

## Thermodynamic analysis of nanocrystal formation in the $\text{TiO}_2\text{--H}_2\text{O}$ (NaOH, HCl) system

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**ABSTRACT** A thermodynamic analysis of the crystallization of titanium dioxide in the anatase, brookite, and rutile modifications from aqueous salt solutions was performed, taking into account the influence of medium pH, temperature, reagent concentration, and the specific surface energy ( $\sigma$ ) of the phases. It was shown that the choice of the  $\sigma$  value for the thermodynamic analysis of anatase crystallization is decisive: at  $\sigma_A = 0.3 \text{ J/m}^2$ , the minimum particle size is determined by the crystallochemical criterion ( $l_{\min} \sim 5\text{--}7 \text{ nm}$ ), while at  $\sigma_A = 1.3 \text{ J/m}^2$ , it is determined by thermodynamic criteria ( $d_{\text{crit}} \sim 8 \text{ nm}$ ,  $d_{\text{eq}} \sim 12 \text{ nm}$ ). Using  $\sigma$  values most closely approximating the conditions of a hydrated  $\text{TiO}_2$  surface ( $\sigma_R = 1.79$ ,  $\sigma_B = 1.0$ ,  $\sigma_A = 1.13 \text{ J/m}^2$ ), the regions of possible crystallization for each modification were determined. Rutile can crystallize in a relatively wide pH range of 0.8–14 (25 °C) and 1.1–10.2 (200 °C), and the minimum particle sizes of rutile under these conditions are determined by thermodynamic criteria –  $d_{\text{crit}}$  and  $d_{\text{eq}}$ . For brookite and anatase in acidic and alkaline conditions (pH  $\sim 1\text{--}3$  and  $9\text{--}14$ ), the minimum particle sizes, as for rutile, are also determined by thermodynamic criteria, whereas in the neutral region, they are determined by the crystallochemical criterion  $l_{\min}$ . Based on the analysis of structural transitions, it was established that anatase can transform into rutile or brookite at particle sizes larger than  $\sim 16 \text{ nm}$ . The calculated size for the brookite  $\rightarrow$  rutile transition is  $\sim 712 \text{ nm}$ .

**KEYWORDS** nanocrystals, titanium oxide, critical nucleus.

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### 1. Introduction

To date, the most studied structural types of titanium dioxide are anatase, brookite, and rutile [1–10]. Research focused on studying the formation processes and structural transformations of  $\text{TiO}_2$  is described in a substantial number of works, some of which are presented here [11–17]. This interest is primarily related to the wide range of applications of titanium oxide in various fields [9, 18, 20–28]. The properties of the resulting  $\text{TiO}_2$  particles and materials based on them are highly sensitive to the choice of the synthesis method [9, 18, 29–31].

Common methods for obtaining specific structural types of oxide nanocrystals include precipitation [32–34], hydrothermal treatment [35–38], sol-gel synthesis [39–41], or their combination at various stages of formation or structural transformations [42–44]. A common feature of these methods is the use of mobile media, particularly aqueous solutions and hydrothermal fluids, to achieve intensive mass transfer of reagents. The sensitive parameters in obtaining nanoparticles by such methods are temperature, pH value, ionic strength of the aqueous salt solution, and component concentrations. All of the above applies fully to the preparation of titanium oxide nanoparticles of various polymorphic modifications as well.

Thermodynamic assessments of the stability of nanoparticles of various structural types of  $\text{TiO}_2$  – anatase, brookite, and rutile – are of interest for the targeted synthesis of  $\text{TiO}_2$ -based nanopowders with specified structures and properties, and can be found, in particular, in works [45, 46]. However, works dedicated to considering the composition of aqueous salt media during the formation of  $\text{TiO}_2$  are absent or have a different focus: [6, 11, 16]. Data on the thermodynamics of formation of  $\text{TiO}_2$  nanoparticles with anatase, brookite, and rutile structures during their crystallization from aqueous salt media at various temperatures and pH values are lacking in the literature. The main problems in such calculations are likely the absence or insufficient accuracy of the necessary thermodynamic data. For example, known databases such as IVTANTHERMO [48], JANAF [49], and HSC 6 [50] lack thermodynamic data for the brookite condensed phase and water-soluble Ti species (with the exception of HSC 6, which contains data for  $\text{Ti}(\text{OH})_4^-(\text{aq})$ ). Numerical values for the enthalpies of the rutile-brookite and anatase-brookite transitions are given in [51]. There are experimental works dedicated to the thermodynamics of  $\text{TiO}_2$  hydrolysis or dissolution processes [52–54]. In the context of studying the thermodynamic feasibility of forming various structural types of  $\text{TiO}_2$ , the estimation of critical and equilibrium nucleus sizes is also of

