31. V.A.Kireev, Zhur.Obshch.Khim., 33, 724 (1962).
32. D.R.Stull and G.C.Sinke, "Thermodynamic Properties of the Elements", Washington, 1956.
33. H.Zeise, "Thermodynamik", Bd III/I, Leipzig, 1954.
34. P.J.Friel and R.C.Goetz, J.Phys.Chem., 64, 175 (1960).
35. F.Burhorn and R.Wieneck, Z.phys.Chem.(Leipzig), 212, 105 (1959); 215, 285 (1960).
36. "Landolt-Börnstein Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik. 6.Aufl. Band II, Teil 4, Kalorische Zustandgrössen", Springer, Göttingen, 1961.
37. J.L.Raymond, J.Chem.Engin.Data, 7, 190 (1962).
38. L.V.Gurvich, V.A.Kvlividze, and N.P.Rtishcheva, Zhur. Fiz.Khim., 36, 219 (1962) [Russ.J.Phys.Chem., 108(1962)].
39. B.J.McBride and S.Gordon, J.Chem.Phys., 35, 2198 (1961).
40. K.K.Kelley, U.S.Bur.Min., Bull.No.584 (1960).
41. J.S.Gordon, J.Chem.Engin.Data, 6, 390 (1961).
42. B.J.McBride and S.Gordon, J.Chem.Phys., 35, 2198 (1961).
43. F.Burhorn and R.Wienecke, Z.phys.Chem.(Leipzig), 213, 37 (1960); 215, 268 (1960).
44. T.J.Katz and J.L.Margrave, J.Chem.Phys., 23, 983(1955).
45. H.G.Kolsky, R.M.Gilmer, and P.W.Gilles, J.Chem.Phys., 27, 494 (1957).
46. J.S.Gordon, J.Chem.Phys., 35, 2252 (1961).
47. D.E.Poland, J.W.Green, and J.L.Margrave, J.Chem. Engin.Data, 7, 389 (1962).
48. O.Sinanoglu, Phys.Fluids, 5, 665 (1962).
49. J.W.Green, D.E.Poland, and J.L.Margrave, J.Chem.Phys., 33, 35 (1960).
50. C.E.Moore, "Atomic Energy Levels", Circ.467, U.S.Nat.Bur. Standards, Washington, Vol.1, 1949; Vol.2, 1952; Vol.3, 1957.
51. V.A.Kireev, Zhur.Fiz.Khim., 35, 1393 (1961) [Russ.J. Phys.Chem., 685 (1961)].
52. V.A.Kireev, Zhur.Fiz.Khim., 36, 2547 (1962) [Russ.J. Phys.Chem., 1389 (1962)].
53. V.A.Kireev, Zhur.Obshch.Khim., 33, 1391 (1963).
54. V.A.Kireev and V.B.Gorbushina, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., 7, 29 (1964).
55. V.A.Kireev, Zhur.Fiz.Khim., 37, 452 (1963) [Russ.J.Phys. Chem., 234 (1963)].
56. G.H.Humfray and E.G.King, J.Amer.Chem.Soc., 74, 2041 (1952).
57. D.W.Good, J.Phys.Chem., 66, 380 (1962).
58. D.Wise, J.L.Margrave, H.M.Feder, and W.N.Hubbard, J.Phys.Chem., 66, 381 (1962); 67, 815 (1963).
59. V.A.Kireev, Paper in "Sbornik Rabot po Fizicheskoi Khimii" (Collection of Papers on Physical Chemistry), Izd.Akad.Nauk SSSR, Moscow, 1947, p.181.
60. V.A.Kireev, Acta Physicochim.URSS, 20, 905 (1945).
61. V.A.Kireev, Zhur.Fiz.Khim., 37, 211 (1963) [Russ.J.Phys. Chem., 106 (1963)].
62. V.A.Kireev, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., 6, 751 (1963).
63. V.A.Kireev, Zhur.Fiz.Khim., 37, 1381 (1963) [Russ.J.Phys. Chem., 737 (1963)].
64. V.A.Kireev, Zhur.Russ.Fiz.-Khim.Obshch., Ch.Khim., 61, 2331 (1929).
65. V.Kirejew [V.A.Kireev], Z.anorg.Chem., 182, 177 (1929).
66. V.A.Kireev, Zhur.Russ.Fiz.-Khim.Obshch., Ch.Khim., 61, 1369 (1929).
67. V.A.Kireev, Zhur.Obshch.Khim., 1, 1057 (1931).
68. V.A.Kireev, Zhur.Obshch.Khim., 3, 622 (1933).
69. V.A.Kireev, Zhur.Fiz.Khim., 34, 945 (1960) [Russ.J.Phys. Chem., 449 (1960)].
70. M.Kh.Karapet'yants, Khim.Prom., 33 (1961).
71. M.Kh.Karapet'yants and Chëng Kuang-yüeh, Khim.Prom., No.3, 32 (1963).
72. M.G.Inghram and J.Drowart, paper in Ref.4, p.274.
73. L.Brewer, Chem.Rev., 61, 425 (1961).
74. P.A.Akishin, L.N.Gorokhov, and L.N.Sidorov, Vestnik Moskov.Gos.Univ., Ser.Matem.Khim., No.6, 194 (1959).
75. P.A.Akishin, L.N.Gorokhov, and L.N.Sidorov, Zhur.Fiz. Khim., 33, 2822 (1959) [Russ.J.Phys.Chem., 648 (1959)].
76. H.M.Rosenstock, J.R.Sites, J.R.Walton, and R.Baldock, J.Chem.Phys., 23, 2442 (1955).
77. R.A.Shelton, Trans.Faraday Soc., 57, 2113 (1961).
78. A.V.Gusarov and L.N.Gorokhov, Vestnik Moskov.Gos. Univ., Ser.2, Khimiya, No.5, 14 (1962).
79. M.B.Panish, J.Chem.Phys., 34, 1079 (1961).
80. J.R.Soulen, P.Sthapitanonda, and J.L.Margrave, J.Phys. Chem., 59, 132 (1955).
81. O.T.Nikitin and P.A.Akishin, Dokl.Akad.Nauk SSSR, 145, 1294 (1961).
82. J.Drowart, G.De Maria, A.J.H.Boergroom, and M.G.Inghram, J.Chem.Phys., 30, 308 (1959).
83. J.Drowart, R.P.Burns, J.De Maria, and M.G.Inghram, J.Chem.Phys., 31, 1131 (1959).
84. K.S.Pitzer and E.Clementi, J.Amer.Chem.Soc., 81, 4477 (1959).
85. A.M.Sladkov and Yu.P.Kudryavtsev, Uspekhi Khim., 32, 509 (1963) [Russ.Chem.Rev., 229 (1963)].
86. P.Codiot, W.Chodkiewicz, and J.Rauss-Godineau, Bull.Soc. chim.France, 2176 (1961); translated into Russian in Uspekhi Khim., 32, 617 (1963).
87. L.N.Sidorov and P.A.Akishin, Dokl.Akad.Nauk SSSR, 151, 136 (1963).
88. L.N.Sidorov, P.A.Akishin, V.I.Belousov, and V.B.Shol'ts, Zhur.Fiz.Khim., 38, 146 (1964) [Russ.J.Phys.Chem., 76 (1964)].
89. L.N.Sidorov, P.A.Akishin, V.I.Belousov, and V.B.Shol'ts, Zhur.Fiz.Khim., 38, 1173 (1964) [Russ.J.Phys.Chem., 641 (1964)].
90. P.A.Akishin, V.P.Spiridonov, G.A.Sobolev, and V.A.Naumov, Zhur.Fiz.Khim., 32, 58 (1958).
91. P.A.Akishin, V.P.Spiridonov, and A.N.Khodchenkov, Zhur. Fiz.Khim., 33, 20 (1959) [Russ.J.Phys.Chem., Abs., 1 (1959)].

