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THERMODYNAMIC CONSIDERATIONS IN METAL-METAL SALT INTERACTIONS¹

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ABSTRACT

The free energies of interaction between isolated metal atoms and the molten chloride of that metal were calculated from thermodynamic considerations. Based on the values of these standard free energies of interaction, metal-salt systems can be classified into two categories. First are those systems exhibiting relatively weak interaction energies (less than 30 kcal.); these include primarily the mono- and divalent metals. In the second group are solutions with relatively strong interaction energies (greater than 40 kcal.); these consist of the transition metals and the metals that are normally trivalent. Solutions of the first category appear to consist of strongly-solvated atoms whereas several of the systems in the second group are known to undergo chemical reaction to form a soluble lower-valent cation species in the melt. This classification of metal-salt systems in terms of weak or strong interactions is a more reasonable one than that based on a nonquantitative property such as subhalide formation. For example, it is shown that the interaction energies of systems containing known solid subhalides, e.g., Hg-HgCl_2 and Bi-BiCl_3 , are no larger and in many cases much less than those for other systems with no known subhalide.

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INTRODUCTION

Solutions of various metals in their respective molten salts have been the subject of numerous investigations^{2a}. Although the existence

(2a) See, for example, M. Bredig, Chapter on "Metal-Metal Salt Solutions" in Selected Topics in the Physical Chemistry of Molten Salts, ed. by M. Blander, Interscience, in press.

of such solutions obviously indicates that appreciable interaction must occur between the two components, only limited discussions^{2b,3} of metal-

(2b) M. Blander as quoted in reference 2a.

(3) K. S. Pitzer, J. Am. Chem. Soc., 84, 2025 (1962).

salt systems in terms of these interactions have as yet been put forth. It is the purpose of this paper to calculate the interaction energies involved between isolated metal atoms and the solvent and to attempt to correlate these values with the chemical properties of metal-salt systems. It is proposed that a classification of these systems in terms of weak or strong interaction energies is more meaningful than a classification based on a nonquantitative property, e.g., subhalide formation.

The dissolution of a metal in its fused salt may be considered to consist of the removal of metal atoms from the bulk metal to the gas phase and then the interaction of the atoms from the gas phase with the solvent to yield a solution of concentration C . (The interaction process includes the formation of holes in the solvent to accomodate the metal atoms.) The work required to overcome the cohesive binding energy of

the metal at the temperature T in the first step is equal to the standard free energy of sublimation or vaporization of the metal to a monatomic gas at that temperature. This work (along with that involved in the formation of holes) is then compensated for by the interaction energy arising in the process given by the second step.

THERMODYNAMIC CONSIDERATIONS

Let us consider a solution of a metal M in a molten salt MX_n in equilibrium with the metal in the gas phase above the solution at a temperature T . The concentrations of metal in the two dispersed phases in similar units give a direct comparison of the difference in the free energy required to form the gas and solution phases. Furthermore, it is quite reasonable to assume that at the low metal vapor pressures that prevail at the temperatures under consideration, the gas is ideal. Thus, a measure of the degree of interaction of metal atoms with the solvent may be obtained from the metal concentration in the two phases, and this interaction is independent of the intermetallic binding of the pure metal. For the molten salt solution we shall assume Henry's law is obeyed by the solute and shall use as the standard state for each component the hypothetical solution with a concentration of one mole per liter. Although this standard state is an unusual one for the solvent, it serves to keep all concentrations in terms of moles per liter. Since the standard chemical potential of the solvent drops out of the final equations to be derived, no complications arise from this choice of standard state. For the gas phase, instead of the usual standard state where the fugacity equals one atmosphere, we shall use the gas at a concentration of one mole per liter also. The use of similar concentration

units in the two phases eliminates the physically unimportant contribution to the standard free energy and entropy⁴ of solution which arises

(4) M. Blander, W. R. Grimes, N. V. Smith and G. M. Watson, J. Phys. Chem., 63, 1164 (1959).

from the arbitrary choice of the concentration scale. The standard free energy change will now depend on the properties of the metal gas atoms in the solvent only since the sole change of significance is the environment of the individual metal atoms.

