

weaker than the hydrogen bond by slightly more than 100 cal. in  $\Delta H$  and of *ca.* 50 cal. in  $\Delta F$ . This conclusion is supported by the higher vapor pressure and the higher heat of vaporization of trifluoroacetic acid-*d* at its boiling point. A possible explanation of the increased strength of the hydrogen bond over that of the deuterium bond lies in the larger volume of the latter, which would result in a much smaller charge density for it. Since the energy of the hydrogen bond is believed to be derived mainly from electrostatic attraction, the weaker deuterium bond is expected.

In Table VIII, the relative order of hydrogen bond strength of the carboxylic acids as measured

TABLE VIII

COMPARISON OF DISSOCIATION DATA OBTAINED FROM SOLUTION STUDIES, AND FROM VAPOR PHASE STUDIES BY TAYLOR

Acid	In benzene		In vapor phase	
	$K_d$ at 30°	$K_{100}$ (mm.)	$\Delta F_{100}$ (cal./mole)	$\Delta H$ (cal./mole)
F <sub>3</sub> CCOOH	..	435	415	14,050
Cl <sub>3</sub> CCOOH	8.8	...	..	....
Formic	7.1	301	686	14,110
Acetic	2.4	92.0	1570	15,270
Propionic	2.3	88.6	1594	15,175

in solution,<sup>15</sup> and as measured in the vapor phase by this investigator are compared. This order is found to be identical with that obtained by Mayotte, Hobbs and Gross<sup>15</sup> and supports their statement: "Other factors being equal, any substituent which, either by inductive or resonance effects, tends to draw electrons away from the carbonyl group and thereby make the effective charge on the oxygens less negative should weaken the hydrogen bond responsible for association." As has been observed before, it appears that the stronger the carboxylic acid the weaker is the hydrogen bond. One would expect that drawing electrons away from the carboxyl group could, in addition to

(15) A. Maryotte, M. E. Hobbs and P. M. Gross, *THIS JOURNAL*, **71**, 1673 (1949).

weakening the hydrogen bond (by making the charge on the oxygen less negative), also strengthen the bond (by increasing the positive charge on the OH hydrogen). Since this strengthening effect takes place to a very small extent, if at all, one must assume that the positive charge on any hydrogen in a carboxyl group is already close to its maximum value.

Data in Table IX show excellent agreement between the values for trifluoroacetic acid obtained

TABLE IX

A SUMMARY OF SIGNIFICANT THERMODYNAMIC PROPERTIES OF ACIDS STUDIED

	A	B	$K_{100}^{\circ}$ (mm.)	$\Delta F_{100}^{\circ}$ cal./mole	$\Delta H$ , cal./mole	$\Delta S_{100}$ , cal./mole deg. <sup>-1</sup>
F <sub>3</sub> CCOOH	-3072	10.869	435	415	14,050	36.5
(by Nash)	-3053	10.800	414	449	13,971	36.2
F <sub>3</sub> CCOOD	-3042	10.815	461	370	13,920	36.3

by Nash and those obtained in this investigation. Failure of such agreement in the case of acetic acid<sup>8</sup> is difficult to understand, as is also the essential constancy of the values for the heat of dissociation for all the acids studied by Nash. Confidence in the results obtained in this series of studies is increased by the findings of Weltner<sup>16</sup> that the thermodynamic constants that we obtained for acetic acid (measured under the same conditions and with the same apparatus used in this study) were essentially in agreement with those determined by him using a completely different procedure.

The precision of the data reported in this investigation is believed to be as follows. For trifluoroacetic acid:  $\pm 100$  cal. in the heat of dissociation with a probability of greater than 95%;  $\pm 10$  in  $K_{100}$  with a probability of greater than 90%. For trifluoroacetic acid-*d*:  $\pm 100$  cal. in the heat of dissociation with a probability of greater than 80%;  $\pm 10$  in  $K_{100}$  with a probability of greater than 70%.

(16) W. Weltner, *ibid.*, **77**, 3941 (1955).

