Chapter 10
Vapor/Liquid Equilibrium

- Previous chapters dealt with ***pure substances*** or with ***constant composition mixtures*** (air).

- But in chemical reactions and number of industrially mass-transfer operations the ***composition changes*** are the desired outcome. (Process such as ***distillation***, ***absorption*** and ***extraction*** bring phases of different composition into contact).

- In such process. The extent of phase change and the rate of mass transfer depend on the departure of the system from the ***equilibrium***.

- For quantitative treatment of mass transfer the equilibrium ***T, P and phase composition*** must be known.

- Two simple formulations that allow calculation of T, P and phase compositions for systems in vapor/liquid systems:

    - Raoult's Law: Valid for systems at ***low to moderate pressure*** and systems of ***chemically similar species***.
    - Henery's Law: Any species present at ***low concentration***. Limited to low to moderate pressure.

- A modification of Raoult's law (removes the restriction of chemically similar species) is treated in section 10.5.

- Finally, in section 10.6, calculations based on equilibrium ratio of K-values are considered.

10.4 Simple Models for a Vapor/Liquid Equilibrium

- ***The goal is to find by calculation the T, P and compositions of phases in equilibrium.***

- **Raoult's Law**:

  Two major assumptions:

  - The vapor phase is an ideal gas.
  - The liquid phase is an ideal solution (11.8).

- It means:

  - Raoult's law can apply only for low to moderate pressures.
  - Raoult's law can apply only when the species that comprise the system are chemically similar.

- **Ideal solution**: Approximated by liquid phases where molecular species are not too different in size and are of the same chemical nature.

  Example: Mixture of isomers such as ortho-, meta-, para- xylene.
  Or adjacent members of homologues series: n-hexane/n-heptane
  Ethanol/propanol
  Benzene/toluene.

- Mathematical Expression:

$$\boxed{y_i P = x_i P_i^{sat}} \qquad (\, i= 1,2,\ldots..,N) \; (10.1)$$

Where:

y_i = Vapor-phase mole fraction.
x_i = Liquid-phase mole fraction.
P_i = Vapor pressure of pure species i at the T of the system.
$y_i P$ = Partial pressure of species i.

- **Limitation**: It can be applied only to a species for which vapor pressure is known.

- Vapor pressure given by empirical equations such as **Antoine equation**, where T is required.

This requires that the species "sub-critical" i.e. that the temperature of application be below the critical temperature of the species.

- Dew point and bubble point calculations with Raoult's law:
    - **Bubl P: Calculate y_i and P**, *given x_i and T.*
    - **Dew P: Calculate x_i and P**, *given y_i and T.*
    - **Bubl T: Calculate y_i and T**, *given x_i and P.*
    - **Dew T: Calculate x_i and T**, *given y_i and P.*
- **Bubble point**: First bubble forms.
- **Dew point**: Liquid droplet remains.
- General procedure:

$$\sum y_i = 1$$

Then equation 10.1 becomes $$P = \sum x_i P_i^{sat} \qquad (10.2)$$

Applied for Bubble point calculations where the vapor phase compositions are unknown.

For a binary system with $$x_2 = 1 - x_1$$
$$P = P_2^{sat} + (P_1^{sat} - P_2^{sat})\, x_1$$

Also 10.1 may be solved for x_i with $$\sum x_i = 1$$
$$P = 1/ \sum y_i P_i^{sat} \qquad (10.3)$$

Applied for Dew point calculations where liquid phase compositions are unknown.

Ex.10.1

Ex. 10.1

Binary system acetonitrite (1) / nitromethane (2)

Vapor Pressures for the Pure species by Antoine eq'n :

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

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

ⓐ Prepare a graph showing P vs x_1 & P vs y_1 for a temp. of ~~80~~ 75°C

ⓑ " " " " t vs x_1 & t vs y_1 @ a Pressure of 70 kPa ~~75~~

Sol'n :

ⓐ $\boxed{\text{BUBL P calc.}}$ From known values of x_1 & t we calculate the bubble (vapor) composition (y_1) & the pressure

As we said (eq'n 10.2) $P = \Sigma x_i P_i^{sat}$ becomes

$$P = P_2^{sat} + (P_1^{sat} - P_2^{sat})\, x_1 \qquad Ⓐ$$

At 75°C , Vapor Pressure from the given Antoine eq'ns

$P_1^{sat} = 83.21$ kPa & $P_2^{sat} = 41.98$ kPa

Now calculate P for any value of x_1 between 0 & 1

x_1, T given $\Rightarrow$ y_1, P find

subs. in Ⓐ for $x_1 = 0.6$

(1) [illegible]

$$\Rightarrow P = 41.98 + (83.21 - 41.98)(0.6) = 66.72 \text{ kPa}$$

From 10.1 $y_i P = x_i P_i^{sat}$

$$\Rightarrow y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{(0.6)(83.21)}{66.72} = 0.7483 \qquad Ⓑ$$

[illegible] → There results mean that @ 75°C a liquid mixture containg 60 mole Percent acetonitrite (1) & 40 mole Percent nitromethane (2) is in equilibrium with a vapor containg 74.83 % acentonitrite (1) & 25.17 % nitromethane (2) @ a Pressure of 66.72 kPa .

Based on similar calculations we can Prepare P-x , P-y diagrams

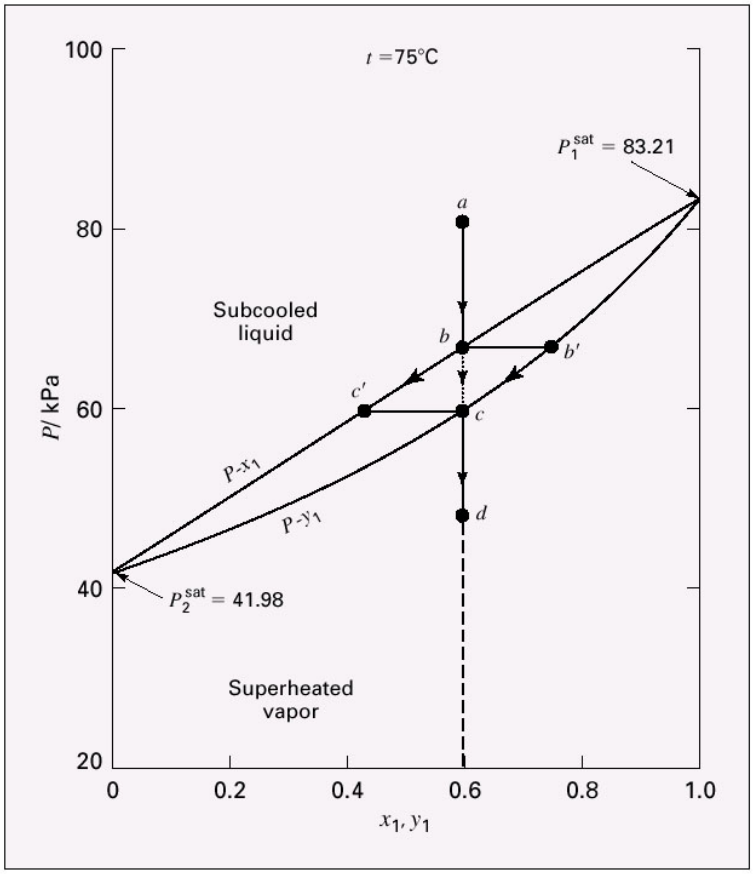


Figure 10.11: *Pxy* diagram for acetonitrile(1)/nitro-methane(2) at 75°C as given by Raoult's law.

P-x_1: Sat'd liquid.
P-y_1: Sat'd vapor.
Above P-x_1: Sub cooled liquid.
Below P-y_1 : Superheated vapor.

