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## PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE RICE UNIVERSITY, HOUSTON, TEXAS]

# Solubility and the Nature of Bonding in Fused Alkali Halide–Metal Systems[1]

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A solution of an alkali metal in a fused halide of the same metal is discussed in terms of the mixing of the two negative species, halide ions and F-center-like electrons in cavities, within the irregular lattice of positive ions. The positive energy of mixing is related to the excess energy of a hypothetical metal comprising an ionic lattice of F-centers and positive ions over that of the true metal. The theory predicts substantial positive excess entropies of mixing. The solubility data of Bredig and collaborators are shown to be consistent with this model and certain parameters are evaluated for each system.

Systems which show a continuous transition from metallic to non-metallic character are of special interest; examples are solutions of the alkali metals in liquid ammonia and in fused alkali halides. Certain conclusions about the nature of the ammonia solutions were presented recently.[2,3] In the present paper the solutions of metals in fused alkali halides are considered from two aspects. First, a qualitative theory is developed for these solutions and, second, the theory is tested against solubility data and certain parameters are evaluated empirically. These calculations are based upon the extensive experimental results of Bredig and collaborators.[4]

These fused salt–metal systems display thermodynamic properties which, except for the high temperatures, are similar to those expected for mixtures of normal non-polar molecular liquids. These latter systems are commonly called regular solutions. It seems surprising that such qualitatively dissimilar substances as fused salts and liquid metals should dissolve in one another in such a simple way. We shall show first that such behavior is, indeed, to be expected, and second, that these systems differ in behavior from regular solutions of molecular liquids in small but significant details.

**Theory.**—A homogeneous mixture, either solid or liquid, of an alkali metal with a halide of the same metal may be regarded as a mixture of the two negative species: the halide ions and the valence electrons of the metal. The positive ions are all the same and will comprise a lattice, regular for the solid or irregular for the liquid, with negative species in the cavities between these positive ions. In the solid state there is difficulty in mixing negative species of substantially different size. Liquid solutions generally show no difficulty in accommodating different sized species and the data on solutions of fused alkali halides[5] conform closely to Raoult's law.

In the range where the salt is the abundant species the electrons from the metal must be confined to isolated cavities. These are the well known F-centers in the solid state. In the liquid state the cavities need no longer conform to the size of the halide ions, but otherwise they should be like F-centers. The formation of such a solution may be considered in two steps: first, the conversion of the metal to a hypothetical ionic lattice of positive ions and F-centers, and second, the mixing with the metal halide. The energy change in the second step would be expected to be small, consequently the observed energy of mixing can be related to the excess energy of the hypothetical ionic lattice metal.

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[1] This research was initiated at the University of California and was assisted by support from the U. S. Atomic Energy Commission. It was reported in part at the International Congress of Pure and Applied Chemistry, Montreal, Canada, August, 1961.

[2] K. S. Pitzer, *J. Am. Chem. Soc.*, **80**, 5046 (1958).

[3] T. A. Beckman and K. S. Pitzer, *J. Phys. Chem.*, **65**, 1527 (1961).

[4] (a) M. A. Bredig, H. R. Bronstein and W. T. Smith, Jr., *J. Am. Chem. Soc.*, **77**, 1454 (1955); (b) J. W. Johnson and M. A. Bredig, *J. Phys. Chem.*, **62**, 604 (1958); (c) M. A. Bredig and H. R. Bronstein, *ibid.*, **64**, 64 (1960); (d) M. A. Bredig and J. W. Johnson, *ibid.*, **64**, 1899 (1960).

[5] E. Aukrust, *et al.*, *Ann. N. Y. Acad. Sci.*, **79**, 830 (1960); R. P. Tastogi and K. T. Varma, *Trans. Faraday Soc.*, **53**, 1165 (1957).

