FREEZING POINT DEPRESSION IN FUSED SALTS

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All elementary texts of physical chemistry (and most of introductory general chemistry) discuss the lowering of the freezing point of a pure solvent caused by the addition of small amounts of solutes. It is demonstrated that the lowering is a quantitative property of the nature of the solvent and the number of solute "particles" (molecules, ions) of the solute added to a given mass of solvent. Thus, from experimental determinations of the freezing point depression, it is possible to compute the molecular weight of undissociated substances or the number of fragments (ions, radicals, etc.) into which a solute dissociates in any particular solvent. Very extensive use has been made of this scheme in studying ionic solutions. I wish to point out a little used application to a very special class of liquids: molten salts, which are also ionic solutions, but ionic solutions in which there need not be any non-ionic diluent as in an aqueous or semi-aqueous solution.

In such a substance as crystalline sodium chloride we are wont to visualize Na^+ and Cl^- ions arranged in a regular three dimensional geometric array with both short range and long range order. When such an ionic crystal melts it is usually considered that the ions acquire at least some degrees of translational freedom, thereby losing the long range order of the crystal, but probably retaining a considerable amount of short range order, the more the nearer the melting point. Thus molten NaCl just above its melting point (801°C.) would be a liquid composed of Na^+ and Cl^- ions and should be looked upon as a very concentrated electrolyte. Indeed it is a good conductor of electricity. Now the freezing point of this ionic liquid is depressed by the addition of a foreign material, in direct proportion to the number of "foreign particles" dissolved in a given mass of molten NaCl. But only those particles which are neither Na^+ nor Cl^- ions cause freezing point lowering. Thus we may anticipate that, per mole of solute added to a fixed mass of NaCl as solvent, NaF, Na_2SO_4, KCl and LiCl would lower the freezing point only half as much as LiF or KF and only one third as much as K_2SO_4. We can explain this behavior by considering that the solvent NaCl is essentially completely dissociated into ions and that the addition of a small amount of the common ion Na^+ does not affect the chemical potential of the sodium ion, μNa^+, and addition of a little Cl^- does not affect μCl^-. On the other hand addition of K^+ or Li^+ does affect the μNa^+ and addition of F^- and $SO_4^=$ does affect μCl^-. We consider that this behavior of freezing point depression is one of the strongest arguments in favor of essentially completely ionic character of these molten salts.

The well known Van't Hoff freezing point depression law,

$$\Delta T_i = \nu \, (RT_o^2/\Delta H_o) \, X_i = \nu \, k \, X_i$$

where ΔT_i is the depression caused by addition of an amount of the i th component corresponding to a mole fraction X_i in a solvent of molar heat of fusion ΔH_o, v is the number of ions per mole of solute, R is the gas constant per mole and T_o the absolute freezing point of the pure solvent; can be used to compute freezing points of fused salt solutions up to surprisingly high concentrations. In using this equation to compute the depression constant, *i.e.,* $RT_o^2/\Delta H_o$, so as not to attempt to lift oneself by his bootstraps, one must be sure to substitute calorimetrically determined heats of fusion and not values estimated from observed freezing point data. We have found remarkably good agreement between calculated and observed depression constants in several cases.
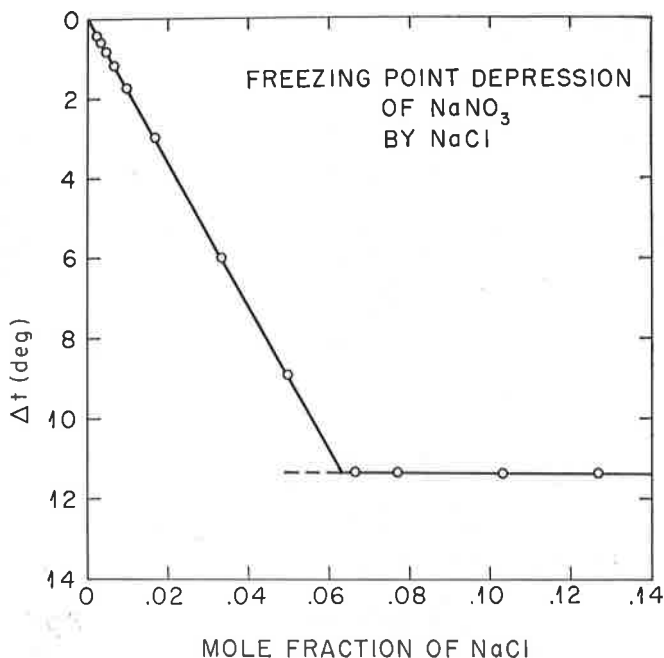

Fig. 1. Freezing point depression (Δt) of sodium nitrate caused by addition of sodium chloride.

