Chapter II

Phase Equilibrium Flash Vaporization
and Partial Condensation

Two-Phase Flash Vapourization

A *flash* is a single-stage distillation in which a feed is partially vaporized to give a vapor that is richer in the more volatile components. In Fig.2.1a a liquid feed is
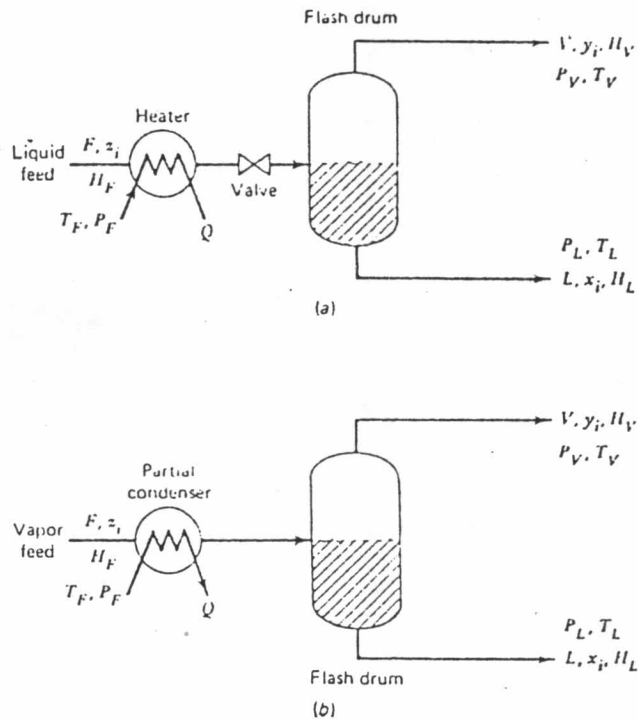

Figure 2.1 Continuous single-stage equilibrium separation. (a) Flash vaporization. (Adiabatic flash with valve: isothermal flash without valve when T_V is specified. (b) Partial condensation. (Analogous to isothermal flash when T_V is specified.

heated under pressure and flashed adiabatically across avalve to a lower pressure. The vapor being saparated from the liquid residue in a flash drum if the valve is omitted, a low-pressure liquid can be partially vaporized in the heater and then separated into two phases. Alternatively, a vopor feed can be cooled and partially condensed, with phase saparation in a flash drum as in Fig.2.1b to give a liquid that is richer in the less volatile component. In both cases, if the component is properly designed, the vapor and liquid leaving the drum are in equilibrium. Unless the relative volatility is very large, the degree of separation achievable between two

Vapor

Composition:

$\Sigma y_I = 1$

$y_I = K^I_I x^I_I$　　　　　$y_I = K^{II}_I x^{II}_I$

Liquid I　　　　　**Liquid II**

Composition:　　　　　Composition:

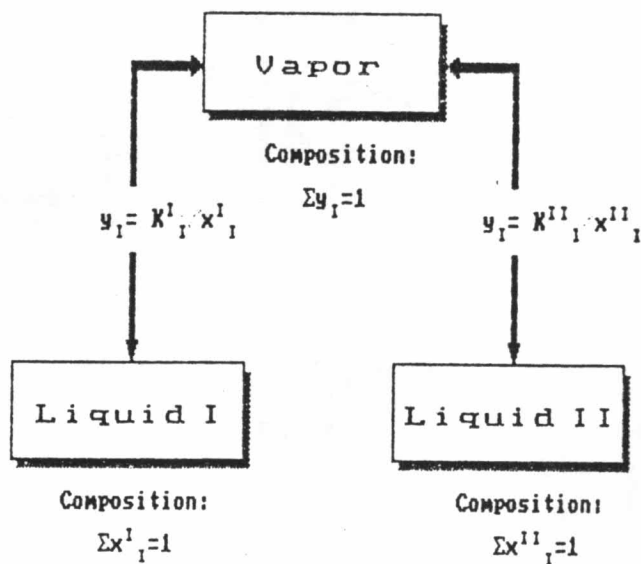$\Sigma x^I_I = 1$　　　　　$\Sigma x^{II}_I = 1$

Figure 2.2

Equilibrium Relationships Between
Immiscible Liquids and Vapor

components in a single stage is poor; so flashing and partial condensation are usually auxiliary operations used to prepare feed streams for further processing.However, the computational methods used in single-stage calculation are of fundamental importance.

