

for the diphenylselenium dibromide<sup>2</sup> molecule. This similarity of molecular structure is in keeping with our observation that the dibromide forms solid solutions with the dichloride having the crystal form and structure of the pure dichloride. This is an interesting fact in view of the lack of isomorphism between the two pure crystalline sub-

stances. An X-ray investigation of a solid solution having 50 mole % of each constituent present shows complete identity of structure with the dichloride.

The observed Se-Cl distance is  $2.30 \pm 0.05 \text{ \AA}$ . and the Cl-Se-Cl bond angle is  $180 \pm 5^\circ$ .

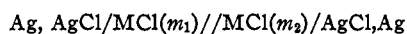
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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF TORONTO]

## The Thermodynamics of Aqueous Solutions of Potassium Chloride at Temperatures from 15–45° from E. m. f. Measurements on Cells with Transference

BY W. J. HORNIBROOK, G. J. JANZ AND A. R. GORDON

Of the thermodynamic investigations by the e. m. f. method of aqueous sodium and potassium chloride solutions, unquestionably the most accurate for the dilute range of concentrations have been those of MacInnes and his associates<sup>1,2</sup> who employed cells of the type



So far such cells with transference have been used only for 25°; recent determinations in this Laboratory of the transport numbers of potassium chloride<sup>3</sup> and of sodium chloride<sup>4</sup> for temperatures from 15–45° now permit similar measurements for temperatures other than 25°. This paper gives the data for potassium chloride and provides (we believe) a satisfactory isotonic standard for dilute solutions for this temperature range. Moreover, thermal and heat capacity data may now be used as an independent check on the self-consistency of the results. Similar measurements on sodium chloride solutions are now under way; we hope to report them in the not too distant future.

### Experimental

The cell, illustrated in Fig. 1, differs from that of Shedlovsky and MacInnes<sup>3</sup> only in the mounting of the electrodes. In our cell, the electrodes are heavy disks of platinum, mounted horizontally in ground glass joints. The disks are about 1 cm. in diameter and 1 mm. thick; in this way, a rigid backing is provided for the active surface of the electrode, while at the same time the electrodes can be silver-plated and chloridized outside the cell. The method of preparing the electrodes was essentially that of Brown and MacInnes.<sup>1</sup> The highly polished surface of the platinum was plated with silver for five hours

at a current of 0.7 ma., the electrolyte being a 10 g. p. l. solution of potassium silver cyanide from which excess cyanide had been precipitated by addition of silver nitrate. After standing in concentrated ammonia and washing in water, the silver surface was chloridized anodically in tenth normal hydrochloric acid for twenty-five minutes at 0.7 ma. To obtain reproducible results we found it necessary during both plating and chloridizing to have a uniform current density over the electrode; this was ensured by the design of the siphon leading into the vessel in which the electrolysis was being carried out. We also found it desirable to keep the solutions well stirred during the electrolyses. After chloridizing, the electrodes were allowed to stand in conductivity water (which was frequently replaced) for twenty-four hours, and then were kept until required in a twentieth molal solution of potassium chloride.

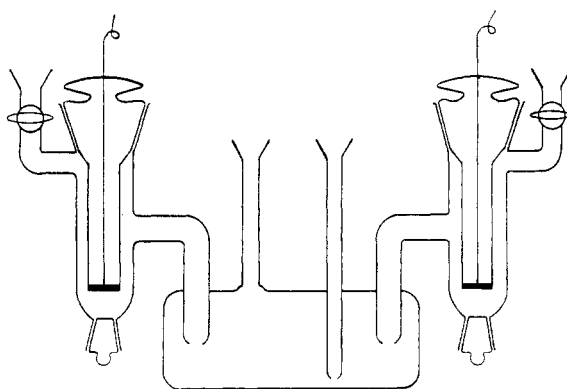


Fig. 1.

The technique of filling the cell has been adequately described by Shedlovsky and MacInnes<sup>3</sup> and need not be discussed here. The solutions were made up gravimetrically from conductivity water (specific conductance  $1.5 \times 10^{-6}$  at 25°) and twice recrystallized B. D. H. Analar potassium chloride which had been fused rapidly in platinum in an atmosphere of dry carbon dioxide-free nitrogen. In computing concentrations, all weights were corrected to vacuum. After filling, the cell was placed in an oil-bath whose temperature was controlled to  $\pm 0.005^\circ$ , bath temperature being read on Beckmann thermometers

(1) A. S. Brown and D. A. MacInnes, *THIS JOURNAL*, **57**, 1356 (1935).

(2) T. Shedlovsky and D. A. MacInnes, *ibid.*, **59**, 503 (1937).

(3) R. W. Allgood, D. J. Le Roy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940).

