SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE
www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – I - Properties of Solutions – SCHA1302

1. Introduction

1.1 Introduction to ideal and non-ideal solutions

The solutions which obey Raoult's law over the entire range of concentration are known as *ideal solutions*. The ideal solutions have two other important properties. The enthalpy of mixing of the pure components to form the solution is zero and the volume of mixing is also zero, i.e.,

$\Delta_{mix}H = 0$, $\Delta_{mix}V = 0$

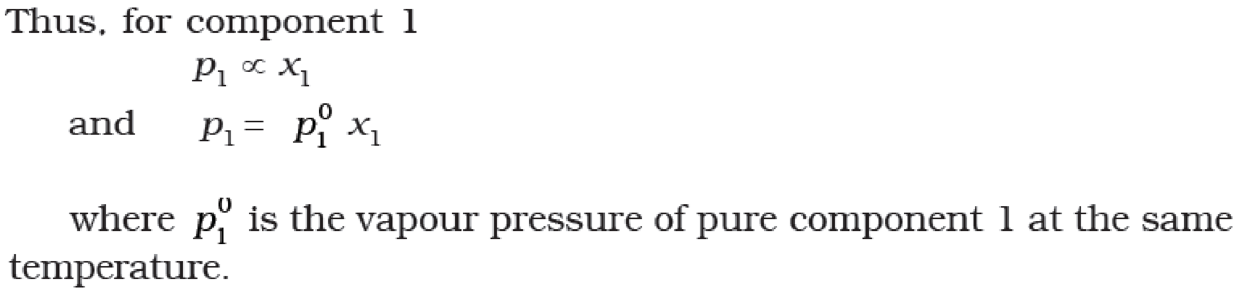
It means that no heat is absorbed or evolved when the components are mixed. Also, the volume of solution would be equal to the sum of volumes of the two components. At molecular level, ideal behavior of the solutions can be explained by considering two components A and B. In pure components, the intermolecular attractive interactions will be of types A-A and B-B, whereas in the binary solutions in addition to these two interactions, A-B type of interactions will also be present. If the intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B, this leads to the formation of ideal solution. A perfectly ideal solution is rare but some solutions are nearly ideal in behavior. Solution of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc. fall into this category.

When a solution does not obey Raoult's law over the entire range of concentration, then it is called *non-ideal solution*. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law. If it is higher, the solution exhibits positive deviation and if it is lower, it exhibits negative deviation from Raoult's law.

1.2 Raoult's law.

Let us consider a binary solution of two volatile liquids and denote the two components as 1 and 2. When taken in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between vapour phase and the liquid phase. Let the total vapour pressure at this stage be P_{total} and P_1 and P_2 be the partial vapour pressures of the two components 1 and 2 respectively. These partial pressures are related to the mole fractions x_1 and x_2 of the two components 1 and 2 respectively.

The French chemist, Francois Marte Raoult (1886) gave the quantitative relationship between them. The relationship is known as the Raoult's law which states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.



Thus, for component 1

$$p_1 \propto x_1$$

and $$p_1 = p_1^0 \, x_1$$

where p_1^0 is the vapour pressure of pure component 1 at the same temperature.

1.3 Partial molar properties

In chemical process plants – the ultimate domain of application of the principles of chemical engineering thermodynamics – matter is dominantly processed in the form of mixtures. Process streams are typically comprised of multiple components, very often distributed over multiple phases. Separation or mixing processes necessitate the use of multiple phases in order to preferentially concentrate the desired materials in one of the phases. Reactors very often bring together various reactants that exist in different phases. It follows that during mixing, separation, inter-phase transfer, and reaction processes occurring in chemical plants multi-component gases or liquids undergo composition changes. Thus, in the thermodynamic description of such systems, in addition to pressure and temperature, composition plays a key role.

Further, whenever multiple phases are present in a system, material and energy transfer occurs between till the phases are in equilibrium with each other, i.e., the system tends to a state wherein the all thermal, mechanical and chemical potential gradients within and across all phases cease to exist.

The present chapter constitutes a systematic development of the concept of a new class of properties essential to description of real mixtures, as well of the idea of the chemical potential necessary for deriving the criterion of phase and chemical reaction equilibrium. Such properties facilitate the application of the first and second law principles to quantitatively describe changes of internal, energy, enthalpy and entropy of multi-component and multiphase systems. Of the separate class of properties relevant to multi-component and multi-phase systems, the partial molar property and the chemical potential are particularly important.

The former is used for describing behavior of homogeneous multi-component systems, while the latter forms the fundament to description equilibrium in multi-phase, as well as reactive systems. As in the case of pure gases, the ideal gas mixture acts as a datum for estimating the properties of real gas mixtures. The comparison of the properties of the real and ideal gas mixtures leads to the introduction of the concept of fugacity, a property that is further related to the chemical potential. Fugacity may also be expressed as a function of volumetric properties of fluids. As we will see, the functional equivalence of fugacity and the chemical potential provides a convenient pathway for relating the temperature, pressure and phase composition of a system under equilibrium.

1.4 Gibbs-Duhem equation:

In order to talk about mixtures, we must define some way of specifying the values of thermodynamic parameters for components of a mixture. Such a description is provided by the concept of a partial molar quantity. The formalism goes like this. If there is some parameter, X, that we wish to describe in terms of its partial value for each component of a solution then the value of X should just be the sum of the values of each of the contributions from the components. Of course, how much a particular component contributes to X will depend on how much of it is present. Thus we write:

$$dX = \left(\frac{\partial X}{\partial n_1}\right)dn_1 + \left(\frac{\partial X}{\partial n_2}\right)dn_2 + \left(\frac{\partial X}{\partial n_3}\right)dn_3 + ...$$

This just says that any change in X will be given by how much the amounts of components 1, 2, 3… are changed (dn_i) and by the coefficient that tells us what the amount of X is per mole of substance 1, 2, 3…, $\left(\frac{\partial X}{\partial n_i}\right)$. These coefficients are called partial molar quantities. For small changes we can often integrate this expression and obtain:

$$X = \left(\frac{\partial X}{\partial n_1}\right)n_1 + \left(\frac{\partial X}{\partial n_2}\right)n_2 + \left(\frac{\partial X}{\partial n_3}\right)n_3 + ...$$

Lets consider an example. One common partial molar quantity is the partial molar volume. The partial molar volume of component i is just given by $\overline{V_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n'}$. Thus it is the amount that the volume would change if we changed the number of moles of substance i on a per mole basis. The simplest case is a mixture of ideal gases, call them A and B. Note that in this case we hold T and P constant as well as the amounts of all other substances in the mixture (n'). We know that ideal gases do not interact and that their volumes depend only on how much is present at constant T and P: $V = \frac{n_A RT}{P} + \frac{n_B RT}{P}$. Thus $\left(\frac{\partial V}{\partial n_A}\right)_{T,P,n'} = \frac{RT}{P}$. So it turns out that the partial molar volume of any component in a mixture of ideal gases is RT/P. It is not always that simple, but more on that later.

OK, now we come to the really important partial molar quantity -- the partial molar Gibbs free energy. Just as for volume, we can write:

$$G = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n'} n_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n'} n_2 + \ldots$$

But we recognize the coefficients in this case as chemical potentials:

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n'}, \mu_2 = \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n'}, \ldots$$

$$Thus$$

$$G = \mu_1 n_1 + \mu_2 n_2 + \ldots$$

$$and$$

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \ldots$$

At constant temperature and pressure and under conditions where the chemical potentials are constant with changing composition. In fact, we can just add these new terms to our previous expression for dG at constant pressure and constant n:

$$dG = Vdp - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \ldots$$

which reduces to the equation just above this if the temperature and pressure are constant.

An aside…

In principle, we could have written dG from the following equation differently

$$G = \mu_1 n_1 + \mu_2 n_2 + \ldots$$

$$and$$

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \ldots + d\mu_1 n_1 + d\mu_2 n_2 + \ldots$$

Yet from the arguments made above, we can see that this equation must be the same as the previous equation for dG:

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + ...$$

Therefore

$$0 = +d\mu_1 n_1 + d\mu_2 n_2 + ...$$

This is an important equation called the **Gibbs-Duhem equation**. What it says is that any change in the chemical potential of one component of a closed system must be balanced by another.

Applications

(i) Gibbs-duhem equation is helpful in calculating partial molar quantity of a binary mixture by measuring the composition of the mixture which depends on the total molar quantity.

(ii) Gibbs-duhem equation is helpful in calculating the partial vapor pressures by calculating the total vapor pressure. All these calculations require a curve-fitting procedure. Using tabulated experimental data the accuracy of the calculated quantities was found to be comparable to the accuracy of the original experimental data.

1.5 Chemical Potential

- If two systems have the same temperature there is no net energy flow between them.
- If two systems have the same pressure, there is no net change of volumes
- If two systems have the same X, there is no net flow of particles What is this X? We call it the chemical potential:
- Physical meaning of chemical potential = tendency of a system to give particles

  The tendency of a substance

  - to react with other substances,
  - to transform into another state,
  - to redistribute in space,

  can be expressed by one and the same quantity – its chemical potential μ.

By definition the partial molar Gibbs free energy is termed the *chemical potential of species i in the mixture, i.e.,:*

$$\mu_i = \left.\frac{\partial(nG)}{\partial n_i}\right|_{T,P,n_{j\neq i}}$$

Or: $\mu_i = \overline{G}_i$

1.5.1 Effect of temperature and pressure on chemical potential

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \overline{V}$$

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -\overline{S}$$

1.6 fugacity and fugacity coefficient

Fugacity is a measure of a chemical potential in the form of 'adjusted pressure.' It reflects the tendency of a substance to prefer one phase (liquid, solid, or gas) over another, and can be literally defined as “the tendency to flee or escape”.

Fugacity is not a physical property of a substance; rather it is a calculated property which is intrinsically related to chemical potential.

The defining equation for fugacity is

$$d\mu = RTd\ln f$$

$$G - G^{ig} = G_i^R = RT\ln\frac{f_i}{P}$$

The dimensionless ratio f_i / P is termed *fugacity coefficient* (ϕ).

Thus: $G_i^R = RT\ln\phi_i$

Where, $\phi_i \equiv f_i / P$

1.7 Lewis Randell rule

$$\hat{f}_i^{id} = x_i f_i$$

The above relation is known as the *Lewis/Randall rule*, and applies to each species in an ideal solution at all conditions of temperature, pressure, and composition. It shows that the fugacity of each species in an ideal solution is proportional to its mole fraction; the proportionality constant being the fugacity of pure species *i* in the same physical state as the solution and at the same T and P.

1.8 Henry's law

Henry was the first to give a quantitative relation between pressure and solubility of a gas in a solvent which is known as Henry's law. The law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

$p = K_H x$

Here K_H is the Henry's law constant.

1.9 activity and activity coefficients in solutions

We have now seen and used several expressions for the chemical potential of a substance or component in a mixture. For a one-component ideal gas we had

$$\mu = \mu^o + RT \ln \frac{p}{p^o}, \qquad (1)$$

where μ^o is the chemical potential when $p = p^o$ and p_o is usually one atmosphere.

For a mixture of ideal gases it can be shown that for each component, *i*, the chemical potential is given by,

$$\mu_i = \mu_i^o + RT \ln \frac{p_i}{p^o}. \qquad (2)$$

For a nonideal gas we used the fugacity, *f*, instead of the pressure and the chemical potential for one component is,

$$\mu = \mu^o + RT \ln \frac{f(p)}{p^o}. \qquad (3)$$

For a mixture of nonideal gases it can be shown that,

$$\mu_i = \mu_i^o + RT \ln \frac{f_i}{p^o}, \qquad (4)$$

only now the fugacity of component *i* is a function of the pressures of all the gases in the mixture,

$$f_i = f_i(p_1, p_2, p_3, \ldots). \tag{5}$$

For ideal solutions we found that,

$$\mu_i = \mu_i^{\circ} + RT \ln X_i. \tag{6}$$

These expressions for chemical potential all have the form of a reference or standard state chemical potential plus *RT* times the logarithm of something related to pressure or concentration. This form turns out to be very important, so important that G. N. Lewis used it to give the most general case of chemical potential as

$$\mu_i = \mu_i^{\circ} + RT \ln a_i. \tag{7}$$

The quantity, a_i, is called the "activity" of component *i* and Equation 7 should be regarded as the definition of activity. Notice that the activity has no units.

All of the special cases we have been considering so far can be reconciled to this definition of activity. Thus, for an ideal gas mixture,

$$a_i = \frac{p_i}{p^{\circ}};$$

for a nonideal gas mixture,

$$a_i = \frac{f_i}{p^{\circ}};$$

for an ideal solution,

$$a_i = X_i,$$

and so on. In a nonideal solution we would have to just write Equation 7 again,

$$\mu_i = \mu_i^{\circ} + RT \ln a_i. \tag{7}$$

In Equation 7 all the non idealities of the solution are absorbed into the activity. We will see a more convenient way to write this below under the heading "activity coefficient."

We can find the activity of a component of a nonideal solution from measurements of the vapor pressure of that component in the vapor in equilibrium with the solution. We know that the chemical potential of a component must be the same in the vapor as in the liquid. that is, from Equations 2 and 7 we obtain,

$$\begin{aligned} \mu_{il} &= \mu_{ig} \\ \mu_{il}^{*} + RT\ln a_i &= \mu_{ig}^{\mathrm{o}} + RT\ln\frac{p_i}{p^{\mathrm{o}}}, \end{aligned} \qquad (8a, b)$$

but for pure component *i*, we must have,

$$\mu_{il}^{*} = \mu_{ig}^{\mathrm{o}} + RT\ln\frac{p_i^{*}}{p^{\mathrm{o}}}. \qquad (9)$$

Subtracting Equation 9 from Equation 8b yields,

$$\begin{aligned} RT\ln a_i &= RT\ln\frac{p_i}{p^{\mathrm{o}}} - RT\ln\frac{p_i^{*}}{p^{\mathrm{o}}} \\ &= RT\ln\frac{p_i}{p_i^{*}}, \end{aligned} \qquad (10a, b)$$

so that

$$a_i = \frac{p_i}{p_i^{*}}. \qquad (11)$$

If the solution were ideal p_i would be given by Raoult's law and the activity would be just the mole fraction.

Activity Coefficient

Sometimes it is convenient to write the activity as the product of an ideal part times a non ideality correction part. For example, in a real solution we might write,

$$a_i = X_i\gamma_i, \qquad (12)$$

or, in a real gas to write,

$$f_i = p_i\gamma_i, \tag{13}$$

so that

$$a_i = \frac{f_i}{p^{\circ}} = \frac{p_i\gamma_i}{p^{\circ}} = \frac{p_i}{p^{\circ}}\gamma_i. \tag{14}$$

In the latter case we already know that

$$f(p) = pe^{\int_0^p \frac{(Z-1)}{p'}dp'}, \tag{15}$$

so that

$$\gamma = e^{\int_0^p \frac{(Z-1)}{p'}dp'}. \tag{16}$$

In the case of the nonideal gas $\gamma \rightarrow 1$ as $p \rightarrow 0$. In the case of a nonideal solution $\gamma_i \rightarrow 1$ as $X_i \rightarrow 1$. From Equations 11 and 12 we see that,

$$a_i = \frac{p_i}{p_i^*} = X_i\gamma_i, \tag{17}$$

from which we conclude that for a nonideal solution,

$$\gamma_i = \frac{p_i}{X_i p_i^*} = \frac{\text{actual vapor pressure}}{\text{Raoult's law vapor pressure}}. \tag{18}$$

In general, the activity coefficient is a unit less parameter that contains all of the nonideality of a system.

1.10 Effect of temperature and pressure on activity coefficients

$$\frac{\overline{V}_i^E}{RT} = \left[\frac{\partial \ln \gamma_i}{\partial P}\right]_{T,x}$$

$$\frac{\overline{H}_i^E}{RT^2} = \left[\frac{\partial \ln \gamma_i}{\partial T}\right]_{P,x}$$

1.11 property changes on mixing

Remember for ideal gases that the chemical potential was given by:

$$\mu_A(g) = \mu_A{}^{\theta} + RT\ln\frac{P_A}{P^{\theta}}$$

and the Gibbs free energy of mixing was

$$\Delta G_{mix} = nRT(X_A \ln X_A + X_B \ln X_B)$$

where the mole fractions are mole fractions in the gas phase.

Well for the liquid, we have

$$\mu_A(l) = \mu_A^*(l) + RT\ln(X_A)$$

where the mole fraction is now in the liquid phase,

and it should not surprise you to learn that the Gibbs free energy of mixing is just

$$\Delta G_{mix} = nRT(X_A \ln X_A + X_B \ln X_B)$$

In other words, the Gibbs free energy of mixing two ideal gases is the same as the Gibbs free energy for forming an ideal solution of two liquids. For more components, you just add more terms. The entropy and enthalpy of mixing are also the same as with ideal gases.

$$\Delta S_{mix} = -nR(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta G_{mix} = -T\Delta S_{mix}$$
$$\Delta H_{mix} = 0$$

Remember, these equations only apply to ideal solutions! In real situations, the enthalpy, in particular, is usually not zero.

Let's just see what effects a mildly nonideal case would have on these (in the book, this is partly covered at the end of the chapter under activities). We can see that for ideal dilute solutions (Henry's law) instead of just X_A in the logarithm, we would have something proportional to X_A. As we saw before:

$$\mu_A(l) = \mu_A^*(l) + RT\ln\left(\frac{X_A K_A}{P_A^*}\right)$$

so for two components, we first consider them separately:

$$G_i = n_A\mu_A + n_B\mu_B$$
$$= n_A\mu_A{}^* + n_B\mu_B{}^*$$

Now for a ideal dilute mixture where there is just a wee bit of A mixed in with a lot of B:

$$G_f = n_A\mu_A + n_B\mu_B$$
$$= n_A\left(\mu_A^*(l) + RT\ln\left(\frac{X_A K_A}{P_A^*}\right)\right) + n_B\mu_B^* + RT\ln(X_B)$$
$$= n_A\mu_A{}^* + n_A RT\ln\frac{X_A K_A}{P_A^*} + n_B\mu_B{}^* + n_B RT\ln X_B$$
$$= n_A\mu_A{}^* + n_A RT\ln\frac{K_A}{P_A^*} + n_A RT\ln X_A + n_B\mu_B{}^* + n_B RT\ln X_B$$

Now subtract the initial from the final Gibbs free energy:

$$\Delta G_{mix} = G_f - G_i = n_A\mu_A{}^* + n_A RT\ln\frac{K_A}{P_A^*} + n_A RT\ln X_A + n_B\mu_B{}^* + n_B RT\ln X_B - n_A\mu_A{}^* - n_B\mu_B{}^*$$
$$\Delta G_{mix} = n_A RT\ln\frac{K_A}{P_A^*} + n_A RT\ln X_A + n_B RT\ln X_B$$
$$\Delta G_{mix} = nRT\left(X_A\ln\frac{K_A}{P_A^*} + X_A\ln X_A + X_B\ln X_B\right)$$
$$or$$
$$\Delta G_{mix} = nRTX_A\ln\frac{K_A}{P_A^*} + nRT(X_A\ln X_A + X_B\ln X_B)$$

How this extra term partitions itself between enthalpy and entropy depends on the details of the liquid interactions and structure. However, usually the bulk of the extra term ends up making the enthalpy of mixing nonzero.

1.12 Enthalpy composition diagrams,

- McCabe Thiele method assumes constant molar flow rate because it considers equal latent heat of vaporization.
- Here we consider varying molar flow rate by solving simultaneous material and energy balances.
- In this case, the operating lines for the enriching and stripping section will be determined from simultaneous solution of mass and energy balance equations.

- To facilitate the solution of the heat balance equation, an enthalpy diagram can be constructed and used.

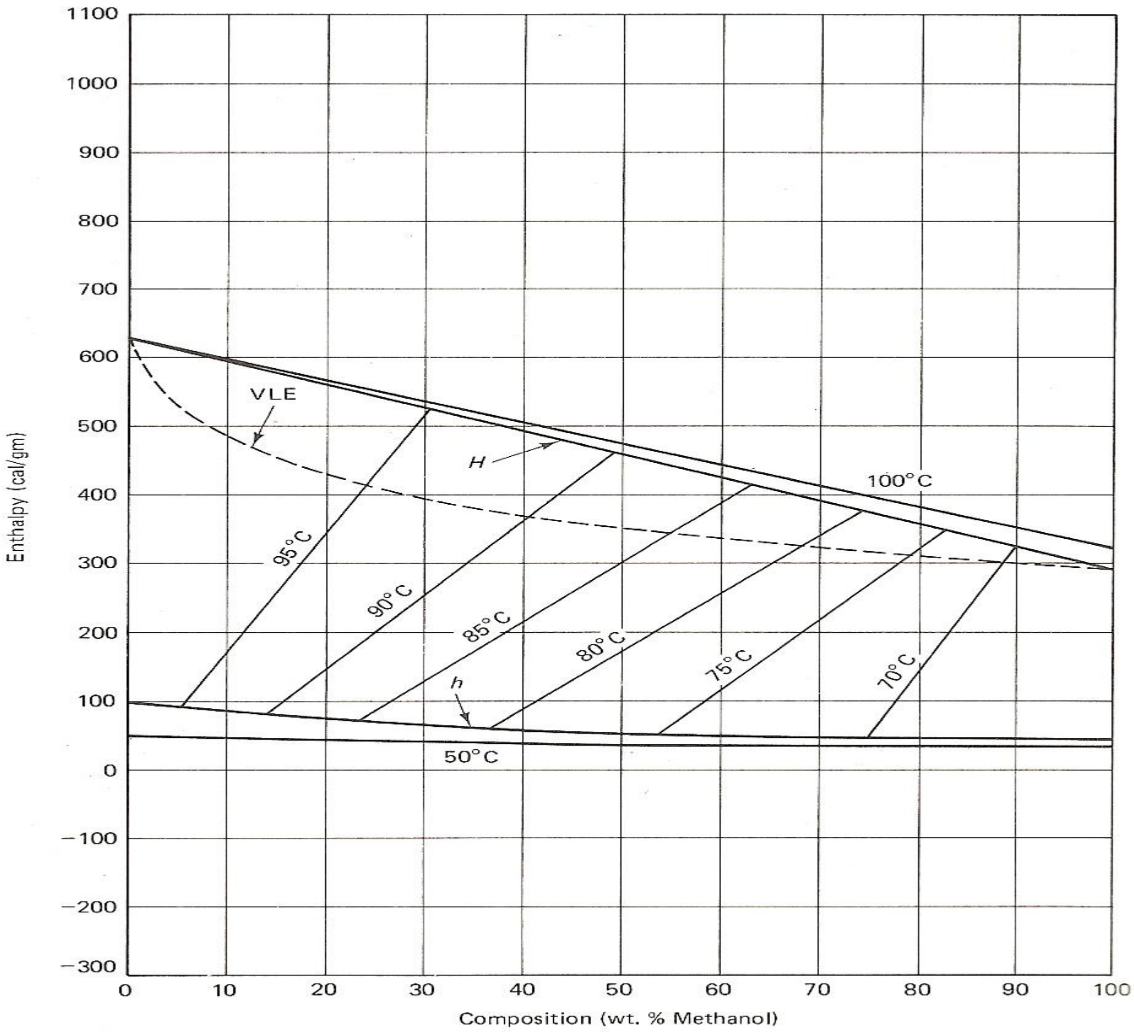
Enthalpy diagram

The liquid enthalpy

$$h = x_A Cp_A (T - T_o) + (1 - x_A) Cp_B (T - T_o) + \Delta H_{sol}$$

The vapor enthalpy

$$H = y_A[\lambda_A + Cv_A(T - T_o)] + (1 - y_A)[\lambda_B + Cv_B(T - T_o)]$$



Hxy diagram for methanol-water system at 1 atm.

