[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Fused Salt Concentration Cells with Transference. Activity Coefficients in the System Silver Nitrate–Sodium Nitrate[1]

BY RICHARD W. LAITY

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An expression relating the electromotive force of a fused salt concentration cell with liquid junction to the activities of the salts present, the temperature and the relative mobilities of the ions involved is derived. The thermodynamic analysis reveals the fact that for solutions having the transport properties of the silver nitrate–sodium nitrate system the junction potential terms vanish from the e.m.f. expression. E.m.f. determinations are described, the results of which show that these solutions deviate appreciably from ideality, but adhere remarkably well to the requirements for a "regular solution."

Twenty-five years ago, in an interesting series of papers the results of which are summarized in the final one,[2] Hildebrand and Salstrom showed that fused mixtures of silver bromide with each of four alkali bromides adhere remarkably well to the criteria for "regular" solutions. The conventional model predicts that regular solutions will exhibit positive deviations from Raoult's Law. The interesting result in this case, however, was that positive deviations were observed only in those melts in which the alkali ion was smaller than silver ion, the deviations becoming more negative as the size of the alkali cation increased. In the paper cited above,[2] these workers attempted to formulate a qualitative explanation of their results in terms of the partial covalent character of the silver–bromine bond. The work also has been discussed by Thurmond, whose optical studies gave no evidence for the existence of complex ions in these solutions.[3]

The results for the silver bromide melts, as well as the explanations offered, suggest that a similar experimental study on silver nitrate–alkali nitrate mixtures might contribute to a further understanding of the situation. The e.m.f. method used by Hildebrand and Salstrom to determine the activity coefficients employed a simple formation cell without transference. Such a cell is, of course, impossible with nitrates due to the non-existence of a reversible nitrate electrode. In the present work the author has therefore carried out measurements on concentration cells with transference using silver electrodes only. Since the thermodynamics of such cells has not yet been treated in the literature for the case of fused salt mixtures, a brief discussion follows.

The derivation of an equation relating the electromotive force of a fused-salt concentration cell with transference to the appropriate transport and thermodynamic properties of the salt mixtures is particularly simple when the melts consist of two salts with one ion in common, the electrodes being reversible to one of the ions of varying concentration. Consider the electrode compartments to be large well-stirred reservoirs, A and B, each containing a mixture of silver nitrate and sodium nitrate at the same temperature T. Let the equivalent (mole) fraction of silver nitrate be X_{1A} in one compartment and X_{1B} in the other, the corresponding concentrations of sodium nitrate being X_{2A} and X_{2B}. These electrode compartments are joined by a tube in which the composition of the melt varies continuously from that in the compartment A to that in compartment B. The conventional thermodynamic analysis of such an arrangement, as normally applied to electrolytic solutions containing more than one salt, predicts that when X_{1A} is greater than X_{1B} the e.m.f. between silver electrodes will be given by

$$-E = RT/F \int_A^B [(1 - t_1)\ \mathrm{d} \ln a_1 - t_2\ \mathrm{d} \ln a_2] \quad (1)$$

where t_1 is the transport number of silver ion, t_2 the transport number of sodium ion, a_1 the activity of silver nitrate and a_2 the activity of sodium nitrate.[4] This equation readily can be derived most rigorously by means of the thermodynamics of irreversible processes. In view of its well-known validity and applicability, however, its derivation will not be discussed further here. Suffice it to say that its application to the fused-salt system described is on even firmer ground, since it is not necessary here to neglect possible activity changes in the solvent.

The lack of a solvent reference frame in molten salts immediately raises a question as to what reference the transport numbers in eq. 1 are based on. In terms of the model on which the equation is based, the answer is clearly the walls of the cell, or, more specifically, the tube connecting the two electrode compartments. It will be shown very shortly, however, that the choice of reference is completely arbitrary in this case. It is also important to note the absolute necessity of placing the t's inside the integral. This is due to the strong concentration dependence of transport numbers in such a system, since the concentration of one cation can only be increased at the expense of the other. It might further be pointed out that eq. 1 is a consolidation of the more customary form in which single ion activities are used. Such equations can always be re-expressed in terms of salt activities, the transport number of the nitrate ion, t_3, disappearing here by virtue of the relation $t_3 = 1 - t_1 - t_2$.

