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LANTHANIDE, YTTRIUM, AND SCANDIUM TRIHALIDES: PREPARATION OF ANHYDROUS MATERIALS AND SOLUTION THERMOCHEMISTRY

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I. Introduction

The primary aim of this review is to collect together information on the solution thermochemistry of the trihalides of the lanthanides,[1] yttrium, and scandium. There is a meager amount of published work relating to nonaqueous solvents, rather more relating to aqueous solu-

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[1] Lanthanum is considered a member of the lanthanide series for the purposes of this review; we shall also from time to time include yttrium and scandium within the generic term "lanthanide."

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tions. We shall deal with both types of solvent, in both cases concentrating on enthalpies of solution and on solubilities.

The determination of many thermodynamic solution properties of these trihalides, especially enthalpies of solution, requires the use of anhydrous materials. These are by no means always readily available for this group of compounds. Therefore we precede our discussion of thermochemical results with a section on preparative methods, in which we deal summarily with many of the relevant papers published since Taylor's extensively referenced review, published in 1962 (*1*).

II. Preparation of Anhydrous Rare-Earth Trihalides

The preparations of rare-earth trihalides can be found in various books (*2–8*) and in Taylor's review (*1*). This review, however, did not include the preparation of scandium and yttrium trihalides, and only covered the preparation of the trifluorides very briefly. We have reviewed the preparation of all the trihalides (including scandium and yttrium) from Taylor's review up to June 1979 and have also included some methods and references missed by Taylor. Although we have mentioned all the methods available for the preparation of the trihalides, emphasis has been placed on the methods used since Taylor's review, and these have been referenced fully, whereas for the other methods, Taylor's review is recommended as a source of references.

The preparation of promethium trihalides has been mentioned by Scherer (*9*). However, the radioactive nature of these compounds has prevented any calorimetric or solubility investigations so far, and they make only one fleeting appearance in this review.

A. TRIFLUORIDES

Taylor's treatment of lanthanide trifluorides was considerably more cursory than that of the other three trihalides, but nonetheless still provides a starting point (*1*). More recently, the extraction, preparation, and treatment of the trifluorides have been dealt with in Gmelin (*4a*).

1. From Solvates

The dehydration of hydrates has been widely used, both by earlier workers (*1*) and recently (*10*). Heating ammoniates $ScF_3 \cdot 0.4NH_3$, $YF_3 \cdot 0.35NH_3$, and $LnF_3 \cdot nNH_3$ also gives anhydrous trifluorides in a convenient manner (*11*).

2. *From Oxides*

Taylor's suggestion (*1*) that heating oxides Ln_2O_3 with ammonium fluoride should prove a satisfactory method for preparing anhydrous lanthanide fluorides has been implemented (*4a, 12*). The trifluorides are also obtained by heating the oxides with fluorine (*4a*), hydrogen fluoride (*1, 4a*), chlorine trifluoride (*13*), bromine trifluoride (*14*), sulfur tetrafluoride (*15*), sulfur hexafluoride (*4a, 16*), and the fluorochlorocarbons CCl_2F_2 (*17*) and CCl_3F (*18*). Reaction in a cadmium fluoride melt also gives lanthanide trifluorides (*19*).

3. *From Trichlorides*

Lanthanide trichlorides can be converted into the corresponding trifluorides by treatment with fluorine (*20*), or aluminum fluoride (melt) (*21*).

4. *Other Methods*

Direct reaction of the metals with anhydrous hydrogen fluoride gives, after removal of absorbed hydrogen fluoride under vacuum, pure trifluorides (*22*). Direct fluorination of the respective carbides has been described for lanthanum, praseodymium, and neodymium (*23*). Several reactions of the nitrates in fluoride melts, including $KF-KBO_3$, $NaF-NaNO_3$, and ammonium fluoride (*24*), give the anhydrous trifluorides. Heating trifluoromethylsulfonates gives very pure samples of the trifluorides (*25*); heating ammonium fluorometallates also gives anhydrous trifluorides (*26*).

B. TRICHLORIDES, TRIBROMIDES, AND TRIIODIDES

1. *General Methods*

First, the methods that apply to all three trihalides are reviewed; then other specific methods are mentioned. Far fewer methods have been perfected for preparing anhydrous lanthanide tribromides than for the trichlorides, though most of them are similar. The triiodides are the most difficult to prepare, as the iodine analogs of several useful chloro and bromo sulfur and carbon compounds are not known. Reaction temperatures for preparation of triiodides have to be carefully controlled, as SmI_3 and YbI_3, for example, decompose easily at elevated temperatures to diiodides. The existence of EuI_3 is questionable, with EuI_2 formed even at room temperature.

2. *Direct Halogenation of the Metals*

Undoubtedly, the best method for the production of pure anhydrous lanthanide trihalides involves direct reaction of the elements. However, suitable reaction vessels, of molybdenum, tungsten, or tantalum, have to be employed; silica containers result in oxohalides (*27*). Trichlorides have been produced by reacting metal with chlorine (*28*), methyl chloride (*28*), or hydrogen chloride (*28–31*). Of the tribromides, only that of scandium has been prepared by direct reaction with bromine (*32*). The triiodides have been prepared by reacting the metal with iodine (*27, 29, 31, 33–41*) or with ammonium iodide (*42*).

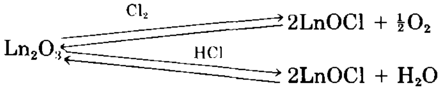
Another attractive method involves reaction of the metals with mercury(II) halides, as the only by-product is mercury:

$$2Ln + 3HgX_2 \rightarrow 2LnX_3 + 3Hg$$

The mercury can be distilled off *in vacuo* (*34, 41–44*). This method works for all three halides.

3. *Conversion of Oxides into Trihalides*

Before the availability of high-purity lanthanide metals, the most popular starting material was the oxide, readily available pure. Because of their high stability, the oxides cannot readily be converted into the respective trihalides simply by reaction with chlorine or hydrogen chloride as oxochlorides are formed; nevertheless, Templeton and Carter (*45*) have prepared pure trichlorides using this method.



$$Ln_2O_3 \xrightarrow{Cl_2} 2LnOCl + \tfrac{1}{2}O_2$$
$$Ln_2O_3 \xrightarrow{HCl} 2LnOCl + H_2O$$

Similarly, tribromides have been prepared by heating the oxide (*46, 47*) or carbonate (*48*) in a stream of dry hydrogen bromide and bromine, and triiodides have been prepared by heating the oxide in a mixture of hydrogen iodide and hydrogen (*49*). However, Block and Campbell (*3b*) obtained only the oxoiodide when they carried out this reaction. If we add a reducing agent—e.g., carbon—to the oxide, then reaction with chlorine (*50–60*) or hydrogen chloride (*56, 61*) gives the trichlorides. The amount of carbon used and the temperature to which the oxides are heated vary for each rare earth. This method also works when bromine is substituted for chlorine, giving pure tribromides (*56*), but no mention of preparing triiodides this way has been found.

The more popular methods of chlorination involve using a volatile chlorinating agent and reducing agent in the same compound, e.g., CCl_4 (*61–67*), CCl_4/Cl_2 (*68, 69*), $CHCl_3$ (*1*), $COCl_2$ (*61, 70*), CO/Cl_2 (*71*), SCl_2 (*1*), S_2Cl_2 (*1*), S_2Cl_2/Cl_2 (*1*), and $SOCl_2$ (*72*). The oxides are converted directly into the trichlorides by passing the vaporized reagent over the heated oxide. Funk obtained $CeCl_3$ by reacting CeO_2 with S_2Cl_2 at a high temperature in a sealed tube (*73*). Similarly, the authors have prepared pure trichlorides by reacting the oxides at 300°C with an excess of CCl_4 in a sealed tube:

$$Ln_2O_3 + 3CCl_4 \rightarrow 2LnCl_3 + 3COCl_2$$

Tribromides have similarly been prepared by treating the heated oxide with CO/Br_2 (*1*), CBr_4 (*74*), S_2Br_2 (*1*), or S_2Cl_2/HBr (*75, 76*).

Trihalides can be produced by heating the oxide with an excess of ammonium halide at a high temperature. The excess ammonium halide is sublimed off in N_2, He (*12*), or *in vacuo* (*39, 77–84*).

The oxides have been converted to the trihalides by reaction with amine hydrohalides with mp <200°C (e.g., $PhNH_2$, $MeNH_2$, Me_2NH, $EtNH_2$, Et_2NH, etc.). A double salt was formed from the reaction with the hydrohalide, which served both as solvent and halogenating agent. The reaction mixture was heated to vaporize the solvent and decompose the double salt, leaving the anhydrous halide (*85*).

4. *Dehydration of Rare-Earth Trihalide Hydrates*

Rare-earth oxides dissolve in dilute hydrohalic acids to produce solutions of the trihalides which can be crystallized, giving six to nine waters of hydration depending upon the halide (cf. Table I). These hydrates cannot be thermally dehydrated, as oxohalides are formed:

$$LnX_3 \cdot nH_2O \xrightarrow{\text{heat}} LnOX + 2HX + (n - 1)H_2O$$

Hence, a variety of dehydrating agents have been used to prevent hydrolysis. However, Brown (*86*) has obtained anhydrous tribromides by thermally dehydrating the hydrates in a vacuum with careful temperature control. In contrast, similar heating of the hydrated triiodides in a vacuum produced oxoiodides rather than anhydrous iodides (*87*).

One of the oldest methods is to pass HX gas over the heated hydrated trihalide. Thus, hydrated trichlorides (*61, 88–92*) are heated initially to 105°C, and then when most of the water has been removed the temperature is raised to 350°C. This method works well for trichlorides, but it does not produce pure tribromides (*93–95*) or triiodides; better results are obtained when the triiodides are heated in a flow of HI and

H_2 (*49*). In place of HCl, other reagents have been used: Cl_2, $COCl_2$, CO/Cl_2, S_2Cl_2/Cl_2, and CCl_4 (*63*).

The hydrates have been heated with an excess of ammonium halide in a stream of air, N_2, CCl_4 (*63*), Cl_2 (*54, 96*), or S_2Cl_2 (*1*) to produce anhydrous trichlorides, or in HBr and N_2 to produce tribromides and in N_2 to give triiodides (*97*).

A better method involves evaporating a solution of LnX_3 containing NH_4X (in a mole ratio of 1:6 for chlorides and 1:12 for iodides) to dryness. The product is transferred to a vacuum line and is slowly heated to 200°C to drive off all the water. The temperature is then raised to 300°C to sublime off the ammonium halide. This method has been used extensively to produce pure trihalides and has proved to give very good results for trichlorides (*52, 78, 79, 98–105*), tribromides (*100–103, 106–108*), and triiodides (*39, 40, 49, 100, 102, 103, 106, 107, 109–111*).

Other dehydrating agents have been used which decompose water—e.g., acetic anhydride, acetyl chloride, and acetyl iodide—with little success. Refluxing the hydrates with thionyl chloride and thionyl bromide gives anhydrous trichlorides and tribromides, but the authors have found that the final traces of thionyl halide could never be removed even on heating in a high vacuum. Reacting the hydrated tribromides or triiodides with thionyl chloride resulted in complete halogen exchange, giving trichlorides in both cases.

Triethyl orthoformate (*112*) and 2,2-dimethoxypropane (*113*) have also been used to dehydrate the trichloride hydrates. They produce solvates—e.g., $LnCl_3 \cdot 4MeOH$ or $LnCl_3 \cdot 3EtOH$—rather than the anhydrous trichlorides, but these alcoholates can be transformed fairly readily into the anhydrous trichlorides (cf. p. 64).

Water is, of course, a particularly difficult solvent to remove from solvates (i.e., hydrates). Thermal decomposition patterns for solvates containing such solvents as tetrahydrofuran suggest that thermal treatment of such solvates may prove a feasible route to anhydrous trihalides.

5. *Halogen Exchange*

An old method of producing anhydrous tribromides and triiodides involves heating the anhydrous trichloride in a stream of HBr or HI at 400–600°C for 7–10 hours. For the triiodides (*39*), a mixture of H_2/HI is normally used, and the conversion takes longer than for the tribromides. This process is difficult to carry out, as the last traces of chloride are very difficult to remove. Recently trifluorides LnF_3 (Ln = Ce, Nd, Y) have been treated with chlorine to produce trichlorides (*114*).

6. *Miscellaneous Methods*

Binary rare-earth compounds such as carbides, sulfides, nitrides, and hydrides have been used to prepare anhydrous trihalides, but they offer no special advantage. Treating these compounds at a high temperature with a halogen (*98*) or hydrogen halide (*115*) produces the trihalide, e.g.,

$$2YC_2 + 3Br_2 \rightarrow 2YBr_3 + 4C$$

$$CeH_3 + 3HBr \rightarrow CeBr_3 + 3H_2$$

Other compounds such as acetates, oxalates, and benzoates have been converted to the trihalides, but in general they do not yield pure products. The acetates have been converted to trichlorides and tribromides by the following method, but no triiodides have been prepared. Ammonia gas is passed through a suspension of the acetate in benzene or toluene; then, after standing for 4 hours, hydrogen halide is passed through the suspension, forming a double metal ammonium halide and ammonium halide. This mixture is filtered off and dried, and the pure trihalide is obtained by subliming off the ammonium halide *in vacuo*. Instead of ammonia, pyridine, piperidine, 2-picoline, or isoquinoline can be used (*116, 117*).

Reaction of the acetate with acetyl chloride or acetyl bromide gives the anhydrous trichloride or tribromide, but on reaction with acetyl iodide anhydrous triiodide cannot be isolated. The oxalates have been converted to trichlorides by reaction with hydrogen chloride, Cl_2/CCl_4 (*88, 118*), or Cl_2/S_2Cl_2 (*88*) at high temperature. Trichlorides and tribromides have also been obtained by treating a suspension of the benzoates in diethyl ether with hydrogen chloride or hydrogen bromide (*46, 47*).

