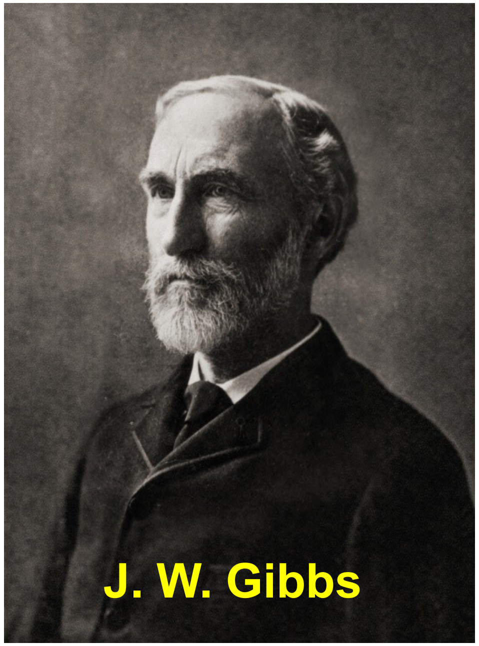
Advanced Chemical Engineering Thermodynamics CHE 622 (1.5 credit hours)



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Course contents

- The current course is divided into the following categories:

- Basic definitions, concepts, and relationships
- *pvT* relationships
- Thermodynamic property relationships for pure components and mixture of components

Relevant books

- Koretsky, M.D. 2013. Engineering and chemical thermodynamics. 2nd ed. John Wiley & Sons, Inc.
- Smith, J. M. Introduction to Chemical Engineering Thermodynamics. 6th ed., McGraw-Hill, Inc.
- Ó Connell, J.P.; Haile, J.M. 2005. Thermodynamics: Fundamentals for Applications. Cambridge University Press.

Values of gas constant in various units

8314.34	m^3	Pa	kmol	K
8.31434	**m^3**	**Pa**	**mol**	**K**
0.00831434	m^3	kPa	mol	K
83.1434	**cm^3**	**bar**	**mol**	**K**
0.0000831434	**m^3**	**bar**	**mol**	**K**
10.731	ft^3	psia	lbmol	°R
8.31434	J		mol	K
0.00831434	kJ		mol	K
1.9872	BTU		lbmol	°R

Basic definitions

System, surroundings, system boundary, universe, closed system, open system, isolated system, adiabatic process, isothermal process, isochoric or isometric process, isentropic process, isenthalpic process, isobaric or isopiestic process, point function or state function or property, path function or path variable, extensive property, intensive property, specific property, pressure, temperature, specific volume, state, process, phase, thermodynamic equilibrium, mechanical equilibrium, thermal equilibrium, chemical equilibrium, chemical reaction equilibrium, phase equilibrium, qausi-equilibrium state, reversible process, internally reversible process, externally reversible process, first law of thermodynamics, second law of thermodynamics, third law of thermodynamics, partial molar property, chemical potential, fugacity, fugacity coefficient, molar property, equation of state, rate, dynamic equilibrium, state postulate, independent variable, dependent variable, corresponding states principle, internal energy, enthalpy, entropy, free energy (Gibbs and Helmholtz), triple point, critical point, work, heat, kinetic energy, potential energy, saturation pressure, saturation temperature, vapor pressure, bubble point, dew point, quality or dryness fraction, wetness fraction, saturated liquid, saturated vapor, saturated wet vapor, superheated vapor, subcooled or compressed liquid, ideal gas, kinetic theory of gases, working fluid, etc.

A few basic definitions [1]

Thermodynamic equilibrium: When two or more phases in contact have equal temperatures, pressures, and chemical potentials then the phases are said to be in thermodynamic equilibrium. In other words, when phases are in thermal, mechanical, and chemical equilibria they are in thermodynamic equilibrium. Truly speaking, this can only occur in a closed system, because in an open system the condition of mechanical equilibrium may not be exactly satisfied. At the thermodynamic equilibrium, the molecular motion does not cease and all the thermodynamic equilibria are therefore dynamic in nature. When two phases such as vapor and liquid in a system have the same temperature, they are said to be in thermal equilibrium. When two phases such as vapor and liquid in a system have the same pressure, they are said to be in mechanical equilibrium. When each of the components in a system of two phases such as vapor and liquid have the same chemical potentials in each phase, then the phases are said to be in chemical equilibrium.

A few basic definitions [1]

Reversible process: Also called as totally reversible process. In a reversible process both system and its surroundings are restored to their original or initial states. In other words, for a process in which a system can be traced back to its original or initial state (with initial state properties) without leaving a change on (the properties of) the surroundings is known as a reversible process. A reversible or totally reversible process should be both externally as well as internally reversible. See internally reversible process and externally reversible process.

Internally reversible process: A process is said to be internally reversible if no irreversibilities occur within a system, i.e., within a system boundary. A reversible or totally reversible process should be both externally as well as internally reversible.

Quasi-static process: A quasi-static process proceeds infinitely slowly and remains close to the equilibrium state at all the times. The process can be reversed at any time.

A few basic definitions [1]

Chemical potential: Chemical potential is the partial molar Gibbs free energy of a component in a binary or multicomponent system. It is therefore the change in Gibbs free energy with the infinitesimal change in number of moles of a component while keeping pressure, temperature, and moles of all the other components as constant. Like entropy, chemical potential is an abstract quantity and the introduction of chemical potential in thermodynamic relationships is useful in explaining various thermodynamic processes. Chemical potential is considered as the escaping tendency of a component to leave a phase where its value is higher and to enter the phase where its value is lower. Chemical potential gradient is therefore the driving force for mass transfer processes. Chemical potential is related to fugacity which is a useful parameter in describing the phase equilibrium relationships. Chemical potential is an intensive property.

For the others, see class notes.

Energy balance for closed system

$$de = \delta q + \delta w$$

$$e = e_K + e_P + u$$

$$de_K + de_P + du = \delta q + \delta w$$

$$\Delta e_K + \Delta e_P + \Delta u = q + w$$

$$m\Delta e_K + m\Delta e_P + m\Delta u = mq + mw$$

$$\Delta E_K + \Delta E_P + \Delta U = Q + W$$

Neglecting kinetic and potential energy contributions,
it may be shown that

$$du = \delta q + \delta w$$

$$\Delta u = q + w$$

The w contains all types of works, but it is most commonly the pv work.

$$w = -\int p_{ex} dv = -\int p dv \qquad \text{(for reversible conditions)}$$

$$W = mw = -m\int p_{ex} dv = -m\int p dv = -\int p dV$$

Energy balance for an open system

$$\Delta e_K + \Delta e_P + \Delta h = q + w_s$$

$$\dot{m}\Delta e_K + \dot{m}\Delta e_P + \dot{m}\Delta h = \dot{m}q + \dot{m}w_s$$

$$\Delta \dot{E}_K + \Delta \dot{E}_P + \Delta \dot{H} = \dot{Q} + \dot{W}_s$$

Develop mechanical energy balance from the total energy balance equation given above.

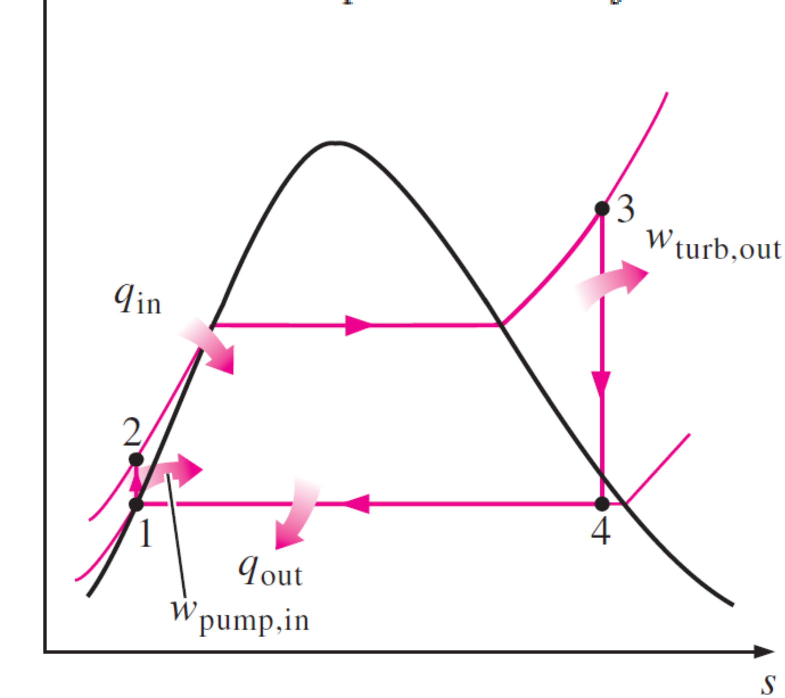
Basic relationships

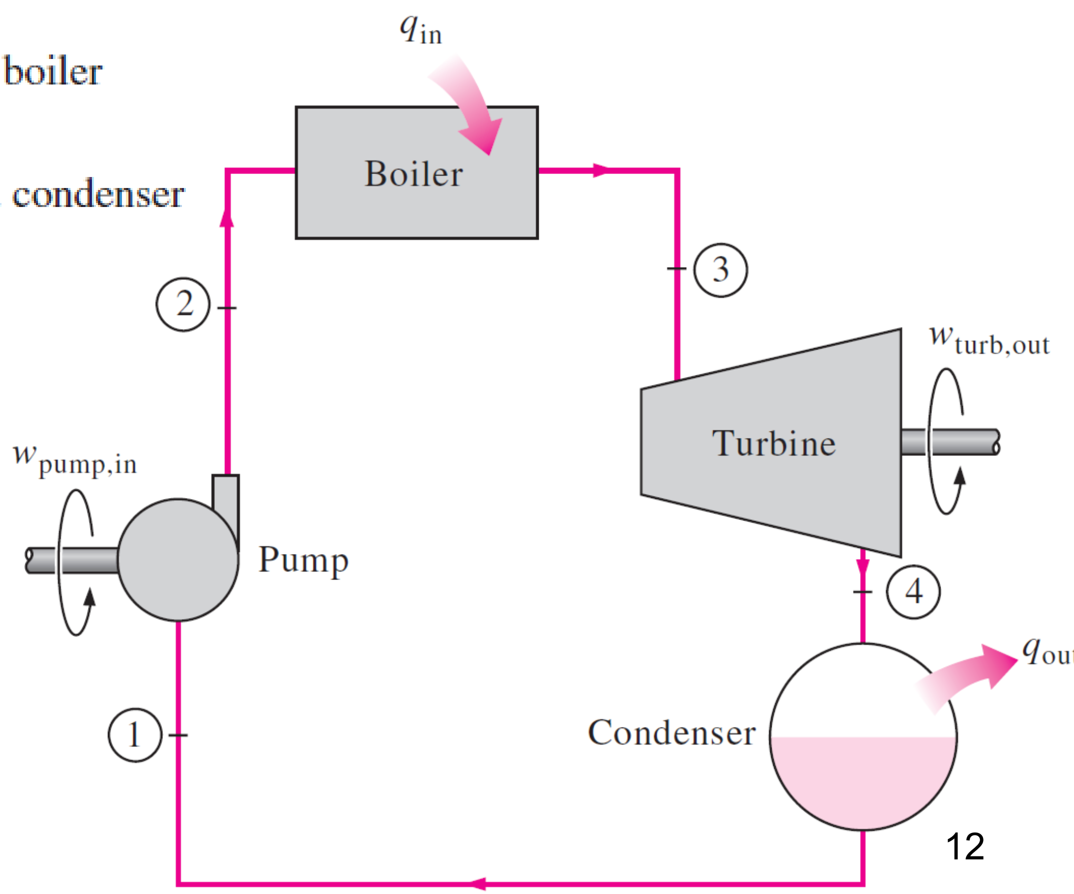
For derivations and the other relationships, see class notes.

Rankine cycle, ideal [2]

Write down the total energy balance (First Law of Thermodynamics) for each unit and neglect the terms having negligible contribution towards energy balance equation. Here, each of the devices is as an open system and not a closed system.

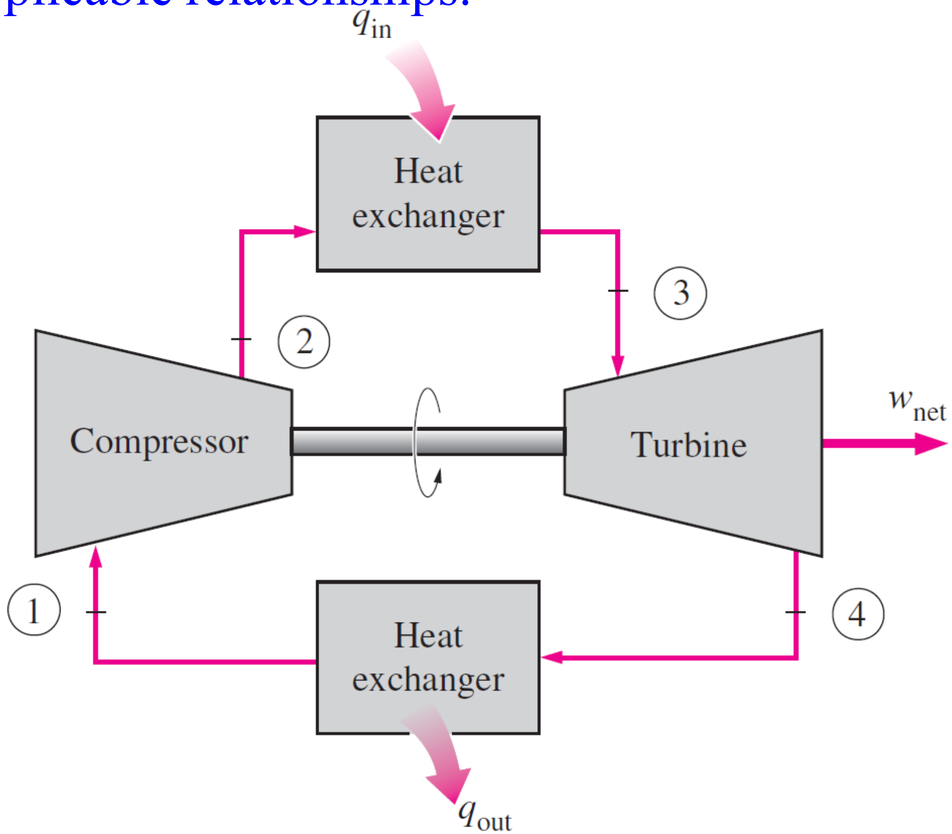
1-2 Isentropic compression in a pump
2-3 Constant pressure heat addition in a boiler
3-4 Isentropic expansion in a turbine
4-1 Constant pressure heat rejection in a condenser

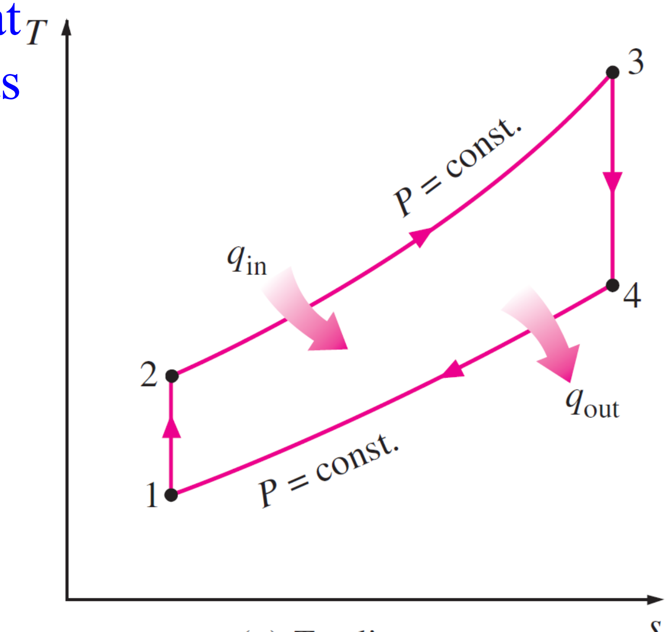




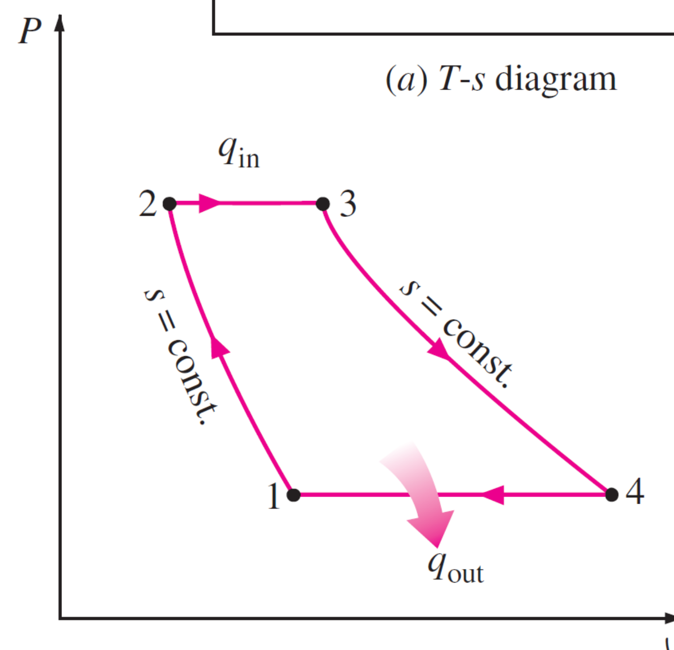
Closed gas turbine (Brayton) cycle, ideal [2]

Using energy balance, the definition of specific heat capacity and ideal gas relationships, workout the various applicable relationships.





(*a*) *T-s* diagram



(*b*) *P-v* diagram

1-2 Isentropic compression (in a compressor)

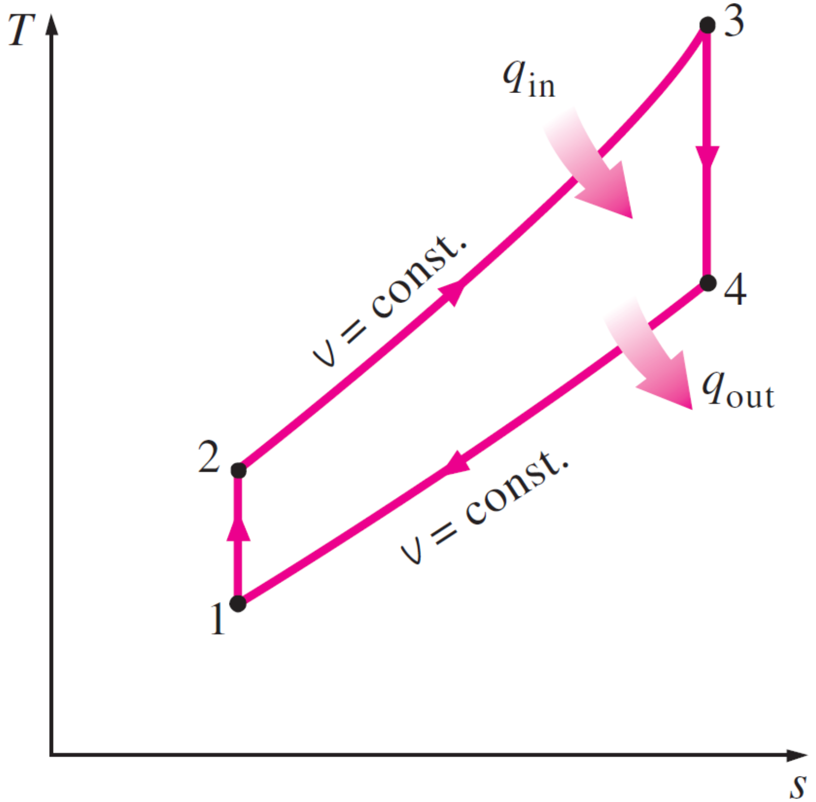
2-3 Constant-pressure heat addition

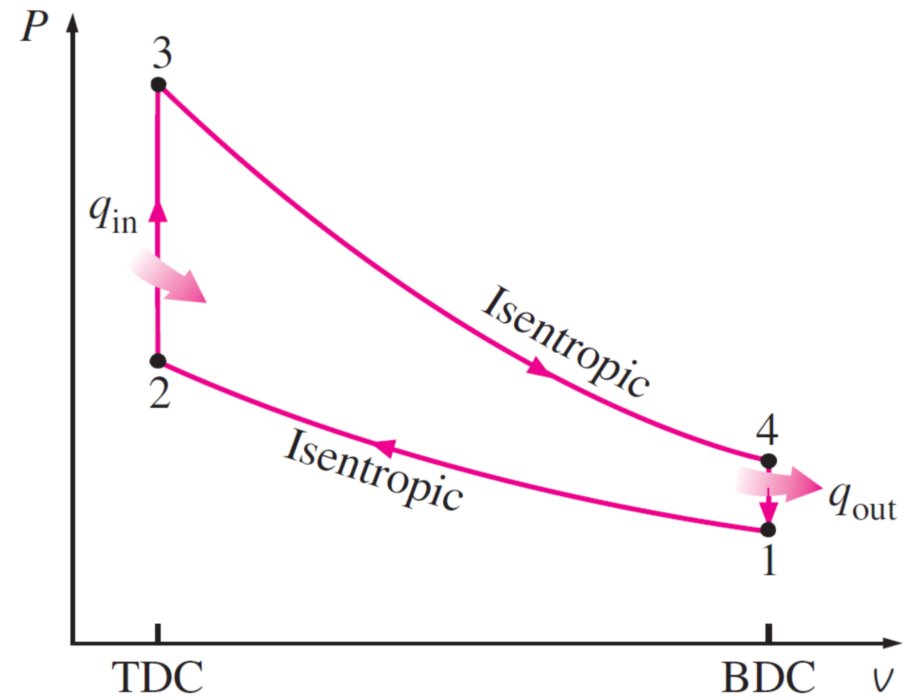
3-4 Isentropic expansion (in a turbine)

4-1 Constant-pressure heat rejection

Otto cycle, ideal [2]

Using energy balance, the definition of specific heat capacity, and ideal gas relationships, workout the various applicable relationships.





1-2 Isentropic compression

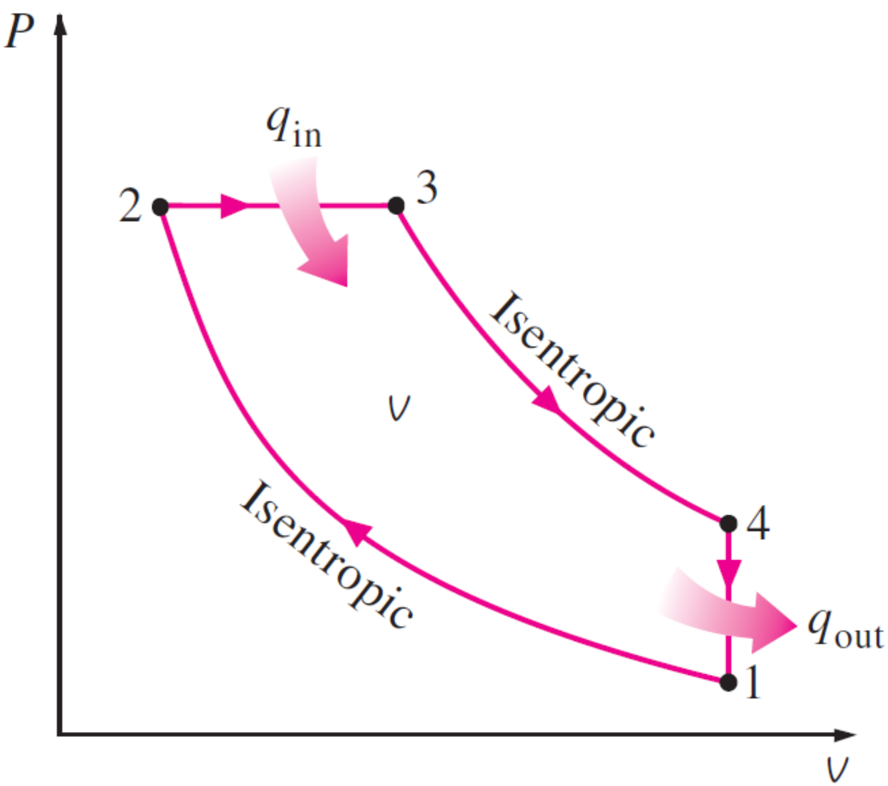
2-3 Constant-volume heat addition

3-4 Isentropic expansion

4-1 Constant-volume heat rejection

Diesel cycle, ideal [2]

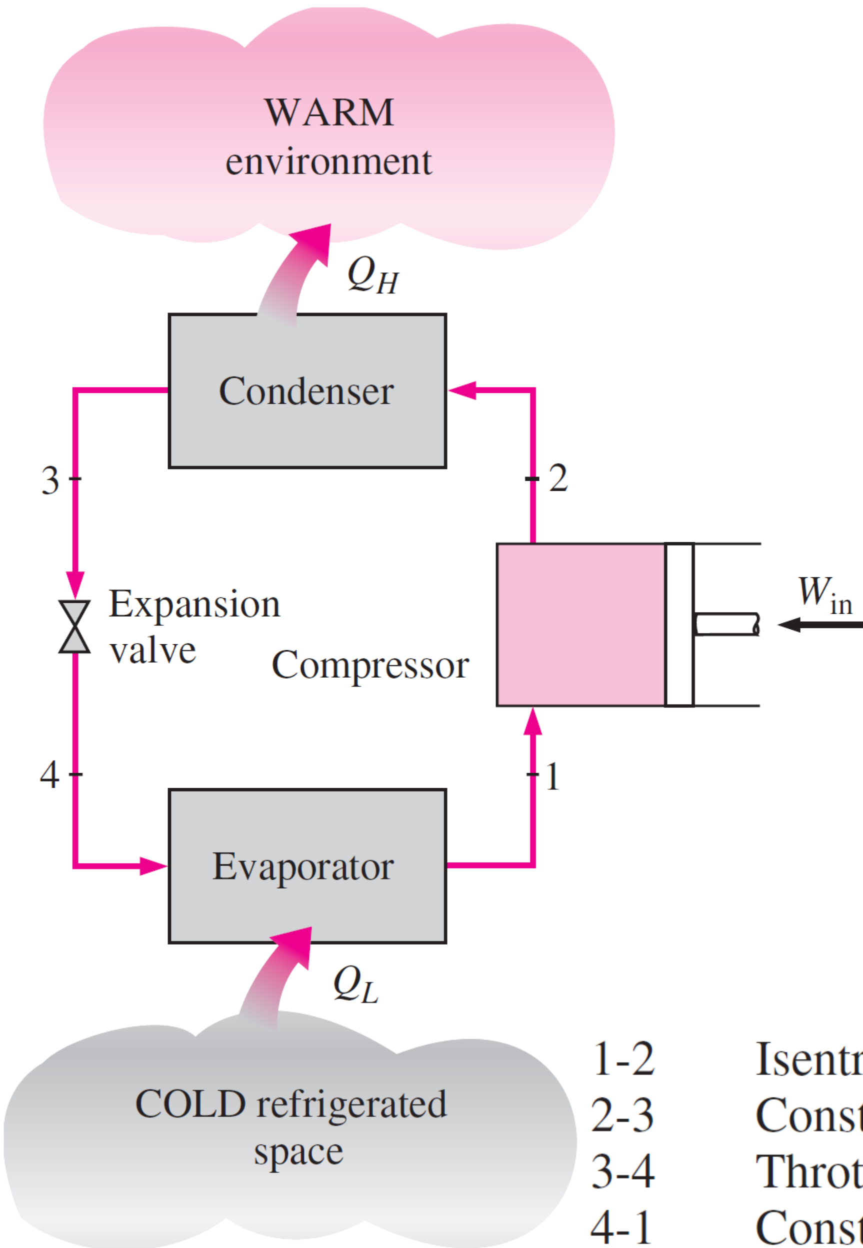
What are the four processes of ideal Diesel cycle? How are these different from ideal Otto cycle? Draw *T-s* diagram of ideal Diesel cycle.

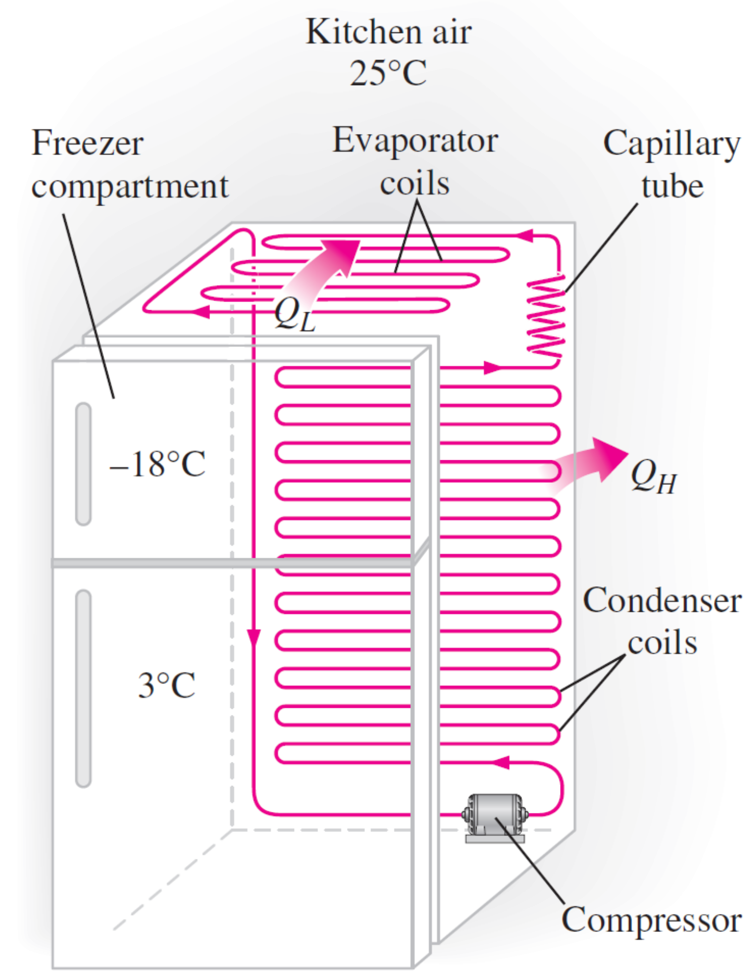


(*a*) *P*- v diagram

Using energy balance, the definition of specific heat capacity and ideal gas relationships, workout the various applicable relationships.

Vapor-compression refrigeration cycle, ideal [2]

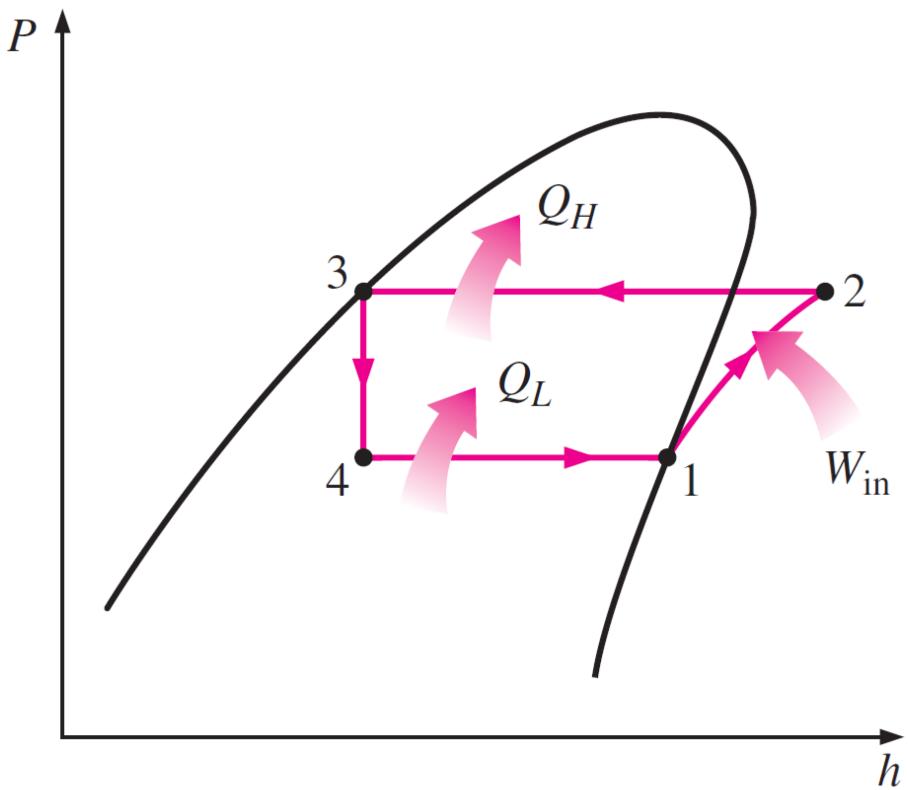


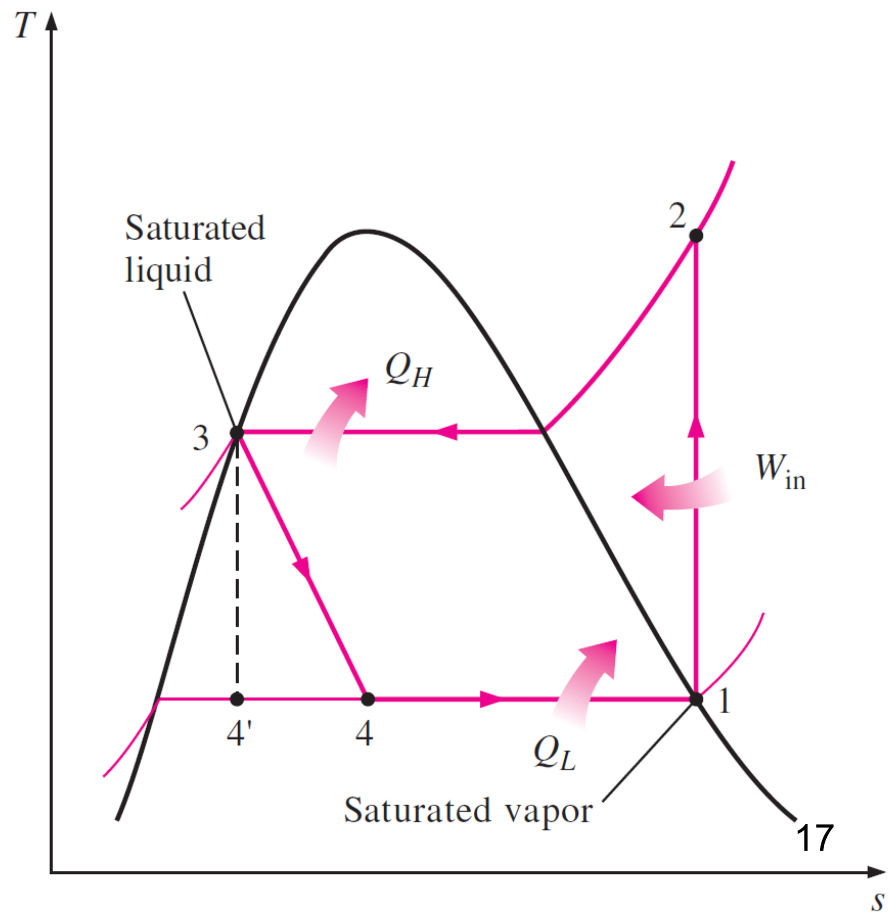


1-2	Isentropic compression in a compressor
2-3	Constant-pressure heat rejection in a condenser
3-4	Throttling in an expansion device
4-1	Constant-pressure heat absorption in an evaporator

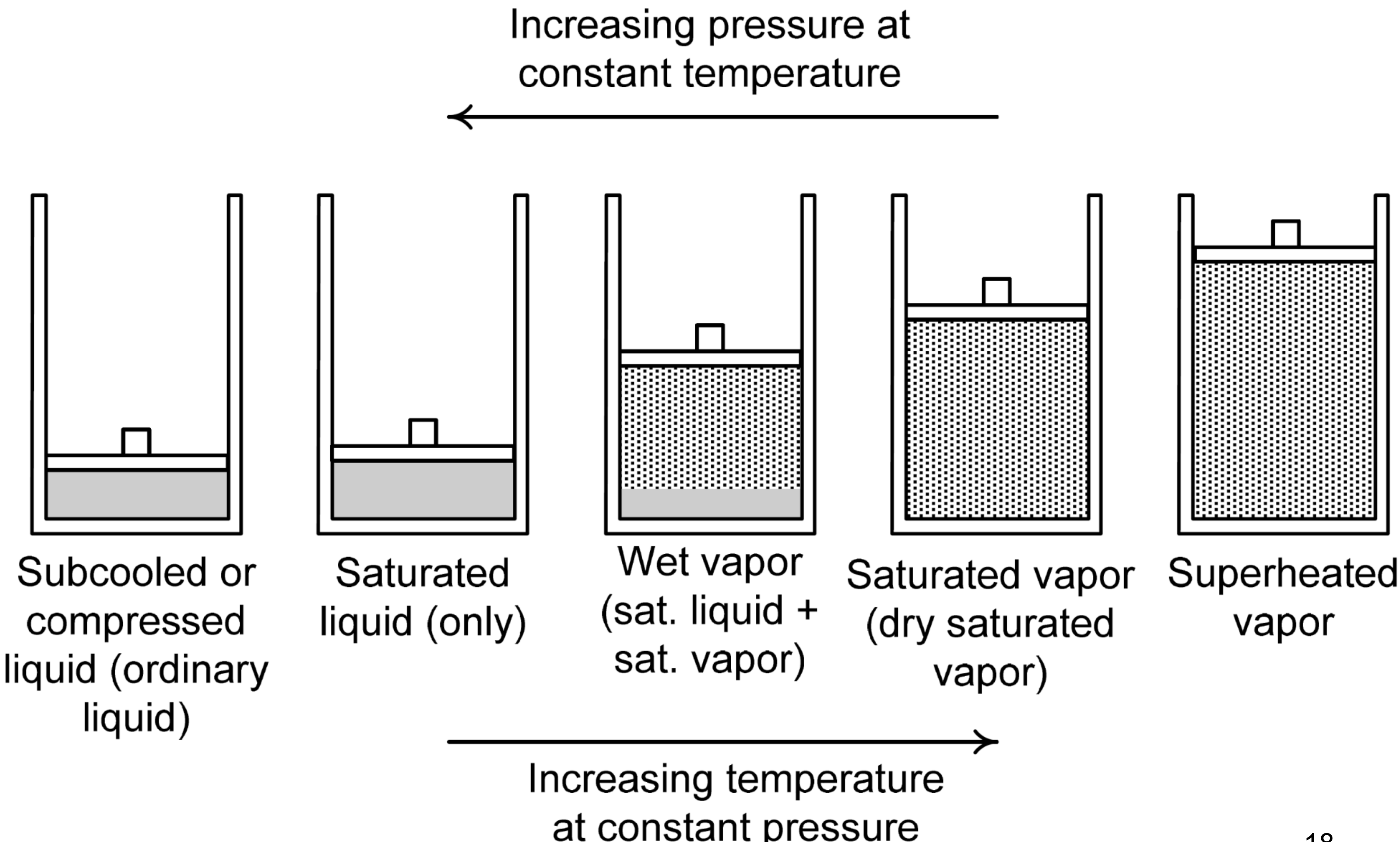
Vapor-compression refrigeration cycle, ideal [2]

Write down the total energy balance (First Law of Thermodynamics) for each unit and neglect the terms having negligible contribution towards energy balance equation. Here, each of the devices is as an open system and not a closed system.

