Thermodynamics II

Vapor/Liquid Equilibrium: Introduction

Chapter 10

Phase equilibrium

- Applications:
  - Distillation, absorption, and extraction bring phases of different composition into contact.
- Both the extent of change and the rate of transfer depend on the departure of the system from equilibrium.
- Quantitative treatment of mass transfer the equilibrium T, P, and phase compositions must be known.

The nature of equilibrium

- Equilibrium: a static condition in which no changes occur in the macroscopic properties of a system with time and phase space.
- At the microscopic level, conditions are not static:
  - Molecules with sufficiently high velocities near the interface overcome surface forces and pass into the other phase.
  - However, the average rate of passage of molecules is the same in both directions, and no net interphase transfer of material occurs.
- An isolated system consisting of liquid and vapor phases in intimate contact eventually reaches a final state wherein no tendency exists for change to occur within the system.
  - Fixed temperature, pressure, and phase composition

Phase rule vs. Duhem's theorem

Gibbs phase rule (intensive properties) :

- For any system at equilibrium, the number of independent variables that must be arbitrarily fixed to establish its *intensive* state is given by J.W. Gibbs (1875).
- The degrees of freedom of the nonreacting systems:

$$\boxed{F = 2 - \pi + N}$$

  - where π is the number of phases, N is the number of chemical species
- A phase is a homogeneous region of matter. A gas or a mixture of gases, a liquid or a liquid solution, and a crystalline solid are examples of phases. Various phases can coexist, but they must be in equilibrium for the phase rule to apply.
- The minimum number of degrees of freedom for any system is zero:

$$\boxed{F = 2 - \pi + N = 0}$$

  - $N = 1$, $\pi = 3$ (i.e. the triple point)

Phase rule vs. Duhem’s theorem

Gibbs phase rule (intensive properties) :

Example 2.5. How many degrees of freedom has each of the following systems:

(1) Liquid water in equilibrium with its vapor.

(2) Liquid water in equilibrium with a mixture of water vapor and nitrogen.

(3) A liquid solution of alcohol in water in equilibrium with its vapor.

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(1) 1 species, 2 phases

$$F = 2 - \pi + N = 2 - 2 + 1 = 1 \rightarrow$$

You can specify just one intensive property and other intensive properties can be found

(2) 2 species, 2 phases

$$F = 2 - \pi + N = 2 - 2 + 2 = 2 \rightarrow$$

You can specify just two intensive property and other intensive properties can be found

(3) 2 species, 2 phases

$$F = 2 - \pi + N = 2 - 2 + 2 = 2 \rightarrow$$

You can specify just two intensive property and other intensive properties can be found

Phase rule vs. Duhem's theorem

Proof of Gibbs phase rule (intensive properties) :

- F ≡ Degrees of Freedom
- F= total # of intensive variables – Total # of independent equations
- Total # of intensive variables for a system of N chemical species and π phases at constant T and P is:
    - 2 : T and P intensive variables
    - (N-1)π : N-1 mole fractions in each phase since $\sum_{i=1}^{N} x_i = 1$

$$\boxed{\text{Total \# of intensive variables} = 2 + (N-1)\pi}$$

- Total # of independent equations≡ equations characterized equilibrium for each species between π phases (for example, Rault's law) is: $\boxed{\text{\# of independent equations} = N(\pi-1)}$

$$\boxed{\therefore F = 2 + (N-1)(\pi) - (\pi-1)(N)} \rightarrow \boxed{F = 2 - \pi + N}$$ **Gibbs's rule**

Phase rule vs. Duhem's theorem

Duhem's rule (intensive and extensive properties) :

- The state of a system described by Duhem's rules is said to be ***completely determined*** since it considers extensive as well as the intensive properties of the system.

- Total # of intensive and extensive variables for a system of N chemical species and π phases at constant T and P are:
  - 2 : T and P intensive variables
  - $(N-1)\pi$: N-1 mole fractions in each phase
  - π: total masses or moles of each phase

$$\boxed{\text{Total \# of variables} = 2 + (N-1)\pi + \pi}$$

Phase rule vs. Duhem's theorem

Duhem's rule (intensive and extensive properties) :

- Total # of independent equations:
  - N(π-1) equilibrium equations for each species between π
  - N material balance equations for N chemical species

$$\boxed{\text{\# of independent equations} = N(\pi-1)+N}$$

Duhem's rule

$$\boxed{\therefore F = \left[2 + (\mathrm{N}\text{-}1)\pi + \pi\right] - \left[(\pi-1)(N) + N\right]} \rightarrow \boxed{F = 2}$$

- Two ? When Gibbs phase rule F = 1, at least one (2-1) of the two variables must be extensive, and when Gibbs F = 0, both (2-0) must be extensive.
- **Duhem's theorem**: "for any closed system formed initially from given masses of prescribed chemical species, the equilibrium state is completely determined when any two independent (extensive or intensive) variables are fixed."

VLE: qualitative behavior

- When two chemical species:
  - phase rule: $F = 4 - \pi$
  - the maximum value of $F = 3$ $(\pi = 1)$, namely, P, T, and one mole fraction. All equilibrium states of the system can be represented in three-dimensional P-T-composition space.

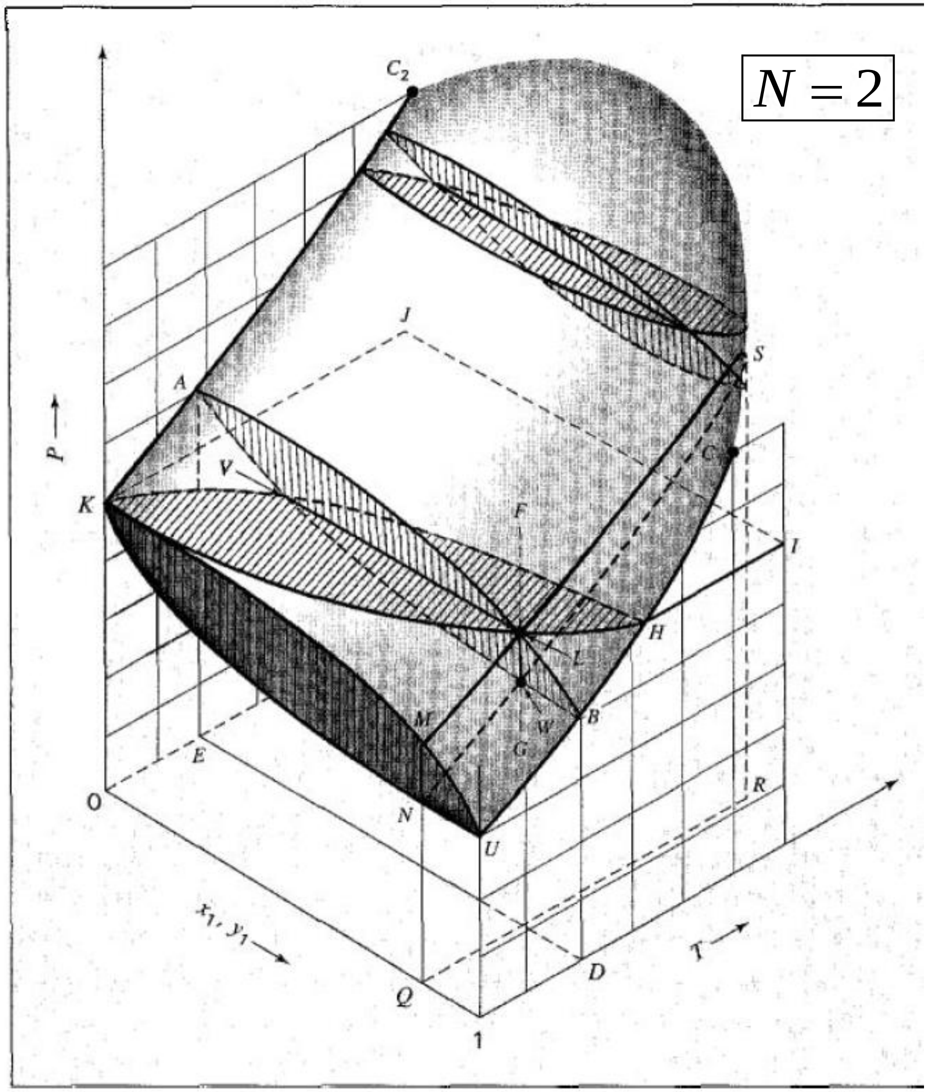


Figure 10.1 $PTxy$ diagram for vapor/liquid equilibrium

VLE: qualitative behavior

- Within this space, the states of pairs of phases coexisting at equilibrium define surfaces.
  - The subcooled-liquid region lies above the upper surface; the superheated-vapor region lies below the under surface.
  - $UBHC_1$ and KAC_2 represent the vapor pressure-vs.-T curves for pure species 1 and 2.
  - C_1 and C_2 are the critical points of pure species 1 and 2.
  - L is a bubble point and the upper surface is the bubblepoint surface.
  - Line VL is an example of a tie line, which connects points representing phases in equilibrium.
  - W is a dewpoint and the lower surface is the dewpoint surface.
- *Pxy* diagram at constant T. See for example Fig. 10.8
- *Txy* diagram at constant P. See for example Fig. 10.9
- *PT* diagram at constant composition

VLE: qualitative behavior

- Fig 10.8 (a)(b), Negative departures from P-x_1 linearity: strong liquid-phase inter-molecular attractions between unlike than between like pairs of molecules.
- Fig 10.8 (c)(d), Positive departures from P-x_1 linearity: strong liquid-phase inter-molecular attractions between like than between unlike pairs of molecules.
- Fig 10.8 (b)(d), the “azeotrope”: the point where $x_1 = y_1$ the dewpoint and bubblepoint curves are tangent to the same horizontal line. The liquid does not change in composition as it evaporates. No separation of such a constant-boiling solution is possible by distillation.

