Faculty of Engineering and Technology
Department of Chemical Engineering
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Thermodynamics II

Lec 3: Vapor Liquid Equilibrium-part 3

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Content

- ➢ ***K-value***
- ➢ ***Relative volatility***
- ➢ ***Bubble and dew point calculations***
- ➢ ***Flash separation***

K-value

$$K_i \equiv \frac{y_i}{x_i}$$ is the equilibrium ratio

- ➢ A measure of the tendency of a given chemical species to partition itself preferentially between liquid and vapor phases
- ➢ It does serve as a measure of the "lightness" of a constituent species,

If Raoult's Law is valid,

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

$$K_i = \frac{P_i^{sat}}{P}$$

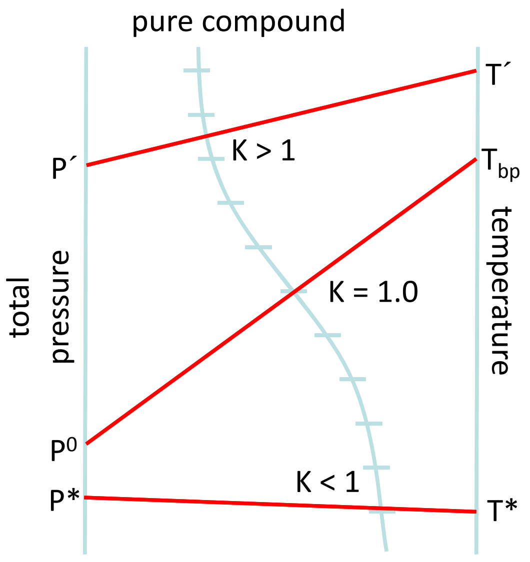
Independent of the V or L composition

If Modified Raoult's Law is valid,

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

$$K_i = \frac{\gamma_i P_i^{sat}}{P}$$

Specify two of (P, T, volatility)



DePriester Chart

Consider a pure compound:

- for a given P, find T_{bp} (i.e., K = 1)
- for a given T, find P_{sat} (i.e., K = 1)
- for a given P, T, find K
  - K > 1 prefers vapor phase
  - K < 1 prefers liquid phase

Don't extrapolate beyond the range of the chart.