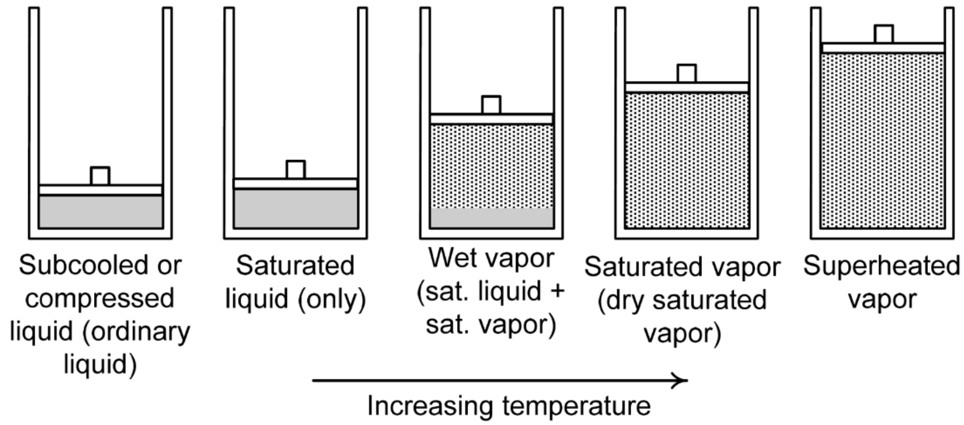


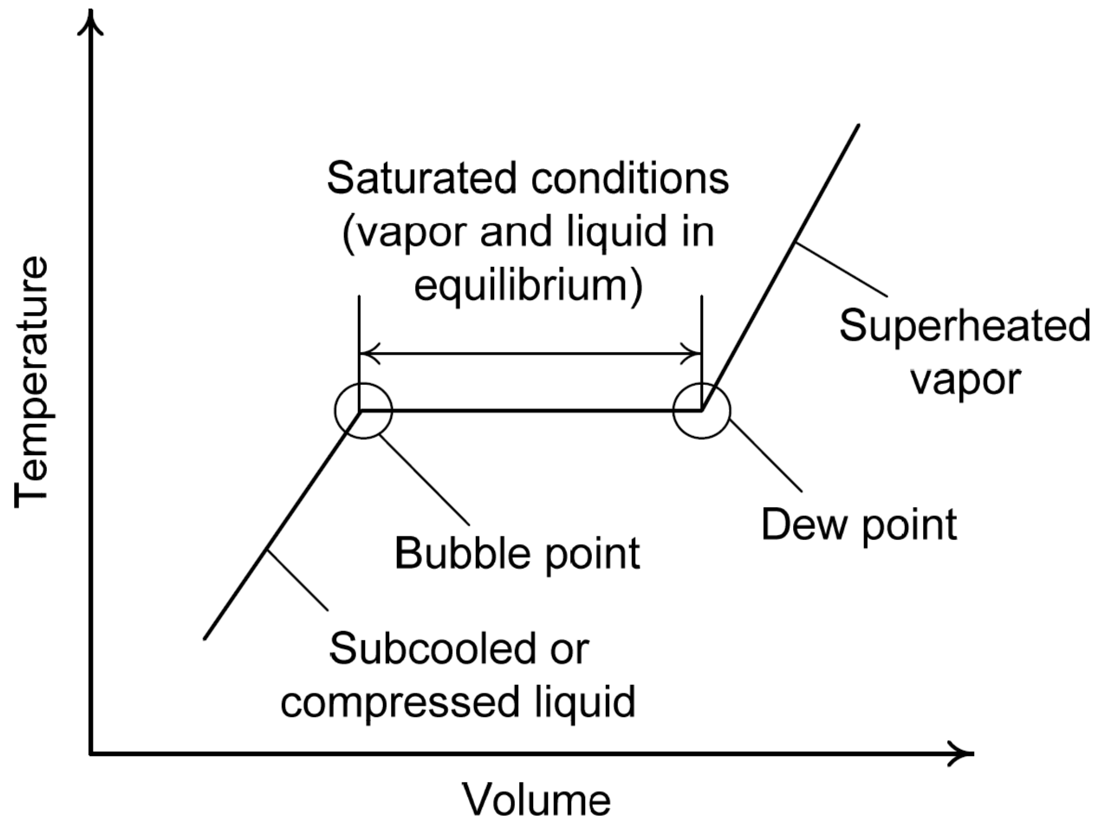


Phase behavior of a pure component [1]



Phase behavior of a pure component [1]

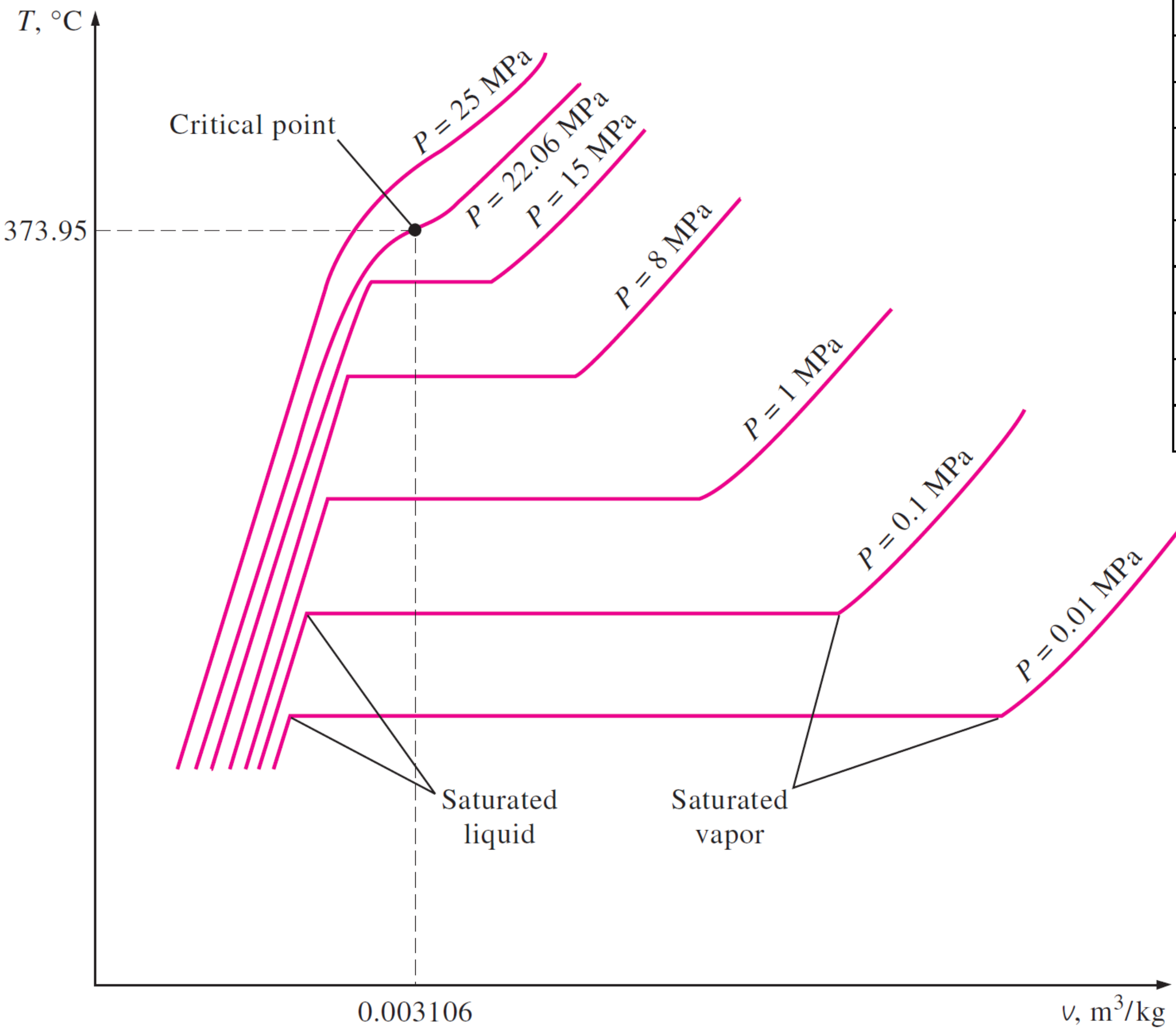




Phase behavior of a pure water [2]

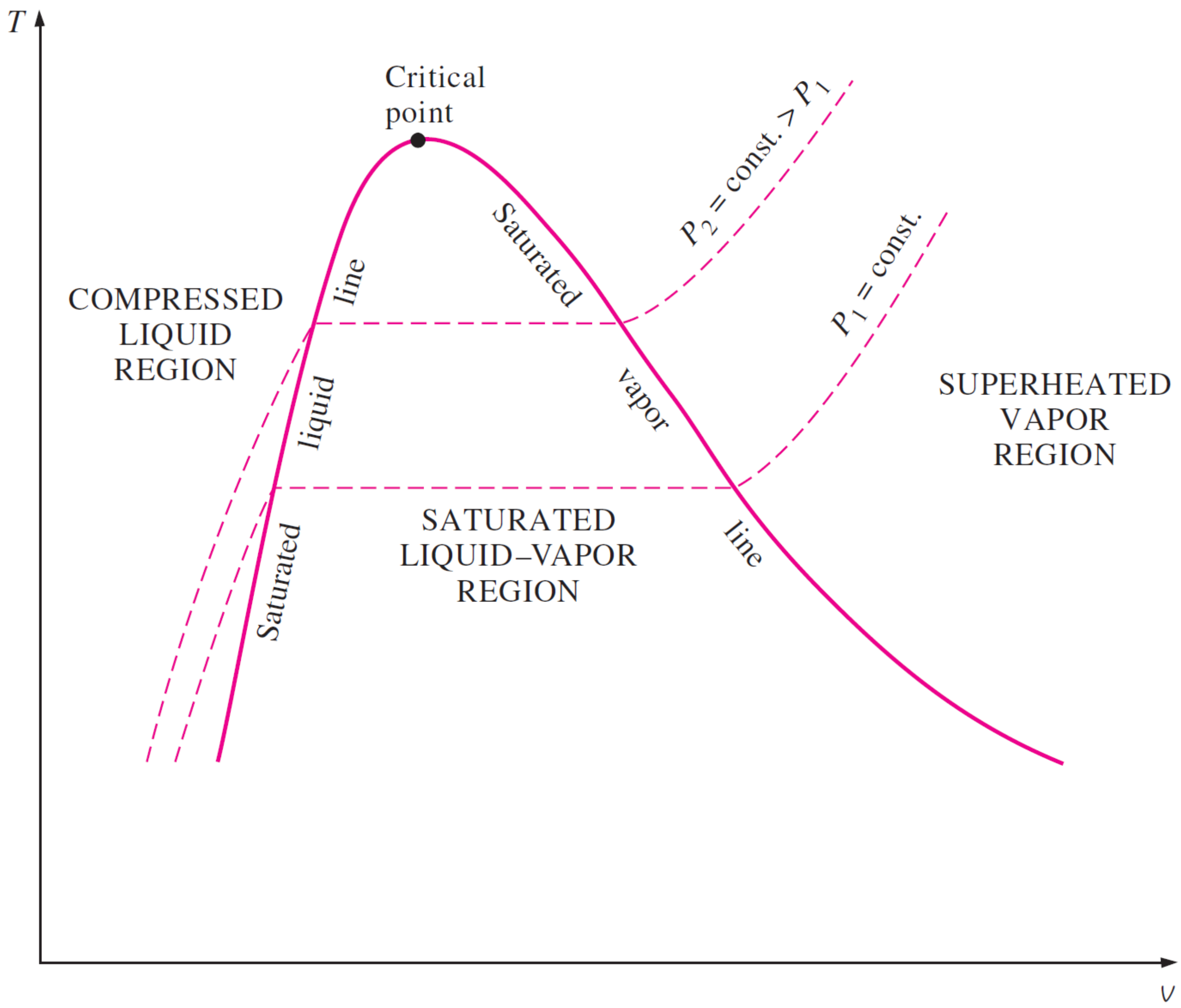
Please go through steam table and see the other values of saturated pressures (vapor pressures) against saturated temperatures (boiling points).

p_{sat}, kPa (vapor pressure)	T_{sat}, °C (boiling point)
0.6113	0.01
1.0	6.98
2.0	17.50
10	45.81
20	60.06
100	99.62
200	120.23
1000	179.91
2000	212.42
10000	311.06
20000	365.81
22089	374.14

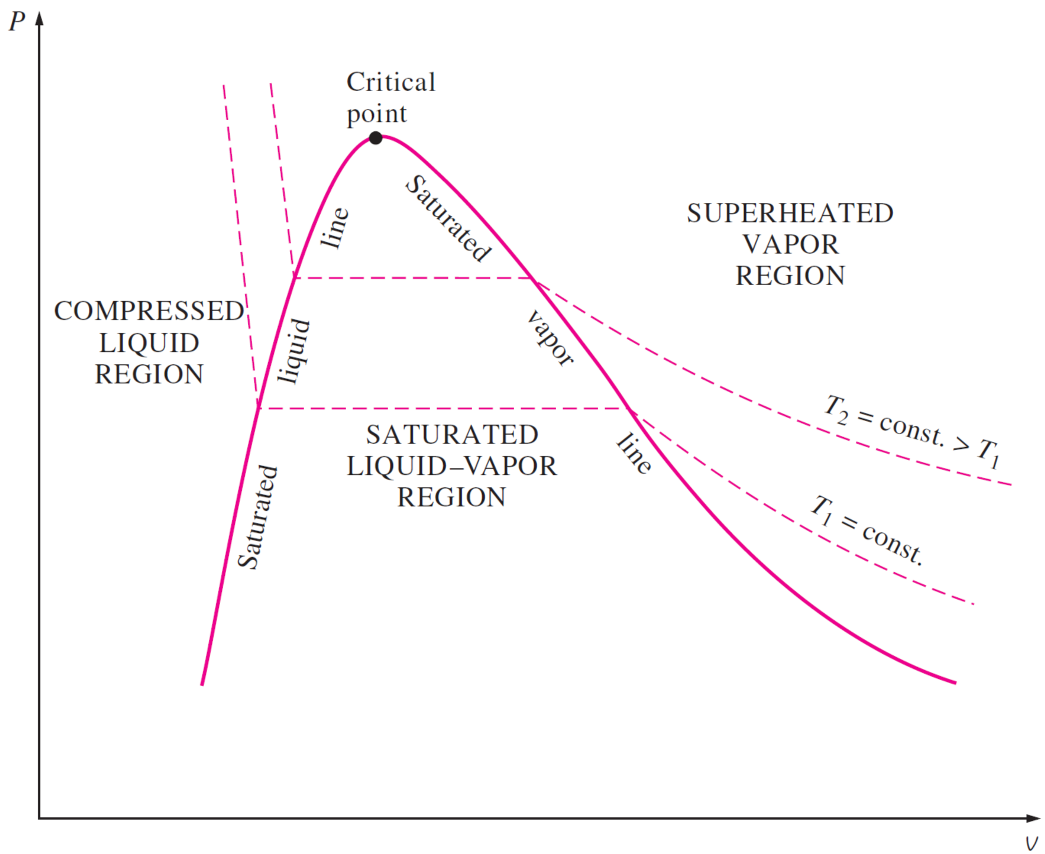


H_2O

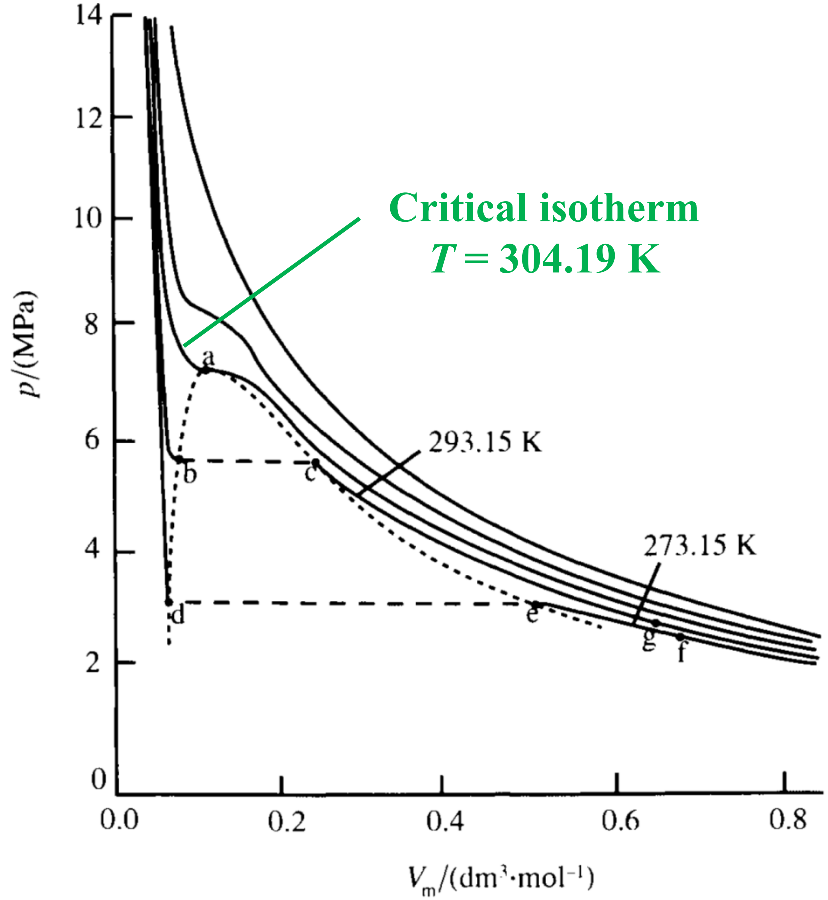
Phase behavior of a pure component [2]



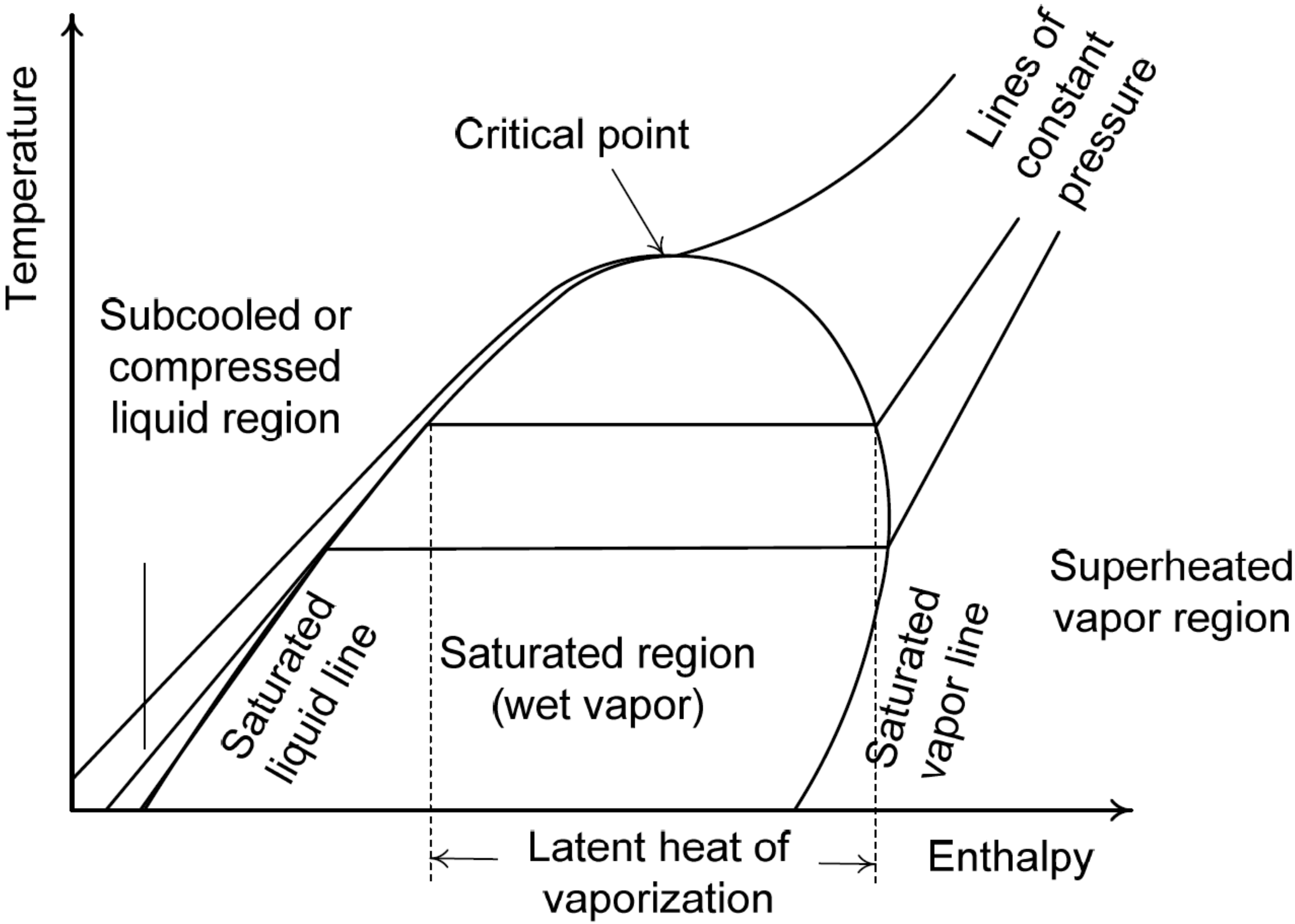
p-v diagram of a pure component



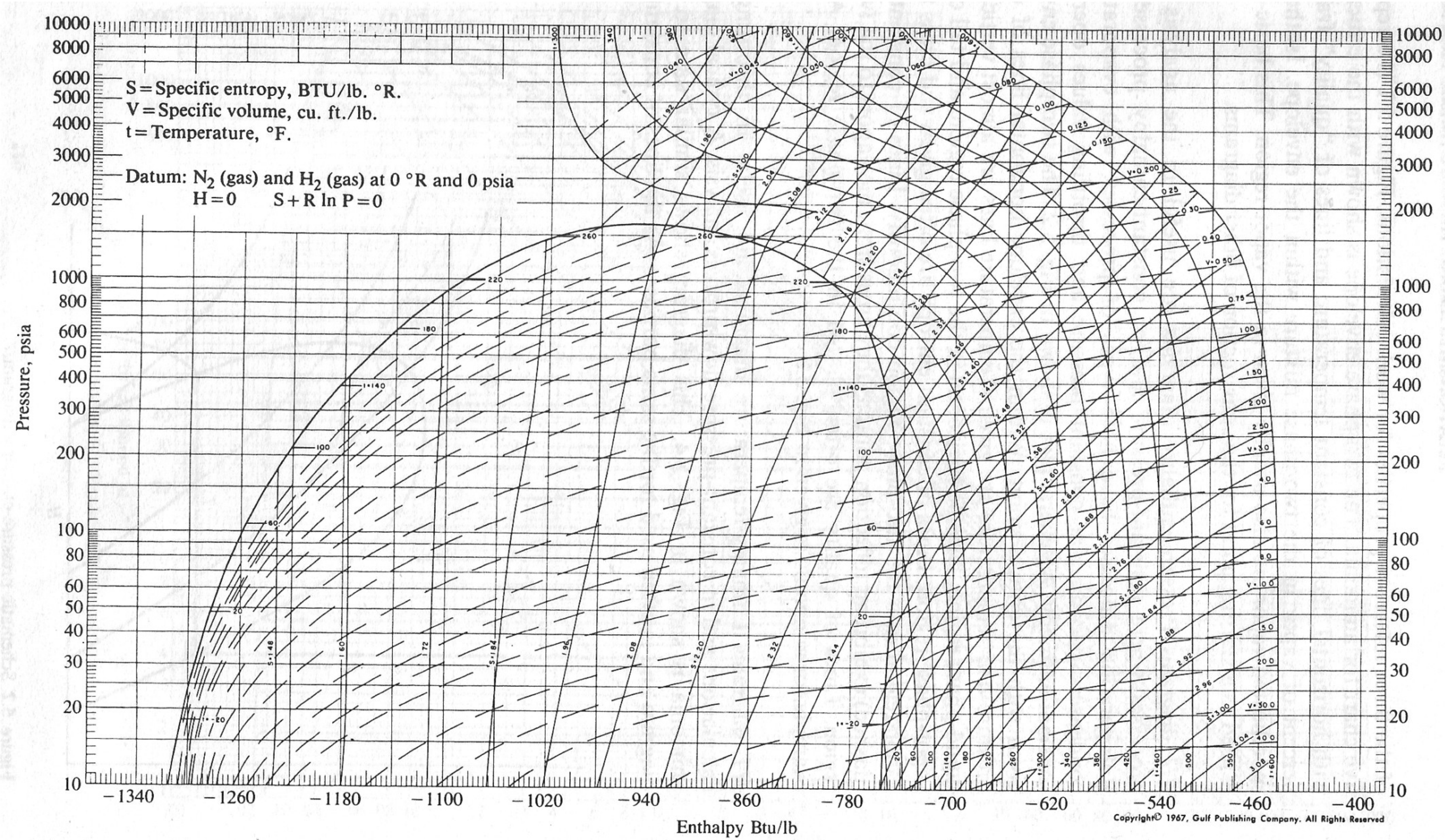
Experimental *p-v* diagram of CO_2 [p.396, 3]



Phase behavior of a pure component [1]

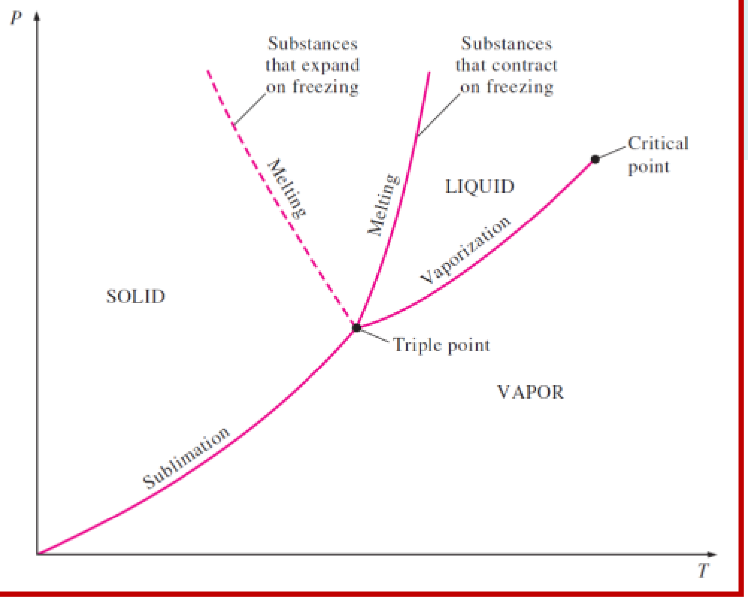


P-h diagram of NH_3 [11]

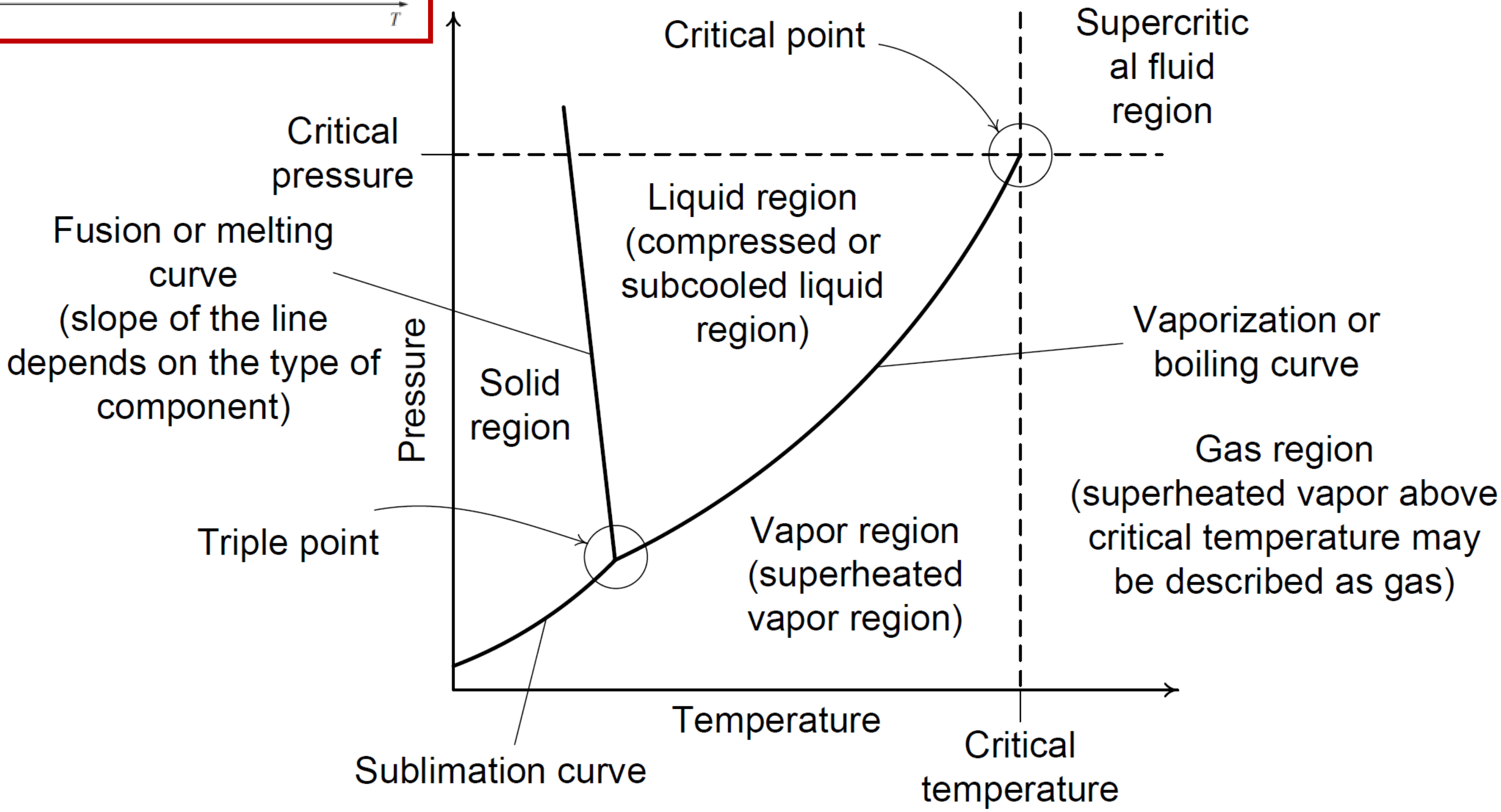


Pressure-enthalpy diagram for ammonia. *(From Lawrence N. Canjar and Francis S. Manning, "Thermodynamic Properties and Reduced Correlations for Gases,"*

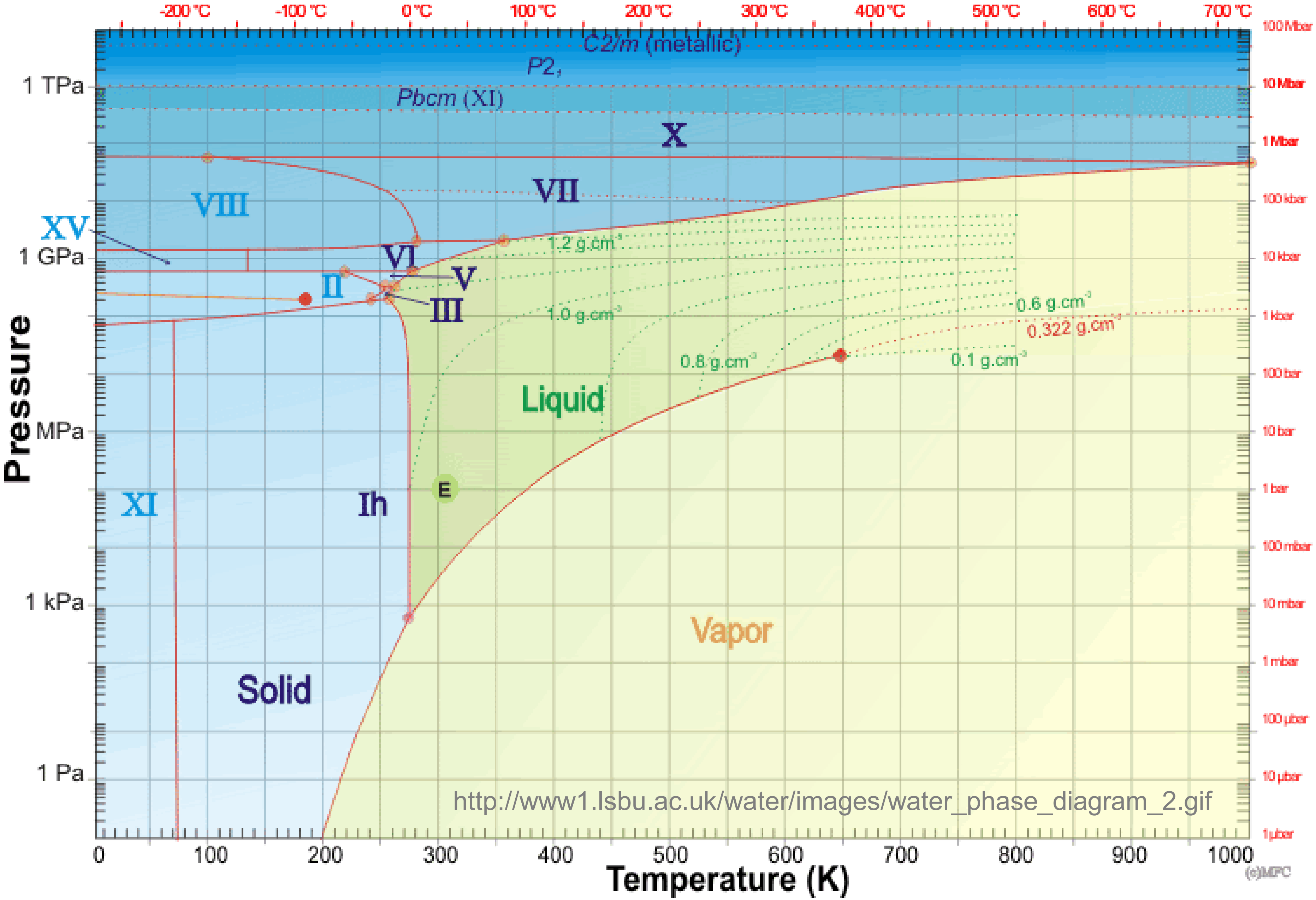
p-T diagram of a pure component [1, 2]



For water like substances if we increase pressure, the solid melts to liquid. So, for water, ice melts to liquid water and is helpful for skating.

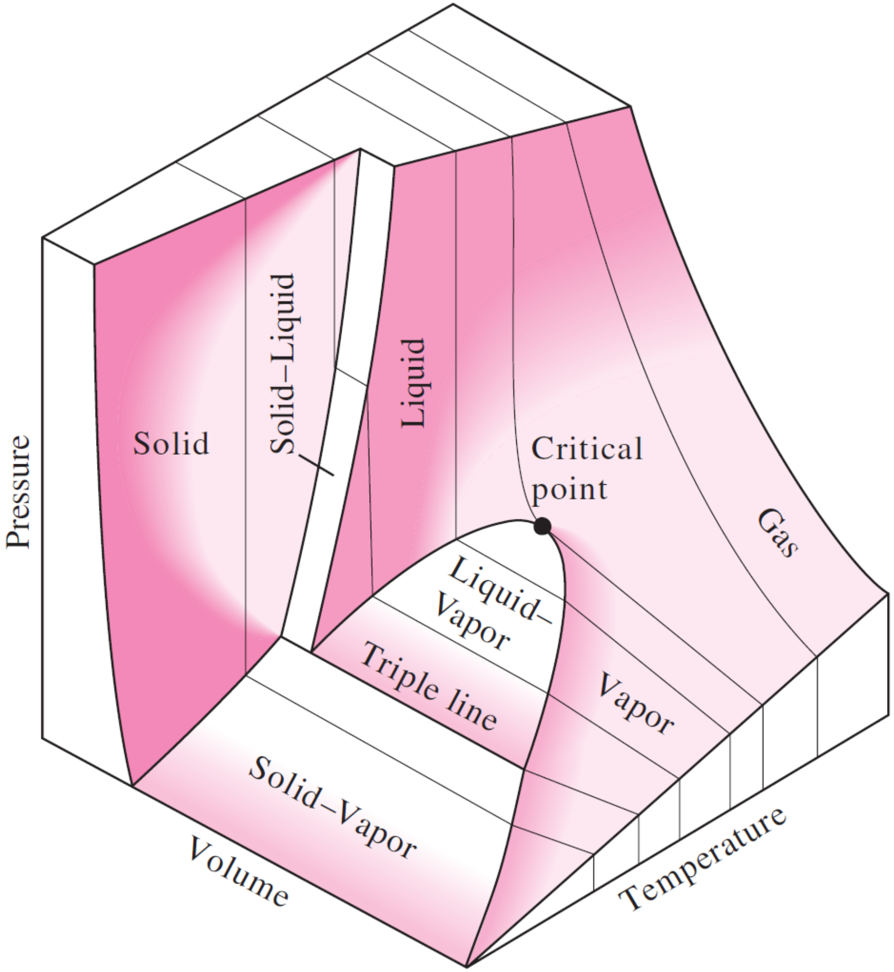


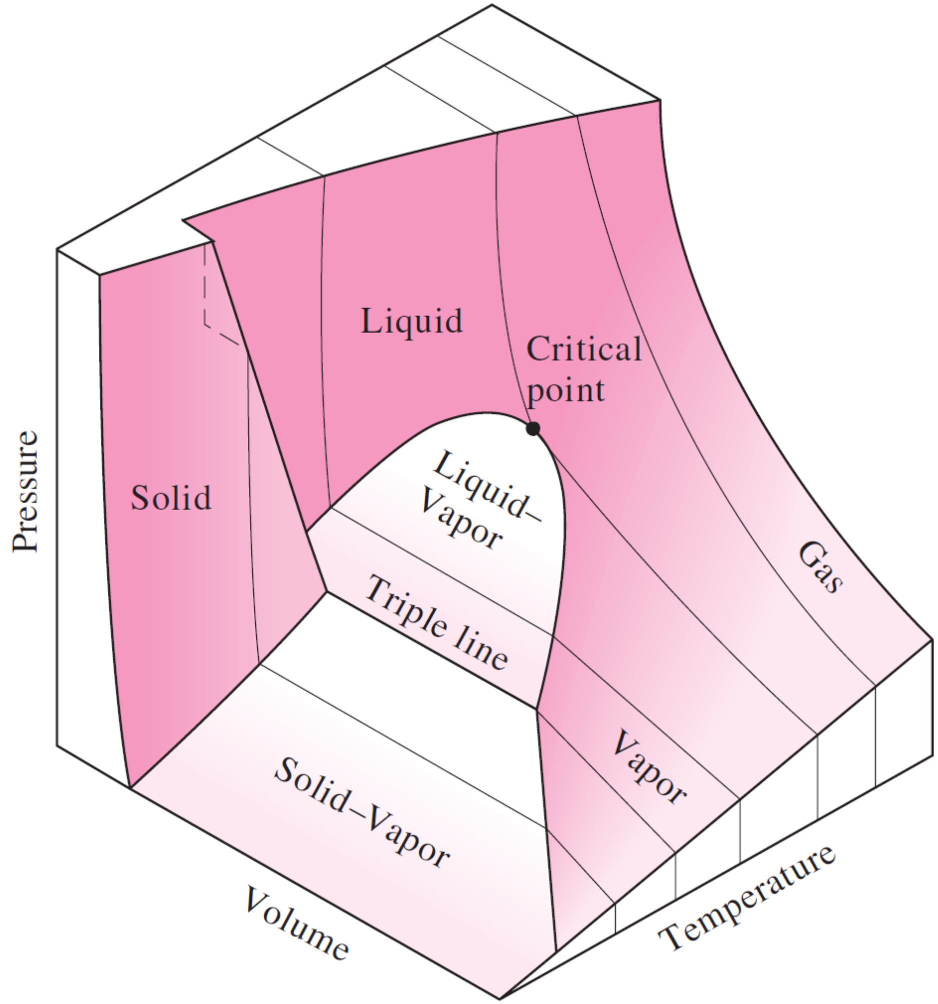
Phase behavior of a pure water



pvT surface of a pure component [2]

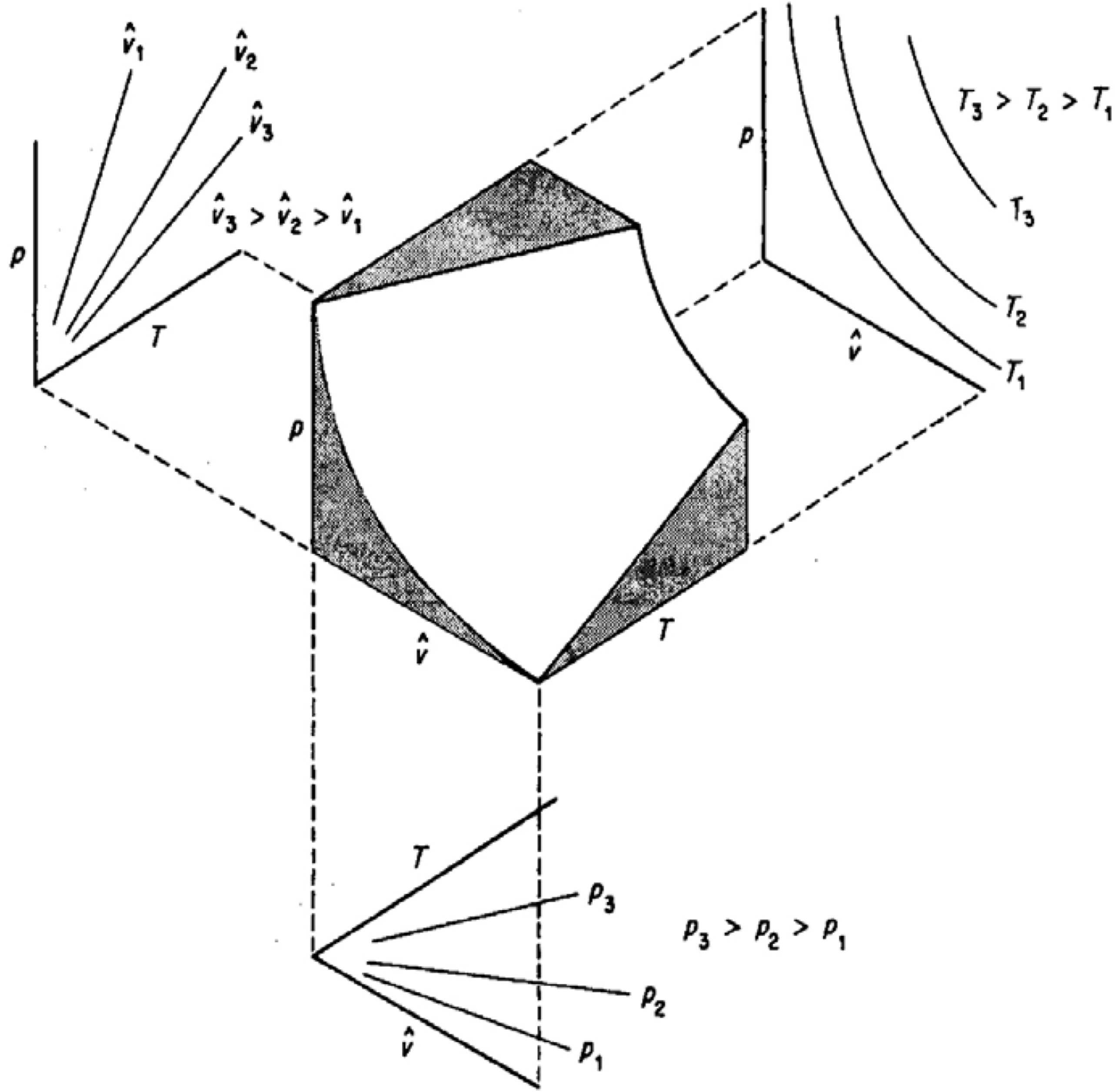
Contracts on freezing



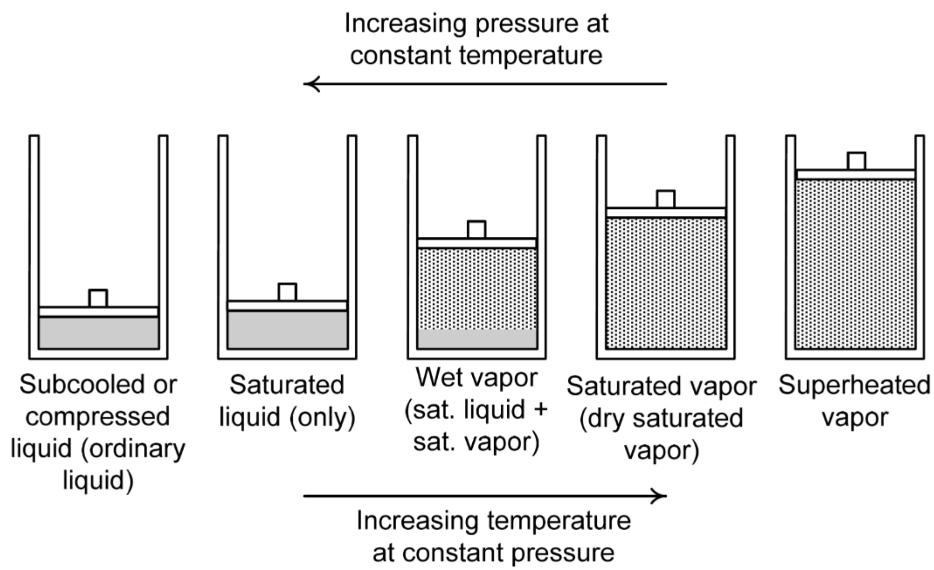


Expands on freezing

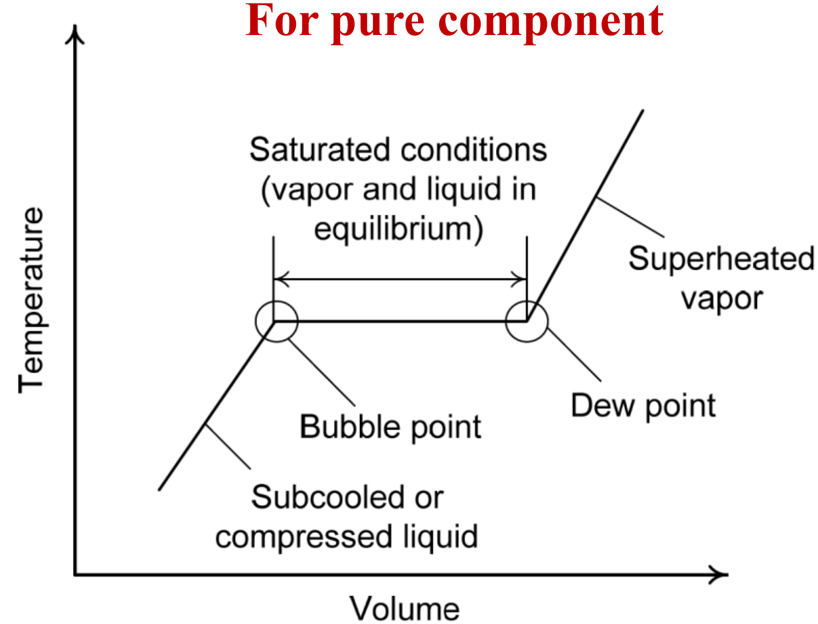
pvT surface of an ideal gas [4]

