CEMG-CC2/GE2

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.

$$A + B \longrightarrow C + D \text{ (Forward reaction)}$$

$$A + B \longleftarrow C + D \text{ (Reverse reaction)}$$

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.

$$A + B \rightleftharpoons C + D$$

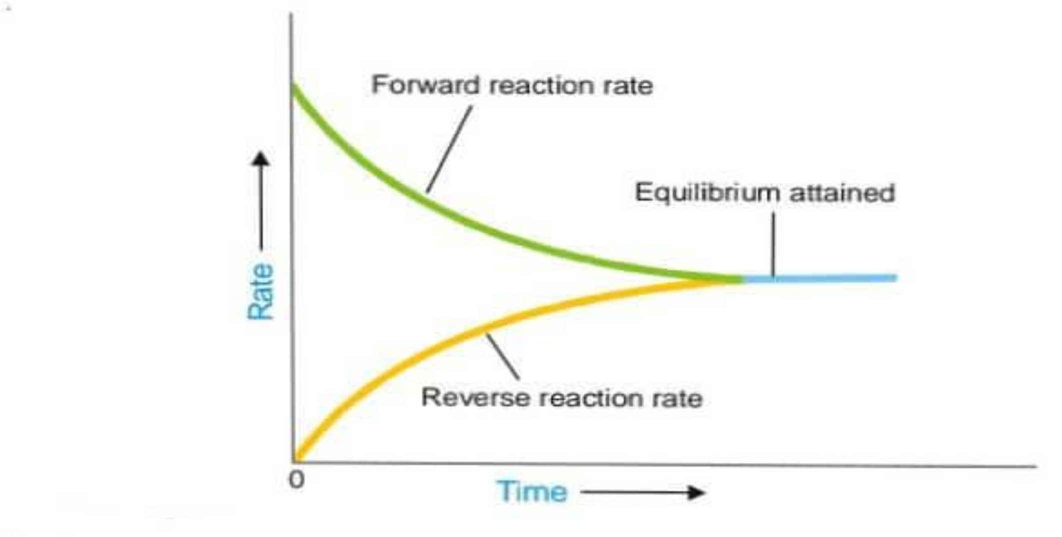
The arrow pointing right indicates the forward reaction, while that pointing left shows the reverse reaction.

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: *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.* 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.



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 $\rightleftharpoons$ 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, Δ_rG, is defined as the change in Gibbs energy with the degree of advancement (ξ) at constant temperature and pressure.

$$\Delta_rG = \left(\frac{\partial G}{\partial \xi} \right)_{P,\,T}$$

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 to the minimum in the Gibbs energy, which is where the slope is zero (fig. 1).

