water solution $H_3N:BF_3$ exists as a monomeric molecular species, and that it is not appreciably dissociated.

3. Optical studies have been made on crystals of ammonia–boron trifluoride, and its powder X-ray diffraction pattern has been established.

4. The heat of formation of solid ammonia–boron trifluoride from the gases at 0° has been determined calorimetrically as 41.3 kcal.

5. It has been shown that the compound undergoes irreversible thermal decomposition at temperatures above 125° according to the equation: $4H_3N:BF_3 \xrightarrow{125°} 3NH_4BF_4 + BN$.

6. Vapor pressure measurements obtained when ammonia–boron trifluoride is heated give values shown to be those of ammonium fluoborate, the only decomposition product volatile in the temperature range studied. The P.T. equation for NH_4BF_4 is $\log_{10} p(\text{mm.}) = -2469/T + 6.82$. The molar heat of sublimation of NH_4BF_4 is 11.3 kcal.

ITHACA, NEW YORK RECEIVED NOVEMBER 1, 1947

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF TORONTO]

Thermodynamics of Sodium Chloride in 50 Mole Per Cent. Aqueous Methanol from E. m. f. Measurements on Cells with Transference

BY J. P. BUTLER AND A. R. GORDON

While concentration cells with transference have been used extensively in the study of electrolytes in aqueous solution[1,2] and have yielded some of the most precise thermodynamic data now available for such solutions, lack of transference numbers has so far prevented their use with solvents other than water. One interesting exception is provided by the work of Harned and Dreby[3] who employed cells with and without transference to yield indirectly transference numbers for hydrochloric acid in dioxane–water mixtures. Recent measurements in this laboratory[4] have now made possible the use of this method for sodium chloride in 50 mole per cent. methanol–water solution. Apart from testing the precision of the measurements with a solvent other than water, the primary purpose of this research was to determine whether the thermodynamic mean ionic diameter was significant when comparing ionic transport processes in two different solvents.

The cells, the preparation of the electrodes, and the general experimental technique have been previously described.[2] In all cases, the observed e. m. f. has been corrected for bias potential as described by Hornibrook, Janz and Gordon. One rather surprising result was that the bias potentials for stable pairs of electrodes were of the same order as those found in aqueous solution, *viz.*, 0.03 mv. or less. Even more surprising was the fact that the bias potential for a given pair was not only independent (within a microvolt or so) of the salt concentration in the mixed solvent, but had also the same value within similar limits after the electrodes had stood for half an hour in a solution with pure methanol or pure water as solvent. This suggests that lightly plated, electrolytically anodized Ag/AgCl electrodes are considerably sturdier than is generally assumed, provided a galvanometer of high currect sensitivity is used.

The solutions were prepared as described by Schiff and Gordon.[5] In computing the volume concentration C from the mass concentration, the density measurements of Shemilt, Davies and Gordon[4] were employed; these give for the range of interest here

$$C/m = 0.88123(1 - 0.0134m) \qquad (1)$$

where m is the molality.

The results are summarized in Table I under the heading E_{obs}. Only average values for round concentrations are given in the table; the method by which these were obtained from the results of individual runs, carried out at concentrations differing slightly from those recorded, will be described below.

TABLE I

m_1 = 0.05 MOLAL; 25°

m_2	$E_{\text{obs.}}$, mv.	$E_{\text{calc.}}$, mv.	m_2	$E_{\text{obs.}}$, mv.	$E_{\text{calc.}}$, mv.
0.003	$+58.07_5$	$+58.07_5$	0.04	+4.386	+4.391
.005	$+47.14_5$	$+47.14_5$	.06	−3.575	−3.564
.01	$+32.56_5$	$+32.56_0$	.07	−6.556	−6.560
.02	+18.293	+18.300	.08	−9.149	−9.147
.03	+10.114	+10.112			

The e. m. f. of a cell of the type Ag,AgCl/NaCl(m_1)//NaCl(m_2)/AgCl,Ag is of course given by the familiar expression

$$E = kt_+^0\ \Delta \log \gamma m + \Delta F(t_+) \qquad (2)$$

Here, k = 118.28 mv., t_+^0 is the limiting transference number for the cation (0.4437), Δ stands for function (m_1) − function (m_2), and $F(t_+)$ is given by

$$F(t_+) = k \int_0^m (t_+ - t_+^0)\ \mathrm{d} \log \gamma m \qquad (3)$$

Eq. 2 can be solved by the usual method of suc-

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(1) Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935); Shedlovsky and MacInnes, *ibid.*, **58**, 1970 (1936); **59**, 503 (1937).