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HALIDES OF RARE-EARTH ELEMENTS IN A LOWER STATE OF OXIDATION

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I. INTRODUCTION

Until recently it was the commonly held opinion that in their compounds most of the rare-earth elements (r.e.e.) are exclusively tervalent, and that only some of them exhibit the so-called "anomalous" valencies of 2 and 4. This view was based mainly on studies carried out in the 1930's, when pure r.e.e. were available only with extreme difficulty, and experimental technique was at an insufficiently high level. However, their properties were so similar in all respects that the particular "anomalous" properties of some of them led to serious doubts, and investigators have never ceased the search for "anomalous" oxidation states in the other elements.

From this point of view, considerable interest attaches to the system of triply charged r.e.e. ions suggested by Klemm[1-3] on the basis of comparison of certain periodic properties of the r.e.e. (valency, colour of compounds, magnetic susceptibility) and constructed by analogy with the Periodic System of the elements:

$$Ce^{3+}Pr^{3+}Nd^{3+}Pm^{3+}Sm^{3+}Eu^{3+}\overset{La^{3+}}{Gd^{3+}},$$

$$Tb^{3+}Dy^{3+}Ho^{3+}Er^{3+}Tm^{3+}Yb^{3+}Lu^{3+}.$$

Here the ions La^{3+}, Gd^{3+}, and Lu^{3+} are analogous to the atoms of the inert gases in Mendeleev's Periodic System, their electron configurations being the most stable (empty, half-full, and full *f* shell). All the other triply--charged r.e.e. ions tend to lose or take up electrons so as to approximate to the most stable configuration. This systematisation of the r.e.e. graphically and in general correctly represents the tendency of lower and higher oxidation states of the r.e.e. to appear, and, what is most important, it gives an insight into the exclusive tervalency of some of the elements and the "anomalous" bivalent and quadrivalent states of the r.e.e., their valency being presented as a periodic function of atomic number.

R.e.e. compounds of lower oxidation state were first obtained at the beginning of this century, but they were not systematically investigated until the middle 1920's, when a series of works by Klemm, Jantsch, and others appeared. These investigated the preparation and chemical and physical properties of samarium, europium, and ytterbium dihalides and the possible existence of such forms with the other r.e.e., and developed methods for the isolation and purification of Sm, Eu, and Yb using compounds of these elements in, bivalent state. Although these papers give hardly any quantitative data on the processes and compounds studied, they contain considerable and interesting factual material on the chemistry of the r.e.e. dihalides.

Interest in this region of their chemistry has considerably increased in recent years because of the increased production of the rare-earth metals, which are normally obtained by electrolysis of the fused chlorides or metallothermic reduction of the anhydrous fluorides or chlorides. The reduction of the triply-charged ions in the melt must inescapably pass through intermediate stages, *i. e.* through ions of lower oxidation states. Knowledge of the properties of the resulting lower halides is necessary for the choice of optimum conditions for the process and to decrease losses in the electrolysis.

The use of differences in the stability of the compounds in the lower state of oxidation is also of promise for the separation of the r.e.e.

Several studies have now been published demonstrating the considerably widespread occurrence of the bivalent state among the r.e.e.

II. SHORT REVIEW OF THE CHEMISTRY OF COMPOUNDS OF RARE-EARTH ELEMENTS IN A LOWER STATE OF OXIDATION

1. Preparation and Some Properties of R. E. E. Dihalides

Of the r.e.e. dihalides, those of Sm, Eu, and Yb are the most stable. Until now the main method for their production has been the reduction of the anhydrous trihalides with hydrogen at elevated temperature[4]; this method is extremely lengthy and demands a number of precautions to prevent considerable contamination of the product with oxide halides and to ensure complete conversion of the trihalides to dihalides. In the production of diiodides by this method, the hydrogen is not so much the reducing agent (the heat of formation of HI is close to zero) as a carrier gas producing a more rapid dissociation of the triiodide.

In many cases it is more convenient to reduce the trihalides with various metals than with hydrogen.

Another method for obtaining the dihalides is the dissociation of the corresponding trihalides in a vacuum, and where applicable this is a more convenient method, since it does not require the production of very pure hydrogen.

The most universal method for the production of the dihalides is the reaction of the trihalides with the corresponding rare-earth metals[5-12], which provides all the known r.e.e. dihalides in the purest form.

In addition to the purity of the reactants, the production of the dihalides requires special care in the choice of material for the reaction vessel. When working with chlorides good results are obtained with metallic molybdenum or tantalum, which are sufficiently inert towards the fused rare-earth metals and their chlorides even at extremely high temperatures[13]; with iodides best results are obtained with metallic tungsten[11].

Brewer[14] has justifiably pointed out that some investigators did not take into account the interaction of the rare--earth metals and dihalides with the material of the vessel (gold, platinum, quartz). The rare-earth metals are known to form very stable intermetallic compounds with

gold and platinum; furthermore, when dissolved in the metal of the boat the activity of the rare-earth metal is greatly reduced. All this displaces the equilibrium towards disproportionation of the dihalide, the more so since the resulting comparatively volatile trihalide is removed from the reaction zone.

There is very scanty information on lower r.e.e. fluorides and bromides. Only the preparation and certain properties of the difluorides and dibromides of Sm, Eu, and Yb have been described[4]. Kirshenbaum and Cahill[15] investigated the reduction of yttrium, lanthanum, cerium, praseodymium, neodymium, and samarium trifluorides with graphite at 1300–2200°, and found that only SmF_3 is reduced, forming the red-brown SmF_2 of m.p. ~1400°. It was also shown that metallic tungsten or molybdenum does not reduce SmF_3 to SmF_2. There are no experimental thermodynamic data on r.e.e. difluorides or dibromides (as with the trifluorides or tribromides). One can only say, in accordance with known relative stabilities of lower and higher halides, that the difluorides should be less stable than the dichlorides, and that the dibromides should be intermediate in stability between the dichlorides and the diiodides.

As regards the latter, the preparation and some of the properties of r.e.e. diiodides, mainly those of Sm, Eu, and Yb, have been studied[4]. Thulium diiodide has only recently been obtained, by reduction of TmI_3 with metallic thulium[10]. This method has also been used to prepare YbI_2.[10] X-Ray crystallography has shown TuI_2 to have the YbI_2 structure.

Druding, Corbett, and their coworkers[9,11,12] have studied the equilibrium diagrams of the La–LaI_3, Ce–CeI_3, Pr–PrI_3, Nd–NdI_3, and Sm–SmI_3 systems, paying particular attention to the purity of the starting materials and absence of reaction with the material of the vessels. The triiodides were prepared from the metals and elemental iodine in a sealed evacuated quartz tube. The metal, in a tungsten crucible, was heated to 800° and the tube with the iodine to 185°. After the reaction the excess of iodine was removed by condensing it. All operations with the iodides and metals were carried out in a dry-box in an atmosphere of argon. Druding and Corbett emphasise[11] that the r.e.e. iodides are extremely sensitive to atmospheric oxygen and moisture. In the case of LaI_3 the product had to be sublimed in vacuum in tantalum apparatus to obtain satisfactory results.

Stable diiodides were obtained in all the systems. In the Nd–NdI_3 and Sm–SmI_3 systems the reduction goes beyond the composition corresponding to the diiodides, and products $NdI_{1.95}$ and $SmI_{1.91}$ were obtained. There was no indication of the existence of neodymium or samarium monoiodide. In the La–LaI_3 and Ce–CeI_3 systems there were observed, in addition to the diiodides, intermediate compounds, melting with decomposition, of the non-stoichiometric composition $LnI_{2.42}$; these were isomorphous with the compound $PrI_3 \cdot PrI_2$, which melts without decomposition, observed in the Pr–PrI_3 system.

The diiodides LaI_2, CeI_2, and PrI_2 are isomorphous, and differ in structure, melting points, colour, and other properties from the "normal" diiodides NdI_2, SmI_2, and YbI_2. While NdI_2 does not pass an electric current, LaI_2, CeI_2, and PrI_2 are good conductors, their electrical conductivity being ~10% of that of the pure metals. The magnetic moment of neodymium in NdI_2 corresponds to the doubly-charged ion Nd^{2+} (Pm^{3+}), while LaI_2 is only weakly paramagnetic.

