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The Solution of Sodium Alloys of Some Post-Transition Metals in Molten Sodium Halides. Evidence for Anions of Bismuth and Antimony¹

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Received March 14, 1968

The solutions of sodium alloys of gold, thallium, tin, lead, antimony, and bismuth particularly in the molten solvent NaCl–NaI (37:63) have been examined as a function of alloy composition and temperature. The first four show relatively small solubilities of the heavy metal, ≤ 1.3 mol % at 700 or 800°. A larger, specific solution of Na_{3.9}Bi occurs with metal phases containing 25–30 atomic % bismuth: 2 mol % at 600° and 27 mol % at 1000°. The solubility data are reasonably consistent with the alloy and melt solute species Na₃Bi plus the substantially less soluble NaBi. Freezing point studies for Na₃Bi in NaCl–NaI, NaI, and KI solvents suggest the simple ionic species Na⁺ and Bi³⁻ are formed in dilute solution. The solubilities for the sodium–antimony system are substantially larger, about 11 mol % Na_{2.6}Sb in equilibrium with Na₃Sb(s), 2 mol % Na₂Sb with NaSb(l), and 1.3 mol % Na_{0.37}Sb with NaBi₃(l), all at 608°. Cryometric data for Na₃Sb and NaSb in sodium iodide suggest the presence of Sb³⁻ and Sb₃³⁻ anions in the melt, respectively. The dependence of solubility on solvent anion and on the heavy metal in the alloy or intermetallic compound are also considered.

Introduction

Although unusual lower oxidation states and bonding of cations are often found for solutions of the post-transition metals in their molten salts and related systems,^{2–4} very little is known about *anions* of these elements even though some of these border on recognized, anion-forming nonmetals. In addition to the pioneering work of Zintl and coworkers⁵ in liquid ammonia, there are the qualitative observations by Heymann and Weber⁶ that sodium alloys with bismuth, antimony, tin, and gold (but not lead, cadmium, or thallium) dissolve to some extent in molten sodium bromide. Recently, the solution of Li₃Bi in an LiCl–LiF mixture (0.05 mol % at 600°, 2 mol % at 1000°) has also been reported⁷ as well as spectral data for solutions of some alkali metal tellurides (M₂Te) in molten alkali metal halides.⁸ The present paper reports more quantitative solubility data in the lower melting NaCl–NaI eutectic composition for many of the alloy systems studied by Heymann and Weber, including temperature and composition dependences for the more interesting antimony and bismuth systems. Cryometric data in several melts pertaining to nature of the solutes have also been obtained.

Experimental Section

Materials.—The bismuth (reactor grade), antimony (Bunker Hill), tin (Vulcan Materials), and thallium (American Smelting and Refining), all stated to be 99.999%, plus lead (American Smelting and Refining, 99.99+%) were purified by fusion in Vycor containers under dynamic vacuum ($\leq 10^{-5}$ torr), a process which either volatilized or brought to the surface nonmetallic impurities. Gold (99.97%, J. Bishop) was used as received. The hydroxide was cut from sodium chunks (Baker, 0.0045% impurities) in the drybox and only the clean center pieces were used for alloy preparations. All compositions with lead, tin, and thallium are sufficiently low melting that they could be prepared by fusion of the weighed components in evacuated, sealed Pyrex or Vycor containers without attack, after which the liquid was poured to the other end of the tube to leave any oxide behind on the glass walls. The same technique was used to obtain a composition near Na₄Au which was then heated with additional gold in sealed tantalum tubes. Tantalum was used for all preparations of the higher melting antimony and bismuth compositions. The actual composition of all alloy samples used was determined by direct analysis either before or after equilibration with melt. In the former case the equilibrium alloy composition was calculated from the initial amounts of salt and known alloy and the solute content of the melt.

The NaI–NaCl eutectic (63 mol % NaI, mp 570°⁹) was made up from Mallinckrodt and Baker reagent grade salts, 0.05% impurities and 99.8% respectively, which were dried in Vycor containers under dynamic vacuum, first at room temperature and then gradually up to the fusion point. The salts used for the antimony solubility studies were also vacuum sublimed separately, though this precaution did not appear to affect the results appreciably.

Solution Studies.—The metallic systems which show appreciable solution in the molten eutectic readily attack Vycor or fused silica. Therefore, all solution measurements were carried out in sealed tantalum apparatus. As described earlier,¹⁰ equilibrations

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) T. C. F. Munday and J. D. Corbett, *Inorg. Chem.*, **5**, 1263 (1966).

(3) J. D. Corbett, *ibid.*, **7**, 198 (1968).

(4) J. D. Corbett in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964, Chapter 6.

(5) E. Zintl, J. Goubeau, and W. Dullenkopf, *Z. Physik. Chem.*, **154A**, 1 (1931).

(6) E. Heymann and H. P. Weber, *Trans. Faraday Soc.*, **34**, 1492 (1938).

(7) M. S. Foster, C. E. Crouthamel, D. M. Gruen, and R. L. McBeth, *J. Phys. Chem.*, **68**, 980 (1964).

