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CLEVELAND 17, OHIO

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

The Electrical Conductivity of Solutions of Alkali Metals in their Molten Halides[1]

BY H. R. BRONSTEIN AND M. A. BREDIG

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The electrical conductivity of alkali metal solutions in their molten halides has been measured by means of a synthetic sapphire conductance cell. The *specific* conductance *increases* with increasing metal concentration. The *equivalent* conductance of K, Λ_K, in both KCl and KBr also *increases*, namely, from 2800 ohm^{-1} cm.^{2} (K–KCl, 820°), 6100 (K–KBr, 760°) and 6500 (K–KBr, 870°) at infinite dilution, to 38,000, 83,000 and 71,000 ohm^{-1} cm.^{2} at 19, 23 and 20 mole % K, respectively, the maximum concentrations measured. However, Λ_{Na}, for Na in NaBr at 895° *decreases* from 12,500 to a minimum of 7300 ohm^{-1} cm.^{2} at *ca.* 9 mole % metal. At 805° Λ_{Na} in NaBr decreases from *ca.* 12,000 at infinite dilution, *i.e.*, approximately the same value as at 895°, to less than 5000, and in NaCl at both 845 and 890° from *ca.* 6000 to less than 3000 ohm^{-1} cm.^{2}. These values are the equivalent conductances at 5, 4 and 3 mole % Na, respectively, representing the metal solubility limits which are too low to permit the equivalent conductance minima to be realized. The different behavior of sodium and potassium may be related to the liquid phase equilibria and to the dissociation energies known for the diatomic gaseous metal molecules, both of which reflect a greater tendency to associate for Na than for K at the test temperatures. Such association, which increases with metal concentration, decreases the number of metal particles per equivalent of metal on which the electronic fraction of the conductance is thought to depend. The effect of the association, not strong enough in the K systems to produce a minimum in equivalent conductance, is, in the Na systems, surpassed, at the minimum, by the effect of the gradual establishment of the metallic conductance band through overlap of the orbitals of the metal polymers. The differences in equivalent conductance at infinite dilution for the various systems may be taken to reflect the influence of the different degrees of polarization of the anions by the cations on electron mobility.

Introduction

Concurrent with the determination of the phase equilibria in the sodium–sodium halide,[2] cesium–cesium halide,[3] potassium–potassium halide[4] and rubidium–rubidium halide[5] systems, a study of some of the more significant physical properties of these solutions was undertaken. Of various measurements, which should help elucidate the state of the electron introduced by the metal atom, such as those of electrical conductance and transport, viscosity, Hall effect, magnetic susceptibility and optical or infrared absorption, the determination of the electrical conductance, as a function of composition and temperature, was chosen as most readily attainable experimentally at the present time.

The literature shows examples of a decrease rather than an increase in electrical conductance on addition of metal to salt in the systems $CdCl_2$–Cd,[6] $BiCl_3$–Bi[7] and $CaCl_2$–Ca.[8] In $CdCl_2$–Cd, this effect was attributed to the formation of $(Cd{:}Cd)^{2+}$ analogous to the complex cation Hg_2^{++}. The existence of similar ions, *e.g.*, K_2^+, in the case of the alkali metal solutions also would lead to a decrease in specific conductance. If, however, the M_2^+ ion is a shallow trap for the electron, an increase in the specific conductivity could be expected. Other models for electron traps from which electrons similarly as in solid semi-conductors would be raised by thermal energy into the conduction band might stress similarity with color centers in halide crystals. However, such similarity has been disputed in the past, and undissociated metal atoms were assumed to be present in the molten state of F-center-colored halides.[9] In any case, additive behavior with respect to electrical conductance, which would correspond to an increase by a factor of little less than 100 of the specific conductivity of the pure salt for every mole per cent. of alkali metal added, is not anticipated. Rather, a pronounced negative deviation from additivity is expected, as the environmental forces acting on the electron in the solution, irrespective of the special model accepted, differ greatly from that in the pure metal.

