Chemical Engineering Thermodynamics II

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Chapter 10. VLE: Introduction

■ Preceding chapters : pure substance or constant composition mixture
  – composition changes: the desired outcome => a primary variable

■ Process (distillation, absorption and extraction) bring phase of different composition into contact, and when the phase are not in equilibrium mass transfer b/w the phase alters their composition.

■ Both the extent of change and the rate of transfer depend on the departure of the system from the equilibrium.

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10.1 The Nature of Equilibrium

■ **Equilibrium** is a static condition in which no changes occur in the macroscopic properties of a system w/ time

=> At the microscopic level, conditions are not static.

=> The molecules comprising a phase at a given instant are not the same molecules that later occupy the same phase.

■ **Measure of composition**

○ Measures of composition: mass fraction, mole fraction, molar concentration

○ **Mass or moles fraction**: the ratio of the mass or number of moles of a species in a mixture to the total mass or number of moles

$$x_i \equiv \frac{m_i}{m} = \frac{\dot{m}_i}{\dot{m}} \qquad \text{or} \qquad x_i \equiv \frac{n_i}{n} = \frac{\dot{n}_i}{\dot{n}}$$

○ **Molar concentration**: the ratio of mole fraction of particular chemical species in a mixture or solution to the molar volume of the mixture.

$$C_i \equiv \frac{x_i}{V} \qquad\qquad \text{For flow process} \quad C_i \equiv \frac{\dot{n}_i}{q}$$

(molar mass) $M = \sum x_i M_i$ => molar mass of a mixture is the mole fraction-weighted sum of the molar masses of all species present

10.2 The Phase Rule

○ Number of variable to be independently fixed in a system at equilibrium
 : the difference b/w the total number of variables that characterized the
  intensive state of the system and the number of independent equations.

○ Intensive state of a PVT system w/ N species and π phase in equilibrium
 : characterized by the intensive variable, T, P, N−1 mole fraction each phase

   => Number of phase-rule variable : $2+(N-1)\pi$ – (1)

○ phase equilibrium equations

$$G_i^\alpha = G_i^\beta = \ldots = G_i^\pi$$

For N species, Number of independent phase-equilibrium eq.
 : $(\pi-1)\,N$ – (2)

■ The difference b/w (1) and (2)
   = $2 + (N-1)' - (\pi-1)N = 2 - \pi' + N$ (Gibbs phase rule)

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■ **Duhem's theorem** :

– closed systems at equilibrium

– extensive state and the intensive state is fixed $2+(N-1)\pi$

– intensive phase-rule variable, π extensive variables

=> **Total number of variables = 2 + N π**

○ **Material balance equation for N chemical species**

=> **Number of independent Eq. = ($\pi-1$)N + N = πN**

=> **Difference : 2 + N π – N π = 2**   [mass is variable]

" For any closed system, the equilibrium state is completely determined when any two independent variables are fixed."

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10.3 VLE : Qualitative Behavior

○ VLE : the state of coexistence of liquid and vapor phase.
○ System comprised of two species (N=2), F = 4 − $\pi \leq 3$
   => system can be represented in 3D graph (P, T, composition)

Figure 10.1

P–T–composition surface equilibrium state of saturate vapor and saturated liquid for species 1 and 2 of a binary system.

○ The under surface contains the saturated vapor state (P–T–y_1)
   The upper surface contains the saturated liquid state (P–T–x_1)
   => Intersect along the line RKAC$_1$ and UBHC$_2$
       which represent the vapor P vs T curve for pure species

○ Critical Point (pure, various mixture of the two species)
  => Highest T & P where a pure chemical species is observed to exist in VLE

   – critical locus : vapor and liquid become identical
   – super cooled, super heated region
   – coexistence of both liquid and vapor

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○ If start with liquid at F and reduce the
  pressure at const. T and composition.
  – First bubble point of vapor appears at point L
  which lies on the upper surface

○ The state of vapor bubble in equilibrium in Equil
    w/ the liquid L is represented by a point on the
    under surface of the T, P of L
    => Point V (Line LV is tie line)

○ As the pressure is further reduced, more liquid
    is vaporized.
    W is the point where last drop of liquid (dew)
    disappear => Dew point

○ Because of the complexity of Fig 10.1, the
    detailed characteristics of binary VLE
    are usually depicted by 2D by cutting the 3–D
    diagram – AEDBL : p–x–y diagram of const T.

