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Chemistry and Thermodynamics of Europium and Some of Its Simpler Inorganic Compounds and Aqueous Species

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I. Introduction

In 1752, A. J. Cronstedt described a new mineral associated with copper pyrite in a Swedish mine near Ryddarhyttan. He named this mineral tungstein or "heavy stone." This name was also applied to a mineral from Bohemia, $CaWO_4$, now known as scheelite. The Swedish mineral was later shown to be different and was then thought to be a Ca–Fe silicate. The rare earths, unknown at that time, were mistaken for calcium.

In 1794, J. Gadolin isolated an oxide from a heavy black mineral at Ytterby and named the oxide ytterbia. C. G. Mosander in 1842 described oxalate precipitation and hydroxide precipitation to separate the ytterbia into three other "earths", which he named yttria, erbia, and terbia. These "earths" turned out to be complicated mixtures also. The isolation of La, lanthanides, yttrium, and scandium was not completed until 1908–1909 owing to the difficulties in separating them by fractional crystallization. Not surprisingly, there are numerous mistaken claims in the early literature as to the nature and number of rare earths.

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Joseph A. Rard was born in St. Louis, Missouri. He received a B.A. in chemistry from Southern Illinois University at Edwardsville (in 1967) and a Ph.D. in physical chemistry from Iowa State University (in 1973) under the direction of Professor Frank H. Spedding. He was a postdoctoral fellow at Ames Laboratory from 1973 to 1976 and a University of Illinois Visiting Research Assistant Professor of Geology during 1977 and 1978 (tenured entirely as a participating guest at Lawrence Livermore National Laboratory, however). He is currently a chemist with the Earth Sciences Department at Lawrence Livermore National Laboratory. His main research interests are in the experimental determination and critical reviews of thermodynamic and transport properties of inorganic compounds, especially their aqueous electrolyte solutions. Major emphasis has been for aqueous lanthanide, transition-metal, brine, and radwaste salts.

Element number 63 is generally considered to have been discovered by E. DeMarcay in 1896 and called element Σ by him. The following year he named it europium (Eu), after Europe. Actually, some of its spectroscopic lines had been noted earlier by de Boisbaudran but were incorrectly attributed to other elements. Mellor's treatise should be consulted for a discussion of the discovery and separation of the various rare earths.[1a]

La through Lu possess a free atom outer electron shell of $5d^16s^2$ or $6s^2$ in their ground state.[1b] These outer electrons are readily lost when these elements form their ions and compounds, and the dominant valence state is plus three for the rare earths. La through Lu differ in their number of 4f electrons, which range from 0 for La to 14 for Lu. They occur below the outer electron orbitals and do not generally participate to a significant degree in chemical bonding. The 4f orbitals are fairly diffuse and do not effectively shield the outer electrons from the nuclear charge. Consequently, there is a gradual decrease in the ionic radius as the number of 4f electrons increase, which is known as the lanthanide contraction.

Element 39, yttrium, is usually classified with the rare earths since it forms a +3 ion with a radius comparable to that of the heavier rare earths and because it occurs with them in nature. Scandium is also called a rare earth, but because of its smaller radius it has significantly different chemistry. We will restrict the term rare earth (abbreviated RE) to La through Lu and Y. Similarly the elemental forms will be denoted as REE. It should be noted that in the German literature SEE is used instead (for Seltenerdelemente). The terms lanthanide, lanthanon, and lanthanoid are usually restricted to Ce through Lu, but some authors also include lanthanum.

Because of the chemical similarity of the REE, early attempts to separate them by fractional crystallization yielded only slight enrichments, so most available samples were not very pure. However, in 1935 McCoy[2] reported purification of "considerable quantities" of Eu by reduction of Eu^{3+} to Eu^{2+} with Zn amalgam in a Jones reductor, followed by precipitation as the nearly insoluble $EuSO_4$. McCoy generously supplied other scientists with samples of his Eu. Marsh[3] modified this procedure by reducing RE ions with Na amalgam to form a Sm–Eu amalgam, followed by dissolution with acid and precipitation with sulfate. The Sm could be selectively oxidized with HNO_3 to effect its separation.

The next major advance in separation of REE resulted from research done as part of the Manhattan project during World War II. The first unclassified reports on the separation of rare earths by ion-exchange chromatography, using differences in the stability of chelates (originally citrate complexes), appeared in the November 1947 issue of the *Journal of the American Chemical Society*. These reports were based on work done at Ames Laboratory (Iowa State University) and Oak Ridge National Laboratory. Government patent lawyers eventually gave the patents to Ames Laboratory, since their process was more advanced and provided better separation. These early results were based on anion-elution chromatography; later results using band-displacement chromatography provide more complete and rapid separation. See Powell[4,5] for more details. Liquid–liquid extraction methods were developed in the early 1950's and also allow separation of large amounts of rare earths.[6-8] Variations on ion-exchange chromatography and liquid–liquid extraction are still the major methods used to separate REE commercially.

REE are more common than the name implies, and over 100 minerals containing them have been described.[9,10] However, only a few of these minerals contain REE in sufficient amounts to warrant commercial extraction. Among the major sources of REE are bastnasite, which is a fluorocarbonate containing mainly La, Ce, Pr, and Nd, monazite, which is a phosphate mineral containing mainly La, Ce, Pr, and Nd along with Th, and xenotime, which is a phosphate containing about 60% Y and about 30% total for Sm through Lu. However, Eu is present only at about 0.1% or less in these ores[8,9-11] and is present in about 1 ppm in the earth's crust.[10]

Data are available for the approximate abundances of REE in specific rocks, for the earth's crust, in meteorites, in lunar rock samples, and in the solar atmosphere.[8-11] In general there is a decrease in abundances of 5- to 30-fold in going from La to Lu. In addition there is an even–odd alternation or zig-zag effect, with even atomic number REE generally being 2–8 times as abundant as their neighboring odd atomic numbered elements (except for Eu, which is sometimes anomalously low). This is a consequence of nuclear stability, since pairing of protons with other protons and of neutrons with other neutrons produces enhanced stability. Thus, when the REE are formed by cosmological processes, their relative amounts follow this trend. Promethium is an exception since it has no stable or very long-lived isotopes.

Natural Eu is a mixture of about 48% ^{151}Eu and 52% ^{153}Eu. Radioactive isotopes of Eu are not observed in minerals (except for trace amounts due to spontaneous fission of U) since its longest-lived radioactive isotopes have half-lives of only 13–16 years.

The distribution of Eu in most minerals is different than expected from trends for other REE, and this is generally called the "europium anomaly". The distribution of Ce is also sometimes anomalous. Most REE form compounds in the +3 state. However, Sm, Eu, Tm, and Yb have some tendency to form +2 compounds, and Ce, Pr, and Tb sometimes form +4 compounds. Only for Eu and Ce are these other valence states sufficiently "stable" to affect the mineralogical distribution and aqueous chemistry. The aqueous chemistry of Eu^{3+} is generally consistent with trends for other RE^{3+} ions.

The present report is a review of the chemical and thermodynamic properties of Eu and some of its inorganic compounds and aqueous species with emphasis on systems with potential geochemical applications. Carbonates are considered as inorganic compounds in this context. Literature coverage is from 1935 through mid 1985. High-temperature chemistry will be discussed in some cases, but only room-temperature thermodynamics will be evaluated except when high-temperature data yield thermodynamic information applicable to room temperature. Compounds of Eu considered are oxides, hydroxides, halides, hydroxyhalides, oxyhalides, sulfides, phosphates, carbonates, sulfates, and nitrates. Aqueous species considered include aquo ions, hydrolyzed species, and complexes of Eu^{3+} with halides, oxyhalides, sulfate, nitrate, carbonate, phosphate, hypophosphite, and triphosphate. Sulfate complexes and, especially at higher pH values, carbonate complexes tend to dominate RE speciation in sea water.[12,13]

A number of reviews are available that give additional details and references about some of the compounds and species considered here. These references also provide comparative information about other REE and about compounds, complexes, and aqueous species not considered here. Sinha[14] has described the crystal structures and coordination geometry of many lanthanide organic and inorganic compounds. Reviews on the REE halides include preparation of anhydrous halides,[15,16] general chemistry including double salts and oxyhalides,[17–19] and thermodynamics and solution chemistry.[16,18,19] A similar review covers oxyhalides, hydroxyhalides, chlorites, chlorates, and perchlorates.[20] Detailed reviews are also available for oxides[21,22] and chalcogenides.[23–25] Herman and Rairden[26] have reviewed REE electrochemistry for aqueous, nonaqueous, and fused-salt systems. Reviews are also available for absorption and fluorescence spectra of RE^{3+} in solution[27–29] and for aqueous hydration and hydrolysis.[30,31]

II. Chemical Properties of Solid, Liquid, and Gaseous Eu and Its Compounds

A. Elemental Europium

Metallic Eu is usually prepared by reduction of Eu_2O_3 with La metal at high temperatures under vacuum, followed by distillation of Eu. It is a fairly reactive metal that reacts with cold water about as fast as Ca to produce hydrogen and a yellow compound. The shredded metal reacts completely with moist air at room temperature within a few hours to produce a yellow compound with an empirical formula of $Eu(OH)_2 \cdot H_2O$.[32] The metal thus needs to be carefully prepared and protected from air and water while being studied. Its melting point is 1099 ± 10 K.[32]

Crystal-structure determinations for solid Eu at 5, 78, and 293 K indicate a body-centered cubic structure with no observed structural transitions.[33] The bcc lattice constant at 298 K is 4.5820 ± 0.0004 Å.[32]

A number of properties indicate an anomaly at about 88 K. These include electrical resistivity, magnetic properties, and heat capacity.[34–36] Neutron diffraction experiments indicate an antiferromagnetic transition with a Néel temperature of 91 K and were interpreted as indicating a helical spin structure below this temperature.[37] Cohen et al.[38] suggested, on the basis of Mössbauer spectra in this region, that Eu actually undergoes a sharp first-order phase transition at 88.6 K, which is slightly below the magnetic-ordering temperature. A λ-like anomaly at about 16 K was reported in heat capacity curves (both used metal from the same supplier),[34,39] but this is now believed to be an impurity effect possibly due to hydrogen.[36]

Vapor pressures for Eu were measured by Spedding et al.[32] from 696 to 900 K by Knudsen effusion–weight loss and by Trulson et al.[40] from 693 to 751 K using Knudsen effusion-mass spectrometry. Habermann and Daane[41] reanalyzed these vapor pressures by the third-law method using the metal entropy at 298 K[35] and high-temperature relative enthalpy data.[42] These recalculations yield enthalpies of sublimation of 175.4 kJ mol^{-1} and 180.3 kJ mol^{-1};[32,40] their average of 177.9 ± 2.5 kJ mol^{-1} is recommended. Three determinations of the first ionization potential of Eu yield 5.68 ± 0.03,[43] 5.61 ± 0.10,[44] and 5.68 ± 0.10 eV.[45] They are in excellent agreement and their average, 5.66 ± 0.04 eV, is recommended.

Entropy data for Eu and enthalpies of combustion and of dissolution in acid will be discussed later along with other thermodynamic data.

B. Anhydrous Europium Oxides

The $Eu–O_2$ phase system contains three major solid oxides. EuO is dark red and possesses the rock salt structure with a = (5.1439 ± 0.0005) Å.[22] Eu_2O_3 is the best known and is a thermodynamically stable oxide. It is white, sometimes with a pale pink cast, and exists in five polymorph forms. The low-temperature form has a body-centered cubic structure with a = 10.869 Å, whereas the next and the major higher temperature form is monoclinic with a = 14.082 Å, b = 3.604 Å, c = 8.778 Å, and β = 100°00′.[22] Their transformation temperature is about 1370 K, but quenched monoclinic Eu_2O_3 is so slow to reach equilibrium that its lower temperature properties can easily be measured. Other structural modifications of Eu_2O_3 occur at ca. 2310, 2410, and 2550 K. See Eyring's review for more details.[22] Dark reddish-violet Eu_3O_4 is orthorhombic with a = 10.094 ± 0.003 Å, b = 12.068 ± 0.003 Å, and c = 3.500 ± 0.001 Å.[22]

Bedford and Catalano[46] have found the melting points of the oxides to be around 2170 ± 50 K for EuO, 2270 ± 100 K for Eu_3O_4, and 2570 ± 50 K for monoclinic Eu_2O_3. They[46] cited three other melting point determinations of 2513 ± 10, 2603, and 2273 K for Eu_2O_3; the last value is much too low. The solidification temperature for Eu_2O_3 in an oxygen atmosphere,[47] 2633

K, agrees fairly well. Eyring[22] cited another value of 2564 K. The mean of 2577 ± 45 K is recommended for Eu_2O_3. Reed and Fahay[48] obtained 2253 ± 20 K for EuO. A superoxide $Eu(O_2)_3$ has also been reported, but it is very unstable and decomposes when heated slightly above room temperature.[49]

Low-temperature bcc Eu_2O_3 is easily obtained by oxidation of Eu below 1370 K; high-purity bcc Eu_2O_3 samples are commercially available, but it is best to calcine them to remove traces of H_2O and CO_2. Monoclinic Eu_2O_3 is obtained at higher temperatures, and crystal growth from a flux such as PbO or NaF yields high-purity single crystals.[50,51a] Eu_2O_3 in air is generally slightly nonstoichiometric with a slight oxygen excess.[51b]

Most RE_2O_3 can be viewed as layer compounds: e.g., layers of $(REO)_n^{+n}$ formed from RE_4O tetrahedra sharing edges in a hexagonal array perpendicular to the *c* axis for the monoclinic sesquioxide. Certain other anions form RE compounds with similar layers. See the discussion in Eyring[22] and references cited by him.

EuO can be obtained by a variety of techniques, such as reduction of Eu_2O_3 with lanthanum followed by "sublimation" and condensation[52] (actually, EuO decomposes and forms Eu(g); reoxidation of the condensate apparently occurs), reduction of EuOCl with LiH,[53] reaction of Eu_2O_3 with excess Eu,[46,48] etc. YbO is the only other RE monoxide that might be "stable" at lower temperatures.[54] However, under conditions of high temperatures and pressures, Leger et al.[55] were able to synthesize LaO, CeO, PrO, NdO, SmO, and YbO. LaO, CeO, PrO, NdO, and SmO are metallic oxides; in contrast EuO and YbO are semiconductors. The REE is divalent in EuO and YbO, trivalent in LaO, CeO, PrO, and NdO (RE^{3+}, O^{2-}, e^-), and intermediate for SmO.

Eu_3O_4 can be prepared by reacting stoichiometric amounts of EuO and Eu_2O_3 at 1170 K in an inert atmosphere[46,56] or by reduction of EuOCl–Eu_2O_3 stoichiometric mixtures with LiH.[57a] McCarthy and White[54] have discussed formation of Eu_3O_4 using H_2 reduction and also using CO–CO_2 gas buffers.

Heating EuO(s) causes decomposition by the reaction

$$4\,EuO(s) = Eu_3O_4(s) + Eu(g) \qquad (1)$$

at high temperatures.[53,57b] Panish[58] found that around 2000 K Eu_2O_3 vaporizes predominantly by

$$Eu_2O_3(c) = 2Eu(g) + 3\,O(g) \qquad (2)$$

whereas Eu_3O_4 decomposes by[57a,b]

$$3Eu_3O_4(c) = 4\,Eu_2O_3(c,\ monoclinic) + Eu(g) \qquad (3)$$

These are the dominant thermal decomposition reactions below about 2000 K. However, EuO(g) can be detected around 1700 K and becomes the dominant vapor species above 2000 K. Eu_2O and Eu_2O_2 have also been detected in the vapor phase above 2000 K, and their formation enthalpies[59,60] are in fair agreement. These high-temperature vapor species are outside the scope of this review.

The reduced valence oxides EuO and Eu_3O_4 readily react with oxygen, and some of their properties are very sensitive to small deviations from stoichiometry. For example, stoichiometric EuO is a semiconductor; an oxygen excess makes EuO an insulator, whereas an oxygen deficiency (excess metal) makes EuO a metallic conductor or produces an insulator–metal transition.[61] Details of the Eu–O_2 phase relationships can be found in McCarthy and White,[54] Bedford and Catalano,[46] and Shafer et al.[61]

Oxygen-exchange reactions of the type[45,62–64]

$$Eu(g) + MO(g) = EuO(g) + M(g) \qquad (4)$$

and the reaction of oxygen with europium vapor[65] have been studied above 2000 K by several workers. Murad and Hildenbrand[64] tabulated most of the published dissociation energies. These and electron-impact measurements[45] yield a dissociation energy for EuO(g) from 4.7 to 5.8 eV and a formation enthalpy ranging from −44.8 to −136.8 kJ mol^{-1}; these various studies are in poor agreement. Fortunately, EuO(g) is not a significant species at the lower temperatures we are interested in. Pedley and Marshall[66] have examined these data and recommend −59 ± 17 kJ mol^{-1} for its formation enthalpy.

Thermodynamic data are available for the enthalpies of formation of EuO(c), Eu_3O_4(c), and Eu_2O_3(c), for the entropy of EuO(c), and for high-temperature relative enthalpies of EuO(c) and both cubic and monoclinic Eu_2O_3. These data will be discussed in sections IV.B, IV.D, and IV.E.

C. Europium Hydroxide and Mixed-Anion Hydroxides

$Eu(OH)_3$(c) is generally prepared by hydrothermal synthesis, i.e., reacting Eu_2O_3 with concentrated alkali at elevated temperatures.[67–69] Temperatures around 500–600 K are best, since by about 770 K EuO(OH) is obtained instead.[70] Crystal structure parameters for $Eu(OH)_3$ are in good agreement;[67,69,70] the two sets in complete agreement[67,69] yield $a = 6.352 \pm 0.001$ Å and $c = 3.653 \pm 0.001$ Å (hexagonal form). All of the $RE(OH)_3$ are isostructural and have the UCl_3 structure. They also form isostructural monoclinic REO(OH) compounds;[70] the unit cell dimensions are $a = 6.10$–6.26 Å, $b = 3.72$–3.75 Å, $c = 4.34$–4.39 Å, and $\beta = 109°$ for EuO(OH).[56,70]

When hydrothermal synthesis is performed at about 620–850 K in the presence of large amounts of Cl^- ions, $Eu(OH)_2Cl$ is obtained.[71,72] $Eu(OH)_2Cl$ is monoclinic with $a = 6.166$ Å, $b = 3.79$ Å, $c = 6.734$ Å, and $\beta = 112.52°$.[72] All $RE(OH)_2Cl$ form isostructural monoclinic crystals,[71,72] but for Dy on they can also form an orthorhombic modification.[71]

Precipitation of Eu^{3+} with OH^- from aqueous Cl^- solutions was found to give $Eu(OH)_2Cl$ initially, but upon aging 50 days at pH 5.8–7.0 $Eu(OH)_{2.5}Cl_{0.5}$ resulted, and further aging for a total of 150 days gave $Eu(OH)_3$.[73] However, Mironov and Polyashov[74] reported a fresh precipitate of $Eu(OH)_{2.7}Cl_{0.3}$. Precipitation from SO_4^{2-} solutions initially gave $Eu(OH)_{2.6}(SO_4)_{0.2}$ and from NO_3^- solutions $Eu(OH)_{2.5}(NO_3)_{0.5}$.[74] It is possible that precipitation of Eu^{3+} with base from solutions containing bulky noncomplexing anions such as ClO_4^- might give $Eu(OH)_3$ directly. However, it is certain that attempts to determine $Eu(OH)_3$ solubilities by pH titration in solutions of Cl^-, NO_3^-, SO_4^{2-}, or most other anions give inaccurate results for fresh precipitates owing to formation of mixed-anion complexes.

Precipitation from $Eu(NO_3)_3$ solutions by aqueous ammonia gave a substance with an empirical formula of $Eu_2O_3{\cdot}4.5H_2O$ (equivalent to $2Eu(OH)_3{\cdot}1.5H_2O$), and its thermal decomposition to Eu_2O_3 was investigated.[75] Since it is possible that not all the NO_3^- was washed out of the precipitate in the study, the exact nature of the hydroxide is unclear.

Spedding et al.[32] found that Eu metal reacts with moist air to form a yellow compound with an empirical formula of $Eu(OH)_2{\cdot}H_2O$. Precipitation of Eu^{2+} with base gave a $Eu(OH)_2{\cdot}H_2O$–$Eu(OH)_3$ mixture,[56] as does reaction of Eu_3O_4 with moist air.[76] Reacting Eu metal with 10 mol L^{-1} NaOH gives pure $Eu(OH)_2{\cdot}H_2O$, which is isostructural with $Sr(OH)_2{\cdot}H_2O$ and $Ba(OH)_2{\cdot}H_2O$. $Eu(OH)_2{\cdot}H_2O$ crystals are orthorhombic with $a = 6.701 \pm 0.002$ Å, $b = 6.197 \pm 0.002$ Å, and $c = 3.652 \pm 0.001$ Å.[76] Even in an inert atmosphere, $Eu(OH)_2{\cdot}H_2O$ gradually decomposes to $Eu(OH)_3$.[56]

D. Anhydrous Chlorides, Fluorides, Bromides, and Iodides

All the REE can form anhydrous trihalides of the type REX_3 where X = F^-, Cl^-, Br^-, or I^- (except, possibly, for EuI_3). Simple dehydration of hydrated or partially hydrated salts is unsatisfactory since there is a tendency to form REOX type oxyhalides instead. However, heating hydrated chlorides in a stream of dry HCl gives $RECl_3$. Several detailed reviews give details for the numerous satisfactory methods for preparing anhydrous halides.[15-19]

Heating anhydrous $EuCl_3$ at 623 K was reported to yield a slightly chloride-deficient product, $EuCl_{2.989\pm0.003}$, and treatment with Cl_2 was necessary to get stoichiometric $EuCl_3$.[77] This is consistent with Ball et al.'s finding[78] that heating $EuCl_3$(s) under vacuum above 570 K caused partial decomposition to $EuCl_2$(s) and a chloride-deficient phase forms that retains the $EuCl_3$(s) lattice structure. $EuCl_3$ has the UCl_3 structure, and published lattice parameters shown significant variations: a = 7.278–7.375 Å and c = 4.071–4.137 Å. See ref 77 and 78 and other work cited by them. Ball et al.'s results[78] suggest that larger a and c values refer to a slightly chloride-deficient phase. $EuCl_3$ melts around 897 K,[79] but the studies cited above suggest this temperature is affected by Cl loss.