VLE: qualitative behavior

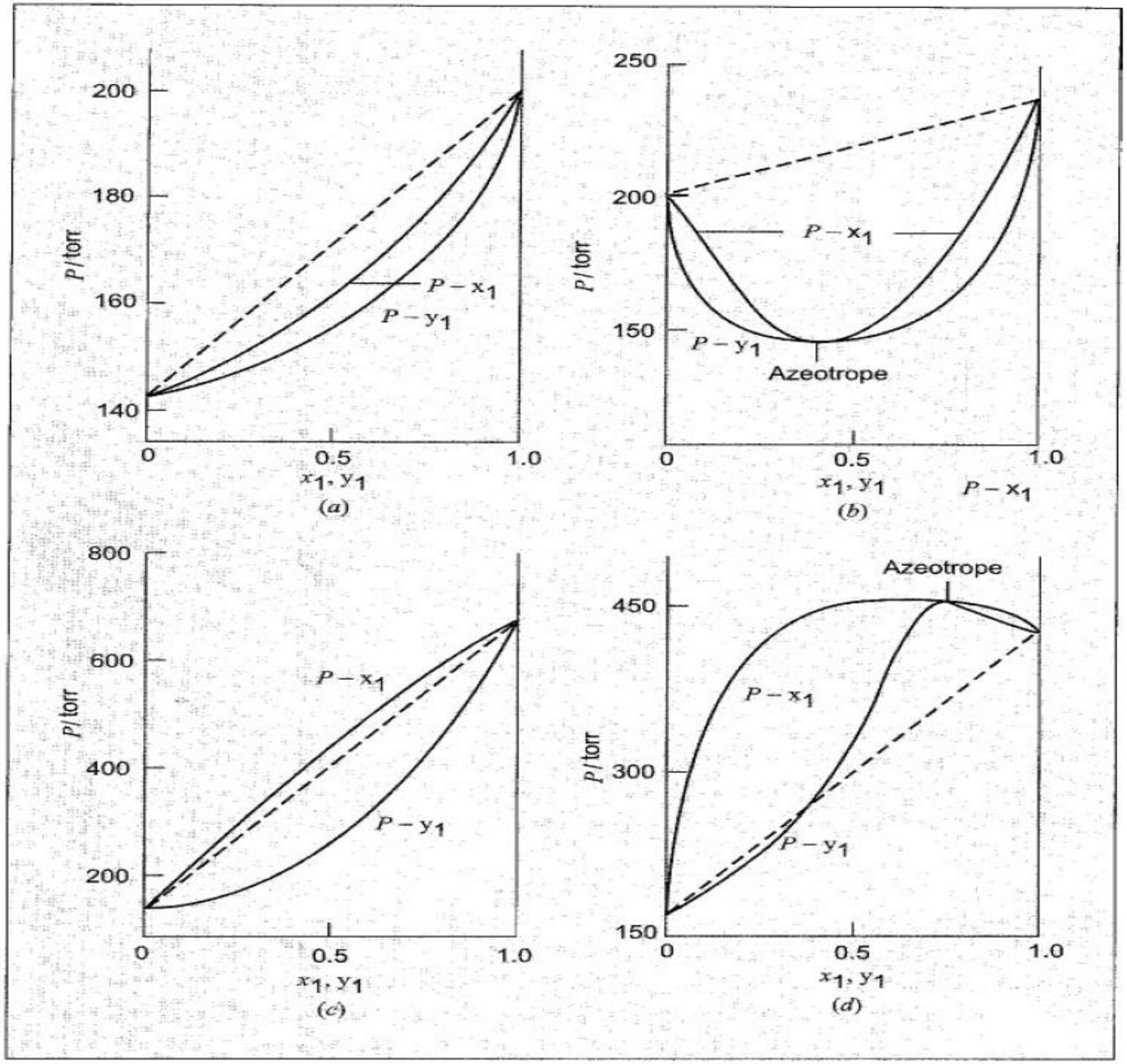


Figure 10.8 *Pxy* diagrams at constant *T*. (a) Tetrahydrofuran(1)/carbon tetrachloride(2) at 303.15 K (30°C); (b) chloroform(1)/tetrahydrofuran(2) at 303.15 K (30°C) (*c*) furan(1)/carbon tetrachloride(2) at 303.15 K (30°C); (*d*) ethanol(1)/toluene(2) at 338.15 K (65°C). Dashed lines: ***Px*** relation for ideal liquid solutions (Raoult's law)

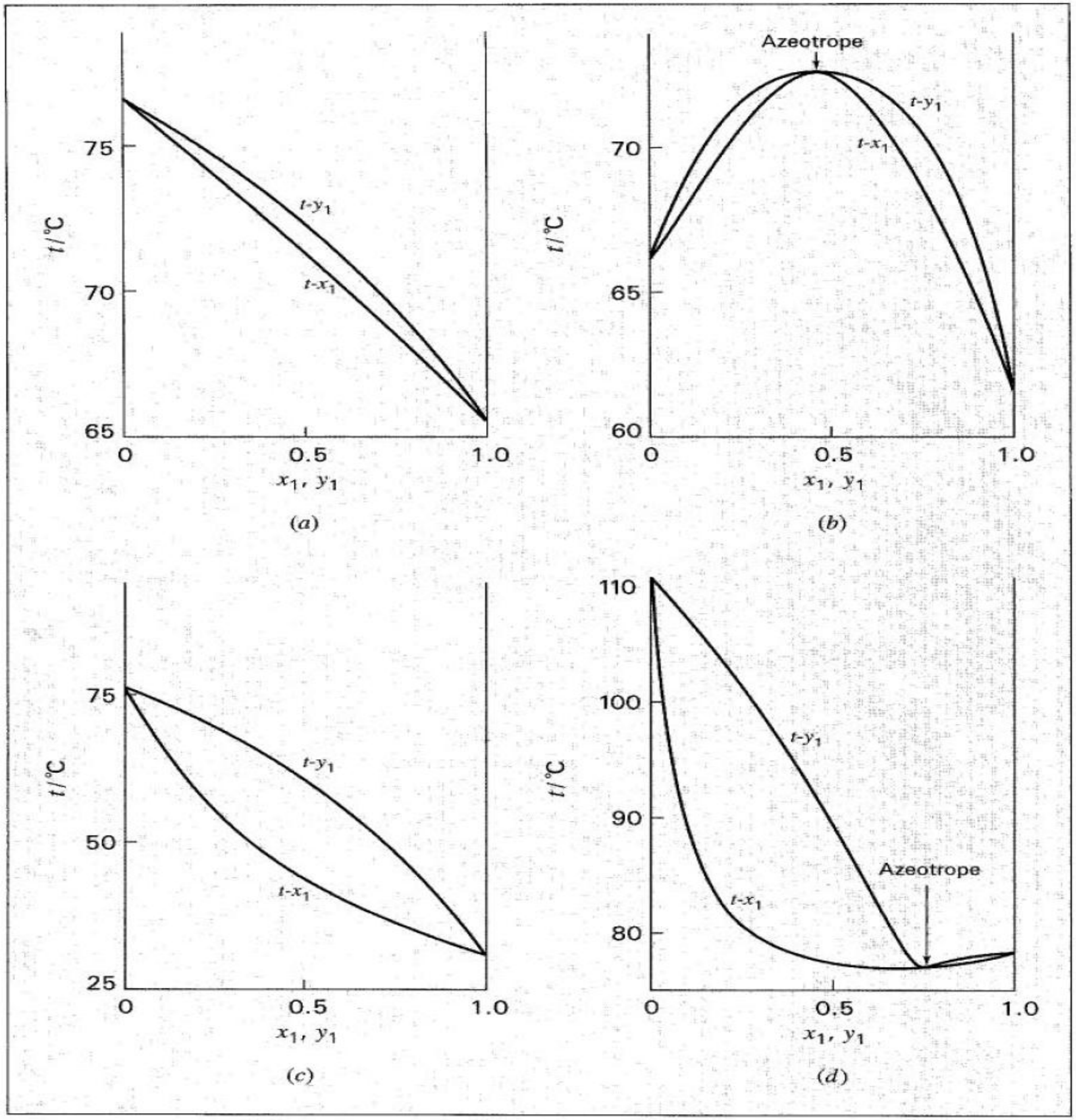


Figure 10.9 *txy* diagrams at 1 atm: (a) tetrahydrofuran(1)/carbon tetrachloride(2); *(b)* chloroform(1)/tetrahydrofuran(2); (c) furan(1)/carbon tetrachloride(2); *(d)* ethanol(1)/ toluene(2)

