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Abstract: Bastnaesite, monazite and xenotime are rare earth minerals (REMs) that are typical sources for rare earth elements (REEs). To advance the understanding of their leaching and precipitation behavior in different hydrometallurgical processes, Eh-pH diagrams were constructed and modified using the HSC 9.9 software. The aqueous stability of rare earth elements in H₂O and acid leaching systems, i.e., the REE-Ligands-H₂O systems, were depicted and studied based on the Eh-pH diagrams. This study considers the most relevant lixiviants, their resulting equilibrium states and the importance in the hydrometallurgical recovery of rare earth elements (REMs). A literature review was performed summarizing relevant Eh-pH diagrams and associated thermodynamic data. Shifting stability regions for REEs were discovered with additions of acid ligands and a narrow stability region for soluble REE-(SO₄/Cl/NO₃) complexes under highly acidic conditions. As such, the recovery of REEs can be enhanced by adjusting pH and Eh values. In addition, the Eh-pH diagrams of the major contaminants (i.e., Fe, Ca and Al) in leaching systems were studied. The resulting Eh-pH diagrams provide possible insights into potential passivation on the particle surfaces due to the formation of an insoluble product layer.

Keywords: Eh-pH diagrams; rare earth minerals; rare earth elements; leaching; solution stability

1. Introduction

Rare earth elements (REEs) are indispensable constituents in many industrial applications including fuel cells, mobile phones, permanent magnets, lamp phosphors, rechargeable batteries and catalysts [1,2]. With the increasing demand and concerns over restricted or constricting supply, increased importance has been assigned to the improvement and recovery of REEs from REE-bearing minerals. The principal mineral sources for REEs are monazite, bastnaesite and xenotime [3]. In addition to the primary mineral sources, it has also become increasingly crucial to recycle REEs from end-of-life products, such as permanent magnets, fluorescent lamps, batteries and catalysts, which contain a fair amount of REEs [4–7]. REE primary and secondary sources are often treated with physical separation processes followed by hydrometallurgical methods. In broad terms, froth flotation is used to produce a REE mineral concentrate followed by leaching, solvent extraction and/or selective precipitation to extract the REEs from their mineral matrix [3,8].

The behavior of REEs during leaching processes is typically evaluated using Eh-pH diagrams. Eh-pH diagrams, also known as Pourbaix diagrams, have played a significant role in understanding the aqueous stability of species that are thermodynamically stable within certain regions of redox potential and pH. The application of Eh-pH diagrams is especially useful when multiple elements, which may interact with each other, co-exist in a solution. In addition, the study of Eh-pH diagrams can help improve the feasibility of the recovery/recycling of REEs by presenting the stable REE species in aqueous solutions regarding the critical processing conditions (i.e., pH, Eh and acid ligands). The Eh-pH diagrams of rare earth metals were initially reported by Pourbaix in 1966 [9], which



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considered REEs only in an H_2O system. Brookins (2012) [10] later presented the Eh-pH diagrams with REEs in carbonate systems in 1988. Hayes et al. (2002) [11] further studied the Eh-pH diagrams of cerium (Ce) species in HClO₄ and H₂O systems with updated thermodynamic data. The early studies of Eh-pH diagrams for REEs focused on their aqueous stability within simple systems, thereby lacking specific applications for more complex systems.

Recently, there have been several important additions to the aqueous stability of REEs that considered the effects of mineralogy. Kim et al. (2012) [12] established the Eh-pH diagrams of REEs in monazite during a hydrometallurgical process, which covered REE-H₂O, REE-SO₄-H₂O, REE-PO₄-H₂O and REE-PO₄-SO₄-H₂O systems, respectively. Their study of Th/REE-H₂O systems revealed notable differences between Th and REEs (Ce, Nd and La). Eh-pH diagrams revealed that Ce³⁺, Nd³⁺ and La³⁺ have higher solubilities under slightly alkaline conditions while Th⁴⁺ only exists in strongly acidic conditions. The results show that most of the REEs (Ce, Nd and La) exist stably in aqueous solutions in their trivalent or tetravalent ionic forms at neutral or acidic conditions. As pH increases to alkaline conditions (pH > 7.5), the insoluble REE hydroxides (Nd(OH)₃, La(OH)₃ and $Ce(OH)_3$) start to form. This supports the theory of the separation between Th oxide (forms at pH > 1.5) and REE hydroxides by solution pH manipulation. Moreover, the insoluble product layer (Th oxide and REE hydroxides) may result in passivation on the mineral surface under alkaline conditions. In REE- (F/PO_4) - H_2O systems, REEs show a propensity to combine with PO_4^{3-} and F^- to form insoluble rare earth phosphates or fluorides within certain pH ranges. Similarly, in REE-H₂O systems, Th and REEs (Ce, Nd and La) in REE-(F/PO₄)-H₂O systems form insoluble products at various pH values. REE phosphates form at pH > 6 while Th phosphate occurs at pH > 0. Thermodynamic data of REE species with suspected variations in crystallinities were applied and the resulting Eh-pH diagrams were compared in Kim's study. The comparison between the stabilities of REE phosphates with different crystalline forms revealed the relationship between monazite dissolution and its crystallinity. It was suggested that naturally occurring monazite ores are more crystalline with higher chemical stability, and less easily dissolved in acid owing to the higher bond energy. Moreover, Kim et al. (2012) [12] examined the effect of sulfate (SO_4^{2-}) concentrations on the stability regions of REEs. In REE-SO₄-H₂O and REE-PO₄-SO₄-H₂O systems, SO_4^{2-} combines with REEs as a complexing ligand that favors the stabilization of REE-SO₄ compounds in solution. In the Eh-pH diagrams by Kim et al., the stability domains of insoluble REE products (REE oxides, REE hydroxides, REE phosphates and REE sulfates) diminished as the SO_4^{2-} concentration increased. Meanwhile, the stability regions of soluble Th/Ce-SO₄ complexes extended with increasing SO_4^{2-} concentration but decreased with an elevation in temperature. Their results are well aligned with the decomposition of monazite in sulfuric acid lixiviants.

Shuai et al. (2017) [13] studied the aqueous equilibrium of bastnaesite in hydrochloric acid leaching systems. Their results showed that trivalent REEs (REE^{3+}) are stable in leaching solutions at a certain acidity (pH < 2), while tetravalent cerium and thorium (Ce^{4+}/Th^{4+}) remain in solid forms. The Eh-pH diagrams in the REE/Th-Cl-H₂O system indicate that trivalent REE ions (REE³⁺) leach into solution at pH values below 6, whereas Ce⁴⁺ and Th⁴⁺ require pH values below 0 and 2, respectively. At pH values below 0, Ce^{4+} can be partially reduced to Ce^{3+} to form CeF_3 precipitates when F^- is present. This result indicates that the separation between REE^{3+} and Ce^{4+}/Th^{4+} can be achieved by manipulating the pH during leaching, which agrees with the leaching data presented later in this study. In addition, Al-Nafai (2015) [14] studied the Eh-pH diagrams of bastnaesite in nitric acid systems. CeNO₃²⁺, LaNO₃²⁺ and NdNO₃²⁺ were found to be stable species in their trivalent state under neutral to acidic conditions with nitrate ions. As the concentration of nitric acid decreases, the stability regions of REE-NO₃ species narrow and eventually disappear from the corresponding Eh-pH diagrams due to the lack of nitrate ions. REEs exist in a soluble form as nitrates below pH 2 and precipitate in sequence as fluorides, fluorine-carbonates and hydroxides, respectively, as the solution pH is increased.

Agarwal et al. (2018) [15] studied monazite and bastnaesite systems with a focus on the yttrium (Y) species in sulfate, nitrate and chloride solutions. The results showed that free Y^{3+} ions are dominant in all considered systems below pH 5 while YSO₄⁺ and YCl²⁺ co-exist with Y^{3+} in the matrix of sulfuric and hydrochloric acids, respectively. Eh-pH diagrams were also compared with speciation diagrams, which depicted the distribution of the Y species in solution as a function of pH at a constant Eh value. The findings from the speciation and Eh-pH diagrams were consistent. Although Agarwal's work revealed the aqueous speciation of yttrium after acid leaching, further speciation investigations are needed to describe the leaching and precipitation processes.

The objective of this study was to determine, from the literature, the appropriate thermodynamic values required to construct Eh-pH diagrams for systems not previously studied and, by so doing, promote a deeper understanding of the dissolution and precipitation processes that are critical to the extraction of REEs from RE minerals. It is anticipated that this work will provide insights into the processing of a wide variety of primary and secondary REE sources. As an example of secondary sources, other researchers found that coal and coal byproducts could be a promising alternative source for REEs [16–19]. RE phosphate minerals (apatite, monazite and xenotime) are discovered as most commonly presented rare earth mineral in coal sources [20–22]. There is also evidence to support the presence of ion-exchangeable REEs in coal byproducts [23,24]. To investigate the thermodynamic aqueous equilibrium of several pertinent systems, literature was consulted for the appropriate elements combined with the associated lixiviant. As shown in Table 1, there have been significant contributions made in the domains of interest. This work will seek to explore the equilibrium data needed to study the effects on leaching and precipitation based on the data from previous leaching tests (as shown in Table 2).

Lixiviant	Bastnaesite (Ce,La)(CO ₃)F	Monazite (Ce,La,Nd,Th)PO ₄	Xenotime YPO ₄
H_2SO_4	Current Study	Kim et al. [12]	Agarwal et al. [15]
HCl	Shuai et al. [13]	Current Study	and
HNO ₃	Al-Nafai [14]	Current Study	Current Study

Table 1. Eh-pH diagrams of three minerals in different acid leaching systems.

Table 2. Parameters in the acid leaching tests reported in this study.

Materials	Acid Type	Acid Conc.(M)	Stirring Speed (rpm)	Temperature(K)	S/L Ratio (g/L)	Time (min)	Particle Size (<mesh)< th=""></mesh)<>
Pure minerals (monazite, bastnaesite, xenotime)	H ₂ SO ₄ , HCl, HNO ₃	1.0	530	298	10	5, 15, 30, 60, 90, 120	80

The highlights of this study are as follows:

- A review of existing research on Eh-pH diagrams and thermodynamic data of REE-Ligands-H₂O systems;
- Development of Eh-pH diagrams for Bastnaesite-H₂SO₄, Monazite-HCl, Monazite-HNO₃ and Xenotime-H₂SO₄/HCl/HNO₃ systems;
- A possible explanation for low Ce recoveries and passivation in tested monazite minerals;
- A likely reason for the lower performance of HCl lixiviant compared to HNO₃ and H₂SO₄ for bastnaesite leaching.

2. Materials and Methods

2.1. Rare Earth Minerals in Leaching Systems

Bastnaesite, monazite and xenotime account for the majority of the REE production from a variety of recognized RE ores [8,25]. For the construction of Eh-pH diagrams, these three minerals are considered as the likely dominant RE sources and thus were the focus in the construction of the corresponding Eh-pH diagrams for the RE minerals-ligands-H₂O systems during acid leaching. The major species studied in the leaching of bastnaesite (chemical formula: (Ce, La)(CO₃)F) are Ce, La and F. Monazite (chemical formula: (Ce, La, Nd, Th)PO₄) is a RE phosphate mineral with a relatively high HREE composition compared to bastnaesite [8]. The Eh-pH diagrams for monazite leaching focused on the (Ce/La/Nd/Th)-PO₄-Ligands-H₂O systems. Xenotime (chemical formula: Y(PO₄)), unlike bastnaesite and monazite, is particularly enriched in large quantities of yttrium and other heavy rare earth elements. The development of the Eh-pH diagrams for xenotime leaching systems consist mostly of yttrium and acid ligands in H₂O and an objective of the study.