We have obtained some very precise data with molten sodium nitrate (melting point 306°C.) as solvent. Figure 1 is a plot of the freezing point of solutions of sodium chloride in sodium nitrate. The flat part of the curve clearly corresponds to formation of a eutectic. Indeed points taken along this part of the graph showed freezing points which did not vary with percentage of solvent frozen in agreement with its being a eutectic. Also a eutectic at about 6 mole percent NaCl has been reported previously. A rising liquidus curve to the right of the eutectic was not observed for two reasons; first, it was not sought, and second, the heat effect of so small an amount would be very

difficult to observe in our experiments. The very fine linearity of the freezing point depression up to the eutectic composition means that in these solutions of molten salts there is but little deviation from ideality. Figure 2 shows freezing point depressions caused by addition of four selected salts (NaCl, KIO_4, $BaCl_2$ and $LaCl_3$) to sodium nitrate, with concentrations expressed as mole fraction of solute. Surprisingly linear plots are obtained and the slopes of the four curves bear a simple integral relationship to one another. According to the Van't Hoff law and earlier remarks on effects of common ions the slopes should be integral multiples of $RT_o^2/\Delta H_o$ if all the salts are essentially totally dissociated into their ions. The slopes actually found are 178° for NaCl, 2 x 177° for KIO_4, 3 x 175° for $BaCl_2$ and 4 x 181° for $LaCl_3$.
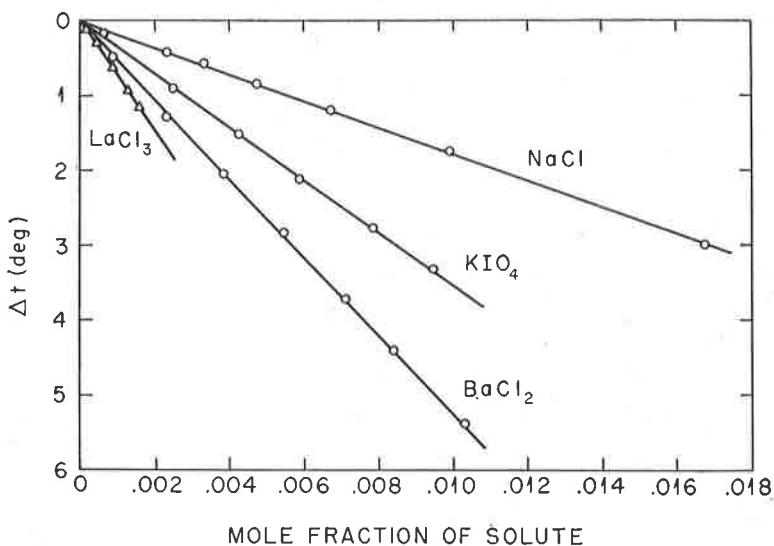

Fig. 2. Freezing point depression (Δt) of sodium nitrate caused by addition of four solutes.

I shall consider the case of KIO_4 further in a moment. Studies with many other solutes in molten sodium nitrate corroborate that $RT_o^2/\Delta H_o$ is 178°; whence one computes that the molar heat of fusion of sodium nitrate is 3740 cal/mole, which agrees closely with values quoted in the literature from direct calorimetric determination.[1]

All of the preceding considerations rest on the assumption that the solvent in these solutions freezes out as a pure phase with no formation of solid solutions. Evidently in many cases this is true within experimental error. However, one must know the situation with respect to solid solutions if he is to draw valid conclusions. An example will illustrate the point. We had found that silver nitrate, silver sulfate, and silver chromate gave depressions in sodium nitrate which correlated beautifully with the concept of the silver ion existing

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[1]Goodwin and Kalmus, *Phys. Rev.*, 28, 1 (1909), report 3690 cal/mole.

as Ag_2^{++} in the melt. And this idea offered a tantalizingly simple explanation of some interesting effects we observed in transport and electrical conductivity of silver ion. But a second, more thorough literature search brought to light some phase equilibrium studies of about 55 years ago which showed that $NaNO_3$ and $AgNO_3$ form a solid solution. Now one can modify the Van't Hoff law in the case of solid solutions to give

$$\Delta T_i = \nu \ (RT_o^2/\Delta H_o) \ (X_i - X^1_i)$$

where X_i is the mole fraction of solute in the molten phase and X^1_i that in the solid phase. Our results with silver salts are explained assuming Ag^+ ion and a solid solution solubility of 50 percent, a value which appears reasonable from the phase studies. It is obvious this sort of freezing point depression work allows one to determine the solid solution solubility rather precisely in the low liquid concentration range where ordinary phase study cannot give a very exact answer.

One of the very important types of information obtainable from freezing point measurements on molten salt solutions is concerned with stability and reactions of complex ions. As an example let us again consider potassium metaperiodate, KIO_4. When this is added to molten sodium nitrate oxygen is evolved and it is of interest to know whether KIO_3 or some other compound is formed. Since IO_3^- is stable in molten nitrate, while I^- and IO^- are unstable (yielding free iodine) and IO_2^- is unknown, we can learn whether a doubling to such an ion as $I_2O_6^-$ takes place. The fact that each IO_4^- initially added gives rise to no free I_2 and exactly one ion indicates that IO_3^- must be formed. Studies may be made to investigate the stability or reaction of an almost unlimited number of complex ions. There are many salts known of the type formula K_2MX_6 where M might be titanium or gold or tin etc., and X is a halide. These salts are frequently well characterized crystalline solids. Certain of them such as K_2TiF_6 give the corresponding complex ions which are quite stable in aqueous solution. We have indications that some are also stable in melts at fairly elevated temperatures. NO_3^- is stable in $NaNO_3$ a little above its melting point; we can investigate it in higher melting salts to find its stability or reactivity.

Basic science of materials at higher and higher temperatures becomes important as industry moves to high temperature reactors and furnaces, jet and rocket propulsion and so on. I should like to suggest, then, that freezing point depression measurements in molten salts offer a hitherto little explored field for much worth-while and fascinating investigation.