UNIT-V

Partial Molar Functions – Concepts of Chemical Potential (Δμ): Gibb’s Duhem Equation and its Application - Chemical Potential for Ideal gases. Variation of Δμ with T and P. Clapeyron Equation, Clausius – Clapeyron Equation: Derivations and their Applications. Activity , fugacity and activity coefficient (definition only). Law of Mass Action: Derivation of Kp and Kc and their relationship – Le Chatelier– Braun Principle – Thermodynamic Interpretation – Application to homogeneous and Heterogeneous Equilibria. Van’t Hoff isotherm and isochore.

Unit - V

Thermodynamics of Open Systems

Partial Molar Properties

- The Thermodynamic Properties U or E, H , S, A and G are extensive properties because of their values change with change in the mass (i.e., no. of moles) of the system.

- A tacit assumption was made that the system under consideration was a closed system ie., there is no change in the mass of the system.

- In the case of open system containing two or more components, there can be change in the number of moles of various components as well.

- Extensive property – X is a function of temperature and pressure but also of the number of moles of the various components present in the system.

- Let T and P be the temperature and Pressure, respectively, of a system and let n_1,n_2, n_3……. n_j be the respective number of moles of the constitutents,1,2,3,……j.

- X= f (T,P, n_1,n_2, n_3……. n_j)

  Where $n_1 + n_2 + n_3 + ……. + n_j$ = Total No. of moles =N

Partial Molar Property

- For a small change in T, P and number of moles of the components, the change in the property dX is given by the expression

$$dX = (\partial X/\partial T)_{P,N}\, dT + (\partial X/\partial P)_{T,N}\, dP +$$

$$(\partial X / \partial n_1)\ T, P, n_2, n_3 \ldots n_j\ dn_1 +$$

$$(\partial X / \partial n_2)_{T, P, n1, n3, n4 \ldots nj\ dn2} +$$

$$(\partial X / \partial n_i)_{T, P, n1, n2, n3 \ldots nj}\, dn_i +$$

$$(\partial X / \partial n_j)_{T, P, n1, n2, n3 \ldots nj-1}\, dn_j$$

…………………(1)

Partial Molar Property

- $(\partial X / \partial n_i)_{T, P, n1,n2,n3\ldots nj}$ is called the partial molar property of that component $\bar{X}_i$.

- Partial molar internal energy

  $= (\partial E / \partial n_i)_{T, P, n1,n2,n3\ldots} = \bar{E}_i$.

- Partial molar enthalpy

  $= (\partial H / \partial n_i)_{T, P, n1,n2,n3\ldots} = \bar{H}_i$.

- Partial molar entropy

  $= (\partial S / \partial n_i)\ T, P, n_{1,} n_2\ , n_3 \ldots\ = \overline{S}_{i}$.

- Partial molar volume

  $= (\partial V / \partial n_i)\ T, P, n_{1,} n_2\ , n_3 \ldots\ = \overline{V}_{i}$.

Partial Molar Free Energy – Concept of Chemical Potential

- It is represented as

$$(\partial G / \partial n_i)\ T, P, n_1 \ldots n_j = \overline{G_i} = \mu_i \quad \ldots\ldots\ldots\ldots\ldots(2)$$

- The chemical potential of a given substance is the change in free energy of the system that results on addition of one mole of that particular substance at a constant temperature and pressure, to such a large quantity of the system that there is no appreciable change in the overall composition of the system.

- For a small free energy change, eqn 1 may be written as

$$dX = (\partial X/\partial T)_{P,N}\, dT + (\partial X/\partial P)_{T,N}\, dP +$$

$$(\partial X / \partial n_1)_{T,\, P,\, n2\, ,n3\ldots nj}\, dn_1 +$$

$$(\partial X / \partial n_2)_{T,\, P,\, n1,n3\, ,n4\ldots nj}\, dn_2 +$$

$$(\partial X / \partial n_i)_{T,\, P,\, n1,n2\, ,n3\ldots nj}\, dn_i +$$

$$(\partial X / \partial n_j)_{T,\, P,\, n1,n2\, ,n3\ldots nj-1}\, dn_j$$

$$dG = (\partial G / \partial T)_{P,N}\, dT + (\partial G / \partial P)_{T,N}\, dP + \mu_1\, dn_1 + \mu_2\, dn_2 + \ldots\ldots \mu_j dn_j \quad \ldots\ldots\ldots\ldots\ldots(3)$$

- μ_1, μ_2 ……………. and μ_j are Chemical potentials of components 1,2….. and j, respectively.

- If temperature and pressure remains constant, then

$$(dG)_{T,P} = \mu_1\, dn_1 + \mu_2\, dn_2 + \ldots\ldots \mu_j dn_j \quad \ldots\ldots\ldots\ldots\ldots(4)$$

- If a system has a definite composition having n_1, n_2 ……n_j moles of constituents 1,2,………..j, respectively, then on integrating eqn (4),we have

$$(G)_{T,P} = n_1\, \mu_1 + n_2\mu_2 + \ldots\ldots n_j\mu_j \quad \ldots\ldots\ldots\ldots\ldots(5)$$

From eqn (5) , chemical potential may be defined as the contribution per mole of each particular constituent of the mixture to the total free energy of the system under conditions of constant temperature and pressure.

Gibbs-Duhem Equation

$(G)_{T,P} = n_1 \mu_1 + n_2\mu_2 + \ldots\ldots n_j\mu_j$ ……………(5)

- Equation (5) shows that the free energy of a system at constant temperature and pressure, can be expressed as sum of $n\mu_j$ terms for the individual components of the system.

- The total differential of G of equation (5) is written as

$$dG = (\mu_1\, dn_1 + n_1\, d\mu_1) + (\mu_2\, dn_2 + n_2\, d\mu_2) \ldots \mu_j dn_j + n_j\, d\mu_j)$$

$$dG = (\mu_1\, dn_1 + \mu_2\, dn_2 + \ldots\ \mu_j\, dn_j) + (n_1 d\mu_1 + n_2 d\mu_2 + \ldots\ldots + n_j\, d\,\mu_j)$$

…………………………………………..(6)

- The first term on the right hand side of equation(6) is equal to dG, at constant temperature and pressure, it follows that at constant temperature and pressure , for a system at definite composition

$$n_1 d\mu_1 + n_2 d\mu_{2} + \dots + n_j\, d\mu_j = 0$$

$$\varepsilon n_j\, d\mu_j = 0$$

This simple relationship is known as **Gibbs-Duhem equation.**

For a system having only two components

(ie., a binary solution), the above equation reduces to

$n_1 d\mu_1 + n_2 d\mu_2 = 0$ or $d\mu 1 = -(n_2/n_1)\, d\mu_2$

- The above equation shows the variation in chemical potential of one components affects the value for the other components as well.

- Thus if $d\mu_j$ is positive, ie., if μ_1 increases, then $d\mu_2$ must be negative ie., μ_2 must decrease and vice-versa.

Important Results

- There is no change in the number of moles of the various constituents of a system, that is when the system is the closed one, then

$dn_1, dn_2 \ldots . dn_j$ are all zero.

$$dG = (\partial G / \partial T)_{P,N}\, dT + (\partial G / \partial P)_{T,N}\, dP + \mu_1\, dn_1 + \mu_2\, dn_2 + \ldots \ldots \mu_j dn_j \quad \ldots\ldots\ldots\ldots\ldots (3)$$

In such case eqn reduces to

$$(\partial G / \partial T)_{P,N}\, dT + (\partial G / \partial P)_{T,N}\, dP$$

- For a closed system

$$dG = VdP - SdT$$

Hence by equating coefficients of dT and dP in the above two equations we get

$$(\partial G / \partial T)_{P,N} = -S$$

$$(\partial G / \partial P)_{T,N} = V$$

Class stopped here

VARIATION OF CHEMICAL POTENTIAL WITH TEMPERATURE

- The variation of chemical potential of any constituent of a system with temperature can be derived by differentiating equation (2) with respect to temperature

$$(\partial G / \partial n_i)_{T,\, P,\, n1\ldots\, nj} = \overline{G_i} = \mu_i \quad \ldots\ldots\ldots\ldots\ldots(2)$$

and equation $(\partial G / \partial T)_{P,N} = - S$

with respect to n,. The results are

$$\partial^2 G/ \partial n_i \partial T = (\partial \mu_i/ \partial T)_{P,N} \ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$\partial^2 G/ \partial T \partial n_i = - (\partial S/ \partial n_i)_{T,P, n_1,n_2, n_3\ldots\ldots n_j} = -\overline{S}_i . \ldots\ldots\ldots (2)$$