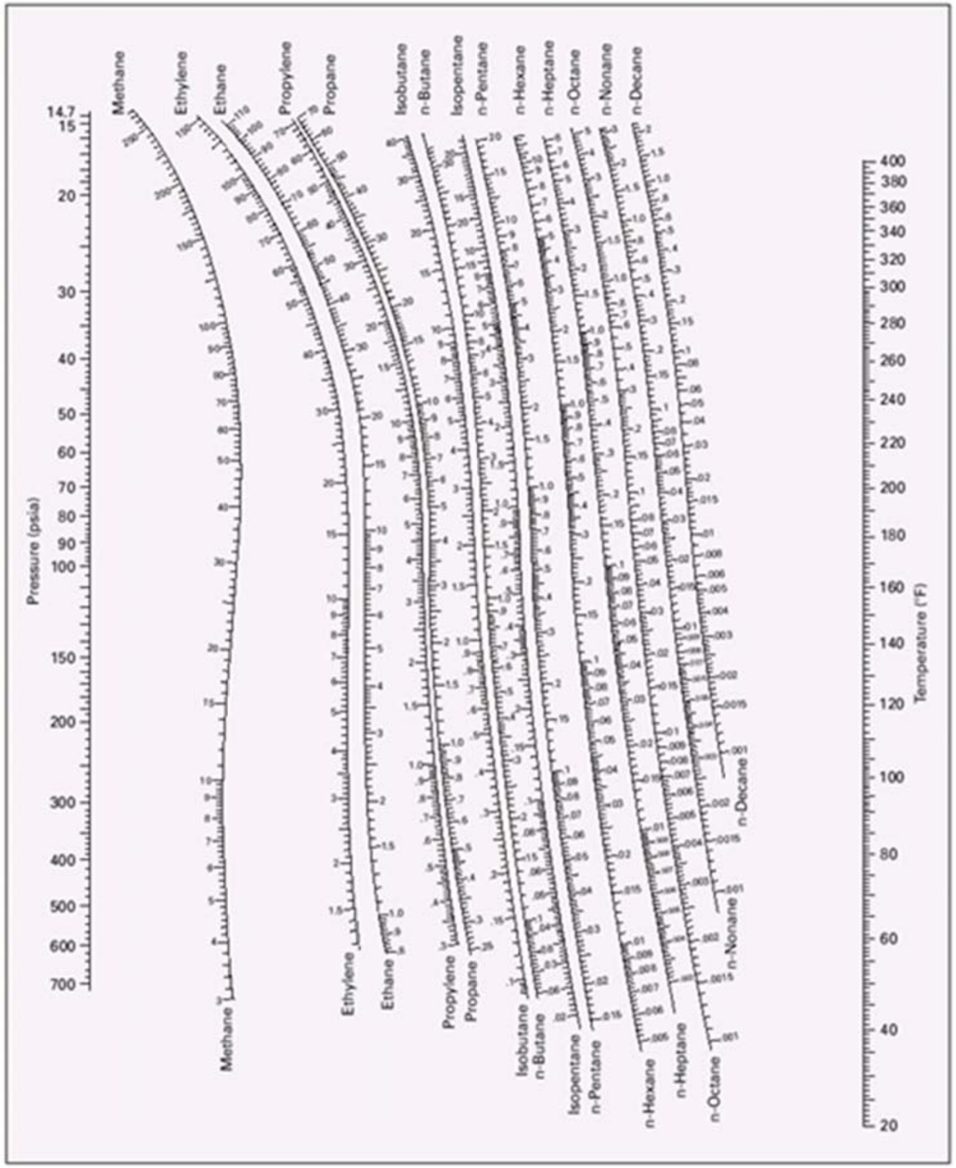


Figure 10.14: K-values for systems of light hydrocarbons. High-temperature range. (Reproduced by permission from C. L. DePriester, *Chem. Eng. Progr. Symp. Ser. No. 7*, vol. 49, p. 42, 1953.)

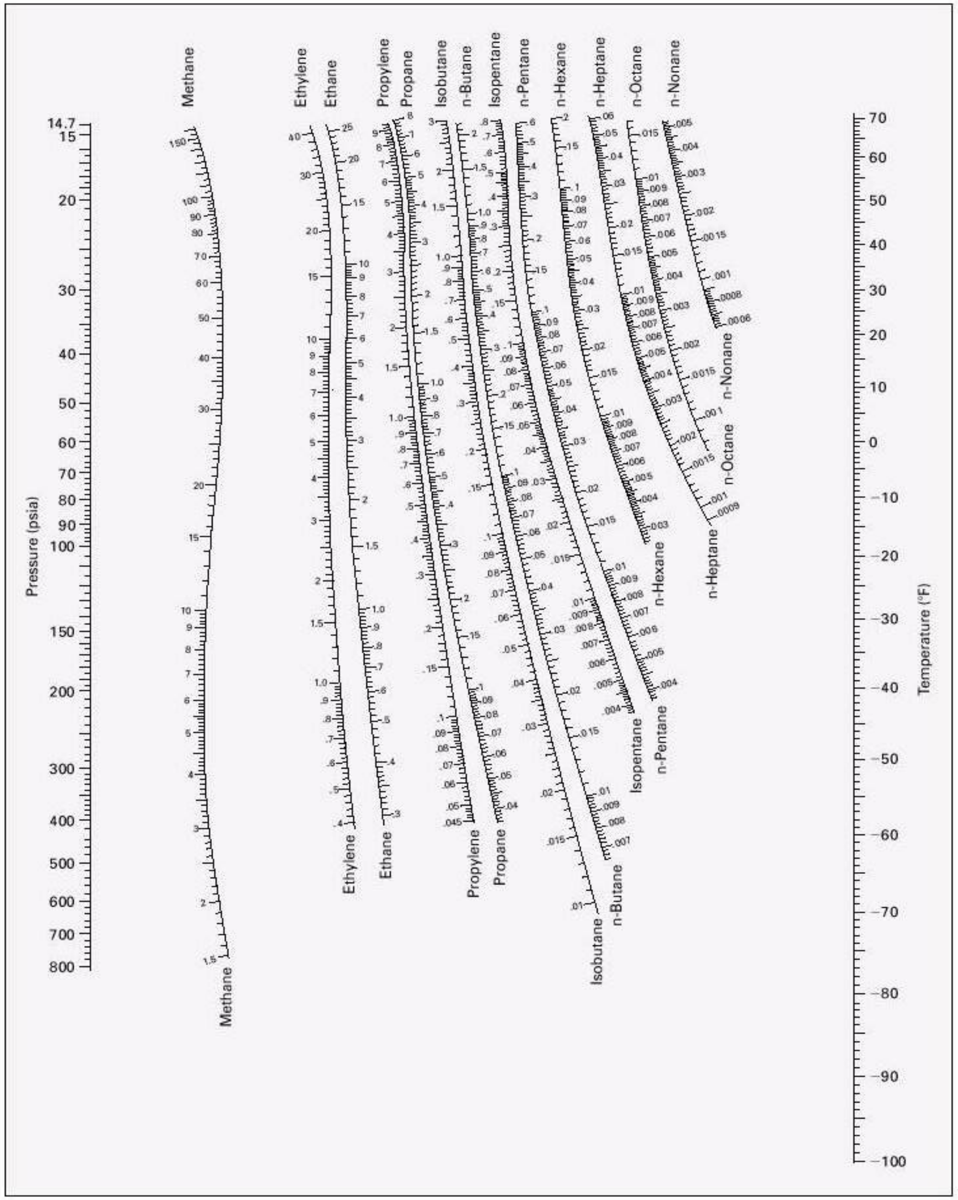


Figure 10.13: K-values for systems of light hydrocarbons. Low-temperature range. (Reproduced by permission from C. L. DePriester, *Chem. Eng. Progr. Symp. Ser. No. 7*, vol. 49, p. 41, 1953.)

