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The Solubility of Some Metals in their Molten Halides[1]

BY J. D. CORBETT AND S. VON WINBUSH

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The apparent solubilities of six metals in their respective molten halides have been measured, using the salts $SnCl_2$, $SnBr_2$, $PbCl_2$, TlCl, AgCl, $GaCl_2$ and AlI_3. A comparison of the lead and tin data with known metal solubilities in the alkaline earth and cadmium(II) halides shows a generally decreasing solubility with decreasing electropositive character of the metal. In contrast to the intensely colored or darkened systems usually obtained in such systems, the Al–AlI_3 and Ga–$GaCl_2$ systems are colorless, and the formation of subhalides seems reasonable. A seemingly significant correlation can be obtained between the solubility of aluminum in AlI_3 and a theoretical calculation of the stability of AlI. The reaction of gaseous tin(II) or lead(II) chloride and excess tin or lead metal in the temperature ranges of 550 to 950° and 500 to 575°, respectively, does not result in the formation of significant amounts of any subhalide.

Introduction

The apparent solution of a number of metals in their molten salts has been known for nearly two centuries. Interpretation of this behavior as being due to colloid formation led Lorenz[2] to introduce the term "pyrosole" to describe the phenomena. The formation of intensely colored melts, the occurrence of visible metal particles in the quenched salt, and the repression of the extent of metal solution by the addition of foreign salts were all considered evidence for the formation of colloidal metal in the molten salts. Early workers in the field also suggested the formation of subhalides in these melts, and the literature is replete with claims for the isolation of such solid compounds as Na_2Cl, CaF, Cd_4Cl_7 and CdI[3]; subsequently it has been shown that most of these preparations were probably only a mixture of the free metal and the normal salt.[4,5,6] Later work has generally also refuted the claims of colloid formation[6,7] although the misconception persists in the modern literature.[8] Most significantly, Cubicciotti[6] has shown that the addition of the metal depresses the freezing point of alkaline earth and cerium halides, such as would be anticipated for a true solution. Cubicciotti has also reported that the repression of the metal solubility in the cadmium[9a] and bismuth[9b] systems by added salts behaves as might be expected from the valence type of the foreign salt. Recently Bredig and co-workers[10] have carried out noteworthy examinations of the phase diagrams for a number of alkali metal–alkali halide systems. They have found that, particularly for the fluorides, complete miscibility of the components occurs at temperatures not too far removed from the melting points of the salts.

Knowledge of the solubilities of metals in their fused halides for elements other than those in the first two representative groups and the zinc family is sparse. We have examined a number of diverse systems in the hope of deriving some criteria by which to correlate such interactions, for the extent and effect of such solutions must be considered in electromotive force and ion transport studies.[11] Systems in which the formation of lower oxidation states might be favored have also been considered.

Experimental

Preparation and Analyses.—Tin(II) chloride was prepared by the dehydration of Baker Reagent grade dihydrate at 300° under a flow of anhydrous HCl. The bromide was obtained by reaction of tin metal (J. T. Baker) with HBr (Matheson Anhyd.) at 400°; its melting point was 232.4 ± 0.2°. Both salts were sublimed after preparation, stored *in vacuo*, and resublimed into the equilibration vessel just before use. All salts were handled with the usual high vacuum techniques.

Lead(II) chloride (Fisher Reagent) was recrystallized from dilute HCl; filtration of the hot solution through a coarse fritted Pyrex funnel was necessary to remove what was apparently a suspended organic impurity, for otherwise the product darkened on heating. The crystals were dried *in vacuo* or under anhyd. HCl by heating slowly to 400°.

Thallium(I) chloride (Fisher C.P.) was either vacuum sublimed, or recrystallized, vacuum dried and melted under anhydrous HCl. Spectrographic analysis showed the thallium metal (Sargent C.P.) contained no In, and only small amounts of Ag and Pb. Tl(III) was shown to be absent in all materials. We are indebted to the Analytical Service Group and Prof. C. V. Banks for analyses verifying the purity of the TlCl.