Three-Phase Flash Vapourization

Conventional two-phase flash caculation methods are often inadequate to handle the situation of a feed being flashed to from three phases:two liquid phases and a vopor phase.For every component in a three-phase system,there will exist two sets of liquid-vapor equilibrium data;one in association with each liquid phase.Compositions of the liquid phases may be calculated,since both liquid phases must be simultaneously in equilibrium with the sigle vapor phase.

Vapour-Liquid-Liquid Equilibrium

For vapor-liquid-liquid equilibrium in term of fugacities becomes

$$f_{iv} = f_{iL}{}' = f_{iL}{}''$$ (2.1)

To from an equilibrium ratio,fugacities are replaced by equivalent expressions involving mole fractions are:

$$f_{iv} = \gamma_{iv} y_i f_{iv} \qquad (2.2)$$

$$f_{iL}{}' = \gamma_{iL}{}' x_i{}' f^{\circ}{}_{iL}{}' \qquad (2.3)$$

$$f_{iL}{}'' = \gamma_{iL}{}'' x_i{}'' f^{\circ}{}_{iL}{}'' \qquad (2.4)$$

or

$$f_{iv} = \phi_{iv} y_i P \qquad (2.5)$$

$$f_{iL}{}' = \phi_{iL}{}' x_{iL}{}' P \qquad (2.6)$$

$$f_{iL}{}'' = \phi_{iL}{}'' x_{iL}{}'' P \qquad (2.7)$$

From equation (2.1) these equations can be rearranged for K-values in terms :

$$K_i{}' = \phi_{iL}{}'/\phi_{iv} = y_i/x_i{}' \qquad (2.8)$$

$$K_i{}'' = \phi_{iL}{}''/\phi_{iv} = y_i/x_i{}'' \qquad (2.9)$$

or

$$K_i{}' = (\gamma_{iL}{}'/\gamma_{iv})(f^{\circ}{}_{iL}{}'/f_{iv}{}^{\circ}) \qquad (2.10)$$

$$K_i{}'' = (\gamma_{iL}{}''/\gamma_{iv})(f^{\circ}{}_{iL}{}''/f_{iv}{}^{\circ}) \qquad (2.11)$$

Isothermal-Isobaric Flash

The material balance for a three phase flash is:

$$f_i = L' x_i{}' + L'' x_i{}'' + V y_i \; ; \; i=1,2\ldots,n. \qquad (2.12)$$

The two liquid-phase mol fractions can.be expressed in terms of the vapor-phase mol-fractions by means of the vapor-liquid equilibrium coefficients. $K_i{}'$ and $K_i{}''$:

$$f_i = L' y_i/K_i{}' + L'' y_i/K_i{}'' + V y_i \qquad (2.13)$$

This equation can be solved for the vopor phase mol fractions;

$$y_1 = f_1 K_1{}' K_1{}'' / (V K_1{}' K_1{}'' + L' K_1{}'' + L'' K_1{}') \qquad (2.14)$$

Alternately,all mol-fractions in equation(2.12) could be related to the mol-fraction in liquid-phase 1 or liquid-phase 2:

$$f_1 = L' x_1{}' + L'' K_1{}' x_1{}' / K_1{}'' + V K_1{}' x_1{}' \qquad (2.15)$$

$$f_1 = L' K_1{}'' x_1{}'' / K_1{}' + L'' x_1{}'' + V K_1{}'' x_1{}'' \qquad (2.16)$$

equation then yield expressions for the mol-fractions in the liquid-phases:

$$x_1{}' = f_1 K_1{}'' / (V K_1{}' K_1{}'' + L' K_1{}'' + L'' K_1{}') \qquad (2.17)$$

$$x_1{}'' = f_1 K_1{}' / (V K_1{}' K_1{}'' + L' K_1{}'' + L'' K_1{}') \qquad (2.18)$$