By definition S_i is the partial molar entropy of component i

It follows from equation 1 and 2 that

$$(\partial \mu_i/ \partial T)_{P,N} = -\overline{S}_i .$$

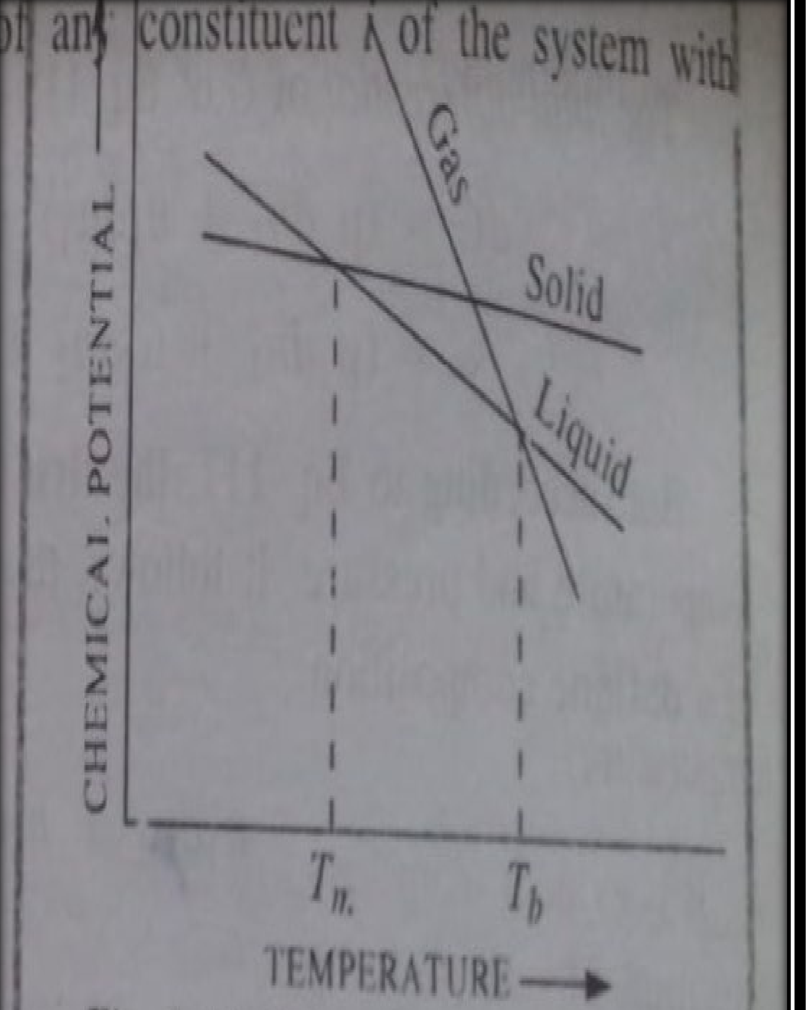


Fig. 3. Variation of chemical potential with temperature.

Reference: Physical Chemistry – Puri & Sharma

- Since the entropy of a substance is always positive, according to the equation

$$(\partial \mu i/ \partial T)_{P,N} = -\bar{S}_{i} .$$

The chemical potential would decrease with increase in temperature.

It is evident that at the melting point (Tm), the chemical potential of solid and liquid phases are same.

It is evident that at the boiling point (T_b), the chemical potential of liquid and gaseous phases are same.

Variation of Chemical Potential with pressure

The variation of chemical potential of any constituent i of the system with pressure may be derived by differentiating equation with respect to pressure

$$(\partial G / \partial n_i)\ T, P, n_1 \ldots n_j = \overline{G_i} = \mu_i$$

and this equation with respect to ni

$$(\partial G / \partial P)_{T,N} = V$$

$$\partial^2 G/\ \partial P\ \partial ni\ \ = (\partial \mu i/\ \partial P)_{T,N} \ldots\ldots\ldots\ldots\ldots\ \ (a)$$

$$\partial^2 G/\ \partial ni\ \partial P = \ (\partial V/\ \partial ni\ )\ _{T,P,\ n1,n2,\ n3\ldots\ldots\ nj} \quad = \overline{V}_{i\ .}\ \ldots\ldots\ldots.(b)$$

It is the partial molar volume of the component i

$$(\partial \mu i/\ \partial P)_{T,N} = \overline{V}_i$$

This equation gives the variation of chemical potential (µi) of any constituent of the system with pressure.

Chemical potential in a system of ideal Gases

- For a system of ideal gases,

Start revision from here

- $PV = nRT$
- Consider a system consisting of a number of ideal gases.
- Let n_1, n_2……. be the number of moles of various constituents present in the mixture.
- Then, in the ideal gas equation, n , the total number of moles may be replaced by $(n_1+n_2 + …..$
- Hence
- $V= nRT/P = (n_1+n_2+……………..)\ RT/P$ ……………………………..(1)
- Differentiating Eqn (1) with respect to ni at constant temperature and pressure, we have
  - $(\partial V/ \partial n_i)_{T,P,n1,n2}$ ………………………….. $= \bar{V}_i = RT/P$
- Substituting the values of $\bar{V}_i = RT/P$ in equation

$$(\partial \mu i/ \partial P)_{T,N} = \bar{V}_i$$

- $(\partial \mu i/ \partial P)_{T,N} = RT/P$ ……………… (2)

- For a constant composition of the gas and at constant temperature

- For a constant composition of the gas and at a constant temperature the equation 2 may also be expressed in the form

- $d\ \mu_i = (RT/P)\ dP = RT\ d\ln P$ ……………………………………………(3)

- Let P_i be the partial pressure of the constituent i present in the mixture. Since each constituent behaves as an ideal gas, therefore

- Since ni and n are constants, therefore on taking logarithms and then differentiating we get

$d\ln P_i = d\ln P$ ……………………………………………..(4)

- Substituting in equation $d\ \mu_i = (RT/P)\ dP = RT\ d\ln P$

$d\ \mu_i = RT\ d\ln P_i$ ……………………………………………………(5)

- On integrating equation (5), we get

$\mu_i = \mu_{i(P)}^0 + RT\ln P_i$ ………………… (6)

Where $\mu_{i(P)}^0$ is the integration constant, the value of which depends upon the nature of the gas and on the temperature.

- It is evident from equation (6) that the chemical potential of any constituent of a mixture of ideal gas is determined by its partial pressure in the mixture, if the partial pressure of the constituent i is unity i..e., pi =1, then

$\mu_i = \mu_{i(P)}^0$

- Thus $\mu_{i(P)}^0$ gives the chemical potential of the gaseous constituent i when the partial pressure of the constituent is unity, at a constant temperature

- According to equation (5) $p_i = (n_i/V)\ RT$

- Now n_i/V represents molar concentration, ie., the number of moles per unit volume of the constituents i in the mixture. If this concentration is represented by ci then equation (5) gives

$p_i = c_i\ RT$

Integrating the value of p_i in equation 6,

$$\mu_i = \mu_{i(P)}^0 + RT\ln P_i \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(6)}$$

we get

$$\mu_i = \mu_{i(P)}^0 + RT\ln (c_i RT) = \underbrace{\mu_{i(P)}^0 + RT\ln RT}_{\text{Constant}} + RT\ln c_i$$

$$= \mu_{i(c)}^0 + RT\ln c_i$$

Where $\mu_{i(c)}^0$ ($= \mu_{i(P)}^0 + RT\ln RT$) is a constant depending upon the nature of the gas and the temperature.

If $c_i = 1$, then $\mu_i = \mu_{i(c)}^0$. Thus $\mu_{i(c)}^0$ represents the chemical potential of the constituent i when the constituent in the mixture is unity at constant temperature.

Lastly since ni/n represents the mole fraction x_i of the constituent I in the mixture may be represented as

$$p_i = x_i P$$

Substituting the value of pi in equation , we have

$$\mu_i = \mu_{i(P)}^0 + RT\ln (x_i P) = \underbrace{\mu_{i(P)}^0 + RT\ln P}_{\text{Constant}} + RT\ln x_i$$

$$\text{Or } \mu_i = \mu_{i(x)}^0 + RT\ln x_i$$

Where the quantity

$$\mu_{i(x)}^0 = (\mu_{i(P)}^0 + RT\ln P)$$

Is also a constant which depends both on the temperature and the total pressure.

$$\text{If } xi = 1, \mu_i = \mu_{i(x)}^0$$

Thus $\mu_{i(x)}^0$ represents the chemical potential of the constituent I when its mole fraction, at a constant temperature and pressure, is unity.

Clapeyron-Clausius Equation

- It finds extensive application in one-component, two-phase systems, derived by Clapeyron and independently by Clausius, from Second law of thermodynamics and is generally known as Clapeyron-Clausius equation.

- The two phases in equilibrium may be any of the following types:

  - (i) Solid and Liquid $S \rightleftharpoons L$, at the melting point of the solid.
  - (ii) Liquid and Vapor $L \rightleftharpoons V$, at the boiling point of the liquid.
  - (iiI) Solid and Vapor $S \rightleftharpoons V$, at the sublimation temperature of the solid.

❖ (iV) One Crystalline Form and Another Crystalline Form as, for example, rhombic and monoclinic sulphur $S_R \rightleftharpoons SM$, at the transition temperature of the two allotropic forms.

❖ Consider any two phases of one and the same substance in equilibrium with each other at a given temperature and pressure.

