Thermodynamic description of mixtures:

We have already seen that the partial pressure, which is the contribution of one component to the total pressure, is used to discuss the properties of mixtures of gases. For a more general description of the thermodynamics of mixtures we need to introduce other analogous 'partial' properties.

1. Partial molar quantities:

The easiest partial molar property to visualize is the 'partial molar volume', the contribution that a component of a mixture makes to the total volume of a sample.

(a) **Partial molar volume:** Imagine a huge volume of pure water at 25°C. When a further 1 mol H_2O is added, the volume increases by 18 cm^3 and we can report that 18 cm3 mol^{-1} is the molar volume of pure water. However, when we add 1 mol H_2O to a huge volume of pure ethanol, the volume increases by only 14 cm^3. The reason for the different increase in volume is that the volume occupied by a given number of water molecules depends on the identity of the molecules that surround them. In the latter case there is so much ethanol present that each H_2O molecule is surrounded by ethanol molecules, and the packing of the molecules results in the H_2O molecules increasing the volume by only 14 cm^3. The quantity 14 cm^3 mol^{-1} is the partial molar volume of water in pure ethanol. In general, the partial molar volume of a substance A in a mixture is the change in volume per mole of A added to a large volume of the mixture.
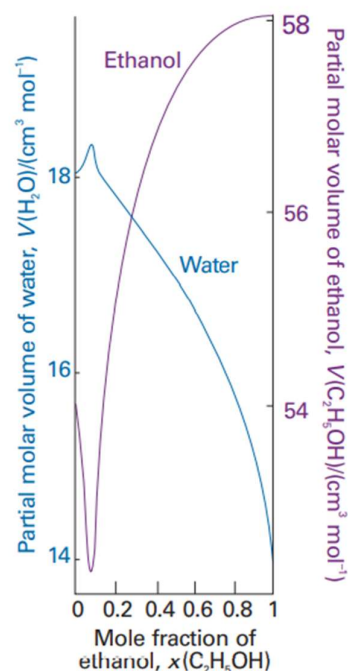

Fig. 1.1 The partial molar volumes of water and ethanol at 25°C. Note the different scales (water on the left, ethanol on the right)

The partial molar volumes of the components of a mixture vary with composition because the environment of each type of molecule changes as the composition changes from pure A to pure B. It is this changing molecular environment, and the consequential modification of the forces acting between molecules, that results in the variation of the thermodynamic properties of a mixture as its composition is changed. The partial molar volumes of water and ethanol across the full composition range at 25°C are shown in **Fig. 1.1**.

The partial molar volume, V_i, of a substance i at some general composition is defined formally as follows:

$$V_i = \left(\frac{\delta V}{\delta n_i}\right)_{p,T,n_j} \qquad \text{... ... ... (1.1)}$$

where the subscript n_j signifies that the amounts of all other substances present are constant. The partial molar volume is the slope of the plot of the total volume as the amount of i is changed, the pressure, temperature, and amount of the other components being constant (Fig. 1.2). Its value depends on the composition, as we saw for water and ethanol. The definition in

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College

eqn 1.1 implies that, when the composition of the mixture is changed by the addition of dn_A of A and dn_B of B, then the total volume of the mixture changes by

$$dV = \left(\frac{\delta V}{\delta n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\delta V}{\delta n_B}\right)_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B \quad \ldots\ldots(1.2)$$

Provided the composition is held constant as the amounts of A and B are increased, the final volume of a mixture can be calculated by integration. Because the partial molar volumes are constant (provided the composition is held constant throughout the integration) we can write

$$dV = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B$$

$$= V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B$$

$$= V_A n_A + V_B n_B \qquad \ldots\ldots\ldots\ldots\ldots(1.3)$$

Although we have envisaged the two integrations as being linked (in order to preserve constant composition), because V is a state function the final result in eqn 1.3 is valid however the solution is in fact prepared. Partial molar volumes can be measured in several ways. One method is to measure the dependence of the volume on the composition and to fit the observed volume to a function of the amount of the substance. Once the function has been found, its slope can be determined at any composition of interest by differentiation.
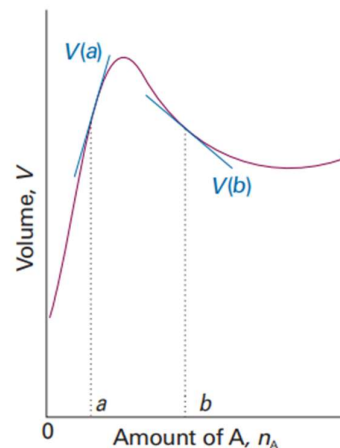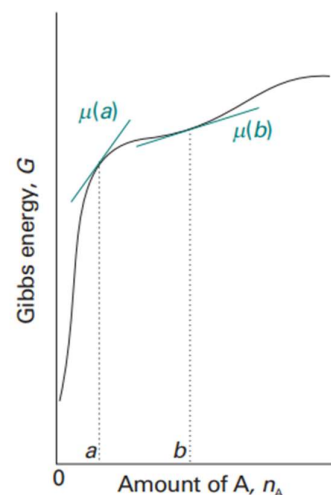
Fig. 1.2 The partial molar volume of a substance is the slope of the variation of the total volume of the sample plotted against the composition. In general, partial molar quantities vary with the composition, as shown by the different slopes at the compositions a and b. Note that the partial molar volume at b is negative: the overall volume of the sample decreases as A is added

