Chapter 7 Vapour-Liquid Equilibria

7.1 Introduction

Both the general criterion of thermodynamic equilibrium as well as the specific condition of equality of chemical potential of each species which hold at equilibrium was introduced in the last chapter. We now develop the detailed relationships connecting the phase variables (T, P and composition) that originate from the concepts of chemical potential and the fugacity coefficient. The basic principle employed in all separation processes is that under equilibrium the compositions of phases differ from each other, and therefore it is possible to preferentially concentrate one species over another (or others) in one particular phase. This feature of phase equilibria is exploited in a wide variety of process equipments such as distillation, extraction, crystallization, etc.

This chapter focuses on the vapour-liquid equilibria (VLE) problem which is depicted schematically in fig. 7.1. When a multi-component, vapour and liquid phase – each (say) containing N chemical species – co-exist in thermodynamic equilibrium at a temperature T and pressure P, the phase compositions $\{y_1, y_2,...y_{N-1}\}$ and $\{x_1, x_2,...x_{N-1}\}$ remain invariant with time, and are related by a unique set of relations. If the relations are known as a function of temperature, pressure and compositions $\{y_i \ and \ x_i\}$ for each species, then provided some of these variables are specified the rest may be calculated. We will derive such relations for real multi-component systems; but as in all cases of thermodynamic modeling we take the ideal system as our starting point. Next the VLE of systems at moderate pressures are treated. Finally the relations for VLE at high pressures are presented. In the following section we derive the relations that hold for pure component VLE before describing those which apply to multi-component systems.
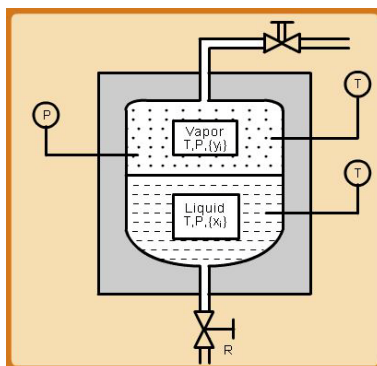

Fig. 7.1 The VLE Problem Description

7.2 Single Component System Phase Equilibria

We start with the general criterion of equality of the chemical potential in the two phases. To generalize the results we assume that any two types of phases α and β of a pure component are at equilibrium. Thus as given by eqn. 6.50:

$$\mu_i^\alpha = \mu_i^\beta \qquad\qquad\qquad\qquad ..(6.50)$$

However, for a pure component the chemical potential is reduces to the pure component molar Gibbs free energy. Therefore:

$$\mu_i^\alpha = G^\alpha \text{ and, } \mu_i^\beta = G^\beta \qquad\qquad\qquad ..(7.1)$$

Thus eqn. 6.50 reduces to:

$$G^\alpha = G^\beta \qquad\qquad\qquad\qquad ..(7.2)$$

On taking a differential:

$$dG^\alpha = dG^\beta \qquad\qquad\qquad\qquad ..(7.3)$$

Using the generic relationship in eqn. 5.7 we may write in keeping with the fact that for a given equilibrium temperature, the equilibrium pressure corresponds to the saturation vapour pressure P^{sat} :

$$V^\alpha dP^{sat} - S^\alpha dT = V^\beta dP^{sat} - S^\beta dT \qquad\qquad ..(7.4)$$

On rearranging:

$$\frac{dP^{sat}}{dT} = \frac{S^\beta - S^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}} \qquad\qquad\qquad ..(7.5)$$

Additionally using the second law we have:

$$dS = dQ/T \qquad\qquad\qquad\qquad ..(7.6)$$

And that for a constant pressure process:

$$dQ = dH \qquad\qquad\qquad\qquad ..(7.7)$$

Using eqns. (7.6) and (7.7) we obtain:

$$\Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta} \qquad\qquad\qquad\qquad ..(7.8)$$

Thus, $\Delta S^{\alpha\beta} = \Delta H^{\alpha\beta}/T$, and substitution in eqn.7.5 gives:

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}} \qquad\qquad\qquad\qquad ..(7.9)$$

The last equation is called the *Clapeyron* equation. For the specific case of phase transition from liquid (l) to vapor (v), it translates into:

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{LV}}{T \Delta V^{LV}} \qquad ..(7.10)$$

Noting that liquid phase molar volumes are relatively much lesser than vapour phase volumes, we may write, $\Delta V^{LV} = V^V - V^V \cong V^v$ ..(7.11)

Further at low to moderate saturation pressures if we assume ideal vapour phase behaviour, then

$$V^v \cong \frac{RT}{P^{sat}} \qquad ..(7.12)$$

Eqn. 7.10 then becomes:

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{LV}}{RT / P^{sat}}$$

Or:

$$\frac{dP^{sat} / P^{sat}}{dT / T^2} = \frac{\Delta H^{LV}}{R} \qquad ..(7.13)$$

Whence, $\Delta H^{LV} = -R[\dfrac{d \ln P^{sat}}{d(1/T)}]$ ..(7.14)

This approximate equation is known as the *Clausius-Clapeyron equation*. The assumptions used in the above derivations have approximate validity only at low pressures. Integrating eqn. 7.14 we have:

$$\ln P^{sat} = A - \frac{B}{T} \qquad ..(7.15)$$

On comparing eqns. 7.14 and 7.15, it follows that: $B = \Delta H^{LV} / R$, while A is the constant of integration. These are generally regarded as constants for a given species. A plot of experimental values of lnP^{sat} vs. *1/T* generally yields a line that is nearly straight between the triple and critical points. However, the validity of eqn. 7.15is questionable at relatively high pressures, and certainly in the critical region. Thus the accuracy of the Clausius-Clapeyron equation reduces at higher pressures. A modified form of eqn. 7.15, called the Antoine Equation, has proved to be more accurate (including at higher pressures), has the following form:

$$\ln P^{sat} = A - \frac{B}{T + C} \qquad ..(7.16)$$

A, B, and C are readily available for a large number of species. Appendix VI provides values of Antoine constants for select substances. More complex forms of equations relation temperature and

vapour pressure of pure substances have been reported in the literature, which provide even greater accuracy. An example of such an equation is the Wagner equation, which is given by:

$$\ln P_r^{sat} = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1-\tau}, \text{ where } \tau = 1 - T_r \qquad ..(7.17)$$

The constants for the Wagner equation for specific substances are available in several reference texts (see R.C. Reid, J.M. Prausnitz and B.E. Poling, *Properties of Gases and Liquids*, 4th ed., McGraw-Hill, 1987).

7.3 Derivation of the Phase Rule

The phase rule was introduced in section 1.5 without proof. Here we develop its mathematical form based on the tenets of solution thermodynamics and phase equilibrium criterion presented in the last chapter. Consider a *non-reactive* system under equilibrium, with π phases each containing N independent chemical species. The degrees of freedom for the system, i.e., the number of intensive variables that may vary independently of each other would be given by:

Degrees of freedom = Total number of systemic intensive variables –number of independent equations relating all the variables.

For the system of interest here the above terms are as follows:

 I.   Total number of systemic intensive variables (also called the phase rule variables)= *T, P and (N-1)* species mole fractions for each of the π phases

 II. Number of independent relations connecting the phase rule variables = $(\pi - 1)N$

The second relation above follows from the fact that for each of the *N* species one may use the chemical potential equality relation across all π phases, as described by eqn. 6.52. It follows that for each component there can be only $(\pi - 1)$ independent relations.

Thus the phase rule may be rewritten as:

$$F = \left[2 + (N-1)\pi\right] - \left[(\pi-1)N\right] = 2 + N - \pi \qquad (7.18)$$

It may be noted that the actual mass of each of the species present are not considered as phase rule variables, as they cannot influence the intensive state of the system. A special case of the phase rule obtains for closed systems for which the initial mass for each species is fixed. Since no mass can

enter or leave the system, the extensive state of the system is rendered fixed along with the intensive variables. Therefore, apart from the $(\pi-1)N$ constraining relations involving the species chemical potentials, there is an additional $\left[(N-1)\pi\right]$ constraint on the mass of each species; this follows from the fact that if a quantum of a species leaves a phase it must reappear in another or more. Thus the phase rule eqn. leads to:

$$F = \left[2 + (N-1)\pi\right] - \left[(\pi-1)N\right] - \left[(N-1)\pi\right] = 2 \qquad\qquad ..(7.19)$$

The above equation is known as the *Duhem's theorem*. It implies that for any closed system formed initially from given masses of a number of chemical species, the equilibrium state is completely determined when any two independent variables are fixed. The two independent variables that one may choose to specify may be either intensive or extensive. However, the number of *independent intensive* variables is given by the phase rule. Therefore, it follows that when F = 1, at least one of the two variables must be extensive, and when F = 0, both must be extensive.

7.4 Description of General VLE Behavior

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 restrict ourselves to description of VLE of multi-component systems to the corresponding mathematical formulation.

When N = 2, the phase rule yields a degree of freedom $F = 4 - \pi$. In the general VLE problem since there are at least two phases, the corresponding number of independent intensive variables become 2. In the case of extractive distillation, there are at least two liquid phases and a vapour phase, whence the degrees of freedom reduce to 1.In the following discussion we present the phase behaviour of the simplest case of a binary VLE. The more volatile of the two is designated as component (1). The phase rule variables for this case are: T, P, y_1 and x_1. Graphical plots of experimentally obtained phase behaviour can then be expressed as a functionof various combinations of these variables. For example at a given temperature one may plot two curves, *P vs. x_1* (or in short *P-x_1*) and *P vs. y_1*. Similarly on specifying a certain pressure, one may plot *T vs. x_1* and *T vs. y_1*. In addition if one fixes either x_1 or y_1 one may plot P-T diagrams. The combination of these diagrams lead to a 3-dimensional surface

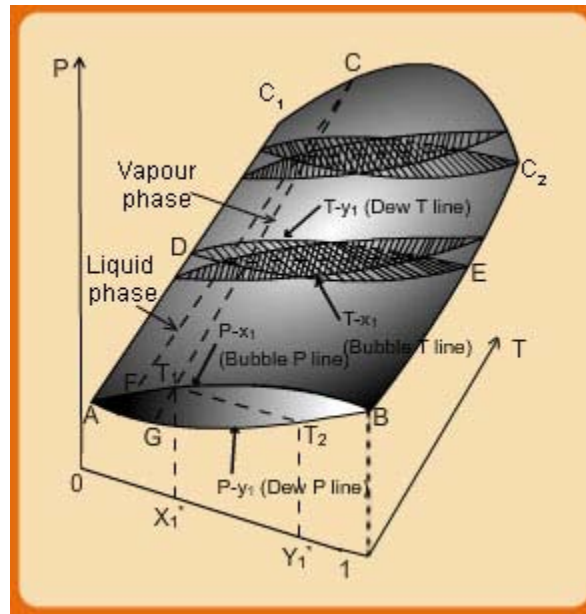involving pressure, temperature and phase compositions on the three axes. A typical plot is shown in fig. 7.2.

