MODULE 6

Lecture No. 48

Date: 22.10.2018

VAPOR-LIQUID EQUILIBRIA

Criteria for Thermodynamic Equilibrium

$T^{\alpha} = T^{\beta}$ (Thermal equilibrium)

$P^{\alpha} = P^{\beta}$ (Mechanical equilibrium)

$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta}$ (Chemical equilibrium)

where $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are two different phases,

$\hat{f}_i$ is fugacity of species $\boldsymbol{i}$ in solution.

Vapor-Liquid Equilibrium

$T^V = T^L$ (Thermal equilibrium)

$P^V = P^L$ (Mechanical equilibrium)

$\boldsymbol{\hat{f}_i^V = \hat{f}_i^L \text{ ---- } -(1)}$ (Chemical equilibrium)

(Starting point for all phase equilibrium calculations)

where V and L are vapor and liquid phases respectively,

$\hat{f}_i$ is fugacity of species $\boldsymbol{i}$ in solution.

Vapor-Liquid Equilibrium

Computation of fugacity of a species in vapor:

Equation of state (EoS)

Computation of fugacity of a species in liquid:

Equation of state (EoS) or

activity coefficient (excess Gibbs energy) models

Two different approaches

If an equation of state is used to describe both phases, the approach is known as

φ-φ method

i.e. fugacity coefficients for the liquid and vapor phases are computed from ***an equation of state***.

If activity coefficient model is used for liquid phase and an equation of state for the vapor phase, the approach is known as

γ-φ method

γ-φ approach

Fugacity coefficient of species *i* in vapor is defined as:

$$\hat{\phi}_i^V = \frac{\hat{f}_i^V}{y_i P} ----(2)$$

Activity coefficient of species *i* in liquid solution is defined as:

$$\gamma_i = \frac{\hat{f}_i^L}{x_i f_i^L} ----(3)$$

From Eq.(1), Eq.(2) and Eq.(3):

$$\hat{\phi}_i^V y_i P = \gamma_i x_i f_i^L ----(4)$$

Ideal gas + Ideal solution

In case of ideal gas, $\hat{\phi}_i^V = 1$

and

In case of ideal solution, $\gamma_i = 1$ and $f_i^L = p_i^{sat}$

$Equation\ (4)\ reduces\ to$:

$$y_i P = x_i\, p_i^{sat} \text{ ---- } (5)$$

Dewpoint and Bubblepoint Calculations

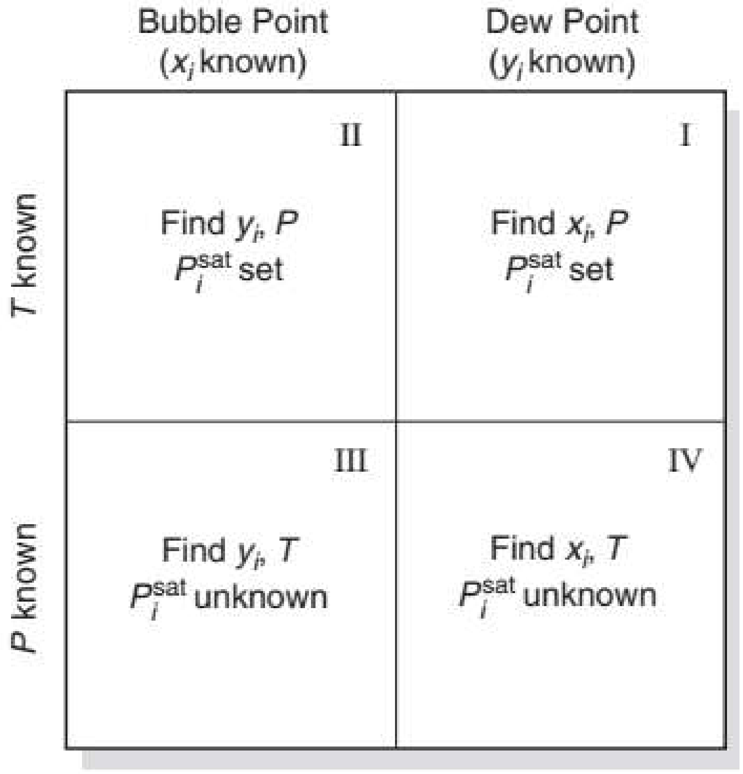
VLE problems with other combinations of variables are possible, engineering interest centres on ***dewpoint*** and ***Bubblepoint*** calculations; there are four classes:

BUBL P: Given $\{x_i\}$ and T, Calculate $\{y_i\}$ and P

BUBL T: Given $\{x_i\}$ and P, Calculate $\{y_i\}$ and T

DEW P: Given $\{y_i\}$ and T, Calculate $\{x_i\}$ and P

DEW T: Given $\{y_i\}$ and P, Calculate $\{x_i\}$ and T



	Bubble Point (x_i known)	Dew Point (y_i known)
T known	II Find y_i, P P_i^{sat} set	I Find x_i, P P_i^{sat} set
P known	III Find y_i, T P_i^{sat} unknown	IV Find x_i, T P_i^{sat} unknown

Grid of common VLE calculations.

Problem 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:

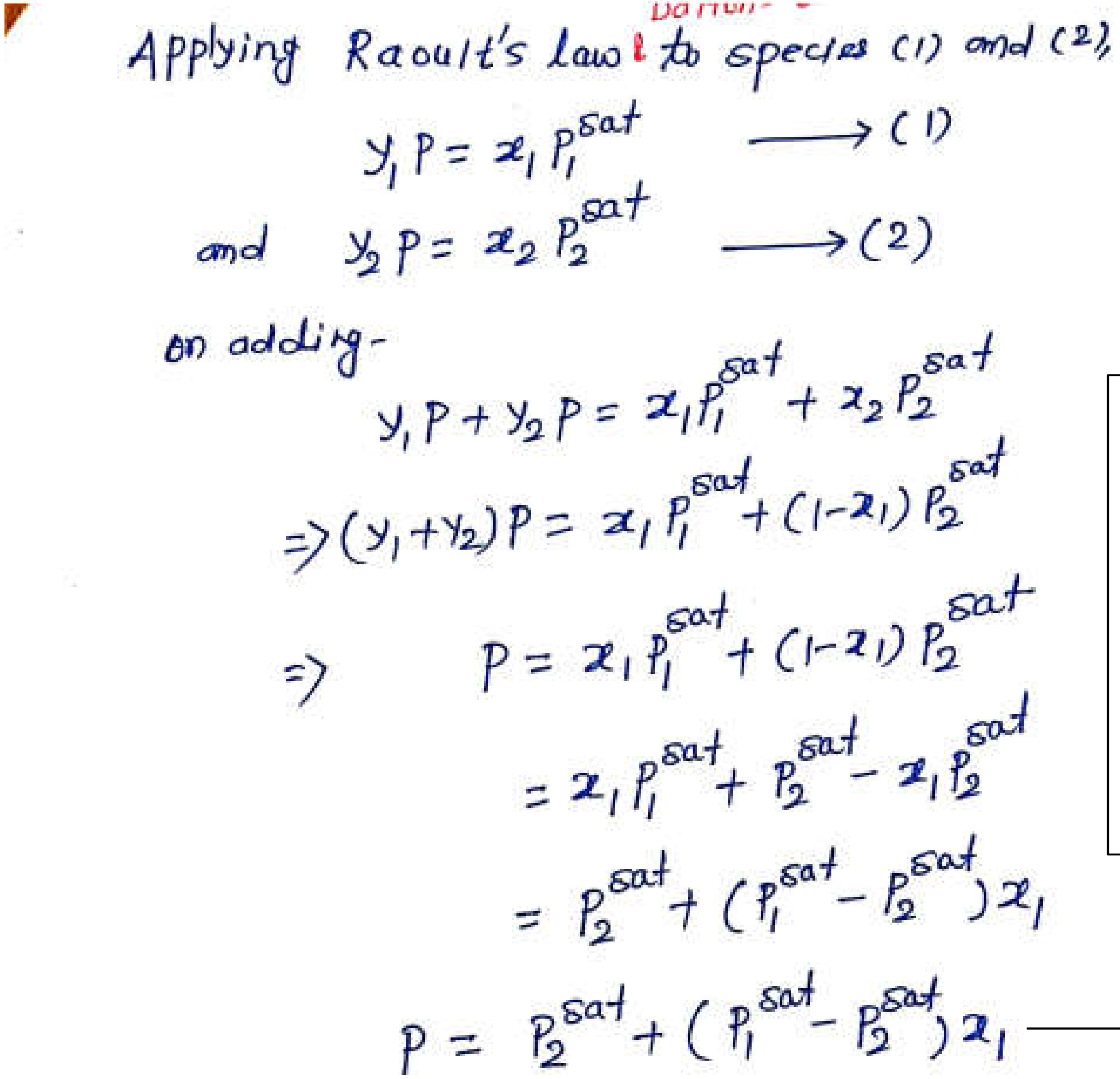
$$\ln P_1^{sat}/kPa = 14.2724 - \frac{2945.47}{T - 49.15}$$

$$\ln P_2^{sat}/kPa = 14.2043 - \frac{2972.64}{T - 64.15}$$

(a) Prepare a graph showing ***y_1 vs. x_1*, *P vs. x_1*** and ***P vs. y_1*** for a temperature of 75 °C (348.15 K).

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

Solution 1 (a): *BUBL P*



Applying Raoult's law to species (1) and (2),

$$y_1 P = x_1 P_1^{sat} \longrightarrow (1)$$

and

$$y_2 P = x_2 P_2^{sat} \longrightarrow (2)$$

on adding-

$$y_1 P + y_2 P = x_1 P_1^{sat} + x_2 P_2^{sat}$$

$$\Rightarrow (y_1 + y_2) P = x_1 P_1^{sat} + (1 - x_1) P_2^{sat}$$

$$\Rightarrow \quad P = x_1 P_1^{sat} + (1 - x_1) P_2^{sat}$$

$$= x_1 P_1^{sat} + P_2^{sat} - x_1 P_2^{sat}$$

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

$$P = P_2^{sat} + (P_1^{sat} - P_2^{sat}) x_1 \longrightarrow (3)$$

Using Eq. **(3)**,
total pressure
Can be calculated for
different values of x_1.