All these unusual properties led Corbett *et al.*[11] to the conclusion that the diiodides LaI_2, CeI_2, and PrI_2 contain the normal triply-charged r.e.e. ions and free electrons forming a metallic bond, *i. e.* their structure is $Ln^{3+}e^-I_2^{2-}$, as in the previously observed r.e.e. sulphides and carbides. The additional energy of the metallic bond stabilises these diiodides against disproportionation into metal and triiodide.

It is a very interesting fact that, judging from the composition of the melt at the melting point of the diiodide, the stability of the diiodides decreases in the series LaI_2–PrI_2. Thus in the cerium group two tendencies in the stability of the diiodides are observed: the stability of the "normal" salt-like diiodides increases in the series La–Eu in accordance with the rapid increase in this series of the third ionisation potential (I_3) of the r.e.e. and the decrease in the energy of sublimation of the metal (see Table 2); the stability of the metal-like compounds increases in the reverse direction, since the decrease in I_3 in this direction favours the appearance of conductivity electrons in the salt lattice. The decrease in I_3 from europium to lanthanum correctly explains also the increased concentration of electron gas in lanthanum metal as compared with europium, *i. e.* the increase in the energy of sublimation from europium to lanthanum. Thus the heats of formation of these unusual metal-like compounds change within the r.e.e. group symbathically with the heats of sublimation of the metals, which is understandable, since these compounds and the metals both have substantially the same type of chemical bond (metallic).

Certain aspects of the chemistry of the r.e.e. dichlorides will be considered in more detail in Part III.

2. Oxide Chlorides, Oxides, and Chalcogenides of R. E. E. in a Lower State of Oxidation

Ivanovskii and coworkers[16] studied the reaction of oxygen and rare-earth metals with fused chlorides of La, Ce, Pr, and Nd, and in all cases observed the formation of red crystals of lower oxide chlorides, insoluble in water, and of composition close to Ln_2OCl_2.

The existence of the gaseous monoxides LnO was first established spectrographically, and then gaseous LaO was observed in mass-spectrometric investigations[17].

Achard[18–20] studied the action of graphite on the r.e.e. oxides. At 1600° and pressure below 10^{-3} mmHg, Sm, Eu, and Yb vaporise from a mixture of the r.e.e. oxides as the monoxides LnO, and this process can be used to isolate and separate these elements. Achard also showed[21,22] that EuO is formed in a mixture of Eu_2O_3 and graphite above 1300°. With excess of graphite the dark red EuO is produced, with a face-centred cubic lattice. The monoxide EuO melts above 1700° and distils in vacuum without decomposition. It is relatively stable in air and is only slowly decomposed by water. The oxide Eu_2O_3 vaporises rapidly at 2500° and 10^{-4} mmHg, the condensate being red-brown because of the presence of EuO.

Other r.e.e. monoxides have only been obtained under specific conditions of high vacuum and elevated temperatures. Goldstein, White, and their coworkers[23–25] have made a mass-spectrometric study of the vaporisation of La_2O_3 and Nd_2O_3 and the exchange of oxygen between La, Ce, Pr, and Nd and their monoxides; they found that La_2O_3 and Nd_2O_3 vaporise stoichiometrically at the com-

position $Ln_2O_{2,96}$. They detected the ions LnO^+, Ln^+, and O^+ in the vapour, the ions Ln^+ appearing at an energy of the ionising electrons greater than a certain definite value, *i. e.* their appearance is due to decomposition of the LnO molecules by electron bombardment. The composition of the vapour was different in the vaporatisation of Lu_2O_3 and Dy_2O_3; in the former case the vapour contained LuO and Lu, and in the latter case almost exclusively Dy; this is due to the lesser stability of the LuO molecules.

The values of ΔH° and ΔS° at ~2000°K were determined for the reactions:

$$Ln'(gas) + Ln''O(gas) \rightleftarrows Ln''(gas) + Ln'O(gas).$$

The calculation of the standard heats of formation from these data contains large errors because of the absence of thermal capacity data. For the gaseous monoxides of La, Ce, Pr, and Nd the values of ΔH° obtained were the same within the limits of experimental error, and were from -27 to -38 kcal. It is interesting that the energies of dissociation of the gaseous monoxides LaO, CeO, PrO, NdO, SmO, EuO, GdO, TbO, LuO, and YO [25] differ exactly by the difference in the heats of sublimation of the corresponding metals.

Shchukarev and Semenov[26] also investigated the composition of the vapour over the oxides of all the r.e.e. except Tm mass-spectrometrically, and showed that the volatility of their oxides in high vacuum and the composition of their vapour differ considerably for the oxides of different elements. There is a general tendency for the stability of the gaseous LnO molecules to decrease from La to Lu. In no case were ions $Ln_2O_3^+$ or $(LnO)_n^+$ observed in the vapour, but the ions CeO_2^+, PrO_2^+, and TbO_2^+ were detected over the corresponding oxides.

There are no data on the stability of the monoxides (except EuO) in the solid state at room temperature. Using the average value of the standard heat of formation of a gaseous monoxide LnO (-30 kcal mole^{-1} [23,24]) and assuming its heat of sublimation to be close to that of BaO and SrO (~120 kcal mole^{-1} [27]), we obtain a value of ~150 kcal mole^{-1} for the standard heat of formation of the solid monoxides of La, Ce, Pr, and Nd. To a first approximation, the monoxide can be considered to be stable in the solid state if ΔH° for the disproportionation into sesquioxide and metal is positive. If the heat of formation of Ln_2O_3 is taken as 430 kcal mole^{-1},[4] ΔH°_{298} for the reaction

$$3LnO \rightleftarrows Ln_2O_3 + Ln$$

is found to be 20 kcal mole^{-1}. Thus it may well be that some r.e.e. monoxides are also stable in the solid state at room temperature.

Klemm and Senff[28] prepared EuS, EuSe, and EuTe by heating $EuCl_2$ in a current of hydrogen with excess of S, Se, or Te, which was then removed by heating in a current of hydrogen at a higher temperature. Magnetic susceptibility measurements showed EuS, EuSe, and EuTe to be compounds with an ionic bond, containing the ions Eu^{2+}. Bivalent Sm and Yb also form monosulphides, and the sulphides Ln_3S_4 have been shown to contain the ions Ln^{2+} and Ln^{3+}.[29-31] The properties and structures of certain other compounds of the r.e.e. with non-metals of Groups V and VI have been described[32-34].

The monosulphides of the r.e.e. for which the bivalent state is less typical possess interesting electrical properties[35-40]; in particular, in the solid state they have considerable conductivity, close to that of the corresponding metals. Conductivity and magnetic susceptibility data on the solid monosulphides demonstrate that the lattice contains the normal triply-charged r.e.e. ions, and also electrons, which produce a metallic bond; these sulphides are therefore intermediate between ionic compounds and compounds with a metallic bond, and they have the general formula $Ln^{3+}e^-S^{2-}$. Certain r.e.e. acetylides in $Ln^{3+}e^-C_2^{2-}$ possess analogous properties[41-44]. As stated above, the diiodides of lanthanum, cerium, and praseodymium exhibit the same effect.

III. CHLORIDES OF RARE-EARTH ELEMENTS IN A LOWER STATE OF OXIDATION

The chemistry of the lower r.e.e. chlorides has been relatively fully investigated, but the existing quantitative data are very often approximate only.