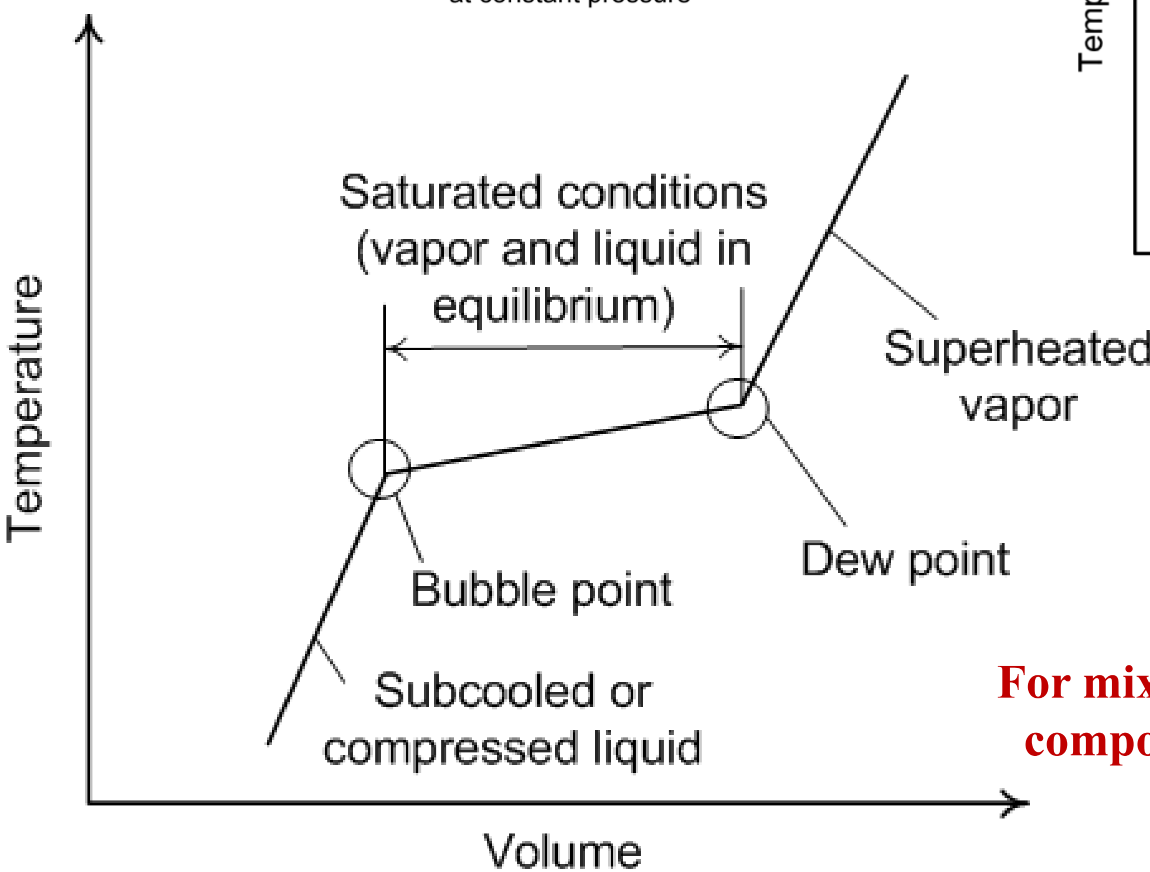


Phase behavior of a mixture of components



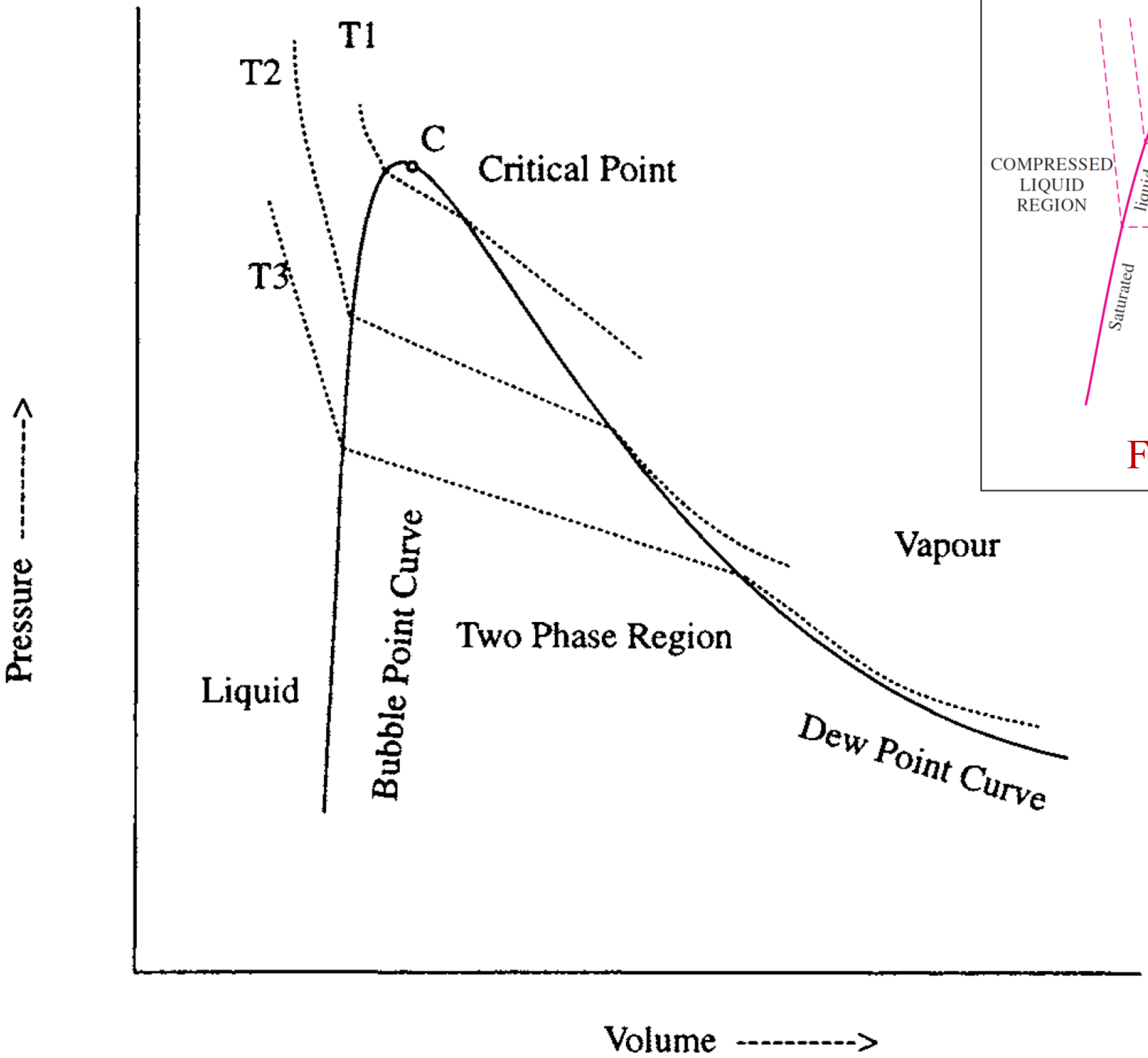
For pure component

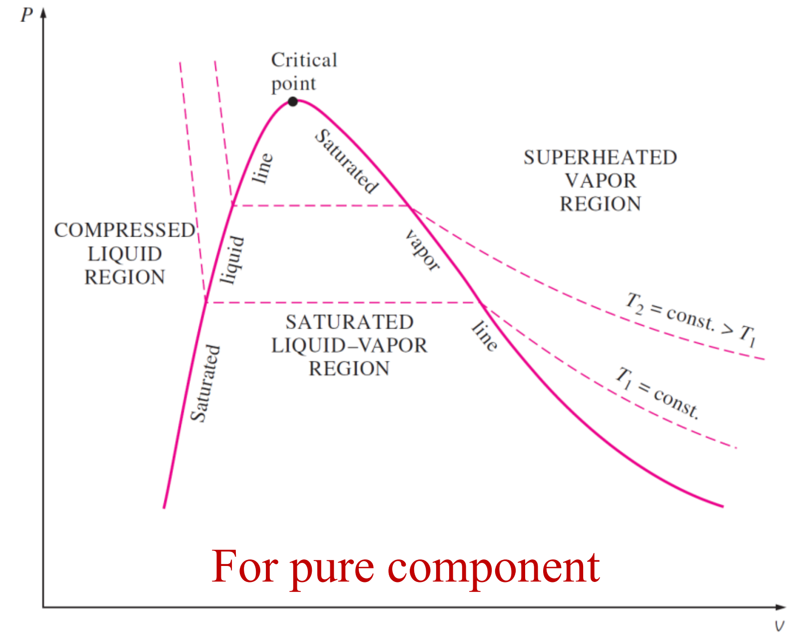




For mixture of components

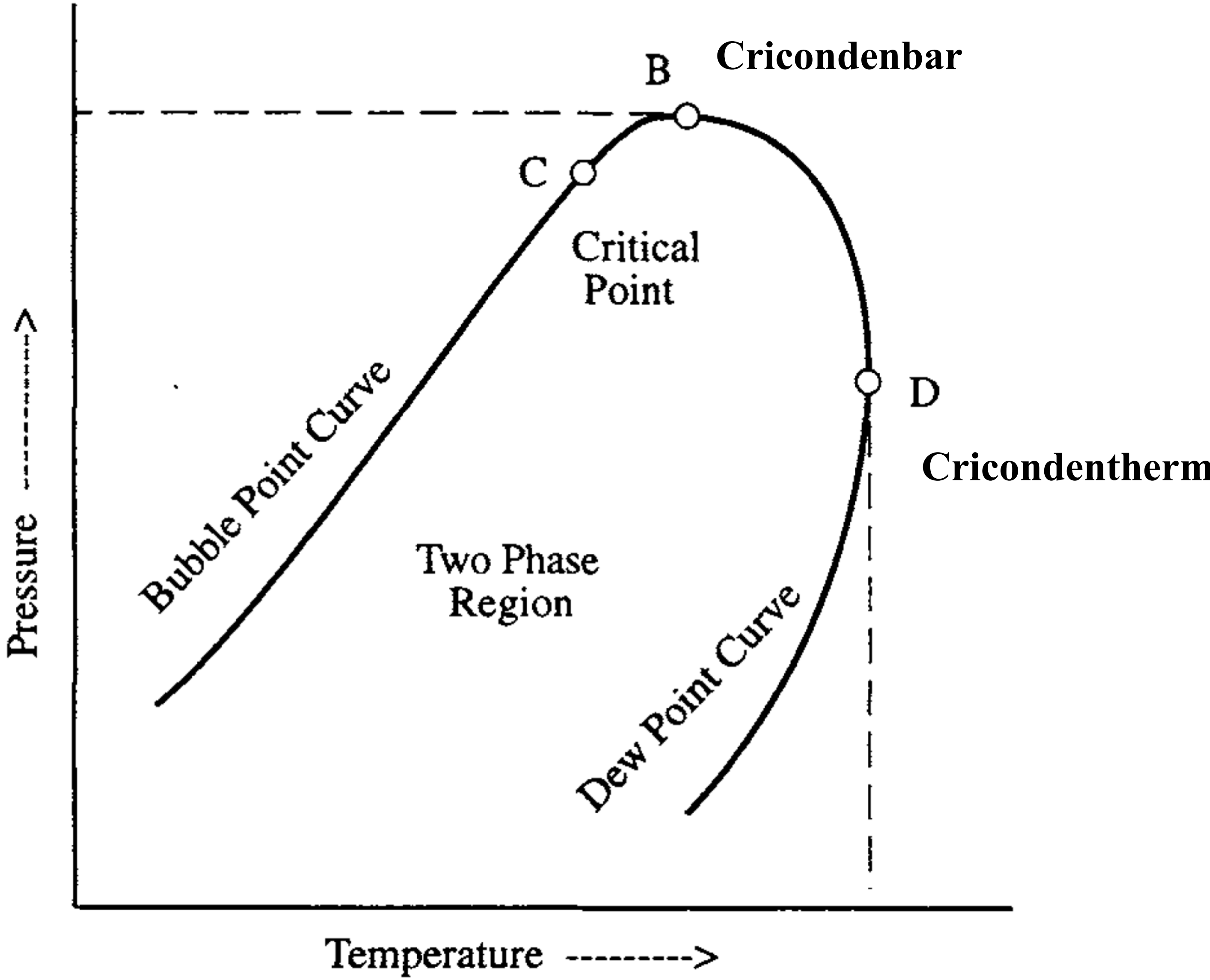
pv diagram of mixture of components [5]



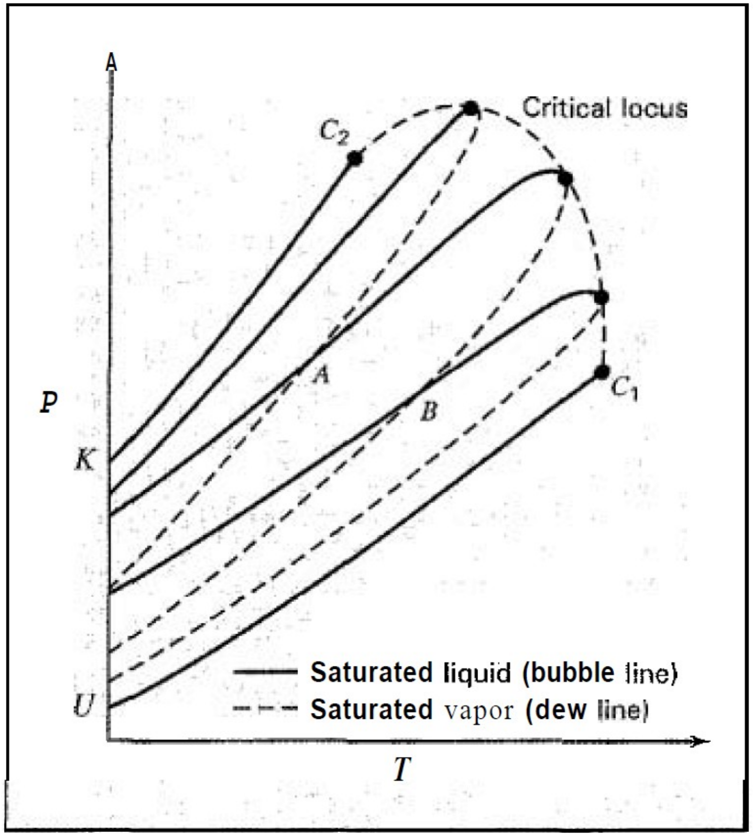


For pure component

p-T diagram of a mixture of components for a fixed composition [5]

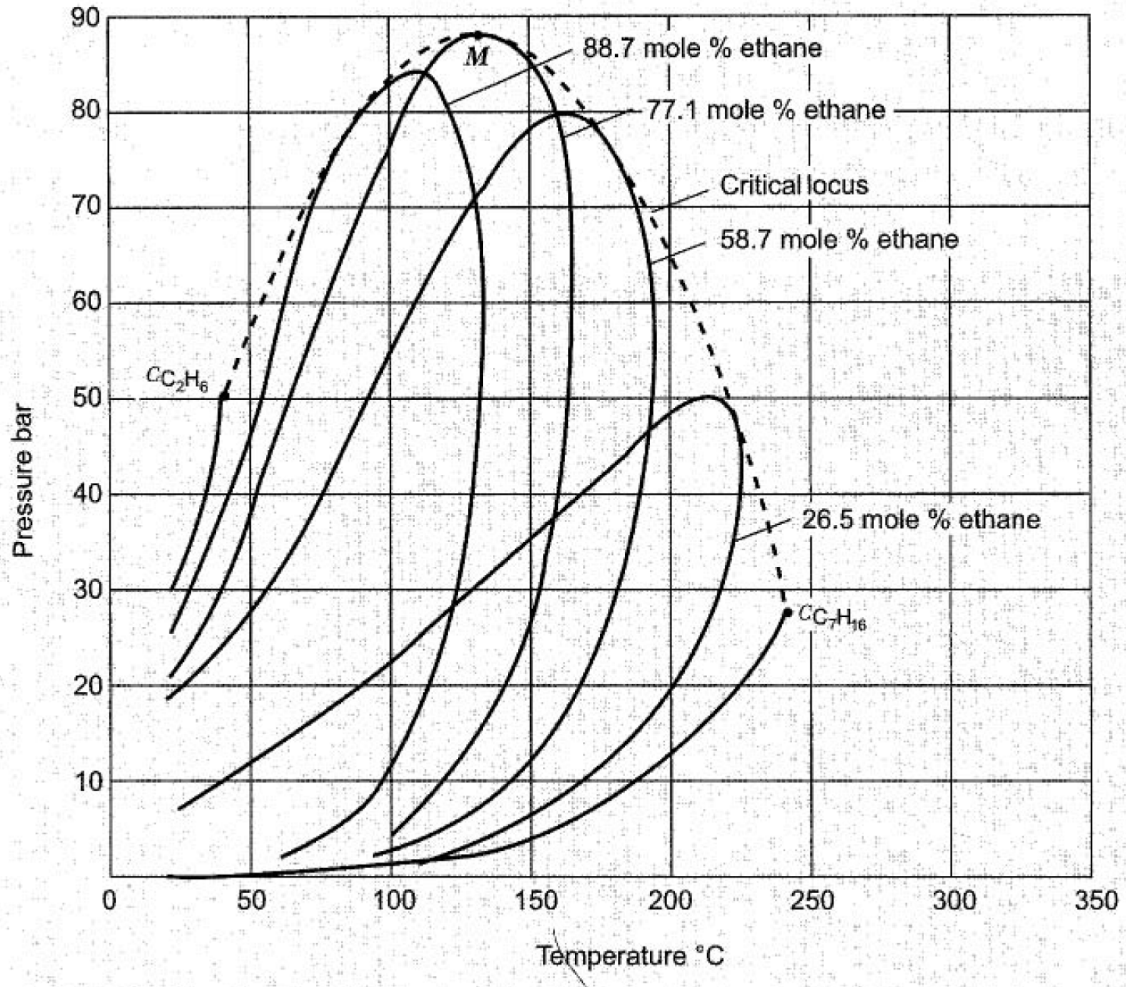


p-T diagram of a mixture of components

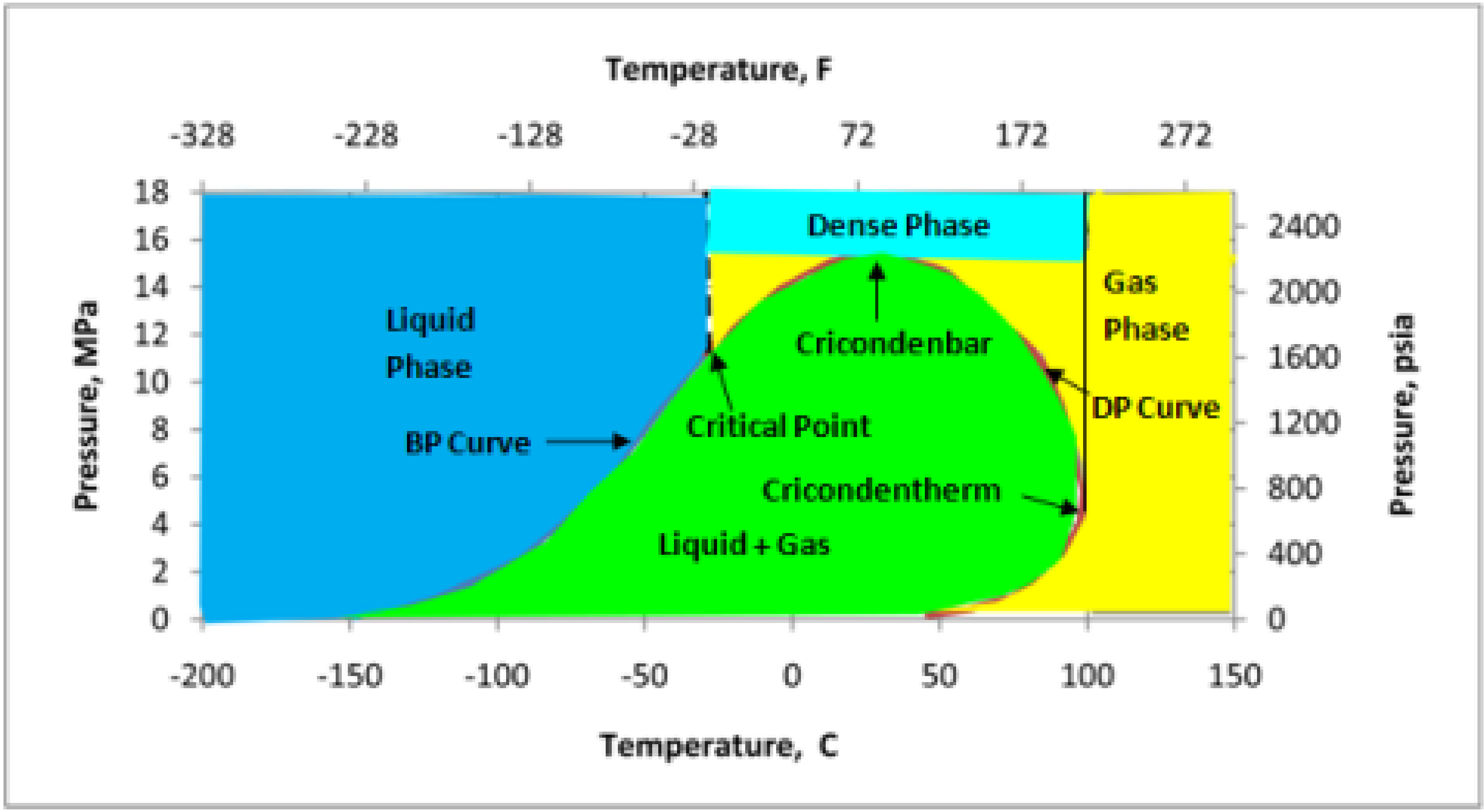


p-T **diagram of a binary mixture at various composition [6]**

p-T **diagram of an ethane-heptane mixture [6]**

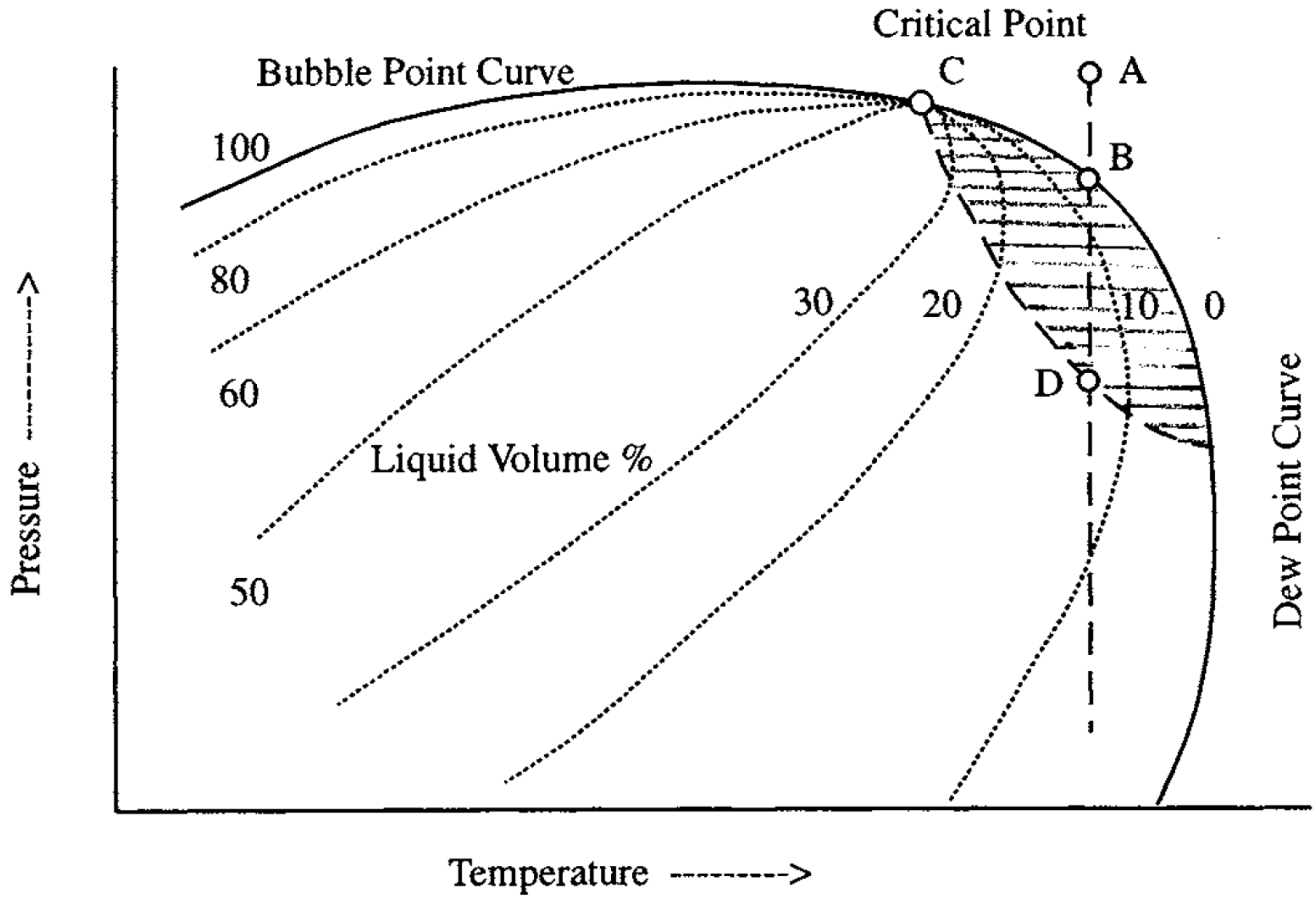


p-T diagram of a typical natural gas



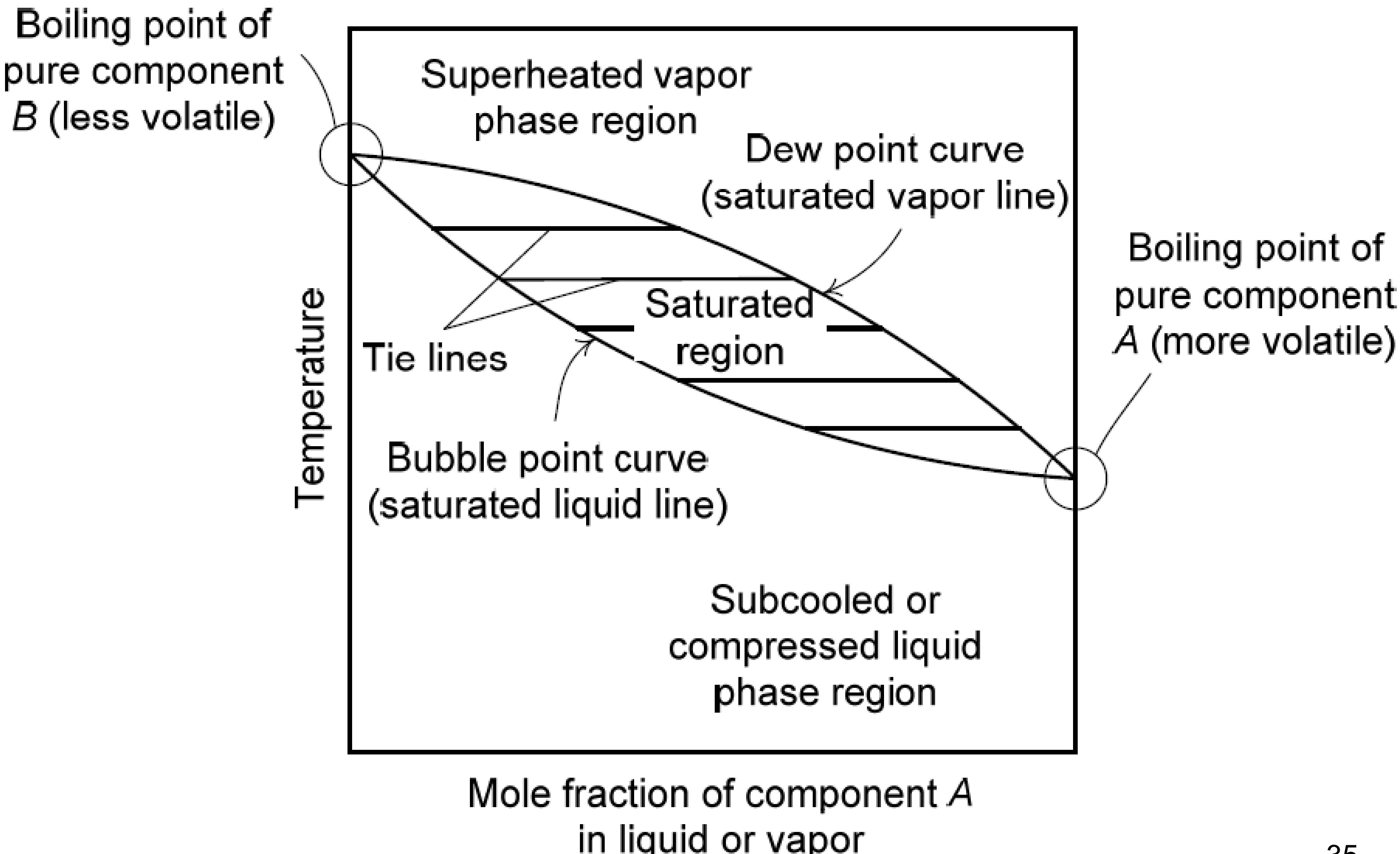
http://www.jmcampbell.com/tip-of-the-month/wp-content/uploads/2011/03/26.png

Retrograde region in a mixture of components [5]

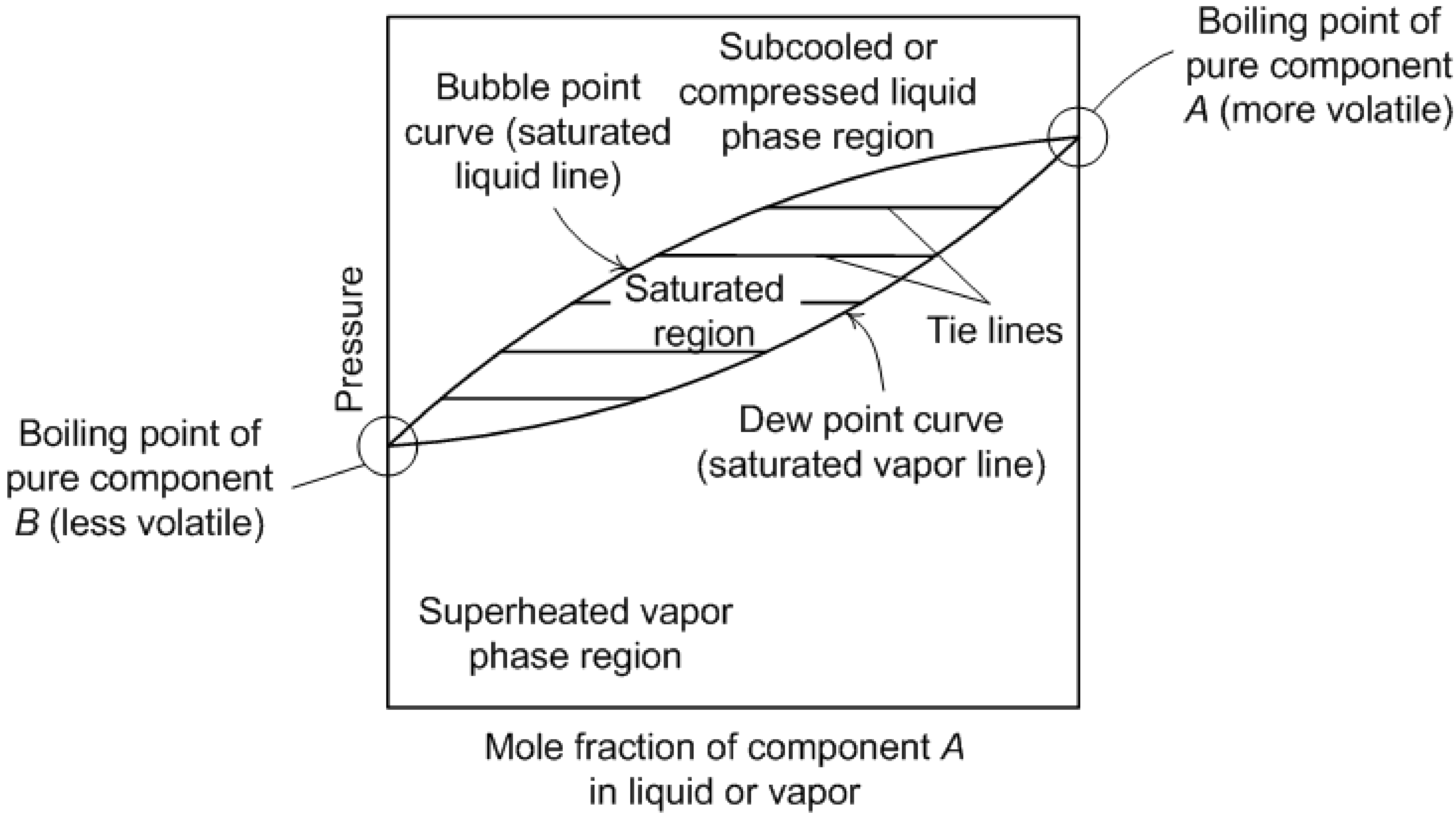


The condensables in a natural gas may condense during natural gas production due to retrograde phenomena. To avoid the gas may be injected to increase the pressure in the lines.

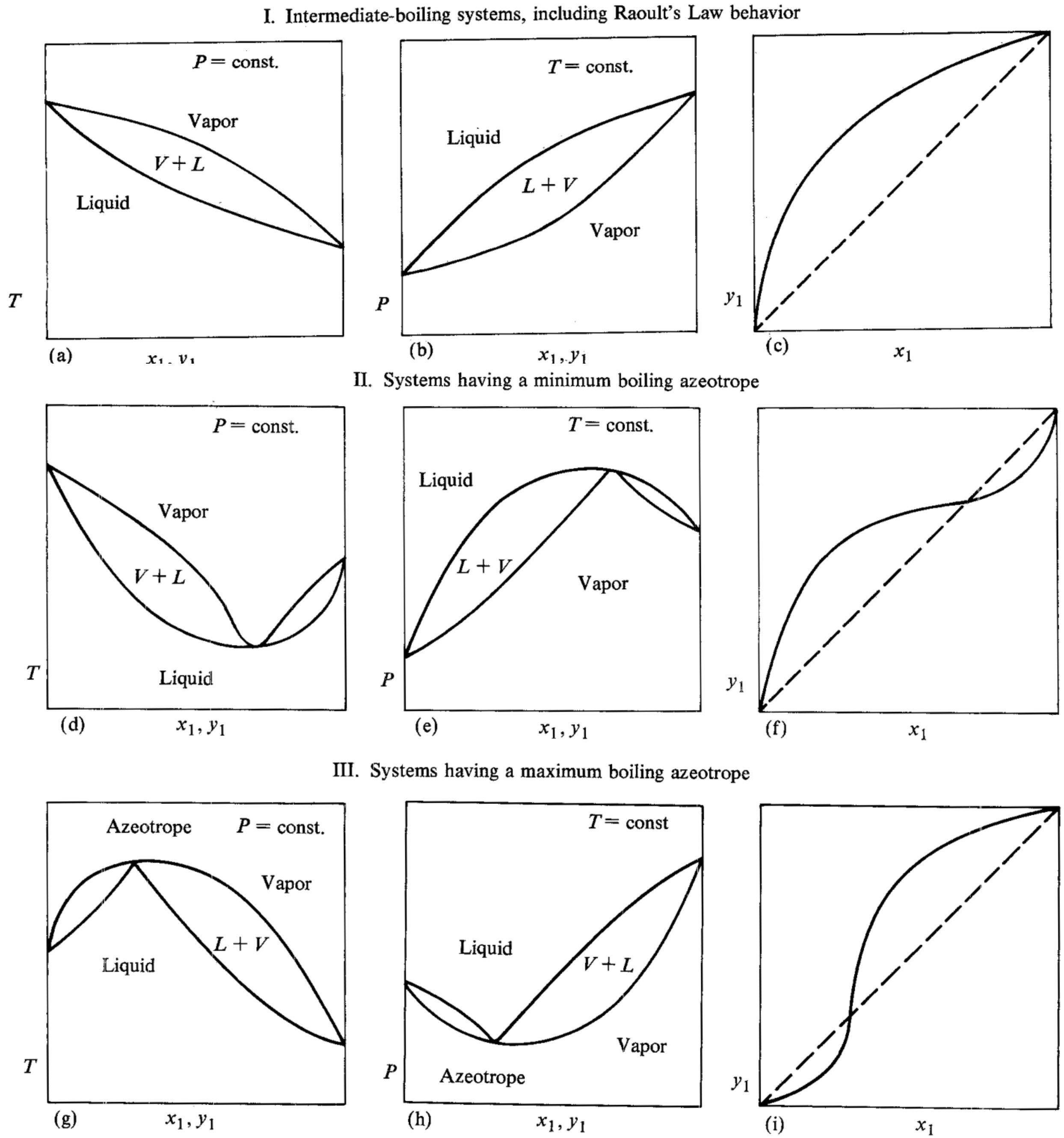
T-x-y diagram of a near ideal binary mixture [1]



p-x-y diagram of a near ideal binary mixture [1]

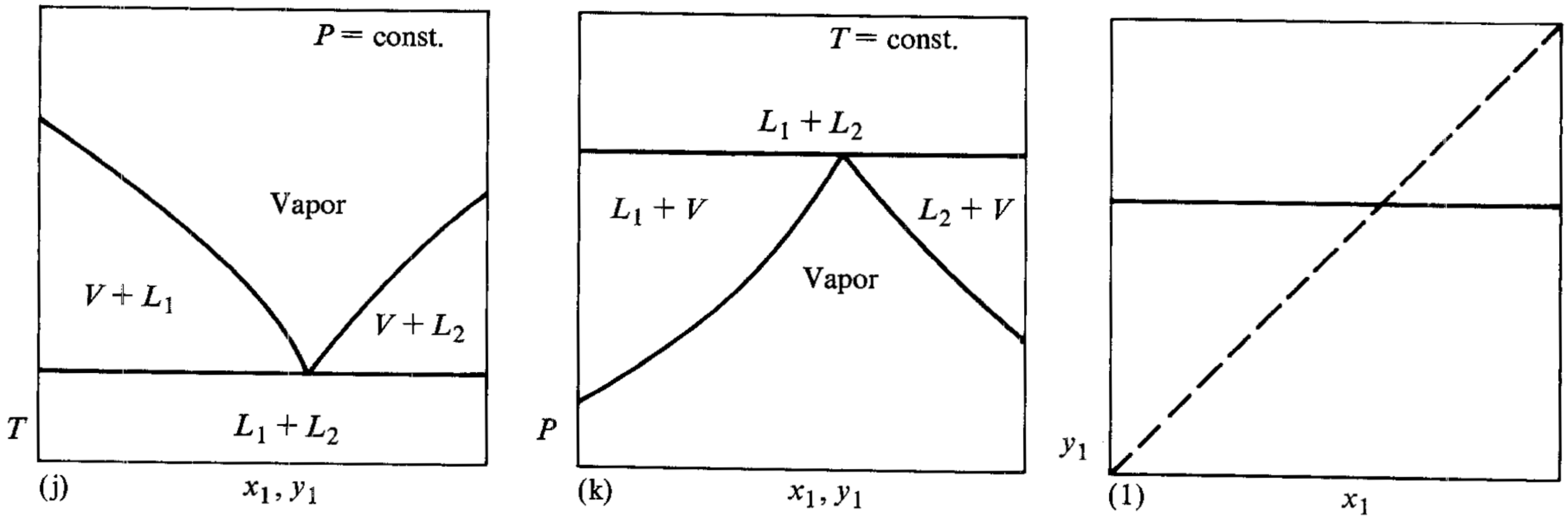


T-x, *p-x*, and *x-y* diagrams of various types [18]

