Chemical Equilibrium

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Overview

- **Describing Chemical Equilibrium**
  - Chemical Equilibrium – A Dynamic Equilibrium (the link to Chemical Kinetics)
  - The Equilibrium Constant.
  - Heterogeneous Equilibria; solvents in homogeneous equilibria.
- **Using the Equilibrium Constant**
  - Qualitatively Interpreting the Equilibrium Constant
  - Predicting the direction of a Reaction
  - Calculating Equilibrium Concentrations
- **Changing Reaction Conditions; Le Châtelier's Principle.**
  - Removing Products or Adding Reactants
  - Changing the Pressure or Temperature
  - Effect of a Catalyst.

The Equilibrium State

- Not all reactants are completely converted to product.
- Reaction equilibria deal with the extent of reaction.
- Arrows between reactants and products separate them and qualitatively indicate the extent of reaction.
  - Single arrow points to dominant side:

    $H_2(g) + O_2(g) \rightarrow H_2O(g)$ –forward reaction
  - Double arrow indicates both reactants and products present after equilibrium obtained:

    $N_2O_4\,(g) \leftrightarrow 2NO_2(g)$. -reversible reaction

- Equilibrium exists when rates of forward and reverse reaction are the same.

E.g. When rate of N_2O_4 decomposition equal the rate of formation of N_2O_4, reaction at equilibrium

$$N_2O_4\,(g) \leftrightarrow 2NO_2(g).$$

- Equilibrium can be obtained from any mixture of reactants and products.

Chemical Equilibrium – Characteristics

- ---represents the condition –there is no apparent change in the composition or other observable properties of the system with time.

- Equilibrium is dynamic since product is constantly made (forward reaction), but at the same rate it is consumed (reverse reaction).

- --the stage at which free energy change(ΔG) for a reaction is zero.

- --disturbed by some external factor, it readjusts with the changing conditions and returns spontaneously to the original state when the disturbing forces are removed.

- Its position is not affected by the catalysts. A catalyst increases the rates of both the forwards and backward reactions to the same extent and thereby merely speeds up the attainment of equilibrium reaction

Chemical Equilibrium

$$A + B \longleftrightarrow C + D$$

The two opposing reactions are

--the reaction between A &B yield product C & D.---- forward reaction.(initial stage-only forward reaction)

---As reaction proceeds the product produced, then C&D react together to form A&B-backward reaction.

At equilibrium, rate of forward reaction =rate of backward reaction

Chemical Equilibrium

----is that stage of a reversible reaction at which both the forward and the backward reactions take place with equal rates without change in the composition of the system.

Law of Mass action

---the rate at which a substance react is directly proportional to its active mass

---- the rate of a chemical reaction is directly proportional to the product of active masses of the reaction.

----the term active mass may be considered as molar concentrations for solutions and gases.

----The active masses of solids are taken as unity.

Law of Mass action

Consider a general eqn.

$$aA+bB \longrightarrow P$$

According to the law of Mass action , the rate of the reaction that any instant is given by

$$r=k(C_A)^a\,(C_B)^b$$

$C_{A,}$ C_{B-} conc. of the reactant at that instant

k-rate constant

The Equilibrium Constant K_c

- Equilibrium constant of reverse reaction: $K_{c,r} = \frac{1}{K_{c,f}}$

aA + bB $\leftrightarrow$ cC + dD

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

cC + dD $\leftrightarrow$ aA + bB

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

Equilibrium constant

$K_c = k_1/k_2$—is a constant called for a reaction Equilibrium constant.

It is the rate constant for the forwarded reaction to that of the backward reaction.

For a reaction,

$$aA + bB \longleftrightarrow lL + mM + \ldots\ldots$$

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

------- the law of chemical equilibrium

Equilibrium constant in terms of concentrations

$$aA + bB \longleftrightarrow lL + mM + \ldots\ldots$$

$$K_c = \frac{[L]^l \times [M]^m x\ldots\ldots}{[A]^a \times [B]^b x\ldots\ldots}$$

----is the ratio of the product of the equilibrium molar concentraions of the product to the product of the equilibrium molar concentrations of the reactant, the concentrations of the concerned species raised to the powers equal to their respective stoichiometric coefficients in the chemical reactions.

Equilibrium constant in terms of partial pressures

- For gases ,at a fixed temp., the partial pressure of a substance is proportional to its molar concentrations.
- Equilibrium constant in terms of partial pressure K_p

$$aA+bB \longleftrightarrow lL+\ mM+\dots\dots$$

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

Equilibrium constant

The values of K_p & K_c for a particular reaction at a constant temp. are unaffected by the factors

(1)Actual quantities of the reactant taken

(2)presence of catalyst

(3) presence of inert materials

(4)the overall pressure of the system.