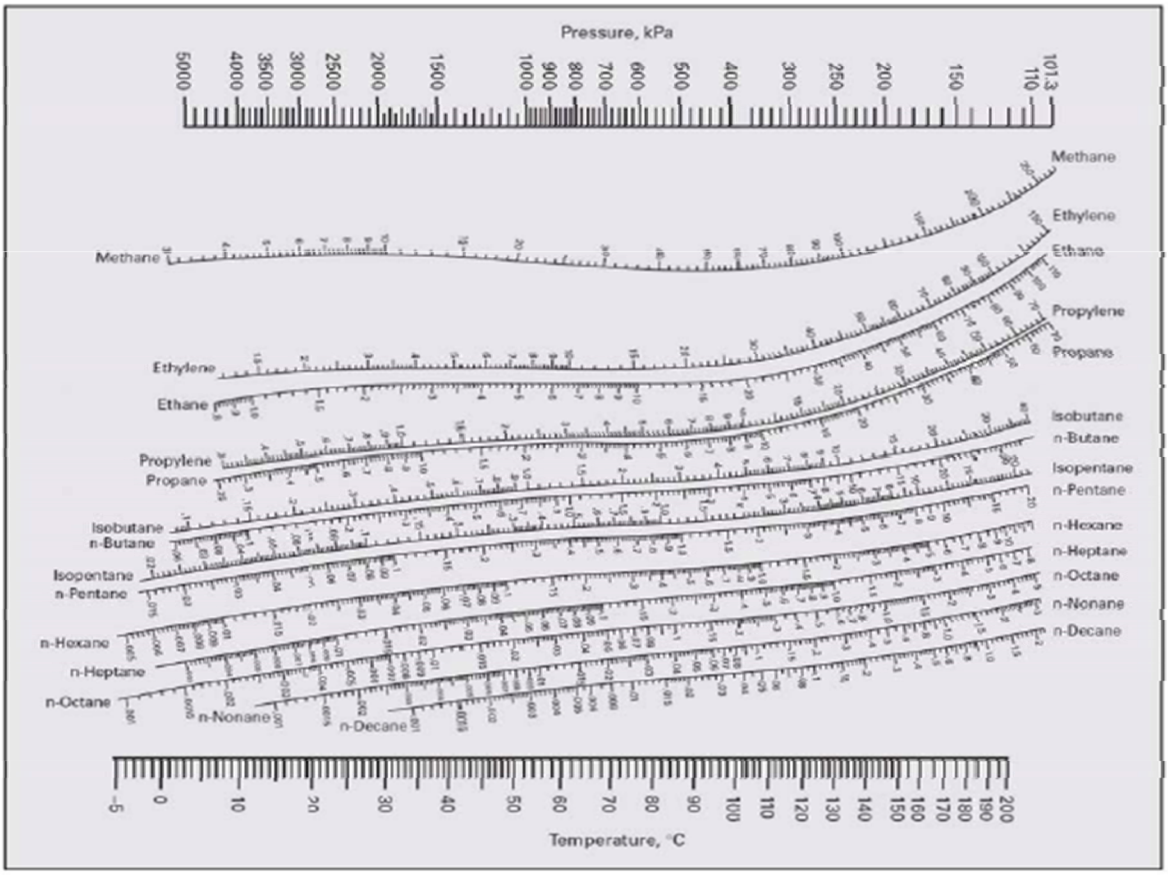


Figure 10.14: *K*-values for systems of light hydrocarbons, high-temperature range (reproduced by permission of the American Institute of Chemical Engineers from D. B. Dadyburjor, *Chemical Engineering Progress*, vol. 74, No. 4, p. 86, 1978)

