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Thermodynamic Description of Oxidized Zinc Minerals and Comparative Analysis of Their Reactivity

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Due to depletion of sulfide zinc ores, the problem of involvement of economically significant oxidized zinc ores into the treatment is a vital task. In this article, the thermodynamic functions have been considered and determined for many oxidized zinc minerals, such as calamine, smithsonite, willemite, hydrozincite and others. The reactivity of minerals was determined by the groups of the same type, and the series were compiled according to the increase in their reactivity. The Gibbs energies $\Delta_r G_T^o$ of the chemical reaction of sphalerite (ZnS), smithsonite ($ZnCO_3$) and calamine $Zn4(Si_2O_7)(OH)_2 \cdot H_2O$ with sulfuric acid were calculated and the following data were obtained per 1 mol of H_2SO_4: for sphalerite (13.27 kJ/mol), for smithsonite (75.46 kJ/mol) and for calamine (154.07 kJ/mol). Based on the calculated thermodynamic analysis of the dissolution of these minerals, the following series of changes in the standard values of Gibbs energies $\Delta_r G_T^o$ was established: ZnS > $ZnCO_3$ > $Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$. The results of thermodynamic calculations make it possible to distinguish the most reactive oxidized zinc minerals, so that in future, when treating oxidized zinc ores, to know about the properties and characteristics of these minerals.

1. Introduction

The burgeoning demand for zinc from its various consumers is forcing them to involve more and more complex and refractory ores, including oxidized ones. In most cases, the recovery of oxidized zinc minerals from oxidized ores is a technological challenge. Meanwhile, they are a major raw materials source for zinc, lead, copper and other non-ferrous metals.

With an increased demand for zinc from developed and developing countries, the commercial interest in oxidized ore deposits has resumed. At the moment, a large number of deposits of rich oxidized zinc ore are known in the world. But an insignificant part of these deposits is involved in the treatment, which reduces the raw material base of zinc production. Principal deposits of oxidized zinc ores, which by now have been involved in industrial treatment, are described in (Ramazanova et al., 2020). Quick depletion of sulphide zinc ores and burgeoning demand for metallic zinc require the involvement of economically significant oxidized zinc ores. With that in mind, the work (Sun et al., 2015) investigated the thermodynamics and kinetics of zinc extraction from oxidized zinc ore. The significance of treatment of oxidized zinc ores such as carbonate and silicate minerals has increased due to the depletion of zinc sulfide ores and the limitation of sulfur emissions during treatment. WIth that in mind, the authors (Soltani et al., 2021) studied the leaching of complex oxidized zinc ore Mehdiabad. In the following work (Wang et al., 2020), devoted to the treatment of oxidized zinc ore, leaching of smithsonite using a $Fe_2(SO_4)_3$ solution is considered. The authors conducted thermodynamic calculations of smithsonite leaching. We studied the kinetics of zinc leaching from calamine (hemimorphite) with sulfuric acid due to the interest in studies of oxidized zinc minerals (Ramazanova et al., 2021). In order to expand the raw material base of zinc production, the kinetics of a promising source of mineral raw materials for the production of zinc -

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smithsonite with sulfuric acid (Ramazanova et al., 2021) was also studied in view of the global concern about the zinc sulfide ores depletion, the study of the thermodynamic characteristics of oxidized zinc minerals is a vital task. The goal of this research is to study thermodynamic parameters of more than 20 oxidized zinc minerals and to compare their reaction capacity.