Concentrate samples of the three RE minerals (bastnaesite, monazite and xenotime) were obtained from the Mineralogical Research Company (San Jose, CA, USA) and used in leaching experiments to provide data for comparison with the Eh-pH diagrams. The monazite sample, which originated from Eureka Farm 99 (Stiplemans mine operation), Namibia, contained about 10% total REEs, including 5.7% Ce, 3.2% La, and 1.0% Nd, while the other REEs accounted for less than 0.1%. As such, the chemical formula representing the mineral type is most likely (Ce_{0.6}La_{0.3}Nd_{0.1})PO₄. The bastnaesite sample ((Ce_{0.5}La_{0.25}Nd_{0.25})CO₃F) was mined from Oregon No. 2 pegmatite from an operation located in Jefferson County, CO. The sample contained 25% total REEs (TREEs), which included 12.5% Ce, 4.3% La, 4.3% Nd and significantly smaller quantities of the other light REEs. The xenotime sample was a product of a mine located in Norway and contained 5.5% yttrium, which accounted for over 63% of the TREEs. Thorium was the second highest, representing 2.5% by weight of the total.

2.2. Leaching Procedures

The mineral samples were crushed and ground in a shatter box to a top size of 15 microns. Leaching experiments were conducted using a triple neck round bottom flask with a total reflux condenser. Temperature was maintained using a water bath at 25 °C. Agitation was provided using a magnetic stirrer at 530 rpm. Leaching experiments were carried out using 1 M H₂SO₄, 1 M HCl and 1 M HNO₃ aqueous solutions with 10 g/L solids concentration. Slurry samples were collected at the following times after test initiation: 5, 15, 30, 60, 90 and 120 min. The solids and liquid samples were immediately separated within one minute of collection using a micro filter. Elemental recovery was calculated using the following expression:

$$R(\%) = \frac{c_L \times V_L}{c_f \times m_f} \times 100 \tag{1}$$

where c_L is the elemental concentration in the leachate, V_L is the leachate volume, c_f is the concentration in feed, and m_f is the mass of the feed solids.

2.3. Construction of Eh-pH Diagrams Using the HSC Software

To simulate the leaching conditions in H_2SO_4 , HNO_3 and HCl systems, the concentrations of the elements (i.e., S/Cl/N) that form the corresponding acid ligands (i.e., $SO_4/Cl/NO_3$) were input as 1 M when constructing the Eh-pH diagrams. The Eh-pH diagrams were generated using HSC 9.9 under 25 °C and 1 bar. The Eh value is presented as relative to the Standard Hydrogen Electrode (SHE) potential. Due to higher temperatures decreasing the solubilities of RE phosphates, the temperature was held constant at 25 °C when constructing the Eh-pH diagrams and comparing different chemical systems. The molarities of REEs were calculated based on the concentrations from the chemical assay.

3. Results and Discussions

3.1. Leaching of REE-Bearing Minerals

As the main component in monazite and bastnaesite minerals, Ce has the ability of changing its valence between +3 and +4. The recovery of Ce is thereby more complicated than that of other REEs in leaching solutions. Efforts were made to leach Ce from pure RE minerals, and the results of Ce recoveries were discussed in this study for monazite and bastnaesite leaching. The results of applying different lixiviants on recovering Ce from monazite are shown in Figure 1. The recoveries of Ce in 1 M H₂SO₄, 1 M HCl and 1 M HNO₃ were only 0.5, 0.7 and 0.7%, respectively. Based on the Eh-pH diagrams produced for the REE-PO₄-SO₄-H₂O system by Kim et al. [12], a surface reaction involving the hydrated insoluble forms of Nd and La may create a product layer that prevents the additional leaching of Ce in the H₂SO₄ leaching system. This hypothesis could possibly explain the low Ce recovery—less than 0.4% when using H₂SO₄ as a lixiviant (Figure 1).



Figure 1. Recovery of Ce from pure monazite using different lixiviants at 25 $^{\circ}$ C and a solids concentration of 10 g/L.

To further investigate the existing species in solution, the speciation diagram for Ce³⁺ in the Ce-SO₄-H₂O system was plotted using data obtained from Visual MINTEQ 3.1 (KTH, Stockholm, Sweden), as shown in Figure 2. Due to the lack of roasting or strong oxidative conditions, the formation of Ce⁴⁺ in the aqueous system is not anticipated. For that reason, only Ce³⁺ species (i.e., Ce(SO₄)₂⁻, Ce³⁺, CeOH²⁺ and CeSO₄⁺) are considered in Figure 2. The dominant Ce species that exist in the given system are cerium sulfate complexes, i.e., Ce(SO₄)₂⁻ and CeSO₄⁺. As the concentration of SO₄²⁻ increases, the distribution percentage of Ce(SO₄)₂⁻ increases, while the distribution percentages of CeSO₄⁺, Ce³⁺, and CeOH²⁺ decrease. Under a SO₄²⁻ concentration of 0.1 M, Ce(SO₄)₂⁻ and CeSO₄⁺ are equally distributed. At SO₄²⁻ concentrations higher than 0.1 M, Ce(SO₄)₂⁻ is predominant in the solution. This result shows consistency with the Eh-pH diagrams for the Ce–SO₄–H₂O system reported by Kim et al., where CeSO₄⁺ is the predominant species at SO₄²⁻ = 0.1 M and decreases dramatically at SO₄²⁻ = 1.0 M [12].



Figure 2. Ce^{3+} speciation in the Ce-SO₄-H₂O system over a range of sulfate concentrations at 25 °C: SO_4^{2-} from 0.01 to 2 M, $Ce^{3+} = 10^{-3}$ M (calculated using the Visual MINTEQ 3.1 software).

The leaching results of Ce from bastnaesite are shown in Figure 3. Improved recoveries are observed in 1 M HNO₃ and 1 M H₂SO₄, whereas the recovery in 1 M HCl leaching is comparatively lower. According to research performed by Shuai et al. [13], Ce⁴⁺ and F^- mainly exist as $[CeF_2]^{2+}$ in sulfuric acid. The cumulative stability constant of $[CeF_2]^{2+}$ is higher than the solubility product constant value of REEF₃. The stronger coordination between Ce⁴⁺ and F^- result in the formation of soluble complexes in solution. However, as reported by Shuai et al., Ce⁴⁺ is reduced to Ce³⁺ during acid leaching and the latter forms insoluble CeF₃ with free F^- ions [13], which explains the low recovery of Ce in our HCl leaching tests when compared to other lixiviants as presented in Figure 3.



Figure 3. Recovery of Ce in bastnaesite leaching with various lixiviants at 25 °C with 10 g/L solid concentration.

The leaching performance of xenotime in different lixiviants shown in Figure 4 revealed characteristics similar to those of monazite due to the similarities in the mineral crystal structure. The recoveries of Y in xenotime were 17, 8 and 11% using 1 M H₂SO₄, 1 M HCl, and 1 M HNO₃, respectively. H₂SO₄ leaching provided the highest yttrium recovery, which may be due to the complexation of sulfate ions to Y. The speciation stability of Ce and Y with SO₄^{2–}, Cl[–] and NO₃[–] in aqueous solutions are further discussed in the following sections.



Figure 4. Recovery of Y in xenotime leaching with various lixiviants at 25 °C with 10 g/L solid concentration.

3.2. Eh-pH Diagrams of Rare Earth Mineral Leachates

To address the systems that have not been previously studied (Table 1), the Eh-pH diagrams of bastnaesite leaching in a H_2SO_4 system, monazite in HCl and HNO₃ systems and xenotime in H_2SO_4 , HCl and HNO₃ systems were investigated. The results and discussions are provided in the following sections.

3.2.1. Bastnaesite Leaching

Bastnaesite (chemical formula: (Ce, La)(CO₃)F) is a major REE-bearing mineral [26]. The primary species in bastnaesite leachate are Ce, La and F, with the corresponding acid ligands in the lixiviants. In most hydrometallurgical processes, bastnaesite is typically roasted under conditions that eliminate carbonate. Therefore, when constructing the Eh-pH diagrams for bastnaesite leaching, CO_3^{2-} is excluded from the system due to the removal of carbonates or the lack of carbonate compounds.

The concentration of the element S composing the acid ligand (i.e., SO_4^{2-}) was 1 M for the construction of the Eh-pH diagrams of bastnaesite leaching in a H_2SO_4 system. The molarities of REEs were calculated based on a chemical assay. The Eh-pH diagrams were generated using HSC 9.9 under 25 °C and 1 bar as presented in Figures 5–7.

As previously shown in Figure 3, the recovery of Ce in bastnaesite reaches 90, 76 and 94% after 2 h of leaching using 1 M H₂SO₄, 1 M HCl, and 1 M HNO₃, respectively. Due to the effect of Ce⁴⁺ and Ce³⁺ on the system, several Eh-pH diagrams are proposed (refer to the bastnaesite summary in Table 1). In a system where bastnaesite is roasted and oxidized, it may be assumed that Ce mainly exists as a tetravalent species. As shown in Figure 5, Ce⁴⁺ forms a hydrated Ce(SO₄)₂ salt, which dominates the water stability region. Anecdotal evidence of the lack of solubility of Ce⁴⁺ compounds is corroborated by processes that roast bastnaesite to selectively leach other REEs. It was found in literature that ionic Ce (Ce³⁺ and Ce⁴⁺) has a strong ability to coordinate with F⁻ and forms a Ce-F complex in the presence of sulfuric acid [14]. The possible existence of a Ce-F complex is indicated by the light blue stability region of CeF₃ below the lower water stability line in the Eh-pH diagram (Figure 5). However, the stability region of CeF₃ was overlapped by Ce(SO₄)₂·5H₂O. It seems that, when Ce-F and Ce-SO₄ compounds co-exist in the system, Ce⁴⁺ tends to complex with SO₄²⁻ in the form of Ce(SO₄)₂ with excess SO₄²⁻ ions.

Although Figure 5 suggests a solid form as a Ce-SO₄ complex at equilibrium in the presence of Ce⁴⁺, the leaching recovery shown in Figure 3 indicates that Ce is soluble at low pH values of around 0 in a 1 M H₂SO₄ solution. Due to the variance between the experimental results in Figure 3 showing excellent solubility of cerium from unroasted bastnaesite and the theoretical Eh-pH diagram proposed in Figure 5 indicating an insoluble form of cerium, the Eh-pH diagram was modified to exclude $Ce(SO_4)_2 \cdot 5H_2O$ while holding all other parameters constant. The reason to discount the Ce⁴⁺ species (i.e., Ce(SO₄)₂ \cdot 5H₂O) is that, due to the lack of pre-roasting/pre-oxidizing or the addition of a strong oxidizer, it is unlikely that Ce⁴⁺ will form across the water stability region, even under highly acidic and oxidative conditions. The modified Eh-pH diagram of the Ce-F-SO₄-H₂O system is shown in Figure 6. Without the formation of $Ce(SO_4)_2 \cdot 5H_2O$, the stability region of Ce^{3+} occurs within a pH range of -2 to 2. The change of Ce species in the modified Eh-pH diagram shows that Ce could exist stably in its ionic Ce³⁺ form at pH values lower than 2 in a 1 M H_2SO_4 leaching system in the absence of Ce^{4+} . This comparison is significant in that the oxidization state of Ce appears to be the single most important factor in the propensity to leach with the associated impact of the oxidation rate of Ce in aqueous systems and the Eh of the solution. In summary, the un-oxidized bastnaesite-sulfate system is better described by the Eh-pH diagram of Figure 6 rather than the more exact thermodynamic predictions presented in Figure 5 given the timescale of the leach test that provided the recovery values presented in Figure 3.

