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The Thermoelectric Properties of Metal–Ammonia Solutions. III. Theory and Interpretation of Results

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Thermodynamic equations are derived for the thermoelectric power of metal–ammonia solutions which include the effects of electron–electron and electron–ion interactions. The previously reported anomalies in thermoelectric behavior of metal and metal–salt solutions are shown *not* to arise from these interactions, but rather from a large *negative* heat-of-transport of the electrons in these solutions ($Q_e^* \approx -.7$ e.v.). This large negative heat-of-transport is accounted for on the assumption that electrons move through the solutions, even at high dilution, by a quantum tunnel process, rather than by the previously considered ionic, or conduction-band processes.

I. Introduction

In the first two papers of this series[1,2] we have presented data on the thermoelectric properties of metal–ammonia solutions which are in many respects quite puzzling. This is perhaps not surprising for our knowledge of the thermostatic properties of these metal–ammonia solutions, to say nothing of their structure or transport mechanisms, is only partially complete. Furthermore, we do not yet have a complete thermodynamic derivation of the thermoelectric power of thermocells involving weak electrolytes with chemical reaction. Since the solutions in question certainly involve at least one and probably several association reactions, a knowledge of how these reactions affect the thermoelectric properties of the system would appear to be essential.

The organization of this paper may be briefly stated. First we derive equations for the thermoelectric power based on a fairly general model of the solutions. Then, using data obtained from other experiments on the solutions, we show that the anomalies in the thermoelectric data are orders of magnitude larger than could arise from any conceivable thermostatic association effects. Then completely neglecting association effects, we "force" the data to fit the thermoelectric equations for an ideal strong electrolyte. We find that all the anomalies in the data may be understood, in at least a semi-quantitative fashion, if one assumes that the electrons move in the solution with a *negative* heat of transport. Finally, a rational model for the conduction process is presented, not very different from the currently popular model, which could give rise to such a phenomenon.

II. The Thermoelectric Power of a Metal–Ammonia Solution with the Inclusion of Electronic and Ionic Association Effects

We wish here to derive equations for the thermoelectric properties of metal–ammonia solutions (and also mixed salt–metal solutions) which will include at least the major contributions of possible association effects and yet which will not be too general or too complex for comparison with the experimental data.

For concreteness let us consider the diagram of the thermocell shown in Fig. 1. The validity of the Thomson relation for such a system may be shown, using the Onsager reciprocal relations, to be quite general so long as Soret diffusion is restricted and there are no concentration gradients. The Thomson relation may be written in the form

$$\frac{d\varphi}{dT} = \frac{1}{T}\frac{(J_H)}{(J_e)_T} \qquad (1)$$

where J_H is the flow of enthalpy from the heat reservoir A which accompanies the isothermal flow of current (J_e) through the thermocell.

Consider now the sub-system within the dotted line in Fig, 1, We assume the electrodes to be inert and reversible to electrons but put no restriction on the mechanism of charge transfer at the electrode or in the solution itself. Now, enthalpy is conserved in any region at constant pressure so we may express J_H as the difference between the enthalpy accumulation rate within the sub-system, ($\dot{H}$), and the enthalpy flows into and out of the sub-system other than that from the heat reservoir. We obtain the equation

$$\frac{(J_H)}{(J_e)_T} = \frac{\dot{H}}{J_e} - (\bar{H}_{el} + Q^*_{el}) - \sum_{\substack{\text{all ions in}\\ \text{soln.}}} [t_i/z_i(\bar{H}_i + Q_i^*)] \qquad (2)$$

where

$\dot{H}$ = enthalpy accumulation rate in the sub-system
$\bar{H}_i$ = partial molar enthalpy of ion i
Q_i^* = molar heat-of-transport (or excess enthalpy) of the ion i (DeGroot's "reduced" heat of transfer)[3]
t_i = fraction of the current carried by ion i
z_i = charge of ion i

H_{el} and Q^*_{el} are, respectively, the enthalpy and heat-of-transport of electrons in the metal wires.

Now it can be shown that, if all of the species in the solution were completely dissociated, the various thermostatic terms ($\dot{H}$, $\bar{H}_{el}$ and H_i) in (2) would, by virtue of the equilibrium across the electrode–solution interface, combine into a single entropy term $T(\bar{S}_e - \bar{S}_{el})$, where the $\bar{S}$'s are the entropies of electrons in the solution and in the metal electrode. The result would be exactly that of Holtan, Mazur and DeGroot.[4] However, if the solutes are weak electroytes we have additional thermostatic terms which must be considered. For the three component system, salt–metal–solvent, we may write

$$\frac{\dot{H}}{J_e} = -t_x\bar{H}_{salt} + (1 - t_e)\bar{H}_{metal} \qquad (3)$$

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(1) J. F. Dewald and G. Lepoutre, THIS JOURNAL, **76**, 3369 (1954).

(2) G. Lepoutre and J. F. Dewald, *ibid.*, **78**, 2953 (1956).

(3) S. R. DeGroot, "Thermodynamics of Irreversible Processes," North Holland Publ. Co., Amsterdam, 1951.

