CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

Rare Earth Metal–Metal Halide Systems. X. Phase Studies of the Yttrium and Erbium Chlorides and Iodides. A Correlation of the Reduction Characteristics of the Rare Earth Elements[1]

BY JOHN D. CORBETT, DANIEL L. POLLARD, AND JACK E. MEE

Received November 29, 1965

Yttrium and erbium react with their respective molten chlorides and iodides without the formation of intermediate phases. The eutectic temperatures and compositions (mole % M) are: YCl_3, 715–716°, 2.3%; YI_3, 948°, 11.8%; $ErCl_3$, 746°, 4.8%; ErI_3, 933°, 11.0%. The cryoscopic analysis of the $ErCl_3$ solution data and the apparently large $\Delta S°_{fus}$ for other halides with the BiI_3-type structure are discussed. The magnitudes of the reaction of the scandium family and lanthanide metals with their respective molten trichlorides exhibit considerable irregularity (1) in the heavy lanthanides, where Yb > Dy (~Tm?) > Ho > Er > Gd, and (2) in the scandium group, Sc > La > Y. The extent of the presumed reduction of $MCl_3(l)$ to $MCl_2(l)$ at 800° for lanthanum through ytterbium is found to correlate very well with $\Delta F°_{subl} + I_1 + I_2$ for the metal. Changes in the sublimation energies appear primarily responsible for the observed trends, with only relatively small effects arising from minor changes in the first two ionization steps and, evidently, in other terms in the complete Born–Haber cycle as well. Predictions of limiting compositions in unknown MCl_3–M systems are made on this basis for Tb (7 mole %), Lu ($\leq 1\%$), and Tm (32%). No clear explanation is evident for the small reduction of yttrium(III) relative to that of lanthanum and scandium. The nature of the lanthanide elements themselves which appears so important in the relative stabilities of the dichlorides as well as other treatments and predictions of stability is also considered.

Introduction

The reduction characteristics of the molten chlorides for the elements lanthanum through gadolinium exhibit a relatively simple trend. The product is evidently solely the dipositive salt and this rather regularly increases in stability with increasing atomic number from lanthanum through europium. At this point the reduced state shows a sharp decrease in stability, as deduced from the small interaction of gadolinium with its molten trichloride (though the formation of the solid $GdCl_{1.6}$ at lower temperatures presents an unusual and not understood digression). The iodides of the same elements present a somewhat different relationship, the solid products dividing between apparently metallic (La, Ce, Pr, Gd) and saltlike (Nd, Sm, Eu) diiodides.[2]

The reduction characteristics of the second half of the series, Tb to Lu, were largely unknown at the time of this research save for the well-known halides of ytterbium(II)[3] and, more recently, thulium(II) iodide.[4] A first guess on the behavior of the intervening elements might be that the chlorides would show a regular trend similar to that in the lighter half, with the stabilities of the presumed divalent states increasing relatively smoothly from terbium through ytterbium but perhaps at a somewhat lower level as ytterbium(II) is known to be somewhat less stable than europium(II).[3] For this reason the chloride and iodide systems have been investigated for erbium, the element immediately preceding thulium. Also the amount of reaction of scandium and lanthanum with their respective molten chlorides decreases in this order (18.5 to 9 mole % at 800°),[5,6] while the stoichiometric reaction of lanthanum with LaI_3 yields the metallic LaI_2 (Sc–ScI_3 is unknown). It therefore was desirable to establish the presumed intermediacy of the same ytterium systems as a measure of the generally stated trend of decreasing stability of lower oxidation states downward in transition families. In fact, an unexpected result, an unusually small amount of reduction, was found in both cases. The erbium results together with recent and equally surprising data for reduction of the dysprosium[7] and holmium[8] chlorides produce an extremely irregular trend in the heavy elements. However, the unusual reduction characteristics of the heavy as well as the regularity of the light rare earth metal series are both found to correlate semiquantitatively with fundamental properties of the elements.

Experimental Section

Materials.—The metals were again obtained through the courtesy of Professors F. H. Spedding and A. H. Daane of this laboratory. The yttrium chunks analyzed (ppm): O, 300; C, 130; N + F, 200; Fe, 350 ± 100; Cu, 250; Ho and Er, <500 each (limit of standard); Yb, trace; and, below the limit of detection, Sm and Tb, ≤100; Dy, ≤50; Ca, Mg, Gd, <20. The erbium, obtained as fine crystals from vacuum distillation, contained <500 ppm Ta, 150 ppm O, a trace of La, and amounts of the neighboring elements comparable to the above. Synthesis of the trihalides was as before,[9] but used commercial HCl for production of the chlorides. Impurities thereby introduced (principally oxide and carbide) were removed by subsequent vacuum sublimation at 800–900°. This was carried out twice for ErI_3 and with a tantalum jacket for the YX_3 salts. Sublimation gives a noticeable improvement in quality, raising the melting point of YI_3 by 8°, for example. Analyses[9] gave X/M = 2.99 ± 0.01 for the chlorides and 3.00 ± 0.01 for the iodides, the mate-

---

[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1829.

