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Thermodynamics of tungsten ores decomposition process options

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Abstract: The thermodynamics of tungsten ore decomposition in mineral acid and alkaline solutions were studied. The published thermodynamic data of tungsten minerals were collected and assessed. The Gibbs energies of CaWO_4 (−1538.43 kJ/mol), FeWO_4 (−1053.91 kJ/mol), MnWO_4 (−1206.08 kJ/mol), H_2WO_4 (−1003.92 kJ/mol), and Na_2WO_4 (−1455.58 kJ/mol, aq) at 25 °C were adopted in the calculation using HSC software. The results show that CaWO_4 is decomposed more readily in Na_2CO_3 solution than in NaOH, while FeWO_4 and MnWO_4 are more reactive in NaOH solutions. From a thermodynamic point of view, tungsten ore decomposes easily in acid solutions despite most ΔG_f° increasing slightly with temperature. Oxidizing Fe^{2+} to Fe^{3+} in acidic solutions facilitates decomposition of FeWO_4 , and the reaction of CaWO_4 in H_2SO_4 solution occurs more easily than in other mineral acids, due to the formation of sparsely soluble CaSO_4 . The results fit well with the experimental data and industrial experience previously reported in the literature.

Keywords: Scheelite; Wolframite; Mineral acid; Alkaline media; Gibbs energy

1. Introduction

Tungsten, a strategic and rare metal, has a wide range of industrial applications, such as hard materials, high temperature technology, lighting, X-ray technology, machine and engine construction, chemical industry, laser technology, armaments and aerospace industry. The key properties are low vapor pressure and thermal expansion, high density and melting point, good thermal and electrical conductivity, and high modulus of elasticity [1, 2]. Due to the lack of viable substitutes, the European Union has included tungsten in the list of critical raw materials [3]. Similarly, the British Geological Survey ranked it as number two in a supply list containing forty one critical elements [4]. The main tungsten minerals in nature are scheelite (CaWO_4) and wolframite ($(\text{Fe,Mn})\text{WO}_4$), with approximately two-thirds of the world tungsten reserves consisting of scheelite [1, 2]. China has more than 60% of tungsten reserves in the world, and accounts for about 80% of the world tungsten production [5]. Ammonium paratungstate (APT), as the main intermediate in industrial tungsten production, is usually obtained from tungsten concentrates by a caustic/soda or hydrochloric acid treatment [6].

In modern industrial production technologies, caustic digestion is employed to treat wolframite producing soluble sodium tungstate and insoluble iron or manganese hydroxide at either atmospheric pressure (75–145 °C), in concentrated NaOH solutions (≥ 10 mol/L) [7], or under high pressures (135–255 °C), in a dilute NaOH solution (1.25–3.75 mol/L) [8]. When tungsten concentrate contains scheelite, Na_2CO_3 is added in NaOH solution to extract tungsten in an autoclave operating under elevated pressures (180–310 °C) [9]. Subsequently, solvent extraction or ion exchange is used to convert Na_2WO_4 to $(\text{NH}_4)_2\text{WO}_4$, which requires excess acid to treat the Na_2WO_4 solution and a large amount of water to dilute the leach solution [10]. Obviously, the caustic/soda leaching method needs a large excess of reagents, and discharges huge volumes of high-salinity wastewater [11]. Furthermore, Leal–Ayala et al. [12] pointed out that 4% of tungsten would be lost in the APT production.

Acid processing, as a classical method, can avoid the use of high temperatures and a large excess of leaching reagents, and treating or even discharging large amounts of sodium salts solutions. Hydrochloric acid, nitric acid, or sulfuric acid is used to decompose tungsten ores and produce insoluble tungstic acid. However, a solid or colloidal H_2WO_4 layer was observed covering the surfaces of the unreacted tungsten particles, thus

hindering the reaction rate and yield. Therefore, some strategies are usually adopted to increase the feasibility, such as reducing particle size [13], using a large excess of concentrated HCl [14], utilizing heated ball mill reactors [15], and employing organic acids to dissolve solid tungstic acid [16].

