Chemical Equilibrium

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What is equlibrium ?

Equilibrium

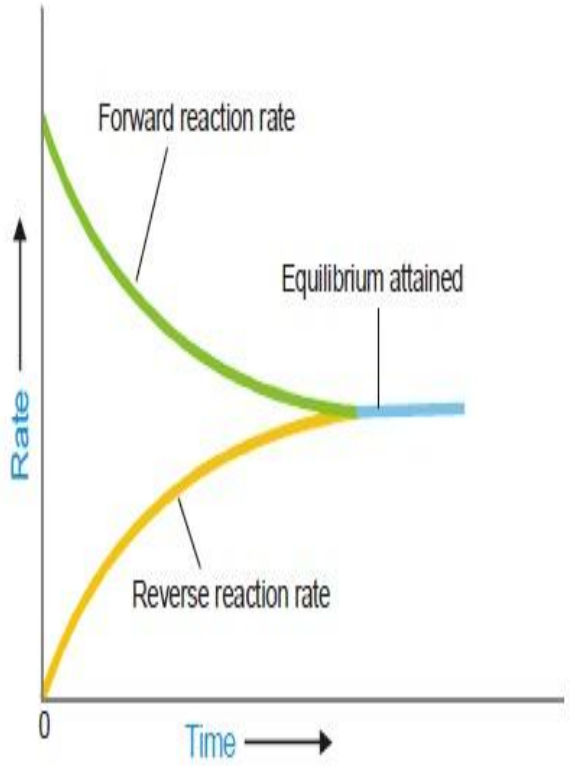
Equilibrium is a state in which there are no observable changes as time goes by.

- There are two types of equilibrium: Physical and Chemical.
  - Physical Equilibrium
    - H_20 (l) $\leftrightarrow$ H_20 (g)

  - Chemical Equilibrium
    - N_2O_4 (g) $\leftrightarrow$ $2NO_2$

Chemical Equilibrium

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



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

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

Characteristic of Chemical Equilibrium

- Chemical equilibrium is dynamic equilibrium
- Constancy of concentrations
- Equilibrium can be initiated from either side
- Equilibrium cannot be attained in an open vessel
- A catalyst cannot change the equilibrium point
- Value of equilibrium constant does not depend upon the initial concentration of reactants
- At equilibrium, $\Delta G = 0$ (the maximum work that can be derived from a chemical reaction is equal to the free energy)

Law of mass action & Eq. constant

- The law of mass action is universal, applicable under any circumstance. The mass action law gives us a general method to write the expression for the equilibrium constant of any reaction. However, for reactions that are complete, the result may not be very useful. Considering the following general chemical reaction

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

- The mass action law states that if the system is at equilibrium at a given temperature, then the following ratio is a constant:

$$\frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} = K \quad \text{(at equilibrium)}$$

- This is the ideal law of chemical equilibrium or law of mass action.
- The ratio of the equilibrium concentrations of products to the equilibrium concentrations of reactants each raised to the power of its stoichiometric coefficient.

Law of mass action

At a constant temperature, the rate of a chemical reaction is proportional to the active masses of the reacting substances.

$$\text{active mass, } a = c\,f$$

Where,

c = molecular concentration

f = activity coefficient

For dilute solution & gases, f =1 [do not deviate appreciably from ideal solutions]

For pure liquids & solids, c =1 [since rate of reaction is independent of amount]

Reaction quotient

A reaction quotient (Q) is a function of the activities or concentrations of the chemical species involved in a chemical reaction.

For any chemical reaction in a system,

$$a\,A + b\,B \rightarrow \quad c\,C + d\,D$$

We can always write a quotient,

$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$ (Q is reaction quotient)

If the system is NOT at equilibrium, the ratio is different from the equilibrium constant. In such cases, the ratio is called a reaction quotient which is designated as Q. A system not at equilibrium tends to become at equilibrium, and the changes will cause changes in Q so that its value approaches the equilibrium constant, K: $Q \rightarrow K$

Reaction quotient

When a chemical reaction in a closed system is at equilibrium, the reaction quotient is defined as the equilibrium constant, K, which depends on T. For a chemical reaction in a closed system, then

$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} = K \quad \text{(at equilibrium)}$$

If Q < K, the reaction goes forward to increase [product]
if Q = K, the system is at equilibrium the law of mass action
if Q > K, the reaction goes backward to decrease [product]

Writing Equilibrium Constant Expressions

- The concentrations of the reacting species in the condensed phase are expressed in M. In the gaseous phase, the concentrations can be expressed in M or in atm.
- The concentrations of pure solids and pure liquids do not appear in the equilibrium constant expressions.
- The equilibrium constant is a dimensionless quantity.
- In quoting a value for the equilibrium constant, you must specify the balanced equation and the temperature.
- If a reaction can be expressed as a sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

Homogeneous Equilibrium

- ***Homogeneous Equilibrium-*** applies to reactions in which all reacting species are in the same phase.

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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

In most cases

$$K_c \neq K_p$$

Relation between Kp and Kc

Since $PV = n\,R\,T$,

$$P = (n/V)\,R\,T = [\,]\,R\,T$$

$[\,] = (n/V)$ is the concentration

For the reaction $a\,A + b\,B \rightarrow c\,C + d\,D$

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

$Kp = Kc\,(RT)^{\Delta n}$

Example 14.2

The following equilibrium process has been studied at 230°C:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

In one experiment the concentrations of the reacting species at equilibrium are found to be [NO] = 0.0542 *M*, [O_2] = 0.127 *M*, and [NO_2] = 15.5 *M*. Calculate the equilibrium constant (K_c) of the reaction at this temperature.

Strategy The concentrations given are equilibrium concentrations. They have units of mol/L, so we can calculate the equilibrium constant (K_c) using the law of mass action [Equation (14.2)].

Solution The equilibrium constant is given by

$$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

Substituting the concentrations, we find that

$$K_c = \frac{(15.5)^2}{(0.0542)^2(0.127)} = 6.44 \times 10^5$$

Check Note that K_c is given without units. Also, the large magnitude of K_c is consistent with the high product (NO_2) concentration relative to the concentrations of the reactants (NO and O_2).

Practice Exercise Carbonyl chloride ($COCl_2$), also called phosgene, was used in World War I as a poisonous gas. The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form carbonyl chloride

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

at 74°C are $[CO] = 1.2 \times 10^{-2}$ *M*, $[Cl_2] = 0.054$ *M*, and $[COCl_2] = 0.14$ *M*. Calculate the equilibrium constant (K_c).

Heterogeneous Equilibrium Constant

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

$[CaCO_3]$ = constant
$[CaO]$ = constant

$$K_p = P_{CO_2}$$

The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant.

Example 14.6

Consider the following heterogeneous equilibrium:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

At 800°C, the pressure of CO_2 is 0.236 atm. Calculate (a) K_P and (b) K_c for the reaction at this temperature.

Strategy Remember that pure solids do not appear in the equilibrium constant expression. The relationship between K_P and K_c is given by Equation (14.5).

Solution (a) Using Equation (14.8) we write

$$\begin{aligned} K_P &= P_{CO_2} \\ &= 0.236 \end{aligned}$$

(b) From Equation (14.5), we know

$$K_P = K_c(0.0821T)^{\Delta n}$$

In this case, $T = 800 + 273 = 1073$ K and $\Delta n = 1$, so we substitute these values in the equation and obtain

$$0.236 = K_c(0.0821 \times 1073)$$
$$K_c = 2.68 \times 10^{-3}$$

Practice Exercise Consider the following equilibrium at 395 K:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

The partial pressure of each gas is 0.265 atm. Calculate K_P and K_c for the reaction.

Thermodynamic Derivation of Law of Chemical Equilibrium

Let us consider a general reaction

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

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

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

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*)

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

and similarly

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

$$c\mu_c = c(\mu^\circ + RT \ln a_c)$$

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

The change in free energy for the reaction is given by

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

On substitution we get

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

$$= [c\{\mu_c^\circ + RT \ln a_c\} + d\{\mu^\circ_D\ RT \ln a_D\}]$$

$$- [a\{\mu^\circ_a + RT \ln a_A\} + b\{\mu^\circ_B RT \ln a_B\}]$$

$$= [\{c\mu_c^\circ + d\mu^\circ_D + \ldots\} - \{a\mu^\circ_A + b\mu^\circ_B + \ldots\ldots\ldots\}] + RT \ln \frac{a_C^c \times a_D^d \times \ldots}{a_A^a \times a_B^b \times \ldots}$$

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{a_C^c \times a_D^d \times \ldots}{a_A^a \times a_B^b \times \ldots} \qquad \ldots (ii)$$

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

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

In equation (*ii*) the factor A given by

$$\frac{a_C^{\,c} \times a_D^{\,d} \times \ldots}{a_A^{\,a} \times a_B^{\,b} \times \ldots}$$

stands for the reaction quotient of activities of the product and reactants. It may be denoted by K. The equation (*ii*) becomes

$$\Delta G = \Delta G^{\circ} + RT \ln K \qquad \ldots (iii)$$

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

Temperature Dependence of Equilibrium Constant (van't Hoff's Equation)

$$\Delta G^\circ = -RT \ln K_p \qquad \ldots(i)$$

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

Differentiating equation (*i*) w.r.t. at constant pressure P, we get

$$\left(\frac{\delta(\Delta G^\circ)}{\delta T}\right)_p = -R \ln K_p - RT\left(\frac{\delta \ln K_p}{\delta T}\right)_p$$