[2] J. E. Mee and J. D. Corbett, *Inorg. Chem.*, **4**, 88 (1965).

[3] W. Klemm and W. Schutt, *Z. Anorg. Allgem. Chem.*, **184**, 352 (1929).

[4] L. B. Asprey and F. H. Kruse, *J. Inorg. Nucl. Chem.*, **13**, 32 (1960).

[5] J. D. Corbett and B. N. Ramsey, *Inorg. Chem.*, **4**, 260 (1965).

[6] F. J. Keneshea and D. Cubicciotti, *J. Chem. Eng. Data*, **6**, 507 (1961).

[7] J. D. Corbett and B. C. McCollum, *Inorg. Chem.*, **5**, 938 (1966).

[8] A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *J. Phys. Chem.*, **67**, 2715 (1963).

[9] L. F. Druding and J. D. Corbett, *J. Am. Chem. Soc.*, **83**, 2462 (1961).

TABLE I

FIXED POINTS AND LIMITING COMPOSITIONS IN MX_3–M SYSTEMS

System	Trihalide mp, °C[a]		Eutectic		Compn at higher temp	
	Obsd	Lit	Mole % M	t, °C[a]	Mole % M	t, °C
YCl_3–Y	721	705 ± 5,[11] 721[12]	2.3 ± 0.3	715–716	2.4 ± 0.3	800
YI_3–Y	997 (978)[b]	965 ± 5[11]	11.8 ± 0.4	948	14.3 ± 0.5	1100
$ErCl_3$–Er	777 ± 0.5	776[11,13]	4.8 ± 0.2	746	6.7 ± 0.2	850
ErI_3–Er	1014	1015[11]	11.0 ± 0.2	933	12.3 ± 0.3	1035

[a] Temperatures are ±1° unless otherwise noted. [b] Solid-state transition.

rial recovery in all cases being within 0.1–0.2 of 100%. Mixtures are considered to be generally ±0.2–0.3 in mole % M, ±0.01 in X/M.

Phase Studies.—Thermal and differential thermal analysis and equilibration experiments were performed as described before.[2] The thermal anslysis measurements were made using capped crucibles to eliminate sublimation of salts, except that Er–ErI_3 samples had to be contained in sealed crucibles.[5] Chunks or buttons of metal, arc-melted in the case of erbium, were employed in equilibration experiments as finer materials gave erratic, time-dependent results, evidently because of suspension. Otherwise self-consistent results were obtained from 1–3-hr equilibrations and, in some instances, for up to 12 hr. X-Ray powder data confirmed the phase analysis conclusions.

Erbium Oxyiodide.—Exploration of the Er_2O_3–ErI_3 system was prompted by a unique residue obtained from an ErI_3 sublimation. Mixtures containing a small excess of either Er_2O_3 or ErI_3 over the stoichiometric requirement which were heated to 1050° in tantalum resulted in X-ray patterns showing strong lines of ErOI plus weak diffractions from only the component in excess. Evidently the intermediate is the only new phase in the Er_2O_3–ErI_3 system at this temperature and it is at least close to the stoichiometry of ErOI. The new pattern is similar but not identical with that reported for TmOI.[10]

Results

Figure 1 illustrates the phase results for the MX_3–M systems studied, M = Y, Er; X = Cl, I. Pertinent data are presented more clearly in Table I.[11–13]

The results are somewhat uniform in the sense that no new solid phase occurs in any of the four systems. This is particularly surprising for erbium inasmuch as it immediately precedes thulium and ytterbium. This contrast will be considered further below. The only new feature of the solid systems is the transition in YI_3 at 978°, above the previously reported melting point. It should be noted that the effect of reduction on this transition was not studied, so that no information was obtained on possible solid solutions in YI_3. The high-temperature form could not be quenched to room temperature.