Molar volumes are always positive, but partial molar quantities need not be. For example, the limiting partial molar volume of $MgSO_4$ in water (its partial molar volume in the limit of zero concentration) is -1.4 cm^3 mol^{-1}, which means that the addition of 1 mol $MgSO_4$ to a large volume of water results in a decrease in volume of 1.4 cm^3. The mixture contracts because the salt breaks up the open structure of water as the ions become hydrated, and it collapses slightly.

(b) Partial molar Gibbs energies

The concept of a partial molar quantity can be extended to any extensive state function. For a substance in a mixture, the chemical potential is defined as the partial molar Gibbs energy:

$$\mu_i = \left(\frac{\delta G}{\delta n_i}\right)_{p,T,n_j} \qquad \ldots\ldots\ldots(1.1)$$

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College

That is, the chemical potential is the slope of a plot of Gibbs energy against the amount of the component i, with the pressure and temperature (and the amounts of the other substances) held constant (Fig. 1.4). For a pure substance we can write $G = n_i G_{i,m}$, and from eqn 1.4 obtain

Fig. 1.4 The chemical potential of a substance is the slope of the total Gibbs energy of a mixture with respect to the amount of substance of interest. In general, the chemical potential varies with composition, as shown for the two values at a and b. In this case, both chemical

$\mu_i = G_{i,m}$: in this case, the chemical potential is simply the molar Gibbs energy of the substance. By the same argument that led to eqn 1.3, it follows that the total Gibbs energy of a binary mixture is

$$G = n_A \mu_A + n_B \mu_B \quad \ldots\ldots\ldots\ldots (1.5)$$

where μ_A and μ_B are the chemical potentials at the composition of the mixture. That is, the chemical potential of a substance in a mixture is the contribution of that substance to the total Gibbs energy of the mixture. Because the chemical potentials depend on composition (and the pressure and temperature), the Gibbs energy of a mixture may change when these variables change, and for a system of components A, B, etc., the equation $dG = Vdp - SdT$ becomes

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots \quad (1.6)$$

This expression is the *fundamental equation of chemical thermodynamics*. Its implications and consequences are explored and developed. At constant pressure and temperature, eqn 1.6 simplifies to

$$dG = \mu_A dn_A + \mu_B dn_B + \cdots \quad (1.7)$$

We know that under the same conditions $dG = dw_{add,max}$. Therefore, at constant temperature and pressure,

$$dw_{add,max} = \mu_A dn_A + \mu_B dn_B + \cdots \quad (1.8)$$

That is, additional (non-expansion) work can arise from the changing composition of a system. For instance, in an electrochemical cell, the chemical reaction is arranged to take place in two distinct sites (at the two electrodes). The electrical work the cell performs can be traced to its changing composition as products are formed from reactants.

(c) The wider significance of the chemical potential

The chemical potential does more than show how G varies with composition. Because G = U + pV − TS, and therefore U = −pV + TS + G, we can write a general infinitesimal change in U for a system of variable composition as

$$dU = -pdV - VdP + SdT + TdS + dG$$
$$= -pdV - VdP + SdT + TdS + (-VdP - SdT + \mu_A dn_A + \mu_B dn_B + \cdots)$$
$$= -pdV + TdS + \mu_A dn_A + \mu_B dn_B + \cdots$$

This expression is the generalization of previous relation (that $dU = TdS - pdV$) to systems in which the composition may change. It follows that at constant volume and entropy

$$dU = \mu_A dn_A + \mu_B dn_B + \cdots \quad (1.9)$$

and hence that

$$\mu_i = \left(\frac{\delta U}{\delta n_i}\right)_{S,V,n_j} \quad \ldots\ldots\ldots (2.0)$$

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College

Therefore, not only does the chemical potential show how G changes when the composition changes, it also shows how the internal energy changes too (but under a different set of conditions). In the same way it is easy to deduce that

(a) $\mu_i = \left(\frac{\delta H}{\delta n_i}\right)_{S,P,n_j}$ (b) $\mu_i = \left(\frac{\delta A}{\delta n_i}\right)_{V,T,n_j}$ $\ldots\ldots\ldots(1.11)$

Thus, we see that the μ_i shows how all the extensive thermodynamic properties U, H, A, and G depend on the composition. This is why the chemical potential is so central to chemistry.

