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Rare Earth Metal–Metal Halide Systems. V. Lanthanum, Cerium, and Praseodymium Bromides[1]

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The $MBr_3 + M$ phase diagrams for lanthanum, cerium, and praseodymium are presented. Lanthanum and cerium exhibit simple solutions of metal, with 14 and 12 mole % dissolved at eutectic temperatures of 728 and 687°, respectively. The compound $PrBr_{2.38}$ is found, melting incongruently to a solution of 16% Pr in $PrBr_3$ and Pr(s) at 601°. For praseodymium the cryoscopic behavior of dilute solutions of metal is consistent with the primary formation of the Pr^{2+} solute, but with lanthanum and cerium the results are anomalous, as the cryoscopic analyses indicate 1.6–1.7 and 2.0 new particles per metal dissolved instead of ~3.

Introduction

Recent investigations[2–6] of the interactions of lanthanum, cerium, and praseodymium with their respective trichlorides and triiodides have yielded rather contrasting results. In the $MCl_3 + M$ systems the metal solubility in the molten halide increases from 9 to 18 mole % without the formation of intermediate phases that are stable at room temperature (although $PrCl_{2.3}$ does exist between 659°, the melting point, and ~594°, below which it disproportionates back into the original components[5]). In contrast, the $MI_3 + M$ phase diagrams indicate the presence of two lower iodides in each system, a stoichiometric diiodide plus an intermediate phase with a composition about either $MI_{2.5}$ or $MI_{2.4}$. Although the latter compounds have not been further characterized, the diiodides are most unusual in that they exhibit marked electronic conduction. A study of their electrical and magnetic properties indicates that the rare earth element is present as the trivalent cation with the extra electron per cation needed for charge balance in a metallic conduction band.[6,7] The present paper answers the natural question as to the behavior of the bromide systems and as to the existence of any lower bromide compounds.

Experimental

The tribromides were prepared by reaction of excess NH_4Br with the rare earth metal oxides (<0.05% other rare earths) at 200–250°. The crude products were distilled twice under vacuum in order to remove oxide contaminants. The pure metals (O, 500–700; C, 100; N, 100; Ca, <200; total other rare earth metals, <500 p.p.m.) were obtained through the courtesy of Drs. F. H. Spedding and A. H. Daane of this Laboratory. The metals and purified salts were stored in evacuated containers and all material transfers were carried out in an argon-flushed drybox.

The phase diagrams were determined by thermal analysis and by equilibration. The thermal apparatus was similar to that used before,[4] but improved somewhat by the use of metal lead-throughs for the thermocouple leads. The entire assembly was taken into the drybox for each addition of material and was thoroughly evacuated before the sample was heated. The system was equilibrated at least 30 min. before a cooling curve was recorded. Repetitive runs were made until the temperature arrests or inflections agreed to within one degree. Since all systems exhibited marked supercooling, only those runs which had ⩽ 6° supercooling were accepted as valid.

The equilibrations were carried out in sealed capsules fabricated from $^1/_4$ in. Ta tubing. The rare earth metal was melted in this before the addition of salt to allow for easier, subsequent separation of the salt and metal phases. The capsules, sealed by arc welding in a He atmosphere, were suspended within an evacuated Vycor tube and heated to above the melting point of the salt. The temperature, as measured by an internal thermocouple with its junction in contact with the Ta tube, then was adjusted to the desired value (requiring about 30 min.). After at least 2 hr. additional equilibration the samples were quenched by dropping them into a silicone oil reservoir at the bottom of the evacuated glass tube. The equilibrations with excess Pr to establish the composition of the intermediate phase were carried out similarly but for 6 and 30 hr.

Analytical samples were put in solution by addition of water followed by dropwise addition of acetic acid to dissolve the hydrolysis products. The solutions were analyzed for metal ions by the EDTA titration using arsenazo as indicator,[8] while bromide was determined by titration with $AgNO_3$ solution using Eosin Y. The precision of the individual compositions is considered to be ±0.3 mole % metal in MBr_3, equivalent to ±0.01 in the Br/M ratio. Material balances were 100 ± 0.3 wt. % or better.

