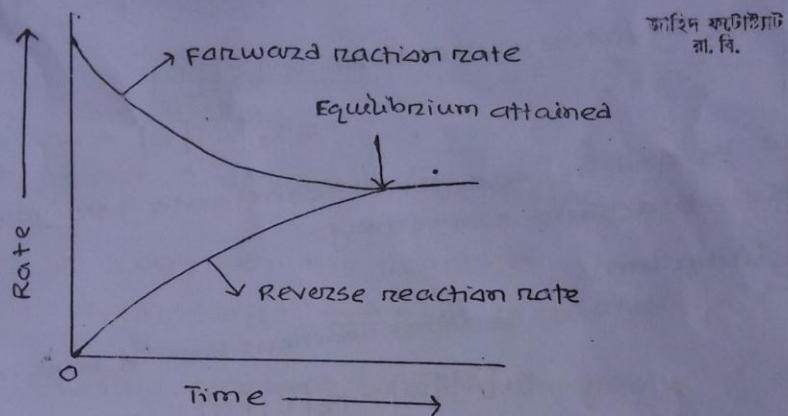


Q1:- Define chemical equilibrium.

Sol:- chemical equilibrium: The ~~chemical~~ equilibrium is the state of reversible reaction when the two opposing reactions occur at the same rate and the concentrations of the reactants and product do not change with time.

Let us consider the reaction, $A + B \rightleftharpoons C + D$

The equilibrium of the reaction can be attained from both sides. Thus the equilibrium concentrations of the reactants and the products are the same and whether we start with A and B or C and D.



जारीदा फॉलोवर
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Fig-TSA- At equilibrium the forward reaction rate equals the reverse reaction rate.

Q2:- State and explain the laws of mass action, with example.

Sol:- Two Norwegian chemists, Gulberg and Waage, postulated a generalisation called the 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.

Ques

How can you use the law for deriving an expression for the equilibrium constant of a reaction?

Mathematical expression of Law of mass action:

Q106

Let us consider a general reversible reaction



and let $[A], [B], [C], [D]$ represents the molar concentrations of A, B, C, D respectively at equilibrium point.

According to the law of mass action,

$$\begin{aligned} \text{Rate of forward reaction} &\propto [A][B] \\ &= k_1 [A][B] \quad \dots \dots (1) \end{aligned}$$

$$\begin{aligned} \text{Rate of reverse reaction} &\propto [C][D] \\ &= k_2 [C][D] \quad \dots \dots (2) \end{aligned}$$

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

At equilibrium,

Rate of forward reaction = Rate of back reverse reaction

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

$$\Rightarrow \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]}$$

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

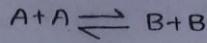
$$we \text{ can write} \quad K_C = \frac{[C][D]}{[A][B]}$$

At any specific temperature k_1/k_2 is constant since k_1 and k_2 are

Equilibrium constant expression for a reaction in general terms.

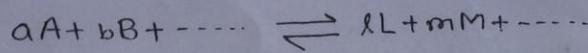
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Let us consider the reaction,



$$\text{Then for the reaction, } K = \frac{[B][B]}{[A][A]} = \frac{[B]^2}{[A]^2}$$

For the general reaction,



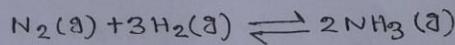
$$K = \frac{[L]^l \times [M]^m \times \dots}{[A]^a \times [B]^b \times \dots}$$

$$\therefore K_c = \frac{c_L^l \times c_M^m \times \dots}{c_A^a \times c_B^b \times \dots}$$

$$K_p = \frac{P_L^l \times P_M^m \times \dots}{P_A^a \times P_B^b \times \dots}$$

where the subscript C represent the molar concentration.

Example: Let us consider the reaction



The equilibrium constant for the reaction is

$$K = \frac{[NH_3]^2}{[N_2] \times [H_2]^3}$$

~~Ques 3:~~ what is the equilibrium constant of a reaction. Define and correlate K_p and K_c and K_e .

Soln:- Equilibrium constant: The equilibrium constant of reaction is (at equilibrium state of the reaction) the ratio of the product of the concentrations of the products to the product of the concentration of the reactants. OR, it is the ratio of forward and reverse rate constant at equilibrium point.

TAREK

a general reaction at equilibrium



Then state constant

$$K = \frac{K_1}{K_2} = \frac{[L]^x \times [M]^m \times \dots}{[A]^a \times [B]^b \times \dots}$$

$$\text{or, } K_c = \frac{c_L^x \times c_m^m \times \dots}{c_A^a \times c_B^b \times \dots}$$

where, c represents the molar concentrations for the elements

K_P if the reactants and products of the reaction are ^{in state} gaseous, then is represented by partial pressure constant for the

above reaction

$$K_p = \frac{P_L^x \times P_m^m \times \dots}{P_A^a \times P_B^b \times \dots}$$

K_x if the reactants and the products of the reaction are represented by mole fraction then the equilibrium constant is represented by K_x

for the above reaction;

$$K_x = \frac{x_L^x \times x_m^m \times \dots}{x_A^a \times x_B^b \times \dots}$$

~~Relation between K_p , K_c and K_x :-~~ Let us consider the general equation



The molar concentration rate constant

$$K_c = \frac{c_L^l \times c_M^m \times \dots}{c_A^a \times c_B^b \times \dots} \quad \dots \quad (1)$$

The partial pressure rate constant

$$K_p = \frac{P_L^l \times P_M^m \times \dots}{P_A^a \times P_B^b \times \dots} \quad \dots \quad (2)$$

