Questions:

1. What is equilibrium state of a system.
2. Mention general conditions of chemical equilibrium.
3. Law of acting mass
4. What expresses the equilibrium constant? What factors does it depends on? What does it mean if the value of equilibrium constant is (a) more than zero, (b) less than zero.
5. In what cases the equilibrium constant is expressed by activity?
6. How is the equilibrium constant distinguished from heterogeneous reactions?
7. What is a equation of isotherm of chemical equilibrium.
8. What are the isochor and isobar equations of the chemical equilibrium. Which relation of equilibrium constant do they express? How is it related to Le Chatelie principle?

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.

$I_2 + H_2 = 2HI$

Vdir = K1 [I] [H]

Vrev = K2 $[HI]^2$

Vdir = Vrev

STABLE CHEMICAL EQUILIBRIUM CHARACTERIZED BY THE FOLLOWING GENERAL CONDITIONS:

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.

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.

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 fugacities 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.

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.

Chemicalequilibriuminheterogeneousreactions

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

$FeO + CO = Fe + CO_2$

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

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 ΔG < 0, a process which can go to the opposite direction spontaneously is in case of ΔG > 0 and if ΔG = 0, the process is in the equilibrium. υ The dependence of maximum work of a reaction upon equilibrium constant was established by Van't Hoff in 1885.

$$dG = VdP - SdT$$

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

$$G = G_0 + RTlnP$$

Consider the reaction in gaseous phase

aA + bB⇔cC + dD

The change of Gibbs energy for this reaction is equal to:

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

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

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

$$\Delta G^0 = -RTln\, K_p$$

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

This is called the equation of the isotherm of the chemical reaction or van't Hoff equation. It links the Gibbs energy and equilibrium constant with partial pressures of the components. We must know, that the partial pressure values of the first member of the equation (in brackets) are changed in every moment of the reaction and aren't equal to the partial pressure values in the expression of ln Kp, which refer only to equilibrium state and have a constant values at a definite temperature. So the difference in the brackets isn't equal to zero.

The equation allows to know the direction of the spontaneous process depending on the substance amount. We know, that if ΔG0, the reverse reaction is spontaneous, and if ΔG=0, the reaction in equilibrium. According to the isotherm equation the condition of the forward 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

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

EQUATIONS OF THE ISOBAR AND ISOCHOR OF CHEMICAL REACTION

As the equilibrium constant depends on the temperature, we can obtain the equation of this dependence.

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

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. The similar equation can be obtained for a process, which takes place at constant volume, and it is called the isochoric equation

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

The equations describe change in the equilibrium constant with change in temperature.the equilibrium constant decreases with a rise in temperature, i.e., the relative content of products become less and the equilibrium is displaced towards the left. In other words, with a rise in temperature the equilibrium is displaced in the direction of the endothermic reaction. Thus, these equations are quantitative expressions **of 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.

Problems

1.A mixture of 11.02 mmol of H_2S and 5.48 mmol of CH_4 was placed in an empty container and the equilibrium for reaction 2H2S + CH4 = $4H_2 + CS_2$ was established at 700oC and 762 torr. Analysis of the equilibrium mixture found 0.711 mmol of CS2. Find K_P and ΔG^0 for the reaction at 700°C.

2. Find *KP* at 600 K for reaction $N_2O_4(g) = 2NO_2(g)$ using the approximation that ΔH^0 is independent on T and equal to 57.20 kJ/mol. It is also known that ΔG^0 = 4730 J/mol.

3. In the reversible reaction $CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$ from 1 mol acid and 1 mol alcohol 0,7 mol of ether is formed. Determine the value of equilibrium constant.

4. The equilibrium constant of the reversible reaction FeO(s) + CO(g) = Fe(s) + CO_2(g) is equal to 0.5. Find the equilibrium amounts of the CO and CO_2, if their initial amounts are: [CO] = 0.05 mol/l and [CO_2] = 0.01 mol/l.