A model of this sort for metals was proposed by Thomson[6] in 1922 and doubtless by others. In our calculations on this model the treatments of F-center wave functions and other properties by Tibbs[7] and by Gourary and Adrian[8] were used to guide the choice of reasonable parameters. The sodium chloride structure was adopted which is equivalent to a cubic closest packed metal. The positive ion radius (Pauling) together with the molal volume of the metal yield the radius of the spherical cavity. It is assumed that the electron spends 70% of the time within the cavity volume which is taken as that of the sphere touching the nearest positive ions increased to include half of the additional empty space associated with the given lattice site. Some overlap of electron orbitals is permitted in view of the probability that at least half of the neighboring electrons will have antiparallel spin. The exact choice of parameters is not essential; these values are reasonable in view of Tibbs' and Gourary and Adrian's results. The usual Madelung formula is used for the electrostatic lattice energy, and the quantum mechanical formula for the energy of a particle in a spherical box yields the kinetic energy of the electron in the cavity. The experimental lattice energies of the real metals are greater than those calculated on this model by 19 kcal./mole for Li, 18 for Na, 10 for K and 9 for Rb and Cs.

These calculations show that the dissolving of an alkali metal in a fused halide of the same metal with a positive heat of solution of several kcal./mole is reasonable. Let us now consider the entropy change to be expected. There is first the entropy of nearly random mixing of unlike species—the usual term for ideal solutions. In addition the electron spins will be uncoupled in the process yielding a positive term $R \ln 2$. Furthermore, the F-centers probably are less rigid in both size and shape than are halide ions. Consequently the vibration frequencies of the surrounding positive and negative ions will be reduced on formation of the solution and this will yield an additional positive entropy contribution. Consequently we may expect substantial positive excess entropies of mixing.

Let us now turn to the other side of the phase diagram where the salt is the dilute component. In this case the metal electrons remain in a metallic state and the halide ions represent foreign particles. Since these foreign particles carry a negative electrical charge, the metal electrons will tend to avoid them by electrostatic forces. Nevertheless the size and rigidity of the halide ions will interfere with the metallic electron system. The halide ion itself will be surrounded by positive ions much as in the pure alkali halide.

It is not easy to calculate the magnitude of this interference of the halide ion with the metallic electron system. Calculation for a neutral sphere from which the neutral particles of a Fermi gas were excluded yielded much too large an effect. But this is to be expected since the correlation of electron motion by the charge of the halide ion would have reduced the free electron density at the ion below the average value. The calculated electron densities for metallic electrons around defects or fixed charges by March and Murray[9] and by Cowan and Kirkwood[10] are informative in this connection. For example, the curves given by Cowan and Kirkwood show for parameters appropriate for sodium a very low density of other electrons out to a radius of 1.3 Å. from a given negative charge. The approximations made by Cowan and Kirkwood probably yield too complete a correlation of electron motion at short distances, but they show that an ion such at $F^-$ with radius 1.4 Å. should cause only a moderate interference with the metallic electrons.

It is found experimentally that fused alkali fluorides are remarkably soluble in the metals. At the respective melting points of the fluoride salts the solubilities are: Na, 17%; K, 40%; Rb and Cs, miscible in all proportions.

The larger halide ions will interfere more with the metallic electrons, particularly for the lighter metals. While the qualitative picture seems clear, it did not prove feasible to make any numerical estimates of the energy of this interference.

Again the entropy effects must be considered. In this case the electron spins remain mostly paired. But the restraining forces for vibration of the alkali metal ions in the metal are much less than in the halide. For example, the vibration frequency of Na in the metal is about 100 cm.$^{-1}$ as inferred from the heat capacity data whereas the $Na^+$ *vs.* $Cl^-$ vibration frequency in NaCl is approximately twice as great or 200 cm.$^{-1}$. The metal ions surrounding an isolated halide ion in solution in the metal may be slightly more restrained than in the pure metal but this effect should be small. Hence, we expect an excess entropy of solution of halide in metal corresponding to the decreased restraint to vibration of the metal ion and presumably also of the halide ion. In view of the three directions of vibration and the frequencies mentioned above, the excess entropy may be expected to fall in the range from $3R \ln 2$ to $6R \ln 2$ or 4 to 8 cal./deg. mole for NaCl in Na.

**Solubility Equilibria.**—Let us now consider the solubility data of Bredig and collaborators[4] in terms of these expectations. Since these very difficult experiments at high temperatures are necessarily of limited precision, it is best to emphasize the solubility itself and to be cautious about derivatives. We take ideal solution behavior (Raoult's law) as a point of departure and deal with excess functions. In particular the excess partial molal Gibbs free energy of the i-th component or the excess chemical potential is

$$\Delta\bar{F}_i^E = \Delta\mu_i^E = \Delta\mu_i - RT \ln x_i = RT \ln \gamma_i$$

where the reference state is the pure liquid component.