(2) Hornibrook, Janz and Gordon, *ibid.*, **64**, 513 (1942); Janz and Gordon, *ibid.*, **65**, 218 (1943); MacWilliam and Gordon, *ibid.*, **65**, 484 (1943); McLeod and Gordon, *ibid.*, **68**, 58 (1946).

(3) Harned and Dreby, *ibid.*, **61**, 3113 (1939).

(4) Shemilt, Davies and Gordon, *J. Chem. Phys.*, **16**, 340 (1948).

(5) Schiff and Gordon, *ibid.*, **16**, 336 (1948).

cessive approximations, employing the transference data of Shemilt, Davies and Gordon,[4] to yield a consistent set of $\Delta \log \gamma = \log \gamma_1 - \log \gamma_2$.

On theoretical grounds, the activity coefficient should be given by

$$\log \gamma^* = -\alpha\sqrt{C}/(1 + \beta\sqrt{C}) + 0.4343\{j^3(X_3/2 - 2Y_3) + j^5(X_5/2 - 4Y_5)\} - \log(1 + 0.05m) \qquad (4)$$

where,[6] for a solvent of dielectric constant[7] 49.84, $\alpha = 1.0072$, $\beta = 0.4125a$, $j = 11.24/a$, and a is the mean ionic diameter in ångströms. The leading term is the usual Debye–Hückel expression, the second contains the "extended terms" of the theory, which have been tabulated as functions of $\beta\sqrt{C}$ by Gronwall, LaMer and Sandved,[8] and the last takes account (with 50 mole per cent. aqueous methanol as solvent) of the change in concentration scale of the electrolyte from mole fraction to molality. If Equation 4 is valid for the concentration range involved, and if the correct value of a has been selected, $\Delta \log \gamma/\gamma^*$ should be uniformly zero. If, on the other hand, Eq. 4 is valid for the lower concentrations but not for those as great as $m_1 = 0.05$, and if once again the correct value of a has been chosen, $\Delta \log \gamma/\gamma^*$ should be a constant for the lower values of m_2, this constant being identically the difference between $\log \gamma$ and $\log \gamma^*$ at 0.05 molal.

Figure 1 shows the result of such an extrapolation with $a = 4.45$ Å.; this corresponds to $\beta = 1.836$ and $j = 2.526$. The quantity plotted is $\Delta \log \gamma/\gamma^*$ for each of the experiments, the abscissas being m_2, expressed in moles per kg. solvent. The value selected for a was chosen after a series of trials with a values ranging from 4 to 5 Å. It is at once evident from the figure that Eq. 4 with $a = 4.45$ adequately represents the activity coefficients up to about 0.025 molal. The figure also gives an idea of the precision and reproducibility of the measurements, the radius of circles corresponding to 5 microvolts in the e. m. f. The maximum deviation of any of the points from the smooth curve corresponds to 0.025 mv., and in only three cases is the discrepancy greater than 0.01 mv. The precision thus is comparable with the best that has been attained in this type of measurement with aqueous solutions.

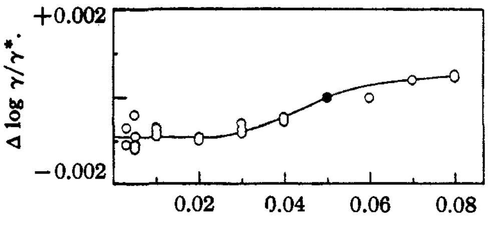

Fig. 1.