The silver chloride was selected from Fisher or Baker Reagent preparations so as to be particularly low in iron. Suitable salts contained no more than 5×10^{-3} wt. % material insoluble in concentrated NH_4OH, as collected in a fine grade sintered glass crucible. The metal used was #26 C.P. wire.

Gallium(II) chloride (saturated with the metal) was prepared from the reaction of excess gallium metal (99.95%, Aluminum Co. of America) with sublimed Ga(III) chloride at 180°. All transfers were carried out in a dry box filled with P_2O_5-dried nitrogen. Gallium was determined by precipitation as the dibromoxinate[12]; chloride volumetrically using 0.1% dichlorofluorescein in 50% polyethylene glycol 400.[13]

Aluminum iodide was prepared by the reaction of 99.99% "iron-free" aluminum wire (A. D. MacKay) with iodine,

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

[2] The work is well summarized in R. Lorenz and W. Eitel, "Pyrosole," Akademische Verlagsgesellschaft, Leipzig, 1926.

[3] (a) W. Borchers, *Z. Elektrochem.*, **8**, 938 (1902); A. Guntz and F. Benoit, *Bull. soc. chim.*, **35**, 709 (1924); H. N. Morse and H. C. Jones, *Am. Chem. J.*, **12**, 488 (1890); K. Siddiqi, *Current Science*, **12**, 147 (1943). (b) Isolation of CaCl has been claimed recently by P. Ehrlich and L. Gentsch, *Naturwiss.*, **40**, 460 (1953); see also G. Wehner, *Z. anorg. allgem. Chem.*, **276**, 72 (1954).

[4] W. Hollens and J. Spencer, *J. Chem. Soc.*, 1062 (1934).

[5] H. Grimm and K. Herzfeld, *Z. Physik*, **19**, 141 (1923).

[6] D. D. Cubicciotti and C. D. Thurmond, THIS JOURNAL, **71**, 2149 (1949); D. Cubicciotti, *ibid.*, **71**, 4119 (1949).

[7] (a) W. Eitel and B. Lange, *Z. anorg. allgem. Chem.*, **171**, 168 (1928); (b) A. H. W. Aten, *Z. physik. Chem.*, **73**, 578 (1910); (c) E. Heymann, J. Martin and M. Mulcahy, *J. Phys. Chem.*, **47**, 473 (1943).

[8] C. Gill, M. E. Straumanis and A. W. Schlechten, *J. Electrochem. Soc.*, **102**, 42 (1955).

[9] (a) G. Cleary and D. Cubicciotti, THIS JOURNAL, **74**, 557 (1952); (b) D. Cubicciotti, *ibid.*, **74**, 1198 (1952).

[10] (a) M. A. Bredig, J. W. Johnson and W. T. Smith, Jr., *ibid.*, **77**, 307 (1955); (b) M. A. Bredig, H. R. Bronstein and W. T. Smith, Jr., *ibid.*, **77**, 1454 (1955).

[11] F. R. Duke and R. W. Laity, *J. Phys. Chem.*, **59**, 549 (1955).

[12] E. Gastinger, *Z. anal. Chem.*, **126**, 373 (1944).

[13] R. Dean, W. Wiser, G. Martin and D. Barnum, *Anal. Chem.*, **24**, 1638 (1952).

Resublimation *in vacuo* into the previously flamed equilibration vessel enabled water-white melts to be obtained. The samples were dissolved in dilute H_2SO_4; the finely divided metal often produced free sulfur. Aluminum was determined as the oxinate; iodide by silver using 0.01% eosin.

No evidence was obtained for the formation of colloidal metals upon aqueous solution of any of the metal–metal salt samples.