Multiplying both sides by T, we get

$$T\left(\frac{\delta(\Delta G^\circ)}{\delta T}\right)_p = -RT \ln K_p - RT^2\left(\frac{\delta \ln K_p}{\delta T}\right)_p$$

From equation (*i*) we get

$$T\left(\frac{\delta(\Delta G^\circ)}{\delta T}\right)_p = \Delta G^\circ - RT^2\left(\frac{\delta(\ln K_p)}{\delta T}\right)_p \qquad \ldots(ii)$$

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

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

or
$$T\left(\frac{\delta(\Delta G)}{\delta T}\right)_p = \Delta G^\circ - \Delta H^\circ \qquad \ldots(iii)$$

Comparing (*ii*) and (*iii*) we get

$$\Delta G^\circ = RT^2\left(\frac{\delta(\ln K_p)}{\delta T}\right)_p$$

Temperature Dependence of Equilibrium Constant (van't Hoff's Equation) Contd.

or $$\frac{\Delta H^\circ}{RT^2} = \frac{\delta(\ln K_p)}{\delta T} \quad \ldots(iv)$$

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 or products.

Therefore, ΔH° may be replaced by ΔH. The equation (iv) becomes

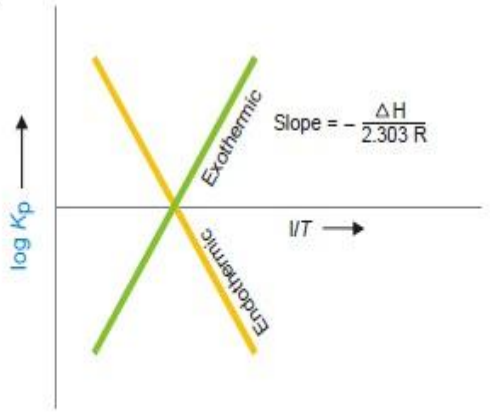
$$\frac{\Delta H}{RT^2} = \frac{d(\ln K_p)}{dT} \quad \ldots(v)$$

Integrating equation (v) we get

$$ln\ K_p = -\frac{\Delta H}{RT} + C$$

or $$\log K_p = -\frac{\Delta H}{2.303RT} + C \quad \ldots(vi)$$

where C is a constant of integration. When a graph of $\log K_p$ against $1/T$ is plotted we get straight line having slope equal to $-\frac{\Delta H}{2.303R}$



Graph between log *Kp* and 1/*T*.

Temperature Dependence of Equilibrium Constant (van't Hoff's Equation) Contd.

From the graph it is clear that

(*a*) For exothermic reaction ΔH is negative and K_p decreases with increase in temperature

(*b*) For endothermic reaction ΔH is positive and K_p increases with increase in temperature.

Integrating equation (*v*) within the limits K_{p2} at temperature T_2 and K_{p1} at temperature T_1

$$\int_{K_{p1}}^{K_{p2}} d \ln K_p = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} dT$$

or

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

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

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

or

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

From this equation the heat of reaction can be determined if the values of equilibrium constant K_{p2} and K_{p1} at temperature T_2 and T_1 are known and vice-versa.

Factors that Affect Chemical Equilibrium

- Chemical Equilibrium represents a balance between forward and reverse reactions.
- Changes in the following will alter the direction of a reaction:
  - Concentration
  - Pressure
  - Volume
  - Temperature

LE CHATELIER'S PRINCIPLE

If a change occurs in one of the variables such as pressure, temperature or concentration, under which a system is in equilibrium, the system will always react in direction which will tend to counteract the effect of change in the variable under considerations.

Changes in Concentration

Change	Shift in Equilibrium
Increase in [Products]	left
Decrease in [Products]	right
Increase in [Reactants]	right
Decrease in [Reactants]	left

Changes in Volume and Pressure

- Changes in pressure primarily only concern gases.
- Concentration of gases are greatly affected by pressure changes and volume changes according to the ideal gas law.

$$PV = nRT$$

$$P = (n/V)RT$$

Changes in Pressure and Volume

Change	Shift in Equilibrium
Increase in Pressure	Side with fewest moles
Decrease in Pressure	Side with most moles
Increase in Volume	Side with most moles
Decrease in Volume	Side with fewest moles

Changes in Temperature

- Equilibrium position vs. Equilibrium constant
- A temperature increase favors an endothermic reaction and a temperature decrease favors an exothermic reaction.