Figure 2-11 Modified DePriester chart (in S.I. units) at low temperatures

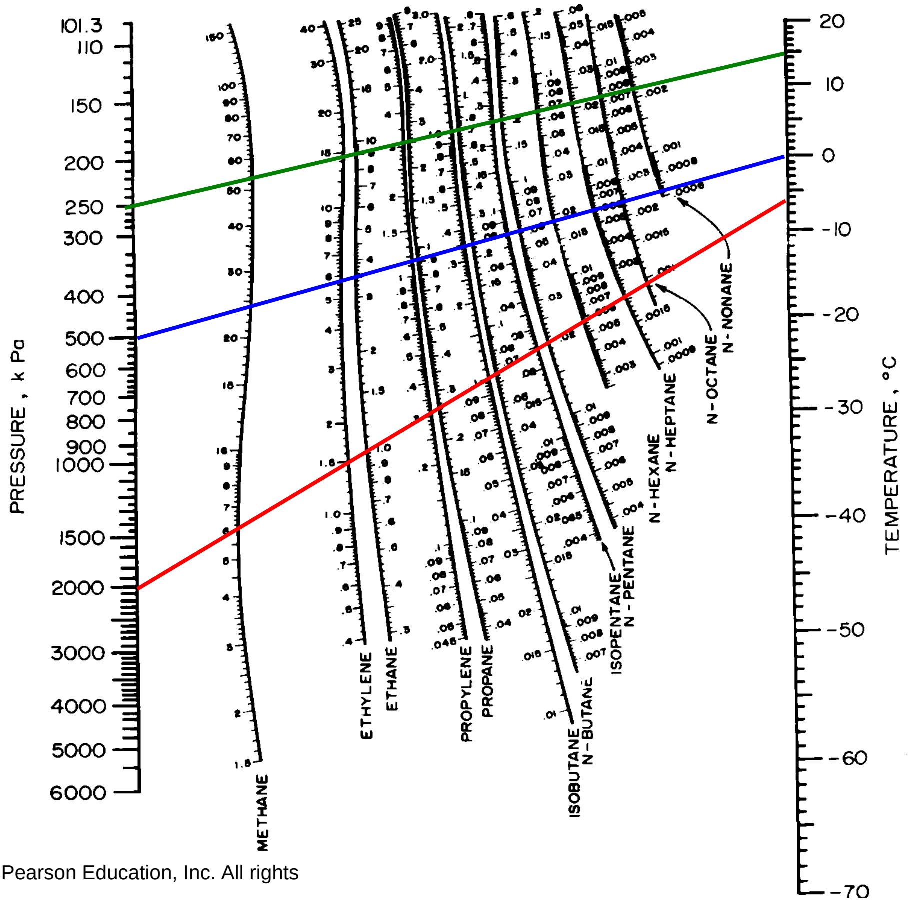
(D. B. Dadyburjor, *Chem. Eng. Prog.*,85, April 1978; copyright 1978, AIChE; reproduced by permission of the American Institute of Chemical Engineers)

At 2000 kPa, what is the boiling point of ethane?

At 15 °C, what is the saturated vapor pressure of isobutane?

At 0 °C and 500 kPa, what is the volatility of n-hexane?

- for a given P, find T_{bp} (i.e., K = 1)
- for a given T, find P_{sat} (i.e., K = 1)
- for a given P, T, find K
  - K > 1 prefers vapor phase
  - K < 1 prefers liquid phase



From *Separation Process Engineering, Third Edition* by Phillip C. Wankat

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Example

- Use the DePriester chart to generate the temperature-composition diagram for isobutane and propane at 1000 kPa.

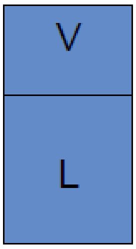
Example Cont.

Example Cont.

Example Cont.

Dew point and Bubble point Calculations

- **For VLE system,**



Overall mole balance

$$T = L + V$$

Component mole balance,

$$Tz_i = Lx_i + Vy_i$$

Let T=1 mol, so V and L are mole fractions,

$$z_i = Lx_i + Vy_i$$

$$z_i = (1-V)x_i + Vy_i \qquad \text{(A)}$$

Note: z_i is overall composition.

Dew point and Bubble point Calculations

Substitute $y_i = K_i x_i$ into (A),

$$z_i = (1-V)x_i + K_i x_i V = x_i(1-V+VK_i) = x_i(1+V(K_i-1))$$

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

Volatility: $K_i = \dfrac{y_i}{x_i}$ (10.10)

Substitute $x_i = \dfrac{y_i}{K_i}$ into (A),

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

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

Dew point and Bubble point Calculations

Also,

$$\sum x_i - \sum y_i = 0$$

$$\sum \frac{z_i}{1+V(K_i-1)} - \sum \frac{z_i K_i}{1+V(K_i-1)} = 0$$

$$\Rightarrow \quad \sum \frac{z_i - z_i K_i}{1+V(K_i-1)} = 0$$

Bubble point Calculations

At bubble point (practically all liquid) L=1, V=0 and $z_i = x_i$

$$\sum \frac{z_i - z_i K_i}{1+V(K_i-1)} = 0 \text{ becomes,}$$

$$\sum (x_i - x_i K_i) = 0$$

$$\sum x_i = \sum x_i K_i$$

$$\Rightarrow \quad \sum x_i K_i = 1$$ Bubblepoint criteria

Bubble point Calculations

If Raoult's Law valid, $y_i P = x_i P_i^{sat}$ ➡ $K_i = \dfrac{P_i^{sat}}{P}$

$$\sum x_i K_i = \sum x_i \frac{P_i^{sat}}{P} = 1 \qquad \text{so,} \quad P = \sum x_i P_i^{sat}$$