Methods and Procedures. A.—Method A employed a direct analysis of the quenched salt. In early experiments, the system of metal and salt (5 to 15 g.) at equilibrium was filtered *in situ* through a medium or fine grade sintered Pyrex filter by means of a slight argon pressure, and a weighed sample of the filtrate analyzed. Experience showed that, at least for these systems, when the experiment was carried out above the melting point of the metal, physical suspension of molten metal particles in the salt did not seem to occur, and the results did not depend on the length of time (beyond a certain minimum) for equilibration. Accordingly, the filtration was dispensed with for all but the AlI_3 system. Here the clearness of the system showed only a few particles floating on the surface. The viscosity of AlI_3 was sufficiently low that the melt could be gravity-filtered in the sealed system.

B.—Method B involved direct measurement of the loss in weight of metal when equilibrated with a known amount of salt at a temperature above the melting point of the metal. The nature of the method allowed accurate determination of much smaller solubilities than possible by direct analysis. In addition to the characteristic colors observed (see Discussion), reuse of metal and sublimed salt samples has eliminated the possibility that the smaller solubilities could have been due to oxidizing or reducing impurities.

The weight of tin(II) halide used (5 to 55 g.) was determined by difference, employing a fragile glass container in which the sublimed and melted salt had been sealed. This was broken with a glass hammer in the vacuum system, the salt resublimed onto the metal and sealed off, and the glass fragments reweighed.

$PbCl_2$ (30 to 40 g.) and TlCl (10 to 30 g.) were weighed directly into a quartz tube, melted under argon, the metal added to the cooled salt, and the container sealed off evacuated. In order to avoid possible loss of dissolved metal from the salt during quenching from the higher temperatures, a small curved finger on one end of the tube allowed the metal to be isolated just before cooling by rotation of the furnace containing the sample. The amount of salt or metal in the gas phase was in all cases negligible.

Tin, lead and thallium were melted *in vacuo* or with a suitable premelted flux until at constant weight (within 0.2, 0.2, 0.4 mg., resp.). The metal buttons recovered were remelted to remove occluded salt. Sublimation of the salt from the tin was a simple matter. The last traces of salt were removed from the lead or thallium by melting with a small amount of KCl–KI or KCl–NaCl eutectic mixture, previously melted *in vacuo*. The added flux was necessary to prevent the very clean metals from sticking to the glass so tightly they could not be removed without loss.

C.—In the determination of the solubility of (solid) silver in AgCl, the weight of dissolved silver was determined directly. The silver wire was equilibrated with 4 to 8 g. of AgCl under 15 cm. of argon; after 3 to 8 hours the entire furnace was rotated and the salt filtered (by the application of argon pressure) through a 10 × 1.5 mm. fine grade sintered quartz filter disk (Thermal Syndicate, 5 to 15 micron aver. pore size) sealed in the tube. A weighed piece of the filtrate was dissolved in concentrated NH_4OH, and the silver metal collected on a fine grade filtering crucible and weighed. Crystallization of AgCl from the solution from evaporation of NH_4OH was avoided, as decomposition in such crusts produced considerable silver. Blanks on the AgCl used were about one-tenth of the quantities obtained here. The amount of undissolved silver possibly passed by the quartz filter is at present unknown; AgCl is too viscous at 480–600° to be filtered through an ultrafine sintered Pyrex disk by reasonable pressures. The Ag–AgCl system was interesting in that ready recrystallization of the metal took place on heating the components overnight at 600° or higher. Occasionally flat crystals of silver were obtained as large as two mm. square; the wire was deeply pitted, although it did not lose its original shape.

In view of the high reactivity that is apt to be obtained with finely divided metals, this method is not widely applicable. For example, when $CdCl_2$ was washed from the once-dissolved metal with distilled water, 10 to 18% of the metal appeared to react and dissolve. This error may influence data reported for this system.[9a]

Equilibrations were in 8 or 12″ tube furnaces with the temperatures controlled by Brown or Wheelco proportioning indicating controllers, using chromel–alumel thermocouples calibrated by Leeds and Northrup.