Fig. 7.2 Three dimensional VLE phase diagram for a binary system

Consider first a case of VLE phase behaviour at a constant temperature. This is in shown as the "lens" AB. The lower part of the lens corresponds to P-y_1 while upper curve is the P-x_1 plot. The values of the vapour and liquid compositions at any system equilibrium pressure are found by drawing a line parallel to the $x_1 - y_1$ axis. The point of intersection of this line with the upper curve provides the saturated liquid phase composition (x_1) and is termed the *bubble pressure line*; while that with the lower curve corresponds to the saturated vapour phase composition (y_1) and is termed the *dew pressure line*. Extending the description the entire upper face of the three dimensional surface constitutes the bubble surface. Any point above it corresponds to the state of sub-cooled liquid. In the same manner, the lower face represents the dew surface. For any point below this face the state is that of a superheated vapour. The line that connects the phase compositions (x_1^* *and* y_1^*) is called the *tie line* (shown as T_1-T_2). Such tie lines may be drawn at any other pressure and the same considerations as above are valid.

Similarly, if one considers isobaric plots (shown as the lens DE), for any equilibrium temperature the vapour and liquid phase compositions are found by drawing a line that passes through the specific temperature and is parallel to the $x_1 - y_1$ axis. The upper intersection point provides the

vapour phase composition (*dew temperature line*), while the lower one corresponds to the liquid phase composition (*bubble temperature line*). Finally if one fixes the composition at a point on the $x_1 - y_1$ axis the intersection of a vertical plane through the composition point with the 3-dimension surface yields the curve FCG. The upper part of this curve, i.e., FC corresponds to the locus of liquid phase compositions while the lower one (CG) is that of the vapour phase compositions. The point C is the meeting point of the two curves and defines the critical point of the mixture at the composition specified by the original vertical plane at a point on the $x_1 - y_1$ axis. At the two end points of the composition axis are the pure component P-T plots which terminate at the critical points, C_1-C_2, of the two substances.

　　If one takes a series of varying isothermal or isobaric "lenses", two types of plots result, which are shown in fig. 7.3. Consider the P-x-y plot. The lowest lens (T_X) corresponds to the situation already described in the last paragraph (i.e., the lens MN). However, the one at T_Y corresponds to a case for which $T_{C1} < T_Y$, but $T_{C2} > T_Y$. Thus at this temperature the vapour and liquid phases of the pure component '1' cannot co-exist, and hence the P-x-y plot vanishes as the composition tends to $x_1 \rightarrow 1$. If one moves to a still higher temperature say T_Z the P-x-y "hangs" at both ends of the $x_1 - y_1$ as both $T_{C1} < T_Z$, and $T_{C2} < T_Z$. The considerations for the isobaric lenses at P_X, P_Y and P_Z are the same as for the isotherms, i,e., for the highest isobar, both $P_{C1} < P_Z$, and $P_{C2} < P_Z$ and so on.
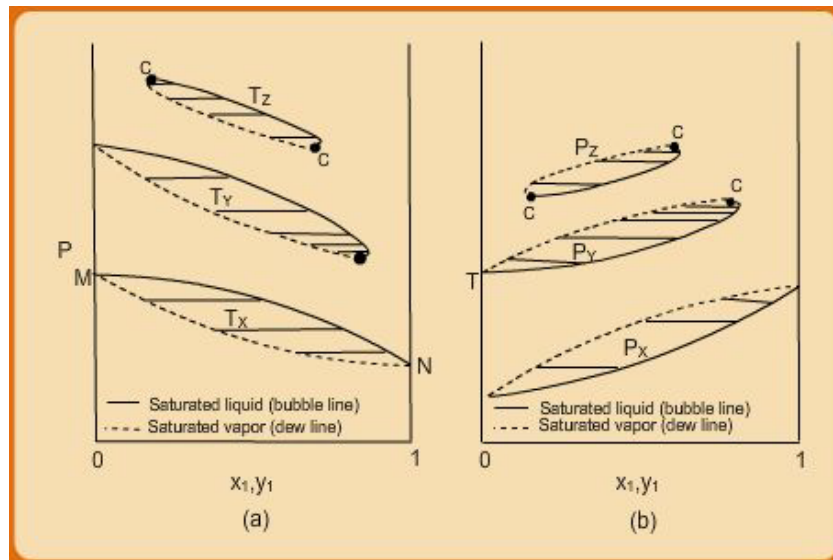

Fig. 7.3 (a) *P-x₁–y₁* diagrams for three temperatures. (b) *T-x₁-y₁* diagrams for three pressures

If one considers now a series of P-T plots they correspond to the curves shown in fig, 7.4. The lines I-J

and K-L which represent the vapour pressure-vs.-T curves for pure species 1 and 2 respectively. At other intermediate compositions the upper and lower plots (obtained by intersection of a vertical plane at constant point on the $x_1 - y_1$ axis, and the P-T-x-y surface of fig. 7.2) constitute a curve that rounds off at the *true* critical point of the mixture (as opposed to the "pseudo-critical" temperature
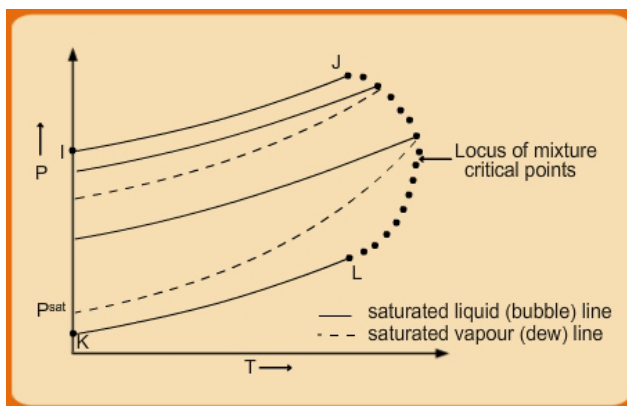

Fig. 7.4 P-T diagram for various compositions

and pressure of mixtures discussed in section 2.4). The critical points of the various mixtures of the two species thus lie along a line on the rounded edge of the surface between J and L; it is, therefore composition dependent. Each interior loop represents the *P-T* behavior of saturated liquid and of saturated vapour for a mixture of *constant composition;* the loops differ from one composition to another. It follows that the *P-T* relation for saturated liquid is different from that for saturated vapour of the same composition. This is in contrast with the behavior of a pure species, for which the bubble and dew lines are the same, as for I-J and K-L.

The above discussion suggests that the phase behaviour of even a simple binary can be relatively more difficult to interpret in its complete three-dimensional form. Reducing such behaviour to two-dimensional plots enables easier visualization of the phase behaviour and understanding their features. However, in many instances, even two dimensional plots can be more complex in nature. Examples of such curves (as are often encountered with solvent mixtures in industrial practice) are shown schematically in the form of *(P-x-y)* in fig. 7.5, for systems at relatively low pressures ($\leq 1\, atm$).
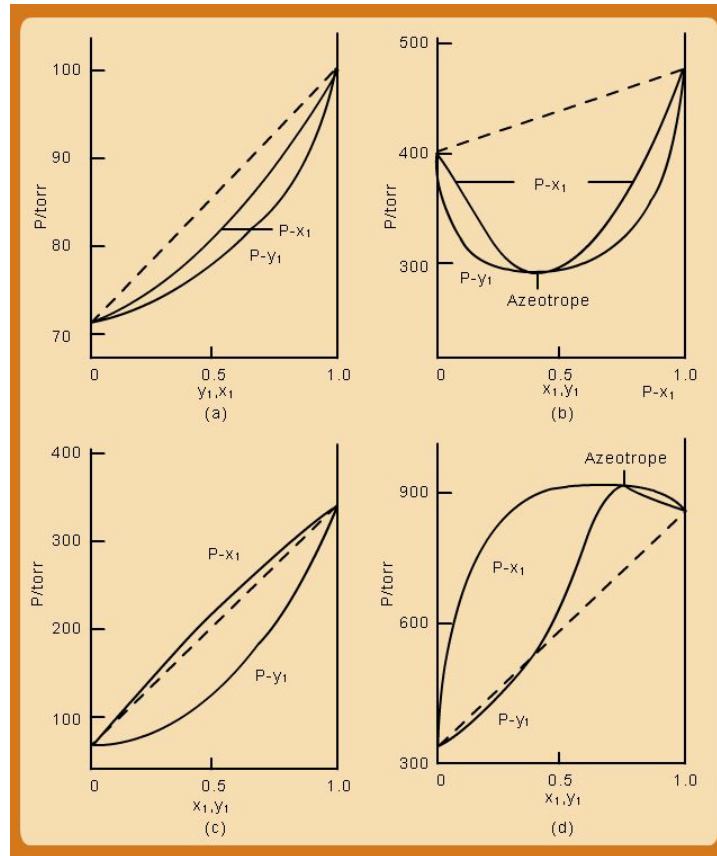
Fig. 7.5 Schematic P-x-y plots showing deviation from ideal VLE behaviour

All the four systemic VLE behaviour exhibits deviation from ideal vapour-liquid systems. As discussed in the next section ideal VLE behaviour is characterized by Raoult's Law (RL). Suffice it mention here that non-ideal VLE systems may exhibit both *negative* (figs. 7.5a & 7.5b) and *positive* deviations (figs. 7.5c and 7.5d) from that which obeys the Raoult's law (RL). The RL behaviour is typified by the dotted P-x_1 lines in each set in fig. 7.5. When the *actual P-x_1* line lies below the RL-line, the system is said to show negative deviation from RL, while if it lies above it is indicative of a positive deviation.

From a molecular thermodynamic viewpoint, negative deviations occur if the 1-2 type (between unlike species) of molecular interactions (attraction) are *stronger* than 1-1 or 2-2 (between like species) type of interaction. As a result, the molecules of the more volatile component (1) are "constrained" by those of component 2 from transiting to the vapour phase to a *greater* extent than in the case when the former is present in a pure form. This effectively translates into an equilibrium pressure less than the RL system at the same liquid phase composition; hence the actual system displays "negative" deviation in comparison to RL for which 1-1, 2-2, and 1-2 types of interactions are

more or less the same. Appreciable negative departures from P-x_1 linearity reflect strong liquid-phase intermolecular interaction. The opposite applies to the case where a system shows a positive deviation from RL; that is, the interaction between the unlike species of molecules is *lower* than that between like molecules.