(8) D. M. Gruen, R. L. McBeth, M. S. Foster, and C. E. Crouthamel, *ibid.*, **70**, 472 (1966).

(9) W. P. Radischtschew, *Zh. Obshch. Khim.*, **5**, 455 (1935).

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

of 2–18 hr, depending on the system, were carried out in sealed tantalum under dynamic vacuum after which the contained sample was quenched to room temperature by dropping it directly into silicone oil within the evacuated apparatus. The control as measured by a thermocouple in contact with the container was $\pm 0.5^\circ$ at 600° and $\pm 1^\circ$ at 1000° . The arrangement provided very rapid quenching since only 1.5–4 g of salt was equilibrated with alloy in short lengths of 6-mm diameter, 10-mil tantalum. As a result agglomeration of the solute which would be suggestive of segregation during the cooling process was not found in any of the measurements; rather, the once-dissolved alloy was always found entirely as a finely divided and highly reactive precipitate uniformly distributed within the salt matrix. The major source of scatter of the data was the visible suspension of small amounts of the solid Na_3M phase in systems in which the alloy phase was all or partly solid at temperature. Even so, reasonably satisfactory cryometric checks of the equilibration data were obtained. Solubility of salt in the metal phase was not specifically studied, but no evidence that such was appreciable was noted either. Cryoscopic measurements were carried out in 13–19-mm diameter sealed tantalum apparatus as before¹¹ so that repeated additions (± 1 mg) of alloy could be made in the drybox. The thermocouple was calibrated with the pure salt at the beginning of each run.

Analyses.—The salt phases containing once-dissolved intermetallics Na_xM as well as many of the alloy compositions themselves react cleanly with water to give hydrogen, sodium hydroxide, and the flocculent heavy metal so that the last two can be directly titrated and weighed, respectively. In practice the metal value is better determined by volumetric methods, and the weight of metal itself was used only for gold in the salt phases. These amounts of hydroxide and metal determined are usually described hereafter in terms of the apparent sodium and metal (M) solubilities in the sodium halide solvent, specifically in terms of $(\text{Na}^+)_x\text{M}^{x-}$ ionic species rather than the elements or molecular units. In this case it is actually the average charge on M^{x-} rather than the sodium content of the solute which is evaluated.

For the gold alloys the reaction of the sodium therein with water went to completion if the solid was amalgamated, after which the gold was recovered by vacuum distillation of the mercury. Substantially the same gold contents were obtained either when the difference was determined according to the hydroxide result for sodium or when the alloy was taken up in aqua regia and fumed with concentrated HCl and the gold was precipitated with oxalic acid at pH 1. Sodium-rich alloys with antimony were treated first with ethanol to allow a milder reaction, while sodium was determined by difference for the less reactive alloys with $\text{Na}/\text{Sb} < 1$. These and the antimony precipitates remaining after treatment of other compositions with water were dissolved in sulfuric acid, tartaric acid was added, and the solution was boiled to remove SO_2 and then titrated with standard solution after addition of Na_2CO_3 and an HCO_3^- buffer. Tests with rhodamine B showed a negligible amount of antimony-(V) was formed in the foregoing process. A few per cent of the total antimony that was found to have dissolved after 24 hr in contact with the basic solution was taken into account.

Lead alloys as well as the precipitates from solution of the salt phase in water were dissolved in aqua regia and taken to dryness with H_2SO_4 , and the PbSO_4 was dissolved in pH 5 acetate-acetic acid buffer and titrated with standard EDTA using xylenol orange indicator. Tin was dissolved in aqueous HCl, excess EDTA was added, and the solution was back-titrated with standard thorium(IV) solution and the same indicator.¹² Bismuth was dissolved in nitric acid and titrated with EDTA using thiourea indicator.¹³

Hydroxide formed by reaction of the alloys or salt phases with water was generally titrated with standard acid and brom cresol green after first boiling at the phenolphthalein end point to expel CO_2 .

Results

Unless otherwise noted the molten salt solvent referred to hereafter is the NaCl – NaI mixture containing 63 mol % NaI .

Thallium.—The liquid¹⁴ compositions NaTl_2 and Na_2Tl gave undetectable (< 0.1 mol %) amounts of thallium in the melt at 687° and so were not studied further.

Gold.—The composition $\text{Na}_{0.9}\text{Au}$ in equilibrium with the solvent gives 1.32 mol % gold in the salt phase at 1010° , 1.24 mol % at 938° , and 0.82 mol % at 858° , with $\text{Na}/\text{Au} \approx 1.2$ in the melt. The composition $\text{Na}_{1.2}\text{Au}$ yields $0.51 \pm 0.05\%$ at 800° with a somewhat higher ratio in the salt (~ 1.8). The alloy $\text{Na}_{2.0}\text{Au}$ gives 0.32 mol % gold in the melt at 712° ; the Na/Au ratio of 3.9 suggests some preferential solution of sodium. According to the phase diagram¹⁵ all of the above data pertain to liquid alloys except $\text{Na}_{0.9}\text{Au}$ at 858° which contains solid NaAu_2 . The relatively small amounts of solution were not studied further.