Once total pressure (P) is
known, y_1 can be
calculated using Eq. **(1)**.

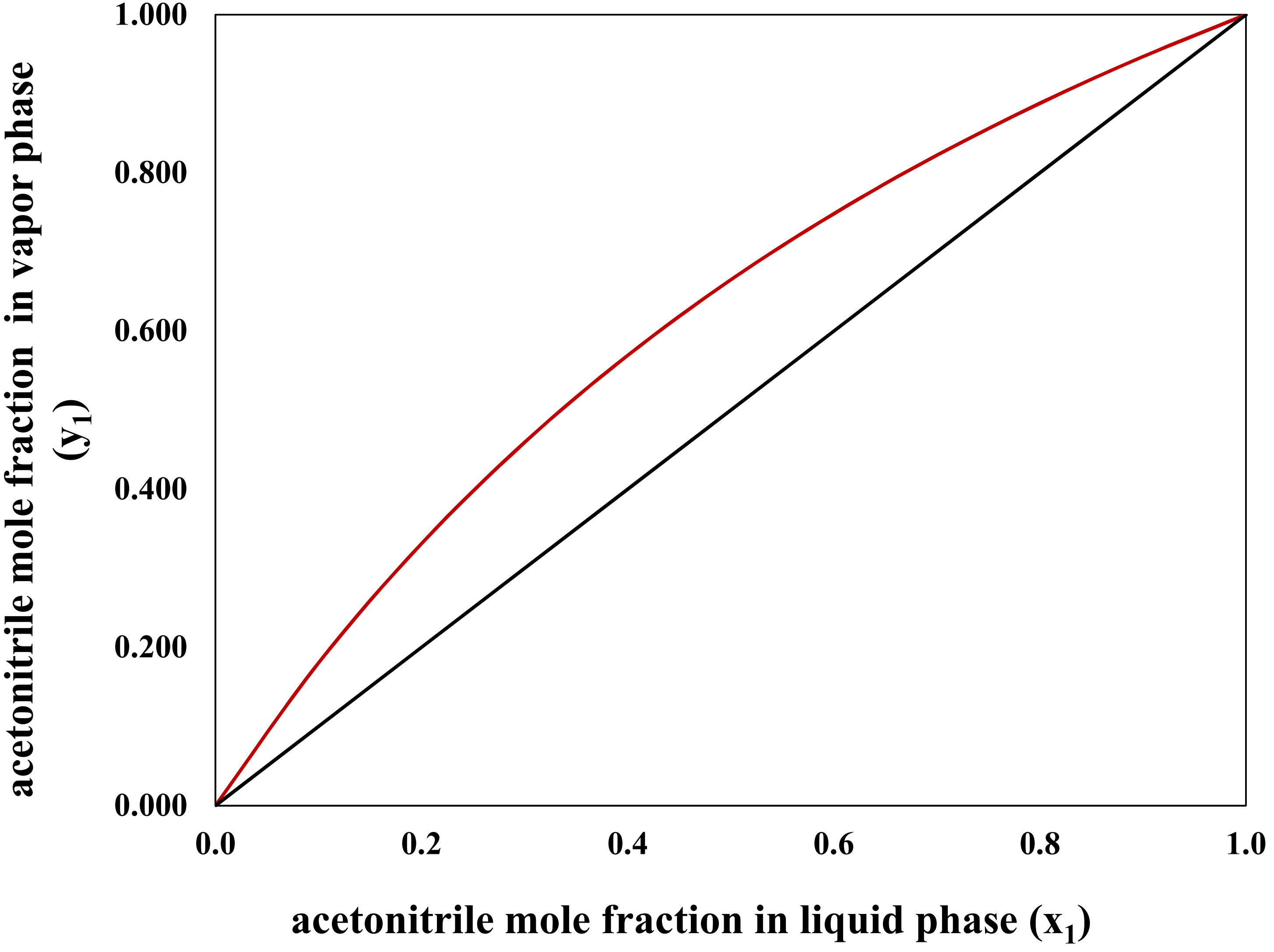
Solution 1 (a): *BUBL P*

acetonitrile (1) and nitromethane (2) **T = 348.15 K**

Raoult's Law

x_1	P (kPa)	y_1
0.0	41.98	0.000
0.1	46.10	0.180
0.2	50.23	0.331
0.3	54.35	0.459
0.4	58.47	0.569
0.5	62.60	0.665
0.6	66.72	0.748
0.7	70.84	0.822
0.8	74.96	0.888
0.9	79.09	0.947
1.0	83.21	1.000

Solution 1 (a): y_1-x_1 diagram at 75 °C ***BUBL P***



THANK YOU

MODULE 6

Lecture No. 49

Date: 23.10.2018

Dewpoint and Bubblepoint Calculations

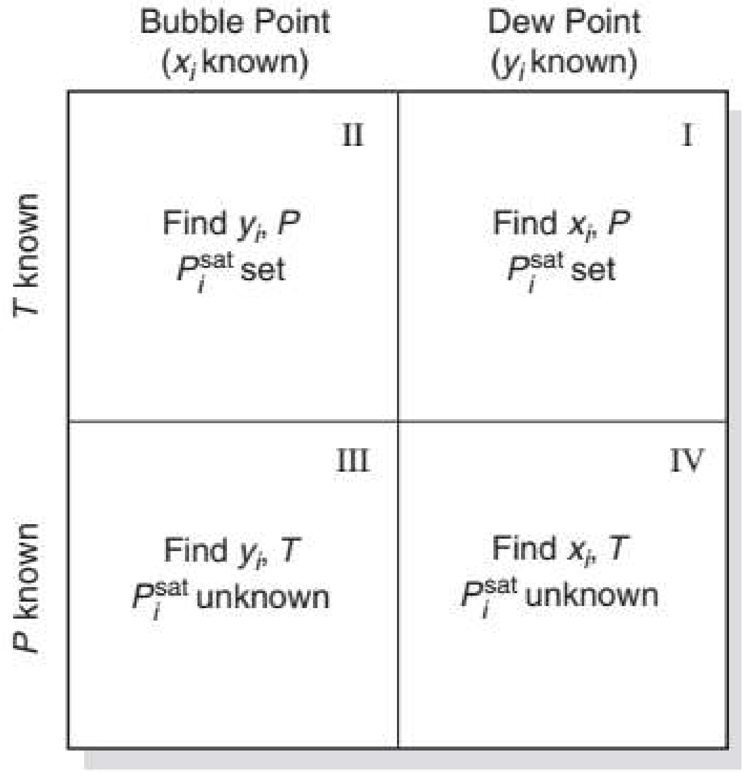
VLE problems with other combinations of variables are possible, engineering interest centres on ***dewpoint*** and ***Bubblepoint*** calculations; there are four classes:

BUBL P: Given $\{x_i\}$ and T, Calculate $\{y_i\}$ and P

BUBL T: Given $\{x_i\}$ and P, Calculate $\{y_i\}$ and T

DEW P: Given $\{y_i\}$ and T, Calculate $\{x_i\}$ and P

DEW T: Given $\{y_i\}$ and P, Calculate $\{x_i\}$ and T



	Bubble Point (x_i known)	Dew Point (y_i known)
T known	II Find y_i, P P_i^{sat} set	I Find x_i, P P_i^{sat} set
P known	III Find y_i, T P_i^{sat} unknown	IV Find x_i, T P_i^{sat} unknown

Grid of common VLE calculations.

Problem 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:

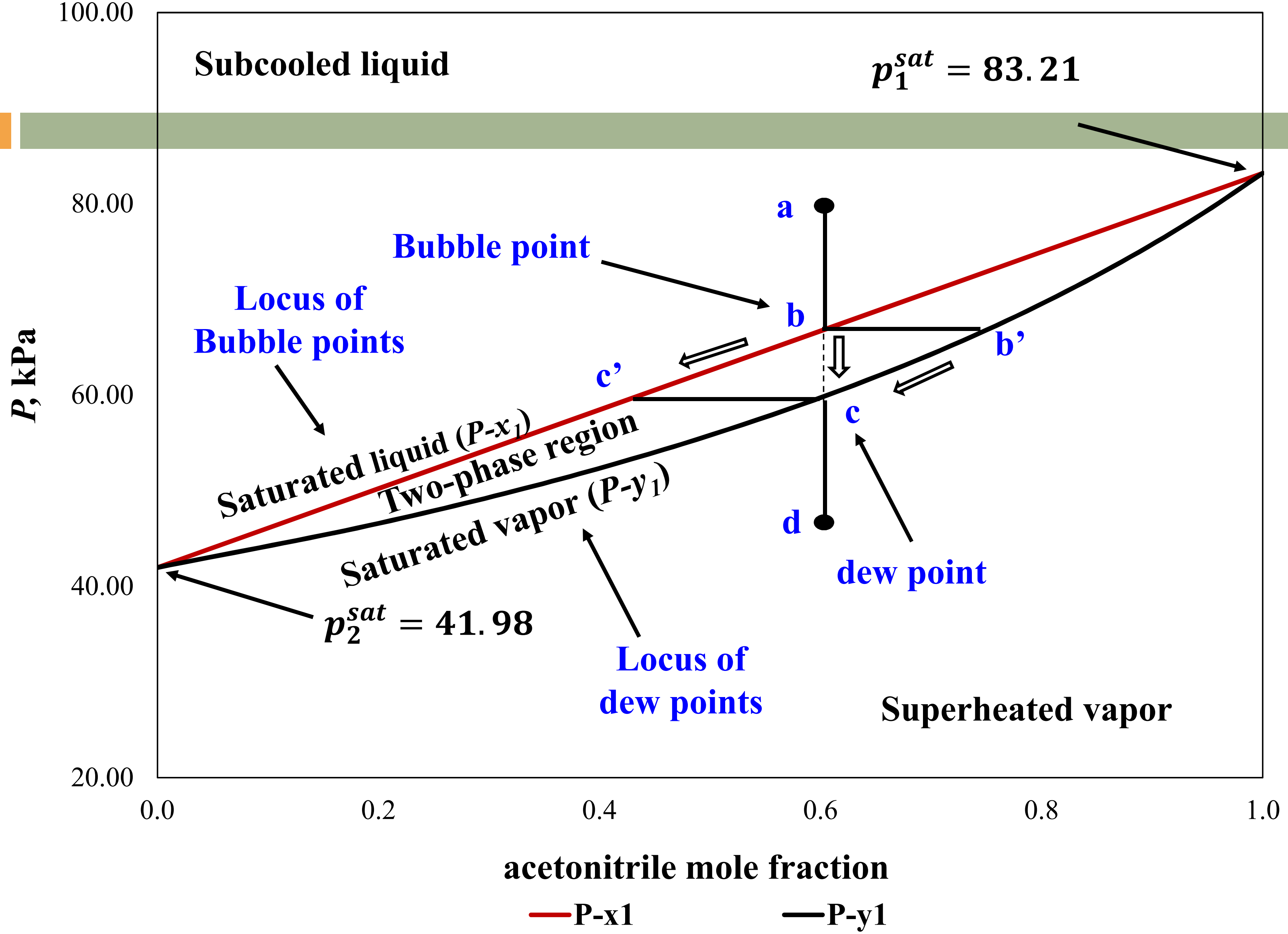
$$\ln P_1^{sat}/kPa = 14.2724 - \frac{2945.47}{T - 49.15}$$