Additionally, many researchers have focused on decomposing tungsten concentrates to produce soluble tungsten compounds. Martins leached synthetic scheelite in hydrochloric or nitric acid at pH 1.5–3.0 in a temperature range of about 25–100 °C to obtain soluble metatungstates [17, 18]. Potashnikov et al. [19] and Kalpakli et al. [20] treated scheelite by oxalic acid to form soluble hydrogen aqua oxalate tungstate ($H_2[WO_3(C_2O_4)H_2O]$). Hydrochloric, nitric or sulfuric acid in the presence of phosphorus was found to decompose scheelite and form a water-soluble phosphotungstic acid chelate compound (12-tungstophosphoric heteropoly acid, $H_3PW_{12}O_{40}$) [21–24]. In previous work, we systematically studied the conversion of scheelite and mixed scheelite-wolframite concentrate in sulfuric acid, and found that the tungsten concentrates can be completely converted in H_2SO_4 solutions by adding an oxidizing agent and controlling the H_2WO_4 formation in moderate acid concentrations [25, 26].

Even though tungsten extraction technology has been developed for more than a hundred years since R. Oxiland in 1874 [1], there is limited thermodynamic information on the tungsten leaching chemistry. Osseo-Asare [27] applied the Pourbaix diagram concept to tungsten hydrometallurgy, but stated a lack of sufficient thermodynamic data. Martins [28] determined the equilibrium constants for wolframite and scheelite leaching systems, and also pointed out some inherent limitations due to the estimation of selected thermodynamic data. Zhao and Li [29] used a pseudo-ternary-system phase diagram to explain scheelite digestion in high concentration NaOH and Na_2CO_3 solutions.

Therefore, this paper focuses on collecting and assessing the thermodynamic data of tungsten minerals previously published. Gibbs free energy changes versus temperature were calculated with HSC software for tungsten minerals decomposing in mineral acid and alkaline solutions, using the adopted thermodynamic data. The calculations were finally compared with the experimental and industrial results previously reported in the literature. This work is beneficial to better understanding of various technologies in industrial tungsten processing.

2. Thermodynamics

2.1 Thermodynamic equation

For a chemical reaction, the Gibbs standard free energy as a function of temperature can be calculated by following equations:

$$\Delta G_T^o = \Delta H_T^o - T \times \Delta S_T^o \quad (1)$$

$$\Delta H_T^o = \Delta H_{298}^o + \int_{298}^T \Delta C_p dT \quad (2)$$

$$\Delta S_T^o = \Delta S_{298}^o + \int_{298}^T \frac{\Delta C_p}{T} dT \quad (3)$$

$$\Delta G_T^o = \Delta G_{298}^o - (T - 298)\Delta S_{298}^o + \int_{298}^T \Delta C_p dT - T \int_{298}^T \frac{\Delta C_p}{T} dT \quad (4)$$

where, ΔG_T^o is the standard Gibbs energy of reaction at temperature T, ($kJmol^{-1}$); ΔH_T^o the standard enthalpy of reaction at temperature T, ($kJmol^{-1}$); ΔS_T^o the standard entropy of reaction at temperature T, ($Jmol^{-1}$); ΔC_p the molar heat capacity of reaction at constant pressure at temperature T, ($Jmol^{-1}K^{-1}$); T is the temperature (K).

In order to calculate more accurate ΔG_T^o , the estimation of the heat capacity term ΔC_p plays a critical role. Barner and Kust [30] has assessed the various approaches for estimating ΔC_p . The molar heat capacity C_p of each substance relating to temperature T was used in the calculation, as shown in empirical equation (5).

$$C_p = A + BT \cdot 10^{-3} + CT^{-2} \cdot 10^5 + DT^2 \cdot 10^{-6} \quad (5)$$

The general equation describing the temperature dependence of equilibrium constant can be derived from

equation (6). The determination of equilibrium constants is dependent on the availability of the relevant thermodynamic data, and this knowledge is essential for understanding the leaching processes, especially when taking the substance concentration into account.

$$\ln K = \frac{-\Delta G_f^o}{RT} \quad (6)$$

2.2 Thermodynamic data

Standard-state thermochemical properties are prerequisites for the modeling of chemical reactions. Various thermodynamic properties of tungsten compounds have been reported. However, there is no assessment of the thermodynamic data available. So the primary target is to select the reliable data for tungsten compounds.