1.13 Excess Properties

Unlike for real gases (pure or mixtures) the EOS based approach to calculation of thermodynamic properties of real liquid solutions have not proved very successful. However, as molar *residual property* is defined for real gases, for *real* liquid solutions one may formulate a different departure function called the molar *excess property* that quantify the deviation from ideal solution property. The mathematical formalism of excess properties is, therefore, analogous to that of the residual properties. If *M* represents the molar (or unit-mass) value of any extensive thermodynamic property(e.g., *V*,***U***, *H*, *S*, *G*, etc.), then an excess property is defined as the difference between the actual property value of a solution and the value it would have as an ideal solution at the same temperature, pressure, and composition. Thus: M

$$M^E \equiv M - M^{id}$$

The excess property bear a relationship to the property change of mixing. One may take the example of excess Gibbs free energy to illustrate the point

$$G^E = G - G^{id}$$

$$\text{Or: } G^E = G - \left(\sum_i x_i G_i + RT \sum_i x_i \ln x_i \right)$$

$$\text{Thus: } G^E = \Delta G_{mix} - RT \sum_i x_i \ln x_i$$

Other relations include:

$$H^E = H - H^{id} = \Delta H_{mix}$$

$$S^E = \Delta S_{mix} + R \sum_i y_i \ln y_i$$

$$\text{Also: } G^E = H - TS^E$$

The non-ideality of real liquid solutions are depicted well by use of excess properties, especially through the behavior of The excess Gibbs energy is typically obtained from low pressure vapour-liquid equilibrium data, while H^E is obtained by measuring isothermal enthalpy change of mixing. Lastly S^E is derived using the following relation:

$$S^E = \frac{H_E - G^E}{T}$$

it shows the variation of each of the excess property as a function of liquid mole fraction for a number of binary solutions.

1.14 Relation between excess Gibbs free energy and activity coefficient

$$\bar{G}_i - \bar{G}_i^{id} = \bar{G}_i^E = RT \ln \frac{\hat{f}_i}{x_i f_i}$$

The left side of this equation is the partial excess Gibbs energy $\bar{G}_i^E$; the dimensionless ratio $\hat{f}_i / x_i f_i$ appearing on the right is the *activity coefficient* of species i in solution, represented by the symbol γ_i.

Thus, by definition:

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i}$$

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

Whence, $\bar{G}_i^E / RT = \ln \gamma_i$

But $G^E = \sum_i x_i \bar{G}_i^E$

On comparing the last two equations we conclude that γ_i is a partial molar property with respect to G^E. Thus, we have:

$$\ln \gamma_i = \left. \frac{\partial (nG^E / RT)}{\partial n_i} \right|_{T,P,n_{j\neq i}}$$

1.15 Standard states definition and choice.

This choice is in principle arbitrary, but the following standard states are usually chosen for practical reasons:

- Mixtures of gases For components in the gaseous phase, the standard state of an ideal gas at standard pressure is used. In the case of this choice, μ_i^{st} is the chemical potential of a pure substance i in the state of an ideal gas at the temperature of the mixture and standard pressure, usually $p^{st} = 101\,325$ Pa.
- Mixtures of liquids and solid substances

For components in a liquid or solid phase, the standard state of a pure substance at the temperature and pressure of the system is used. μ_i^{st} is the chemical potential of a pure substance i, which at the temperature and pressure of the mixture is in the same phase as the mixture.

The standard states of individual components may be chosen arbitrarily within certain limits. The first limitation is that the standard temperature is always the temperature of the system. Further on, the standard state of individual components of a system is usually chosen at fixed composition. The standard pressure is either constant, or it changes with the system pressure.

- Standard state: the state of a pure substance in a given state of matter or modification at the temperature of the system and a standard pressure.

Solved problems

1.1

Consider a solution of two species S1/S2 at 25°C such that $x_1 = 0.4$. If $\overline{V}_1 = 40 \text{ x } 10^{-6}\ m^3/mol$, find $\overline{V}_2$. The solution specific gravity is = 0.90 and the molecular weights of the species are 32 and 18 respectively.

Molar mass of solution = $x_1M_1 + x_2M_2$ (M = MW)

$$= 0.4 \text{ x } 32 + 0.6 \text{ x } 18$$

$$= 23.433 \text{ gm/mol} = 23.6 \text{ x } 10^{-3} \text{ kg/mol}$$

$$\text{Solution molar volume} = \frac{\text{Molar mass}}{\text{Density}} \Rightarrow$$

$$= \frac{23.6x10^{-3}\,kg/mol}{900kg/m^3} = 26.2 \text{ x } 10^{-6}\ m^3/mol$$

Now $V = x_1\overline{V}_1 + x_2\overline{V}_2$

$$\Rightarrow \overline{V}_2 = (V - x_1\overline{V}_1)/x_2 = \frac{(26.2\ -\ 0.4\ x\ 40)\ x10^{-6}}{0.6}$$

$$= 17.0 \text{ x } 10^{-6}\ m^3/mol.$$

1.2

The molar enthalpy of a binary solution is given by:

$V = 500\ x_1 + 1000\ x_2 + x_1x_2\ (50\ x_1+40x_2)\ cm^3/mol$. Find the expressions for $\overline{V}_1$, and $\overline{V}_1^{\infty}$.

Putting $x_1 = 1 - x_2$; it follows:

$$V = 500 + 550\ x_2 - 60\ x_2^2 + 10\ x_2^3$$

$$\frac{dV}{dx_2} = 550 - 120\ x_2 + 30\ x_2^2$$

$$\overline{V_1} = V - x_2 \frac{dV}{dx_2}$$

$= 500\ x_1 + 1000\ x_2 + x_1x_2\ (500x_1 + 40\ x_2)\ -x_2\ [550 - 120\ x_2 + 30\ x_2^2]$

Putting $x_2 = 1-x_1$; and simplifying:

$$\overline{V_1} = 540 - 60\ x_1 + 20\ x_1^3$$

$$\overline{V_1}^{\infty} = \lim_{x_1 \to 0} \overline{V_1} = 540\ \text{J / mol}$$

1.3

What is the change in entropy when 0.6 m^3 of CO_2 and 0.4 m^3 of N_2, each at 1 bar and 25°C blend to form a gas mixture at the same conditions? Assume ideal gases.

For an ideal gas, mole fraction = volume fraction

CO_2 (1) / N_2(2); $y_1 = 0.6$, $y_2=0.4$

$$(\Delta S)_{mix} = -R \sum y_i \ln y_i = 5.5 J / molK$$

REFERENCES

1. Smith J.M. and Van Ness H.C., Introduction to Chemical Engineering Thermodynamics, 7th Edition, McGraw Hill, 2005.
2. Narayanan K.V., A Text Book of Chemical Engineering Thermodynamics, 3rd Edition, Prentice Hall of India Pvt. Ltd., 2013.
3. Gopinath Halder, Introduction to Chemical Engineering Thermodynamics, 2nd Edition, PHI Learning Pvt. Ltd., 2009.

SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE
www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – II - Phase Equilibria – SCHA1302

2.Introduction

2.1 Criteria of Thermodynamic Equilibrium

The nature of thermodynamic equilibrium is as we know that , it involves simultaneous thermal and mechanical equilibrium within a system. Apart from these constraints, the system must also be in a state of chemical equilibrium. In the most general sense, chemical equilibrium subsumes the following restrictions: (i) the various phases that may exist within the system are in equilibrium with each other in that there is no mass transfer of any chemical species between the phases; (ii) all reactions occurring in the system are also equilibrated, i.e., there is no further progress of the reaction in terms of conversion of the reactants to products.

The last two criteria are better understood in terms of the property called chemical potential, which we shall introduce in the following section. Here we focus on the overall, general criterion that must be in obeyed for any chemical system in equilibrium regardless of whatever species, phases or reactions that defines it. Consider a closed system, which can be either homogeneous or heterogeneous, and which exists in a state of thermal and mechanical equilibrium with its surroundings. However, we assume that it is not under equilibrium with respect to possible inter-phase transfer of the chemical species or reactions between them. If the latter conditions prevail, all inter-phase transfer processes or reactive transformation of species must continue to occur till the point when the system is also at chemical equilibrium. In all real systems such changes are induced by finite gradients and are therefore are irreversible in nature. Applying the first law equation for all such changes for the system.

$$dU^t = dQ + dW$$

We next consider that the system is under thermal and mechanical equilibrium with the surroundings. Under such a situation,

$$dW = -PdV^t$$

And also: $dS_{surr} = \frac{dQ_{surr}}{T_{surr}} = -\frac{dQ^t}{T}$ (note that $dQ_{surr} = -dQ^t$ for system)

But by the second law: $dS_{surr} + dS^t \geq 0$

Combining the above equations,

$$dU^t + PdV^t - TdS^t \leq 0$$

It follows that for all incremental changes within the system, which take it closer to the final thermodynamic equilibrium, the property changes must satisfy the constraint imposed by the above eqn. If the changes internal to the system occur under reversible conditions, the *equality* sign is valid; on the other hand, for irreversible processes the inequality condition holds. The above equation can be used to generate alternate criteria of thermodynamic equilibrium, namely:

$$(dU^t)_{V^t,S^t} \leq 0$$

$$(dS^t)_{U^t,V^t} \leq 0$$

The other two criteria which are most apt in relation to thermodynamics of phase equilibria involve the use of Helmholtz and Gibbs free energy. If a process takes place under the constraints of constant temperature and volume then:

$$\left[dU^t - d(TS^t)\right]_{T,V^t} \leq 0$$

Or:

$$\left[d(U^t - TS^t)\right]_{T,V^t} \leq 0$$

$$(dA^t)_{T,V^t} \leq 0$$

And, if the process occurs under constant temperature and pressure one may write:

$$\left[dU^t + d(PV^t) - d(TS^t)\right]_{T,P} \leq 0$$

Or: $\left[dG^t\right]_{T,P} \leq 0$

This equation provides the most practical of the three versions of general criteria of approach to equilibrium, as temperature and pressure are the most easily measurable of all the thermodynamic properties. As we have argued at the early part of this section at total thermodynamic equilibrium not only are thermal and mechanical gradients non-existent, there can be no further change in either the composition of any of the phases, or that of the reactive species. If there are any such incremental, *infinitesimal* changes of composition variables at the state of complete equilibrium the system once again must return to its stable state. the following equation to characterize thermodynamic equilibrium:

$$\left[dG^t\right]_{T,P} = 0$$

In summary, therefore, the above equation constitutes a generalized description of thermodynamic equilibrium, which may be stated as follows: **“**The equilibrium state of a closed system is that state for which the total Gibbs energy is a minimum with respect to all possible changes at the given T and P”.

The criterion of equilibrium can be employed for determination of equilibrium states of a system in terms of its T, P and compositions. In principle, one first expresses G_t (at a given temperature and pressure) as a function of the numbers of moles of each chemical species present in the various phases. Next one makes a partial differential operation on G_t with respect to moles of each species in the phases, and sets each such differential to zero to obtain the set of values for the mole numbers that *minimizes* G_t, subject to the constraints of conservation of mass. This procedure can be applied to problems of phase, chemical-reaction equilibria; and, of course, the most complex of chemical thermodynamic problems, where the criteria of phase and chemical-reaction equilibrium are valid simultaneously. As we will see, this eqn. forms the foundation for developing more *specific* criteria that can help describe both phase and chemical reaction equilibria.

2.2 Single Component Phase equilibria:

The Chemical Potential μ controls phase transitions and phase equilibria. Equilibrium condition – at equilibrium μ must be identical throughout the system When multiple phases are present in equilibrium, μ must be the same in all phases For example, consider two phases (liquid and solid) of water at a fixed (T, p). If $\mu_s(T, p) = \mu_\ell(T, p)$ then… liquid water and ice coexist If $\mu_s(T, p) > \mu_\ell(T, p)$ then… the water is in the liquid phase If $\mu_s(T, p) < \mu_\ell(T, p)$ then… the water is in the solid phase. 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 a and b of a pure component are at equilibrium. Thus as given by equation

$$\mu_i^{\alpha} = \mu_i^{\beta}$$

However, for a pure component the chemical potential is reduces to the pure component molar Gibbs free energy. Therefore: $\mu_i^{\alpha} = G^{\alpha}$ and, $\mu_i^{\beta} = G^{\beta}$

Hence the equation reduces to:

$$G^{\alpha} = G^{\beta}$$

On taking a differential:

$$dG^{\alpha} = dG^{\beta}$$

Using the generic relationship ,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} :

$$V^{\alpha} dP^{sat} - S^{\alpha} dT = V^{\beta} dP^{sat} - S^{\beta} dT$$

On rearranging:

$$\frac{dP^{sat}}{dT} = \frac{S^{\beta} - S^{\alpha}}{V^{\beta} - V^{\alpha}} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}$$

Additionally using the second law we have:

$$dS = dQ/T$$

And that for a constant pressure process:

$$dQ = dH$$

Using the above equations and we obtain:

$$\Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta}$$

Thus, $\Delta S^{\alpha\beta} = \Delta H^{\alpha\beta} / T$,

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}$$

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

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T\Delta V^{lv}}$$

Noting that liquid phase molar volumes are relatively much lesser than vapour phase volumes, we may write,

$$\Delta V^{LV} = V^{V} - V^{V} \cong V^{v} = \frac{RT}{P^{sat}}$$

Further at low to moderate saturation pressures if we assume ideal vapor phase behavior, then

$$V^{v} \cong \frac{RT}{P^{sat}}$$

Above Equation becomes:

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

Or:

$$\frac{dP^{sat} / P^{sat}}{dT / T^{2}} = \frac{\Delta H^{LV}}{R}$$

$$\Delta H^{LV} = -R[\frac{d \ln P^{sat}}{d(1/T)}]$$

approximate equation is known as the *Clausius-Clapeyron equation*. The assumptions used in the above derivations have approximate validity only at low pressures.

$$\ln P^{sat} = A - \frac{B}{T}$$

and comparing these equations 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 equation is 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. called the Antoine Equation, has proved to be more accurate, including at higher pressures, has the following form:

$$\ln P^{sat} = A - \frac{B}{T + C}$$

2.2.1 Fugacity of Pure substances:

It has been shown that the chemical potential provides a fundamental description of phase equilibria. As we shall further, it also proves an effective tool for depicting chemical reaction equilibria. Nevertheless, its direct usage is restricted, as it is not easy to directly relate the chemical potential to thermodynamic properties amenable to easy experimental determination, such as the volumetric properties. The definition of a new function called fugacity, itself related to the chemical potential, helps bridge the gap. The concept of fugacity is advanced based on the following thermodynamic relation for an ideal gas. For a single component closed system containing an ideal gas we have:

$$dG = VdP - SdT$$

At constant temperature, for a pure ideal gas ‘i’ the above equation reduces to:

$$dG_i^{ig} = V_i^{ig}dP = RTdP / P = RTd\ln P$$

$$G_i^{ig} = \Gamma_i(T) + RTd\ln P$$

[Where, Gi(T) is the constant of integration]

Utilizing the essential simplicity we apply it a real fluid but by replacing pressure with fugacity, since it is not valid for a real fluid:

$$dG_i = V_i dP$$

(At const T)

Thus, $dG_i = RTd\ln f_i$;

Hence $G_i = \Gamma_i(T) + RTd\ln f_i$

Since f_i has the units of pressure, it is often described as a “fictitious pressure”. It may be noted that the definition of fugacity as provided and is completely general in nature, and so can be extended to liquids and solids as well.

$$G - G^{ig} = G_i^R = RT\ln\frac{f_i}{P}$$

The dimensionless ratio f_i / P is termed *fugacity coefficient* (ϕ).

Thus: $G_i^R = RT\ln \phi_i$

Where, $\phi_i \equiv f_i / P$

Clearly for an ideal gas the following relations hold: $G_i^R = 0;\ f_i^{ig} = P;$ accordingly, $\phi_i = 1$.

However, by equation : $\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dP}{P}$

Thus, using the last relation

$$\ln \phi_i = \int_0^P (Z_i - 1)\frac{dP}{P}$$

(At const. T)

The general criterion of thermodynamic equilibrium has been defined by eqn. Applying it to, for example, a vapour (V) and liquid (L) system of a pure component '*i*' we have:

$$\mu_i^V = \mu_i^L$$

However, for a pure component system: $\lim_{x_i \to 1} \bar{M}_i = M_i$.

Thus: $\mu_i^V \equiv \bar{G}_i^V = G_i^V$ and $\mu_i^L \equiv \bar{G}_i^L = G_i^L$

Thus, using these eqn. we have:

$$G_i^V = G_i^L$$

The above equation may be generalized for any other types of phases. However, the eqn. is rendered more easily applicable if the chemical potential is replaced by fugacity. Thus integrating eqn. between vapour and liquid states of a pure component:

$$\int_L^V dG_i = RT\int_L^V d\ln f_i$$

$$G_i^V - G_i^L = RT\ln(f_i^V / f_i^L)$$

Now applying eqn. to it follows $RT\ln(f_i^V / f_i^L) = 0$

Or:

$$f_i^V = f_i^L = f_i^{sat}$$

In eqn. f_i^{sat} indicates the value for either saturated liquid or saturated vapor, this is because the coexisting phases of saturated liquid and saturated vapor are in equilibrium. Since under such condition the pressure is P_i^{sat}, we can write:

$$\phi_i^V = \frac{f_i^V}{P_i^{sat}}$$

$$\phi_i^L = \frac{f_i^L}{P_i^{sat}}$$

$$\phi_i^{sat} = \frac{f_i^{sat}}{P_i^{sat}}$$

Thus, employing eqn. again, it follows:

$$\phi_i^V = \phi_i^L = \phi_i^{sat}$$

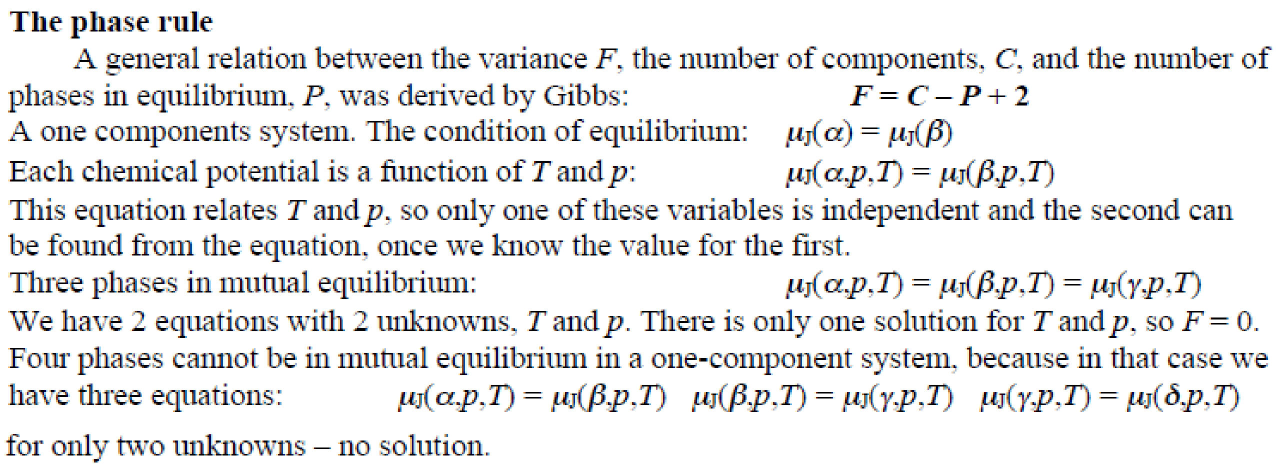
Fugacity coefficient (and hence fugacity) of pure gases may be conveniently evaluated by applying eqn. to a *volume-explicit* equation of state. The truncated virial EOS is an example of the latter type, for which the compressibility factor of pure species (*i*) is given by:

$$Z_i = 1 + \frac{B_{ii}P}{RT}$$

Or

$$Z_i - 1 = \frac{B_{ii}P}{RT}$$

2.3 phase rule & its application



The phase rule

A general relation between the variance *F*, the number of components, *C*, and the number of phases in equilibrium, *P*, was derived by Gibbs: $\boldsymbol{F = C - P + 2}$

A one components system. The condition of equilibrium: $\mu_J(\alpha) = \mu_J(\beta)$

Each chemical potential is a function of *T* and *p*: $\mu_J(\alpha,p,T) = \mu_J(\beta,p,T)$

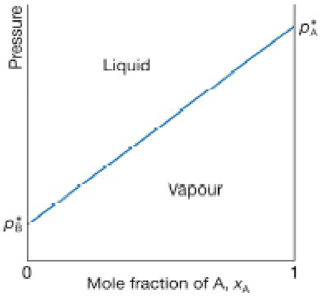
This equation relates *T* and *p*, so only one of these variables is independent and the second can be found from the equation, once we know the value for the first.

Three phases in mutual equilibrium: $\mu_J(\alpha,p,T) = \mu_J(\beta,p,T) = \mu_J(\gamma,p,T)$

We have 2 equations with 2 unknowns, *T* and *p*. There is only one solution for *T* and *p*, so $F = 0$.

Four phases cannot be in mutual equilibrium in a one-component system, because in that case we have three equations: $\mu_J(\alpha,p,T) = \mu_J(\beta,p,T)$ $\mu_J(\beta,p,T) = \mu_J(\gamma,p,T)$ $\mu_J(\gamma,p,T) = \mu_J(\delta,p,T)$

for only two unknowns – no solution.