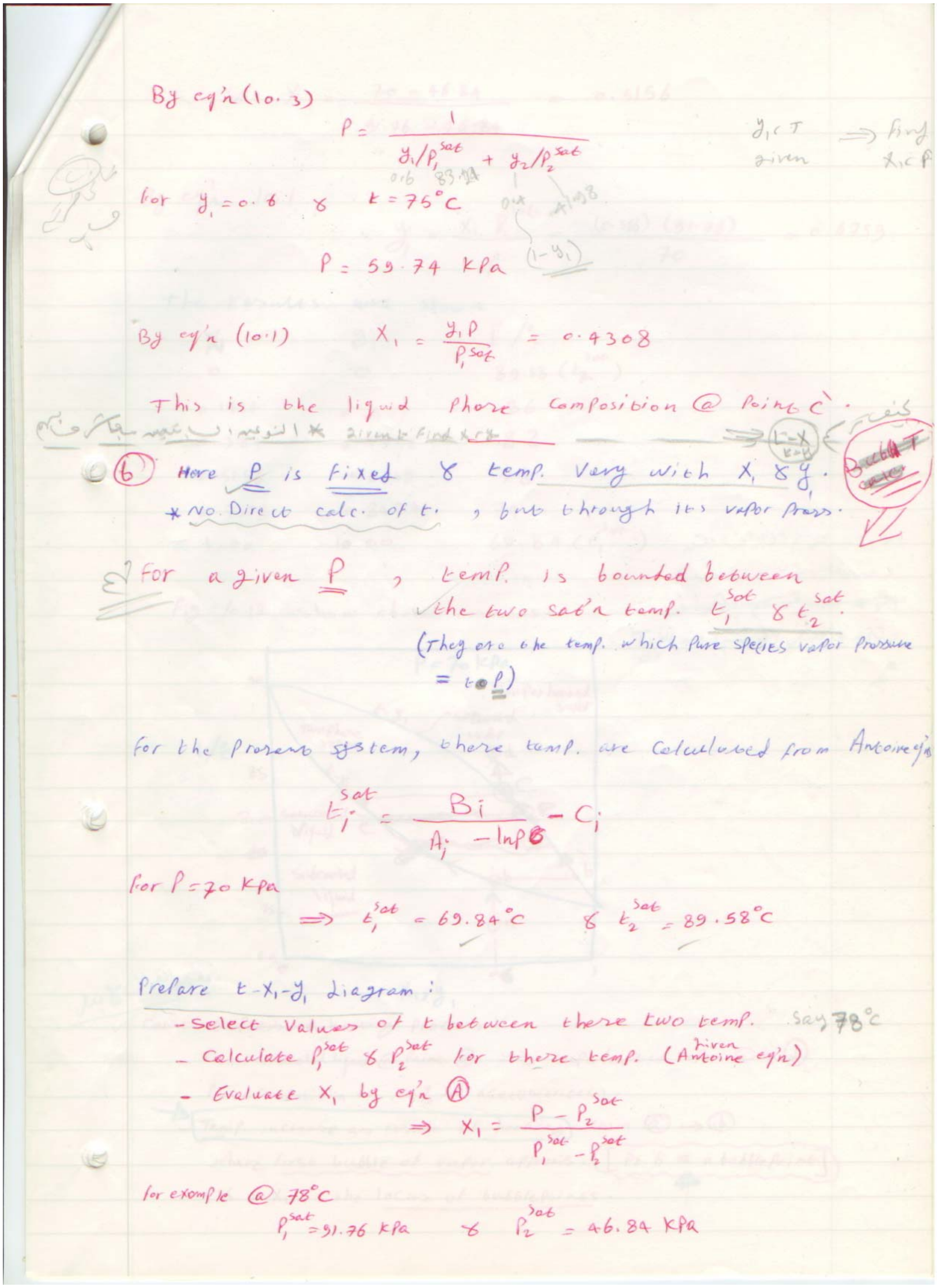
Between P-x_1 & P-y_1 two phase region.

Lines meet at edges of the diagram: P_1^{sat} and P_2^{sat}.

- **Point a: sub cooled liquid mixture 60 mol% & 40 mol% at 75°C.**
- **Reduce pressure slowly so that system is always in equilibrium until point b.**
- **Point b: Sat'd liquid on the edge of vaporization.**
- **Further reduce the pressure till point b^-, bubble of vapor appears.**
- **Points b and b^- are the equilibrium state @ x_1= 0.6, P= 66.72, and y_1= 0.7483(as we did calculated)**
- **Point b is a bubble point, P-x_1 line is the locus of bubble points.**
- **As pressure reduced, vapor increase and liquid decrease following the two paths b^-c and bc-.**
- **Finally, approach point C where only a droplet of liquid remains. C is a dew point, P-y_1 line is the locus of dew points.**
- **Point c- read from the graph or calculated.**

DEW P calculation: Calculate x_i and P, *given y_i and T*

T= 75°c, y_1= 0.6 **Find x_1 and P.**



By eq'n (10.3)

$$P = \frac{1}{y_1/P_1^{sat} + y_2/P_2^{sat}}$$

0.6 83.21 0.4 41.98 (1−y_1)

y_1, T given ⟹ find x_1, P

for $y_1 = 0.6$ & $t = 75°C$

$$P = 59.74 \text{ kPa}$$

By eq'n (10.1) $x_1 = \dfrac{y_1 P}{P_1^{sat}} = 0.4308$

This is the liquid phase composition @ point C'.

[illegible] given t Find x, y ⟹ (1−x) [illegible]

⑥ Here P is fixed & temp. very with x_1 & y_1.

~~Bubble T calc~~

* No Direct calc. of t., but through its vapor press.

For a given P, temp. is bounded between the two sat'n temp. t_1^{sat} & t_2^{sat}.
(They are the temp. which pure species vapor pressure = to P)

for the present system, these temp. are calculated from Antoine eq'ns

$$t_i^{sat} = \frac{B_i}{A_i - \ln P} - C_i$$

for P = 70 kPa

$$\Rightarrow t_1^{sat} = 69.84°C \quad \& \quad t_2^{sat} = 89.58°C$$

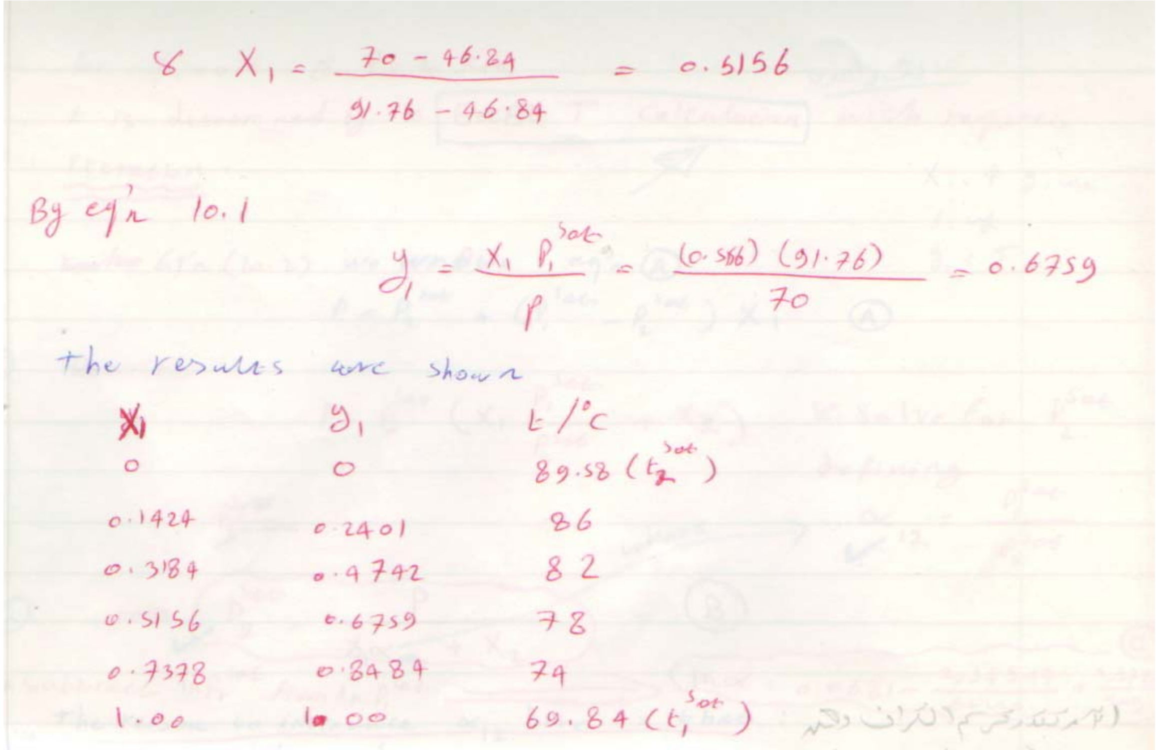
Prepare t-x_1-y_1 diagram:

- Select values of t between these two temp. say 78°C
- Calculate P_1^{sat} & P_2^{sat} for these temp. (given Antoine eq'n)
- Evaluate x_1 by eq'n Ⓐ

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

for example @ 78°C

$$P_1^{sat} = 91.76 \text{ kPa} \quad \& \quad P_2^{sat} = 46.84 \text{ kPa}$$



8 $$X_1 = \frac{70 - 46.24}{91.76 - 46.84} = 0.5156$$

By eq'n 10.1

$$y_1 = \frac{X_1 P_1^{sat}}{P} = \frac{(0.5156)(91.76)}{70} = 0.6759$$

The results are shown

X_1	y_1	t /°C
0	0	89.58 (t_2^{sat})
0.1424	0.2401	86
0.3184	0.4742	82
0.5156	0.6759	78
0.7378	0.8484	74
1.00	1.00	69.84 (t_1^{sat})

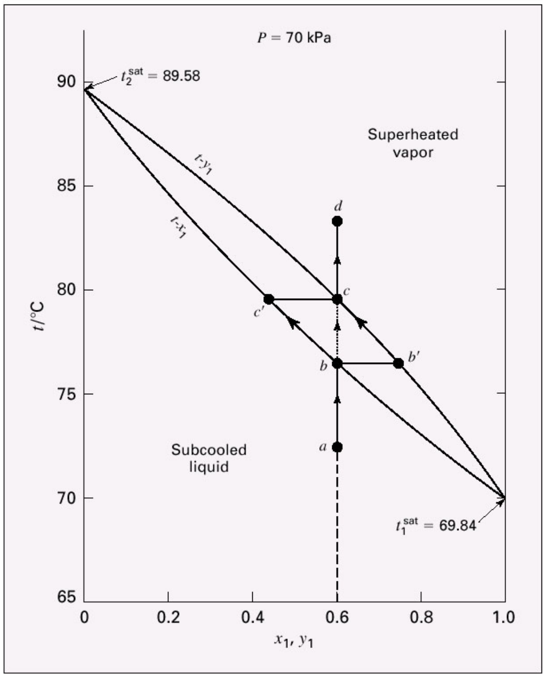


Figure 10.12: *txy* diagram for acetonitrile(1)/nitromethane(2) at 70 kPa as given by Raoult's law.

Constant pressure heating process:

- **Point a: Sub cooled liq. of a composition of 60% acetonitrite.**
- **Temp. increase as a result of heating from a to b.**
- **Point b: first bubble of vapor appears. Bubble point. t-x_1 is the locus of bubble points.**

Bubl T calculation: Calculate y_i and T, *given x_i and P.*

P= 70 kpa, x_1= 0.6 **Find y_1 and P.** **{Iteration}**

- **From eq. (10.2) write** $P = P_2^{sat}(x_1(P_1^{sat}/P_2^{sat}) + x_2)$ **A**
- **Solve for** P_2^{sat} **, defining** $\alpha = P_1^{sat}/P_2^{sat}$
- $P_2^{sat} = P/x_1\alpha + x_2$ **B**
- $\ln \alpha = \ln (P_1^{sat} / P_2^{sat})$ $(= \ln P_1^{sat} - P_2^{sat})$
- **From Antoine equation** $\ln\alpha = 0.0681 - 2{,}945.47/t+224 + 2{,}972.64/209$ **C**
- **α is a weak function of t.**

Iteration procedure:

1- **Calculate P_2^{sat} from equation B with the current value of α. (From part a @ 75°c).**

2- **Calculate t from Antoine equation for species 2:**

$$t = 2{,}972.64/(14.2043-\ln P_2^{sat}) - 209$$

3- **Find a new value of a by equation C.**

4- **Return to the initial step and iterate to converge for final value of t.**

The result is t = 76.42°c (Temp. of points b and b^-).
From Antoine equation P_1^{sat} = 87.17 kpa.

From 10.1 b^- composition:

$$y_1 = x_1 P_1^{sat} /P = 0.6 * 87.17/70 = 0.7472$$

Vaporizing a mixture at constant P, unlike vaporizing a pure species DOES NOT occur at constant temperature.

As heating continue beyond b, temp raises and the amount of vapor increases. During this process, vapor and liquid compositions change as in path b^-c and bc^-.

- Dew point is reached at c where last droplet of liquid disappears (Dew point), t-y_1 is locus of dew points.

Dew T calculation: Calculate x_i and T, *given y_i and P.*

P= 70 kpa, y_1= 0.6 **Find x_1 and T. {Iteration}**

$$\alpha = P_1^{sat}/P_2^{sat}$$

$$P_1^{sat} = P\,(y_1 + y_2\alpha)$$

Same iteration procedure as before but based on P_1^{sat} instead of P_1^{sat} with

$$t = 2{,}972.64/(14.2424 - \ln P_1^{sat}) - 224$$

The result is t = 79.58°c (Temp. of points c and c^-).
From Antoine equation P_1^{sat} = 96.53 kpa.

From 10.1 b^- composition:

$$x_1 = y_1 P / P_1^{sat} = 0.6 * 70/96.53 = 0.4351$$

Temperature raises from 76.42°c to 79.58°c during the vaporization step from point b to c.
Continue heating to super heated at point d.

- **<u>Henry's Law</u>**:

  - Raoult's law **requires** $\mathbf{P_i^{sat}}$ value at application temperature.

  - For species whose critical T is less than the application temperature, this is not appropriate.

  - For example, **air dissolved in water** at equilibrium.
    (Air T_C = 132.2°K = -140.95 °C is much lower than 25°C).

  - Use Henry's law for **dilute solute in the liquid phase** (liq. Mole fraction < 0.01 in system).

  - **Henry's law**: <u>The partial pressure of the species in the vapor phase is directly proportional to its liquid phase mole fraction.</u>

  - $$\boxed{y_i P = x_i \mathcal{H}_i} \quad (10.4)$$

    Where, $\mathcal{H}_i$ from experiment (table 10.1) values at 25°C.