Not surprisingly, Eu forms a fairly stable dichloride $EuCl_2$. It is usually prepared by hydrogen reduction of $EuCl_3$ at high temperatures. It has both a high-temperature CaF_2 type structure and low-temperature $PbCl_2$ type structure with a transformation temperature of 1020 ± 5 K.[79,80a,b] Laptev et al.[80a] found its melting point to be 1127 ± 2 K. They cited earlier studies which may have misinterpreted the structural change for melting. Matrix-isolated $EuCl_2$ and EuF_2 molecules have also been investigated.[81]

A high-pressure study found that $EuBr_2$ transforms from the $SrBr_2$ structure to the $PbCl_2$ structure at high pressures.[82] Hodorowicz et al.[83,84a] have investigated $EuCl_2$–$EuBr_2$, $EuCl_2$–EuI_2, and $EuBr_2$–EuI_2 solid phases and their structures. Also see the single-crystal X-ray and Mössbauer studies of Sanchez et al.[84b]

Laptev et al.[85] have investigated the $EuCl_3$–$EuCl_2$ phase diagram in detail. Intermediate phases are $EuCl_3{\cdot}2EuCl_2$ ($EuCl_{2.333}$), $EuCl_3{\cdot}3EuCl_2$ ($EuCl_{2.25}$), and $EuCl_3{\cdot}4EuCl_2$ ($EuCl_{2.20}$).[85] $EuCl_3{\cdot}2EuCl_2$ is hexagonal with $a = 4.841 \pm 0.005$ Å and $c = 12.41 \pm 0.01$ Å;[86] $EuCl_3{\cdot}4EuCl_2$ is tetragonal with $a = 4.970 \pm 0.007$ Å and $c = 6.76 \pm 0.02$ Å.[87]

Polyachenok and Novikov reported that molten $EuCl_3$ near its melting point contains about 8% $EuCl_2$.[88] Hastie et al. found by using mass spectrometry that $EuCl_3^+$ occurs in the vapor above solid $EuCl_3$, but upon melting this species disappears rapidly and the $EuCl_2^+$ ion current becomes larger.[89] This strongly indicates that $EuCl_3$ rapidly decomposes to form $EuCl_2$ upon melting. Consequently, vapor pressures for molten $EuCl_3$ are not very accurate,[90-92] and recommended thermodynamic values for it are suspect. Polyachenok and Novikov[88] studied the $EuCl_3$–$EuCl_2$ liquid equilibrium using Cl_2 vapor pressure measurements.

Hastie et al.[89] stabilized the Eu(III) state by using molten $EuCl_3$–$LuCl_3$ mixtures and detected $EuCl_3^+$ and $Eu_2Cl_5^+$ in the vapor. Their measurements yield a vapor dimerization enthalpy of −134 ± 25 kJ mol^{-1}.

The situation is simpler for $EuCl_2$(l) since it vaporizes congruently. Vapor pressure studies have been made by using boiling point[93] and Knudsen-effusion methods.[94] Of these, Hariharan and Eick's[94] is the more detailed and probably the more accurate. Polyachenok and Novikov's data[93] extrapolated to 1 atm gives a normal boiling point of 2463 K, whereas Hariharan and Eick obtained 2335 ± 35 K.[94] Their vaporization enthalpies also differ by 115 kJ mol^{-1}. $EuCl_2$ vapor pressures were also investigated with gas-phase equilibria involving other RE metals and also Ba.[95,96]

A large number of ternary Eu chlorides have been prepared. For example, the KCl–$EuCl_3$ phase diagram contains KEu_2Cl_7, K_2EuCl_5, and two crystalline modifications of K_3EuCl_6.[97] The dieuropium phyllochlorides KEu_2Cl_7, $RbEu_2Cl_7$, and $CsEu_2Cl_7$ were investigated by Meyer et al.[98] Morss[99a] prepared a number of triple salts of the type $Cs_2NaRECl_6$ (Eu was not studied) and measured their enthalpies of solution. These mixed salts are outside the scope of this review.

EuF_3 has a lower temperature hexagonal modification (below about 920 or 1125 K) and a higher temperature orthorhombic modification.[17a,b,99b] It melts at 1531 ± 8 K.[99b] EuF_3 can be reduced to EuF_2 at elevated temperatures by using H_2 or Ca.[17a,b] EuF_2 melts at 1670 ± 5 K.[99c] The Eu_2O_3–EuF_3 phase diagram contains low-temperature rhombohedral and high-temperature cubic EuOF.[99d]

Asprey et al.[99e] attempted to prepare EuI_3 by reaction of Eu and I_2 vapor under pressure. They could not identify the product by X-ray diffraction; either it was not EuI_3 or EuI_3 has a different structure from the other REI_3. Whether or not EuI_3 can be prepared is uncertain, since most methods give EuI_2 instead.[16]

Anhydrous $EuBr_3$ is dark rust brown at room temperature,[99f] in contrast to most other Eu^{3+} ionic compounds (including $EuBr_3{\cdot}6H_2O$), which are colorless. This color becomes lighter at lower temperatures. Haschke[99f] suggested that an electron transition is involved but that some Schottky type point defects may also have been present. A bromide to europium charge transfer now seems more likely.[99g] $EuBr_3$ decomposes incongruently to form light gray $EuBr_2$ above 500 K.[99f]

E. Hydrated Chlorides and Their Thermal Decomposition, Oxychlorides, and Other Hydrated Halides

$RECl_3$, $REBr_3$, and REI_3 are readily soluble in water, whereas REF_3 salts are sparingly soluble.[16] At room temperature, the solid phases precipitating out from chloride solutions are $RECl_3{\cdot}7H_2O$ for La through Pr. The stable solid phases are $RECl_3{\cdot}6H_2O$ for Nd through Lu and Y, and their crystals are isostructural.[100,101] $EuCl_3{\cdot}6H_2O$ is monoclinic with $a = 9.67 \pm 0.03$ Å, $b = 6.52 \pm 0.01$ Å, $c = 7.99 \pm 0.02$ Å, and $\beta = 94°36' \pm 30'$ from single-crystal determination.[102] These parameters are in good agreement with powder-pattern data.[100] The Eu^{3+} is coordinated by six waters and two chlorides.

$EuCl_2{\cdot}2H_2O$ is monoclinic with $a = 11.661$ Å, $b = 6.404$ Å, $c = 6.694$ Å, and $\beta = 105°37'$, and it is isostructural with $SrCl_2{\cdot}2H_2O$.[103]

Thermal decomposition of $EuCl_3{\cdot}6H_2O$ yields EuOCl, which then reacts with air at high temperatures to form Eu_2O_3.[104-107] Intermediate products of decomposition are under dispute, with $2EuCl_3{\cdot}EuOCl$ (= Eu_3OCl_7), $Eu(OH)Cl_2$, and/or $EuCl_3{\cdot}0.5H_2O$ claimed by various workers. Sokolova et al.[107] reported a four-stage dehydration of $EuCl_3{\cdot}6H_2O$ (intermediate hydrates not specified). $EuCl_3{\cdot}6H_2O$ fuses at 425 K in a sealed tube.[108]

Haase and Brauer[109] studied the thermal decomposition of $EuCl_2{\cdot}2H_2O$ in N_2, Ar, and He and observed the sequence $EuCl_2{\cdot}2H_2O \rightarrow EuCl_2{\cdot}H_2O \rightarrow EuCl_2{\cdot}wH_2O$ ($w < 1$) $\rightarrow$ $EuCl_2$ (orthorhombic) $\rightarrow$ $EuCl_2$ (cubic). Further heating yields EuOCl.

Baev and Novikov[110] studied the equilibrium

$$2\ RECl_3(s) + O_2(g) = 2\ REOCl(s) + 2\ Cl_2(g) \quad (5)$$

for several REE, but unfortunately EuOCl was not studied. Hariharan and Eick[111] studied the reaction

$$3\ EuOCl(s) = Eu_2O_3(s,\ monoclinic) + EuCl_2(g) + Cl(g) \quad (6)$$

at elevated temperatures, so thermodynamic data can be derived for EuOCl(s). However, Bunda et al.[112a] claimed that $EuCl_3(g)$ forms instead. All REOCl have the PbFCl structure; for EuOCl, $a = 3.964$–3.965 Å and $c = 6.695$–6.696 Å.[20]

Tanguy et al.[112b] investigated heating EuO and $EuCl_2$ together under vacuum and produced Eu_4OCl_6, which has the Ba_4OCl_6 type structure. Unit cell parameters are $a = 9.45 \pm 0.01$ Å and $c = 7.16 \pm 0.01$ Å. A similar reaction also occurs for the bromide analogue.[112b]

EuF_3 forms a hemihydrate as the stable hydrated phase at room temperature, $EuF_3{\cdot}0.5H_2O$.[16,17b] It has a solubility around 10^{-5} mol L^{-1}.[16] However, Batsanova and Lukina's X-ray powder pattern and refractometric study[113a] suggests that "hydrated trifluorides" are not true hydrates but rather the water is in vacancy sites. $EuF_3{\cdot}0.5H_2O$ precipitated from aqueous HF has two nonequivalent types of water, as indicated by thermal dehydration.[113b] Heating to higher temperatures gives EuOF. A claim[113c] that $EuF_3{\cdot}4H_2O$ precipitates from aqueous HF at 293 K needs to be confirmed.

Very soluble $EuI_3{\cdot}9H_2O$ was reported as the solid hydrated iodide phase at around 273 K.[113d,e] Partial drying under vacuum gave $EuI_3{\cdot}6H_2O$.[113e] Reacting EuI_2 with moist O_2 gives EuOI.[17a]

$REBr_3{\cdot}6H_2O$ are isostructural with $RECl_3{\cdot}6H_2O$.[113f] Heating or vacuum drying of $EuBr_3{\cdot}6H_2O$ gave $EuBr_3{\cdot}H_2O$ followed by anhydrous $EuBr_3$.[106,113g] Further heating gave EuOBr.

F. Europium Sulfides

Solid compounds that have been reported to form in the Eu–sulfur system include EuS, Eu_3S_4, Eu_4S_7, $Eu_2S_{3.81}$, and EuS_2.[25] Eu_2S_3 has been claimed, but evidence is limited, and it is probably metastable.[25] Only EuS and Eu_3S_4 have been studied in any detail, and they will be emphasized here. EuS is a magnetically ordered semiconductor with much industrial interest.[24]

EuS can be prepared by a wide variety of techniques. Examples include reaction of Eu_2O_3, H_2, and sulfur gas at about 1300 K,[114] direct reaction of equivalent amounts of Eu and sulfur at about 770 K,[115] reaction of Eu_2O_3 with flowing H_2S at 1470 K,[116] reaction of $EuSO_4$ with H_2S at 1125 K,[60] high-temperature thermal decomposition of Eu_3S_4,[117] etc. Chemical transport of EuS by high-temperature vaporization can yield large single crystals.[117,118a] EuS has the fcc rock salt structure with $a = 5.945$–5.971 Å.[24,25,118a] Heating EuS in air at ca. 750 K was reported to give Eu_2O_2S.[119]

Eu_3S_4 can be prepared by reacting EuS and S in stoichiometric amounts in an evacuated ampoule at 870 K, by reacting $Eu_2O_2(CO_3)$ with a H_2S stream at 690 K,[25] or by thermal decomposition of Eu thiocyanate in an Ar–CS_2 stream at 770–870 K. It has the cubic Th_3P_4 structure with $a = 8.527$–8.537 Å. Heating it in air can give Eu_2O_2S, $Eu_2O(SO_4)_2$, $Eu_2(SO_4)_3$, and $Eu_2O_2(SO_4)$ at different temperatures, with the latter product being produced by about 1000 K.[25,119] Solid Eu_2S_3 is usually considered to be nonexistent, but metastable α and β forms were claimed that spontaneously transform into Eu_3S_4 in a few weeks.[25] Other phases reported in the Eu–S phase diagram are Eu_4S_7, EuS_2, and the sulfur-deficient phase $Eu_2S_{3.81}$. These phases have been studied very little. See the Gmelin volume[25] for references and details.

Eliseev[118b] studied the lattice constant of the Eu–S system from 15 to 54 at % sulfur. The lattice constant was around 5.965 Å up to 50% sulfur and about 5.97 Å at higher sulfur concentrations. A value of about 5.56 Å would be expected for Eu_2S_3.[118b]

The higher sulfides of Eu decompose to EuS upon heating in the absence of oxygen. For example

$$2\ Eu_3S_4(s) = 6\ EuS(s) + S_2(g) \quad (7)$$

occurs at high temperature.[118] EuS is generally considered to sublime incongruently according to

$$EuS(s) = Eu(g) + \alpha S(g) + [(1 - \alpha)/2]S_2(g) \quad (8)$$

where the sulfur exists as an equilibrium mixture of S and S_2.[116] Some workers have assumed that all gaseous S is dissociated to the monomer at experimental temperatures of around 2000 K. Nagai et al.[114] and Gordienko and Fenochka[120] found that some EuS(g) is also present. Smoes et al.[60] used mass spectrometry to show that at 2100 K the amounts of vapor species above EuS (relative to Eu(g) = 1) are 0.22 S, 0.07 S_2, 0.05 EuS, 3×10^{-4} EuS_2, 2×10^{-4} Eu_2S, 6×10^{-4} Eu_2S_2, and 5×10^{-7} Eu_2S_3. Thus, only three of these species need be considered in most cases. Smoes et al. obtained enthalpy of formation data for the vapor species EuS, EuS_2, Eu_2S, and Eu_2S_2 and also Eu_2OS formed by reaction with oxygen impurities.[60]

G. Europium Orthophosphate and Other Oxyphosphorus Compounds

REE orthophosphates, $REPO_4$, are of some importance since they occur with Th in one of the major REE minerals (monazite), and with Y in another (xenotime). The $REPO_4$ from La to Gd are isostructural with the monazite structure, whereas Tb to Lu have the zircon structure.[121a] Reported unit cell parameters for $EuPO_4$ are a = 6.61–6.65 Å, b = 6.81–6.84 Å, c = 6.29–6.33 Å, and β = 103°05′–104°00′.[121a,b] Single crystal structure data are available for $EuPO_4$.[121a] They can be prepared by precipitating soluble REE salts with Na_2HPO_4 and then thermally drying the product.[121b] Thermal decomposition above 2300 K was reported to give $Eu_7P_3O_{18}$, Eu_3PO_7, and $Eu_8P_2O_{17}$, with ultimate decomposition to Eu_2O_3.[122] It is quite likely that Eu^{3+} will form basic phosphates and hydrogen pyrophosphates as have been described for La^{3+}.[123]

Bamberger et al.[124] have reviewed claims of alkali metal–REE double phosphates and concluded that most claims are based on misidentification of the solid phases.

H. Carbonates and Basic Carbonates

Precipitation of the slightly soluble carbonate of Eu^{3+} generally gives $Eu_2(CO_3)_3 \cdot 3H_2O$.[125–127] This can be dehydrated to give anhydrous $Eu_2(CO_3)_3$.[128] However, when free alkali is present, basic carbonates $Eu(OH)CO_3 \cdot nH_2O$ are obtained with n = 0.25–0.6.[127] Hydrothermal synthesis[129a] for several REE's gave salts such as $RE_2O(OH)_2CO_3$ and $RE_2O_2(CO_3)$, and similar phases form for Eu.[129b] Thermal decomposition of $Eu_2(CO_3)_3$ also gives $Eu_2O_2(CO_3)$.[130] Double carbonates such as $Na[Eu(CO_3)_2] \cdot 6H_2O$ and $K[Eu(CO_3)_2] \cdot 3H_2O$ have also been prepared.[131] Nonstoichiometric basic carbonates $Eu_2(CO_3)_x(OH)_{2(3-x)} \cdot nH_2O$ have been described in the Eu_2O_3–CO_2–H_2O system.[132]

I. Europium Nitrates and Oxynitrates

Europium forms a trinitrate that is fairly soluble in aqueous solution. Mironov et al.[133] were able to prepare $Eu(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 5H_2O$, $Eu(NO_3)_3 \cdot 4H_2O$, $Eu(NO_3)_3 \cdot 3H_2O$, $Eu(NO_3)_3 \cdot 2H_2O$, $Eu(NO_3)_3 \cdot H_2O$, and $Eu(NO_3)_3$. Methods used include precipitation from H_2O or aqueous HNO_3, dehydration of higher hydrates by P_2O_5 or by vacuum dehydration, and reaction of water with the anhydrous salt. Their results indicate that the thermodynamically stable form is $Eu(NO_3)_3 \cdot 6H_2O$ from about 238 to 306 K, $Eu(NO_3)_3 \cdot 5H_2O$ from about 306 to 333 K, and $Eu(NO_3)_3 \cdot 4H_2O$ from 333 to 364 K. The melting point of $Eu(NO_3)_3 \cdot 4H_2O$ is 364 K.[108,133] Other studies[134,135] confirm that the hexahydrate is the stable form at room temperature.

Thermal decomposition of the hydrated nitrate produced slight inflections due to stepwise dehydration and $Eu(NO_3)_3$ formation,[133] but these intermediate stages are not usually observed due to a considerable tendency to decompose to $EuO(NO_3)$.[136,137] $Eu_3O_4(NO_3)$ has been claimed to form around 800 K,[136,137] and Eu_2O_3 begins to form around 1000 K. Very careful heating of hydrated nitrates under vacuum (maximum temperature about 470 K) is required to get fairly pure anhydrous $Eu(NO_3)_3$.[138] A phase of the type $Eu_2O_3 \cdot nN_2O_5 \cdot pH_2O$ has also been claimed to form during thermal decomposition of hydrated $Eu(NO_3)_3$.[139]

Crystal structures for $Eu(NO_3)_3 \cdot nH_2O$ are unknown. However, $Eu(NO_3)_3 \cdot 6H_2O$ is isostructural with the Pr, Nd, Sm, and (possibly) Gd analogues.[134,135] Siekierski et al.[140] examined available solubility data for $RE(NO_3)_3 \cdot nH_2O$ in water in detail and suggested correlations of solubility changes with crystal structure changes. They also found that Mironov et al.'s[133] $Eu(NO_3)_3 \cdot nH_2O$ solubilities were much too low and were inconsistent with data for other REE. Rard[141] determined the aqueous solubility of $Eu(NO_3)_3 \cdot 6H_2O$ at 298.15 K.

Heating $EuCl_3$ in molten $LiNO_3$–KNO_3 and $NaNO_3$–KNO_3 eutectics produced $EuO(NO_3)$, whereas further heating gave Eu_2O_3.[142] It has been suggested[142] that $Eu_2O(NO_3)_2$ was another possible decomposition product. Similar oxynitrites, $Eu_2O(NO_2)_2$ and $EuO(NO_2)$, were suggested in $NaNO_2$–KNO_2 eutectics.[143] No direct evidence was obtained in either study for these chemical formulas, but they were suggested by weight loss data upon thermal decomposition.

A number of double nitrates of the type $A_2RE(NO_3)_5$ are known for Eu and other REE where A denotes a monovalent cation. See Bünzli et al.[144] and references cited by them for details.

J. Europium Sulfates

REE from Pr through Lu and Y form isostructural $RE_2(SO_4)_3 \cdot 8H_2O$ as the stable solid hydrated form at room temperature.[145] These crystals are monoclinic, and $Eu_2(SO_4)_3 \cdot 8H_2O$ has a = 18.317 ± 0.003 Å, b = 6.75 ± 0.02 Å, c = 13.564 ± 0.004 Å, and β = 102°15′. Wendlandt[146] studied several of these salts and found that thermal decomposition of light RE sulfates gave intermediate hydrates, whereas heavy RE sulfates generally went directly to the anhydrous sulfate. Ivanov[145] studied most of the $RE_2(SO_4)_3 \cdot 8H_2O$, including Eu, and in contrast found that they dehydrated directly to $RE_2(SO_4)_3$ between 373 and 523 K, that anhydrous sulfates decomposed to oxysulfates around 970–1070 K, and that further decomposition occurred around 1470–1570 K. These oxysulfates were not described in detail but were presumably of the type $RE_2O(SO_4)_2$ or $RE_2O_2(SO_4)$ that were reported for Gd.[147a] $RE_2O_2SO_4$ form around 1300 K.[147b]

Double salts of the type $RE_2(SO_4)_3 \cdot Cs_2SO_4 \cdot 8H_2O$ are also known; they dehydrate in stages when heated.[148a] REE's from Sm to Lu form double salts with the empirical formula $K_6RE_4(SO_4)_9$.[148b]

$RE_2(SO_4)_3$ solubilities in water decrease with increasing temperature, in contrast with most other salts.[149]

Saturated aqueous solutions at 298 K contain about 4×10^{-2} mol L^{-1} of $Eu_2(SO_4)_3$[149] and about 10^{-5} mol L^{-1} of $EuSO_4$.[150] This lower solubility for $EuSO_4$ is the basis for separation methods described in the introduction. A dihydrate of $EuSO_4$ has also been reported.[3]

Zaidi et al.[151a] prepared a number of $RE(SO_3Cl)_3$ salts by reacting chlorosulfuric acid with the corresponding anhydrous RE benzoates.