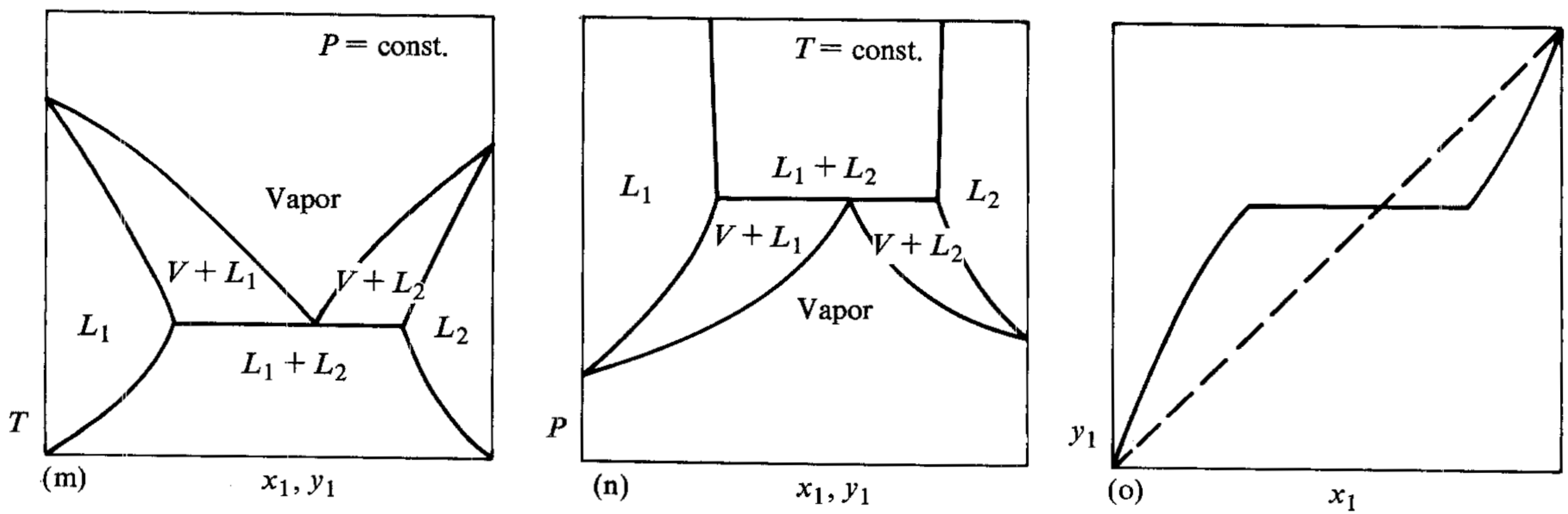


T-*x*, *p*-*x*, and *x*-*y* diagrams of various types [18]

IV. Systems having immiscible liquid phases



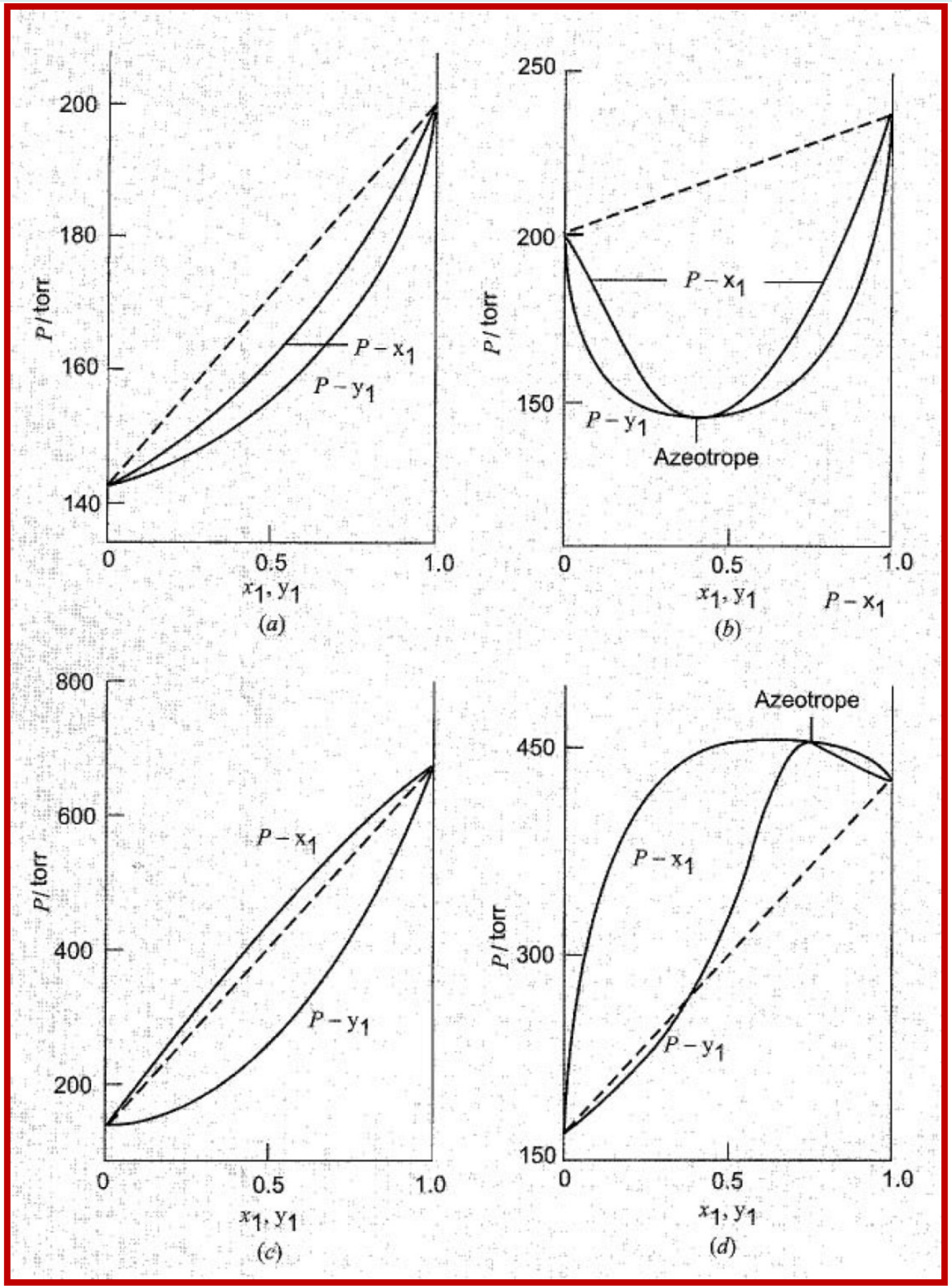
V. Systems having partially miscible liquid phases



p-x-y diagrams of various binary mixtures [6]

(a) Tetrahydrofuran (1)-carbon tetrachloride (2) at 303.15 K

(b) Chloroform (1)-tetrahydrofuran (2) at 303.15 K



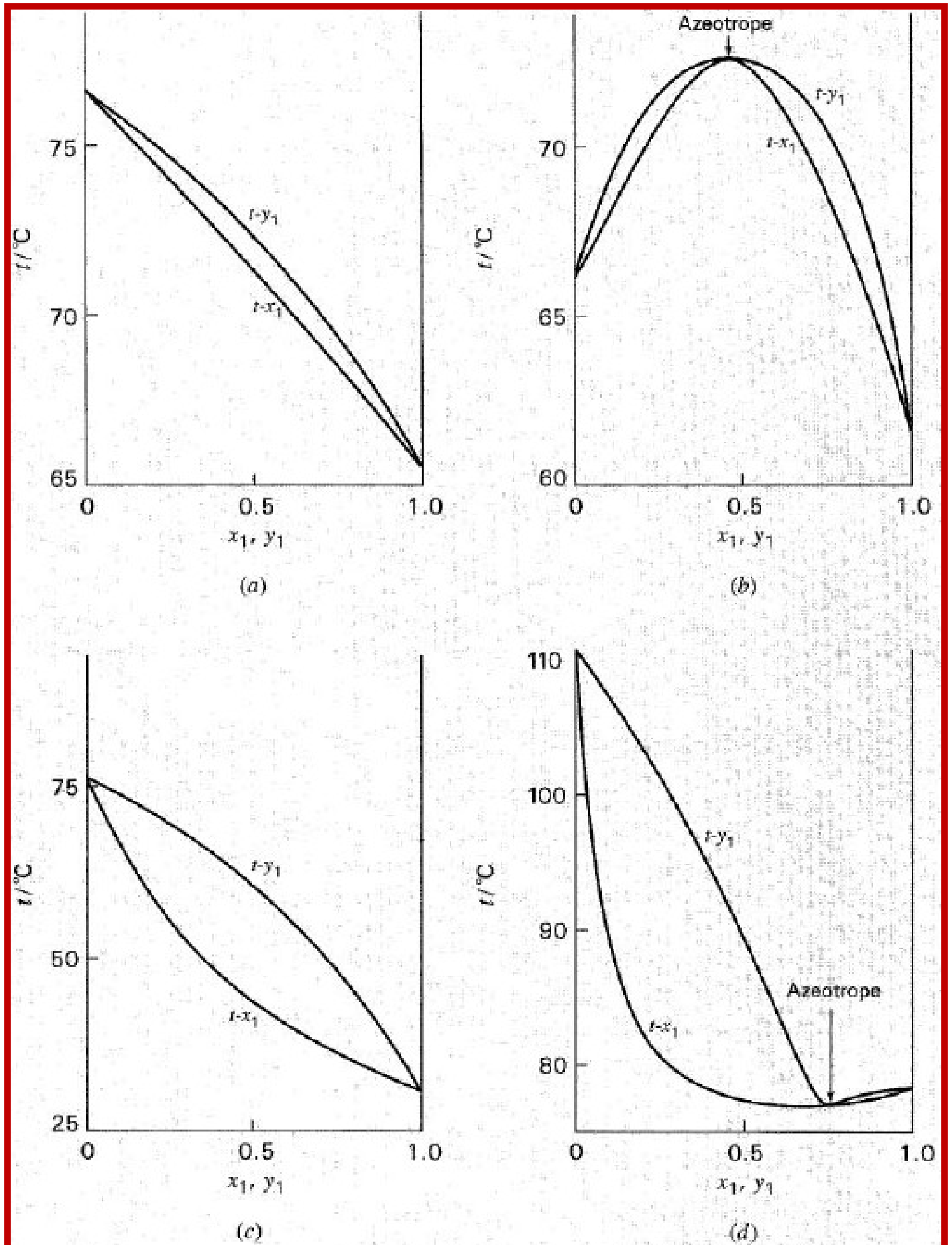
(c) Furan (1)-carbon tetrachloride (2) at 303.15 K

(d) Ethanol (1)-toluene (2) at 338.15 K

T-x-y diagrams of various binary mixtures [6]

(a) Tetrahydrofuran (1)-carbon tetrachloride (2) at 1 atm

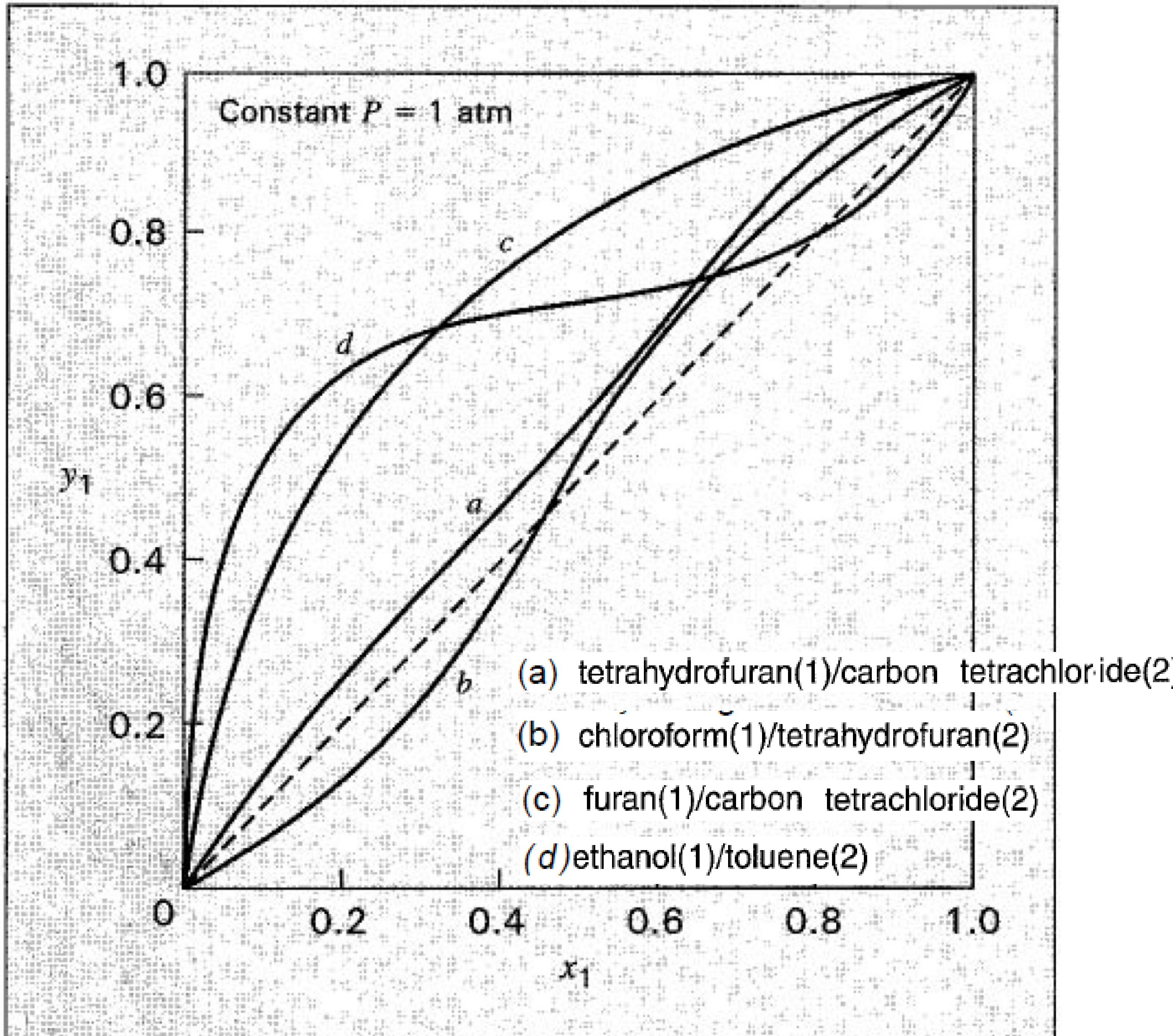
(b) Chloroform (1)-tetrahydrofuran (2) at 1 atm



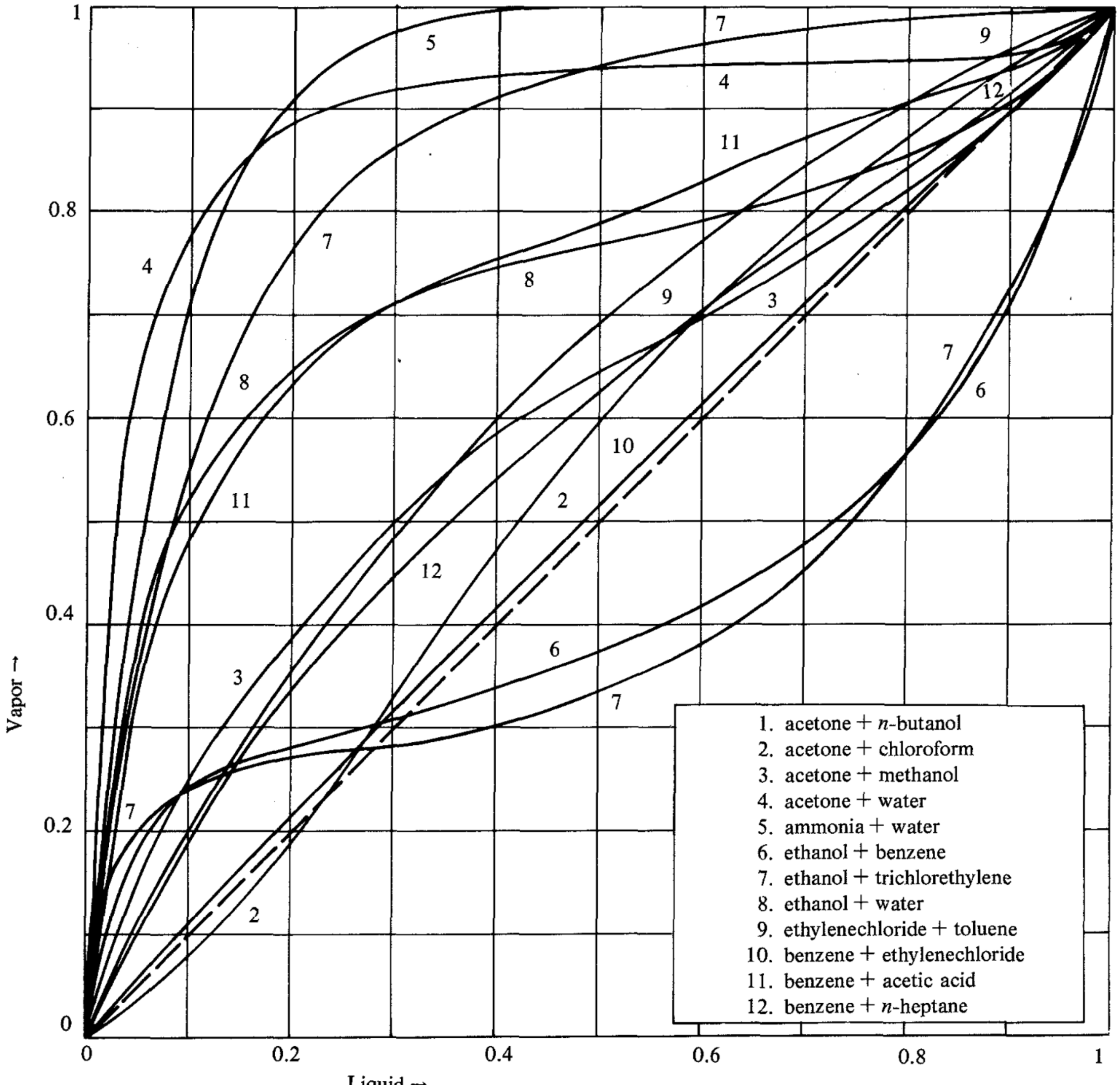
(c) Furan (1)-carbon tetrachloride (2) at 1 atm

(d) Ethanol (1)-toluene (2) at 1 atm

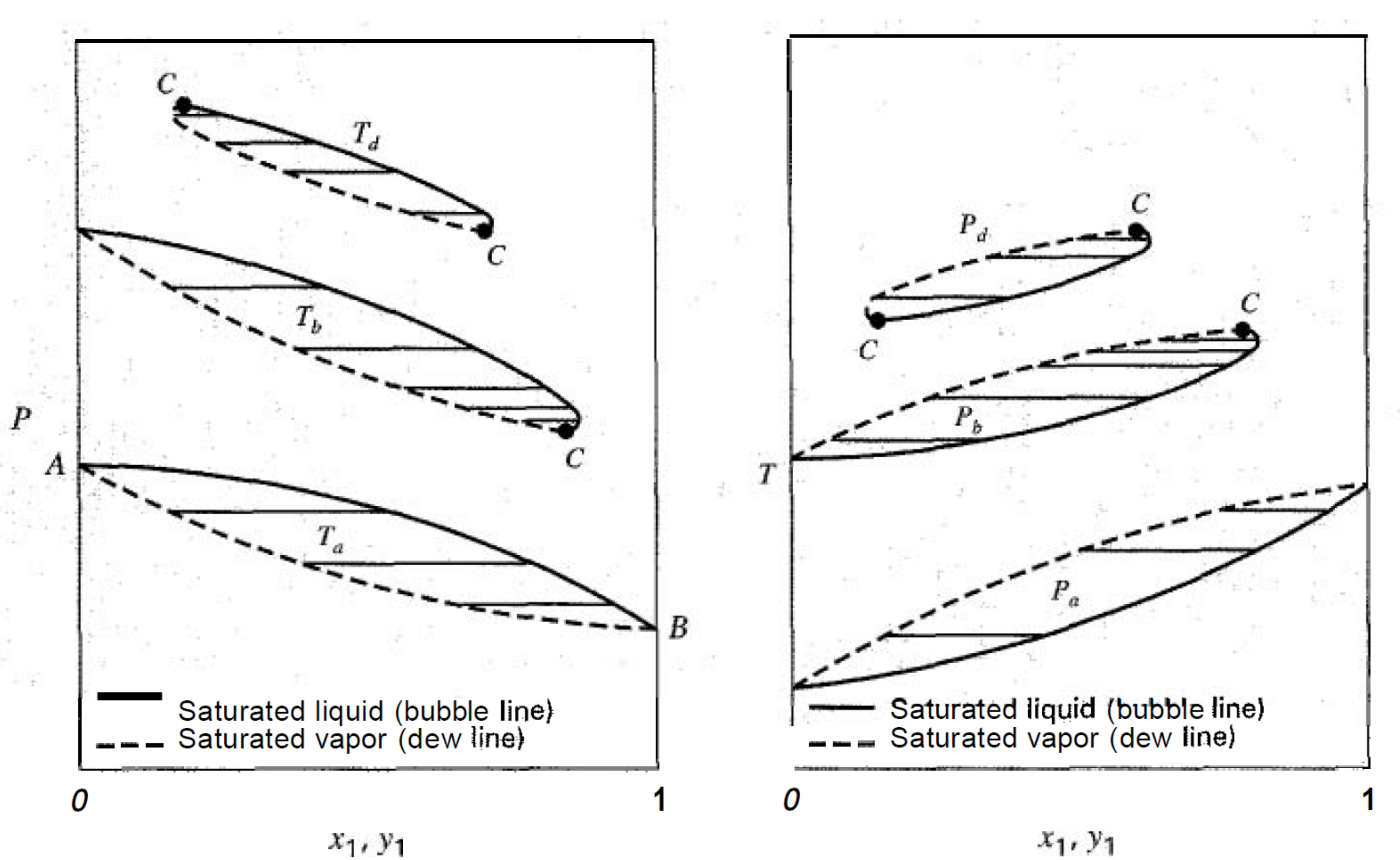
x-y diagrams of various binary mixtures [6]



x-y diagrams of various binary mixtures at 1 atm [18]

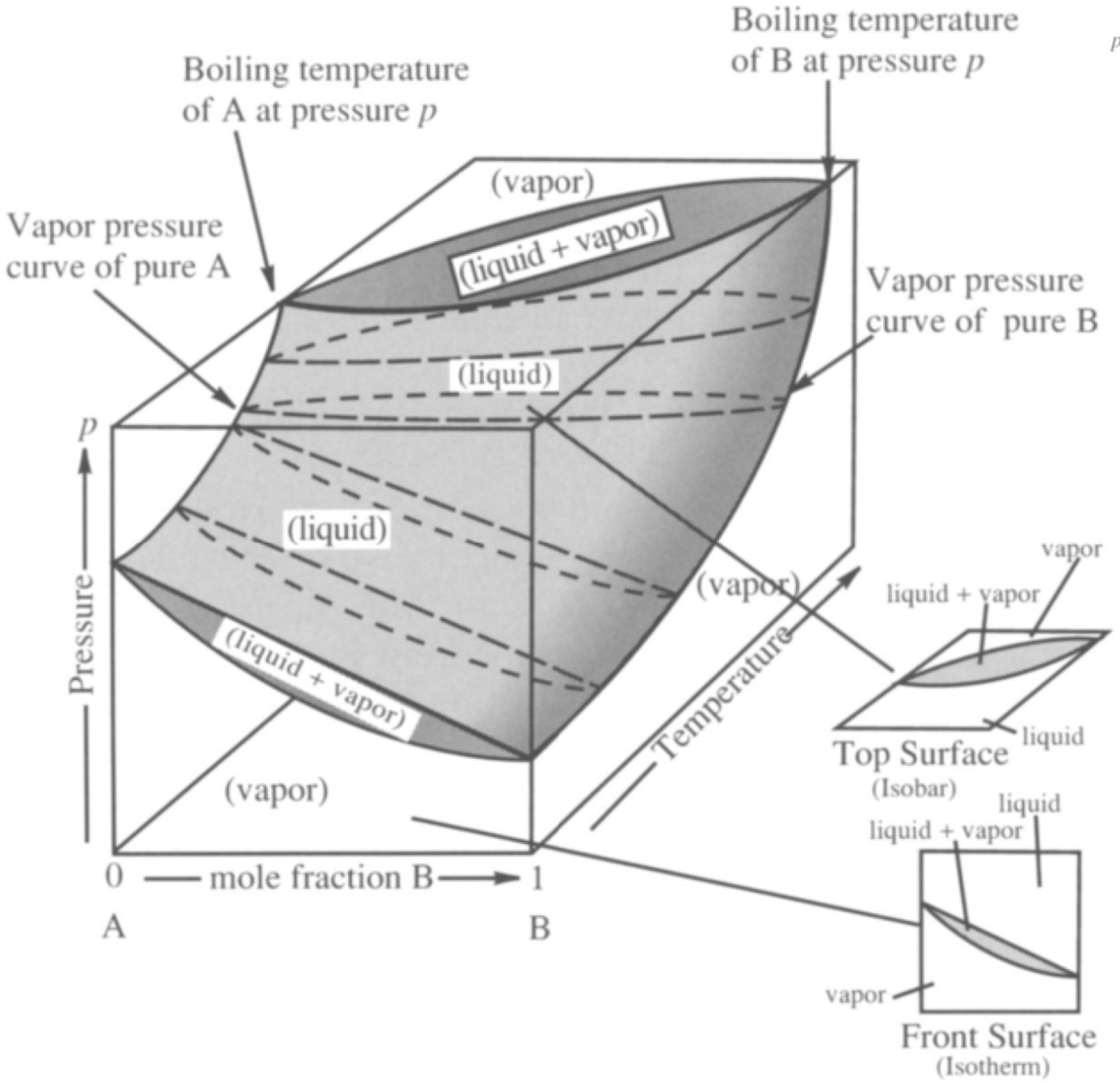


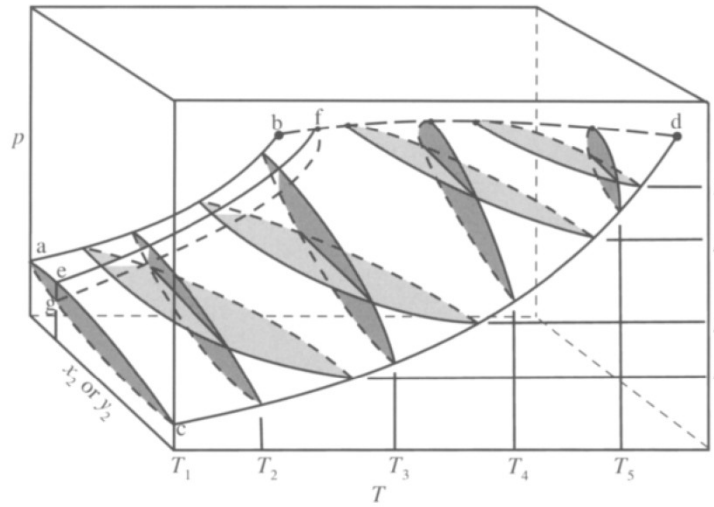
P-x-y and T-x-y diagrams of a binary near ideal system [6]



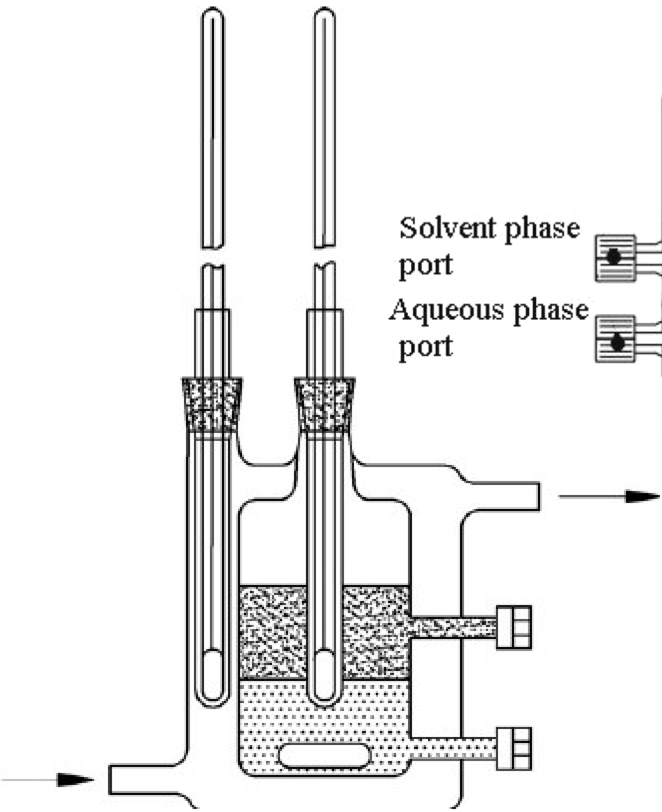
No two-phase region beyond critical point.

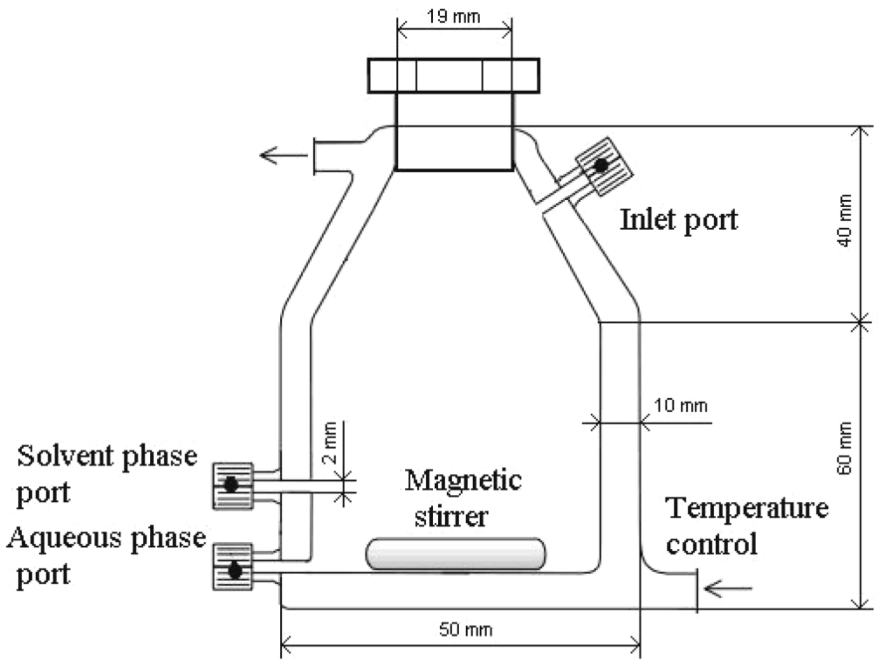
p-T-x-y diagram of a binary near ideal solution [3]





Simple liquid-liquid equilibrium cells



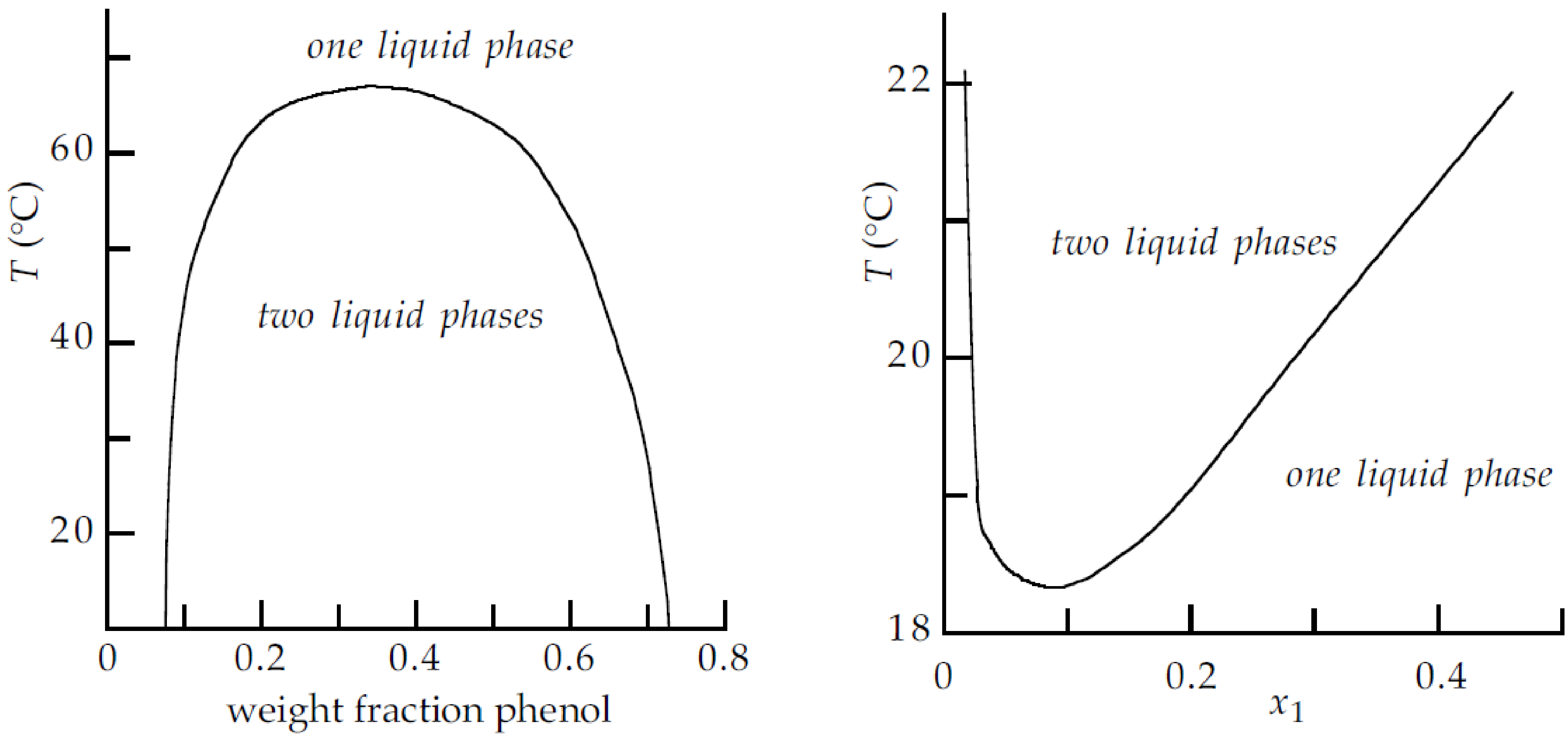


http://www.scielo.br/pdf/bjce/v23n3/10.pdf

https://www.researchgate.net/profile/Xuenong_Gao/publication/244343478/figure/fig1/AS:298489847271424@1448176933158/Fig-1-Liquid-liquid-equilibrium-cell.png

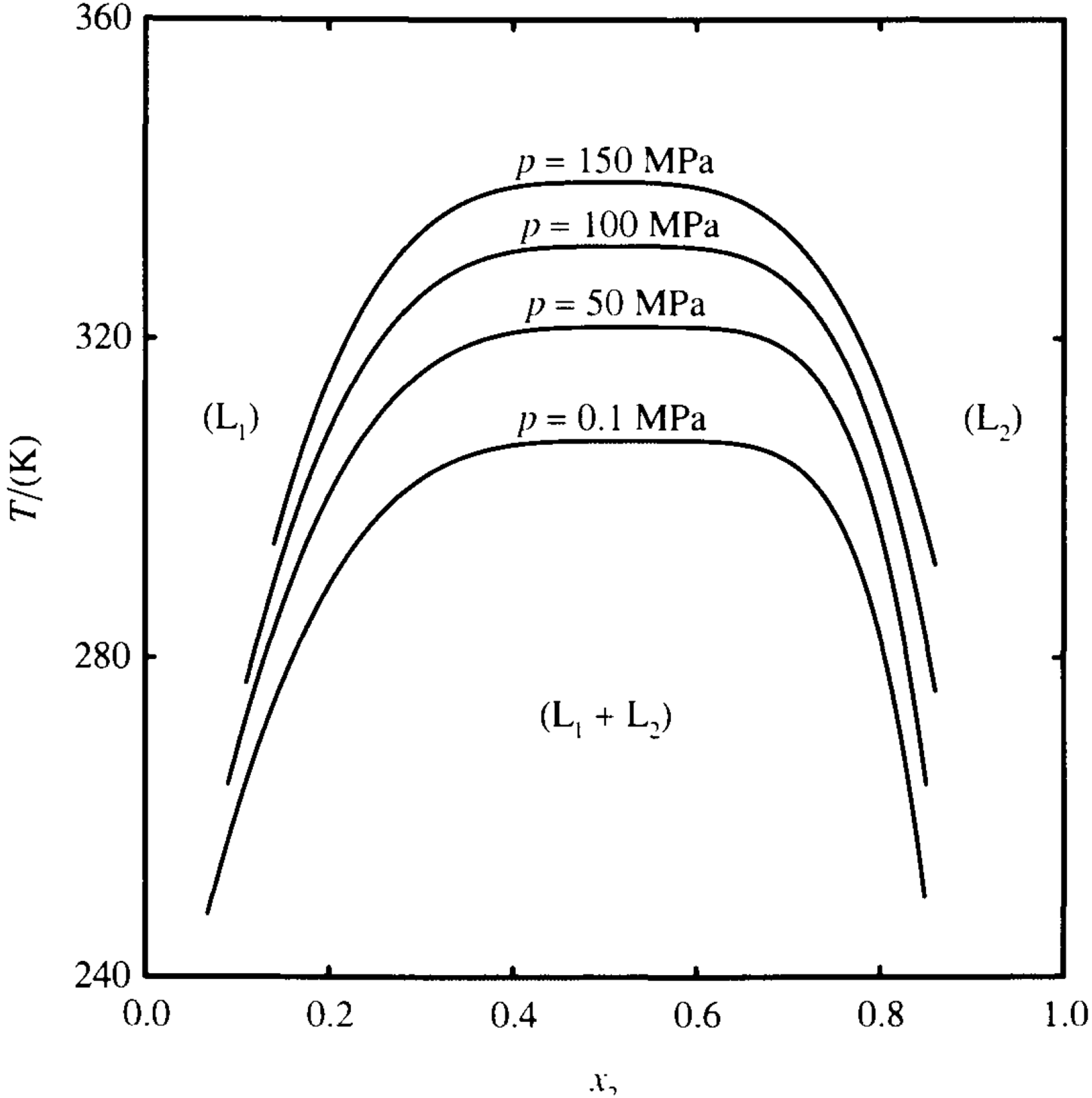
http://chemtech.aalto.fi/en/midcom-serveattachmentguid-1e4082b533635c8082b11e481ccdb51c8f8081e081e/big_lle_analytical_method.JPG

T-x diagram of a liquid-liquid system [7]

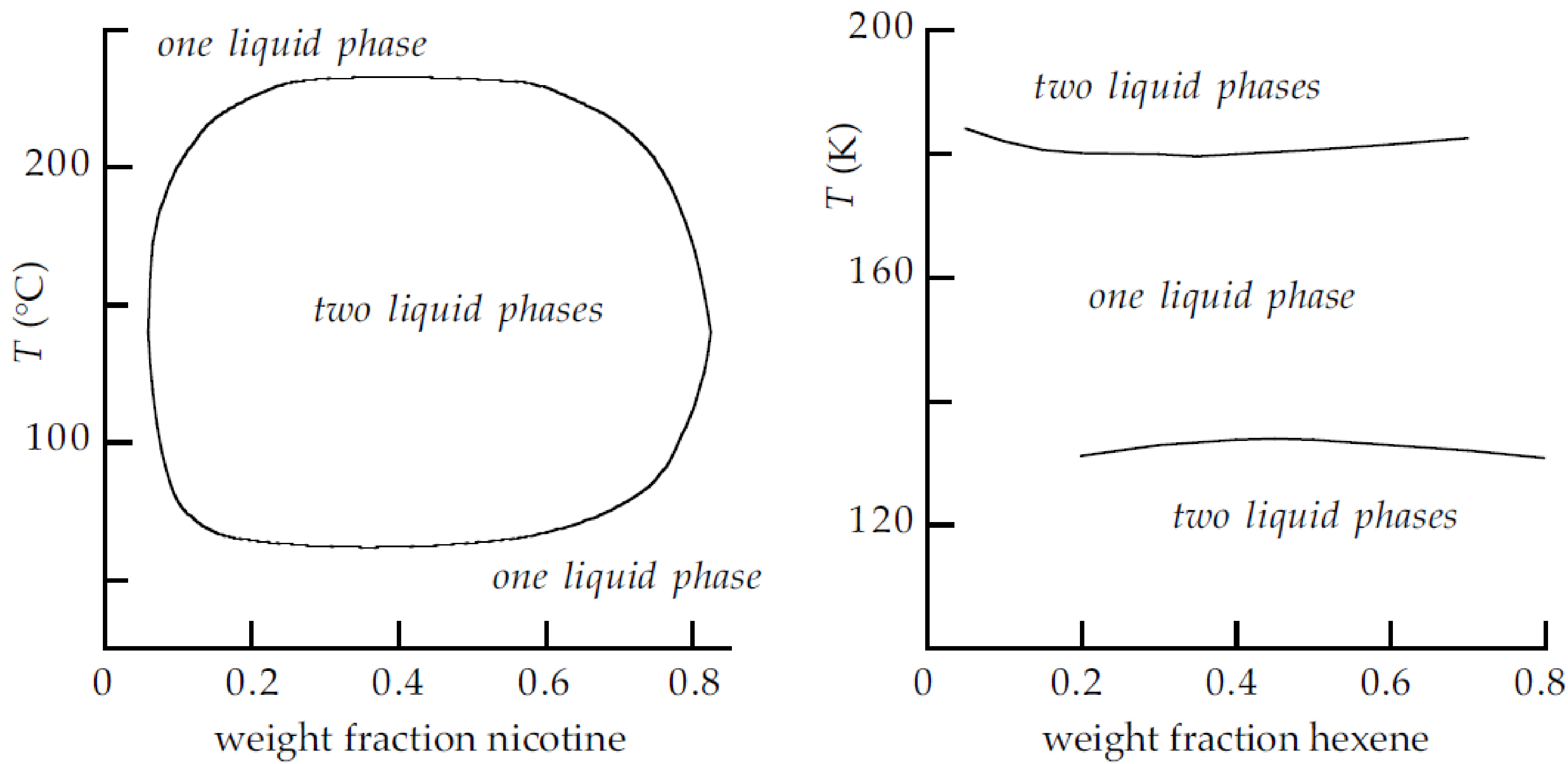


Left: Mixtures of phenol (C_6H_6O) and water have a UCST near 67°C and 0.35 weight fraction phenol *Right*: Mixtures of triethylamine(1) ($C_6H_{15}N$) and water(2) have an LCST near 18.3°C and $x_1 \approx 0.095$