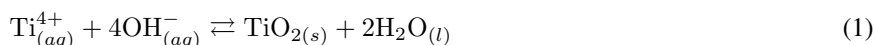
interest. Such estimates are presented in a number of works for crystallization from a melt, for example [55]. In the case of crystallization from aqueous solutions, the analysis of the influence of aqueous salt media on crystallization processes is limited [56], or focused on kinetic aspects of crystallization [56, 57], or does not account for the medium's influence [6, 59]. Furthermore, the majority of works are dedicated to the thermodynamic assessment of size effects and their connection to structural transitions [6, 45, 46]. The main problem in such calculations that account for the liquid phase, besides the lack of thermodynamic data, is the problem of choosing a correct value for the specific surface energy ( $\sigma$ ) for anatase, brookite, and rutile crystallizing under different conditions (particularly from aqueous salt media). There are two main types of approaches to determining specific surface energy: experimental and theoretical. Experimental approaches are typically based on the analysis of thermodynamic data from aggregation, sintering, adsorption processes, and the interpretation of temperature dependencies of changes in specific surface area and particle growth activation energy. These approaches allow only an indirect estimation of the specific surface energy and often yield significantly differing results [6, 45, 51, 60]. Theoretical approaches are based on quantum-mechanical calculation methods and allow for the estimation of specific surface energy values for individual crystallographic planes, taking into account atomic relaxation, as well as possible adsorption of water molecules or hydroxyl groups [6, 61, 62]. However, even in this case, the results of such calculations depend on the chosen interaction parameters, simulation conditions, and the degree to which surface defects are accounted for. Data on specific surface energy in various aqueous salt media are very limited, not to mention the temperature dependence  $\sigma = \sigma(T)$ . It should also be noted that when determining the minimum possible crystal sizes for various  $\text{TiO}_2$  modifications, crystallochemical constraints described in [63] are practically not taken into account. This also limits the reliability of the calculated data obtained regarding the sizes of forming  $\text{TiO}_2$  nanocrystals.

Thus, the uncertainty in selecting the correct specific surface energy value for the anatase, brookite, and rutile structural types remains one of the key factors limiting the reliability and accuracy of thermodynamic calculations for the sizes of critical and equilibrium nuclei and the stability of nano-sized  $\text{TiO}_2$  particles in various aqueous media. Therefore, a thermodynamic analysis of the influence of the pH of the aqueous salt medium, reagent concentration, temperature, specific surface energy value, as well as crystallochemical constraints on crystallite sizes, on the crystallization processes of  $\text{TiO}_2$  solid phases with anatase, brookite, and rutile structural types from aqueous media is of significant interest.

## 2. Calculation

The thermodynamic analysis of  $\text{TiO}_2$  crystallization processes from aqueous salt solutions was carried out with the following assumptions: the aqueous salt solution remains a liquid phase upon heating. The resulting solid particles have an isometric shape, close to spherical, with a size  $d$ . The influence of pressure on the thermodynamic properties of condensed phases was neglected, as pressure within the considered range of its variation has a negligible effect on these properties [48–50].

The following heterogeneous equilibrium is established in the reaction medium:



In an aqueous salt solution, depending on the pH value, the following equilibria of water-soluble Ti(IV) species are established:



To calculate the change in the molar Gibbs energy ( $\Delta_r G_m$ ) of reaction (1), taking into account the influence of particle size ( $d$ ) and the pH of the reaction medium, the following equation was used:

$$\Delta_r G_m(T, \text{pH}, d) = \Delta_r G_m^\circ(T) + RT \ln K + \frac{6\sigma V_m}{d},$$

$$K = \frac{1}{x_{\text{Ti}^{4+}} \cdot a_{\text{Ti}^{4+}} \cdot a_{\text{OH}^-}^4} \quad x_{\text{Ti}^{4+}} = \frac{1}{1 + \sum \beta_i a_{\text{OH}^-}^i},$$

where  $\Delta_r G_m^\circ(T)$  is the change in the standard molar Gibbs energy of reaction (1) (kJ/mol) at temperature  $T(K)$ ;  $R$  is the universal gas constant (kJ/(mol·K));  $K$  is the equilibrium constant of reaction (1);  $a_{\text{Ti}^{4+}}$  is the activity of bound and unbound  $\text{Ti}_{(aq)}^{4+}$  ions;  $a_{\text{OH}^-}$  is the activity of  $\text{OH}_{(aq)}^-$  ions;  $x_{\text{Ti}^{4+}}$  is the mole fraction of unbound water-soluble  $\text{Ti}_{(aq)}^{4+}$  cations;  $\sigma$  is the specific surface energy (kJ/nm<sup>2</sup>);  $V_m$  is the molar volume of  $\text{TiO}_2$  (nm<sup>3</sup>/mol);  $d$  is the particle diameter (nm);  $\beta_i$  is the stability constant of the water-soluble  $i$ -th aquahydroxo complex based on equilibria (2)–(7) in the aqueous salt medium.