The mole fraction rate constant

$$K_x = \frac{x_L^l \times x_M^m \times \dots}{x_A^a \times x_B^b \times \dots} \quad \dots \quad (3)$$

In an ideal gas mixture, if a gas having molar partial pressure P and if the gas occupy a volume V at temp T then

$$PV = nRT$$

$$\Rightarrow P = \frac{n}{V} RT$$

$$\therefore P = CRT \quad \left[\because c = \frac{n}{V} = \text{molar conc.} \right]$$

substituting the value of P in equation (2) we get

$$K_p = \frac{c_L^l \times (RT)^l \times c_M^m \times (RT)^m \times \dots}{c_A^a \times (RT)^a \times c_B^b \times (RT)^b \times \dots}$$

$$\Rightarrow K_p = \frac{c_L^l \times c_M^m \times \dots}{c_A^a \times c_B^b \times \dots} \times \frac{(RT)^{l+m+\dots}}{(RT)^{a+b+\dots}}$$

$$\Rightarrow K_p = K_c (RT)^{(l+m+\dots)-(a+b+\dots)}$$

$$\therefore K_p = K_c (RT)^{\Delta n} \quad \dots \quad (4)$$

where, $\Delta n = (l+m+\dots) - (a+b+\dots) = \text{change in mole number of the reaction.}$

In a gas mixture the partial pressure of a gas is P , the total pressure is P . Then we can write $P = xP$, where, $x = \text{mole fraction.}$

substituting the value of P in equation (2) we get

$$K_p = \frac{x_L^l P^l \times x_M^m P^m \times \dots}{x_A^a P^a \times x_B^b P^b \times \dots}$$

$$\Rightarrow K_p = \frac{x_L^l \times x_M^m \times \dots}{x_A^a \times x_B^b \times \dots} \times P^{(l+m+\dots) - (a+b+\dots)}$$

$$K_p = K_x P^{\Delta n} \quad \dots \dots \dots (5)$$

From (4) and (5) we can write

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

$$\Rightarrow K_c = K_x \left(\frac{P}{RT} \right)^{\Delta n}$$

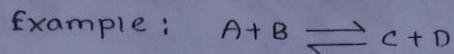
$$\Rightarrow K_c = K_x \left(\frac{1}{V} \right)^{\Delta n}$$

$$\therefore K_x = K_c V^{\Delta n} \quad \dots \dots \dots (6) \quad \checkmark$$

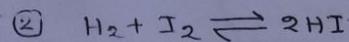
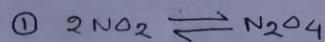
Equation (4), (5) and (6) are the required relation between K_p , K_c and K_x .

Q: No: 4:- What do you mean by reversible reaction.

Soln:- A reaction which can go in the forward and backward direction simultaneously is called a reversible reaction.



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



Q: No: 5: Deduce the relation $\Delta G^\circ = -RT \ln K$. (M74 G74)

OR Deduce van't Hoff's isothermal equation.

OR Thermodynamic derivation of law of chemical equilibrium

Soln:- Let us consider a general reaction



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

$$\mu = \mu_0^\circ + RT \ln a \quad \text{--- (1)}$$

where, μ_0 is the chemical potential of the pure substance when all reactants and products are in their standard state, R is the gas constant and T is the absolute temp.

For a mole of the reactant A using (1) we can write

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

and similarly.

$$b\mu_B = b(\mu_B^\circ + RT \ln a_B)$$

$$c\mu_C = c(\mu_C^\circ + RT \ln a_C)$$

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

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the change in free energy ΔG can be written as

$$\begin{aligned}\Delta G &= G_{\text{products}} - G_{\text{reactants}} \\ &= (c\mu_c + d\mu_D + \dots) - (a\mu_A + b\mu_B + \dots) \\ &\equiv [c(\mu_c^0 + RT \ln a_c) + d(\mu_D^0 + RT \ln a_D)] - [a(\mu_A^0 + RT \ln a_A) + b(\mu_B^0 + RT \ln a_B)] \\ &= [c(\mu_c^0 + d\mu_D^0 + \dots) - (a\mu_A^0 + b\mu_B^0)] + RT \ln \frac{a_c^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots} \\ \Rightarrow \Delta G &= \Delta G^0 + RT \ln \frac{a_c^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots} \quad \text{--- (2)}\end{aligned}$$

where ΔG^0 is the difference in the free energy of the reaction when all the reactants and products are in their standard state, and the factor $\frac{a_c^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots}$ is the quotient of activities of the products and reactants. It may be denoted by J .

$$\therefore \Delta G = \Delta G^0 + RT \ln J$$

This is the van't Hoff equation of isotherm.

At equilibrium $\Delta G = 0$, we get

$$\Delta G^0 = -RT \ln J \quad \text{--- (3)}$$

where, ΔG^0 is the free energy of the reaction when the reactants and products are in their standard state and it is constant at a given temperature. R is constant and T is constant. So the factor $\frac{a_c^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots}$ is also constant.

we can write. $\frac{a_c^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots} = K$

$$\text{Using (3)} \quad \Delta G^0 = -RT \ln K$$

$$\text{or } \Delta G^0 = -2.303 RT \log K.$$

Derive an equation showing the effect of temperature on equilibrium constant. Q5, Q4

Soln: There is appreciable change in the value of equilibrium constant with the change in temperature. It can be determined thermodynamically using the relation.

$$\Delta G^\circ = -RT \ln K_P \quad \dots (1)$$

where ΔG° is the ^{change in} standard free energy of the reaction.