VLE: qualitative behavior

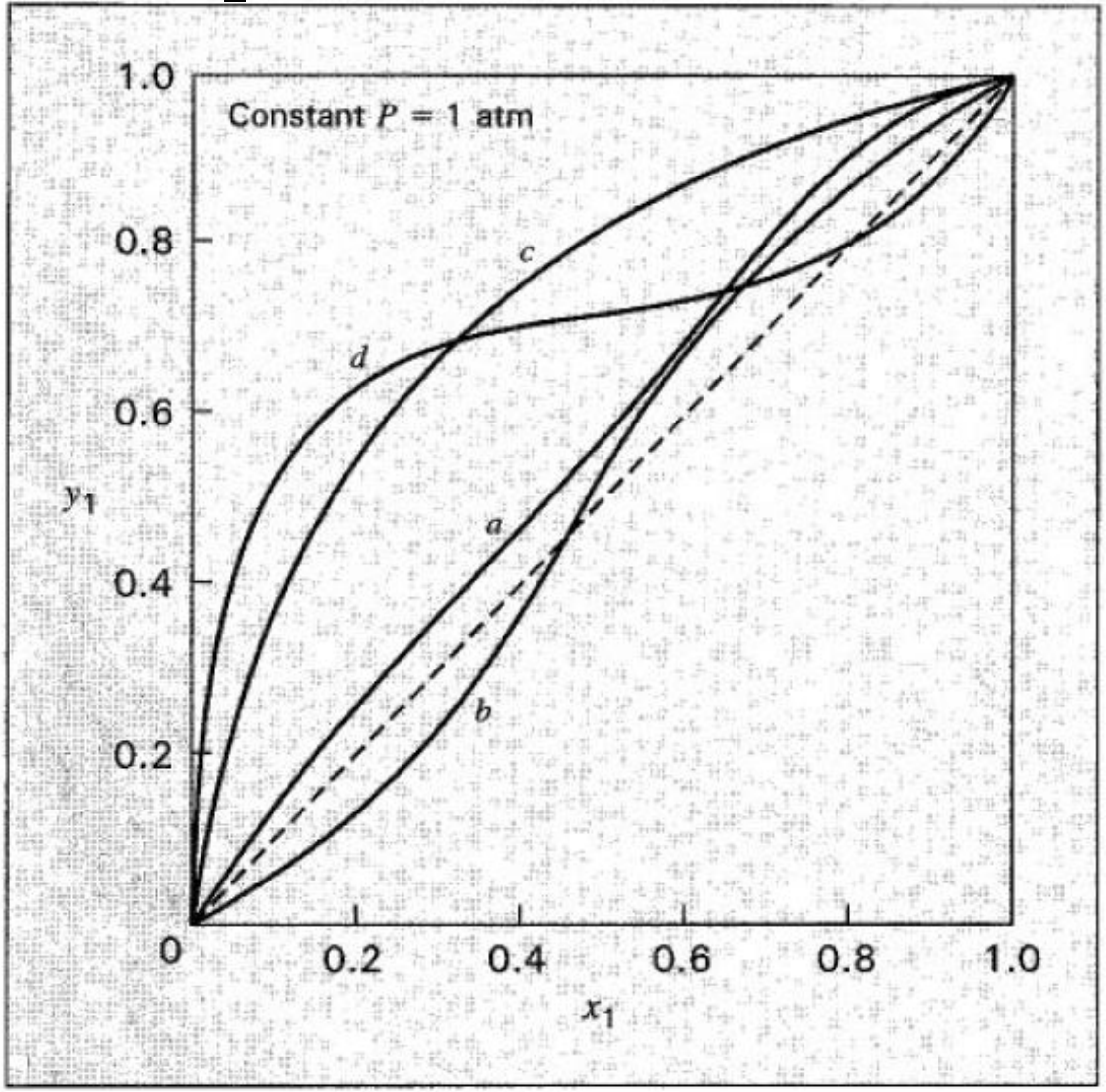


Figure 10.10 yx diagrams at 1 atm: (a) tetrahydrofuran(1)/carbon tetrachloride(2); (b) chloroform(1)/tetrahydrofuran(2); (c) furan(1)/carbon tetrachloride(2); *(d)* ethanol(1)/toluene(2)

Simple models for VLE

- The simplest are Raoult's law and Henry's law.
- Raoult's law:
  - the vapor phase is an ideal gas (apply for low to moderate pressure)
- the liquid phase is an ideal solution (apply when the species that are chemically similar; Examples: n-hexaneln-heptane, ethanol/propanol, and benzene/toluene, acetone/acetonitrile and acetonitrile/nitromethane.

  - $\boxed{y_i P = x_i P_i^{sat} \quad (i = 1, 2, \ldots, N)}$ **Raoult's law**
    - although it provides a realistic description of actual behavior for a small class of systems, it is valid for any species present at a mole fraction approaching unity, provided that the vapor phase is an ideal gas.

Dewpoint and bubble point Calculations

BUBL P: Calculate ***{yi) and P, given {xi} and T***

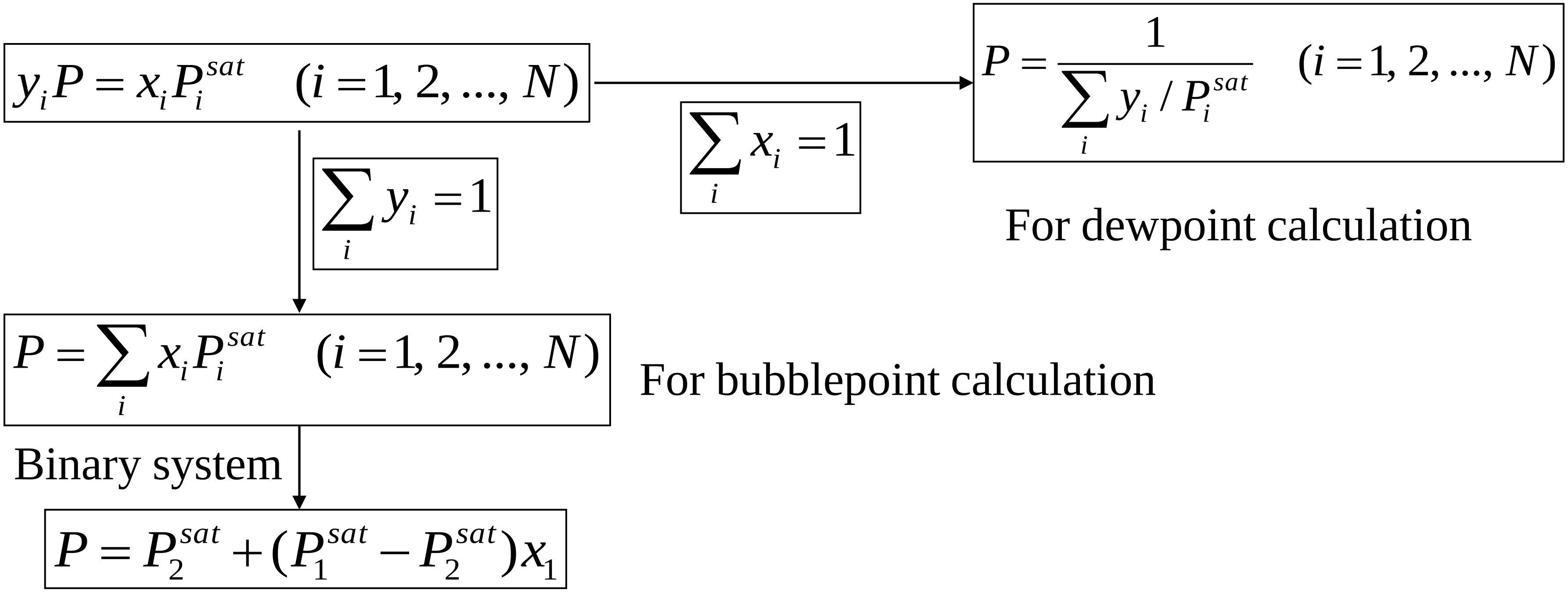
DEW P: Calculate ***{xi} and P, given {yi} and T***

BUBL T: Calculate ***{yi} and T, given {x_i} and P***

DEW T: Calculate ***{xi} and T, given {yi} and P***

Flash Caluations: Calculate ***{xi} and {yi}, given T, P*****, and** ***{zi}***.

Dewpoint and bubble point Calculations



$$\boxed{y_i P = x_i P_i^{sat} \quad (i = 1, 2, \ldots, N)}$$

$$\boxed{\sum_i x_i = 1}$$

$$\boxed{P = \frac{1}{\sum_i y_i / P_i^{sat}} \quad (i = 1, 2, \ldots, N)}$$

For dewpoint calculation

$$\boxed{\sum_i y_i = 1}$$

$$\boxed{P = \sum_i x_i P_i^{sat} \quad (i = 1, 2, \ldots, N)}$$

For bubblepoint calculation

Binary system

$$\boxed{P = P_2^{sat} + (P_1^{sat} - P_2^{sat}) x_1}$$

Dewpoint and bubble point Calculations

Example 10.1

Binary system acetonitrile (1)/nitromethane(2) conforms closely to Raoult’s law. Vapor pressures for the pure species are given by the following Antoine equations:

$$\boxed{\ln P_1^{sat}/kPa = 14.2724 - \frac{2945.47}{t/^\circ C + 224.00}} \quad \boxed{\ln P_2^{sat}/kPa = 14.2043 - \frac{2972.64}{t/^\circ C + 209.00}}$$

(a) Prepare a graph showing P vs. x_1 and P vs. y_1 for a temperature of 75°C.

(b) Prepare a graph showing t vs. x_1 and t vs. y_1 for a pressure of 70 kPa.