Treating the oxide, trichloride, or metal with boron tribromide or boron triiodide has produced tribromides and triiodides for lanthanum (*119*). Presumably, treating the metal or the oxide with boron trichloride will produce the trichloride.

7. *Methods for Individual Trihalides*

$CeCl_3 \cdot 7H_2O$ has been treated with pyridinium hydrochloride in ethanol to give a white precipitate (which can be completed by adding acetone) of $CeCl_3 \cdot pyHCl \cdot 2H_2O$. This is filtered off, washed with acetone, and dried *in vacuo*. Dry hydrogen chloride is then passed over the salt, which is heated in a glass tube. Most of the water is removed between 100 and 150°C; at 200°, pyridinium hydrochloride starts subliming, and the tube is finally heated to 300–350°C, leaving pure $CeCl_3$ (*120, 121*).

$LaCl_3$, $NdCl_3$, and $GdCl_3$ have been produced from the oxides by heating them with $MoOCl_4$ or WCl_6 (*122*). PCl_5 and $PCl_5/AlCl_3$ have been used to chlorinate the oxides at 900°C (46.8% PCl_5) (*123*). The oxochloride has been converted to the trichloride by treatment with CCl_4 at 550–650°C (*66*). The rate of production of the trichloride by treatment of the dichloride with hydrogen chloride has been studied (*124, 125*).

$EuBr_2$ reacts with bromine at 12–70 atm to give the anhydrous tribromide (*126, 127*). Tribromides and triiodides have been produced by heating the oxide with $AlBr_3$ (*1*), AlI_3 (*128–130*), or Al/I_2 (*40*).

Anhydrous lanthanum and praseodymium trichlorides have been prepared from the hydrates by transforming them into alcohol solvates and breaking them down at 150–180°C in a vacuum (*131*).

8. Conclusions

The methods discussed produce trihalides of varying purity; however, if very pure trihalides are required, they can be sublimed at high temperature from any oxide or oxohalide impurities. The trichlorides can usually be obtained pure, but the tribromides and triiodides tend to be contaminated with oxides and oxoiodides. The various methods of preparing triiodides are compared by a few authors (*39, 40, 49, 132*), and they recommend their preferred route, which generally is the direct reaction between the metal and iodine.

III. Hydrates and Solvates

A. General

The existence of solvates of lanthanide halides may be taken as an indication of favorable interaction between the halides and solvent in question. Evidence of this type may suggest solvents which could prove useful or interesting for calorimetric or solubility studies. However, the existence of stable solvates is no guarantee of marked solubility for the halide in the solvent in question. One need look no further than lanthanide fluorides and water for cautionary examples, for despite their very low solubility in water these fluorides form a series of stable hemihydrates, $LnF_3 \cdot \frac{1}{2}H_2O$.

TABLE I

HYDRATES THAT CRYSTALLIZE FROM AQUEOUS SOLUTION

	Number of water molecules																
MX_3	Sc	Y	La	Ce	Pr	Nd	(Pm)	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
MCl_3	6	6			6	6	6	6	6	6	6	6	6	6	6	6	6
			7	7	7												
MBr_3	5																
		6		6		6	6	6	6	6	6	6	6	6	6	6	6
			7		7												
																	8
MI_3	6																
										8	8	8	8	8	8	8	8
		9	9	9	9	9	9	9	9	9	9	9					

B. HYDRATES

The lanthanide fluorides precipitate from aqueous solution as the hemihydrates; hydrates $LnF_3 \cdot 3H_2O$, $\cdot 4H_2O$, and $\cdot 4.5H_2O$ (the last for NdF_3) have also been claimed (*4a*). The very much more soluble chlorides, bromides, and iodides generally crystallize with between six and nine waters of crystallization (Table I). A variety of lower hydrates, often produced by careful heating of these "normal" hydrates under reduced pressure, are also known. Thus, the octa- and enneahydrates $MI_3 \cdot 8HO$ and $MI_3 \cdot 9H_2O$ give hexahydrates and sometimes tetrahydrates, while for yttrium iodide, $YI_3 \cdot 6H_2O$ and $YI_3 \cdot 3H_2O$ are well characterized. Scandium iodide hexahydrate readily gives the pentahydrate, but further heating gives hydroxo species rather than lower hydrates.

C. OTHER SOLVATES

1. Inorganic Solvents

The inorganic nonaqueous solvents ammonia and hydrogen fluoride form series of solvates with lanthanum trihalides. The latter solvent is, understandably, particularly important in relation to the trifluorides. Both ScF_3 and YF_3 form solvates with HF, for yttrium $YF_3 \cdot HF$ and $YF_3 \cdot 2HF$; but for scandium stoichiometries, $ScF_3 \cdot 0.85HF$, $ScF_3 \cdot 1.85HF$, and $ScF_3 \cdot 2.85HF$ have been claimed (*133*). Interestingly, crystallization of lanthanide trifluorides from aqueous hydrofluoric acid leads exclusively to hydrates, giving some idea of the relative affinities of hydrogen fluoride and of water for these compounds.

Ammonia adducts or solvates include a lanthanide series $LnF_3 \cdot 1.5 NH_3$; YF_3 adds less ammonia, ScF_3 adds only $0.4NH_3$ (*4a*). The other trihalides also form series of ammoniates, for example $CeBr_3 \cdot 8NH_3$ and $CeI_3 \cdot 8NH_3$ (*134*). There are numerous references to species $LnCl_3 \cdot xNH_3$ (*135*), and to ammoniates of $ScCl_3$ and $ScBr_3$ (*136–140*), and of YCl_3 (*141*). Lanthanide chlorides also form mixed solvates with hydrazine (*vide infra*).

2. *Organic Solvents*

The lanthanide halides form a wide range of solvates with a variety of organic solvents; for a given halide and solvent, a range of stoichiometries may be exhibited. Some idea of the range of solvents involved is given by Table II (*108, 112, 142–166*), which gives references to numerous solvates. The collection of citations in this table is illustrative, not comprehensive.

Solvates of the monohydroxylic alcohols have been extensively studied. The expected pattern of more solvent molecules per chloride molecule is reported for the lanthanide and yttrium trichlorides. For scandium trichloride, the existence of $ScCl_3 \cdot 2EtOH$ and $ScCl_3 \cdot 2C_6H_{13}OH$ compares unexpectedly with the tris-alcoholates reported for the n-C_6

TABLE II

SOLVATES OF LANTHANIDE TRIHALIDES

Solvent	Reference		
	$LnCl_3$	$LnBr_3$	LnI_3
Alcohols	*a*		
Dioxane	*142*		
Tetrahydrofuran	*143, 144*	*108*	*145*
Diethyl ether	*146*		
Dimethylformamide	*147*	*148*	*149*
Dimethylacetamide	*150*		*151*
Acetonitrile	*112, 152*	*148*	
Dimethyl sulfoxide[b]	*147, 153*	*154*	*155*
Pyridine	*156*	*148, 157*	
Hexamethylphosphoramide	*158, 159*	*160*	

[a] See Table III.

[b] Also dipropyl sulfoxide [$LnBr_3$ (*161*)], diphenyl sulfoxide [LnI_3 (*155*)], tetramethylene sulfoxide [$LnCl_3$ (*162*), $LnBr_3$ (*163*), LnI_3 (*164*)], and thioxane oxide [$LnCl_3$ (*165*), $LnBr_3$ (*163*), LnI_3 (*166*)].

TABLE III

ALCOHOLATES OF LANTHANIDE TRICHLORIDES[a]

	Stoichiometry							
			$NdCl_3$					
Alcoholate	$LaCl_3$ (*112*)	$PrCl_3$ (*169*)	(*169*)	(*112*)	$SmCl_3$ (*112*)	$DyCl_3$ (*112*)	$ErCl_3$ (*112*)	$YbCl_3$ (*112*)
MeOH	4	3.5	3	4	4	4	4	4
EtOH	3	2.5	2	3	3	3	3	3
*n*PrOH		2	2					
*i*PrOH	3			3	3	3	3	3
*n*BuOH		1.5	1.5					
n$C_5H_{11}OH$		1.5	1					

[a] For alcoholates of $ScCl_3$, see references (*167*) and (*168*); for alcoholates of YCl_3, see reference (*170*).

to *n*-C_9 alcohols (*167*), although other workers have found both $ScCl_3{\cdot}2ROH$ and $ScCl_3{\cdot}3ROH$ for a range of alcohols (*168*). There are minor disagreements about the stoichiometry of the alcoholates of the lanthanide trichlorides (selected data in Table III) (*112, 167–170*) within the agreed trend stated earlier.

Tetrahydrofuran solvates of the lanthanide trichlorides show a somewhat irregular pattern. $LaCl_3$ and $CeCl_3$ crystallize with 3THF; $PrCl_3$ and $NdCl_3$ with 2THF, $SmCl_3$ to $TmCl_3$ (and YCl_3) with 3.5THF, and $YbCl_3$ and $LuCl_3$ with 3THF. The action of heat and reduced pressure on these solvates leads to $LnCl_3{\cdot}THF$ and $LnCl_3{\cdot}0.5THF$. For all the trichlorides except $YbCl_3$, it is possible to obtain anhydrous trichlorides from THF solvates (*171*).

The pattern of a range of solvates for a given halide–solvent system may also be illustrated by pyridine solvates. These have been prepared for several lanthanide halides; the stoichiometry $LnX_3{\cdot}3.5py$ is common. In the particular case of cerium tribromide, it has been found that the solvate in equilibrium with saturated solution ranges from $CeBr_3{\cdot}3py$ in the region of 0°C through $CeBr_3{\cdot}2py$, $CeBr_3{\cdot}1.5py$, and $CeBr_3{\cdot}py$ to $CeBr_3{\cdot}0.67py$ above 30°C (*157*).

A fair number of mixed solvates, compounds containing molecules of crystallization of two different solvents, are also known. Generally, these are obtained either by recrystallizing halide hydrates from a nonaqueous solvent, or by crystallizing a halide from an appropriate solvent mixture, such as an alcohol intentionally or unintentionally containing significant amounts of water. Examples include

$LaCl_3 \cdot 2EtOH \cdot H_2O$ (*172*); $LaCl_3 \cdot 4NH_3 \cdot 2H_2O$ (*173*); $LnCl_3 \cdot 3N_2H_4 \cdot nH_2O$, with Ln being, for example, Sm (*174*) or Ce (*175*); $PrI_3 \cdot 3N_2H_4 \cdot nH_2O$, (*176*); a series of compounds $LnBr_3 \cdot 4HMPA \cdot 3H_2O$ (*177*); and mixed $HF-H_2O$ solvates (*133b*).

Apart from the qualitative observations made previously about suitable solvents for study, the subject of solvates has two important bearings on the topics of thermochemistry which form the main body of this review. The first is that measured solubilities relate to the appropriate hydrate in equilibrium with the saturated solution, rather than to the anhydrous halide. Obviously, therefore, any estimate of enthalpy of solution from temperature dependence of solubility will refer to the appropriate solvate. The second area of relevance is to halide–solvent bonding strengths. These may be gauged to some extent from differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC); solvates of "aprotic" solvents such as pyridine, tetrahydrofuran, and acetonitrile will give clearer pictures here than solvates of "protic" solvents such as water or alcohols.

IV. Enthalpies of Solution

A. In Water

1. *Trichlorides*

a. Anhydrous. Enthalpies of solution of anhydrous lanthanide trichlorides are collected together in Table IV (*178–188*). The isolated results of Matignon (*178*), at temperatures of 16–18°C, obtained in the early years of this century, are given in the first column. The first report of enthalpies of solution of the full series of these trichlorides contained only a graphical presentation of the results (*179*). The same authors shortly afterwards produced a full report, whose values are given in the second column of Table IV (*180*). These values were obtained at 20°C. Much later studies of the temperature dependence of solution enthalpies (*184b*) suggest that values at 25°C would be 2–3 kJ mol^{-1} more negative. Such an adjustment does bring these 20°C values closer to the remaining columns, containing more recent values obtained at 25°C. Overall, there is a fair measure of agreement between enthalpies reported by different groups of workers, apart from an uncomfortably large range for yttrium chloride, and one or two of the miscellaneous results in the final column.

The general trend of increasingly negative enthalpies of solution

TABLE IV

ENTHALPIES OF SOLUTION OF ANHYDROUS TRICHLORIDES IN WATER[a]

Trichloride	Enthalpy of solution (kJ mol^{-1}) Matignon (1906) 16–18°C (*178*)	Bommer and Hohmann (1941) 20°C (*179, 180*)	Spedding *et al.* (1952, 1954) 25°C (*181, 182*)	Morss (1971) 25°C (*183*)	Krestov (1972, 1973) 25°C (*184*)	Blachnik and Selle (1979) 25°C[h]	Miscellaneous
$ScCl_3$		−197					
YCl_3	−189.9	−218.8	−203.7	−224.7	−194.5		
$LaCl_3$	−131.0	−132.2	−137.8	−137.7	−134.7		−133.7[i]
$CeCl_3$		−136.8	−144.0	−143.9		−140.7	−137.2[i]
$PrCl_3$	−140.2	−141.8	−149.3	−149.4	−149.1	−147.7	−144.3[i]
$NdCl_3$	−148.1	−150.2	−156.9	−156.9	−155.3	−153.3	−147.7[i]
$PmCl_3$				−161.9[d]			−163.2[e]
$SmCl_3$	−156.5	−163.2	−167.1	−166.9	−166.9	−165.9	
$EuCl_3$		−172.2		−170.3			−174.9[e]
$GdCl_3$		−177.4	−180.0	−181.6	−181.8	−180.8	−181.8[f]
$TbCl_3$		−191.8		−192.5	−186.9		−186.6[e]
$DyCl_3$		−197.9[b,c]		−209[d]		−198.1	−193.3[e]
$HoCl_3$		−209.2		−213.4		−210.3	−199.6[e]
$ErCl_3$		−207.3	−208.3	−215.1	−210.0	−215.0	−215.3[g]
$TmCl_3$		−213		−215.9			−186.6[g] −211.7[e] −187.2[g]
$YbCl_3$		−213.2	−216.1	−215.9		−215.4	
$LuCl_3$		−214.6		−218.4			−222.6[e]

[a] Estimated at infinite dilution, except for Matignon's values (*178*) which refer to final concentrations of between 0.5 and 2% trichloride.