Two parts of the phase results are comparable to published information. A value of 6.1 ± 0.2 mole % Er in $ErCl_3$ at 820° interpolated from the present diagram agrees very well with the 6% limit reported by Dworkin, *et al.*,[8] from a final analysis of the saturated system in a conductivity study. Also, the eutectic point found here for Y in YCl_3 agrees with that given by Polyachenok and Novikov,[12] 2% metal and 716°. However, they also indicate an additional halt at 740° extending from the liquidus line to at least 35% Y. This was attributed to a monotectic transformation, apparently for a metal-rich phase, as reference was made to such observations in the $LaCl_3$–La and $CeCl_3$–Ce systems.[6,14] However, there is no evidence for a solid-state transformation in Y metal anywhere near this temperature let alone a fusion necessary for a monotectic relationship. Instead, the respective transitions have been reported to be at 1495 and 1509° in the pure metal.[11]

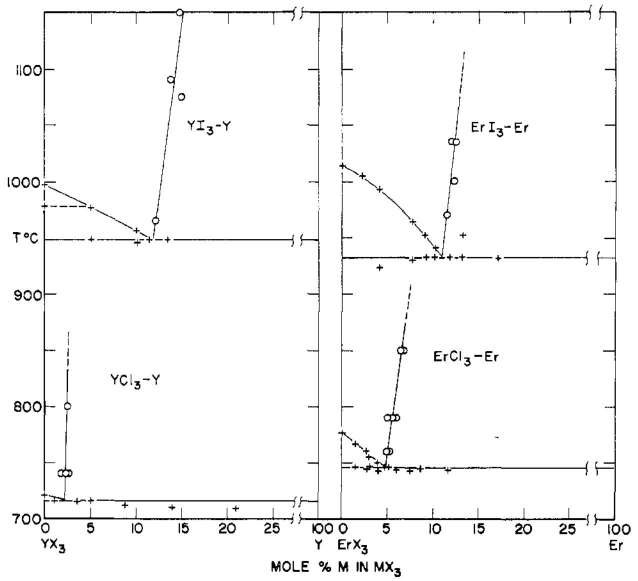

Figure 1.—Phase diagrams for YCl_3–Y and YI_3–Y (left) and $ErCl_3$–Er and ErI_3–Er (right): +, thermal analysis; ○, equilibration with excess metal.

Discussion

Phase Results.—In view of the behavior of the light rare earth metal systems[2] as well as of the neighboring thulium,[4] ytterbium,[3] and dysprosium,[7] it seems reasonable that the erbium solutions, and perhaps those of yttrium as well, would contain an M^{2+} ion of limited stability. Analysis of the depression of the melting point of $ErCl_3$ by Er appears to support this view, the calorimetric heat of fusion[13] yielding a cryoscopic number (ν) of 2.3–2.4. Remembering the usual specter of solid solution formation, and the sort of deviations observed in other, better known systems (compare the tabulations by Bredig[15]), this result appears to support Er^{2+} (ν = 3) over Er^{+} (ν = 1.5). Although the evidence is not conclusive, it should also be observed that

---

(10) F. J. Kruse, L. B. Asprey, and B. Morosin, *Acta Cryst.*, **14**, 541 (1961).

(11) F. H. Spedding and A. H. Daane, *Metallurgical Rev.*, **5**, 297 (1961).

(12) O. G. Polyachenok and G. I. Novikov, *Russ. J. Inorg. Chem.*, **8**, 1478 (1963).

(13) A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, **67**, 2499 (1963).

(14) G. W. Mellors and S. Senderoff, *ibid.*, **63**, 1110 (1959).

(15) M. A. Bredig in "Molten Salt Chemistry," M. Blander, Ed., Wiley-Interscience, New York, N. Y., 1964, p 408.

there is no evidence whatsoever for a unipositive ion for any rare earth element in a condensed system.

Calorimetric fusion data are not available for the other three trihalides studied here. Although the solution of Er in ErI_3 presumably takes place by the same means as in $ErCl_3$, the melting point depressions are quite different (Figure 1) and a comparable entropy of fusion yields a surprising cryoscopic number of 1.1–1.2. The same estimate also gives about the same answer for Y in YI_3. (It is difficult to judge whether Y in YCl_3 is comparable because of the small solubility and limited data.) In addition, very much the same situation has recently been noted for Sc in $ScCl_3$.[16] It does not seem likely that just these three diverse systems of all those studied would contain either such substantial solid solutions or, as already considered, sufficiently unique solute species to account for the cryoscopic differences. On the other hand, it seems more than coincidental that the three exceptional cases, $ScCl_3$, YI_3, and ErI_3 (together with the rest of the heavy rare earth metal iodides), all have the h.c.p. BiI_3-type structure,[17] while all calorimetric fusion data published for rare earth metal trihalides pertain to compounds with other structures (UCl_3, $PuBr_3$, $AlCl_3$). These observations thus suggest that the halides with the BiI_3-type structure may have relatively high entropies of fusion, 15 to 16 eu, as has been estimated for $ScCl_3$,[16] which would be sufficient to make the cryoscopic data for these fall into the general category found elsewhere.[18] In the way of interpretation it might be noted that these salts also have substantially higher melting points and smaller liquid ranges than the other rare earth metal halides (Cl, Br, I) which, with the apparently high $\Delta S°_{fus}$, suggest a relatively greater covalency in the liquid state and/or a substantial decrease in coordination number on fusion. The lower-melting parent BiI_3 and the isotopic $FeCl_3$ are evidently in this category, with relatively high values for $\Delta S°_{fus}$, 13.8 eu at 408°[19] and 17.8 eu at 304°,[20] respectively.

The Reducibility of the Tripositive Rare Earth Elements.—Sufficient information is now available for the rare earth metal–metal chloride systems to enable a meaningful discussion of trends in the extent of the reduction reaction. However, only a relatively limited comparison could be made if this were limited to solid phases which separate, and this would be complicated by special lattice effects which are evidently responsible for the formation of some compounds of different and irregular stoichiometries (*e.g.*, $PrCl_{2.31}$, $GdCl_{1.58}$). Therefore, a better and more general comparison of the reduction reaction can be made in terms of the composition of the salt-rich phase in equilibrium with solid metal above the melting point of any intermediate phase; that is, the apparent metal "solubility" which leads to the presumed solution of MCl_3 and MCl_2 in equilibrium with metal M. Reasons for a uniform choice of MCl_2 as the other compound in solution have been stated earlier here and elsewhere.[2,7] Choice of chloride over iodide for the anion not only allows more elements to be included but also avoids what are apparently rather special effects which give an unusual stability to the "metallic" diiodide melts.[21,22]

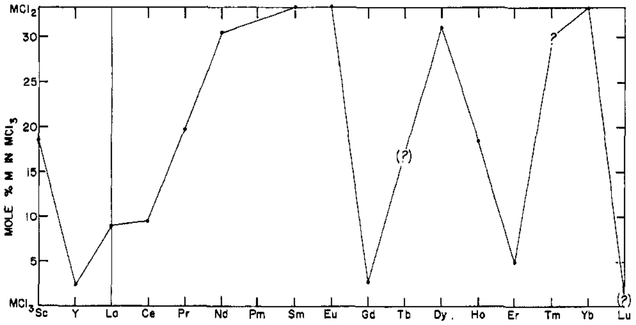

Figure 2.—Compositions of molten chloride melts of scandium, yttrium, and the rare earth metals in equilibrium with excess solid metal, expressed as apparent mole % dissolved metal (MCl_2 = 33.3% M *in* MCl_3). Sources: Sc, ref 5; Y, Er, this work; La, ref 6; Ce, ref 14; Pr, ref 22; Nd, ref 9; Sm, ref 12; Eu, Yb, ref 30; Gd, ref 2; Dy, ref 7; Ho, ref 8.

For this comparison, a plot of the limit of reduction for the chlorides of the lanthanide elements as well as for the related scandium family is given in Figure 2 in terms of mole % metal, where MCl_2 corresponds to 33.3% M in MCl_3. Temperatures chosen for this are generally just above the melting points of any intermediate chlorides and are in the range 800–840° for the series Sc–La–Eu and 760–800° for Gd through Yb; in any case temperature coefficients of the reduction limits are quite small (except perhaps for Sc in $ScCl_3$[5]). The datum for $SmCl_2$, mp 859°,[12] then applies to the slightly supercooled liquid, though this is of no subsequent consequence.

The necessary information for the $TmCl_3$–Tm reaction is not available, although the existence of solid $TmCl_2$, melting somewhat incongruently, is quite likely based on the known TmI_2.[4] No information is available on the terbium or lutetium systems although sometimes fallible intuition would suggest a very small reduction of $LuCl_3$.

Although the elements lanthanum through europium, Figure 2, exhibit a relatively smooth increase in the extent of reduction of the tripositive states, striking irregularities in this property are evident elsewhere, in the Sc–Y–La triad and, more extensively, in the heavy elements gadolinium through ytterbium. In the latter an almost complete lack of any single trend is in complete contrast to the behavior of the lighter elements and perhaps to expectations. Clearly a more or less classical consideration of stability solely in terms of electronic configuration is inapplicable. On the other hand, a substantial correlation and explana-

---

(16) Footnote 9 in ref 5.

(17) L. B. Asprey, T. K. Keenan, and F. H. Kruse, *Inorg. Chem.*, **3**, 1137 (1964).

(18) A $\Delta S°_{fus}$ of only about 12 eu is indicated for the isostructural GdI_3, the lower value coming about because of the solid-state transition about 200° below the melting point.[2,15]

(19) M. A. Bredig and A. S. Dworkin, unpublished research.

(20) K. K. Kelley, *U. S. Bur. Mines Bull.*, **584**, 97 (1960).

(21) J. D. Corbett, L. F. Druding, W. J. Burkhard, and C. B. Lindahl, *Discussions Faraday Soc.*, **32**, 79 (1961).

(22) L. F. Druding, J. D. Corbett, and B. N. Ramsey, *Inorg. Chem.*, **2**, 869 (1963).

tion of the extent of reduction of all of the lanthanides is possible in terms of known thermodynamic properties.

In principle the enthalpy of the equilibrium reduction

$$2MCl_3(soln) + M(s) = 3MCl_2(soln)$$

is given by a Born–Haber cycle as

$$\Delta H°_T = -2U_3 + \Delta H°_{subl\ M} + I_1 + I_2 - 2I_3 + 3U_2$$

where U_n denotes the enthalpy change for formation of pure liquid MX_n from gaseous M^{n+} and nX^-. The cycle of course also presumes the two liquids have negligible heats of mixing, as at least suggested by cryoscopic data at moderate concentrations of metal (5 to 15 mole %). Such conditions, together with the reasonable assumption that $\Delta S°$ for the above reaction is about constant, or, at worst, changes relatively smoothly across the series lanthanum to lutetium (or scandium to lanthanum), will then result in a recognizable correlation between the above $\Delta H°_T$ and the amount of reduction (or better, log K).[23] Although all terms in the enthalpy cycle are obviously not available, the most important ones evidently are.

Again, all that can be asserted regarding the influence of the terms $3U_2 - 2U_3$ is that they should probably vary relatively smoothly across each of the two series (La to Lu and Sc to La), being mainly responsive to regular and, in the first case, small changes in radii. The third ionization energies I_3, though a principal exothermic effect, for the main part must be hopefully placed in the same category. However, it is clear that the sum $I_1 + I_2$[24] exhibits *no* irregular trends which might be used to interpret the results in Figure 2 (except perhaps for the high value at the less interesting element Gd). On the other hand, just the *heats of sublimation of the metals*[25] substantially mirror the stability to reduction in the lanthanides; that is, a high heat change is reflected in a small amount of reduction and *vice versa*. This simple effect thus appears to be responsible for the major part of the differences observed in Figure 2 for the elements La to Lu; effects within the scandium family will be considered later.

The relationship may be demonstrated by a plot of extent of reduction of the lanthanides (mole % M or K_{app}) *vs.* $\Delta H°_{subl\ 298}$ wherein two smooth curves connect the data points, one each for the elements lanthanum to europium and gadolinium to ytterbium. The two groups substantially result from the fact that there is a break in $\Delta H°_{subl}$ at gadolinium whereas other terms, particularly U_n, presumably show a more or less regular change with atomic number, such that a comparable heat change corresponds to less reduction in the heavier group (*e.g.*, Gd *vs.* La). Although this simple treatment accounts for the major reduction characteristics of the lanthanides, especially the inversion with dysprosium, holmium, and thulium, small irregularities still remain for Dy *vs.* Ho and, less noticeable, Ce *vs.* La, the first in each pair appearing too reduced for the value of $\Delta H°_{subl}$. These are evidently second-order effects which can be accounted for in terms of small changes in the known ionization energies. In addition it is somewhat better to express the sublimation term as $\Delta F°_{1073}$, using the $\Delta H°_{298}$ summary[25] together with recent compilations of heat content and free energy functions[26–29] for the solid and gaseous elements, although the $\Delta H°_{1073} - \Delta H°_{298}$ and $1073\Delta S°$ quantities are within a range of only 1.8 and 8 kcal/g-atom, respectively, for all the elements considered. The calculations thus apply to the high-temperature, solid forms of Ce, Pr, Eu, and Yb.

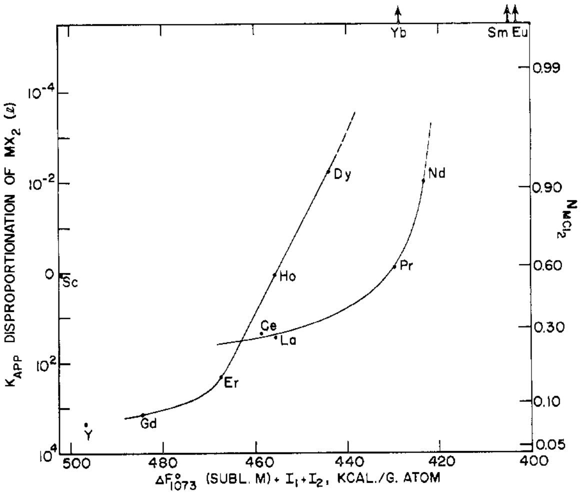

Figure 3.—Log K_{app} at 800° for the disproportionation $3MCl_2(soln) = 2MCl_3(soln) + M(s)$ as a function of $I_1 + I_2 + \Delta F°_{subl}$ for the metal.

