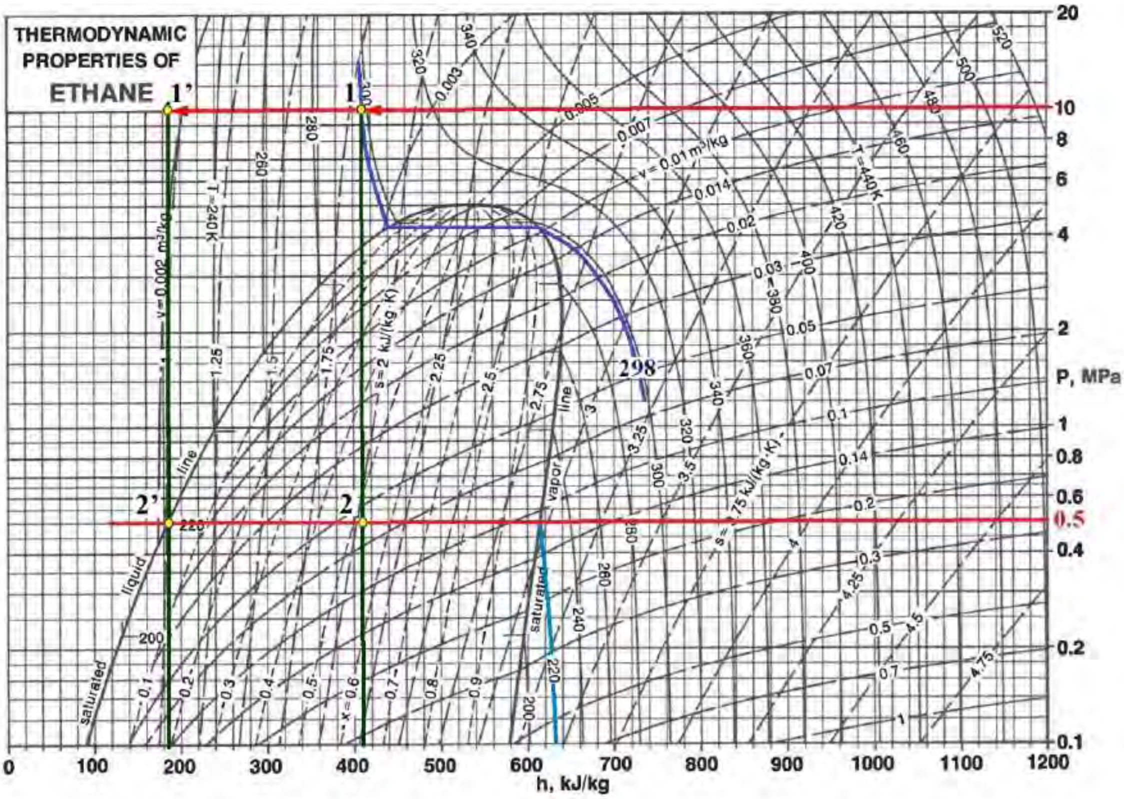




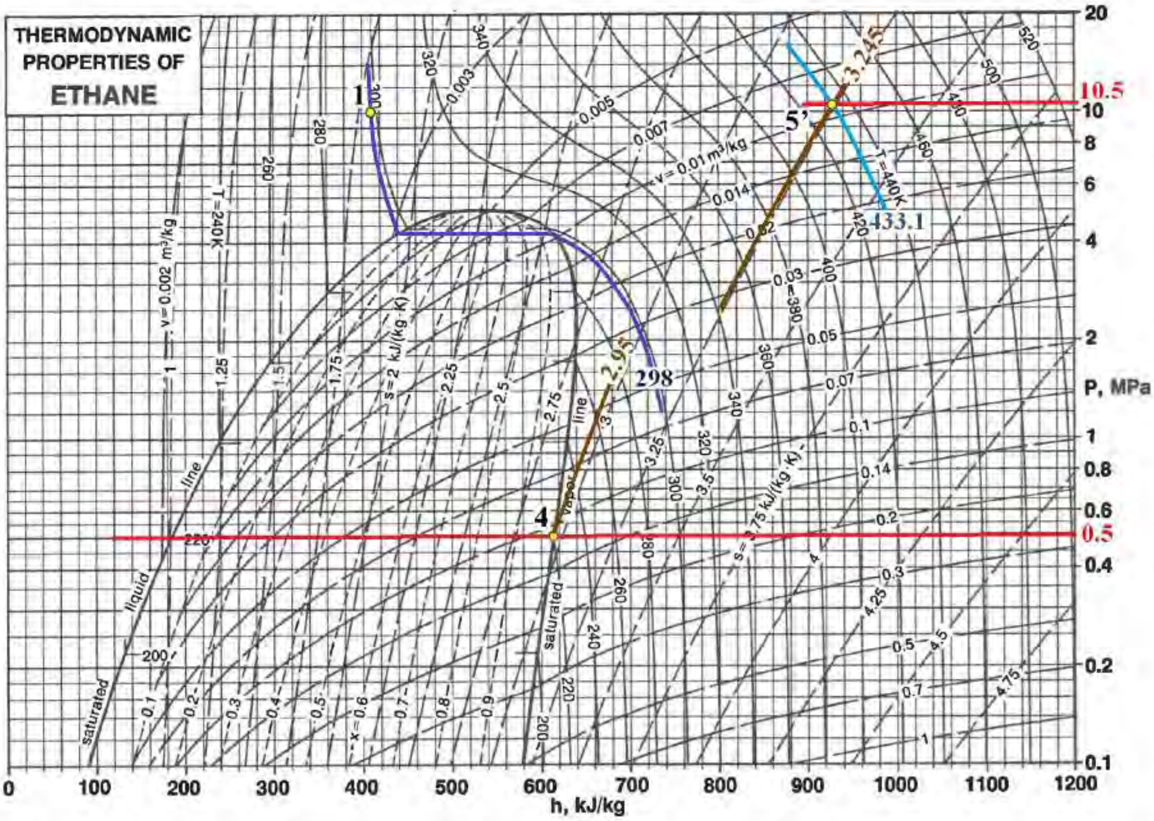




Question g. In order to only produce saturated liquid (point 2'), both $\widehat{\mathcal{W}}_0$ and $\widehat{\mathcal{W}}_v$ would have to be cooled to a temperature close to 220 K (point 1'). But then the heat exchanger would have to employ a refrigerant at a temperature lower than that, which is absurd.

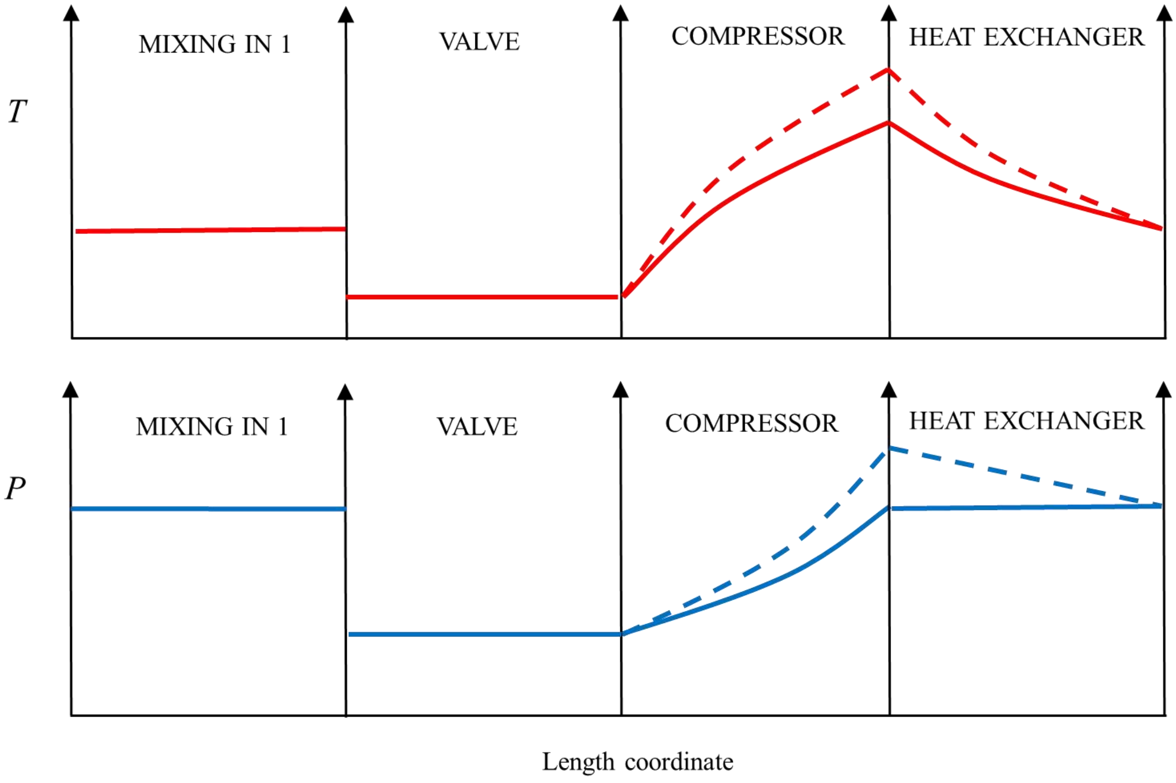


Question h. If the entropy increases in the compressor by 10% it means that $\hat{S}_{5'} = 1.1\hat{S}_4$ =1.1(2.95 kJ/kg·K)=3.245 kJ/kg·K and if the pressure in the heat exchanger drops a 5%, $P_{5'} = 1.05P_1 = 1.05(10\ \text{MPa})$ =10.5 MPa.



The intersection between the 10.5 MPa isobar and the 3.245 kJ/kg·K isentropic takes place on the isotherm $T_{5'}$=433.1 K.

Finally, in the qualitative representation (assuming piston flow in the compressor) dashed lines are used in those operations where the evolution of T and P is not the same as in the case of adiabatic compressor and isobaric exchanger.



6.16. Propane at 20ºC and 80 bar is employed to produce 15 L/s of liquid hydrocarbon at 3 bar. The licuefaction cycle consist of four successive operations: an isenthalpic expansion of the available hydrocarbon in a valve (obtaining a mixture of liquid and vapor), a phase separation and the recycling of the vapor (which is in equilibrium with the liquid at 3 bar), an isentropic compression and cooling in an isobaric heat exchanger with water. The compressed and cooled fluid is mixed with a feed (to compensate the flow of withdrawn liquid) and the resulting stream enters the isenthalpic valve. By means of a specific *PH*(ρ,*T*,*S*) diagram for propane, calculate:

a) The temperature at which the liquid propane leaves the phase separator and the mass flow rate of this liquid stream.
b) The temperature and state of the propane leaving the isentropic compressor and the specific enthalpies at all significant points of the process.
c) The flow rate of the feed, the flow rate of the vapor recycled and the flow rate that enters the isenthalpic valve.
d) The compression power and the heat flow removed by the cooling water.

Question a. Let “1” be the point where propane is at 20ºC (293 K) and 80 bar (8000 kPa) –where the feed is mixed with the stream leaving the heat exchanger–, “2” be the point corresponding to the mixture of liquid and vapor that results from the expansion in the valve, “4” be the liquid stream, “3” the vapor stream, and “5” the compressed vapor before entering the heat exchanger.

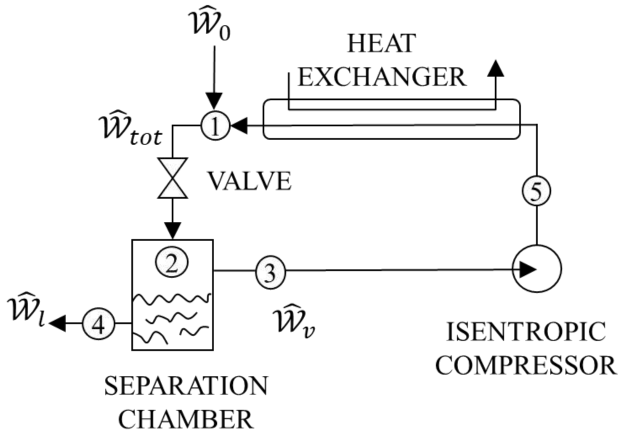
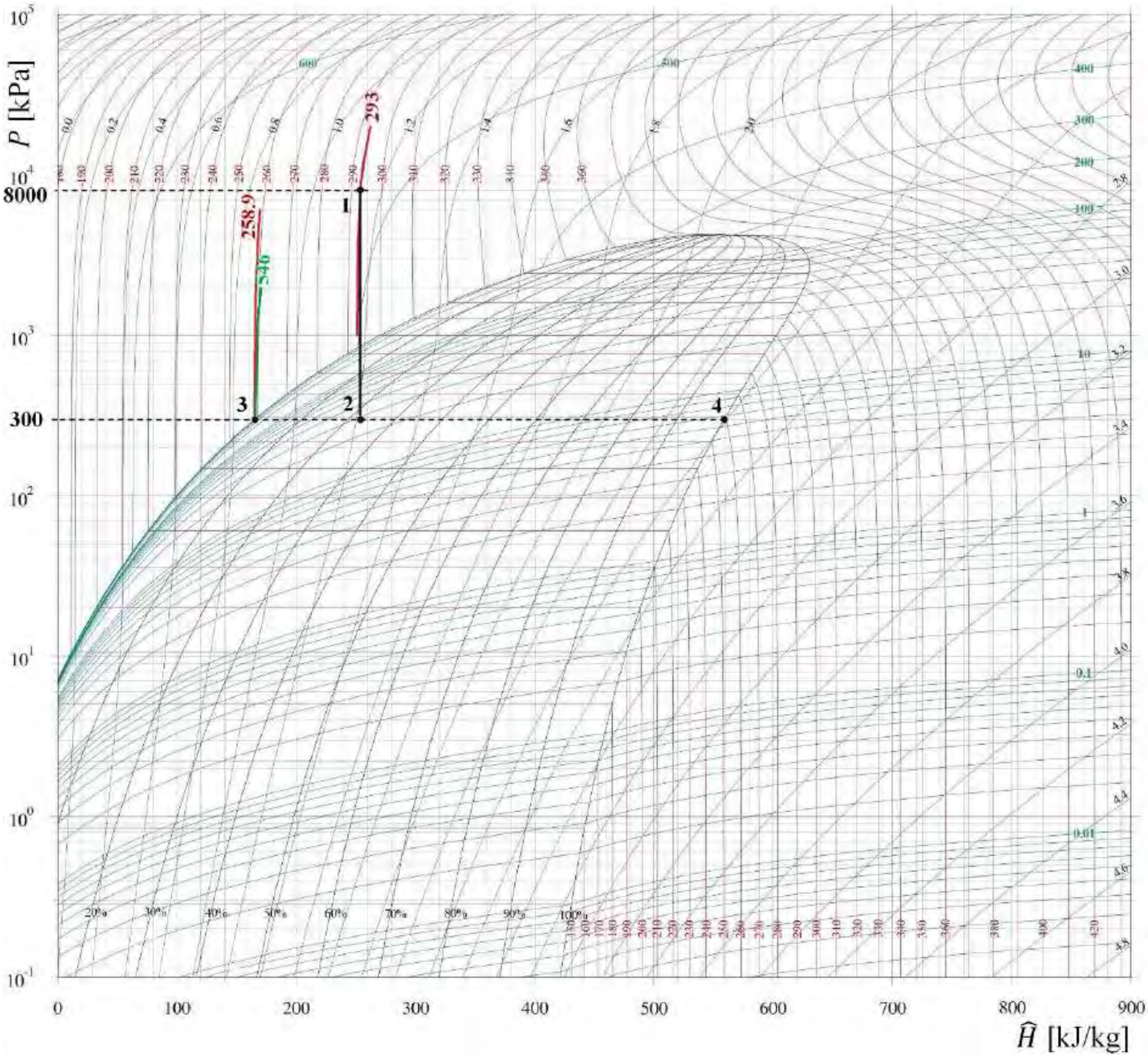


Figure V.8 of appendix V (a specific *PH* diagram for propane) will be used for calculations. Due to the fact that the transit from 1 to 2 is isoenthalpic, and that 2, 3 and 4 are at the same pressure and temperature (equilibrium), point 2 will be placed in the diagram by drawing a vertical line as operation line and looking for the intersection with the isobar of 3 bar (300 kPa). The point where this isobar cuts the saturated liquid curve will be "3" and the point where it cuts the saturated vapor curve will be "4". The isotherm that passes through 3-2-4 corresponds to the temperature of 258.9 K.



On the other hand, the mass flow of liquid propane at point 3 can be calculated as

$$\hat{\mathcal{W}}_l = \breve{\mathcal{W}}_l \hat{\rho}_3$$

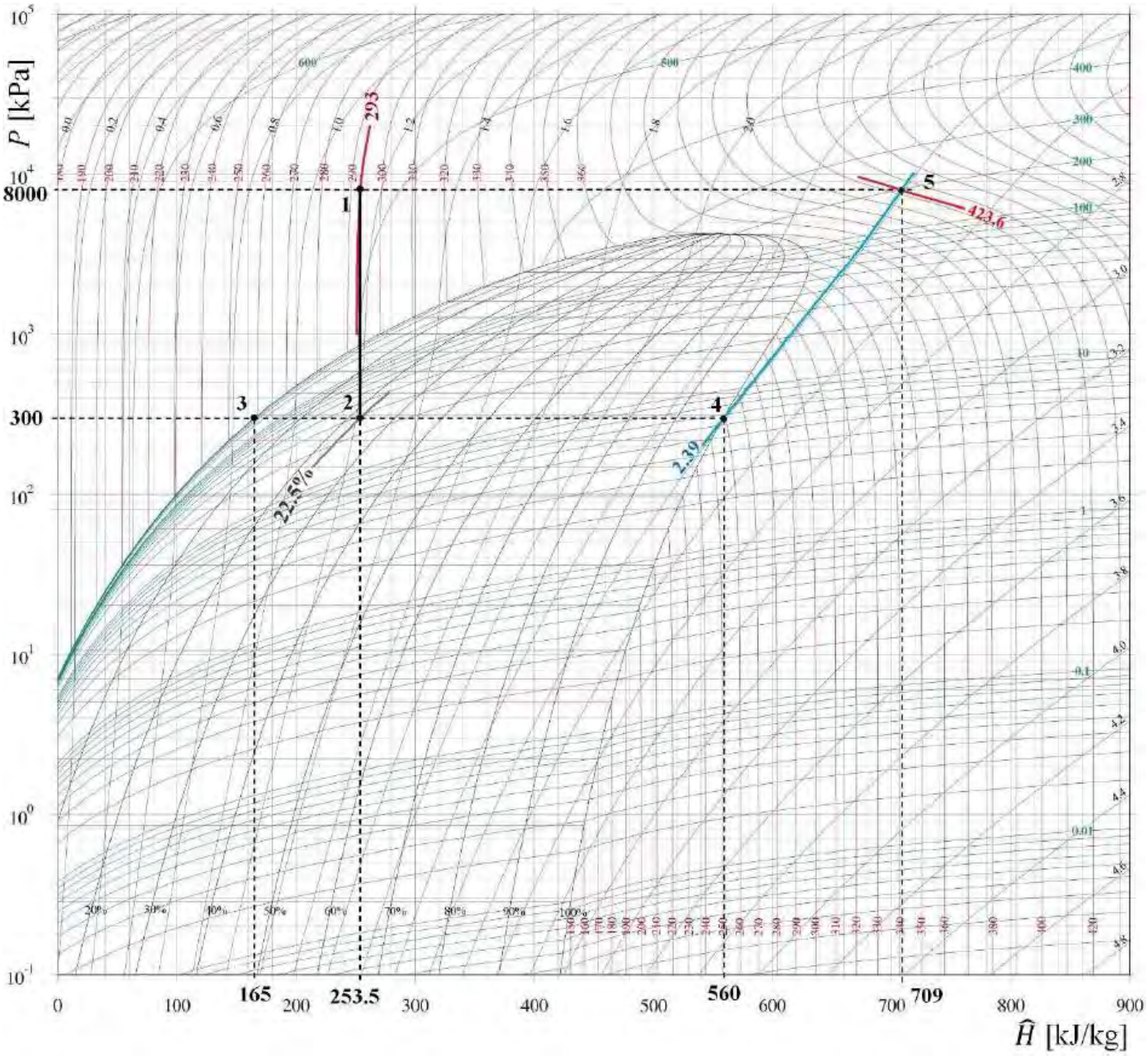
where $\hat{\rho}_3$ is the isochore which passes through 3. In this case, 546 kg/m^3 =546 g/L

$$\hat{\mathcal{W}}_l = \left(15\ \frac{\mathrm{L}}{\mathrm{s}}\right)\left(546\ \frac{\mathrm{g}}{\mathrm{L}}\right) = 8190\ \frac{\mathrm{g}}{\mathrm{s}} = 8.19\ \frac{\mathrm{kg}}{\mathrm{s}}$$

Question b. Since the compressor is isentropic, the saturated vapor (point 4) and the propane leaving the compressor (point 5) will be on the same isentropic line. Graphically the intersection of the one that passes through 4 ($\hat{S}_4$ =2.39 kJ/kg·K) with the 8000 kPa isobar corresponds to the 423.6 K isotherm (supercritical fluid).

When point 5 is determined, all the specific enthalpies of interest can be read in the diagram.

Point	$\hat{H}$ (kJ/kg)
1	253.5
2	253.5
3	165
4	560
5	709



Question c. The feed flow ($\hat{\mathcal{W}}_0$) is determined through a total mass balance to the system

$$\hat{\mathcal{W}}_0 = \hat{\mathcal{W}}_l = 8.19\ \frac{\text{kg}}{\text{s}}$$

while the flow rate of recycled vapor ($\hat{\mathcal{W}}_v$) and of propane which enters the valve ($\hat{\mathcal{W}}_{tot}$) can be calculated in two ways: by combining the mass and enthalpy balances to the valve and the separator

$$\widehat{\mathcal{W}}_{tot} = \widehat{\mathcal{W}}_l + \widehat{\mathcal{W}}_v$$

$$\widehat{\mathcal{W}}_{tot}\widehat{H}_1 = \widehat{\mathcal{W}}_{tot}\widehat{H}_2 = \widehat{\mathcal{W}}_l\widehat{H}_3 + \widehat{\mathcal{W}}_v\widehat{H}_4$$

$$\widehat{\mathcal{W}}_{tot} = \frac{\left(\widehat{H}_3 - \widehat{H}_4\right)}{\left(\widehat{H}_1 - \widehat{H}_4\right)}\widehat{\mathcal{W}}_l = \frac{(165 - 560)}{(253.5 - 560)}\left[8.19\ \frac{\text{kg}}{\text{s}}\right] = 10.55\ \frac{\text{kg}}{\text{s}}$$

$$\widehat{\mathcal{W}}_v = \widehat{\mathcal{W}}_{tot} - \widehat{\mathcal{W}}_l = 10.55\ \frac{\text{kg}}{\text{s}} - 8.19\ \frac{\text{kg}}{\text{s}} = 2.36\ \frac{\text{kg}}{\text{s}}$$

or by interpolating the title line which passes through point 2 in the $PH(\rho,\ T,\ S)$ diagram (in this case, 22.5%) and introducing the datum in the mass balance to the valve and the separator

$$\frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}} = 0.225 \quad \rightarrow \quad \widehat{\mathcal{W}}_v = 0.225\widehat{\mathcal{W}}_{tot}$$

$$\widehat{\mathcal{W}}_{tot} = \widehat{\mathcal{W}}_l + 0.225\widehat{\mathcal{W}}_{tot} \quad \rightarrow \quad \widehat{\mathcal{W}}_{tot} = \frac{\widehat{\mathcal{W}}_l}{0.775} = \frac{8.19\ \text{kg/s}}{0.775} = 10.57\ \frac{\text{kg}}{\text{s}}$$

$$\widehat{\mathcal{W}}_v = \widehat{\mathcal{W}}_{tot} - \widehat{\mathcal{W}}_l = 10.57\ \frac{\text{kg}}{\text{s}} - 8.19\ \frac{\text{kg}}{\text{s}} = 2.38\ \frac{\text{kg}}{\text{s}}$$

Question d. The compression power (passage from point 4 to point 5) is given by the integral

$$\Delta\widehat{W}^{\text{fl}}_{54} = \int_4^5 \widehat{V}\text{d}P$$

while the heat in the exchanger (transit from 5 to 1) will be

$$\Delta\widehat{Q}_{15} = \int_5^1 T\text{d}\widehat{S}$$

But according to reference problem 0.3

$$\text{d}\widehat{H} = \text{d}\widehat{Q} + \text{d}\widehat{W}^{\text{fl}} = T\text{d}\widehat{S} + \widehat{V}\text{d}P$$

If the compression is isentropic ($\text{d}\widehat{S}$=0)

$$\text{d}\widehat{W}^{\text{fl}} = \text{d}\widehat{H}$$

$$\Delta\widehat{W}^{\text{fl}}_{54} = \Delta\widehat{H}_{54} = \left(709\ \frac{\text{kJ}}{\text{kg}} - 560\ \frac{\text{kJ}}{\text{kg}}\right) = 149\ \frac{\text{kJ}}{\text{kg}}$$

and if the heat exchange is isobaric (dP=0)

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q}$$

$$\Delta\hat{Q}_{15} = \Delta\hat{H}_{15} = \left(235.5\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 709\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -473.5\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

If these intensive values are extended to steam streem (multiplied by the vapor mass flow rate)

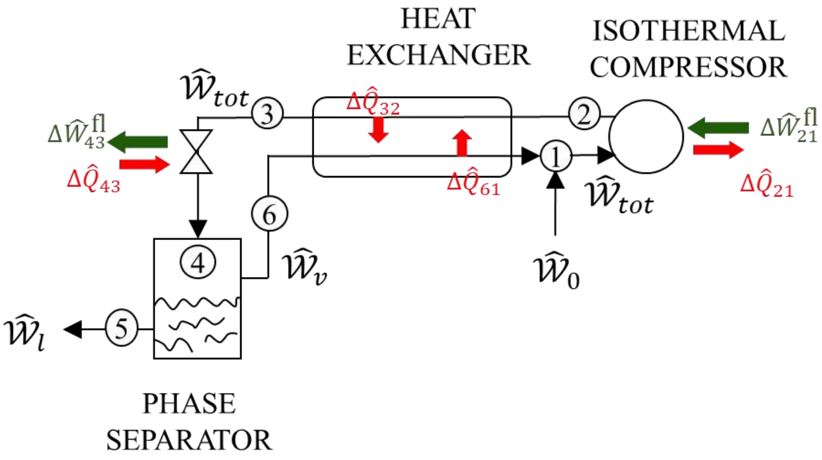
$$\mathscr{p}_{54} = \hat{\mathcal{W}}_v \Delta\hat{W}_{54}^{\mathrm{fl}} = \left(2.36\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(149\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 351.64\ \frac{\mathrm{kJ}}{\mathrm{s}}$$

$$q_{15} = \hat{\mathcal{W}}_v \Delta\hat{Q}_{15} = \left(2.36\ \frac{\mathrm{kg}}{\mathrm{s}}\right)\left(-473.5\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = -1117.46\ \frac{\mathrm{kJ}}{\mathrm{s}}$$

6.17. Dry decontaminated ambient air at 0ºC and 1 atm is mixed with the recycled air vapor from the liquefaction process described below, giving a flow rate of 100 m³/h. This flow is isothermally compressed to 200 atm and subsequently cooled to -136°C in an isobaric heat exchanger, which uses the aforementioned recycled air vapor as a refrigerant (in counterflow mode). A valve causes an isenthalpic expansion to the initial pressure obtaining liquefied air (that is extracted from the process) and vapor (that is sent to the aforementioned exchanger and reaches the conditions of the feed after leaving it).

- **a) Draw the flowchart of the process.**
- **b) Determine the total air mass flow rate in lb/h.**
- **c) With the help of a quantitative $TS(H,P)$ diagram of air, estimate the specific enthalpies and entropies at the main points.**
- **d) Evaluate the flow rates of saturated liquid and vapor that are produced.**
- **e) Quantify the heat flow of the compressed stream in the heat exchanger.**
- **f) Quantify the heat flow of the recycled stream in the heat exchanger.**
- **g) Calculate the heat and work flows in the isenthalpic valve.**
- **h) Calculate the heat flow and power in the isothermal compressor.**
- **i) Compare the real compression work with that calculated if air behaves as ideal gas.**
- **j) Qualitatively represent in $PV(T,H)$ and $TS(P,H)$ diagrams the heats and works involved in the process.**
- **k) If a reversible adiabatic expander is employed instead of the isenthalpic expansion valve, estimate the power which is now obtained and the global impact of the change on the process.**

Question a. The attached figure is the process flowchart.



Point “1” represents the place where the feed mass flow rate ($\hat{\mathcal{W}}_0$) joins the recirculated vapor stream leaving the heat exchanger (whose mass flow is the same than that at point “6”, but its temperature and pressure are those of “1”). Point “2” is located at the outlet of the isothermal compressor, point “3” at the exit of the heat exchanger and point “4” after the isenthalpic expansion. $\hat{\mathcal{W}}_{tot}$ is the mass flow rate of the mixture feed + recycled vapor, which passes through the compressor, the exchanger and the valve. Points “5” and “6” represent the liquid (mass flow $\widehat{\mathcal{W}}_l$) and vapor (mass flow $\widehat{\mathcal{W}}_v$) that leave the phase separator, respectively. Heats and works are also indicated, and will be discussed later.

Question b. Point “1” is at 0ºC and 1 atm, conditions in which the gas ideal behaviour can be assumed. The volume and mass flow of an ideal gas are related through

$$\widehat{\mathcal{W}}_{tot} = \frac{\breve{\mathcal{W}}_{tot}}{\widehat{V}_1} = \breve{\mathcal{W}}_{tot}\frac{P_1\mathfrak{M}_{air}}{RT_1}$$

By taking into account the usual conversion factors

$$T_1(\mathrm{K}) = T_1(^\circ\mathrm{C}) + 273 = 0^\circ\mathrm{C} + 273 = 273\ \mathrm{K}$$

$$1\ \mathrm{m}^3 = 1000\ \mathrm{L}$$

and that the table of appendix II gives $\mathfrak{M}_{air} = 28.97$ g/mol-g

$$\widehat{\mathcal{W}}_{tot} = \left(100\cdot 10^3\,\frac{\mathrm{L}}{\mathrm{h}}\right)\frac{(1\ \mathrm{atm})\left(28.97\,\frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)}{\left(0.082\,\frac{\mathrm{atm}\cdot\mathrm{L}}{\mathrm{K}\cdot\mathrm{mol\text{-}g}}\right)(273\ \mathrm{K})} = 129.41\cdot 10^3\ \frac{\mathrm{g}}{\mathrm{h}}$$

flow rate that, expressed in lb/h becomes

$$\widehat{\mathcal{W}}_{tot} = 129.41\cdot 10^3\ \frac{\mathrm{g}}{\mathrm{h}}\times\frac{1\ \mathrm{kg}}{1000\ \mathrm{g}}\times\frac{2.2\ \mathrm{lb}}{1\ \mathrm{kg}} = 284.702\ \frac{\mathrm{lb}}{\mathrm{h}}$$

Question c. Calculations will be carried out with figure V.16 of appendix V, which is the diagram of Landsbaum et al. (1955) for dry air. Since temperatures are expressed in degrees Rankine, those of the statement of the problem have to be converted to the same units.

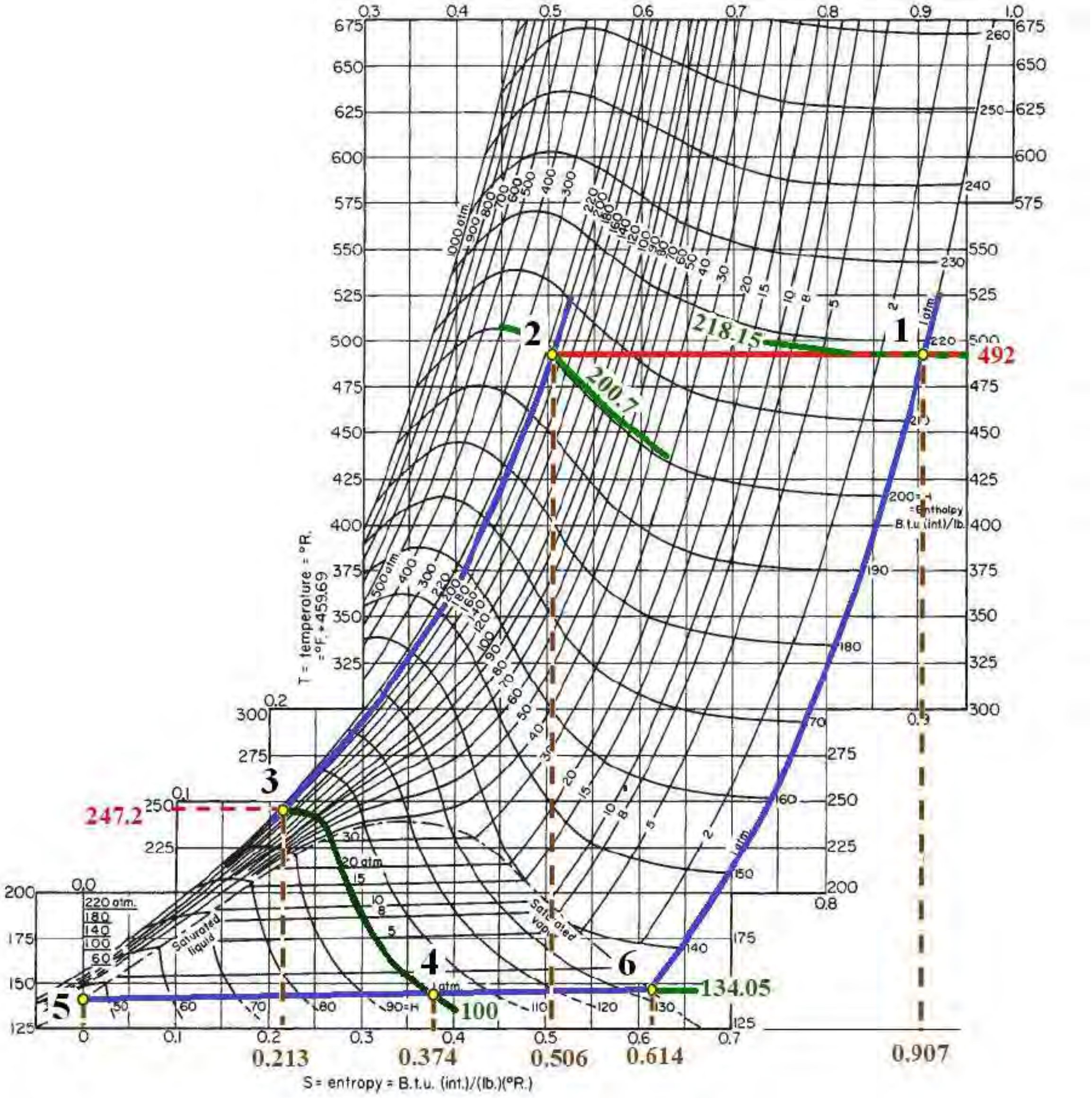
$$T_1(^\circ\mathrm{R}) = T_2(^\circ\mathrm{R}) = 1.8(0^\circ\mathrm{C}) + 492 = 492^\circ\mathrm{R}$$

$$T_3(^\circ\mathrm{R}) = 1.8(-136^\circ\mathrm{C}) + 492 = 247.2^\circ\mathrm{R}$$

and, by reading and interpolating isotherms, isoenthalpics and isentropics are

Point	$\widehat{H}$ (BTU/lb)	$\widehat{S}$ (BTU/lbºR)
1	218.15	0.907
2	200.7	0.506
3	100	0.213
4	100	0.374
5	-	0
6	134.05	0.614

The only enthalpy value that cannot be strictly determined is that of point 5 (saturated liquid), since it is lower than the minimum enthalpy shown in the figure (50 BTU/lb), but by assuming that between 40 and 50 BTU/lb exists the same functional space that between 50 and 60 BTU/lb, a value of $\widehat{H}_5$ =46 BTU/lb could be extrapolated.



Question d. According to the mass balance to the phase separator

$$\widehat{\mathcal{W}}_{tot} = 284.702\ \frac{\text{lb}}{\text{h}} = \widehat{\mathcal{W}}_l + \widehat{\mathcal{W}}_v$$

and if it is combined with the entropy balance to the same apparatus

$$\widehat{\mathcal{W}}_{tot}\hat{S}_4 = \widehat{\mathcal{W}}_l\hat{S}_5 + \widehat{\mathcal{W}}_v\hat{S}_6$$

the mass flow rates are

$$\widehat{\mathcal{W}}_l = \frac{\left(\hat{S}_4 - \hat{S}_6\right)}{\left(\hat{S}_5 - \hat{S}_6\right)} \widehat{\mathcal{W}}_{tot} = \frac{(0.374 - 0.614)}{(0.0 - 0.614)} \left[284.702\ \frac{\text{lb}}{\text{h}}\right] = 111.28\ \frac{\text{lb}}{\text{h}}$$

$$\widehat{\mathcal{W}}_v = \widehat{\mathcal{W}}_{tot} - \widehat{\mathcal{W}}_l = 284.702\ \frac{\text{lb}}{\text{h}} - 111.28\ \frac{\text{lb}}{\text{h}} = 173.422\ \frac{\text{lb}}{\text{h}}$$

However, the mass balance could also be combined with the enthalpy balance to the separator (although results will not be exactly the same due to the error inherent to reading data in graphs)

$$\widehat{\mathcal{W}}_{tot}\widehat{H}_4 = \widehat{\mathcal{W}}_l\widehat{H}_5 + \widehat{\mathcal{W}}_v\widehat{H}_6$$

$$\widehat{\mathcal{W}}_l = \frac{\left(\widehat{H}_4 - \widehat{H}_6\right)}{\left(\widehat{H}_5 - \widehat{H}_6\right)} \widehat{\mathcal{W}}_{tot} = \frac{(100 - 134.05)}{(46 - 134.05)} \left[284.702\ \frac{\text{lb}}{\text{h}}\right] = 110.098\ \frac{\text{lb}}{\text{h}}$$

$$\widehat{\mathcal{W}}_v = \widehat{\mathcal{W}}_{tot} - \widehat{\mathcal{W}}_l = 284.702\ \frac{\text{lb}}{\text{h}} - 110.098\ \frac{\text{lb}}{\text{h}} = 174.604\ \frac{\text{lb}}{\text{h}}$$

In order not to duplicate calculations, only the values obtained with the entropy balance will be used below.

Question e. The heat transfer in the exchanger (passage from point 2 to point 3) is determined by the integral

$$\Delta\hat{Q}_{32} = \int_2^3 T\mathrm{d}\hat{S}$$

But equations of reference problem 0.3 indicate that

$$\mathrm{d}\widehat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\widehat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \qquad [1]$$

and if pressure remains constant (dP=0) there is no flow work, $\mathrm{d}\widehat{H} = \mathrm{d}\hat{Q}$ and the exchanged heat will be the difference between enthalpies at the final and initial points (avoiding the numerical integration)

$$\Delta\hat{Q}_{32} = \Delta\widehat{H}_{32} = \widehat{H}_3 - \widehat{H}_2 = 100\ \frac{\text{BTU}}{\text{lb}} - 200.7\frac{\text{BTU}}{\text{lb}} = -100.7\frac{\text{BTU}}{\text{lb}}$$

The multiplication by the corresponding mass flow (feed+recycled vapor) gives the heat flow

$$q_{32} = \widehat{\mathcal{W}}_{tot}\Delta\hat{Q}_{32} = \left(284.702\ \frac{\text{lb}}{\text{h}}\right)\left(-100.7\ \frac{\text{BTU}}{\text{lb}}\right) = -28.7 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

Question f. The simplification of the preceding question is also applicable to the heat exchanged by the recycled vapor (transit form 6 to 1), so

$$\Delta\hat{Q}_{16} = \Delta\hat{H}_{16} = \hat{H}_1 - \hat{H}_6 = 218.15\ \frac{\mathrm{BTU}}{\mathrm{lb}} - 131.95\frac{\mathrm{BTU}}{\mathrm{lb}} = 86.2\ \frac{\mathrm{BTU}}{\mathrm{lb}}$$

$$q_{16} = \widehat{W}_v\Delta\hat{Q}_{16} = \left(173.422\ \frac{\mathrm{lb}}{\mathrm{h}}\right)\left(86.2\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right) = 14.9\cdot 10^3\ \frac{\mathrm{BTU}}{\mathrm{h}}$$

Notice that the absolute value of q_{32} is higher than that of q_{16}. This means that the recycled vapor can not remove the heat required to decrease the temperature of the compressed stream from 492ºR to 247.2ºR. Additional cooling will be needed.

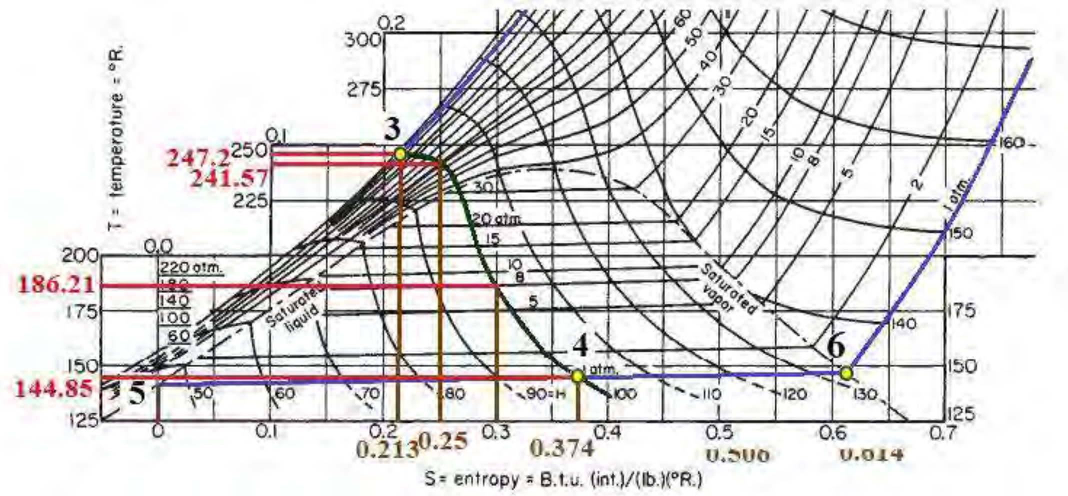
Question g. The heat and work changes in the valve (passage from 3 to 4) are

$$\Delta\hat{Q}_{43} = \int_3^4 T\mathrm{d}\hat{S} \quad ; \quad \Delta\widehat{W}_{43}^{\mathrm{fl}} = \int_3^4 \hat{V}\mathrm{d}P$$

but the device is isenthalpic, and in this case, equation [1] indicates that

$$\mathrm{d}\hat{H} = 0 = \mathrm{d}\hat{Q} + \mathrm{d}\widehat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \quad \rightarrow \quad \mathrm{d}\hat{Q} = -\mathrm{d}\widehat{W}^{\mathrm{fl}} \quad \rightarrow \quad \Delta\hat{Q}_{43} = -\Delta\widehat{W}_{43}^{\mathrm{fl}}$$

One of the integrals has to be numerically evaluated (for example, by the trapezoidal rule). Since figure V.16 does not include isochores, only $\Delta\hat{Q}_{43}$ can be determined.



T (ºR)	$\hat{S}$ (BTU/lbºR)	$[\hat{S}_i - \hat{S}_{i-1}]\left(\frac{T_i + T_{i-1}}{2}\right)$
247.2	0.213	
241.57	0.25	9.043
186.21	0.3	10.694
144.85	0.374	12.249
	Sum=	31.986

Thus, $\Delta\hat{Q}_{43} = -\Delta\widehat{W}^{\text{fl}}_{43}$ =31.986 BTU/lb, and

$$q_{43} = \mathcal{W}_{tot}\Delta\hat{Q}_{43} = \left(284.702\ \frac{\text{lb}}{\text{h}}\right)\left(31.986\ \frac{\text{BTU}}{\text{lb}}\right) = 9.1\cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

$$\wp_{43} = -q_{43} = -9.1\cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

Question h. In the isothermal compressor (transition from point 1 to point 2) the integral corresponding to the heat change becomes simpler because T is constant

$$\Delta\hat{Q}_{21} = \int_1^2 T\mathrm{d}\hat{S}\ = T_1\int_1^2 \mathrm{d}\hat{S}\ = T_1\left(\hat{S}_2 - \hat{S}_1\right)$$

and so

$$\Delta\hat{Q}_{21} = (492°\text{R})\left(0.506\ \frac{\text{BTU}}{\text{lb°R}} - 0.907\ \frac{\text{BTU}}{\text{lb°R}}\right) = -197.3\ \frac{\text{BTU}}{\text{lb}}$$

$$q_{21} = \mathcal{W}_{tot}\Delta\hat{Q}_{21} = \left(284.702\ \frac{\text{lb}}{\text{h}}\right)\left(-197.3\ \frac{\text{BTU}}{\text{lb}}\right) = -56.2\cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

With regards to the compression work, equation [1] indicates that

$$\mathrm{d}\widehat{W}^{\text{fl}} = \mathrm{d}\widehat{H} - \mathrm{d}\hat{Q} =\ \mathrm{d}\widehat{H} - T\mathrm{d}\hat{S}$$

$$\Delta\widehat{W}^{\text{fl}}_{21} = \int_1^2 \left(\mathrm{d}\widehat{H} - T\mathrm{d}\hat{S}\right) = \Delta\widehat{H}_{21} - T_1\left(\hat{S}_2 - \hat{S}_1\right) = \Delta\widehat{H}_{21} - \Delta\hat{Q}_{21}$$

which gives

$$\Delta\widehat{W}^{\text{fl}}_{21} = \left(200.7\ \frac{\text{BTU}}{\text{lb}} - 218.15\frac{\text{BTU}}{\text{lb}}\right) - \left(-197.3\ \frac{\text{BTU}}{\text{lb}}\right) = 179.85\ \frac{\text{BTU}}{\text{lb}}$$

$$\wp_{21} = \mathcal{W}_{tot}\Delta\widehat{W}^{\text{fl}}_{21} = \left(284.702\ \frac{\text{lb}}{\text{h}}\right)\left(179.85\ \frac{\text{BTU}}{\text{lb}}\right) = 51.2\cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

Question i. If air behaves as ideal gas between points 1 and 2

$$\Delta\widehat{W}^{\text{fl}}_{21} = \int_1^2 \hat{V}\mathrm{d}P = \int_1^2 \left(\frac{RT}{\mathfrak{M}_{air}P}\right)\mathrm{d}P = \frac{RT_1}{\mathfrak{M}_{air}}[\ln P]_1^2 = \frac{RT_1}{\mathfrak{M}_{air}}\ln\left(\frac{P_2}{P_1}\right)$$

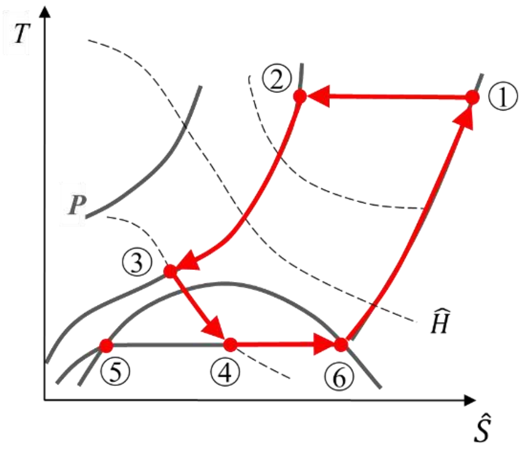
$$\Delta \widehat{W}_{21}^{\mathrm{fl}} = \frac{\left(0.082\,\dfrac{\mathrm{atm \cdot L}}{\mathrm{K \cdot mol\text{-}g}}\right)(273\ \mathrm{K})}{\left(28.97\,\dfrac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)} \ln\left(\frac{200\ \mathrm{atm}}{1\ \mathrm{atm}}\right) = 4.094\ \frac{\mathrm{atm \cdot L}}{\mathrm{g}}$$

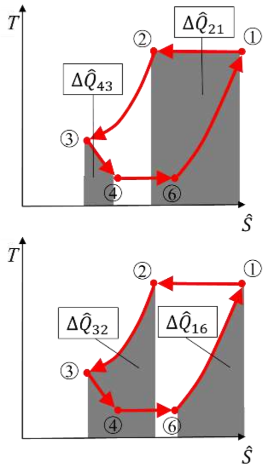
by taking into account the conversion factors of appendix I

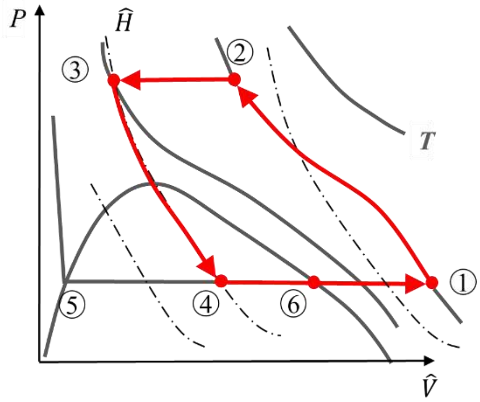
$$4.094\ \frac{\mathrm{atm \cdot L}}{\mathrm{g}} \times \frac{0.0961\ \mathrm{BTU}}{1\ \mathrm{atm \cdot L}} \times \frac{1000\ \mathrm{g}}{1\ \mathrm{kg}} \times \frac{1\ \mathrm{kg}}{2.2\ \mathrm{lb}} = 178.83\ \frac{\mathrm{BTU}}{\mathrm{lb}}$$

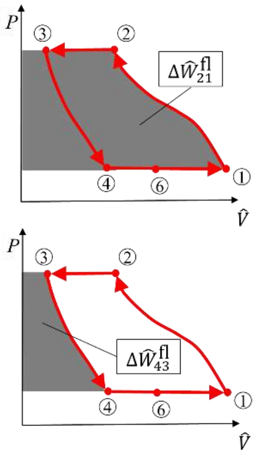
This value is very close to that of the preceding question (179.85 BTU/lb).

Question j. The attached figures represent the heats and works





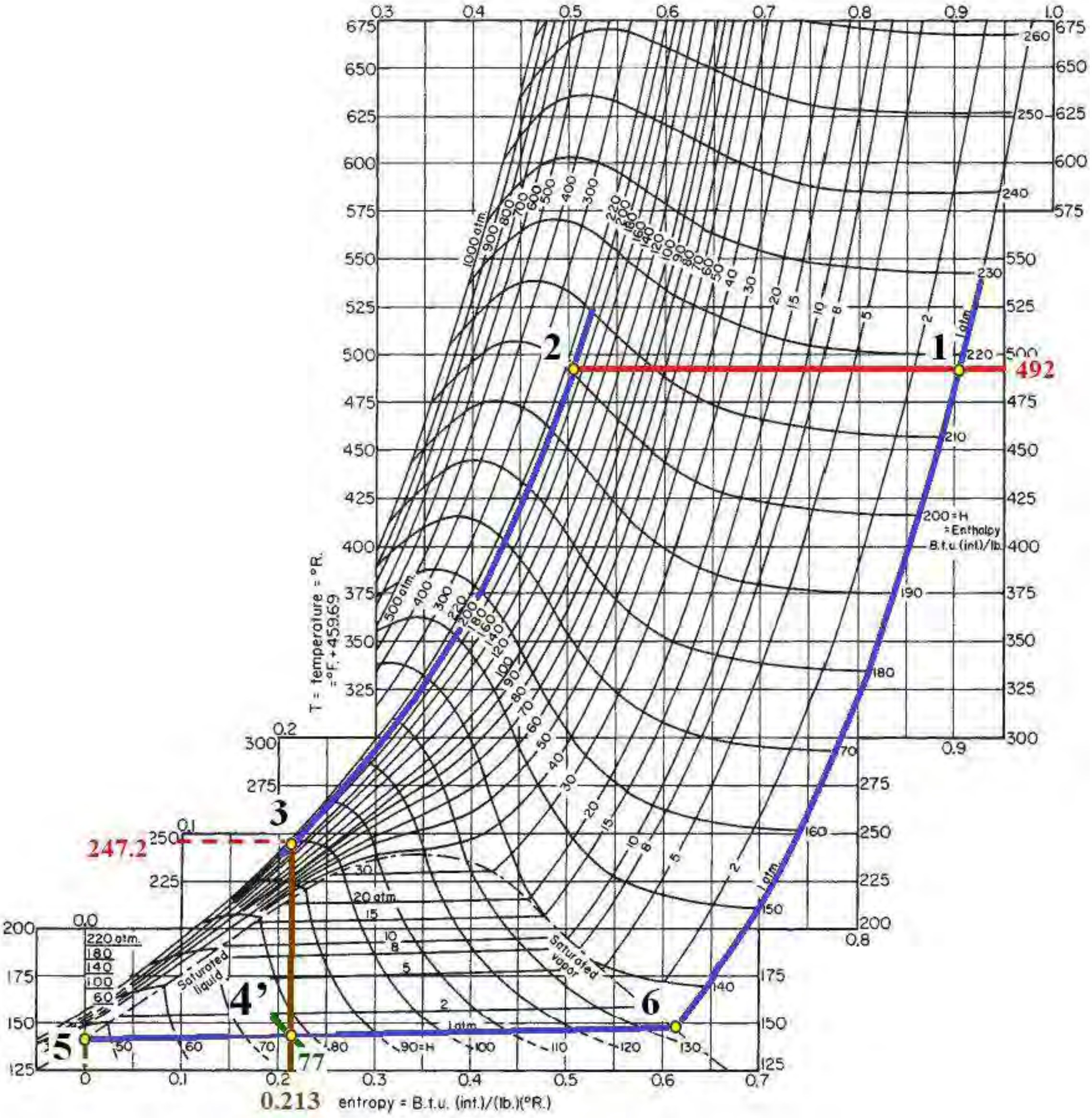




Question k. If a reversible adiabatic expander was used (i.e., isentropic), point 4 would become 4’ ($\hat{S}_{4'}$ =0.213 BTU/lb°R, $\hat{H}_{4'}$ =77 kJ/kg). This would require increasing the liquid flow and decreasing the vapor one, because the combination of the mass and entropy balances leads to

$$\widehat{\mathcal{W}}_{l'} = \frac{\left(\hat{S}_{4'} - \hat{S}_6\right)}{\left(\hat{S}_5 - \hat{S}_6\right)}\widehat{\mathcal{W}}_{tot} = \frac{(0.213 - 0.614)}{(0.0 - 0.614)}\left[284.702\ \frac{\text{lb}}{\text{h}}\right] = 185.937\ \frac{\text{lb}}{\text{h}}$$

$$\widehat{\mathcal{W}}_{v'} = \widehat{\mathcal{W}}_{tot} - \widehat{\mathcal{W}}_{l'} = 284.702 - 185.937 = 98.765\ \frac{\text{lb}}{\text{h}}$$



and according to equation [1], the power in this isentropic device will be

$$\mathrm{d}\hat{Q} = T\mathrm{d}\hat{S} = 0 \quad \rightarrow \quad \mathrm{d}\hat{H} = \mathrm{d}\widehat{W}^{\text{fl}} \quad \rightarrow \quad \Delta\widehat{W}^{\text{fl}}_{4'3} = \Delta\hat{H}_{4'3} = \hat{H}_{4'} - \hat{H}_3$$

$$\Delta\widehat{W}^{\text{fl}}_{4'3} = 77\ \frac{\text{BTU}}{\text{lb}} - 100\,\frac{\text{BTU}}{\text{lb}} = -23\,\frac{\text{BTU}}{\text{lb}}$$

$$\wp_{4'3} = \widehat{\mathcal{W}}_{tot'}\Delta\widehat{W}^{\mathrm{fl}}_{4'3} = \left(284.702\ \frac{\mathrm{lb}}{\mathrm{h}}\right)\left(-23\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right) = -6.55 \cdot 10^3\ \frac{\mathrm{BTU}}{\mathrm{h}}$$

The power and heat flow in the compressor and the heat exchanged by the compressed stream remain unchanged, but the heat flow of the recycled vapor stream will decrease, because $\widehat{\mathcal{W}}_{v'} < \widehat{\mathcal{W}}_v$

$$q_{16} = \widehat{\mathcal{W}}_{v'}\Delta\hat{Q}_{16} = \left(98.765\ \frac{\mathrm{lb}}{\mathrm{h}}\right)\left(86.2\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right) = 8.5 \cdot 10^3\ \frac{\mathrm{BTU}}{\mathrm{h}}$$

6.18. Liquid air at 1 atm is obtained from a feed stream of 10^5 L/h of dry air at 20°C and the same pressure. The process consist of isothermal compression up to 200 atm, subsequent cooling in an isobaric heat exchanger to -95°C and a final isentropic expansion which generates two phases in equilibrium. Liquid is removed, and the vapor stream at 1 atm is recycled to the head of the process (but in order to save energy, it is previously passed through the same heat exchanger than the compressed stream in counterflow mode).

a) Draw the flowchart of the process, and the information flow diagram.

b) Determine the mass flow rate of the feed in lb/h.

c) With the help of a quantitative *TS*(*H,P*) diagram of air, estimate the specific enthalpies and entropies at the main points.

d) Evaluate the flow rates of saturated liquid and vapor that are produced.

e) Quantify the heat flow of the compressed stream in the heat exchanger.

f) Quantify the heat flow of the stream at 1 atm in the heat exchanger.

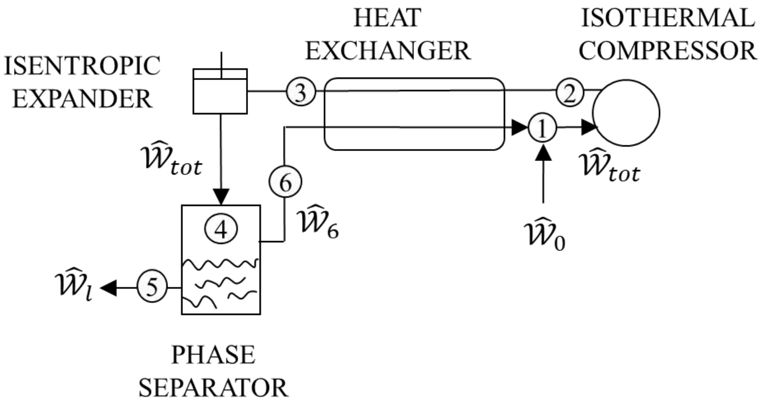
g) Calculate the power in the isentropic expander.

h) Calculate the heat flow and power in the isothermal compressor.

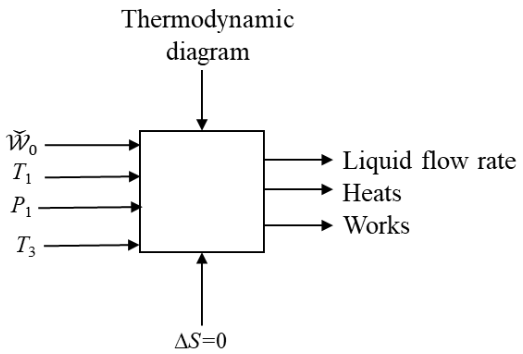
i) Qualitatively represent the cycle in *TH*(*P,S*), *TV*(*P,S*), *PT*(*S*) and $z(T_r,P_r)$ diagrams.

j) Does the refrigeration capacity compensates the cooling requirements? What would happen if the temperature of the compressed stream that leaves the exchanger was of -65ºC? What if it was of -74ºC?

Question a. Let point "1" be the place where the feed mass flow rate ($\widehat{\mathcal{W}}_0$) joins the recycled vapor stream leaving the heat exchanger (whose mass flow is the same than that at point "6") giving a total flow $\widehat{\mathcal{W}}_{tot}$. Let "2" be the air that leaves the compressor, "3" be the compressed stream after cooling and "4" after expansion. Let $\widehat{\mathcal{W}}_l$ be the mass flow rate of liquid air and $\widehat{\mathcal{W}}_v$ that of vapor air in the phase separator. The flowchart of the process will be



and the information flow diagram



Question b. At 1 atm, the feed can be assumed to be an ideal gas, where the mass and volume flow rates are related through

$$\hat{\mathcal{W}}_0 = \frac{\breve{\mathcal{W}}_0}{\hat{V}_0} = \breve{\mathcal{W}}_0 \frac{P_1 \mathfrak{M}_{air}}{RT_1}$$

by converting the units of the temperature (appendix I) and selecting the molecular mass of air (appendix II)

$$T_1(\mathrm{K}) = T_1(^\circ\mathrm{C}) + 273 = 20^\circ\mathrm{C} + 273 = 293\ \mathrm{K}$$

$$\mathfrak{M}_{air} = 28.97\ \mathrm{g/mol\text{-}g}$$

$$\hat{\mathcal{W}}_0 = \left(10^5 \frac{\mathrm{L}}{\mathrm{h}}\right) \frac{(1\ \mathrm{atm})\left(28.97 \frac{\mathrm{g}}{\mathrm{mol\text{-}g}}\right)}{\left(0.082 \frac{\mathrm{atm \cdot L}}{\mathrm{K \cdot mol\text{-}g}}\right)(293\ \mathrm{K})} = 120.58 \cdot 10^3\ \frac{\mathrm{g}}{\mathrm{h}}$$

mas flow rate that expressed in lb/h becomes

$$\hat{\mathcal{W}}_0 = 120.58 \cdot 10^3\ \frac{\mathrm{g}}{\mathrm{h}} \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}} \times \frac{2.2\ \mathrm{lb}}{1\ \mathrm{kg}} = 265.276\ \frac{\mathrm{lb}}{\mathrm{h}}$$

Question c. The diagram of Landsbaum et al. (1955) was employed for calculations (figure V.16 of this book's appendix V). Since the temperatures in this diagram are expressed in degrees Rankine, the two temperatures in the statement of the problem (expressed in degrees Kelvin) must be converted by the factors of appendix I

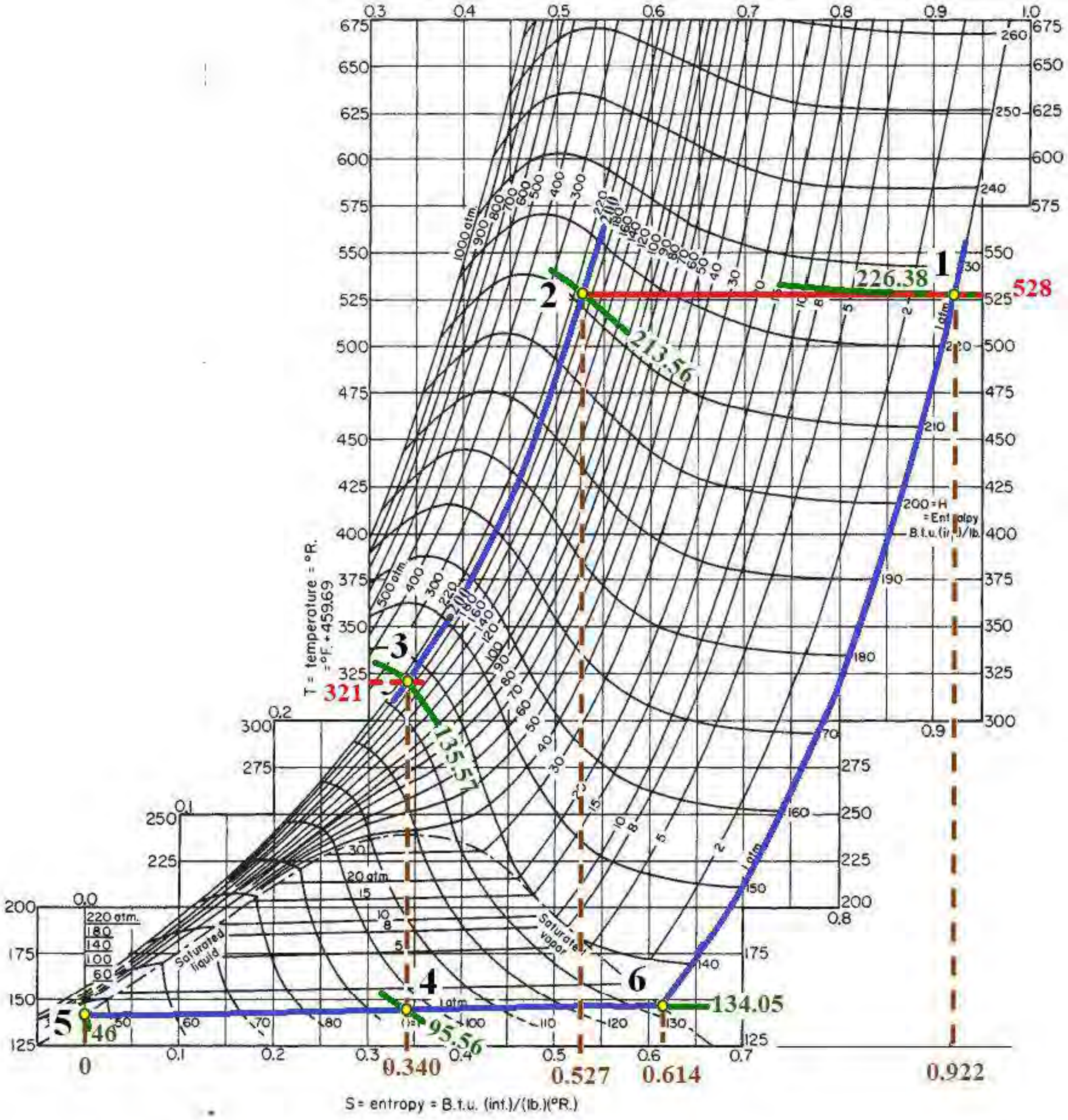
$$T_1(^\circ\mathrm{R}) = T_2(^\circ\mathrm{R}) = 1.8(20^\circ\mathrm{C}) + 492 = 528^\circ\mathrm{R}$$

$$T_3(^\circ\mathrm{R}) = 1.8(-95^\circ\mathrm{C}) + 492 = 321^\circ\mathrm{R}$$

After placing points 1 – 6, the requested data will be

Point	$\hat{H}$ (BTU/lb)	$\hat{S}$ (BTU/lb°R)
1	226.38	0.922
2	213.56	0.527
3	135.57	0.340
4	95.56	0.340
5	46	0
6	134.05	0.614

Notice that the enthalpy of point 5 (saturated liquid) has been extrapolated (there are not isenthalpic lines lower than 40 BTU/lb and it has been assumed that between 40 and 50 BTU/lb there is the same functional space as between 50 and 60 BTU/lb). All other enthalpies and entropies have been found by interpolation between existing values.



Question d. According to the total mass balance to the system

$$\hat{\mathcal{W}}_0 = \hat{\mathcal{W}}_l = 265.276\ \frac{\text{lb}}{\text{h}}$$

and according to the balance to the phase separator

$$\hat{\mathcal{W}}_{tot} = \hat{\mathcal{W}}_l + \hat{\mathcal{W}}_v$$

If both are combined with the entropy balance to the expander and the separator

$$\hat{\mathcal{W}}_{tot}\hat{S}_3 = \hat{\mathcal{W}}_{tot}\hat{S}_4 = \hat{\mathcal{W}}_l\hat{S}_5 + \hat{\mathcal{W}}_v\hat{S}_6$$

the other mass flow rates are

$$\hat{\mathcal{W}}_{tot} = \frac{\left(\hat{S}_5 - \hat{S}_6\right)}{\left(\hat{S}_4 - \hat{S}_6\right)}\hat{\mathcal{W}}_l = \frac{(0.0 - 0.614)}{(0.340 - 0.614)}\left[265.276\ \frac{\text{lb}}{\text{h}}\right] = 594.45\ \frac{\text{lb}}{\text{h}}$$

$$\hat{\mathcal{W}}_v = \hat{\mathcal{W}}_{tot} - \hat{\mathcal{W}}_l = 594.45\frac{\text{lb}}{\text{h}} - 265.276\frac{\text{lb}}{\text{h}} = 329.174\ \frac{\text{lb}}{\text{h}}$$

Question e. The compressed stream that passes through the heat exchanger (from point 2 to point 3) suffers a heat change per unit mass of

$$\Delta\hat{Q}_{32} = \int_2^3 T\mathrm{d}\hat{S}$$

but due to the fact that the pressure does not vary in the apparatus (dP=0), equations of reference problem 0.3 indicates that $\mathrm{d}\hat{H} = \mathrm{d}\hat{Q}$ because

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\text{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \qquad [1]$$

and no numerical integration is required.

$$\Delta\hat{Q}_{32} = \Delta\hat{H}_{32} = \hat{H}_3 - \hat{H}_2 = 135.57\ \frac{\text{BTU}}{\text{lb}} - 213.56\frac{\text{BTU}}{\text{lb}} = -77.99\frac{\text{BTU}}{\text{lb}}$$

Regarding the heat flow

$$q_{32} = \hat{\mathcal{W}}_{tot}\Delta\hat{Q}_{32} = \left(594.45\ \frac{\text{lb}}{\text{h}}\right)\left(-77.99\ \frac{\text{BTU}}{\text{lb}}\right) = -46.4\cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

Question f. The heat exchanged by the stream at a 1 atm corresponds to the step from 6 to 1. Since the exchange is isobaric, it is also satisfied that $\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} \ \rightarrow\ \Delta\hat{H} = \Delta\hat{Q}$, so

$$\Delta\hat{Q}_{16} = \Delta\hat{H}_{16} = \hat{H}_1 - \hat{H}_6 = 226.38\ \frac{\mathrm{BTU}}{\mathrm{lb}} - 134.05\frac{\mathrm{BTU}}{\mathrm{lb}} = 92.33\ \frac{\mathrm{BTU}}{\mathrm{lb}}$$

and the heat flow

$$q_{16} = \hat{\mathcal{W}}_v\Delta\hat{Q}_{16} = \left(329.174\ \frac{\mathrm{lb}}{\mathrm{h}}\right)\left(92.33\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right) = 30.4\cdot 10^3\ \frac{\mathrm{BTU}}{\mathrm{h}}$$

Question g. The work flow per unit mass in the expander (passage from 3 to 4) is calculated as

$$\Delta\widehat{W}_{43}^{\mathrm{fl}} = \int_3^4 \hat{V}\mathrm{d}P$$

but if the operation is isentropic, $\mathrm{d}\hat{S} = 0$ and equation [1] becomes

$$\mathrm{d}\hat{H} = \mathrm{d}\widehat{W}^{\mathrm{fl}} \quad \rightarrow \quad \Delta\widehat{W}_{43}^{\mathrm{fl}} = \Delta\hat{H}_{43}$$

$$\Delta\widehat{W}_{43}^{\mathrm{fl}} = \hat{H}_4 - \hat{H}_3 = 95.56\ \frac{\mathrm{BTU}}{\mathrm{lb}} - 135.57\frac{\mathrm{BTU}}{\mathrm{lb}} = -40.01\frac{\mathrm{BTU}}{\mathrm{lb}}$$

and the power is

$$\mathcal{P}_{43} = \hat{\mathcal{W}}_{tot}\Delta\widehat{W}_{43}^{\mathrm{fl}} = \left(594.45\ \frac{\mathrm{lb}}{\mathrm{h}}\right)\left(-40.01\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right) = -23.8\cdot 10^3\ \frac{\mathrm{BTU}}{\mathrm{h}}$$

Question h. In the isothermal compressor (transit from 1 to 2) the heat change per unit mass is

$$\Delta\hat{Q}_{21} = \int_1^2 T\mathrm{d}\hat{S}$$

but due to the fact that T_1=T_2

$$\Delta\hat{Q}_{21} = T_1\int_1^2 \mathrm{d}\hat{S}\ = T_1\left(\hat{S}_2 - \hat{S}_1\right)$$

$$\Delta\hat{Q}_{21} = (528°\mathrm{R})\left(0.527\ \frac{\mathrm{BTU}}{\mathrm{lb°R}} - 0.922\ \frac{\mathrm{BTU}}{\mathrm{lb°R}}\right) = -208.56\ \frac{\mathrm{BTU}}{\mathrm{lb}}$$

and the heat flow is the multiplication of $\Delta\hat{Q}_{21}$by the corresponding mass flow

$$q_{21} = \hat{\mathcal{W}}_1\Delta\hat{Q}_{21} = \hat{\mathcal{W}}_2\Delta\hat{Q}_{21} = \left(594.45\ \frac{\mathrm{lb}}{\mathrm{h}}\right)\left(-208.56\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right) = -124\cdot 10^3\ \frac{\mathrm{BTU}}{\mathrm{h}}$$

On the other hand, equation [1] says that the compression work is

$$\mathrm{d}\widehat{W}^{\mathrm{fl}} = \mathrm{d}\hat{H} - \mathrm{d}\hat{Q} = \ \mathrm{d}\hat{H} - T\mathrm{d}\hat{S}$$

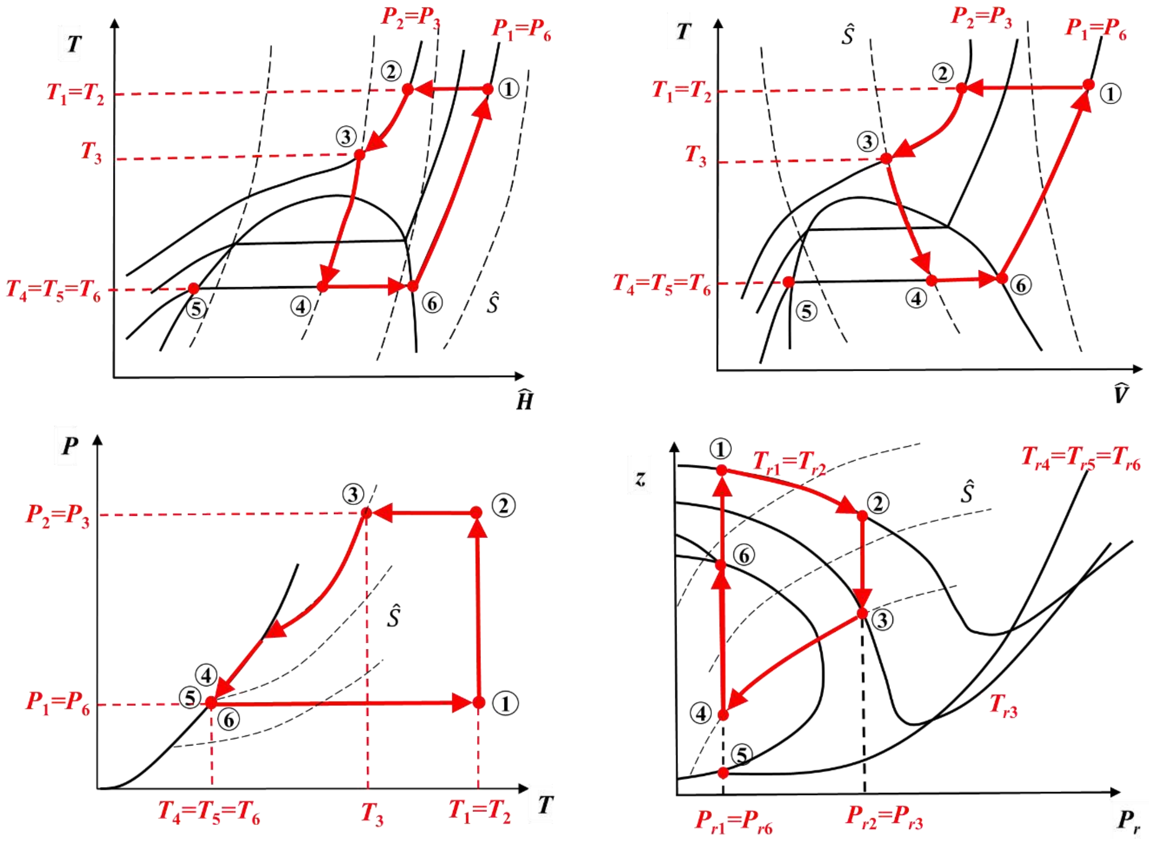
$$\Delta\widehat{W}^{\mathrm{fl}}_{21} = \int_1^2 \left(\mathrm{d}\widehat{H} - T\mathrm{d}\hat{S}\right) = \Delta\widehat{H}_{21} - T_1\left(\hat{S}_2 - \hat{S}_1\right) = \Delta\widehat{H}_{21} - \Delta\widehat{Q}_{21}$$

$$\Delta\widehat{W}^{\mathrm{fl}}_{21} = \left(213.56\ \frac{\mathrm{BTU}}{\mathrm{lb}} - 226.38\frac{\mathrm{BTU}}{\mathrm{lb}}\right) - \left(-208.56\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right) = 195.74\ \frac{\mathrm{BTU}}{\mathrm{lb}}$$

and the power

$$\wp_{21} = \widehat{\mathcal{W}}_{tot}\Delta\widehat{W}^{\mathrm{fl}}_{21} = \left(594.45\ \frac{\mathrm{lb}}{\mathrm{h}}\right)\left(195.74\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right) = 116.36\cdot 10^3\ \frac{\mathrm{BTU}}{\mathrm{h}}$$

Question i. The requested representations will be



Question j. There is no compensation, because $|q_{32}| > |q_{16}|$. The flow rate of the recycled vapor is not enough to refrigerate the compressed stream.