[b] This value is for β-$DyCl_3$.

[c] The enthalpy of solution of γ-$DyCl_3$ is −210.2 kJ mol^{-1} (*180*).

[d] Estimated by interpolation.

[e] Estimates; from Finogenov (*185*).

[f] From Jekel *et al.* (*186*).

[g] U.S. Bureau of Mines Reports (*187, 188*).

[h] Recent values, added in proof. Blachnik, R., and Selle, D., *Thermochim. Acta* **33**, 301 (1979).

[i] Values added in proof. Novikov, G. I., and Baev, A. K., *Vestn. Leningrad Univ.* **22**, 4 (1961).

going from $LaCl_3$ to $LuCl_3$ (Fig. 1) (*183, 189–192*) indicates that hydration enthalpies, which for the 3+ cations increase in this direction as ionic radii (see Table V) (*193*) decrease, dominate increasingly over lattice enthalpies. If size is the controlling factor, then one would expect the enthalpy of solution of yttrium trichloride to be approximately the

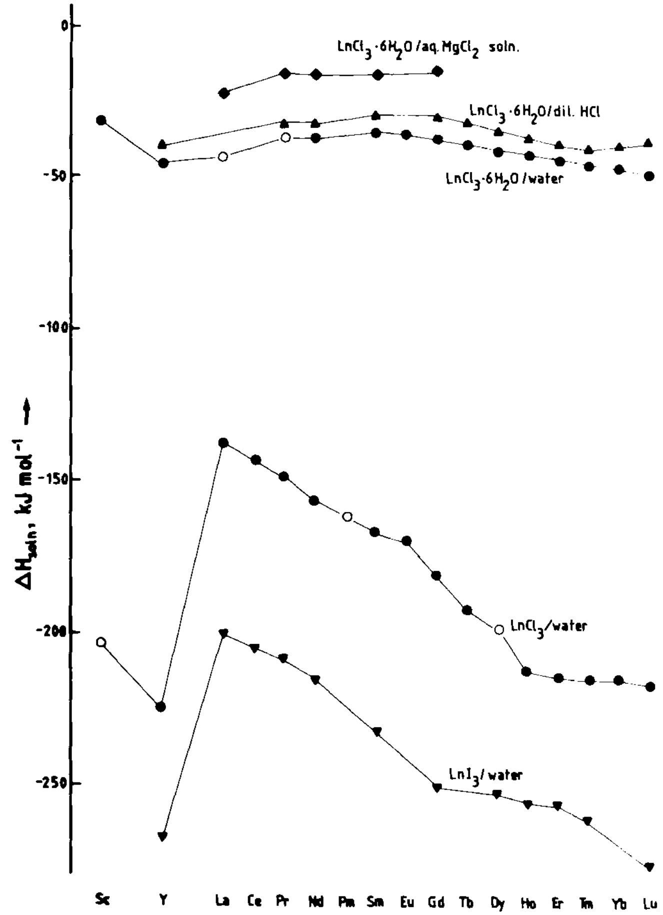


FIG. 1. Enthalpies of solution of lanthanide trihalides in aqueous media: (●) anhydrous trichlorides (*183*) and trichloride hexahydrates (*189*) in water; (▲) trichloride hexahydrates in dilute hydrochloric acid (*190*); (◆) trichloride hexahydrates in aqueous magnesium chloride solution (*191*); (▼) anhydrous triiodides in water (*192*). Values for the trichlorides refer to 25°C, for the triiodides to 20°C. Filled symbols represent experimental determinations, open symbols represent estimates.

same as that for holmium trichloride (*194*). Perhaps an estimate of about -210 kJ mol^{-1} obtained from this point of view may be used in assessing the relative merits of the five discordant published values for YCl$_3$ given in Table IV. It is unfortunate that the only value for ScCl$_3$ is the early one at 20°C. On ionic-radius grounds (Table V), one might expect a more negative enthalpy of solution in water than -197 kJ mol^{-1} for this compound. Perhaps the equilibrium $Sc^{3+}_{(aq)} \rightleftharpoons Sc(OH)^{2+}_{(aq)}$ +

TABLE V

IONIC RADII (Å)[a]

Ion	Radius	Ion	Radius	Ion	Radius	Ion	Radius
Al^{3+}	0.67	Ce^{3+}	1.17	Mg^{2+}	0.86	Na^{+}	1.16
Sc^{3+}	0.87	Pr^{3+}	1.15	Ca^{2+}	1.14	K^{+}	1.52
Y^{3+}	1.03	Nd^{3+}	1.14	Sr^{2+}	1.30	Rb^{+}	1.63
La^{3+}	1.20	Sm^{3+}	1.10	Ba^{2+}	1.50	Cs^{+}	1.84
		Eu^{3+}	1.09				
		Gd^{3+}	1.08				
		Tb^{3+}	1.06				
		Dy^{3+}	1.05				
		Ho^{3+}	1.03				
		Er^{3+}	1.02				
		Tm^{3+}	1.01				
		Yb^{3+}	1.00				
		Lu^{3+}	0.99				

[a] From Adams (*193*). In all cases, the radii apply to a coordination number of six (radii for coordination number eight are generally about 0.12 Å larger).

$H^{+}_{(aq)}$ is interfering; of the ions considered in this review, only $Sc^{3+}_{(aq)}$ has a sufficiently low pK_a [4.6–5.1 (*195*)] to be considered remotely acidic. It is possible that lower chlorides of yttrium and of scandium may contribute to these difficulties, together with the problems associated with all the trihalides of this review of the presence of small amounts of hydrates or oxochlorides. While on the matter of possible impurities, it may be recalled that in Bommer and Hohmann's early work there is a discrepancy between enthalpies of solution of anhydrous trichlorides and of respective metals in hydrochloric acid. Here the more likely impurity to be responsible is unreacted potassium metal in the lanthanide metal used in the hydrochloric acid dissolution experiments.

The range of enthalpies of solution of anhydrous lanthanide trichlorides in water may be compared with those for other anhydrous chlorides. They are considerably more negative (Table IV) than those for the alkaline-earth metals [$MgCl_2$, −155 kJ mol^{-1}, to $BaCl_2$, −13 kJ mol^{-1} (*196*)] and for the alkali metals [LiCl, −37 kJ mol^{-1}, to CsCl, +18 kJ mol^{-1} (*197*)].

Thus far we have dealt with enthalpies of solution at the standard temperature of 25°C, or slightly less. For several trichlorides ($LaCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$, $GdCl_3$, $TbCl_3$, $ErCl_3$, and YCl_3), enthalpies of solution in water have been measured over the temperature range 14.8–92.8°C. Thence values at 10° intervals from 0 to 100°C have been interpolated and extrapolated (*184*). The enthalpies of solution become more negative as the temperature increases. Thus, for example, the enthalpies of solution of $LaCl_3$ and of $SmCl_3$ are given as -27.93 and -36.28 kcal mol^{-1} at 0°C, -42.79 and -49.63 kcal mol^{-1} at 100°C. The temperature variation of ΔH gives, of course, C_p.

b. Hydrates. Several sets of values for enthalpies of dissolution of lanthanide chloride hexa- and heptahydrates exist. The lesser practical problems in obtaining these materials in a pure state should mean that the enthalpies obtained are more accurate than those for the anhydrous chlorides. But of course these enthalpies of hydrated materials are of less interest and value than those for the anhydrous materials.

As so often, Matignon was responsible for the earliest efforts here, with determinations of the enthalpies of solution of $PrCl_3{\cdot}7H_2O$ of -22.2 kJ mol^{-1} (*178*) and of $NdCl_3{\cdot}6H_2O$ of -32.8 (*198*) and -31.8 (*199*) kJ mol^{-1}, at 15–17°C. These values are tolerably close to recent estimates. Modern values for enthalpies of solution of lanthanide chloride hydrates, extrapolated to infinite dilution with the aid of measured enthalpies of dilution, are listed in Table VI (*182, 189, 191, 200–202a*). The values are quoted, as in the original references, to four significant figures, which seems somewhat ambitious.

The variation in enthalpies of solution of the hexahydrates parallels approximately that for the values for the anhydrous compounds (Fig. 1). It is interesting that the difference between the enthalpies of solution of the hexa- and heptahydrates of praseodymium trichloride is approximately 14 kJ mol^{-1}, which compares closely with a mean value of 13 kJ mol^{-1} per water molecule for salts of sp- and of d-block elements (*203*). The differences between the enthalpies of solution of the hexahydrates and of the respective anhydrous trichlorides correspond to 20–25 kJ mol^{-1} per water molecule.

In principle, it should be possible to estimate enthalpies of solution of these hydrates from the temperature dependence of solubility, using the standard van't Hoff equation. Of course, the solid phase in equilibrium with the saturated solution has to be of constant composition throughout the temperature range involved. In practice, the solubilities of the lanthanide chlorides in water are far too high for this approach to be successful. Activity coefficients are very much less than unity (*4b, 189*), and their variation with temperature will make a large contribution to the apparent solution enthalpy [cf., for example, the case of sodium hydroxide (*204*)]. A van't Hoff treatment of the solubility data for, for example, $LaCl_3{\cdot}7H_2O$, $PrCl_3{\cdot}7H_2O$, and $NdCl_3{\cdot}6H_2O$ (*205*), gives much lower solution enthalpies than those obtained by direct cal-

TABLE VI

ENTHALPIES OF SOLUTION OF TRICHLORIDE HYDRATES IN WATER (25°C AND INFINITE DILUTION)[a]

	Enthalpy of solution (kJ mol^{-1})	
Trichloride	$6H_2O$	$7H_2O$
$ScCl_3$	−31.8[b]	
YCl_3	−46.24[c]	
$LaCl_3$	[−44.6][d]	−28.00
$CeCl_3$		−28.9[c]
$PrCl_3$	[−38.06][e]	−23.91 [−29.16][f]
$NdCl_3$	−38.21	
$SmCl_3$	−36.04	
$EuCl_3$	−36.46; −36.69[c]	
$GdCl_3$	−38.15	
$TbCl_3$	−39.97; −40.00[g]	
$DyCl_3$	−41.73	
$HoCl_3$	−43.58; −43.64[g]	
$ErCl_3$	−44.95	
$TmCl_3$	−46.53	
$YbCl_3$	−48.18	
$LuCl_3$	−49.62; −49.83[c]	

[a] From Spedding *et al.* (*189*) except where otherwise stated; values in brackets may not refer to infinite dilution.

[b] Estimated, from Travers *et al.* (*200*).

[c] From Hinchey and Cobble (*201*).

[d] From Nosova (*191*).

[e] From Spedding and Flynn (*182*).

[f] From Maier *et al.* (*202*).

[g] From deKock and Spedding (*202a*).

orimetry (Table VI). Indeed in many cases, for instance yttrium trichloride (*206, 207*), the temperature variation of solubility is too irregular for a meaningful van't Hoff treatment. However, although we reject this route to estimating enthalpies of solution of hydrates in water here, we do employ it elsewhere for some nonaqueous systems, albeit for much more dilute solutions where its use is considerably less unacceptable.

c. Dissolution in Aqueous Hydrochloric Acid. There have been numerous calorimetric determinations of enthalpies of dissolution of lanthanide chlorides in aqueous hydrochloric acid at various concentrations. Such measurements started with Matignon, who reported

TABLE VII

ENTHALPIES OF SOLUTION OF ANHYDROUS TRICHLORIDES IN AQUEOUS HYDROCHLORIC ACID (AT 25°C)[a]

[HCl]	Enthalpy of solution (kJ mol^{-1})								
(m)	$LaCl_3$	$CeCl_3$[b]	$PrCl_3$	$NdCl_3$[b]	$GdCl_3$	$ErCl_3$[e]	$TmCl_3$[c]	$YbCl_3$[c]	YCl_3
0.0[d]	−137.8	−144.0	−149.3	−156.9	−179.9	−208.3	−215.9	−215.9	−203.7
0.1324		−137.4							
0.1432				−149.1					
0.1505		−136.7							
0.1885				−148.3					
0.1990		−134.1							
0.2475		−133.4							
0.5014	−128.2		−142.2		−174.1				
1.2122			−125.6						
1.2134						−193.3			−195.1
4.36							−186.6	−187.2	

[a] From Spedding and Flynn (*182b*) except where otherwise stated.

[b] From Spedding and Miller (*181*).

[c] From Stuve (*188*).

[d] From same authors' work for direct comparison.

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[e] Enthalpies of solution of $ErCl_3$ in 10^{-3} and 1.428 M HCl are −215.3 and −201.7 kJ mol^{-1}, respectively [Fuger, J., Morss, L., and Brown, D. *J. Chem. Soc. Dalton Trans.* p. 1076 (1980)].

values for the trichlorides of praseodymium and neodymium in 1906 (*178*). The most detailed series of measurements have been made by Spedding and co-workers (*181, 182b*), who have studied the trichlorides of lanthanum, cerium, praseodymium, neodymium, gadolinium, erbium, and yttrium. Values are given in Table VII, which also includes isolated values from other references. The general trend in these values is of a significant decrease in the enthalpy of solution as the concentration of hydrochloric acid increases. This decrease seems to be slightly less marked on going from left to right across the lanthanide series; the decrease for erbium is about two-thirds that for lanthanum and praseodymium.