Based on homogeneous equilibria in the aqueous medium (2)–(7) and the condition  $\sum_{k=0}^i x_{Ti(OH)_n^{4-n}} = 1$ , the mole fraction of unbound water-soluble  $Ti_{(aq)}^{4+}$  cations was calculated as a function of the pH value in the aqueous salt medium. The ionic strength of the solution was estimated for an aqueous solution with the composition  $TiCl_4$  and  $NaOH$ , assuming that  $C(Ti^{4+})=C(TiCl_4)$  and  $C(OH^-)=C(NaOH)$  at each calculation point. The activity coefficients of the  $Ti^{4+}(aq)$  and  $OH^-(aq)$  ions, required for estimating their activities in the aqueous salt solution, were calculated using the Davies equation [64] for each pH value, total molar concentration of  $Ti^{4+}$  ( $C$ , mol/L), and solution ionic strength. The temperature dependence of activity coefficients in the Davies equation was accounted for using data from [65] at 25 and 200 °C.

The necessary data for calculating the  $\Delta_r G_m^\circ(T)$  values for equilibrium (1) were taken from the JANAF, IVTANTHERMO, and HSC 6 databases. The molar Gibbs energy of formation for the brookite modification was estimated based on the molar enthalpy of the rutile-brookite transformation ( $0.71 \pm 0.38$  kJ/mol) according to data from [51] and the molar entropy of brookite formation at different temperatures [66], using the thermodynamic properties of rutile from the three databases mentioned above. Thus, the molar Gibbs energy of formation of brookite at 25 °C, using the thermodynamic properties of rutile from JANAF, IVTANTHERMO, and HSC 6, is  $-383.90$ ,  $-383.21$ , and  $-384.28$  kJ/mol, respectively. At 200 °C, these values are  $-529.69$ ,  $-529.06$ , and  $-530.11$  kJ/mol.

The values of  $\Delta_f G_m^\circ(Ti(OH)_{n(aq)}^{4-n})$  for  $n = 0-6$ , which are absent in the databases (except for the case  $n = 4$ ), were estimated based on experimental data presented in [52, 54, 67]. Thus, the molar Gibbs energy of formation of the  $Ti_{(aq)}^{4+}$  ion is:  $-350.2$  kJ/mol at 25 °C. An estimate of this value at 200 °C ( $-317$  kJ/mol) was made based on data from [53] and the thermodynamic data for  $Ti(OH)_4(aq)$  specified in the HSC 6 database.

Based on data on the hydrolysis constants of the rutile modification [53] and the molar Gibbs energy of formation of the  $Ti_{(aq)}^{4+}$  ion, the molar Gibbs energies of formation of  $Ti(OH)_{3(aq)}^+$  and  $Ti(OH)_{5(aq)}^-$  at 200 °C were estimated. Based on this, dependencies of the molar Gibbs energy of formation of the  $Ti(OH)_{n(aq)}^{4-n}$  complexes on the number  $n$  (Fig. 1) were constructed for temperatures of 25 °C and 200 °C, and the stability constants (eq. (2)–(6)) at 200 °C were estimated, which had not been explicitly presented in the scientific literature before.

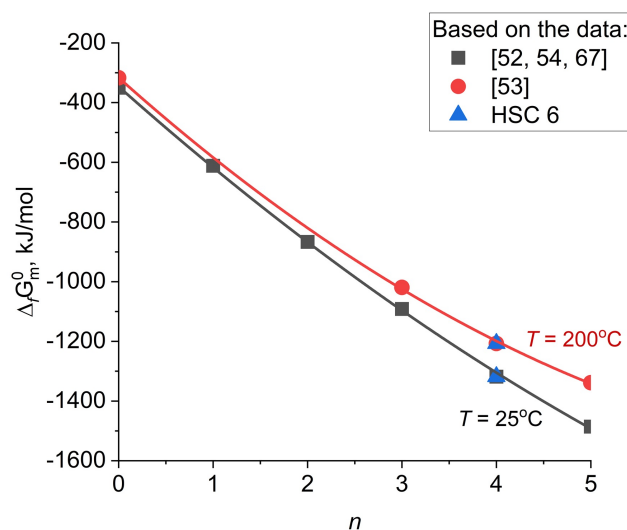


FIG. 1. Dependence of the molar Gibbs energy of formation of water-soluble  $Ti(OH)_{n(aq)}^{4-n}$  species on the number  $n$  at temperatures of 25 and 200 °C

Thus, for all subsequent calculations, the following stability constant ( $\lg \beta$ ) data for mononuclear hydroxo complexes  $Ti(OH)_{n(aq)}^{4-n}$  were used: At a temperature of 25 °C:  $18.51 \pm 0.40$ ,  $34.53 \pm 0.36$ ,  $48.06 \pm 0.41$ ,  $59.09 \pm 0.43$ ,  $61.17 \pm 0.38$ , and  $56.22 \pm 0.51$  for  $n = 1-6$ , respectively. At a temperature of 200 °C:  $14.31 \pm 0.25$ ,  $29.03 \pm 0.32$ ,  $41.95 \pm 0.35$ ,  $50.80 \pm 0.52$ , and  $53.43 \pm 0.45$  for  $n = 1-5$ , respectively.

