

KINETICS OF THE PROCESSES OF ROASTING, LEACHING, WASHING AND CEMENTATION

A. L. Rotinyan and B. V. Drozdov

Institute of the Nickel-Cobalt and Tin Industry, Leningrad

INTRODUCTION

In spite of the great importance of problems of reaction rates in roasting, leaching, washing, and cementation, no generalized laws governing the kinetics of these reactions have been established as yet. Only a few endeavors have been made to substantiate the applicability of Nernst's diffusion theory. In practice, we have been confined to purely empirical data, as Nernst's theory is inapplicable to hydrometallurgical processes, and the equations derived from it yield results that depart considerably from experiment.

The present paper investigates the general laws governing the kinetics of the processes of roasting, leaching, washing, and cementation. The formula derived agrees with numerous experiments performed by various authors.

The foundation underlying this work has been the conclusion reached by B.B.Drozov in his study of the cementation process.*

DEVELOPMENT OF THE BASIC FORMULA

In developing this formula we started with the condition of uniform distribution of the solid reacting component within the aggregate mass of solid particles. In actuality, the distribution of the solid component may vary considerably in individual grains, but this distribution is evened out when a large number of grains is taken.

Likewise, the diffusion rate varies not only in different particles, but in different directions within a single particle. Hence, we shall henceforth have to use as the diffusion rate and the coefficient of diffusion the mean values for material at a given stage of fineness.

We also assume that the reaction is formally a first-order one, taking place under isothermal conditions, and without secondary reactions or mechanical crushing of the grains.

Despite the marked differences in the chemical nature of the roasting, leaching, washing, and cementation reactions, their kinetics have much in common.

All the processes discussed are heterogeneous reactions that take place between solid particles and a gas (roasting) or a liquid (leaching, washing,

* Reported at the 2nd All-Union Conference on Electrochemistry (Kiev, 1948).

and cementation).

The distinguishing characteristic of the foregoing reactions is the gradual growth of a diffusion layer through which liquid or gaseous reagents pass in one direction, with the liquid or gaseous reaction products passing through it in the opposite direction.

As a rule, the reaction commences at the surface of the solid particle, penetrating into the interior of the grain as it proceeds, gradually forming a growing, porous, solid crust of reaction products or of inert unreacted material, or finally, of both together.

Thus, in the initial stage of the process, when the reaction occurs at the particle's surface, the kinetics are governed by the velocity of the chemical reaction itself. As the crust grows, its role in the reaction kinetics increases. There are three possible cases, depending on the structure and other peculiarities of the crust:

1. The crust is highly porous; when this is so, the overall velocity of the process is determined entirely by the chemical reactions themselves, as the rate of diffusion is many times the reaction rate. Despite the continuous increase in thickness of the crust, it exerts no effect upon the nature of the kinetics.

In this case, therefore, the usual first-order kinetics equation applies.

2. The crust has low porosity; in this case, the kinetics are, in general, limited by the rate of diffusion of the liquid or gaseous reagents through the porous crust into the reaction zone.

3. The crust is of average porosity; the diffusion and reaction rates are then commensurable.

The operations set forth in the title of this article are either performed at constant volume (agitation), or in a current of liquid or gas (percolation, most kinds of roasting).

Let us derive the kinetics equation for the processes that occur at constant volume. Our notation is as follows:

a = initial concentration of reagent.

x = concentration of the reagent that has already reacted at time t .

D = mean coefficient of diffusion of the reagent through the crust.

S = phase separation surface.

λ = thickness of crust.

v = volume of reagent.

ζ = reagent concentration at surface where reaction is occurring at given instant.

k = constant of first-order reaction rate.

μ = coefficient allowing for the transition from surface to volume concentration.

Let us consider the kinetics when the diffusion rate is commensurable with the reaction rate [1].

