

29. (a) Criteria for phase equilibrium:

Clausius inequality:

$$dS \geq \frac{dQ}{T} \quad \text{--- (1)}$$

The first law of thermodynamics expressed mathematically can be rewritten as

$$dQ = dU + dW \quad \text{--- (2)}$$

Substituting eqn (2) in eqn (1)

$$TdS \geq dU + dW$$

$$dU \leq TdS - dW \quad \text{--- (3)}$$

$$dU \leq TdS - PdV \quad \text{--- (4)}$$

Equation (4) can be treated as the combined statement of the first and second law of thermodynamics applied to a closed system which interact with its surroundings through heat transfer and work of volume displacement. This equation is utilised for deriving the criteria of equilibrium under various sets of constraints, each set corresponding to a physically realistic & commonly encountered situation. These different criteria are discussed now.

(i) Constant U and V:

An isolated system does not exchange mass, heat & work with the surroundings.

In equation (2), $dQ = 0$, $dW = 0$ and hence $dU = 0$.

A well insulated vessel of constant volume would

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closely approximate this behaviour. Thus in equation (4)

$dU=0$ and $dV=0$ so that

$$\boxed{dS_{U,V} \geq 0} \quad - (5)$$

The entropy is constant in a reversible process and increases in a spontaneous process occurring in a system of constant U and V .

(ii) Constant T and V :

Helmholtz free energy is defined by

$$A = U - TS$$

$$U = A + TS$$

$$dU = dA + Tds + SdT$$

Substitute this result in eqn (4) and rearrange the resulting expression to the following form

$$dA \leq -pdV - SdT \quad - (6)$$

Under the restriction of constant temperature and volume, the latter implying no work, the equation simplifies to

$$\boxed{dA_{T,V} \leq 0} \quad - (7)$$

Equation (7) means the spontaneous process occurring at constant temperature and volume is accompanied by a decrease in the work function and consequently, in a state of thermodynamic equilibrium under these conditions the Helmholtz free energy or the work function is a minimum.

(iii) Constant P and T:

Gibbs free energy as

$$G = H - TS$$

Since $H = U + PV$,

$$G = U + PV - TS$$

$$dG = dU + PdV + VdP - TdS - SdT$$

rearranging these as

$$dU = dG - PdV - VdP + TdS + SdT$$

and combining this result with eqn (4)

$$dG \leq VdP - SdT \quad \text{--- (8)}$$

At constant temperature and pressure, eqn (8) reduces to

$$\boxed{dG_{T,P} \leq 0} \quad \text{--- (9)}$$

Equation (9) means that the free energy either decreases or remains unaltered depending upon whether the process is spontaneous or reversible. It implies that for a system in equilibrium at a given temperature and pressure the free energy must be minimum.

Since most chemical reactions and many physical changes are carried out under conditions of constant temperature and pressure, equation (9) is the commonly used criterion of thermodynamic equilibrium.

In the equilibrium state, differential variations can occur in the system at constant T & P without producing any change in the Gibbs function. Thus, the equality in equation (9) can be used as the

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General Criterion of equilibrium on as a thermodynamic statement that characterises the equilibrium state.

$$\boxed{dG=0} \text{ (at constant } T \text{ and } P) \text{ — (10)}$$

(b) VLE for Single Component System:

Consider the thermodynamic equilibrium in a system consisting of two or more phases of a single substance. Though the individual phases can exchange mass with each other and are therefore open, the system as a whole is closed. As an example, treating the equilibrium between vapour and liquid phase of a single substance at a constant temperature and pressure. Applying the criterion of equilibrium to this closed system,

$$dG=0$$

$$dG^a + dG^b = 0 \text{ — (1)}$$

where the dG^a and dG^b are the changes in free energies of the phases 'a' and 'b' respectively. Since each phase is open, the change in its free energy may be due to the changes in temperature, pressure and the number of moles of the component that constitute the phase.

$$dG = VdP - SdT + \sum \bar{G}_i dn_i$$

Applying this equation to the phases 'a' and 'b'

$$dG^a = v^a dp^a - s^a dT^a + G^a dn^a ; dG^b = v^b dp^b - s^b dT^b + G^b dn^b$$

At constant temperature and pressure,

$$dG^a = G^a dn^a ; dG^b = G^b dn^b \text{ — (2)}$$

As the system as a whole is closed, (59)

$$dn^a + dn^b = 0 \quad \& \quad dn^a = -dn^b \quad \text{--- (3)}$$

Substitute eqns (2) and (3) into eqn (1)

$$(G^a - G^b) dn^a = 0 \quad \text{--- (4)}$$

Equation (4) means that $G^a = G^b$ --- (5)
whenever two phases of the same substance are

in equilibrium under a given temperature and pressure, the molar free energy is the same in each phase.