(d) The Gibbs–Duhem equation:
Because the total Gibbs energy of a binary mixture is given by eqn 1.5 and the chemical potentials depend on the composition, when the compositions are changed infinitesimally, we might expect G of a binary system to change by
$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$$
However, we have seen that at constant pressure and temperature a change in Gibbs energy is given by eqn 1.7. Because G is a state function, these two equations must be equal, which implies that at constant temperature and pressure
$$n_A d\mu_A + n_B d\mu_B = 0 \quad \ldots\ldots(1.12a)$$

This equation is a special case of the Gibbs–Duhem equation:

$$\sum_i n_i d\mu_i = 0 \qquad \ldots\ldots(1.12b)$$

The significance of the Gibbs–Duhem equation is that the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components. In a binary mixture, if one partial molar quantity increases, then the other must decrease, with the two changes related by

$d\mu_B = -\frac{n_A}{n_B} d\mu_A$ $\ldots\ldots\ldots\ldots\ldots(1.13)$

The same line of reasoning applies to all partial molar quantities. We can see in Fig. 1.1, for example, that, where the partial molar volume of water increases, that of ethanol decreases. Moreover, as eqn 1.13 shows, and as we can see from Fig. 1.1, a small change in the partial molar volume of A corresponds to a large change in the partial molar volume of B if n_A/n_B is large, but the opposite is true when this ratio is small. In practice, the Gibbs-Duhem equation is used to determine the partial molar volume of one component of a binary mixture from measurements of the partial molar volume of the second component.

Chemical Potential:

$$\left(\frac{\delta G}{\delta n_i}\right)_{T,P,n_j} = \mu_i$$

G is an extensive, n_i is extensive, so μ_i is intensive. μ_i has the same value everywhere within a system at equilibrium.

Let us transfer dn_i amount of $_i$ from A to B

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College
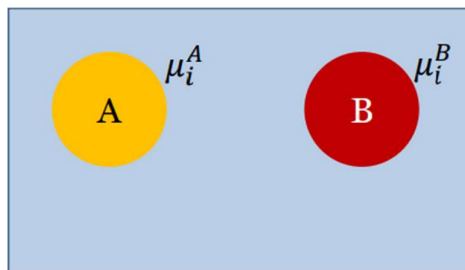
$$dG^A = \mu_i^A(-dn_i)$$

$$dG^B = \mu_i^B(dn_i)$$

Total change in Gibbs free energy of the system,

$$dG = dG^A + dG^B = \mu_i^A(-dn_i) + \mu_i^B(dn_i)$$

$$dG = (\mu_i^B - \mu_i^A)dn_i$$

If $\mu_i^B > \mu_i^A$, then $dG > 0$; Nonspontaneous Process

If $\mu_i^A > \mu_i^B$, then $dG < 0$; Spontaneous Process

Substance i flows from area of high chemical potential to area of low chemical potential.

All flow stops when $\mu_i^A = \mu_i^B$, and, dG=0; and the system is in equilibrium!!

μ_i is hence called "**Chemical Potential**". It is a measure of escaping tendency. If μ_i is high at a point in the system, substance wants to escape from there.

For a mixture, $G = \sum_i \mu_i n_i$ *For pure substancs*, $G = \mu\, n$

Molar Gibbs free energy $\mu = \dfrac{G}{n} = \bar{G} = G_m$

Now, $dG = SdT + Vdp + \mu\, dn$

At constant T and n, dG=Vdp

$$G_m(p) = G_m^0 + \int_{p_0}^{p} V_m dp$$

For an ideal gas,

$$G_m(p) = G_m^0 + RT ln\frac{p}{p_0}$$

At constant T, the pressure, p gives the measure of potential of a gas (p_0=1atm)

$$\mu = \mu^0 + RT ln\, p$$

Gas flows from areas of high pressure to low, till pressure is uniform throughout: mechanical equilibrium!

Variation of Chemical Potential (μ) with Temperature and Pressure:

Thermodynamics of Mixing

When solids, liquids or gases are combined, the thermodynamic quantities of the system experience a change as a result of the mixing. This module will discuss the effect that mixing

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College

has on a solution's Gibbs energy, enthalpy, and entropy, with a specific focus on the mixing of two gases.

A solution is created when two or more components mix homogeneously to form a single phase. Studying solutions is important because most chemical and biological life processes occur in systems with multiple components. Understanding the thermodynamic behavior of mixtures is integral to the study of any system involving either ideal or non-ideal solutions because it provides valuable information on the molecular properties of the system.

Most real gases behave like ideal gases at standard temperature and pressure. This allows us to combine our knowledge of ideal systems and solutions with standard state thermodynamics in order to derive a set of equations that quantitatively describe the effect that mixing has on a given gas-phase solution's thermodynamic quantities.