A number of values of ΔH_f^o have been reported for scheelite (CaWO_4) at 298 K. The proposed value changes in the range of -1623.00 to -1683.70 kJmol^{-1} , as reviewed by Wood and Samon [31], and the adopted value is -1645.1 kJmol^{-1} . This value is widely accepted by Lange's Handbook of Chemistry [32], HSC software [33], and last by Martins [28]. King and Weller [34] determined the heat capacity of scheelite at low temperatures (up to 298.15 K), and from this they derived a third law entropy, $S_{298}^o = 126.4$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}$, which has been adopted in all major compilations of thermodynamic data on scheelite. Combined with the heat capacity of scheelite (298–1000 K) from Barin and Knacke [35], the parameters for temperature dependence of C_p are obtained. The values of ΔH_{298}^o and S_{298}^o result in $\Delta G_{298}^o = -1538.43$ $\text{kJ}\cdot\text{mole}^{-1}$. The thermodynamic data adopted for scheelite are shown in Table I.

Table I. Adopted thermodynamic data for tungsten compounds

Compound	ΔH_{298}^o	ΔG_{298}^o	S_{298}^o	$C_p = A + BT \cdot 10^{-3} + CT^{-2} \cdot 10^5 + DT^2 \cdot 10^{-6}$			
				A	B	C	D
CaWO_4	-1645.10	-1538.43	126.4	134.56	20.67	-24.4	0
FeWO_4	-1154.80	-1053.91	131.8	132.42	29.75	-23.93	0
MnWO_4	-1035.83	-1206.08	127.4	120.68	36.51	-3.69	0
H_2WO_4	-1131.77	-1003.92	112.6	13.25	350.6	10.1	-186
$\text{Na}_2\text{WO}_4(\text{aq})$	-1554.02	-1455.58	160.3	105.41	118	0	0

ΔH_{298}^o and ΔG_{298}^o , kJmol^{-1} ; S_{298}^o and C_p , $\text{Jmol}^{-1}\text{K}^{-1}$

Similarly to scheelite, the values of ΔH_f^o reported for ferberite (FeWO_4) at 298 K have been also reviewed by Wood and Samon [31]. As with scheelite, the standard entropy of ferberite, $S_{298}^o = 131.8$ $\text{JK}^{-1}\text{mole}^{-1}$, was calculated from the low-temperature calorimetric measurements of heat capacity by Weller [36]. This value was adopted in this research. Combined with the heat capacity of ferberite (5–500 K), measured by Lyon and Westrum [37] using adiabatic calorimetry, the parameters for temperature dependence of C_p were fitted by HSC software. However, there are big differences in the values of ΔH_{298}^o and ΔG_{298}^o for ferberite. The more negative values are in the range -1184 to -1192 kJmol^{-1} and -1085 to -1089 kJmol^{-1} , while the opposed higher values range from -1154 to -1158 kJmol^{-1} and -1054 to -1057 kJmol^{-1} [31]. We favor the higher values because thermodynamic calculation result show an accordant trend with the experimental results [26], while the more negative values seem more suited to pyrometallurgical calculations. So we accept, respectively, -1154.8 and -1053.91 kJmol^{-1} for ΔH_{298}^o and ΔG_{298}^o of ferberite in this paper, which was also accepted in the recent research of Martins [28] and Lange's Handbook of Chemistry [32].

There are limited thermodynamic data available for huebnerite (MnWO_4). In the HSC Database, the ΔH_{298}^o , ΔG_{298}^o , and S_{298}^o for huebnerite are -1305.83 kJmol^{-1} , -1053.08 kJmol^{-1} , and 140.58 $\text{JK}^{-1}\text{mole}^{-1}$, respectively. These data, together with the parameters for C_p , originate from Barin and Knacke [35], and they are very similar to the values adopted by Horner [38].