If the temperature of the compressed air that leaves the heat exchanger was of -65ºC

$$T_{3'}(^{\circ}\mathrm{R}) = 1.8(-65^{\circ}\mathrm{C}) + 492 = 375^{\circ}\mathrm{R}$$

It is only necessary to substitute $\widehat{H}_3$ =135.57 BTU/lb by $\widehat{H}_{3'}$ =160 BTU/lb and $\hat{S}_3$ =0.340 BTU/lb°R by $\hat{S}_{3'}$ = 0.411 BTU/lb°R in the previous calculations

$$\widehat{\mathcal{W}}_{tot'} = \frac{\left(\hat{S}_5 - \hat{S}_6\right)}{\left(\hat{S}_{3'} - \hat{S}_6\right)}\widehat{\mathcal{W}}_l = \frac{(0.0 - 0.614)}{(0.411 - 0.614)}\left[265.276\ \frac{\mathrm{lb}}{\mathrm{h}}\right] = 802.36\ \frac{\mathrm{lb}}{\mathrm{h}}$$

$$\widehat{\mathcal{W}}_{v'} = \widehat{\mathcal{W}}_{tot'} - \widehat{\mathcal{W}}_l = 802.36\ \frac{\mathrm{lb}}{\mathrm{h}} - 265.276\frac{\mathrm{lb}}{\mathrm{h}} = 537.084\ \frac{\mathrm{lb}}{\mathrm{h}}$$

to see that there is an excess of refrigeration

$$q_{3'2} = \widehat{\mathcal{W}}_{tot'}\left(\widehat{H}_{3'} - \widehat{H}_2\right) = \left(802.36\ \frac{\mathrm{lb}}{\mathrm{h}}\right)\left(160\ \frac{\mathrm{BTU}}{\mathrm{lb}} - 213.56\frac{\mathrm{BTU}}{\mathrm{lb}}\right) = -42.97\cdot 10^3\ \frac{\mathrm{BTU}}{\mathrm{h}}$$

$$q_{16} = \widehat{\mathcal{W}}_{v'}\Delta\hat{Q}_{16} = \left(537.084\ \frac{\mathrm{lb}}{\mathrm{h}}\right)\left(94.43\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right) = 50.72\cdot 10^3\ \frac{\mathrm{BTU}}{\mathrm{h}}$$

If the temperature is of -74ºC

$$T_{3''}(°\mathrm{R}) = 1.8(-74°\mathrm{C}) + 492 = 358.8°\mathrm{R}$$

and $\widehat{H}_3$ is substituted by $\widehat{H}_{3''}$ =152.73 BTU/lb and $\hat{S}_3$ by $\hat{S}_{3''}$ = 0.392 BTU/lb°R

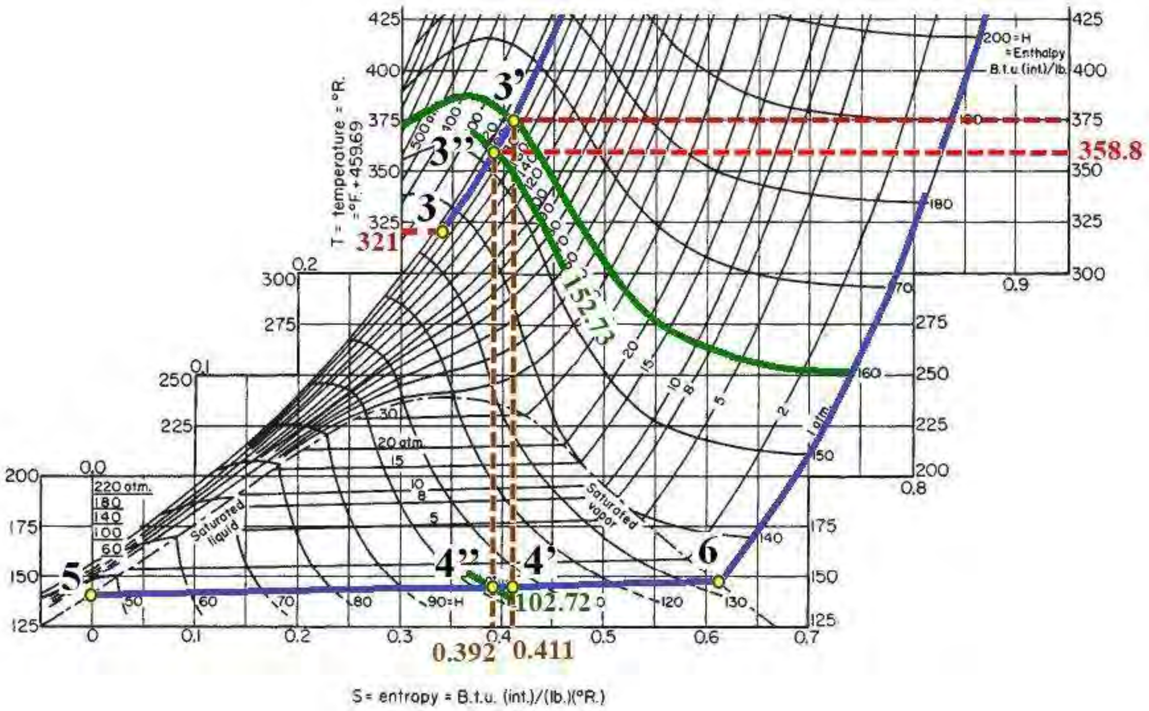
$$\widehat{\mathcal{W}}_{tot''} = \frac{\left(\hat{S}_5 - \hat{S}_6\right)}{\left(\hat{S}_{3''} - \hat{S}_6\right)}\widehat{\mathcal{W}}_5 = \frac{(0.0 - 0.614)}{(0.392 - 0.614)}\left[265.276\ \frac{\mathrm{lb}}{\mathrm{h}}\right] = 733.69\ \frac{\mathrm{lb}}{\mathrm{h}}$$

$$\widehat{\mathcal{W}}_{v''} = \widehat{\mathcal{W}}_{tot''} - \widehat{\mathcal{W}}_l = 733.69\frac{\mathrm{lb}}{\mathrm{h}} - 265.276\frac{\mathrm{lb}}{\mathrm{h}} = 468.414\ \frac{\mathrm{lb}}{\mathrm{h}}$$

the heat flows will be very close

$$q_{3''2} = \widehat{\mathcal{W}}_{tot''}\left(\widehat{H}_{3''} - \widehat{H}_2\right) = \left(733.69\frac{\mathrm{lb}}{\mathrm{h}}\right)\left(152.73\frac{\mathrm{BTU}}{\mathrm{lb}} - 213.56\frac{\mathrm{BTU}}{\mathrm{lb}}\right) = -44.6\cdot 10^3\ \frac{\mathrm{BTU}}{\mathrm{h}}$$

$$q_{16} = \widehat{\mathcal{W}}_{v''}\Delta\hat{Q}_{16} = \left(468.414\ \frac{\mathrm{lb}}{\mathrm{h}}\right)\left(94.43\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right) = 44.2\cdot 10^3\ \frac{\mathrm{BTU}}{\mathrm{h}}$$



As a curiosity, notice that if the saturated liquid and vapor flows had been evaluated by combining mass and enthalpy balances in the latter case, $\hat{\mathcal{W}}_{tot''}$ and $\hat{\mathcal{W}}_{v''}$ would have been 1.6 – 2.5% higher than using the entropy balance, but $q_{3''2}$ and q_{16} would be practically equal to each other.

$$\hat{\mathcal{W}}_{tot''} = \hat{\mathcal{W}}_l + \hat{\mathcal{W}}_{v''}$$

$$\hat{\mathcal{W}}_{tot''}\hat{H}_{4''} = \hat{\mathcal{W}}_{tot''}\hat{H}_{4''} = \hat{\mathcal{W}}_l\hat{H}_5 + \hat{\mathcal{W}}_{v''}\hat{H}_6$$

$$\hat{\mathcal{W}}_{tot''} = \frac{(\hat{H}_5 - \hat{H}_6)}{(\hat{H}_{4''} - \hat{H}_6)}\hat{\mathcal{W}}_l = \frac{(46 - 134.05)}{(102.72 - 134.05)}\left[265.276\ \frac{\text{lb}}{\text{h}}\right] = 745.53\ \frac{\text{lb}}{\text{h}}$$

$$\hat{\mathcal{W}}_{v''} = \hat{\mathcal{W}}_{tot''} - \hat{\mathcal{W}}_5 = 745.53 - 265.276 = 480.254\ \frac{\text{lb}}{\text{h}}$$

$$q_{3''2} = \hat{\mathcal{W}}_{tot''}(\hat{H}_{3''} - \hat{H}_2) = \left(745.53\frac{\text{lb}}{\text{h}}\right)\left(152.73\frac{\text{BTU}}{\text{lb}} - 213.56\frac{\text{BTU}}{\text{lb}}\right) = -45.35{\cdot}10^3\frac{\text{BTU}}{\text{h}}$$

$$q_{16} = \hat{\mathcal{W}}_{v''}\Delta\hat{Q}_{16} = \left(480.254\ \frac{\text{lb}}{\text{h}}\right)\left(94.43\ \frac{\text{BTU}}{\text{lb}}\right) = 45.35 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

6.19. Air at 15ºC and 2 atm is isothermally compressed to 100 atm. It is then isobarically cooled in a heat exchanger and then expanded in a suitable device up to 2 atm, which generates a mixture of saturated liquid and vapor. After separation, this saturated vapor is heated isobarically up to 15ºC (in the same exchanger than the stream at 100 atm to save energy) and mixed with the feed.

a) Represent the flowchart and describe the temperature evolution of both streams in the heat exchanger.

b) Obtain the energy balance to the heat exchanger as a function of the liquefied air fraction.

c) If an isenthalpic valve is employed, determine the fraction of liquefied air and the temperature of the stream at 100 atm when leaving the heat exchanger.

d) If an isentropic expander is employed, determine the fraction of liquefied air and the temperature of the stream at 100 atm when leaving the heat exchanger.

e) Compare the heat flows in the exchangers of questions c) and d) for a feed flow rate of 10 lb/h.

f) Compare the heat flows and the powers in the isothermal compressors of question c) and d) for the same feed flow rate of 10 lb/h.

g) If the isenthalpic valve is used but the air is isentropically compressed to 100 atm (instead of isothermically compressed), estimate the fraction of liquefied air and the temperature of the stream at 100 atm when leaving the heat exchanger.

h) In view of the results of question c) someone proposed to replace the process by: isentropic compression of the saturated vapor at 2 atm to 100 atm, mixing with the feed (which was previously compressed to 100 atm in an isothermal compressor), isobaric cooling to the temperature of question c) and expansion in the isenthalpic valve. Estimate their energy differences for the 10 lb/h feed flow rate.

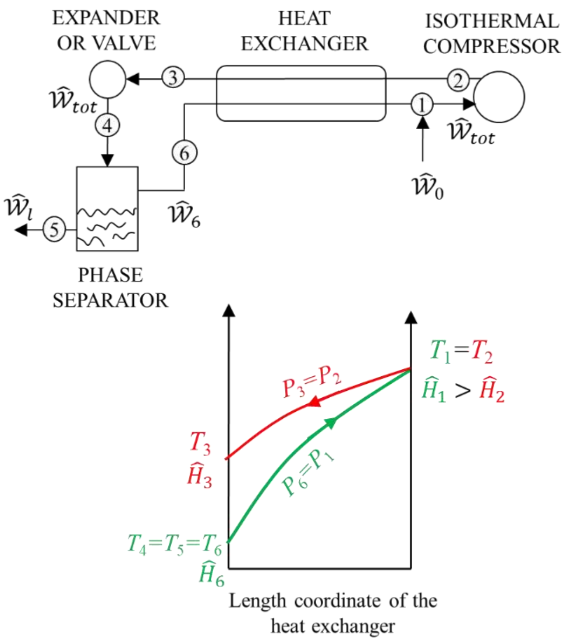
If necessary, use the following data for air (Perry et al.,1997). Take into account that $\widehat{H}$=0 kJ/kg at 0 K and 0 atm and that $\widehat{S}$ =3.0 kJ/kg·K for the saturated liquid at 1 atm, whereas in the well-known Landsbaum diagram, $\widehat{S}$ =0 for the saturated liquid at 1 atm and $\widehat{H}$=100 BTU/lb at 0ºR and 0 atm.

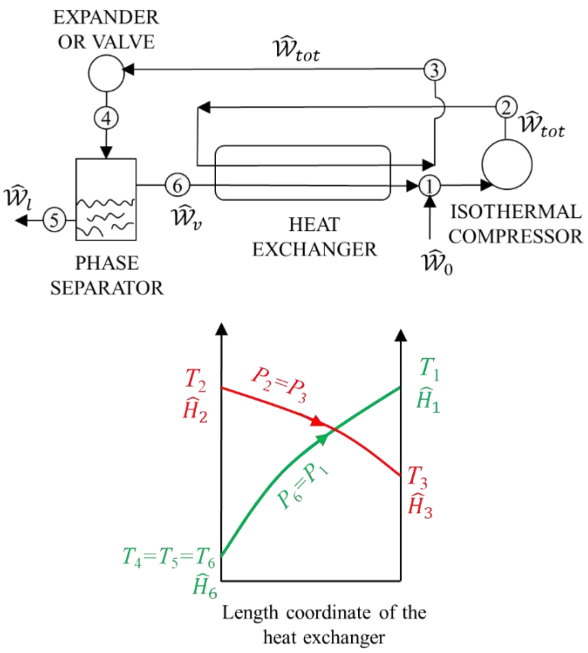
	***P*=80 bar**		***P*= 100 bar**		***P*=150 bar**	
***T* (K)**	**$\widehat{H}$ (kJ/kg)**	**$\widehat{S}$ (kJ/kg·K)**	**$\widehat{H}$ (kJ/kg)**	**$\widehat{S}$ (kJ/kg·K)**	**$\widehat{H}$ (kJ/kg)**	**$\widehat{S}$ (kJ/kg·K)**
350	339	5.733	336.5	5.661	330.9	5.525
400	393.1	5.878	391.3	5.807	387.5	5.677
450	446.5	6.004	445.3	5.935	442.9	5.807
500	499.8	6.116	499	6.048	497.5	5.922
600	606.7	6.311	606.6	6.244	606.6	6.121
800	825.1	6.624	825.8	6.559	827.8	6.439
1000	1051.1	6.877	1052.4	6.812	1055.5	6.693

	P=80 bar		**P= 100 bar**		**P=150 bar**	
T (K)	**$\hat{H}$ (kJ/kg)**	**$\hat{S}$ (kJ/kg·K)**	**$\hat{H}$ (kJ/kg)**	**$\hat{S}$ (kJ/kg·K)**	**$\hat{H}$ (kJ/kg)**	**$\hat{S}$ (kJ/kg·K)**
1200	**1284**	**7.089**	**1286**	**7.024**	**1290**	**6.906**
1400	**1522**	**7.273**	**1524**	**7.208**	**1529**	**7.092**
1600	**1772**	**7.437**	**1774**	**7.373**	**1779**	**7.256**
1800	**2025**	**7.586**	**2027**	**7.522**	**2033**	**7.405**
2000	**2285**	**7.723**	**2288**	**7.659**	**2294**	**7.543**
2500	**2971**	**8.029**	**2972**	**7.964**	**2977**	**7.848**

Question a. Let $\widehat{W}_0$ be the mass flow rate of the feed, $\widehat{W}_l$ be the mass flow rate of the saturated liquid, $\widehat{W}_v$ be the mass flow rate of the saturated vapor and $\widehat{W}_{tot}$ the mass flow rate of the stream that leaves the compressor. The quotient $\widehat{W}_l / \widehat{W}_{tot}$ is the mass fraction of liquefied air.

The heat exchanger can work in counterflow or in parallel flow. In both cases, the maximum efficiency would be reached when T_1=T_2 (which requires an infinite length of the apparatus). However, the representation of the temperature evolution shows that the heat exchange in parallel flow is impossible, since the thermal potential becomes zero at an intermediate point.





Question b. In the heat exchanger

$$\begin{bmatrix}\text{heat flow}\\ \text{given in the}\\ \text{cooling}\\ \text{from 2 to 3}\end{bmatrix} = \begin{bmatrix}\text{heat flow}\\ \text{gained in the}\\ \text{heating}\\ \text{from 6 to 1}\end{bmatrix}$$

$$q_{32} = -q_{16}$$

$$\widehat{\mathcal{W}}_{tot}\Delta\hat{Q}_{32} = -\widehat{\mathcal{W}}_{v}\Delta\hat{Q}_{16}$$

$$\widehat{\mathcal{W}}_{tot}\int_2^3 T\mathrm{d}\hat{S} = -\widehat{\mathcal{W}}_{v}\int_1^6 T\mathrm{d}\hat{S} \qquad [1]$$

However, equations of reference problem 0.13 say that

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\widehat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \qquad [2]$$

and if the heat exchanger is isobaric (dP=0), then $\mathrm{d}\hat{H} = \mathrm{d}\hat{Q}$ and equation [1] becomes

$$\widehat{\mathcal{W}}_{tot}\Delta\hat{H}_{32} = -\widehat{\mathcal{W}}_{v}\Delta\hat{H}_{16}$$

$$\widehat{\mathcal{W}}_{tot}\left(\hat{H}_3 - \hat{H}_2\right) = -\widehat{\mathcal{W}}_{v}\left(\hat{H}_1 - \hat{H}_6\right) \qquad [3]$$

$$\left(\hat{H}_3 - \hat{H}_2\right) = -\frac{\widehat{\mathcal{W}}_{v}}{\widehat{\mathcal{W}}_{tot}}\left(\hat{H}_1 - \hat{H}_6\right) \qquad [4]$$

On the other hand, and according to the mass balance to the phase separator

$$\widehat{\mathcal{W}}_{tot} = \widehat{\mathcal{W}}_{l} + \widehat{\mathcal{W}}_{v}$$

$$1 = \frac{\widehat{\mathcal{W}}_{l}}{\widehat{\mathcal{W}}_{tot}} + \frac{\widehat{\mathcal{W}}_{v}}{\widehat{\mathcal{W}}_{tot}} \qquad \rightarrow \qquad \frac{\widehat{\mathcal{W}}_{v}}{\widehat{\mathcal{W}}_{tot}} = 1 - \frac{\widehat{\mathcal{W}}_{l}}{\widehat{\mathcal{W}}_{tot}}$$

By introducing this relation in expression [4], the energy balance as a function of the liquefied air fraction can be obtained.

$$\left(\hat{H}_3 - \hat{H}_2\right) = -\left(1 - \frac{\widehat{\mathcal{W}}_{l}}{\widehat{\mathcal{W}}_{tot}}\right)\left(\hat{H}_1 - \hat{H}_6\right) \qquad [5]$$

Question c. Enthalpies of points 1, 2 and 6 can be read in figure V.16 of appendix V, where the temperature is expressed in degrees Rankine.

$$T_1(°\mathrm{R}) = T_2(°\mathrm{R}) = 1.8(15°\mathrm{C}) + 492 = 519°\mathrm{R}$$

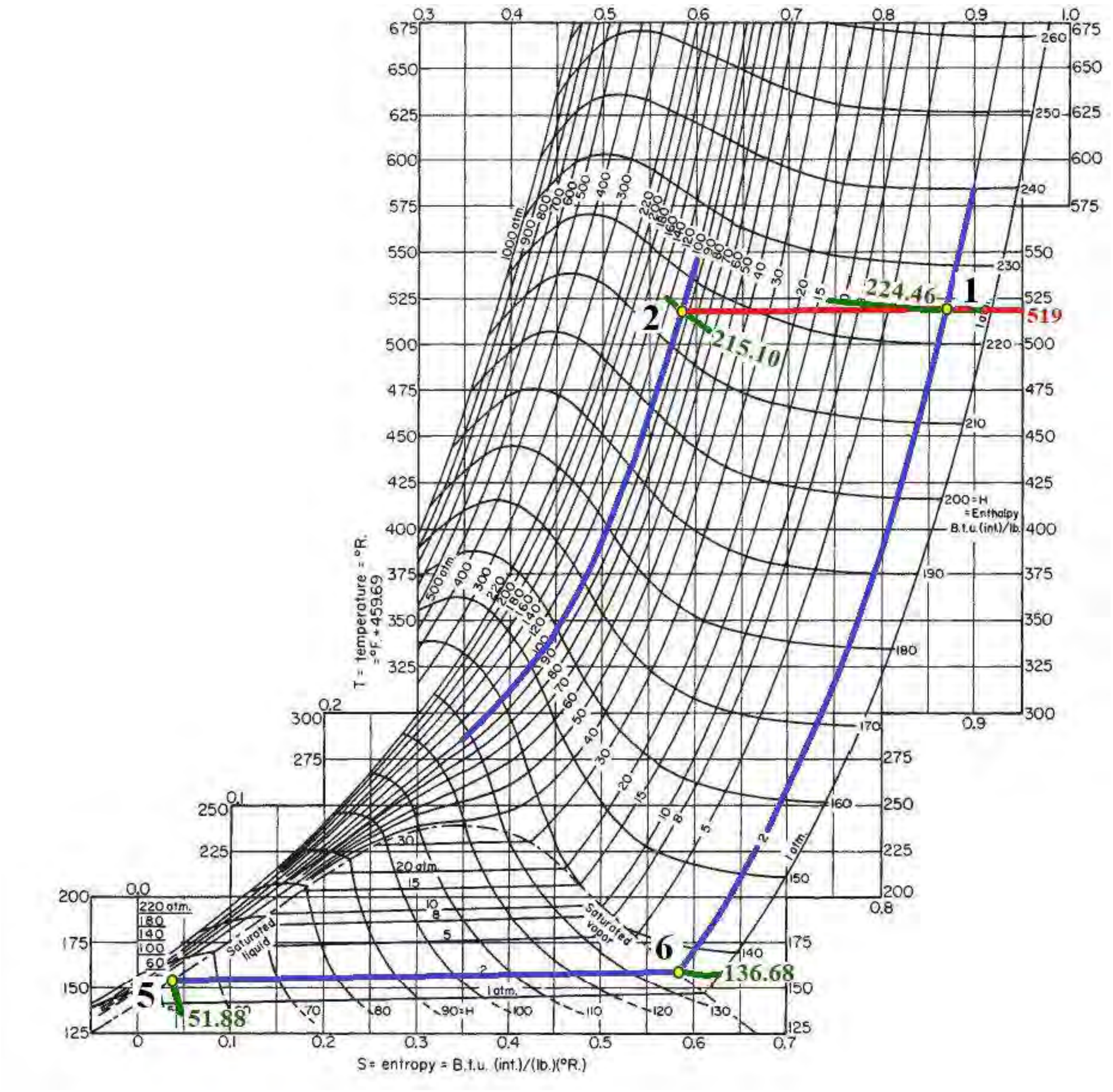
By graphically placing the data of the statement of the problem, it can be found that $\hat{H}_1$ =224.46 BTU/lb, $\hat{H}_2$ =215.10 BTU/lb and $\hat{H}_6$ =136.68 BTU/lb. Since an isenthalpic valve is between points 2 and 4, $\hat{H}_3 = \hat{H}_4$, and $\hat{H}_4$ will be calculated from the enthalpies of the saturated liquid and the saturated vapor as

$$\hat{H}_4 = \left(\frac{\widehat{\mathcal{W}}_{l}}{\widehat{\mathcal{W}}_{tot}}\right)\hat{H}_5 + \left(1 - \frac{\widehat{\mathcal{W}}_{l}}{\widehat{\mathcal{W}}_{tot}}\right)\hat{H}_6 \qquad [6]$$

where $\widehat{H}_5 = 51.88$ BTU/lb. By substituting [6] in equation [5]

$$\left[\left(\frac{\widehat{\mathcal{W}}_l}{\widehat{\mathcal{W}}_{tot}}\right)51.88+\left(1-\frac{\widehat{\mathcal{W}}_l}{\widehat{\mathcal{W}}_{tot}}\right)136.68-215.10\right]=-\left(1-\frac{\widehat{\mathcal{W}}_l}{\widehat{\mathcal{W}}_{tot}}\right)(224.46-136.68)$$

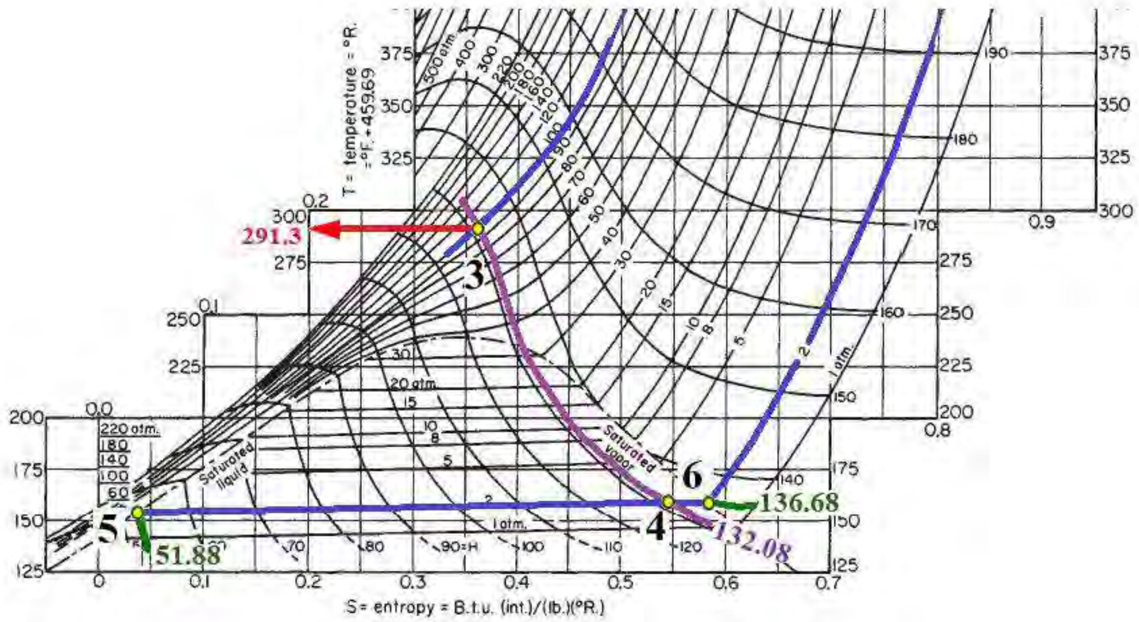
$$\frac{\widehat{\mathcal{W}}_5}{\widehat{\mathcal{W}}_3}=0.0542$$



and temperature T_3 will be found in the intersection of the isenthalpic line

$$\widehat{H}_4=\widehat{H}_3=0.0542\left(51.88\ \frac{\text{BTU}}{\text{lb}}\right)+(1-0.0542)\left(136.68\ \frac{\text{BTU}}{\text{lb}}\right)=132.08\ \frac{\text{BTU}}{\text{lb}}$$

with the 100 atm isobar, which in this case is of 219.3ºR



Question d. When employing an isentropic expander, $\widehat{H}_3 \neq \widehat{H}_4$ and the calculation of the liquefied fraction is not as easy as in the previous question. It has to be determined by trial and error in the following way:

- Assume a value of $\widehat{H}_4$.
- Read in figure V.16 the enthalpy $\widehat{H}_3$ which is placed on the same isentropic line that $\widehat{H}_4$.
- Obtain the liquefied fraction from equation [6] and $\widehat{H}_4$

$$\frac{\widehat{\mathcal{W}}_l}{\widehat{\mathcal{W}}_{tot}} = \frac{\widehat{H}_4 - \widehat{H}_6}{\widehat{H}_5 - \widehat{H}_6} = \frac{\widehat{H}_4 - 136.68}{51.88 - 136.68}$$

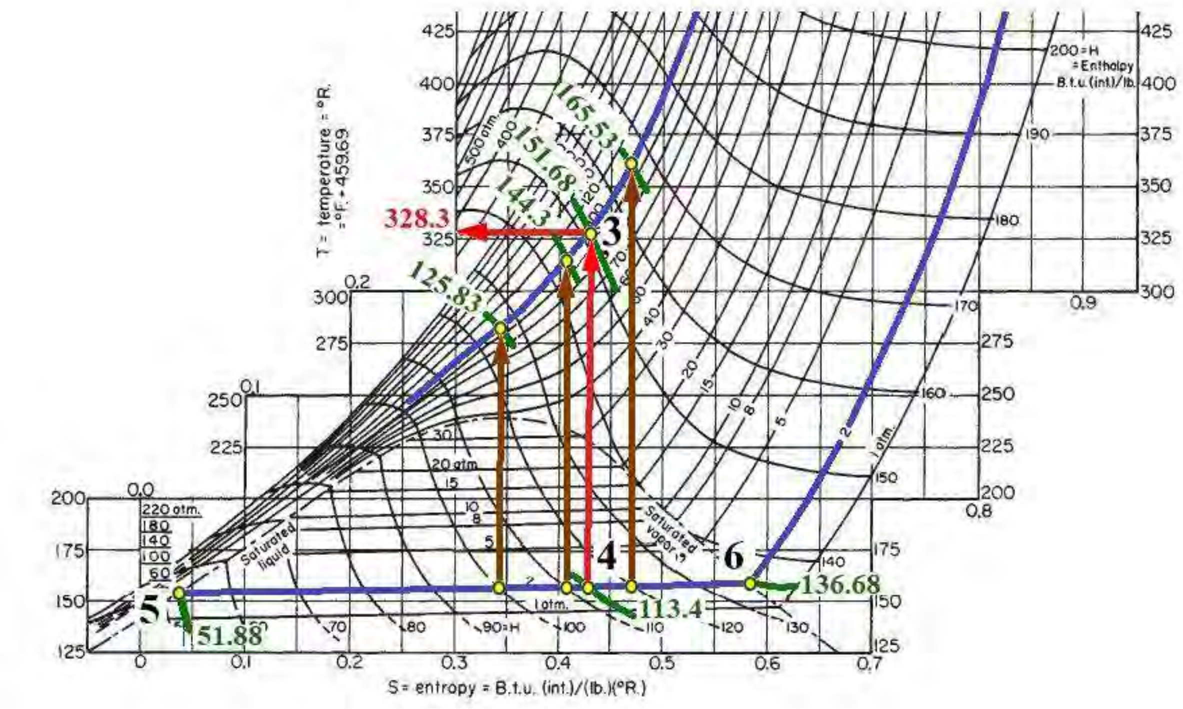
- Obtain the liquefied fraction from equation [5] and $\widehat{H}_3$

$$\frac{\widehat{\mathcal{W}}_l}{\widehat{\mathcal{W}}_{tot}} = 1 + \frac{\left(\widehat{H}_3 - \widehat{H}_2\right)}{\left(\widehat{H}_1 - \widehat{H}_6\right)} = 1 + \frac{\widehat{H}_3 - 215.10}{224.46 - 136.68}$$

- If both fractions are not the same, assume another enthalpy in point 4. If both fractions coincide, then the assumed enthalpy is the correct one. The intersection between the isoenthalpic line $\widehat{H}_3$ with the 100 atm isobar will graphically indicate the value of T_3.

$\widehat{H}_4$ (BTU/lb)	$\widehat{H}_3$ (BTU/lb)	liquefied fraction, eq. [6]	liquefied fraction, eq. [5]	Comments
100	125.83	0.4325	-0.0169	$\widehat{H}_3$ must be higher
110	144.35	0.3146	0.1940	$\widehat{H}_3$ must be higher
120	165.53	0.1967	0.4353	$\widehat{H}_3$ must be lower
113.4	151.68	0.2745	0.2775	Reasonable match

Therefore T_3=328.3ºR. The trial and error could also be done by assuming T_3 and reading $\widehat{H}_3$ and $\widehat{H}_4$ in the figure, but this would have saturated the diagram with lines.



Question e. The global mass balance shows that

$$\widehat{\mathcal{W}}_0 = \widehat{\mathcal{W}}_l = 10\ \frac{\text{lb}}{\text{h}}$$

and by using the liquefied mass fraction of question **c**

$$\frac{\widehat{\mathcal{W}}_l}{\widehat{\mathcal{W}}_{tot}} = 0.0542 \qquad \rightarrow\ \widehat{\mathcal{W}}_{tot} = \frac{\widehat{\mathcal{W}}_l}{0.0542} = \frac{(10\ \text{lb/h})}{0.0542} = 184.5\ \frac{\text{lb}}{\text{h}}$$

$$\widehat{\mathcal{W}}_v = \widehat{\mathcal{W}}_{tot} - \widehat{\mathcal{W}}_l = 184.5\ \frac{\text{lb}}{\text{h}} - 10\frac{\text{lb}}{\text{h}} = 174.5\ \frac{\text{lb}}{\text{h}}$$

If these data and the corresponding enthalpies are introduced in equation [3], the heat flows in the heat exchanger will be

$$q_{32} = \widehat{\mathcal{W}}_{tot}\left(\hat{H}_3 - \hat{H}_2\right) = \left(184.5\ \frac{\text{lb}}{\text{h}}\right)\left(132.08\ \frac{\text{BTU}}{\text{lb}} - 215.15\ \frac{\text{BTU}}{\text{lb}}\right) = -15.3 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

$$-q_{16} = -\widehat{\mathcal{W}}_v\left(\hat{H}_1 - \hat{H}_6\right) = -\left(174.5\frac{\text{lb}}{\text{h}}\right)\left(224.46\ \frac{\text{BTU}}{\text{lb}} - 136.68\ \frac{\text{BTU}}{\text{lb}}\right) = -15.3 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

On the other hand, by employing an average liquefied fraction of 0.5(0.2745+0.2775) =0.2760 for question **d**

$$\frac{\widehat{\mathcal{W}}_l}{\widehat{\mathcal{W}}_{tot}} = 0.2760 \qquad \rightarrow \quad \widehat{\mathcal{W}}_{tot} = \frac{\widehat{\mathcal{W}}_l}{0.2760} = \frac{(10\ \text{lb/h})}{0.2760} = 36.23\ \frac{\text{lb}}{\text{h}}$$

$$\widehat{\mathcal{W}}_v = \widehat{\mathcal{W}}_{tot} - \widehat{\mathcal{W}}_l = 36.23 - 10 = 26.23\ \frac{\text{lb}}{\text{h}}$$

$$q_{32} = \widehat{\mathcal{W}}_{tot}\left(\hat{H}_3 - \hat{H}_2\right) = \left(36.23\ \frac{\text{lb}}{\text{h}}\right)\left(151.68\ \frac{\text{BTU}}{\text{lb}} - 215.15\ \frac{\text{BTU}}{\text{lb}}\right) = -2.3 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

$$-q_{16} = -\widehat{\mathcal{W}}_v\left(\hat{H}_1 - \hat{H}_6\right) = \left(26.23\ \frac{\text{lb}}{\text{h}}\right)\left(224.46\ \frac{\text{BTU}}{\text{lb}} - 136.68\ \frac{\text{BTU}}{\text{lb}}\right) = -2.3 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

As can be seen, the heat flows are higher in the case of an isenthalpic valve, mainly because the flow rate of the recycled saturated vapor ($\widehat{\mathcal{W}}_v$) is higher than in the case of an isentropic expander.

Question f. In the isothermal compressor (transit from point 1 to point 2), the integral which evaluates the heat change becomes simpler because T is constant

$$\Delta\hat{Q}_{21} = \int_1^2 T\mathrm{d}\hat{S} = T_1\int_1^2 \mathrm{d}\hat{S} = T_1\left(\hat{S}_2 - \hat{S}_1\right)$$

And the compression work, according to equation [2] can be calculated as

$$\mathrm{d}\widehat{W}^{\text{fl}} = \mathrm{d}\hat{H} - \mathrm{d}\hat{Q} = \mathrm{d}\hat{H} - T\mathrm{d}\hat{S}$$

$$\Delta\widehat{W}^{\text{fl}}_{21} = \int_1^2 \left(\mathrm{d}\hat{H} - T\mathrm{d}\hat{S}\right) = \Delta\hat{H}_{21} - T_1\left(\hat{S}_2 - \hat{S}_1\right) = \Delta\hat{H}_{21} - \Delta\hat{Q}_{21}$$

Figure V.16 indicates that $\hat{S}_1$ =0.870 BTU/lb°R and $\hat{S}_2$ =0.584 BTU/lb°R; thus

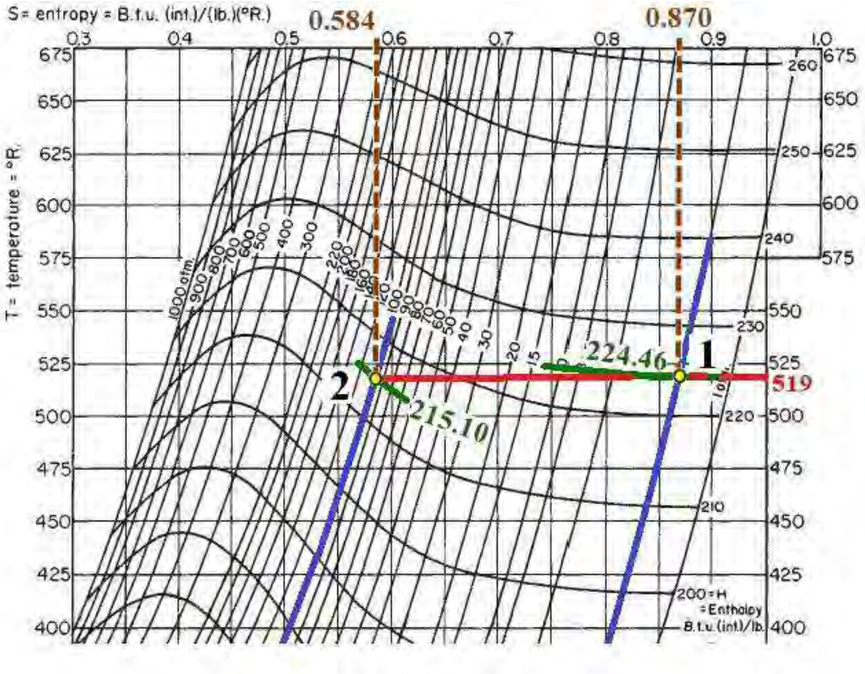
$$\Delta\hat{Q}_{21} = (519°\text{R})\left(0.584\ \frac{\text{BTU}}{\text{lb°R}} - 0.870\frac{\text{BTU}}{\text{lb°R}}\right) = -148.43\ \frac{\text{BTU}}{\text{lb}}$$

$$\Delta\widehat{W}^{\text{fl}}_{21} = \left(215.10\ \frac{\text{BTU}}{\text{lb}} - 224.46\frac{\text{BTU}}{\text{lb}}\right) - \left(-148.43\ \frac{\text{BTU}}{\text{lb}}\right) = 139.07\ \frac{\text{BTU}}{\text{lb}}$$

The multiplication of this heat and this work by the flow through the compressor ($\widehat{\mathcal{W}}_{tot}$) gives the heat flows and the powers involved. When using an isenthalpic valve

$$q_{21} = \widehat{\mathcal{W}}_{tot} \Delta \hat{Q}_{21} = \left(184.5\ \frac{\text{lb}}{\text{h}}\right)\left(-148.43\ \frac{\text{BTU}}{\text{lb}}\right) = -27.4 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

$$\wp_{21} = \widehat{\mathcal{W}}_{tot} \Delta \widehat{W}^{\text{fl}}_{21} = \left(184.5\ \frac{\text{lb}}{\text{h}}\right)\left(139.07\ \frac{\text{BTU}}{\text{lb}}\right) = 25.66 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$



and when using an isentropic expander

$$q_{21} = \widehat{\mathcal{W}}_{tot} \Delta \hat{Q}_{21} = \left(36.23\ \frac{\text{lb}}{\text{h}}\right)\left(-148.43\ \frac{\text{BTU}}{\text{lb}}\right) = -5.38 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

$$\wp_{21} = \widehat{\mathcal{W}}_{tot} \Delta \widehat{W}^{\text{fl}}_{21} = \left(36.23\ \frac{\text{lb}}{\text{h}}\right)\left(139.07\ \frac{\text{BTU}}{\text{lb}}\right) = 5.04 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

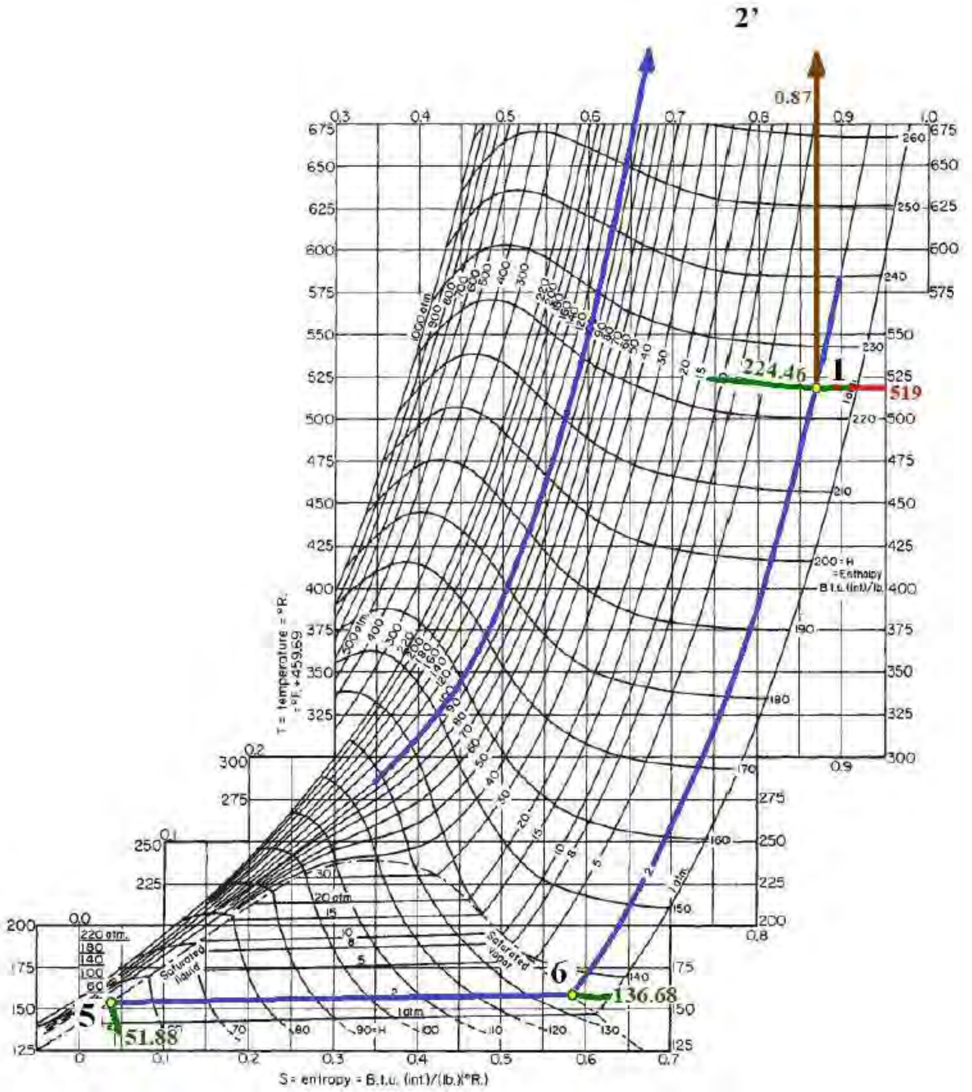
Question g. This question is similar to question **c**, its main difference being that $\widehat{H}_2 \neq$215.10 BTU/lb, but rather a value corresponding to the intersection of the 100 atm isobar with the isentropic that passes through point 1 ($\hat{S}_1$ =0.87 BTU/lb°R). Since this intersection is beyond the limits of figure V.16, the table in the statement of the problem has to be employed. It provides values of enthalpies and entropies at high temperatures. However, in this table the temperatures are in K, the pressures in bar, the entropies in kJ/kg and the entropies in kJ/kg·K, so they have to be expressed in the same units as figure V.16 by means of the conversion factors in appendix I

$$T\ \text{K} \times \frac{1.8\ \text{°R}}{1\ \text{K}} = 1.8T$$

$$P\ \text{bar}\times\frac{0.987\ \text{atm}}{1\ \text{bar}}=0.987P$$

$$\hat{H}\ \frac{\text{kJ}}{\text{kg}}\times\frac{1000\ \text{J}}{1\ \text{kJ}}\times\frac{0.000948\ \text{BTU}}{1\ \text{J}}\times\frac{1\ \text{kg}}{2.2\ \text{lb}}=0.43090909\ \hat{H}$$

$$\hat{S}\ \frac{\text{kJ}}{\text{kg}\cdot\text{K}}\times\frac{1000\ \text{J}}{1\ \text{kJ}}\times\frac{0.000948\ \text{BTU}}{1\ \text{J}}\times\frac{1\ \text{kg}}{2.2\ \text{lb}}\times\frac{1\ \text{K}}{1.8\ \text{°R}}=0.23939394\ \hat{S}$$



Additionally, in figure V.16 (Landsbaum diagram), the reference states for enthalpy and entropy are not the same as those in the table given by the statement of the problem. Therefore, 100 BTU/lb have to be substracted to all enthalpies and 3.0 kJ/kg·K (or what is the same, 1.293 BTU/lb°R) to all the entropies.

T (ºR)	P=78.96 atm		P= 98.7 atm		P=148.05 atm	
	$\widehat{H}$ (BTU/lb)	$\hat{S}$(BTU/lbºR)	$\widehat{H}$ (BTU/lb)	$\hat{S}$(BTU/lbºR)	$\widehat{H}$ (BTU/lb)	$\hat{S}$(BTU/lbºR)
630	246.08	0.6543	245.00	0.6370	242.59	0.6045
720	269.39	0.6890	268.61	0.6720	266.98	0.6409
810	292.40	0.7191	291.88	0.7026	290.85	0.6720
900	315.37	0.7460	315.02	0.7297	314.38	0.6995
1080	361.43	0.7926	361.39	0.7766	361.39	0.7471
1440	455.54	0.8676	455.84	0.8520	456.71	0.8233
1800	552.93	0.9281	553.49	0.9126	554.82	0.8841
2160	653.29	0.9789	654.15	0.9633	655.87	0.9351
2520	755.84	1.0229	756.71	1.0074	758.86	0.9796
2880	863.57	1.0622	864.43	1.0469	866.59	1.0189
3240	972.59	1.0979	973.45	1.0825	976.04	1.0545
3600	1084.63	1.1307	1085.92	1.1153	1088.51	1.0876
4500	1380.23	1.2039	1380.66	1.1884	1382.82	1.1606

By interpolating in this new table the temperature and pressure of the point whose entropy is 0.87 BTU/lbºR at 100 atm, the values of $T_{2'}$=1552 ºR and $\widehat{H}_{2'}$= 486 BTU/lb can be found. When this enthalpy is combined with equations [5] and [6] it is obtained that

$$\left[\left(\frac{\widehat{\mathcal{W}}_l}{\widehat{\mathcal{W}}_{tot}}\right)51.88+\left(1-\frac{\widehat{\mathcal{W}}_l}{\widehat{\mathcal{W}}_{tot}}\right)136.68-486\right]=-\left(1-\frac{\widehat{\mathcal{W}}_l}{\widehat{\mathcal{W}}_{tot}}\right)(224.46-136.68)$$

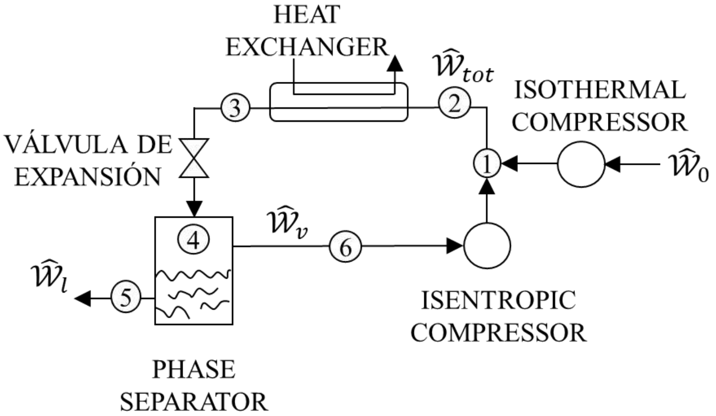
$$\frac{\widehat{\mathcal{W}}_l}{\widehat{\mathcal{W}}_{tot}}=-1.51$$

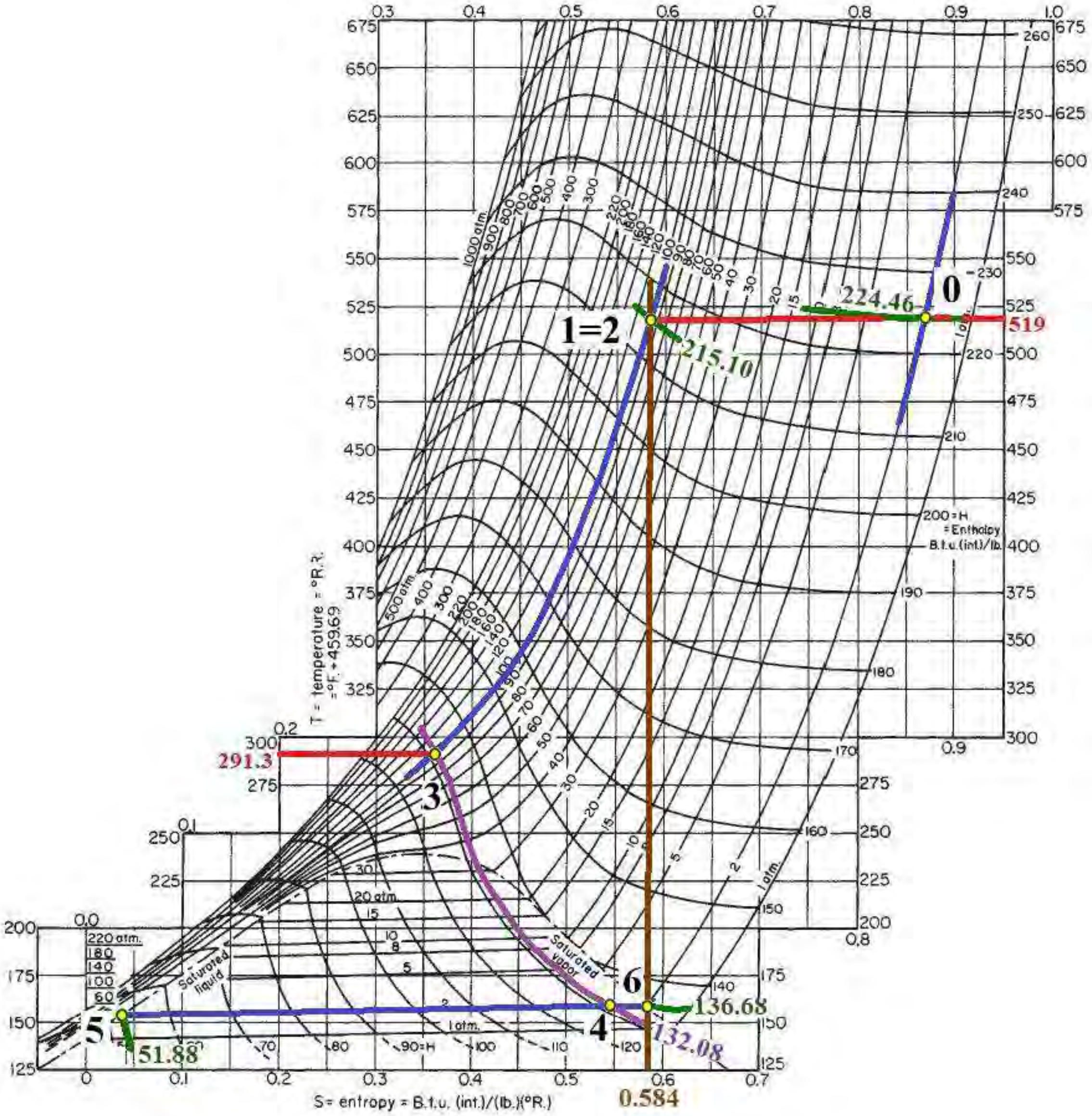
$$\widehat{H}_4=\widehat{H}_3=-1.51\left(51.88\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right)+(1+1.51)\left(136.68\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right)=264.728\ \frac{\mathrm{BTU}}{\mathrm{lb}}$$

The negative sign of the liquefied fraction, its value higher than unity and the fact that the calculated enthalpy is not located within the biphasic region, imply that the desired result cannot be achieved: the saturated vapor stream is unable of refrigerating the stream at 100 atm.

Question h. The flowchart and the representation of the process in the *TS*(*P*,*H*) diagram show that the main difference with that of question **c** is the absence of heat exchange between the compressed stream at 100 atm and the saturated vapor stream. An additional refrigerant will therefore be required in the heat exchanger to remove

$$q_{32}=\widehat{\mathcal{W}}_{tot}\left(\widehat{H}_3-\widehat{H}_2\right)=\left(184.5\ \frac{\mathrm{lb}}{\mathrm{h}}\right)\left(132.08\ \frac{\mathrm{BTU}}{\mathrm{lb}}-215.15\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right)=-15.3\cdot 10^{3}\ \frac{\mathrm{BTU}}{\mathrm{h}}$$





On the other hand, the heat flow and the power of the isothermal compressor will decrease, because the flow to be compressed is that of the feed

$$q_{10} = \hat{\mathcal{W}}_0 \Delta\hat{Q}_{10} = \left(10\ \frac{\text{lb}}{\text{h}}\right)\left(-148.43\ \frac{\text{BTU}}{\text{lb}}\right) = -1.45 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

$$\wp_{10} = \hat{\mathcal{W}}_0 \Delta\hat{W}^{\text{fl}}_{10} = \left(10\ \frac{\text{lb}}{\text{h}}\right)\left(139.07\ \frac{\text{BTU}}{\text{lb}}\right) = 1.39 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

although the power of the new isentropic compressor has to be included now. If $\text{d}\hat{S}=0$ equation [2] gives

$$\text{d}\hat{W}^{\text{fl}} = \text{d}\hat{H} \quad \rightarrow \quad \Delta\hat{W}^{\text{fl}}_{26} = \int_6^2 \text{d}\hat{H} = \Delta\hat{H}_{26}$$

$$\Delta\hat{W}^{\text{fl}}_{26} = \hat{H}_2 - \hat{H}_6 = \left(215.10\ \frac{\text{BTU}}{\text{lb}} - 136.68\frac{\text{BTU}}{\text{lb}}\right) = 78.42\ \frac{\text{BTU}}{\text{lb}}$$

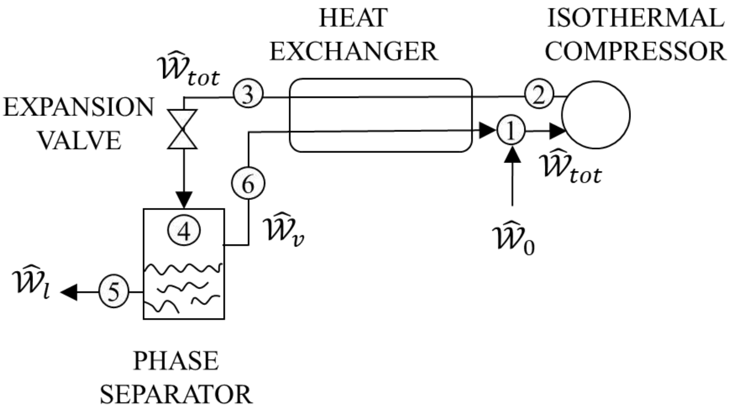
and

$$\wp_{26} = \hat{\mathcal{W}}_v \Delta\hat{W}^{\text{fl}}_{26} = \left(174.5\ \frac{\text{lb}}{\text{h}}\right)\left(78.42\ \frac{\text{BTU}}{\text{lb}}\right) = 13.7 \cdot 10^3\ \frac{\text{BTU}}{\text{h}}$$

6.20. A system operating according to the Linde cycle is fed with ammonia at 0.1 MPa and 450 K to obtain a saturated liquid at the same pressure. The process has been optimized so that the saturated steam resulting from the phase separation is recirculated to cool the compressed NH_3 stream (which is at 10 MPa) in a counterflow heat exchanger before reaching the same conditions as the feed.

- **a) Represent the flowchart and obtain the energy balance to the heat exchanger as a function of the fraction of liquefied NH_3.**
- **b) Determine the fraction of liquefied ammonia and the temperature at which the stream at 10 MPa leaves the heat exchanger.**
- **c) Qualitatively represent the operating lines in *PT*(*H*), *PV*(*T,H*) and *TS*(*P,H*) diagrams.**

Question a. According to section e of reference problem 0.13, the Linde cycle consists of isothermal compression, isobaric heat exchange, isenthalpic expansion and recycling of the vapor to mix it with the feed (after passing through the heat exchanger). Its flowchart can be approximated by



where $\hat{\mathcal{W}}_0$ is the mass flow of feed, $\hat{\mathcal{W}}_l$ the mass flow of saturated liquid, $\hat{\mathcal{W}}_v$ the mass flow of the saturated vapor and $\hat{\mathcal{W}}_{tot}$ the mass flow of the stream that passes through the compressor and the valve (and is the sum of the feed flow and the saturated vapor flow).

On the other hand, the energy balance in the heat exchanger indicates that the heat flow given in the cooling from 2 to 3 must be the same than the heat flow gained in the heating from 6 to 1; thus

$$q_{32} = -q_{16}$$

$$\hat{\mathcal{W}}_{tot}\Delta\hat{Q}_{32} = -\hat{\mathcal{W}}_v\Delta\hat{Q}_{16}$$

$$\hat{\mathcal{W}}_{tot}\int_2^3 T\mathrm{d}\hat{S} = -\hat{\mathcal{W}}_v\int_1^6 T\mathrm{d}\hat{S} \qquad [1]$$

Nevertheless, equations of reference problem 0.3 establish that

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P$$

and if the exchange is isobaric (dP=0), then d$\hat{H}$ = d$\hat{Q}$ and equation [1] gives

$$\hat{\mathcal{W}}_{tot}\Delta\hat{H}_{32} = -\hat{\mathcal{W}}_{v}\Delta\hat{H}_{16}$$

$$\left(\hat{H}_3 - \hat{H}_2\right) = -\frac{\hat{\mathcal{W}}_v}{\hat{\mathcal{W}}_{tot}}\left(\hat{H}_1 - \hat{H}_6\right) \qquad [2]$$

By combining this equation with the mass balance to the phase separator

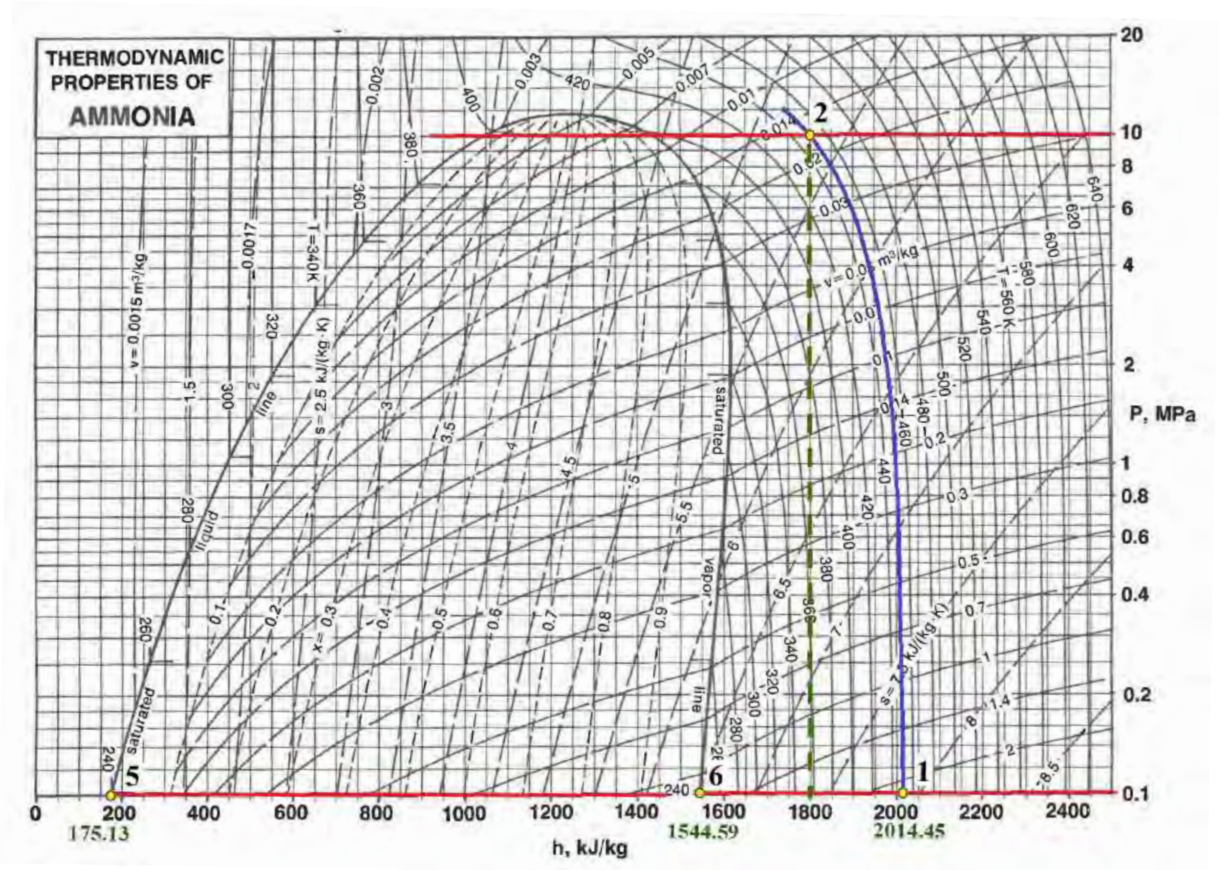
$$\hat{\mathcal{W}}_{tot} = \hat{\mathcal{W}}_l + \hat{\mathcal{W}}_v$$

it can be obtained that

$$\left(\hat{H}_3 - \hat{H}_2\right) = -\left(1 - \frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}\right)\left(\hat{H}_1 - \hat{H}_6\right) \qquad [3]$$

being $\hat{\mathcal{W}}_l / \hat{\mathcal{W}}_{tot}$ the fraction of liquefied ammonia.

Question b. Enthalpies of points 1, 2 and 6 are read in figure V.12 of appendix V, where $\hat{H}_1$ = 2014.42 kJ/kg, $\hat{H}_2$ =1800 kJ/kg and $\hat{H}_6$ =1544.59 kJ/kg.



Since there is an isenthalpic valve between points 3 and 4, $\hat{H}_3 = \hat{H}_4$, and $\hat{H}_4$ can be calculated from the enthalpies of the saturated liquid and vapor as

$$\hat{H}_4 = \left(\frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}\right)\hat{H}_5 + \left(1 - \frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}\right)\hat{H}_6 \qquad [4]$$

being $\hat{H}_5 = 175.13$ kJ/kg. By substituting [4] in [3]

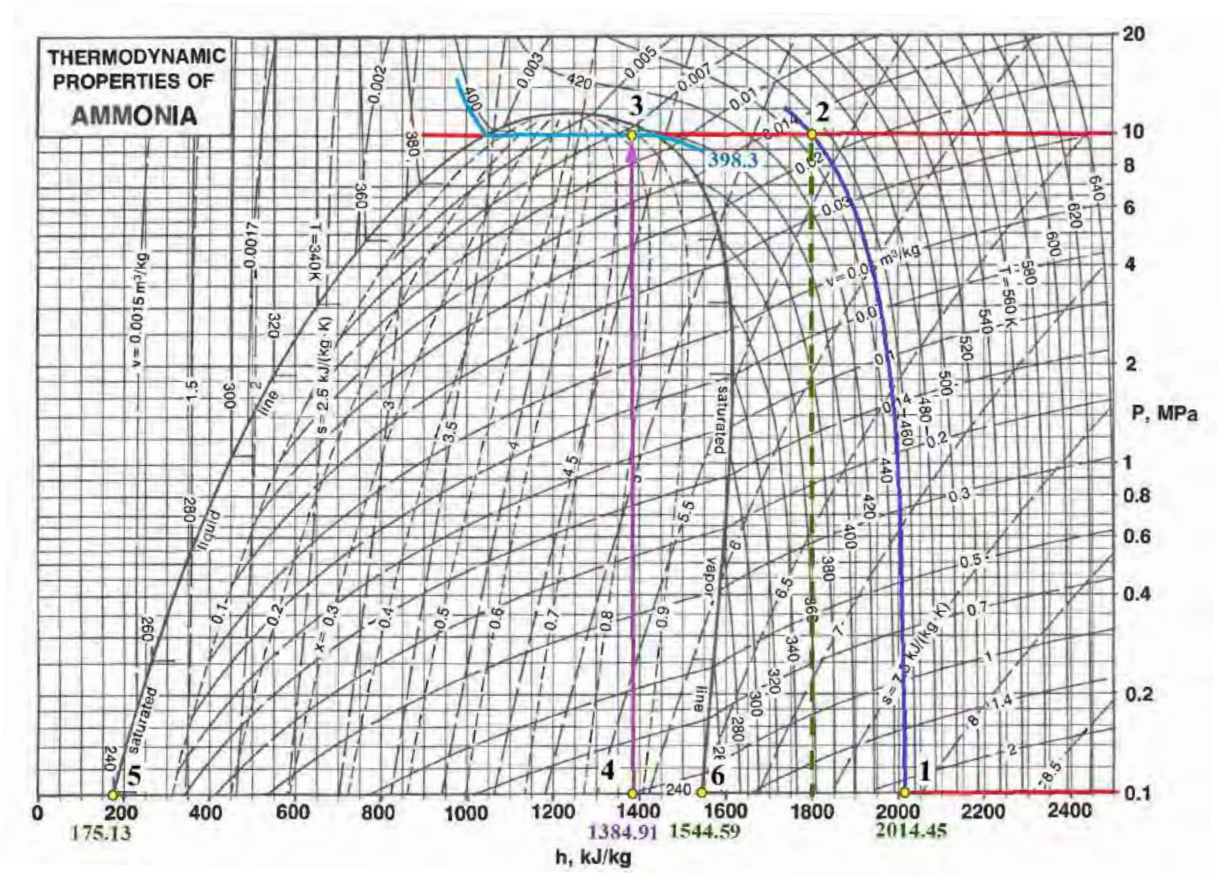
$$\left[\left(\frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}\right)175.13 + \left(1 - \frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}\right)1544.59 - 1800\right] = -\left(1 - \frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}\right)(2014.45 - 1544.59)$$

$$\frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}} = 0.1166$$

and introducing this value in [4] the following enthalpy is obtained

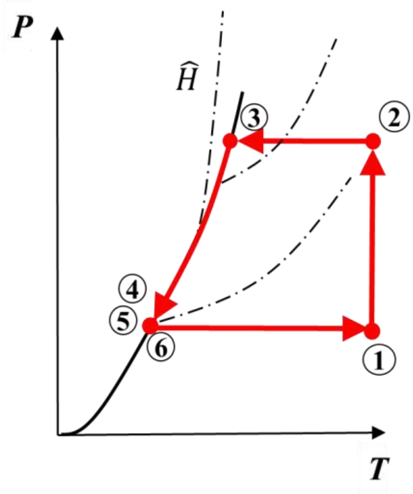
$$\hat{H}_4 = (0.1166)\left(175.13\ \frac{\text{kJ}}{\text{kg}}\right) + (1 - 0.1166)\left(1544.59\ \frac{\text{kJ}}{\text{kg}}\right) = 1384.91\,\frac{\text{kJ}}{\text{kg}}$$

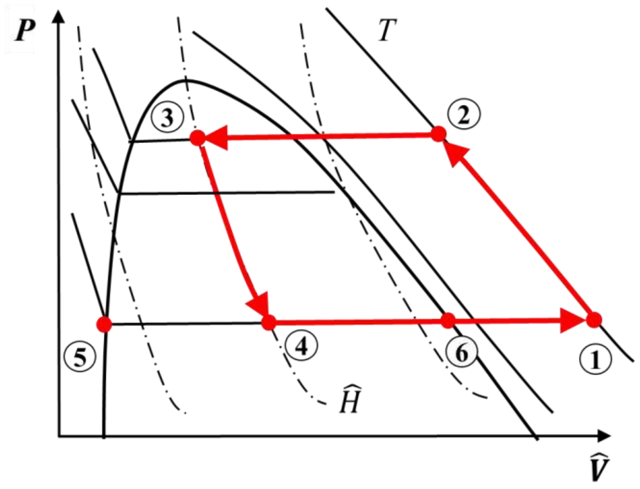
which placed in figure V.12 allows the determination of T_3 in the intersection of the $\hat{H}_4$ isoenthalpic (vertical line) with the 10 MPa isobar (horizontal line).

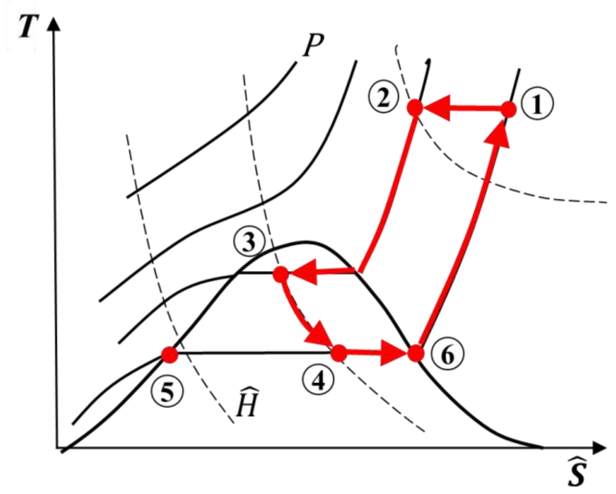


This intersection tooks place in the biphasic zone, approximately at 398.3 K.

Question c. The qualitative representations of the operating lines in the *PT*(*H*), *PV*(*T*,*H*) and *TS*(*P*,*H*) diagrams will be





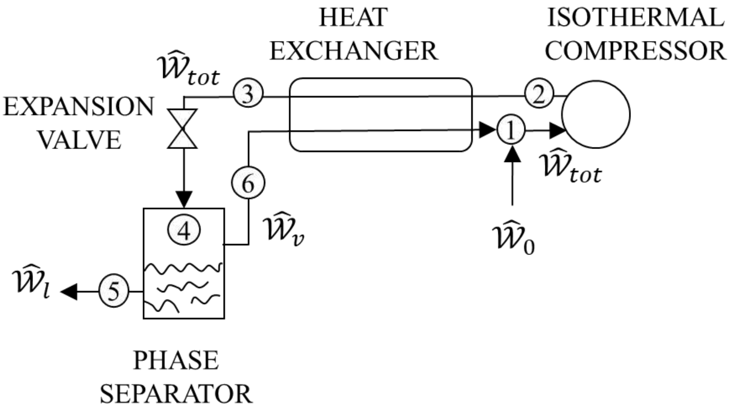


6.21. A stream of 1000 kg/h of ethane at 75°C and 1 bar will be liquefied to obtain ethane at the same pressure and at its normal boiling temperature.

In the Linde cycle, the mass flow that results from mixing this feed with recycled heated vapor is isothermally compressed to 80 bar, isobarically cooled to the appropiate temperature by means of a counterflow heat exchanger (that uses as the only cooling medium the recycled vapor) and isenthalpically expanded to 1 atm. After the expansion, the two phases are separated.

- **a) Represent the flowchart.**
- **b) Obtain the energy balance to the heat exchanger as a function of the liquefied fraction.**
- **c) Determine the fraction of liquefied ethane and the temperature before the isenthalpic expansion by means of a *PH*(*T*,*S*,*V*) diagram.**
- **d) Calculate the heat flow in the heat exchanger.**
- **e) Calculate the heat flow and the power consumed in the compression.**
- **f) Qualitatively explain how to perform a quasi-isothermal compression by means of three stages of isentropic compression followed by isobaric cooling.**

Question a. By following the description given in the statement of the problem, the flowchart will be



where $\widehat{W}_0$ is the mass flow rate of the feed, $\widehat{W}_l$ the mass flow rate of the saturated liquid, $\widehat{W}_v$ the mass flow rate of saturated vapor and $\widehat{W}_{tot}$ the mass flow rate of the stream that passes through the compressor, the heat exchanger and the valve (and whose mass flow rate is the sum of those of the feed and the saturated vapor).

Question b. According to the energy balance to the heat exchanger, the heat flow given by the stream that cools between 2 and 3 must be the same as the heat flow gained by the stream that heats between 6 and 1

$$q_{32} = -q_{16}$$

$$\widehat{W}_{tot}\Delta\hat{Q}_{32} = -\widehat{W}_v\Delta\hat{Q}_{16}$$

$$\hat{\mathcal{W}}_{tot}\int_2^3 T\mathrm{d}\hat{S} = -\hat{\mathcal{W}}_v\int_1^6 T\mathrm{d}\hat{S} \qquad [1]$$

If the heat exchange is isobaric, dP=0. Having in mind that

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\hat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \qquad [2]$$

it turns out that $\mathrm{d}\hat{H} = \mathrm{d}\hat{Q}$ and the integrals of equation [1] become

$$\hat{\mathcal{W}}_{tot}\Delta\hat{H}_{32} = -\hat{\mathcal{W}}_v\Delta\hat{H}_{16} \qquad [3]$$

$$\left(\hat{H}_3 - \hat{H}_2\right) = -\frac{\hat{\mathcal{W}}_v}{\hat{\mathcal{W}}_{tot}}\left(\hat{H}_1 - \hat{H}_6\right) \qquad [4]$$

where $\hat{\mathcal{W}}_v/\hat{\mathcal{W}}_{tot}$ is the non-liquefied fraction of ethane, which is related with the liquiefied fraction ($\hat{\mathcal{W}}_l/\hat{\mathcal{W}}_{tot}$) by the mass balance to the phase separator

$$\hat{\mathcal{W}}_{tot} = \hat{\mathcal{W}}_l + \hat{\mathcal{W}}_v$$

$$1 = \frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}} + \frac{\hat{\mathcal{W}}_v}{\hat{\mathcal{W}}_{tot}} \qquad \rightarrow \qquad \frac{\hat{\mathcal{W}}_v}{\hat{\mathcal{W}}_{tot}} = 1 - \frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}$$

Hence, equation [4] gives

$$\left(\hat{H}_3 - \hat{H}_2\right) = -\left(1 - \frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}\right)\left(\hat{H}_1 - \hat{H}_6\right) \qquad [5]$$

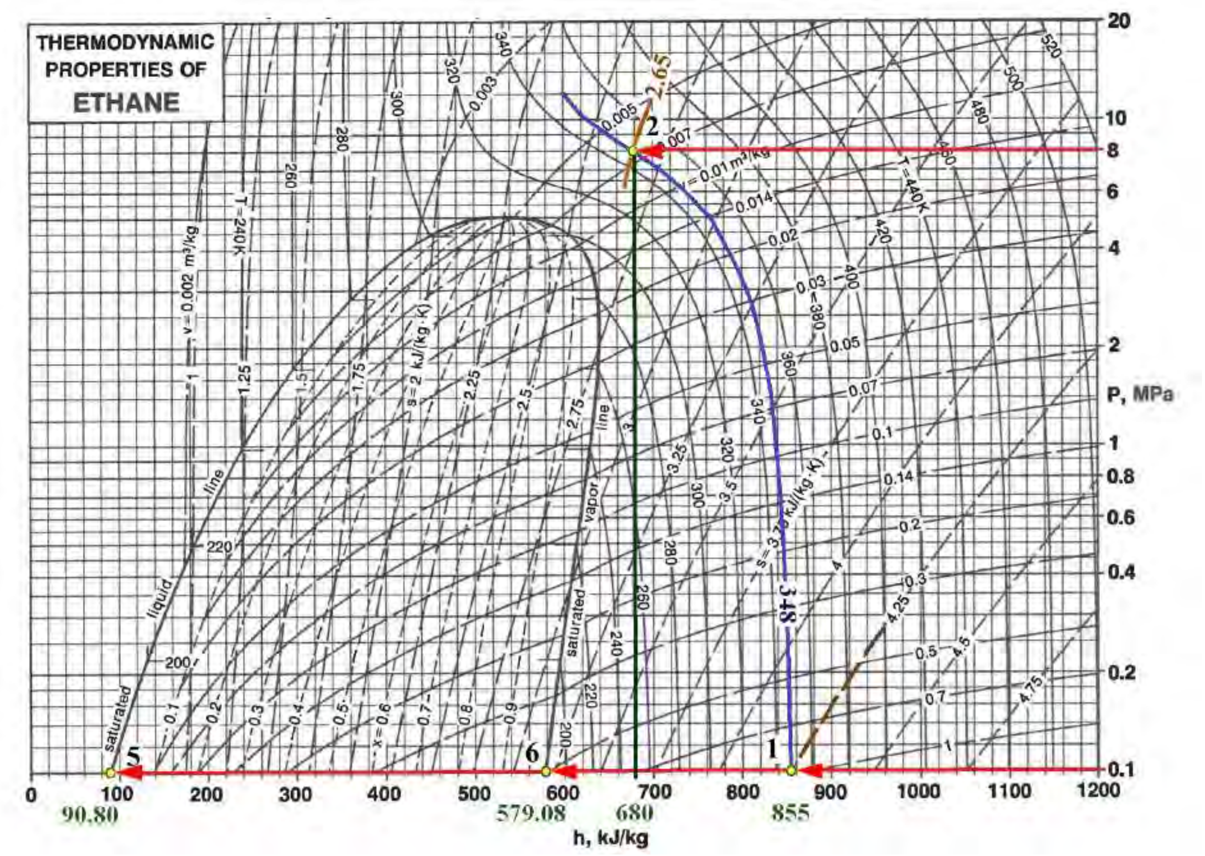
Question c. Figure V.15 of appendix V is a diagram such as the requested one. In it, the temperatures are expressed in K and the pressures in MPa; thus, by means of the conversion factors of appendix I

$$T_1(\mathrm{K}) = 75^\circ\mathrm{C} + 273 = 348\ \mathrm{K}$$

$$P_1 = 80\ \mathrm{bar}\times\frac{0.1\ \mathrm{MPa}}{1\ \mathrm{bar}} = 8\ \mathrm{MPa}$$

$$P_2 = 1\ \mathrm{bar}\times\frac{0.1\ \mathrm{MPa}}{1\ \mathrm{bar}} = 0.1\ \mathrm{MPa}$$

With these data the enthalpies in the points 1, 2 and 6 can be read, which are $\hat{H}_1$ =855 kJ/kg, $\hat{H}_2$ =680 kJ/kg and $\hat{H}_6$ =579.08 kJ/kg.



$\hat{H}_3 = \hat{H}_4$ because points 3 and 4 are separated by an isenthalpic valve. $\hat{H}_4$ will be determined by the enthalpies of the saturated liquid and vapor as

$$\hat{H}_4 = \left(\frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}\right)\hat{H}_5 + \left(1-\frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}\right)\hat{H}_6 \qquad [6]$$

where $\hat{H}_5 = 90.80$ kJ/kg. By introducing [6] in equation [5], it can be obtained that

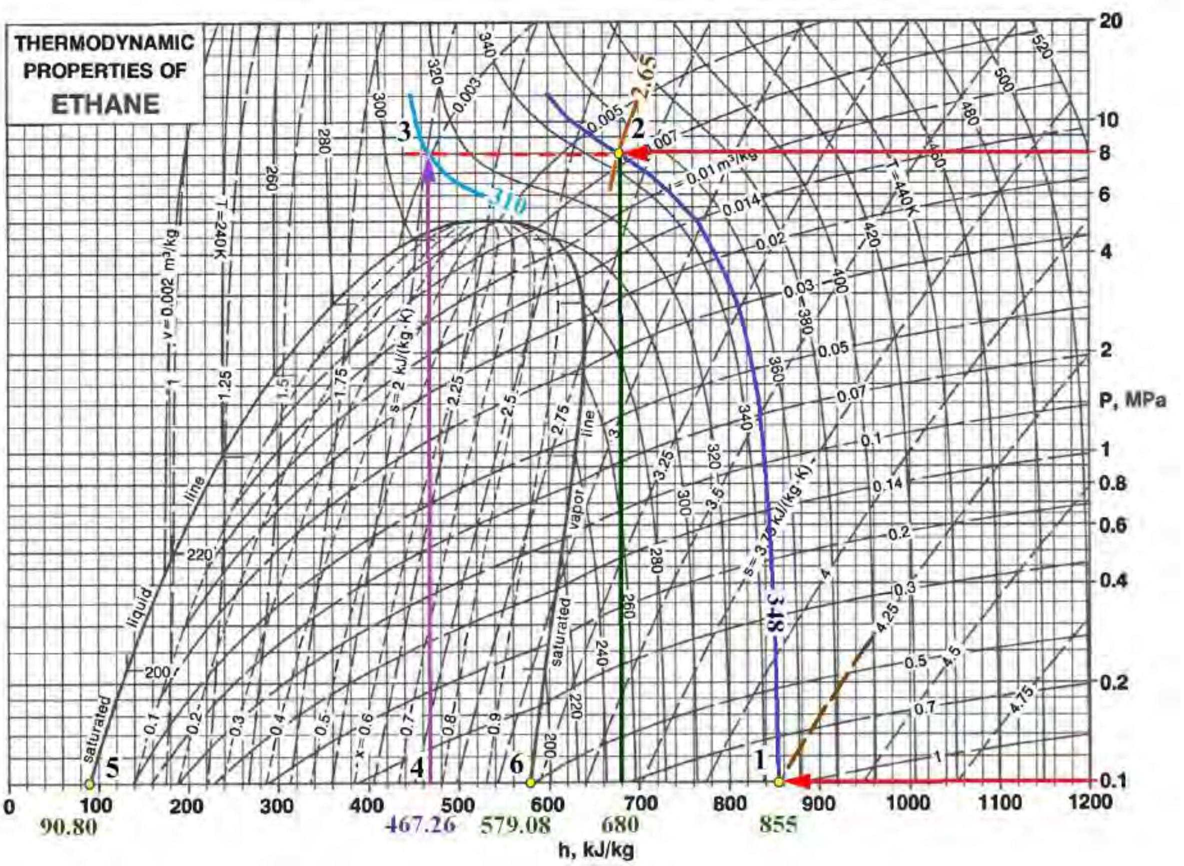
$$\left[\left(\frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}\right)90.80 + \left(1-\frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}\right)579.08 - 680\right] = -\left(1-\frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}}\right)(855-579.08)$$

$$\frac{\hat{\mathcal{W}}_l}{\hat{\mathcal{W}}_{tot}} = 0.229$$

and by substituting this value of $\hat{\mathcal{W}}_v / \hat{\mathcal{W}}_{tot}$ in [6]

$$\hat{H}_4 = (0.229)\left(90.80\ \frac{\text{kJ}}{\text{kg}}\right) + (1-0.229)\left(579.08\ \frac{\text{kJ}}{\text{kg}}\right) = 467.26\,\frac{\text{kJ}}{\text{kg}}$$

The intersection between the 467.26 kJ/kg isenthalpic and the 8 MPa isobar will give point 3, and the isotherm that passes through this point will be T_3.



In this case, T_3=310 K.