(C) VLE for Multicomponent Systems:

Consider a heterogeneous system consisting of π phases indicated by the letters, $\alpha, \beta, \gamma, \dots, \pi$.

The various components that constitute the system are 1, 2, 3, ... C. The symbol μ_i^k denotes the chemical potential of component 'i' in phase 'k'.

Suppose that small amounts of various components are transferred from one phase to another, the system being in equilibrium and the temperature and pressure kept constant. Since the system as a whole is closed, the proposed transfer should satisfy the following criterion.

$$dG = 0 \quad (\text{at Const } T \text{ and } P) \quad \text{--- (1)}$$

The free energy change in a multicomponent system is given by

$$dG = VdP - SdT + \sum \mu_i dn_i$$

At constant temperature and pressure, ⁽⁶⁰⁾ the above equation becomes

$$dG = \sum \mu_i dn_i$$

Substitute this into Eqn ① to get

$$\sum \mu_i dn_i = 0 \quad \text{--- ②}$$

Let dn_i^k denote the increase in the number of moles of component i in phase k . Equation ②

may then be written as

$$\sum_{i=1}^c \sum_{k=\alpha}^{\pi} \mu_i^k dn_i^k = 0$$

Expanding this equation

$$\begin{aligned} & \mu_1^\alpha dn_1^\alpha + \mu_1^\beta dn_1^\beta + \dots + \mu_1^\pi dn_1^\pi + \\ & \mu_2^\alpha dn_2^\alpha + \mu_2^\beta dn_2^\beta + \dots + \mu_2^\pi dn_2^\pi + \\ & \vdots \\ & \mu_c^\alpha dn_c^\alpha + \mu_c^\beta dn_c^\beta + \dots + \mu_c^\pi dn_c^\pi = 0 \quad \text{--- ③} \end{aligned}$$

Since the system as a whole is closed, it should satisfy the mass conservation equation given below

$$\begin{aligned} dn_1^\alpha + dn_1^\beta + \dots + dn_1^\pi &= 0 \\ dn_2^\alpha + dn_2^\beta + \dots + dn_2^\pi &= 0 \\ \vdots \\ dn_c^\alpha + dn_c^\beta + \dots + dn_c^\pi &= 0 \quad \text{--- ④} \end{aligned}$$

The variation in the number of moles dn_i are independent of each other. However, they are subject to the constraints imposed by

Eqn (4). For all possible variations dn_i^k , eqn (3) is to be satisfied. This is possible only if

$$\begin{aligned} \mu_1^{\alpha} &= \mu_1^{\beta} = \dots = \mu_1^{\pi} \\ \mu_2^{\alpha} &= \mu_2^{\beta} = \dots = \mu_2^{\pi} \\ &\vdots \\ \mu_c^{\alpha} &= \mu_c^{\beta} = \dots = \mu_c^{\pi} \end{aligned} \quad \text{--- (5)}$$

Equation (5) means that when a system consisting of several components distributed between various phases is in thermodynamic equilibrium at a definite temperature and pressure, the chemical potential of each component is the same in all the phases.

$$\begin{aligned} T &= \text{Constant}; & P &= \text{Constant} \\ \mu_i^{\alpha} &= \mu_i^{\beta} = \dots = \mu_i^{\pi} & \text{for } i &= 1, 2, 3, \dots, C \end{aligned}$$

--- (6)

Thus the equality of chemical potential along with the requirement of uniformity of temperature and pressure serves as the general criterion of thermodynamic equilibrium in a closed heterogeneous multicomponent system.

30. Solution:

$$n_i = n_{i0} + v_i \xi \quad \text{--- (1)}$$

(a)

$$y_i = \frac{n_i}{\sum n_i} = \frac{n_{i0} + v_i \xi}{\sum n_{i0} + \xi \sum v_i} = \frac{n_{i0} + v_i \xi}{n_0 + \xi V} \quad \text{--- (2)}$$

where $n_0 = \sum n_{i,0}$, the total number of moles initially present in the system and $V = \sum v_i$, the sum of the stoichiometric numbers.