Equation(2.14)may be summed over all components to yield:

$$1 = \sum_{i=1}^{c} (f_1 K_1{}' K_1{}'' / (V K_1{}' K_1{}'' + L' K_1{}'' + L'' K_1{}')) \qquad (2.19)$$

By an overall material balance:

$$V = F - L' - L'' \qquad (2.20)$$

Inserting equation(2.20) into equation(2.19)and rearranging.

where: $\qquad u_1 = L' / F$ and $u_2 = L'' / F$

$$P_1(u_1, u_2)$$

$$= \sum_{i=1}^{c} z_i K_i{}' K_i{}'' / (K_i{}' K_i{}'' + u_1 K_i{}'' (1 - K_i{}') + u_2 K_i{}' (1 - K_i{}'')) - 1$$

$$= \sum_{i=1}^{c} z_i (- u_1 K_i{}'' (1 - K_i{}') - u_2 K_i{}' (1 - K_i{}'')) / (K_i{}' K_i{}'' +$$

$$u_1 K_i{}'' (1 - K_i{}') + u_2 K_i{}' (1 - K_i{}''))$$

$$= 0 \qquad\qquad (2.21)$$

Likewise, equations (2.17) and (2.18) become;

$$P_2(u_1, u_2) = \sum_{i=1}^{c} z_i (1 - u_1) K_i{}'' (1 - K_i{}') - u_2 K_i{}' (1 - K_i{}''))/$$

$$(K_i{}' K_i{}'' + u_1 K_i{}'' (1 - K_i{}') + u_2 K_i{}' (1 - K_i{}''))$$

$$= 0 \qquad\qquad (2.22)$$

$$P_3(u_1, u_2) = \sum_{i=1}^{c} z_i (- u_1 K_i{}'' (1 - K_i{}') + (1 - u_2) K_i{}' (1 - K_i{}''))/$$

$$(K_i{}' K_i{}'' + u_1 K_i{}'' (1 - K_i{}') + u_2 K_i{}' (1 - K_i{}''))$$

$$= 0 \qquad\qquad (2.23)$$

Two independent functions which have properties more suitable for numerical solution can be derived from equations(2.21-2.23).These are;

$$Q_1(u_1,u_2) = P_2(u_1,u_2) - P_1(u_1,u_2)$$

$$= \sum_{i=1}^{c} z_i K_i''(1 - K_i')/(K_i' K_i''$$

$$+ u_1 K_i''(1 - K_i') + u_2 K_i'(1 - K_i'')) \qquad (2.24)$$

$$Q_2(u_1,u_2) = P_3(u_1,u_2) - P_1(u_1,u_2)$$

$$= \sum_{i=1}^{c} z_i K_i'(1 - K_i'')/(K_i' K_i''$$

$$+ u_1 K_i''(1 - K_i') + u_2 K_i'(1 - K_i'')) \qquad (2.25)$$

The P-functions can be written in terms of the Q-functions:

$$P_1(u_1,u_2) = - u_1 Q_1(u_1,u_2) - u_2 Q_2(u_1,u_2) \qquad (2.26)$$

$$P_2(u_1,u_2) = (1-u_1)Q_1(u_1,u_2) - u_2 Q_2(u_1,u_2) \qquad (2.27)$$

$$P_3(u_1,u_2) = - u_1 Q_1(u_1,u_2) - (1-u_2)Q_2(u_1,u_2) \qquad (2.28)$$

Simultaneous solution of equation(2.24,2.25)will yield the same values of u_1 and u_2 as simultaneous solution of equation(2.21-2.23). But the Q-function are more suitable for iterative solution because they contain no superfluous roots in the domain of interest.Once it has been determined that three phases are present,a (2*2 matrix) search must be performed for the values of u_1 and u_2 which cause equations(2.24,2.25) to be satisfied.If the flash is being performed with recalculated K-values from a previously

$$
\begin{vmatrix} u_1 \\ \\ u_2 \end{vmatrix}_m = \begin{vmatrix} \\ \\ \end{vmatrix} - (1/D) \begin{vmatrix} dQ_2/du_2 & - dQ_1/du_2 \\ \\ - dQ_2/du_1 & dQ_1/du_1 \end{vmatrix}_m \begin{vmatrix} Q_1 \\ \\ Q_2 \end{vmatrix}_m
\qquad (2.32)
$$

where D is the determinant of the Jacobian matrix

$$
D = dQ_1/du_1 . dQ_2/du_2 - dQ_1/du_2 . dQ_2/du_1 \qquad (2.33)
$$

Convergence is declared when Q_1 and Q_2 are zero to within tolerance.