In this case, a stationary state sets in within an extremely short interval of time after the beginning of the reaction, which may be characterized by the following equation:

$$\frac{dc}{dt} = \frac{1}{\mu} \frac{dx}{dt} = k \zeta = \frac{D}{\lambda} [(a - x) - \mu \zeta]. \quad (1)$$

The thickness of the crust does not remain constant, but grows continuously, and hence may be replaced by $\underline{x}$ on the basis of the following equation:

$$B = \frac{xv}{S\lambda}. \quad (2)$$

Here $\underline{B}$ is the quantity of reagent that reacts per unit volume of the solid phase. When the useful constituents are evenly distributed throughout the material, $\underline{B}$ is a constant.

Combining (1) and (2), we get:

$$k\zeta = \frac{DSB}{xv} [(a - x) - \mu \zeta]. \quad (3)$$

whence:

$$\zeta = \frac{DSB(a - x)}{kxv + DSB\mu} \quad (4)$$

and

$$\frac{dx}{dt} = \frac{kDSB\mu(a - x)}{kxv + DSB\mu}. \quad (5)$$

Integrating Equation (5) over the following boundary conditions:

$$t = 0; \quad x = 0 \quad (6)$$

yields the equation:

$$\frac{1}{t} \ln \frac{a}{a - x} - \beta \frac{x}{t} = M, \quad (7)$$

in which:

$$\beta = \frac{vk}{kva + DSB\mu} \quad (8)$$

and

$$M = \frac{kDSB\mu}{kva + DSB\mu}. \quad (9)$$

Let us now examine the two boundary cases: a) when the diffusion rate is much higher than the reaction rate; and b) when the diffusion rate is much lower than the reaction rate.

* Equation (7) in its outward form is identical with the empirical formula of A. I. Duntseess and A. V. Frost [2] for the kinetics of the self-inhibiting homogeneous monomolecular decomposition reactions of hydrocarbons. Equation (7) differs from Duntseess and Frost equation in that the constants β and M are derived rationally.

In the first case, the process kinetics will be wholly governed by chemical factors. Mathematically, this may be expressed as:

$$D \longrightarrow \infty; \quad \beta \longrightarrow 0$$

$$DSB\mu \gg kva; \quad M \longrightarrow k.$$

Thus, in the first case Equation (7) is transformed into the usual equation for the velocity of a first-order reaction.

In the second case, the reaction rate is mainly determined by the rate at which the reagent is supplied to the reaction zone, and the relationships are as follows:

$$DSB\mu \ll kva; \quad \beta \longrightarrow \frac{1}{a}; \quad M \longrightarrow \frac{DSB\mu}{va}.$$

Thus the limiting value of the coefficient of inhibition β equals $\frac{1}{a}$.

Strictly speaking, the coefficient of inhibition approaches $\frac{1}{a}$ but is not equal to it. If $\beta = \frac{1}{a}$, it would mean that $D = 0$, and hence the reaction would terminate at the surface layer of the grain.

Process kinetics are usually judged by the quantity of reacted solid substance, and not by the quantity of reacted reagent.

If $\underline{m}$ gram molecules of the reacting solid substance correspond to one gram molecule of reagent, and if the recovery (degree of conversion) $\underline{x}'$ is figured in parts of unity ($a = 1$), Equation (7) becomes:

$$\frac{1}{t} \ln \frac{1}{1 - x'} - \beta' \frac{x'}{t} = M. \quad (10)$$

Here

$$\beta' = \frac{mvk}{DSB\mu + kv} = m\beta. \quad (11)$$

In the limit, β' will approach $\underline{m}$, and β will approach unity.

The equation of the reaction kinetics in a current of liquid or gas at constant pressure ought not to differ, in principle, from Equation (10), for, as G.M.Panchenkov [3] has pointed out, the reaction rate at constant volume is directly proportional to the rate in a current of liquid.