There is an additional complexity evident in figs. 7.5c and 7.5d. Considering the former we see that it is defined by two distinct types of behaviour on either sides of the point termed as the "azeotrope". At this point the *P*-x_1 and the *P*-y_1 curves converge; i.e., the two phases are identical in composition at this point. On left side of the azeotrope $x_1 > y_1$, while on the other side, $x_1 < y_1$. The reverse situation holds for the system depicted in fig. 7.4d. Such systems are not uncommon in the process industry and always pose a difficulty in purifying a mixture to compositions higher than the azeotropic point. This is because during a distillation process when the mixture composition arrives at the azeotropic point the two phases become identical in composition, and the liquid composition does not alter further during evaporation.

The phase behaviour of the same systems as in fig. 7.5 is depicted as *T-x-y* diagrams in fig. 7.6. In particular we refer to the figs 7.6b and 7.6d. As expected the P-x curves *appear inverted* on a T-x diagram. The first kind of system (fig. 7.6b) is said to show a *maximum* boiling point azeotrope, while that depicted by fig. 7.5d shows a *minimum* boiling point azeotropic behaviour.
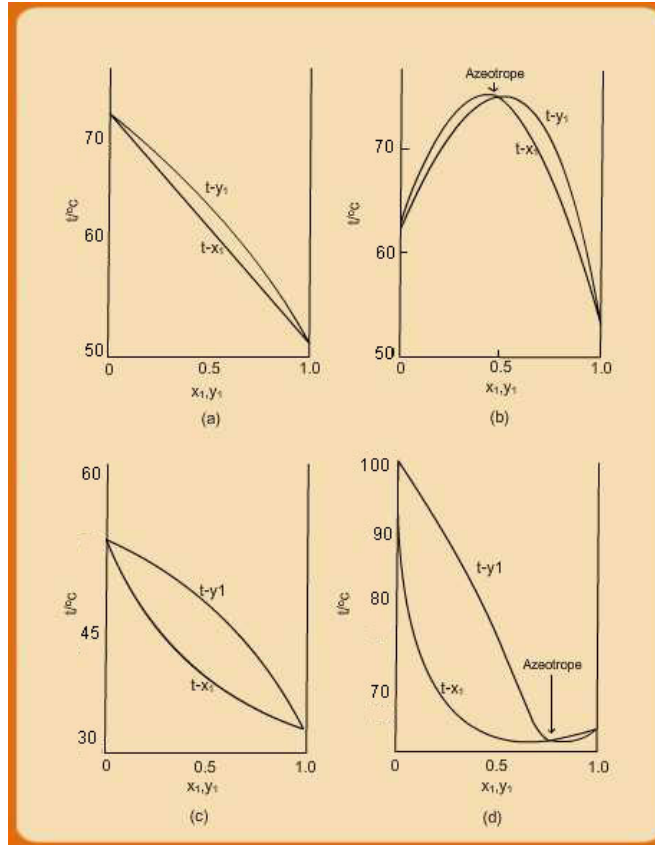
Fig. 7.6 Schematic T-x-y plots showing deviation from ideal VLE behaviour

7.5 Raoult's Law for VLE

As mentioned in the concluding part of the last section, vapour-liquid systems which are *ideal* in nature display a behaviour corresponding to Raoult's Law. In such a system, both the vapour and the liquid phases essentially behave as ideal mixtures. For describing the VLE for such systems we start by applying eqn. 6.50, to the vapour and liquid phases:

$$\mu_i^V = \mu_i^L \qquad \qquad ..(7.20)$$

For an ideal vapor mixture by eqn. 6.72 we have:

$$\mu_i^{ig} \equiv G_i^{ig} + RT \ln y_i$$

Similarly for an ideal liquid solution eqn. 6.77 provides:

$$\mu^{id} = G_i^{id} + RT \ln x_i$$

Thus rewriting eqn. 7.20 (using expressions provided by eqns. 6.72 and 6.77):

$$\mu_i^{ig} \equiv \mu_i^{id} \qquad \qquad ..(7.21)$$

$$G_i^{ig} + RT \ln y_i = G_i + RT \ln x_i \qquad\qquad ..(7.22)$$

Or: $RT \ln(y_i / x_i) = G_i - G_i^{ig}$ ..(7.23)

Since effect of pressure is negligible on liquid properties we assume that:

$$G_i^l(T,P) \simeq G_i^l(T,P_i^s) \qquad\qquad ..(7.24)$$

Now for the gas phase: $dG_i^{ig} = V_i^{ig} dP$ (at const T) ..(7.25)

Thus: $G_i^{ig}(T,P_i^s) - G_i^{ig}(T,P) = RT \int_P^{P_i^s} dP/P = RT \ln P_i^s / P$ ..(7.26)

Combining eqns. 7.23, 7.24 and 7.26 gives:

$$RT \ln(y_i / x_i) = G_i^l(T,P_i^s) - G_i^{ig}(T,P_i^s) + RT \ln(P_i^s / P) \qquad\qquad ..(7.27)$$

The first two terms on the RHS in equation above correspond to the Gibbs free energy of *pure* liquid and vapour phases under equilibrium conditions, i.e., at (T,P_i^s); hence, as shown in section 7.1, these terms equal. Therefore, it follows that:

$$y_i / x_i = P_i^s / P \qquad\qquad ..(7.28)$$

Alternately: $y_i P = x_i P_i^s$ ..(7.29)

Equation 7.29 is known as the Raoult's Law.

It may be noted that the conditions for ideal mixture behaviour for the gas and liquid phases are not the same in general. For the gas mixture to be ideal the pressures need to be close to atmospheric or less. While a liquid solution is ideal if the interaction between the *same* molecular species is identical to that between *dissimilar* molecules.

The algorithms needed for generating RL phase diagrams are discussed later in this section. But prior to that, we present examples of *typical* phase diagrams that obtain from the application of the Raoult's law (RL) equations. Consider again a binary system for which a representative *isothermal* plot is depicted in fig. 7.7. (The more volatile of the two components is designated as component '1'). The upper *straight* line represents the saturated liquid compositions, while the lower curve corresponds to the saturated vapour compositions. At any pressure, the phase compositions are found at the intersections of a line parallel to the *x-y* axis with the P-x and P-y curves. The straight line connecting these compositions is the tie line (such as A_1-B_1, A_2-B_2, etc.). The portion of the diagram enclosed by the *P-x-y* curves corresponds to the two phase region where the vapour and liquid phases co-exist. Any point lying outside of this two-phase envelope corresponds to a state where only a single phase is

present. Now consider the point L which lies above the phase envelope. At this condition the mixture exists as a *compressed* (or *sub-cooled*) state whose composition corresponds to x_1^*. Lowering the pressure at this fixed composition eventually brings the liquid mixture to the point A_3, where any further reduction of pressure leads to the formation of a vapour phase whose composition is given by B_3. Thus this point is characterized by the formation of the first bubble of vapour, and hence is termed the *bubble point*, the corresponding pressure being the *bubble pressure*, at the given composition.
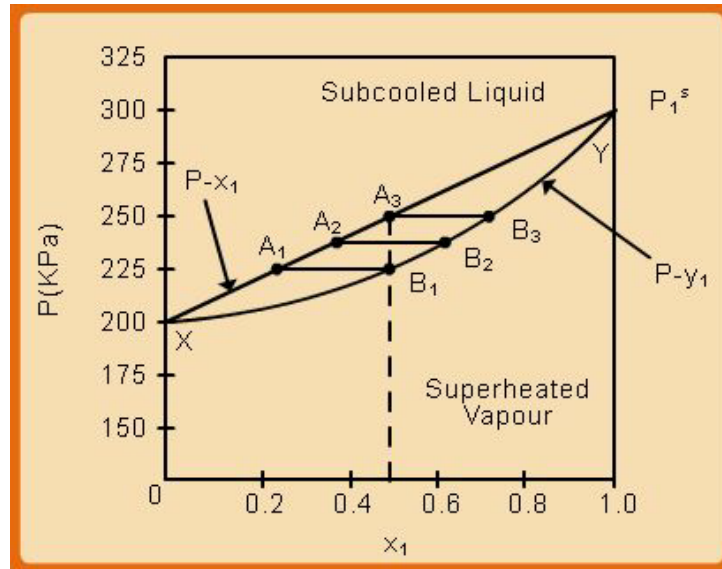

Fig. 7.7 Model P-x-y plot for a system obeying Raoult's Law

Next consider the point V in the above diagram. At this state the mixture is at the same overall composition as at L, but the state is one of single phase, *superheated vapour*. Increasing the pressure at the same composition eventually brings the mixture to the point B_1, where any further increase of pressure leads to the formation of the liquid phase, whose composition is given by the point A_1. Thus this point is said to be the *dew point* corresponding to the vapour phase composition given by y_1^*, while the pressure at this point is termed the dew pressure.

We revert to the discussion on the system state at the bubble point A_3. If one reduces the pressure progressively formation of more bubbles of vapour occurs, which coalesce and lead to the development of a bulk vapour phase. The system eventually reaches the point B_1 where practically the entire mixture exists in the vapour form; further reduction of pressure renders the mixture superheated and finally one reaches the point V (and beyond). Let us focus on what happens as the system transits through the two-phase region defined by the end points A_3 and B_1. Note that the *overall* composition of the system remains invariant as the pressure reduces. However, since now the original amounts of

each species need to be distributed across the co-existing vapour and liquid phases the actual composition in each phase must change in accordance with the following mass conservation equation: $z_1 (\equiv x_1^* \ or \ y_1^*) = x_1 L + y_1 V$; where, $z_1 =$ overall composition; x_1 and y_1 are compositions of the liquid and vapour phases at equilibrium, and L and V are the relative amounts of moles (per mole of the original mixture) in the liquid and vapour phases, respectively (thus $L + V = 1$). The liquid phase composition progressively changes along the line A_3 to A_1 (*bubble curve*), while the composition of the vapour phase in equilibrium with the liquid phase transits from B_3 to B_1 (*dew curve*). At each pressure between the bubble pressure (P_b) and the dew pressure (P_d) the equilibrium vapour and liquid phase compositions, as well as the relative amounts of mass in each phase are constrained by the relations: $z_1 (\equiv x_1^* \ or \ y_1^*) = x_1 L + y_1 V$; and $L + V = 1$.

The associated, isobaric T-x-y plots for the same system are shown in fig.7.7. As is expected the dew temperature curve lies *above* the bubble temperature curve. The lens-like region corresponds to the two-phase states of the system. At the point V the system is in a single phase, super-heated state.
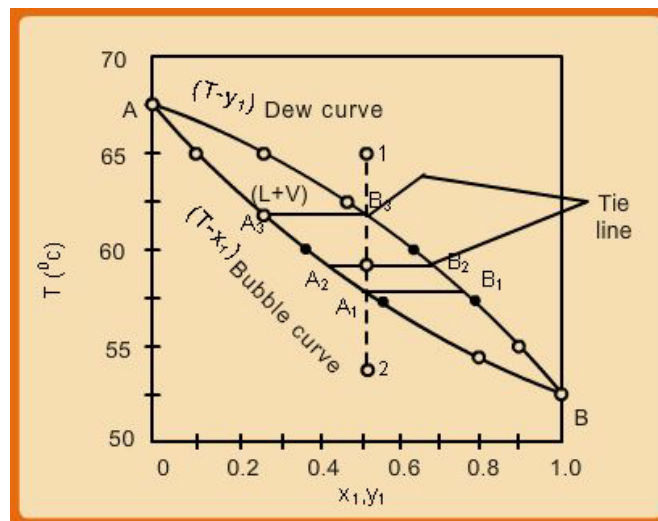
Fig. 7.8 Model T-x-y plot for a system obeying Raoult's Law

Progressive reduction of temperature brings it to the point B_3 where the *first* dew of liquid forms, whose composition is provided by the point A_3. Thus this point is referred to as the *dew point*, and the corresponding temperature called the *dew temperature*(T_d) for the given vapour phase composition (y_1^*). On the other hand if one starts from the point L (single-phase, compressed liquid state) gradual increase of temperature brings the system to A_1, the *bubble point*, where the first bubble of vapour forms. The associated temperature then is the *bubble temperature* (T_b) for the composition x_1^*. At any

other temperature intermediate to T_d and T_b, the system contains co-existing vapour and liquid phases whose compositions are constrained by the same mass conservation relations provided above, i.e., $z_1 (\equiv x_1^* \ or \ y_1^*) = x_1 L + y_1 V$; and $L + V = 1$. Note that as in the P-x-y plot the T-x-y plots also are characterized by horizontal tie lines that connect the compositions of the equilibrated vapour and liquid phases.

The data in figures 7.7 and 7.8 may be may be alternately displayed in the form of a *y-x* plot (fig. 7.9). It shows the equilibrium vapour and liquid phase compositions in a more immediate manner. Note that, as required by the phase rule, each pair of equilibrium *y* and *x* values correspond to a different combination of equilibrium temperature and pressure.
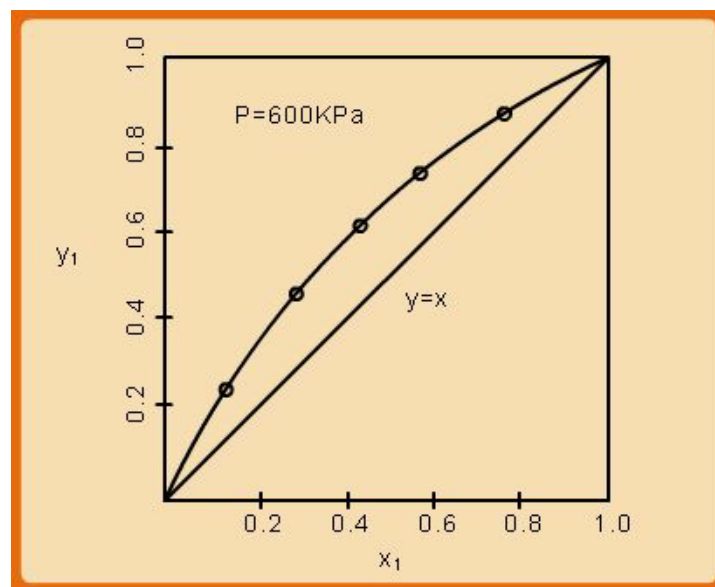
Fig. 7.9 Model y-x plot for a system obeying Raoult's Law

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 Raoult's Law (eqn. 7.29) 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 enumerated below in table 7.1 first and then the relevant algorithms used are presented.

Table 7.1 Types of VLE calculations

VLE Type	Specified Variables	Computed Variables
Bubble Pressure	T and $\{x_i\}$	P and $\{y_i\}$
Dew Pressure	T and $\{y_i\}$	P and $\{x_i\}$
Bubble Temperature	P and $\{x_i\}$	T and $\{y_i\}$
Dew Temperature	P and $\{y_i\}$	T and $\{x_i\}$
Flash Distillation	T, P and $\{z_i\}$	L or V, $\{x_i\}$ and $\{y_i\}$

In the above table the notations used signify the following:

$\{x_i\} \equiv overall\ liquid\ phase\ compoition \equiv \{x_1, x_2,...x_{N-1}\}$

$\{y_i\} \equiv overall\ vapour\ phase\ compoition \equiv \{y_1, y_2,...y_{N-1}\}$

$\{z_i\} \equiv overall\ feed\ composition\ to\ flash\ vessel \equiv \{z_1, z_2,...z_{N-1}\}$

$L \equiv moles\ of\ liquid\ phase\ formed\ per\ mole\ of\ feed\ to\ flash\ vessel$

In summary, therefore, one specifies either T or P and either the liquid-phase or the vapor-phase composition, thus fixing 1+(N-1) or N phase rule variables as required by the phase rule for VLE calculation. The variants of Raoult's Law (eqn. 7.29) which are used are as follows:

$$y_i = x_i P_i^s / P \qquad\qquad ..(7.30)$$

Thus:

$$\sum_i^N x_i P_i^s / P = 1$$

Or:

$$P = \sum_i^N x_i P_i^s \qquad\qquad ..(7.31)$$

Also:

$$x_i = y_i P / P_i^s \qquad\qquad ..(7.32)$$

Thus:

$$\sum_i^N y_i P / P_i^s = 1$$

Or:

$$P = 1 \bigg/ \sum_{i}^{N} y_i / P_i^s \qquad\qquad ..(7.33)$$

For computation of vapour pressures the Antoine equation (or another suitable equation) may be used:

$$\ln P_i^s = A_i - \frac{B_i}{t + C_i}; \text{ where } t = {}^0K \ (or \ {}^0C) \qquad\qquad ..(7.34)$$

Values of Antoine constants for a select group of substances are tabulated in Appendix IV. More exhaustive tabulation is available at:

http://www.eng.auburn.edu/users/drmills/mans486/Diffusion%20Tube/Antoine_coefficient_table.PDF

Bubble Pressure:

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

   a) Use eqn. 7.31 to compute P

   b) Next use eqn. 7.30 to obtain $\{y_i\}$

Dew Pressure:

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

   a) Use eqn. 7.33 to compute P

   b) Use eqn. 7.32 to obtain $\{x_i\}$

Bubble Temperature:

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

   a) For the given pressure compute $\{T_i^s\}$ using the following form of Antoine eqn.

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

   b) Initialize the bubble temperature as: $T_{b(i)} = \sum_{i}^{N} x_i T_i^s$

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

   d) Use equation 7.30 to compute $\{y_i\}$

e) Is $\left| \sum_i y_i - 1 \right| < \varepsilon$?   (ε = pre - defined acceptable error for convergence)

f) If yes, $T_{last} = T_{b(f)}$; where $T_{b(f)}$ = final acceptable bubble temperature

g) At $T_{b(f)}$ compute final $\{y_i\}$

h) If $\sum_i y_i - 1 > \varepsilon$, then $T_{last} > T_{b(f)}$; revise to *new* T as: $T_{new} = T_{last}\left(\dfrac{\varepsilon}{\sum_i y_i - 1} \right)$ and return to step (c).

i) If $\sum_i y_i - 1 < -\varepsilon$, then the assumed $T < T_{b(f)}$; where $T_{b(f)}$ = final acceptable bubble temperature

   Revise to *new* T using: $T_{new} = T_{last}\left(\dfrac{\left| \sum_i y_i - 1 \right|}{\varepsilon} \right)$ and return to step (c).

Dew Temperature:

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

a) For the given pressure compute $\{T_i^s\}$ using the following form of Antoine eqn.

b) $T_i^s = \dfrac{B_i}{A_i - \ln P} - C_i$

c) Initialize the dew temperature as: $T_{d(i)} = \sum_i^N x_i T_i^s$

d) Using computed T calculate $\{P_i^s\}$

e) Use equation 7.33 to compute $\{x_i\}$

f) Is $\left| \sum_i x_i - 1 \right| < \varepsilon$?   (ε = pre - defined acceptable error for convergence)

g) If yes, $T_{last} = T_{d(f)}$; where $T_{d(f)}$ = final acceptable bubble temperature

h) At $T_{d(f)}$ compute final $\{x_i\}$

j) If $\sum_i x_i - 1 > \varepsilon$, then $T_{last} < T_{d(f)}$; revise to *new* T as: $T_{new} = T_{last}\left(\dfrac{\sum_i x_i - 1}{\varepsilon} \right)$ and return to step (c).

k) If $\sum_i x_i - 1 < -\varepsilon$, then $T_{last} > T_{d(f)}$; revise to *new* T as: $T_{new} = T_{last} \left(\dfrac{\left| \left| \sum_i x_i - 1 \right| \right|}{\varepsilon} \right)$ and return to step

(c).

Example 7.1

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

$$\ln P_1^S = 14.5463 - \frac{2940.46}{t + 237.22}; \ln P_2^S = 14.5463 - \frac{2940.46}{t + 237.22}; \ln P_3^S = 14.2043 - \frac{2972.64}{t + 209.00}$$

$P_i^S (KPa); t(^0C).$

Calculate: (a) P, $\{y_i\}$ for a temperature = 80°C, $x_1 = 0.3$, $x_2 = 0.3$ (b) P, $\{x_i\}$, for t = 70°C, $y_1 = 0.5$, $y_2 = 0.3$.