K. Europium Salts with Oxyanions XO_n^-

Hydrated chlorite (ClO_2^-) and chlorate (ClO_3^-) salts are known for several REE, but there is an almost total lack of data for Eu.[20] Much more data are available for perchlorates.[20] Petrov et al.[151b] prepared $Eu(ClO_4)_3 \cdot 9H_2O$. However, various other studies for REE reported 5, 6, 7, 8, 9, and occasionally 10 hydrates,[151b,152] so it is likely that these hydrates differ little in thermodynamic stability. Thermal decomposition yields dehydration followed by decomposition to REOCl or $RECl_3$,[152,153] but the individual steps are not well separated.

$Eu(TcO_4)_3 \cdot 3H_2O$ has been prepared, and it can be dehydrated to the monohydrate and anhydrous salts, but little else is known about it.[154a] Varfolomeev et al.[154b] reported preparation of $RE(ReO_4)_3 \cdot 4H_2O$ for several RE; dehydration gave lower hydrates and anhydrous salts. Thermal decomposition of $RE(ReO_4)_3$ gave RE_3ReO_8.

$RE(IO_3)_3 \cdot nH_2O$ are well-known and are soluble to about 10^{-3} mol L^{-1}.[155,156] Unit cell parameters are available for triclinic $Eu(IO_3)_3 \cdot 2H_2O$ crystals:[157] $a = 7.47 \pm 0.03$ Å, $b = 10.66 \pm 0.03$ Å, $c = 7.33 \pm 0.02$ Å, $\alpha = 105.1 \pm 0.2°$, $\beta = 110.9 \pm 0.3°$, and $\gamma = 97.6 \pm 0.3°$. Bromate salts $RE(BrO_3)_3 \cdot 9H_2O$ are interesting in that the 9 waters directly surround the RE^{3+} and the anions are further away from the hydrated cation (ethyl sulfates are similar).[158] $Eu(BrO_3)_3 \cdot 9H_2O$ has a solubility of 1.21 mol kg^{-1} at 298.15 K.[159]

III. Properties of Aqueous Solutions

A. Hydrated Ions

Below a pH of about 5 or 6, RE^{3+} ions in aqueous noncomplexing media exist predominantly as unhydrolyzed aquo ions. The ionic radius of RE^{3+} decreases from La^{3+} to Lu^{3+} due to the lanthanide contraction. This change in ion size and the resulting change in the ratio of the ionic charge to the radius down the series obviously should result in significant changes in hydration. Despite numerous studies, there is no general consensus about the actual hydration changes that occur. For example, there are conflicting claims that the inner-sphere hydration number is constant across the series (at 6, 8, or 9 waters!) or that there is a decrease of one water between Nd and Tb (usually from 9 to 8, but 10 to 9 and 8 to 6 have also been suggested), and there are a few claims that the inner-sphere hydration increases. In addition, there is an increase in total hydration (inner- plus outer-sphere hydration) in going from La^{3+} to Lu^{3+}, and hydration trends may also be modified when complexing anions like NO_3^- disturb the hydration spheres. It is thus worth briefly considering hydration claims. Only a few anions such as Cl^- and ClO_4^- form complexes that are weak enough to preserve the basic hydration trends of RE^{3+} ions.

The earliest advocates of a RE^{3+} hydration number decrease in the inner coordination sphere for noncomplexing media were Spedding and co-workers, who based their argument on changes in the partial molal volume at infinite dilution (and analogies with hydrated salts).[160] This same trend persists to about 3 mol kg^{-1} in $RECl_3$ solutions.[161] Other properties such as enthalpies of dilution exhibit similar sharp breaks,[162] but the argument as to whether a hydration change should cause an increase or decrease in their properties is less clear cut. Electrical conductances of aqueous $RE(ClO_4)_3$ show a prominant reversal between Nd and Tb above about 3.0 mol kg^{-1},[163] and a similar reversal also occurs in the viscosities.[164] Mioduski and Siekierski[165] studied cocrystallization of lanthanide ethyl sulfates (which have only waters around the RE^{3+} in the crystals) and found the free energies of cocrystallization showed breaks at Pm and Gd. Since the crystals have no structural changes, this suggests coordination changes in the aqueous phase.

A number of other properties show a more gradual S-shaped trend, which is usually interpreted in terms of an overall hydration-number increase as the RE radius decreases. Relative viscosities[164,166] and electrical conductances[163] below about 2 mol kg^{-1} show this behavior and were interpreted with this model (but shape factors rather than hydration could possibly explain the viscosity data).[166] Both hydration entropies[167] and standard-state ionic entropies[168a] support the overall hydration-increase model. Bertha and Choppin[167] discussed available data and concluded that there is between a 10% and 20% increase in net hydration in going from La^{3+} to Lu^{3+}; capillary diffusion data yield a similar estimate.[168b] Water activity data[169,170] very clearly show this increasing hydration.

In brief, the hydration number decrease model is the following. The lanthanide contraction causes the ionic radius to decrease from La to Lu. As this occurs, the surface charge density on the RE ion increases, and this causes an increase in the ion-dipole forces that affect hydration. Thus total hydration increases from La to Lu. However, the decreasing ionic radius means that the inner-sphere radius decreases until the inner sphere can no longer accommodate as many waters, and then one water is gradually displaced between Nd and Tb. When this occurs, the inner hydrated radius decreases more rapidly so outer-sphere waters can approach more closely; thus interaction of the RE^{3+} with outer-sphere water increases more rapidly with atomic number in this region. Changes in the hydrogen bonding between inner- and outer-sphere waters may also be involved.[171] This yields the familiar S-shape.[170,172a]

Spedding et al.[160] suggested that equilibrium mixtures of the 9 and 8 hydrates are present between Nd and Tb. However, Mioduski and Siekierski[165] suggested that fractional coordination may be involved instead. Kanno and Hiraishi[172b] studied the Raman spectra of H_2O bound to RE^{3+} in glassy (frozen) $RECl_3$ solutions. Two types of bound water were found for Eu and Gd but only one for the other REE's. This suggests that a mixture of $RE(H_2O)_9^{3+}$ and $RE(H_2O)_8^{3+}$ is present for solutions of these two elements.[172b] The relative amounts of each species varied opposite to that expected from simple mass-action considerations![172b]

In contrast, several other studies were interpreted as indicating no hydration change. Reuben and Fiat[173] found no anomalous shift in water NMR peaks for RE perchlorates with concentration, whereas some shifting would be expected for intermediate RE if an equilibrium is involved. Heat capacities of RE^{3+} in perchlorate solutions also exhibit no maximum with ionic radius as would be expected for such an equilibrium.[174] Hinchey and Cobble[175a] found that the standard-state ionic entropies plotted vs. the inverse of the ionic radius squared were nearly linear. This was later shown to result from inaccurate and, in some cases, estimated input data; these entropies do in fact show an S-shape when more accurate input data are used.[168] Marcus[30] has reviewed hydration trends in detail and cites references for other studies that indicate a constant hydration number, especially the work of Geier and Karlen.[175b] Some of these authors consider the two-series trends to be due to structural changes rather than a hydration number change.

A very plausible resolution to some of these apparently contradictory conclusions about RE^{3+} inner-sphere hydration has been given by Marcantonatos et al.[175c] They noted that if only the simple inner-sphere hydration equilibrium is considered, increasing either the REX_3 concentration, or the X^- concentration (X^- = halide, perchlorate, or other simple monovalent anion) at constant RE^{3+} concentration, should cause the inner-sphere hydration to decrease. However, if outer-sphere ion pairs are also considered, then four equilibria are present involving $RE(H_2O)_n{}^{3+}$, $RE(H_2O)_{n-1}{}^{3+}$, $RE(H_2O)_nX^{2+}$, and $RE(H_2O)_{n-1}X^{2+}$. They showed that given reasonable values for the equilibrium constants, increasing the electrolyte concentration could actually increase the inner-sphere hydration number. Thus, even though outer-sphere ion pairs do not remove inner-sphere waters, they can shift the equilibria to favor higher primary hydration numbers for RE^{3+} from Sm^{3+} to Gd^{3+}. Also see the discussion in section III.F.

Habenschuss and Spedding[176a] did X-ray scattering measurements for concentrated $RECl_3$ solutions and found that the inner-sphere hydration number decreases by one. This is one of the strongest pieces of evidence for their model. They obtained a hydration number of 8.3 for Eu^{3+}. Results from neutron scattering[176b,c] give hydration numbers of 8.5 ± 0.2 for Nd^{3+} and 7.4 ± 0.5 for Dy^{3+}; although the absolute values are smaller, the hydration number decrease is observed.

Fluorescence lifetime measurements[177] for $Eu(ClO_4)_3$ in water–acetonitrile mixtures yield a hydration number of 8.9, laser-induced luminescence decay[178a] measurements in water yield 9.6 ± 0.5 waters, and fluorescence lifetimes[178b] in water yield 9.0. Thus the only agreement is that the hydration number of Eu^{3+} is around 8 or 9. Krestov and Kurakina's[179] hydration numbers of 6 for the whole RE series, from derivatographic measurements, obviously refer to the hydrated nitrate crystals and not to the aquo ions.

Since the inner-sphere hydration number of Eu^{3+} is somewhat uncertain, it is not surprising that so is its symmetry. Sayre et al.[180] used fluorescence spectra measurements to conclude the symmetry is either D_{2h}, C_{2h}, or C_i, and "presumed" D_{2h}. Sage et al.'s[181] magnetic circular dichroism (MCD) measurements of the $^7F_0 \rightarrow {}^5D_1$ transition indicate the symmetry is D_{2h} *or lower*. A conflicting MCD study[182] concluded that only a threefold axis, D_{3h} or C_{3v}, could explain their results.

We conclude that the RE^{3+} ions very likely undergo an inner-sphere hydration number decrease between Nd^{3+} and Tb^{3+}, Eu^{3+} has an inner-sphere hydration number around 8 or 9, the Eu^{3+} aquo ion has low symmetry (probably D_{2h} or less), and the inner-sphere hydration number probably is changed by outer-sphere complex formation at higher Cl^- and $ClO_4{}^-$ concentrations. More work needs to be done to resolve some apparently conflicting conclusions mentioned above.

B. Hydrolyzed Species in Eu^{3+} Solutions

Titration of aqueous RE^{3+} salt solutions with alkali metal hydroxides produces precipitation between pH values of 6 and 8, but the actual precipitation pH depends on concentration, anion, and RE, and it is affected by aging. Several studies have been made for Eu^{3+} salts. Moeller and Kremers[183,184] titrated 0.1 mol L^{-1} RE nitrate, sulfate, and acetate solutions with 0.1 mol L^{-1} NaOH. The pH at incidence of precipitation was 6.82 for $Eu(NO_3)_3$, 6.68 for $Eu_2(SO_4)_3$, and 7.18 for $Eu(OAc)_3$. Another study of titration of 0.03 mol L^{-1} solutions with NaOH gave initial precipitation around pH 6 for $EuCl_3$ and $Eu_2(SO_4)_3$ and around 6.5 for $Eu(NO_3)_3$.[74] Grebenshchikova et al.[185] reported the start of precipitation at pH 6.2–6.3 in nitrate solutions and Weaver and Shoun[186] got ca. pH 7.5 for 0.002 mol L^{-1} $Eu(NO_3)_3$. In principle, these data could be used to extract solubility products for $Eu(OH)_3$. However, it is well-known that the solid phase generally contains mixed anions.[73,74] Since in most cases the composition of the solid phase is not accurately known, these data cannot be utilized for solubilities. Only Askel'rud and Ermolenko's[73] data (analyzed in section IV.F.3) are free of these objections. Also see the discussion in Gmelin.[31]

The solubility of $RE(OH)_3$ increases slightly in concentrated base,[187,188] and this was attributed for some REE to reactions of the type

$$RE(OH)_3(s) + OH^-(aq) = RE(OH)_4{}^-(aq) \qquad (9)$$

Baes and Mesmer[187] give approximate formation constants for several $RE(OH)_4{}^-$, but no data are available for Eu. It is unlikely that $Eu(OH)_4{}^-$ forms to any major extent, since the solubility of $Gd(OH)_3$ increases only fourfold in 18.8 mol L^{-1} NaOH and $La(OH)_3$ shows even less solubility variation with concentration of base.[188] $Yb(OH)_3$ shows a much larger solubility change with added base and has a solubility maximum in 14 mol L^{-1} NaOH. This was attributed to formation of $Yb(OH)_6{}^{3-}$,[188] and similar reactions probably occur just for the heavier lanthanides Yb and Lu, which can form solid salts with the empirical compositions $Na_4RE(OH)_7 \cdot nH_2O$[189] or $Na_3RE(OH)_6 \cdot nH_2O$.[190] In addition, all of the RE^{3+} form $RE(OH)^{2+}$, and most form $RE_2(OH)_2{}^{4+}$ and $RE_3(OH)_5{}^{4+}$ in aqueous solution.[187]

Kragten and Decnop-Weever[191,192] have recently studied the precipitation behavior of the elements adjacent to Eu (Sm and Gd) in aqueous perchlorate solutions. Aqueous species observed were $RE(OH)^{2+}$, $RE(OH)_2{}^+$, $RE(OH)_3$, and $RE_3(OH)_4{}^{5+}$ for freshly precipitated solutions. Many of the above species may disappear upon aging, which will cause the hydroxide solubility to vary with time. Pershin[193] monitored pH changes of Eu(III) solutions with aging.

The first hydrolysis of Eu^{3+} in aqueous solution

$$Eu^{3+}(aq) + H_2O(l) = Eu(OH)^{2+}(aq) + H^+(aq) \qquad (10)$$

has been studied a number of times.[194-200] There is much less information for the second step[199,201]

$$Eu(OH)^{2+}(aq) + H_2O(l) = Eu(OH)_2{}^+(aq) + H^+(aq) \qquad (11)$$

These experimental data will be discussed in section IV.G.1.

C. General Comments on Aqueous Complex Formation

Although RE^{3+} tend to form weaker complexes with anions than many transition metals, they do form complexes with nearly every anion and, in some cases, these complexes are quite strong. Direct evidence for this comes from polarographic measurements.[202-205] Half-wave potentials have been measured in a variety of media including aqueous solutions of Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, SCN^-, CH_3COO^-, and EDTA. All of these anions affect the half-wave potential for the Eu(III)/Eu(II) reduction; the reduction curves are shifted different amounts for different anions, and all of them are shifted relative to the presumably weakly complexing ClO_4^- media. Weaker complexes such as with Cl^-, Br^-, I^-, NO_3^-, and SCN^- shift the half-wave potentials to less negative values, whereas stronger complexes such as with SO_4^{2-} and CH_3COO^- generally shift the curve to more negative values. The relative shifts depend on the strength of these complexes for both Eu(III) and Eu(II). Some of these complexes will be discussed in the following sections.

D. Aqueous Complexes of Eu^{3+} with Cl^-, Br^-, and I^-

Aqueous complexes of Eu^{3+} with Cl^-, Br^-, and I^- will be discussed together since they have similar complex formation chemistry and they all form fairly soluble hydrated salts.

The dominant if not entire mode of complex formation in these solutions is outer-sphere. Evidence for this includes the small negative enthalpy and the small positive entropy[206] of complex formation of $EuCl^{2+}$ (but much more negative enthalpy values were reported by other workers[207]), the similarity of series trends with ionic radius for thermodynamic and transport properties of aqueous rare earth chlorides at high concentrations to those at low concentrations,[161,162,166,169] and the absence of major changes in the RE^{3+} absorption spectra with increasing Cl^- concentration.[208a] Absorption and luminescence spectra confirm that $EuBr^{2+}$ complexes are also outer-sphere.[175c] The I^- salt has been studied much less, but since its stability constants are similar to those of the chloride and bromide salts, its chemistry should also be similar. The absence of excess sound absorption in $REBr_3$ and REI_3 solutions indicates the absence of strong complex formation.[208b]

Fukasawa et al.[209] calculated approximate outer-sphere stability constants for $RECl^{2+}$ and $REBr^{2+}$ theoretically, which were only slightly smaller than the observed total constants; this implies the dominant complex formation mode is outer-sphere. A conflicting claim has been made by Breen and Horrocks[210] using luminescence excitation spectroscopy. They reported an inner-sphere formation constant for $EuCl^{2+}$ that is only slightly smaller than the total complex formation constant (inner- plus outer-sphere) reported by others, which implies the dominant complex formation mode is inner-sphere. Tanaka and Yamashita,[211] however, used the same approach and concluded that inner-sphere complex formation was unlikely.

There are a large number of studies that report stability constants for Cl^-, Br^-, or I^- complexes of Eu^{3+}.[206-208a,209,210,212-216] Some derive both the first and second constants, whereas others report only the first *K* value from their data. The calculated value of the first constant is sensitive to whether a second complex is assumed to form. This will be discussed in more detail in the thermodynamic section.

In addition, a number of thermodynamic and transport properties are available for aqueous $EuCl_3$ solutions (and most other $RECl_3$) at 298 K from low concentrations to saturation. These properties are densities,[161] enthalpies of dilution,[162] activity coefficients,[169] heat capacities,[217] electrical conductances,[218] and relative viscosities.[219] Adiabatic compressibilities are also available from low to moderate concentrations.[220,221]

E. Aqueous Complexes of Eu^{3+} with F^-

REF_3 are very much less soluble than the other RE halides in aqueous solution, their REF^{2+} formation constants are about 10^3 larger than for other REX^{2+},[207,222,223a,b] and their enthalpies and entropies of complex formation are large and positive.[222] This suggests that RE^{3+}–F^- complexes are largely inner-sphere, in contrast to the other halides, which are predominantly outer-sphere. Moulin et al.,[207] in contrast, found the enthalpies of formation of REF^{2+} to be negative. However, the positive enthalpies from direct calorimetry should be more reliable.[222] A mixed-anion aqueous species, $EuF(OH)_2$, has recently been reported.[224]

F. Aqueous $RE(ClO_4)_3$ Solutions

Most of the available information suggests that RE^{3+} and ClO_4^- ions interact very little in aqueous solution, although they obviously must form water-sharing ion pairs by saturation (4.60–4.76 mol kg^{-1} at 298 K).[163] The crystal structures of $La(ClO_4)_3 \cdot 6H_2O$, $Tb(ClO_4)_3 \cdot 6H_2O$, and $Er(ClO_4)_3 \cdot 6H_2O$ have been reported.[225] Each RE^{3+} ion is surrounded by a cubic close-packed $RE(H_2O)_6^{3+}$ arrangement with ClO_4^- occupying all octahedral and tetrahedral holes.

Two studies report $Eu(ClO_4)^{2+}$ formation constants. Fluorescence lifetime measurements yield 24 mol^{-1} L,[226] whereas electromigration velocity measurements yield 0.6 ± 0.1 mol^{-1} L.[227] These values are so discrepant that they will not be used to extract thermodynamic data.

Another fluorescence lifetime study,[228] unlike that of Giuliani and Donohue,[226] found no significant effect of ClO_4^- on Eu^{3+} fluorescence lifetime, so the larger stability constant is suspect. Bünzli and Yersin[228] also concluded that $Eu(ClO_4)^{2+}$ ion pairs were outer sphere.

Breen and Horrocks[210] and Tanaka and Yamashita[211] suggested that these outer-sphere ClO_4^- ion pairs actually cause the inner-sphere hydration number of Eu^{3+} to increase at high ClO_4^- concentrations. However, since transport properties[163,164] for stoichiometric $RE(ClO_4)_3$ solutions still seem to exhibit the hydration number decrease even at saturation, the very high ClO_4^- to RE^{3+} ratio in the fluorescence studies may be the critical factor for altering the inner-sphere hydration number.

Thermodynamic and transport data have been reported at 298 K for aqueous rare earth perchlorate solutions, including $Eu(ClO_4)_3$. They are densities,[229] heat capacities,[230] and viscosities[164] (all from low concentrations to saturation), and adiabatic compressibilities[220,231] (to moderate concentrations). Several other properties have been measured for a number of other lanthanides, so that properties for $Eu(ClO_4)_3$ can be accurately estimated by interpolation. They include activity coefficients,[170,232] enthalpies of dilution,[233] and electrical conductances.[163]

G. Aqueous Eu^{3+} Halates: ClO_3^-, BrO_3^-, and IO_3^-

Stability constant data have been reported for aqueous Eu^{3+} with ClO_3^-, BrO_3^-, and IO_3^-,[234-236] and are concordant to a factor of 2 or 3. Reaction enthalpies are discordant: enthalpies of formation of $Eu(ClO_3)^{2+}$ have been reported to be −21[234] and 0 kJ mol^{-1},[236] and for $Eu(IO_3)^{2+}$ are −11[234] and +11 kJ mol^{-1}.[235] The discrepancies are partly resolved by direct enthalpy of complex formation measurements; this leads to the claim that the IO_3^- complex is predominantly inner sphere whereas the ClO_3^- and BrO_3^- complexes are predominantly outer sphere.[237] Crystal structure data for bromates show RE^{3+} surrounded by 9 H_2O's,[158] which is consistent with an outer-sphere assignment for their aqueous complexes. Solubility data for $Eu(IO_3)_3$ at 298.15 K are in remarkably good agreement, 7.8–8.2 × 10^{-4} mol L^{-1}.[155,156,167,238]

H. Aqueous RE^{3+} Complexes with $H_2PO_4^-$, $H_2PO_2^-$, and $P_3O_{10}^{5-}$

Addition of phosphoric acid to RE^{3+} solutions causes much less RE^{3+} to be absorbed on ion-exchange resins than when only perchloric acid is present. This suggests that complexes form, although they are weaker than for trivalent ions of Al, Fe, Ti, In, and Sc.[239] Formation constants of $RE(H_2PO_4)^{2+}$ are available for Ce^{3+}, Pm^{3+}, and Y^{3+} at $I = 0.2$ mol L^{-1};[240] since their formation constants vary only by a factor of 2 a rough estimate could be made for Eu^{3+}. Similarly, a stability constant for $Eu(H_2PO_2)^{2+}$ has been published.[241a]

Nieuwenhuizen et al.[241b] used ^{17}O NMR to investigate complex formation between RE^{3+} and sodium triphosphate. Hydrated $RE(P_3O_{10})_2^{7-}$ formed in each case.