Question d. The total mass balance to the system indicates that

$$\widehat{\mathcal{W}}_l = \widehat{\mathcal{W}}_0 = 1000\ \text{kg/h}$$

and with the liquefied fraction of question **c**, it can be obtained that

$$\frac{\widehat{\mathcal{W}}_l}{\widehat{\mathcal{W}}_{tot}} = 0.229 \qquad \rightarrow \qquad \widehat{\mathcal{W}}_{tot} = \frac{\widehat{\mathcal{W}}_l}{0.229} = \frac{1000\ \text{kg/h}}{0.229} = 4366.8\ \frac{\text{kg}}{\text{h}}$$

$$\widehat{\mathcal{W}}_v = \widehat{\mathcal{W}}_{tot} - \widehat{\mathcal{W}}_l = 4366.8\frac{\text{kg}}{\text{h}} - 1000\frac{\text{kg}}{\text{h}} = 3366.8\ \frac{\text{kg}}{\text{h}}$$

By introducing these flow rates together with the corresponding enthalpies in equation [3], the heat flow in the heat exchanger is obtained

$$q_{32} = \widehat{\mathcal{W}}_{tot}\left(\widehat{H}_3 - \widehat{H}_2\right) = \left(4366.8\ \frac{\text{kg}}{\text{h}}\right)\left(467.26\frac{\text{kJ}}{\text{kg}} - 680\frac{\text{kJ}}{\text{kg}}\right) = -929 \cdot 10^3\ \frac{\text{kJ}}{\text{h}}$$

$$-q_{16} = -\widehat{\mathcal{W}}_v\left(\widehat{H}_1 - \widehat{H}_6\right) = -\left(3366.8\ \frac{\text{kg}}{\text{h}}\right)\left(855\frac{\text{kJ}}{\text{kg}} - 579.08\frac{\text{kJ}}{\text{kg}}\right) = -929 \cdot 10^3\ \frac{\text{kJ}}{\text{h}}$$

Question e. The integral that evaluates the heat per unit mass in the isothermal compressor (step from point 1 to 2) becomes simpler due to the fact that T is constant

$$\Delta\hat{Q}_{21} = \int_1^2 T\mathrm{d}\hat{S} = T_1\int_1^2 \mathrm{d}\hat{S} = T_1\left(\hat{S}_2 - \hat{S}_1\right)$$

and the compression work per unit mass, according to equation [2] is

$$\mathrm{d}\widehat{W}^{\mathrm{fl}} = \mathrm{d}\widehat{H} - \mathrm{d}\hat{Q} = \mathrm{d}\widehat{H} - T\mathrm{d}\hat{S}$$

$$\Delta\widehat{W}_{21}^{\mathrm{fl}} = \int_1^2\left(\mathrm{d}\widehat{H} - T\mathrm{d}\hat{S}\right) = \Delta\widehat{H}_{21} - T_1\left(\hat{S}_2 - \hat{S}_1\right) = \Delta\widehat{H}_{21} - \Delta\hat{Q}_{21}$$

Figure V.15 shows that $\hat{S}_1$ =4.25 kJ/kg·K and that $\hat{S}_2$ =2.65 kJ/kg·K, so

$$\Delta\hat{Q}_{21} = (348\ \mathrm{K})\left(2.65\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}} - 4.25\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = -556.8\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

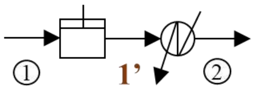
$$\Delta\widehat{W}_{21}^{\mathrm{fl}} = \left(680\ \frac{\mathrm{kJ}}{\mathrm{kg}} - 855\frac{\mathrm{kJ}}{\mathrm{kg}}\right) - \left(-556.8\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 381.8\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

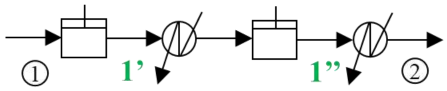
By extending this heat and this work to the flow through the compressor, the heat flows and powers are obtained

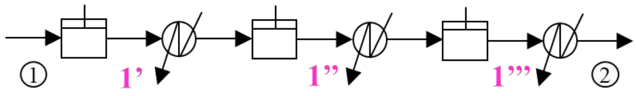
$$q_{21} = \widehat{\mathcal{W}}_{tot}\Delta\hat{Q}_{21} = \left(4366.8\ \frac{\mathrm{kg}}{\mathrm{h}}\right)\left(-556.8\ \frac{\mathrm{BTU}}{\mathrm{lb}}\right) = -24.31\cdot 10^5\ \frac{\mathrm{kJ}}{\mathrm{h}}$$

$$\wp_{21} = \widehat{\mathcal{W}}_{tot}\Delta\widehat{W}_{21}^{\mathrm{fl}} = \left(4366.8\ \frac{\mathrm{kg}}{\mathrm{h}}\right)\left(381.8\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 16.67\cdot 10^5\ \frac{\mathrm{kJ}}{\mathrm{h}}$$

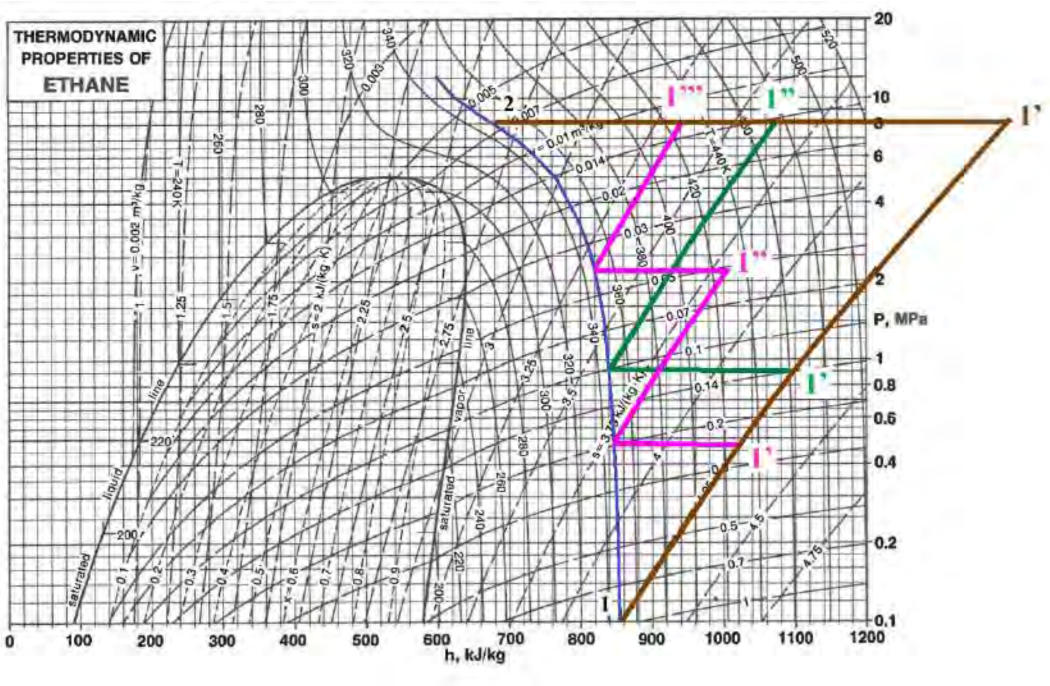
Question f. Isothermal compression requires a very controlled refrigeration of the compressor. Therefore, it is easier to approach it by successive stages of isentropic compression + isobaric cooling, which minimizes operating costs (power consumed and heat removed).







Assuming compressors of equal power and efficiency, it would be necessary a trial-and-error procedure to find the pressure at the exit of each stage. See in the figure below how for one stage (brown line) point 1' is very far from point 2, but for two stages (green line) point 1" is closer, and for three stages (fuchsia line) the point 1'" is even closer to 2.



It can be easily intuited that the stepped line will coincide with the isotherm when the number of stages tends to infinity.

6.22. It will be produced liquid oxygen at 15 lb$_f$/in^2 and saturation temperature from a feed of 100 mol-lb/s at the same pressure and -70°F.

The proposed modified Linde cycle operates as follows: the stream at the initial conditions is first subjected to three successive stages of isentropic compression, each followed by subsequent isobaric cooling (in the first one, the fluid is compressed to 100 lb$_f$/in^2 and cooled to the initial temperature, in the the second one it is compressed from 100 to 400 lb$_f$/in^2 and cooled to the initial temperature as well, and in the third stage it is compressed to 1500 lb$_f$/in^2 and cooled to -140°F).

Next, compressed oxygen is subjected to a practically isenthalpic expansion, followed by an immediate and total separation into two phases. Liquid oxygen at the predetermined conditions is then obtained.

The non-liquefied oxygen is recycled as cooling fluid (circulating in counterflow in the heat exchangers that cool the streams leaving the compression stages). It heats isobarically to the initial conditions and then is mixed with the 100 mol-lb/s feed.

- **a) Draw an approximate flowchart of the process and write the mass balances.**
- **b) Quantitatively represent the cycle in a *PH*(*T*,*S*,*V*) diagram and determine the specific enthalpies of the main streams involved.**
- **c) Qualitatively represent the cycle in *PT*(*H*,*S*) and *PV*(*T*,*S*,*H*) diagrams.**
- **d) Calculate the flow rates of the recycled O$_2$ stream and of that circulating through the compression + refrigeration stages.**
- **e) Quantify the heat flow transferred in the three cooling stages and the heat flow gained by the recycled O$_2$.**
- **f) Evaluate the power required for compression in stages.**
- **g) Why are three compression stages followed by cooling proposed? Why not one compression stage to the desired final pressure followed by cooling to the temperature that precedes the isenthalpic expansion?**
- **h) Redo question d), e) and f) if the expansion is isentropic instead of isenthalpic.**

Question a. In the following figure, let point "1" be the place where the feed (mass flow rate $\widehat{\mathcal{W}}_0$) mixes with the stream leaving the heat exchangers (which was originally saturated vapor with mass flow rate $\widehat{\mathcal{W}}_v$). Let point "10" be the place where the liquefied oxygen (mass flow rate $\widehat{\mathcal{W}}_l$) leaves the process and "8" be the biphasic mixture resulting from isenthalpic expansion in the valve. The global mass balance says that

$$\widehat{\mathcal{W}}_0 = \widehat{\mathcal{W}}_l = 100\ \frac{\text{mol-lb O}_2}{\text{s}} \times \frac{32\ \text{lb O}_2}{1\ \text{mol-lb O}_2} = 3200\ \frac{\text{lb}}{\text{s}} \qquad [1]$$

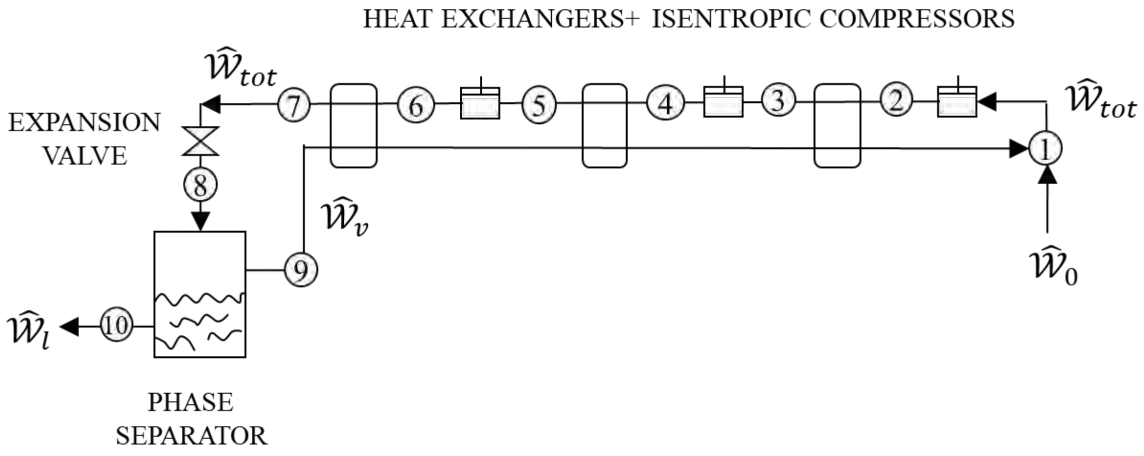
while the balance to the phase separator indicates that

$$\widehat{\mathcal{W}}_{tot} = \widehat{\mathcal{W}}_v + \widehat{\mathcal{W}}_l \qquad [2]$$

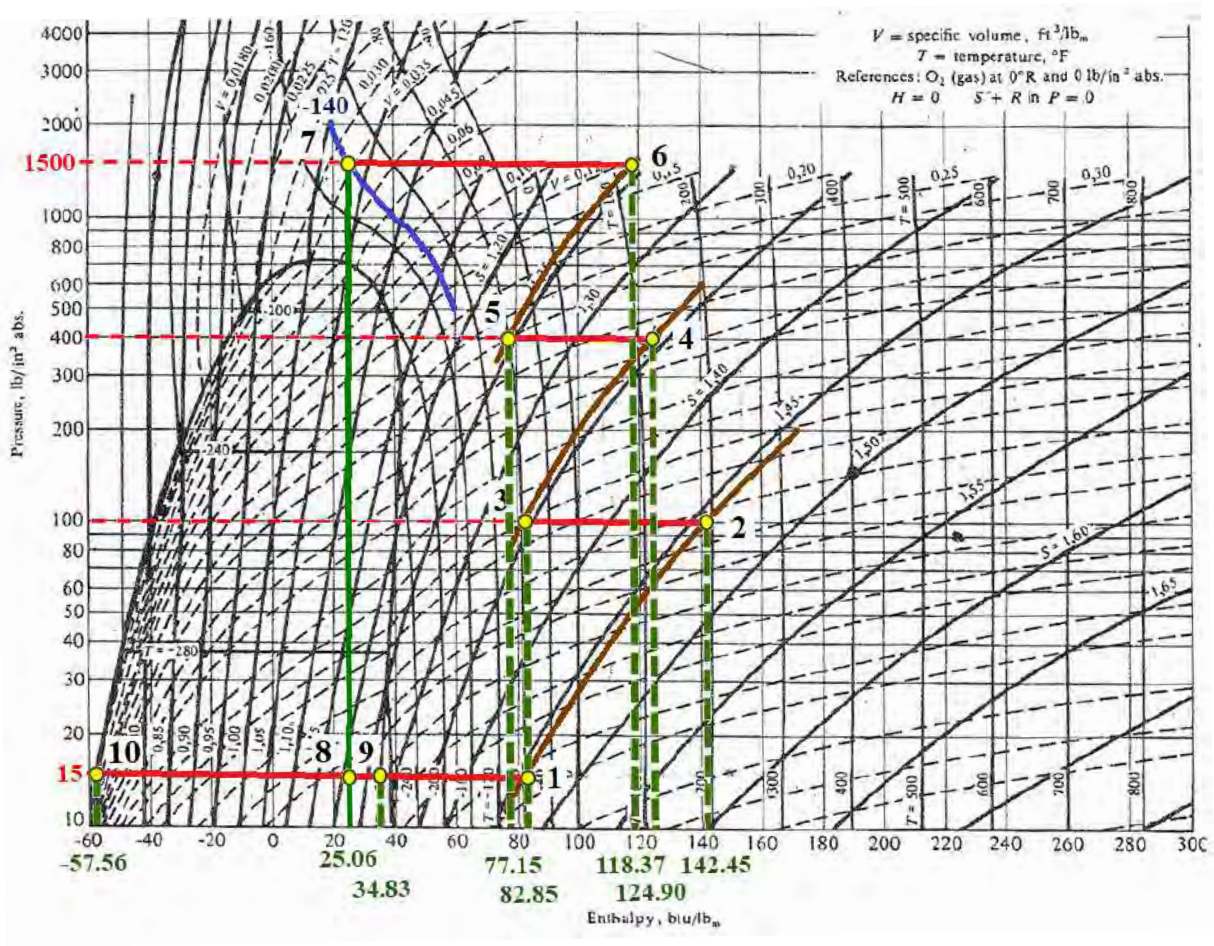
and the balance to point "1"

$$\widehat{\mathcal{W}}_{tot} = \widehat{\mathcal{W}}_0 + \widehat{\mathcal{W}}_v \qquad [3]$$

being $\widehat{\mathcal{W}}_{tot}$ constant between points 1 and 8.



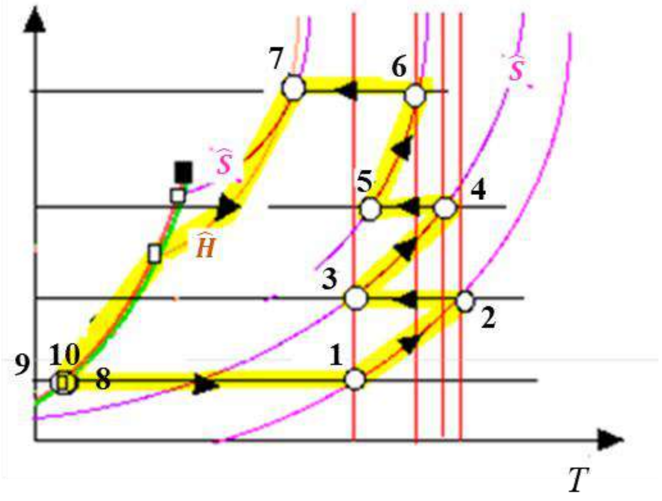
Question b. Figure V.1 of this book's appendix V is a *PH*(*T,S,V*) of oxygen.

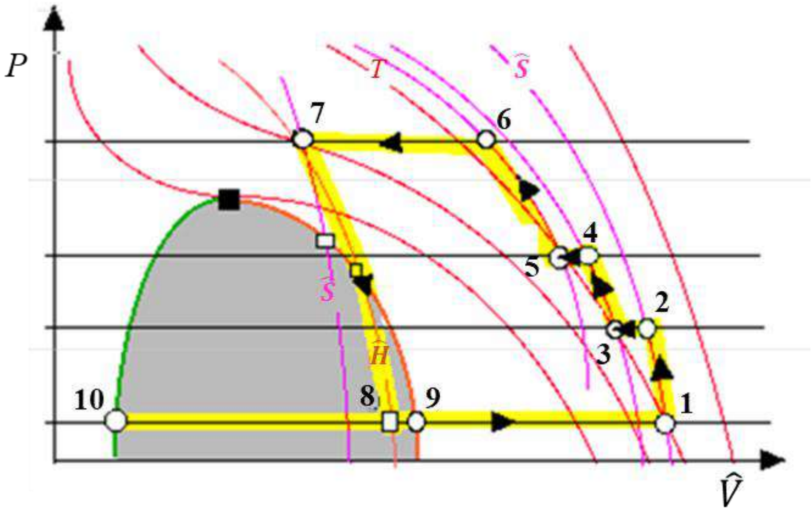


After representing the process on it, the specific enthalpies of the main points can be read

Point	$\hat{H}$ (BTU/lb)
1	82.85
2	142.45
3	82.85
4	124.90
5	77.15
6	118.37
7	25.06
8	25.06
9	34.83
10	-57.56

Question c. The qualitative representations will be





Question d. By combining the enthalpy balance to the phase separator

$$\widehat{\mathcal{W}}_{tot}\hat{H}_8 = \widehat{\mathcal{W}}_v\hat{H}_9 + \widehat{\mathcal{W}}_l\hat{H}_{10}$$

with equations [1] and [2], the mass flow rate of the recycled vapor is obtained

$$\widehat{\mathcal{W}}_v = \left(\frac{\widehat{H}_8 - \widehat{H}_{10}}{\widehat{H}_9 - \widehat{H}_8}\right)\widehat{\mathcal{W}}_l = \left[\frac{25.06 - (-57.56)}{34.83 - 25.06}\right]\left(3200\ \frac{\text{lb}}{\text{s}}\right) = 27060.8\ \frac{\text{lb}}{\text{s}} \qquad [4]$$

And having in mind equation [3], the mass flow rate which passes through the compression + cooling stages will be

$$\widehat{\mathcal{W}}_{tot} = 27060.8\ \frac{\text{lb}}{\text{s}} + 3200\ \frac{\text{lb}}{\text{s}} = 30260.8\ \frac{\text{lb}}{\text{s}} \qquad [5]$$

Question e. The heat (per unit mass) given by the compressed stream in the three cooling stages will be

$$\Delta\hat{Q}_{72} = \int_2^7 T\mathrm{d}\hat{S} = \int_2^3 T\mathrm{d}\hat{S} + \int_4^5 T\mathrm{d}\hat{S} + \int_6^7 T\mathrm{d}\hat{S}$$

Since they are isobaric (dP=0)

$$\mathrm{d}\widehat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\widehat{W}^{\text{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \quad \xrightarrow{\mathrm{d}P=0} \quad \mathrm{d}\widehat{H} = \mathrm{d}\hat{Q}$$

and the heat could be easily calculated as

$$\Delta\hat{Q}_{72} = \Delta\hat{Q}_{32} + \Delta\hat{Q}_{54} + \Delta\hat{Q}_{76} = \Delta\widehat{H}_{32} + \Delta\widehat{H}_{54} + \Delta\widehat{H}_{76}$$

$$\Delta\hat{Q}_{72} = (82.85 - 142.45) + (77.15 - 124.90) + (25.06 - 118.37) = -200.66\ \frac{\text{BTU}}{\text{lb}}$$

Hence, the heat flow of the compressed stream will be

$$q_{72} = \widehat{\mathcal{W}}_{tot}\Delta\hat{Q}_{72} = \left(30260.8\ \frac{\text{lb}}{\text{s}}\right)\left(-200.66\ \frac{\text{BTU}}{\text{lb}}\right) = -607 \cdot 10^4\ \frac{\text{BTU}}{\text{s}} \qquad [6]$$

With regards to the heat gained during the exchange by the recycled stream

$$\Delta\hat{Q}_{19} = \int_9^1 T\mathrm{d}\hat{S} \quad \xrightarrow{\mathrm{d}P=0} \quad \Delta\hat{Q}_{19} = \Delta\widehat{H}_{19}$$

$$q_{19} = \widehat{\mathcal{W}}_v\Delta\hat{Q}_{19} = \left(27060.8\ \frac{\text{lb}}{\text{s}}\right)\left(82.85\ \frac{\text{BTU}}{\text{lb}} - 34.83\ \frac{\text{BTU}}{\text{lb}}\right) = 130 \cdot 10^4\ \frac{\text{BTU}}{\text{s}} \qquad [7]$$

it is found that $|q_{72}| > |q_{19}|$, so the recycled oxygen is unable of cooling the compressed one.

Question f. The compression work (per unit mass) in the three stages is evaluated as

$$\Delta\widehat{W}^{\text{fl}}_{61} = \int_1^6 \hat{V}\,\mathrm{d}P = \int_1^2 \hat{V}\,\mathrm{d}P + \int_3^4 \hat{V}\,\mathrm{d}P + \int_5^6 \hat{V}\,\mathrm{d}P$$

but due to the fact that they are isentropic ($\mathrm{d}\hat{S}$=0)

$$\mathrm{d}\widehat{H} = \mathrm{d}\widehat{Q} + \mathrm{d}\widehat{W}^{\text{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \quad \xrightarrow{\mathrm{d}\hat{S}=0} \quad \mathrm{d}\widehat{W}^{\text{fl}} = \mathrm{d}\widehat{H}$$

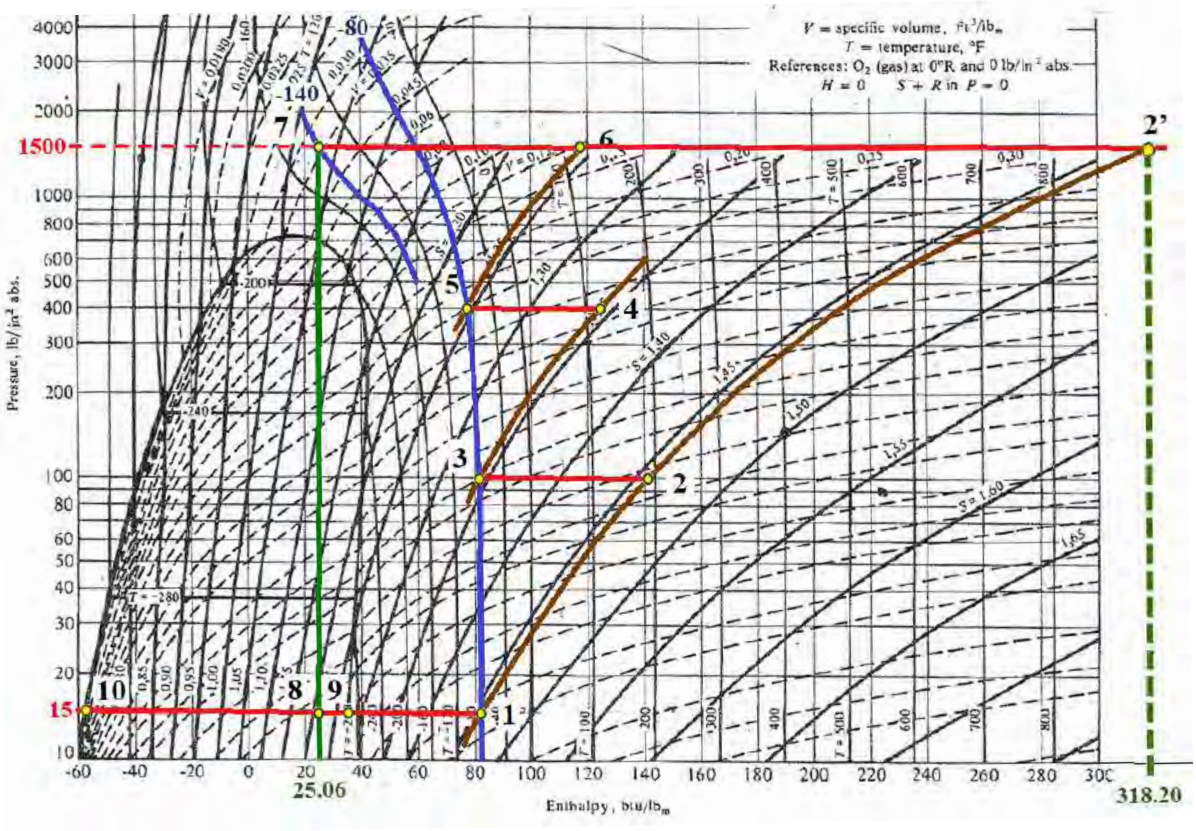
$$\Delta\widehat{W}^{\text{fl}}_{61} = \Delta\widehat{W}^{\text{fl}}_{21} + \Delta\widehat{W}^{\text{fl}}_{43} + \Delta\widehat{W}^{\text{fl}}_{65} = \Delta\widehat{H}_{21} + \Delta\widehat{H}_{43} + \Delta\widehat{H}_{65}$$

$$\Delta\widehat{W}^{\text{fl}}_{61} = (142.45 - 82.85) + (124.9 - 82.85) + (118.37 - 77.15) = 142.87\ \frac{\text{BTU}}{\text{lb}}$$

and the power is

$$\mathscr{P}_{61} = \widehat{\mathcal{W}}_{tot}\Delta\widehat{W}^{\text{fl}}_{61} = \left(30260.8\ \frac{\text{lb}}{\text{s}}\right)\left(142.87\ \frac{\text{BTU}}{\text{lb}}\right) = 432 \cdot 10^4\ \frac{\text{BTU}}{\text{s}} \qquad [8]$$

Question g. If a single compression stage had been chosen (from 1 to the new point 2') followed by a cooling from 2' to 7



the heat flow in the exchanger

$$\Delta\hat{Q}_{72'} = \Delta\hat{H}_{72'} = 25.06\,\frac{\text{BTU}}{\text{lb}} - 318.20\,\frac{\text{BTU}}{\text{lb}} = -293.14\,\frac{\text{BTU}}{\text{lb}}$$

$$q_{72'} = \widehat{\mathcal{W}}_{tot}\Delta\hat{Q}_{72'} = \left(30260.8\,\frac{\text{lb}}{\text{s}}\right)\left(-293.14\,\frac{\text{BTU}}{\text{lb}}\right) = -887\cdot 10^{4}\,\frac{\text{BTU}}{\text{s}}$$

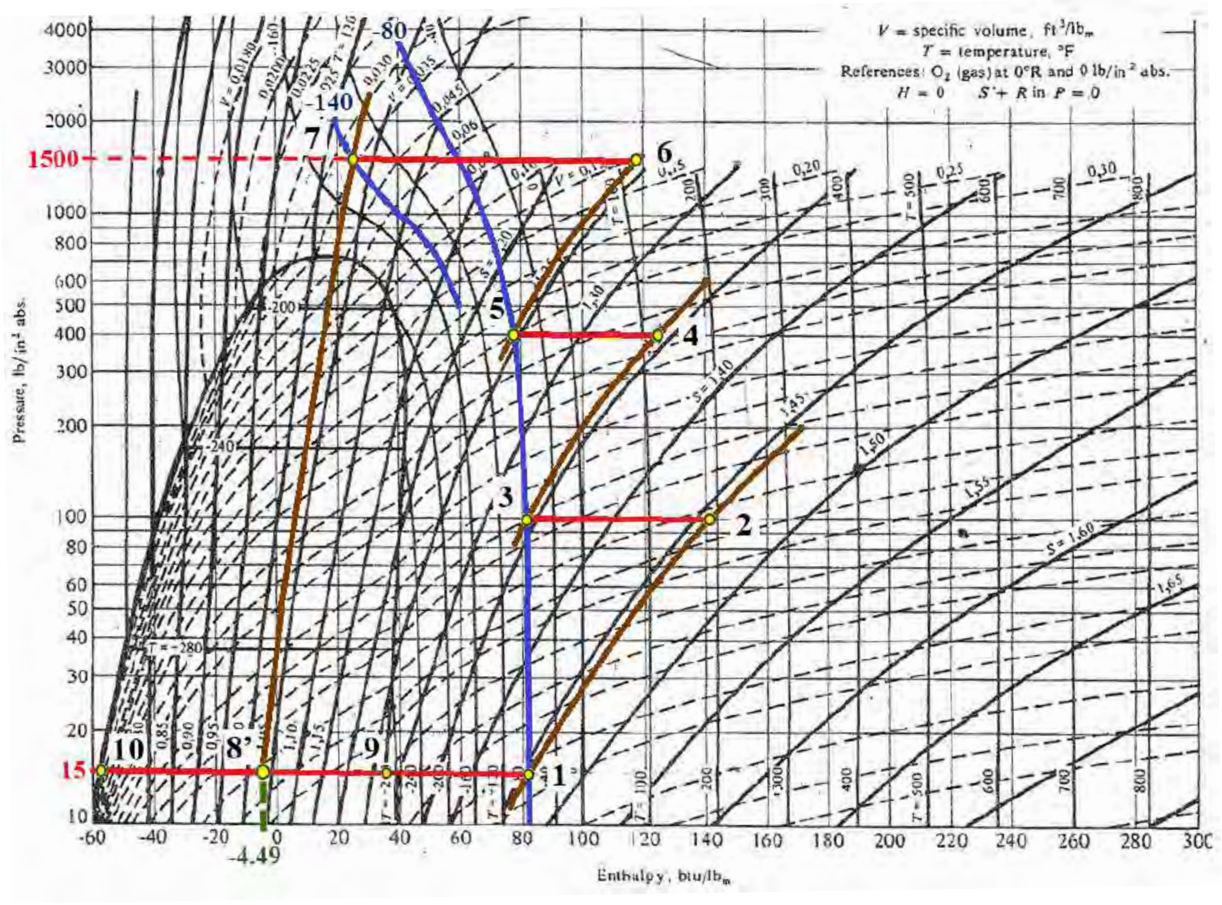
and the power consumed in the compressor

$$\Delta\widehat{W}^{\text{fl}}_{2'1} = \Delta\hat{H}_{2'1} = 318.20\,\frac{\text{BTU}}{\text{lb}} - 82.85\,\frac{\text{BTU}}{\text{lb}} = 235.35\,\frac{\text{BTU}}{\text{lb}}$$

$$\wp_{2'1} = \widehat{\mathcal{W}}_{tot}\Delta\widehat{W}^{\text{fl}}_{2'1} = \left(30260.8\,\frac{\text{lb}}{\text{s}}\right)\left(235.35\,\frac{\text{BTU}}{\text{lb}}\right) = 712\cdot 10^{4}\,\frac{\text{BTU}}{\text{s}}$$

would be higher than those with three stages.

Question h. If the isentropic line that passes through point 7 is interpolated (between 1.00 BTU/lb°R and 1.05 BTU/lb°R) it can be observed that point 8 moves to 8', whose enthalpy is of -4.49 BTU/lb.



Therefore, equations [4] and [5] will give

$$\hat{\mathcal{W}}_v = \left(\frac{\hat{H}_{8'} - \hat{H}_{10}}{\hat{H}_9 - \hat{H}_8}\right)\hat{\mathcal{W}}_l = \left[\frac{-4.49 - (-57.56)}{34.83 - 25.06}\right]\left(3200\ \frac{\text{lb}}{\text{s}}\right) = 17382.2\ \frac{\text{lb}}{\text{s}}$$

$$\hat{\mathcal{W}}_{tot} = \hat{\mathcal{W}}_v + \hat{\mathcal{W}}_l = 17382.2\ \frac{\text{lb}}{\text{s}} + 3200\ \frac{\text{lb}}{\text{s}} = 20582.2\ \frac{\text{lb}}{\text{s}}$$

while expressions [6], [7] and [8] take the values

$$q_{72} = \hat{\mathcal{W}}_{tot}\Delta\hat{Q}_{72} = \left(20582.2\ \frac{\text{lb}}{\text{s}}\right)\left(-200.66\ \frac{\text{BTU}}{\text{lb}}\right) = -413 \cdot 10^4\ \frac{\text{BTU}}{\text{s}}$$

$$q_{19} = \hat{\mathcal{W}}_v\Delta\hat{Q}_{19} = \left(17382.2\ \frac{\text{lb}}{\text{s}}\right)\left(82.85\ \frac{\text{BTU}}{\text{lb}} - 34.83\ \frac{\text{BTU}}{\text{lb}}\right) = 83.5 \cdot 10^4\ \frac{\text{BTU}}{\text{s}}$$

$$\mathcal{p}_{61} = \hat{\mathcal{W}}_{tot}\Delta\hat{W}_{61}^{\text{fl}} = \left(20582.2\ \frac{\text{lb}}{\text{s}}\right)\left(142.87\ \frac{\text{BTU}}{\text{lb}}\right) = 294 \cdot 10^4\ \frac{\text{BTU}}{\text{s}}$$

which are lower than those corresponding to the isenthalpic expansion because the involved flow rates are lower as well.

6.23. In order to produce saturated liquid air at 2 atm from a feed of 100 lb/min at the same pressure and 500ºR, the following modified Claude cycle is proposed: the stream at the initial conditions is first subjected to five successive stages of isentropic compression (2 to 5 atm, 5 to 10 atm, 10 to 20 atm, from 20 to 50 atm and from 50 to 140 atm), each followed by subsequent isobaric cooling. Next, the gas at 140 atm and 500°R suffered an isentropic expansion, followed by an immediate and total separation into two phases. Liquid air at the predetermined conditions is then obtained.

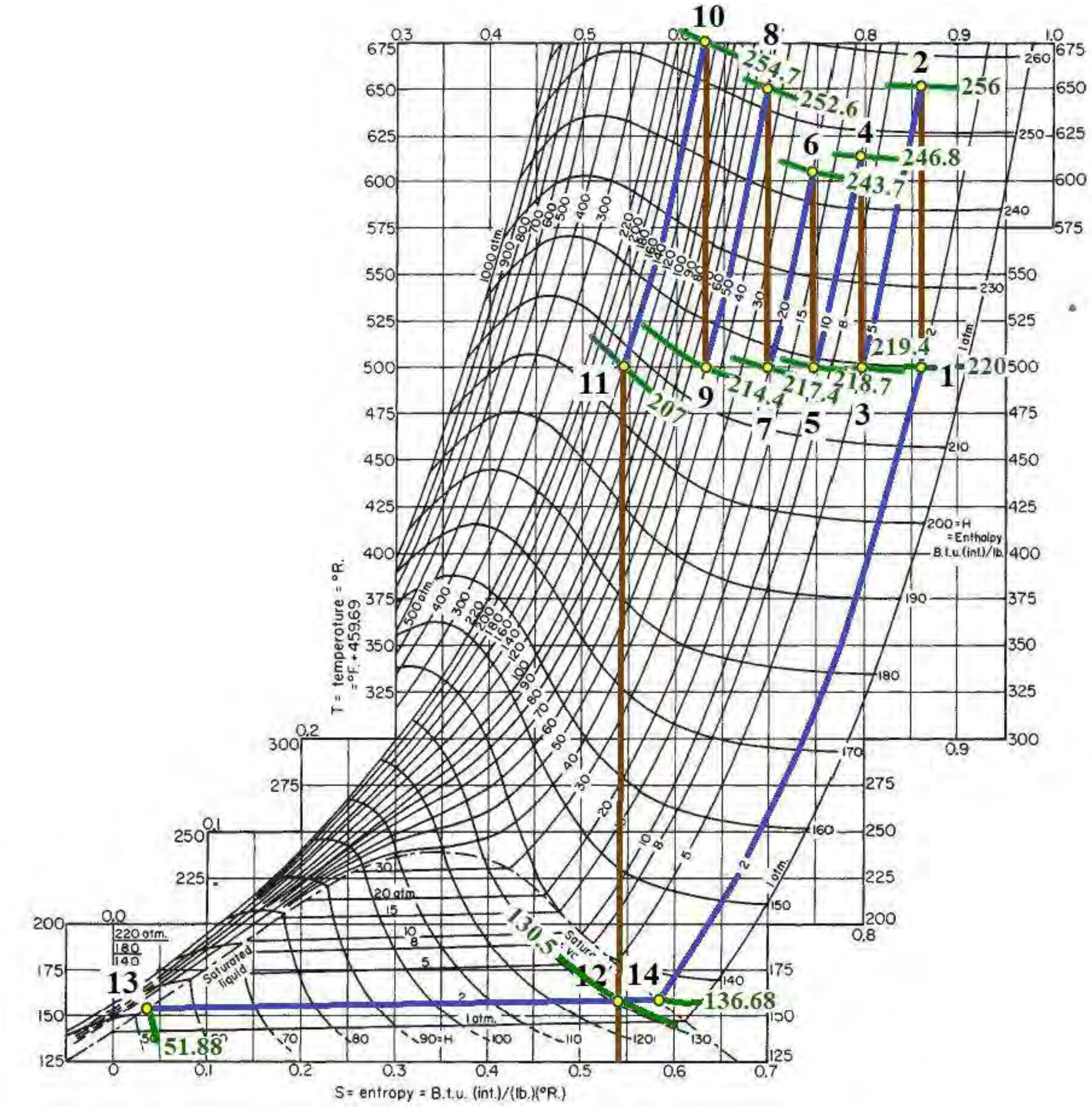
To save energy, the non-liquefied air is recycled as cooling fluid (circulating in counterflow in the heat exchangers that cool the streams leaving the compression stages). It heats isobarically to the initial conditions and then is mixed with the 100 lb/min feed.

- **a) Draw the cycle in a quantitative *TS*(*P,H*) diagram, indicating the specific enthalpies at the main points.**
- **b) Calculate the mass flow rate of recycled air.**
- **c) Estimate the heat transferred in the cooling stages and the power required in the compression stages.**
- **d) Determine the heat flow gained by the recycled air. Is an additional refrigeration needed?**

Question a. Figure V.16 of this book's appendix V is the *TS*(*P*,*H*) diagram of Landsbaum et al. (1955) for dry air.

If the indications given by the statement of the problem are followed, the process can easily be represented on this diagram, and the enthalpies at the main points will be

Point	$\hat{H}$ (BTU/lb)
1	220
2	256
3	219.4
4	246.8
5	218.7
6	243.7
7	217.4
8	252.6
9	214.4
10	254.7
11	207
12	130.5
13	51.88
14	136.68



Question b. Let $\widehat{\mathcal{W}}_0$ be the mass flow rate of the feed, $\widehat{\mathcal{W}}_l$ be the mass flow rate of the saturated liquid, $\widehat{\mathcal{W}}_v$ the mass flow rate of the saturated vapor and $\widehat{\mathcal{W}}_{tot}$ the mass flow rate of the stream that passes through the compressors, the heat exchangers and the expander. The total mass balance says that

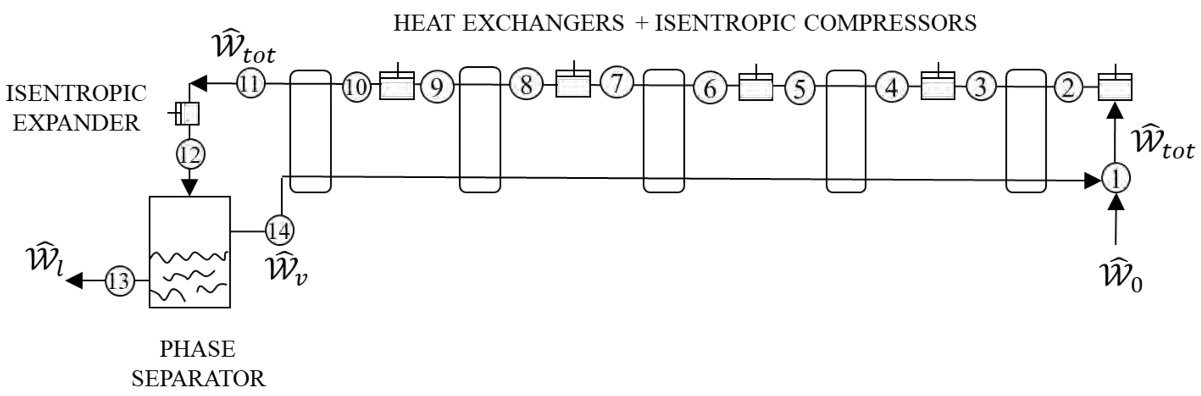
$$\widehat{\mathcal{W}}_0 = \widehat{\mathcal{W}}_l = 100\ \frac{\text{lb}}{\text{min}} \tag{1}$$

while the balance to the phase separator indicates that

$$\widehat{\mathcal{W}}_{tot} = \widehat{\mathcal{W}}_l + \widehat{\mathcal{W}}_v \tag{2}$$

and the balance to point “1”

$$\widehat{\mathcal{W}}_1 = \widehat{\mathcal{W}}_0 + \widehat{\mathcal{W}}_v$$



By combining equations [1] and [2] with the enthalpy balance to the phase separator

$$\hat{\mathcal{W}}_{tot}\hat{H}_{12} = \hat{\mathcal{W}}_l\hat{H}_{13} + \hat{\mathcal{W}}_v\hat{H}_{14}$$

the mass flow rate of recycled air is obtained

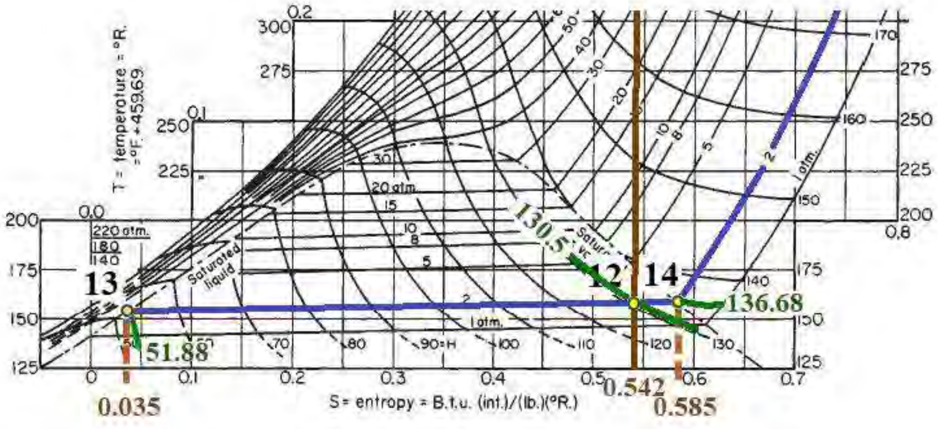
$$\hat{\mathcal{W}}_v = \frac{\hat{H}_{13} - \hat{H}_{12}}{\hat{H}_{12} - \hat{H}_{14}}\hat{\mathcal{W}}_l = \left[\frac{51.88 - 130.5}{130.5 - 136.68}\right]\left(100\ \frac{\text{lb}}{\text{min}}\right) = 1272.17\ \frac{\text{lb}}{\text{min}}$$

together with that of total air through the system

$$\hat{\mathcal{W}}_{tot} = 100\ \frac{\text{lb}}{\text{min}} + 1272.17\frac{\text{lb}}{\text{min}} = 1372.17\ \frac{\text{lb}}{\text{min}}$$

Additionally, the mass balances could be combined with the entropy balances to the phase separator and to the expander

$$\hat{\mathcal{W}}_{tot}\hat{S}_{11} = \hat{\mathcal{W}}_{tot}\hat{S}_{12} = \hat{\mathcal{W}}_l\hat{S}_{13} + \hat{\mathcal{W}}_v\hat{S}_{14}$$



and then

$$\widehat{W}_v = \frac{\hat{S}_{13} - \hat{S}_{12}}{\hat{S}_{12} - \hat{S}_{14}} \widehat{W}_l = \left[\frac{0.035 - 0.542}{0.542 - 0.585}\right] \left(100\ \frac{\text{lb}}{\text{min}}\right) = 1179\ \frac{\text{lb}}{\text{min}}$$

$$\widehat{W}_{tot} = 100 \frac{\text{lb}}{\text{min}} + 1179 \frac{\text{lb}}{\text{min}} = 1279\ \frac{\text{lb}}{\text{min}}$$

Values that are 7% lower than those calculated with enthalpies because the error inherent to reading and interpolating graphical data. In order not to duplicate calculations, only the values obtained with the enthalpy balance will be used below.

Question c. The heat and work changes during the compression+cooling stages are

$$\Delta\hat{Q}_{11-2} = \int_2^{11} T\mathrm{d}\hat{S} = \int_2^3 T\mathrm{d}\hat{S} + \int_4^5 T\mathrm{d}\hat{S} + \int_6^7 T\mathrm{d}\hat{S} + \int_8^9 T\mathrm{d}\hat{S} + \int_{10}^{11} T\mathrm{d}\hat{S}$$

$$\Delta\widehat{W}^{\text{fl}}_{10-1} = \int_1^{10} \hat{V}\mathrm{d}P = \int_1^2 \hat{V}\mathrm{d}P + \int_3^4 \hat{V}\mathrm{d}P + \int_5^6 \hat{V}\mathrm{d}P + \int_7^8 \hat{V}\mathrm{d}P + \int_9^{10} \hat{V}\mathrm{d}P$$

According to equations of reference problem 0.3

$$\mathrm{d}\widehat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\widehat{W}^{\text{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P$$

if the cooling stages are isobaric ($\mathrm{d}P$=0)

$$\mathrm{d}\widehat{H} = \mathrm{d}\hat{Q}$$

$$\Delta\hat{Q}_{11\text{-}2} = \Delta\hat{Q}_{32} + \Delta\hat{Q}_{54} + \Delta\hat{Q}_{76} + \Delta\hat{Q}_{98} + \Delta\hat{Q}_{11\text{-}10} = \Delta\widehat{H}_{32} + \Delta\widehat{H}_{54} + \Delta\widehat{H}_{76} + \Delta\widehat{H}_{98} + \Delta\widehat{H}_{11\text{-}10}$$

$$\begin{aligned}\Delta\hat{Q}_{11\text{-}2} = (219.4 - 256) + (218.7 - 246.8) + (217.4 - 243.7) + \\ +(214.4 - 252.6) + (207 - 254.7) = -176.9\ \frac{\text{BTU}}{\text{lb}}\end{aligned}$$

if the compression stages are isentropic ($\mathrm{d}\hat{S}$=0)

$$\mathrm{d}\widehat{W}^{\text{fl}} = \mathrm{d}\widehat{H}$$

$$\Delta\widehat{W}^{\text{fl}}_{10\text{-}1} = \Delta\widehat{W}^{\text{fl}}_{21} + \Delta\widehat{W}^{\text{fl}}_{43} + \Delta\widehat{W}^{\text{fl}}_{65} + \Delta\widehat{W}^{\text{fl}}_{87} + \Delta\widehat{W}^{\text{fl}}_{10\text{-}9} = \Delta\widehat{H}_{21} + \Delta\widehat{H}_{43} + \Delta\widehat{H}_{65} + \Delta\widehat{H}_{87} + \Delta\widehat{H}_{10\text{-}9}$$

$$\begin{aligned}\Delta\widehat{W}^{\text{fl}}_{10\text{-}1} = (256 - 220) + (246.8 - 219.4) + (243.7 - 218.7) + \\ +(252.6 - 217.4) + (254.7 - 214.4) = 163.9\ \frac{\text{BTU}}{\text{lb}}\end{aligned}$$

and the heat flow and power will be

$$q_{11\text{-}2} = \widehat{\mathcal{W}}_{tot}\Delta\hat{Q}_{11\text{-}2} = \left(1372.17\ \frac{\text{lb}}{\text{min}}\right)\left(-176.9\ \frac{\text{BTU}}{\text{lb}}\right) = -24.3 \cdot 10^4\ \frac{\text{BTU}}{\text{min}}$$

$$\wp_{10\text{-}1} = \widehat{\mathcal{W}}_{tot}\Delta\widehat{W}^{\text{fl}}_{10\text{-}1} = \left(1372.17\ \frac{\text{lb}}{\text{min}}\right)\left(163.9\ \frac{\text{BTU}}{\text{lb}}\right) = 22.5 \cdot 10^4\ \frac{\text{BTU}}{\text{min}}$$

Question d. Due to the assumed isobaricity of the heat exchanger, the simplification of the previous question is applied here. Thus

$$q_{1\text{-}14} = \widehat{\mathcal{W}}_v\Delta\hat{Q}_{1\text{-}14} = \widehat{\mathcal{W}}_v\int_{14}^{1} T\mathrm{d}\hat{S}\ = \widehat{\mathcal{W}}_v\Delta\widehat{H}_{1\text{-}14}$$

$$q_{1\text{-}14} = \left(1272.17\ \frac{\text{lb}}{\text{min}}\right)\left(220\ \frac{\text{BTU}}{\text{lb}} - 136.68\ \frac{\text{BTU}}{\text{lb}}\right) = 10.6 \cdot 10^4\ \frac{\text{BTU}}{\text{min}}$$

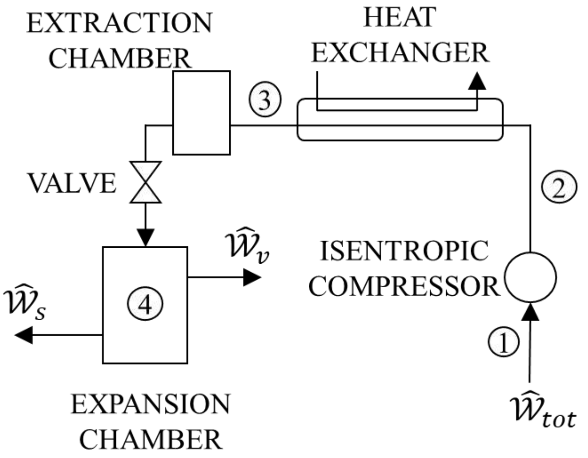
$|q_{11\text{-}2}| > |q_{1\text{-}14}|$, so the recycled stream is not sufficient to remove all the heat given by the compressed stream. Additional refrigeration is needed.

6.24. A pilot-plant supercritical extractor consists of an adiabatic frictionless compressor programmed to reach 100 bar, an isobaric heat exchanger programmed to reach 50ºC, an extraction chamber that operates at conditions of complete mixing and an expansion chamber connected to the previous one through an isenthalpic valve, where occurs an expansion to 1 bar. A flash evaporation separates the liquid extract from the solvent (which can be recycled or eliminated).

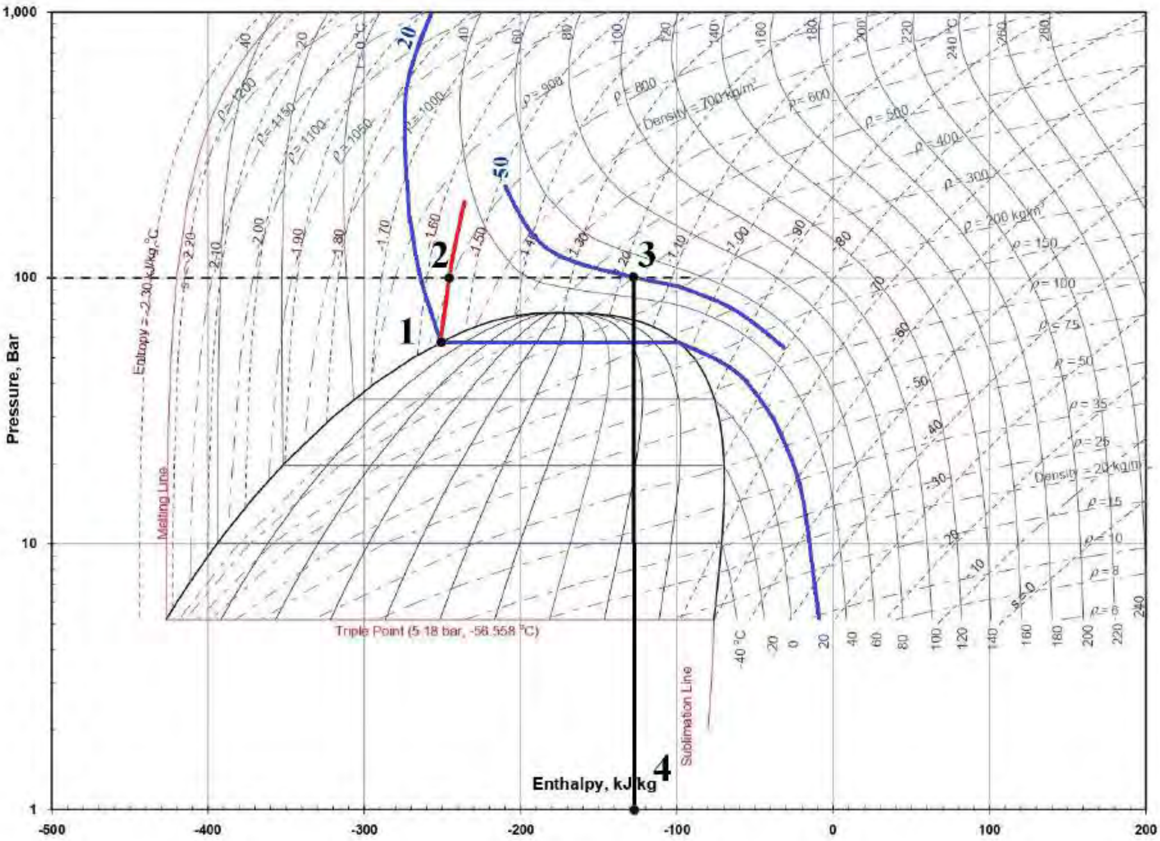
The system is fed at 1 kg/min through a siphon tube from the liquid phase of a commercial cylinder containing CO_2 in liquid-vapor equilibrium at 20ºC.

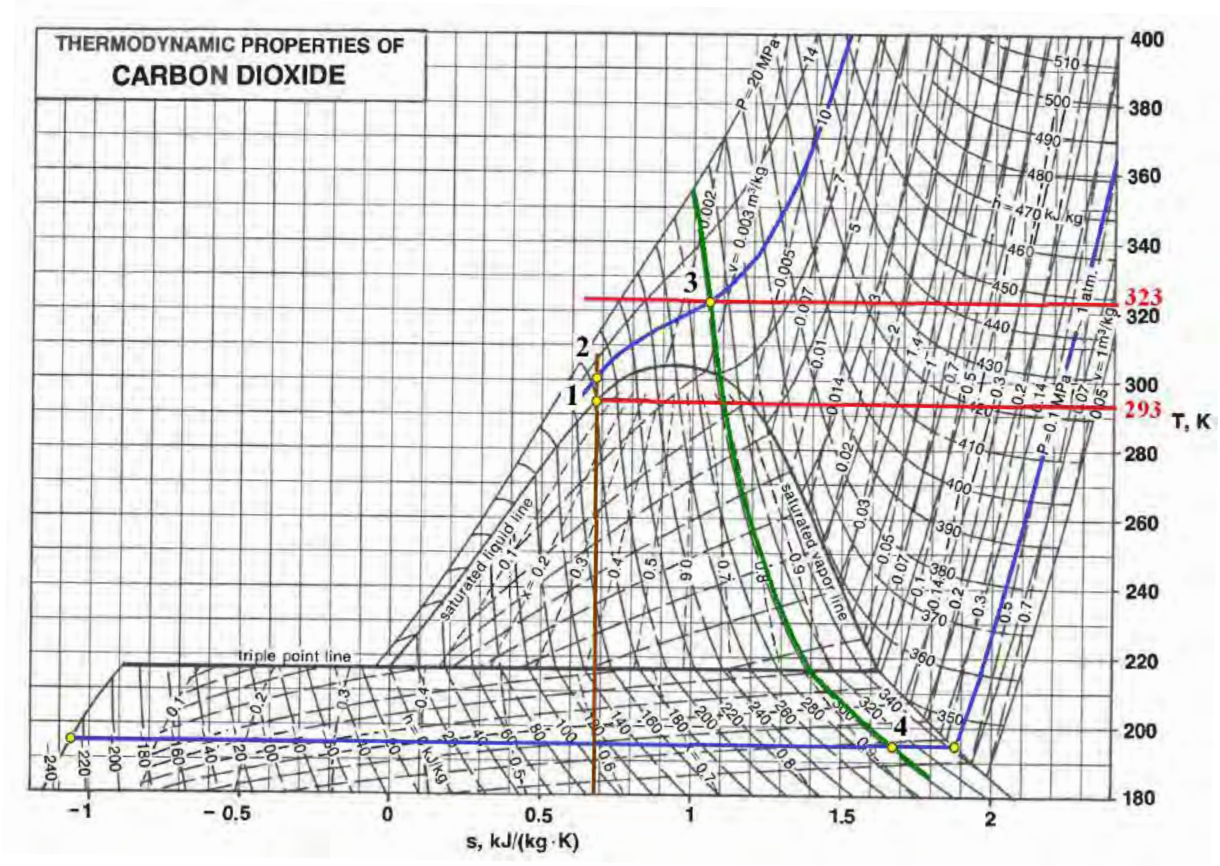
- **a) Drawn the flowchart.**
- **b) Represent the process quantitatively in *PH*(*T*,*S*,ρ) and *TS*(*P*,*V*,*H*) diagrams and qualitatively in *PT*, *PV*(*T*) and *z*(P_r,T_r) diagrams.**
- **c) Indicate if simplifications can be made to calculate the power consumed in the compressor and the heat flow in the exchanger.**
- **d) Determine the power and heat flow from the previous section with the help of the *PH*(*T*,*S*,ρ) and *TS*(*P*,*V*,*H*) diagrams.**
- **e) Calculate the conditions of CO_2 after expansion.**

Question a. Let "1" be the conditions of CO_2 before the compression (saturated liquid at 20ºC), "2" be these conditions after the adiabatic frictionless compression to 100 bar (i.e., isentropic), "3" be the stream after the heating to 50ºC and "4" be the conditions after the isenthalpic expansion to 1 bar. The flow chart is

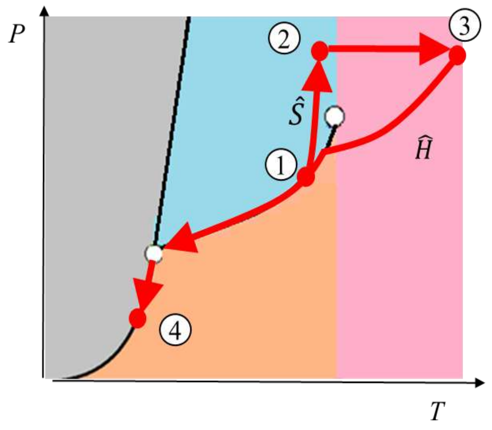


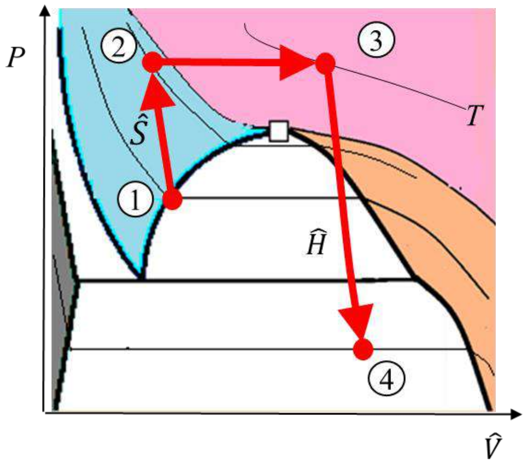
Question b. The quantitative representation of the process on figures V.2 (*P* vs. *H* diagram with isolines of *T*, *S* and ρ) and V.3 (*T* vs. *S* with isolines of *P*, *V* and *H*) of this book's appendix V after the corresponding unit conversion (20ºC=293 K, 50ºC=323 K, 1 bar=0.1 MPa, 100 bar= 10 MPa) will be

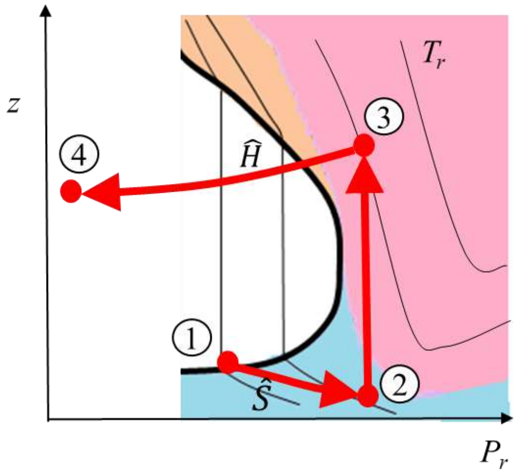

Pressure, Bar
1,000
100
10
1
Enthalpy, kJ/kg
-500
-400
-300
-200
-100
0
100
200
1
2
3
4
20
50
Entropy = -2.30 kJ/kg.°C
Density = 700 kg/m³
Density = 20 kg/m³
ρ = 200 kg/m³
Melting Line
Sublimation Line
Triple Point (5.18 bar, -56.558 °C)


THERMODYNAMIC PROPERTIES OF
CARBON DIOXIDE
s, kJ/(kg·K)
-1
-0.5
0
0.5
1
1.5
2
T, K
400
380
360
340
323
320
300
293
280
260
240
220
200
180
1
2
3
4
P = 20 MPa
v = 0.003 m³/kg
h = 470 kJ/kg
1 atm.
P = 0.1 MPa
v = 1 m³/kg
saturated liquid line
saturated vapor line
triple point line
x = 0.2
h = 0 kJ/kg

It can be seen that, after the final isenthalpic expansion, a solid (dry ice) and a vapor in equilibrium at a very low temperature are generated. The qualitative representation of the multiple line of operation in the *PT*, *PV*(*T*) and $z(P_r,T_r)$ diagrams is







Question c. The compression power between points 1 and 2 will be given by the integral

$$\wp_{21} = \widehat{\mathcal{W}}_{tot}\Delta\widehat{W}^{\text{fl}}_{21} = \widehat{\mathcal{W}}_{tot}\int_1^2 \hat{V}\mathrm{d}P$$

while the heat flow between points 2 and 3 are

$$q_{32} = \widehat{\mathcal{W}}_{tot}\Delta\hat{Q}_{32} = \widehat{\mathcal{W}}_{tot}\int_2^3 T\mathrm{d}\hat{S}$$

However, according to reference problem 0.3

$$\mathrm{d}\hat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\widehat{W}^{\text{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P$$

If the compression is adiabatic and frictionless ($\mathrm{d}\hat{Q}$=0)

$$\mathrm{d}\widehat{W}^{\mathrm{fl}} = \mathrm{d}\widehat{H}$$

$$\mathscr{p}_{21} = \widehat{\mathcal{W}}_{tot}\Delta\widehat{H}_{21} = \widehat{\mathcal{W}}_{tot}\left(\widehat{H}_2 - \widehat{H}_1\right) \qquad [1]$$

and if the heat exchange is isobaric (dP=0)

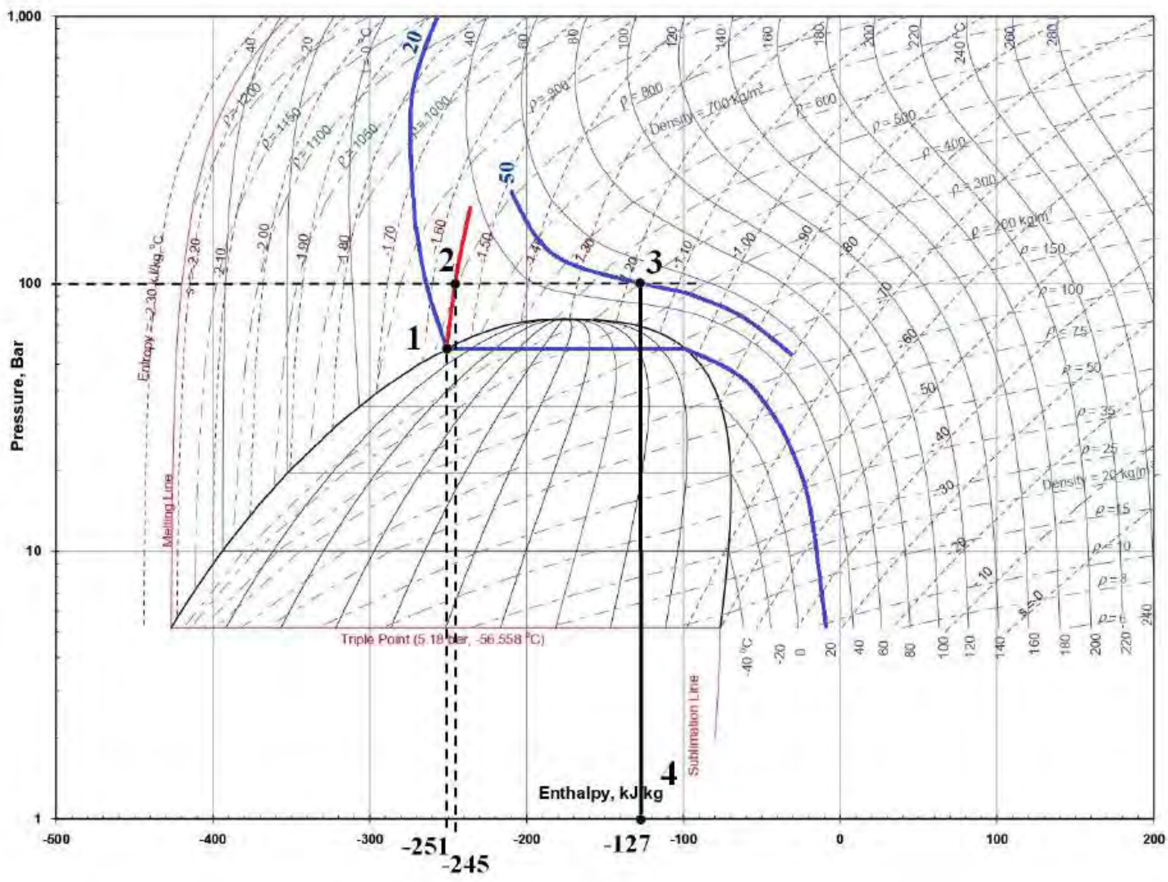
$$\mathrm{d}\widehat{H} = \mathrm{d}\widehat{Q}$$

$$q_{32} = \widehat{\mathcal{W}}_{tot}\Delta\widehat{H}_{32} = \widehat{\mathcal{W}}_{tot}\left(\widehat{H}_3 - \widehat{H}_2\right) \qquad [2]$$

Question d. In figure V.2, the enthalpies are $\widehat{H}_1$ = -251 kJ/kg, $\widehat{H}_2$ = -245 kJ/kg and $\widehat{H}_3 = \widehat{H}_4$ = -127 kJ/kg, so equations [1] and [2] will give

$$\mathscr{p}_{21} = \left(1\ \frac{\mathrm{kg}}{\mathrm{min}}\right)\left[-245\ \frac{\mathrm{kJ}}{\mathrm{kg}} - \left(-251\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right)\right] = 6\ \frac{\mathrm{kJ}}{\mathrm{min}}$$

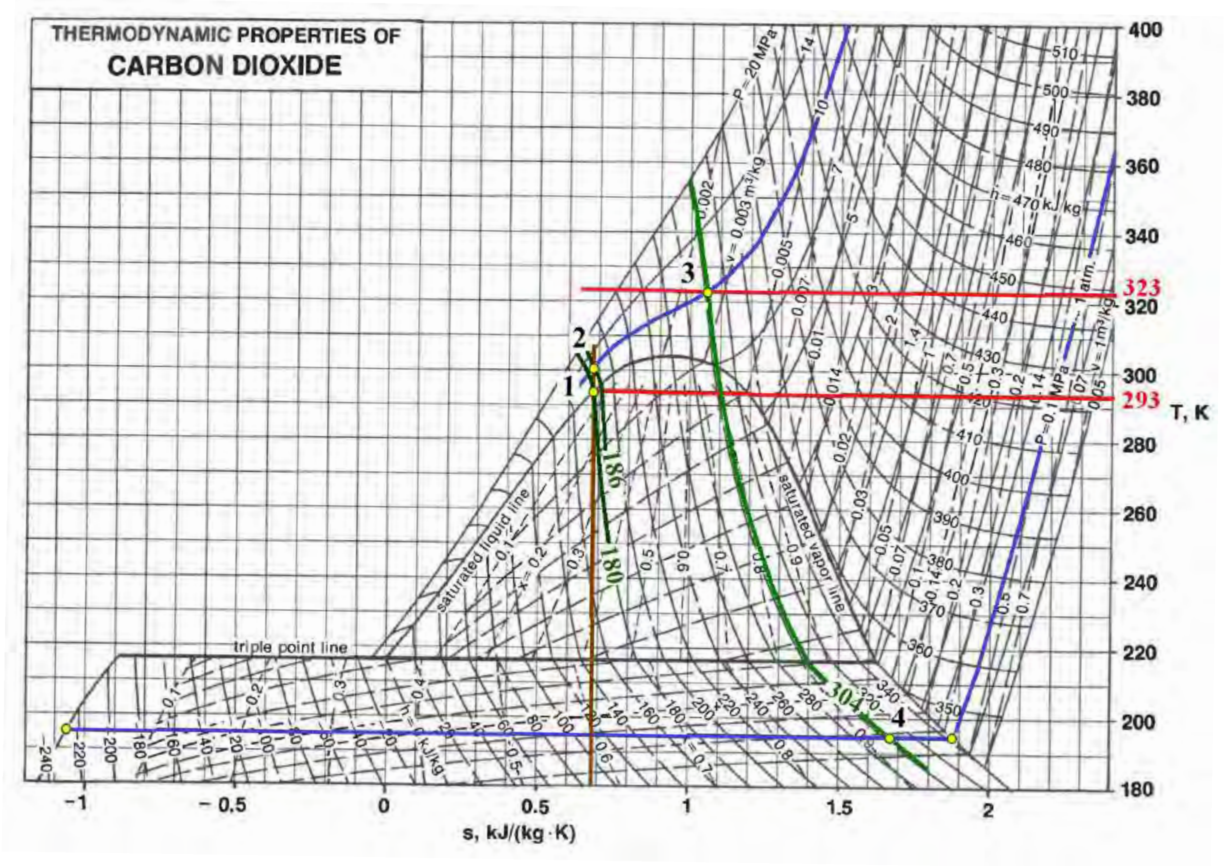
$$q_{32} = \left(1\ \frac{\mathrm{kg}}{\mathrm{min}}\right)\left[-127\ \frac{\mathrm{kJ}}{\mathrm{kg}} - \left(-245\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right)\right] = 118\ \frac{\mathrm{kJ}}{\mathrm{min}}$$



While in figure V.3, $\widehat{H}_1$ =180 kJ/kg, $\widehat{H}_2$ =186 kJ/kg and $\widehat{H}_3 = \widehat{H}_4$ =304 kJ/kg, which leads to the same results

$$\wp_{21} = \left(1\ \frac{\text{kg}}{\text{min}}\right)\left[186\ \frac{\text{kJ}}{\text{kg}} - 180\ \frac{\text{kJ}}{\text{kg}}\right] = 6\ \frac{\text{kJ}}{\text{min}}$$

$$q_{32} = \left(1\ \frac{\text{kg}}{\text{min}}\right)\left[304\ \frac{\text{kJ}}{\text{kg}} - 186\ \frac{\text{kJ}}{\text{kg}}\right] = 118\ \frac{\text{kJ}}{\text{min}}$$



Question e. The carbon dioxide conditions after the isenthalpic expansion can only be determined with figure V.3, since the other one obviates the solid-vapor equilibrium. Its temperature is of 195 K, and as previously mentioned, it will be divided into two phases whose flow rates can be calculated by combining the mass balance in the expansion chamber

$$\widehat{\mathcal{W}}_{tot} = \widehat{\mathcal{W}}_s + \widehat{\mathcal{W}}_v$$

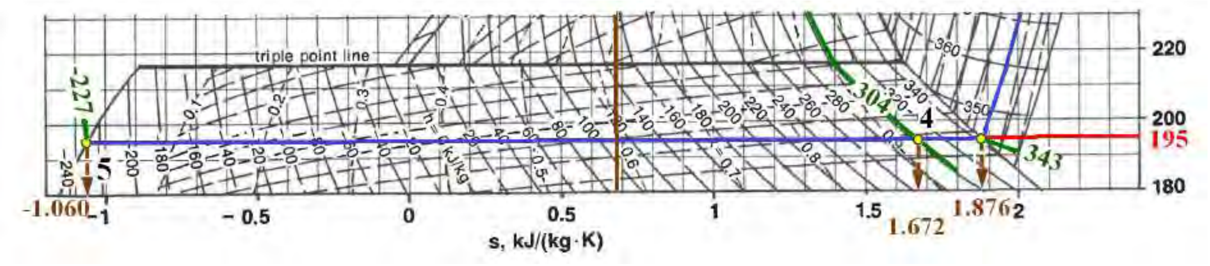
with the enthalpy balance to this chamber

$$\widehat{\mathcal{W}}_{tot}\hat{H}_4 = \widehat{\mathcal{W}}_s\hat{H}_s^{sat} + \widehat{\mathcal{W}}_v\hat{H}_v^{sat}$$

obtaining

$$\widehat{\mathcal{W}}_s = \frac{\left(\hat{H}_4 - \hat{H}_v^{sat}\right)}{\left(\hat{H}_s^{sat} - \hat{H}_v^{sat}\right)}\widehat{\mathcal{W}}_{tot} = \frac{(304 - 343)}{(-227 - 343)}\left[1\ \frac{\text{kg}}{\text{min}}\right] = 0.068\ \frac{\text{kg}}{\text{min}}$$

$$\widehat{W}_v = \widehat{W}_{tot} - \widehat{W}_s = 1\ \frac{\text{kg}}{\text{min}} - 0.068\ \frac{\text{kg}}{\text{min}} = 0.932\ \frac{\text{kg}}{\text{min}}$$



Although it could also have been done by combining the mass balance with that of entropy to the chamber

$$\widehat{W}_{tot}\hat{S}_4 = \widehat{W}_s\hat{S}_s^{sat} + \widehat{W}_v\hat{S}_v^{sat}$$

$$\widehat{W}_s = \frac{\left(\hat{S}_4 - \hat{S}_v^{sat}\right)}{\left(\hat{S}_s^{sat} - \hat{S}_v^{sat}\right)}\widehat{W}_{tot} = \frac{(1.672 - 1.876)}{(-1.060 - 1.876)}\left[1\ \frac{\text{kg}}{\text{min}}\right] = 0.069\ \frac{\text{kg}}{\text{min}}$$

$$\widehat{W}_v = \widehat{W}_{tot} - \widehat{W}_s = 1\ \frac{\text{kg}}{\text{min}} - 0.069\ \frac{\text{kg}}{\text{min}} = 0.931\ \frac{\text{kg}}{\text{min}}$$

the small differences being due to the error in reading and interpolating the graphical data.

6.25. An experimental plant that manufactures dry ice operates in the following way: CO_2 at 293 K and 0.1 MPa is isothermically compressed to 10 MPa, then cooled to one temperature in an isobaric heat exchanger (circulating in counterflow with the recycle, as explained below) and isenthalpically expanded. The result of this expansion is a biphasic mixture of solid and vapor in equilibrium at 1 atm (in a proportion of 2/3 by weight).

After removing the dry ice, the saturated vapor is recycled, being heated in the heat exchanger from the equilibrium temperature to 293 K. Under these conditions it is mixed with a CO_2 feed (added to replace the flow of removed solids and to keep the process in a steady state) and the resulting stream enters the compressor, closing the cycle.

a) Draw the flowchart of the cycle and qualitatively represent it on *PT*, *PV*(*T*) and *TH*(*P*) diagrams.

b) With the help of *PH*(ρ,*T*,*S*) or *TS*(*V*,*P*,*H*) diagrams, estimate the entropy, enthalpy and temperature of the stream leaving the isenthalpic valve.

c) Estimate the entropy, enthalpy and temperature of the compressed stream leaving the heat exchanger.

d) Quantify the specific enthalpies and entropies of the stream at the entrance and the exit of the isothermal compressor.

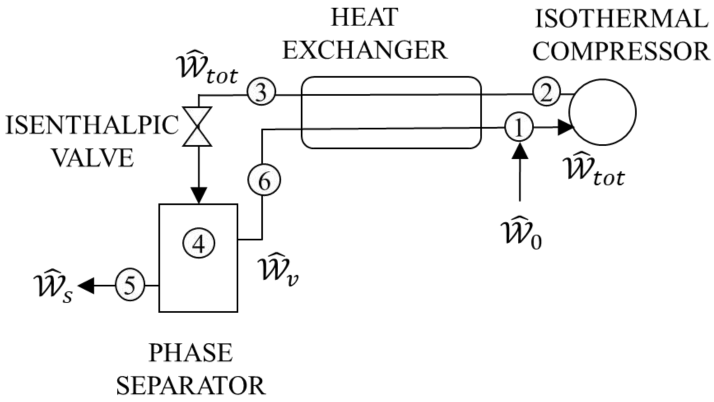
e) Calculate the heat exchanged in the heat exchanger.

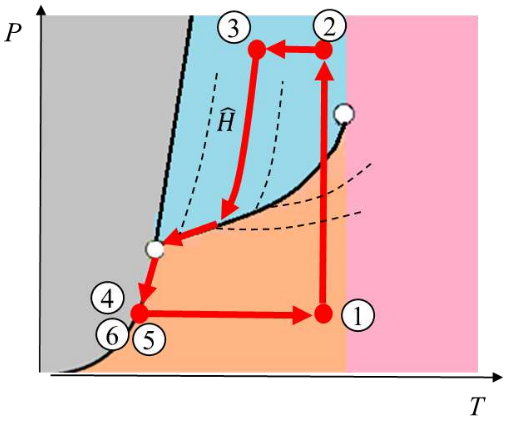
f) Calculate the heat and work in the compressor and express them per kilogram of snow produced.

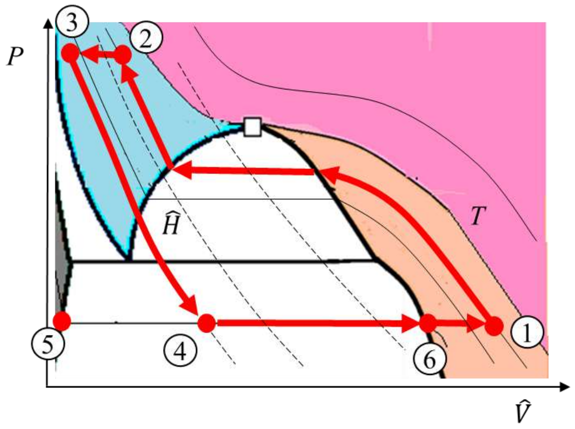
Use, if necessary, the following data for the 10 MPa isobar. The reference state of entropies and enthalpies is the liquid at the temperature and pressure of the triple point (Reynolds, 1979).