Now, with the vapor and solution phases in equilibrium

$$\mu_M^{(\text{soln})} = \mu_M^{(\text{g})} \quad (1)$$

where μ_M is the partial molar free energy of the metal and the superscripts soln and g denote the solution and gas phases, respectively. When the solution is sufficiently dilute so that Henry's law can be assumed, and if ideal gas behavior holds

$$\mu_M^{(\text{soln})} = \mu_M^{*(\text{soln})} + RT \ln C_M^{(\text{soln})} \quad (2)$$

and

$$\mu_M^{(\text{g})} = \mu_M^{*(\text{g})} + RT \ln C_M^{(\text{g})} \quad (3)$$

where μ_M^* denotes the chemical potential of the metal in the respective standard state.

Equating (2) and (3), we obtain

$$\mu_M^{*(\text{soln})} - \mu_M^{*(\text{g})} = RT \ln C_M^{(\text{g})} / C_M^{(\text{soln})} \quad (4)$$

where C represents the equilibrium concentration of metal in similar

units, e.g., moles/liter, in the two phases. Equation (4) gives the change in the standard free energy of a mole of isolated metal atoms going from the gas phase into solution and this change in the chemical potential or the Helmholtz standard free energy ΔA° includes the energy required for hole formation in the solvent as well as the energy of interaction between individual metal atoms and the solvent. From equation (4) it can be seen that $C_M^{(g)}/C_M^{(soln)}$ equals the Henry's law constant in concentration units. In the application of equation (4) to systems that have been studied, the concentration or partial pressure of the metal in the vapor phase above the solution must be known. Since these values are usually available only for saturated solutions of the metal, where the partial pressure of the metal in the gas phase is equal to the vapor pressure of the pure metal, one is restricted to the consideration of saturated solutions. A similar approach to the above was suggested by Blander^{2b} and used to calculate the interaction energy of a hypothetical alkali-alkali halide melt^{2a}.

In the present study this procedure has been applied to known metal-salt systems and also has been extended to include cases where solid subhalide formation is known to occur, e.g., Hg-HgCl₂, Bi-BiCl₃, Nd-NdCl₃ systems. Needless to say, this method is not restricted to metal-salt solutions but can be applied to any type of saturated solution.

For systems in which a reaction occurs to form a solid lower-valent compound of the type M₂X₂ the above treatment must be modified. For example, in the case of the reaction

let us designate Hg_2Cl_2 , HgCl_2 and the metal by the subscripts 1, 2 and M, respectively. Then for the solid phase in equilibrium with the solution

$$\mu_1^{\circ} = \mu_M^{(\text{soln})} + \mu_2^{(\text{soln})} \quad (6)$$

and

$$\mu_1^{\circ} = \mu_M^{\circ} + \mu_2^{\circ} + \Delta\mu^{\circ} \quad (7)$$

where μ° refers to the pure condensed phase and $\Delta\mu^{\circ}$ is the standard free energy of formation of the solid subhalide from the metal and normal halide. Equating equations (6) and (7) and substituting for μ_M°

$$\mu_M^{\circ} = \mu_M^{*(g)} + RT \ln C_M^{(g)} \quad (8)$$

and for μ_2°

$$\mu_2^{\circ} = \mu_2^{*(1)} + RT \ln C_2^{(1)} \quad (9)$$

where $C_M^{(g)}$ is obtained from the vapor pressure of the pure metal and $C_2^{(1)}$ refers to the pure liquid, we obtain

$$\mu_M^{(\text{soln})} + \mu_2^{(\text{soln})} = \mu_M^{*(g)} + RT \ln C_M^{(g)} + \mu_2^{*(1)} + RT \ln C_2^{(1)} + \Delta\mu^{\circ} \quad (10)$$

Now substituting

$$\mu_i^{(\text{soln})} = \mu_i^{*(\text{soln})} + RT \ln C_i^{(\text{soln})} \quad (11)$$

into (10) for $\mu_M^{(\text{soln})}$ and $\mu_2^{(\text{soln})}$, recognizing that $\mu_2^{*(1)} = \mu_2^{*(\text{soln})}$

and rearranging terms, we find

$$\mu_M^{*(\text{soln})} - \mu_M^{*(g)} = RT \ln C_M^{(g)} / C_M^{(\text{soln})} + RT \ln C_{\text{MX}_2}^{(1)} / C_{\text{MX}_2}^{(\text{soln})} + \Delta\mu^{\circ} \quad (12)$$