Gibbs Free Energy Mixing:

Unlike the extensive properties of a one-component system, which rely only on the amount of the system present, the extensive properties of a solution depend on its temperature, pressure and composition. This means that a mixture must be described in terms of the partial molar quantities of its components. The total Gibbs free energy of a two-component solution is given by the expression

$$G = n_1 \bar{G}_1 + n_2 \bar{G}_2 \quad \ldots\ldots(1)$$

Where G is the total Gibbs energy of the system, n_i is the number of moles of component i, and $\bar{G}_i$ is the partial molar Gibbs energy of component i.

The molar Gibbs energy of an ideal gas can be found using the equation

$$\bar{G} = \bar{G}^\circ + RT \ln P_1$$

where $\bar{G}^\circ$ is the standard molar Gibbs energy of the gas at 1 bar, and P is the pressure of the system. In a mixture of ideal gases, we find that the system's partial molar Gibbs energy is equivalent to its chemical potential, or that

$$\bar{G}_i = \mu_i$$

This means that for a solution of ideal gases, Equation can become

$$\bar{G} = \mu_i = \mu_i^0 + RT \ln \frac{P_i}{1bar} \quad \ldots\ldots(2)$$

Where, μ_i is the chemical potential of the ith component, μ_i^0 is the standard chemical potential of component i at 1 bar, and P_i is the partial pressure of component i.

Now pretend we have two gases at the same temperature and pressure, gas 1 and gas 2. The Gibbs energy of the system before the gases are mixed is given by Equation1, which can be combined with Equation2 to give the expression

$$G_{initial} = n_1 (\mu_i^0 + RT \ln P) + n_2 (\mu_2^0 + RT \ln P)$$

If gas 1 and gas 2 are then mixed together, they will each exert a partial pressure on the total system, P_1 and P_2, so that final Gibbs free energy of the final solution can be found using equation

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College

$$G_{final} = n_1(\mu_i^0 + RTlnP_1) + n_2(\mu_2^0 + RTlnP_2)$$

The Gibbs energy of mixing, $\Delta_{mix}G$, can then be found by subtracting G_{final} and $G_{initial}$

$$\Delta_{mix}G = G_{final} - G_{initial}$$

$$= n_1 RTln\frac{P_1}{P} + n_2 RTln\frac{P_2}{P}$$

$$= n_1 RTlnx_1 + n_2 RTlnx_2 \quad .....(3)$$

Where, $P_i = x_i P$ and x_i is the mole fraction of gas i. This equation can be simplified further that the mole fraction of a component is equal of moles of that components over the total moles of the system, or

$$x_i = \frac{n_i}{n}$$

Equation 3 then becomes

$$\Delta_{mix}G = nRT(lnx_1 + lnx_2) \quad .....(4)$$

This expression gives us the effect that mixing has on the Gibbs free energy of a solution. Since x_1 and x_2 are mole fractions that range from 0 to 1, we can conclude that $\Delta_{mix}G$ will be a negative number. This is consistent with the idea that gases mix spontaneously at constant pressure and temperature.
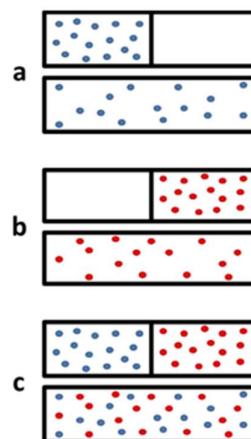
Equation4 can be written as,

$$\Delta_{mix}G = nRT \sum_i x_i lnx_i$$

Entropy of mixing:

Figure 1 shows that when two gases mix, it can really be seen as two gases expanding into twice their original volume. This greatly increases the number of available microstates, and so we would therefore expect the entropy of the system to increase as well.

Thermodynamic studies of an ideal gas's dependence of Gibbs free energy of temperature have shown that

$$\left(\frac{dG}{dT}\right)_P = -S$$

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College

This means that differentiating equation 4 at constant pressure with respect to temperature will give an expression for the effect that mixing has on the entropy of a solution.

Figure 1: The mixing of two gases can be seen as two expansions. (a) Expansion of gas 1 alone when teh barrier is removed. The molecules have twice as many microstates in the open box. (b) Expansion of gas 2 along. (c) the simultaneous expansion of gases 1 and 2 is equivalent to mixing

$$\left(\frac{dG_{mix}}{dT}\right)_P = nR(x_1 lnx_1 + x_2 lnx_2)$$

$$= \Delta_{mix}S$$

$$\Delta_{mix}S = nR(x_1 lnx_1 + x_2 lnx_2) \ ....(5)$$

Since the mole fractions again lead to negative values for lnx_1 and lnx_2. The negative sign in front of the equation makes $\Delta_{mix}S$ positive, as expected. This agrees with the idea that mixing is a spontaneous process.