According to the dependencies of the molar Gibbs energy for reaction (1) on pH, constructed using the three databases, it can be concluded that the resulting values show minor differences (Fig. 2). In this case, the range of values for anatase, according to IVTANTHERMO, almost always lies between the values determined using the JANAF and HSC 6 databases (Fig. 2). Therefore, subsequent calculations were performed using thermodynamic data taken from the IVTANTHERMO database.

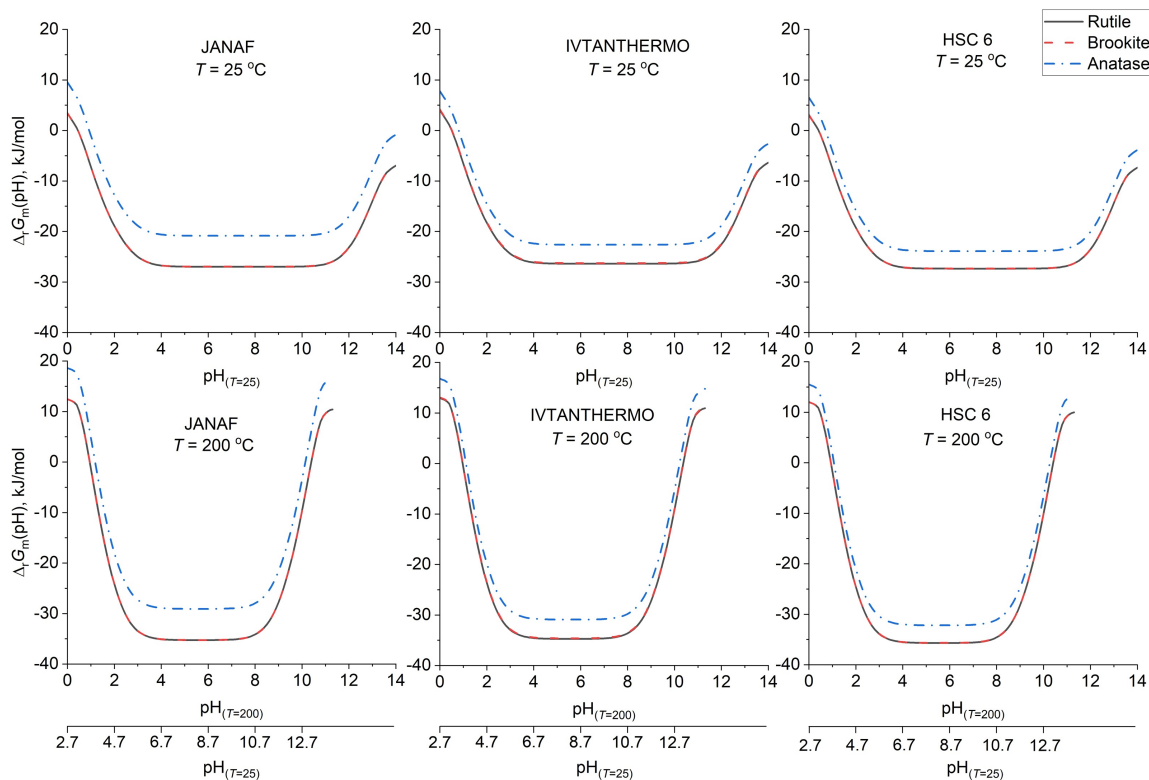


FIG. 2. Dependencies of the change in molar Gibbs energy for equilibrium (1) on pH value ( $T = 25$  and  $200$  °C,  $C = 10^{-3}$  M), plotted using thermodynamic data taken from the JANAF, IVTANTHERMO, and HSC 6 databases for the rutile, brookite, and anatase modifications

