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A SELECTED THERMODYNAMIC DATABASE FOR REE TO BE USED IN HLNW PERFORMANCE ASSESSMENT EXERCISES

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ABSTRACT

A selected thermodynamic database for the Rare Earth Elements (REE) to be used in the safety assessment of high-level nuclear waste has been compiled. Thermodynamic data for the aqueous species of the REE with the most important ligands relevant for granitic groundwater conditions have been selected and validated. The dominant soluble species under repository conditions are the carbonate complexes of REE. The solubilities of the oxides, hydroxides, carbonates, hydroxycarbonates, phosphates and other important solids have been selected and validated. Solubilities and solubility limiting solids in repository conditions have been estimated with the selected database. At the initial stages of fuel dissolution, the UO_2(s) matrix dissolution will determine the concentrations of REE. Later on, solid phosphates, hydroxycarbonates and carbonates may limit their solubility. Recommendations for further studies on important systems in repository conditions have been presented.

ABSTRACT (Swedish)

En utvald termodynamisk databas för de sällsynta jordartsmetallerna (lantaniderna), för användning i säkerhetsanalyser av förvaring av högaktivt radioaktivt avfall, har kompilerats. Termodynamiska data för vattenlösliga specier av lantaniderna med de viktigaste liganderna i granitiska grundvatten har valts ut och validerats. Den dominerande specien under förvarsförhållanden är lantanidernas karbonatkomplex. Löslighetsprodukterna av oxider, hydroxider, karbonater, hydroxykarbonater, fosfater och andra viktiga mineral har valts och validerats. Lösligheter och löslighetsbegränsande faser under förvarsförhållanden har bestämts med den utvalda databasen. I den tidiga skedena av bränsleupplösningen kommer UO_2 - matrisens upplösning att bestämma koncentrationen av lantanider. I senare skeden kommer fosfater, hydroxykarbonater och karbonater att bestämma lösligheten. Rekomendationer för fortsatta studier av, under förvarsförhållanden, viktiga system har gjorts.

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INTRODUCTION

The cycling of the rare earth elements (REE) in Nature has been largely increased in the past 30 years due to their anthropogenic usage. Particularly, in the electronic industry with the developement of semi- and supraconductor materials. The production of significant amounts of REE during the fission of uranium and plutonium nuclear reactor fuels constitutes another potential anthropogenic source.

The geochemistry of REE has been thoroughly studied, mainly as indicator of selective water rock interactions where the REE have been used to differentiate between various alteration processes. The study of the low temperature geochemistry of the REE has increased steadily in the last decades and several compilations have been produced concerning particular aspects of the REE coordination chemistry and thermodynamics(e.g. 1-13, 17-21). However, no attempt has been made so far to produce a selected thermodynamic database of REE to be used in the safety assessment of high-level nuclear waste.

Our objective is therefore to produce an up to date thermodynamic data base that includes the aqueous and solid phases specificly relevant for granitic groundwater conditions.

1. DATA SELECTION

The thermodynamic databases associated to the geochemical modelling computer codes, normally used in performance assessment exercises (i. e. Harphreeqe (134) and EQ 3/6 (135)) contain very few data on REE and their compounds. This is also true for working data bases that have been produced in international efforts like Chemval (136). Only data on europium, based on the selection by Rard (5) and some sporadic data for La and Sm species and solids are available in the databases associated to the Phreeqe and EQ 3/6 code packages. The main sources of information for our compilation of soluble species have been a review paper by Wood (1) and the later ones by Millero (2) and Lee and Byrne (3). In addition, we have derived most of the solubility constants from primary literature data. The details of the data compilation and selection are given in the appropriate sections.

1.1. Simple lanthanide ions.

The dominant oxidation state of the REE in aqueous solution at 25 °C is the +3 state. However under oxidizing conditions Ce^{4+} and under extremely reducing conditions Eu^{2+}, Sm^{2+} and Yb^{2+} are formed. The values chosen in the database for the redox potentials are those reported in the review of Morss (21), compared whenever possible with experimental determinations and with the spectroscopic estimations of Nuggent et al.(23). The standard state thermodynamic properties at 25 °C of Morss (21) are in good agreement with NBS Technical Notes 270-5(18) and 270-7(19). The standard reduction potentials of the reaction (in EQ 3/6 format):

$$Ln^{3+} + 0.5\ H_2O \rightleftharpoons Ln^{2+} + H^+ + 0.25\ O_2(g)$$

for ytrium, lanthanum and the lanthanides reported in the tables were calculated from the $\Delta G_f°(Ln^{3+})$ and $\Delta G_f°(Ln^{2+})$ of reference (21) and the equilibrium:

$$2\ H_2O \rightleftharpoons 4\ H^+ + O_2(g) + 4e^- \qquad \log K = -83.106$$

The only lanthanide(II) ion which can exist in water for an appreciable period of time at 25 °C is Eu(II). Wood (4) calculates an increase of the stability of the two valent state with temperature, to the point of its domination above 250 °C. Even though temperatures other than 25 °C are not considered in this work, the values of the constants for this equilibrium have been included in the database for all REE.

For europium, Rard (5) uses a slightly different value from (21), based on new experimental determinations (26), which has been accepted in this work. For the other REE, the accuracy of the estimated redox(II)-(III) values is of the order of 0.1 V (21), which we consider quite acceptable for our pourposes.

The redox potential for the Ce(III)-Ce(IV) couple

$$Ce^{3+} + H^+ + 0.25\ O_2(g) \rightleftharpoons Ce^{4+} + 0.5\ H_2O$$

is the only one of significance for performance assessment calculations. Since the estimations of these potentials are more uncertain (21) and the importance of the four valent state is reduced with the increase of the temperature (4), the rest of the REE(III)-REE(IV) redox potentials were not included in the database.

1.2. Solution species

As mentioned above, at 25 °C the main oxidation state of lanthanum, the lanthanides and yttrium is the +3 state. Since very few data are available for complexes of only Eu(II) and Ce(IV), and no recent data on the complexation and solubility of the REE in oxidation state other than +3 were found, in the following the discussion is centered on the complexation of trivalent REE.

Several reviews on the aqueus chemistry of the REE have been published (1, 7 - 11) and the short summary given in this paragraph is based on this work.

The REE(III) ions are hard acceptors in the Pearson-Ahrland sense and form strong complexes with hard ligands containing highly electronegative donor atoms such as carbonate, phosphate, hydroxide, fluoride, and sulfate. The bonds between REE^{3+} ions and hard ligands such as CO_3^{-2} or F^- are mainly electrostatic in character and the 4f electrons do not seem to participate to a large extent in the bonding. An approximately linear dependence of the log β_1 on the inverse of the sum of anionic and cationic radii has been reported (11) . The deviations from this general behavior, with a break in the slope most often occurring at Gd (named "tetrad" or "nephelauxetic" effect), are often very small to be detected for most geochemically important ligands. Another consequence of the dominantly electrostatic nature of bonding is that the coordination number and the geometry of REE ions are less constrained than those of transition metal ions. The coordination number of the REE in solid compounds ranges from 3 to 12, while in solution it is generally accepted that for heavy REE(HREE) it is mainly 8 and for LREE 8 or 9.

The stabilities of the solution species of the lanthanides are mainly based on the recent reviews of Wood (1), Millero (2) and Lee and Byrne (3). It should be pointed out that the primary experimental data used in these works to calculate thermodynamic values of the constants are in some cases the same, as e. g. for carbonate or phosphate complexes, but the calculation of activity coefficients to extract thermodynamic values differs. In the process of selecting the values in this work the following was considered:

Wood (1) uses a modified extended Debye - Huckel expression and assumes the log K values to be linear with $\sqrt{I}/(1+\sqrt{I})$. While this is quite acceptable for low ionic strengths and for complex formation reactions of the REE^{3+} ions with high charge ligands, the same can not be expected at high ionic strengths and for monovalent ligands, since the Debye-Huckel contribution to the activity coefficient expression is not as dominant.

Millero (6) has proposed a mixture of the ion association approach and specific ion interaction approach of Pitzer. The main assumptions of the ion association approach, such as the use of the mean salt method, based on the dependence of the activity coefficients only on the ionic strength, are not true within the frame of the Pitzer or any ion interaction approach. Byrne and coworkers (3,64,65,66) use the ion association approach modified by Millero which for the lanthanides gives in general slightly higher values of the constants than the values obtained by the method used by Wood.

In another work (2) Millero modifies Pitzer's equations to functions of only ionic strength. From the equations thus obtained, values of the thermodynamic constants of lanthanide complexes with the most important ligands in natural waters are calculated. This form of Pitzer equations is correctly applied in calculating activity coefficients of trace species in ionic media, but the lack of parameter values makes necessary other simplifications. For example, the calculation of the thermodynamic constants for various lanthanide ion pairs is carried out considering only the $\beta^{(0)}$ parameter for ion pairs, while all Pitzer parameters are considered for the other ions. The neglection of the $\beta^{(1)}$ parameter for the ion pairs leaves without compensation the respective large $\beta^{(1)}$ values for the lanthanide ions. This results in values at $I=0$ smaller than the ones obtained with any one of the other methods. Also the unsymetrical mixing terms for highly charged ions should influence appreciably the results obtained by using the Pitzer method, and in Millero's treatement these terms are considered for univalent ions, but have not been taken into account for the much higher same sign and triple interactions of the lanthanide ions.

The selected values were extracted from the data of Lee and Byrne, Wood and Millero, taking into account the above effects for each reaction. In cases when recent and reliable experimental determinations were available, they were included in the analysis.

1.2.1. Hydrolytic solution species

The hydrolysis of the lanthanides has been reviewed in the competent work of Baes and Mesmer (29) and their values have been accepted by Wood (1). A linear free energy relationship was used to evaluate the hydrolysis constants of several elements for which no sufficient good quality data were available. In the cases when new data have been published after this compilation, they have been included in the tables. In general, there is agreement between the values reported by Baes and Mesmer and the most reliable recent measurements, as discussed shortly in the following.

Kragten and Dencop-Weever (30-37) have studied the hydrolysis of La, Ce, Nd, Sm, Gd, Tb and Yb measuring the solubility of their freshly precipitated (5 min. aged) hydroxides. Their values measured at 1M $NaClO_4$ agree reasonably well with the values selected by Baes and Mesmer, after accounting for the difference in the ionic strength.

Davidov and Voronik (43) have used ion-exchange and spectrophotometry and obtain -6.4 for the first hydrolysis constant of yttrium, in good agreement with the value accepted in this work.

M'Halla et al. (40) have measured conductometrically the first hydrolysis constants of La, Eu, Gd and Lu. Their values for the first hydrolysis constant (-7.6 for La, -7.3 for Eu, -9.3 for Gd and $\leq$ - 5 for Lu) are too high compared to the ones proposed by Baes and Mesmer (29) (respectively -5.5, -6.2, -6.0, -6.4). One possible explanation may be carbonate complexation due to carbon dioxide contamination of the solution. Schmidt et al. (42) find weaker hydrolysis for Eu and Yb using measurements of transient conductivity changes after pulse radiation (-5.3±0.2 for both Eu and Yb, compared with -6.2 for Eu and -6.3 for Yb). Bilal and Koss(44) have determined very large first hydrolysis constants for Ce, Eu, Tb and Yb at 1 M $NaClO_4$ (-log β_1= -6.6, $\leq$ -5, -7.4, -8.4, and for β_2, -11.8, -13.7, -14.30, -15.9 respectively). According to Bingler and Byrne (85) this overestimation is due to the use of phosphate buffers, which complex the lanthanide ions. The value -log β_1 = -6.43 of the first hydrolysis constant for Eu at 0.7 M Cl^- reported by Caceci and Choppin (41) was calculated from competitive reactions with oxalate complexing and assuming no hydrolysis at pH=5.9. Lundqvist (52) estimates -5.7 for the same constant at 1 M $NaClO_4$, while Nair et al.(44) report -5.71 for Eu and -5.0 for Sm at the same conditions and -logβ_2 = -11.9 and -12.2 for their respective second hydrolysis constants. These values are in fair agreement with the values selected here, after accounting for the ionic strength difference. As a conclusion, the data reported in ref.(29) for the hydrolysis of the REE have been accepted in this work. They are changed only slightly in some cases when reliable new measurements have been reported.

Ciavatta and coworkers (38, 39) have shown that at higher temperatures (50 or 60 °C) the polynuclear hydrolytic complexes predominant in lanthanide systems may be different from those at 25 °C. For this reason, and because polynuclear complexes are seldom formed in natural waters, owing to the low concentrations of the lanthanide ions, the corresponding constants have been included only in the cases reported in ref. (29).

1.2.2 Carbonate complexes.

In most natural waters, the carbonate complexes are accepted as the dominant soluble species of the rare earths (1, 3, 11, 12, 16, 64). There seems to be agreement about the speciation and the stability constants for the carbonate complexation of the lanthanides. The bicarbonate complex and the various carbonate complexes $REE(CO_3)_n$, n = 1 - 4, have been reported. The values chosen in the database mainly rely on the measurements of Byrne and coworkers (3, 58, 60, 61, 64), Lundqvist (52), Ciavatta et al. (50), Ferri et al. (53) and Spahiu (56, 57). Since the position of yttrium in the lanthanide series varies with the ligand, the experimental values of Spahiu (56, 57) for $YHCO_3^{2+}$ and YCO_3^+ were used to interpolate the value for $Y(CO_3)_2^-$ from data of Lee and Byrne (64). The values reported by Chat (62) are in good agreement with the accepted values.

Dumenceau and coworkers (54, 55) have reported constants for the tetracarbonate complexes of the lanthanides, while Ferri (53) reports the tri and tetracarbonate complex of Ce. The values given by Ferri (53) for the first and second carbonate complex are higher than the values we have selected for Ce and the neighbouring elements, even after accounting for the ionic strength difference, while Wood (1) indicates shortcomings in the work of Dumenceau et al. (55, 56). Thus the higher carbonate complexes (tri - and tetracarbonate) were not considered, untill new experimental evidence becomes available. On the other hand their importance would be limited in carbonate concentration and pH ranges of most groundwaters.

Bernkopf (94) and Bidoglio and Marcandalli (130) propose mixed hydroxocarbonate complexes of Eu, but the speciation schemes used in these works seem problematic (1), and have not been confirmed in later studies. Further experimental evidence is needed to confirm the existence of the mixed complexes.

1.2.3 Phosphate complexes

The phosphate complexation of the REE has recently been studied by Byrne and coworkers (85,86) and the species $REEH_2PO_4^{2+}$, $REEHPO_4$ and $REE(HPO_4)_2$ have been proposed. The species $REEH_2PO_4^{2+}$ seems to be well established also in other works. Thus Rao et al. (83) report $-\log \beta_1 = -1.61$ for La at 0.5 M $NaClO_4$, while Afonin and Pechurova (84) report -1.24 for Nd at ≈ 0.7 M (Na, H)Cl. Borisov et al. (82) report for the same constant (at zero ionic strength) -2.33 for Ce, -2.51 for Pm and -2.65 for Y.

The other species, $GdHPO_4^+$ and $Gd(HPO_4)_2^-$, have been directly measured only for Gd (85), while the values for the other REE have been estimated by us using linear free energy relationships and parameters reported in refs. (3) and (86), in order to compare them with the values reported by Millero (2).

In a recent work on phosphate complexation of Gd and Ce (86), Byrne and coworkers report stability constants for the complexes of $GdPO_4^0$ and $CePO_4^0$ and linear free energy estimates for all $LnPO_4^0$ and $Ln(PO_4)_2^{-3}$ complexes. The outcome of this work indicates that in previous works the stability of these species have been overestimated by several orders of magnitude (87, 88) [Mayer and Schwartz (81) propose a $CePO_4$ constant of -18.5 instead of -11.35 estimated by Byrne et al.]. These species become more important for the heavy lanthanides, as shown in the figures 1a, 1b. and 1c. In these figures the speciation of La, Eu and Lu has been calculated with the present database for soluble species (the precipitation of solids was suppressed) in a typical granitic ground water. The total concentration of the various REE and of the ligands in the granitic ground water [Allard (96)] were as given below:

$\Sigma\, REE^{3+} = 2\ 10^{-7}$ M, $\Sigma\, CO_3^{2-} = 1.8\ 10^{-3}$ M, $\Sigma\, Cl^- = 1\ 10^{-3}$ M, $\Sigma\, SO_4^{-2} = 1\ 10^{-4}$ M,
$\Sigma\, F^- = 5\ 10^{-5}$ M, $\Sigma\, PO_4^{-3} = 2\ 10^{-6}$ M,

As seen from the diagrams, the carbonate complexation dominates the speciation of REE in granitic groundwaters. This is in agreement with geological information (14, 15) which link the REE mobility in uranium mineralisations to the carbonate and exclude the importance of phosphate in this process. Anyhow, for ratios of total carbonate/total phosphate lower than 100, the phosphate complexes become dominant, especially for heavy REE. These species have been included in the database, but since they are obtained from only one measurement for Gd (the value for the Ce complex is estimated from linear free energy relationships, the measured one is considered unreliable by the authors), the values of these phosphate complexes are given in italics in the tables 1-16.

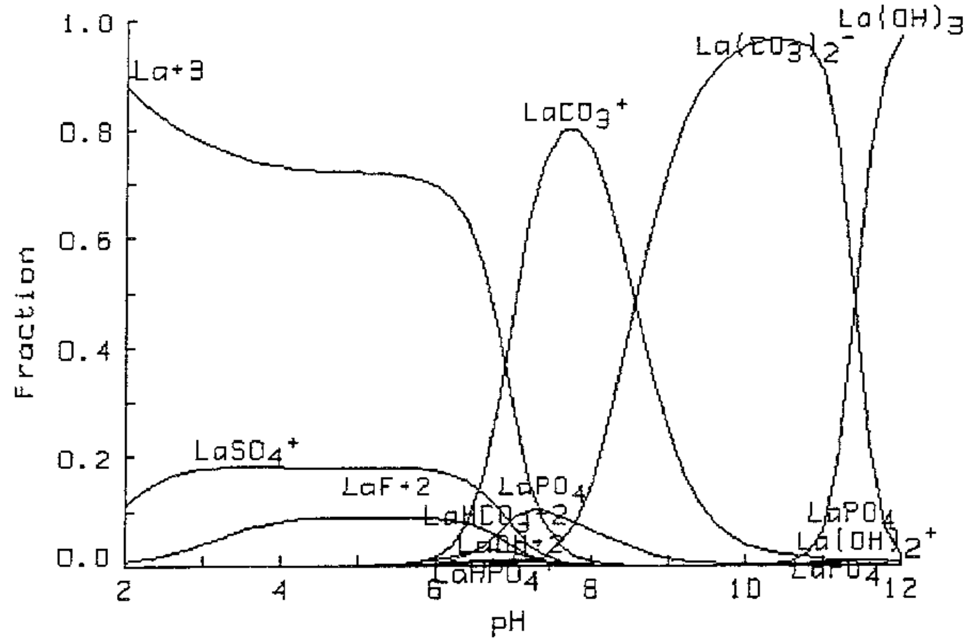

Fig 1a. Aqueous speciation of lanthanum in granitic ground water calculated with the data selected in the present work.

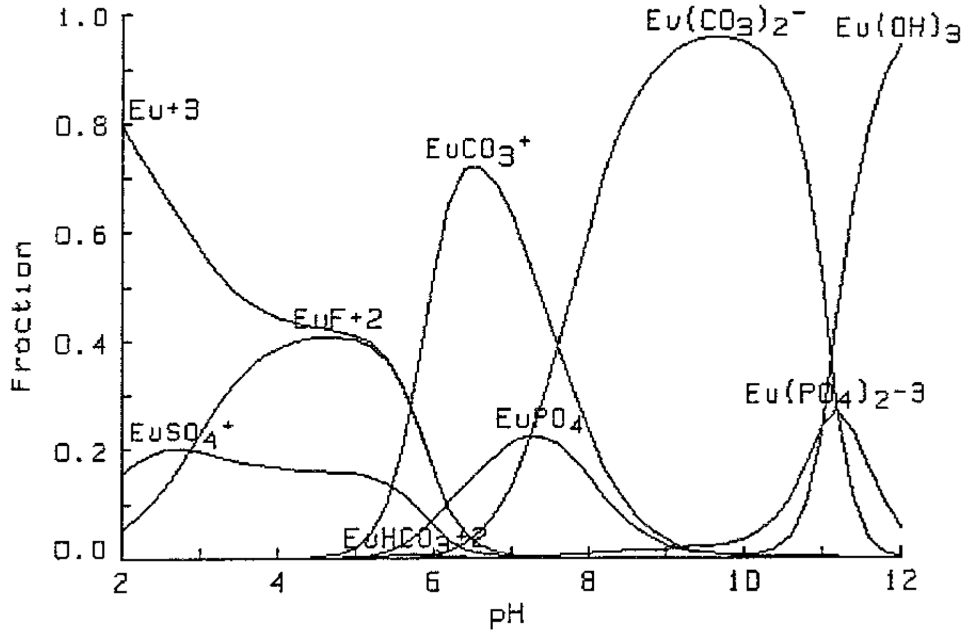

Fig **1b.** Speciation of europium calculated with data from this work.

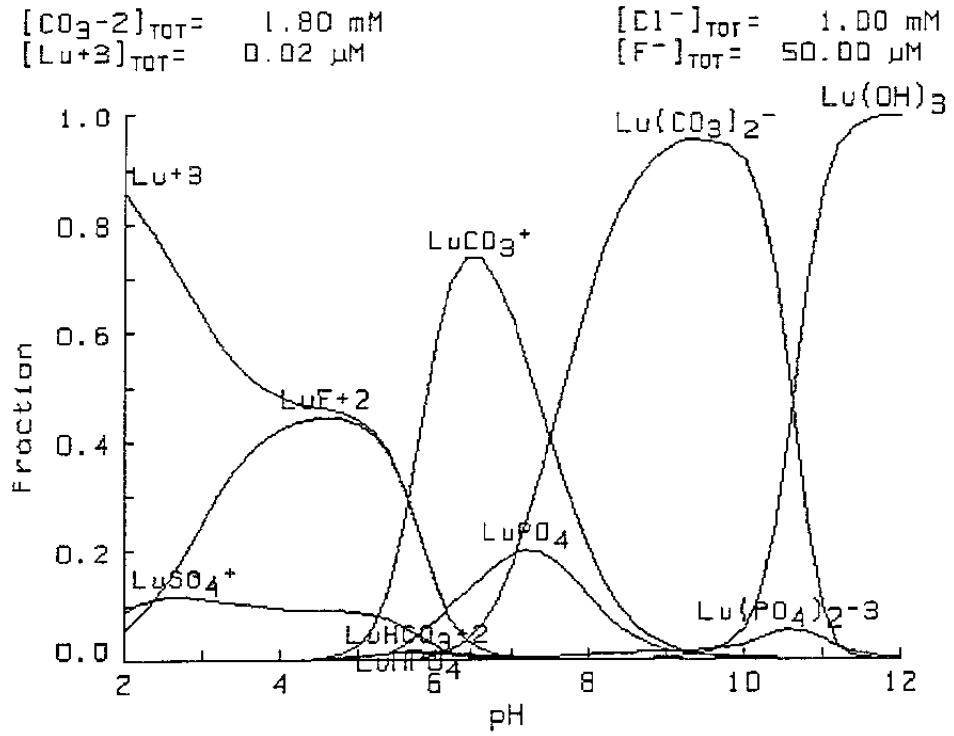

Fig. 1c. Speciation of lutetium in groundwater, calculated with the present database.