Transport Experiments.—Lead or tin(II) chloride was slowly sublimed over the corresponding heated metal in an evacuated fused-quartz tube. The salts were heated to temperatures that would give (static) vapor pressures of from 25 to 100 μ, although the actual pressures were somewhat lower. The lead and tin metals were heated by means of a separate furnace to temperatures of from 500 to 575°, and 550 to 950°, respectively. (At higher temperatures the vapor pressure of lead became appreciable.) The condensed salts appeared no different from the pure components indicating that any amounts of metal transported as subhalides must be significantly less than observed in the equilibrium experiments.

Freezing Point Depression.—Cooling curves were run on a 10-g. sample of TlCl with the thermocouple packed in a thin-walled tube that extended into the middle of the salt. Consistent values of 429° were obtained. The furnace was then tilted so as to spill thallium metal into the salt, and the cooling curves repeated. The freezing point was then 428 ± 0.5°.

Results and Discussion

Table I summarizes the data obtained; the number of significant figures reported is indicative of the reproducibility of the measurements.

TABLE I

System	Equilibration temp., °C.	Dissolved metal, mole %	Method[a]
Sn–$SnCl_2$	500	0.0032	B
Sn–$SnBr_2$	500	.068	B
Pb–$PbCl_2$	600	.020	B
	700	.052	B
	800	.123	B
Tl–TlCl	550	.009	B
	650	.009	B
Ag–AgCl	490	.03	C
	700	.06	C
Ga–$GaCl_2$	180	1.92	A
Al–AlI_3	380	0.0	A
	423	.3	A

[a] Methods: A, direct analysis; B, loss in weight of metal; C, weight of dissolved metal.

Sn–$SnCl_2$, Sn–$SnBr_2$.—No previous determinations of these quantities have been published. Addition of metal to the fused halide caused a slight darkening, although the melts were not opaque. The quenched solids were distinctly gray.

Pb–$PbCl_2$.—These small amounts of dissolved lead were sufficient to color the liquid an opaque black; the quenched salt was gray. Lorenz[14] obtained a value of 5×10^{-4} mole per cent. at 610°, approximately one hundredth as large, by a "titration" of the metal-saturated melt with PbO_2. Later workers[7a] reported 1.55×10^{-2}% at the one temperature of 509°, a value somewhat higher than an extrapolation of our data would yield.

Tl–TlCl.—No quantitative data are available in the literature. Addition of the metal colors the normally orange liquid a very dark orange-brown;

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(14) R. Lorenz, G. von Hevesy and E. Wolff, *Z. physik. Chem.*, **76**, 732 (1911); "International Critical Tables," **IV**, 40, quotes this work with the omission of a factor of 10^{-1}.

the quenched solid is yellow-brown to gray-brown. The solubility of Tl in TlCl is only about 1% of that found in the alkali chloride systems near the melting point of the salts[10]; the fugacity of thallium metal here is about 10^{-5} of that of the alkali metals at those temperatures. The freezing point depression observed corresponds to a metal solubility of 0.4 ± 0.2%; the failure of ideal solution laws in such a solution is not surprising.

Ag–AgCl.—Reinders[15] reported a solubility of 0.13% at 1000°. The values reported here are to be considered as possibly maximum values, limited by the filtration technique applied to the melt (see Experimental section, method C). The liquid saturated with silver, and the solidified salt were distinctly different in color from that of the pure salt, being dark yellow to yellow-brown, depending on the temperature, and blue or greenish-gray, respectively; a real solubility accordingly appears indicated.

Ga–$GaCl_2$.—The liquid was colorless; the quenched melt, gray. The temperature used was nine degrees above the melting point of the pure chloride. Taube, Friedman and Wilson[16] appear to have obtained a value of 2.5% at 200 to 250°. They suggested the formation of a subhalide in the colorless liquid that disproportionated on solidification.

