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SOLUTION OF METALS IN THEIR MOLTEN SALTS.

SOME MANGANESE, CHROMIUM, URANIUM AND ANTIMONY SYSTEMS.*

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Abstract-Preparations of high purity MnCl_2 , CrCl_2 , CrI_2 , UBr_4 , UI_3 and Sb_2S_3 are described; the melting points obtained for CrI_2 (868°) and Sb_2S_3 (559.5°) are significantly higher than previously reported. The small solubilities of manganese and chromium in the respective halides studied were characterized primarily by the depression of the freezing points of the salts by excess metal. For $\text{MnCl}_2 + \text{Mn}$ (in Ta), ΔT is $1.5 \pm 1^\circ$, for $\text{CrCl}_2 + \text{Cr}$, 6° , and for $\text{CrI}_2 + \text{Cr}$, 3° .

The UBr_3 -U and UI_3 -U systems were studied by equilibration in tantalum containers followed by analysis of the saturated salt phase. Uranium dissolves in liquid UBr_3 to 4 ± 1 mole per cent over the range of 800 to 912° , and in $\text{UI}_3(l)$, from 5.7 per cent at 784° to ~ 9 per cent at 1020° . The liquidus curve for $\text{Sb}_2\text{S}_3 + \text{Sb}$ was investigated by thermal analysis; the salt-rich eutectic is at 524.5° and 18.0 ± 0.5 per cent Sb. At 780° the equilibrium salt phase contains 42.0 ± 0.5 per cent Sb. The UBr_3 and Sb_2S_3 compositions are somewhat lower in metal content than previously reported.

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Hitherto the only knowledge of metal-metal halide interactions for metals of the first transition series has been for nickel, where solutions of up to 9 mole per cent metal in liquid NiCl_2 have been observed.⁽¹⁾ Investigation of the system MnCl_2 -Mn was prompted principally by the report⁽²⁾ that the use of thermodynamic half cell potential for a Mn/MnCl_2 reference cell gave a potential for the U/UCl_3 couple 0.1 v lower than obtained with Fe/FeCl_2 or Ag/AgCl . This suggested that an appreciable solution of Mn in liquid MnCl_2 have been responsible for the observed deviation even though one possible solution mode, the formal reduction of the $3d^5$ solvent ion Mn^{2+} , could be considered unusual. Conversely, the CrX_2 -Cr systems, $\text{X} = \text{Cl}, \text{I}$, have been examined to establish whether the simple Cr^+ ion might possess a stability sufficient to exist in a more or less dilute solution in liquid CrX_2 .

An appreciable solution of uranium metal in certain of the liquid uranium(III) halides has been reported. With UCl_3 , this has been given as 4 per cent metal at 820° , the eutectic, and 6 per cent at 1140° ,⁽³⁾ while in UBr_3 a much larger dependence of solubility on temperature has been suggested, increasing from about 4 per cent at the eutectic (743°) to roughly 21 per cent at only 950° .⁽⁴⁾ In view of the admittedly tentative nature of the published results for the bromide system and also the probable presence of side reactions with the containers used in the prior study, the system has been reexamined. In addition, reaction of $\text{UI}_3(l)$ with metal has been explored to establish whether the trend suggested by the above chloride and bromide data would result in an even larger interaction in this case, or perhaps the separation of a lower phase.

Finally, the Sb_2S_3 system presents an interesting example of a relatively large solubility of metal, 20 to 30 per cent at the eutectic at 520° ^(5, 6) and 42 per cent at 615° , the monotectic,⁽⁷⁾ without the formation of an intermediate phase. As is frequently the case with chalcogenide vs. halide systems, the interaction is far greater than in the corresponding halides, where formation of Sb_2I_4 is indicated in the iodide melt,⁽⁸⁾ In similar contrast, the sulfide melts apparently show a definite electronic conductivity with relatively large amounts of dissolved metal.⁽⁷⁾ Inasmuch as a technical grade of Sb_2S_3 was employed in recent studies of the system, the Sb_2S_3 liquidus curve as well as the solubility of liquid metal at 780° have been reinvestigated with higher purity materials.