(Click for solution)

Flash Distillation Calculations

This is an operation, often exploited in the chemical industry to achieve the desired enrichment of a feedstock through a one-step distillation process. A schematic of the process is shown in fig. 7.6. A liquid at a pressure equal to or greater than its bubble point pressure is introduced into the flash by passing it through a pressure reduction valve. The abrupt reduction in pressure "flashes" or partially evaporates the feed liquid, which results in the formation of a vapour and a liquid stream which are typically assumed to leave the flash vessel in equilibrium each other.
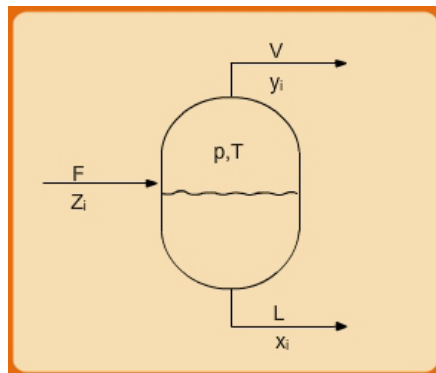

Fig. 7.10 Schematic of Flash Distillation Process

One of the common forms of flash calculation typically involves the determination of the liquid and vapour stream composition that results from process as well also the resultant liquid or vapour phase mole fractions that obtains per mole of feed. Consider a system containing one mole of mixture of chemical species with an *overall* composition represented by the set of mole fractions $\{z_i\}$. Let L and V be the moles of liquid and vapour formed per mole of feed. The corresponding stream compositions are denoted as $\{x_i\}$ and $\{y_i\}$ respectively. The material-balance equations are:

$$F = L + V = 1 \quad\quad\quad ..(7.35)$$

$$z_i F = x_i L + y_i V$$

$$z_i = x_i(1-V) + y_i V; \quad\quad\quad ..(7.36)$$

Now: $K_i = y_i/x_i = P_i^s/P \quad\quad\quad ..(7.37)$

Putting $x_i = y_i/K_i$ and using relations in (7.44) one obtains:

$$y_i = \frac{z_i K_i}{1+V(K_i-1)} \quad\quad\quad ..(7.38)$$

$$\sum_i y_i = 1$$

Using this condition in eqn. 7.38:

$$\sum_i \frac{z_i K_i}{1+V(K_i-1)} = 1 \quad (i = 1, 2....N) \quad\quad\quad ..(7.39)$$

Since $x_i = y_i/K_i$, an alternative equation is:

$$x_i = \frac{z_i}{1+V(K_i-1)} \quad (i = 1,2,....N) \quad\quad\quad ..(7.40)$$

It follows that: $\sum_i \dfrac{z_i}{1+V(K_i-1)} = 1 \quad\quad\quad ..(7.41)$

Subtracting eqn. 7.41 from 7.39 and defining a function φ we get

$$\varphi = \sum_i \frac{z_i(K_i-1)}{1+V(K_i-1)} = 0 \quad\quad\quad ..(7.42)$$

It follows that: $\dfrac{d\varphi}{dV} = -\sum_i \dfrac{z_i(K_i-1)^2}{[1+V(K_i-1)]^2}$ ..(7.43)

The derivative $\dfrac{d\varphi}{dV}$ is always negative; in other words the relation between φ vs. V is monotonic, and this makes for convenient application of the well-known Newton-Raphson method of solution (see Appendix VII); this leads to the following equation for the nth iteration:

$$V_{n+1} = V_n - \dfrac{\varphi_n}{\left(\dfrac{d\varphi}{dV}\right)_n}$$ ..(7.44)

Where, the values for φ and $\left(\dfrac{d\varphi}{dV}\right)$ may be computed using eqns. 7.42 and 7.43 respectively.

Example 7.2

A liquid mixture containing equimolar amounts of benzene (1) /toluene (2) and ethylbenzene (3) is flashed to conditions of T = 110°C, P = 90 kPa, determine the equilibrium mole fractions $\{x_i\}$ and $\{y_i\}$ of the liquid and vapor phase formed and the molar fraction V of the vapor formed. Assume that Raoult's law applies. $\ln P^{sat}(Pa) = A - \dfrac{B}{t(^{0}K)+C}$

	A	B	C
Benzene	13.8594	2773.78	-53.08
Ethylbenzene	14.0045	3279.47	-59.95
Toluene	14.0098	3103.01	-53.36

(Click for solution)

7.6 VLE Algorithms for Low to Moderate Pressures

The next level of complexity in VLE algorithms arise when one has to account for non-ideal behaviour for both the gas and liquid phases. This may obtain at pressures away from atmospheric and if the constituent molecules form a non-ideal liquid phase. The general approach to VLE of such system involves correcting both sides of the Raoult's law to incorporate the effect of non-ideal behaviour. If the pressures are moderately high the truncated virial EOS may be used to describe the gas phase

behaviour, whereas the liquid phase non-ideality is defined by a suitable activity coefficient model. The activity coefficient based approach is preferred for moderate pressures, as under such conditions the liquid phase properties may be conveniently regarded as independent of pressure, hence only temperature effects on the activity coefficients need be accounted for. This approach, of course, is rendered inaccurate at relatively high pressures, where both the gas and liquid phases need to be described using fugacity coefficients derived typically from a cubic (or a higher order) EOS. This is dealt with in the next section. Presently the VLE algorithms for low to moderate pressure range are introduced. The starting point is the eqn. (6.126):

$$\hat{f}_i^\alpha = \hat{f}_i^\psi \qquad\qquad ..(6.126)$$

Applying it to VLE:

$$\hat{f}_i^V = \hat{f}_i^L \qquad\qquad ..(6.127)$$

For gas phase, we use eqn. 6.129:

$$\hat{f}_i^V = y_i \hat{\phi}_i P$$

For liquid phase (using eqn. 6.164):

$$\hat{f}_i^L = x_i \gamma_i f_i$$

Applying eqn. 6.127:

$$y_i \hat{\phi}_i P = x_i \gamma_i f_i \qquad\qquad ..(7.45)$$

From basic fugacity function for liquid phase (eqn.6.119):

$$f_i(T,P) = \phi_i^{sat} P_i^{sat} \exp[\frac{V_i^l (P - P_i^{sat})}{RT}] \qquad\qquad ..(6.119)$$

Using eqn. 6.119 in 6.128 we may write the phase equilibria relation as:

$$y_i \Phi_i P = x_i \gamma_i P_i^S ; \qquad\qquad (i = 1,2,... \text{ N}) \qquad\qquad ..(7.46)$$

Where $\Phi_i = (\hat{\phi}_i / \hat{\phi}_i^s) \exp[-\frac{V_i^L (P - P_i^s)}{RT}] \qquad\qquad ..(7.47)$

One may show that the Pontying (exponential factor) in the last equation is usually ~ 1 for low to moderate pressure range, hence one may write:

$$\Phi_i \approx (\hat{\phi}_i / \phi_i^s) \qquad\qquad ..(7.48)$$

For a gas mixture obeying the truncated virial EOS (by eqn. 6.98):

$$\phi_i^{sat} = \exp[\frac{B_{ii} P_i^s}{RT}]$$ ..(7.49)

Specifically for a binary using eqns. 6.149 and 6.150:

$$\ln \hat{\phi}_1 = \frac{P}{RT}(B_{11} + y_2^2 \delta_{12})$$ ..(6.149)

$$\hat{\phi}_2 = \exp[\frac{P}{RT}(B_{22} + y_1^2 \delta_{12})]$$ ..(6.150)

Using the last four equations it follows that:

$$\Phi_1 = \exp[\frac{B_{11}(P - P_1^s) + Py_2^2 \delta_{12}}{RT}]$$ ..(7.50)

And $$\Phi_2 = \exp[\frac{B_{22}(P - P_2^s) + Py_1^2 \delta_{12}}{RT}]$$ ..(7.51)

It may be shown that for a multi-component the general expression for Φ_i is provided by:

$$\Phi_i = \exp \frac{B_{ii}\left(P - P_i^s\right) + \frac{1}{2}P\sum_j\sum_k y_i y_k\left(\delta_{ji} - \delta_{jk}\right)}{RT}$$ ..(7.52)

Now, $\Phi_i = \Phi_i(T, P, y_1, ..., y_{N-1})$

And:

$$\gamma_i = \gamma_i(T, P, x_1, ..., x_{N-1}) \cong \gamma_i(T, x_1, ..., x_{N-1})$$ ..(7.53)

The approximation made in eqn. 7.53 is a reasonable one, as at low to moderate pressures the dependence of $\gamma_i \gamma_i$ on 'P' may be neglected (as at such conditions the liquid phase properties are not strongly pressure dependent).

The same five classes as provided in table 7.1 may be solved using this modified form of the Raoult's law. In all cases eqn. 7.46 provides the starting point for calculation, which may be re-written is two principal alternate forms as follows:

$$y_i = x_i \gamma_i P_i^s / \Phi_i P$$ ..(7.54)

$$x_i = y_i \Phi_i P / \gamma_i P_i^s$$ ..(7.55)

Since $\sum_i y_i = 1$

$$\sum x_i \gamma_i P_i^s / \Phi_i P = 1$$

Or:

$$P = \sum x_i \gamma_i P_i^s / \Phi_i \qquad\qquad ..(7.56)$$

Similarly since $\sum x_i = 1 = \sum y_i \Phi_i P / \gamma_i P_i^s$; it follows that:

$$P = 1 / \sum y_i \Phi_i / \gamma_i P_i^s \qquad\qquad ..(7.57)$$

We may also re-write eqn. 7.46 in terms of the K-factor (as used for Raoult's Law in eqn. 7.37) as follows:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^s}{\Phi_i P} \qquad\qquad ..(7.58)$$

Accordingly:

$$y_i = K_i x_i \qquad\qquad ..(7.59)$$

Or:

$$x_i = \frac{y_i}{K_i} \qquad\qquad ..(7.60)$$

From eqn. 7.59, it follows that:

$$\sum_i K_i x_i = 1 \qquad\qquad ..(7.61)$$

From eqn. 7.60:

$$\sum_i \frac{y_i}{K_i} = 1$$

Note that when $\Phi_i = \gamma_i = 1$ eqn. 7.46 reduces to the ideal case of Raoult's Law.