Liquid-liquid equilibria for n-C_6H_{14}+CH_3OH system [3]

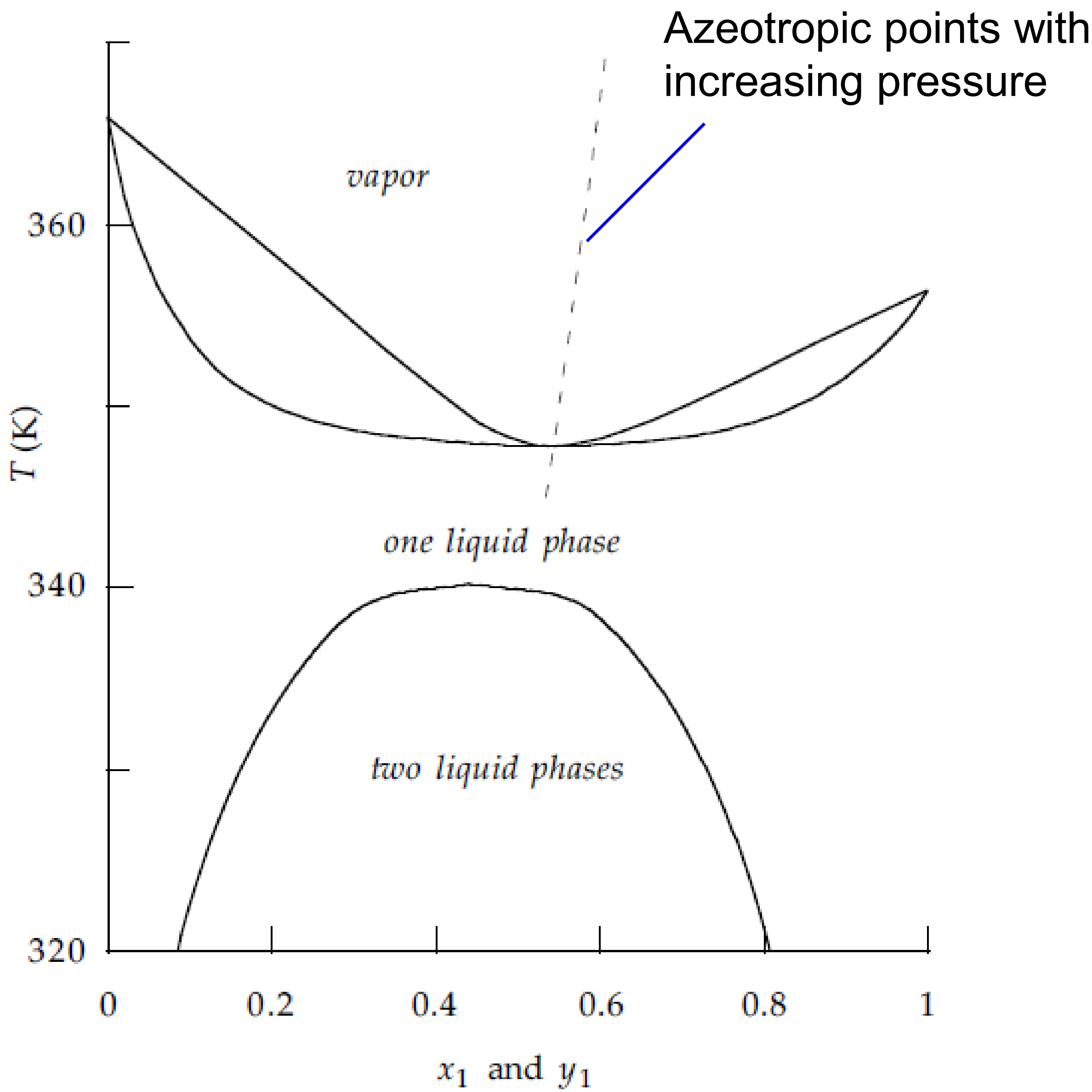


T-x diagram of a liquid-liquid system [7]

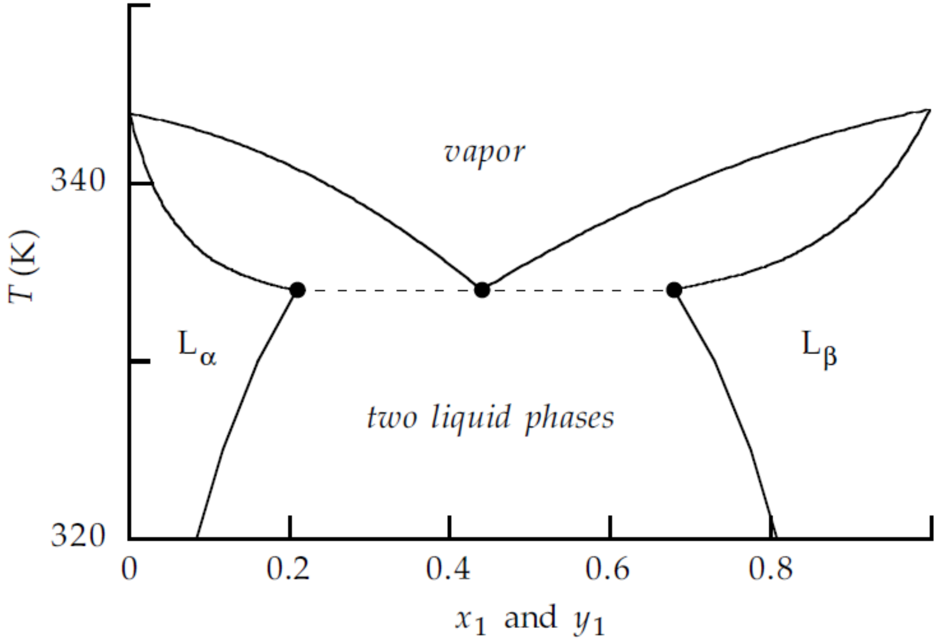


Examples of binary mixtures that have both a UCST and an LCST. *Left*: Mixtures of nicotine ($C_{10}H_{14}N_2$) and water have a closed solubility loop, with UCST = 233°C and LCST = 61.5°C *Right*: Mixtures of 1-hexene (C_6H_{12}) and methane have a miscibility gap, with UCST = 133.8 K and LCST = 179.6 K

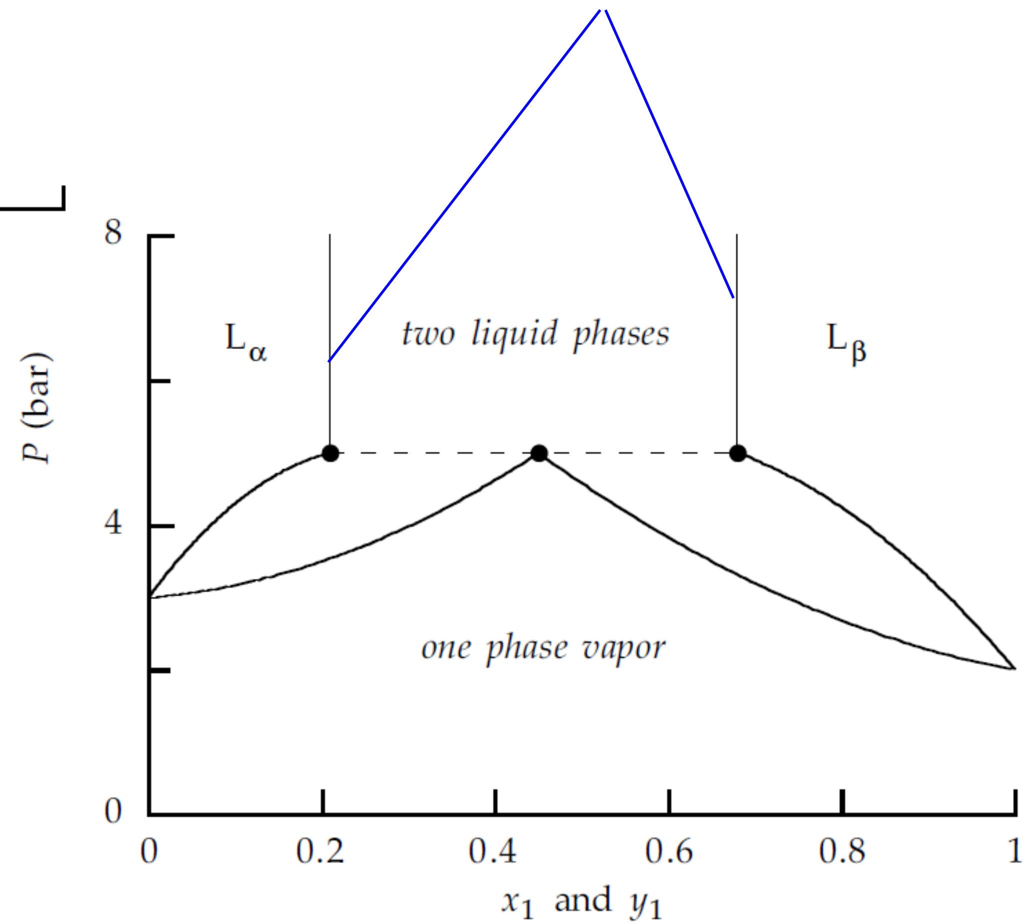
T-*x* diagram of a vapor-liquid-liquid system [7]



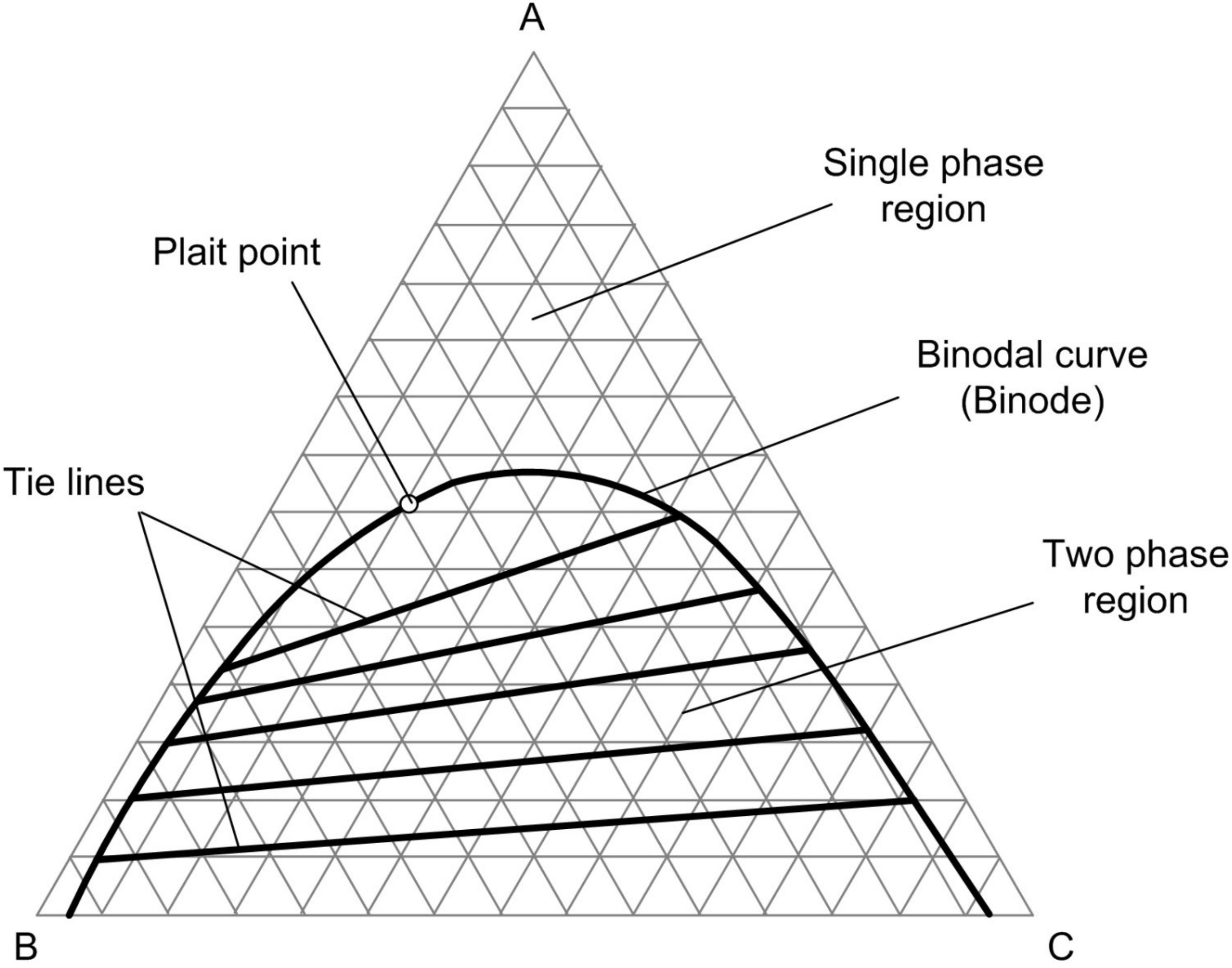
T-x and *p-x* diagrams of a liquid-liquid system [7]



Straight lines show negligible miscibility of phases with increase in pressure

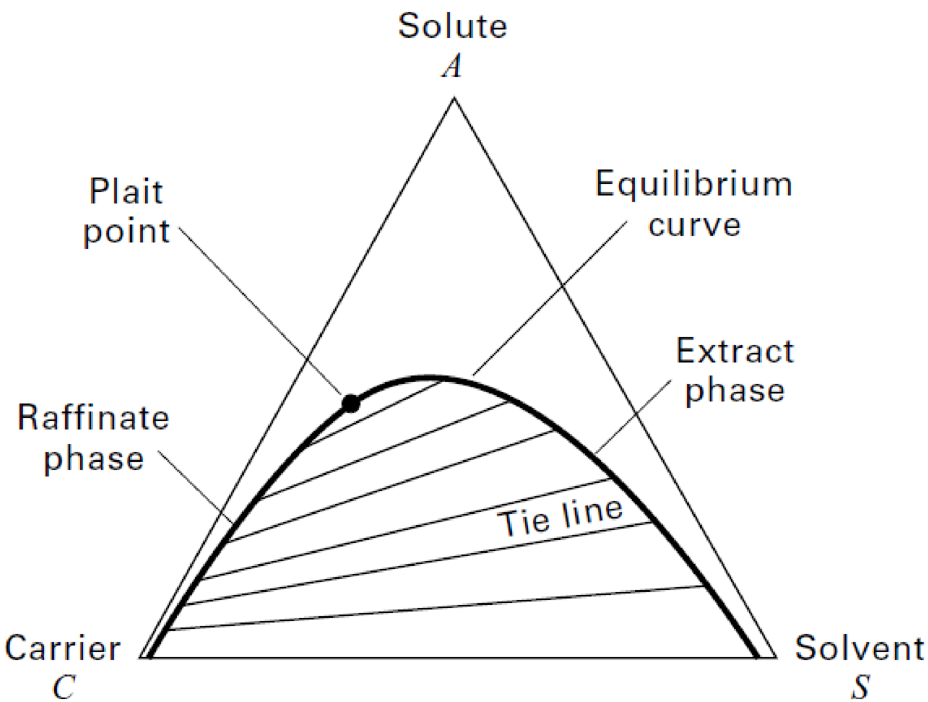


Ternary diagram for liquid-liquid extraction system

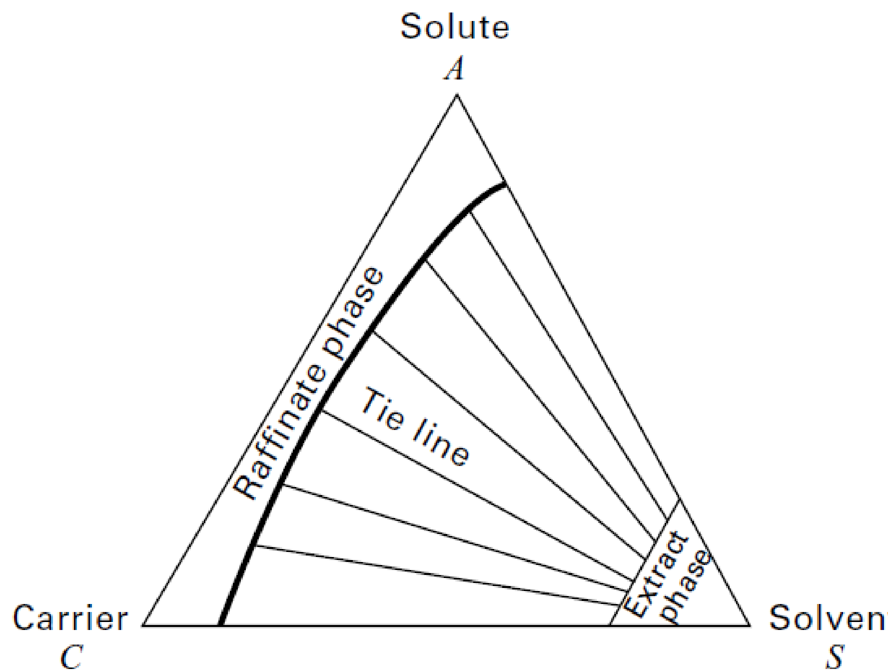


Common ternary phase diagrams for liquid-liquid extraction systems [8]

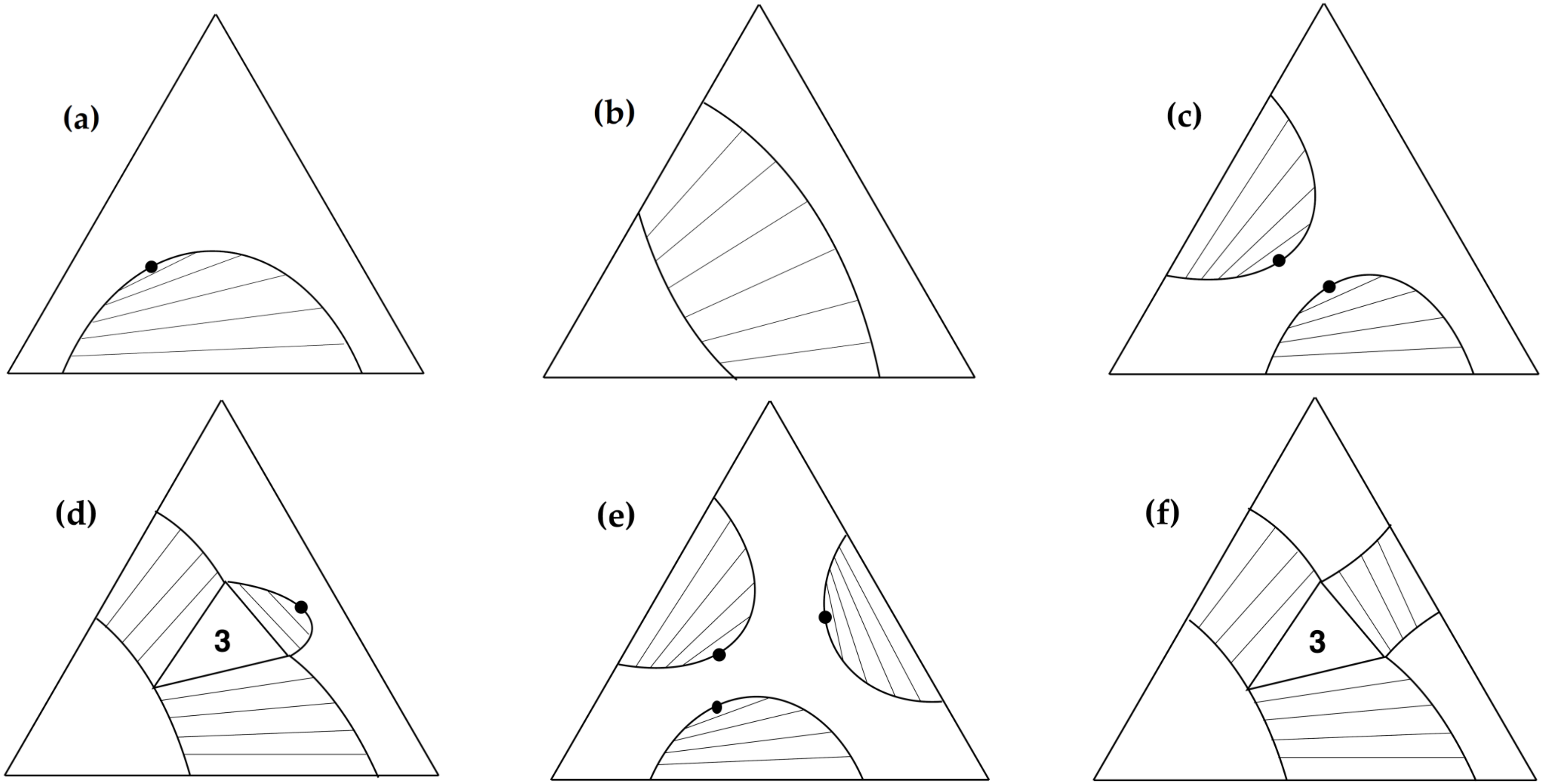
Type I: One immiscible pair



Type II: Two immiscible pairs

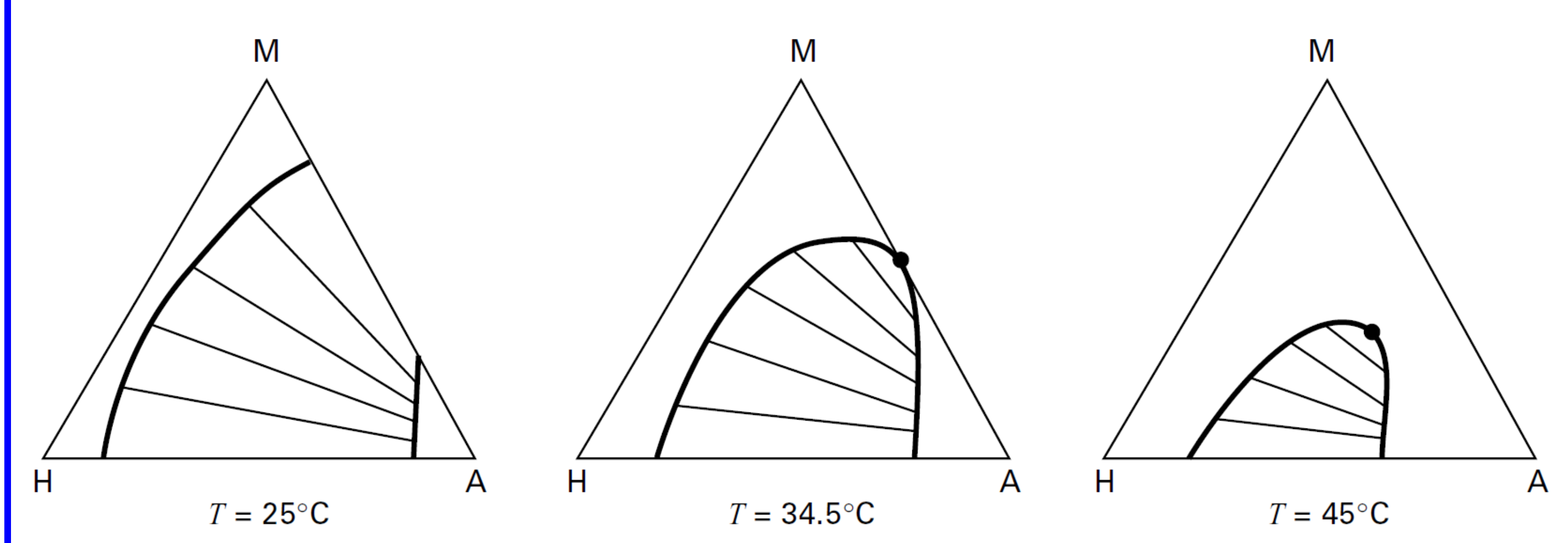


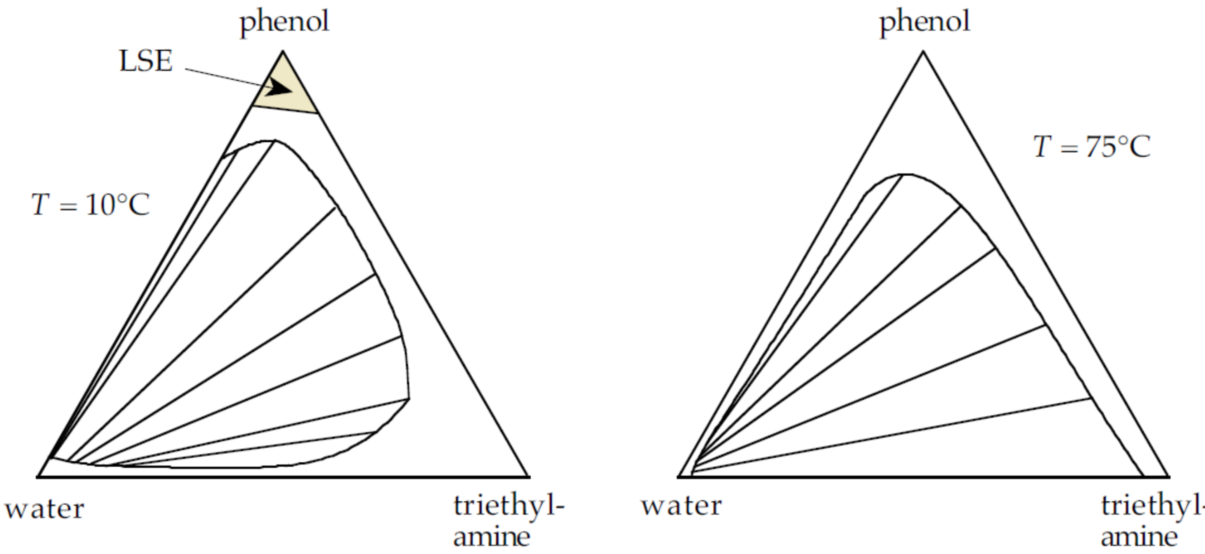
Ternary diagrams for liquid-liquid extraction system [7]

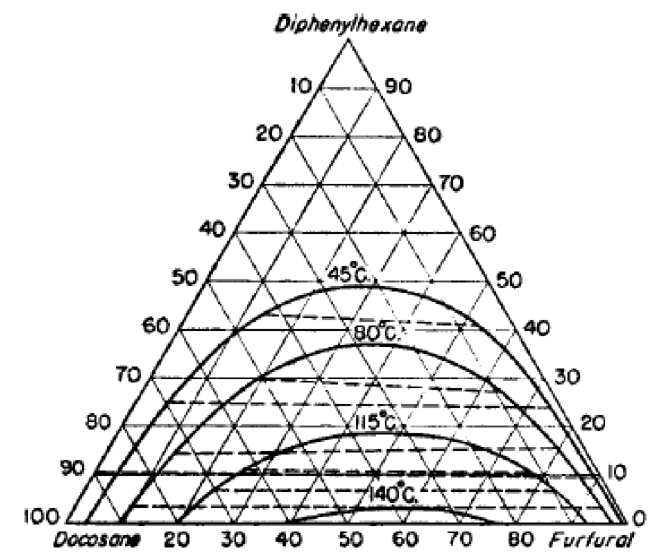


"Filled circles locate consolute points. Numeral 3 inside a triangle identifies three-phase LLLE; the compositions of the three phases are given by the vertices of the triangles. These six diagrams are arranged by the number of two-phase regions: (a) and (b) each have one, (c) has two, and (d)-(f) each have three." [7]

Effect of temperature on miscibility of the multicomponent mixtures [7, 8, 18]

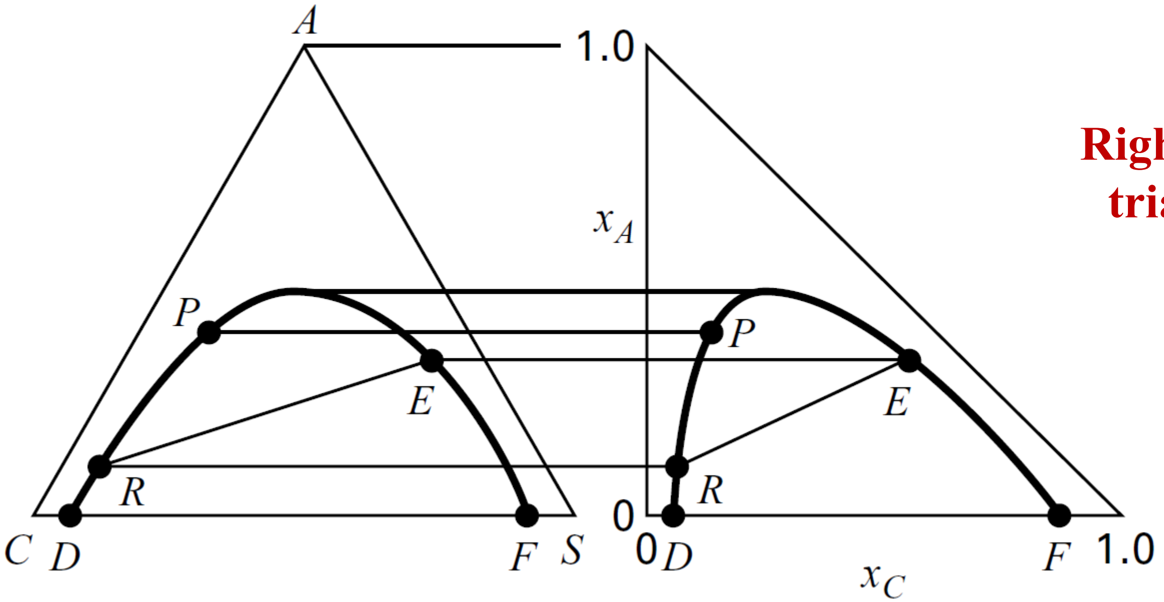




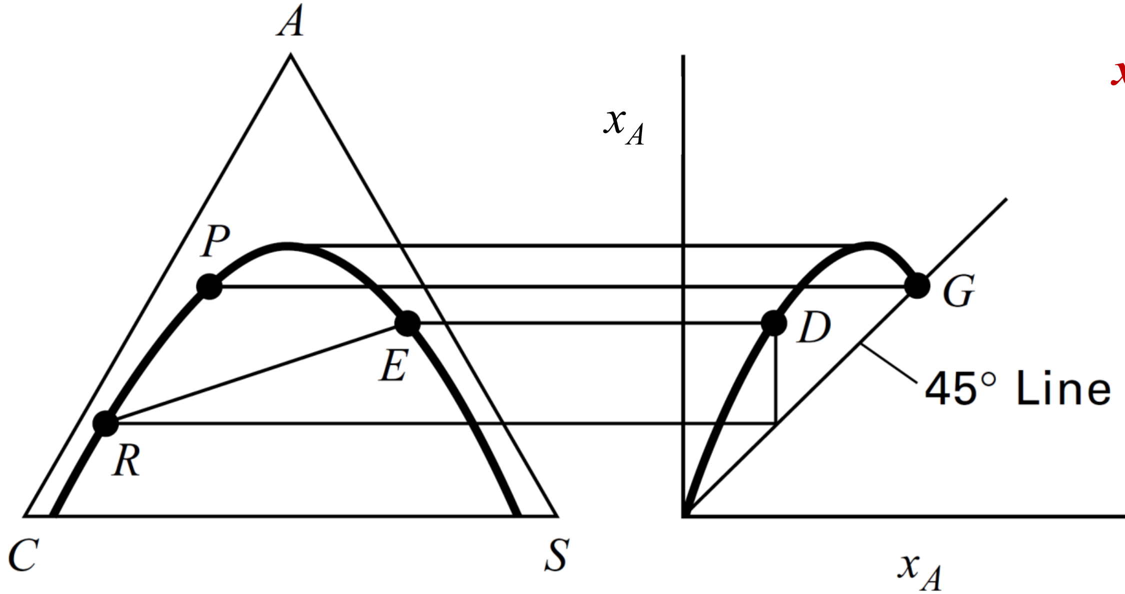


Other ternary component diagrams [8]

Right-angled triangular

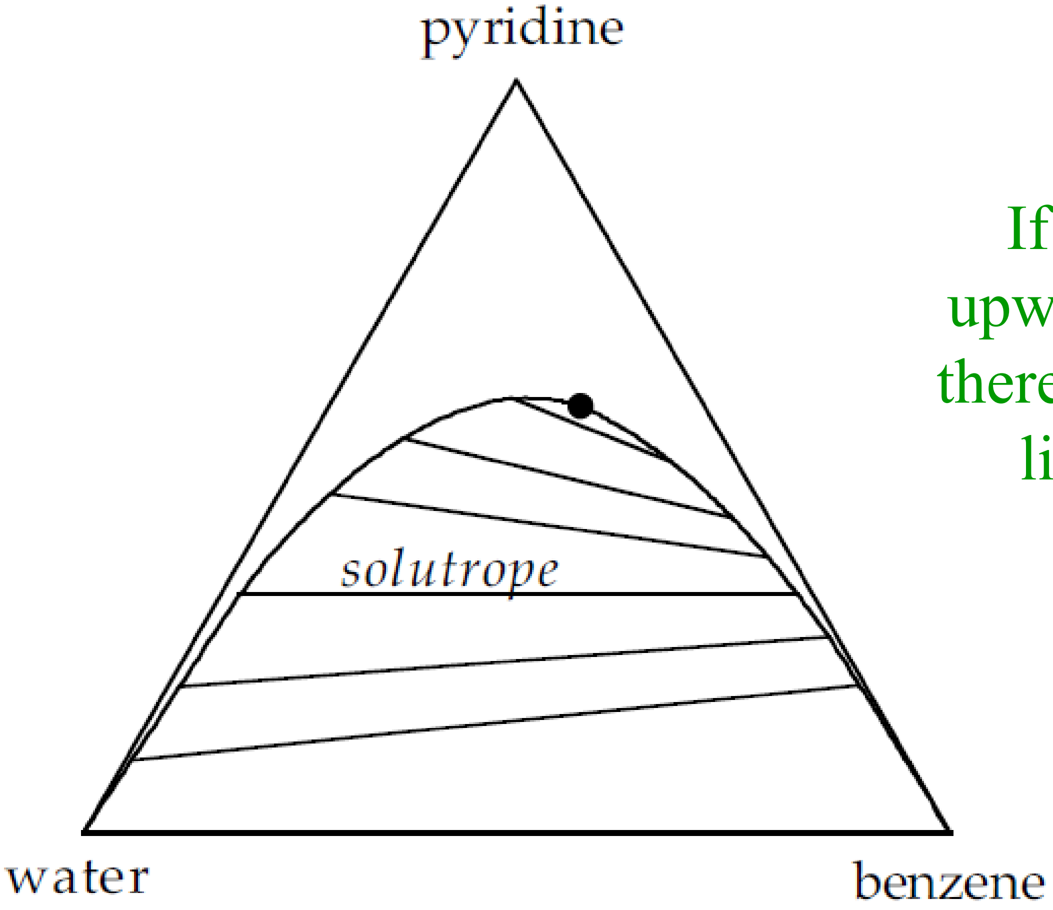


***x-x* diagram**



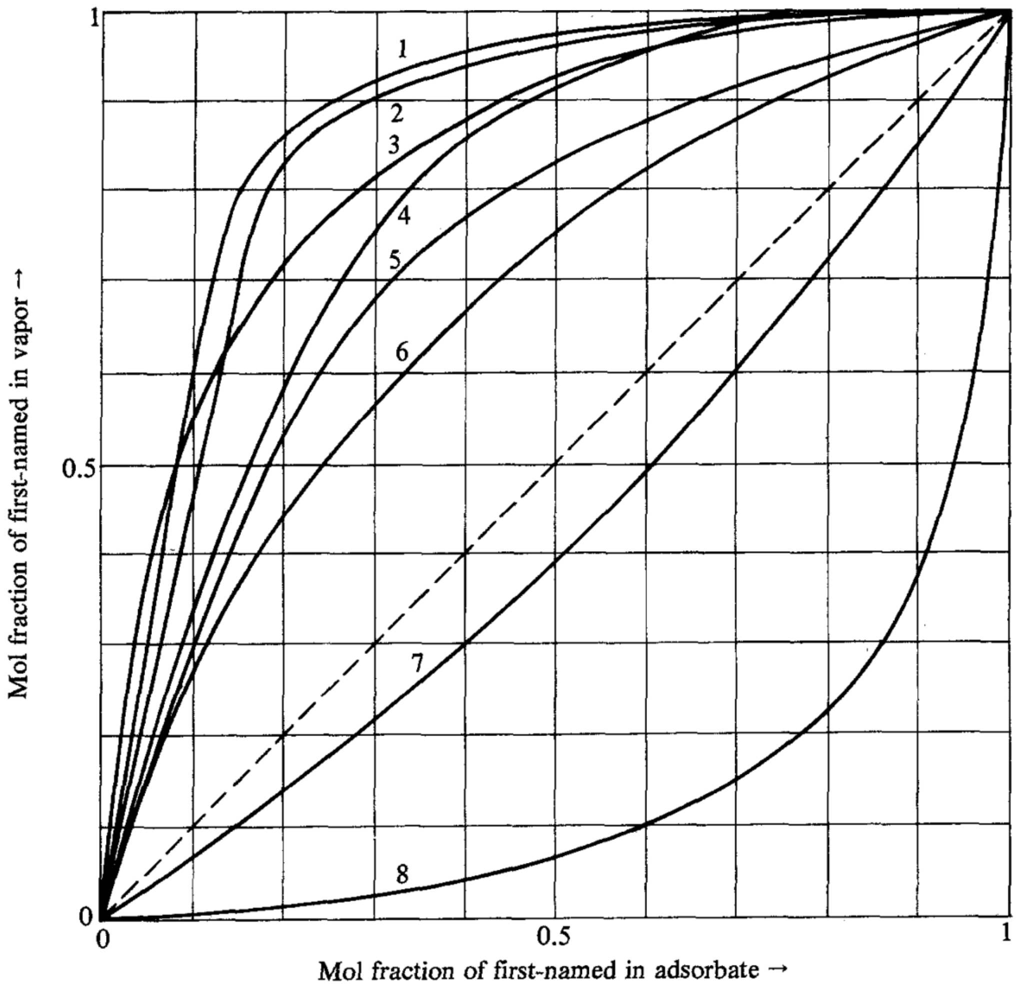
The concept of solutrope [7]

The horizontal line showing solutrope gives the same composition of pyridine in water and benzene phases.



If some tie lines slope upwards some downwards there is always a horizontal line called solutrope.

Adsorption equilibria [18]



Adsorption of Binary Mixtures (Data of Union Carbide Corporation).

1. Ethane + ethylene, type 4A MS, 25 C, 250 Torr.
2. Ethane + ethylene, type 4A MS, 25 C, 730 Torr.
3. Ethane + ethylene, type 4A MS, 75 C, 730 Torr.
4. Carbon dioxide + hydrogen sulfide, type 5A MS, 27 C, 760 Torr.
5. *n*-Pentane + *n*-hexane, type 5A MS, 100 C, 760 Torr.
6. Ethane + ethylene, silica gel, 25 C, 760 Torr.
7. Ethane + ethylene, Columbia G carbon, 25 C, 760 Torr.
8. Acetylene + ethylene, type 4A MS, 31 C, 740 Torr.

pvT properties of pure components and mixture of components

The following methods can be used to determine the *pvT* properties of pure and mixture of components:

- Experimental determination in the laboratory (most often tedious, needs availability of equipment and chemicals, and requires extra amount of money)
- Search experimental values through handbooks, research journals, and databases such as Dortmund data bank and DIPPR
- Use of generalized compressibility factor charts
- Use of analytical equations of state such as ideal gas law and van der Waals equations of state

Process simulators such as Aspen Hysys can be used to find pure component and mixture properties (using databases and various equations of state)

pvT properties of pure components and mixture of components

Accurate experimental data is always preferred over theory.