(4) (a) H. Holtan, Jr., P. Mazur and S. R. DeGroot, *Physica*, **XIX**, 1109 (1953); (b) there appears to be a minus sign missing from the second half of their equation 48.

where t_x and t_e are the Hittorf transport numbers, respectively, of X^- and electrons. Equation 3 expresses the fact that since the temperature and pressure of the sub-system remain constant, the enthalpy of the sub-system can change only to the extent that there is an over-all change in the material content of the sub-system. We assume that only the ions are mobile, the solvent and any neutral molecules remaining fixed. $\bar{H}_{\text{salt}}$ and $\bar{H}_{\text{metal}}$ are the partial molar enthalpies of salt and metal considered as thermostatic components.

Our next problem is to evaluate $\bar{H}_{\text{el}}$ in equation 2 in terms of the properties of the solution and the metal electrode. Since the electrodes are assumed reversible to electrons, the electrochemical potential of the electrons in the metal must be equal to that of the electrons in the solution. This may be expressed in the form

$$\bar{H}_{\text{el}} = \bar{H}_s - T(\bar{S}_s - \bar{S}_{\text{el}}) \tag{4}$$

where the $\bar{H}$'s contain the electrostatic potential and where the subscript "el" refers to electrons in the metal lead wires, and the subscript "s" refers to the single electrons in the solution. The use of the single electrons in this connection is purely for convenience, since the electrochemical potentials of the electrons in all forms are equal by virtue of the equilibrium condition.

We now substitute (3) and (4) into (2), obtaining

$$\begin{aligned}\frac{(J_{\text{H}})}{(J_e)_{\text{T}}} = {} & -t_x\bar{H}_{\text{salt}} + (1 - t_e)\bar{H}_{\text{metal}} \\ & -H_s + T(\bar{S}_s - \bar{S}_{\text{el}}) - \sum_{\substack{\text{all ions in} \\ \text{soln.}}} t_i/z_i\bar{H}_i \\ & -Q_{\text{el}}^* - \sum_{\text{all ions}} t_i/z_iQ_i^*\end{aligned} \tag{5}$$

Equation 5 involves no assumptions about the detailed constitution of the solutions. To this extent it is both exact and unenlightening. Now we follow Bingel[5] and assume the presence of metal ions (M^+), single electrons (s), paired electrons (p), metallide ions (M^-), in addition to X^- ions and neutral salt molecules (MX) arising from the presence of salt. Expressing the sum over the enthalpies, $\bar{H}_i$ explicitly, and then combining terms appropriately, we obtain equation 6 below. The entropy and heat-of-transport terms of the electrons in the metal have been discarded, since these are orders of magnitude smaller than the terms arising from the solution.[6]

$$\begin{aligned}T\frac{d\varphi}{dT} = \frac{(J_{\text{H}})}{(J_e)_{\text{T}}} = {} & T\bar{S}_s - \sum_{\text{all ions}} t_i/z_iQ_i^* \\ & -t_pW_p - 2t_mW_m - (1 - t_s - t_p - 2t_m)(\alpha_pW_p + \alpha_mW_m) \\ & +t_XW_X(1 - \alpha_X)\end{aligned} \tag{6}$$

The terms have the following meanings

t_X = fraction of current carried by X^-
t_s = fraction of current carried by e^-
t_p = fraction of current carried by $e_2^=$
t_m = fraction of current carried by M^-
α_X = fraction of the salt existing as X^-
α_p = fraction of the electrons existing as $e_2^=$
α_m = fraction of the electrons existing as M^-
$W_X = \bar{H}_{M^+} + \bar{H}_{X^-} - \bar{H}_{MX}$ = enthalpy of ionization of MX
$2W_p = 2\bar{H}_s - \bar{H}_p$ = enthalpy of pair dissociation
$2W_m = 2\bar{H}_s + \bar{H}_{M^+} - \bar{H}_{M^-}$ = enthalpy of metallide dissociation

The first two terms in (6) constitute the complete solution for the strong electrolyte case, or for weak electrolyte systems at infinite dilution. This can be seen from the fact that in these two cases $\alpha_x = 1$, $t_p = t_m = 0$, $\alpha_p = 0$, $\alpha_m = 0$, and the last four terms are zero. The last four terms represent the effects of association.

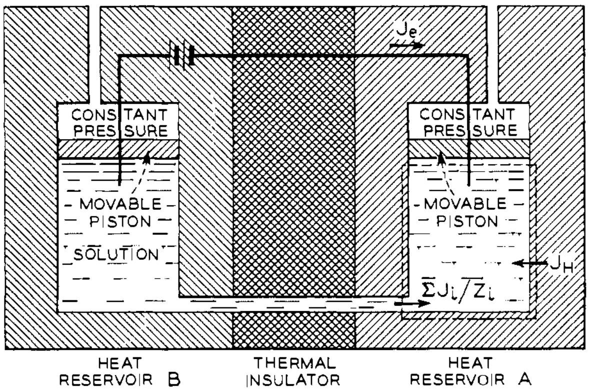

Fig. 1.—Thermodynamic representation of a constant pressure thermocell.

III. Comparison with Experiment

Three major anomalies in the thermoelectric behavior of these solutions have been observed and reported by us. These are: (1) the large dilution effects; (2) the large temperature effects; (3) the very large effect of added salt. Since it is both the largest and the least ambiguous of the three effects we concentrate our attention first on the salt effect.