Lead.—The liquid alloys also exhibited only small solubilities and so were not investigated extensively. At 600° the lead content of the same solvent in equilibrium with NaPb is $(4.5 \pm 0.6) \times 10^{-2}$ mol %; with Na_2Pb , 0.27 ± 0.07 mol %; and with $\text{Na}_{15}\text{Pb}_4$, 0.3 ± 0.1 mol %.

Tin.—The small solubility values given are based on sodium concentrations alone assuming the solution process is congruent: $\text{Na}_{2.0}\text{Sn}$, 1.3 ± 0.2 mol % at 600° ; $\text{Na}_{3.0}\text{Sn}$, 1.1 ± 0.2 mol % at 600 and 700° ; $\text{Na}_{4.0}\text{Sn}$, 0.8 ± 0.05 mol % at 600° , 1.2 ± 0.2 mol % at 700° . All alloy compositions are liquid at temperature.

Bismuth.—Preliminary measurements showed that Na_3Bi dissolves congruently and substantially in the melt. The results of measurements between 600 and 1000° with alloys containing 26–57 atom % Bi ($\text{Na}_{2.84}\text{Bi}$ to $\text{Na}_{0.76}\text{Bi}$) are collected in Table I. The dependence of the bismuth solubility on alloy composition and (rounded) temperature is shown in Figure 1. The composition ranges wherein solid Na_3Bi is present were estimated from recent corrections^{16,17} to the published diagram.¹⁵ The solubilities with $\text{Na}_3\text{Bi(s)}$ present may be somewhat high at the lower temperatures (600 and 700°) because of suspension of the solid in the melt, as evident from the results of longer equilibrations than reported in Table I.

The dependencies of solubility and of solute composition on alloy composition suggest that there is a preferential solution of Na_3Bi in the melt and that at least one more species with a lower sodium content (NaBi?) dissolves from alloys richer in bismuth but to a substantially smaller degree. The first 16 data in Table I, which include all of those systems in equi-

(14) R. P. Elliott, "Constitution of Binary Alloys—First Supplement," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(15) M. Hansen and K. Anderko, "Constitution of Binary Alloys," 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1958.

(16) A. K. Fischer, S. A. Johnson, and S. E. Wood, *J. Phys. Chem.*, **71**, 1465 (1967).

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

(12) J. Korb and R. Pribil, *Chemist Analyst.*, **45**, 102 (1956).

(13) J. S. Fritz, *Anal. Chem.*, **26**, 1978 (1954).

TABLE I
 SOLUBILITY OF Na-Bi ALLOYS IN MOLTEN NaCl-NaI

$10^2 N_{\text{Bi}}$ (alloy)	Temp, °C	$10^2 N_{\text{Bi}}$ (salt melt) ^a	Na/Bi (salt melt)	$10^2 N_{\text{Bi}}$ (alloy)	Temp, °C	$10^2 N_{\text{Bi}}$ (salt melt) ^a	Na/Bi (salt melt)
26	605 ^b	2.25	3.01	44.5	798	2.78	2.56
26	594 ^b	3.01	2.93	45	890	3.3	2.65
26.6	618 ^b	1.96	3.02	46	600	1.59	2.89
26	690 ^b	3.09	3.02	46	800	2.71	2.60
26	693 ^b	4.05	2.94	46	1011	4.77	...
28	800 ^{b?}	8.36	3.02	47	595	1.37	2.94
26	901	21.9	2.93	50.3	600	0.87	2.72
26	897	15.0	2.95	50.6	594	0.87	2.72
27	897	16.0	...	51.5	694	1.15	...
27.3	903	17.1	2.94	51.7	694	1.42	2.49
28	1000	26.6	2.91	52	956	1.87	2.49
29	800 ^{b?}	9.45	2.96	52.7	895	1.53	2.34
29	1005	25.1	3.02	56.9	885	0.99	2.31
31.7	992	19.2	2.97	57	736	0.67	2.54
34.5	605 ^b	1.85	2.89	57	797	0.72	...
34.5	699 ^b	3.13	2.87	57	1003	1.11	2.32
37	794	5.08	2.81	57.2	600	0.41	...

^a $N_{\text{Bi}}(\text{salt melt}) = n(\text{Na}_3\text{Bi})/[n(\text{Na}_3\text{Bi}) + n(\text{eu})]$. ^b Liquid alloy contains $\text{Na}_3\text{Bi}(\text{s})$ at temperature.