○ If the lines from several planes are projected
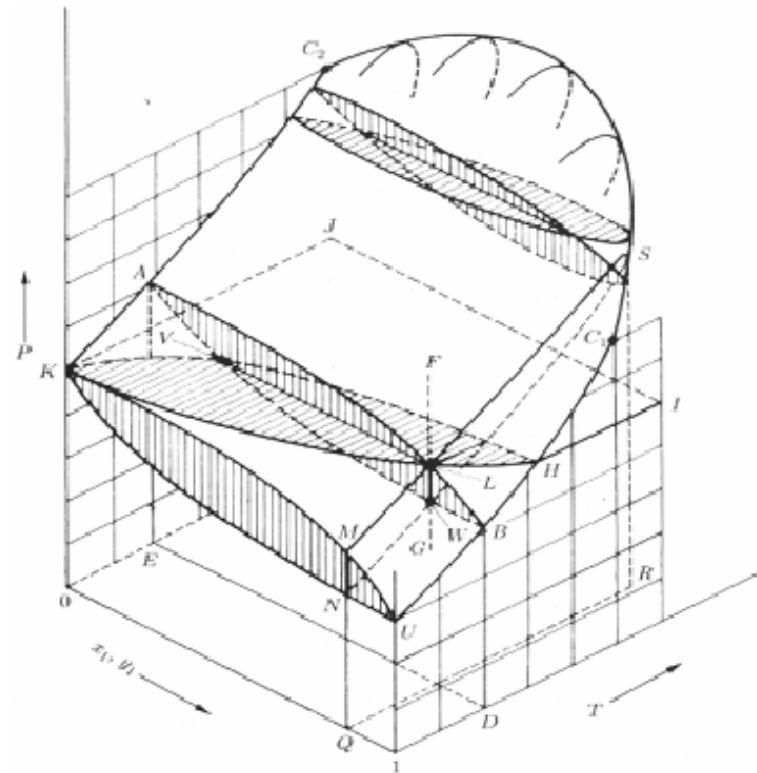   on a single parallel plane,
    –> 10.2(a)
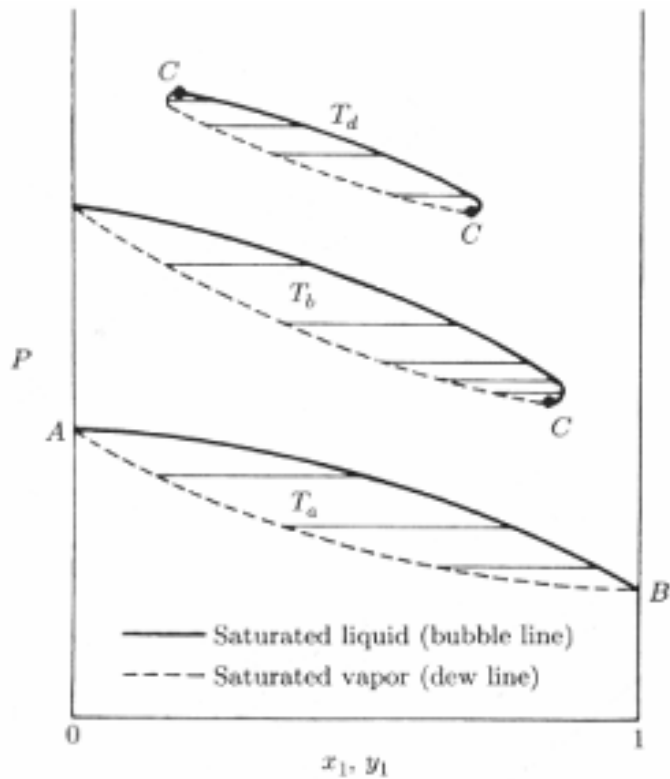