Vapor pressure diagrams

The partial vapor pressures of the components of an ideal solution of two volatile liquids are related to the composition of the liquid mixture by Raoult's law:

$$p_A = x_A p_A^* \qquad p_B = x_B p_B^*$$

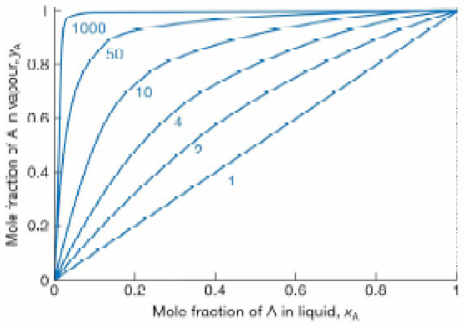
The total pressure:

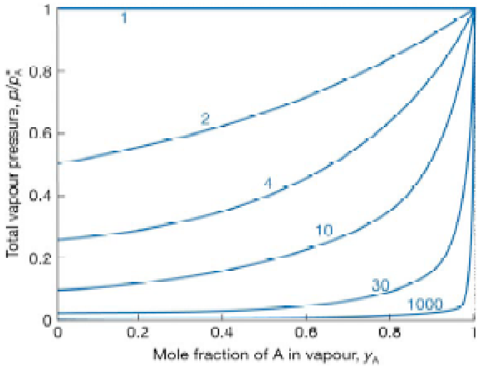
$$p = p_A + p_B = x_A p_A^* + x_B p_B^*$$

$$p = p_B^* + (p_A^* - p_B^*)x_A$$

The total vapor pressure changes linearly with the composition from p_B^* to p_A^* as x_A changes from 0 to 1.

The composition of the vapor





The compositions of the liquid and vapor that are in mutual equilibrium are not necessarily the same. Common sense: the vapor should be richer in the more volatile component. The partial pressures of the components are given by Raoult's law.

From Dalton's law, the mole fractions in gas are: $y_A = p_A/p \quad y_B = p_B/p$

Provided the mixture is ideal, the partial pressures and the total pressure may be expressed in terms of the mole fractions in the liquid:

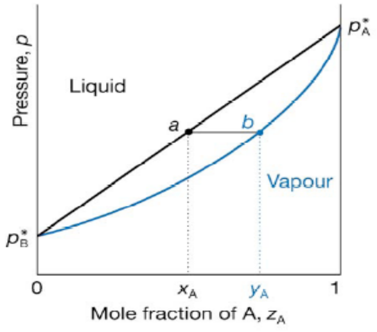
$$y_A = \frac{x_A p_A^*}{p_B^* + \left(p_B^* - p_A^*\right)x_A} \qquad y_B = 1 - y_A$$

The figure shows the composition of the vapor plotted against the composition of the liquid for various values of $p_A^*/p_B^* > 1$: in all cases $y_A > y_B$ – the vapor is richer than the liquid in the more volatile component. If B is not volatile, $p_B^* = 0$ and $y_B = 0$.

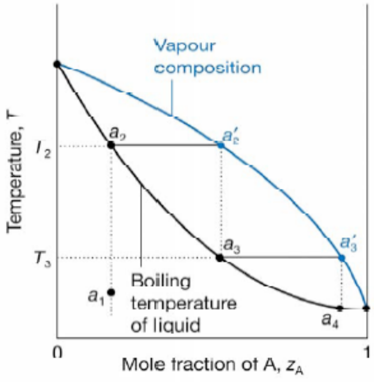
We can relate the total vapor pressure to the composition of the vapor

$$p = \frac{p_A^* p_B^*}{p_A^* + \left(p_B^* - p_A^*\right)y_A}$$

The interpretation of the diagrams



If we are interested in distillation, both the vapor and the liquid compositions are of equal interest and the two preceding diagrams can be combined into one: The point *a* indicates the vapor pressure of a mixture of composition x_A, and the point *b* indicates the composition of the vapor that is in equilibrium with the liquid at that pressure. When two phases are in equilibrium, $P = 2$ and $F' = 1$: if the composition is specified, the pressure at which the two phases are in equilibrium is fixed.



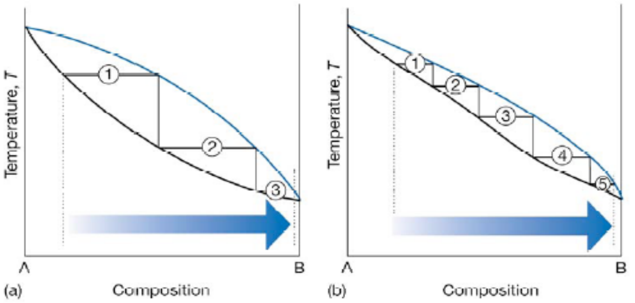
Temperature-composition diagrams

A **temperature-composition diagram** – a phase diagram in which the boundaries show the composition of the phases in equilibrium at various temperatures (at a given pressure, typically, 1 atm). The liquid phase now lies in the lower part of the diagram.

The distillation of mixtures

The region between the lines is a two-phase region with $F' = 1$. The regions outside the phase lines correspond to a single phase and $F' = 2$ (the temperature and composition are both independently variable).

When a liquid of composition a_1 is heated, it boils at the temperature T_2. Then the liquid has composition a_2 (the same as a_1) and the vapor (present only as a trace) has composition a_2'. The vapor is richer in the more volatile component A (with the lower boiling point). From the location of a_2, we can state the vapor's composition at the boiling point, and from the location of the tie line joining a_2 with a_2' we can read off the boiling temperature (T_2) of the original liquid mixture. In a **simple distillation**, the vapor is withdrawn and condensed. In **fractional distillation**, the boiling and condensation cycle is repeated successively until almost pure A is obtained.



The efficiency of a fractionating column is expressed in terms of the number of **theoretical plates**, the number of effective vaporization and condensation steps that are required to achieve a condensate of given composition from a given distillate (three and five for (a) and (b)).

Vapor pressure and boiling

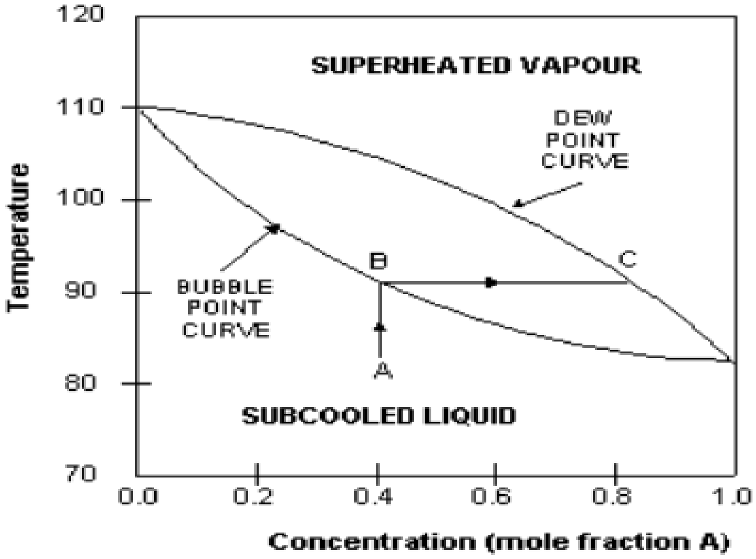
The vapor pressure of a liquid at a particular temperature is the equilibrium pressure exerted by molecules leaving and entering the liquid surface.

Here are some important points regarding vapor pressure:

- Energy input raises vapor pressure
- Vapor pressure is related to boiling
- A liquid is said to 'boil' when its vapor pressure equals the surrounding pressure
- The ease with which a liquid boils depends on its volatility
- Liquids with high vapor pressures (volatile liquids) will boil at lower temperatures
- The vapor pressure and hence the boiling point of a liquid mixture depends on the relative amounts of the components in the mixture

- Distillation occurs because of the differences in the volatility of the components in the liquid mixture.

  THE BOILING POINT DIAGRAM



- The Boiling Point Diagram The boiling point diagram shows how the equilibrium compositions of the components in a liquid mixture vary with temperature at a fixed pressure.
- Consider an example of a liquid mixture containing 2 components (A and B) - a binary mixture..

  The boiling point of A is that at which the mole fraction of A is 1. The boiling point of B is that at which the mole fraction of A is 0. In this example, A is the more volatile component and therefore has a lower boiling point than B.

  The upper curve in the diagram is called the dew-point curve while the lower one is called the bubble-point curve.

- Dew-point: is the temperature at which the saturated vapor starts to condense.
- Bubble-point: is the temperature at which the liquid starts to boil.
- The region above the dew-point curve shows the equilibrium composition of the superheated vapor while the region below the bubble-point curve shows the equilibrium composition of the sub-cooled liquid.

- For example, when a subcooled liquid with mole fraction of A=0.4 (point A) is heated, its concentration remains constant until it reaches the bubble-point (point B), when it starts to boil. The vapors evolved during the boiling has the equilibrium composition given by point C, approximately 0.8 mole fraction A. This is approximately 50% richer in A than the original liquid. ™
- This difference between liquid and vapor compositions is the basis for distillation operations.

Relative Volatility

- Relative volatility: is a measure of the differences in volatility between 2 components, and hence their boiling points. It indicates how easy or difficult a particular separation will be.
- The relative volatility of component ‘i’ with respect to component ‘j’ is defined as

$$\alpha_{ij} = \left(\frac{yi}{xi}\right) \Big/ \left(\frac{yj}{xj}\right)$$

yi = mole fraction of component ‘i’ in the vapour

xi = mole fraction of component ‘i’ in the liquid

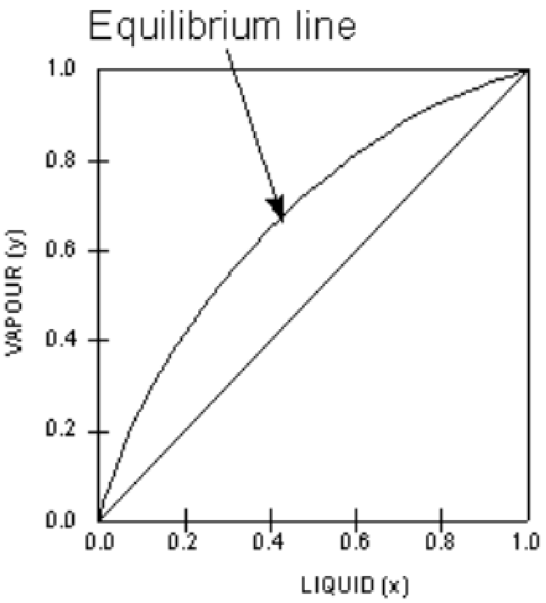
Thus if the relative volatility between 2 components is very close to one, it is an indication that they have very similar vapor pressure characteristics. This means that they have very similar boiling points and therefore, it will be difficult to separate the two components via distillation.

2.4 vapour liquid equilibria

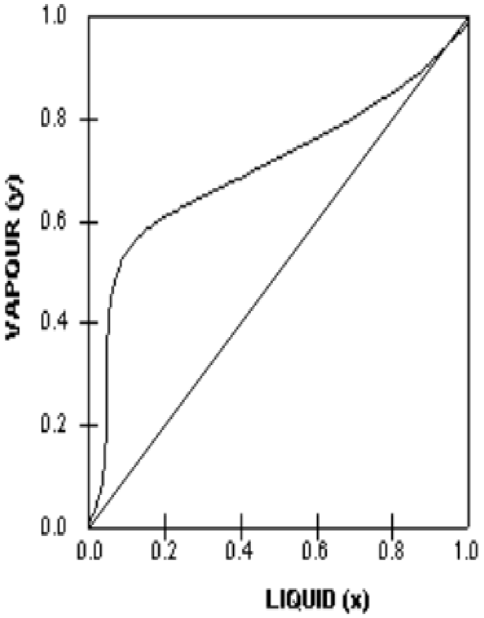
Distillation columns are designed based on the boiling point properties of the components in the mixtures being separated. Thus the sizes, particularly the height, of distillation columns are determined by the vapor liquid equilibrium (VLE) data for the mixtures.

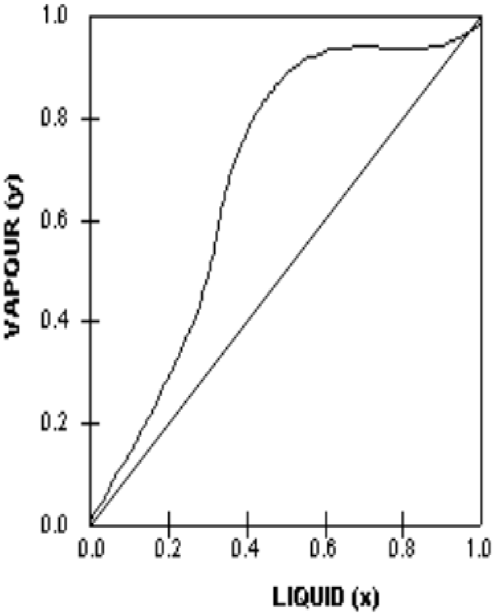
Vapor-Liquid-Equilibrium (VLE) Curves

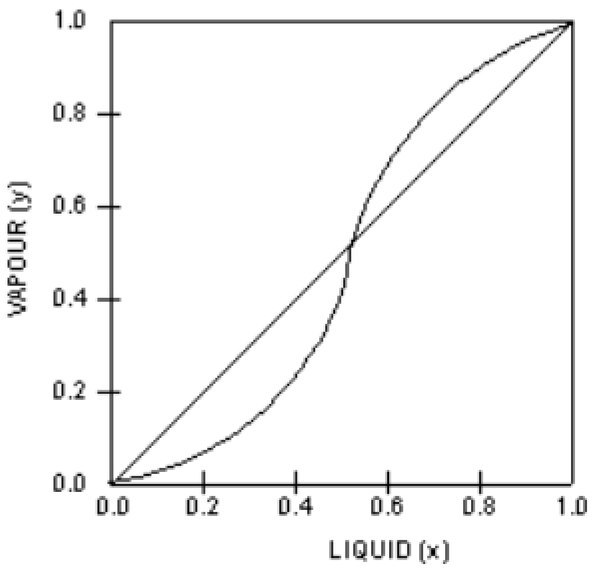
Constant pressure VLE data is obtained from boiling point diagrams. VLE data of binary mixtures is often presented as a plot, as shown in the figure. The VLE plot expresses the bubble-point and the dew-point of a binary mixture at constant pressure. The curved line is called the equilibrium line and describes the compositions of the liquid and vapour in equilibrium at some fixed pressure



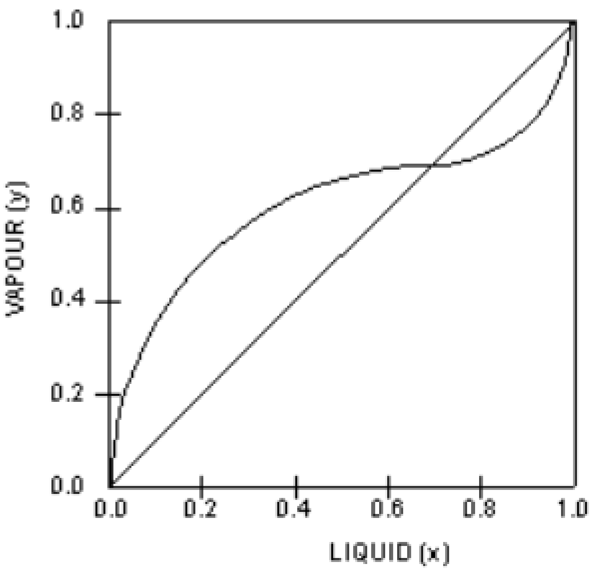
The previous particular VLE plot shows a binary mixture that has a uniform vapor-liquid equilibrium that is relatively easy to separate. The next two VLE plots below on the other hand, shows non-ideal systems which will present more difficult separations.







Maximum Boiling Point



Minimum Boiling Point

The most intriguing VLE curves are generated by azeotropic systems. An azeotrope is a liquid mixture which when vaporised, produces the same composition as the liquid. The two VLE plots below, show two different azeotropic systems, one with a minimum boiling point and one with a maximum boiling point. In both plots, the equilibrium curves cross the diagonal lines, and this are azeotropic points where the azeotropes occur. In other words azeotropic systems give rise to VLE plots where the equilibrium curves crosses the diagonals

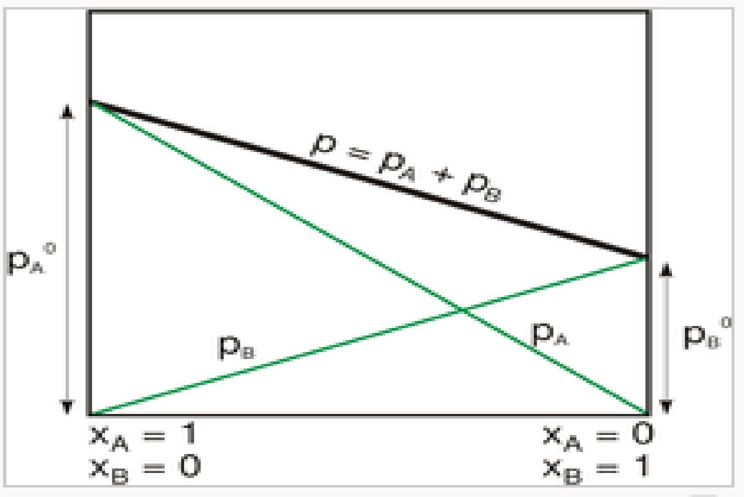
Raoult's law

It states that the partial vapor pressure of each component of an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture.

Mathematically, Raoult's law for a single component in an ideal solution is stated as

$$p_i = p_i^{\star} x_i,$$

where p_i is the partial vapor pressure of the component i in the gaseous mixture (above the solution), $p_i^{\star}$ is the vapor pressure of the pure component i, and x_i is the mole fraction of the component i in the mixture (in the solution).



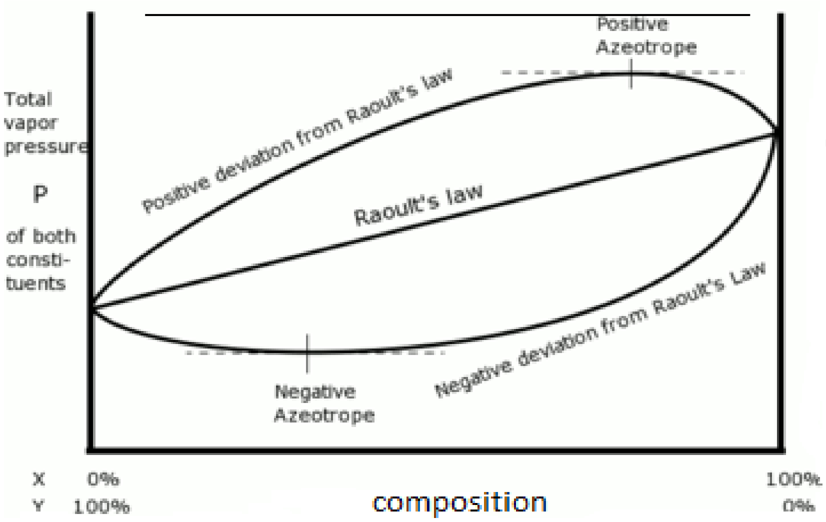
Once the components in the solution have reached equilibrium, the total vapor pressure of the solution can be determined by combining Raoult's law with Dalton's law of partial pressures to give

$$p = p_A^\star x_A + p_B^\star x_B + \cdots.$$

If a non-volatile solute (zero vapor pressure, does not evaporate) is dissolved into a solvent to form an ideal solution, the vapor pressure of the final solution will be lower than that of the pure solvent.

Ideal solution: An ideal solution will obey Raoult's Law,

Real solutions: Solutions which deviate from Raoults law are called as real solutions. Many pairs of liquids are present in which there is no uniformity of attractive forces, i.e., the adhesive and cohesive forces of attraction are not uniform between the two liquids, so that they deviate from the Raoult's law.



Negative deviation:

If the vapor pressure of a mixture is lower than expected from Raoult's law, there is said to be a negative deviation. This is evidence that the adhesive forces between different components are stronger than the average cohesive forces between like components. In consequence each component is retained in the liquid phase by attractive forces that are stronger than in the pure liquid so that its partial vapor pressure is lower.

For example, the system of chloroform ($CHCl_3$) and acetone(CH_3COCH_3) has a negative deviation from Raoult's law

Positive deviation

When the cohesive forces between like molecules are greater than the adhesive forces between dissimilar molecules, the dissimilarities of polarity leads both components to escape solution more easily. Therefore, the vapor pressure is greater than expected from the Raoult's law, showing positive deviation. If the deviation is large, then the vapor pressure curve shows a maximum at a particular composition and form a positive azeotrope. Some mixtures in which this happens are (1)benzene and methanol, (2) carbon disulfide and acetone, and (3) chloroform and ethanol.

The concentration of a vapor in contact with its liquid, especially at equilibrium, is often expressed in terms of vapor pressure, which will be a partial pressure (a part of the total gas pressure) if any other gas(es) are present with the vapor. The equilibrium vapor pressure of a liquid is in general strongly dependent on temperature. At vapor–liquid equilibrium, a liquid with individual components in certain concentrations will have an equilibrium vapor in which the concentrations or partial pressures of the vapor components have certain values depending on all of the liquid component concentrations and the temperature.

The converse is also true: if a vapor with components at certain concentrations or partial pressures is in vapor–liquid equilibrium with its liquid, then the component concentrations in the liquid will be determined dependent on the vapor concentrations and on the temperature. The equilibrium concentration of each component in the liquid phase is often different from its concentration (or vapor pressure) in the vapor phase, but there is a relationship. The VLE concentration data can be determined experimentally, or computed or approximated with the help of theories such as Raoult's law, Dalton's law, and Henry's law.

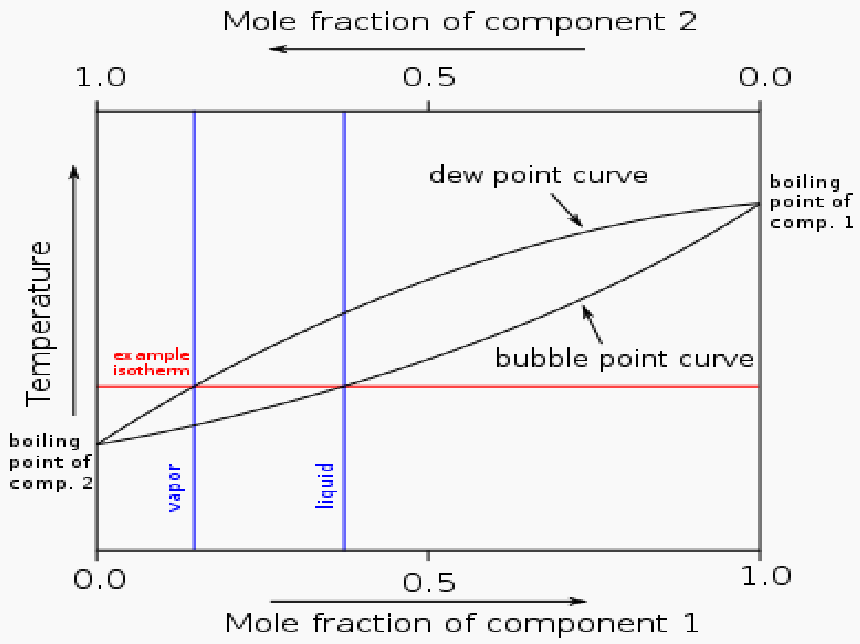
Such VLE information is useful in designing columns for distillation, especially fractional distillation, which is a particular specialty of chemical engineers. Distillation is a process used to separate or partially separate components in a mixture by boiling (vaporization) followed by condensation. Distillation takes advantage of differences in concentrations of components in the liquid and vapor phases.