I. Aqueous Eu^{3+} Carbonate Complexes

Freezing point depression data for RE^{3+} in the presence of excess carbonate[242] indicate the formation of $RE(CO_3)_4^{5-}$. Stability constant data are available for $Eu(CO_3)^+$ and $Eu(CO_3)_2^-$ at an ionic strength of 1 mol L^{-1} [243] and for $Eu(CO_3)_4^{5-}$ at $I = 2.5$ mol L^{-1}.[244]

J. Eu^{3+} Sulfate Complexes

Stability constant data are available for sulfate complexes of Eu^{3+} from a variety of methods.[155,214,215,241a,245-249] Most of these studies are in reasonable agreement, but a few of the earlier studies are less accurate due to the neglect of $Eu(SO_4)_2^-$ when calculating stability constants for $Eu(SO_4)^+$. Both enthalpy and entropy of complex formation are moderately to fairly large and positive.[246-248,250] These enthalpy and entropy values, together with the moderately large stability constants, suggest that sulfate complexes could be predominantly inner sphere rather than outer sphere. Other evidence supporting the presence of extensive complex formation includes excess sound absorption maxima[251] and low values for electrical conductances.[149,252a]

Aqueous complexes of the type $RE(S_2O_3)_3^{3-}$ and $RE(S_2O_3)_4^{5-}$ have been reported for several RE in the presence of excess thiosulfate ions.[252b]

K. Eu^{3+} Nitrate Complexes

Eu^{3+} nitrate solutions have properties that are intermediate in behavior between the weakly complexed chlorides and perchlorates and the more strongly complexed sulfates. This suggests that there may be a mixture of inner- and outer-sphere nitrate complexes present. On the basis of small negative enthalpies and entropies of formation, Choppin and Strazik[253] concluded that the dominant complexes were outer sphere. In contrast, Breen and Horrocks' fluorescence lifetime measurements[210] were interpreted as indicating the dominant complexes were inner sphere. Other spectroscopic measurements[254] were used to claim that inner-sphere complexes form only for the excited $^5D_0$ state of Eu^{3+} but not for the ground state. Crystal structures are known for several hydrated $RE(NO_3)_3 \cdot 6H_2O$, and all have three NO_3^- ions bound to the RE by two oxygens and also four or five directly coordinated H_2O's.[140] This indicates that some inner-sphere complexes could well form in their solutions.

Many properties of aqueous $RE(NO_3)_3$ show large differences from the weakly complexed Cl^- and ClO_4^- salts, and this indicates that NO_3^- solutions are more extensively and also probably more strongly complexed. Water activities of $RE(NO_3)_3$ solutions[255,256] are much higher than for the Cl^- and ClO_4^- series, and cation hydration numbers from adiabatic compressibilities[220,257] are much lower. In addition, adding NO_3^- ions to RE^{3+} solutions causes large shifts in the water NMR frequency.[173] All of these effects suggest that significant amounts of bound water are liberated by complex formation. Also, electrical conductance data are lower than expected for a highly dissociated salt.[258]

Fluorescence (line) spectra measurements[259] for aqueous $Eu(NO_3)_3$ solutions indicate a constant number of lines above about 0.01 mol L^{-1}, but at lower concentrations the nitrate solution spectra changes and approaches that of chloride solutions. This apparently indicates that inner-sphere nitrate complexes dissociate to form outer-sphere complexes or uncomplexed solutions at lower concentrations.

There are numerous studies[207,210,212,215,216,253,254,260,261] of the complex formation constants of Eu nitrates. They indicate that both $Eu(NO_3)^{2+}$ and $Eu(NO_3)_2^+$ form in aqueous solutions. However, when large amounts of HNO_3 are present, $RE(NO_3)_3 \cdot HNO_3$ and $RE(NO_3)_3 \cdot 3HNO_3$ can apparently form.[262]

Pitzer et al.[263] have compared and correlated published thermodynamic data for aqueous RE^{3+} salts with Cl^-, ClO_4^-, and NO_3^- anions, and Onstott et al.[264] discussed the thermodynamics of crystallization for these same salts.

L. Aqueous Eu^{2+}

Sm, Eu, Tm, and Yb can be reduced to the +2 state in aqueous solution by chemical, electrochemical,[26] or electron-beam pulse radiolysis.[265] Of these, only Eu^{2+} is "sufficiently stable" to be readily characterized by standard electrochemical methods. However, Eu^{2+} is gradually oxidized to Eu^{3+} by atmospheric air. This oxidation causes changes with time in the electrical conductances for $EuCl_2$ and EuI_2 solutions.[266]

A number of redox potential measurements are available, which will be used below to yield Gibbs energy data for the Eu^{2+} ion. All redox potentials cited in this paper are reduction potentials relative to the normal hydrogen electrode (NHE). McCoy[267] reported the Eu^{3+}/Eu^{2+} reduction potential to be −0.43 V in formic acid, and Holleck[268] obtained −0.49 V in chloride solutions. Eu^{3+} forms complexes (and, presumably, Eu^{2+} also) with almost any ion except possibly ClO_4^-, so potentials in these media do not yield results for the aquo ions. Macero et al.[269] studied formate complexes and concluded that correction of McCoy's data[267] for complex formation gives −0.36 V for the aquo ion case. This value agrees with the majority of potential measurements in ClO_4^- solutions, −0.35 to −0.38 V.[202,270–273] Three studies in Cl^- media also fall in this range,[204,274,275] which suggests a compensating effect for the weak Eu^{3+} and Eu^{2+} chloride complexes. However, Shul'gin and Koz'min[276] obtained −0.428 V for $EuCl_3$, which suggests they had problems with their liquid junction potential.

Older enthalpy of solution data for $EuCl_2$ and for EuO in aqueous HCl could be used to yield enthalpy of formation data for the Eu^{2+} ion. Unfortunately, these results show considerable variation due to oxidation problems and to complex reaction mechanisms. Morss and Haug performed new experiments[275] and very carefully reanalyzed previous literature data.[275,277] They produced a very plausible resolution of these problems. These data will be discussed in Section IV.D.

IV. Thermodynamic Data

A. General Comments

This section is concerned with the analysis of thermodynamic data for aqueous species and for the pure compounds discussed previously. In those cases where data of sufficient quality are available, values of thermodynamic quantities are recommended. Solid compounds with evaluated thermodynamic data are (in addition to Eu(c)): EuO, Eu_2O_3, Eu_3O_4, EuS, $EuCl_2$, $EuCl_3$, $EuBr_3$, EuOCl, $Eu(OH)_3$, $Eu(OH)_2Cl$, $Eu(OH)_{2.5}Cl_{0.5}$, $EuCl_3{\cdot}6H_2O$, $EuF_3{\cdot}0.5H_2O$, $Eu_2(SO_4)_3{\cdot}8H_2O$, $EuSO_4$, $Eu(NO_3)_3{\cdot}6H_2O$, $Eu_2(CO_3)_3{\cdot}3H_2O$, $Eu_2(CO_3)_3$, $Eu(BrO_3)_3{\cdot}9H_2O$, and $Eu(IO_3)_3{\cdot}2H_2O$. Aqueous species evaluated are Eu^{2+}, Eu^{3+}, and aqueous complexes of Eu^{3+} with OH^-, F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}, BrO_3^-, IO_3^-, and CO_3^{2-}. Other systems lacking all or part of the required data are also considered, and recommendations are made as to what needs to be measured or remeasured.

In the following sections, thermodynamic data are evaluated mainly by properties, such as entropies, stability constants, etc. However, there is one major exception that concerns EuO(c), Eu_2O_3(c), $EuCl_2$(c), $EuCl_3$(c), Eu^{2+}(aq), and Eu^{3+}(aq). These data are interrelated through enthalpies of solution (Eu, EuO, Eu_2O_3 in aqueous HCl; $EuCl_3$ and $EuCl_2$ in acidified H_2O), combustion enthalpies of Eu and EuO, and Eu^{3+}/Eu^{2+} redox equilibria. Thus they will be evaluated together and appropriately averaged. Two previous evaluations of data for these oxides, chlorides, and aquo ions are worthy of note: Morss and Haug's[275] careful evaluation of experimental data for Eu that resolves many earlier discrepancies, and Morss' later evaluation[277] for all the lanthanides. Another important paper is Nugent et al.'s correlation[278] of redox potentials with spectroscopic properties.

In all of the following sections, calculations for Eu species and compounds have been made thermodynamically consistent whenever possible. Thus our reported results generally differ slightly from values given in the cited literature. Thermodynamic data for HCl and H_2O in aqueous HCl were taken from NBS technical note 270-3[279] as reanalyzed by Morss[277] and for most other (non Eu) compounds from the 1977 CODATA tables. Values for oxyanions not in CODATA and for H_2O_2(aq) are from the NBS technical note 270-3.[279]

B. Entropies and Relative Enthalpies of Solid Compounds

1. Eu Metal

Lounasmaa reported heat capacity data for Eu(c) from 0.36 to 4.03 K[280] and from 3.02 to 24.76 K,[39] Krusius et al. from 0.03 to 0.8 K,[281] Teaney and Moruzzi from 10.66 to 273.03 K,[36] Gerstein et al. from 5.06 to 323.60 K,[35] and Polovov and Maĭstrenko from 80 to 850 K.[282] Two studies found a heat capacity anomaly at 16 K[36,39] that was absent from a later study.[35] The studies with the 16 K anomaly and two others[280,281] had obtained their Eu(c) from the same supplier, and it may have contained a second-phase hydride or some other unknown impurity at lower temperatures.[36] Since Gerstein et al.'s results[35] seem to be the more accurate they were accepted (they also ran a second sample that was probably of lower purity, but which gave results in fairly reasonable agreement at room temperature). Best values of the entropies and heat capacities are $S^\circ_{298.15}(\mathrm{Eu(c)}) = 77.81$ J K^{-1} mol^{-1} and $C_{p,298.15}(\mathrm{Eu(c)}) = 27.65$ J K^{-1} mol^{-1}. Polovov and Maĭstrenko[282] only presented their data graphically so entropies cannot be derived.

High-temperature data for both Eu crystal and gas are required for analyzing high-temperature decomposition pressures. Berg et al.[42] performed relative enthalpy measurements for Eu up to 1373 K. These data were represented by the published equations (T in K)[21,42]

$$H_T - H_{273.15} = 24.55(T - 273.15) + 4.289 \times 10^{-3}(T^2 - 273.15^2) \qquad 273 \le T \le 503 \quad (12)$$

$$H_T - H_{273.15} = 40.50(T - 273.15) - 1.979 \times 10^{-2}(T^2 - 273.15^2) + 1.255 \times 10^{-5}(T^3 - 273.15^3) - 665 \qquad 503 \le T \le 1090 \quad (13)$$

$$H_T - H_{273.15} = 38.12(T - 273.15) + 4335 \qquad 1090 \le T \le 1373 \quad (14)$$

Reported units were converted to J mol^{-1} by us. Maximum errors are about 1.5 kJ mol^{-1} at higher temperature. A thermal anomaly at 503 K was attributed by them to a possible polymorphic transformation.[42] The third equation is for liquid Eu. These equations give an enthalpy of fusion of 9.1 ± 0.2 kJ mol^{-1} and an enthalpy of transition of 57 ± 84 J mol^{-1} at the transition temperature of 503 K.[21] This alleged polymorphic transtiion may or may not be real; its enthalpy of transition is so uncertain as to be doubtful. Polovov and Maĭstrenko did not observe this transition but found a λ-like anomaly around 765 K.[282] Stull and Sinke[283] reported ideal gas thermodynamic values of

$S°_{298.15}$ = 188.7 J K^{-1} mol^{-1} and $C_{p,298.15}$ = 20.8 J K^{-1} mol^{-1}.

2. EuO and EuS

Teaney and Moruzzi[36] reported heat capacities for EuO powder from 19.37 to 299.25 K and for EuS powder from 9.61 to 285.27 K. McMasters et al.[284] made relative enthalpy measurements by drop calorimetry (relative to 298.15 K) from 419 to 1724 K for EuO and from 404 to 1605 K for EuS. McMasters et al. combined these two sources of thermal data to calculate $S°_{298.15}(EuO(s))$ = 83.64 J K^{-1} mol^{-1}, $C_{p,298.15}(EuO(s))$ = 48.74 J K^{-1} mol^{-1}, $S°_{298.15}(EuS(s))$ = 95.77 J K^{-1} mol^{-1}, and $C_{p,298.15}(EuS(s))$ = 50.96 J K^{-1} mol^{-1}. Their relative enthalpy equations were converted to J mol^{-1}

$$H_T - H_{298.15} = -14239 + 46.714T + 3.6100 \times 10^{-3}T^2 \quad (15)$$

for EuO, and

$$H_T - H_{298.15} = -14123 + 46.268T + 4.1497 \times 10^{-3}T^2 \quad (16)$$

for EuS. Uncertainties are about 500 J mol^{-1}.

3. $EuCl_3$, $EuBr_3$, and $Eu(OH)_3$

Sommers and Westrum[77] reported heat capacity data for $EuCl_3$(c) from 4.95 to 346.44 K, Deline et al.[99g] for $EuBr_3$(c) from 5.18 to 338.08 K, and Chirico and Westrum[285] for $Eu(OH)_3$ from 4.99 to 346.69 K. These data yield $S°_{298.15}(EuCl_3(s))$ = 144.1 J K^{-1} mol^{-1}, $C_{p,298.15}(EuCl_3(s))$ = 107.0 J K^{-1} mol^{-1}, $S°_{298.15}(EuBr_3(c))$ = 182.8 J K^{-1} mol^{-1}, $C_{p,298.15}(EuBr_3(c))$ = 110.6 J K^{-1} mol^{-1}, $S°_{298.15}(Eu(OH)_3(s))$ = 119.9 J K^{-1} mol^{-1}, and $C_{p,298.15}(Eu(OH)_3(c))$ = 122.6 J K^{-1} mol^{-1}. The enthalpy of fusion of $EuCl_3$ was reported to be 51.0 ± 2.1 kJ mol^{-1}.[79]

4. Eu_2O_3

There is no calorimetrically determined entropy for Eu_2O_3, but since it is an important substance it is necessary to estimate its value. The most popular value is Westrum's estimate of 146 J K^{-1} mol^{-1}.[286] However, we prefer to estimate the entropy of cubic Eu_2O_3 by comparison of REE oxides with their corresponding hydroxides and chlorides.[77,285,287-291]

Differences between the entropy of REX_3 (X = OH^- or Cl^-) and RE_2O_3 can be represented by

$$2S°_{298.15}(REX_3(s)) - S°_{298.15}(RE_2O_3) = A \quad (17)$$

for various RE in each series. If A is roughly constant for each series, then its value can be used to estimate the entropy of Eu_2O_3 from the $Eu(OH)_3$ and $EuCl_3$ entropies. Although La_2O_3, Pr_2O_3, and Nd_2O_3 have a different structure than Eu_2O_3 and other RE_2O_3, the effect of lattice entropy differences on A should be small enough that data for lighter lanthanides can be averaged with the heavier lanthanides. Data for X = OH^- yield A = 103.3 ± 2.6 J K^{-1} mol^{-1}, so $S°_{298.15}(Eu_2O_3(s))$ = 136.5 ± 2.6 J K^{-1} mol^{-1}. Similarly, for X = Cl^-, A = 149.2 ± 2.0 J K^{-1} mol^{-1}, so $S°_{298.15}(Eu_2O_3(s))$ = 139.1 ± 2.0 J K^{-1} mol^{-1}. Our best estimate is then the average of 137.8 ± 2.3 J K^{-1} mol^{-1} for cubic Eu_2O_3.

High-temperature relative enthalpy (drop calorimetry) data are available for cubic Eu_2O_3 (relative to 298.15 K) up to 1350 and 1371 K and for the monoclinic form up to 1802 and 1589 K.[292,293] Cubic Eu_2O_3 is stable below about 1370 K and monoclinic Eu_2O_3 at higher temperatures, but their transformation is so slow below 1370 K that both forms can be studied. Data for cubic Eu_2O_3 are in excellent agreement and for monoclinic Eu_2O_3 are in fairly reasonable agreement. We accept Holley et al.'s[21] least-squares equations (converted to J mol^{-1}). For cubic Eu_2O_3

$$H_T - H_{298.15} = 136.9(T - 298.15) + 7.196 \times 10^{-3}(T^2 - 298.15^2) + 1.556 \times 10^6\left(\frac{1}{T} - \frac{1}{298.15}\right) \quad 298 \leq T \leq 1371 \text{ K} \quad (18)$$

For monoclinic Eu_2O_3

$$H_T - H_{298.15} = 133.8(T - 298.15) + 7.866 \times 10^{-3}(T^2 - 298.15)^2 + 1.728 \times 10^6\left(\frac{1}{T} - \frac{1}{298.15}\right) \quad 298 \leq T \leq 895 \text{ K} \quad (19)$$

$$H_T - H_{298.15} = 132.2(T - 298.15) + 7.866 \times 10^{-3}(T^2 - 298.15^2) - 2498 \quad 895 \leq T \leq 1800 \text{ K} \quad (20)$$

The uncertainty in $H_T - H_{298.15}$ is about 10^3 J mol^{-1} at 1400 K and 3 × 10^3 J mol^{-1} at 2000 K. There is a minor thermal anomaly for monoclinic Eu_2O_3 at 895 K with a transformation enthalpy of 423 ± 268 J mol^{-1}. Heat capacities from differential scanning calorimetry[294] are as much as 15 J K^{-1} mol^{-1} lower and so were rejected.

5. $EuCl_3 \cdot 6H_2O$

Entropy data are also required for $EuCl_3 \cdot 6H_2O$ but, unfortunately, only the heat capacity at 298.15 K, $C_{p,298.15}$ = 366.9 J K^{-1} mol^{-1}, is available.[175a] However, data are available for several other $RECl_3 \cdot 6H_2O$, and it is possible to obtain their lattice entropy by subtracting off the "magnetic" peaks. Hinchey and Cobble[175a] found that the lattice entropy divided by the heat capacity of the crystal at 298 K was 1.09–1.10 for $RECl_3 \cdot 6H_2O$. This yields the estimate of $S°_{298.15}(EuCl_3 \cdot 6H_2O(c))$ = (366.9)(1.095) + 9.33 = 411.1 J K^{-1} mol^{-1}. The second term is the electronic contribution to the entropy. Interpolation of lattice heat capacities for $RECl_3 \cdot 6H_2O$ and addition of the electronic term give an estimate of 407.1 J K^{-1} mol^{-1}.[295] The mean of 409.1 J K^{-1} mol^{-1} is accepted and is probably reliable to 2–3 J K^{-1} mol^{-1}.

6. Eu_3O_4, EuOCl, and $EuCl_2$

High-temperature data are available for the decomposition of Eu_3O_4 and EuOCl and for the sublimation of $EuCl_2$. Entropies for these compounds are required to further utilize these data, and no direct experimental values are available. Consequently, it is necessary to estimate them. McMasters et al.[284] noted that the entropy of Fe_3O_4 is less than the sum for FeO and Fe_2O_3. They thus estimated that $S°_{298.15}(Eu_3O_4)$ = 0.99[$S°_{298.15}$(EuO) + $S°_{298.15}(Eu_2O_3)$]. Recalculation to our recommended values gives $S°_{298.15}(Eu_3O_4)$ = 0.99(83.64 + 137.8) = 219.2 ± 3.0 J K^{-1} mol^{-1}. Haschke and Eick[57a] estimated an entropy of 205 J K^{-1} mol^{-1} using the sum of lattice and electronic terms and 203.3 ± 10.9 J K^{-1} mol^{-1} from an approximate second-law extrapolation of their decomposition pressure measurements. The average of 209.2 ± 8.8 J K^{-1} mol^{-1} is our recommended value for Eu_3O_4.

Hariharan and Eick[111] estimated $S°_{298.15}$(EuOCl(s)) = 102.5 ± 4.2 J K^{-1} mol^{-1} from various additivity schemes and 101.1 ± 3.1 J K^{-1} mol^{-1} from an approximate third-law extrapolation of their decomposition pressures; these values have been made consistent with our new $S°$ for Eu_2O_3 and the $EuCl_2$ value given below. The recommended value is the average of 101.8 ± 3.7 J K^{-1} mol^{-1} for EuOCl.

Hariharan and Eick[94] estimated that $S°_{298.15}$ = 144.3 J K^{-1} mol^{-1} for solid $EuCl_2$ from various estimation schemes and 137.7 J K^{-1} mol^{-1} from an approximate third-law extrapolation of their sublimation pressures. Their average value is recommended: $S°_{298.15}$($EuCl_2$(s)) = 141.0 ± 3.3 J K^{-1} mol^{-1}.

C. Enthalpies and Gibbs Energies for EuS(s) and Comments on Eu_2O_2S(s)/$Eu_2O_2SO_4$(s)

Thermal decomposition of EuS(s) proceeds mainly by formation of Eu(g) and an equilibrium mixture of S(g) and S_2(g) around 2000 K. Below this temperature some sublimation of EuS can occur, and above this temperature EuS_2(g), Eu_2S(g), and Eu_2S_2(g) can also form, as discussed earlier. Here we are concerned only with decomposition to the elements since it yields enthalpies of formation for EuS(s). Note that these decomposition pressure measurements yield the enthalpy of formation from the gaseous elements, which must be converted to the solid elements for $\Delta H°_{f,298.15}$ data. The CODATA entropy of 32.05 J K^{-1} mol^{-1} was used for rhombohedral sulfur at 298.15 K.

Since Kaldis and Peteler[296] concluded that their earlier vapor pressure study[118a] was in error, it is not considered further.

