[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Miscibility of Liquid Metals with Salts. I. The Sodium–Sodium Halide Systems[1]

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Techniques have been developed for the determination of the equilibria existing between liquid sodium metal and the four sodium halides up to approximately 1050°. All these systems are similar in that a monotectic exists a few degrees below the melting point of the pure salt. Mutual solubility of salt and metal in their liquid phases was actually measured up to approximately 25 mole per cent. Since it increases rather rapidly with temperature it was possible to estimate the temperatures of miscibility in all proportions by extrapolation. For all four systems these were found to be in the neighborhood of 1000 to 1100°. The difference between the monotectic and the consolute temperatures, or the area of immiscibility in the liquid state, thus increases as the salt component changes from fluoride to iodide. Heats of solution of the solid salts in the liquid metal were calculated from the temperature coefficients of solubility. The nature of the liquid metal–salt solutions is discussed briefly and tentatively in terms of the packing of ions and of mutual substitution of electrons and anions.

Introduction

Systems comprising liquid metals with their halogen salts have merited interest in connection with such varied problems as metal "fogs" in fused salt electrolysis,[3] "color centers" in crystals[4] and the existence of metal subhalides.[3,5] These subhalides are usually assumed to contain the metallic element rather than the halogen in an uncommon valence state, *e.g.*, Bi^+ and Cl^- in BiCl, or Ca^+ and Cl^-, rather than Ca^{++} and Cl^{--}, in—controversial—solid "CaCl." Complex cations such as Hg_2^{++} in HgCl[6] seem to have been more generally accepted. While on theoretical grounds the existence of solid subhalides such as CaCl is highly improbable,[7] a considerable solubility of alkaline earth metals in their molten halides, and a low, yet not at all negligible solubility of these halides in the metals has been demonstrated.[8,9] Cubicciotti[10] has recently studied the cerium–cerium chloride system and the effect of various metal chlorides on the solubility of cadmium metal in molten cadmium chloride. The solubility of sodium metal in fused sodium chloride at 800 and 850° has been reported[11] as 4 and 15 mole per cent., respectively. Much smaller values, of the order of 1 mole per cent., for the solubilities of sodium and potassium in their respective molten bromides near 850° have been derived from electromotive force measurements.[12]

While the possibility of producing solid subhalides in the alkali metal–halide systems was considered remote, a new attack on the general problem of miscibility of metals and salts especially in the liquid state seemed worthwhile. The present study is the first in a series devoted to alkali metal–alkali halide systems. These systems were assumed to be the most simple ones among salt–metal systems. It is to be followed by work on other groups of elements later.

Experimental

Methods of sampling different from those usually employed in solubility studies had to be devised. The reactivity and volatility of sodium at high temperatures did not permit the use of quartz even as windows, thus eliminating the possibility of visual observation. In addition, it was imperative that no traces of oxygen or water be present.

Purification of Materials.—The salts of reagent grade were heated in an evacuated quartz test-tube, 2 × 24 in., which was fitted with a rubber stopper and two stopcocks. The pressure did not exceed 5×10^{-2} mm. at any time until a temperature of 500° was reached, when pumping was discontinued and a flow of dry argon was maintained through the tube during the remainder of the process. The temperature was slowly raised to approximately 50° above the melting point and held there for one hour. After slow cooling to room temperature, clear fragments of fused salt found in the center of the ingot were stored in a desiccator over phosphorus pentoxide while the top and bottom portions were discarded.

In the case of sodium fluoride a covered platinum boat in a McDanel porcelain tube was employed.

Fusion reduced the ratio of surface area to mass, and thus the amount of atmospheric gases and moisture adsorbed. It also removed the last traces of moisture from the salt. The salts purified in this way gave a negative test with phenolphthalein for free alkali in water solution.

The sodium metal was heated to a temperature slightly above its melting point and forced through a sintered stainless steel filter into a stainless steel beaker containing mineral oil. The filtering process effectively removed the oxide which is insoluble in the liquid metal at that temperature.

Design of Containers for Equilibrations.—The several forms of containers used in these tests were constructed of type 316 or 304 stainless steel tubing with 0.035″ wall. Both types exhibited very little if any corrosion under the test conditions. However, type 316 was better for use with sodium bromide and iodide as the other was darkened slightly by these salts.

Because considerable segregation occurred on cooling even when the container was quenched in a mixture of ice and water, it was necessary to separate sample portions of the phases at the test temperature and to keep them separated during the cooling period.

For sampling the heavier, salt-rich phase containers of the type shown in Fig. 1a, b, were employed. The side-arm of the tube shown there was used to hold a stainless steel ball (Fig. 1a) which by tilting the capsule could be transferred to the constriction, thus sealing off the lower portion of the salt-rich phase (Fig. 1b).

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(2) This paper is based on a thesis by J. Warren Johnson presented to the Department of Chemistry of the University of Tennessee in partial fulfillment of the requirements for the Ph.D. degree, December, 1953.

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(7) *Cf. e.g.*, O. K. Rice, "Electronic Structure and Chemical Binding," McGraw–Hill Book Co., New York, N. Y., 1940, pp. 244–249.

(8) E. D. Eastman, D. D. Cubicciotti and C. D. Thurmond, "National Nuclear Energy Series," Vol. IV, **19B**, "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," edited by L. L. Quill, p. 6–12, 1950.

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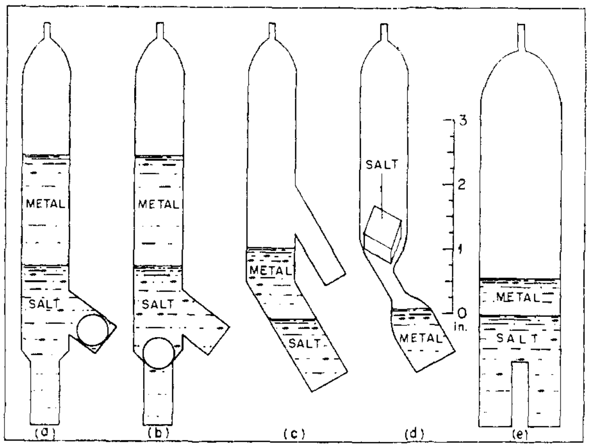

Fig. 1.

To sample the less dense, metal-rich phase a container (Fig. 1c) was designed, which permitted decantation of a portion of the equilibrated metal-rich phase into a side arm.

To determine the solubility of sodium metal in the *solid* salts a *straight* tube was employed. The tube was crimped almost closed above the metal charge (Fig. 1d) and a fragment of the salt, too large to fall through the crimped section even after equilibration, was placed in the tube above the crimping.

Tubes containing a thermocouple well (Fig. 1e) were used to obtain cooling and heating curves for the determination of the melting points of the pure salts and the monotectic temperatures of the four systems.

Cleaning, Loading and Sealing of Capsules.—To remove the oxide scale[13] from the containers they were immersed for 20 minutes, at a temperature of 60–70°, in a solution containing five weight per cent. ferric sulfate and ten volume per cent. sulfuric acid. After rinsing with water the tubes were treated for 15 minutes with a solution containing 15% nitric acid and 2% hydrofluoric acid by volume. They were rinsed again, scrubbed with a brush to remove any loose scale, and dried at 110°.

The salts were weighed and loaded into capsules in a dry box containing dry nitrogen. The capsules were then immediately attached to a vacuum line by means of a glass ball joint inserted through a one-holed rubber stopper.

The sodium metal, stored under mineral oil, was cut into cylinders with a cork borer and the top and bottom of the core discarded. The cylinder of sodium metal was weighed under mineral oil, rinsed in hexane, and placed in the capsule while still wet with hexane. The capsule was again evacuated to a pressure of 1×10^{-3} mm. or less. Gentle heating of the capsule melted the sodium and facilitated the removal of hexane.

After evacuation the capsules were removed from the vacuum line by sealing off the glass tube with a torch, crimped flat in a large vise for a length of $^3/_4$ in. at a point 2 in. below the top of the tube, and sawed off at the crimp. The edges of the cut were welded together with a Heliarc Welder.

For the equilibrations in the ball capsules 30, 22, 34 and 40 g., respectively, of sodium fluoride, chloride, bromide and iodide were used with enough sodium metal to make 40 mole per cent. of free metal. The size of the salt charges was so chosen that the level of the molten salt phase would be above the side-arm when the capsule was in a vertical position.

For the capsules designed for decanting the metal-rich phase, charges of 8, 6, 10, 11 g., respectively, of the salts were used together with 10 g. of sodium metal. The weights of the salts were such as to give approximately 4 ml. of pure molten salt. This was not large enough to flow into the side-arm when it pointed downward with the tube in a horizontal position.

Furnace, Temperature Measurement and Equilibration of Sample.—A 3 in. bore Marshall tube furnace 16 in. long, having ten external taps for the attachment of shunt resistors to eliminate the temperature gradient, was used. The furnace could be tilted from a horizontal to a vertical position and during equilibration was mechanically rocked at a rate of 18 cycles a minute in the horizontal position through an angle of 20°.

A stainless steel tube 20 in. long and $2^7/_8$ in. outside diameter was used as a furnace liner and container for the inert atmosphere maintained around the capsule.

Temperatures were measured with several chromel–alumel thermocouples spot welded along the capsule. The e.m.f. of the thermocouples was read on a Brown Electronik recorder, the major part of the voltage being bucked by a Rubicon precision potentiometer. The recorder had a chart span of 3 mv. graduated in 0.01 mv. corresponding to 0.25°. The recorder reading was checked periodically by measuring the entire e.m.f. on the precision potentiometer. The method of spot welding thermocouples to the capsule rendered calibration of individual couples impractical. However, couples prepared in this manner gave the same voltages as the conventional fused tip type when checked at the melting points of the four salts used.

The capsules were mounted rigidly in a stainless steel holder furnished with a lead-out tube for thermocouples and clamped to the top of the strainless steel liner. During the equilibration period, usually two to three hours, the capsules were oriented with the side-arm upward to allow uninterrupted flow of the contents from one end to the other. In the salt phase tests stirring was aided by the ball rolling back and forth in the main body of the tube. After the equilibration the capsule was first rotated 180° in the furnace to trap the ball in the side-arm and then the furnace was turned to a vertical position to allow the phases to separate. After that the furnace was tilted slightly to allow the ball to fall from the side-arm and to seal off the sample portion of the salt phase. In the metal phase tests, after equilibration no rotation of the capsule as above was performed but the furnace was turned to a vertical position. After a brief period of gentle tapping to facilitate phase separation, a portion of the metal phase was decanted into the side-arm by tilting the furnace momentarily.

Using the same thermocouples in all runs two cooling curves were obtained on each pure salt, then two curves on the metal–salt mixture. This was followed by two more curves on the pure salt.

Analytical Methods.—The salt phase samples were analyzed by dissolving in a mixture of ethyl alcohol and distilled water and titrating with standard acid. From the weight of the sample and the alkalinity the mole per cent. of free metal could be calculated. The metal phase samples were dissolved in alcohol and water, the alkalinity developed was determined with nitric acid, and the halide ion determined as the silver salt. Compositions calculated from these alkalinity and halide determinations were usually in excellent agreement with values calculated from the alkalinity and total weight of the sample. The sodium fluoride was weighed directly since it was found to be quite insoluble in alcohol containing sodium ethoxide.

Results and Discussion

The measurements of this investigation are summarized in Tables I, II and III and Figs. 2, 3 and 4. All four systems investigated exhibit monotectic reactions a few degrees below the melting points of the pure salts. Both the melting points and the monotectic temperatures were derived from halts in cooling curves. The term "monotectic," following the practice of the metallurgists (*cf.* "Metals Handbook of the ASM," 1948, page 9), is used here rather than the term "upper eutectic" which has been used by others, but which does not properly apply to the reaction of a liquid to form on cooling a solid plus another liquid of different composition. Distinct kinks (Fig. 4, log mole fraction of salt *vs.* $1/T°$ K.) in the curves for the solubilities of the salts in the liquid metal occur at the same temperatures at which cooling curves for salt-rich compositions show large evolution of heat (essentially the heat of fusion of the salt). This

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[13] "Metals Handbook," edited by Taylor Lyman, American Society for Metals, Cleveland, Ohio, 1948, p. 585.

TABLE I

EQUILIBRIUM COMPOSITIONS IN THE SODIUM–SODIUM HALIDE SYSTEMS

Salt	Salt phase Temp., °C. ± 3°	Salt phase Mole % sodium	Metal phase Temp., °C. ± 3°	Metal phase Mole % salt
NaF	979	0.19[a]	801	2.4[b]
	983	0.96[a]	849	5.3[b]
	1000	7.6	900	8.1[b]
	1001	15.8	952	10.7[b]
	1015	14.8	976	14.6[b]
			983	16.4[b]
			1004	17.3
			1026	19.5
			1048	20.0
			1078	23.6
NaCl	750	0.08[a]	550	0.12[b]
	784	0.11[a]	649	0.75[b]
	790	0.15[a]	750	1.8[b]
	809	2.8	781	2.2[b]
	811	2.8	784	2.4[b]
	826	4.9	790	2.9[b]
	889	9.3	832	4.2
	890	10.2	874	5.8
	929	21.3	913	8.3
	949	25.6	957	11.1
	950	25.1		
	975	27.8[c]		
	976	32.0		
	1001	33.0		
NaBr	650	0.04[a]	550	0.21[b]
	685	0.07[a]	600	0.41[b]
	720	0.15[a]	660	1.1[b]
	750	4.5–4.7	687	1.3[b]
	799	6.8	721	2.4[b]
	849	6.4	757	3.3
	852	7.3	825	4.6
	909	12.2	894	7.8
	943	14.7	955	12.1
	953	14.7–15.3		
NaI	674	3.1–3.3	550	0.06[b]
	722	4.1	584	0.28[b]
	763	6.2	608	0.60[b]
	810	8.3–8.3	637	0.80[b]
	849	9.9	652	1.2[b]
	909	14.9	699	1.5
	954	20.8	800	2.8
			882	5.7
			959	10.5

[a] Solubility in *solid* salt phase. [b] The phase in equilibrium with the liquid metal phase is *solid* salt. [c] Equilibrated one hour only.

TABLE II

SUMMARY OF PRINCIPAL DATA FOR SODIUM–SODIUM HALIDE SYSTEMS

Salt	M.p., °C. ±0.5	Monotectic Temp., °C. ±0.5	Monotectic Solid salt, mole % Na	Monotectic Liquid salt, mole % Na	Monotectic Liquid metal, mole % salt	Consolute (estimated) Temp., °C.	Consolute (estimated) Mole % salt
NaF	995	990	~1	(2)[a]	17.0	(1100)[a]	(30)[a]
NaCl	803	794	~0.2	2.4	2.3	1060 ± 40	40
NaBr	747	740	~0.3	4.2	3.4	1090 ± 50	50
NaI	661	656	. . .	2.9	1.4	1110 ± 50	40

[a] Rough estimate.

TABLE III

MELTING POINT DEPRESSIONS

Salt	M.p. salt, °K.	ΔH[a]fusion, cal./mole	Mole fraction metal	ΔT^0 Calcd.	ΔT^0 obsd.
NaF	1268	7800	(0.020)[b]	(8)[b]	5
NaCl	1076	6800	.024	8	9
NaBr	1020	6100	.042	14	7
NaI	934	5200	.029	10	5

[a] National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Washington, D. C., 1952, Series II, pp. 796–797. [b] Rough estimate.

permits drawing a horizontal line across the equilibrium diagram at the monotectic temperature, and is proof of the assumption that no solid compounds such as Na_2X exist at these temperatures. No indications were obtained for the occurrence of such compounds at any other temperatures and their existence is considered highly improbable, even though Ag_2F is known. In this respect the sodium systems seem to resemble those of the alkaline earth metals. The more recent study[8–10] appears to have refuted former allegations[5a] of the existence of compounds, *i.e.*, subhalides such as CaCl.[14] In the sodium systems comparatively large positive temperature coefficients of mutual salt–metal solubility permit extrapolation to what definitely appears to be consolute, or critical solution temperatures, at and above which only one liquid phase exists. These temperatures are rather moderate, namely, in the vicinity of 1000 to 1100°. The estimated compositions at these temperatures are listed in Table II. The only record found in the literature of a salt being completely, *i.e.*, in all proportions, miscible in liquid phase with a metal is the finding, reported recently,[15] of a consolute temperature of 1010° in the system Ba–$BaCl_2$. Some slight indications of this phenomenon have appeared in the calcium chloride–calcium metal system,[8,9] but a strong temperature dependence of the solubility of the salt in the metal seemed to be missing in that case. Lorenz and Winzer[11] mention having observed a rapid increase in the solubility with temperature of sodium metal in fused sodium chloride and "complete disappearance of the metal phase at temperatures above 850°." However, it was not made clear how the phenomenon was observed and whether "disappearance of the metal

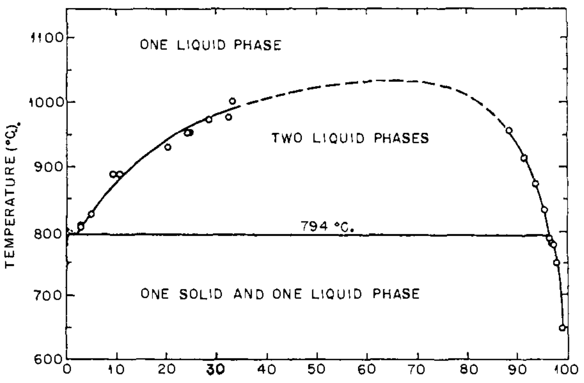

Fig. 2.—Sodium chloride–sodium system.

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(14) *Cf.*, however, latest evidence for CaCl in reference (5b).

(15) Harald Schäfer and Andreas Niklas, *Angew. Chem.*, **64**, 611 (1952).

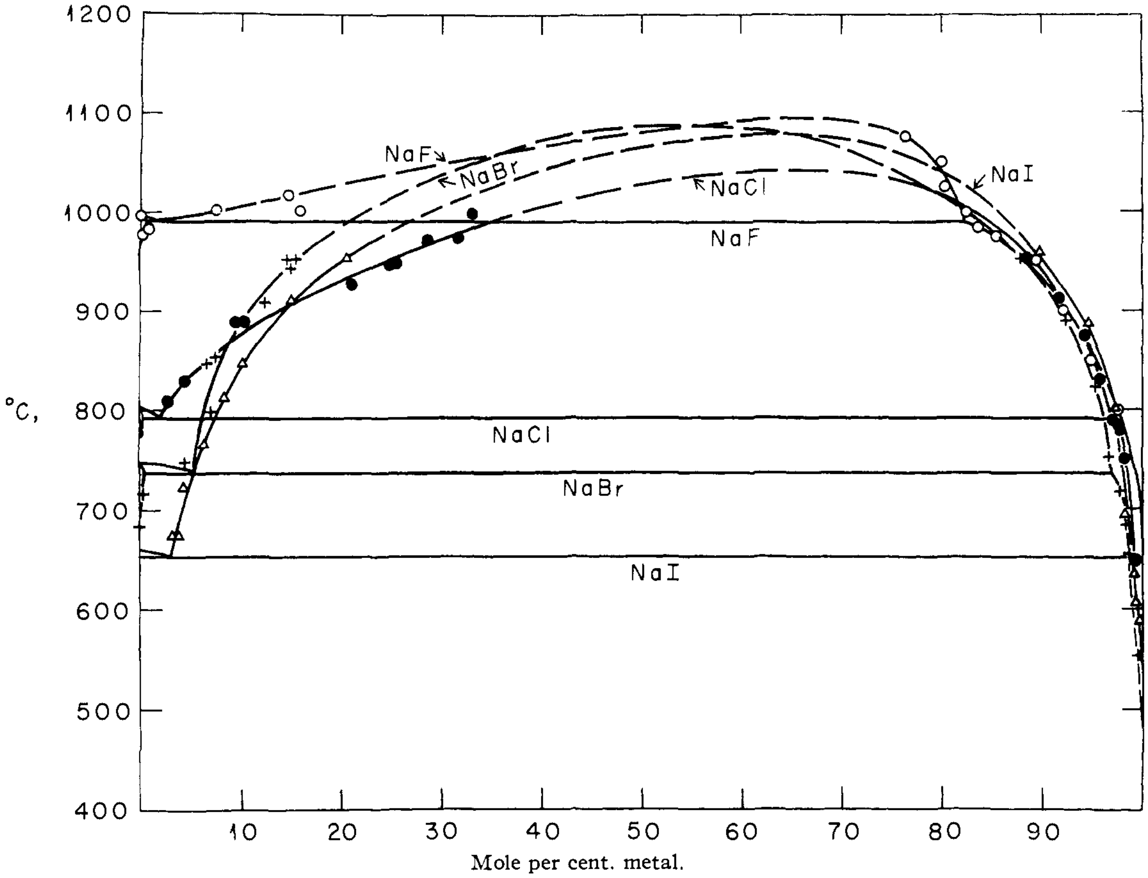

Fig. 3.—Sodium halide–sodium metal systems.

phase" referred to a given limited amount of metal rather than to miscibility in all proportions. In investigations of similar salt–metal systems to be reported in a later paper, it was possible to make measurements actually at and above consolute temperatures, and thus directly demonstrate complete miscibility. This was not feasible in the present study because of mechanical difficulties connected with sampling the liquid salt phase near and above 1000°. Experimental techniques are at present being modified in an attempt to extend these measurements to higher temperatures.

The four systems dealt with here are not only rather similar with respect to the consolute temperatures, but Fig. 3 also reflects a high degree of similarity in the solubilities at any given temperature. This is particularly pronounced on the metal side of the diagrams. This behavior indicates the predominant influence of the metal as a solvent for these various salts, and the lesser importance of the variation of the anion of the salt.

The depressions of the melting points of the salts produced by the addition of sodium metal, $\Delta T_{\text{exp.}}$, were measured, as described, with a precision better than $\pm 0.5°$. They are compared in Table III with depressions, $\Delta T_{\text{calc.}}$, obtained by means of the Clausius–Clapeyron equation

$$\Delta T_{\text{calc.}} = \frac{RT^2}{\Delta H_f} \times N_2$$

with the assumption of Raoult's law, or ideal solution (ΔH_f = heat of fusion of salt). The mole fraction N_2 of metal in the salt-rich monotectic liquid was arrived at by using the intersection of the solubility curve of the metal in the liquid salt phase with the monotectic horizontal. With this somewhat uncertain extrapolation, the agreement between calculated and experimental depressions for sodium chloride and their disagreement in the cases of sodium bromide and sodium iodide may not be significant. The disagreement, if real, could be indicative of either solutions of sodium metal in the solid salts or of considerable deviation from ideality even in the comparatively dilute liquid solutions, or most probably a combination of both. The data of Table I indicate a solubility of sodium in solid sodium bromide at the monotectic temperature of not more than 0.3 mole per cent., *i.e.* not large enough to contribute significantly to the disagreement.

The solubility values for the solid salts in the liquid metal (Table I and Fig. 4) were measured in the range between temperatures slightly below the monotectics and 550°. In this region where the solubility of the metal in the solid salts is negligible, an at least approximately straight line function is indicated between the logarithm of the solubility and the reciprocal of the absolute temperature. From the slopes of these lines the following partial heats of solution per mole of salt, at saturation, are obtained—NaF–Na, 26 ± 2; NaCl–Na, 20 ± 3; NaBr–Na, 24 ± 1; and NaI–Na, 28 ± 2 kcal. It is interesting to note that the fluoride does not fit the trend of decreasing heats of solution from iodide to chloride. This trend may be connected with the decreasing degree of disturbance produced in the liquid metal structure by the smaller anion when substituted for an electron. The concept of substitution of halide ions for electrons is a convenient one in thinking of the structure of the solution of the salts in the liquid metal. With increasing salt concentration there is naturally a transition from the liquid metallic structure to that of the liquid salt. It is possible in most general terms to use in the salt-rich solution the same concept of substitution, in this case, of electrons for halide ions. However, especially when the results of measurements of the physical properties such as electronic conductance or electrical transport, Hall effect, magnetic susceptibility, density, viscosity and optical or infrared absorption are available, it will be desirable and perhaps feasible to specify more definitely the state of the electron introduced by the metal atom. An interaction of calcium atoms and Ca^{++} ions, perhaps equivalent to the formation of the complex cation Hg_2^{++} from Hg^{++} ions and Hg atoms in solid or fused HgCl, has been assumed in the solutions of calcium metal in calcium chloride.[8] In the case of the alkali metals, there could also be Na_2^+, etc., ions. The valence electron engaged in this interaction may be confined to such a molecule ion. On the other hand it may be mobile enough to contribute electronic conductance to the solution and thus be assigned, not to a pair of sodium cores, but, by analogy to the band theory of solids, to the conduction band of energy levels.

Reference may also be made here to a structural picture for the solutions of the alkaline earth and other metals in their fused halide salts, advanced by D. D. Cubicciotti on the suggestion of D. Harker.[10] It was proposed that what was then considered a comparatively high solubility (not more than 40 mole per cent. in the case of Ba in $BaCl_2$) was largely due to the presence of "octahedral holes" in the packing of the anions of the fused salt, only half of which are occupied by the cations in the case of the dihalides. Part of the other half was thought to be thus available for occupancy by solute metal atoms, which would enter into some sort of interaction with the ions of the salt, particularly the cations. What was then considered to be known as a much lower solubility of the alkali metals in their halides (*e.g.*, of the order of one mole per cent. of potassium in potassium bromide[12]) was attributed to the filling of all the "octahedral holes" in the anion structure of the alkali halide since its stoichiometric composition is one cation per anion. The results of the present investigation, with its finding of very high solubilities at least at the higher temperatures, seemingly, but not necessarily, contradict this picture. If the two groups of systems were to be compared at a given temperature and at the same partial pressures of the metal, sodium metal would exhibit perhaps a 1/1000 smaller solubility in its salts than the alkaline earth metals in theirs.

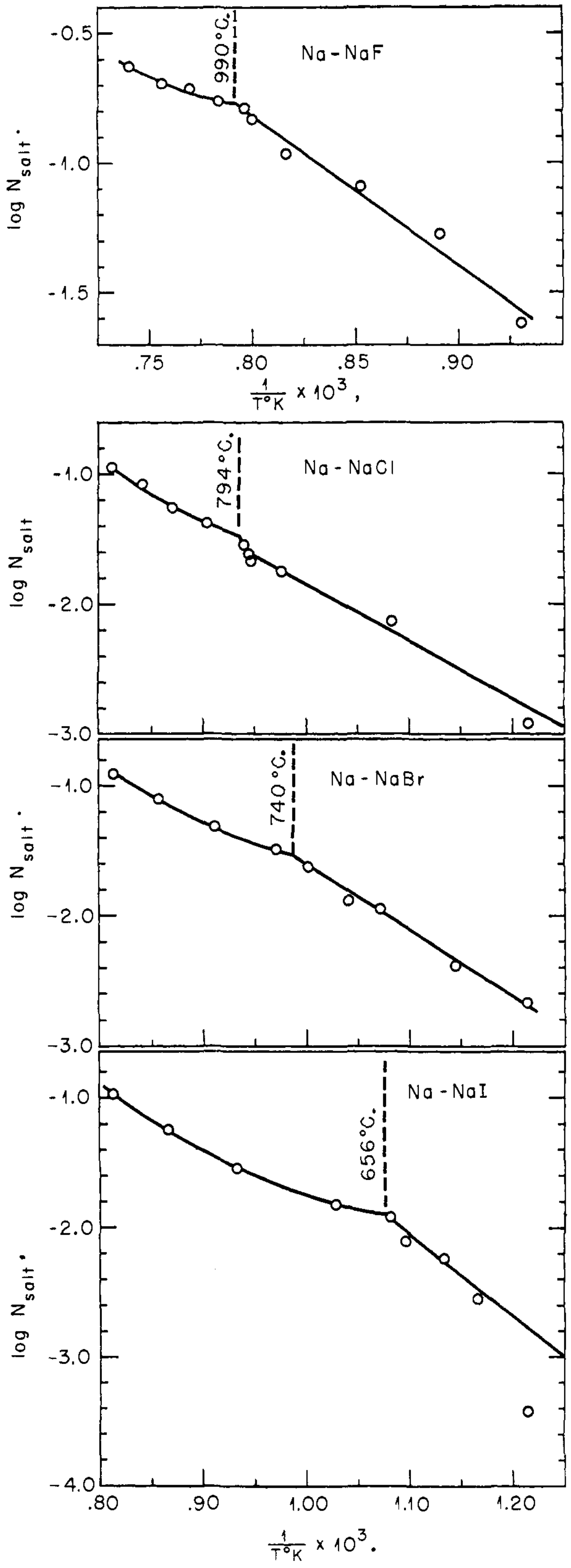

Fig. 4.—Solubility of sodium halides in sodium metal (N_{salt} = mole fraction of salt).

A very great discrepancy exists between the present results and those obtained by E. Mollwo[12] in 1935 on the basis of electromotive force measurements. From the latter a value not exceeding one mole per cent. at 870° was derived for the solubility of sodium in fused sodium bromide, but the present determinations show a solubility of 9 ± 0.5 mole per cent. at that temperature (Table I and Fig. 3). It is difficult to establish with certainty the cause of this discrepancy. The use of glass for the cell and of platinum for the electrodes, both of which are very likely to be heavily attacked by alkali metals, raises serious doubts as to whether the potentials measured were representative of the sodium concentration cell as believed by the investigator or rather of some other not immediately obvious electrode process.

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[Contribution from the Department of Chemistry of The University of Texas]

The Ammonolysis of the Halides of Carbon(IV)[1]

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The rate of formation of guanidine and ammonium iodide from carbon tetraiodide and ammonia increases with temperature from 25 to 150°. Ammonolysis, however, is complete at 100° and the limiting rate in the formation of guanidine is the reaction of an intermediate which may be cyanogen iodide; the reaction is markedly catalyzed by iodide ion. With carbon tetrabromide and ammonia at 125°, ammonolysis is rate limiting; this reaction is catalyzed by ammonium bromide and other ammonia-soluble bromides. Carbon tetrachloride and ammonia do not react at an appreciable rate at temperatures below 300°; at this temperature, however, ammonolysis is rate limiting as in the case of the tetrabromide. Copper and iodine, previously reported as catalysts for this reaction, are relatively ineffective; the ammonolysis is catalyzed by ammonium iodide and conversions in excess of 80% have been observed.

On the basis of the available information relative to the interaction of ammonia and the normal halides of the non-transitional elements of Group IV, it appears that with increase in atomic number there is a decrease in tendency toward solvolytic cleavage and an increase in tendency toward the formation of stable ammonates.[2-10] Although only very limited information is available relative to the halides of carbon(IV), it should be anticipated that just as they are completely hydrolyzed to carbonic acid and hydronium halide,[11] so complete ammonolysis should yield ammonium halide and the nitrogen system analog of carbonic acid, *i.e.*, the ammonocarbonic acid, guanidine.[12] Alternatively, by analogy with partial hydrolysis of carbon tetraiodide to iodoform and hypoiodous acid,[13] comparably extensive ammonolysis should yield iodoform, and iodoamide which is the nitrogen system analog of hypoiodous acid.

It is commonly considered that carbon tetrachloride is unreactive toward ammonia[14] although Stähler[15] has reported that at 140° (*i.e.*, above the critical temperature of ammonia), carbon tetrachloride reacts with ammonia in the presence of copper and iodine to provide a 35–40% yield of guanidine together with lesser quantities of hydrocyanic acid and cyanogen. Apparently the ammonolysis of the other halides of carbon(IV) has not been studied.

The experiments described below are concerned with the interaction of ammonia and the chloride, bromide and iodide of carbon(IV).

Experimental

Materials.—The following materials were prepared and purified by the methods described in the literature to which reference is made: carbon tetrabromide,[16] carbon tetraiodide,[17] cyanogen iodide,[18] cyanuric iodide,[19] silver cyanamide,[20] bismuth(III) iodide,[21] aluminum(III) bromide.[22] X-Ray diffraction data for carbon tetrabromide, carbon tetraiodide and silver cyanamide are given in Table I. All other materials consisted of reagent grade chemicals, or were prepared for use as described previously.[23]

Analytical Methods.—With the exception noted below, all analytical determinations were made using standard procedures.

Guanidine was determined as the picrate in the manner described elsewhere[23] except that the solubility correction factor that must be added to compensate for the appreciable solubility of guanidine picrate was redetermined as a function of temperature. From a stock solution containing 989 mg. of high purity guanidine nitrate dissolved in 100 ml. of water, 10-ml. aliquots (each equivalent to 233 mg. of guanidine picrate) were taken and each was treated with 300 mg. of ammonium iodide, 40 ml. of water and 85 ml. of saturated ammonium picrate solution. Duplicate samples were equilibrated at 25, 30 and 35°, and from the weights of guanidine picrate found, it was computed that the correc-

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[1] This work was supported in part by the U. S. Navy, Bureau of Ordnance, Contract N123s-67363, Task Order I.

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