In mixtures containing two or more components, the concentrations of each component are often expressed as mole fractions. The mole fraction of a given component of a mixture in a particular phase (either the vapor or the liquid phase) is the number of moles of that component in that phase divided by the total number of moles of all components in that phase. Binary mixtures are those having two components. Three-component mixtures are called ternary mixtures. There can be VLE data for mixtures with even more components, but such data is often hard to show graphically. VLE data is a function of the total pressure, such as 1 atm or whatever pressure the process is conducted at.

When a temperature is reached such that the sum of the equilibrium vapor pressures of the liquid components becomes equal to the total pressure of the system (it is otherwise smaller), then vapor bubbles generated from the liquid begin to displace the gas that was maintaining the overall pressure, and the mixture is said to boil. This temperature is called the *boiling point* of the liquid mixture at the given pressure. (It is assumed that the total pressure is held steady by adjusting the total volume of the system to accommodate the specific volume changes that accompany boiling.) The boiling point at an overall pressure of 1 atm is called the *normal boiling point* of the liquid mixture. Binary mixture VLE data at a certain overall pressure, such as 1 atm, showing mole fraction vapor and liquid concentrations when boiling at various temperatures can be shown as a two-dimensional graph called a **boiling-point diagram**. The mole fraction of component 1 in the mixture can be represented by the symbol x_1. The mole fraction of component 2, represented by x_2, is related to x_1 in a binary mixture as follows:

$x_1 + x_2 = 1$ In multi-component mixtures in general with n components, this becomes:

$x_1 + x_2 + ... + x_n = 1$



Boiling-point diagram

The preceding equilibrium equations are typically applied for each phase (liquid or vapor) individually, but the result can be plotted in a single diagram. In a binary boiling-point diagram, temperature (T) is graphed vs. x_1. At any given temperature where both phases are present, vapor with a certain mole fraction is in equilibrium with liquid with a certain mole fraction. The two mole fractions often differ. These vapor and liquid mole fractions are represented by two points on the same horizontal isotherm (constant T) line. When an entire range of temperatures vs. vapor and liquid mole fractions is graphed, two (usually curved) lines result. The lower one, representing the mole fraction of the boiling liquid at various temperatures, is called the *bubble point curve*. The upper one, representing the mole fraction of the vapor at various temperatures, is called the *dew point curve*.

These two lines (or curves) necessarily meet where the mixture becomes purely one component, namely where $x_1 = 0$ (and $x_2 = 1$, pure component 2) or $x_1 = 1$ (and $x_2 = 0$, pure component 1). The temperatures at those two points correspond to the boiling points of each of the two pure components.

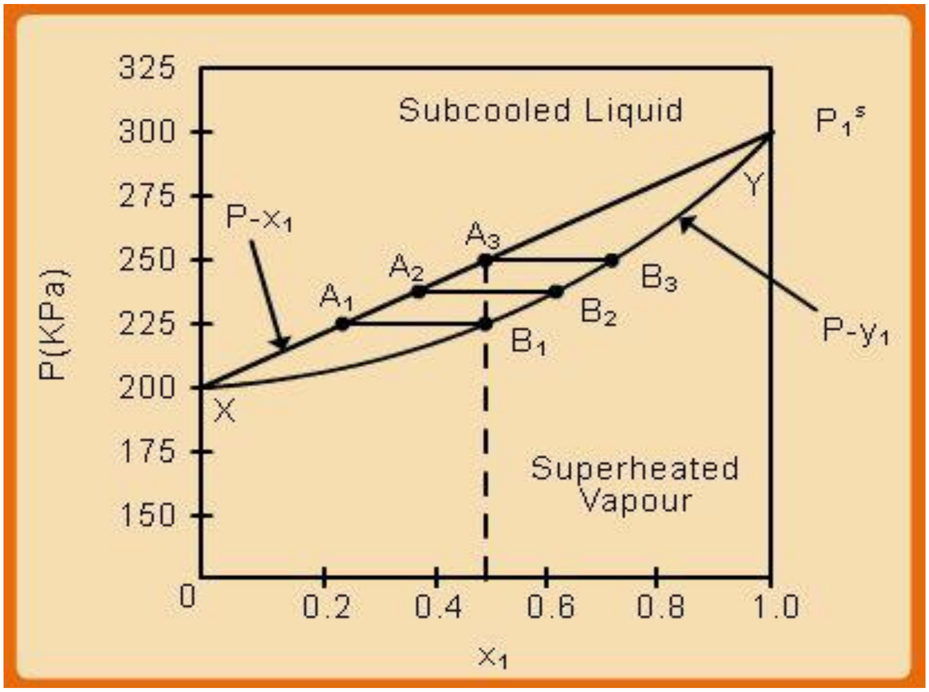
For certain pairs of substances, the two curves also coincide at some point strictly between $x_1 = 0$ and $x_1 = 1$. When they meet, they meet tangently; the dew-point temperature always lies above the boiling-point temperature for a given composition when they are not equal. The meeting point is called an azeotrope for that particular pair of substances. It is characterized by an azeotrope temperature and an azeotropic composition, often expressed as a mole fraction. There can be maximum-boiling azeotropes, where the azeotrope temperature is at a maximum in the boiling curves, or minimum-boiling azeotropes, where the azeotrope temperature is at a minimum in the boiling curves.

If one wants to represent a VLE data for a three-component mixture as a boiling point "diagram", a three-dimensional graph can be used. Two of the dimensions would be used to represent the composition mole fractions, and the third dimension would be the temperature. Using two dimensions, the composition can be represented as an equilateral triangle in which each corner represents one of the pure components. The edges of the triangle represent a mixture of the two components at each end of the edge. Any point inside the triangle represents the composition of a mixture of all three components. The mole fraction of each component would correspond to where a point lies along a line starting at that component's corner and perpendicular to the opposite edge. The bubble point and dew point data would become curved surfaces inside a triangular prism, which connect the three boiling points on the vertical temperature "axes". Each face of this triangular prism would represent a two-dimensional boiling-point diagram for the corresponding binary mixture. Due to their three-dimensional complexity, such boiling-point diagrams are rarely seen. Alternatively, the three-dimensional curved surfaces can be represented on a two-dimensional graph by the use of curved isotherm lines at graduated intervals, similar to iso-altitude lines on a map. Two sets of such isotherm lines are needed on such a two-dimensional graph: one set for the bubble point surface and another set for the dew point surface.

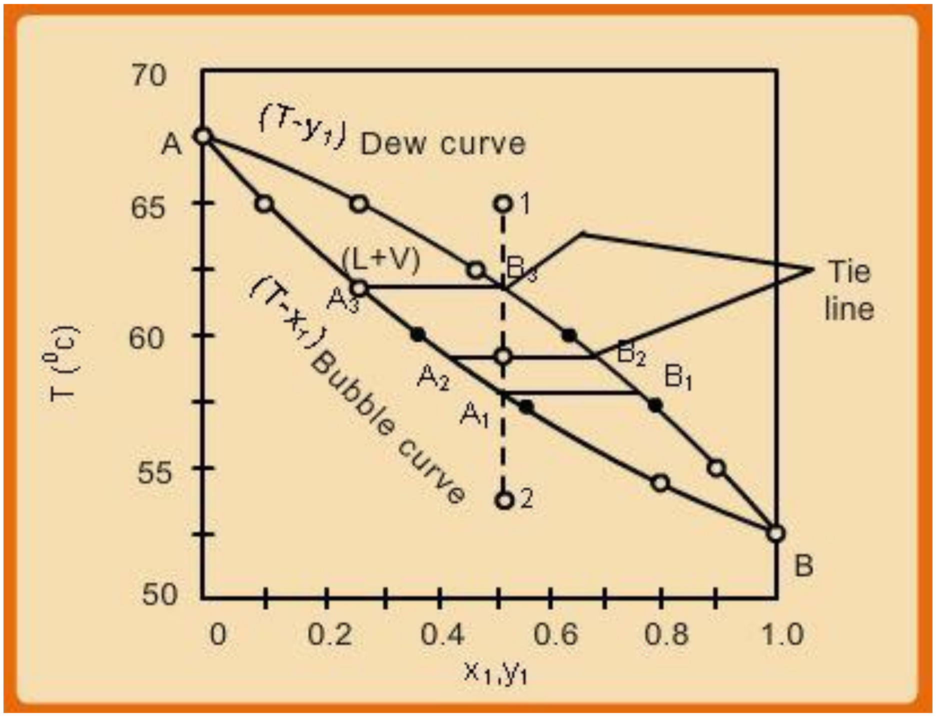
2.5 Duhem's theorem.

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

2.6 Pxy and Txy diagrams.



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



Model T-x-y plot for a system obeying Raoult's Law

Solved problems

2.1

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, $y_1 = 0.5$, $y_2 = 0.3$.

(a) For 80°C, $P_1^S = 195.75$, $P_2^S = 97.84$, $P_3^S = 50.32$ KPa. Thus:

$$P = \sum x_i P_i^S = 108.3 KPa$$

Next:

$$y_i = x_i P_i^S / P$$

Thus:

$$y_1 = 0.54,\ y_2 = 0.27,\ y_3 = 0.19$$

(b) For 70°C, $P_1^S = 144.77$, $P_2^S = 70.37$, $P_3^S = 43.80$ KPa

$$P = 1 / \sum y_k / P_k^S = 81.4 \text{ KPa}$$

Next:

$$x_i = y_i P / P_i^S$$

Thus:

$$x_1 = 0.28,\ x_2 = 0.34,\ x_3 = 0.38$$

2.2

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. $\ln P^{sat}(Pa) = A - \frac{B}{t(^0K)+C}$

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

At T = 383K, the saturation vapour pressures are: $P_1^S = 233.2$; $P_2^S = 99.1$; $P_3^S = 47.1kPa$

Thus: $K_1 = P_1^S / P = 2.6$; similarly $K_2 = 1.1$; $K_3 = 0.52$

For flash $\sum_{i=1}^{n} \frac{Z_i K_i}{1 + V(K_i - 1)} = 1$

Thus: $\frac{Z_1 K_1}{1 + V(K_1 - 1)} + \frac{Z_2 K_2}{1 + V(K_2 - 1)} + \frac{Z_3 K_3}{1 + V(K_3 - 1)} = 1$ ..(1)

$Z_1 = Z_2 = Z_3 = 0.33$

On substituting the values of K_i and Z_i by solving eqn. (1) on obtains: V = 0.834

REFERENCES

1. Smith J.M. and Van Ness H.C., Introduction to Chemical Engineering Thermodynamics, 7th Edition, McGraw Hill, 2005.

2. Narayanan K.V., A Text Book of Chemical Engineering Thermodynamics, 3rd Edition, Prentice Hall of India Pvt. Ltd., 2013.

3. Gopinath Halder, Introduction to Chemical Engineering Thermodynamics, 2nd Edition, PHI Learning Pvt. Ltd., 2009.

SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited “A” Grade by NAAC | 12B Status by UGC | Approved by AICTE
www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT– III - Correlation and Prediction of Phase Equilibria - SCHA1302

3. Vapour Liquid Equilibria

3.1 VLE: State of coexistence of L & V phases

- ✓ A condition where a liquid phase and vapor phase are in equilibrium with each other
- ✓ At this condition: rate of evaporation (liquid → vapor) = rate of condensation (vapor → liquid)

Binary mixture: Mixture that contains two constituents

- ✓ e.g: mixture of liquid and vapor at an equilibrium level takes place when liquid and vapor are allowed to contact to each other in a closed location

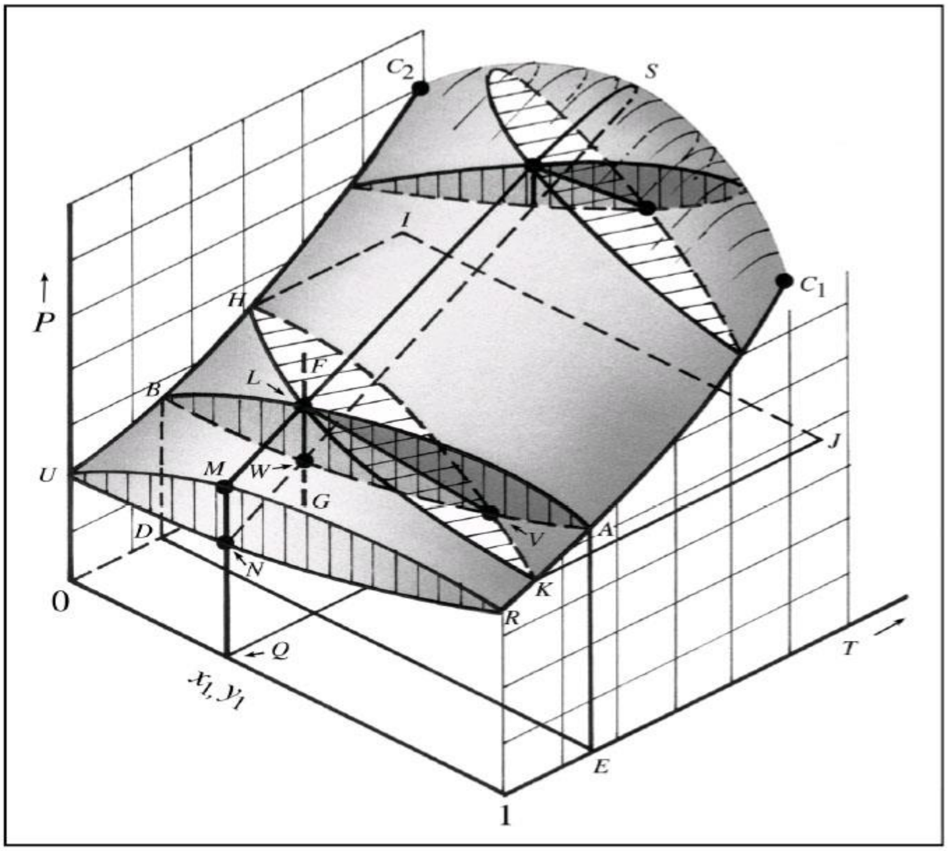


Figure 10.1: $PTxy$ diagram for vapor/liquid equilibrium.

- ✓ Under surface- sat. V states (P-T-y_1)

- ✓ Upper surface- sat. L states (P-T-x_1)
- ✓ Liquid at F, reduces pressure at constant T & composition along FG, the first bubble appears at L – bubble point: a point when a liquid forms the first bubble of vapor and begins to evaporate
- ✓ As pressure reduces, more & more L vaporizes until completed at W; point where last drop of L (dew) disappear – dew point: a point when a vapor forms the first droplet of liquid and begins to condense

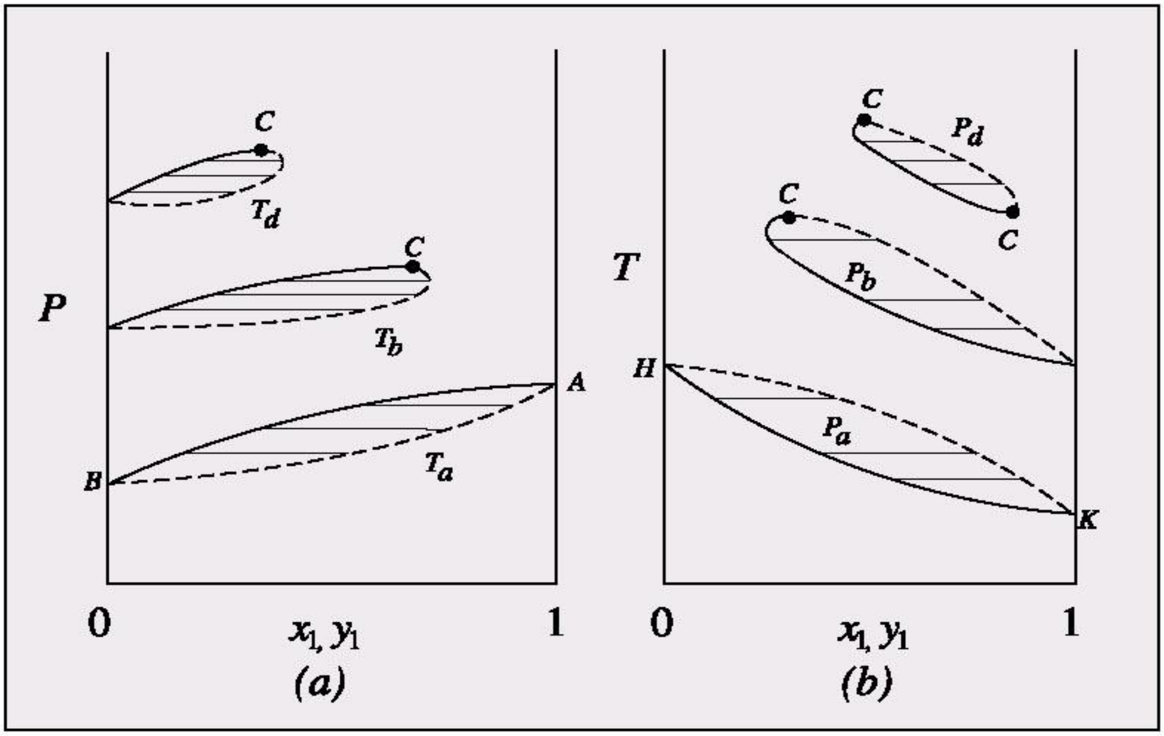


Figure 10.2: (*a*) *Pxy* diagram for three temperatures. (*b*) *Txy* diagram for three pressures.
—— Saturated liquid (bubble line); - - - Saturated vapor (dew line)

3.2 Simple models for vapour liquid equilibrium

Rault's law

Assumptions;

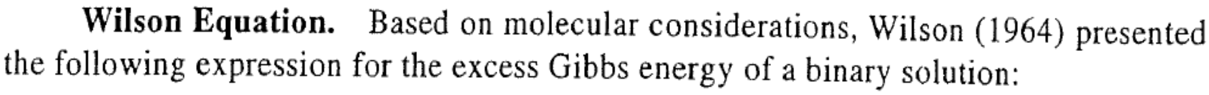
- Vapor phase is an ideal gas
    - Applicable for low to moderate pressure

- Liquid phase is an ideal solution
    - Valid only if the species are chemically similar (size, same chemical nature e.g. isomers such as ortho-, meta- & para-xylene)

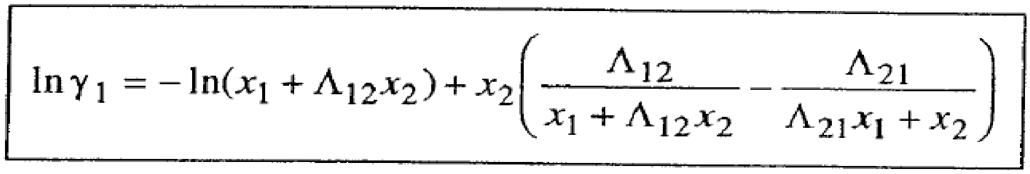
$$y_i P = x_i P_i^{sat} \quad (i = 1, 2, \ldots, N)$$

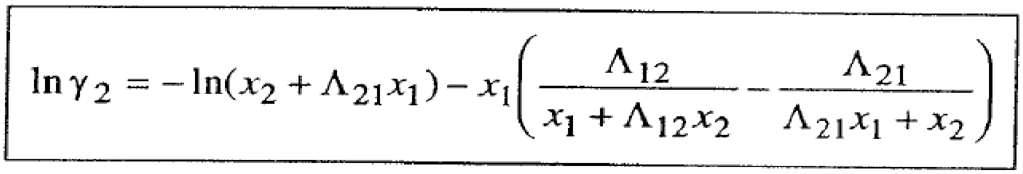
x_i : $L -$ phase mole fraction
y_i : $V -$ phase mole fraction
P_i^{sat} : Vapor pressure of pure species i
P : Total pressure

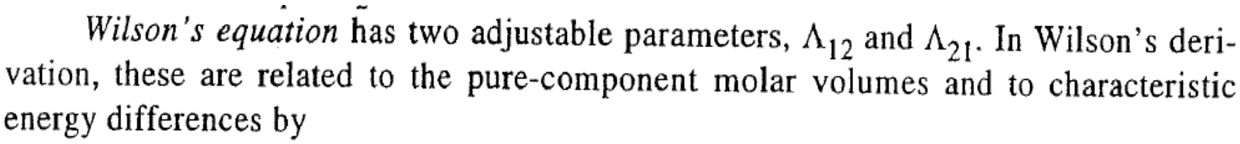
3.3 Wilson equation


Wilson Equation. Based on molecular considerations, Wilson (1964) presented the following expression for the excess Gibbs energy of a binary solution:


The activity coefficients derived from this equation are


$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$$


$$\ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$$


Wilson's equation has two adjustable parameters, Λ_{12} and Λ_{21}. In Wilson's derivation, these are related to the pure-component molar volumes and to characteristic energy differences by

$$\Lambda_{12} \equiv \frac{v_2}{v_1}\exp\left(-\frac{\lambda_{12}-\lambda_{11}}{RT}\right)$$

$$\Lambda_{21} \equiv \frac{v_1}{v_2}\exp\left(-\frac{\lambda_{21}-\lambda_{22}}{RT}\right)$$

3.4 NRTL

$$\frac{g^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1+x_2G_{21}}+\frac{\tau_{12}G_{12}}{x_2+x_1G_{12}}\right)$$

where

$$\tau_{12} = \frac{g_{12}-g_{22}}{RT} \qquad \tau_{21} = \frac{g_{21}-g_{11}}{RT}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \qquad G_{21} = \exp(-\alpha_{12}\tau_{21})$$

3.5 UNIQUAC

UNIQUAC (short for UNIversal QUAsi Chemical model) builds on the work of Wilson by making three primary refinements. First, the temperature dependence of W*ij* is modified to depend on surface areas rather than volumes, based on the hypothesis that the interaction energies that determine local compositions are dependent on the relative surface areas of the molecules. If the parameter *qi* is proportional to the surface area of molecule *i*,

$$\Omega_{ij} = \frac{q_i}{q_j}\exp\left(\frac{-N_A z(\varepsilon_{ij}-\varepsilon_{jj})}{2RT}\right) = \frac{q_i}{q_j}\exp\left(\frac{-a_{ij}}{T}\right) = \frac{q_i}{q_j}\tau_{ij}$$

3.6 UNIFAC

This is an extension of UNIQUAC with no adjustable parameters for the user to input or fit to experimental data. Instead, all of the adjustable parameters have been characterized by the developers of the model based on group contributions that correlate the data in a very large data base. The assumptions regarding coordination numbers, etc., are similar to the assumptions in UNIQUAC. The same strategy is applied,

$$\boxed{\ln \gamma_k = \ln \gamma_k^{COMB} + \ln \gamma_k^{RES}}$$

3.7 Van Laar equation

The **Van Laar equation** is an activity model, which was developed by Johannes van Laar in 1910-1913, to describe phase equilibria of liquid mixtures. The equation was derived from the Van der Waals equation. The original van der Waals parameters didn't give good description of vapor-liquid phase equilibria, which forced the user to fit the parameters to experimental results. Because of this, the model lost the connection to molecular properties, and therefore it has to be regarded as an empirical model to correlate experimental results.

$$\ln \gamma_1 = A_{12} \left(\frac{A_{21}X_2}{A_{12}X_1+A_{21}X_2}\right)^2$$
$$\ln \gamma_2 = A_{21} \left(\frac{A_{12}X_1}{A_{12}X_1+A_{21}X_2}\right)^2$$

This shows that the constants A_{12} and A_{21} are equal to logarithmic limiting activity coefficients $ln(\gamma_1^{\infty})$ and $ln(\gamma_2^{\infty})$ respectively. The model gives increasing (A_{12} and $A_{21} > 0$) or only decreasing (A_{12} and $A_{21} < 0$) activity coefficients with decreasing concentration. The model can not describe extrema in the activity coefficient along the concentration range.