In general, *equation5* can be written as

$$\Delta_{mix}S = nR \sum_i x_i lnx_i$$

Enthalpy of mixing:

We know that in an ideal system ΔG=ΔH−TΔS, but this equation can also be applied to the thermodynamics of mixing and solved for the enthalpy of mixing so that it reads

$$\Delta_{mix}H = \Delta_{mix}G + T\Delta_{mix}S ......(6)$$

Plugging in our expressions for $\Delta_{mix}G$ (Equation4) and $\Delta_{mix}S$ (Equation5), we get

$$\Delta_{mix}H = nRT(lnx_1 + lnx_2) + T[nR(x_1 lnx_1 + x_2 lnx_2)]$$
$$= 0$$

This result makes sense when considering the system. The molecules of ideal gas are spread out enough that they do not interact with one another when mixed, which implies that no heat absorbed or produced and results in a $\Delta_{mix}H$ of zero. Figure2 illustrates how $T\Delta_{mix}S$ $\Delta_{mix}G$ change as a function of the mole fraction so that $\Delta_{mix}H$ of a solution will always be equal to zero (this is for the mixing of two ideal gasses).
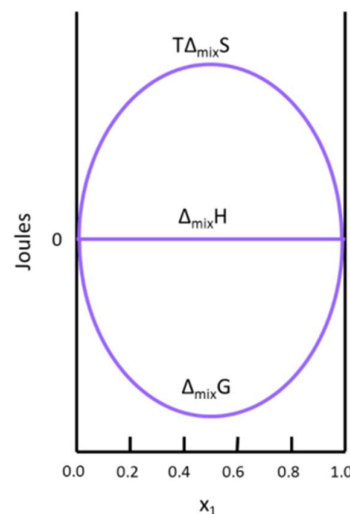
Figure 2. A graph of $T\Delta_{mix}S, \Delta_{mix}H, \Delta_{mix}G$ as a function x_1
For the mixing

Gibbs energy of mixing:

$$\Delta_{mix}G = nRT \sum_i x_i lnx_i$$

For a pure substance, $x_i = 1$, hence, $\Delta_{mix}G = 0$
For a mixture of two substances, if $x_1 = x, then \ x_2 = 1 - x$

$$\Delta_{mix}G = nRT[xlnx + (1 - x)\ln(1 - x)]$$

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College

Now, x<1 $\quad\quad\quad \Delta_{mix}G < 0$

Spontaneous process!

$$\Delta_{mix}S = nR \sum_i x_i \ln x_i$$

$$\Delta_{mix}S > 0$$

Ideal binary mixture
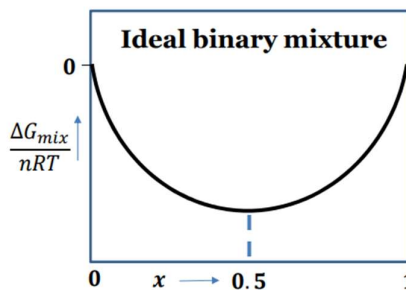
Chemical equilibrium

p, T constant
Is a chemical reaction Spontaneous?

$$dG = \sum_i \mu_i\, dn_i$$

Let ξ be advancement of the reaction
$$n_i = n_i^0 + v_i \xi$$
$$dn_i = v_i\, d\xi$$
$$dG = \sum_i \mu_i v_i\, d\xi$$

$\left(\dfrac{\delta G}{\delta \xi}\right)_{T,p} = \sum_i v_i \mu_i$ $\quad$ Rate of increase of Gibbs free energy with the advancement of the reaction.

If $\left(\dfrac{\delta G}{\delta \xi}\right)_{T,p} < 0$ $\quad$ *the reaction spntaneous*

If $\left(\dfrac{\delta G}{\delta \xi}\right)_{T,p} > 0$ $\quad$ *the reaction proceeds in backward direction*

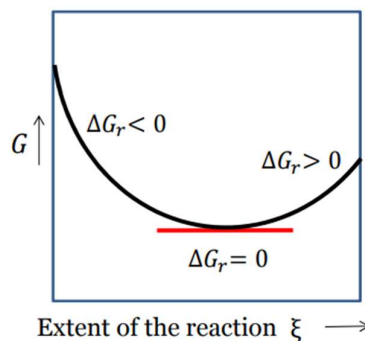*If* $\left(\dfrac{\delta G}{\delta \xi}\right)_{T,p} = 0$ $\quad$ *G has minimum value, the reaction is in equilibrium*

$$\left(\frac{\delta G}{\delta \xi}\right)_{T,p,eq} = 0 \quad\quad \sum_i v_i \mu_i = 0$$