1.2.4. Sulfate and fluoride complexes.

Considerable effort has been devoted to the study of the sulfate complexation of the REE [e. g. 108-112; more complete reference list in (1)]. Wood (1) selects the values of Powell (112), while most of Millero's (2) primary data are those of Choppin and coworkers (110), and the values from different sources seem to be in reasonable agreement. No recent measurements were considered and the values in the tables were extracted from the reports mentioned above.

Fluoride complexes also seem to be well determined and their importance increases in the acidic range, especially for natural waters with high fluoride content. The values of the higher fluoride complexes are less certain and were included only for some elements, mostly as reported by Wood (1).

1.2.5 Chloride, nitrate and other solution species

The complexes of REE with chloride and nitrate are weak (114-120), generally outer sphere complexes and the studies on these systems are in fair agreement. Wood accepts the values of Mironov (117), which are in fair agreement with the values reported in the two other sources (2,3). The same holds for the nitrate complexes. No recent measurements were considered for these complexes and the values were selected based on the reports already mentioned (1,2,3).

There are indications that the complexation of the REE with geochemically important organic ligands is strong (131, 132, 12,13), but very few reliable data are available. Thus only the values of fulvic and humic acid complexes for Eu have been included in this work as tentative ones.

1.3. Solid phases.

A number of sparingly soluble solid phases are formed by the REE. The most important as potential solubility limiting solids in many natural systems include hydroxides, carbonates, hydroxycarbonates, fluorocarbonates, fluorides and phosphates. In spite of their importance, very few data exist in literature and for important systems as hydroxydes, carbonates and fluorides the agreement between the results of different researchers is poor, often spanning several orders of magnitude. In this context, we agree with the statement by Wood(1) "*The major missing piece of information which prevents the modeling of such chemical dispersion processes at the present time is accurate solubility products for the most common primary and secondary REE-bearing phases such as bastnaesite, monazite, allanite etc.*"

The REE form amorphus hydroxides which may incorporate substantial quantities of anions present in the system as in the case of hydroxychlorides, but with aging the solubility often drops several orders of magnitude and the solid phase is transformed to normal hydroxide (48). The same holds for carbonates, which can form hydroxyl carbonates or fluorocarbonates, accompanied with changes in the solubility. On the other hand for solid phosphates (89) or fluorides (5, 10) of REE, slow hydration equilibria influence the solubility. These possible phase changes during the measurements, together with other factors discussed in the following paragraphs, may explain the scatter in the reported solubility products.

Only in a few recent studies a careful characterisation of the solid phase before and after the experiment has been performed. On the other hand the importance of americium in nuclear waste management has resulted in a considerable effort in the study of its chemistry in the last years. In many cases recent results on americium show much lower solubilities than accepted previously, thus the comparison of e. g. Nd solubilities with recent data on Am has been taken into account in selecting the solid phase data.

1.3.1 Solubility of the oxides and hydroxides

The oxides of REE are easily hydrated and quite soluble in water to be the solubility limiting solids. The data for the solubility of the oxides, that is for the reaction:

$$REE_2O_3(s) + 6\ H^+ \rightleftharpoons 2\ REE^{3+} + 3H_2O$$

were calculated from $\Delta G_f^o(Ln_2O_3)$ values as reported in ref.(19) and based in ref.(17,18), considered the most reliable ones and from $\Delta G_f^o(REE^{3+})$ for aqua ions of Morss(21), using CODATA values for water.

The values of the solubilities for the amorphous hydroxides are based on data of Kragten and Denkop-Weever (30-37) for freshly precipitated hydroxides, after extrapolation to zero ionic strength.

The data of Baes and Mesmer for the solubility of the hydroxides have been reported as a summary of the previous work in the tables. They based their estimations in the data of Akselrud (48) for aged precipitates (more than 150 days). Anyhow, recent measurements on well characterized crystalline neodymium hydroxide (46) or on europium hydroxide (94) and americium hydroxide (47, 49) report lower solubilities. The correlation of the *a* parameter of the unit cell and the solubility product, used by Baes and Mesmer(29), does not seem reliable in the case of Eu, when the experimental value (48) seems to be in better agreement with more recent results (94) than the estimated one. Furthermore, a common feature of the few validations of REE thermodynamic databases are the larger solubilities calculated e.g. in Nd-glass dissolution tests (74) than the ones measured. Thus Rai and coworkers (74) propose that the solubility of $Nd(OH)_3(s)$ glass) of the same magnitude as that reported by Bernkopf (94) for Am (-28.9) to explain their solubility data. This value is even lower than the one measured by Silva (46) for the corresponding crystalline solid (-26.2).

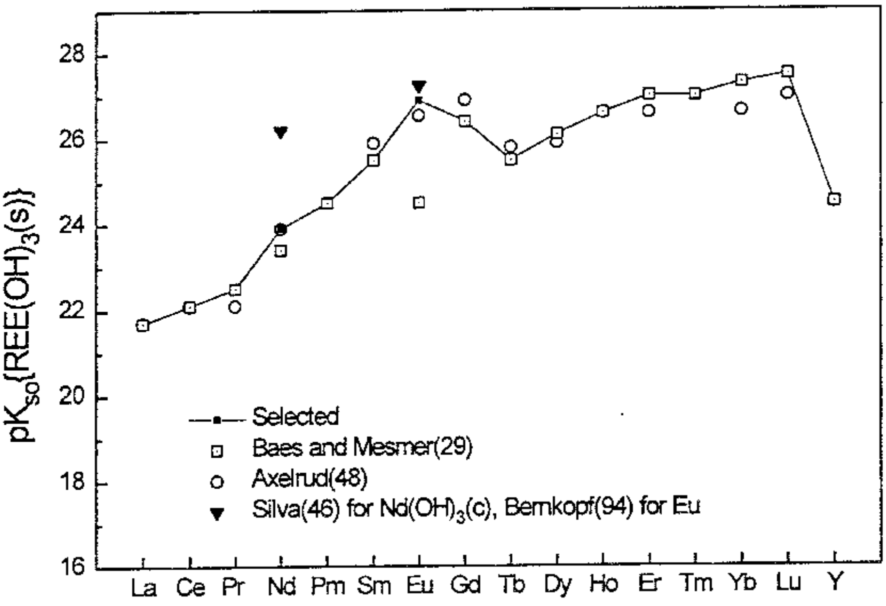

Fig. 2. Solubility products of REE hydroxides.

The solubilities reported by Baes and Mesmer (29) are recomended for the other REE solid hydroxides (fig. 2). It is difficult to predict the solubility products of the crystalline hydroxides without having new experimental evidence, so only the value of Silva (46) for Nd has been selected.

1.3.2 Solubility of the carbonates and hydroxycarbonates.

Solid REE carbonates and hydroxocarbonates have been proposed (11,12) to be solubility limiting in natural waters. However, the experimental data concerning the solubility of REE carbonates and hydroxycarbonates are quite scattered. There are several reasons for this scattering.

As already mentioned, a carefull characterization of the solid phase before and after the solubility measurements is very important because of the possible phase transformations. It is not straightforward to predict which solid phase is stable at 25 °C and a given set of conditions in the REE^{3+} - $CO_2(g)$ - H_2O system. In the following, a summary of the chemical and geochemical literature concerning this problem is given.

Caro and coworkers (67,122) have measured solubilities and identified solid phases in the $REE_2O_3(s)$-$CO_2(g)$-H_2O system. Normal carbonates of the type $REE_2(CO_3)_3 \cdot nH_2O$ with n=8 for La through Nd, n=3 for Sm through Tm and Y, n=6 for Yb and Lu were identified by equilibrating the corresponding hydroxides with 1 atm. $CO_2(g)$. The reaction kinetics is slow for oxides and oxycarbonates obtained through thermal decomposition of oxalates, but rapid and complete for hydroxydes. This is expected following the discussion of the reaction kinetics of the CO_2 attachment to hydroxides as given in ref. (133). The difficulties caused by the influence of very fine particles(under 1 µm), especially for the amorphous carbonates (Yb, Lu), in the solubility measurements have been stressed.

In another work of Caro et al. (68), the phases formed at lower partial pressures of $CO_2(g)$ and room temperature have been studied. The results are that the hydroxides transform to normal carbonates for $P_{CO2} \geq 0.1$ atm., while at the P_{CO2} of air ($3\ 10^{-4}$ atm.) the hydroxides of La through Eu give well crystallized phases with ratios CO_2/Ln_2O_3 near 2, that is hydroxycarbonates. For Gd through Lu this ratio is between 1 and 1.5, the solids are amorphous and the results hardly reproducible. The normal carbonates are stable for $P_{CO2} \geq 0.01$ atm., but in air hydrolyze rapidly for Pr and Nd (24 hours) or slowly for Sm and Eu (8 days) to form hydroxycarbonates $Ln(OH)CO_3$, similar to those obtained from the hydroxides at the P_{CO2} of air. The carbonates of Gd through Lu and also of La are very resistant to the hydrolysis and after several weeks the X-ray spectra are only slightly altered (enlargement of lines), while the ratio CO_2/Ln_2O_3 is near 2.8. The prolonged hydrolysis of the carbonates of Pr through Eu in argon atmosphere permits to lower the ratio CO_2/Ln_2O_3 to 2.3 till 1, but the hydrolysis product has essentially the same X-ray diffraction pattern, This is explained by the authors by the formation of a nonstoichiometric phase of the composition $Ln_2(CO_3)_x(OH)_{2(3-x)}$ nH_2O. In argon atmosphere the carbonates of Gd through Lu, including that of La, behave like in air.

Even though no solubility products of the hydroxycarbonates are reported in this study, we have given the results in some detail to show the complexity of the system.

In the geochemical literature, the interest in the hydroxycarbonates is connected with the importance of the mineral bastnaesite, $LnCO_3F(s)$, which is analogous to the hydroxycarbonate (the corresponding mineral is named hydroxyl-bastnaesite). Minerals with high coordination numbers (10-12) are LREE selective, while those with low coordination number (6) are HREE selective. The coordination number of REE in bastnaesite is 11. Thus Williams-Jones and Wood (80) conclude that apparently high contents of HREE and Y in bastnaesite represent intergrowths and inclusions of other minerals. Furthermore, attempts to synthesize bastnaesite analogues containing HREE's have not been successful. This agrees with the results of Caro and coworkers (68), that the hydroxycarbonates are formed easier for the light REE.

The most studied hydroxyl-bastnaesite has been $Nd(OH)CO_3$, while limited hydrothermal synthesis studies have been carried out on those of La, Gd, Pr, Er and Y (78, 79, 124, 125). From these studies it follows that the T-X_{CO2} stability field of hydroxyl-bastnaesite decreases with decreasing ionic radius of the REE and Y. From the study of Wakita and Kinoshita (88) it follows that the hydroxyl-bastnaesite of La is synthesized at atmospheric pressure in air over 65 °C, while normal carbonate (lanthanite) forms at lower temperatures. Tareen and Kutty(87) find that for X_{CO2} =0.01 and below 250 °C $Gd_2(CO3)_3$. $2H_2O$ is synthesized in the Gd-CO_2-$H2O$ system at 1.5 kbar, while the hydroxycarbonate is stable over this temperature.

Owing to the similarity with americium, the Eu and Nd solid carbonates and hydroxy carbonates have been extensively studied in the last years. Thus the hydroxy carbonate solubility products have been reported only for these systems for which direct experimental data exist, while for the rest of the REE only the values for the normal carbonate have been reported. Very possibly in repository conditions the hydroxycarbonates of Ce, Pr and Pm form and as a crude approximation the values given for Nd and Eu can be used, while for the rest of the REE further experimental evidence is preferred. The values reported for Nd and Eu are based on the measurements of Kim and coworkers (71, 72), accompanied by a complete characterization of the solid phases using X-ray, FTIR and DTA. The data of Bernkopf (94) for Eu those of Rai et al. (74) for Nd have also been considered, while data of Silva and Nitsche (127), Felmy et al. (70) on Am have been used for comparison with Nd. Runde et al. (72) report for both Nd and Eu the formation of normal carbonate for P_{CO2} = 1 atm and 0.01 atm., while the $Ln(OH)CO_3(s)$ forms at P_{CO2} of air (0.0003 atm.). Carroll (77) claims the formation of the hydroxycarbonate of Nd at 0.1 and 1 atm. $CO_2(g)$ for long equilibration times, which seems in discordance with all previous information.

The solubility products of the normal carbonates are reported for the reaction:

$$REE_2(CO_3)_3(s) \rightleftharpoons 2\ REE^{3+} + 3\ CO_3^{-2}$$

which involves high charge ions and depends strongly on activity coefficient estimation. Thus already the pure electrostatic contribution accounted for by the Debye-Hückel term gives around 3 logarithmic units difference between the constant measured at 0.1 M and the value at zero ionic strength. The carbonic acid dissociation equilibria also influence in the values of the reported constants, since the dissolution equilibrium which is measured experimentally in the presence of carbon dioxide is

$$REE_2(CO_3)_3(s) + 6\ H^+ \rightleftharpoons 2\ REE^{3+} + 3\ CO_2(g) + 3\ H_2O$$

and has to be combined with the constants of the carbonic acid dissociation to derive the constant for the solubility.

The most complete set of measurements of the REE normal carbonates are those of Firshing and Mohammadzadel (69) and Jordanov and Havezov (66). In both these studies no characterization of the solid phase after equilibration has been performed and the carbonate complexes at equilibrium pH 4.8-6.15 in (69), and 4.76-5.75 in solutions saturated with $CO_2(g)$ or 7.55-8.16 in presence of bicarbonate in (66), have been neglected. This would result in both cases in higher solubility products than the true ones. Thus Choppin (12) recalculates a value of -35.3 for Nd carbonate accounting for carbonate complexation from data in (69) instead of -34.1 reported by the authors. While in (66) a regular increase of solubility is observed from La to Yb and Y, in (69) the behaviour is much different (see fig. 3). It is evident that higher solubilities in (69) are observed in the cases of the higher equilibrium pH (for La and Er) showing the influence of carbonate complexes. On the other hand the partial dissolution of solid carbonates with 10 mM perchloric acid may cause losses of $CO_2(g)$ at the initial stages of the experiment, while latter, $CO_2(g)$ from air may have been absorbed (P_{CO2} is substantially lower than that of air in their equilibrium solutions, even assuming no losses of CO_2). This is most possible during the manipulations in the three months period of equilibration. Another point which makes difficult recalculations in this case is the possibility of phase changes due to the low partial pressure of $CO_2(g)$ and the long equilibration time.

In the studies of Grenthe et al. (73) for Y and Gamsjäger (76) for La, the Pitzer approach has been used with excellent results to describe the ionic strength influence on the solubility product of REE carbonates. Since proper characterization of the solid phase together with controlled conditions as P_{CO2} pressure and carbonate complexation were used in the studies of Ferri et al.(53) for Ce, Ciavatta et al. (50) for La, Meinrath and Kim for Nd (71) and Runde et al. (72) for Nd and Eu, we have used the Pitzer approach to obtain the thermodynamic solubility products of these carbonates (fig. 3). These values were used as reference ones to estimate the solubility products of the other lanthanide carbonates.

For the REE Gd through Lu, the values of the solubility products were selected on the basis of the recalculated values of Jordanov and Havezov (66) potentiometric data in the presence of 1 atm. $CO_2(g)$. From the results of Caro et al. (68) this should assure the stability of the normal carbonates. The data were recalculated using mixed activity-concentration constants for the carbonic acid and assuming a liquid junction potential of 0.08 pH units for 0.1 M $NaClO_4$, then were extrapolated to zero ionic strength using the same method as for La and Y.

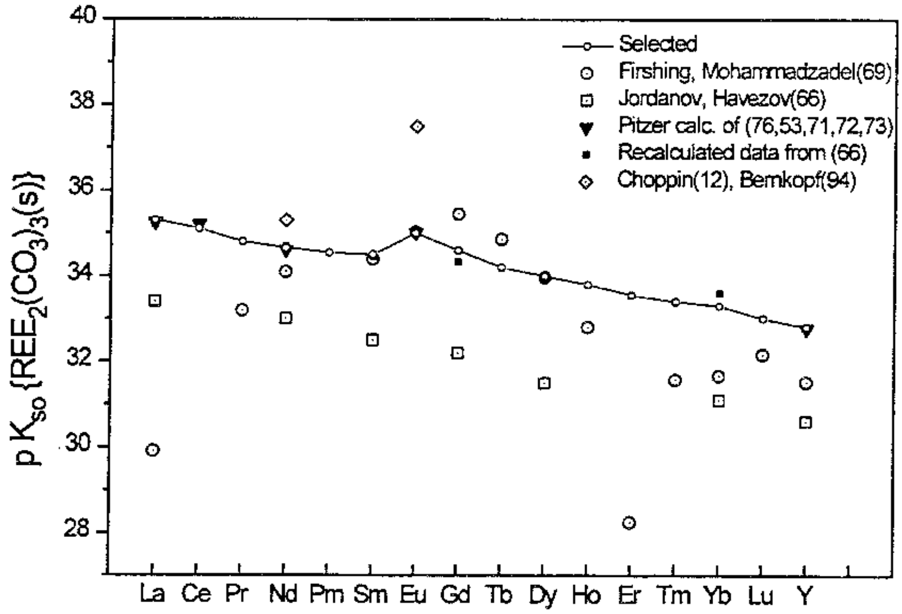

Fig 3. Solubility products of REE normal carbonates

Besides much higher solubilities of carbonates of REE, (e. g. in Rard (5) for Eu from old values which the same author (51) has corrected later), also some much lower ones have been reported. Bernkopf (94), measured the solubility of Eu carbonate in a pH region where complexes form, assuming mixed hydroxocarbonate complexes. As discussed above, this speciation scheme is not confirmed in later studies, and this may explain the low solubility product deduced together with the constants for the complexes. In Chemval 5 database a value of -41.6 is calculated from data of Shiloh et al. (127) for americium carbonate, measured at variable moderate ionic strengths and high carbonate concentrations, together with improper speciation (128). Choppin (12) recently reports -37.9 for Nd carbonate in sea water, but this is probably a sign error in the activity coefficient calculations, since all experimental studies show an increase of the solubility with ionic strength.

Double solid carbonates as $NaCe(CO_3)_2(s)$, which are reported (53) to form at high sodium concentrations, were not considered relevant for the present applications.

It is clear that owing to the importance of carbonates and hydroxy carbonates as potential solubility limiting solids, more experimental data are highly needed for these systems. The solubilities of at least two HREE carbonates from over and undersaturation, at well controlled ionic strengths, with a careful characterization of the solid phases before and after equilibration and known partial pressure of CO_2 should be performed to fully understand these systems.

1.3. 3 Solubility of phosphates

In nature the LREE commonly occur as the phosphate mineral monazite, while the HREE and yttrium form the phosphate mineral xenotime, with similar composition, but different coordination of the cation. Monazite type minerals are usually formed under hydrothermal conditions. However, recent studies in Belgium indicate the formation of monazites at low temperatures. Rare earth phosphate phases are very insoluble, therefore it is likely that one or more such phases control the concentrations of the REE in natural systems.

The data in the tables are based mainly in the work of Jonasson et al. (89) on the solubilities of the hydrated phosphate phase of La, Pr, Nd and Er, measured at 25 and 100 °C. The solid phase $LnPO_4\ xH_2O$ was produced in reflux for 24 hours and may have a better crystallinity than the corresponding amorphous phases (see discussion in test cases). There seems to be a reasonable agreement between their data and other measurements reported (74, 90, 91). The change in the logarithm of the solubility product from La ($\log K_{s0} = -24.5$) to Er (-24.18) seems to be small. Rai et al. (74) report $\log K_{s0} = -24.45$ for Nd, which compares well with our estimates of $\log K_{s0} = -24.6$ for Nd and $\log K_{s0} = -24.7$ for Pr. These estimates have been made from data at 100 °C in (89), assuming the same temperature dependence in solubility as for Er ($\log K_{s0}(100) - \log K_{s0}(25) \cong -1.3$). Jonasson et al. (89) compare their measurements with those of Tananaev and coworkers (90, 91), accounting for the ionic strength differences and estimate $\log K_{s0} = -25.3$ for La and $\log K_{s0} = -25.1$ for Gd. A regular linear increase of the cell parameters of the monazite type phosphates of La through Gd with the ionic radius of the REE has been reported (93). This may explain the small and regular increase in the solubility products noted in (89). This allowed us to assume a linear correlation to interpolate the values of the solubility products for all REE phosphates reported in the tables.

1.3.4. Other solids.

There are data on the solubilities of chlorides and bromides(10), sulfates (113), nitrates (121) and iodates of the REE, but we considered them not relevant for safety assessment reasons, due to their high solubility.

Rare earth fluorides are quite insoluble and precipitate from aqueous media as the hemihydrates, $REEF_3 \cdot 0.5\ H_2O(s)$. The data on the solubility of REE fluorides are quite spread, with solubility products ranging from $\log K_{s0} = -14$ to -29. Even in the same study (106) the solubility product for the same element, measured with three different methods differs more than two orders of magnitude. The values of the solubility product of $LaF_3(s)$ obtained with fluoride ion-selective electrodes, constructed from lanthanum trifluoride result extremely low (-24 to -29) and scattered. This is due to aging and hydration effects in the electrode monocrystal (5), and these data were not considered in the selection. The available literature data, together with the selected values are shown in fig. 4. From the selected values and the typical fluoride concentrations in ground waters, it follows that the importance of fluorides as potential solubility limiting solids is small as compared to other solids (e.g. phosphates or hydroxycarbonates).