where $C_M^{(\text{soln})}$ and $C_{\text{MX}_2}^{(\text{soln})}$ are the equilibrium concentrations of M and MX_2 , respectively, in the saturated solution. For reactions of the type

e.g.,

a similar treatment yields

$$\mu_M^*(\text{soln}) - \mu_M^*(g) = RT \ln C_M^{(g)}/C_M^{(\text{soln})} + \frac{1}{2} RT \ln C_{\text{MX}_3}^{(l)}/C_{\text{MX}_3}^{(\text{soln})} + \frac{1}{2} \Delta\mu^\circ \quad (15)$$

and for a reaction such as

e.g., Nd-NdCl₃, one finds

$$\mu_M^*(\text{soln}) - \mu_M^*(g) = RT \ln C_M^{(g)}/C_M^{(\text{soln})} + 2RT \ln C_{\text{MX}_3}^{(l)}/C_{\text{MX}_3}^{(\text{soln})} + \Delta\mu^\circ \quad (17)$$

where $\Delta\mu^\circ$ is the standard free energy change of reaction (13) or (16). From the above relations involving subhalide formation and equation (4) it can be seen that for dilute solutions where a solid subhalide is the separating phase the magnitude of the standard free energy of interaction is essentially increased by a quantity proportional to $\Delta\mu^\circ$. Unfortunately, for many subhalides the values of $\Delta\mu^\circ$ are unknown. However, for the calomel reaction (5) $\Delta\mu^\circ$ at 280° is about -5.7 kcal⁵. For the Bi-BiCl₃ system,

(5) L. Brewer, Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, ed. by L. L. Quill, McGraw-Hill, 1950.

reaction (14) with all three components in the solid state has a $\Delta\mu^\circ$ of -2.1 kcal⁶ at 450°K. Using 5.68⁷ and 2.60⁸ kcal/mole for the heats of

(6) A. J. Darnell and S. J. Yosim, *J. Phys. Chem.*, **63**, 1813 (1959).

(7) L. E. Topol, S. W. Mayer and L. D. Ransom, *J. Phys. Chem.*, **64**, 862 (1960).

(8) D. Stull and G. Sinke, Thermodynamic Properties of the Elements, Am. Chem. Soc., Washington, D. C., 1956.

fusion of BiCl_3 and Bi, respectively, and the relation

$\Delta F_f = \Delta H_f(1 - T/T_f)$, where ΔF_f is the Gibbs' free energy change on fusion and T_f is the melting point of the pure substance, 544.1°K and 506.6°K for Bi and BiCl_3 , respectively, we obtain a $\Delta\mu^*$ of -2.7 kcal for reaction (14) at 553°K .

The standard free energy of interaction of metal atoms with the salt solvent, $\Delta\mu_{\text{int}}^*$, is actually given by

$$\Delta\mu_{\text{int}}^* = (\mu_M^*(\text{soln}) - \mu_M^*(g)) - \Delta\mu_h^* \quad (18)$$

where $\Delta\mu_h^*$ is the chemical potential for holes. This energy for hole formation varies from about 3 to 10 kcal from one fused salt system to another but is always positive and thus will make the interaction energy more negative⁹.

- (9) The expression for the work involved in the formation of Avogadro's number N of holes derived by Reiss et al.¹⁰ is given by

$\Delta\mu_h^* = p(4/3\pi r^3) + 4\pi r^2\sigma N(1 - 2\delta/r)$ where p is the pressure of the fluid, σ is the interfacial tension between the fluid and the hole, δ is a distance of the order of the thickness of the inhomogeneous layer near the hole-fluid interface, and r equals the sum of the radius of the metal atom plus the average radius of the solvent ions. Since the p - V term is negligible (of the order of one calorie) for the systems under consideration, the above expression can be approximated by

$\Delta\mu_h^* = 18.1 r^2\sigma(1 - 2\delta/r)$ where r is expressed in angstroms and $\Delta\mu_h^*$ is given in calories. Taking average radii of $1.5 \text{ \AA}$ for both metal atoms and salt ions and substituting typical values of r , $2\delta/r$ and σ of $3.0 \text{ \AA}$, 0.64 ¹⁰, and 100 dynes/cm^2 , respectively, into the above equation, we find a $\Delta\mu_h^*$ of approximately 6 kcal.