The correlation is shown in Figure 3, where log K_{app} for the disproportionation of $MCl_2(l)$ is plotted as a function of $\Delta F°_{subl\ 1073} + I_1 + I_2$ for M. K_{app} is evidently very small for disproportionation of the dichlorides of Sm, Eu, and Yb as they apparently melt congruently.[12,30] In addition, combination of the chlorine dissociation pressures measured above liquid $SmCl_3$ and $YbCl_3$[31] with data for their formation gives

---

(23) There are not sufficient data on heats of formation at temperature or on temperature dependencies of the melt equilibria to allow an alternate, direct evaluation of these quantities.

(24) In order of elements shown in Figure 2, $I_1 + I_2$ is, in ev: 19.34, 18.61, 16.66, 16.45, 16.03, 16.24, –, 16.67 ± 0.1, 16.92, 18.26 ± 0.4, 17.48, 17.47, 17.99, 18.01, 17.85, 18.39, 20.05 ± 0.4. I_3 data for the first five elements are, in ev: 24.75, 20.5, 19.20, 20, 23.2, respectively. Sources are: $I_{1,2,3}$ for Sc and Y, I_1 for La, C. E. Moore, National Bureau of Standards Circulars 467-1 (1949), -2 (1952), -3 (1958), U. S. Government Printing Office, Washington, D. C.; I_1 for Ce through Lu, C. E. Moore, *Appl. Opt.*, **2**, 665 (1963), except I_1 for Dy and Ho, N. I. Alekseev and D. L. Kaminskii, *Soviet Phys.-Tech. Phys.*, **9**, 1177 (1964); for La through Lu, J. Sugar and J. Reader, *J. Opt. Soc. Am.*, **55**, 1286 (1965); I_3 for Pr, J. Sugar, *ibid.*, **53**, 831 (1963); I_3 for La, J. Sugar, *ibid.*, **55**, 1283 (1965).

(25) C. E. Habermann and A. H. Daane, *J. Chem. Phys.*, **41**, 2818 (1964).

(26) D. H. Dennison, K. A. Gschneidner, Jr., and A. H. Daane, *J. Phys. Chem.*, in press (data for solid Sc, Gd through Tm, Lu).

(27) J. Berg, Ph.D. Thesis, Iowa State University, 1961 (data for solid La, Pr, Eu, Yb).

(28) R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley and Sons, Inc., New York, N. Y., 1963 (data for solid Y, Ce, Nd, Sm; gaseous Sc, Y, La, Nd through Tb, Yb, Lu).

(29) R. C. Feber and C. C. Herrick, Los Alamos Scientific Laboratory Report LA-3184, Dec 1964 (data for gaseous Ce, Pr, Dy through Tm).

(30) O. G. Polyachenok and G. I. Novikov, *Russ. J. Inorg. Chem.*, **8**, 1378 (1963).

(31) G. I. Novkkov and O. G. Polyachenok, *Russ. Chem. Rev.*, **33**, 342 (1964).

$K_{1073} \sim 10^{-25}$ for the disproportionation reaction. Although the original dissociation measurements pertain to melts in which Henry's law probably applies to MCl_2, whereas MCl_3 is presumably in this region in the present comparison, the difference is probably not large. A very literal interpretation should of course not be applied to the shapes of the curves in Figure 3 as they are simply a reflection of the assumptions of a smooth variation in I_3 and $3U_2 - 2U_3$, as appears to be the case, plus any nonideality of the solutions including the effect of an expected transition of the dilute component to a Henry's law behavior at either extreme.

The relationship indicated in Figure 3, in comparison with the irregularity presented in Figure 2, satisfactorily accounts for the principal factors involved, in particular, not only the substantial inversion for Dy, Ho, and Er, but also the similar amounts of reduction of $CeCl_3$ and $LaCl_3$, which has been considered somewhat anomalous. On this basis, the melt interactions for unmeasured MCl_3–M systems are predicted to be about 7 mole % Tb, 32% Tm, and ≤1% Lu in their respective molten chlorides at 800°. In general, it may be observed that since the presence of a measurable equilibrium is the result of small differences of large numbers, this kind of observation is much more sensitive to relatively small irregularities, as in $\Delta H°_{subl}$. In opposition, variations attributable to the differences in the sublimation energies are not evident in the large enthalpies of formation of the tripositive oxides or chlorides, for example.