Results and Discussion

The phase diagrams characterizing the $LaBr_3 + La$, $CeBr_3 + Ce$, and $PrBr_3 + Pr$ systems are presented in Fig. 1, 2, and 3, respectively.[9] The first two are very similar to the corresponding $MCl_3 + M$ diagrams[2,3]; that is, without the formation of intermediate phases but with somewhat greater metal solubility than in the chlorides. Metal solubilities of lanthanum and cerium in the bromides at the eutectic temperatures are 14.2

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[1] Work was performed in the Ames Laboratory of the United States Atomic Energy Commission.

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

[3] G. W. Mellors and S. Senderoff, *J. Phys. Chem.*, **63**, 1110 (1959).

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

[5] L. F. Druding, J. D. Corbett, and B. N. Ramsey, *Inorg. Chem.*, in press.

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

[7] R. A. Sallach and J. D. Corbett, to be published.

[8] J. S. Fritz, R. T. Oliver, and D. J. Pietrzyk, *Anal. Chem.*, **30**, 1111 (1958).

[9] Thermal studies were not carried into the region where transitions within the metal phase, when present, would be detected. These are therefore drawn as dashed lines in the figures at the temperatures found for the transformations in the pure metals, although a noticeable depression of these would be expected (ref. 2, 4, and 6).

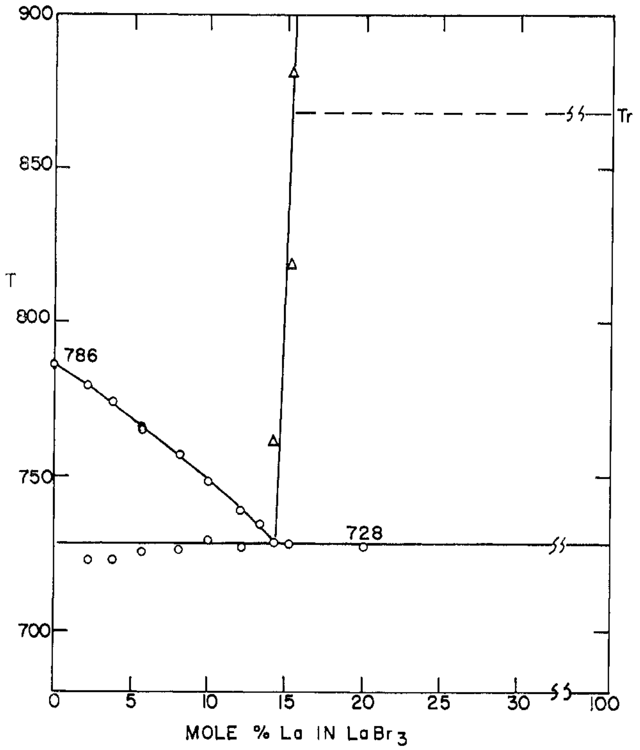

Fig. 1.—The system LaBr$_3$–La: thermal analysis, cooling, ○; equilibration, Δ.[9]

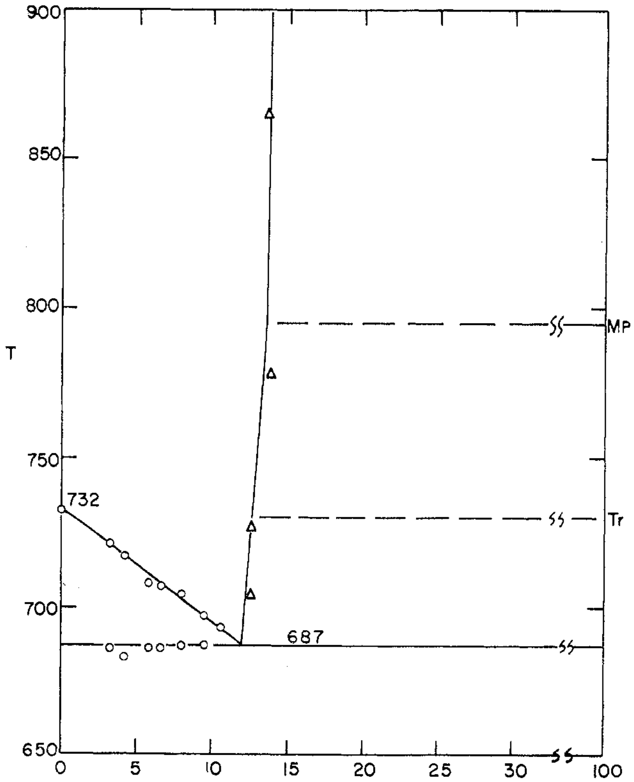

Fig. 2.—The system CeBr$_3$–Ce: thermal analysis, cooling, ○; equilibration, Δ.[9]