A. Demonstration of the Second Order Nature of the Thermostatic Contributions to the Salt Effect.—Equation 6 shows that there are two possible ways in which the addition of salt might affect the thermoelectric power of a metal–ammonia solution. It could, by a common ion effect, alter the concentrations of the various electronic and ionic species and thus alter the α's and $\bar{S}_s$ in (6). More generally, the addition of the salt would change the transference numbers of the various electronic and ionic species, thus affecting the thermoelectric power to the extent that the various enthalpies of association and heats-of-transport are finite. Each of the terms in (6) is thus seen to be a possible source of a salt effect. Our problem is to eliminate those terms which play only a minor role.

1. The Entropy Term.—The entropy term in (6) may be shown to be roughly independent of the presence of salt by a simple mass-action argument. The entropy of single electrons, $\bar{S}_s$, may be approximated as

$$\bar{S}_s = \bar{S}_0 - k \ln [e^-]$$

where $[e^-]$ is the concentration of single electrons and $\bar{S}_0$ is a constant. Thus the change in $\bar{S}_s$ on adding salt may be written

$$\Delta S = k \ln \frac{[e^-]_{R=0}}{[e^-]_{R=R}} \tag{1'}$$

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[5] W. Bingel, *Ann. Physik*, **12**, 57 (1953). To our knowledge Bingel's is the most general model considered so far in the literature, all others being special cases of Bingel's.

[6] M. I. Temkin and A. V. Khorochin, *J. Phys. Chem.*, (*U.S.S.R.*), **26**, 500 (1952).

Now we may write the mass action expression for the dissociation of the M^- ion as

$$K = \frac{[e^-][M^+]}{[M^-]} = [e^-]^2 \frac{\left(1 + \frac{2[X^-]}{C} + \frac{[e^-]}{C} + \frac{2[e_2^=]}{C}\right)}{\left(1 - \frac{[e^-]}{C} - \frac{2[e_2^=]}{C}\right)} \tag{2'}$$

Since the addition of salt will, if anything, decrease the concentration of both the single and the paired electrons, (2′) may be expressed as an inequality

$$\frac{[e^-]_{R=0}}{[e^-]_{R=R}} \lesssim \sqrt{1 + \frac{2[X^-]}{C}} \lesssim \sqrt{1 + 2R} \tag{3'}$$

From (3′) and (1′) we then obtain

$$\Delta S \lesssim \frac{k}{2} \ln (1 + 2R) \tag{4'}$$

For the largest value of R employed in our experiments, ($R = 28.5$), equation 4′ predicts a maximum variation $\bar{S}_s$ of about 175 μv./°C. which is only a small fraction of the experimentally observed change in thermoelectric power on adding sodium chloride at this salt/metal ratio. At 0.002 molar metal concentration the change is ∼1600 μv./°C. and at higher dilutions it is even greater than this. Thus the entropy term in (6) makes only a minor contribution, if any, to the salt effect. This is not to say that the term itself is negligible, only that it does not vary much on addition of salt.

2. **The $t_m W_m$ and $t_p W_p$ Terms.**—There are a number of ways to show that these terms cannot account for more than a small fraction of the experimentally observed salt effect. Both terms will decrease on addition of salt through the decrease in t_m and t_p. Thus the maximum possible contribution to the salt effect would be the value of the terms in the pure metal solution. Since, as Bingel[5a] has calculated, and Hutchison's[7] magnetic data confirmed, $W_p < W_m$, we may write

$$t_p W_p + 2t_m W_m \lesssim (t_p + 2t_m) W_m$$

Now the magnetic data indicate that at 0.002 molar about 80% of the electrons are single electrons. Thus since the mobilities of the pairs and metallide ions should be, if anything, smaller than the single electron mobility, we may write

$$t_p + t_m \lesssim 0.2$$

from which

$$t_p + 2t_m \lesssim 0.4$$

The magnetic data indicate a value of $W_m \approx 0.15$ e.v. Thus using this figure we find that at −33°

$$\frac{1}{T}(t_p W_p + 2t_m W_m)_{\text{pure metal}} < 250 \text{ μv./°C.}$$

This is to be compared again with the experimental value of 1600 μv./°C. Since even with the extreme assumptions used here we cannot account for more than a small fraction of the effects observed, the origin of the large salt effect must lie elsewhere.

3. **The Last Two Terms.**—The last two terms in (6) may be shown to operate in the wrong *direction* to account for a positive salt effect. W_x, which appears in the last term, may be shown from conductance measurements[8] to be both small and negative; thus, since addition of salt causes an increase in t_x, the last term can only give rise to a negative salt effect.

As shown above, $W_m > W_p > 0$. Thus, since any common ion effect on the α's must increase α_m by more than it decreases α_p, the factor $(\alpha_p W_p + \alpha_m W_m)$ in the next-to-last term is positive and can only increase on salt addition. The factor $(1 - t_s - t_p - 2t_m)$ is quite readily shown to be positive and can only become more positive on salt addition. Thus the next-to-last term can only give a negative salt effect.

We conclude from the reasoning above that the very large effect of salt addition on the thermoelectric power must arise from sum over the heats-of-transport in equation 6.

