Thermodynamics (Part 3)

EQUILIBRIUM

- Equilibrium is a state in which there are no observable changes as time goes by.
- Equilibrium could be physical when it states between two phases of the same substrate (such as liquid water and water vapor) and chemical equilibrium between left and right sides of the chemical equation.

CHEMICAL EQUILIBRIUM

$$I_2 + H_2 = 2HI$$

$$V_{dir} = K_1[I_2]\,[H_2]$$

$$V_{rev} = K_2\,[HI]^2$$

$$V_{dir} = v_{rev}$$

STABLE CHEMICAL EQUILIBRIUM CHARACTERIZED BY THE FOLLOWING GENERAL CONDITIONS:

1. The equilibrium of the system remains unchanged when the external conditions are kept constant.
2. If an external force causes a slight displacement from equilibrium, the system tends to return by itself to the equilibrium state.
3. Equilibrium has a dynamic character.

STABLE CHEMICAL EQUILIBRIUM CHARACTERIZED BY THE FOLLOWING GENERAL CONDITIONS:

4. Tendency to the equilibrium state approaches from two opposite directions - both reactants and products.
5. Rates of both direct and reverse reactions are |equal.
6. The Gibbs free energy of the system has the least value.
7. Amounts of both reactants and products are constant.

EQUILIBRIUM CONSTANT

The quantitative relation between amounts of components in equilibrium state gives by ***equilibrium constant***. The equation of the equilibrium constant is deduced kinetically, based on the equality both of the rates direct and reverse reactions and on the dependence of the reaction rate on the concentrations of the reactants and products, according the ***law of mass actions.***

LAW OF ACTING MASS

- The rate of a chemical reaction is proportional to the product of the concentrations of the reactant.
- This very important principle was established in 1867 by two Norwegian scientists Guldberg and Waage and is known as the Law of Mass Action or the Law of Acting Mass.

EQUILIBRIUM CONSTANT

$$aA + bB = cC + dD$$

$$V_{dir} = k_{dir}[A]^a[B]^b \quad and \quad V_{rev} = k_{rev}[C]^c[D]^d$$

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

Equilibrium constant of a reaction is expressed as a ratio of the rate constants of the forward and reverse reactions.

EQUILIBRIUM CONSTANT

Kc is the equilibrium constant deduced for reactions in dilute solutions. For solutions of higher concentrations the activities ai should be used in place of the concentrations **(Ka)**:

$$K_a = \frac{a_c a_d}{a_b a_a}$$

For ideal gases the expression of the equilibrium constant includes the partial pressures of reagents (**Kp**), and for nonideal gases – the fugaci-ties f (**Kf**).

CONNECTION BETWEEN K_P AND K_C

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

where **Δn** is a difference between the number of moles in the products and reactants.

EQUILIBRIUM CONSTANT

The equilibrium constant depends only on the temperature and the nature of the components and does not depend on the amounts of the reagents. The equilibrium constant helps us to predict the direction in which a reaction mixture will proceed to achieve equilibrium and to calculate the concentrations of reactants and products in equilibrium state.

Chemical equilibrium in heterogeneous reactions

When the reactants are in different phases, then at constant temperature equilibrium partial pressure of each of solid substances is a constant and equal to the saturated vapor pressure over the pure phase of those substances. Due to it their partial pressures are not involved in the equilibrium constant equation

$$\mathrm{FeO} + \mathrm{CO} = \mathrm{Fe} + \mathrm{CO_2}$$

$$K_p = \frac{P_{CO_2}}{P_{CO}}$$

EQUATION OF THE ISOTHERM OF A CHEMICAL REACTION

- Any reaction is spontaneous, if it takes place with decreasing energy. Hence, a spontaneous direct process is characterized by $\Delta G < 0$, a process which can go to the opposite direction spontaneously is in case of $\Delta G > 0$ and if $\Delta G = 0$, the process is in the equilibrium.
- The dependence of maximum work of a reaction upon equilibrium constant was established by Van't Hoff in 1885.

EQUATION OF THE ISOTHERM OF A CHEMICAL REACTION

$$dG = VdP - SdT$$

$$G_2 - G_1 = \int_{P_1}^{P_2} \frac{RT}{P} dP = RT \ln \frac{P_2}{P_1}$$

$$G = G_0 + RT\ln P$$

EQUATION OF THE ISOTHERM OF A CHEMICAL REACTION

Let’s consider the reaction in gaseous phase

$$aA + bB \Leftrightarrow cC + dD$$

$$\Delta G = cG_C + dD_D - aA_A - bB_B$$

$$\Delta G = \Delta G^0 + RT\ln\frac{P_C^c P_D^d}{P_A^a P_B^b}$$

$$\Delta G = \Delta G^0 + RT\ln\frac{P_C^c P_D^d}{P_A^a P_B^b}$$

$$\frac{P_C^c P_D^d}{P_A^a P_B^b} = K_p$$

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

The equation of the isotherm of the chemical reaction or van’t Hoff equation

$$\Delta G = RT\left(\ln\frac{P_C^c P_D^d}{P_A^a P_B^b} - \ln K_p\right)$$

THE EQUATION ALLOWS TO KNOW THE DIRECTION OF THE SPONTANEOUS PROCESS DEPENDING ON THE SUBSTANCE AMOUNT

According to the isotherm equation the condition of the for-ward reaction to be spontaneous is