Differentiating equation (1) w.r.t T at constant pressure P we get.

$$\frac{d}{dT}(\Delta G^\circ) = -R \ln K_P - RT \frac{d}{dT}(\ln K_P)$$

Multiplying both sides by -T we get.

$$-T \frac{d}{dT}(\Delta G^\circ) = RT \ln K_P + RT^2 \frac{d}{dT}(\ln K_P)$$

$$\Rightarrow -T \frac{d}{dT}(\Delta G^\circ) = -\Delta G^\circ + RT^2 \frac{d}{dT}(\ln K_P)$$

$$\Rightarrow \Delta G^\circ - T \frac{d}{dT}(\Delta G^\circ) = RT^2 \frac{d}{dT}(\ln K_P) \quad \dots (2)$$

Comparing equation (2) with Gibbs-Helmholtz equation

$$\Delta G^\circ = \Delta H^\circ + T \frac{d}{dT}(\Delta G^\circ) \text{ we get,}$$

$$\Delta H^\circ = RT^2 \frac{d}{dT} \ln K_P$$

$$\Rightarrow \frac{\Delta H^\circ}{RT^2} = \frac{d}{dT} \ln K_P \quad \dots (3)$$

This equation is known as Van't Hoff equation. Where ΔH° is the enthalpy change of the reaction at constant pressure when all reactants and products are in their standard state. It has been found that the enthalpy change does not vary much with change in partial pressures of the reactants and products.

TARE
In these cases, ΔH° may be replaced by ΔH . The equation (3) becomes

$$\frac{\Delta H}{RT^2} = \frac{d}{dT} (\ln K_p) \quad \text{--- (4)}$$

Integrating equation (4) within the limits K_p_2 at temp T_2 and K_p_1 at temperature T_1 .

$$\int_{K_p_1}^{K_p_2} d \ln K_p = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} dT$$

$$\Rightarrow \ln \frac{K_p_2}{K_p_1} = - \frac{\Delta H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\Rightarrow \ln \frac{K_p_2}{K_p_1} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\Rightarrow \ln \frac{K_p_2}{K_p_1} = \frac{\Delta H}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\therefore \log \frac{K_p_2}{K_p_1} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

From this equation the heat of reaction can be determined if the values of equilibrium constant K_p_2 and K_p_1 at temperature T_2 and T_1 are known and vice-versa.

Q7. Deduce Van't Hoff equation in terms of K_c . Using this equation how can you proceed to determine ΔE for a reaction?

Soln:- We know that the 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 w.r.t temperature get

$$\frac{d}{dT}(\ln K_P) = \frac{d}{dT}(\ln K_C) + \frac{\Delta n}{T}$$

$$\Rightarrow \frac{d}{dT}(\ln K_C) = \frac{d}{dT}(\ln K_P) - \frac{\Delta n}{T} \quad \text{--- (1)}$$

$$\Delta n \frac{1}{RT} R = \frac{\Delta n}{T}$$

we know that $\frac{d}{dT}(\ln K_P) = \frac{\Delta H}{RT^2}$

Substituting this into equation (1) we get.

$$\frac{d}{dT}(\ln K_C) = \frac{\Delta H}{RT^2} - \frac{\Delta n}{T}$$

$$\Rightarrow \frac{d}{dT}(\ln K_C) = \frac{\Delta H}{RT^2} - \frac{\Delta n RT}{T^2}$$

$$\Rightarrow \frac{d}{dT}(\ln K_C) = \frac{\Delta H - \Delta n RT}{RT^2}$$

But we know $\Delta H = \Delta E + \Delta n RT$

$$\therefore \frac{d}{dT}(\ln K_C) = \frac{\Delta E}{RT^2} \quad \text{--- (2)}$$

Equation (2) is the van't Hoff equation in terms of K_C

where ΔE is the heat of the reaction at constant volume.

Integrating (2) within the limits K_C_2 at temp. T_2 and K_C_1 at temp. T_1 we get.

$$\int_{K_C_1}^{K_C_2} d \ln K_C = \int_{T_1}^{T_2} \frac{\Delta E}{RT^2} dT$$

$$\Rightarrow \ln \frac{K_C_2}{K_C_1} = - \frac{\Delta E}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

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$$\Rightarrow \ln \frac{K_C_2}{K_C_1} = \frac{\Delta E}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\Rightarrow \ln \frac{K_C_2}{K_C_1} = \frac{\Delta E}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\therefore \log \frac{K_C_2}{K_C_1} = \frac{\Delta E}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

From this equation the value of ΔE can be calculated if the values of equilibrium constant K_C_2 at T_2 and K_C_1 at T_1 are known.

~~Q8~~ Write down van't Hoff equation for K_P and K_C and define the different terms involved in each case.

~~Soln~~:- van't Hoff equation for K_P is

$$\underbrace{\frac{d}{dT} (\ln K_P)}_{\text{where, } K_P = \text{Equilibrium constant in terms of partial pressure.}} = \frac{\Delta H}{RT^2}$$

where, K_P = Equilibrium constant in terms of partial pressure.

ΔH = Heat of the reaction at constant pressure.

T = Absolute temperature.

R = Gas constant.

van't Hoff equation for K_C is

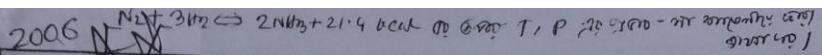
$$\frac{d}{dT} (\ln K_C) = \frac{\Delta E}{RT^2}$$

where, K_C = Equilibrium constant in terms of concentration.

ΔE = Heat of the reaction at constant volume.

T = Absolute temperature.

R = Gas constant.