The thermodynamic value for H_2WO_4 , ΔG_{298}^o , is in the range of -1003.9 to -1006.9 kJmol^{-1} except for the estimate by Osseo-Asare [27], which has been compared by Martins [28]. The value in the HSC Database is -1003.92 kJmol^{-1} , similar to Lange's Handbook of Chemistry [32]. This was adopted in the calculations together with the other data.

The ΔG_{298}^o of Na_2WO_4 in aqueous solution was reviewed by Martins [28], ending up with a value of about -1455 kJmol^{-1} . This value is also available in the HSC Database. As for CaWO_4 and FeWO_4 , the entropy, $S_{298}^o = \sim 160.3$ $\text{JK}^{-1}\text{mole}^{-1}$, was calculated from low-temperature calorimetric measurements of heat capacity by King and Weller [34]. Combined with the heat capacity in Barin and Knacke [35], the parameters for temperature dependence of C_p were fitted at temperatures of 275–800 K (see Table I).

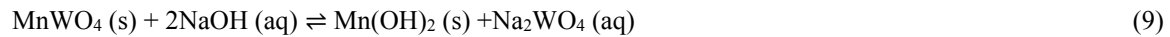
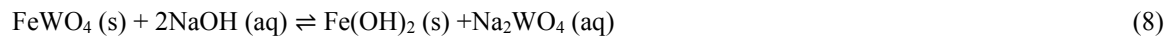
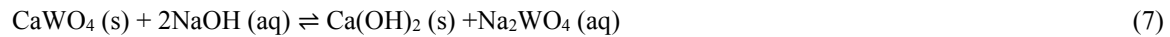
The adopted thermodynamic data for tungsten compounds are presented in Table I. The other data for substances used in the calculation were taken from the HSC Database. They are close to the values adopted by Martins [28], except the C_p parameters.

3. Thermodynamic results

3.1 Tungsten ores decomposing in NaOH and Na_2CO_3 solutions

The decompositions of tungsten ores (CaWO_4 , FeWO_4 , and MnWO_4) in NaOH and Na_2CO_3 solutions are expressed with equations (7)–(12). The standard Gibbs energy changes versus temperature for these reactions are depicted in Fig. 1 and Fig. 2 for sodium hydroxide and carbonate solutions, respectively.

In NaOH solutions



In Na_2CO_3 solutions

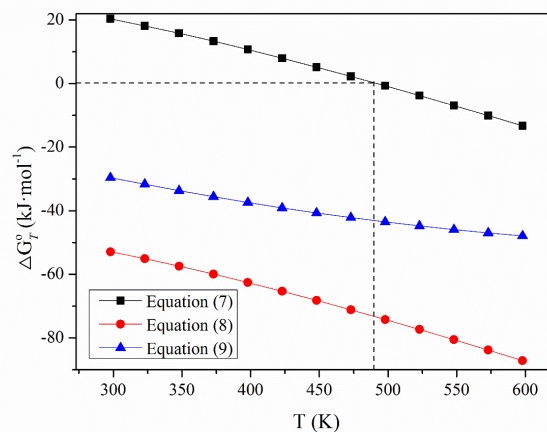
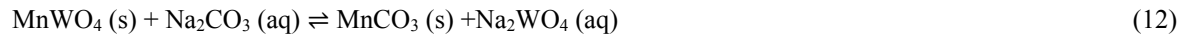
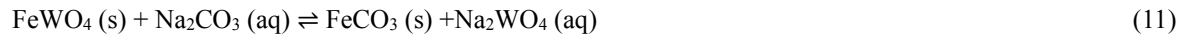
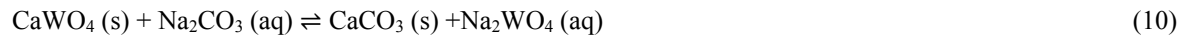


Fig. 1 Standard Gibbs energy changes versus temperature of tungsten ores decomposing in NaOH solutions.