Experimental

Apparatus.—The reactivity and volatility of the alkali metals at high temperatures necessitated the rather complicated apparatus to be described (Fig. 1). Quartz was not used for the dip cell as it is strongly attacked by alkali metals at high temperatures. Hot pressed beryllium oxide, though resistant to attack by alkali metals, was slightly porous. Single crystals of magnesium oxide, also resistant to alkali metal attack, were subject to easy fracture. Finally, a cell constructed from a large, single crystal of synthetic sapphire, Al_2O_3, was found excellent for use in these solutions. It cannot, of course, be used in fluoride salt melts.

The rotatable turret and entry ports were necessary for introducing the liquid alkali metal as well as the cell and sampler assemblies. The closure pads were incorporated in the apparatus to eliminate as much as possible the loss of alkali metal from the solution by vaporization and diffusion to the cold portion of the apparatus. The auxiliary heaters around the shield tubes permitted the cell and sampler to be heated to the solution temperature, so that their entry into the solution would not cause localized change in concentration by partial solidification of the salts.

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[1] Work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, operated by Union Carbide Nuclear Company, Oak Ridge, Tennessee. Presented at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 8–13, 1957.

[2] M. A. Bredig, J. W. Johnson and Wm. T. Smith, Jr., THIS JOURNAL, **77**, 307 (1955).

[3] M. A. Bredig, H. R. Bronstein and W. T. Smith, Jr., *ibid.*, **77**, 1454 (1955).

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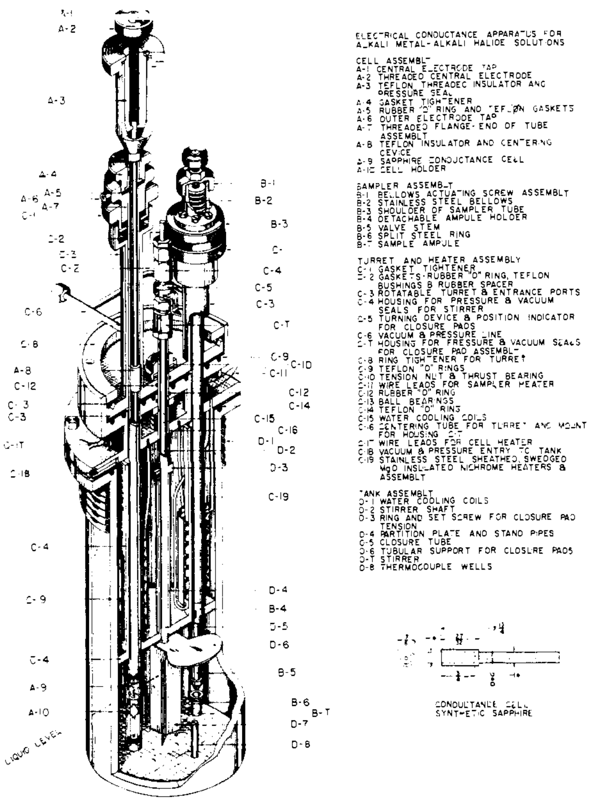

Fig. 1.—Apparatus for measuring electrical conductance of solutions of metals in molten salts.

The stirrer permitted agitation of the solution periodically and eliminated concentration gradients in the solution, due to some reflux of metal condensing from the vapor.

The apparatus, then, consists of a tank portion D, constructed of 347 stainless steel pipe of 5″ i.d. and 5.5″ o.d. of over-all height of 13.75″. The tank, partitioned by a horizontal plate with shield tubes D-4, is fitted with a mechanical, hand-operated stirrer, D-7, and closure pads, D-7, that are actuated through pressure seals, C-4 and C-7, in the upper portion of the apparatus. A pointer indicates the position of the pads on a calibrated scale not illustrated. Two thermocouple wells, D-8, extend 1.5″ and 2.75″, respectively, into the bottom unit.