- (10) H. Reiss, H. L. Frisch, E. Helfand and J. L. Lebowitz, J. Chem. Phys., 32, 119 (1960).
 (11) H. Bloom and J. O'M. Bockris, Modern Aspects of Electrochemistry No. 2, ed. by J. O'M. Bockris, Academic Press, N.Y., 1959, Chap. 3.

RESULTS

In Table I are listed $\Delta\mu_{\text{int}}^*$ values calculated for various metal-metal salt solutions with a $\Delta\mu_h^* = 6$ kcal used throughout since the variation in $\Delta\mu_h^*$ for different systems is small compared to the energy of interaction.

In addition, we have made the assumptions

that Henry's law and ideal gas behavior hold. In those cases where departure from Henry's law occurs, the corrections should not be more and in most instances are much less than 4-5 kilocalories, and these corrections will always make the interaction energy less negative. (The standard state is not the pure metal, but a hypothetical solution of the metal at 1 mole/l.) However, these corrections would not effect any conclusions in this paper. The vapor pressure of the pure metal existing as monomers⁸ in the gas, has been used. Thus, even if an appreciable amount of the gas consists of metal polymers, equations (3) and (8) still hold as long as the concentration of monomer, $C_M^{(g)}$, is known. In those systems where salt solubility in the metal occurs, Raoult's law has been applied to calculate the vapor pressure of the metal above the solution. In most cases, the solubility of salt in metal is extremely small and the extent of departure from Raoult's law should also be correspondingly small. However, even in those systems where the salt solubility in the metal is appreciable, e.g., K-KCl, Rb-RbCl, the error involved in the use of the ideal vapor pressure value should not be greater than 1-2 kcal and the correction to the interaction energy is in the opposite direction to the Henry's law correction.

The typical effects of temperature on these systems are illustrated by Bi-BiCl₃ at 553 and 973°K and Ag-AgCl at 763 and 973°K. The Bi system was chosen to show the apparent temperature dependence of the interaction energy because of the change in phases that occurs. At the lower temperature a solid subhalide, BiCl, is in equilibrium with the melt whereas at the higher temperature two liquid phases exist. The Ag-AgCl system is typical of the many metal-salt melts in which no solid subhalide

exists. Nevertheless, in both systems a decrease in the negative partial molar free energy of interaction with increasing temperature occurs and this behavior exemplifies the temperature dependence of virtually all of the systems considered in Table I. This can also be readily seen from equations (4), (12), (15) or (17) since the metal vapor pressure (and thus $C_M^{(g)}$) increases more rapidly with temperature than does the metal solubility in most instances. From the examples above, approximate corrections to the $\Delta\mu_{int}^*$ values in Table I may be estimated to afford a direct comparison at a common temperature. Such corrections would not change the order of the systems essentially. (The interaction energy of Hg-HgCl₂ at 973°K is calculated to be about the same as at 553°K since the increase in metal vapor pressure and the disappearance of the $\Delta\mu^*$ contribution for the solid Hg₂Cl₂ in equation (12) is compensated by the increased metal solubility and temperature contributions.)

The effect of varying the anion is shown by the increase in interaction energy as one goes from chloride to iodide in the lead system and this behavior is typical of most of the cations listed in Table I (with the exception of the Cd system). This variation is due to the increase in solubility of the metal in its halides in the order I > Br > Cl. Since the solubility of Al in AlCl₃ is not known but appears to be about five orders of magnitude smaller²³ than in AlI₃, a less negative value of $\Delta\mu_{int}^*$ of about -45 to -50 kcal/mole appears likely in the chloride.