Enthalpies of solution of lanthanum (*180*) and scandium (*208*) trichlorides in 14.1% and in 0.5 *M* aqueous hydrochloric acid, respectively, are also smaller than the respective enthalpies of solution in water. In the former case the values −26.4 and −31.6 kcal mol^{-1} were measured at 20°C; in the latter, a value of −43.0 kcal mol^{-1} for dissolution in hydrochloric acid at 25°C has to be compared with a value of −47.1 kcal mol^{-1} for dissolution in water at 20°C (*180*). Enthalpies of

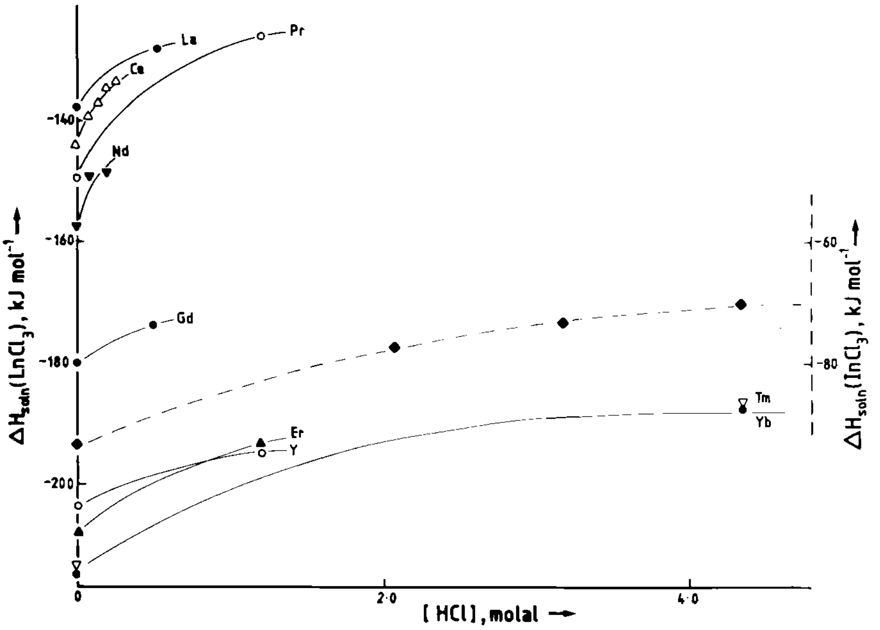

FIG. 2. The variation of the enthalpies of solution of lanthanide trichlorides and, for comparison, indium trichloride (dashed line), with acid concentration in aqueous hydrochloric acid, at 25°C (*182b*).

solution have also been reported for lanthanum (*209*) and erbium (*210*) trichlorides in hydrochloric acid at 54.5°C. The enthalpy of solution of erbium trichloride in hydrochloric acid at 25°C is -48.25 kcal mol^{-1}, again smaller than the corresponding value in water, -50.48 kcal mol^{-1} (*187*).

The effects of varying the hydrochloric acid concentration here are similar to those on enthalpies of solution of indium trichloride (*210a*) (Fig. 2). They are much larger than those observed in analogous measurements on the alkaline-earth halides. Selected values (*196*) for the latter are given in Table VIII to illustrate this. Both for the lanthanide trichlorides and for the alkaline-earth chlorides, the salts of the larger cations show the largest variation in enthalpies of solution on varying the hydrochloric acid concentration.

Enthalpies of solution of the series of chloride hydrates in aqueous hydrochloric acid (approximately 0.1 mol dm^{-3}) are listed in Table IX (*190*). In Fig. 1, the trend in these values across the lanthanide series is compared with the trends for enthalpies of solution of the hydrates and of the anhydrous salts in water.

d. Dissolution in Aqueous Salt Solutions. Several investigations have been made of the variation in enthalpy of solution of certain lanthanide trichlorides in aqueous salt solutions, including those containing ammonium chloride, alkali-metal chlorides, and alkaline-earth metal chlorides. The results of a study of the trichlorides of lanthanum, praseodymium, neodymium, and gadolinium in solutions of various concentrations of the chlorides of lithium, sodium, potassium, cesium, magnesium, calcium, and barium (*211*) have proved in-

TABLE VIII

ENTHALPIES OF SOLUTION OF ANHYDROUS ALKALINE-EARTH METAL CHLORIDES IN AQUEOUS HYDROCHLORIC ACID (AT 25°C)

[HCl] (mol dm^{-3})	Enthalpy of solution (kJ mol^{-1})		
	$CaCl_2$	$SrCl_2$	$BaCl_2$
0.0	−76.9	−48.6	−13.0
1.0	−74.7	−43.4	−8.9
2.0	−71.0	−40.2	
4.0	−64.1		
6.0	−55.6	−28.9	

[a] From Perachon and Thourey (*196*).

TABLE IX

ENTHALPIES OF SOLUTION OF CHLORIDE HYDRATES IN DILUTE HYDROCHLORIC ACID[a]

Chloride hydrate	Enthalpy ($kJ\ mol^{-1}$)	Chloride hydrate	Enthalpy ($kJ\ mol^{-1}$)
$LaCl_3 \cdot 7H_2O$	−21.8	$PrCl_3 \cdot 6H_2O$	−33.6
$CeCl_3 \cdot 7H_2O$	−20.3	$NdCl_3 \cdot 6H_2O$	−32.8
		$SmCl_3 \cdot 6H_2O$	−30.2
		$EuCl_3 \cdot 6H_2O$	−29.4
		$GdCl_3 \cdot 6H_2O$	−31.1
		$TbCl_3 \cdot 6H_2O$	−33.6
		$DyCl_3 \cdot 6H_2O$	−35.6
$YCl_3 \cdot 6H_2O$	−40.5	$HoCl_3 \cdot 6H_2O$	−38.2
		$ErCl_3 \cdot 6H_2O$	−39.8
		$TmCl_3 \cdot 6H_2O$	−41.6
		$YbCl_3 \cdot 6H_2O$	−40.6
		$LuCl_3 \cdot 6H_2O$	−39.0

[a] From Karapet'yants *et al.* (*190*). The hydrochloric acid concentration is mole fraction 5.9×10^{-3}.

accessible. Effects of ammonium chloride on enthalpies of solution of lanthanum and samarium trichlorides are surprisingly different (*191*). The only satisfactory pattern emerges from reported effects of magnesium chloride on enthalpies of solution of a selection of five lanthanide trichlorides (*191*) (Fig. 1). Plots of solution enthalpies (Table X) against magnesium chloride concentration are linear, and the slopes for the five trichlorides are, as one would expect, essentially equal. The

TABLE X

ENTHALPIES OF SOLUTION FOR LANTHANIDE TRICHLORIDE HEXAHYDRATES IN AQUEOUS MAGNESIUM CHLORIDE SOLUTIONS AT 25°C[a]

$[MgCl_2]$ (*m*)	Enthalpy of solution ($kJ\ mol^{-1}$) $LnCl_3 \cdot 6H_2O$				
	La	Pr	Nd	Sm	Gd
0.0	−44.6	−36.2	−35.9	−35.6	−32.9
1.02, 1.06	−33.9	−23.4	−24.1	−24.3	−23.4
2.11	−24.1	−16.7	−17.1	−17.6	−16.0
3.25, 3.28	−15.1	−7.7		−8.8	−6.4

[a] From Nosova (*191*).

decrease in solution enthalpy going from water to molal magnesium chloride, about 12 kJ mol^{-1}, is somewhat smaller than that (about 18 kJ mol^{-1}) for the decrease on going from water to molal hydrochloric acid.

The temperature dependences of solubilities of the trichlorides of lanthanum, praseodymium, and neodymium in aqueous ammonium chloride solutions (*212*) are so irregular that no estimate of solution enthalpies can be made from them by the van't Hoff method.

e. Enthalpies of Dilution. These represent a special case of the last section, in which the lanthanide trichloride is acting both as solute and as added electrolyte. The importance of the measurement of enthalpies of dilution lies in their use in extrapolating enthalpies of solution to the theoretically desirable but experimentally unattainable state of infinite dilution. Early measurements of enthalpies of dilution are reported and referenced in (*213*), while more recent determinations may be found in (*181–182b, 189, 214, 215*).

f. D_2O. Enthalpies of solution of anhydrous lanthanum trichloride in D_2O and in H_2O have been reported as −30.48 and −32.16 kcal mol^{-1} (−127.5 and −134.6 kJ mol^{-1}, respectively) (*216*). The difference, 7.1 kJ mol^{-1}, is, as one might expect, larger than the D_2O–H_2O differences observed for chlorides of the alkali metals (1.6–2.5 kJ mol^{-1}) and for the chlorides of calcium and barium (4.2 and 5.4 kJ mol^{-1}). These differences are a rational function of cation and anion charge and size, and are attributed to the disturbing of hydrogen (deuterium) bonding. About 10 hydrogen (deuterium) bonds per lanthanum trichloride are said to be affected.

2. *Tribromides*

There appear to be no enthalpies of solution of rare-earth tribromides published in the available literature.[2] However, Bommer and Hohmann reported a value of −230.5 kJ mol^{-1} (at 20°C) for the enthalpy of solution of scandium tribromide in water (*180*). This value may be compared with −197.1 kJ mol^{-1} for the chloride, and an estimate (from the published LnI_3 series, *q.v.*) of −240 to −250 kJ mol^{-1} for the iodide. The markedly more negative values for the heavier ha-

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[2] Since this review was written, enthalpies of solution of several lanthanide tribromides in various concentrations of hydrochloric acid have been reported [C. Hurtgen, D. Brown, and J. Fuger, *J. Chem. Soc. Dalton Trans.* p. 70 (1980)].

lides suggest that the lattice enthalpies for these halides decrease more rapidly than the hydration enthalpies of the respective halide anions.

3. *Triiodides*

The situation for the triiodides is only slightly better than for the tribromides. There is only one set of values, obtained many years ago at 20°C (*192*). These are listed, and compared with the analogous set of solution enthalpies for the trichlorides obtained under analogous conditions by the same workers, in Table XI (and see Fig. 1). As for the chlorides, the solution enthalpies for the iodides must be subject to some small degree of uncertainty in view of the possible presence of impurities (oxoiodides, lower iodides, etc.) in the samples used. It is harder to obtain really pure anhydrous iodides than chlorides in the lanthanide series (cf. Section II). As for the chlorides, solution enthalpies for the iodides become more negative going across the lanthanide

TABLE XI

ENTHALPIES OF SOLUTION OF ANHYDROUS TRIIODIDES AND, FOR COMPARISON, ANHYDROUS TRICHLORIDES IN WATER AT 20°C

	Enthalpy of solution ($kJ\ mol^{-1}$)	
Element	LnI_3[a]	$LnCl_3$[b]
Y	−268[c]	−219
La	−201[d]	−132
Ce	−205[d]	−137
Pr	−209[d]	−142
Nd	−216[d]	−150
Sm	−233	−163
Gd	−252	−177
Dy	−253[c]	−198
Ho	−256[c]	−209
Er	−257	−207
Tm	−262	−213
Lu	−276	−215

[a] From Bommer and Hohmann (*192*).
[b] From Table IV.
[c] Also see Bommer, (*194*).
[d] α-LnI_3; other iodides are β-modification.

series of elements from lanthanum to lutetium; differences are slightly bigger for the chlorides than for the iodides. As ever, the dependences of ion solvation and lattice energies on ion size partially compensate.

As the characterization of scandium triiodide has been considered to be uncertain (*6*), it is understandable that no enthalpy of solution of this compound in water was reported by early investigators such as Bommer and Hohmann.

4. *Conclusions*

The results in the three preceding subsections conform fairly well to a consistent pattern. However, there are gaps and inconsistencies that require further thermochemical, and in some cases chemical, study. The series of solution enthalpies for the lanthanide trichlorides is satisfactory, but disagreements over the value for the enthalpy of solution of yttrium trichloride in water need resolving, and a modern value for scandium trichloride (at 25°C) would be welcome. The complete absence of enthalpies of solution of tribromides of the lanthanide elements and yttrium is regrettable, as is the lack of a value for scandium triiodide.

The direct measurement of enthalpies of solution of lanthanide trifluorides in water is hardly practicable, in view of their very small solubilities in this solvent. Enthalpies of hydration of lanthanide trifluorides have been measured (*217*). It should be possible to derive enthalpies of solution, at least for the hemihydrates $LnF_3 \cdot \frac{1}{2}H_2O$, by measuring enthalpies of precipitation.

B. IN NONAQUEOUS SOLVENTS

1. *Trichlorides*

In 1906, Matignon reported an enthalpy of solution of -21.54 kcal mol^{-1} (-90 kJ mol^{-1}) for neodymium trichloride in ethanol (*178*). His ethanol may have been less than perfectly anhydrous, and the value for pure ethanol somewhat less negative than this, perhaps -80 or -70 kJ mol^{-1}. Certainly a value in this region is considerably less negative than his value for the enthalpy of solution of neodymium trichloride in water, -148 kJ mol^{-1}. The difference may reasonably be attributed to less favorable solvation of the constituent ions in ethanol than in water. Ion solvation would be expected to be even less favorable in isopropanol, so it is not surprising to find an enthalpy of solution of about $+40$ kJ mol^{-1} for neodymium trichloride in this alcohol. This estimate must be considered as only approximate, as it is derived from

TABLE XII

ENTHALPIES OF SOLUTION OF LANTHANIDE TRICHLORIDES IN NONAQUEOUS SOLVENTS AT 25°C

	Enthalpy of solution (kJ mol^{-1})					
Trichloride	MeOH	EtOH	*i*PrOH	DMSO[a]	DMF	Water[b]
$LaCl_3$	−92.6[c]	(−60)[c,d]		−163	−47[c]	−138
$CeCl_3$			(+60)[f,g]			−144
$NdCl_3$		−90[e]	(+40)[f,h]	−183		−157
$SmCl_3$				−206		−167
$GdCl_3$				−208	*i*	−182
$DyCl_3$				−217		−209
$HoCl_3$				−219		−213
$ErCl_3$				−221		−215
$YbCl_3$	−167[c]			−226		−216

[a] From Clark and Bear (*220*); all values are ±2–6 kJ mol^{-1}.

