

J. J. R. FRAÚSTO DA SILVA

M. MANUELA QUEIMADO

Centro de Estudos de Química Nuclear (I. A. C.)
Instituto Superior Técnico
Lisboa



SOLUBILITY PRODUCTS OF LANTHANIDE FLUORIDES

The solubility products of the lanthanide fluorides at 25.0 °C and $p = 0.1$ (NaNO_3) have been measured using a fluoride ion specific electrode. Consistent values were obtained after aging of the precipitates for 5-10 days. The pK_s values decrease from 18.9 for lanthanum to 15.0, for lutecium fluorides. This trend is in agreement with that to be expected from a theoretical treatment of the thermodynamic parameters involved, using a Born-Haber cycle and Kapustinskii's equation to estimate the thermochemical radii of rare earth ions.

1 — INTRODUCTION

The lanthanide elements have attracted much attention in the last few years not only for reasons related to the increasing number of applications in metalurgy and electronic devices but also for the peculiarities of their chemistry which, in many aspects, is still not well understood.

The lack of reasonable quantities of sufficiently pure compounds of these elements has been partly responsible for the neglect of research in this area, which, furthermore, was considered rather uninteresting face to the spectacular developments that took place in the chemistry of the main transition series.

The development of better separation methods, using either ion-exchange or fractional precipitation techniques, solved the problems of price and supply but, at the same time, several questions related to the particularities of the electronic distribution in the lanthanides and its effect on the relative sizes of the respective ions, the anomalies registered in the properties of many of their compounds and, more recently, the possibility of their use as probes for alkali and alkaline-earth metals in biological systems, aroused widespread interest in the chemistry of those elements and several studies have been undertaken to elucidate different aspects of their behaviour.

One of the problems which has called for some attention is that of the correlation between the free-energies of formation of several species — hydrated ions, complexes of various ligands, sparingly soluble salts — and the atomic number of the elements. Unlike what seems to be rather general for the main transition metals, such correlations are here most variable: sometimes, the free energies of formation increase with the atomic number, sometimes they decrease and still other times non-systematic variations are obtained.

Many explanations have been advanced for this behaviour and some generalisations have been put forward, particularly for the formation of sparingly soluble salts. Hence, it is generally assumed that the solubility of the lanthanide salts increase with the atomic number when the anion of the salt considered derives from a strong acid and decreases with the atomic number in the opposite case (1). As examples, one may quote the case of the lantha-

nide sulfates (solubility increases with atomic number) and those of the hydroxides and dimethylphosphates (solubility decreases with atomic number).

This generalisation is not satisfactory for many exceptions are known and the division strong acid-weak acid is not a clear-cut one. We have thus decided to undertake a study of the problem and try to formulate it more adequately in precise thermodynamic terms. The fluorides were chosen for this first study due to a combination of reasons which include the fact that hydrofluoric acid is a moderately strong acid, the fact the F^- in solution penetrates the internal hydration sheath of the lanthanide ions, contrarily to what happens with many other inorganic anions, the fact that fluoride selective precipitation of lanthanides is a separation technique with practical importance and, last but not the least, the recent availability of reliable solid state fluoride specific electrodes.

2 — EXPERIMENTAL

2.1 — REAGENTS

The oxides of the lanthanide elements, of purity above 99.9 %, were ignited at 800-900 °C, cooled in a desiccator, accurately weighed to give 0.035M solutions and dissolved in the minimum amount of HNO_3 . The excess of acid was removed by repeated evaporation to dryness in a steam bath. Sodium fluoride was of Analar grade; all water used in this work was deionised.

2.2 — INSTRUMENTS

All measurements were made with a Beckman Research pH meter equipped with an ORION solid-state fluoride electrode and an ORION sleeve calomel reference.

2.3 — TECHNIQUE

Since titration techniques proved to be subject to a number of errors and are exceedingly time-

consuming to achieve reproducible results, a batch procedure was adopted, which gave quite satisfactory results.

Equal samples of a 0.035M solution of sodium fluoride were measured into double walled cells with an inner polyethylene lining with thermostated circulating water at 25 °C and an excess of a 0.035M solution of lanthanide nitrate was added with stirring.

The total volume was adjusted with distilled water to which the calculated amount of $NaNO_3$ was added to keep the ionic strength to 0.1M the precipitates formed were left to age with occasional stirring and the potential was measured after regular intervals until a constant value was obtained. This took usually between 4 and 10 days and permanent stirring didn't make appreciable change although it shortened the period required for equilibrium to be reached.

pH values were also measured and found to be of the order of 5; although some of the fluoride is in the form of HF this doesn't cause any problem, since the electrode was calibrated in free F^- concentration; on the other hand, the correction in the concentration of lanthanide ion due to the solubilisation of the respective fluoride was found to be negligible face to the excess of precipitant used.

