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Keywords: leaching, chemical kinetics, homogeneous–heterogeneous catalysis, thermodynamic parameter evaluation, equilibrium Gibbs free energy, fluoride ions, sulfuric acid, rutile, titanium dioxide, altered ilmenite

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Rutile decomposition by sulfuric acid, including the formation of two salts, $Ti(SO_4)_2/TiOSO_4$, is thermodynamically modelled. It is shown that TiO_2 can spontaneously dissolve in H_2SO_4 solutions. However, titania is considered as an inert (ballast) phase component of titanium-containing raw materials due to the decelerated separate nature of such chemical transformations. It is concluded that the hampered related kinetics of dissolution can be attributed to the lability of $Ti(IV)$ cations/the specific engineered features of the hierarchical crystalline structure. It is suggested that the breaking of $Ti-O-Ti$ bonds without additional mechanical strains in crystal lattice geometry becomes more advantageous when smaller negative anions/fluoride ions can be used. The analysis of sulfate-fluoride extraction leaching of titanium confirmed that a decrease in the Gibbs energy in the presence of F occurs. It is indicated by kinetic research studies that the addition of corrosive sodium reagent (NaF) reduces the activation by 45 kJ/mol, which results in intensification. A mechanism is proposed for the interactions involving the $Ti-O-Ti$ cleavage on the surface/the H_2SO_4 -induced Ti dioxide degradation on the sites of defects. Moreover, F acts as a homogeneous/heterogeneous bifunctional catalyst.

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Article

Mechanism, Thermodynamics and Kinetics of Rutile Leaching Process by Sulfuric Acid Reactions

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Abstract: Rutile decomposition by sulfuric acid, including the formation of two salts, $\text{Ti}(\text{SO}_4)_2/\text{TiOSO}_4$, is thermodynamically modelled. It is shown that TiO_2 can spontaneously dissolve in H_2SO_4 solutions. However, titania is considered as an inert (ballast) phase component of titanium-containing raw materials due to the decelerated separate nature of such chemical transformations. It is concluded that the hampered related kinetics of dissolution can be attributed to the lability of Ti(IV) cations/the specific engineered features of the hierarchical crystalline structure. It is suggested that the breaking of Ti–O–Ti bonds without additional mechanical strains in crystal lattice geometry becomes more advantageous when smaller negative anions/fluoride ions can be used. The analysis of sulfate-fluoride extraction leaching of titanium confirmed that a decrease in the Gibbs energy in the presence of F occurs. It is indicated by kinetic research studies that the addition of corrosive sodium reagent (NaF) reduces the activation by 45 kJ/mol, which results in intensification. A mechanism is proposed for the interactions involving the Ti–O–Ti cleavage on the surface/the H_2SO_4 -induced Ti dioxide degradation on the sites of defects. Moreover, F acts as a homogeneous/heterogeneous bifunctional catalyst.

Keywords: altered ilmenite; titanium dioxide; rutile; sulfuric acid; fluoride ions; equilibrium Gibbs free energy; thermodynamic parameter evaluation; homogeneous–heterogeneous catalysis; chemical kinetics; leaching

1. Introduction

Currently, the global yearly production of titanium dioxide is approximately 6 million tons, and its demand grows continuously by an average of 2.5% per year [1]. Ilmenite is a widespread raw material for the production of titanium dioxide by both the chloride [2–4] and sulfate methods. Sulfuric acid leaching of mineral rocks and concentrates containing titanium is a common method for the production of a pigment titanium dioxide. Presently, ways to intensify this leaching method are sought for using three activation methods: mechanical, thermal and chemical. The mechanical activation of raw materials significantly increases the rate of dissolution of solid minerals, as reported in a number of works [5–13]. It was shown in several publications that the mechanical dispersion of raw material can either change or remain constant, depending on various factors—among them, the ore grinding method (“dry” or in a solution medium), different process duration, etc.

Studies investigating the thermal activation of raw materials have shown that the degree of titanium extraction increases with an increase in temperature [14–17]. The degree of titanium leaching rapidly increases with an increase in temperature, with a maximum value at 160 °C during processing of a titanium-containing feed [17].

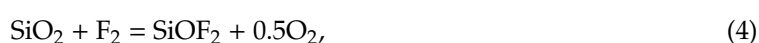
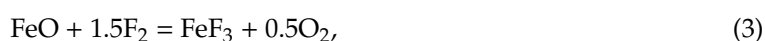
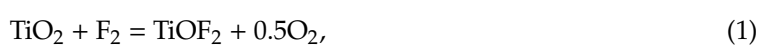
At higher temperatures, titanium salt undergoes hydrolysis in the solution, which results in the decrease in its content therein. In the reaction mixture, at 200 °C, agglomerates are formed and cannot be leached. These agglomerates are presumably the products of the polymerization of hydrolysis forms of titanium. The formation of agglomerates insoluble in 5% sulfuric acid was observed in a few works [18,19].

Nowadays, the chemical activation of raw materials with sulfuric acid solutions is also debatable. The influence of the concentration and mass module of sulfuric acid on the decomposition of ilmenite was investigated repeatedly [8,15,20–28]. The degree of titanium extraction into solution was found to increase with increasing sulfuric acid concentration [18]. However, when using H₂SO₄ solutions with a concentration above 14 M, reduced efficiency of the leaching process was observed. According to the literature, maximum efficiency was found to be within a sulfuric acid concentration of 9–17 M. This can be attributed to the fact that ore raw materials taken from different deposits have different chemical compositions and, therefore, different optimal leaching process conditions.