$$\ln P_2^{sat}/kPa = 14.2043 - \frac{2972.64}{T - 64.15}$$

(a) Prepare a graph showing y_1 **vs.** x_1, P **vs.** x_1 and P **vs.** y_1 for a temperature of 75 °C (348.15 K).

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

Solution 1 (a): P vs. x_1 and P vs. y_1 diagram at 75 °C ***BUBL P***



Solution 1 (a): *BUBL P*

Description of Figure in slide no. 4:

- This figure is a phase diagram on which the straight line labelled ***P-x_1*** represents states of saturated liquid; the subcooled-liquid region lies above this line.
- The curve ***P-y_1*** represents states of saturated vapour; the superheated-vapour region lies below this line.
- Points lying between the saturated liquid and saturated vapour lines are in the two-phase region, where saturated liquid and saturated vapour coexist in equilibrium.
- ***P-x_1*** and ***P-y_1*** lines meet at the edges of the diagram, where saturated liquid and saturated vapour of the pure species coexist at the vapor pressures P_1^{sat} and P_2^{sat}.

Solution 1 (a): *BUBL P*

Description of Figure in slide no. 4:

- Imagine a subcooled liquid mixture of 60 mol% acetonitrile and 40 mol% nitromethane at 75 °C. Its state is represented by point ***a***.
- Now reduce the pressure while maintaining the system at equilibrium at 75 °C.
- When the pressure reaches the value at point ***b***, the system is saturated liquid on the verge of vaporizing. A minuscule further decrease in pressure produces a bubble of vapor, represented by point ***b'***. The two points b and b' (x_1=0.6, P=66.72 kPa and y_1=0.748) together represent the state determined by earlier calculations. Point ***b*** is a bubble point, and the ***P*-x_1** line is the locus of bubble points.

Solution 1 (a): *DEW P*

Description of Figure in slide no. 4:

- As the pressure is further reduced, the amount of vapor increases and the amount of liquid decreases, with the states of the two phases following paths ***b’c*** and ***bc’*** respectively.
- Finally as point ***c*** is approached, the liquid phase represented by point ***c’***, has almost disappeared, with only droplets (dew) remaining. Point ***c*** is therefore a dew point, and the P-y_1 curve is the locus of dewpoints. Once the dew has evaporated, only saturated vapor at point ***c*** remains, and further pressure reduction leads to superheated vapor at point ***d***.

Solution 1 (a): *DEW P*

The composition of the vapor at point ***c*** is y_1=0.6, but the composition of the liquid at point ***c'*** and the pressure must be either be read from the graph or calculated.

This is ***DEW P*** calculation:

Applying Raoult's Law and Dalton's law to species (1) and (2)

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

$$\Rightarrow \quad x_1 = \frac{y_1 P}{P_1^{sat}} \longrightarrow (1)$$

and,

$$x_2 = \frac{y_2 P}{P_2^{sat}} \longrightarrow (2)$$

Adding Eq^n. (1) and Eq^n. (2)

$$x_1 + x_2 = \frac{y_1 P}{P_1^{sat}} + \frac{y_2 P}{P_2^{sat}}$$

$$\Rightarrow \quad 1 = \left(\frac{y_1}{P_1^{sat}} + \frac{y_2}{P_2^{sat}}\right) P$$

Solution 1 (a): *DEW P*

$$\boxed{P = \frac{1}{\left[\frac{y_1}{P_1^{sat}} + \frac{y_2}{P_2^{sat}}\right]}} \longrightarrow (3)$$

For $y_1 = 0.6$ and $t = 75°C$,

$$P = \frac{1}{\left(\frac{0.6}{83.21} + \frac{0.4}{41.98}\right)} = \underline{\underline{59.74}} \text{ kpa}$$

From eqn. (1),

$$x_1 = \frac{y_1 P}{P_1^{sat}} = \frac{0.6 \times 59.74}{83.21} = \underline{\underline{0.4308}}$$

This is the liquid-phase composition at point c'.

THANK YOU

MODULE 6

Lecture No. 50

Date: 24.10.2018

VAPOR-LIQUID EQUILIBRIA

Dewpoint and Bubblepoint Calculations

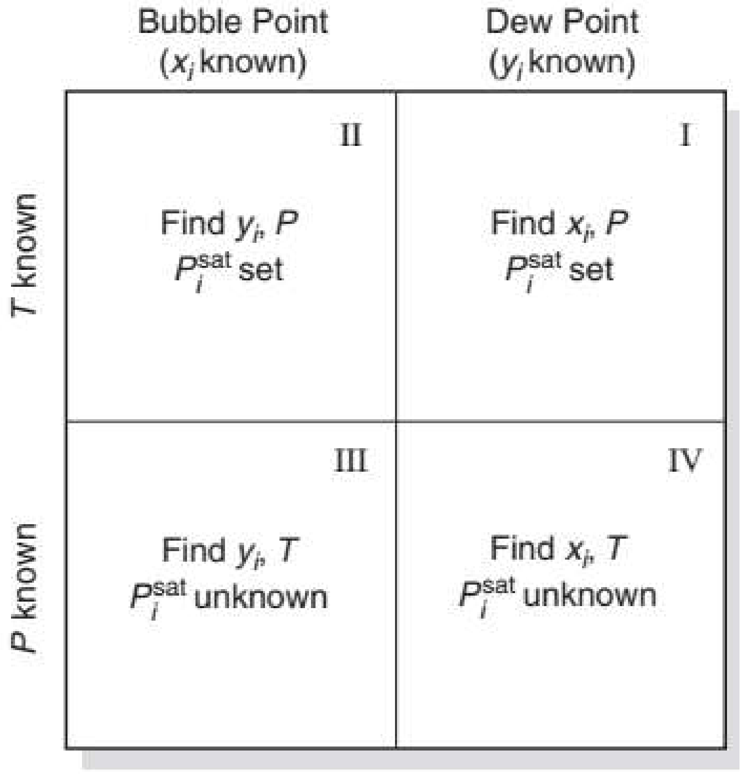
VLE problems with other combinations of variables are possible, engineering interest centres on ***dewpoint*** and ***Bubblepoint*** calculations; there are four classes:

BUBL P: Given $\{x_i\}$ and T, Calculate $\{y_i\}$ and P

BUBL T: Given $\{x_i\}$ and P, Calculate $\{y_i\}$ and T

DEW P: Given $\{y_i\}$ and T, Calculate $\{x_i\}$ and P

DEW T: Given $\{y_i\}$ and P, Calculate $\{x_i\}$ and T



	Bubble Point (x_i known)	Dew Point (y_i known)
T known	II Find y_i, P P_i^{sat} set	I Find x_i, P P_i^{sat} set
P known	III Find y_i, T P_i^{sat} unknown	IV Find x_i, T P_i^{sat} unknown

Grid of common VLE calculations.

Problem 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:

$$\ln P_1^{sat}/kPa = 14.2724 - \frac{2945.47}{T - 49.15}$$

$$\ln P_2^{sat}/kPa = 14.2043 - \frac{2972.64}{T - 64.15}$$

(a) Prepare a graph showing ***y_1 vs. x_1, P vs. x_1*** and ***P vs. y_1*** for a temperature of 75 °C (348.15 K).

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

Problem 1 (b)

When pressure ***P*** is fixed, the temperature varies along with $\boldsymbol{x_1}$ and $\boldsymbol{y_1}$. For a given pressure, the temperature range is bounded by saturation temperatures $\boldsymbol{T_1^{sat}}$ and $\boldsymbol{T_2^{sat}}$, the temperatures at which the pure species exert vapor pressures equal to ***P***.

These temperatures are calculated from the given Antoine equations:

$$\ln P_1^{sat}/kPa = 14.2724 - \frac{2945.47}{T - 49.15}$$

On arrangement,

$$T_1^{sat} = \frac{2945.47}{14.2724 - \ln P_1^{sat}} + 49.15$$

For $P_1^{sat} = 70$ kPa, $\boldsymbol{T_1^{sat}}$**=342.99 K**.