In case $A_{12} = A_{21} = A$, which implies that the molecules are of equal size but different in polarity, then the equations become:

$$\begin{cases} \ln \gamma_1 = Ax_2^2 \\ \ln \gamma_2 = Ax_1^2 \end{cases}$$

In this case the activity coefficients mirror at $x_1=0.5$. When A=0 the model the activity coefficients are unity, thus describing an ideal mixture.

Dewpoint & Bubblepoint Calculations with Raoult's Law

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

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

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

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

For binary systems to solve for
bubblepoint calculation (T is given);

$$\sum_i y_i = 1$$

$$\downarrow$$

$$P = \sum_i x_i P_i^{sat}$$

$$P = P_2^{sat} + \left(P_1^{sat} - P_2^{sat}\right)x_1$$

$$\downarrow$$

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

Raoult's law equation can be solved for x_i to solve for dewpoint calculation (T is given)

$$\sum_i x_i = 1$$

↓

$$P = \frac{1}{\sum_i y_i / P_i^{sat}}$$

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

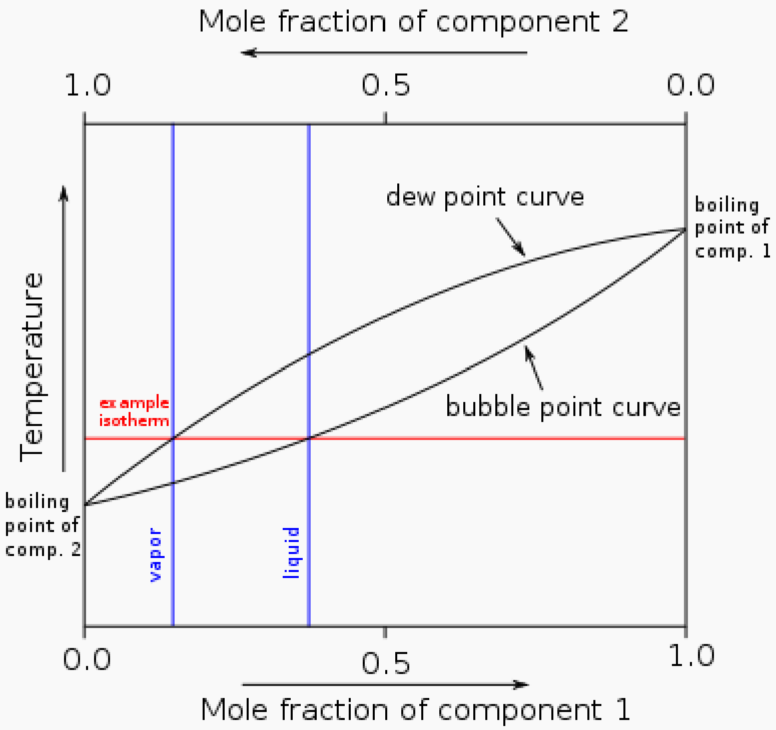
↓

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

The vapor pressure of a liquid at a particular temperature is the equilibrium pressure exerted by molecules leaving and entering the liquid surface.

Here are some important points regarding vapor pressure:

- Energy input raises vapor pressure
- Vapor pressure is related to boiling
- A liquid is said to 'boil' when its vapor pressure equals the surrounding pressure
- The ease with which a liquid boil depends on its volatility
- Liquids with high vapor pressures (volatile liquids) will boil at lower temperatures
- The vapor pressure and hence the boiling point of a liquid mixture depends on the relative amounts of the components in the mixture
- Distillation occurs because of the differences in the volatility of the components in the liquid mixture.



Boiling-point diagram

The preceding equilibrium equations are typically applied for each phase (liquid or vapor) individually, but the result can be plotted in a single diagram. In a binary boiling-point diagram, temperature (T) is graphed vs. x_1. At any given temperature where both phases are present, vapor with a certain mole fraction is in equilibrium with liquid with a certain mole fraction. The two mole fractions often differ. These vapor and liquid mole fractions are represented by two points on the same horizontal isotherm (constant T) line. When an entire range of temperatures vs. vapor and liquid mole fractions is graphed, two (usually curved) lines result. The lower one, representing the mole fraction of the boiling liquid at various temperatures, is called the *bubble point curve*. The upper one, representing the mole fraction of the vapor at various temperatures, is called the *dew point curve*.

These two lines (or curves) necessarily meet where the mixture becomes purely one component, namely where $x_1 = 0$ (and $x_2 = 1$, pure component 2) or $x_1 = 1$ (and $x_2 = 0$, pure component 1).

The temperatures at those two points correspond to the boiling points of each of the two pure components.

For certain pairs of substances, the two curves also coincide at some point strictly between x_1 = 0 and x_1 = 1. When they meet, they meet tangently; the dew-point temperature always lies above the boiling-point temperature for a given composition when they are not equal. The meeting point is called an **azeotrope** for that particular pair of substances. It is characterized by an azeotrope temperature and an azeotropic composition, often expressed as a mole fraction. There can be **maximum-boiling azeotropes**, where the azeotrope temperature is at a maximum in the boiling curves, or **minimum-boiling azeotropes**, where the azeotrope temperature is at a minimum in the boiling curves.

If one wants to represent a VLE data for a three-component mixture as a boiling point "diagram", a three-dimensional graph can be used. Two of the dimensions would be used to represent the composition mole fractions, and the third dimension would be the temperature. Using two dimensions, the composition can be represented as an equilateral triangle in which each corner represents one of the pure components. The edges of the triangle represent a mixture of the two components at each end of the edge. Any point inside the triangle represents the composition of a mixture of all three components. The mole fraction of each component would correspond to where a point lies along a line starting at that component's corner and perpendicular to the opposite edge. The bubble point and dew point data would become curved surfaces inside a triangular prism, which connect the three boiling points on the vertical temperature "axes". Each face of this triangular prism would represent a two-dimensional boiling-point diagram for the corresponding binary mixture. Due to their three-dimensional complexity, such boiling-point diagrams are rarely seen. Alternatively, the three-dimensional curved surfaces can be represented on a two-dimensional graph by the use of curved isotherm lines at graduated intervals, similar to iso-altitude lines on a map. Two sets of such isotherm lines are needed on such a two-dimensional graph: one set for the bubble point surface and another set for the dew point surface.

The tendency of a given chemical species to partition itself preferentially between liquid and vapor phases is the Henry's law constant. There can be VLE data for mixtures of four or more components, but such a boiling-point diagram is hard to show in either tabular or graphical form.

For such multi-component mixtures, as well as binary mixtures, the vapor–liquid equilibrium data are represented in terms of *K* values (vapor–liquid distribution ratios) defined by

$$K_i = \frac{y_i}{x_i}$$

where y_i and x_i are the mole fractions of component *i* in the phases *y* and *x* respectively.

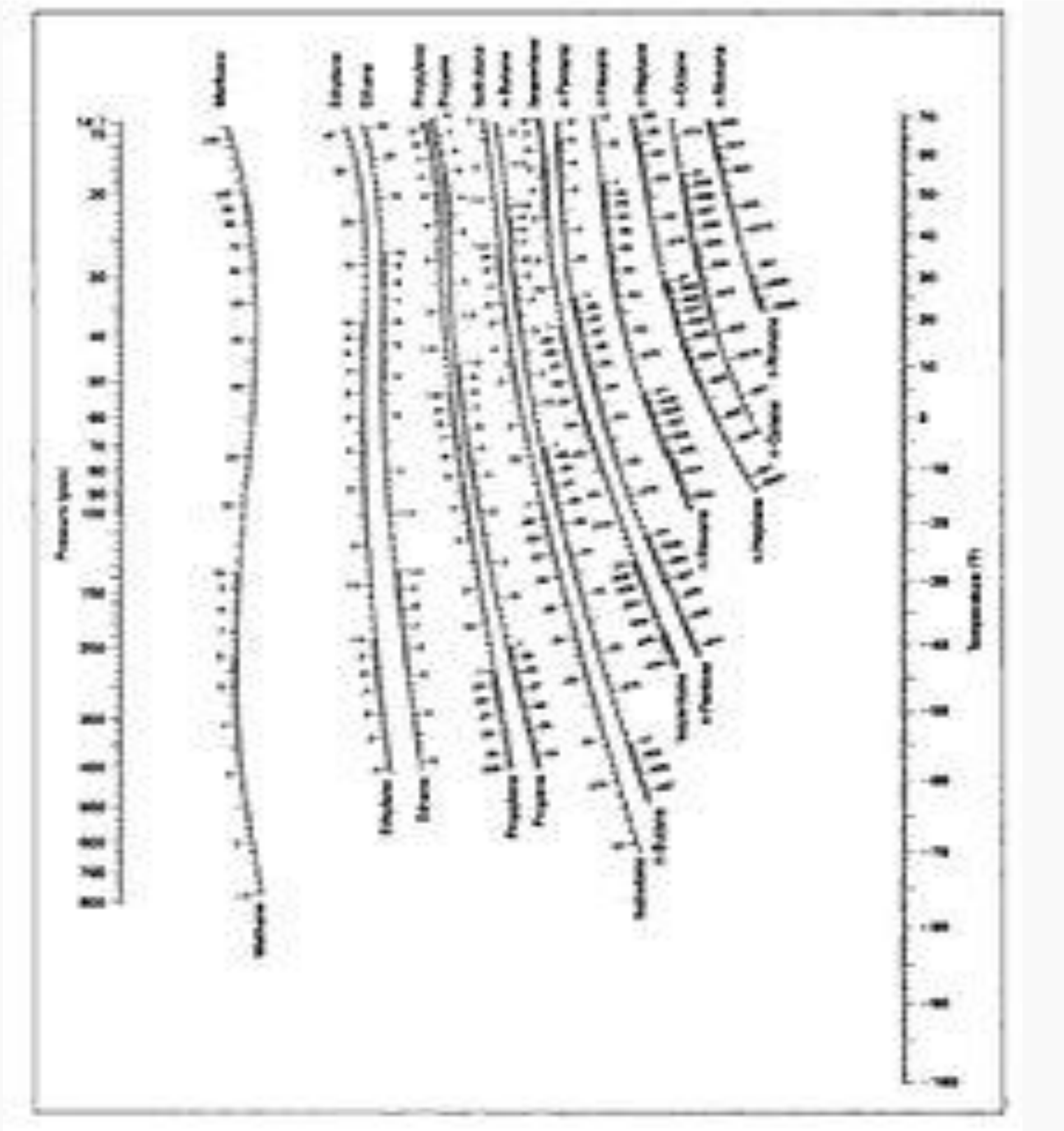
For Raoult's law

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

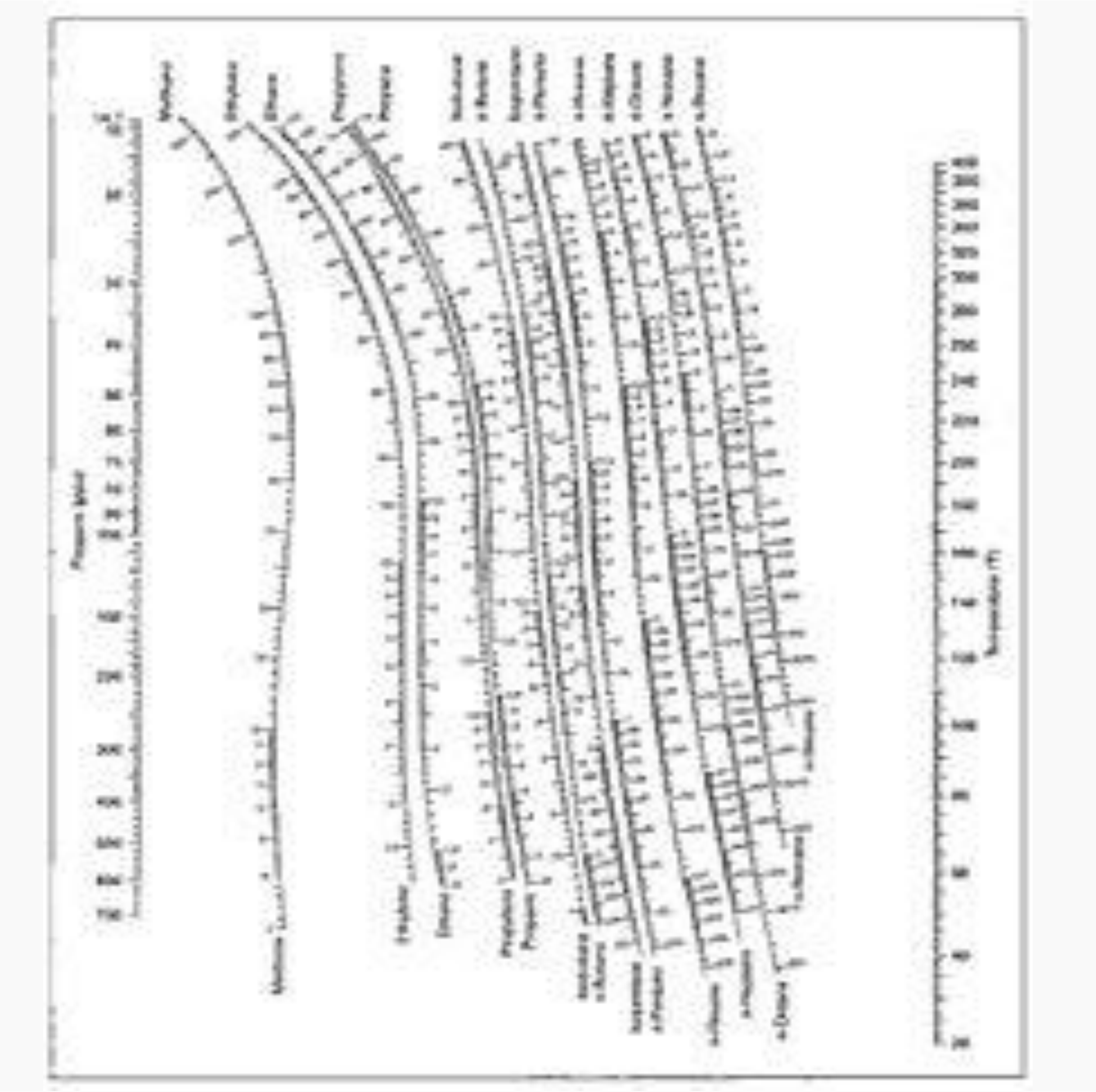
For modified Raoult's law

$$K_i = \frac{\gamma_i P_i^\star}{P}$$

where γ_i is the activity coefficient, P_i is the partial pressure and P is the pressure The values of the ratio K_i are correlated empirically or theoretically in terms of temperature, pressure and phase compositions in the form of equations, tables or graph such as the De-Priester charts (Shown on the right).



K-Values for systems of light hydrocarbons Low Temperature Range



K-Values for systems of light hydrocarbons High Temperature Range

For binary mixtures, the ratio of the *K* values for the two components is called the relative volatility denoted by α

$$\alpha = \frac{K_i}{K_j} = \frac{(y_i/x_i)}{(y_j/x_j)}$$

which is a measure of the relative ease or difficulty of separating the two components. Large-scale industrial distillation is rarely undertaken if the relative volatility is less than 1.05 with the volatile component being *i* and the less volatile component . *K* values are widely used in the design calculations of continuous distillation columns for distilling multi-component mixtures.

Vapor Liquid Equilibrium Calculations:

For each component in a binary mixture, one could make a vapor–liquid equilibrium diagram. Such a diagram would graph liquid mole fraction on a horizontal axis and vapor mole fraction on a vertical axis. In such VLE diagrams, liquid mole fractions for components 1 and 2 can be represented as x_1 and x_2 respectively, and vapor mole fractions of the corresponding components are commonly represented asy_1 and y_2.[3] Similarly for binary mixtures in these VLE diagrams:

$$x_1 + x_2 = 1 \text{ and } y_1 + y_2 = 1$$

Such VLE diagrams are square with a diagonal line running from the ($x_1 = 0, y_1 = 0$) corner to the ($x_1 = 1, y_1 = 1$) corner for reference.

These types of VLE diagrams are used in the McCabe–Thiele method to determine the number of equilibrium stages (or theoretical plates) needed to distill a given composition binary feed mixture into one distillate fraction and one bottoms fraction. Corrections can also be made to take into account the incomplete efficiency of each tray in a distillation column when compared to a theoretical plate.

Vapor-Liquid Equilibrium Calculations Using K Values

The vapor-liquid equilibrium constant or distribution coefficient for component A is defined as

$$K_A = \frac{y_A}{x_A}$$

where y_A = mole fraction of A in the vapor phase and x_A = mole fraction of A in the liquid phase

For light hydrocarbon systems (methane to decane), the K values have been determined semi-emperically and can be evaluated from the equations given in Table 3.1. In general, K is a function of temperature, pressure, and composition.

Table 3.1. Equilibrium K values for light hydrocarbon systems

(1) $\ln K = -A/T^2 + B - C \ln(P) + D/P^2$
(2) $\ln K = -A/T^2 + B - C \ln(P) + D/P$
(3) $\ln K = -A/T + B - C \ln(P)$, where P is in psia, T is in ^oR

compound	A	B	C	D	Form
Methane	292860	8.2445	.8951	59.8465	(1)
Ethylene	600076.9	7.90595	.84677	42.94594	(1)
Ethane	687248.2	7.90694	.866	49.02654	(1)
Propylene	923484.7	7.71725	.87871	47.67624	(1)
Propane	970688.6	7.15059	.76984	6.90224	(2)
i-Butane	1166846	7.72668	.92213	0	(1)
n-Butane	1280557	7.94986	.96455	0	(1)
i-Pentane	1481583	7.58071	.93159	0	(1)
n-Pentane	1524891	7.33129	.89143	0	(1)
n-Hexane	1778901	6.96783	.84634	0	(1)
n-Heptane	2013803	6.52914	.79543	0	(1)
n-Octane	7646.816	12.48457	.73152		(3)
n-Nonane	2551040	5.69313	.67818	0	(1)
n-Decane	9760.457	13.80354	.7147		(3)

The relative volatility α_i for each individual component in a multicomponent mixture is defined with respect to a reference component C.

$$\alpha_i = \frac{y_i/x_i}{y_C/x_C} = \frac{K_i}{K_C}$$

The values of α_i will be less dependent on temperature than the values of K_i since the K_i all increase with temperature in a similar manner.

Boiling (Bubble) point calculation using K values

The liquid composition x_i of a mixture is given at a specified pressure P, the temperature T and composition y_i of the vapor in equilibrium with the liquid can be calculated with the following procedure:

- Choose a component C to be the reference (base) component.

- Assume a temperature T ($T = \bullet\ x_i T_{bi}$)

T_{bi} = Boiling point of pure component i at pressure P. If an equation for K is given as function of temperature and pressure, this temperature can be obtained by setting K = 1.

Iteration steps:

1. Let T_{save} = T. Determine K_i (From table 7.1). $y_i = K_i x_i$

2. Evaluate Sumy = $\bullet\ y_i$

3. Let $K_C = K_C$/Sumy

4. Determine T from K_C and P

5. **If** abs(T - T_{save}) > 1Δ^{o}R goto step 1 **else** $y_i = y_i$/Sumy

Dew point calculation using K values

The vapor composition y_i of a mixture is given at a specified pressure P, the temperature T and composition x_i of the liquid in equilibrium with the vapor can be calculated with the following procedure:

- Choose a component C to be the reference (base) component.

- Assume a temperature T ($T = \bullet\ y_i T_{bi}$)

T_{bi} = Boiling point of pure component i at pressure P. If an equation for K is given as function of temperature and pressure, this temperature can be obtained by setting K = 1.

Iteration steps:

1. Let T_{save} = T. Determine K_i (From table 7.1). $x_i = y_i/K_i$

2. Evaluate Sumx = $\bullet\ x_i$

3. Let K_C = K_C Sumx

4. Determine T from K_C and P

5. **If** abs(T - T_{save}) > 1Δ^{o}R goto step 1 **else** x_i = x_i/Sumy

Solved problems

3.1 A mixture contains 35 mole % isobutane, 35 mole % isopentane, and 30 mole % n-hexane is at 30 psia. The K values for these compound can be obtained from

$\ln K = A/T^2 + B + C \ln P$ where T is in ^{o}R and P is in psia

Compound	A	B	C
Isobutane	-1,166,846	7.72668	-.92213
Isopentane	-1,481,583	7.58071	-.93159
n-hexane	-1,778,901	6.96783	-.84634

The boiling point of (pure) n-hexane at 30 psia is 659.6^{o}R

This mixture is flashed at 582.74^{o}R where 60 % of the feed is evaporated and at this conditions K_{iC4} = 3.1718, K_{iC5} = 1.051, K_{nC6} = 0.3169

Let isopentane be the reference compound and T = 582.74^{o}R be a guessed value for the bubble point calculation (for the above mixture), the next calculated temperature T_{cal} can be determined from

K_{iC5} (at T_{cal}) = K_{iC5} (at 582.74^{o}R) /● y_i = 0.66814

Let isopentane be the reference compound and T = 582.74^{o}R be a guessed value for the dew point calculation (for the above mixture), the next calculated temperature T_{cal} can be determined from

K_{iC5} (at T_{cal}) = K_{iC5} (at 582.74^{o}R) *● x_i = 1.4609

3.2

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 55.7^0C.