Equations (1) and (2) relate the mole fraction of various constituents in the system to the extent of reaction

$$n_0 = \sum n_{i,0} = 2 + 7 + 1 = 10$$

$$V = \sum v_i = 2 - 1 - 3 = -2$$

$$y_{N_2} = \frac{n_{N_2,0} + v_{N_2} \xi}{n_0 + \xi V} = \frac{2 - \xi}{10 - 2\xi}$$

$$y_{H_2} = \frac{n_{H_2,0} + v_{H_2} \xi}{n_0 + \xi V} = \frac{7 - 3\xi}{10 - 2\xi}$$

$$y_{NH_3} = \frac{n_{NH_3,0} + v_{NH_3} \xi}{n_0 + \xi V} = \frac{1 + 2\xi}{10 - 2\xi}$$

(b) The limiting reactant here is Nitrogen.

Let the fractional conversion of nitrogen be x . Then

Moles of nitrogen in the reaction mixture is $n_{N_2,0} - x n_{N_2,0}$

Moles of nitrogen in the mixture in terms of the extent of reaction is $n_{N_2,0} + v_{N_2} \xi$

Comparing the two results,

$$x = - \frac{v_{N_2} \xi}{n_{N_2,0}}$$

Since the stoichiometric number is negative for a reactant, the conversion given by the above

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equation will be always positive. The relationship between conversion and the extent of reaction can be written as

$$x = \frac{|v_{N_2}| \xi}{n_{N_2,0}}$$

In general, conversion can be treated as the fractional extent of reaction and is written as

$$x = \frac{\xi}{n_{i0} |v_i|} \quad \text{--- (3)}$$

31. Solution:

Let benzene be component 1 and cyclohexane be component 2. For the azeotrope

$$y_1^L = \frac{P}{P_1^s} = \frac{101.3}{100.59} = 1.007$$

$$y_2^L = \frac{P}{P_2^s} = \frac{101.3}{99.27} = 1.020$$

$$x_1 = 0.532 \quad \text{and} \quad x_2 = 0.468$$

Van Laar equation:

$$A = \ln y_1^L \left(1 + \frac{x_2 \ln y_2^L}{x_1 \ln y_1^L} \right)^2$$

$$= \ln(1.007) \left(1 + \frac{0.468 \ln(1.02)}{0.532 \ln(1.007)} \right)^2$$

$$A = 0.0853$$

$$B = \ln y_2^L \left(1 + \frac{x_1 \ln y_1^L}{x_2 \ln y_2^L} \right)^2 = \ln 1.02 \left(1 + \frac{0.532 \ln 1.007}{0.468 \ln 1.02} \right)^2$$

$$B = 0.0388$$

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 For a solution containing 10% benzene, $x_1 = 0.1$ & $x_2 = 0.9$
 For calculating the activity coefficient at this
 concentration, van Laar equations

$$\ln \gamma_1 = \frac{Ax_2^2}{\left[\frac{A}{B}x_1 + x_2 \right]^2} = \frac{0.0853 \times 0.9^2}{\left[\frac{0.0853}{0.0388} \times 0.1 + 0.9 \right]^2}$$

$$\ln \gamma_1 = 0.055 \Rightarrow \gamma_1 = 1.0566$$

$$\ln \gamma_2 = \frac{Bx_1^2}{\left[x_1 + \frac{B}{A}x_2 \right]^2} = \frac{0.0388 \times 0.1^2}{\left[0.1 + \frac{0.0388}{0.0853} \times 0.9 \right]^2}$$

$$\ln \gamma_2 = 1.4953 \times 10^{-3} \Rightarrow \gamma_2 = 1.001$$

32. Solution:

The standard free energy of reaction is

$$\Delta G^\circ = \sum_{\text{Products}} |V_i| \Delta G_{i,f}^\circ - \sum_{\text{Reactants}} |V_i| \Delta G_{i,f}^\circ$$

$$\Delta G^\circ = \sum_{\text{Products}} |V_i| \Delta G_{i,f}^\circ = 2 \times (-16,500) = -33,000 \frac{\text{J}}{\text{mol}}$$

The standard heat of reaction

$$\Delta H^\circ = -92,200 \frac{\text{J}}{\text{mol}}$$

WKT,

$$\Delta G^\circ = \Delta H^\circ - \Delta \alpha T \ln T - \frac{\Delta \beta}{2} T^2 - \frac{\Delta \gamma}{6} T^3 \quad \text{--- (1)}$$

$$\Delta \alpha = 2 \times 29.75 - 27.27 - 3 \times 27.01 = -48.8$$

$$\Delta \beta = (2 \times 25.11 - 4.93 - 3 \times 3.51) \times 10^{-3} = 34.76 \times 10^{-3}$$