Available decomposition pressure data for EuS extend from about 1500 to 2500 K, but most measurements are between 1800 and 2400 K.[60,114-116,118a,120,296,297] Thus most of the data are above the EuS(s) drop calorimetry data range (maximum of 1605 K) and all are above the Eu(c) data (maximum of 1373 K).[42] We thus made no attempt to recalculate the literature high-temperature atomization enthalpies to our best values of thermal data for Eu and EuS(s) since an extrapolation outside the temperature ranges of some of the necessary data is required anyway, the enthalpy corrections are very small, and several sets of data[114,120,297] do not provide enough details to allow recalculation.

McMasters et al.[284] did third-law extrapolations of Hariharan and Eick's[116] results and Kaldis and Simanovski's unpublished results, which we revise slightly to $\Delta H°_{f,298.15}$(EuS(s)) = −448.9 ± 9.6 and 440.5 ± 3.3 kJ mol^{-1}, respectively. Kaldis and Peteler's[296] results yield −443.0 ± 2.1 kJ mol^{-1}, Nagai et al.[114] obtained −472.7 ± 18.8 kJ mol^{-1}, Fenochka and Gordienko[120,297] obtained −402.0 ± 9.2 kJ mol^{-1}, and Smoes et al.[60] obtained −456.8 ± 10.9 kJ mol^{-1}. Averaging the four values in best agreement[60,284,296] gives the recommended result of $\Delta H°_{f,298.15}$(EuS(s)) = −447.3 ± 7.2 kJ mol^{-1}. These enthalpies of formation were calculated from reported atomization enthalpies but have been adjusted to our recommended enthalpy of sublimation of Eu(g) and the CODATA values for S(rh) and S(g). The entropy of formation of EuS(s) is given by

$$\Delta S°_{f,298.15}(\mathrm{EuS(s)}) = S°_{298.15}(\mathrm{EuS(s)}) - S°_{298.15}(\mathrm{S(rh)}) - S°_{298.15}(\mathrm{Eu(c)}) \quad (21)$$

Our recommended values thus yield $\Delta S°_{f,298.15}$(EuS(s)) = 95.77 − 32.05 − 77.81 = −14.09 J K^{-1} mol^{-1}. This yields a standard Gibbs energy of formation of −443.1 ± 7.9 kJ mol^{-1}, assuming an uncertainty of 0.7 J K^{-1} mol^{-1} for the formation entropy.

Dwivedi and Kay[298] investigated the thermodynamics of oxidation of Eu_2O_2S(s) to $Eu_2O_2SO_4$(s) using oxygen concentration cells, from 1020 to 1320 K. These measurements yield reaction free energies, but there are no independent data for either compound so no Gibbs energies of formation can be derived.

D. Data for Solid EuO, Eu_2O_3, $EuCl_2$, $EuCl_3$, and $EuCl_3$·$6H_2O$ and for Aqueous Eu^{2+} and Eu^{3+}

A variety of compounds and aqueous species are considered together in this section because their data are interrelated. For example, data for EuO are available from combustion with O_2 to form Eu_2O_3 and by dissolution of EuO in HCl to form aquo ions.

Eu_2O_3 has been studied by several workers. Huber et al.[299] used combustion of Eu by O_2(g) to obtain an enthalpy of formation of monoclinic Eu_2O_3 of −1648.1 ± 3.8 kJ mol^{-1}. Enthalpies of solution of cubic and monoclinic Eu_2O_3 in 6 mol L^{-1} HNO_3 gave the enthalpy of transformation of stable cubic to metastable monoclinic Eu_2O_3 as −18.0 ± 2.5 kJ mol^{-1}. Stuve[300] used enthalpies of solution of Eu(c) and Eu_2O_3(cubic) in 4 mol L^{-1} HCl to calculate the formation enthalpy of Eu_2O_3(cubic) to be −1619.1 ± 5.0 kJ mol^{-1}. Yashvili and Gvelesiani[301] obtained an enthalpy of formation of Eu_2O_3 from dissolution of it and of Eu(c) in aqueous HCl, −1725.5 ± 5.1 kJ mol^{-1}. These various studies are in poor agreement, and, in the case of the latter study, the authors admitted that their Eu was of inadequate purity. The source of the problems is easy to see: Eu is a very reactive metal and it readily reacts with atmospheric moisture and oxygen. Thus "pure metal" samples generally contain some oxide and/or hydride, and these impurities are difficult to detect by most standard analytical chemistry methods.

Fortunately, the combustion enthalpy of Eu(c) and solution enthalpies of monoclinic and cubic Eu_2O_3 have been reexamined in detail and with care by Fitzgibbon et al.[302] Their combustion of Eu(c) by O_2 gave an enthalpy of formation of −1651.0 ± 3.8 kJ mol^{-1} for monoclinic Eu_2O_3. Measurements of the enthalpies of solution of Eu and Eu_2O_3 in 4 mol L^{-1} HCl yield another value of −1653.2 ± 3.4 kJ mol^{-1}. Averaging these with earlier results from their laboratory[299] yields $\Delta H°_{f,298.15}$(Eu_2O_3, monoclinic) = −1650.8 ± 2.6 kJ mol^{-1}. Combining Fitzgibbon et al.'s[302] enthalpy of solution of monoclinic Eu_2O_3 in 6 mol L^{-1} HCl with Stubblefield et al.'s[303] enthalpy of solution of Eu(c) in this medium yields −1624.3 ± 4.3 kJ mol^{-1}, which implies the Eu(c) solution data probably are in error so they were not included in the average.

Fitzgibbon et al.[302] also did a large number of experiments for the dissolution of cubic and monoclinic Eu_2O_3 in HCl and HNO_3, and consistent results were obtained in both media. They yield an enthalpy of transformation of cubic to monoclinic of 11.1 ± 1.2 kJ mol^{-1}. Their earlier negative value[299] of this quantity was attributed by them[302] to CO_2 and H_2O impurities. Using the newer result[302] gives $\Delta H^\circ_{f,298}(Eu_2O_3, \text{cubic}) = -1661.9 \pm 3.8$ kJ mol^{-1}.

The entropy of formation of cubic Eu_2O_3 is given by $\Delta S^\circ_{f,298.15}(Eu_2O_3, \text{cubic}) = S^\circ_{298.15}(Eu_2O_3, \text{cubic}) - 2S^\circ_{298.15}(Eu(c)) - (3/2)S^\circ_{298.15}(O_2(g)) = 137.8 - 2(77.81) - 1.5(205.04) = -325.4 \pm 3.0$ J K^{-1} mol^{-1}. Then, $\Delta G^\circ_{f,298.15}(Eu_2O_3, \text{cubic}) = -1564.9 \pm 4.7$ kJ mol^{-1}. Fitzgibbon et al.[302] estimated that $\Delta S = 6.3 \pm 2.1$ J K^{-1} mol^{-1} for the cubic to monoclinic transition. Then, $\Delta S^\circ_{f,298.15}(Eu_2O_3, \text{monoclinic}) = -319.1 \pm 3.7$ J K^{-1} mol^{-1}, and $\Delta G^\circ_{f,298.15}(Eu_2O_3, \text{monoclinic}) = -1555.7 \pm 3.7$ kJ mol^{-1}.

Five studies of the enthalpy of solution of Eu(c) in aqueous HCl show large differences.[300-304] Fitzgibbon et al.'s value[302] is probably the only reliable one, and only for their results, Huber et al.'s,[299] and Stuve's[300] were the impurity contents of Eu(c) adequately known. Bommer and Hohmann's enthalpy of solution[305] of $EuCl_3(c)$ in H_2O is also significantly in error due both to impurities and because adding anhydrous RE chlorides directly to water can give some hydrolysis and formation of hydroxide; thus their reaction may not have solely been dissolution of $EuCl_3(c)$. This hydrolysis problem can be avoided by dissolution of $EuCl_3(c)$ into HCl solutions.[300,306]

Data for EuO(s), $EuCl_2(s)$, and $Eu^{2+}(aq)$ are also related. Data are available for the dissolution of EuO(s) in aqueous HCl[304] and for the combustion of EuO(s) by O_2.[307] Enthalpies of solution and of oxidation of aqueous $EuCl_2$[275,303,308] are also available. However, especially for $EuCl_2$,[308] there is a considerable variation of the experimental enthalpies with experimental conditions.

Morss and Haug,[275] in addition to doing new measurements on $EuCl_2$, reanalyzed literature data. Some discrepancies in previous literature data were due to other workers assuming that Eu^{2+} oxidation in air-saturated HCl proceeded with water formation. In fact, they[275] showed that the main reaction was actually

$$Eu^{2+}(aq) + H^+(aq) + (^1/_2)O_2(aq) = Eu^{3+}(aq) + (^1/_2)H_2O_2(aq) \quad (22)$$

Our discussion will be largely based on theirs and will yield only minor revisions in their recommended values.

Morss and Haug's[275] recalculations yield enthalpies of formation of EuO(s) from Burnett and Cunningham's enthalpies of solution of EuO in O_2-saturated HCl[304] (corrected for 2.2% monoclinic Eu_2O_3) of −586.8 kJ mol^{-1} and a value of -591.5 ± 2.8 kJ mol^{-1} from Huber and Holley's combustion data,[307] after recalculation to our Eu_2O_3 results. McMasters et al.[284] reanalyzed Haschke and Eick's[53] decomposition pressure data for EuO(s) and obtained a third-law enthalpy of -599.1 ± 15.9 kJ mol^{-1}. Our recommended value is the average of $\Delta H^\circ_{f,298.15}(EuO(s)) = -592.2 \pm 5.5$ kJ mol^{-1}, giving double weight to the more precise combustion data. Using our evaluated entropies yields the entropy of formation of EuO(s) of $\Delta S^\circ_{f,298.15}(EuO(s)) = 83.64 - 77.81 - {}^1/_2(205.04) = -96.69$ J K^{-1} mol^{-1}, and $\Delta G^\circ_{f,298.15}(EuO(s)) = -563.4 \pm 5.7$ kJ mol^{-1}.

Morss and Haug[275] also combined Fitzgibbon et al.'s[302] enthalpy of dissolution data for Eu(c) in HCl

$$Eu(c) + 3HCl\ (\text{in 4 mol } L^{-1}\ HCl) = EuCl_3\ (\text{in 4 mol } L^{-1}\ HCl) + (^3/_2)H_2(g) \quad (23)$$

and Stuve's[300] enthalpy of solution of $EuCl_3(s)$ in 4 mol L^{-1} HCl to obtain the enthalpy of formation of $EuCl_3(s)$. These data yield -937.1 ± 3.6 kJ mol^{-1}, but the error in the enthalpy change for reaction 23 could possibly be larger. They also used the enthalpy of dissolution of monoclinic Eu_2O_3 in 4 mol L^{-1} HCl[302] and Stuve's enthalpy of solution of $EuCl_3(s)$ in this same medium[300] to obtain $\Delta H^\circ_{f,298.15}(EuCl_3(s))$; we revise their result to -935.9 ± 3.3 kJ mol^{-1} using our recommended Eu_2O_3 value. Similarly, we combine Machlan et al.'s[306] enthalpy of solution of $EuCl_3(s)$ in 6 mol L^{-1} HCl with Fitzgibbon et al.'s data[302] for dissolution of monoclinic Eu_2O_3 in this same medium to obtain $\Delta H^\circ_{f,298.15}(EuCl_3(s)) = -934.2 \pm 4.1$ kJ mol^{-1}. The best value of $\Delta H^\circ_{f,298.15}(EuCl_3(s)) = -935.8 \pm 4.0$ kJ mol^{-1} was obtained by averaging these results.

The entropy of formation of $EuCl_3(s)$ is $\Delta S^\circ_{f,298.15}(EuCl_3(s)) = 144.1 - 77.81 - {}^3/_2(222.97) = -268.2$ J K^{-1} mol^{-1}. Thus, $\Delta G^\circ_{f,298.15}(EuCl_3(c)) = -855.8 \pm 4.3$ kJ mol^{-1}.

The only value of the enthalpy of solution of $EuCl_3(s)$ into dilute HCl is Machlan et al.'s results[306] into 0.015 mol L^{-1} HCl, and it can be approximately extrapolated to infinite dilution to obtain the enthalpy of formation of Eu^{3+}. Morss and Haug's calculations[275] then give $\Delta H^\circ_{f,298.15}(Eu^{3+}(aq)) = -604.8 \pm 4.2$ kJ mol^{-1}, after correction to our revised $EuCl_3(s)$ data. Morss and Haug also studied the oxidation of argon-flushed $EuBr_2$ solutions with both aqueous Br_2 and liquid Br_2.[275] Their data yield $\Delta H^\circ_{f,298.15}(Eu^{3+}(aq)) - \Delta H^\circ_{f,298.15}(Eu^{2+}(aq)) = -76.8 \pm 4.2$ and -77.4 ± 8.4 kJ mol^{-1} by the two different methods. Thus, $\Delta H^\circ_{f,298.15}(Eu^{2+}(aq)) = -527.7 \pm 7.6$ kJ mol^{-1}. Previous determinations of these quantities by other workers are considered inaccurate by Morss and Haug.[275] Il'ina and Khanaev's[309a] enthalpy of oxidation of Eu^{2+} was unavailable to us.

Two determinations of the enthalpy of solution of $EuCl_3 \cdot 6H_2O(c)$ into water are in excellent agreement: -36.46 ± 0.03 and -36.69 ± 0.13 kJ mol^{-1} after extrapolation to infinite dilution.[162,175a] Hydrolysis problems are not present for dissolution of the hydrated salt. Karapet'yants et al.'s enthalpy of solution[128] into 0.239 mol kg^{-1} HCl yields about −37.9 kJ mol^{-1}, but the correction to infinite dilution in water makes this value less certain than the direct solution into water results. The best value is the average of solution into water, -36.58 ± 0.13 kJ mol^{-1}. The solution process is given formally by

$$EuCl_3 \cdot 6H_2O(c) = Eu^{3+}(aq) + 3Cl^-(aq) + 6H_2O(l) \quad (24)$$

Thus, $\Delta H^\circ_{f,298.15}(EuCl_3 \cdot 6H_2O(c)) = 36.58 + (-604.8)\ 3(-167.08) + 6(-285.83) = -2784.5 \pm 4.3$ kJ mol^{-1}. The entropy of formation is $\Delta S^\circ_{f,298.15}(EuCl_3 \cdot 6H_2O)(c)) = 409.1 - 77.81 - {}^3/_2(229.97) - 6(130.57) - 3(205.04) = -1412.2 \pm 11.6$ J K^{-1} mol^{-1}, and $\Delta G^\circ_{f,298.15}(EuCl_3 \cdot 6H_2O(c)) = -2363.4 \pm 7.8$ kJ mol^{-1}.

Solubility data are available for $EuCl_3 \cdot 6H_2O$ in water at 298.15 K. Spedding et al.[161] reported a value of 3.5889 mol kg^{-1} by direct determination and 3.5839 mol kg^{-1} by isopiestic equilibration.[169] Powell's value[309b] of 3.621 mol kg^{-1} is about 1% higher. The two values in agreement were averaged for 3.5864 ± 0.0025 mol kg^{-1}.

The activity of H_2O, $a_w = 0.4918 \pm 0.0004$ and the solute activity coefficient $\gamma_\pm = 5.221 \pm 0.013$ for the saturated solution were taken from the revised values reported by Spedding et al.,[168a] where we assume a 2.5% uncertainty for $\gamma_\pm$. These results yield the standard Gibbs energy of solution, $\Delta G° = -RT \ln (27m^4\gamma_\pm{}^4a_w{}^6) = -26.67 \pm 0.04$ kJ mol^{-1}. The entropy of solution is thus -33.25 ± 0.57 J K^{-1} mol^{-1}.

Mason[310] also reported activity data for $EuCl_3$ from 0.20 to 2.08 mol kg^{-1}, but his osmotic coefficients are 0.15–1.5% too high. This is most likely due to low-purity reagents and to hydrolysis when his anhydrous salt was added to water. Kotlyar-Shapirov et al.'s activity data[311] are too scattered to be of any use.

The above data for reaction 24 yield the entropy of Eu^{3+}, $S°_{298.15}(Eu^{3+}(aq)) = 409.1 - 33.25 - 6(69.95) - 3(56.73) = -214.0 \pm 3.1$ J K^{-1} mol^{-1}. Then, the entropy of formation is $\Delta S°_{f,298.15}(Eu^{3+}(aq)) = -214.0 - 77.81 + 3(65.285) = -96.0 \pm 3.6$ J K^{-1} mol^{-1}. This last term of 65.285 J K^{-1} mol^{-1} is the "entropy" of the electron (= $^1/_2$ the $H_2(g)$ value) and is required to maintain consistency with the hydrogen ion convention. Thus, $\Delta G°_{f,298.15}(Eu^{3+}(aq)) = -576.2 \pm 5.3$ kJ mol^{-1}.

Numerous measurements have been made of the aqueous redox potential involving Eu^{3+}/Eu^{2+}, which allow the free energy of formation of Eu^{2+} to be calculated from the Eu^{3+} data. There is evidence (discussed earlier) that Cl^- ions form weak complexes with aqueous Eu^{3+} and ClO_4^- ions probably form very weak complexes also. Since the Eu^{3+} perchlorate stability constant is poorly known and almost nothing is known about these chloride and perchlorate complexes in Eu^{2+} solutions, the electrode potentials cannot be properly corrected for complex formation. Consequently, we chose an empirical extrapolation, of E vs. $(I)^{1/2}$, for the data given below. Here E is the reduction potential in volts vs. the normal hydrogen electrode, and I is the ionic strength in mol L^{-1}.

McCoy,[267] Holleck,[268] and Shul'gin and Koz'min[276] reported E values in chloride solutions of −0.43 to −0.49 V. However, more recent results are consistently less negative, which suggests that these three studies are in error. McCoy's solutions[267] contained formic acid but when corrected for complex formation with Eu^{3+} yield −0.36 V for Eu^{3+}/Eu^{2+},[269] which agrees with more recent work. This corrected value, the results of Vlček in $HClO_4$,[202] and eleven other studies[203-205,269-275,312] were used to obtain the recommended results. The Gierst and Cornelissen[312] polarographic measurements in various $NaClO_4$ concentrations yield −0.350 V at infinite dilution. Morss and Haug's cell measurements[275] in dilute HCl yield −0.349 V but show an opposite variation with concentration than Gierst and Cornelissen,[312] and their higher ionic strength value is less negative than all the other studies. However, since these two sets of data both yield −0.35 V when separately extrapolated to infinite dilution, we have more confidence in the results. The other studies were each at one ionic strength, usually 1 mol L^{-1}. Based on the reported variations[203-205,270-274,312] of −0.350 to −0.386 V at $I = 1$ mol L^{-1}, we estimate an uncertainty of 0.016 V. Thus, $E° = -0.349 \pm 0.016$ V is the best value for this potential. It should be noted that $E°$ values in Cl^- solutions tend to be slightly more negative than in ClO_4^- solutions at the same ionic strength; this may indicate that Eu^{3+} forms stronger complexes with Cl^- than does Eu^{2+}.

This potential yields $\Delta G°_{rxn} = \Delta G°_{f,298.15}(Eu^{2+}(aq)) - \Delta G°_{f,298.15}(Eu^{3+}(aq)) = 33.7 \pm 1.5$ kJ mol^{-1}. Then, $\Delta G°_{f,298.15}(Eu^{2+}(aq)) = -542.5 \pm 6.8$ kJ mol^{-1}. Also, $\Delta S°_{f,298.15}(Eu^{2+}(aq)) = 49.7 \pm 10$ J K^{-1} mol^{-1}, so $S°_{298.15}(Eu^{2+}(aq)) = 49.7 + 77.81 - 2(65.285) = -3.1 \pm 11$ J K^{-1} mol^{-1}.

Stubblefield and Eyring[308] investigated the dissolution of $EuCl_2(s)$ both in O_2- and H_2-saturated HCl solutions. The enthalpy of solution of $EuCl_2(s)$ in O_2-saturated HCl was about twice as negative as for the H_2-saturated case, which clearly establishes that the oxygen was causing extensive oxidation. However, results were highly irreproducible in both cases (about 38 kJ mol^{-1} variation).

Stubblefield et al. reinvestigated the solution of $EuCl_2(s)$ in H_2-saturated 6 mol L^{-1} HCl and obtained enthalpy data about a factor of 10 more reproducible.[303] They obtained evidence for the reaction being oxidation of $Eu^{2+}(aq)$ by $H^+(aq)$

$$EuCl_2(s) + HCl\ (\text{in 6 mol } L^{-1}\ HCl) = EuCl_3\ (\text{in 6 mol } L^{-1}\ HCl) + (^1/_2)H_2(g) \quad (25)$$

Assuming that their reaction was complete, $\Delta H°_{f,298.15}(EuCl_2(s)) = -935.7 - 129.3 + 153.5 + 90.8 = -820.8 \pm 5.7$ kJ mol^{-1} from these data[303] and from enthalpy of solution of $EuCl_3$ in 6 mol L^{-1} HCl.[306]

Morss and Haug[275] measured the dissolution enthalpy of $EuCl_2(s)$ in dilute (0.001–0.1 mol L^{-1}) HCl saturated with argon. At these low HCl concentrations, oxidation of Eu^{2+} by H^+ is much less of a problem. Thus they obtained an enthalpy of solution (corrected to infinite dilution) of -37.7 ± 0.2 kJ mol^{-1} for the reaction

$$EuCl_2(s) = Eu^{2+}\ (\text{in dilute HCl}) + 2Cl^-\ (\text{in dilute HCl}) \quad (26)$$

Combining these data with the enthalpies of formation of Eu^{2+} and Cl^- gives $\Delta H°_{f,298.15}(EuCl_2(s)) = -527.7 + 2(-167.08) + 37.7 = -824.2 \pm 7.8$ kJ mol^{-1}. Similar solution measurements for $EuCl_2(s)$ in O_2-saturated 0.1 mol L^{-1} HCl were shown to occur predominantly by reaction 22; i.e., H_2O_2 is formed.[275] However, a smaller fraction could have gone by H_2O formation, so these data will not be used here (note: $\Delta H°_{f,298.15}(EuCl_2(s))$ from O_2-saturated solution data agrees well with the other two results if reaction 22 is *assumed* to go to completion).