Most of the works have dealt with the processing of ilmenite concentrates with FeTiO₃ content above 90%, which are almost completely leached by concentrated sulfuric acid. However, the content of TiO₂ can increase in the geochemical transformation (leukoxenization) of ilmenite ores with the formation of the so-called altered ilmenite. The content of ilmenite FeTiO₃ decreases and the proportion of pseudobrookite Fe₂Ti₃O₉ increases due to the removal and oxidation of ferrous iron to the trivalent state in ore rocks. The rutile content can exceed 65 wt% in altered ilmenites. It was experimentally proved that the leaching degree of titanium from altered ilmenites barely reaches 15% with a leaching process duration of 5 h, even when 90–95% sulfuric acid solutions are used [29]. Leaching with sulfuric acid cannot ensure complete recovery of titanium from this ore due to the chemical inertness of rutile with respect to concentrated sulfuric acid. The undissolved rutile in the composition of the sludge after processing of ilmenite ores moves into dumps, which leads to accumulation of waste products in the production area, environmental degradation and losses of the target component (titanium).

In our opinion, it is possible to improve the technological parameters of sulfuric acid leaching of titanium from the rutile fraction of altered ilmenites by adding a fluorinating reagent to the reaction mixture. As is known, fluoride ions can bind titanium (IV) ions to fairly strong complexes. Fluorides are assumed to be able to “activate” a rutile surface due to the destruction of its crystal lattice and, thereby, fluorides shift the equilibrium of the reaction of rutile dissolution with sulfuric acid towards the formation of soluble titanium salts. Obviously, the fluoride ions will be bound to hydrogen ions in acidic media, because hydrogen fluoride is a weak acid and, due to its volatility, HF must continuously evaporate from the reaction mixture. The efficiency of such sulfate-fluoride processing of ilmenite ores is expected to be determined by the ratio of the rates of at least three processes: the diffusion of hydrogen fluoride molecules into the reaction zone on the surface of rutile particles, the chemical decomposition of titanium dioxide due to interaction with sulfuric and hydrofluoric acids, and the evaporation of HF from the reaction mixture at the interface between the reaction mixture and air.

Fluorination of ilmenite ores is described in the literature [30–35]. Fluorination reactions with F₂ [31] are governed by successive substitution of oxygen atoms by fluorine atoms on the surface of ore particles in a temperature range of 298–1800 K.





The literature also describes a method for indirect fluorination of ilmenites using solutions of hydrogen fluoride [36,37]. It is interesting to note that fluorination of TiO_2 with anhydrous HF is impossible and the presence of water is necessary for reactions to occur. This was concluded by the authors [31] based on thermodynamic calculations. In our opinion, an explanation of this effect is possible from the standpoint of the dissociation of HF ($\text{H}_2\text{O} + \text{HF} = \text{H}_3\text{O}^+ + \text{F}^-$), with subsequent participation of fluoride ions in the substitution reaction. Obviously, fluoride ions can also be considered as an “activator” of ore decomposition in this case. A method for indirect fluorination of ilmenites by using saturated aqueous solutions of hydrodifluoride or ammonium fluoride at boiling point was proposed [32,38]. Such a fluoride method is considered quite promising not only due to the possibility of efficient processing of altered ilmenites, but also due to recycling of the main components [39–42]. Significant disadvantages include the relatively high consumption of a leaching reagent (fluorides are consumed in reactions not only by titanium (IV), but also by iron (III)) and the large number of process steps. These disadvantages lead to an increase in costs compared to the sulfuric acid leaching method.

In our opinion, the combination of fluoride and sulfuric acid methods will overcome these disadvantages due to possible synergies in the simultaneous interaction of sulfuric and hydrofluoric acids with titanium dioxide, as the main source of titanium losses remaining in the sludge during sulfuric leaching of altered ilmenites. In order to verify this hypothesis, we studied the thermodynamic probability of possible reactions in the $\text{TiO}_2\text{--SO}_3\text{--H}_2\text{O}$ system in the absence and presence of fluoride ion additives. A comparative analysis of the thermodynamic probability of possible chemical transformations is the first stage of research. The efficiency of this approach was demonstrated by the authors earlier, in the publications [43–45]. The second stage of research is the kinetic analysis of patterns that occur when titanium is leached [46]. It is of interest to study the effect of fluorides on the rate of sulfuric acid dissolution of titanium oxide compounds. Thus, thermodynamic and kinetic modeling of the decomposition of rutile by sulfuric acid in the absence and presence of fluoride ion additives was the aim of this work.

2. Materials and Methods

2.1. Calculation Methods

Titanium dioxide as the main component of the sludge, 100 and 85 wt% solutions of sulfuric acid and crystalline sodium fluoride, as a source of fluoride ions, were considered as initial materials for thermodynamic modeling of the leaching process. It was assumed that the reactants and reaction products are in the form of pure phases, i.e., in the standard conditions. The necessary thermodynamic data for the participants of the chemical transformation were taken from the reference literature [47–49].

The change in standard Gibbs energies during chemical transformations was determined by the Temkin–Schwartzman method [50] according to the formula:

$$\Delta G^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 - T \int_{298}^T \frac{dT}{T^2} \int_{298}^T \Delta C_p dT, \quad (6)$$

where ΔC_p is the change in heat capacity during the transition from pure reagents to reaction products.