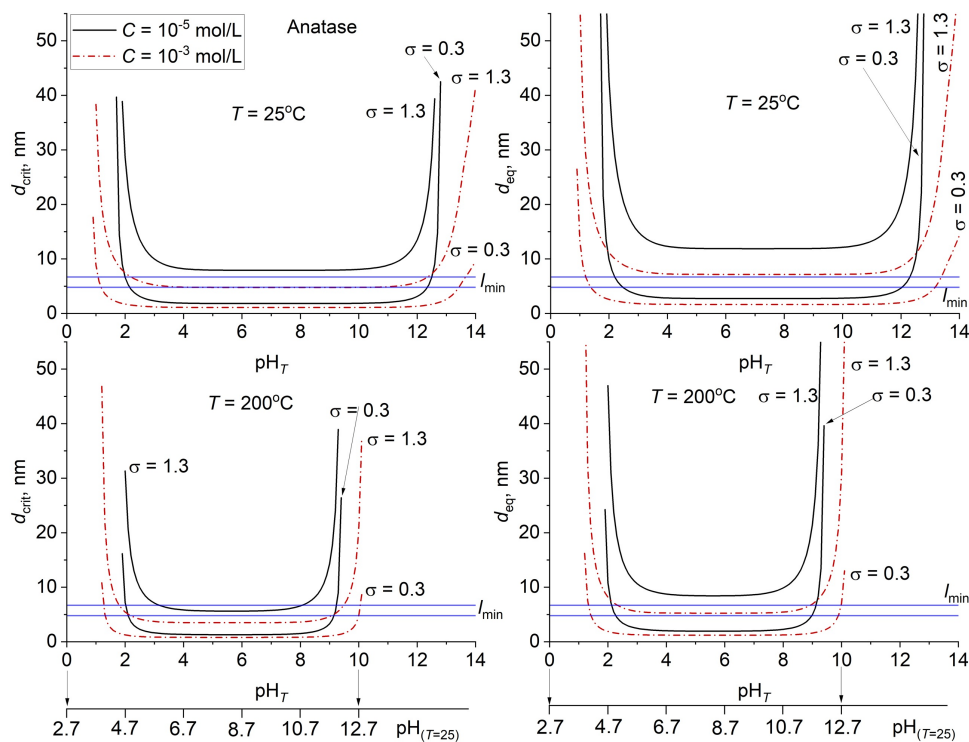


FIG. 3. Dependencies of the critical ( $d_{crit}$ ) and equilibrium ( $d_{eq}$ ) nucleus sizes of the anatase modification of  $\text{TiO}_2$  on the pH of the aqueous salt medium, the value of specific surface energy ( $\sigma$ ,  $\text{J/m}^2$ ), and the concentration of the titanium-containing component ( $C$ ) at  $10^{-5}$  and  $10^{-3}$  mol/L at temperatures of  $25$  and  $200$  °C. The double line indicates the estimated limits of variation for the minimum possible sizes of anatase crystals from a crystallochemical perspective ( $l_{min}$ )

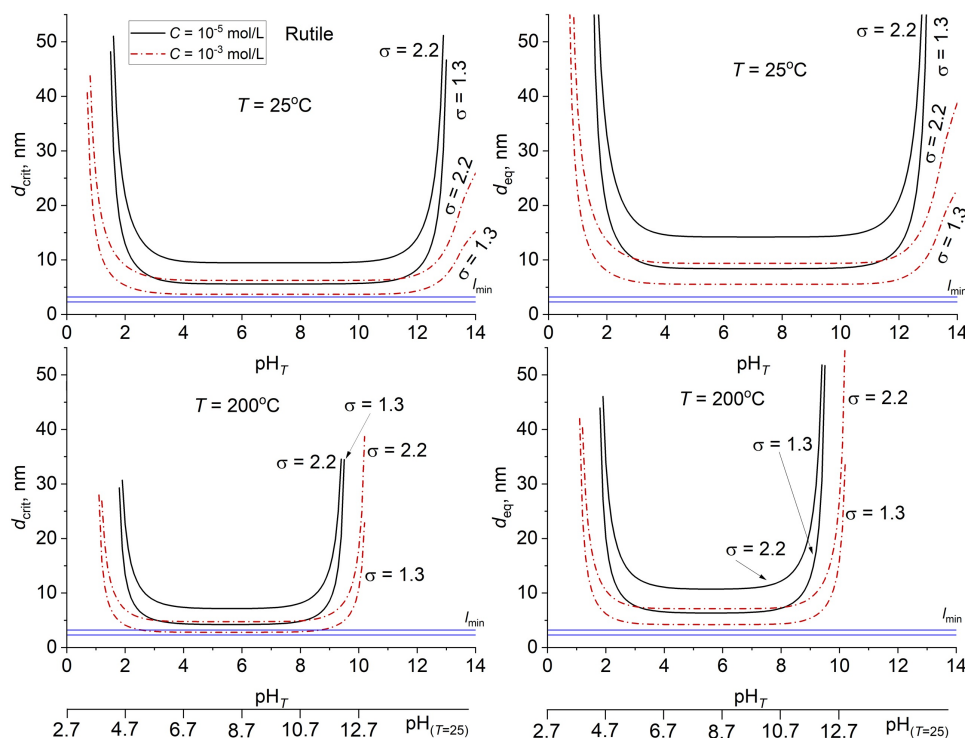


FIG. 4. Dependencies of the critical ( $d_{crit}$ ) and equilibrium ( $d_{eq}$ ) nucleus sizes of the rutile modification of  $\text{TiO}_2$  on the pH of the aqueous salt medium, the specific surface energy value ( $\sigma$ ,  $\text{J/m}^2$ ), and the concentration of the titanium-containing component ( $C$ ) at  $10^{-5}$  and  $10^{-3}$  mol/L at temperatures of 25 and 200 °C. The double line indicates the estimated limits of variation for the minimum possible sizes of anatase crystals from a crystallochemical perspective ( $l_{min}$ )

The dependence of the critical ( $d_{crit}$ ) and equilibrium ( $d_{eq}$ ) nucleus sizes of various polymorphic modifications of  $\text{TiO}_2$  on temperature and pH value was determined based on expressions (8) and (9), respectively:

$$d_{crit}(T, pH) = -\frac{4\sigma V_m}{\Delta_r G_m^\circ(T) + RT \ln K},$$

$$d_{eq}(T, pH) = -\frac{6\sigma V_m}{\Delta_r G_m^\circ(T) + RT \ln K}.$$

An estimation of the minimum possible size of crystalline  $\text{TiO}_2$  particles with different structures, based on crystallochemical concepts, was performed using the empirical expression proposed in the work [63]:

$$l_{min} = \max(a, b, c) \cdot N, [nm] \quad (8)$$

where  $a$ ,  $b$ ,  $c$  are the values of the unit cell parameters (nm);  $N$  is an empirical parameter ( $N \approx 5-7$ ). The values of the unit cell parameters for various polymorphic modifications of  $\text{TiO}_2$  were taken from the work [68,69].

