**AL-FARABI KAZAKH NATIONAL UNIVERSITY**

**CHEMISTRY AND CHEMICAL TECHNOLOGY DEPARTMENT**

**Physical chemistry, catalysis and petrochemistry branch**

Guidelines for laboratory work

**Spectrophotometric measurement of the decomposition rate of complex manganese oxalate**

ACCORDING TO THE COURSE "PHYSICAL CHEMISTRY"

Approved at the meeting of the Department of Physical Chemistry, Catalysis and Petrochemistry from " \_\_\_ " \_\_\_\_\_ 202\_\_\_ year, protocol №\_\_\_

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1. **THE PURPOSE OF THE WORK**

The aim of the work is to determine the order of the decomposition reaction of manganese oxalate, the rate constant at several temperatures, as well as the calculation of the activation energy of this process based on the use of absorption spectra.

1. **THEORETICAL PROVISIONS**

Chemical kinetics considers the rates of chemical reactions and the parameters on which they depend. The most important parameters are concentration, temperature, pressure.

The reaction rate is generally determined by the change in the amount of substance per unit of time, in a unit of reaction space:

 (1),

where R is the reaction space, n is the number of moles of a given component at time t.

For homogeneous reactions, R is the volume and, subject to its constancy, expression (1) is simplified:

 (2),

The reaction rate is determined by the change in the concentration of the reacting substance per unit of time.

For heterogeneous reactions, R is the specific surface area (A) and expression (1) for such reactions is written as:

 (3).

The reaction rate is always positive, but the signs (+) or (-) are used depending on whether the concentration of the starting substances (-) or reaction products (+) changes the speed of this process. The reaction rate is expressed as a derivative of the concentration over time for any substance involved in the reaction. The starting substances are consumed, and the reaction products are formed in equivalent quantities in accordance with their stoichiometric coefficients, therefore, when determining the reaction rate, there is no need to monitor the change in the concentration of all interacting substances. In the general case, the reaction rate proceeding according to the equation:

n1A + n2B ↔ n3C + n4D

can be adequately represented by several equations:



where n1, n2, n3, n4 are stoichiometric coefficients.

The dependence of the velocity on the concentration of the starting substances is expressed by the law of acting masses:

 (4),

where is the reaction rate constant; n1 and n2 are numbers indicating the particular order of the reaction by components A and B, respectively. The total order of the reaction is: n= n1 +n2. Dependence (4) is called the basic postulate of chemical kinetics: the reaction rate at each moment of time is proportional to the product of the concentration of reacting substances raised to a certain degree.

An important characteristic in chemical kinetics is the velocity constant. Its physical meaning is that, provided that the concentration of reacting substances is equal to (CA = CB =…= 1) for homogeneous reactions the rate constant is equal to the reaction rate W =k, and for heterogeneous reactions W ≠ k. The dimension of the velocity constant is determined by the kinetic equation by which it is calculated depending on the reaction order. In general, this can be represented as follows: {k}=(conc) n+1. (time) -1, where n is the reaction order.

There are average and true reaction rates. The average reaction rate ($\overbar{W}$) for a given period of time is the ratio of the change in the concentration of the reagent (starting substance or reaction product) to the time during which this change occurred:

 (5).

The true reaction rate (w) at a given time can be expressed as an infinitesimal change in the concentration of the reagent over an infinitesimal period of time, i.e. as a derivative of the concentration over time:

.

For reactions of different orders, the differential and integral forms of kinetic equations will have different dependencies. For a first–order reaction:(А→В) , differential equations:

or ,

where x is the amount of substance that has acted by time t, and a is the initial concentration of the substance.

Integral forms of the kinetic equation:



where *С*0 is the initial concentration, C is the concentration of the substance at time t.

An important characteristic in kinetics is the half–life or half-conversion period - the time during which half the amount of a substance reacts. For first-order reactions, the half-life *t1/2* is determined by the equation:

 (6).

For second-order reactions (А+В→С+D), if the initial concentrations of the reagents are the same,  , the differential forms of the kinetic equation have the form:

 or ,

and the integral forms of the kinetic equation:

 

For second–order reactions (А+В→С+D), if the initial concentrations of reagents are not the same (CA≠CB), , the differential equations take the following form:

 or , ,

where a and b are the initial concentrations of reagents A and B.

The integral form of the kinetic equation will be:



For reactions of other orders, differential and integral kinetic the equations have more complex dependencies, the conclusions and analysis of which are available in the literature.

An important characteristic of chemical reactions is the molecularity. The molecular nature of the reaction is determined by the number of particles involved in one elementary act of chemical transformation. At the same time, the number of molecules of the substances formed does not matter. Reactions are monomolecular. The order of the reaction and the molecularity may coincide for the simplest homogeneous reactions, and most often they differ. The reason for this is the course of the reaction by a complex mechanism. In addition, the reason for the discrepancy may be a significant excess of one of the reagents in the reaction mixture. Then the concentration of this reagent remains practically constant during the reaction, and the order is less than that determined by the stoichiometric equation. The order of the reaction depends on the conditions of its course. It can be changed, for example, by varying the concentration or pressure.