(a) *BUBL P* $\boxed{P = P_2^{sat} + (P_1^{sat} - P_2^{sat})x_1}$

At 75°C $\boxed{P_1^{sat} = 83.21}$ $\boxed{P_2^{sat} = 41.98}$

$$\boxed{P = 41.98 + (83.21 - 41.98)x_1} \xrightarrow[\boxed{P = 66.72}]{\text{e.g. } x_1 = 0.6} \boxed{y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{(0.6)(83.21)}{66.72} = 0.7483}$$

At 75°C, a liquid mixture of 60 mol-% (1) and 40 mol-% (2) is in equilibrium with a vapor containing 74.83 mol-% (1) at pressure of 66.72 kPa.

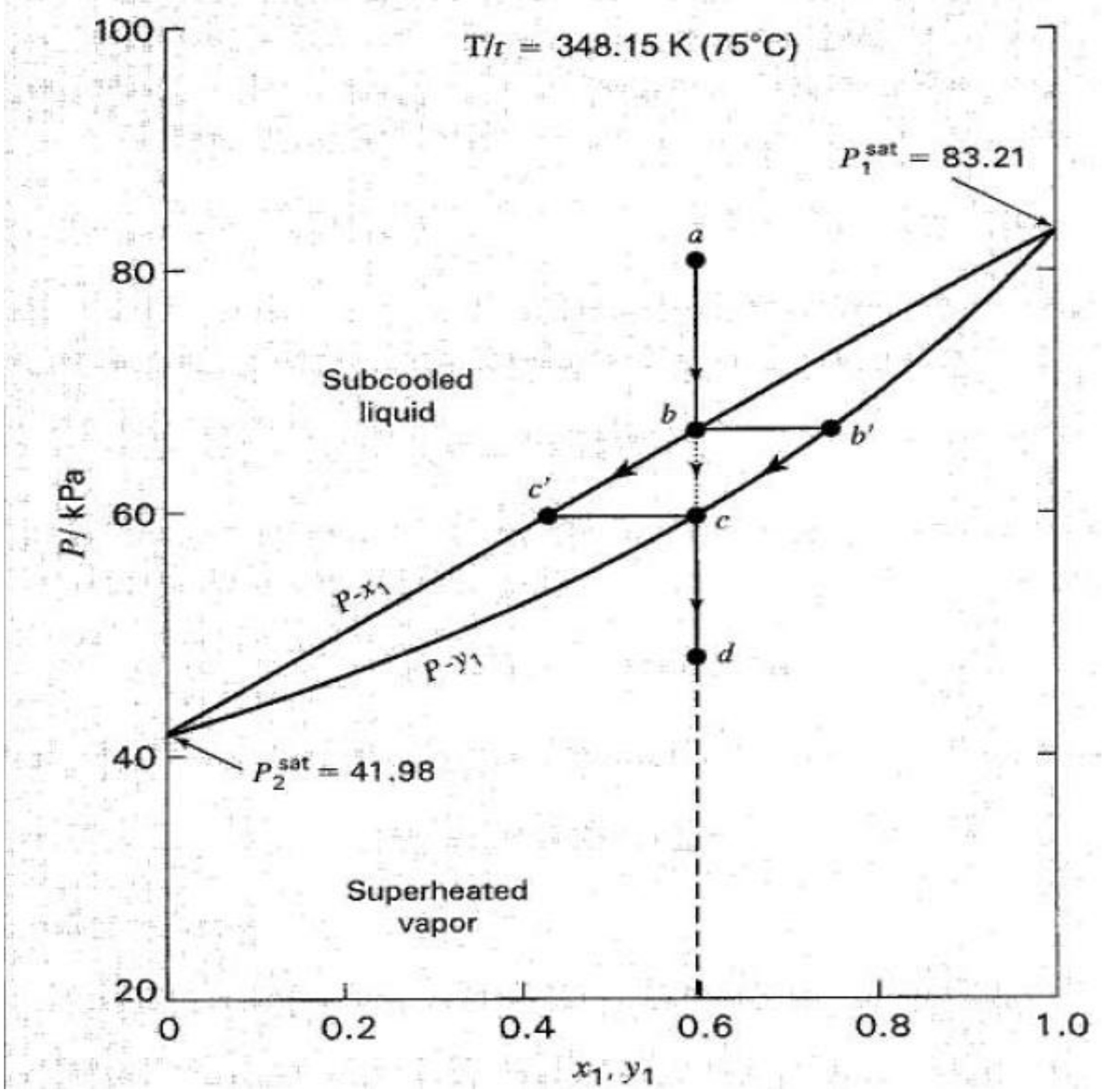
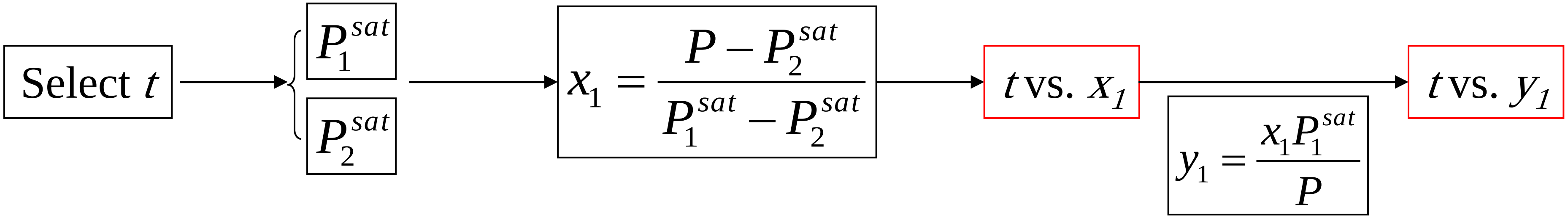


Figure 10.11 Pxy diagram for acetonitrile(1)/nitromethane(2) at 348.15 K (75°C) as given by Raoult's law

(b) *Flash –like calculation T,* having P = 70 kPa and specify *T* to calculate x_1 and y_1

$$\ln P_1^{sat}/kPa = 14.2724 - \frac{2945.47}{t/^\circ C + 224.00}$$

$$\ln P_2^{sat}/kPa = 14.2043 - \frac{2972.64}{t/^\circ C + 209.00}$$



Select *t*

P_1^{sat}

P_2^{sat}

$$x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}}$$

t vs. x_1

$$y_1 = \frac{x_1 P_1^{sat}}{P}$$

t vs. y_1

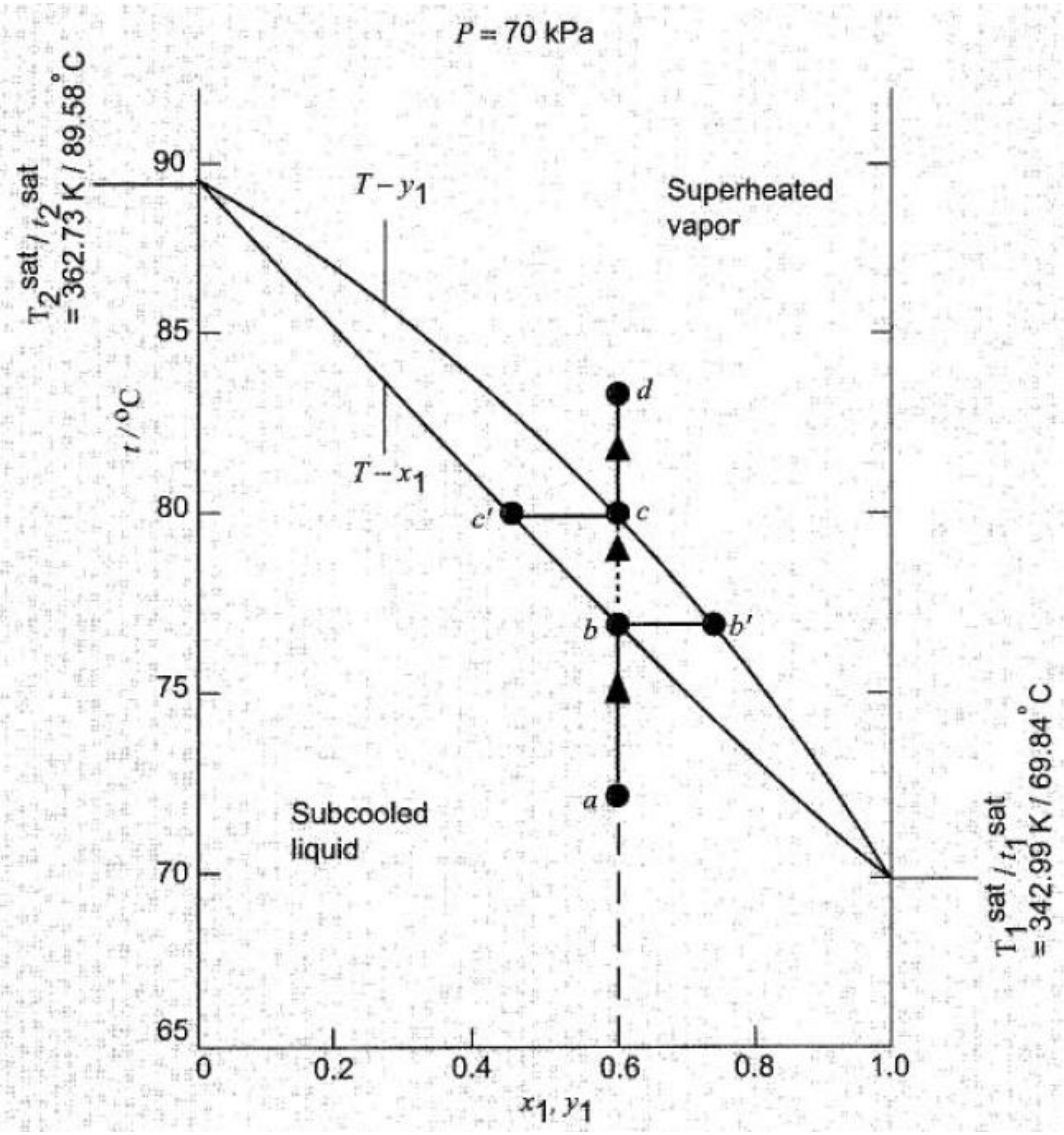


Figure 10.12 *txy* diagram for acetonitrile(1)/nitromethane(2) at 70 kPa as given by Raoult's law

