DOI: 10.17344/acsi.2025.9348 *Acta Chim. Slov.* **2025,** *72,* 774–780

Scientific paper

Kinetic Parameters of Mineral Dissolution and Gibbs Free Energy

Alma Ryskaliyeva[*,1], Murat Baltabayev[1], Yerassyl Mukhamediyar[2], Aigul Zhubatova[1] and Nurzhamal Khokhanbayeva[3]

[1] *Kazakh National Agrarian Research University, Department of Horticulture, Plant Protection and Quarantine, 8 Abay Ave., 050010 Almaty, Kazakhstan*

[2] *Higher School of Economics, International College of Economics and Finance, 11 Pokrovsky Bulvar, building T, 109028 Moscow, Russia*

[3] *Kazakh National Agrarian Research University, Department of Soil Science, Agrochemistry and Ecology, 8 Abay Ave., 050010 Almaty, Kazakhstan*

* *Corresponding author: E-mail: aryskalieva@mail.ru*
Phone: +7705-981-82-60

Received: 05-31-2025

Abstract

This study investigates the quantitative relationship between the kinetics and thermodynamics of mineral dissolution in heterogeneous reactions, specifically focusing on the dissolution of sparingly soluble minerals. Building on historical developments in chemical kinetics and thermodynamics, we propose empirical equations that describe experimental data and enable predictive modeling of dissolution processes. Two descriptors were evaluated: the normalized Gibbs energy of oxidation ($\Delta_r G^0/\sigma$) and the average atomic Gibbs energy of mineral formation ($\Delta_f G^0/n$). Experimental values of the apparent rate constant (k) and specific dissolution rate (W) were obtained under strictly controlled conditions. Linear regression models were developed. The regression coefficients were interpreted in terms of reagent selectivity and aggressiveness, consistent with the Bell–Evans–Polanyi principle. These findings support the use of $\Delta_f G^0/n$ as a reliable predictor of mineral reactivity and provide a thermodynamic basis for rational selection of leaching agents.

Keywords: Mineral dissolution, heterogeneous reactions, chemical reactivity, selectivity, aggressiveness, empirical modeling.

1. Introduction

One of the earliest advances in quantitative chemical kinetics was the law of mass action, formulated by Guldberg and Waage. It established a fundamental relationship between the reaction rate and the concentrations of reactants,[1] laying the groundwork for connecting kinetic and thermodynamic parameters. For reversible homogeneous reactions, this was expressed as:

$$K = \frac{k_1}{k_{-1}}, \tag{1}$$

where K is the equilibrium constant, and k_1 and k_{-1} are the rate constants of the forward and reverse reactions, respectively. Based on this principle, models that relate reaction rates to the equilibrium constant were developed. In particular, for proton transfer reactions, the Brønsted equation[2] gained widespread application:

$$\ln k = \alpha \ln K + a, \tag{2}$$

where α and a are empirical parameters depending on the nature of the reagents. Substituting the Gibbs-Helmholtz relation

$$\ln K = \frac{-\Delta G}{RT} \tag{3}$$

into the Brønsted equation, one gets:

$$\ln k = \frac{-\alpha \Delta G}{RT} + a, \tag{4}$$

indicating an exponential dependence of the reaction rate

on the Gibbs free energy change. Such models are widely accepted in homogeneous chemistry, where the mechanisms are relatively well defined.

However, for heterogeneous processes, such as mineral dissolution, this classical kinetic–thermodynamic relationship loses its rigor. The multistep nature of the reactions, heterogeneity of the solid phase, presence of defects, variable surface activity, and uncertainty in the composition of reaction products complicate the direct application of such relations. As a result, dependencies like the Brønsted equation cannot be directly transferred to heterogeneous processes.

Nevertheless, analogies with proton transfer reactions suggest that an empirical relationship between the rate and the thermodynamic driving force may still be valid if an appropriate thermodynamic descriptor is chosen. Two such descriptors are considered in this study: 1) the normalized Gibbs energy of reaction, $\Delta_r G^0/\sigma$, where σ is the stoichiometric coefficient of the oxidant; 2) the average atomic Gibbs energy of mineral formation, $\Delta_f G^0/n$, where n is the number of atoms in the formula unit. These quantities reflect the energy cost per unit transformation and may serve as indicators of mineral reactivity. We hypothesize that the logarithms of kinetic parameters (apparent rate constant k and specific dissolution rate W) are linearly dependent on the selected thermodynamic descriptors.

To test this hypothesis, we experimentally evaluate the reaction rates for selected copper and iron sulfides, dissolved in various oxidizing media under strictly controlled conditions. As a result, two kinetic parameters were measured: 1) the apparent rate constant k, which characterizes the integral process rate; and 2) the specific dissolution rate W, normalized to the mineral surface area. Linear regression models were constructed to correlate $\ln k$ and $\ln W$ with the two thermodynamic descriptors: $\Delta_r G^0/\sigma$ and $\Delta_f G^0/n$.

This approach allowed us to quantitatively link thermodynamics and kinetics in heterogeneous systems and interpret regression coefficients physically. We also observed an inverse proportionality between these coefficients, representing a manifestation of the Bell–Evans–Polanyi principle in heterogeneous systems. Overall, the approach supports the use of the average atomic Gibbs energy of formation as a universal reactivity descriptor, particularly in cases where the reaction products are not well defined. Thus, this study contributes to the development of a thermodynamically grounded framework for predicting dissolution kinetics and selecting effective leaching agents.

2. Methodology

2. 1. Determining the Kinetic Parameters of Mineral Dissolution (*k, W*)

The chemical activity of minerals was compared based on the method proposed by Kh. Ospanov,[3] which requires strictly controlled conditions such as the same temperature, degree of dispersion, reagent concentration, and sample purity. Experiments were conducted under vigorous stirring, which eliminated the influence of external diffusion. Under these conditions, the initial stage of the reaction proceeds with a stable concentration of active sites on the mineral surface.

To calculate the kinetic parameters, we used the initial section method within the framework of the Shchukarev–Dolivo–Dobrovolsky kinetic equation:[4,5]

$$\frac{dC_M}{dt} = \frac{k \cdot S_0 \cdot C^n}{\sigma} \tag{5}$$

When the dissolving reagent is in excess and the interaction time between the minerals and the oxidizing agent is short, both the reagent concentration and the initial surface area of the mineral can be considered approximately constant: $C \approx const$, $S_0 \approx const$. This assumption allows for the derivation of an integral expression:

$$C_M = \frac{k \cdot S_0 \cdot C^n \cdot t}{\sigma} \tag{6}$$

where C_M is the amount of metal transferred into solution; k is the apparent rate constant; S_0 is the initial surface area of the mineral; C is the concentration of the dissolving reagent; n is the order of the reaction; t is the time; σ is the stoichiometric coefficient.

Taking the logarithm of the integral form of the kinetic equation yields a relationship that can be used to determine the reaction order, n:

$$ln\left(\frac{C_M}{t}\right) = n \cdot lnC + ln\left(\frac{k \cdot S_0}{\sigma}\right), \tag{7}$$

which can be used to determine the order of a chemical reaction n, the numerical value of which allows the calculation of the apparent reaction rate constant k.

2. 2. Theoretical Foundations of Normalization

The transition from homogeneous reactions described by the Brønsted equation to heterogeneous mineral dissolution processes requires a rethinking of the choice of a thermodynamic parameter. In the conditions of a multi-stage dissolution mechanism and the specificity of the solid phase, it is necessary to take into account the form of the Gibbs energy adequate to the description of heterogeneous interaction.

The Shchukarev–Dolivo–Dobrovolsky method normalizes not only the kinetic but also the geometric characteristics of the process. The rate constant takes into account σ, a parameter reflecting the reagent consumption, and the specific rate W is initially normalized per unit of mineral surface. Such a formulation of the problem requires a similar normalized approach to thermodynamic functions.

To compare thermodynamics and kinetics, we divide the standard Gibbs energy of the reaction by the stoichiometric coefficient σ, reflecting the number of electrons or moles of the reagent participating in the elementary act of the reaction. The resulting value $\Delta_r G^0/\sigma$ is the normalized energy characterizing the energy expenditure for one ion-atom transition,[6-8] that is, for one elementary stage of interaction between the mineral and the reagent. For example, for the reaction $Cu_2S+2FeCl_3 \rightarrow 2CuCl+2FeCl_2+S$, the value $\Delta_r G^0/\sigma$ shows how much Gibbs energy is spent for every one mole of electrons transferred from the reducing agent (Cu_2S or S^{2-}) to the oxidizing agent (Fe^{3+}).

The lower the value of this normalized thermodynamic parameter, the less energy consuming is the transfer of an ion from the solid phase to the solution, and the higher the reaction rate, all other things being equal. This makes $\Delta_r G^0/\sigma$ a convenient and justified parameter for quantitative comparison with kinetic characteristics such as the apparent rate constant and the specific dissolution rate.[3]

However, the use of the normalized Gibbs energy $\Delta_r G^0/\sigma$ as a predictor of kinetic characteristics has certain limitations. This parameter is based on the complete thermodynamic characteristic of the dissolution reaction, including knowledge of the composition of all reaction products and the amount of oxidizer consumed. In the case of natural minerals, which may have a defective structure, inclusions of foreign phases, and an uncertain composition of the final products, the exact determination of $\Delta_r G^0/\sigma$ becomes difficult. In such cases, the use of this parameter is permissible only as an *approximate* measure of the thermodynamic 'driving force' of the reaction and requires special attention in the physicochemical interpretation of the results.[9]

Practical hydrometallurgy shows that in the conditions of multicomponent and defective natural minerals, it is often impossible to accurately determine the products of dissolution. In such cases, it is difficult to correctly determine the total Gibbs energy of the reaction as well. In this regard, some scholars proposed to use the average atomic Gibbs energy of mineral formation as a thermodynamic parameter.[9] They demonstrate that normalization of the energy per mole of atoms allows identifying patterns between the dissolution rate and the stability of the solid phase. Therefore, this study considers the use of the average atomic Gibbs energy as a normalized thermodynamic parameter comparable to the specific rate and apparent rate constant of dissolution.

2. 3. Methodology for Determining the Average Atomic Gibbs Energy

The values of the standard Gibbs energy of formation of a number of sulfide minerals, in particular non-stoichiometric and thermodynamically poorly studied compounds, were calculated using the comparative analogy method proposed by Karapetyants.[10–12] This method is based on a comparison of the thermodynamic characteristics of chemically and structurally related compounds. It enables the interpolation or extrapolation of the Gibbs energy in the absence of direct experimental data.

We calculated the average atomic Gibbs energy in two stages. First, the standard Gibbs energy of formation of the mineral ($\Delta G°$) was determined using reference data and/or calculations using the Karapetyants' method described above. Then, the obtained value was divided by the total number of atoms in the formula unit of the mineral (e.g., for Cu_2S, one needs to divide by 3), as a result of which we calculated the average energy of formation per mole of atoms included in the gross formula of the mineral.

2. 4. Statistical Analysis and Physicochemical Interpretation

Based on the experimental data, we determined two key kinetic parameters: the apparent dissolution rate constant, k and the specific reaction rate, W. Statistical analysis was performed to evaluate the relationships between thermodynamic and kinetic characteristics.[13,14] First, a pairwise correlation analysis was performed and the determination coefficients R/R^2 were calculated. Then, linear regression analysis, analogous to the Brønsted equation was performed. We assessed the reliability of the resulting regression models using t-test and F-test, and the mean approximation error. The obtained regression coefficients were interpreted within the framework of physical chemistry, including analogies with the Brønsted and Hammett equations.[14] Overall, this approach provides a deeper understanding of the reactivity of minerals and oxidizing agents and contributes to the development of generalized solubility models for natural minerals.

3. Experimental

Monominerals from the Maykain, Akchatau, and Zhezkazgan deposits in Kazakhstan were used as research objects in the study. The samples were carefully selected under a microscope and tested for purity using chemical, spectral, and X-ray phase analysis. The experiments were carried out using a fraction (74–104 μm) obtained after grinding in an agate mortar and subsequent sieve analysis. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method[15,16] with nitrogen purge. The mineral samples were placed in a hermetically sealed reaction cell (150 mL) with a solution of a dissolving oxidizer at a temperature of (25 ± 0.1)°C. The mixture was stirred at a frequency of 140–150 oscillations per minute for specified time intervals. After the reaction was complete, the solution was filtered, the precipitate was washed with a solution of the original composition 5–6 times. The content of metal transferred from the solid phase to the

solution was determined by the atomic absorption spectroscopy (AAS) method. A 0.05 M iron (III) chloride in 1 M HCl and 0.01 M sodium nitrite in 0.05 M HCl were used as dissolving oxidizing reagents. The acquisition of experimental data involved several stages.

First, the concentration of copper (II) ions was determined by molecular absorption spectrophotometry with a Shimadzu UV-1800 UV-Vis spectrophotometer. Measurements were carried out in quartz cuvettes with an optical path thickness of 1 cm at a wavelength corresponding to the maximum absorption of the complex. The concentration was calculated using the following equation:

$$C_M = \frac{A}{\varepsilon \cdot l} \quad (8)$$

where C_M is the copper (II) concentration, M; A is the optical density; ε is the molar absorption coefficient, l mol^{-1} cm^{-1}; l is the length of the cuvette, cm (in this case l = 1 cm).

The C_M = f(t) dependencies were plotted to determine the linear section of the initial dissolution stage. The kinetic curve looked like a typical saturation curve with a rectilinear initial section.

Then, the specific dissolution rate was determined as:

$$W = \frac{\Delta C_M}{\Delta t \cdot S_0} \quad (9)$$

where C_M is the change in metal concentration in the solution, M; Δt is the time interval, s; is the specific surface area of the mineral (according to BET), cm^2; W is the specific dissolution rate, mol/(s·cm^2).

The order of a reaction n was determined as the slope of the pair regression equation (7).

After determining the reaction order n, the values of the apparent rate constant were calculated according to the formula:

$$k = \frac{C_M \cdot \sigma}{S_0 \cdot C^n \cdot t} \quad (10)$$

Where C_M is metal concentration, M; C is the initial concentration of the oxidizing agent, M; t is the dissolution time, s; σ is the stoichiometric coefficient; k is the apparent dissolution rate constant, 1/(s cm^2) at n = 1.

Experimental conditions for both series were as follows. Temperature: T = 298 K; particle size: 74–104 μm; number of experiments: n = 6; reaction order: n ~ 1. Results were evaluated at a 95% confidence level.

4. Results and Discussion

Tables 1 and 2 present the results of the measurements described above, including the values of the thermodynamic parameters.

Table 1. Kinetic parameters of the interaction of copper sulfides with 0.05 M iron(III) chloride in 1 M hydrochloric acid medium; reduced values of the Gibbs energy of oxidation of copper sulfides – $\Delta_r G^0/\sigma$ and Gibbs average atomic energy of copper sulfide formation - $\Delta_f G^0/n$

Mineral	Formula	$-\Delta_f G^0/n$, kJ/(mol·atom)	Rate constant k, s^{-1} t = 120s	Specific rate W, mol/(sm^2 s) t = 120–240s	$-\Delta_r G^0/\sigma$, kJ/mol; σ –consumption of iron (III) chloride for 1 mole of mineral
Chalcocite (orthorhombic)	Cu_2S-o	26.4	$1.06 \cdot 10^{-7}$	$1.42 \cdot 10^{-9}$	53.2
Chalcocite (hexagonal)	Cu_2S-h	28.7	$0.78 \cdot 10^{-7}$	$1.37 \cdot 10^{-9}$	34.9
Bornite (I)	Cu_5FeS_4	32.2	$1.56 \cdot 10^{-8}$	$0.57 \cdot 10^{-10}$	30.3
Bornite (II)	Cu_3FeS_3	33.7	$1.18 \cdot 10^{-8}$	$0.23 \cdot 10^{-10}$	27.6
Covellite	CuS	38.6	$3.28 \cdot 10^{-9}$	$0.19 \cdot 10^{-11}$	16.7
Cubanite	$CuFe_2S_3$	43.6	$0.72 \cdot 10^{-10}$	$0.13 \cdot 10^{-12}$	4.8
Chalcopyrite	$CuFeS_2$	44.7	$0.65 \cdot 10^{-12}$	$0.09 \cdot 10^{-12}$	3.6

Table 2. Kinetic parameters of the interaction of copper sulfides with 0.01 M sodium nitrite in 0.05 M hydrochloric acid medium; reduced values of the Gibbs energy of oxidation of copper sulfides $-\Delta_r G^0/\sigma$ and the average Gibbs atomic energy of the formation of copper sulfides $-\Delta_f G^0/n$

Mineral	Formula	$-\Delta_f G^0/n$, kJ/(mol atom)	Rate constant k, s^{-1} t = 120 s	Specific rate W, mol/(sm^2 s)	$-\Delta_r G^0/\sigma$, kJ/mol; σ –consumption of oxidant as for 1 mole of mineral
Chalcocite (orthorhombic)	Cu_2S-o	26.4	$3.29 \cdot 10^{-7}$	$8.50 \cdot 10^{-10}$	87.6
Chalcocite (hexagonal)	Cu_2S-h	28.7	$2.56 \cdot 10^{-7}$	$5.90 \cdot 10^{-10}$	53.2
Bornite (I)	Cu_5FeS_4	32.2	$2.12 \cdot 10^{-8}$	$5.40 \cdot 10^{-11}$	49.8
Bornite (II)	Cu_3FeS_3	33.7	$1.64 \cdot 10^{-8}$	$3.47 \cdot 10^{-11}$	27.4
Covellite	CuS	38.6	$2.51 \cdot 10^{-9}$	$4.70 \cdot 10^{-12}$	18.8
Cubanite	$CuFe_2S_3$	43.6	$2.39 \cdot 10^{-10}$	$5.66 \cdot 10^{-13}$	7.8
Chalcopyrite	$CuFeS_2$	44.7	$1.44 \cdot 10^{-10}$	$3.32 \cdot 10^{-13}$	5.8
Galena	PbS	49.4	$0.50 \cdot 10^{-10}$	$1.00 \cdot 10^{-13}$	2.9

Figures 1–4 demonstrate the experimental dependences of the logarithm of the rate constant ln*k* and the logarithm of the dissolution rate ln*W* on two different thermodynamic characteristics: normalized Gibbs energy of the chemical reaction and average atomic Gibbs energy of mineral formation. Each graph shows the experimental data points and the corresponding regression lines. These graphs highlight an important conceptual feature. The normalized Gibbs energy of a chemical reaction, $\Delta_r G^0/\sigma$, reflects the thermodynamic driving force of dissolution, including the contribution of the final reaction products. It is directly related to the direction and energy potential of the chemical transformation. In contrast, the average atomic Gibbs energy of mineral formation, $\Delta_f G^0/n$, describes the internal thermodynamic stability of the initial solid phase and is determined essentially by the depth of the potential well of the crystal structure.

Hence, the opposite direction of trends is observed. When using $\Delta_r G^0/\sigma$, an increase in the driving force (i.e. a decrease in the value of $\Delta_r G^0/\sigma$) corresponds to an increase in the logarithms of the kinetic parameters ln*k* and ln*W*, which is consistent with the provisions of the transition state theory. When using $\Delta_f G^0/n$, on the contrary, more thermodynamically stable (energetically more favorable) minerals dissolve more slowly, which is also justified from the point of view of the equilibrium between the crystal and the solution.

Four regression equations were evaluated to examine the correlation between kinetic parameters (ln*k* and ln*W*) and two normalized thermodynamic quantities: the Gibbs energy of the chemical reaction ($\Delta_r G^0/\sigma$) and the average atomic Gibbs formation energy of the mineral ($\Delta_f G^0/n$):

$$ln\ k = a(-\Delta_r G^0/\sigma) + b \quad (11)$$

$$ln\ W = a(-\Delta_r G^0/\sigma) + b \quad (12)$$

$$ln\ k = a(\Delta_f G^0/n) + b \quad (13)$$

$$ln\ W = a(\Delta_f G^0/n) + b \quad (14)$$

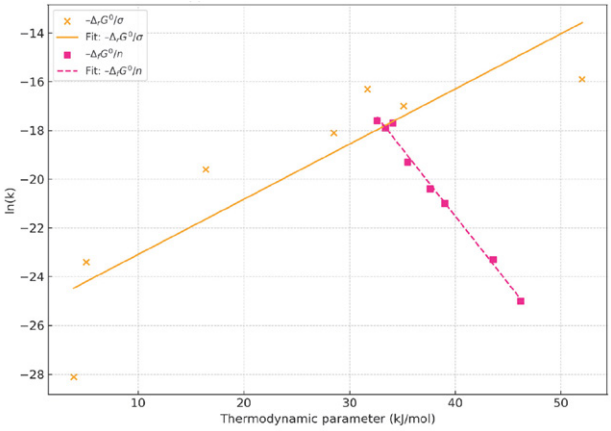

Figure 1. Correlation between ln*k* and thermodynamic parameters for copper sulfide dissolution in 0.05M $FeCl_3$ in 1M HCl

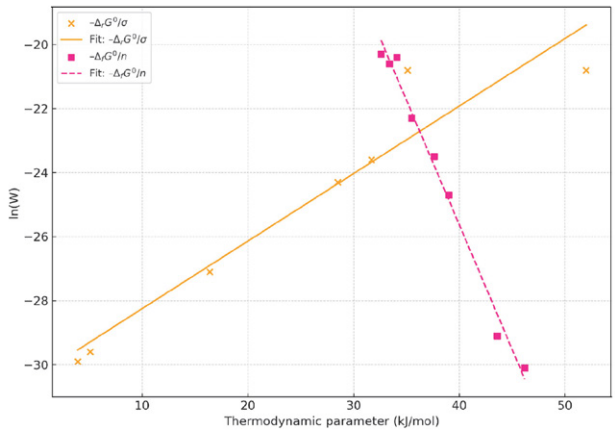

Figure 2. Correlation between ln*W* and thermodynamic parameters for copper sulfide dissolution in 0.05M $FeCl_3$ in 1M HCl

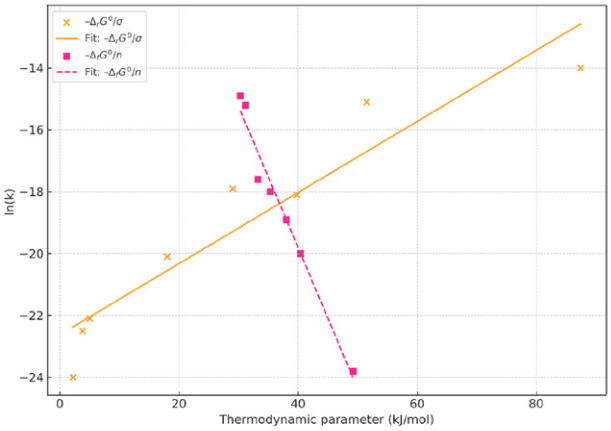

Figure 3. Correlation between ln*k* and thermodynamic parameters for copper sulfide dissolution in 0.01M $NaNO_2$ in 0.05M HCl

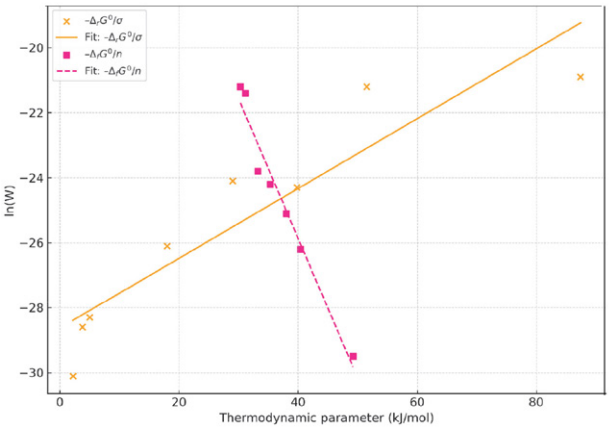

Figure 4. Correlation between ln*W* and thermodynamic parameters for copper sulfide dissolution in 0.01M $NaNO_2$ in 0.05M HCl

It should be emphasized that the regression coefficients a and b in Equations (11)– (14) are determined independently for each correlation. Therefore, lnk and lnW are not mathematically identical, even though the functional form of the equations is the same. Each pair of

coefficients reflects the specific dependence of the chosen kinetic parameter on the corresponding thermodynamic descriptor.