1. Calorimetry of R. E. E. Dichlorides

Although the dichlorides of Sm, Eu, and Yb have been known for a comparatively long time, only one attempt has been made to determine their heats of formation calorimetrically[45-47]. The heats of solution of these dichlorides in 6 M HCl were determined in a microcalorimeter. It was found that $EuCl_2$ reacts very slowly with the HCl solution in the absence of air, while in the presence of air differing amounts of the Eu^{2+} ions undergo the side reaction:

$$Eu^{2+} + {}^1/_4O_2 + H^+ \rightarrow Eu^{3+} + {}^1/_2H_2O,$$

so that the heat of formation of $EuCl_2$ could not be determined. Atmospheric oxygen does not oxidise Sm^{2+} to Sm^{3+}, since identical results were obtained whether the acid was saturated with hydrogen or with air. With $YbCl_2$ there is only slight oxidation.

The dichlorides were obtained by reduction of the anhydrous trichlorides for 6 h at 650° with hydrogen. With samarium the reduction product contained only 69.4% $SmCl_2$. Since the heats of solution of metallic Sm and Yb are not known, the reduction potentials of Sm^{3+} and Yb^{3+} on a mercury cathode[48,49] were used in calculating the heats of formation of the dichlorides. The standard enthalpy of formation was calculated to be -195.6 kcal mole^{-1} for $SmCl_2$ and -184.5 kcal mole^{-1} for $YbCl_2$.

The enthalpy of formation of neodymium dichloride has been determined by dissolving the metal and the dichloride in 0.2 *N* HCl.[5,50] The $NdCl_2$ was prepared by melting the stoichiometric quantities of the trichloride and metal in molybdenum crucibles in an atmosphere of argon. The enthalpy of formation of $NdCl_2$ obtained, -163.2 kcal mole^{-1}, is in good agreement with the value calculated from the equilibrium diagram and pressure data in the Nd–$NdCl_3$ system[5,7].

2. Dissociation of Samarium, Europium, and Ytterbium Trichlorides

The dissociation of the fused trichlorides of Sm, Eu, and Yb with evolution of chlorine:

$$LnCl_3(liq.) \rightleftarrows LnCl_2(liq.) + {}^1/_2Cl_2(gas),$$

has been employed in the determination of the thermodynamic characteristics of the di- and tri-chlorides[50,51]. The equilibrium chlorine pressure was determined over the temperature range 600–960° with a quartz membrane

zero-manometer[52]. From the equilibrium chlorine pressure, and knowing the weight of chloride taken and the volume of the membrane chamber, the concentrations of the di- and tri-chlorides in the melt were calculated, and hence the corresponding equilibrium constants, from which ΔF°, ΔH°, and ΔS° for the dissociation were obtained.

At the average temperature of ~800° ΔH° for the dissociation is 28.8 kcal for $SmCl_3$, 11.6 kcal for $EuCl_3$, and 24.0 kcal for $YbCl_3$, and ΔS° for all three chlorides is close to 9 entropy units. The calculation of the standard heats of formation of the dichlorides of Sm, Eu, and Yb included the use of the standard enthalpies of formation of $SmCl_3$ (-243 kcal mole^{-1}), $EuCl_3$ (-241 kcal mole^{-1}), and $YbCl_3$ (-223 kcal mole^{-1}) obtained by interpolation of the data for the trichlorides of the other r.e.e.,[53,54] and also the approximate value of ΔC_p for the dissociation, equal to -12 kcal mole^{-1} deg^{-1} in the temperature interval 25–900°. The standard enthalpies of formation obtained[50,51] were -203 kcal mole^{-1} for $SmCl_2$, -217 kcal mole^{-1} for $EuCl_2$, and -186 kcal mole^{-1} for $YbCl_2$. The value for $SmCl_2$ is closer to Brewer's estimate (-203 ± 7 kcal mole^{-1} [14]) than to the calorimetrically determined value of -195.6 kcal × × mole^{-1}. The value obtained for $EuCl_2$ is also close to Brewer's estimate (-210 ± 7 kcal mole^{-1} [14]), but the value obtained for $YbCl_2$ is in good agreement with the value of -184.5 kcal mole^{-1} determined calorimetrically. The dissociation of the trichlorides has also provided a value for the absolute entropy S°_{298} of the trichlorides (34 entropy units), taking S°_{298} for the dichlorides as 32 entropy units. The thermodynamic data obtained can be used in considering certain equilibria in which the di- and tri-chlorides of Sm, Eu, and Yb take part.

The anhydrous r.e.e. trichlorides are normally prepared by chlorination of the corresponding oxides[7,55]. With $SmCl_3$, $EuCl_3$, and $YbCl_3$ there is the danger of their partial dissociation to form the dichlorides as impurities. Calculation shows that in the case of chlorination in a current of chlorine ($P_{Cl_2} \simeq 1$ atm) the fused trichlorides near their melting points will contain the following amounts of dichloride (in mole %): $SmCl_3$ 0.005, $EuCl_3$ 8, and $YbCl_3$ 0.1. Under these conditions $SmCl_3$ and $YbCl_3$ will be obtained sufficiently pure, even if chlorination is carried out in the fused state, while $EuCl_3$, which because of its low melting point is usually obtained in the fused state, must be finely ground and heated in the current of chlorine but not so as to melt it. The solid $EuCl_2$ should then be fully converted into $EuCl_3$, since the chlorine pressure over the solid trichlorides of these elements is considerably lower (where no solid solutions are formed) than over the fused trichlorides, being at 620° 5×10^{-7} mmHg for $SmCl_3$, 5 mmHg for $EuCl_3$ and 2×10^{-5} mmHg for $YbCl_3$. In a vacuum solid $EuCl_3$ should completely dissociate into $EuCl_2$. In the fused state $SmCl_3$ and $YbCl_3$ also dissociate to the dichlorides to a considerable extent in a vacuum.

Reduction of the trichlorides with hydrogen is the usual method for the preparation of $SmCl_2$, $EuCl_2$, and $YbCl_2$. The free energy change ΔF° for the reduction of solid $SmCl_3$, $EuCl_3$, and $YbCl_3$ with hydrogen:

$$LnCl_3 + {}^1/_2H_2 \rightleftarrows LnCl_2 + HCl$$

at 620° is respectively -5, -20, and -9 kcal. Taking into account the formation of the intermediate compound $LnCl_3 \cdot nLnCl_2$ in the $LnCl_2$–$LnCl_3$ systems[7,50], it is doubtful whether solid $SmCl_3$ can be completely reduced. Reduction in the melt should theoretically go to completion, but in the case of $SmCl_3$ the rate of the reaction is apparently too low. In most cases reduction of the trichlorides of the other r.e.e. can be ignored. Calculation using the approximate heats of formation of the dichlorides shows[5] that marked reduction can only be expected in the case of the chlorides of Nd, Pm, Er, Tm, and Sc.

3. Equilibrium Diagrams of Rare-Earth Metal–Trichloride Systems

The dichlorides of the other r.e.e. are less stable than those of Sm, Eu, and Yb, and can be obtained by reduction of the trichlorides with the corresponding rare-earth metal. Study of the equilibrium diagrams of Ln–$LnCl_3$ systems can not only demonstrate the existence of the dichlorides, but can also give certain information on the interaction between the tri- and di-chlorides in the solid state and in the melt, and when the dichloride melts incongruently its approximate heat of formation can be calculated. The study of these systems is complicated by the high reactivity of the dichlorides and the metals. The melt is usually held in molybdenum or tantalum apparatus in an atmosphere of carefully purified argon or helium; other metals or ceramics are unsuitable for use in these investigations. The attention which must be directed towards the experimental technique can be judged from the measurements of conductivity in the Ce–$CeCl_3$ system[56–58], where reaction of the melt with the material of the container completely distorted the results.

At present, equilibrium diagrams have been obtained for the systems La–$LaCl_3$,[59] Ce–$CeCl_3$,[60] Pr–$PrCl_3$,[7,50,61,86], Nd–$NdCl_3$,[7–9,50] Sm–$SmCl_3$, Y–YCl_3, and Sc–$ScCl_3$.[6,50]

There is no evidence of the formation of any chemical compound of lower oxidation state in the La–$LaCl_3$, Ce–$CeCl_3$, or Y–YCl_3 systems. The solubility of the metal at the eutectic point is respectively 9 (826°), 9.3 (777°), and 2 mole % (716°).