B. **Interpretation with Neglect of Association Effects—the Salt Effect.**—In this section we attempt an explanation of the experimental data by completely neglecting the association effects and assuming that the only species in solution are metal ions, X^- ions and single electrons. Equation 6 may be written for this case as (7)

$$\frac{d\varphi}{dT} = \bar{S}_e - \frac{1}{T} \sum_{\text{all ions}} \frac{t_j Q_j^*}{z_j} = \bar{S}_e + \frac{1}{T}(t_e Q_e^* + t_x Q_x^* - t_+ Q_+^*) \tag{7}$$

Rather little is known about the absolute values of the heats-of-transport of even the simplest electrolyte systems. However, studies dating back to Richards[9] in the 19th Century, and continuing in the recent work of Bonnemay,[10] Goodrich and coworkers,[11] Tyrrell, and Hollis[12] and Chanu,[13] indicate that, in aqueous solution at least, the heats-of-transport of "normal" ions do not vary greatly from one ion to another; the only "abnormal" ions in this respect seem to be the hydrogen and hydroxide ions, and even these do not differ from the "normal" ions by much more than 0.1 e.v. These results imply that the heats-of-transport of normal ions in aqueous solution are at most a few kT and it seems quite reasonable to postulate a similar behavior for "normal" ions like Na^+ and Cl^- in liquid ammonia solution. Thus, since the transference numbers of the sodium and chloride ions are either quite small or roughly equal (depending on the salt/metal ratio) in our experiments, we may further simplify equation 6 by cancelling the $t_x Q_x^*$ term against the $t_+ Q_+^*$ term. Equation 7 then becomes

$$\frac{d\varphi}{dT} = \bar{S}_e + \frac{t_e Q_e^*}{T} \tag{8}$$

Equation 8 is in a form suitable for direct comparison with the experimental data. We may plot

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(7) C. A. Hutchison, Jr., and R. C. Pastor, *J. Chem. Phys.*, **21**, 1959 (1953).

(8) (a) E. C. Franklin and C. A. Kraus, THIS JOURNAL, **27**, 191 (1905); (b) A. I. Shatenshtein, *J. Phys. Chem.* (*U.S.S.R.*), **15**, 974 (1941).

(9) T. W. Richards, *Z. physik. Chem.*, **24** 39 (1897).

(10) M. Bonnemay, *J. Chem. Phys.*, **46**, 176 (1949).

(11) J. C. Goodrich, *et al.*, THIS JOURNAL, **72**, 4411 (1950).

(12) H. J. V. Tyrrell and G. L. Hollis, *Trans. Faraday Soc.*, **45**, 411 (1949).

(13) J. Chanu, *J. chim. phys.*, **51**, 390 (1954).

the thermoelectric power at any given concentration of metal as a function of the transference number of the electrons in the mixed salt–metal solutions. If (8) is a valid approximation, we may expect an essentially linear plot, the slope of which will yield the heat of transport of electrons in the solution. Such a plot is shown in Fig. 2. The thermoelectric data, taken from the second paper in this series,[2] are for solutions 0.01 molar in metal content.[14] The transference number of the electrons is calculated, for each value of the salt/metal ratio, from the conductivity and transference data of Franklin and Kraus,[8a] and of Kraus,[15] the assumption being made that there are no interactions between the salt and the metal. The qualitative result is unaffected by other more complex assumptions. Details of the calculation are shown in Appendix I.

As seen from Fig. 2, the thermoelectric data conform in not unreasonable fashion to the linear behavior predicted by equation 8. The slope of the thermoelectric power *vs.* t_e curve multiplied by the absolute temperature yields a value for the heat-of-transport of the electrons

$$Q_e^* = -0.70 \text{ e.v.}$$

This large negative value for the heat-of-transport is a surprising result; at first glance it seems to contradict many of the ideas which have been presented in the past regarding the structure of these metal–ammonia solutions, and if the salt effect stood by itself as the only anomalous feature of the data one would be strongly tempted to discard such an explanation. In this connection it should be mentioned that one could quite readily understand a *positive* heat of transport of 0.7 e.v. This would be roughly the value to be expected if the electrons moved *via* the conduction band which, according to Jolly,[16] is located ~0.8 e.v. above the electron pair level. The result that the mobile electrons appear to carry considerably *less* than the thermostatic enthalpy requires extensive confirmation from other sources.

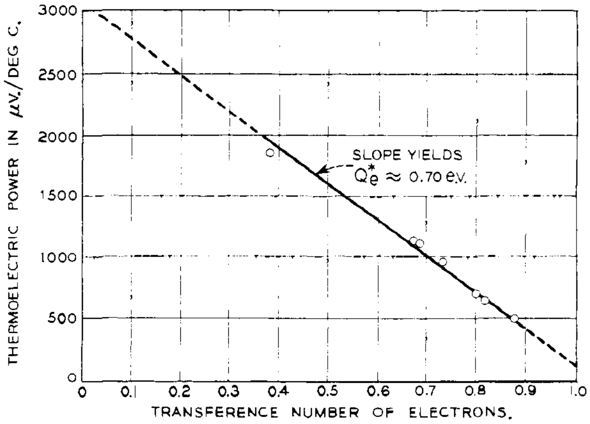

Fig. 2.—The thermoelectric power of mixed sodium–sodium chloride solutions as a function of the transference number of the electrons (calculated). Data are for solutions 0.01 molar in metal at −33°.