$\Delta G_r = \sum_i v_i \mu_i$ $\quad$ *by definition* $\left(\dfrac{\delta G}{\delta \xi}\right)_{T,p} = \Delta G_r$

At equilibrium $\quad \Delta G_r = 0$

$\Delta G_r < 0$ $\quad$ Forward reaction is spontaneous, Exergonic (work producing) e.g., carbohydrate oxidation

$\Delta G_r > 0$ $\quad$ Backward reaction is spontaneous, Endergonic (work consuming) e.g., electrolysis of water

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College

For reaction of an ideal mixture of gases

$$\Delta G_r = \sum_i \nu_i \, \mu_i = \sum_i \nu_i(\mu_i^0 + RT \, lnp_i) = \sum_i \left(\nu_i \, \mu_i^0 + RT \, ln \, Q_p\right) \qquad Q_p = \prod_i p_i^{\nu_i}$$

$$\Delta G_r = \Delta G_r^0 + RT \ln Q_p$$

At equilibrium $\quad \Delta G_r^0 = -RT \ln Q_p$ where $\quad K_p = \prod_i (p_i)_e^{\nu_i}\quad$ equilibrium constant
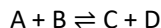
Chemical Equilibrium:

REVERSIBLE REACTIONS

Not all chemical reactions proceed to completion. In most reactions two or more substances react to form products which themselves react to give back the original substances. Thus A and B may react to form C and D which react together to reform A and B.
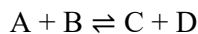
A + B $\longrightarrow$ C + D (Forward reaction)

A + B $\longleftarrow -$ C + D (Reverse reaction)
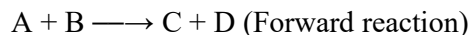
A reaction which can go in the forward and backward direction simultaneously is called a Reversible reaction. Such a reaction is represented by writing a pair of arrows between the reactants and products.
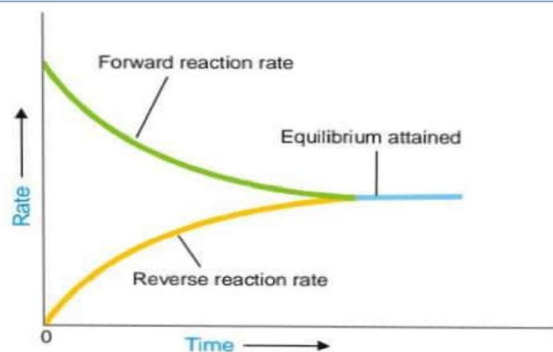
A + B $\rightleftharpoons$ C + D

The arrow pointing right indicates the forward reaction, while that pointing left shows the reverse reaction.

NATURE OF CHEMICAL EQUILIBRIUM: ITS DEFINITION

Let us consider the reaction

A + B $\rightleftharpoons$ C + D

If we start with A and B in a closed vessel, the forward reaction proceeds to form C and D. The concentrations of A and B decrease and those of C and D increase continuously. As a result, the rate of forward reaction also decreases and the rate of the reverse reaction increases. Eventually, the rate of the two opposing reactions equals and the system attains a *state of equilibrium.* Thus, *Chemical equilibrium* may be defined as: <u>the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of reactants and products do not change with time.</u> Furthermore, the true equilibrium of a reaction can be attained from both sides. Thus, the equilibrium concentrations of the reactants and products are the same whether we start with A and B, or C and D.

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College

At equilibrium the forward reaction rate equals the reverse reaction rate.

Chemical Equilibrium is Dynamic Equilibrium:

We have shown above that as the reaction, A + B ⇌ C + D attains equilibrium, the concentrations of A and B, as also of C and D remain constant with time. Apparently, it appears that the equilibrium is dead. But it is not so. The equilibrium is dynamic. Actually, the forward and the reverse reactions are taking place at equilibrium but the concentrations remain unchanged.

When a chemical equilibrium is established in a *closed vessel* at constant temperature, concentrations of the various species in the reaction mixture become constant. The reaction mixture at equilibrium is called *Equilibrium mixture*. The concentrations at equilibrium are called *Equilibrium concentrations*. The equilibrium concentrations are represented by square brackets with [ ]. Thus [A] denotes the equilibrium concentration of substance A in moles per litre.

Thermodynamic conditions for equilibrium:

At constant temperature and pressure, the composition of a reaction mixture tends to change until the *Gibbs energy is a minimum*.

DEGREE OF ADVANCEMENT AND GIBBS ENERGY

Consider the equilibrium

$$A \rightleftharpoons B.$$

If an infinitesimal amount $d\xi$ of A turns into B, the change in the amount of A is $-d\xi$ and the change in the amount of B is $+d\xi$. The quantity ξ is called the *extent of reaction or degree of advancement.* it has the dimensions of amount of substance and is represented in moles.