[b] From Table IV [from Morss (*183*) values].

[c] J. Burgess and J. Kijowski, unpublished observations.

[d] Estimated from values measured in wet ethanol (1% water).

[e] Matignon's value (*178*); cf. text.

[f] Obtained from the temperature dependence of solubilities.

[g] Solubilities from Saad and Soliman (*221*).

[h] Solubilities from Hopkins and Quill (*218*).

[i] Reasonable estimate from Held and Criss (*222*) impossible to make.

the temperature variation of solubility in isopropanol (*218*); rare-earth chlorides dissolve far too slowly and reluctantly in higher alcohols for direct calorimetry in conventional apparatus to be successful. A similar van't Hoff estimate of enthalpy of solution from the temperature dependence of solubility indicates an enthalpy of solution of around +60 kJ mol^{-1} for cerium trichloride in isopropanol. We have recently measured the enthalpy of solution of anhydrous lanthanum trichloride in methanol, finding a value of −92.6 kJ mol^{-1} (*219*). Anhydrous lanthanum trichloride dissolves too slowly in pure dry ethanol for us to obtain an accurate enthalpy, but measurements in ethanol containing a small amount of water suggest an enthalpy of solution of approximately −60 kJ mol^{-1} in anhydrous ethanol (*219*).

Enthalpies of solution of anhydrous rare-earth chlorides in nonhydroxylic solvents are also scant. What values exist are collected together in Table XII (*178, 183, 218, 220–222*), which includes alcohol and water values for ease of comparison. The values in this table are direct calorimetric measurements, performed on anhydrous trichlorides. The value for gadolinium trichloride in dimethylformamide is very uncertain because the enthalpy of solution of this compound in DMF varies markedly and irregularly with concentration (*222*); the corresponding value for lanthanum trichloride is less uncertain as it was obtained at a very low final concentration of trichloride (*219*).

Enthalpies of solution of rare-earth trichlorides in dimethyl sulfoxide are markedly more negative than in water, though the difference decreases on going from lanthanum across to ytterbium. Less favorable solvation of the chloride ions by the dimethyl sulfoxide must be more than balanced by favorable solvation of the rare-earth 3+ cations (cf. Section VI,B). This dimethyl sulfoxide-versus-water comparison should be contrasted with the alcohol-versus-water comparisons discussed earlier.

An extreme example of the measurement of solution enthalpies is provided by that of lanthanum trichloride in molten potassium chloride. The value reported, which refers to infinite dilution, is -20.8 kcal mol^{-1} (-87.0 kJ mol^{-1}), at 890°C (*223*). This value is comparable with those for dissolution in lower alcohols at normal temperatures.

2. *Tribromides*

There seem to be no direct calorimetric determinations of enthalpies of solution of rare-earth tribromides in nonaqueous solvents,[3] and very few reports on the temperature variation of solubilities whence solution enthalpies might be roughly estimated. The most detailed set of data concerns cerium tribromide in pyridine (*157*). In this system there exists a series of solvates (cf. Section III,C,2), but sufficient solubilities were determined for the estimation of enthalpies of solution of each solvate. These enthalpies are included in Fig. 3, which shows an extraordinary zig-zag variation of solubility with temperature. The actual values of enthalpies of solution cannot be accurate, but at least it is clear that they change sign and magnitude in an eccentric manner.

3. *Triiodides*

The enthalpy of solution of the ammoniate $LaI_3 \cdot 6NH_3$ in liquid ammonia at 25°C is -178.5 kJ mol^{-1}. This value is close to that at infinite dilution, for it was determined at a concentration of LaI_3 in the product solution of only 1 in 18,500 (*224*). Comparisons of this value with those for other iodides, or for aqueous media, are complicated by the fact that the ammoniate rather than anhydrous LaI_3 was used for this calori-

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[3] Since this review was written, enthalpies of solution of lanthanum tribromide in methanol and ethanol have been reported [G. A. Krestov, V. A. Kobenin, and S. V. Semenovskii, *Khim. Termodin. Termokhim.* p. 170 (1979)].

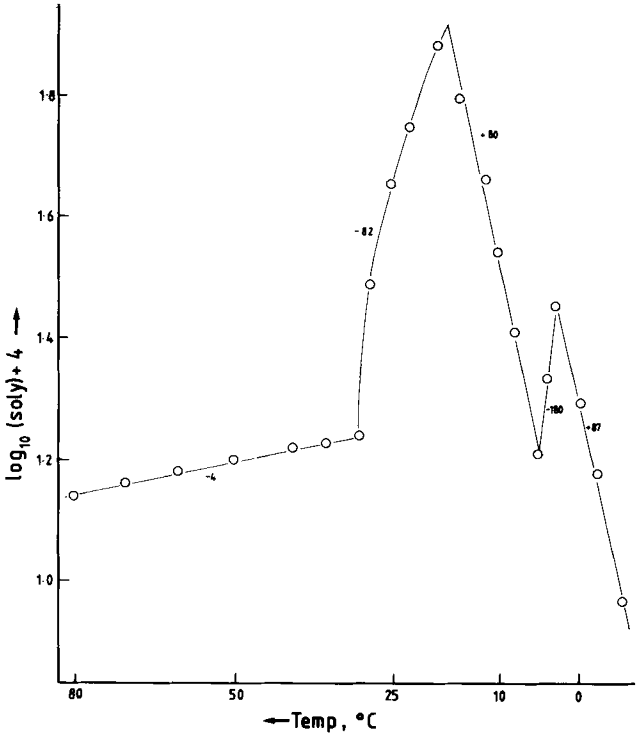

FIG. 3. The dependence of the solubility (mole fraction) of cerium tribromide in pyridine on temperature (*157*). The numbers adjacent to the various lines and curves are the respective estimates for enthalpies of solution.

metric determination. However, comparisons can be made with the use of appropriate estimates, as set out in the following paragraphs.

The enthalpy of solution of anhydrous LaI_3 in water is -201 kJ mol^{-1}, as already listed. Using the data discussed in the section on enthalpies of solution of hydrates of lanthanide chlorides in water, it can thence be deduced that the enthalpy of solution of a hexahydrate, $LaI_3 \cdot 6H_2O$, would be between -100 and -120 kJ mol^{-1}. Certainly the enthalpy of solution of $LaI_3 \cdot 6H_2O$ in water would be much less negative than that of $LaI_3 \cdot 6NH_3$ in liquid ammonia.

Alternatively, an approximate value for the enthalpy of solution of anhydrous LaI_3 in liquid ammonia can be made by using enthalpy data for other ammoniates, particularly for $NaCl \cdot 5NH_3$ (*225*). Hence one would expect the difference between LaI_3 and $LaI_3 \cdot 6NH_3$ to be around 60 kJ mol^{-1}, suggesting an enthalpy of solution of roughly -240 kJ mol^{-1} for anhydrous LaI_3 in liquid ammonia. The qualitative comparison between the solvents liquid ammonia and water here is the same as that in the previous paragraph.

The estimate of −240 kJ mol^{-1} for dissolving anhydrous LaI_3 in liquid ammonia may be compared with values of −70 to −130 kJ mol^{-1} for various diiodides (ZnI_2, HgI_2, SrI_2, and PbI_2) at various temperatures and concentrations, and of −33 kJ mol^{-1} for potassium iodide at −33°C and at infinite dilution (*226*). The comparisons in this and the preceding paragraphs are consistent with the normal pattern of ion size and charge effects, with stronger solvation of cations by ammonia than by water.

4. *Miscellaneous*

For enthalpies of solution of rare-earth salts in a really wide range of solvents, one has to look outside the halide family to nitrates. Enthalpies of solution of lanthanum(III) nitrate have been measured in 15 solvents, under comparable conditions. Unfortunately, it was the hexahydrate rather than the anhydrous nitrate that was used (*227*).

V. Solubilities

A. IN WATER

1. *Trifluorides*

The lanthanide fluorides are all sparingly soluble in water, as are the fluorides of yttrium and scandium. Thus, solubility information is generally presented in the form of the solubility product K_{sp}:

$$K_{sp} = [Ln^{3+}][F^-]^3$$

This expression has been written in terms of concentration; if activity coefficients are known or estimated, then a thermodynamically ideal solubility product may be obtained from the analogous product of ionic activities. As the concentration of ions in solutions of lanthanide fluorides is low, the concentration and activity solubility products will not differ markedly, although activity coefficients for these salts of 3+ cations are significantly less than unity even in such dilute solutions (*4a*).

Fluorides of the lanthanides, yttrium, and scandium normally precipitate from aqueous media as the hemihydrates, $LnF_3 \cdot \frac{1}{2}H_2O$. It is these hemihydrates which are in equilibrium with saturated solution, and the solubility-product measurements refer to these hemihydrates.

There have been many determinations of solubility products for lanthanide fluorides over the years. We shall try to show the range of values presented for a given element, as well as the chemically important variation of solubility with the nature of the metal. Values for aqueous solution will be reviewed first, then the effects of added acid or salts on solubility considered.

a. Scandium Trifluoride. We have traced only one value, of 3×10^{-20}, for the solubility product of this compound in aqueous solution (*6*). A recent review of the thermochemistry of scandium details stability constants for scandium(III)–fluoride interaction, but does not report a K_{sp} value (*200*).

b. Yttrium Trifluoride. Values of 18.3 (*228*) and 14.8 (*229*) for pK_{sp} have appeared in the recent Russian literature. Of these two wildly discordant values, the former seems, in the context of values for other elements and an earlier estimate of 17.3 [$K_{sp} = 4.96 \times 10^{-18}$ (*230*)], more attractive.

c. Lanthanum Trifluoride. This has been the most studied of the trifluorides covered in this review. Values for its solubility product in aqueous solution at 298.25 K are listed, in chronological order in Table XIII (*228–235*). Recent critical evaluation of these values, and of their relation to other thermodynamic parameters, leads to a recommended value of 3×10^{-19} for K_{sp} (*231*). Lower solubility-product values of 10^{-29} (*236*), 3×10^{-25} (*237*), and 10^{-24} (*238*) are derived from experiments

TABLE XIII

SOLUBILITY PRODUCTS FOR LANTHANUM TRIFLUORIDE AND CERIUM TRIFLUORIDE IN AQUEOUS SOLUTION AT 25°C[a]

Year (Ref.)	$K_{sp}(LaF_3)$ (mol^4 dm^{-12})	Year (Ref.)	$K_{sp}(CeF_3)$ (mol^4 dm^{-12})
1953 (*230*)	1.4×10^{-18}	1953 (*230*)	1.4×10^{-18}
1953 (*231*)	1.9×10^{-20}	1959 (*235*)	1.1×10^{-15}
1968 (*232*)	3×10^{-19}	1965 (*230*)	1.3×10^{-19}
1969 (*231*)	$6.3–160 \times 10^{-23}$	1976 (*229*)	1.1×10^{-17}
1973 (*233*)	6.2×10^{-21}	1977 (*228*)	1.3×10^{-19}
1974 (*234*)	1.1×10^{-18}		
1976 (*229*)	7.6×10^{-18}		
1977 (*228*)	2.0×10^{-19}		

[a] Most values refer to infinite dilution, but some to salt concentrations of up to 0.5 mol dm^{-3} (not always specified clearly).

with fluoride-ion-selective electrodes constructed from lanthanum trifluoride. Disagreements here are due to some extent to difficulties with respect to aging of the lanthanum trifluoride precipitate.

d. Cerium Trifluoride. Solubility products are listed in Table XIII. As for lanthanum trifluoride, reported values cover a range of over 100-fold, not all of which spread can be attributed to differences in conditions or assumptions. However, as one would expect, values for K_{sp} for LaF_3 and for CeF_3 from a given investigation are extremely similar.

e. Other Trifluorides. Table XIV includes several sets of values plus some isolated values for the trifluorides of the lanthanide elements, in all cases in aqueous solution at 298.15 K. Agreement is less than satisfactory, especially at the beginning of the series. The two complete sets of values agree in showing a fairly steady decrease in K_{sp} along the lanthanide series, with a drop of several thousand times from LaF_3 to LuF_3. However the most recent set, of five values only, shows an increase from LaF_3 to EuF_3, and only then a decrease to ErF_3.

TABLE XIV

SOLUBILITY PRODUCTS FOR LANTHANIDE TRIFLUORIDES IN AQUEOUS SOLUTION AT 25°C

	pK_{sp}			
	(233)			
Trifluoride	Stoichiometric	Thermochemical	*(228)*	*(229)*
LaF_3[a]	18.9	20.2	18.7	17.1
CeF_3[a]	19.2	20.5	19.1	17.1
PrF_3	18.9	20.2		17.0
NdF_3	18.6	19.9	20.3	17.1
SmF_3	17.9	19.3		16.0
EuF_3	17.2	18.5	21.9	15.4[b]
GdF_3	16.8	18.1		15.3
TbF_3	16.7	18.0		14.9
DyF_3	16.3	17.6		14.6
HoF_3	15.8	17.2		14.6
ErF_3	15.5	16.8	18.0	14.5
TmF_3	15.8	17.1		14.6
YbF_3	15.0	16.3		14.6
LuF_3	15.0	16.4		14.6

[a] See also Table XIII.