Lanthanum, as shown in Figure 7, also has the ability of complexing with F^- and forms insoluble LaF₃. However, the La-SO₄ compound is soluble in the water stability region within the pH range of 1.5 to 8.5. This finding suggests promising La leachability in sulfuric acid systems for bastnaesite leaching.



Figure 5. Eh-pH diagram of the Ce-F-SO₄-H₂O system for bastnaesite leaching in H₂SO₄ at 25 °C: Ce = 10^{-3} M, F = 10^{-3} M, S = 1.0 M.



Figure 6. Modified Eh-pH diagram of the Ce-F-SO₄-H₂O system for bastnaesite leaching in H₂SO₄ at 25 °C: Ce = 10^{-3} M, F = 10^{-3} M, S = 1.0 M (excluding the Ce(SO₄)₂·5H₂O species from Figure 5).



Figure 7. Eh-pH diagram of the La-F-SO₄-H₂O system for bastnaesite leaching in H₂SO₄ at 25 °C: La = 10^{-3} M, F = 10^{-3} M, S = 1.0 M.

3.2.2. Monazite Leaching

The leaching of monazite using 1 M H_2SO_4 , 1 M HCl and 1 M HNO₃ resulted in Ce recovery values of 0.5, 0.7 and 0.7%, respectively (Figure 1). The results indicate the poor leachability of monazite under the designed leaching conditions. To further investigate the leaching reaction of Ce in monazite, Eh-pH diagrams of monazite solubility in HCl and HNO₃ systems were developed as shown in Figures 8–15, respectively.

In the HCl leaching system, Ce is leached into the solution in its trivalent state and subsequently forms a soluble complex with Cl^- in the solution as indicated by the gray region of Ce³⁺ in Figure 8 [13]. A similar result occurs in the HNO₃ leaching system, wherein Ce mainly exists in its trivalent state at pH values lower than 3.5, either as a free ion or complexed with NO₃⁻. From pH 3.5 to 11, the main species of Ce are phosphate and oxide compounds, which are insoluble forms. The precipitation of Ce hydroxide occurs at pH values higher than 11.

According to the Eh-pH diagrams, the leachability of Ce is comparatively higher under low pH conditions (pH < 3.5). Under these conditions, Ce is in an ionic trivalent form across the water stability region. However, experimental data indicates that the leaching recovery of Ce is less than 1% in 1 M H₂SO₄, 1 M HCl and 1 M HNO₃ solutions (Figure 1). This result is likely due to the occurrence of Ce in the feed material in a crystalline state, which requires more energy for Ce to be leached from the associated minerals [27]. As previously reported, a possible reason for low monazite leaching is the difficulty to chemically decompose the mineral structure of monazite and dissolve the REEs into solution [28–30]. As shown in Figure 9 through Figures 11, 13 and 14, La and Nd are not soluble except under very acidic conditions. As such, only surface amounts of Ce may be solubilized and leaching diminishes due to the impenetrability (Nd and La insoluble compounds) into the mineral particle. Furthermore, any leaching results in the formation of insoluble complexes in the leaching solution, such as CePO₄, LaPO₄ and NdPO₄, which accumulates on the mineral surfaces, thereby preventing a further reaction between the minerals and leaching agents, and consequently resulting in low recovery values. Therefore, more aggressive leaching conditions, such as a higher temperature or stronger acidity, may favor the leaching process.

The Eh-pH diagrams of Th shown in Figures 11 and 15 indicate that, in both the HCl and HNO₃ systems, Th has a wider stability region from pH -2 to 8 due to its ionic forms, i.e., ThH₃PO₄⁴⁺ and Th(HPO₄)₃²⁻. This result indicates that Th will likely stay in the solution after being leached rather than precipitating as a solid.

Unlike other rare earth elements, which are only stable in their trivalent state (REE³⁺), Ce commonly exists in trivalent (Ce³⁺) and tetravalent states (Ce⁴⁺) in solution. Tetravalent Ce (Ce⁴⁺) is more stable than its trivalent state (Ce³⁺). Insoluble complexes formed by Ce⁴⁺ and phosphate (i.e., CePO₄) show a higher stability than their sulphate or hydroxide forms [31]. The Eh-pH diagrams of Ce species in the Cl⁻ and NO₃⁻ systems indicate that Ce cannot exist in solutions as its ionic tetravalent form (Ce⁴⁺). Instead, it either exists as Ce³⁺ or forms complexes as CeClO₄²⁺ and CeNO₃²⁺ in the presence of Cl⁻ and NO₃⁻, respectively, as indicated by Figures 8 and 12. In other words, if Ce is pre-oxidized to Ce⁴⁺, it will not be easily leached into solution and the separation between Ce⁴⁺ and other REE³⁺ species can therefore be achieved.



Figure 8. Eh-pH diagram of the Ce-PO₄-Cl-H₂O system for monazite leaching in HCl at 25 °C: Ce = 10^{-3} M, P = 10^{-3} M, Cl = 1.0 M.



Figure 9. Eh-pH diagram of the La-PO₄-Cl-H₂O system for monazite leaching in HCl at 25 °C: La = 10^{-3} M, P = 10^{-3} M, Cl = 1.0 M.



Figure 10. Eh-pH diagram of the Nd-PO₄-Cl-H₂O system for monazite leaching in HCl at 25 °C: Nd = 10^{-3} M, P = 10^{-3} M, Cl = 1.0 M.



Figure 11. Eh-pH diagram of the Th-PO₄-Cl-H₂O system for monazite leaching in HCl at 25 °C: Th = 10^{-3} M, P = 10^{-3} M, Cl = 1.0 M.



Figure 12. Eh-pH diagram of the Ce-PO₄-NO₃-H₂O system for monazite leaching in HNO₃ at 25 °C: Ce = 10^{-3} M, P = 10^{-3} M, N = 1.0 M.



Figure 13. Eh-pH diagram of the La-PO₄-NO₃-H₂O system for monazite leaching in HNO₃ at 25 °C: La = 10^{-3} M, P = 10^{-3} M, N = 1.0 M.



Figure 14. Eh-pH diagram of the Nd-PO₄-NO₃-H₂O system for monazite leaching in HNO₃ at 25 °C: Nd = 10^{-3} M, P = 10^{-3} M, N = 1.0 M.



Figure 15. Eh-pH diagram of the Th-PO₄-NO₃-H₂O system for monazite leaching in HNO₃ at 25 °C: Th = 10^{-3} M, P = 10^{-3} M, N = 1.0 M.

3.2.3. Xenotime Leaching

The Eh-pH diagrams for xenotime leaching in the H_2SO_4 , HCl and HNO₃ systems are shown in Figures 16–18. The gray region in all three charts represent the ionic region of Y³⁺ (in the Y-PO₄-SO₄ and Y-PO₄-NO₃ systems) and YCl²⁺ (in the Y-PO₄-Cl system), respectively. The wide regions of yttrium phosphate overlapping with the water stability region (within the two dash lines) indicate that the leaching of xenotime in H_2SO_4 , HCl and HNO₃ was limited by the formation of a phosphate precipitant. The recovery of Y in xenotime was 17, 8 and 11% using 1 M H_2SO_4 , 1 M HCl and 1 M HNO₃, respectively. In sulfate systems, the formation of ionic species YSO₄⁺ at pH values from 0 to 0.5 indicates higher leachability of xenotime in sulfuric acid. This correlates well with our experimental data where the highest recovery occurs when using sulfuric acid is used as the lixiviant (Figure 4).



Figure 16. Eh-pH diagram of the Y-PO₄-SO₄-H₂O system for xenotime leaching in H₂SO₄ at 25 °C: $Y = 10^{-3}$ M, $P = 10^{-3}$ M, S = 1.0 M.



Figure 17. Eh-pH diagram of the Y-PO₄-Cl-H₂O system for xenotime leaching in HCl at 25 °C: $Y = 10^{-3}$ M, $P = 10^{-3}$ M, Cl = 1.0 M.



Figure 18. Eh-pH diagram for the Y-PO₄-NO₃-H₂O system for xenotime leaching in HNO₃ at 25 °C: $Y = 10^{-3}$ M, $P = 10^{-3}$ M, N = 1.0 M.

3.3. Eh-pH Diagrams of the Main Contaminants

Commonly associated contaminants in REE systems include iron, calcium and aluminum. The Eh-pH diagrams showed some solubility of $\text{REE}^{3+}/\text{Ce}^{3+}$ in low pH regions. However, the actual leach recovery values were lower than anticipated. A possible explanation is the formation of a product or precipitation layer on the surface of the minerals by contaminants. The product layer may block the mineral surface, thereby inhibiting the reaction between the acids and the minerals. Similar phenomena have been reported by other researchers [15,31,32]. To further understand the impact of contaminants on leaching, Eh-pH diagrams (Figures 19–22) of the three major contaminating elements, i.e., Fe, Ca and Al, were generated for the 1 M H₂SO₄, 1 M HCl and 1 M HNO₃ systems, respectively. In the three acid leaching systems, Fe shows the ability to form different species of precipitants, which may be the main factor that causes the passivation effect on the mineral surfaces.

The Eh-pH diagram of Fe, Ca and Al in the sulfuric acid leaching system (Figure 19) shows the presence of goethite (FeO·OH), hydrated rhomboclase (H₃OFe(SO₄)₂·3H₂O) and calcium ferrite (CaO·Fe₂O₃), under corresponding leaching conditions. However, the stability region of H₃OFe(SO₄)₂·3H₂O and Fe(SO₄)₃·5.03H₂O overshadowed the stability region of Fe³⁺ and FeO·OH across the water stability region (from pH –2 to 12). The stable occurrence of H₃OFe(SO₄)₂·3H₂O and Fe(SO₄)₃·5.03H₂O contradicts the fact that Fe³⁺ and FeO·OH should be the dominant Fe species in the sulfate system. Moreover, (H₃OFe(SO₄)₂·3H₂O and Fe(SO₄)₃·5.03H₂O) may form at time scales beyond those of typical leaching due to slow kinetics. Therefore, the Eh-pH diagram for the Fe-Ca-Al-NO₃-H₂O system was modified by omitting H₃OFe(SO₄)₂·3H₂O and Fe(SO₄)₃·5.03H₂O, while keeping all other conditions the same. As shown in the modified Eh-pH diagram (Figure 20), the dominant Fe species under pH 1 is either Fe³⁺ (at Eh above 0.65 V vs. SHE) or Fe²⁺ (at Eh below 0.65 V vs. SHE). As pH and Eh increase, FeO·OH starts to form and dominates the stability region in the sulfate system. The Eh-pH diagram for the Fe-S-H₂O system at 298 K reported by Bernardez et al. also corroborates our findings [33].

In the modified Eh-pH diagram (Figure 20), goethite (FeO·OH) is considered the main product that could cause passivation on the mineral surface. The formation of FeO·OH can be described as:

$$Fe_2(SO_4)_3 + 4H_2O \rightarrow 2FeOOH + 3H_2SO_4$$
(2)

For REE leaching, the formation of FeO·OH, Fe_3O_4 and $CaO·Fe_2O_3$ (as shown in Figure 20) can inhibit the leaching process by preventing contact between the mineral surfaces and the leaching agent in solution.

In HCl leaching systems, Fe mainly exists at a +3 state at pH values lower than 6.0 and starts to form a FeO·OH precipitate at pH values above 6.0, as shown in Figure 21. In HNO₃ systems, Fe exists as either Fe^{2+} or Fe^{3+} below pH 1.0, as shown in Figure 22. Generally, Fe exists in its ionic forms at low pH and low Eh conditions, which indicates that the leaching of RE minerals containing Fe may be more favorable under these conditions.