Equation (7) not only makes it possible to determine the degree of completeness of the reaction at any instant from two experimental points for different time values, but it also enables one to compute the values of the constant of first-order velocity and of the coefficient of diffusion from Equations (8) and (9). If experimental data are available for various temperatures, the possibility arises of computing the activation energies of the chemical reaction and diffusion. Unfortunately, however, the available experimental material is insufficient for such calculations.

CHECKING THE FORMULA AGAINST EXPERIMENTAL DATA

To check the formula we made use of the circumstance that the equation is

a straight line when plotted in $\frac{1}{t} \ln \frac{1}{1-x'} - \frac{x'}{t}$ co-ordinates. Hence, if the experimental data lie along a straight line when plotted in these co-ordinates, this testifies to the applicability of the equation. To cite all the examples that confirm Equation (10) would take too much space here, and we shall therefore confine ourselves to a few characteristic cases.

Roasting. Roasting consists of heterogeneous reactions between a solid or several solids and the gas phase.

During the roasting process the gaseous substances diffuse through a stratum of solid reaction products or a mixture of solid reaction products and inert materials.

In dissociating roasting, the diffusion of the gases through the crust takes place in one direction only.

Naturally, the gases encounter a certain resistance in the process of diffusion. But, since a highly porous material is usually formed during dissociation, and what is more, the grains are broken down into more or less small pieces during roasting, there is reason to believe that the growing crust will not affect the course of the reaction, and that the latter will proceed in accordance with a first-order equation.

Table 1
Kinetics of the Dissociative Roasting of Alunite

Roasting time, hours	3	4	5	6	7	8	10	12
Elimination of chemically combined water, %	38.5	50.0	57.7	65.3	73.1	77.0	84.5	88.4
k	0.162	0.173	0.172	0.176	0.187	0.183	0.186	0.179

Let us cite data on the roasting of alunite, in which the latter loses its chemically combined water, by way of illustration [4] (Table 1).

The constancy of the constant of velocity of the first order reaction is satisfactory down to 90% of disintegration.

In all other types of roasting, we have to deal with both the diffusion of the reacting gas into the granule and with the diffusion of the gaseous reaction products outward.

Plenty of data is available on the kinetics of reducing roasting. By way of illustration, the data of D.P. Bogatsky [5] on the reduction of nickel-aluminum silicate by carbon monoxide are plotted in Fig. 1. As the temperature is raised, the coefficient β increases, which indicates that the diffusion and reaction rates are commensurable. The growth of β is due to the fact that the temperature variation of the coefficient of diffusion is less marked than that of the reaction-rate constant. Equation (10) also covers the other data in that paper satisfactorily.

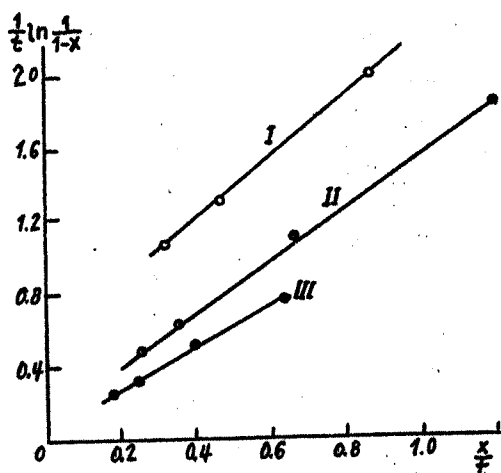


Fig. 1. Checking Equation (10) against data on the reducing roasting of nickel-aluminum silicate by carbon monoxide

I-Roasting temperature 800° , $\beta' = 1.7$; II-Roasting temperature 700° , $\beta' = 1.4$; III-Roasting temperature 600° , $\beta' = 1.2$.

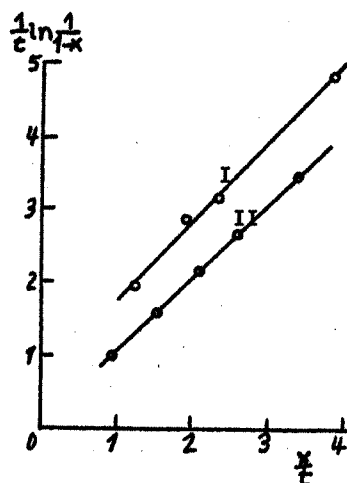


Fig. 2. Checking Equation (10) against data on the chlorination of wolfram ores by liquid sulfur chlorides.