To increase the efficiency of experimental studies, it is necessary to first carry out a theoretical analysis of the properties of the objects under study in order to assume the nature of the interaction of the object under study with the solvent. In the works cited, the thermodynamic parameters of some oxidized zinc minerals were determined. The authors (Bissengaliyeva et al., 2010) investigated the thermodynamic properties of hemimorphite by low-temperature adiabatic and quantum calorimetry and calculated thermodynamic functions: heat capacity, entropy, enthalpy. In work (Dachs and Geiger, 2009), the calorimetric and thermodynamic phase transitions of hemimorphite $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$ and its dehydrated analogue $Zn_4Si_2O_7(OH)_2$ were studied. Two different model approaches have been taken to describe the low temperature behavior and derive the phase transition thermodynamic properties of both phases. The authors (Terry and Monhemius, 1983) investigated the effect of temperature, pH, acid type and surface area on the kinetics of acid dissolution of natural and synthetic willemites and natural hemimorphites. A quantitative mixed kinetics model has been developed that predicts the rate of dissolution for willemite in sulfuric acid. In the work (Bissengaliyeva et al., 2012), the heat capacity of smithsonite was investigated by the method of low-temperature adiabatic calorimetry, and the thermodynamic functions were calculated on the basis of experimental data for the heat capacity. The authors (Preis et al., 2000) investigated the solubility and thermal decomposition of smithsonite and determined the thermodynamic data for $ZnCO_3$: solubility constant, standard Gibbs energy of formation, standard enthalpy of formation and standard entropy.

In this work, it became necessary to determine the thermodynamic properties of the oxidized zinc minerals we are interested in and to compare their reactivity. It should be noted that a special place in the consideration of this issue deserves the ones developed by Ospanov general principles of predicting the sequence of dissolution of solids (Ospanov, 2012). For a qualitative prediction of the difference in the reactivity of sulfides, an unconventional thermodynamic approach was proposed - by using standard value of the average Gibbs atomic energy of the formation of a solid $\Delta_f \underline{G^o}$, taking into account the properties of the mineral, depending not only on the nature of the constituent atoms, but also on the different numbers of dissimilar atoms and different types of bonds included in the formula of this compound (Ospanov, 2012). The proposed principle of predicting the sequential dissolution of minerals has been tested and confirmed by the example of a number of classes of compounds (sulfides, oxides, phosphates) and is successfully used in the processing of mineral raw materials in the Republic of Kazakhstan.

2. Choice of methods for calculating thermodynamic parameters

Considering that, all natural minerals (as well as many solid substances) differ greatly in composition, the author (Ospanov, 2012) considered it expedient to use the values of $\Delta_f G^o$ related to the number of atoms corresponding to the simplest formula of the mineral. Finding the value of the average Gibbs atomic energy of the formation of solids was carried out according to Eq.(1) proposed by Ospanov (2012):

$$-\Delta_f \overline{G}^o = \frac{-\Delta_f G^o}{n} \qquad (1)$$

where “n” is the number of atoms (in the gross formula) in a solid.

In (Ospanov, 2012), oxidized zinc minerals that are frequently found in nature were given and the standard Gibbs energies and average Gibbs atomic energies of oxide formation were calculated (Table 1).

Table 1: Standard Gibbs energies and average Gibbs atomic energies of formation of oxidized zinc minerals

Mineral	Formula	$-\Delta_f G^o$, Kcal/ mol	$-\Delta_f \overline{G}^o$ Kcal/mol · atom
Hydrozincite	$Zn_5(CO_3)_2(OH)_2$	586.00	23.40
Smithsonite	$ZnCO_3$	175.40	35.10
Zincite	ZnO	76.66	38.80
Calamine	$Zn_4(Si_2O_7)(OH)_2{\cdot}H_2O$	789.10	39.60
Willemite	$Zn_2(SiO_4)$	365.10	52.30

Based on a comparison of the average Gibbs atomic energy of formation, the thermodynamic series Eq.*(2)* of dissolution sequence of oxidized zinc minerals that are often found in nature was compiled:

$$Zn_5(CO_3)_2(OH)_2 > ZnCO_3 > ZnO > Zn_4(Si_2O_7)(OH)_2{\cdot}H_2O > Zn_2(SiO_4) \qquad (2)$$