Figure 19. Eh-pH diagram for the Fe-Ca-Al-SO₄-H₂O system at 25 °C: Fe = 10^{-3} M, Ca = 10^{-3} M, Al = 10^{-3} M, S = 1.0 M.



Figure 20. Modified Eh-pH diagram for the Fe-Ca-Al-SO₄-H₂O system at 25 °C: Fe = 10^{-3} M, Ca = 10^{-3} M, Al = 10^{-3} M, N = 1.0 M (excluding the H₃OFe(SO₄)₂·3H₂O and Fe(SO₄)₃·5.03H₂O from Figure 19).



Figure 21. Eh-pH diagram for the Fe-Ca-Al-Cl-H₂O system at 25 °C: Fe = 10^{-3} M, Ca = 10^{-3} M, Al = 10^{-3} M, Cl = 1.0 M.



Figure 22. Eh-pH diagram for the Fe-Ca-Al-NO₃-H₂O system at 25 °C: Fe = 10^{-3} M, Ca = 10^{-3} M, Al = 10^{-3} M, N = 1.0 M.

4. Thermodynamic Data from the HSC Database and Other Sources

The data used in generating the Eh-pH diagrams are listed in Table 1 (see Appendix A). The various Gibbs free energies are listed because there are different values of the same species reported in other resources due to the difference in crystallinity. The species with multiple values reported are indicated in Table 1. It is noted that the Gibbs free energy for ThH₂PO₄²⁺ varies from -434.174 to -723.550 kcal/mol in the HSC 9.9 and the HSC 5.11 databases, respectively, which causes differences in the corresponding Eh-pH diagrams. In addition, new species that are not included in the HSC 9.9 database but are reported in other publications are also included in Table 1 (see Appendix A). For example, the Gibbs free energy for an insoluble cerium sulphate, $Ce_2(SO_4)_3 \cdot 8H_2O$, is excluded in the HSC database but reported in other studies by Dean and Wagman [34,35]. The importance of having all the available thermodynamic data of the requisite species is that the effect of different thermodynamic data and the presence of different species on the Eh-pH diagrams can be determined. Future work will be focused on importing the missing species and updating the thermodynamic data to see how the Eh-pH diagrams change accordingly. The comparison between Eh-pH diagrams resulting from different thermodynamic data will also help to gain a better understanding of how species with different crystallinities behave chemically in solution.

5. Conclusions

In this work, a literature review was performed relating to the Eh-pH diagrams of three RE minerals, i.e., bastnaesite, monazite and xenotime, in aqueous systems. Eh-pH diagrams of RE minerals in hydrometallurgical systems that were not previously reported in the literature were developed in this study. Furthermore, leaching tests using RE minerals in the considered aqueous systems, i.e., acid leaching using H₂SO₄, HCl and HNO₃, were performed to provide experimental data for comparison with theoretical findings from the corresponding Eh-pH diagrams.

Using 1 M inorganic acid concentrations at 25 °C with 10 g/L solid concentration, the Ce recovery from bastnaesite leaching showed over 90% recovery in the 1 M sulfuric acid and 1 M nitric acid leaching systems, whereas 1 M hydrochloric acid provided about 75% leaching recovery. The Eh-pH diagrams of REEs associated with bastnaesite leaching in the Ce-F-SO₄-H₂O system indicate that Ce has a strong affinity for SO₄^{2–} and forms a Ce-SO₄ complex, under the excess SO₄^{2–}. It was interpreted from the modified Eh-pH diagram and the speciation plot that, in bastnaesite leaching using 1 M H₂SO₄, Ce mainly existed

in ionic (Ce^{3+}) form, which resulted in a high leaching recovery of Ce. However, it might form $Ce(SO_4)_2$ pentahydrate under strongly oxidative conditions.

Under the same leaching conditions, Ce in monazite showed leaching recoveries lower than 1%, regardless of the acid type. The Eh-pH diagrams of monazite indicate that Ce can stably exist as Ce^{3+} in both HCl and HNO₃ systems. However, the leaching recovery of Ce in these two solutions was lower than 1%. A possible reason for the low Ce recovery in monazite may be the passivation effect by other insoluble species formed during leaching, such as NdPO₄ and LaPO₄. In addition, the strong crystallinity of monazite minerals indicates that more intensive leaching conditions, such as higher temperature and stronger acidity, may be required to chemically decompose the monazite structure and promote the Ce recovery.

Yttrium leaching recovery from xenotime showed that sulfuric acid is a preferential leaching reagent with a relatively higher Y recovery (over 15%) compared to nitric and hydrochloric systems. The Eh-pH diagrams of xenotime in leaching solutions indicate that Y has some solubility in the H_2SO_4 solution under oxidative and highly acidic conditions, which results in the highest recovery among the three lixiviants tested.

According to the Eh-pH diagrams of contaminating elements in the three leaching systems, Fe is likely to form precipitants under specific conditions and block the surface of minerals, thereby inhibiting the recovery of other REEs during leaching. It is suggested that the leaching recovery can be enhanced in the stability regions where Fe and other contaminating elements exist in ionic forms.

The compilation of thermodynamic data (Gibbs free energy) of possible RE mineral species reported in the literature presented the hypothesis that such differences were the result of variations in the crystallinity of REE mineral forms.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

The thermodynamic data of the involved species was compiled from the HSC database and supplemented from other available resources, as shown in Table 1.

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Species	$\Delta G_{f,298}^0$ (kcal/mol)	References	Species	$\Delta G_{f,298}^0$ (kcal/mol)	References
H ₂ O	-56.678	HSC 5.11	LaF ₃	-388.093	HSC 9.9
Р	0.000	HSC 9.9	$La_2O_2SO_4$	-511.334	HSC 9.9
H_3PO_4	-267.428	HSC 9.9	LaS	-107.728	HSC 9.9
HPO_3^{2-}	-193.968	HSC 9.9	LaS_2	-146.785	HSC 9.9
HPO_4^{2-}	-261.949	HSC 9.9	La_2S_3	-288.790	HSC 9.9
	-260.296	HSC 5.11	$La_2(SO_4)_3$	-859.824	HSC 9.9
$H_2PO_3^-$	-202.326	HSC 9.9		-859.291	HSC 5.11
$H_2PO_4^-$	-271.786	HSC 9.9	$La_2(SO_4)_3 \cdot 9H_2O$	-1380.146	HSC 9.9
	-270.126	HSC 5.11		-1399.880	Dean
PO_{4}^{3-}	-245.098	HSC 9.9	$La_2(SO_4)_3(a)$	-877.762	HSC 5.11
	-243.364	HSC 5.11	LaF ²⁺	-236.572	HSC 9.9
HF(l)	-65.91	HSC 9.9	LaF_2^+	-307.773	HSC 9.9
F^-	-67.3294	HSC 9.9	LaF_4^-	-447.461	HSC 9.9
HF_2^-	-139.495	HSC 9.9	$LaSO_4^+$	-346.908	HSC 9.9
S	0.000	HSC 9.9	$La(SO_4)_2^-$	-526.596	HSC 9.9
SO ₃ (l)	-89.3045	HSC 9.9	$La_2(CO_3)_3$	-750.900	Brookins
H_2SO_4	-164.894	HSC 9.9			
SO_3	-88.1433	HSC 9.9	Nd	0.000	HSC 9.9
HS ⁻	2.9063	HSC 9.9	NdH ₂	-38.120	HSC 9.9
HSO_3^-	-126.103	HSC 9.9	NdN	-66.489	HSC 9.9
HSO_4^-	-180.524	HSC 9.9	Nd_2O_3	-411.102	HSC 9.9
2	-180.609	HSC 5.11		-411.300	Brookins
SO_3^{2-}	-116.287	HSC 9.9		-411.436	HSC 5.11
SO_4^{2-}	-177.907	HSC 9.9	Nd(OH) ₃	-306.629	HSC 9.9
$HClO_4(l)$	18.646	HSC 9.9		-305.200	Brookins
Cl-	-31.372	HSC 9.9		-305.308	Baes and Mesmer
Cl ₃ -	65.864	HSC 9.9	$NdPO_4$	-442.053	HSC 9.9
ClO-	-8.668	HSC 9.9		-439.200	Liu and Byrne
ClO_2^-	4.108	HSC 9.9		-423.461	HSC 5.11
ClO_3^-	-1.886	HSC 9.9	$Nd(PO_3)_3$	-766.726	HSC 9.9
ClO_4^-	-1.886	HSC 9.9	$NdPO_4 \cdot 2H_2O$	-566.731	HSC 9.9
$PCI_3(I)$	-65.496	HSC 9.9	Nd ²⁺	-100.198	HSC 9.9
$POCI_3(I)$	-134.790	HSC 9.9	Nd ³⁺	-160.205	HSC 9.9
PCI ₄	-83.145	HSC 9.9		-160.500	Brookins
PCI ₅	-78.147	HSC 9.9		-160.100	HSC 5.11
$HN_3(I)$	78.216	HSC 9.9	Nd ⁴⁺	-47.031	HSC 9.9
$HNO_3(I)$	-19.300	HSC 9.9	$NdHPO_4^+$	-427.460	Poitrasson
NH ₃ (I)	-0.217	HSC 9.9	$Nd(HPO_4)_2^-$	-692.500	Poitrasson
$NH_4OH(I)$	-60.710	HSC 9.9	$NdH_2PO_4^{2+}$	-433.937	HSC 9.9
NH ₃	-0.566	HSC 9.9		-433.510	Poitrasson
NH4OH	-52.381	HSC 9.9	NdNO ₃ ²⁺	-188.223	HSC 9.9
NH_4NO_3	-43.921	HSC 9.9	NdO ⁺	-203.068	HSC 9.9
$NH_4 \cdot H_2PO_4$	-289.399	HSC 9.9	NdO_2^-	-218.630	HSC 9.9
NH_4	-18.977	HSC 9.9	NdOH ²	-206.797	HSC 9.9
NO_3^-	-26.489	HSC 9.9		-206.410	HSC 5.11
HNO ₂	11.221	HSC 9.9	Nd(OH) ₂	-250.800	Baes and Mesmer
0	0.000	HSC 9.9	Nd(OH) ₄	-336.700	Brookins
Ce	0.000	HSC 9.9	NIL (OID) 4+	-336.610	Baes and Mesmer
CeH ₂	-35.731	H5C 9.9	$Na_2(OH)_2^{\pm}$	-415.451	baes and Mesmer
CeO_2	-245.301	HSC 9.9	NaCl ₂	-154.111	HSC 9.9
	-244.400	vvagman	NaCl ₃	-230.804	HSC 9.9
C = O	-244.900	ПЭС 3.11 НКС 0.0	INACI3.6H2U	-583.064	HSC 9.9
Ce_2O_3	-411.58/	DSC 9.9	INdUCI NJCI ²⁺	-225.415	HSC 0.0
	-407.800	Drookins	NdCI ²	-192.530	TOC 9.9

 Table 1. Thermodynamic data from the HSC software and other literatures [10,34–43].