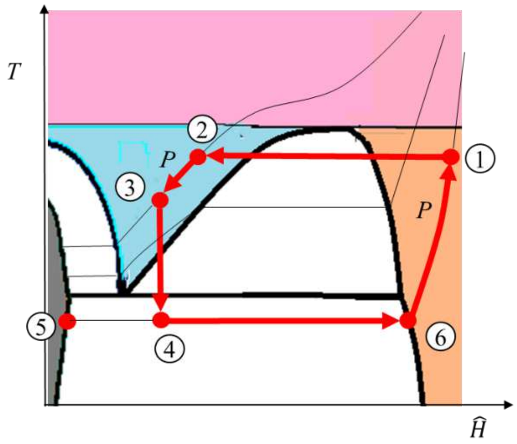
T(K)	$\hat{\rho}\ (\mathrm{kg/m^3})$	$\hat{H}\ (\mathrm{kJ/kg})$	$\hat{S}\ (\mathrm{kJ/kg{\cdot}K})$
220	1187.2	9.59	0.0073
230	1152	29.94	0.0977
240	1115.3	49.88	0.1826
250	1076.7	69.75	0.2637
260	1035.2	89.87	0.3426
270	989.97	110.59	0.4208
280	939	132.36	0.4999
290	878.96	155.97	0.5827
300	802.05	183.07	0.6746

Question a. By denominating “1” to the place where the feed joins the recycled heated vapor, “2” to this mixture after isothermal compression, “3” to the compressed and cooled mixture, “4” to the stream after the isenthalpic expansion, “5” to the removed solid and “6” to the CO_2 in equilibrium with that solid, the flow diagram and the requested representations are









Question b. Since figure V.2 of appendix V (*PH* diagram) does not include the region of the solid, figure V.3 of the same appendix (*TS* diagram) should be used to solve the problem. According to this figure, the 0.1 MPa isobar intersects the solid-vapor biphasic region at a temperature of 195 K. On the other hand, the entropy of the biphasic stream (4) can be determined from the entropies of the saturated solid and the liquid by combining the mass and entropy balances as

$$\hat{S}_4 = \frac{\hat{\mathcal{W}}_s}{\hat{\mathcal{W}}_{tot}}\hat{S}_s + \frac{\hat{\mathcal{W}}_v}{\hat{\mathcal{W}}_{tot}}\hat{S}_v = \frac{\hat{\mathcal{W}}_s}{\hat{\mathcal{W}}_{tot}}\hat{S}_5 + \frac{\hat{\mathcal{W}}_v}{\hat{\mathcal{W}}_{tot}}\hat{S}_6$$

Taking into account that the statement of the problem says

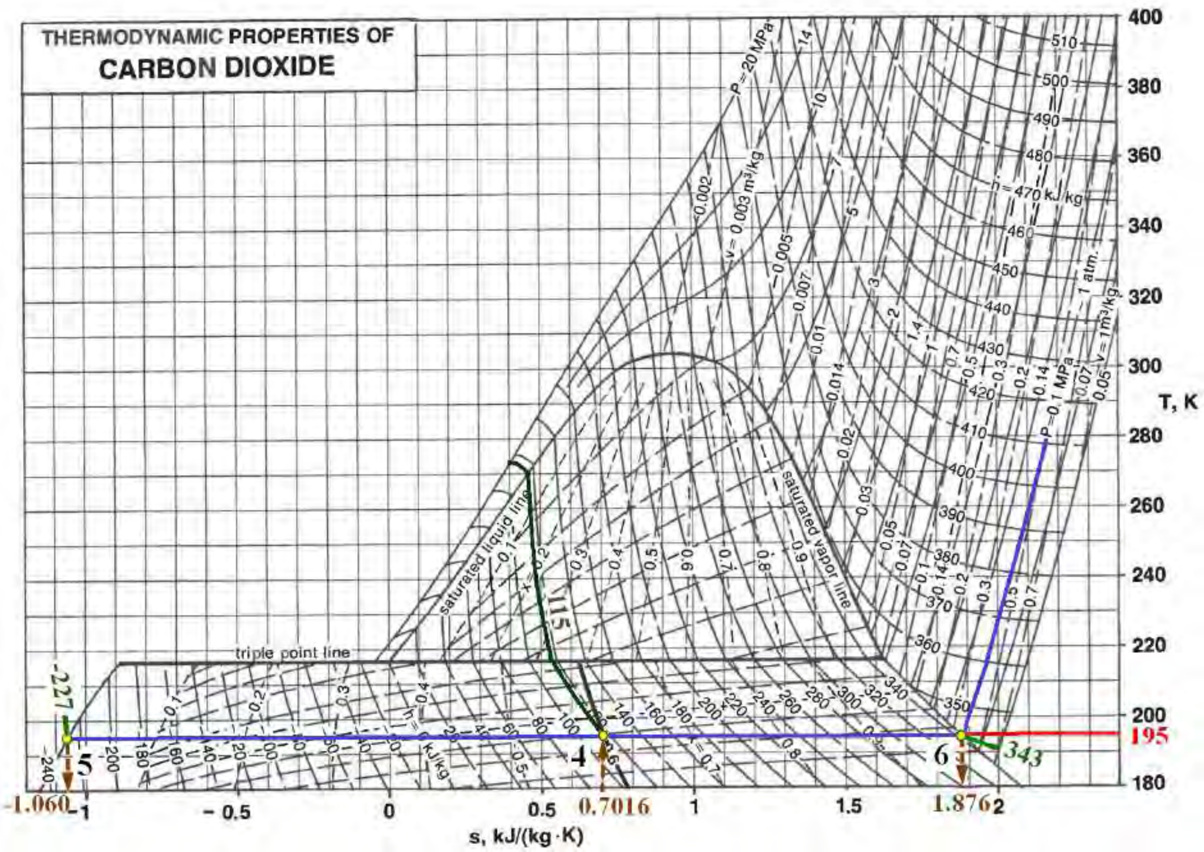
$$\frac{\widehat{\mathcal{W}}_s}{\widehat{\mathcal{W}}_v} = \frac{2}{3}$$

the mass balance to the phase separator allows the calculation of the title or quality of vapor in point 4

$$\widehat{\mathcal{W}}_{tot} = \widehat{\mathcal{W}}_s + \widehat{\mathcal{W}}_v = \frac{2}{3}\widehat{\mathcal{W}}_v + \widehat{\mathcal{W}}_v = \frac{5}{3}\widehat{\mathcal{W}}_v \quad \rightarrow \quad \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}} = \frac{3}{5} = 0.6$$

so

$$\hat{S}_4 = \left(1 - \frac{3}{5}\right)\left(-1.060\ \frac{\text{kJ}}{\text{kg·K}}\right) + \frac{3}{5}\left(1.876\ \frac{\text{kJ}}{\text{kg·K}}\right) = 0.7016\ \frac{\text{kJ}}{\text{kg·K}}$$



The specific enthalpy of the stream can be calculated in three ways:

- By interpolating the isenthalpic line that passes through the intersection of the $\hat{S}_4$ isentropic with the 0.1 MPa isobar.

- By interpolating the isenthalpic that passes through the intersection of the 0.6 title line with the 0.1 MPa isobar.

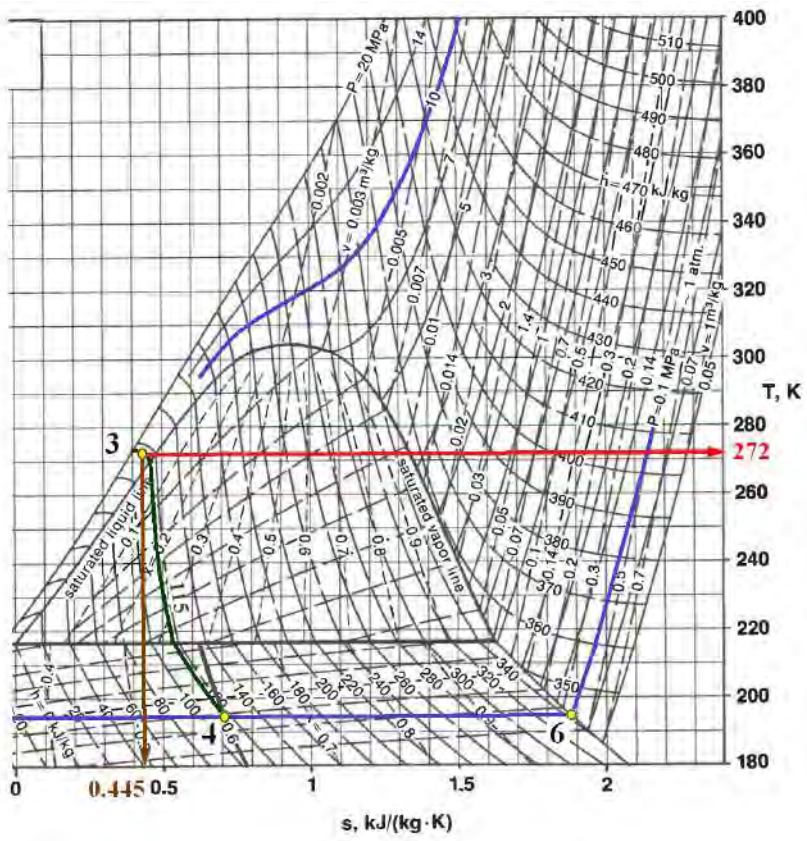
- From the enthalpies of the saturated solid (-227 kJ/kg) and saturated vapor (343 kJ/kg) at 0.1 MPa, by combining the mass and enthalpy balances in point 4

$$\hat{H}_4 = \frac{\hat{\mathcal{W}}_s}{\hat{\mathcal{W}}_{tot}}\hat{H}_s + \frac{\hat{\mathcal{W}}_v}{\hat{\mathcal{W}}_{tot}}\hat{H}_v = \frac{\hat{\mathcal{W}}_s}{\hat{\mathcal{W}}_{tot}}\hat{H}_5 + \frac{\hat{\mathcal{W}}_v}{\hat{\mathcal{W}}_{tot}}\hat{H}_6$$

In all cases $\hat{H}_4 = 115$ kJ/kg.

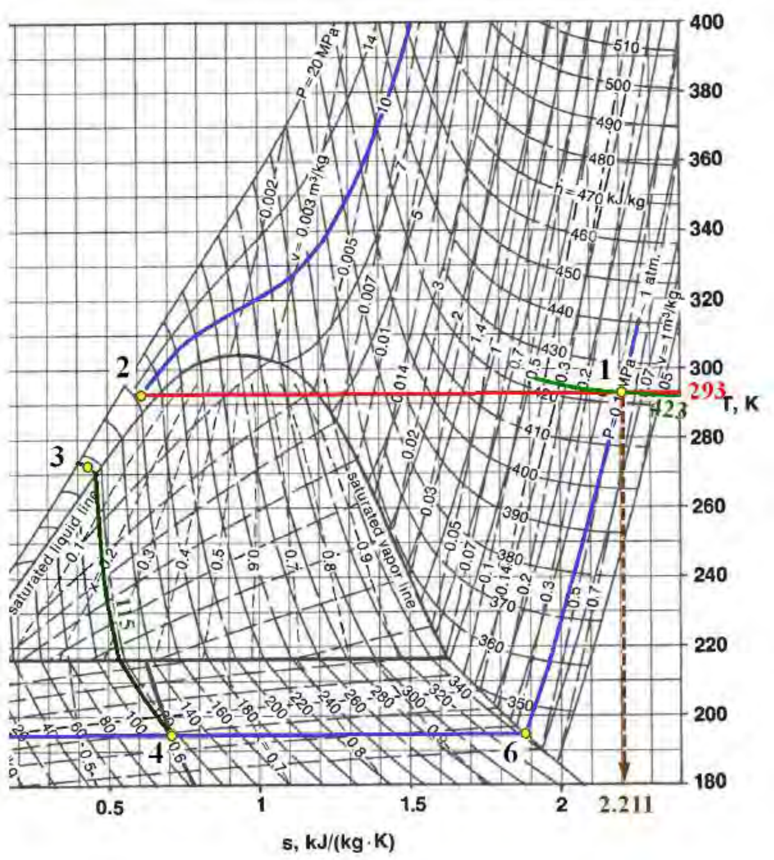
Question c. The stream that leaves the heat exchanger is the same that enters the isenthalpic valve, so $\hat{H}_4 = \hat{H}_3$ =115 kJ/kg. In the $TS(V,P,H)$ diagram, the intersection of the 115 kJ/kg isoenthalpic line with the 10 MPa isobar (pressure of the compressed fluid leaving the heat exchanger) would allow finding both the entropy and the temperature of point 3. However, by visual inspection of figure V.3, it is seen that this intersection occurs at a temperature lower than 295 K, where the 10 MPa isobar is not drawn.

Fortunately, the statement supplies data up to 220 K. Comparison of this table with Figure V.3 shows that both have the same reference state for enthalpies and entropies, so the data can be used without any adjustment.



By interpolating the temperature at which the enthalpy is of 115 kJ/kg, it results that T_3=272 K. Additionally, the entropy at this temperature is $\hat{S}_3 = 0.445$ kJ/kg·K.

Question d. Due to the fact that T_1=T_2=293 K, the intersection of this isotherm with the isobars 0.1 MPa and 10 MPa will allow the reading of the entropies and enthalpies at the entrance and the exit of the compressor, respectively. In point 1 it can be obtained that $\hat{S}_1$ = 2.211 kJ/kg·K and $\widehat{H}_1$ =423 kJ/kg. Nonetheless, point 2 is placed below the 10 MPa isobar, and the table given by the statement of the problem has to be employed to interpolate them. Thus, at 293 K results are $\hat{S}_2$ = 0.61 kJ/kg·K and $\widehat{H}_2$ =163 kJ/kg.



Question e. The heat flow given by the compressed stream ($\widehat{W}_{tot}$) will be that of the transit from point 2 to point 3, while the heat flow gained by the fluid at 0.1 MPa ($\widehat{W}_v = 0.6\widehat{W}_{tot}$) will be that of the step from 6 to 1.

$$q_{32} = \widehat{W}_{tot}\Delta\hat{Q}_{32} = \widehat{W}_{tot}\int_2^3 T\mathrm{d}\hat{S}$$

$$q_{16} = \widehat{W}_v\Delta\hat{Q}_{16} = 0.6\widehat{W}_{tot}\int_6^1 T\mathrm{d}\hat{S}$$

However, if the heat exchanger is isobaric (dP=0), equations of reference problem 0.13

$$\mathrm{d}\widehat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\widehat{W}^{\mathrm{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \qquad [1]$$

indicate that $\mathrm{d}\hat{H} = \mathrm{d}\hat{Q}$, so the exchanged heat can be determined by a simple difference of enthalpies

$$q_{32} = \widehat{\mathcal{W}}_{tot}\Delta\hat{H}_{32} = \widehat{\mathcal{W}}_{tot}\left(\hat{H}_3 - \hat{H}_2\right) = \widehat{\mathcal{W}}_{tot}\left(115\ \frac{\text{kJ}}{\text{kg}} - 163\frac{\text{kJ}}{\text{kg}}\right) = -48\widehat{\mathcal{W}}_{tot}$$

$$q_{16} = 0.6\widehat{\mathcal{W}}_{tot}\Delta\hat{H}_{16} = 0.6\widehat{\mathcal{W}}_{tot}\left(\hat{H}_1 - \hat{H}_6\right) = 0.6\widehat{\mathcal{W}}_{tot}\left(423\ \frac{\text{kJ}}{\text{kg}} - 343\frac{\text{kJ}}{\text{kg}}\right) = 48\widehat{\mathcal{W}}_{tot}$$

These results reveal that the system is energetically optimized.

Question f. Since the compressor (passage from point 1 to point 2) is isothermal (constant *T*), the integral that defines the exchanged heat becomes

$$\Delta\hat{Q}_{21} = \int_1^2 T\mathrm{d}\hat{S}\ = T_1\int_1^2 \mathrm{d}\hat{S}\ = T_1\left(\hat{S}_2 - \hat{S}_1\right)$$

$$\Delta\hat{Q}_{21} = (293\text{ K})\left(0.61\frac{\text{kJ}}{\text{kg·K}} - 2.211\ \frac{\text{kJ}}{\text{kg·K}}\right) = -469.1\ \frac{\text{kJ}}{\text{kg}}$$

and the compression work according to equation [1] is

$$\mathrm{d}\widehat{W}^{\text{fl}} = \mathrm{d}\hat{H} - \mathrm{d}\hat{Q} = \ \mathrm{d}\hat{H} - T\mathrm{d}\hat{S}$$

$$\Delta\widehat{W}^{\text{fl}}_{21} = \int_1^2\left(\mathrm{d}\hat{H} - T\mathrm{d}\hat{S}\right) = \Delta\hat{H}_{21} - T_1\left(\hat{S}_2 - \hat{S}_1\right) = \Delta\hat{H}_{21} - \Delta\hat{Q}_{21}$$

$$\Delta\widehat{W}^{\text{fl}}_{21} = \left(163\ \frac{\text{kJ}}{\text{kg}} - 423\frac{\text{kJ}}{\text{kg}}\right) - \left(-469.1\frac{\text{kJ}}{\text{kg}}\right) = 209.1\ \frac{\text{kJ}}{\text{kg}}$$

As is well known, heat flow and power in the compressor are determined by multiplying these results by the flow rate of CO_2 in the apparatus ($\widehat{\mathcal{W}}_{tot}$). However, the statement asks that they be expressed per kilogram of snow produced, i.e., they have to be divided by $\widehat{\mathcal{W}}_s = \left(1 - \frac{3}{5}\right)\widehat{\mathcal{W}}_{tot} = 0.4\widehat{\mathcal{W}}_{tot}$

$$\frac{q_{21}}{\widehat{\mathcal{W}}_s} = \frac{\widehat{\mathcal{W}}_{tot}}{\widehat{\mathcal{W}}_s}\Delta\hat{Q}_{21} = \left(\frac{\widehat{\mathcal{W}}_{tot}}{0.4\widehat{\mathcal{W}}_{tot}}\right)\left(-469.1\ \frac{\text{kJ}}{\text{kg}}\right) = -1172.75\ \frac{\text{kJ}}{\text{kg}}$$

$$\frac{\wp_{21}}{\widehat{\mathcal{W}}_s} = \frac{\widehat{\mathcal{W}}_{tot}}{\widehat{\mathcal{W}}_s}\Delta\widehat{W}^{\text{fl}}_{21} = \left(\frac{\widehat{\mathcal{W}}_{tot}}{0.4\widehat{\mathcal{W}}_{tot}}\right)\left(209.1\ \frac{\text{kJ}}{\text{kg}}\right) = 522.75\ \frac{\text{kJ}}{\text{kg}}$$

6.26. To obtain 10 kg/min of dry ice (solid CO_2) from vapor of this substance at 290 K and 10 MPa, two cycles have been considered:

- **Isenthalpic expansion (in a valve) of the stream at 290 K and 10 MPa to 0.1 MPa, obtention of saturated solid and vapor at this pressure in a separation chamber that follows the valve, isentropical compression of the vapor at 0.1 MPa to 10 MPa, cooling with water in an isobaric heat exchanger to 298 K and final mixing with a feed stream (added to replace the flow of removed solids).**
- **Heating of the saturated vapor at 0.1 MPa through an isobaric heat exchanger of infinite length (in counterflow to the CO_2 at 290 K and 10 MPa) to 290 K, isentropical compression to 10 MPa, passage through a second isobaric heat exchanger fed with water until reaching 298 K and final mixing with the feed. This mixture is the stream that enters the infinite length heat exchanger and isenthalpically expands in the valve.**

Draw both flowcharts and by means of a specific $TS(V,P,H)$ diagram for CO_2, estimate:

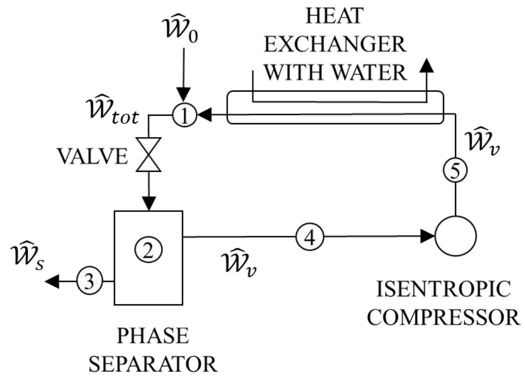
a) **Specific enthalpy and entropy of the feed.**
b) **Specific enthalpy and entropy of the stream leaving the expansion valve in the first process, as well as its temperature and its mass flow.**
c) **The mass flow rates of all the other streams involved in the first process.**
d) **The power consumed in the compressor of the first process.**
e) **The heat flow in the heat exchanger of the first process.**
f) **The mass flow rates of all the streams in the second process.**
g) **The temperature of the compressed stream entering the valve in the second process.**
h) **The specific enthalpy and entropy of the stream leaving the expansion valve in the second process.**
i) **The power consumed in the compressor of the second process.**
j) **The heat flow in the heat exchanger with water of the second process.**

Use, if necessary, the following data for the 10 MPa isobar. The reference state for enthalpies and entropies is the saturated liquid at the triple point (Reynolds, 1979).

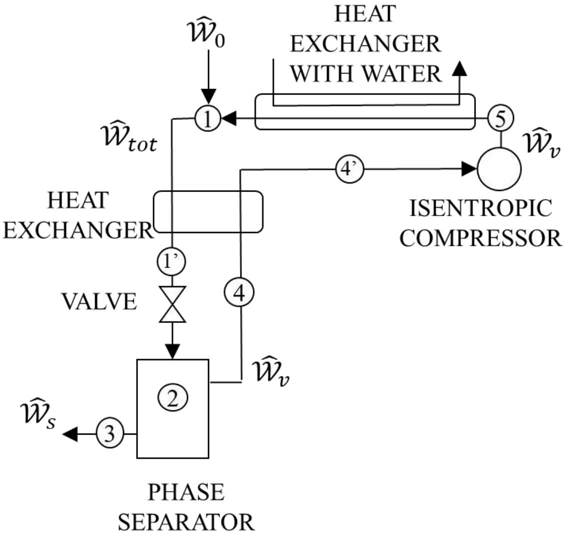
T(K)	$\hat{\rho}\ (\mathrm{kg/m^3})$	$\hat{H}\ (\mathrm{kJ/kg})$	$\hat{S}\ (\mathrm{kJ/kg{\cdot}K})$
220	1187.2	9.59	0.0073
230	1152	29.94	0.0977
240	1115.3	49.88	0.1826
250	1076.7	69.75	0.2637
260	1035.2	89.87	0.3426
270	989.97	110.59	0.4208
280	939	132.36	0.4999
290	878.96	155.97	0.5827

T(K)	$\hat{\rho}$ (kg/m^3)	$\hat{H}$ (kJ/kg)	$\hat{S}$ (kJ/kg·K)
300	802.05	183.07	0.6746
400	161.29	463.19	1.5127
500	112.99	584.73	1.7846
600	89.928	700.24	1.9952
700	75.472	816.97	2.1751
800	65.359	936.2	2.3343
900	57.770	1058.02	2.4777
1000	51.840	1182.21	2.6086

The two flowcharts (with significant points and streams) are shown below.



First process



Second process

Question a. The intersection of the 290 K isotherm with the 10 MPa isobar should give both the required entropy and enthalpy values. However, by visual inspection of figure V.3 of this book's appendix V (TS diagram of CO_2) it is seen that this intersection occurs at a temperature lower than 295 K, where the 10 MPa isobar is not drawn.

The statement of the problem provides numerical data for this isobar up to 220 K. Comparison of the table with Figure V.3 reveals that both have the same reference state for enthalpies and entropies, so the data can be used without any adjustment. Additonally, 290 K is one of the entries in the table: this avoids interpolations.

Therefore, $\hat{S}_0 = 0.5827$ kJ/kg·K and $\hat{H}_0$ =155.97 kJ/kg.

Question b. Due to the fact that the valve is isenthalpic, the specific enthalpy of the stream in point 2 will be the same as in point 1, and coincides with that of the feed. $\widehat{H}_2 = \widehat{H}_1 = \widehat{H}_0$ =155.97 kJ/kg.

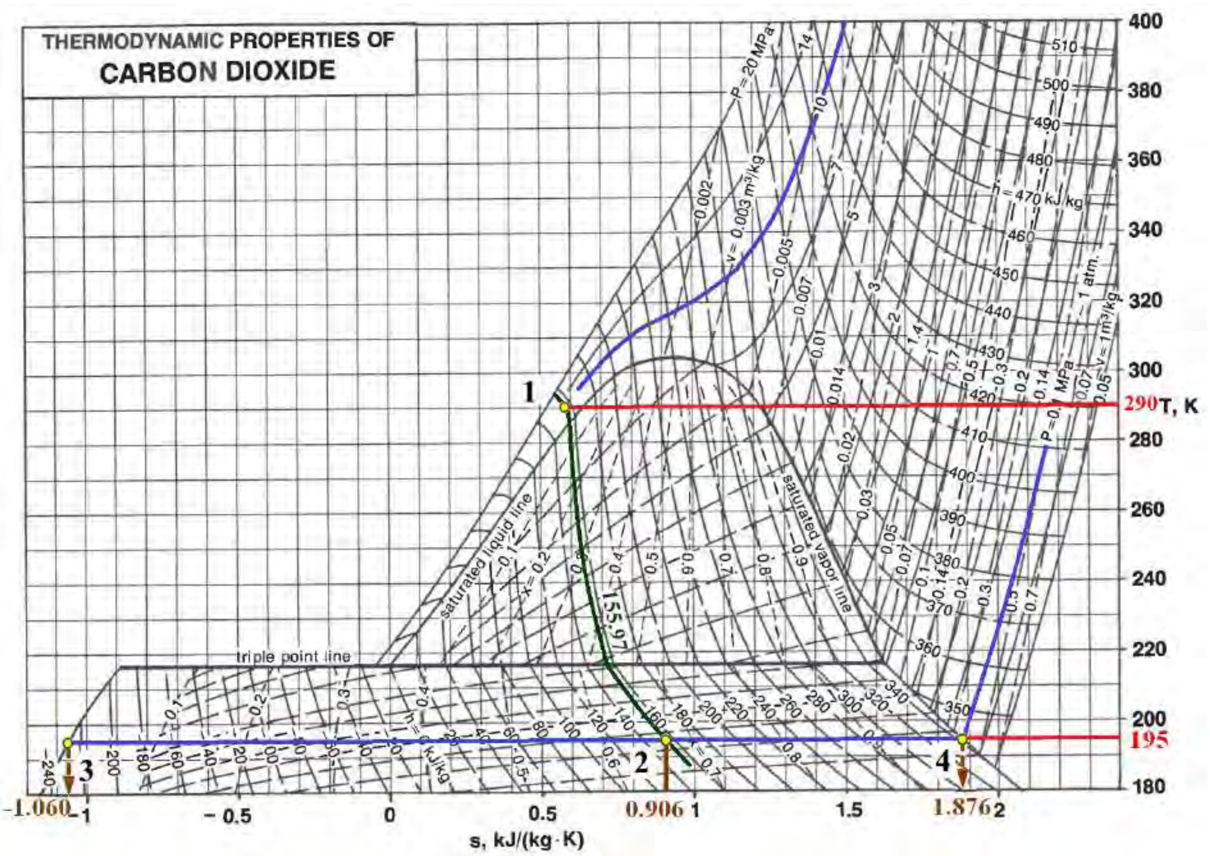
On the other hand, since point 2 is at 0.1 MPa, its specific entropy will be at the intersection of this isobar with the 155.97 kJ/kg isenthalpic, which turns out to be $\hat{S}_2 = 0.906$ kJ/kg·K. The temperature of the stream, like that of solid and vapor, is of 195 K. The saturated liquid and saturated vapor have the same pressure and temperature that this point.

Finally, by combining the mass and entropy balances to the phase separator, the mass flow rate $\widehat{\mathcal{W}}_{tot}$ is obtained

$$\widehat{\mathcal{W}}_{tot}\hat{S}_2 = \widehat{\mathcal{W}}_s\hat{S}_3 + \widehat{\mathcal{W}}_v\hat{S}_4$$

$$\widehat{\mathcal{W}}_{tot} = \widehat{\mathcal{W}}_s + \widehat{\mathcal{W}}_v$$

$$\widehat{\mathcal{W}}_{tot} = \frac{(\hat{S}_3 - \hat{S}_4)}{(\hat{S}_2 - \hat{S}_4)}\widehat{\mathcal{W}}_s = \frac{(-1.060 - 1.876)}{(0.906 - 1.876)}\left[10\ \frac{\text{kg}}{\text{min}}\right] = 30.27\ \frac{\text{kg}}{\text{min}}$$



Question c. According to the mass balance to the aforementioned separator

$$\widehat{\mathcal{W}}_v = \widehat{\mathcal{W}}_{tot} - \widehat{\mathcal{W}}_s = 30.27\frac{\text{kg}}{\text{min}} - 10\frac{\text{kg}}{\text{min}} = 20.27\ \frac{\text{kg}}{\text{min}}$$

and the global mass balance to the system allows to say that

$$\widehat{W}_0 = \widehat{W}_s = 10\ \frac{\text{kg}}{\text{min}}$$

Question d. The power in the compressor will be the multiplication of the vapor mass flow rate by the specific flow work carried out in the apparatus, which is

$$\mathrm{d}\widehat{W}^{\mathrm{fl}} = \widehat{V}\mathrm{d}P \quad \rightarrow \ \Delta\widehat{W}^{\mathrm{fl}}_{54} = \int_4^5 \widehat{V}\mathrm{d}P$$

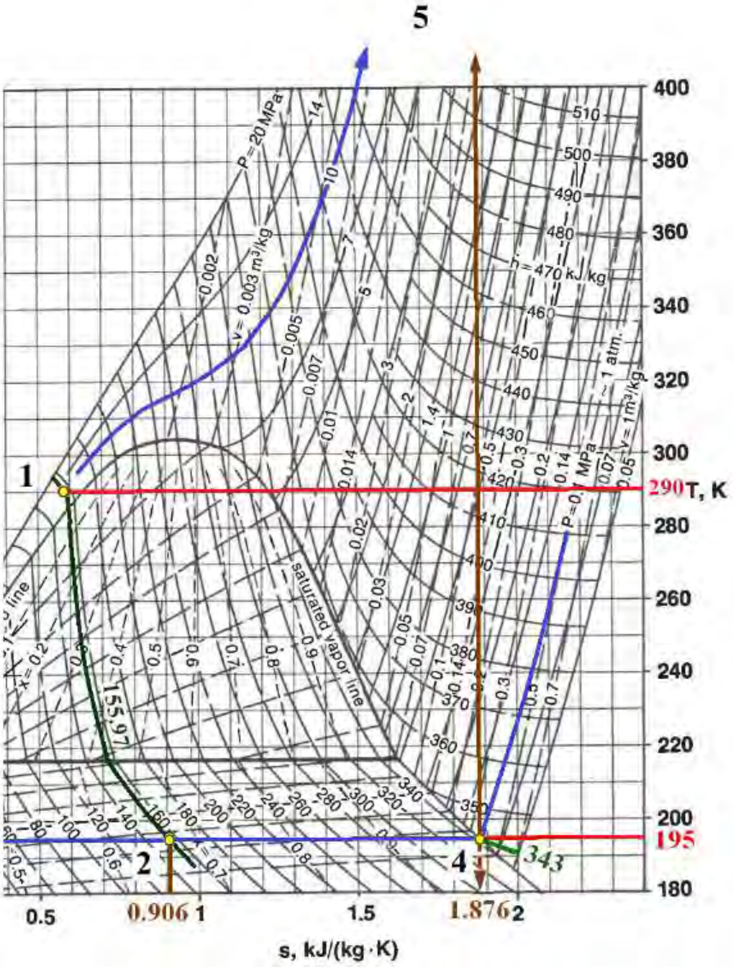
However, equations of reference problem 0.3 say that

$$\mathrm{d}\widehat{H} = \mathrm{d}\widehat{Q} + \mathrm{d}\widehat{W}^{\mathrm{fl}} = T\mathrm{d}\widehat{S} + \widehat{V}\mathrm{d}P \qquad [1]$$

and, if the compression is isentropic, then $\mathrm{d}\widehat{S} = 0$ and

$$\mathrm{d}\widehat{W}^{\mathrm{fl}} = \mathrm{d}\widehat{H} \quad \rightarrow \ \Delta\widehat{W}^{\mathrm{fl}}_{54} = \Delta\widehat{H}_{54}$$

The enthalpy at point 4 is that of the saturated vapor (343 kJ/kg), but that at point 5 (10 MPa and the same entropy as point 4) is beyond the limit of the graph. It has to be interpolated from the table provided by the statement of the problem.



Thus, for $\hat{S}_5 = \hat{S}_4 = 1.876$ kJ/kg·K, it is found that $\widehat{H}_4$ =634.86 kJ/kg (and the temperature, 543.4 K). Then, the power

$$\wp_{54} = \widehat{\mathcal{W}}_v \Delta \widehat{W}^{\text{fl}}_{54} = \left(20.27\ \frac{\text{kg}}{\text{min}}\right)\left(634.86\ \frac{\text{kJ}}{\text{kg}} - 343\frac{\text{kJ}}{\text{kg}}\right) = 5916\ \frac{\text{kJ}}{\text{min}}$$

Question e. The heat flow in the heat exchanger can be calculated through

$$q_{15} = \widehat{\mathcal{W}}_v \Delta \hat{Q}_{15} = \widehat{\mathcal{W}}_v \int_5^1 T \mathrm{d}\hat{S}$$

Formula that can be simplified because the apparatus is isobaric (dP=0) and according to equation [1]

$$\mathrm{d}\widehat{H} = \mathrm{d}\hat{Q} + \mathrm{d}\widehat{W}^{\text{fl}} = T\mathrm{d}\hat{S} + \hat{V}\mathrm{d}P \quad \xrightarrow{\mathrm{d}P=0} \quad \mathrm{d}\widehat{H} = \mathrm{d}\hat{Q}$$

$$q_{15} = \widehat{\mathcal{W}}_v \Delta \widehat{H}_{15} = \left(20.27\ \frac{\text{kg}}{\text{min}}\right)\left(155.97\ \frac{\text{kJ}}{\text{kg}} - 634.86\frac{\text{kJ}}{\text{kg}}\right) = -9707.1\ \frac{\text{kJ}}{\text{min}}$$

Question f. To calculate these flow rates, the first thing that must be done is the energy balance to the heat exchanger where the saturated vapor and the compressed CO$_2$ are treated. Since it is isobaric, the simplification of question **e** is applicable to it.

$$\begin{bmatrix} \text{heat flow} \\ \text{given in the} \\ \text{cooling from} \\ \text{1 to 1}' \end{bmatrix} = \begin{bmatrix} \text{heat flow} \\ \text{gained in the} \\ \text{heating from} \\ \text{4 to 4}' \end{bmatrix}$$

$$q_{1'1} = -q_{4'4}$$

$$\widehat{\mathcal{W}}_{tot} \Delta \hat{Q}_{1'1} = -\widehat{\mathcal{W}}_v \Delta \hat{Q}_{4'4} \quad \rightarrow \quad \widehat{\mathcal{W}}_{tot} \Delta \widehat{H}_{1'1} = -\widehat{\mathcal{W}}_v \Delta \widehat{H}_{4'4}$$

$$\widehat{\mathcal{W}}_{tot}\left(\widehat{H}_{1'} - \widehat{H}_1\right) = -\widehat{\mathcal{W}}_v\left(\widehat{H}_{4'} - \widehat{H}_4\right)$$

$$\widehat{H}_{1'} = \widehat{H}_1 - \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}}\left(\widehat{H}_{4'} - \widehat{H}_4\right) \qquad [2]$$

Taking into account that the mass balance to the phase separator says that

$$\widehat{\mathcal{W}}_{tot} = \widehat{\mathcal{W}}_s + \widehat{\mathcal{W}}_v$$

$$\frac{\widehat{\mathcal{W}}_s}{\widehat{\mathcal{W}}_{tot}} + \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}} = 1 \quad \rightarrow \quad \frac{\widehat{\mathcal{W}}_s}{\widehat{\mathcal{W}}_{tot}} = 1 - \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}} \qquad [3]$$

and that the streams in points 1' and 2 have the same enthalpy

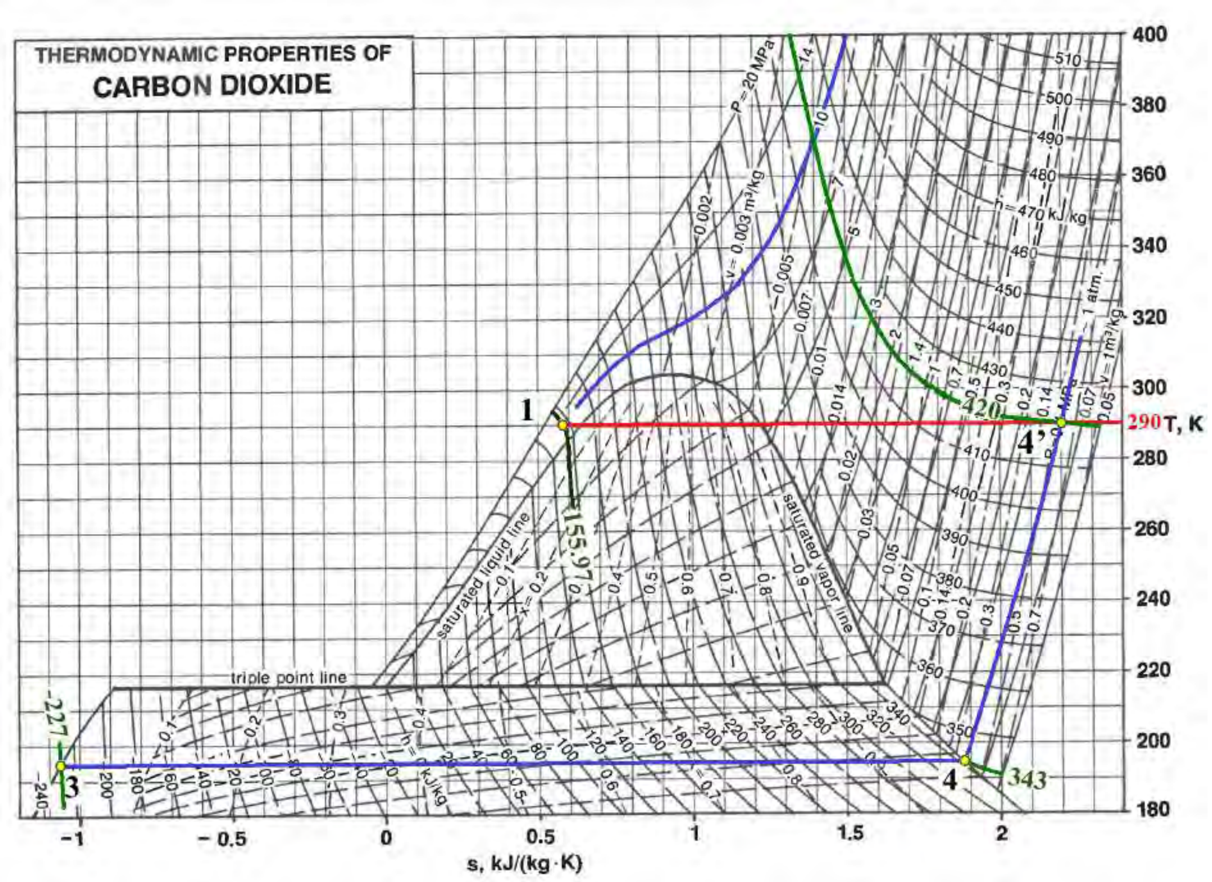
$$\widehat{\mathcal{W}}_{tot}\hat{H}_{1'} = \widehat{\mathcal{W}}_{tot}\hat{H}_2 = \widehat{\mathcal{W}}_s\hat{H}_3 + \widehat{\mathcal{W}}_v\hat{H}_4$$

$$\hat{H}_{1'} = \frac{\widehat{\mathcal{W}}_s}{\widehat{\mathcal{W}}_{tot}}\hat{H}_3 + \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}}\hat{H}_4 \qquad [4]$$

Replacing the quotient $\widehat{\mathcal{W}}_s/\widehat{\mathcal{W}}_{tot}$ of expressions [2] and [4] by that of [3], and then equating [2] to [4]

$$\hat{H}_1 - \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}}\left(\hat{H}_{4'} - \hat{H}_4\right) = \left(1 - \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}}\right)\hat{H}_3 + \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}}\hat{H}_4$$

a function is obtained where the only unknown parameter is the quotient between the solid mass flow rate and the mass flow rate that enters the phase separator because $\hat{H}_1$ and $\hat{H}_4$ have been determined in previous questions and $\hat{H}_{4'}$ and $\hat{H}_3$ can be directly read in figure V.3.



$$155.97 - \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}}(420 - 343) = \left(1 - \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}}\right)(-227) + \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}}(343)$$

$$\frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}} = 0.5919$$

from where

$$\frac{\widehat{\mathcal{W}}_s}{\widehat{\mathcal{W}}_{tot}} = 1 - 0.5919 = 0.4081$$

$$\widehat{\mathcal{W}}_{tot} = \frac{\widehat{\mathcal{W}}_s}{0.4081} = \frac{10\ \mathrm{kg/min}}{0.4081} = 24.5\ \frac{\mathrm{kg}}{\mathrm{min}}$$

$$\widehat{\mathcal{W}}_v = 24.5\frac{\mathrm{kg}}{\mathrm{min}} - 10\frac{\mathrm{kg}}{\mathrm{min}} = 14.5\ \frac{\mathrm{kg}}{\mathrm{min}}$$

Question g. The requested temperature is that of stream $\widehat{\mathcal{W}}_{1'}$, whose enthalpy can be calculated with formulas [2] or [4]

$$\widehat{H}_{1'} = \widehat{H}_1 - \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}}\left(\widehat{H}_{4'} - \widehat{H}_4\right) = 155.97\frac{\mathrm{kJ}}{\mathrm{kg}} - (0.5919)\left(420\frac{\mathrm{kJ}}{\mathrm{kg}} - 343\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 110.39\ \frac{\mathrm{kJ}}{\mathrm{kg}}$$

$$\widehat{H}_{1'} = \left(1 - \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}}\right)\widehat{H}_3 + \frac{\widehat{\mathcal{W}}_s}{\widehat{\mathcal{W}}_{tot}}\widehat{H}_4 = (1 - 0.5919)\left(-227\frac{\mathrm{kJ}}{\mathrm{kg}}\right) + 0.5919\left(343\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 110.38\frac{\mathrm{kJ}}{\mathrm{kg}}$$

that differ in the last decimal because of numerical rounding (and therefore, an average value $\widehat{H}_{1'}$ =110.385 kJ/kg will be taken). The intersection of the corresponding isenthalpic with the 10 MPa isobar will provide the requested temperature. However, it can be observed that this temperature is going to be quite low, and it will be necessary the interpolation in the table of the statement. For an enthalpy of 110.385 kJ/kg a value of 269.9 K is found.

Question h. The valve is isenthalpic, so $\widehat{H}_2 = \widehat{H}_{1'}$ =110.385 kJ/kg. The entropy can be calculated by combining the mass and entropy balances to the phase separator

$$\hat{S}_2 = \left(1 - \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}}\right)\hat{S}_3 + \frac{\widehat{\mathcal{W}}_v}{\widehat{\mathcal{W}}_{tot}}\hat{S}_4$$

$$\hat{S}_2 = (1 - 0.5919)\left(-1.060\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) + 0.5919\left(1.876\frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}\right) = 0.678\ \frac{\mathrm{kJ}}{\mathrm{kg{\cdot}K}}$$

or by finding in the diagram the intersection between the 110.385 kJ/kg isenthalpic and the 0.1 MPa isobar.

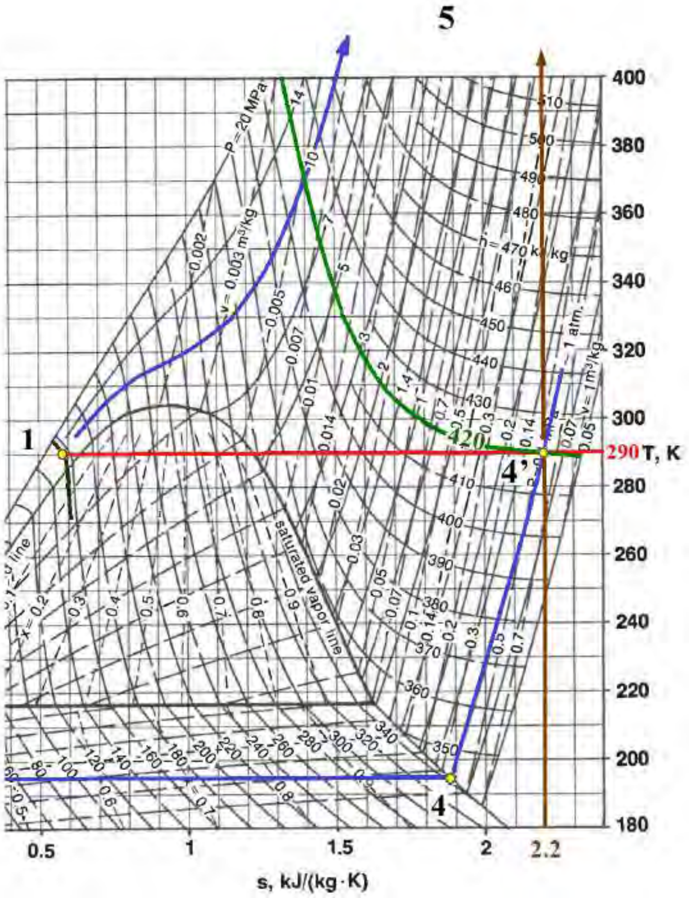
Question i. As in question **d**, the power in the isentropic compressor will be

$$\mathcal{P}_{54'} = \widehat{\mathcal{W}}_v \Delta\widehat{W}^{\mathrm{fl}}_{54'} = \widehat{\mathcal{W}}_v \Delta\widehat{H}_{54'} = \widehat{\mathcal{W}}_v\left(\widehat{H}_5 - \widehat{H}_{4'}\right)$$

and the enthalpy in point 5 has to be taken from the table given by the problem.

When reading the entropy at point 4' in the figure (2.2 kJ/kg·K), the temperature which will have the same entropy at 10 MPa will be T_5=716 K, and the enthalpy will be $\widehat{H}_5$ =835.62 kJ/kg, so

$$\wp_{54'} = \left(14.5\ \frac{\text{kg}}{\text{min}}\right)\left(835.62\ \frac{\text{kJ}}{\text{kg}} - 420\,\frac{\text{kJ}}{\text{kg}}\right) = 6026.49\ \frac{\text{kJ}}{\text{min}}$$



Question j. By following the same procedure as in question **e**

$$q_{15} = \widehat{\mathcal{W}}_v \Delta\widehat{H}_{15} = \left(14.5\ \frac{\text{kg}}{\text{min}}\right)\left(155.97\ \frac{\text{kJ}}{\text{kg}} - 835.62\,\frac{\text{kJ}}{\text{kg}}\right) = -9854.93\ \frac{\text{kJ}}{\text{min}}$$

SERIES 7

MIXING AND SEPARATION OPERATIONS

Problem Page

7.1. A mixture of 60% benzene and 40% toluene (by weight) with a flow rate of 1000 kg/h is subjected to a flash distillation at 760 mm Hg of pressure, achieving an evaporation of 60% of the feed.

a) Check that the mixture is ideal, knowing that the vapor pressures (in mm Hg) can be empirically correlated as

$$\log P_v = 6.906 - \frac{1211.0}{220.8 + T(°\mathrm{C})} \quad \textbf{for benzene}$$

$$\log P_v = 6.953 - \frac{1343.9}{219.4 + T(°\mathrm{C})} \quad \textbf{for toluene}$$

a) Determine the amounts of liquid and vapor produced, as well as their composition when distillation occurs at 91°C.

b) Calculate the distillation temperature if the same molar flow rate in both the liquid and vapor phases is desired.

Vapor-liquid equilibrium data for the system benzene+toluene at 760 mm Hg

Temperature (°C)	Molar fraction of benzene in the liquid	Molar fraction of benzene in vapor
83	0.860	0.940
86	0.729	0.873
89	0.611	0.798
95	0.403	0.626
98	0.312	0.526
101	0.229	0.418
103	0.176	0.340
109	0.035	0.078

Let A be benzene, B be toluene and $\mathcal{W}_0$ be the feed flow rate.

Question a. According to reference problem 0.17 the mole fractions, vapor pressures and total pressure in an ideal binary mixture will be exactly related by the expressions

$$\tilde{x}_A P_{vA} + (1 - \tilde{x}_A) P_{vB} = P_{tot} \quad \rightarrow \quad \tilde{x}_A = \frac{P_{tot} - P_{vB}}{P_{vA} - P_{vB}} \qquad [1]$$

$$\tilde{x}_A P_{vA} = \tilde{y}_A P_{tot} \quad \rightarrow \quad \tilde{y}_A = \frac{\tilde{x}_A P_{vA}}{P_{tot}} \qquad [2]$$

Thus, at each temperature the molar fractions of benzene in the vapor and in the liquid can be calculated with [1] and [2] and compared with those given in the statement of the problem.

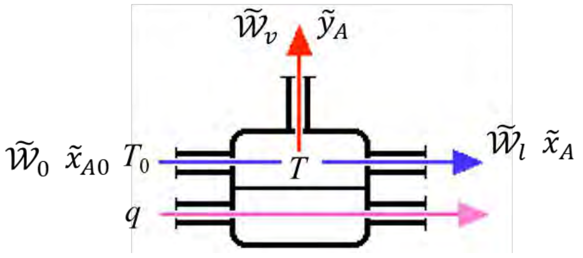
T (ºC)	P_{vA} (mm Hg)	P_{vB} (mm Hg)	$\frac{760-P_{vB}}{P_{vA}-P_{vB}}$	$\frac{\tilde{x}_A P_{vA}}{760}$
83	831.428	322.765	0.85957	0.940363
86	909.501	356.896	0.72946	0.872955
89	993.176	393.865	0.61092	0.798364
95	1178.405	476.989	0.40348	0.625616
98	1280.502	523.493	0.31242	0.526393
101	1389.290	573.529	0.22858	0.417856
103	1465.673	608.942	0.17631	0.340035
109	1714.263	725.662	0.03473	0.078345

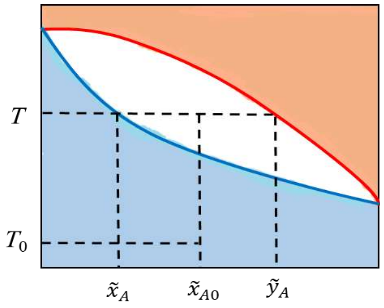
As shown, the calculated values practically coincide with the experimental ones.

Question b. During a flash distillation, heat (q) is communicated to a feed stream $\tilde{\mathcal{W}}_0$ at a temperature T_0 and with an initial composition $\tilde{x}_{A0}$, increasing its temperature to T and creating a metastable situation that splits into a vapor stream $\tilde{\mathcal{W}}_v$ with a mole fraction $\tilde{y}_A$ and a liquid stream $\tilde{\mathcal{W}}_l$ whose composition is $\tilde{x}_A$. In this way, the produced amounts of liquid and vapor can be calculated using the corresponding mass balances.

Total $$\tilde{\mathcal{W}}_0 = \tilde{\mathcal{W}}_l + \tilde{\mathcal{W}}_v \qquad [3]$$

Partial to benzene $$\tilde{x}_{A0}\tilde{\mathcal{W}}_0 = \tilde{\mathcal{W}}_l\tilde{x}_A + \tilde{\mathcal{W}}_v\,\tilde{y}_A \qquad [4]$$





But in order to apply them, unit conversion has to be carried out. The mole fraction of benzene is calculated from the mass fraction as

$$\tilde{x}_{A0} = \frac{n_{A0}}{n_{A0}+n_{B0}} = \frac{\frac{M_{A0}}{\mathfrak{M}_A}}{\frac{M_{A0}}{\mathfrak{M}_A}+\frac{M_{B0}}{\mathfrak{M}_B}} = \frac{\frac{\hat{x}_{A0}M_{tot}}{\mathfrak{M}_A}}{\frac{\hat{x}_{A0}M_{tot}}{\mathfrak{M}_A}+\frac{\hat{x}_{B0}M_{tot}}{\mathfrak{M}_B}} =$$

$$= \frac{\hat{x}_{A0}}{\hat{x}_{A0}+\frac{\mathfrak{M}_A}{\mathfrak{M}_B}(1-\hat{x}_{A0})} = \frac{0.6}{0.6+\frac{78.114\text{ g/mol-g}}{92.141\text{ g/mol-g}}(1-0.6)} = 0.6389$$

where 78.114 and 92.141 are the molecular weights of A and B, respectively, taken from appendix II. The molar flow rates of these substances in the feed will be

$$\widetilde{\mathcal{W}}_{A0} = \frac{\widehat{\mathcal{W}}_A}{\mathfrak{M}_A} = \frac{\hat{x}_{A0}\widehat{\mathcal{W}}_0}{\mathfrak{M}_A} = \frac{0.6\left(1000\ \frac{\text{kg}}{\text{h}} \times \frac{1000\ \text{g}}{1\ \text{kg}}\right)}{78.114\ \frac{\text{g}}{\text{mol-g}}} = 7681.1\ \frac{\text{mol-g}}{\text{h}}$$

$$\widetilde{\mathcal{W}}_{B0} = \frac{\widehat{\mathcal{W}}_B}{\mathfrak{M}_B} = \frac{\hat{x}_{B0}\widehat{\mathcal{W}}_0}{\mathfrak{M}_B} = \frac{0.4\left(1000\ \frac{\text{kg}}{\text{h}} \times \frac{1000\ \text{g}}{1\ \text{kg}}\right)}{92.141\ \frac{\text{g}}{\text{mol-g}}} = 4341.2\ \frac{\text{mol-g}}{\text{h}}$$

and by adding both, the total molar flow rate of the feed takes the value

$$\widetilde{\mathcal{W}}_0 = 7681.1 + 4341.2 = 12022.3\ \frac{\text{mol-g}}{\text{h}}$$

Finally, the mole fractions of A in the produced liquid and vapor streams have to be obtained from the equilibrium data. They could be interpolated graphically from the table in the statement of the problem, but since in question **a** it was shown the ideality of the mixture, it is easier to calculate them by employing equations [1] and [2]

T (ºC)	P_{vA} (mm Hg)	P_{vB} (mm Hg)	$\tilde{x}_A$ from [1]	$\tilde{y}_A$ from [2]
91	1052.20	420.17	0.5377	0.7444

The introduction of these values in balances [3] and [4] generates a system of linear equations

$$12022.3\ \frac{\text{mol-g}}{\text{h}} = \widetilde{\mathcal{W}}_l + \widetilde{\mathcal{W}}_v$$

$$0.6389\left(12022.3\ \frac{\text{mol-g}}{\text{h}}\right) = 0.5377\widetilde{\mathcal{W}}_l + 0.7444\widetilde{\mathcal{W}}_v$$

By obtaining $\widetilde{\mathcal{W}}_l$ from the first equation and substituting it in the second one, it results that

$$0.6389\left(12022.3\ \frac{\text{mol-g}}{\text{h}}\right) = 0.5377\left(12022.3\ \frac{\text{mol-g}}{\text{h}} - \widetilde{\mathcal{W}}_v\right) + 0.7444\widetilde{\mathcal{W}}_v$$

$$\widetilde{\mathcal{W}}_v = \frac{0.6389(12022.3) - 0.5377(12022.3)}{0.7444 - 0.5377} = 5886.1\,\frac{\text{mol-g}}{\text{h}}$$

and from the first equation

$$\widetilde{\mathcal{W}}_l = 12022.3 - 5886.1 = 6136.2 \frac{\text{mol-g}}{\text{h}}$$

Question c. Obviously, if both the liquid and the vapor have the same molar flow, this must be half of the liquid feed

$$\widetilde{\mathcal{W}}_v = \widetilde{\mathcal{W}}_l = \frac{\widetilde{\mathcal{W}}_0}{2}$$

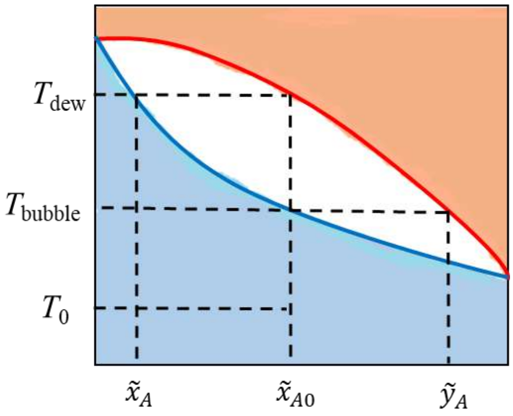
and therefore, the partial balance [4] will give

$$0.6389\widetilde{\mathcal{W}}_0 = \frac{\widetilde{\mathcal{W}}_0}{2}\tilde{x}_A + \frac{\widetilde{\mathcal{W}}_0}{2}\tilde{y}_A \quad \rightarrow \quad 0.6389 = 0.5(\tilde{x}_A + \tilde{y}_A) \qquad [5]$$

The working temperature will be that at which the molar fractions of A in the liquid and in the vapor meet this condition, and will be found by trial and error: choosing a temperature, calculating $\tilde{x}_A$ and $\tilde{y}_A$ (by graphical interpolation or by means of equations [1] and [2] as in the previous question) and introducing these molar fractions in expression [5]. If $0.6389 > 0.5(\tilde{x}_A + \tilde{y}_A)$ a lower temperature should be selected for the next trial and if $0.6389 < 0.5(\tilde{x}_A + \tilde{y}_A)$ a higher one should be chosen.

As a curiosity, all the values will be placed between the bubble point (which is that of the saturated liquid when a first vapor bubble appears) and the dew point (which is that of the saturated vapor when only one drop of liquid phase remains).

T (ºC)	P_{vA} (mm Hg)	P_{vB} (mm Hg)	$\tilde{x}_A$ with [1]	$\tilde{y}_A$ with [2]	[5]	Comments
88.28	972.569	384.725	0.63839	0.81694	0.72767	*T* bubble
90	1022.359	406.847	0.57375	0.77181	0.67278	*T* should be higher
91	1052.204	420.170	0.53767	0.74440	0.64103	*T* should be higher
94.58	1164.629	470.751	0.41685	0.63879	0.52782	*T* dew
92	1082.721	433.839	0.50265	0.71609	0.60937	*T* should be lower
91.5	1067.378	426.961	0.52003	0.73035	0.62519	*T* should be lower
91.068	1054.258	421.089	0.53526	0.74250	0.63888	OK



7.2. 100 kg of a binary mixture of water and 20% ethanol by weight will be treated by two stages of distillation and condensation at atmospheric pressure in order to obtain the maximum amount of final concentrate (at 75% ethanol by weight).

a) Schematically represent the process.

b) Estimate the performance of the operation (amount of concentrate produced per kg of feed).

c) Determine the amount of vapor and liquid produced in the first stage.

d) Calculate the energy cost of the different stages.

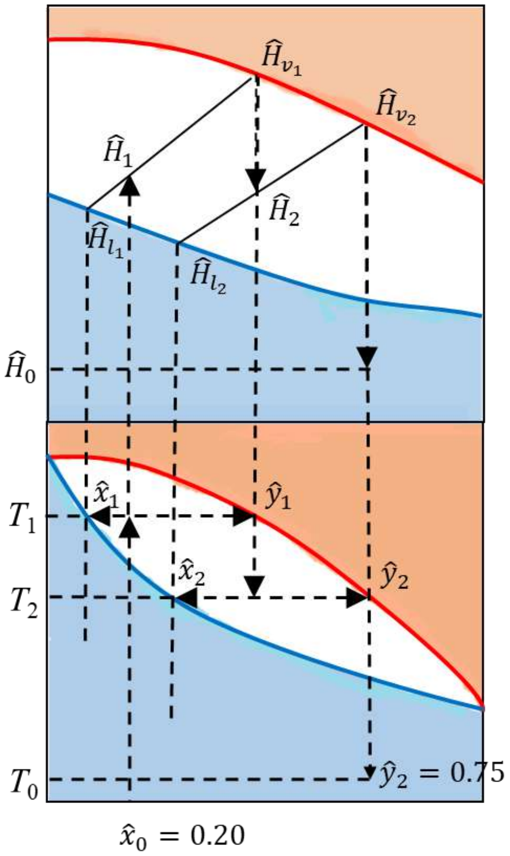
e) Find the heating time, if the heater consists of a chamber with an electrical resistance at 300ºC, embedded in a rolled ceramic tube of 3 cm in diameter and 1 m in length and its total heat transfer coefficient is of 9934 kcal/(h·m^2·ºC).

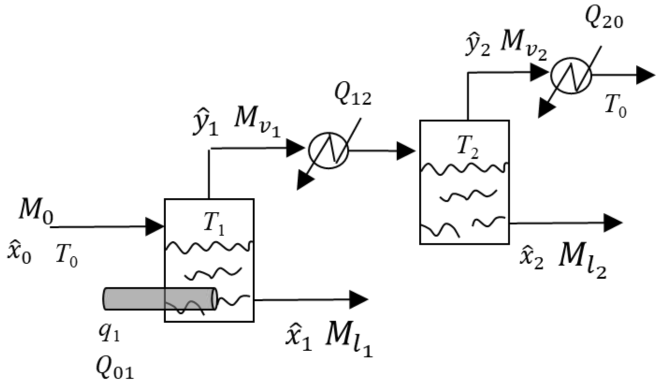
Equilibrium data for the ethanol-water system:

Temperature (ºC)	Liquid phase		Vapor phase	
	% etanol by weight	Enthalpy at saturation (kcal/kg)	% etanol by weight	Enthalpy at saturation (kcal/kg)
100	0	100	0	639
99	1	94.8	11	594
96	4	95	33	514
91	10	89	54	433
88	20	77.8	66	384
85	30	72	72	361
82	40	69.5	75	353
81.5	50	67.8	77	345
81	60	66.7	79	334
80	70	61.2	83	320
79	80	58.4	86	306
78.5	90	55.6	92	289
78	100	57.7	100	256

The enthalpy of liquids at room temperature (T_0) can be taken as 20 kcal/kg.

Question a. The process consists of charging the initial mass of the mixture (M_0 with an ethanol mass fraction of $\hat{x}_0$) at room temperature (T_0) in the first stage, heating it by means of a heat flow q_1 to a temperature T_1 which generates a metastable situation that splits into a liquid mass (M_{l_1} with an etanol mass fraction of $\hat{x}_1$) and a vapor one ($M_{v_1}$with an etanol mass fraction of $\hat{y}_1$). This mass of vapor is cooled to a temperature T_2 and introduced into the second stage, generating another metastable situation with the corresponding masses of liquid M_{l_2}(composition $\hat{x}_2$) and of vapor M_{v_2} (composition $\hat{y}_2$). Finally, M_{v_2} is cooled to room temperature. The statement of the problem indicates that $\hat{x}_0 = 0.20$ and $\hat{y}_2 = 0.75$.





Equilibrium data show that the vapor composition in the second stage (75%) corresponds to a liquid composition $\hat{x}_2 = 0.40$ and to a temperature T_2=82ºC.

Question b. The recovery percentage can be defined as

$$100\,\frac{\text{kg of alcohol in the vapor of the 2}^{\text{nd}}\text{ stage}}{\text{kg of alcohol in the feed}} = 100\,\frac{M_{v_2}\hat{y}_2}{M_0\hat{x}_0} \qquad [1]$$

where M_{v2} remains unknown and has to be obtained from the mass balances to the two stages.

Stage 1

Total $$M_0 = M_{l_1} + M_{v_1} \quad [2]$$

Partial to ethanol $$M_0\hat{x}_0 = M_{l_1}\hat{x}_1 + M_{v_1}\hat{y}_1 \quad [3]$$

Combination of [2] and [3]

$$M_0\hat{x}_0 = \left(M_0 - M_{v_1}\right)\hat{x}_1 + M_{v_1}\hat{y}_1$$

$$M_0(\hat{x}_0 - \hat{x}_1) = M_{v_1}(\hat{y}_1 - \hat{x}_1) \quad \rightarrow \quad M_{v_1} = M_0\frac{(\hat{x}_0 - \hat{x}_1)}{(\hat{y}_1 - \hat{x}_1)} \quad [4]$$

Stage 2

Total $$M_{v_1} = M_{l_2} + M_{v_2} \quad [5]$$

Partial to ethanol $$M_{v_1}\hat{y}_1 = M_{l_2}\hat{x}_2 + M_{v_2}\hat{y}_2 \quad [6]$$

Combination of [5] and [6]

$$M_{v_1}\hat{y}_1 = \left(M_{v_1} - M_{v_2}\right)\hat{x}_2 + M_{v_2}\hat{y}_2$$

$$M_{v_1}(\hat{y}_1 - \hat{x}_2) = M_{v_2}(\hat{y}_2 - \hat{x}_2) \rightarrow M_{v_2} = M_{v_1}\frac{(\hat{y}_1 - \hat{x}_2)}{(\hat{y}_2 - \hat{x}_2)} \quad [7]$$

From [4] and [7] it can be obtained

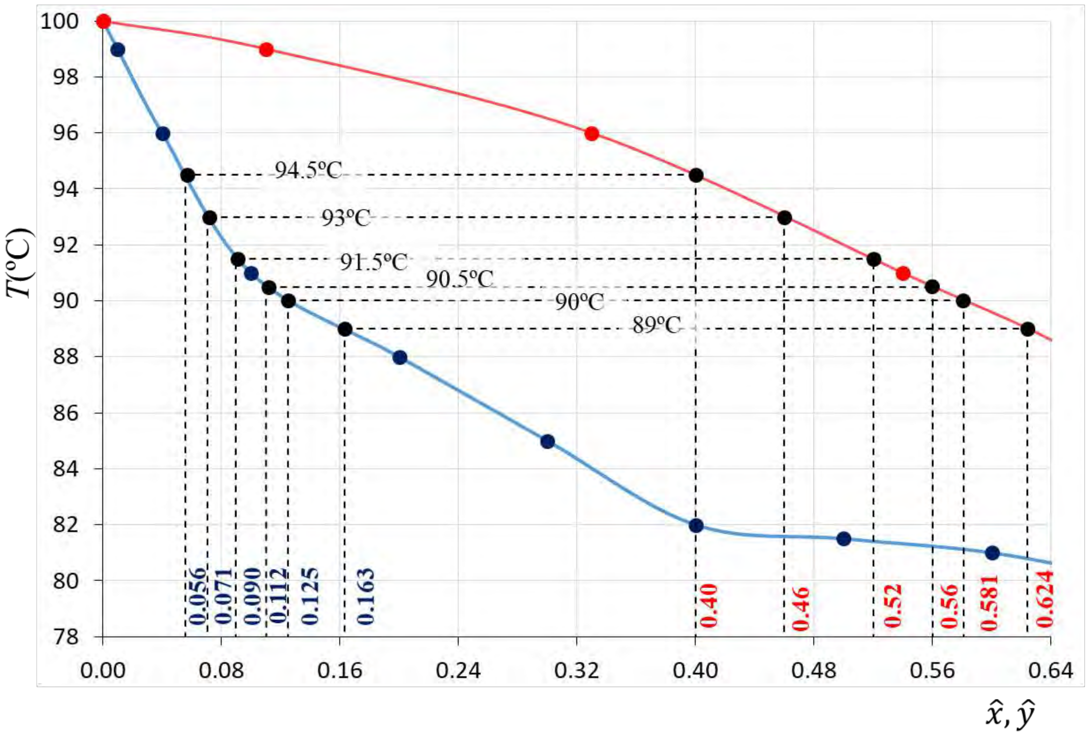
$$M_{v_2} = M_0\frac{(\hat{x}_0 - \hat{x}_1)}{(\hat{y}_1 - \hat{x}_1)}\frac{(\hat{y}_1 - \hat{x}_2)}{(\hat{y}_2 - \hat{x}_2)} \quad [8]$$

$\hat{x}_1$ and $\hat{y}_1$ are unknown as well, but since the statement of the problem says that the amount of vapor produced in the second stage is maximum, these concentrations will be those that meet this condition or what is the same, that the function

$$\frac{(\hat{y}_1 - \hat{x}_1)}{(\hat{x}_0 - \hat{x}_1)}\frac{(\hat{y}_2 - \hat{x}_2)}{(\hat{y}_1 - \hat{x}_2)} = \frac{(\hat{y}_1 - \hat{x}_1)}{(0.20 - \hat{x}_1)}\frac{(0.75 - 0.40)}{(\hat{y}_1 - 0.40)} \quad [9]$$

take its minimum value. This calculation will be done by trial and error: chosing several T_1 values, interpolating $\hat{x}_1$ and $\hat{y}_1$, introducing these mass fractions in expression [9] and choosing that which minimize it. Selected temperatures will lie between the one that produces a liquid of composition $\hat{x}_1 = 0.2$ and that which generates a vapor of composition $\hat{y}_1 = 0.4$, because in both cases the function [9] adopts an infinite value.

T_1(°C)	$\hat{x}_1$	$\hat{y}_1$	Value of [9]	Comments
88	0.2	0.66	∞	Mass fractions read in the table of the statement
89	0.163	0.624	19.468	Mass fractions interpolated in the graph
90	0.125	0.581	11.757	Mass fractions interpolated in the graph
90.5	0.112	0.56	11.136	Mass fractions interpolated in the graph
91	0.10	0.54	11.00	Mass fractions read in the table of the statement
91.5	0.091	0.52	11.479	Mass fractions interpolated in the graph
93	0.071	0.46	17.590	Mass fractions interpolated in the graph
94.5	0.056	0.40	∞	Mass fractions interpolated in the graph



The mínimum value of function [9] is 11.00 and occurs at T=91°C, so equation [8] gives

$$M_{v_2} = \frac{M_0}{11} = \frac{100\ \text{kg}}{11} = 9.09\ \text{kg}$$

and introducing this amount of vapor in equation [1] the recovery percentage will be obtained

$$100\frac{M_{v_2}\hat{y}_2}{M_0\hat{x}_0} = 100\frac{(9.09\ \text{kg})(0.75)}{(100\ \text{kg})(0.20)} = 34.1\%$$

Question c. From equation [4]

$$M_{v_1} = M_0\frac{(\hat{x}_0 - \hat{x}_1)}{(\hat{y}_1 - \hat{x}_1)} = (100\ \text{kg})\frac{0.2 - 0.1}{0.54 - 0.1} = 22.73\ \text{kg}$$

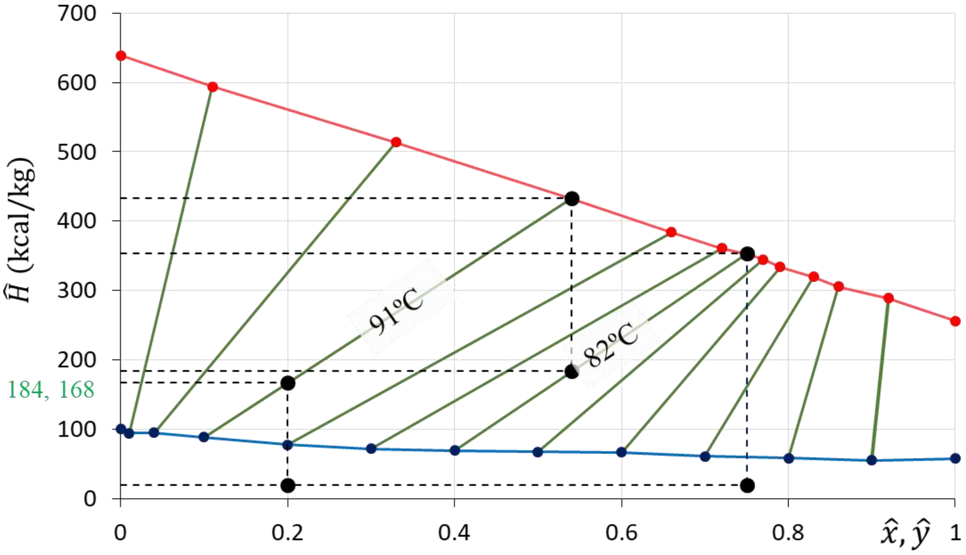
and from [2]

$$M_{l_1} = M_0 - M_{v_1} = 100 - 22.73 = 77.27 \text{ kg}$$

Question d. The energy cost will consist of:

- Heating of M_0 from T_0 (where the specific enthalpy is $\widehat{H}_0$) to T_1 (where the enthalpy is $\widehat{H}_1$).
- Phase separation, each one with a different specific enthalpy.
- Cooling of the vapor M_{v_1} from T_1 to T_2 (where the specific enthalpy is $\widehat{H}_2$).
- Phase separation, each one with a different specific enthalpy.
- Cooling of the vapor M_{v_2} from T_2 to temperature T_0 (where the specific enthalpy is again $\widehat{H}_0$).

According to the statement of the problem, $\widehat{H}_0$ =20 kcal/kg and according to the equilibrium data table, $\widehat{H}_{v_1}$= 433 kcal/kg and $\widehat{H}_{v_2}$=353 kcal/kg. $\widehat{H}_1$ and $\widehat{H}_2$ have to be interpolated from the *H-xy* diagram, taking values of 168 and 184 kcal/kg, respectively.



Hence

$$Q_{01} = M_0\left(\widehat{H}_1 - \widehat{H}_0\right) = 100(168 - 20) = 14800 \text{ kcal}$$

$$Q_{12} = M_{v_1}\left(\widehat{H}_2 - \widehat{H}_{v_1}\right) = 22.73(184 - 433) = -5659.77 \text{ kcal}$$

$$Q_{20} = M_{v_2}\left(\widehat{H}_0 - \widehat{H}_{v_2}\right) = 9.09(20 - 353) = -3026.97 \text{ kcal}$$

Question e. Regarding the heating time, it will be the quotient between the 14800 kcal calculated (required heat) and the kcal/h supplied by the heater (heat flow), which, according to reference problem 0.12 are calculated as

$$q_1 = k_T A \Delta T$$

where the area of the cylinder 3 cm in diameter and 1 m in length is

$$A = \pi d L = \pi\left(3\ \mathrm{cm} \times \frac{1\ \mathrm{m}}{100\ \mathrm{cm}}\right)(1\ \mathrm{m}) = 0.094\ \mathrm{m}^2$$

and the temperature difference between stage 1 (which operates at 91ºC) and the electrical resistance (which is at 300ºC) will be

$$\Delta T = 300℃ - 91℃ = 209℃$$

Therefore

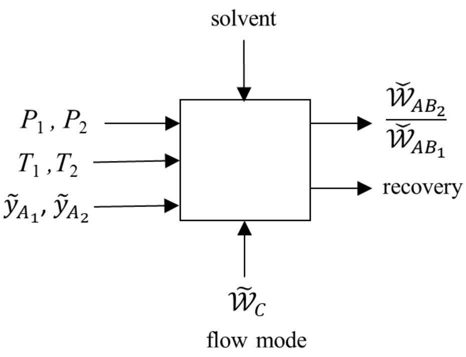
$$q_1 = \left(9934 \frac{\mathrm{kcal}}{\mathrm{h} \cdot \mathrm{m}^2 \cdot ℃}\right)(0.094\ \mathrm{m}^2)(209℃) = 195163\ \frac{\mathrm{kcal}}{\mathrm{h}}$$

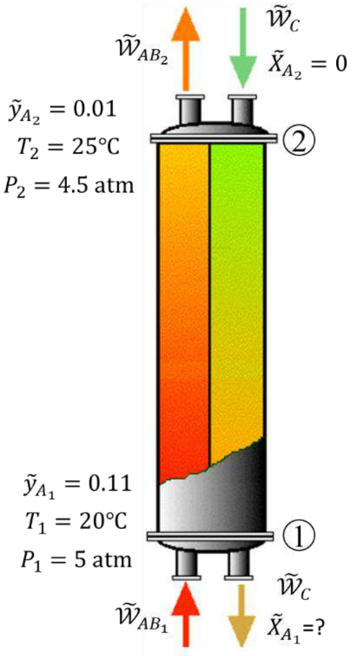
and

$$t = \frac{Q_{01}}{q_1} = \frac{14800\ \mathrm{kcal}}{195163\ \frac{\mathrm{kcal}}{\mathrm{h}}} = 0.076\ \mathrm{h} \quad \rightarrow \quad 0.076\ \mathrm{h} \times \frac{60\ \mathrm{min}}{1\ \mathrm{h}} = 4.56\ \mathrm{min}$$

7.3. It is required to separate carbon dioxide from a gaseous mixture containing 89% inert substances (by volume) through absorption with a counterflow diethanolamine solution. The gases enter the absorption column at 5 atm and 20°C and leave it at 4.5 atm and 25°C, with a 1% CO_2 (by volume). Draw the information flow diagram and the flowchart. By assuming that only CO_2 is absorbed, that there are no equilibrium restrictions, and that the gas is ideal, calculate the ratio between the volume gas flow rate at the outlet and the flow rate at the inlet, and the percent recovery.

For the sake of clarity, the substance being transferred will be called A (CO_2), the inerts of the gaseous stream will be called B, the mixture of CO_2 and gaseous inerts will be denoted as AB and the liquid diethanolamine as C.





If the gas is ideal, the ratio between the volumetric flows can be calculated from the molar flows and the molar volumes (by means of their equation of state) as

$$\frac{\tilde{W}_{AB_2}}{\tilde{W}_{AB_1}} = \frac{\tilde{W}_{AB_2}\tilde{V}_2}{\tilde{W}_{AB_1}\tilde{V}_1} = \frac{\tilde{W}_{AB_2}\left(\frac{RT_2}{P_2}\right)}{\tilde{W}_{AB_1}\left(\frac{RT_1}{P_1}\right)} = \frac{\tilde{W}_{AB_2}T_2P_1}{\tilde{W}_{AB_1}T_1P_2}$$

where T_1 and T_2 are the absolute temperatures at points 1 and 2, respectively, which according to appendix I will be

$$T_1(\mathrm{K}) = 20°\mathrm{C} + 273 = 293\ \mathrm{K}$$

$$T_2(\mathrm{K}) = 25°\mathrm{C} + 273 = 298\ \mathrm{K}$$

The molar flow rate of the gaseous mixture varies throughout the column since moles of A are lost by transference, but the composition can be expressed as a function of the molar flow rate of gaseous inerts, which remains constant along the process ($\widetilde{W}_{B_1} = \widetilde{W}_{B_2} = \widetilde{W}_B$), allowing a simpler direct relationship between flow rates and compositions

$$\text{total flow} = \text{flow of B} + \text{flow of A} = \text{flow of B}\left(1+\frac{\text{flow of A}}{\text{flow of B}}\right) =$$

$$=\text{flow of B}\left(1+\frac{\text{moles of A}}{\text{moles of B}}\right)=\text{flow of B (1+mole ratio of A in the gas)}$$

and so

$$\frac{\widetilde{W}_{AB_2}}{\widetilde{W}_{AB_1}} = \frac{\widetilde{W}_B(1+\tilde{Y}_{A_2})T_2P_1}{\widetilde{W}_B(1+\tilde{Y}_{A_1})T_1P_2} = \frac{(1+\tilde{Y}_{A_2})T_2P_1}{(1+\tilde{Y}_{A_1})T_1P_2} \qquad [1]$$

On the other hand, the molar ratios of A can be calculated from the mole fractions of A (section e of reference problem 0.14) which are equal to the volume fractions in the case of ideal gas: 1–0.89 =0.11 at the entrance of the column and 0.01 at the exit.

$$\tilde{Y}_{A_1} = \frac{\tilde{y}_{A_1}}{1-\tilde{y}_{A_1}} = \frac{0.11}{1-0.11} = 0.1236$$

$$\tilde{Y}_{A_2} = \frac{\tilde{y}_{A_2}}{1-\tilde{y}_{A_2}} = \frac{0.01}{1-0.01} = 0.0101$$

By introducing all these data in equation [1] it results that

$$\frac{\widetilde{W}_{AB_2}}{\widetilde{W}_{AB_1}} = \frac{(1+0.0101)(298\text{ K})(5\text{ atm})}{(1+0.1236)(293\text{ K})(4.5\text{ atm})} = 1.016$$

Regarding the recovery percentage, it can also be defined as a function of the mole ratios of A in the liquid stream and in the gaseous stream as

$$100\times\frac{\text{A in the liquid that leaves the column}}{A\text{ in the gas that enters the column}} = 100\times\frac{\widetilde{W}_C\tilde{X}_{A_1}}{\widetilde{W}_B\tilde{Y}_{A_1}}$$

expression in which the numerator has to be calculated from the mass balance to compound A by employing the flow of inerts and the mole ratios

$$\begin{bmatrix}\text{A in the}\\\text{entering gas}\end{bmatrix}+\begin{bmatrix}\text{A in the}\\\text{entering liquid}\end{bmatrix}=\begin{bmatrix}\text{A in the}\\\text{leaving gas}\end{bmatrix}+\begin{bmatrix}\text{A in the}\\\text{leaving liquid}\end{bmatrix}$$

$$\widetilde{W}_B\tilde{Y}_{A_1} + \widetilde{W}_C\tilde{X}_{A_2} = \widetilde{W}_B\tilde{Y}_{A_2} + \widetilde{W}_C\tilde{X}_{A_1}$$

Since no carbon dioxide is present in the diethanolamine which enters the absorption column ($\tilde{X}_{A_2} = 0$)

$$\tilde{\mathcal{W}}_C \tilde{X}_{A_1} = \tilde{\mathcal{W}}_B \tilde{Y}_{A_1} - \tilde{\mathcal{W}}_B \tilde{Y}_{A_2} = \tilde{\mathcal{W}}_B \left(\tilde{Y}_{A_1} - \tilde{Y}_{A_2} \right)$$

$$100 \times \frac{\tilde{\mathcal{W}}_B \left(\tilde{Y}_{A_1} - \tilde{Y}_{A_2} \right)}{\tilde{\mathcal{W}}_B \tilde{Y}_{A_1}} = 100 \times \frac{\tilde{Y}_{A_1} - \tilde{Y}_{A_2}}{\tilde{Y}_{A_1}} = 100 \times \frac{0.1236 - 0.0101}{0.1236} = 91.83\%$$

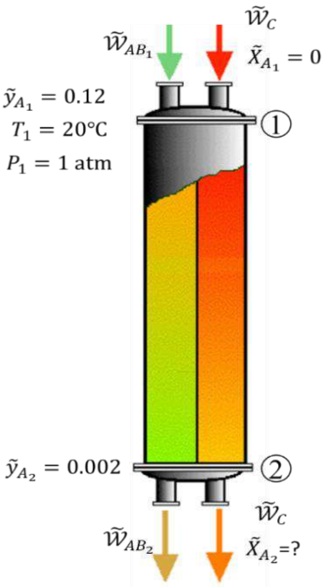
7.4. In a thermal power station it is desired to purify by absorption a residual stream of air at 1 atm which contains a 12% SO_2 (by volume). The flow rate of this stream is 28 m^3/h, the absorption tower operates in parallel flow and the treated stream should not contain more than 0.2% SO_2 (by volume). Assuming the ideal gas behaviour, a constant density of liquid water of 1000 g/L and no humidification of air in presence of water:

a) What will be the SO_2 percentage in the water leaving the tower if the gas stream enters at 20ºC? What is the volumetric flow rate of water necessary to perform the operation?

b) What will be the SO_2 percentage in the water leaving the tower and the volumetric flow rate of this water if the gas stream enters at 40ºC?