WKT,

$$\Delta H_T^\circ = \Delta H^\circ + \Delta \alpha T + \frac{\Delta \beta}{2} T^2 + \frac{\Delta \gamma}{3} T^3 \quad \text{--- (2)}$$

$$\ln K = \frac{-\Delta H_T^\circ}{RT} + \frac{\Delta \alpha}{R} \ln T + \frac{\Delta \beta}{2R} T + \frac{\Delta \gamma}{6R} T^2 + A \quad \text{--- (3)}$$

$$-92,200 = \Delta H' - 48.8T + 17.38 \times 10^{-3} T^2$$

$$= \Delta H' - 48.8 \times 298 + 17.38 \times 10^{-3} \times (298)^2$$

$$-92,200 = \Delta H' - 1.3 \times 10^4$$

$$\Delta H' = -7.9201 \times 10^4$$

Substitute in eqn (1) and third term ΔS° can be neglected.

$$-33000 = \Delta H' - \Delta \alpha T \ln T - \frac{\Delta \beta}{2} T^2 - AT$$

$$-33000 = -7.9201 \times 10^4 + 48.8 \times 298 \times \ln 298 - 17.38 \times 10^{-3} \times 298^2 - A \times 8.314 \times 298$$

$$-33000 = 2105 - 2477.57 A$$

$$A = 14.169$$

Substitute $\Delta H'$ and A into eqn (1) and eqn (3)

$$\ln K = \frac{79201}{RT} - \frac{48.8}{R} \ln T + \frac{17.38 \times 10^{-3}}{R} T + 14.169$$

$$\Delta G^\circ = -79201 + 48.8T \ln T - 17.38 \times 10^{-3} T^2 - 14.169 RT$$

Put $T = 700K$ in the above equations, we get

$K = 1 \times 10^{-4}$
$\Delta G^\circ = 53607 \text{ J/mol}$

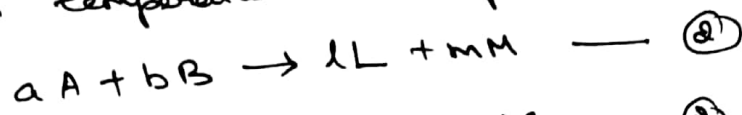
33. Relationship between standard free energy change and equilibrium constant:

The criterion of equilibrium for chemical reactions are

$$\sum \mu_i \nu_i = 0 \quad \text{--- (1)}$$

Consider a closed system in which a chemical reaction represented by the following general equation

has been allowed to reach a ^(6b) state of equilibrium at a given temperature and pressure.



The criterion of equilibrium for eqn (2) can be written for the general chemical reaction as

$$(l\mu_L + m\mu_M) - (a\mu_A + b\mu_B) = 0 \quad \text{--- (3)}$$

The chemical potential of a component in the equilibrium state of the reaction mixture is related to its fugacity in that state as given below

$$\mu_i = RT \ln \bar{f}_i + C \quad \text{--- (4)}$$

Suppose that at the same temperature, but at another state, which may be called the standard state, the free energy of component i is μ_i° .

$$\text{Then, } \mu_i^\circ = RT \ln \bar{f}_i^\circ + C \quad \text{--- (5)}$$

C is a constant that depends only on temperature. Since the temperature in the standard state is the same as that in the equilibrium state, C can be eliminated from eqn (4) using eqn (5) as,

$$\mu_i = \mu_i^\circ + RT \ln \frac{\bar{f}_i}{\bar{f}_i^\circ} = \mu_i^\circ + RT \ln a_i \quad \text{--- (6)}$$

where a_i is the activity of species i in the mixture.