Criteria of Phase Equilibria

For each phase in a multiphase,multicomponent system ,the Gibbs free energy is given functionally as

$$
G = G(T,P,n_1,n_2,\ldots\ldots\ldots n_c) \qquad (2.34)
$$

where n = moles and subscripts refer to species.The total differential of G is

$$
DG = (dG/dT)_{P,n_1} DT + (dG/dP)_{T,n_1} DP + \sum_{i=1}^{c}(dG/dn_i)_{P,T,n_i} Dn_i \qquad (2.35)
$$

where j 1. From classical thermodynamics

$$
(dG/dT)_{P,n_1} = - S \qquad (2.36)
$$

and
$$\left(dG/dP\right)_{T,n_i} = V \tag{2.37}$$

where S = entropy and V = volume. Defining the *chemical potential*, μ, of species i as

$$\mu_i = \left(dG/dn_i\right)_{P,T,n_i} \tag{2.38}$$

and substituting into (2.35), we have

$$DG = -S\ DT + V\ DP + \sum_{i=1}^{c}\mu_i Dn_i \tag{2.39}$$

When (2.39) is applied to a closed system consisting of two phases in equilibrium at uniform temperature and pressure, where each phase is an open system capable of mass transfer with another phase

$$DG_{system} = \sum_{k=1}^{p}\left(\sum_{i=1}^{c}\mu_i^{\ k}Dn_i^{\ k}\right) = 0 \tag{2.40}$$

where the superscript (k) refers to each of p phases. Conservation of moles of each species requires that

$$Dn_i^{\ 1} = -\sum_{k=2}^{p}Dn_i^{\ k}$$

which, upon substitution into (2.39), gives

$$\sum_{k=2}^{p}\left(\sum_{i=1}^{c}\left(\mu_i^{\ k}-\mu_i^{\ 1}\right)Dn_i^{\ k}\right) = 0 \tag{2.41}$$

with dn_1^1 eliminated in (2.41), each dn_1^k term can be varied independently of any other dn_1^k term. But this requires that each coefficient of dn_1^k in(2.41) be zero. Therefore,

$$\mu_1^1 = \mu_1^2 = \mu_1^3 = \ldots \mu_1^p \qquad (2.42)$$

Thus, the chemical potentials of any species in a multicomponent system are identical in all phases at physical equilibrium. Chemical potential cannot be expressed as an absolute quantity, and the numerical values of chemical potential are difficult to more easily understood physical quantities. Furthermore, the chemical potential are approaches an infinite negative value as pressure approaches zero. For these reasons, the chemical potential is not directly useful for phase equilibria calculations. Instead, fugacity, as defined below, is employed, as a surrogate. Equation(2.38) restated in terms of chemical potential is

$$(d\mu_1/dP)_T = \bar{v}_1 \qquad (2.43)$$

where $\bar{v}_1$ = partial molal volume. For a pure substance that behaves as an ideal gas

$$\bar{v}_1 = RT/P$$

and (2.43) can be integrated to give

$$\mu_1 = RT \ln P + C_1(T) \qquad (2.44)$$

where C_1 depend on T.Unfortunately,(2.44)does not describe real multicomponent gas or liquid behavior.However,(2.44)was rescued by G.M.Lewis,who in 1901 invented the fugacity f, a pseudopressure when used in place of pressure in (2.44),thus for a component in a mixture.

$$f_1 = C_2(T) \exp(\mu_1/RT) \qquad (2.45)$$

where C_2 is related to C_1.Regardless of the value of C_1 at phycical equilibrium,(2.42) can be replaced with

$$f_1^1 = f_1^2 = f_1^3 = \ldots \ldots f_1^p \qquad (2.46)$$

For a pure,ideal gas,fugacity is equal to the pressure and, for a componet in an ideal gas mixture,it is equal to its partial pressure, $p_1 = y_1 P$.