The change in heat capacity is determined by the equation $\Delta C_p = \Delta a + \Delta b \cdot T + \Delta c \cdot T^{-2}$, where writing heat capacity is represented in the form of an interpolation expression $C_p = a + b \cdot T + c \cdot T^{-2}$. The last term in the right side of Equation (6) was calculated by the formula:

$$\int_{298}^T \frac{dT}{T^2} \int_{298}^T \Delta C_p dT = \Delta a M_0 + \Delta b M_1 + \Delta c M_{-2}, \quad (7)$$

where M_0 , M_1 and M_{-2} are temperature-dependent coefficients:

$$M_0 = \ln \frac{T}{298.16} + \frac{298.16}{T} - 1, \quad (8)$$

$$M_1 = \frac{1}{2T}(T - 298.16)^2, \quad (9)$$

$$M_{-2} = \frac{1}{2} \left(\frac{1}{298.16} - \frac{1}{T^2} \right). \quad (10)$$

2.2. Experimental Methods and Procedures

Titanium dioxide (for optical glass melting) was used in the experiments. Titanium dioxide was preliminarily crushed in a drum mill under the following conditions: sample mass 100 g, mass of cylindrical grinding bodies (40 × 40 mm) 3 kg, container volume of drum mill 2 L, rotation speed 60 rpm, grinding time 1 h, and dry grinding process. Afterwards, titanium oxide was calcined in a muffle furnace at 900 °C for 3 h. The phase composition of the oxide was confirmed by X-ray diffraction (100% rutile phase was detected).

A powder fraction < 40 μm, at a mass ratio of $\text{TiO}_2/\text{H}_2\text{SO}_4 = 0.5$ and $\text{TiO}_2/\text{NaF} = 1$, was used in the sulfuric acid leaching process. The weight samples (0.50 g) of rutile were put into heat-resistant tubes, and then the same weight sample of NaF (analytical grade, Rechem supplier) and 0.70 mL of 85 wt% sulfuric acid (analytical grade, Rechem supplier) were added into tubes. The tubes were placed into a glycerin bath, which was heated to the necessary temperature. The tubes were cooled under running water in order to stop the leaching process; the contents of the tubes were quantitatively transferred to a volumetric flask, using a 5 wt% H_2SO_4 solution to prevent the hydrolysis of titanium salts. The solutions were adjusted to the mark, stirred and left for a day to completely dissolve the titanium salts and precipitate the unreacted part of rutile. The aliquots of these solutions were transferred to heat-resistant glasses to evaporate traces of hydrogen fluoride and then the aliquots were quantitatively transferred to volumetric flasks. The titanium concentration was determined by the spectrophotometric peroxide method with a wavelength of 410 nm.

Each individual tube is a separate point on the kinetic curves. Each tube was taken out from a glycerin bath at a specific time. Measurements at each point are the result of at least three experiments, and therefore error markers are plotted for each point.

3. Results and Discussion

3.1. Model Selection for Thermodynamic Modeling

It is known [51] that in the $\text{TiO}_2\text{--SO}_3\text{--H}_2\text{O}$ system, the formation of six titanium sulfate salts is possible. The composition of these salts is determined by the SO_3 content and the temperature range (indicated in brackets): $\text{Ti}(\text{SO}_4)_2$ (90–100%, below 250 °C), TiOSO_4 (60–90%, 150–250 °C), $\text{TiOSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (70–90%, below 150 °C), $\text{TiOSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (60–70%, below 100 °C), $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ (45–60%, below 180 °C) and $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ (30–45%, below 80 °C).

High concentrations of sulfuric acid (85–90%) are used to increase the efficiency of leaching processes. At the same time, the temperature in the reaction mixture rises to a temperature range of 200–220 °C due to the exothermic reactions of the leaching process and the interaction of concentrated acid with sharp water steam. The composition of titanium sulfates does not remain constant in sulfuric acid leaching of altered ilmenites; this was experimentally proved by the authors in the previous work [52]. At the first stage, the salt of $\text{Ti}(\text{SO}_4)_2$ is the dominant form when the temperature of the reaction medium reaches 200 °C. As compared to all other sulfate salts, this titanium salt is the most soluble in the dilute acid solutions. A decrease in the acid concentration and in the temperature from the moment of sludge formation (solidification of the reaction mixture) during the chemical reaction leads to the formation of TiOSO_4 salt, which also becomes crystallized when the titanium content

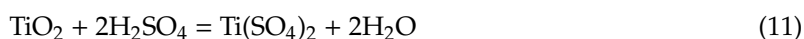
increases in the reaction medium. This salt does not contain crystallization water. It is well explained by the fact that water, which remains unevaporated before the solidification of sludge, is bound into relatively strong hydrates of sulfuric acid $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$.

It is known that the solubility of TiOSO_4 becomes decreased after ageing of precipitate. This property is important for the next stage of the process, the dissolution of the sludge in the 5 wt% solution of sulfuric acid. From the standpoint of the chemistry of coordination compounds, the difference in the solubility of $\text{TiO}(\text{HSO}_4)$ and TiOSO_4 salts can be explained by the difference in the properties of monodentate HSO_4^- ions and bidentate SO_4^{2-} ions. These last ones can act as bridging ligands which bind titanyl cations to the polymer structure. The formation of bridging bonds between TiO^{2+} cations in titanium sulfate solutions has been experimentally proved by IR and Raman spectroscopy [27,53]. The ligand exchange rate in the coordination sphere of Ti(IV) ions becomes increased at high temperatures, which promotes the transition of the $\text{TiO}_2\text{--SO}_3\text{--H}_2\text{O}$ system from a metastable to an equilibrium state, with formation of less soluble products of TiOSO_4 .

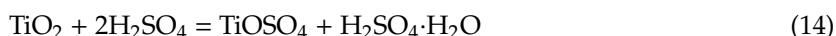
Therefore, we considered $\text{Ti}(\text{SO}_4)_2$ and TiOSO_4 as the main products of the reaction between sulfuric acid and titanium dioxide in model calculations in order to thermodynamically substantiate sulfuric acid leaching of titanium in industrial conditions.