K_p & K_c are vary with temp

Equilibrium constant in terms of Mole fractions

Equilibrium constant for gaseous equilibria also considered in terms of mole fractions of the reactant and products.

----is the ratio of the product of the equilibrium mole fractions of the product to the product of the equilibrium mole fractions of the reactant, the mole fractions being raised to the powers equal to their respective stoichiometric coefficients in the chemical reactions.

$$aA + bB \longrightarrow lL + mM + \ldots\ldots\ldots$$

$$K_x = \frac{P_L^{\,l} \text{ x } P_M^{\,m} \text{ x} \ldots\ldots\ldots}{P_A^{\,a} \text{ x } P_B^{\,b} \text{ x} \ldots\ldots\ldots}$$

K_p & K_c are vary with temp, but K_x depends also on pressure, when the change in no of moles in the reaction (Δn)is not zero.

Equilibrium constant in terms of activities

For thermodynamics, equilibrium constant widely used in terms of activities of the products and reactant.

- ----is the ratio of the product of the equilibrium activities of the product to the product of the equilibrium activities of the reactant, the activities of the concerned species being raised to the powers equal to their respective stoichiometric coefficients in the chemical reactions.

$$aA + bB \longleftrightarrow lL + mM + \ldots\ldots$$

$$K = \frac{a_L^{\,l} \times a_M^{\,m} \times \ldots\ldots}{a_A^{\,a} \times a_B^{\,b} \times \ldots\ldots}$$

- a-activities of the constant

- K dependent only on temp.

Relationship between K_c and K_p

- Relationship between concentration and pressure obtained from the ideal gas law.
  - Recall PV = nRT or $$P_A = \frac{n_A}{V}RT$$ $$= [A]RT$$
  - Substitute for P in equilibrium expression. Consider the reaction:

aA + bB $\leftrightarrow$ cC + dD

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b} = \frac{([C]RT)^c([D]RT)^d}{([A]RT)^a([B]RT)^b}$$

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

$$K_P = K_c(RT)^{(c+d)-(a+b)} = K_c(RT)^{\Delta n}$$

  - Use this relationship to relate K_P and K_c

Relationship between(i) K_p and K_x (ii) K_c and K_x

The partial pressure(p) of any gas in mixture of ideal gases is related to the total pressure(P)

partial pressure(p) =xP where x=mole fraction in a mixture

Substitute ‘xP’ for each partial pressure in the eqn.

$$K_p = \frac{p_L^{\,l} \times p_M^{\,m} \times ....}{p_A^{\,a} \times p_B^{\,b} \times ....}$$

$$= \frac{(x_L P)^l \times (x_M P)^m \times ....}{(x_A P)^a \times (x_B P)^b \times ....}$$

$$= \frac{x_L^{\,l} \times x_M^{\,m} \times ....}{x_A^{\,a} \times x_B^{\,b} \times ....} \times P^{(l+m+....)} \quad (a+{-}b+....)$$

$$K_p = K_x P^{(\Delta n)} \quad \text{---------}(`1)$$

(Δn)=(no. of pdt. Molecules - no. of reactant mole.)

Relationship between(i) K_p and K_x (ii) K_c and K_x

- We know, $K_p = K_c \times (RT)^{\Delta n}$

  since, $K_p = K_x P^{(\Delta n)}$, substituting the value of K_p

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

  $K_x = K_c \times \left[RT/P\right]^{\Delta n}$ PV=RT, V=RT/P

  $K_x = K_c \times V^{\Delta n}$ --------(2)

  V=vol. of system containing 1 mole of the gas

  V=total volume/ no of moles

If $\Delta n = 0$, all the equilibrium constant are same, otherwise they differ.

From (1) and (2) K_x *depends on the total pressure or volume*

Factors influencing the value of equilibrium constant

The value of K_p & K_c independent of the initial concentrations of the reactant and the catalyst.

Depend on the following factors

(1) Temp.----The rate of the reaction increases with increasing the temp.-because activation energy decreases

--the forward & backward reactions differ in their activation energies.

---value of equilibrium constant change with changing the temp.

As temp increases,

----- forward reaction endothermic,

equilibrium constant increases

---if it is exothermic,

equilibrium constant decreases

Factors influencing the value of equilibrium constant

(2) The mode of section of the reactant.