The best value for the enthalpy of formation of $EuCl_2(s)$ is the average of -822.5 ± 6.7 kJ mol^{-1}. Our earlier entropy estimate for $EuCl_2(s)$ yields $\Delta S°_{f,298.15}(EuCl_2(s)) = 141.0 - 77.81 - 222.97 = -159.8 \pm 3.8$ J K^{-1} mol^{-1}. Thus our free energy of formation is $\Delta G°_{f,298.15}(EuCl_2(s)) = -774.8 \pm 7.9$ kJ mol^{-1}.

Heating $EuCl_3(s)$ high enough to give a significant vapor pressure causes melting, and upon melting $EuCl_3$ extensively decomposes to $EuCl_2$. Also, heating $EuCl_2$ produces predominantly $EuCl_2(g)$ by congruent vaporization. Thus these vaporization data do not directly yield Gibbs energy results for the solid phases. Consequently, solution calorimetry was used to derive most of the above results. However, Polyachenok and Novikov[88] studied the liquid $EuCl_3/EuCl_2$ decomposition equilibrium. They used their results to obtain rough values of the enthalpies of formation of $EuCl_3(l)$ (−1008 kJ mol^{-1}) and $EuCl_2$(l) (−908 kJ mol^{-1}), which are within 10% of the more accurate solid state results discussed above.

E. Thermodynamics of Solid Eu_3O_4, EuOCl, $EuBr_3$, $EuBr_2$, and EuI_2

Hashcke and Eick[57a] studied the decomposition of Eu_3O_4(s) between 1604 and 2016 K by target collection–mass spectrometry. By far the dominant decomposition reaction was the formation of monoclinic Eu_2O_3 and Eu(g) by eq 3. Using estimated heat capacities, they obtained the enthalpy of formation of Eu_3O_4. Revising their calculations to our recommended results for Eu_2O_3(monoclinic) and Eu(g) gives $\Delta H^\circ_{f,298.15}$($Eu_3O_4$(s)) = −2270.5 ± 12 kJ mol^{-1}. Our recommended entropies yield $\Delta S^\circ_{f,298.15}$($Eu_3O_4$(s)) = $S^\circ_{298.15}$(Eu_3O_4(s)) − $3S^\circ_{298.15}$(Eu(s)) − $2S^\circ_{298.15}$(O_2(g)) = 209.2 − 3(77.81) − 2(205.04) = −434.3 ± 8.8 J K^{-1} mol^{-1}. Thus, $\Delta G^\circ_{f,298.15}$($Eu_3O_4$(s)) = −2141.0 ± 14 kJ mol^{-1}.

Hariharan and Eick[111] studied the thermal decomposition of EuOCl(s) from Knudsen effusion vapor pressure measurements from 1236 to 1617 K. The predominant reaction is given by eq 6, and monoclinic Eu_2O_3 and gaseous $EuCl_2$ and Cl were the products. However, traces of cubic Eu_2O_3 were generally observed, which suggests that the initial decomposition could have been to the cubic form (or that some cubic Eu_2O_3 formed during quenching). Being unsure of that, however, we and they made thermodynamic calculations assuming formation of monoclinic Eu_2O_3.

Hariharan and Eick[111] gave a third-law decomposition enthalpy of 727.2 ± 18.4 kJ per 3 mols of EuOCl(s) for reaction 6. Combining our selected data for $EuCl_2$(s) and Eu_2O_3(monoclinic) with Hariharan and Eick's[94] vaporization enthalpy for $EuCl_2$ yields $\Delta H^\circ_{f,298.15}$(EuOCl(s)) = −911.1 ± 7.3 kJ mol^{-1}. Although the vaporization enthalpy of $EuCl_2$ of 346.0 ± 11 kJ mol^{-1} from Hariharan and Eick[94] was felt to be the best available result for our calculations, it is in poor agreement both with Polyachenok and Novikov's value[93] of 231 kJ mol^{-1} and with Hastie et al.'s[89] 255 ± 4 kJ mol^{-1}. Thus the EuOCl enthalpy of formation may have much larger error than estimated above.

Using our selected entropy for EuOCl(s) yields an entropy of formation of $\Delta S^\circ_{f,298.15}$(EuOCl(s)) = −190.0 ± 3.7 J K^{-1} mol^{-1}; therefore $\Delta G^\circ_{f,298.15}$(EuOCl(s)) = −854.4 ± 8.4 kJ mol^{-1}. Again, the errors could actually be larger.

Hariharan and Eick[313a] studied the congruent vaporization of EuI_2. To calculate $\Delta H^\circ_{f,298.15}$($EuI_2$(s)) requires estimating molecular parameters for EuI_2(g). Since this is rather uncertain, we choose not to reanalyze these data. Data for EuF_2(s) and EuF_3(s) are discussed in Section IV.F.9.

Haschke[99f] studied the incongruent vaporization of $EuBr_3$(s) to form $EuBr_2$(s) and Br_2(g), using a spectrophotometer to monitor the Br_2(g) vapor pressure. To calculate enthalpy of formation data for $EuBr_3$(s) requires enthalpy of formation data for $EuBr_2$(s). Two vaporization studies have been made for $EuBr_2$;[313b,c] the more recent one[313c] is undoubtedly more accurate and was accepted. Haschke[313c] estimated the dissociation energy for $EuBr_2$(g) from that of the other europium dihalides. The calculated $\Delta H^\circ_{f,298.15}$($EuBr_2$(g)) was then combined with the sublimation enthalpy to yield $\Delta H^\circ_{f,298.15}$($EuBr_2$(s)) = −720 ± 33 kJ mol^{-1}. Then, the decomposition pressure measurements[99f] yield $\Delta H^\circ_{f,298.15}$($EuBr_3$(s)) = −753 ± 33 kJ mol^{-1}.

The selected entropy of $EuBr_3$ yields $\Delta S^\circ_{f,298.15}$($EuBr_3$(s)) = 182.8 − $^3/_2$(152.21) − 77.81 = −123.3 ± 1.0 J K^{-1} mol^{-1}, and $\Delta G^\circ_{f,298.15}$($EuBr_3$(s)) = −716 ± 33 kJ mol^{-1}. A redetermination of the enthalpy of formation of $EuBr_3$(s) using solution calorimetry would yield much more precise values for ΔH and ΔG.

F. Thermodynamic Data for Hydrated Salts

$EuCl_3{\cdot}6H_2O$ falls in this classification but was treated earlier since it was needed for evaluation of the aqueous solution data. Also, $Eu(OH)_3$ and $EuSO_4$ will be treated in this section since they precipitate from aqueous solutions, although they will be treated as unhydrated. In addition, both hydrated and anhydrous europium fluorides and discussed together here.

1. *Europium Nitrate*

$Eu(NO_3)_3{\cdot}6H_2O$ is the stable hydrate precipitating from a saturated $Eu(NO_3)_3$ solution from about 237 to 300 K. Mironov et al.'s solubilities[133] are generally inconsistent with published data for other $RE(NO_3)_3{\cdot}6H_2O$ and are usually too low.[140] Rard[141] determined the aqueous solubility to be 4.2732 ± 0.0061 mol kg^{-1} at 298.15 K. The solubility reaction is given formally as

$$Eu(NO_3)_3{\cdot}6H_2O(c) = Eu^{3+}(aq) + 3NO_3^-(aq) + 6H_2O(l) \quad (27)$$

which has a thermodynamic solubility product given by

$$K_s = a_c a_a^3 a_w^6 \quad (28)$$

where the subscript c denotes the Eu^{3+} cation, a the NO_3^- anion, and w water. Using published activity coefficient data,[256] Rard[141] reported that K_s = 69.8 ± 9.3, where the main uncertainty comes from the low concentration extrapolation of activity coefficient data. This yields a Gibbs energy of formation of $\Delta G^\circ_{f,298.15}$($Eu(NO_3)_3{\cdot}6H_2O$(c)) = −576.2 + 3(−111.34) + 6(−237.19) + 10.52 = −2322.8 ± 5.4 kJ mol.$^{-1}$ Afanas'ev and Koroleva[313d] reported an enthalpy of solution for $Eu(NO_3)_3{\cdot}6H_2O$, but it is not clear if or how they extrapolated their data to infinite dilution. Also, their data for other $RE(NO_3){\cdot}6H_2O$ are quite scattered and indicate errors of at least 10–30%. This is inadequate for our purpose.

A more reliable estimate of the enthalpy of solution of $Eu(NO_3)_3{\cdot}6H_2O$ can be made from the more precise enthalpy of solution data for La, Nd, Gd, Ho, and Er nitrate hexahydrates.[314] Graphical interpolation yields 13.8 ± 0.8 kJ mol^{-1} for $Eu(NO_3)_3{\cdot}6H_2O$. Then, the enthalpy of formation of $Eu(NO_3)_3{\cdot}6H_2O$ is given by $\Delta H^\circ_{f,298.15}$($Eu(NO_3)_3{\cdot}6H_2O$(c)) = −604.8 + 3(−207.36) + 6(−285.83) − 13.8 = −2955.7 ± 5.0 kJ mol^{-1}, and the entropy of formation is $\Delta S^\circ_{f,298.15}$($Eu(NO_3)_3{\cdot}6H_2O$(c)) = −2122.5 ± 20 J K^{-1} mol^{-1}. Thus, $S^\circ_{298.15}$($Eu(NO_3)_3{\cdot}6H_2O$(c)) = −2122.5 + 77.81 + $^3/_2$(191.50) + 6(130.57) + $^{15}/_2$(205.04) = 563.8 ± 21 J K^{-1} mol^{-1}. Comparison with the $Gd(NO_3)_3{\cdot}6H_2O$ experimental entropy[295] of 557.3 J K^{-1} mol^{-1} from heat capacity data suggests that the mean value for $Eu(NO_3)_3{\cdot}6H_2O$ could actually be more accurate than these uncertainty limits indicate.

2. Europium Iodate

Laurie and Monk[155] found the solubility of Eu^{3+} iodate at 298.15 K to be 8.18×10^{-4} mol L^{-1}, Firsching and Paul[156] obtained 8.0×10^{-4} mol L^{-1}, Bertha and Choppin[167] obtained 8.0×10^{-4} mol L^{-1}, and Miyamoto et al.[238] obtained 7.8×10^{-4} mol L^{-1}. The best value of the solubility is $(7.97 \pm 0.14) \times 10^{-4}$ mol L^{-1}, which equals $(7.99 \pm 0.14) \times 10^{-4}$ mol kg^{-1}. In most of these studies the composition of the solid phase was not analyzed. Nassau et al.[315] and Abrahams et al.[157] found that precipitation of $RE(NO_3)_3$ solutions with HIO_3 near room temperature gave $RE(IO_3)_3{\cdot}4H_2O$ or $RE(IO_3)_3{\cdot}2H_2O$ for Eu to Lu, with the dihydrate usually obtained for Eu; however Yakunina et al.[316] and Hâjek and Hradilovâ.[317] obtained the tri- and tetrahydrates. Miyamoto[238] prepared the dihydrates for most RE and measured solubilities for these same samples that generally agree with the other studies. Thus, solubility data probably refer to $Eu(IO_3)_3{\cdot}2H_2O$, and the various hydrates probably differ little in stability.

The solubility equilibrium is then given formally by

$$Eu(IO_3)_3{\cdot}2H_2O(s) = Eu^{3+}(aq) + 3IO_3^-(aq) + 2H_2O(l) \tag{29}$$

and the solubility product by

$$K_s = a_c a_a^3 a_w^2 = 27m^4\gamma_c\gamma_a^3 a_w^2 = (4.7 \pm 0.4) \times 10^{-12} \tag{30}$$

Calculations were made with the Debye–Hückel equation assuming an ion size of 6.6 Å, as was found for Sm-Gd perchlorates.[318] The resulting activity coefficients are assumed uncertain by 10%. These values yield a standard Gibbs energy of solution of 64.7 ± 0.2 kJ mol^{-1}, and $\Delta G^\circ_{f,298.15}(Eu(IO_3)_3{\cdot}2H_2O(s)) = -576.2 + 3(-128.2) + 2(-237.19) - 64.7 = -1499.7 \pm 5.7$ kJ mol^{-1}. Bertha and Choppin[167] determined the enthalpy of precipitation of $Eu(IO_3)_3$ and other RE iodates at several ionic strengths. Data at an ionic strength of 0.05 mol L^{-1} were unreliable owing to formation of colloids, but data of other ionic strengths showed no trend with concentration. Their data yield an enthalpy of solution of 21.3 ± 2.1 kJ mol^{-1} assuming a 10% uncertainty and an enthalpy of formation of $\Delta H^\circ_{f,298.15}(Eu(IO_3)_3{\cdot}2H_2O(s)) = -604.8 + 3(-221.3) + 2(-285.83) - 21.3 = -1861.8 \pm 8.0$ kJ mol^{-1}. Then, $\Delta S^\circ_{f,298.15}(Eu(IO_3)_3{\cdot}2H_2O(s)) = -1214.3 \pm 26$ J K^{-1} mol^{-1}. Also, $S^\circ_{298.15}(Eu(IO_3)_3{\cdot}2H_2O(s)) = -1214.3 + 77.81 + {}^3/_2(116.14) + 2(130.57) + {}^{11}/_2(205.04) = 426.6 \pm 27$ J K^{-1} mol^{-1}.

3. Europium Hydroxide and Hydroxychlorides

It was noted earlier that precipitation of hydroxides from Eu^{3+} salt solutions generally gives a mixed-anion hydroxide. Aksel'rud and Ermolenko[73] studied the precipitation of Eu^{3+} by OH^- from solutions containing 0.1, 0.2, 0.5, 1.0, and 2.0 mol L^{-1} NaCl and also studied the changes in precipitate composition with aging. After aging 150 days, the composition in all cases was found to be chloride-free, i.e., $Eu(OH)_3$. Solubilities of "$RE(OH)_3$" are well-known to change as the solutions age and part of this is due to removal of other anions from the hydroxide precipitate. Other factors affecting solubility are changes in the relative amounts of monomers and polymers in the aqueous phase and possible changes in the solid hydroxide phase (such as crystal growth, crystals forming from amorphous hydrous oxides, etc.).

"Pure" $Eu(OH)_3$ was found after 150 days, and the solubility product showed only a slight ionic strength dependence.[73] No trend was observed for ln K_s as a function of pH or Eu^{3+} concentration, so the solution phase was assumed to be unhydrolyzed Eu^{3+} in these well-aged solutions. Under these conditions the solubility reaction is given by

$$Eu(OH)_3(s) = Eu^{3+}(aq) + 3OH^-(aq) \tag{31}$$

Extrapolation of ln K_s as a function of the square root of ionic strength gave ln $K_s = -60.8 \pm 0.5$ at infinite dilution. Thus, the standard Gibbs energy of solution is $\Delta G^\circ_{298.15} = -RT \ln K_s = 150.7 \pm 5.7$ kJ mol^{-1}, where K_s is now assumed to be uncertain by a factor of 10 to account for possible future aging effects. Then, $\Delta G^\circ_{f,298.15}(Eu(OH)_3(s)) = -576.2 + 3(-157.34) - 150.7 = -1198.9 \pm 7.9$ kJ mol^{-1}, $\Delta S^\circ_{f,298.15}(Eu(OH)_3(s)) = 119.9 - 77.81 - {}^3/_2(205.04) - {}^3/_2(130.57) = -461.3 \pm 1.2$ J K^{-1} mol^{-1}, and $\Delta H^\circ_{f,298.15}(Eu(OH)_3(s)) = -1336.5 \pm 8.3$ kJ mol^{-1}. A direct determination of the enthalpy of solution of $Eu(OH)_3$ in acid would be desirable as a check.

Their precipitate was $Eu(OH)_{2.5}Cl_{0.5}$ after 50 days of aging and had a solubility that depended on the 0.52 power of the chloride activity (theoretically 0.50 power).[73] For this material

$$Eu(OH)_{2.5}Cl_{0.5}(s) = Eu^{3+}(aq) + 2.5\ OH^-(aq) + 0.5\ Cl^-(aq) \tag{32}$$

and ln $K_s = -50.9$. Thus, the standard Gibbs energy of solution is 126.2 ± 5.7 kJ mol^{-1}, and $\Delta G^\circ_{f,298.15}(Eu(OH)_{2.5}Cl_{0.5}(s)) = -1161.4 \pm 7.8$ kJ mol^{-1}. It is not clear whether $Eu(OH)_{2.5}Cl_{0.5}$ is a stoichiometric compound or simply a mixture of $Eu(OH)_2Cl$ and $Eu(OH)_3$ but the dependence of solubility on chloride activity suggests the former may be true.

Similar calculations for the fresh precipitate $Eu(OH)_2Cl(s)$ yield ln $K_s = -43.4$, so the standard Gibbs energy of solution is 107.7 ± 5.7 kJ mol^{-1} and $\Delta G^\circ_{f,298.15}(Eu(OH)_2Cl(s)) = -1129.9 \pm 7.8$ kJ mol^{-1}.

All of the K_s values in this section were assumed uncertain by a factor of 10 for thermodynamic calculations.

4. Europium Perchlorate

The solubility of $Eu(ClO_4)_3$ was reported to be 4.6334 mol kg^{-1},[163,229] with an uncertainty of about 0.2%. This value could, in principle, be combined with an estimated value for the activity coefficient interpolated from data for the other $RE(ClO_4)_3$[170] to yield a thermodynamic solubility product for $Eu(ClO_4)_3{\cdot}nH_2O$. Since no analysis was made for the hydrate, we do not further analyze these data, but it may well have been $Eu(ClO_4)_3{\cdot}8H_2O$ or a lower hydrate.

5. Europium Bromate

Staveley et al.[159] determined the enthalpy of solution of $Eu(BrO_3)_3{\cdot}9H_2O$ in water and found its solubility to be 1.21 mol kg^{-1} at 298 K. They determined the integral enthalpy of solution to be about 68.6 ± 0.2 kJ mol^{-1} for dilution to 0.010 mol L^{-1}. There are no enthalpy of dilution data for $Eu(BrO_3)_3$, so the correction to infinite dilution of -2.0 ± 0.3 kJ mol^{-1} was made by averaging the data for the chloride[162] and perchlorate.[233] The enthalpy of solution to infinite dilution is then 66.6 ±

1.0 kJ mol^{-1}, where the uncertainty limit has been increased due to the uncertainty in the approximate extrapolation and because of the somewhat low purity of their $Eu(BrO_3)_3{\cdot}9H_2O$. Then, $\Delta H^\circ_{f,298.15}(Eu(BrO_3)_3{\cdot}9H_2O(c)) = -604.8 + 3(-83.68) + 9(-285.83) - 66.6 = -3494.9 \pm 7.8$ kJ mol^{-1}. There are no activity data for aqueous $RE(BrO_3)_3$, so the solubility data cannot presently be used to obtain Gibbs energies of solution.

6. Europium Carbonates

Karapet'yants et al.[128] measured the enthalpies of dissolution of $Eu_2(CO_3)_3$ and $Eu_2(CO_3)_3{\cdot}3H_2O$ in 0.33 mol kg^{-1} HCl to form solutions with final Eu^{3+} concentrations of 0.030 mol kg^{-1}. Their enthalpies of dissolution were -141.4 ± 1.7 kJ mol^{-1} for the anhydrous compound and -91.2 ± 1.7 kJ mol^{-1} for the trihydrate. The solution processes were

$$Eu_2(CO_3)_3{\cdot}nH_2O(s) + 6HCl \text{ (in aq HCl)} = 2Eu^{3+} \text{ (in aq HCl)} + 6\,Cl^- \text{ (in aq HCl)} + (3+n)H_2O \text{ (in aq HCl)} + 3CO_2(g) \quad (33)$$

and the final solutions were in 0.239 mol kg^{-1} HCl. Their results for the enthalpy of solution of $EuCl_3{\cdot}6H_2O$ in this medium and our selected value for the formation enthalpy of $EuCl_3{\cdot}6H_2O$ were used in these calculations. Then, $\Delta H^\circ_{f,298.15}(Eu_2(CO_3)_3(s)) = -3092.5 \pm 11$ kJ mol^{-1}, and $\Delta H^\circ_{f,298.15}(Eu_2(CO_3)_3{\cdot}3H_2O(s)) = -4000.4 \pm 11$ kJ mol^{-1}.

Karapet'yants et al.[319] utilized Caro et al.'s $Eu_2(CO_3)_3$ solubilities[126] to calculate thermodynamic data. However, Caro et al.'s data at 296 ± 1 K were for 1 atm CO_2 pressure, which should decrease the pH and increase the solubility. Sklyarenko and Ruzaikina[127] found that $Eu_2(CO_3)_3$ has a minimum solubility between pH 7.0 and 8.0, with an increase in solubility at lower and higher pH values. They reported a solubility of 3.88×10^{-6} mol L^{-1} for $Eu_2(CO_3)_3$ at 303 K. This will also be taken for the 298 K solubility, but the uncertainty will be assumed to be a factor of 5. Also, the solid phase under these conditions is $Eu_2(CO_3)_3{\cdot}3H_2O$.[125-127] Thus

$$Eu_2(CO_3)_3{\cdot}3H_2O(s) = 2Eu^{3+}(aq) + 3\,CO_3^{2-}(aq) + 3H_2O(l) \quad (34)$$

is the formal solubility reaction. For it

$$K_s = a_c^2 a_a^3 a_w^3 = (2m)^2(3m)^3\gamma_\pm^5 = 108m^5\gamma_\pm^5 \quad (35)$$

where $a_w \simeq 1$ since the solution is dilute and $m = (1/2)(3.88 \times 10^{-6}) = 1.94 \times 10^{-6}$ mol kg^{-1}. Under the assumption of an arbitrary ion size of 5.0 Å for this system, the Debye–Hückel equation yields $\gamma_\pm = 0.963$. Then, $\ln K_s = -61.3 \pm 8.1$, the standard Gibbs energy of solution is 151.9 ± 20 kJ mol^{-1}, and $\Delta G^\circ_{f,298.15}(Eu_2(CO_3)_3{\cdot}3H_2O(s)) = 2(-576.2) + 3(-527.84) + 3(-237.19) - 151.9 = -3599.4 \pm 30$ kJ mol^{-1}. Also $\Delta S^\circ_{f,298.15}(Eu_2(CO_3)_3{\cdot}3H_2O(s)) = -1344.9 \pm 100$ J K^{-1} mol^{-1} and $S^\circ_{298.15}(Eu_2(CO_3)_3{\cdot}3H_2O(s)) = -1344.9 + 2(77.81) + 3(5.74) + 6(205.04) + 3(130.57) = 449.9 \pm 100$ J K^{-1} mol^{-1}. The average value seems to be somewhat high, so some of the input data may have larger errors than estimated here.