$$\ln K_p > \ln \frac{P_C^c P_D^d}{P_A^a P_B^b},$$

and the reverse reaction to be spontaneous is

$$\ln \frac{P_C^c P_D^d}{P_A^a P_B^b} > \ln K_p.$$

CHEMICAL EQUILIBRIUM

Different chemical reactions can be compared with respect to their ability to proceed spontaneously. This is usually carried out for conditions in which all the substances are in standard states. Thus, the value of ΔG^0 is constant at a certain temperature for a certain reaction and depends only on the nature of substances. The ΔG and, hence, the direction of spontaneous process depends on the concentrations or partial pressures of the substances taking part in it.

LINK BETWEEN EQUILIBRIUM CONSTANT, AND ENTHALPY AND ENTROPY

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

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

$$\ln K_p = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

DEPENDENCE THE EQUILIBRIUM CONSTANT ON TEMPERATURE FOR EXOTHERMIC (1) AND ENDOTHERMIC (2) PROCESS

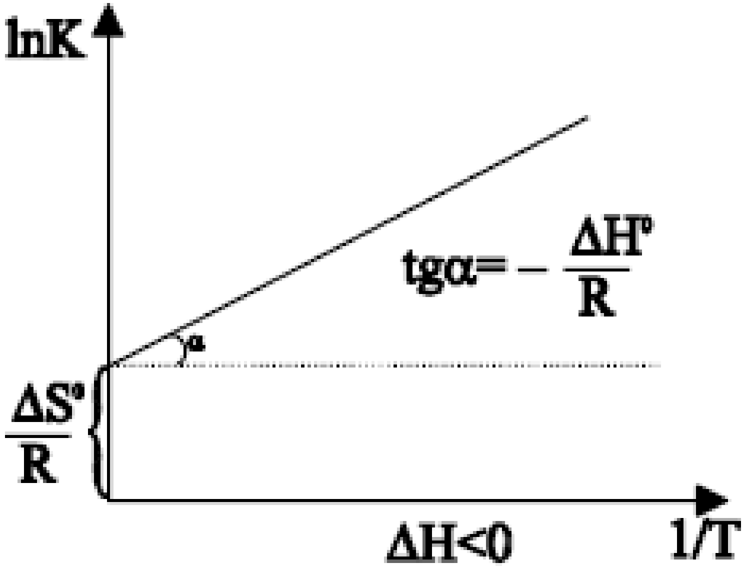

Fig. 1.

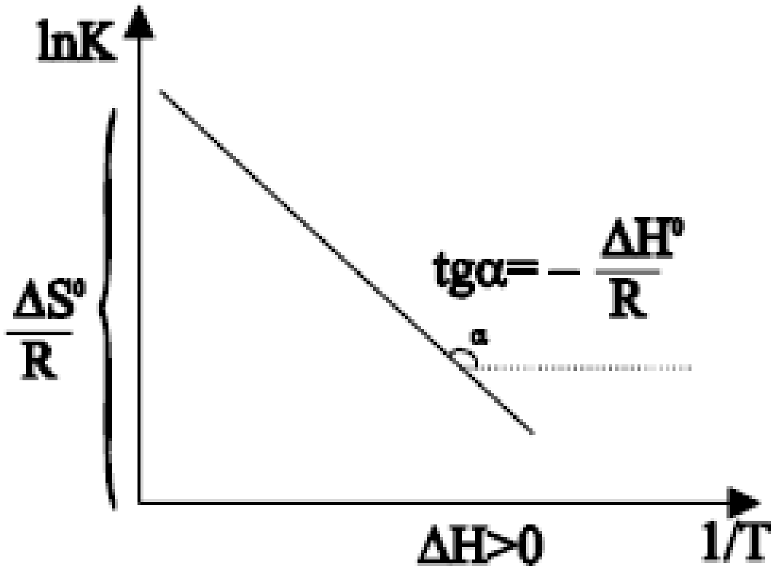

Fig. 2.

IF WE KNOW THE VALUES OF EQUILIBRIUM CONSTANTS AT TWO TEMPERATURES, WE CAN FIND THE VALUE OF THE REACTION HEAT EFFECT FROM THE FOLLOWING

$$\ln K_1 = -\frac{\Delta H^0}{RT_1} + \frac{\Delta S^0}{R} \qquad \ln K_2 = -\frac{\Delta H^0}{RT_2} + \frac{\Delta S^0}{R}$$

$$\ln \frac{K_1}{K_2} = -\frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

EQUATIONS OF THE ISOBAR OF CHEMICAL REACTION

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

This equation establishes a relation between the change in the equilibrium constant with temperature and the heat effect of the reaction. It is called the isobar equation and valid for the processes, which take place at constant pressure.

Equations of the isochor of chemical reaction

$$\frac{d \ln K_C}{dT} = \frac{\Delta U}{RT^2}$$

LE CHATELIER PRINCIPLE

A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance.