**Lecture 1.** Tasks, sections and fields of application of chemical physics. Elementary processes in chemistry. Collision theory.

**The purpose of the lecture:** to familiarize students with the tasks, sections of chemical physics, consider elementary processes in chemistry and explain collision theory.

**Expected results:** students getting information about the problems and branches of chemical physics, knowledge about elementary processes in chemistry and understanding of collision theory.

The introduction of the general course "chemical physics" is connected with the problems of extraction and processing of various raw materials of the Republic of Kazakhstan, meeting the needs of the economy and defense. This urgently requires the organization of training of domestic personnel of chemists who own the entire arsenal of modern non-traditional technologies.

These technologies are based on the use of physical phenomena such as plasma, discharge, laser radiation, surface treatment by flows of various particles, etc. The development of new methods of analysis using laser technology, the initiation and stimulation of chemical processes require the study of the mechanisms of chemical reactions at the level of elementary events in both the gas and condensed phases and at the interfaces.

Chemists, especially those with a technical background, must now deeply understand the interconnections of the basic physical and chemical processes that take place in technological reactors, be prepared for the rapid implementation and use of the latest innovative technologies. The theoretical basis of such technologies is provided precisely by chemical physics, as defined by Nobel laureate academician N.N. Semenov, on the physical foundations of chemical transformations.

Currently, in a number of areas of chemical physics there are monographic studies of scientists from Russia, foreign countries and, including Kazakhstan scientists, a number of international journals are published. Achievements of chemical physics are widely used in educational processes in a number of leading foreign universities.

Semenov emphasizes that CHEMISTRY is the science of chemical transformations and the properties of individual chemical compounds.

### Elementary processes in chemistry

All chemical reactions are complex, i.e. consist of a set of interconnected elementary reactions, usually called the mechanism of chemical processes. The most important role is played by labile short-lived intermediate particles. One act (stage) with a duration of $10^{-13}$-$10^{-15}$ s is usually classified as elementary, and their study is one of the most important tasks of the discipline "chemical physics". Atoms, radicals, ions, excited atoms and molecules have excess energy compared to the average energy of the reacting molecules. There are two main theories of chemical kinetics: transition state and collisions. The first one requires the determination of potential energy surfaces for interacting particles. It is easier to apply for "purely" monomolecular reactions, i.e. to calculate the decay rate of "isolated" particles with a fixed energy. By the experimental method of molecular beams, single molecular collisions are now directly studied when the reactants have a precisely set speed, and sometimes precisely set quantum states, and even spatial orientation.

Collisions of particles are divided into three types: elastic, inelastic and accompanied by reactions.

Elastic - internal quantum states of colliding pairs do not change.

Inelastic - quantum numbers of colliding pairs change.

Accompanied by a reaction - there is a chemical change in the reactants.

The intermolecular distances are shorter with a significant overlap of electron clouds, which leads to the formation of a new chemical bond.

Therefore, the internal energy states of the reactants, as well as the collision energy, play an important role in the reaction.

As is known, at a given temperature, the molecules have an equilibrium thermal distribution of the translational energy and the internal quantum states. And for reactions under known macroscopic conditions, the physical characteristics of the system averaged over the thermal distribution of the characteristics of all particles participating in the reaction are obtained. This makes it very difficult to obtain information about microscopic characteristics, because most of it is lost due to multiple collisions.

Gas-phase reactions can be studied experimentally at the microscopic level due to the correlation between specific initial conditions and the corresponding measured quantities (reaction cross section, angular scattering, etc.).

This allows you to get a lot of valuable information:
- about the dynamics of reactions;
- about chemical reactivity;
- On the redistribution of energy over all degrees of freedom of all colliding particles.

Therefore, we will further interpret the presented material precisely in the framework of the collision theory (the classical version, even without quantum-mechanical refinements). Let us briefly recall its essence.