Since this approach is effective, in our work we used the above considered theoretical concept proposed by Kh.K. Ospanov. Table 2 shows the standard Gibbs energies $\Delta_f G^o$ and the average Gibbs atomic energies $\Delta_f\overline{G}^o$ of formation of a number of oxidized zinc compounds of various classes. This table contains a list of the main oxidized zinc minerals with an increased zinc content in the mineral and is divided into groups of the same type. Kh.K. Ospanov used an approximate method for calculating the standard Gibbs energy $\Delta G^\circ_{f(298)}$ in the absence of crystal chemical data for many minerals (Ospanov, 2006). Accordingly, our calculations were carried out by summing the data on thermodynamic characteristics in Eq.(3) taking into account their stoichiometric coefficients in the mineral, for example:

$$\Delta G^\circ_{f(298)}/Zn_4(Si_2O_7)(OH)_2/ = 4\,\Delta G^\circ_{f(298)}/ZnO/ + 2\,\Delta G^\circ_{f(298)}/SiO_2/ + \Delta G^\circ_{f(298)}/H_2O/ \quad (3)$$

3. Results and discussion

Table 2 shows the calculated values of the average Gibbs atomic energy of formation in (kJ/mol · atom) for all oxidized zinc minerals. On the basis of comparison of this value, the reactivity of these minerals was determined, and series of increasing their reactivity were drawn up.

Table 2: Energy parameters of the formation of oxidized zinc minerals

Mineral name	Formula	– $\Delta G^\circ_{f(298)}$, kJ/mol	– $\Delta_f\overline{G}^o$, kJ/mol · atom	Zn content in the mineral, % mass.	Data used for calculation of $\Delta G^\circ_{f(298)}$
Zinc sulfate minerals					
Goslarite	$Zn(SO_4)\cdot 7H_2O$	2,564. 08 (Naumov, 1976)	94.96	40.40*	Reference value used $\Delta G^\circ_{f(298)}$ = –2,564.08 kJ / mol
Zincosite	$ZnSO_4$	869.17 (Naumov, 1976)	144.86	40.37*	Reference value used $\Delta G^\circ_{f(298)}$ = – 869.17 kJ / mol
$ZnSO_4 < Zn(SO_4)\cdot 7H_2O$					
Zinc carbonate minerals					
Monheimite	$(Zn, Fe)CO_3$	701.84	116.97	27.30	$(Zn, Fe)CO_3 = ZnO + FeO + CO$
Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	3,105.93	124.24	59.30	$Zn_5(CO_3)_2(OH)_6 = 5ZnO + 2CO_2 + 3H_2O$
Zincrosazite	$Zn_2(CO_3)(OH)_2$	1,273.83	127.38	58.03*	$Zn_2(OH)_2CO_3 = 2ZnO + CO_2 + H_2O$
Smithsonite	$ZnCO_3$	734.36 (Naumov, 1976)	146.87	52.15	Reference value used $\Delta G^\circ_{f(298)}$ =– 734.36 kJ/mol
$ZnCO_3 < Zn_2(CO_3)(OH)_2 < Zn_5(CO_3)_2(OH)_6 < (Zn, Fe)CO_3$					
Anhydrous and Hydrated Zinc Oxide Minerals					
Zinccolivenite	$CuZnAsO_4(OH)$	958.25	106.47	22.80*	$CuZnAsO_4(OH) = CuO + ZnO + 0.5As_2O_5 + 0.5H_2O$
Zincospiroffite	$Zn_2Te_3O_8$	1,432.17	110.16	20.28*	$Zn_2Te_3O_8 = 2ZnO + 3TeO_2$
Tsinkalstibit	$Zn_2AlSb(OH)_{12}$	3,286.14	117.36	26.90*	$Zn_2AlSb(OH)_{12} = 0.5Sb_2O_5 + 2ZnO + 0.5Al_2O_3 + 6H_2O$
Adamin	$Zn_2AsO_4(OH)$	1,150.97	127.88	56.78	$Zn_2AsO_4(OH) = 2ZnO + 0.5As_2O_5 + 0.5H_2O$
Legrandite	$Zn_3(AsO_4)_2\cdot 2{,}5H_2O$	2,611.23 (Naumov, 1976)	145.06	33.60*	Reference value used $\Delta G^\circ_{f(298)}$ = – 2,611.23 kJ / mol
Dekloisite	$PbZn_2VO_4OH$	1,518.40	151.84	27.80*	$PbZn_2VO_4OH = 0.5V_2O_3 + PbO + 2ZnO + 0.5H_2O$