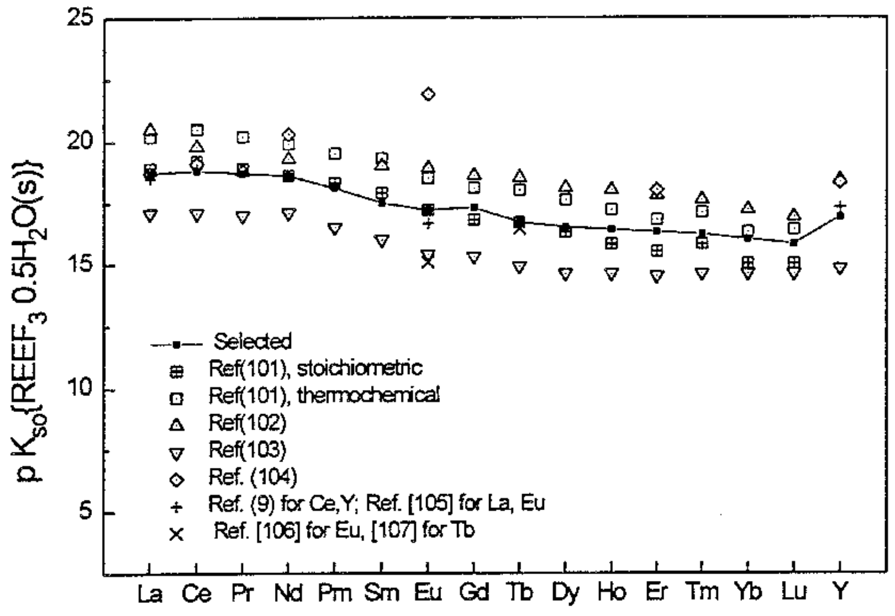

Fig. 4. Literature data and selected values for the solubility product of REE fluorides.

William-Jones and Wood (80) mention a variety of low solubility mineral phases such as bastnaesite and its solid solutions with calcite as parisite, synchisite, roentgenite or oxycarbonates etc, but no solubility data were found for them in the literature.

1.4 Data tables

All data correspond to 25 °C and data from all sources have been converted in EQ 3/6 format using CODATA key values. The values of the constants as reported in literature are shown with the reference number followed by a star, when this value does not correspond to the standard state ($I \neq 0$). When the value of the constant for a given reaction has been estimated by us from literature values, it is included in square brackets. The values of some of the selected constants are given in italics when we consider that they need further confirmation. In all this work the values of the constants correspond to the reaction as written in the tables. Tables for Eu and Sm are given before, since there are some data (given in the first column) for these elements in the EQ 3/6 and in the Hatches (HARPHRQ) databases .

Table 1. Europium solution species.

Reaction	log K EQ3/6 Hat.(H)	log K Millero	log K Wood	log K Lit.(ref)	Selec-ted.
$EuOH^{2+} \rightleftharpoons Eu^{3+} + OH^-$	-7.10 -6.2(H)	-5.83	-6.2	-6.1(3), -6.2(29), -6.4(94) -7.3(33),-5.3(34),-5.7(44,52*)	-6.2
$Eu(OH)_2^+ \rightleftharpoons Eu^{3+} + 2OH^-$	-13.12	-	-	-11.63(3),-11.9(94*), -11.4(29), 11.9(44*)	-11.6
$Eu(OH)_3 \rightleftharpoons Eu^{3+} + 3OH^-$	-	-	-	-16.6(3),-16.6(29) 17.1(94*)	-16.8
$EuCO_3^+ \rightleftharpoons Eu^{3+} + CO_3^{-2}$	-8.13	-7.37	-8.00	-8.0(3,64), -8.08(62), -5.93(52*)	-7.9
$Eu(CO_3)_2^- \rightleftharpoons Eu^{3+} + 2CO_3^{-2}$	-13.52	-12.24	-12.96	-13.52(3),-12.8(62) -13.4(61,64), -10.7(52*)	-12.9
$EuHCO_3^{2+} \rightleftharpoons Eu^{3+} + HCO_3^-$	-	-1.60	-2.08	[-2.54](64)	-2.1
$EuH_2PO_4^{2+} \rightleftharpoons Eu^{3+} + H_2PO_4^-$	-	-2.21	-	[-2.82](3,86)	-2.4
$EuHPO_4^+ \rightleftharpoons Eu^{3+} + HPO_4^{2-}$	-	-5.42	-	[-5.95](3,86)	-5.7
$Eu(HPO_4)_2^- \rightleftharpoons Eu^{3+} + 2\ HPO_4^{2-}$	-	-9.10	-	[-10.0](3,86)	-9.6
$EuPO_4 \rightleftharpoons Eu^{3+} + PO_4^{3-}$	-	-		-12.22(3)	*-12.2*
$Eu(PO_4)_2^{3-} \rightleftharpoons Eu^{3+} + 2\ PO_4^{3-}$	-	-		-20.66(3)	*-20.66*

Table 1. Europium solution species. (continued)

Reaction	log K EQ3/6 Hat.$^{(H.)}$	log K Millero	log K Wood	log K Lit.$^{(ref)}$	Selec-ted.
$EuSO_4^+ \rightleftharpoons Eu^{3+} + SO_4^{-2}$	-3.58 -3.67$^{(H)}$	-3.37	-3.67		-3.5
$Eu(SO_4)_2 \rightleftharpoons Eu^{3+} + 2SO_4^{-2}$	-5.13	-	-5.42		-5.2
$EuF^{+2} \rightleftharpoons Eu^{3+} + F^-$	-3.35	-3.63	-4.24		-3.9
$EuF_2^+ \rightleftharpoons Eu^{3+} + 2F^-$	-5.80	-	-7.96		-6.9
$EuF_3 \rightleftharpoons Eu^{3+} + 3F^-$	-10.60	-	-		-10.6
$EuCl^{+2} \rightleftharpoons Eu^{3+} + Cl^-$	-0.38	-0.28	-0.34		-0.34
$EuCl_2^+ \rightleftharpoons Eu^{3+} + 2Cl^-$	0.05	-	-		0.05
$EuBr^{2+} \rightleftharpoons Eu^{3+} + Br^-$	-0.25	-	-		-0.25
$EuBr_2^+ \rightleftharpoons Eu^{3+} + 2Br^-$	0.09	-	-		0.09
$EuNO_3^{+2} \rightleftharpoons Eu^{3+} + NO_3^-$	-0.65	-0.83	-1.23		-0.8
$EuBrO_3^{+2} \rightleftharpoons Eu^{3+} + Br^- + 1.5\ O_2(g)$	17.21	-	-		17.21
$EuIO_3^{+2} \rightleftharpoons Eu^{3+} + I^- + 1.5\ O_2(g)$	-15.18	-	-		-15.18
$Eu(HumAc)^{2+} \rightleftharpoons Eu^{3+} + HumAc^-$	- -13.3$^{(H)}$	-	-		-13.3
$Eu(HumAc)_2^+ \rightleftharpoons Eu^{3+} + 2\ HumAc^-$	- -14.6$^{(H)}$	-	-		-14.6
$Eu(FulAc)^{2+} \rightleftharpoons Eu^{3+} + FulAc^-$	- -6.49$^{(H)}$	-	-		-6.49
$Eu(FulAc)_2^+ \rightleftharpoons Eu^{3+} + 2FulAc^-$	- -10.5$^{(H)}$	-	-		-10.5
Eu(II)					
$Eu^{+3} + 0.5\ H_2O \rightleftharpoons Eu^{2+} + H^+ + 0.25O_2(g)$	26.68	-	-	26.69$^{(26)}$, 25.56$^{(21)}$	26.68

Table 1.2. Europium solids.

Reaction	log K EQ36	log K Hatch.	log K Lit.(ref.)	Selec-ted.
Eu(s)		-		
$Eu(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Eu^{3+} + 1.5\ H_2O$	163.27	163.23	162.96(26) 162.88(21)	163.2
Eu(III)				
$Eu(OH)_3(s) \rightleftharpoons Eu^{3+} + 3OH^-$	-26.39	-24.5	-24.5(29) -26.54(48), -27.2(94)	-26.9
$Eu_2O_3(cubic) + 6H^+ \rightleftharpoons 2\ Eu^{3+} + 3\ H_2O$	52.39	52.4		52.4
$Eu_2O_3(monoclinic) + 6H^+ \rightleftharpoons 2\ Eu^{3+} + 3\ H_2O$	54.00	54.01	54.08(19)	54.0
$Eu_2(CO_3)_3{\cdot}3H_2O(s) \rightleftharpoons 2Eu^{3+} + 3CO_3^{2-} + 3H_2O$	-26.59	-26.58	-35.03(69),-34.64(94*) -32.46(51),-31.78(72*)	-35.0
$Eu(OH)CO_3(s) \rightleftharpoons Eu^{3+} + OH + CO_3^{2-}$	-	-	-20.49(94*),-20.18(72*)	-21.8
$EuPO_4{\cdot}xH_2O(s) \rightleftharpoons Eu^{3+} + PO_4^{2-} + x\ H_2O$	-	-	[-24.4](89, 74)	-24.4
$Eu_2(SO_4)_3{\cdot}8H_2O(s) \rightleftharpoons 2Eu^{3+} + 3SO_4^{2-} + 8H_2O$	-10.20	-10.18		-10.2
$EuF_3{\cdot}0.5H_2O(s) \rightleftharpoons Eu^{3+} + 3F^- + 0.5H_2O$	-16.21	-16.21	-18.5(101), -17.2(101) -18.9(102), -15.4(103) -21.9(104),-16.7(105)	-17.2
$EuCl_3{\cdot}6H_2O(s) \rightleftharpoons Eu^{3+} + 3Cl^-$	5.21	5.22		5.2
$EuOCl\ (s) + 2H^+ \rightleftharpoons Eu^{3+} + H_2O + Cl^-$	15.81	15.82		15.81
$Eu(OH)_2Cl\ (s) \rightleftharpoons Eu^{3+} + 2OH^- + Cl^-$	-18.87	-18.87		-18.87
$Eu(OH)_{2.5}Cl_{0.5}\ (s) \rightleftharpoons Eu^{3+} + 2.5\ OH^- + 0.5\ Cl^-$	-22.11	-22.11		-22.11
$EuBr_3\ (s) \rightleftharpoons Eu^{3+} + 3Br^-$	30.19	30.19		30.19
$Eu(NO_3)_3{\cdot}6H_2O(s) \rightleftharpoons Eu^{3+} + 3NO_3^- + 6H_2O$	1.84	1.85		1.84
$Eu(IO_3)_3{\cdot}2H_2O(s) \rightleftharpoons Eu^{3+} + 3I^- + 2H_2O + 4.5O_2(g)$	-51.39	-51.11		-51.4
Eu(II)				
$Eu_3O_4(s) + 9H^+ + 0.25O_2(g) \rightleftharpoons Eu^{3+} + 4.5H_2O$	114.74	114.73		114.74
$EuO(s) + 3H^+ + 0.25O_2(g) \rightleftharpoons Eu^{3+} + 1.5H_2O$	64.57	-64.56		64.57
$EuSO_4(s) + H^+ + 0.25O_2(g) \rightleftharpoons Eu^{3+} + SO_4^{2-} + 0.5H_2O$	18.26	-18.25		18.26
$EuS(s) + 2H^+ + 0.25O_2(g) \rightleftharpoons Eu^{3+} + HS^- + 0.5H_2O$	41.99	41.97		41.98
$EuCl_2(s) + H^+ + 0.25O_2(g) \rightleftharpoons Eu^{3+} + 2Cl^- + 0.5H_2O$	31.99	-31.98		31.99

Table 2. Lanthanum solution species.

Reaction	log K EQ3 or Hatch.$^{(H)}$	log K Wood	log K Mill.	log K Lit.$^{(ref.)}$	Selec-ted.
$LaOH^{2+} \rightleftharpoons La^{3+} + OH^-$	-5.5$^{(P)}$	-5.5	-5.10	-5.34$^{(3)}$ -5.2$^{(37*)}$, -7.6$^{(40)}$	-5.4
$La(OH)_2^+ \rightleftharpoons La^{3+} + 2OH^-$	-	-	-	-9.86$^{(3)}$ -9.7$^{(37*)}$	-9.8
$La(OH)_3 \rightleftharpoons La^{3+} + 3OH^-$	-	-	-	-14.1$^{(3)}$ -14.04$^{(37*)}$	-14.0
$La_2(OH)_2^{4+} \rightleftharpoons 2\,La^{3+} + 2\,OH^-$	-5.0$^{(H)}$	-	-	≥-10.5$^{(29)}$	-5.0
$La_5(OH)_9^{+4} \rightleftharpoons 5La^{3+} + 9OH^-$	-54.8$^{(H)}$	-	-	-54.8$^{(29)}$	-54.8
$LaCO_3^+ \rightleftharpoons La^{3+} + CO_3^{-2}$	-	[-7.42]	-6.82	-7.12$^{(3,64)}$ -7.78$^{(50)}$ -7.74$^{(20)}$	-7.3
$La(CO_3)_2^- \rightleftharpoons La^{3+} + 2CO_3^{-2}$	-	[-12.0]	-11.31	-11.59$^{(3)}$ -12.0$^{(64)}$	-11.8
$LaHCO_3^{2+} \rightleftharpoons La^{3+} + HCO_3^-$	-	[-2.5]	-2.02	-2.5$^{(50)}$ [-2.46]$^{(64)}$	-2.3
$LaH_2PO_4^{2+} \rightleftharpoons La^{3+} + H_2PO_4^-$	-	-	-2.50	[-2.42]$^{(86,3)}$ -1.61$^{(83*)}$	-2.5
$LaHPO_4^+ \rightleftharpoons La^{3+} + HPO_4^{-2}$	-	-	-4.87	[-5.27]$^{(86,3)}$	-5.1
$La(HPO_4)_2^- \rightleftharpoons La^{3+} + 2\,HPO_4^{-2}$	-	-	-8.17	[-8.61]$^{(86,3)}$	-8.4
$LaPO_4 \rightleftharpoons La^{3+} + PO_4^{-3}$	-	-	-	-10.96$^{(3)}$	*-10.96*
$La(PO_4)_2^{3-} \rightleftharpoons La^{3+} + 2\,PO_4^{-3}$	-	-	-	-17.63$^{(3)}$	*-17.6*
$LaSO_4^+ \rightleftharpoons La^{3+} + SO_4^{-2}$	-	-3.62	-3.21	-0.8$^{(20)}$	-3.4
$La(SO_4)_2 \rightleftharpoons La^{3+} + 2SO_4^{-2}$	-	-5.29	-	-1.0$^{(20)}$	-5.1
$LaF^{2+} \rightleftharpoons La^{3+} + F^-$	-	-3.72	-3.12	-2.02$^{(20)}$	-3.4
$LaF_2^+ \rightleftharpoons La^{3+} + 2\,F^-$	-	-6.84	-		-6.2
$LaF_3 \rightleftharpoons La^{3+} + 3\,F^-$	-	-10.20	-		-10.2
$LaCl^{2+} \rightleftharpoons La^{3+} + Cl^-$	-	-0.48	-0.29	-0.64$^{(20)}$	-0.38
$LaNO_3^+ \rightleftharpoons La^{3+} + NO_3^-$	-	[-1.1]	-0.58		-0.8
La(II)					
$La^{+3} + 0.5\,H_2O \rightleftharpoons La^{2+} + H^+ + 0.25O_2(g)$	-	-	-	73.2$^{(21)}$ 84.0$^{(23)}$	73.2

Table 2.1. Lanthanum solids.

Reaction	log K EQ36 Hat.(H)	log K Literature(ref.)	Selec-ted.
La(s)			
$La(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons La^{3+} + 1.5\ H_2O$	-	182.5(21)	182.5
La(III)			
$La(OH)_3(am) \rightleftharpoons La^{3+} + 3OH^-$	-	-22.48(20), [-18.5](37)	-18.5
$La(OH)_3(s) \rightleftharpoons La^{3+} + 3OH^-$	-20.7(H)	-21.7(29), -21.05(20)	-21.7
$La_2O_3(c, hex.) + 6H^+ \rightleftharpoons 2\ La^{3+} + 3\ H_2O$	-	66.23(20), 66.13(19)	66.2
$La_2(CO_3)_3{\cdot}8H_2O(s) \rightleftharpoons 2La^{3+} + 3CO_3^{2-} + 8H_2O$	-33.4(H)	-35.25(76),[-35.45](50,73,76) -29.91(69), -32.6(20), -33.4(66), [-35.2](66)	-35.3
$La(OH)CO_3(s) \rightleftharpoons La^{3+} + OH + CO_3^{2-}$	-	-	-
$LaPO_4\ x\ H_2O(s) \rightleftharpoons La^{3+} + PO_4^{3-} + x\ H_2O$	-	-24.5(89) -25.3(90, 89)	-24.7
$LaF_3\ 0.5\ H_2O(s) \rightleftharpoons La^{3+} + 3\ F^- + 0.5\ H_2O$	-	-18.9(101), -20.2(101), -20.5(102), -17.1(103), -18.7(104), -18.5(105)	-18.7
$LaCl_3\ (s) \rightleftharpoons La^{3+} + 3\ Cl^-$	-	14.43(20)	14.4
$LaCl_3{\cdot}7H_2O(s) \rightleftharpoons La^{3+} + 3Cl^- + 7H_2O$	-	4.73(20)	4.7

Table 3. Cerium solution species.

Reaction	log K Lee&By.	log K Wood	log K Mill.	log K Lit.(ref.)	Selec-ted.
$CeOH^{2+} \rightleftharpoons Ce^{3+} + OH^-$	-5.59	-5.7	-5.60	-5.7(29) -5.7(30*)	-5.65
$Ce(OH)_2^+ \rightleftharpoons Ce^{3+} + 2OH^-$	-10.40	-	-	-10.4(29) -11.3(30*)	-10.4
$Ce(OH)_3 \rightleftharpoons Ce^{3+} + 3OH^-$	-14.77	-	-	-14.8(29) -14.9(30*)	-14.8
$Ce_3(OH)_5^{4+} \rightleftharpoons 3Ce^{3+} + 5OH^-$	-	-	-	-36.5(29)	-36.5
$CeCO_3^+ \rightleftharpoons Ce^{3+} + CO_3^{-2}$	-7.40	-7.56	-6.95	-8.4(53) -7.4(64)	-7.5
$Ce(CO_3)_2^- \rightleftharpoons Ce^{3+} + 2CO_3^{-2}$	-12.18	-12.19	-11.50	-13.7(53) -12.63(64)	-12.5
$CeHCO_3^{2+} \rightleftharpoons Ce^{3+} + HCO_3^-$	-	-2.42	-1.95	-1.49(56*) [-2.46](64)	-2.2
$CeH_2PO_4^{2+} \rightleftharpoons Ce^{3+} + H_2PO_4^-$	-	-	-2.43	[-2.56](86,3) -2.33(82)	-2.5
$CeHPO_4^+ \rightleftharpoons Ce^{3+} + HPO_4^{-2}$	-	-	-4.98	[-5.5](86,3)	-5.2
$Ce(HPO_4)_2^- \rightleftharpoons Ce^{3+} + 2\ HPO_4^{-2}$	-	-	-8.34	[-9.1](86,3)	-8.7
$CePO_4 \rightleftharpoons Ce^{3+} + PO_4^{-3}$	-11.35	-	-	-11.73(86) -18.53(81)	*-11.35*
$Ce(PO_4)_2^{3-} \rightleftharpoons Ce^{3+} + 2\ PO_4^{-3}$	-18.48	-	-	-15.7(86*)	*-18.5*
$CeSO_4^+ \rightleftharpoons Ce^{3+} + SO_4^{-2}$	-	[-3.62]	-3.29		-3.4
$CeF^{2+} \rightleftharpoons Ce^{3+} + F^-$	-	-3.86	-3.28		-3.6
$CeF_2^+ \rightleftharpoons Ce^{3+} + 2\ F^-$		-7.30	-	[-6.4](1,2,5)	-6.4
$CeCl^{2+} \rightleftharpoons Ce^{3+} + Cl^-$	-	-0.47	-0.31		-0.4
$CeNO_3^+ \rightleftharpoons Ce^{3+} + NO_3^-$	-	-1.13	-0.69		-0.9
Ce(IV)					
$Ce^{3+} + H^+ + 0.25\ O_2(g) \rightleftharpoons Ce^{4+} + 0.5\ H_2O$	-	-	-	-8.64(25) -8.97(21)	-8.64
$CeOH^{3+} \rightleftharpoons Ce^{4+} + OH^-$	-	-	-	-15.2(29*) -14.5(95) -19.2(21)	-17.2
$Ce(OH)_2^{2+} \rightleftharpoons Ce^{4+} + 2OH^-$	-	-	-	-28.5(29*) -30(95)	-30.0
$Ce_2(OH)_2^{6+} \rightleftharpoons 2Ce^{4+} + 2OH^-$	-	-	-	-31.8(29*) -31(95)	-31.0
Ce(II)					
$Ce^{+3} + 0.5\ H_2O \rightleftharpoons Ce^{2+} + H^+ + 0.25\ O_2(g)$	-	-	-	76.6(23) 84.4(21)	84.4

Table 3.1. Cerium solids.

Reaction	log K Literature(ref.)	Selec-ted.
Ce(s)		
$Ce(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Ce^{3+} + 1.5\ H_2O$	180.7(21)	180.7
Ce(III)		
$Ce(OH)_3(am) \rightleftharpoons Ce^{3+} + 3OH^-$	-21.24(30*),	-20.8
$Ce(OH)_3(s) \rightleftharpoons Ce^{3+} + 3OH^-$	-22.1(29),	-22.1
$Ce_2O_3(c, hex., \alpha) + 6H^+ \rightleftharpoons 2\ Ce^{3+} + 3\ H_2O$	62.3(19)	62.3
$Ce_2(CO_3)_3{\cdot}8H_2O(s) \rightleftharpoons 2Ce^{3+} + 3CO_3^{2-} + 8H_2O$	-35.55(53), -35.24(53,73,76)	-35.1
$Ce(OH)CO_3(s) \rightleftharpoons Ce^{3+} + OH + CO_3^{2-}$	-	-
$CePO_4\ x\ H_2O \rightleftharpoons Ce^{3+} + PO_4^{3-} + x\ H_2O$	-21.3(92*), [-24.6](89, 74)	-24.6
$CeF_3\ 0.5\ H_2O \rightleftharpoons Ce^{3+} + 3\ F^- + 0.5\ H_2O$	-18.7(9),-19.2(101),-20.5(101), -19.8(102),-17.1(103),-19.1(104)	-18.8
Ce(IV)		
$CeO_2(c) + 4\ H^+ \rightleftharpoons Ce^{4+} + 2\ H_2O$	-8.16(17, 29)	-8.16
$Ce_3(PO_4)_4(s) \rightleftharpoons Ce^{4+} + 3\ PO_4^{3-}$	-90.1(92*)	*-90.1*

Table 4. Samarium solution species.