[b] Also 16.7, in Lingane *(232)*.

f. Solubility in Aqueous Electrolytes. Some data are available on solubilities of lanthanide trifluorides in aqueous electrolyte solutions. The presence of acids increases solubilities. Thus at pH 4 and 25°C, solubilities of yttrium, cerium, and europium trifluorides are 30.5, 8.74, and 2.61 $\times$ 10^{-6} mol dm^{-3}, respectively (*4a*); solubilities in water under analogous conditions are 20.7, 8.29, and 1.53 $\times$ 10^{-6} mol dm^{-3}, respectively. Marked increases in solubility for the trifluorides of yttrium, praseodymium, neodymium, samarium, and europium have been noted on going from water to nitric acid of concentration 3 to 6 mol dm^{-3}. Trifluoride concentrations are then between 1 and 6 $\times$ 10^{-4} mol dm^{-3} (*239*). Further increase in nitric acid concentration leads to a slight drop in solubility, here and for LaF_3 and ScF_3 (*240a*). Solubility increases of comparable magnitude are observed for ammonium fluoride solutions, although here increasing concentration of salt, up to 13.6 mol dm^{-3}, leads to continuously increasing solubility. Thus, for example, the solubility of lutetium trifluoride is 3.63, 13.0, 70.5, and 93.0 $\times$ 10^{-4} mol dm^{-3} at ammonium fluoride concentrations of 3.0, 6.0, 12.0, and 13.6 mol dm^{-3} (*4a*). Information is also available for several lanthanide trifluorides in aqueous hydrofluoric acid (*133b, 240b*), and in aqueous hydrochloric acid (*240c*). The solubility product for lanthanum trifluoride in aqueous solutions containing sodium perchlorate shows a small and curved dependence on added salt concentration, both at 20° and at 25°C, as shown in Table XV (*234*). The ready dissolution of lanthanum trifluoride in solutions of disodium ethylenediaminetetraacetate can be ascribed to complex formation (*4a*).

2. *Trichlorides*

As so often in this review, Matignon was the first to provide quantitative information, reporting the solubility of neodymium chloride in

TABLE XV

VARIATION OF THE SOLUBILITY PRODUCT FOR LANTHANUM FLUORIDE WITH SODIUM PERCHLORATE CONCENTRATION[a]

[NaClO$_4$] (mol dm^{-3})	pK_{sp}					
	0.0	0.1	0.2	0.3	0.4	0.5
At 20°C	17.65	17.29	17.18	17.03	17.16	17.47
At 25 °C	17.95	17.69	17.50	17.49	17.73	17.80

[a] From Pan *et al.* (*234*).

TABLE XVI

SOLUBILITIES OF TRICHLORIDES IN WATER AT 25°C[a]

Trichloride	Solubility (mol/kg water)	Trichloride	Solubility (mol/kg water)	Trichloride	Solubility (mol/kg water)
		$ScCl_3 \cdot 6H_2O$	[b]		
		$YCl_3 \cdot 6H_2O$	3.948		
$LaCl_3 \cdot 7H_2O$	3.8944			$GdCl_3 \cdot 6H_2O$	3.5898
$CeCl_3 \cdot 7H_2O$	3.748			$TbCl_3 \cdot 6H_2O$	3.5795
$PrCl_3 \cdot 7H_2O$	3.975			$DyCl_3 \cdot 6H_2O$	3.6302
				$HoCl_3 \cdot 6H_2O$	3.739
$NdCl_3 \cdot 6H_2O$	3.9307			$ErCl_3 \cdot 6H_2O$	3.7840
$SmCl_3 \cdot 6H_2O$	3.6414			$YbCl_3 \cdot 6H_2O$	4.0028
$EuCl_3 \cdot 6H_2O$	3.619			$LuCl_3 \cdot 6H_2O$	4.136

[a] From Hinchey and Cobble (*201*).

[b] A solubility of 4.65 mol dm^{-3} at 25°C has been reported (*53*), but should be regarded with caution as there is likely to be considerable hydrolysis in such a strong solution when derived from the hydrate and neutral water.

water, at 13° and 100°C, and of praseodymium chloride at 13°C (*178*). Further sporadic reports appeared at intervals. These dealt with yttrium trichloride [from two independent sources in close agreement in 1925 (*206, 207*)], neodymium and samarium trichlorides [also in 1925 (*207*)], and the trichlorides of lanthanum, praseodymium, and neodymium [in 1940 (*205*)]. These sources all reported solubilities over a wide range of temperature. More recent determinations of solubilities of the whole range of trichlorides, at 25°C, are listed in Table XVI (*201*). In the past few years, another set of solubilities has been emerging, from a mammoth series of Russian investigations of lanthanide trihalide/electrolyte or nonelectrolyte/water ternary systems. Some idea of the range of values from these sources is given in Table XVII (*241–257*).

There is tolerable agreement between the values in Tables XVI and XVII, in such cases as direct or almost direct comparison is possible. Thus, for example, the Russian value of 48.52% by weight for the solubility of neodymium chloride at 30°C may be compared with 49.7% by Hinchey and Cobble, at 25°C. Indeed, if one follows the solubilities reported for neodymium chloride back to Matignon, the values at or near 25°C are all reasonably close together (*178, 201, 205, 207, 258, 259*). On the question of comparability, it may be remarked here that solubility comparisons are from time to time precluded by the preference of some authors for weight units, and of others for volume concentration units. When densities are also given, then of course interconversion is straightforward, but densities are by no means always available when needed.

TABLE XVII

SOLUBILITIES OF TRICHLORIDES IN WATER AS TAKEN FROM TERNARY PHASE DIAGRAMS

Trichloride	Solubility (g per 100 g soln.)					
	18°C	20°C	25°C	30°C	40°C	50°C
$LaCl_3$				48.07 (*241*)		
$CeCl_3$	48.0 (*242*)		49.3 (*242, 243*)[a]	49.09 (*244*)		51.7 (*242, 243*)
$PrCl_3$				50.6 (*245*)		
$NdCl_3$				48.52 (*246*)		
$SmCl_3$		48.0 (*247*) 48.3 (*248*)			49.0 (*247*) 49.2 (*248*)	
$GdCl_3$		47.5 (*249*) 48.0 (*250*)		48.32 (*251*)	48.2 (*249*) 49.0 (*250*)	
$DyCl_3$		48.5 (*252*) 49.5 (*253*)			50.5 (*252, 253*)	
$ErCl_3$				48.05 (*254*) 48.06 (*255*)		

[a] But 48.63% has been reported elsewhere [cf. references (*256*) and (*257*)].

Early studies of the temperature variation of the solubilities of lanthanide trichlorides have already been mentioned. More recently, comprehensive data from −15° to +50°C have been presented (*259, 260*); a representative selection is given in Table XVIII. Here and elsewhere, the dependence of solubility on temperature does not conform

TABLE XVIII

TEMPERATURE DEPENDENCE OF SOLUBILITIES OF TRICHLORIDES IN WATER[a]

Trichloride	Solubility					
	−10°C	0°C	10°C	25°C	30°C	50°C
YCl_3		43.3	43.4	43.5	44.0	45.2
$LaCl_3$	47.4	47.2	48.2	48.8	49.8	51.6
$NdCl_3$	49.1	49.2	49.3	49.7	50.5	52.2
$GdCl_3$	48.4	48.2	48.3	48.7	49.3	50.8
$ErCl_3$		50.7	51.0	51.3	51.6	52.5
$LuCl_3$		52.6	54.2	54.2	54.6	55.1

[a] Solubilities are quoted in grams trichloride per 100 g solution (*259, 260*). Further data, for other trichlorides and for other temperatures, can be found in Nikolaev *et al.* (*259, 260*).

well to the linear log versus 1/*T* van't Hoff plot, hardly surprising in view of the very high concentrations involved. Estimates of enthalpies of solution of the appropriate hydrates by this method are therefore not of significant value. Other miscellaneous references to temperature dependence of solubilities of lanthanide trichlorides include those relating to cerium and neodymium (*258*), and to lanthanum (*261*). The last-cited reference is of interest in that solubilities both of the hexahydrate and of the heptahydrate were determined over the ranges 40–72.5°C and 0–95°C, respectively.

All the solubilities so far mentioned have been presented in weight or concentration units. These may be converted via standard thermodynamic formulas into Gibbs free energies of solution. One group of authors, however, has preferred to present their data in this form, for YCl_3, $LaCl_3$, and six other lanthanide trichlorides (*184*).

a. Solubility in Aqueous Acids. Matignon noted that whereas 50.96 g of praseodymium trichloride was present in 100 g of saturated aqueous solution (at 13°C), only 41.05 g was present when the 100 g of saturated solution contained 7.25 g of hydrogen chloride (*178*). The solubility of yttrium trichloride decreases from 3.95 molal in water to 1.71 molal in aqueous hydrochloric acid of density 1.1051 g cm^{-3} (at 25°C) (*207*). Similarly, cerium trichloride dissolves to the extent of 50% by weight (grams $CeCl_3$ per 100 g solution) in water, but only 27% in 15% hydrochloric acid, at 40°C (*258*). The pattern for scandium trichloride is similar (*262*), as is that for ytterbium trichloride.

The dependence of the solubility of $LaCl_3 \cdot 7H_2O$ on acid concentration at 25°C is indicated in Table XIX (*205*). The dependence at 50°C is the same. The dependence of solubilities of trichlorides of scandium (*263*), yttrium (*264, 265*), and several rare-earth elements (*265*) on hydrochloric acid concentration has been established at 0°C.

b. Solubility in Aqueous Salt Solutions. Solubilities of the trichlorides of lanthanum, praseodymium, and neodymium in ammonium

TABLE XIX

DEPENDENCE OF SOLUBILITY OF $LaCl_3 \cdot 7H_2O$ ON ACID CONCENTRATION[a] (AT 25°C)

[Acid], mol dm^{-3}	0.0	0.714	0.817	1.471	1.644	2.611
Solubility	49.27	48.79	45.87	43.55	42.78	39.47

[a] Solubilities are quoted in grams $LaCl_3$ per 100 g solution; from Friend and Hale (*205*). The acid used was not specified by the authors, but may be presumed to be hydrochloric.

chloride solutions of concentrations 1.0, 2.0, 3.0, 4.0, and 5.0 mol dm^{-3} at 15°, 30°, and 50°C have been presented graphically (*212*). The dependences of solubilities on ammonium chloride concentration and on temperature are complex. The solubility of lanthanum trichloride decreases steadily as magnesium chloride is added, falling from 48.9 g per 100 g solution in water to 10.8 g per 100 g solution containing 29% magnesium chloride (at 25°C) (*266*). Solubility isotherms for some ternary systems have been established: for example, cerium trichloride/sodium or lithium chloride/water (*256*), cerium trichloride/guanidinium chloride/water (*242*), gadolinium or dysprosium trichloride/pyridinium chloride/water (*253*), and, slightly different in recipe, cerium trichloride/cerium nitrate/water (*257*).

c. Solubility in Aqueous Solutions of Nonelectrolytes. Solubilities of various lanthanide trichlorides in aqueous solutions of sundry nonelectrolytes at varying concentrations have been reported, at a selection of temperatures. Randomly chosen examples include erbium trichloride/acetylurea (*254*), and praseodymium chloride or erbium trichloride/semicarbazide (*245, 255*). When the nonelectrolyte is liquid, the system comes within the province of mixed aqueous solvents, dealt with later.

3. Tribromides

a. Yttrium Tribromide. The solubility of yttrium tribromide in water was measured at five temperatures in the range 0–95°C more than half a century ago (*206*). At 25°C, the solubility is approximately 44% by weight, which is surprisingly close to that of the chloride (43.5%).

b. Lanthanide Tribromides. These figure in some of the detailed studies of halide/nonelectrolyte/water systems so extensively pursued by Russian chemists. Hence, solubilities in water can be obtained from the extreme cases of zero concentration of nonelectrolyte (cf. the chlo-

TABLE XX

SOLUBILITIES OF LANTHANIDE TRIBROMIDES IN WATER (AT 30°C)

REE	Solubility $LnBr_3$ (g per 100 g soln.)	Reference	Solubility $LnCl_3$ (g per 100 g soln.)	Reference
Nd	63.08	*246*	48.52	*246*
Tb	62.01	*267*		
Er	65.12	*268*	48.05	*254*

TABLE XXI

SOLUBILITIES OF YTTRIUM AND LANTHANIDE TRIIODIDES[a,b] IN WATER (AT 0°C)

Compound	Solubility (g per 100 g soln.)	Compound	Solubility (g per 100 g soln.)
YI_3	66.98 (*269*)	NdI_3	66.64 (*273*)
			69.77 (*272*)
LaI_3	68.74 (*270*)	SmI_3	85.71[c,d] (*274*)
	68.96 (*271*)	EuI_3	63.84 (*275*)
CeI_3	66.56 (*270*)	GdI_3	67.29 (*276*)
PrI_3	68.07 (*272*)		67.32 (*271*)

[a] From ternary phase diagrams (cf. trichlorides and tribromides in Tables XVII and XX).

[b] The enneahydrate is the solid phase in equilibrium with saturated solution in all cases.

[c] *Sic,* but must be wrong by comparison with the other triiodide solubilities in this table.

[d] From the reported density, this can be converted into a molar concentration of 4.53.

ride set). Such solubilities are given in Table XX (*246, 254, 267, 268*), which also shows how markedly more soluble are the bromides than the chlorides.

4. *Triiodides*

The triiodides are slightly more soluble in water than the tribromides [Table XXI (*269–276*)]; the published value for samarium triiodide looks suspiciously high. The addition of hydrogen iodide produces a large decrease in the solubility of yttrium triiodide, from 66.98 wt % in water to 4.90 wt % in 63.45 wt % HI (in both cases at 0°C) (*269*). Other lanthanide triiodides behave similarly (*271–274*).

5. *Trihalide Mixtures*

In what may well prove to be only the first in a series, solubility isotherms have been reported for MF_3/MCl_3/water systems, for M = Y, La, and Gd (*277*).