see example 10.1

If Modified Raoult's Law valid, $y_i P = x_i \gamma_i P_i^{sat}$ ➡ $K_i = \dfrac{\gamma_i P_i^{sat}}{P}$

$$\sum x_i K_i = \sum x_i \frac{\gamma_i P_i^{sat}}{P} = 1 \qquad \text{so,} \quad P = \sum x_i \gamma_i P_i^{sat}$$

Dew point Calculations

At dewpoint (practically all vapor): L=0, V=1 and $z_i = y_i$

$$\sum \frac{z_i - z_i K_i}{1 + V(K_i - 1)} = 0 \qquad \text{becomes,}$$

$$\sum \frac{y_i - y_i K_i}{K_i} = 0$$

$$\sum \frac{y_i}{K_i} - \sum y_i = 0$$

➡ $\displaystyle\sum \frac{y_i}{K_i} = 1$ Dewpoint criteria

Dew point Calculations

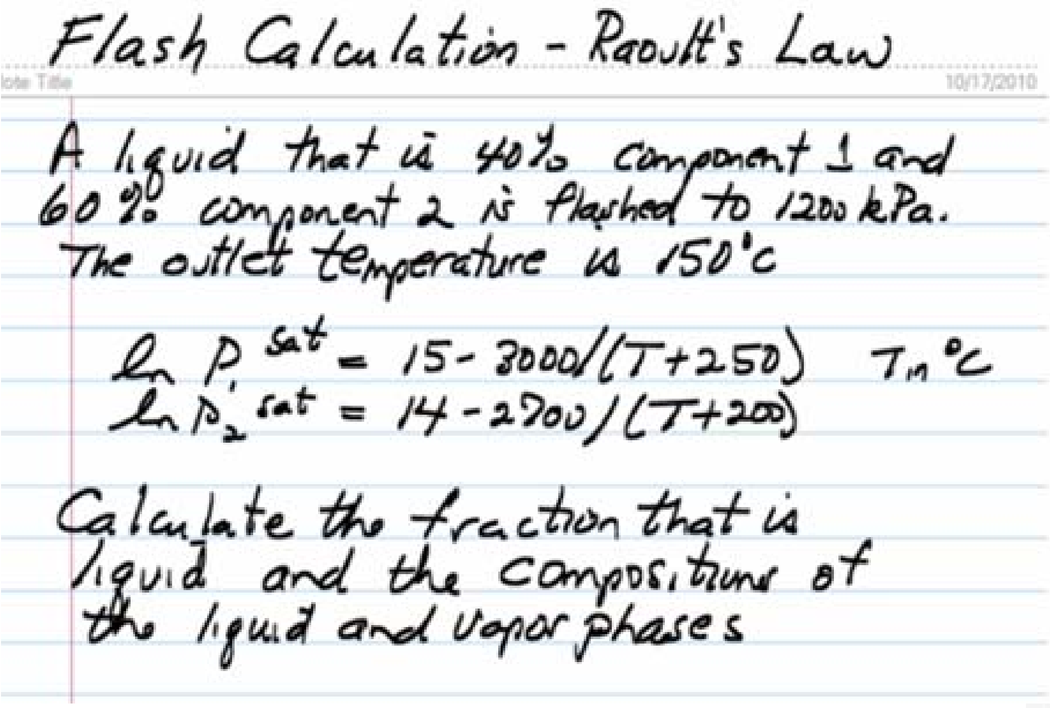
If Raoult's Law valid,

$$\sum \frac{y_i}{K_i} = \sum \frac{y_i}{\frac{P_i^{sat}}{P}} = 1 \qquad P = \frac{1}{\sum \frac{y_i}{P_i^{sat}}}$$

If Modified Raoult's Law valid,

$$\sum \frac{y_i}{K_i} = \sum \frac{y_i}{\frac{\gamma_i P_i^{sat}}{P}} = 1 \qquad P = \frac{1}{\sum \frac{y_i}{\gamma_i P_i^{sat}}}$$

Example



Flash Calculation - Raoult's Law

Note Title 10/17/2010

A liquid that is 40% component 1 and 60% component 2 is flashed to 1200 kPa. The outlet temperature is 150°C