The main difficulties derived from the lack of strict compliance of the fluoride electrode with Nernst's law below $[F^-] < 10^{-5}$ and a certain tendency for decreasing reproductibility at low fluoride concentrations. For these reasons the values of the solubility products obtained in the present work are more precise for the heavier and more soluble lanthanide fluorides than for the lighter and less soluble ones, although the errors in the last case are not likely to exceed 0.3 units in pK_s values.

3 — CALCULATIONS

Solubility products were calculated at 0.1M ionic strength and 25.0 °C temperature as $K_s = [M^{3+}][F^-]^3$; $[M^{3+}]$ was determined from the excess of tritrant used and $[F^-]$ from the calibration curve for the fluoride electrode, which was repeated

before final measurements were made. Each value of K_s presented is the mean of 4 different sets of experiments, in which 50 %, 75 %, 125 % and 175 % excess of lanthanide nitrate was used relatively to the fluoride present.

Thermodynamic solubility products $K_s^0 = (M^{3+})(F^-)^3$ were obtained using the expression $K_s^0 = \gamma_{\pm}^4 \cdot K_s$ where the activity coefficient γ_{\pm} may be calculated with reasonable approximation by Davies' expression:

$$\log \gamma_{\pm} = -A |Z_i Z_j| \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right)$$

4 — RESULTS AND DISCUSSION

The results obtained in the present work are summarized in Table 1 and pK_s values are correlated with the atomic number of the lanthanides in fig. 1. The precision of the determinations is of the order of ± 0.3 pK unit for the lighter lanthanides and ± 0.1 pK for the heavier ones.

As it can be seen in the figure, pK_s values decrease

with the atomic number of lanthanides, corresponding to an increase of the solubility of the heavier fluorides. The values of pK_s for LaF_3 and EuF_3 are higher than those obtained by Lingane for the freshly precipitated fluorides (respectively 17,9 and 16,7) (2) which are obtained in a hydrated sometimes colloidal, metastable form. Titration curves obtained using this author's technique exhibited a pronounced tendency to shift to higher potentials after the equivalence point, which corresponds to a decrease in solubility.

The trend represented in fig. 1 is in agreement with that referred for the sparingly soluble salts derived from the anions of strong acids, which is not exactly the case with hydrofluoric acid since its pK_a is of the order of 3.2. On the other hand, in terms of the lattice energies of the different fluorides, one would expect that solubility decreased with the atomic number, since the lanthanide ions decrease in size and the lattice energy is inversely proportional to the sum of the anion and the cation radii.

Both arguments are, however, rather crude, because solubility is the result of a complex process which may be visualised with the help of a Born-Haber

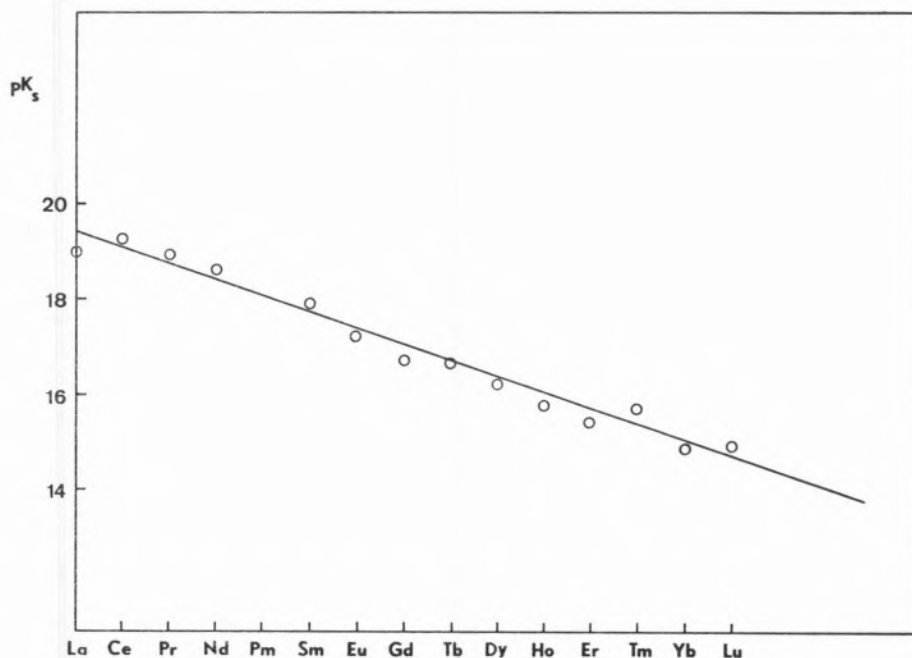


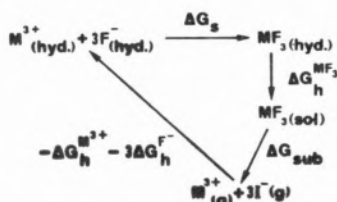
Fig. 1
Variation of pK_s with atomic number for the series of lanthanide fluorides.