Q. State and explain Le Chatelier's principle.

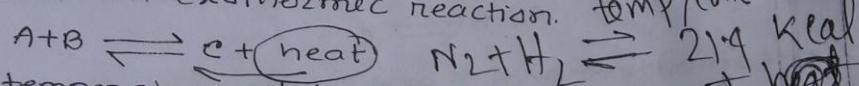
Ans - For chemical equilibrium Le Chatelier's principle can be stated as:

If a change in concentration, pressure or temperature is caused to a chemical reaction in equilibrium, the equilibrium will shift to the right or to the left so as to minimize the change.

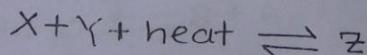
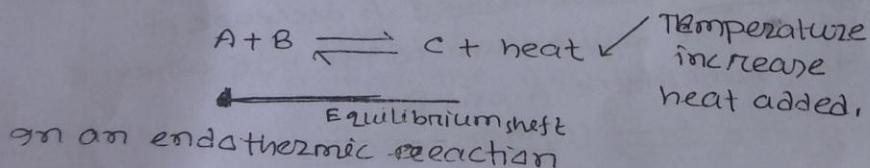
Now we proceed to illustrate the above statement by taking examples of each type of stress.

① Effect of change of temperature: When temperature of a reaction is increased, the equilibrium shifts in a direction in which heat is absorbed.

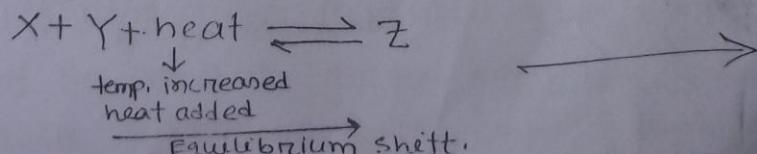
Let us consider an exothermic reaction.



When the temperature of the system is increased, heat is supplied to it from outside. According to this principle, the equilibrium will shift to the left which involves the absorption of heat.



The increase of temperature will shift the equilibrium to the right as it involves the absorption of heat.



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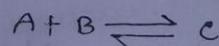
In general, we can say that the increase of temp. favours the reverse change in an exothermic reaction and the forward change in an endothermic reaction.

Left to right

② Effect of change in pressure: If the pressure of a gaseous equilibrium state is increased, the equilibrium will shift in a direction which tends to decrease in pressure.

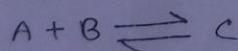
The pressure of a gaseous equilibrium state is determined by the total number of molecules it contains. If the forward reaction proceeds by the reduction of molecules, it will accompanied by the decrease of the pressure of the system and vice-versa.

Let us consider an equilibrium reaction



The combination of A and B produces a reduction of number of molecules while the decomposition of C into A and B produces an increase in the number of molecules. Therefore the increase of pressure on the equilibrium will shift to the right and produce more C. A decrease of pressure will shift the equilibrium to the left when C will decompose to form more A and B.

moles decrease

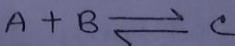


→

Equilibrium shift

in increase of P

moles increases



→

Equilibrium shift on

decrease of P.

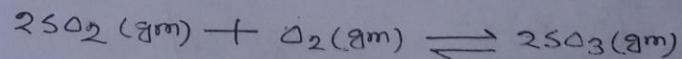
Therefore we can conclude that the increase of pressure in a chemical equilibrium shifts it in a direction in which the number of moles decrease and vice-versa.

② Effect of change in concentration:

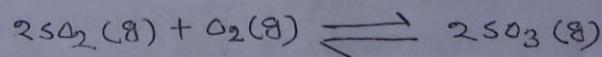
When the concentration of any of the reactants or products is changed the equilibrium shifts in a direction so as to minimize the change in concentration that was made

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Q: Derive an equation to show that the effect of pressure on the following equilibrium.



Sol: Given that the reaction is



At initial state. 2 1 0 mole

At equilibrium state. $2-2\alpha$ $1-\alpha$ 2α mole.

Let at initial state the mole number of SO_2 and O_2 are 2 and 1 respectively. At equilibrium, by reacting α mole of SO_2 and O_2 form SO_3 . The mole number of SO_2 , O_2 and SO_3 are $(2-2\alpha)$, $(1-\alpha)$ and 2α respectively.

$$\begin{aligned} \text{At equilibrium, the total mole number} \\ &= 2-2\alpha + 1-\alpha + 2\alpha \\ &= 3-\alpha \end{aligned}$$

Let us consider the ^{total} pressure of the system $3 = P$

We know that,

Partial pressure = Total pressure \times mole fraction.

$$\therefore P_{SO_2} = \frac{2-2\alpha}{3-\alpha} P$$

$$P_{O_2} = \frac{1-\alpha}{3-\alpha} P$$

$$P_{SO_3} = \frac{2\alpha}{3-\alpha} P$$

$$\therefore K_p = \frac{(P_{SO_3})^2}{(P_{SO_2})^2 \times P_{O_2}} = \frac{\left(\frac{2\alpha}{3-\alpha}\right)^2 P^2}{\left(\frac{2-2\alpha}{3-\alpha}\right)^2 \times \left(\frac{1-\alpha}{3-\alpha}\right) P}$$

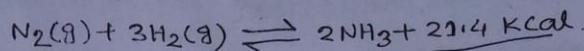
$$\therefore K_p = \frac{(3-\alpha)\alpha^2}{(1-\alpha)^3 P} \quad \text{--- (1)}$$

We can conclude from (1) if the pressure increases then the ^{equilibrium} constant K_p decreases. But at constant temp K_p is constant, so far keeping the value of K_p constant, the value of α must be increased if the pressure increases.

So if the pressure increase the equilibrium will go forward and the ^{Production} of SO_3 will be increased.