Pycnometer

Vibrating tube densitometer

http://www.apexchemicals.co.th/addons/default/modules/other_product/uploads/category_sub/img_zoom_1418115695.jpg
http://www.anton-paar.com/corp-en/products/details/density-meter-for-the-petroleum-industry-dma-4200-m/

Generalized compressibility factor method

A modification may be made in ideal gas law to be used for real gas or liquid systems by introducing the compressibility factor as follows:

$$pV = ZnRT$$

$$pv = ZRT \qquad (n = 1)$$

Density can be calculated by:

$$\rho = \frac{pM}{ZRT}$$

Compressibility factor

The *pvT* properties of a component are expressed in terms of compressibility factor (Z) and Z can be related to p, T, and v (or V) as below:

$$Z = \frac{pV}{nRT}$$

$$Z = \frac{pv}{RT} \qquad (n = 1)$$

For ideal gas: $Z = 1.0$

For liquids: $Z = 0.01$ to 0.2 [9]

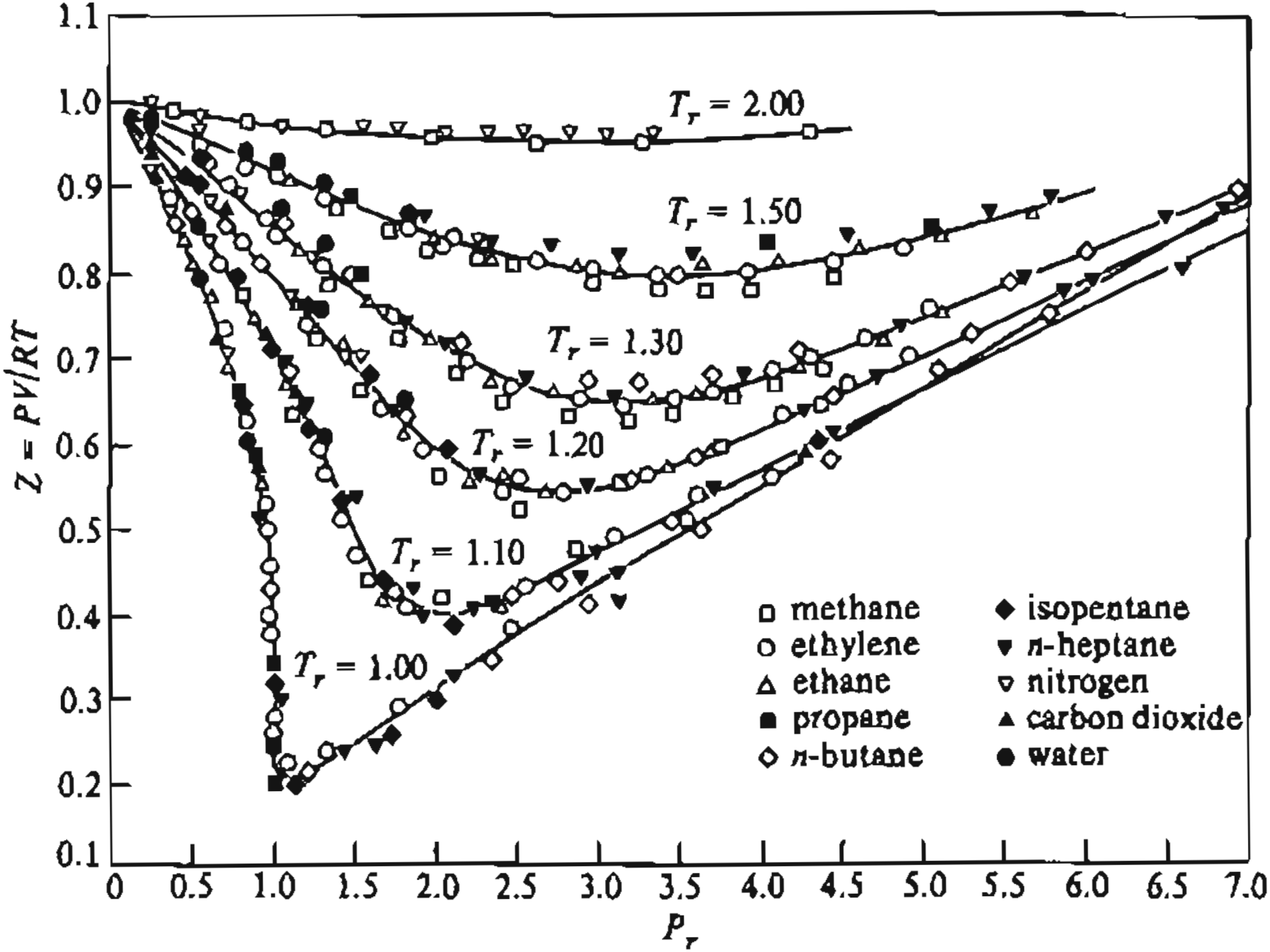
Z at the critical point is usually in the range of 0.27 to 0.29. For most substances, Z_c is 0.27.

Corresponding states principles

Two-parameter corresponding states principle:
For the same reduced temperature and reduced pressure, the compressibility factor is the same.

Three-parameter corresponding states principle:
For the same reduced temperature and reduced pressure and the same third parameter such as critical compressibility factor, acentric factor, or Riedel alpha the value of the compressibility factor is the same.

Experimental Z values [9]



Corresponding states method

Two-parameter corresponding states method describes that for the same reduced temperature and pressure compressibility factor (Z) is the same. The two-parameter method (based on T_r and p_r) is less accurate compared to three- or four-parameters methods. In a three-parameter method, critical compressibility factor (Z_c) and Pitzer acentric factor (ω) are commonly used. Riedel alpha as the third parameter is not common. Lydersen et al. (Lydersen method) uses critical compressibility factor method while Pitzer et al. (Pitzer method) applies acentric factor (ω). Lee-Kesler method is a modification of Pitzer method.

Lydersen method

Lydersen and coworkers used critical compressibility factor as the third parameter. Critical compressibility factor can be calculated using p_c, T_c, and v_c data.

Z at the critical point, i.e., Z_c is usually in the range of 0.27 to 0.29. For most substances, it is 0.27.

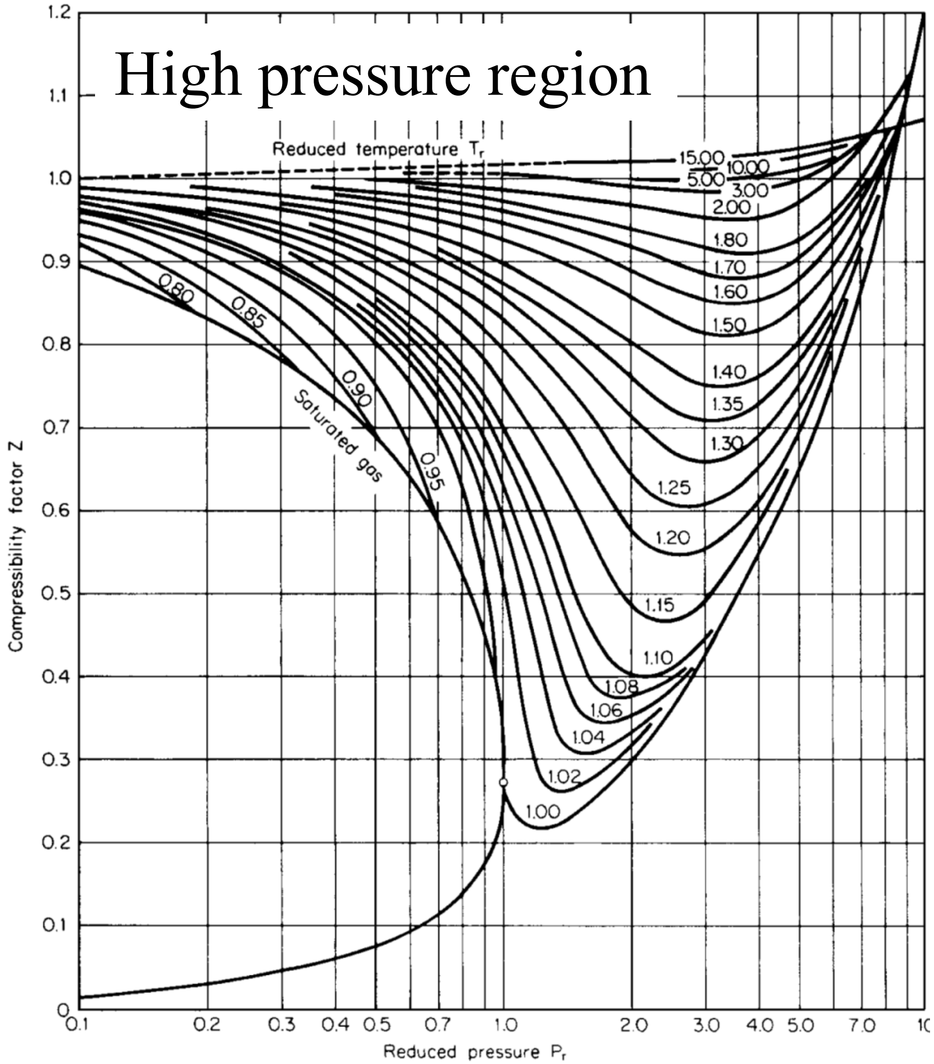
Lydersen method

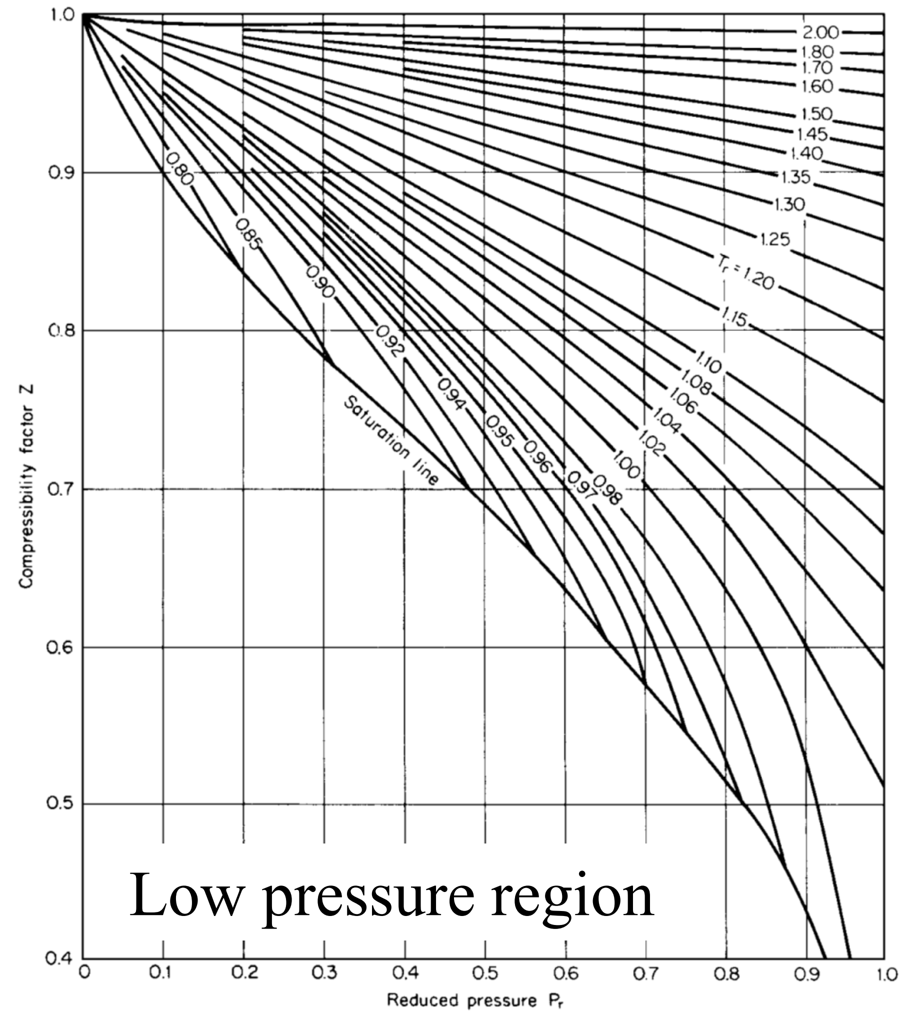
We need T_r = ratio of temperature of interest to critical temperature of substance and p_r = ratio of pressure of interest to critical pressure of substance to locate Z for a constant value of Z_c.

$$T_r = \frac{T}{T_c} \qquad p_r = \frac{p}{p_c}$$

If two charts at, say, $Z_c = 0.27$ and $Z_c = 0.29$ are given, then two Z values using T_r and p_r can be viewed from each of these charts. If the Z_c value for the component or mixture of components lies between the above two Z_c values, then the required Z can be calculated using two-point interpolation (between two Z_cs and two Zs).

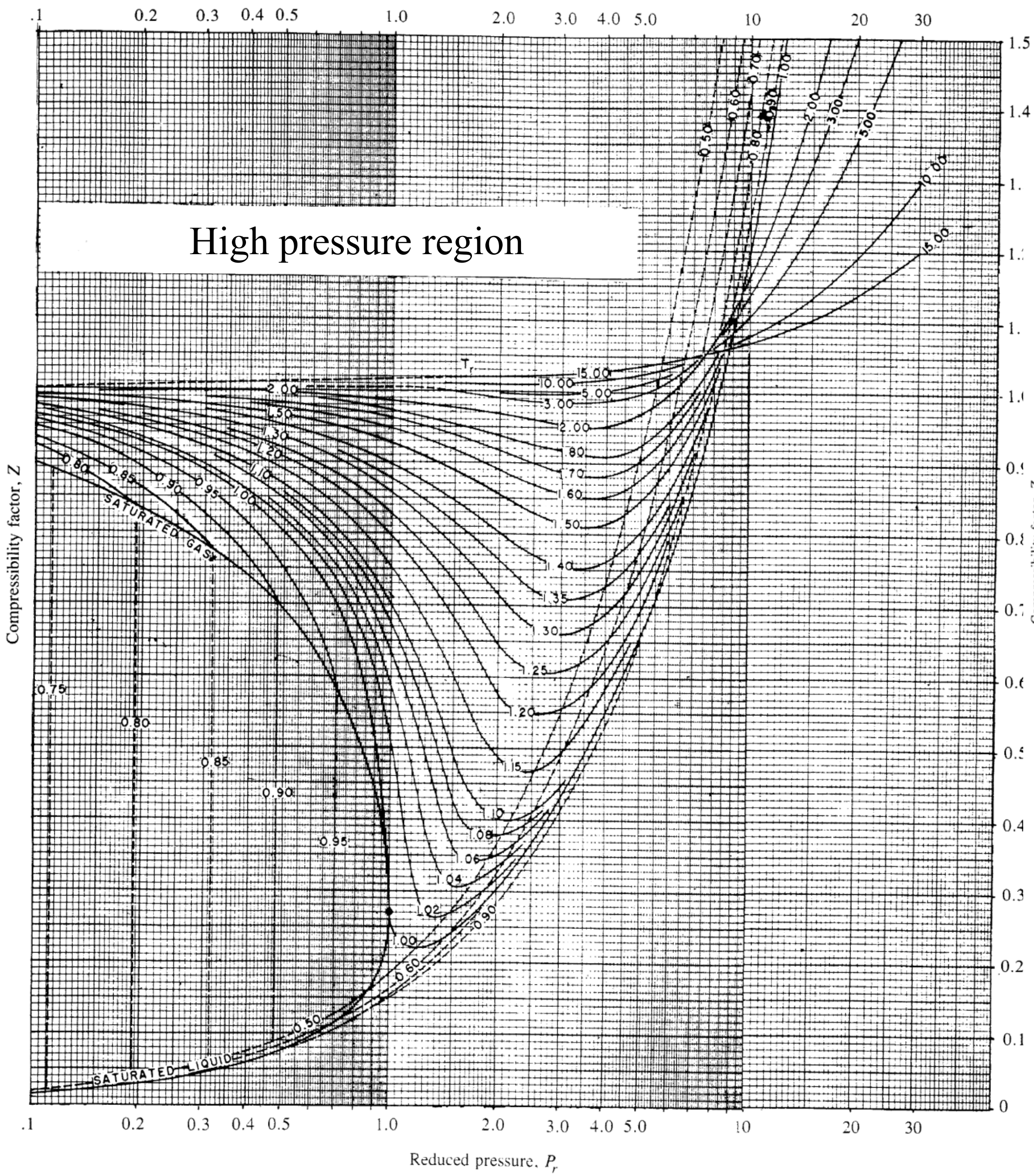
Lydersen method [10]



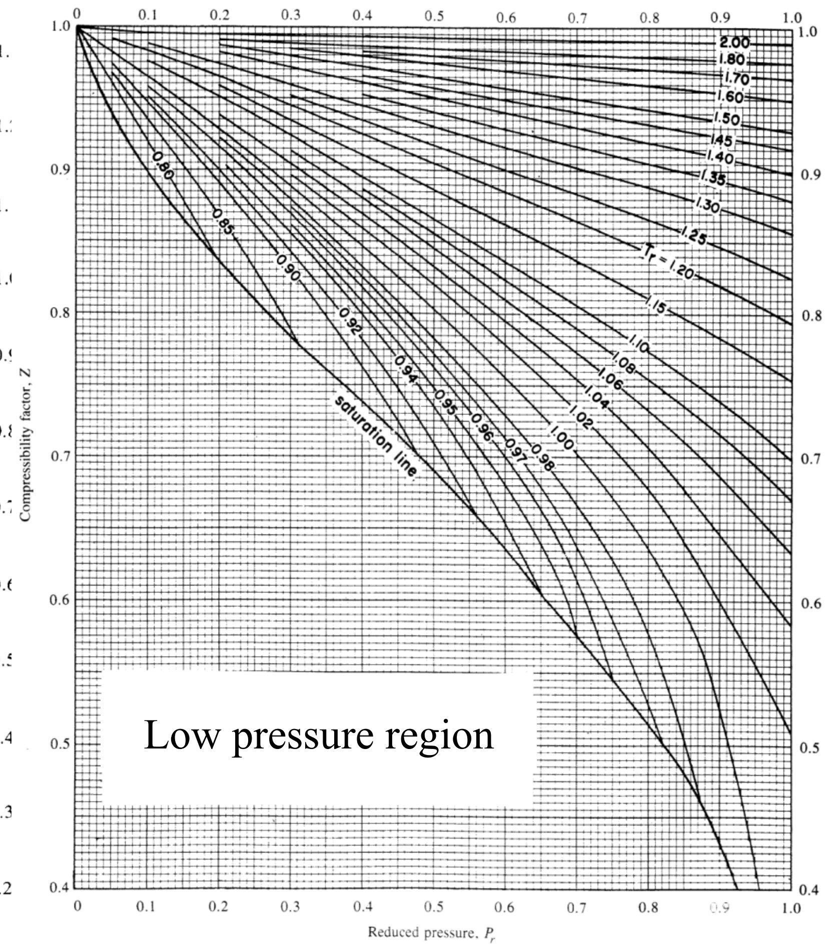


(Z_c = 0.27)

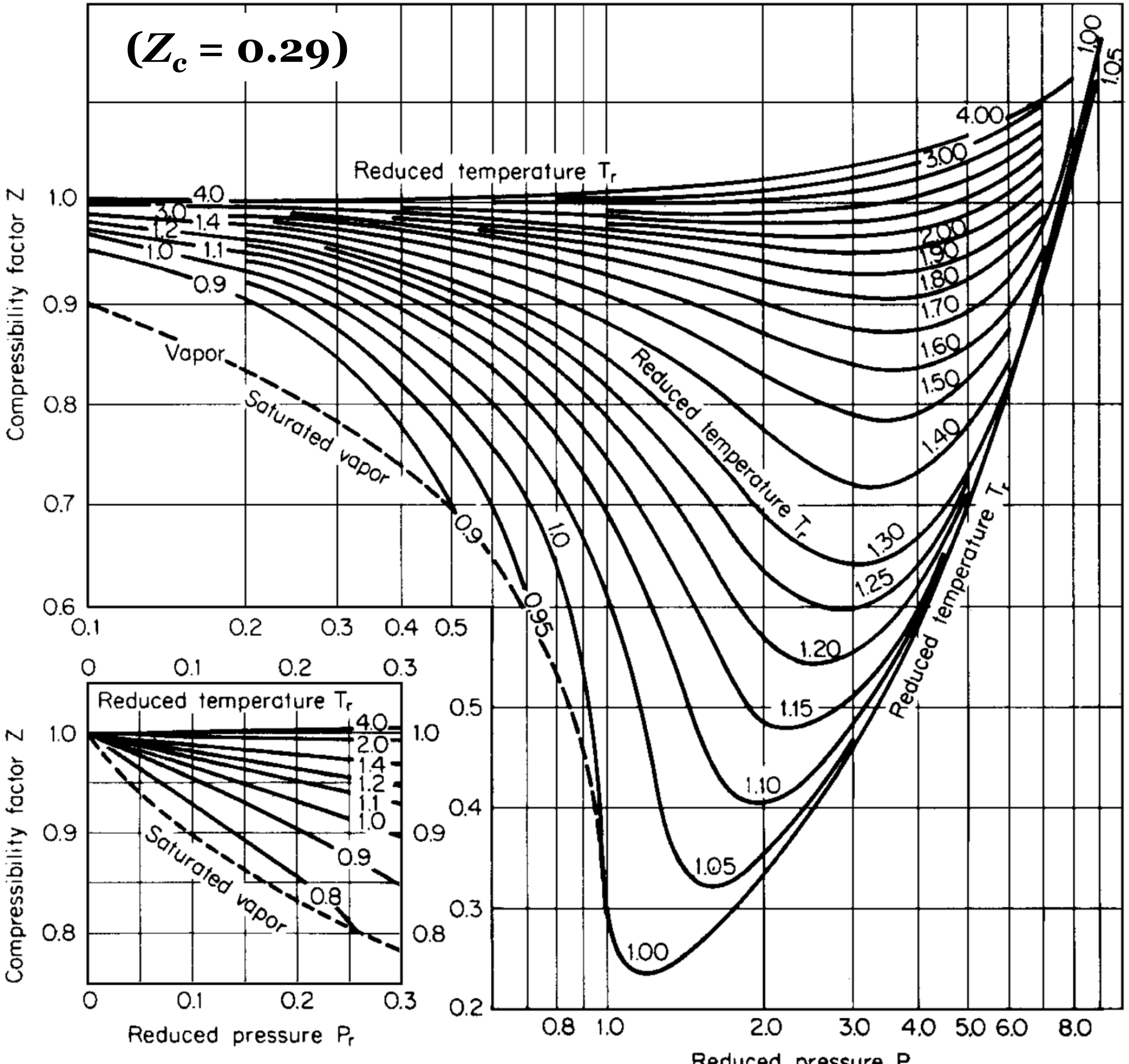
Lydersen method [11]



$Z_c = 0.27$



Lydersen method [10]



Use of Lydersen method

100 moles of ethylene at 50°C and 40 atm is present in a container. Compute the volume of the container using the Lydersen method. Use $T_c = 283$ K, $p_c = 50.5$ atm, and $Z_c = 0.276$.

Hint:

$T_r = (50+273.15)/283 = 1.142$

$p_r = 40/50.5 = 0.792$

For $Z_c = 0.27$, $Z = 0.81$

For $Z_c = 0.29$, $Z = 0.80$

Now interpolate

Lydersen method: Alternate approach [11]

$$Z = Z_{0.27} + D(Z_c - 0.27)$$

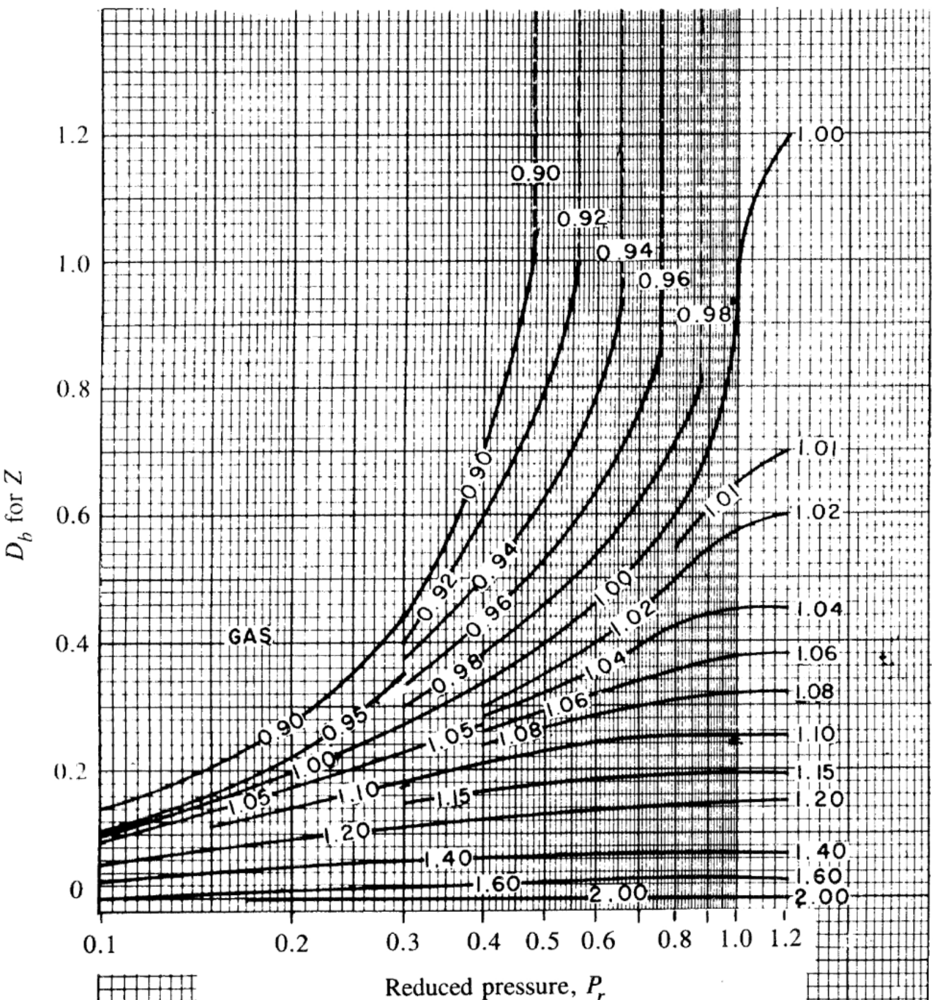
D is deviation term, and

$$D = D_a \; for \; Z_c > 0.27$$

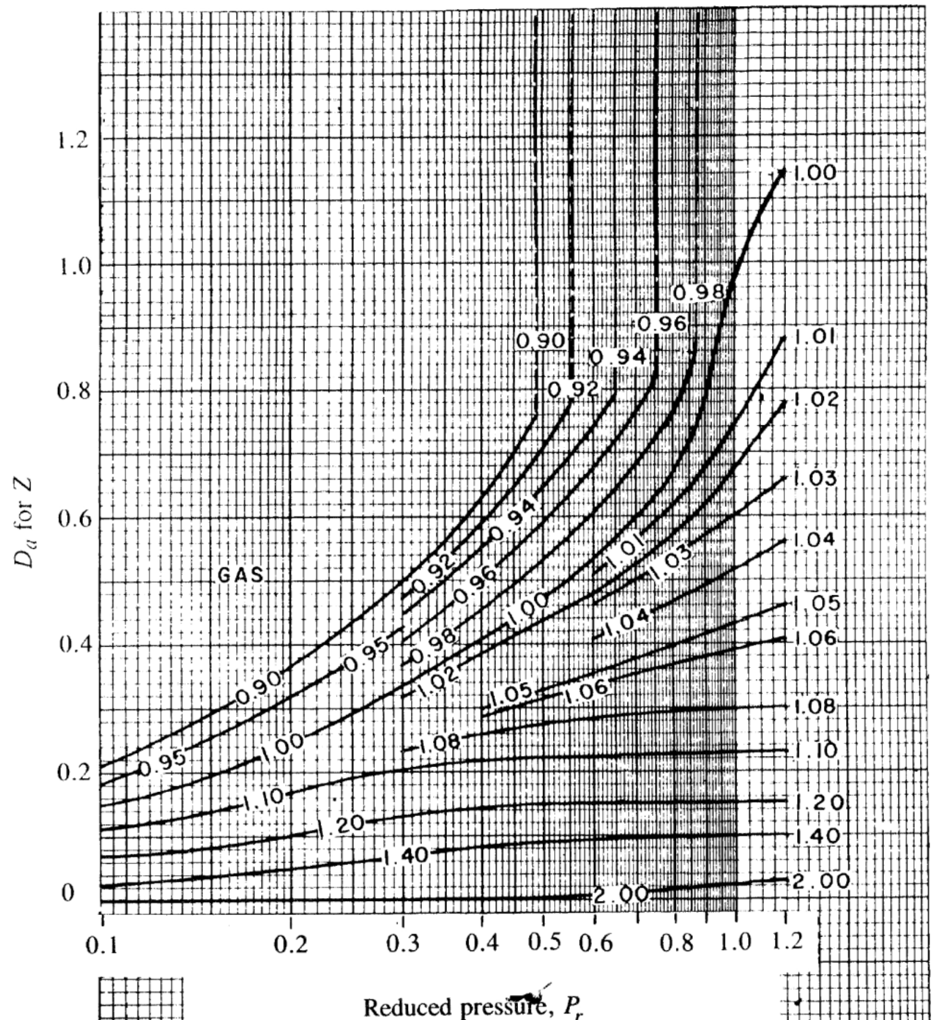
$$D = D_b \; for \; Z_c < 0.27$$

$$Z_{0.27} = value of \; Z \; for \; Z_c = 0.27$$

Lydersen method: Alternate approach [11]



D_b for values of $Z_c < 0.27$



D_a for values of $Z_c > 0.27$

Use of Lydersen (alternate) method [11]

Determine the compressibility factor of water at 700°C and 25 MPa pressure by using the Lydersen generalized technique. Compare your answer with the value of $Z = 0.97$ derived from experimental data. Use $T_c = 647.3$ K, $p_c = 22.12$ MPa, and $Z_c = 0.234$.

Pitzer Method

In the Pitzer method, acentric factor is used as a third parameter and Z is written as a sum of two parts as shown below:

$$Z = Z^{(0)} + \omega Z^{(1)}$$

The first part on the right side indicates compressibility factor for spherically symmetric molecules ($\omega = 0$) while the second part accommodates the nonsphericity of the molecule. Values of $Z^{(0)}$ and $Z^{(1)}$ are plotted or tabulated as function of T_r and p_r.

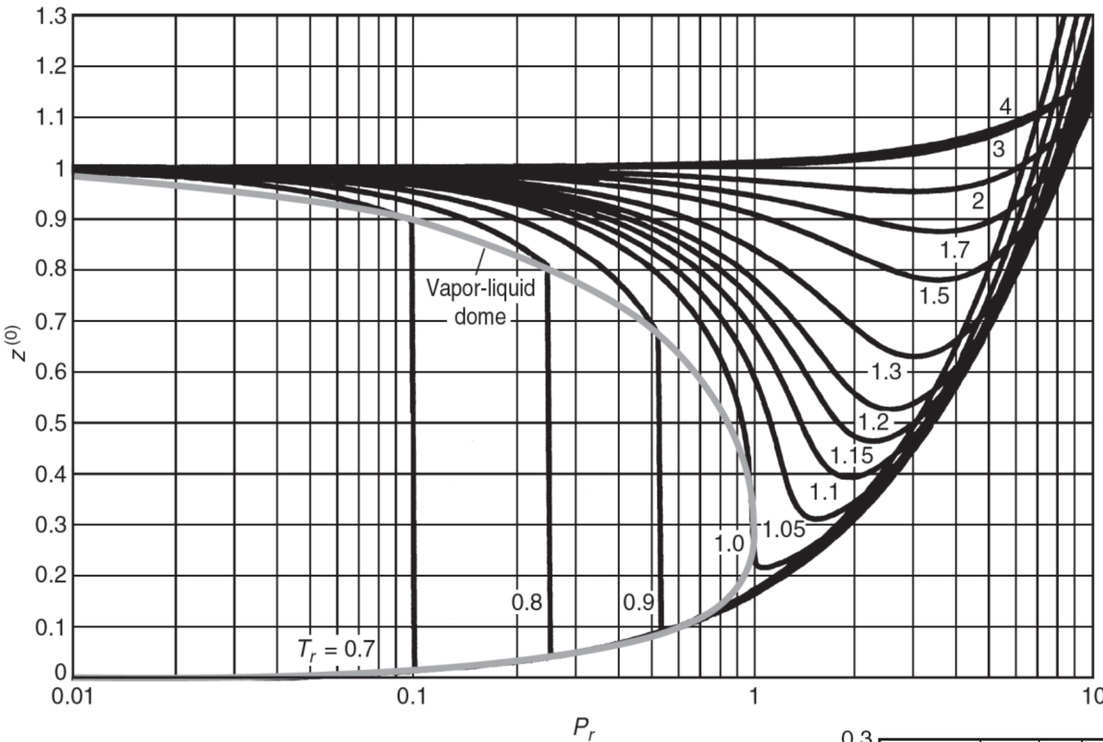
Pitzer acentric factor

Acentric factor is a measure of deviation in spherically symmetric molecules such as argon, krypton, and xenon (acentric factor equal to zero). In other words, it gives the information about the nonsphericity of a molecule.

$$\omega \equiv -1 - \log_{10}[P^{sat}(T_r = 0.7)/P_c]$$

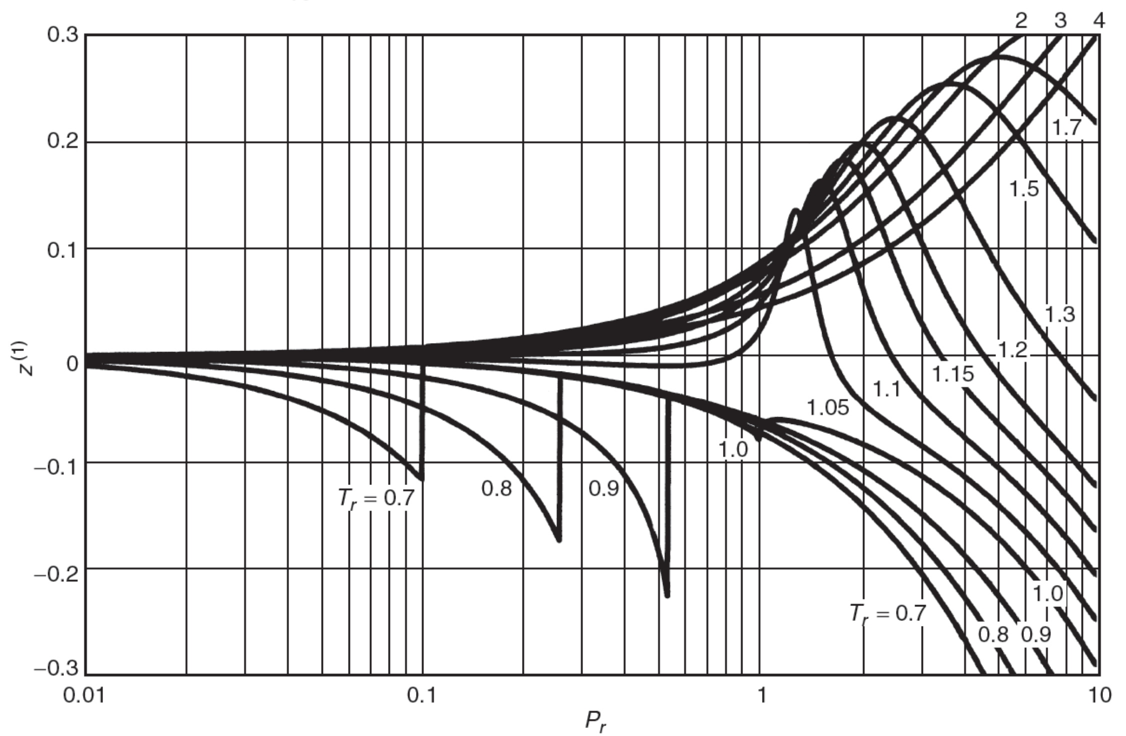
Acentric factor for CO_2 is 0.225, n-butane 0.200; benzene 0.210, n-hexane 0.300, and hydrogen has –0.217.

Lee-Kesler charts [12]



The charts to be used in Pitzer method are modified by Lee and Kesler.

The Lee-Kesler charts shown here are available in tabulated form and analytical form to be used with computers. See Ref. 1.



Lee-Kesler analytical equation

$$Z = Z^{(0)} + \frac{\omega}{\omega^{(h)}}(Z^{(h)} - Z^{(0)}) = Z^{(0)} + \omega Z^{(1)} \qquad (1)$$

where Z = compressibility factor, dimensionless

$Z^{(0)}$ = compressibility factor for the simple fluid obtained from Eq. 2

$Z^{(h)}$ = compressibility factor for the heavy reference fluid (n-octane) obtained from Eq. 2

ω = acentric factor of the compound for which Z (volume) is sought

$\omega^{(h)}$ = acentric factor for the heavy reference fluid (n-octane) = 0.3978

The compressibility factors for the simple fluid $Z^{(0)}$ and the heavy reference fluid $Z^{(h)}$ are obtained from the following equation (Eq. 2)

$$Z^{(i)} = \frac{p_r v_r'}{T_r} = 1 + \frac{B}{v_r'} + \frac{C}{(v_r')^2} + \frac{D}{(v_r')^5} + \frac{c_4}{(T_r)^3 (v_r')^2}\left(\beta + \frac{\gamma}{(v_r')^2}\right)\exp\left(\frac{-\gamma}{(v_r')^2}\right) \qquad (2)$$

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{(T_r)^2} - \frac{b_4}{(T_r)^3}$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{(T_r)^3}$$

$$D = d_1 + \frac{d_2}{T_r}$$

$Z^{(i)} = Z^{(0)}$ when the constants in the equation correspond to the simple fluid

$Z^{(i)} = Z^{(h)}$ when the constants in the equation correspond to the heavy reference fluid

p_r = reduced pressure, $\frac{p}{p_c}$

Lee-Kesler analytical equation

p_c = critical pressure of the compound whose Z is sought, kPa

$$v_r' = \frac{p_c v}{RT_c}$$

v = molar volume of the simple fluid or of the heavy reference fluid, as the case may be, m^3/kmol

R = gas constant = 8.3140 ($m^3 \cdot$kPa)/(kmol·K)

T_c = critical temperature of the compound whose Z is sought, K

T_r = reduced temperature, $\frac{T}{T_c}$

T = temperature, K

Constant	Simple fluid	Heavy reference fluid
b_1	0.1181193	0.2026579
b_2	0.265728	0.331511
b_3	0.154790	0.027655
b_4	0.030323	0.203488
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0.0	0.016901
c_4	0.042724	0.041577
d_1	1.55488×10^{-5}	4.8736×10^{-5}
d_2	6.23689×10^{-5}	7.40336×10^{-6}
β	0.65392	1.226
γ	0.060167	0.03754

Use of Pitzer (Lee-Kesler method) method

Estimate the specific volume for CO_2 (in cm^3/g) at: a) 310 K and 8 bar, b) 310 K and 75 bar. The experimental values at these conditions are 70.58 cm^3/g and 3.90 cm^3/g, respectively. Use Pitzer method (Lee-Kesler method).

Mixing rules for generalized charts for compressibility factor [12]

$$T_{pc} = \sum y_i T_{c,i}$$

$$P_{pc} = \sum y_i P_{c,i}$$

$$\omega_p = \sum y_i \omega_i$$

$$Z_{pc} = \sum y_i Z_{c,i}$$

Mixing rules for generalized charts for compressibility factor [13]

Pseudocritical Property	*Kay (1938)*	*Prausnitz & Gunn (1958)*	*Lorentz-Berthelot Type (LB)*
T_c	$\Sigma y_i T_{ci}$	$\Sigma y_i T_{ci}$	$(1 - k_{ij})\sqrt{T_{ci}T_{cj}}$
V_c	$\Sigma y_i V_{ci}$	$\Sigma y_i V_{ci}$	$(V_{ci}^{1/3} + V_{cj}^{1/3})^3/8$
z_c	$\Sigma y_i z_{ci}$	$\Sigma y_i z_{ci}$	$0.5(z_{ci} + z_{cj}) = 0.291 - 0.080\omega$
ω	$\Sigma y_i \omega_i$	$\Sigma y_i \omega_i$	$0.5(\omega_i + \omega_j)$
P_c	$\Sigma y_i P_{ci}$	$z_c RT_c/V_c$	$z_c RT_c/V_c$

Note: Binary interaction parameters, k_{ij}, are given for some substances in Table E.3. The rules for T_c and V_c in the last column are known as the Lorentz-Berthelot Rules. They apply only to pairs of substances and are used to find the cross parameters a_{ij} of cubic equations or the B_{ij} of the virial equation.

Activity

A gaseous mixture at 25°C (298K) and 120 atm (12,162 kPa) contains 3.0% He, 40.0%Ar, and 57.0% C2H4 on a mole basis. Compute the volume of the mixture per mole using the following: a) generalized compressibility factor method (Lydersen method), b) generalized compressibility factor method (Pitzer method using Lee-Kesler charts).

Component, i	Y_i	$T_{c,i}$ (K)	$P_{c,i}$ (atm)
He	0.03	5.2	2.24
A	0.40	150.7	48.00
C_2H_4	0.57	283.0	50.50

Homework Problems

✓Estimate the specific volume for CO_2 (in cm^3/g) at: a) 310 K and 8 bar, b) 310 K and 75 bar. The experimental values at these conditions are 70.58 cm^3/g and 3.90 cm^3/g, respectively. Use the Lydersen method and analytical Lee-Kesler equation.

✓Estimate the specific volume for CH_4 (in cm^3/g) at: a) 310 K and 8 bar, b) 310 K and 75 bar. Use both Lydersen and Pitzer methods.

✓Calculate the density of a natural gas that contains 60% CH_4, 20% C_2H_6, 10% N_2, and 10% CO_2 at 40 bar and 80°C using both Lydersen and Pitzer methods.

Simplest *pvT* relationship valid only for gases (but at low pressures): ideal gas law

The expression given below is the ideal gas law.

$$pV = nRT$$

$$pv = RT \qquad (n = 1)$$

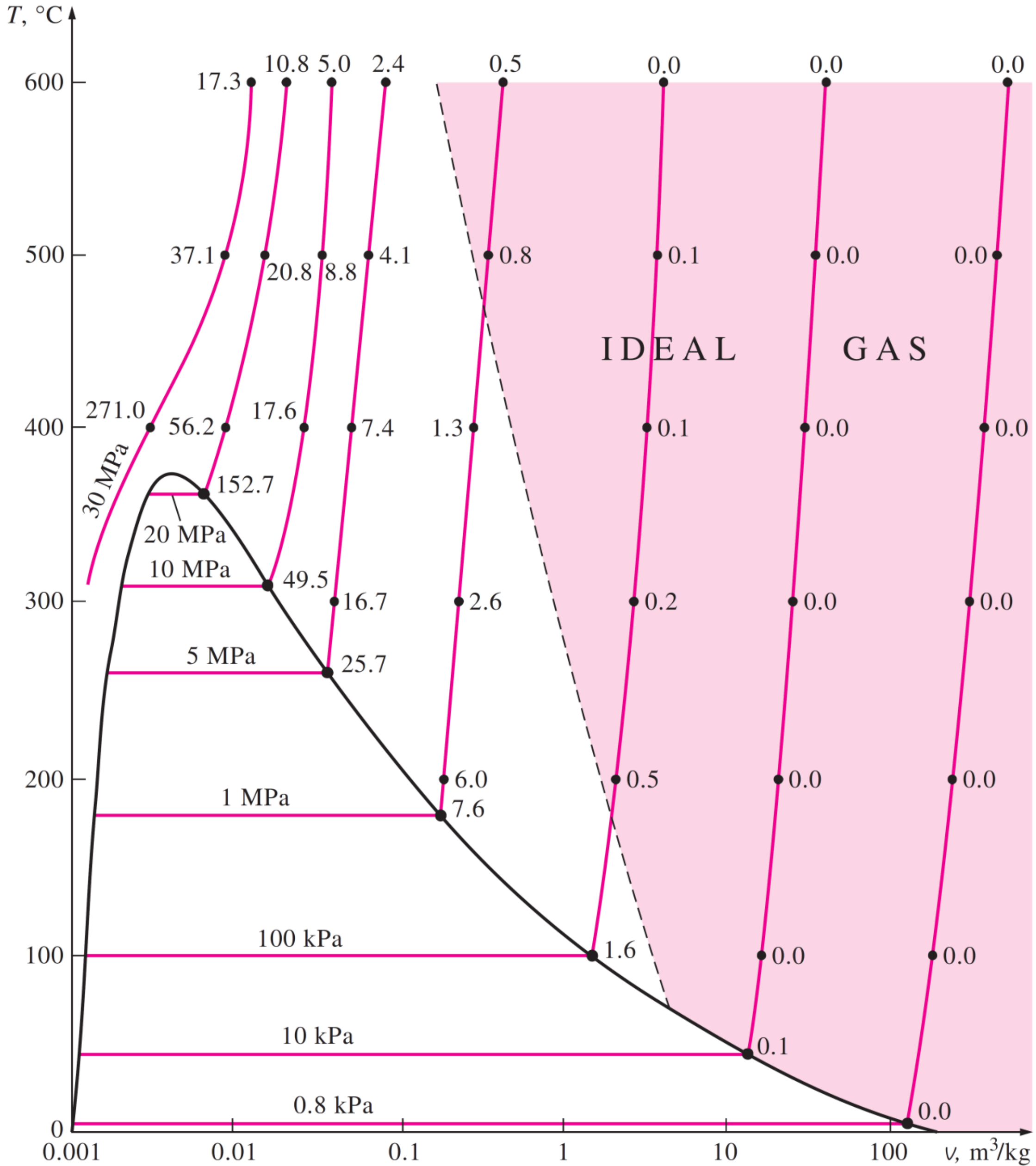
A useful form of the ideal gas law is:

$$\left(\frac{p_1}{p_2}\right)\left(\frac{V_1}{V_2}\right) = \left(\frac{n_1}{n_2}\right)\left(\frac{T_1}{T_2}\right)$$

Gas density can be calculated by:

$$\rho = \frac{pM}{RT}$$

Steam as ideal gas [2]



Percentage of error ($[|v_{table} - v_{ideal}|/v_{table}] \times 100$) involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal gas with less than 1 percent error.