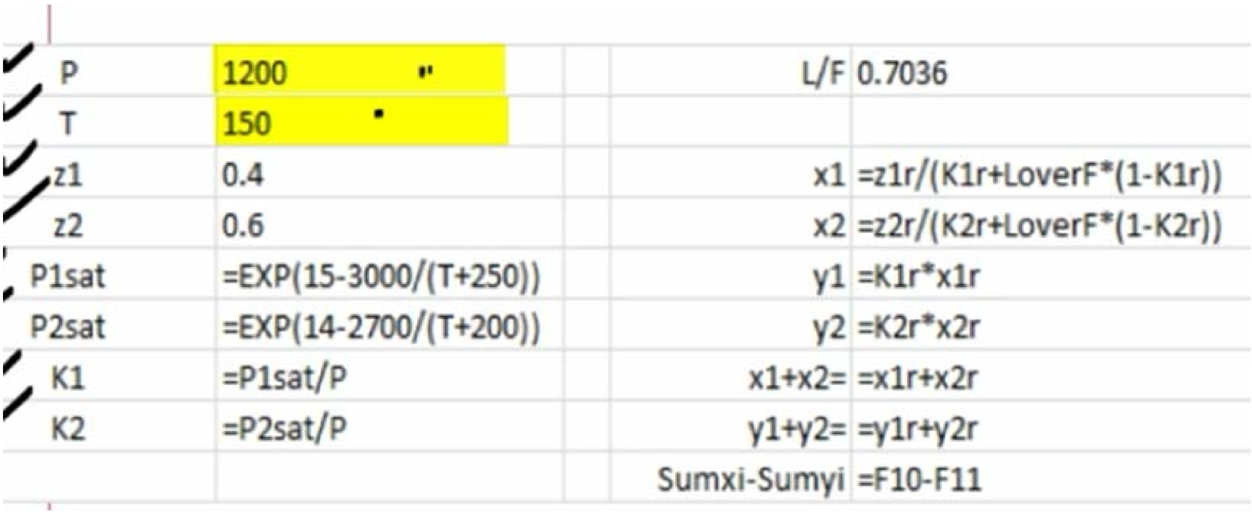
$$\ln P_1^{sat} = 15 - 3000/(T+250) \qquad T \text{ in } ^\circ C$$
$$\ln P_2^{sat} = 14 - 2700/(T+200)$$

Calculate the fraction that is liquid and the compositions of the liquid and vapor phases

Example Cont.

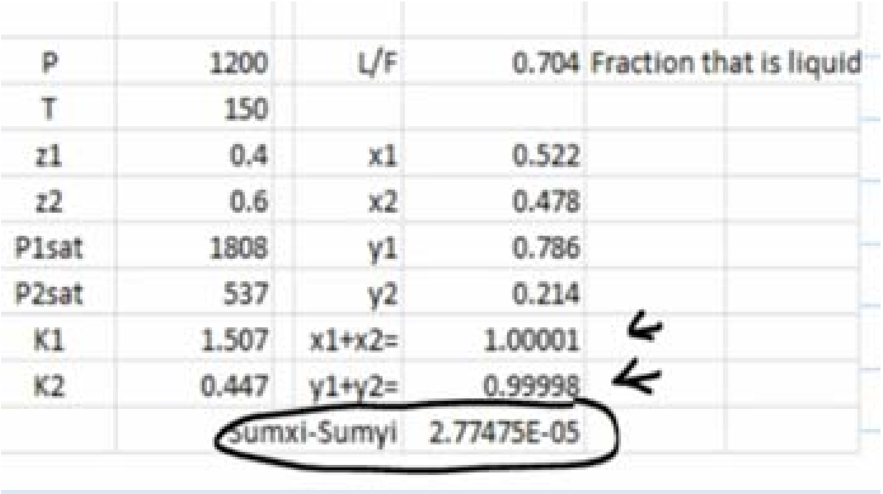
Example Cont.

Example Cont.



P	1200	L/F	0.7036
T	150		
z1	0.4	x1	=z1r/(K1r+LoverF*(1-K1r))
z2	0.6	x2	=z2r/(K2r+LoverF*(1-K2r))
P1sat	=EXP(15-3000/(T+250))	y1	=K1r*x1r
P2sat	=EXP(14-2700/(T+200))	y2	=K2r*x2r
K1	=P1sat/P	x1+x2=	=x1r+x2r
K2	=P2sat/P	y1+y2=	=y1r+y2r
		Sumxi-Sumyi	=F10-F11

Example Cont.