~~Ques. 5~~ With the help of Le-Chatelier's principle, explain the effect of temperature and pressure on the reaction.

TARI



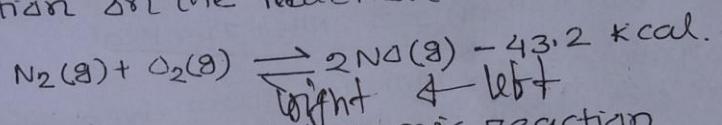
Soln:- The synthesis of ammonia from Hydrogen and Nitrogen is an exothermic reaction.

Effect of temperature:- When the temperature of the system is raised the equilibrium will shift from ~~right-to-left~~ ^{right-to-left} to right. On the other hand by lowering the temperature the equilibrium will shift from ~~right-to-left~~ ^{left-to-right} which evolves the heat in an attempt to raise the temperature.

Effect of pressure:- High pressure on the reaction at equilibrium favours the shift of the reaction to the right. Because the forward reaction proceed a decrease in the number of moles.

Effect of concentration:- If the concentration of the elements of the reactants (i.e., H₂ and N₂) is increased the equilibrium will shift from right-to-left and if the concentration of the element of product is increased the equilibrium will shift from right-to-left-to-right.

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Q10: (i) With the help of the Le Chatelier's principle explain the effect of temperature, pressure and concentration on the reaction.



Soln:- This is an endothermic reaction.

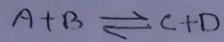
① Effect of temperature:- When the temperature of the system is raised the equilibrium will shift from left-to-right and if the temperature of the system is lowered the equilibrium will shift from right-to-left.

② Effect of Pressure:- There is no effect of change in pressure on the equilibrium of the reaction because forward reaction involves no change in the number of moles.

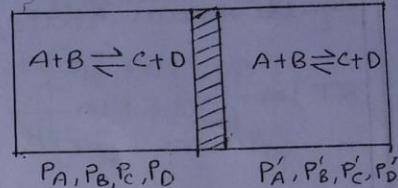
③ Effect of concentration:- The formation of nitric-oxide is favoured by using the high concentration of the reactants i.e., N_2 and O_2 .

thermodynamic derivation of equilibrium constant.

Soln: Let us consider a reaction.



takes place at the same temp. in two large containers. Each of the two containers A, B, C, D are in equilibrium state and there is a semipermeable membrane between the two containers.



Let the partial pressure of A, B, C, D in the 1st container is P_A, P_B, P_C and P_D and that of the second container is P'_A, P'_B, P'_C, P'_D .

$$dG = VdP - SdT$$

$$dG = VdP \quad [dT = 0, \text{ isothermal process}]$$

Now, free energy change of A, $\Delta G_{1A} = \int_{P_A}^{P'_A} VdP$

$$= \int_{P_A}^{P'_A} \frac{RT}{P} dP$$
$$= RT \ln \frac{P'_A}{P_A}$$

Free energy change of B, $\Delta G_{1B} = RT \ln \frac{P'_B}{P_B}$

" " " " " C, $\Delta G_{1C} = RT \ln \frac{P'_C}{P_C}$

" " " " " D, $\Delta G_{1D} = RT \ln \frac{P'_D}{P_D}$

Total free energy change

$$\Delta G = RT \ln \frac{P_A}{P_A} + RT \ln \frac{P_B'}{P_B} + RT \ln \frac{P_C'}{P_C} + RT \ln \frac{P_D}{P_D}$$

At equilibrium state, $\Delta G = 0$

$$\therefore RT \ln \frac{P_A}{P_A} + RT \ln \frac{P_B'}{P_B} = RT \ln \frac{P_C'}{P_C} + RT \ln \frac{P_D}{P_D}$$

$$\Rightarrow \ln \frac{P_A'}{P_A} + \ln \frac{P_B'}{P_B} = \ln \frac{P_C'}{P_C} + \ln \frac{P_D}{P_D}$$

$$\Rightarrow \ln \frac{P_A' \times P_B'}{P_A \times P_B} = \ln \frac{P_C' \times P_D}{P_C \times P_D}$$

$$\therefore \frac{P_C' \times P_D}{P_A \times P_B} = \frac{P_C' \times P_D}{P_A' \times P_B'} = K_P$$

[For this system the partial pressure is proportional to molar concentration]

$$\frac{c_C \times c_D}{c_A \times c_B} = K_C$$

Q: Now consider the reaction



where, a, b, c, d are the mole numbers of A, B, C, D respectively.

Let the partial pressure of a mole A, b mole B, c mole C, d mole D are P_A, P_B, P_C, P_D respectively.

$$\text{Free energy of a mole } A = aG_A = a[G_A^{\circ} + RT \ln P_A]$$

$$\text{ " " " b " } B = bG_B = b[G_B^{\circ} + RT \ln P_B]$$

$$\text{ " " " c " } C = cG_C = c[G_C^{\circ} + RT \ln P_C]$$

$$\text{ " " " d " } D = dG_D = d[G_D^{\circ} + RT \ln P_D]$$

Where, $G_A^{\circ}, G_B^{\circ}, G_C^{\circ}, G_D^{\circ}$ are the standard free energy of A, B, C, D respectively.

The free energy change of the reaction.

$$\Delta G = G_{\text{Product}} - G_{\text{Reactant}}$$

$$= (cG_C + dG_D) - (aG_A + bG_B)$$

$$= (cG_C^{\circ} + cRT \ln P_C + dG_D^{\circ} + dRT \ln P_D)$$

$$- (aG_A^{\circ} + aRT \ln P_A + bG_B^{\circ} + bRT \ln P_B)$$

$$= (cG_C^{\circ} + dG_D^{\circ} - aG_A^{\circ} - bG_B^{\circ}) + (cRT \ln P_C + dRT \ln P_D - aRT \ln P_A - bRT \ln P_B)$$

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b} \quad \text{--- ①}$$

This is the van't Hoff isothermal equation.

At equilibrium $\Delta G = 0$

$$\therefore \boxed{\Delta G^{\circ} = -RT \ln K_P}$$



The equilibrium constants (K_P) for a reaction are 1.22×10^3 and 2.16 at 298K and 498K , respectively. Calculate ΔH for the reaction, $2\text{K} + ?$

∴ We know,

$$\log \frac{K_{P2}}{K_{P1}} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\Rightarrow \log \frac{2.16}{1.22 \times 10^3} = \frac{\Delta H}{2.303 \times 8.314} \left[\frac{498 - 298}{298 \times 498} \right]$$

$$\Rightarrow 3.24 = \frac{\Delta H}{19.147} \times \frac{200}{148404}$$

$$\Rightarrow \Delta H = 46.03 \times 10^3 \text{ J}$$

$$\therefore \Delta H = 46.03 \text{ KJ} \text{ (Ans)}$$

Here,

$$K_{P1} = 1.22 \times 10^3$$

$$K_{P2} = 2.16$$

$$T_1 = 298\text{K}$$

$$T_2 = 498\text{K}$$

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta H = ?$$

3/ The equilibrium constant K_C for a reaction $A \rightleftharpoons B$ at 25°C and 45°C are 0.143 and 0.293 . Calculate ΔH for this reaction, $2\text{K} + \Delta, 2\text{K} + ?$

Soln:- We know,

$$\log \frac{K_{C2}}{K_{C1}} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right]$$

$$\Rightarrow \log \frac{0.293}{0.143} = \frac{\Delta H}{2.303 \times 8.314} \left[\frac{318 - 298}{298 \times 318} \right]$$

$$\Rightarrow 0.1304 = \frac{\Delta H}{19.147} \times \frac{20}{94764}$$

$$\Rightarrow \Delta H = 11.83 \times 10^3 \text{ J}$$

$$\therefore \Delta H = 11.83 \text{ KJ} \text{ (Ans)}$$

Here,

$$K_{C1} = 0.143$$

$$K_{C2} = 0.293$$

$$T_1 = (25 + 273) \text{ K}$$

$$= 298 \text{ K}$$

$$T_2 = 318 \text{ K}$$

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta H = ?$$

TAREK

- At 100°C, ΔG° for the dissociation $N_2O_4 \rightleftharpoons 2NO_2(g)$ is -16.676 kJ .
- (i) Calculate K_p and K_c for this dissociation at this temperature.
 - (ii) Find out the degree of dissociation of N_2O_4 under the total pressure of 10 atm.
 - (iii) Explain the effect of temperature on the dissociation. 2K+5

Soln:- we know,

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

$$\Rightarrow -7039.2 = -8.314 \times 373 \times \ln K_p$$

$$\Rightarrow \ln K_p = 2.26$$

$$K_p = 9.67$$

Ans.

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

$$\Rightarrow 9.67 = K_c (8.314 \times 373)^1$$

$$\Rightarrow K_c = 3.12 \times 10^3$$

Here,

$$\Delta G^\circ = -16.676 \text{ kJ}$$

$$= -1.676 \times 10^3 \times 4.2$$

$$= -7039.2 \text{ J}$$

$$T = 373 \text{ K}$$

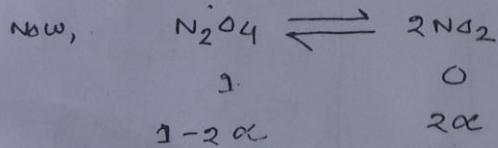
$$K_p = ?$$

$$K_c = ?$$

$$\alpha = ?$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta n = 2 - 1 = 1$$



$$P = 10 \text{ atm}$$

$$P_{NO_2} = 2\alpha$$

$$P_{N_2O_4} = 1$$

$$\text{Now, } K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \times P = \frac{(2\alpha)^2}{1} \times P = 4\alpha^2 P \therefore \alpha = \sqrt{\frac{K_p}{4P}}$$
$$= \sqrt{\frac{9.67}{4 \times 10}}$$
$$= 0.489$$

Effect of pressure:- If the pressure increase the production of NO_2 will be ~~decrease~~ if α increase, N_2O_4 decrease and NO_2 increase.

TAREF

equilibrium constants (K_p) for reaction are 0.773 at 500°C and 12.06 at 600°C , calculate ΔH for the reaction. 2K+4.

Soln:- we know that

$$\log \frac{K_p 2}{K_p 1} = \frac{\Delta H}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\Rightarrow \log \frac{12.06}{0.773} = \frac{\Delta H}{2.303 \times 8.314} \left[\frac{873 - 773}{773 \times 873} \right]$$

$$\Rightarrow 1.293 = \frac{\Delta H}{19.147} \times \frac{100}{674829}$$

$$\Rightarrow \Delta H = 154146.9 \text{ J}$$

$$\therefore \Delta H = 154.146 \text{ kJ (Ans)}$$

Here,

$$K_p 1 = 0.773$$

$$K_p 2 = 12.06$$

$$T_1 = 773 \text{ K}$$

$$T_2 = 873 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H = ?$$

For a reaction, K_c is 1.22×10^{-3} at 298 K and 2.16×10^{-3} at 498 K. calculate ΔE for the reaction. 2K+3, 2K+1