3.2. Leaching of Titanium from Rutile with Sulfuric Acid

The dissolution of titanium dioxide in sulfuric acid with the formation of two products, $\text{Ti}(\text{SO}_4)_2$ and TiOSO_4 , was considered at the first stage of thermodynamic modeling. It is generally accepted to consider such reactions in the most simplified form, as the reactions which are accompanied by the release of water:



Obviously, water cannot be considered as a pure phase in concentrated solutions of sulfuric acid, i.e., in the standard state, due to the formation of relatively strong hydrates $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$. Therefore, reactions (11) and (12) were rewritten taking into account the formation of sulfuric acid hydrate:



Similarly, it is possible to write the equations for the dissolution of titanium dioxide in 85% sulfuric acid (the molar ratio $\text{H}_2\text{SO}_4/\text{H}_2\text{O} = 1$). The number of moles of sulfuric acid in such equations should generally depend on the degree of conversion of titanium dioxide and excess sulfuric acid. We considered one of the possible options which involve two acid hydrates with $n = 1$ and 2:

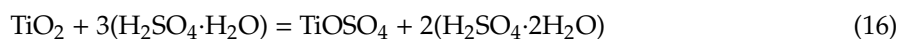
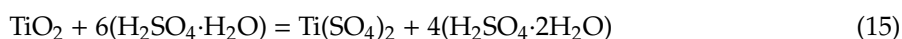
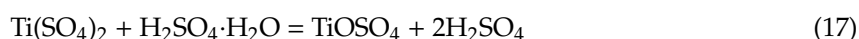


Table 1 shows the calculated values of ΔH_{298}^0 , ΔS_{298}^0 , ΔG_{298}^0 and the coefficients Δa , Δb and Δc in the expression for change in heat capacity ($\Delta C_p = \Delta a + \Delta b \cdot T + \Delta c \cdot T^{-2}$) during transformations in the $\text{TiO}_2\text{--SO}_3\text{--H}_2\text{O}$ system according to Equations (13)–(16).

Table 1. Thermodynamic data for chemical transformations in the TiO₂–SO₃–H₂O system.

Reaction	ΔH_{298}^0 [kJ/mol]	ΔS_{298}^0 [kJ/mol·K]	ΔG_{298}^0 [kJ/mol]	Δa	$\Delta b \cdot 10^3$	$\Delta c \cdot 10^{-5}$
TiO ₂ + 4H ₂ SO ₄ = Ti(SO ₄) ₂ + 2(H ₂ SO ₄ ·H ₂ O)	−235.2	−79.9	−211.3	−226.7	−58	56.9
TiO ₂ + 6(H ₂ SO ₄ ·H ₂ O) = Ti(SO ₄) ₂ + 4(H ₂ SO ₄ ·2H ₂ O)	−178.8	−38.7	−167.2	−226.7	−58	56.9
TiO ₂ + 2H ₂ SO ₄ = TiOSO ₄ + H ₂ SO ₄ ·H ₂ O	−157.3	20.4	−163.4	−69.8	−30	33.4
TiO ₂ + 3(H ₂ SO ₄ ·H ₂ O) = TiOSO ₄ + 2(H ₂ SO ₄ ·2H ₂ O)	−129.1	41.0	−141.3	−69.8	−30	33.4
Ti(SO ₄) ₂ + H ₂ SO ₄ ·H ₂ O = TiOSO ₄ + 2H ₂ SO ₄	77.9	100.3	48.0	156.9	28	−23.5

It was found that the largest decrease in the standard Gibbs energy is observed for the reaction of Ti(SO₄)₂ formation as a result of the dissolution of rutile in 100% sulfuric acid. The standard formation energy of Ti(SO₄)₂ decreases by almost 50 kJ/mol in 85% sulfuric acid. However, this salt is the most thermodynamically stable sulfate compound of titanium (IV) even in this case. To confirm this general property, it can be shown that the value of ΔG_{298}^0 (48 kJ/mol) for the reaction of the transformation of Ti(SO₄)₂ to titanium oxysulfate TiOSO₄ is positive:



This reaction also shows that the spontaneous dehydration of H₂SO₄·H₂O with the formation of 100% sulfuric acid is impossible. The dissolution of titanium dioxide in sulfuric acid with the formation of TiOSO₄ oxysulfate is also characterized by negative values of the standard Gibbs energy (Equations (14) and (16)). The Ti(SO₄)₂→TiOSO₄ transition according to reaction (17) is thermodynamically impossible, and therefore the formation of both salts should be considered as two independent reactions of the dissolution of rutile in sulfuric acid with the formation of Ti(SO₄)₂ and TiOSO₄.

Temperature dependences of the change in standard Gibbs energies for the reactions (13)–(16) are presented in Figure 1. The calculations were made for a temperature range of 298–510 K. The upper temperature value is limited by the boiling point of 85 wt% sulfuric acid solution at 237 °C. Such a temperature range makes it possible to disregard the thermal effects of the evaporation and decomposition of sulfuric acid onto water and sulfur oxide(VI). In addition, temperatures above 500 K are not used in sulfuric acid leaching of ilmenites. The thermal effects of water evaporation and an additional hydration of sulfuric acid were neglected in the calculations because of the presence of water, which is formed upon dissolution of TiO₂ and remains in the reaction mixture upon evaporation. In fact, it is impossible to estimate the ratio of evaporated water to the water which remains bound to hydrates with sulfuric acid.

It can be seen from the obtained data that temperature dependences of Gibbs energies for the reactions of Ti(SO₄)₂ formation according to reactions (13) and (15) are characterized by positive slopes. This general property is explained by the fact that reactions (13) and (15), unlike all other considered reactions, proceed with a decrease in entropy. Obviously, such ΔS_{298}^0 values are caused by a higher degree of ordering of Ti(SO₄)₂ crystal lattice as compared to TiO₂ or TiOSO₄.