Express the chemical potential of all the components as in equation (6)

$$(l\mu_L^\circ + m\mu_M^\circ) - (a\mu_A^\circ + b\mu_B^\circ) + RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b} = 0 \quad \text{--- (7)}$$

Equation (7) can be put into the following form:

$$\left(\sum \mu_i^\circ + m \mu_M^\circ \right) - \left(a \mu_A^\circ + b \mu_B^\circ \right) = -RT \ln \frac{a_L^1 a_M^m}{a_A^a a_B^b} \quad \text{--- (8)}$$

That is,

$$\sum \mu_i^\circ \nu_i = -RT \ln \frac{a_L^1 a_M^m}{a_A^a a_B^b}$$

The left-hand side gives the standard free energy change ΔG° , the free energy change accompanying the reaction when each of the reactants and the products is in its standard state. Using the definition of the equilibrium constant $K = \frac{a_L^1 a_M^m}{a_A^a a_B^b}$

$$\Delta G^\circ = -RT \ln K \quad \text{--- (9)}$$

Thus the equilibrium constant is determined by the standard free energy change and the temperature.

34. Models for vapour liquid equilibrium:

Among a number of equations between x and x that are available, as far as phase equilibrium problems are concerned, some equations have got wide acceptance. They are discussed in the following sections.

(i) Wohl's three-suffix equation:

$$\left. \begin{aligned} \ln x_1 &= x_2^2 \left[A + 2 \left(B \frac{v_1}{v_2} - A \right) x_1 \right] \\ \ln x_2 &= x_1^2 \left[B + 2 \left(A \frac{v_2}{v_1} - B \right) x_2 \right] \end{aligned} \right\} \quad \text{--- (1)}$$

x_1 and x_2 are the effective volume fraction of the

Separate components in the solution and v_1 and v_2 are the effective molar volumes, v_1 and v_2 are related as

$$v_1 = \frac{v_1}{x_1 + x_2 \left(\frac{v_2}{v_1}\right)} ; v_2 = \frac{v_2}{x_2 + x_1 \left(\frac{v_1}{v_2}\right)}$$

Equation (1) is known as Wohl's three-suffix equation. It involves three parameters, A, B and (v_1/v_2) which are characteristics of the binary system.

(ii) Margules equation:

When the term (v_1/v_2) is unity in eqn (1), the following expression, which is known as the Margules three-suffix equation.

$$\ln \gamma_1 = x_2^2 [A + 2(B-A)x_1] = (2B-A)x_2^2 + 2(A-B)x_2^3$$

$$\ln \gamma_2 = x_1^2 [B + 2(A-B)x_2] = (2A-B)x_1^2 + 2(B-A)x_1^3$$

The constant A in the above equation is the terminal value of $\ln \gamma_1$ at $x_1=0$ and the constant B is the terminal value of $\ln \gamma_2$ at $x_2=0$. The three-suffix Margules equation adequately represents the VLE data of systems like acetone-methanol, acetone-chloroform, chloroform-methanol etc.,

When $A=B$ in eqn (2), the Margules equation takes the following simple form

$$\ln \gamma_1 = Ax_2^2 ; \ln \gamma_2 = Ax_1^2 \quad \text{--- (3)}$$

Equation (3) is called the Margules two-suffix equation. It represents sufficiently and accurately the activity

Coefficients of Simple liquid mixtures.

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(iii) Van Laar equation:

Let $(a_1/a_2) = (A/B)$ in equation (1). The resulting two-parameter equation is known as the Van Laar equation.

$$\ln \gamma_1 = A x_2^2 = \frac{A x_2^2}{[(A/B)x_1 + x_2]^2}; \quad \ln \gamma_2 = B x_1^2 = \frac{B x_1^2}{[x_1 + (B/A)x_2]^2} \quad (4)$$

The Van Laar equation (4) may be rearranged to the following forms, which are very convenient for the evaluation of constants A and B.

$$A = \ln \gamma_1 \left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1} \right)^2; \quad B = \ln \gamma_2 \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2} \right)^2 \quad (5)$$

(iv) Wilson equation:

All the activity coefficient equations discussed so far can be deduced from the original Wohl's equation under proper simplifying assumptions. However, there are many equations that cannot be derived from the Wohl's general equation. Among such equations, the Wilson equation, the NRTL equation and the UNIQUAC equation are important from practical point of view. All these are based on the concept of local compositions, which are different from the overall mixture compositions.

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \quad (70)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \quad (6)$$

Wilson equations have two adjustable positive parameters Λ_{12} and Λ_{21} . These are related to the pure component molar volumes and to the characteristic energy differences by

$$\Lambda_{12} = \frac{V_2}{V_1} \exp \left[-\frac{\lambda_{12} - \lambda_{11}}{RT} \right] = \frac{V_2}{V_1} \exp \left[-\frac{a_{12}}{RT} \right]$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp \left[-\frac{\lambda_{21} - \lambda_{22}}{RT} \right] = \frac{V_1}{V_2} \exp \left[-\frac{a_{21}}{RT} \right] \quad (7)$$

where V_1 and V_2 are the molar volumes of pure liquids and λ 's are the energies of interaction between the molecules designated in the subscripts.