❖ It is possible to transfer any definite amount of the substance from one phase to another in a thermodynamically reversible manner, ie., infinitesimally slowly , the system remaining in a state of equilibrium all along.

❖ For example, by applying heat infinitesimally slowly to the system, it is possible to change any desired amount of the substance from the liquid to the vapor phase at the same temperature and pressure.

❖Similarly by withdrawing heat is infinitesimally slowly from the system, it is possible to change any desired amount of the substance from the vapor to the liquid phase without any change in temperature and pressure.

❖Since the system remains in the state of equilibrium, the free energy change of either process will be zero.

- Hence equal amount of a given substance must have exactly the same free energy in the two phases at equilibrium with each other.

- Consider, in general the change of a pure substance from phase A to another phase B in equilibrium with it at a given temperature and pressure.

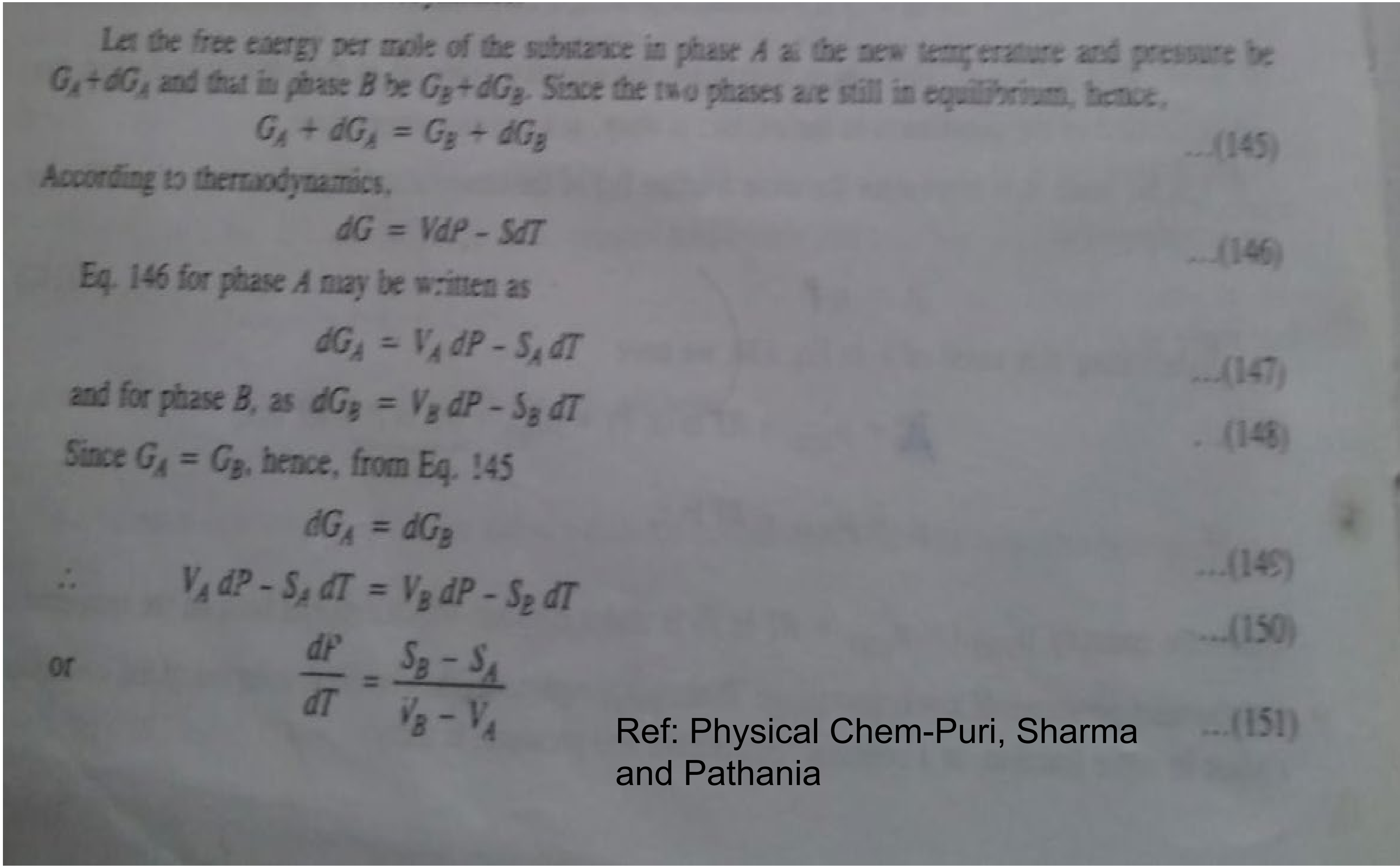
- If G_A is the free energy mole of the substance in the initial phase A and G_B is the free energy mole of the substance in the final phase B, then $G_A = G_B$ hence there will be no free energy change i.e.,

$$\Delta G = G_B - G_A = 0$$

- if the temperature of such a system is raised say from T to T+dT, the pressure will also will have to change from P to P+dP, in order to maintain the equilibrium.

- The relationship between dT and dP can be derived from thermodynamics.

- Let the free energy per mole of the substance in phase A at the new temperature and pressure be $G_A + dG_A$



Let the free energy per mole of the substance in phase A at the new temperature and pressure be G_A+dG_A and that in phase B be G_B+dG_B. Since the two phases are still in equilibrium, hence,

$$G_A + dG_A = G_B + dG_B \qquad \ldots(145)$$

According to thermodynamics,

$$dG = VdP - SdT \qquad \ldots(146)$$

Eq. 146 for phase A may be written as

$$dG_A = V_A\,dP - S_A\,dT \qquad \ldots(147)$$

and for phase B, as $dG_B = V_B\,dP - S_B\,dT$ ...(148)

Since $G_A = G_B$, hence, from Eq. 145

$$dG_A = dG_B \qquad \ldots(149)$$

$$\therefore \quad V_A\,dP - S_A\,dT = V_B\,dP - S_B\,dT \qquad \ldots(150)$$

or

$$\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} \qquad \ldots(151)$$

Ref: Physical Chem-Puri, Sharma and Pathania

It may be noted that since V_A and V_B are the molar volumes of the pure substance in the two phases A and B, respectively, $V_B - V_A$ represents the change in volume when one mole of the substance passes from the initial phase A to the final phase B. It may be represented by ΔV. Similarly, $S_B - S_A$, being the change in entropy for the same process, may be put as ΔS. Hence,

$$dP/dT = \Delta S/\Delta V \qquad \text{...(152)}$$

If q is the heat exchanged reversibly per mole of the substance during the phase transformation at temperature T, then the change of entropy (ΔS) in this process is given by $\Delta S = q/T$.

Hence,
$$\frac{dP}{dT} = \frac{q}{T\Delta V} \qquad \text{...(153)}$$

Thus,
$$\frac{dP}{dT} = \frac{q}{T(V_B - V_A)} \qquad \text{...(154)}$$

This is **Clapeyron equation.**

This equation, evidently, gives change in pressure dP which would accompany the change in temperature dT or *vice versa*, in the case of a system containing two phases of a pure substance in equilibrium with each other. Suppose the system consists of water in the two phases, *viz.*, liquid and vapour, in equilibrium with each other at the temperature T, *i.e.*,

$$\text{Water } (\textit{liquid}) \rightleftharpoons \text{Water } (\textit{vapour})$$

Then,

q = Molar heat of vaporisation, ΔH_v

V_B = Volume of one mole of water in the vapour state, say, V_g

V_A = Volume of one mole of water in the liquid state, say, V_l

Eq. 154, therefore, takes the form

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_g - V_l)} \qquad \text{...(155)}$$

Ref: Physical Chem-Puri, Sharma and Pathania

...(155)

If the system consists of water at its freezing point, then, the two phases in equilibrium will be

$$\text{Water } (\textit{Solid}) \textit{ i.e.}, \text{ ice} \rightleftharpoons \text{Water } (\textit{liquid})$$

Eq. 154 may then be written as

$$\frac{dP}{dT} = \frac{\Delta H_f}{T(V_l - V_s)} \qquad \text{...(156)}$$

where ΔH_f is the molar heat of fusion of ice.

Integrated Form of the Clapeyron Equation for Liquid $\rightleftharpoons$ Vapour Equilibrium. The Clapeyron equation (155), as applied to liquid $\rightleftharpoons$ vapour equilibrium, can be easily integrated. The molar volume of a substance in the vapour state is considerably greater than that in the liquid state. In the case of water, for example, the value of V_g at 100°C is $18 \times 1670 = 30060$ ml while that of V_l is only a little more than 18 ml. Thus, $V_g - V_l$ can be taken as V_g without introducing any serious error. The Clapeyron equation (155), therefore, may be written as

$$\frac{dP}{dT} = \frac{\Delta H_v}{TV_g} \qquad \text{...(157)}$$

Assuming that the gas law is applicable, *i.e.*, $PV = RT$ (per mole), $V_g = RT/P$

Hence,
$$\frac{dP}{dT} = \frac{\Delta H_v}{T} \times \frac{P}{RT} = P\frac{\Delta H_v}{RT^2} \qquad \text{...(158)}$$

or
$$\frac{1}{P} \times \frac{dP}{dT} = \frac{\Delta H_v}{RT^2} \quad \text{or} \quad \frac{d(\ln P)}{dT} = \frac{\Delta H_v}{RT^2} \qquad \text{...(159)}$$

Ref: Physical Chem-Puri, Sharma and Pathania

Assuming that ΔH_v remains constant over a small range of temperature, we have

$$\int d(\ln P) = \frac{\Delta H_v}{R}\int \frac{dT}{T^2} \quad \text{or} \quad P = -\frac{\Delta h_v}{R}\left(\frac{1}{T}\right) + C \qquad \text{...(160)}$$

where C is integration constant.

