Vapour-Liquid Equilibrium (VLE): Qualitative Behavoiur

Thermodynamics is an abstract subject, it takes an abstract mind to understand it.

Introduction

- Before presenting the mathematical formulation of the multi-component VLE problem, it is pertinent to discuss some key features of typical vapour-liquid phase behaviour.
- The description of phase behaviour of vapour and liquid phases co-existing under equilibrium can be complex and difficult to visualize for systems containing a large number of chemical species. Thus, to clarify matters it is useful to consider a binary system.
- The considerations for such a system may, in principle, be generalized to understand the behaviour of multi-component systems. However, we shall restrict ourselves to description of VLE of multi-component systems to the corresponding mathematical formulation.

Introduction (2)

Vapour/liquid equilibrium is the state of coexistence of liquid and vapour phases.

- In the qualitative discussion, we shall focus on systems comprised of two chemical species, because systems of greater complexity cannot be adequately represented graphically.
- When N = 2 the phase rule becomes F = 4 π. Since there must be at least one phase (π = 1), the maximum number of phase rule variables which must be specified to fix the intensive state of the system is three: namely, pressure P, temperature T and mole fraction (or mass) fraction.
- All equilibrium states of the system can therefore be represented in three-dimensional P-T-Composition space. Within the space, the state of pairs of phases coexisting at equilibrium (F = 4 2 = 2) define surfaces. A schematic three-dimensional diagram is shown in Fig. 1.

Introduction (3)



Figure 1: PT xy diagram for vapour/liquid equilibrium

Description of general VLE behaviour

- Fig. 1 shows schematically the *P*-*T*-composition surfaces which contain the equilibrium states of saturated vapor and saturated liquid for a binary system. The lower surface contains the saturated-vapor states; it is the *P*-*T*-*y*₁ surface. The upper surface contains the saturated-liquid states; it is the *P*-*T*-*x*₁ surface. These surfaces intersect along the lines *UBHC*₁ and *KAC*₂ which represent the vapour pressure-vs.-*T* curves for the pure species 1 and 2.
- However, the lower and upper surfaces form a continuous rounded surface across the top of the diagram between C_1 and C_2 , the critical points of pure species 1 and 2; the critical points of the various mixtures of the two species lie along a line on the rounded edge of the surface between C_1 abd C_2 .
- This critical locus is defined by the points at which vapour and liquid phases in equilibrium become identical.

Description of general VLE behaviour (2)

- The subcooled-liquid region lies above the upper surface of Fig. 1; the superheated vapour region lies below the lower surface. The interior space between the two surfaces is the region of coexistence of both liquid and vapor phases.
- If one starts with a liquid at F and reduces the pressure at constant temperature and composition along vertical line \overline{FG} , the first bubble of vapour appears at point L, which lies on the upper surface. Thus, L is a *bubblepoint*, and the upper surface is the bubblepoint surface.
- The state of the vapour bubble in equilibrium with the liquid at *L* must be represented by a point on the lower surface at the temperature and pressure of *L*. This point is indicated by *V*. Line *VL* is an example of a tie line, which connects points representing phases in equilibrium.

Description of general VLE behaviour (3)

- As the pressure is further reduced along line *FG*, more and more liquid vaporizes until at *W* the process is complete. Thus *W* lies on the under surface and represents a state of saturated vapor having the mixture composition. Since *W* is the point at which the last drops of liquid (*dew*) disappear, it is a *dewpoint*, and the lower surface is the dewpoint surface.
- Because of the complexity of Fig. 1, the detailed characteristics of binary VLE are usually depicted by two-dimensional graphs that display what is seen on various planes that cut the three-dimensional diagram. The three principal planes, each perpendicular to one of the coordinate axes, are illustrated in Fig. 1. Thus a vertical plane perpendicular to the temperature axis is outlined as *ALBDEA*.

Description of general VLE behaviour (4)



Figure 2: (a) Pxy diagram for three temperatures. (b) Txy diagram for three pressures 9/46

Description of general VLE behaviour (5)

- The lines on this plane form a *P*-*x*₁-*y*₁ phase diagram at constant *T*. If the lines from several such planes are projected on a single parallel plane, a diagram like Fig.2(a). It shows *P*-*x*₁-*y*₁ plots for three different temperatures.
- The one for T_a , represents the section of Fig. 1 indicated by ALBDEA. The horizontal lines are tie lines connecting the compositions of phases in equilibrium. The temperature T_b lies between the two pure- species critical temperatures identified by C_1 and C_2 in Fig. 1, and temperature T_d is above both critical temperatures. The curves for these two temperatures therefore do not extend all the way across the diagram. However, the first passes through one mixture critical point, and the second through two such points.