Henry's law

- For a species present as a very dilute solute in the liquid phase, the partial pressure of the species in the vapor phase is directly proportional to its liquid-phase mole fraction:

$$\boxed{y_i P = x_i H_i}$$

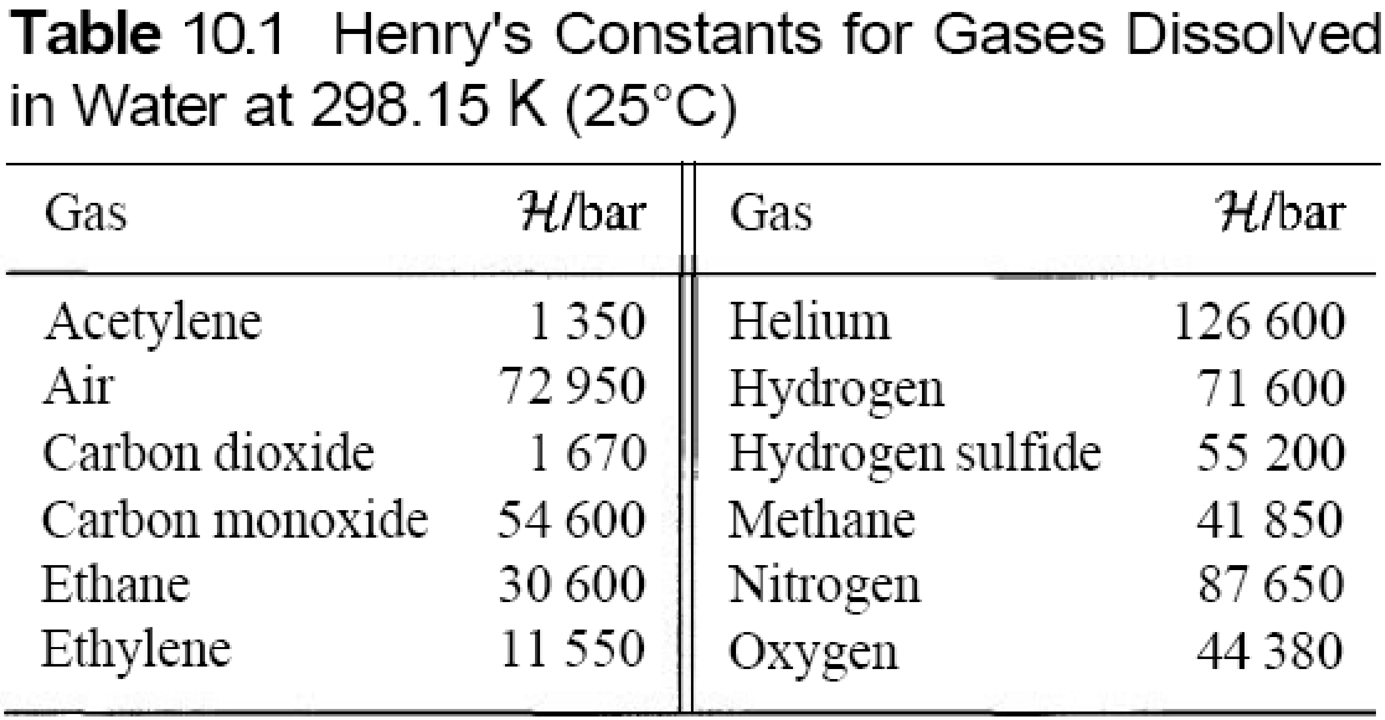


Table 10.1 Henry's Constants for Gases Dissolved in Water at 298.15 K (25°C)

Gas	$\mathcal{H}$/bar	Gas	$\mathcal{H}$/bar
Acetylene	1 350	Helium	126 600
Air	72 950	Hydrogen	71 600
Carbon dioxide	1 670	Hydrogen sulfide	55 200
Carbon monoxide	54 600	Methane	41 850
Ethane	30 600	Nitrogen	87 650
Ethylene	11 550	Oxygen	44 380

Henry’s law

Example 10.2. Assuming that carbonated water contains only CO_2 (species 1) and H_2O (species 2) , determine the compositions of the vapor and liquid phases in a sealed can of “soda” and the pressure exerted on the can at 10°C. Henry’s constant for CO_2 in water at 10°C is about 990 bar.

$F = 2 - \pi + N = 2 - 2 + 2 = 2 \rightarrow$ Two intensive variables must be specified

With the given condition, the problem can not be solved. Suppose that the mole fraction of CO_2 is 0.01.

$\rightarrow x_1 = 0.01,\ x_2 = 1\text{-}0.01\text{=}0.99$

Henry’s law for species 1: $\boxed{y_1 P = x_1 H_1}$ Raoult’s law for species 2: $\boxed{y_2 P = x_2 P_2^{sat}}$

$$\boxed{P = x_1 H_1 + x_2 P_2^{sat}}$$

$$\downarrow$$

$$\boxed{P = (0.01)(990) + (0.99)(0.01227) = 9.912}$$

$$\boxed{y_2 P = x_2 P_2^{sat}} \quad \boxed{y_1 P = x_1 H_1}$$

$$\downarrow$$

$$\boxed{y_1 = 0.9988} \quad \boxed{y_2 = 0.0012}$$

VLE by modified Raoult’s law

- Account is taken of deviation from solution ideality in the liquid phase by a factor inserted into Raoult’s law:

$$\boxed{y_i P = x_i \gamma_i P_i^{sat} \quad (i = 1, 2, 3, \ldots N)}$$

The activity coefficient, f (T, x_i)

$$\boxed{P = \sum_i x_i \gamma_i P_i^{sat}}$$

$$\boxed{P = \frac{1}{\sum_i y_i / \gamma_i P_i^{sat}}}$$

Visit: **http://vle-calc.com/**

VLE by modified Raoult’s law

Relative volatility:

For binary VLE system the relative volatility is defined as:

$$\boxed{\alpha_{12} \equiv \frac{y_1/x_1}{y_2/x_2}} \xrightarrow{\boxed{y_i P = x_i \gamma_i P_i^{sat}}} \boxed{\alpha_{12} = \frac{\gamma_1 P_1^{sat}}{\gamma_2 P_2^{sat}}}$$

$$\text{Azeotrope} \longrightarrow \boxed{y_1 = x_1}\ \boxed{y_2 = x_2} \longrightarrow \boxed{\alpha_{12} = 1}$$

Example 10.3. For the system methanol (1)/methyl acetate (2), the following equations provide a reasonable correlation for the activity coefficients:

$$\boxed{\ln \gamma_1 = (2.771 - 0.00523T)x_2^2} \qquad \boxed{\ln \gamma_2 = (2.771 - 0.00523T)x_1^2}$$

The Antoine equations provide vapor pressures:

$$\boxed{\ln P_1^{sat} / kPa = 16.59158 - \frac{3643.31}{T(K) - 33.424}}$$

$$\boxed{\ln P_2^{sat} / kPa = 14.25326 - \frac{2665.54}{T(K) - 53.424}}$$

Calculate

(a): P and $\{y_i\}$ for T = 318.15 K and $x_1 = 0.25$

(b): P and $\{x_i\}$ for T = 318.15 K and $y_1 = 0.60$

(c): T and $\{y_i\}$ for P = 101.33 kPa and $x_1 = 0.85$

(d): T and $\{x_i\}$ for P = 101.33 kPa and $y_1 = 0.40$

(e): the azeotropic pressure and the azeotropic composition for T = 318.15 K

Example 10.3

(a) for T = 318.15, and $x_1 = 0.25$ ***BUBL P***

$$\boxed{P_1^{sat} = 44.51} \qquad \boxed{P_2^{sat} = 65.64}$$

$$\boxed{\gamma_1 = 1.864} \qquad \boxed{\gamma_2 = 1.072}$$

$$\boxed{P = \sum_i x_i \gamma_i P_i^{sat} = (0.25)(1.864)(44.51) + (0.75)(1.072)(65.64) = 73.50}$$

$$\boxed{y_i P = x_i \gamma_i P_i^{sat}}$$

$$\downarrow$$

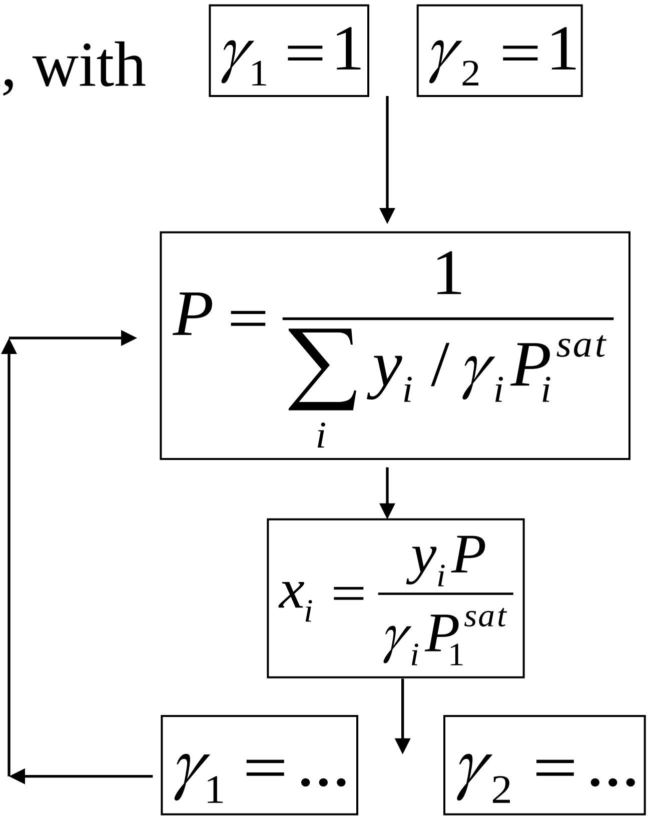
$$\boxed{y_1 = 0.282} \qquad \boxed{y_2 = 0.718}$$