The plot also serves as a convenient and precise means of obtaining the "observed" value of the e. m. f. for the round concentrations entered in Table I; from the mean of the observed values of $\Delta \log \gamma/\gamma^*$ for the individual runs and the known value of $\Delta \log \gamma^*$ for the round concentrations, an observed value of $\Delta \log \gamma$ and consequently of the e. m. f. may be obtained at once. From the continuous curve of the figure, the values of $\log \gamma$ entered in Table II were obtained; obviously, the first four entries are also identically $\log \gamma^*$. Table II also gives the values of $F(t_+)$ corresponding to the tabulated values of the activity coefficients.[9] The self-consistency of the two tables is shown by the column headed $E_{\text{calcd.}}$ in Table I, which gives the e. m. f. computed from Eq. 2 by interpolation in Table II. While the precision and reproducibility of the measurements leaves little to be desired, it must nevertheless be remembered that the transference data on which the calculation of the activity coefficients is based, are at best accurate to a part in four thousand; this would correspond for the first entry in Table I to an uncertainty of 0.0003 in $\log \gamma$. We believe, however, that the results recorded here show that cells with transference can yield thermodynamic data of high precision with solvents other than water.

TABLE II

$m^{1/2}$	$1 + \log \gamma$	$F(t_+)$, mv.	$m^{1/2}$	$1 + \log \gamma$	$F(t_+)$, mv.
0.04	0.9639	−0.150	0.20	0.8552	−0.492
.08	.9318	.272	.24	.8343	.549
.12	.9034	.362	.28	.8157	.607
.16	.8782	.434	.32	(.7987)	(− .661)

Two other points deserve mention. The mean ionic diameter found here is the same as that reported by Brown and MacInnes[1] for sodium chloride in aqueous solution.[10] Thus, if a mean ionic diameter determined thermodynamically is significant in transport processes, the ratio of the limiting ion conductances in the mixture to those in water should (on the simple hydrodynamic picture) be close to the reciprocal of the ratio of the viscosities. Actually, as Schiff and Gordon[5] have shown, the limiting conductances in the mixture for sodium and chloride ions are 13% and 28% less than would be predicted from viscosity alone.

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(6) The values of *k* and of the universal constants are those suggested by Manov, Bates, Hamer and Acree, THIS JOURNAL, 65, 1765 (1943).

(7) Albright and Gasting, 68, 1061 (1964).

(8) Gronwall, LaMer and Sandved, *Physik. Z.*, 29, 358 (1928).

(9) For convenience in interpolating, the values of $F(t_+)$ in the table are carried to a greater number of significant figures than is entirely justified by the precision of the transference data.

(10) The smaller value (4.12 Å.) reported by Janz and Gordon[3] results from their use of the empirical Hückel extension to the original Debye–Hückel equation involving the introduction of a term linear in the concentration. It is well known that while this form is applicable over a wider concentration range than is the Debye–Hückel equation itself, its use removes any precise significance from the value of β used in the extrapolation; actually, the activity coefficients reported by Brown and MacInnes and by Janz and Gordon are in excellent agreement in spite of the different analytic forms used to represent the data in the two cases. It is the mean ionic diameter obtained when the linear term is not employed that should be compared with that derived from Eq. 4. In this connection see Brown and MacInnes[1] and Hornibrook, Janz and Gordon.[3]

If ion solvation in the mixture is primarily by water rather than methanol molecules, and if the Debye–LaMer diameter is a true measure of the diameter of the solvated ions, this would account for the surprising agreement between the values of *a* in the two cases. It would still leave unexplained, however, the decreased ion conductances in the mixture as compared with those predicted by the Walden rule, unless some additional factor, significant only in the transport process, is postulated, *e. g.*, hydrogen bonding between the water molecules in the hydrated sheath about the ions and the "free" methanol molecules of the solvent.