The turret and heater assembly C consists of a rotatable plate containing the two entry ports, C-3, closure plate to the tank, the heater assemblies, C-19, and entries for vacuum and pressure lines, C-6, C-18. The rotatable turret was constructed of a circular plate 6.25″ diameter × $^1/_2$″ thick, the entry ports were of $^3/_4$″ pipe, schedule 40, 1.050″ o.d., 0.824″ i.d. welded onto the plate at 3.25″ centers. The sampler and cell port were 6$^1/_8$″ and 7$^5/_8$″ in height, respectively, including 1″ for the threaded gasket well. The center of the plate contained a $^5/_8$″ diameter hole for placement of the turret onto the centering tube, C-16, which also acted as a guide tube for the closure pad assembly. A groove was machined out along the outer top edge of the turret plate for a ball bearing run. The ring tightener, C-8, is seated upon the ball bearings. The tension nut and thrust bearing, C-10, allows pressure to be applied to the center of the plate. This design permits good sealing by the rubber backed Teflon "O" rings, C-9. Rubber "O" rings are placed in machined grooves, C-12, as further protection against pressure leaks. This design permits the rotation of the turret without affecting the pressure seal. The heater elements were made from stainless steel-sheathed, swaged, magnesia-insulated nichrome wire. The coiled heater cables were fastened to stainless steel envelopes by welding, and the envelopes were supported by tie rods to the closure plate as illustrated. The sheathed cables were brought out through the closure plate and the sheath welded to the plate. Coiled copper tubing for water cooling, C-15 and D-1, are for the protection of the Teflon "O" rings.

The cell assembly is a dip cell arrangement consisting of a central electrode, A-2, extending into the cup of the sapphire cell, A-9, the other electrode being represented by the main body of the cell assembly. The main tube of the assembly is made of 0.675″ o.d., 0.423″ i.d. 347 stainless steel pipe. The tip of the central electrode can be positioned inside the cup of the conductance cell by means of the threaded portion at the top and the threaded Teflon plug, A-3. For ease of cleaning the main tube, the central electrode is fitted to the tube at A-5 by means of a rubber "O" ring and Teflon gaskets and tightened to the flanged end of the assembly, A-7. A Teflon sleeve, A-8, acts as a centering device.

The cell holder, A-10, an open end tube, is threaded to the main tube. Slots in the holder give the solution free access to the cell. The sapphire cell, A-9, is positioned by two tiers of three pins each near the top and bottom of the capillary tube. The cell is supported by a knife-edged pin under the cup. The over-all length of this assembly is 33 inches.

The sampling device is a long stemmed valve actuated through a stainless steel bellows, B-2. The stem of the valve is welded to the top of the bellows. The top of the bellows is attached to the actuating screw assembly, B-1, by means of a flat head bolt passing through the hollow lifting screw. The upward travel of the lifting screw against the flat headed bolt opens the valve, the downward travel closes the valve. The sample ampule, B-7, 1$^1/_8$″ in height, $^3/_8$″ i.d., $^1/_2$″ o.d. with a $^1/_{16}$″ × $^1/_{16}$″ shoulder at the top, slips into the sample holder, B-4, with its shoulder supported by the inner shoulder of the ampule holder. The ampule is held in place by a split steel ring, B-6, placed in the groove provided. The ring provides the necessary anchorage of the ampule for sufficient force to be placed on the upward thrust of the valve stem to break the stopper loose from its seat in case some self-welding occurs. The over-all length of this assembly is 27 inches. The casing of the sampler tube is 0.675″ o.d., 0.423″ i.d.

The synthetic sapphire cell was constructed from a solid boule of single crystal Al_2O_3 of approximately $^5/_8$″ diameter and 3″ in length. The cup was first cut to a depth of $^3/_4$″ by a $^1/_4$″ diameter diamond-edged doughnut cutter. The capillary was drilled in the ultrasonic Cavitron drilling machine by means of a hollow stainless steel tube of 0.040″ o.d. with a carborundum–water slurry.