7. Europium(III) Sulfates

Long and Degraff[320] measured the heat capacities of $Eu_2(SO_4)_3{\cdot}8H_2O(c)$ from 62.83 to 295.23 K. These have been analyzed[295] to yield an entropy of 672.0 J K^{-1} mol^{-1}; it is probably uncertain by several J K^{-1} mol^{-1} owing to the long extrapolation below 63 K. Interpolation of solubility curves for several $RE_2(SO_4)_3$ gives about 0.038 mol kg^{-1} for the solubility of the Eu salt at 298.15 ± 0.02 K.[149] This is in rough agreement with linear interpolation of Jackson and Rienäcker's data at 293 and 313 K.[321] Jackson and Rienäcker incorrectly used the temperature dependence of the log of solubility and not of the solubility product in calculating their ΔH. Unfortunately, there is no available activity coefficient data to allow free energies of solution to be calculated. Also, because of extensive ionic association, it is difficult to reliably estimate its activity coefficients.

A rough calculation of the solubility product using 0.038 mol kg^{-1} for the solubility[149] and the Debye–Hückel equation with an arbitrary ion size of 5 Å[248] gives $\ln K_s = -23.6 \pm 5$ and a standard Gibbs energy of solution of 58.4 ± 12 kJ mol^{-1}. Then, $\Delta G^\circ_{f,298.15}(Eu_2(SO_4)_3{\cdot}8H_2O(s)) = 2(-576.2) + 3(-744.46) + 8(-237.19) - 58.4 = -5341.7 \pm 17$ kJ mol^{-1}. The entropy of formation is $\Delta S^\circ_{f,298.15}(Eu_2(SO_4)_3{\cdot}8H_2O(s)) = 672.0 - 2(77.81) - 3(32.05) - 8(130.57) - 10(205.04) = -2674.7 \pm 5.0$ J K^{-1} mol^{-1}, and $\Delta H^\circ_{f,298.15}(Eu_2(SO_4)_3{\cdot}8H_2O(s)) = -6139.2 \pm 19$ kJ mol^{-1}. It is possible that the errors for ΔG and ΔH are larger than estimated owing to the limited solubility data.

Differential scanning microcalorimetry was used to determine heat capacities above room temperature for $Eu_2(SO_4)_3{\cdot}8H_2O$, $Eu_2(SO_4)_3{\cdot}2H_2O$, $Eu_2(SO_4)_3$, and several $K_2SO_4{\cdot}Eu_2(SO_4)_3$ double salts.[322] These results are not analyzed here since we are interested in 298 K data and because these types of measurements have fairly large uncertainties.

8. Europium(II) Sulfate

Solubility data have also been reported for aqueous $EuSO_4$.[150,272,323-325] Its solubility is affected by the presence of other ions and by changes in pH, so only solubilities in pure water were considered. Three values in water at 298.15 K range from 3.8×10^{-5} to 1.08×10^{-4} mol L^{-1}.[150,324,325] Averaging these values on the log scale gives $(6.7 \pm 4.6) \times 10^{-5}$ mol L^{-1}. Anhydrous $EuSO_4$ is the solid phase precipitating from these solutions,[323,326] so the solubility product is given by

$$K_s = a_c a_a = m^2\gamma_\pm^2 \quad (36)$$

No activity coefficient data are available for $EuSO_4$ solutions, but all divalent metal sulfates have very similar activity coefficients. For example, at $(6.7 \pm 4.6) \times 10^{-5}$ mol kg^{-1}, $MgSO_4$[327] and $MnSO_4$[328] data yield $\gamma_\pm = 0.908 \pm 0.016$. This $\gamma_\pm$ value yields $\ln K_s = -19.4 \pm 1.1$ and $\Delta G^\circ_{f,298.15}(EuSO_4(s)) = -1335.1 \pm 7.3$ kJ mol^{-1}. Koz'min et al.[150] measured their solubilities at three temperatures, and their data yield an approximate enthalpy of solution of 33.7 ± 5.0 kJ mol^{-1}. Then, $\Delta H^\circ_{f,298.15}(EuSO_4(s)) = -527.7 - 909.60 - 33.7 = -1471.0 \pm 9.1$ kJ mol^{-1}, $\Delta S^\circ_{f,298.15}(EuSO_4(s)) = -455.8 \pm 54$ J K^{-1} mol^{-1}, and $S^\circ_{298.15}(EuSO_4(s)) = -455.8 + 77.81 + 32.05 + 2(205.04) = 64.1 \pm 55$ J K^{-1} mol^{-1}. A value near the upper uncertainty limit would be more realistic, and the enthalpy of solution may have larger uncertainty than estimated.

9. Europium Fluorides

Solubility product determinations for REF_3 in aqueous solution show considerable variation. For example, data for K_s of LaF_3 cited by Burgess and Kijowski[16] range from 6.3×10^{-23} to 1.1×10^{-15} $mol^4\ kg^{-4}$. Unfortunately, EuF_3 is no exception in this regard.[329-334] There is agreement that $EuF_3 \cdot 0.5H_2O$ is the solid phase in equilibrium with the saturated solutions.[16,17b,335a] Thus, the solubility equilibrium is

$$EuF_3 \cdot 0.5H_2O = Eu^{3+}(aq) + 3F^-(aq) + 0.5\ H_2O(l) \qquad (37)$$

for which

$$K_s = a_c a_a^3 a_w^{0.5} = 27m^4\gamma_\pm^4 a_w^{0.5} \qquad (38)$$

Since the solubility is fairly low, $a_w \simeq 1$ for K_s calculations. K_s values show large variations with pH and have a minimum value around pH 4 or 5;[329-334] the solubility increase at lower pH values is probably due to formation of molecular HF. Solubility values in 0.1 mol L^{-1} $NaNO_3$ seem concordant with the aqueous solution values.[336]

For $EuF_3 \cdot 0.5H_2O$ at 298.15 K, Vasil'ev and Kozlovskii's analysis[333] of published data[329] gave ln Q_s = −50.4, Lingane's potentiometric titration[330] gave ln Q_s = −38.36 ± 0.09, Koroleva et al.[332] obtained −35.41 ± 0.23, and Frausto Da Dilva and Queimado[336] give −39.6 to −42.6. Menon[334] obtained −34.75 ± 0.11 radiometrically, −28.94 ± 0.09 potentiometrically, and −29.83 ± 0.05 conductometrically, but considered the radiometric value to be more reliable. Here Q_s is the apparent solubility constant. The recommended solubility value is the average of the four results in best agreement: ln Q_s = −37.0 ± 2.3. Correction to infinite dilution by means of the Debye–Hückel limiting law gives −37.2 ± 2.3. Discrepant values of Vasil'ev and Kozlovskii[333] and Menon's[334] conductometric and potentiometric data were rejected.

The recommended solubility data yield a standard Gibbs energy of solution of 92.3 ± 5.8 kJ mol^{-1} and $\Delta G^\circ_{f,298.15}(EuF_3 \cdot 0.5H_2O(s)) = -576.2 + 3(-281.74) + {}^1/_2(-237.19) - 92.3 = -1632.4 \pm 12$ kJ mol^{-1}. Menon[334] determined the solubility of $EuF_3 \cdot 0.5H_2O$ at five temperatures and used these results to estimate an enthalpy of solution of 39.8 ± 4.0 kJ mol^{-1}, which indicates an increasing solubility with increasing temperature. Thus, $\Delta H^\circ_{f,298.15}(EuF_3 \cdot 0.5H_2O(s)) = -604.8 + 3(-335.35) + {}^1/_2(-285.83) - 39.8 = -1793.6 \pm 10$ kJ mol^{-1}. Then, $\Delta S^\circ_{f,298.15} = -540.8 \pm 54$ J K^{-1} mol^{-1} and $S^\circ_{298.15}(EuF_3 \cdot 0.5H_2O(s)) = -540.8 + 77.81 + {}^3/_2(202.69) + {}^1/_2(130.57) + {}^1/_4(205.04) = -42.4 \pm 55$ J K^{-1} mol^{-1}. Obviously this value should be positive; the negative mean value is a reflection of the large imprecision of the input data and suggests that the enthalpy and thus the entropy of solution have much large errors than estimated by Menon.

Itoh et al.[337] recently reported solubilities from dissolution of powdered EuF_3 and other REF_3 using fluoride ion sensitive electrodes. Their solubilities seem to be somewhat low; ln K_s = −43.4 for EuF_3. They investigated LaF_3 in more detail. Single crystals of LaF_3 did not reach saturation after 3 months, although the powdered crystals did so much more rapidly. Surface effects and difficulty in hydrating REF_3 probably caused these differences. Their solubility values thus may possibly refer to anhydrous or partially hydrated REF_3.

Storozhenko et al.[335a] studied the enthalpy of solution of EuF_3 and $EuF_3 \cdot 0.44H_2O$ in a mixture of HCl and boric acid. These data yield an enthalpy of hydration of 3.9 ± 0.3 kJ mol^{-1}, which we adjust to 4.4 ± 0.4 kJ mol^{-1} for $EuF_3 \cdot 0.5H_2O$. Then, $\Delta H^\circ_{f,298.15}(EuF_3(s)) = -1793.6 - {}^1/_2(-285.83) - 4.4 = -1655.1 \pm 11$ kJ mol^{-1}. As for $EuF_3 \cdot 0.5H_2O$, the enthalpy of formation could have larger errors than estimated here. Kim and Johnson[338] estimated that the value of $\Delta H^\circ_{f,298.15}$ should be ca. −1610 kJ mol^{-1} for EuF_3, based on correlations with experimental values for other REF_3.

In 1976 Storozhenko et al.[335a] reported enthalpies of reaction of Eu metal with oxygen-free aqueous HF and with aqueous HF containing small amounts of H_2O_2. They used their results to calculate $\Delta H^\circ_{f,298.15}(EuF_3 \cdot 0.52H_2O(s)) = -1701.8 \pm 4.6$ kJ mol^{-1}, $\Delta H^\circ_{f,298.15}(EuF_3(s)) = -1557.7 \pm 4.6$ kJ mol^{-1}, and $\Delta H^\circ_{f,298.15}(EuF_2 \cdot 0.76H_2O(s)) = -1393.8 \pm 2.2$ kJ mol^{-1}. Considering the difficulties in obtaining pure metallic Eu and being uncertain about their choice of data for F_2 and HF(aq), we consider these results to be fairly uncertain. However, use of the 1976 values would at least give a positive entropy for $EuF_3 \cdot 0.5H_2O$.

Zmbov and Margrave[335b] used high-temperature gas-phase mass spectrometry and enthalpy of sublimation data to calculate $\Delta H^\circ_{f,298.15}(EuF_3(s)) = -1720 \pm 42$ kJ mol^{-1}.

Combining Zmbov and Margrave's[335b] enthalpy of formation of EuF_2(g) with Petzel and Greis's[335c] third-law enthalpy of sublimation yields $\Delta H^\circ_{f,298.15}(EuF_2(s)) = -1081 \pm 50$ kJ mol^{-1}.

In view of the large variation of the enthalpies of formation of EuF_3 and $EuF_3 \cdot 0.5H_2O$ and the large uncertainty for EuF_2, we do not recommend enthalpy data for any of the europium fluorides.

High-temperature relative enthalpies are also available for EuF_3 up to 1252 K from drop calorimetry for both orthogonal and hexagonal forms in their corresponding stability regions.[339] Greis and Haschke[17b] estimated that $S^\circ_{298.15}(EuF_3(c)) \simeq 115.1$ J K^{-1} mol^{-1}.

Table I summarizes thermodynamic data for solid Eu compounds.

G. Thermodynamic Data for Aqueous Species

This section is concerned with thermodynamic data for aqueous complexes at 298.15 K. Three separate problems need to be dealt with when analyzing aqueous solution thermodynamic and chemical information:

(1) Most studies of stability constants are done at constant ionic strength, and only a few were done with ionic strength varied to allow extrapolation to infinite dilution. However, significant media effects are sometimes observed. For example, Khopkar and Narayanankutty[216] measured the formation constants of $EuCl^{2+}$ and $Eu(NO_3)^{2+}$ at an ionic strength of 1, with $LiClO_4$, $HClO_4$, $NaClO_4$, and NH_4ClO_4 being used to adjust the ionic strength. Stability constants for $Eu(NO_3)^{2+}$ showed 10% variation with media, but $EuCl^{2+}$ constants varied by more than a factor of 2. Similarly, Choppin et al.[261] obtained 25% variations of K of $Eu(NO_3)^{2+}$ for HNO_3, $LiNO_3$, NH_4NO_3, and $NaNO_3$ solutions. These differences are clearly due to changes in $\gamma_\pm$ and a_w due to varying the "inert cation". This media effect may make derived stability constants uncertain by at least 10–30%. These differences can, in principle, be eliminated by extrapolation of data to infinite dilution. Unfortunately, since many studies are at a single

TABLE I Thermodynamic Data for Eu(c) and Solid Eu Compounds at 298.15 K

substance	$\Delta G^\circ_{f,298.15}$, kJ mol^{-1}	$\Delta H^\circ_{f,298.15}$, kJ mol^{-1}	$S^\circ_{298.15}$, J K^{-1} mol^{-1}
Eu(c)	0	0	77.81[a]
EuS(s)	-443.1 ± 7.9	-447.3 ± 7.2	95.77
Eu_2O_3 (monoclinic)	-1555.7 ± 3.7	-1650.8 ± 2.6	144.1 ± 3.7
Eu_2O_3 (cubic)	-1564.9 ± 4.7	-1661.9 ± 3.8	137.8 ± 2.3
EuO(s)	-563.4 ± 5.7	-592.2 ± 5.5	83.64
Eu_3O_4(s)	-2141.0 ± 14	-2270.5 ± 12	209.2 ± 8.8
$EuCl_3$(s)	-855.8 ± 4.3	-935.8 ± 4.0	144.1
$EuCl_3{\cdot}6H_2O$(c)	-2363.4 ± 7.8	-2784.5 ± 4.3	409.1 ± 3
$EuCl_2$(s)	-774.8 ± 7.9	-822.5 ± 6.7	141.0 ± 3.3
EuOCl(s)	-854.4 ± 8.4	-911.1 ± 7.3	101.8 ± 3.7
$EuBr_3$(c)	-716 ± 33	-753 ± 33	182.8
$Eu(OH)_3$(c)	-1198.9 ± 7.9	-1336.5 ± 8.3	119.9
$Eu(NO_3)_3{\cdot}6H_2O$(c)	-2322.8 ± 5.4	-2955.7 ± 5.0	563.8 ± 21
$Eu(IO_3)_3{\cdot}2H_2O$(c)	-1499.7 ± 5.7	-1861.8 ± 8.0	426.6 ± 27
$Eu(OH)_{2.5}Cl_{0.5}$(s)	-1161.4 ± 7.8		
$Eu(OH)_2Cl$(s)	-1129.9 ± 7.8		
$Eu(BrO_3)_3{\cdot}9H_2O$(c)		-3494.9 ± 7.8	
$Eu_2(CO_3)_3$(s)		-3092.5 ± 11	
$Eu_2(CO_3)_3{\cdot}3H_2O$(s)	-3599.4 ± 30	-4000.4 ± 11	449.9 ± 100
$Eu_2(SO_4)_3{\cdot}8H_2O$(s)	-5341.7 ± 17	-6139.2 ± 19	672.0
$EuSO_4$(s)	-1335.1 ± 7.3	-1471.0 ± 9.1[b]	64.1 ± 55[b]
$EuF_3{\cdot}0.5H_2O$(s)	-1632.4 ± 12		

[a] Entropy values without assigned error limits are for systems with heat capacity data to low temperature but for which the authors assigned no uncertainty limit to the entropies. [b] Based in part on enthalpy of solution estimated from the temperature dependence of the solubility; the actual errors for ΔH_f° and S° could possibly be larger.

ionic strength, this extrapolation cannot be done for them.

(2) At some anion to cation concentration ratios, more than one complex may be present. It has been found that neglecting a second complex can cause the calculated first formation constant to be in error by as much as 50%.[213,248] Consequently, preference will be given to those investigations that considered higher order complexes or that controlled the anion to cation ratio so as to make higher order complexes negligible.

(3) Some methods, such as liquid–liquid extraction, are sometimes used without proper understanding of the extraction mechanisms. For example, formation constants for $Eu(IO_3)^{2+}$ measured by Choppin and Bertha[235] and Roulet and Chenaux[234] using this method show opposite trends with temperature. Direct enthalpy of complex formation measurements[237] agree with Choppin and Bertha.[235] Conflicting trends in stability constants will be reconciled whenever direct calorimetric results are available.

1. Hydrolyzed Europium Species

A large number of studies have been made for the first hydrolysis of Eu^{3+} by water,[194-201,243] eq 10, for which

$$Q_{h1} = [Eu(OH)^{2+}][H^+]/[Eu^{3+}] \qquad (39)$$

Here $a_w \simeq 1$ for dilute solutions. Whenever data have been extrapolated to infinite dilution (or corrected for activity coefficients), the Q values will be changed to K in this report. Two of these studies[195,196] are considerably discrepant from all the others and so were not considered further. Five of the other six studies[194,197-199,243] are in good agreement and fall in the range −18.49 to −20.03 for $\ln Q_{h1}$. There is no trend with ionic strength within the scatter of the data. The recommended value is their average of $\ln K_{h1} = -19.00 \pm 0.62$. Then, the standard Gibbs energy change for eq 39 is 47.1 ± 1.6 kJ mol^{-1}, and $\Delta G^\circ_{f,298.15}(Eu(OH)^{2+}(aq)) = 47.1 - 576.2 - 237.19 = -766.3 \pm 6.9$ kJ mol^{-1}. Caceci and Choppin's value[200] also was not included in the average since their Q_{h1} appears to be slightly too large by about a factor of 10.

If a second hydrolysis step also occurs, then

$$Eu^{3+}(aq) + 2H_2O(l) = Eu(OH)_2^+(aq) + 2H^+(aq) \qquad (40)$$

for which

$$\beta_{h2} = [Eu(OH)_2^+][H^+]^2/[Eu^{3+}] \qquad (41)$$

assuming, again, that solutions are sufficiently dilute so $a_w \simeq 1$. β_{h2} is defined as the cumulative hydrolysis constant; $\beta_{h2} = Q_{h1}Q_{h2}$. Nair et al.[199] reported that $\ln \beta_{h2} = -35.57 \pm 0.09$ in 1 mol L^{-1} $NaClO_4$, and Bilal and Koss[201] got $\ln \beta_{h2} = -32.87 \pm 0.22$ in 1 mol L^{-1} NaCl. The average of −34.2 ± 1.4 is recommended for $\ln \beta_{h2}$. No attempt was made to extrapolate this value to infinite dilution owing to a factor of 15 difference in these β_{h2} values, and the results were assumed uncertain by a factor of 50. Then, the free energy change for reaction 40 is 84.8 ± 9.7 kJ mol^{-1}, and $\Delta G^\circ_{f,298.15}(Eu(OH)_2^+(aq)) = 84.8 - 576.2 - 2(237.19) = -965.8 \pm 16$ kJ mol^{-1}. This β_{h2} value is in fair agreement with the estimate of Baes and Mesmer.[187]

2. Europium Halate Complexes

Roulet and Chenaux[234] measured the $Eu(ClO_3)^{2+}$, $Eu(BrO_3)^{2+}$, and $Eu(IO_3)^{2+}$ formation constants in 0.1 mol L^{-1} $NaClO_4$, from 275 to 313 K, using liquid extraction. Choppin and Bertha[235] did similar measurements for $Eu(IO_3)^{2+}$, also in 0.1 mol L^{-1} $NaClO_4$. Not only were Choppin and Bertha's formation constant[235] for $Eu(IO_3)^{2+}$ much larger than Roulet and Chenaux'-s,[234] but also their K's increased with increasing temperature, whereas Roulet and Chenaux's decreased. Direct enthalpy of reaction measurements[237] confirm Choppin and Bertha's results for this salt, so Roulet and Chenaux's $Eu(IO_3)^{2+}$ data were rejected.

The sign of the enthalpy of complex formation suggests that $Eu(IO_3)^{2+}$ aqueous complexes are predominantly inner sphere. From the Debye–Hückel activity coefficient equation with an appropriate ion size for this complex,[235] the formation constant is 68 ± 11. Thus the standard Gibbs energy of reaction is $-RT \ln K = -10.5 \pm 0.4$ kJ mol^{-1}. Then, $\Delta G^\circ_{f,298.15}(Eu(IO_3)^{2+}(aq)) = -10.5 + (-576.2) + (-128.16) = -714.8 \pm 7.8$ kJ mol^{-1}. Choppin and Bertha's[235] data for the change in stability constant with temperature gave an enthalpy of reaction of 11.1 ± 1.8 kJ mol^{-1}, which agrees with their direct calorimetric result of 11.3 ± 0.8 kJ mol^{-1}.[237] Both values are for 0.1 mol L^{-1}. We assume they approximate the infinite dilution value, so their mean of 11.2 ± 2.5 kJ mol^{-1} is accepted. The error limit has been increased to account for lack of an enthalpy extrapolation. Then, $\Delta H^\circ_{f,298.15}(Eu(IO_3)^{2+}(aq)) = 11.2 - 604.8 - 221.3 = -814.9 \pm 8.7$ kJ mol^{-1}, $\Delta S^\circ_{f,298.15}(Eu(IO_3)^{2+}(aq)) = -335.8 \pm 35$ J K^{-1} mol^{-1}, and $S^\circ_{298.15}\,(Eu(IO_3)^{2+}(aq)) = -335.8 + 77.81 + {}^1/_2(116.14) + {}^3/_2(205.04) - 2(65.285) = -22.9 \pm 36$ J K^{-1} mol^{-1}.