C. The Concentration and Temperature Dependences in the Pure Metal Solutions.—We obtain at least a partial confirmation of the negative heat-of-transport from the anomalous concentration and temperature dependences. Consider first the concentration dependence of the pure metal solutions. There are two major sources of a concentration dependence of thermoelectric power exhibited by equation 8, the entropy term ($\bar{S}_e$) and the transference number (t_e). For an ideal solution the entropy term is of the form

$$\bar{S}_e = \bar{S}_0 - 2.303\, k \log_{10} C$$

For a real solution the entropy variation will be somewhat less than this, but still roughly of this form. The transference number of the electrons may also be empirically approximated as a logarithmic function of concentration in the range from approximately 0.002 to 0.05 molar. From Kraus' transference data[15] we obtain

$$t_e \approx 1.048 + 0.065 \log C$$

Inserting these values and the value of Q_e^* derived above into (8) and differentiating, we obtain at −33°

$$\frac{\mathrm{d}(\mathrm{d}\varphi)/\mathrm{d}T)}{\mathrm{d}\log_{10} C} \approx -2.303k - 190 = -375\ \mu\text{v./°C.}$$

This value is to be compared with the experimental value of −340 μv./°C. for sodium and potassium solutions at −33°. The agreement is good, probably fortuitously good, in view of the many approximations involved. Regardless of this, at least a major portion of the anomalous concentration dependence of the pure solutions can be accounted for if the heat of transport is negative.

A second confirmation of the large negative heat of transport of electrons is obtained from the fact that the large Thomson coefficients observed for the pure metal solutions are of the order predicted by equation 8. The Thomson coefficient, (σ), may be obtained from (8) by differentiating with respect to T.

$$\sigma = \frac{(\mathrm{d}^2\varphi)}{(\mathrm{d}T^2)} = \frac{\mathrm{d}\bar{S}_e}{\mathrm{d}T} - \frac{Q_e^*}{T_2}\, t_e + \frac{Q_e^*}{T}\frac{\mathrm{d}t_e}{\mathrm{d}T} \qquad (9)$$

We expect that (9) will be valid only in very dilute solution since the Thomson coefficient is a second-order term. Where the discard of association effects at finite concentration might be justified in treating the first-order effects, this cannot be done for the second-order terms. Now, unfortunately, we do not have any precise data to evaluate the first and last terms in (9). However, orders of magnitude for these terms may be obtained, from the Sackur equation for the first, and from the temperature dependence of conductivity of solutions in ammonia for the second. The two terms act in opposite directions and are both appreciably smaller than the observed Thomson coefficients at high dilution. The second term may then be taken to be the major factor in the Thomson coefficient at high dilution. Using the value −0.7 e.v. for Q_e^* and a value of 7/8 for t_e we find

$$-\frac{(Q_e^* t_e)}{(T^2)_{\mathrm{Na}}} = 10.6\ \mu\text{v./°C.}^2 \text{ (at } -33°)$$

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[14] The result is very nearly independent of the metal concentration in the range of concentration studied here. See below under "concentration dependence."

[15] C. A. Kraus, "Properties of Electrically Conducting Systems, ACS Monograph, 1922.

[16] See the reference cited by Kaplan and Kittel.[17]

This is to be compared with the value of the Thomson coefficient obtained at the lowest concentration studied by us (0.001 *M*)

$$\sigma_{\mathrm{Na}}(0.001) = 6.5\ \mu\mathrm{v.}/^{\circ}\mathrm{C.}^2$$

The discrepancy between the two values is relatively small and since the experimental value is still rising with dilution at 0.001 molar, the real discrepancy may well be even smaller than this.

The difference between the Thomson coefficients observed for sodium and for potassium solutions is also understandable, in terms of the differences in t_e for the two solutions, if the heat of transport is large and negative. Using the ionic conductances at infinite dilution of Kraus and $Q_e = -0.7$ e.v., we predict that at infinite dilution the difference between the Thomson coefficients of the two metals should be

$$\sigma_{\mathrm{Na}} - \sigma_{\mathrm{K}} \approx -\frac{Q_e^*}{T^2}\,(t_e{}^{\mathrm{Na}} - t_e{}^{\mathrm{K}}) = 0.4\ \mu\mathrm{v.}/^{\circ}\mathrm{C.}^2$$

The experimental coefficients for the two metals differ by about 0.7 μv./°C.^{2} at 0.001 molar, in order of magnitude agreement with the prediction.

One final correlation of the experimental data can be made with the assumption of a negative heat of transport. It was shown in paper 2 of this series that the concentration dependence of the mixed salt–metal solutions could be expressed as a linear function of the quantity $1/(1 + 0.3R)$ where R was the salt/metal ratio.

The concentration dependence in the mixed solutions was defined and empirically expressed as

$$\text{“Concn. dependence”} \equiv -\left[\frac{\partial(\mathrm{d}\varphi/\mathrm{d}T)_{\mathrm{R,C}}}{\partial \log C_{\mathrm{metal}}}\right]_{\mathrm{R}} \approx A - B/(1 + 0.3R) \quad (10)$$

The experimental values of A and B were found to be, respectively, 670 μv./°C. and 330 μv./°C. We have already shown that the absolute value of the concentration dependence in the pure metal solutions, ($R = 0$) can be understood in terms of the negative heat of transport. This is also the case for the mixed solutions as can be seen by differentiating equation 8 with respect to concentration at constant salt/metal ratio. Using only conductivity data and the value derived above for Q_e^* we may calculate the value of B in (10). The calculated value is +370 μv./°C. which is in surprisingly good agreement with the experimental value of 330 μv./°C. Physically what this means is that dilution at constant salt/metal ratio has two effects; it changes the entropy and also the transference number of electrons. At finite concentration the latter effect is appreciably larger in the presence of added salt than in its absence because the sodium chloride is more strongly associated than the sodium metal. Because of this the equivalent conductance of the salt will increase on dilution by a larger amount, percentagewise, than does that of the metal. Thus the fraction of the current carried by the salt will increase with dilution at constant salt/metal ratio.