$$\Delta_rG = 0 \text{ , Condition of equilibrium}$$

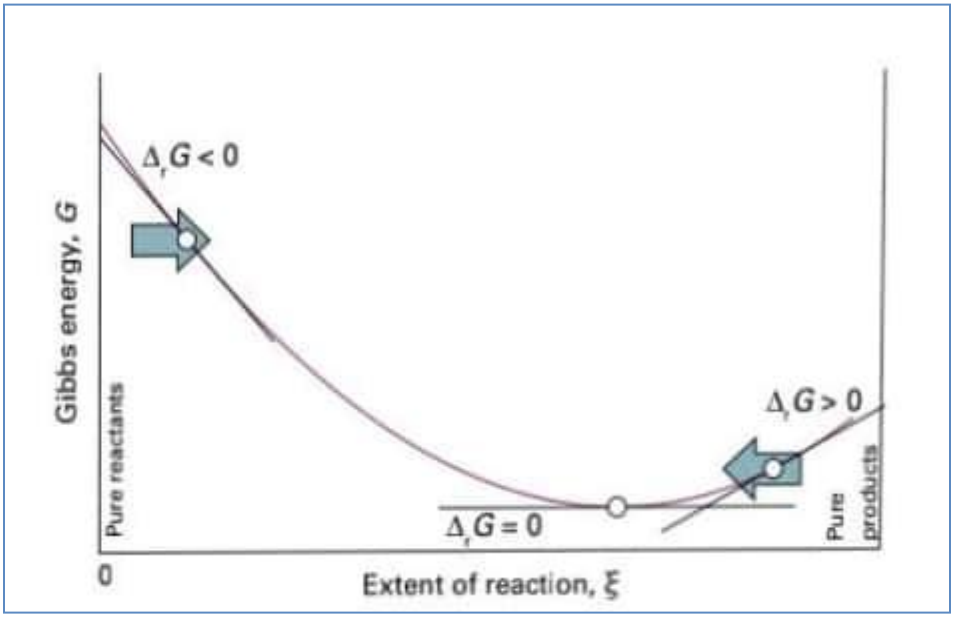


Fig. 1

LAW OF MASS ACTION

It states that : the rate of a chemical reaction is proportional to the active masses of the reactants.

By the term ‘active mass’ is meant the molar concentration i.e., number of moles per litre.

In a reaction, A + B ⟶ the number of collisions between A and B depends on the concentration of each reactant.

$$\text{Therefore, Rate of reaction} \propto [A]\,[B] = k\,[A]\,[B]$$

where k = rate constant of the reaction

From the above considerations, it stands proved that the rate of a reaction is proportional to the molar concentrations of the reactants.

EQUILIBRIUM CONSTANT: EQUILIBRIUM LAW

Let us consider a general reaction

$$A + B \rightleftharpoons C + D$$

and let [A], [B], [C] and [D] represent the molar concentrations of A, B, C and D at the equilibrium point. According to the Law of Mass action.

$$\text{Rate of forward reaction} \propto [A]\,[B] = k_1\,[A]\,[B]$$

$$\text{Rate of reverse reaction} \propto [C][D] = k_2\,[C]\,[D]$$

where k_1 and k_2 are rate constants for the forward and reverse reactions.

At equilibrium, rate of forward reaction = rate of reverse reaction.

Therefore,

$$k_1[A]\,[B] = k_2\,[C]\,[D]$$

or

$$k_1/k_2 = \frac{[C][D]}{[A][B]} \qquad \ldots (1)$$

At any specific temperature k_1/k_2 is constant since both k_1 and k_2 are constants. The ratio k_1/k_2 is called *Equilibrium constant* and is represented by the symbol K_c, or simply K. The subscript 'c' indicates that the value is in terms of concentrations of reactants and products. The equation (1) may be written as

$$K_c = \frac{[C][D]}{[A][B]}$$

This equation is known as the Equilibrium constant expression or Equilibrium law.

Equilibrium Constant Expression for a Reaction in General Terms

The general reaction may be written as

$$aA + bB \rightleftharpoons cC + dD$$

where a, b, c and d are numerical quotients of the substance, A, B, C and D respectively. The equilibrium constant expression is

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

where K_C is the Equilibrium constant. The general definition of the equilibrium constant may thus be stated as : the product of the equilibrium concentrations of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balanced equation.

EQUILIBRIUM CONSTANT EXPRESSION IN TERMS OF PARTIAL PRESSURES

When all the reactants and products are gases, we can also formulate the equilibrium constant expression in terms of partial pressure. The relationship between the partial pressure (p) of any one gas in the equilibrium mixture and the molar concentration follows from the general ideal gas equation

$$pv = nRT \quad \text{or} \quad p = \left(\frac{n}{V}\right) RT$$

The quantity $\frac{n}{V}$ is the number of moles of the gas per unit volume and is simply the molar concentration. Thus,

$$p = (\text{Molar concentration}) \times RT$$

i.e., the partial pressure of a gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature. Therefore, we can write the equilibrium constant expression in terms of partial pressure instead of molar concentrations. For a general reaction

$$l\,L(g) + mM(g) \rightleftharpoons yY(g) + zZ(g)$$

the equilibrium law or the equilibrium constant may be written as

$$K_p = \frac{(p_Y)^y \; (p_Z)^z}{(p_L)^l \; (p_M)^m}$$

Here K_p is the equilibrium constant, the subscript ‘p’ referring to partial pressure. Partial pressures are expressed in atmospheres.