Morris and Tharwat[236] and Roulet and Chenaux[234] studied the formation constant for $Eu(BrO_3)^{2+}$ at ionic strengths of 1.0 and 0.1 mol L^{-1}, respectively, as a function of temperature, and both found that the stability constant decreased with increasing temperature. Roulet and Chenaux[234] reported an enthalpy of formation of −13.8 ± 3.8 kJ mol^{-1}, Morris and Tharwat[236] reported −12 kJ mol^{-1}, but Choppin and Ensor[237] found −2.5 ± 1.3 kJ mol^{-1} by direct calorimetry. Owing to disagreement between direct calorimetry and the temperature dependence of stability constants, these enthalpy data will not be analyzed further.

Stability constants for $Eu(BrO_3)^{2+}$ from these two studies differ by a factor of three, with the values of Roulet and Chenaux[234] being larger. Some of this difference arises because Morris and Tharwat[236] allowed for $Eu(BrO_3)_2^+$ formation whereas Roulet and Chenaux[234] did not. Insufficient data were presented to allow recalculations on a consistent basis. The $RE(BrO_3)_3{\cdot}9H_2O$ crystals[158] contain only water surrounding the RE^{3+}, so complexes in solution are assumed to be outer sphere. Thus the ion size was chosen to be the sum of the anion + cation + water radii, and activity coefficients were calculated with the extended Debye–Hückel equation recommended by Choppin and Bertha.[235] Then, $\ln K_1 = 2.95 \pm 0.40$, the standard Gibbs energy of complex formation is $-RT \ln K_1 = -7.32 \pm 0.99$, and $\Delta G^\circ_{f,298.15}(Eu(BrO_3)^{2+}(aq)) = -7.32 - 576.2 + 1.5 = -582.0 \pm 7.3$ kJ mol^{-1}. No attempt was made to analyze stability constant data for $Eu(BrO_3)_2^+$ since it has a reported temperature dependence opposite $Eu(BrO_3)^{2+}$, which seems unlikely.

Morris and Tharwat[236] found that the $Eu(ClO_3)^{2+}$ stability constants were independent of temperature, whereas Roulet and Chenaux[234] found they decreased by a factor of four when the temperature was increased from 275 to 313 K. Heats of complex formation from these two studies are 0 and −21 ± 8 kJ mol^{-1}, whereas direct calorimetry gave −6.3 ± 1.7 kJ mol^{-1}.[237] Additional data will be required before thermodynamic values are recommended for this system.

3. Europium Phosphite and Phosphate Complexes

Barnes[241a] measured the stability constant for $Eu(H_2PO_2)^{2+}$ at 298 K using absorption spectra. Measurements were for ionic strengths of 0.042–0.065 mol L^{-1}, and extrapolation to infinite dilution by Davies' equation gave $K_1 = 186 \pm 5$ mol^{-1} L. Although enthalpy data are available for the $H_2PO_2^-$ ion,[279] we could find no free energy of formation so we cannot utilize these results. $Eu(H_2PO_2)_3{\cdot}H_2O$ has a layered structure with Eu ions bound through hypophosphite ions,[340] and it is conceivable that polymeric structures may also form in aqueous solution.

Borisov et al.[240] reported stability constants at $I = 0.2$ mol L^{-1} for $RE(H_2PO_4)^{2+}$, where RE = Ce, Pm, and Y. Since only three REE were studied and Y varies in its "position" in the RE series with anion, no attempt was made to estimate a value for Eu.

4. Europium Nitrate Complexes

The stability constant of $Eu(NO_3)^{2+}$ has been reported in numerous studies.[207,210,212,215,216,228,253,254,260,261] A wide variety of techniques have been used, including spectroscopic methods, liquid extraction, and ion exchange. Most of these studies are in reasonable agreement. Three studies were made of the temperature dependence of the equilibrium,[207,253,261] and the reaction was exothermic (but the ΔH values differ by a factor of 4). Moulin et al.'s stability constants[207] for $RE(NO_3)^{2+}$ are about a factor of 10 larger than values from the other studies and were rejected. Attempts have been made to separate the stability constants into inner- and outer-sphere components by spectroscopic techniques.[228,254] This distinction will not be considered further since we desire the total thermodynamic formation constants. Formation constants from luminescence spectra are about a factor of 2 lower than expected for that ionic strength and may just represent the inner-sphere fraction rather than the total amount of complex formation.[210]

Most of the $Eu(NO_3)^{2+}$ stability studies were measured at 298 K but some were at 295 or 303 K. The temperature dependence of K_1 is small enough that the variable temperature will be neglected. The more reliable data[212,215,216,253,260,261] were plotted as $\ln Q_1$ vs. the square root of ionic strength, where Q_1 refers to the reaction

$$Eu^{3+}(aq) + NO_3^-(aq) = Eu(NO_3)^{2+}(aq) \qquad (42)$$

Extrapolation to infinite dilution gave $\ln K_1 = 1.5 \pm 0.3$. Thus, the free energy change for reaction 42 is −3.72 ± 0.74 kJ mol^{-1}, and $\Delta G^\circ_{f,298.15}(Eu(NO_3)^{2+}(aq)) = -3.72 - 576.2 - 111.34 = -691.3 \pm 7.0$ kJ mol^{-1}. Data for the second association step are too scattered and the enthalpy of reaction for eq 42 is too media dependent to allow values to be recommended for them at this time.

5. Europium Chloride Complexes

A number of studies have been made of the formation constant of $EuCl^{2+}$.[206–208a,209,210,212–216] Two studies have been made of the enthalpy change from temperature dependences of $\ln K_1$ and both indicate an exothermic complex formation reaction.[206,207] Most studies were made at 298 K but range from 293 to 303 K. This small temperature difference will be neglected when stability constants are recalculated. The ionic strength was varied in these studies between 0.87 and 4.0 mol L^{-1}, but most runs were done at unit ionic strength. Using a plot of $\ln Q_1$ vs. square root of ionic strength gives a limiting value equal to $\ln K_1$.

The intercept for the $EuCl^{2+}$ formation constant is $\ln K_1 = 0.9 \pm 0.9$, the free energy of complex formation is −2.2 ± 2.2 kJ mol^{-1}, and $\Delta G^\circ_{f,298.15}(EuCl^{2+}(aq)) = -576.2 - 131.29 - 2.2 = -709.7 \pm 7.5$ mol^{-1}. Some of the large scatter in $\ln K_1$ may come from the variation in K_1 with different ionic media at a fixed ionic strength.[213]

Several studies also reported values of Q_2 for

$$EuCl^{2+}(aq) + Cl^-(aq) = EuCl_2^+(aq) \qquad (43)$$

Values are $Q_2 = 0.19$ at $I = 0.87$ mol L^{-1},[206] $Q_2 = 0.15$–0.66 at $I = 1.0$ mol L^{-1},[206,213,215,216] $Q_2 = 0.41 \pm 0.04$ at $I = 3.0$ mol L^{-1},[209] and $Q_2 = 0.19$ at $I = 4.0$ mol L^{-1}.[214] There is no obvious trend with ionic strength, so the average of $\ln K_2 = -1.03 \pm 0.8$ was used. This given error limit is 1.5 times the actual value to account for the inability to extrapolate to infinite dilution. Then, for reaction 43, the standard Gibbs energy change is $-RT \ln K_2 = 2.55 \pm 1.88$ kJ mol^{-1}, and $\Delta G^\circ_{f,298.15}(EuCl_2^+(aq)) = 2.55 - 709.7 - 131.29 = -838.5 \pm 9.4$ kJ mol^{-1}.

6. Europium Iodide Complex

For EuI^{2+}, Choppin and Unrein[206] reported that $Q_1 = 0.49 \pm 0.06$, whereas Moulin et al.[207] reported $Q_1 = 1.7$, with both studies at $I = 1.0$ mol L^{-1} and 298 K. Owing to the poor agreement, no values are recommended for that system. However, Moulin et al.'s ΔH and/or ΔG data for $EuCl^{2+}$ and $Eu(NO_3)^{2+}$ by the same method were in error so their EuI^{2+} data may be also.

7. Europium Bromide Complexes

Three studies reported data for $EuBr^{2+}(aq)$,[206,207,209] and two of them also reported values for $EuBr_2^+(aq)$.[206,209] Moulin et al.'s Q_1 values[207] at 298 K are about three times larger than Q_1 values from the other two studies. Our calculations are based on the two data sets in good agreement.[206,209] Choppin and Unrein[206] reported $Q_1 = 0.58 \pm 0.09$ and $Q_2 = 0.35 \pm 0.20$ at 1.0 mol L^{-1}, and Fukasawa et al.[209] recommended $Q_1 = 0.38 \pm 0.02$ and $Q_2 = 0.59 \pm 0.05$ at $I = 3.0$ mol L^{-1}. Kozachenko et al.[341] reported stability constants for $PrBr^{2+}$, $SmBr^{2+}$, $HoBr^{2+}$, and $ErBr^{2+}$ at $I = 3.0$ mol L^{-1} and 298 K. Their data indicate that Q_1 should be about 0.6–0.7 for $EuBr^{2+}$ at this ionic strength, which further supports our choice. These data are too sparse to allow an accurate extrapolation to infinite dilution, so we assumed a concentration dependence similar to the chloride complexes. This yields $\ln K_1 \simeq 0.6 \pm 0.5$, a standard Gibbs energy of complex formation of $-RT \ln K_1 = -1.5 \pm 1.2$ kJ mol^{-1}, and $\Delta G^\circ_{f,298.15}(EuBr^{2+}(aq)) = -1.5 - 576.2 - 104.04 = -681.7 \pm 6.7$ kJ mol^{-1}. Also, $\ln K_2 \simeq -0.8 \pm 0.5$, so ΔG° for complex formation is $-RT \ln K_2 = 2.0 \pm 1.3$ kJ mol^{-1} and $\Delta G^\circ_{f,298.15}(EuBr_2^+(aq)) = 2.0 - 681.7 - 104.04 = -783.8 \pm 8.1$ kJ mol^{-1}.

8. Europium Fluoride Complexes

It was earlier noted that, whereas the hydrated $RECl_3$, $REBr_3$, and REI_3 salts are highly soluble in aqueous solution, the REF_3 salts have very low solubilities. Their aqueous complexes also exhibit significant differences since REF^{2+} complexes have formation constants about 10^3 larger than for the corresponding Cl^-, Br^-, and I^- salts.

A number of studies have been reported of the first stability constant for EuF^{2+} formation in aqueous solution.[207,222,223a,b,332,334,342,343] These values are generally in fairly good agreement. Only Aziz and Lyle's data[342] as recalculated by Makarova et al.[343] are somewhat high ($\simeq$50%) and were the only results rejected. The other data were plotted as $\ln Q_1$ vs. $(I)^{1/2}$ and the intercept is $\ln K_1 = 7.70 \pm 0.16$. Thus, the standard Gibbs energy of solution is $-RT \ln K_1 = -19.1 \pm 0.4$ kJ mol^{-1}, and $\Delta G^\circ_{f,298.15}(EuF^{2+}(aq)) = -19.1 - 576.2 - 281.74 = -877.0 \pm 6.2$ kJ mol^{-1}.

Although Moulin et al.'s[207] stability constant at 298 K agreed with others, their enthalpy of complex formation is opposite in sign to the probably more reliable direct calorimetric determination.[222]

Bilal and co-workers[223a,b] also determined the second stability constant for

$$EuF^{2+}(aq) + F^-(aq) = EuF_2^+(aq) \tag{44}$$

at 298 K and $I = 1$ mol L^{-1}. Their results are $Q_2 = 277 \pm 35$ and 264 ± 49 mol^{-1} L. If, as for $EuCl_2^+$, this constant varies little with ionic strength (at least relative to experimental error), then $-RT \ln K_2 = -13.9 \pm 0.4$ kJ mol^{-1}. This uncertainty limit will be increased to 6.0 kJ mol^{-1} to account for the possible error in assuming no change with ionic strength. Thus, $\Delta G^\circ_{f,298.15}(EuF_2^+(aq)) = -13.9 - 877.0 - 281.74 = -1172.7 \pm 13$ kJ mol^{-1}.

Bilal and Koss[224] also reported a formation constant for $Eu(OH)_2F(aq)$ at $I = 1.0$ mol L^{-1} and 298 K. Since their solutions also contained $H_2PO_4^-$ and HPO_4^{2-}, which could also be complexing with the Eu^{3+}, we did not analyze these data.

9. Europium Carbonate Complexes

Eu^{3+} reacts with CO_3^{2-} in basic aqueous solution by the reactions

$$Eu^{3+}(aq) + CO_3^{2-}(aq) = Eu(CO_3)^+(aq) \tag{45}$$

$$Eu(CO_3)^+(aq) + CO_3^{2-}(aq) = Eu(CO_3)_2^-(aq) \tag{46}$$

$$Eu(CO_3)_2^-(aq) + CO_3^{2-}(aq) = Eu(CO_3)_3^{3-}(aq) \tag{47}$$

$$Eu(CO_3)_3^{3-}(aq) + CO_3^{2-}(aq) = Eu(CO_3)_4^{5-}(aq) \tag{48}$$

Lundqvist[243] used liquid extraction to determine $\ln Q_1 = 13.65 \pm 0.12$ and $\ln Q_2 = 11.03 \pm 0.18$, for $Eu(CO_3)_n^{3-2n}$ at 298 K and $I = 1$ mol L^{-1}. He also cited a value of β_4 at $I = 2.5$ mol L^{-1} from a thesis by Dumonceau.[244] Here β_4 is the cumulative formation constant; i.e., $\beta_4 = Q_1Q_2Q_3Q_4$. However, this value of β_4 seems too small when compared to Q_1, Q_2, and Q_3 for various REE,[243] so the β_4 data were not analyzed. It is difficult to correct the Q_1 and Q_2 values to infinite dilution with any degree of confidence. However, data for $Eu(SO_4)^+$ and $Eu(SO_4)_2^-$, which have the same charges as $Eu(CO_3)^+$ and $Eu(CO_3)_2^-$, respectively, indicate that extrapolation to infinite dilution from $I = 1$ mol L^{-1} increases Q_1 by roughly a factor of 165 and Q_2 by about a factor of 4. We will use these approximations for our calculations with an assumed 30% uncertainty. Then, $-RT \ln K_1 = -46.5 \pm 0.9$ kJ mol^{-1}, $\Delta G^\circ_{f,298.15}(Eu(CO_3)^+(aq)) = -46.5 - 576.2 - 527.8 = -1150.5 \pm 7.2$ kJ mol^{-1}, $-RT \ln K_2 = -30.8 \pm 1.1$ kJ mol^{-1}, and $\Delta G^\circ_{f,298.15}(Eu(CO_3)_2^-(aq)) = -30.8 - 1150.5 - 527.9 = -1709.2 \pm 9.0$ kJ mol^{-1}.

10. Europium Sulfate Complexes

The stability constant for

$$Eu^{3+}(aq) + SO_4^{2-}(aq) = Eu(SO_4)^+(aq) \tag{49}$$

has been studied numerous times and with several different methods.[155,214,215,241a,245–249,251] Bansal et al.[215] also list several unpublished values by other workers. Techniques used include spectroscopy, ion exchange, liquid–liquid extraction, conductance measurements, and the change in solubility of $Eu(IO_3)_3$ with concentration of added sulfate. Plotting $\ln Q_1$ vs. $(I)^{1/2}$ yields $\ln K_1 = 8.27 \pm 0.98$. Then, the standard Gibbs energy of reaction is $-RT \ln K_1 = -20.5 \pm 2.4$ kJ mol^{-1} and $\Delta G^\circ_{f,298.15}(Eu(SO_4)^+(aq)) = -20.5 - 576.2 - 744.46 = -1341.2 \pm 5.5$ kJ mol^{-1}.

Several values have also been reported for the second association reaction[214,215,246,247,248]

$$Eu(SO_4)^+(aq) + SO_4^{2-}(aq) = Eu(SO_4)_2^-(aq) \tag{50}$$

Apparent stability constants for the formation of the second complex are reasonably concordant and yield $\ln K_2 = 3.61 \pm 0.49$, a standard reaction Gibbs energy of -8.95 ± 1.2 kJ mol^{-1}, and $\Delta G^\circ_{f,298.15}(Eu(SO_4)_2^-(aq)) =$

TABLE II Thermodynamic Data for Eu Aqueous Species at 298.15 K

aqueous species	$\Delta G^\circ_{f,298.15}$, kJ mol^{-1}	$\Delta H^a_{f,295.15}$ kJ mol^{-1}	$S^\circ_{298.15}$, J K^{-1} mol^{-1}
Eu^{3+}	-576.2 ± 5.3	-604.8 ± 4.2	-214.0 ± 3.1
Eu^{2+}	-542.5 ± 6.8	-527.7 ± 7.6	-3.1 ± 11
$Eu(OH)^{2+}$	-766.3 ± 6.9		
$Eu(OH)_2{}^+$	-965.8 ± 16		
$Eu(IO_3)^{2+}$	-714.8 ± 7.8	-814.9 ± 8.7	-22.9 ± 36
$Eu(BrO_3)^{2+}$	-582.0 ± 7.3		
$Eu(NO_3)^{2+}$	-691.3 ± 7.0		
$EuCl^{2+}$	-709.7 ± 7.5		
$EuCl_2{}^+$	-838.5 ± 9.4		
$EuBr^{2+}$	-681.7 ± 6.7		
$EuBr_2{}^+$	-783.8 ± 8.1		
EuF^{2+}	-877.0 ± 6.2		
$EuF_2{}^+$	-1172.7 ± 13		
$Eu(CO_3)^+$	-1150.5 ± 7.2		
$Eu(CO_3)_2{}^-$	-1709.2 ± 9.0		
$Eu(SO_4)^+$	-1341.2 ± 5.5	-1497.4 ± 6.0	-69.4 ± 20
$Eu(SO_4)_2{}^-$	-2094.6 ± 6.9	-2398.8 ± 8.2	6.9 ± 30

$-8.95 - 1341.2 - 744.5 = -2094.6 \pm 6.9$ kJ mol^{-1}. Bilal and Koss[249] claimed that $Eu(SO_4)_3{}^{3-}$ forms rather than $Eu(SO_4)_2{}^-$. Since the other studies[214,215,247,248] reported $Eu(SO_4)_2{}^-$ instead, no analysis was made for $Eu(SO_4)_3{}^{3-}$.

Five of the above studies also report enthalpies of reaction corresponding to reaction 49.[246-248,250,251] They are in fairly good agreement and show no trend with concentration, so they were averaged to yield the recommended value of 17.0 ± 1.4 kJ mol^{-1}. Thus, $\Delta H^\circ_{f,298.15}(Eu(SO_4)^+(aq)) = 17.0 - 604.8 - 909.60 = -1497.4 \pm 6.0$ kJ mol^{-1}, $\Delta S^\circ_{f,298.15}(Eu(SO_4)^+(aq)) = -524.1 \pm 18.5$ J K^{-1} mol^{-1}, and $S^\circ_{298.15}(Eu(SO_4)^+(aq)) = -524.1 + 77.81 + 32.05 + 2(205.04) - 65.285 = -69.4 \pm 20$ J K^{-1} mol^{-1}.

Two reported values for the enthalpy of reaction 50 are 10.0 kJ mol^{-1} at $I = 2.0$ mol L^{-1} [246] and 6.3 ± 0.4 kJ mol^{-1} in dilute solution.[247] The data are too sparse to determine the dependence on ionic strength, so the average of 8.2 ± 1.9 was accepted. Then, $\Delta H^\circ_{f,298.15}(Eu(SO_4)_2{}^-(aq)) = 8.2 - 1497.4 - 909.60 = -2398.8 \pm 8.2$ kJ mol^{-1}, $\Delta S^\circ_{f,298.15}(Eu(SO_4)_2{}^-(aq)) = -1020.4 \pm 29$ J K^{-1} mol^{-1}, and $S^\circ_{298.15}(Eu(SO_4)_2{}^-(aq)) = -1020.4 + 77.81 + 2(32.05) + 4(205.04) + 65.285 = 6.9 \pm 30$ J K^{-1} mol^{-1}.

Table II summarizes thermodynamic data for these aqueous species.

V. Recommendations

This report is a review of the thermodynamics of Eu, its oxides, sulfides, chlorides, oxychlorides, hydroxides, hydroxychlorides, fluorides, bromides, halates, sulfates, nitrates, carbonates, and a number of related aqueous species. The publication of new thermodynamic data for several of the above systems would be very desirable to improve the thermodynamic data base. Heat capacity data for the solid oxides Eu_2O_3 (especially the cubic form) and Eu_3O_4 are needed to yield more reliable entropy values. Enthalpies of solution of $Eu(OH)_3(s)$ in acid would serve as a check on the Gibbs energy results obtained from solubility data. More extensive heat capacity, solubility, and enthalpy of solution data for $Eu_2(SO_4)_3 \cdot 8H_2O$ and EuF_3 are also needed. In addition, further studies of complex formation for several of the aqueous species as a function of ionic strength and temperature (especially the carbonates) would be desirable. Even more important are additional enthalpies of solution of $EuCl_3(s)$ in dilute HCl, since all of the enthalpies of formation for aqueous species are based on a single determination of this quantity (as described in section IV.D).

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Registry No. Eu, 7440-53-1.

VII. References

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