Reaction	log K Hatches	log K Wood	log K Mill.	log K Lit.(ref.)	Selec-ted.
$SmOH^{2+} \rightleftharpoons Sm^{3+} + OH^-$	-6.1	-6.1	-5.81	-6.04(3), -6.4(31*) -4.97(45*)	-6.1
$Sm(OH)_2^+ \rightleftharpoons Sm^{3+} + 2OH^-$	-	[-11.5](29)	-	-11.5(3), -12.8(31*) -11.9(45*)	-11.5
$Sm(OH)_3 \rightleftharpoons Sm^{3+} + 3OH^-$	-	[-16.1](29)	-	-16.09(3) -18.6(31*)	-16.1
$Sm(OH)_4 \rightleftharpoons Sm^{3+} + 4OH^-$	-	-	-	-19.0(35*) [-19.1](29)	-19.1
$SmCO_3^+ \rightleftharpoons Sm^{3+} + CO_3^{-2}$	-	[-7.92]	-7.30	-7.93(3) -7.88(64)	-7.8
$Sm(CO_3)_2^- \rightleftharpoons Sm^{3+} + 2CO_3^{-2}$	-	[-12.81]	-12.11	-13.37(3, 64)	-12.8
$SmHCO_3^{2+} \rightleftharpoons Sm^{3+} + HCO_3^-$	-	[-2.12]	-1.75	[-2.52](64)	-2.1
$SmH_2PO_4^{2+} \rightleftharpoons Sm^{3+} + H_2PO_4^-$	-	-	-2.23	[-2.79](3, 86)	-2.35
$SmHPO_4^+ \rightleftharpoons Sm^{3+} + HPO_4^{-2}$	-	-	-5.35	[-5.9](3, 86)	-5.6
$Sm(HPO_4)_2^- \rightleftharpoons Sm^{3+} + 2\ HPO_4^{-2}$	-	-	-8.96	[-9.9](3, 86)	-9.4
$SmPO_4 \rightleftharpoons Sm^{3+} + PO_4^{-3}$	-	-	-	-12.11(3)	*-12.1*
$Sm(PO_4)_2^{3-} \rightleftharpoons Sm^{3+} + 2\ PO_4^{-3}$	-	-	-	-20.42(3)	*-20.4*
$SmSO_4^+ \rightleftharpoons Sm^{3+} + SO_4^{-2}$	-3.54	-3.66	-3.28		-3.5
$Sm(SO_4)_2 \rightleftharpoons Sm^{3+} + 2SO_4^{-2}$	-	-5.24	-		-5.2
$SmF^{2+} \rightleftharpoons Sm^{3+} + F^-$	-	-4.17	-3.58		-3.8
$SmCl^{2+} \rightleftharpoons Sm^{3+} + Cl^-$	-	-0.48	-0.30		-0.4
$SmNO_3^+ \rightleftharpoons Sm^{3+} + NO_3^-$	-	[-1.2]	-0.78		-0.9
Sm(II)					
$Sm^{+3} + 0.5\ H_2O \rightleftharpoons Sm^{2+} + H^+ + 0.25O_2(g)$	-	-	-	47.0(23) 47.2(21)	47.2

Table 4.1. Samarium solids.

Reaction	log K Hatches	log K Literature(ref.)	Selec- ted.
Sm(s)			
$Sm(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Sm^{3+} + 1.5\ H_2O$	-	178.8(21)	178.8
Sm(III)			
$Sm(OH)_3(am) \rightleftharpoons Sm^{3+} + 3OH^-$	-	-23.84(31*),	-23.4
$Sm(OH)_3(s) \rightleftharpoons Sm^{3+} + 3OH^-$	-25.5	-25.5(29),	-25.5
Sm_2O_3(c, mon.) $+ 6H^+ \rightleftharpoons 2\ Sm^{3+} + 3\ H_2O$	-	42.9(19),	42.9
$Sm_2(CO_3)_3 \rightleftharpoons 2\ Sm^{3+} + 3\ CO_3^{2-}$	-26.75	-34.4(69), -32.5(66)	-34.5
$Sm(OH)CO_3(s) \rightleftharpoons Sm^{3+} + OH + CO_3^{2-}$	-	-	-
$SmPO_4\ x\ H_2O\ (s) \rightleftharpoons Sm^{3+} + PO_4^{3-} + x\ H_2O$	-	[-24.5](89,91,92,74)	-24.5
$SmF_3\ 0.5\ H_2O\ (s) \rightleftharpoons Sm^{3+} + 3\ F^- + 0.5\ H_2O$	-	-17.9(101),-19.3(101) -19.0(102),-16.0(103)	-17.5
$Sm_2(SO_4)_3(s) \rightleftharpoons 2\ Sm^{3+} + 3\ SO_4^{2-}$	-9.8		-9.8

Table 5. Praseodymium solution species.

Reaction	log K Lee&By.	log K Wood	log K Mill.	log K Lit.(ref.)	Selec-ted.
$PrOH^{2+} \rightleftharpoons Pr^{3+} + OH^-$	-5.73	-5.9	-5.60	-5.9(29)	-5.8
$Pr(OH)_2^+ \rightleftharpoons Pr^{3+} + 2OH^-$	-10.73	-	-	[-11.0](29)	-10.8
$Pr(OH)_3 \rightleftharpoons Pr^{3+} + 3OH^-$	-15.37	-	-	[-15.6](29)	-15.4
$PrCO_3^+ \rightleftharpoons Pr^{3+} + CO_3^{-2}$	-7.57	[-7.65]	-7.03	-7.56(64)	-7.55
$Pr(CO_3)_2^- \rightleftharpoons Pr^{3+} + 2CO_3^{-2}$	-12.54	[-12.35]	-11.65	-12.91(64)	-12.55
$PrHCO_3^{2+} \rightleftharpoons Pr^{3+} + HCO_3^-$	-	[-2.24]	-1.89	[-2.48](64)	-2.15
$PrH_2PO_4^{2+} \rightleftharpoons Pr^{3+} + H_2PO_4^-$	-	-	-2.37	[-2.63](3,86)	-2.45
$PrHPO_4^+ \rightleftharpoons Pr^{3+} + HPO_4^{-2}$	-	-	-5.08	[-5.63](3,86)	-5.4
$Pr(HPO_4)_2^- \rightleftharpoons Pr^{3+} + 2\ HPO_4^{-2}$	-	-	-8.50	[-9.3](3,86)	-8.9
$PrPO_4 \rightleftharpoons Pr^{3+} + PO_4^{-3}$	-11.60	-	-		*-11.60*
$Pr(PO_4)_2^{3-} \rightleftharpoons Pr^{3+} + 2\ PO_4^{-3}$	-19.08	-	-		*-19.08*
$PrSO_4^+ \rightleftharpoons Pr^{3+} + SO_4^{-2}$	-	-3.62	-3.27		-3.4
$Pr(SO_4)_2 \rightleftharpoons Pr^{3+} + 2SO_4^{-2}$	-	-4.92	-		-4.9
$PrF^{2+} \rightleftharpoons Pr^{3+} + F^-$	-	-4.06	-3.48		-3.7
$PrCl^{2+} \rightleftharpoons Pr^{3+} + Cl^-$	-	-0.44	-0.32		-0.3
$PrNO_3^+ \rightleftharpoons Pr^{3+} + NO_3^-$	-	-1.2	-0.69		-0.9
Pr(II)					
$Pr^{+3} + 0.5\ H_2O \rightleftharpoons Pr^{2+} + H^+ + 0.25\ O_2(g)$	-	-	-	66.4(23) 80.7(21)	80.7

Table 5.1 Praseodymium solids.

Reaction	log K Literature(ref.)	Selec-ted.
Pr(s)		
$Pr(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Pr^{3+} + 1.5\ H_2O$	181.4(21)	181.4
Pr(III)		
$Pr(OH)_3(am) \rightleftharpoons Pr^{3+} + 3OH^-$	[-20.9](30-37),	-20.9
$Pr(OH)_3(s) \rightleftharpoons Pr^{3+} + 3OH^-$	-22.5(29), -22.08(48)	-22.4
Pr_2O_3(c, hex.) $+ 6H^+ \rightleftharpoons 2\ Pr^{3+} + 3\ H_2O$	61.4(19),	61.4
$Pr_2(CO_3)_3(s) \rightleftharpoons 2\ Pr^{3+} + 3\ CO_3^{2-}$	-33.2(69), -27.0(65*),	-34.8
$Pr(OH)CO_3(s) \rightleftharpoons Pr^{3+} + OH + CO_3^{2-}$	-	-
$PrPO_4\ x\ H_2O\ (s) \rightleftharpoons Pr^{3+} + PO_4^{3-} + x\ H_2O$	-26.0(89*), [-24.6](89, 74)	-24.6
$PrF_3\ 0.5\ H_2O\ (s) \rightleftharpoons Pr^{3+} + F^- + 0.5\ H_2O$	-18.9(101), -20.2(101), -18.8(102), -17.0(103)	-18.7

Table 6. Neodymium solution species.

Reaction	log K Lee&Byr.	log K Wood	log K Mill.	log K Lit.(ref.)	Selec-ted.
$NdOH^{2+} \rightleftharpoons Nd^{3+} + OH^-$	-5.84	-6.0	-5.67	-6.0(29) -5.7(36*)	-5.9
$Nd(OH)_2^+ \rightleftharpoons Nd^{3+} + 2OH^-$	-10.96	-	-	-11.4(36*) -11.1(29)	-11.1
$Nd(OH)_3 \rightleftharpoons Nd^{3+} + 3\ OH^-$	-15.60	-	-	-17.0(36*) -15.5(29)	-15.6
$Nd(OH)_4^- \rightleftharpoons Nd^{3+} + 4\ OH^-$	-	-	-	-18.9(29)	-18.9
$Nd_2(OH)_2^{+4} \rightleftharpoons 2Nd^{3+} + 2OH^-$	-	-	-	-15.9(36*) -14.14(29)	-14.1
$NdCO_3^+ \rightleftharpoons Nd^{3+} + CO_3^{-2}$	-7.69	[-7.75]	-7.13	-7.67(64)	-7.6
$Nd(CO_3)_2^- \rightleftharpoons Nd^{3+} + 2CO_3^{-2}$	-12.79	[-12.5]	-11.80	-13.09(64)	-12.6
$NdHCO_3^{2+} \rightleftharpoons Nd^{3+} + HCO_3^-$	-	[-2.14]	-1.83	[-2.51](64)	-2.12
$NdH_2PO_4^{2+} \rightleftharpoons Nd^{3+} + H_2PO_4^-$	-	-	-2.31	[-2.68](3,86) -1.28(84*)	-2.4
$NdHPO_4^+ \rightleftharpoons Nd^{3+} + HPO_4^{-2}$	-	-	-5.18	[-5.72](3,86)	-5.4
$Nd(HPO_4)_2^- \rightleftharpoons Nd^{3+} + 2\ HPO_4^{-2}$	-	-	-8.66	[-9.47](3,86)	-9.1
$NdPO_4 \rightleftharpoons Nd^{3+} + PO_4^{-3}$	-11.78	-	-	-	-11.8
$Nd(PO_4)_2^{3-} \rightleftharpoons Nd^{3+} + 2\ PO_4^{-3}$	-19.50	-	-	-	-19.5
$NdSO_4^+ \rightleftharpoons Nd^{3+} + SO_4^{-2}$	-	-3.65	-3.26		-3.5
$Nd(SO_4)_2 \rightleftharpoons Nd^{3+} + 2SO_4^{-2}$	-	-5.15	-		-5.1
$NdF^{2+} \rightleftharpoons Nd^{3+} + F^-$	-	-4.14	-3.56		-3.8
$NdCl^{2+} \rightleftharpoons Nd^{3+} + Cl^-$	-	-0.40	-0.32		-0.35
$NdNO_3^+ \rightleftharpoons Nd^{3+} + NO_3^-$		-1.25	-0.79		-1.0
Nd(II)					
$Nd^{+3} + 0.5\ H_2O \rightleftharpoons Nd^{2+} + H^+ + 0.25\ O_2(g)$				64.7(23) 65.1(21)	65.1

Table 6.1. Neodymium solids.

Reaction	log K Literature(ref.)	Selec-ted.
Nd(s)		
$Nd(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Nd^{3+} + 1.5\ H_2O$	180.0(21)	180.0
Nd(III)		
$Nd(OH)_3(am) \rightleftharpoons Nd^{3+} + 3OH^-$	-22.4(36*),	-21.5
$Nd(OH)_3(s) \rightleftharpoons Nd^{3+} + 3OH^-$	-23.4(29), -23.9(48), [-28.7](74*)	-23.9
$Nd(OH)_3(c) \rightleftharpoons Nd^{3+} + 3OH^-$	-26.2(46)	-26.2
Nd_2O_3(c, hex.) $+ 6H^+ \rightleftharpoons Nd^{3+} + 3\ H_2O$	58.6(19)	58.6
$Nd_2(CO_3)_3 \rightleftharpoons 2\ Nd^{3+} + 3\ CO_3^{2-}$	-33.0(66), -34.1(69), -31.35(71*,72*), -35.3(12,69), [-34.6](71,72,76,73), [-34.7](66)	-34.65
$Nd(OH)CO_3(s) \rightleftharpoons Nd^{3+} + OH + CO_3^{2-}$	-19.94(72*), -21.74(77) -19.19(71*), -22.54(74)	-21.5
$NdPO_4$ x H_2O (s) $\rightleftharpoons Nd^{3+} + PO_4^{3-}$ + x H_2O	-25.9(89), -24.45(74) [-24.6](89)	-24.5
$NdF_3\ 0.5\ H_2O$ (s) $\rightleftharpoons Nd^{3+} + 3\ F^- + 0.5\ H_2O$	-18.6(101),-19.9(101), -19.3(102) -17.1(103), - 20.3(104)	-18.6

Table 7. Prometium solution species.

Reaction	log K Lee&By.	log K Wood	log K Mill.	log K Lit.(ref.)	Selec-ted.
$PmOH^{2+} \rightleftharpoons Pm^{3+} + OH^-$	-5.94	-6.05	-5.77	[-6.05](29)	-6.0
$Pm(OH)_2^+ \rightleftharpoons Pm^{3+} + 2OH^-$	-11.22	-	-		-11.2
$Pm(OH)_3 \rightleftharpoons Pm^{3+} + 3OH^-$	-15.85	-	-		-15.8
$PmCO_3^+ \rightleftharpoons Pm^{3+} + CO_3^{-2}$	-7.81	[-7.84]	-7.22	7.78(64)	-7.7
$Pm(CO_3)_2^- \rightleftharpoons Pm^{3+} + 2CO_3^{-2}$	-13.08	[-12.65]	-11.96	-13.23(64)	-12.7
$PmHCO_3^{2+} \rightleftharpoons Pm^{3+} + HCO_3^-$	-	[-2.11]	-1.79	[-2.52](64)	-2.1
$PmH_2PO_4^{2+} \rightleftharpoons Pm^{3+} + H_2PO_4^-$	-	-	-2.27	[-2.74](3,86) -2.51(82)	-2.4
$PmHPO_4^+ \rightleftharpoons Pm^{3+} + HPO_4^{-2}$	-	-	-5.27	[-5.8](3,86) -4.05(82*,85)	-5.5
$Pm(HPO_4)_2^- \rightleftharpoons Pm^{3+} + 2\ HPO_4^{-2}$	-	-	-8.81	[-9.6](3,86)	-9.2
$PmPO_4 \rightleftharpoons Pm^{3+} + PO_4^{-3}$	-11.95	-	-		*-11.95*
$Pm(PO_4)_2^{3-} \rightleftharpoons Pm^{3+} + 2\ PO_4^{-3}$	-19.96	-	-		*-19.96*
$PmSO_4^+ \rightleftharpoons Pm^{3+} + SO_4^{-2}$	-	[-3.66]	-3.34		-3.5
$Pm(SO_4)_2 \rightleftharpoons Pm^{3+} + 2SO_4^{-2}$	-	[-5.33]	-		-5.2
$PmF^{2+} \rightleftharpoons Pm^{3+} + F^-$	-	[-4.16]	-3.63		-3.8
$PmCl^{2+} \rightleftharpoons Pm^{3+} + Cl^-$	-	[-0.38	-0.31		-0.34
$PmNO_3^+ \rightleftharpoons Pm^{3+} + NO_3^-$	-	-1.31	-0.88		-1.1
Pm(II)					
$Pm^{+3} + 0.5\ H_2O \rightleftharpoons Pm^{2+} + H^+ + 0.25O_2(g)$				64.7(23) 66.0(21)	66.0

Table 7.1. Prometium solids.

Reaction	**log K Literature(ref.)**	**Selec-ted.**
Pm(s)		
$Pm(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Pm^{3+} + 1.5\ H_2O$	178.5(21)	178.5
Pm(III)		
$Pm(OH)_3\ (am) \rightleftharpoons Pm^{3+} + 3OH^-$	[-24.1](30-37*)	-23.7
$Pm(OH)_3\ (s) \rightleftharpoons Pm^{3+} + 3OH^-$	-24.5(29)	-24.5
Pm_2O_3 (c, hex.) $+ 6H^+ \rightleftharpoons Pm^{3+} + 3\ H_2O$	[48.8](19)	*48.8*
$Pm_2(CO_3)_3\ (s) \rightleftharpoons 2\ Pm^{3+} + 3\ CO_3^{2-}$	[-34.3](69), [-34.55](76,73)	-34.55
$Pm(OH)CO_3\ (s) \rightleftharpoons Pm^{3+} + OH + CO_3^{2-}$	-	-
$PmPO_4\ x\ H_2O\ (s) \rightleftharpoons Pm^{3+} + PO_4^{3-} + x\ H_2O$	[-24.5](89, 74)	*-24.5*
$PmF_3\ 0.5\ H_2O\ (s) \rightleftharpoons Pm^{3+} + 3\ F^- + 0.5\ H_2O$	-18.3(101),-19.5 (101), -16.5(103)	-18.1

Table 8. Gadolinium solution species.

Reaction	log K Lee&By.	log K Wood	log K Miller.	log K Lit.$^{(ref.)}$	Selec-ted.
$GdOH^{2+} \rightleftharpoons Gd^{3+} + OH^-$	-6.07	-6.0	-5.79	$-6.0^{(29)}$, $-9.3^{(40)}$ $-6.0^{(32^*)}$	-6.0
$Gd(OH)_2^+ \rightleftharpoons Gd^{3+} + 2OH^-$	-11.63	-	-	$-11.6^{(29)}$ $-12.4^{(32^*)}$	-11.8
$Gd(OH)_3 \rightleftharpoons Gd^{3+} + 3OH^-$	-16.72	-	-	$-16.8^{(29)}$ $-19.0^{(32^*)}$	-17.5
$Gd(OH)_4^- \rightleftharpoons Gd^{3+} + 4OH^-$	-	-	-	$-21.6^{(29)}$	-22.1
$GdCO_3^+ \rightleftharpoons Gd^{3+} + CO_3^{-2}$	-7.97	[-8.05]	-7.44	$-7.82^{(64)}$	-7.8
$Gd(CO_3)_2^- \rightleftharpoons Gd^{3+} + 2CO_3^{-2}$	-13.52	[-13.08]	-12.39	$-13.35^{(64)}$	-13.1
$GdHCO_3^{2+} \rightleftharpoons Gd^{3+} + HCO_3^-$	-	[-2.1]	-1.72	$-2.57^{(64,86)}$	-2.1
$GdH_2PO_4^{2+} \rightleftharpoons Gd^{3+} + H_2PO_4^-$	-	-	-2.20	$-2.81^{(85)}$ $-2.74^{(86)}$	-2.4
$GdHPO_4^+ \rightleftharpoons Gd^{3+} + HPO_4^{-2}$	-	-	-5.49	$-5.70^{(85)}$ $-5.91^{(86)}$	-5.7
$Gd(HPO_4)_2^- \rightleftharpoons Gd^{3+} + 2\ HPO_4^{-2}$	-	-	-9.24	$-9.5^{(85)}$ $-9.97^{(86)}$	-9.6
$GdPO_4 \rightleftharpoons Gd^{3+} + PO_4^{-3}$	-12.20	-	-	$12.19^{(86)}$	-12.2
$Gd(PO_4)_2^{3-} \rightleftharpoons Gd^{3+} + 2\ PO_4^{-3}$	-20.71	-	-	-	-20.7
$GdSO_4^+ \rightleftharpoons Gd^{3+} + SO_4^{-2}$	-	-3.66	-3.25		-3.4
$Gd(SO_4)_2 \rightleftharpoons Gd^{3+} + 2SO_4^{-2}$	-	-5.20	-		-5.1
$GdF^{2+} \rightleftharpoons Gd^{3+} + F^-$	-	-4.36	-3.75		-4.1
$GdF_2^{2+} \rightleftharpoons Gd^{3+} + 2F^-$	-	-8.27	-		-7.2
$GdCl^{2+} \rightleftharpoons Gd^{3+} + Cl^-$	-	-0.33	-0.28		-0.3
$GdNO_3^+ \rightleftharpoons Gd^{3+} + NO_3^-$	-	-1.1	-0.47		-0.8
Gd(II)					
$Gd^{+3} + 0.5\ H_2O \rightleftharpoons Gd^{2+} + H^+ + 0.25O_2(g)$	-	-	-	$86.7^{(23)}$ $85.4^{(21)}$	85.4

Table 8.1. Gadolinium solids.