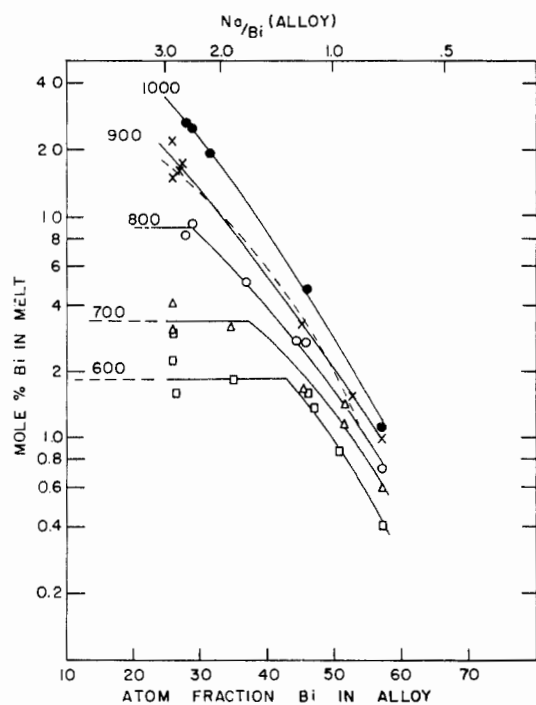


Figure 1.—Bismuth solubility in NaCl-NaI (37:63) as a function of temperature and composition of the metal phase. The dashed line is calculated (see Discussion).

librium with $\text{Na}_3\text{Bi}(\text{s})$ as well as liquid compositions containing 26–29 atom % bismuth ($\text{Na/Bi} = 2.85\text{--}2.45$) give an average Na/Bi ratio of 2.96 ± 0.04 in the melt. With increasing bismuth content in the metal phase, the decrease in solubility is accompanied by a decrease in the Na/Bi ratio of the solute, more rapidly at the higher temperatures, reaching 2.3–2.5 with a 57 atom % alloy ($\text{Na}_{0.75}\text{Bi}$). When fused silica is used as the container rather than tantalum, the dilute melts containing Na_3Bi are observed to be ruby red before attack of the walls commences. Solutions of Li_3Bi in LiCl-LiF (70:30) are deep red.⁸

Cryometric studies in NaCl-NaI, NaI, and KI

strongly support the notion that the solute is the ionic $(\text{Na}^+)_3\text{Bi}^{3-}$. The results are shown in Figure 2. In NaCl-NaI the limiting slope and the appropriate mean heat of fusion calculated from calorimetric data for the

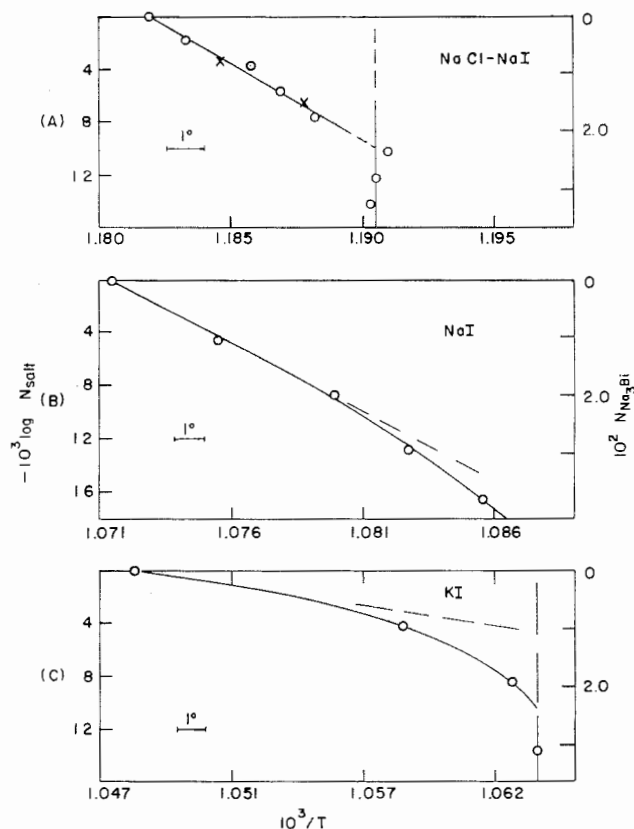


Figure 2.—Freezing point depressions for Na_3Bi in various solvents: (A) NaCl-NaI (37:63) (two separate measurements); (B) NaI; (C) KI. The dashed lines correspond to $\nu = 1.13, 1.17$, and 4.0, respectively; the vertical lines, to eutectic temperatures.

component salts¹⁸ give a cryoscopic number ν (the number of foreign ions per solute) of 1.13 ± 0.04 , the uncertainty indicated being solely that for determination of the slope. A eutectic with $\text{Na}_3\text{Bi}(\text{s})$ was so observed at 2.2 ± 0.2 mol % and 566.8° ,¹⁹ a condition which compares with about 1.9 mol % at 600° obtained from direct measurements (Figure 1). In NaI, Figure 2B, $\nu = 1.17 \pm 0.03$, with the eutectic (not shown) at 5.1 ± 0.2 mol % Na_3Bi and 645° ; for comparison a direct determination of the saturation value at 667° gave 5.2 mol %. Since the presumed solute cation Na^+ cannot be detected in the above solvents, data were also secured in KI, Figure 2C, where four foreign ions would be expected. The cryoscopic number obtained is indeed about 4.0, with an uncertainty of at least 0.2 based only on the difficulty of estimating the slope. (Even with no curvature ν is 3.0.) Of course, some solid solution of NaI in KI is also to be expected. The invariance of the 667.0° eutectic temperature observed with excess Na_3Bi present (not shown) suggests that the solid phase present is Na_3Bi and not K_3Bi , which is con-

(18) A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, **64**, 269 (1960).