Eq. 160 is, the equation of a straight line. Hence, the plot of $\ln P$ against $1/T$ should yield a straight line with slope = $-\Delta H_v/R$ and intercept $= C$. This enables evaluation of ΔH_v.

Eq. 159 can also be integrated between limits of pressures P_1 and P_2 corresponding to temperatures T_1 and T_2. Thus,

$$\int_{P_1}^{P_2} d(\ln P) = \frac{\Delta H_v}{R}\int_{T_1}^{T_2} \frac{dT}{T^2} \qquad \text{...(161)}$$

$$\therefore \quad \ln\frac{P_2}{P_1} = -\frac{\Delta H_v}{R}\left[\frac{1}{T}\right]_{T_1}^{T_2} = \frac{\Delta H_v}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{\Delta H_v}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad \text{...(162)}$$

The integrated form of Clapeyron equation is known as the Clapeyron–Clausius equation.

Ref: Physical Chem-Puri, Sharma and Pathania

Applications of Clapeyron-Clausius Equation

1.Calculation of Molar heat of Vaporization

- Molar heat of Vaporization of a liquid can be calculated if its vapor pressure at two different temperatures are known.

$$\ln\frac{P_2}{P_1} = -\frac{\Delta H_v}{R}\left[\frac{1}{T}\right]_{T_1}^{T_2} = \frac{\Delta H_v}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] = \frac{\Delta H_v}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

2. Effect of temperature on Vapor pressure of a liquid

- If vapor pressure of a liquid at one temperature is known, the other temperature can be calculated.

3. Effect of Pressure on boiling point

- If the boiling point of a liquid at one pressure is known, the other pressure can be calculated.

Clapeyron-Clausius Equation for Solid ⇌ Vapour Equilibria. The Clapeyron equation for solid ⇌ vapour equilibrium may be written as

$$\frac{dP}{dT} = \frac{\Delta H_s}{T(V_g - V_s)} \qquad ...(163)$$

where ΔH_s stands for the molar heat of sublimation of the substance. Since the molar volume of a substance in the gaseous state is very much greater than that in the solid state, $V_g - V_s$ can be safely taken as V_g. Eq. 163 can thus be easily integrated, as before, to given the following expression ·

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_s}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad ...(164)$$

Eq. 164 can be put to the same use for solid ⇌ vapour equilibria as Eq.162 for liquid ⇌ vapour equilibria.

Application of the Clapeyron Equation for Solid ⇌ Liquid Equilibria. The Clapeyron equation (156) for solid ⇌ liquid equilibrium cannot be integrated easily since V_s cannot be ignored in comparison with V_l. Also the laws of liquid state are not so simple as those for gaseous state. However, this equation as such can be used for calculating the effect of pressure on the melting point of a solid and also for calculating heats of fusion from vapour pressure data obtained at different temperatures.

Ref: Physical Chem-Puri, Sharma and Pathania

Fugacity

- Fugacity (f) is a sort of ‘fictitious pressure’ which is used in order to retain for real gases simple forms of equations which are applicable to ideal gases only.

While for an ideal gas,

- $\Delta G = nRT \ln P_2/P_1$

for a real gas

$\Delta G = nRT \ln f_2/f_1$

The physical significance of fugacity is that it measures the escaping tendency of a substance from its own state to another state.

Activity & Activity coefficient

Activity

It is defined as the ratio of the fugacity of the substance in that state to the fugacity of the same substance in the pure state

$$a = f/ f^{o}$$

Activity Coefficient

For an ideal gas

$a = P$

While for a real gas $a \propto P$

$a = Y P$ Where Y is known as the activity coefficient

Chemical Equilibrium

Experimental results suggest that most of the chemical reactions when carried out in closed vessels do not go to completion.

Under these conditions, a reaction starts by itself by initiation, continues for some time at diminishing rates and ultimately appears to stop.

The reactants may still be present but they do not appear to change into products any more.

In such cases, the product of the reaction start reacting at the same rate as the reactants.

The rate of the backward reaction becomes equal to the forward reaction.

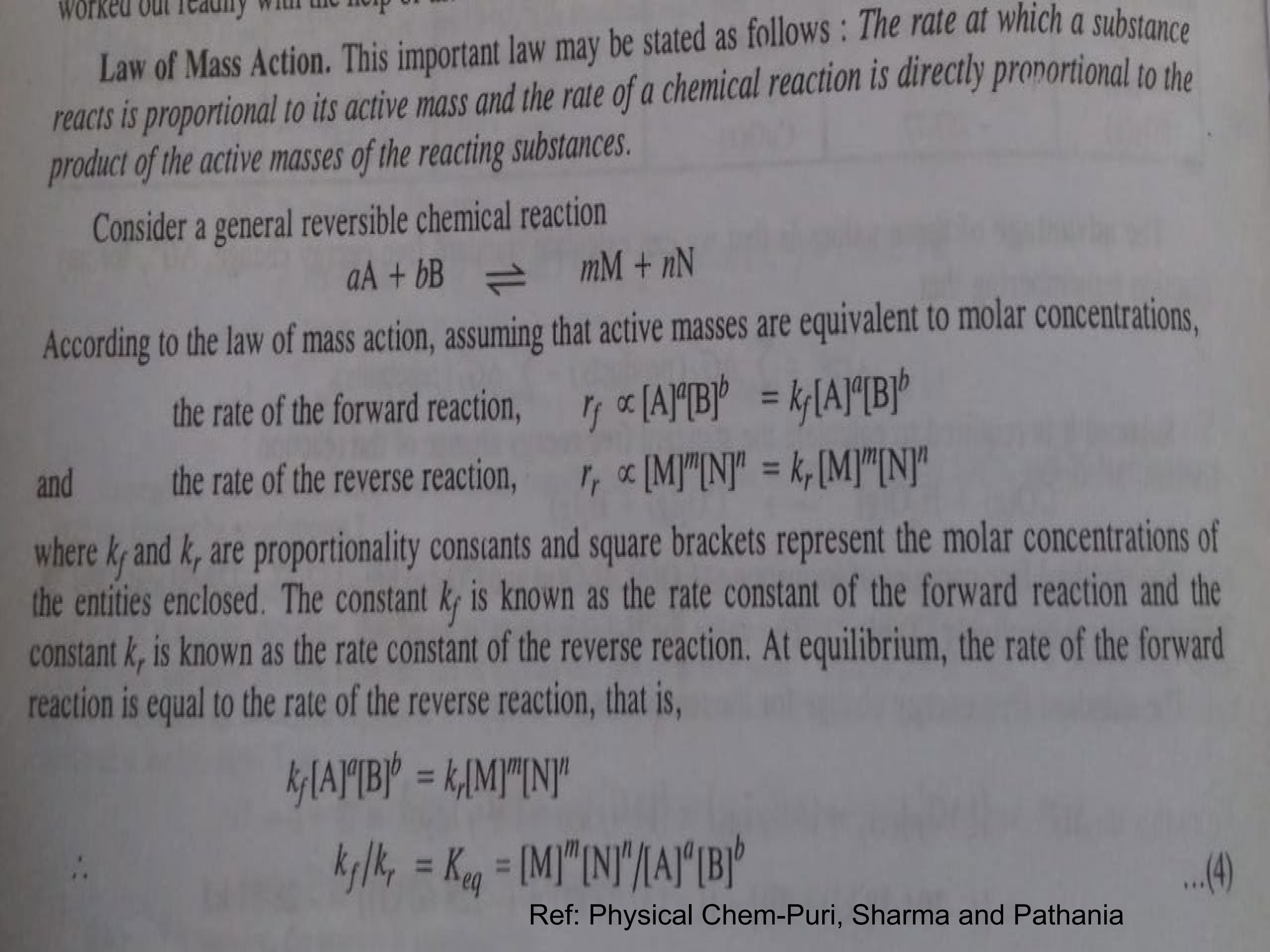
Thus, in a given time as much of the products are formed as react back to give the reactants.

The composition of the reaction mixture at a given temperature is the same irrespective of the initial state of the system i.e., irrespective of the fact whether we start with the reactants or the products.

The reaction in such condition is said to be in a state of equilibrium.

The attainment of equilibrium can be recognized by noting constancy of observable properties such as pressure, concentration, density or color whichever may be suitable in a given case.