EXPERIMENTAL

MnCl_2 -Mn: The salt was prepared by dehydration of the reagent grade tetrahydrate under anhydrous HCl at 500° , followed by treatment with Cl_2 up to 700° , and vacuum distillation at 800° . The chlorination step was found necessary in order to obtain a clear, yellow-brown melt without deposition of a black solid. The metal (99.9 per cent A. D. MacKay) attacked Vycor in the presence of molten MnCl_2 so that thermal analysis studies were carried out in tantalum containers, and then only with excess metal because of the simultaneous formation of a TaMn_2 coating on the container. Thermocouples were periodically checked against the melting point of NaI. Separate MnCl_2 samples gave melting points of 653.5 and 654° , each $\pm < 1^{\circ}$, compared to 650° given by Moore.⁽⁹⁾

CrCl_2 -Cr: Since preparation of CrCl_2 via H_2 or HCl treatment of CrCl_3 or Cr respectively could give a product contaminated with one or

the other starting material which would thereby vitiate subsequent results, the stoichiometric compound was prepared from CrCl_3 and Cr. Reaction of the metal (Electromet 99.9+ per cent) with dry Cl_2 at 960° gave CrCl_3 , and this was sublimed under Cl_2 . The proper proportions of metal and CrCl_3 (to ± 0.001 in Cl/Cr) were then reacted completely (without exposure to the atmosphere) in a sealed, fused silica container at 890° to give the pure, asbestos-like CrCl_2 . Thermal analyses were performed in sealed glass containers, with weighed amounts of metal added through a break-seal. The melting point of CrCl_2 was found to be 824° , compared to the "selected" 815° ⁽¹⁰⁾ and 824° reported by Fischer and Gewehr.⁽¹¹⁾

CrI_2 -Cr: Metal at 800° was reacted with I_2 from a reservoir at 175° in a sealed, evacuated, glass container to give a mixture of CrI_2 and CrI_3 . Sublimation of this product in vacuo at 700° gave the red-brown CrI_2 plus a trace of the black CrI_3 , with metal in the residue and considerable amounts of I_2 in the cold trap. Additional vacuum sublimation continued to give small amounts of CrI_3 in the product. This was finally removed by sublimation from the CrI_2 in a sealed tube at 555° . Alternatively, Cr and I_2 in stoichiometric proportions (± 0.001 in I/Cr) were transferred in an inert atmosphere box and reacted to produce CrI_2 , red in transmitted, and yellow-brown in reflected light. Both products gave a melting point of 868° in sealed tubes, which is far in excess of the 790 to 795° inferred by Hein and Wintner-Holder from resistance measurements.⁽¹²⁾

UBr_3 -U: UBr_4 was used as the starting salt since it could be readily sublimed to reduce impurities. The metal was cut from a rod (Mallinckrodt, principal metallic impurities, in ppm: 50 Fe, 44 Al, 14 Mg) and

cleaned with 1:1 HNO_3 while the bromine (< 0.02 per cent Cl, A. D. MacKay) was dried over P_4O_{10} and subsequently sealed in ampoules equipped with break-seals. The Br_2 container and the metal were placed in opposite ends of a Vycor tube in the form of a shallow, inverted V, and this was evacuated. Hydrogen, purified by passage through a trap filled with Linde Molecular Sieve 4A cooled to -196° , was reacted with the metal at 250° for 1 to 2 hr, and the hydride so formed then decomposed under vacuum at 500° . The apparatus was then sealed, the spectacular reaction initiated by breaking the ampoule, and completed by heating the metal end to 570° and the Br_2 , to 40 to 50° .

Purification of the UBr_4 by sublimation at 450° plus all subsequent UBr_4 -U reactions were executed in Ta so as to eliminate side reactions with glass. For the first step a two-piece, Ta apparatus was constructed from 3/4 in. tubing so as to provide an extended crucible for the crude material and a closely fitting cylinder on the open end for the condensate. The UBr_4 product had an average Br content of 57.43 per cent vs. the theoretical 57.32 per cent.

Known quantities of U and UBr_4 were contained in 1/4 in. x 2 in. Ta tubes arc welded under $\sim 1/3$ atm. of He. These were heated in a glass container under proportional temperature control with measuring thermocouple junction in contact with the metal wall, and were quenched by dropping them into a silicone oil reservoir in the bottom of the glass envelope. The composition of the salt phase was usually determined from the loss in weight of the added metal, as the massive U did not disintegrate at or below 915° , the adhering salt could be easily removed by a H_2O wash, and an appreciable solubility of salt in the solid metal was not

evident. Direct analysis of the salt phase was in good agreement when checked; for example, 49.30 per cent Br vs. 49.36 per cent calculated from the weight loss. The product gave a powder pattern of only UBr_3 . Analysis for bromide was gravimetric; the silver precipitated by reaction of the ion with U(IV) was redissolved by heating for an hour with dil. HNO_3 .

