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A NEW MODEL OF CHEMICAL DISSOLUTION OF SOLIDS: AN ANALYSIS OF THE MECHANISM OF DISSOLUTION OF MONODISPERSED MATERIALS

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Abstract. On the basis of a new model of chemical dissolution, an analysis of the kinetic parameters obtained using the modified Dolivo-Dobrovolsky equation was carried out. It shows that the change in parameters during the transition from one mineral to another is subject to a compensation effect. This means that there is a temperature point at which all minerals dissolve at the same rate. Therefore, at temperatures below that temperature, the reactivity of minerals settles in one sequence, and at temperatures above, in the opposite sequence. In addition, a new equation for the rate constant of chemical dissolution of minerals has been obtained. Calculations based on the new dissolution model made it possible to distinguish between the systemic and individual properties of minerals of the same nature in the process of dissolution. These minerals differ from each other by the concentration of active surface complexes, and are combined into a system by a single transmission coefficient and the same value of the lifetime of the active complex.

Keywords: mineral, dissolution, kinetics, thermodynamics, reactivity.

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Introduction

The kinetic parameters of chemical dissolution, which are determined in the kinetic region, where the rate of the dissolution reaction is not limited by the rate of diffusion exchange of reagents and reaction products in the layer at the interface between the solid and liquid phases, are important for a quantitative description of the reactivity of minerals. Ospanov, Kh. *et al.* at the Faculty of Chemistry, Al-Farabi Kazakh National University carried out an experimental study of the kinetics of dissolution of sparingly soluble minerals based on Dolivo-Dobrovolsky's equation of the kinetics of dissolution of dispersed solid matter Eq.(1) [1].

$$U = k\cdot\frac{S_0\cdot C_0^{\alpha}}{\sigma}\cdot t \qquad (1)$$

where, U- the reduced extraction, 1/L;
k- the dissolution rate constant, 1/s·cm^2;
$\frac{S_0\cdot C_0^{\alpha}}{\sigma}$- the reduced dissolution rate;
S_o- the surface area of 1 mol of solid at the initial moment, cm^2/mol;
C_o- the initial concentration of the dissolving reagent, mol/L;
α= 1- the order of the reaction according to the reagent;
σ- a stoichiometric coefficient indicating the number of moles of solvent required to dissolve one mole of a solid;
t- the time of contact of the solid phase with the solvent, s.

According to the methodology of Dolivo-Dobrovolsky, the kinetics of dissolution of a dispersed solid can be studied following the assumptions and conditions listed below [2]:

- the solid that is subject to dissolution is grained in a way that its geometric shape is not too different from its isometric shape (for example, a cube, an octahedron, a tetrahedron, a sphere, *etc.*);
- the dissolution rate at any given moment is the same on all grain faces;
- only the initial stage of the dissolution process is studied, when the proportion of the still undissolved substance is relatively large ($\eta \geq$ 0.8-0.9) and therefore, the size of the grain surface S changes according to the formula $S = S_0\cdot \eta^{\beta}$, where the exponent β is in the range between 2/3 and 0 (2/3> β> 0);

- the dissolution process is carried out with a large excess of the solvent, when its concentration remains practically constant during the experiment and the reduced extraction U is expressed by the Eq.(2).

$$U = \frac{1-\eta^{1-\beta}}{1-\eta} \qquad (2)$$

However, Ospanov, Kh., instead of the theoretical value of the reduced extraction *U*, intuitively used the experimental values of the extraction of metal ions from solids into solution. Further, in this work, Eq.(1) with such a replacement will be referred to as a modified Eq.(1). Despite the theoretical groundlessness of such a replacement, the kinetic parameters obtained on the basis of the modified Eq.(1) made it possible to reach amazingly effective results in chemical technology [2]. Therefore, the analysis of this phenomenon is an actual theoretical task that has to be addressed. The work presented here fulfills this gap by studying the kinetics and the mechanism of dissolution of sparingly soluble natural minerals based on the existing theories and a new model of chemical dissolution of solids [3] and as well as an empirical work guided by Ospanov, Kh. [4]. Thus, the goal of this study was set to give a theoretical interpretation to the modified V.V. Dolivo-Dobrovolsky equation and to draw a number of conclusions about the mechanism of chemical dissolution of minerals.