The reaction order and the molecularity differ in that:

* the reaction order can take any values (Negative, positive, fractional numbers and zero), and the molecularity is one, two and three.
* the order is an experimental quantity and refers to the reaction as a whole, and the molecularity is only an elementary act of chemical transformation and is a theoretical quantity.

Of all the kinetic characteristics of chemical reactions, the most important is the rate constant. The greater the magnitude of the velocity constant, the greater the velocity.

For reactions of the nth order (except the first), with equal concentrations of all starting substances, the rate constant is expressed by the equation:

 (7).

It is possible to compare the rate constants of chemical reactions only if the reaction order for the studied processes is the same.

Methods for determining the reaction order are divided into two large groups: integral and differential, which are described in detail in all textbooks on physical chemistry /1-4/.

**Influence of temperature on the rate of chemical reaction**

The rate of chemical reactions increases with increasing temperature most often. The dependence of the reaction rate on temperature is approximately described by the Van’t-Hoff rule:

 (8),

where  and  are the rate constants at temperatures T2 and T1; γ is the temperature coefficient of the reaction rate constant.

The temperature coefficient shows that when heated at 100C, the rate constant increases 2-4 times. The Van't-Hoff rule is used for approximate calculations, and the temperature coefficient is determined from the ratio:

 (9).

More precisely, the dependence of the reaction rate on temperature is described by the Arrhenius equation:

 (10),

where k is the velocity constant; T is the temperature, K; R is the universal gas constant; E is the activation energy.

After integration, equation (10) takes the form:

 (11),

and in exponential form:

*k*=Аое-Е/RT (12),

where A0 is the pre–exponential multiplier.

Often the integral form of the Arrhenius equation is used in analytical calculations:

 (13).

The activation energy of the reaction E is the minimum energy (per 1 mole of matter) that reacting particles must possess in order for their collision to lead to chemical interaction.

Particles whose energy is greater than or equal to the activation energy are called active. This energy is necessary to overcome the energy barrier of the reaction. A collision will be effective if the total energy of the colliding particles is equal to or greater than the activation energy characteristic of this reaction. Schematically, the formation of active particles can be represented as follows: A +A+E → A\*+A\*, where A\* are active particles.

The activation energy is a potential barrier that must be overcome by particles whose energy is greater than or equal to E (active particles).

A0 is a pre–exponential multiplier – according to the theory of active collisions, it is a collision factor (Z0), which is associated with the total number of double collisions (Z) of 1 cm3 in 1 sec. The values of Z0 and Z can be determined on the basis of molecular kinetic theory /4/. Therefore, by replacing A with Z0, the velocity constant can be calculated by the equation:

*k*= Z ое-Е/RT (14).

Very often, not all active particles in a collision enter into a chemical reaction. This is due to the necessary specific orientation of the reacting particles in space, i.e. with certain favorable steric conditions. Taking into account these conditions, an additional multiplier P is introduced into equation (14), called a steric or probabilistic factor:

*k*= РZ ое-Е/RT (15).

This equation reveals the physical meaning of A0. Since A0 = PZ0, A0 is a function of the total number of collisions and the steric factor.

Thus, the activation energy characterizes the dependence of the reaction rate on temperature. The greater the E, the faster the reaction rate increases with increasing temperature, and the lower the activation energy, the greater the reaction rate constant, since a large proportion of particles can overcome the energy barrier.

Thus, the most important kinetic characteristics of a chemical reaction are the rate, the rate constant, the reaction order, the activation energy and the pre-exponential multiplier. Therefore, the tasks of chemical kinetics are to determine these parameters by various physico-chemical methods. The most common methods based on the dependence of the physical properties of a mixture on its composition, such as spectrophotometry, spectroscopy, mass spectrometry, chromatography. The use of these methods is based on preliminary obtaining calibration graphs of the dependence of the physical property on the concentration, and then determining the concentration of reacting substances.

Spectrophotometry is a method of investigation and analysis of substances based on the measurement of absorption spectra in the optical region of electromagnetic radiation. The spectrophotometric method is applicable in cases when the initial substance or one of the reaction products is absorbed in a given spectral region (colored), and the remaining substances involved in the reaction are colorless.

The decomposition of a complex compound of manganese proceeds by a first - order reaction according to the equation:

 Mn(C2O4)33- = Mn2+ + 5/2 C2O42- + CO2

In this case, the complex ion is colored, the decay products are colorless. The equation for the first - order reaction has the form:

k =  (16),

where K is the rate constant, t is the reaction time, C0 and C are the concentrations of the initial substance at the initial time and time t. According to the Booger–Lambert–Behr law, the concentration of the substance is directly proportional to the optical density:

 (17),

where D0 and D are the optical density of the solution of the initial substance, respectively, at the initial moment of time and at time t.