The statistical estimates of the regression quality are summarized in Tables S1–S4 presented in Appendix 1. Each equation was tested using two datasets: calculated values of ln*k* and ln*W* for the oxidation of copper sulfides with either 0.01 M $NaNO_2$ or 0.05 M $FeCl_3$ in acidic medium. The coefficient of determination (R^2) for all cases exceeded 0.90, confirming a strong linear correlation. The regression with the highest R^2 value (0.94) was observed for ln*W* versus $\Delta_f G^0/n$ in the $NaNO_2$ system. This suggests that the specific dissolution rate *W* is more sensitive to the thermodynamic stability of the mineral than the rate constant *k*, which additionally depends on geometric and surface parameters. The observed correlation between ln*W* and $\Delta_f G^0/n$ supports the assumption that mineral dissolution, like homogeneous acid–base proton transfer, follows a linear free energy relationship. This supports the theoretical foundation for using $\Delta_f G^0/n$ as a descriptor of mineral reactivity in oxidative leaching.

The use of the average atomic Gibbs formation energy $\Delta_f G^0/n$ instead of $\Delta_r G^0/\sigma$ allowed a broader unification of kinetic and thermodynamic data. $\Delta_f G^0/n$ is a structural and energetic characteristic of the solid phase, and it is independent of the stoichiometry of the chemical reaction, which can vary depending on the oxidant and pH. This makes $\Delta_f G^0/n$ a more universal descriptor for comparing dissolution kinetics across a wide range of minerals and reagents.

Among the four regression equations examined, Equations (13) and (14) present practical interest, with Equation (14) possessing a theoretical value as well.[17,18] Therefore, it is important to provide the physicochemical interpretation of the regression coefficients in Equation (14). The slope *a* could be related to the reaction constant ρ in the well-known Hammett equation:

$$log\ (k/k_0)\ = \rho \cdot \sigma \qquad (15)$$

In this analogy, the role of the reaction rate constant *k* is played by the specific dissolution rate *W*, and the factor $\Delta_f G^0/n$, the average atomic Gibbs formation energy, serves as a thermodynamic analog of the substituent constant σ, reflecting structural or energetic effects within the solid phase. If we compare dissolution rates of two minerals, we can rewrite Equation (4) in differential form:

$$ln\ (W/W_0)\ = a \cdot \left[\left(\Delta_f G^0/n\right) - \left(\Delta_f G^0/n\right)_0\right] \qquad (16)$$

This relationship fits the form of a Hammett-type correlation, where *a* functions as a measure of the reagent's selectivity. The logarithmic difference in dissolution rates is directly proportional to the difference in thermodynamic stabilities of the solid phases. Since $\Delta_f G^0/n$ has units of kJ/(mol atom), the slope *a* must have units of mol atom/kJ to preserve the dimensionlessness of the left-hand side.

Equation (16) can therefore be interpreted as a linear free energy relationship (LFER), where the slope *a* quantifies the sensitivity of dissolution kinetics to changes in the thermodynamic stability of the mineral. This reinforces the interpretation of *a* as a selectivity coefficient and of *b* as an indicator of the intrinsic aggressiveness of the reagent.

$$\gamma = W/W_0 \qquad (17)$$

Thus, in terms of both Equation (16) and this definition, the coefficient *a* can be seen as a generalization of selectivity. While γ depends on a specific mineral pair, *a* reflects a broader property of the reagent across a series of solids.

Furthermore, since the Gibbs energy of formation $\Delta_f G^0$ for elements in their standard states is zero, the intercept *b* acquires a clear physical meaning. The intercept could be interpreted as the logarithm of the dissolution rate of pure metallic copper under identical experimental conditions in the studies of the dissolution of copper-containing minerals. While *a* characterizes selective reactivity, *b* corresponds to nonselective, or background, aggressiveness, *i.e.* the ability to extract copper ions regardless of the mineral structure. These two parameters, *a* and *b*, are conceptually complementary and inversely related, consistent with the Bell–Evans–Polanyi (BEP) principle.[19] Thus, they can be viewed as the two dimensions of reagent reactivity – selectivity and aggressiveness. Figure 5 graphically illustrates this relationship for two oxidizing systems: $FeCl_3$ and $NaNO_2$.