Bubble pressure:

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

  a) Start with given T, $\{x_i\}$, Antoine constants, $\in$ (error value for convergence)

  b) Set all $\{\Phi_i\} = 1.0$, Evaluate $\{P_i^s\}, \{\gamma_i\}$, Calculate P using eqn. 7.56

  c) Calculate $\{y_i\}$ using eqn.7.54

  d) Now evaluate $\{\Phi_i\}$, using eqns. 7.52

  e) Calculate P_{new} using eqn. 7.56

  f) Is $\delta P < \in$?

g) If 'No', go to step 'c' and calculate new $\{y_i\}$ with last $\{\Phi_i\}$

h) If 'Yes', end at last P, and $\{y_i\}$

Dew Point Pressure:

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

a) Start with T and $\{y_i\}$; Antoine constants; ε and δ (error values for convergence); start with Raoult's law by setting all $\{\Phi_i\} = 1.0$, and all $\{\gamma_i\} = 1.0$; Evaluate $\{P_i^s\}$, then calculate P using eqn. 7.57; Now evaluate $\{x_i\}$ by eqn. 7.55; Evaluate $\{\gamma_i\}$ using appropriate activity coefficient model Liquid-phase; recalculate P using eqn. (7.65), revise $\{\Phi_i\}$ using given $\{y_i\}$ and last P.

b) Calculate new set $\{x_i\}$ using eqn. 7.55

c) Normalize $\{x_i\}$ using $x_{i(n)} = \dfrac{x_i}{\sum x_i}$, and use normalized $\{x_i\}$ to compute $\{\gamma_i\}$

d) Use last $\{\gamma_i\}$ to calculate P by eqn. 7.57

e) Is $\delta P < \varepsilon$?

f) If 'Yes' then $P_{last} = P_{d(f)}$

Bubble Temperature:

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

a) Solve for T and $\{y_i\}$ first by assuming Raoult's Law algorithm for bubble temperature

b) Using solution in 'a' estimate $\{K_i\}$ using eqn. 7.58 with the given values of P and $\{x_i\}$; latest values of T and $\{y_i\}$

c) Next calculate $\{K_i x_i\}$

d) Calculate all $y_i = K_i x_i \Big/ \sum_i K_i x_i$

e) Using normalized $\{y_i\}$, recalculate $\{K_i\}$ and $\sum_i K_i x_i$

f) Has $\sum_i K_i x_i$ changed? If yes return to step 'd'

g) If $\sum_i K_i x_i$ has not changed between two successive iterations between steps 'c' and 'd' is

$$\sum_i K_i x_i = 1?$$

h) If *yes*, the last values of T and $\{y_i \equiv K_i x_i\}$ give the final bubble temperature $T_{b(f)}$, and vapour compositions.

i) If *no*, and last $\sum_i K_i x_i > 1$, then $T_{last} > T_{b(f)}$; revise to *new* T as: $T_{new} = T_{last} \left(\dfrac{1}{\sum_i K_i x_i} \right)$ and return to

step (c).and return to step 'b'.

j) If *no*, and last $\sum_i K_i x_i < 1$, then $T_{last} < T_{b(f)}$; revise to *new* T as: $T_{new} = T_{last} \sum_i K_i x_i$ and return to

step (c).and return to step 'b'.

Dew Temperature:

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

a) Solve for T and $\{x_i\}$ first by assuming Raoult's Law algorithm for dew temperature

b) Using solution in 'a' estimate $\{K_i\}$ using eqn. 7.58 with the given values of P and $\{y_i\}$;

latest values of T and $\{x_i\}$

c) Next calculate $\{y_i / K_i\}$

d) Calculate all $x_i = (y_i / K_i) \Big/ \sum_i (y_i / K_i)$

e) Using normalized $\{x_i\}$, recalculate $\{K_i\}$ and $\sum_i y_i / K_i$

f) Has $\sum_i y_i / K_i$ changed? If yes return to step 'd'

g) If $\sum_i y_i / K_i$ has not changed between two successive iterations between steps 'c' and 'd' is

$$\sum_i y_i / K_i = 1?$$

h) If *yes*, the last values of T and $\{x_i \equiv y_i / K_i\}$ give the *final* dew temperature $T_{d(f)}$, and liquid phase compositions.

i) If *no, and* $\sum_i y_i / K_i > 1$, then $T_{last} < T_{d(f)}$; revise to *new* T as: $T_{new} = T_{last} \sum_i x_i / K_i$ and return to step (b).

j) If *no, and* $\sum_i y_i / K_i < 1$, then $T_{last} > T_{d(f)}$; revise to *new* T as: $T_{new} = T_{last} \sum_i x_i / K_i$ and return to step (b).

Example 7.3

Methanol (1)-acetone (2) forms an azeotrope at 760 Torr with $x_1 = 0.2$, T = 55.7^{0}C. Using van Laar model predict the bubble pressure for a system with for $x_1 = 0.1$ at 55.7^{0}C.

$$\log_{10} P_1^s = 8.0897 - [1582.271 / (t + 239.726)]; \log_{10} P_2^s = 7.1171 - [1210.595 / (t + 229.664)]$$

$$P_i^s (torr); t(^0C)$$

(Click for solution)

Example 7.4

For a binary, the activity coefficients are $\ln \gamma_1 = Ax_2^2$ and $\ln \gamma_2 = Ax_1^2$. Show that the system forms an azeotrope when $A > \left| \ln \left(P_2^s / P_1^s \right) \right|$

(Click for solution)

Flash Distillation Calculations

The procedure for non-ideal systems takes a form similar to that adopted for systems obeying Raoult's Law except that one needs to additionally check for existence of both liquid and vapour phases following flash. The algorithm comprises the following steps.

a) Start with flash T, P and feed composition $\{z_i\}$

b) At the given T, calculate dew pressure P_d by putting $\{y_i\} = \{z_i\}$

c) Next calculate bubble pressure P_b by putting $\{x_i\} = \{z_i\}$

d) Is $P_d < P < P_b$? If *no*, the vapour phase has not formed.

e) If *yes*, compute $\{\Phi_i\}, \{\gamma_i\}$, and V as $\simeq \dfrac{P_b - P}{P_b - P_d}$

f) Use $\{\Phi_i\}, \{\gamma_i\}$, to get $\{K_i\}$ using eqn. 7.58

g) Then use eqn. 7.42 and 7.43 to evaluate φ and $d\varphi / dV$.

h) Using Newton-Raphson method, find V

i) With last V compute $\{x_i\}$ using eqn. 7.40 and $\{y_i\}$ by eqn. 7.38

j) Re-calculate $\{\Phi_i\}, \{\gamma_i\}$, and $\{K_i\}$ using eqn. 7.58

k) Check if the change in each parameter x_i, y_i, and V between steps 'e' and 'j' is within pre-defined error values chosen for convergence.

l) If *yes*, then the last values of x_i, y_i, and V constitute the solution

m) If *no*, return to step 'f' with the last values of x_i, y_i, and V

7.7 High Pressure Vapour Liquid Equilibria

At relatively high pressures the VLE relations used in the last section lose exactness especially with respect to the activity coefficient-based approach for description of the non-ideal behaviour of the liquid phase. This is because the assumption that the activity coefficients are weakly dependent on pressure no longer remains a realistic approximation. In addition, the gas phase *P-V-T* behaviour can no longer be described by the truncated virial EOS. Under such conditions a use of a higher order EOS, which may be applied both to the gas and liquid phase is preferred. As we have seen in chapter 2, the cubic EOS provides just that advantage; besides they offer a reasonable balance between accuracy and computational complexity. We start with the general criterion for phase equilibria as applied to vapour-liquid systems, given by eqn. 6.127:

$$\hat{f}_i^V = \hat{f}_i^L \qquad (i = 1,2, \ldots, N) \qquad\qquad\qquad ..(7.62)$$

An alternative form of the last equation results from introduction of the fugacity coefficient using eqn. 6.129 and 6.130:

$$y_i \hat{\phi}_i^V P = x_i \hat{\phi}_i^L P \qquad (i=1,2, \ldots N) \qquad\qquad\qquad ..(7.63)$$

The last equation reduces to:

$$y_i \hat{\phi}_i^V = x_i \hat{\phi}_i^L \qquad\qquad\qquad\qquad ..(7.64)$$

VLE of pure species

For the special case of pure species *i*, equation 7.64 reduces to:

$$\phi_i^V = \phi_i^L \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad ..(7.65)$$

If both ϕ_i^V and ϕ_i^L are expressed in terms of cubic EOS as defined by any of the eqns. 6.104 to 6.107, for a given T one may obtain the saturation vapour pressure by means of suitable algorithm as shown by the worked out example below.

Example 7.5

Estimate the vapour pressure of a substance "A' using PR-EoS, at T = 428°K. For the substance A: T_C = 569.4 K, P_C = 2.497 MPa, = 24.97 bar, ω = 0.398.

(Click for solution)

VLE from K-value Correlations for Hydrocarbon Systems

Using eqn. 7.64 one can write, $K_i = y_i / x_i$

Alternately: $K_i = \hat{\phi}_i^V / \hat{\phi}_i^L$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad ..(7.66)$

As evident from eqns. 6.155 to 6.157, the expression for species fugacity coefficients for mixtures described by cubic EOS are relatively complex, which in turn makes the estimation of the K-factors difficult as iterative solutions to obtaining T, P and/or compositions are inevitable. As demonstrated in the last section, this is true even for the fugacity and activity coefficient based formulation of the VLE problem. The use of cubic EOS for description of fugacity coefficients of species in both phases poses additional difficulty owing to the intrinsic complexity of the expressions shown in eqns. 6.155 to 6.157.

However, in the case of VLE of light hydrocarbon mixtures a reasonable simplification may be achieved by assuming *ideal solution* behaviour for both the phases. This is a relatively practical approximation as hydrocarbons being non-polar in nature, the intermolecular interactions are generally weaker than amongst polar molecules. In effect in the case of lighter hydrocarbons (C_1-C_{10}) the interactions between the same species and those between dissimilar species are not significantly different. This forms the basis of assuming ideal solution behaviour for such system. It may be noted that since equilibrium pressures in light hydrocarbon systems tend to be 'high' (as they are low-boiling) under practical conditions of distillation processes, ideal solution behaviour yields far more accurate results than would be possible by *ideal gas* assumption.