In the Pr–$PrCl_3$ system an unstable intermediate compound is formed, apparently of composition $PrCl_3 \cdot PrCl_2$, and existing in the solid state in the narrow temperature interval 665–640°. Below 640° it decomposes into solid $PrCl_3$ and metal. X-Ray diffraction could detect no compounds of lower oxidation state in this system at room temperature[8]. There is a report[62] that an unstable intermediate compound has been observed in this system.

In the Nd–$NdCl_3$ system[8,9], $NdCl_2$ melting with decomposition has been observed, and also two intermediate compounds of composition $NdCl_{2.27}$ and $NdCl_{2.37}$. It has been shown by X-ray diffraction that $NdCl_2$ is isomorphous with $SmCl_2$ and $EuCl_2$. This system has also been investigated by Polyachenok[7,50], who confirmed the formation of the stable dichloride $NdCl_2$. The stoichiometric compositions $NdCl_3 \cdot 2NdCl_2$ and $NdCl_3 \cdot 3NdCl_2$ were found for the intermediate compounds.

The dichloride $SmCl_2$ melting at 859° is formed in the Sm–$SmCl_3$ system[6,50], and also the intermediate compound $SmCl_3 \cdot 4SmCl_2$. The $SmCl_2$ obtained by fusing $SmCl_3$ with metallic Sm differs in appearance and melting point from the $SmCl_2$ obtained by hydrogen reduction of $SmCl_3$, and is very like $NdCl_2$.

Just as in the Nd–$NdCl_3$ system, a phase transformation has been observed in the Sm–$SmCl_3$ system in the region of compositions Sm–$SmCl_2$, lying below the melting point of the dichloride. No satisfactory explanation of this effect

has yet been given, but at any rate it demonstrates the complex nature of $NdCl_2$ and $SmCl_2$. These are apparently transitional between the normal dichlorides $EuCl_2$ and $YbCl_2$ and the metal-like compounds observed with the iodides[11]. The possibility of these transformations being associated with further reaction between the dichlorides and the metals is also not excluded. From this point of view the study of the Eu–$EuCl_2$ and Yb–$YbCl_2$ systems formed by the salt-like dichlorides of europium and ytterbium is of interest.

The dichloride $ScCl_2$, melting with decomposition, has been observed in the Sc–$ScCl_3$ system[6,50], and also an intermediate compound of composition $2ScCl_3.ScCl_2$. Barber and coworkers[63] had previously calculated the heat of formation of $ScCl_2$ by the Born–Haber cycle, and concluded that $ScCl_2$ should not be very stable. The heat of formation of $ScCl_2$ calculated from the equilibrium diagram data is 145 kcal $mole^{-1}$.[6,50,51]

4. Saturated Vapour Pressure in Rare-Earth Metal–Trichloride Systems

Another method of investigation of the lower r.e.e. chlorides is the measurement of the saturated vapour pressure over the fused trichlorides containing the dissolved metal. Information on the solubility of the rare-earth metals in the melt at elevated temperature is obtained at the same time. Novikov and Polyachenok[64,65] developed a variation of the "boiling point" method suitable for this purpose, and measured the pressure of the saturated vapour in the Sc–$ScCl_3$, Y–YCl_3, La–$LaCl_3$, Pr–$PrCl_3$, Nd–$NdCl_3$, and Er–$ErCl_3$ systems in the temperature range 1000–1400°.[6,7,50,51,66] The quartz ampoules employed were coated inside with a dense layer of metallic molybdenum by reduction of $MoCl_5$ vapour with hydrogen[67]. These ampoules enable a point to be obtained on the equilibrium diagram with a sample of only 0.2–0.5 g, with measurement of the saturated vapour pressure at any desired temperature up to 1400°.

The saturated vapour pressure *vs.* composition isotherms obtained with the systems named can be divided into three types.

In the La–$LaCl_3$ and Y–YCl_3 systems the experimental points, right up to the region of stratification, lie on a straight line intersecting the composition axis at the point corresponding to the metal. This corresponds to atomic dissolution of the metal, or dissolution by the Bredig mechanism[62]:

$$Ln(solid) \rightleftarrows Ln^{3+}(liq.) + 3e^-.$$

The Nd–$NdCl_3$ and Er–$ErCl_3$ systems exhibit only slight positive or negative deviations from the line intersecting the composition axis at the composition corresponding to the dichloride, *i. e.* the doubly-charged ions Nd^{2+} and Er^{2+} are formed in the melt.

The Pr–$PrCl_3$ and Sc–$ScCl_3$ systems are intermediate in type. On the basis of the information available, it is difficult to say whether this is due to the simultaneous presence of doubly-charged ions and free electrons (Bredig mechanism) in the melt or to dimerisation of the doubly-charged ions, and, apparently, Bredig's data[62] on the conductivity of the melts in the La–$LaCl_3$, Pr–$PrCl_3$, and Nd–$NdCl_3$ systems cannot distinguish between the two mechanisms.

In all cases only the corresponding trichlorides were observed visually in the distillate, the dichlorides $PrCl_2$, $NdCl_2$, $ErCl_2$, and $ScCl_2$ being unstable in the vapour at the temperatures indicated, and disproportionating exothermically into the corresponding gaseous trichloride and molten metal. The heats of vaporisation of the trichlorides from melts not saturated with respect to the metal are close to the heats of vaporisation of the pure trichlorides[50,68]. Assuming that with Sc, Pr, Nd, and Er all the metal is present in the melt as the dichloride, the equilibrium constant of the disproportionation reaction

$$3LnCl_2(liq.) \rightleftarrows 2LnCl_3(liq.) + Ln(liq.)$$

can be calculated and ΔS° for the reaction evaluated, and the heat of formation of the dichloride can be determined. Calculations using the average thermal capacities of the components have given values close to those obtained from the equilibrium diagrams.

In the Pr–$PrCl_3$ and Nd–$NdCl_3$ systems it was possible to construct saturated vapour pressure *vs.* melt composition isotherms for several temperatures, so that ΔF°, ΔH°, and ΔS° for the disproportionation at the mean experimental temperature of 1250° could be calculated. For the above disproportionation of the dichlorides, ΔH° is 24 ± ± 10 kcal for $PrCl_2$ and 38 ± 10 kcal for $NdCl_2$, with ΔS° = = 15 entropy units for both dichlorides.

The conversion to standard conditions of the thermodynamic data obtained at high temperatures introduces considerable errors, because of the almost complete absence of experimental data on the thermal capacities of the reaction components; however, the heat of formation of $NdCl_2$ determined calorimetrically is in good agreement with the value calculated by the method indicated above from equilibrium diagram and vapour pressure data[5,50].

5. Saturated Vapour Pressure of Samarium, Europium, and Ytterbium Dichlorides

We have measured[50,51] the saturated vapour pressure of the pure dichlorides $SmCl_2$, $EuCl_2$, and $YbCl_2$ over the temperature range 1200–1400°; $SmCl_2$ was obtained by fusing stoichiometric amounts of $SmCl_3$ and metallic Sm, and $EuCl_2$ and $YbCl_2$, by reducing the trichlorides with metallic zinc.

The r.e.e. dichlorides have very low volatility, the saturated vapour pressures at the maximal experimental temperature of 1400° being ~10 mmHg for $SmCl_2$, ~3 mmHg for $EuCl_2$, and ~5 mmHg for $YbCl_2$. Only with $SmCl_2$, therefore, could the heat of vaporisation be found with satisfactory accuracy (60 kcal $mole^{-1}$ at the mean temperature of 1300°), while with $EuCl_2$ and $YbCl_2$ the heats of vaporisation were calculated from the experimental results on the saturated vapour pressure by assuming ΔS for the vaporisation of these dichlorides to be the same (at the corresponding vapour pressure) as that for $SmCl_2$.