B. IN NONAQUEOUS SOLVENTS

1. *Trifluorides*

Cerium trifluoride is known to be insoluble in liquid ammonia (*278*). Lanthanum trifluoride is very sparingly soluble in bromine trifluoride;

TABLE XXII

SOURCES OF SOLUBILITY DATA FOR TRICHLORIDES IN MONOHYDROXYLIC ALCOHOLS

	Reference					
Trichloride	MeOH	EtOH	*n*PrOH	*i*PrOH	BuOH[a]	AmOH
ScCl$_3$	←		*167*			→
YCl$_3$	*112*	*112, 178*		*112*		
LaCl$_3$	*112*	*112, 218*	*218*	*112, 218*		
CeCl$_3$	*284*	*284*	*284*	*221, 284*	*284*	*284*
PrCl$_3$	*169*	*169, 178*	*169*		*169*	*169*
NdCl$_3$	*112, 169, 218, 285*	*112, 169, 178, 218, 285*	*169, 218, 285*	*112, 218*		*169, 218*
LnCl$_3$[b]	*112*	*112*		*112*		

[a] For qualitative information on relative solubilities of lanthanide trichlorides in *n*-butanol and in water, see Asselin *et al.* (*286*).

[b] Ln = Sm, Gd, Dy, Er, Yb.

less than 0.02 g dissolves in 100 g BrF$_3$ over the temperature range 25–70°C (*279*). Its solubility in liquid uranium hexafluoride has also been measured (*280*).

Solubilities of the later lanthanide trifluorides are similar in liquid hydrogen fluoride and in water, though they are slightly more soluble in the former. Solubilities in liquid hydrogen fluoride (probably 98% HF) decrease steadily from a value of 4×10^{-5} mol EuF$_3$ per 100 g HF to 2.1×10^{-5} mol LuF$_3$ per 100 g HF, at 0°C (*281*).

2. *Trichlorides*

Much information is available on the solubilities of various trichlorides in a wide variety of solvents. This material will be presented here arranged according to solvent type.

a. Alcohols. It has been recognized since the time of Matignon that lanthanide trichlorides are somewhat soluble in ethanol.[4] He reported solubilities for four lanthanide trichlorides (*178*) and for yttrium trichloride (*178*) at temperatures between 15 and 20°C. West and King later reported solubilities for neodymium trichloride in the lower alcohols at 20°C (*282, 283*). Subsequently, all solubilities have been determined at 25°C, to which temperature the data presented and discussed below refer. The availability of solubility data is indicated in Table XXII (*112, 167, 169, 178, 218, 221, 284–286*). Before considering values and trends in detail, however, it is necessary to consider accuracy.

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[4] But Mellor (*8*) claimed scandium trichloride to be insoluble in ethanol.

TABLE XXIII

INTERCOMPARISON OF REPORTED SOLUBILITIES FOR NEODYMIUM TRICHLORIDE IN METHANOL AND IN ETHANOL[a] (AT 25°C)

Source	Solubility in MeOH	Source	Solubility in EtOH
218	570 g dm^{-3}[a]	*218*	360 g dm^{-3}[b]
285	529.7 g dm^{-3}	*285*	249.8 g dm^{-3}
169	52.81 g/100 g soln.	*169*	43.56 g/100 g soln.[c]
112	40.8 g/100 g soln.	*112*	25.3 g/100 g soln.

[a] Compare 48 to 50 g per 100 g solution in water (Section V,A,2).
[b] West and King reported about 530 g dm^{-3} at 20°C (*282, 283*).
[c] Matignon reported 30.8 g per 100 g solution at 20°C (*178*).

In the section on solubilities in water it was stated that the various determinations of the solubility of neodymium trichloride were tolerably consistent. Neodymium trichloride is, again, the compound for which most information is available in respect of solubilities in alcohols. But here agreement, where compatible concentration units permit comparison, is less good, as shown in Table XXIII. The solubilities tend to decrease as the years pass, and some of the earlier values are surprisingly close to the respective solubilities in water. One suspects that the methanol and ethanol used were dried more efficiently in the later determinations. From this point of view at least, Merbach's 1972 values (*112*) are to be preferred. This problem of incompletely dried alcohols has been encountered above in connection with enthalpy measurements (Section IV,B); it crops up repeatedly with solubilities. Thus, a 1962 set of solubilities of cerium trichloride in a series of monohydroxylic alcohols (*284*) contains some surprisingly high values, especially for the C_3 to C_6 alcohols—although it must be said that other workers have also reported fairly high solubilities for these trichlorides in higher alcohols (*282, 283*).[5] Another possible complication, especially for higher alcohols where solubility equilibria take a long time to establish, is that one might get μ-chloropolynuclear species building up (*287*). However, at least in dilute solution in methanol, this process does take place slowly, over a period of several weeks.

In view of the aforementioned difficulties, both of incompatibility of concentration units and of chemistry and accuracy, we have selected sets of data to illustrate trends in solubilities. Only one paper deals with a selection of trichlorides across the lanthanide series; its results

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[5] Though some workers ensure scrupulously anhydrous conditions in their solubility determinations [e.g., Saad and Soliman (*221*)], others may have been less careful.

TABLE XXIV

SOLUBILITIES OF TRICHLORIDES IN ALCOHOLS (AT 25°C)[a]

Trichloride	Solubility (mol $LnCl_3$ per 1000 g alcohol)		
	MeOH	EtOH	*i*PrOH
YCl_3	4.38	2.92	0.91
$LaCl_3$[b]	2.45	1.26	0.004
$NdCl_3$	2.75	1.35	0.04
$SmCl_3$	3.33	1.97	0.23
$GdCl_3$	4.21	2.43	0.32
$DyCl_3$	4.00	2.85	1.14
$ErCl_3$	4.53	3.41	0.84
$YbCl_3$	4.90	4.26	0.80

[a] From Merbach *et al.* (*112*). The solids in equilibrium approximate to $LnCl_3 \cdot 4ROH$; for details consult reference (*112*).

[b] Results for methanol and ethanol at 0° and 50°C are also available (*112*).

are summarized in Table XXIV. There is a general, but far from steady, increase in solubilities as one proceeds from lanthanum (f^0) across to ytterbium (f^{13}). This sequence is followed for methanol, ethanol, and isopropanol. For the various trichlorides here, and for the trichlorides of scandium (*283*), cerium (*284*), and praseodymium (*169*), solubilities decrease as the size of the alkyl group increases. This is shown by the selected data collected in Table XXV. Intercomparisons are sometimes complicated by differences in the numbers of molecles of alcohol of crystallization, $LnCl_3 \cdot nROH$, in the solid phase in equilibrium with saturated solution.

Lanthanum and neodymium trichlorides are readily soluble in ethylene glycol and in glycerol [Table XXVI (*218, 288*)].

Finally, in this section on alcohols, we should mention investigations in which the trichloride/alcohol systems are acknowledged to be not anhydrous. Solubilities of yttrium trichloride and of most of the lanthanide trichlorides have been determined in 96.8% ethanol over the temperature range 20–60°C (*289*), while the solubilities of the hydrates $LaCl_3 \cdot 7H_2O$ and $CeCl_3 \cdot 6H_2O$ have been determined in an extensive range of alcohols at 25°C, with a few data at 35° and at 45°C (*290*).

b. Ethers. Matignon found that neodymium and praseodymium trichlorides were effectively insoluble in diethyl ether (*178*), but later

TABLE XXV

SOLUBILITIES OF TRICHLORIDES IN MONOHYDROXYLIC ALIPHATIC ALCOHOLS (25°C)

	Solubility										
Trichloride	MeOH	EtOH	*n*PrOH	*n*BuOH	*n*-$C_5H_{11}OH$	*n*-$C_6H_{13}OH$	*n*-$C_7H_{15}OH$	*n*-$C_8H_{17}OH$	*n*-$C_9H_{19}OH$	*i*PrOH	*t*BuOH
$ScCl_3$ (*283*) [g/100 g soln][a]	45.5	37.3	26.1	25.2	23.7	21.5	19.3	16.9	13.5		
$LaCl_3$ (*218*) [g dm^{-3}]		425	330[c]							7	
$LaCl_3$ (*112*) [mol/1000 g ROH]	2.45	1.26								0.004	
$CeCl_3$ (*284*) [g/100 g soln]	39.4	27.6	25.4	34.5	29.6	26.8				4.2	0.5
$CeCl_3$ (*221*) [g/100 g soln]										0.23	
$PrCl_3$ (*169*) [g/100 g soln]	53.69	43.76	32.04	23.62	24.35						
$NdCl_3$ (*218*) [g dm^{-3}]	570	360	285	330	380					3.5	
$NdCl_3$ (*285*) [g dm^{-3}]	529.7	249.8	249.5	317.8							
$NdCl_3$ (*169*) [g/100 g soln][b]	52.81	43.56	28.46	17.64	15.30						
$YbCl_3$ (*112*) [mol/1000 g ROH]	4.90	4.26								0.80	

[a] At 18°C. [b] Values also available for 0°, 40°, and 50°C. [c] Compare 300 g dm^{-3} at 20°C (*288*).

TABLE XXVI

SOLUBILITIES OF RARE-EARTH TRICHLORIDES IN ETHYLENE GLYCOL AND IN GLYCEROL

	Solubility (g dm^{-3})				
	Glycol			Glycerol	
Trichloride	20°C	25°C	40°C	30°C	40°C
$LaCl_3$ (*288*)	166		450	50	150
$LaCl_3$ (*218*)		305			
$NdCl_3$ (*218*)		415			

workers have found and measured significant solubilities for the trichlorides of scandium, yttrium, and the lanthanides in various ethers, including dialkyl ethers, tetrahydrofuran, dioxane, and diglyme [Table XXVII (*143, 146, 285, 291–295*)]. Solubilities are generally lowest in diethyl ether and largest in tetrahydrofuran. In diglyme, in tetrahydrofuran, and, most markedly, in higher aliphatic ethers, there is a large increase in solubility at the right-hand end of the lanthanide series (Ho to Yb). Solubilities of scandium and of yttrium trichlorides have values appropriate to the ionic radii of these cations.

c. Ketones. Trichlorides are sparingly soluble in ketones, both aliphatic and aromatic (Table XXVIII) (*296*). The trend of solubilities of lanthanum trichloride from acetone through acetophenone to diphenyl ketone is not regular.

d. Simple N-Donor Solvents. Cerium trichloride, like cerium trifluoride, is insoluble in liquid ammonia (*278*). The trichlorides of lanthanum, praseodymium, and neodymium are said to be insoluble in hydrazine, but cerium trichloride is claimed to dissolve to the extent of 3 g in 100 g of hydrazine, with evolution of gas (*297*). Yet, a recent reference reports a stable hydrazine adduct of cerium trichloride (*175*).

The most studied solvent here is pyridine (Table XXIX (*178, 298*). The reported solubilities parallel the affinities suggested by known solvates—e.g., $YCl_3 \cdot 3py$, $SmCl_3 \cdot 3py$, but $PrCl_3 \cdot 2py$ (cf. Section III,C,2). Qualitative information on related solvents is that neodymium trichloride is very sparingly soluble in aniline, but insoluble in toluidine, pyrrole, piperidine, and quinoline. Praseodymium trichloride is also insoluble in quinoline, but yttrium trichloride is slightly soluble in this solvent (*178*).

TABLE XXVII

SOLUBILITIES OF TRICHLORIDES IN ETHERS[a,b]

	Solubility (g $LnCl_3$ per 100 g soln.)									
	Et O Et	Me O nBu	Me O nAm	Me O C_7H_{15}	nPr O nPr	Diglyme		Dioxane	THF[c]	
	(146)	(291)	(291, 292)	(291)	(292)	(293)	(292)	(292)	(294)	(143)
Trichloride	20°C	←			25°C			→	~20°C	~22°C
$ScCl_3$		6.5				1.22			d	
YCl_3			1.6, 3.0	2.7			0.4	0.1	0.930	0.252
$LaCl_3$	0.045			0.6			0.02	0.02	0.126	
$CeCl_3$	0.0073			0.1					0.593	
$PrCl_3$				0.8			0.04	0.04	0.590	
$NdCl_3$	0.0058		0.07	0.4			0.04	0.1	1.16	0.812
$SmCl_3$	0.0074						0.4_5	0.07	1.49[e]	1.47[e]
$EuCl_3$			0.4	0.5		0.25	0.6	0.07		1.26
$GdCl_3$	0.028		0.08			0.33	0.5_5	0.1	1.91	1.25
$TbCl_3$		0.23	0.7	3.3		0.22	0.6	0.3		0.685
$DyCl_3$	0.032		0.08			0.25	0.6	0.4	0.645	0.512
$HoCl_3$			2.4	1.0	0.1	0.37	0.6_5	0.5_5	0.698	0.307
$ErCl_3$			33.5		0.2	0.67	0.9	0.7	0.786	0.397
$TmCl_3$	0.053					0.88				0.486
$YbCl_3$	0.085		43.5		13.7	1.15	1.4_5	0.8	1.98	1.08
$LuCl_3$										0.880

[a] Reference (*291*) contains data for further dialkyl ethers.

[b] Reference (*292*) also contains some solubilities in 1,3-dioxolan.

[c] Concentrations in THF are in g per 100 ml solution (*143*) or g per 100 ml solvent (*294*).

[d] Solubility 1% at 25°C (*295*).

[e] Compare 8.07 g dm^{-3} (*285*).

TABLE XXVIII

SOLUBILITIES OF TRICHLORIDES IN KETONES (20°C)[a]

Ketone	Solubility	
	$LaCl_3$	$CeCl_3$
Acetone	0.0012	0.0043
Acetophenone	0.022	0.10
Benzophenone	0.00026[b]	
Cyclohexanone	0.018	0.38
Acetylacetone	0.40	0.10

[a] Solubilities expressed as grams $LnCl_3$ per 100 g solvent, from Sheka and Kriss (*296*).