P	1200	L/F	0.704	Fraction that is liquid
T	150			
z1	0.4	x1	0.522	
z2	0.6	x2	0.478	
P1sat	1808	y1	0.786	
P2sat	537	y2	0.214	
K1	1.507	x1+x2=	1.00001	
K2	0.447	y1+y2=	0.99998	
		Sumxi-Sumyi	2.77475E-05	

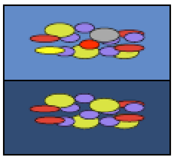
General VLE equilibrium criteria

Consider a multicomponent system in a VLE condition, the fugacity (to be defined in Chapter 11) of species *i* for each phase is given by,

For vapor mixture $\hat{f}_i^v = \hat{\phi}_i y_i P$

For liquid solution $\hat{f}_i^l = \gamma_i x_i f_i$

VLE criteria (to be shown/derived in chapter 11),



$$\hat{f}_i^l = \hat{f}_i^v$$

so $$\hat{\phi}_i y_i P = \gamma_i x_i f_i$$

where,

$\hat{\phi}_i$ fugacity coefficient species i in gas mixture

f_i fugacity of pure species i

γ_i *activity* coefficient of species i in liquid solution

General equilibrium criteria

$\hat{\phi}_i = 1$

For ideal gas vapor mixture in equilibrium with ideal liquid solution

$\gamma_i = 1$

equation becomes $y_i P = x_i f_i$

and also for pure species in equlibrium and ideal gas vapor,

$$f_i = f_i^l = f_i^v = P = P_i^{sat}$$

we get, $y_i P = x_i P_i^{sat}$ Raoult's Law (10.1)

General VLE equilibrium criteria

$$\hat{\phi}_{\mathrm{i}} = 1$$

For ideal-gas mixture in equilibrium with non-ideal liquid solution

$$\cancel{\hat{\phi}_{\mathrm{i}}} y_i P = \gamma_i x_i f_i$$

$$y_i P = \gamma_i x_i P_i^{\mathrm{sat}}$$ Modified Raoult's Law

where γ_i is a function of T and $\mathrm{x_i}$.

Using data from vapor pressure tables

Raoult's Law

vapor pressure

ideal liquid: $P_A = x_A P_A^{sat}(T)$

non-ideal liquid: $P_A = \gamma_A x_A P_A^{sat}(T)$

activity coefficient

Dalton's Law

ideal gas: $y_A = \dfrac{P_A}{P_{TOTAL}}$

non-ideal gas: $y_A = \dfrac{P_A}{\phi_A P_{TOTAL}}$

fugacity coefficient

$$K_A = \frac{y_A}{x_A} = \frac{P_A^{sat}(T)}{\varphi_A P_{TOTAL}} \cong \frac{P_A^{sat}(T)}{P_{TOTAL}}$$

Relative volatility

volatility $$K_A = \frac{y_A}{x_A} = K_A(T)$$ strong function of temperature

relative volatility of A wrt B $$\alpha_{AB} = \frac{K_A}{K_B} = \frac{y_A/x_A}{y_B/x_B}$$ not a strong function of temperature; often assumed independent

for a binary system, substitute and rearrange:

$$y_B = 1 - y_A$$

$$x_B = 1 - x_A$$

$$\boxed{y_A = \frac{\alpha_{AB} x_A}{1 + (\alpha_{AB} - 1) x_A}}$$

Relative volatility

at azeotrope $\alpha_{ik} = \frac{1}{1} = 1$

$\alpha_{ik}>1$ Species i is relatively more volatile
$\alpha_{ik}<1$ Species k is relatively more volatile

If Raoult's Law valid,

$$\alpha_{12} = \frac{P_1^{sat}/P}{P_2^{sat}/P} = \frac{P_1^{sat}}{P_2^{sat}}$$

Note: for higher vapor pressure means more volatile $\alpha_{12}>1$

If Modified Raoult's Law valid,

$$\alpha_{12} = \frac{\gamma_1 P_1^{sat}/P}{\gamma_2 P_2^{sat}/P} = \frac{\gamma_1 P_1^{sat}}{\gamma_2 P_2^{sat}}$$

Relative volatility

For Raoult's Law, $P_b = \sum x_i P_i^{sat}$ (10.2)

$$P_b = \frac{P_k^{sat}}{P_k^{sat}} \sum x_i P_i^{sat} = P_k^{sat} \sum x_i \frac{P_i^{sat}}{P_k^{sat}} = P_k^{sat} \sum x_i \alpha_{ik}$$

where k is a component that arbitrarily chosen.

$$P_b = P_k^{sat} \sum x_i \alpha_{ik} \qquad \text{where } \alpha_{ik} = \frac{P_i^{sat}}{P_k^{sat}}$$

$$\Rightarrow \quad P_k^{sat} = \frac{P_b}{\sum x_i \alpha_{ik}}$$

Also,

$$\ln \alpha_{ik} = \ln \frac{P_i^{sat}}{P_k^{sat}} = \ln P_i^{sat} - \ln P_k^{sat} = \left(A_i - \frac{B_i}{T + C_i} \right) - \left(A_k + \frac{B_k}{T + C_k} \right)$$

Example

Ex: Calculate T_b and y_1, given x_1=0.6 and P=70kPa.