In the case of solid salt in equilibrium with solution the usual freezing point equations apply with heats of fusion given by Dworkin and Bredig.[11] The effect on salt activity of any metal dissolved in the solid salt was neglected.

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[6] J. J. Thomson, *Phil. Mag.*, **43**, 721; **44**, 657 (1922).

[7] S. R. Tibbs, *Trans. Faraday Soc.*, **35**, 1471 (1939).

[8] B. S. Gourary and F. J. Adrian, *Phys. Rev.*, **105**, 1180 (1957).

[9] N. H. March and A. M. Murray, *Proc. Roy. Soc. (London)*, **A256**, 400 (1960).

[10] R. D. Cowan and J. G. Kirkwood, *Phys. Rev.*, **111**, 1460 (1958).

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

The case of two liquid phases is more complex in that the activity of the abundant component (solvent) in each phase is decreased somewhat from unity. Where the solubility is small, however, it is easy to estimate the activity coefficient $\gamma$ of the solvent with sufficient accuracy and then to calculate $\gamma$ for the same component as the solute in the other phase. As the solubilities increase at higher temperatures, it is sometimes necessary to use successive approximations with the assumption at this stage that the regular solution equation

$$RT \ln \gamma_i = \Delta\mu_i^0(1 - x_i)^2 \qquad (1)$$

applies accurately enough for the small corrections to solvent activity. $\Delta\mu_i^0$ is the excess chemical potential at zero concentration which is also the difference in chemical potential between the solute and solvent standard states. Where the two components have substantially different volumes the corresponding equation

$$RT \ln \gamma_i = \Delta\mu_i^0(1 - \phi_i)^2 \qquad (2)$$

was used where $\phi_i$ is the volume fraction. The solute activity coefficient is just $\gamma_i = a_i/x_i$ where $x_i$ is the solute mole fraction and $a_i$ has been estimated from the composition of the other phase in which $i$ is the solvent.

The data on sodium systems cover a particularly extensive temperature range and will be treated first. Most of the values come from liquid–liquid equilibria which were corrected by equation 1 except for NaF where equation 2 was used because of the large volume ratio. The results are summarized by the linear expressions for $\Delta\mu_i$ as a function of $T$ in Table I.

TABLE I

EXCESS CHEMICAL POTENTIALS FOR SODIUM HALIDE–SODIUM SOLUTIONS

| Salt | Temp. range, °K. | $\Delta\mu^0_{salt}$, kcal./mole | $\Delta\mu^0_{metal}$, kcal./mole | $T_c$, °K. | $(\Delta\mu^0/RT)$ at $T_c$ Salt | $(\Delta\mu^0/RT)$ at $T_c$ Metal |
|---|---|---|---|---|---|---|
| NaF | 1120–1400 | 10.7–0.004 $T$ | ......... | 1453 | 1.7 | .. |
| NaCl | 1070–1230 | 15.3– .007 $T$ | 18.1–0.009 T | 1353 | 2.2 | 2.2 |
| NaBr | 1020–1230 | 13.7– .006 $T$ | 18.1– .010 T | 1299 | 2.3 | 2.0 |
| NaI | 930–1230 | 14.2– .006 $T$ | 16.3– .009 T | 1306 | 2.5 | 1.8 |

There are several interesting features of the results of Table I. First one notes that the $\Delta\mu^0$ values vary quite appreciably over the temperature range of measurement. The negative of the coefficient of $T$ in each expression is, of course, the excess partial molal entropy. These values must be multiplied by 1000 to convert from kcal. to cal., and have the sign and order of magnitude suggested by the discussion above. Also the $\Delta\mu^0_{metal}$ values are in the range indicated for the excess energy of the hypothetical metal comprised of F-centers and positive ions. This excess energy for the hypothetical sodium metal is, of course, the same for each system in Table I, and we find only a modest variation of the $\mu^0_{metal}$ values for the various halide systems.