(19) Although the ternary eutectic need not lie in the pseudo-binary section between the NaCl-NaI eutectic and Na_3Bi (or NaSb), no thermal analysis evidence to the contrary was observed with the relatively small solubilities of these alloys.

sistent with the estimated enthalpy change;²⁰ the composition of the saturated melt is about 2.4 mol % Na₃Bi.

Antimony.—Preliminary studies revealed that sodium-antimony compositions showed a very considerable solubility in the NaCl-NaI melt at moderate temperatures, *e.g.*, about 20 mol % antimony from solid Na₃Sb at 700° and even 8 mol % above Na_{0.29}Sb at 720°. Accordingly, the solutions were studied as a function of composition primarily at a lower temperature, 608°. The results are given in Table II for 24.8–74.8 atom %

TABLE II
SOLUTION OF SODIUM-ANTIMONY ALLOYS IN
NaCl-NaI EUTECTIC AT 608°

$10^2 N_{\text{Sb}}$ (alloy)	$10^2 N_{\text{Sb}}$ (salt melt) ^a	Na/Sb (salt melt)	$10^2 N_{\text{Sb}}$ (alloy)	$10^2 N_{\text{Sb}}$ (salt melt) ^a	Na/Sb (salt melt)
24.9 ^b	7.94	3.02	50.45	1.51	1.88
24.8 ^b	10.1	2.98	51.0	1.59	1.87
29.2 ^b	14.9	2.46	51.0	1.59	1.91
35.2 ^b	9.24	2.55	51.0	1.89	1.70
35.8 ^b	11.6	2.50	74.4	2.50	0.355
35.8 ^b	11.5	2.48	74.6	1.13	0.385
40.6	10.2	2.35	74.8	1.22	0.424
41.0	9.92	2.29	74.8	1.46	0.373
47.2	5.93	1.75	75.9	1.29	0.331
47.2	4.78	1.93			

^a $N_{\text{Sb}} = n(\text{Na}_x\text{Sb})/[n(\text{Na}_x\text{Sb}) + n(\text{eu})]$. ^b Solid Na₃Sb present.

antimony in the metal phase. A measure of the residual oxidizing impurities in the salt is presumably given by the apparent solubilities of pure antimony of 0.03 and 0.07 atom % found after 13 hr at 670°. The mole per cent of dissolved metal and sodium or concentration of antimony and its average charge are both shown in Figure 3 as a function of alloy composition. Some visible suspension of solid Na₃Sb in the salt phase was evident, particularly after equilibration for longer times than the 2–2.5 hr used for the data reported, and this appears to be the principal reason for scatter of the data with alloys containing less than 39 atom % Sb. However, a small amount of suspended alloy has a much smaller effect on the Na/Sb ratio than on the solubilities of the individual components so that the apparent limit of existence of solid Na₃Sb used was deduced much better from a plot of the Na/Sb ratio *vs.* alloy composition. This result, 39% antimony, compares with 41% estimated from the published phase diagram.¹⁵ The rather sharp increase in the Na/Sb ratio in the melt above Na₃Sb(s) from ~2.5 in the presence of excess antimony to 3.00 ± 0.02 with a small excess of sodium (Table II) appears to reflect the sharp drop in the activity and hence solubility of an antimony-rich species such as NaSb as one crosses the Na₃Sb composition. At the same time the activity of sodium increases as the liquid phase changes from *ca.* 61 to 91 atom % sodium, though it will be noted later that the solubility of elemental sodium under the conditions studied probably is not very significant. The rapid decrease in solute concentration with increasing antimony content of the alloy phase will be considered later.

(20) O. Kubaschewski, E. L. L. Evans, and C. B. Alcock, "Metallurgical Thermochemistry," Pergamon Press Ltd., London, 1967, pp 212, 304.

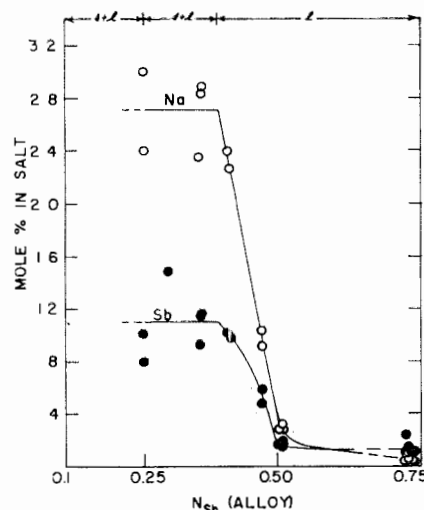


Figure 3.—Solubility of antimony and sodium in NaCl-NaI (37:63) at 608° as a function of composition of the metal phase.

The solutions of Na₃Sb and NaSb were observed to be tan to black and dark reddish brown, respectively, at about 580°. Both attacked the fused-silica container.

