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Influence of Dispersity on the Thermodynamics of Chemical Reactions of Nanominerals

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According to the definition given in [1], specific groups of minerals (clays, graphites, and others) can be assigned to the class of so-called nanocrystal materials (NM), which are interesting in nanotechnologies. The main peculiarity of NM is the notable influence of the size of particles on the properties of nanocrystals (the so-called size effect). Despite the long-term history of the size effect, some of its aspects, in particular, the role of dispersity in the thermodynamics of chemical reactions, are poorly developed [2]. This problem will be considered in our paper.

We shall consider a natural NM (for example, clay mineral) as an ensemble of independent nanoparticles with one interface surface (interphase surface). According to Gibbs, the surface is described by the same thermodynamic functions as the volume phases. For example, according to Gibbs, the isobaric–isothermal potential G for nanocrystalline state of matter is equal to

$$G = G_\infty + \sigma A, \tag{1}$$

where, G_∞ is the free Gibbs energy of a mineral in the macrocrystalline state, A is the area of the NM surface (m^2/mol), and σ is the surface energy of nanoparticle (J/m^2).

Let a chemical reaction occur in the system

$$\mathrm{A_{sm}} + \nu_\mathrm{B}\mathrm{B_{gas(solution)}} = \nu_\mathrm{C}\mathrm{C_{sm}} + \nu_\mathrm{D}\mathrm{D_{gas(solution)}}. \tag{2}$$

The stoichiometric coefficient is equal to $\nu_\mathrm{A} = 1$; i.e., all calculations are related to a mole of the initial substance.

The assumption that the transformation process in a system can be described by one chemical reaction is equivalent to the assumption that this process depends on one independent variable. The number of moles of any reaction component can be selected as such a variable, but it is more convenient to introduce a new variable η, which is known as the reaction coordinate, i.e., the degree of transformation. Henceforth, we shall designate η as the intensity of the transformation. According to the definition, $\eta = \frac{n_{0i} - n_i}{\nu_i}$. A more convenient concept of the relative degree of transformation is introduced in chemical kinetics [3]: $\alpha = \frac{\eta}{n_{0i}}$, where α is a dimensionless variable and $0 \le \alpha \le 1$.

If we assume that all components are mutually insoluble, the reaction in the system should go up to the end ($\alpha = 1$), unless one of the components is exhausted. Under this assumption, the isobaric–isothermal potential of reaction ΔG_R is determined as

$$\Delta G_R = \sum_{i=1}^{n} G_i \nu_i, \tag{3}$$

where $\nu_i < 0$ for reagents and $\nu_i > 0$ for the reaction products; G_i is the thermodynamic potential of component i.

Let us consider individual types of transformations described by Eq. (2).

Phase transitions ($\nu_\mathrm{B} = \nu_\mathrm{D} = 0$, $\nu_\mathrm{C} = 1$). With account for (3) and (1), we can write the following for phase transitions (polymorphic transformations, melting, and so on) in NM:

$$\Delta G_R = G_\mathrm{C} - G_\mathrm{A} = (G_\infty)_\mathrm{C} - (G_\infty)_\mathrm{A} + \sigma_\mathrm{C} A_\mathrm{C} - \sigma_\mathrm{A} A_\mathrm{A}. \tag{4}$$

In the equilibrium state, we have $\Delta G_R = 0$. Taking into account equality $G = H - TS$, the formula for the specific area of the surface $A = \Gamma/\rho r$, and constant mass, we get (for spherical particles)

$$Q_\infty \frac{\Delta T}{(T_0)_\infty} = \frac{3}{\rho_\mathrm{A} r}\left(\sigma_\mathrm{A} - \sigma_\mathrm{C}\left(\frac{\rho_\mathrm{C}}{\rho_\mathrm{A}}\right)^{2/3}\right), \tag{5}$$

where $Q_\infty = (H_\infty)_\mathrm{C} - (H_\infty)_\mathrm{A}$ is the heat of phase transition related to the macrocrystalline state, $\Delta T = (T_0)_\infty - T_0$ is temperature difference between phase transitions for

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the microcrystalline and nanodispersed state of the substance, Γ is the coefficient of the form (for spherical particles, $\Gamma = 3$), ρ is the mole density of nanoparticles, and r is the characteristic size.

Equation (5), which was first derived by Hill [4], can be considered a generalized analog of the known Gibbs–Thomson formula. Other modifications of Eq. (5) are known in the literature [5].

The vast experimental experience accumulated in recent years has revealed the strong influence of dispersity on the melting temperature of some metals [1] and the temperature of polymorphic transitions in minerals [6]. For example, the temperature of gold melting decreases from 1064 to 427°C when the size of particles decreases to 4 nm [7]. However, examples of the opposite influence are also known when the melting temperature increases with increasing dispersity [8]. According to Eq. (5), this is possible at $\sigma_A < \sigma_C\left(\frac{\rho_C}{\rho_A}\right)^{2/3}$.

Heterogeneous endothermic reactions ($\nu_B = 0$). This class includes, for example, reactions of dissociation or dehydration of minerals. The isobaric–isothermal potential of such a reaction for a macrocrystal system is written as

$$(\Delta G_R)_\infty = \nu_D G_D + \nu_C G_C - G_A. \tag{6}$$

Taking (1) into account, we get for a nanodispersed system

$$\Delta G_R = (\Delta G_R)_\infty + \nu_C \sigma_C A_C - \sigma_A A_A, \tag{7}$$

where $((\Delta G_R)_\infty)$ is the reaction potential for the macrocrystal system specified by Eq. (6).

On the other hand, the isotherm equation is true for an endothermic reaction (at not very high temperatures and pressures):

$$RT[\ln(P^{\nu_D}) - \ln(K_E)]$$
$$= RT[\ln(P^{\nu_D})_\infty - \ln(K_E)_\infty] + \nu_C\sigma_C A_C - \sigma_A A_A, \tag{8}$$

where P is the initial pressure in a gas system and K_E is the equilibrium constant.

If we assume that the initial pressures in both systems are equal to $P = P_\infty$, which can be easily obtained in an experiment, we get a fundamental equation for the dispersity of matter and the equilibrium constant

$$K_E = K_{E\infty}\exp\frac{\sigma_A A_A - \nu_C\sigma_C A_C}{RT}. \tag{9}$$

Equation (9) can be a basis for constructing equilibrium diagrams of the P–T–r type, which reflect a displacement of the equilibrium caused by variation in dispersity, for example, of clayey material.

Let us consider some consequences of Eq. (9).

1. Let us assume that $\sigma_A A_A - \nu_C\sigma_C A_C > 0$. In this case, the equilibrium constant would increase with increasing dispersity of the initial substance. On the other hand, according to Le Chatelier's principle, the equilibrium constant for endothermic reactions also increases with increasing temperature. We come to an interesting conclusion: an increase in the dispersity of a material can displace the equilibrium of an endothermic reaction in the same direction as the temperature increase.

2. After taking the logarithm and differentiation (7) with respect to T and neglecting the dependence $\sigma = f(T)$ for a small temperature interval, we get the following relation:

$$Q \approx Q_\infty - (\sigma_A A_A - \nu_C\sigma_C A_C), \tag{10}$$

where Q and Q_∞ are the thermal effects of reactions for nanodispersed and macrocrystalline states of the matter.

In the endothermic reaction, $Q > 0$ (according to the thermodynamic system of signs). Taking into account that usually $\sigma_A > \sigma_C$ (the surface energy of the low-temperature phase is greater than that of the high-temperature phase) and assuming that $(\sigma_A A_A - \nu_C\sigma_C A_C) > 0$, we come to the conclusion that the thermal effect of the endothermic reaction can decrease with increasing dispersity.

For example, a decrease in the heat of the endothermic reaction of calcite dissociation from 41.1 to 21.9 kcal/mol was observed when calcite was ground for 140 min [9].

3. In the case of equilibrium, $\Delta G_R = 0$. Taking into account that $A = \Gamma M/\rho r$, we get an equation similar to (5):

$$Q_\infty\frac{\Delta T}{(T_0)_\infty} = \frac{\Gamma M_A}{\rho_A r_A}\left[\sigma_A - \sigma_C\left(\frac{\nu_C M_C}{M_A}\frac{\rho_A}{\rho_C}\right)^{2/3}\right], \tag{11}$$

where M_i are the molecular masses of minerals A and C and ρ_i are their densities (g/m^3). $\Delta T = (T_0)_\infty - T_0$ is the difference between equilibrium temperatures for the macrocrystalline and nanodispersed states of the matter. Complex $\frac{\nu_C M_C}{M_A}$ is known as the Pilling–Bedward coefficient in the literature [10]. We assume as before $\sigma_A > \sigma_B$ and $\left[\sigma_A - \sigma_C\left(\frac{\nu_C M_C}{M_A}\frac{\rho_A}{\rho_A}\right)^{2/3}\right] > 0$. Then, we come to a conclusion: the temperature of the process in endothermic reactions (as well as in phase transitions) can displace to lower temperatures when dispersity increases.

For large crystal kaolinite reported in [11], the temperature peak in the DTA curves appeared equal to 700 instead of 560°C, which is typical for usual dispersed kaolinite.

Heterogeneous exothermic reactions ($\nu_D = 0$). In exothermic reactions $Q < 0$, therefore, the influence of dispersity upon such reactions can be the opposite.

According to Eq. (10), the heat of an exothermic reaction can increase with increasing dispersity. Experimental data confirm this conclusion: when the size of particles decreased from 95 to 9.5 nm, the thermal effect of the reaction of synthetic magnetite oxidation increased (by the absolute value) from 61 to 77.3 kJ/mole [12].

All previous formulas were based on the assumption that the reaction goes to the end; i.e., $\alpha = 1$. However, in many cases, the reaction can slow down owing to some diffuse kinetic causes and $\alpha \neq 1$. For example, oxidation of Al produces a film of Al_2O_3, which slows down the metal oxidation. When $\alpha \neq 1$, the model considered here becomes more complex. A nanoparticle becomes multilayered as a result of the reaction. We assume that as a result of the reaction, the initial nanoparticle (mineral A) is transformed into a two-layer nanoparticle, in which the core is represented by the initial material A and the surface layer is represented by mineral C formed as a result of the reaction. An additional interface appears and separates mineral A from mineral C. Let the specific area of the new surface be A_{AC} and the surface energy be σ_{AC}. It is possible to show that in this case Eq. (7) is transformed to the following:

$$\Delta G_R = \alpha(\Delta G_R)_\infty + \alpha(\nu_C\sigma_C A_C + \sigma_{AC}A_{AC} - \sigma_A A_A). \tag{12}$$

Areas of surfaces A_C, A_{AC}, and A_A, in turn, are interrelated by means of the relative intensity of transformation α. For example, the following relations exist for spherical particles

$$A_A = \frac{3M_A}{\rho_A r_A}, \quad A_C = A_A\left(1 - \alpha\left(1 - \frac{\nu_C M_C}{M_A}\frac{\rho_A}{\rho_C}\right)\right)^{2/3}, \quad A_{AC} = A_A(1-\alpha)^{2/3}. \tag{13}$$

Substituting (13) into (12), we obtain ($\Gamma = 3$ for spherical particles):

$$\Delta G_R = \alpha(\Delta G_R)_\infty + \alpha\frac{3M_A}{\rho_A r_A}\left(\nu_C\sigma_C\left(1 - \alpha\left(1 - \frac{K\rho_A}{\rho_C}\right)\right)^{2/3} + \sigma_{AC}(1-\alpha)^{2/3} - \sigma_A\right), \tag{14}$$

where $K = \frac{\nu_C M_C}{M_A}$.

We obtained a general formula for the thermodynamic potential of chemical reaction (2) in a nanodispersed system. At $\alpha = 1$, we get Eq. (7). At $\alpha = 1$ and $K = 1$, we get Hill's formula (5).

The application of the generalized thermodynamic potential provides the following facilities: (1) it easily explains some facts, which go beyond classical thermodynamics, for example, the appearance of high-temperature phases in the low-temperature range (synthesis of high-temperature tetragonal ZrO_2 in the stability range of low-temperature monoclinic $ZrO_2$and so on); (2) it theoretically forecasts a method to synthesize some compounds that can be interesting for nanotechnology; and (3) it develops more realistic models of the initial stages of the mineral-forming process.

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