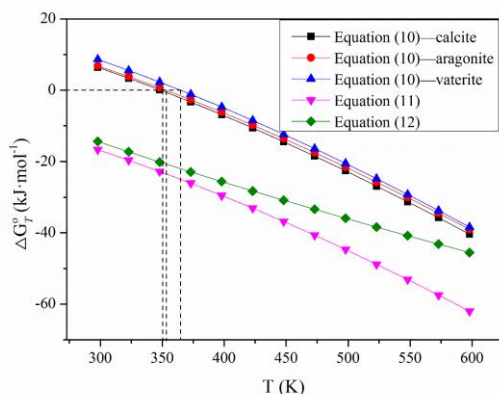
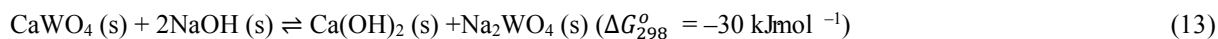


Fig. 2 Standard Gibbs energy changes versus temperature of tungsten ores decomposing in Na_2CO_3 solutions.

The results in Fig. 1 indicate that raising temperature favors the decomposition of tungsten ores in NaOH solution thermodynamically, especially for CaWO_4 . The standard Gibbs energy change of CaWO_4 becomes negative at the temperature of above about 220 °C, while for FeWO_4 and MnWO_4 it decreases slightly with increasing temperature but is negative over the whole temperature range. The results indicate that the decomposition of CaWO_4 in NaOH solutions should be done at elevated temperatures.

When these tungsten compounds are decomposed in Na_2CO_3 solutions, as shown in Fig. 2, the trend is similar to that in NaOH solutions. However, the temperature, at which the standard Gibbs energy change of CaWO_4 decomposition in Na_2CO_3 solutions becomes negative, significantly decreases to ~75 °C, 80 °C, and 90 °C when producing calcite, aragonite, and vaterite, respectively. The standard Gibbs energy changes of FeWO_4 and MnWO_4 decomposition in Na_2CO_3 solutions are more positive than in NaOH solutions at the same temperature.

It should be noted that the equilibrium constants of CaWO_4 decomposition in NaOH and Na_2CO_3 solutions are positive at temperatures above 50 °C and 25 °C, respectively, as reported by reference [28]. These results differ from the above calculation according to equation (6). Wan et al. [39] synthesized scheelite by adding $\text{Ca}(\text{OH})_2$ into Na_2WO_4 solution in a temperature range of 20–110 °C. However, Zhao et al. [40] studied the kinetics of sodium hydroxide leaching of scheelite at 60–100 °C. The results seem to be in disagreement. Considering that Zhao et al. [40] used NaOH concentrations in the range of 8–16 mol/L, these conditions cannot be assumed to be ideal as adopted in thermodynamic calculation. Kinetic theory can be used to explain those results. Chen et al. [41] extracted tungsten mechanochemically using caustic processing of scheelite according to reaction (13), and found a reverse reaction when washing the products in water. So NaOH concentration plays a key role in CaWO_4 decomposition. This is evidence that our thermodynamic calculation is reliable for CaWO_4 decomposing in NaOH solutions.



Furthermore, the stability of the products seems to influence the thermodynamic reaction sequence based on Fig. 1 and Fig. 2, especially for scheelite which has a very small equilibrium constant. The solubility product K_{sp} values at 298 K for $\text{Ca}(\text{OH})_2$, CaCO_3 , $\text{Fe}(\text{OH})_2$, FeCO_3 , $\text{Mn}(\text{OH})_2$, and MnCO_3 are $10^{-4.38}$, $10^{-7.91}$ (calcite), $10^{-8.22}$ (aragonite), and $10^{-8.47}$ (vaterite), $10^{-16.31}$, $10^{-10.5}$, $10^{-12.72}$ and $10^{-10.63}$, respectively [32, 42], which is in accordance with thermodynamic calculation sequence. Chen et al. [41] used a 0.1 M Na_2CO_3 solution washing the compositions of Na_2WO_4 and $\text{Ca}(\text{OH})_2$ by forming more stable CaCO_3 and added $\text{Al}(\text{OH})_3$ to the co-grinding of CaWO_4 and NaOH for producing more stable katoite [$\text{Ca}_3\text{Al}_2(\text{OH})_{12}$] and in order to avoid the reverse reaction. All these observations verify the above analysis.