  - Examples: Removing Ammonia from air stream containing 2% Ammonia to become odorless.
  - Co_2 + Water

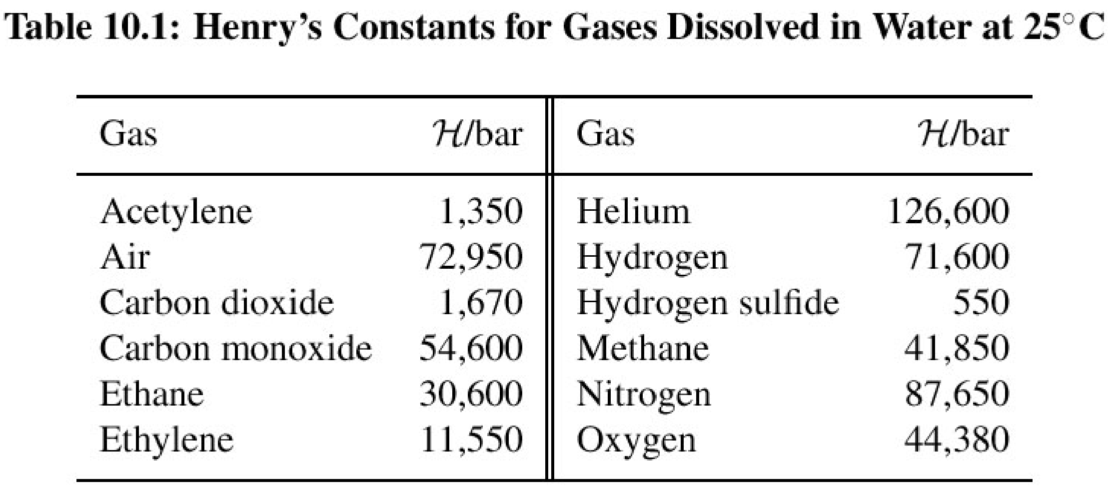


Table 10.1: Henry's Constants for Gases Dissolved in Water at 25°C

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	550
Carbon monoxide	54,600	Methane	41,850
Ethane	30,600	Nitrogen	87,650
Ethylene	11,550	Oxygen	44,380

EX 10.2

CO_2 & H_2O x_i & y_i = ? in soda can
& P = ? on 10°C

$\mathcal{H}_{CO_2} = 990$ bar @ 10°C

(CO_2 very diluted in H_2O)

[illegible]

Sol'n

CO_2 (1) & H_2O (2)

Henery law for CO_2 $\Rightarrow y_1 P = x_1 \mathcal{H}_1$

& Raoult's law H_2O $\Rightarrow y_2 P = x_2 P_2^{sat}$

$$\Rightarrow P = x_1 \mathcal{H}_1 + x_2 P_2^{sat}$$

steam table

$$x_1 = \frac{P - P_2^{sat}}{\mathcal{H} - P_2^{sat}} = \frac{1 - 0.01227}{990 - 0.01227} = 9.98 \times 10^{-4}$$

* Assume $x_1 = 0.01$ (very low)

$\mathcal{H}_1 = 990$ bar (given)

$P_2^{sat} = 0.01227$ bar (steam table @10°C)

table (F.1) $P^{sat} = 1.227$ kPa

$$\Rightarrow P = (0.01)(990) + (0.99)(0.01227) = 9.912 \text{ bar}$$ ✓

* use in Henery's law, find new value of x_1

$y_1 \simeq 1$ $\Rightarrow$ eq'n (10.4) becomes

when P vapor phase is nearly pure CO_2(1)

$$x_1 = \frac{P}{\mathcal{H}_1} = \frac{9.912}{990} = 0.01$$ ✓

Confirms original assumption.

[illegible] فرضنا

* By Raoult's law Eq'n (6.1) for species (2)

$$y_2 = \frac{x_2 P_2^{sat}}{P} = \frac{(0.99)(0.01227)}{9.912} = 0.0012$$

$y_1 = 1 - y_2 = 1.0 - 0.0012 = 0.9988$

& Vapor phase is nearly pure CO_2 as assumed.

10.5 VLE by Modified Raoult's Law

- ***Deviation from solution ideality*.**

$$\boxed{y_i P = x_i \gamma_i P_i^{sat}} \quad (\text{ i= } 1,2,\ldots..,N) \quad (10.5)$$

Where γ_i = **Activity coefficient**.

- It is function of T and liquid composition and based on experiments. (12.1 give correlations to calculate γ).
- As a result, bubble point and dew point calculations are more complex.
- In this chapter γ values are assumed known.
- General solution:

$$\sum y_i = 1$$

Sum equation 10.5 becomes

$$P = \sum x_i \gamma_i P_i^{sat} \quad (10.6)$$

Also you can solve for x_i from 10.5.

$$\sum x_i = 1$$

$$P = 1/\sum y_i \gamma_i P_i^{sat} \quad (10.7)$$

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EX 10.3 given Corr. for activity coeff

~~$\ln$~~ $\ln \gamma_1 = A x_2^2$ $\quad$ $\ln \gamma_2 = A x_1^2$ $\quad$ $A = 2.771 - 0.00523T$

Antoine eq'ns for vapor Press:

$\ln P_1^{sat} =$ $\quad$ & $\ln P_2^{sat} =$

T(K) & P(kPa), eq'n (10.5) valid, Calculate:

ⓐ P & y_i for $T = 318.15\,K$ & $x_1 = 0.25$ (BubI P calc.)

ⓑ P & x_i for $T = \cancel{}$ & $y_1 = 0.6$ (Dew P calc.)

ⓒ T & y_i for $P = 101.33\,kPa$ & $x_1 = 0.85$ (BubI T calc.)

ⓓ T & x_i for $P = 101.33\,kPa$ & $y_1 = 0.44$ (Dew T calc.)

ⓔ The azeotropic Pressure, and the azeotropic composition, for $T = 318.5\,K$.

Solution:

ⓐ BUBL P Calculation. $T = 318.15\,K$, Antoine eq'ns

① $\Rightarrow P_1^{sat} = 44.51$ $\quad$ $P_2^{sat} = 65.64\ kPa$

② Activity Coeff. $A = 2.771 - (0.00523)(318.15) = 1.107$

$\gamma_1 = \exp(A x_2^2) = \exp((1.107)(0.75)^2) = 1.864$

$\gamma_2 = \exp(A x_1^2) = \exp((1.107)(0.25)^2) = 1.072$

③ From Eq'n (10.6) find $\underline{P}$ $\quad$ $P = \sum_i x_i \gamma_i P_i^{sat}$ (10.6)

$P = (0.25)(1.864)(44.51) + (0.75)(1.072)(66.64) = 73.5\ kPa$

④ From eq'n (10.5) find y_i $\quad$ $y_i = \dfrac{x_i \gamma_i P_i^{sat}}{P}$

$y_1 = 0.282$ $\quad$ $y_2 = 0.718$

ⓑ DEW P calculation $y_1 = 0.6$ T = 318.15K

∵ T same as in Part ⓐ

∴ P_1^{sat} & P_2^{sat} are the same.

Here, liquid phase composition X_i = ?? unknown.
but we need it for γ calculation

∴ Iterative Procedure is required.

① Initial value $\gamma_1 = \gamma_2 = 1.0$

② calculate P by eq'n (10.7) $P = \dfrac{1}{y_1/\gamma_1 P_1^{sat} + y_2/\gamma_2 P_2^{sat}}$

③ Calculate X_1 by eq'n (10.5) $X_1 = \dfrac{y_1 P}{\gamma_1 P_1^{sat}}$

then $X_2 = 1 - X_1$

④ Recalculate activity coeff., go to the first step, continue to convergence

$\gamma_1 = \exp(A x_2^2)$ $\gamma_2 = \exp(A x_1^2)$

After going through this process,

$\Rightarrow P = 62.89$ kPa $X_1 = 0.8169$ $\gamma_1 = 1.0378$

$\gamma_2 = 2.0935$

ⓒ BUBL T Calculation

$\because$ T is unknown
$\therefore$ A can't be calculated so γ_1 & γ_2
$\Rightarrow$ Iterative Procedure

① Solve Antoine eq'n for the sat. temp.

$$T_i^{sat} = \frac{B_i}{A_i - \ln P} - C_i$$

$\because P = 101.33$ kPa (given)

$$\therefore T_1^{sat} = 337.71 \qquad T_2^{sat} = 330.08 \text{ K}$$

* Initial T, is found by calculating a mole-fraction-weighted average of these values:

x_1 given

$$T = (0.85)(337.71) + (0.15)(330.08) = 336.57 \text{ K}$$

② Iterative Procedure start:
for the current value of T find A & γ_1 & γ_2 and $\alpha = \frac{P_1^{sa}}{P_2^{sa}}$
from the given eq'ns.