Temperature 100° . I-artificial mixture, $\beta' = 1.1$; II-scheelite concentrate, $\beta' = 1$. Scale $\times 10$

As an example of chlorination roasting covered by Equation (10), we may cite the data of Y.B. Fridman and Y. Bogarad [8] on the chlorination of wolfram ores by liquid sulfur monochloride (Fig. 2). In contradistinction to this, the chlorination roasting of polymetallic sulfide ore by gaseous chlorine at 300° apparently satisfies the equation for the velocity of a first-order reaction, according to the data of D.M. Chizhikov [7]. The computed values of the constants are as follows:

Time, min.	40	60	80	100	120
$\frac{k}{-PbCl_2}$	0.020	0.024	0.022	0.020	—
$\frac{k}{-ZnCl_2}$	—	0.014	0.013	0.011	0.012

Much data has been collected in our institute on oxidation, sulfating, and reduction roasting, all of which fully confirm Equation (10).

Leaching. The lixiviation reaction takes place between a solid and a liquid solvent. In the leaching process there is gradually formed a crust of inert elixivated material, through which the fresh solvent diffuses into the reaction zone, the substance dissolved as the result of the reaction passing through in the opposite direction.

The leaching process resembles the process of dissolution of a solid body, and consequently many endeavors have been made [8,9] to apply Nernst's diffusion theory to it, as expressed by the following equation:

$$\frac{dx}{dt} = \frac{D}{\lambda} (\rho - \delta), \quad (12)$$

where ρ = saturation concentration; and δ = volumetric concentration at time t .

Integration of this equation yields the usual equation for first-order kinetics. In actuality, the constant of leaching rate computed from a first-order equation does not remain constant, growing gradually but uninterruptedly smaller as time goes on. This is due to the fact that the analogy between dissolution and leaching processes is not far-reaching enough to enable the direct application of solution laws to the leaching process. As has been pointed out already, the main difference in principle consists of the gradual increase of the diffusion layer during leaching, whereas the thickness of the diffusion layer remains constant in the solution process.

It may be expected that Equation (10) is applicable to instances of leaching from fairly dense material. If the granule is porous enough, leaching, like roasting, can take place without inhibition in accordance with the first-order law. This assumption is graphically illustrated in Fig. 3, in which the leaching rate of two kinds of natural covellite and "artificial" covellite, obtained by the preliminary leaching of secondary mineral chalcocite, [10], is shown. "Artificial" covellite is much more porous than the natural mineral; it is leached out in a few days in accordance with the first-order equation, whereas the dense natural minerals are leached out in accordance with Equation (10), their leaching rate being limited by the diffusion. Kennecott covellite evidently has a higher coefficient of diffusion than that from Butte.

One of the basic problems of lixiviation practice is the effect of temperature upon the leaching rate.

It is evident from Fig. 4, for the kinetics of the leaching of covellite, that the 50° straight line is shifted upward parallel to the 35° straight line [10].

Consequently, the kinetics of the lixiviation of CuS lie in the diffusion region under the conditions, and a rise in temperature results solely in an increase in the coefficient of diffusion.