The reaction Gibbs energy, $\Delta_r G$, is defined as the change in Gibbs energy with the degree of advancement (ξ) at constant temperature and pressure

$$\Delta G_r = \left(\frac{\delta G}{\delta \xi}\right)_{T,p}$$

As the reaction proceeds, represented by the degree or advancement ξ increasing, the slope of a plot of total Gibbs energy of the reaction mixture against ξ changes. Equilibrium corresponds
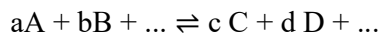
Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College

to the minimum in the Gibbs energy, which is where the slope is zero (fig. 1). $\Delta_r G = 0$, Condition of equilibrium
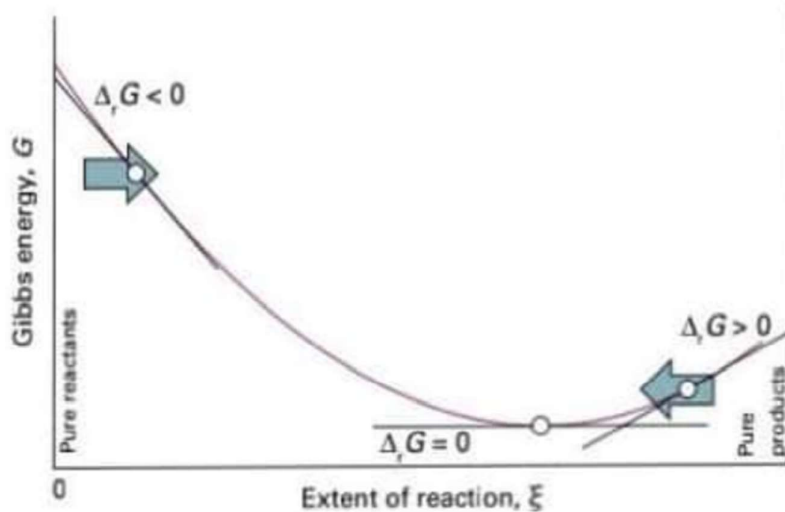
Van't Hoff Reaction Isotherm:

Let us consider a general reaction

$$aA + bB + ... \rightleftharpoons c C + d D + ...$$

The chemical potential of a substance in a mixture is related to its activity by the expression

$$\mu = \mu° + RT \ln a ... (i)$$

where $\mu°$ is the chemical potential of the pure substance in standard state of unit activity, R is gas constant and T the absolute temperature.

For a mole of the substance 'A' we can write using the equation (i)

$$a\,\mu_A = a\,(\mu_A° + RT \ln a_A)$$

and similarly

$$b\,\mu_B = b\,(\mu_B° + RT \ln a_B)$$

$$c\,\mu_C = c\,(\mu_C° + RT \ln a_C)$$

$$d\,\mu_D = d\,(\mu_D° + RT \ln a_D)$$

The change in free energy for the reaction is given by

$\Delta G = G_{products} - G_{reactants}$

Now,

$\Delta G = (c\,\mu_C + d\,\mu_D + ...) - (a\,\mu_A + b\,\mu_B + ...)$

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College

$= [c \{\mu_C° + RT \ln a_C\} + d \{\mu_D° RT \ln a_D\}] - [a \{\mu_A° + RT \ln a_A\} + b \{\mu_B° RT \ln a_B\}]$

$= [\{c \mu_C° + d \mu_D° + ...\} - \{a \mu_A° + b\mu_B° + ...\}] + RT \ln \dfrac{(a_C)^c \times (a_D)^d \times ...}{(a_A)^a \times (a_B)^b \times ...}$

where $\Delta G°$ is the difference in free energy of the reaction when all reactants and products are in their standard state. It is given by

$\Delta G° = \{c \mu_C° + d \mu_D° + ...\} - \{a \mu_A° + b \mu_B° + ...\}$

$\Delta G = \Delta G° + RT \ln Q$ …………………… (3)

Where, $Q = \dfrac{(a_C)^c \times (a_D)^d \times ...}{(a_A)^a \times (a_B)^b \times ...}$

'Q' stands for the reaction quotient of activities of the product and reactants.

The equation (3) is called *van't Hoff reaction isotherm*.

For the reaction at equilibrium $\Delta G = 0$

therefore, from equation (3) $\Delta G° = - RT \ln Q$

An equilibrium constant 'K' expressed in terms of activities is called a thermodynamic equilibrium constant. So,

$$\Delta G° = - RT \ln K \text{ …….(4)}$$

$$\Delta G° = -2.303 \ RT \log K$$

The equation (4) is also called *van't Hoff Isotherm*

SOLVED PROBLEM 1: Calculate K for reaction which has $\Delta G°$ value -20 kcal at 25°C.

SOLUTION We know that $\Delta G° = -2.303 \ RT \log K$ ... (a)

where $\Delta G°$ is standard free energy; R is gas constant; T is absolute temperature; and K is equilibrium constant.