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## The Thermoelectric Properties of Metal-Ammonia Solutions. II. The Thermoelectric Power of Sodium and Potassium Solutions at $-78^{\circ}$ and the Effect of Added Salt on the Thermoelectric Power of Sodium at $-33^{\circ}$

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Measurements of the thermoelectric power of sodium and potassium solutions in liquid ammonia at  $-78^{\circ}$  and of mixed sodium-sodium chloride solutions at  $-33^{\circ}$  are reported. The results in dilute solution show an anomalously large dependence of thermoelectric power on temperature and on concentration of salt, as well as a small but significant dependence on the nature of the metal ion.

### Introduction

The first paper in this series<sup>2</sup> reported on the thermoelectric power of solutions of sodium and potassium in liquid ammonia at  $-33^{\circ}$ . While the data at high concentration were in remarkably

good accord with present day ideas of the nature of these solutions, an anomalously large concentration dependence of thermoelectric power was observed in the concentration region below 0.1 molar. In this latter region the data for sodium were essentially indistinguishable from those for potassium solutions. The present paper reports our in-

(1) Bell Telephone Laboratories, Murray Hill, N. Y.

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

vestigation of the effects of temperature and salt addition on the thermoelectric power of dilute solutions.

### Experimental

The general experimental techniques have been described previously.<sup>2</sup> The only new features in the present work were in the manner of thermal control at  $-78^\circ$  and in the handling of the sodium chloride which was used in the mixed metal-salt experiments.

**Cell.**—The thermoelectric cell employed in the low temperature work was quite similar to that previously described. The entire cell was immersed in a Dry Ice-alcohol slurry. The cold side of the cell was jacketed by a region of partly frozen ammonia, and the "warm" side was wrapped with a finely wound heating coil. A thermal probing of this warm side showed that a steady state could be achieved in which the temperature was uniform within a few hundredths of a degree over about three quarters of the length of the tube. The platinum electrode was placed in the center of this constant temperature region.

**NaCl Preparation and Analysis.**—In the metal-salt experiments, solutions were prepared by placing an aliquot of a stock solution of recrystallized reagent grade sodium chloride in the preparation cell and evaporating off the water; then, after pumping overnight to a vacuum better than  $10^{-6}$  mm., the sodium was distilled into the cell and a known quantity of ammonia was condensed onto the sodium-sodium chloride mixture exactly as previously described. Solutions were diluted successively by removing a known quantity of solution and replacing with a known quantity of pure ammonia. Each such series of dilutions yielded a curve of thermoelectric power *vs.* concentration at a constant ratio of salt to metal, this ratio being determined after completion of a series of dilutions by analysis of the solution for sodium metal. Check analyses were performed for chloride ion to assure that the ratio of salt to metal was in fact maintained constant through the entire series of dilutions. The details of the entire procedure are contained in the Ph.D. thesis.<sup>3</sup>

**Decomposition.**—The decomposition of the solutions has been discussed at length in our previous report. The extent of decomposition was again monitored by measurement of the conductance of the solutions. In the work at  $-78^\circ$  there was not the slightest indication of any decomposition. In the salt experiments however, the rate of decomposition was significantly larger and experiments were performed as rapidly as possible in order to minimize the effects of decomposition. A series of experiments was terminated whenever the total decomposition exceeded about 2%.

### Experimental Results and Discussion

**The Data at  $-78^\circ$ .**—The experimental data for the pure sodium and potassium solutions at  $-78^\circ$  are shown graphically in Fig. 1, where the thermo-

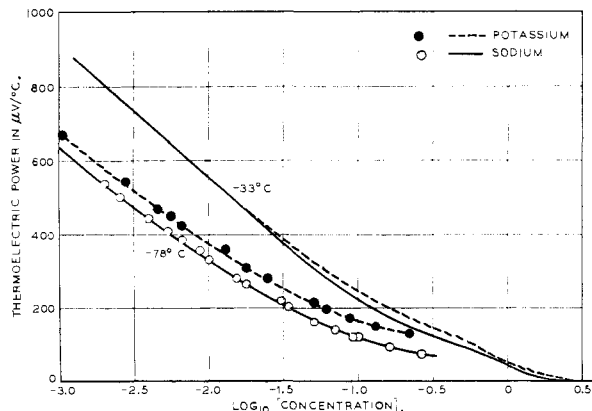


Fig. 1.—The thermoelectric power of dilute sodium and potassium solutions at  $-78^\circ$ .

electric power is plotted against the logarithm of the metal concentration. The experimental curve at

(3) G. Lepoutre, Yale University, 1953.