Table 2 (continuation): Energy parameters of the formation of oxidized zinc minerals

Mineral name	Formula	$-\Delta G^{\circ}_{f(298)}$, kJ/mol	$-\Delta_f \overline{G}^{\circ}$, kJ/mol · atom	Zn content in the mineral, % mass.	Data used for calculation of $\Delta G^{\circ}_{f(298)}$
Franklinite	$ZnFe_2O_4$	1,065.87 (Naumov, 1976)	152.26	26.90*	Reference value used $\Delta G^{\circ}_{f(298)}$ = – 1,065.87 kJ / mol
Sendekloisite	$(PbZn_2AsO_4OH)$	1,538.32	153.83	26.40*	$(PbZn_2AsO_4OH) = 0.5As_2O_3 + 2ZnO + PbO + 0.5H_2O$
Zincite	ZnO	320.96 (Naumov, 1976)	160.48	80.30	Reference value used $\Delta G^{\circ}_{f(298)}$ = – 320.96 kJ / mol
Yafsoanit	$Ca_3Te_2Zn_3O_{12}$	3,303.06	165.15	25.56*	$Ca_3Te_2Zn_3O_{12} = 3ZnO + 3CaO + 2TeO_2 + O_2$
Moresnetite	$4SiO_2 \cdot 2Al_2O_3 \cdot 3ZnO \cdot 9H_2O$	9,686.41	176.11	28.38* without H_2O	$4SiO_2 \cdot 2Al_2O_3 \cdot 3ZnO \cdot 9H_2O = 4SiO_2 + 2Al_2O_3 + 3ZnO + 9H_2O$
Zinccochromite	$ZnCr_2O_4$	1,379.25	197.03	27.89*	$ZnCr_2O_4 = ZnO + Cr_2O_3$
Ganit	$Zn(Al_2O_4)$	1,903.00	271.85	35.52*	$Zn(Al_2O_4) = Al_2O_3 + ZnO$
$Zn(Al_2O_4) < ZnCr_2O_4 < 4SiO_2 \cdot 2Al_2O_3 \cdot 3ZnO \cdot 9H_2O < Ca_3Te_2Zn_3O_{12} < ZnO < (PbZn_2AsO_4OH) < ZnFe_2O_4 < PbZn_2VO_4OH < Zn_3(AsO_4)_2 \cdot 2{,}5H_2O < Zn_2AsO_4(OH) < Zn_2AlSb(OH)_{12} < Zn_2Te_3O_8 < CuZnAsO_4(OH)$					
Anhydrous and hydrated zinc silicate minerals					
Zinccolibetite	$CuZnPO_4OH$	1,238.42	137.60	27.02*	$CuZnPO_4OH = 0.5P_2O_5 + 0.5H_2O + CuO + ZnO$
Zincylite	$Zn_3Si_4O_{10}(OH)_2 \cdot 4H_2O$	5,574.63	168.92	34.03*	$Zn_3Si_4O_{10}(OH)_2 \cdot 4H_2O = 3ZnO + 4SiO_2 + 5H_2O$
Calamine	$Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$	3,232.87	190.17	54.67	$Zn_4(Si_2O7)(OH)_2 = 4ZnO + 2SiO_2 + H_2O$
Larsenite	$(Pb, Zn)SiO_4$	1,365.57	195.08	45.20	$(Pb, Zn)SiO_4 = PbO + ZnO + SiO_2$
Sokonit	$Zn_3(Si_4O_{10})(OH)_2 \cdot nH_2O$	4,861.17	202.54	38.90* without H_2O	$Zn_3(Si_4O_{10})(OH)_2 \cdot nH_2O = 2ZnO + Zn(OH)_2 + 4SiO_2 + nH_2O$
Willemite	$Zn_2(SiO_4)$	1,529.10 (Naumov, 1976)	218.44	59.13	Reference value used $\Delta G^{\circ}_{f(298)}$ = – 1,529.10 kJ / mol
Gentgelvin	$Zn_4(BeSiO_4)_3S$	5,537.70	240.70	43.70*	$2Zn_4(BeSiO_4)_3S = 2ZnS + 3Be_2SiO_4 + 3Zn_2(SiO_4)$
$Zn_4(BeSiO_4)_3S < Zn_2(SiO_4) < Zn_3(Si_4O_{10})(OH)_2 \cdot nH_2O < (Pb, Zn)SiO_4 < Zn_4(Si_2O_7)(OH)_2 \cdot H_2O < Zn_3Si_4O_{10}(OH)_2 \cdot 4H_2O < CuZnPO_4OH$					
Phosphorous zinc minerals					
Hepeitis	$Zn_3(PO_4)_2 \cdot 4H_2O$	3,613.20 (Naumov, 1976)	144.53	42.67*	Reference value used $\Delta G^{\circ}_{f(298)}$ = – 3,613.20 kJ / mol
Tarbuttite	$Zn_2(PO_4)(OH)$	1,433.60	159.28	53.72*	$Zn_2(PO_4)(OH) = 2ZnO + 0.5P_2O_5 + 0.5H_2O$
$Zn_2(PO_4)(OH) < Zn_3(PO_4)_2 \cdot 4H_2O$					