Reaction	log K Literature(ref.)	Selec-ted.
Gd(s)		
$Gd(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Gd^{3+} + 1.5\ H_2O$	178.6(21)	178.6
Gd(III)		
$Gd(OH)_3(am) \rightleftharpoons Gd^{3+} + 3OH^-$	-24.34(32*)	-24.0
$Gd(OH)_3(s) \rightleftharpoons Gd^{3+} + 3OH^-$	-26.4(29), -26.9(48)	-26.4
Gd_2O_3(c, monocl.) $+ 6H^+ \rightleftharpoons Gd^{3+} + 3\ H_2O$	53.8(19)	53.8
$Gd(OH)CO_3\,(s) \rightleftharpoons Gd^{3+} + OH^- + CO_3^{2-}$	-	-
$Gd_2(CO_3)_3\ (S) \rightleftharpoons 2\ Gd^{3+} + 3\ CO_3^{2-}$	-35.45(69),-32.2(66), [-34.4](66)	-34.7
$GdPO_4\ x\ H_2O\ (s) \rightleftharpoons Gd^{3+} + PO_4^{3-} + x\ H_2O$	-25.1(91,89), [-24.3](89, 74)	-24.3
$GdF_3\ 0.5\ H_2O\ (s) \rightleftharpoons Gd^{3+} + 3\ F^- + 0.5\ H_2O$	-16.8(101), -18.1(101), -18.6(102), -15.3(103),	-16.9

Table 9. Terbium solution species.

Reaction	log K Lee&By.	log K Wood	log K Mill.	log K Lit.(ref.)	Selec-ted.
$TbOH^{2+} \rightleftharpoons Tb^{3+} + OH^-$	-6.14	-6.1	-5.98	-6.1(29) -8.4(44*)	-6.1
$Tb(OH)_2^+ \rightleftharpoons Tb^{3+} + 2OH^-$	-11.82	-	-	[-11.7](29) -14.3(44*)	-11.7
$Tb(OH)_3 \rightleftharpoons Tb^{3+} + 3OH^-$	-16.92	-	-	[-16.95](29)	-16.9
$TbCO_3^+ \rightleftharpoons Tb^{3+} + CO_3^{-2}$	-8.08	[-8.1]	-7.50	-7.93(64)	-7.9
$Tb(CO_3)_2^- \rightleftharpoons Tb^{3+} + 2CO_3^{-2}$	-13.73	[-13.2]	-12.52	-13.53(64)	-13.1
$TbHCO_3^{2+} \rightleftharpoons Tb^{3+} + HCO_3^-$	-	[-2.13]	-1.71	[-2.55](64)	-2.1
$TbH_2PO_4^{2+} \rightleftharpoons Tb^{3+} + H_2PO_4^-$	-	-	-2.19	[-2.77](86,3)	-2.4
$TbHPO_4^+ \rightleftharpoons Tb^{3+} + HPO_4^{-2}$	-	-	-5.54	[-5.97](86,3)	-5.8
$Tb(HPO_4)_2^- \rightleftharpoons Tb^{3+} + 2\ HPO_4^{-2}$	-	-	-9.37	[-10.1](86,3)	-9.7
$TbPO_4 \rightleftharpoons Tb^{3+} + PO_4^{-3}$	-12.39	-	-	-	-12.4
$Tb(PO_4)_2^{3-} \rightleftharpoons Tb^{3+} + 2\ PO_4^{-3}$	-21.02	-	-	-	-21.0
$TbSO_4^+ \rightleftharpoons Tb^{3+} + SO_4^{-2}$	-	-3.63	-3.20		-3.4
$Tb(SO_4)_2 \rightleftharpoons Tb^{3+} + 2SO_4^{-2}$	-	-5.13	-		-5.0
$TbF^{2+} \rightleftharpoons Tb^{3+} + F^-$	-	-4.47	-3.85		-4.2
$TbCl^{2+} \rightleftharpoons Tb^{3+} + Cl^-$	-	-0.32	-0.27		-0.3
$TbNO_3^+ \rightleftharpoons Tb^{3+} + NO_3^-$	-	-0.97	-0.51		-0.7
Tb(II)					
$Tb^{+3} + 0.5\ H_2O \rightleftharpoons Tb^{2+} + H^+ + 0.25\ O_2(g)$	-	-	-	83.3(23) 79.5(21)	79.5

Table 9.1. Terbium solids.

Reaction	log K Literature(ref.)	Selec-ted.
Tb(s)		
$Tb(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Tb^{3+} + 1.5\ H_2O$	179.2(21)	
Tb(III)		
$Tb(OH)_3(am) \rightleftharpoons Tb^{3+} + 3OH^-$	[-23.2](30-37),	-23.2
$Tb(OH)_3(s) \rightleftharpoons Tb^{3+} + 3OH^-$	-25.5(29), -26.31(48)	-26.3
Tb_2O_3(c, cub.) $+ 6H^+ \rightleftharpoons Tb^{3+} + 3\ H_2O$	47.1(19),	47.1
$Tb(OH)CO_3(s) \rightleftharpoons Tb^{3+} + OH^- + CO_3^{2-}$	-	-
$Tb_2(CO_3)_3\ (s) \rightleftharpoons 2\ Tb^{3+} + 3\ CO_3^{2-}$	-34.86(68),	-34.2
$TbPO_4\ x\ H_2O\ (s) \rightleftharpoons Tb^{3+} + PO_4^{3-} + x\ H_2O$	[- 24.3](89, 74)	-24.3
$TbF_3\ 0.5\ H_2O\ (s) \rightleftharpoons Tb^{3+} + 3\ F^- + 0.5\ H_2O$	-16.7(101),-18.0(101),-18.5(102) -14.9(103), -16.44(107)	-16.7

Table 10. Dysprosium solution species.

Reaction	log K Lee&Byr	log K Wood	log K Mill.	log K Lit.(ref.)	Selec-ted.
$DyOH^{2+} \rightleftharpoons Dy^{3+} + OH^-$	-6.19	-6.0	-6.04	-6.0(29)	-6.05
$Dy(OH)_2^+ \rightleftharpoons Dy^{3+} + 2OH^-$	-11.90	-	-	-11.8(29)	-11.8
$Dy(OH)_3 \rightleftharpoons Dy^{3+} + 3OH^-$	-17.17	-	-	-17.3(29)	-17.3
$Dy(OH)_4^- \rightleftharpoons Dy^{3+} + 4OH^-$				-22.5(29)	-22.5
$DyCO_3^+ \rightleftharpoons Dy^{3+} + CO_3^{-2}$	-8.14	[-8.13]	-7.55	-8.0(64)	-7.95
$Dy(CO_3)_2^- \rightleftharpoons Dy^{3+} + 2CO_3^{-2}$	-13.83	[-13.3]	-12.65	-13.66(64)	-13.2
$DyHCO_3^{2+} \rightleftharpoons Dy^{3+} + HCO_3^-$	-	[-2.15]	-1.72	[-2.48](64)	-2.15
$DyH_2PO_4^{2+} \rightleftharpoons Dy^{3+} + H_2PO_4^-$	-	-	-2.20	[-2.76](86,3)	-2.4
$DyHPO_4^+ \rightleftharpoons Dy^{3+} + HPO_4^{-2}$	-	-	-5.60	[-6.0](66,3)	-5.8
$Dy(HPO_4)_2^- \rightleftharpoons Dy^{3+} + 2\ HPO_4^{-2}$	-	-	-9.49	[-10.2](86,3)	-9.8
$DyPO_4 \rightleftharpoons Dy^{3+} + PO_4^{-3}$	-12.52	-	-		*-12.5*
$Dy(PO_4)_2^{3-} \rightleftharpoons Dy^{3+} + 2\ PO_4^{-3}$	-21.22	-	-		*-21.2*
$DySO_4^+ \rightleftharpoons Dy^{3+} + SO_4^{-2}$	-	-3.83	-3.15		-3.5
$Dy(SO_4)_2 \rightleftharpoons Dy^{3+} + 2SO_4^{-2}$	-	-5.03	-		-5.0
$DyF^{2+} \rightleftharpoons Dy^{3+} + F^-$	-	-4.51	-3.89		-4.2
$DyCl^{2+} \rightleftharpoons Dy^{3+} + Cl^-$	-	-0.31	-0.27		-0.3
$DyNO_3^+ \rightleftharpoons Dy^{3+} + NO_3^-$	-	[-1.05]	-0.15		-0.6
Dy(II)					
$Dy^{+3} + 0.5\ H_2O \rightleftharpoons Dy^{2+} + H^+ + 0.25\ O_2(g)$	-	-	-	64.7(23) 61.8(21)	61.8

Table 10.1. Dysprosium solids.

Reaction	log K Literature(ref.)	Selected.
Dy(s)		
$Dy(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Dy^{3+} + 1.5\ H_2O$	178.6(21)	178.6
Dy(III)		
$Dy(OH)_3(am) \rightleftharpoons Dy^{3+} + 3OH^-$	[-24.5](30-37),	-24.5
$Dy(OH)_3(s) \rightleftharpoons Dy^{3+} + 3OH^-$	-26.1(29)	-26.1
Dy_2O_3(c, cub.) + $6H^+ \rightleftharpoons Dy^{3+} + 3\ H_2O$	47.0(19),	47.0
$Dy(OH)CO_3(s) \rightleftharpoons Dy^{3+} + OH^- + CO_3^{2-}$	-	-
$Dy_2(CO_3)_3\ (s) \rightleftharpoons 2\ Dy^{3+} + 3\ CO_3^{2-}$	-31.5(66), -33.97(69), [-34.0](66)	-34.0
$DyPO_4\ x\ H_2O\ (s) \rightleftharpoons Dy^{3+} + PO_4^{3-} + x\ H_2O$	[-24.3](89,74)	-24.3
$DyF_3\ 0.5\ H_2O\ (s) \rightleftharpoons Dy^{3+} + 3\ F^- + 0.5\ H_2O$	-16.3(101),-17.6(101), -18.2(102), -14.6(103)	-16.5

Table 11. Holmium solution species.

Reaction	log K Lee&Byr	log K Wood	log K Mill.	log K Lit.(ref.)	Selec-ted.
$HoOH^{2+} \rightleftharpoons Ho^{3+} + OH^-$	-6.22	-6.0	-6.01	-6.0(29)	-6.1
$Ho(OH)_2^+ \rightleftharpoons Ho^{3+} + 2OH^-$	-11.93	-	-	-11.95(29)	-11.9
$Ho(OH)_3 \rightleftharpoons Ho^{3+} + 3OH^-$	-17.44	-	-	-17.55(29)	-17.5
$HoCO_3^+ \rightleftharpoons Ho^{3+} + CO_3^{-2}$	-8.18	[-8.17]	-7.59	-8.04(64)	-8.0
$Ho(CO_3)_2^- \rightleftharpoons Ho^{3+} + 2CO_3^{-2}$	-13.86	[-13.5]	-12.77	-13.71(64)	-13.3
$HoHCO_3^{2+} \rightleftharpoons Ho^{3+} + HCO_3^-$	-	[-2.2]	-1.73	[-2.44](64)	-2.17
$HoH_2PO_4^{2+} \rightleftharpoons Ho^{3+} + H_2PO_4^-$	-	-	-2.21	[-2.75](86,3)	-2.3
$HoHPO_4^+ \rightleftharpoons Ho^{3+} + HPO_4^{-2}$	-	-	-5.64	[-6.03](86,3)	-5.8
$Ho(HPO_4)_2^- \rightleftharpoons Ho^{3+} + 2\ HPO_4^{-2}$	-	-	-9.62	[-10.2](86,3)	-9.9
$HoPO_4 \rightleftharpoons Ho^{3+} + PO_4^{-3}$	-12.59	-	-	-	-12.6
$Ho(PO_4)_2^{3-} \rightleftharpoons Ho^{3+} + 2\ PO_4^{-3}$	-21.27	-	-	-	*-21.3*
$HoSO_4^+ \rightleftharpoons Ho^{3+} + SO_4^{-2}$	-	-3.60	-3.16		-3.4
$Ho(SO_4)_2 \rightleftharpoons Ho^{3+} + 2SO_4^{-2}$	-	-4.90	-		-4.9
$HoF^{2+} \rightleftharpoons Ho^{3+} + F^-$	-	-4.57	-3.95		-4.3
$HoCl^{2+} \rightleftharpoons Ho^{3+} + Cl^-$	-	-0.30	-0.27		-0.3
$HoNO_3^+ \rightleftharpoons Ho^{3+} + NO_3^-$	-	[-0.8]	-0.25		-0.5
Ho(II)					
$Ho^{+3} + 0.5\ H_2O \rightleftharpoons Ho^{2+} + H^+ + 0.25\ O_2(g)$	-	-	-	69.8(23) 68.1(21)	68.1

Table 11.1. Holmium solids.

Reaction	log K Literature(ref.)	Selec-ted.
Ho(s)		
$Ho(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Ho^{3+} + 1.5\ H_2O$	180.6(21)	180.6
Ho(III)		
$Ho(OH)_3(am) \rightleftharpoons Ho^{3+} + 3OH^-$	[-24.2](30-37),	-24.2
$Ho(OH)_3(s) \rightleftharpoons Ho^{3+} + 3OH^-$	-26.6(29), -26.6(48)	-26.6
Ho_2O_3(c, cub.) $+ 6H^+ \rightleftharpoons Ho^{3+} + 3\ H_2O$	47.3(19),	47.3
$Ho(OH)CO_3(s) \rightleftharpoons Ho^{3+} + OH^- + CO_3^{2-}$	-	-
$Ho_2(CO_3)_3\ (s) \rightleftharpoons 2\ Ho^{3+} + 3\ CO_3^{2-}$	-32.8(69), [-33.8](66, 73,76)	-33.8
$HoPO_4 \times H_2O\ (s) \rightleftharpoons Ho^{3+} + PO_4^{3-} + x\ H_2O$	[-24.2](89, 74)	-24.2
$HoF_3\ 0.5\ H_2O\ (s) \rightleftharpoons Ho^{3+} + 3\ F^- + 0.5\ H_2O$	-15.8(101),-17.2(101), -18.0(102), -14.6(103)	-16.4

Table 12. Erbium solution species.

Reaction	log K Lee&By.	log K Wood	log K Mill.	log K Lit.(ref.)	Selec-ted.
$ErOH^{2+} \rightleftharpoons Er^{3+} + OH^-$	-6.27	-6.1	-6.15	-6.1(29) -7.0(34*)	-6.13
$Er(OH)_2^+ \rightleftharpoons Er^{3+} + 2OH^-$	-12.04	-	-	-12.1(29) -12.5(34*)	-12.1
$Er(OH)_3 \rightleftharpoons Er^{3+} + 3OH^-$	-17.65	-	-	-17.8(29) -17.8(34*)	-17.8
$Er(OH)_4^- \rightleftharpoons Er^{3+} + 4OH^-$	-	-	-	-23.4(29)	-23.4
$ErCO_3^+ \rightleftharpoons Er^{3+} + CO_3^{-2}$	-8.24	[-8.2]	-7.63	-8.11(64)	-8.05
$Er(CO_3)_2^- \rightleftharpoons Er^{3+} + 2CO_3^{-2}$	-13.98	[-13.6]	-12.88	-13.89(64)	-13.4
$ErHCO_3^{2+} \rightleftharpoons Er^{3+} + HCO_3^-$	-	[-2.26]	-1.76	[-2.38](86,3)	-2.2
$ErH_2PO_4^{2+} \rightleftharpoons Er^{3+} + H_2PO_4^-$	-	-	-2.24	[-2.77](86,3)	-2.4
$ErHPO_4^+ \rightleftharpoons Er^{3+} + HPO_4^{-2}$	-	-	-5.68	[-6.07](86,3)	-5.9
$Er(HPO_4)_2^- \rightleftharpoons Er^{3+} + 2\ HPO_4^{-2}$	-	-	-9.73	[-10.3](86,3)	-10.0
$ErPO_4 \rightleftharpoons Er^{3+} + PO_4^{-3}$	-12.69	-	-	-	*-12.7*
$Er(PO_4)_2^{3-} \rightleftharpoons Er^{3+} + 2\ PO_4^{-3}$	-21.41	-	-	-	*-21.4*
$ErSO_4^+ \rightleftharpoons Er^{3+} + SO_4^{-2}$	-	-3.59	-3.15		-3.4
$Er(SO_4)_2 \rightleftharpoons Er^{3+} + 2SO_4^{-2}$	-	-5.05	-		-5.0
$ErF^{2+} \rightleftharpoons Er^{3+} + F^-$	-	-4.59	-3.98		-4.3
$ErCl^{2+} \rightleftharpoons Er^{3+} + Cl^-$	-	-0.26	-0.28		-0.27
$ErNO_3^+ \rightleftharpoons Er^{3+} + NO_3^-$	-	[-0.74]	-0.15		-0.4
Er(II)					
$Er^{+3} + 0.5\ H_2O \rightleftharpoons Er^{2+} + H^+ + 0.25\ O_2(g)$				70.9(21)	70.9

Table 12.1. Erbium solids.

Reaction	log K Literature(ref.)	Selec-ted.
Er(s)		
$Er(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Er^{3+} + 1.5\ H_2O$	179.5(21)	179.5
Er(III)		
$Er(OH)_3(am) \rightleftharpoons Er^{3+} + 3OH^-$	-23.7(34*),	-23.0
$Er(OH)_3(s) \rightleftharpoons Er^{3+} + 3OH^-$	-27.0(29), -26.6(48)	-27.0
$Er_2O_3(c, cub.) + 6H^+ \rightleftharpoons Er^{3+} + 3\ H_2O$	42.1(19)	42.1
$Er(OH)CO_3(s) \rightleftharpoons Er^{3+} + OH^- + CO_3^{2-}$	-	-
$Er_2(CO_3)_3\ (s) \rightleftharpoons 2\ Er^{3+} + 3\ CO_3^{2-}$	-28.25(69), -22.9(65*), [-32.2](69), [-33.6](66, 73,76)	-33.6
$ErPO_4\ x\ H_2O\ (s) \rightleftharpoons Er^{3+} + PO_4^{3-} + x\ H_2O$	-24.18(89)	-24.2
$ErF_3\ 0.5\ H_2O\ (s) \rightleftharpoons Er^{3+} + 3\ F^- + 0.5\ H_2O$	-15.5(101), -16.8(101), -17.8(102),-15.5(103),	-16.3

Table 13. Thulium solution species.

Reaction	log K Lee&By.	log K Wood	log K Mill.	log K Lit.(ref.)	Selec-ted.
$TmOH^{2+} \rightleftharpoons Tm^{3+} + OH^-$	-6.32	-6.3	-6.19	-6.3(29)	-6.25
$Tm(OH)_2^+ \rightleftharpoons Tm^{3+} + 2OH^-$	-12.12	-	-	-12.15(29)	-12.1
$Tm(OH)_3 \rightleftharpoons Tm^{3+} + 3OH^-$	-17.82	-	-	-17.85(29)	-17.8
$TmCO_3^+ \rightleftharpoons Tm^{3+} + CO_3^{-2}$	-8.32	[-8.27]	-7.66	-8.19(64)	-8.1
$Tm(CO_3)_2^- \rightleftharpoons Tm^{3+} + 2CO_3^{-2}$	-14.07	[-13.7]	-13.0	-14.03(64)	-13.5
$TmHCO_3^{2+} \rightleftharpoons Tm^{3+} + HCO_3^-$	-	[-2.29]	-1.79	[-2.33](64)	-2.25
$TmH_2PO_4^{2+} \rightleftharpoons Tm^{3+} + H_2PO_4^-$	-	-	-2.27	[-2.78](86,3)	-2.5
$TmHPO_4^+ \rightleftharpoons Tm^{3+} + HPO_4^{-2}$	-	-	-5.71	[-6.11](86,3)	-5.9
$Tm(HPO_4)_2^- \rightleftharpoons Tm^{3+} + 2\ HPO_4^{-2}$	-	-	-9.84	[-10.3](86,3)	-10.1
$TmPO_4 \rightleftharpoons Tm^{3+} + PO_4^{-3}$	-12.82	-	-	-	*-12.8*
$Tm(PO_4)_2^{3-} \rightleftharpoons Tm^{3+} + 2\ PO_4^{-3}$	-21.57	-	-	-	*-21.6*
$TmSO_4^+ \rightleftharpoons Tm^{3+} + SO_4^{-2}$	-	-3.60	-3.07		-3.3
$Tm(SO_4)_2 \rightleftharpoons Tm^{3+} + 2SO_4^{-2}$	-	-5.15	-		-5.1
$TmF^{2+} \rightleftharpoons Tm^{3+} + F^-$	-	-4.61	-3.99		-4.3
$TmCl^{2+} \rightleftharpoons Tm^{3+} + Cl^-$	-	-0.25	-0.27		-0.26
$TmNO_3^+ \rightleftharpoons Tm^{3+} + NO_3^-$	-	-0.67	-0.20		-0.4
Tm(II)					
$Tm^{+3} + 0.5\ H_2O \rightleftharpoons Tm^{2+} + H^+ + 0.25O_2(g)$	-	-	-	59.6(23) 59.1(21)	59.1

Table 13.1. Thulium solids.

Reaction	log K Literature(ref.)	Selec- ted.
Tm(s)		
$Tm(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Tm^{3+} + 1.5\ H_2O$	179.5(21)	179.5
Tm(III)		
$Tm(OH)_3(am) \rightleftharpoons Tm^{3+} + 3OH^-$	[-24.7](30-37*),	-24.7
$Tm(OH)_3(s) \rightleftharpoons Tm^{3+} + 3OH^-$	-27.0(29)	-27.0
$Tm_2O_3(c) + 6H^+ \rightleftharpoons Tm^{3+} + 3\ H_2O$	44.7(19)	44.7
$Tm(OH)CO_3(s) \rightleftharpoons Tm^{3+} + OH^- + CO_3^{2-}$	-	-
$Tm_2(CO_3)_3\ (s) \rightleftharpoons 2\ Tm^{3+} + 3\ CO_3^{2-}$	-31.67(69), [-33.4](66, 73,76)	-33.4
$TmPO_4\ x\ H_2O\ (s) \rightleftharpoons Tm^{3+} + PO_4^{3-} + x\ H_2O$	[-24.2](89,91,92,74)	-24.2
$TmF_3\ 0.5\ H_2O\ (s) \rightleftharpoons Tm^{3+} + 3\ F^- + 0.5\ H_2O$	-15.8(101), -17.1(101), -17.6(102), -14.6(103)	-16.2

Table 14. Ytterbium solution species.