The picture is somewhat different in Fig. 5 [10]. As the

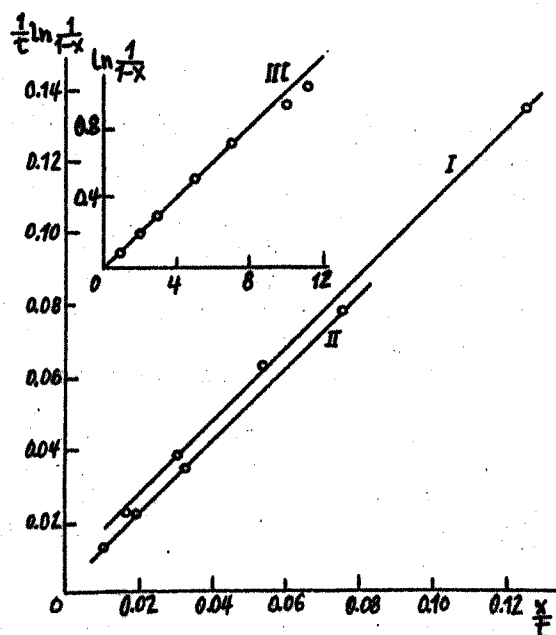


Fig. 3. Checking Equation (10) against data on the leaching rate of covellite in an acidulated solution of iron sulfate.

I-Kennecott covellite; II-Butte covellite;
III-artificial covellite. Temperature 35°
 $m = 1, \quad \beta = 1$

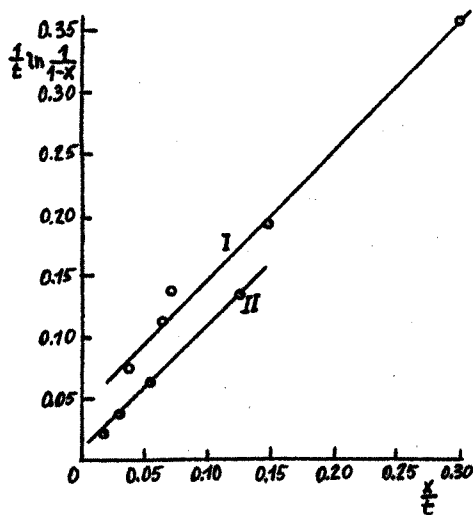


Fig. 4. Checking Equation (10) against data on the leaching rate of Kennecott covellite, -100+200 screen mesh, in an acidulated solution of iron sulphate.

I-50°; II-35°; $m = 1$, $\beta' = 1$

temperature rises, β' first drops and then rises again. This is evidently due to the fact that in this case, the variation of the coefficient of diffusion with temperature is greater at low temperatures than that of the velocity constant, whereas at higher temperatures the conditions are reversed; as a result, β' begins to rise and at 50° almost attains the limiting value, corresponding to the diffusion kinetics.

Fig. 6 illustrates the effect of the material's grain size [10]. As the degree of dispersion increases, the straight lines are displaced upward parallel to one another, which indicates the diffusional nature of the kinetics. The increase of M is linked to the growth of the phase separation surface with pulverization.

Fig. 7 shows the influence of the solvent anion upon the leaching rate [10]. Processing the experimental material in accordance with Equation (10) enabled us to prove that with iron sulfate, increased lixiviation is due not to the high rate of solution of the mineral in $\text{Fe}_2(\text{SO}_4)_3$ as compared with FeCl_3 , but to the high coefficient of diffusion of $\text{Fe}_2(\text{SO}_4)_3$, which results in accelerating the lixiviation.

Equation (10) was likewise checked against other data, being completely substantiated.

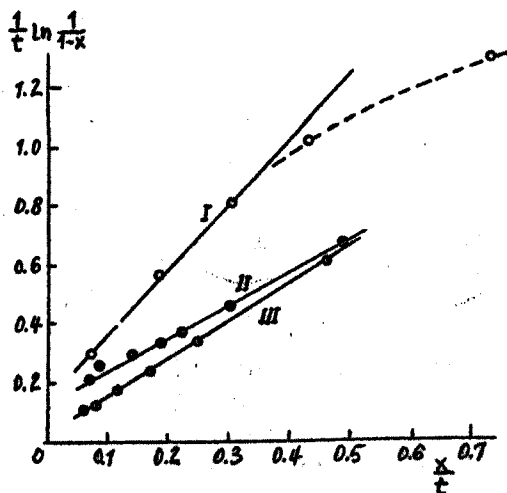


Fig. 5. Checking Equation (10). Effect of temperature on the leaching rate of chalcocite, -100+200 screen mesh, in an acidulated solution of iron sulphate.