## Collision theory

The molecularity of a simple reaction is determined by the number of particles involved in one act - mono-, bi- and trimolecular. The theory itself is the application of the kinetic theory of gases to gas-phase bi- and trimolecular reactions. The rate of the bimolecular reaction A and B is determined by the product of the frequency of collisions A and B and the probability factor - the fraction of collisions leading to the reaction. Frequency i.e. the number of collisions A and B in a unit volume per unit time $Z_{AB}$ is proportional to the product of concentrations:

$$Z_{AB} = z_{AB}C_A C_B,$$

where $z_{AB}$ is the factor of the frequency of double collisions, which is numerically equal to the frequency of collisions A and B at $C_A = C_B = 1$.

According to kinetic theory, if A and B are structureless rigid balls, then

$$z_{AB} = \pi(r_A+r_B)^2 u_{AB}.$$

According to kinetic theory

$$<u_{AB}> = [8kT/\pi\mu]^{1/2},$$

where $\mu=m_A m_B(m_A+m_B)^{-1}$. From here:

$$z_{AB} = 4{,}57 \cdot 10^4 (r_A+r_B)^2 [1/M_A+1/M_B]^{1/2}\sqrt{T} \text{ cm}^3 \cdot \text{s}^{-1}.$$

Usually $z_{AB} \cong 10^{-10}$ cm$^3$·s$^{-1}$ or $10^{11}$ l·mole·s$^{-1}$. The factor of the frequency of collisions A and B with a relative speed from u to u+du is equal to:

$$z_{AB} = \pi(r_A+r_B)^2 [4\pi(\mu/2\pi kT)^{3/2}\exp(-\mu n^2/2kT)u^3 du]$$

Passing to the kinetic collision energy $U_K$ (per mole) and introducing the factor $P(U_K)$ - the probability of the reaction as a function of $U_K$, we find:

$$z_{AB} = [8\pi(\tfrac{1}{M_A} + \tfrac{1}{M_B})]^{1/2} (RT)^{-3/2} (r_A + r_B)^2 \int\limits_0^\infty U_K P(U_K) e^{-U_K/RT} dU_K$$

For comparison with experiment, especially in the molecular beam method, another form is convenient. We take into account that $k = P_Z \cdot z_{AB}$ (where P is the steric factor, see below) and denote $\pi(r_A+r_B)^2 P(U_K) = \sigma(E_K)$ - reaction cross section. Then:

$$k = [8(\tfrac{1}{M_A} + \tfrac{1}{M_B}) \cdot \tfrac{1}{\pi}]^{1/2} (RT)^{3/2} \int\limits_{E_0}^\infty U_K \sigma(E_K) e^{-U_K/RT} dU_K$$

In order for the reaction to take place, the colliding particles need to overcome the threshold energy $E_0$. Particles collide at different angles, and to overcome $E_0$, the velocity component along the line connecting the centers is important, therefore for $\sigma(E_K)$ we have:

$$\sigma(E_K) = \{0 \ (E_K < E_0); \ \pi(r_A+r_B)^2(1-E_0/E_K) \ (E_K \geq E_0).$$

In general, for a bimolecular reaction

$$k = [8 \cdot 10^7 \pi RT(1/M_A+1/M_B)]^{1/2}\pi(r_A+r_B)^2 \exp(-E_0/RT).$$

Arrhenius energy

$$E = R\frac{d\ln k}{d(1/T)} = E_0 + \tfrac{1}{2} RT \ ,$$

and preexponential factor

$$A = [8 \cdot 10^7 \pi RT (\tfrac{1}{M_A} + \tfrac{1}{M_B})]^{1/2} (r_A + r_B)^2$$

The second factor in the expression for the rate of a chemical reaction is called the steric factor $P_Z$ — the probability of a reaction occurring in a collision of particles whose collision energy is sufficient for the reaction to proceed. $P_Z$ includes, first of all, the probability of proper orientation of colliding particles relative to each other (for the reaction to occur, the overlapping of well-defined atomic orbitals is necessary). In addition, particles collide at different vibrational and rotational levels. Because instead $\sigma(U_K)$ must be considered $\sigma(U_K, i, j)$, where i and j are different energy states of the particle. Therefore, $P_Z$ and $\sigma$ are related to each other, i.e. $P_Z$ depends on the reaction cross section for different energy states of particles.