Soln:- we know,

$$\log \frac{K_c 2}{K_c 1} = \frac{\Delta E}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{2.16 \times 10^{-3}}{1.22 \times 10^{-3}} = \frac{\Delta E}{2.303 \times 8.314} \left[\frac{498 - 298}{298 \times 498} \right]$$

$$\Rightarrow 0.248 = \frac{\Delta E}{19.147} \times \frac{200}{148404}$$

$$\Rightarrow \Delta E = 3523.45 \text{ J}$$

Here,

$$K_c 1 = 1.22 \times 10^{-3}$$

$$K_c 2 = 2.16 \times 10^{-3}$$

$$T_1 = 298 \text{ K}$$

$$T_2 = 498 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

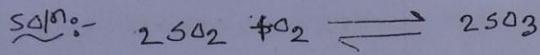
$$\Delta E = ?$$

$$\therefore \Delta E = 3.52 \text{ kJ (Ans)}$$

Tuli \rightarrow P-582, No: ①, 578, ②, 566, ①, ②

TAREX PRACTICAL

6. A mixture of 2.0 moles of SO_2 and 1.0 mole of O_2 is present in a 10 litre reacting vessel at 800K and at equilibrium 0.6 mole of SO_3 is formed. Calculate the total pressure of the reaction mixture and K_p . $2\text{K}+2$.



At initial state. 2 1 Δ mole

At equilibrium $2-2\alpha$ $1-\alpha$ 2α mole.

According to the question. $2\alpha = 0.6$

$$\alpha = 0.3 \text{ mole}$$

$$T = 800\text{K}$$

$$V = 10 \text{ litre}$$

$$\text{Now, } K_c = \frac{\left(\frac{2\alpha}{V}\right)^2}{\left(\frac{2-2\alpha}{V}\right)^2 \times \frac{1-\alpha}{V}} = \frac{4\alpha^2/V^2}{4(1-\alpha)^2 \times \frac{(1-\alpha)^2}{V^2}} = \frac{V^2 \alpha^2}{(1-\alpha)^3}$$

$$\therefore K_c = \frac{(10)^2 \times 0.3^2}{(1-0.3)^3} = 26.24$$

$$\text{we know, } K_p = K_c (RT)^{\Delta n}$$

$$= 26.24 \times (0.0821 \times 800)^{-1}$$

$$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$\Delta n = 2-3 = -1$$

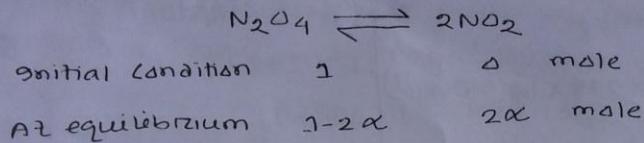
$$= 0.04$$

$$\text{Again, } K_p = \frac{(1-\alpha)^{\Delta n}}{P} \Rightarrow P = \frac{(1-\alpha)^{\Delta n}}{K_p}$$

$$= \frac{(1-0.3)^2}{0.04 \times (1-0.3)^3} = 19.71 \text{ atm}$$

At a certain temp. the equilibrium constant of a reaction is 0.21
 $N_2O_4 \rightleftharpoons 2NO_2$. calculate the partial pressure. The dissociation
 of N_2O_4 is 35%. at atm $2K-1$

Soln



$$\text{Total mole} = 1 - 2\alpha + 2\alpha = 1 \text{ mole}$$

$$\text{Now, } K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{4\alpha^2}{1^2} \cdot P \quad \left| \begin{array}{l} \alpha = 0.35 \\ K_p = 0.21 \end{array} \right.$$

$$\Rightarrow P = \frac{K_p}{4\alpha^2} = \frac{0.21}{4 \times (0.35)^2} = 0.42 \text{ atm} \quad \text{Ans}$$

8. The value of K_p at 298 K for the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$
 is found to be 826. Partial pressure being measured in atmospheric
 unit. calculate ΔG° at 298 K.

Soln: We know,

$$\begin{aligned} \Delta G^\circ &= -2.303 RT \log K_p \\ &= -2.303 \times 0.0821 \times 298 \times \log 826 \\ &= -3977.78 \text{ cal} \end{aligned}$$

Ans

Here,

$$T = 298 \text{ K}$$

$$K_p = 826$$

$$R = 8.314 \text{ L atm}$$

$$R = 0.0821 \text{ L atm} \text{ per mole}$$

$$\Delta G^\circ = ?$$

$$R = 1.987 \text{ cal mole}^{-1} \text{ K}^{-1}$$

Formation enthalpy of 1 mole NH_3 is $\frac{\Delta H}{2}$

Because $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$\begin{array}{l} \Delta H^\circ \text{ of formation cal, 298 K} \\ R = 1.99 \end{array}$$

$$\begin{array}{l} \Delta G^\circ \text{ of formation 298 K} \\ R = 8.314 \end{array}$$

TAREX

Q. The equilibrium constant K_p for the reaction $C_2H_2(g) + H_2(g) \rightleftharpoons C_2H_6(g)$ is 5.04 atm^2 at 25°C . Calculate ΔG° .

Soln:

$$\Delta G^\circ = -2.303 RT \ln K_p$$

$$= -2.303 \times 8.314 \times 298 \times \ln(5.04 \times 10^2)$$

$$= -200 \text{ kJ}$$

Ans

Here,

$$K_p = 5.04 \text{ atm}^2$$

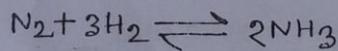
$$T = 298 \text{ K}$$

$$\Delta G^\circ = ?$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Q. At 500°C the reaction between N_2 and H_2 to form ammonia has $K_c = 6 \times 10^2$. What is the numerical value of K_p for the reaction.