I- 50°, $\beta'=2$; II-35°, $\beta'=1.1$; III-22°, $\beta'=1.3$. m, in accordance with the reaction $\text{Cu}_2\text{S} + 2\text{Fe}_2(\text{SO}_4)_3 = 2\text{CuSO}_4 + 4\text{FeSO}_4$, equaling 2; consequently, the limiting value of $\beta' \rightarrow 2$. The first point of Line I dropped out, which indicates that inhibition does not set in at once, but only after some time has elapsed after the beginning of leaching.

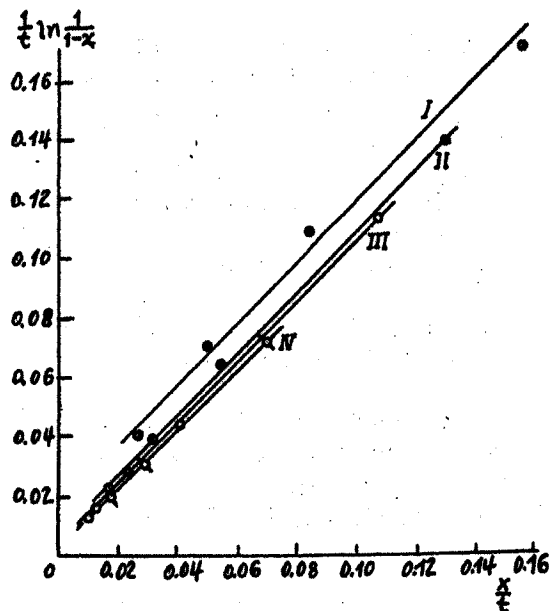


Fig. 6. Checking Equation (10). Effect of grain size upon the leaching rate of Kennecott covellite in an acidulated solution of iron sulfate.

I- 200 mesh; II-1pp + 200 mesh; III-10 + 28 mesh; IV-3 + 10 mesh; $\beta' = 1$.

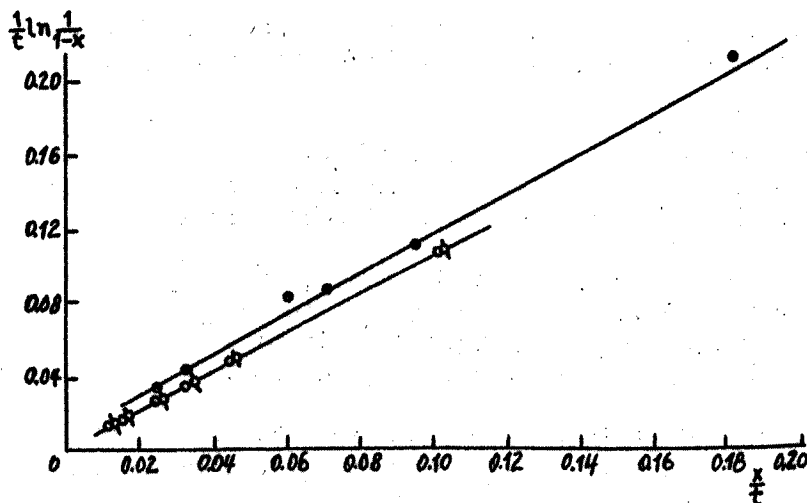


Fig. 7. Checking Equation (10). Influence of solvent upon the leaching rate of covellite, 200 mesh grain size.

I-1% solution of Fe as $\text{Fe}_2(\text{SO}_4)_3 + 0.5\% \text{H}_2\text{SO}_4$; II-0-1% solution of Fe as $\text{FeCl}_3 + 0.5\% \text{HCl}$; II-0-1% solution of Fe as FeCl_3 ; $\beta' = 1$; $m = 1$.