Al–AlI_3.—Examination of this system was undertaken also because of the likelihood of subhalide formation.[17,18] The resulting melt was again colorless. The quenched salt was usually gray, although occasionally a white solid was obtained which darkened on heating briefly to 100°. If the solubility at 423° is indeed due to the formation of AlI, an interesting correlation with theoretical predictions of the stability of such a compound can be obtained. Assuming an ideal solution in AlI_3, use of Brewer's free energy function and entropy data,[19] together with a more recent value for the free energy of formation of AlI_3,[20] gives $\Delta F_{700°K.} =$ −13 kcal. for AlI. If S^0_{298} for AlI is taken as about 24 e.u. (from comparison with gallium and indium monohalide data),[19] a corresponding ΔF_{700} for the formation of AlI(s) of −15 kcal. can be estimated from the ΔH^0_{298} calculated theoretically by Irmann.[21] (Std. state = I_2 (g.), 1 atm.) The agreement seems significant; reasonable errors appear to affect the calculated values by less than 2 kcal. A value of −22 ± 2 kcal. for ΔF^0_{298} for the formation of AlI is consistent with both sets of data.

For the two post-transition elements that show disproportionately large solubilities in their halides, cadmium[7b] and bismuth,[22] the formation of subhalides in melts that are also intensly colored has been suggested.[23] As described in the Experimental section, the lack of transport of tin and lead metals by reaction with their gaseous dihalides in the temperature ranges of 550 to 950° and 500 to 575°, respectively, appears to rule out the presence of appreciable quantities of gaseous subhalides of these elements under the specified conditions. This observation may be significant in a consideration of the solute species present in the metal-saturated molten salts, although such evidence is far from conclusive. Direct evidence for the presence or absence of discrete lower oxidation states in intensely colored melts, as opposed to energy bands for the sites of the electrons,[9b] or other interpretations,[10] is completely lacking.

Cubicciotti[6] noted that within the alkaline earth and zinc groups the solubilities of the metals in their respective divalent salts generally increased with increasing atomic number, but that an over-all correlation of solubilities between the two groups could not be found. Addition of our lead and tin data to his table shows, with the apparent exception of zinc, a general trend toward a smaller solubility in the groups containing the less electropositive metals. While the fugacity of the metal at the experimental temperature may be significant, the heat of vaporization of the metal does not seem to be a determining factor. Comparison of the tin chloride and bromide solubilities does not appear fruitful. Compilation of all known data on the miscibilities of metals with their halides shows no consistent trend on the variation of solubility with change in halide anion. The phenomena we are concerned with here is doubtlessly complex, and simple correlations of the effect of cation or anion alteration may not be possible.

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(15) W. Reinders, *Z. physik. Chem.*, **77**, 213, 366 (1911).

(16) H. Taube, H. Friedman and A. Wilson, NP-636, Progress Report, "The Chemistry of Gallium," Navy Contract N6-ori-20, Univ. of Chicago, October and November, 1948. The figure quoted was recalculated from their chloride analyses.

(17) W. Klemm, E. Voss and K. Geiersberger, *Z. anorg. allgem. Chem.*, **256**, 15 (1938).

(18) W. C. Schumb and H. H. Rogers, THIS JOURNAL, **73**, 5806 (1951).

(19) "The Chemistry and Metallurgy of Miscellaneous Materials—Thermodynamics," L. L. Quill, Ed., NNES IV-19B, McGraw-Hill Book Co., New York, N. Y., 1950, papers 3 and 6.

(20) J. D. Corbett and N. W. Gregory, THIS JOURNAL, **76**, 1446 (1954).

(21) F. Irmann, *Helv. Chim. Acta*, **188**, 1449 (1950).

(22) B. Eggink, *Z. physik. Chem.*, **64**, 419 (1908).

(23) Ref. 19, pp. 242, 251.