③ find new value for P_1^{sat} from eq'n (10.6) written as

$$P_1^{sat} = \frac{P}{x_1\gamma_1 + x_2\gamma_2/\alpha}$$

④ find a new value for T from Antoine eq'n for species 1

$$T = \frac{B_1}{A_1 - \ln P_1^{sat}} - C_1$$

⑤ Return to the initial step ②, iterate to convergence on value for T.

$$\Rightarrow T = 331.20 \text{ K} \qquad P_1^{sat} = 95.24 \text{ kPa} \qquad P_2^{sat} = 48.73$$

$$A = 1.0388 \qquad \gamma_1 = 1.0236 \qquad \gamma_2 = 2.1182$$

The vapor-phase mole fraction $y_1 = \frac{x_1\gamma_1 P_1^{sat}}{P} = 0.67 \qquad y_2 = 1 - y_1 = 0.330$

② DEW T calculation

$\because$ $P = 101.33$ kPa

$\therefore$ T_1^{sat} & T_2^{sat} same as Part $\underline{\underline{C}}$

The initial value for the unknown temp. is found as mole-fraction weighted average of these values:

Assume T, $T = (0.4)(337.71) + (0.6)(330.08) = 333.13$ K

$\gamma_1 = \gamma_2 = 1$

$\because$ liquid phase composition $x_i \equiv ?$ not known

$\therefore$ γ_1 and γ_2 can't be calculated.

Then, iterative procedure as Part $\underline{\underline{C}}$ ($\gamma_1 = \gamma_2 = 1$) is required:

① Evaluate A, P_1^{sat}, P_2^{sat} and $\alpha = \frac{P_1^{sat}}{P_2^{sat}}$ at the current value of T from Antoine eq'ns.

② Calculate x_1 by eq'n (10.5)

$$x_1 = \frac{y_1 P}{\gamma_1 P_1^{sat}} \quad \text{and} \quad x_2 = 1 - x_1$$

③ Calculate values of γ_1 and γ_2 from the given eq'ns.

④ Find a new value for T from Antoine eq'n written to species 1:

$$T = \frac{B_1}{A_1 - \ln P_1^{sat}} - C_1$$

⑤ Return to the initial step and iterate withe the current values of γ_1 and γ_2 until the process converges on a final value for T.

final values $T = 326.7$ K $\quad P_1^{sat} = 64.63$ kPa $\quad P_2^{sat} = 90.89$ kPa

$A = 1.0624 \quad \gamma_1 = 1.3629 \quad \gamma_2 = 1.2523$

$x_1 = 0.4602 \quad x_2 = 0.5398$

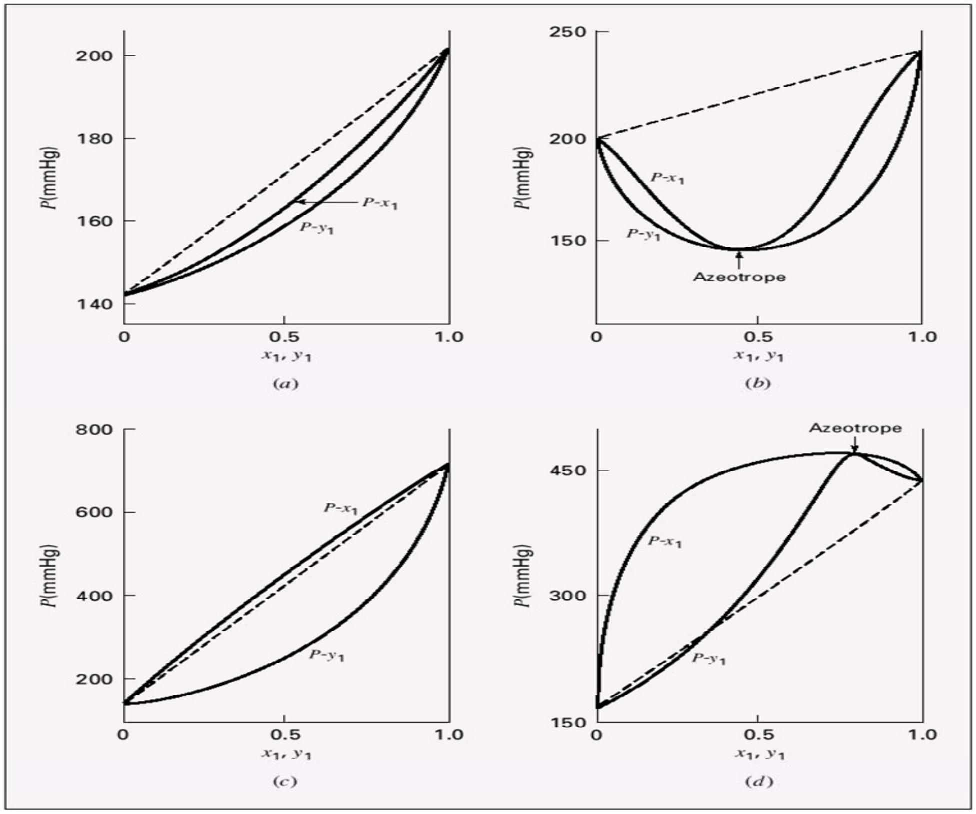


Figure 10.8: *Pxy* diagrams at constant *T*: (*a*) tetrahydrofuran(1)/carbon tetrachloride(2) at 30°C; (*b*) chloroform(1)/tetrahydrofuran(2) at 30°C; (*c*) furan(1)/carbon tetrachloride(2) at 30°C; (*d*) ethanol(1)/toluene(2) at 65°C. Dashed lines: *Px* relation for Raoult's law.

- (a): P-x_1 (or bubble point curve) lies below the linear P-x_1 relation characteristics of Raoult's law.

- (b): P-x_1 curve exhibits a minimum, when the negative departures from linearity become sufficiently large, relative to the difference between the two pure species vapor pressure. Also P-y_1 curve has a minimum at the same point.

- (c): P-x_1 (or dew point curve) lies above the linear P-x_1 relation.

- (d): P-x_1 curve exhibits a maximum, when the positive departures from linearity become sufficiently large, relative to the difference between the two pure species vapor pressure. Also P-y_1 curve has a maximum at the same point.

- At this point,
  - $x = y$
  - Dew point and bubble curves are tangent to the sane horizontal line.
  - For minimum pressure, the vapor and liquid phases in equilibrium have identical composition.
- This is called **"Azetrope".**

- It means:
  A boiling liquid of this composition produces a vapor of exactly the same composition as the liquid; therefore does not change in composition as it evaporate.
  NO SEPERATION of such a constant-boiling solution is possible by distillation.

- Negative departure from linearity ≡ Stronger liquid phase intermolecular attractions between unlike than between like pairs of molecules.

- Positive departure from linearity ≡ Stronger liquid phase intermolecular attractions between like than between unlike pairs of molecules.

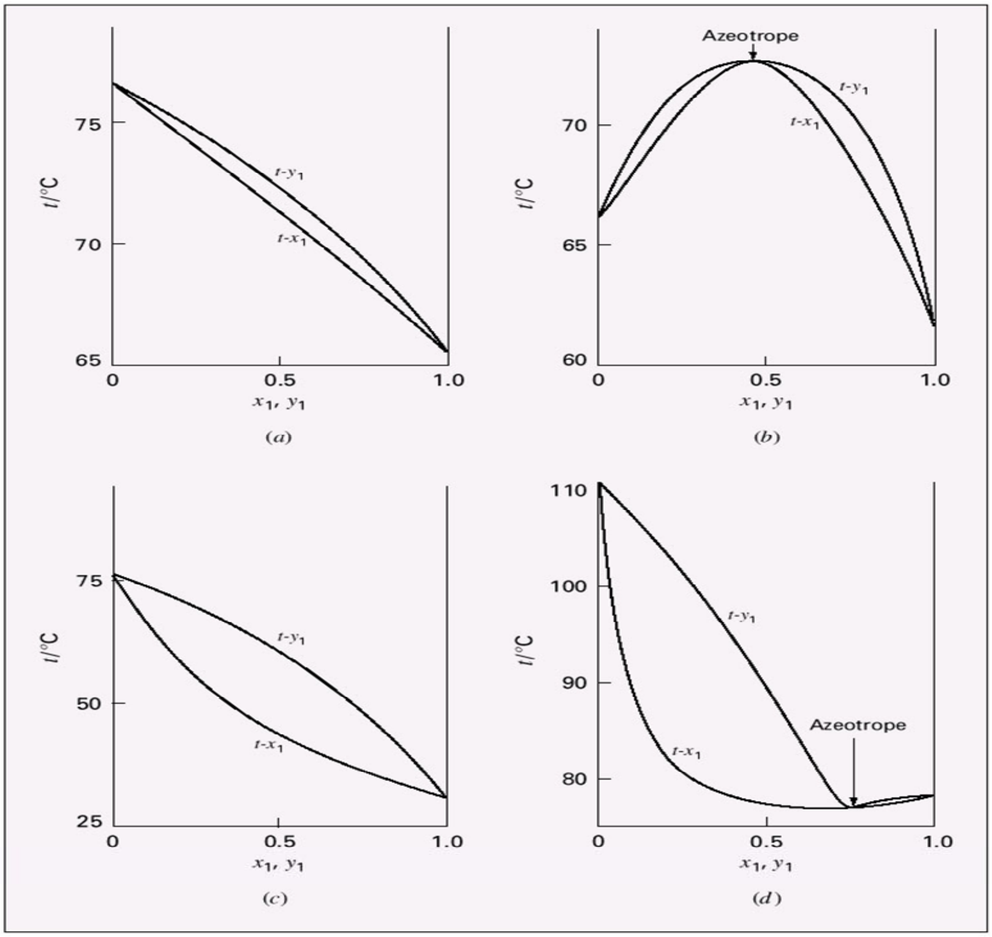


Figure 10.9: *txy* diagrams at 1(atm): (*a*) tetrahydrofuran(1)/carbon tetrachloride(2); (*b*) chloroform(1)/tetrahydrofuran(2); (*c*) furan(1)/carbon tetrachloride(2); (*d*) ethanol(1)/ toluene(2).

- t-x_1-y_1 diagram of data at constant P.
- This is more of interest because distillation process is carried out more nearly at constant P than constant temperature.
- Opposite to figure 10.8. (Azetrope in opposite sides).

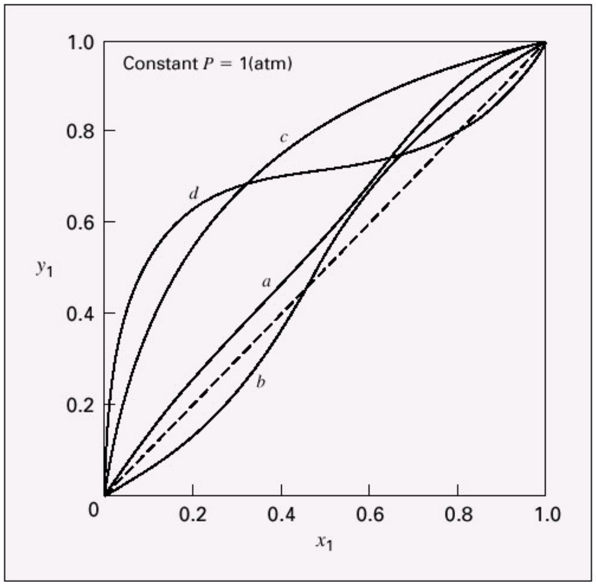


Figure 10.10: *yx* diagrams at 1(atm):
(*a*) tetrahydrofuran(1)/carbon tetrachloride(2);
(*b*) chloroform(1)/tetrahydrofuran(2);
(*c*) furan(1)/carbon tetrachloride(2);
(*d*) ethanol(1)/toluene(2).

- x_1-y_1 at constant pressure for the same systems.
- Point at which curve crosses the diagonal line of diagram is Azetrope ($x_1 = y_1$).
- (a) and (c) no azetrope.
- (b) and (d) azetrope across the diagonal.

e- There are two kinds of questions about azetrops:

1- Do we have azetrope at this given temperature for this given system?
2- What are azetropic pressure and azetropic compositions?

1- Do we have azetrope at this given temperature for this given system?

- Let Relative Volatilty, $\alpha_{12} = (y_1/ x_1) / (y_2/ x_2)$ (10.8)
- At an Azetrope, $y_1= x_1$, $y_1= x_1$ and $\alpha_{12} =1$
- From modified Raoult's law, eq'n (10.5):

$$y_1/ x_1 = \gamma_1 P_1^{sat} / P$$

- Substitute in 10.8,

$$\alpha_{12} = \gamma_1 P_1^{sat} / \gamma_2 P_2^{sat} \qquad (10.9)$$

- Since $\ln\gamma_2 = Ax_1^2$ and $\ln\gamma_1 = Ax_2^2$ (given)
- Then, When $x_1 = 0 \rightarrow \gamma_2=1$ and $\gamma_1 =\exp(A)$
- And, When $x_1 = 1 \rightarrow \gamma_1=1$ and $\gamma_2 =\exp(A)$
- In these limits, substitute in 10.9,

$$(\alpha_{12})_{x1=0} = P_1^{sat} \exp(A) / P_2^{sat} \quad \text{and} \quad (\alpha_{12})_{x1=1} = P_1^{sat} / P_2^{sat} \exp(A)$$

- For the temperature of interest, $P_1^{sat} = 44.51$, $P_2^{sat} = 65.64$ kpa
- The limiting values of α_{12} from the above equations;
  $(\alpha_{12})_{x1=0} = 2.052$ Value of one limit > 1 and
  $(\alpha_{12})_{x1=1} = 0.224$ Value of one limit < 1
- So Azetrope does exist.
- α_{12} is a continues function of x_1 and must pass through the value of 1.0 at some intermediate composition.

2- What are azetropic pressure and azetropic compositions?

- Since for azetrope $\alpha_{12} = 1$

  Then eq'n 10.9 becomes, $\gamma_1^{az} / \gamma_2^{az} = P_2^{sat} / P_1^{sat} = 65.64/44.51 = 1.4747$

- The difference between the correlation equations for $\ln\gamma_1$ and $\ln\gamma_2$ provides the general relation:

$$\ln \gamma_1/\gamma_2 = A x_2^2 - A x_1^2 = A(x_2 - x_1)(x_2 + x_1)$$
$$= A(x_2 - x_1) = A(1-2x_1)$$

- $\ln \gamma_1 / \gamma_2 = \ln 1.4747 = 0.388$

- Then $0.388 = A(1-2x_1^{az}) \rightarrow x_1^{az} = 0.325$

- And $\gamma_1^{az} = 1.657$

- With $x_1^{az} = y_1^{az}$

- $P^{az} = \gamma_1^{az} P_1^{sat} = (1.657)(44.51) = 73.76$ kpa, and

- $x_1^{az} = y_1^{az} = 0.325$

10.6 VLE from K-value correlations

$$K_i = y_i/x_i$$

K -value measure the tendency of species to favor the vapor phase.

$K_i > 1$	Species I exhibit a higher concentration in the vapor phase.
$K_i < 1$	Species I exhibit a higher concentration in the liquid phase.

Allowing elimination of one set of mole fractions x or y, two types of calculations result:

Bubble point calculation: $y_i = k_i x_i$ and $\sum y_i = 1$

$$\text{Then} \quad \sum k_i x_i = 1 \qquad (10.13)$$

Find the set of K-values that satisfies equation 10.13

Dew point calculation: $x_i = y_i / k_i$ and $\sum x_i = 1$

$$\text{Then} \quad \sum y_i / k_i = 1 \qquad (10.14)$$

Find the set of K-values that satisfies equation 10.14

- Figures 10.13 1nd 10.14 show monographs for the k-values of light hydrocarbons as function of T and P. They are prepared for average effect of compositions.

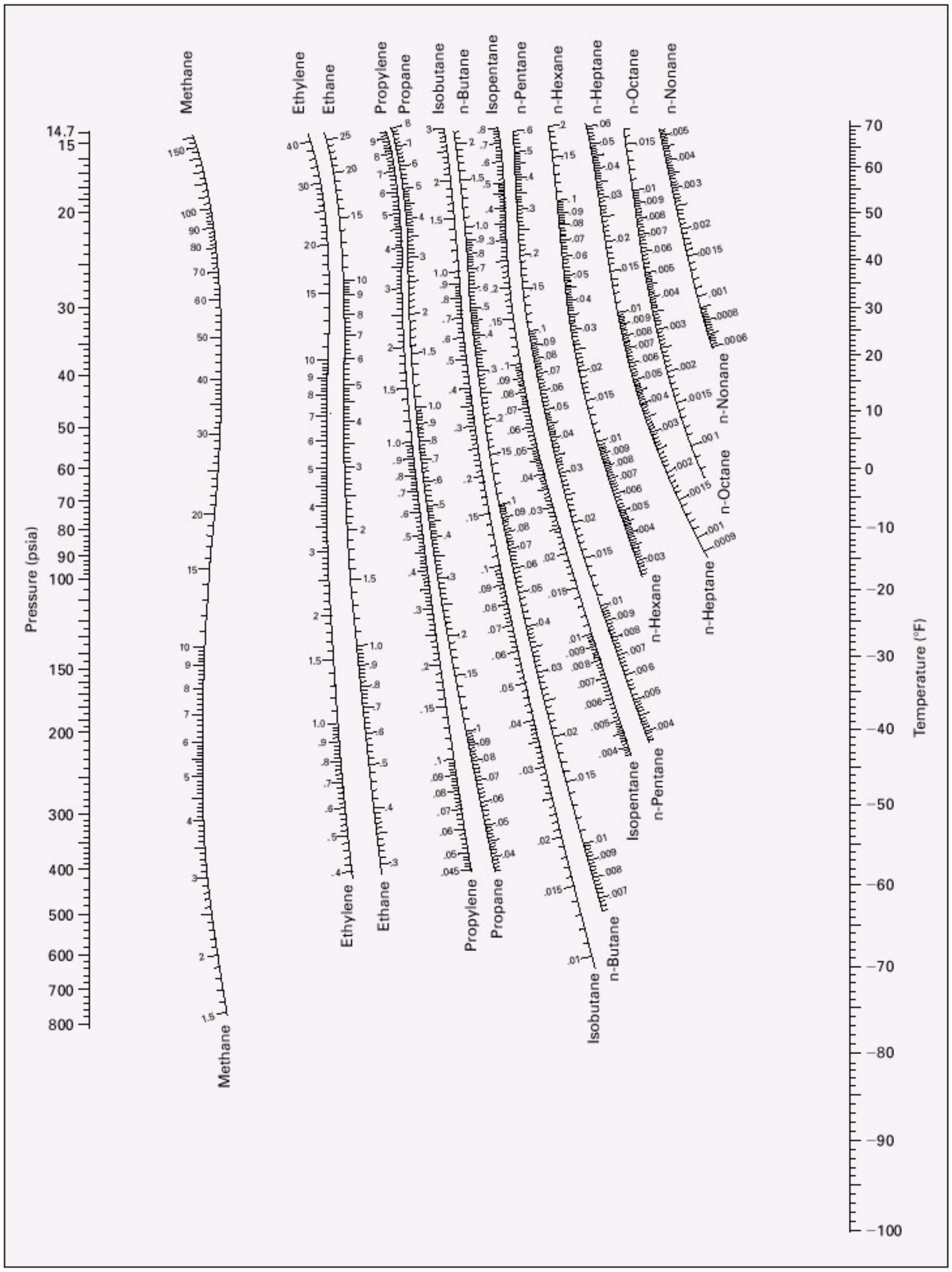


Figure 10.13: K-values for systems of light hydrocarbons. Low-temperature range. (Reproduced by permission from C. L. DePriester, *Chem. Eng. Progr. Symp. Ser. No. 7*, vol. 49, p. 41, 1953.)

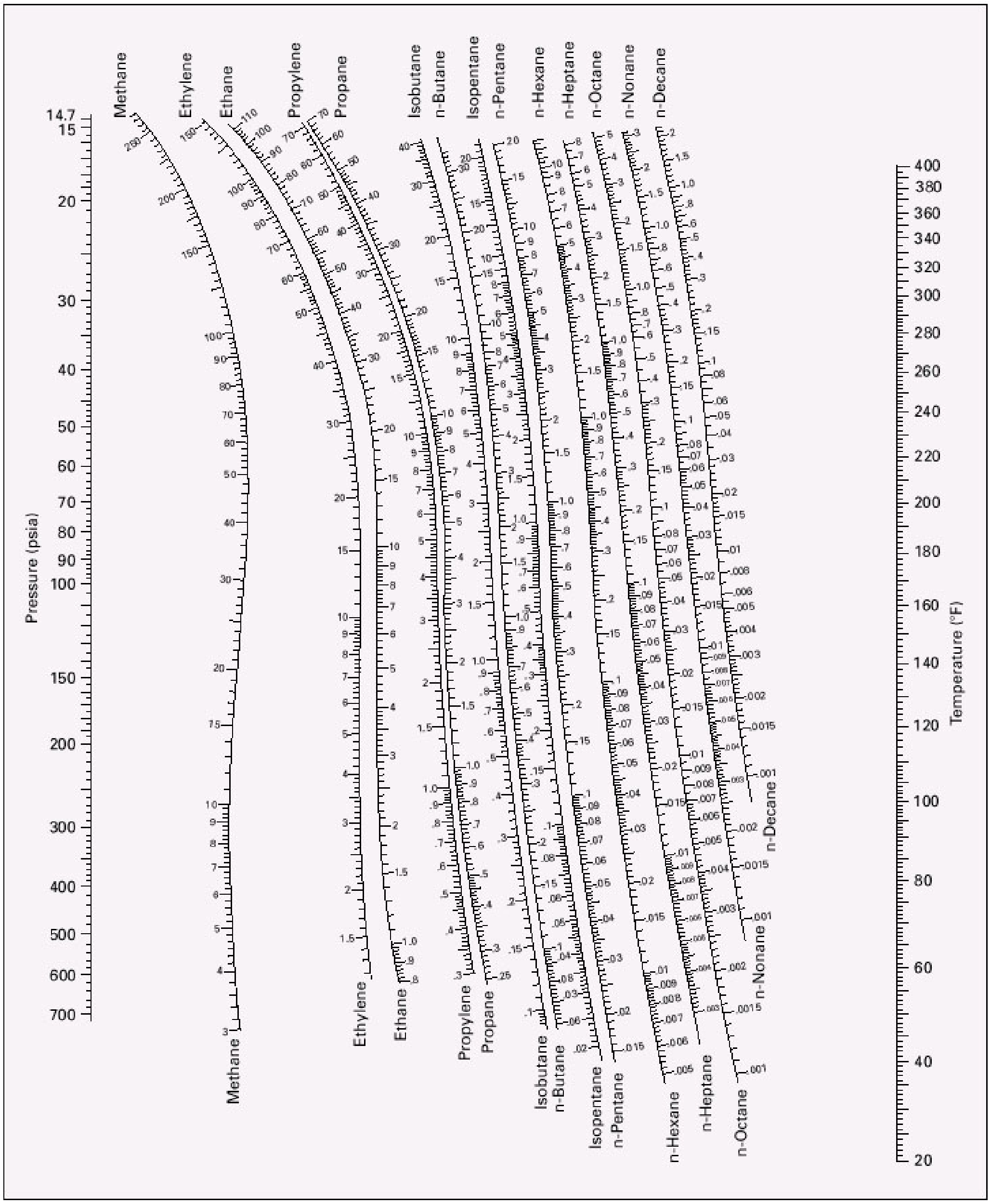
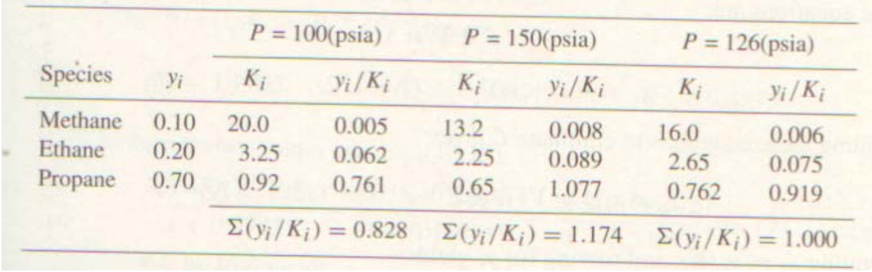