Example 10.3

(b): for T = 318.15 K and $y_1 = 0.60$ ***DEW P***

$\boxed{P_1^{sat} = 44.51}$ $\boxed{P_2^{sat} = 65.64}$

An iterative process is applied, with



$\boxed{\gamma_1 = 1}$ $\boxed{\gamma_2 = 1}$

$$\boxed{P = \frac{1}{\sum_i y_i / \gamma_i P_i^{sat}}}$$

$$\boxed{x_i = \frac{y_i P}{\gamma_i P_1^{sat}}}$$

$\boxed{\gamma_1 = \ldots}$ $\boxed{\gamma_2 = \ldots}$

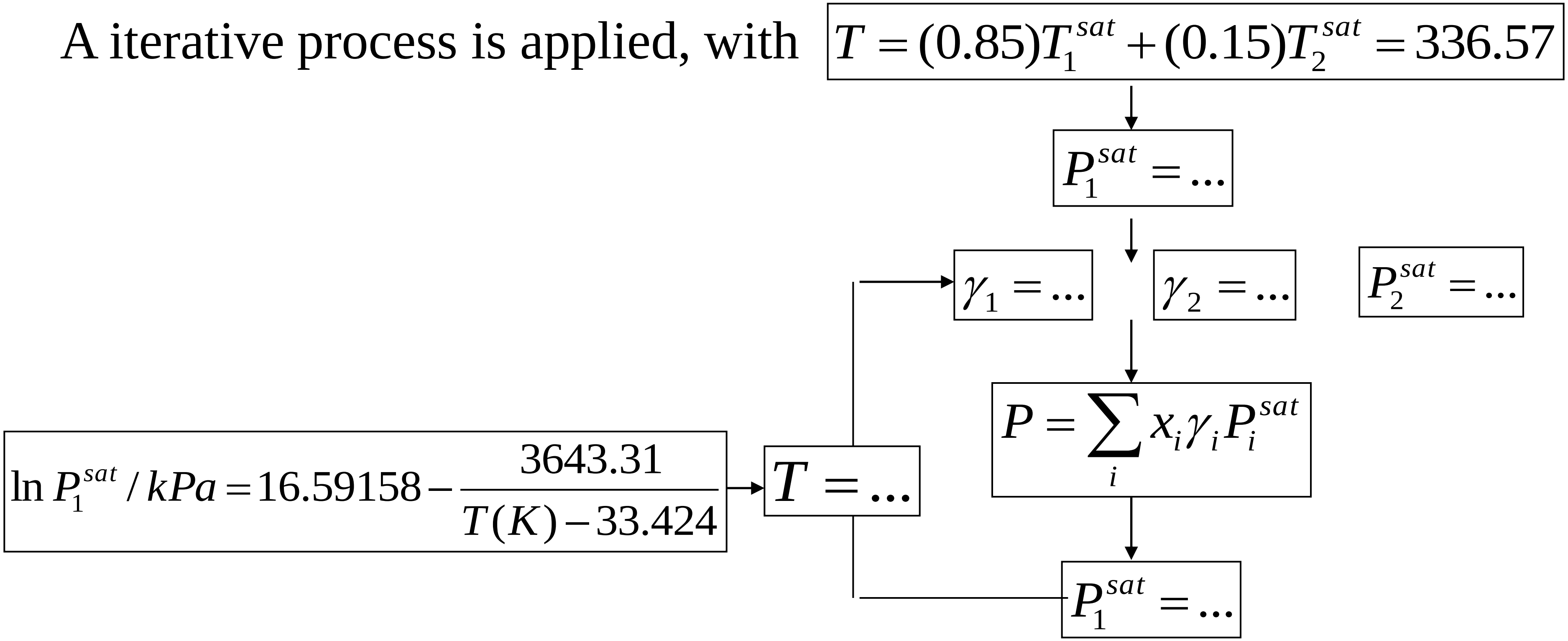
Converges at: $\boxed{P = 62.89\ kPa}$ $\boxed{\gamma_1 = 1.0378}$ $\boxed{\gamma_2 = 2.0935}$ $\boxed{x_1 = 0.8169}$

Example 10.3

(c): for P = 101.33 kPa and x_1 = 0.85 ***BUBL T***

$\boxed{T_1^{sat} = 337.71}$ $\boxed{T_2^{sat} = 330.08}$

A iterative process is applied, with



$$\boxed{T = (0.85)T_1^{sat} + (0.15)T_2^{sat} = 336.57}$$

$$\boxed{P_1^{sat} = ...}$$

$$\boxed{\gamma_1 = ...} \quad \boxed{\gamma_2 = ...} \quad \boxed{P_2^{sat} = ...}$$

$$\boxed{P = \sum_i x_i \gamma_i P_i^{sat}}$$

$$\boxed{P_1^{sat} = ...}$$

$$\boxed{\ln P_1^{sat} / kPa = 16.59158 - \frac{3643.31}{T(K) - 33.424}} \rightarrow \boxed{T = ...}$$

Converges at:

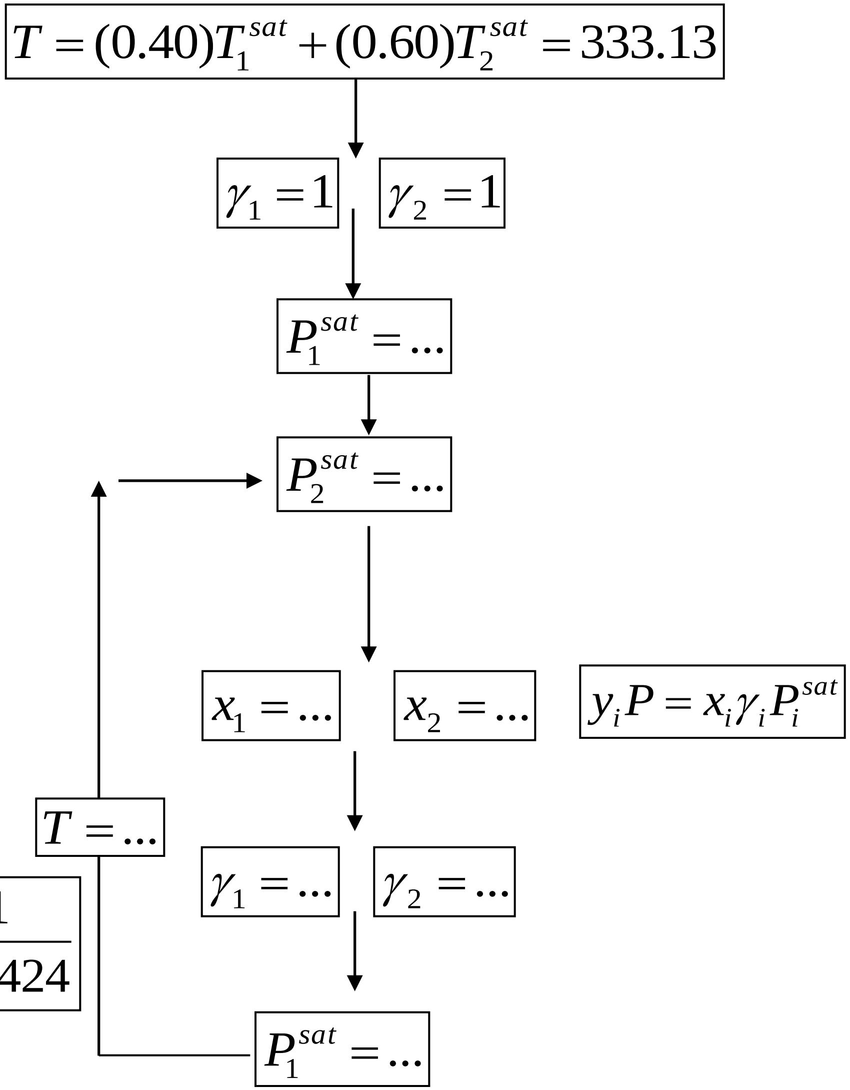
$\boxed{T = 331.20K}$ $\boxed{\gamma_1 = 1.0236}$ $\boxed{\gamma_2 = 2.1182}$ $\boxed{y_1 = 0.670}$ $\boxed{y_2 = 0.330}$