The substantial excess entropies found in Table I constitute a departure from the behavior of regular solutions which were postulated by Hildebrand to have ideal entropies of mixing. The effect of volume differences between components has long been discussed for molecular solutions and considerable evidence has accumulated in favor of equation 2 which shows the activity coefficient dependence on volume fraction. If equation 2 holds for each component, then the ratio of the coefficients is expected to follow the equation

$$\frac{\Delta\mu_1^0}{\Delta\mu_2^0} = \frac{V_1}{V_2} \qquad (3)$$

where $V_1$ and $V_2$ are the molal volumes of the respective components. Bredig and Bronstein[4c] gave the following molal volumes: Na, 33; NaF, 22; NaCl, 38; NaBr, 45; NaI, 55 cc. While the ratios of $\Delta\mu_i^0$ values do not conform accurately to equation 3, there is approximate agreement. Indeed, the temperature coefficients of $\Delta\mu^0_{salt}$ and $\Delta\mu^0_{metal}$ differ, and it would be surprising if the temperature dependence of the volume ratio was such to fit equation 3 exactly.

It is also interesting to note the values of $(\Delta\mu_i^0/RT)$ at the critical temperature for liquid–liquid mixing which are given in the last two columns of Table I. The regular solution equation 1 is applicable for nearly equal molal volumes and for $\Delta\mu^0_{salt} = \Delta\mu^0_{metal}$. This equation yields the value $(\Delta\mu^0/RT) = 2.0$ at the critical temperature. The value for Na–NaCl in Table I is 2.2 which indicates a small but significant deviation from equation 1.

The data on the heavier alkali metal systems cover narrower temperature ranges and sometimes show no liquid–liquid phase separation. It is difficult or impossible in most of these cases to unambiguously determine the temperature coefficient of $\Delta\mu$, hence the data are summarized in Table II as $\Delta\mu^0$ values assuming no temperature dependence. As many as three values are given; the basis for each is explained in the table. The values are given as $A_{12} = (\Delta\mu_i^0/V_i)$ which is constant in the volume fraction system of regular solution equations. The value from the critical mixing temperature obviously applies to that temperature. The value from $\gamma_{metal}$ applies at the melting point of the salt while the value from $\gamma_{salt}$ arises from data at temperatures somewhat below the salt melting point.

TABLE II

EXCESS CHEMICAL POTENTIALS FOR ALKALI HALIDE–ALKALI METAL SOLUTIONS

$$A_{12} = \frac{\Delta\mu_i^0}{V_i} \begin{cases} \text{top value from } \gamma_{salt} \text{ at low salt concn.} \\ \text{middle value from } T_c \text{ of liquid mixing} \\ \text{bottom value from } \gamma_{metal} \text{ at low metal concn.} \end{cases}$$

| | Units, cal./cc. F | Cl | Br | I |
|---|---|---|---|---|
| K | 110 | 90 | 80 | 70 |
| | 105 | 78 | 69 | 65 |
| | 115 | 94 | .. | 80 |
| Rb | .. | 70 | 62 | 53 |
| | 82 | 64 | .. | 50 |
| | .. | .. | .. | .. |
| Cs | 45 | 55 | .. | 42 |
| | .. | .. | .. | .. |
| | .. | .. | .. | .. |

Volumetric data for the systems in Table II are sparse at the temperature of interest for these calculations. Literature[12] values were used, but the change to the temperature of interest had to be estimated in many cases. The values adopted were: K, 60; KF, 31; KCl, 49; KBr, 56; KI, 69; Rb,

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(12) See J. W. Johnson, P. A. Agron and M. A. Bredig, *J. Am. Chem. Soc.*, **77**, 2734 (1955), and references there cited.

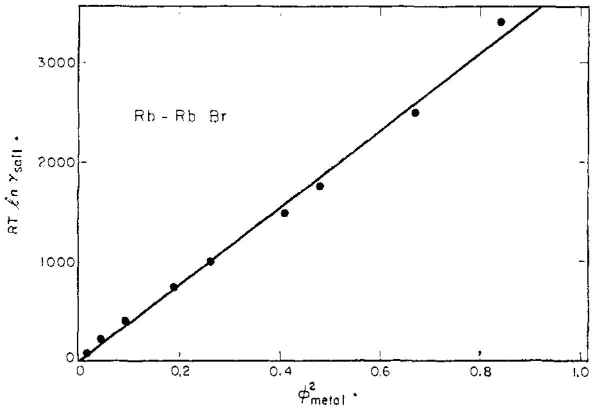

Fig. 1.

70; RbF, 36; RbCl, 54; RbBr, 62; RbI, 76; Cs 85; CsF, 45; CsCl, 60; CsBr, 68; CsI, 81 cc./mole.