$\Delta G° = -20$ kcal $= -20,000$ cal

$R = 1.99$ cal

$T = 25 + 273 = 298$ K

The value of K from expression (a) may be calculated as

$\log K = -\Delta G°/2.303 \ RT$

$\qquad = 20,000/2.303 \times 1.99 \times 298$

$K = 5 \times 10^{14}$

PROBLEM 2. The standard free energy change for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is $+173.1$ kJ. Calculate K_P for the reaction at 25°C.

Try at home   Ans: 4.6×10^{-31}

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College

Van`t Hoff Reaction Isobar:

The equation for reaction isotherm when the reactants and products are gaseous and are also in their standard states is represented as,

$$\Delta G^0 = -RTlnK_p \qquad \dots\dots(1)$$

Where, ΔG^0 is the change in standard free energy of the reaction

Differentiating eqn (1) w.r.t T at constant pressure p, we get

$$\left(\frac{\delta(\Delta G^0)}{\delta T}\right)_p = -RlnK_p - RT\left(\frac{d(lnK_p)}{dT}\right)_p$$

Multiplying both sides by T, we get

$$T\left(\frac{\delta(\Delta G^0)}{\delta T}\right)_p = -RTlnK_p - RT^2\left(\frac{d(lnK_p)}{dT}\right)_p$$

From equn (1), we get

$$T\left(\frac{\delta(\Delta G^0)}{\delta T}\right)_p = \Delta G^0 - RT^2\left(\frac{d(lnK_p)}{dT}\right)_p \qquad \dots\dots(2)$$

We know that Gibbs Helmholtz equation for a reaction in the standard state can be written as

$$\Delta G^0 = \Delta H^0 + T\left(\frac{\delta(\Delta G^0)}{\delta T}\right)_p$$

Or,

$$T\left(\frac{\delta(\Delta G^0)}{\delta T}\right)_p = \Delta G^0 - \Delta H^0 \qquad \dots\dots(3)$$

Comparing equation (2) and (3) we get,

$$\Delta H^0 = RT^2\left(\frac{d(lnK_p)}{dT}\right)_p$$

Or, $\left(\frac{d(lnK_p)}{dT}\right)_p = \frac{\Delta H^0}{RT^2} \qquad \dots\dots(4)$

Equation 4 is known as van`t Hoff reaction isobar.

van`t Hoff reaction isochore

We know that equilibrium constant in terms of partial pressure (Kp) and in terms of concentration (Kc) are related to each other by the relation,

$$K_p = K_c(RT)^{\Delta n}$$

Taking logarithms, we get

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$$lnK_p = lnK_c + \Delta n \ln RT$$

Differentiating w.r.t Temperature (T), we get

$$\frac{d(lnK_p)}{dT} = \frac{d(lnK_c)}{dT} + \frac{\Delta n}{T}$$

$$or, \quad \frac{d(lnK_c)}{dT} = \frac{d(lnK_p)}{dT} - \frac{\Delta n}{T}$$

$$or, \quad \frac{d(lnK_c)}{dT} = \frac{\Delta H}{RT^2} - \frac{\Delta n}{T} \quad \left[\because \quad \frac{d(lnK_p)}{dT} = \frac{\Delta H}{RT^2}\right]$$

$$= \frac{\Delta H}{RT^2} - \frac{\Delta n . RT}{T . RT}$$

$$or, \quad \frac{d(lnK_c)}{dT} = \frac{\Delta H - \Delta n . RT}{RT^2}$$

We know, $\Delta H = \Delta U + \Delta n . RT$

$$\frac{d(lnK_c)}{dT} = \frac{\Delta U}{RT^2} \quad\quad\quad ……..(1)$$

Where, ΔU is the heat of the reaction at constant volume.

Equation (1) is called van`t Hoff reaction isochore.

LE CHATELIER'S PRINCIPLE:

Le Chatelier's principle can be stated as: *if a change in concentration, pressure or temperature is caused to a chemical reaction in equilibrium, the equilibrium will shift to the right or the left so as to minimise the change.*

EFFECT OF CHANGE OF PRESSURE

The pressure of a gaseous reaction at equilibrium is determined by the total number of molecules it contains. If the forward reaction proceeds by the reduction of molecules, it will be accompanied by a decrease of pressure of the system and vice versa.

Let us consider a reaction,

$$A + B \rightleftharpoons C$$

The combination of A and B produces a decrease of number of molecules while the decomposition of C into A and B results in the increase of molecules. Therefore, by the increase of pressure on the equilibrium it will shift to right and give more C. A decrease in pressure will cause the opposite effect. The equilibrium will shift to the left when C will decompose to form more of A and B.

Dr. Rajib Pramanik
Associate Professor, Dept. of Chemistry, Berhampore Girls College