Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (First Year)

Subject: Chemistry

Paper Code: CHC-102

Paper Title : Physical Chemistry and Organic Chemistry

Unit: Unit 2- Chemical Equilibrium

Module Name: Thermodynamic Derivation of Law of Chemical Equilibrium

Module No : 10

Name of the Presenter: Mrs Pooja D. Gadekar

Notes

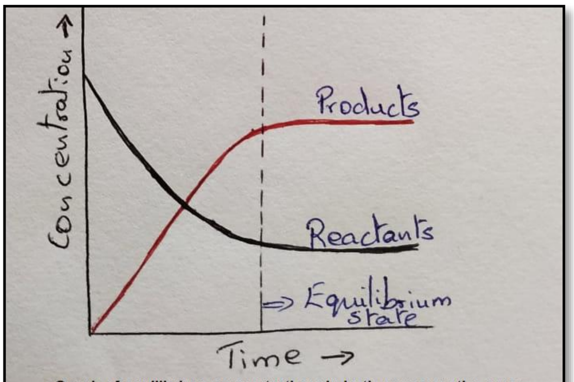
CHEMICAL EQUILIBRIUM

- Let us consider the reaction in a closed vessel:

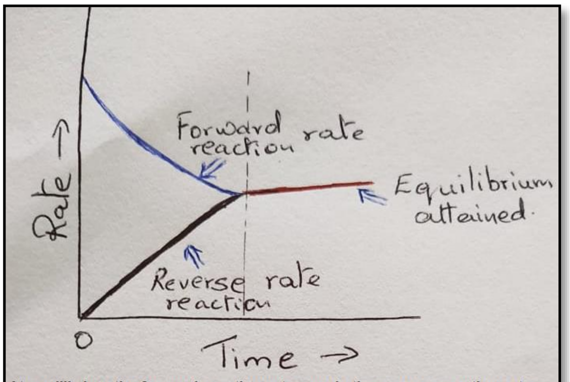
$$A + B \leftrightarrow C + D$$

Such that A and B proceeds in the forward direction to form C and D.

- As a result the rate of forward reaction decreases while the rate of the reverse reaction increases. i.e. the rate of the two opposing reactions equals and the system attains a *state of equilibrium*
- **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.**
- Also known as **dynamic equilibrium state.**
- It is divided into two types i.e. Homogenous and Heterogeneous.



Graph of equilibrium concentrations in both cases are the same.



At equilibrium the forward reaction rate equals the reverse reaction rate

Some Examples of Reversible Reactions

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

$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \leftrightarrow CH_3COOC_2H_{5(l)} + H_2O_{(l)}$

$PCl_{5(s)} \leftrightarrow PCl_{3(s)} + Cl_{2(g)}$

$CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)}$

CHARACTERISTICS OF CHEMICAL EQUILIBRIUM

- **Constancy of concentrations.**

When a chemical equilibrium is established in a closed vessel at constant temperature, concentrations of the various species in the reaction mixture become constant.

- **Equilibrium can be initiated from either side.**

The state of equilibrium of a reversible reaction can be approached whether we start with reactants or products,

Example: $H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$

The equilibrium is established if we start the reaction with H_2 & I_2 or 2 HI.

- **Equilibrium cannot be Attained in an Open Vessel**

The equilibrium can be established only if the reaction vessel is closed and no part of the reactants or products is allowed to escape out.

- **A catalyst cannot change the equilibrium point**

When a catalyst is added to a system in equilibrium, it speeds up the rate of both the forward and the reverse reaction to an equal extent. Therefore a catalyst cannot change the equilibrium point except that it is achieved earlier.

- **Value of Equilibrium Constant does not depend upon the initial concentration of reactants**

It has been found that equilibrium constant must be the same when the concentrations of reacting species are varied over a wide range.

At Equilibrium $\Delta G = 0$

At equilibrium the Gibbs free energy (G) is minimum and any change taking place proceeds without change in free energy *i.e.* $\Delta G = 0$.

Norwegian chemists Cato Maxmillian Guldberg and Peter Waage proposed that for a chemical reaction

$$aA + bB \leftrightarrow cC + dD$$

The rate of reaction in either direction is proportional to the active mass (concentration) of the reactants.

By applying the Law of Mass Action;

The rate of forward reaction;

$$R_f = K_f [A]^a [B]^b$$

The rate of back ward reaction;

$$R_b = K_b [C]^c [D]^d$$

Where,

[A], [B], [C] and [D] - equilibrium concentrations of A, B, C and D.

a, b, c, and d- stoichiometric coefficients of A, B, C and D

K_f and K_b - rate constants of forward and backward reaction.

However, at equilibrium,

Rate of forward reaction = Rate of backward reaction.

$$K_f [A]^a [B]^b = K_b [C]^c [D]^d$$

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

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

OR

$$K_c = \frac{K_f}{K_b}$$

K_c is called the equilibrium constant expressed in terms of molar concentrations and the equation is known as the Law of Chemical Equilibrium.

Write Equilibrium constant for the following reactions:

1) $N_{2\,(g)} + 3H_{2\,(g)} \leftrightarrow 2NH_{3\,(g)}$

Solution:

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

2) $2N_2O_{5(g)} \leftrightarrow 4NO_{2(g)} + O_{2\,(g)}$

Solution: $$K_c = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$

Thermodynamic Derivation of Law of Chemical Equilibrium

Let us consider a general reaction

$$aA + bB + ... \leftrightarrow c\,C + d\,D + ...$$

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

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

Where

μ° -chemical potential of pure substance in standard state of unit activity

R - gas constant

T - 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

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

$= [c\ \{\mu_c° + RT \ln a_c\} + d\{\ \mu°_D\ RT \ln a_D\}] - [a\{\mu°_a + RT \ln a_A\ \} + b\{\mu°_B RT \ln a_B\}]$

$$= [\ \{\ c\ \mu c° + d\ \mu° D + ...\} - \{a\ \mu° A + b\ \mu° B + ...\}] + RT \ln \frac{a^c_C \times a^d_D \times ....}{a^a_A \times a^b_B \times ...}$$

$$\Delta G = \Delta G^o + RT \ln \frac{a^c_C \times a^d_D \times ....}{a^a_A \times a^b_B \times ...} \qquad ... (ii)$$

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

$$\Delta G° = \{c\mu c° + d\ \mu D° + ...\ \} - \{a\mu A° + b\ \mu B° + ...\}$$

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

$$\frac{a^c_C \times a^d_D \times ....}{a^a_A \times a^b_B \times}$$

stands for the reaction quotient of activities of the product and reactants. It may be denoted by *J*.

The equation (*ii*) becomes

$$\Delta G = \Delta G° + RT \ln J \qquad ... (iii)$$

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

At equilibrium, $\Delta G = 0$

thus, $\Delta G° = - RT \ln J$

$\Delta G°$ - free energy of the reaction in the standard state and is constant at a given temperature.

Also, the gas constant *R* and *T* are constant, the factor is a constant i.e.

$$\frac{a^c_C \times a^d_D \times ....}{a^a_A \times a^b_B \times .....} = K$$

It is nothing but the law of chemical equilibrium. Thus, from equation (*iii*) we have

$$\Delta G° = -RT \ln K \qquad ... (iv)$$

or

$$\Delta G° = -2.303\ RT \log K \qquad ... (v)$$

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