The boiling points of $SmCl_2$, $EuCl_2$, and $YbCl_2$ are 1950°, 2100°, and 2050°. The change in volatility in the series $SmCl_2$–$EuCl_2$–$YbCl_2$ does not follow the increase in atomic number of the metal, as is found with the r.e.e. trichlorides, but obeys the rule that the less stable the dichloride, the greater its volatility. This suggests that it is not the dichlorides themselves which vaporise, but their disproportionation products: the metals and trichlorides, which recombine to form the dichlorides in the

cooler parts of the apparatus (only the dichlorides are observed visually in the distillate). However, approximate thermodynamic calculations do not confirm this suggestion, particularly in the case of $EuCl_2$ and $YbCl_2$.

It may also be thought that this volatility relationship is a consequence of the nature of the dichlorides themselves, and in fact if the boiling points of the fluorides of elements of Group II of the Periodic System are compared[69] with the ionic radii of the corresponding doubly-charged cations, it is seen that the boiling points for the alkaline earth metal difluorides lie on a smooth line with a maximum at an ionic radius of 1.1–1.2 Å; the alkaline earth metal dichlorides also show a maximum boiling point at this ionic radius[69]. From this aspect the appearance of a maximum boiling point in the r.e.e. dichlorides around $EuCl_2$ (the ionic radius of Eu^{2+} is 1.24 Å) falls in with the general properties of the dihalides.

6. Electrical Conductivity and Density in Rare-Earth Metal–Trichloride Systems

Investigation of the electrical properties of melts containing dissolved metals is a common and convenient method for studying the nature of the melts and thermodynamic characteristics of lower halides if they are formed when the metals dissolve[70,71].

In their investigation of e.m.f., density, and conductivity in the Ce–$CeCl_3$ system, Mellors and Senderoff[56,72] concluded that the metal dissolves in the $CeCl_3$ to form Ce^+ ions, but this was later shown to be incorrect[57], because the melt was in contact with Al_2O_3. Bredig and coworkers[58,62] repeated the conductivity measurements in this system, and investigated the La–$LaCl_3$, Pr–$PrCl_3$, and Nd–$NdCl_3$ systems similarly. The conductivity of the melt, in the case of lanthanum and cerium, increases sharply when the metal is added, which can only be explained by the formation of free electrons in the melt, by ionisation of the atoms of dissolved metal:

$$\mathrm{Ln(solid)} \rightleftarrows \mathrm{Ln^{3+}} + 3e^- \text{ or } \mathrm{Ln(solid)} \rightleftarrows \mathrm{Ln^{2+}} + 2e^-.$$

In the Nd–$NdCl_3$ system the conductivity increases only very slightly as the concentration of metal is increased, *i. e.* there is practically no dissociation of Nd^{2+} ions into Nd^{3+} and e^-. The Pr–$PrCl_3$ system occupies an intermediate position, but is much closer to the Nd–$NdCl_3$ system. It has been suggested[62] that this demonstrates the existence of Pr^{2+} ions in the melt, of similar stability to the Nd^{2+} ions.

TABLE 1. Some characteristics of r.e.e. di- and tri-chlorides.

Element	$-\Delta H^\circ_{298}$ (kcal mole^{-1}) for the formation of dichloride	$-\Delta H^\circ_{298}$ (kcal mole^{-1}) for the formation of trichloride	Melting point of the dichlorides, °C
Sc	145 [50,51]	221 [76]	805(decomp.)[5,60]
Pr	163 [50,51]	252 [54]	—
Nd	163.2 [5,50]	246.5 [5,50]	835(decomp.)[7,60]
Sm	203 [50,51] / 195.6 [45]	243 *	859
Eu	217 [50,51]	241 *	738 [50]
Er	150 [50]	229 [54]	—
Yb	186 [50,51] / 184.5 [45]	223 *	723 [4]

* Extrapolation of Spedding's data[54].

Attempts have also been made[73–75] to provide a theoretical foundation for the effects observed on the dissolution of the metals in the fused halides.

Table 1 collects together the available standard enthalpies of formation of the solid r.e.e. dichlorides and the corresponding trichlorides; in most cases the values for the dichlorides have been calculated from those for the trichlorides. The melting points of the dichlorides given in Table 1 demonstrate that like the diiodides[11] they fall into two groups which have different physical and chemical properties: the comparatively unstable $ScCl_2$, $NdCl_2$, and $SmCl_2$, which have relatively high melting points and are black lustrous crystalline substances, and the more stable $EuCl_2$ and $YbCl_2$, which melt at a comparatively low temperature.

IV. POSSIBILITY OF EXISTENCE OF RARE-EARTH ELEMENT DIHALIDES

The experimental chemistry of lower r.e.e. halides which has been reviewed shows that work in this field is really only just beginning, and that there are no experimental data for the halides of many of the r.e.e., especially the fluorides and bromides. All the elements of the cerium group form diiodides. Judging by the ionisation potentials and energies of sublimation of the metals, the relationships observed in the cerium group should also apply to the elements of the yttrium group, so that diiodides would be expected to be formed by all the elements of the yttrium group and yttrium and scandium. Of these, ScI_2 and ErI_2, together with the known TmI_2 and YbI_2, will apparently be "normal" diiodides, while the others will possibly be metal-like compounds. The metal-like compounds of the yttrium group should be less stable than those of the cerium group, since I_3 for the yttrium group elements is somewhat higher.

With the r.e.e. dibromides also, typical salt-like and metal-like compounds should apparently be found.

Metal-like r.e.e. dichlorides have not been and can hardly be expected to be found in so clearly expressed a form as in the diiodides ($NdCl_2$, $SmCl_2$, and $ScCl_2$ retain only some indications of this type of compounds, *e.g.*, colour), probably because the chlorine atom has a greater affinity for the electron than the iodine atom. In actual fact, in the fused state the differences largely disappear[11], and solutions of La and Ce in the fused trichlorides are true ionic-electronic liquids[77].

It is improbable that metal-like compounds will be found among r. e.e. fluorides.

Since for r.e.e. dichlorides and difluorides the component of the energy of formation associated with the presence of the additional metallic bond in the crystal can apparently be ignored, the heats of formation of the salt-like (ionic) dihalides can be calculated[5] from the Born–Haber cycle, using Kapustinskii's equation for calculating the energy of the crystal lattice†:

$$Q = U + 2E - \sigma - D - \Sigma I_1 + I_3,$$

where U is the crystal lattice energy, E is the electron

† The errors arising in such an approximate calculation, which may be particularly large in the case of the fluorides, are to a large extent systematic in nature when the variation in stability throughout the rare-earth group is being considered.

affinity of the halogen atom, σ is the heat of sublimation of the metal, D is the dissociation energy of the halogen molecule, and $\Sigma I_1 + I_2$ is the sum of the first and second ionisation potentials of the r.e.e. atoms.

As early as 1950 Brewer[14] tried to assess the possibility of obtaining certain r.e.e. dichlorides, and suggested that in addition to $SmCl_2$, $EuCl_2$, and $YbCl_2$, the stable $NdCl_2$ and $TmCl_2$ and the unstable $PrCl_2$. $HoCl_2$, and $ErCl_2$ would be obtained. He also suggested that the r.e.e. monohalides are unstable. Our calculations have confirmed that all the r.e.e. monohalides must disproportionate strongly exothermically into the trihalide and the metal[5].

The best agreement of the calculated crystal lattice energies with existing experimental data was obtained for the trichlorides with the normal, and in the case of the dichlorides, with the improved Kapustinskii equation[78]. In calculations with the fluorides the improved Kapustinskii equation was also only used for the difluorides.

Since the radii of the doubly-charged r.e.e. ions are only known for samarium, europium, and ytterbium, in calculating the crystal lattice energy we have used the approximate radii obtained by analogy with the ion pairs $Sm^{2+}-Sm^{3+}$, $Eu^{2+}-Eu^{3+}$, and $Yb^{2+}-Yb^{3+}$.