3.2 Tungsten ores decomposing in mineral acid

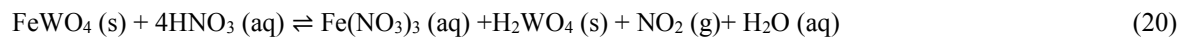
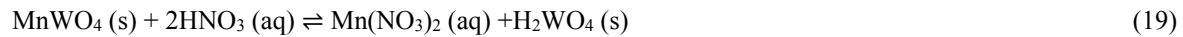
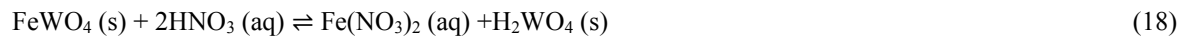
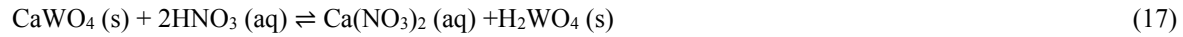
The decompositions of tungsten ore (CaWO_4 , FeWO_4 , and MnWO_4) in HCl, HNO_3 , and H_2SO_4 solutions

occur according to reactions (14)–(23). The oxidation of Fe^{2+} to Fe^{3+} is also taken into account below, due to the strong oxidation power of HNO_3 solutions.

In HCl solutions



In HNO₃ solutions



In H₂SO₄ solutions

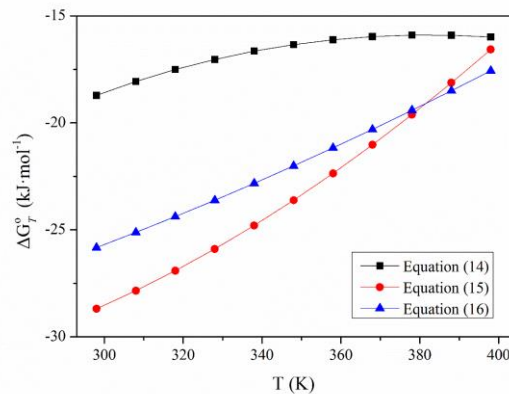
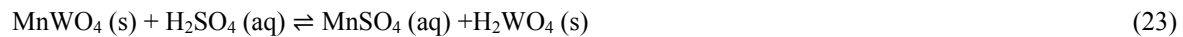
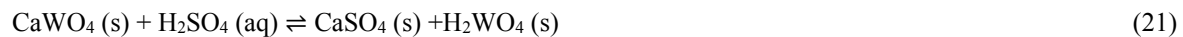


Fig. 3 Standard Gibbs energy changes versus temperature for tungsten ore decomposition in HCl solutions.

As seen in Fig. 3, raising temperature does not favor the tungsten ore decomposition in HCl solutions thermodynamically. The standard Gibbs energy changes of CaWO_4 , MnWO_4 , and FeWO_4 decomposition increase slightly, but keep a relatively negative value with increasing temperature. In addition, the preferential conversion order or driving force of reaction is $\text{FeWO}_4 > \text{MnWO}_4 > \text{CaWO}_4$ at $<100^\circ\text{C}$, from a thermodynamic point of view.

The relationships of the standard Gibbs energy changes of CaWO_4 , MnWO_4 , and FeWO_4 decomposition in HNO_3 solutions versus temperature are depicted in Fig. 4, showing similar trends as in HCl solutions. Considering the oxidation of ferrous to ferric by HNO_3 , the standard Gibbs energy change of FeWO_4 decreases significantly in HNO_3 solution. This implies that the equilibrium end product in the solution has an obvious influence on the decomposition.