The capillary was not of uniform dimensions, 0.040″ i.d., due to the length of the drilling. Also, in starting the bore, some widening near the cup portion occurred. The conductivity cell is shown in Fig. 1. The outer and inner portions of the cup were polished to a high degree of smoothness, to prevent wetting of the cell by the solution and establishment of an electrical path from inside the cup over to the outer solution.

To each entry port, supports (not shown in illustration) are mounted for attachment of safety rods, which prevent the cell and sampler assemblies from being blown out of the entry ports in case of failure of the gaskets.

The alkali metal injector was constructed of tubing of the same dimension as that of the cell assembly tube. To one end was welded a connecting flange, and the bottom end closed by welding to it a narrow tip having a small hole (No. 80 drill) in its side.

The tank portion was set to a depth of 9″ into a large vertical tube furnace of 6″ i.d. by 24″ in height. The furnace was provided with 12 shunts to reduce the thermal gradient. Four chromel–alumel thermocouples were spot-welded on the outside of the tank spaced between the bottom and the partition plate.

Temperatures were measured in a manner previously described.[2]

Procedure.—Chemical reagent grade salts were predried at 180° for several days before loading into the apparatus. The salt was further dehydrated in the apparatus by vacuum drying at temperatures up to 50° below the melting point until a pressure of 20 μ of Hg was obtained. At this point, the apparatus was pressurized with argon to 43 p.s.i. absolute using a nullimatic pressure regulator, and the salt melted. After reaching test temperature, thermal gradients were removed by adjusting the furnace shunts.

Reagent grade potassium metal came as cast rods of approximately 1″ diameter by 2.25″ in length. Approximately $^1/_4$″ was cut off from either end, and a center core was obtained by using a tubular cutter of $^7/_{16}$″ diameter. This operation was carried out under mineral oil. The center cores contained 0.27% sodium, by spectrographic analysis, and 0.3% oxygen, determined[10] using the Wurtz reaction. Similarly, sodium metal contained 0.2% potassium and 0.1% oxygen. The small hole in the bottom of the injector tube was sealed by allowing molten salt to freeze into it. This seal prevented the alkali metal from being prematurely ejected into the entry port. The alkali metal cores were washed with dry hexane to remove the mineral oil, and the predetermined charge obtained by weighing under hexane. To the gasketed flange of the tube is bolted a plate having connections through valves for attachment of vacuum and pressure lines. As a precautionary measure against small leaks, a rubber tube was slipped over the bottom of the tube and clamped shut. The excess hexane adhering to the cores was removed by evacuation. After pressurizing the injector with 3 p.s.i. of argon, the rubber tube was removed, the injector placed into the cell port and the pressure seal tightened. The sampler assembly was placed into the other port. The ports, at first evacuated, were then pressurized to the tank pressure by an interconnecting valve. The turret was turned, by means of a special wrench which clamped about the entry ports, to the proper position aligning the entry ports with the shield tubes. The closure pads were rotated by means of the turning device in such a way that only the shield tube for the injector opened. The injector was pushed down into the molten salt, and a short time allowed for melting the plug. Due to an excess pressure of 2 p.s.i. maintained in the injector, the molten metal was forced out through the small hole into the molten salt. During this period, the stirrer was actuated, either by hand or by motor. The injector was then pulled up into the entry port, and the closure pads and turret rotated to the closed positions. After releasing the argon pressure, the injector was removed.

The cell and sample assemblies were introduced into the tank in a similar way and positioned into the heater zones. The heater current was adjusted to the amperage necessary to raise the cell and sampler to the solution temperature as previously calibrated. After 1 hr., the closure pads were moved to allow both the cell and sampler to be pushed down into the solution. The cell depth was determined by observing the point of first electrical contact for the central electrode.