The one effect which is not understandable in terms of this qualitative picture is the concentration dependence of the Thomson coefficient. Since this is, in effect, a third-order term it could very well arise from one or more of the discarded association terms of equation 6. More extensive knowledge of the thermostatic properties of the solutions is required before consideration of this effect would be profitable.

IV. Physical Basis for a Large Negative Heat-of-transport

A. General Discussion.—The preceding semiquantitative interpretation of all the major anomalies in the thermoelectric data seems to establish the validity of large negative heat-transport fairly unambiguously. We attempt now to understand this thermodynamic result in terms of a physical conductance mechanism.

Several conduction mechanisms have been considered in the past. Perhaps the earliest view with any claim to present-day consideration was that of Kraus, that the electrons were "solvated" and moved, essentially as ions, in the form of $(\mathrm{NH_3})_n^-$ ions. More recently the tendency has been to view the dilute solutions as semi-conductors, with most of the electrons trapped in solvent cavities, and conduction taking place by thermal, or photoactivation to a "conduction band," located some 0.7 to 1.0 volt above the trapping level. Kittel and Kaplan[17] have recently questioned this view,—at least for the thermal process—and have in effect returned to the earlier model of Kraus. They picture that the electron-cavity complex moves as a unit. They make an order of magnitude calculation of the mobility of such an aggregate, obtaining a value of the order of typical ionic mobilities, and then ascribe the extra mobility to other causes.

The reasoning used by Kittel and Kaplan to discard the conduction band process appears to be simply that the electron mobility is much too low. This argument is unconvincing, for the equivalent conductance of the electrons which they use in their calculation, (1000 mhos), represents the number average mobility of *all* the electrons, trapped and untrapped; we would normally expect that the number of *conduction* electrons would be very small compared to the total number of electrons. Without some estimate of the population of the conduction band, calculation of the mobility of the *conduction electrons* from the average mobility is clearly not possible. This is not to say that the mechanism of Kaplan and Kittel is incorrect, merely that it was not demonstrated.

A much more convincing argument for abandonment of the conduction band hypothesis is the relatively small temperature coefficient of conductivity observed in these solutions. If the conduction band were located 0.8 e.v. above the trapped level, as is indicated by the photo-absorption and photo-conductivity experiments, and the dark conductivity were by excitation to this level, we would expect a temperature coefficient of dark conductivity given roughly by[18]

$$\frac{\partial \ln \Lambda}{\partial 1/T} \approx \frac{\Delta\epsilon}{2k} \approx 4600^{\circ}\mathrm{K}. \quad (11)$$

The experimental value of the temperature co-

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[17] J. Kaplan and C. Kittel, *J. Chem. Phys.*, **21**, 1429 (1953).

[18] The factor of 2 is used in (11) to take at least order-of-magnitude account of the positive polarization energy of the solvent around a trapped electron. (See below for discussion.)

efficient of dark conductivity is only ~600°K. Thus the conduction band model for the dark conductivity seems highly unlikely.

To our knowledge no other mechanisms have been advanced for the conduction process in dilute solutions. This is rather surprising for we can see no reason to exclude a quantum "tunnel" mechanism. If such a process were in fact operative in the dilute range of concentration one could readily understand both the sign and order of magnitude of the observed heat-of-transport of electrons. Neither the "ionic" type of flow, pictured by Kraus and by Kaplan and Kittel, nor the conduction band model can predict such behavior.

To see how a tunnel conduction process could give rise to a large negative heat-of-transport we need to consider the nature of the electron trapping process. In these liquid solutions the trap may best be visualized, as Ogg[19] has done, as a center of dipole polarization. An electron, finding itself in a region where by chance a few of the solvent dipoles are favorably oriented, will tend to remain in that region and remaining there, will tend to polarize the permanent dipoles of the solvent further, until eventually a fairly stable configuration is achieved. The solvent dipoles will not be able to follow the detailed motion of the electron and thus the electron will "see" an effective charge located at the polarization center, and the electron wave function will be hydrogen-like around this center. Now if another polarization center approaches a trapped electron, the trapped electron may well make a quantum transition to this new center. If it does so, it will leave the energy of dipole polarization behind and since this *positive* energy is included in the thermostatic energy (and enthalpy), a negative heat-of-transport would result, *i.e.*, the mobile species would carry less than the thermostatic energy (or enthalpy).

The details of the process described above are doubtless quite complicated. However we may make an order of magnitude calculation of the size of the heat-of-transport by assuming that the entire polarization energy is left behind when an electron tunnels out of a solvent trap. The repulsive dipolar energy remaining in the dielectric once the electron is removed may be approximated by the Born expression

$$E_{\mathrm{D}} \approx \frac{e^2}{2a}\left(1 - \frac{1}{k}\right) \approx \frac{e^2}{2a} \qquad (12)$$

We may take the result of Lipscomb,[20] that a trapped electron in these solutions is confined very largely in a sphere of radius ~ 3.5 Å. and, assuming that the solvent polarization is largely dipolar, *i.e.*, cannot follow the detailed electronic motion, use it in (12) to find

$$E_{\mathrm{D}} \approx 1.0 \text{ e.v.} \approx -Q_{\mathrm{e}}^*$$

The result is certainly in order-of-magnitude agreement with the experimental value derived from the thermoelectric data, and in the absence of any other plausible mechanism is taken to imply the operation of a tunnel effect in the dark conduction process in these solutions.