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Species	$\Delta G_{f,298}^0$ (kcal/mol)	References	Species	$\Delta G_{f,298}^0$ (kcal/mol)	References
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ce(OH) ₃	-307.247	HSC 9.9	NdCl ₂ ⁺	-223.435	HSC 9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-303.600	Brookins	NdCl ₄ ⁻	-285.157	HSC 9.9
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		-303.490	Baes and Mesmer	$Nd_2(SO_4)_3$	-847.843	HSC 5.11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CePO ₄	-432.959	HSC 9.9	NdSO4 ⁺	-343.500	HSC 5.11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-439.796	Liu and Byrne	$Nd(SO_4)_2^-$	-523.379	HSC 5.11
$ \begin{array}{cccc} CePQ_4, 2H_2O & -545.820 & HSC 9.9 & Nd_2(CO_3)_3 & -741.400 & Brookins \\ Ce^{2+} & -162.105 & HSC 9.9 & Th & 0.000 & HSC 9.9 \\ \hline Ce^{4+} & -162.105 & HSC 9.9 & Th & 0.000 & HSC 9.9 \\ \hline Ce^{4+} & -121.348 & HSC 9.9 & Th(HPQ_1)_2.4H_2O & -952.667 & HSC 9.9 \\ \hline CeH_2PQ_4^{2+} & -435.081 & HSC 9.9 & Th(NO_3)_4 & -250.762 & HSC 9.9 \\ \hline CeNO_3^{2+} & -139.025 & HSC 9.9 & Th(NO_3)_4.4H_2O & -500.379 & HSC 9.9 \\ \hline CeO^+ & -205.111 & HSC 9.9 & ThO & -138.800 & HSC 9.9 \\ \hline CeO^+ & -205.111 & HSC 9.9 & ThO & -138.800 & HSC 9.9 \\ \hline CeO^+ & -205.111 & HSC 9.9 & ThO & -138.800 & HSC 9.9 \\ \hline CeOH^{2+} & -209.611 & HSC 9.9 & ThO & -138.800 & HSC 9.9 \\ \hline CeOH^{2+} & -209.611 & HSC 9.9 & -279.340 & Wagman \\ \hline CeOH^{2+} & -209.611 & HSC 9.9 & Th^{4+} & -168.502 & Wagman \\ \hline CeOH^{2+} & -209.611 & HSC 9.9 & Th^{4+} & -168.502 & Wagman \\ \hline CeOH^{2+} & -209.611 & HSC 9.9 & Th^{4+} & -168.502 & Wagman \\ \hline CeOH^{2+} & -209.611 & HSC 9.9 & Th^{4+} & -168.502 & Wagman \\ \hline Ce(OH)_2^{2+} & -242.50 & HSC 9.9 & Th^{4+} & -168.502 & Wagman \\ \hline Ce_{COH}_{2+}^{2+} & -242.50 & HSC 9.9 & Th^{4+} & -168.502 & Wagman \\ \hline Ce_{CO}(Dh)_2^{4+} & -719.496 & Baes and Mesmer & ThHPO_4^{2+} & -401.224 & HSC 9.9 \\ \hline Ce_{2}(OH)_2^{4+} & -719.496 & Baes and Mesmer & ThH_2PO_4^{2+} & -444.174 & HSC 9.9 \\ \hline Ce_{2}(OH)_2^{5+} & -449.430 & Baes and Mesmer & ThH_2PO_4^{2+} & -446.378 & HSC 9.9 \\ \hline Ce_{2}(OH)_2^{5+} & -419.430 & Baes and Mesmer & ThH_2PO_4^{2+} & -446.378 & HSC 9.9 \\ \hline Ce_{2}(OH)_2^{5+} & -419.430 & Baes and Mesmer & ThH_2PO_4^{3+} & -446.378 & HSC 9.9 \\ \hline Ce_{5} & -107.259 & HSC 9.9 & Th(HPO_4)_2^{4} - 224.250 & HSC 9.9 \\ \hline Ce_{5} & -385.311 & HSC 9.9 & Th(HPO_4)_2^{4} - 224.250 & HSC 9.9 \\ \hline Ce_{5} & -107.259 & HSC 9.9 & Th(HPO_4)_2^{4} - 224.657 & HSC 5.11 \\ \hline Ce_{5}(O_{4})_{2} & -385.652 & HSC 9.9 & Th(HPO_{4})_{2} - 224.667 & HSC 5.11 \\ \hline Ce_{5}(O_{4})_{3} & -386.652 & HSC 9.9 & Th(HPO_{4})_2^{4} - 220.070 & HSC 9.9 \\ \hline Ce(SO_{4})_{2} & -506.184 & HSC 9.9 & Th(HPO_{4})_{2} + 422.0 & -952.667 & HSC 5.11 \\ \hline Ce_{5}(O_{4})_{3} & -386$		-421.750	Byrne and Kim	Nd ₂ (SO ₄) ₃ ·8H ₂ O	-1335.000	HSC 5.11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CePO ₄ ·2H ₂ O	-545.820	HSC 9.9	$Nd_2(CO_3)_3$	-741.400	Brookins
$\begin{array}{cccccc} Ce^{3^{4}} & -162.105 & HSC 9.9 & Th & 0.000 & HSC 9.9 \\ & -160.600 & Brookins & ThH_2 & -25.527 & HSC 9.9 \\ & -120.440 & Wagman & Th(NO_3)_4 & -250.762 & HSC 9.9 \\ & -120.440 & Wagman & Th(NO_3)_4 & -250.762 & HSC 9.9 \\ & -120.440 & Wagman & Th(NO_3)_4 & -250.762 & HSC 9.9 \\ & -433.904 & HSC 5.11 & Th(NO_3)_4 & -510.378 & HSC 9.9 \\ & -433.904 & HSC 5.11 & Th(NO_3)_4 & -510.378 & HSC 9.9 \\ & CeNO_3^{2^{+}} & -189.025 & HSC 9.9 & ThO & -138.800 & HSC 9.9 \\ & CeO^{-} & -205.111 & HSC 9.9 & ThO_2 & -279.340 & Wagman \\ & CeO^{+} & -209.611 & HSC 9.9 & -278.330 & HSC 9.9 \\ & CeO^{+^{2^{+}}} & -178.830 & HSC 9.9 & Th^{4^{+}} & -168.507 & HSC 9.9 \\ & -275.506 & HSC 5.11 & Th(OH)_4 & -382.263 & HSC 9.9 \\ & -275.906 & HSC 5.9 & Th^{4^{+}} & -168.507 & HSC 9.9 \\ & -178.580 & Baes and Mesmer & -168.520 & Wagman \\ & Ce(OH)_2^{2^{+}} & -224.250 & HSC 9.9 & -178.580 & HSC 5.11 \\ & Ce_2(OH)_2^{4^{+}} & -413.410 & Baes and Mesmer & ThH_2O_4^{2^{+} b} & -434.174 & HSC 9.9 \\ & Ce_3(OH)_5^{4^{+}} & -719.496 & Baes and Mesmer & ThH_2O_4^{2^{+} b} & -434.174 & HSC 9.9 \\ & Ce_2(OH)_2^{2^{+}} & -235.670 & Baes and Mesmer & ThH_2O_4^{2^{+} b} & -434.174 & HSC 9.9 \\ & Ce_2(OH)_2^{5^{+}} & -362.070 & Baes and Mesmer & ThH_2O_4^{2^{+} b} & -434.174 & HSC 9.9 \\ & Ce_2(OH)_5^{4^{+}} & -119.430 & Baes and Mesmer & -446.150 & HSC 5.11 \\ & Ce_2(OH)_5^{4^{+}} & -419.430 & Baes and Mesmer & -446.150 & HSC 5.11 \\ & Ce_2(OH)_3^{5^{+}} & -419.430 & Baes and Mesmer & -446.150 & HSC 9.9 \\ & CeF_3 & -385.311 & HSC 9.9 & Th(HPO_4)_3^{2^{-}} & -100.1906 & HSC 9.9 \\ & CeF_3 & -385.311 & HSC 9.9 & Th(HPO_4)_1^{4^{+}} & -220.070 & HSC 5.11 \\ & CeS_5 & -107.259 & HSC 9.9 & Th(HPO_4)_1^{4^{+}} & -220.070 & HSC 5.11 \\ & CeS_5 & -107.259 & HSC 9.9 & Th(HPO_4)_1^{4^{-}} & -220.070 & HSC 9.9 \\ & Ce(SO_4)_2 & -506.184 & HSC 9.9 & Th(HPO_4)_2^{-4} & -220.000 & Wagman \\ & Ce_2(SO_4)_3 & HSC 9.9 & Th(HPO_4)_2^{-4} & -220.000 & Wagman \\ & Ce_2(SO_4)_3 & HSC 9.9 & Th(HPO_4)_2^{-4} & -220.000 & Wagman \\ & Ce_2(SO_4)_3 & HSC 9.9 & Th(HPO_4)_2^{-4} & -220.00$	Ce ²⁺	-74.898	HSC 9.9			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ce ³⁺	-162.105	HSC 9.9	Th	0.000	HSC 9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-160.600	Brookins	ThH ₂	-25.527	HSC 9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ce^{4+}	-121.348	HSC 9.9	Th(HPO ₄) ₂ ·4H ₂ O	-952.667	HSC 9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-120.440	Wagman	$Th(NO_3)_4$	-250.762	HSC 9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CeH ₂ PO ₄ ²⁺	-435.081	HSC 9.9	Th(NO ₃) ₄ ·4H ₂ O	-500.379	HSC 9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-433.904	HSC 5.11	$Th(NO_3)_4 \cdot 5H_2O$	-555.786	HSC 9.9
$\begin{array}{cccc} {\rm CeO}^+ & -205.111 & {\rm HSC} 9.9 & {\rm ThO}_2 & -279.455 & {\rm HSC} 9.9 \\ {\rm CeO}_2^- & -217.402 & {\rm HSC} 9.9 & -279.340 & {\rm Wagman} \\ {\rm CeOH}^2 + & -209.611 & {\rm HSC} 9.9 & -278.330 & {\rm HSC} 5.11 \\ & -205.960 & {\rm HSC} 5.11 & {\rm Th(OH)}_4 & -382.263 & {\rm HSC} 9.9 \\ & -178.830 & {\rm HSC} 9.9 & {\rm Th}^{4+} & -168.507 & {\rm HSC} 9.9 \\ & -178.580 & {\rm Baes and Mesmer} & -168.520 & {\rm Wagman} \\ {\rm Ce(OH)}_2^{2+} & -224.250 & {\rm HSC} 9.9 & -167.800 & {\rm HSC} 5.11 \\ {\rm Ce}_2(OH)_2^{4+} & -413.410 & {\rm Baes and Mesmer} & {\rm ThHPO}_4^{2+} & -401.224 & {\rm HSC} 9.9 \\ {\rm Ce(OH)}_2^{4+} & -719.496 & {\rm Baes and Mesmer} & {\rm ThH}_2{\rm PO}_4^{2+} b & -434.174 & {\rm HSC} 9.9 \\ {\rm Ce}_3(OH)_5^{4+} & -719.496 & {\rm Baes and Mesmer} & {\rm ThH}_2{\rm PO}_4^{3+} & -446.378 & {\rm HSC} 9.9 \\ {\rm Ce}_2(OH)_2^{5+} & -362.070 & {\rm Baes and Mesmer} & {\rm Th}_2{\rm PO}_4^{3+} & -446.378 & {\rm HSC} 9.9 \\ {\rm Ce}_2(OH)_5^{5+} & -419.430 & {\rm Baes and Mesmer} & {\rm -446.150} & {\rm HSC} 5.11 \\ {\rm Ce}_2(OH)_5^{5+} & -419.430 & {\rm Baes and Mesmer} & {\rm -446.150} & {\rm HSC} 9.9 \\ {\rm Cef}_3 & -385.311 & {\rm HSC} 9.9 & {\rm Th}_3{\rm PO}_4^{4+} & -445.706 & {\rm HSC} 9.9 \\ {\rm Cef}_4 & -418.999 & {\rm HSC} 9.9 & {\rm Th}({\rm HPO}_4)_3^2^- & {\rm -1001.906} & {\rm HSC} 9.9 \\ {\rm Cef}_5 & -107.259 & {\rm HSC} 9.9 & {\rm Th}({\rm HPO}_4)_2({\rm HPO}_4)^{4-} & {\rm -722.489} & {\rm HSC} 5.11 \\ {\rm Ce}_2{\rm So}_4 & -388.652 & {\rm HSC} 9.9 & {\rm Th}({\rm HPO}_4)_2({\rm HPO}_4)_{-120} & {\rm -1230.166} & {\rm Kerdaniel} \\ {\rm Ce}_3{\rm S}_4 & -388.652 & {\rm HSC} 9.9 & {\rm Th}O{\rm H}^3^+ & -220.070 & {\rm HSC} 9.9 \\ {\rm -506.366} & {\rm HSC} 5.11 & {\rm -220.000} & {\rm Wagman} \\ {\rm Ce}_2({\rm SO}_4)_2 & -506.184 & {\rm HSC} 9.9 & {\rm Th}O{\rm H}^3^+ & -220.070 & {\rm HSC} 9.9 \\ {\rm -506.366} & {\rm HSC} 5.11 & {\rm Th}(O{\rm H})_2^{4+} & -226.683 & {\rm HSC} 9.9 \\ {\rm -506.366} & {\rm HSC} 5.11 & {\rm Th}(O{\rm H})_2^{6+} & -444.241 & {\rm HSC} 9.9 \\ {\rm Ce}_2({\rm SO}_4)_2 & -506.184 & {\rm HSC} 9.9 & {\rm ThOH}^3 & -220.070 & {\rm HSC} 9.9 \\ {\rm -506.366} & {\rm HSC} 5.11 & {\rm Th}(O{\rm H})_2^{6+} & -444.241 & {\rm HSC} 9.9 \\ {\rm Ce}_2({\rm SO}_4)_2 & -506$	CeNO ₃ ²⁺	-189.025	HSC 9.9	ThO	-138.800	HSC 9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CeO ⁺	-205.111	HSC 9.9	ThO ₂	-279.455	HSC 9.9
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	CeO_2^-	-217.402	HSC 9.9		-279.340	Wagman