Problem 1 (b)

$$\ln P_2^{sat}/kPa = 14.2043 - \frac{2972.64}{T - 64.15}$$

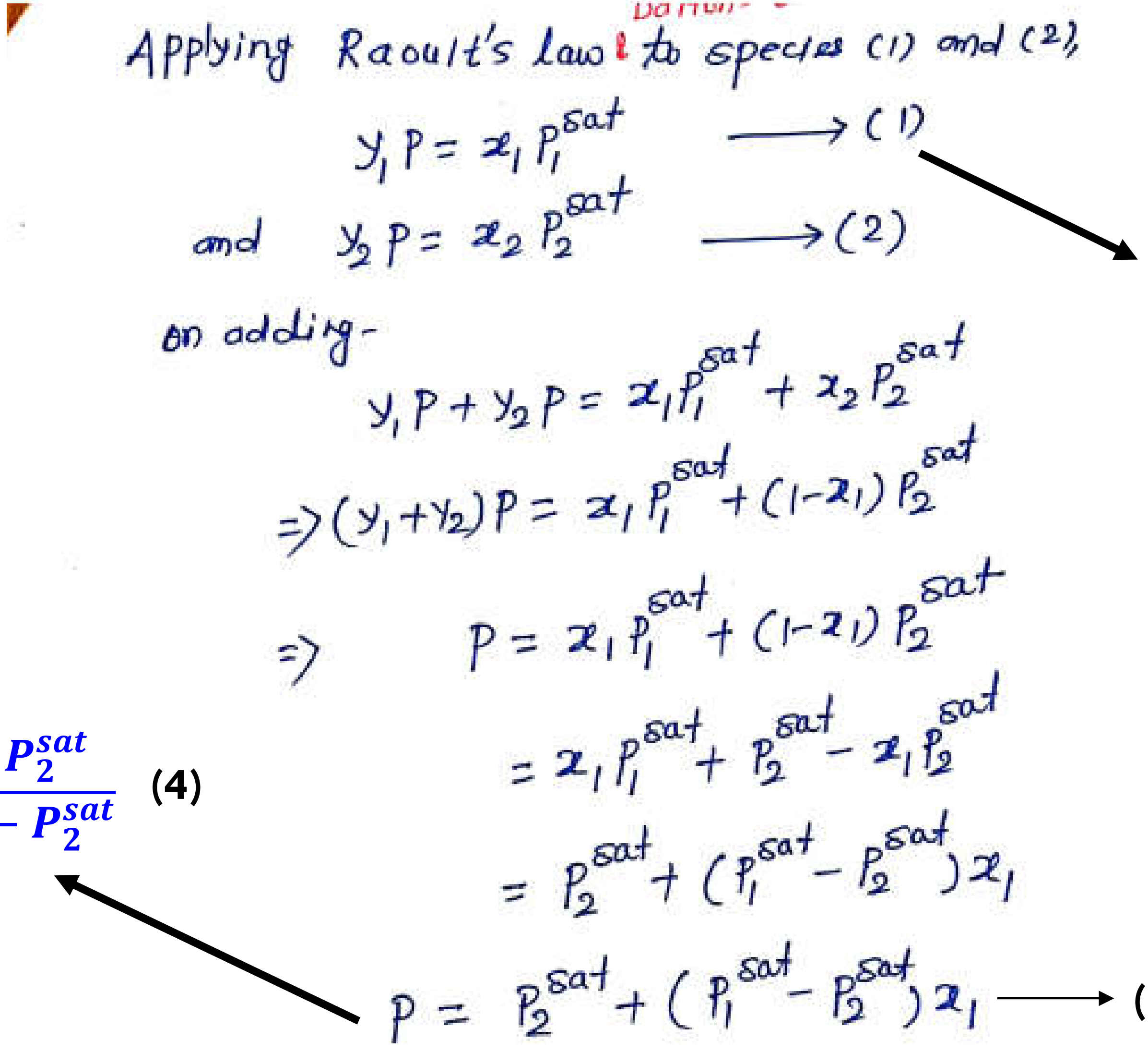
On arrangement,

$$T_2^{sat} = \frac{2972.64}{14.2043 - \ln P_2^{sat}} + 64.15$$

For $P_2^{sat} = 70$ kPa, $\boldsymbol{T_2^{sat}}$**=362.73 K**.

*The simplest way to prepare a ***T-x_1-y_1*** diagram is to select values of ***T*** between these two temperatures, calculate $\boldsymbol{P_1^{sat}}$ and $\boldsymbol{P_2^{sat}}$ for these temperatures, and evaluate ***x_1*** and ***y_1*** by the following expression (***see next slide***):

Solution 1 (b):



Applying Raoult's law to species (1) and (2),

$$y_1 P = x_1 P_1^{sat} \longrightarrow (1)$$

and $$y_2 P = x_2 P_2^{sat} \longrightarrow (2)$$

on adding -

$$y_1 P + y_2 P = x_1 P_1^{sat} + x_2 P_2^{sat}$$

$$\Rightarrow (y_1 + y_2) P = x_1 P_1^{sat} + (1 - x_1) P_2^{sat}$$

$$\Rightarrow \quad P = x_1 P_1^{sat} + (1 - x_1) P_2^{sat}$$

$$= x_1 P_1^{sat} + P_2^{sat} - x_1 P_2^{sat}$$

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

$$P = P_2^{sat} + (P_1^{sat} - P_2^{sat}) x_1 \longrightarrow (3)$$

$$y_1 = \frac{x_1 P_1^{sat}}{P} \quad (5)$$

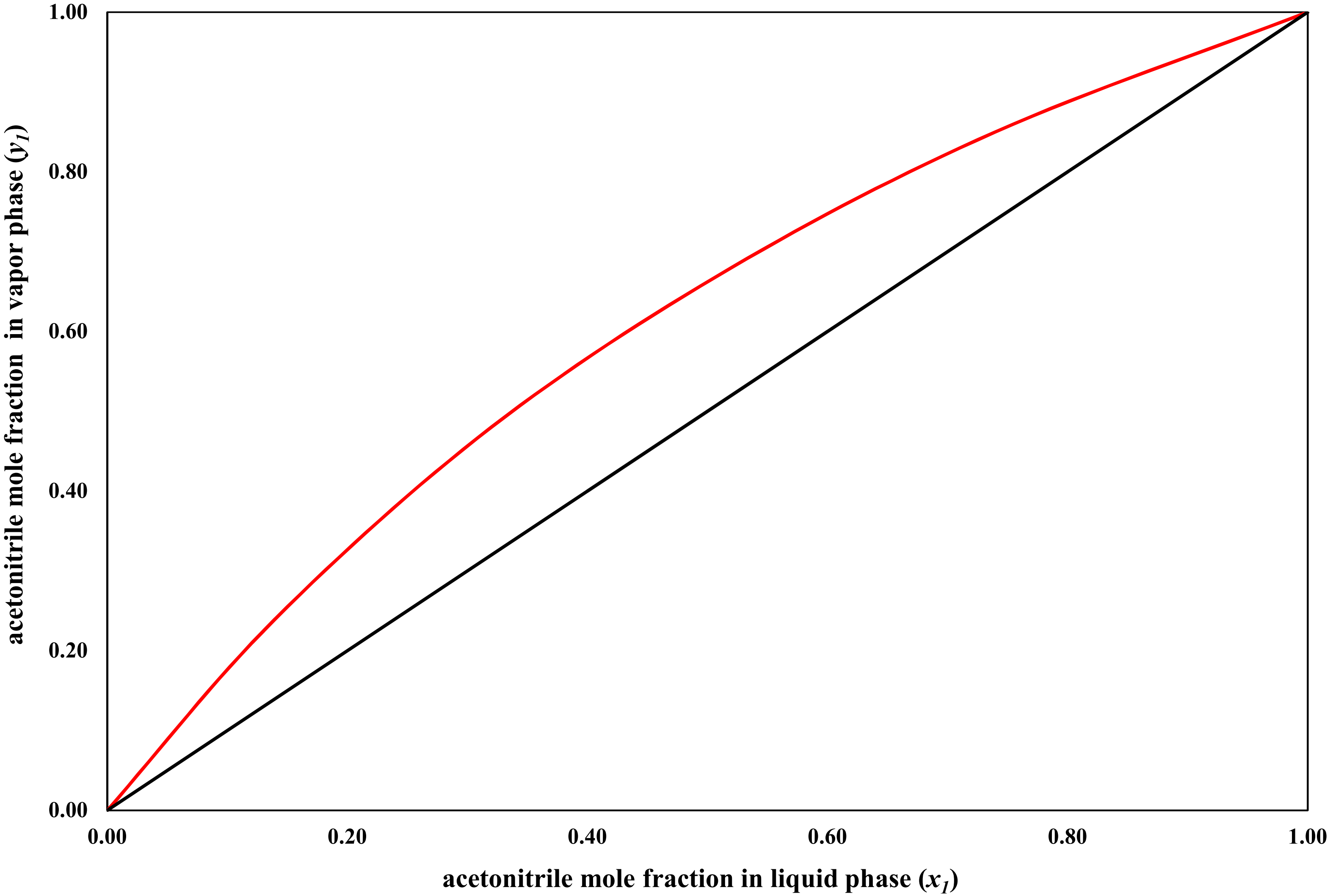
$$x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}} \quad (4)$$

Solution 1 (b):