(V) Non-random two-liquid (NRTL) equation:

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

(8)

The two adjustable parameters are evaluated as

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

$$\text{and } \tau_{12} = \frac{b_{12}}{RT}; \quad \tau_{21} = \frac{b_{21}}{RT}$$

(vi) Universal quasi-chemical (UNIQUAC) equation:

$$\ln \gamma_1 = \ln \frac{\phi_1^*}{x_1} + \frac{z}{2} q_1 \ln \frac{Q_1}{\phi_1^*} + \phi_2^* \left(l_1 - \frac{q_1}{q_2} l_2 \right) - q_1' \ln(Q_1' + Q_2' \tau_{21}) + Q_2' q_1' \left(\frac{\tau_{21}}{Q_1' + Q_2' \tau_{21}} - \frac{\tau_{12}}{Q_2' + Q_1' \tau_{12}} \right)$$

$$\ln \gamma_2 = \ln \frac{\phi_2^*}{x_2} + \frac{z}{2} q_2 \ln \frac{Q_2}{\phi_2^*} + \phi_1^* \left(l_2 - \frac{q_2}{q_1} l_1 \right) - q_2' \ln(Q_2' + Q_1' \tau_{12}) + Q_1' q_2' \left(\frac{\tau_{12}}{Q_2' + Q_1' \tau_{12}} - \frac{\tau_{21}}{Q_1' + Q_2' \tau_{21}} \right)$$

(vii) Universal functional activity Coefficient (UNIFAC) method:

In the UNIFAC method, the activity coefficients are estimated through group contributions.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

$\gamma_i^C \Rightarrow$ Activity Coefficient of the Combinatorial part (the molecular size contribution)

$\gamma_i^R \Rightarrow$ Activity Coefficient of the Residual part (the interactions contributions).

35. Solution:

The mole fractions of the species at equilibrium are related to the equilibrium constant which is

given by

$$K_y = \frac{K}{K_\phi} P^{-v} \quad \text{--- (1)}$$

where v is the sum of stoichiometric numbers.

Here, $v = 1 + 1 - 1 - 1 = 0$. As the gas mixture behaves as an ideal gas, $K_\phi = 1$. Eqn (1) gives

$$K_y = K = 1$$

K_y is related to the mole fractions of various components as $K_y = \prod y_i^{v_i}$.

The relationship between mole fractions and extent of reaction at equilibrium as

$$y_i = \frac{n_i}{\sum n_i} = \frac{n_{i0} + v_i \xi}{\sum n_{i0} + \xi \sum v_i} = \frac{n_{i0} + v_i \xi}{n_0 + \xi V}$$

(a) The mole fractions of the constituents in the equilibrium mixture are expressed in terms of the extent of reaction as given in the table below:

Component	v_i	n_{i0} , mol	y_i
CO	-1	1	$(1-\xi)/2$
H ₂ O	-1	1	$(1-\xi)/2$
CO ₂	+1	0	$\xi/2$
H ₂	+1	0	$\xi/2$
n_0		2	

$$K_y = 1 = \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} = \frac{(\xi/2)(\xi/2)}{\left[\frac{(1-\xi)}{2}\right]\left[\frac{(1-\xi)}{2}\right]} = \frac{\xi^2}{(1-\xi)^2}$$

Solving the above, $\xi = 0.5$

Conversion of steam x is obtained from

$$\text{equation } x = \frac{|v_i| \xi}{n_{i0}} = 0.5$$

This means that 50% of steam is converted in the reaction.

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(b) Component	ν_i	$n_{i0, \text{mol}}$	y_i
CO	-1	1	$(1-\xi)/4$
H ₂ O	-1	1	$(1-\xi)/4$
CO ₂	+1	0	$\xi/4$
H ₂	+1	0	$\xi/4$
N ₂		2	
n_0		4	

$$K_y = 1 = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} = \frac{(\xi/4)(\xi/4)}{\left[\frac{(1-\xi)}{4}\right]\left[\frac{(1-\xi)}{4}\right]} = \frac{\xi^2}{(1-\xi)^2}$$

$\xi = 0.5$. The conversion of water vapour is 50%.