The quantity $2E-D$ was taken as 118 kcal for the dichlorides and 130 kcal for the difluorides[79]. The heats of sublimation of the metals have been determined by Spedding and White and their coworkers[80-82].

Data obtained for the first ionisation potentials[83-85] indicate values of 5.6 ± 0.1 eV for cerium group elements and 6.2 ± 0.2 eV for yttrium group elements. The existing data on the second ionisation potentials of the cerium group elements[83] and those calculated by the Born–Haber cycle from thermodynamic data enable $\Sigma I_1 + I_2$ to be taken as constant for all the cerium group elements, and equal to 16.9 ± 0.3 eV. For the yttrium group elements $\Sigma I_1 + I_2$ was also taken to be constant at 18.9 eV.

Table 2 gives the approximate heats of formation of the dichlorides and difluorides that we have calculated by the above method, and also the corresponding heats of formation of the trichlorides found experimentally[53,54] or by interpolation of experimental data.

The heats of formation of the trifluorides were calculated from the thermochemical cycle, using the values of the sum of the three ionisation potentials of the r.e.e. $\Sigma I_1 + I_2 + I_3$ obtained, using the same cycle, from the heats of formation of the corresponding trichlorides.

The heats of formation of only the difluorides and dichlorides are as yet insufficient to assess their stability. For this it is necessary to consider the disproportionation of the dihalides into metal and the stable trihalide, *i.e.* the reaction:

$$3LnX_2(\text{solid}) \rightleftarrows 2LnX_3(\text{solid}) + Ln(\text{solid}).$$

The heats of disproportionation of the difluorides and dichlorides are also given in Table 2.

Certain qualitative conclusions can be drawn from Table 2 regarding the stability of the r.e.e. dichlorides and difluorides:

(1) In addition to the known $NdCl_2$, $SmCl_2$, $EuCl_2$, $YbCl_2$, and $ScCl_2$, the stable $PmCl_2$ and $TmCl_2$ may also be obtained.

(2) Of the less stable dichlorides, $HoCl_2$ and $ErCl_2$ may apparently be obtained in the solid state, in addition to the known $PrCl_2$.

(3) The dichlorides $LaCl_2$, $CeCl_2$, $GdCl_2$, $TbCl_2$, and YCl_2 are not expected to be formed in the solid state. These compounds, or more accurately the ions La^{2+}, Ce^{2+}, Gd^{2+}, Tb^{2+}, and Y^{2+}, apparently do not exist in the melt.

(4) Of the difluorides, apparently only SmF_2, EuF_2, and YbF_2 are stable at room temperature. There may be indications, however, that at high temperatures compounds intermediate between LnF_2 and LnF_3 may be produced in the case of scandium, thulium, and promethium. The formation of other r.e.e. difluorides must be considered improbable.

TABLE 2. Calculation of the stability of r.e.e. dihalides.

Element	σ, kcal per g-atom	Ionic radius, Å		Ionisation potentials			$-\Delta H^\circ_{298}$ (kcal mole^{-1}) for					
		r^{3+}	r^{2+}	$\Sigma I_1 + I_2$	$\Sigma I_1 + I_2 + I_3$	I_3	formation of dichloride	formation of trichloride	disproportionation of dichloride	formation of difluoride	formation of trifluoride	disproportionation of difluoride
La	97	1.22	1.38	390	832	443	128	256	128	213	435	231
Ce	96	1.18	1.36	390	848	459	131	253	113	217	435	219
Pr	78	1.16	1.31	390	873	482	156	252	36	244	436	140
Nd	76	1.15	1.29	390	884	494	161	246	9	250	431	112
Pm	62	1.14	1.27	390	901	510	178	246	— 42	268	432	60
Sm	50	1.13	1.26	390	919	528	192	243	—102	282	431	16
Eu	42	1.13	1.24	390	929	540	200	241	—118	294	429	—24
Gd	84	1.11	1.22	436	894	459	117	240	129	209	430	233
Tb	87	1.09	1.19	436	901	466	118	236	118	212	428	220
Dy	62	1.07	1.16	436	945	510	148	233	22	243	418	107
Ho	70	1.05	1.13	436	936	501	145	231	27	241	427	131
Er	66	1.04	1.12	436	945	510	150	229	8	247	426	111
Tm	58	1.04	1.11	436	956	519	159	226	— 25	257	423	75
Yb	40	1.00	1.06	436	990	554	185	223	—109	286	425	—8
Lu	95	0.99	1.04	436	940	503	133	221	43	235	425	145
Y	97	1.06	1.12	436	903	466	119	233	109	216	429	210
Sc	79	0.83	0.9—1.0	447	1012	565	151[63]	221	— 11	272	445	74

1. W.Klemm, Z.anorg.Chem., 184, 345 (1929).
2. W.Klemm, Z.anorg.Chem., 187, 29 (1930).
3. G.Jantsch and W.Klemm, Z.anorg.Chem., 216, 80 (1933).
4. V.V.Serebrennikov, "Khimiya Redkozemel'nykh Elementov", (Chemistry of the Rare-Earth Elements), Vol.I, Izd.Tomsk Univ., Tomsk, 1959.
5. O.G.Polyachenok and G.I.Novikov, Zhur.Neorg.Khim., 8, 1567 (1963) [Russ.J.Inorg.Chem., 816 (1963)].
6. O.G.Polyachenok and G.I.Novikov, Zhur.Obshch.Khim., 33, 2797 (1963).
7. G.I.Novikov and O.G.Polyachenok, Zhur.Neorg.Khim., 8, 1053 (1963) [Russ.J.Inorg.Chem., 545 (1963)].
8. L.F.Druding and J.D.Corbett, J.Amer.Chem.Soc., 81, 5512 (1959).
9. L.F.Druding and J.D.Corbett, J.Amer.Chem.Soc., 83, 2462 (1961).
10. L.B.Asprey and F.H.Kruse, J.Inorg.Nuclear Chem., 13, 32 (1960).
11. J.D.Corbett, L.F.Druding, W.J.Burkhard, and C.B.Lindahl, Discuss.Faraday Soc., 79 (1961).
12. J.D.Corbett, L.F.Druding, and C.B.Lindahl, J.Inorg. Nuclear Chem., 17, 176 (1961).
13. A.N.Zelikman, "Metallurgiya Redkozemel'nykh Metallov, Toriya i Urana" (Metallurgy of the Rare-Earth Metals, Thorium, and Uranium), Metallurgizdat, Moscow, 1961.
14. L.L.Quill (Editor), "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics", McGraw-Hill, New York, 1950.