and 12.0 mole %, respectively, *vs.* 9% for each in its trichloride.

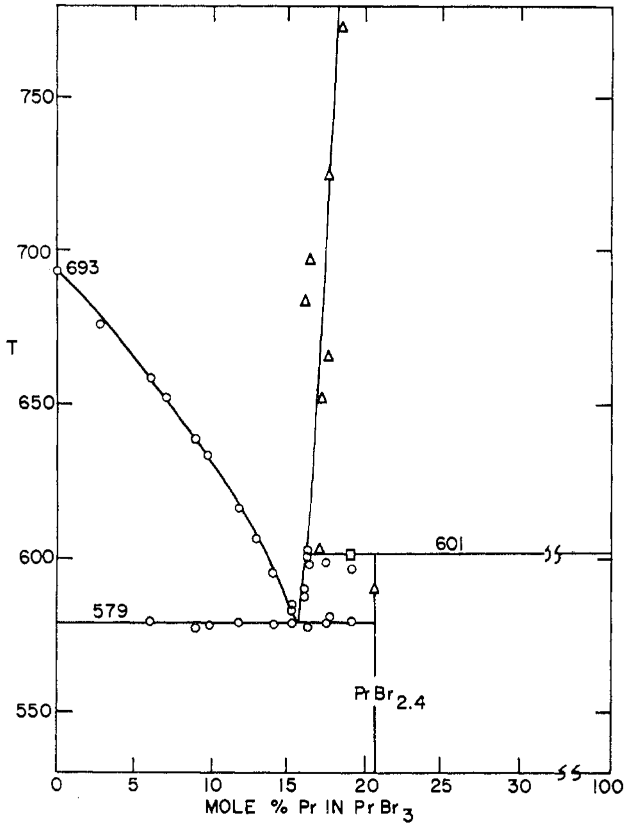

Fig. 3.—The system PrBr$_3$–Pr: thermal analysis, cooling, ○, heating, □; equilibration, Δ.

The PrBr$_3$ + Pr diagram also appears to be related to that of the corresponding chloride system in that an intermediate phase is formed, with the primary difference being that the resulting bromide is stable at room temperature. The composition of this was determined to be PrBr$_{2.38\pm0.01}$ (abbreviated to PrBr$_{2.4}$ in the figure) by analysis of the salt phase that was in equilibrium with the metal at 590°. This composition compares to PrCl$_{2.3}$ and PrI$_{2.50}$ mentioned previously and to NdCl$_{2.37\pm0.02}$ reported for the next heavier element.[4] An X-ray powder pattern of PrBr$_{2.4}$ showed no lines due to PrBr$_3$ and only one weak reflection that possibly could be attributed to the metal; however, more than trace amounts (~0.5 wt. %) of the latter would be evident on the initial solution of an analytical sample in dilute acetic acid. The stronger lines, with their estimated intensities, are: 6.63 (10), 3.89 (3), 3.52 (3), 3.21 (7), 2.84 (7), 2.59 (10), 2.17 (5), 2.08 (3), 2.00 (3), and 1.98 (3) Å. It is interesting that pieces of this compound (~0.25 in. long) showed electrical resistances in the order of a kiloöhm. This is not unexpected in view of the metallic behavior of PrI$_2$ and the fact that both the PrI$_3$ + Pr[10] and the PrCl$_3$ + Pr[11] melts show electronic conduction, although it is the first example of such behavior in solid bromides. However the magnitude of the resistance suggests a semiconduction process rather than the presence of a metal-like conduction band, and hence the probable occurrence of Pr^{2+} as well as Pr^{3+} in the lattice. The stabilized Pr(Nd)Cl$_{2.3}$ appears to be typically salt-like in this property.[5]

[10] A. S. Dworkin, R. A. Sallach, H. R. Bronstein, M. A. Bredig, and J. D. Corbett, *J. Phys. Chem.*, **67**, 1145 (1963).