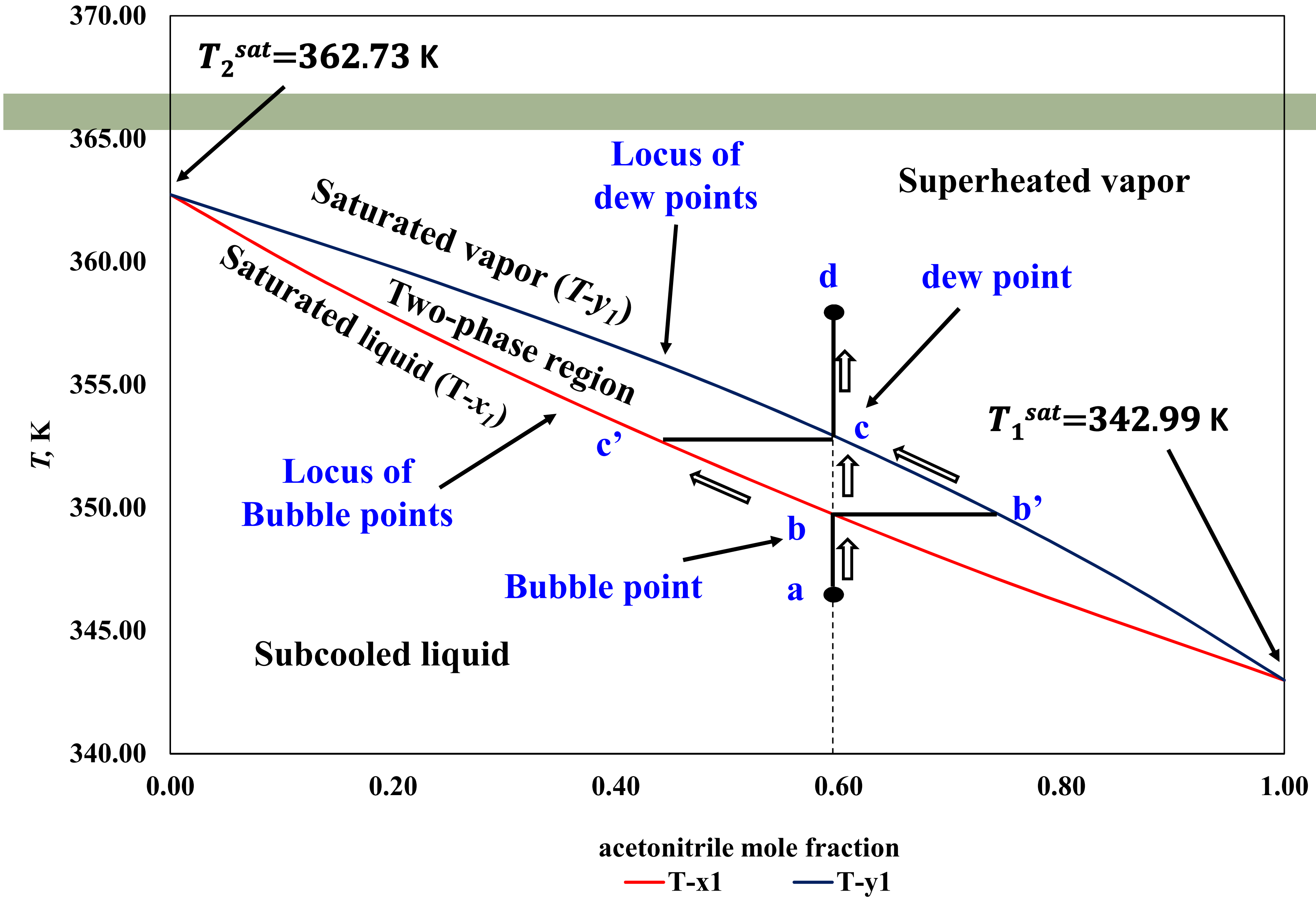
acetonitrile (1) and nitromethane (2)

T/K	x_1	y_1
362.73	0.00	0.00
359.15	0.14	0.24
355.15	0.32	0.48
351.15	0.52	0.68
347.15	0.74	0.85
342.99	1.00	1.00

Solution 1 (b): y_1-x_1 diagram at 70 kPa



Solution 1 (b): T vs. x_1 and P vs. y_1 diagram at 70 kPa



Solution 1 (b):

Description of Figure in slide no. 10:

- This figure is a phase diagram on which the curve labelled $T\text{-}y_1$ represents states of saturated vapor; the superheated vapor region lies above this line.
- The curve $T\text{-}x_1$ represents states of saturated liquid; the subcooled liquid region lies below this line.
- Points lying between the saturated liquid and saturated vapour lines are in the two-phase region, where saturated liquid and saturated vapour coexist in equilibrium.

Solution 1 (b):

Description of Figure in slide no. 10:

- Imagine a subcooled liquid mixture of 60 mol% acetonitrile and 40 mol% nitromethane at 70 kPa. Its state is represented by point ***a***.
- Now increase the temperature while maintaining the system at equilibrium at 70 kPa.
- When the temperature reaches the value at point ***b***, the system is saturated liquid on the verge of vaporizing. A minuscule further increase in temperature produces a bubble of vapor, represented by point ***b'***. Point ***b*** is a bubble point, and the T-x_1 line is the locus of bubble points.

Solution 1 (b): ***BUBL T***

The composition of the liquid at point ***b*** is x_1=0.6, but the composition of the vapor at point ***b'*** and the temperature must be either be read from the graph or calculated.

This is ***BUBL T*** calculation.

Solution 1 (b): *BUBL T*

STEP-1: Guess a Temperature and calculate P_1^{sat} & P_2^{sat} using Antoine equation.

STEP-2: Calculate total pressure (P_{calc}) using Eqn. (3).

STEP-3: Calculate $del\,p = P_{calc} - P_{given}$;

if $del\,P < 1E\text{-}5$ (convergence criterion), P has converged.

Otherwise, return to STEP-1.

Final values:

T = 349.57 K, P_1^{sat}=87.18 kPa, P_2^{sat} = 44.23 kPa, y_1=0.7473.

Solution 1 (b): *DEW T*

Description of Figure in slide no. 10:

As the heating process continues beyond point ***b***, the amount of vapor increases and the amount of liquid decreases. During this process, the vapor- and liquid-phase compositions change as indicated by paths ***b'c*** and ***bc'*** , until the dew point is reached at point ***c***, where the last droplets of liquid disappear. The ***T-y***$_1$ curve is the locus of dew points.

The vapor composition at point ***c*** is y_1=0.6, but the composition of the liquid at point ***c'*** and the temperature must be either be read from the graph or calculated.

This is ***DEW T*** calculation.

Solution 1 (b): *DEW T*

Applying Raoult's law and Dalton's law to species (1) and (2)

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

$$\Rightarrow \quad x_1 = \frac{y_1 P}{P_1^{sat}} \longrightarrow (1)$$

and,

$$x_2 = \frac{y_2 P}{P_2^{sat}} \longrightarrow (2)$$

Adding Eqn. (1) and Eqn. (2)

$$x_1 + x_2 = \frac{y_1 P}{P_1^{sat}} + \frac{y_2 P}{P_2^{sat}}$$

$$\Rightarrow \quad 1 = \left(\frac{y_1}{P_1^{sat}} + \frac{y_2}{P_2^{sat}}\right) P$$

$$\boxed{P = \frac{1}{\left[\frac{y_1}{P_1^{sat}} + \frac{y_2}{P_2^{sat}}\right]}} \longrightarrow (3)$$

Solution 1 (b): *DEW T*

STEP-1: Guess a Temperature and calculate P_1^{sat} & P_2^{sat} using Antoine equation.

STEP-2: Calculate total pressure (P_{calc}) using Eqn. (3).

STEP-3: Calculate $del\,p = P_{calc} - P_{given}$;

if $del\,P < 1E\text{-}5$ (convergence criterion), P has converged.

Otherwise, return to STEP-1.

Final values:

$T = 352.72$ K, $P_1^{sat} = 96.51$ kPa, $P_2^{sat} = 49.56$ kPa, $x_1 = 0.4352$.

THANK YOU

Problem

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

$\ln \gamma_1 = A x_2^2$ $\ln \gamma_2 = A x_1^2$ where $A = 2.771 - 0.00523\,T$

In addition, the following Antoine equations provide vapor pressures:

$$\ln P_1^{sat}/kPa = 16.59158 - \frac{3643.31}{T\ [K] - 33.424}$$

$$\ln P_2^{sat}/kPa = 14.25326 - \frac{2665.54}{T\ [K] - 53.424}$$

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 $y_1 = 0.40$

BUBBLE PRESSURE CALCULATION

(*BUBL P*)

Part (a): *BUBL P*

Given: x_i and T.

Calculate: y_i and P.

Equations

Writing Modified Raoult's law and Dalton's law for components:

$$y_1P = x_1\gamma_1P_1^{sat} ---- -(1)$$

$$y_2P = x_2\gamma_2P_2^{sat} ---- -(2)$$

Adding Eqn. (1) and (2),

$$y_1P + y_2P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat}$$

$$(y_1+y_2)P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat}$$

Since, $(y_1+y_2)=1$

$$P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat} ---- -(3)$$

ALGORITHM

STEP-1: Calculate P_1^{sat} & P_2^{sat} at given temperature (T) using Antoine equation.

$$P_1^{sat} = 44.51 \text{ kPa}; P_2^{sat} = 65.64 \text{ kPa}$$

STEP-2: Calculate activity coefficients (γ_1 and γ_2) using the given equations.

$$A = 1.107; \gamma_1 = 1.864; \gamma_2 = 1.072$$

STEP-3: Calculate total pressure (P) using Eqn. (3).

$$P = 73.52 \text{ kPa}$$

STEP-4: Calculate y_1 and y_2 using Eqn. (1) and (2) respectively.

$$y_1 = 0.282 \text{ and } y_1 = 0.718$$

DEW PRESSURE CALCULATION

(*DEW P*)

Part (b): *DEW P*

Given: y_i and T.

Calculate: x_i and P.

Equations

Writing Raoult's law and Dalton's law for components:

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

$$x_1 = \frac{y_1 P}{\gamma_1 P_1^{sat}} ----(4)$$

Similarly,

$$x_2 = \frac{y_2 P}{\gamma_2 P_2^{sat}} ----(5)$$

Adding Eqn. (4) and (5),

$$x_1 + x_2 = \frac{y_1 P}{\gamma_1 P_1^{sat}} + \frac{y_2 P}{\gamma_2 P_2^{sat}}$$

DEW PRESSURE CALCULATION

Since, $(x_1+x_2)=1$,

$$1 = \frac{y_1 P}{\gamma_1 P_1^{sat}} + \frac{y_2 P}{\gamma_2 P_2^{sat}}$$

$$1 = \left(\frac{y_1}{\gamma_1 P_1^{sat}} + \frac{y_2}{\gamma_2 P_2^{sat}}\right) P$$

$$P = \frac{1}{\left(\frac{y_1}{\gamma_1 P_1^{sat}} + \frac{y_2}{\gamma_2 P_2^{sat}}\right)} ----(6)$$

ALGORITHM

STEP-1: Calculate $\boldsymbol{P_1^{sat}}$ & $\boldsymbol{P_2^{sat}}$ at given temperature (T) using Antoine equation.