V. The Standard Molar Entropy of Ammoniated Electrons

One of the original purposes of this work was to study the entropy of the electrons in these solutions. Now as Holtan, Mazur and DeGroot[4] have shown, and as will be elaborated by one of us in a subsequent paper, one cannot determine either the thermostatic or the transport quantities for individual ions by strictly thermodynamic measurements. Absolute ionic *entropies*-of-transport may appear to be measurable, however in a strictly thermodynamic sense they are no different from the thermostatic entropies since they involve assuming some value for the entropy-of-transport of electrons in a metal, and while this may well be quite small, only a mechanistic argument can demonstrate this.

Realizing the validity of the above reasoning, we may still use equation 8 above (this equation contains mechanistic as well as thermodynamic elements) and, to the extent that the mechanistic arguments used are valid, obtain a value for the absolute "ionic" entropy of ammoniated electrons in the standard state. Using the value of Q_{e}^* derived above, we find for the entropy at 0.01 molar metal concentration and −33°

$$\bar{S}_{\mathrm{e}} = \frac{\mathrm{d}\varphi}{\mathrm{d}T} - \frac{t_{\mathrm{e}}Q_{\mathrm{e}}^*}{T} \approx +74 \text{ e.u.}$$

or for the standard molar entropy at −33°

$$\bar{S}_{\mathrm{e}}^0 = 65 \pm \sim 5 \text{ e.u.}$$

The value above is in sizable disagreement with the value implied by the recent paper of Latimer and Jolly.[21] Using Hutchison's[7] magnetic data we find that if the absolute standard equivalent entropy of electron pairs is 25 e.u., as given by Latimer and Jolly, the absolute standard entropy of single electrons must be 30 e.u., roughly one-half the value calculated above. The discrepancy is not understood at present.

Appendix I

The Calculation of the Transference Number of Electrons in the Mixed Metal–Salt Solutions.—As a crude first approximation to the transference number of electrons in the mixed solutions, we might assume that both salt and metal were completely dissociated, and that the relative mobilities were given, at finite concentration, by the relative ion conductances at infinite dilution. In this case, using the values of λ_0 given by Kraus,[15] we would find

$$t_{\mathrm{e}} = \frac{1}{1 + \frac{\lambda_{\mathrm{Na^+}}}{\lambda_{\mathrm{e^-}}}(1 + R) + \frac{\lambda_{\mathrm{Cl^-}}}{\lambda_{\mathrm{e^-}}} R} = \frac{0.875}{1 + 0.3R} \qquad (1'')$$

This gives the transference number of electrons in the mixed solutions at infinite dilution and is the origin of the abscissa of Fig. 3 in our previous paper.[2]

An appreciably more realistic approximation than this may be obtained for finite concentrations by allowing for the incomplete dissociation of both the salt and the metal. The only assumption which we make is that there are no interactions be-

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[19] R. A. Ogg, Jr., *J. Chem. Phys.*, **14**, 295 (1946); **14**, 114 (1946); THIS JOURNAL, **68**, 155 (1946).

[20] W. N. Lipscomb, *J. Chem. Phys.*, **21**, 52 (1953).

[21] W. M. Latimer and W. L. Jolly, THIS JOURNAL, **75**, 4147 (1953).

tween salt and metal in the solution. We may then write

$$t_e(c,m) = \frac{t_e(c,O)}{\left(1 + R\,\frac{\Lambda_{NaCl}(m)}{\Lambda_{Na}(c)}\right)} \qquad (2'')$$

where

c = concentration of metal
m = concentration of salt
R = salt/metal ratio = m/c

The Λ's are the equivalent conductances of the salt and metal at the concentrations m and c, respectively, and the t_e's are the transference numbers of electrons in the pure metal and mixed solutions.

The transference numbers shown in Fig. 2 of this paper were calculated using equation 2″ with $t_e(c, 0)$ calculated from the ratio of ion conductances at infinite dilution. Other methods of approximating t_e yield comparable values.

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Kinetics of the Formation of the Formal of Polyvinyl Alcohol

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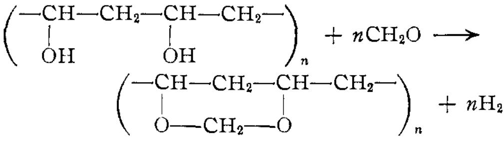
The sulfuric, perchloric or hydrochloric acid-catalyzed formation of the formal of polyvinyl alcohol in aqueous media has been investigated kinetically at 70° by estimating iodometrically the formaldehyde consumed. It was found that the rate was proportional to the product of the stoichiometric concentrations of formaldehyde and the hydroxyl group of polyvinyl alcohol. A linear relationship with almost unit slope (−1.07) was obtained between log k and the acidity function, H_0, of the solution. A mechanism is postulated which involves the rate-determining attack of protonated formaldehyde on the hydroxyl group of polyvinyl alcohol followed by the rapid cyclization with the neighboring hydroxyl group.