The results in Table I indicate that all the energies of interaction are appreciable and, although these values may be somewhat in error, they illustrate, with a few exceptions, some interesting relations between the interaction energies and the periodicity of the metals. For the alkali metal systems, with the exception of Li, the energies of interaction at $T \approx 1000^\circ\text{K}$ are all approximately equal and exhibit only a slight trend. The alkaline earths have interaction energies of similar magnitude as those above but the energies essentially become increasingly more negative with increasing atomic number. Similar interaction energies as those for Groups IA and IIA are observed for systems containing the Group IIB metals, Zn, Cd and Hg, and also for Tl (in TlCl) and Pb. Much larger energies are present in the Ag, Sn, Tl (in TlCl_3), Sb and Bi solutions and still larger values are evident with Al, Ga, the lanthanides, Ni and U. The Δu_{int}^* values for Tl in TlCl_3 and Ga in GaCl_3 were calculated from the Tl-TlCl and Ga-Ga₂Cl₄ data by adding the ideal free energy change involved in the solution of the amount of metal required to change the composition from the pure trichloride to that of the salt measured, i.e., 66.7 mole % Tl to yield TlCl and 33.3 mole % Ga to form GaCl₂. The larger interaction energy of Ag-AgCl compared to that of Tl-TlCl and the alkali-alkali halides is surprising; also, the large difference between the values for the tin and lead systems cannot be readily explained. The experimental data for these systems (Ag, Sn, Pb) should be confirmed. However, the chemical similarity of the lanthanides is again shown in the almost identical interaction energy values. Further, since the actinides are also expected to show mutually similar interaction energies (about -94 kcal/mole as for U-UCl₃), one would expect a large increase in inter-

action energy as one goes from the lanthanides to the actinides. It should also be noted that the energies for systems containing solid subhalides, e.g., Hg, Bi, are approximately the same as those for their congeners with no solid subhalide present. (Although the $\Delta\mu^\circ$ for the Nd-NdCl₃ reaction (16) is not known; it thus appears likely that it is of the order of -1 to -4 kcal.)

DISCUSSION

From the values of the interaction energies in Table I it is interesting to compare the different groups of metals. First, there are the alkali and alkaline earth metals, the interaction energies of which, with the exception of Li, are in the range -12 to -23 kcal/mole metal and become essentially more negative with each successive congener in the group. The anomalous behavior of Li is probably related to its small size and its presence largely as atom dimers^{2a}, Li₂, in the melt. A second group consists of the other mono- and divalent metals whose ions do not have an inert gas electron configuration and thus should exhibit greater polarization effects; interaction energies here vary from -17 to -27 kcal/mole with the exceptions of Ag and Sn. A third category of systems is that composed of the transition metals and the trivalent metals where negative interaction energies of about 40 kcal and higher are found. Thus, all the systems considered above can be categorized in terms of weak (less negative than -30 kcal) or strong (more negative than -40 kcal) interaction energies. This delineation is more meaningful than the use of a nonquantitative property such as subhalide or nonsubhalide formation as a measure of the strength of metal-salt interactions. As can be seen from Table I there are many systems containing no known solid subhalide

that have interaction energies as large or larger than systems with a solid subhalide present. Thus the existence of a solid subhalide cannot be taken as confirmation that a stable subhalide species may exist in the liquid; conversely, the nonoccurrence of a solid subhalide does not preclude the existence of a lower-valent cation species in solution. In addition, the systems (Bi-BiCl₃, Bi-BiBr₃, Sb-SbI₃, Ga-GaCl₃, Tl-TlCl₃) that are known to contain in solution lower-valent species of the types depicted by reactions (13) and (16), where an actual exchange of electrons between the metal and solvent cations occurs, all fall in the strong interaction class (see below).

Some of the factors that should affect the interactions of metal atoms and molten salts are the ionization energy of the metal, size and polarizabilities of the entities and polarization strengths or charge densities of the cations. Metal atoms in these ionic melts would be expected to be highly polarized, and it is interesting to note that the energies in Table I are approximately those one would expect from ion-induced dipole interactions. (The potential energy for such interactions is given to a first approximation by

$$E = - \alpha (Ze)^2 / 2a^4 \quad (19)$$

where α is the polarizability of the uncharged species and is about $2-6 \times 10^{-24}$ cc/atom, Ze the charge of the ion, and a the distance between the ion and dipole.) Unfortunately, since the force fields around an induced dipole in a fused salt cannot be evaluated at the present, no accurate values for such interactions can be calculated.

It is interesting to note that the transition metals and all the metals with three or more valence electrons exhibit large interaction energies. In addition, many of these metals are known to exist in these melts as lower-valent cations, e.g., Bi^{+33} , Sb^{+34} , Ga^{+35} , Tl^{+17} .

(33) L. E. Topol, S. J. Yosim and R. A. Osteryoung, J. Phys. Chem., 65, 1511 (1961).

(34) J. D. Corbett and F. C. Albers, J. Am. Chem. Soc., 82, 533 (1960).