Experimental

Materials

Monominerals of malachite $CuCO_3 \cdot Cu(OH)_2$, azurite $(CuCO_3)_2 \cdot Cu(OH)_2$, chrysocolla $CuSiO_3$, elite $Cu_5[(PO_3)_2 \cdot (OH)_4] \cdot H_2O$, cuprite Cu_2O and tenorite CuO used in this study were obtained from the Dzhezkazgan deposit (Kazakhstan). Grinding of minerals was carried out in an agate mortar and the particle size of the monodisperse material for experiments ranged from -0.104 to 0.074 mm. The reagents used in the study included extra pure grade ethylenediaminetetraacetic acid (EDTA), extra pure grade sodium acetate, and high purity electrolytic copper.

Methods

Preparation of model working solutions

Aqueous solutions of ethylenediaminetetraacetic acid (EDTA) of “extra pure” grade were used as a dissolving reagent. Sodium acetate 4 M was used as a background. A typical copper solution 1 mg/mL was made from high purity electrolytic copper 500 mg EDTA solutions of 50 mL were poured on crushed mineral samples of 50 mg (malachite, azurite, chrysocolla, elite, cuprite and tenorite) in a thermostated cell [4] with a capacity of 150 mL. The cell was sealed hermetically and stirred for a specified period of time: 180, 300, 600, 1200, 2400 and 3600 s. After the end of shaking, the solution was filtered off. The filtrate was placed in sodium acetate 25 mL, 4 M, and the content of copper ions in the resulting solution was determined by the polarographic method.

The rate of extraction of copper ions from minerals into EDTA solution depended on the following factors: the duration of stirring (30-60 min), concentration of EDTA solutions (0.01 mol/L; 0.025 mol/L; 0.05 mol/L), temperature, and intensity of stirring (100-300 vibrations per minute). To determine the parameters of the Arrhenius equation, the experiments were carried out at temperatures of 25, 35, 45, 55, and 65°C. The values of the dissolution rate constants were obtained as a result of 5 parallel experiments with a confidence level of 0.95.

Determination of copper ions content

The mineral samples were dissolved in a thermostatically controlled cell 150 mL. The cell was shaken on an orbital shaker with 100-200 vibrations per minute. A ‘Zp–60’ polarograph was used to determine the content of copper ions.

Results and discussion

In the course of theoretical analysis, a compensation effect that is a correlation between Arrhenius ln*A* and a change in the value of activation energies was found. The effect can sometimes be an erroneous consequence of the fact that equations that do not correspond to the basic law of chemical kinetics can be used to describe the kinetics of the process. The modified Eq.(1) contains information about the acting masses and surfaces; therefore, it is worth applying the theory of the isokinetic effect [5] to analyze the processes under consideration.

According to Shakhparonov’s theory [5], it is necessary to make the following assumptions in the new model of chemical dissolution [3]:

- the total change in the Gibbs energy during the chemisorption of ligands on active ion-copper atoms on the crystal surface and subsequent activation should be the Gibbs energy of formation of surface active complexes $\Delta G^{\neq}$;
- the number of available active centers should be much greater than the number of ligands in contact with them; therefore, the unit in the denominator in

the basic equation of the new model [3] should be neglected.

Taking these assumptions into account, the basic equation of the model takes the form of Eq.(3).

$$\frac{dn_{AL}}{Vdt} = \varphi \nu e^{-\Delta G^{\neq}/RT} C_A \cdot S \cdot C_L \qquad (3)$$

where, $\frac{dn_{AL}}{Vdt}$- the increase in the concentration of metal ion-atoms that have passed into the solution volume V;

φ- the transmission coefficient;

$\Delta G^{\neq}$ - the Gibbs energy of the dissolution process activation, kJ/mol;

C_A- the surface concentration of metal atoms A, mol/cm^2;

S- the size of the reacting surface of the solid, cm^2;

C_L- the concentration of the reagent, mol/L.