The sodium iodide freezing point depressions by Na₃Sb and NaSb are shown in Figure 4. The data for

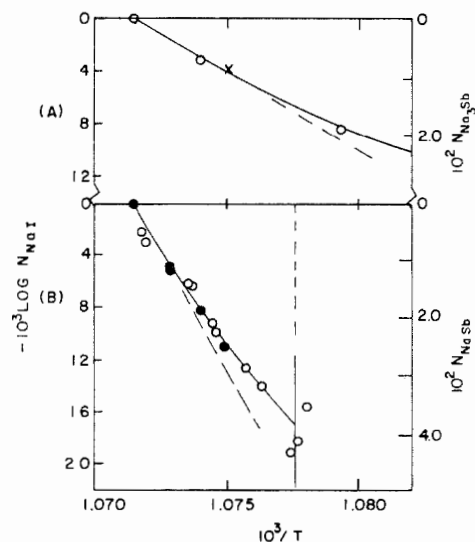


Figure 4.—Freezing point depressions for (A) Na₃Sb and (B) NaSb in NaI. The dashed lines correspond to $\nu = 1.04$ and 0.34, respectively.

the former yield a cryoscopic number of 1.04. Extension to higher concentrations than shown yields a eutectic at 11.6 mol % and 622.7°; the saturation value determined directly at 655° is 12.3 mol %, with Na/Sb = 2.7 in solution. The data shown for NaSb comprise two independent studies which yield 0.33 ± 0.03 and 0.338 ± 0.01 new ions per mol of Na_{0.973}Sb and Na_{1.02}Sb, respectively. The eutectic obtained with the former is at 3.7 ± 0.1 mol % and 654.8°. If the solution process in NaI is similar to that found in NaCl-NaI (Figure 3), a saturated solution somewhat richer in sodium will be in equilibrium with an alloy richer in antimony (~60 atom % Sb). Such is consistent with the curvature in Figure 4B, the higher slope corresponding to

ultimate cosolution of a species richer in sodium, *e.g.*, Na_3Sb . The converse is observed for Na_3Sb in NaI at higher concentrations than shown, presumably because the solution above $\text{Na}_3\text{Sb(s)}$ at saturation is poorer in sodium. An exploratory run with $\text{Na}_{0.97}\text{Sb(l)}$ in NaCl-NaI gave $\nu = 0.41 \pm 0.07$, with saturation at 1.8 ± 0.4 mol % and 568° , compared with about 1.6 mol % at 608° from Figure 3. In contrast, only about 1.1 mol % NaSb dissolves in NaCl-NaI (70:30) (rather than 37:63) at 694° .

Discussion

The melt solubilities of the bismuth and antimony alloys with sodium are the largest for the heavy metals studied and give the most information. The evidence obtained suggests that the process involves the solution of substantially ionic sodium compounds in the melt. A complete description of the solution equilibrium of course requires knowledge of the activities in the melt as well as in the metal phase or at least some faith that the melt species behave ideally. Fortunately the activities for the liquid sodium-bismuth alloys at 900° have recently been reported by Fischer and coworkers.¹⁶ Furthermore they made the very suggestive observation that the data over the entire composition range could be described quite well by a quasi-ideal model involving ideal solutions of the components and of the assumed species NaBi and Na_3Bi , with formation constants of the latter from the components of about 300 (K_1) and 2×10^5 (K_2), respectively. (These are the only compounds found in the binary system, melting at 446° ¹⁵ and 842° ,¹⁶ respectively.) If it is assumed that the same species dissolve in the NaCl-NaI melt, the two distribution constants ($N(\text{melt})/N(\text{alloy})$) of $k_1 = 2.55 \times 10^{-3}$ for NaBi and $k_2 = 0.210$ for Na_3Bi yield the dashed line for total solubility shown in Figure 1 and at the same time describe the observed variation of solute composition fairly well. The observed solubilities are described even better, particularly above 50 atom % Bi, with the empirical constants $K_1 = 600$, $K_2 = 8 \times 10^5$, $k_1 = 7.5 \times 10^{-3}$, and $k_2 = 0.203$. Of course, the deviations otherwise found could well be the result of solution nonideality considering the range of concentrations involved. In any case a preferential solution of Na_3Bi from the alloys is evident from the data; the solubility of the assumed NaBi is too small to ascertain anything definite about its possible association.

The cryoscopic numbers of about 1.1 for Na_3Bi solutions in NaCl-NaI and in NaI are consistent with either a solute $3\text{Na}^+ + \text{Bi}^{3-}$ or an un-ionized Na_3Bi . However, the solution of such a molecular species in an ionic melt would be very unusual. The case for complete ionization is better established by the apparent formation of about four ions in liquid KI (see Results). The substantial positive deviation observed in the liquidus curve (Figure 2C) is in accord with the theory of reciprocal systems in which the components are stable toward the ion-exchange reaction;²¹ this appears to be the case in the present case where coulombic considerations sug-

gest that the reaction $\text{Na}_3\text{Bi} + 3\text{KI} \rightarrow \text{K}_3\text{Bi} + 3\text{NaI}$ should not be favorable.