$-33^\circ$  from our previous work is shown for comparison with the present results.

Three features of the data are to be noted; first, a large and positive temperature dependence, second, a fairly large and essentially logarithmic dependence of thermoelectric power on metal concentration and, finally, in contrast to the behavior at  $-33^\circ$ , a significant difference between the sodium and the potassium curves. The third observation is rather interesting when taken in conjunction with data previously reported on the magnetic properties of these solutions. It suggests that the specific nature of the positive ion has important bearing on the electronic properties of the dilute solutions. On the basis of our results alone one might be tempted to assume that the positive ion played a significant role only at low temperatures, since at "high" temperature ( $-33^\circ$ ) the thermoelectric behavior of the potassium solutions is indistinguishable from that of the sodium solutions. Hutchison's magnetic resonance data<sup>4</sup> make this assumption untenable, for only at his lowest temperature is the magnetic behavior of the two metals the same, while sizable differences between the two metals are observed at high temperatures. The apparent discrepancy is immediately rationalized when we realize that Hutchison's lowest temperature is our highest temperature, namely,  $-33^\circ$ —the boiling point of ammonia. Apparently this temperature is a singular one, at which the effects of the sodium and potassium ions are the same, but not negligible. This is contrary to recent views of the structure of these solutions.<sup>5,6</sup> We consider this question in a subsequent paper.

Figure 2 shows the temperature dependence of thermoelectric power directly. Here we have

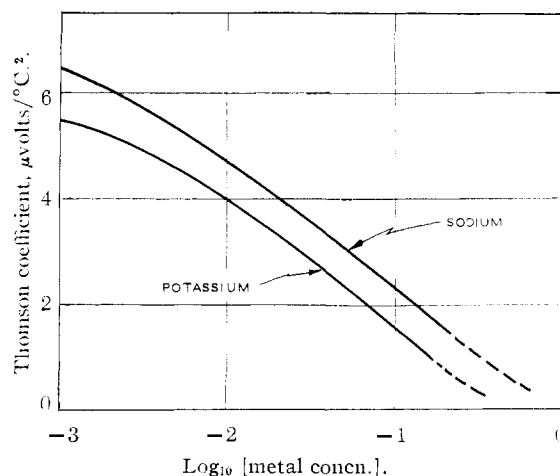


Fig. 2.—The Thomson coefficients of dilute sodium and potassium solutions.

plotted the Thomson coefficient ( $\partial^2\phi/\partial T^2$ ) as a function of the concentration of the solutions. The two curves are calculated from the change in thermoelectric power between  $-33^\circ$  and  $-78^\circ$ . The form of the concentration dependence of the Thomson coefficient is very similar to that of the

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

(5) R. A. Ogg, *ibid.*, **14**, 114, 295 (1946).

(6) J. Kaplan and C. Kittel, *ibid.*, **21**, 1429 (1953).

thermoelectric power itself, showing a roughly logarithmic increase with dilution in the range of concentration which has been studied.

**The Effects of Salt Addition.**—The data on the effects of adding salt to the metal solutions, are shown in Table I and in Fig. 3. For convenience, the original data, obtained at different concentrations of metal in the concentration range from 0.005 to 0.05 molar, have been converted, by graphical interpolation, to a uniform concentration of dissolved metal (arbitrarily taken as 0.01 molar). The original data are contained in the Ph.D. thesis of one of us.<sup>9</sup> The choice of the abscissa in Fig. 3 is made primarily for convenience in obtaining a linear relationship. Use of a function of the form  $1/(1 + aR)$ , where  $R$  is the salt-metal ratio, and "a" is a constant, can be shown to be physically reasonable, as a rough expression for the transference number of electrons in the mixed salt-metal solutions, but for the present we view the form of Fig. 3 as purely empirical.