The relationship between the quantities of the reacting substances and the products formed can be worked out readily with the help of **Law of mass action.**



worked out readily with the help of

Law of Mass Action. This important law may be stated as follows : *The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is directly proportional to the product of the active masses of the reacting substances.*

Consider a general reversible chemical reaction

$$aA + bB \rightleftharpoons mM + nN$$

According to the law of mass action, assuming that active masses are equivalent to molar concentrations,

the rate of the forward reaction, $r_f \propto [A]^a[B]^b = k_f[A]^a[B]^b$

and the rate of the reverse reaction, $r_r \propto [M]^m[N]^n = k_r[M]^m[N]^n$

where k_f and k_r are proportionality constants and square brackets represent the molar concentrations of the entities enclosed. The constant k_f is known as the rate constant of the forward reaction and the constant k_r is known as the rate constant of the reverse reaction. At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction, that is,

$$k_f[A]^a[B]^b = k_r[M]^m[N]^n$$

$$\therefore \quad k_f/k_r = K_{eq} = [M]^m[N]^n/[A]^a[B]^b \qquad \text{...(4)}$$

Ref: Physical Chem-Puri, Sharma and Pathania

The constant K_{eq} is called the **equilibrium constant** of the reaction. Eq. 4 represents the law of **chemical equilibrium.**

The equilibrium concentrations in Eq. 4 can be written in terms of activities (a_i), partial pressures (p_i), molar concentrations (c_i) or mole fractions (x_i) of the species involved in the reaction. Consequently, K_{eq} will have different numerical values for a given chemical reaction.

Thermodynamic Treatment of the Law of Mass Action. It may be pointed out that we cannot derive the law of mass action from thermodynamic considerations. We can only obtain an expression for the equilibrium constant thermodynamically.

Consider the general reversible reaction

$$aA + bB \rightleftharpoons mM + nN$$

where the reactants and the products are assumed to be *ideal gases.*

We know that chemical potential (*i.e.*, Gibbs free energy) of reactants consisting of *a* moles of A and *b* moles of B is given by the expression

$$G_{reactants} = a\mu_A + b\mu_B \qquad ...(5)$$

where μ_A and μ_B are the chemical potentials of the species A and B, respectively. Similarly, for the products we have

$$G_{products} = m\mu_M + n\mu_N \qquad ...(6)$$

In each case, pressure and temperature are constant. The free energy of the reaction is equal to the difference between the free energy of the products and that of the reactants, that is,

$$\begin{aligned}(\Delta G)_{reaction} &= G_{products} - G_{reactants} \\ &= (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) \qquad ...(7)\end{aligned}$$

Ref: Physical Chem-Puri, Sharma and Pathania

ctants, that is,

$$(\Delta G)_{\text{reaction}} = G_{\text{products}} - G_{\text{reactants}}$$

$$= (m\mu_{\text{M}} + n\mu_{\text{N}}) - (a\mu_{\text{A}} + b\mu_{\text{B}}) \qquad \text{...(7)}$$

At equilibrium, the free energy change $\Delta G=0$ so that Eq. 7 becomes

$$(m\mu_{\text{M}} + n\mu_{\text{N}}) - (a\mu_{\text{A}} + b\mu_{\text{B}}) = 0 \qquad \text{...(8)}$$

The chemical potential of the *i*th species in the gaseous state is given by

$$\mu_i = \mu_i^\circ + RT \ln p_i \qquad \text{(Chapter 11)} \qquad \text{...(9)}$$

where p_i is the partial pressure of the *i*th component and μ_i° is its standard chemical potential (*i.e.*, when partial pressure of the *i*th component is unity). From Eqs. 8 and 9, we obtain

$$[m(\mu_{\text{M}}^\circ + RT \ln p_{\text{M}}) + n(\mu_{\text{N}}^\circ + RT \ln p_{\text{N}})] - [a(\mu_{\text{A}}^\circ + RT \ln p_{\text{A}}) + b(\mu_{\text{B}}^\circ + RT \ln p_{\text{B}})] = 0 \qquad \text{...(10)}$$

or

$$RT \ln\, (p_{\text{M}}^m p_{\text{N}}^n)/(p_{\text{A}}^a p_{\text{B}}^b) = -[(m\mu_{\text{M}}^\circ + n\mu_{\text{N}}^\circ) - (a\mu_{\text{A}}^\circ - b\mu_{\text{B}}^\circ)]$$

$$= -[G_{\text{products}}^\circ - G_{\text{reactants}}^\circ] = -(\Delta G^\circ)_{\text{reaction}} \qquad \text{...(11)}$$

or

$$(p_{\text{M}}^m p_{\text{N}}^n)/(p_{\text{A}}^a p_{\text{B}}^b) = e^{-\Delta G^\circ/RT} \qquad \text{...(12)}$$

Since ΔG° depends only on temperature and R is the gas constant, hence the right hand side of Eq. 12 is a constant at constant temperature. Thus,

$$(p_{\text{M}}^m p_{\text{N}}^n)/(p_{\text{A}}^a p_{\text{B}}^b) = \text{constant} = K_p \qquad \text{...(13)}$$

If the chemical potentials of various species are expressed in terms of mole fractions (x_i), then

$$\mu_i = \mu_i^\circ + RT \ln x_i \qquad \text{...(14)}$$

From this the following expression analogous to Eq. 13 is obtained :

$$(x_{\text{M}}^m\, x_{\text{N}}^n)/(x_{\text{A}}^a\, x_{\text{B}}^b) = K_x \qquad \text{...(15)}$$

Ref: Physical Chem-Puri, Sharma and Pathania

$$(m\mu^0_M + mRT\ln P_M + n\mu^0_N + nRT\ln P_N)$$

$$-\Big[(a\mu^0_A + aRT\ln P_A) + b\mu^0_B + bRT\ln P_B)\Big] = 0$$

$$mRT\ln P_M \Rightarrow RT\ln P_M^m$$

IIIly for others

$$(RT\ln P_M^m + RT\ln P_N^n) - (RT\ln P_A^a + RT\ln P_B^b)$$

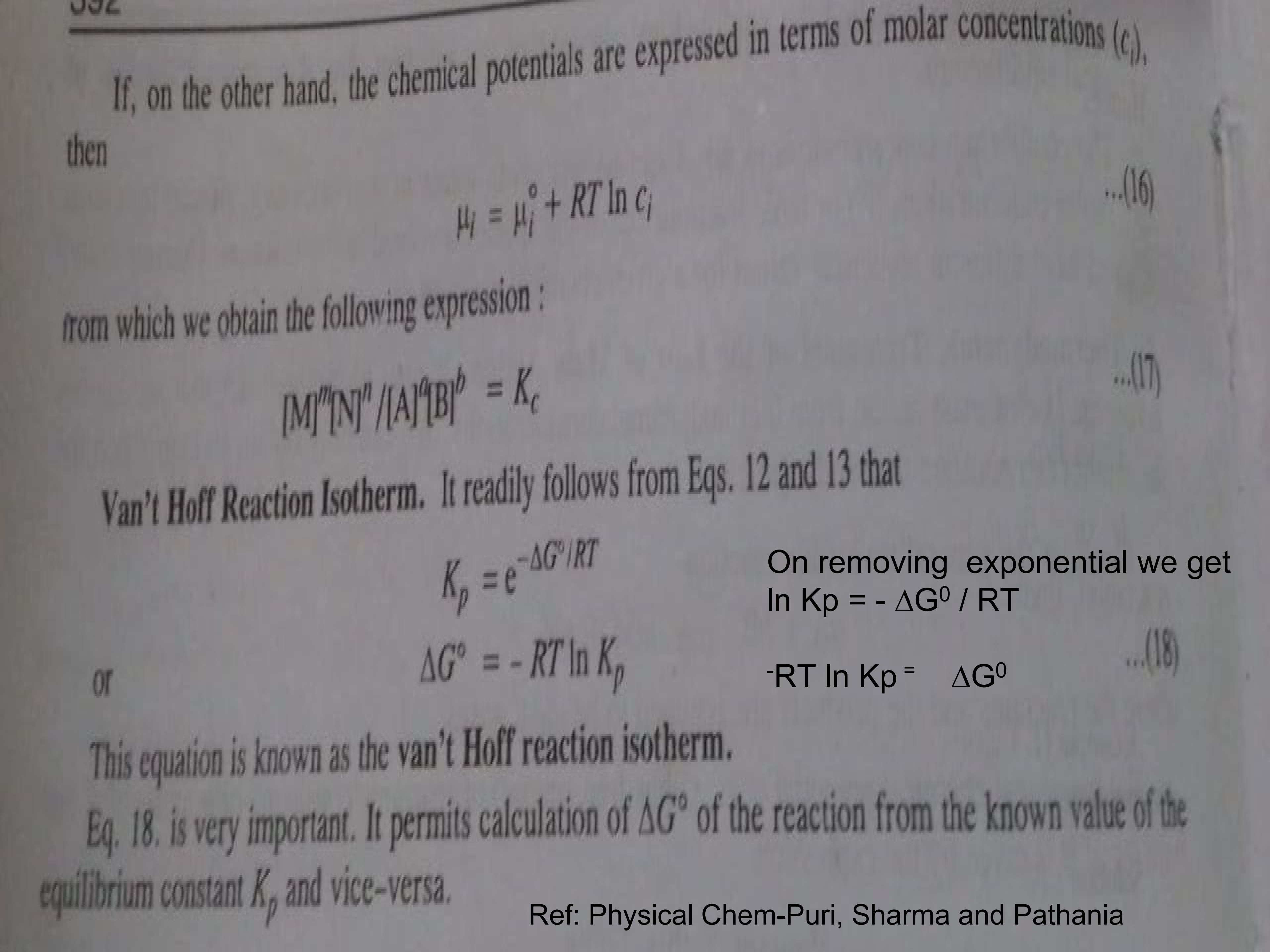
$$= \frac{RT\ln P_M^m P_N^n}{P_A^a P_B^b}$$