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CeOH ²⁺	-209.611	HSC 9.9		-278.330	HSC 5.11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-205.960	HSC 5.11	Th(OH) ₄	-382.263	HSC 9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CeOH ³⁺	-178.830	HSC 9.9	Th^{4+}	-168.507	HSC 9.9
$\begin{array}{cccc} {\rm Ce}({\rm OH})_2^{2+} & -224.250 & {\rm HSC}9.9 & -167.800 & {\rm HSC}5.11 \\ {\rm Ce}_2({\rm OH})_2^{4+} & -413.410 & {\rm Baes} and {\rm Mesmer} & {\rm ThHPO4}^{2+} & -401.224 & {\rm HSC}9.9 \\ {\rm Ce}_3({\rm OH})_5^{4+} & -719.496 & {\rm Baes} and {\rm Mesmer} & {\rm ThH}_2{\rm PO4}^{2+} & -434.174 & {\rm HSC}9.9 \\ {\rm Ce}({\rm OH})_2^{2+} & -235.670 & {\rm Baes} and {\rm Mesmer} & {\rm ThH}_2{\rm PO4}^{2+} & -436.378 & {\rm HSC}9.9 \\ {\rm Ce}_2({\rm OH})_5^{5+} & -419.430 & {\rm Baes} and {\rm Mesmer} & {\rm ThH}_2{\rm PO4}^{3+} & -446.378 & {\rm HSC}9.9 \\ {\rm Ce}_2({\rm OH})_5^{5+} & -419.430 & {\rm Baes} and {\rm Mesmer} & -446.150 & {\rm HSC}5.11 \\ {\rm Ce}_{\rm ClO}_4^{2+} & -166.270 & {\rm HSC}9.9 & {\rm ThH}_3{\rm PO4}^{4+} & -445.706 & {\rm HSC}9.9 \\ {\rm CeF}_3 & -385.311 & {\rm HSC}9.9 & {\rm Th}{\rm HSC}9.9 & -444.030 & {\rm HSC}5.11 \\ {\rm CeF}_4 & -418.999 & {\rm HSC}9.9 & {\rm Th}({\rm HO}_4)_3^{2-} & -1001.906 & {\rm HSC}9.9 \\ {\rm CeS} & -107.259 & {\rm HSC}9.9 & {\rm Th}({\rm HPO4})_3^{2-} & -1001.906 & {\rm HSC}9.9 \\ {\rm Ce}_5_3 & -279.743 & {\rm HSC}9.9 & {\rm Th}({\rm HPO}_4)_2.4{\rm H_2O} & -952.667 & {\rm HSC}5.11 \\ {\rm Ce}_2{\rm S}_4 & -388.652 & {\rm HSC}9.9 & {\rm Th}_2({\rm PO}_4)_2({\rm HPO}_4)\cdot{\rm H_2O} & -1230.166 & {\rm Kerdaniel} \\ {\rm Ce}_3{\rm S}_4 & -388.652 & {\rm HSC}9.9 & {\rm Th}({\rm OH}^{3+} & -220.070 & {\rm HSC}9.9 \\ & -506.366 & {\rm HSC}5.11 & {\rm Th}({\rm OH}^{3+} & -220.070 & {\rm HSC}9.9 \\ & -506.366 & {\rm HSC}5.11 & {\rm Th}({\rm OH}^{3+} & -220.069 & {\rm HSC}5.11 \\ & -861.115 & {\rm HSC}9.9 & {\rm Th}({\rm OH}^{3+} & -220.069 & {\rm HSC}5.11 \\ & -861.115 & {\rm HSC}9.9 & {\rm Th}({\rm OH}^{3+} & -220.069 & {\rm HSC}5.11 \\ & -861.115 & {\rm HSC}9.9 & {\rm Th}({\rm OH}^{3+} & -220.069 & {\rm HSC}9.9 \\ & {\rm Ce}_{({\rm SO}_4)_2}\cdot{\rm SH}_2{\rm O} & -1191.210 & {\rm HSC}9.9 & {\rm -220.069} & {\rm HSC}5.11 \\ & -861.115 & {\rm HSC}9.9 & {\rm -220.069} & {\rm HSC}5.11 \\ & {\rm Ce}_{2}({\rm SO}_4)_3\cdot{\rm SH}_2{\rm O}({\rm S}^{3-} & {\rm -322.610} & {\rm Dean}, {\rm Wagman} & {\rm Th}({\rm OH})_3^{+} & {\rm -322.711} & {\rm HSC}9.9 \\ & {\rm Ce}_{({\rm S}^{3+} & {\rm -204.692} & {\rm HSC}9.9 & {\rm Th}_{2}({\rm OH})_2^{6+} & {\rm -444.241} & {\rm HSC}9.9 \\ &$		-178.580	Baes and Mesmer		-168.520	Wagman
$\begin{array}{ccccc} {\rm Ce}_2({\rm OH})_2^{4+} & -413.410 & {\rm Baes and Mesmer} & {\rm Th}{\rm HPO4}_2^{2+} & -401.224 & {\rm HSC 9.9} \\ {\rm Ce}_3({\rm OH})_5^{4+} & -719.496 & {\rm Baes and Mesmer} & {\rm Th}{\rm H_2PO4}_2^{2+} & {\rm b} & -434.174 & {\rm HSC 9.9} \\ {\rm Ce}({\rm OH})_2^{2+} & -235.670 & {\rm Baes and Mesmer} & {\rm Th}{\rm H_2PO4}_3^{3+} & -446.378 & {\rm HSC 9.9} \\ {\rm Ce}_2({\rm OH})_2^{6+} & -362.070 & {\rm Baes and Mesmer} & {\rm Th}{\rm H_2PO4}_3^{3+} & -446.378 & {\rm HSC 9.9} \\ {\rm Ce}_2({\rm OH})_3^{5+} & -419.430 & {\rm Baes and Mesmer} & {\rm Th}{\rm H_2PO4}_3^{4+} & -446.570 & {\rm HSC 9.9} \\ {\rm Ce}_2({\rm OH})_4^{2+} & -166.270 & {\rm HSC 9.9} & {\rm Th}{\rm H_3PO_4}^{4+} & -445.706 & {\rm HSC 9.9} \\ {\rm CeF}_3 & -385.311 & {\rm HSC 9.9} & {\rm m}{\rm HSC 9.9} & {\rm m}{\rm H}3{\rm PO}_4^{4+} & -445.706 & {\rm HSC 9.9} \\ {\rm CeF}_4 & -418.999 & {\rm HSC 9.9} & {\rm Th}({\rm HPO4}_3)_3^{2-} & {\rm -1001.906} & {\rm HSC 9.9} \\ {\rm CeS} & -107.259 & {\rm HSC 9.9} & {\rm Th}({\rm HPO4}_3)_4^{2-} & {\rm -222.489} & {\rm HSC 5.11} \\ {\rm Ce}_2{\rm S}_2 & -145.208 & {\rm HSC 9.9} & {\rm Th}({\rm HPO4}_3)_4^{2-} & {\rm -1001.906} & {\rm HSC 9.9} \\ {\rm Ce}_3{\rm S}_4 & -388.652 & {\rm HSC 9.9} & {\rm Th}({\rm HPO4}_3)_2^{-4}{\rm H_2O} & {\rm -952.667} & {\rm HSC 5.11} \\ {\rm Ce}_2{\rm S}_4 & -388.652 & {\rm HSC 9.9} & {\rm Th}_2({\rm PO4}_3)_2({\rm HPO4}_3)^{-1}{\rm H_2O} & {\rm -1230.166} & {\rm Kerdaniel} \\ {\rm Ce}_3{\rm S}_4 & -388.652 & {\rm HSC 9.9} & {\rm Th}{\rm OH}^{3+} & {\rm -220.070} & {\rm HSC 9.9} \\ {\rm -506.184} & {\rm HSC 9.9} & {\rm Th}{\rm OH}^{3+} & {\rm -220.000} & {\rm Wagman} \\ {\rm Ce}_2({\rm SO4}_3)_2 & {\rm -860.943} & {\rm HSC 9.9} & {\rm -1001.91} & {\rm HSC 9.9} \\ {\rm -506.366} & {\rm HSC 5.11} & {\rm Th}({\rm OH}_3)_2^{-4} & {\rm -272.693} & {\rm HSC 9.9} \\ {\rm Ce}_5{\rm O4}_3)_2{\rm H_2O}({\rm S})^{\rm a} & {\rm -1322.620} & {\rm Dean}, {\rm Wagman} & {\rm Th}({\rm OH}_3^{-4} & {\rm -222.0100} & {\rm Wagman} \\ {\rm Ce}_2({\rm SO4}_4)_2{\rm H_2O}({\rm S})^{\rm a} & {\rm -1322.620} & {\rm Dean}, {\rm Wagman} & {\rm Th}({\rm OH}_3^{-6} & {\rm -444.241} & {\rm HSC 9.9} \\ {\rm Ce}_5{\rm F}^{+} & {\rm -234.692} & {\rm HSC 9.9} & {\rm Th}{\rm COH}_3^{-6} & {\rm -4441.241} & {\rm HSC 9.9} \\ {\rm Ce}_5{\rm F}^{+} & {\rm -234.692} & {\rm HSC $	$Ce(OH)_2^{2+}$	-224.250	HSC 9.9		-167.800	HSC 5.11
$\begin{array}{cccc} Ce_3(OH)_5^{4+} & -719.496 & Baes and Mesmer & ThH_2PO_4^{2+b} & -434.174 & HSC 9.9 \\ Ce(OH)_2^{2+} & -235.670 & Baes and Mesmer & -723.550 & HSC 5.11 \\ Ce_2(OH)_2^{6+} & -362.070 & Baes and Mesmer & ThH_2PO_4^{3+} & -446.378 & HSC 9.9 \\ Ce_2(OH)_3^{5+} & -419.430 & Baes and Mesmer & -446.150 & HSC 5.11 \\ CeClO_4^{2+} & -166.270 & HSC 9.9 & ThH_3PO_4^{4+} & -445.706 & HSC 9.9 \\ CeF_3 & -385.311 & HSC 9.9 & -444.030 & HSC 5.11 \\ CeF_4 & -418.999 & HSC 9.9 & Th(HPO_4)_3^{2-} & -1001.906 & HSC 9.9 \\ CeS & -107.259 & HSC 9.9 & Th(HPO_4)_3^{4+} & -722.489 & HSC 5.11 \\ Ce_5S_3 & -279.743 & HSC 9.9 & Th_2(PO_4)^{3+} & -722.489 & HSC 5.11 \\ Ce_5S_4 & -388.652 & HSC 9.9 & Th_2(PO_4)_2(HPO_4)_{-12}O & -952.667 & HSC 5.11 \\ Ce_3S_4 & -388.652 & HSC 9.9 & Th_2(PO_4)_2(HPO_4)_{-12}O & -1230.166 & Kerdaniel \\ Ce_3S_4 & -388.652 & HSC 9.9 & Th_0H^{3+} & -220.070 & HSC 9.9 \\ Ce(SO_4)_2 & -506.184 & HSC 9.9 & ThOH^{3+} & -220.070 & HSC 9.9 \\ -506.366 & HSC 5.11 & -220.000 & Wagman \\ Ce_2(SO_4)_3 & -860.943 & HSC 9.9 & ThOH^{3+} & -220.069 & HSC 5.11 \\ -861.115 & HSC 5.11 & Th(OH)_2^{2+} & -272.693 & HSC 9.9 \\ Ce_3(SO_4)_2 \cdot 5H_2O & -1191.210 & HSC 9.9 & Th(OH)_3^{+} & -322.711 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 860.943 & HSC 9.9 & Th_2(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_5C_4(SO_4)_3 \cdot 860.943 & HSC 9.9 & Th_2(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_5C_4(SO_4)_3 \cdot 860.943 & HSC 9.9 & Th_2(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_5C_4(SO_4)_3 \cdot 812O(s)^{-3} & -1322.620 & Dean, Wagman & Th(OH)_3^{+} & -322.711 & HSC 9.9 \\ Ce_5C_4 & -306.163 & HSC 9.9 & Th_2(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_5C_4 & -306.163 & HSC 9.9 & Th_2(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_5C_4 & -306.163 & HSC 9.9 & -441.241 & HSC 5.11 \\ Ce_5C_4 & -306.163 & HSC 9.9 & -441.241 & HSC 5.11 \\ Ce_5C_4 & -306.163 & HSC 9.9 & -441.241 & HSC 5.11 \\ Ce_5C_4 & -306.163 & HSC 9.9 & -441.241 & HSC 5.11 \\ Ce_5C_4 & -306.163 & HSC 9.9 & -441.241 & HSC 9.9 \\ Ce_5C_4 & -306.163 & HSC 9.9 & -441.241 & HSC 9.9 \\ Ce_5C_4 & -306.163 & HSC 9.9 & -441.241 & HSC 9.9 \\ Ce_5C_4 & -30$	$Ce_2(OH)_2^{4+}$	-413.410	Baes and Mesmer	ThHPO ₄ ²⁺	-401.224	HSC 9.9