Table I

Stoichiometric and thermodynamic solubility products of lanthanide fluorides, $T = 25.0^\circ\text{C}$, $\mu = 0.1\text{ M}$

Lanthanide	K_s	pK_s	K_s°	pK_s°
La	1.19×10^{-19}	18.9 (2)	6.19×10^{-21}	20.2
Ce	5.58×10^{-20}	19.2 (5)	2.90×10^{-21}	20.5
Pr	1.09×10^{-19}	18.9 (6)	5.69×10^{-21}	20.2
Nd	2.36×10^{-15}	18.6 (3)	1.23×10^{-20}	19.9
Sm	1.01×10^{-18}	17.9 (9)	5.27×10^{-20}	19.3
Eu	5.98×10^{-18}	17.2 (2)	3.11×10^{-19}	18.5
Gd	1.58×10^{-17}	16.8 (0)	8.22×10^{-19}	18.1
Tb	1.85×10^{-17}	16.7 (3)	9.61×10^{-19}	18.0
Dy	4.67×10^{-17}	16.3 (3)	2.43×10^{-18}	17.6
Ho	1.33×10^{-16}	15.8 (7)	6.93×10^{-18}	17.2
Er	2.96×10^{-16}	15.5 (3)	1.54×10^{-17}	16.8
Tm	1.50×10^{-16}	15.8 (2)	7.82×10^{-18}	17.1
Yb	9.62×10^{-16}	15.0 (2)	5.00×10^{-17}	16.3
Lu	8.42×10^{-16}	15.0 (7)	4.38×10^{-17}	16.4

cycle (in which one assumes that the value of pH is such that no HF is formed):



The meaning of the symbols is as follows:

ΔG_s — Gibbs' free energy of dissolution of MF_3

$\Delta G_h^{M^{F_3}}$ — Gibbs' free energy of hydration of MF_3

ΔG_{sub} — Gibbs' free energy of sublimation of the lattice into the separate gaseous ions at 1 atm

$\Delta G_h^{M^{3+}}, \Delta G_h^{F^-}$ — Gibbs' free energy of hydration of gaseous ions

According to the first principle of thermodynamics

$$\Delta G_s + \Delta G_h^{M^{F_3}} + \Delta G_{\text{sub}} - \Delta G_h^{M^{3+}} - 3\Delta G_h^{F^-} = 0 \quad (1)$$

One may admit that $\Delta G_h^{M^{F_3}}$ can be disregarded, since the solids have been found to be anhydrous; hence, if ΔG_s is replaced by $-2.303 RT pK_s^\circ$,

$$2.303 RT pK_s^\circ = \Delta G_{\text{sub}} - \Delta G_h^{M^{3+}} - 3\Delta G_h^{F^-} \quad (2)$$

If all the Gibbs free energies are known, pK_s° values for the several lanthanide fluorides can be derived and their order compared with that obtained from direct determinations.

Now $\Delta G_h^{F^-} = 103.1$ Kcal/mole in the absolute scale ($\Delta G_h^{H^+} = 0$) and the Gibbs' free energies of hydration of the lanthanides can be approximated by the equation:

$$\Delta G_h^{M^{3+}} = -163.9 \cdot \frac{Z^2}{r_{\text{ef}}} \text{ Kcal/mole} \quad (3)$$

where Z is the charge of the ion and r_{ef} their effective radii, which equals the Pauling's crystalline radii plus 0.75 \AA (4).