* The liquid-phase composition is unknown, but is required in the calculation of activity coefficients. An iterative procedure is required; initial values are provided by Raoult's law, for which $\boldsymbol{\gamma_1 = \gamma_2 = 1.0}$. The required steps, with current values of γ_1 and γ_2 are:

STEP-2: Calculate $\boldsymbol{P}$ using Eq. (6).

STEP-3: Calculate $\boldsymbol{x_1}$ and $\boldsymbol{x_2}$ using Eq. (4) and Eq. (5) respectively.

STEP-4: Using new values of $\boldsymbol{x_1}$ and $\boldsymbol{x_2}$ evaluate activity coefficients ($\boldsymbol{\gamma_1}$ and $\boldsymbol{\gamma_2}$) and return to STEP-2. The iteration will continue until we get a converged value of $\boldsymbol{P}$.

Final values: $\boldsymbol{P} = 62.89$ kPa, $\boldsymbol{x_1}=0.8169$; $\boldsymbol{\gamma_1} = 1.0378$; $\boldsymbol{\gamma_2}=2.0933$

MODULE 6

Lecture No. 52

Date: 29.10.2018

Problem

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

$\ln \gamma_1 = A x_2^2$ $\ln \gamma_2 = A x_1^2$ where $A = 2.771 - 0.00523\,T$

In addition, the following Antoine equations provide vapor pressures:

$$\ln P_1^{sat}/kPa = 16.59158 - \frac{3643.31}{T\ [K] - 33.424}$$

$$\ln P_2^{sat}/kPa = 14.25326 - \frac{2665.54}{T\ [K] - 53.424}$$

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 $y_1 = 0.40$**

BUBBLE TEMPERATURE CALCULATION

(*BUBL T*)

Part (c): *BUBL T*

Given: x_i and P.

Calculate: y_i and T.

Equations

Writing Modified Raoult's law and Dalton's law for components:

$$y_1 P = x_1 \gamma_1 P_1^{sat} ----(1)$$

$$y_2 P = x_2 \gamma_2 P_2^{sat} ----(2)$$

Adding Eqn. (1) and (2),

$$y_1 P + y_2 P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$$

$$(y_1 + y_2) P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$$

Since, $(y_1 + y_2) = 1$

$$P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} ----(3)$$

ALGORITHM

STEP-1: An initial value for the unknown temperature is found from the saturation temperatures of the pure species at the known pressure. The Antoine equation, solved for ***T***, becomes:

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

Application for $\boldsymbol{P}$ = 101.33 kPa leads to

$$\boldsymbol{T_1^{sat}} = 337.71 \text{ K}; \boldsymbol{T_2^{sat}} = 330.08 \text{ K}$$

Start with initial Guess of $\boldsymbol{T = 335\ K}$.

ALGORITHM

STEP-2: With the current value of T, calculate **A**, $\boldsymbol{\gamma_1}$ and $\boldsymbol{\gamma_2}$, $\boldsymbol{P_1^{sat}}$, $\boldsymbol{P_2^{sat}}$.

STEP-3: Calculate total pressure (P_{calc}) using Eqn. (3).

STEP-4: Calculate $del\,p = P_{calc} - P_{given}$;

if $del\,P <$ **1E-5** (convergence criterion), P has converged.

Otherwise, return to STEP-2.

Final values:

$T = 331.20$ K, $P_1^{sat} = 77.98$ kPa, $P_2^{sat} = 105.35$ kPa,

$\gamma_1 = 1.0237$; $\gamma_2 = 2.1184$, $y_1 = 0.67$; $y_2 = 0.33$.

DEW TEMPERATURE CALCULATION

(*DEW T*)

Part (b): *DEW T*

Given: y_i and P.

Calculate: x_i and T.

Equations

Writing Raoult's law and Dalton's law for components:

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

$$x_1 = \frac{y_1 P}{\gamma_1 P_1^{sat}} ---- -(4)$$

Similarly,

$$x_2 = \frac{y_2 P}{\gamma_2 P_2^{sat}} ---- -(5)$$

Adding Eqn. (4) and (5),

$$x_1 + x_2 = \frac{y_1 P}{\gamma_1 P_1^{sat}} + \frac{y_2 P}{\gamma_2 P_2^{sat}}$$

DEW TEMPERATURE CALCULATION

Since, $(x_1+x_2)=1$,

$$1 = \frac{y_1 P}{\gamma_1 P_1^{sat}} + \frac{y_2 P}{\gamma_2 P_2^{sat}}$$

$$1 = \left(\frac{y_1}{\gamma_1 P_1^{sat}} + \frac{y_2}{\gamma_2 P_2^{sat}}\right) P$$

$$P = \frac{1}{\left(\frac{y_1}{\gamma_1 P_1^{sat}} + \frac{y_2}{\gamma_2 P_2^{sat}}\right)} ---- -(6)$$

ALGORITHM

STEP-1: An initial value for the unknown temperature is found from the saturation temperatures of the pure species at the known pressure. The Antoine equation, solved for ***T***, becomes:

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

Application for $\boldsymbol{P} =$ 101.33 kPa leads to

$$\boldsymbol{T_1^{sat}} = 337.71\ \mathrm{K};\ \boldsymbol{T_2^{sat}} = 330.08\ \mathrm{K}$$

Start with initial Guess of ***T* = 335 *K***.

ALGORITHM

STEP-2: Because the liquid phase composition is not known, the activity coefficients are initialized as $\gamma_1 = \gamma_2 = 1$.

STEP-3: With current value of T, calculate A, P_1^{sat}, P_2^{sat}.

STEP-4: Calculate x_1 *(Eq. 4)*, x_2 *(Eq. 5) and* $x = x_1 + x_2$.

STEP-5: Calculate $del\,x = 1 - x$. Iterate the value of T, until the process converges on a value of T with $del\,X <$ 1E-5 (convergence criterion).

STEP-6: With new values of x_1 *and* x_2, calculate γ_1 **and** γ_2. Guess a new value of T and Return to STEP-3.

Final values: T = 326.70 K, P_1^{sat}=64.64 kPa, P_2^{sat} = 89.95 kPa, γ_1 = 1.3623; γ_2=1.2524, x_1=0.4603; y_2=0.5397.

VLE FROM *K*-VALUE CORRELATIONS

K-value

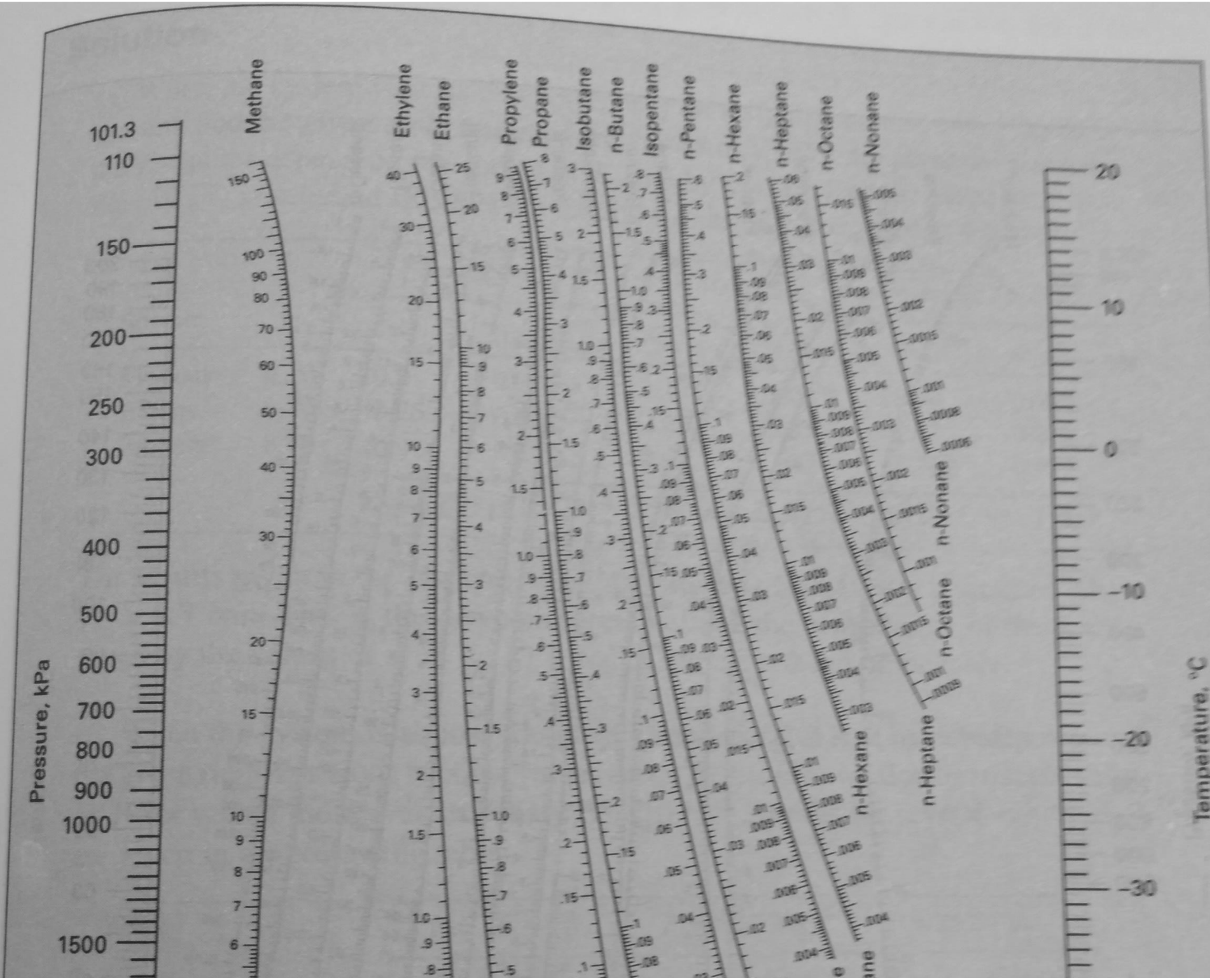
A convenient measure of the tendency of a given chemical species to partition itself preferentially between liquid and vapor phases is the **equilibrium ratio K_i,** defined as

$$K_i = \frac{y_i}{x_i} ----(1)$$

This quantity is usually called a ***K*-value**.