Description of general VLE behaviour (6)

- All three of these critical points are denoted by the letter C. Each is a tangent point at which a horizontal line touches the curve. This is so because all tie lines connecting phases in equilibrium are horizontal, and the tie line connecting identical phases (the definition of a critical point) must therefore be the last such line to cut the diagram. A horizontal plane passed through Fig. 1 perpendicular to the P axis is identified by C_1 and C_2 in Fig. 1, and temperature T_d is above both critical temperatures.
- A horizontal plane passed through Fig. 1 perpendicular to the P axis is identified by *HIJKLH*. Viewed from the top, the lines on this plane represent a T- x_1 -y diagram. When lines for several pressures are projected on a parallel plane, the resulting diagram appears as in Fig. 2(b). This figure is analogous to Fig. 2(a), except that it represents values for three constant pressures, P_a , P_b , and P_d .

Description of general VLE behaviour (7)



Figure 3: PT diagram for several compositions

Description of general VLE behaviour (8)

- Other possible plots are vapor mole fraction y_1 vs. liquid mole fraction x_1 for either the constant-T conditions of Fig. 2(a) or the constant-P conditions of Fig. 2(b). The third plane identified in Fig. 1, vertical and perpendicular to the composition.
- The critical point of a binary mixture occurs where the nose of a loop in Fig. 3 is tangent to the envelope curve. Put another way, the envelope curve is the critical locus. Fig. 3 illustrates that the location of the critical point on the nose of the loop varies with composition. For a pure species, the critical point is the highest temperature and highest pressure at which vapor and liquid phases can coexist, but for a mixture it is in general neither. Therefore under certain conditions a condensation process occurs as the result of a *reduction* in pressure.

Description of general VLE behaviour (9)

- Consider the enlarged nose section of a single P-T loop shown in Fig. 4. The critical point is at C. The points of maximum pressure and maximum temperature are identified as M_p and M_T . The interior dashed curves indicate the fraction of the overall system that is liquid in a two-phase mixture of liquid and vapor. To the left of the critical point C a reduction in pressure along a line such as BD is accompanied by vaporization of liquid from bubblepoint to dewpoint, as would be expected.
- However, if the original condition corresponds to point *F*, a state of saturated vapour, liquefaction occurs upon reduction of the pressure and reaches a maximum at point *G*, after which vaporization takes place until the dewpoint is reached at point *H*. This phenomenon is called *retrograde condensation*.

Description of general VLE behaviour (10)

- It can be important in the operation of deep natural-gas wells where the pressure and temperature in the underground formation are at conditions represented by point *F*. If the pressure at the wellhead is that of point *G*, considerable liquefaction of the product stream is accomplished along with partial separation of the heavier species of the mixture.
- Within the underground formation itself, the pressure tends to drop as the gas supply is depleted. If not prevented, this leads to the formation of a liquid phase and a consequent reduction in the production of the well. Repressuring is therefore a common practice; i.e., a lean gas (gas from which the heavier species have been removed) is returned to the underground reservoir to maintain an elevated pressure.

Description of general VLE behaviour (11)



Figure 4: Portion of a PT diagram in the critical region

Vapour-Liquid Equilibrium (VLE) Models

Vapour-Liquid Equilibrium (VLE) Models

- When thermodynamics is applied to vapour/liquid equilibrium, the goal is to find by calculation the temperatures, pressures, and compositions of phases in equilibrium.
- Of course, Equilibrium provides the mathematical framework for the systematic correlation, extension and generalization, evaluation, and interpretation of data.
- It is also the means by which the predictions of various theories of molecular physics and statistical mechanics may be applied for practical purposes.
- This cannot be accomplished without *models* for the behaviour of systems in vapour/liquid equilibrium.
- The two simplest models are Raoult's law and Henry's law.

Vapour-Liquid Equilibrium (VLE) Models (2)



Figure 5: Pxy diagrams at constant T: (a) tetrahydrofuran(1)/carbon'tetrachloride(2) at 30 °C; (b) chloroform(1)/tetrahydrofuran(2) at 30 °C. Dashed lines: P - x relation for Raoult's law

Two major assumptions required to reduce VLE calculations to *Raoult's law* are:

- The vapour phase is an ideal gas.
- The liquid phase is an ideal solution.