For reactions (14) and (16), the plot of the $\Delta G(T)$ dependence exhibits a monotonous decrease with increasing temperature. It is well explained by the fact that the crystal lattice of the reaction product of TiOSO₄ is less ordered as compared to TiO₂.

In the case of reaction (17), the change in the Gibbs energy remains positive throughout the entire studied temperature range. It shows that the spontaneous conversion of Ti(SO₄)₂ to TiOSO₄ is impossible. At the same time, extrapolation of the $\Delta G(T)$ curves for reactions (13)–(17) into the area of higher temperatures shows the fundamental possibility of shifting the equilibrium of the reaction (17) towards the formation of TiOSO₄ as the least soluble sulfate titanium salt.

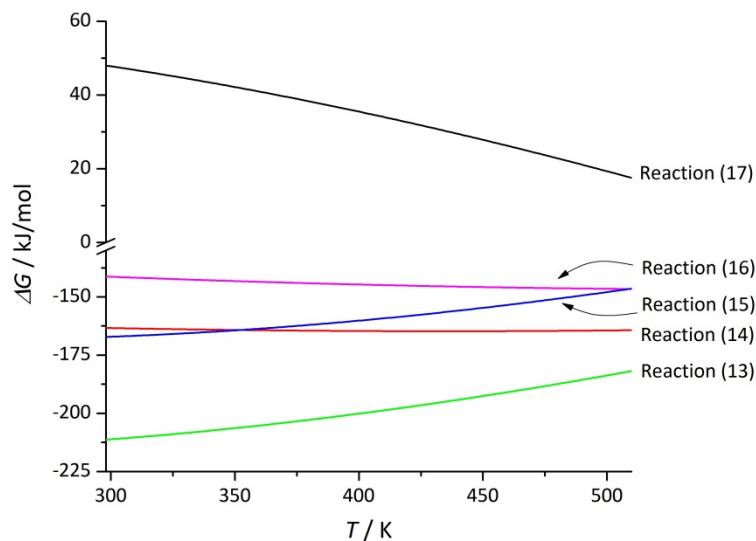


Figure 1. Temperature dependences of changes in the Gibbs energy. Each curve corresponds to the individual reaction.

The obtained results of thermodynamic calculations of the interaction between rutile and sulfuric acid confirm the widespread opinion that titanium dioxide can be dissolved in concentrated sulfuric acid with the formation of tetravalent titanium salts. However, in cases where the dissolution of rutile is considered, it is usually indicated that such dissolution is rather slow (even in concentrated sulfuric acid at the temperature of its decomposition onto SO_3 and H_2O). Such slow dissolution of rutile shows that it can be considered as a chemically inert (ballast) component of the raw material in the sulfuric acid decomposition of altered ilmenites.

In our opinion, the kinetic hampering of reactions (13)–(16) should be explained by the features of the properties of Ti(IV) cation and the crystal structure of rutile. It is known that Ti(IV) ions belong to a group of cations with a low degree of lability in coordination chemistry. The large positive charge of the titanium cation and its relatively small radius is believed to increase the activation energy of the substitution reaction, which reduces the rate of exchange of intrasphere ligands (oxygen ions in rutile) for other ligands from the solution (in our case, these are sulfuric acid ions whose concentrations in H_2SO_4 concentrated solutions are rather small).

Each titanium ion is surrounded by six oxygen ions, located at the angles of the octahedron in the rutile crystal lattice. The octahedrons are connected by two common edges and form chains parallel to the layers of the densest hexagonal packing. Although the tetragonal structure is typical for many other oxides, rutile possesses some features different from those characteristic for close-packed structures such as corundum. The layers of the densest packing of oxygen ions in the crystal structure of corundum are perpendicular to the triple axis, while these layers are parallel to the faces of the octahedron in the spinel structure; on the contrary, in the rutile structure, the layers of the densest packing are parallel to the main (quadruple) axis of rutile crystals. Obviously, a local widening of the crystal lattice would occur if oxygen ions in such layers are replaced by larger anions of sulfuric acid. This process is associated with the additional energy consumption. The $-\text{Ti}-\text{O}-\text{Ti}-$ bond breaking without additional deformation of the crystal lattice is also obviously more advantageous with smaller anions, the fluoride ones in this case. In fact, the reference data indicate the sequence of ionic radii $\text{SO}_4^{2-}-0.295$; $\text{O}^{2-}-0.136$; $\text{F}^- -0.133$ nm.

Therefore, it is interesting to consider the effect of fluorides on the efficiency of the rutile dissolution process.

3.3. Sulfate-Fluoride Leaching of Titanium from Rutile

Hydrochloric acid, calcium fluoride and sodium fluoride were used as a fluoride precursor. The best results were obtained using sodium fluoride, which can be explained by the rapid evaporation of HF from the reaction area and differences in the solubilities of CaF_2 , NaF and the products of its reactions with sulfuric acid.

Figure 2 shows the results of the effect of sodium fluoride addition on the efficiency of the dissolution of rutile in sulfuric acid for 1.5 h, under isothermal conditions at a temperature range of 70–165 °C.

It was found that the rutile does not completely dissolve in 85% sulfuric acid solution in the absence of fluoride ions even at 100 °C. NaF additives at a mass ratio of $\text{TiO}_2/\text{NaF} = 1$ dramatically accelerate the dissolution of rutile. Curves 2–6 in Figure 2 have the shape of convex curves at the beginning of the leaching process.