Equilibrium data

Parts by weight of SO_2 per 100 parts by weight of H_2O	Partial pressure of SO_2 (mm Hg) in the air	
	20ºC	40ºC
10	698	-
7.5	517	-
5.0	336	665
2.5	161	322
1.5	92	186
1.0	59	121
0.7	39	87
0.5	26	57
0.3	14.1	-
0.2	8.5	-
0.15	5.8	12.9
0.10	3.2	7.5
0.05	1.2	2.8
0.02	0.5	0.8



Let A be the substance being transferred (SO_2), B be the air without SO_2, AB be the mixture of SO_2 with air and C be the liquid water. Because the characteristics of the problem, it will be convenient to work with mole ratios instead of with molar fractions (equal to volume ones when dealing with ideal gases). Therefore, the equilibrium data supplied by the problem have to be converted to these mole ratios as well:

$$\tilde{X}_A = \frac{n_A}{n_C} = \frac{\left(\frac{M_A}{\mathfrak{W}_A}\right)}{\left(\frac{M_C}{\mathfrak{W}_C}\right)}$$

$$\tilde{Y}_A = \frac{n_A}{n_B} = \frac{P_A}{P_B} = \frac{P_A}{P_{tot} - P_A}$$

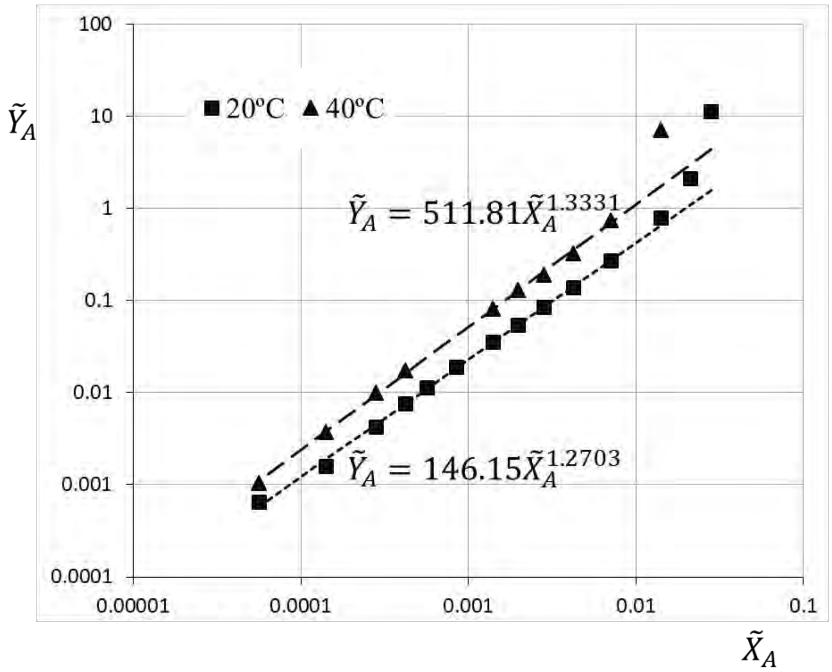
By taking M_C=100 g, P_{tot}=760 mm Hg, and from appendix II $\mathfrak{W}_A$=64.07 g/mol-g and $\mathfrak{W}_C$=18.015 g/mol-g, it results that

$\tilde{X}_A$	$\tilde{Y}_A(20°C)$	$\tilde{Y}_A(40°C)$
0.02811	11.25806	-
0.02108	2.127572	-
0.01406	0.792452	7
0.00703	0.268781	0.735159
0.00422	0.137724	0.324041
0.00281	0.084165	0.189358
0.00197	0.054091	0.129271
0.00140	0.035422	0.081081
0.00084	0.018903	-
0.00056	0.011311	-
0.00042	0.007690	0.017266
0.00028	0.004228	0.009966
0.00014	0.001581	0.003698
$5.6235\cdot10^{-5}$	0.000658	0.001054

Data that can be fitted to empirical expressions when $\tilde{X}_A < 0.014$ (correlation coefficients of 0.999)

$$\tilde{Y}_A(20°C) = 146.15\tilde{X}_A^{1.2703} \quad [1]$$

$$\tilde{Y}_A(40°C) = 511.81\tilde{X}_A^{1.3331} \quad [2]$$



Question a. According to the mass balance to substance A by employing the flow of inerts and the mole ratios

$$\begin{bmatrix}\text{A in the}\\\text{entering gas}\end{bmatrix}+\begin{bmatrix}\text{A in the}\\\text{entering liquid}\end{bmatrix}=\begin{bmatrix}\text{A in the}\\\text{leaving gas}\end{bmatrix}+\begin{bmatrix}\text{A in the}\\\text{leaving liquid}\end{bmatrix}$$

$$\tilde{W}_B\tilde{Y}_{A_1}+\tilde{W}_C\tilde{X}_{A_1}=\tilde{W}_B\tilde{Y}_{A_2}+\tilde{W}_C\tilde{X}_{A_2} \qquad [3]$$

Being the molar flow rate of B calculable from that of the AB mixture in point 1 as

$$\tilde{W}_B=\tilde{W}_{AB_1}-\tilde{W}_{A_1}=\tilde{W}_{AB_1}-\tilde{y}_{A_1}\tilde{W}_{AB_1}=\tilde{W}_{AB_1}\left(1-\tilde{y}_{A_1}\right)$$

And the molar flow rate of AB is related to the volume flow rate by

$$\tilde{W}_{AB_1}=\frac{\breve{W}_{AB_1}}{\tilde{V}_{AB_1}}=\frac{P_1\breve{W}_{AB_1}}{RT_1}$$

Having in mind that T_1(K) =T_1(ºC) + 273 = 20ºC+273=293 K, that 1 m^3 =1000 L, and that molar fractions in ideal gases are equal to volume fractions (as mentioned above)

$$\tilde{W}_{AB_1}=\frac{\left(28\cdot 10^3\,\frac{\text{L}}{\text{h}}\right)(1\text{ atm})}{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(293\text{ K})}=1165.4\;\frac{\text{mol-g}}{\text{h}}$$

$$\tilde{W}_B=\left(1165.4\;\frac{\text{mol-g}}{\text{h}}\right)(1-0.12)=1025.55\;\frac{\text{mol-g}}{\text{h}}$$

On the other hand, according to equations of reference problem 0.13, molar ratios can be estimated from the molar fractions by means of

$$\tilde{Y}_A=\frac{\tilde{y}_A}{1-\tilde{y}_A}$$

Thus,

$$\tilde{Y}_{A_1}=\frac{0.12}{1-0.12}=0.1363$$

$$\tilde{Y}_{A_2}=\frac{0.002}{1-0.002}=0.002004$$

and by knowing that there is no SO$_2$ in the liquid that enters at point 1 ($\tilde{X}_{A_1}=0$), equation [3] will allow the calculation of the water flow as

$$\tilde{W}_C=\frac{\tilde{W}_B}{\tilde{X}_{A_2}}\left(\tilde{Y}_{A_1}-\tilde{Y}_{A_2}\right) \qquad [4]$$

The main shortcoming of expression [4] is that the SO_2 concentration in the liquid leaving the column is unknown. In the absence of such datum, it is assumed that the apparatus works with 100% efficiency, reaching equilibrium at point 2 (which is equivalent to calculating the maximum required water flow). Equation [1] indicates that the liquid mole ratio in equilibrium with a gas mole ratio of 0.002004 is

$$0.002004 = 146.15\tilde{X}_{A_2}^{1.2703} \quad \rightarrow \tilde{X}_{A_2} = 0.000148$$

obtaining that

$$\tilde{\mathcal{W}}_C = \frac{\tilde{\mathcal{W}}_B}{\tilde{X}_{A2}}\left(\tilde{Y}_{A_1} - \tilde{Y}_{A_2}\right) = \frac{\left(1025.55\ \frac{\text{mol-g}}{\text{h}}\right)}{0.000148}(0.1363 - 0.002004) = 930.6 \cdot 10^3\,\frac{\text{mol-g}}{\text{h}}$$

Finally, if the density of 1000 g/L is taken for liquid water, its volumetric flow will be

$$\breve{\mathcal{W}}_C = \frac{\mathfrak{M}_C\tilde{\mathcal{W}}_C}{\hat{\rho}_C} = \frac{\left(18.015\ \frac{\text{g}}{\text{mol-g}}\right)\left(930.6 \cdot 10^3\,\frac{\text{mol-g}}{\text{h}}\right)}{\left(1000\ \frac{\text{g}}{\text{L}}\right)} = 16764.8\ \frac{\text{L}}{\text{h}}$$

Question b. At 40ºC (313 K), the procedure will be the same as in the previous question, but the equilibrium composition and the air flow will vary.

$$\tilde{\mathcal{W}}_{AB_1} = \frac{P_1\breve{\mathcal{W}}_{AB_1}}{RT_1} = \frac{\left(28 \cdot 10^3\,\frac{\text{L}}{\text{h}}\right)(1\ \text{atm})}{\left(0.082\,\frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol-g}}\right)(313\ \text{K})} = 1090.9\ \frac{\text{mol-g}}{\text{h}}$$

$$\tilde{\mathcal{W}}_B = \left(1090.9\ \frac{\text{mol-g}}{\text{h}}\right)(1 - 0.12) = 960\ \frac{\text{mol-g}}{\text{h}}$$

Equation [2] gives

$$0.002004 = 511.81\tilde{X}_{A_2}^{1.3331} \quad \rightarrow \tilde{X}_{A_2} = 8.788 \cdot 10^{-5}$$

and equation [4]

$$\tilde{\mathcal{W}}_C = \frac{\tilde{\mathcal{W}}_B}{\tilde{X}_{A_2}}\left(\tilde{Y}_{A_1} - \tilde{Y}_{A_2}\right) = \frac{\left(960\ \frac{\text{mol-g}}{\text{h}}\right)}{8.788 \cdot 10^{-5}}(0.1363 - 0.002004) = 1467 \cdot 10^3\,\frac{\text{mol-g}}{\text{h}}$$

being the volume flow rate of

$$\breve{\mathcal{W}}_C = \frac{\mathfrak{M}_C\tilde{\mathcal{W}}_C}{\hat{\rho}_C} = \frac{\left(18.015\ \frac{\text{g}}{\text{mol-g}}\right)\left(1467 \cdot 10^3\,\frac{\text{mol-g}}{\text{h}}\right)}{\left(1000\ \frac{\text{g}}{\text{L}}\right)} = 26428\ \frac{\text{L}}{\text{h}}$$

7.5. A residual gaseous stream of 4.4·10³ Nm³/h at 25°C and 1 atm contains a mole fraction of 0.009 SO_2, which has to be reduced by 90% by absorption with water. The Henry's law constant is 0.8 atm. Estimate the maximum molar flow rate of water required in both counterflow and parallel flow modes. Assume no humidification of the gas in presence of water.

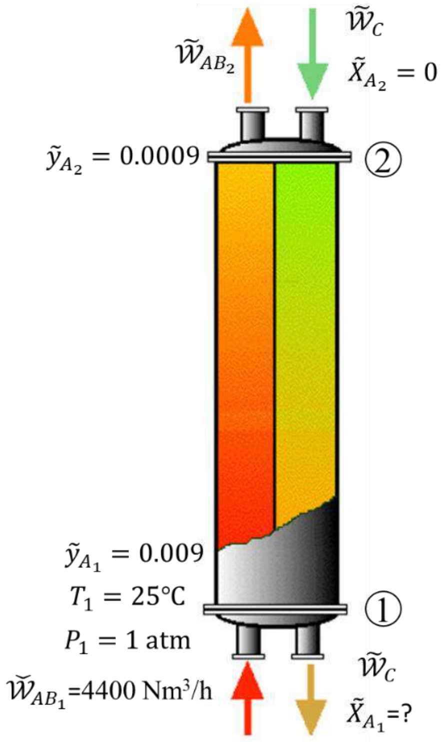
Let A be the substance that is transferred (SO_2), B be the gas without SO_2 (inerts), AB be the mixture of SO_2 and gas and C be the liquid water: the mass balance to compound A employing the flow of inerts and the mole ratios during a counterflow operation will be

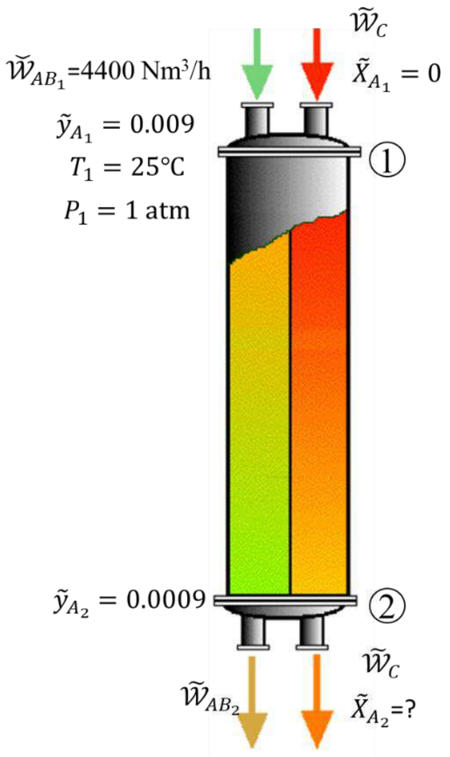
$$\left[\begin{array}{c}\text{A in the}\\ \text{entering gas}\end{array}\right]+\left[\begin{array}{c}\text{A in the}\\ \text{entering liquid}\end{array}\right]=\left[\begin{array}{c}\text{A in the}\\ \text{leaving gas}\end{array}\right]+\left[\begin{array}{c}\text{A in the}\\ \text{leaving liquid}\end{array}\right]$$

$$\tilde{W}_B\tilde{Y}_{A_1}+\tilde{W}_C\tilde{X}_{A_2}=\tilde{W}_B\tilde{Y}_{A_2}+\tilde{W}_C\tilde{X}_{A_1} \qquad [1]$$

and in parallel flow mode

$$\tilde{W}_B\tilde{Y}_{A_1}+\tilde{W}_C\tilde{X}_{A_1}=\tilde{W}_B\tilde{Y}_{A_2}+\tilde{W}_C\tilde{X}_{A_2} \qquad [2]$$





where the molar flow rate of gaseous inerts (which does not vary along the column in any case, $\tilde{W}_{B_1} = \tilde{W}_{B_2} = \tilde{W}_B$) can be calculated from that of the AB mixture at point 1 as

$$\tilde{W}_B = \tilde{W}_{AB_1} - \tilde{W}_{A_1} = \tilde{W}_{AB_1} - \tilde{y}_{A_1}\tilde{W}_{AB_1} = \tilde{W}_{AB_1}\left(1 - \tilde{y}_{A_1}\right)$$

and the molar flow of the gaseous mixture is related to the volumetric flow by means of

$$\tilde{W}_{AB_1} = \frac{W_{AB_1}}{\tilde{V}_{AB1}} = \frac{P_1 W_{AB_1}}{RT_1}$$

being

$$T_1(\mathrm{K}) = 25°\mathrm{C} + 273 = 293\ \mathrm{K}$$

$$W_{AB_1} = 4400\ \frac{\mathrm{m}^3}{\mathrm{h}} \times \frac{1000\ \mathrm{L}}{1\ \mathrm{m}^3} = 4.4 \cdot 10^6\,\frac{\mathrm{L}}{\mathrm{h}}$$

and therefore

$$\tilde{W}_{AB_1} = \left(4.4 \cdot 10^6\,\frac{\mathrm{L}}{\mathrm{h}}\right)\frac{1\ \mathrm{atm}}{\left(0.082\,\frac{\mathrm{atm}\cdot\mathrm{L}}{\mathrm{K}\cdot\mathrm{mol\text{-}g}}\right)(298\ \mathrm{K})} = 180062\ \frac{\mathrm{mol\text{-}g}}{\mathrm{h}}$$

$$\tilde{W}_B = 180062\ \frac{\mathrm{mol\text{-}g}}{\mathrm{h}}(1 - 0.009) = 178441\,\frac{\mathrm{mol\text{-}g}}{\mathrm{h}}$$

On the other hand, according to reference problem 0.14, mole ratios can be calculated from mole fractions as

$$\tilde{Y}_A = \frac{\tilde{y}_A}{1 - \tilde{y}_A}$$

and taking into account that the molar fraction at the entrance is of 0.009, and that at the exit is a 90% lower

$$\tilde{y}_{A_1} = 0.009 \qquad \rightarrow \qquad \tilde{Y}_{A_1} = \frac{0.009}{1 - 0.009} = 0.009082$$

$$\tilde{y}_{A_2} = 0.009(1 - 0.9) = 0.0009 \qquad \rightarrow \qquad \tilde{Y}_{A_2} = \frac{0.0009}{1 - 0.0009} = 0.000901$$

In counterflow mode, $\tilde{X}_{A_2} = 0$, and in parallel flow, $\tilde{X}_{A_1} = 0$, because there is no SO_2 in the water that enters the column. Thus, equation [1] gives

$$\tilde{W}_C = \frac{\tilde{W}_B}{\tilde{X}_{A_1}}\left(\tilde{Y}_{A_1} - \tilde{Y}_{A_2}\right) \qquad [3]$$

and equation [2]

$$\tilde{\mathcal{W}}_C = \frac{\tilde{\mathcal{W}}_B}{\tilde{X}_{A2}}\left(\tilde{Y}_{A_1} - \tilde{Y}_{A_2}\right) \qquad [4]$$

In both cases, the mole ratio of sulfur dioxide in the water leaving the column is unknown, but since the statement of the problem refers to the maximum amount of liquid, it can be assumed that the apparatus reaches the maximum possible efficiency, i.e., the concentrations of equilibrium, which are given by Henry's law (section c of reference problem 0.17)

$$P_A = \mathcal{H}\tilde{x}_A \quad \rightarrow \quad \tilde{y}_A P = \mathcal{H}\tilde{x}_A \quad \rightarrow \quad \tilde{y}_A = \frac{\mathcal{H}}{P}\tilde{x}_A = \frac{0.8\ \text{atm}}{1\ \text{atm}}\tilde{x}_A = 0.8\tilde{x}_A$$

and by introducing mole ratios instead of mole fractions, this expression becomes

$$\frac{\tilde{Y}_A}{1+\tilde{Y}_A} = 0.8\frac{\tilde{X}_A}{1+\tilde{X}_A}$$

When operating in counterfow, $\tilde{X}_{A_1}$ is in equilibrium with $\tilde{Y}_{A_1}$

$$\frac{\tilde{Y}_{A_1}}{1+\tilde{Y}_{A_1}} = 0.8\frac{\tilde{X}_{A_1}}{1+\tilde{X}_{A_1}}$$

$$\frac{0.009082}{1+0.009082} = 0.8\frac{\tilde{X}_{A_1}}{1+\tilde{X}_{A_1}} \quad \rightarrow \quad \tilde{X}_{A_1} = 0.01125\left(1+\tilde{X}_{A_1}\right) \quad \rightarrow \quad \tilde{X}_{A_1} = 0.011378$$

and therefore, the water flow calculated by equation [3] will be

$$\tilde{\mathcal{W}}_C = \left(178441\frac{\text{mol-g}}{\text{h}}\right)\frac{(0.009082 - 0.000901)}{(0.011378)} = 128302.5\frac{\text{mol-g}}{\text{h}}$$

When operating in parallel flow, $\tilde{X}_{A_2}$ is in equilibrium with $\tilde{Y}_{A_2}$

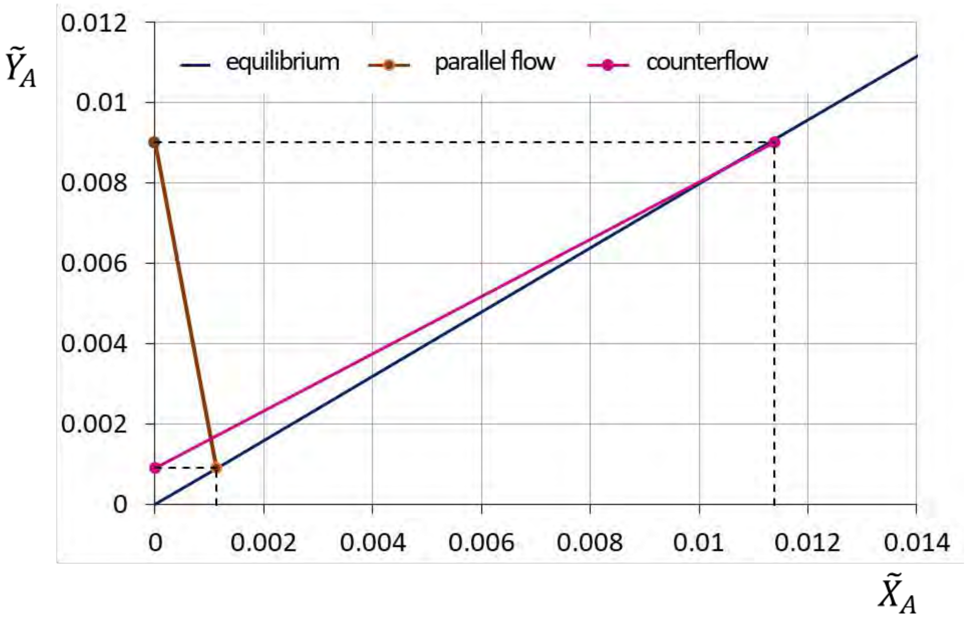
$$\frac{\tilde{Y}_{A_2}}{1+\tilde{Y}_{A_2}} = 0.8\frac{\tilde{X}_{A_2}}{1+\tilde{X}_{A_2}}$$

$$\frac{0.000901}{1+0.000901} = 0.8\frac{\tilde{X}_{A_2}}{1+\tilde{X}_{A_2}} \quad \rightarrow \quad \tilde{X}_{A_2} = 0.001125\left(1+\tilde{X}_{A_2}\right) \quad \rightarrow \quad \tilde{X}_{A2} = 0.001127$$

and the water flow calculated by equation [4] will be

$$\widetilde{W}_C = \left(178441\,\frac{\text{mol-g}}{\text{h}}\right)\frac{(0.009082 - 0.000901)}{(0.001127)} = 1295320\,\frac{\text{mol-g}}{\text{h}}$$

Notice that the amount of water in the parallel flow mode is almost ten times higher than the amount in the counterflow one, highlighting the greater efficiency of the second mode of contact.



7.6. A valuable substance A, present in a waste effluent (which is a binary gaseous mixture of A with an inert diluent B), can be selectively separated by a liquid non-volatile absorbent C in which B is insoluble. To carry out the operation, a mass transfer column and the following data are available:

- **Flow rate of the mixture to be treated: 1000 kg/h; composition: 10% A (by weight).**
- **Flow rate of the pure absorbent: 320 kg/h.**
- **Objective: recovering 95% of A present in the mixture.**
- **The equilibrium conditions of the system at the operating temperature are given by $\widetilde{Y}_A^{eq} = \widetilde{X}_A^{eq}/5$, where $\widetilde{Y}$ are the mole ratios in the gaseous mixture and $\widetilde{X}$ those in the absorbent phase.**
- **The mass transfer conditions (moles of component A transferred per unit time) at the operating temperature can be represented by the formula $\mathrm{d}\mathcal{N}_A = \mathrm{k}_{M(g)}\left(\widetilde{Y}_A - \widetilde{Y}_A^{eq}\right)\mathrm{d}A$. It is a function of the difference at each point in the column between the global composition of the effluent ($\widetilde{Y}_A$) and that at the interphase, assumed to be that of equilibrium ($\widetilde{Y}_A^{eq}$) with the global composition $\widetilde{X}_A$ of the liquid phase (i.e., all the resistance to the mass transfer is assumed to be located in the gaseous phase). $\mathrm{k}_{M(g)}$ is a mass transport coefficient whose value ($8\cdot 10^{-3}$ mol-g/cm^{2}s) remains practically constant through the column.**
- **Molar masses: A (100), B (120), C (80).**
- **For the purposes of the problem, the physical properties of both streams do not vary during the operation, and they can be assimilated to those of pure water in the corresponding state of aggregation.**
  - **a) Calculate the mass fraction of A in the absorbent stream leaving the column.**
  - **b) Represent the operation in a $\widetilde{Y}_A$ vs. $\widetilde{X}_A$ diagram and justify why it should operate in counterflow.**
  - **c) Calculate the theoretical contact surface between phases to carry out this operation.**
  - **d) Could you use an expression such as $\mathrm{d}\mathcal{N}_A=\mathbf{k}_{M(gl)}\left(\widetilde{Y}_A - \widetilde{X}_A\right)\mathrm{d}A$, where the transferred moles are a function of the difference in A concentrations between the phases in contact and $\mathrm{k}_{M(gl)}$ is a global transport coefficient?**

Question a. First, all the mass flow rates at the entrance of the apparatus are calculated. Since the statement of the problem says that the mixture is binary, and that the mass fraction of A is 0.1, it follows that the mass fraction of B is 0.9. Having in mind that the flow of the waste stream ($\widehat{\mathcal{W}}_{AB_{in}}$) is of 1000 kg/h

$$\widehat{\mathcal{W}}_{A_{in}} = \hat{y}_A \widehat{\mathcal{W}}_{AB_{in}} = 0.1\left(1000\ \frac{\mathrm{kg}}{\mathrm{h}}\right) = 100\ \frac{\mathrm{kg}\,A}{\mathrm{h}} \rightarrow 100\ \frac{\mathrm{kg}}{\mathrm{h}} \times \frac{1000\ \mathrm{g}}{1\ \mathrm{kg}} \times \frac{1\ \mathrm{h}}{3600\ \mathrm{s}} = 27.78\ \frac{\mathrm{g}}{\mathrm{s}}$$

$$\widehat{\mathcal{W}}_{B_{in}} = \hat{y}_B \widehat{\mathcal{W}}_{AB_{in}} = 0.9\left(1000\ \frac{\mathrm{kg}}{\mathrm{h}}\right) = 900\ \frac{\mathrm{kg}\,B}{\mathrm{h}} \rightarrow 900\ \frac{\mathrm{kg}}{\mathrm{h}} \times \frac{1000\ \mathrm{g}}{1\ \mathrm{kg}} \times \frac{1\ \mathrm{h}}{3600\ \mathrm{s}} = 250\ \frac{\mathrm{g}}{\mathrm{s}}$$

By means of the molecular masses, molar flow rates are determined

$$\tilde{\mathcal{W}}_{A_{in}} = \frac{\hat{\mathcal{W}}_{A_{in}}}{\mathfrak{M}_A} = \frac{\left(27.78\ \frac{\text{g}}{\text{s}}\right)}{\left(100\ \frac{\text{g}}{\text{mol-g}}\right)} = 0.2778\ \frac{\text{mol-g}}{\text{s}}$$

$$\tilde{\mathcal{W}}_{B_{in}} = \frac{\hat{\mathcal{W}}_{B_{in}}}{\mathfrak{M}_B} = \frac{\left(250\ \frac{\text{g}}{\text{s}}\right)}{\left(120\ \frac{\text{g}}{\text{mol-g}}\right)} = 2.0833\ \frac{\text{mol-g}}{\text{s}}$$

And in the case of the absorbent stream

$$\hat{\mathcal{W}}_{C_{in}} = 320\ \frac{\text{kg}}{\text{h}} \times \frac{1000\ \text{g}}{1\ \text{kg}} \times \frac{1\ \text{h}}{3600\ \text{s}} = 88.889\ \frac{\text{g}}{\text{s}}$$

$$\tilde{\mathcal{W}}_{C_{in}} = \frac{\hat{\mathcal{W}}_{C_{in}}}{\mathfrak{M}_C} = \frac{\left(88.889\ \frac{\text{g}}{\text{s}}\right)}{\left(80\ \frac{\text{g}}{\text{mol-g}}\right)} = 1.111\ \frac{\text{mol-g}}{\text{s}}$$

Due to the fact that the molar flows of B and C does not vary along the column

$$\tilde{\mathcal{W}}_{B_{in}} = \tilde{\mathcal{W}}_{B_{out}} = \tilde{\mathcal{W}}_B$$
$$\tilde{\mathcal{W}}_{C_{in}} = \tilde{\mathcal{W}}_{C_{out}} = \tilde{\mathcal{W}}_C$$

On the other hand, the mass ratio of A in the waste stream at the entrance will be

$$\tilde{Y}_{A_{in}} = \frac{\tilde{y}_{A_{in}}}{\tilde{y}_{B_{in}}} = \frac{\left(\frac{\hat{y}_{A_{in}}}{\mathfrak{M}_A}\right)}{\left(\frac{\hat{y}_{B_{in}}}{\mathfrak{M}_B}\right)} = \frac{\left(\frac{\hat{y}_{A_{in}}}{\mathfrak{M}_A}\right)}{\left(\frac{1-\hat{y}_{A_{in}}}{\mathfrak{M}_B}\right)} = \frac{\left(\frac{0.1}{100\ \text{g/mol-g}}\right)}{\left(\frac{1-0.1}{120\ \text{g/mol-g}}\right)} = 0.1333$$

and at the exit, the recovery of 95% implies that the ratio between the amount of A which leaves the column and the amount of A which enters is of 5%

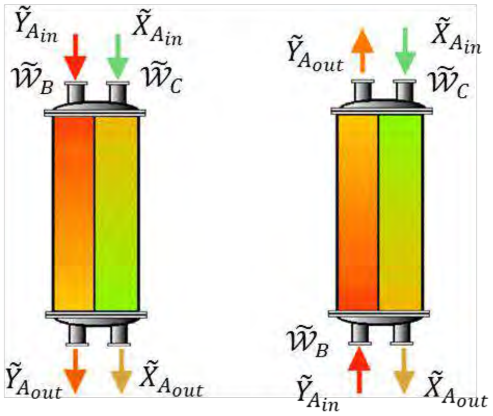
$$\frac{\text{flow of A which leaves the column with the stream B}}{\text{flow of A which enters the column with the stream B}} = \frac{\tilde{Y}_{A_{out}}\tilde{\mathcal{W}}_B}{\tilde{Y}_{A_{in}}\tilde{\mathcal{W}}_B} = 0.05$$

Therefore

$$\tilde{Y}_{A_{out}} = 0.05\tilde{Y}_{A_{in}} = 0.05(0.1333) = 0.00666$$

By applying the mass balance, and knowing that there is no A in the the absorbent stream that enters the apparatus ($\tilde{X}_{A_{in}} = 0$)

$$\tilde{\mathcal{W}}_B\tilde{Y}_{A_{in}} + \tilde{\mathcal{W}}_C\tilde{X}_{A_{in}} = \tilde{\mathcal{W}}_B\tilde{Y}_{A_{out}} + \tilde{\mathcal{W}}_C\tilde{X}_{A_{out}}$$



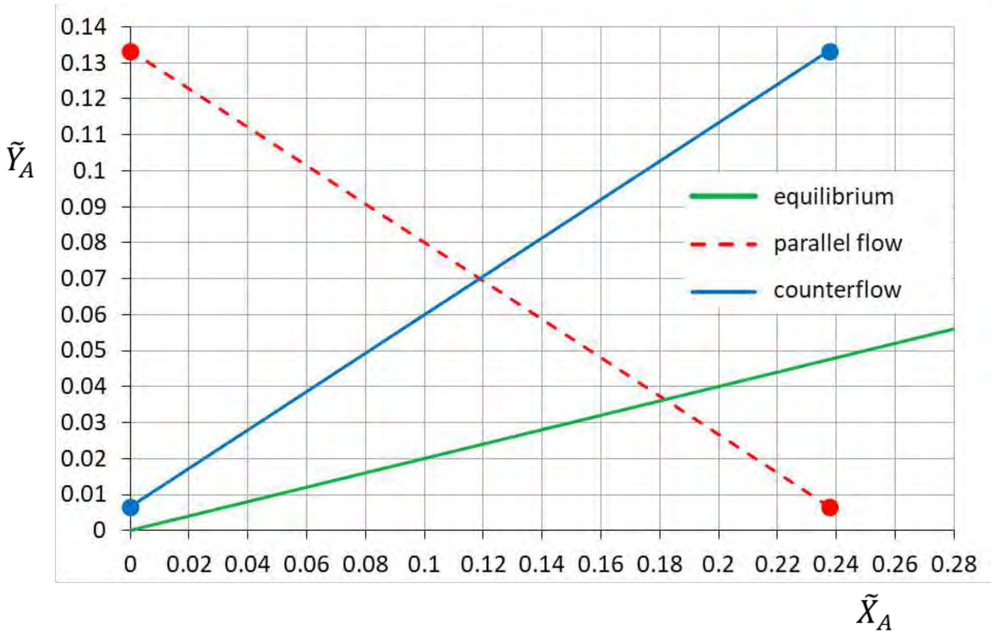
$$\tilde{X}_{A_{out}} = \frac{\widetilde{\mathfrak{W}}_B\left(\tilde{Y}_{A_{in}} - \tilde{Y}_{A_{out}}\right)}{\widetilde{\mathfrak{W}}_C} = \frac{\left(2.0833\ \frac{\text{mol-g}}{\text{s}}\right)(0.1333 - 0.00666)}{\left(1.111\ \frac{\text{mol-g}}{\text{s}}\right)} = 0.2375$$

value that, converted to mass fractions, gives

$$\hat{x}_{A_{out}} = \frac{M_A}{M_A + M_C} = \frac{n_A\mathfrak{W}_A}{n_A\mathfrak{W}_A + n_C\mathfrak{W}_C} = \frac{\left(\frac{n_A}{n_C}\right)\mathfrak{W}_A}{\left(\frac{n_A}{n_C}\right)\mathfrak{W}_A + \mathfrak{W}_C} = \frac{\tilde{X}_{A_{out}}\mathfrak{W}_A}{\tilde{X}_{A_{out}}\mathfrak{W}_A + \mathfrak{W}_C} =$$

$$= \frac{0.2375(100\ \text{g/mol-g})}{0.2375(100\ \text{g/mol-g}) + (80\ \text{g/mol-g})} = 0.2289$$

Question b. An operation line that passes through the points (0, 0.00666) and (0.2375, 0.1333) correspond to the counterflow process, while a line that passes through points (0.2375, 0.00666) and (0, 0.1333) corresponds to the parallel flow one.



When representing the operation and equilibrium lines it is observed that the line corresponding to parallel flow intersects the equilibrium one ($\tilde{Y}_A = \tilde{X}_A/5$) at the point

$$\frac{\left(2.0833\ \frac{\text{mol-g}}{\text{s}}\right)\left(0.1333-\tilde{Y}_A\right)}{\left(1.111\ \frac{\text{mol-g}}{\text{s}}\right)} = 5\tilde{Y}_A \quad \rightarrow \tilde{Y}_A = 0.03635 \quad \rightarrow \tilde{X}_A = 0.1818$$

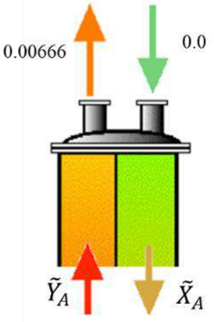
It is demonstrable that, as long as the two flow modes are feasible, the counterflow operation is the most efficient. Additionally, in this case, the conditions imposed by the compositions at the entrance and at the exit would not be achieved in parallel flow, because the system should reach the equilibrium and go beyond (where mass transfer would occur against chemical potential), which is impossible in a spontaneous way.

Question c. According to reference problem 0.18, a differential mass balance leads to

$$-\widetilde{\mathcal{W}}_B \mathrm{d}\tilde{Y}_A = \widetilde{\mathcal{W}}_C \mathrm{d}\tilde{X}_A = \mathrm{k}_{M(g)}\left(\tilde{Y}_A - \tilde{Y}_A^{eq}\right)\mathrm{d}A \qquad [1]$$

$$\mathrm{d}A = -\frac{\widetilde{\mathcal{W}}_B \mathrm{d}\tilde{Y}_A}{\mathrm{k}_{M(g)}\left(\tilde{Y}_A - \tilde{Y}_A^{eq}\right)} \qquad \rightarrow \qquad A = -\frac{\widetilde{\mathcal{W}}_B}{\mathrm{k}_{M(g)}} \int_{\tilde{Y}_{A_{in}}}^{\tilde{Y}_{A_{out}}} \frac{\mathrm{d}\tilde{Y}_A}{\left(\tilde{Y}_A - \tilde{Y}_A^{eq}\right)} \qquad [2]$$

where $\tilde{Y}_A^{eq}$ is related to $\tilde{X}_A$ by the equilibrium equation $\tilde{Y}_A^{eq} = \tilde{X}_A/5$ (the statement of the problem says that the mass transfer resistance in the liquid phase is negligible, so $\tilde{X}_A^{eq} \approx \tilde{X}_A$) and the relation between $\tilde{Y}_A$ and $\tilde{X}_A$ is obtained from a macroscopic balance similar to that of question **a**, but at an indeterminate point of the column when operating in counterflow



$$\tilde{X}_A = \frac{\widetilde{\mathcal{W}}_B\left(\tilde{Y}_A - \tilde{Y}_{A_{out}}\right)}{\widetilde{\mathcal{W}}_C} + \tilde{X}_{A_{in}} =$$

$$= \frac{\left(2.0833\ \frac{\text{mol-g}}{\text{s}}\right)\left(\tilde{Y}_A - 0.00666\right)}{\left(1.111\ \frac{\text{mol-g}}{\text{s}}\right)} + 0.0 =$$

$$= 1.875\tilde{Y}_A - 0.0125$$

Hence

$$A = -\frac{\left(2.0833\ \frac{\text{mol-g}}{\text{s}}\right)}{\left(8{\cdot}10^{-3}\ \frac{\text{mol-g}}{\text{cm}^2 s}\right)} \int_{0.1333}^{0.00666} \frac{\mathrm{d}\tilde{Y}_A}{\left[\tilde{Y}_A - \frac{1}{5}\left(1.875\tilde{Y}_A - 0.0125\right)\right]} =$$

$$= 260.41\ \text{cm}^2 \int_{0.00666}^{0.1333} \frac{5\mathrm{d}\tilde{Y}_A}{\left(5\tilde{Y}_A - 1.875\tilde{Y}_A + 0.0125\right)} =$$

$$= 5\left(\frac{260.41\ \text{cm}^2}{3.125}\right)\left[\ln\left(3.125\tilde{X}_A + 0.0125\right)\right]_{0.00666}^{0.1333} =$$

$$= 5\left(\frac{260.41\ \text{cm}^2}{3.125}\right)\ln\left\{\frac{3.125(0.1333) + 0.0125}{3.125(0.00666) + 0.0125}\right\} = 1064.84\ \text{cm}^2$$

Question d. If a global transfer coefficient is applied and the transferred moles become a function of the difference in concentrations between the phases in contact, equations [1] and [2] will be

$$-\tilde{W}_B \mathrm{d}\tilde{Y}_A = \tilde{W}_C \mathrm{d}\tilde{X}_A = \mathrm{k}_{M(gl)}\left(\tilde{Y}_A - \tilde{X}_A\right)\mathrm{d}A$$

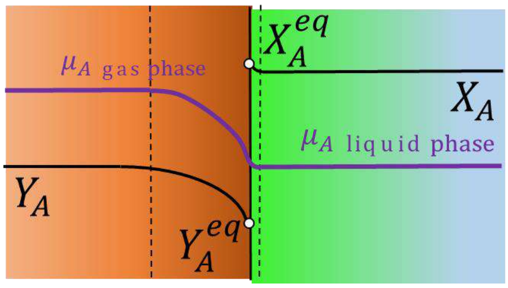
$$\mathrm{d}A = -\frac{\tilde{W}_B \mathrm{d}\tilde{Y}_A}{\mathrm{k}_{M(gl)}\left(\tilde{Y}_A - \tilde{X}_A\right)} \qquad \rightarrow \qquad A = -\frac{\tilde{W}_B}{\mathrm{k}_{M(gl)}}\int_{\tilde{Y}_{A_{in}}}^{\tilde{Y}_{A_{out}}} \frac{\mathrm{d}\tilde{Y}_A}{\left(\tilde{Y}_A - \tilde{X}_A\right)}$$

the main difference being the denominator of the function to integrate, which is now

$$\tilde{Y}_A - \tilde{X}_A = \tilde{Y}_A - \left(1.875\tilde{Y}_A - 0.0125\right) = 0.0125 - 0.875\tilde{Y}_A$$

By operating as in the previous question, it will be found that the result of the integral is not a real number: the potential $\left(\tilde{Y}_A - \tilde{X}_A\right)$ is positive at one end of the column (0.00666–0= 0.00666) and negative at the other (0.1333–0.2375 =–0.1042).

This does not imply the impossibility of mass transfer, only that expression $\mathrm{k}_{M(gl)}\left(\tilde{Y}_A - \tilde{X}_A\right)$ is not suitable to represent the chemical potential (μ_A) which is the true driving force of mass transfer. In opposition to the concentration, which shows discontinuities in the interface, μ is a continuous and monotonic function.



7.7. Commercial single-stage dehydrators have been installed in 1000 m^3 classrooms. They operate by passing the air through a cold surface where the water condenses, being it collected in a tank. If humidity in the clasrooms has to be reduced from 0.020 kg water/(kg dry air) to 0.002 kg water/(kg dry air) at 20ºC, calculate the minimum volume of the tank. Assume that air behaves like an ideal gas and that the density of the condensed water is of 1 kg/L.

Since the initial and final humidities are expressed as mass ratios (humidity ratios), it will be necessary to calculate the mass of dry air involved in the process, M

$$M = \frac{V_{classrooms}}{\hat{V}}$$

where $V_{classrooms}$ is the total volume of the clasrooms (coinciding with the total volume of moist air to be treated) and $\hat{V}$ the specific volume of the initial moist air, which is determined as (section d of reference problem 0.19)

$$\hat{V} = \left(\frac{1}{\mathfrak{M}_{air}} + \frac{\hat{Y}_1}{\mathfrak{M}_{water}}\right)\frac{RT}{P}$$

By knowing that

$$T(\mathrm{K}) = 20℃ + 273 = 293\ \mathrm{K}$$

and by taking the molar masses from appendix II, and introducing the initial humidity ratio, it is obtained

$$\hat{V} = \left(\frac{1}{28.97\frac{\mathrm{g}}{\text{mol-g}}} + \frac{0.02}{18.015\frac{\mathrm{g}}{\text{mol-g}}}\right)\frac{\left(0.082\frac{\mathrm{atm}\cdot\mathrm{L}}{\mathrm{K}\cdot\text{mol-g}}\right)(293\ \mathrm{K})}{1\ \mathrm{atm}} = 0.856\ \frac{\text{L moist air}}{\text{g dry air}}$$

and due to the fact that the units L/g are equivalent to m^3/kg

$$M = 1000\ \mathrm{m}^3 \times \frac{1\ \text{kg dry air}}{0.856\ \mathrm{m}^3\ \text{moist air}} = 1168.22\ \text{kg dry air}$$

This mass of dry air remains constant during dehydration, so the total amount of water removed will be

$$M\left(\hat{Y}_1 - \hat{Y}_2\right) = (1168.22\ \text{kg dry air})\left(0.020\frac{\text{kg water}}{\text{kg dry air}} - 0.002\frac{\text{kg water}}{\text{kg dry air}}\right) = 21.03\ \text{kg water}$$

datum that will allow the calculation of the tank volume by using the water density

$$21.03\ \mathrm{kg} \times \frac{1\ \mathrm{L}}{1\ \mathrm{kg}} = 21.03\ \mathrm{L}$$

7.8. Analytically determine the humidity ratio, the specific volume, the specific heat, the specific enthalpy and the dewpoint temperature of an air-water mixture at atmospheric pressure whose dry-bulb temperature is 35ºC and the relative humidity is 30%.

Section c of reference problem 0.19 establishes that humidity ratio ($\tilde{Y}$) and relative humidity (φ) are related by the expression

$$\tilde{Y} = \frac{\varphi P_{v(water)}}{P_{tot} - \varphi P_{v(water)}} \qquad \rightarrow \qquad \hat{Y} = \frac{\mathfrak{M}_{water}}{\mathfrak{M}_{air}}\left(\frac{\varphi P_{v(water)}}{P_{tot} - \varphi P_{v(water)}}\right)$$

where P_{tot} is 1 atm (1.013 bar) and $P_{v(water)}$ is the vapor pressure of pure water at the dry-bulb temperature. By interpolation from table VI.1 of this book's appendix VI, it is found that this pressure at 35ºC is of 0.055 bar, and by taking the molecular masses from appendix II

$$\hat{Y} = \left(\frac{18.015\,\frac{\text{g}}{\text{mol-g}}}{28.97\,\frac{\text{g}}{\text{mol-g}}}\right)\left[\frac{(0.30)(0.055\text{ bar})}{1.013\text{ bar} - (0.30)(0.055\text{ bar})}\right] = 0.0103\ \frac{\text{kg moisture}}{\text{kg dry air}}$$

Additonally, in section d of the aforementioned reference problem 0.19, the specific volume of moist air is given by

$$\hat{V} = \left(\frac{1}{\mathfrak{M}_{air}} + \frac{\hat{Y}}{\mathfrak{M}_{water}}\right)\frac{RT}{P_{tot}}$$

therefore

$$\hat{V} = \left(\frac{1}{28.97\,\frac{\text{g}}{\text{mol-g}}} + \frac{0.0103}{18.015\,\frac{\text{g}}{\text{mol-g}}}\right)\frac{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(35 + 273\text{ K})}{1\text{ atm}} = 0.886\ \frac{\text{L moist air}}{\text{g dry air}}$$

On the other hand, the specific heat capacity and enthalpy are estimated as (section e of problem 0.19)

$$\hat{C}_P = \hat{C}_{P_{air(35℃)}} + \hat{Y}\hat{C}_{P_{steam(35℃)}}$$

$$\hat{H} = \hat{H}_{air(35℃)} + \hat{Y}\hat{H}_{steam(35℃)}$$

being interpolated the individual parameters of steam and air from tables VI.1 and VI.2 of appendix VI, respectively.

$$\hat{C}_P = 1.007\,\frac{\text{kJ}}{(\text{kg dry air})\ \text{K}} + \left(0.0103\,\frac{\text{kg moisture}}{\text{kg dry air}}\right)\left[1.88\,\frac{\text{kJ}}{(\text{kg water})\ \text{K}}\right] = 1.031\,\frac{\text{kJ}}{(\text{kg dry air})\ \text{K}}$$

$$\widehat{H} = 35.28\,\frac{\text{kJ}}{\text{kg dry air}} + 0.0103\,\frac{\text{kg moisture}}{\text{kg dry air}}\left(2564.32\,\frac{\text{kJ}}{\text{kg water}}\right) = 61.69\,\frac{\text{kJ}}{\text{kg dry air}}$$

Finally, the dewpoint temperature will be that at which this mixture whose partial pressure of water vapor is $\varphi P_{v(water)}$ becomes saturated, i.e., the temperature at which

$$(0.30)(0.055\ \text{bar}) = 0.0165\text{bar}$$

is the new vapor pressure of the water. By interpolation in table VI.1 it results to be 14.9ºC.

7.9. A 900 m^3 public space remains at a temperature of 20ºC and its humidity is of 90% at the end of the day. For hygiene and comfort, it have to be reduced to 37.5% in 12 hours without modifying the temperature. Therefore, a dehumidifier is employed: it cools the air until saturation to the desired moisture and, after water removal, it heats the low-humidity air to the initial temperature. Calculate:

a) The volumetric flow rate of moist air to be treated.

b) The mass flow of water to be removed and that of dry air to be treated.

c) The heat flow that has to be removed (in watts) in order to cool the high-humidity air from 20ºC to the saturation temperature.

d) The heat flow required by the low-humidity air to return to 20ºC (in watts).

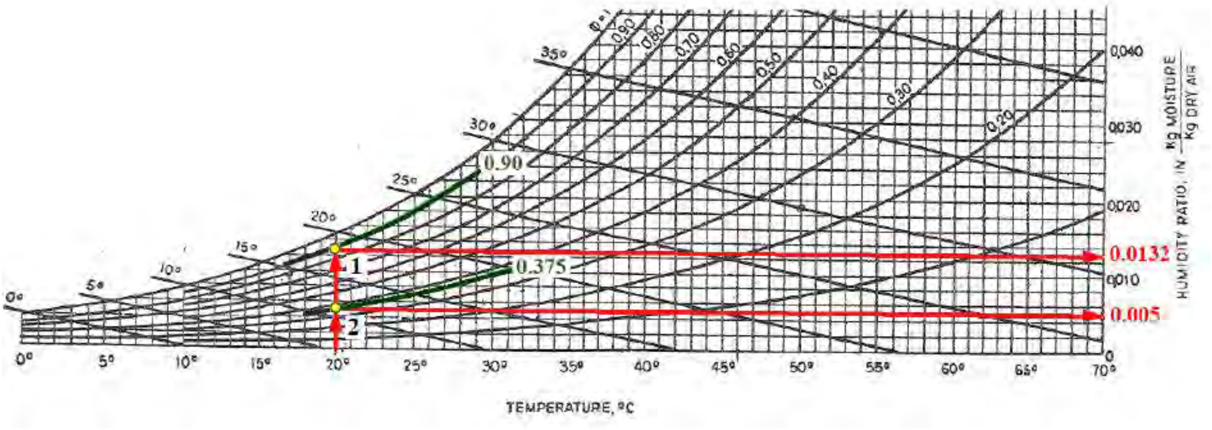
e) The heat flow to condense the water at saturation temperature (in watts).

Let 1 be the point at 20ºC and 90% relative humidity, 2 be the point at the same temperature and 37.5% relative humidity, and 3 be the point where moisture condenses.

Question a. From the volume of the room and the operating time, it can be obtained

$$\breve{\mathcal{W}}_{air} = \frac{V}{t} = \frac{900\ \mathrm{m}^3}{12\ \mathrm{h}} = 75\ \frac{\mathrm{m}^3}{\mathrm{h}} \quad \rightarrow \quad 75\ \frac{\mathrm{m}^3}{\mathrm{h}} \times \frac{1000\ \mathrm{L}}{1\ \mathrm{m}^3} \times \frac{1\ \mathrm{h}}{3600\ \mathrm{s}} = 20.83\ \frac{\mathrm{L}}{\mathrm{s}}$$

Question b. To estimate the water flow to be removed, the humidity ratios at 20ºC have to be read from the psychrometric diagram (figure VII.1 of appendix VII)



$$\hat{Y}_1 = 0.0132\,\frac{\text{kg moisture}}{\text{kg dry air}} \quad \text{when } \varphi = 0.9$$

$$\hat{Y}_2 = 0.005\,\frac{\text{kg moisture}}{\text{kg dry air}} \quad \text{when } \varphi = 0.375$$

The first one allows the obtention of the specific volume of moist air at the initial conditions (section d of reference problem 0.19)

$$\hat{V} = \left(\frac{1}{\mathfrak{W}_{air}} + \frac{\hat{Y}_1}{\mathfrak{M}_{water}}\right)\frac{RT_1}{P}$$

and together with the volume flow rate of moist air, the calculation of the mass flow rate of dry air to be treated gives

$$T_1(\mathrm{K}) = T_2(\mathrm{K}) = 20°\mathrm{C} + 273 = 293\ \mathrm{K}$$

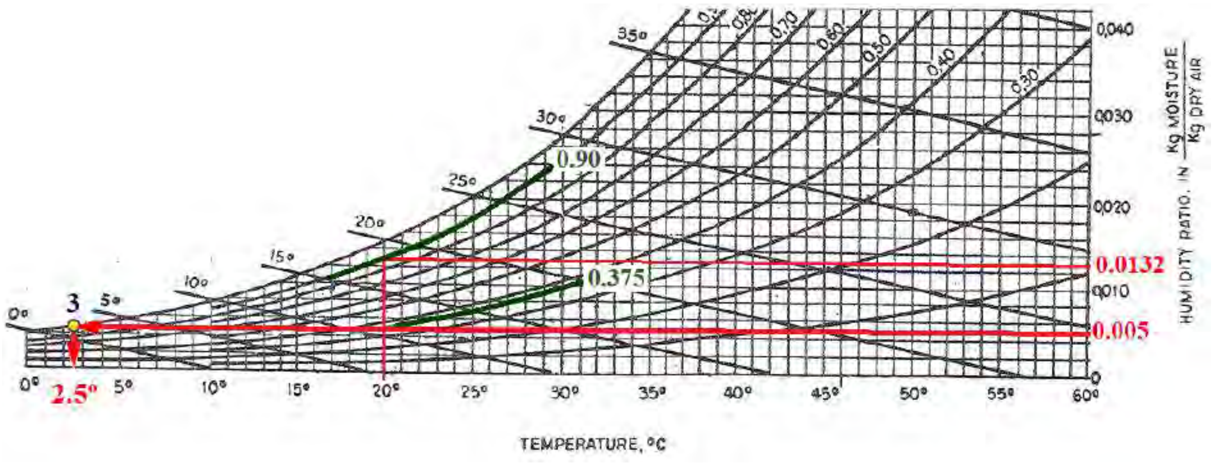
$$\hat{V} = \left(\frac{1}{28.97\,\dfrac{\mathrm{g}}{\text{mol-g}}} + \frac{0.0132}{18.015\,\dfrac{\mathrm{g}}{\text{mol-g}}}\right)\frac{\left(0.082\,\dfrac{\mathrm{atm\cdot L}}{\mathrm{K\cdot mol\text{-}g}}\right)(293\ \mathrm{K})}{1\ \mathrm{atm}} = 0.847\ \frac{\text{L moist air}}{\text{g dry air}}$$

$$\hat{\mathcal{W}} = \frac{\breve{\mathcal{W}}}{\hat{V}} = 20.83\ \frac{\text{L moist air}}{\mathrm{s}} \times \frac{1\ \text{g dry air}}{0.847\ \text{L moist air}} = 24.59\ \frac{\text{g dry air}}{\mathrm{s}}$$

By combining the two humidity ratios and this mass flow rate of dry air (converted to kg/s) it is found that

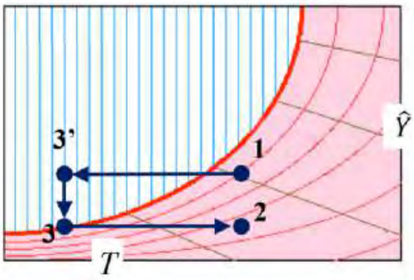
$$\hat{\mathcal{W}}_{water} = \hat{\mathcal{W}}_{air}\left(\hat{Y}_1 - \hat{Y}_2\right) = \left(0.02459\ \frac{\text{kg air}}{\mathrm{s}}\right)(0.0132 - 0.005) = 20.16 \cdot 10^{-5}\,\frac{\text{kg water}}{\mathrm{s}}$$

Question c. To determine this heat, temperature T_3 (at which the 0.005 humidity ratio line intersects the 100% relative humidity line) is needed.



But the first stage of the apparatus is not from 1 to 3, but from 1 to the metastable point 3' (at the same temperature as 3), so

$$q_{3'1} = \hat{\mathcal{W}}_{air}\left(\hat{H}_{3'} - \hat{H}_1\right)$$



where the specific enthalpies of moist air per kilogram of dry air (assuming ideal mixture) are estimated as

$$\hat{H}_1 = \hat{H}_{air(20°C)} + \hat{Y}_1 \hat{H}_{steam(20°C)}$$
$$\hat{H}_{3'} = \hat{H}_{air(2.5°C)} + \hat{Y}_1 \hat{H}_{steam(2.5°C)}$$

By interpolating from tables VI.1 and VI.2 of this book's appendix VI

$$\hat{H}_1 = 20.15\ \frac{\text{kJ}}{\text{kg dry air}} + 0.0132\ \frac{\text{kg moisture}}{\text{kg dry air}} \left(2537.97\ \frac{\text{kJ}}{\text{kg water}}\right) = 53.65 \frac{\text{kJ}}{\text{kg dry air}}$$

$$\hat{H}_{3'} = 2.50\ \frac{\text{kJ}}{\text{kg dry air}} + 0.0132\ \frac{\text{kg moisture}}{\text{kg dry air}} \left(2507.23\ \frac{\text{kJ}}{\text{kg water}}\right) = 35.59 \frac{\text{kJ}}{\text{kg dry air}}$$

it results that

$$q_{3'1} = \left(0.02459\ \frac{\text{kg dry air}}{\text{s}}\right)\left(35.59 \frac{\text{kJ}}{\text{kg dry air}} - 53.65 \frac{\text{kJ}}{\text{kg dry air}}\right) = -0.4441\ \text{kW}$$

and obviously

$$q_{31} = -444.1\ \text{W}$$

Question d. In order to increase the temperature from T_3 to T_2

$$q_{23} = \hat{W}_{air}\left(\hat{H}_2 - \hat{H}_3\right)$$

By operating as in the previous question

$$\hat{H}_2 = \hat{H}_{air(20°C)} + \hat{Y}_2 \hat{H}_{steam(20°C)}$$
$$\hat{H}_3 = \hat{H}_{air(2.5°C)} + \hat{Y}_2 \hat{H}_{steam(2.5°C)}$$

$$\hat{H}_2 = 20.15\ \frac{\text{kJ}}{\text{kg dry air}} + 0.005\ \frac{\text{kg moisture}}{\text{kg dry air}} \left(2537.97\ \frac{\text{kJ}}{\text{kg water}}\right) = 32.84 \frac{\text{kJ}}{\text{kg dry air}}$$

$$\widehat{H}_3 = 2.50\ \frac{\text{kJ}}{\text{kg dry air}} + 0.005\ \frac{\text{kg moisture}}{\text{kg dry air}}\left(2507.23\ \frac{\text{kJ}}{\text{kg water}}\right) = 15.04\,\frac{\text{kJ}}{\text{kg dry air}}$$

Hence

$$q_{23} = \left(0.02459\ \frac{\text{kg dry air}}{\text{s}}\right)\left(32.84\,\frac{\text{kJ}}{\text{kg dry air}} - 15.04\,\frac{\text{kJ}}{\text{kg dry air}}\right) = 0.4377\ \text{kW} = 437.7\ \text{W}$$

which are 437.7 W

Question e. The condensation heat will be

$$q_{33'} = \widehat{\mathcal{W}}_{air}\left(\widehat{H}_3 - \widehat{H}_{3'}\right)$$

$$q_{33'} = \left(0.02459\ \frac{\text{kg dry air}}{\text{s}}\right)\left(15.04\,\frac{\text{kJ}}{\text{kg dry air}} - 35.59\,\frac{\text{kJ}}{\text{kg dry air}}\right) = -0.505\ \text{kW}$$

which are -505 W. Notice that this heat flow is only related to water, and therefore it can also be obtained from the enthalpy of condensation of this pure substance at 2.5ºC

$$q_{33'} = \widehat{\mathcal{W}}_{water}\left[\widehat{H}^{sat}_{l(2.5°\text{C})} - \widehat{H}^{sat}_{v(2.5°\text{C})}\right]$$

In table VI.1, $\widehat{H}^{sat}_{l(2.5°\text{C})}$ =10.53 kJ/kg and $\widehat{H}^{sat}_{v(2.5°\text{C})}$ =2506.17 kJ/kg; thus

$$q_{33'} = \left(20.16 \cdot 10^{-5}\,\frac{\text{kg water}}{\text{s}}\right)\left(10.53\,\frac{\text{kJ}}{\text{kg water}\cdot\ \text{K}} - 2506.17\ \frac{\text{kJ}}{\text{kg water}}\right) = -0.503\ \text{kW}$$

7.10. A cottage uninhabited from Monday to Friday consists of two floors of 8×4 m (one with an average height of 3 m, the other with 2.5 m) and remains hermetically closed. The air inside is saturated with moisture and at an average temperature of 20°C. The house owners consider that such moisture should be reduced to 30% in order to find aceptable conditions during the weekend.

A commercial thermal dehumidifier is employed. It includes a suction pump capable of pumping 100 L/min and a heat exchanger with an effective area of 0.25 m^2 and an overall heat transfer coefficient of 100 kcal/(h·m^2·°C). The interior temperature of the exchanger is roughly constant.

- **a) Calculate the time required to perform the desired operation.**
- **b) Analytically calculate the humidity ratios in the cottage before and after the dehumidification.**
- **c) Determine the amount of removed water.**
- **d) Evaluate the enthalpy change of the air throughout the process, and the heat flow associated with it.**
- **e) Determine the temperature increase in the atmosphere if all the heat produced by the machine is dispersed inside the house. This heat is 1.25 times higher than the enthalpy change of the air and is released without varying the humidity ratio.**
- **f) Estimate the heat removed in the heat exchanger if the dehumidifier works by vaporizating saturated liquid Freon 503 at -28.8°C in its interior.**

Let 1 be the cottage at 20°C and 100% relative humidity and 2 be the house at the same temperature and 30% relative humidity.

Question a. This time can be defined as the ratio between the volume of air to be treated and the air flow of the device (100 L/min=0.1 m^3/min). The air volume will coincide with that of the cottage, which consists of a floor of 8×4×3=96 m^3 and another one of 8×4×2.5=80 m^3, i.e., a total volume of 176 m^3.

$$t=\frac{176\ \mathrm{m}^3}{0.1\ \mathrm{m}^3/\mathrm{min}}=1760\ \mathrm{min} \quad \rightarrow \quad 1760\ \mathrm{min}\times\frac{1\ \mathrm{h}}{60\ \mathrm{min}}=29.33\ \mathrm{h}$$

which is much lower than the time during which the house is uninhabited (5 days, from Monday to Friday).

Question b. Section c of reference problem 0.19 indicates that the humidity mass ratio ($\hat{Y}$) and the relative humidity (φ) are related by

$$\hat{Y}=\frac{\mathfrak{M}_{water}}{\mathfrak{M}_{air}}\left(\frac{\varphi P_{v(water)}}{P_{tot}-\varphi P_{v(water)}}\right)$$

where P_{tot} is 1 atm (1.013 bar) and $P_{V(water)}$ is the vapor pressure of pure water at the dry-bulb temperature. By interpolating from table VI.1 of appendix VI, this pressure at 20°C results to be of 0.023 bar, and by taking the molar masses from appendix II, it is obtained

$$\hat{Y}_1 = \left(\frac{18.015\,\frac{\text{g}}{\text{mol-g}}}{28.97\,\frac{\text{g}}{\text{mol-g}}}\right)\left[\frac{(1.0)(0.023\text{ bar})}{1.013\text{ bar} - (1.0)(0.023\text{ bar})}\right] = 0.01445\;\frac{\text{kg moisture}}{\text{kg dry air}}$$

$$\hat{Y}_2 = \left(\frac{18.015\,\frac{\text{g}}{\text{mol-g}}}{28.97\,\frac{\text{g}}{\text{mol-g}}}\right)\left[\frac{(0.30)(0.023\text{ bar})}{1.013\text{ bar} - (0.30)(0.023\text{ bar})}\right] = 0.00426\;\frac{\text{kg moisture}}{\text{kg dry air}}$$

Question c. To estimate the flow rate of removed water, the specific volume of moist air when the relative humidity is of 100% has to be determined first.

$$\hat{V} = \left(\frac{1}{\mathfrak{M}_{air}} + \frac{\hat{Y}_1}{\mathfrak{M}_{water}}\right)\frac{RT_1}{P}$$

$$T_1(\text{K}) = T_2(\text{K}) = 20^\circ\text{C} + 273 = 293\text{ K}$$

$$\hat{V} = \left(\frac{1}{28.97\,\frac{\text{g}}{\text{mol-g}}} + \frac{0.01445}{18.015\,\frac{\text{g}}{\text{mol-g}}}\right)\frac{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(293\text{ K})}{1\text{ atm}} = 0.8486\;\frac{\text{L moist air}}{\text{g dry air}}$$

If the volumetric flow rate of moist air is considered

$$\widehat{\mathcal{W}} = \frac{\breve{\mathcal{W}}}{\hat{V}} = 100\;\frac{\text{L moist air}}{\text{min}} \times \frac{1\text{ g dry air}}{0.8486\text{ L moist air}} = 117.84\;\frac{\text{g dry air}}{\text{min}}$$

and by converting this result to kg/min and using the humidity ratios of question **b**, the removed water will be

$$\widehat{\mathcal{W}}_{water} = \widehat{\mathcal{W}}_{air}\left(\hat{Y}_1 - \hat{Y}_2\right) = \left(0.11784\;\frac{\text{kg air}}{\text{min}}\right)(0.01445 - 0.00426) = 12\cdot 10^{-4}\,\frac{\text{kg water}}{\text{min}}$$

Question d. Enthalpies of states 1 and 2 are given by

$$\hat{H}_1 = \hat{H}_{air(20^\circ\text{C})} + \hat{Y}_1\hat{H}_{steam(20^\circ\text{C})}$$

$$\hat{H}_2 = \hat{H}_{air(20^\circ\text{C})} + \hat{Y}_2\hat{H}_{steam(20^\circ\text{C})}$$

After interpolating from tables VI.1 and VI.2 of appendix VI

$$\hat{H}_1{=}20.15\ \frac{\text{kJ}}{\text{kg dry air}}{+}0.01445\ \frac{\text{kg moisture}}{\text{kg dry air}}\left(2537.97\ \frac{\text{kJ}}{\text{kg water}}\right){=}56.82\frac{\text{kJ}}{\text{kg dry air}}$$

$$\hat{H}_2{=}20.15\ \frac{\text{kJ}}{\text{kg dry air}}{+}0.00426\ \frac{\text{kg moisture}}{\text{kg dry air}}\left(2537.97\ \frac{\text{kJ}}{\text{kg water}}\right){=}30.96\frac{\text{kJ}}{\text{kg dry air}}$$

Then

$$\Delta\hat{H}_{21} = \hat{H}_2 - \hat{H}_1 = 30.96\frac{\text{kJ}}{\text{kg dry air}} - 56.82\frac{\text{kJ}}{\text{kg dry air}} = -25.86\ \frac{\text{kJ}}{\text{kg dry air}}$$

Finally, the total heat removed is obtained by referring this difference to the mass flow rate of dry air

$$q_{air} = \left(0.11784\ \frac{\text{kg dry air}}{\text{min}}\right)\left(-25.86\frac{\text{kJ}}{\text{kg dry air}}\right) = -3.05\ \frac{\text{kJ}}{\text{min}}$$

Question e. If the dispersed heat is 1.25 times that calculated in question **d** but $\hat{Y}_2$ remains constant, the cottage will reach a state 3 where

$$-1.25q_{air} = \hat{W}_{air}\left(\hat{H}_3 - \hat{H}_2\right)$$

$$-1.25\left(-3.05\ \frac{\text{kJ}}{\text{min}}\right) = \left(0.11784\ \frac{\text{kg dry air}}{\text{min}}\right)\left(\hat{H}_3 - 30.96\frac{\text{kJ}}{\text{kg dry air}}\right)$$

$$\hat{H}_3 = 63.31\ \frac{\text{kJ}}{\text{kg dry air}}$$

But since

$$\hat{H}_3 = \hat{H}_{air(T_3)} + \hat{Y}_2\hat{H}_{steam(T_3)}$$

the requested temperature will be found by assuming a T_3 value, interpolating the enthalpies of steam and air from tables VI.1 and VI.2 of appendix VI, respectively, and comparing the calculated value with 63.31 kJ/kg

T_3(°C)	$\hat{H}_{air(T_3)}$ kJ/kg	$\hat{H}_{steam(T_3)}$ kJ/kg	$\hat{H}_3$ kJ/kg	Comments
30	30.23	2555.54	41.12	T_3 is higher
40	40.32	2573.11	51.28	T_3 is higher
50	50.40	2590.67	61.44	T_3 is higher
60	60.49	2608.24	71.59	T_3 is lower
51.8	52.22	2593.84	63.27	OK

Hence

$$T_3 = 51.8\text{°C}$$

This theoretical result suggests a potentially dangerous situation, but in practice it would be partially solved by the natural heat losses (the building is not totally thermally insulated) and by the adequate evacuation of the dehumidifier to the outside.

Question f. According to section c of reference problem 0.12, the exchanged heat is related to the exchange area and the overall heat transfer coefficient by the expression

$$q_{removed} = \mathrm{k}_T A \Delta T$$

where the gradient ΔT is the difference between the air temperature (20ºC) and that inside the dehumidifier, which remains constant (-28.8ºC).

$$q_{removed} = \left(100\ \frac{\text{kcal}}{\text{h·m}^2\text{·°C}}\right)(0.25\ \text{m}^2)(20\text{°C} + 28.8\text{°C}) = 1220\ \frac{\text{kcal}}{\text{h}}$$

value that converted to kJ/min gives

$$1220\ \frac{\text{kcal}}{\text{h}} \times \frac{1\ \text{J}}{0.000239\ \text{kcal}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} \times \frac{1\ \text{h}}{60\ \text{min}} = 85.08\ \frac{\text{kJ}}{\text{min}}$$

Notice that this heat is almost twenty-eight times higher than that obtained in question **d**, which indicates that the dehumidifier could perform the task twenty-eight times faster than in the first question of the problem. This reveals that the system is overspecified.

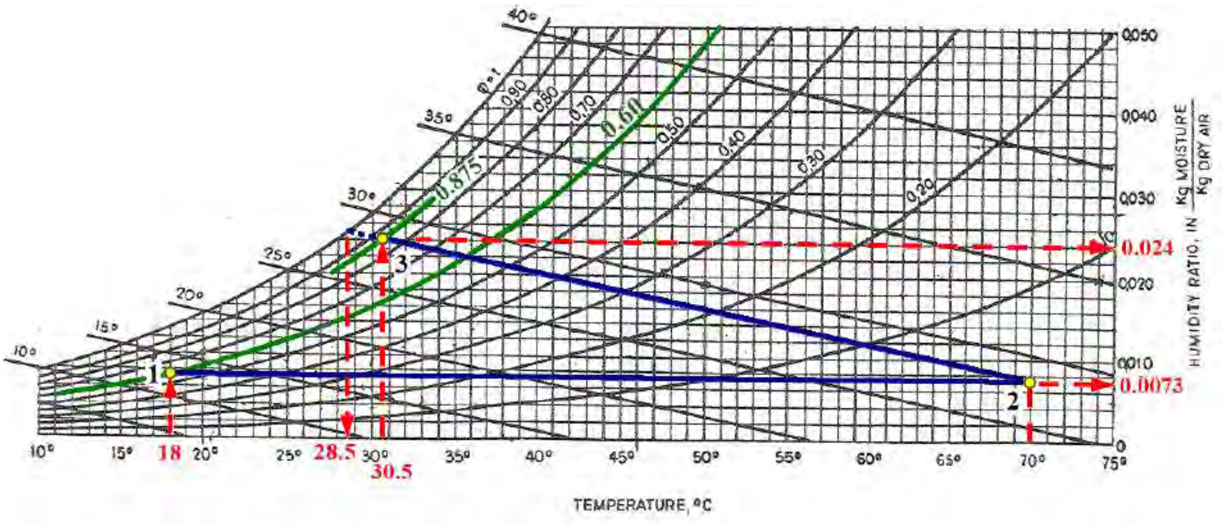
7.11. Air is available at 18°C with a relative humidity of 60% at 760 mm Hg. This air is preheated to 70°C, then employed to evaporate 100 kg/h of water in an adiabatic dryer, and finally leaves the dryer 2°C above saturation temperature. Calculate the air volumetric flow used (measured at 18°C and 60% humidity) and the heat flow to be supplied in the preheating.

Let point 1 be the air at 18°C and 60% humidity, point 2 be the preheated air and 3 be the air leaving the dryer. The mass flow of air to perform the operation is

$$\widehat{\mathcal{W}}_{air} = \frac{\widehat{\mathcal{W}}_{water}}{\left(\hat{Y}_3 - \hat{Y}_1\right)}$$

The humidity ratio at point 1 is that of the intersection between the 18°C dry-bulb temperature and the 60% relative humidity in figure VII.1 of this book's appendix VII (psychrometric diagram)

$$\hat{Y}_1 = \hat{Y}_2 = 0.0073$$



Calculation of humidity ratio at point 3 is more complex. Graphically it requires drawing the adiabatic line that passes through 2 (parallel, in this case, to the adiabatic lines of 25° and 30° in the psychrometric diagram) and calculating the saturation temperature (28.5°C). When this temperature is found, 2°C are added to it and then the intersection between the dry-bulb temperature T_3 (28.5+2=30.5°C) and the previously drawn adiabatic line will give $\hat{Y}_3$ (0.024 kg moisture/kg dry air) and φ (approximately 87.5%). Thus

$$\widehat{\mathcal{W}}_{air} = \frac{\left(100\ \frac{\text{kg water}}{\text{h}}\right)}{\left(0.024\ \frac{\text{kg moisture}}{\text{kg dry air}} - 0.0073\ \frac{\text{kg moisture}}{\text{kg dry air}}\right)} = 5988\ \frac{\text{kg dry air}}{\text{h}}$$

On the other hand, the mass and volume flow rates are related by the expression

$$\breve{\mathcal{W}} = \hat{\mathcal{W}}\hat{V}$$

where the specific volume is

$$\hat{V} = \left(\frac{1}{\mathfrak{M}_{air}} + \frac{\hat{Y}_1}{\mathfrak{M}_{water}}\right)\frac{RT_1}{P_{tot}}$$

By taking the molar masses from appendix II and remembering that 18ºC are 291 K (18+273)

$$\hat{V} = \left(\frac{1}{28.97\,\frac{\text{g}}{\text{mol-g}}} + \frac{0.0073}{18.015\,\frac{\text{g}}{\text{mol-g}}}\right)\frac{\left(0.082\,\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(291\text{ K})}{1\text{ atm}} = 0.8333\,\frac{\text{L moist air}}{\text{g dry air}}$$

$$\breve{\mathcal{W}}_{air} = 5988\,\frac{\text{kg dry air}}{\text{h}} \times \frac{0.8333\text{ m}^3\text{ moist air}}{1\text{ kg dry air}} = 4988\,\frac{\text{m}^3\text{ moist air}}{\text{h}}$$

Finally, the heat flow required to raise the temperature of the 4988 m^3/h air from 18ºC to 70ºC is estimated as

$$q_{21} = \hat{\mathcal{W}}\left(\hat{H}_2 - \hat{H}_1\right)$$

where

$$\hat{H}_1 = \hat{H}_{air(18^\circ\text{C})} + \hat{Y}_1\hat{H}_{steam(18^\circ\text{C})}$$

$$\hat{H}_2 = \hat{H}_{air(70^\circ\text{C})} + \hat{Y}_1\hat{H}_{steam(70^\circ\text{C})}$$

From tables VI.1 and VI.2

$$\hat{H}_1 = 18.13\,\frac{\text{kJ}}{\text{kg dry air}} + 0.0073\,\frac{\text{kg moisture}}{\text{kg dry air}}\left(2534.46\,\frac{\text{kJ}}{\text{kg water}}\right) = 36.63\,\frac{\text{kJ}}{\text{kg dry air}}$$

$$\hat{H}_2 = 70.57\,\frac{\text{kJ}}{\text{kg dry air}} + 0.0073\,\frac{\text{kg moisture}}{\text{kg dry air}}\left(2625.81\,\frac{\text{kJ}}{\text{kg water}}\right) = 89.74\,\frac{\text{kJ}}{\text{kg dry air}}$$

$$q_{21} = \left(5988\,\frac{\text{kg dry air}}{\text{h}}\right)\left(89.74\,\frac{\text{kJ}}{\text{kg dry air}} - 36.63\,\frac{\text{kJ}}{\text{kg dry air}}\right) = 318023\,\frac{\text{kJ}}{\text{h}}$$

7.12. An air stream of 300 m³/min at 65°C (dewpoint temperature of 28°C) is treated in an adiabatic humidifier with an area of 2 m² and an overall heat transfer coefficient $k_T a$=85 Btu/(h·ft³·°F). The air leaves the apparatus with a relative humidity of 90%. Calculate:

a) The temperature and humidity of the air leaving the humidifier.

b) The mass of evaporated water.

c) The height of the humidification chamber, if $dq = k_T a(T_{sat} - T)dV_{ap}$, where V_{ap} is the apparatus volume.

d) The temperature of the leaving air if the humidifier length is doubled.

Figure VII.1 of this book's appendix VII (psychrometric diagram) and molecular weights from appendix II will be taken for solving this problem.

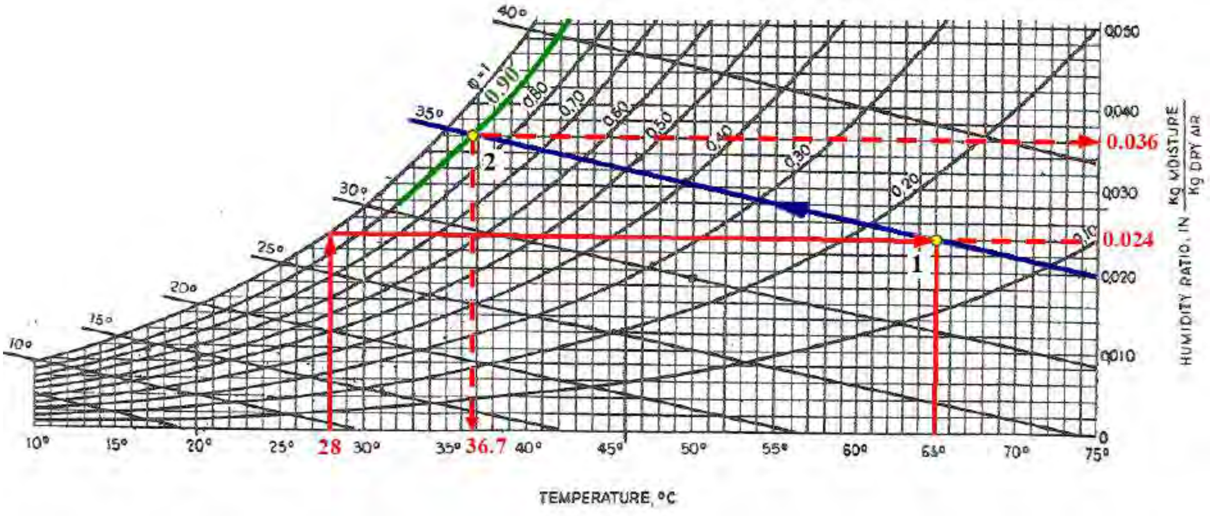
Unit conversions will be performed by means of factors of appendix I

$$T_1(\text{K}) = 65°\text{C} + 273 = 338\ \text{K}$$

$$\breve{\mathcal{W}} = 300\ \frac{\text{m}^3\text{moist air}}{\text{min}} \times \frac{60\ \text{min}}{1\ \text{h}} = 1800\ \frac{\text{m}^3\ \text{moist air}}{\text{h}}$$

$$\text{k}_T\text{a} = 85\frac{\text{BTU}}{\text{h·ft}^3\text{·°F}} \times \frac{1050\ \text{J}}{1\text{BTU}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} \times \frac{1\ \text{ft}^3}{0.028\ \text{m}^3} \times \frac{1.8°\text{F}}{1°\text{C}} = 5737.5\ \frac{\text{kJ}}{\text{h·m}^3\text{·°C}}$$

Question a. The dewpoint temperature is that which corresponds to saturation, and allows obtaining the humidity ratio at the entrance of the device (1), because it does not change with the dry-bulb temperature ($\hat{Y}_1$ =0.024 kg moisture/ kg dry air at 28° and at 65°). On the other hand, the intersection of the 65°C isotherm and the $\hat{Y}_1$ isoline allows determining the operation line of the adiabatic humidifier (corresponding to a wet-bulb temperature of 35°).