Fig. 10.1 *PTxy* diagram for VLE

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Fig. 10.2 (a) P–x–y plot for 3 T

- T_a : AEDBLA
- Horizontal lines –> tie line
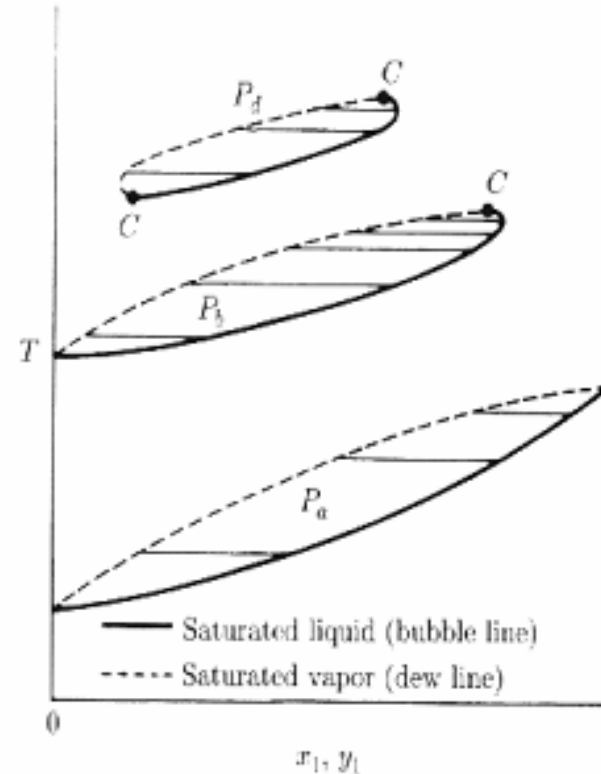- T_b & T_d lie between the two pure
  species T_c

Fig. 10.2 (b) T–x–y diagram

P_a –> KJIHLK
P_b –> between P_c
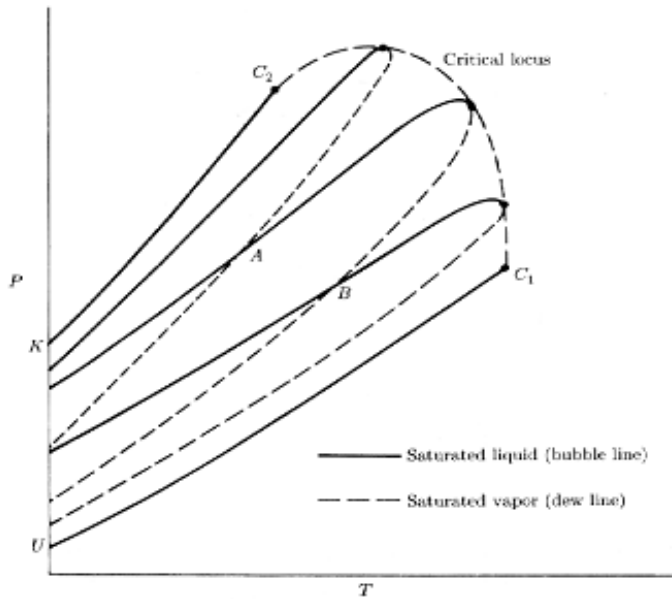P_d –> above P_c of both species –> island

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Fig. 10.3 PT diagram

○ UC_2, RC_1 are vapor-pressure curves for the pure species.

– Each interior loop represents the P–T behavior of saturated liquid and of saturated vapor for mixture of fixed composition

○ P–T relation for saturated liquid is different from the saturated vapor of the same composition.