Other analytical equations of state

Engineers have developed two types of empirical analytical equations of state.

✓Truncated virial type equation
✓van der Waals type (cubic equation of state) equation

The virial equation can be written as:

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \cdots \qquad B' = \frac{B}{RT}$$

$$z = \frac{Pv}{RT} = 1 + B'P + C'P^2 + D'P^3 + \ \ldots \qquad C' = \frac{C - B^2}{(RT)^2}$$

Truncated virial equations

Upto 15 bar B-truncated (upto second virial coefficient) virial equation is better:

$$z = \frac{Pv}{RT} = 1 + B'P = 1 + \frac{BP}{RT}$$

From 15 to 50 bar, C-truncated (upto third virial coefficient) is better:

$$z = 1 + \frac{B}{v} + \frac{C}{v^2}$$

Virial equation does not apply to liquids.

Truncated virial equations [12]

Principle of corresponding states is normally applied to a truncated virial equation. For *B*-truncated virial equation:

$$B_r = B^{(0)} + \omega B^{(1)}$$

$$B_r = \frac{BP_c}{RT_c}$$

Abbot proposed that

$$B^{(0)} = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad B^{(1)} = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Other virial type equations: Beattie-Bridgeman EoS

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3}$$

$$B = B_0 - \frac{A_0}{RT} - \frac{c}{T^3}$$

$$C = -B_0 b + \frac{A_0 a}{RT} - \frac{c B_0}{T^3}$$

$$D = \frac{b c B_0}{T^3}$$

A_0, B_0, a, b, and c are adjustable parameters

Other virial type equations: Benedict-Webb-Rubin (BWR) EoS

$$z = 1 + \left(B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3}\right)v^{-1} + \left(b - \frac{a}{RT}\right)v^{-2} + \frac{a\alpha}{RT}v^{-5}$$

$$+ \frac{\beta}{RT^3v^2}\left(1 + \frac{\gamma}{v^2}\right)\exp\left(-\frac{\gamma}{v^2}\right)$$

Requires the values of 8 coefficients, however, good to correlate data of both liquid and gas, and *pvT* properties near critical point.

van der Waals type equations:
van der Waals equation

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$a = \frac{27}{64}\frac{(RT_c)^2}{P_c}$$

$$Pv^3 - (RT + Pb)v^2 + av - ab = 0$$

$$b = \frac{(RT_c)}{8P_c}$$

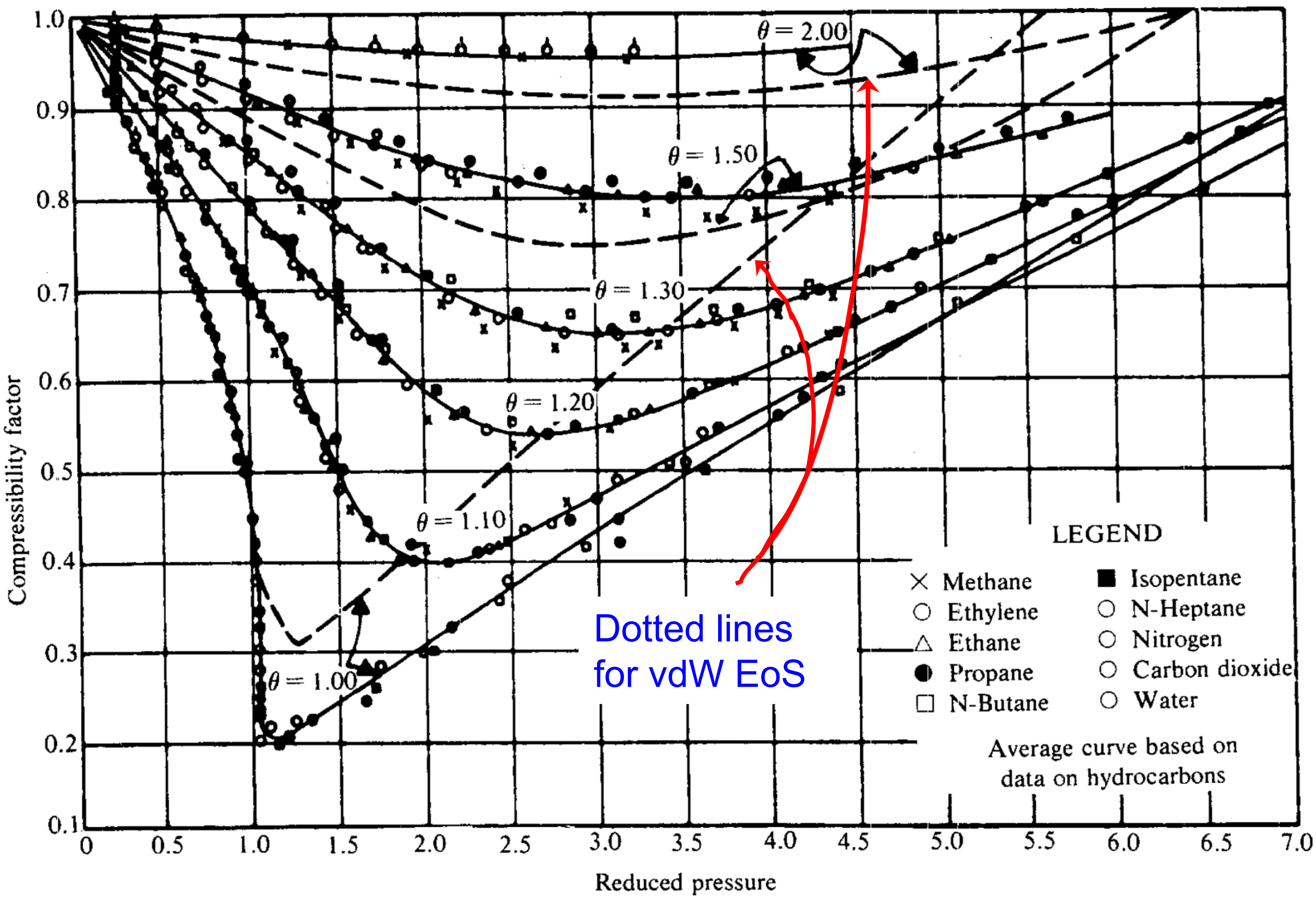
Z_c comes out be 0.375.

$$v^3 - \left[\frac{RT}{P} + b\right]v^2 + \frac{a}{P}v - \frac{ab}{P} = 0$$

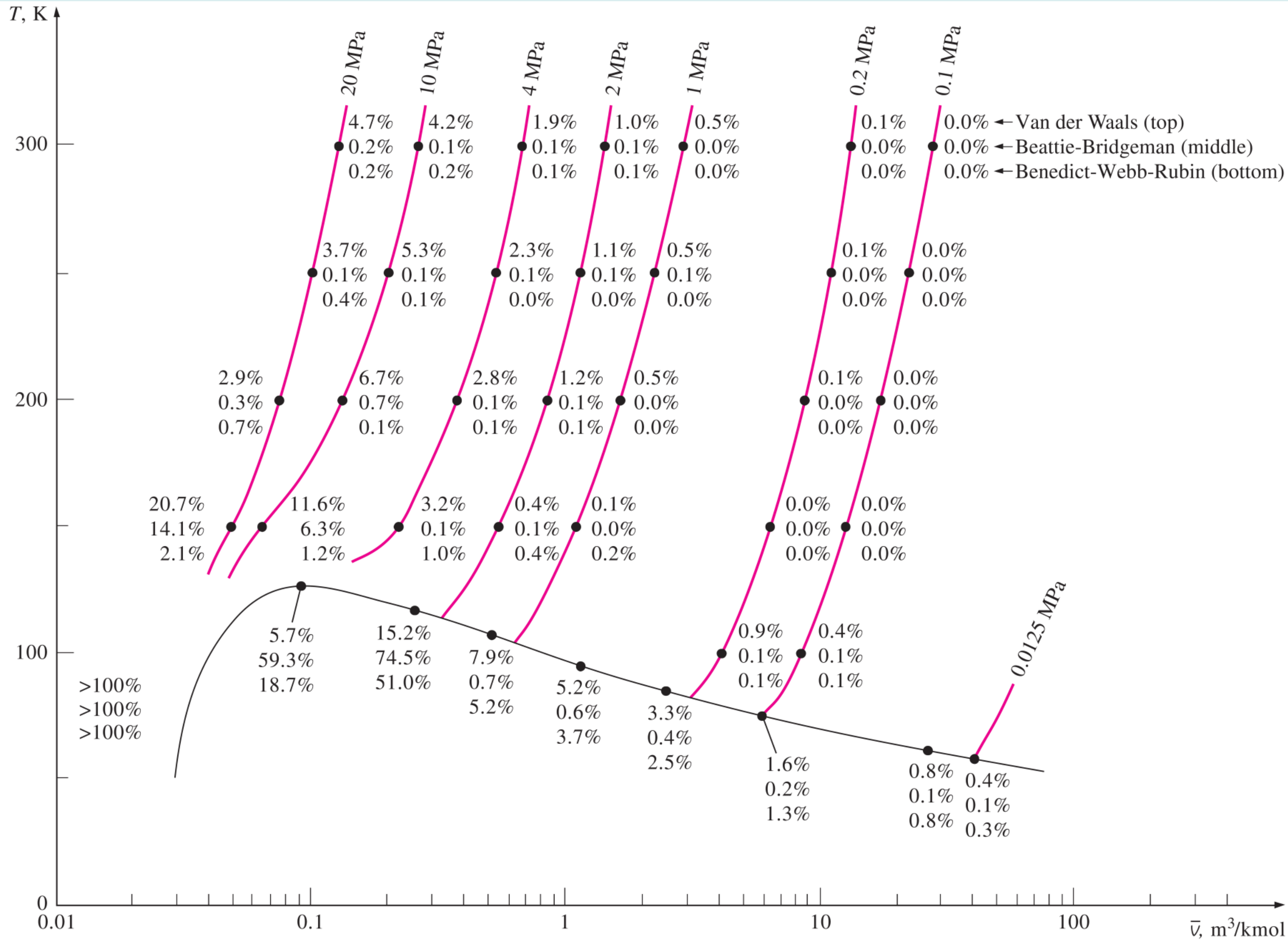
The best values of *a* and *b* can be obtained by fitting experimental *pvT* data.

The solution of a cubic equation may result in three volumes. The largest volume is meant for gas and the lowest volume is meant for liquid while the middle root or volume has no significance. Above critical point there will be only one positive root which will give volume of the supercritical fluid.

van der Waals type equations: van der Waals equation [13]



Comparison of some equations of states with experimental values of N2 [2]



Percentage of error involved in various equations of state for nitrogen (% error $= [(|v_{table} - v_{equation}|)/v_{table}] \times 100$).

van der Waals type equations: Redlich-Kwong (RK)EoS (Two-parameter equation)

$$P = \frac{RT}{v - b} - \frac{a}{T^{1/2} v(v + b)}$$

$$a = \left(\frac{1}{9(\sqrt[3]{2} - 1)}\right)\frac{R^2 T_c^{2.5}}{P_c} = \frac{0.42748 R^2 T_c^{2.5}}{P_c}$$

$$b = \left(\frac{\sqrt[3]{2} - 1}{3}\right)\frac{RT_c}{P_c} = \frac{0.08664 RT_c}{P_c}$$

Z_c comes out be 0.333.

The equation depart significantly from measured values near the critical point.

van der Waals type equations: Soave-Redlich-Kwong (SRK)EoS (Three-parameter equation)

$$p = \frac{RT}{(v-b)} - \frac{a}{v(v+b)}$$

$$a = 0.42748\frac{(RT_c)^2}{p_c}\left(1 + m\left(1 - \sqrt{\frac{T}{T_c}}\right)\right)^2$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2$$

$$b = 0.08664\frac{RT_c}{p_c}$$

Z_c comes out be 0.333.

van der Waals type equations: Peng-Robinson (PR) EoS (Three-parameter equation)

$$P = \frac{RT}{v - b} - \frac{a\alpha(T)}{v(v + b) + b(v - b)}$$

$$a = 0.45724 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.07780 \frac{RT_c}{P_c}$$

$$\alpha(T) = [1 + \kappa(1 - \sqrt{T_r})]^2$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

Z_c comes out be 0.307.

Mixing rules for analytical equations of state: binary system [12]

$$a_{\mathrm{mix}} = y_1^2 a_1 + 2 y_1 y_2 a_{12} + y_2^2 a_2$$

$$a_{12} = \sqrt{a_1 a_2}$$

$$a_{12} = \sqrt{a_1 a_2}(1 - k_{12})$$

$$b_{\mathrm{mix}} = y_1 b_1 + y_2 b_2$$

Mixing rules for analytical equations of state: multicomponent system [12]

For RK type equations

$$a_{\text{mix}} = \sum_i \sum_j y_i y_j a_{ij}$$

$$b_{\text{mix}} = \sum_i y_i b_i$$

For PR and SRK type equations

$$a_{\text{mix}} = \sum_i \sum_j y_i y_j [a\alpha(T)]_{ij}$$

$$b_{\text{mix}} = \sum_i y_i b_i$$

Mixing rules for analytical equations of state: example for three-component system

Please write here for three components

van der Waals type equations: Peng-Robinson (PR) EoS (Three-parameter equation)

For a mixture of components, measure $a\alpha(T)$ for each component and then use the mixing rule.

Problem

Calculate the pressure exerted by a mixture of 20 mol propane and 30 mol ethane present in a 0.1 m^3 vessel at 373 K. Use Redlich-Kwong (RK) equation for the purpose. Use simple mixing rules.

$$P = \frac{RT}{v - b} - \frac{a}{T^{1/2} v(v + b)}$$

$$a = \left(\frac{1}{9(\sqrt[3]{2} - 1)} \right) \frac{R^2 T_c^{2.5}}{P_c} = \frac{0.42748 R^2 T_c^{2.5}}{P_c}$$

$$b = \left(\frac{\sqrt[3]{2} - 1}{3} \right) \frac{RT_c}{P_c} = \frac{0.08664 RT_c}{P_c}$$

Homework probelms [10]

1. Calculate the density of a natural gas mixture containing 32.1% methane, 41.2% ethane, 17.5% propane, and 9.2% nitrogen (mole basis) at 3550 kPa and 394 K. Use Lydersen method as well as Pitzer method.

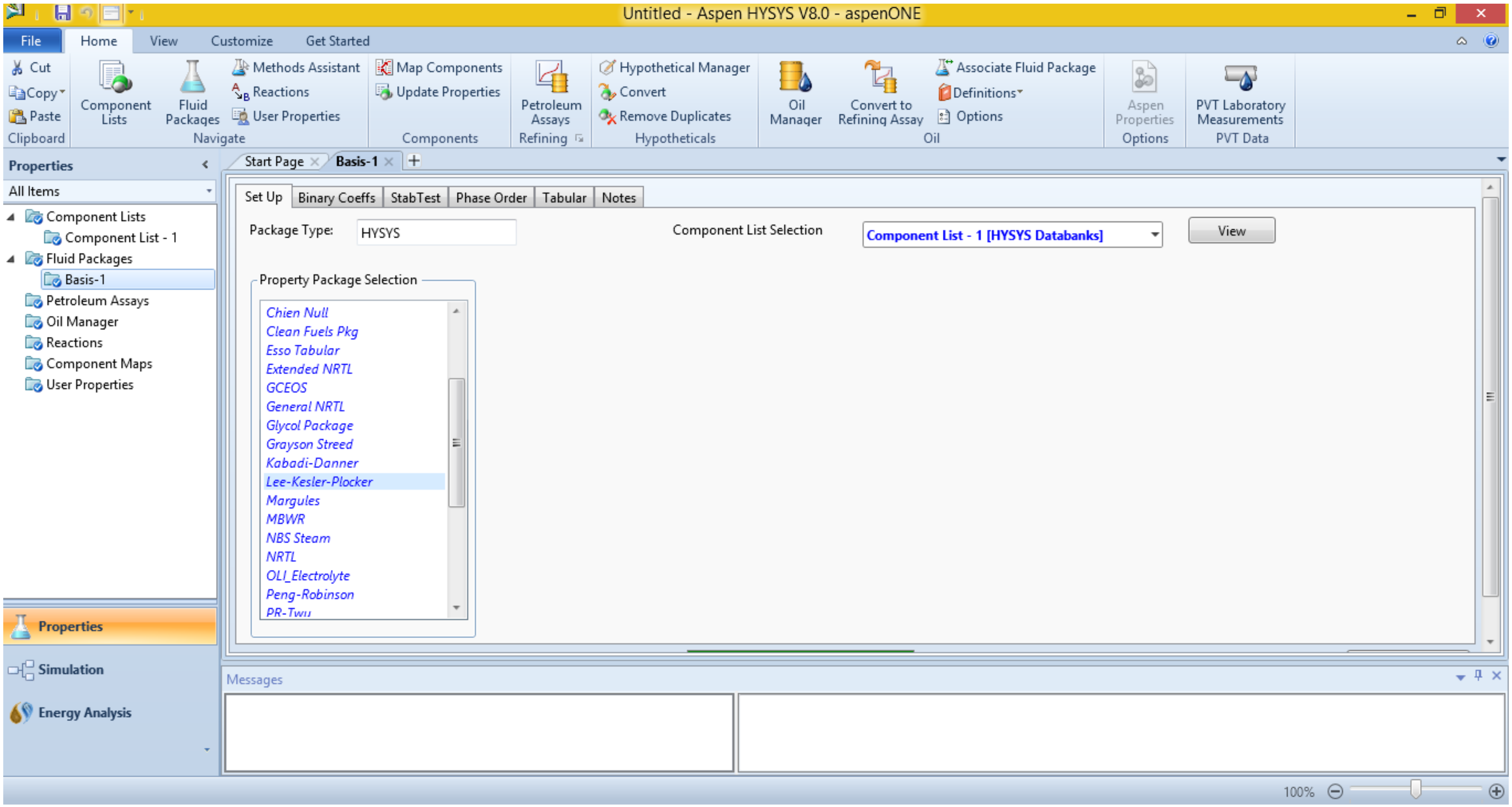
2. A gaseous mixture at 298 K and 120 atm contains 3% He, 40% Ar, and 57% C_2H_4 on a mole basis. Calculate the volume of the mixture per mole using the following:
a) Ideal gas law, b) Pitzer method, and c) Lydersen method.

Rackett equation for liquid density

A few equations have been explicitly applicable to liquid phase only, one such equation is Rackett equation. Rackett equation is used to find the density of saturated liquid, i.e., when component is at its bubble point. As density of a liquid is only marginally influenced by pressure, so the equation can be used for density of a subcooled (compressed) liquid as well.

$$v^{\mathrm{l,sat}} = \frac{RT_c}{P_c}(0.29056 - 0.08775\omega)^{[1+(1-T_r)^{2/7}]}$$

Use of Aspen Hysys for property measurements



Homework problem

Estimate the specific volume in cm^3/g for carbon dioxide at (a) 310 K and 8 bar (b) 310 K and 75 bar by the following methods and compare to the experimental values of 70.58 at 310 K and 8 bar and of 3.90 cm^3/g at 310 K and 75 bar , respectively. Use T_c = 304.2 K, p_c = 73.82 bar, and ω = 0.228.

1. Ideal gas law
2. *B*-truncated virial equation
3. van der Waals equation
4. Redlich-Kwong equation
5. Peng-Robinson equation
6. Peng-Robinson equation in Aspen HYSYS
7. Soave-Redlich-Kwong equation
8. Soave-Redlich-Kwong equation in Aspen HYSYS
9. Lydersen method
10. Pitzer method (Lee-Kesler charts)

Homework problem

Calculate the molar volume of 40% N_2 and 60% NH_3 mixture at 200 bar and 250 ºC. Use simple mixing rules and apply:

1. Ideal gas law
2. van der Waals equation
3. Redlich-Kwong equation
4. Soave-Redlich-Kwong equation
5. Peng-Robinson equation
6. Peng-Robinson equation in Aspen HYSYS
7. Lydersen method
8. Pitzer Method (Lee-Kesler charts)

Problem

Estimate the specific volume of NH_3 in mol/L at

a) 1 bar and 300, 400, 500, and 600 K

b) 10 bar and 400, 500, and 600 K

c) 100 bar and 400, 500, and 600 K, using each of the following methods and compare the results with the data given in the next slide. Work in excel, write in word as table, print, and submit as hard copy.

1. Ideal gas law
2. *B*-truncated virial equation
3. van der Waals equation
4. Redlich-Kwong equation
5. Peng-Robinson equation
6. Peng-Robinson equation in Aspen HYSYS
7. Soave-Redlich-Kwong equation
8. Soave-Redlich-Kwong equation in Aspen HYSYS
9. Lydersen method
10. Pitzer method (Lee-Kesler charts)
11. Pitzer method (Lee-Kesler equation)

Data for NH_3

Temperature K	Pressure MPa	Density mol/dm^3	Volume dm^3/mol
200.00	0.10000	42.756	0.023388
239.56	0.10000	40.064	0.024960
239.56	0.10000	0.051595	19.382
300.00	0.10000	0.040502	24.690
400.00	0.10000	0.030171	33.144
500.00	0.10000	0.024091	41.509
600.00	0.10000	0.020060	49.849
700.00	0.10000	0.017188	58.179
200.00	1.0000	42.774	0.023379
298.05	1.0000	35.403	0.028246
298.05	1.0000	0.45697	2.1883
300.00	1.0000	0.45215	2.2117
400.00	1.0000	0.31157	3.2095
500.00	1.0000	0.24426	4.0940
600.00	1.0000	0.20197	4.9513
700.00	1.0000	0.17248	5.7977
200.00	5.0000	42.852	0.023336
300.00	5.0000	35.450	0.028209
362.03	5.0000	28.505	0.035081
362.03	5.0000	2.4828	0.40277
400.00	5.0000	1.8706	0.53459
500.00	5.0000	1.3046	0.76650
600.00	5.0000	1.0412	0.96040
700.00	5.0000	0.87563	1.1420
200.00	10.000	42.947	0.023284
300.00	10.000	35.714	0.028000
398.32	10.000	20.945	0.047744
398.32	10.000	7.1390	0.14008
400.00	10.000	6.5455	0.15278
500.00	10.000	2.8656	0.34897
600.00	10.000	2.1650	0.46190
700.00	10.000	1.7835	0.56069

From Perry's Chemical Engineers' Handbook, 2008, 8th ed, p. 2-218.

Thermodynamic property relationships

Objective

To develop mathematical expressions by which various thermodynamic properties can be related and non-measurable properties such as change in entropy, internal energy, etc., can be expressed in terms of measurable properties. We can have measured thermodynamic data in terms of pressure (p), temperature (T), molar volume (v), constant volume specific heat capacity (c_v), constant pressure specific heat capacity (c_p), isothermal compressibility (κ), and isobaric volume expansivity (β).

Types of thermodynamic properties

- Measured thermodynamic properties
- Fundamental thermodynamic properties
- Derived thermodynamic properties

Measured thermodynamic properties

- Pressure
- Temperature
- Volume

Experimentally measurable in a laboratory are measured properties. As p, v, and T are measurable properties so equations of state are commonly known as pvT relationships.

Fundamental thermodynamic properties

Those appear from fundamental laws of thermodynamics.

- Internal energy
- Entropy

These are not measurable and required for mathematical formulations and understanding of thermodynamic laws.

Derived thermodynamic properties

- Enthalpy
- Helmholtz free energy
- Gibbs free energy

Merely derived from other properties and defined for convenience such as enthalpy is a combination of internal energy and *pv* work. Enthalpy is important in closed systems for constant pressure processes and includes flow work so that one does not separately measure flow work in thermodynamic calculations.

Fundamental property relationships

$$du = Tds - pdv$$

$$dh = Tds + vdp$$

$$da = -sdT - pdv$$

$$dg = -sdT + vdp$$

Thermodynamic property relationships

These equations are called as fundamental property relationships. Though these are derived for reversible process but they are applicable for both reversible and irreversible processes as they are defined in terms of only state functions.

For derivation of these equations see class notes.

Thermodynamic property relationships

If z is a function of x and y, then we may write

$$z = f(x, y)$$

For above equation, the total derivative of z is written mathematically as:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

State postulate

For a pure (constant composition) system, the values of two independent, intensive properties are required to completely describe the state of a system.

For a substance of fixed composition, state postulate suggests that a state property to be calculated requires the information of at least two other state properties. So as an example, internal energy, u, may be written as a function of s and v, i.e., $u = f(s, v)$ and total differential of u can be written mathematically as described below:

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$$

Fundamental property relationships

$z = f(x, y)$	Partial derivatives		Fundamental group
$u = f(s, v)$	$\left(\frac{\partial u}{\partial s}\right)_v = T$	$\left(\frac{\partial u}{\partial v}\right)_s = -p$	$\{u, s, v\}$
$h = f(s, p)$	$\left(\frac{\partial h}{\partial s}\right)_p = T$	$\left(\frac{\partial h}{\partial p}\right)_s = v$	$\{h, s, p\}$
$a = f(T, v)$	$\left(\frac{\partial a}{\partial T}\right)_v = -s$	$\left(\frac{\partial a}{\partial v}\right)_T = -p$	$\{a, T, v\}$
$g = f(T, p)$	$\left(\frac{\partial g}{\partial T}\right)_p = -s$	$\left(\frac{\partial g}{\partial p}\right)_T = v$	$\{g, T, p\}$

Thermodynamic property relationships

Say, for the first two derivatives (2nd row of the table in the previous slide)! Are there any other properties apart from *s* and *v* that can define the partial derivatives in terms of a state function? of course not! This suggests us to define the set containing *u*, *s*, and *v* as a fundamental set of properties [9]. Similarly one can obtain other fundamental groupings.

Maxwell relationships

For any three properties z, x, and y mathematics helps us to write

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y$$

So for the fundamental set $\{u, s, v\}$, it may be shown that

$$\left[\frac{\partial}{\partial v}\left(\frac{\partial u}{\partial s}\right)_v\right]_s = \left[\frac{\partial}{\partial s}\left(\frac{\partial u}{\partial v}\right)_s\right]_v$$

Maxwell relationships

Maxwell Relationship	Fundamental group
$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$	$\{u, s, v\}$
$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$	$\{h, s, p\}$
$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$	$\{a, T, v\}$
$-\left(\frac{\partial s}{\partial p}\right)_T = \left(\frac{\partial v}{\partial T}\right)_p$	$\{g, T, p\}$

Thermodynamic property relationships

These equations are called as Maxwell relationships. It is observed that in the last two Maxwell equations, the right-hand side is composed of only measured properties [12].

For derivation of these equations see class notes.

Other partial derivatives

Some other common thermodynamic properties in the form of which experimental thermodynamic data is usually reported are:

- Thermal expansion coefficient or isobaric volume expansivity (β)
- Isothermal compressibility (κ)
- Constant volume molar heat capacity (c_v)
- Constant pressure molar heat capacity (c_p)

Other partial derivatives

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \qquad c_v = \left(\frac{\partial u}{\partial T}\right)_v$$

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \qquad c_p = \left(\frac{\partial h}{\partial T}\right)_p$$

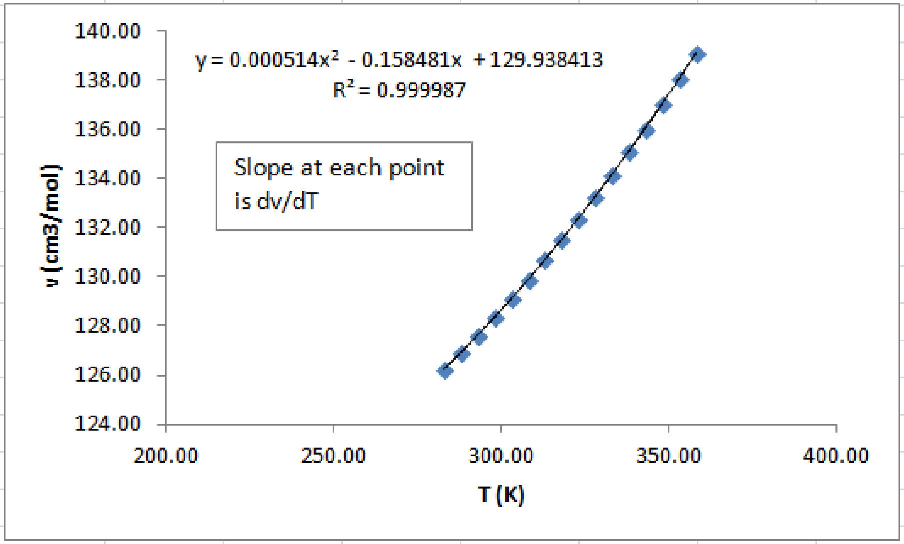
Why negative sign in the second equation?

Other partial derivatives

How can we measure β using experimental data of v and T? Below is example in Excel.

MCH			
Mol wt		98.186	g/mol

T	T	Density	Specific vol	Molar vol, v	dv/dT	Beta
oC	K	g/cm3	cm3/g	cm3/mol	cm3/K	(1/K)
10.00	283.15	0.78	1.29	126.22	0.13	0.00
15.00	288.15	0.77	1.29	126.93	0.14	0.00
20.00	293.15	0.77	1.30	127.65	0.14	0.00
25.00	298.15	0.76	1.31	128.38	0.15	0.00
30.00	303.15	0.76	1.32	129.13	0.15	0.00
35.00	308.15	0.76	1.32	129.89	0.16	0.00
40.00	313.15	0.75	1.33	130.69	0.16	0.00
45.00	318.15	0.75	1.34	131.52	0.17	0.00
50.00	323.15	0.74	1.35	132.37	0.17	0.00
55.00	328.15	0.74	1.36	133.25	0.18	0.00
60.00	333.15	0.73	1.37	134.15	0.18	0.00
65.00	338.15	0.73	1.38	135.09	0.19	0.00
70.00	343.15	0.72	1.39	136.04	0.19	0.00
75.00	348.15	0.72	1.40	137.03	0.20	0.00
80.00	353.15	0.71	1.41	138.04	0.20	0.00
85.00	358.15	0.71	1.42	139.10	0.21	0.00



Values of molar volume, expansion coefficient and compressibilty for various substances [12]

	v[cm^3/mol]	$\beta[K^{-1}] \times 10^3$	$\kappa[Pa^{-1}] \times 10^{10}$
Liquid			
Acetone	73.33	1.49	12.7
Benzene	86.89	1.24	9.4
Methanol	39.56	1.12	12.1
Ethanol	58.24	1.12	11.1
n-Hexane	130.77		15.5
Mercury	14.75	0.181	0.40
Solid			
Aluminum	9.96	0.0672	0.145
Copper	7.11	0.0486	0.091
Iron	7.10	0.035	0.048
Diamond	3.42	0.0036	0.010

Source: R. H. Perry, D. W. Green, and J. O. Maloney (eds.), *Perry's Chemical Engineers' Handbook*, 7th ed. (New York: McGraw-Hill, 1997); D. R. Lide, *CRC Handbook of Chemistry and Physics, 83rd ed.* (Boca Raton, FL: CRC Press, 2002–2003).

Example 4.11 [12]

Determine the molar volume of copper at 500 ^{o}C using expansion coefficient of copper. Volume of copper at 20 ^{o}C is given as 7.11 cm^3/mol. Assume expansion coefficient is constant in this range.

Other partial derivatives

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \longrightarrow \left(\frac{\partial v}{\partial T}\right)_p = \beta v$$

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \longrightarrow \left(\frac{\partial v}{\partial p}\right)_T = -v\kappa$$

Other partial derivatives

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \quad \Longrightarrow \quad \left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T}$$

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p \quad \Longrightarrow \quad \left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T}$$

Relationships of *ds*, *du*, and *dh*

Bring to mind steam table and other thermodynamic tables that contain the data of six thermodynamic properties including the data of s, h, and u. How are these tables developed where only p, T, and v are measurable? We need equations for ds, du, and dh in many of our thermodynamic calculations.

Relationship of *ds* in terms of *T* and *v*

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dT$$

$$ds = \frac{c_v}{T} dT + \left(\frac{\partial p}{\partial T}\right)_v dv$$

Integrating, one may have

$$\Delta s = \int \frac{c_v}{T} dT + \int \left(\frac{\partial p}{\partial T}\right)_v dv$$

Relationship of *ds* in terms of *T* and *v*

The second term in the equation on the previous slide can be solved by knowing experimental p and T values at constant v and thereby taking derivative of the fitted function. Moreover, a suitable pressure explicit equation of state that well describes the component in hand can be used after taking derivative with respect to T at constant v.

How can be this equation simplified for an ideal gas law?

Relationship of *ds* in terms of *T* and *p*

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$$

$$ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp$$

Integrating, one may have

$$\Delta s = \int \frac{c_p}{T} dT - \int \left(\frac{\partial v}{\partial T}\right)_p dp$$

Relationship of ds in terms of T and v

The second term in the equation on the previous slide can be solved by knowing experimental v and T values at constant p and thereby taking derivative of the fitted function. Moreover, a suitable volume explicit equation of state that well describes the component in hand can be used after taking derivative with respect to T at constant p.

How can be this equation simplified for an ideal gas law?

Homework problem

Find relationships of ds in terms of p and v.

Relationship of du in terms of T and v

$$du = c_v dT + \left(T\left(\frac{\partial p}{\partial T}\right)_v - p \right) dv$$

$$\Delta u = \int c_v dT - \int \left(T\left(\frac{\partial p}{\partial T}\right)_v - p \right) dv$$

$$c_v^{\text{real}} = c_v(T, v_1) = c_v^{\text{ideal gas}} + \int_{v_{\text{ideal gas}}}^{v_1} \left[T\left(\frac{\partial^2 P}{\partial T^2}\right)_v \right] \mathrm{d}v$$

Relationship of *dh* in terms of *T* and *p*

$$\mathrm{d}h = c_P \mathrm{d}T + \left[-T\left(\frac{\partial v}{\partial T}\right)_P + v \right]\mathrm{d}P$$

$$\Delta h = \int c_P \mathrm{d}T + \int \left[-T\left(\frac{\partial v}{\partial T}\right)_P + v \right]\mathrm{d}P$$

$$c_P^{\text{real}} = c_P(T, P) = c_P^{\text{ideal gas}} - \int_{P_{\text{ideal gas}}}^{P_{\text{real}}} \left[T\left(\frac{\partial^2 v}{\partial T^2}\right)_P \right]\mathrm{d}P$$

Class activity

Find relationships of dh in terms of T and v.

Example 5.2 [12]

One mole of propane gas is to be expanded from 0.001 m^3 to 0.040 m^3 while in contact with a heating bath that keeps the temperature constant at 100°C. The expansion is not reversible. The heat extracted from the bath is 10.4 kJ. Using the van der Waals equation of state, determine the work for the expansion.

van der Waals EoS

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \qquad a = \frac{27}{64}\frac{(RT_c)^2}{P_c} \qquad b = \frac{(RT_c)}{8P_c}$$

Cyclic rule

For any three properties x, y, and z, mathematically one can write (using cyclic rule)

$$-1 = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial z}{\partial y}\right)_x$$

So involving v, p, and T, it may be shown that

$$-1 = \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial T}{\partial p}\right)_v$$

Class activity

Prove cyclic rule for ideal gas law.

Example 5.4 [12]

The first step in manufacturing isobutane from isomerization of n-butane is to compress the feed stream of n-butane. It is fed into the compressor at 9.47 bar and 80 ^{o}C and optimally exists at 18.9 bar and 120 ^{o}C, so that it can be fed into the isomerization reactor. The work supplied to the compressor is 2100 J/mol. Calculate the heat that needs to be supplied into the unit per mole of n-butane that passes through. Use Redlich-Kwong equation of state.

Class activity: Problem 5.60 [12]

5.60 Gas A expands through an *adiabatic* turbine. The inlet stream flows in at 100 bar and 600 K while the outlet is at 20 bar and 445 K. Calculate the work produced by the turbine. The following data are available for gas A. The *ideal* gas heat capacity for this process is:

$$c_P = 30.0 + 0.02T$$

where c_P is in [J/(mol K)] and T is in [K]. PvT data has been fit to the following equation:

$$P(v - b) = RT + \frac{aP^2}{T}$$

where, $a = 0.001[(\text{m}^3\text{K})/(\text{bar mol})]$ and, $b = 8 \times 10^{-5}[\text{m}^3/\text{mol}]$

Homework: Problem 5.32 [12]

5.32 Propane at 350°C and 600 cm^3/mol is expanded in an isentropic turbine. The exhaust pressure is atmospheric. What is the exhaust temperature? PvT behavior has been fit to the van der Waals equation with:

$$a = 92 \times 10^5 \left[(\text{atm cm}^6)/\text{mol}^2\right]$$

$$b = 91 \left[\text{cm}^3/\text{mol}\right]$$

(a) Solve this problem using T and v as the independent properties, that is,

$$s = s(T, v)$$

(b) Solve this problem using T and P as the independent properties.

Alternate method for changes in enthalpy, entropy, and internal energy

Changes in enthalpy, entropy, and internal energy, etc., in terms of β and κ.

Alternate method for changes in enthalpy, entropy, and internal energy

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \longrightarrow \left(\frac{\partial v}{\partial T}\right)_p = \beta v$$

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \longrightarrow \left(\frac{\partial v}{\partial p}\right)_T = -v\kappa$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{\beta}{\kappa}$$

Relationship between isobaric volume expansivity and isothermal compressibilty

$$\boxed{\left(\frac{\partial p}{\partial T}\right)_v = \frac{\beta}{\kappa}} \qquad (1)$$

Eq. 1 can be proved by cyclic rule.

Using cyclic rule:

$$-1 = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial z}{\partial y}\right)_x \qquad (2)$$

So involving v, p, and T, it may be shown from Eq. 2 that

$$-1 = \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial T}{\partial p}\right)_v \qquad (3)$$

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \qquad (4)$$

Relationship between isobaric volume expansivity and isothermal compressibilty

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \qquad (5)$$

Dividing Eq. 4 by Eq. 5, it may be shown that

$$\frac{\beta}{\kappa} = -\frac{\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_T} \qquad (6)$$

$$\frac{\beta}{\kappa} = -\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial v}\right)_T \qquad (7)$$

Relationship between isobaric volume expansivity and isothermal compressibilty

From Eq. 3, it may be shown that

$$\frac{1}{\left(\frac{\partial T}{\partial p}\right)_v} = -\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T$$

Or

$$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T \qquad (8)$$

Comparing Eq. 7 and Eq. 8, Eq. 1 can be proved

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{\beta}{\kappa} \qquad (1)$$

Alternate method for changes in enthalpy, entropy, and internal energy

$$dh = (c_v + \frac{\beta v}{\kappa})dT + (\frac{\beta T}{\kappa} - \frac{1}{\kappa})dv$$

$$ds = \frac{c_p}{T}dT - \beta v dp$$

$$du = (c_p - \beta p v)dT + (\kappa p v - \beta v T)dp$$

Isobaric volume expansivity and isothermal compressibilty for an ideal gas

$$v = \frac{RT}{P}$$

$$\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{Pv} = \frac{1}{T} \qquad \text{(ideal gas)}$$

$$\kappa \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = \frac{RT}{P^2 v} = \frac{1}{P} \qquad \text{(ideal gas)}$$

Alternate method for changes in enthalpy, entropy, and internal energy for an ideal gas

Class activity

Changes in enthalpy, entropy, and internal energy in terms of β and κ for an ideal gas.

$\mathbf{c_p - c_v = ?}$

$$c_p - c_v = -T\left(\frac{\partial v}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial v}\right)_T$$

$$c_p - c_v = \frac{Tv\beta^2}{\kappa}$$

$$c_p - c_v = R\,(ideal\,gas)$$

$c_p - c_v = ?$

- As $\left(\frac{\partial v}{\partial T}\right)_p^2$ cannot be negative as squared and $\left(\frac{\partial p}{\partial v}\right)_T$ is negative so, c_p is either equal or greater than c_v, it cannot be less than c_v.
- At absolute zero, $T = 0$ K, $c_p = c_v$.
- For the component such as liquid water where density increases and then decreases with temperature, $\left(\frac{\partial v}{\partial T}\right)_p$ will be zero at the minima of volume (for water at 4°C density is the maximum at 1.0 bar), again $c_p = c_v$.