Since the statement of the problem says that the air leaves at a relative humidity of 90%, the crossing between this relative humidity line and the operation line of the adiabatic apparatus will indicate both the temperature and the humidity ratio at the exit.

$$T_2 = 36.7\text{°C} \qquad\qquad \hat{Y}_2 = 0.036\ \frac{\text{kg moisture}}{\text{kg dry air}}$$

Question b. The amount of evaporated water will be

$$\hat{Y}_2 - \hat{Y}_1 = 0.036 - 0.024 = 0.012\ \frac{\text{kg moisture}}{\text{kg dry air}}$$

and the mass flow rate of dry air has to be calculated from the volume flow rate which enters the dehumidifier at 338 K as

$$\hat{\mathcal{W}} = \frac{\breve{\mathcal{W}}}{\hat{V}}$$

$$\hat{V} = \left(\frac{1}{\mathfrak{W}_{air}} + \frac{\hat{Y}_1}{\mathfrak{M}_{water}}\right)\frac{RT_1}{P_{tot}}$$

$$\hat{V} = \left(\frac{1}{28.97\frac{\text{g}}{\text{mol-g}}} + \frac{0.024}{18.015\frac{\text{g}}{\text{mol-g}}}\right)\frac{\left(0.082\frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol-g}}\right)(338\ \text{K})}{1\ \text{atm}} = 0.9936\ \frac{\text{L}}{\text{g dry air}}$$

$$\hat{\mathcal{W}} = 1800\ \frac{\text{m}^3\text{moist air}}{\text{h}} \times \frac{1\ \text{kg dry air}}{0.9936\ \text{m}^3\ \text{moist air}} = 18116\ \frac{\text{kg dry air}}{\text{h}}$$

Therefore, the mass flow rate of evaporated water is

$$\left(0.012\ \frac{\text{kg moisture}}{\text{kg dry air}}\right)\left(18116\ \frac{\text{kg dry air}}{\text{h}}\right) = 217.4\ \frac{\text{kg water}}{\text{h}}$$

Question c. According to the differential energy balance

$$\hat{\mathcal{W}}\langle\hat{C}_P\rangle \mathrm{d}T = \mathrm{k}_T \mathrm{a}(T_{sat} - T)\mathrm{d}V_{ap}$$

where the saturation temperature is that which corresponds to the adiabatic line (35°C) and $\langle\hat{C}_P\rangle$ is a specific heat capacity averaged between the two states

$$\hat{C}_{P1} = \hat{C}_{P_{air(65°\mathrm{C})}} + \hat{Y}_1 \hat{C}_{P_{steam(65°\mathrm{C})}}$$

$$\hat{C}_{P2} = \hat{C}_{P_{air(36.7°\mathrm{C})}} + \hat{Y}_2 \hat{C}_{P_{steam(36.7°\mathrm{C})}}$$

From tables VI.1 and VI.2

$$\hat{C}_{P1} = 1.0085\ \frac{\mathrm{kJ}}{\mathrm{kg\ dry\ air{\cdot}K}} + \left(0.024\ \frac{\mathrm{kg\ moisture}}{\mathrm{kg\ dry\ air}}\right)\left(1.924\ \frac{\mathrm{kJ}}{\mathrm{kg\ water{\cdot}K}}\right) = 1.0547\ \frac{\mathrm{kJ}}{\mathrm{kg\ dry\ air{\cdot}K}}$$

$$\hat{C}_{P2} = 1.0074\ \frac{\mathrm{kJ}}{\mathrm{kg\ dry\ air{\cdot}K}} + \left(0.036\ \frac{\mathrm{kg\ moisture}}{\mathrm{kg\ dry\ air}}\right)\left(1.881\ \frac{\mathrm{kJ}}{\mathrm{kg\ water{\cdot}K}}\right) = 1.0437\ \frac{\mathrm{kJ}}{\mathrm{kg\ dry\ air{\cdot}K}}$$

$$\langle\hat{C}_P\rangle = \frac{\hat{C}_{P1} + \hat{C}_{P2}}{2} = \frac{1}{2}\left(1.0547\ \frac{\mathrm{kJ}}{\mathrm{kg\ dry\ air{\cdot}K}} + 1.0437\ \frac{\mathrm{kJ}}{\mathrm{kg\ dry\ air{\cdot}K}}\right) = 1.0492\ \frac{\mathrm{kJ}}{\mathrm{kg\ dry\ air{\cdot}K}}$$

Additionally, having in mind that the area of the apparatus (A) is constant

$$\hat{\mathcal{W}}\langle\hat{C}_P\rangle \mathrm{d}T = \mathrm{k}_T\mathrm{a}(35 - T)A\mathrm{d}h \quad \rightarrow \quad \mathrm{d}h = \frac{\hat{\mathcal{W}}\langle\hat{C}_P\rangle}{A(\mathrm{k}_T\mathrm{a})}\frac{\mathrm{d}T}{(35 - T)}$$

and by integrating the expression between 65ºC and 36.7ºC it is obtained that

$$h = -\frac{\left(18116\ \frac{\mathrm{kg\ aire\ seco}}{\mathrm{h}}\right)\left(1.0492\ \frac{\mathrm{kJ}}{\mathrm{kg\ aire\ seco{\cdot}°C}}\right)}{(2\ \mathrm{m}^2)\left(5737.5\ \frac{\mathrm{kJ}}{\mathrm{h{\cdot}m^3{\cdot}°C}}\right)}\ln\left(\frac{35 - 36.7}{35 - 65}\right) = 4.75\ \mathrm{m}$$

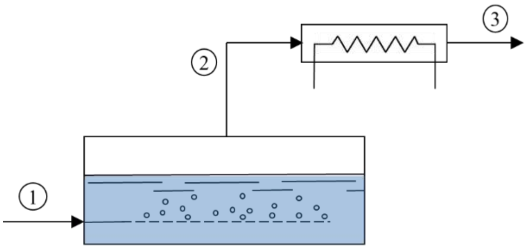
Question d. Let assume that the average specific heat capacity remains constant. If the height is doubled to 9.5 m

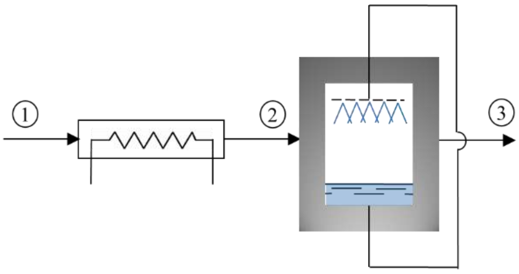
$$-\frac{(18116)(1.0492)}{(2)(5737.5)}\ln\left(\frac{35 - T_2}{35 - 65}\right) = 9.5$$

the temperature of the leaving air would be T_2=35.096ºC.

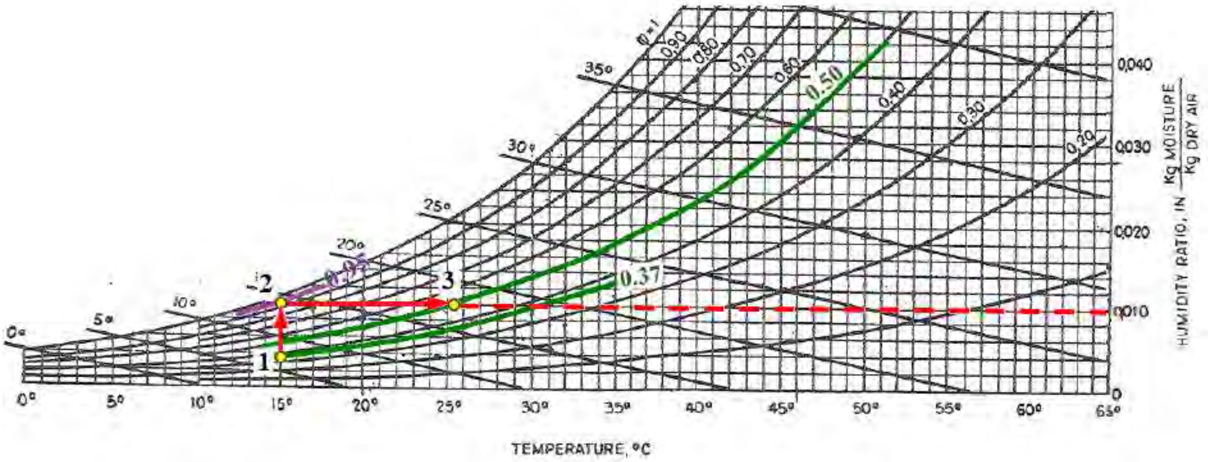
7.13. An air stream of 1500 m^3/h at 15°C and 760 mm Hg with a relative humidity of 37% is passed through a diffuser immersed in a water pond so that its humidity increases isothermally up to a unknown value. After leaving the pond, the stream is heated to 25°C (and its relative humidity decreases to 50%).

- **a) Calculate the humidity reached in the pond.**
- **b) If instead of entering the pond, the air is preheated at constant humidity to an unknown temperature and then adiabatically humidified to 25°C and 50% relative humidity, estimate the preheating temperature.**
- **c) Determine the mass flow of dry air which is treated.**
- **d) Evaluate the energy consumption in both cases.**



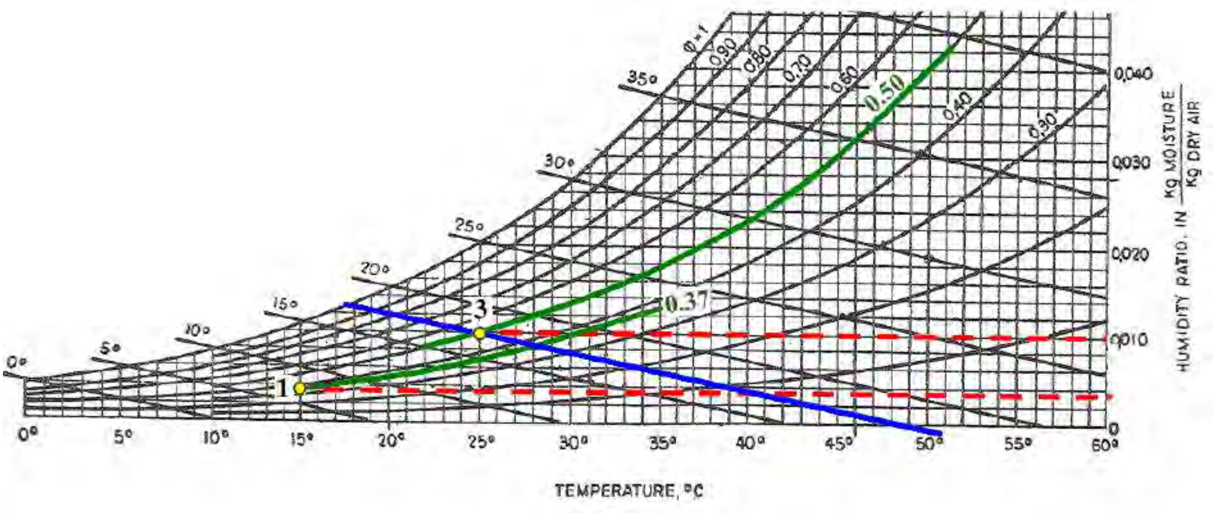


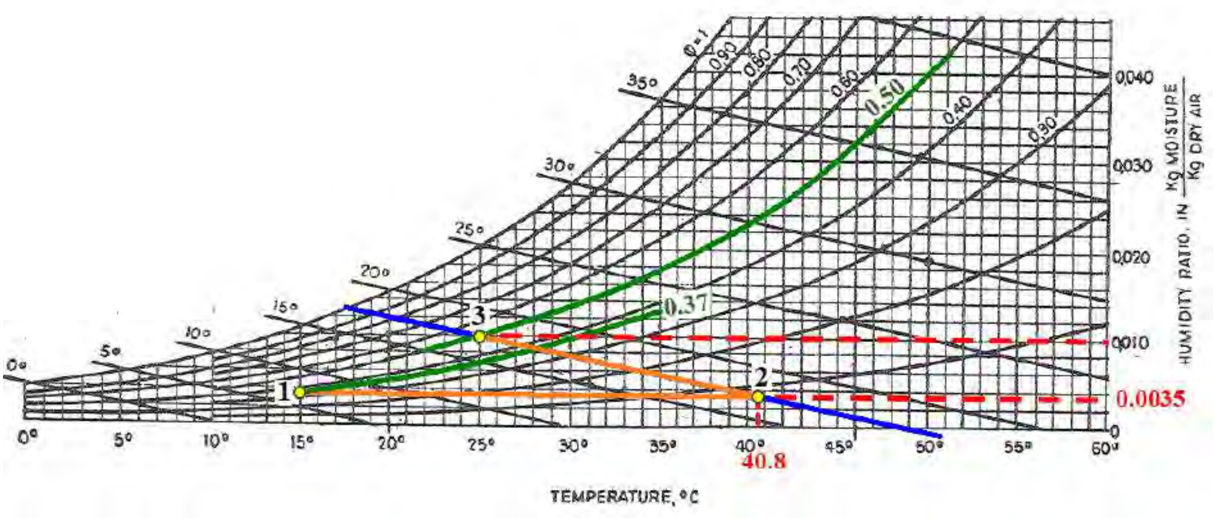
Question a. In figure VII.1 of appendix VII, the relative humidity reached in the pond is graphically found by the intersection between the vertical line corresponding to 15ºC (isotherm) and the horizontal line that passes through point 3 (25ºC and relative humidity of 50%), which is around 95%.



The humidity ratio in the final condition is $\hat{Y}_2 = \hat{Y}_3 = 0.01$ kg moisture/ kg dry air.

Question b. The graphical solution of the mass and energy balances involved in the described process will be the intersection between the adiabatic line that passes through point 3 (25ºC and 50% relative humidity) and the horizontal line that passes through point 1 (15ºC and 37% humidity).





The adiabatic line has to be interpolated (it lies between those of 20º and 15º) and it can be observed that the sought intersection (point 2) takes place at 40.8ºC.

Question c. At point 1, air has a humidity ratio of 0.0035 kg moisture/kg dry air, and it is at an absolute temperature of 15ºC + 273= 288 K. Thus, its specific volume will be

$$\hat{V} = \left(\frac{1}{\mathfrak{W}_{air}} + \frac{\hat{Y}_1}{\mathfrak{M}_{water}}\right)\frac{RT_1}{P_{tot}}$$

$$\hat{V} = \left(\frac{1}{28.97\,\frac{\text{g}}{\text{mol-g}}} + \frac{0.0035}{18.015\,\frac{\text{g}}{\text{mol-g}}}\right)\frac{\left(0.082\,\frac{\text{atm·L}}{\text{K·mol-g}}\right)(288\text{ K})}{(1\text{ atm})} = 0.82\ \frac{\text{L moist air}}{\text{g dry air}}$$

By having in mind that the volume flow rate is of 1500 m^3/h and that 1 L/g= 1 m^3/kg, the mass flow rate will be determined as

$$\hat{\mathcal{W}} = 1500\ \frac{\text{m}^3\text{moist air}}{\text{h}} \times \frac{1\text{ kg dry air}}{0.82\text{ m}^3\text{ moist air}} = 1829.27\ \frac{\text{kg dry air}}{\text{h}}$$

Question d. In both cases the energy consumption will be the same, because

$$q_{31} = q_{21} + q_{32} = \hat{\mathcal{W}}\left(\hat{H}_2 - \hat{H}_1\right) + \hat{\mathcal{W}}\left(\hat{H}_3 - \hat{H}_2\right) = \hat{\mathcal{W}}\left(\hat{H}_3 - \hat{H}_1\right)$$

Therefore

$$\hat{H}_1 = \hat{H}_{air(15℃)} + \hat{Y}_1\hat{H}_{steam(15℃)}$$

$$\hat{H}_3 = \hat{H}_{air(25℃)} + \hat{Y}_3\hat{H}_{steam(25℃)}$$

From tables VI.1 and VI.2

$$\hat{H}_1 = 15.11\ \frac{\text{kJ}}{\text{kg dry air}} + 0.0035\ \frac{\text{kg moisture}}{\text{kg dry air}}\left(2529.19\ \frac{\text{kJ}}{\text{kg water}}\right) = 23.96\,\frac{\text{kJ}}{\text{kg dry air}}$$

$$\hat{H}_3 = 25.19\ \frac{\text{kJ}}{\text{kg dry air}} + 0.01\ \frac{\text{kg moisture}}{\text{kg dry air}}\left(2546.75\ \frac{\text{kJ}}{\text{kg water}}\right) = 50.66\,\frac{\text{kJ}}{\text{kg dry air}}$$

$$q_{31} = \left(1829.27\ \frac{\text{kg dry air}}{\text{h}}\right)\left(50.66\,\frac{\text{kJ}}{\text{kg dry air}} - 23.96\,\frac{\text{kJ}}{\text{kg dry air}}\right) = 48841.51\ \frac{\text{kJ}}{\text{h}}$$

7.14. A mixture of air and carbon tetrachloride at 760 mm Hg and 50°C, with a wet-bulb temperature (T^{sat}) of 40°C passed through a heat exchanger where it is cooled to 10°C. Determine the amount of CCl_4 that condenses if the mixture flow is of 1500 m^3/h in the initial conditions. The vapor pressure of carbon tetrachloride is

***T* (°C)**	**10**	**20**	**30**	**40**	**50**
P_v (mm Hg)	**25**	**91**	**143**	**215.8**	**317.1**

and in this mixture, the following relation is satisfied

$$\frac{\hat{Y}^{sat}-\hat{Y}}{T-T^{sat}}=0.0483\ \frac{1}{^{\circ}\mathrm{C}}$$

being $\hat{Y}^{sat}$ the mass of CCl_4 per kg of dry air at T^{sat}.

The problem is conceptually and phenomenologically analogous to any other of humidification with the typical air + water system, and consequently it can also be treated in an analogous way. The only difference is that the available information is not a psychrometric diagram, but fragmentary data. Thus, section c of reference problem 0.19 establishes that the humidity mass ratio ($\hat{Y}$) and the relative humidity (φ) are related by the expression

$$\tilde{Y}=\frac{\varphi P_{v(\mathrm{CCl_4})}}{P_{tot}-\varphi P_{v(\mathrm{CCl_4})}}\quad\rightarrow\quad\hat{Y}=\frac{\mathfrak{M}_{\mathrm{CCl_4}}}{\mathfrak{M}_{air}}\left(\frac{\varphi P_{v(\mathrm{CCl_4})}}{P_{tot}-\varphi P_{v(\mathrm{CCl_4})}}\right)$$

When φ=1, air is saturated of CCl_4 (and $\hat{Y}=\hat{Y}^{sat}$). By employing the molecular masses of appendix II (28.97 for air and 153.84 for CCl_4) and the vapor pressures listed in the statement of the problem, it is found that

T(°C)	10	20	30	40	50
P_v (mm Hg)	25	91	143	215.8	317.1
$\hat{Y}^{sat}\left(\frac{\mathrm{kg\ CCl_4}}{\mathrm{kg\ dry\ air}}\right)$	0.1806	0.7223	1.2307	2.1058	3.802

By taking into account that this curve gives a $\hat{Y}^{sat}$ = 2.1058 kg CCl_4/ kg dry air at the wet-bulb temperature of 40ºC (T^{sat}), the humidity ratio of the feed (at T=50ºC) will be obtained by means of the adiabatic line as

$$\hat{Y}=\hat{Y}^{sat}-0.0483(T-T^{sat})=2.1058-0.0483\frac{1}{^{\circ}\mathrm{C}}(50^{\circ}\mathrm{C}-40^{\circ}\mathrm{C})=1.6228$$

On the other hand, the specific volume of the mixture at 50ºC+273= 323 K will be

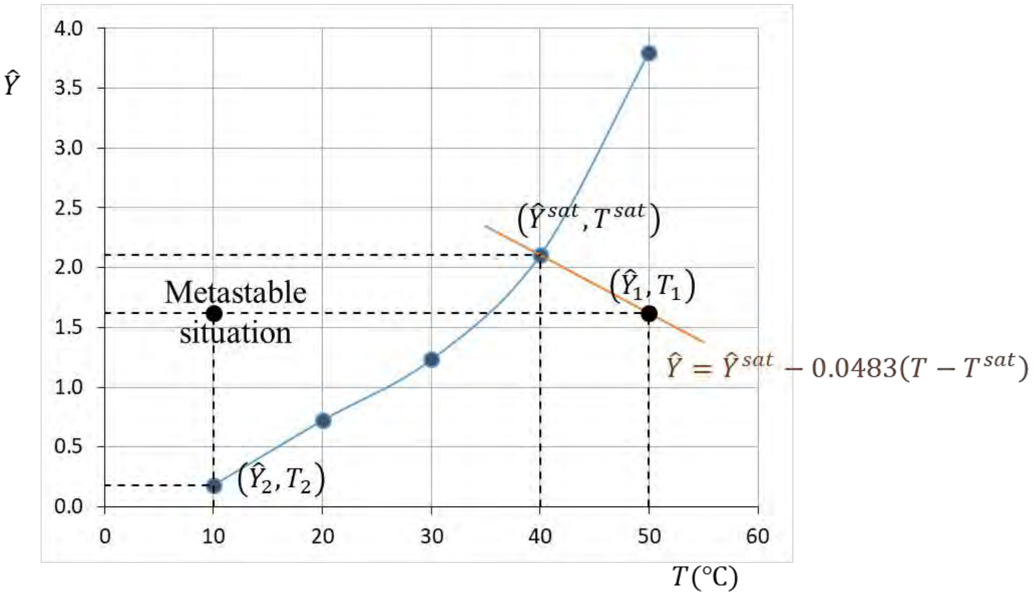
$$\hat{V} = \left(\frac{1}{28.97\,\frac{\text{g}}{\text{mol-g}}} + \frac{1.6628}{153.84\,\frac{\text{g}}{\text{mol-g}}}\right)\frac{\left(0.082\,\frac{\text{atm·L}}{\text{K·mol-g}}\right)(323\text{ K})}{(1\text{ atm})} = 1.2\ \frac{\text{L moist air}}{\text{g dry air}}$$

and therefore, its mass flow rate

$$\hat{\mathcal{W}}_{air} = \frac{\breve{\mathcal{W}}_{air}}{\hat{V}} = \frac{\left(1500\ \frac{\text{m}^3\text{moist air}}{\text{h}}\right)}{\left(1.2\ \frac{\text{m}^3\text{moist air}}{\text{kg dry air}}\right)} = 1250\ \frac{\text{kg dry air}}{\text{h}}$$

The cooling of the mixture to 10ºC will generate a metastable situation, which will split into an air stream saturated of CCl_4 (φ=1.0, $\hat{Y}^{sat}$ = 0.1806 kg CCl_4/kg dry air) and a condensed stream of carbon tetracloride, whose mass flow rate will be

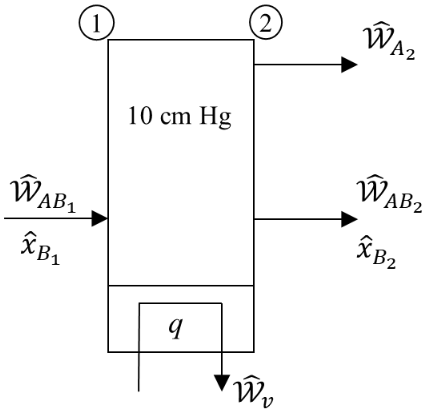
$$\hat{\mathcal{W}}_{\text{CCl}_4} = \left(1250\ \frac{\text{kg dry air}}{\text{h}}\right)\left(1.6228\ \frac{\text{kg CCl}_4}{\text{kg dry air}} - 0.1806\,\frac{\text{kg CCl}_4}{\text{kg dry air}}\right) = 1802.75\ \frac{\text{kg CCl}_4}{\text{h}}$$



7.15. A single-stage evaporator is employed to concentrate a sodium hydroxide solution from 10 to 30% by weight. The feed is at 50ºC and has a flow rate of 1500 kg/h. The absolute pressure in the boiling chamber is of 10 cm Hg and the overall heat transfer coefficient is of 1540 kcal/ (m²·h·ºC), using saturated steam at 102ºC as a heating source. Estimate:

- **a) The flow rate of the concentrated solution and that of the evaporated water.**
- **b) The specific enthalpy of the feed (in kcal/kg).**
- **c) The specific enthalpy of the concentrated solution (in kcal/kg).**
- **d) The specific enthalpy of the evaporated water (in kcal/kg), assuming a constant specific heat capacity of 0.46 cal/(g·ºC) for the vapor.**
- **e) The heat supplied by the condensing steam (in kcal/h).**
- **f) The flow of saturated steam necessary to produce evaporation and the heating area for this operation (in kg/h).**

By the sake of simplicity, the mixture of water + NaOH will be called AB and the evaporated water will be called A. The inlet of the evaporator will be denoted as 1 and the outlet as 2.



Question a. The mass flow rates of these streams can be obtained from macroscopic mass balances

Total mass balance $\widehat{\mathcal{W}}_{AB_1} = \widehat{\mathcal{W}}_{AB_2} + \widehat{\mathcal{W}}_{A_2}$

Partial balance to solute B $\widehat{\mathcal{W}}_{AB_1}\hat{x}_{B_1} = \widehat{\mathcal{W}}_{AB_2}\hat{x}_{B_2}$

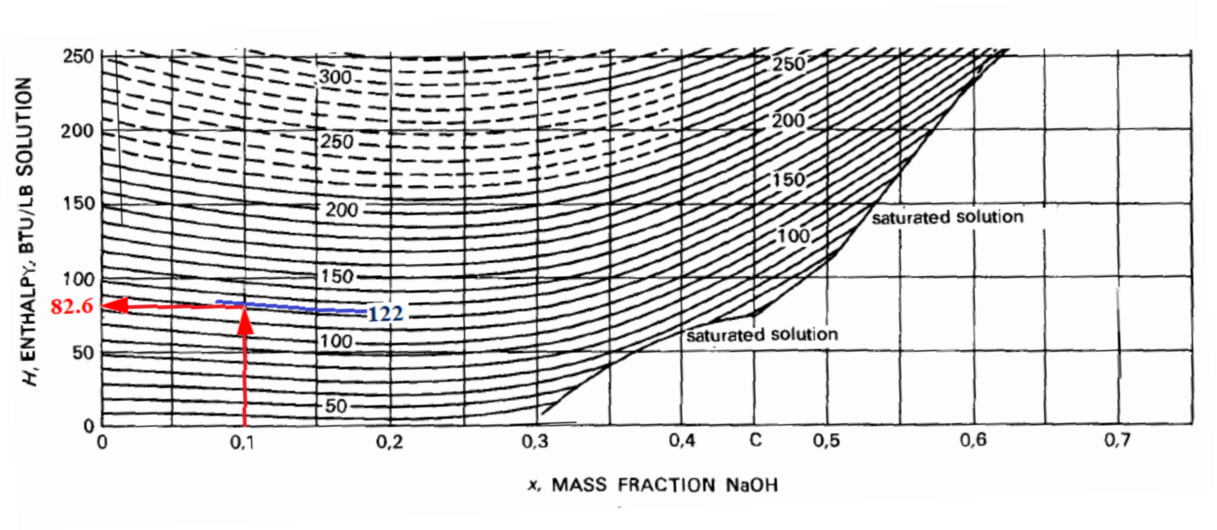
By introducing the available data (from the statement of the problem)

$$\widehat{\mathcal{W}}_{AB_2} = \frac{\widehat{\mathcal{W}}_{AB_1}\hat{x}_{B_1}}{\hat{x}_{B_2}} = \frac{\left(1500\ \frac{\mathrm{kg}}{\mathrm{h}}\right)(0.10)}{0.30} = 500\frac{\mathrm{kg}}{\mathrm{h}}$$

$$\widehat{\mathcal{W}}_{A_2} = \widehat{\mathcal{W}}_{AB_1} - \widehat{\mathcal{W}}_{AB_2} = 1500\ \frac{\mathrm{kg}}{\mathrm{h}} - 500\frac{\mathrm{kg}}{\mathrm{h}} = 1000\frac{\mathrm{kg}}{\mathrm{h}}$$

Question b. To calculate the specific enthalpy of the feed, figures such as VII.2 of appendix VII can be used, but first the temperatures have to be converted to degrees Fahrenheit, which are the ones used in it.

$$T_1(°\mathrm{F}) = 1.8\,T_1(°\mathrm{C}) + 32 = 1.8(50°\mathrm{C}) + 32 = 122°\mathrm{F}$$



By converting the read value to kcal/kg with the factors of appendix I, it is obtained that

$$82.6\,\frac{\mathrm{BTU}}{\mathrm{lb}} \times \frac{0.252\ \mathrm{kcal}}{1\ \mathrm{BTU}} \times \frac{1\ \mathrm{lb}}{0.454\ \mathrm{kg}} = 45.85\,\frac{\mathrm{kcal}}{\mathrm{kg}}$$

Question c. The chamber is at 10 cm Hg (vacuum), or what is the same, at

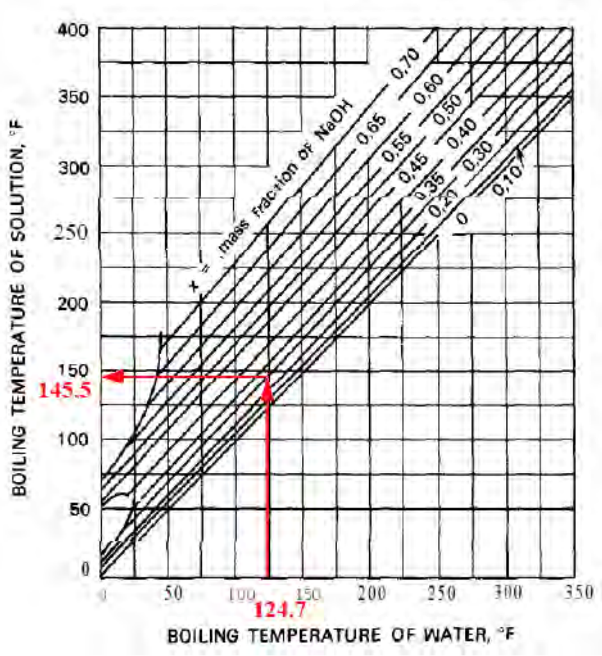
$$10\ \mathrm{cm\ Hg} \times \frac{1\ \mathrm{m\ Hg}}{100\ \mathrm{cm\ Hg}} \times \frac{1.33\ \mathrm{bar}}{1\ \mathrm{m\ Hg}} = 0.133\ \mathrm{bar}$$

For this vapor pressure, interpolation in table VI.1 of appendix VI leads to a boiling temperature of 51.5°C (pure water). However, the presence of solute will cause an ebullioscopic increase, estimable by means of a Dühring diagram (figure VII.3 of appendix VII)

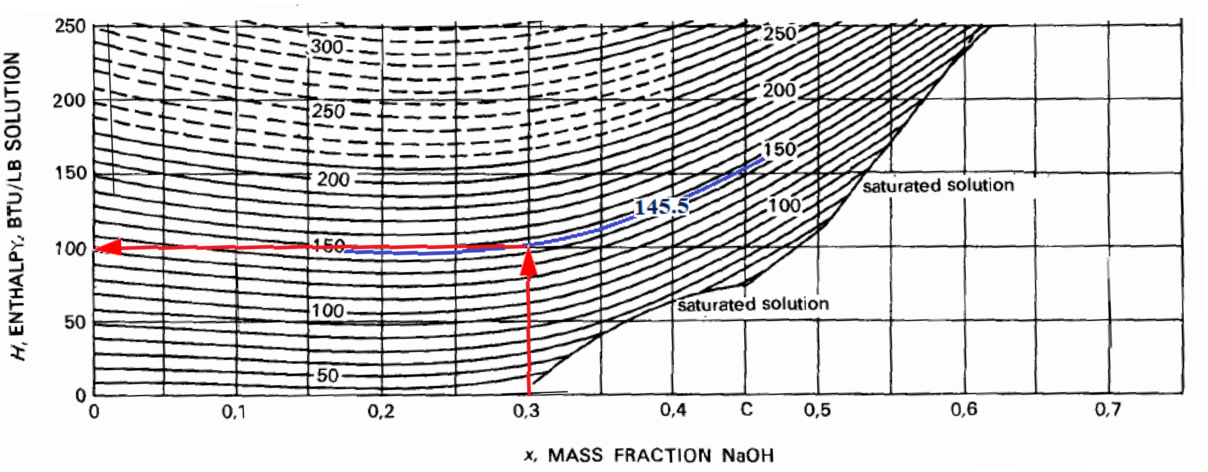
$$T(°\mathrm{F}) = 1.8\,T(°\mathrm{C}) + 32 = 1.8(51.5°\mathrm{C}) + 32 = 124.7°\mathrm{F}$$

The corresponding reading for this temperature and for 30% NaOH gives 145.5°F, which converted to degrees centigrades

$$T_2(°\mathrm{C}) = \frac{T_2(°\mathrm{F}) - 32}{1.8} = \frac{145.5 - 32}{1.8} = 63.05°\mathrm{C}$$



And turning again to figure VII.2 of appendix VII, the enthalpy of the concentrated solution is of 100 BTU/lb.



$$100\ \frac{\text{BTU}}{\text{lb}} \times \frac{0.252\ \text{kcal}}{1\ \text{BTU}} \times \frac{1\ \text{lb}}{0.454\ \text{kg}} = 55.51\,\frac{\text{kcal}}{\text{kg}}$$

Question d. The enthalpy of the evaporated water will be that of the saturated steam at 51.5°C plus superheating to 63.05°C. The one of the saturated steam can be interpolated from table VI.1 of appendix VI, being approximately of 2594 kJ/kg, which converted to kcal/kg with the factors of appendix I gives

$$\widehat{H}_{v(51.5^{\circ}\text{C})}^{sat} = 2594\ \frac{\text{kJ}}{\text{kg}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} \times \frac{0.000239\ \text{kcal}}{1\ \text{J}} = 619.97\ \frac{\text{kcal}}{\text{kg}}$$

and by taking the specific heat capacity provided by the statement of the problem, the requested specific enthalpy will be

$$\widehat{H}_{v(63.05℃)} = \widehat{H}^{sat}_{v(51.5℃)} + \hat{C}_P(63.05℃ - 51.5℃) =$$

$$= 619.97\frac{\text{kcal}}{\text{kg}} + 0.46\frac{\text{kcal}}{\text{kg}\cdot℃}(63.05℃ - 51.5℃) = 625.283\frac{\text{kcal}}{\text{kg}}$$

Question e. In order to calculate the heat flow q, a macroscopic energy balance to the system will be necessary

$$\begin{bmatrix}\text{heat flow}\\ \text{given by the}\\ \text{condensing}\\ \text{vapor}\end{bmatrix} + \begin{bmatrix}\text{energy flow}\\ \text{of the feed}\end{bmatrix} = \begin{bmatrix}\text{energy flow}\\ \text{of the}\\ \text{concentrated}\\ \text{solution}\end{bmatrix} + \begin{bmatrix}\text{energy}\\ \text{flow of the}\\ \text{evaporated}\\ \text{water}\end{bmatrix}$$

$$q \quad + \quad \widehat{W}_{AB_1}\widehat{H}_{AB_1} \quad = \quad \widehat{W}_{AB_2}\widehat{H}_{AB_2} \quad + \quad \widehat{W}_{A_2}\widehat{H}_{A_2}$$

and introducing the data obtained in the previous questions

$$q + \left(1500\ \frac{\text{kg}}{\text{h}}\right)\left(45.85\frac{\text{kcal}}{\text{kg}}\right) = \left(500\frac{\text{kg}}{\text{h}}\right)\left(55.51\frac{\text{kcal}}{\text{kg}}\right) + \left(1000\frac{\text{kg}}{\text{h}}\right)\left(625.283\frac{\text{kcal}}{\text{kg}}\right)$$

so that

$$q = 584263\ \frac{\text{kcal}}{\text{h}}$$

Question f. According to section c of reference problem 0.12, the transferred heat is related to the heating area (A) by

$$q = A\text{k}_T\Delta T$$

where ΔT is the difference between the temperature of the condensing steam (102ºC) and that of the NaOH solution leaving the evaporator (63.05ºC). Moreover, when the steam condenses, this transferred heat will be equal to

$$q = \widehat{W}_v\Delta\widehat{H}_{vap}$$

where $\widehat{W}_v$ is the mass flow rate of steam employed and $\Delta\widehat{H}_{vap}$ is the latent heat of vaporization at 102ºC, calculable by substracting the saturated liquid enthalpy ($\widehat{H}^{sat}_l$=427 kJ/kg) from that of the saturated vapor ($\widehat{H}^{sat}_v$ =2680 kJ/kg). These enthalpies can be interpolated from table VI.1 of appendix VI

$$\Delta\hat{H}_{vap} = \hat{H}_v^{sat} - \hat{H}_l^{sat} = 2680\,\frac{\text{kJ}}{\text{kg}} - 427\,\frac{\text{kJ}}{\text{kg}} = 2253\ \frac{\text{kJ}}{\text{kg}}$$

$$2253\ \frac{\text{kJ}}{\text{kg}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} \times \frac{0.000239\ \text{kcal}}{1\ \text{J}} = 538.47\ \frac{\text{kcal}}{\text{kg}}$$

By using the heat flow q calculated in question **e**

$$A = \frac{q}{\text{k}_T \Delta T} = \frac{\left(584263\ \frac{\text{kcal}}{\text{h}}\right)}{\left(1450\ \frac{\text{kcal}}{\text{m}^2 \cdot \text{h} \cdot ^\circ\text{C}}\right)(102^\circ\text{C} - 63.05^\circ\text{C})} = 10.345\ \text{m}^2$$

$$\hat{\mathcal{W}}_v = \frac{q}{\Delta\hat{H}_{vap}} = \frac{\left(584263\ \frac{\text{kcal}}{\text{h}}\right)}{\left(538.47\ \frac{\text{kcal}}{\text{kg}}\right)} = 1085.04\ \frac{\text{kg}}{\text{h}}$$

7.16. It is necessary to produce 50 t/day of caustic soda in the form of a 70% solution (by weight) through evaporation of a 50% saline solution at 100°C. The evaporator employs steam at 3.4 bar as heating fluid, which leaves the boiler at 11°C below its condensation temperature. The water evaporated in the boiling chamber is liquefied in a counterflow condenser at 38°C (an expected temperature for the boiling of pure water at the operating pressure of the evaporator). Calculate:

a) The flow rate of the feed, of the concentrated solution and of the evaporated water (in kg/h).

b) The specific enthalpy of the feed (in kcal/kg).

c) The specific enthalpy of the concentrated solution (in kcal/kg).

d) The specific enthalpy of the evaporated water (in kcal/kg), assuming a constant specific heat capacity of 0.46 cal/(g·°C) for the vapor.

e) The heat supplied by the condensing steam in the boiler (in kcal/h).

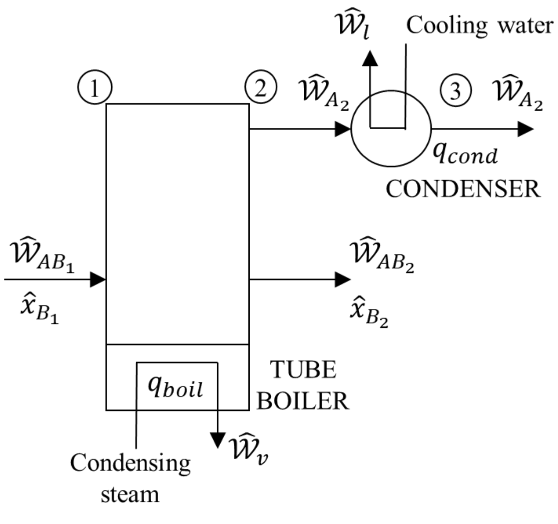
f) The enthalpy change that results from condensing the steam at 3.4 bar in the boiler (in kcal/kg), assuming a constant specific heat capacity of 1 cal/(g·°C) for the liquid.

g) The consumption of condensing steam necessary to carry out the required operation if losses due to faulty insulation are around 7%.

h) The number of tubes through which the steam circulates in the boiler (each one is 2.5 m long and 2.22 cm in outer diameter) if the overall heat transmission coefficient is of 1750 kcal/(h·m^2·°C) and perfect mixing is assumed in both the stream that gives heat and the stream that gains it.

i) The amount of cooling water required in the counterflow condenser (it enters at 10°C and leaves at 20°C) and the exchange surface (average heat transfer coefficient of 500 kcal/(h·m^2·°C)).

Let the term AB be the mixture H_2O + NaOH and let A be the evaporated water.



Question a. It is known that

$$\hat{W}_B = 50\ \frac{\text{t}}{\text{day}} \times \frac{1000\ \text{kg}}{1\ \text{t}} \times \frac{1\ \text{day}}{24\ \text{h}} = 2083.33\ \frac{\text{kg}}{\text{h}}$$

Carrying out mass balances

Total $\hat{W}_{AB_1} = \hat{W}_{AB_2} + \hat{W}_{A_2}$

Partial (to solute B) $\hat{W}_{AB_1}\hat{x}_{B_1} = \hat{W}_{AB_2}\hat{x}_{B_2} = \hat{W}_B$

and introducing the available data in them

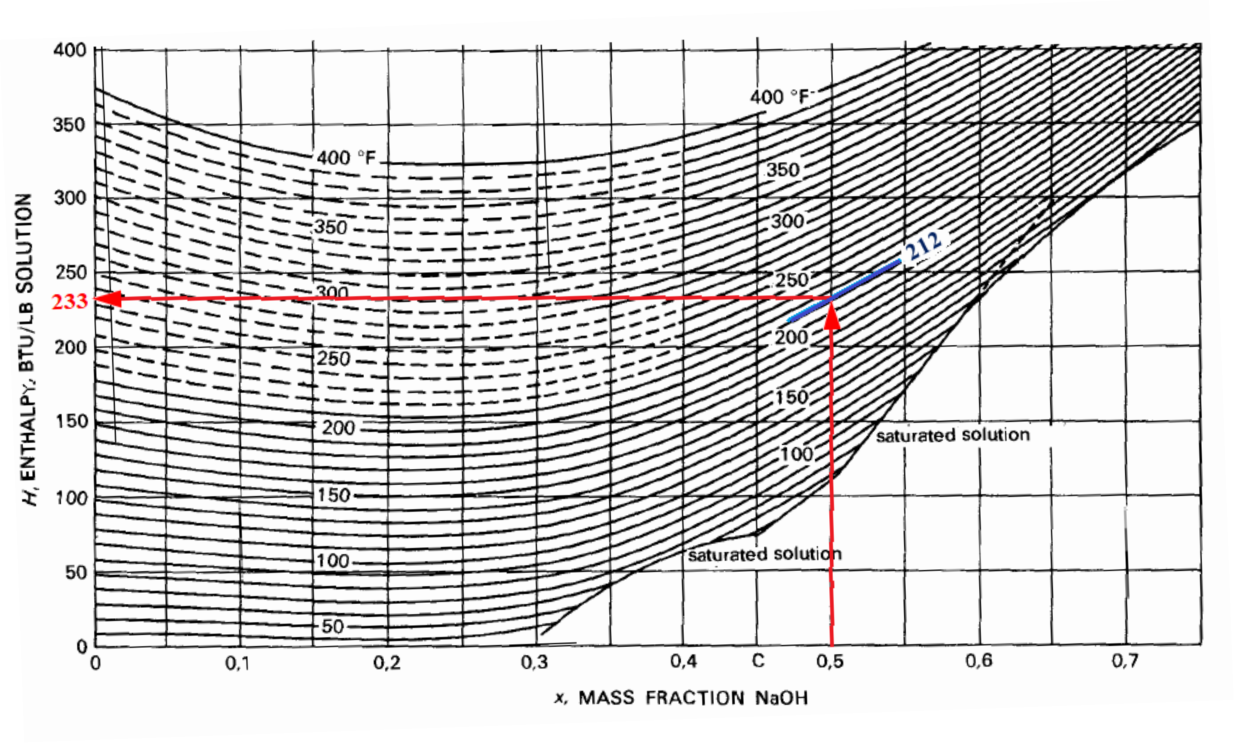
$$\hat{W}_{AB_1} = \frac{\hat{W}_B}{\hat{x}_{B_1}} = \frac{\left(2083.33\ \frac{\text{kg}}{\text{h}}\right)}{0.50} = 4166.66\frac{\text{kg}}{\text{h}}$$

$$\hat{W}_{AB_2} = \frac{\hat{W}_B}{\hat{x}_{B_2}} = \frac{\left(2083.33\ \frac{\text{kg}}{\text{h}}\right)}{0.70} = 2976.18\frac{\text{kg}}{\text{h}}$$

$$\hat{W}_{A_2} = \hat{W}_{AB_1} - \hat{W}_{AB_2} = 4166.66\ \frac{\text{kg}}{\text{h}} - 2976.18\frac{\text{kg}}{\text{h}} = 1190.48\frac{\text{kg}}{\text{h}}$$

Question b. By using figure VII.2 of appendix VII with the feed temperature converted to degrees Fahrenheit

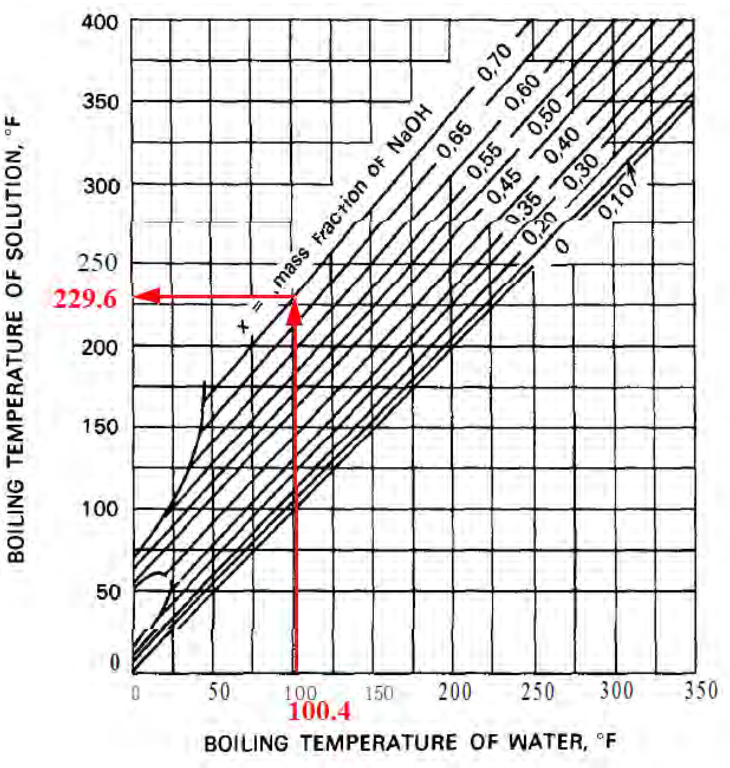
$$T_1(^{\circ}\text{F}) = 1.8\ T_1(^{\circ}\text{C}) + 32 = 1.8(100^{\circ}\text{C}) + 32 = 212^{\circ}\text{F}$$



$$233\,\frac{\text{BTU}}{\text{lb}}\times\frac{0.252\text{ kcal}}{1\text{ BTU}}\times\frac{1\text{ lb}}{0.454\text{ kg}}=129.33\,\frac{\text{kcal}}{\text{kg}}$$

Question c. If pure water boils in the evaporator at 38ºC, the presence of solute will cause a ebullioscopic increase that is estimable by figure VII.3 of appendix VII (Dühring diagram of the system H_2O+NaOH)

$$T(\text{°F}) = 1.8T(\text{°C}) + 32 = 1.8(38\text{°C}) + 32 = 100.4\text{°F}$$

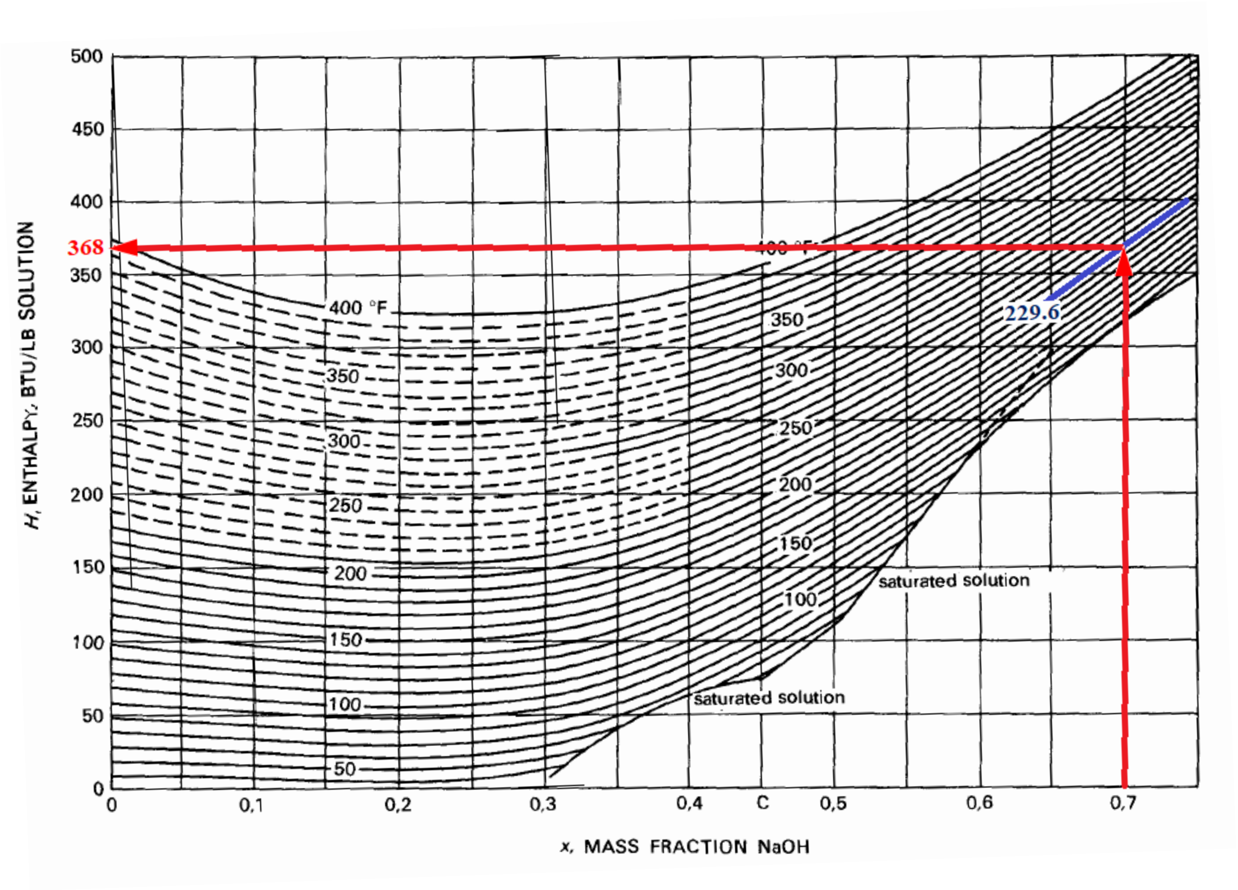


The diagram gives 229.6 ºF, which in the usual way is equivalent to

$$T_2(\text{°C})=\frac{T_2(\text{°F})-32}{1.8}=\frac{229.6-32}{1.8}=109.78\text{°C}$$

and with this temperature and the feed composition, figure VII.2 of appendix VII allows the reading of

$$368\,\frac{\text{BTU}}{\text{lb}}\times\frac{0.252\text{ kcal}}{1\text{ BTU}}\times\frac{1\text{ lb}}{0.454\text{ kg}}=204.26\,\frac{\text{kcal}}{\text{kg}}$$



Question d. The enthalpy of the evaporated water will be that of the saturated vapor at 38ºC plus a superheating until 109.78ºC

$$\widehat{H}_{v(109.78℃)} = \widehat{H}^{sat}_{v(38℃)} + \hat{C}_{Pv}(109.78℃ - 38℃)$$

By interpolating $\widehat{H}^{sat}_{v(38℃)}$ from table VI.1 of appendix VI (2570 kJ/kg), and converting it to kcal/kg

$$2570\ \frac{\text{kJ}}{\text{kg}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} \times \frac{0.000239\ \text{kcal}}{1\ \text{J}} = 614.23\ \frac{\text{kcal}}{\text{kg}}$$

the requested parameter is

$$\widehat{H}_{v(109.78℃)} = 614.23 \frac{\text{kcal}}{\text{kg}} + 0.46 \frac{\text{kcal}}{\text{kg} \cdot ℃}(109.78℃ - 38℃) = 647.25\ \frac{\text{kcal}}{\text{kg}}$$

Question e. From an energy balance to the system and the data of the previous questions

$$\left[\begin{array}{c}\text{heat flow}\\ \text{given by the}\\ \text{steam in}\\ \text{the boiler}\end{array}\right]+\left[\begin{array}{c}\text{energy flow}\\ \text{of the feed}\end{array}\right]=\left[\begin{array}{c}\text{energy flow}\\ \text{of the}\\ \text{concentrated}\\ \text{solution}\end{array}\right]+\left[\begin{array}{c}\text{energy}\\ \text{flow of the}\\ \text{evaporated}\\ \text{water}\end{array}\right]$$

$$q_{boil} \quad + \quad \widehat{W}_{AB_1}\widehat{H}_{AB_1} \quad = \quad \widehat{W}_{AB_2}\widehat{H}_{AB_2} \quad + \quad \widehat{W}_{A_2}\widehat{H}_{A_2}$$

$$q_{boil}+\left(4166.66\frac{\text{kg}}{\text{h}}\right)\left(129.33\frac{\text{kcal}}{\text{kg}}\right)=\left(2976.18\frac{\text{kg}}{\text{h}}\right)\left(204.26\frac{\text{kcal}}{\text{kg}}\right)+\left(1190.48\frac{\text{kg}}{\text{h}}\right)\left(647.25\frac{\text{kcal}}{\text{kg}}\right)$$

the heat flow supplied by the steam in the boiler will be

$$q_{boil}=839578.57\ \frac{\text{kcal}}{\text{h}}$$

Question f. If the vapor condenses at 3.4 bar, its condensation temperature should be 138ºC (table VI.1 of appendix VI), but since the statement of the problem indicates that it leaves the boiler at 11ºC below this temperature (i.e., 127ºC)

$$\Delta\widehat{H}_{lv}=\Delta\widehat{H}_{cond(138^\circ\text{C})}+\hat{C}_{Pl}(127^\circ\text{C}-138^\circ\text{C})$$

being the heat of condensation also calculated from table VI.1 as the enthalpy of the saturated liquid at 138ºC (582 kJ/kg) minus that of the saturated vapor at 138ºC (2730.5 kJ/kg)

$$\Delta\widehat{H}_{cond}=\widehat{H}_l^{sat}-\widehat{H}_v^{sat}=580\frac{\text{kJ}}{\text{kg}}-2730.5\frac{\text{kJ}}{\text{kg}}=-2150.5\ \frac{\text{kJ}}{\text{kg}}$$

$$-2150.5\ \frac{\text{kJ}}{\text{kg}}\times\frac{1000\ \text{J}}{1\ \text{kJ}}\times\frac{0.000239\ \text{kcal}}{1\ \text{J}}=-513.97\ \frac{\text{kcal}}{\text{kg}}$$

so that

$$\Delta\widehat{H}_{lv}=-513.97\frac{\text{kcal}}{\text{kg}}-1.0\frac{\text{kcal}}{\text{kg}\cdot{}^\circ\text{C}}(11^\circ\text{C})=-524.97\frac{\text{kcal}}{\text{kg}}$$

Question g. The heat transferred by the condensing steam is

$$q_{boil}+q_{loss}=-\widehat{W}_v\Delta\widehat{H}_{lv}$$

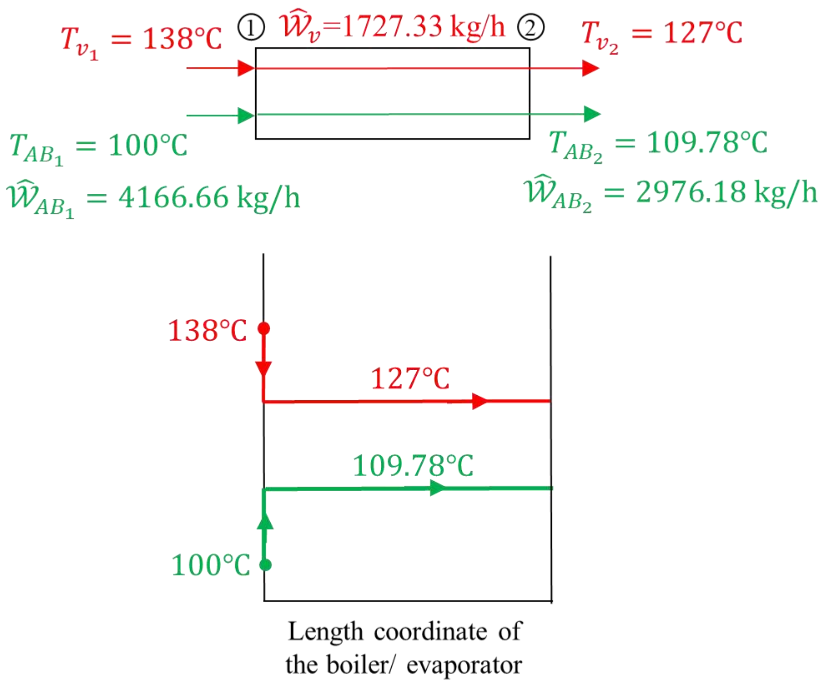
where $\widehat{\mathcal{W}}_v$ is the mass flow rate of the employed condensing steam, $\Delta\widehat{H}_{lv}$ its specific enthalpy change (calculated in the previous question) and q_{loss} the heat flow due to losses (7% of q_{boil}).

$$\widehat{\mathcal{W}}_v = \frac{\left(839578.57\ \dfrac{\text{kcal}}{\text{h}}\right)(1+0.07)}{\left(524.97\dfrac{\text{kcal}}{\text{kg}}\right)} = 1711.24\ \frac{\text{kg}}{\text{h}}$$

Question h. From section c of reference problem 0.12, the heat transferred in the boiler is related with the transfer surface (A) by the equation

$$q_{boil} + q_{loss} = Ak_T\Delta T$$

where k_T is the overall heat transfer coefficient and ΔT is the difference between the temperature of the vapor and that of the NaOH solution. Since the statement of this problem says that there is perfect mixing, when the feed enters the evaporator, it suddenly reaches the temperature of 109.78ºC, and at the moment when the vapor enters the boiler, its temperauture abruptly decreases from 138ºC to 127ºC.



Thus, ΔT= 127–109.78= 17.22ºC and

$$A = \frac{\left(839578.57\ \frac{\text{kcal}}{\text{h}}\right)(1+0.07)}{\left(1750\frac{\text{kcal}}{\text{h}\cdot\text{m}^2\cdot{}^{\circ}\text{C}}\right)(17.22^{\circ}\text{C})} = 29.81\ \text{m}^2$$

Additionally, the surface area of one tube is

$$\pi dL = \pi(0.0222\ \text{m})(2.5\ \text{m}) = 0.174\ \text{m}^2$$

And, obviously, the number of tubes will be the quotient between the total heat exchange surface and the area of a single tube

$$\frac{29.81\ \text{m}^2}{0.174\ \text{m}^2} = 171.3$$

Question i. From an energy balance to the counterflow condenser, the cooling water flow rate ($\widehat{\mathcal{W}}_l$) can be obtained

$$\widehat{\mathcal{W}}_{A_2}\widehat{H}_{A_2} = q_{cond} + \widehat{\mathcal{W}}_{A_2}\widehat{H}^{sat}_{Al(38^{\circ}\text{C})}$$

$$\widehat{\mathcal{W}}_l\hat{C}_{Pl}(20^{\circ}\text{C} - 10^{\circ}\text{C}) = q_{cond}$$

being $\widehat{H}_{A_2}$ the enthalpy of the superheated vapor evaluated in question **d** and $\widehat{H}^{sat}_{Al(38^{\circ}\text{C})}$ that of the saturated liquid at 38ºC, which has to be read in table VI.1 of appendix VI

$$\widehat{H}^{sat}_{Al(38^{\circ}\text{C})} = 160\ \frac{\text{kJ}}{\text{kg}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} \times \frac{0.000239\ \text{kcal}}{1\ \text{J}} = 38.24\ \frac{\text{kcal}}{\text{kg}}$$

$$q_{cond} = \left(1190.48\frac{\text{kg}}{\text{h}}\right)\left(647.25\frac{\text{kcal}}{\text{kg}} - 38.24\frac{\text{kcal}}{\text{kg}}\right) = 725014.23\ \frac{\text{kcal}}{\text{h}}$$

By assuming 1 kcal/(kg·ºC) for the liquid water as in question **f**

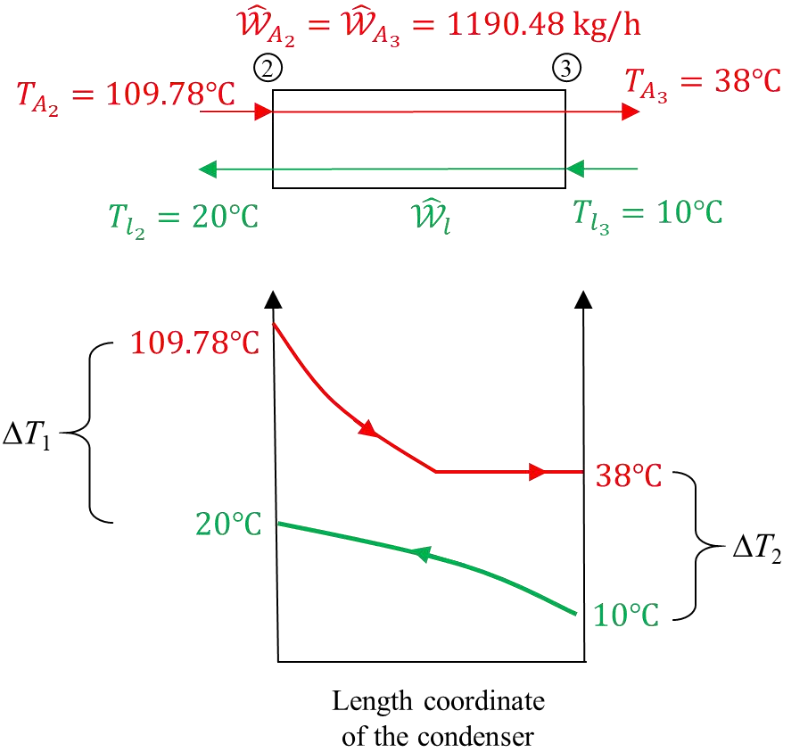
$$\widehat{\mathcal{W}}_l = \frac{\left(725014.23\ \frac{\text{kcal}}{\text{h}}\right)}{\left(1\ \frac{\text{kcal}}{\text{kg}\cdot{}^{\circ}\text{C}}\right)(10^{\circ}\text{C})} = 72501.4\ \frac{\text{kg}}{\text{h}}$$

On the other hand, the surface area of the condenser will be related to the heat flow by means of an equation similar to that of question **h**, with the difference that perfect mixing can no longer be assumed, and therefore the temperature gradient has to be logarithmically averaged between the entrance and the exit of the apparatus.

$$A = \frac{q_{cond}}{k_T \langle \Delta T \rangle_{ln}} = \frac{q_{cond}}{k_T \left\{ \dfrac{\Delta T_2 - \Delta T_3}{\ln\left(\dfrac{\Delta T_2}{\Delta T_3}\right)} \right\}}$$

The attached figure shows that ΔT_2=109.78–20= 89.78ºC and that ΔT_3=38–10= 28ºC; thus

$$A = \frac{\left(725014.23\ \dfrac{\text{kcal}}{\text{h}}\right)}{\left(500\,\dfrac{\text{kcal}}{\text{h}\cdot\text{m}^2\cdot{}^\circ\text{C}}\right)\left\{\dfrac{89.78^\circ\text{C} - 28^\circ\text{C}}{\ln\left(\dfrac{89.78^\circ\text{C}}{28^\circ\text{C}}\right)}\right\}} = 27.34\ \text{m}^2$$

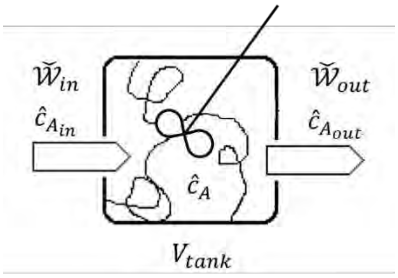


7.17. An amount of 125 kg of common salt is added into a 800 L tank, full of water and perfectly stirred. When the total dissolution of the salt has been achieved, a constant water flow of of 100 L/min is passed through the tank, removing a similar flow of dissolution to keep the level constant.

a) **Is it a continuous or discontinuous, stationary or transitory process?**
b) **How much salt will be removed after 1 h of operation under these conditions?**
c) **After how long will the salt concentration be reduced to one tenth of the initial content?**
d) **Redo the problem in a 800 m^3 tank with a water flow of 10 m^3/min.**

Question a. It is a continuous process in transitory mode.

Question b. To solve the problem, a mass balance of salt in the system has to be carried out



$$\begin{bmatrix}\text{Rate of}\\ \text{entry of A}\\ \text{into the system}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{exit of A}\\ \text{from the system}\end{bmatrix} + \begin{bmatrix}\text{Rate of}\\ \text{generation of A}\\ \text{because reaction}\\ \text{or mass transfer}\end{bmatrix} = \begin{bmatrix}\text{Accumulation}\\ \text{of A}\end{bmatrix}$$

$$\breve{W}_{in}\hat{c}_{A_{in}} - \breve{W}_{out}\hat{c}_{A_{out}} + 0 = \frac{\mathrm{d}M_A}{\mathrm{d}t}$$

and due to the fact that the tank is perfectly stirred and that the level is kept constant, it can be assimilated to the continuous stirred tank reactor (CSTR) model, with a constant volume flow rate ($\breve{W}_{in} = \breve{W}_{out}$), a constant tank volume, no chemical reaction and no mass transfer. Furthermore, the salt concentration in the stream that leaves the tank is the same as that inside the tank ($\hat{c}_{A_{out}}$=$\hat{c}_A$).

$$\breve{W}_{in}\hat{c}_{A_{in}} - \breve{W}_{in}\hat{c}_A = \frac{\mathrm{d}(V_{tank}\hat{c}_A)}{\mathrm{d}t} = V_{tank}\frac{\mathrm{d}\hat{c}_A}{\mathrm{d}t}$$

Since $\hat{c}_{A_{in}}$=0, the integration will give

$$\frac{\breve{W}_{in}}{V_{tank}}(-\hat{c}_A) = \frac{\mathrm{d}\hat{c}_A}{\mathrm{d}t}$$

$$\frac{\breve{\mathcal{W}}_{in}}{V_{tank}}\mathrm{d}t = -\frac{\mathrm{d}\hat{c}_A}{\hat{c}_A} \quad \rightarrow \quad \frac{\breve{\mathcal{W}}_{in}}{V_{tank}}\int_0^t \mathrm{d}t = -\int_{\hat{c}_{A_o}}^{\hat{c}_A}\frac{\mathrm{d}\hat{c}_A}{\hat{c}_A}$$

$$\frac{\breve{\mathcal{W}}_{in}}{V_{tank}}t = -[\ln \hat{c}_A]_{\hat{c}_{A_o}}^{\hat{c}_A} = -\ln\left(\frac{\hat{c}_A}{\hat{c}_{A_o}}\right) \quad \rightarrow \quad \hat{c}_A = \hat{c}_{A_o}\exp\left(-\frac{\breve{\mathcal{W}}_{in}}{V_{tank}}t\right)$$

By takint into account that the initial concentration is

$$\hat{c}_{A_o} = \frac{125\ \mathrm{kg\ salt}}{800\ \mathrm{L}} = 0.156\ \mathrm{kg/L}$$

the concentration after 1 h (60 min) of applying the 100 L/min flow will be

$$\hat{c}_A = \left(0.156\frac{\mathrm{kg}}{\mathrm{L}}\right)\exp\left(-\frac{100\ \mathrm{L/min}}{800\ \mathrm{L}} \times 60\ \mathrm{min}\right) = 8.628 \cdot 10^{-5}\frac{\mathrm{kg}}{\mathrm{L}}$$

and the amount of salt removed

$$\Delta M_A = V_{tank}\left(\hat{c}_{A_o} - \hat{c}_A\right) = (800\ \mathrm{L})\left(0.156\frac{\mathrm{kg}}{\mathrm{L}} - 8.628 \cdot 10^{-5}\frac{\mathrm{kg}}{\mathrm{L}}\right) = 124.73\ \mathrm{kg}$$

Question c. The reduction to one tenth of the initial salt concentration will occur at

$$t = -\frac{V_{tank}}{\breve{\mathcal{W}}_{in}}\ln\left(\frac{\hat{c}_A}{\hat{c}_{A_o}}\right) = -\frac{800\ \mathrm{L}}{\left(100\frac{\mathrm{L}}{\mathrm{min}}\right)}\ln(0.1) = 18.42\ \mathrm{min}$$

Question d. In a 800 m^3 tank and a water flow of 10 m^3/min

$$\hat{c}_{A_o} = \frac{125\ \mathrm{kg\ sal}}{800\ \mathrm{m}^3} = 0.156\ \frac{\mathrm{kg}}{\mathrm{m}^3}$$

$$\hat{c}_A = \hat{c}_{A_o}\exp\left(-\frac{\breve{\mathcal{W}}_{in}}{V_{tank}}t\right) = \left(0.156\frac{\mathrm{kg}}{\mathrm{m}^3}\right)\exp\left(-\frac{10\ \mathrm{m}^3/\mathrm{min}}{800\ \mathrm{m}^3} \times 60\ \mathrm{min}\right) = 0.0737\frac{\mathrm{kg}}{\mathrm{m}^3}$$

$$\Delta M_A = V_{tank}\left(\hat{c}_{A_o} - \hat{c}_A\right) = (800\ \mathrm{m}^3)\left(0.156\frac{\mathrm{kg}}{\mathrm{m}^3} - 0.0737\frac{\mathrm{kg}}{\mathrm{m}^3}\right) = 65.84\ \mathrm{kg}$$

$$t = -\frac{V_{tank}}{\breve{\mathcal{W}}_{in}}\ln\left(\frac{\hat{c}_A}{\hat{c}_{A_o}}\right) = -\frac{800\ \mathrm{m}^3}{\left(10\frac{\mathrm{m}^3}{\mathrm{min}}\right)}\ln(0.1) = 184.2\ \mathrm{min}$$

7.18. A 99 kg mixture of A and B of composition 35% A (by weight) is treated with a solvent C in a single extraction contact. Calculate:

- **a) Minimum and maximum amounts of solvent to be employed.**
- **b) Total masses of the produced phases if 66 kg of solvent C are employed.**
- **c) Percentage of A separated in the extracted product.**

Equilibrium data (percentage by weight)

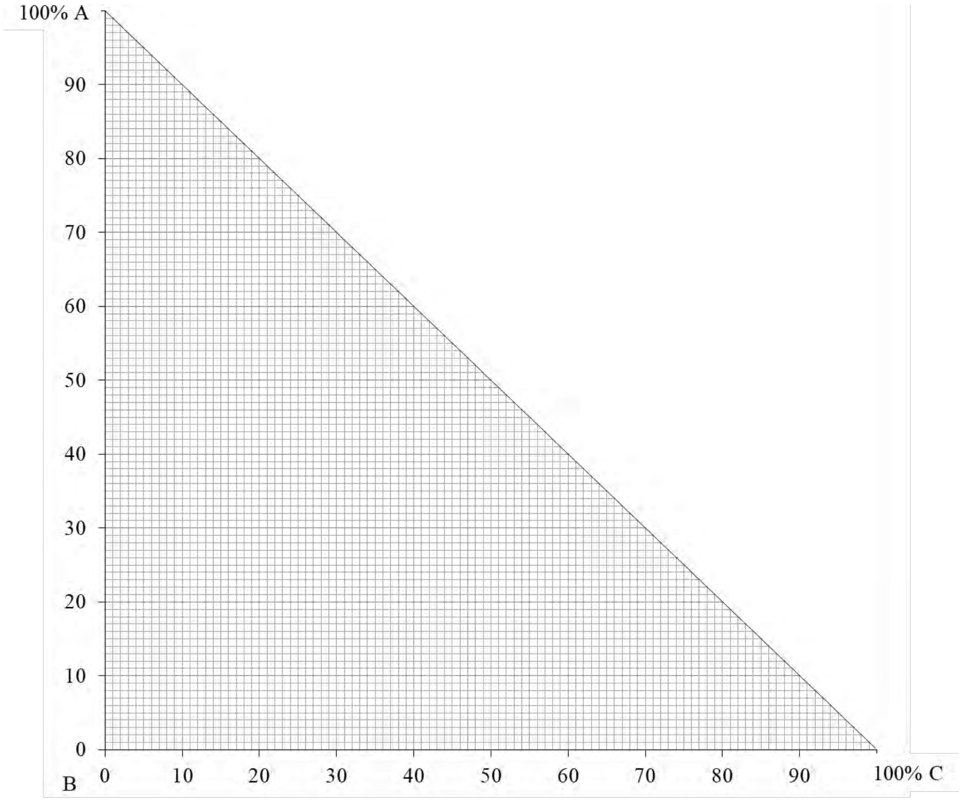
% A	% C	% B
0	98.3	1.7
4.6	93.2	2.2
18.95	77.3	3.75
24.4	71	4.6
28.9	65.5	5.6
37.6	54.7	7.7
43.2	46.2	10.6
47	38.3	14.7
48.3	32.8	18.9
48.4	27.4	24.2
46.3	20.1	33.6
42.7	12.4	44.9
30.9	5.01	64.09
20.9	3.23	75.87
3.73	2.12	94.15

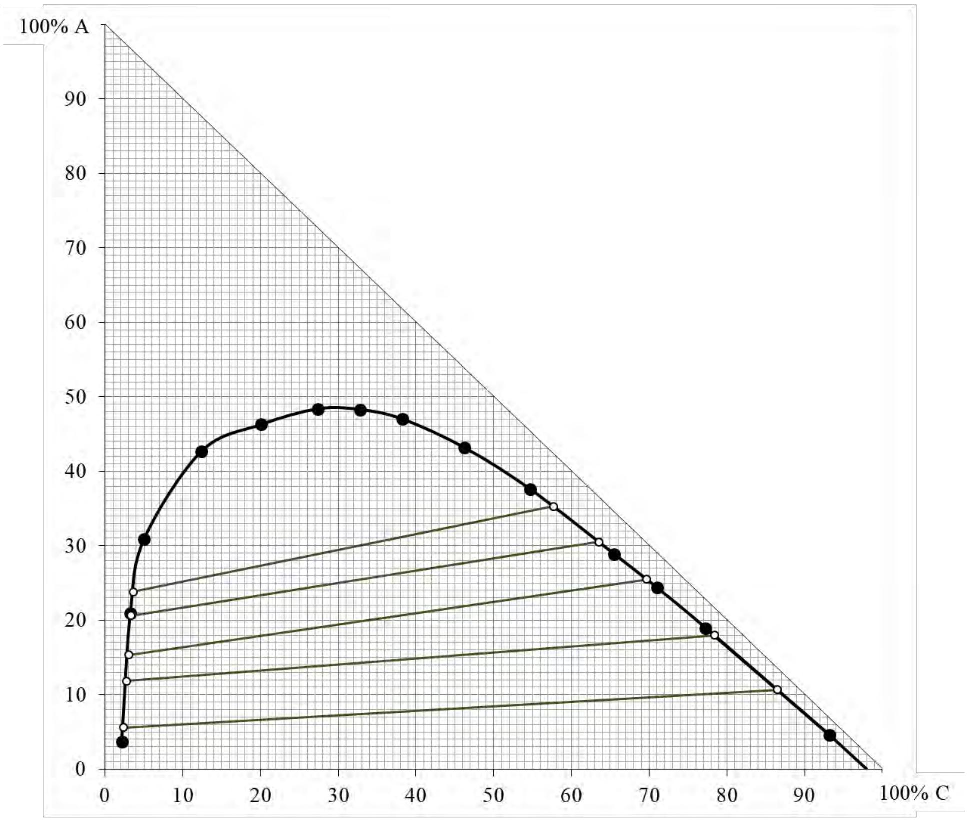
Equilibrium compositions that determine tie lines (% by weight as well)

C-enriched phase			B-enriched phase		
% A	% C	% B	% A	% C	% B
10.66	86.5	2.84	5.58	2.4	92.02
18.0	78.4	3.6	11.83	2.75	85.42
25.5	69.7	4.8	15.35	3.0	81.65
30.5	63.5	6.0	20.6	3.3	76.1
35.3	57.5	7.0	23.8	3.6	72.6

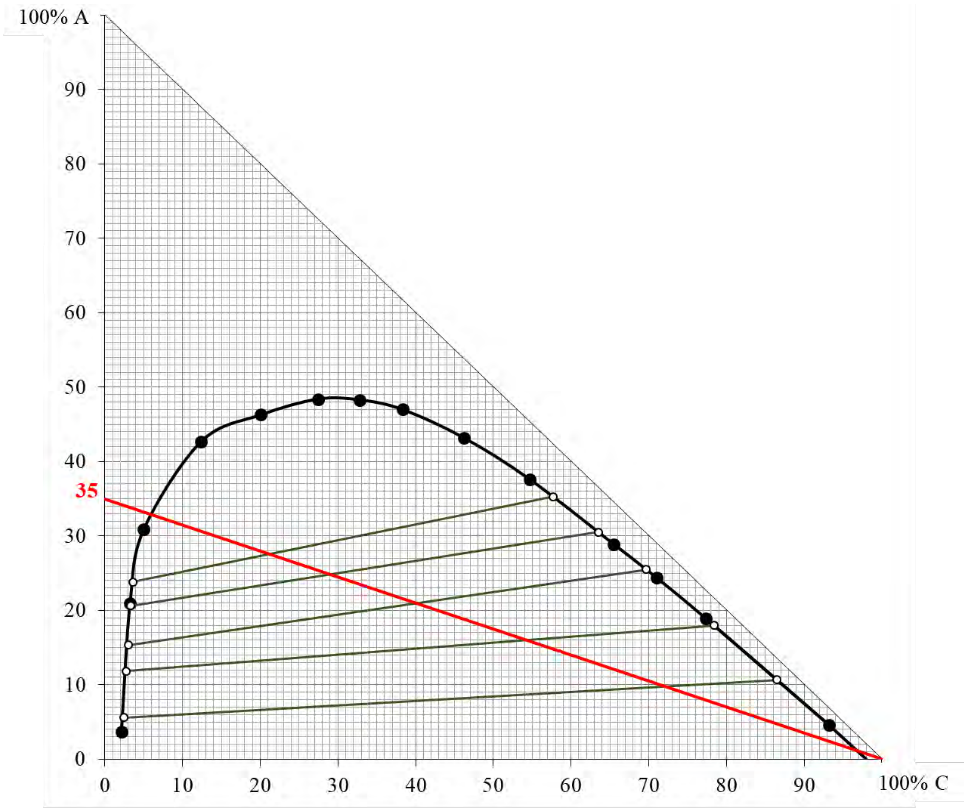
It is a liquid-liquid extraction and its resolution has to be carried out by means of the ternary diagrams explained in reference problem 0.21.

First, the triangle is represented, placing the 100% of the substance of interest (A) at its upper corner and the 100% of solvent (C) at its lower right corner. Then, with the data in the statement of the problem, the equilibrium curve and the tie lines are drawn.

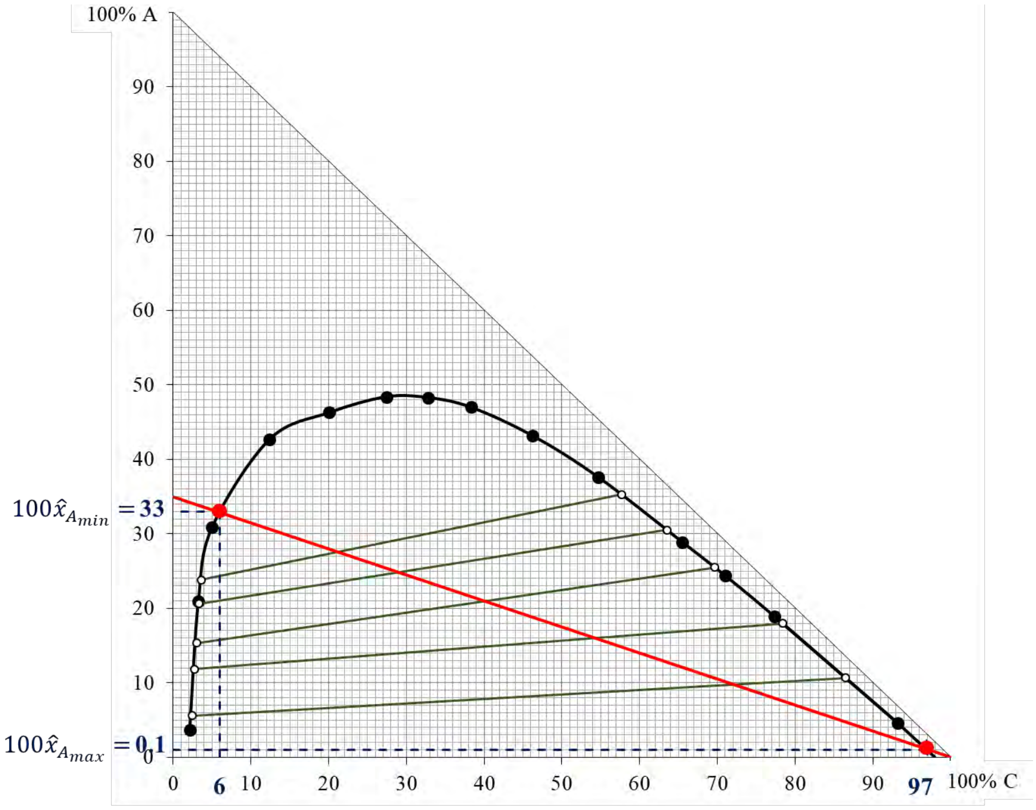




Finally, the percentage of A in the binary mixture is placed on the vertical axis (35%) and this point is joined with the vertex of 100% C. This red line represents the geometric location of the compositions of all ternary mixtures generated from the binary one with 35% by weight of A.