Reaction	log K Lee&Byr	log K Wood	log K Mill.	log K Lit.(ref.)	Selec-ted.
$YbOH^{2+} \rightleftharpoons Yb^{3+} + OH^-$	-6.40	-6.3	-6.22	-6.3(29) -5.6(33*) -5.3(42) -8.4(44*)	-6.35
$Yb(OH)_2^+ \rightleftharpoons Yb^{3+} + 2OH^-$	-12.26	-	-	-12.2(29), -15.9(44*) -11.5(33*)	-12.3
$Yb(OH)_3 \rightleftharpoons Yb^{3+} + 3OH^-$	-18.15	-	-	-17.9(29) -17.8(33*)	-18.0
$Yb(OH)_4^- \rightleftharpoons Yb^{3+} + 4OH^-$	-	-	-	-23.3(29)	-23.3
$YbCO_3^+ \rightleftharpoons Yb^{3+} + CO_3^{-2}$	-8.40	-8.31	-7.67	-8.28(64)	-8.15
$Yb(CO_3)_2^- \rightleftharpoons Yb^{3+} + 2CO_3^{-2}$	-14.22	-13.81	-13.08	-14.21(64)	-13.6
$YbHCO_3^{2+} \rightleftharpoons Yb^{3+} + HCO_3^-$	-	-2.33	-1.84	[-2.27](64)	-2.25
$YbH_2PO_4^{2+} \rightleftharpoons Yb^{3+} + H_2PO_4^-$	-	-	-2.32	[-2.8](86,3)	-2.4
$YbHPO_4^+ \rightleftharpoons Yb^{3+} + HPO_4^{-2}$	-	-	-5.73	[-6.2](86,3)	-6.0
$Yb(HPO_4)_2^- \rightleftharpoons Yb^{3+} + 2\ HPO_4^{-2}$	-	-	-9.95	[-10.4](86,3)	-10.2
$YbPO_4 \rightleftharpoons Yb^{3+} + PO_4^{-3}$	-12.94	-	-	-	*-12.9*
$Yb(PO_4)_2^{3-} \rightleftharpoons Yb^{3+} + 2\ PO_4^{-3}$	-21.79	-	-	-	*-21.9*
$YbSO_4^+ \rightleftharpoons Yb^{3+} + SO_4^{-2}$	-	-3.59	-3.06		-3.3
$Yb(SO_4)_2 \rightleftharpoons Yb^{3+} + 2SO_4^{-2}$	-	-5.18	-		-5.1
$YbF^{2+} \rightleftharpoons Yb^{3+} + F^-$	-	-4.63	-4.02		-4.3
$YbCl^{2+} \rightleftharpoons Yb^{3+} + Cl^-$	-	-0.24	-0.16		-0.2
$YbNO_3^+ \rightleftharpoons Yb^{3+} + NO_3^-$		[-0.6]	-0.25		-0.4
Yb(II)					
$Yb^{+3} + 0.5\ H_2O \rightleftharpoons Yb^{2+} + H^+ + 0.25\ O_2(g)$	-	-	-	40.2(23) 38.3(21)	38.3

Table 9.1. Ytterbium solids.

Reaction	log K Literature(ref.)	Selec-ted.
Yb(s)		
$Yb(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Yb^{3+} + 1.5\ H_2O$	175.1(21)	175.1
Yb(III)		
$Yb(OH)_3(am) \rightleftharpoons Yb^{3+} + 3OH^-$	-22.94(33*),	-23.0
$Yb(OH)_3(s) \rightleftharpoons Yb^{3+} + 3OH^-$	-27.3(29), -26.64(48)	-27.3
$Yb_2O_3(c, cub.) + 6H^+ \rightleftharpoons Yb^{3+} + 3\ H_2O$	47.8(19)	47.8
$Yb(OH)CO_3(s) \rightleftharpoons Yb^{3+} + OH^- + CO_3^{2-}$	-	-
$Yb_2(CO_3)_3\ (s) \rightleftharpoons 2\ Yb^{3+} + 3\ CO_3^{2-}$	-31.67(69),-31.1(66) , [-33.6](66)	-33.3
$YbPO_4\ x\ H_2O\ (s) \rightleftharpoons Yb^{3+} + PO_4^{3-} + x\ H_2O$	[-24.1](89,74)	-24.1
$YbF_3\ 0.5\ H_2O\ (s) \rightleftharpoons Yb^{3+} + 3\ F^- + 0.5\ H_2O$	-15.0(101), -16.3(101), -17.2(102), -14.6(103)	-16.0

Table 15. Lutetium solution species.

Reaction	log K Lee&By.	log K Wood	log K Mill.	log K Lit.(ref.)	Selec-ted.
$LuOH^{2+} \rightleftharpoons Lu^{3+} + OH^-$	-6.41	-6.4	-6.24	-6.4(29) ≥-5.0(40)	-6.4
$Lu(OH)_2^+ \rightleftharpoons Lu^{3+} + 2OH^-$	-12.33	-	-	[-12.3](29)	-12.3
$Lu(OH)_3 \rightleftharpoons Lu^{3+} + 3OH^-$	-18.15	-	-	[-18.0](29)	-18.1
$LuCO_3^+ \rightleftharpoons Lu^{3+} + CO_3^{-2}$	-8.43	[-8.35]	-7.70	-8.29(64)	-8.2
$Lu(CO_3)_2^- \rightleftharpoons Lu^{3+} + 2CO_3^{-2}$	-14.29	[-13.9]	-13.20	-14.2(64)	-13.8
$LuHCO_3^{2+} \rightleftharpoons Lu^{3+} + HCO_3^-$	-	[-2.35]	-1.90	[-2.22](64*)	-2.3
$LuH_2PO_4^{2+} \rightleftharpoons Lu^{3+} + H_2PO_4^-$	-	-	-2.38	[-2.82](86,3)	-2.5
$LuHPO_4^+ \rightleftharpoons Lu^{3+} + HPO_4^{-2}$	-	-	-5.75	[-6.2](86,3)	-6.0
$Lu(HPO_4)_2^- \rightleftharpoons Lu^{3+} + 2\ HPO_4^{-2}$	-	-	-10.05	[-10.5](86,3)	-10.3
$LuPO_4 \rightleftharpoons Lu^{3+} + PO_4^{-3}$	-12.99	-	-		*-13.0*
$Lu(PO_4)_2^{3-} \rightleftharpoons Lu^{3+} + 2\ PO_4^{-3}$	-21.90	-	-		*-21.9*
$LuSO_4^+ \rightleftharpoons Lu^{3+} + SO_4^{-2}$	-	-3.60	-3.01		-3.3
$Lu(SO_4)_2 \rightleftharpoons Lu^{3+} + 2SO_4^{-2}$	-	-5.39	-		-5.3
$LuF^{2+} \rightleftharpoons Lu^{3+} + F^-$	-	-4.66	-4.05		-4.3
$LuCl^{2+} \rightleftharpoons Lu^{3+} + Cl^-$	-	-0.23	0.03		-0.1
$LuNO_3^+ \rightleftharpoons Lu^{3+} + NO_3^-$	-	[-0.6]	-0.56		-0.6

Table 15.1. Lutetium solids.

Reaction	log K Literature(ref.)	Selec-ted.
Lu(s)		
$Lu(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Lu^{3+} + 1.5\ H_2O$	179.2(21)	179.2
Lu(III)		
$Lu(OH)_3(am) \rightleftharpoons Lu^{3+} + 3OH^-$	[-23.0](30-37*),	-23.0
$Lu(OH)_3(s) \rightleftharpoons Lu^{3+} + 3OH^-$	-27.5(29), -27.0(48)	-27.5
Lu_2O_3(c, hex.) $+ 6H^+ \rightleftharpoons Lu^{3+} + 3\ H_2O$	45.0(19)	45.0
$Lu(OH)CO_3(s) \rightleftharpoons Lu^{3+} + OH^- + CO_3^{2-}$	-	-
$Lu_2(CO_3)_3\ (s) \rightleftharpoons 2\ Lu^{3+} + 3\ CO_3^{2-}$	-32.16(69), [33.0](66, 73)	-33.0
$LuPO_4\ x\ H_2O\ (s) \rightleftharpoons Lu^{3+} + PO_4^{3-} + x\ H_2O$	[-24.0](89,74)	-24.0
$LuF_3\ 0.5\ H_2O\ (s) \rightleftharpoons Lu^{3+} + 3\ F^- + 0.5\ H_2O$	-15.0(101), -16.4(101) -16.9(102), -14.6(103),	-15.9

Table 16. Yttrium solution species.

Reaction	log K Lit.(ref.)	Selec-ted.
$YOH^{2+} \rightleftharpoons Y^{3+} + OH^-$	-6.3(29), -6.4(43*)	-6.3
$Y(OH)_2^+ \rightleftharpoons Y^{3+} + 2OH^-$	-11.6(29)	-11.6
$Y(OH)_3 \rightleftharpoons Y^{3+} + 3OH^-$	-16.0(29)	-16.0
$Y(OH)_4^- \rightleftharpoons Y^{3+} + 4OH^-$	-19.5(29)	-19.5
$Y_2(OH)_2^{4+} \rightleftharpoons 2\,Y^{3+} + 2\,OH^-$	-13.8(29)	-13.8
$Y_3(OH)_5^{4+} \rightleftharpoons 3\,Y^{3+} + 5\,OH^-$	-38.4(29)	-38.4
$YCO_3^+ \rightleftharpoons Y^{3+} + CO_3^{-2}$	-8.07(56) ,	-8.05
$Y(CO_3)_2^- \rightleftharpoons Y^{3+} + 2CO_3^{-2}$	[-13.3](56,64)	-13.3
$YHCO_3^{2+} \rightleftharpoons Y^{3+} + HCO_3^-$	-2.36(56) , [-2.38](57, 64)	-2.3
$YH_2PO_4^{2+} \rightleftharpoons Y^{3+} + H_2PO_4^-$	[-2.4](86,3,2), -2.65(82),	-2.4
$YHPO_4^+ \rightleftharpoons Y^{3+} + HPO_4^{-2}$	[-6.0](86,3), [-5.7](2)	-5.9
$Y(HPO_4)_2^- \rightleftharpoons Y^{3+} + 2\,HPO_4^{-2}$	[-10.2](86,3), [-9.6](2)	-9.9
$YPO_4 \rightleftharpoons Y^{3+} + PO_4^{-3}$	[-12.6](3)	*-12.6*
$Y(PO_4)_2^{3-} \rightleftharpoons Y^{3+} + 2\,PO_4^{-3}$	[-21.4](3)	*-21.4*
$YSO_4^+ \rightleftharpoons Y^{3+} + SO_4^{-2}$	[-3.4](1,2)	-3.4
$Y(SO_4)_2 \rightleftharpoons Y^{3+} + 2SO_4^{-2}$	[-4.9](1)	-4.9
$YF^{2+} \rightleftharpoons Y^{3+} + F^-$	-4.3(1,2)	-4.3
$YF_2^{2+} \rightleftharpoons Y^{3+} + 2F^-$	-8.58(1) [-7.8](1,2,5)	-7.8
$YF_3^{2+} \rightleftharpoons Y^{3+} + 3F^-$	-12.49(1) [-11.2](1,2,5)	-11.2
$YCl^{2+} \rightleftharpoons Y^{3+} + Cl^-$	[-0.3](1,2)	-0.3
$YNO_3^+ \rightleftharpoons Y^{3+} + NO_3^-$	[-0.4](1,2)	-0.4

Table 16.1. Yttrium solids.

Reaction	log K Literature(ref.)	Selec-ted.
Y(s)		
$Y(s) + 3H^+ + 0.75\ O_2(g) \rightleftharpoons Y^{3+} + 1.5\ H_2O$	182.3(21)	182.3
Y(III)		
$Y(OH)_3(am) \rightleftharpoons Y^{3+} + 3OH^-$	[-22.6](30-37*), -23.2(48)	-23.0
$Y(OH)_3(s) \rightleftharpoons Y^{3+} + 3OH^-$	-24.5(29), -24.5(48)	-24.5
$Y_2O_3(c, cub.) + 6H^+ \rightleftharpoons Y^{3+} + 3\ H_2O$	46.4(19)	46.4
$Y(OH)CO_3(s) \rightleftharpoons Y^{3+} + OH^- + CO_3^{2-}$	-	-
$Y_2(CO_3)_3\ 3H_2O\ (s) \rightleftharpoons 2\ Y^{3+} + 3\ CO_3^{2-} + 3H_2O$	-32.77(73), -30.6(66) -31.52(69) , [-32.8](66)	-32.8
$YPO_4\ x\ H_2O\ (s) \rightleftharpoons Y^{3+} + PO_4^{3-} + x\ H_2O$	[-24.2](89,74)	-24.2
$YF_3\ 0.5\ H_2O\ (s) \rightleftharpoons Y^{3+} + 3\ F^- + 0.5\ H_2O$	-17.3(9), -17.3(101),-18.4(102) -14.8(103), -18.3(104)	-16.9

2. TEST CASES.

A rigorous validation of the selected data base is difficult, owing to the lack of independent solubility data as a function of the different master variables. As an example, most of the carbonate solubility studies used to derive the solubility products (fig. 3) have been performed at one particular set of conditions. Neodymium and europium, as chemical analogs of Am, have received special attention in the last years and there are some data concerning the solubility of Nd, Eu or Am hydroxide, carbonate, hydroxycarbonate, and phosphate at various conditions. These data have been reported mainly by Kim and coworkers (71, 72, 94) and Rai and coworkers (70,74, 129).

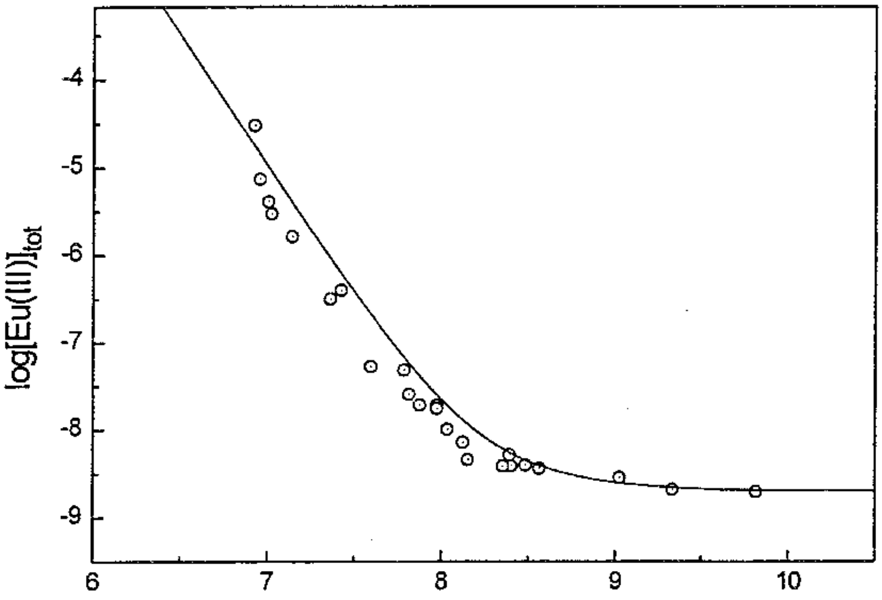

Fig. 5. Solubility of $Eu(OH)_3(s)$ from ref. (94). The theoretical curve was calculated by using the constants selected in the present work.

In fig. 5 the experimental data by Bernkopf (94) for the solubility of $Eu(OH)_3(s)$ until pH =10.5 are represented, together with the prediction from this work.

In fig. 6 the data of Ferri et al. (53) for the solubility of $Ce_2(CO_3)_3(s)$ are represented, together with the theoretical curve calculated with the constants selected in this work. As seen the agreement is good, except for the part of the lower solubilities. We have recalculated the carbonate constants at 3 M $NaClO_4$ using $\varepsilon(Na^+, CO_3^{-2})$= -0.08 and $\varepsilon(Na^+, HCO_3^-)$= -0.002

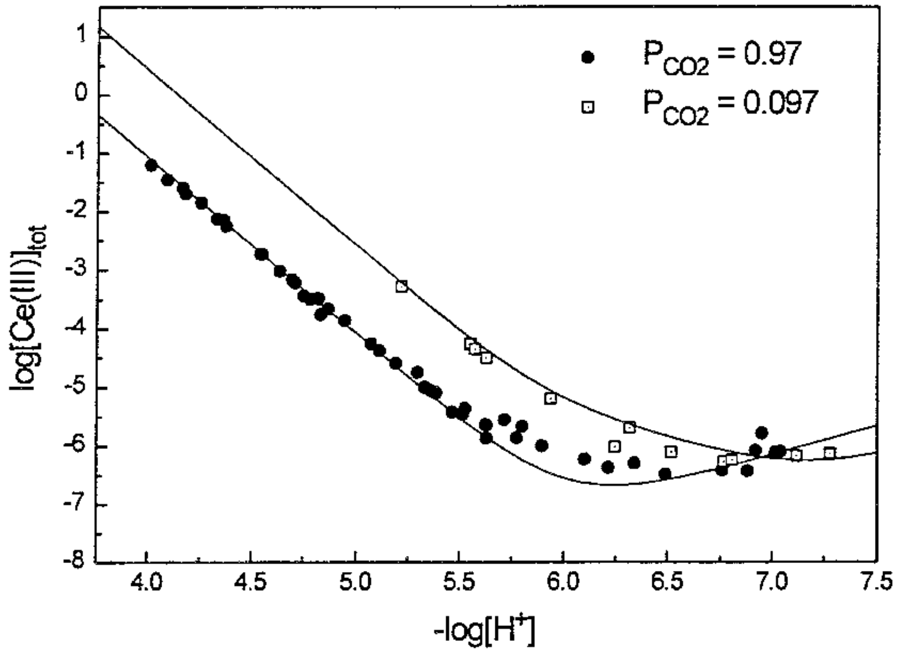

Fig 6. Solubility data for cerium carbonate from ref.(53) calculated with the constants selected in this work.

The data of Runde, Meinrath and Kim(72) for the solubility of europium carbonate and hydroxycarbonate were digitized as represented in fig. 7, together with the model calculations using the constants selected this work. As seen the agreement is good and in the same work reference is made to similar solubilities for Nd and Am carbonates and hydroxycarbonates.

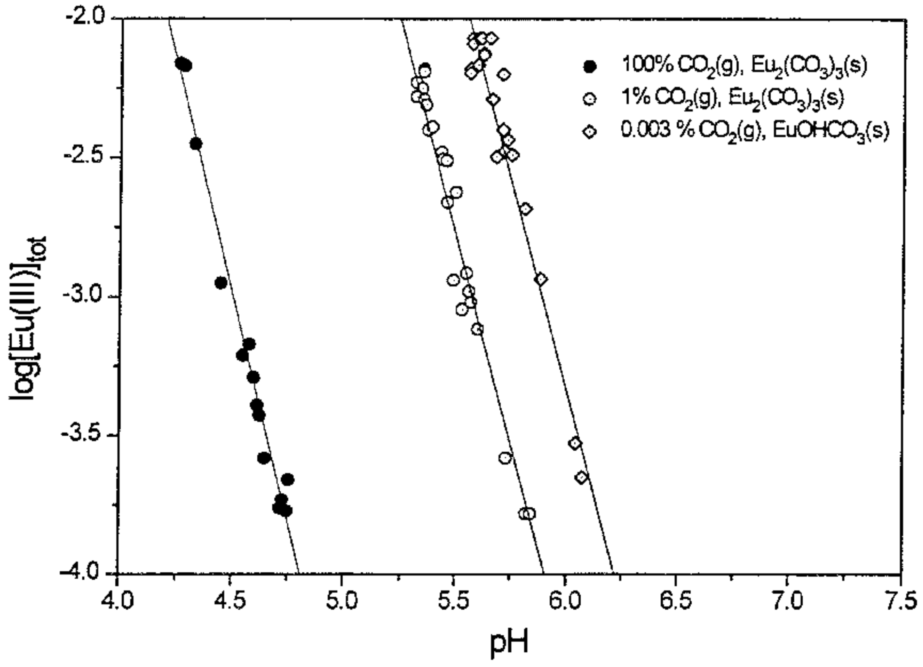

Fig. 7. Solubilities of $Eu_2(CO_3)_3(s)$ and $EuOHCO_3(s)$ from ref. (72).

In fig. 8 the data on the solubility of neodymium carbonate and hydroxycarbonate as reported by Meinrath and Kim (71) are represented together with the model calculations using the solubility products from this work.

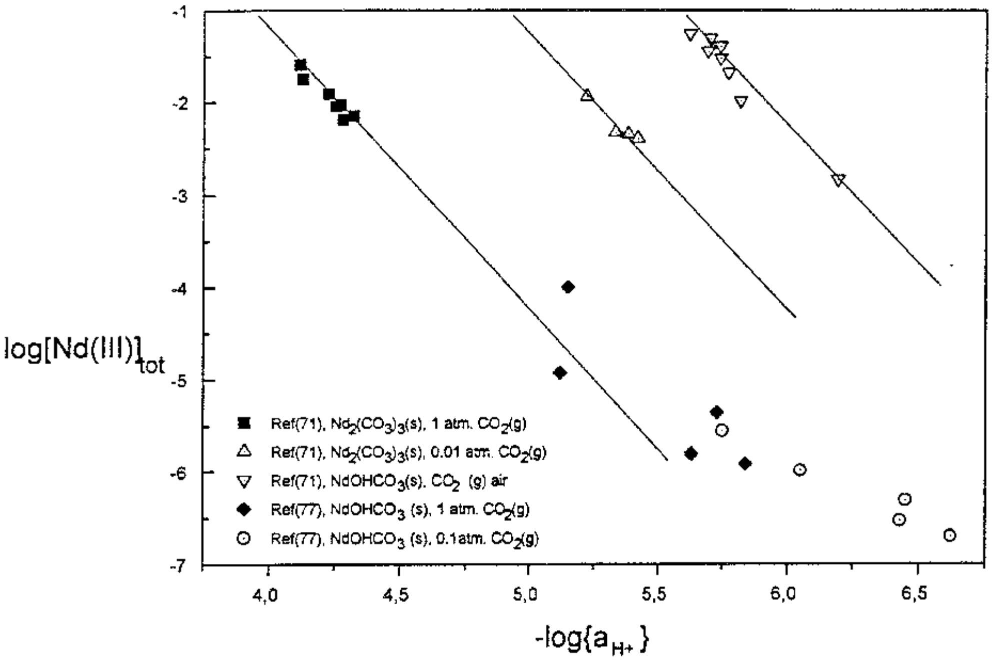

Fig. 8. Solubilities of $Nd(CO_3)_3(s)$ and $Nd(OH)CO_3(s)$ from ref. (71) and (77) and model calculations with the constants selected in this work.

In the same figure are represented the data of Caroll (77) which claims to have determined only the hydroxycarbonate of Nd at all partial pressures of $CO_2(g)$. Even though phase transformations at prolonged equilibration times in this system are an open question, it seems that some data of Carroll fit well with the solubility of the normal carbonate as calculated from the constants selected in this work.