UI_3 -U: Preparation and purification of the pure uranium iodides is more difficult due to the ease of disproportionation or dissociation. To avoid reaction of UI_3 with glass at elevated temperatures the synthesis procedure used for the rare earth metal triiodides⁽¹³⁾ was employed, so that metal in a W crucible at 800° reacted with I_2 vapor from a reservoir at 100 to 120° . The reaction was still slow and incomplete, and massive metal remained after 48 hr. Reaction of iodine with powdered "hydride" U was more successful, giving a product $\text{UI}_{2.98}$ (99.87 per cent I + U) with a melting point of $771-772^\circ$ ($766.5 \pm 1^\circ$ lit.⁽¹⁴⁾). Thermal analysis and equilibration experiments were again carried out in sealed Ta tubes; in this case recrystallized metal was evident in the salt matrix after 3 hr at 1020° so that salt analysis rather than weight loss of the metal was more reliable at the higher temperatures. Because ready sublimation of the iodide was not feasible some oxygen contamination is to be expected; 0.1 per cent was found in one sample by inert gas fusion. Reduced salts showed only the powder pattern of UI_3 .

Sb_2S_3 -Sb: Technical Sb_2S_3 (Fisher) was found to have very unsatisfactory melting characteristics, and spectrographic examination showed major amounts of Si, Fe, Ca and Cu. Although vacuum sublimation gave a considerably better material, the majority of the starting salt used was

synthesized from the elements. Purified sulfur was vacuum sublimed at 140° , discarding about the first and last third, and was subsequently handled only in a dry box. The metal, 99.999 per cent with respect to metal content (A. D. MacKay), was fused in vacuum to reduce the oxide content. The elements were reacted in the desired proportions in evacuated and sealed glass tube as before, with the metal heated to about 600° and the sulfur, to 400° . For pure Sb_2S_3 rather than mixtures, a final vacuum sublimation at 540° was added. Spectrographic analysis of this showed only traces of Pb and Si, and the melting point of 559.5° obtained compares to 547° in a recent compilation⁽¹⁵⁾ and 546° in the most complete phase diagram of the Sb_2S_3 -Sb system.⁽⁵⁾

The Sb_2S_3 liquidus curve was studied on mixtures synthesized in situ from the elements, equilibrated at 600 - 650° in the sealed Vycor cell, and cooled at 1 to $5^{\circ} \text{ min}^{-1}$. The thermocouple, calibrated by the 630.5° melting point of the metal, was contained in a well projecting into the melt. Serious supercooling was reduced by the presence of powdered Vycor and by mechanically shaking the entire cell through an attached quartz rod operated by a motorized cam. Compositions were altered by sublimation of the entire contents of the cell through a break-seal into a like cell containing additional metal.

Since the above data disagreed noticeably with previous results, the composition of the salt-rich phase in equilibrium with liquid Sb at 780° was also checked. Known weights of Sb and sublimed Sb_2S_3 were equilibrated in short lengths of sealed Vycor tubing, cooled quickly, and the recovered metal button was cleaned with aqu. HCl and weighed. In order to correct for the significant solubility of salt

in liquid metal that was retained within the button, values of the apparent solubility vs. wt. ratio of metal to salt at equilibrium for several experiments were extrapolated back to zero metal phase. The result agreed to within 0.1 per cent dissolved metal with that obtained directly through use of a button previously saturated with salt. Powder pattern data confirmed that a new solid phase is not formed.

RESULTS AND DISCUSSION

Metal interactions with the liquid manganese and chromium halides were found to be so small that direct methods for the determination of the composition were concluded to be generally unreliable. Accordingly, the magnitude of the solubility was inferred from the depression of the freezing point of MX_2 by added metal. Excess Mn lowers the $MnCl_2$ point by only $1.5 \pm 1^\circ$; from the calorimetric heat of fusion⁽⁹⁾ this corresponds to an ideal solution of about 0.8 ± 0.5 mole per cent Mn as atoms, or half as much as Mn^+ . With $CrCl_2 + Cr$, the liquidus data for mixtures containing 0.7 to 6 per cent Cr indicate a eutectic at $818 \pm 1^\circ$, a depression of 6° , with the composition near 3 to 4 per cent. A composition of 1.9 per cent metal as atoms is calculated from the ΔT of 6° and the accepted⁽¹⁰⁾ heat of fusion. The 868° melting point of CrI_2 is depressed only 3° by excess chromium, so any reaction must be even less favorable than with the chloride.