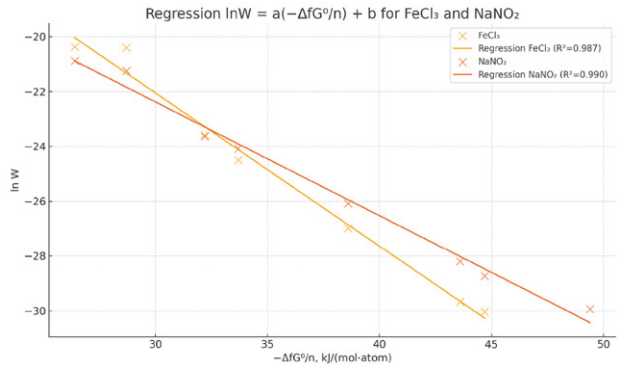

Figure 5. Dependence of the logarithm of the specific dissolution rate (ln*W*) of copper sulfide minerals on the average atomic Gibbs energy of mineral formation $\Delta_f G^0/n$ for two oxidants: $FeCl_3$ and $NaNO_2$.

The regression lines demonstrate that the logarithm of the dissolution rate decreases linearly with increasing thermodynamic stability (more negative $-\Delta_f G^0/n$), in line with the BEP principle. The steeper slope for $FeCl_3$ reflects its higher selectivity, while the higher intercept for $NaNO_2$ reflects its greater aggressiveness. This inverse relationship provides a clear manifestation of the dual nature of reagent reactivity in heterogeneous mineral dissolution. However,

further experimental and theoretical studies are required to refine these concepts.

4. Conclusion

This study established a strong linear relationship between thermodynamic descriptors and kinetic parameters of sulfide mineral dissolution. Statistical analysis confirmed the significance of the identified regression models, indicating the reliability and reproducibility of the observed correlations. The regression coefficients were interpreted as indicators of reagent selectivity (slope *a*) and aggressiveness (intercept *b*), providing a conceptual framework for characterizing dissolution processes. These findings validate the applicability of the Bell–Evans–Polanyi principle to heterogeneous mineral dissolution and support the use of $\Delta_f G^0/n$ as a practical predictor of reactivity. The proposed approach can be applied in the design of efficient leaching technologies in hydrometallurgy and in the further development of the general theory of chemical reactivity of compounds.

Acknowledgements

The authors are grateful to Gaukhar Baltabayeva for proofreading the final version of the manuscript. This work is dedicated to the memory of our supervisor, Khabibulla Ospanov, whose insight and encouragement were instrumental in the development of this research at its initial stages. All remaining errors are the responsibility of the authors.

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Povzetek

Študija preučuje kvantitativni odnos med kinetiko in termodinamiko raztapljanja mineralov v heterogenih reakcijah, s posebnim poudarkom na slabo topnih mineralih. Na podlagi zgodovinskega razvoja kemijske kinetike in termodinamike smo predlagali empirične enačbe, ki opisujejo eksperimentalne podatke in omogočajo napovedno modeliranje procesov raztapljanja. Ocenili smo dva deskriptorja: normalizirano prosto (Gibbsovo) energijo oksidacije ($\Delta_r G^0/\sigma$) in povprečno atomsko Gibbsovo energijo tvorbe minerala ($\Delta_f G^0/n$). Eksperimentalno smo določili konstanto hitrosti (k) in specifično hitrost raztapljanja (W) pod strogo nadzorovanimi pogoji. Razvili smo modele linearne regresije in interpretirali koeficiente regresije v smislu selektivnosti in agresivnosti reagentov, skladno s principom Bell–Evans–Polanyi. Rezultati kažejo, da $\Delta_f G^0/n$ zanesljivo napoveduje reaktivnost mineralov in ponuja termodinamično osnovo za racionalno izbiro izločilnih reagentov.