– This is in contrast w/ the behavior of a pure species, for which the bubble as dew lines coincide

○ critical locus

10.4 Simple models for vapor/liquid equilibrium

■ Goal in VLE: to find by calculation the P, T, composition of phase
=> needs the models for behavior of systems in VLE
=> Two simplest are Raoult's law and Henry's law

Raoult's Law

○ Assumption:
(1) Vapor phase is an ideal gas –> low pressure
(2) Liquid phase is an ideal solution –> species that comprise the system
are chemically similar.

$$y_i P = x_i P_i^{sat} \qquad (10\text{–}1)$$

$y_i P$; Partial pressure

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■ Dew point & Bubble point calculation with Raoult's Law

Bubble P : calculate (y_i, P) given (x_i, T)
Dew P   : calculate (x_i, P) given (y_i, T)
Bubble T : calculate (y_i, T) given (x_i, P)
Dew T   : calculate (x_i, T) given (y_i, P)

=> Need iterative calculation

From eq (10.1)
$$\sum y_i P = \sum x_i P_i^{sat} \quad \Rightarrow \quad P = \sum x_i P_i^{sat} \quad \text{(BUBL P)}$$

$$P = x_1 P_1^{sat} + x_2 P_2^{sat} = x_1 P_1^{sat} + (1 - x_1) P_2^{sat} = P_2^{sat} + (P_1^{sat} - P_2^{sat}) x_1$$

=> P vs x_1 at constant T -> straight line connecting P_2^{sat} at x_1=0 to P_1^{sat} at x_1 =1

○ solve eq (10.1) for x_i

$$x_i = \frac{y_i}{P_i^{sat}} P \qquad \text{summation} \qquad P = \frac{1}{\sum_i y_i / P_i^{sat}} \quad \text{(DEW P)}$$

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■ Henry's Law

○ Application of Raoult's law to species i requires a value for P_i^{sat} at the temperature of application, therefore is not appropriate for species whose critical temperate is less than the temperate of application

○ For species present as a very dilute solute in the liquid phase, Henry' law then states that the partial pressure of the species in the vapor phase is directly proportional its liquid-phase mole fraction

$$y_i P = x_i H_i$$

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10.5 VLE by modified Raoult's Law

■ Modified Raoult's Law : when 2nd assumption is abandoned and account is taken of deviations from solution identity in the liquid phase

$$y_i P = x_i \gamma_i P_i^{sat} \qquad \gamma_i \;:\; \text{activity coeff.}$$

Example 10.3
$$P = \sum_i x_i \gamma_i P_i^{sat} \qquad P = \frac{1}{\sum_i y_i / \gamma_i P_i^{sat}}$$

10.6 VLE from K-value correlations

○ Tendency of chemical species to partition itself preferentially between Liquid/Vapor **equilibrium ratio K$_i$,** defined as $K_i = \dfrac{y_i}{x_i}$

If Ki > 1 -> higher concentration in the vapor phase

Raoult's Law : $K_i = \dfrac{P_i^{sat}}{P}$ **modified Raoult's Law :** $K_i = \dfrac{\gamma_i P_i^{sat}}{P}$

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Flash calculation

○ Reduction of pressure from bubble point => produce two phase system of V/L

○ For Flash Calculation => Calculations of the quantity and compositions of the vapor/liquid consisting of two phases.

○ Consider a system
   ▶ one mole of nonreacting chemical species
   ▶ Overall composition => Z_i
   ▶ L : moles of liquid, V : moles of vapor

○ For species i , overall composition $Z_i = x_i L + y_i V$

$$Z_i = x_i(1 - V) + y_i V \quad \text{by eliminating L}$$

Substitute $x_i = y_i / K_i$ and solving for y_i $y_i = \dfrac{z_i K_i}{1 + V(K_i - 1)}$

Since $\sum y_i = 1$ $\displaystyle\sum_i \dfrac{Z_i K_i}{1 + V(K_i - 1)} = 1$

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