Constant temperature in this two-component system permits application of the Gibbs–Duhem equation

$$\mathrm{d} \ln a_2 = -X_1/X_2\ \mathrm{d} \ln a_1 \quad (2)$$

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[1] Presented in part at the Atlantic City Meeting of the American Chemical Society, September, 1956.

[2] J. H. Hildebrand and E. J. Salstrom, THIS JOURNAL, **54**, 4257 (1932).

[3] C. D. Thurmond, *ibid.*, **75**, 3928 (1953).

[4] See, for example, E. A. Guggenheim, "Thermodynamics," North-Holland Publishing Co., Amsterdam, 1949, pp. 349–352.

Substituting (2) in (1) and rearranging gives

$$E = RT/F \int_{\mathrm{B}}^{\mathrm{A}} [(X_2 - X_2t_1 + X_1t_2)/X_2] \mathrm{d} \ln a_1 \quad (3)$$

Now eq. 3 contains inside the parentheses an expression identical to that which Aziz and Wetmore have designated as ϕ in their transport measurements on this system.[5] It remains only to establish whether the transport numbers, t_i, as defined here can be identified with the "transport fractions," θ_i, of Aziz and Wetmore.

Examination of the Aziz and Wetmore derivation of ϕ, the quantity that is measured in a Hittorf-type experiment on a fused-salt mixture, reveals that at no point do these authors define the reference with respect to which the transport fractions are measured. The only implication inherent in the derivation is that all three transport fractions are referred to the same reference. With this one qualification, then, the value of ϕ must be independent of the choice of reference. That such is indeed the case may clearly be seen by carrying out a transformation of reference on the equation defining the value of ϕ, that is, by taking one point as reference for the θ_i and expressing these θ_i in terms of new transport fractions θ_i' in which the ionic velocities are referred to some other point. It is found that the equation transforms into itself, *i.e.*, an equation identical in form to the original, but containing θ_i' in place of the θ_i. The value of ϕ thus gives one equation in two unknowns, and only when the reference is decided upon can the individual transport numbers be assigned values. Aziz and Wetmore's procedure of giving approximate figures for the transport numbers consisted essentially in limiting the choice of references to those for which the transport number of each ion lies between zero and one.

It readily can be shown that the part of eq. 3 involving transport numbers, $-X_2t_1 + X_1t_2$, depends only on the velocity of silver ion relative to sodium ion. The reason that ϕ is independent of reference thus becomes immediately apparent, since the difference between two velocities does not depend on their "absolute" values.

On the basis of the above discussion eq. 3 may now be rewritten

$$E = RT/F \int_{\mathrm{B}}^{\mathrm{A}} (\phi/X_2) \mathrm{d} \ln a_1 \quad (4)$$

where ϕ is a quantity measurable by means of a Hittorf-type transport experiment. Dissecting the activity in the usual way

$$E = RT/F \int_{\mathrm{B}}^{\mathrm{A}} (\phi/X_2) \,\mathrm{d} \ln X_1 + RT/F \int_{\mathrm{B}}^{\mathrm{A}} (\phi/X_2) \,\mathrm{d} \ln \gamma_1 \quad (5)$$

where γ_1 is the activity coefficient of silver nitrate in the mixture of composition X_1, the standard state being arbitrary.

The derivation is now complete, eq. 5 representing the most useful form of the expression. Thus, after experimentally determining ϕ as a function of composition, the first member on the right can readily be integrated. This gives the e.m.f. that would be found if the solutions were ideal. The second member on the right contains the activity coefficient whose concentration dependence is sought in the e.m.f. measurements. In general, this can be found by a method of successive approximations. First, integrate by taking ϕ/X_2 to be a constant midway between its values at A and B. On the basis of e.m.f. data an approximate concentration dependence for $\ln \gamma_1$ may now be obtained. Expressing $\mathrm{d} \ln \gamma_1$ in concentration terms only, eq. 5 may now be integrated again without holding ϕ/X_2 constant. Combining the result with e.m.f. data again gives a more exact concentration dependence for γ_1, which may again be inserted into eq. 5, etc.