- The first assumption means that Raoult's law can be applied for low to moderate pressure.
- The second implies that it can have approximate validity only when the species that comprise the system are chemically similar.
- Just as the ideal gas serves as a standard to which real gas behaviour may be compared, the ideal solution also serves as standard to which real solution behaviour may be compared.

- Ideal solution behaviour is often approximated by liquid phases where molecular species are not too different in size and are of the same chemical nature. for example, the mixture of isomers, such as *ortho-, meta- and para-*xylene conforms very closely to idela solution behaviour.
- So also do mixtures of adjacent members in the homologous series, such as *n*-hexane/*n*-heptane, ethanol/propanol, benzene/toluene, acetone/acetonitrile and acetonitrile/nitromethane.

• The mathematical expression which reflects the two major assumptions and which gives the quantitaive expression to Raoult's law is:

$$y_i P = x_i P_i^{sat}$$
 (i = 1, 2, ..., N) (1)

where

 $x_i =$ liquid-phase mole fraction

 y_i = vaour-phase mole fraction

 P_i^{sat} = vapour pressure of pure species *i* at the temperature of the system. $v_i P$ = partial pressure of species *i*.

- The simple model for VLE represented by Eq. (1) provides a realistic description of the actual behaviour for a relatively small class of systems.
- A limitation of Raoult's law is that it can be applied only to species for which vapour pressure is known and this requires that the species must be "subcritical," i.e., that the temperature of application be below the critical temperature of the species.
- An important and useful feature of Raoult's law is that it is valid for any *species* present at a mole fraction approaching unity, provided only that the vapour phase is an ideal gas. Chemical similarity of the constituent species is not a requirement.

Multi-Component VLE Calculations using Raoult's Law

- For generality we consider a system containing N chemical species. Then by phase rule, for a VLE situation, the degrees of freedom are 2N, the phase rule variables being x_i, y_i , T, and P.
- The Raoults Law (RL) provides N constraining relations connecting these variables. Thus, for solving the VLE problem, N variables need to be specified, so that the values of the other N variables may be determined.
- Five types of VLE computations are commonly encountered in practice. They are:

Multi-Component VLE Calculations using Raoult's Law (2)

- **Bubble Pressure:** Calculate y_i and P, given x_i and T
- **Dew pressure:** Calculate x_i and P, given y_i and T
- **Bubble Temperature:** Calculate y_i and T, given x_i and P
- **Dew Temperature:** Calculate x_i and T, given y_i and P
- Flash Calculation: Calculate L or V, x_i and y_i , given T, P and z_i .

Multi-Component VLE Calculations using Raoult's Law (3)

The variant of RL used are as follows:

Thus:

 $\sum_{i}^{N} \frac{x_i P_i^s}{P} = 1$

 $y_i = \frac{x_i P_i^s}{P}$

Or

 $P = \sum_{i=1}^{N} x_i P_i^s$

(4)

(2)

(3)

(7)

(5)

(6)

Multi-Component VLE Calculations using Raoult's Law (4)

Also:

Thus:

Or

 $x_i = \frac{y_i P}{P_i^s}$

 $\sum_{i}^{N} \frac{y_i P}{P_i^s} = 1$

 $P = \frac{1}{\sum_{i}^{N} \frac{y_i}{P^s}}$

Multi-Component VLE Calculations using Raoult's Law (5)

• For computation of vapour pressures the Antoine equation may be used:

$$logP^{sat} = A - \frac{B}{T+C}$$
(8)

where T is in ^{o}C or K

• The Wagner equation can also be used:

$$log \mathcal{P}^{sat} = rac{A au + B au^{1.5} + C au^3 + D au^6}{1- au}$$

where $\tau = 1 - T_r$

(9)

Multi-Component VLE Calculations using Raoult's Law (6)

Bubble pressure

Given T and $\{x_i\}$, to calculate P and $\{y_i\}$.

a. use

$$P=\sum_{i}^{N}x_{i}P_{i}^{s}$$

to compute *P*.

b. use

$$y_i = \frac{x_i P_i^s}{P}$$

to compute $\{y_i\}$

Multi-Component VLE Calculations using Raoult's Law (7)

Dew pressure

Given T and $\{y_i\}$, to calculate P and $\{x_i\}$.

a. use

$$\frac{1}{P} = \sum_{i}^{N} \frac{y_i}{P_i^s}$$

to compute *P*.

b. use

$$x_i = \frac{y_i P}{P_i^s}$$

to compute $\{x_i\}$

Multi-Component VLE Calculations using Raoult's Law (8)

Bubble temperature

Given P and $\{x_i\}$, to calculate T and $\{y_i\}$.

a. For the given pressure compute $\{T_i^s\}$ using the Antoine equation:

$$T_i^s = \frac{B_i}{A_i - logP} - C_i$$

b. Initialize the bubble temperature as:

$$T_{bi} = \sum_{i}^{N} x_i T_i^s$$

c. Using computed T calculate $\{P_i^s\}$

Multi-Component VLE Calculations using Raoult's Law (9)

d. Use

$$y_i = \frac{x_i P_i^s}{P}$$

to compute $\{y_i\}$. e. Is $|\sum_i y_i - 1| < \epsilon$? f. If yes, $T_{last} = T_{bf}$, T_{bf} = final acceptable bubble temperature. g. At T_{bf} compute final $\{y_i\}$ h. If $\sum_i y_i - 1 > \epsilon$, then $T_{last} > T_{bf}$; revise to new T as: $T_{new} = T_{last} \left(\frac{\epsilon}{\sum_i y_i - 1}\right)$

and return to step (c).

i. If $\sum_{i} y_i - 1 < -\epsilon$, the assumed $T < T_{bf}$; revise to new T and return to step(c).

$$T_{new} = T_{last} \left(\frac{\left|\sum_{i} y_{i} - 1\right|}{\epsilon} \right)$$

Multi-Component VLE Calculations using Raoult's Law (10)

Dew temperature

Given P and $\{y_i\}$, to calculate T and $\{x_i\}$.

a. For the given pressure compute $\{T_i^s \text{ using the Antoine equation:} \}$

$$T_i^s = \frac{B_i}{A_i - logP} - C_i$$

b. Initialize the dew temperature as:

$$T_{di} = \sum_{i}^{N} x_i T_i^s$$

c. Using computed T calculate $\{P_i^s\}$

Multi-Component VLE Calculations using Raoult's Law (11)

d. Use

$$x_i = \frac{y_i P}{P_i^s}$$

to compute $\{x_i\}$. e. Is $|\sum_i x_i - 1| < \epsilon$? f. If yes, $T_{last} = T_{df}$, T_{df} = final acceptable dew temperature. g. At T_{df} compute final $\{x_i\}$ h. If $\sum_i x_i - 1 > \epsilon$, then $T_{last} < T_{df}$; revise to new T and return to step (c).

$${{{T}_{\textit{new}}}={{T}_{\textit{last}}}{\left({rac{{{\sum _{i}{x_{i}}}-1}}{\epsilon }}
ight)}}$$

i. If $\sum_{i} x_i - 1 < -\epsilon$, then $T_{last} > T_{df}$; revise to new T and return to step(c).

$$T_{new} = T_{last} \left(\frac{\left| \sum_{i} x_{i} - 1 \right|}{\epsilon} \right)$$

Example 1

Consider the ternary system Acetone(1)/Acetonitrile(2)/Nitromethane(3) for which:

$$\begin{split} &log P_1^{sat}/\text{kPa} = 14.5463 - \frac{2940.46}{t/^\circ C + 237.22} \\ &log P_2^{sat}/\text{kPa} = 14.2724 - \frac{2945.47}{t/^\circ C + 224.0} \\ &log P_3^{sat}/\text{kPa} = 14.2043 - \frac{2972.64}{t/^\circ C + 209.0} \end{split}$$

Calculate:

- a. P, $\{y_i\}$ for a temperature of 80°C, $x_1 = 0.3$, $x_2 = 0.3$
- b. P, $\{x_i\}$ for a temperature of 70°C, $y_1 = 0.5$, $y_2 = 0.3$
- c. T, $\{y_i\}$ for a pressure of 70kPa, $x_1 = 0.3$, $x_2 = 0.5$
- d. *T*, $\{x_i\}$ for a pressure of 70kPa, $y_1 = 0.35$, $y_2 = 0.45$

- An important application of VLE is the flash calculations.
- The name originates from the fact thata 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 vapour and liquid in equilibrium.
- This is an operation, often exploited in the chemical industry to achieve the desired enrichment of a feedstock through a one-step distillation process.
- Flash calculations are used for processes with vapour/liquid equilibrium. A typical process that requires flash calculations, is when a feed stream (F) is separated into a vapour (V) and liquid (L) product.