Metal interactions of this sort as possible evidence for monovalent ions of the first transition series thus continue to be substantially negative other than for nickel and, of course, its neighbor copper. Indirect evidence suggests a similarly negligible reaction in $FeCl_2-Fe$,⁽²⁾ while metal solution in molten CoI_2 appears very minor.⁽¹⁶⁾ The behavior of this series

may be roughly correlated with fundamental thermodynamic quantities to the extent that the relative enthalpy for the solution reaction $M^{2+} + M \rightarrow 2M^+$ will be more favorable for a small value of $(I_1 - I_2 + \Delta H_{\text{subl.}})$ for the element M. These terms for the elements Ti to Cu clearly support the predominance of Cu^+ and indicate that Ni^+ and Cr^+ should be next most stable, with Mn^+ in fourth place. The difference observed experimentally in the amount of reaction of Cr and Ni with their chlorides amounts to a free energy difference of only about 2 kcal per mole of the M^+ presumed formed, and this scarcely could have been predicted by such means.

The solution of U in UBr_3 was investigated between 800 and 915°. The solubility of 4 ± 1 per cent is substantially independent of temperature within the reproducibility of the measurements although there may be a small retrograde solubility effect within the quoted uncertainty. This amount agrees with the approximate 3 to 5 per cent at the 743° eutectic concluded earlier⁽⁴⁾ (although their experimental data appear to allow this composition to be as high as 8 per cent). On the other hand, the much greater metal content in the liquidus compositions previously reported at higher temperatures must have been due to extensive attack of the alumina and porcelain apparatus.

Investigation of the UI_3 -U reaction was not carried out extensively when it became apparent that the solubility was not significantly greater than in the bromide. At 784°, about 18° above the reported⁽¹⁴⁾ melting point, the solubility is 5.7 per cent and this increases to 6.3 per cent at 865 and ~9 per cent at 1020°. Uranium(II) would thus appear to have only a very limited stability. Incidentally, it was also established that UI_3

exhibits a very high resistance typical of a salt. This eliminates the possibility, apparently not previously clarified, that UI_3 might be a metallic salt (e. g. $U^{4+}(I^-)_3e^-$) such as recently found with ThI_2 .⁽¹⁷⁾

The improved quality of the Sb_2S_3 indicated by the higher melting point obtained also resulted in a significant change in the liquidus curve obtained on addition of metal. The temperatures observed ($\pm 1^\circ$) for the respective mole per cent of dissolved metal (± 0.1 per cent) (based on Sb_2S_3 solvent) are: 551.5°, 4.3; 547, 7.9; 533, 14.0; 526, 16.5; 529, 16.7; 524°, 17.8, with the eutectic temperature at 524-5°. The eutectic composition of 18.0 ± 0.5 per cent when compared to the earlier 21 per cent at 520°⁽⁵⁾ and about 30 per cent at 519°⁽⁶⁾ suggests that oxidizing impurities may have been present in the salt used previously. Similarly, the sulfide-rich phase in equilibrium with the liquid metal-rich phase at 780° was found to contain 42.0 ± 0.5 per cent metal, somewhat less than the 48 per cent interpolated from the most recent data.⁽⁹⁾

Analysis of the above liquidus data in terms of $Sb + Sb_2S_3$ mixtures gives a limiting heat of fusion of 8 to 9 kcal per mole of Sb_2S_3 , compared to 5.6 kcal mole⁻¹ in the literature.⁽⁵⁾ The latter, or actually twice this value, was deduced from the liquidus curves for solutions of SnS and PbS in what was presumed to be the molecular solvent Sb_4S_6 . In the absence of more specific knowledge of the solvent characteristics and constitution of liquid Sb_2S_3 , the only substantial conclusion that can be reached is that Sb metal effectively produces about one-third fewer solute particles on solution in Sb_2S_3 than do SnS or PbS.

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