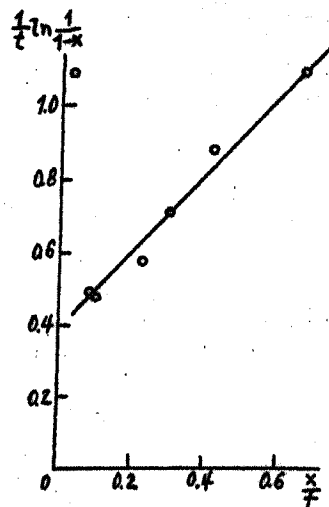


Fig. 8. Checking Equation 10 against data on the washing rate of leached sand containing gold as $\text{KAu}(\text{CN})_2$. Intermittent washing. In the original the washing quantity is cited instead of the leaching time.

$\beta' = 1.1$.

Washing. In the washing process, there occurs the diffusion of the substance dissolved in the liquid contained in the pores of the granule.

During lixiviation, in most cases there exists a well-known relationship between the molecules of the soluble solid component and the solvent, based upon the stoichiometry of the given reaction, whereas there is no fixed stoichiometric relationship in washing, and the magnitude of β' in Equation (10) depends on the experimental conditions.

Fig. 8 reproduces data confirming Equation (10) for the process of washing gold out of sand after it had been dissolved by potassium cyanide, [9].

Cementation. The applicability of Equation (10) to cementation processes may also be considered proved by the work of B.V.Drozdo. Inhibition of the reaction is governed by the degree of porosity of the film of cement metal and by the coefficient of diffusion of the metal's ions.

SUMMARY

1. All the examples cited, as well as a large number of computations made by us, indicate the applicability of the formula developed to processes of roasting, leaching, washing and cementation.

2. Despite all the differences between these various processes from the standpoint of chemical reactions, they may be collated kinetically under one generalized law based upon a calculation of the gradual increase in the thickness of the diffusing layer that is proportional to the amount of the reacted diffusing substance. The applicability of Equation (10) likewise indicates that most of these reactions take place in several stages.

3. In actuality, Equation (10) postulates that the reaction proceeds in accordance with the first-order law, but nonetheless, it is valid even for extremely complicated processes.

4. The only possible explanation for this is that the overall equation for the chemical action consists at bottom of several simple stages (that are of the first order), one of which limits the overall process rate.

5. It should be borne in mind that although study of the kinetics often yields valuable information to explain the mechanism of the reactions, final evaluation of the mechanism can be made only when the kinetics data are in agreement with the results obtained by other research methods.

In the computational part of this research considerable assistance was rendered us by A. M. Yakovleva, to whom we wish to express our gratitude.

LITERATURE CITED

- [1] D.A.Frank-Kamenetsky, Diffusion and Heat Transfer in Chemical Kinetics, Publishing House of the USSR Acad. Sci., 1947.
- [2] Cf. A.D.Stepukhovich, J. Gen. Chem. USSR, 15, 341 (1945).
- [3] G.M.Panchenkov, J. Phys. Chem. USSR, 22, 209 (1948).
- [4] Cf. S.S.Smirnov-Verin, Alunites and their Use. ONTI, 1933.

- [5] D.P. Bogatsky, J. Phys. Chem. USSR, 20, 81 (1947).
- [6] Y.D. Friedman and Y. Bogorod, J. Appl. Chem., 19, 837 (1946)
- [7] D.M. Chizhikov. The Chlorine Method of Treating Polymetallic Ores and Concentrates. ONTI, 1936, p. 93.
- [8] T.P. Campbell, The Hydrometallurgy of Nonferrous Metals, 1934.
- [9] V.I. Smirnov. The Hydrometallurgy of Copper, 1947
- [10] J.D. Sullivan. Symposium on The Metallurgy of Copper, ed. A.M. Gazaryan, ONTI, 1937, p. 338.

Received July 1, 1948.