15. A.D.Kirshenbaum and J.A.Cahill, J.Inorg.Nuclear Chem., 14, 148 (1960).
16. L.E.Ivanovskii, N.G.Illyushchenko, V.L.Zyazev, and A.F.Plekhanov, Trudy Inst.Elektrokhim.Akad.Nauk Ukrain. SSR, 55 (1960).
17. W.A.Chupka, M.G.Inghram, and R.F.Porter, J.Chem. Phys., 24, 792 (1956).
18. J.-C.Achard, Compt.rend., 245, 1064 (1957).
19. J.-C.Achard, Compt rend., 244, 3059 (1957).
20. "Methods for the Separation of the Rare-Earth Metals" (Translated into Russian), Inostr.Lit., Moscow, 1961.
21. J.-C.Achard, Compt.rend., 250, 3025 (1960).
22. J.-C.Achard, Bull.Soc.chim.France, 31 (1961).
23. H.W.Goldstein and D.White, J.Phys.Chem., 65, 1400 (1961).
24. P.N.Walsh, D.F.Dever, and D.White, J.Phys.Chem., 65, 1410 (1961).
25. D.White, P.N.Walsh, L.L.Ames, and H.W.Goldstein, in "Thermodynamics of Nuclear Materials", International Atomic Energy Agency, Vienna, 1962, p.417.
26. S.A.Shchukarev and G.A.Semenov, Dokl.Akad.Nauk SSSR, 141, 652 (1961).
27. V.A.Medvedev, Zhur.Fiz.Khim., 35, 1481 (1961) [Russ.J. Fiz.Chem., 729 (1961)].
28. W.Klemm and H.Senff, Z.anorg.Chem., 241, 259 (1939).
29. L.Domange, J.Flahaut, and M.Guittard, Compt.rend., 249, 697 (1959).
30. J.Flahaut, L.Domange, M.Guittard, and J.Loriers, Bull. Soc.chim.France, 102 (1961).
31. M.D.Houston, Ceram.Age, 77, 50 (1961).
32. L.H.Brixner, J.Inorg.Nuclear Chem., 15, 199 (1960).
33. A.Iandelli, Atti Accad.naz.Lincei, Rend.Classe Sci.fis.mat. nat., 30, 201 (1961).
34. G.L.Olcese, Atti Accad.naz.Lincei, Rend.Classe Sci.fis. mat.nat., 30, 195 (1961).
35. M.Picon, L.Domange, and J.Flahaut, Bull.Soc.chim. France, 221 (1960).
36. E.D.Eastman, L.Brewer, L.A.Bromley, P.W.Gilles, and N.L.Lofgren, J.Amer.Chem.Soc., 72, 2248 (1950).
37. E.D.Eastman, L.Brewer, L.A.Bromley, P.W.Gilles, and N.L.Lofgren, J.Amer.Chem.Soc., 72, 4019 (1950).
38. J.Flahaut, Bull.Soc.chim.France, 1282 (1960).
39. G.V.Samsonov, N.M.Popova, and L.I.Tikhomirova, Zhur. Prikl.Khim., 31, 153 (1958).
40. S.V.Radzikovskaya and G.V.Samsonov, Zhur.Prikl.Khim., 34, 671 (1961).
41. F.H.Spedding, K.Gschneider, and A.H.Daane, J.Amer. Chem.Soc., 80, 4499 (1958).
42. M.Atoji, K.Gschneider, A.H.Daane, R.E.Rundle, and F.H.Spedding, J.Amer.Chem.Soc., 80, 1804 (1958).
43. F.H.Spedding, K.Gschneider, and A.H.Daane, Trans.AIME, 215, 192 (1959).
44. R.C.Vickery, R.Sedlacek, and A.Ruben, J.Chem.Soc., 498, 503 (1959).
45. G.R.Machlan, C.T.Sutbblefield, and L.Eyring, J.Amer. Chem.Soc., 77, 2975 (1955).
46. C.T.Stubblefield and L.Eyring, J.Amer.Chem.Soc., 77, 3004 (1955).
47. C.T.Stubblefield, Diss.Abs., 15, 1180 (1955).
48. H.A.Laitinen, J.Amer.Chem.Soc., 64, 1133 (1942).
49. A.Timnick and G.Glockler, J.Amer.Chem.Soc., 70, 1347 (1948).
50. O.G.Polyachenok, Abstract of Candidate's Thesis, Leningrad. Gos.Univ., Leningrad, 1963.
51. O.G.Polyachenok and G.I.Novikov, Vestnik Leningrad.Gos. Univ., (16), 134 (1963).
52. G.I.Novikov and A.G.Suvorov, Zavod.Lab., 25, 750 (1959).
53. F.H.Spedding and C.F.Miller, J.Amer.Chem.Soc., 74, 4195 (1952).
54. F.H.Spedding and J.P.Flynn, J.Amer.Chem.Soc., 76, 1474 (1954).
55. M.D.Taylor, Chem.Rev., 62, 503 (1962).
56. G.W.Mellors and S.Senderoff, J.Phys.Chem., 64, 294 (1960).
57. H.R.Bronstein, A.S.Dworkin, and M.A.Bredig, J.Phys. Chem., 64, 1344 (1960).
58. H.R.Bronstein, A.S.Dworkin, and M.A.Bredig, J.Phys. Chem., 66, 44 (1962).
59. F.J.Keneshea and D.Cubbicciotti, J.Chem.Eng.Data, 6, 507 (1961).
60. G.W.Mellors and S.Senderoff, J.Phys.Chem., 63, 1110 (1959).
61. G.I.Novikov and O.G.Polyachenok, Zhur.Neorg.Khim., 7, 1209 (1962) [Russ.J.Inorg.Chem., 622 (1962)].
62. A.S.Dworkin, H.R.Bronstein, and M.A.Bredig, J.Phys. Chem., 66, 1201 (1962).
63. M.Barber, J.W.Linnett, and N.H.Taylor, J.Chem.Soc., 3323 (1961).
64. G.I.Novikov and O.G.Polyachenok, Zhur.Neorg.Khim., 6, 1951 (1961) [Russ.J.Inorg.Chem., 996 (1961)].
65. O.G.Polyachenok and G.I.Novikov, Zhur.Neorg.Khim., 8, 2631 (1963) [Russ.J.Inorg.Chem., 1378 (1963)].
66. O.G.Polyachenok and G.I.Novikov, Zhur.Neorg.Khim., 8, 2818 (1963) [Russ.J.Inorg.Chem., 1478 (1963)].
67. O.G.Polyachenok and G.I.Novikov, Zhur.Neorg.Khim., 8, 1785 (1963) [Russ.J.Inorg.Chem., 927 (1963)].
68. O.G.Polyachenok and G.I.Novikov, Zhur.Neorg.Khim., 8, 1526 (1963) [Russ.J.Inorg.Chem., 793 (1963)].
69. G.I.Novikov and F.G.Gavryuchenkov, Zhur.Neorg.Khim., 9, 475 (1964) [Russ.J.Inorg.Chem., 260 (1964)].
70. Yu.K.Delimarskii and B.F.Markov, "Elektrokhimiya Rasplavlennykh Solei" (Electrochemistry of Fused Salts), Metallurgizdat, Moscow, 1960.
71. E.A.Ukshe and N.G.Bukun, Uspekhi Khim., 30, 243 (1961) [Russ.Chem.Rev., 90 (1961)].
72. S.Senderoff and G.W.Mellors, J.Electrochem.Soc., 105, 224 (1958).
73. A.S.Dworkin, H.R.Bronstein, and M.A.Bredig, Discuss. Faraday Soc., 188 (1961).
74. S.A.Rice, Discuss.Faraday Soc., 181 (1961).
75. K.S.Pitzer, J.Amer.Chem.Soc., 84, 2025 (1962).
76. H.Bommer and E.Hohmann, Z.anorg.Chem., 248, 373 (1941).
77. Ya.I.Ol'shanskii, Dokl.Akad.Nauk SSSR, 61, 701 (1950).
78. K.B.Yatsimirskii, Zhur.Neorg.Khim., 6, 518 (1961) [Russ. J.Inorg.Chem., 265 (1961)].
79. "Kratkii Spravochnik Fiziko-Khimicheskikh Velichin" (Short Handbook of Physicochemical Quantities), 3rd Edn., GKhI, Leningrad, 1959.
80. W.R.Savage, D.E.Hudson, and F.H.Spedding, J.Chem. Phys., 30, 221 (1959).
81. O.C.Trulson, D.E.Hudson, and F.H.Spedding, J.Chem. Phys., 35, 1018 (1961).
82. D.White, P.N.Walsh, H.W.Goldstein, and D.F.Dever, J.Phys.Chem., 65, 1404 (1961).
83. A.N.Zaidel', V.K.Prokof'ev, and S.M.Raiskin, "Tablitsy Spektral'nykh Linii" (Tables of Spectral Lines), Gostekhizdat, Moscow, 1952.
84. N.I.Ionov and M.A.Mittsev, Zhur.Eksper.Teor.Fiz., 38, 1350 (1960).
85. N.I.Ionov and M.A.Mittsev, Zhur.Eksper.Teor.Fiz., 40, 741 (1961).
86. L.F.Druding and J.D.Corbett, Inorg.Chem., 2, 869 (1963).

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