$$\Big[(m\mu^0_M + n\mu^0_N) - (a\mu^0_A + b\mu^0_B)\Big]$$

$$\frac{RT\ln P_M^m P_N^n}{P_A^a P_B^b} = -\Big[(m\mu^0_M + n\mu^0_N) - (a\mu^0_A + b\mu^0_B)\Big]$$

$$= -\Big[G_{products} - G_{reactant}\Big]$$

$$= -(\Delta G^0)_{reaction}$$



If, on the other hand, the chemical potentials are expressed in terms of molar concentrations (c_i), then

$$\mu_i = \mu_i^\circ + RT \ln c_i \qquad \text{...(16)}$$

from which we obtain the following expression :

$$[M]^m[N]^n/[A]^a[B]^b = K_c \qquad \text{...(17)}$$

Van't Hoff Reaction Isotherm. It readily follows from Eqs. 12 and 13 that

$$K_p = e^{-\Delta G^\circ/RT}$$

or

$$\Delta G^\circ = -RT \ln K_p \qquad \text{...(18)}$$

This equation is known as the **van't Hoff reaction isotherm.**

Eq. 18. is very important. It permits calculation of ΔG° of the reaction from the known value of the equilibrium constant K_p and vice-versa.

On removing exponential we get

$\ln Kp = - \Delta G^0 / RT$

$^{-}RT \ln Kp\ ^{=}\ \Delta G^0$

Ref: Physical Chem-Puri, Sharma and Pathania

- Derivation of Kp and Kc and their relationship – Le Chatelier–Braun Principle – Thermodynamic Interpretation – Application to homogeneous and Heterogeneous Equilibria. Vont Hoff isotherm and isochore.

Distinction between ΔG and ΔG°. We must emphasize the distinction between ΔG and ΔG° for a reaction. ΔG° is the difference in the free energy of products and reactants when all of them are in their standard states. This does not refer to the actual reaction at equilibrium. ΔG, however, refers to the difference in the free energy of products and reactants at the actual measured concentrations (or partial pressures) of the components. When $\Delta G=0$, the reaction is at equilibrium and the concentrations (or partial pressures) of the components are those which appear in the equilibrium constant expression.

Relations between K_p, K_c and K_x

We shall now proceed to establish the relations between the three equilibrium constants K_p, K_c and K_x.

a. Relation between K_p and K_x. In an ideal gaseous mixture, each component obeys Dalton's law of partial pressures, *i.e.*, $p_i = x_iP$ where P is the total pressure and p_i is the partial pressure of the ith component with mole fraction x_i in the mixture. For the reaction

$$aA + bB \rightleftharpoons mM + nN$$

we have $p_A = x_AP,\ \ p_B = x_BP,\ \ p_M = x_MP,\ \ P_N = x_NP$

$$\therefore \qquad K_p = \frac{p_M^m\, p_N^n}{p_A^a\, p_B^b} = \left(\frac{x_M^m\, x_N^n}{x_A^a\, x_B^b}\right) P^{(m+n)-(a+b)} = K_x(P)^{\Delta n} \qquad \text{...(19)}$$

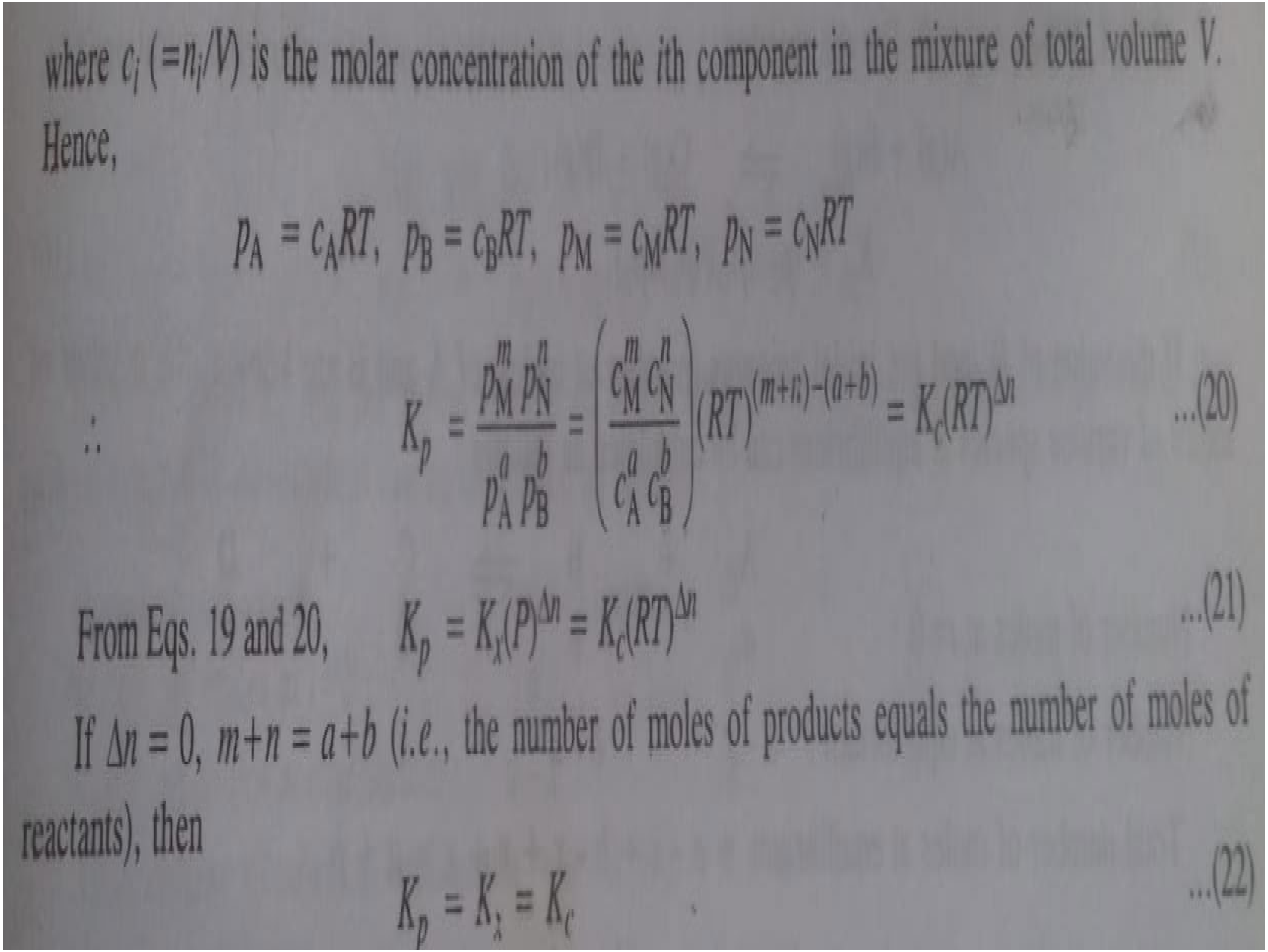
where $\Delta n = (m + n) - (a + b)$.

b. Relation between K_p and K_c. For an ideal gaseous mixture,

$$p_iV = n_iRT$$

$$\therefore \qquad p_i = (n_i/V)RT = c_i/RT$$

Ref: Physical Chem-Puri, Sharma and Pathania



where c_i ($=n_i/V$) is the molar concentration of the ith component in the mixture of total volume V.