The solubilities for the sodium-antimony system are not so easily explained. Although there are no activity data for the alloy system at this temperature, the similarity of the antimony and bismuth phase diagrams with sodium tempts a comparable description of the alloy and hence of the species in the melt. However, Na_3Sb and NaSb species in the alloy and their Raoultian solutions in the salt cannot describe the experimental data in the range of about 39–50 atom % Sb in the metal phase. The antimony solubility, Figure 3, shows about a sixfold decrease over this range, with a sharp break near 50 atom % Sb which certainly suggests the presence of NaSb in at least the alloy, but at the same time the Na/Sb ratio in the melt decreases only from about 2.5 to 1.85, corresponding to only a moderate increase in the concentration of the presumed NaSb . Positive deviations of NaSb in the alloy or negative deviations of the same in the melt could be responsible, as could the alternate of an intermediate solute species such as Na_2Sb . Considering the large solubility of Na_3Sb , it is interesting but perhaps coincidental that an estimated entropy of fusion of Na_3Sb (14.8 eu²⁰) leads to a predicted solubility for an ideal solution²² at 608° that is very close to that observed, 12.3 mol % *vs.* ~ 11 mol %.

The cryometric data for the composition Na_3Sb in NaI ($\nu = 1.04$) again are consistent with, but not proof of, an ionic solute $(\text{Na}^+)_3\text{Sb}^{3-}$. Interestingly, the Na-Sb composition gives $\nu = 0.33$, which for a single ionic species corresponds to $(\text{Na}^+)_3\text{Sb}^{3-}$. The same product was inferred (without much evidence for its degree of association) by Zintl, *et al.*,⁵ in liquid ammonia, certainly an extreme in conditions. Solid NaSb is known to contain spiral antimony chains coaxial with larger spirals of sodium,²³ *i.e.*, $\text{Na}_\infty\text{Sb}_\infty$. The antimony chains presumably break up to some extent on fusion, and the solution data suggest the trimeric ion Sb_3^{3-} is extracted into the melt. The curvature of the freezing point-composition curve, Figure 4B, is inconsistent with an equilibrium mixture of polymers, as these would associate on increasing concentration and give positive deviation for the solvent rather than the negative deviation observed. It is noteworthy that the data for the system indicate that a species still richer in antimony may also be obtained in the melts since a 75 atom % antimony alloy is in equilibrium with 1.3 mol % of a solute having an empirical composition near $\text{Na}_{0.37}\text{Sb}$. The formation of Na_3Sb_7 ($\text{Na}_{0.43}\text{Sb}$) was deduced by Zintl, *et al.*,⁵ in liquid ammonia, and such compositions are found in the binary antimony systems with rubidium and cesium.¹⁴

Throughout the previous discussion a significant cosolution of elemental sodium in the NaCl-NaI melt has been neglected. Known data for the Na-NaX binary systems²⁴ indicate that pure sodium should dissolve in

(22) K. S. Pitzer and L. Brewer in revision of G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 228.

(23) D. T. Cromer, *Acta Cryst.*, **12**, 41 (1959).

(24) M. A. Bredig and H. R. Bronstein, *J. Phys. Chem.*, **64**, 64 (1960).

(21) M. Blander, "Molten Salt Chemistry," Interscience Publishers, Inc., New York, N. Y., 1964, p 197.

the mixed halide melt to the order of 5-10 mol % at 900° and, by extrapolation, 0.6-1.2 mol % at 630°. In the sodium-bismuth system at 900° the highest sodium activity in the alloys studied is about 0.1 at 26 atom % Bi,¹⁶ so that the sodium contribution to the solution should be small compared with about 18 mol % Na₃Bi therein. For antimony the extreme case studied involves Na₃Sb(s) in equilibrium with liquid metal containing about 91 atom % Na at 600°,¹⁵ which for an ideal solution of Na and Na₃Sb would correspond to $N_{\text{Na}} = 0.88$. Such would indicate that of the order of 0.5-1 atom % sodium would dissolve in the melt, which is still significantly less than the 2.5 mol % increase in sodium in the melt found on crossing the Na₃Sb composition (Table II).

The solubilities of the Na₃M compounds collected in Table III show a plausible dependence on the nature of the solvent. In general the effect of the anion is most pronounced, the solubility decreasing markedly when NaI is diluted with NaCl for both solid Na₃Bi and liquid NaSb. The change seen for NaSb with different amounts of NaCl is not as clear because of the lack of temperature dependences, though the contrast with pure NaI is obvious. With Na₃Sb(s) the data are insufficient to make the relationship clear. Although many factors are certainly involved, the dependence of solubility on the anion in the sodium melts suggests a simple explanation involving three factors: the smaller work involved in substituting a large solute anion in an iodide melt, the better solvation of the solute anion by sodium when the counteranion of the solvent is large, and, probably the least important, the greater dispersion forces with larger anions. The inferior solvating power of KI vs. NaI is also reasonable in this view. The much smaller solubility of Li₃Bi in LiCl-LiF (70:30), only about 0.05 mol % at 600°,⁷ is striking but involves many variables, the most important of which is probably the greater stability of Li₃Bi(s).²⁰