[11] A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *ibid.*, **66**, 1201 (1962).

With many metal–salt systems a discussion of the mechanism of metal solubility evokes diverse theories, ranging from solution as metal atoms to the formation of lower-valent cations. In the present case, the freezing point depression of the tribromides by added metal suggests that there may be two, or a range of, types of behavior. First, the $PrBr_3$ data appear consistent with the primary formation of the reduced ion Pr^{2+}. With this model, the heat of fusion is calculated from the limiting slope to be 11 ± 1 kcal. $mole^{-1}$, in good agreement with 11.0 kcal. $mole^{-1}$ computed from ΔS_f for the isostructural chloride or 11.6 kcal. $mole^{-1}$ from an average of ΔS_f for $PrCl_3$ and PrI_3.[12] In principle solution of the metal atom to form Pr^{3+} and three electrons also is allowed[13] by this cryoscopic result if the electrons are taken to be trapped in anion "vacancies" and therefore effectively foreign anions. However, there is no direct evidence for this latter mode of solution; an additional unresolved problem is whether such "electronide" solution would behave reasonably ideally at these concentrations. On the other hand, the existence of Ce^{2+} and Pr^{2+} in the solid state is indicated by studies of their solid solutions with the reduced neodymium chlorides.[4,5]

The foregoing cryoscopic interpretation is substantially the same as can be deduced for the chloride and iodide systems of lanthanum through neodymium.[10, 14] Also, at concentrations comparable to those used for the cryoscopic calculations the electronic contribution to the total conductivity of the chloride and iodide melts is of the character to indicate that the electrons are energetically trapped with respect to conduction, *e.g.*, as M^{2+} ions or solvated electrons. Thus the phase results and, to a less conclusive degree, the conductivity of dilute solutions point to a M^{2+} solute with a stability that increases with increasing atomic number of the metal.

In contrast, the $MBr_3 + M$ systems for the lighter elements lanthanum and cerium show what appears to be a real deviation from the generally consistent cryoscopic behavior found in all the systems discussed above. As comparison of the liquidus curves will show (Fig. 1-3), the depression of the melting points of $LaBr_3$ and $CeBr_3$ by added metal is markedly less than that of $PrBr_3$, so that heats of fusion calculated for the M^{2+} (or e^-) model are much too large. Instead, the best agreement between the limiting, dilute solution behavior and the heats of fusion estimated as above is obtained if 1.6 to 1.7 particles are produced on solution of La in $LaBr_3$ and 2.0, with Ce in $CeBr_3$. Although the exact values must not be taken too literally, the contrast to $PrBr_3 + Pr$ is clear. It is interesting to note that cryoscopic numbers somewhat less than three (*ca.* 2.5) also are found for the chloride and iodide systems of the same two elements,[10,15] but these are not as strikingly low as with the bromides.

The foregoing results for lanthanum and cerium bromides could of course be explained by invoking mixtures of the M^{2+} (or e^-) species with M^+, M^0, or more complex entities. This does not appear particularly desirable in view of the trends observed for metal–salt systems of the just-heavier metals, and, for the main part, the chloride and iodide systems of lanthanum and cerium as well. Significant solid solution formation in the tribromides seems to be a more plausible alternative, although the thermal analysis data given here offer no good evidence for or against this. At present any further attempt at explanation of what appears to be an anomaly in the general properties of these systems is largely speculation.

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(12) The heats of fusion for most of the chlorides and iodides were kindly supplied to us by A. S. Dworkin and M. A. Bredig prior to their publication (*J. Phys. Chem.*, **67**, 697 (1963)).

(13) In this case the Tempkin expression in terms of ionic mole fractions is $N_{MX_3} = N_{M^+}(N_{X^-})^3$.

(14) A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *Discussions Faraday Soc.*, **32**, 188 (1961).

(15) M. A. Bredig, private communication.