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

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

At 55.7^0C $P_1^s = 541.75 torr; P_2^s = 745.5 torr$

We assume that the vapour phase is ideal. Hence the VL equation is given by:

$y_i P = x_i \gamma_i P_i^S$

At the azeotropic condition: $y_i = x_i$

Hence,

$\gamma_i = P / P_i^S$

Thus $\gamma_1 = 1.4313, \ln \gamma_1 = 0.3607$ and $\gamma_2 = 1.0318, \ln \gamma_2 = 0.0137$

The Van Laar parameters are estimated next using the azeotropic composition given by $x_1 = 0.2$ and $x_2 = 0.8$:

$$A_{12} = \ln \gamma_1 \left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right)^2 = 0.4786$$

$$A_{21} = \ln \gamma_2 \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 = 0.7878$$

Thus $\ln \gamma_1 = \dfrac{A_{12}}{\left(1 + \dfrac{A_{12} x_1}{A_{21} x_2}\right)^2}; \ln \gamma_2 = \dfrac{A_{21}}{\left(1 + \dfrac{A_{21} x_2}{A_{12} x_1}\right)^2}$

For $x_1 = 0.1$, $\gamma_1 = 1.5219$, $\gamma_2 = 1.0032$

$\therefore P = \sum x_i \gamma_i P_i^s = 757.62$ torr, $y_1 = \gamma_1 x_1 P_1^s / P = 0.1067$

REFERENCES

1. Smith J.M. and Van Ness H.C., Introduction to Chemical Engineering Thermodynamics, 7th Edition, McGraw Hill, 2005.

2. Narayanan K.V., A Text Book of Chemical Engineering Thermodynamics, 3rd Edition, Prentice Hall of India Pvt. Ltd.,
2013.

3. Gopinath Halder, Introduction to Chemical Engineering Thermodynamics, 2nd Edition, PHI Learning Pvt. Ltd., 2009.

SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE
www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – IV - Application of Phase Equilibria – SCHA1302

4. Application of Phase Equilibria

4.1 Excess Gibbs free energy model

Practicing engineers find most of the liquid-phase information needed for equilibrium calculations in the form of excess Gibbs Energy models. These models:

- reduce vast quantities of experimental data into a few empirical parameters,
- provide information an equation format that can be used in thermodynamic simulation packages (Provision)

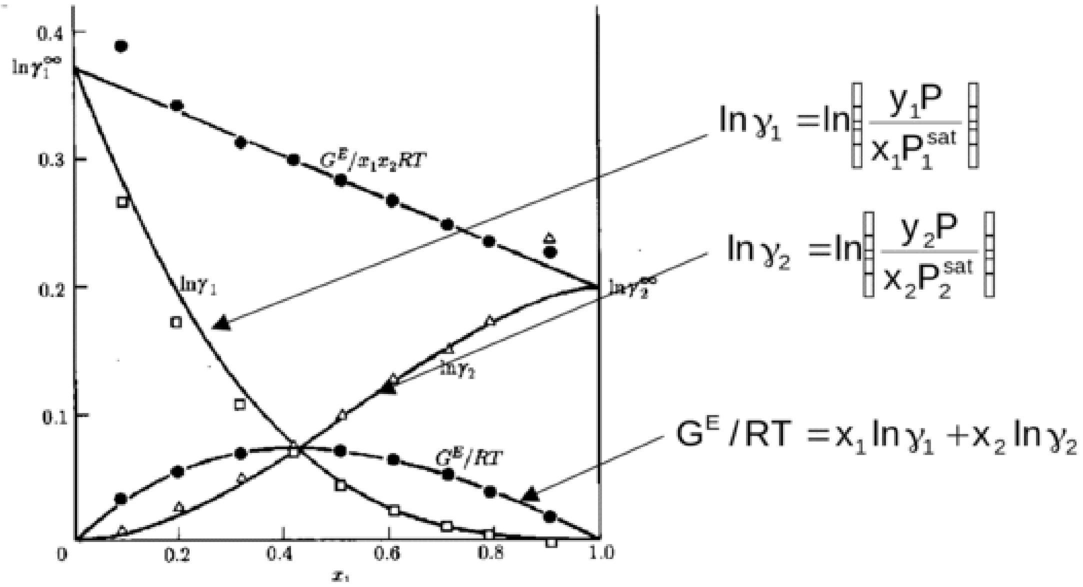
"Simple" empirical models

- Symmetric, Margule's, vanLaar
- No fundamental basis but easy to use
- Parameters apply to a given temperature, and the models usually cannot be extended beyond binary systems.

Local composition models

- Wilsons, NRTL, Uniquac
- Some fundamental basis
- Parameters are temperature dependent, and multi-component behaviour can be predicted from binary data.

Our objectives are to learn how to fit Excess Gibbs Energy models to experimental data, and to learn how to use these models to calculate activity coefficients.



$$\ln\gamma_1 = \ln\left(\frac{y_1P}{x_1P_1^{sat}}\right)$$

$$\ln\gamma_2 = \ln\left(\frac{y_2P}{x_2P_2^{sat}}\right)$$

$$G^E/RT = x_1\ln\gamma_1 + x_2\ln\gamma_2$$

Margule's Equations

While the simplest Redlich/Kister-type expansion is the Symmetric Equation, a more accurate model is the Margule's expression:

$$\frac{G^E}{RTx_1x_2} = A_{21}x_1 + A_{12}x_2$$

Note that as x_1 goes to zero,

$$\left.\frac{G^E}{RTx_1x_2}\right|_{x_1 \to 0} = A_{12}$$

and from L'hopital's rule we know:

$$\lim_{x_1 \to 0} \frac{G^E}{RTx_1x_2} = \ln \gamma_1^{\infty}$$

therefore,

$$A_{12} = \ln \gamma_1^{\infty} \quad \text{and similarly} \quad A_{21} = \ln \gamma_2^{\infty}$$

van Laar Equations

Another two-parameter excess Gibbs energy model is developed from an expansion of $(RTx_1x_2)/G^E$ instead of G^E/RTx_1x_2. The end results are:

$$\frac{G^E}{RTx_1x_2} = \frac{A'_{12}A'_{21}}{A'_{21}x_1 + A'_{12}x_2}$$

for the excess Gibbs energy and:

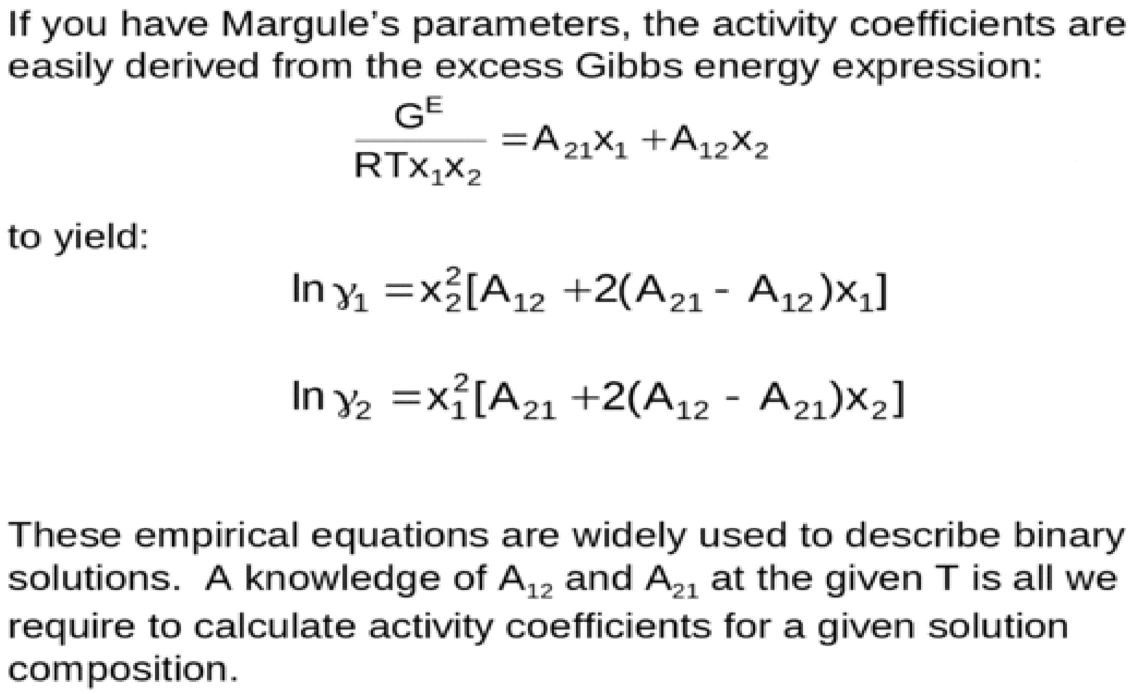
$$\ln \gamma_1 = A'_{12}\left(1 + \frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2}$$

$$\ln \gamma_2 = A'_{21}\left(1 + \frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2}$$

for the activity coefficients.

Note that: as $x_1 \to 0$, $\ln\gamma_1^{\infty} \to A'_{12}$

and as $x_2 \to 0$, $\ln\gamma_2^{\infty} \to A'_{21}$



If you have Margule's parameters, the activity coefficients are easily derived from the excess Gibbs energy expression:

$$\frac{G^E}{RTx_1x_2} = A_{21}x_1 + A_{12}x_2$$

to yield:

$$\ln\gamma_1 = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1]$$

$$\ln\gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2]$$

These empirical equations are widely used to describe binary solutions. A knowledge of A_{12} and A_{21} at the given T is all we require to calculate activity coefficients for a given solution composition.

4.2 Thermodynamic consistency of phase equilibria

- The Gibbs/Duhem Equation imposes a constraint on activity coefficient that may not be satisfied by a set of experimental values derived from P-xy data.

- The experimental values of ln γ_1 and ln γ_2 combine by (excess Gibbs free energy) to give values of G^E/RT.

- This addition process is independent of the Gibbs/Duhem Equation
- Nor can a P-xy correlation Calculated by modify Roults low be consistent with experimental values.
- If the experimental data are inconsistent with the Gibbs/Duhem equation , they are necessarily incorrect as the result of systematic error in the data.
- Because correlating equations for G^E/RT impose consistency on derived activity coefficients, no such correlation exists that can precisely reproduce P-xy data that are inconsistent.
- Our purpose now is to develop a simple test for the consistency with respect to the Gibbs/Duhem equation of a P-xy data set.

- $\left(\frac{GE}{RT}\right)^{*}$ = x1 ln γ1* + x2 ln γ2*
- Differentiation gives

$$\frac{d\left(\frac{GE}{RT}\right)^{*}}{dx1} = \text{x1}\ \frac{d\ ln\,\gamma 1*}{dx1} + \ln \gamma1* + \text{x2}\ \frac{d\ ln\,\gamma 2*}{dx1} - \ln \gamma2* \qquad \text{or}$$

$$\frac{d\left(\frac{GE}{RT}\right)^{*}}{dx1} = \ln \frac{\gamma1*}{\gamma2*} + \text{x1}\ \frac{d\ ln\,\gamma 1*}{dx1} + \ \text{x2}\ \frac{d\ ln\,\gamma 2*}{dx1}$$

- Written for derived property values , i.e.,those given by a correlation , such as the Margules equation :

$$\frac{d\left(\frac{GE}{RT}\right)}{dx1} - \frac{d\left(\frac{GE}{RT}\right)^{*}}{dx1} = \ln \frac{\gamma1}{\gamma2} - \ln \frac{\gamma1*}{\gamma2*} - (\text{x1}\ \frac{d\ ln\,\gamma 1*}{dx1} + \text{x2}\ \frac{d\ ln\,\gamma 2*}{dx1})$$

- The difference between like terms are residual , which may be represented by a δ notation.
- The preceding equation then becomes

$$\frac{d\ \delta\left(\frac{G^{E}}{RT}\right)}{dx1} = \delta \ln \frac{\gamma1}{\gamma2} - (\text{x1}\ \frac{d\ ln\,\gamma 1*}{dx1} + \text{x2}\ \frac{d\ ln\,\gamma 2*}{dx1})$$

- If a data set is reduced so as to make the residuals in G^E/RT scatter about zero , then the derivative d δ (G^E/RT) / dx1 is effectively zero , reducing the preceding equation to

$$\delta \ln \frac{\gamma1}{\gamma2} = \text{x1}\ \frac{d\ ln\,\gamma 1*}{dx1} + \text{x2}\ \frac{d\ ln\,\gamma 2*}{dx1}$$

- $\delta \ln \frac{\gamma 1}{\gamma 2} = x1 \frac{d\ ln\, \gamma 1*}{dx1} + x2 \frac{d\ ln\, \gamma 2*}{dx1}$

- The right side of this equation is exactly the quantity that eq. for binary system , Gibbs/Duhem equation, requires to be zero for consistent data. The residual on the left therefore provides a direct measure of deviation from the Gibbs/Duhem equation. The extent to which these residuals fail to scatter about zero.

4.2.1 Using slope in $\ln \gamma_i$ curve

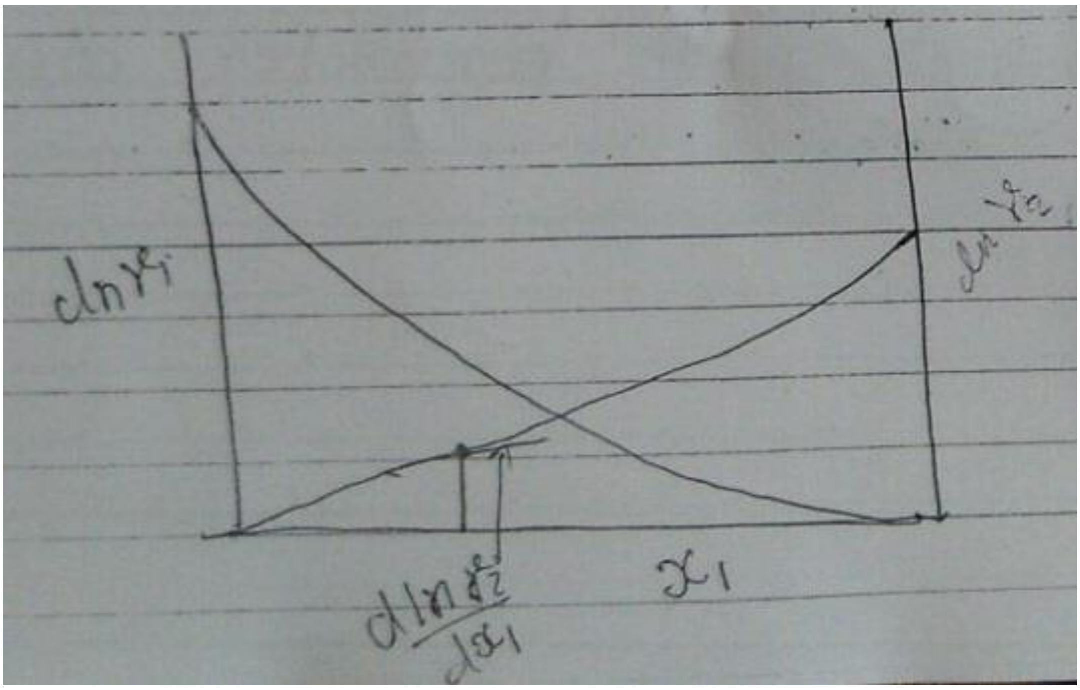
$$x_1 \left[\frac{d\ln\gamma_1}{dx_1}\right] = x_2 \left[\frac{d\ln\gamma_2}{dx_2}\right]$$

$$x_1 \left[\frac{d\ln\gamma_1}{dx_1}\right] = -(1 - x_1) \left[\frac{d\ln\gamma_2}{dx_1}\right]$$

$$x_1 = 1 - x_1$$

$$dx_2 = -dx_1$$

- To verify consistancy exit or not plot,graph



4.2.2 Using mid point data

Using Mid-Point Data

- In Van- Laar equation.

  put

$$x_1 = x_2 = 0.5$$

$$\ln\gamma_1 = A'_{12}\left[1 + \frac{x_1 A'_{12}}{x_2 A'_{21}}\right]^{-2}$$

$$\ln\gamma_1 = A'_{12}\left[1 + \frac{A'_{12}}{A'_{21}}\right]^{-2}$$

$$\frac{A'_{12}}{[\frac{A'_{21} + A'_{12}}{A'_{21}}]^2} = \frac{A'_{12} A'^2_{21}}{[A'_{21} + A'_{12}]^2}$$

$$\ln\gamma_2 = A'_{21}[1 + \frac{A'_{21}}{A'_{12}}]^{-2}$$

$$= \frac{A'_{12} A'^2_{21}}{[A'_{21} + A'_{12}]^2}$$

$$\frac{\ln\gamma_1}{A'_{21}} = \frac{\ln\gamma_2}{A'_{12}} \qquad \text{at } x_1 = x_2 = 0.5$$

$$A'_{12} = A'_{21} \rightarrow \frac{A'^3_{21}}{4A'^2_{21}}$$

$$\ln\gamma_1 = \frac{A'_{21}}{4}$$

$$\ln\gamma_2 = \frac{A'_{12}}{4}$$

4.2.3Redlich/ Kister method

$$\Delta G^E = RT\sum_i x_i \ln\gamma_i$$

$$\Delta G^E = RT[x_1\ln\gamma_1 + x_2\ln\gamma_2]$$

- Diff … w.r.t x1

$$\frac{dG^E}{dx_1} = RT\left[\ln\frac{\gamma_1}{\gamma_2} + x_1\frac{d\ln\gamma_1}{dx_1} + (1-x_1)\frac{d\ln\gamma_1}{dx_1}\right]$$

- Now , $x_1 = 1 - x_1$

$$\frac{dG^E}{dx_1} = RT\left[\ln\frac{\gamma_1}{\gamma_2}\right]$$

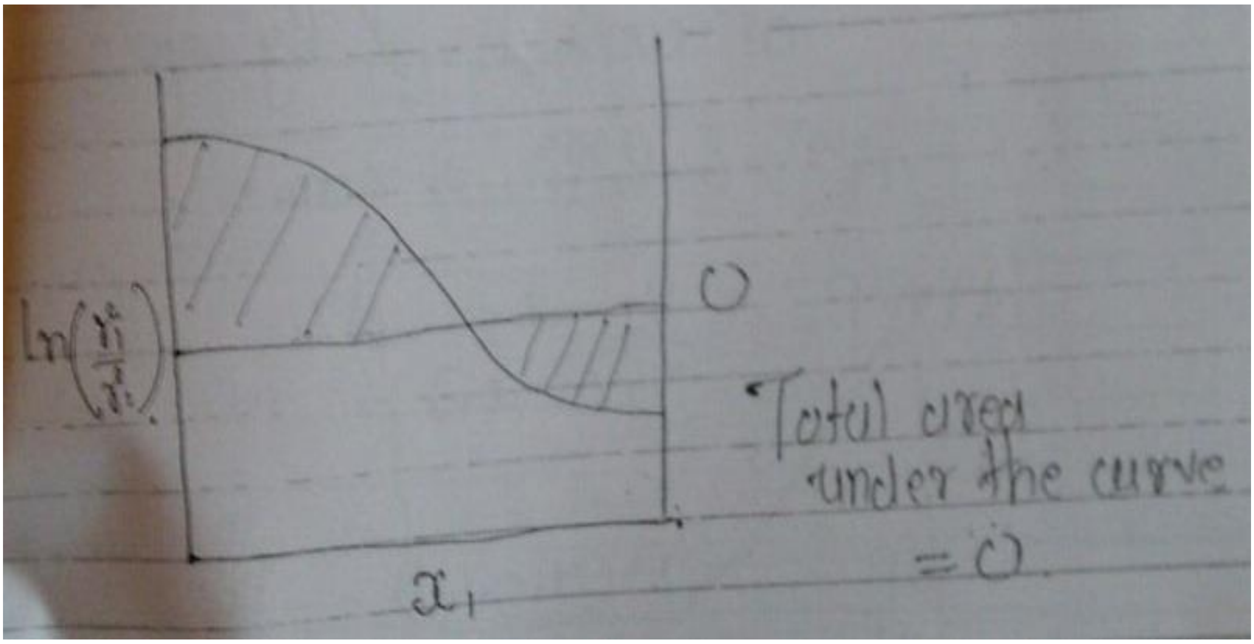
- In between x1=0 to x2=1

$$\Delta G^E = RT\ln\frac{\gamma_1}{\gamma_2}\int_0^1 dx_1$$

- ΔG^E at $x_1 = 0 \to 0$
- ΔG^E at $x_2 = 1 \to 0$

- Plot $\ln\frac{\gamma_1}{\gamma_2}$ Vs x_1

$$\ln\frac{\gamma_1}{\gamma_2}\int_0^1 dx_1 = 0$$



4.2.4 Using coexistence equation:-

Modified Raoult's law

consider vap. Phase is ideal gas

$$y_i P = \gamma_i x_i P_i^{sat}$$

$$\gamma_i = \frac{y_i P}{x_i P_i^{sat}}$$

Gibbs/Duhem equation

$$x_1 d(ln\gamma_1) = -(1 - x_1)d(lnx_2)$$

$$x_1 dln\left(\frac{y_1 P}{x_1 P_1^{sat}}\right) = -(1 - x_1)dln(\frac{y_1 P}{x_1 P_2^{sat}})$$

at const T. by Antion eq^n.

$$[P_1^{sat} \,\&\, P_2^{sat} \; is \; same]$$

$$dlnP = \frac{y_1 - x_1}{y_1(1 - x_1)} dy_1$$

$$\frac{dP}{dy_1} = \frac{P(y_1 - x_1)}{y_1(1 - x_1)}$$

$$x_1 \frac{dln\overline{P_1}}{dx_2} = -x_2 \frac{dln\overline{P_2}}{dx_1}$$

$$\frac{x_1}{P_1}\frac{d\overline{P_1}}{dx_1} = -\frac{x_2}{P_2}\frac{d\overline{P_2}}{dx_1}$$

4.3 Flash distillation of multicomponent mixture using K values

A liquid mixture is partially vaporized and the vapor is allowed to come to equilibrium with the liquid. The process flow diagram is shown in Fig. 4.1. The vapor and liquid phases are then separated.

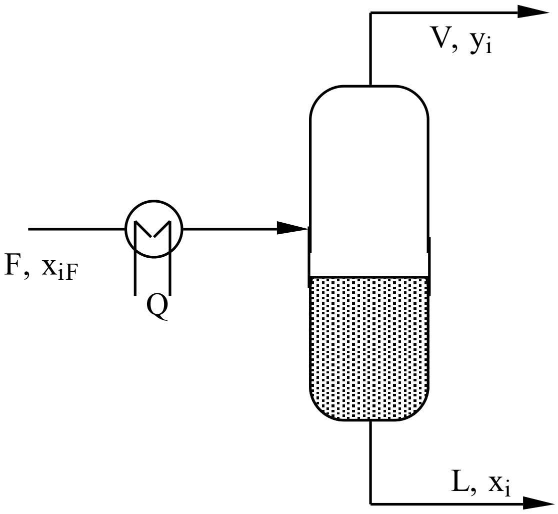


Fig. 4.1 Flash distillation.