3. SOLUBILITIES OF REE IN REPOSITORY CONDITIONS.

The REE in the fuel are present as oxides in solid solution with uranium dioxide. Hence their solubility in the first period will be limited by matrix dissolution and very low concentrations are to be expected. Anyhow, after some time the saturation with respect to various secondary solid phases should be reached and their solubility will be further governed by these phases. We have used as example our Eu database and the groundwater with the composition given in paragraph 1. 2. 3. to calculate solubilities and solubility limiting solids in repository conditions. From the reported solubilities, the normal phosphates seem the most insoluble (fig 9) and should limit the solubility of the REE in the interval 10^{-10} - 10^{-12} in typical pH values for most groundwaters.

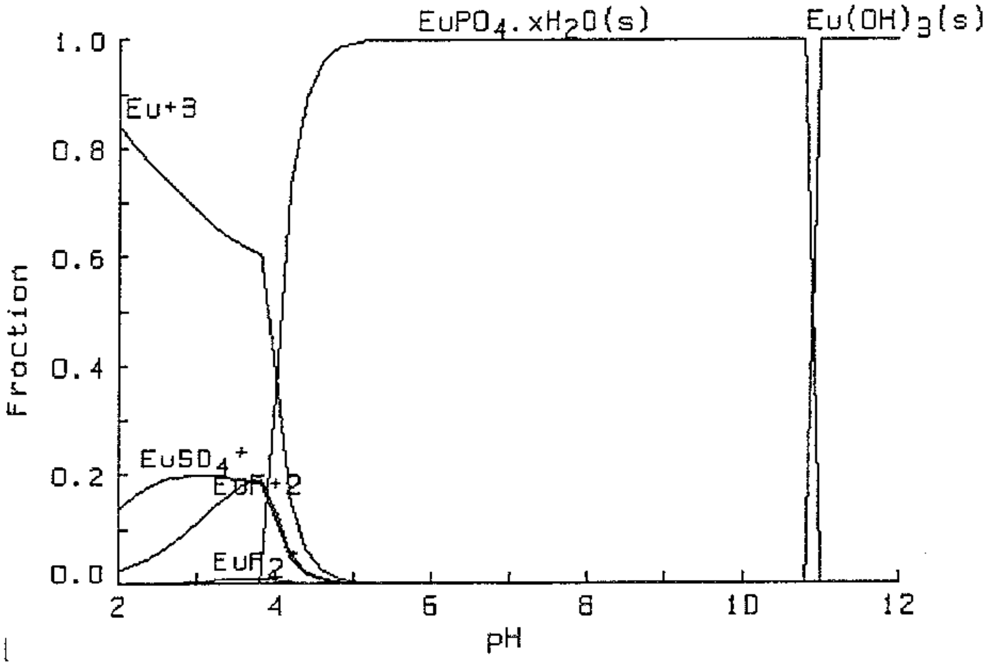

Fig 9. Distribution of Eu at the 2 10^{-7} M level among solids and solute species in groundwater.

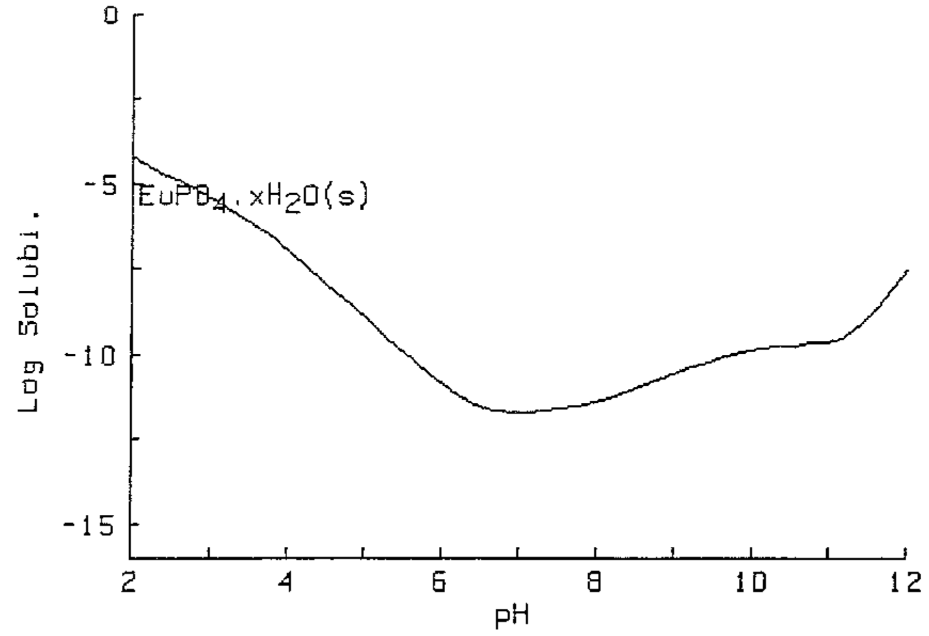

Fig. 10. Solubility of $EuPO_4$.x $H_2O(s)$ in ground water.

Anyhow, in a validation of the Nd database (74) for the solubility of neodymium doped glass, solubilities several orders of magnitude higher than the one predicted assuming formation of $NdPO_4$ $xH_2O(s)$ were observed in the presence of phosphate. The authors suppose the formation of a much more soluble than $NdPO_4$ x $H_2O(s)$ phosphate phase in the Nd - PO_4 - H_2O system. This is also a very important point to be clarified by further experimental work.

As the next less soluble phase most studies indicate the hydroxycarbonates, but only data for Eu and Nd are available. In fig. 11 is shown the solubility of $EuOHCO_3(s)$ in the granitic ground water given above, calculated with the values of the constants from this work. As seen, solubilities of the order of 10^{-8}-10^{-9} M are to be expected in the presence of this solid phase.

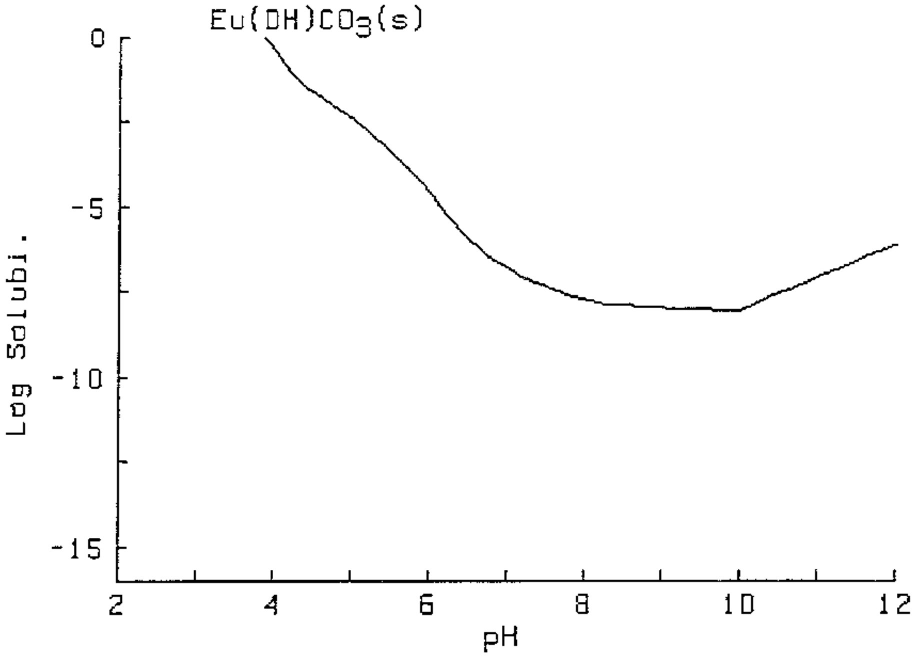

Fig. 11. Solubility of $EuOHCO_3(s)$ in granitic ground water as calculated with values of the constants selected in this work.

On the other hand the solubilities in the case of the carbonate as the solubility limiting phase would be of the order 10^{-7} - $10^{-7.5}$ M, as shown in fig 11 for $Eu_2(CO_3)_3(s)$.

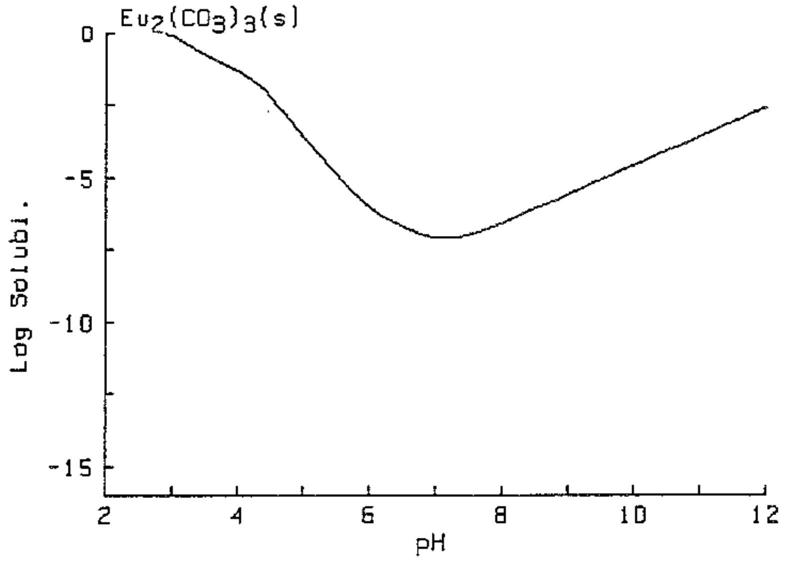

Fig.12. Solubility of $Eu_2(CO_3)_3$ $3H_2O(s)$ in granitic ground water as calculated with values of the constants selected here.

In this work it is considered that these two phases, i. e. carbonate and hydroxycarbonate form at different P_{CO2} pressures as reported in most studies (67, 68, 71, 72, 75) and their stability fields can be calculated from the constants reported in the database and the known constants of the carbon dioxide-water system.

Thus for Eu(III) the constant of the reaction:

$$Eu(OH)_3(s) + CO_2(g) \rightleftharpoons Eu(OH)CO_3(s) + H_2O$$

can be calculated from the solubility constants of $Eu(OH)_3(s)$, $Eu(OH)CO_3(s)$, $K_w{}^{o}$= -14 and the constant $K_HK_1K_2$ = -18.15 for the reaction $CO_2(g) + H_2O \rightleftharpoons CO_3{}^{2-} + 2H^+$ as K= -4.85. This corresponds to a $CO_2(g)$ partial pressure for the equilibrium between these two solids of $0.14 \cdot 10^{-4}$ bar. In the same way may be obtained the constants for the equilibrium:

$Eu(OH)_3(s) + 1.5\ CO_2(g) \rightleftharpoons 0.5\ Eu_2(CO_3)_3\ (s) + 1.5\ H_2O$ K= 5.48

corresponding to an equilibrium P_{CO2} = 0.033 10^{-4} bar, and for the reaction:

$Eu(OH)CO_3(s) + 0.5\ CO_2(g) \rightleftharpoons 0.5\ Eu_2(CO_3)_3\ (s) + 0.5\ H_2O$ K= 0.63

which gives an equilibrium P_{CO2} = 0.23 bar.

A typical predominance diagram for Eu at the 2 10^{-7} M level in ground water, calculated with the constants selected in this work, but excluding phosphate for the above mentioned reasons, is presented in fig. 13.

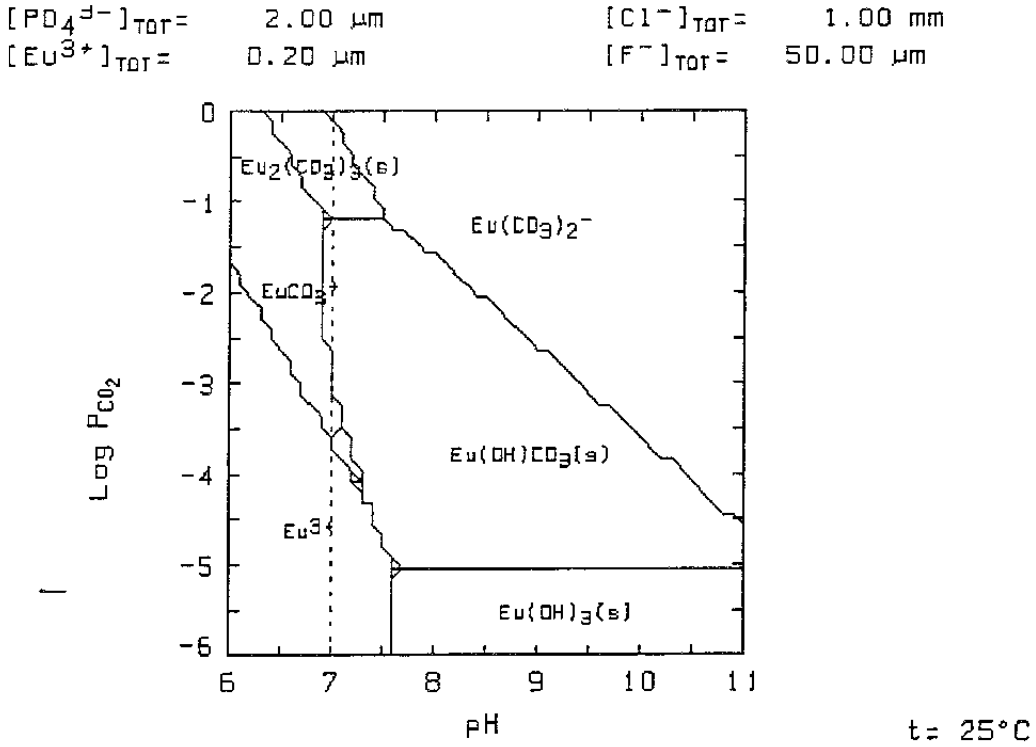

Fig. 13. Predominance area diagram for the Eu^{3+}-CO_2(g)-H_2O system.

As seen for P_{CO2} typical for air, the hydroxycarbonate is the dominant phase, while at higher carbonate contents the normal carbonate forms. As discussed above, more work is needed to fully understand this system for all the REE, since it is difficult to make predictions when neither the existence nor the solubility of the hydroxycarbonates of the heavy REE is known.

3. CONCLUSIONS AND RECOMMENDATIONS.

1. We have compiled a selected thermodynamic database for the REE under repository conditions.

1. The solution speciation of the REE is known with an acceptable degree of accuracy for most important ligands, especially as compared to the known solubilities of the most important solids.

2. Carbonate complexes of the REE are the dominant soluble species under repository conditions.

3. More reliable data on the stability of inorganic aqueous complexes like hydroxide, phosphate, higher carbonate, are of particular importance in the speciation of REE in hyperalkaline(cement) environments. Additionally, the increase of the stability of the two valent state with temperature and its complexation represent areas where more future studies are needed.

4. At the initial stages of fuel dissolution, UO_2(s) matrix dissolution will determine the concentrations of REE. Later, solid phosphates, hydroxycarbonates and carbonates may limit their solubility, probably under 10^{-7} M.

5. Neither the solids formed, nor their solubilities are known with any degree of reliability in many important systems as $Ln\text{-}H_2O\text{-}CO_3$, $Ln\text{-}CO_3\text{-}F$, $Ln\text{-}H_2O\text{-}PO_4$. There is a need for accurate studies on these systems, with good control of the solid phase and solution parameters, to model the behaviour of the REE in repository conditions.

References

1. Wood S. A. (1990) The aqueous geochemistry of the rare-earth elements and yttrium. 1. Review of available low temperature data for inorganic complexes and the inorganic REE speciation of natural waters, *Chem. Geol.,* **82**, 159-186.

2. Millero, F. J. (1992) Stability constants for the formation of rare earth inorganic complexes as a function of ionic strength, *Geochim. Cosmochim. Acta*, **56**, 3123-3132.

3. Lee, J. H., Byrne, R. H. (1992) Examination of comparative rare earth element complexation behaviour using linear free energy relationships, *Geochim. Cosmochim. Acta* , **56**, 1127-1137.

4. Wood S. A. (1990) The aqueous geochemistry of the rare-earth elements and yttrium. 2. Theoretical predictions of speciation in hydrothermal solutions to 350 °C at saturation water vapor pressure, *Chem. Geol.,* **88**, 99-125.

5. Rard, J. A. (1985), Chemistry and thermodynamics of europium and some of its simpler inorganic compounds, *Chem. Rew.*, **85**, 555-582.

6. Millero F. J. and Schreiber D. R.(1982) Use of the ion pairing model to estimate activity coefficients of the ionic components of natural waters, *Am. J. Sci.*, **282**, 1508-1540.

7. Karraker, D. G. (1970) Coordination of the trivalent lanthanide ions, *J. Chem. Educ.* **47**, 424-430.

8. Sinha, S. P. (1976) Structure and bonding in highly coordinated lanthanide complexes, Struct. Bonding (Berlin), **25**, 69-149.

9. Czack, G., Flachsbart, I., Hein, H., Koch, E., Kreuzbichler, I., Kuhn, P., Lehl, H., Vetter, U. (1982) "Gmelin Handbook of Inorganic Chemistry", Springer-Verlag, Berlin, System No **39**, Vol. C4b.

10. Burgess, J., Kijowski, J. (1981) In "Adv. Inorg. Chem. Radiochem." , Vol. **24**., p 57-114, Acad. Press, New York.

11. Choppin, G.R.(1984) Lanthanide complexation in aqueous solutions, *J. Less-Common Met.*, **100**, 141-151.

12. Choppin, G. R. (1986) Speciation of trivalent f elements in natural waters, *J. Less-Common Met.*, **126**, 307- 313.

13. Chopin, G. R. (1989) Soluble rare earth and actinide species in sea water, *Mar. Chem.* **28**, 19-26.

14. McLennan, S. M., Taylor, S. R. (1979) Rare earth element mobility associated with uranium mineralisation, *Nature*, **282**, 147-250.

15. Fryer B. J., Taylor, R. P., (1987) Rare-earth element distributions in uraninites: implications for ore genesis, *Chem. Geol.*, **63**, 101-108.

16. Byrne, R. H., Kim, K. H. (1990) Rare earth element scavenging in seawater, *Geochim. Cosmochim. Acta*, **54**, 2654-2656.

17. Schumm, R. H., Wagman, D. D., Bailey, S. H., Evans, W. H., Parker, V. B. (1973) Selected values of chemical thermodynamic properties. Tables for the lanthanide (rare earth) elements , U. S. Natl. Bur. Standards, *Tech. Note 270-7*, 75 p.

18. Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. H., Schumm, R. H., Churney, K.H. (1971) Selected values of chemical thermodynamic properties. Tables for elements 54 through 61 in their standard order of arrangement, U. S. Natl. Bur. Standards, *Tech. Note 270-5*, 37 p.

19. Robie, R. A., Hemingway, B. S., Fisher, J. R. (1979) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar(10^5 pascals) pressure and at higher temperatures, *U. S. Geological Survey Bulletin 1452*, U. S. Gov. Printing Office, Washington D. C. 20402.

20. Phillips, S. L., Hale F. V., Silvester L. F., Siegel, M. D. (1988) Thermodynamic tables for nuclear waste isolation, Aqueous solutions database, Vol. 1, *Report NUREG/CR-4864, LBL-22860, SAND87-0323*, U. S. NRC, Washington, D. C. 20665.

21. Morss, L. R. (1976) Thermochemical properties of yttrium, lanthanum and the lanthanide elements and ions, *Chem. Rew.*, **76**, 827-841.

22. David, F. (1976) Mise au point systematique des propriétés thermodynamiques des ions actinides en solution aqueuse, *J. Chim. Phys.*, **83**, 393-401.

23. Nugent, L. J.,Baybarz, R. D., Burnett, J. L., Ryan, J. L. (1973) Electron-transfer and f-d adsorption bands of some lanthanide and actinide complexes and the standard (II - III) oxidation potential for each member of the lanthanide and actinide series, *J. Phys. Chem.*, **77**, 1528-1539.

24. Bratsch, S. G. (1989) Standard electrode potentials and temperature coefficients in water at 298.15 K, *J. Phys. Chem. Ref. Data*, **18**, 1-21.

25. Conley, H.L. (1960) *M. S. Thesis*, University of California, Berkley, California. *LBL Report* UCRL-9332.

26. Morss, L. R., Haug, H. O. (1973) Enthalpy of formation of europium dichloride and thermodynamic properties of the +2 and +3 aqueous ions of europium, *J. Chem. Thermodyn.*, **5**, 513-524 .

27. Biedermann, G., Terjosin, G. S. (1969) On the standard potentialof the Europium (II - III) couple, *Acta Chem. Scand.*, **23**, 1986-1902.

28. Hinshey, R. J., Cobble, J. W. (1970) Standard-state entropies for the aqueous trivalent lanthanide and yttrium ion, *Inorg. Chem.*, **9**, 917-921.

29. Baes, C. F., Mesmer, R. E. (1976) *The Hydrolysis of cations*, Wiley-Interscience, New York.

30. Kragten, J., Decnop-Weever, L. G. (1978) Hydroxide complexes of cerium(III), *Talanta,* **25**, 147-150.

31. Kragten, J., Decnop-Weever, L. G. (1979) Hydroxide complexes of lanthanides - II. Samarium(III) in perchlorate medium, *Talanta,* **26**, 1105-1109.

32. Kragten, J., Decnop-Weever, L. G. (1980) Hydroxide complexes of lanthanides - III. Gadolinium(III) in perchlorate medium, *Talanta,* **27**, 1047-1050.

33. Kragten, J., Decnop-Weever, L. G. (1982) Hydroxide complexes of lanthanides - IV. Ytterbium(III) in perchlorate medium, *Talanta,* **29**, 219-222.

34. Kragten, J., Decnop-Weever, L. G. (1983) Hydroxide complexes of lanthanides - V. Erbium(III) in perchlorate medium, *Talanta,* **30**, 131-133.

35. Kragten, J., Decnop-Weever, L. G. (1983) Hydroxide complexes of lanthanides-V, *Talanta,* **30**, 134.

36. Kragten, J., Decnop-Weever, L. G. (1984) Hydroxide complexes of lanthanides - VII. Neodymium(III) in perchlorate medium, *Talanta,* **31**, 731-733.

37. Kragten, J., Decnop-Weever, L. G. (1987) Hydroxide complexes of lanthanides - VIII. Lanthanum(III) in perchlorate medium, *Talanta,* **34**, 861-864.

38. Ciavatta, L., Iuliano, M., Porto, R. (1987) The hydrolysis of lanthanum(III) ion in aqueous perchlorate solutions at 60 °C, *Polyhedron,* **6**, 1283-1290.