- When K_i is greater than unity, species ***i*** exhibit a higher concentration in the vapor phase; when less, a higher concentration in the liquid phase, and is considered a "heavy" constituent.
- The use of *K*-values makes for computational convenience, allowing elimination of one set of mole fractions $\{y_i\}$ or $\{x_i\}$ in favour of the other.

K-VALUES FOR SYSTEMS OF LIGHT HYDROCARBONS (LOW-TEMPERATURE RANGE)


Pressure, kPa
101.3
110
150
200
250
300
400
500
600
700
800
900
1000
1500
Methane
Ethylene
Ethane
Propylene
Propane
Isobutane
n-Butane
Isopentane
n-Pentane
n-Hexane
n-Heptane
n-Octane
n-Nonane
Temperature, °C
20
10
0
−10
−20
−30

K-VALUES FOR SYSTEMS OF LIGHT HYDROCARBONS (HIGH-TEMPERATURE RANGE)

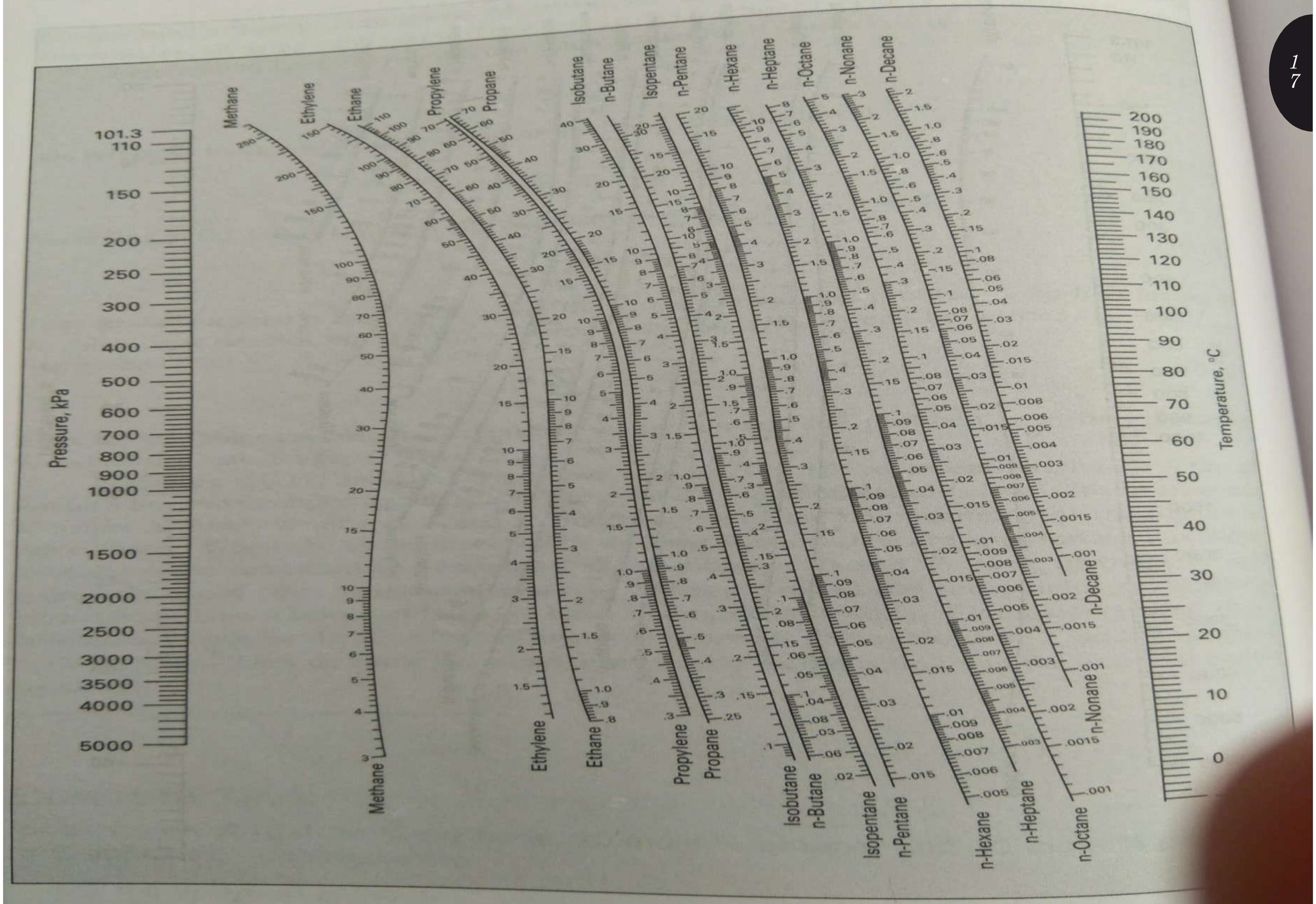


Figure 10.14: *K*-values for systems of light

Writing Raoult's law and Dalton's law for component *i* :

$$y_i P = x_i P_i^{sat} ---- -(2)$$

From Eq.(1) and Eq.(2):

$$K_i = \frac{P_i^{sat}}{P} ---- -(3)$$

Writing Modified Raoult's law and Dalton's law for component *i* :

$$y_i P = x_i \gamma_i P_i^{sat} ---- -(4)$$

From Eq.(1) and Eq.(4):

$$K_i = \frac{\gamma_i P_i^{sat}}{P} ---- -(5)$$

From Eq.(1):

$$y_i = K_i x_i ---- -(6)$$

Summation with $\sum_i y_i = 1$ yields; $\sum_i K_i x_i = 1 ---- -(7)$

Thus, for bubble point calculations, where the x_i are known, the problem is to find the set of *K*-values that satisfies Eq.(7).

Alternatively, Eq. (1) can be written,

$$x_i = \frac{y_i}{K_i} ---- -(8)$$

Summation with $\sum_i x_i = 1$ yields; $\sum_i \frac{y_i}{K_i} = 1 ---- -(9)$

Thus, for dew point calculations, where the y_i are known, the problem is to find the set of *K*-values that satisfies Eq.(9).

Example

For a mixture of 10 mole % methane, 20 mole % ethane and 70 mole % propane at 10 °C. Determine the

(a) Dew point pressure.

(b) Bubble point pressure.

Solution (a):

When the system is at its dew point, only an insignificant amount of liquid is present, and the given mole fractions are values of y_i. For the given temperature, the K-values depend on the choice of P, and by trial we find the value for which Eq.(9) is satisfied.

Results for several values of P are given as follows:

		$P = 6.9$ bar		**$P = 10.34$ bar**		**$P = 8.7$ bar**	
	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
		$\sum y_i/Ki$	**0.828**		**1.174**		**1.000**

Solution (a):

The results given in the last two column show that Eq. (9) is satisfied when $P =$ 8.7 bar. This is the dew point pressure, and the composition of the dew is given by the values of $x_i = y_i/K_i$ listed in the last column of the table.

Solution (b):

When the system is at its bubble point, the given mole fractions are values of x_i. For the given temperature, the *K*-values depend on the choice of *P*, and by trial we find the value for which Eq.(7) is satisfied.

Results for several values of *P* are given as follows:

		P = 26.2 bar		***P = 27.6 bar***		***P = 26.54 bar***	
	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
		$\sum K_i x_i$	**1.017**		**1.174**		**1.000**

Solution (b):

The results given in the last two column show that Eq. (7) is satisfied when $P =$ 26.54 bar. This is the bubble point pressure, and the composition of the bubble of vapor is given by the values of $y_i = K_i x_i$ listed in the last column of the table.

MODULE 6

Lecture No. 53 & 54

Date: 30.10.2018 / 31.10.2018

ISOTHERMAL FLASH CALCULATIONS

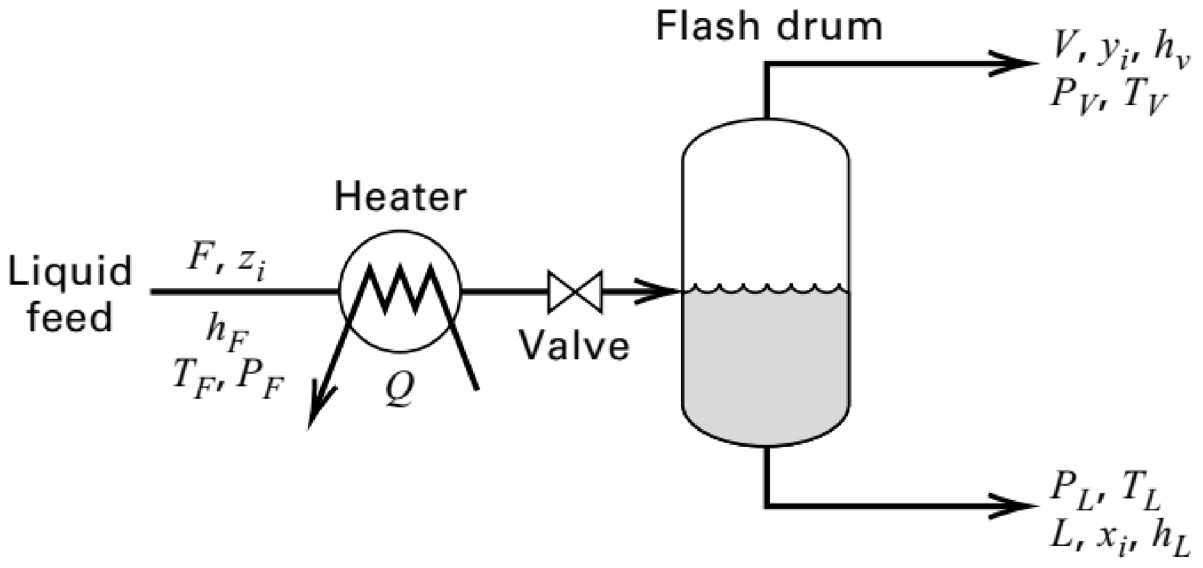
(*PT*-Flash Calculations)

Single-stage flash calculations are among the most common calculations in chemical engineering.