Soln: The equilibrium reaction is



we know,

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

$$= 6 \times 10^2 \times (0.0821 \times 773)^{-2}$$

$$= 1.5 \times 10^{-5}$$

Ans

Here,

$$T = 500^\circ\text{C} = 773 \text{ K}$$

$$K_c = 6 \times 10^2$$

$$\Delta n = 2 - (1 + 3)$$

$$= -2$$

$$R = 0.0821 \text{ Latm K}^{-1} \text{ mol}^{-1}$$

Q. In a reversible reaction the value of Δn is $\frac{1}{2}$. At what temp. the value of K_p and K_c will be 40.5 and 5.5, $R = 0.0821 \text{ Latm K}^{-1} \text{ mol}^{-1}$

Soln: we know,

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

$$\Rightarrow \frac{40.5}{5.5} = (0.0821 \times T)^{\frac{1}{2}}$$

$$\Rightarrow T = \frac{1}{0.0821} \times \left(\frac{40.5}{5.5} \right)^2$$

$$T = 661.22 \text{ K}$$

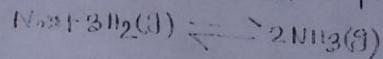
$$\Delta n = \frac{1}{2}$$

$$K_p = 40.5$$

$$K_c = 5.5$$

$$R = 0.0821 \text{ Latm K}^{-1} \text{ mol}^{-1}$$

Write the equilibrium constant expression for the reaction

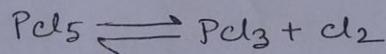


Sol:- The equation is already balanced. The numerical quotient of H_2 and NH_3 are 3 and 2 respectively. The concentration of the product is $[NH_3]^2$ and partial pressure is $P_{NH_3}^2$, the product of the concentration of the reactant is $[N_2][H_2]^3$. The product of the partial pressure of the reactants is $P_{N_2} \times P_{H_2}^3$

$$\text{So, } K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \text{and, } K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$

13. with the help of law of mass action calculate the values of K_p and K_c for the reaction. $P_{Cl_5} = P_{Cl_3} + Cl_2$

Sol:- Let us consider the reaction is performed in pressure P , and volume V . Let, and the degree of dissociation is x .



| | | | | |
|---------------------------------|-------|-------|-------|------|
| At initial state | 1 | 0 | 0 | mole |
| At ^{equilibrium} state | $1-x$ | $1-x$ | $1-x$ | mole |

At ~~final~~ state
mole number

Q At equilibrium state the molar concentration of the ~~reactants~~ ^{elements} ~~molecules~~

$$[P_{Cl_5}] = \frac{1-x}{V} \text{ mol/L} \quad [P_{Cl_3}] = \frac{x}{V} \text{ mol/L} \quad [Cl_2] = \frac{x}{V} \text{ mol/L}$$

$$\therefore K_c = \frac{[P_{Cl_3}] \times [Cl_2]}{[P_{Cl_5}]} = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{1-x}{V}} = \frac{x^2}{(1-x)V}$$

$$\boxed{\therefore K_c = \frac{x^2}{(1-x)V}}$$

TAREE

[Q] Let at equilibrium the total mole number α
 $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

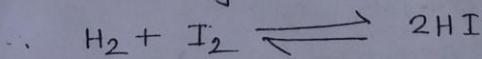
$$\therefore P_{PdS} = \frac{1 - \alpha}{1 + \alpha} P_{atm}, P_{Pd3} = \frac{\alpha}{1 + \alpha} P_{atm}, P_{Cl2} = \frac{\alpha}{1 + \alpha} P_{atm}$$

$$\therefore K_p = \frac{P_{Pd3} \times P_{Cl2}}{P_{PdS}} = \frac{\frac{\alpha}{1 + \alpha} P \times \frac{\alpha}{1 + \alpha} P}{\frac{1 - \alpha}{1 + \alpha} P} = \frac{\alpha^2 P^2}{(1 + \alpha)^2} \times \frac{1 + \alpha}{1 - \alpha} P = \frac{\alpha^2}{1 - \alpha^2} P$$

$$K_p = \frac{\alpha^2}{1 - \alpha^2} P$$

34. With the help of the law of mass action calculate the value of K_p and K_c from the reaction: $H_2 + I_2 \rightleftharpoons 2HI$

Soln:- Let us consider the reaction is performed at pressure P atm. volume V litre and degree of dissociation is α



At initial state mole number $a \quad b \quad 0$ mole

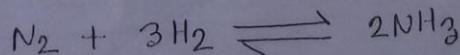
At equilibrium mole number $a - \alpha \quad b - \alpha \quad 2\alpha$ mole

$$\therefore K_c = \frac{4\alpha^2}{(a - \alpha)(b - \alpha)}$$

$$K_p = \frac{4\alpha^2}{(a - \alpha)(b - \alpha)}$$

35. With the help of the law of mass action calculate the value of K_p and K_c for the equilibrium: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

According to (2)



At initial state mole number $a \quad b \quad 0$ mole

At equilibrium state mole number $a - \alpha \quad b - 3\alpha \quad 2\alpha$ mole

$$K_p = \frac{4\alpha^2 (a + b - 2\alpha)^2}{(a - \alpha)(b - 3\alpha)^3}$$

$$K_p = \frac{16\alpha^2 (2\alpha)^2}{27P^2 (5 - \alpha)^4}$$

$$K_c = \frac{4\alpha^2 V^2}{(a - \alpha)(b - 3\alpha)^3}$$