Substituting equation (17) into equation (16) we obtain:

k =  (18).

Therefore, to calculate the reaction rate constant, it is necessary to measure the optical density of the solution and its change over time.

1. **THE ORDER OF WORK**

Devices and materials: photoelectrocolorimeter FEC, light filter – blue, thermostat, reagents: 0.01 М КMnO4, 0.1 M MnSO4, 0.1 M H2C2O4.

The initial solutions are pre–maintained at a given temperature for 10-15 minutes. Having prepared the measuring device, solutions of 0.1 M MnSO4 and 0.1 M H2C2O4 are mixed in relation to 1:7. To 4 parts of the resulting colorless mixture, 1 part of a 0.01 M КMnO4 solution is added, while a brown complex salt is quickly formed. A reaction vessel with a complex salt is kept in a thermostat at a given temperature and samples are taken into a centimeter cuvette, installed in a device for measuring optical density. The report is conducted from the first dimension. During the experiment, a constant temperature t1 is maintained. Reports are made first every minute, then after 2-4 minutes. The experiment is stopped when the optical density reaches values close to 0.10.

1. **PROCESSING OF RESULTS**

The results are recorded in the table in the following form:

Initial solutions……………………Temperature.........................

|  |  |  |
| --- | --- | --- |
| Time | Optical density D | k, time-1 |
|  |  |  |
|  |  |  |

1. From the obtained values D0 and D, k is calculated, and then the average value of the velocity constant at a given temperature, which can be found from the graph of the dependence lgD = f (t).
2. The experiment is repeated at a temperature of t2 = t1  100С and the activation energy is calculated using two values of constants.

In research practice, two methods are usually used to determine the activation energy:

a) The calculation method, which is based on the application of a certain integral form of the Arrhenius equation:

 (19).

According to equation (16), the activation energy can be calculated from the rate constants at two temperatures:

 (20).

b) A graphical method based on the use of an indefinite integral form of the Arrhenius equation: ln*k* = lnA0 - .

3. The half-life in both cases is also calculated and the values obtained are compared.

1. **SAFETY PRECAUTIONS**

In the process of performing the work , it is prohibited:

1. Turn on and off the installation without the permission of the teacher.
2. Leave the energized installation unattended.
3. Work with ungrounded equipment.

When performing laboratory work, the student is obliged to:

* work in a bathrobe, if necessary, use personal protective equipment;
* work carefully, keep clean;
* drain waste solutions into drain tanks specially designed for this purpose;
* carefully handle chemical utensils, reagents, equipment;
* perform the work in the described sequence.
1. **REQUIREMENTS TO THE REPORT**

The report should contain the following sections:

1. The purpose of the work.
2. Intermediate and final results of experiments.
3. Calculations for processing the results.
4. Conclusion based on the results of experiments and calculations.
5. The work must be signed by the student and the teacher.
6. **CONTROL QUESTIONS**
7. Give a definition of the following concepts: chemical kinetics, average and true rates of chemical reaction, reaction mechanism, elementary reaction act. Factors affecting the reaction rate.
8. Reaction rate constant, physical meaning. The law of the acting masses. The order and the molecular nature of the reaction. Methods for determining the reaction order.
9. Reactions of different orders. Kinetics of simple irreversible homogeneous reactions of zero, first and second orders. Equations for calculating reaction constants and half-conversion times for reactions of various orders.
10. Spectrophotometric method of analysis. The law on which it is based.
11. The effect of temperature on the rate of chemical reaction. The Van't-Goff rule. The Arrhenius equation. Activation energy.
12. What order does the decomposition reaction of complex manganese oxalate follow?
13. Why is it convenient to use the spectrophotometric method to study the kinetics of this reaction?
14. **LIST OF RECOMMENDED LITERATURE**
15. Stromberg A.G., Semchenko D.P. Physical chemistry. M.: Higher School, - 2006, 527 p.
16. Damaskin B.B., Petri O.A., Cirlina G.A. Electrochemistry. M.: Chemistry, Kolos, 2006, 672 p.
17. Kamysbaev, D. H. Conceptual apparatus of physical chemistry// Study guide. - Almaty: Kazak University, 2015, 126 p.
18. Ospanova A.K., Seilkhanova G.A. Selected chapters of physical chemistry // Textbook. – Almaty. - 2011, 146 p
19. Ospanova A.K., Seilkhanova G.A., Syzdykov L.I., Zhusupova A.K. Test questions on physical chemistry (kinetics and electrochemistry) // Textbook. - Almaty: Kazak University, 2016, 186 p.
20. Eremin V.V., Kargov S.I., Uspenskaya I.A., etc. Tasks in physical chemistry. M.: Exam, 2005, 318 p.
21. Ospanova A.K., Seilkhanova G.A., Murzagalieva M.G. Laboratory workshop on electrochemistry//Study guide. - Almaty: Kazak University, 2008, 72 p.