Formation of Ammonia $N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$

$$K_c = \frac{[NH_{3(g)}]^2}{[N_{2(g}] \times [H_2]^3}$$

The reaction is reversed

Decomposition of NH$_3$ $2NH_{3(g)} \leftrightarrow N_{2(g)} + 3H_{2(g)}$

$$K'_c = \frac{[N_{2(g}] \times [H_2]^3}{[NH_{3(g)}]^2}$$

$$K'_c = 1/\ K_c$$

Factors influencing the value of equilibrium constant

(3)Mode of representing the stoichiometric equation

Decomposition of NH_3 $$2NH_{3(g)} \longleftrightarrow N_{2(g)} + 3H_{2(g)}$$

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

Suppose the reaction changes, $$NH_{3(g)} \longleftrightarrow 1/2N_{2(g)} + 3/2H_{2(g)}$$

$$K'_c = \frac{[N_2]^{1/2} \times [H_2]^{3/2}}{[NH_3]}$$

$$K'_c = \sqrt{Kc}$$

Factors influencing the value of equilibrium constant

(4)Concentration of the partial pressure units used for the calculation of the equilibrium constant.

For a reaction, if $\Delta n \neq 0$,

the value of K_c depends on the unit at which the conc. of the reactant or product

the value of K_p depends on the unit at which the partial pressure of the reactant or product

Units

$K_c = (molL^{-1})^{\Delta n}$ or $(moldm^{-3})^{\Delta n}$ or $(molm^{-3})^{\Delta n}$

$K_p = (atm)^{\Delta n}$ or $(bar)^{\Delta n}$ or $(Pa)^{\Delta n}$

Thermodynamic treatment of the law of mass action

(a) Introduction

For this derivation we know two thermodynamic terms., chemical potential and activity

If system is gaseous,

Activity of a substance in an equilibrium as considered as pressure in thermodynamic terms

If system is ideal, activity=pressure

If system is a solution, activity as a measure of concentration.

Chemical molar potential or partial molar free energy (µ)of a component in a mixture is the contribution per mole of that particular component to the total free energy of the system under conditions of constant temp. and pressure.

Thermodynamic treatment of the law of mass action

If free energy (G) of mixture of components 1,2 etc.. at constant temp. and pressure,

$$(G)_{T,P} = n_1 \mu_1 + n_2 \mu_2 + \ldots\ldots.$$

n_1 n_2 = no of moles

μ_1 μ_2 = chemical potentials of components 1,2

Activity a_i of the ith constituent in a mixture at constant temp and pressure is related to its chemical potential μ_i

$$\mu_i = \mu_i^0 + RT\ln a_i$$

μ_i^0=standard chemical potential ,R=universal gas constant

----Chemical potential in its standard state at the same temp.

Thermodynamic treatment of the law of mass action

(b) Derivation of the van’t Hoff reaction isotherm and the law of chemical equilibrium

Consider a general reaction,

$$aA+bB+.... \longleftrightarrow lL+mM+....$$

----under any conditions of pressure and composition.

Total free energy of the reactant ($G_{\text{reactants}}$) consisiting ‘a’ moles of A , ’b’ moles of B.

$$G_{\text{reactants}} = a\mu_A + b\mu_B + ... \qquad (1)$$

Total free energy of the product,

$$G_{\text{products}} = l\mu_L + m\mu_M + ... \qquad (2)$$

μ=chemical potential of species

Thermodynamic treatment of the law of mass action

At constant temp. And pressure,

Change in free energy(ΔG)= $G_{\text{products}} - G_{\text{reactants}}$

$$=(l\mu_L + m\mu_M + \dots\dots\dots) - (a\mu_A + b\mu_B + \dots\dots\dots)$$

Substitute the eqn., $\mu = \mu^0 + RT\ln a$

$$\Delta G=[l\,(\mu_L^0 + RT\ln a_L^{l}\,) + m(\,\mu_M^0 + RT\ln a_M^{m}\,)] - [a(\,\mu_A^0 + RT\ln a_A^{a}\,) + b(\mu_B^0 + RT\ln a_B^{b}\,)] \quad \text{-------------} \quad (5)$$

$$= [l\,\mu_L^0 + m\mu_M^0) - (\,a\mu_A^0 + b\mu_B^0)] + [(RT\ln a^l_L + RT\ln a_M^m\,) - (RT\ln a_A^a + RT\ln a_B^b\,)] \quad \text{----------}(6)$$

$$\Delta G = \Delta G^0 + RT\ln \left\{ \frac{a^l_L \times a_M^m}{a_A^a \times a_B^b} \right\} \quad \text{-------------------}(7)$$

-----van’t Hoff reaction isotherm

Thermodynamic treatment of the law of mass action

If the reaction is in the state of equilibrium

$$\Delta G = 0$$

$$0 = \Delta G^0 + RT \ln \left[\frac{a_L^l \times a_M^m}{a_A^a \times a_B^b}\right]_{equb} \text{----------}(8)$$

$$\Delta G^0 = -RT \ln \left[\frac{a_L^l \times a_M^m}{a_A^a \times a_B^b}\right]_{equb} \text{----------}(9)$$

ΔG^0 for a reaction is constant at constant temp

$$\left[\frac{a_L^l \times a_M^m}{a_A^a \times a_B^b}\right]_{equb} = K \text{----------}(10)$$

K=thermodynamic equilibrium constant

Eqn (10) –represents ***law of mass action***

Thermodynamic treatment of the law of mass action

At constant temp. and pressure ,

activity of each component α molar concentrations

α partial pressure(if gaeous)

$$\left[\frac{C_L^l \text{x } C_M^m}{C_a^a \text{x } C_B^b}\right]_{equb} = Kc\text{, constant} \qquad -(11)$$

$$\left[\frac{P_L^l \text{x } P_M^m}{P_a^a \text{x } P_B^b}\right]_{equb} = K_P\text{ , constant} \qquad -(12)$$

Thermodynamic treatment of the law of mass action

(C) The standard free energy change and equilibrium constant

$\Delta G = -RT \ln K$ K=thermodynamic equilibrium constant

For ideal gaseous reactions, activities replaced by partial pressure

$$\Delta G^0 = -RT \ln K_p$$

$$\Delta G^0 = -2.303RT \log K_p$$

If we know Kp, can calculate ΔG^0

Thermodynamic treatment of the law of mass action

Temperature dependence of equilibrium constant

Equilibrium constant varies with change in temp

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

$$\log \frac{[K_p]_2}{[K_p]_1} = \frac{\Delta H^0}{2.303} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

$[K_p]_1$ & $[K_p]_2$ = value of equilibrium constant at T_1 & T_2

ΔH^0 - standard enthalpy change of a reaction- standard heat of reaction

Homogeneous equilibria

----in which all the constituents present in a single phase.

Gas Phase

Homogenous equilibria exist in two types-first & second type.

FIRST TYPE

no of reacting molecules=no of molecules of product Δn=0, $K_c = K_P$

$$H_{2(g)} + I_{2(g)} \longleftrightarrow 2HI_{(g)}$$

For these

equilibrium constant and on the equilibrium composition in depend on the pressure and volume of the reaction vessel (V).

SECOND TYPE

$$PCl_{5(g)} \longleftrightarrow PCl_{3(g)} + Cl_{2(g)}$$ $\Delta n \neq 0$, $K_c \neq K_P$

equilibrium constant and on the equilibrium composition depend on the pressure and volume of the reaction vessel (V).

Factors that Alter the Composition of an Equilibrium Mixture
Le Châtelier's Principle

Le Châtelier's Principle: "If a stress is applied to a reaction mixture at equilibrium, reaction occurs in the direction that relieves the stress."

- Types of stress on equilibrium:
  - Concentration of reactants or products. You can add or remove one or more components in a reaction mixture.
  - With gases changing the pressure or volume is a way of changing the concentrations of all components in the mixture.
  - Change temperature.

Le Châtelier's Principle: Changes in Concentrations

- If the conc. of a particular reactant increased, the system would like to reduce the amount of the added substance.

when the conc. of the reactant increases

---forward reaction occurs and equilibrium shifts towards right

- If the concentrations of the product increased the equilibrium shits left in order to reduce the amount of added substance.

$$A+B \longleftrightarrow C+D$$

(conc. reactant increased - equilibrium shifts towards right)

(conc. product increased - equilibrium shifts towards left)

Le Châtelier’s Principle: Changes in pressure

---It is significant in gaseous substance in which $\Delta n \neq 0$

---P’ of the gaseous system α to the total no of moles of substance present in it

----In a reaction, if no. of moles decreases, i.e., “P” of the system will decreases.

In a reaction, if no. of moles increases, i.e., “P” of the system will increases.

Law- when “P” increased (decreased) on a system containing gaseous substance in equilibrium, the equilibrium shifts in a direction which tends to decreases (or increases) the pressure and hence to decrease (or increase) the no. of moles.

Le Châtelier's Principle: Changes in temp.

If the temp. increased, the equilibrium shifts in the direction in which heat is absorbed-forward reaction

$A+B \leftrightarrow C+D$ heat (exothermic-absorption of heat)

If, forward reaction is exothermic, backward reaction is endothermic

In exothermic reaction

IF THE TEMP.

--------increases, equilibrium shifts in the backward direction to absorb excess of heat.