(4) R. W. Allgood and A. R. Gordon, to appear shortly.

which had been set by means of a platinum resistance thermometer with National Bureau of Standards certificate. The electromotive force readings were made on a calibrated Leeds and Northrup type K<sub>2</sub> potentiometer by means of a galvanometer of sensitivity  $2 \times 10^{-10}$  amp./mm. scale deflection. The Eppley cell, with National Bureau of Standards certificate was checked at intervals against similar standards in the laboratory.

As Shedlovsky and MacInnes found, once thermal equilibrium was attained, the e. m. f. showed fluctuations of only a few microvolts over a period of hours. Following Brown and MacInnes' technique, the cell was then drained, and refilled but with the electrode that had been in the stronger solution now in the weaker and *vice versa*. After following the e. m. f. with this reversed filling, the true reversible e. m. f. was taken to be the average of the two steady readings. As an additional check, the bias potential between the two electrodes when both were in the same solution was read frequently both before and after a run (see below).

A feature inherent in the treatment by Brown, Shedlovsky and MacInnes of cells with transference has been the assumption that reversing the electrodes so that the electrode which had been in the stronger solution was now in the weaker, served to eliminate the random bias potential between the electrodes. This is obviously equivalent to assuming that such a bias potential is independent of the concentration of the solution, and Brown and MacInnes<sup>1</sup> gave good experimental evidence in favor of this. Some time later, however, Smith and Taylor<sup>5</sup> showed that the potentials of a group of silver-silver chloride electrodes, while reasonably self-consistent among themselves, showed a steady drift with time over a period of several days when compared with an older group of electrodes; they ascribed this drift to diffusion from the body of the solution into the pores in the active surface of the electrode—a suggestion which threw some doubt on Brown and MacInnes' conclusion. The duration of the effect seemed to argue against their explanation since (to take the simple case of plane diffusion) concentration differences tend to disappear with exp.  $(-\pi^2 kt/x^2)$  where  $k$  is the diffusion constant,  $t$  the time, and  $x$  the distance from the plane where the concentration is constant. For potassium chloride at 25°,  $k = 2 \times 10^{-5}$  cm./sec.; if  $x$  be taken as 0.1 cm. (a liberal estimate for the length of a pore plus the thickness of an adherent diffusion layer in the solution), the exponential falls to 0.0001 within less than ten minutes.

One test of Smith and Taylor's explanation

(5) E. R. Smith and J. R. Taylor, *National Bureau of Standards J. Research*, **20**, 833 (1938).

may be cited. Two electrodes prepared at the same time were immersed in a 0.05 *M* potassium chloride solution, and electrode A showed a potential of  $-0.017$  mv. against electrode B for a period of twelve hours with fluctuations of only one or two microvolts. A was then transferred to a 0.01 *M* solution; twelve hours later, B was transferred to the 0.01 *M* solution, and after twenty-five minutes A showed a potential against B of  $-0.019$  mv., which was again steady within a microvolt or so for a further twelve hours.

Another test is afforded by the first 25° entry in Table I. With electrode A in the stronger solution and B in the weaker, the steady value of the e. m. f. was 38.164 mv.; with B and A interchanged, the steady value was 38.118 mv., corresponding to a true reversible e. m. f. of 38.141 mv. and a bias potential of A against B of  $+0.023$  mv. After completion of the run, both electrodes were placed in the stronger solution, and after forty minutes showed a steady bias potential of A against B of  $+0.020$  mv. We believe that such results, typical of those obtained from many similar tests, amply justify Brown and MacInnes' averaging procedure. Naturally, such measurements only show that if the potentials of two electrodes, prepared to be as nearly identical as possible and of the same age, are changing with time, they are changing at the same rate, and that this rate is independent (for considerable periods at any rate) of the concentration of the solution. On the other hand, we have frequently found that a pair of supposedly identical electrodes will show a drifting or fluctuating bias of several hundredths of a millivolt; we believe the explanation of this, as well as of Smith and Taylor's results, is change in the nature of the active surface of the electrode, *e. g.*, solution of the smaller silver chloride crystals, uncovering of "hot spots" on silver crystals, etc., and not diffusion.

Table I gives the results; here  $m_1$  and  $m_2$  are the molalities of the two solutions, and the observed e. m. f. in millivolts is entered in the column headed  $E_{\text{obs}}$ . The theory of such cells is now well understood<sup>1,2</sup> and need not be discussed here. The electromotive force is given by

$$E = k \int_{m_2}^{m_1} t_+ d \log \gamma m \quad (1)$$

$$= kt_+^0 (\Delta \log m + \Delta \log \gamma) + k \int_{m_2}^{m_1} t_3 d \log \gamma m \quad (2)$$

where  $k = 2.3026 \times 2RT/F$ ,  $t_+$  (equal to  $t_+^0 + t_3$ ) is the transference number of the cation,  $t_+^0$  is the