Hence,

$$p_A = c_A RT,\quad p_B = c_B RT,\quad p_M = c_M RT,\quad p_N = c_N RT$$

$$\therefore \qquad K_p = \frac{p_M^m\, p_N^n}{p_A^a\, p_B^b} = \left(\frac{c_M^m\, c_N^n}{c_A^a\, c_B^b}\right)(RT)^{(m+n)-(a+b)} = K_c(RT)^{\Delta n} \qquad \text{...(20)}$$

From Eqs. 19 and 20, $K_p = K_x(P)^{\Delta n} = K_c(RT)^{\Delta n}$ ...(21)

If $\Delta n = 0$, $m+n = a+b$ (*i.e.*, the number of moles of products equals the number of moles of reactants), then

$$K_p = K_x = K_c \qquad \text{...(22)}$$

Ref: Physical Chem-Puri, Sharma and Pathania

Le Chatelier's Principle

Source: Internet

Statement :

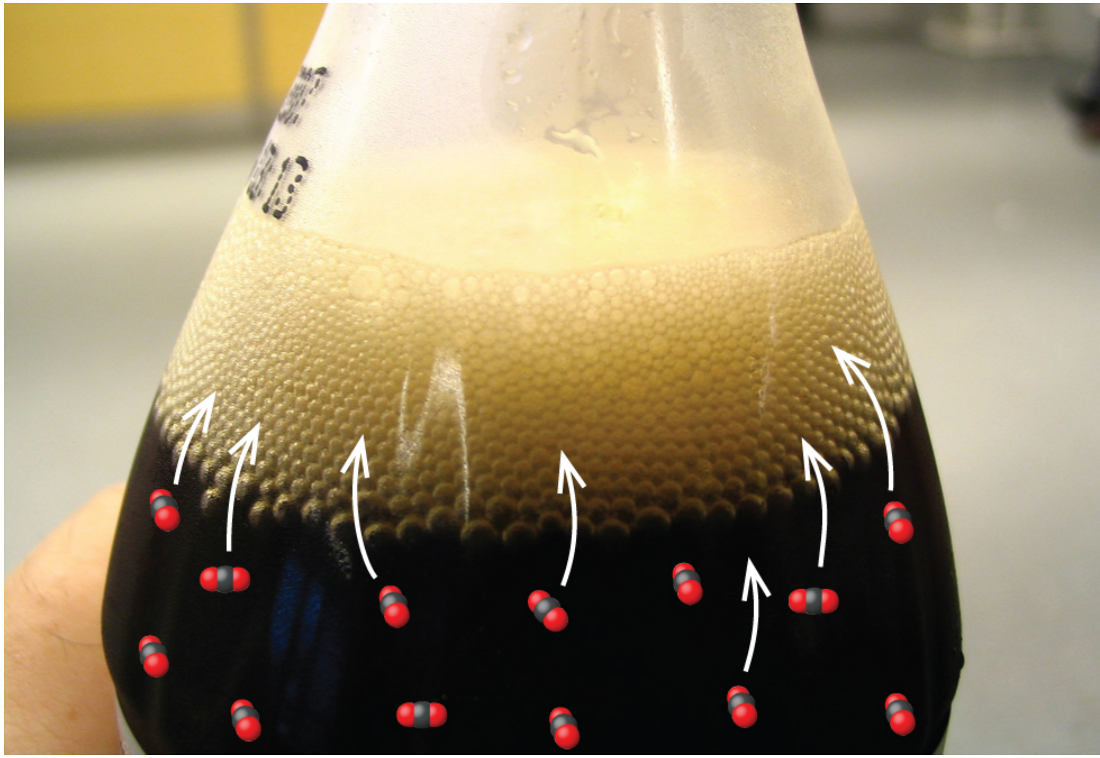
which states that any change in a substance on one side of the equation in concentration, temperature, or pressure results in an equilibrium shift to oppose the change until a new equilibrium is reached.

Or

If an equilibrium is subjected to a stress, the equilibrium shifts in such a way to reduce the stress.

For instance, you know that the volume of a gas decreases with increased pressure. So, if you have two volumes of gas in equilibrium, if one volume decreases with increased pressure, the other volume must increase with decreased pressure.

Source: Internet



Effect of Change of Concentration

Example

$$Fe^{3+} + SCN^{-} \longrightarrow [Fe(SCN)]^{2+}$$

aq aq aq

Pale Yellow Colorless Dark Yellow

Ferric salt is added to this equilibrium, the color of the solution will darken immediately – due to the increase in the concentration of the colored complex ion $[Fe(SCN)]^{2+}$

This is in accordance with Le Chatlier’s principle.

Addition of more Fe^{3+} ion has resulted in increasing the concentration of the complex ferri-sulphocyanide ion.

The change imposed on the system was meant to raise the concentration of one of the reactant (Ferric ions) resulted in the raising the concentration of the product.

If Sulphocyanide is added to the equilibrium the color will darken due to the formation of the ferri-sulphocyanide ion.

Addition of reactant has led to the formation of the product.

Now suppose a small amount of potassium ferri-sulphocyanide capable of giving the complex ion $[\mathrm{Fe(SCN)}]^{2+}$ is added to the equilibrium .

The solution will be less dark showing that the dark colored $[\mathrm{Fe(SCN)}]^{2+}$ complex ion has changed back to Fe^{3+} and SCN^{-} ion.

In general, increase in concentration of the reactants results in shifting the equilibrium towards the product and , increase in concentration of the product results in shifting the equilibrium towards the reactants.

Effect of Change of Temperature

A chemical equilibrium actually involves two opposing reactions , one favoring the reactant and the other favoring the product.

If one is exothermic, the other is endothermic. This follows First law of thermodynamics.

$$N_2O_{4\,(g)} \rightleftharpoons 2NO_{2\,(g)}$$

In this equilibrium, the reaction favoring the product (NO_2) is seen to be endothermic..

∴ The opposing reaction favoring the reactant (N_2O_4) must be exothermic.

Now suppose the system is heated and the temperature is allowed to rise

According to Le Chatlier Principle ..
The equilibrium will shift towards cooling.

Dissociation of N_2O_4 to NO_2

Now suppose the system is cooled vice-versa occurs.

Effect of Change of Pressure

If the system in equilibrium consists of gases, then the concentration of all the components can be altered by changing the pressure.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2\ (g)}$$

1 mole 2 mole

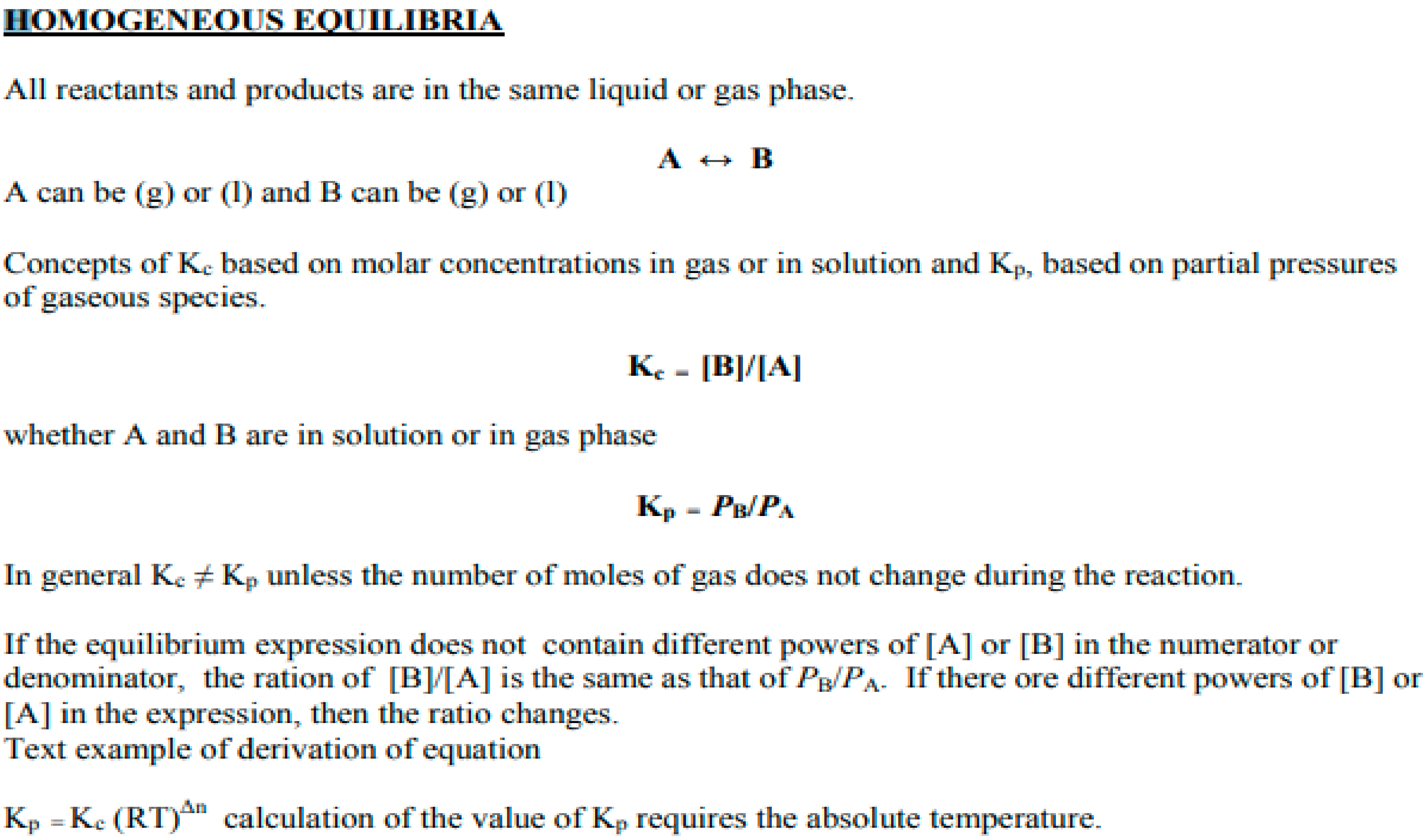
Suppose the pressure of the system is increased. The volume of the system decreases.