Secondly, it should be observed that the *a* value found here is considerably less than the critical Bjerrum[11] distance, given for 1:1 electrolytes by $e^2/2DkT = 5.6$ Å. for a solvent of dielectric constant 50 at 25°. Thus on the Bjerrum picture there should be considerable ion-pair formation, yet the form of the ion conductance *vs.* concentration curves[5] for this salt shows that association must be slight.

A consideration of the data presented here and of the ion conductances suggests (to us at any rate) that the use of a mixed solvent complicates the problem considerably, and that measurements in a one-component non-aqueous solvent may yield data which are more easily interpreted.

Summary

1. The e. m. f. of the cell with transference Ag,AgCl/NaCl(m_1)//NaCl(m_2)/AgCl,Ag, with 50 mole per cent. aqueous methanol as solvent, has been measured at 25° for sodium chloride concentrations from 0.003 to 0.08 *M*.

2. The precision and reproducibility of the results are comparable with those obtained with this type of cell for aqueous solutions. The bias potential between stable pairs of electrodes is 0.03 mv. or less, and is independent within one or two microvolts of the electrolyte concentration, just as is the case when water is solvent.

3. The activity coefficients, computed from the e. m. f. data and the known transference numbers, were extrapolated by means of the Gronwall, LaMer and Sandved extension to the Debye–Hückel equation, which represents the coefficients up to 0.025 *M* when the value selected for the mean ionic diameter is 4.45 Å. For higher concentrations, the observed values lie below those predicted by the equation.

4. The value found for the ionic diameter is in fortuitously exact agreement with that for this salt in water, and is definitely less than the critical Bjerrum distance for this solvent. The significance of the mean ionic diameter in its relation to the ion conductances for the salt in water and in methanol–water solution is discussed.

TORONTO, CANADA RECEIVED MARCH 13, 1948

[11] Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY]

Mixed Adsorption of Radon and Argon on Silica Gel

BY BENJAMIN P. BURTT[1] AND J. D. KURBATOV

Mixed adsorption studies using radon in various gases at 1 atm. have been made by Siebert[2] at −80°, by Francis[3] with silica gels of various states of hydration, by Becker and Stehberger[4] and, using charcoal, by Nikitin and Joffe.[5]

The present work lies in the general field of mixed gas adsorption. The adsorbent was silica gel and all the experiments were conducted at 25 ± 3°. Adsorption isotherms of radon in air, in carbon dioxide and in argon at near atmospheric pressure were obtained. Approximately 1×10^{-16} g. atom of radon at partial pressures around 1×10^{-10} mm. was used.

Adsorption isotherms for air, argon and carbon dioxide were determined under the same experimental conditions as for radon. A brief study was also made of the mixed adsorption of carbon dioxide and air using conventional pressure–volume methods with subsequent analysis of the gas. A more thorough study was made of the mixed adsorption of argon and carbon dioxide applying both methods of conventional analysis and radioactive tracer technique. The adsorption of argon from air was investigated using radioactive argon as a tracer.

Description of the Apparatus and Procedure

The apparatus shown in Fig. 1 was constructed for mixed adsorption studies using radioactive gases. It was also suitable for the measurement of the simple adsorption of gases by pressure–volume methods.

The mixture of radioactive gas and the gas accompanying it is stored in buret S. Chosen volumes of the mixture can be transferred to the evacuated system as well as to the ionization chamber for analysis. The ionization chamber was connected to a Wulf bifilar electrometer. The gas is confined during adsorption in the system, A and E (total volume 26 cc.). About 0.8 g. of silica gel is placed in the removable adsorption flask E. With-

[1] At present in the Department of Chemistry, Syracuse University, Syracuse, New York.

[2] W. Siebert, *Z. physik. Chem.*, **A180**, 169 (1937).

[3] M. Francis, *Kolloid-Z.*, **59**, 292 (1932).

[4] A. Becker and K. H. Stehberger, *Ann. Physik*, [5] 1, 529 (1929).

[5] B. A. Nikitin and E. M. Joffe, *Bull. acad. sci. U. R. S. S., Classe sci chim.*, **1944**, 210–215 (English Summary).