Note * - Calculated values.

As can be seen from Table 2, each type of oxidized zinc compounds has its own series of reactivity. The values of the average Gibbs atomic energy of the formation of oxidized zinc minerals obtained in this way make it possible to predict the thermodynamic capabilities of the minerals themselves and are interesting for further study of the reactivity of these minerals in relation to certain reagents.

At present, concerned with the increased requirements for the efficiency of using mineral raw materials, the problem of its complex processing and the development of waste-free technology is acute. Hydrochemical methods of treatment of zinc-containing ores (flotation, hydrometallurgy) are widely used in connection with the involvement in the production of ores that are poorer in the content of valuable components of ores, which are not profitable for treating them by pyrometallurgical methods. Since the physicochemical substantiation of hydrochemical processes occurring at the solid-liquid interface is based on the laws of chemical thermodynamics, it was advisable to calculate the average Gibbs atomic energies ($\Delta_f\bar{G}^{\circ}$) for all oxidized zinc minerals, which are a guideline in choosing the optimal conditions for their separation during the selective dissolution of solids (minerals).

Sulfuric acid is an effective solvent for some less thermodynamically stable oxidized zinc minerals (Abdel-Aal, 2000). And also serves as an optimal reagent for the leaching of zinc sulfide minerals (Guler, 2016). The thermodynamic analysis of the interaction of these minerals with sulfuric acid is shown in Table 3. The table shows oxidized zinc minerals such as calamine, smithsonite and the sulfide mineral sphalerite, which is an accompanying mineral in the oxidized zinc ore of the Shaimerden deposit.

Table 3: The change in Gibbs energy $\Delta_r G_T^o$ from the chemical reaction of oxidized and sulfide zinc minerals with sulfuric acid

Reactions	- $\Delta_r G_T^o$, kJ/mol	- $\Delta_r G_T^o$,counting on 1 mol of H_2SO_4, kJ/mol
$ZnS + 4H_2SO_4 \rightarrow ZnSO_4 + 4SO_2 + 4H_2O$	53.07	13.27
$ZnCO_3 + H_2SO_4 \rightarrow ZnSO_4 + CO_2 + H_2O$	75.46	75.46
$Zn_4(Si_2O_7)(OH)_2 \cdot H_2O + 4H_2SO_4 \rightarrow 4ZnSO_4 + 2SiO_2 + 6H_2O$	616.31	154.07