Acetonitrile (1) / nitromethane (2)

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

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

Example cont.

Example cont.

T	α_{12}	P_2^{sat}	T
77.74	1.9611	44.39	76.53
76.53	1.9703	44.24	76.43
76.43	1.9717	44.22	76.42

Answer
(point b)

Bubble point calculation using relative volatility

definition of relative volatility:

$$\alpha_i = \frac{K_i}{K_{ref}} = \frac{y_i / x_i}{K_{ref}}$$

solve for y_i:

$$y_i = \alpha_i x_i K_{ref}$$

sum:

$$\sum_i y_i = 1.0 = \sum_i (\alpha_i x_i) K_{ref}$$

solve for K_{ref}:

$$K_{ref} = \frac{1}{\sum_i \alpha_i x_i}$$

Algorithm:

given a solution composition (x_i values), find relative volatilities (α_i values), then

1. guess $T_{initial}$
2. calculate K_{ref}
3. find $T = T_{bp}$ corresponding to K_{ref}

Ex.: Finding Tbp using relative volatilities

Find the bubble point of a mixture of n-pentane ($x_P = 0.3$), n-hexane ($x_X = 0.3$) and n-heptane ($x_H = 0.4$), at 1 atm total pressure. Find the composition of the first vapor bubble.

Example cont.

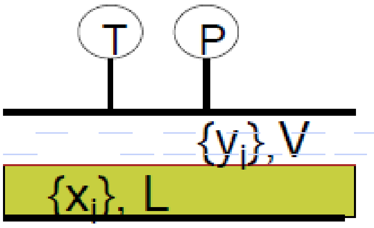
Fin

Flash separation

- Another type of vapor-liquid equilibrium problem, and one that is more important for mass **balances for** designing separation equipment, is computing the two-phase equilibrium state when VLE either a liquid of known composition is partially vaporized or a vapor is partially condensed as a result of a change in temperature and/or pressure. This is referred to as a flash calculation.
- The term *flash* arises from the fact that if the pressure is suddenly lowered (or the temperature raised) on a mixture that is at its boiling temperature, it will flash-vaporize; that is, there will be a sudden partial vaporization of the liquid.
- The partial vaporization or partial condensation problem is somewhat more difficult to solve than bubble point and dew point calculations for the following reason:
- In a bubble point calculation an infinitesimal amount of vapor is produced, so the liquid composition is that of the original mixture; and
- In a dew point calculation, an infinitesimal amount of liquid forms, so the vapor composition is that of the original mixture.

Flash separation

- 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 and liquid in equilibrium.
- Flash calculation refers to any calculation of the quantities and compositions of the vapor and liquid phases making up a two-phase system in equilibrium at known T, P, and overall composition



- Consider a system containing **1 mol** with overall composition ***z***z_i (given) ***L*** the moles of liquid, ***V*** the moles of vapor

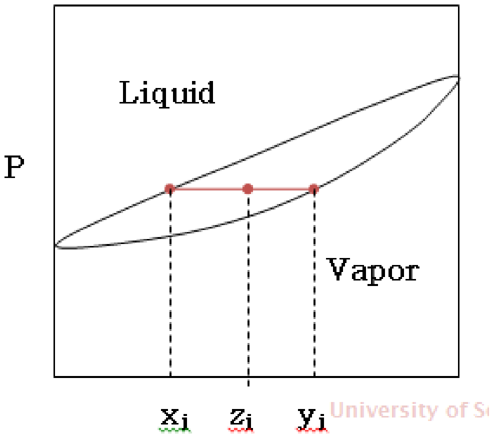
$$1 = L + V \qquad \textbf{(A)}$$

$$z_i = x_i L + y_i V \qquad i = 1, 2, \ldots, N \qquad \textbf{(B)}$$

Eq. (A) × z_i ➡ $$z_i = z_i L + z_i V \qquad \textbf{(C)}$$

Flash separation

Eq. (B) – Eq. (C) ➡ $$L(z_i - x_i) = V(y_i - z_i)$$ **Lever rule**



- **Substituting** $x_i = y_i / K_i$

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \qquad i = 1, 2, \ldots, N$$

- **Because** $\sum y_i = 1$

➡ $$\sum_i \frac{z_i K_i}{1 + V(K_i - 1)} = 1$$

Flash separation

Solution is by trial and error.

Guess V until the summation term equal to 1.
But………

………first we need to know whether the system is actually two-phase.

In general ……

If $P_d < P < P_b$, two phase or If $T_b < T < T_d$, two phase

Example

Example 10.5 acetone (1) / acetonitrile (2) / nitromethane (3)

T = 80°C P = 110 kPa and z_1 = 0.45 z_2 = 0.35 z_3 = 0.20

Example Cont.

Example Cont.