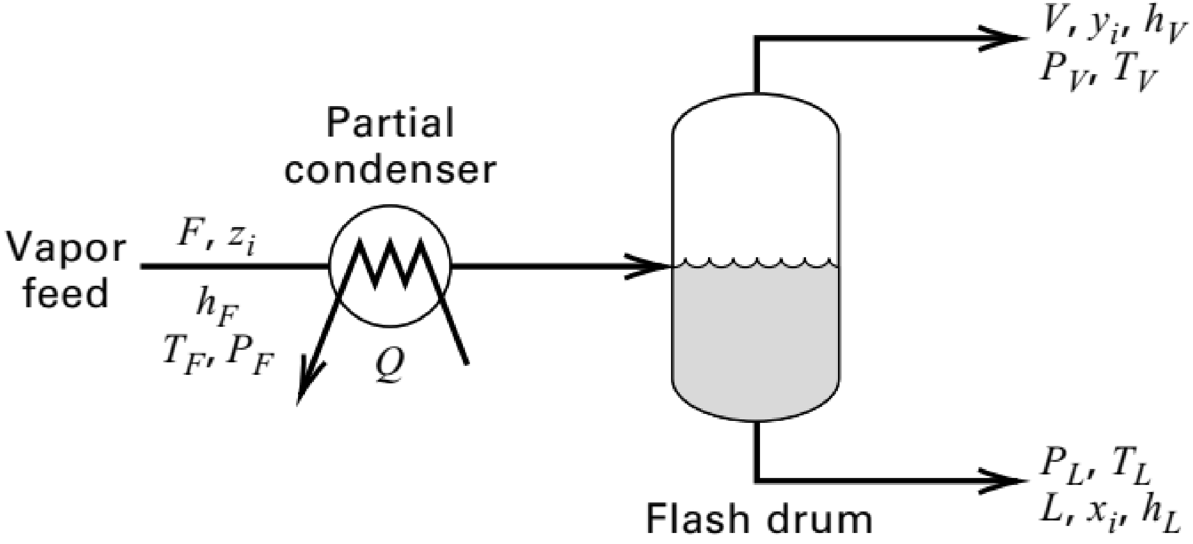
A flash is a single-equilibrium-stage distillation in which a feed is partially vaporized to give a vapor richer than the feed in the more volatile components.

In Figure (a), a pressurized liquid feed is heated and flashed across a valve to a lower pressure, resulting in creation of a vapor phase that is separated from the remaining liquid in a flash drum, or (2) if the valve is omitted, a liquid can be partially vaporized in a heater and then separated into two phases.

Alternatively, a vapor feed can be cooled and partially condensed, as in Figure (b), to give, after phase separation, a liquid richer in the less-volatile components.



(a) flash vaporization (a)



(b) partial condensation. (b)

Unless the relative volatility, is very large, flashing (partial vaporization) or partial condensation is not a replacement for distillation, but an auxiliary operation used to prepare streams for further processing.

Total Material balance:

$$F = L + V ----(1)$$

Component Material Balance:

$$FZ_i = Lx_i + Vy_i ----(2)$$

Phase Equilibrium:

$$y_i = K_i x_i ----(3)$$

From Eq.(1):

$$L = F - V ----(4)$$

Using Eq.(4) and Eq.(3) in Eq.(2):

$$FZ_i = (F - V)x_i + Vy_i$$

$$FZ_i = (F - V)\frac{y_i}{K_i} + Vy_i$$

Dividing throughout by F:

$$Z_i = (1 - \frac{V}{F})\frac{y_i}{K_i} + \frac{V}{F}y_i$$

Assuming, $\Psi = V/F ----(5)$

$$Z_i = (1-\Psi)\frac{y_i}{K_i} + \Psi y_i$$

$$Z_i K_i = (1-\Psi)y_i + \Psi y_i K_i$$

$$Z_i K_i = (1-\Psi+\Psi K_i)y_i$$

$$y_i = \frac{Z_i K_i}{1+\Psi(K_i-1)} ----(6)$$

and

$$x_i = \frac{Z_i}{1+\Psi(K_i-1)} ----(7)$$

Summations:

$$\sum_i x_i - \sum_i y_i = 0$$

$$\sum_i \frac{Z_i(1-K_i)}{1+\Psi(K_i-1)} = 0 ----(8)$$

The initial step in solving a *P,T*-flash problem is to find the value of Ψ which satisfies Eq.(8)

Rachford-Rice Procedure for Isothermal-Flash Calculations:

Specified variables: $F, T_F, P_F, z_1, z_2, \ldots, z_C, T_V, P_V$

Steps

(1) $T_L = T_V$

(2) $P_L = P_V$

(3) Solve

$$f\{\Psi\} = \sum_{i=1}^{C} \frac{z_i(1 - K_i)}{1 + \Psi(K_i - 1)} = 0$$

for $\Psi = V/F$, where $K_i = K_i\{T_V, P_V\}$.

(4) $V = F\Psi$

(5) $x_i = \dfrac{z_i}{1 + \Psi(K_i - 1)}$

(6) $y_i = \dfrac{z_i K_i}{1 + \Psi(K_i - 1)} = x_i K_i$

(7) $L = F - V$

Equation (8) can be solved iteratively by guessing values of Ψ between 0 and 1 until the function $f\{\Psi\}=0$. The most widely employed procedure for solving Eq. (8) is **Newton Raphson method.** A value of the Ψ root for iteration $k+1$ is computed by the recursive relation

$$\Psi^{(k+1)} = \Psi^{(k)} - \frac{f\{\Psi^k\}}{f'\{\Psi^k\}} ---- -(9)$$

where the superscript is the iteration index, and the derivative of $f\{\Psi\}$, with respect to Ψ is

$$f'\{\Psi^k\} = \sum_i \frac{Z_i(1-K_i)^2}{[1+\Psi^k\,(K_i-1)]^2} ---- -(10)$$

The iteration can be initiated by assuming $\Psi^1 = 0.5$. Sufficient accuracy is achieved by terminating the iterations when

$$\frac{\left|\Psi^{(k+1)} - \Psi^{(k)}\right|}{\Psi^{(k)}} < 0.0001 ----(11)$$

The existence of a valid root must be checked before employing the procedure, by checking if the equilibrium condition corresponds to subcooled liquid or superheated vapor rather than partial vaporization or condensation.

A first estimate of whether a multicomponent feed gives a two-phase mixture is made by inspecting the K-values. If all K-values are > 1, the phase is superheated vapor. If all K-values are < 1, the single phase is a subcooled liquid. If one or more K-values are greater than 1 and one or more K-values are less than 1, the check is made by first computing $f\{\Psi\}$ for $\Psi=0$.

If the resulting $f\{0\} > 0$, the mixture is below its bubble point (subcooled liquid). Alternatively, if $f\{1\} < 0$, the mixture is above the dew point (superheated vapor).

EXAMPLE:

A 100-kmol/h feed consisting of 10, 20, 30, and 40 mol% of propane, n-butane, n-pentane, and n-hexane, respectively, enters a distillation column at 689.5 kPa and 366.5 K. Assuming equilibrium, what fraction of the feed enters as liquid, and what are the liquid and vapor compositions?

Given, $K_3 = 4.2$, $K_4 = 1.75$, $K_5 = 0.74$, $K_6 = 0.34$.

Solution:

Because some *K*-values are greater than 1 and some less than 1, it is necessary first to compute values of $f\{0\}$ and $f\{1\}$ to see if the mixture is between the bubble and dew points. (Use eq. 8)

$$f\{0\} = \frac{0.1(1-4.2)}{1} + \frac{0.2(1-1.75)}{1} + \frac{0.3(1-0.74)}{1} + \frac{0.4(1-0.34)}{1} = -0.128$$

Since $f\{0\}$ is not more than zero, the mixture is above the bubble point.

Now compute $f\{1\}$:

$$f\{1\} = \frac{0.1(1-4.2)}{1+(4.2-1)} + \frac{0.2(1-1.75)}{1+(1.75-1)} + \frac{0.3(1-0.74)}{1+(0.74-1)} + \frac{0.4(1-0.34)}{1+(0.34-1)} = 0.720$$

Since $f\{1\}$ is not less than zero, the mixture is below the dew point.

Therefore, the mixture is part vapor.

Using the Rachford–Rice procedure and substituting z_i and K_i values in eq. 8:

$$0 = \frac{0.1(1-4.2)}{1+\Psi(4.2-1)} + \frac{0.2(1-1.75)}{1+\Psi(1.75-1)} + \frac{0.3(1-0.74)}{1+\Psi(0.74-1)} + \frac{0.4(1-0.34)}{1+\Psi(0.34-1)}$$

Solving this equation by Newton-Raphson method using an initial guess for Ψ of 0.50 gives the following iteration history:

K	$\Psi^{(k)}$	$f\{\Psi^{(k)}\}$	$f'\{\Psi^{(k)}\}$	$\Psi^{(k+1)}$	$\frac{\left\|\Psi^{(k+1)}-\Psi^{(k)}\right\|}{\Psi^{(k)}}$
1	0.5000	0.2515	0.6529	0.0982	0.8037
2	0.0982	-0.0209	0.9111	0.1211	0.2335
3	0.1211	-0.0007	0.8539	0.1219	0.0065
4	0.1219	0.0000	0.8521	0.1219	0.0000

Convergence is rapid, giving $\Psi = V/F = 0.1219$.

The vapor flow rate is 0.1219(100) = 12.19 kmol/h, and the liquid flow rate is (100 - 12.19) = 87.81 kmol/h.

Liquid and vapor compositions are (Eq. 6 and Eq. 7):

	x	y
Propane	0.0719	0.3021
***n*-Butane**	0.1833	0.3207
***n*-Pentane**	0.3098	0.2293
***n*-Hexane**	0.4350	0.1479