Flash Calculations (2)

In principle, flash calculations are straight forward and involve combining the VLE equations with the component mass balances and in some cases the energy balance.

Some flash calculations are:

- 1. Bubble point at given T (easy).
- 2. Bubble point at given P (need to iterate on T).
- 3. Dew point at given T (easy).
- 4. Dew point at given P (need to iterate on T).
- 5. Flash at given P and T (relatively easy)
- 6. Flash at given P and H ("standard" flash e.g. for a flash tank after a valve).
- 7. Flash at given P and S (e.g. for condensing turbine).
- 8. Flash at given U and V (e.g. for dynamic simulation of an adiabatic flash drum).

Flash Calculations (3)

- We shall concern ourselves only with the P T-flash, which refers to any calculation of the quantities and compositions of the vapour and liquid phases of a two-phase system in equilibrium at known T, P, and overall composition.
- Consider a system containing one mole of nonreacting chemical species with an overall composition represented by the set of mole fractions $\{z_i\}$. Let L be the moles of liquid, with mole fractions $\{x_i\}$, and let V be the moles of vapour, with mole fractions $\{y_i\}$.

The material balance equations are:

$$L + V = F$$

 $z_i = x_i L + y_i V$ (*i* = 1, 2, ..., *N*)

Flash Calculations (4)

• Combining the equations to eliminate *L* gives:

$$z_i = x_i(F - V) + y_iV$$
 (i = 1, 2, ..., N) (10)

• Substituting $x_i = \frac{y_i}{K_i}$ and solving for y_i yields:

$$y_i = \frac{z_i K_i}{1 + \frac{V}{F}(K_i - 1)} \tag{11}$$

• Since $\sum_{i} = 1$, Eq. (10) is summed over all species:

$$\sum_i rac{z_i \mathcal{K}_i}{1 + V(\mathcal{K}_i - 1)} = 1$$

(12)

Flash Calculations (5)

- The initial step in solving a P T-flash problem is to find the value of V which satisfies Eq. (12). Note that V = 1 is a trivial solution.
- Substituting $x_i = \frac{y_i}{\kappa_i}$, an alternative solution is:

$$x_i = \frac{z_i}{1 + V(K_i - 1)}$$
(13)

$$\sum_{i} rac{z_i}{1 + V(K_i - 1)} = 1$$
 (14)

• Subtracting Eq. (14) from Eq. (13) and defining a function ϕ we get

$$\phi = \sum_{i} \frac{z_i(K_i - 1)}{1 + V(K_i - 1)} = 0$$
(15)

Flash Calculations (6)

• It follows that:

$$\frac{d\phi}{dV} = -\sum_{i} \frac{z_i (K_i - 1)^2}{[1 + V(K_i - 1)]^2}$$
(16)

The derivative ^{dφ}/_{dV} is always negative, meaning that the relation between φ and V is monotonic, and the makes convenient application for the well-known Newton-Raphson method of solution; leading to the equation for the nth iteration:

$$V_{n+1} = V_n - \frac{\phi}{\left(\frac{d\phi}{dV}\right)_n} \tag{17}$$

Example 2: Flash calculation

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

Solution 2: Flash calculation

• Do a bubble pressure calculation with $\{z_i\} = \{x_i\}$.

$$P_b = \sum_i x_i P_i^s$$

• Do a dew pressure calculation with $\{z_i\} = \{y_i\}$.

$$\frac{1}{P_d} = \sum_i \frac{y_i}{P_i^s}$$

• If the given pressure lies between the P_b and P_d , the system is in two-phase and a flash calculation can be carried out.

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

Solution 2: Flash calculation (2)

• Solve the Rachford-Rice equation:

$$\phi = \sum_{i}^{N} \frac{z_i(K_i - 1)}{1 + V(K_i - 1)} = 0$$

• Obtain $\{y_i\}$ and $\{x_i\}$:

$$egin{aligned} y_i &= \sum_i^N rac{z_i \mathcal{K}_i}{1 + V(\mathcal{K}_i - 1)} \ x_i &= \sum_i^N rac{z_i}{1 + V(\mathcal{K}_i - 1)} \end{aligned}$$

VLE algorithms for Low to Moderate Pressure