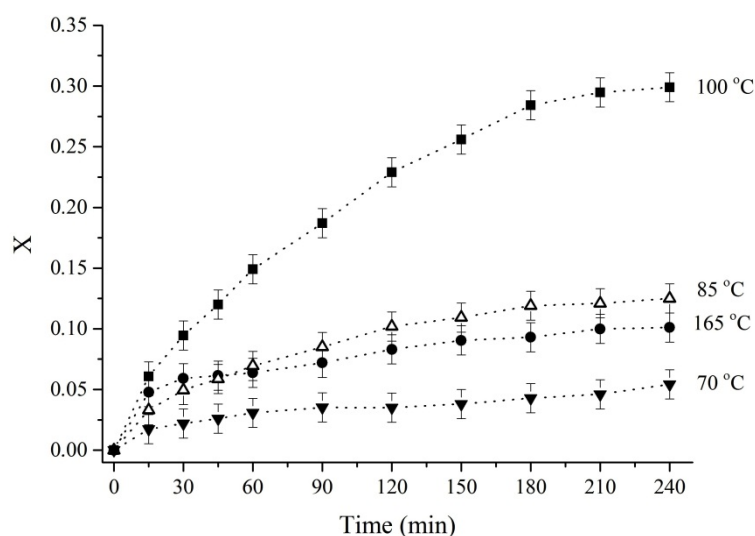
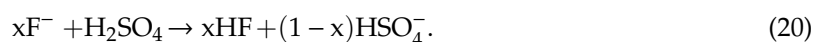
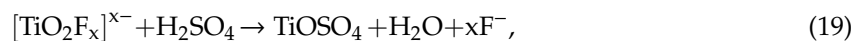


Figure 2. The kinetics of leaching of rutile during processing in H_2SO_4 (85 wt%) at a mass ratio of $\text{Ti}/\text{F} = 1/1$ at temperatures: 70, 85, 100 and 165 °C.

As can be seen from Figure 2, the highest degree of titanium leaching with increasing temperature is achieved during the leaching process at 100 °C. The low degree of titanium leaching in the solution at 165 °C can be explained by the fact that HF quickly evaporates from the reaction mixture at this temperature. It is known that an azeotropic mixture with a HF concentration of 37.5% and a boiling point of 109 °C is formed on heating of HF solutions. Therefore, increasing the temperature to above 100 °C increases the evaporation of HF, leading to a decrease in fluoride ion concentration in the reaction mixture.

Data on the leaching kinetics at different temperatures for the initial sections of the kinetic curves $X(t)$ made it possible to calculate the activation energy of this process: 45.0 kJ/mol. The values of activation energies are important data to determine the mechanisms of leaching processes. The literature gives rather different values of activation energies for sulfuric acid leaching of ilmenite and its altered form. For example, as reported earlier [8,13], the activation energies are in the range of 28–48 kJ/mol, whereas other authors list activation energies as 75.0 [54], 72.6 [17] and 64.4 [18] kJ/mol. Further, activation energies in the ranges of 52–62 kJ/mol [13–15] and 80–100 kJ/mol [28] were also mentioned by different authors. The different activation energies are explained by the difference in the chemical compositions of the researched ilmenite ores. According to our research [52], the first stage of sulfuric acid leaching of ilmenite concentrates is characterized by activation energies of 62.5 kJ/mol for titanium and 63.1 kJ/mol for iron. These activation energies, calculated according to the kinetic data on the accumulation of titanium and iron salts in solutions, indicate that the parallel extraction of Ti(IV) and

Fe(II, III) ions from ilmenite takes place. Therefore, one can compare the dissolution of ilmenite and rutile in sulfuric acid based on a comparison of the magnitude of the activation energies required for these chemical reactions. The addition of NaF into the reaction mixture reduces the activation energy required from 63 to 45 kJ/mol; therefore, fluorides can be considered as activators of the process which accelerate the interaction of rutile with sulfuric acid. Thus, the process can be represented as a series of stages:



The dissolution of titanium dioxide begins with the breaking of $-Ti-O-Ti-$ bonds on its surface due to the addition of fluoride ions. This initiates the subsequent sulfuric acid decomposition of titanium dioxide on the sites of surface “defects” that are formed in the rutile lattice. The stage of gradual removal of fluorides from the reaction system due to the formation of low-dissociating hydrogen fluoride is also added because it was shown by additional experiments that fluorides are absent in $TiO(OH)_2$ precipitates. The precipitates were obtained by ammonia deposition from titanium salt solutions after the sulfate-fluoride decomposition of rutile.

Figure 3 shows a photograph of the sludge obtained during leaching of ilmenite ore by the sulfate-fluoride method in a hermetically sealed RVD-200 Teflon reactor. Holes and recesses are visible on the sample surface, which, in our opinion, can be explained by the formation of gaseous HF bubbles.

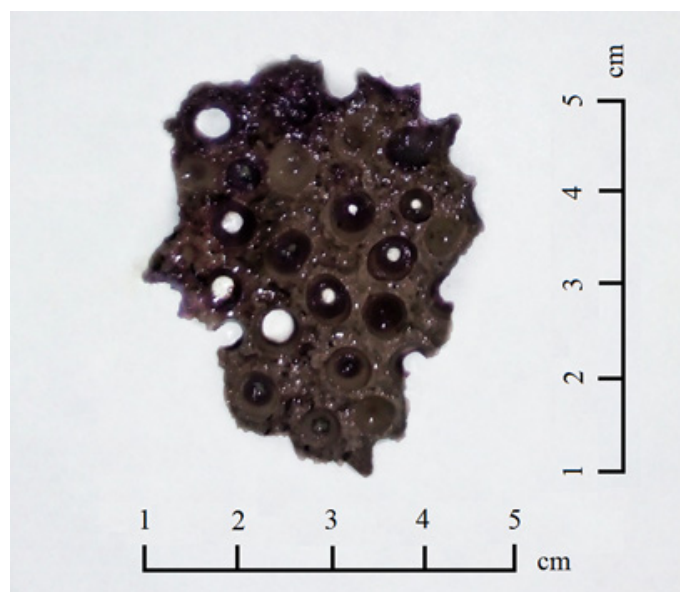


Figure 3. A photograph of the sludge after sulfuric leaching of ilmenite in the presence of sodium fluoride.