TABLE I  
THE DEPENDENCE OF THERMOELECTRIC POWER OF MIXED SODIUM-SODIUM CHLORIDE SOLUTIONS ON THE SALT TO METAL RATIO ( $R$ ) AND ON DILUTION ( $V$ ) AT  $-33^\circ$

$R$	Thermoelectric power (at 0.01 $M$ metal concn.) ( $\mu V./^\circ C.$ )	Slope of thermoelectric power vs. $\log(V)$ curves ( $\mu V./^\circ C.$ )
0	517	340
0.29	664	370
0.44	708	365
1.46	985	( )
2.60	1142	485
2.92	1163	495
28.5	1867	635

One of the important features to note from Table I and Fig. 3 is that the addition of salt to a metal solution causes a very large increase in thermoelectric power; the effect is in the direction to be expected if the salt were decreasing the concentration of the electrons, by common ion effect for example. However, as will be shown in an accompanying paper, the observed changes in thermoelectric power are nearly ten times as large as can be accounted for by such a thermostatic mechanism. The origin of the large salt effect appears to lie in the thermal diffusion potential.

In our original work at  $-33^\circ$  we observed an anomalously large concentration dependence of the thermoelectric power. Figure 3 shows how this concentration dependence is affected by the addition of salt. Here we have plotted the slopes of the thermoelectric power vs. log of dilution curves as a function of the salt-metal ratio. The mixed salt-metal solutions show an even larger, and thus presumably more anomalous, dependence on dilution. At the highest salt-metal ratios studied, the concentration dependence is more than three times the dependence which could possibly arise from the electron entropy term in the thermoelectric power. Rather surprisingly, the variation of the concentration dependence with salt-metal ratio is very nearly of the same form as the variation of the thermoelectric power itself.

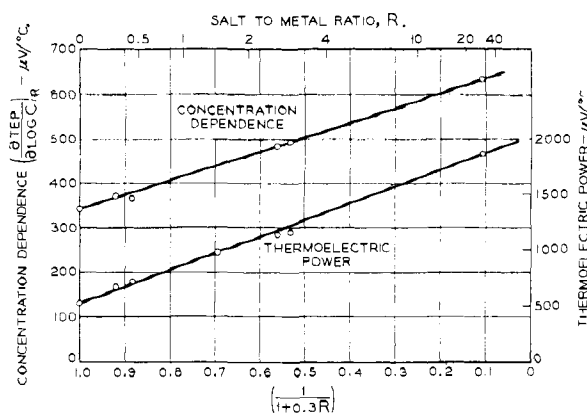


Fig. 3.—The thermoelectric power and the concentration dependence of thermoelectric power of mixed sodium-sodium chloride solutions at  $-33^\circ$ . The data are for solutions 0.01 molar in metal at salt/metal ratio  $R$ . The concentration dependence is defined as  $[\partial(\partial\phi/\partial T)_{C,R}/\partial \log C_{\text{metal}}]_R$ .

### Discussion

Three apparently anomalous dependences of the thermoelectric power of metal-ammonia solutions have been observed and reported; the solutions exhibit large Thomson coefficients, extremely large salt effects and large dilution effects. If one uses the equations derived by Holten, DeGroot and Mazur<sup>7</sup> for the thermoelectric power of thermocells involving strong electrolytes, one can account for all three of these dependences with the single assumption—that the heat of transport of electrons is negative, *i.e.*, that when electrons move through the solution, heat is transported in the opposite direction. Such a behavior, while certainly not one to be anticipated, could arise if the primary mode of electron transport in the solutions were by a tunnel process; in making transitions from one polarization center to another, an electron would then leave the dipole polarization energy of the center behind and, with the electron gone, this energy would eventually be transformed into heat. In its "new" environment the electron would polarize the solvent at the expense of the thermal energy of the surroundings. Thus, polarization energy would flow in a direction opposite to the electron flow.

The tunnel process has not been given much credence in previous considerations of the conduction mechanism in these solutions and therefore we hesitate to introduce this view before eliminating simpler explanations such as the questionable use of the strong electrolyte equations to describe associating systems like these metal-ammonia solutions. However, the demonstration that the effects of association are in fact much smaller than the observed anomalies, is a lengthy process and it is therefore made in an accompanying paper; the detailed interpretation of the data in terms of the tunnel hypothesis is made in the same paper.

(7) H. Holten, Jr., P. Mazur and S. R. DeGroot, *Physica*, **XIX**, 1109 (1953).