(d): for P = 101.33 kPa and y_1 = 0.40

DEW T

$\boxed{T_1^{sat} = 337.71}$ $\boxed{T_2^{sat} = 330.08}$

A iterative process is applied, with



$$\boxed{T = (0.40)T_1^{sat} + (0.60)T_2^{sat} = 333.13}$$

$\boxed{\gamma_1 = 1}$ $\boxed{\gamma_2 = 1}$

$\boxed{P_1^{sat} = ...}$

$\boxed{P_2^{sat} = ...}$

$\boxed{x_1 = ...}$ $\boxed{x_2 = ...}$ $\boxed{y_i P = x_i \gamma_i P_i^{sat}}$

$\boxed{\gamma_1 = ...}$ $\boxed{\gamma_2 = ...}$

$\boxed{P_1^{sat} = ...}$

$\boxed{T = ...}$

$$\boxed{\ln P_1^{sat} / kPa = 16.59158 - \frac{3643.31}{T(K) - 33.424}}$$

Converges at: $\boxed{T = 326.70K}$ $\boxed{\gamma_1 = 1.3629}$ $\boxed{\gamma_2 = 1.2523}$ $\boxed{x_1 = 0.4602}$ $\boxed{x_2 = 0.5398}$

(e): the azeotropic pressure and the azeotropic composition for T = 318.15 K

$$\text{Azeotrope} \longrightarrow \boxed{y_1 = x_1}\ \boxed{y_2 = x_2} \longrightarrow \boxed{\alpha_{12} = 1}$$

$$\boxed{\alpha_{12}\Big|_{x_1=0} = \frac{P_1^{sat}\exp(2.771-0.00523T)}{P_2^{sat}} = 2.052}\quad \boxed{\alpha_{12}\Big|_{x_1=1} = \frac{P_1^{sat}}{P_2^{sat}\exp(2.771-0.00523T)} = 0.224}$$

Since α$_{12}$ is a continuous function of x$_1$: from 2.052 to 0.224, α$_{12}$ = 1 at some point

There exists the azeotrope!

$$\boxed{\alpha_{12} = \frac{\gamma_1 P_1^{sat}}{\gamma_2 P_2^{sat}} = 1} \longrightarrow \boxed{\frac{\gamma_1^{az}}{\gamma_2^{az}} = \frac{P_2^{sat}}{P_1^{sat}} = 1.4747}$$

$$\left.\begin{array}{l}\boxed{\ln\gamma_1 = (2.771-0.00523T)x_2^2}\\ \boxed{\ln\gamma_2 = (2.771-0.00523T)x_1^2}\end{array}\right\}\ \boxed{\ln\frac{\gamma_1}{\gamma_2} = (2.771-0.00523T)(x_2-x_1) = (2.771-0.00523T)(1-2x_1)}$$

$$\downarrow$$

$$\boxed{x_1^{az} = 0.325 = y_1^{az}} \longrightarrow \boxed{\gamma_1^{az} = 1.657}$$

$$\boxed{P^{az} = \gamma_1^{az}P_1^{sat} = 73.76kPa}$$

VLE from K-value correlations

- A convenient measure, the *K-value*: $\boxed{K_i \equiv \frac{y_i}{x_i}}$
- It measures the “lightness” of a constituent species, i.e., of its tendency to favor the vapor phase. When K_i is greater than unity, species i exhibits a higher concentration in the vapor phase; when less, a higher concentration in the liquid phase, and is considered a "heavy" constituent. Moreover, the use of K-values makes for computational convenience, allowing elimination of one set of mole fractions.$\{y_i\}$ or {xi} in favor of the other.
- The Raoult’s law: $\boxed{K_i = \frac{P_i^{sat}}{P}}$
- The modified Raoult’s law: $\boxed{K_i = \frac{\gamma_i P_i^{sat}}{P}}$

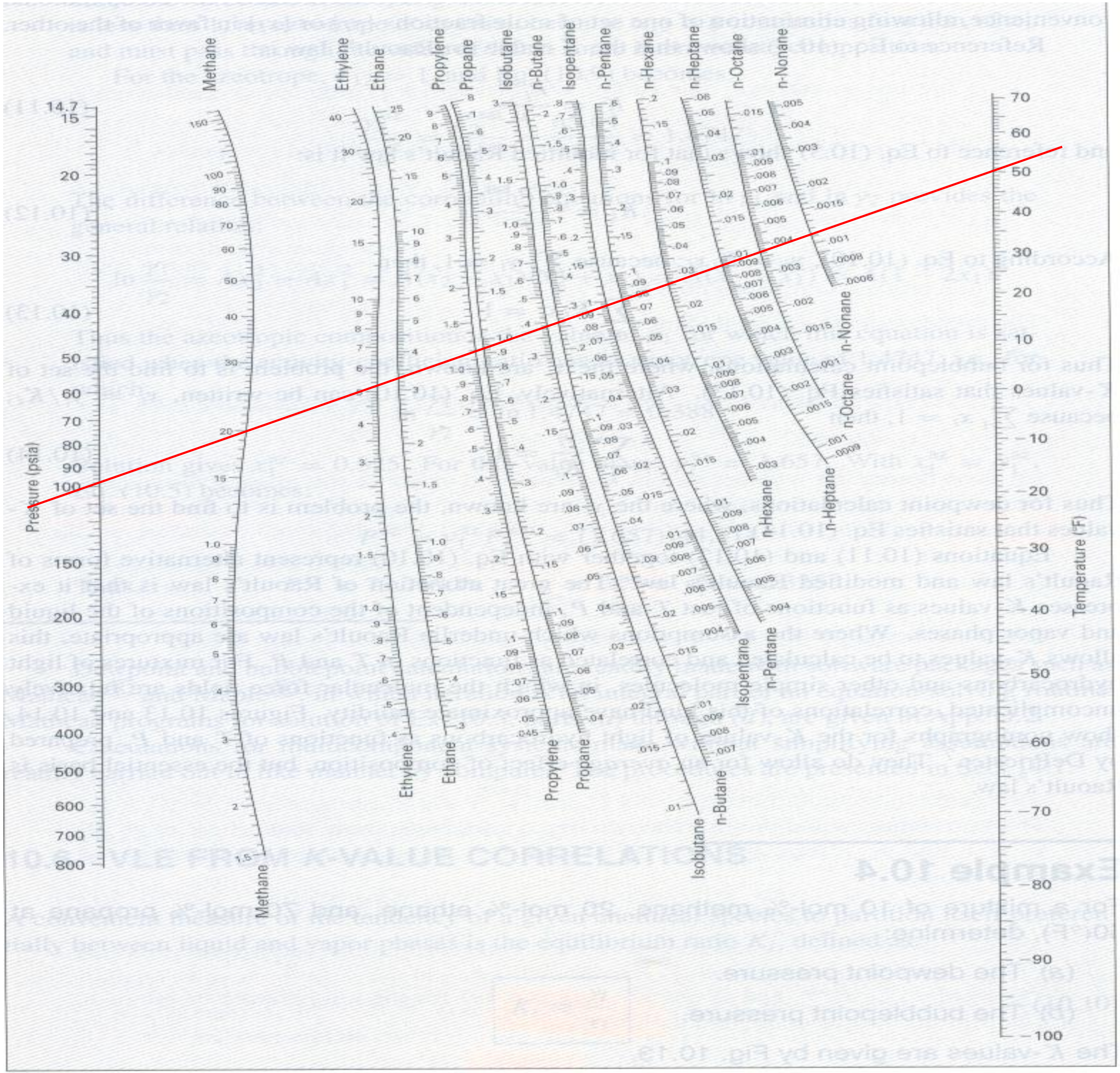

Methane
Ethylene
Ethane
Propylene
Propane
Isobutane
n-Butane
Isopentane
n-Pentane
n-Hexane
n-Heptane
n-Octane
n-Nonane
Pressure (psia)
14.7
15
20
30
40
50
60
70
80
90
100
150
200
300
400
500
600
700
800
Temperature (°F)
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100