Comparing Eq.(1) and Eq.(3), an equation for the rate constants of chemical dissolution is derived in Eq.(4).

$$k = \varphi \cdot \frac{k_B T}{h} \cdot \exp\left(\frac{\Delta G^{\neq}}{RT}\right) \cdot C_A \cdot \sigma \qquad (4)$$

Using the Arrhenius equation and Eq.(4), it can be found that:

$$\Delta H^{\neq} = E - RT \qquad (5)$$

Then, substituting the obtained Eq.(5) into the expression for the logarithm of the rate constant in Eq.(4) gives the Eq.(6).

$$\Delta S_a^{\neq} = R\left(\ln A - \ln\frac{k_B T}{h} - lnC_A - \ln\sigma - 1\right) \qquad (6)$$

where, $\Delta S_q^{\neq}$ is the apparent entropy of activation, *i.e.* activation entropy, calculated under the assumption that the transmission coefficient φ= 1 (Table 1).

According to Eq.(5), the enthalpy of activation $\Delta H^{\neq}$ does not depend on φ; therefore, the true enthalpy of activation coincides with the apparent enthalpy of activation and there is no "*k*" index for $\Delta H^{\neq}$.

Calculation of the true values of the thermodynamic parameters of the activation process

The analysis of the change in the enthalpy of activation depending on the apparent entropy of activation of the process of extracting copper from the studied copper minerals in EDTA solution shows the presence of a pair regression (r= 0.983) represented by Eq.(7).

$$\Delta H^{\neq}\ (\text{kJ/mol}) = 220.4 + 384\ \Delta S^{\neq}\ (\text{J/mol}) \qquad (7)$$

According to Shakhparonov's methodology [5], and the numerical values of the coefficients in Eq.(7), A= 220.4 kJ/mol and B= 384 K, according to the formula φ= exp($-\frac{A}{RB}$) from the same chapter, the transmission coefficient can be calculated.

Then, according to the formulas $\Delta G^{\neq} = \Delta G_k^{\neq} + RT\ln\varphi$ and $\Delta S^{\neq} = \Delta S_q^{\neq} - R\ln\varphi$, it can be obtained the true values of the Gibbs energy and the activation entropy of the dissolution reactions (Table 2).

Table 1

Rate constants and characteristics of the active complex of the reaction of dissolution of oxidized copper minerals in EDTA, calculated under the condition that φ= 1.

Minerals	*k·10^7, 1/s·cm^2 (at 25°C)*	*E, kJ/mol*	*lnA*	*$\Delta H^{\neq}$, kJ/mol*	*-$\Delta S_q^{\neq}$, J/mol·K*	*$-T\Delta S_k^{\neq}$, kJ/mol*	*$\Delta G_k^{\neq}$ kJ/mol*
Malachite	49.00	36.4	2.5	33.9	480.9	143.3	177.2
Azurite	35.00	41.2	4.1	38.7	465.0	138.6	177.3
Chrysocolla	5.60	47.5	4.8	45.0	460.7	137.3	182.3
Elite	3.20	50.1	5.2	47.6	451.8	134.6	182.3
Cuprite	3.10	53.4	6.5	50.9	450.8	134.3	185.3
Tenorite	3.00	74.8	15.1	72.3	382.5	114.0	186.3

Table 2

True values of the enthalpy $\Delta H^{\neq}$ of Gibbs energies $\Delta G^{\neq}$, and the entropy $\Delta S^{\neq}$ of activation of the reaction of dissolution of oxidized minerals in 0.025 M aqueous EDTA solution.

Minerals	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, $J/mol{\cdot}K$	$\Delta G^{\neq}$, kJ/mol
Malachite	33.9	92.8	6.0
Azurite	38.7	108.7	6.1
Chrysocolla	45.0	113.0	11.1
Elite	47.6	121.9	11.1
Cuprite	50.9	122.9	14.1
Tenorite	72.3	191.2	15.1

Rate constants of fast processes

The chemisorption of the ligand on the surface of the single crystal and the activation of the surface chemisorption complex can be considered as one reaction in the course of which the Gibbs energy of the system changes by $\Delta G + \Delta G^{\neq}_{s.c.} = \Delta G^{\neq}$. Therefore, the equilibrium constant of the reaction of the formation of an active complex looks as Eq.(8).

$$K = \frac{k^{\neq}}{k_f^{\neq}} = \exp\left(-\frac{\Delta G_i^{\neq}}{RT}\right) \qquad (8)$$

where, $k^{\neq}, k_f^{\neq}$ are rate constants of the fast processes of activation and deactivation.