---------it cause backward reaction, hence increase the conc. of the reactant

-------- for greater yield of product can be achieved by lowering of temp.

Le Châtelier’s Principle: Changes in temp.

Endothermic

$A+B \longleftrightarrow C+D-\text{Heat}$ (endothermic-absorption of heat)

If, forward reaction is endothermic, backward reaction is exothermic

In such cases, if the temp. increases, ie, heat is supplied to it from the outside.

In endothermic reaction, for greater yield of product can be achieved by increasing of temp.

Le Châtelier's Principle: Application

1. Haber Process-manufacture of NH_3

$$N_{2(g)} + 3H_{2(g)} \longleftrightarrow 2NH_{3(g)} \quad \Delta H = -93.74 KJ$$

(forward ren: exo)

backward rexn –endo

(a) Effect of temp.

--Increase the temp backward rexn increases (endo.— decompositon of NH_3)

---decrease the temp would favors exothermic rexn-forward rexn- formation of NH_3

(b) Effect of "P"

---when P increase ,ie no of moles of molecules increases

------forwards rexn- decrease no of molecules

-----increase in 'P'-leads to the formation of NH_3- better yield.

Le Châtelier's Principle: Application

Haber Process-manufacture of NH_3

$N_{2(g)}$+ $3H_{2(g)}$ $\longleftrightarrow$ $2NH_{3(g)}$ ΔH= -93.74KJ (exo)

backward rexn –endo

(c) Effect of "conc."

If N_2 or H_2 added to the system- equilibrium shifts to get more NH_3

If NH_3 is removed from the system- equilibrium shifts to produced more NH_3

According to principle, to get high yield of NH_3

Conditions- low temp, high 'P' & constant removal of NH_3

In actual practice,

1. High 'p'(100-1000atm)
2. temp.-500^{O}C(to increase the rate rexn ,by increasing the threshold energy)
3. Constant removal of NH_3

use of catalyst- Finally divided Fe

Le Châtelier's Principle: Application

2.Contact Process-manufacture of H_2SO_4

$$2SO_{2(g)} + O_{2(g)} \longleftrightarrow 2SO_{3(g)} \quad \Delta H = -192.5KJ \text{ (exo)}$$

backward rexn –endo

(a) Effect of temp.

--Increase the temp backward rexn increases (endo.—decompositon of SO_3)

---decrease the temp would favors exothermic rexn-forward rexn-formation of SO_3

(b) Effect of "P"

---when P increase ,ie no of moles of molecules increases

------forwards rexn- decrease no of molecules

-----increase in 'P'-leads to the formation of NH_{3-}better yield.

Le Châtelier's Principle: Application

Contact Process-manufacture of H_2SO_4

$2SO_{2(g)} + O_{2(g)} \longleftrightarrow 2SO_{3(g)}$ ΔH= -192.5KJ (exo)

backward rexn –endo

(c) Effect of "conc."

If SO_2 or O_2 added to the system- equilibrium shifts to get more SO_3

If SO_3 is removed from the system- equilibrium shifts to produced more SO_3

According to principle, to get high yield of SO_3

Conditions- low temp, high 'P' (not use high "p"-SO_3 is highly corrosive & damage the walls of the chamber)

& constant removal of SO_3

In actual practice,

1. High 'p'(Max.1.7 atm)
2. temp.-450^OC(to increase the rate rexn ,by increasing the threshold energy)
3. Constant removal of SO_3

use of catalyst- Platinised asbestos V_2O_5

Le Châtelier's Principle: Application

3. Brikeland & Eyde Process-manufacture of HNO_3

$N_{2(g)} + O_{2(g)} \longleftrightarrow 2NO_{(g)}$ ΔH= +192.5KJ (endo)

backward rexn –exo

(a) Effect of temp.

--Increase in the temp. –endothermic -forward rexn- formation of NO increases

(b) Effect of "P"

--- there is no change in no. of molecules $\Delta n=0$

------no effect in "p"

Application

Brikeland & Eyde Process-manufacture of HNO_3

$$N_{2(g)} + O_{2(g)} \longleftrightarrow 2NO_{(g)} \quad \Delta H= +192.5KJ \text{ (endo)}$$

backward rexn –exo

(c) Effect of “conc.”

If N_2 or O_2 added to the system- equilibrium shifts to get more NO

If NO is removed from the system- equilibrium shifts to produced more NO

According to principle, to get high yield of NO

Conditions- high temp, & constant removal of NO

In actual practice,

1. High temp.-an electric arc is struck betn the reactant to produce NO

3. Constant removal of NO

NO is oxidised to NO_3 and dissolved in water to get HNO_3