Up to this point little has been said regarding the irregular relationship of scandium, yttrium, and lanthanum. Figure 3 suggests that yttrium behaves as a member of the heavier group, as it also does in properties largely dependent on size and complexing ability, while scandium seems anomalous here as it is in many respects in any comparison with the lanthanides.[32] However, inclusion of the available data for I_3, which drops disproportionately rapidly from scandium to yttrium, simply inverts the problem in the present model, as now the scandium reduction agrees very well with data for La, Ce, and Pr, while that for yttrium is much too low. Both of these may be coincidental, as it would seem more appropriate to consider the scandium family separately. In this case the reduction of yttrium is too low for it to show a properly intermediate position in the chlorides and probably in the iodides as well based on expectations for the ScI_3–Sc system derived from $ScCl_3$–Sc. Perhaps U_3 and U_2 do not vary regularly in the scandium family; YCl_3 melts much lower (721°) than either $ScCl_3$ (967°[5]) or $LaCl_3$ (862°[11]), but the liquid has a properly intermediate vapor pressure.[12] In any case, the trend in reduction properties of the scandium family does not appear parallel to that in subsequent transition groups.

The third ionization energies available for La, Ce, and Pr also may be utilized in a comparison of an alternate model for these solutions. It has often been observed that solvent activity measurements (cryoscopy) in dilute solution cannot rigorously distinguish the formation of M^{2+} from the equivalent amount of anion-like electrons plus M^{3+} from the dissolved metal, although the near-ideality observed for the solutions does not seem as reasonable in this situation.[33] In the literal sense, one should then compare $\Delta F°_{subl} + \Sigma I$, but these are 898, 920, and 964 kcal/g-atom for La, Cd, and Pr, respectively, in inverse order to the change in metal solubility. However, this interpretation is probably specious in that such an "electronide" species would doubtless interact strongly with the neighboring cations and thereby recover a substantial fraction of the I_3 which differentiates its formation from that of M^{2+}. If so, the modal differences are far more subtle; if not, it appears that solvated electrons are not a satisfactory, alternate description of the ground state of the solute. Incidentally, the Sc, Y, La problem is not resolved in this picture either (1072, 969, 898 kcal/g-atom, respectively); Y does *not* have the highest ΣI, as has been stated.[12]

Since the tendency of the metal to reduce its trichloride seems to vary inversely with the energy of sublimation (and ionization) of the metal, while other factors appear to be much less important, presumably the same disposition toward divalency must be manifested to some extent in the solid metal itself. It is well-known that the two elements forming the most stable dipositive states, europium and ytterbium, also are divalent (two-electron) metals, and, in fact, the general decrease in $\Delta H°_{subl}$ from La to Eu (and, less regularly, from Gd to Yb) has been attributed to an increasing propensity toward divalency *in the metal* at high temperatures.[25,32] Conversely, high values for cerium and terbium have been related to an opposite tendency toward tetravalent (four-electron) metals, while the high energies for sublimation of La, Ce, Gd, Lu are also associated with the only elements of the series which retain a $5d^1$ electron on vaporization.[25,32] At present there seems to be no suitable explanation of the particularly large sublimation energy at erbium, although other irregularities are also evident at that point, such as in $\Delta S°_{fus}$.[26] In the present treatment small changes in I_1 and I_2 generally oppose $\Delta F°_{subl}$ trends, except at Gd and Lu where ionization energy peaks reinforce the large sublimation energies. It would be noted that valencies of these metals deduced from dT/dP for fusion[34] do not correspond very well to those considered here.

Finally, the present state of knowledge on the reduction of the rare earth elements and the above correlation may be compared with two other recent treatments and their predictions. Polyachenok and Novikov[35] used a scheme more dependent on unknown quantities, the calculation of stabilities of all of the solid dichlorides by a complete Born–Haber cycle. They recognized that $\Delta H°_{subl}$ of the metal was a main factor

---

[32] K. A. Gschneidner, Jr., in "Solid State Physics," Vol. 16, F. Seitz and D. Turnbull, Ed., Academic Press, New York, N. Y., 1964, p 342.

[33] R. A. Sallach and J. D. Corbett, *Inorg. Chem.*, **2**, 459 (1963).

[34] A. Jayaraman, *Phys. Rev.*, **139A**, 690 (1965).