The Gibbs' free energy of sublimation of the lattice G_{sub} may be calculated by the expression (3)

$$G_{\text{sub}} = \frac{287.2(a+c)Z^+ \cdot Z^-}{r^+ + r^-} \left(1 - \frac{0.345}{r^+ + r^-}\right) - 7.4(a+c) \quad (4)$$

where the lattice energy is given by Kapustinskii

Table II

Comparison of «Thermochemical» and Pauling's ionic radii of rare earth ions

Lanthanide	pK_s^0 experimental	$G_{hid}^{M^{3+}}$ kcal/mole	r^+ Pauling Å	r^+ experimental Å	$r^+ - r^-$ Pauling exp. Å
La	20.2	776.4	1.15	1.26	0.11
Ce	20.5	793.1	1.11	1.21	0.10
Pr	20.2	801.7	1.09	1.19	0.10
Nd	19.9	806.1	1.08	1.18	0.10
Pm	—	—	—	—	—
Sm	19.3	824.1	1.04	1.14	0.10
Eu	18.5	828.7	1.03	1.13	0.10
Gd	18.1	833.4	1.02	1.12	0.10
Tb	18.0	842.9	1.00	1.08	0.08
Dy	17.6	847.8	0.99	1.09	0.10
Ho	17.2	857.6	0.97	1.06	0.09
Er	16.8	862.6	0.96	1.05	0.09
Tm	17.1	867.7	0.95	1.04	0.09
Yb	16.3	872.8	0.94	1.03	0.09
Lu	16.4	878.1	0.93 —	1.05	0.12

equation since the Madelung constant for the structures of rare earth fluorides is unknown and, therefore, the more rigorous Born-Mayer equation cannot be used.

In this expression a and c are the stoichiometric coefficients of the compound (in the case of MF_3 , $a = 3$ and $c = 1$), Z^+ and Z^- are the charges and r^+ , r^- the radii of the cation and the anion.

A problem arises concerning the most adequate values to be used for $r^+ + r^-$, since the rare earth fluorides crystallize in two types of structure, one hexagonal (La to Sm) and the other orthorhombic (Sm to Lu) and in both cases there are two different $M^{3+} - F^-$ distances (5); furthermore, the

radii for the M^{3+} ions have been tabulated from results obtained with different compounds, namely the oxides.

In this conditions it is interesting to adopt the experimental pK_s^0 values and calculate «thermochemical» radii for the rare earth ions from equation 4 to be compared with the tabulated Pauling's ionic radii — Table II.

As it is shown the deviations among the several pairs of values are of the order of only 0.1 Å and practically constant; it is then reasonable to assume that the use of Kapustinskii's equation is legitimate, given the approximations of all the calculations.

The thermochemical radii decrease from La^{3+} to Lu^{3+} , hence the order of experimental pK_s is correct and explained on the basis of the combined effects of lattice and hydration energies.

It is interesting to note that although the lanthanide fluorides crystallize in two different structure types already referred to, there seems to be no appreciable differences in behaviour. The solubility of both types of species should then be of the same order of magnitude; on the other hand the empirical assumption of higher solubilities for the lanthanide salts derived from strong (and moderately strong) acids receives some support. However this cannot be taken as a general rule since cases are known of weak acids (such as carbonic and oxalic acids) whose lanthanide salts also exhibit increasing solubility with the increase in atomic number. Since in these cases the formation of protonated species has to be considered there may not be any real contradiction, but the theoretical derivation of the equation necessary to calculate solubility products is rather involved and the lack of adequate data prevents its use for prediction or comparison purposes.

REFERENCES

1. Phillips, C. S. G. and Williams, R. J. P., «Inorganic Chemistry», Vol. 2, Oxford at the Clarendon Press, Oxford, 1966, p. 112.
2. Lingane, J. J., *Anal. Chem.*, **40**, 935 (1968).

3. Johnson, D. A., «Thermodynamic Aspects of Inorganic Chemistry», Cambridge University Press, Cambridge, 1968, Chapt. 5.
4. Harvey, K. B. and Porter, G. B., «Physical Inorganic Chemistry», Addison Wesley Publ. Co., Reading, Mass., 1963, pp. 332-333.
5. Phillips, C. S. G. and Williams, R. J. P., «Inorganic Chemistry», Vol. 2, Oxford at the Clarendon Press, Oxford, 1966, p. 109.

RESUMO

Utilizando um eléctrodo específico para o ião fluoreto mediram-se os produtos de solubilidade dos fluoretos dos lantanídeos à temperatura de 25 °C e força iónica = 0,1 (NaNO_3). Deixando envelhecer os precipitados durante 5 a 10 dias obtêm-se valores de pK_s bastante concordantes. Os valores de pK_s diminuem desde 18,9 para o fluoreto de lantânio até 15,0 para o fluoreto de lutécio. Esta tendência está de acordo com o que seria de esperar a partir dum tratamento teórico dos parâmetros termodinâmicos envolvidos usando um ciclo de Born-Haber assim como a equação de Kapustinskii para determinar os raios termodinâmicos dos iões dos lantanídeos.