Fig 10.13

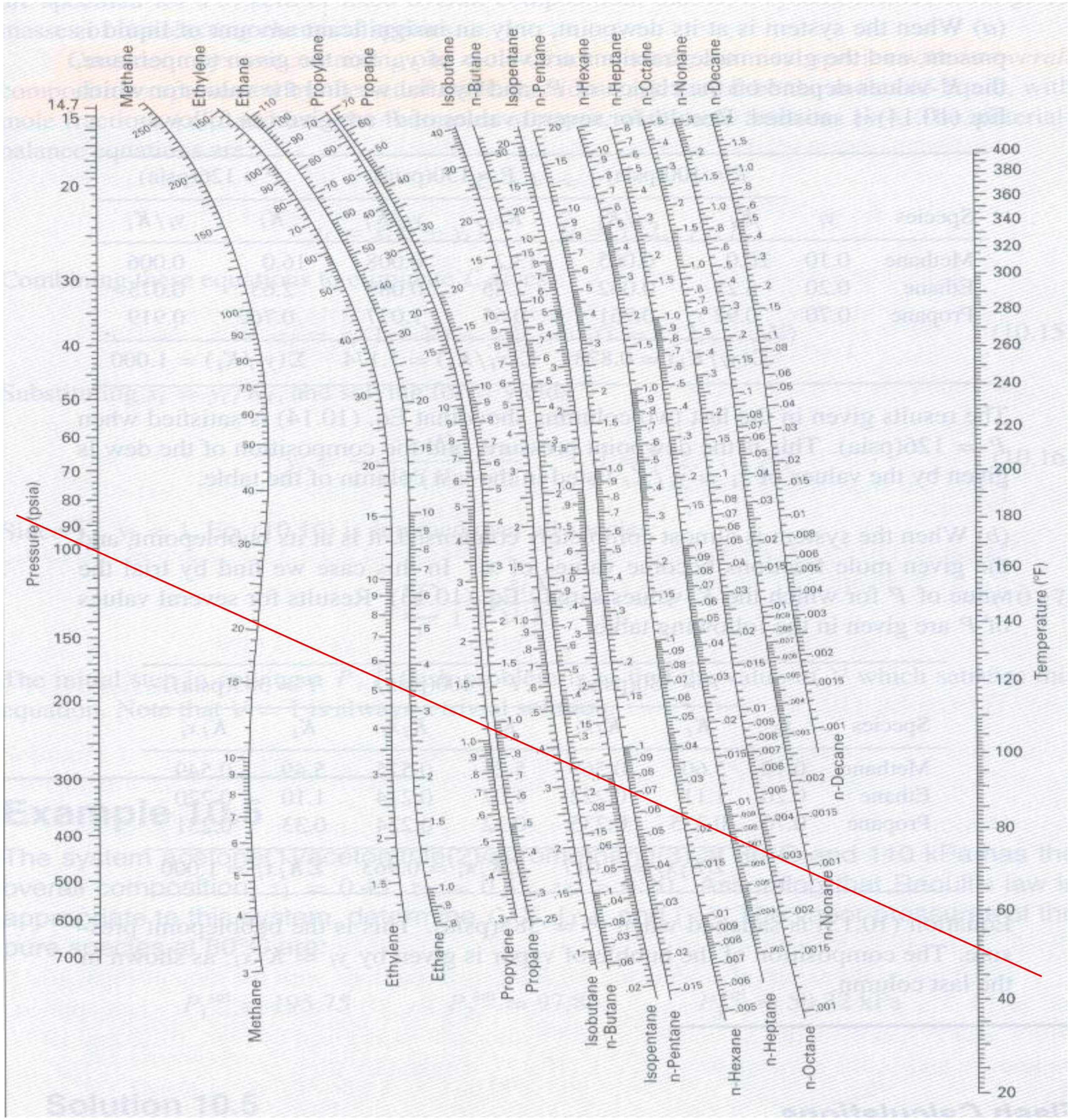

Pressure (psia)
14.7
15
20
30
40
50
60
70
80
90
100
150
200
300
400
500
600
700
Methane
Ethylene
Ethane
Propylene
Propane
Isobutane
n-Butane
Isopentane
n-Pentane
n-Hexane
n-Heptane
n-Octane
n-Nonane
n-Decane
Temperature (°F)
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20

Fig 10.14

Example 10.4. For a mixture of 10 mol-% methane, 20 mol-% ethane, and 70 mol-% propane at 50°F, determine: (a) the dewpoint pressure, (b) the bubblepoint pressure. The K-values are given by Fig. 10.13.

(a) at its dewpoint, only an insignificant amount of liquid is present:

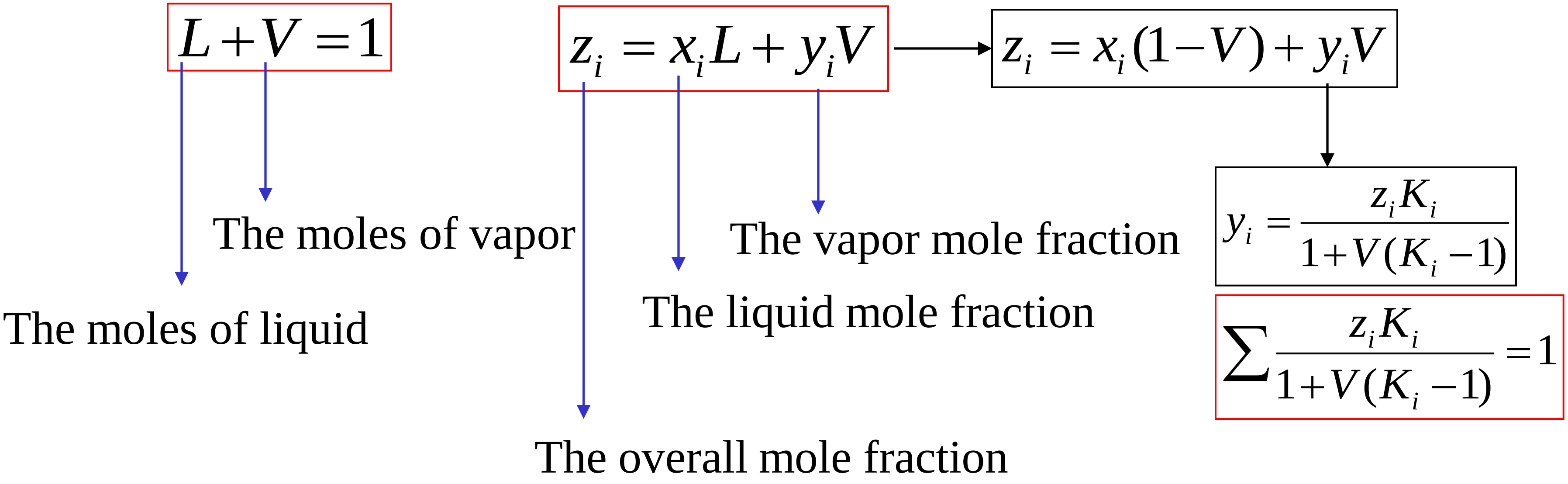
		P = 100 (psia)		P = 150 (psia)		P = 126 (psia)	
Species	y_i	K_i	y_i/K_i	K_i	y_i/K_i	K_i	y_i/K_i
Methane	0.10	20.0	0.005	13.2	0.008	16.0	0.006
Ethane	0.20	3.25	0.062	2.25	0.089	2.65	0.075
Propane	0.70	0.92	0.761	0.65	1.077	0.762	0.919
		$\Sigma (y_i/K_i) = 0.828$		$\Sigma (y_i/K_i) = 1.174$		$\Sigma (y_i/K_i) = 1.000$	

(b) at bubblepoint, the system is almost completely condensed:

		P = 380 (psia)		P = 400 (psia)		P = 385 (psia)	
Species	x_i	K_i	$x_i K_i$	K_i	$x_i K_i$	K_i	$x_i K_i$
Methane	0.10	5.60	0.560	5.25	0.525	5.49	0.549
Ethane	0.20	1.11	0.222	1.07	0.214	1.10	0.220
Propane	0.70	0.335	0.235	0.32	0.224	0.33	0.231
		$\Sigma (x_i K_i) = 1.017$		$\Sigma (x_i K_i) = 0.963$		$\Sigma (x_i K_i) = 1.000$	

Flash calculations

- A liquid at a pressure equal to or greater than its bubblepoint pressure “flashes” or partially evaporates when the pressure is reduced, producing a two-phase system of vapor and liquid in equilibrium.
- Consider a system containing one mole of nonreacting chemical species:



$$\boxed{L+V=1}$$

The moles of vapor

The moles of liquid

$$\boxed{z_i = x_i L + y_i V} \longrightarrow \boxed{z_i = x_i(1-V) + y_i V}$$

The vapor mole fraction

The liquid mole fraction

The overall mole fraction

$$\boxed{y_i = \frac{z_i K_i}{1+V(K_i-1)}}$$

$$\boxed{\sum \frac{z_i K_i}{1+V(K_i-1)} = 1}$$

Example 10.5. The system acetone (1)/acetonitrile (2)/nitromethane(3) at 80°C and 110 kPa has the overall composition, $z_1 = 0.45$, $z_2 = 0.35$, $z_3 = 0.20$, Assuming that Raoult's law is appropriate to this system, determine L, V, $\{x_i\}$, and $\{y_i\}$. The vapor pressures of the pure species are given.

Do a *BUBL P* calculation, with $\{z_i\} = \{x_i\}$:

$$\boxed{P_{bubl} = x_1 P_1^{sat} + x_2 P_2^{sat} + x_3 P_3^{sat} = (0.45)(195.75) + (0.35)(97.84) + (0.20)(50.32) = 132.40\ kPa}$$

Do a *DEW P* calculation, with $\{z_i\} = \{y_i\}$:

$$\boxed{P_{dew} = \frac{1}{y_1 / P_1^{sat} + y_2 / P_2^{sat} + y_3 / P_3^{sat}} = 101.52\ kPa}$$

Since $P_{dew} < P = 110\text{ kPa} < P_{bubl}$, the system is in the two-phase region,

$$\boxed{K_i = \frac{P_i^{sat}}{P}} \rightarrow \boxed{K_1 = 1.7795}\ \boxed{K_2 = 0.8895}\ \boxed{K_3 = 0.4575} \rightarrow \boxed{\sum \frac{z_i K_i}{1 + V(K_i - 1)} = 1} \rightarrow \boxed{V = 0.7364\ mol}$$

$$\boxed{L = 1 - V = 0.2636\ mol}$$

$$\boxed{y_i = \frac{z_i K_i}{1 + V(K_i - 1)}}$$

$$\boxed{y_1 = 0.5087}\quad \boxed{y_2 = 0.3389}\quad \boxed{y_3 = 0.1524}$$

$$\boxed{K_i \equiv \frac{y_i}{x_i}}$$

$$\boxed{x_1 = 0.2859}\quad \boxed{x_2 = 0.3810}\quad \boxed{x_3 = 0.3331}$$