Duke, Laity and Owens have shown the determinations of ϕ for the silver nitrate–sodium nitrate system by Aziz and Wetmore[5] to be in error.[6] Additional transport experiments by the present author[7] confirm that at all concentrations employed in the present work $\phi = X_2$ to within less than 1% deviation. This result states that the silver ion does not move relative to the sodium ion during electrolysis of these mixtures, *i.e.*, both ions have the same mobility. Substituting this experimental value of ϕ into eq. 5, it is seen that the silver nitrate–sodium nitrate case can be described by a particularly simple expression

$$E = RT/F \int_{\mathrm{B}}^{\mathrm{A}} \mathrm{d} \ln X_1 + RT/F \int_{\mathrm{B}}^{\mathrm{A}} \mathrm{d} \ln \gamma_1 \quad (6)$$

$$= RT/F \ln X_{1\mathrm{A}}/X_{1\mathrm{B}} + RT/F \ln \gamma_{1\mathrm{A}}/\gamma_{1\mathrm{B}} \quad (7)$$

This result may at first seem surprising, since the "liquid junction potential" apparently comes out to be zero in this cell. A brief qualitative discussion will show why eq. 7 is clearly correct for this case. If a sharp boundary between the solutions could be maintained in such a cell, the position of this boundary would be defined as the point at which the ratio of silver ion to sodium ion per unit volume undergoes an abrupt change from its value in one solution to its value in the other. The cations in the melt thus define the position of the boundary. Now it has just been shown that transport experiments reveal the sodium and silver ion to have the same mobility in these mixtures, *i.e.*, when a current is passed, silver and sodium ions move along together at the same rate, regardless of their relative concentrations. Thus, the ions defining the liquid junction all move along together and the junction therefore moves with them. The only ions crossing the junction during electrolysis would be the nitrate ions, which must therefore carry all the current with respect to the boundary. The reversible passage of one faraday through the cell would thus transfer one equivalent of nitrate from A to B across the boundary and one equivalent of silver ion from A to B at the electrodes. From the free energy change accompanying the transfer of one equivalent of silver nitrate from A to B, it is clear that eq. 7 predicts the correct e.m.f. of the cell.

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[5] P. M. Aziz and F. E. W. Wetmore, *Can. J. Chem.*, **30**, 779 (1952). The identity is established readily by substituting $t_3 = 1 - t_1 - t_2$ into the expression given above.

[6] F. R. Duke, R. W. Laity and B. Owens, *J. Electrochem. Soc.*, in press.

[7] R. W. Laity (to be published).

Experimental

Materials.—Reagent grade silver nitrate and sodium nitrate were melted together in varying proportions to form the solutions initially placed in the cell. Very fine silver wire of high purity was used for the electrodes.

Apparatus.—The transference cell was a Pyrex U-tube 13 mm. in diameter and about 4.5 inches high containing a fritted glass disk at the bottom to separate the two compartments while permitting the solution to be in contact within the pores. Varying porosities of disks were used with no apparent effect on the results. Into the top of each arm fitted a stopper, through which passed a 4 mm. tube which extended almost to the bottom of the cell. Fine silver wires wrapped around the bottoms of these tubes were passed up through them, the other ends being connected across a Leeds and Northrup Model K potentiometer. The salt mixtures usually filled about one third of the tube, although considerable variations in the amounts used gave only random deviations in the results.

Constant and uniform temperature was maintained by immersing the cell in a well-stirred bath composed of a molten mixture of sodium and potassium nitrates. The bath itself was set in the top of a cylindrical furnace, the whole system being insulated at the top with a thick sheet of asbestos. Lack of interfering thermal e.m.f.'s was established when it was found that placing identical mixtures in both sides produced a potential of less than one microvolt. A thermal e.m.f. of several tenths of a millivolt could be developed, however, by discontinuing stirring in the bath.