For calculations involving variation of the specific surface energy ( $\sigma$ ,  $\text{J/m}^2$ ), ranges of values obtained experimentally and reported in works [6,45,51,60] for rutile and anatase were used:  $\sigma_R = 1.3-2.2$ ,  $\sigma_A = 0.3-1.3$   $\text{J/m}^2$ . For calculations with a fixed specific surface energy value, the values reported in [6] and calculated using the DFT method, taking into account the influence of the aqueous environment (surface hydration), were used:  $\sigma_R = 1.79$ ,  $\sigma_A = 1.13$   $\text{J/m}^2$ . These values satisfactorily agree with the experimental data from [45] and are apparently the most applicable within the scope of this work. For all calculations involving brookite, the value  $\sigma_B = 1.0$   $\text{J/m}^2$  [51] was used. The influence of temperature on the specific surface energy values was not considered due to limited literature data.

### 3. Result and discussion

Due to the significant spread in data on the specific surface energy of anatase and rutile modifications, it is necessary to examine the influence of this parameter's value on the results of thermodynamic calculations of the critical and equilibrium nucleus sizes of  $\text{TiO}_2$  for these modifications.

As can be concluded from the analysis of the calculation results presented in Fig. 3, the sizes of the critical and equilibrium nuclei of anatase practically do not change during crystallization from aqueous salt media in the pH range of 4–11 (25 °C) and 4–8 (200 °C), but strongly depend on the chosen value of the specific surface energy. Increasing the specific surface energy values from 0.3 to 1.3  $\text{J/m}^2$  when estimating the  $d_{crit}$  of anatase in aqueous salt solutions

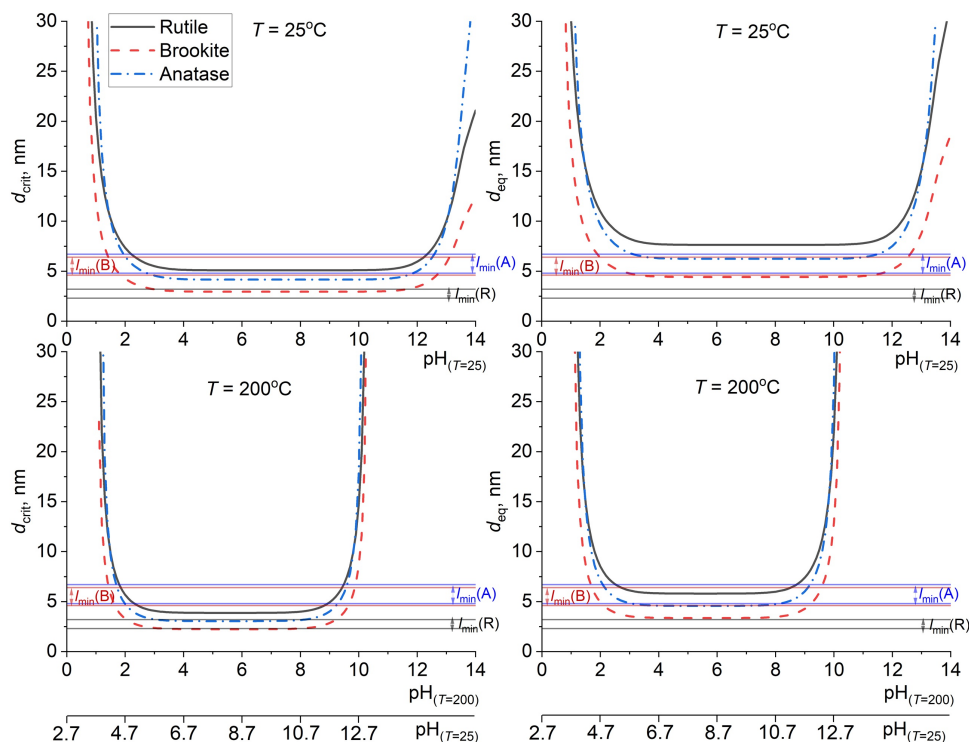


FIG. 5. Dependencies of the critical ( $d_{crit}$ ) and equilibrium ( $d_{eq}$ ) nucleus sizes of various  $\text{TiO}_2$  modifications on the pH of the aqueous salt medium at temperatures of 25 °C and 200 °C and a titanium-containing component concentration ( $C$ ) of  $10^{-3}$  mol/L. The specific surface energy values were taken as follows ( $\text{J/m}^2$ ):  $\sigma_R = 1.79$ ,  $\sigma_A = 1.13$ ,  $\sigma_B = 1.0$ . Double lines indicate the estimated limits of variation for the minimum possible sizes of rutile, anatase, and brookite crystals from a crystallochemical perspective –  $l_{min}(R)$ ,  $l_{min}(A)$ ,  $l_{min}(B)$ , respectively