[35] O. G. Polyachenok and G. I. Novikov, *Russ. J. Inorg. Chem.*, **8**, 816 (1963).

in determining the relative stabilities of the MCl_2 phases, but the sublimation enthalpy changes available to them were much poorer, 10 to 15 kcal too low in the critical cases of Sc,[31] Pr, Dy, and Er for example. Estimates of some I_1 and I_2 values led to a number of significant errors, especially in the heavier half, where $I_1 + I_2$ was taken as constant at 18.9 ev, up to 1.4 ev higher than now reported.[24] Since borderline stabilities are very dependent on small differences in a quantitative calculation, errors resulted in the prediction of a regular trend in the second half of the lanthanides analogous to that in the first, particularly for Dy, Er, (Lu?), and Sc. Correction with present data would put the calculations largely in agreement with experiment.

Topol[36] has treated relative metal solubilities in a somewhat different manner, one which essentially used the logarithm of the Henry's law constant $[C_M(g)/C_M(\text{melt})]$ at constant temperature to describe an "interaction energy" or standard free energy of metal dissolution. These were observed to group roughly according to charge type and position in the periodic table. The few energies determinable at that time for rare earth metal systems were in the range of -62 ± 3 kcal/mole, which, with again erroneous vapor pressure data, led to predictions of generally large metal solubilities (>10%) for the heavy elements Tb to Er and "even complete miscibilities" for Sm, Eu, Tm, Yb, and Lu(!) with their molten chlorides. Although the literal attainment of the last condition does not seem likely,[37] the procedure would probably predict results comparable to those known with better vapor pressure data now available. Although different standard states and dimensions (and philosophy) are involved in Topol's procedure, it actually parallels that found suitable here in that, for constant interaction energy, $-\Delta F^\circ_{\text{subl}}$ was taken as proportional to log N_M, which is in turn proportional to log K_{assoc} for small N_M. The other terms in the cycle used here are then included in the "interaction energy" range considered as constant. General applicability to other groups of systems involving chemical equilibria then depends on $\Delta F^\circ_{\text{subl M}}$ being of major importance relative to other quantities, particularly on the absence of disproportionate ionization energies not reflected in $\Delta F^\circ_{\text{subl}}$. Of course, the more physical nature of the treatment does not consider or interpret the chemistry involved, but, on the other hand, the prime importance of the sublimation energy found in the present work supports a chemical model largely in its continuity with known dihalides, in small but significant ionization factors, and in any explanation of trends in the metals themselves.

Acknowledgments.—The authors are indebted to Dr. K. A. Gschneidner, Jr., for sources of some of the ionization and sublimation data and to B. N. Ramsey for thermal analysis of the YCl_3–Y system.

---

[36] L. E. Topol, *J. Phys. Chem.*, **69**, 11 (1965).

[37] The interaction energy of M with MCl_2 would be considerably less than with MCl_3 to form MCl_2—compare Tl with $TlCl_3$ and TlCl.[36]

CONTRIBUTION FROM THE CHEMISTRY DIVISION,
ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Observation of Astatine Compounds by Time-of-Flight Mass Spectrometry[1]

BY E. H. APPELMAN, E. N. SLOTH, AND M. H. STUDIER

Received January 7, 1966

Astatine compounds were prepared and were identified in a time-of-flight mass spectrometer. The compounds observed were HAt, CH_3At, AtI, AtBr, and AtCl. No evidence was found for the existence of At_2. An attempt to identify astatine fluorides was unsuccessful.

Introduction

Astatine is a synthetic halogen element with no long-lived nuclides. As a result, all investigations of astatine chemistry to date have been carried out at extremely low concentrations, and the astatine has been detected only by its radioactivity. Such investigations can never unambiguously establish the identity of astatine species, and some sort of independent verification of the conclusions of these studies is therefore desirable.

In the case of volatile astatine compounds, such verification can be obtained through the use of a mass spectrometer to measure directly the masses, and hence the probable identities of the principal molecular species present. The Bendix time-of-flight mass spectrometer, with its source modified for continuous duty,[2] has an ultimate sensitivity of about 40 atoms/cc and is thus quite suitable for the examination of astatine species. We have therefore set out to prepare and to identify with this instrument a number of astatine compounds, particularly those that we would expect astatine to form with other members of the halogen family.

Experimental Section

Preparation and Isolation of Astatine.—Astatine-211 was synthesized by bombardment of bismuth with 29-Mev α particles in the 60-in. cyclotron at Argonne National Laboratory. The

---

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) M. H. Studier, *Rev. Sci. Instr.*, **34**, 12 (1963).