We develop next the result that obtains owing to the assumption of ideal solution behaviour. The chemical potential of all species in an ideal solution is given by eqn. 6.77:

$$\mu_i^{id} = \overline{G}_i^{id} = G_i + RT \ln x_i \qquad\qquad ..(7.67)$$

For a real solution: $d\overline{G}_i = RTd \ln \hat{f}_i$ \hfill ..(7.68)

At the same time for pure species at same T&P: $dG_i = RTd \ln f_i$ \hfill ..(7.69)

From eqns. (7.68) and (7.69) it follows that:

$$\overline{G}_i - G_i = RT \ln(\hat{f}_i / f_i) \qquad\qquad ..(7.70)$$

From (7.67) $\overline{G}_i^{id} - G_i = RT \ln x_i$ \hfill ..(7.71)

Thus from eqns. (7.70) and (7.71):

$$\overline{G}_i - \overline{G}_i^{id} = RT \ln(\hat{f}_i / x_i f_i) \qquad\qquad ..(7.72)$$

For an ideal solution LHS of (7.72) is identically zero; hence for such a solution:

$$\hat{f}_i = x_i f_i \qquad\qquad ..(7.73)$$

For a real gas mixture the fugacity coefficient $\hat{\phi}_i$ is defined by: $\hat{f}_i = y_i \hat{\phi}_i P$

In analogy, for a real solution we define $\hat{\phi}_i$ by: $\hat{f}_i = x_i \hat{\phi}_i P$

Or: $\hat{\phi}_i = \hat{f}_i / x_i P$ \hfill ..(7.74)

Using (7.74) for an ideal solution: $\hat{\phi}_i^{id} = \hat{f}_i^{id} / x_i P$ \hfill ..(7.75)

Using (7.73) in (7.75) it follows: $\hat{\phi}_i^{id} = x_i f_i / x_i P = f_i / P = \phi_i$

Thus for an ideal solution: $\hat{\phi}_i = \phi_i$ \hfill ..(7.76)

Now considering the light hydrocarbon systems, the application of eqn. 7.76 in 7.66 gives:

$$K_i = \frac{\phi_i^L (T,P)}{\phi_i^V (T,P)} = \frac{f_i^L(T,P)}{P\phi_i^V (T,P)} \qquad\qquad ..(7.77)$$

Using eqn. 6.119 we substitute for the fugacity $f_i^L(T,P)$. Thus:

$$f_i^L = P_i^{sat} \phi_i^{sat} \exp[\frac{V_i^L(P - P_i^{sat})}{RT}]$$

Where, V_i^l is the molar volume of pure species i as a saturated liquid. Thus the K-value is given by:

$$K_i = \frac{P_i^{sat} \phi_i^{sat}(T, P_i^{sat})}{P \phi_i^V(T, P)} \exp\left[\frac{V_i^L(P - P_i^{sat})}{RT}\right]$$

..(7.78)

The advantage of eqn. 7.78 is that it is a function of the properties of the pure species only, and therefore its dependence on composition of the vapour and liquid phases is eliminated. The K-factor then is a function of temperature and pressure alone. The terms ϕ_i^{sat} and ϕ_i^V in eqn. 7.78 can in principle be computed using expression provided by cubic EOS (i.e., eqns. 6.104 – 6.107) or a corresponding expression from an higher order EOS, including the generalized correlation (section 6.9). This allows K-factors for light hydrocarbons to be as functions of T and P.

However, it may be noted that the computation of fugacities at high pressures (and/or temperatures) can potentially be rendered difficult as above the critical temperature the liquid state is necessarily hypothetical, while at pressures higher than the saturation pressure the vapour state is hypothetical. This is corrected for by some form of extrapolations to those hypothetical states. Various approaches have been described in the literature (T.E. Daubert, *Chemical Engineering Thermodynamics*, McGraw-Hill, 1985). The nomographs of K-factors (see figs. 7.11 and 7.12) reported by Dadyburjor (D.B. Dadyburjor, *Chem. Eng. Progr.,* vol. 74(4), 85-86, 1978) provide an example of one such approach.
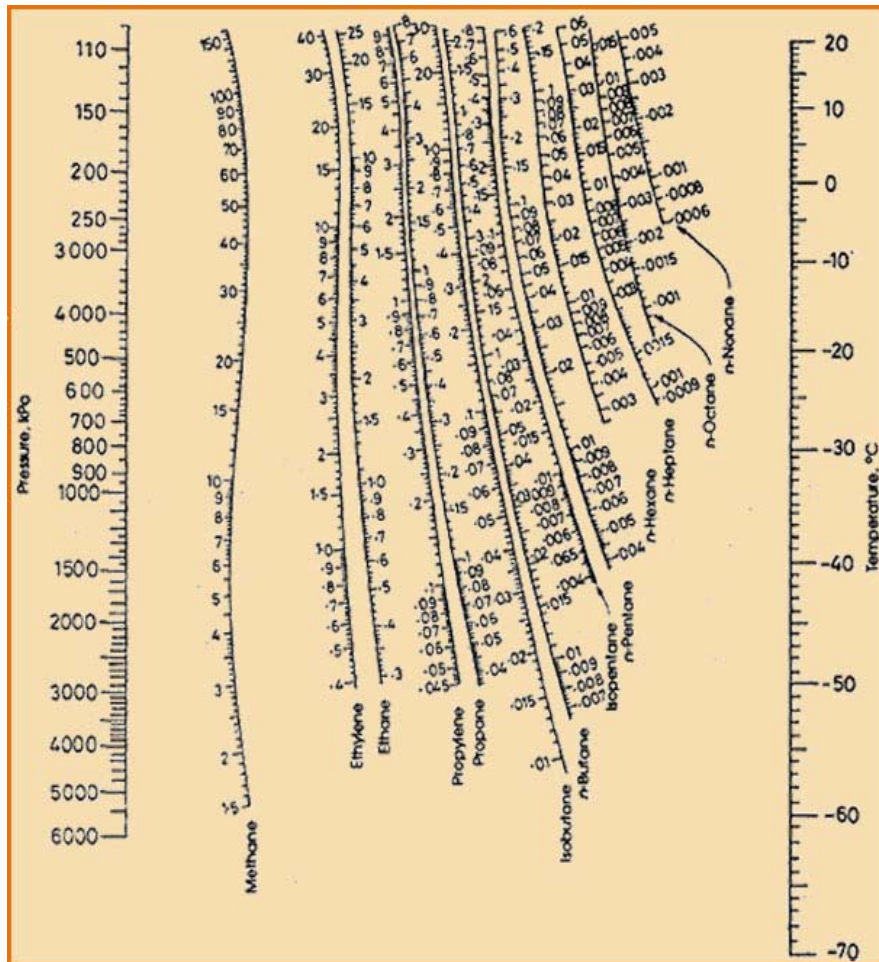
Fig. 7.11 K-factors in light hydrocarbon systems (low temperature range) [Source: Dadyburjor; D.B., *Chem. Eng.Progr.*, Vol. 74 (4) pp.85-86 (1978)].
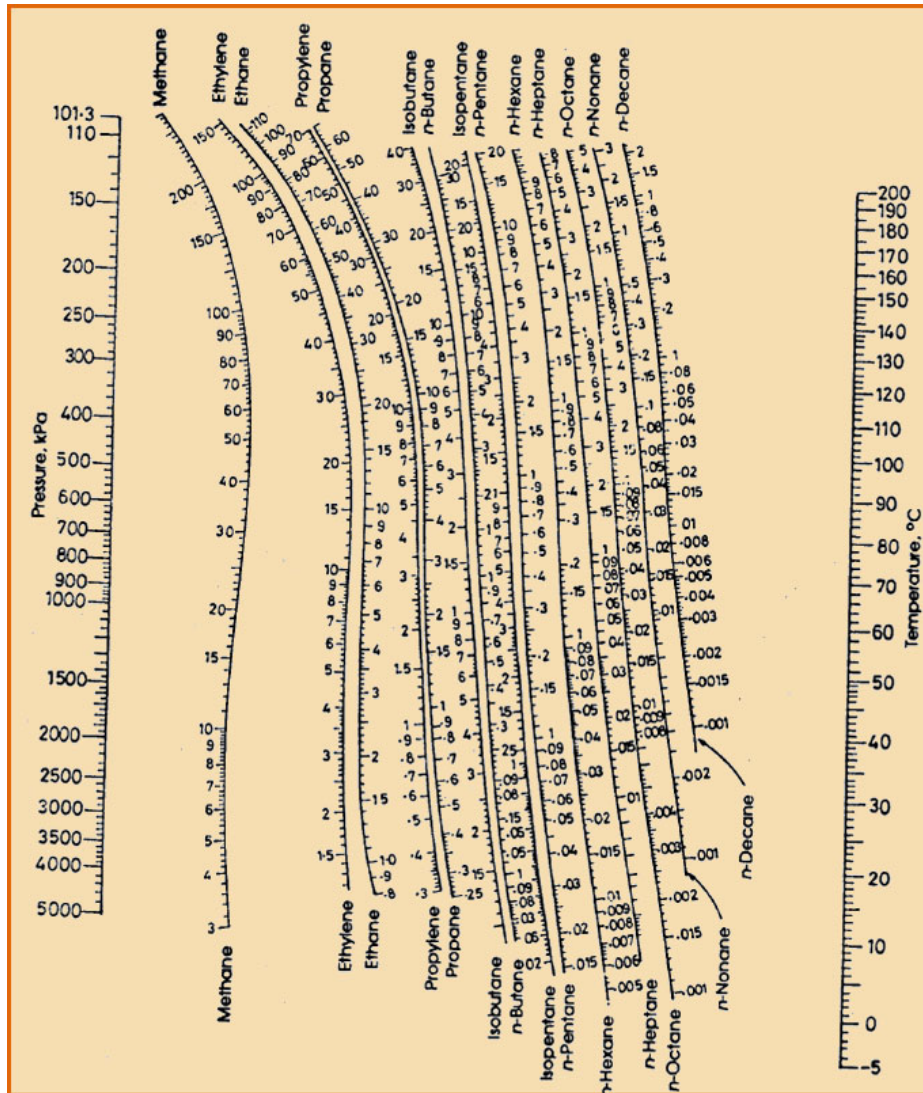
Fig. 7.12 K-factors in light hydrocarbon systems (high temperature range) [Source: Dadyburjor; D.B., *Chem. Eng.Progr.*, Vol. 74 (4) pp.85-86 (1978)].

The nomographs may be conveniently used purpose of VLE calculations in hydrocarbon systems as they the K-factors for each species can be estimated at a given T and P. This is done by drawing a straight line connecting the given temperature and pressure; the corresponding K_i value is read off from the point of intersection of this line with the K_i curve for a particular species. For *bubble point* (either T or P) calculations one uses:

$$\sum_i y_i = \sum_i K_i x_i = 1 \qquad\qquad ..(7.79)$$

- For **pressure** calculation: If $\sum_i K_i x_i > 1$, assumed pressure is *lower* than the correct value; if $\sum_i K_i x_i < 1$ the assumed pressure is *higher* than the correct pressure. Thus, pressure needs to be revised for the next step of calculation.

- Similarly, for **temperature** calculation: if $\sum_i K_i x_i > 1$, assumed temperature is *higher* than the correct value; if $\sum_i K_i x_i < 1$ the assumed temperature is *lower* than the correct value. Thus, temperature needs to be revised for the next step of calculation.

On the other hand the solution for **dew point** calculations derives from:

$$\sum_i x_i = \sum_i \frac{y_i}{K_i} = 1 \qquad\qquad ..(7.80)$$

- For **pressure** calculation: If, $\sum_i (y_i / K_i) > 1$ assumed pressure is *higher* than the correct value; if $\sum_i (y_i / K_i) > 1$ the assumed pressure is *lower* than the correct pressure. Thus, pressure needs to be revised for the next step of calculation.

- Similarly, for **temperature** calculation: if $\sum_i (y_i / K_i) > 1$, assumed temperature is *lower* than its correct value; if $\sum_i (y_i / K_i) < 1$ the assumed temperature is *higher* than its correct value. Thus, temperature needs to be revised for the next step of calculation.