Procedure.—Salt mixtures of different concentrations were placed in each arm of the cell. Heavy silver wires were then left dipping in each mixture at temperatures higher than those to be used in the measurements in order to "saturate" the mixtures with silver. This eliminated the dissolution of the electrodes and erratic initial behavior of the e.m.f. observed when this precaution was not taken. The nature of this phenomenon is not understood.

The heavy wires were now removed and the electrodes inserted. The e.m.f. was followed until it showed the slow, steady downward drift caused by diffusion through the disk, the solutions in each compartment being stirred by agitation of the electrodes between readings. Theoretical treatment showed that the e.m.f. should decay logarithmically with time when diffusion was the controlling step, a relation which was found to hold precisely. After the final reading the cell was removed quickly and its contents poured into two beakers. The salt remaining in the cell was washed out with water, the washings being added to the salt already poured out. The resulting solutions were analyzed for total cation concentration by passing aliquots through a cation-exchange resin and titrating the liberated acid with standard base. Silver ion was then determined in other aliquots by the Volhard method.

Results and Discussion

The experimental results for the five cells studied are shown in the first four columns of Table I. It is seen that a wide range of concentrations and concentration differences was used. Some spread in temperatures employed will also be noted. The range is not very wide in this respect, however, due to the uncertainty of ϕ outside this range. All transport studies on this system to date have been made at approximately 330°, so it was not felt that e.m.f. measurements very far from this temperature could justifiably be interpreted with respect to eq. 7. The first two cells, in which the concentrations were nearly the same, indicate the reproducibility of the method. In the first of these the quantity of solution in the cell was more than twice that used in the second.

TABLE I

RESULTS OF E.M.F. MEASUREMENTS ON SILVER NITRATE–SODIUM NITRATE MIXTURES

X_{1A}	X_{1B}	T, °C.	E.m.f., mv.	E_{ideal}, mv.	$RT/F \ln \gamma_{1A}/\gamma_{1B}$, mv.	A, cal./mole
0.2211	0.07961	335	44.56	53.50	−8.94	858
.2228	.07679	333	46.12	55.65	−9.53	885
.1254	.07800	344	22.15	25.24	−3.09	838
.3499	.3367	314	1.34	1.93	−0.59	800
.4900	.06396	329	83.28	105.66	−22.38	838

The fifth column shows the e.m.f. that would be calculated for each cell if the solutions were ideal. Comparison of columns four and five reveals that these solutions deviate appreciably from ideality. From eq. 7 it is apparent that $E - E_{\text{ideal}} = RT/F \ln \gamma_{1A}/\gamma_{1B}$. These values are tabulated in the sixth column.

In view of Hildebrand and Salstrom's results for the bromide melts the possibility that this nitrate system might form regular solutions immediately suggests itself. To be a regular solution the system must meet the requirement that

$$RT \ln \gamma_1 = AX_2^2 \tag{8}$$

where A is a constant independent of composition and temperature. From eq. 8 it follows that for two solutions, A and B

$$RT \ln \gamma_{1A}/\gamma_{1B} = A(X_{2A}^2 - X_{2B}^2) \tag{9}$$

The activity coefficient ratios found in the e.m.f. measurements on the silver nitrate–sodium nitrate mixtures were tested to determine whether the relation in eq. 9 holds for this system. The last column in Table I shows the value of A calculated for each cell. The deviations from the average value of 840 cal./mole are seen to be not greater than 5%, showing that A is indeed a constant within the experimental error. Although the temperature range employed is perhaps not sufficient to warrant the definite conclusion, it appears highly probable that these solutions are regular. In this connection it might be pointed out that the "ideality" of the transport properties mentioned earlier ($\phi = X_2$ at all concentrations) indicates that the entropy of mixing is probably ideal in this system.

An attempt to explain these results in terms of a model will not be made until further studies have been completed. It might be noted, however, that the heat of mixing in these mixtures, which depends directly on the value of A, is positive and, in fact, is very close to the value found by Hildebrand and Salstrom for silver bromide–sodium bromide melts (840 *vs.* 1050 cal./mole). Similar experiments on the silver nitrate–potassium nitrate system are at present under way in this Laboratory.

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PRINCETON, NEW JERSEY