The total number of moles per unit volume will be more than before.

The change can be counteracted if equilibrium shifts in that direction in which the total number of moles is decreased.

This can take place by the combination of NO_2 molecules to produce N_2O_4.

According to Le Chatlier Principle, application of pressure on the above system tends to shift the equilibrium in favor of $N_2O_{4.}$



HOMOGENEOUS EQUILIBRIA

All reactants and products are in the same liquid or gas phase.

$$A \leftrightarrow B$$

A can be (g) or (l) and B can be (g) or (l)

Concepts of K_c based on molar concentrations in gas or in solution and K_p, based on partial pressures of gaseous species.

$$K_c = [B]/[A]$$

whether A and B are in solution or in gas phase

$$K_p = P_B/P_A$$

In general $K_c \neq K_p$ unless the number of moles of gas does not change during the reaction.

If the equilibrium expression does not contain different powers of [A] or [B] in the numerator or denominator, the ration of [B]/[A] is the same as that of P_B/P_A. If there ore different powers of [B] or [A] in the expression, then the ratio changes.
Text example of derivation of equation

$K_p = K_c (RT)^{\Delta n}$ calculation of the value of K_p requires the absolute temperature.

Examples

$$N_{2\,(g)} + O_{2\,(g)} \longrightarrow 2NO_{2\,(g)}$$

HETEROGENEOUS EQUILIBRIA

If a solid or liquid is part of a chemical equilibrium, its "concentration" is taken as unity and may be eliminated from the equilibrium expression.

$NH_3(g) + HCl(g) \leftrightarrow NH_4Cl(s)$

$K_{eq} = [NH_4Cl] / [NH_3]\cdot[HCl]$

Since NH_4Cl is a solid, its effective concentration in the reaction does not change as long as some solid is present. Since $[NH_4Cl]$ is constant, it can be eliminated from the right side of the equation and incorporated into the K_{eq} constant, which them becomes

$K_{eq} = 1/[NH_3]\cdot[HCl]$ if the molar concentrations of the gases will be expressed, or

$K_p = 1/P_{NH3} \cdot P_{HCl}$ if the gas pressures will be expressed.

$$CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)}$$

Van’t Hoff isotherm

- It gives the net work that can be obtained from a gaseous reactant at constant temperature when both the reactants and the products are at suitable arbitrary pressures.
- It can be derived using the equilibrium box which is a theoretical device with the supposition that of its four walls , one is permeable to A, the second to B, the third to C and the fourth to D during the gaseous reaction.

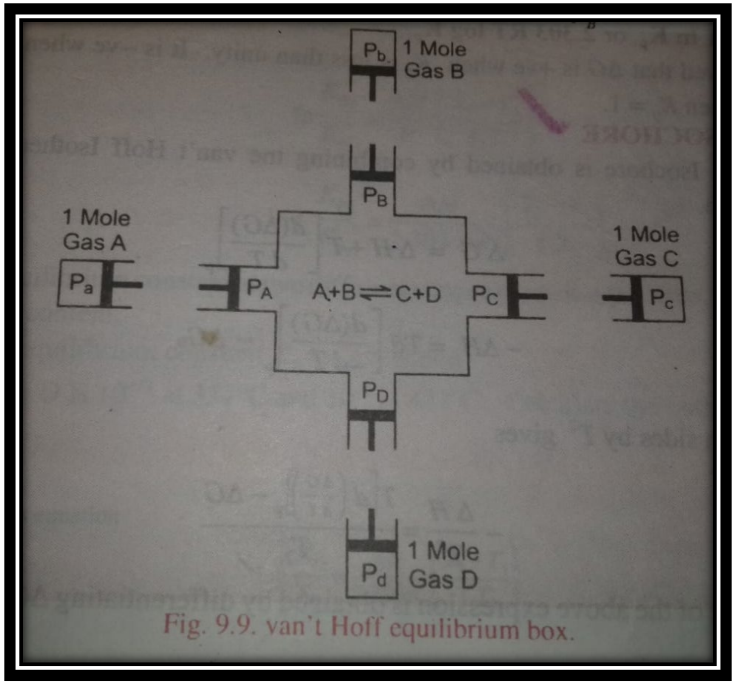


Fig. 9.9. van't Hoff equilibrium box.

Figure: Ref: Physical Chem-Puri, Sharma and Pathania

- The following theoretical operations can be performed .

(1) Change the pressure on A from the initial pressure P_a to the equilibrium pressure P_A.

- Work done by the gas $= RT \ln \dfrac{P_a}{P_A}$.

(2) Change the pressure on B from the initial pressure P_b to the equilibrium pressure P_B.

- Work done by the gas $= RT \ln \dfrac{P_b}{P_B}$.

(3) Introduce 1 gm mole of A and 1 gm mole of B through their respective semi permeable membranes into the equilibrium box which contains the reactants and products at equilibrium pressure.

No work is done as the partial pressure in A and B inside the box are equal to the pressures of the gases coming in

A and B react to form 1 gm mole of C and 1 gm mole of D..

(4) Withdraw 1 gm mole of C and 1 gm mole of D from the equilibrium box through their respective semi permeable walls.

No work is done in this process as the gases come out at the equilibrium pressure P_C and P_D

(5) Now alter the pressure on the gas from the equilibrium pressure P_C and P_D to the final pressure P_c and P_d

- Work done by the gas C = RT In $\frac{P_C}{P_c}$.

- Work done by the gas C = RT ln $\frac{P_D}{P_d}$.

As the change in free energy is equal to the total work done by the gases:

$$-\Delta G = RT \ln \frac{P_C\,P_D}{P_A.\,P_B.} - RT \ln \frac{P_c\,P_d}{P_a.\,P_b.}$$

$$= RT \ln K_p - RT \ln \frac{P_c\,P_d}{P_a.\,P_b.}$$

- If the reaction is started with reactants at a partial pressure of 1 atmosphere and the resulting products are also at 1 atmosphere pressure, we have,

$$-\Delta G = RT \ln K_p - RT \ln 1$$

$$-\Delta G = RT \ln K_p$$

- ie.,the net work of the reaction is equal to the decrease in free energy of the system and is given by the expression

$$-\Delta G = RT \ln K_p \text{ or } 2.303\ RT \log K_p$$

- It will be observed that ΔG is positive when K_p is less than unity. It is negative when K_p is greater then unity and is zero when $K_p = 1$.

Van’t Hoff isochore

- The van’t Hoff Isochore is obtained by combining the van’t Hoff isotherm with the Gibbs-Helmholtz equation.

$$\Delta G = \Delta H + T \left[\frac{d\,\Delta G}{dt} \right]_p$$

$$-\Delta H = T \left[\frac{d\,\Delta G}{dt} \right]_p - \Delta G$$

Dividing both sides by T^2 gives

$$-\frac{\Delta H}{T^2} = \frac{T\,d\left[\frac{\Delta G}{dt}\right]_p - \Delta G}{T^2}$$

- ❖ The right hand side of the above expression is obtained by differentiating

$$\frac{\Delta G}{T}$$ with respect to temperature at constant pressure.

$$\left\{ \frac{d\,(\Delta G)\,/T}{dt} \right]_p = \frac{T \left[\frac{\Delta G}{dt} \right]_p - \Delta G}{T^2}$$

$$\frac{-\Delta H}{T^2} = \left[\frac{d\ (\Delta G\,/T)}{dt} \right]_p \ \ldots\ldots\ldots\ldots \ (1)$$

According to van’t Hoff isotherm

$$- \Delta G = RT \ln K_p \text{ ----------------------}(2)$$

- Combining this with equation (1) ,we have

$$\frac{\Delta H}{T^2} = \frac{RT\, d(\ln K_p) / T}{dT}$$

$$\frac{\Delta H}{RT^2} = \frac{d(\ln K_p)}{dT}$$

Van’t Hoff Isochore

- For applying isochore to any particular reaction ,it is necessary to integrate it. If ΔH remains constant over a range of temperatures , we have on integration

$$\ln K_p = \int \frac{\Delta H}{R\,T^2}\, dT$$

$$= -\frac{\Delta H}{R\,T} + \text{Constant}$$

Applying the limits T_1 and T_2 at which the equilibrium constants are K_{p1} and K_{p2} respectively, we have

$$\ln K_{p2} - \ln K_{p1} = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln K_{p2} - \ln K_{p1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln \frac{K_{p2}}{K_{p1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{K_{p2}}{K_{p1}} = \frac{\Delta H}{2.303 \times R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

❖ Knowing the equilibrium constant at two different temperatures it is possible, therefore , to calculate the change in heat content.