(35) L. A. Woodward, G. Garton and H. L. Roberts, J. Chem. Soc., 3723 (1956).

(Although the data in Sb-SbI_3 are consistent with the species Sb^+ , Corbett and Albers³⁴ assumed Sb_2I_4 entities because these melts are diamagnetic. However, in analogy with Bi-BiI_3 , Sb^+ would be expected to be diamagnetic³⁶

(36) L. E. Topol and L. D. Ransom, J. Chem. Phys., 38, 1663 (1963).

also.) It thus appears that lower oxidation states containing fully paired electrons are favored, and the large energies in the trivalent metal solutions are probably associated with the shift of electrons from a metal atom (or pair of atoms) to localized orbitals around the trivalent cation as depicted in reactions (13) and (16). For divalent metals the dimerization reaction (5) is consistent with the tendency for the s electrons to remain paired. Although there is no evidence at present for the existence of monovalent monomeric cations of normal divalent

metals³⁷ except for Ni^{29,38}, no distinction can be made from existing

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- (37) L. E. Topol, "E.M.F. Measurements in Molten Divalent Metal-Metal Halide Solutions", J. Phys. Chem., to be published.
- (38) The evidence for the apparent anomaly with Ni in NiCl₂ results from a cryoscopic study which favors the species Ni⁺. These results are based on a heat of fusion³⁹ of 18.45 kcal/mole for NiCl₂ but this value, together with the melting point of the salt, 1282°K²⁹, yields an entropy of fusion of 14.4 e.u. or 4.8 e.u. per gm-ion. Virtually all ionic salts have entropies of fusion of 2.5-3.5 e.u. per gm-ion and FeCl₂ and CoCl₂ have values⁵ of 3.6 and 2.5 e.u. per gm-ion, respectively. If the measured heat of fusion of NiCl₂ is in error and a more normal value of 10 kcal/mole taken, i.e., an entropy of fusion of 3.0 e.u. per gm-ion assumed, then the cryoscopy results are in accord with Ni atoms or Ni₂⁺. Although the removal of an electron to form Ni⁺ is consistent with the high interaction energy found in Ni-NiCl₂, it is difficult to see why Ni⁺ should be more stable than Ni₂⁺, and a redetermination of the heat of fusion of NiCl₂ seems warranted.
- (39) J. P. Coughlin, J. Am. Chem. Soc., 73, 5314 (1951).
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evidence between entities of the type M₂⁺² and metal atoms. Actually the difference is a subtle one since metal atoms, being very polarizable, would presumably exist in these melts as solvated species of the type M-M⁺². The difference between such a solvate and the entity M₂⁺² is then mainly due to a difference in the degree of interaction between the metal atom and cation. With the monovalent metals such as the alkalis, silver and thallium the formation of fully paired electronic structures does not appear feasible except by dimerization of the atoms, and it is difficult to postulate a subhalide species although solvated species may exist.

CONCLUSIONS

On the basis of the magnitude of the standard free energies of interaction between individual atoms of metals and their molten chlorides, two chief classifications of systems can be made. In the first category

are systems which exhibit relatively weak interaction energies (less negative than -30 kcal) and these primarily consist of the mono- and divalent metals. The second category includes the transition metals and the trivalent metals, and these systems are characterized by relatively strong interaction energies (more negative than -40 kcal). Solutions of metals of the first category appear to consist of strongly-solvated atoms and the magnitude of the interaction energy is a measure of the degree of solvation. The high energies of interaction characteristic of the last group of metals are consistent in many cases with other facts which indicate that an electron or pair of electrons are removed from the metal in the melt. This classification of metal-salt systems in terms of weak or strong interaction energies appears to be a more reasonable delineation than one based on a nonquantitative property such as subhalide formation. For example, the interaction energies for Hg-HgCl_2 and Bi-BiCl_3 , where solid subhalides exist, are much less than those for many other systems which do not contain a solid subhalide phase. Thus, solid subhalide formation is not necessarily indicative of a large energy of interaction.