Several authors have reported kinetic studies of the formation of acetals from aliphatic alcohols.[1] A mechanism which involves the rapid reversible formation of hemiacetal,[2] followed by the rate-determining condensation of it with another alcohol molecule, appears to gain general acceptance.[3] However, the analysis of the kinetic data does not seem satisfactory. Polyvinyl alcohol is different from ordinary alcohols in that it forms a cyclic acetal with a six-membered ring.



$$(\text{—CH—CH}_2\text{—CH—CH}_2\text{—}(\text{OH})(\text{OH}))_n + n\text{CH}_2\text{O} \longrightarrow (\text{—CH—CH}_2\text{—CH—CH}_2\text{—}(\text{O—CH}_2\text{—O}))_n + n\text{H}_2\text{O} \quad (1)$$

Previous velocity measurements for this reaction have only qualitative meaning.[4] The present paper summarizes the results of kinetic studies of the formal formation of polyvinyl alcohol.

Experimental

Materials.—Nippon Gosei Chemical Co. polyvinyl alcohol (the average degree of polymerization, 1930) was used. Aqueous formaldehyde and sulfuric, perchloric and hydrochloric acids of the best grade were used.

A Typical Procedure for the Rate Measurements.—A mixture of 50 cc. of 0.60 M aqueous polyvinyl alcohol solution,[5] 80 cc. of 2.50 N sulfuric acid and 60 cc. of distilled water was placed in a flask dipped in a thermostat (70 ± 0.2°). After the temperature equilibrium was established, 10 cc. of 1.50 M aqueous formaldehyde solution, previously allowed to attain the same temperature, was added with stirring to the flask from a calibrated pipet. A 10-cc. aliquot was pipetted out at regular time intervals and added to an aqueous solution of *ca.* 50 cc. of 0.5 N sodium hydroxide. To this solution was added 30 cc. of 0.1 N iodine solution, then *ca.* 25 cc. of 1 N sulfuric acid; after standing *ca.* 20 minutes, the solution was titrated with 0.05 N sodium thiosulfate.[6,7] Since the reaction system usually became turbid after 30–40% of the equivalent amount of formaldehyde was consumed, the estimation was limited to this range.

Experimental Results and Calculations.—Apparent second-order rate constants, k, were calculated by means of the equations: if $p \neq 2f$

$$k = \frac{1}{t(p - 2f)} \ln \frac{f(p - 2x)}{p(f - x)} \qquad (2)$$

and if $p = 2f$

$$k = \frac{1}{2t}\left(\frac{1}{f - x} - \frac{1}{f}\right) \qquad (3)$$

Here, p and f are the initial concentrations of polyvinyl alcohol[8] and formaldehyde, respectively, and x is the consumed formaldehyde after t seconds. Table Ia shows the effect of the molar ratio and the initial concentration of reactants on the rate. The effect of the concentration of catalytic acids is given in Table Ib. Values of pH's were determined at 30°.

Some Complementary Experiments. (a) **Reversibility of the Reaction.**—In order to check the reversibility of this reaction[9] the amount of formaldehyde produced from the product was estimated as follows. Partially (*ca.* 40%) reacted polyvinyl alcohol which deposited during the rate measurement was collected, washed thoroughly with water, and dried. About 1.3 g. (0.03 mole) of it was heated for two hours in 100 cc. of 0.25 M aqueous sulfuric acid at 70°,

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[1] H. Adkins and E. W. Adams, THIS JOURNAL, **47**, 1368 (1925); H. Adkins and A. E. Broderick, *ibid.*, **50**, 178 (1928).

[2] *Cf.* H. L. de Leeuw, *Z. physik. Chem.*, **77**, 284 (1911); H. Adkins and A. E. Broderick, THIS JOURNAL, **50**, 499 (1928); W. Herold and K. L. Wolf, *Z. physik. Chem.*, **B12**, 165 (1931); I. Lauder, *Trans. Faraday Soc.*, **48**, 1015 (1952).

[3] For example, L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 304.

[4] N. Fujimoto, T. Osugi and I. Sakurada, *Chem. High Polymers Japan*, **7**, 14 (1950) [*C. A.*, **46**, 883 (1952)].

[5] The concentration of polyvinyl alcohol is represented by that of its hydroxyl group.

[6] *Cf.* J. F. Walker, "Formaldehyde," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1953, p. 385.

[7] Since polyvinyl alcohol forms an addition compound with iodine [*cf.* H. Staudinger, K. Frey and W. Starck, *Ber.*, **60**, 1791 (1927); W. Gallay, *Can. J. Res.*, **14**, B 105 (1936)], it is necessary to correct the titer from the value of the blank test in the same condition, and to use a large excess of the iodine solution.

[8] Strictly speaking, in the initial concentration of hydroxyl group, a maximum reaction percentage (86.5%) should be taken into consideration [*cf.* P. J. Flory, THIS JOURNAL, **61**, 1518 (1939)]; but such accurate treatment seems unnecessary, because kinetics in this case were restricted only to the initial stage of reaction.

[9] I. Sakurada and N. Nakamura, *Bull. Inst. Chem. Research Kyoto Univ.*, **28**, 78 (1952) [*C. A.*, **46**, 8861 (1952)].