As can be seen from Table 3, the oxidation process of sphalerite (ZnS), smithsonite ($ZnCO_3$) and calamine ($Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$) with sulfuric acid depends not only on the nature of the reactants, but also on the molar ratio of the oxidizing agent. Based on the calculated thermodynamic analysis of the dissolution of oxidized and sulfide zinc minerals with sulfuric acid, the following series of changes Eq.(4) in the standard values of Gibbs energies $\Delta_r G_T^o$ was found (Table 3).

$$ZnS > ZnCO_3 > Zn_4(Si_2O_7)(OH)_2 \cdot H_2O \tag{4}$$

As can be seen from Table 3, the reactivity of calamine and smithsonite in the H_2SO_4 solvent correlates very well with the reactivity of the minerals themselves, which are given above. On the basis of the data obtained, a number of reactivity we compiled (Table 2) and a number the author obtained are confirmed (Ospanov, 2012).

Thus, the fact of relationship between $\Delta_r G_T^o$ and $\Delta_f \bar{G}^0$, previously established by Kh.K. Ospanov (Ospanov, 2012) using the example of the oxidation of some copper sulfides, beryllium minerals, phosphates and silicates in appropriate solvents, is actually confirmed in this study and when considering the occurrence of the probability of the reaction of dissolution of zinc minerals in sulfuric acid.

The considered two parameters $\Delta_r G_T^o$ and $\Delta_f \bar{G}^0$ characterize different properties of the system: the first is the destruction of the crystal lattice under the action of the solvent and the transition of metal ions from the solid phase to the solution (dissolution process), and the second is the difference in the chemical activity of minerals within the limits of similar substances. The observed fact of the relationship between $\Delta_r G_T^o$ and $\Delta_f \bar{G}^0$ the dissolution process of oxidized zinc minerals in sulfuric acid solutions is of great applied importance for the qualitative prediction of the possibility of competing processes occurring within the same type of reactions, similar in mechanism, when a strict quantitative assessment of thermodynamic properties is difficult due to the uncertain composition of the reaction products.

The results of thermodynamic calculations we obtained make it possible to distinguish the most reactive oxidized zinc minerals, so that in future, when treating the oxidized zinc ores, to know about the properties and characteristics of these minerals. The advantage of our work is that data analysis allows us to involve in the treatment of the oxidized zinc minerals with an industrially acceptable zinc content (hydrozincite, zincrosazite, smithsonite, calamine, adamine, willemite and others). This makes it possible to increase the economic efficiency of zinc hydrometallurgy.

4. Conclusions

The values of the average Gibbs atomic energy of formation $\Delta_f \bar{G}^0$ for large amounts of oxidized zinc minerals are calculated. On the basis of a comparison of this value, the reactivity of these minerals was determined and rows were compiled for the same type of groups according to the increase in their reactivity.

The Gibbs energies $\Delta_r G^o_T$ were determined from the chemical reaction of sphalerite (ZnS), smithsonite ($ZnCO_3$) and calamine ($Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$) with sulfuric acid, and the following data were obtained per 1 mol of H_2SO_4: for sphalerite (13.27 kJ/mol), for smithsonite (75.46 kJ/mol) and for calamine (154.07 kJ/mol). The following series of changes in the standard values of Gibbs energies $\Delta_r G^o_T$ was established: ZnS > $ZnCO_3$> ($Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$). The given series of changes in the standard values of Gibbs energies correlates very well with the reactivity of the minerals themselves.

The analysis of the obtained thermodynamic calculations makes it possible to involve in the treatment of oxidized zinc minerals with an industrially acceptable zinc content, such as hydrozincite ($Zn_5(CO_3)_2(OH)_6$), zincrosazite ($Zn_2(CO_3)(OH)_2$), smithsonite ($ZnCO_3$), calamine ($Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$), adamine ($Zn_2AsO_4(OH)$), willemite ($Zn_2(SiO_4)$), which can improve economic efficiency.

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