Resistance measurements were made with a Leeds and Northrup precision "Jones" bridge. No mutual inductance effects were noted because of the close proximity to each other of the electrodes. Resistance measurements made at 500, 1,000, 2,000 and 10,000 c.p.s. varied less than 0.3%. The conductance cells were calibrated in 1-demal aqueous potassium chloride solution at 25.00° and rechecked in the pure molten salts using the values of Van Artsdalen and Yaffe.[11] Agreement to within 0.2% was found. The cell constants were of the order of 300 cm.$^{-1}$. The resistance of the cell was found to be determined exclusively by the solution within the capillary. Recalibration of the cells after usage, with 1-demal aqueous potassium chloride and with pure molten salt, showed that the cell constants had not changed by more than 0.1%.

A special jig was used for removing the sample ampule from the holder. The jig consists of clamps to hold the main tube of the sampler body and a screw piston to press against the sample ampule. This arrangement permitted the removal of the ampule holder and the cleaning of the outside of the ampule and the valve stem before breaking the valve seat. The ampule and material adhering to the valve stopper was weighed. The sample was first treated with ethyl alcohol, under a protective blanket of argon for controlled reaction with the alkali metal, before water was added for final dissolution. Weight of the sample and alkalinity determined by titration gave the free metal content.

Results and Discussion

Table I contains the results for the following solutions: sodium dissolved in molten sodium bromide, sodium in molten sodium chloride, potassium in molten potassium chloride and potassium in molten potassium bromide. Maximum concentration limits in the case of the sodium bromide and sodium chloride solutions were imposed by the phase equilibria and the temperature limitation of the apparatus.[12] In the measurements on the potassium solutions in chloride and bromide, made above the consolute temperature, the limitation was imposed both by the cell constant of the cell employed and the sensitivity of the bridge.

TABLE I

CONDUCTIVITY OF SOLUTIONS OF ALKALI METALS IN THEIR MOLTEN HALIDES

Potassium–potassium chloride			Sodium–sodium chloride		
Temp., °C.	Mole % metal	Sp. cond., ohm^{-1} cm.$^{-1}$	Temp., °C.	Mole % metal	Sp. cond., ohm^{-1} cm.$^{-1}$
818	0.50	2.600	851	0.30	4.156
818	1.03	2.910	852	1.10	4.673
818	2.65	4.032	843	1.47	5.336
804	3.58	5.451	844	2.93	5.894
818	3.61	6.102	845	3.10	5.661
811	7.24	13.995	854	3.16	6.255
823	8.16	17.160			
814	10.60	30.410	896	0.81	4.526
823	11.27	32.390	889	1.87	5.692
821	16.15	93.190	891	3.84	6.540
809	18.93	144.45	895	3.87	6.513
			895	4.25	7.381
859	4.23	6.980			
862	4.53	7.700			
Potassium–potassium bromide			Sodium–sodium bromide		
759	0.55	2.313	801	0.45	4.043
763	1.98	4.231	801	0.50	4.008
766	5.25	10.628	799	1.19	5.161
763	7.85	20.353	806	1.40	5.359
761	9.80	28.054	805	2.53	6.634
763	10.30	32.437	805	2.79	6.800
761	11.84	50.226	797	4.12	7.899
767	14.52	67.695	802	4.86	8.450
765	16.30	86.500	808	4.97	8.525
763	16.70	94.363	811	5.20	8.919
761	16.95	119.77			
764	19.80	155.70	886	0.24	3.853
761	22.75	346.00	890	1.17	5.815
			894	3.34	9.505
874	1.51	4.152	896	5.84	12.715
872	2.45	5.580	896	5.85	12.511
870	5.00	12.659	896	6.64	14.495
868	7.91	25.736	897	7.04	15.755
872	10.71	40.974	897	8.92	18.465
871	12.25	63.551	896	9.10	18.291
868	14.81	84.162			
872	16.10	124.56			
871	16.70	135.39			
866	20.04	239.54			

Figure 2 is a plot of *specific* conductance as a function of concentration expressed in mole per cent. metal. The *specific*, and thus also the *molecular*, conductance of the solution increases continuously in all four cases with the addition of the metal. This distinguishes these systems from others, for instance cadmium in molten cadmium chloride, where the specific and molecular conductivity of the solution was found to decrease with the addition of metal.[5] As a consequence, the equiva-

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[12] It was as a result of this investigation that the earlier data[3] for the solubility of Na in NaCl were found to be in error. A paper on this subject is in preparation.

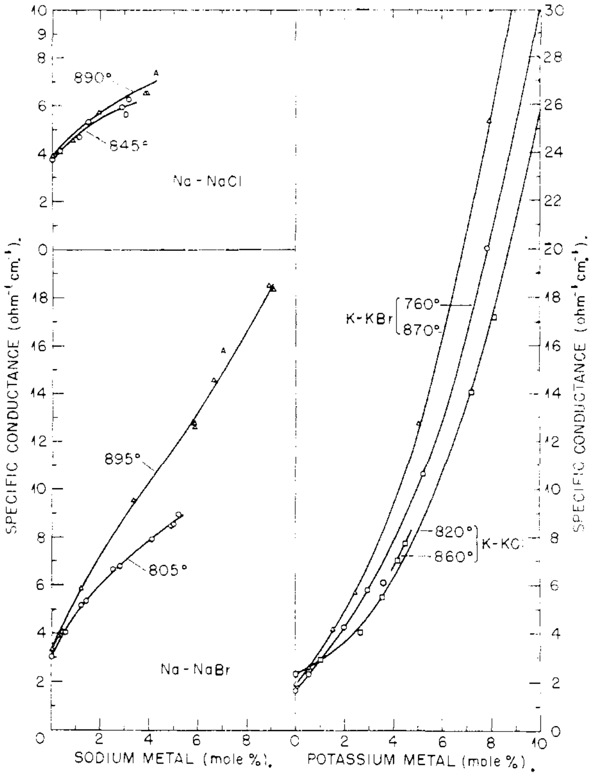

Fig. 2.—Specific conductance of solutions of sodium and potassium metals in their molten chlorides and bromides.

lent conductance of cadmium in dilute solution was computed to approach 8 ohm^{-1} cm.^2, that is, an order of magnitude smaller than the salt and several orders of magnitude smaller than that of the metal in the alkali halide solutions. The decrease in molecular conductance of the solution in the case of cadmium has been attributed to the formation of complexes such as Cd_2^{2+}. In spite of the observed large increase in molecular conductance in the case of alkali metal solutions, the formation of Na_2^+ or K_2^+ ions cannot be ruled out. The contribution to the total conduction of comparatively few mobile electrons would far outbalance any decrease in the mobility of the cations by complexing. Any possible small decrease, of the order of 1 ohm^{-1} cm.^2 per mole % of metal, due to complexing, in the equivalent conductances of the salts, which are of the order of only 100 to 150 ohm^{-1} cm.^2, would be lost in the very much larger increase, of the order of 100 ohm^{-1} cm.^2 per mole % metal, of the molecular conductance of the solutions.

In order to calculate the equivalent conductance of the metal, Λ_{metal}, additivity of volumes is assumed, which seems to be indicated by some preliminary density determinations. Another approximation is involved in the assumption—admittedly less valid at high than at low metal concentrations—that the product of the mole fraction of the salt and its equivalent conductivity essentially represents the contribution of the salt to the measured molecular conductance of the solution, or, for the purposes of this discussion, the equivalent conductance of the salt is not materially altered by the presence of the metal. The following simple equation, then, was used

$$\Lambda_{metal} = \frac{\kappa_{soln}V_{soln} - X_1\Lambda_{salt}}{X_2}$$

X_2 = mole fraction of the metal
X_1 = mole fraction of the salt
κ_{soln} = specific conductivity of the soln.
V_{soln} = molar volume of the soln.

The density and specific conductivity of the molten salts were taken from the data of Van Artsdalen and Yaffe.[11]

Figure 3 is a plot of the equivalent conductance of the metal, calculated from smoothed curves of the specific conductivities, as a function of concentration expressed as mole per cent. metal. This plot shows that the two types of sodium solutions differ quite strikingly from the two types of potassium solutions studied thus far. The potassium solutions exhibit a continuous increase of the equivalent conductance of the potassium metal. The values at infinite dilution are approximately 2,800 ohm^{-1} cm.^2 for the K–KCl at 820°, 6,100 and 6,500 ohm^{-1} cm.^2 for the K–KBr at 760 and 870°, respectively. At the highest concentrations measured thus far, the values are 38,000 for 19 mole % K at 820° in the chloride, 83,000 and 71,000 ohm^{-1} cm.^2 for 23 and 20 mole % K in the bromide at 760 and 870°, respectively. In the Na–NaBr solutions, on the other hand, the equivalent conductance decreases at 895° from approximately 12,000 at infinite dilution to a minimum of 7,500 ohm^{-1} cm.^2 at approximately 9 mole % of metal. The conductance should increase with further addition of sodium; however, the solubility limit of sodium in the salt already has been reached at this temperature.

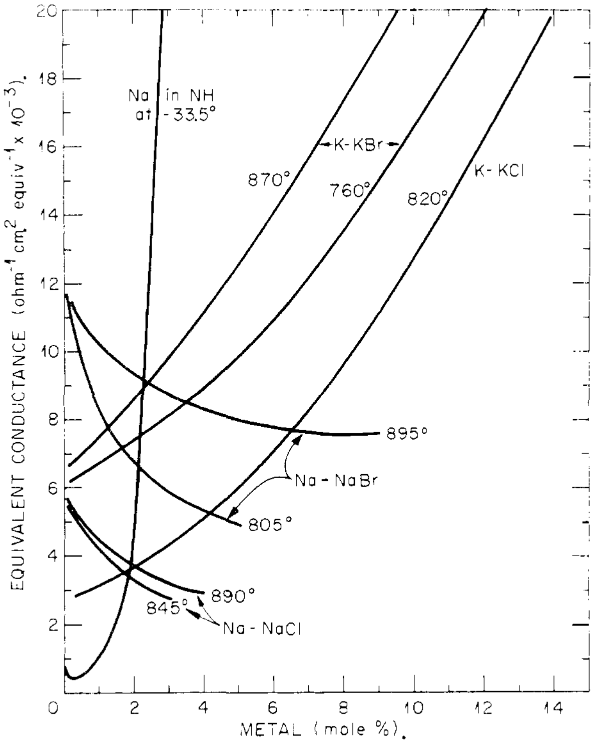

Fig. 3.—Equivalent conductance of sodium and potassium metals in their molten chloride and bromide solutions.

At 805°, the same system exhibits a steeper decrease, and a minimum is also approached but not reached because of the limited solubility of the metal at this lower temperature. In the Na–NaCl solutions, the equivalent conductance of the metal decreases from approximately 6,000 ohm^{-1} cm.^{2} at infinite dilution, and again because of limited solubility, the minimum is not reached at either the high or low test temperatures.

Before a complete theoretical discussion of the conductance mechanism can be attempted, more must be known about other physical properties of these solutions. However, based on the results of this investigation, a tentative interpretation is developed which appears to be in accord with the present experimental observations.

The ionization energy, which is greater by approximately 1 e.v. for sodium than for potassium, does not seem to be a critical factor. At infinite dilution, the equivalent conductance of the sodium metal is not lower but is higher than that of potassium by several thousand ohm^{-1} cm.^{2}. With the increase in the equivalent conductance of sodium, after it has passed through the minimum, the low-energy "conduction band," characteristic of the pure metal, must gradually be established. The data indicate some mobility of electrons at infinite dilution, but as the concentration of sodium is increased, the product of mobility and number of electrons per equivalent of metal is found to decrease. A lowering of the number of mobile electrons might result from association of sodium to polymers, among which Na_2 molecules might be predominant. This would cause a shift, to higher values than without association, of those metal concentrations expressed as atom per cent., at which the gradual establishment of the metallic conduction band by overlap of the orbitals of the metal molecules occurs in the salt melt.

With this explanation, it is possible to connect the observed difference in the behavior of the sodium and potassium solutions with differences in the corresponding phase diagrams[2,4] at the temperature of the conductance measurements. The test temperatures of 800 to 900° in the case of the sodium solutions were far below the consolute temperatures of these two systems (1,080° for Na–NaCl and 1,026° for Na–NaBr).[13] The separation into two immiscible liquid phases is linked with some sort of association of one of the components. Furthermore, the freezing point depressions of both NaCl and NaBr by the sodium differ from the ideal depressions in a manner which may be explained by association of the solute, sodium metal, possibly to Na_2 molecules, which are known to exist in the vapor state in equilibrium with Na atoms.[14] The K–KBr and K–KCl systems[4] show less association of the potassium as indicated by a less rapid deviation from ideality in the freezing point depression of the salt with concentration than in the sodium systems. Most significant is that the test temperatures were well above the consolute temperatures of the systems, 790° (K–KCl) and 728° (K–KBr), where the solutions approach ideality, *i.e.*, monatomic dispersion of the potassium metal in the molten salt.

With an increase in temperature, causing dissociation of the sodium polymers, to some sufficiently high temperature above the consolute, it is expected that the conductance behavior of the sodium solutions would resemble that of the potassium solutions.

The increase, with the atomic number of the halide ion, in the equivalent conductance of the metal at infinite dilution (*e.g.*, Λ_{0Na}, in bromide = 12,000, as against 6,000 ohm^{-1} cm.^{2} in chloride), may be related to observations both in aqueous solutions and in solids, that electron transfer between two oxidation states of a metallic element is greatly facilitated by greater polarizability of the anion.[15,16] The similar difference, at infinite dilution, between the solutions of sodium and potassium in the salts with the same anion seems to demonstrate the stronger effect of the polarization with the smaller cation, Na^+, ($\Lambda_{0Na} = 6,000$ against $\Lambda_{0K} = 2,800$ in the chlorides and $\Lambda_{0Na} = 12,000$ against $\Lambda_{0K} = 6,000$ ohm^{-1} cm.^{2} in the bromides).

For comparison, there is included in Fig. 3 the equivalent conductance of sodium metal in liquid ammonia at −33.5°, as measured by Gibson and Phipps.[17] It appears that the state of the electron must be rather different in the two types of solutions. A conductance minimum also was observed in liquid ammonia solutions, but at values of concentration and conductance, of approximately 0.2 mole % and 500 ohm^{-1} cm.^{2}, much lower than in the molten salt solutions. The minimum in liquid ammonia is followed by a much steeper rise than in the molten salts. The initial decrease in NH_3 has been attributed to the decreasing dissociation of the metal atoms into solvated electrons and sodium ions with increasing concentration.[18] The rise is connected with the rapid establishment of a truly metallic type of conductance by the electrons (large mean free path). The fact that the equivalent conductance at infinite dilution is very much larger in the molten salt is perhaps due to the influence of the ions of the salts, which may enhance electron mobility by the mechanism above, involving polarized anions. Part of the large difference in the metallic conductance at higher meta concentration may—in view of the negative temperature coefficient of metallic conductance—be attributed to the large difference in the absolute temperature, four to five times higher for the molten salts than for the liquid ammonia.

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OAK RIDGE, TENNESSEE

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