Figure 10.14: *K*-values for systems of light hydrocarbons. High-temperature range. (Reproduced by permission from C. L. DePriester, *Chem. Eng. Progr. Symp. Ser. No. 7*, vol. 49, p. 42, 1953.)

Ex. 10.4:

a- When system is at its dew point:

- **Only an insignificant amount of liquid is present.**
- **The given mole fraction are values of y_i.**
- **For the given T, K-values depend on the choice of P, by trial and error find the value for which equation 10.14 satisfied.**
- **Drew a line between the selected pressure and T=50^{O}F and find k-values.**

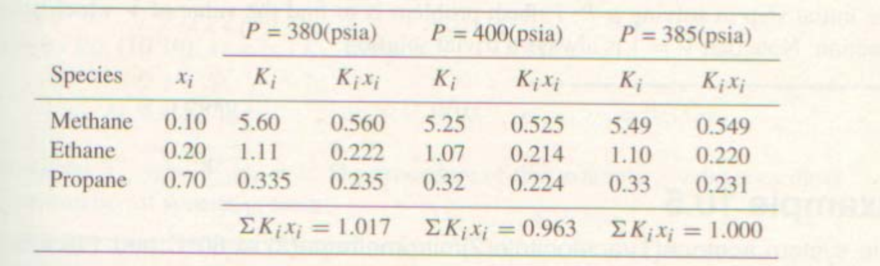


		$P = 100$(psia)		$P = 150$(psia)		$P = 126$(psia)	
Species	y_i	K_i	y_i/K_i	K_i	y_i/K_i	K_i	y_i/K_i
Methane	0.10	20.0	0.005	13.2	0.008	16.0	0.006
Ethane	0.20	3.25	0.062	2.25	0.089	2.65	0.075
Propane	0.70	0.92	0.761	0.65	1.077	0.762	0.919
		$\Sigma(y_i/K_i) = 0.828$		$\Sigma(y_i/K_i) = 1.174$		$\Sigma(y_i/K_i)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

- **Equation 10.14 satisfied when P=126 psia. This is the dew point P. The dew compositions are given by the values of x_i listed in the last column.**

b- The system is completely condensed, it is at its bubble point.

- **The given mole fraction are values of x_i.**
- **By trial and error find the value of P for which k-values satisfy equation 10.13.**
- **Drew a line between the selected pressure and T=50^{O}F and find k-values.**

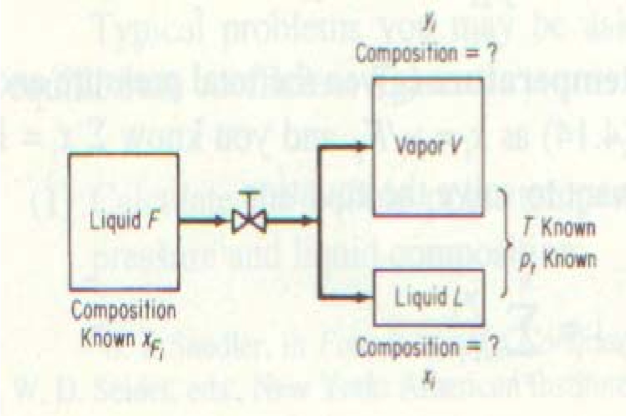


		$P = 380$(psia)		$P = 400$(psia)		$P = 385$(psia)	
Species	x_i	K_i	$K_i x_i$	K_i	$K_i x_i$	K_i	$K_i x_i$
Methane	0.10	5.60	0.560	5.25	0.525	5.49	0.549
Ethane	0.20	1.11	0.222	1.07	0.214	1.10	0.220
Propane	0.70	0.335	0.235	0.32	0.224	0.33	0.231
		$\Sigma K_i x_i = 1.017$		$\Sigma K_i x_i = 0.963$		$\Sigma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

- **Equation 10.13 satisfied when P=385 psia. This is the bubble point P. The bubble compositions are given by the values of y_i listed in the last column.**

Flash Calculations

A liquid at a pressure equal to or greater than its bubble point pressure "flashes" or partially evaporates when the pressure is reduced producing a two phase system of vapor-liquid in equilibrium.



Flash vaporization with V and L in equilibrium

- **L ≡ moles of liquid, with mole fraction [x_i].**
- **V ≡ moles of vapor, with mole fraction [y_i].**
- **Z_i ≡ over all mole fraction.**
- **$L + V = 1$**
- **$Z_i = x_i L + y_i V$**
- **Combine equations to eliminate L and substitute with $x_i = y_i / k_i$ then solve for y_i**

$$y_i = Z_i k_i / 1 + V(k_i - 1) \qquad (10.16)$$

Since $\sum y_i = 1$, then

$$\sum Z_i k_i / 1 + V(k_i - 1) = 1 \qquad (10.17)$$

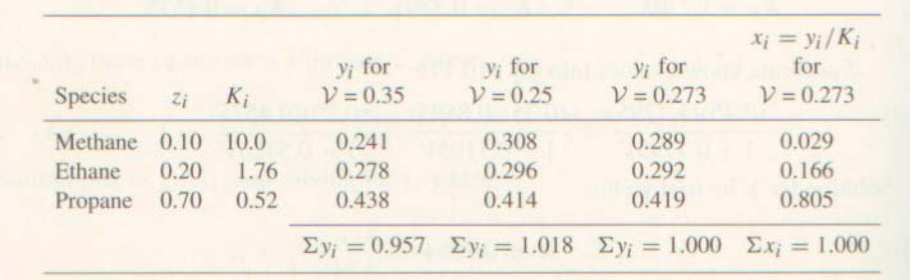
The initial step for solving a P-T flash problem is to find the value of V that satisfies this equation.

Read Ex. 10.5

Flash calculations can also be made for light hydrocarbons with data from figures 10.13 and 10.14.

Ex. 10.6

- The given pressure (200 psia) between bubblepoint and dewpoint pressures as found in Ex.10.4.
- So the system consists of two phases.
- K-values from fig. 10.13.
- By trial and error find value of V for which equation 10.17 satisfied.



Species	z_i	K_i	y_i for $\mathcal{V} = 0.35$	y_i for $\mathcal{V} = 0.25$	y_i for $\mathcal{V} = 0.273$	$x_i = y_i/K_i$ for $\mathcal{V} = 0.273$
Methane	0.10	10.0	0.241	0.308	0.289	0.029
Ethane	0.20	1.76	0.278	0.296	0.292	0.166
Propane	0.70	0.52	0.438	0.414	0.419	0.805
			$\Sigma y_i = 0.957$	$\Sigma y_i = 1.018$	$\Sigma y_i = 1.000$	$\Sigma x_i = 1.000$

- Equation 10.17 satisfied when V=0.273
- The phase compositions are given in the last two columns.