$\begin{array}{cccc} {\rm Ce}({\rm OH})_2^{2+} & -235.670 & {\rm Baes and Mesmer} & -723.550 & {\rm HSC 5.11} \\ {\rm Ce}_2({\rm OH})_2^{6+} & -362.070 & {\rm Baes and Mesmer} & {\rm ThH}_2{\rm PO}_4^{3+} & -446.378 & {\rm HSC 9.9} \\ {\rm Ce}_2({\rm OH})_3^{5+} & -419.430 & {\rm Baes and Mesmer} & -446.150 & {\rm HSC 5.11} \\ {\rm CeClO}_4^{2+} & -166.270 & {\rm HSC 9.9} & {\rm ThH}_3{\rm PO}_4^{4+} & -445.706 & {\rm HSC 9.9} \\ {\rm CeF}_3 & -385.311 & {\rm HSC 9.9} & -444.030 & {\rm HSC 9.9} \\ {\rm CeF}_4 & -418.999 & {\rm HSC 9.9} & {\rm Th}({\rm HPO}_4)_3^{2-} & -1001.906 & {\rm HSC 9.9} \\ {\rm CeS} & -107.259 & {\rm HSC 9.9} & {\rm Th}({\rm HPO}_4)_2 \cdot {\rm H_2O} & -952.667 & {\rm HSC 5.11} \\ {\rm Ce}_2{\rm S}_3 & -279.743 & {\rm HSC 9.9} & {\rm Th}({\rm HPO}_4)_2 \cdot {\rm H_2O} & -952.667 & {\rm HSC 5.11} \\ {\rm Ce}_3{\rm S}_4 & -388.652 & {\rm HSC 9.9} & {\rm Th}O^+ & -204.534 & {\rm HSC 9.9} \\ {\rm Ce}({\rm SO}_4)_2 & -506.184 & {\rm HSC 9.9} & {\rm ThOH}^{3+} & -220.070 & {\rm HSC 9.9} \\ & -506.366 & {\rm HSC 5.11} & {\rm ThOH}^{3+} & -220.070 & {\rm HSC 9.9} \\ {\rm Ce}({\rm SO}_4)_3 & -860.943 & {\rm HSC 9.9} & {\rm Th}({\rm OH})_2^{2+} & -272.693 & {\rm HSC 9.9} \\ {\rm Ce}({\rm SO}_4)_2 \cdot {\rm 5H}_2O & -1191.210 & {\rm HSC 9.9} & {\rm Th}({\rm OH})_3^{+} & -220.069 & {\rm HSC 5.11} \\ {\rm Ce}_2({\rm SO}_4)_3 \cdot {\rm a} & -332.620 & {\rm Dean, Wagman} & {\rm Th}({\rm OH})_3^{+} & -322.711 & {\rm HSC 9.9} \\ {\rm Ce}_2^{\rm F^2+} & -234.692 & {\rm HSC 9.9} & {\rm Th}_2({\rm OH})_2^{6+} & -444.241 & {\rm HSC 9.9} \\ {\rm CeF}_2^{+} & -306.163 & {\rm HSC 9.9} & {\rm Th}_2({\rm OH})_2^{6+} & -444.241 & {\rm HSC 9.9} \\ {\rm CeF}_2^{+} & -306.163 & {\rm HSC 9.9} & {\rm Th}_2({\rm OH})_2^{6+} & -444.241 & {\rm HSC 9.9} \\ {\rm CeF}_2^{+} & -306.163 & {\rm HSC 9.9} & {\rm Th}_2({\rm OH})_2^{6+} & -444.241 & {\rm HSC 9.9} \\ {\rm CeF}_2^{+} & -306.163 & {\rm HSC 9.9} & {\rm Th}_2({\rm OH})_2^{6+} & -444.241 & {\rm HSC 9.9} \\ {\rm CeF}_2^{+} & -306.163 & {\rm HSC 9.9} & {\rm Th}_2({\rm OH})_2^{6+} & -444.241 & {\rm HSC 9.9} \\ {\rm CeF}_2^{+} & -306.163 & {\rm HSC 9.9} & {\rm Th}_2({\rm OH})_2^{6+} & -444.241 & {\rm HSC 9.9} \\ {\rm CeF}_2^{+} & -306.163 & {\rm HSC 9.9} & {\rm Th}_2({\rm OH})_2^{6+} & -444.241 & {\rm HSC 9.9} \\ {\rm CeF}_2^{+} & -306.163 & {\rm$	$Ce_{3}(OH)_{5}^{4+}$	-719.496	Baes and Mesmer	$ThH_2PO_4^{2+b}$	-434.174	HSC 9.9
$\begin{array}{cccc} {\rm Ce}_2({\rm OH})_2^{6+} & -362.070 & {\rm Baes and Mesmer} & {\rm Th}H_2{\rm PO}_4^{3+} & -446.378 & {\rm HSC } 9.9 \\ {\rm Ce}_2({\rm OH})_3^{5+} & -419.430 & {\rm Baes and Mesmer} & -446.150 & {\rm HSC } 5.11 \\ {\rm CeClO}_4^{2+} & -166.270 & {\rm HSC } 9.9 & {\rm Th}H_3{\rm PO}_4^{4+} & -445.706 & {\rm HSC } 9.9 \\ {\rm CeF}_3 & -385.311 & {\rm HSC } 9.9 & -444.030 & {\rm HSC } 5.11 \\ {\rm CeF}_4 & -418.999 & {\rm HSC } 9.9 & {\rm Th}({\rm HPO}_4)_3^{2-} & -1001.906 & {\rm HSC } 9.9 \\ {\rm CeS} & -107.259 & {\rm HSC } 9.9 & {\rm Th}({\rm HPO}_4)_2 \cdot {\rm H_2O} & -952.667 & {\rm HSC } 5.11 \\ {\rm Ce}_2{\rm S}_3 & -279.743 & {\rm HSC } 9.9 & {\rm Th}({\rm HPO}_4)_2 \cdot {\rm H_2O} & -1230.166 & {\rm Kerdaniel} \\ {\rm Ce}_3{\rm S}_4 & -388.652 & {\rm HSC } 9.9 & {\rm Th}O^+ & -204.534 & {\rm HSC } 9.9 \\ {\rm Ce}({\rm SO}_4)_2 & -506.184 & {\rm HSC } 9.9 & {\rm Th}O^+^{3+} & -220.070 & {\rm HSC } 9.9 \\ & -506.366 & {\rm HSC } 5.11 & {\rm Ce}_2{\rm SO}_4)_3 & -860.943 & {\rm HSC } 9.9 & {\rm Th}O{\rm HSC } 9.9 \\ {\rm Ce}({\rm SO}_4)_2 \cdot {\rm 5H}_2{\rm O} & -1191.210 & {\rm HSC } 9.9 & {\rm Th}({\rm OH})_2^{2+} & -272.680 & {\rm Wagman} \\ {\rm Ce}_2({\rm SO}_4)_3 \cdot {\rm 8H}_2{\rm O(s)}^{\rm a} & -1322.620 & {\rm Dean, Wagman } {\rm Th}({\rm OH})_3^+ & -322.711 & {\rm HSC } 9.9 \\ {\rm Ce}_4^{\rm c}^{\rm c}$	$Ce(OH)_2^{2+}$	-235.670	Baes and Mesmer	<u> </u>	-723.550	HSC 5.11
$\begin{array}{cccc} Ce_2(OH)_3^{5+} & -419.430 & Baes and Mesmer & -446.150 & HSC 5.11 \\ CeClO_4^{2+} & -166.270 & HSC 9.9 & ThH_3PO_4^{4+} & -445.706 & HSC 9.9 \\ CeF_3 & -385.311 & HSC 9.9 & -444.030 & HSC 9.9 \\ CeF_4 & -418.999 & HSC 9.9 & Th(HPO_4)_3^{2-} & -1001.906 & HSC 9.9 \\ CeS & -107.259 & HSC 9.9 & Th(H_3PO_4)(H_2PO_4)^{3+} & -722.489 & HSC 5.11 \\ Ce_2S_2 & -145.208 & HSC 9.9 & Th(H_2O_4)_2.4H_2O & -952.667 & HSC 5.11 \\ Ce_2S_3 & -279.743 & HSC 9.9 & Th_2(PO_4)_2(HPO_4)\cdot H_2O & -1230.166 & Kerdaniel \\ Ce_3S_4 & -388.652 & HSC 9.9 & ThO^+ & -204.534 & HSC 9.9 \\ Ce(SO_4)_2 & -506.184 & HSC 9.9 & ThO^+ & -220.070 & HSC 9.9 \\ & -506.366 & HSC 5.11 & Th(OH)_3^{++} & -220.000 & Wagman \\ Ce_2(SO_4)_3 & -860.943 & HSC 9.9 & -272.680 & Wagman \\ Ce_2(SO_4)_2 \cdot 5H_2O & -1191.210 & HSC 9.9 & -272.680 & Wagman \\ Ce_2(SO_4)_2 \cdot 5H_2O & -1191.210 & HSC 9.9 & Th(OH)_3^{++} & -322.711 & HSC 9.9 \\ Ce(SO_4)_2 \cdot 5H_2O & -1191.210 & HSC 9.9 & Th_2(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th(OH)_3^{++} & -322.711 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th(OH)_3^{-6+} & -444.241 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th(OH)_3^{-6+} & -322.711 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th(OH)_2^{6+} & -444.241 & HSC 9.9 \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th$	$Ce_2(OH)_2^{6+}$	-362.070	Baes and Mesmer	ThH ₂ PO ₄ ³⁺	-446.378	HSC 9.9
$\begin{array}{cccc} CeClO_4^{2+} & -166.270 & HSC 9.9 & ThH_3PO_4^{4+} & -445.706 & HSC 9.9 \\ CeF_3 & -385.311 & HSC 9.9 & -444.030 & HSC 5.11 \\ CeF_4 & -418.999 & HSC 9.9 & Th(HPO_4)_3^{2-} & -1001.906 & HSC 9.9 \\ CeS & -107.259 & HSC 9.9 & Th(HPO_4)_2(PO_4)^{3+} & -722.489 & HSC 5.11 \\ Ce_2S_2 & -145.208 & HSC 9.9 & Th(HPO_4)_2.4H_2O & -952.667 & HSC 5.11 \\ Ce_2S_3 & -279.743 & HSC 9.9 & Th_2(PO_4)_2(HPO_4)-H_2O & -1230.166 & Kerdaniel \\ Ce_3S_4 & -388.652 & HSC 9.9 & ThO^+ & -204.534 & HSC 9.9 \\ Ce(SO_4)_2 & -506.184 & HSC 9.9 & ThOH^{3+} & -220.070 & HSC 9.9 \\ & -506.366 & HSC 5.11 & -220.000 & Wagman \\ Ce_2(SO_4)_3 & -860.943 & HSC 9.9 & -220.069 & HSC 5.11 \\ Ce_2(SO_4)_2 & -506.184 & HSC 9.9 & -220.069 & HSC 5.11 \\ -861.115 & HSC 5.11 & Th(OH)_2^{2+} & -272.693 & HSC 9.9 \\ Ce(SO_4)_2 \cdot 5H_2O & -1191.210 & HSC 9.9 & -272.680 & Wagman \\ Ce_2(SO_4)_3 \cdot 8H_2O(s)^a & -1322.620 & Dean, Wagman & Th(OH)_3^+ & -322.711 & HSC 9.9 \\ CeF^{2+} & -234.692 & HSC 9.9 & Th_2(OH)_2^{6+} & -444.241 & HSC 9.9 \\ CeF_2^+ & -306.163 & HSC 9.9 & -441.241 & HSC 9.1 \\ \end{array}$	$Ce_2(OH)_3^{5+}$	-419.430	Baes and Mesmer	2 1	-446.150	HSC 5.11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CeClO ₄ ²⁺	-166.270	HSC 9.9	ThH₃PO₄ ⁴⁺	-445.706	HSC 9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CeF ₃	-385.311	HSC 9.9	5 - 1	-444.030	HSC 5.11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CeF₄	-418.999	HSC 9.9	$Th(HPO_4)_3^{2-}$	-1001.906	HSC 9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CeS	-107.259	HSC 9.9	$Th(H_3PO_4)(H_2PO_4)^{3+}$	-722.489	HSC 5.11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CeS ₂	-145.208	HSC 9.9	Th(HPO ₄) ₂ ·4H ₂ O	-952.667	HSC 5.11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ce_2S_3	-279.743	HSC 9.9	$Th_2(PO_4)_2(HPO_4) \cdot H_2O$	-1230.166	Kerdaniel
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ce_3S_4	-388.652	HSC 9.9	ThO ⁺	-204.534	HSC 9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$Ce(SO_4)_2$	-506.184	HSC 9.9	ThOH ³⁺	-220.070	HSC 9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(1/2	-506.366	HSC 5.11		-220.000	Wagman
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$Ce_2(SO_4)_3$	-860.943	HSC 9.9		-220.069	HSC 5.11
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2. 1.0	-861.115	HSC 5.11	$Th(OH)_2^{2+}$	-272.693	HSC 9.9
$\begin{array}{cccc} Ce_2(SO_4)_3 \cdot 8H_2O(s) \ ^a & -1322.620 \\ CeF^{2+} & -234.692 \\ CeF_2^{+} & -306.163 \\ CeF_2^{+} & -306.163 \\ \end{array} \begin{array}{cccc} Dean, Wagman \\ HSC \ 9.9 \\ HSC \ 9.9 \\ HSC \ 9.9 \\ -441.241 \\ HSC \ 5.11 \\ HSC \ 5.11 \\ \end{array}$	$Ce(SO_4)_2 \cdot 5H_2O$	-1191.210	HSC 9.9	() <u>-</u>	-272.680	Wagman
CeF^{2+} -234.692 HSC 9.9 $Th_2(OH)_2^{6+}$ -444.241 HSC 9.9 CeF_2^+ -306.163 HSC 9.9 -441.241 HSC 5.11	$Ce_2(SO_4)_3 \cdot 8H_2O(s)^a$	-1322.620	Dean, Wagman	Th(OH) ₃ ⁺	-322.711	HSC 9.9
CeE_{2}^{+} -306.163 HSC 9.9 -441.241 HSC 5.11	CeF ²⁺	-234.692	HSC 9.9	$Th_2(OH)_2^{6+}$	-444.241	HSC 9.9
	CeF_2^+	-306.163	HSC 9.9		-441.241	HSC 5.11
CeF_4^{-} -446.467 HSC 9.9 $Th(OH)_6^{2-}$ -445.000 Wagman	CeF_4^-	-446.467	HSC 9.9	$Th(OH)_6^{2-}$	-445.000	Wagman
CeSO ₄ ⁺ -344.445 HSC 9.9 Th ₄ (OH) ₈ ⁸⁺ -1099.168 HSC 5.11	$CeSO_4^+$	-344.445	HSC 9.9	$Th_4(OH)_8^{8+}$	-1099.168	HSC 5.11
-344.627 HSC 5.11 Th ₄ (OH) ₁₂ ⁴⁺ -1312.614 Rand	1	-344.627	HSC 5.11	$Th_4(OH)_{12}^{4+}$	-1312.614	Rand
$Ce(SO_4)_2^-$ -523.696 HSC 9.9 $Th_6(OH)_{14}^{10+}$ -1747.287 Rand	$Ce(SO_4)_2^-$	-523.696	HSC 9.9	$Th_{6}(OH)_{14}^{10+}$	-1747.287	Rand
-523.878 HSC 5.11 Th ₆ (OH) ₁₅ ⁹⁺ -1811.602 HSC 5.11	(1)2	-523.878	HSC 5.11	$Th_{6}(OH)_{15}^{9+}$	-1811.602	HSC 5.11
$Th_{0}(OH)_{15}^{5+}$ -495.755 Rand				$Th_2(OH)_2^{5+}$	-495.755	Rand
La 0.000 HSC 9.9 ThCl ₂ -161.045 HSC 9.9	La	0.000	HSC 9.9	ThCl	-161.045	HSC 9.9
LaH ₂ -38.415 HSC 9.9 ThCl ₃ -213.197 HSC 9.9	LaH ₂	-38.415	HSC 9.9	ThCl ₃	-213.197	HSC 9.9
LaN -64.779 HSC 9.9 ThCl ₄ -261.724 HSC 9.9	LaN	-64.779	HSC 9.9	ThCl	-261.724	HSC 9.9
$La_2O_3 -407.239 HSC 9.9 ThOCl_2 -276.399 HSC 9.9$	La ₂ O ₃	-407.239	HSC 9.9	ThOC ₁₂	-276.399	HSC 9.9
-407.700 Brookins ThCl ³⁺ -201.623 HSC 9.9	2 0	-407.700	Brookins	ThCl ³⁺	-201.623	HSC 9.9