Joule-Thomson coefficient

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial P}\right)_h = \frac{\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right]}{c_p} = \frac{\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right]}{c_P^{\text{ideal gas}} - \int_{P_{\text{ideal gas}}}^{P_{\text{real}}} \left[T\left(\frac{\partial^2 v}{\partial T^2}\right)_P\right] \mathrm{d}P}$$

Use any suitable volume explicit EoS, if experimental *pvT* data is not available. You may use Virial EoS.

$$v = \frac{RT}{P}(1 + B'P)$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} \qquad (ideal\,gas)$$

$$\mu_{JT} = 0\,(ideal\,gas)$$

Homework: Modified example 5.9 [12]

Develop an expression for the Joule-Thomson coefficient using the pressure-based expansion of the virial equation of state truncated to the second virial coefficient. What is a pressure-explicit equation such as van der Waals equation of state is appropriate.

Departure functions

The departure function of any thermodynamic property is the difference between the real, physical state in which it exists and that of a hypothetical ideal gas at the same T and p. For example, the enthalpy departure is given by:

$$\Delta h_{T,\,P}^{\text{dep}} = h_{T,\,P} - h_{T,\,P}^{\text{ideal gas}}$$

Enthalpy departure function

The enthalpy departure is given by:

$$\Delta h_{T,\ P}^{\text{dep}} = h_{T,\ P} - h_{T,\ P}^{\text{ideal gas}}$$

$$\Delta h_{T,P}^{\text{dep}} = h_{T,P} - h_{T,P=0}^{\text{ideal gas}}$$

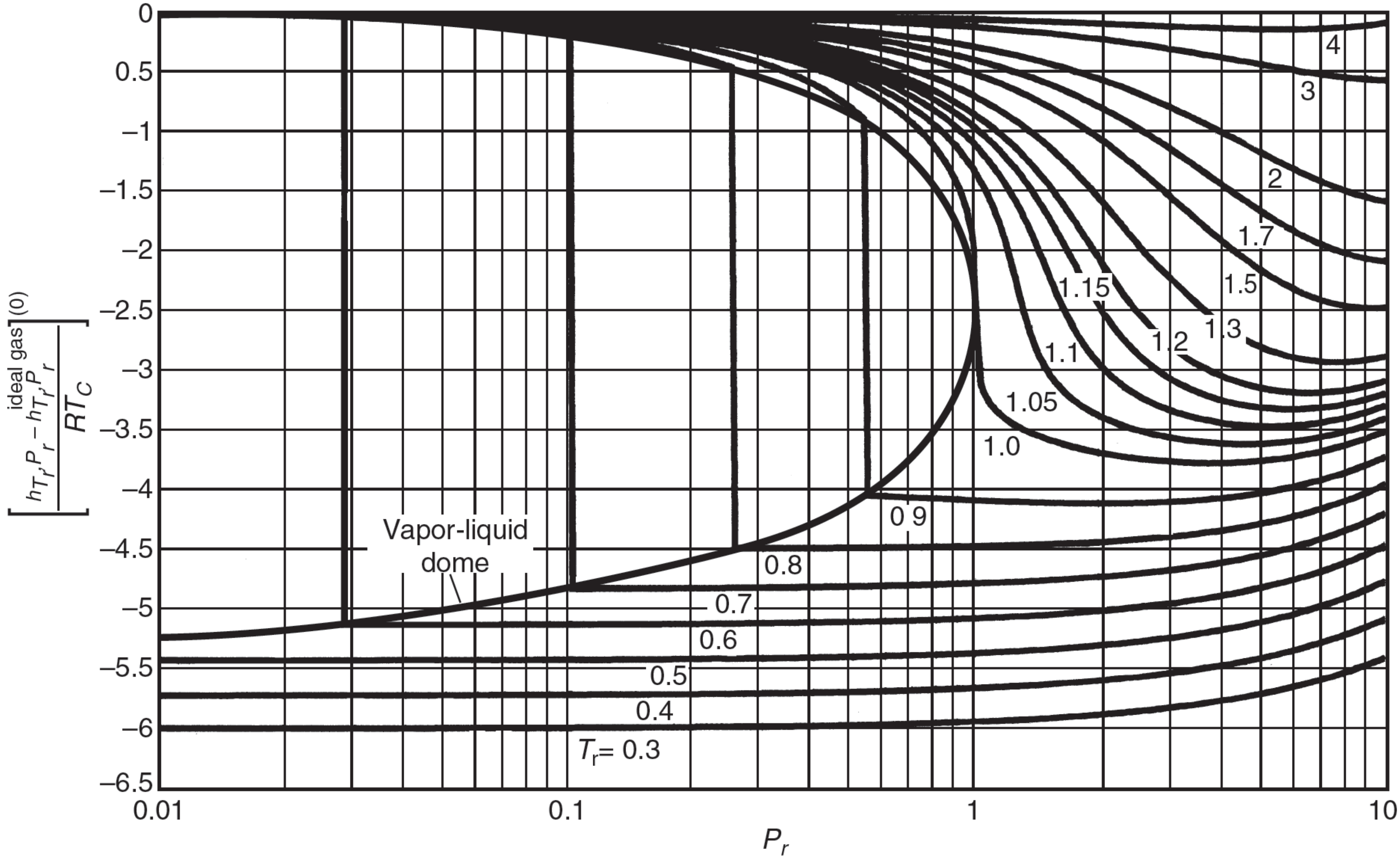
(As enthalpy of an ideal gas is independent of *p*)

Enthalpy departure function

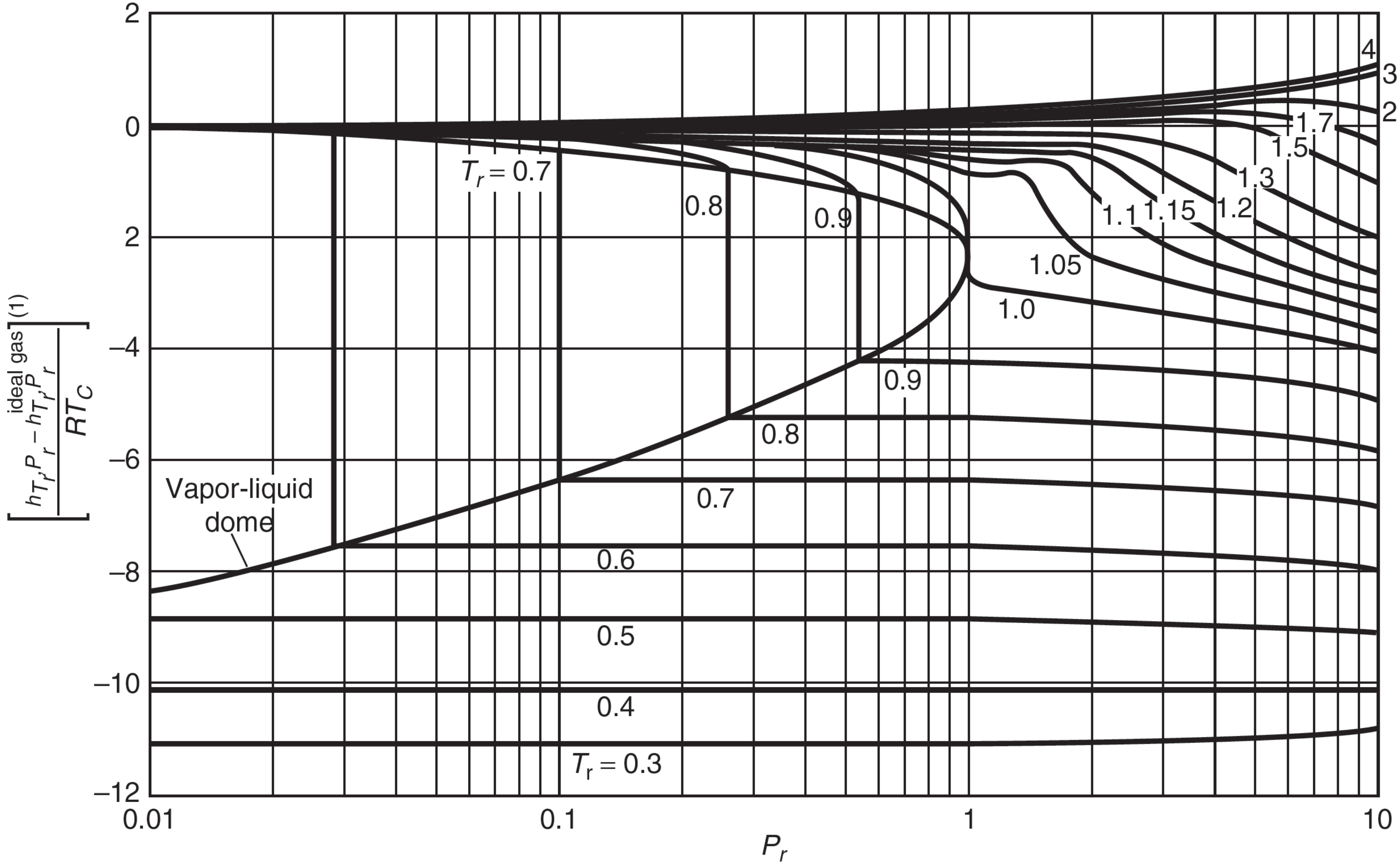
Develop expression for enthalpy departure function in terms of

$$pv = zRT$$

Enthalpy departure function [12]



Enthalpy departure function [12]



Entropy departure function

Entropy departure is given by:

$$\Delta s_{T,P}^{\text{dep}} = s_{T,P} - s_{T,P}^{\text{ideal gas}}$$

$$\Delta s_{T,P}^{\text{dep}} = s_{T,P} - s_{T,P}^{\text{ideal gas}} = \left(s_{T,P} - s_{T,P=0}^{\text{ideal gas}}\right) - \left(s_{T,P}^{\text{ideal gas}} - s_{T,P=0}^{\text{ideal gas}}\right)$$

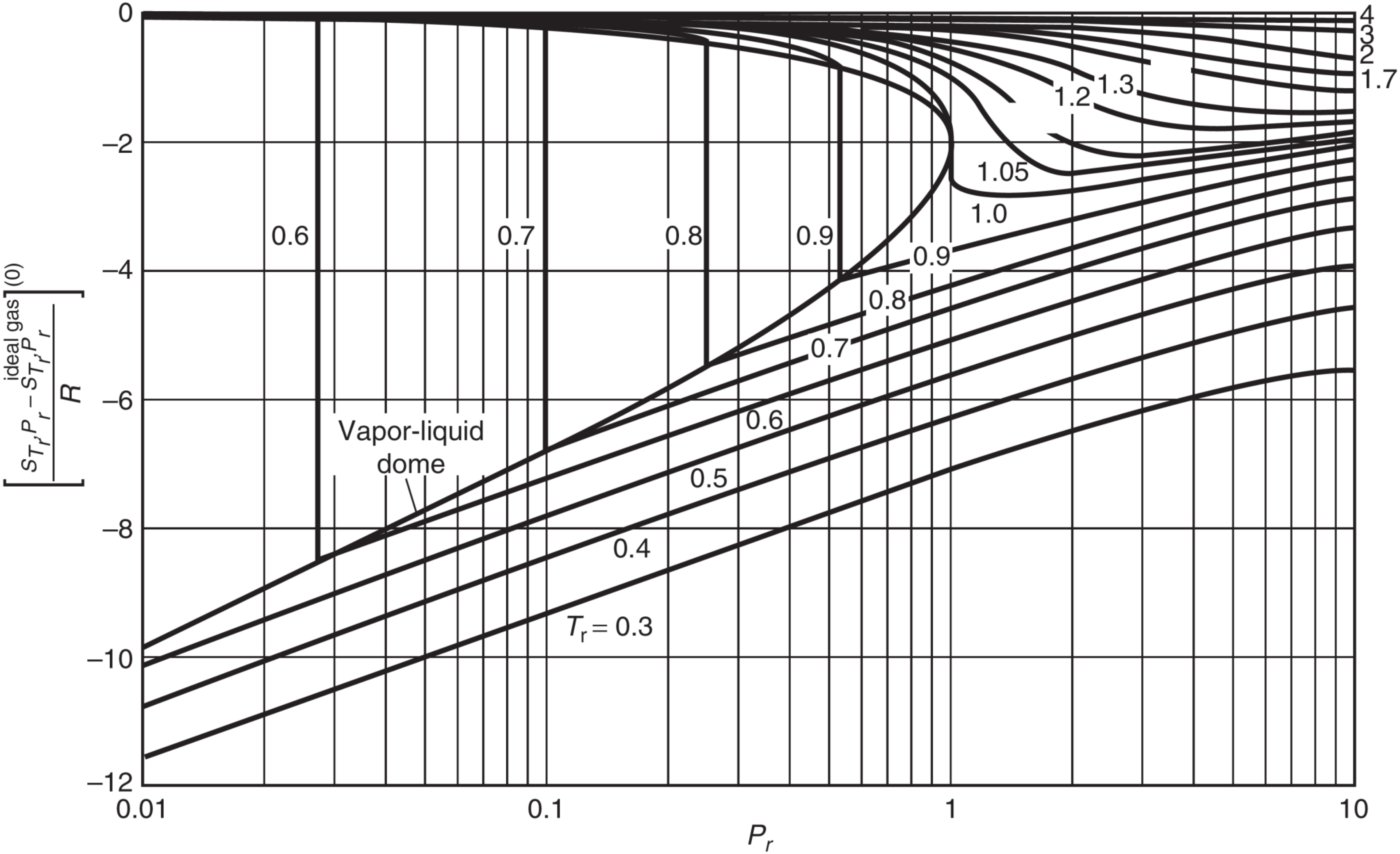
(As entropy of an ideal gas is not independent of p)

Entropy departure function

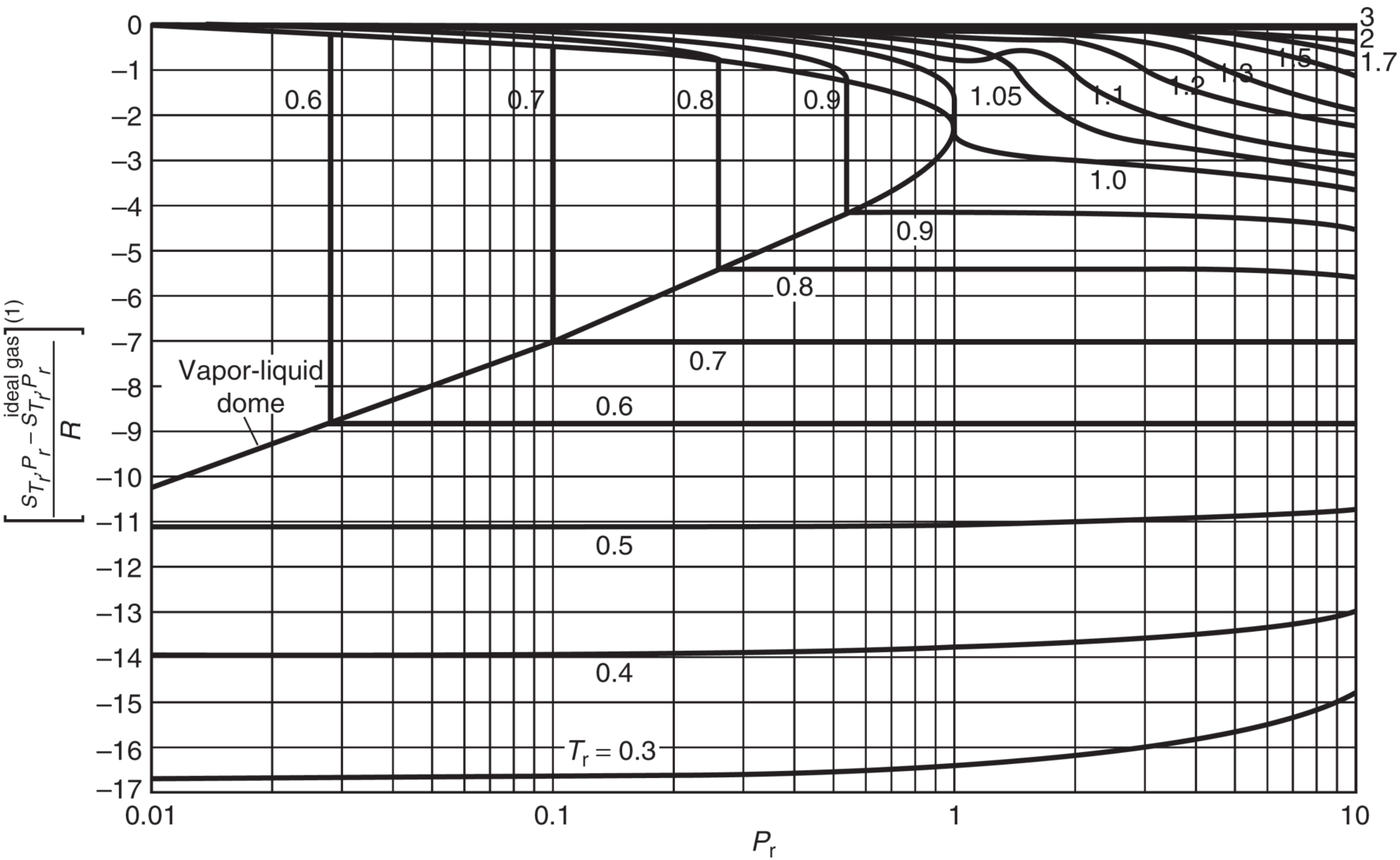
Develop expression for entropy departure function in terms of

$$pv = zRT$$

Entropy departure function [12]



Entropy departure function [12]



Other departure functions

$$(\Delta u)_{T,p}^{dep} = (\Delta h)_{T,p}^{dep} - p(\Delta v)_{T,p}^{dep}$$

$$(\Delta u)_{T,p}^{dep} = (u_{T,p} - u_{T,p}^{iG}) = (h_{T,p} - h_{T,p}^{iG}) - p(v_{T,p} - v_{T,p}^{iG})$$

Similarly,

$$(\Delta a)_{T,p}^{dep} = (a_{T,p} - a_{T,p}^{iG}) = (u_{T,p} - u_{T,p}^{iG}) - T(s_{T,p} - s_{T,p}^{iG})$$

$$(\Delta g)_{T,p}^{dep} = (g_{T,p} - g_{T,p}^{iG}) = (h_{T,p} - h_{T,p}^{iG}) - T(s_{T,p} - s_{T,p}^{iG})$$

Homework problems

- Develop expression for enthalpy departure function for a gas that obeys van der Waals equation of state.

- Develop expression for entropy departure function for a gas that obeys van der Waals equation of state.

- Determine enthalpy and entropy departure functions for n-heptane at 500 K and 2.0 bar. Assume van der Waals equation is applicable in this region.

- Example 5.7 [12]

Practice problems

Text Book

Koretsky, M.D. 2013. Engineering and chemical thermodynamics. 2nd ed. John Wiley & Sons, Inc.

Problems

5.20, 5.26, 5.32, 5.34, 5.45, 5.46, 5.48, 5.49, 5.50, and 5.51.

Thermodynamics of mixtures

For a two-component system, when composition of the system is changing, i.e., when moles of one or more components are changing, then for *i*th number of components, one can write

$U = f(S, V, n_1, n_2)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_1,n_2} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_1,n_2} dV + \left(\frac{\partial U}{\partial n_1}\right)_{S,V,n_2} dn_1 + \left(\frac{\partial U}{\partial n_2}\right)_{S,V,n_1} dn_2$$

From fundamental equation for constant n_1 and n_2, $dU = TdS - pdV$, it may shown that

$$dU = TdS - pdV + \mu_1 dn_1 + \mu_2 dn_2$$

$$\mu_1 = \left(\frac{\partial U}{\partial n_1}\right)_{S,V,n_2}, \quad \mu_2 = \left(\frac{\partial U}{\partial n_2}\right)_{S,V,n_1}$$

Thermodynamics of mixtures [14]

For *i*th number of components

$U = f(S, V, n_1, n_2, \ldots, n_i)$

$$dU = TdS - pdV + \sum \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} dn_i$$

$$dH = Vdp + TdS + \sum \left(\frac{\partial H}{\partial n_i} \right)_{p,S,n_j} dn_i$$

$$dA = -SdT - pdV + \sum \left(\frac{\partial A}{\partial n_i} \right)_{T,V,n_j} dn_i$$

$$dG = Vdp - SdT + \sum \left(\frac{\partial G}{\partial n_i} \right)_{p,T,n_j} dn_i$$

Thermodynamics of mixtures

$$dU = TdS - pdV + \sum \mu_i dn_i$$

$$dH = Vdp + TdS + \sum \mu_i dn_i$$

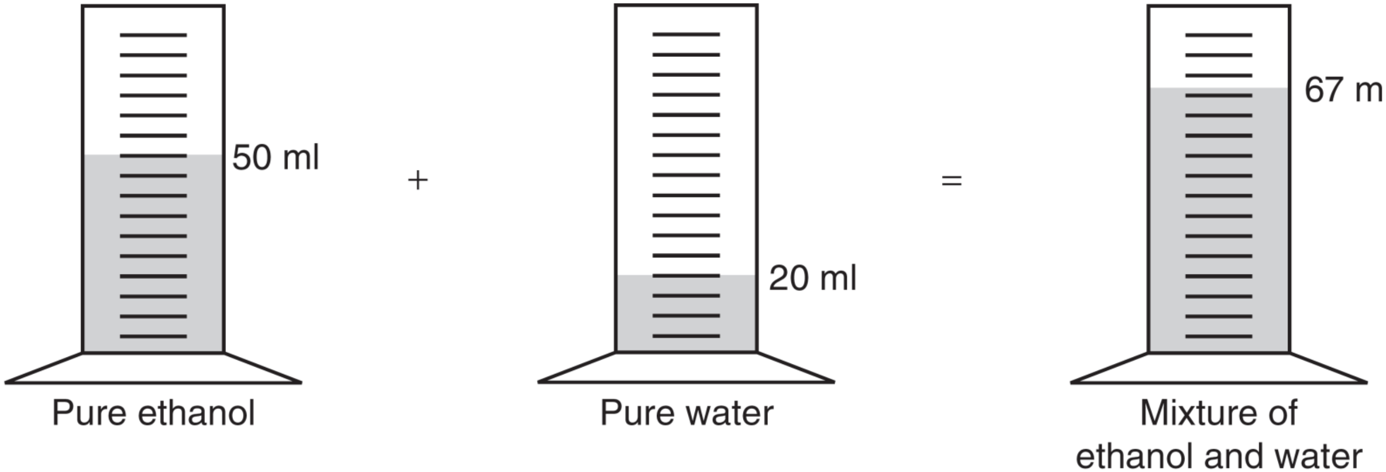
$$dA = -SdT - pdV + \sum \mu_i dn_i$$

$$dG = Vdp - SdT + \sum \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{p,S,n_j} = \left(\frac{\partial A}{\partial n_2}\right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_j}$$

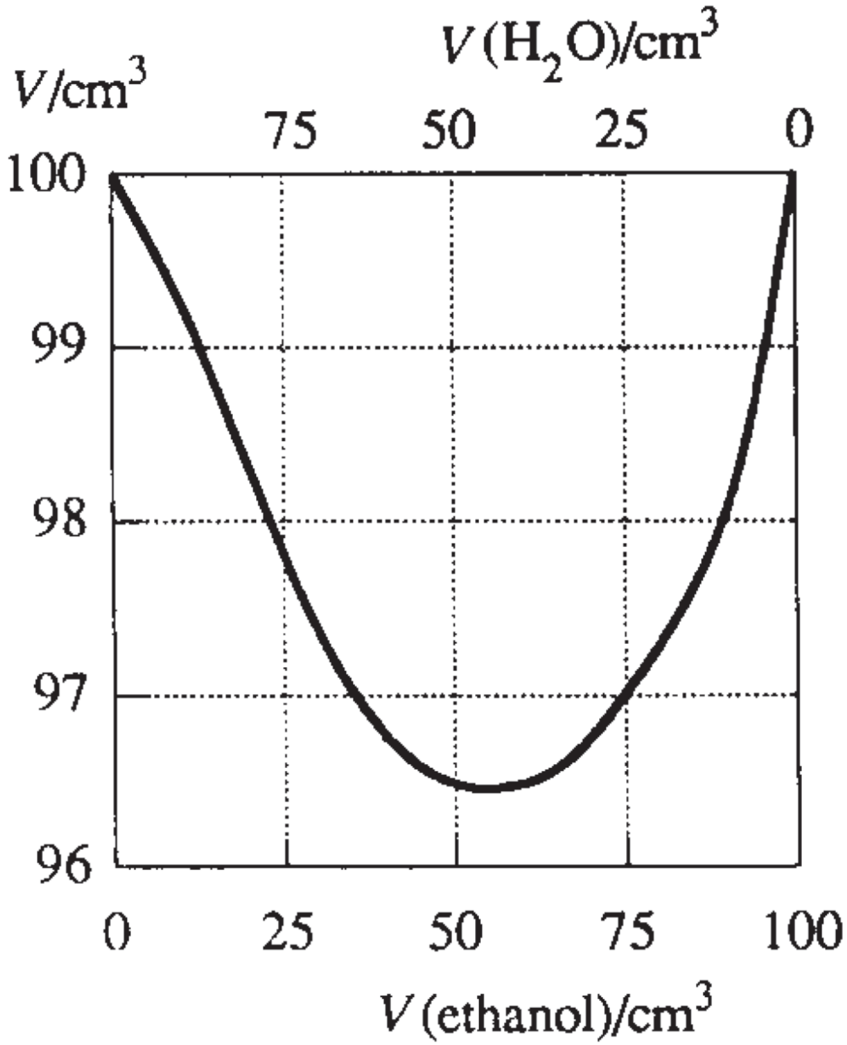
Thermodynamics of mixtures [12]

Where has the other 3.0 mL gone?



"When a species becomes part of a mixture, it losses its identity; yet it still contributes to the properties of the mixture, since the total solution properties of the mixture depend on the amount present of each species and its resultant interactions."

Thermodynamics of mixtures [15]



Volume V of a solution formed by mixing a volume $V_{ethanol}$ of pure ethanol with a volume ($100\ cm^3 - V_{ethanol}$) of pure water at 20°C and 1 atm.

Partial molar properties

A partial molar property, say, $\overline{K}_i$ is equal to the change in the extensive property K of the solution with change (infinitesimal) in number of moles of species i when temperature, pressure, and number of moles of all the other species are held constant. It is itself an intensive property.

$$\overline{K}_i \equiv \left(\frac{\partial K}{\partial n_i}\right)_{T,P,n_{j \neq 1}}$$

always in terms of n_i never x_i

always hold the intensive properties P and T constant

the number of moles of all other species except i are held constant

Partial molar properties

A partial molar property is a measure of the contribution of a component towards that extensive property of the solution.

Examples are partial molar volume and partial molar enthalpy. Similarly, other partial molar properties can be defined.

$$\overline{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq 1}}$$

$$\overline{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq 1}}$$

Partial molar properties [16]

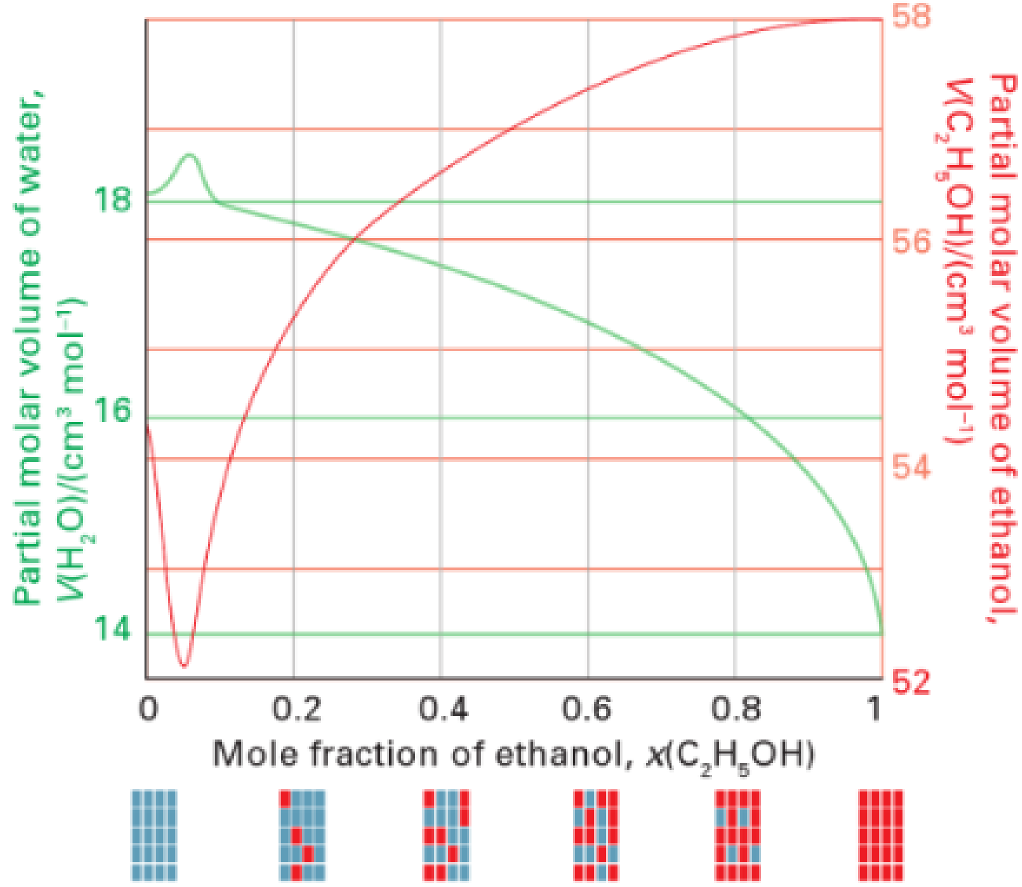


Fig. 6.1 The partial molar volumes of water and ethanol at 25 °C. Note the different scales (water on the left, ethanol on the right).

Partial molar properties

For a total change in property, K, of a mixture:

$$dK = \left(\frac{\partial K}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial K}{\partial P}\right)_{T,n_i} dP + \sum_{i=1}^{m} \overline{K}_i dn_i$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n_i} dP + \sum_{i=1}^{m} \overline{V}_i dn_i$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial H}{\partial P}\right)_{T,n_i} dP + \sum_{i=1}^{m} \overline{H}_i dn_i$$

Partial molar properties

For a total change in property, K, of a mixture at constant T and p:

$$dK = \sum \overline{K}_i dn_i$$

Upon integration,

$$K = \sum n_i \overline{K}_i \longrightarrow$$

$$V = \sum n_i \overline{V}_i$$

$$H = \sum n_i \overline{H}_i$$

$$k = \frac{K}{n_{\text{total}}} = \sum x_i \overline{K}_i \longrightarrow$$

$$v = \sum x_i \overline{V}_i$$

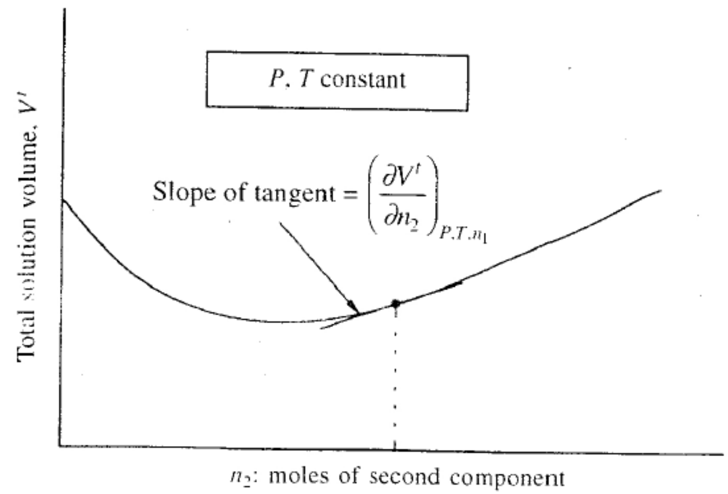
$$h = \sum x_i \overline{H}_i$$

k is intensive property

Measurement of partial molar properties [17]

If an analytical equation is available between an extensive property such as V of solution and moles of component i at constant T , p, and n_j, then partial molar volume can be obtained by taking the following derivative at any required number of moles.

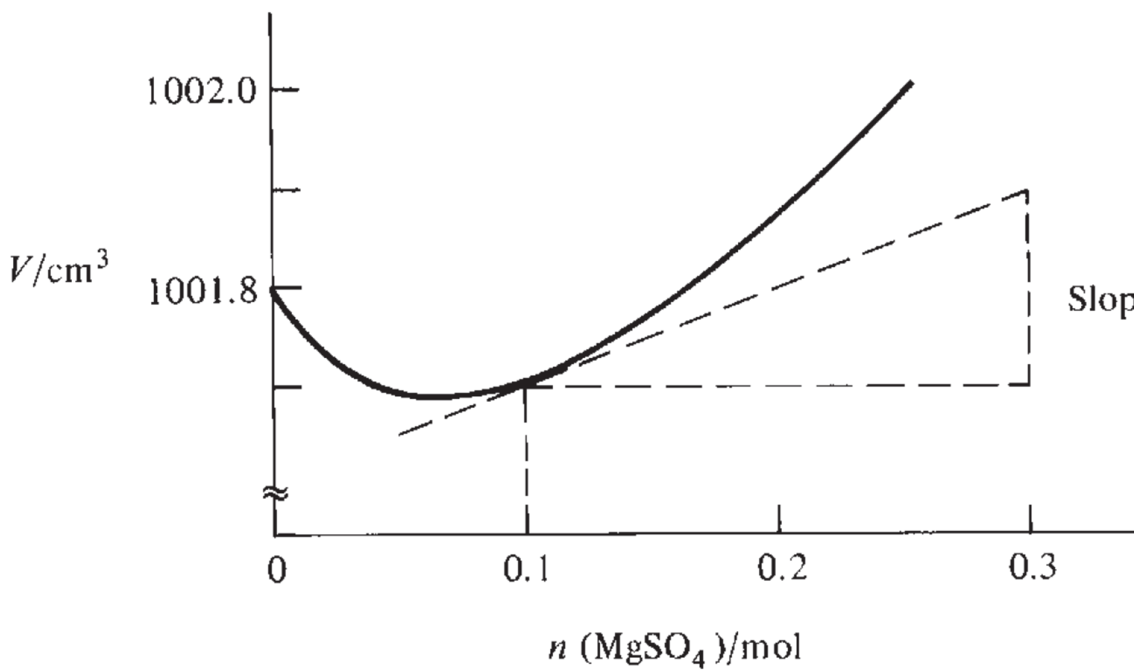
$$\overline{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_j}$$



The same can be obtained by plotting V and n_i and taking slope at required number of moles.

Measurement of partial molar properties [15]

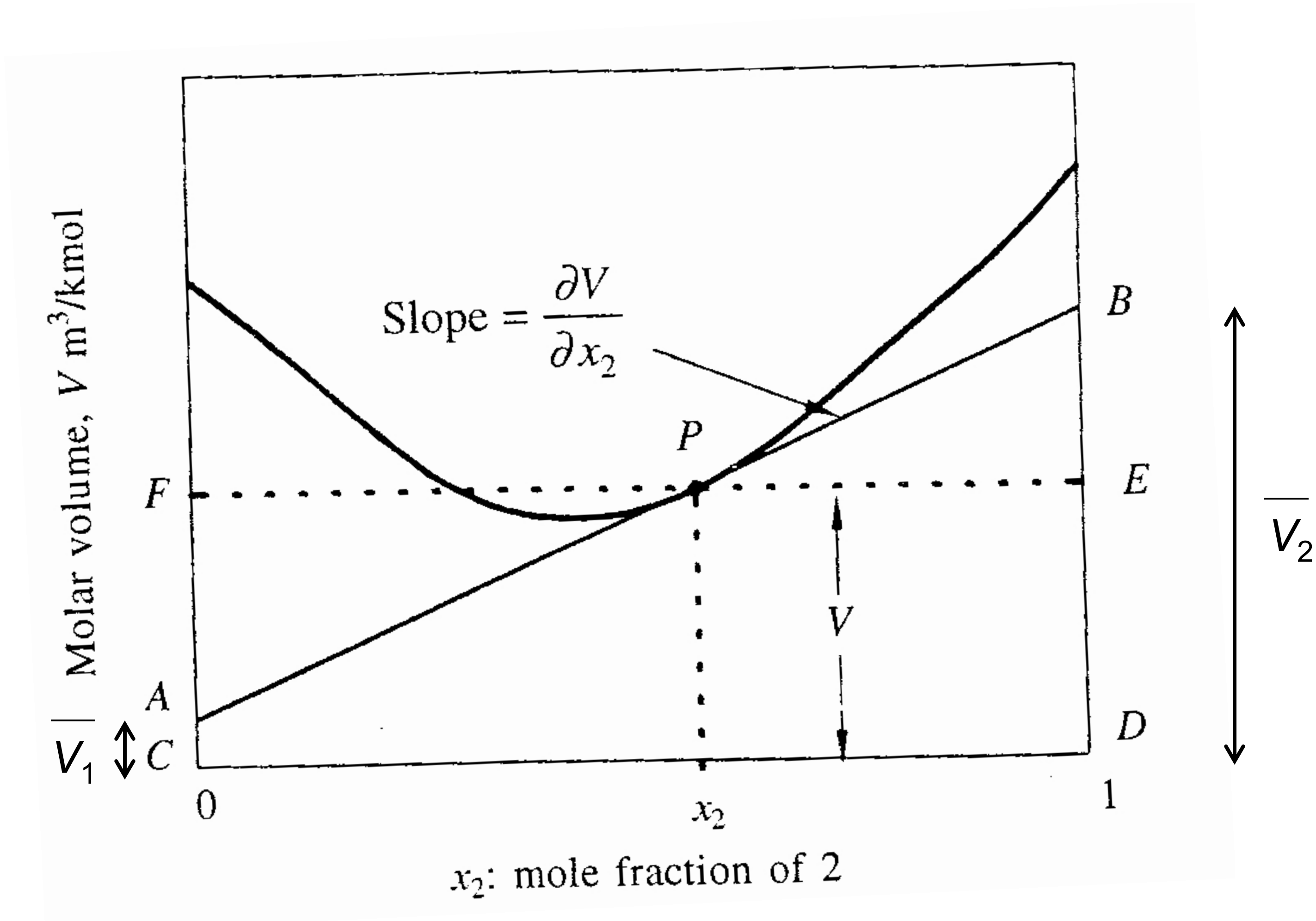
Volumes at 20°C and 1 atm of solutions containing 1000 g of water and n moles of $MgSO_4$. The dashed lines are used to find that $\bar{V}_{MgSO_4}$ = 1.0 cm^3/mol at molality 0.1 mol/kg.



$$\text{Slope} = \frac{(1001.90 - 1001.70)\ \text{cm}^3}{(0.30 - 0.10)\ \text{mol}} = 1.0\ \text{cm}^3/\text{mol}$$

Measurement of partial molar properties [17]

Alternately, tangent-slope method can be applied as shown below:



Partial molar properties using EoS

Use virial equation of state to workout the expression for partial molar volume.

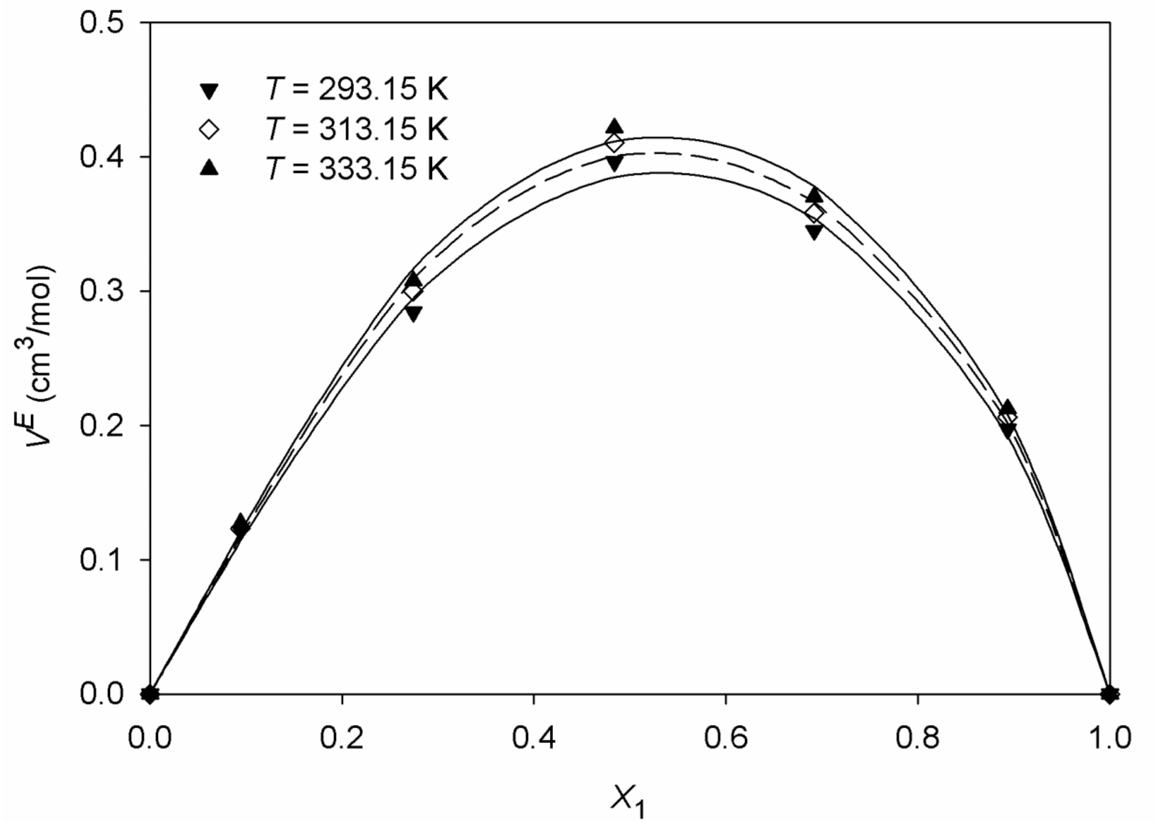
Excess properties

For liquid solutions, excess properties such as excess volume can be defined, where excess volume (V^E) is the difference between the actual volume (V) of the mixture at a fixed T, p, and composition (Xi) and the ideal solution volume (V^{iD}) at the same conditions.

$$V^E = V - V^{iD}$$

$$V^E = \frac{\sum_{i=1}^{i=N} (X_i M_i)}{\rho} - \sum_{i=1}^{i=N} \left(\frac{X_i M_i}{\rho_i} \right)$$

Excess properties



Excess molar volumes of methylcyclohexane (1) + toluene binary system at various temperatures. The solid curves are based on Redlich-Kister fitting.

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