The concentration of surface active complexes can be calculated using Eq.(9).

$$C_{AL}^{\neq} = C_{\mathrm{Me}} \cdot n_L \exp\left(-\frac{\Delta G^{\neq}}{RT}\right) \qquad (9)$$

where, $C_{AL}^{\neq}$- the surface concentration of active complexes, mol/L;

C_{Me}- the surface concentration of metal ion-atoms, mol/cm^2;

n_L- the number of particles of the dissolving agent in the system;

$\Delta G^{\neq}$- true Gibbs energy of activation of the dissolution process, kJ/mol.

It is necessary to calculate the concentration of metal atoms C_{Me} on the surface of minerals to calculate the surface concentration of active complexes. In the experiment, the monominerals were grinded to a particle size of 0.074 mm. Therefore, for the convenience of calculations, it can be assumed that the particles have a spherical shape with a radius of R= 0.037 mm. On the surface of these balls, clusters of atoms can be located in a monolayer, each of which represents the gross formula of the mineral. For example, for malachite $CuCO_3{\cdot}Cu(OH)_2$, the cluster consists of two copper atoms, one carbon atom, five oxygen atoms, and two hydrogen atoms. The cluster radius r can be calculated using $r^3 = \sum\lambda_i\ r_i^3$ formula, where λ_i are the number of atoms of type i in the cluster and r_i- their radius.

The number of clusters in the volume of a particle N is equal to R^3/r^3. The fraction of clusters located in the near-surface monolayer η is equal to the fraction of this layer in the volume of the particle $(R^3 - R_o^3)/R^3$, where R_o is the radius of the particle minus the thickness of the monolayer equal to cluster diameter $2r$. Consequently, the surface concentration of clusters will be equal to $C_c = N\eta/S$, where S is the surface area of the particle. Therefore, the surface concentration of metal ion-atoms in mol/cm^2 will be equal to: $C_{Me} = N\eta x/(4\pi R^2 N_A)$, where N_A is Avogadro's number, x is the volume fraction of metal atoms in the cluster volume: $x = \lambda_i\ rMe^3/\sum\lambda_i\ r_i^3$, where λ_{Me}, r_{Me} are the number in the cluster and the radius of the metal atom.

An abbreviated scheme of chemical dissolution can be represented as Eq.(10), in which the next stage after the formation of an active complex is the formation of a transition state $AL^{\neq} \xrightarrow{k^+} AL^+$.

$$A_s + L \underset{k_f^{\neq}}{\overset{k^{\neq}}{\leftrightarrow}} (AL)^{\neq} \overset{k^+}{\to} (AL)^+ \qquad (10)$$

The rate constant of this stage is proportional to the transmission coefficient φ, the numerical value of which is very small; therefore, this reaction is the limiting stage of the mineral dissolution reaction, *i.e.* the numerical values of k^+ are equal to the experimentally found dissolution rate constants k in Eq.(1).

The transmission coefficient φ is expressed through the rate constants of the decay of $AL^{\neq}$: $\varphi = \frac{k^+}{k^+ + k_f^{\neq}}$, and therefore the decontamination rate constant can be represented as Eq.(11).

$$k_f^{\neq} = \frac{k^+(1-\varphi)}{\varphi} \cong \frac{k^+}{\varphi} \qquad (11)$$

Hence, according to Eq.(8), one can find the rate constant of the direct reaction in Eq.(9) as in Eq.(12).

$$k^{\neq} = k_f^{\neq} \exp\left(\frac{\Delta G_i^{\neq}}{RT}\right) \qquad (12)$$

The lifetime of the active complex $AL^{\neq}$

The number of disintegrating particles of the active complex $dn^{\neq}$ on the surface area S during the time dt is: $dn^{\neq} = k^{+} \cdot Sdt + k_f^{\neq} \cdot Sdt$. Calculations show that $k_f^{\neq} \gg k^{+}$, therefore:

$$dn^{\neq} = k_f^{\neq} \cdot Sdt \qquad (13)$$

By definition, the number of active complexes $AL^{\neq}$ on the surface of a mineral particle is $n^{\neq} = C_{AL}^{\neq} . S$, where S is the surface area of the particle. Therefore, replacing $dn^{\neq}$ and dt with integral values of $n^{\neq}$ and , $\tau_{AL}^{\neq}$ accordingly, taking into account Eq.(13), Eq.(14) was obtained for the average lifetime of active complexes.

$$\tau_{AL}^{\neq} = \frac{C_{AL}^{\neq}}{k_f^{\neq}} \qquad (14)$$

The calculated values of the rate constants of the considered processes, as well as the concentrations and the average lifetime of active complexes are given in Table 3.