 Table 1. Cont.

Species	$\Delta G_{f,298}^0$ (kcal/mol)	References	Species	$\Delta G_{f,298}^0$ (kcal/mol)	References
LaO ₂ H	-239.621	HSC 9.9	$Th(SO_4)_2(a)$	-537.701	HSC 5.11
La(OH) ₃	-305.945	HSC 9.9	$ThSO_4^{2+}$	-353.900	Wagman
	-305.800	Brookins	-	-354.099	HSC 5.11
	-305.745	HSC 5.11	$Th(SO_4)_3^{2-}$	-713.840	Rand
LaPO ₄	-442.238	HSC 9.9	Th(SO ₄) ₂ .9H ₂ O	-1045.540	Rand
	-441.887	Liu and Byrne			
	-425.785	HSC 5.11	Y	0.000	HSC 9.9
$La(PO_3)_3$	-764.090	HSC 9.9	YN	-64.165	HSC 9.9
LaPO ₄ ·2H ₂ O	-569.549	HSC 9.9	YH ₂	-43.233	HSC 9.9
La ²⁺	-77.666	HSC 9.9	YH ₃	-49.328	HSC 9.9
La ³⁺	-163.997	HSC 9.9	Y_2O_3	-434.061	HSC 9.9
	-163.400	Brookins		-434.200	Brookins
	-164.010	HSC 5.11	Y(OH) ₃	-319.870	HSC 9.9
LaH ₂ PO ₄ ²⁺	-437.575	HSC 9.9		-308.600	Brookins
LaNO ₃ ²⁺	-191.232	HSC 9.9	YPO_4	-446.402	HSC 9.9
LaO ⁺	-204.935	HSC 9.9	YPO ₄ ·2H ₂ O	-552.328	HSC 9.9
LaO_2^-	-216.948	HSC 9.9	YS	-108.884	HSC 9.9
LaOH ²⁺	-209.524	HSC 9.9	Y_2S_3	-296.898	HSC 9.9
$La_2(OH)_2^{4+}$	-416.286	Baes and Mesmer	$Y_2(SO_4)_3 \cdot 8H_2O$	-1320.595	HSC 9.9
$La_3(OH)_5^{4+}$	-721.350	Baes and Mesmer	Y ³⁺	-163.788	HSC 9.9
LaCl ₂	-109.004	HSC 9.9		-165.800	Brookins
LaCl ₃	-237.904	HSC 9.9	YO ⁺	-198.099	HSC 9.9
LaCl ₃ ·7H ₂ O	-645.182	HSC 9.9	YO_2^-	-227.335	HSC 9.9
LaOCl	-230.090	HSC 9.9	YOH ²⁺	-209.927	HSC 9.9
LaCl ²⁺	-195.747	HSC 9.9	YSO_4^+	-347.459	HSC 9.9
$LaCl_2^+$	-226.743	HSC 9.9	$Y(SO_4)_2^-$	-526.127	HSC 9.9
$LaCl_4^-$	-288.371	HSC 9.9	$Y(OH)_4^-$	-341.200	Brookins
			YCl ₃	-221.713	HSC 9.9
			YCl ₃ ⋅6H ₂ O	-591.468	HSC 9.9
			YOCI	-225.617	HSC 9.9
			YCl ²⁺	-198.520	HSC 9.9
			$Y_2(CO_3)_3$	-752.400	Brookins

Table 1. Cont.

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