[b] Solubility at 50°C.

e. Other Solvents. Solubilities of trichlorides in hexamethylphosphoramide (*159*), tributyl phosphate (*299, 300*), and hexachlorobutadiene (*301*) are given in Table XXX (*159, 299–301*). Cerium trichloride is insoluble in acetonitrile (*302*), but samarium trichloride dissolves to the extent of 0.82 g per liter at 25°C (*285*), and scandium trichloride to 3.7% by weight (*295*). Scandium trichloride is slightly more soluble in dimethylformamide (5.5%; *295*). The trichlorides of praseodymium, neodymium, and holmium are soluble, at least 2%, in dimethylformamide, *N*-methylformamide, formamide, and diethylformamide (*303*). Praseodymium and neodymium trichlorides are insoluble in chloroform (*178*). Extrapolation from published data (*304*) suggests that these trichlorides might dissolve in propylene carbonate, but we have recently found that lanthanide trichlorides are very sparingly soluble in this solvent. However, they dissolve fairly readily in dimethyl sulfoxide (*219*).

TABLE XXIX

SOLUBILITIES OF TRICHLORIDES IN PYRIDINE[a]

Trichloride	Temperature	Solubility	Reference
YCl_3	15°C	6.5	*178*
$CeCl_3$	0°C	1.58	*298*
$PrCl_3$	15°C	2.14	*178*
$NdCl_3$	15°C	1.8	*178*
$SmCl_3$	15°C	6.38	*178*

[a] Solubilities expressed in grams $LnCl_3$ per 100 g pyridine.

TABLE XXX

SOLUBILITIES OF LANTHANIDE TRICHLORIDES IN HEXAMETHYLPHOSPHORAMIDE (HMPA), TRIBUTYL PHOSPHATE (TBP), AND HEXACHLOROBUTADIENE (HCB)

	Solubility		
$LnCl_3$	HMPA[a] (mol dm^{-3}) 23 ± 3°C (*159*)	TBP[b] (g/100 g soln.) 25°C (*299*)	HCB (g/100 g soln.) 25°C[c] (*301*)
$LaCl_3$	0.107		0.040
$CeCl_3$	0.107		0.036
$PrCl_3$	0.128	30.0	0.039
$NdCl_3$	0.125	31.8	0.029
$SmCl_3$	0.126	33.4	0.024
$EuCl_3$	0.121	35.2	
$GdCl_3$	0.125	37.8	
$TbCl_3$	0.128	38.5	
$DyCl_3$	0.109	39.2	
$HoCl_3$	0.108	41.0	
$ErCl_3$	0.098	41.3	
$TmCl_3$	0.093	41.4	
$YbCl_3$	0.085		
$LuCl_3$	0.073		

[a] Addition of ammonium chloride increases the solubility of $SmCl_3$, $ErCl_3$, and $TmCl_3$ in HMPA (*159*).

[b] Solubilities between 0.89 and 1.79 mol dm^{-3} have been reported (*300*).

[c] Solubilities also reported at 50° and 75°C.

3. *Tribromides*

The information available is collected in Table XXXI (*46, 149, 157, 160, 291, 292, 305–310*). There are remarkably few data for hydroxylic solvents, but a reasonable amount for some aprotic solvents, especially ethers. Cerium tribromide is sparingly soluble in liquid ammonia (*278*); information on solubilities of tribromides in other inorganic nonaqueous solvents seems entirely lacking. Comparisons between tribromide and trichloride solubilities can readily be made using Tables XXIV to XXXI.

4. *Triiodides*

Quantitative information is given in Table XXXII (*149, 292, 306, 311*); there are also some solubilities reported for several triiodides in

TABLE XXXI

SOLUBILITIES OF LANTHANIDE TRIBROMIDES IN NONAQUEOUS SOLVENTS

	Solubility										
			Ethers (g/100 g soln.) 25°C (*291*)								
$LnBr_3$	THF[a] (g/100 ml soln.) ~22°C (*305*)	Dioxane (g/100 g soln.) 25°C (*292*)	Me O *n*Bu	Me O $H_{15}C_7$	Me O $H_{19}C_9$	Me O $H_{26}C_{11}$	Pyridine ($g\ dm^{-3}$) 25°C (*4b*)	Acetonitrile ($g\ dm^{-3}$) 25°C (*4b*)	Ethylenediamine (g/100 g en) 30°C (*306*)	HMPA ($mol\ dm^{-3}$) 25 ± 3°C (*160*)	DMF ($g\ dm^{-3}$) 30°C (*149*)
$ScBr_3$		1.0[b]									
YBr_3	0.16	1.6									
$LaBr_3$	0.57	0.2					162.0	4.55–4.58	0.14	0.0365	251.2
$CeBr_3$	0.60						*c*			0.0371	
$PrBr_3$	0.62	0.3_5					278.5	5.9–11.3		0.0425	
$NdBr_3$	0.71	0.9_5	1.6	7.1	2.1	3.6	109.2	7.6–12.3	0.936[d]	0.0461	
$SmBr_3$	0.55	1.3	3.0	7.3	7.6	4.6	111.6	52.3		0.0450	
$EuBr_3$	0.45		0.15	1.5	0.04	0.7				0.0495	
$GdBr_3$	0.38	0.9_5					117.8	62.4		0.0489	
$TbBr_3$	0.29	0.9								0.0502	
$DyBr_3$	0.26	0.9_5								0.0499	
$HoBr_3$	0.38									0.0503	
$ErBr_3$	0.41	0.6								0.0471	
$TmBr_3$	0.41									0.0486	
$YbBr_3$	0.25	1.7								0.0423	
$LuBr_3$	0.30									0.0454	

[a] Exactly the same trend as reported earlier (*307, 308*); recent qualitative comparison of $LnCl_3$ and $LnBr_3$ solubilities in THF can be found in Deacon and Koplick (*309*).

[b] From Kirmse (*310*).

[c] The solubility of $CeBr_3$ in pyridine has been reported over the range −5 to +80°C (*157*); at 25°C it is 2.12 g per 100 g solution.

[d] Solubilities of $NdBr_3$ in monoethanolamine and morpholine are 3.20 and 0.099 g per 100 g solvent, respectively, at 30°C (*306*).

TABLE XXXII

SOLUBILITIES OF LANTHANIDE TRIIODIDES IN NONAQUEOUS SOLVENTS

	Solubility					
				g/100 g solvent 30°C (*306*)		
LnI_3	THF g dm^{-3} 20°C (*311*)	Dioxane g/100 g soln 25°C (*292*)	DMF[a] g dm^{-3} 25°C (*149*)	Ethylenediamine	Monoethanolamine	Morpholine
YI_3	1.53					
LaI_3			578.7[b]			
CeI_3	0.14					
PrI_3		2.7	735.8			
NdI_3		1.6	657.1	2.53	1.93	0.50
SmI_3			520.7			
GdI_3	2.67	0.4	451.0			
TbI_3	8.63					
DyI_3	3.55					
YbI_3		0.1_5				

[a] Solubilities expressed in grams $LnI_3 \cdot 8DMF$ rather than grams anhydrous LnI_3 per dm^3.

[b] 0.524 mol dm^{-3}.

four alkylamines (*310*). Qualitative observations include the ready solubility of YI_3 in ethanol (*6*), that the solubility of LaI_3 in liquid ammonia increases as the temperature falls, and that CeI_3 is less soluble in liquid ammonia than LaI_3 (*278*).

5. *Miscellaneous*

Comparisons of solubilities of trichlorides, tribromides, and triiodides of the lanthanides in a variety of nonaqueous solvents can be found in a Russian review (*310*). Perhaps the widest range of solubilities of lanthanide(III) salts in nonaqueous media refers not to the trihalides but to the nitrates, whose solubilities in 31 solvents have been measured (*312*). Unfortunately, these measurements were carried out on the hexahydrates rather than anhydrous materials.

C. MIXED AQUEOUS SOLVENTS

Strictly, the solubilities of salt hydrates in nonaqueous solvents, and of lanthanide trichlorides in 97% ethanol, mentioned in Section V,B,2,a, come into this category, as may other solubilities measured unwittingly in damp solvents. There has, in fact, been very little work devoted to measuring solubilities in series of mixed aqueous solvents, and much of this has been reported in obscure or inaccessible publications.

Solubilities of $LaCl_3 \cdot 7H_2O$ and of $NdCl_3 \cdot 6H_2O$ in acetone/water mixtures have been reported, and compared with those for chlorides of barium and of the alkali metals (*313*). For these trichlorides, the solubility increases as acetone is added to water up to about 15% acetone, then decreases ($LaCl_3$ and $NdCl_3$ are effectively insoluble in acetone itself). There is also some information, presented only in graphical form, on solubilities of praseodymium trichloride in water-rich methanol, ethanol, and ether mixtures (*314*), and one fact on yttrium trichloride in a water/ether mixture (*264*).

Other solubilities relevant to this section include those for $LaCl_3$ in aqueous ammonia (*173*), lanthanide trifluorides in aqueous hydrofluoric acid (*133b, 240b, 281, 315*), and lanthanide trifluorides in aqueous trifluoroacetic acid (*316*). Trifluoroacetic acid seems to have a marked solubilizing effect on these trifluorides.

D. MIXED NONAQUEOUS SOLVENTS

The trifluorides LaF_3, CeF_3, PrF_3, and SmF_3 are soluble to a limited degree in nitrosyl fluoride/hydrogen fluoride mixtures. Solubilities are in the range 0.05–0.09% by weight at room temperature (*317*).

Solubilities of YCl_3 and of $LaCl_3$ have been measured in mixtures of dimethylformamide or dimethyl sulfoxide with benzene or dioxane. Results for $LaCl_3$ are tabulated, but those for YCl_3 are presented graphically in order to demonstrate linear dependences on mole-fraction composition of the solvent mixtures (*318*). Solubilities of YCl_3, $LaCl_3$, and $LaBr_3$ in mixtures of alcohols (MeOH, EtOH, *n*PrOH) with benzene or dioxane are presented in a similar manner (*319*).

VI. Other Quantities

A. TRANSFER PARAMETERS

Enthalpies of transfer of trihalides from water into nonaqueous and mixed solvents can be obtained by simple arithmetic for all the cases where enthalpies of solution in nonaqueous and mixed aqueous media are known. As long as the enthalpies concerned have been measured in reasonably dilute conditions, or have been estimated for infinite dilution, then close approximations to ideal enthalpies of transfer will be obtained (assuming that pure, dry materials were used, of course!).

In principle, Gibbs free energies of transfer for trihalides can be obtained from solubilities in water and in nonaqueous or mixed aqueous solutions. However, there are two major obstacles here. The first is the prevalence of hydrates and solvates. This may complicate the calculation of $\Delta G_{tr}(LnX_3)$ values, for application of the standard formula connecting ΔG_{tr} with solubilities requires that the composition of the solid phase be the same in equilibrium with the two solvent media in question. The other major hurdle is that solubilities of the trichlorides, tribromides, and triiodides in water are so high that knowledge of activity coefficients, which indeed are known to be far from unity (*4b*), is essential (*201*). These can, indeed, be measured, but such measurements require much time, care, and patience.

B. SINGLE-ION PARAMETERS

The enthalpies of solution and solubilities reviewed here provide much of the experimental information required in the derivation of single-ion hydration and solvation enthalpies, Gibbs free energies, and entropies for scandium, yttrium, and lanthanide 3+ cations.

The derivation of enthalpies of transfer (ΔH_{tr}) of La^{3+} and Yb^{3+} from water into methanol, dimethylformamide, and dimethyl sulfoxide, using published values for $\Delta H_{tr}(Cl^-)$ (*320*) and the enthalpies of solution of the lanthanide trichlorides included in Table XII, is set out in Table XXXIII. Values for $\Delta H_{tr}(K^+)$ (*320*) are included in this table for comparison. Whereas $\Delta H_{tr}(K^+)$ is negative for transfer from water into all three organic solvents, $\Delta H_{tr}(Ln^{3+})$ values are positive for transfer from water into methanol or into dimethylformamide, but negative for transfer into dimethyl sulfoxide, suggesting very favorable solvation of Ln^{3+} ions in this solvent, but only relatively little solvation of Ln^{3+} ions in methanol or dimethylformamide. Values of $\Delta H_{tr}(Yb^{3+})$ are more positive (less negative) than those for the larger La^{3+}. There are uncertainties of several kJ mol^{-1} in the $\Delta H_{tr}(Cl^-)$ values, whose magnitude depends on the extrathermodynamic assumptions used in deriving single-ion values. Therefore, there are rather large uncertainties in the $\Delta H_{tr}(Ln^{3+})$ values shown in Table XXXIII. However, all the single-ion values in this table have been derived using the same assumption [$\Delta H_{tr}(AsPh_4^+) = \Delta H_{tr}(BPh_4^-)$], so differences are reliable even if absolute values may be significantly in error.

As indicated in the previous section, the derivation of Gibbs free energies of transfer, and thence of entropies of transfer, from trichloride

TABLE XXXIII

ENTHALPIES OF TRANSFER OF La^{3+} AND OF Yb^{3+} FROM WATER INTO ORGANIC SOLVENTS (25°C)[a]

ΔH	Enthalpy ($kJ\ mol^{-1}$)			
	Water	Methanol	DMF	DMSO
$\Delta H_{soln}(LaCl_3)$	−138	−93	−47	−163
$\Delta H_{soln}(YbCl_3)$	−216	−167		−226
$\therefore \Delta H_{tr}(LaCl_3)$		+45	+91	−25
$\therefore \Delta H_{tr}(YbCl_3)$		+49		−10
$\Delta H_{tr}(Cl^-) \times 3$		+25	+64	+57
$\therefore \Delta H_{tr}(La^{3+})$		+20	−27	−82
$\therefore \Delta H_{tr}(Yb^{3+})$		+24		−67
$\Delta H_{tr}(K^+)$ [for reference]		−18	−39	−35

[a] Data from Table XII and from Cox (*320*).

solubilities is not a recommendable procedure. Information is need for other salts that crystallize as anhydrous materials and that are much less soluble in water. In view of this, and as the results are of more general relevance than the present review, we refer the reader to a recent book in which these and other single ion thermodynamic parameters are listed, discussed, and referenced (*195*).

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