TABLE III
SOLUBILITY OF BISMUTH AND ANTIMONY ALLOY PHASES
IN DIFFERENT MELTS

Solvent	Saturating alloy compn	Mol % Bi or Sb	Temp, °C
NaI	Na ₃ Bi(s)	5.2	667
NaCl-NaI (37:63)	Na ₃ Bi(s)	~2.8	667
KI	Na ₃ Bi(s)	2.4	667
NaI	NaSb(l)	3.7	655
NaCl-NaI (37:63)	NaSb(l)	2.0	600
NaCl-NaI (70:30)	NaSb(l)	1.1	694
NaI	Na ₃ Sb(s)	11.6	623
NaCl-NaI (37:63)	Na ₃ Sb(s)	11	600

To some extent intermetallic phases and liquid alloys of elements of widely different electronegativities (in the Mulliken sense) should approach salts in their properties so that their solution in salt melts would not be particularly surprising. Valence-type compounds typified by Na₃Sb and Na₃Bi are therefore likely candidates, and in fact these two, both with the Na₃As structure,²⁵ are designated according to Zintl's rules^{26,27} as

(25) G. Brauer and E. Zintl, *Z. Physik. Chem.*, **37B**, 323 (1937).

"salt like," as opposed to the "intermetallic" character of the Cu₃Al structure shown by Li₃Bi. Qualitative indications that Na₃Sb and Na₃Bi differ from typical metallic phases are also given by their brittleness, their steel-blue and blue-violet colors, respectively, and the fact that their enthalpies of formation may be accounted for relatively well in an ionic model.²⁸ Both NaSb and Na₃Sb are semiconductors, whereas Na₃Bi is metallic in its conduction property.^{29,30} Of course the latter is a property of the dense solid state whereas the salt melt solubility presumably manifests an incipient ionic character of Na₃Bi in a more dilute state. Obviously one must then consider solvation of ions and a favorable entropy of solution in competition with metallic binding in the solid phase. A more substantial rearrangement occurs on the transition from the spiral chain structure of antimony in NaSb to small, evidently polyatomic anions in the melt, but in both phases localized metal-metal bonding is important. The AuCu (distorted CsCl) structure for NaBi³¹ certainly puts it in a different category, and at best a small solubility is indicated.

About 30 years ago Heymann and Weber⁶ reported the first indications of the solution of alloys in molten salts. Their qualitative observations were that some heavy metals which in themselves were insoluble in molten NaBr at 770° passed into solution when alloyed with generally unspecified amounts of sodium, namely, bismuth, antimony, tin, and gold. Thallium, cadmium, and lead were, on the other hand, insoluble even in the presence of sodium. The observed solution was correlated with a high enthalpy of formation of the highest melting phase with sodium (for antimony and bismuth) and with a high melting point of this phase relative to the experimental temperature. Thus the insolubilities of thallium, cadmium, and lead were attributed to decomposition of the intermetallic phases since their binary systems with sodium all showed maximum melting points of the order of 400° or lower. Although the observations were only qualitative and were probably complicated by attack of the glass containers (Supremax), they are in substantial agreement with those reported here. Thallium and lead systems show only very small solubilities, $< \sim 0.1$ %, but in their "soluble" group there is a considerable difference between tin and gold (~ 1 %) and the much more soluble antimony and bismuth phases. The melting point of the intermetallic compound does not seem to be as good a criterion with the present data, and an additional bonding consideration seems more pertinent. Solution of heavy metals as simple, monatomic anions is rather unlikely for such as thallium, lead, and tin because of the higher charges required (e.g., Pb⁴⁻) and what must be diminished elec-

(26) E. Zintl, *Angew. Chem.*, **52**, 1 (1939).

(27) W. Klemm, *Proc. Chem. Soc.*, 329 (1958).

(28) P. M. Robinson and M. B. Bever in "Intermetallic Compounds," J. H. Westbrook, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 3.

(29) W. E. Spicer, *Phys. Rev.*, **112**, 114 (1958).

(30) Ya. A. Ugai and T. N. Vigutova, *Soviet Phys. Solid State*, **1**, 635 (1959).

(31) E. Zintl and W. Dullenkopf, *Z. Physik. Chem.*, **B16**, 183 (1932).

tron affinities for the elements. In these cases polyatomic anions of the general sort deduced by Zintl⁵ are presumably better candidates. However the thermal stabilities of these must be limited, and the entropy change for decomposition of at least the more complex examples should be substantial at the temperatures necessary to observe solution in simple molten salts such as the alkali metal halides. Unfortunately the intermetallics of interest readily reduce the useful solvent NaAlCl_4 .

Particularly for bismuth and antimony the explorations reported here indicate the existence of an in-

teresting solution chemistry involving unusual anions, and additional characterization by several means is needed. Emf methods could be particularly useful if electronic conduction in the melts is not bothersome. The small changes in conduction properties generally observed on fusion of pure semiconductors³² suggest that there should not be a substantial electronic conduction in the solutions of NaSb or Na_3Sb , but this property for the Na_3Bi solutions is more uncertain.

(32) A. F. Ioffe and A. R. Regel in "Progress in Semiconductors," Vol. IV, A. F. Gibson, R. E. Burgess, and F. A. Korger, Ed., Heywood and Co., London, 1960, p 238.