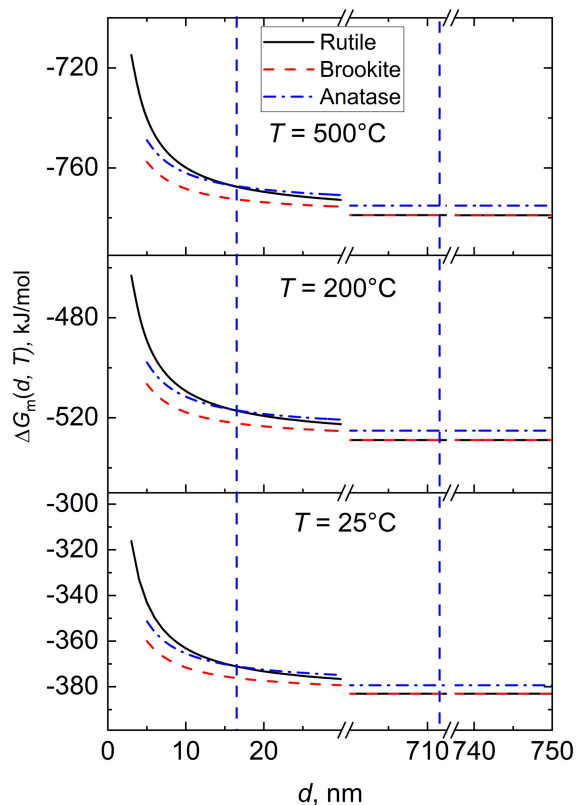


FIG. 6. Dependencies of the molar Gibbs energy of formation of  $\text{TiO}_2$  on particle size at different temperatures



( $C = 10^{-5}$  mol/L) leads to its increase by a factor of four: approximately 2 nm ( $\sigma_A = 0.3$  J/m<sup>2</sup>) and 8 nm ( $\sigma_A = 1.3$  J/m<sup>2</sup>) at 25 °C. At the same time, the minimum size for crystallochemically stable existence ( $l_{min}$ ) [63] of anatase crystals lies in the range of approximately 5–7 nm. This means that when using the value  $\sigma_A = 0.3$  J/m<sup>2</sup> in calculations, the determining criterion for the minimum particle sizes of anatase will be the crystallochemical criterion. In the case where the value  $\sigma_A = 1.3$  J/m<sup>2</sup> is used in calculations, the minimum particle sizes of anatase will be determined by thermodynamic criteria ( $d_{crit} \sim 8$  nm,  $d_{eq} \sim 12$  nm).

Shifting the pH of the aqueous salt solution into more acidic or alkaline regions leads to an increase in the values of  $d_{crit}$  and  $d_{eq}$ . However, the pH ranges for the existence of anatase under such conditions are quite narrow due to the dominance of the particle dissolution process (Fig. 3).

The problem of choosing the specific surface energy value for the rutile modification is not as significant as in the case of anatase. The calculation results indicate that the minimum particle size of rutile, under the considered crystallization conditions, is determined by the thermodynamic criterion, as the minimum possible sizes from a crystallochemical perspective ( $l_{min}$ ) are significantly lower (Fig. 4).

Using the specific surface energy values most closely approximating the case of hydrated TiO<sub>2</sub> surfaces for thermodynamic analysis (Fig. 5), several regions of possible crystallization and relatively stable existence of nanocrystals can be identified. In this case, the main criterion for determining these regions is the comparison of  $d_{crit}$ ,  $d_{eq}$ , and  $l_{min}$  values.

Rutile, as the most thermodynamically stable modification, can crystallize at a temperature of 25 °C in a relatively wide pH range of 0.8–14 of the aqueous salt solution. When the temperature increases to 200 °C, this pH range is: 1.1–10.2.

Brookite is a metastable modification [45], although its molar Gibbs energy of formation is close to that of rutile. An important criterion for determining the boundaries of brookite crystallization is the  $l_{min}$  value, which is significantly higher than the size of the critical nucleus and practically twice the  $l_{min}$  value of rutile (Fig. 5).

Brookite can crystallize at a temperature of 25 °C in acidic and alkaline media within the pH range of approximately 1–2 and 12–14 ( $d_{crit} > l_{min}$ ). When the temperature increases to 200 °C, this pH range becomes approximately 1–2 and 9–10, respectively. This indicates that brookite has a greater tendency to crystallize from acidic and alkaline aqueous salt solutions, according to the calculation results (Fig. 5).