Question a. Since the objective is the separation into two phases (one enriched in C and the other in B), the maximum and minimum amount of solvent will be those in which the line that joins 35% of A and 100% of C intersects with the equilibrium curve, as follow



By calling M_0 to the mass of the initial binary solution, $\hat{x}_{A0}$ to the mass fraction of A and M_C to the mass of solvent added, the mass balance in any case indicates that

$$\begin{bmatrix}\text{Mass of A in}\\ \text{the initial}\\ \text{solution}\end{bmatrix} = \begin{bmatrix}\text{Mass of A in the}\\ \text{mixture of solution}\\ \text{and solvent}\end{bmatrix} \qquad [1]$$

The red line intersects the equilibrium curve for the first time in a mixture whose composition of A is 33%; thus

$$M_0\hat{x}_{A0} = \left(M_0 + M_{C_{min}}\right)\hat{x}_{A_{min}}$$

$$(99\text{ kg initial})\left(\frac{35\text{ kg A}}{100\text{ kg initial}}\right) = \left(99\text{ kg initial}+M_{C_{min}}\right)\left(\frac{33\text{ kg A}}{100\text{ kg mixture}}\right)$$

$$M_{C_{min}} = \frac{(99\text{ kg})(0.35)}{0.33} - 99\text{ kg} = 6\text{ kg}$$

and the last intersection tooks place in a mixture whose composition of A (within the reading error) is 1%.

$$M_0\hat{x}_{A0} = \left(M_0 + M_{C_{max}}\right)\hat{x}_{A_{max}}$$

$$(99\text{ kg initial})\left(\frac{35\text{ kg A}}{100\text{ kg initial}}\right) = \left(99\text{ kg initial}+M_{C_{max}}\right)\left(\frac{1\text{ kg A}}{100\text{ kg mixture}}\right)$$

$$M_{C_{max}} = \frac{(99\text{ kg})(0.35)}{0.01} - 99\text{ kg} = 3366\text{ kg}$$

Question b. By applying equation [1] when M_C= 66 kg, it is obtained that

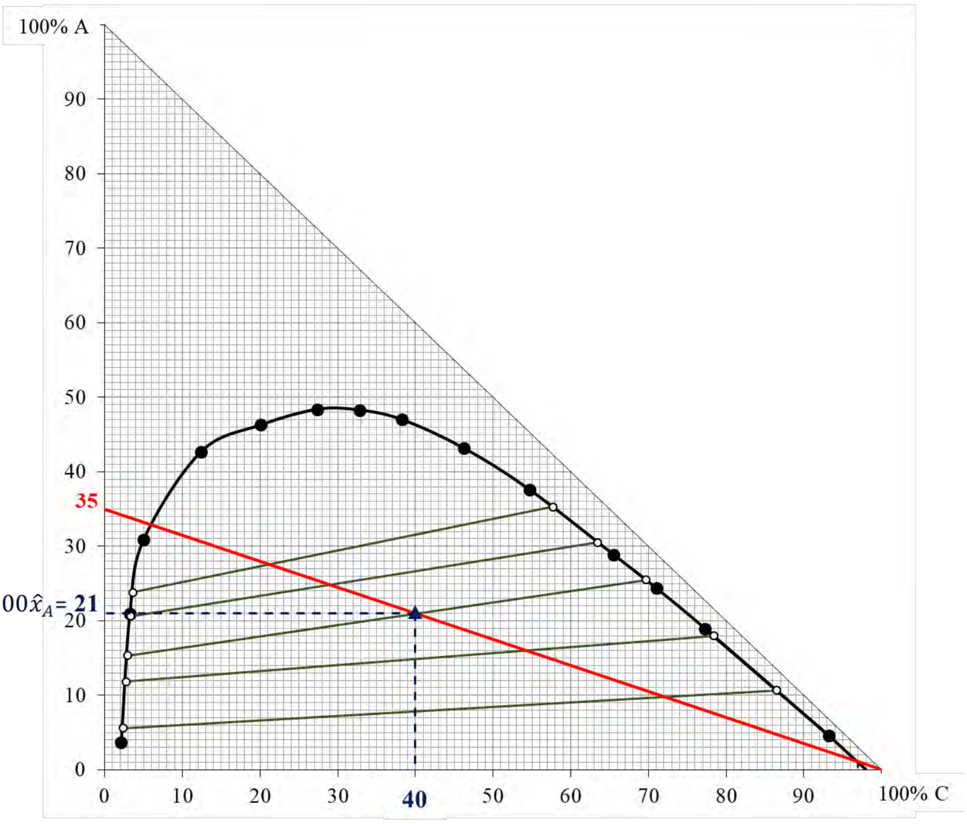
$$M_0\hat{x}_{A0} = (M_0 + M_C)\hat{x}_A$$

$$(99\text{ kg initial})\left(\frac{35\text{ kg A}}{100\text{ kg initial}}\right) = (99\text{ kg initial}+66\text{ kg C})\hat{x}_A$$

$$\hat{x}_A = \frac{(99\text{ kg})(0.35)}{99\text{ kg} + 66\text{ kg}} = 0.21$$

If this composition of A is placed on the red line, it is seen that it corresponds to a value $\hat{x}_C$=0.4 and falls on a tie line given by the statement of the problem, the one whose ends are

C-enriched phase			B-enriched phase		
% A	% C	% B	% A	% C	% B
25.5	69.7	4.8	15.35	3.0	81.65



Now, for the sake of simplicity, the solvent-enriched phase will be called "phase I" and the B-enriched phase will be denoted as "phase II" so that their respective masses will be M_I and M_{II}. The total mass balance establishes that

$$\begin{bmatrix}\text{Total mass of the}\\ \text{mixture of solution}\\ \text{and solvent}\end{bmatrix} = \begin{bmatrix}\text{Mass of the}\\ \text{C-enriched phase}\end{bmatrix} + \begin{bmatrix}\text{Mass of the}\\ \text{B-enriched phase}\end{bmatrix}$$

$$M_0 + M_C = M_I + M_{II}$$

$$99 \text{ kg initial} + 66 \text{ kg C} = M_I + M_{II}$$

and the partial mass balance to compound A indicates that

$$\begin{bmatrix}\text{Mass of A in the total mixture}\\ \text{of solution and solvent}\end{bmatrix} = \begin{bmatrix}\text{Mass of A in the}\\ \text{C-enriched phase}\end{bmatrix} + \begin{bmatrix}\text{Mass of A in the}\\ \text{B-enriched phase}\end{bmatrix}$$

$$(M_0 + M_C)\hat{x}_A = M_I\hat{x}_{I_A} + M_{II}\hat{x}_{II_A}$$

$$(\text{99 kg initial+66 kg C})\left(\frac{\text{21 kg A}}{\text{100 kg mixture}}\right) = M_I\left(\frac{\text{25.5 kg A}}{\text{100 kg phase I}}\right) + M_{II}\left(\frac{\text{15.35 kg A}}{\text{100 kg phase II}}\right)$$

which generates a system of linear equations, whose solutions are M_I=91.85 kg and M_{II}=73.15 kg.

Question c. The amount of A recovered in phase I is

$$M_{I_A} = M_I\hat{x}_{I_A} = (\text{91.85 kg phase I})\left(\frac{\text{25.5 kg A}}{\text{100 kg phase I}}\right) = \text{23.42 kg A}$$

By taking into account that the initial amount of A in the binary solution was

$$M_{A0} = M_0\hat{x}_{A0} = (\text{99 kg initial})\left(\frac{\text{35 kg A}}{\text{100 kg initial}}\right) = \text{34.65 kg A}$$

the parameter requested by the statement of the problem takes a value of

$$\text{Recovery} = \frac{M_{I_A}}{M_{A0}} \times 100 = \frac{\text{23.42 kg}}{\text{34.65 kg}} \times 100 = 67.6\%$$

SYMBOLS

ROMAN AND GREEK LETTERS, SUPERSCRIPTS AND SUBSCRIPTS

Roman letters

A	Surface area
a	Parameter of the Van der Waals equation of state
a	Specific area
b	Parameter of the Van der Waals equation of state
C	Heat capacity; C_P, at constant pressure; C_V, at constant volume
c	Concentration
cte	Generic constant
D	Molecular diffusivity
d	Generic diameter
E	Energy
F	Helmholtz free energy
$\mathbb{F}$	Force
f()	Generic function
f	Fugacity
G	Gibbs free energy
$\mathbb{g}$	Gravitational acceleration
H	Enthalpy
$\mathcal{H}$	Henry's constant
h	Height
J	Flow density (flow rate per unit area in Laplace coordinates)
$\mathbb{Ky}$	Dimensionless conversion factor
$\mathbb{ky}$	Dimensionless conversion factor
k_M	Mass transfer coefficient; $\mathrm{k}_{M(g)}$, in the gas phase; $\mathrm{k}_{M(l)}$, in the liquid phase; $\mathrm{k}_{M(gl)}$, in the two phases
k_T	Heat transfer coefficient
k_v	Momemtum transfer coefficient
k	Boltzman constant=(R/N_{av})
L	Length
M	Mass
$\widetilde{\mathbb{M}}$	Molarity
$\mathfrak{M}$	Molar mass
m	Molecular mass ($\mathfrak{M}/N_{av}$)
$\mathbb{m}$	Molality
n	Number of moles
N_{av}	Avogadro number ($6.023 \cdot 10^{23}$ particles/mol-g)
$\mathcal{N}$	Number of moles transferred per unit time
P	Pressure
$\mathscr{p}$	Power or work flow
Q	Heat
q	Heat flow
$\mathbb{q}$	Heat flow density (heat flow per unit area)
R	Universal gas constant
S	Entropy
T	Temperature
t	Time
U	Internal energy
$\mathbb{u}$	Unities

V	Volume
v	Velocity
W	Work
$\mathcal{W}$	Flow
X	Cartesian coordinate or variable
X	Mass or mole ratio (in the liquid phase)
x	Mass or mole fraction (in the liquid phase)
$\mathbb{x}$	Quantity
Y	Cartesian coordinate or variable
Y	Mass or mole ratio (in the vapor phase)
y	Mass or mole fraction (in the vapor phase)
Z	Cartesian coordinate or variable
z	Compressibility factor

Greek letters

α	Temperature interval
β	Intercept (temperature scale)
γ	Quotient between C_P and C_V
Δ_T, Δ_P, Δ_V	Group contributions of the Lydersen equations
δ	Boundary layer thickness
ε^{LJ}	Characteristic energy of the Lennard-Jones potential
η	Viscosity
Θ	Thermometric magnitude
λ	Thermal conductivity
μ	Chemical potential
ρ	Density
ξ_0, ξ_1, ξ_2, ξ_3, ξ_4	Empirical constants (in equations of the specific heat capacity)
σ	Characteristic diameter of the hard-sphere or Lennard-Jones potentials
τ	Shear stress
υ	Kinematic viscosity
φ	Relative humidity
Ω	Collison integral (Lennard-Jones potential); Ω_η, for the viscosity; Ω_λ, for the thermal conductivity; Ω_D, for the diffusivity
ω_M, ω_L, ω_T, ω_t	Real numbers (dimensional analysis)
Ψ	Correction functions when $z_c \neq 0.27$; Ψ_z, for the compressibility factor; Ψ_H, for the enthalpy departure; Ψ_U, for the internal energy departure; Ψ_S, for the entropy departure

Superscripts

*	Ideal behavior of a real substance
e-c	Expansion-compression
eq	Equilibrium
fl	Flow
HS	Hard-sphere
int	Interphase
LJ	Lennard-Jones
sat	Saturation

Subscripts

A,B,C	Generic substances
AB	Binary mixture of substances A and B
b	Referred to normal boiling conditions
c	Referred to critical point conditions
kin	Kinetic
g	Referred to gas phase
i, j	Generic elements of a mixture, sequence or series
l	Referred to liquid phase
pot	Potential
r	Reduced property
rad	Radiation
s	Referred to solid phase
sol	Solidification
t	Referred to triple point conditions
tot	Total
v	Referred to vapor phase
vap	Vaporization

APPENDICES

DATA

Tables and diagrams (from the Bibliography) used to solve the original problems here proposed

In the academic and scientific field, it is a well-known fact that the reference to the books of other authors plays a role of mutual benefit. On the one hand, whoever cites a previous work uses it as a tacit support from an authorized source. On the other hand, those who are cited receive the express recognition of the person who cites, and their work is diffused in other complementary scenarios.

Unlike commercial patents or other property rights, the use and diffusion of teaching and learning materials is a less regulated field, and rests mostly on responsibility of the parties and on good practices. Such is the case of transcribing, copying, using and developing (mostly without taxes) concepts, theories, models, physicochemical constants, mnemonic rules, correlations, estimation equations, operators, algorithms, nomograms, data tables, charts, images... in short, scientific knowledge.

With this regard, our objective has been (and will continue to be so while the edition of this monograph is active) to add to the citation not only a consent that is presupposed, but also the proof of this consent by the owner of the intellectual property. This has been possible when the publishers have cordially responded to us during the last two years, but in three cases it has not been possible, because the publishing houses have ceased to exist, the writers have died, and their work centers were not able to provide us with any other closer contact.

Since this textbook is primarily focused on the training of students, we have been very aware of the aforesaid words: they are an express declaration of intentions in an area in which the irregular reproduction of information has become a poor habit.

Thanks to all the authors whose contributions are included in these appendices and to all those whose magisterium, explicit or implicit here, has supported the specialization of the signing authors for years.

APPENDIX I. UNIT CONVERSION

Universal gas constant

$$R = 0.082 \frac{\mathrm{atm \cdot L}}{\mathrm{K \cdot mol\text{-}g}} = 8.314 \frac{\mathrm{J}}{\mathrm{K \cdot mol\text{-}g}} = 1.9872 \frac{\mathrm{cal}}{\mathrm{K \cdot mol\text{-}g}} = 10.7316 \frac{\mathrm{psi \cdot ft^3}}{\mathrm{°R \cdot mol\text{-}lb}}$$

Boltzman constant

$$k = 1.362 \cdot 10^{-25} \frac{\mathrm{atm \cdot L}}{\mathrm{K}} = 1.38 \cdot 10^{-23} \frac{\mathrm{J}}{\mathrm{K}} = 3.297 \cdot 10^{-24} \frac{\mathrm{cal}}{\mathrm{K}}$$

Gravitational acceleration

$$g = 9.80665 \frac{\mathrm{m}}{\mathrm{s^2}} = 1.27094 \cdot 10^8 \frac{\mathrm{m}}{\mathrm{h^2}} = 32.174 \frac{\mathrm{ft}}{\mathrm{s^2}} = 4.16975 \cdot 10^8 \frac{\mathrm{ft}}{\mathrm{h^2}}$$

CONVERSION OF THERMOMETRIC READINGS

	T(°C)	T(°F)	T(K)	T(°R)
T(°C)	T(°C)	$\frac{T(°\mathrm{F}) - 32}{1.8}$	T(K) + 273	$\frac{T(°R) - 492}{1.8}$
T(°F)	1.8T(°C) + 32	T(°F)	1.8T(K) – 460	T(°R) – 460
T(K)	T(°C) + 273	$\frac{T(°\mathrm{F}) - 32}{1.8} + 273$	T(K)	$\frac{T(°R)}{1.8}$
T(°R)	1.8T(°C) + 492	T(°F) + 460	1.8 T(K)	T(°R)

TEMPERATURE INTERVALS

	°C	°F	K	°R
°C	°C	1.8°F	K	1.8°R
°F	$\frac{°\mathrm{C}}{1.8}$	°F	$\frac{\mathrm{K}}{1.8}$	°R
K	°C	1.8°F	K	1.8°R
°R	$\frac{°\mathrm{C}}{1.8}$	°F	$\frac{\mathrm{K}}{1.8}$	°R

MASS

	kg	U.T.M	pound	slug	ton(short)	ton(large)
kg	1	0.102	2.2	0.068	$1.102{\cdot}10^{-3}$	$9.84{\cdot}10^{-4}$
U.T.M	9.8	1	21.6	0.671	0.0108	$9.64{\cdot}10^{-3}$
pound	0.454	0.046	1	0.031	$5{\cdot}10^{-4}$	$4.5{\cdot}10^{-4}$
slug	14.605	1.489	32.17	1	0.0160	0.0143
ton(short)	907.2	92.6	2000	62.5	1	0.892
ton(large)	1016	103.7	2240	70	1.120	1

LENGTH

	inche	meter	foot	yard	mile
inche	1	0.0254	0.0833	0.0276	$1.57{\cdot}10^{-5}$
meter	39.37	1	3.28	1.09	$6.2{\cdot}10^{-4}$
foot	12	0.3048	1	0.33	$1.8{\cdot}10^{-4}$
yard	36	0.9144	3	1	$5.6{\cdot}10^{-4}$
mile	63358.14	1609.3	5279.85	1760	1

VOLUME

	in^3	L	m^3	ft^3	gal (USA)
in^3	1	0.00164	$1.63{\cdot}10^{-5}$	$5.78{\cdot}10^{-4}$	$4.3{\cdot}10^{-3}$
L	61.056	1	10^{-3}	0.035	0.264
m^3	$6.105{\cdot}10^{4}$	1000	1	35.3	264
ft^3	1728.5	28.31	0.028	1	7.485
gal (USA)	231	3.785	0.0038	0.134	1

FORCE

	Newton	kg$_f$	poundal	lb$_f$
Newton	1	0.1020	7.219	0.224
kg$_f$	9.8	1	70.8	2.2
poundal	0.138	0.014	1	0.031
lb$_f$	4.45	0.454	32.7	1

PRESSURE

	bar	kg$_f$/cm^2	atm	m Hg	in Hg	m H$_2$O	lb$_f$/ft^2	MPa
bar	1	1.02	0.987	0.750	29.5	10.2	2090	0.1
kg$_f$/cm^2	0.981	1	0.968	0.736	29	10.0	2050	0.0981
atm	1.013	1.03	1	0.761	29.9	10.3	2120	0.1013
m Hg	1.33	1.36	1.32	1	39.4	13.6	2780	0.133
in Hg	0.0339	0.0345	0.0334	0.0254	1	0.346	70.7	0.00339
m H$_2$O	0.0980	0.0999	0.0967	0.0735	2.89	1	205	0.0098
lb$_f$/ft^2	0.000479	0.000487	0.000473	0.000359	0.0141	0.00489	1	$47.9\cdot10^{-6}$
MPa	10	10.2	9.87	7.50	2.95	102	20900	1

HEAT, ENERGY, WORK

	J	kg$_f$·m	lb$_f$·ft	kW·h	atm·L	kcal	BTU	erg
J	1	0.102	0.738	$2.78\cdot10^{-7}$	0.009987	0.000239	0.000948	10^{7}
kg$_f$·m	9.8	1	7.23	$2.74\cdot10^{-6}$	0.0968	0.00234	0.00930	$9.8\cdot10^{7}$
lb$_f$·ft	1.36	0.138	1	$3.77\cdot10^{-7}$	0.0134	0.000324	0.00129	$1.36\cdot10^{7}$
kW·h	$3.6\cdot10^{6}$	$3.67\cdot10^{5}$	$2.66\cdot10^{6}$	1	$35.5\cdot10^{3}$	860	3420	$3.6\cdot10^{13}$
atm·L	101	10.3	74.7	$2.82\cdot10^{-5}$	1	0.0242	0.0961	$1.01\cdot10^{9}$
kcal	4180	427	3090	0.00116	41.3	1	3.97	$4.18\cdot10^{10}$
BTU	1050	108	778	0.000293	10.4	0.252	1	$1.05\cdot10^{10}$
erg	10^{-7}	$1.02\cdot10^{-8}$	$7.38\cdot10^{-8}$	$2.78\cdot10^{-14}$	$9.987\cdot10^{-10}$	$2.39\cdot10^{-11}$	$9.48\cdot10^{-11}$	1

APPENDIX II. CRITICAL PROPERTIES AND SPECIFIC HEAT CAPACITIES OF IDEAL GASES

According to Bird et al. (1989) and Poling et al.(2001). Reproduced with permission.

Substance	$\mathfrak{M}$ (g/mol-g)	σ^{LJ} (Å)	ε^{LJ}/k (K)	T_c (K)	P_c (atm)	$\tilde{V}_c$ (cm³/mol-g)	z_c	$\eta_c \times 10^6$ (g/cm.s)	$\lambda_c \times 10^6$ (cal/cm.s.K)	$\tilde{C}_P^* = \xi_0 + \xi_1 T + \xi_2 T^2 + \xi_3 T^3 + \xi_4 T^4$, T in K					
										T range (K)	$\frac{\xi_0}{R}$	$\frac{\xi_1}{R}\times 10^3$	$\frac{\xi_2}{R}\times 10^5$	$\frac{\xi_3}{R}\times 10^8$	$\frac{\xi_4}{R}\times 10^{11}$
H_2	2.016	2.915	38	33.3	12.8	65	0.304	34.7	-	50-1000	2.883	3.681	-0.772	0.692	-0.213
Ar	39.944	3.418	124	151	48	75.2	0.291	264	71	50-1000	-	-	-	-	-
Kr	83.8	3.498	225	209.4	54.3	92.2	0.291	396	49.4	50-1000	-	-	-	-	-
Xe	131.3	4.055	229	289.8	58	118.8	0.290	490	40.2	50-1000	-	-	-	-	-
air	28.97	3.617	97	-	-	-	-	193	90.8	50-1000	-	-	-	-	-
N_2	28.02	3.681	91.5	126.2	33.5	90.1	0.291	180	86.8	50-1000	3.539	-0.261	0.007	0.157	-0.099
O_2	32	3.433	113	154.4	49.7	74.4	0.292	250	105.3	50-1000	3.63	-1.794	0.658	-0.601	0.179
Cl_2	70.91	4.115	357	417	76.1	124	0.276	420	97	50-1000	3.056	5.3708	-0.8098	0.5693	-
CO	28.01	3.59	110	133	34.5	93.1	0.294	190	86.5	50-1000	3.912	-3.913	1.182	-1.302	0.515
CO_2	44.01	3.996	190	304.2	72.9	94	0.274	343	122	50-1000	3.259	1.356	1.502	-2.374	1.056
SO_2	64.07	4.29	252	430.7	77.8	122	0.268	411	93.6	50-1000	4.417	-2.234	2.344	-3.271	1.393
methane	16.04	3.822	137	190.7	45.8	99.3	0.290	159	158	50-1000	4.568	-8.975	3.631	-3.407	1.091
ethane	30.07	4.418	230	305.4	48.2	148	0.284	210	203	50-1000	4.178	-4.427	5.66	-6.651	2.487
propane	44.09	5.061	254	370	42	200	0.276	228	-	50-1000	3.847	5.131	6.011	-7.893	3.079
butane	58.12	-	-	425.5	37.5	255	0.274	239	-	200-1000	5.547	5.536	8.057	-10.571	4.134
benzene	78.114	5.27	440	562.0	48.3	256	0.268	312	-	50-1000	3.551	-6.184	14.365	-19.365	8.234
toluene	92.141	-	-	591.7	40.5	316	0.264	-	-	50-1000	3.866	3.558	13.356	-18.659	7.69
CCl_4	153.84	5.881	327	556.4	45	276	0.272	413	-	200-1000	2.518	41.882	-7.16	5.739	-1.756
water	18.015	-	-	647.1	217.	55.95	0.229	-	-	50-1000	4.395	-4.186	1.405	-1.564	0.632
methanol	32.042	-	-	512.6	79.9	118	0.224	-	-	50-1000	4.714	-6.986	4.211	-4.443	1.535
ethanol	46.069	-	-	513.9	60.6	167	0.240	-	-	50-1000	4.396	0.628	5.546	-7.024	2.685
propanol	60.096	-	-	536.7	51.0	219	0.254	-	-	50-1000	4.712	6.565	6.31	-8.341	3.216
ammonia	17.031	-	-	405.4	112.	72.47	0.244	-	-	50-1000	4.238	-4.215	2.041	-2.126	0.761

APPENDIX III. GROUP CONTRIBUTIONS OF LYDERSEN

Adapted from Perry et al. (1997). Reproduced with permission.

	Δ_T	Δ_P	Δ_V
Nonring increments:			
$-CH_3$, $>CH_2$	0.020	0.227	55
>CH-	0.012	0.210	51
>C<	0.000	0.210	41
$=CH_2$, =CH-	0.018	0.198	45
=C<, =C=	0.000	0.198	36
≡CH, ≡C-	0.005	0.153	(36)
Ring increments:			
$-CH_2-$	0.013	0.184	44.5
>CH-	0.012	0.192	46
>C<	(-0.007)	(0.154)	(31)
=CH-	0.011	0.154	37
=C<, =C=	0.011	0.154	36
Halogen increments:			
-F	0.018	0.224	18
-Cl	0.017	0.320	49
-Br	0.010	(0.500)	(70)
-I	0.012	(0.830)	(95)
Oxygen increments:			
-OH (alcohols)	0.082	0.060	(18)
-OH (phenols)	0.031	(-0.020)	(3)
-O- (nonring)	0.021	0.160	20
-O- (ring)	(0.014)	(0.120)	(8)
>C=O (nonring)	0.040	0.290	60
>C=O (ring)	(0.033)	(0.200)	(50)
O=CH- (aldehyde)	0.048	0.330	73
-COOH (acid)	0.085	(0.400)	80
-COO- (ester)	0.047	0.470	80
=O (except for combinations above)	(0.020)	(0.120)	(11)
Nitrogen increments:			
$-NH_2$	0.031	0.095	28
>NH (nonring)	0.031	0.135	(37)
>NH (ring)	(0.024)	(0.090)	(27)
>N- (nonring)	0.014	0.170	(42)
>N- (ring)	(0.007)	(0.130)	(32)
-CN	(0.060)	(0.360)	(80)
$-NO_2$	(0.055)	(0.420)	(78)
Sulfur increments:			
-SH	0.015	0.270	55
-S- (nonring)	0.015	0.270	55
-S- (ring)	(0.008)	(0.240)	(45)
=S	(0.003)	(0.240)	(47)
Organometallic increments			
>Si<	0.026	0.468	
>SiH-	0.040	0.513	
$-SiH_3$	0.027		
>SiO-	0.025	0.730	
>SiO- (cyclic)	0.027	0.668	

NOTES:
- There are no hydrogen increments
- All bonds in the table are connections with atoms other than hydrogen
- Values in parentheses are based on few experimental points

APPENDIX IV. GENERALIZED DIAGRAMS OF THERMODYNAMIC AND TRANSPORT PROPERTIES

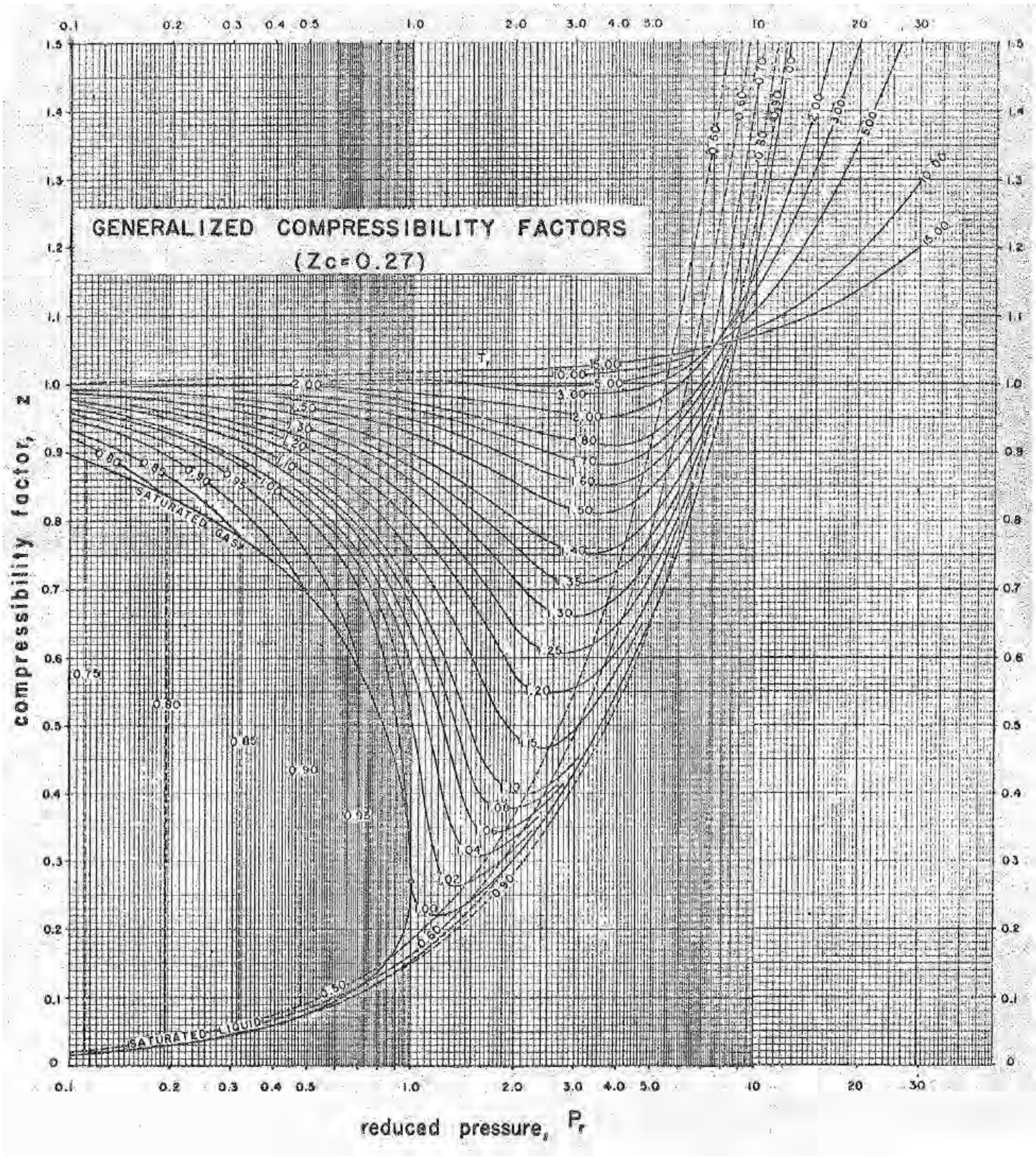


Figure IV.1. Compressibility factor as a function of reduced temperature and reduced pressure when z_c=0.27 (Lydersen et al., 1955). Reproduced with permission.

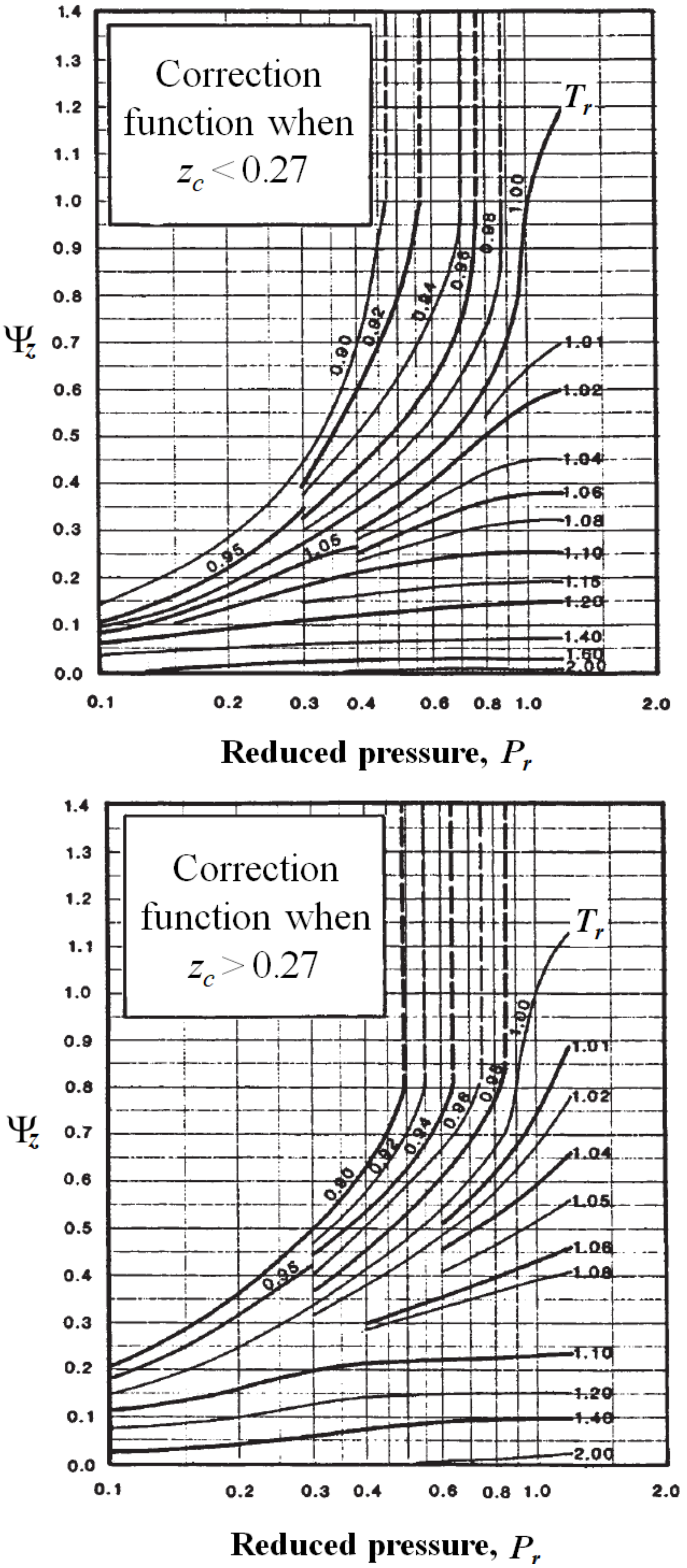


Figure IV.2. Correction functions for the compressibility when $z_c \neq 0.27$ (adapted from Perry et al., 1997). Reproduced with permission.

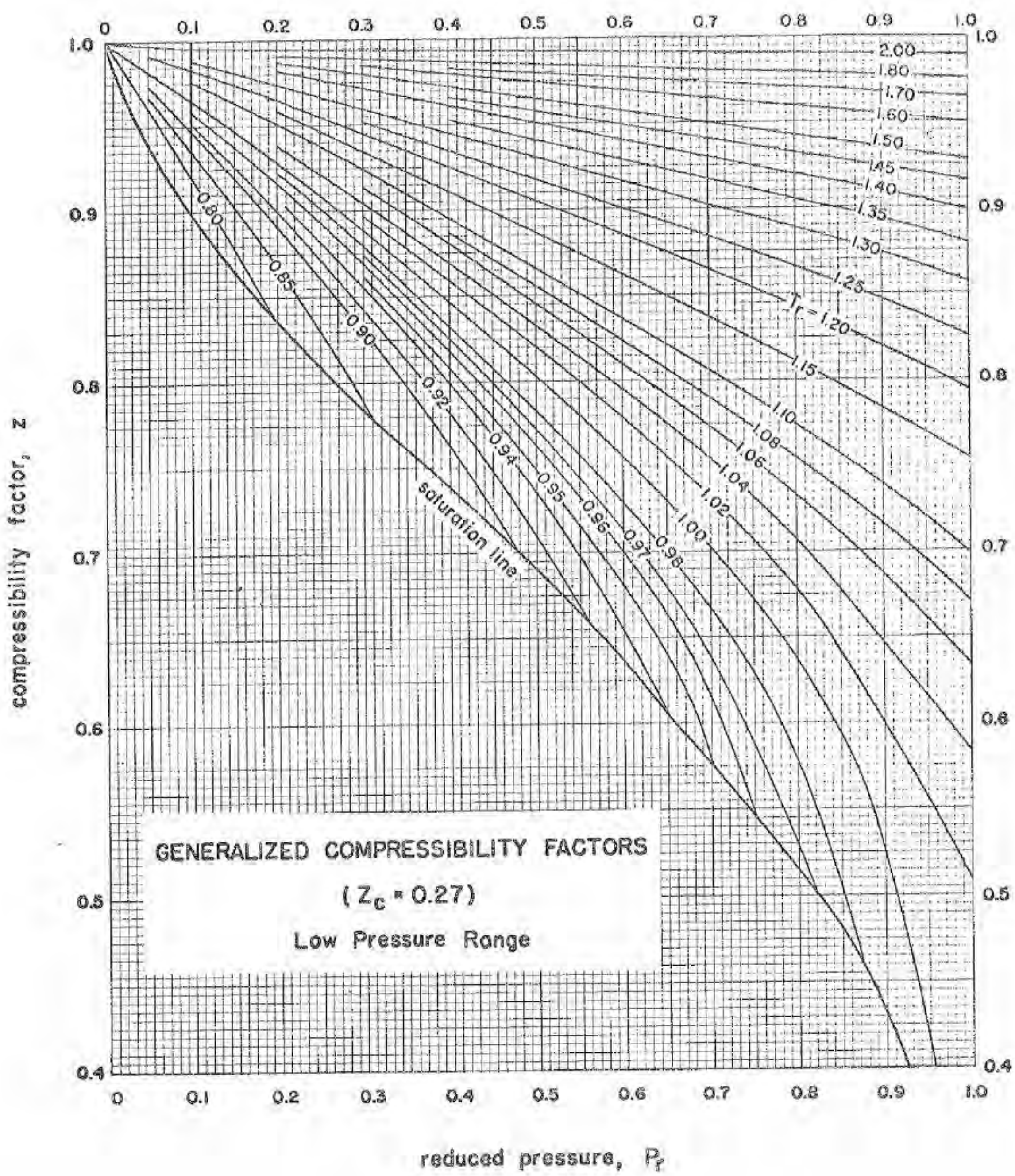


Figure IV.3. Compressibility factor as a function of reduced temperature and reduced pressure when z_c=0.27 in the low-density region (Lydersen et al., 1955). Reproduced with permission.

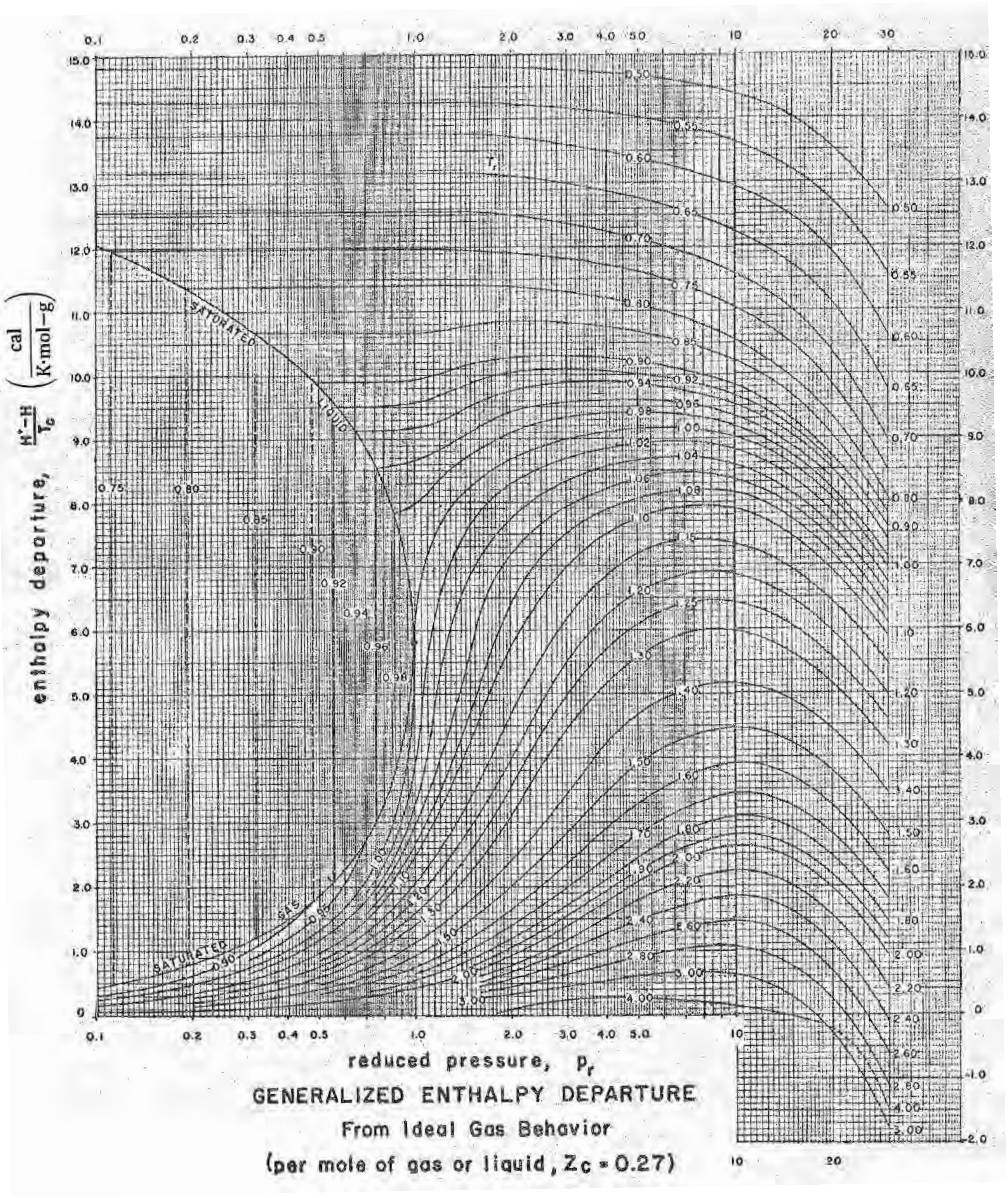


Figure IV.4. Enthalpy departure as a function of reduced temperature and reduced pressure when z_c=0.27 (adapted from Lydersen et al., 1955). Reproduced with permission.

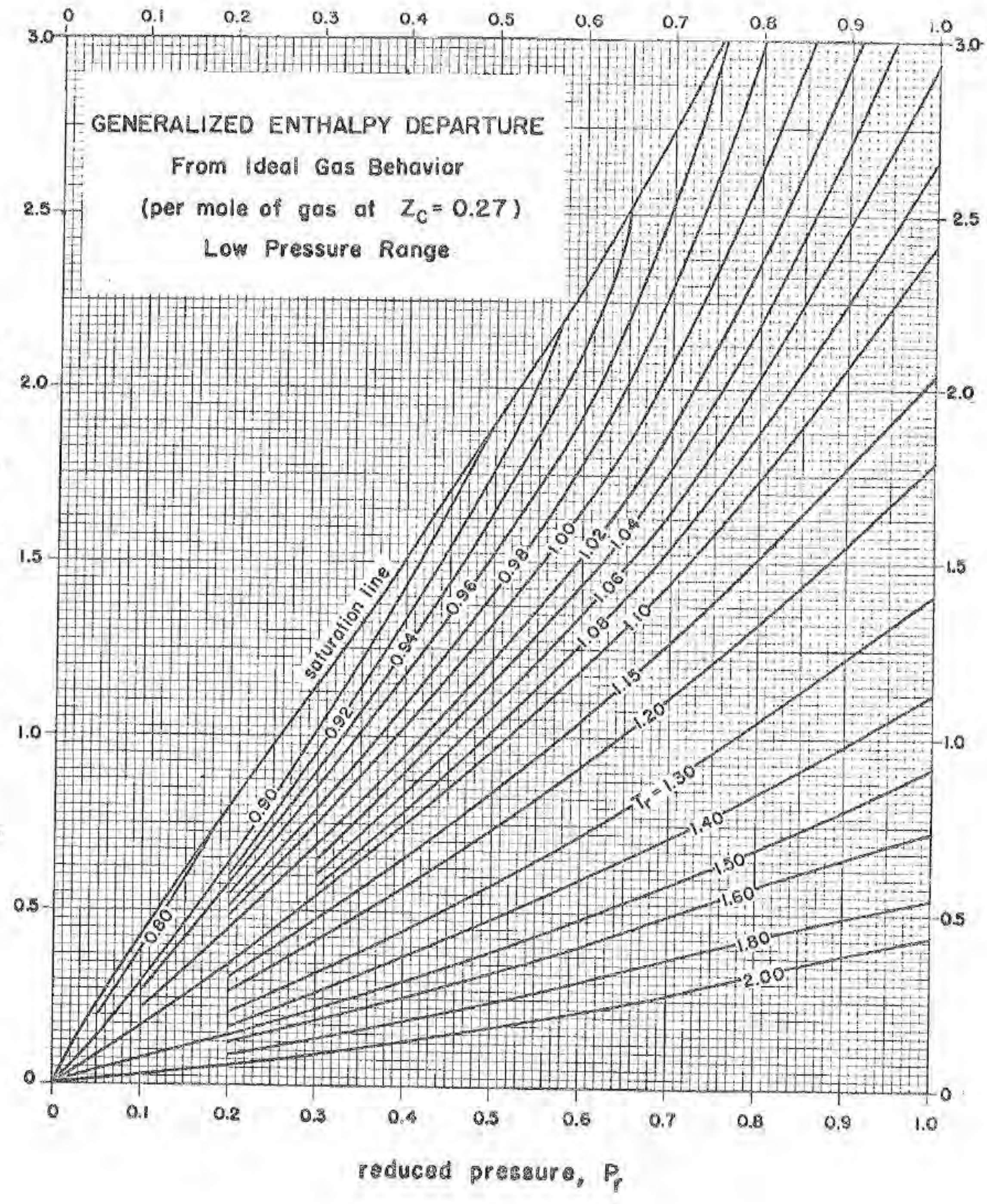


Figure IV.5. Enthalpy departure as a function of reduced temperature and reduced pressure when z_c=0.27 in the low-density region (adapted from Lydersen et al., 1955). Reproduced with permission.

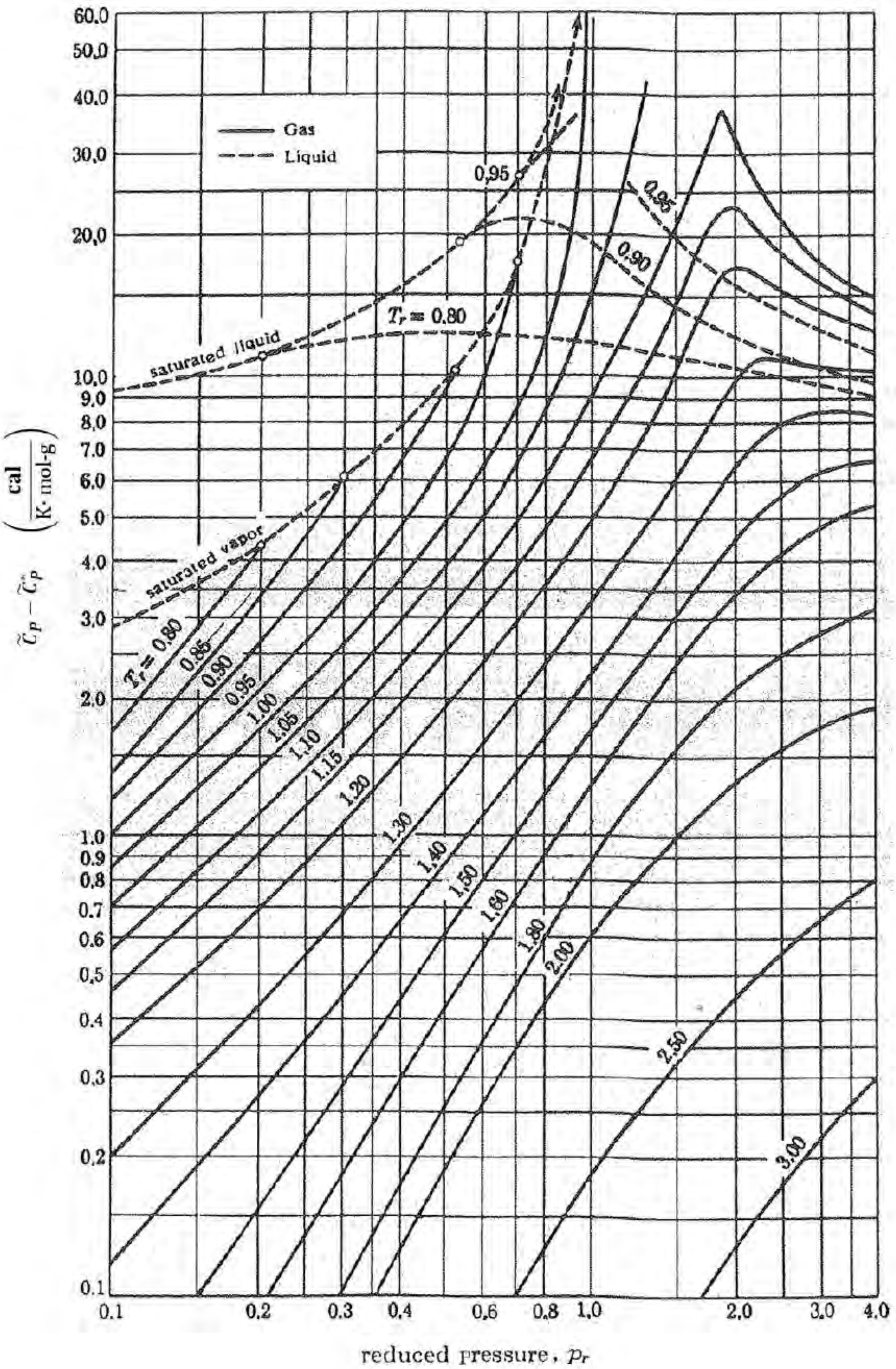


Figure IV.6. Heat capacity departure as a function of reduced temperature and reduced pressure when z_c=0.27 (adapted from Hougen et al., 1982). Reproduced with permission.

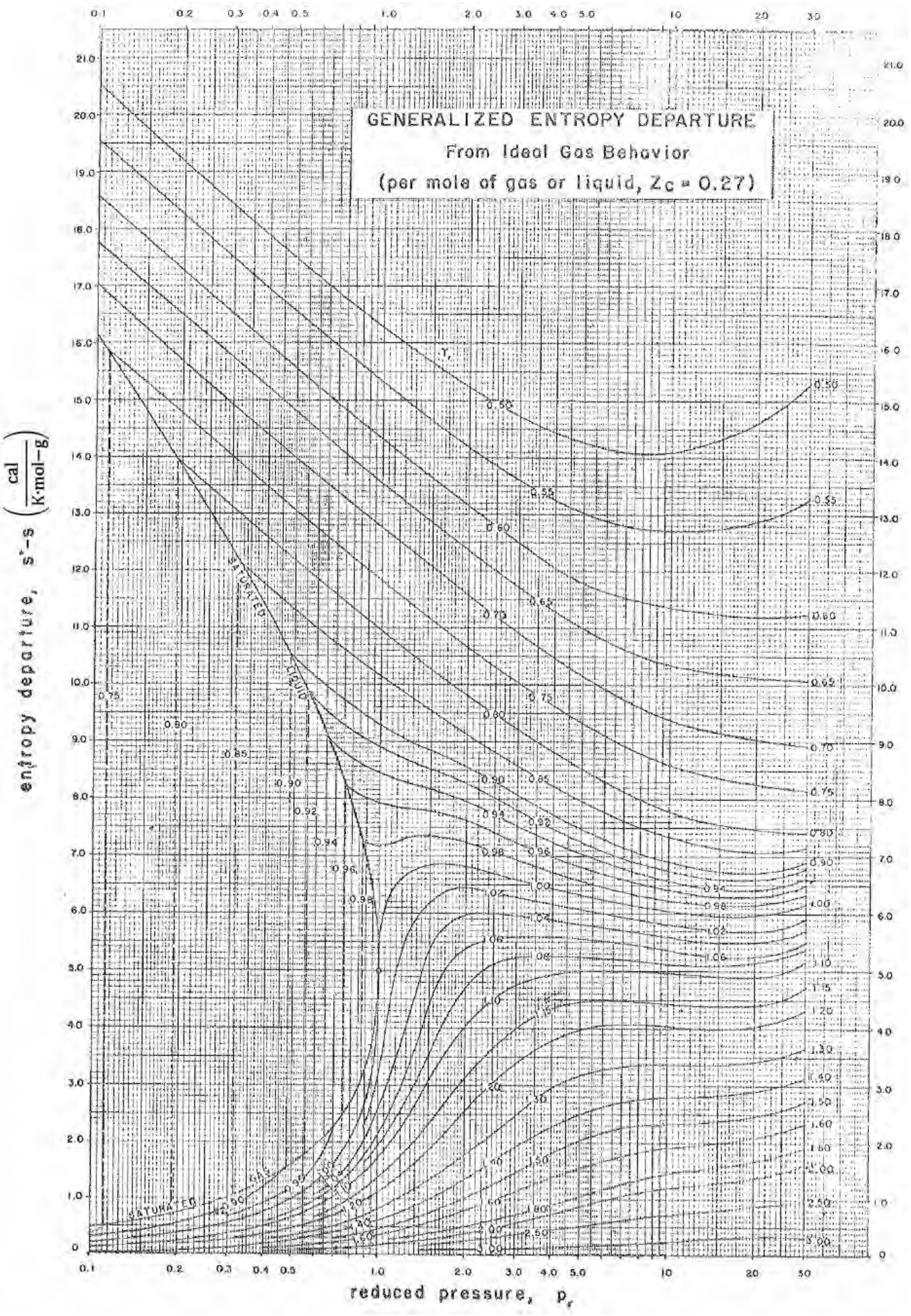


Figure IV.7. Entropy departure as a function of reduced temperature and reduced pressure when z_c=0.27 (adapted from Lydersen et al., 1955). Reproduced with permission.

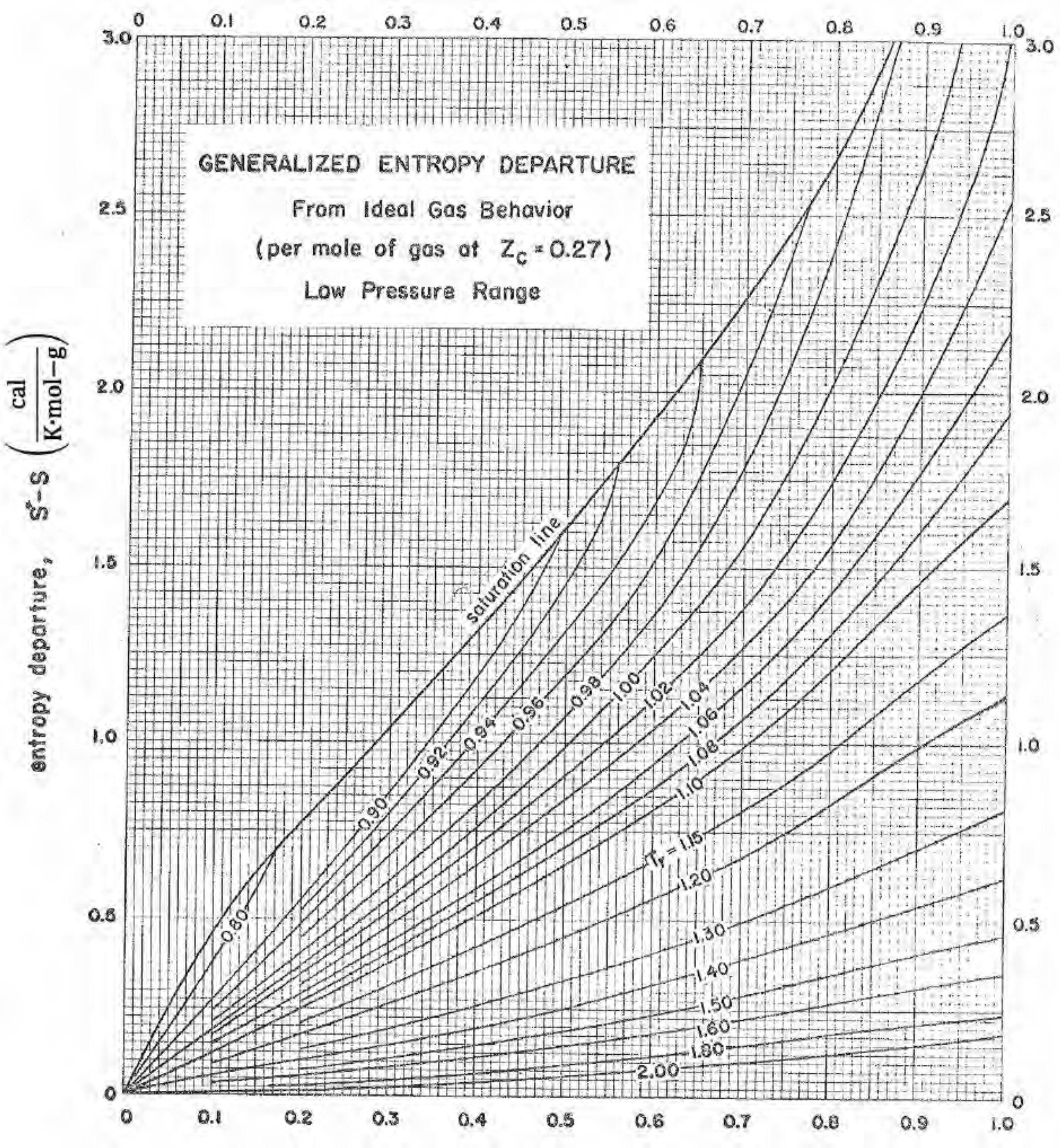


Figure IV.8. Entropy departure as a function of reduced temperature and reduced pressure when z_c=0.27 in the low-density region (adapted from Lydersen et al., 1955). Reproduced with permission.

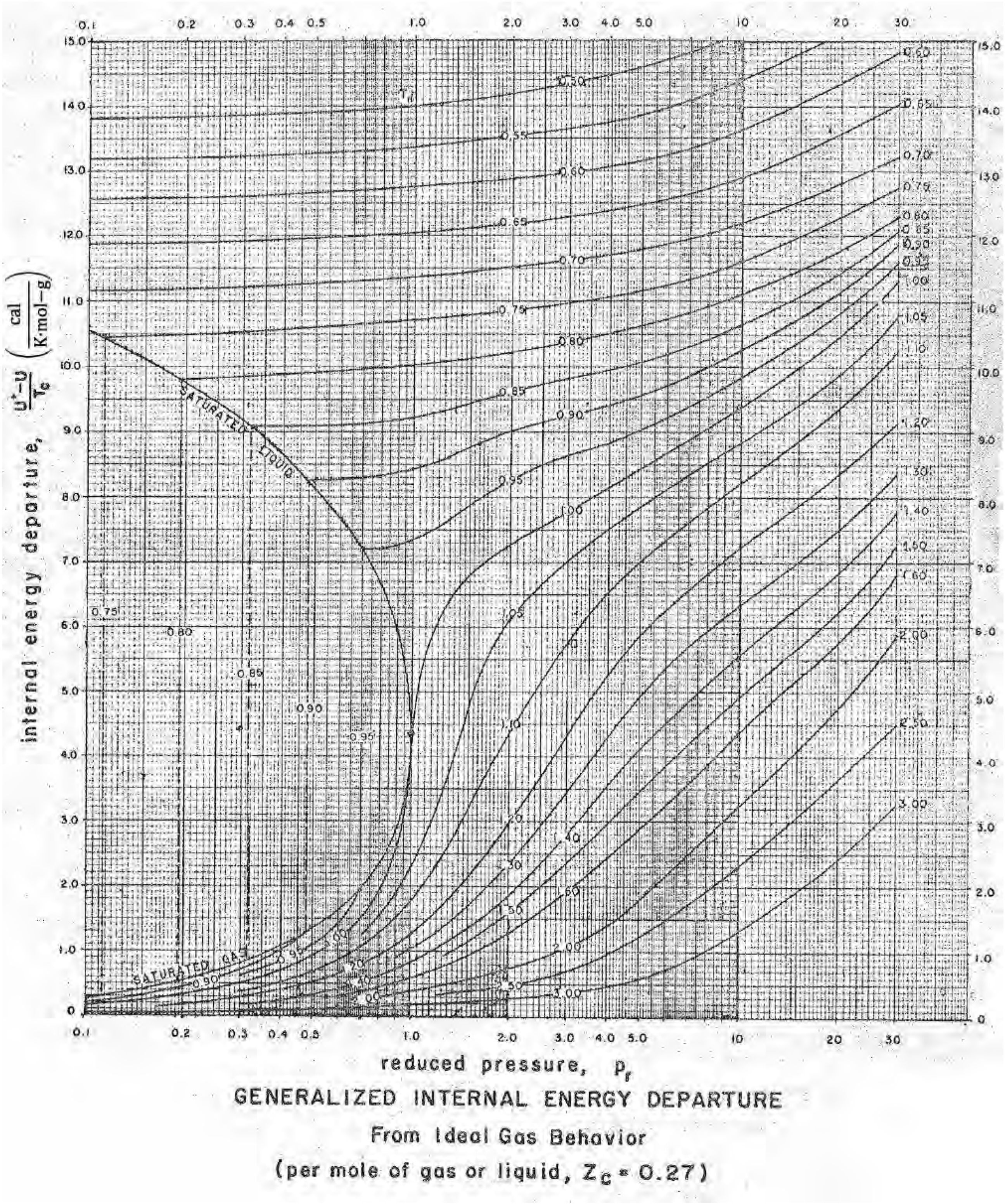


Figure IV.9. Internal energy departure as a function of reduced temperature and reduced pressure when z_c=0.27 (adapted from Lydersen et al., 1955). Reproduced with permission.

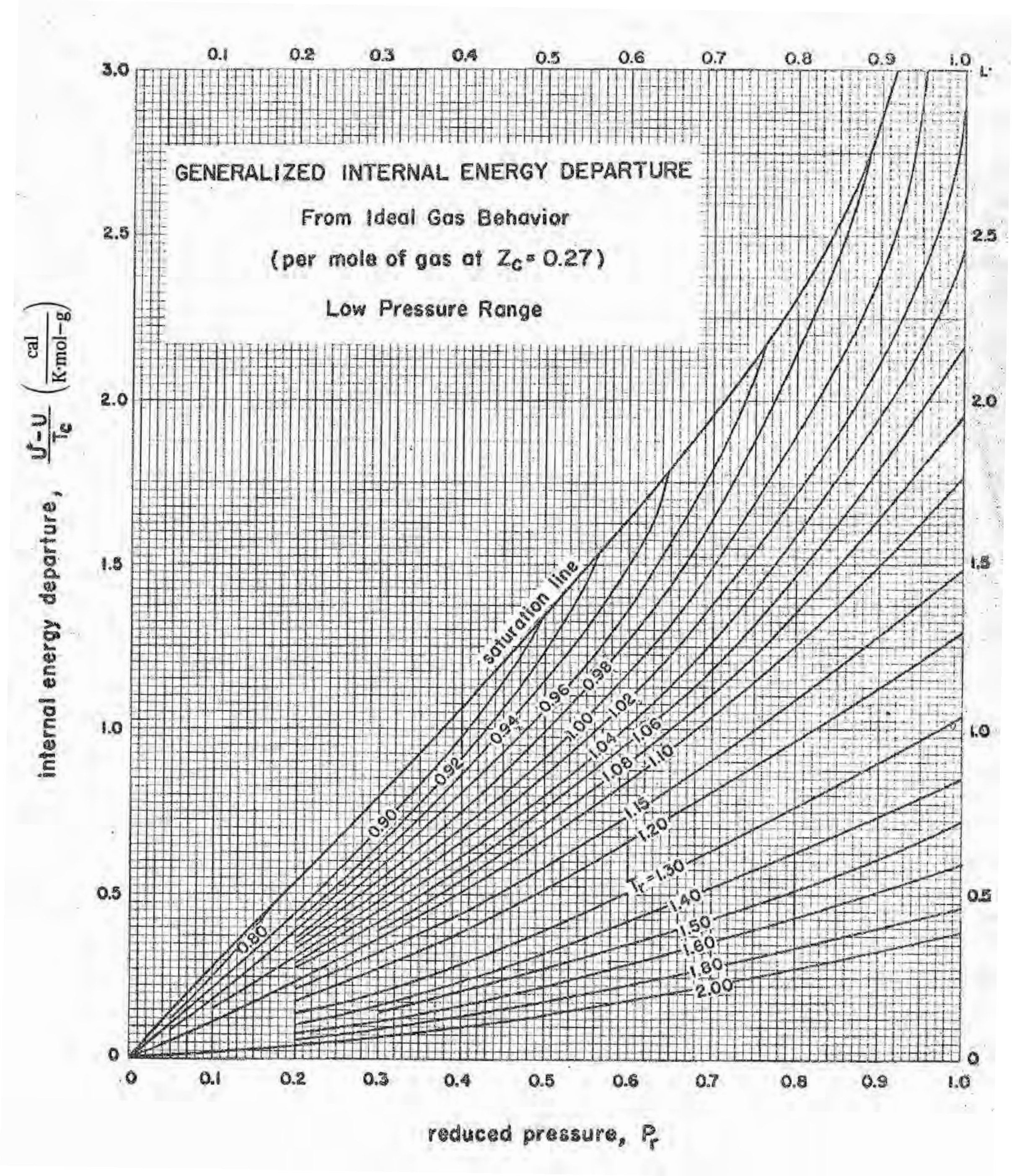


Figure IV.10. Internal energy departure as a function of reduced temperature and reduced pressure when z_c=0.27 in the low-density region (adapted from Lydersen et al., 1955). Reproduced with permission.

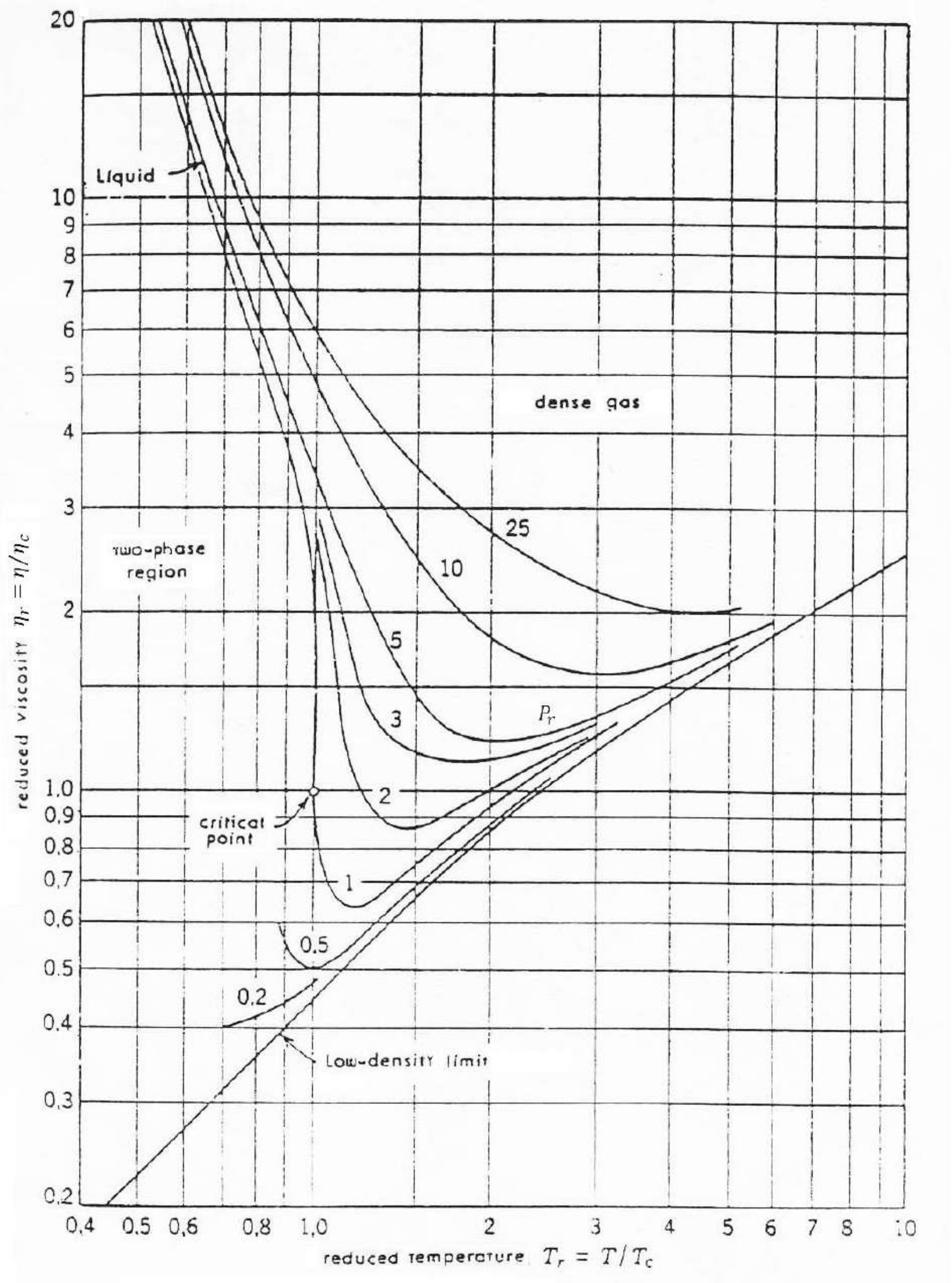


Figure IV.11. Reduced viscosity as a function of reduced temperature and reduced pressure (adapted from Bird et al., 1982). Reproduced with permission.

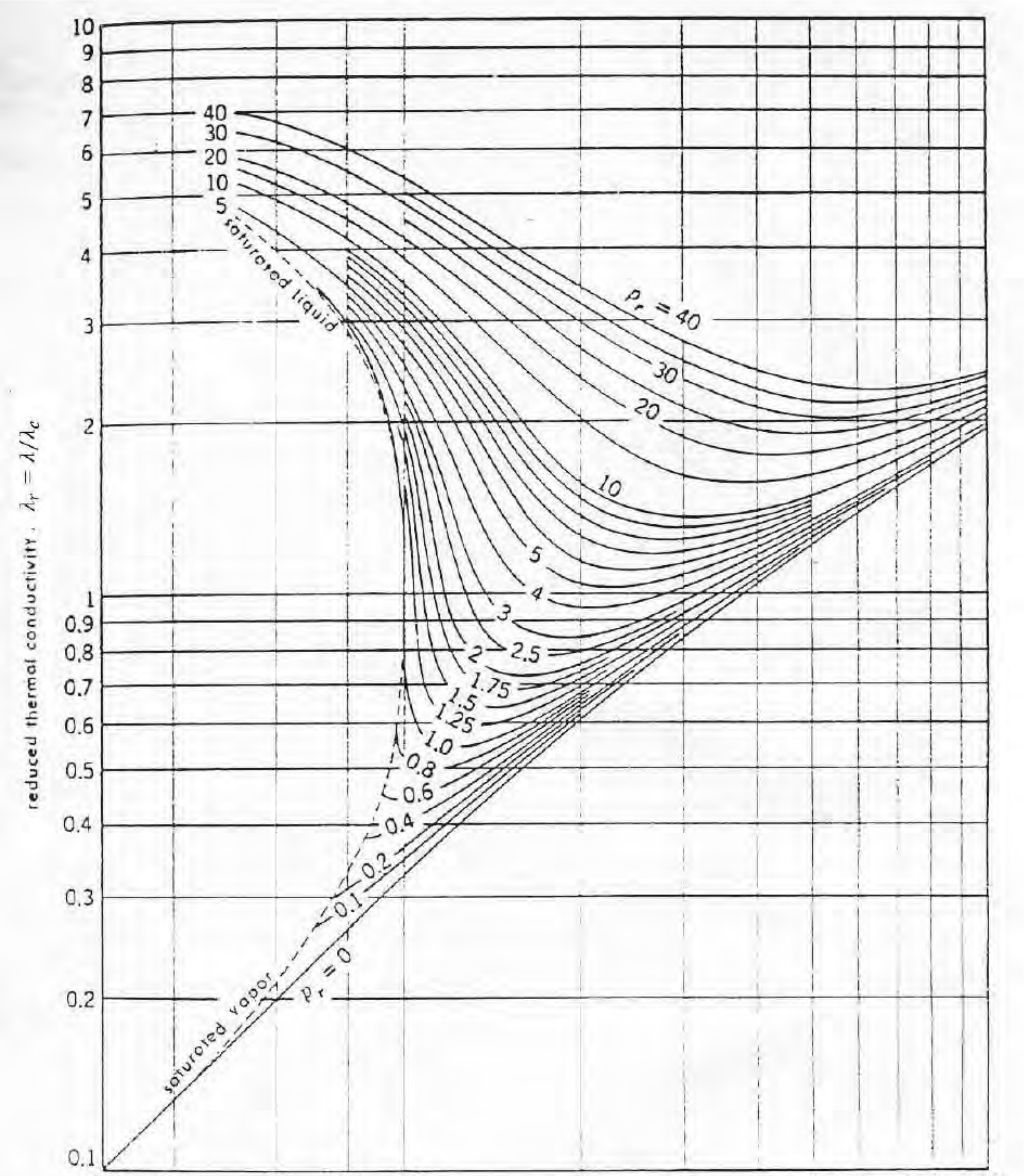


Figure IV.12. Reduced thermal conductivity as a function of reduced temperature and reduced pressure (adapted from Bird et al., 1982). Reproduced with permission.

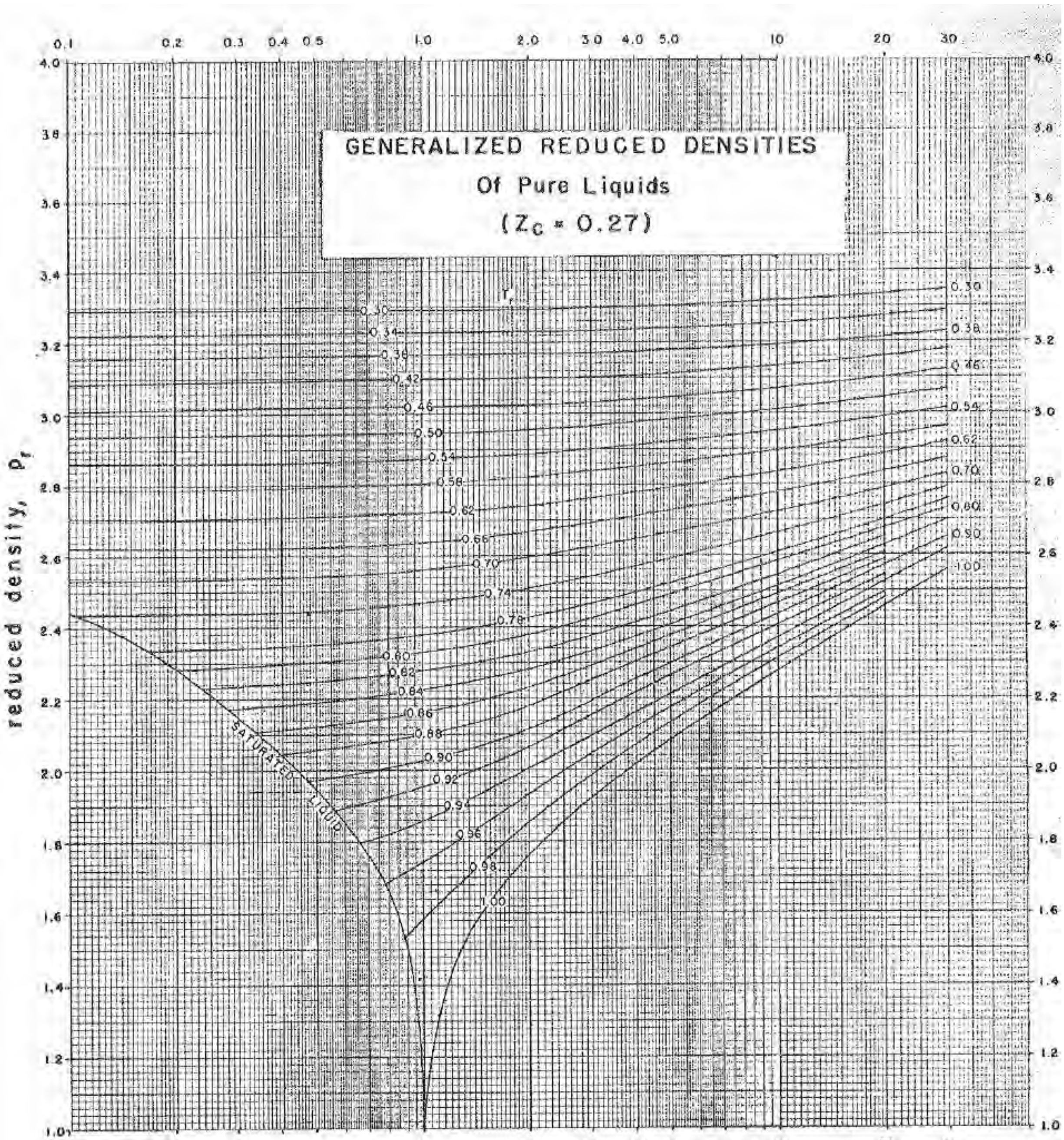


Figure IV.13. Reduced densities as a function of reduced temperature and reduced pressure when z_c=0.27 (Lydersen et al., 1955). Reproduced with permission.

APPENDIX V. THERMODYNAMIC DIAGRAMS FOR PARTICULAR SUBSTANCES

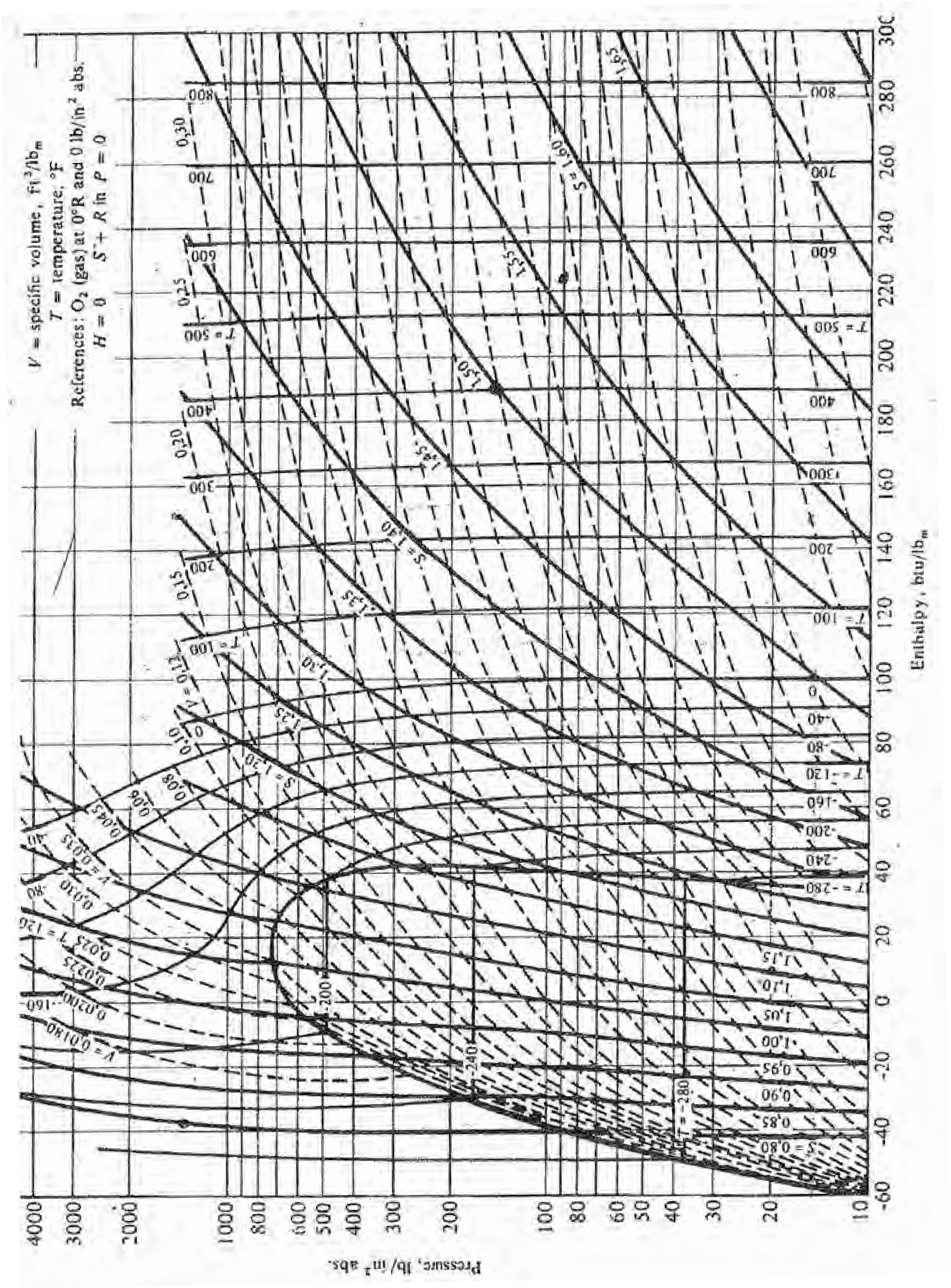


Figure V.1. Pressure-enthalpy diagram of oxygen (Canjar and Manning, 1967). Reproduced with permission.