Fig. 5 presents the standard Gibbs energy changes versus temperature for the decomposition of CaWO_4 , MnWO_4 , and FeWO_4 in H_2SO_4 solutions. The trends for FeWO_4 and MnWO_4 are similar to those in HCl and HNO_3 solutions. The standard Gibbs energy change of CaWO_4 notably decreases in H_2SO_4 solutions. The effect may be increased by the lower concentration of Ca^{2+} compared to Fe^{2+} and Mn^{2+} in the leaching solutions, due to the formation of sparingly soluble CaSO_4 ($K_{\text{sp}} = 10^{-4.38}$). The solubility of CaSO_4 decreases with increasing temperature [43, 44], which further explains this trend reversal.

Our previous research [26] showed that increasing Fe^{2+} in the solution hinders the FeWO_4 decomposition, while oxidation of Fe^{2+} to Fe^{3+} or/and renewing the acid solution by a two-stage decomposition favors FeWO_4

reaction. This explains the impact of oxidization by HNO_3 in Fig. 4 and the difference between scheelite and wolframite decomposition in sulfuric acid in Fig. 5.

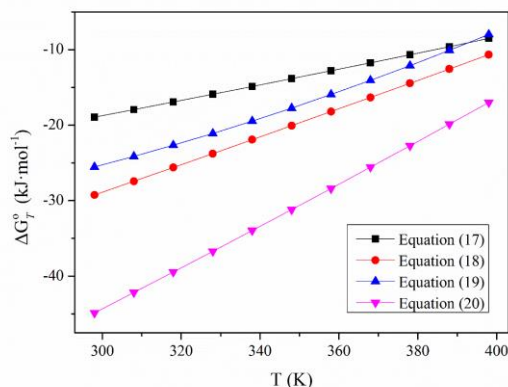


Fig. 4 Standard Gibbs energy changes versus temperature of tungsten ore decomposition in HNO_3 solutions.

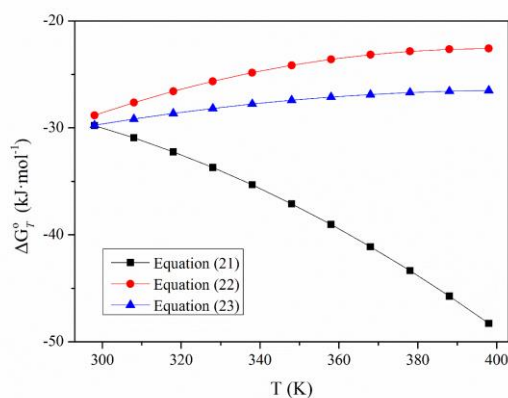


Fig. 5 Standard Gibbs energy changes versus temperature of tungsten ore decomposition in H_2SO_4 solutions.

The current thermodynamic results give an explanation of wolframite treatment by caustic soda when scheelite is digested by soda in modern industrial APT practices. When tungsten ore is decomposed in acid solutions, a solid H_2WO_4 product layer will form on the surfaces of unreacted tungsten mineral particles. It can be dissolved incorporating actions, such as controlling the acid concentration and adding an oxidizing agent [25, 26, 45]. Due to the absence of thermodynamic data, unfortunately, this paper does not carry out a detailed thermodynamic analysis on tungsten ore decomposition to $\text{H}_2[\text{WO}_3(\text{C}_2\text{O}_4)\text{H}_2\text{O}]$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

4. Conclusion

Thermodynamics is fundamental in metallurgical research. It plays an active role in high-temperature metallurgy, but seems to have been left out of hydrometallurgy in recent years. This paper studied the thermodynamics of tungsten ore decomposition, combining the available experimental and industrial experience. The previously published thermodynamic data of tungsten minerals were assessed to obtain a more reliable thermodynamic picture. The results explain why, in modern industrial APT practice, wolframite is usually treated with caustic soda while scheelite is treated with soda ash. Tungsten ores decompose easily in acid solutions from a thermodynamic point of view. The concentration of metal ion influences the decomposition of tungsten ores, which can be explained by kinetics, such as oxidizing to high valence ion, forming insoluble product, and multi-step decomposition. For that purpose, a dilute solution approach is inadequate in strong e.g. caustic or salt solutions, and proper solution models are needed to describe the solution properties accurately [46, 47]. This work is beneficial for further understanding the tungsten minerals decomposition process thermodynamically.

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