The use of these equations illustrated below using an example.

<u>**Example 7.6**</u>

A vapour mixture contains 20mol% methane (1), 30mol% ethane (2) , and rest propane (3), at 30^0C. Determine the dew composition.

(Click for solution)

High Pressure VLE using cubic EOS

This constitutes a generalized approach without any simplifying assumptions such as employed for light hydrocarbons. The governing relation thus is eqn. 7.66.

$$K_i = \hat{\phi}_i^V / \hat{\phi}_i^L$$

The fugacity of each species, either in vapour or liquid phase, is computed using the expressions that apply to use of cubic EOS (eqns. 6.155 to 6.157). For relevant VLE calculations once again the eqns. 7.79 and 7.80 are employed. The steps for computing (for example) the bubble pressure are enlisted below. The basic principle used for other types of standard calculations (such as discussed for low to moderate pressure VLE systems, table 7.1) remains the same.

Bubble pressure algorithm:

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

a) Solve for P and $\{y_i\}$ first by assuming Raoult's Law algorithm for bubble pressure

b) Using solution in 'a' estimate $\{K_i\}$ using eqn. 7.66 with the given values of T and $\{x_i\}$; and the latest values of P and $\{y_i\}$

c) Next calculate $\{K_i x_i\}$ and $\sum_i K_i x_i$

d) Calculate all $y_i = K_i x_i / \sum_i K_i x_i$

e) Using normalized $\{y_i\}$, recalculate $\{K_i\}$ and $\sum_i K_i x_i$

f) Has $\sum_i K_i x_i$ changed between steps 'c' and 'e'? If *yes* return to step 'd'

g) If $\sum_i K_i x_i$ has not changed between two successive iterations between steps 'c' and 'e' is

$$\sum_i K_i x_i = 1?$$

h) If *yes*, the last values of P and $\{y_i \equiv K_i x_i\}$ give the final bubble temperature $P_{b(f)}$, and vapour compositions.

i) If *no*, and last $\sum_i K_i x_i > 1$, then $P_{last} < P_{b(f)}$; revise to *new P* as: $P_{new} = P_{last} \sum_i K_i x_i$ and return to step (c).and return to step 'b'.

j)   If *no*, and last $\sum_i K_i x_i < 1$, then $P_{last} > P_{b(f)}$; revise to *new P* as: $P_{new} = P_{last} \sum_i K_i x_i$ and return to step (c).and return to step 'b'.

We illustrate the above methodology by a calculation of bubble pressure for an example binary system below.

Example 7.7

For the system of methane (1) and butane (2) compute the bubble pressure for a liquid phase composition of $x_1 = 0.2$ at a temperature of 310K, using the PR-EOS.

(Click for solution)

7.8 Henry's Law

The solubility of gases that are *sparingly* soluble in solvents constitutes a special application of the general VLE relations developed in sections 7.3 and 7.4. There are numerous real-life examples of such situations; for example, the solubilization of oxygen in water, which sustains aqueous life. Similarly, gases such as nitrogen, carbon dioxide, etc., display relatively low solubility (mole fraction: $10^{-5} - 10^{-2}$) in water or many solvents of industrial interest. Further, in many such instances, the solubility of a gas in a solvent is required at temperatures beyond the critical temperature of the gas. Application of vapour-liquid phase equilibria relations given by Raoult's law or its modified versions (discussed in the foregoing sections) to a solute species i (in a solvent) requires the saturation vapour pressure P_i^{sat} at the temperature of application. Clearly if the temperature of interest exceeds the critical temperature of the solute, the parameter P_i^{sat} is not definable, and hence such VLE relations presented in sections 7.5 and 7.6 are not appropriate in such cases.

As for any VLE problem the starting point for determining the solubility of a gaseous species 'i' in a liquid is the equality of the fugacity of the solute species and liquid (liq) phases:

$$\hat{f}_i^{gas} = \hat{f}_i^{liq} \qquad\qquad\qquad ..(7.81)$$

Using eqn. 7.45 (considering low to moderate pressures):

$$y_i \hat{\phi}_i P = x_i \gamma_i f_i$$ ..(7.45)

Denoting the gaseous solute as '1' and the solvent as '2', one may write:

$$\hat{f}_1^{\,gas} = \hat{f}_1^{\,liq}$$ ..(7.82)

And: $\hat{f}_2^{\,gas} = \hat{f}_2^{\,liq}$ ..(7.83)

Using eqn. 7.45 the last two equations may be re-written as:

$$y_1 \hat{\phi}_1 P = x_1 \gamma_1 f_1$$ ..(7.84)

$$y_2 \hat{\phi}_2 P = x_2 \gamma_2 f_2$$ ..(7.85)

If we further assume that the gas is very sparingly soluble in the solvent, the liquid phase is essentially pure solvent and the following relations derive:

$$\gamma_1 \cong \gamma_1^{\infty}$$

$$\gamma_2 \approx 1$$

Therefore, for component 1 we may rewrite the eqn. 7.84 as:

$$y_1 \hat{\phi}_1 P = x_1 \gamma_1^{\infty} f_1$$ ..(7.86)

Or alternately:

$$y_1 \hat{\phi}_1 P = x_1 H_1$$ ..(7.87)

Where:

$$H_1 = \gamma_1^{\infty} f_1$$ ..(7.88)

Equation 7.88 is termed the Henry's law, and H_1 the Henry's constant, which is defined at the system temperature. If one plots the value of $\hat{f}_1$ as a function of the gas mole fraction x_1 in the solvent phase (as shown schematically in fig. 7.13), the parameter H_1 corresponds to the slope of the tangent drawn on the curve at the limiting condition of $x_1 \rightarrow 0$.
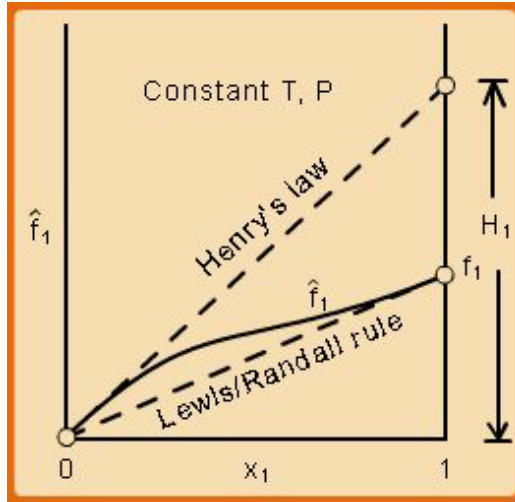
Fig. 7.13 Plot of $\hat{f}_1$ as a function of the gas mole fraction x_1

Similarly for component 2 the phase equilibrium equation 7.85 may be rewritten as:

$$y_2\hat{\phi}_2 P = x_2 H_2 \qquad\qquad\qquad ..(7.89)$$

Where: $H_2 = \gamma_2 f_2$ ..(7.90)

Since $\gamma_2 \approx 1,$ it follows that:

Where: $H_2 = f_2$ ..(7.91)

Thus: $\hat{f}_2 = x_2 f_2$ ..(7.92)

It may be noted that eqn. 7.92 is the same as 6.162 (section 6.15), which describes the Lewis -Randall rule. Thus when Henry's law is applicable for the solute then Lewis-Randall rule is applicable for the solvent. Since for a system temperature $T > T_{c,1}$ the fugacity $\hat{f}_1$ of pure liquid phase for '1' is hypothetical, it follows that the Henry's law constant $H_1 (= \gamma_1^\infty f_1)$ is necessarily a hypothetical quantity as well. Since solubility of a gas is temperature dependent, it follows that H_i is also a function of temperature. The Henry's law constant for a large number of gases with water as the solvent has been reported in the literature. For example for acetylene the value is 1350bar, for carbon dioxide 1670bar, and for air 72950bar). Fig. 7.14 presents the value of Henry's law constant for a number of gases in water as a function of temperature.

Example 7.8

A concentrated binary solution containing mostly species $2 (but X_2 \neq 1)$ 2 (but $x_2 \neq 1$) is in equilibrium with a vapor phase containing both species 1 and 2. The pressure of this two-phase system is 1 bar; the temperature is 298.0K. Determine from the following data good estimates of x_1 and y_1. $H_1 = 200$ bar; $P_2^{sat} = 0.10$ bar.
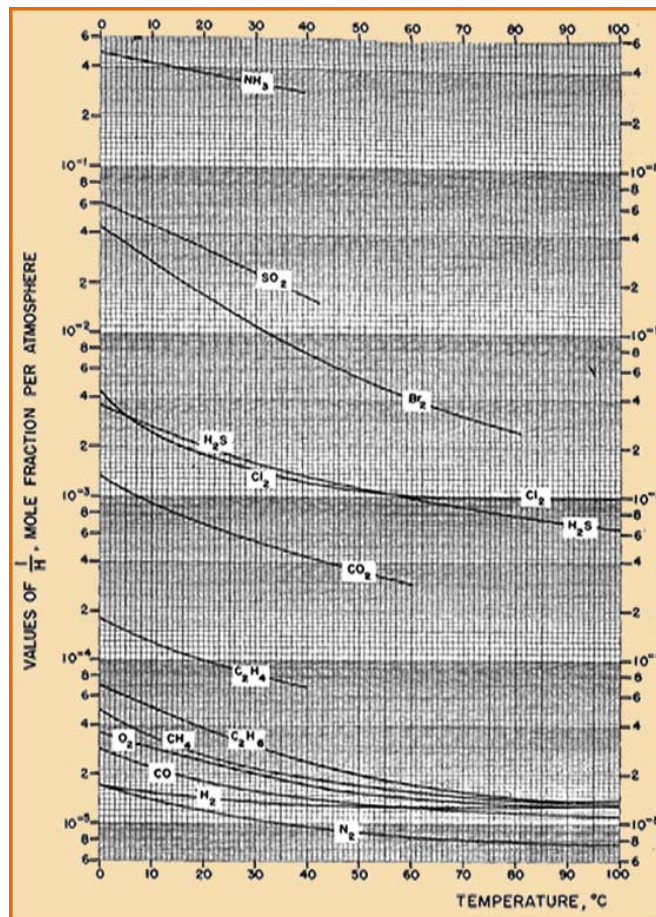
(Click for solution)

Fig. 7.14 Plot of Henry's Constant vs. Temperature, $\left[(1/H) = N(mole\ fraction)/P(atm) \right]$ [Reprinted with permission from O.A. Hougen, K.M. Watson, and R.A. Ragatz (1960), *Chemical Process Principles Charts,* 2nd ed., John Wiley & Sons, New York]

Assignment- Chapter 7