Making a component i balance,

$$Fx_{iF} = Vy_i + Lx_i = Vy_i + (F - V)x_i$$

Defining f = V/F,

$$x_{iF} = fy_i + (1 - f)x_i$$

The above equation can be solved for y_i,

$$y_i = K_i x_i = \frac{f - 1}{f} x_i + \frac{x_{iF}}{f}$$

or for x_i,

$$x_i = \frac{x_{iF}}{f\{K_i - 1\} + 1}$$

The feed composition $x_{iF}$and the fraction f of the feed vaporized are given at a specified separator pressure P, the temperature T and compositions x_i and y_i can be calculated with the following procedure:

- Assume a temperature $T = fT_d + (1 - f)T_b$

T_b, T_d = Bubble point and dew point of mixture at pressure P.

Let T_1 = T and $\text{Sumx1} = \sum \frac{x_{iF}}{f\{K_i(T_1,P) - 1\} + 1}$

Let $T_2 = T_1 \times \text{Sumx1}$ and $\text{Sumx2} = \sum \frac{x_{iF}}{f\{K_i(T_2,P) - 1\} + 1}$

Iteration steps:

```
1. $T = (T_1 - T_2 - T_1 \times \text{Sumx2} + T_2 \times \text{Sumx1})/(\text{Sumx1} - \text{Sumx2})$

2. Evaluate Sumx = $\sum x_i$ at T, P

3. Let $T_1 = T_2$, $T_2 = T$, Sumx1 = Sumx2, and Sumx2 = Sumx

4. If abs(Sumx - 1) > .001
then   goto step 1
else   $T = (T_1 - T_2 - T_1 \times \text{Sumx2} + T_2 \times \text{Sumx1})/(\text{Sumx1} - \text{Sumx2})$
EndIf
```

$$x_i = \frac{x_{iF}}{f\{K_i - 1\} + 1} \text{ and } y_i = K_i x_i$$

If the feed composition x_{iF}, temperature T and pressure P of separator are given, then the fraction of the feed vaporized V/F and compositions x_i and y_i can be calculated

$$\bullet \; y_i - \bullet \; x_i = 0$$

$$\bullet \; \frac{K_i x_{iF}}{f(K_i - 1) + 1} - \bullet \; \frac{x_{iF}}{f(K_i - 1) + 1} = 0$$

$$F = \bullet \; \frac{(K_i - 1)x_{iF}}{f(K_i - 1) + 1} = 0$$

which is known as the Rachford-Rice equation, has excellent convergent properties and can be solved by Newton's method. Take the derivative of the function F with respect to V/F (or f),

$$\frac{dF}{df} = - \bullet \; \frac{(K_i - 1)^2 x_{iF}}{[f(K_i - 1) + 1]^2}$$

The following procedure can be used to solve for V/F:

- Check to see if T is between T_b and T_d.

- $f = (T - T_b)/(T_d - T_b)$

Iteration steps:

1. Evaluate $F = \bullet \; \frac{(K_i - 1)x_{iF}}{f(K_i - 1) + 1}$

2. Evaluate $\frac{dF}{df} = - \bullet \; \frac{(K_i - 1)^2 x_{iF}}{[f(K_i - 1) + 1]^2}$

3. Let $ER = F/\frac{dF}{df}$. $f = f - ER$

4. **If**abs(ER) > .001 goto step 1

$x_i = \frac{x_{iF}}{f(K_i - 1) + 1}$ and $y_i = K_i x_i$

Solved problems

4.1

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

Assume $P = 2.15\ MPa$

$At\ 30°C, and\ 2.15\ MPa$ read off the K factors from the charts.

$K_1 = 8.1,\ K_2 = 1.82,\ K_3 = 0.62$

$$x_1 = \frac{y_1}{K_1} = \frac{0.2}{8.1} = 0.0247$$

$$x_2 = \frac{y_2}{K_2} = \frac{0.3}{1.82} = 0.1648$$

$$x_3 = \frac{y_3}{K_3} = \frac{0.5}{0.62} = 0.8065$$

$$\sum x_i = 0.9960{\sim}1$$

Hence dew pressure = 2.15 MPa. The dew composition therefore corresponds to the values of x_i computed above.

REFERENCES

1. Smith J.M. and Van Ness H.C., Introduction to Chemical Engineering Thermodynamics, 7th Edition, McGraw Hill, 2005.

2. Narayanan K.V., A Text Book of Chemical Engineering Thermodynamics, 3rd Edition, Prentice Hall of India Pvt.Ltd.,
2013.

3. Gopinath Halder, Introduction to Chemical Engineering Thermodynamics, 2nd Edition, PHI Learning Pvt. Ltd., 2009.

SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE
www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – V- Chemical Reaction Equilibria – SCHA1302

5.Introduction

The standard state of a material (pure substance, mixture or solution) is a reference point used to calculate its properties under different conditions.

Standard free energy changes of formation, ΔG^o_f, of each species in a change we can determine the standard state free energy change, ΔG^o, for the change using the following equation:

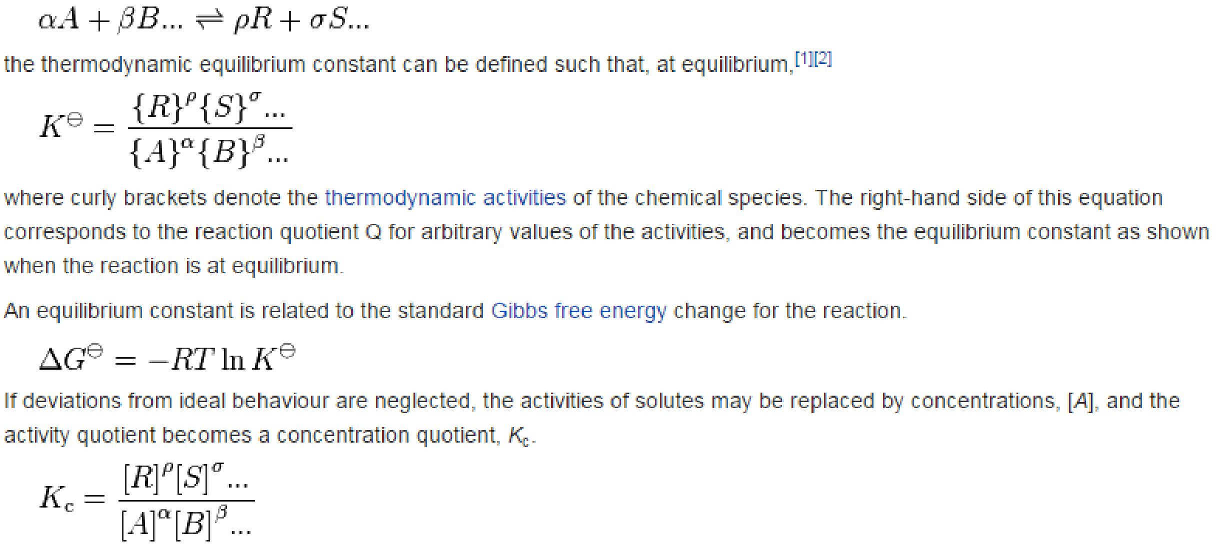
$$\Delta G^o = \Sigma\ \Delta G^o_{f(products)} - \Sigma\ \Delta G^o_{f(reactants)}$$

Reaction equilibrium constant

The equilibrium constant of a chemical reaction is the value of the reaction quotient when the reaction has reached equilibrium. An equilibrium constant value is independent of the analytical concentrations of the reactant and product species in a mixture, but depends on temperature and on ionic strength. Known equilibrium constant values can be used to determine the composition of a system at equilibrium.

Evaluation of Reaction equilibrium constant

For a general chemical equilibrium



$$\alpha A + \beta B ... \rightleftharpoons \rho R + \sigma S ...$$

the thermodynamic equilibrium constant can be defined such that, at equilibrium,[1][2]

$$K^\ominus = \frac{\{R\}^\rho \{S\}^\sigma ...}{\{A\}^\alpha \{B\}^\beta ...}$$

where curly brackets denote the thermodynamic activities of the chemical species. The right-hand side of this equation corresponds to the reaction quotient Q for arbitrary values of the activities, and becomes the equilibrium constant as shown when the reaction is at equilibrium.

An equilibrium constant is related to the standard Gibbs free energy change for the reaction.

$$\Delta G^\ominus = -RT \ln K^\ominus$$

If deviations from ideal behaviour are neglected, the activities of solutes may be replaced by concentrations, [*A*], and the activity quotient becomes a concentration quotient, K_c.

$$K_c = \frac{[R]^\rho [S]^\sigma ...}{[A]^\alpha [B]^\beta ...}$$

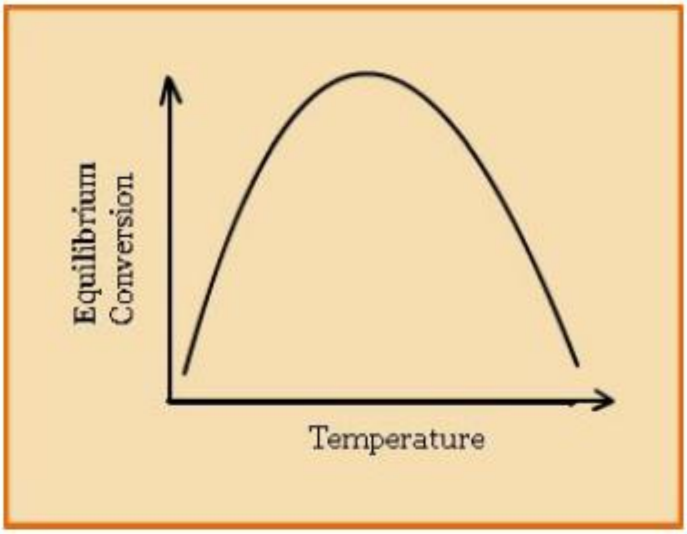
K_c is defined as equal to the thermodynamic equilibrium constant but with concentrations of reactants and products instead of activities. (K_c appears here to have units of concentration raised to some power while $K^{\ominus}$ is dimensionless; however as discussed below under Definitions, the concentration factors in K_c are properly divided by a standard concentration so that K_c is dimensionless also.)

Again assuming ideal behavior, the activity of a solvent may be replaced by its mole fraction, or approximately by 1 in dilute solution. The activity of a pure liquid or solid phase is exactly 1. The activity of a species in an ideal gas phase may be replaced by its partial pressure.

Knowledge of equilibrium constants is essential for the understanding of many chemical systems, as well as biochemical processes such as oxygen transport by hemoglobin in blood and acid-base homeostasis in the human body.

Stability constants, formation constants, binding constants, association constants and dissociation constants are all types of equilibrium constant. See also Determination of equilibrium constants for experimental and computational methods.

Reaction chemistry forms the essence of chemical processes. The very distinctiveness of the chemical industry lies in its quest for transforming less useful substances to those which are useful to modern life. The perception of old art of ‘alchemy’ bordered on the magical; perhaps in today’s world its role in the form of modern chemistry is in no sense any less. Almost everything that is of use to humans is manufactured through the route of chemical synthesis. Such reactive processes need to be characterized in terms of the maximum possible yield of the desired product at any given conditions, starting from the raw materials (i.e., reactants). The theory of chemical reactions indicates that rates of reactions are generally enhanced by increase of temperature. However, experience shows that the maximum quantum of conversion of reactants to products does not increase monotonically. Indeed for a vast majority the maximum conversion reaches a maximum with respect to reaction temperature and subsequently diminishes.



Fiq-5.1 Schematic of Equilibrium Reaction vs. Temperature

The reason behind this phenomenon lies in the molecular processes that occur during a reaction. Consider a typical reaction of the following form occurring in gas phase:

$A(g) + B(g) \rightarrow C(g) + D(g)$

The reaction typically begins with the reactants being brought together in a reactor. In the initial phases, molecules of A and B collide and form reactive complexes, which are eventually converted to the products C and D by means of molecular rearrangement. Clearly then the early phase of the reaction process is dominated by the presence and depletion of A and B.

However, as the process, continues, the fraction of C and D in the reactor increases, which in turn enhances the likelihood of these molecules colliding with each other and undergoing transformation into A and B. Thus, while initially the forward reaction dominates, in time the backward reaction becomes increasingly significant, which eventually results in the two rates becoming equal. After this point is reached the concentrations of each species in the reactor becomes fixed and displays no further propensity to change unless propelled by any externally imposed “disturbance”(say, by provision of heat).

Under such a condition the reaction is said to be in a state of equilibrium. The magnitude of all measurable macroscopic variables (T, P and composition) characterizing the reaction remains constant. Clearly under the equilibrium state the percentage conversion of the reactants to products must be the maximum possible at the given temperature and pressure. Or else the reaction would progress further until the state of equilibrium is achieved. The principles of chemical reaction thermodynamics are aimed at the prediction of this equilibrium conversion. The reason why the equilibrium conversion itself changes with variation of temperature may be appreciated easily. The rates of the forward and backward reactions both depend on temperature; however, an increase in temperature will, in general, have different impacts on the rates of each. Hence the extent of conversion at which they become identical will vary with temperature; this prompts a change in the equilibrium conversion. Reactions for which the conversion is 100% or nearly so are termed irreversible, while for those which never attains complete conversion are essentially reversible in nature.

The fact that a maxima may occur in the conversion behavior suggests that for such reactions while the forward reaction rates dominate at lower temperatures, while at higher temperatures the backward reaction may be predominant. The choice of the reaction conditions thus depends on the maximum (or equilibrium) conversion possible. Further, the knowledge of equilibrium conversions is essential to intensification of a process. Finally, it also sets the limit that can never be crossed in practice regardless of the process strategies. This forms a primary input to the determination of the economic viability of a manufacturing process. If reaction equilibria considerations suggest that the maximum possible conversion over practical ranges of temperature is lower than that required for commercial feasibility no further effort is useful in its further development. On the other hand if the absolute maximum conversion is high then the question of optimizing the process conditions attain significance. Exploration of the best strategy for conducting the reaction (in terms of temperature, pressure, rate enhancement by use of catalytic aids, etc) then offers a critical challenge.

This chapter develops the general thermodynamic relations necessary for prediction of the equilibrium conversion of reactions. As we shall see, as in the case of phase equilibria, the Gibbs free energy of a reaction constitutes a fundamental property in the estimation of equilibrium conversion. The next section presents method of depicting the conversion by the means of the reaction co-ordinate, which is followed by estimation of the heat effects associated with all reactions. The principles of reaction equilibria are then developed.

5.1 Prediction of free energy data

Free energy: the Gibbs function

The Gibbs [free] energy (also known as the Gibbs function) is defined as

In a spontaneous change, Gibbs energy always decreases and never increases. This of course reflects the fact that the entropy of the world behaves in the exact opposite way (owing to the negative sign in the TΔS term).

$$H_2O(l) \rightarrow H_2O(s)$$

water below its freezing point undergoes a decrease in its entropy, but the heat released into the surroundings more than compensates for this, so the entropy of the world increases, the free energy of the H_2O diminishes, and the process proceeds spontaneously.

An important consequence of the one-way downward path of the free energy is that once it reaches its minimum possible value, all net change comes to a halt. This, of course, represents the state of chemical equilibrium. These relations are nicely summarized as follows:

- $\Delta G < 0$: reaction can spontaneously proceed to the right:

$$A \rightarrow B$$

- $\Delta G > 0$: reaction can spontaneously proceed to the left:

$$A \leftarrow B$$

- $\Delta G = 0$: the reaction is at equilibrium; the quantities of [A] and [B] will not change

Finding the value of ΔG: do not bother!

This might seem strange, given the key importance ΔG in determining whether or not a reaction will take place in a given direction. It turns out, however, that it is almost never necessary to explicitly evaluate ΔG. As we will show in the lesson that follows this one, it is far more convenient to work with the equilibrium constant of a reaction, within which ΔG is "hidden". This is just as well, because for most reactions (those that take place in solutions or gas mixtures) the value of ΔG depends on the proportions of the various reaction components in the mixture; it is not a simple sum of the "products minus reactants" type, as is the case with ΔH.

Recalling the condition for spontaneous change

$$\Delta G=\Delta H-T\Delta S<0$$

it is apparent that the temperature dependence of ΔG depends almost entirely on the entropy change associated with the process. (We say "almost" because the values of ΔH and ΔS are themselves slightly temperature dependent; both gradually increase with temperature). In particular, notice that in the above equation the sign of the entropy change determines whether the reaction becomes more or less spontaneous as the temperature is raised. For any given reaction, the sign of ΔH can also be positive or negative. This means that there are four possibilities for the influence that temperature can have on the spontaneity of a process:

5.2 Criteria for Chemical Reaction Equilibrium

The general criterion for thermodynamic equilibrium

$$(dG^t)_{T,P} \leq 0$$

As already explained, the above equation implies that if a closed system undergoes a process of change while being under thermal and mechanical equilibrium, for all incremental changes associated with the compositions of each species, the total Gibbs free energy of the system would decrease. At complete equilibrium the equality sign holds; or, in other words, the Gibbs free energy of the system corresponds to the minimum value possible under the constraints of constant (and uniform) temperature and pressure. Since the criterion makes no assumptions as to the nature of the system in terms of the number of species or phases, or if reactions take place between the species, it may also be applied to determine a specific criterion for a reactive system under equilibrium.

The general criterion for thermodynamic equilibrium implies that if a closed system undergoes a process of change while being under thermal and mechanical equilibrium, for all incremental changes associated with the compositions of each species, the total Gibbs free energy of the system would decrease. At complete equilibrium the equality sign holds; or, in other words, the Gibbs free energy of the system corresponds to the minimum value possible under the constraints of constant (and uniform) temperature and pressure. Since the criterion makes no assumptions as to the nature of the system in terms of the number of species or phases, or if reactions take place between the species, it may also be applied to determine a specific criterion for a reactive system under equilibrium. As has been explained in the opening a paragraph of this chapter, at the initial state of a reaction, when the reactants are brought together a state of non-equilibrium ensues as reactants begin undergoing progressive transformation to products. However, a state of equilibrium must finally attain when the rates of forward and backward reactions equalize. Under such a condition, no further change in the composition of the residual reactants or products formed occurs. However, if we consider this particular state, we may conclude that while in a macroscopic sense the system is in a state of static equilibrium, in the microscopic sense there is dynamic equilibrium as reactants convert to products and vice versa. Thus the system is subject to minute fluctuations of concentrations of each species.

5.3 The Reaction Coordinate

During the progress of the reaction, at each point the extent of depletion of the reactants, and the enhancement in the amount of product is exactly in proportion to their respective stoichiometric coefficients. Thus for any change dn_i in the number of moles of the ith species for a differential progress of the reaction one may write

$$\frac{dn_1}{\alpha_1}=\frac{dn_2}{\alpha_2}=\ldots=\frac{dn_3}{\alpha_3}=\frac{dn_4}{\alpha_4}$$

Since all terms are equal, they can all be set equal to a single quantity, defined to represent *the extent of reaction* as follows: $d\xi$

$$\frac{dn_1}{\alpha_1}=\frac{dn_2}{\alpha_2}=\ldots=\frac{dn_3}{\alpha_3}=\frac{dn_4}{\alpha_4}=d\xi$$

The general relation between a differential change $dn$is therefore: ($i = 1,2, ...N$) $_{i}$in the number of moles of a reacting species and $d\xi$

$$dn_i=\alpha_i d\xi \quad (i = 1,2, \ldots N)$$

This new variable, called the *reaction coordinate*, describe the extent of conversion of reactants to products for a reaction. Thus, it follows that the value of is zero at the start of the reaction. On the other hand when, it follows that the reaction has progressed to an extent at which point each reactant has depleted by an amount equal to its stoichiometric number of moles while each product has formed also in an amount equal to its stoichiometric number of moles.