Concluding remarks

Experiments are usually carried out at a constant volume of the reaction cell and a constant volume of the dissolving reagent. In practice, when dissolving poorly soluble natural inorganic minerals in experiments, the reaction order often has a fractional value, fluctuating around unity [7]. Under these conditions, the modified Eq.(1) with the reaction order equal to unity and taking into account the stoichiometric coefficient σ completely coincides with the theoretical Eq.(3) of the new dissolution model.

According to Eq.(7), the isokinetic temperature for the system under consideration is 384 K. This means that the entire system of the same type of substances - malachite, azurite, chrysocolla, elite, cuprite, and tenorite at this temperature dissolve at the same rate. At temperatures below the isokinetic temperature, the dissolution rates of minerals are arranged in the sequence: malachite › azurite › chrysocolla › elite › cuprite › tenorite, and at temperatures above 384 K, they are arranged in the reverse order: tenorite › cuprite › elite › chrysocolla › azurite › malachite.

According to Table 3, the average lifetime of the surface-active complexes in the dissolution reactions of malachite, azurite, chrysocolla, elite, cuprite, and tenorite in an aqueous solution of EDTA remains constant. This can be explained by the fact that the reactions under consideration proceed with the formation and decomposition of the surface active complex $(CuY^{2-})_{surf, solv.}$, which is identical for the dissolution reactions of all considered minerals.

Based on Eq.(11) and Eq.(14), one can obtain a formula that gives a new theoretical interpretation to the rate constants of chemical dissolution:

$$k = \frac{C_{AL}^{\neq}}{\tau_{AL}^{\neq}} \varphi \qquad (15)$$

According to Eq.(15) and Table 3, the individual differences of the studied materials are associated with the difference in the concentrations of active complexes on their surfaces. The generality and consistency of solids of the same type is associated with a single value of the transmission coefficient for all minerals and a single value for the lifetime of the active complex.

Table 3

Kinetic characteristics of the reduced dissolution scheme, according to Eq.(10).

Minerals	$k^{\neq} \times 10^{-22}$ $1/s \cdot cm^2$	$k_f^{\neq} \times 10^{-23}$ $1/s \cdot cm^2$	$k^{+} \times 10^{7}$ $1/s \cdot cm^2$	$C_{AL}^{\neq} \times 10^{-8}$ $1/cm^2$	$\tau_{AL}^{\neq} \times 10^{15}$ s
Malachite	41.71	47.04	49.00	11.38	2.4
Azurite	28.61	33.60	35.00	8.074	2.4
Chrysocolla	0.63	5.38	5.60	1.26	2.3
Elite	0.35	3.07	3.20	0.73	2.4
Cuprite	0.10	2.98	3.10	0.73	2.4
Tenorite	0.06	2.88	3.00	0.662	2.3

Conclusions

The new dissolution model is built based on a rigorous application of the Gibbs grand canonical ensemble and therefore gives a sufficiently deep theoretical interpretation of the modified equation with help of which the experimental data were obtained. The apparent and true values of the entropy and Gibbs energy of activation, rate constants of the processes of emergence and decay of surface-active complexes, surface concentrations and the average lifetime of the surface active complex were calculated. Calculations show that the lifetime of active surface complexes in the reactions of dissolution of the studied minerals remains constant.

A theoretical equation for the rate constant of chemical dissolution is obtained. The experimental data considered in this work on this equation indicate that the same type of oxidized copper minerals differ from each other in the surface concentration of active surface complexes, and are combined into a system of the same type of minerals by a single transmission coefficient and a certain value of the lifetime of the active complex.

The theoretical equation for the rate constant of chemical dissolution was obtained. The experimental data considered in the work according to this equation indicate that the same type of oxidized copper minerals differ from each other by the surface concentration of active surface complexes, and are combined into a system of the same type of minerals by a single transmission coefficient and by a certain value of the lifetime of the active complex.

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