The regions of anatase modification crystallization from an aqueous salt medium can be characterized, according to the calculation results (Fig. 5), as follows: at a temperature of 25 °C within the pH range of 1–3 and 11.5–14; at a temperature of 200 °C within the range of 1.2–2.4 and 8.9–10.1. In general, the crystallization boundaries for anatase are similar to those for brookite in an alkaline medium. In an acidic medium, these boundaries for anatase lie within a wider pH range (1.2–2.4) at 200 °C compared to brookite (pH = 1.1–1.8). This suggests that anatase has a greater tendency to crystallize in an acidic environment than brookite does. However, the minimum sizes from a crystallochemical perspective for anatase and brookite are quite similar (Fig. 5). It is likely that the crystallization of either anatase or brookite under these conditions will be determined to a greater extent by synthesis specifics and kinetic factors.

Following the analysis of TiO<sub>2</sub> crystallization in the rutile, brookite, and anatase structures, determining the possibilities of structural transitions between these modifications is important. According to the calculation (Fig. 6), the intersection points of the molar Gibbs energy of formation for the anatase and rutile modifications of TiO<sub>2</sub> are practically independent of temperature. For anatase crystal sizes larger than approximately 16 nm, TiO<sub>2</sub> can transit either into the rutile structure, which aligns with the conclusions of the work [51], or into the brookite structure. Starting from particle sizes of 40–60 nm, the specific surface energy contributes insignificantly to the molar Gibbs energy value. Consequently, from a particle size of about 40 nm onwards, the molar Gibbs energy values for rutile and brookite become very close. However, if the specific surface energy values are taken as 1.79 J/m<sup>2</sup> for rutile and 1.0 J/m<sup>2</sup> for brookite, then the brookite-to-rutile transition becomes thermodynamically feasible at particle sizes of approximately 712 nm. The estimation of stability boundaries and structural transitions strongly depends on the choice of the specific surface energy value for the calculation. It is quite possible that the specific surface energy of brookite, for which data in the literature is very limited, could be higher if surface hydration is taken into account. It should be noted that the large particle size of brookite at which its transformation into rutile becomes thermodynamically possible indicates that, in practice, one can expect to obtain macrocrystals of brookite in a relatively stable state due to the kinetically hindered nature of the brookite-to-rutile transition for such particles.

#### 4. Conclusions

Thus, it was shown that the choice of the specific surface energy value for anatase, which according to literature data varies within a relatively wide range (0.3–1.3 J/m<sup>2</sup>), significantly influences the calculation results. For instance, when using the value  $\sigma_A = 0.3$  J/m<sup>2</sup> in calculations, the determining criterion for the minimum particle sizes of anatase will be the crystallochemical criterion. Conversely, when the value  $\sigma_A = 1.3$  J/m<sup>2</sup> is used, the minimum particle sizes of anatase will be determined by thermodynamic criteria ( $d_{crit} \sim 8$  nm,  $d_{eq} \sim 12$  nm). Based on the thermodynamic analysis of TiO<sub>2</sub> particle crystallization using specific surface energy values most closely approximating these conditions for rutile ( $\sigma_R = 1.79$  J/m<sup>2</sup>), brookite ( $\sigma_B = 1.0$  J/m<sup>2</sup>), and anatase ( $\sigma_A = 1.13$  J/m<sup>2</sup>), the regions of possible crystallization was determined. Rutile can crystallize in a relatively wide pH range of 0.8–14 at 25 °C and 1.1–10.2 at 200 °C, and the

minimum particle sizes of rutile under these conditions are determined by thermodynamic criteria –  $d_{crit}$  and  $d_{eq}$ . The minimum sizes of brookite crystalline particles in acidic and alkaline media within the pH ranges of 0.7–2 and 12–14 at 25 °C, and 1.1–1.8 and 9.2–10.2 at 200 °C, are determined by thermodynamic criteria. In other considered conditions (pH 2–12 at 25 °C and 1.8–9.2 at 200 °C), the minimum brookite particle sizes are determined by the crystallochemical criterion ( $l_{min} \sim 5\text{--}7$  nm). The minimum sizes of anatase crystals in acidic and alkaline media within the pH ranges of 1–3 and 11.5–14 at 25 °C, and 1.2–2.4 and 8.9–10.1 at 200 °C, are determined by thermodynamic criteria ( $d_{crit}$ ,  $d_{eq}$ ). In the remaining considered conditions, as in the case of brookite, the crystallochemical criterion applies. Given that the minimum sizes from a crystallochemical perspective for anatase and brookite are very similar, the crystallization of these modifications under the considered conditions will be largely determined by the specifics of the synthesis conditions and kinetic factors. Based on the thermodynamic analysis of structural transitions, it was shown that anatase can transform into rutile or brookite at particle sizes larger than approximately 16 nm. Starting from particle sizes of about 40–60 nm, the specific surface energy does not contribute significantly to the molar Gibbs energy value. According to the calculation results, the structural transition from brookite to rutile occurs at particle sizes of 712 nm. However, prior to this transition, the molar Gibbs energies of rutile and brookite are so close that the difference between these values falls within the error frameworks for determining thermodynamic properties.

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