5.4 Nature of Chemical Equilibrium

- reaction ***must*** be reversible:

$A \leftrightarrows B$

  - product formation rate = $k_f [A]$
  - reactant formation rate = $k_r [B]$
- at equilibrium, $k_f [A] = k_r [B]$
- start with pure A, [A] decreases with time as [B] increases
- in addition, ***rate*** of A consumption, the forward rate, decreases with time; conversely, reverse rate increases with time, until they are equal
- rearrange above equation:

$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = \text{a constant}$$

- this ratio independent of whether reaction started with A or B or a mixture of both (as long as temp constant)
- forward and reverse reactions do not stop, hence referred to as ***dynamic equilibrium***
- eg. carbonate equilibria (both directions):

$$Ca^{2+}(aq) + 2\,HCO_3^-(aq) \leftrightarrows CaCO_3(s) + CO_2(g) + H_2O(l)$$

- Co^{2+}-complexes:

$[Co(H_2O)_6]^{2+} + 4\,Cl^- \leftrightarrows [CoCl_4]^{2-} + 6\,H_2O$

- eg.

$$H_2(g) + I_2(g) \rightleftarrows 2\,HI(g)$$

- eg. start with 1:1 H_2:I_2 ratio, reaction reaches equilibrium with all 3 components in certain proportions
  - start with different ratio of H_2:I_2, different proportions of 3 components at equ'm
  - start with pure HI, same proportions as first case

  - *i.e.*- can approach equ'm from either direction
- quantitative: ***Law of Mass Action***
- general reaction, balanced equation:

$$a\,\mathrm{A} + b\,\mathrm{B} \leftrightarrows p\,\mathrm{P} + q\,\mathrm{Q}$$

- where *a, b, p, q* are ***stoichiometry coefficients*** (or stoichiometry numbers) of the balanced equation
  - at equilibrium:

$$K_c = \frac{[\mathrm{P}]^p[\mathrm{Q}]^q}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

  - K_c is equilibrium constant (sub "c" denotes concentrations in molarity; sub "p" below)
  - numerator for "right side" - prod. of [prod]'s
  - denominator for "left side" - prod. of [reactant]'s
- eg. the HI reaction above:

$$K_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}]\,[\mathrm{I_2}]}$$

- equilibrium constant depends only on stoichiometry from balanced equation, ***not*** on the reaction mechanism
- K is a true constant at a given temp (varies with temp)
- note: equilibrium constants given with***out*** units (above K_c, and K_p below, first developed as *empirical* constants; later, *thermodynamic* equilibrium constants, which are dimensionless)

5.5 Expressing Equilibrium Constants in Terms of Pressure, K_p

- when reactants and products are gases, can use pressure instead of molarity
- eg.

$$\mathrm{N_2O_4(g)} \leftrightarrows 2\,\mathrm{NO_2(g)}$$

$$K_c = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} \; ; \quad K_p = \frac{P^2_{\mathrm{NO_2}}}{P_{\mathrm{N_2O_4}}}$$

5.6 Thermodynamic Description of the Equilibrium State

- Ideal gas at constant T, change pressure:

  $\Delta G = \Delta H - T\Delta S = -T\Delta S$, since $\Delta H = 0$

  $$\text{but } \Delta S = \frac{q_{rev}}{T} \quad \text{and } q_{rev} = nRT \ln\left(\frac{V_2}{V_1}\right), \ (\text{ch } 7.6)$$

  $$\therefore \ \Delta S = nR \ln\left(\frac{V_2}{V_1}\right), \quad (\text{ch } 8.5)$$

  $$= nR \ln\left(\frac{P_1}{P_2}\right) = -nR \ln\left(\frac{P_2}{P_1}\right)$$

  $$\Delta G = nRT \ln\left(\frac{P_2}{P_1}\right) = nRT \ln\left(\frac{P}{P_{ref}}\right)$$

  if choose $P_1 = 1$ atm, the reference state, (then ignore $P_1 = P_{ref}$ ***only if*** in units of atm)

- **Gas-phase reactions**

  Eg. $3\ NO(g) \leftrightarrows N_2O(g) + NO_2(g)$

  If all at 1 atm, 25°C, then $\Delta G = \Delta G^o$

  If not, then treat as 3-step process:

  $3\ NO(P_{NO}) \rightarrow 3\ NO(P_{ref}), \quad \Delta G_1$

  $3\ NO(P_{ref}) \rightarrow N_2O(P_{ref}) + NO_2(P_{ref}), \quad \Delta G_2 = \Delta G^o$

  $N_2O(P_{ref}) + NO_2(P_{ref}) \rightarrow N_2O(P_{N2O}) + NO_2(P_{NO2}), \quad \Delta G_3$

  Overall: $\Delta G = \Delta G_1 + \Delta G^o + \Delta G_3$

  $$= \Delta G^o + RT \ln \{(P_{N2O})(P_{NO2})/(P_{NO})^3\}$$

  but at equilibrium, $\Delta G = 0$, hence $\Delta G^o = -RT \ln K_p$ (constant T)

  note: K is dimensionless when P's in atm and P_{ref}'s = 1 atm

  In general:

  For $aA + bB \leftrightarrows cC + dD$

  $$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Reactions in Ideal Solution

- Concentrations in M, reference state 1 M; then, by extension:

$$\Delta G^{o} = -RT \ln\left(\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}\right) = -RT \ln K_{c}$$

Reactions Involving Pure Solids and Liquids and Multiple Phases; Activity

- Read for interest

Equilibrium Calculations

Evaluating Equilibrium Constants from Reaction Data

- practical applications, once known
  - predict the direction of reaction as a given mixture proceeds to equilibrium (see above)
  - calculate the conc'ns of reactants and products once equ'm established
- ***but***, often do not know equ'm conc'ns of ***all*** reactants and products
- if equ'm conc'n of at least one species, the initial conc'ns of all species and stoichiometry known, can calculate K
- four-step procedure:
  1. ***tabulate*** known initial and equ'm conc'ns of all species involved
  2. for species for which initial and equ'm conc'ns known, calculate ***change*** in conc'n
  3. use the ***stoichiometry*** of the reaction to calculate changes in conc'ns of all other species
  4. calculate remaining equilibrium conc'ns and ***calculate*** equ'm constant

5.7 Relationships Among Equilibrium Constants

- if stoichiometric coefficients multiplied, new equ'm constant raised to the power of mult'n factor:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

$$K_1 = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = 3.5 \times 10^8$$

but for: $1/2\ N_2(g) + 3/2\ H_2(g) \rightleftarrows NH_3(g)$

$$K_2 = \frac{[NH_3]}{[N_2]^{\frac{1}{2}}\ [H_2]^{\frac{3}{2}}} = K_1^{\frac{1}{2}} = \sqrt{K_1} = 1.9 \times 10^4$$

- if an equilibrium equation is written in the opposite (left-to-right) sense, the equilibrium constant is inverted

$$2\ NH_3(g) \rightleftarrows N_2(g) + 3\ H_2(g)$$

$$K_3 = \frac{[N_2][H_2]^3}{[NH_3]^2} = K_1^{-1} = \frac{1}{K_1} = 2.9 \times 10^{-9}$$

- if two or more equations are added to produce a net equation, the equilibrium constant for the net equation is the product of the equilibrium constants of the equations added:
  - given 3 reactions:

$$H_2(g) + Br_2(g) \leftrightarrows 2\ HBr(g); \quad K_p = 7.9 \times 10^{11}$$
$$H_2(g) \leftrightarrows 2\ H(g); \quad K_p = 4.8 \times 10^{-41}$$
$$Br_2(g) \leftrightarrows 2\ Br(g); \quad K_p = 2.2 \times 10^{-15}$$

  - calculate K_p for the following reaction:

$$H(g) + Br(g) \leftrightarrows HBr(g)$$

  - reverse equ’ns 2 & 3, add them to equ’n 1:

$$\begin{array}{c} 2\ H(g) \leftrightarrows H_2(g) \\ 2\ Br(g) \leftrightarrows Br_2(g) \\ \underline{H_2(g) + Br_2(g) \leftrightarrows 2\ HBr(g)} \\ 2\ H(g) + 2\ Br(g) \leftrightarrows 2\ HBr(g) \end{array}$$

$$K_p = \left[\left(\frac{1}{4.8 \times 10^{-41}}\right)\left(\frac{1}{2.2 \times 10^{-15}}\right)\left(7.9 \times 10^{11}\right)\right]^{\frac{1}{2}}$$
$$= 2.7 \times 10^{33}$$

5.8 Using Equilibrium Constants for Calculation of Equilibrium Concentrations

- using initial concentrations of all components and the equilibrium constant, can also do it using equilibrium concentrations of some components and the equilibrium constant

Magnitude of K and the Direction of Change

- if K >> 1, reaction proceeds to right; little of A left at equ'm; product(s) predominate
- if K << 1, reaction proceeds very little; mostly A left at equ'm; reactant(s) predominate
- reaction reversible; left-to-right sense of writing it is arbitrary:
  - eg.

$$N_2O_4(g) \leftrightarrows 2\ NO_2(g)\ ; \quad K_c = 0.212$$

  - for

$$2\ NO_2(g) \leftrightarrows N_2O_4(g)\ ; \quad K_c = \frac{1}{0.212} = 4.72$$

The Reaction Quotient, Predicting the Direction of a Reaction

- reactant and product concentrations in expression for K gives **reaction Quotient, Q:**

$$a\,A + b\,B \leftrightarrows c\,C + d\,D$$

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

  - note: concentrations in Q are *not necessarily* equilibrium concentrations
- Q is used to predict the direction a reversible reaction will take to reach equilibrium from given initial concentrations of reactant(s) and product(s)
  - Q = K, system at equilibrium
  - Q > K, reaction moves to left (to reactant(s))
  - Q < K, reaction moves to right (to product(s))

5.9 Disturbing a Chemical Equilibrium: Le Chatelier's Principle

- if a system at equilibrium is disturbed by a change in temperature, concentration of one of the components or volume/pressure, the system will shift its equilibrium position to counteract the effect of this disturbance

Change in Reactant or Product Conc'ns

- eg. the Haber Process for commercial production of ammonia:

$$N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g)$$

  - add H_2 (or N_2), system reacts to reduce [H_2] towards original value & produce NH_3

  - add NH_3, system reacts to reduce $[NH_3]$ towards original value & produce $H_2 + N_2$
- same conclusion by considering Q:

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = Q\,, \text{ at equ'm}$$

  - remove NH_3, $Q < K_c$, reaction shifts to right, to form more NH_3
  - analogous change, add H_2
- exploited in actual industrial process, see pages 297-8 and Figure 9.10, continuously remove NH_3 as formed

5.10 Effects of Volume & Pressure Changes

- if volume reduced, pressure increases; system responds in the direction that reduces the number of moles of gas
- following eg., pressure increase causes shift to left:

$$N_2O_4(g) \leftrightarrows 2\ NO_2(g)$$

- note: these changes do ***not*** change K (const. T), but change Q; re-adjustment until Q = K

5.11 Effect of Temperature Changes

- almost all K values change with temp (contrast foregoing)

eg. colour changes in following equ'm

$$\underset{\text{pink}}{Co(H_2O)_6^{2+}(aq)} + 4Cl^-(aq) \rightarrow \underset{\Delta H\ >\ 0\qquad \text{blue}}{CoCl_4^{2-}(aq)} + 6H_2O(l)$$

  - cooled soln: pink
  - warmed soln: blue
  - room temp soln: violet
- consider ***heat*** as a reaction component:
  - endothermic ($\Delta H > 0$):

Reactants + *heat* ⇆ products

  - exothermic ($\Delta H < 0$):

Reactants ⇆ products + *heat*

- when heat added to a system, equilibrium shifts to absorb heat:
  - endothermic: increase in T, increased K
  - exothermic: increase in T, decreased K

$2\ NO_2(g) \leftrightarrows N_2O_4(g); \quad \Delta H^o = -57.2$ kJ

brown colorless

$K_c = 170$ at 298 K, 1300 at 273 K

5.12 Effect of a Catalyst

- no effect (actually ***equal*** effect on forward and reverse rates)
- speeds up the approach to equ'm but not the position

Temperature Dependence of Equilibrium Constants

- Le Chatelier's principle qualitative; here a little more quantitative with a thermodynamic explanation, based on:

$$- RT \ln K = \Delta G^o = \Delta H^o - T\Delta S^o$$

  - As long as ΔH^o and ΔS^o not temp-dependent, then T-factor above determines

Extraction and Separation Processes

- Distribution between phases, ***partitioning, partition coefficient***, an equilibrium constant
- Exploited in extraction processes and separation by chromatography
- Read for interest

5.13 The Phase Rule

The phase rule was formulated by J. Willard Gibbs (1874) to determine the variance or degrees of freedom of a system "f" of a known # of components "c" and phases "p". The variance of a system can be expressed as the total variables of this system minus the "fixed variables". For any system of "**c**" components and containing "**p**" phases, the total number of variables is **c.p + 2**, where the "2" represents the two variables P and T. The fixed variables are given by the number of equations needed to fully define the composition of the system, and expressed as: **$c(p-1) + p$**. Accordingly, the degrees of freedom will be given by:

$$\mathbf{f = cp + 2 - [cp - c + p]}$$

$$\therefore \mathbf{f = c - p + 2}$$

The phase rule therefore allows us to determine the minimum number of variables that must be fixed in order to perfectly define a particular condition of the system from a knowledge of the number of system components and phases. Note that this "number of variables" cannot be negative (i.e. $f \geq 0$). The phase rule also allows us to determine the maximum number of phases that can coexist stably in equilibrium; e.g. if a system has 20 components, according to the phase rule, the maximum number of phases in equilibrium will be 22 (when $f = 0$). *Accordingly, if the number of phases present exceeds that calculated by the phase rule (after the number of components has been correctly identified), then not all these phases are in equilibrium!*

Based on the phase rule, the condition of a system can be described as invariant, univariant, divariant .....etc., if f = 0, 1, 2,.....etc. respectively, where:

(i) an invariant state is one in which neither P nor T nor X (composition) can be changed without causing a change in the number of phases present in the system. On the P-T diagram for the one-component system "SiO_2" (which shows the P-T stability fields of the silica polymorphs; Fig. 1), an invariant state is represented by a *point* as "C" where three phases (cristobalite, high quartz and tridymite) coexist.

(ii) a univariant state is one in which either P or T need to be specified in order to fully define the system. A univariant mineral assemblage can therefore be maintained if a change in one variable (e.g. P) is accompanied by a <u>dependent</u> change in another (e.g. T), but if one of these two variables is held constant while the other is changed, the assemblage is no longer stable, and the system is no longer univariant. An example of this is given by point "B" of Fig. 1 (or any point lying along any of the *curves* defining the P-T limits of the different phases).

(iii) a divariant state is one in which two variables have to be specified in order to fully define or characterize the system. An example of a divariant state is given by point "A" (Fig. 1), or any point lying in the stability *fields* of one of the polymorphs.

The condensed Phase rule: In cases where either P or T are held constant, one can apply the "condensed phase rule" given by the formula:

$f = c - p + 1$

This is simply because the total number of variables within the system has now become pc+1, since only one of the two intensive properties of the system (P and T) is allowed to vary. The condensed phase rule is quite helpful in understanding isobaric T-X or isothermal P-X diagrams, and in experimental geochemistry, where either P or T are held constant to investigate the dependence of the system on the other intensive variable.

Application of Phase Rule to a system with dissolved species:

In cases where the system consists of dissolved species, defining the number of components may become challenging. If we decide to consider every dissolved ionic species a component, then the phase rule is best expressed by the formula:

$f = c' - p - r + 2$

where c' is the number of different chemical species in the system, and r the number of "auxiliary" restrictions necessary to fully define the system.

To fully appreciate this, we consider the example of a system containing the mineral calcite at saturation and in equilibrium with gaseous CO_2. The system contains 3 phases (water, calcite, and CO_2), and may be considered to conatin 3 components as well (as we attempt to minimize c in accordance with the definition). Application of the phase rule f = c-p+2 would indicate that the system is bivariant (3-3+2). However, calcite dissociates in water giving ionic species, water dissociates to H^+ and OH^-, whereas CO_2 dissolves in water to form carbonic acid. Possible equilibria in the system therefore include:

$CO_2 + H_2O = H_2CO_3$

$H_2CO_3 = H^+ + HCO_3^-$

HCO_3- = $H^+ + CO_3^{2-}$

$H_2O = H^+ + OH^-$

$CaCO_3 = Ca^{2+} + CO_3^{2-}$

Once we decide to consider the ionic species as system components, c’ = 9 (Ca^{2+}, CO_3^{2-}, HCO_3^-, H^+, OH^-, H_2O, CO_2, H_2CO_3, and $CaCO_3$). “r” then becomes the number of equations necessary to fully define the system (solve for some concentrations knowing others). Because c = c’-r, r must be equal to 6. The six equations necessary to fully define the system become the 5 reactions listed above (one equation for each reaction, each expressing the equilibrium constant), and an equation that defines the charge balance of the system (all waters have to be charge – balanced):

$2[Ca^{2+}] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$

Solved problems

5.1

Consider the reaction: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the degree of conversion, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K).

Species	**a**	**bx10^3**	**cx10^6**	**dx10^9**	**ex10^{-5}**
C_2H_4	20.691	205.346	– 99.793	18.825	-
H_2O	4.196	154.565	– 81.076	16.813	-
C_2H_5OH	28.850	12.055	-	-	1.006

From standard tables $\Delta H^0_{R,298} \approx -52.7$ KJ; $\Delta G^0_{R,298} = 14.5$ KJ

Now $\Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^{T} \Delta C_P^0 dT$ ---------------------- (A)

$\Delta C_P^0 = \sum \alpha_i C_{P,i}^0 = \Delta a + \Delta bT + \Delta CT^2 + \Delta dT^3 + \Delta e / T^2$ ------------- (B)

Where:

$\Delta a = \sum \alpha_i a_i, \Delta b = \sum \alpha_i b_i, etc$

For example $\Delta a = 20.691 – 4.196 -28.850 = -12.355$

$\Delta b = (205.346 – 154.565 – 12.055) \times 10^{-3} = 3.8726 \times 10^{-2}$

Similarly $\Delta c = -1.8717 \times 10^{-5}$; $\Delta d = 2.012 \times 10^{-9}$; $\Delta e = -1.006 \times 10^{5}$

Putting B in A and integrating A we get:

$$\Delta H_T^0 = -50.944(KJ) - 12.355T + \frac{3.8726\times10^{-2}}{2}T^2 - \frac{1.8717\times10^{-5}}{3}T^3 + \frac{2.012\times10^{-9}}{4}T^4 + 1.006\times10^5/T \quad \ldots\ldots\ldots\ldots.(C)$$

By Vant Hoff equation: $\frac{d(\Delta G_T^0/RT)}{dT} = -\frac{\Delta H_T^0}{RT^2}$

$$\therefore \frac{\Delta G_T^0}{RT} - \frac{\Delta G_{298}^0}{R(298)} = -\int_{298}^{T} \frac{\Delta H_T^0}{RT^2} dT \quad \text{---} \quad D$$

We already know ΔH_T^0 from (C); putting C in D and integrating we obtain:

$$\Delta G_T^0 = -50.944 + 12.355T\ln T - \frac{3.8726\times10^{-2}}{2}T^2 + \frac{1.8718\times10^{-5}}{6}T^3 - \frac{2.012\times10^{-9}}{12}T^4 + \frac{1.006\times10^5}{2T} + 56.681T$$

Putting T=500k, ΔG_T^0= 11.43kJ

5.2

Consider the following reaction: A(g) + B(g) = C(g) + 3D(g) $CH_4 + H_2O \rightarrow CO + 3H_2$

Intially the following number of moles are introduced in the reactor. Obtian the mole fraction expressions in terms of reaction coordinate.

$n_{0,A}$ = 2 mol, $n_{0,B}$ = 1 mol, $n_{0,C}$ = 1 mol $n_{0,D}$ = 4 mol

$\alpha \sum \alpha_i$ = -i = -1-1+1+3 = 2

$n_o = \sum_i n_{i_o}$ = 2+ 1 +1 + 4 = 8

$$y_i = \frac{n_i}{n} = \frac{n_{i_o} + \alpha_i \xi}{n_o + \alpha\xi}$$

$$\therefore\therefore\ y_A = \frac{2-\xi}{8+2\xi}; \quad y_B = \frac{1-\xi}{8+2\xi}; \quad y_C = \frac{1+\xi}{8+2\xi}; \quad y_{H_2} = \frac{4+\xi}{8+2\xi}$$

5.3

Consider the following simultaneous reactions. Express the reaction mixture composition as function of the reaction co-ordinates. All reactants and products are gaseous.

A + B = C + 3D ..(1)

A + 2B = E + 4D ..(2)

Initial number of moles:

$n_{0,A} = 2$ mol; $n_{0,B} = 3$ mol

Let the reaction co-ordinates for each reaction be ξ_1 *and* ξ_2 respectively.

j	A	B	C	D	E	$\alpha_j=\Sigma\alpha_{i,j}$
1	- 1	-1	1	3	0	2
2	-2	-2	0	4	1	2

$$y_i = \frac{n_{io} + \sum_j \alpha_{i,j}\xi_j}{n_o + \sum_j \alpha_j \xi_j}; \qquad n_o = 2+3 = 5$$

$$\therefore\ y_A = \frac{2-\xi_1-\xi_2}{5+2\xi_1+2\xi_2};\ y_B = \frac{3-\xi_1-2\xi_2}{5+2\xi_1+2\xi_2};\ y_C = \frac{\xi_1}{5+\ 2\xi_1+2\xi_2}$$

$$y_D = \frac{3\xi_1+4\xi_2}{5+\ 2\xi_1+2\xi_2};\ y_E = \frac{\xi_2}{5+\ 2\xi_1+2\xi_2}$$

5.4

The following two independent reactions occur in the steam cracking of methane at 1000 K and 1 bar: $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$; and $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$. Assuming ideal gas behaviour determine the equilibrium composition of the gas leaving the reactor if an equimolar mixture of CH_4 and H_2O is fed to the reactor, and that at 1000K, the equilibrium constants for the two reactions are 30 and 1.5 respectively.

Let ξ_1 and ξ_2 be the reaction co-ordinate for the two reactions, we have

Comp	n_{i0}	n_{exit}	y_{exit}
CH_4	1	$1 - \xi_1$	$(1 - \xi_1) / 2(1 + \xi_1)$
H_2O	1	$1 - \xi_1 - \xi_2$	$(1 - \xi_1 - \xi_2) / 2(1 + \xi_1)$
CO	0	$\xi_1 - \xi_2$	$(\xi_1 - \xi_2) / 2(1 + \xi_1)$
CO_2	0	ξ_2	$\xi_2 / 2(1 + \xi_1)$
H_2	0	$3\xi_1 + \xi_2$	$(3\xi_1 + \xi_2) / 2(1 + \xi_1)$

Total moles at equilibrum: $2(1 + \xi_1)$

$K = K_\varphi K_y P^\alpha$ (for each reaction); $K_\varphi = 1.0$ (ideal gas assumption); P = 1 bar

Thus $K_1 = \left[\frac{(\xi_1 - \xi_2)}{2(1+\xi_1)}\right]\left[\frac{(3\xi_1 + \xi_2)}{2(1+\xi_1)}\right]^3 \Big/ \left[\frac{(\varepsilon_1 - \xi_2)}{2(1+\xi_1)}\right]\left[\frac{(3\xi_1 + \xi_2)}{2(1+\xi_1)}\right]$

$$= \frac{(\xi_1 - \xi_2)(3\xi_1 + \xi_2)^3}{4(1+\xi_1)^2(1-\xi_1)(1-\xi_1-\xi_2)} = 30 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad A$$

Similarly $K_2 = \dfrac{(3\xi_1 + \xi_2)\xi_2}{(\xi_1 - \xi_2)(1-\xi_1-\xi_2)} = 1.5$ …………………………………… B

A and B needs to be solved simultaneously; a simple way to do this is to

(i) Assume ε_2 , calculate ε_1 using B

(ii) Use ξ_2 and ξ_1 in A to check if $K_1 = 30$

(iii) If $K_1 \neq 30$, assume new ε_2 and go to step 1

Using the above algorithm, one finally obtains: $\xi_1 = 0.7980$, $\xi_2 = 0.0626$.

Thus: $y_{CO_2} = 0.0174, y_{CH_4} = 0.0562, y_{H_2O} = 0.0388, y_{CO} = 0.2045, y_{H_2} = 0.6831$

5.5

Consider the following reaction: A(s) + B(g) → C(s) + D(g). Determine the equilibrium fraction of B which reacts at 500°C if equal number of moles of A and B are introduced into the reactor initially. The equilibrium constant for the reaction at 500°C is 2.0.

The reaction is:

$A(s)+B(g)\rightarrow C(s)+D(g)$; basis 1 mole of A & B each initially

$$K=\hat{a}_C\hat{a}_D\Big/\hat{a}_A\hat{a}_B$$

For solids: $\hat{a}=1$

Thus:

$$K=\hat{a}_D\Big/\hat{a}_B=K_\phi K_y P^\alpha\,;\alpha=0, \mathit{and}\ K_\phi=1$$

$$\therefore K=K_y$$

If one assumes equimolar feed of reactants:

$$y_B=(1-\xi);\ y_D=\xi$$

$$\therefore K=K_y=2.0=\frac{\xi}{1-\xi}\Rightarrow\xi=0.67$$

Thus 67% of B reacts.

REFERENCES

1. Smith J.M. and Van Ness H.C., Introduction to Chemical Engineering Thermodynamics, 7th Edition, McGraw Hill, 2005.

2. Narayanan K.V., A Text Book of Chemical Engineering Thermodynamics, 3rd Edition, Prentice Hall of India Pvt. Ltd., 2013.

3. Gopinath Halder, Introduction to Chemical Engineering Thermodynamics, 2nd Edition, PHI Learning Pvt. Ltd., 2009.