In virtually all systems (with the exception of the monovalent metals) the metal and cation species are stabilized by forming a completely paired electron structure. Unfortunately, both additional and more reliable data are necessary to complete the characterization of metal-salt systems and to enable one to make accurate predictions on unknown systems. Some untested systems which should be feasible for study are Cu in CuCl ,

Co in CoCl_2 , Fe in FeCl_2 , Ac in AcCl_3 and Th in ThCl_3 . The copper system would serve as an interesting comparison with Ag-AgCl, and the cobalt (and iron) and actinium and thorium systems would shed more light on the variation of interaction energy among transition metals as well as between different periods of these metals.

ACKNOWLEDGMENT

The author would like to extend his gratitude to Dr. M. Blander for his many helpful comments and suggestions.

TABLE I

System	T (°K)	Vap. Press. Metal ⁸ (atm)	Metal Soly. (mole %)	$\rho^{11,12}$ soln. (g/cc)	$-(\mu_H^*(\text{soln}) - \mu_H^*(g))$ (kcal/mole)	$-\Delta\mu_{\text{int}}^*$ (kcal/mole)
Li-LiCl ¹³	913	1.64×10^{-4}	0.50	1.49	20	26
Na-NaCl ¹⁴	1068	0.344	2.1	1.56	10	16
K-KCl ¹⁵	1025	0.70	10.5	1.53	11	17
Rb-RbCl ¹⁶	969	0.57	18	2.05	12	18
Ag-AgCl ¹⁷	763	1.1×10^{-13}	0.03	4.80	44	50
Ag-AgCl ¹⁷	973	1.81×10^{-9}	0.06	4.60	40	46
Tl-TlCl ¹⁷	923	3.52×10^{-5}	0.009	5.23	15	21
Mg-MgCl ¹⁸	1073	0.034	0.30	1.66	6	12
Ca-CaCl ^{19,20}	1093	1.52×10^{-3}	2.70	2.06	12	18
Sr-SrCl ^{20,21}	1112	7.10×10^{-3}	5.5	2.75	11	17
Ba-BaCl ²²	1151	1.60×10^{-3}	15.0	3.23	17	23
Zn-ZnCl ²³	973	0.076	1.64	2.35	11	17
Cd-CdCl ²⁴	973	0.44	18.0	3.60	13	19
Hg-HgCl ²⁵	553	0.184	5.0	4.55	11	17
Al-AlI ¹⁷	696	6.8×10^{-18}	0.3	2.5	55	61
Ga-Ga ₂ Cl ₃ ¹⁷	453	4.1×10^{-26}	1.92	2.41	55	61
Ga-GaCl ₃ ^a	453	4.1×10^{-26}	35.2 ^a	2.41	57	63 ^a
Tl-TlCl ₃ ^a	923	3.52×10^{-5}	66.7 ^a	5.23	32	38 ^a
La-LaCl ₃ ²⁶	1193	1.5×10^{-12}	11.0	3.20	65	71
Ce-CeCl ₃ ²⁷	1050	2.5×10^{-11}	9.3	3.60	61	67
Nd-NdCl ₃ ²⁸	1128	7.1×10^{-10}	30.5	4.0	~60	~66

TABLE I (CONTINUED)

System	T (°K)	Vap. Press. Metal ⁸ (atm)	Metal Soly. (mole %)	$\rho_{\text{soln.}}$ 11,12 (g/cc)	$-(\mu_H^*(\text{soln}) - \mu_H^*(g))$ (kcal/mole)	$-\Delta u_{\text{int.}}^*$ (kcal/mole)
Ni-NiCl ₂ ²⁹	1250	1.0×10^{-10}	9.1	2.6	70	76
U-UCl ₃ ³⁰	1093	1.2×10^{-16}	4.1	4.1	88	94
Sn-SnCl ₂ ¹⁷	773	2.1×10^{-15}	3.2×10^{-3}	3.09	46	52
Pb-PbCl ₂ ¹⁷	973	1.5×10^{-5}	0.052	4.65	21	27
Pb-PbI ₂ ²³	973	1.5×10^{-5}	0.41	5.5	25	31
Sb-SbCl ₃ ²³	546	4.8×10^{-19}	0.018	2.1	43	49
Bi-BiCl ₃ ³¹	553	5.7×10^{-13}	35.0	4.65 ³³	38	44
Bi-BiCl ₃ ³¹	973	2.3×10^{-5}	35.0	3.75 ³³	32	38

a) calculated from data in lower-valent salt (see text)

- (12) See reference 2a, Chapter by A. Klemm, "Transport Properties of Molten Salts".
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