39. Ciavatta, L., Porto, R., Vasca, E (1988) The hydrolysis of cerium(III) ion in aqueous perchlorate solutions at 50 °C, *Polyhedron,* **7**, 1355-1361.

40. M'Halla, J., Chemla, M., Bury, R., David, F. (1988) Étude conductimétrique de l'hydrolyse des ions lanthanides dans l'eau, *J. Chim. Phys.*, **85**, 121-133.

41. Caceci, M.S. , Choppin, G. R. (1983) The Determination of the first hydrolysis constant of Eu(III) and Am(III), *Radiochimica Acta* , **33**, 101-104.

42. Schmidt, K. H., Sullivan, J. C., Gordon, S., Thompson, R. C. (1978) Determination of hydrolysis constants of metal cations by a transient conductivity method, *Inog. Nucl. Chem. Letters,* **14**, 429-434.

43. Davidov, Yu. P., Voronik, N. I. (1983) The hydrolysis of the Y^{3+} cation in solution, *Russ. J. Inorg. Chem.*, **28**, 1270-1272.

44. Bilal, B. A., Koss, V. (1981) Complex formation of trace elements in geochemical systems, 5. Study of the distribution of hydroxy complexes of rare earth elements, *J. Inorg. Nucl. Chem.*, **43**, 3393-3394.

45. Nair, G. M., Chander, K.. Joshi, J. K. (1982) Hydrolysis constants of plutonium (III) and americium(III), *Radiochim. Acta*, **30**, 37-40.

46. Silva, R. J. (1982) The Solubilities of Crystalline Neodymium and Americium Trihydroxides, *Report LBL-15055,* Lawrence Berkley Laboratory, Berkley, California, 57 p.

47. Rai, D., Strickert, R. G. , Moore, D. A., Ryan, J. L. (1983) Am(III) Hydrolysis Constants and Solubility of Am(III) Hydroxide. *Radiochimica Acta*, **33**, 201-206.

48. Aksel'rud, N. V. (1963) Hydroxide chlorides and hydroxides of elements of the scandium subgroup and of the lanthanides, *Russ. Chem. Rev.*, **32**, 353-366.

49. Kim, J. I., Bernkopf, M., Lierse, Ch., Koppold, F. (1984) Hydrolysis reactions of Am(III) and Pu(VI) ions in near-neutral solutions, *ACS Symp. Series,* **246**, Amer. Chem. Soc., Washington D. C. p. 115-134.

50. Ciavatta, L., Ferri, D., Grenthe, I., Salvatore, F., Spahiu, K. (1981) Studies on metal carbonate equilibria. 3. The lanthanum(III) carbonate complexes in aqueous perchlorate media, *Acta Chem. Scand.,* **A 35**, 403-413.

51. Ruzaikina, L. V., Marov, I. N., Ryabukhin, V. A., Ermakov, A. N., Filimonova, V. N. (1978) Investigation of the complexing of europium with carbonate ions, *Zh. Analit. Khim.*, **33**, 1082.

52. Lundqvist, R. (1982) Hydrophilic complexes of Actinides. I. Carbonates of Trivalent Americium and Europium. *Acta Chem. Scan.* **A 36**, 741-750.

53. Ferri, D., Grenthe, I., Hietanen, S., Salvatore, F. (1983) Studies on metal carbonate equilibria. 5. The cerium(III) carbonate complexes in aqueous perchlorate media, *Acta Chem. Scand.,* **A 37**, 359-365.

54. Dumonceau, J., Bigot, S., Treuil, M., Faucherre, J., Fromage, F. (1979) Determination des constantes de formation des tétracarbonatolanthanides(III) - Note rectificative, *Comp. Rend. Ac. Sci.* Paris, Serie C, **288**, 415.

55. Dumonceau, J., Bigot, S., Treuil, M., Faucherre, J., Fromage, F. (1979) Étude spectrophotométrique des tétracarbonatolanthanides(III), *Comp. Rend. Ac. Sci. Paris*, Serie C, **289**, 165-166.

56. Spahiu, K. (1983) Carbonate complex formation in lanthanoid and actinoid systems, *Ph. D. Thesis*, TRITA-OOK-1007, Royal Institute of Technology, Stockholm.

57. Spahiu, K. (1985) Studies on metal carbonate equilibria. 11. Yttrium(III) carbonate complex formation in aqueous perchlorate media of various ionic strengths, *Acta Chem. Scand.,* **A 39**, 33-45.

58. Cantrell, K. J., Byrne, R. H. (1987) Rare earth element complexation by carbonate and oxalate ions, *Geochim. Cosmochim. Acta* , **51**, 597-605.

59 Cantrell, K. J. (1987) Actinide(III) Carbonate Complexation, *Polyhedron,* **7**, 573-574.

60. Cantrell, K. J., Byrne, R. H. (1988) Temperature dependence of europium carbonate complexation , *J. Solution Chem.*, **16**, 555-556.

61. Thompson, S. W., Byrne, R. H. (1988) Indicator ligands in metal complexation studies: Role of 4-(2-pyridylazo) rezorcinol in europium carbonate equilibrium investigations, *Anal. Chem.*, **60**, 19-22.

62. Chatt, A., Rao, R. R. (1989) Complexation of europium(III) with carbonate ions in groundwater, *Mat. Res. Soc. Symp. Proc.*, **127**, 697-704

63. Meinrath, G., Kim, J. I. (1991) The carbonate complexation of the Am(III) ion, *Radiochimica Acta* , **52/53**, 29-34.

64. Lee, J. H., Byrne, R. H. (1993) Complexation of trivalent rare earth elements (Ce, Eu, Gd, Tb, Yb) by carbonate ions, *Geochim. Cosmochim. Acta* , **57**, 295-302.

65. Fridman, Ya. D., Dolgashova, N. V. (1964) The fluorocarbonates of the rare earth elements, *Zhur. Neorg. Khim.*, **9**, 623-632.

66. Jordanov, N, Havezov, I. (1966) Löslichkeitsprodukte der normalen carbonate einiger dreiwertiger seltener erden ($E_2(CO_3)_3 \cdot n H_2O$), *Z. Anorg. Chem.*, **347**, 101-106.

67. Caro, P., Lemaître-Blaise, M., Trombe, F. (1968) Identification et solubilités des phases solides à l'equilibre sous une atmosphère de gaz carbonique dans les systèmes ternaires oxydes de terres rares -gaz carbonique-eau , *Comp. Rend. Ac. Sci. Paris*, Serie C, **267**, 1594-1597.

68. Caro, P., Lemaitre-Blaise, M. (1969) Hydroxycarbonates des terres rares $Ln_2(CO_3)_x(OH)_{2(3-x)}$ nH_2O, *Comp. Rend. Ac. Sci. Paris*, Serie C, **269**, 687-690.

69. Firsching, F. H., Mohammadzadel, J. (1986) Solubility products of the rare earth carbonates, *J. Chem. Eng. Data,* **31**, 40-42.

70. Felmy, A. R., Rai, D., Fulton R. W. (1990) The Solubility of $AmOHCO_3(s)$ and the Aqueous Thermodynamics of the System Na^+ - Am^{3+} - HCO_3^- - CO_3^{2-} - OH^- - H_2O, *Radiochimica Acta* , **50**, 193-204.

71. Meinrath, G., Kim, J. I. (1991) Solubility products of different Am(III) and Nd(III) carbonates, *Eur. J. Solid State Inorg. Chem.*, **28**, 383-388.

72. Runde, W., Meinrath, G., Kim, J. I. (1992) A Study of Solid-Liquid Phase Equilibria of Trivalent Lanthanide and Actinide Ions in Carbonate Systems, *Radiochimica Acta*, **58/59**, 93-100.

73. Grenthe, I., Spahiu, K., Eriksen, T. (1992), Studies on metal carbonate equilibria. 24. Analysis of the solubility equilibria of yttrium carbonate in aqueous perchlorate media using the Pitzer and Bronsted-Guggenheim-Scatchard ion interaction models, *J. Chem.Soc. Faraday Trans.*, **88**, 1267-1273.

74. Rai, D., Felmy, A. R., Fulton R. W., Ryan, J. L. (1992) Aqueous chemistry of Nd in borosilicate-glass / water systems, *Radiochimica Acta* , **58/59**, 9-16.

75. Vitorge, P. (1992) $Am(OH)_3(s)$, $AmOHCO_3(s)$, $Am_2(CO_3)_3(s)$ Stabilities in Environmental Conditions, *Radiochimica Acta* , **58/59**, 105-107.

76. Gamsjäger, H. (1993) Solid-solute phase equilibria: From thermodynamic basis information to multicomponent systems, *Aquatic Sciences*, **55**, 314-323.

77. Carroll, S. (1993) Precipitation of Nd-Ca carbonate solid solution at 25 °C, *Geochim. Cosmochim. Acta,* **57**, 3383-3393.

78. Wakita, H., Kinoshita, S. (1979) A synthetic study of the solid solutions in the system $La_2(CO_3)_3.8H_2O-Ce_2(CO_3)_3.8H_2O$ and $La(OH)CO_3-Ce(OH)CO_3$, *Bull. Chem. Soc. Japan*, **52**, 428-432.

79. Tareen, J. A., Kutty, T. R. N. (1980) Hydrothermal phase equilibria in $Ln_2O_3-H_2O-CO_2$ systems. I. The lighter lanthanides, *J. Crystal Growth*, **50**, 527-532.

80. Williams-Jones, A. E., Wood, S. A. (1993) A preliminary petrogenetic grid for REE fluorocarbonates and associated minerals, *Geochim. Cosmochim. Acta* , **57**, 725-738.

81. Mayer, S. W., Schwartz, S. W. (1950) The association of cerous ion with sulphite, phosphate and pyrophosphate ions, *J. Amer. Chem. Soc.*, **72**, 5106-5110.

82. Borisov M. S., Yelesin, A. A., Lebedev, I. A., Filimonov, V. T., Yakovliev, G. I. (1966) Investigations of complex formation of trivalent actinides and lanthanides in phosphoric acid solutions, *Radiokhimyia*, **8**,1966, 42-48.

83. Rao, V. K., Shahani, C. J., Rao, C. L. (1970) Studies on the phosphate complexes of actinium and lanthanum, *Radiochimica Acta*, **14**, 32-34.

84. Afonin, E. G., Pechurova, N. I. (1987) Complex formation of Nd (III) with phosphoric acid, *Zhur. Neorg. Khim.*, **33**, 2141-2142.

85. Bingler, L. S., Byrne, R. H. (1989) Phosphate complexation of Gd(III) in aqueous solutions, *Polyhedron,* **8**, 1315-1320.

86. Byrne, R. H., Lee, J. H., Bingler, L. S. (1991) Rare earth element complexation by PO_4^{3-} ions in aqueous solutions, *Geochim. Cosmochim. Acta*, **55**, (1991), 2729-2735.

87. Byrne R. H., Bingler L. S. (1989) Comment on " Cerium : A chemical tracer for paleo-oceanic redox conditions " by Liu, Y. G., Miah, M. R. U., Schmitt, R. A., *Geochim. Cosmochim. Acta* , **53**,1475-1476.

88. Liu, Y. G., Miah, M. R. U., Schmitt, R. A. (1989) Reliability of the reported stability constant for $CePO_4^{\circ}$, as related to Ce redox formulations in sea water, *Geochim. Cosmochim. Acta*, **53**, 1477-1479.

89. Jonasson, R. G., Bancroft, G. M., Nesbit, H. W. (1985) Solubilities of some hydrous REE phosphates with implications for diagenesis and sea water concentrations, *Geochim. Cosmochim. Acta*, **49**, 2133-2139.

90. Tananaev, I. V., Vasil'eva, V. P. (1963) Lanthanum phosphates, *Russ. J. Inorg. Chem.*, **8**, 555-558.

91. Tananaev, I. V., Petrushkova, S. M. (1967) A study of the interaction of gadolinium chloride with orthophosphate ions in aqueous solution at 25 °C, *Russ. J. Inorg. Chem.*, **12**, 81-86.

92. Chukhlantsev, V. G., Alyamovskaya, K. V. (1961) *Izvest. VUZ*, **4**, 359.

93. Pepin, J. G., Vance, E. R. (1981) Crystal data for rare earth orthophosphates of the monazite type structure. *J. Inorg. Nucl. Chem.* **43**, 2807-2809.

94. Bernkopf, M. F.(1984) Hydrolysereaktionen und karbonatkomplexierung von dreiwertigem Americium in naturlichen aquatischen System, *Ph. D. Thesis,* Institut für Radiochemie der Technischen Universität München.

95. Allard, B., Kipatsi, H., Liljenzin, J. O. (1980) Expected species of uranium, neptunium and plutonium in neutral aqueous solutions, *J. Inorg. Nucl. Chem.,* **42**, 1015-1027.

96. Allard, B.(1982) Sorption of actinides in granitic rock, *SKB Techical Report*, SKB-TR-82-21, and: Allard, B. (1983) Actinide solution equilibria and solubilities in geologic systems, SKB Technical Report SKB-TR-83-35.

97. Paul, A. D., Gallo, L. S. VanCamp, J. B. (1961) The fluoride complexing of yttrium(III) in aqueous solution, *J. Phys. Chem.* **65**, 441-443.

98. Walker, J. B., Choppin, G. R., (1967) Thermodynamic parameters of fluoride complexes of the lanthanides, *Adv. Chem.*, **71**, 127-140.

99. Aziz, A., Lyle, S. J. (1969) Equilibrium constants for aqueous fluoro complexes of scandium, yttrium, americium(III) and curium(III) by extraction into di-2-ethylhexyl phosphoric acid, *J. Inorg. Nucl. Chem.*, **31**, 3471-3480.

100. Aziz, A., Lyle, S. J. (1970) Complexes of lanthanum and actinum with fluoride, oxalate and sulphate in aqueous solutions, *J. Inorg. Nucl. Chem.*, **32**, 1925-1932.

101. Fraustro da Silva, J. R., Queimado, M. M. (1973) *Rev. Port. Quim.* **15**, 29.

102. Itoh, H., Hachiya, H., Tsuchiya, M., Suzuki, Y. (1984) Determination of solubility products of rare earth fluorides by fluoride ion selective electrode, *Bull. Chem. Soc. Japan,* **57**, 1689-1690.

103. Koroleva, G. N., Gava, S. A., Poluektov, N. S., Kirillov, A. I., Kornelli, M. E. (1976), *Dokl. Acad. Nauk. SSSR*, **228**, 1384.

104. Vasil'ev, V. P., Kozlovskii, E. V., *Russ. J. Inorg. Chem. (Engl. Transl.),* **22**, 472.

105. Lingane, J. J. (1968) Further study of lanthanum fluoride membrane electrode for potentiometric determination and titration of fluoride, *Anal. Chem.*, **40**, 935-939.

106. Menon, M. P. (1981) Radiometric, potentiometric and conductimetric measurements of the solubility and solubility product of europium trifluoride, *J. Radioanal. Chem.*, **62**, 283-294.

107. Menon, M. P. (1982) Solubility product constant and thermodynamic values for the terbium trifluoride-water system, *J. Chem. Eng. Data,* **27**, 81-84.

108. Spedding, F. H., Jaffe, S. (1954) Conductances, solubilities and ionization constants of some rare earth sulfates in aqueous solutions at 25 °C, *J. Am. Chem. Soc.*, **76**, 882-884.

109. Sekine, T. (1965) Solvent extraction study of trivalent actinide and lanthanide complexes in aqueous solutions. II. Sulfate complexes of La(III), Eu(III), Lu(III) and Am(III) in 1 M $NaClO_4$. *Acta Chem. Scand.*, **19**, 1469-1475.

110. De Carvalho, R. G., Choppin, G. R. (1967) Lanthanide and actinide sulphate complexes. I. Determination of stability constants. *J. Inorg. Nucl. Chem.* **29**, 725-735.

111. Izatt, R. M., Eatough, D., Christensen, J. J., Bartholomew, C. H. (1969) Calorimetrically determined log K, H°, and S° values for the interaction of sulphate ion with several bi-and ter-valent ions, *J. Chem. Soc. London*, 47-53.

112. Powell, H. P. K. (1974) Entropy titrations: A reassessment of data for the reaction of the sulphate ion with trivalent lanthanoid ions, *J. Chem. Soc. Dalton Trans.*, 1108-1112.

113. Rard, J. A. (1988) Aqueous solubilities of praseodimium, europium and lutetium sulphates, *J. Solution. Chem.*, **17**, 499-517.

114. Paul, A. D. (1962) The chloride and bromide complexing of scandium(III) and yttrium(III) in aqueous solution., *J. Phys. Chem.* **66**, 1248-1252.

115. Choppin; G. R., Unrein, P. J. (1963) Halide complexes of the lanthanide elements, *J. Inorg. Nucl. Chem.* **25**, 387-393.

116. Bansal, B. M. L., Patil, S. K., Sharma, H. D. (1964) Chloride, nitrate, and sulphate complexes of europium(III) and americium(III) *J. Inorg. Nucl. Chem.* **26**, 993-1000.

117. Mironov, V. E., Avramenko, N. I., Koperin, A. A., Blokhin, V. V., Eike, M. Yu, Isayev, I. D. (1982) Thermodynamics of the formation reaction of the monochloride complexes of the rare earth metals in aqueous solution, *Koord. Khim.* **8**, 636-638.

118. Choppin, G. R., Strazik, W. F. (1965) Complexes of trivalent lanthanide and actinide ions. I. Outer-sphere ion pairs., *Inorg. Chem.* **25**, 387-393.

119. Sekine, T, Sakamoto, I, Sato, T., Taira, T., Hasegawa, Y. (1967) Complexes of europium(III) with nitrate and chloride ions in 4 M $NaClO_4$, *Bull. Chem. Soc. Japan*, **40**, 251-254.

120. Breen, P. J., Horrocks, Jr. W. (1983) Europium(III) luminiscence excitation spectroscopy - Inner sphere complexation of europium(III) by chloride, thiocyanate and nitrate ions., *Inorg. Chem.*, **22**, 536-540.

121. Siekierski, S., Misoudski, T., Salomon, M. "Solubility data series, Volume 13. Scandium, yttrium, lanthanum and lanthanide nitrates", Pergamon Press , Oxford., 1983.

122. Trombe, F., Blaise, M., Caro, P. (1966) Sur la solubilité des carbonates d'yttrium, de scandium et des quelques éléments des terres rares dans l'eau chargée de gaz carbonique, *Comp. Rend. Ac. Sci. Paris*, Serie C, **263**, 521-524.

123. Caro, P., Lemaitre-Blaise, M., Dexpert, H., Sawyer, J. (1971) Un hydroxycarbonate de terres rares Ln(OH)CO_3 (Ln=Terres rares) isomorphe du fluorocarbonate bastnaesite LnFCO_3, *Comp. Rend. Ac. Sci. Paris*, Serie C, **272**, 57-59.

124. Haschke, J. M., Eyring, L. (1971) Hydrothermal equilibria and crystal growth of rare earth oxides, hydroxides, hydroxynitrates and hydroxycarbonates, *Inorg. Chem.*, **10**, 2267-2274.

125. Chai, B. T. H., Mroczkowski, S. (1978) Synthesis of rare earth carbonates under hydrothermal conditions, *J. Cryst. Growth,* **44**, 84-97.

126. Silva, R. J., Nitsche, H. (1983) Thermodynamic properties of chemical species of waste radionuclides, Report, NUREG/CP-0052, U. S. Nuclear Regulatory Commission.

127. Shiloh, M., Givon, M, Marcus, Y. (1969) A spectrophotometric study of trivalent actinide complexes in solution. III. Americium with bromide, iodide, nitrate and carbonate ligands, *J. Inorg. Nucl. Chem.* **31**, 1807-1814.

128. Newton, T. W., Sullivan, J.C. (1985) Actinide carbonate complexes in aqueous solution, in: Handbook of the physics and chemistry of the actinides (Freeman, A., Keller, C. eds.), Vol. 3, Amsterdam, North Holland, 1985.

129. Rai D., Felmy A. R., Fulton R. W. (1992) Solubility and ion activity product of $AmPO_4 \cdot x\ H_2O$(am). *Radiochimica Acta*, **56**, 7-14.

130. Bidoglio, G., Marcandalli, B, (1983) Caratterizzazione e determinazione di constanti di stabilita di carbonato complessi di lantanidi, Comm. Eur. Comm., Rep. EUR 8275, 97 pp.

131. Torres R. A., Choppin G. (1984) Europium(III) and Americium(III) Stability Constants with Humic Acid, *Radiochimica Acta*, **35**, 143-148.

132. Maes, A., De Brabandere, J., Cremers, A. (1991) Complexation of Eu^{3+} and Am^{3+} with Humic Substances, *Radiochimica Acta*, **52/53**, 41-47.

133. Bruno J. (1986) Stoichiometric and structural sudies on the Be^{2+} - H_2O - $CO_2(g)$ system, Ph. D. dissertation, Royal Inst. of Technol., Stockholm.

134. Parkhurst, D. L., Thorstenson, D. C., Plummer, L. N. PHREEQE- A computer program for geochemical calculations. US Geologicl Survey-Water Resources Investigations. Report 80-96, 1980. *also* Brown, P. L., Haworth, A., Sharland, S. M., Tweed, C. J. (1991) HARPHRQ-A geochemical speciation program based on PHREEQE. Nirex safety Studies. *Report* NSS/R188.

135. Wolery, T. J., Calculation of chemical equilibrium between aqueous solution and minerals; the EQ 3/6 software package. UCRL-52658, Lawrence Livermore National Laboratory, Livermore, CA, 1979. *also* Wolery, T. J., Isherwood, D. J., Jackson, K. J., Delany, J. M, Puigdomenech, I. EQ 3/6: Status and applications, in "*Proceedings conference on application of geochemical models to high-level nuclear waste repository assessment*", (K. G. Jacobs and S. K. Whatley *editors*) Oak Ridge, Tennesee, 1984. NUREG/CP -0062, ORNL/TM-9585, pp. 54-65.

136. Chandratillake, M., Falk, W. E., Read, D.(1992) CHEMVAL project. Guide to the CHEMVAL thermodynamic database. UK DoE *Report No.* UK/DoE/HMIP/RR/92/094, 24 p.

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[1] GeoPoint AB, Sollentuna, Sweden
[2] Conterra AB, Uppsala, Sweden
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[1] Conterra AB
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[1] Clay Technology AB, Lund, Sweden
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[2] Itasca Consulting Group Inc.
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