RELATIONSHIP BETWEEN K_c AND K_p

Let us consider a general reaction

$$aA + bB \rightleftharpoons cC + dD$$

where all reactants and products are gases. We can write the equilibrium constant expression in terms of partial pressures as

$$K_p = \frac{(p_C)^c \; (p_D)^d}{(p_A)^a \; (p_B)^b} \qquad \text{...............(1)}$$

Assuming that all these gases constituting the equilibrium mixture obey the ideal gas equation, the partial pressure (p) of a gas is

$$p = \left(\frac{n}{V}\right)\ RT$$

Where $\frac{n}{V}$ is the molar concentration. Thus the partial pressures of individual gases, A, B, C and D are:

$$p_A = [A]\,RT\ ;\ \ p_B = [B]\,RT\ ;\ \ p_C = [C]\,RT\ ;\ \ p_D = [D]\,RT$$

Substituting these values in equation (1), we have

$$K_p = \frac{[C]^c(RT)^c\ [D]^d\ (RT)^d}{[A]^a\ (RT)^a\ [B]^b\ (RT)^b}$$

$$K_p = \frac{[C]^c\ \ [D]^d}{[A]^a\ \ [B]^b}\ \ x\ \ \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

$$K_p = K_c\ \ x\ \ (RT)^{(c+d)-(a+b)}$$

$$K_p = K_c\ \ x\ \ (RT)^{\Delta n} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where Δn = (c+d) – (a+b), the difference in the sums of the coefficients for the gaseous products and reactants. From the expression (2) it is clear that when Δn = 0, $K_p = K_c$.

SOLVED PROBLEM 1. At 500°C, the reaction between N_2 and H_2 to form ammonia has $K_c = 6.0 \times 10^{-2}$. What is the numerical value of K_p for the reaction?

SOLUTION: Here, we will use the general expression

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

For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$

we have, Δn = (sum of quotients of products) – (sum of quotients of reactants) = 2 – 4 = – 2
$K_c = 6.0 \times 10^{-2}$
T = 500 + 273 = 773 K
R = 0.0821 $\text{lit.atm.mol}^{-1}\text{K}^{-1}$
Substituting the value of R, T, Kc and Δn in the general expression, we have
$Kp = (6.0 \times 10^{-2})\ [(0.0821) \times (773)]^{-2} = 1.5 \times 10^{-5}$

PROBLEM 2. The value of K_p at 25°C for the reaction

$$2NO(g) + Cl_2\ (g) \rightleftharpoons 2NOCl(g)$$

is $1.9 \times 103\ \text{atm}^{-1}$. Calculate the value of K_C at the same temperature.

Try at home Ans: 4.6×10^4

EQUILIBRIUM CONSTANT EXPRESSION IN TERMS OF MOLE FRACTIONS

When equilibrium constant is expressed in terms of mole fractions of reactants and products, it is expressed as, K_X

$$aA + bB \rightleftarrows cC + dD$$

$$K_x = \frac{(x_C)^c \ (x_D)^d}{(x_A)^a \ (x_B)^b}$$

Where, X_A, x_B, X_C and x_D represents the mole fractions of A, B, C and D.

RELATIONSHIP BETWEEN K_p AND K_x

The partial pressure ‘p’ of a gas in an ideal gas mixture is related to pressue ‘P’ as

$$p = xP$$

where x is the mole fraction of the gas in the mixture. Substituting for the partial pressure of A, B, C and D in equation (1), we get

$$K_p = \frac{(p_C)^c \ (p_D)^d}{(p_A)^a \ (p_B)^b}$$

$$K_p = \frac{(x_C)^c \ (x_D)^d}{(x_A)^a \ (x_B)^b} \times \frac{(P)^{c+d}}{(P)^{a+b}}$$

$$K_p = K_X \ (P)^{(c+d) - (a+b)}$$

$$K_p = K_X \ (P)^{\Delta n} \quad \ldots\ldots\ldots\ldots.(3)$$

where $\Delta n = (c+d) - (a+b)$, the difference in the sums of the coefficients for the products and reactants. From the expression (3) it is clear that when $\Delta n = 0$, $K_p = K_X$.

RELATIONSHIP BETWEEN K_C AND K_x

From equation (2) and (3), we have

$$K_C(RT)^{\Delta n} = K_x(P)\ )^{\Delta n}$$

$$K_C = K_x\,(P/RT)^{\Delta n}$$

$$K_C = K_x\,(V)^{\Delta n}$$

Where V is the volume of the system containing 1 mol of an ideal gas. when $\Delta n = 0$, $K_p = K_c = K_x$

Van’t Hoff Reaction Isotherm:

Let us consider a general reaction

$$aA + bB + \ldots \rightleftharpoons cC + dD + \ldots$$

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

$$\mu = \mu^\circ + RT \ln a \qquad \ldots (i)$$

where μ° 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)

$$a\mu_A = a(\mu_A^\circ + RT \ln a_A)$$

and similarly

$$b\mu_B = b(\mu_B^\circ + RT \ln a_B)$$
$$c\,\mu_C = c(\mu_C^\circ + RT \ln a_C)$$

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

The change in free energy for the reaction is given by

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

Now,

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

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

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

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

$$\Delta G^o = \{c\,\mu_C^\circ + d\,\mu_D^\circ + \ldots\} - \{a\,\mu_A^\circ + b\,\mu_B^\circ + \ldots\ldots\}$$

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where,

$$Q = \frac{(a_C)^C \times (a_D)^d \times \ldots..}{(a_A)^a \times (a_B)^b \times \ldots.}$$

‘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) $\Delta G^\circ = -RT \ln Q$

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

$$\Delta G^\circ = -RT \ln K \qquad ....(4)$$

$$\Delta G^\circ = -2.303\ RT \log K$$

The equation (4) is also called van’t Hoff Isotherm.

SOLVED PROBLEM 1: Calculate K for reaction which has ΔG° value –20 kcal at 25°C.

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

where ΔG° is standard free energy; R is gas constant; T is absolute temperature; and K is equilibrium constant.

$\Delta G^\circ = -20$ kcal $= -20{,}000$ cal

$R = 1.99$ cal

$T = 25 + 273 = 298$ K

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

$\log K = -\Delta G^\circ/2.303\ RT$

$= 20{,}000/2.303 \times 1.99 \times 298$

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

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}

Van't Hoff reaction isochore :-

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

$$\Delta G^\circ = -RT \ln K_p \quad \cdots\cdots ①$$

Where, ΔG° is the change in standard free energy of the reaction.

Differentiating eq^n ① with respect to T at constant pressure P, we get

$$\left(\frac{\partial(\Delta G^\circ)}{\partial T}\right)_P = -R \ln K_p - RT\left(\frac{d(\ln K_p)}{dT}\right)_P$$

Multiplying both sides by T, we get

$$T\left(\frac{\partial(\Delta G^\circ)}{\partial T}\right)_P = -RT \ln K_p - RT^2\left(\frac{d(\ln K_p)}{dT}\right)_P$$

From equation ① we get

$$T\left(\frac{\partial(\Delta G^\circ)}{\partial T}\right)_P = \Delta G^\circ - RT^2\left(\frac{d(\ln K_p)}{dT}\right)_P \quad \cdots ②$$

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

$$\Delta G^\circ = \Delta H^\circ + T\left(\frac{\partial(\Delta G^\circ)}{\partial T}\right)_P$$