Therefore, for thermodynamic modeling of the sulfate-fluoride leaching process, we used reactions which involve the formation of hydrogen fluoride.

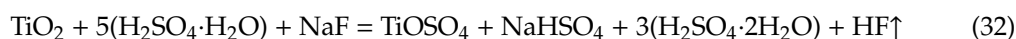
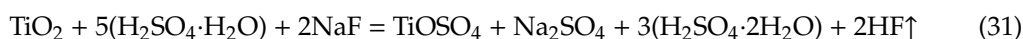
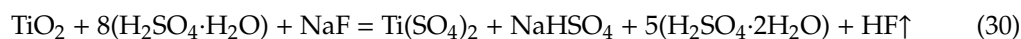
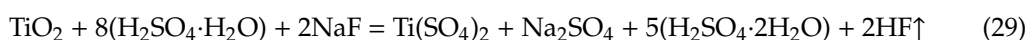


As was mentioned above, water cannot be considered as a pure phase (in the standard state) in concentrated solutions of sulfuric acid due to the formation of hydrates $H_2SO_4 \cdot nH_2O$. Therefore, reactions (21)–(24) were rewritten taking into account the formation of sulfuric acid hydrates:

(a) For 100% acid:



(b) For 85% acid:



The possible formation and decomposition of an intermediate product (a titanium (IV) fluoride compound) was disregarded in the calculations.

The calculated values of ΔH_{298}^0 , ΔS_{298}^0 , and ΔG_{298}^0 and the coefficients Δa , Δb and Δc of the heat capacity change equations for reactions (25)–(32) are listed in Table 2. Figures 4 and 5 for these reactions show the results of calculations of the change in Gibbs energies of the rutile in a temperature range of 298–510 K.

Table 2. Thermodynamic data for chemical transformations in the TiO_2 – NaF – SO_3 – H_2O system.

Reaction	ΔH_{298}^0 [kJ/mol]	ΔS_{298}^0 [kJ/mol·K]	ΔG_{298}^0 [kJ/mol]	Δa	$\Delta b \cdot 10^3$	$\Delta c \cdot 10^{-5}$
$TiO_2 + 5H_2SO_4 + 2NaF = Ti(SO_4)_2 + Na_2SO_4 + 2HF\uparrow + 2(H_2SO_4 \cdot H_2O)$	−206.4	157.8	−253.4	−334.5	43	85.3
$TiO_2 + 5H_2SO_4 + NaF = Ti(SO_4)_2 + NaHSO_4 + HF\uparrow + 2(H_2SO_4 \cdot H_2O)$	−251.2	11.2	−254.6	−317.9	55	82.8
$TiO_2 + 3H_2SO_4 + 2NaF = TiOSO_4 + Na_2SO_4 + 2HF\uparrow + H_2SO_4 \cdot H_2O$	−128.5	258.1	−205.4	−177.6	71	61.8
$TiO_2 + 3H_2SO_4 + NaF = TiOSO_4 + NaHSO_4 + HF\uparrow + H_2SO_4 \cdot H_2O$	−173.4	111.5	−206.6	−161.0	84	59.4
$TiO_2 + 8(H_2SO_4 \cdot H_2O) + 2NaF = Ti(SO_4)_2 + Na_2SO_4 + 2HF\uparrow + 5(H_2SO_4 \cdot 2H_2O)$	−135.9	209.3	−198.3	−334.5	43	85.3
$TiO_2 + 8(H_2SO_4 \cdot H_2O) + NaF = Ti(SO_4)_2 + NaHSO_4 + HF\uparrow + 5(H_2SO_4 \cdot 2H_2O)$	−180.7	62.7	−199.4	−631.7	55	82.8
$TiO_2 + 5(H_2SO_4 \cdot H_2O) + 2NaF = TiOSO_4 + Na_2SO_4 + 2HF\uparrow + 3(H_2SO_4 \cdot 2H_2O)$	−86.2	289.0	−172.4	−177.6	71	61.8
$TiO_2 + 5(H_2SO_4 \cdot H_2O) + NaF = TiOSO_4 + NaHSO_4 + HF\uparrow + 3(H_2SO_4 \cdot 2H_2O)$	−131.1	142.4	−173.5	−161.0	84	59.4

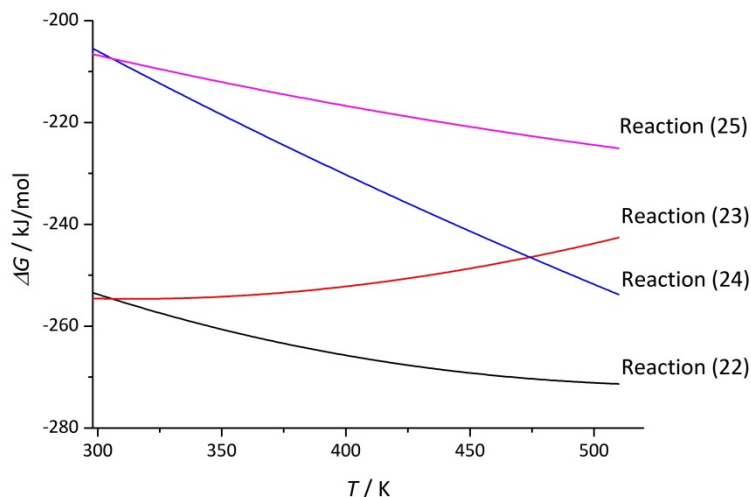


Figure 4. Temperature dependences of the change in the Gibbs energy in rutile dissolution reactions in 100% sulfuric acid, with NaF as the activator reagent. Each curve corresponds to the individual reaction.