The values of $A_{12}$ for the sodium systems from $T_c$ are, respectively, 215, 155, 136, 120 cal./cc., which are considerably larger than those in Table II for the heavier metals. We note that the value of $A_{12}$ from $T_c$ is the lowest for each potassium system and corresponds, of course, to the highest temperature. Presumably this is the result of a large excess partial molal entropy, as was found for the the sodium systems, and which yields a negative temperature coefficient for $\Delta\mu^0$. Where values based upon both $\gamma_{metal}$ and $\gamma_{salt}$ are available in Table II, they are nearly equal, which indicates conformity to the volume fraction equations. This is further indicated in Fig. 1 which shows the data for RbBr in a manner to test equation 2.

## Discussion

The preceding calculations and arguments have shown that the valence electrons from the alkali metal atoms in a metal–fused salt solution may be considered to be a negative ion species much like the halide ions themselves. The general similarity of the solubility properties of these systems to the corresponding properties of mixtures of non-polar molecules has been noted as well as the significant differences. It is clear that the mixing of the two negative species must be nearly random. However, if the metal concentration is high, we know that the valence electrons assume metallic character and that it is no longer a useful approximation to regard a particular electron localized in a particular cavity. One must now regard the array of cavities as an irregular lattice of sites of low potential energy for electrons and solve the many-electron problem for electronic motion in and among these sites. The work of Lax and Phillips[13] shows that the irregular geometry itself does not qualitatively change the electronic energy level pattern. The decisive matters with respect to metallic *vs.* non-metallic character are those discussed by Mott.[14] The overlap of the wave functions between the F-center cavities is a critical factor. As Mott predicts, intermediate states are unstable at low temperatures, and one finds the continuous transition from metallic to non-metallic character only above a critical mixing temperature.

The metal to non-metal transition composition may be taken to be that of the critical point for phase separation. It is interesting to note that this composition is of the order of 50 mole % metal for the fused salt solutions whereas it is only 4.2% metal in solutions of sodium in liquid ammonia. Apparently the electronic wave functions are much more localized in the fused salts than in ammonia.

Additional properties such as electrical conductance[15] can be shown to be consistent with our general model. We may also note that the system[16] Li–LiH appears to be similar to the halide systems.

(13) M. Lax and J. C. Phillips, *Phys. Rev.*, **110**, 41 (1958).

(14) N. F. Mott, *Phil. Mag.*, [8] **6**, 287 (1961); N. F. Mott and W. D. Twose, *Adv. in Phys.*, **10**, 107 (1961); and earlier papers there cited.

(15) H. R. Bronstein, A. S. Dworkin and M. A. Bredig, *J. Chem. Phys.*, **34**, 1843 (1961); also *J. Am. Chem. Soc.*, **80**, 2077 (1958).

(16) C. E. Meiser, *et al.*, *J. Phys. Chem.*, **62**, 220 (1958).

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[CONTRIBUTION FROM THE REACTOR CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY,[4] AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

# Association Constants in the System $AgNO_3$–NaBr–$NaNO_3$ and their Comparison with the Quasi-lattice Theory

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The association constants $K_1$, $K_2$ and $K_{12}$ for the formation of AgBr, $AgBr_2^-$ and $Ag_2Br^+$ have been evaluated from electromotive force measurements in $AgNO_3$–NaBr–$NaNO_3$ mixtures at 402, 438, 460 and 500°. The constants, $K_1$, $K_2$ and $K_{12}$, in mole fraction units, are, respectively, 633, 246 and 280 at 402°, 500, 180 and 200 at 438°, 430, 151 and 167 at 460° and 325, 103 and 120 at 500°. The temperature dependence of the association constants, within the experimental error, is predictable from calculations based on the quasi-lattice model. The differences between values of $K_1$ for the formation of AgBr in $NaNO_3$ and $KNO_3$ are consistent with the "reciprocal coulomb effect."

## Introduction

Measurements of the activity coefficients of $AgNO_3$ in molten $NaNO_3$ in dilute solutions of $Ag^+$ and $Br^-$ ions at four temperatures ranging from 402 to 500° are described in this paper. One of the

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(3) On Sabbatical Leave from the University of Maine with the Reactor Chemistry Division of Oak Ridge National Laboratory, Sept. 1960–Aug. 1961.

(4) Operated for the United States Atomic Energy Commission by Union Carbide Corporation.