Or,
$$T\left(\frac{\partial(\Delta G^\circ)}{\partial T}\right)_P = \Delta G^\circ - \Delta H^\circ \quad \cdots\cdots ③$$

Comparing equation ② and ③ we get

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

or,
$$\left[\frac{d(\ln K_p)}{dT}\right]_P = \frac{\Delta H^\circ}{RT^2} \quad —— ④ \quad \text{or,} \quad \frac{d(\ln K_p)}{dT} = \frac{\Delta H}{RT^2}$$

Equation ④ is known as Van't Hoff reaction isochore.

Van't Hoff reaction isobar :-

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

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

Taking logarithms we get

$$\ln K_p = \ln K_c + \Delta n \ln RT$$

Differentiating with respect to temperature (T), we get

$$\frac{d(\ln K_p)}{dT} = \frac{d(\ln K_c)}{dT} + \frac{\Delta n}{T}$$

or, $$\frac{d(\ln K_c)}{dT} = \frac{d(\ln K_p)}{dT} - \frac{\Delta n}{T}$$

~~From equation~~

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

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

or, $$\frac{d(\ln K_c)}{dT} = \frac{\Delta H - \Delta n RT}{RT^2}$$

We know, $\Delta H = \Delta E + \Delta n RT$

$$\therefore \frac{d(\ln K_c)}{dT} = \frac{\Delta E}{RT^2} \quad \text{———} ①$$

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

Equation ① is called van't Hoff reaction isobar.

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.

The reactions in which the number of product molecules is equal to the number of reactant molecules, e.g.,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI$$

are unaffected by pressure changes.

EFFECT OF PRESSURE ON VARIOUS GASEOUS EQUILIBRIA

System	Pressure increased	Pressure decreased
(1) $N_2O_4 \rightleftharpoons 2NO_2$	Backward	Forward
(2) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$	Backward	Forward
(3) $2SO_2 + O_2 \rightleftharpoons 2SO_3$	Forward	Backward
(4) $N_2 + 3H_2 \rightleftharpoons 2NH_3$	Forward	Backward
(5) $H_2 + I_2 \rightleftharpoons 2HI$	No effect	No effect
(6) $N_2 + O_2 \rightleftharpoons 2NO$	No effect	No effect

EFFECT OF CHANGE OF TEMPERATURE

Let us consider an exothermic reaction

$$A + B \rightleftharpoons C + \text{heat}$$

When the temperature of the system is increased, heat is supplied to it from outside. According to Le Chatelier's principle, the equilibrium will shift to the left which involves the absorption of heat. This would result in the increase of the concentration of the reactants A and B.

In an endothermic reaction

$$X + Y + \text{heat} \rightleftharpoons Z$$

the increase of temperature will shift the equilibrium to the right as it involves the absorption of heat. This increases the concentration of the product Z.

In general, we can say that the increase of temperature favours the reverse change in an exothermic reaction and the forward change in an endothermic reaction.

THE DIRECTION OF EQUILIBRIUM SHIFT IN SOME REACTIONS ON INCREASE OF TEMPERATURE

Reaction	Equilibrium Shift
$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2 + 284$ kcal	Backward
$H_2 + Cl_2 \rightleftharpoons 2HCl + 44.2$ kcal	Backward
$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O + 212.8$ kcal	Backward
$2CO_2 + 135.2$ kcal $\rightleftharpoons 2CO + O_2$	Forward
$N_2O_4 + 14$ kcal $\rightleftharpoons 2NO_2$	Forward
$H_2 + I_2 + 12.4$ kcal $\rightleftharpoons 2HI$	Forward

Effect of addition of inert gas

Let us add an inert gas to an equilibrium mixture while the volume of the reaction vessel remains the same. The addition of the inert gas increases the total pressure but the partial pressures of the reactants and products are not changed. Thus the addition of an inert gas has no effect on the position of the equilibrium.