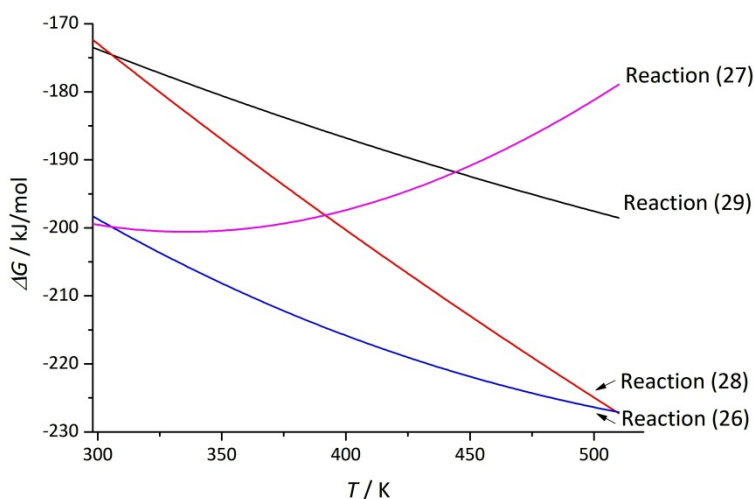


Figure 5. Temperature dependences of the change in the Gibbs energy in rutile dissolution reactions in 85% sulfuric acid, with NaF as the activator reagent. Each curve corresponds to the individual reaction.

The calculated values of the change in the Gibbs energy show that reactions (25)–(32) are thermodynamically possible because the change in the Gibbs energy is negative throughout the whole studied temperature range. The addition of sodium fluoride leads to a decrease in the standard Gibbs energy by approximately 30 kJ/mol, and this difference is almost doubled with increasing temperature to 500 K. The exceptions are reactions (26) and (30). The temperature dependences of Gibbs energies for these reactions pass through a small minimum and then monotonically decrease in absolute value. Despite the nature of the curves, the ΔG values remain negative. The ΔS_{298}^0 values for these reactions are positive, although their orders of magnitude are lower than those for other reactions. Therefore, positive angular coefficients of the dependences $\Delta G(T)$ in this case can be explained by a change in the heat capacity of the participants in the chemical transformation, which is described by the last term of the Temkin–Schwartzman equation.

Temperature dependences of Gibbs energies are characterized by relatively large negative angular coefficients for all other reactions considered above which involved NaF addition. This feature is explained by the fact that these reactions are accompanied by a large increase in entropy caused by the formation of gaseous HF. If we take into account that the removal of gaseous HF from the reaction zone displaces its equilibrium to the right according to the Le Chatelier principle, then it should be concluded that the rutile can be completely dissolved. Further, it should be noted that reactions (26),

(28), (30) and (32) make it possible to reduce the molar ratio of NaF/TiO₂ from 2 to 1. However, the complete conversion of TiO₂ will require the use of an excess of fluorides in the reaction mixture because of possible losses of hydrogen fluoride during the leaching process.

It can be concluded from the above analysis of the scheme of chemical transformations that the fluorides which participate in reactions (25)–(32) can be regenerated in HF form. Therefore, fluorides can be considered as a homogeneous–heterogeneous (so-called bifunctional) catalyst, which increases the sulfate-fluoride decomposition of rutile. The simultaneous homogeneity and heterogeneity of such a catalyst is due to the fact that the fluorine ions do not form an independent phase in a sulfuric acid solution, but exhibit their effect only at the phase boundary of both reagents, i.e., on the surface of titanium dioxide.

4. Conclusions

The rutile can spontaneously dissolve in H₂SO₄ solutions with the formation of salts Ti(SO₄)₂ and TiOSO₄, as shown by thermodynamic analysis of leaching of titanium in the TiO₂–SO₃–H₂O system. At the same time, the experimentally proven inhibition effect of such reactions forces technologists to consider rutile as an inert (ballast) component of titanium-bearing raw materials. In our opinion, the kinetic difficulties in the reactions of sulfuric acid dissolution of rutile should be explained by the features of Ti(IV) cation properties and the rutile crystal structure. The low degree of lability of Ti(IV) cations increases the activation energy of substitution reactions in its coordination sphere and reduces the rate of exchange of oxygen ions to sulfate ions. It should be noted that the concentration of sulfate ions in the concentrated H₂SO₄ solutions is rather small and further reduces the rate of the substitution reaction. Further, it should be borne in mind that the size of sulfate ions is more than two times larger than oxygen ions. Therefore, the exchange of oxygen ions to sulfate ions in the rutile lattice should be inhibited by local expansion of the rutile crystal lattice. The breaking of Ti–O–Ti bonds without additional strains in the crystal lattice is suggested to be more beneficial using smaller anions, specifically fluoride ions.

The thermodynamic analysis of sulfate-fluoride leaching of titanium confirmed an additional decrease in the Gibbs energy of the dissolution reaction of rutile in sulfuric acid in the presence of fluoride ions.

The sodium fluoride additive increases the reaction between sulfuric acid and rutile by reducing the activation energy to 45 kJ/mol, as shown by the kinetic studies. A reaction mechanism was proposed for the interaction of rutile with sulfuric acid, which includes the breaking of Ti–O–Ti bonds on the surface of rutile due to the replacement of oxygen ions by fluoride ions and the sulfuric acid decomposition of titanium dioxide on the sites of surface “defects” in the rutile lattice. It was proposed to consider the decomposition of rutile by the sulfuric acid in the presence of NaF additives as a homogeneous–heterogeneous catalytic process, where fluoride ions play the role of a bifunctional catalyst.

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