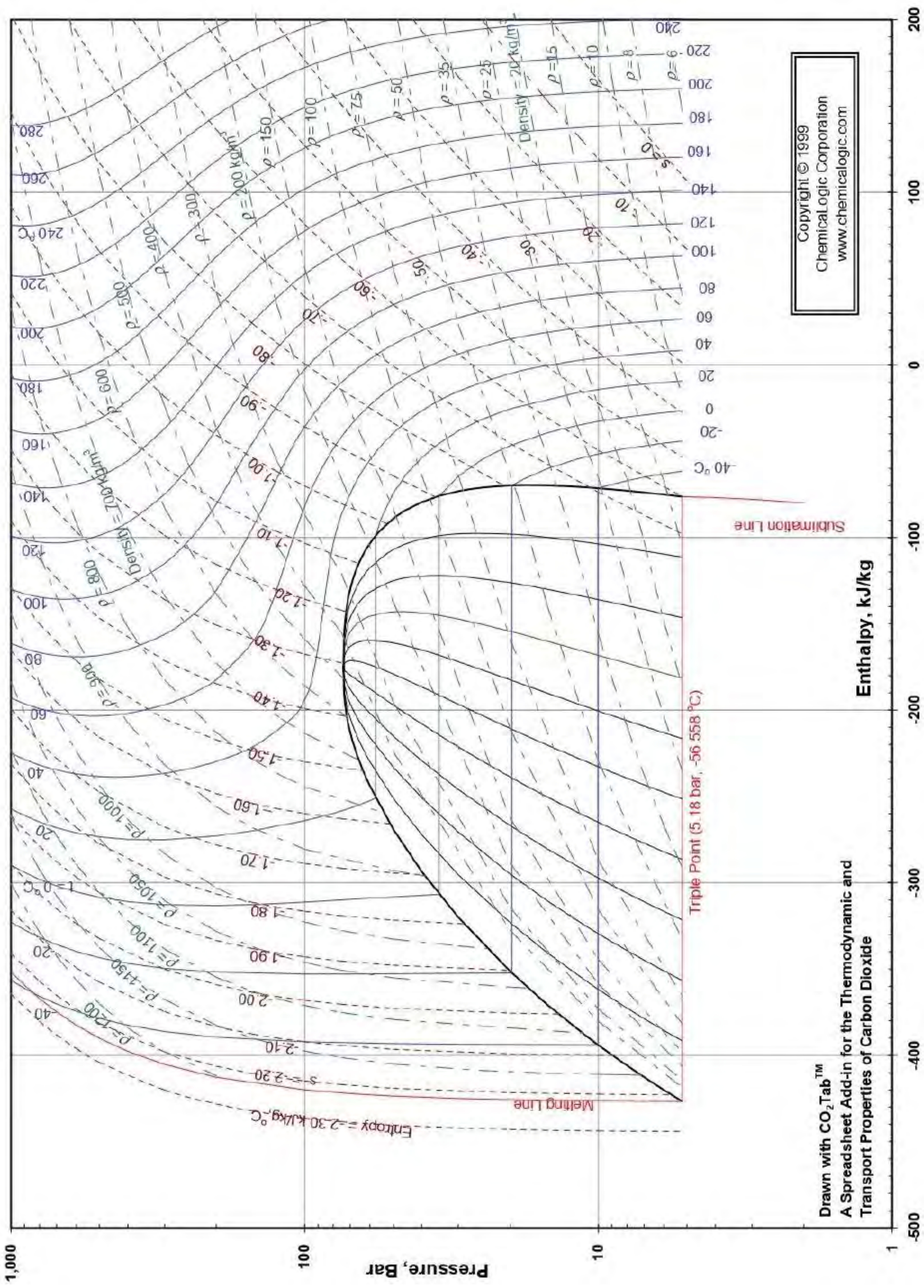


Figure V.2. Pressure-enthalpy diagram of carbon dioxide (adapted from the website www.chemicalogic.com). Reproduced with permission.

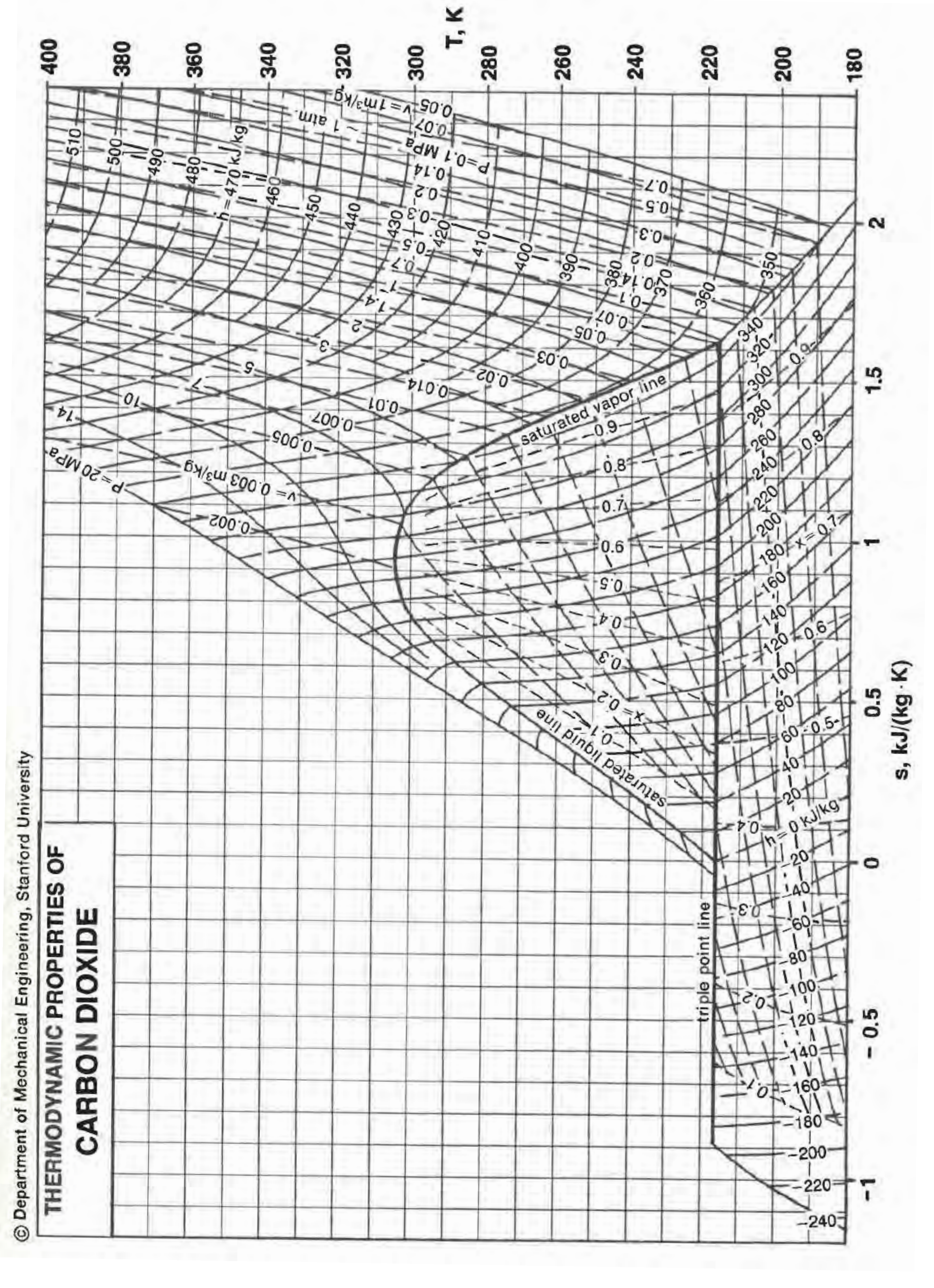


Figure V.3. Temperature-entropy diagram of carbon dioxide (Reynolds, 1979).

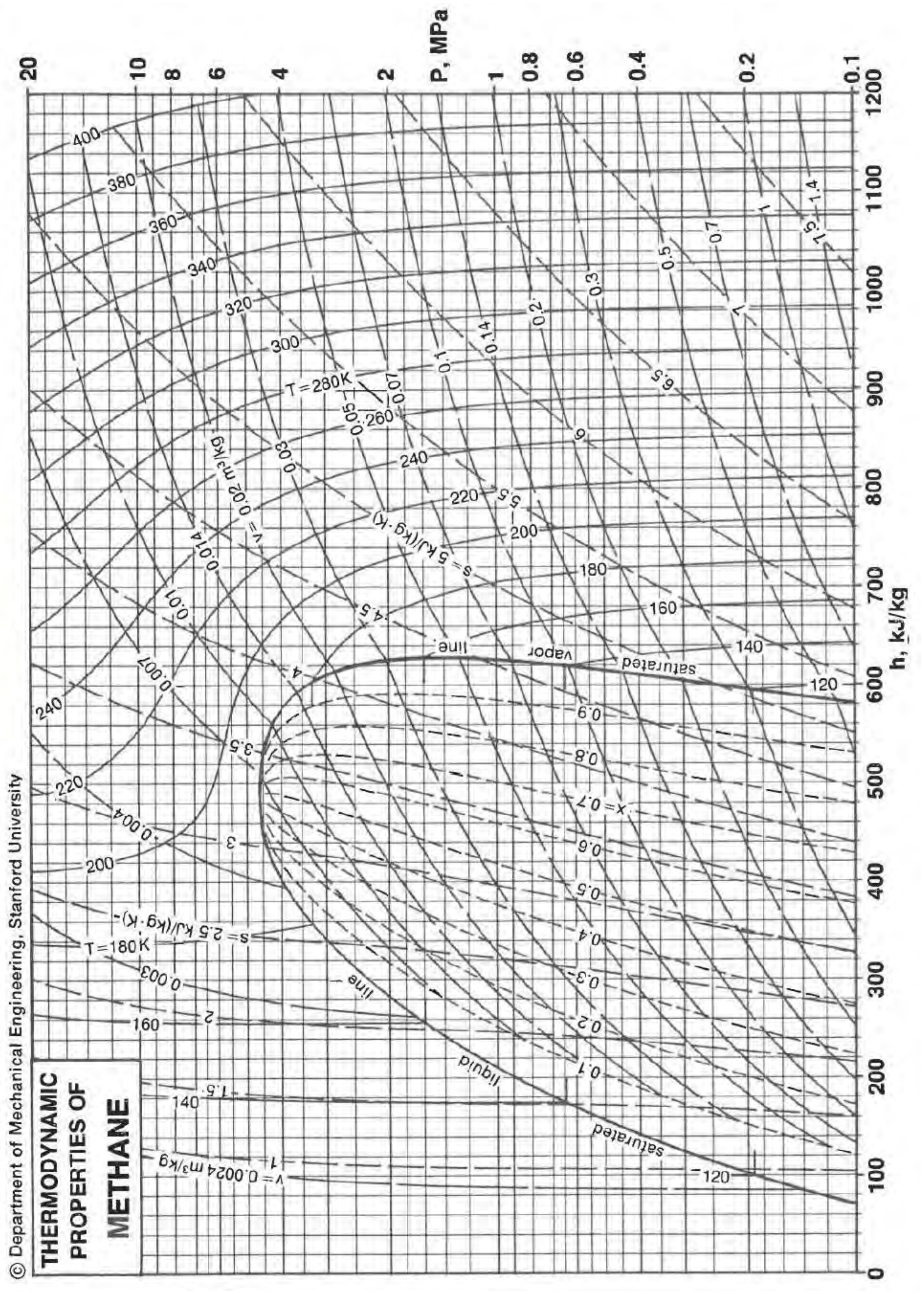


Figure V.4. Pressure-enthalpy diagram of methane (Reynolds, 1979).

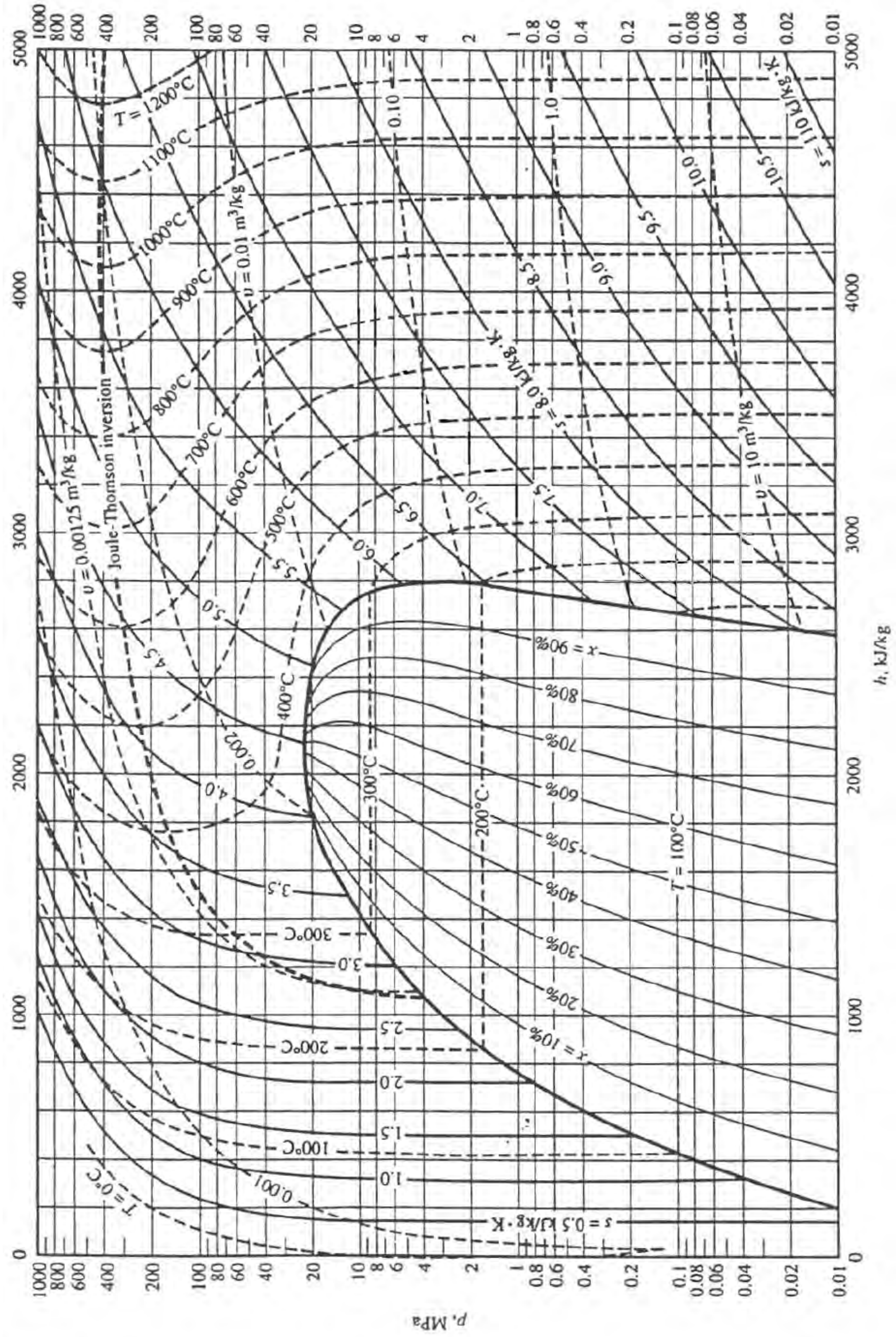


Figure V.5. Pressure-enthalpy diagram of water (Jones and Dugan, 1997).

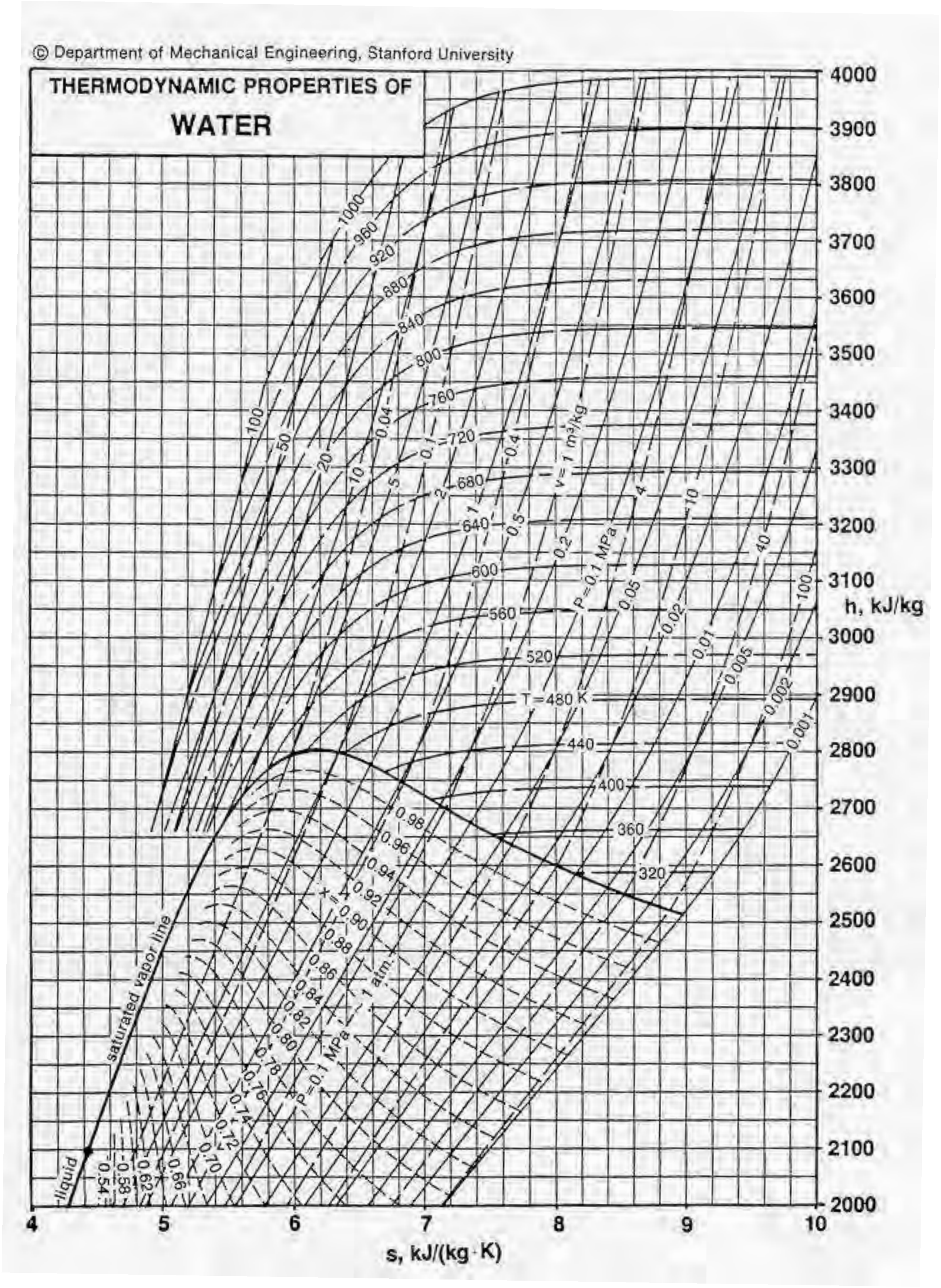


Figure V.6. Mollier diagram of water (Reynolds, 1979).

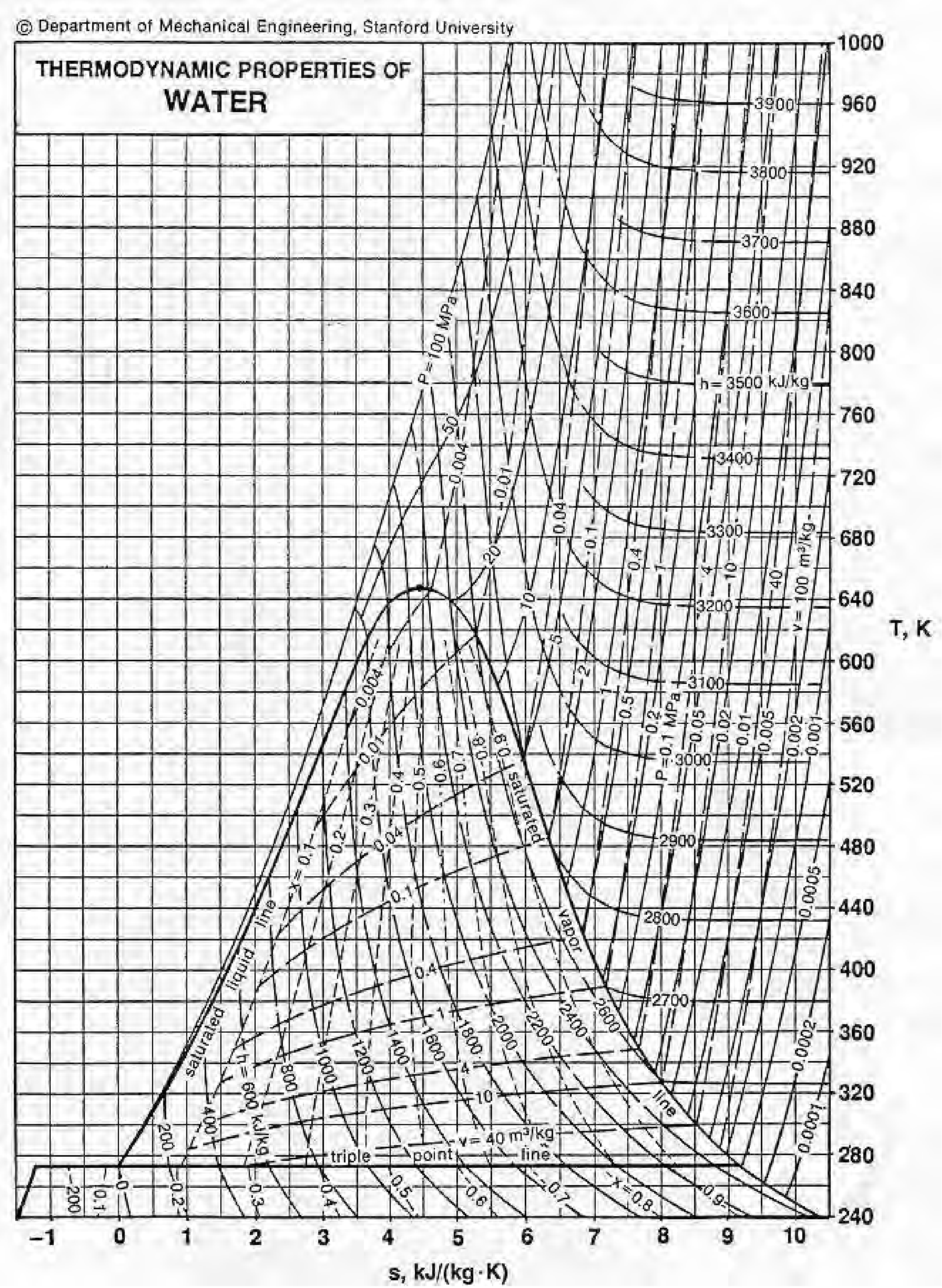


Figure V.7. Temperature-entropy diagram of water (Reynolds, 1979).

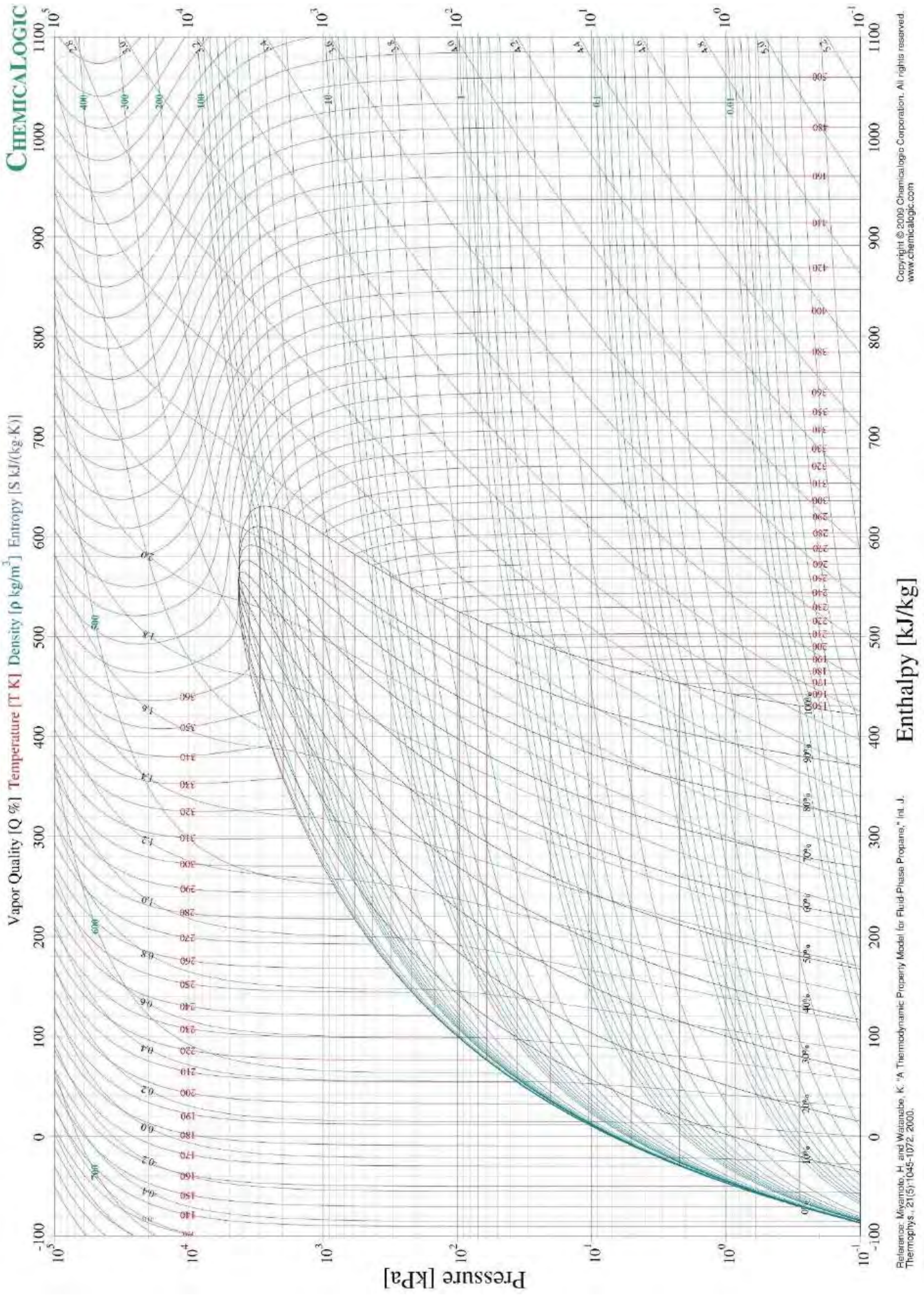


Figure V.8. Pressure-enthalpy diagram of propane (adapted from the website www.chemicalogic.com). Reproduced with permission.

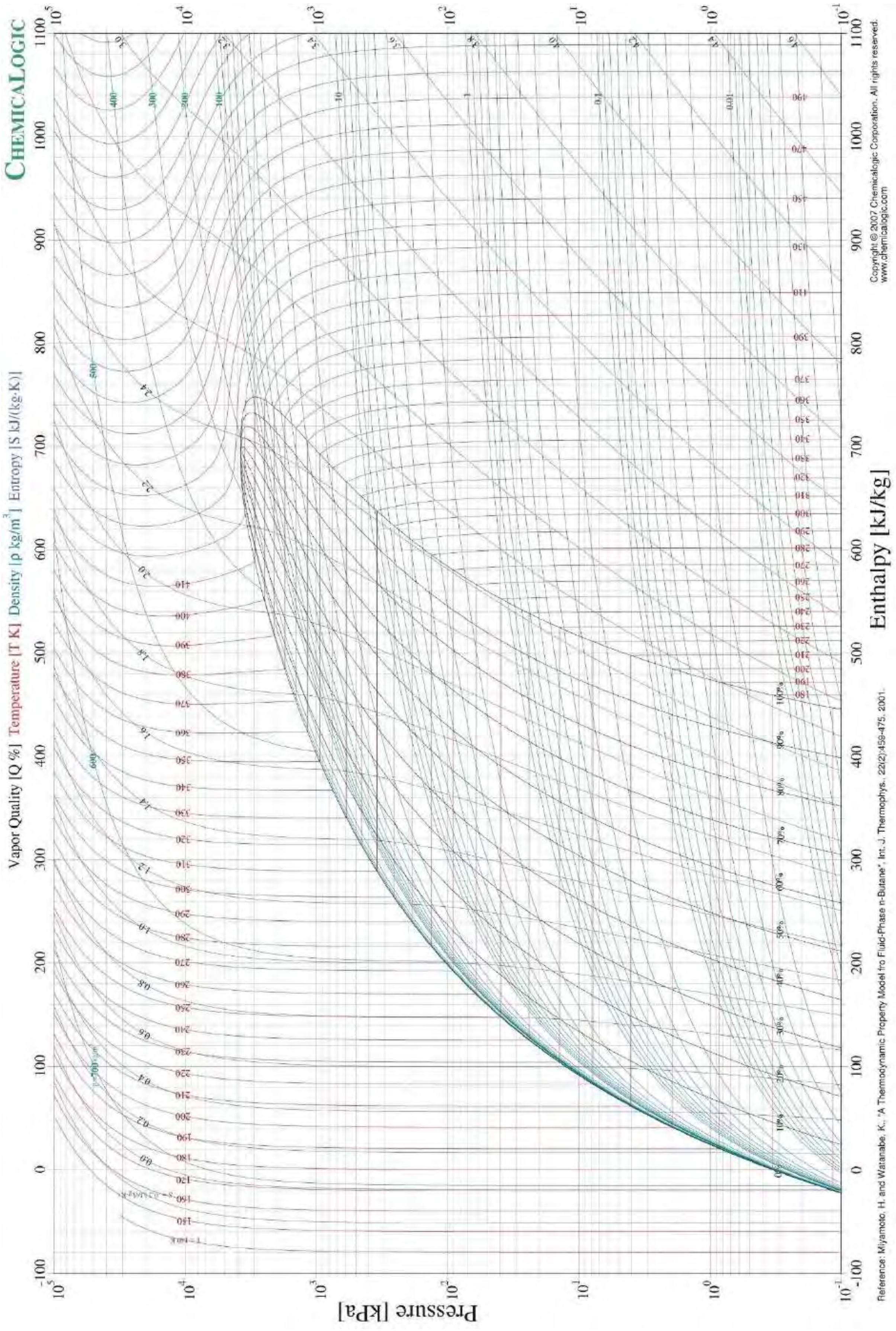


Figure V.9. Pressure-enthalpy diagram of butane (adapted from the website www.chemicalogic.com). Reproduced with permission.

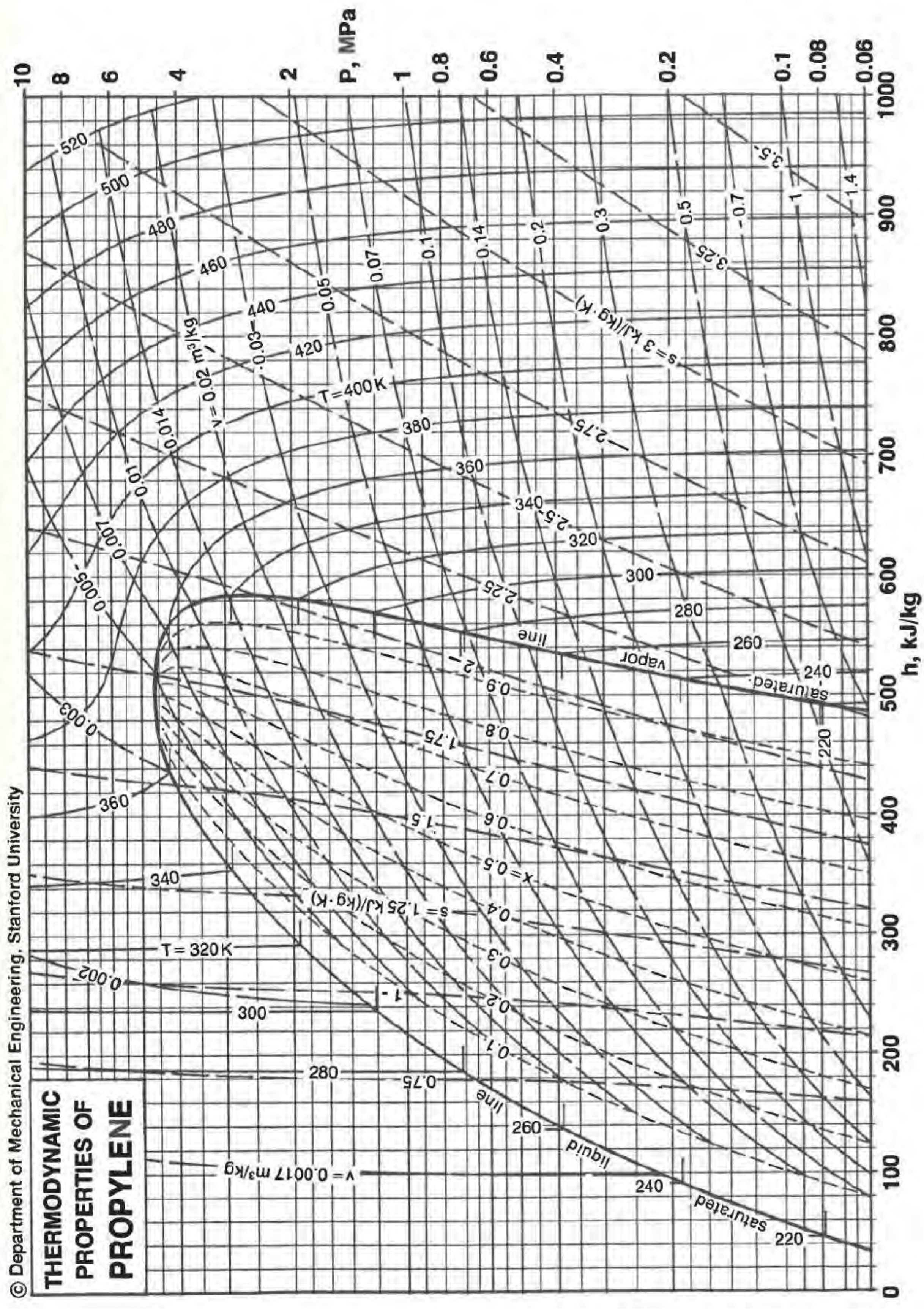


Figure V.10. Pressure-enthalpy diagram of propylene (Reynolds, 1979).

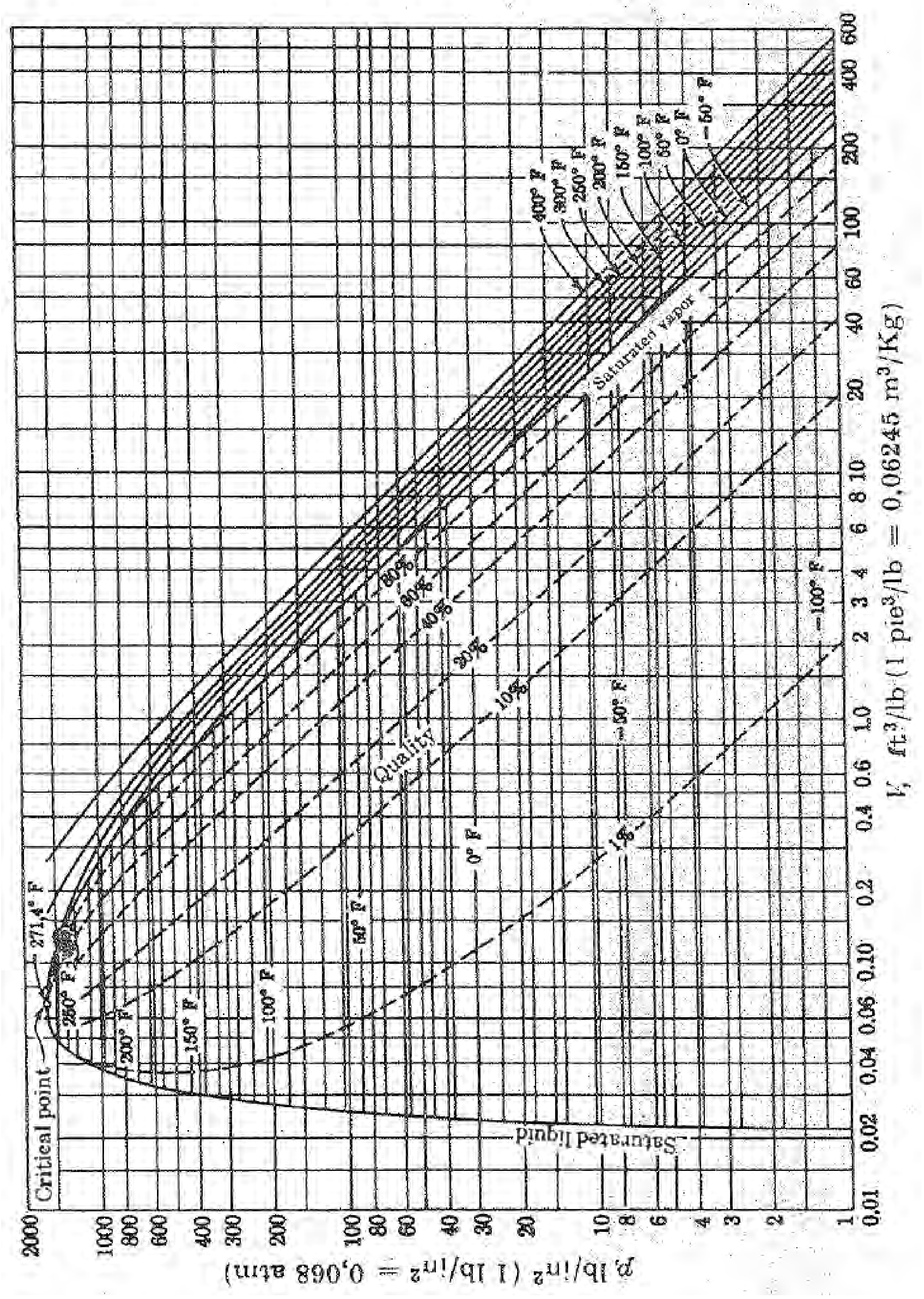


Figure V.11. Pressure-volume diagram of ammonia (adapted from Hougen et al., 1982). Reproduced with permission.

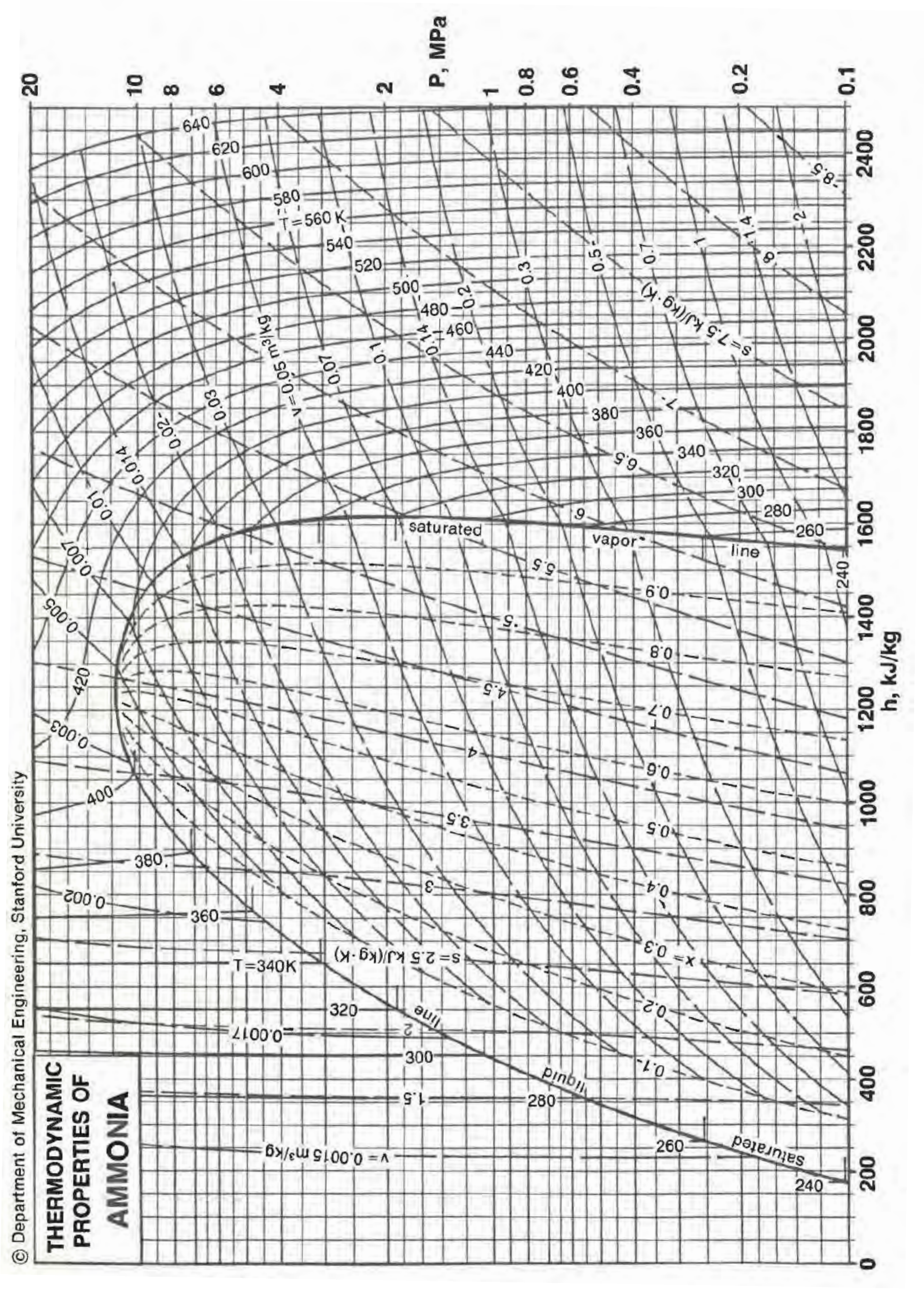


Figure V.12. Pressure-enthalpy diagram of ammonia (Reynolds, 1979).

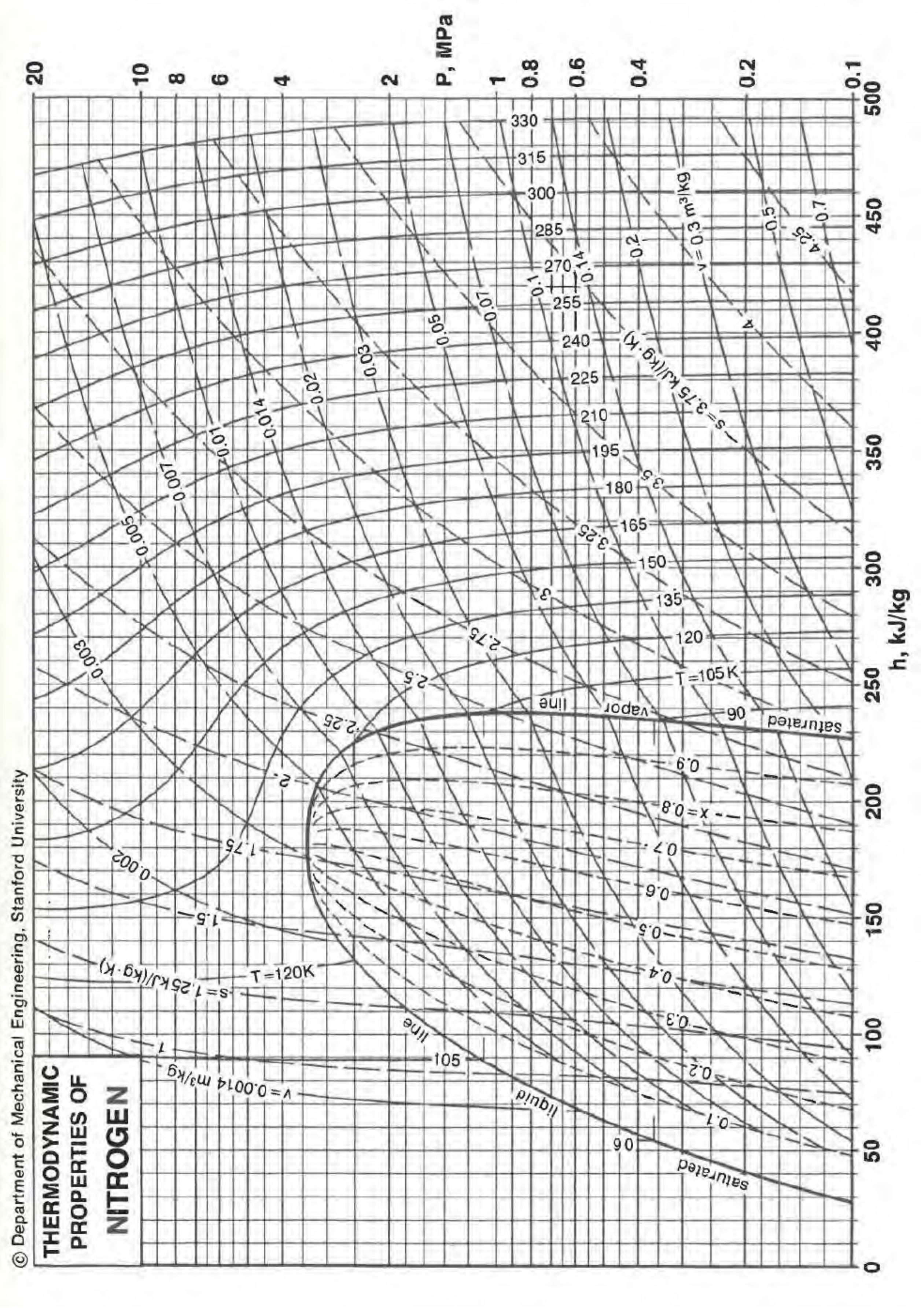


Figure V.13. Pressure-enthalpy diagram of nitrogen (Reynolds, 1979).

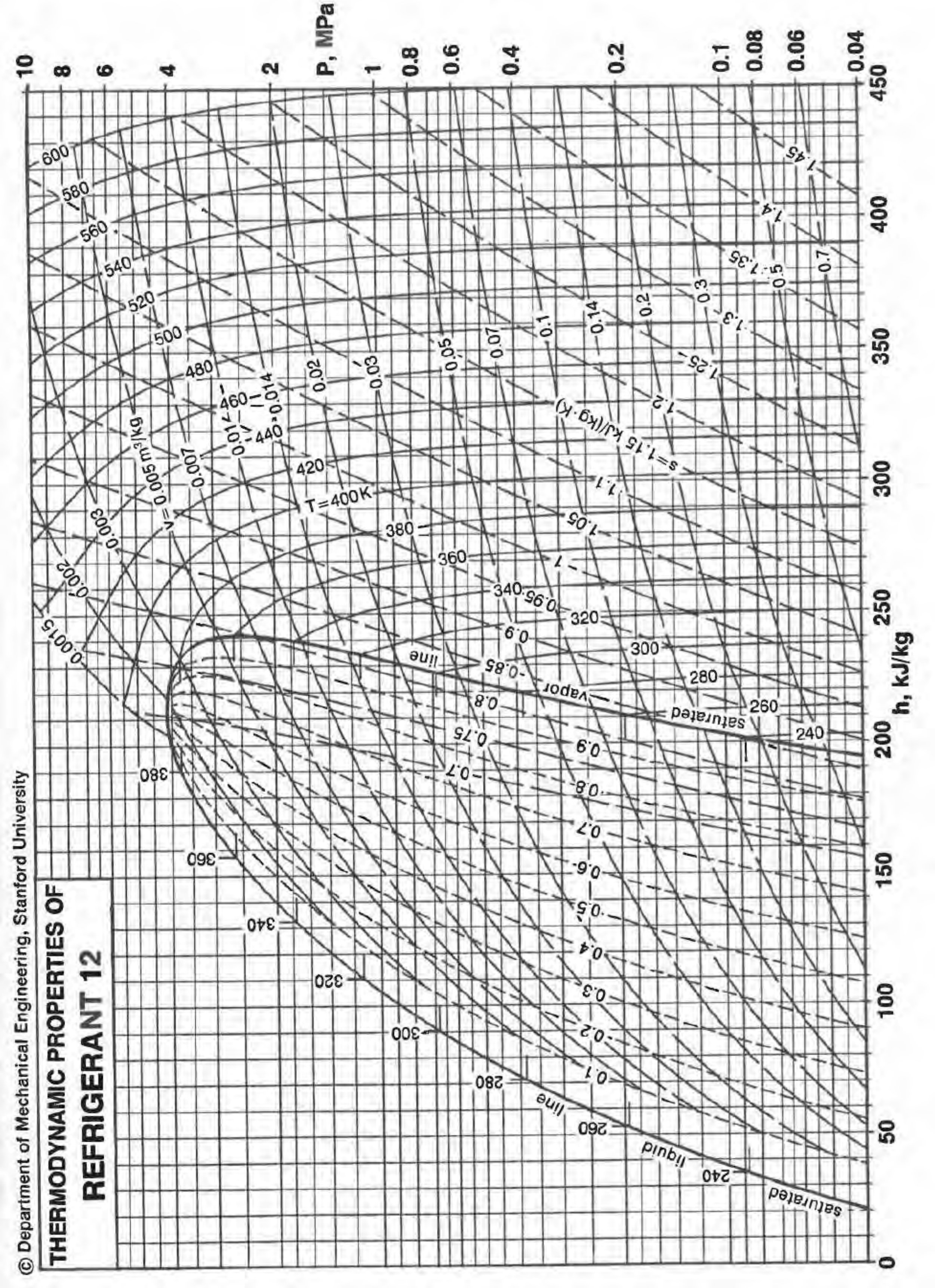


Figure V.14. Pressure-enthalpy diagram of refrigerant 12 (Reynolds, 1979).

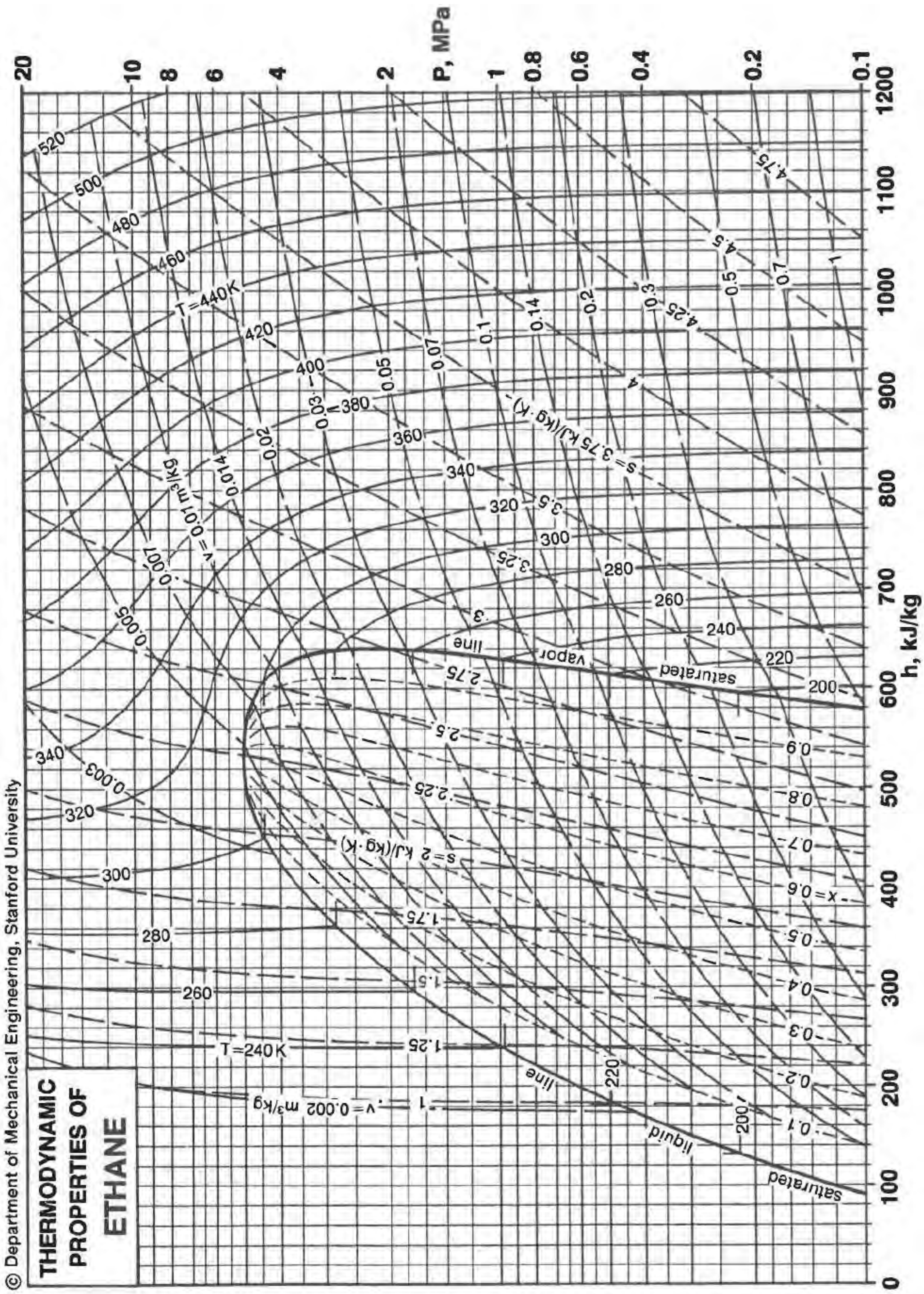


Figure V.15. Pressure-enthalpy diagram of ethane (Reynolds, 1979).

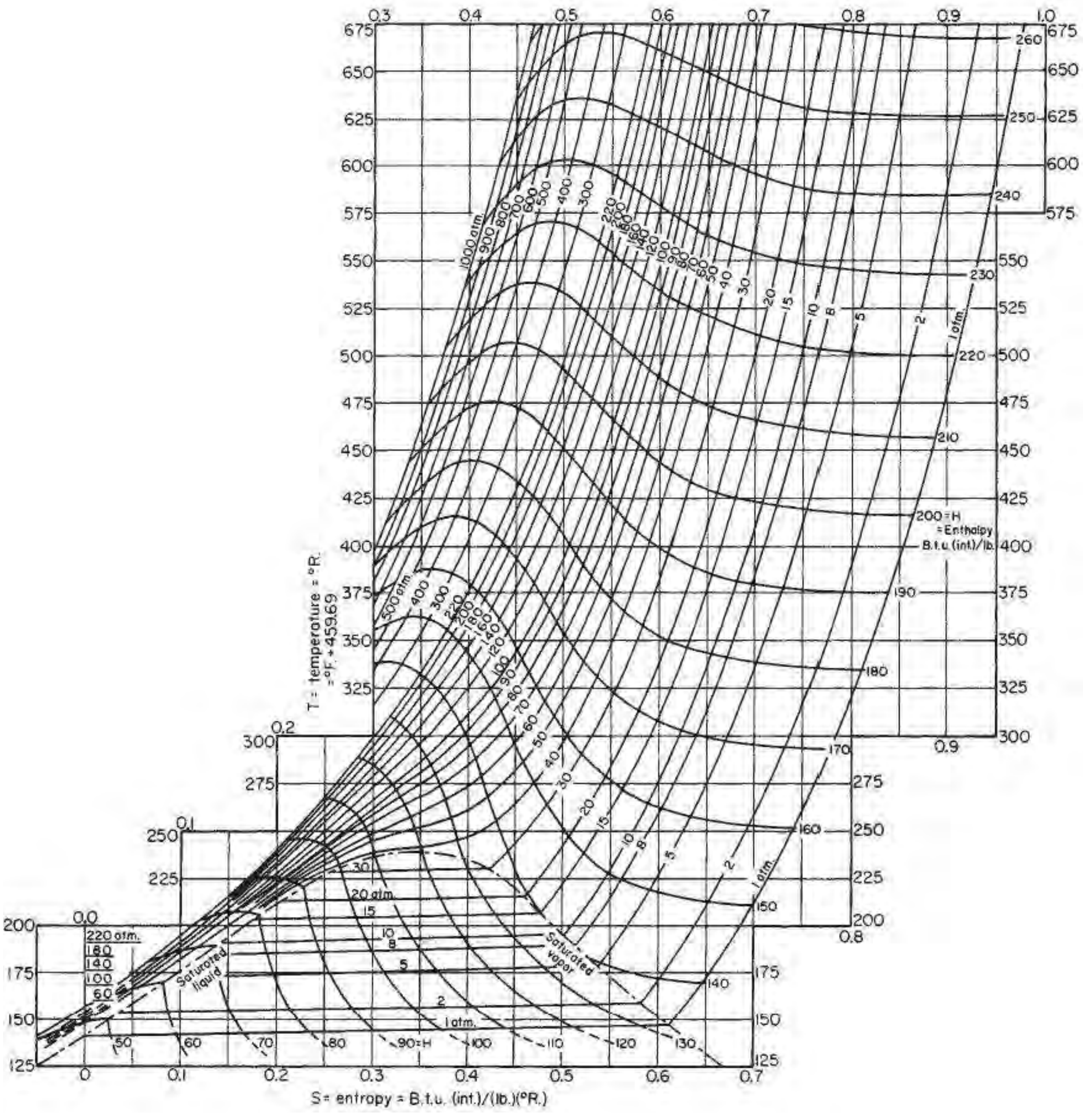


Figure V.16. Temperature-entropy diagram of dry air (Landsbaum et al, 1955 according to Perry et al., 1997). Reproduced with permission.

APPENDIX VI. THERMODYNAMIC PROPERTIES: NUMERICAL DATA OF WATER AND AIR

Table VI.1. Properties of saturated water: liquid and vapor (Perry et al., 1997). Reproduced with permission.

T (ºC)	P (bar)	Specific volume (m^3/kg)		Enthalpy (kJ/kg)		Entropy (kJ/kg·K)		Heat capacity (kJ/kg·K)	
		liquid	vapor	liquid	vapor	liquid	vapor	liquid	vapor
0.00	0.00611	0.001000	206.3	0.0	2502	0.000	9.158	4.217	1.854
1.85	0.00697	0.001000	181.7	7.8	2505	0.028	9.109	4.211	1.855
6.85	0.00990	0.001000	130.4	28.8	2514	0.104	8.980	4.198	1.858
11.85	0.01387	0.001000	99.4	49.8	2523	0.178	8.857	4.189	1.861
16.85	0.01917	0.001001	69.7	70.7	2532	0.251	8.740	4.184	1.864
21.85	0.02617	0.001002	51.94	91.6	2541	0.323	8.627	4.181	1.868
26.85	0.03531	0.001003	39.13	112.5	2550	0.393	8.520	4.179	1.872
31.85	0.04712	0.001005	27.9	133.4	2559	0.462	8.417	4.178	1.877
36.85	0.06221	0.001007	22.93	154.3	2568	0.530	8.318	4.178	1.882
41.85	0.08132	0.001009	17.82	175.2	2577	0.597	8.224	4.179	1.888
46.85	0.10530	0.001011	13.98	196.1	2586	0.649	8.151	4.180	1.895
51.85	0.13510	0.001013	11.06	217	2595	0.727	8.046	4.182	1.903
56.85	0.17190	0.001016	8.82	237.9	2604	0.791	7.962	4.184	1.911
61.85	0.21670	0.001018	7.09	258.8	2613	0.854	7.881	4.186	1.920
66.85	0.27130	0.001021	5.74	279.8	2622	0.916	7.804	4.188	1.930
71.85	0.33720	0.001024	4.683	300.7	2630	0.977	7.729	4.191	1.941
76.85	0.41630	0.001027	3.846	321.7	2639	1.038	7.657	4.195	1.954
81.85	0.51000	0.001030	3.18	342.7	2647	1.097	7.588	4.199	1.968
86.85	0.62090	0.001034	2.645	363.7	2655	1.156	7.521	4.203	1.983
91.85	0.75140	0.001038	2.212	384.7	2663	1.214	7.456	4.209	1.999
96.85	0.90400	0.001041	1.861	405.8	2671	1.271	7.394	4.214	2.017
100.00	1.01330	0.001044	1.679	419.1	2676	1.307	7.356	4.217	2.029
101.85	1.08150	0.001045	1.574	426.8	2679	1.328	7.333	4.220	2.036
106.85	1.28690	0.001049	1.337	448	2687	1.384	7.275	4.226	2.057
111.85	1.52330	0.001053	1.142	469.2	2694	1.439	7.218	4.232	2.080
116.85	1.79400	0.001058	0.98	490.4	2702	1.494	7.163	4.239	2.104
126.85	2.45500	0.001067	0.731	532.9	2716	1.605	7.058	4.256	2.158
136.85	3.30200	0.001077	0.553	575.6	2729	1.708	6.959	4.278	2.221
146.85	4.37000	0.001088	0.425	618.6	2742	1.810	6.865	4.302	2.291
156.85	5.69900	0.001099	0.331	661.8	2753	1.911	6.775	4.331	2.369
166.85	7.33300	0.001110	0.261	705.3	2764	2.011	6.689	4.360	2.460
176.85	9.31900	0.001123	0.208	749.2	2773	2.109	6.607	4.400	2.560
186.85	11.7100	0.001137	0.167	793.5	2782	2.205	6.528	4.440	2.680
196.85	14.5500	0.001152	0.136	838.2	2789	2.301	6.451	4.480	2.790
206.85	17.9000	0.001167	0.111	883.4	2795	2.395	6.377	4.530	2.940

T (ºC)	*P* (bar)	Specific volume (m^3/kg)		Enthalpy (kJ/kg)		Entropy (kJ/kg·K)		Heat capacity (kJ/kg·K)	
		liquid	vapor	liquid	vapor	liquid	vapor	liquid	vapor
216.85	21.8300	0.001184	0.0922	929.1	2799	2.479	6.312	4.590	3.100
226.85	26.4000	0.001203	0.0766	975.6	2801	2.581	6.233	4.660	3.270
236.85	31.6600	0.001222	0.0631	1023	2802	2.673	6.163	4.740	3.470
246.85	37.7000	0.001244	0.0525	1071	2801	2.765	6.093	4.840	3.700
256.85	44.5800	0.001268	0.0445	1119	2798	2.856	6.023	4.950	3.960
266.85	52.3800	0.001294	0.0375	1170	2792	2.948	5.953	5.080	4.270
276.85	61.1900	0.001323	0.0317	1220	2784	3.039	5.882	5.240	4.640
286.85	71.08	0.001355	0.0269	1273	2772	3.132	5.808	5.430	5.090
296.85	82.16	0.001392	0.0228	1328	2757	3.225	5.733	5.680	5.670
306.85	94.51	0.001433	0.0193	1384	2737	3.321	5.654	6.000	6.400
316.85	108.3	0.001482	0.0163	1443	2717	3.419	5.569	6.410	7.350
326.85	123.5	0.001541	0.0137	1506	2682	3.520	5.480	7.000	8.750
336.85	137.3	0.001612	0.0115	1573	2641	3.627	5.318	7.850	11.10
346.85	159.1	0.001705	0.0094	1647	2588	3.741	5.259	9.350	15.40
351.85	169.1	0.001778	0.0085	1697	2555	3.805	5.191	10.60	18.30
356.85	179.7	0.001856	0.0075	1734	2515	3.875	5.115	12.60	22.10
361.85	190.9	0.001935	0.0066	1783	2466	3.950	5.025	16.40	27.60
366.85	202.7	0.002075	0.0057	1841	2401	4.037	4.912	26.00	42.00
371.85	215.2	0.002351	0.0045	1931	2292	4.223	4.732	90.00	-
374.15	221.2	0.003170	0.0032	2107	2107	4.443	4.443	∞	∞

Table VI.2. Properties of air at atmospheric pressure (Perry et al., 1997). Reproduced with permission.

T (ºC)	Specific volume (m^3/kg)	Enthalpy$^+$ (kJ/kg)	Entropy$^+$ (kJ/kg·K)	Heat capacity (kJ/kg·K)
-183.15	0.251	-185.37	-1.130	1.044
-173.15	0.281	-174.97	-1.021	1.032
-153.15	0.34	-154.47	-0.834	1.020
-133.15	0.399	-134.17	-0.677	1.014
-113.15	0.457	-113.97	-0.542	1.010
-93.15	0.515	-93.77	-0.423	1.008
-73.15	0.537	-73.57	-0.317	1.007
-53.15	0.631	-53.47	-0.221	1.006
-33.15	0.688	-33.37	-0.133	1.006
-13.15	0.746	-13.27	-0.053	1.006
6.850	0.803	6.93	0.022	1.006
26.85	0.861	27.03	0.091	1.007

T (ºC)	Specific volume (m^3/kg)	Enthalpy[+] (kJ/kg)	Entropy[+] (kJ/kg·K)	Heat capacity (kJ/kg·K)
76.85	1.005	77.43	0.246	1.009
126.85	1.148	127.93	0.381	1.014
176.85	1.292	178.83	0.502	1.021
226.85	1.436	230.13	0.609	1.030
326.85	1.723	334.23	0.799	1.051
526.85	2.297	549.23	1.108	1.099
726.85	2.872	773.53	1.358	1.141
926.85	3.446	1004.73	1.569	1.175
1126.85	4.020	1241.73	1.751	1.207
1326.85	4.594	1490.73	1.915	1.248
1526.85	5.168	1743.73	2.064	1.286
1726.85	5.743	2005.73	2.203	1.337
2226.85	7.200	2737.73	2.528	1.665

[+] Unlike the original text, the origin of enthalpies and entropies here is established at 0°C

APPENDIX VII. EQUILIBRIUM DIAGRAMS OF PARTICULAR MIXTURES

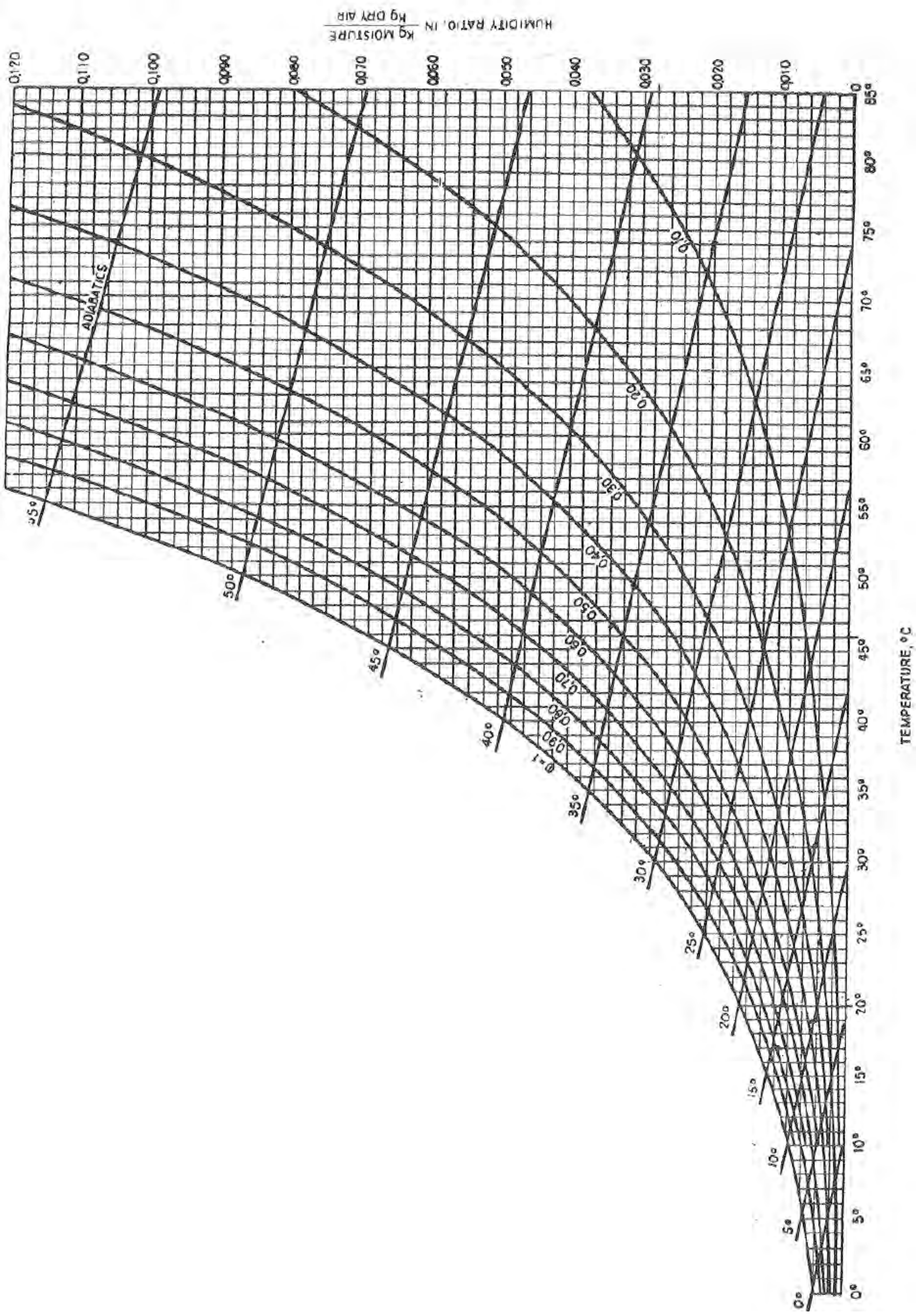


Figure VII.1. Psychrometric chart (adapted from Vian and Ocón, 1979).

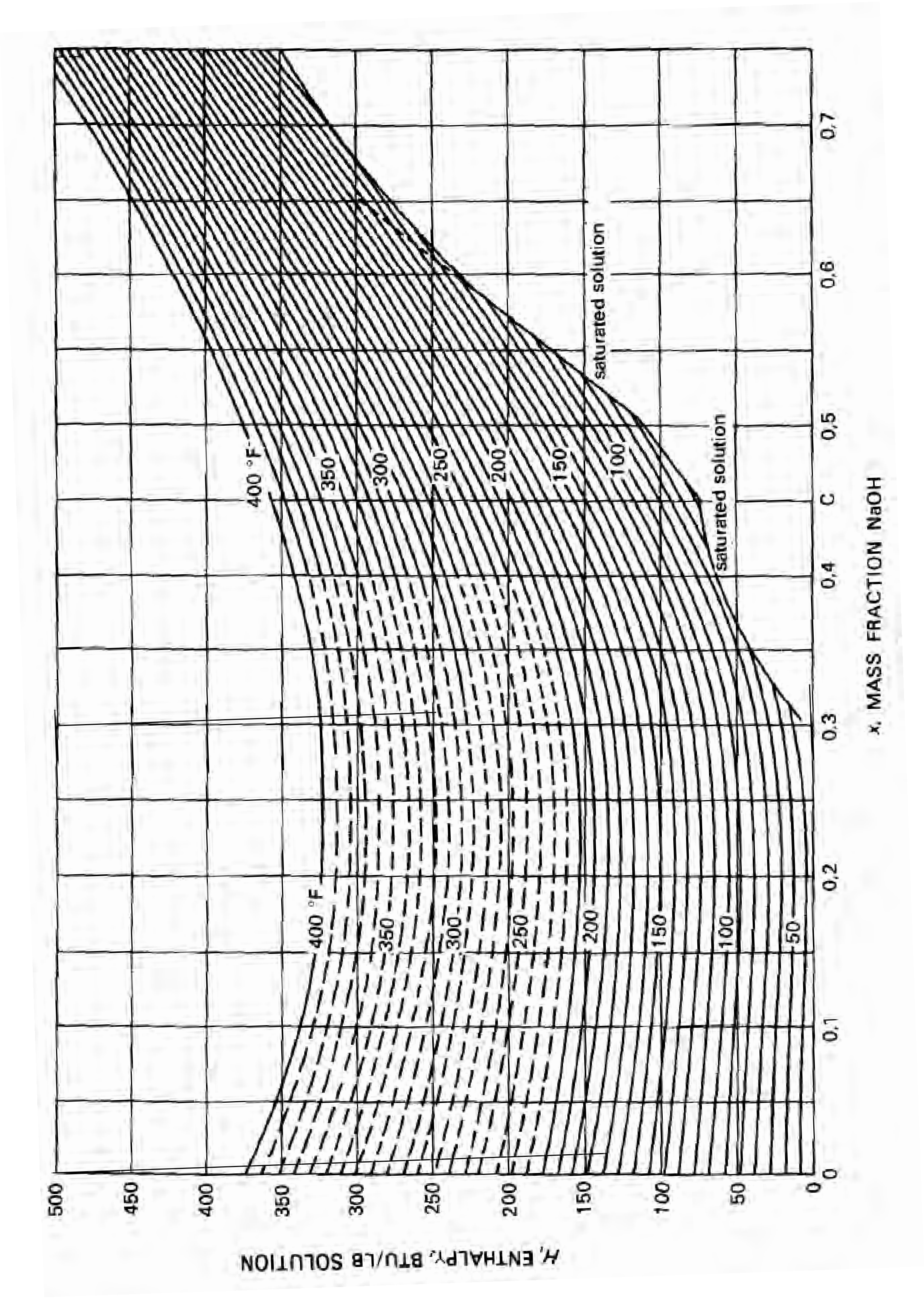


Figure VII.2. Enthalpy of the mixtures H_2O+NaOH (adapted from McCabe and Smith, 1998). Reproduced with permission.

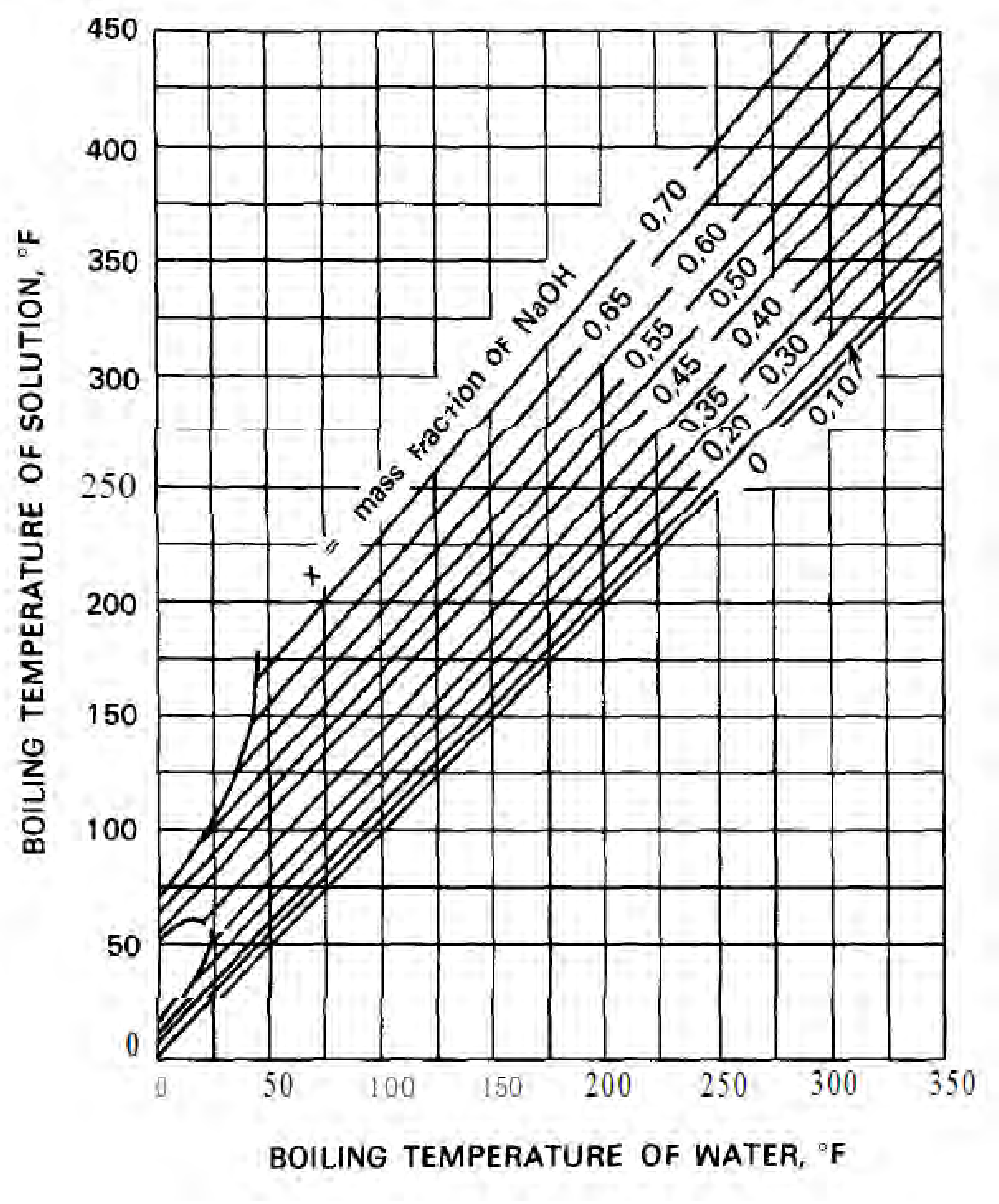


Figure VII.3. Dühring diagram of mixtures H_2O+NaOH (adapted from McCabe and Smith, 1998). Reproduced with permission.

BIBLIOGRAPHY

EXPRESSLY USED SOURCES

In order not to disperse the sources of information in a text aimed primarily to students, data points, tables and diagrams employed in solving the problems of Series 1 to 7 have been obtained from the following recomendable and most accesible sources cited here.

As stated in the Introduction, the material of Series 0 has been taken from the basic applied theory book of Bueno J. (2018) without further references. That textbook contained a lot of concerned bibliography, and we would like to acknowledge the role of all those sources mentioned there that, although not expresely cited below, are on the minds of all of us as basic references in thermodynamic knowledge.

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Problems of Thermodynamics applied to Chemical Engineering

Thermodynamics is a *legendary subject*! Its academic origins lie definitely within the field of Physics, and it concerns certain limitations that Nature imposes on our interactions with the world around us. Most science courses deal with operations, processes, reactions, etc., *that can proceed* – and thus *we have reason to study them*! Thermodynamics deals with things *we can't do*, and thus we are *forced* to study them to know what situations to avoid! The subject speaks to us through *Four Laws*. The First and Second Laws can be stated as the energy of the universe is constant and the entropy of the universe tends to a maximum. The Third Law involves the absolute zero, and the Zeroth Law deals with equilibrium. These are glorious ideas, with implications for lengthy, academic discussion. But scientists, engineers, and technicians in general need ways to apply thermodynamics to practical situations.

Only a few years after Rudolph Clausius made his philosophical statements about the Laws, an unknown, unpaid, professor of mathematical physics at Yale University, Josiah Willard Gibbs, translated them into an analysis system that could model real processes in thermodynamic terms. So thanks to Gibbs there was now a data-based mathematical structure that could predict the possibility of a given system undergoing a given change. But the mathematics was almost always complex and easy to misinterpret, and that caught the eye of one of Gibbs's contemporaries -- the Scottish physicist James Clerk Maxwell – who recommended visualizing the Math using a graph, a surface, a group of surfaces, a sculpture, or some other artistic model. Today we call that idea *scientific visualization*..

Kenneth R Jolls
Emeritus Professor. Iowa State University USA
Visiting Professsor at the Universidad de Oviedo
"Engineering, Entropy and Art: A Tour Through the Thermodynamics of J. W Gibbs"

One more book and, above all, one more book of problems on a widely visited field but, like so many others, misunderstood in what is already known and not appreciated in all its dimensions and scientific implications yet to be known, it just intends – and it is not little– to strengthen the path so far traveled for those who have to continue advancing and exploring, making steps forward. It is therefore simply a matter of putting at your disposal - at your disposal, reader of this epilogue - a few more keys to answer minor questions- for example, being able to see with different eyes a liquefied gas tank, a refrigeration cycle or a supercritical extractor; or been able to optimize an operating line through the twists and turns of a polyphase and multicomponent state diagram, and do so with the certainty of traveling through a stimulating natural park with reliable equipment and cartography.

Both in the theory text and in this one, of a more practical nature, an attempt has been made to promote a spatial vision or analogy of physical-chemical phenomenology, to which Prof. Jolls, an expert in both languages, could also have added a musical interpretation.

We believe that, with this new training table, those interested in the subject will have additional resources and stimuli to make progress in the thermodynamic expert knowledge of the natural and the technological. It is about helping to leave some issues duly settled and ready the tools to deal with others of greater scope and significance. Making way, which is what it is all about.

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