transference number at infinite dilution, and  $\Delta$  indicates function ( $m_1$ ) - function ( $m_2$ ). As a first approximation,  $\gamma$  is set equal to 1 in the last term of (2); from the resulting provisional  $\Delta \log \gamma$ , the last term is evaluated, and thus a second approximation to  $\Delta \log \gamma$  is obtained; a third approximation is unnecessary. Table II gives the  $k$  and  $t_+^0$  used in the calculations, while the last term of Eq. 2 is tabulated<sup>6</sup> in Table III. To extrapolate to infinite dilution  $\Delta \log \gamma + \Delta (a\sqrt{m}/(1 + b\sqrt{m}))$  is plotted against  $m$ ; here  $a = \alpha d_0^{1/2}$ ,  $b = \beta d_0^{1/2}$  where  $\alpha$  and  $\beta$  are the characteristic parameters of the Debye-Hückel theory, and  $d_0$  is the density of water. If an appropriate value of  $b$  has been selected, the resulting plot is a straight line whose slope is the coefficient of the linear term in the usual expression for the activity coefficient

$$\log \gamma = - a\sqrt{m}/(1 + b\sqrt{m}) + Dm \quad (3)$$

This form is, of course, valid only for dilute solutions; the linear term then serves as an *omnium gaiherum* correction for a possible linear term in the volume concentration  $C$ , for the term correcting Raoult law activity coefficients to molal activity coefficients, and for the slight change in the leading term brought about by replacing  $C$  by  $md_0$ . Table II gives the values of  $a$ ,  $b$  and  $D$  used in the calculations; those for  $b$  correspond to a distance of closest approach of the ions of 3.98 Å. A point that has been frequently emphasized, however, is that there is nothing unique about the  $b$  of Eq. 3;  $b$  can be varied by several per cent., and a new  $D$  can then be found which will give an equally satisfactory representation of  $\Delta \log \gamma$  and will lead to the same absolute values of the activity coefficients.

Table IV gives  $\log \gamma$  for round values of  $m^{1/2}$ , while Table V gives values of the osmotic coefficient defined by

$$\varphi = 1 + \frac{1}{m} \int_0^m md \ln \gamma \quad (4)$$

The self-consistency of Tables III and IV with Table I is shown by the column headed  $E_{\text{calcd.}}$ , which gives to the nearest 5 microvolts the electromotive force calculated from the entries of Tables III and IV by means of Eq. 2. It is apparent that the agreement is satisfactory—in the majority of cases to 0.01 mv. or better.

Our results for 25° are in satisfactory agreement with those of Shedlovsky and MacInnes<sup>2</sup>;

(6) For convenience in interpolating, the entries in Table III have been recorded to a greater number of significant figures than is justified by the accuracy of the transference data.

TABLE I

$m_1$	$m_2$	$E_{\text{obs.}}$	$E_{\text{calcd.}}$
15° Centigrade			
0.050210	0.009986	+37.065	+37.070
.050000	.010010	+36.941	+36.925
.050084	.020092	+20.803	+20.805
.050084	.029697	+11.850	+11.845
.049581	.029697	+11.604	+11.605
.049581	.039889	+ 4.938	+ 4.900
.050210	.039845	+ 5.224	+ 5.225
.050256	.060127	- 4.011	- 4.030
.050256	.069734	- 7.344	- 7.340
.049860	.080157	-10.609	-10.630
.049860	.099633	-15.461	-15.460
25° Centigrade			
0.049845	0.009922	+38.141	+38.145
.049941	.010015	+37.961	+37.970
.049791	.020015	+21.372	+21.370
.049941	.020032	+21.437	+21.425
.049831	.020105	+21.295	+21.285
.050179	.030000	+12.005	+12.000
.049919	.070304	- 7.894	- 7.905
.050056	.080010	-10.804	-10.815
.050164	.085368	-12.260	-12.250
.049845	.099554	-15.920	-15.915
.049856	.099516	-15.901	-15.900
35° Centigrade			
0.050064	0.009990	+39.182	+39.195
.049895	.010022	+39.037	+39.035
.049916	.020044	+22.009	+22.015
.050033	.029895	+12.360	+12.365
.049916	.041018	+ 4.716	+ 4.700
.050064	.041018	+ 4.777	+ 4.770
.049916	.071700	- 8.602	- 8.605
.050033	.080703	-11.326	-11.350
.049844	.090446	-14.123	-14.125
.049844	.099108	-16.275	-16.275
45° Centigrade			
0.050818	0.010025	+40.563	+40.565
.050198	.010002	+40.295	+40.285
.049857	.020022	+22.610	+22.630
.050851	.029922	+13.095	+13.090
.049994	.059868	- 4.414	- 4.410
.050097	.069815	- 8.113	- 8.110
.049973	.082338	-12.161	-12.170
.050118	.090819	-14.475	-14.480
.050198	.10684	-18.356	-18.370

TABLE II

	15°	25°	35°	45°
$k$ , mv.	114.32	118.29	122.26	126.23
$t_+^0$	0.4928	0.4905	0.4889	0.4872
$a$	0.4966	0.5049	0.5141	0.5244
$b$	1.300	1.307	1.314	1.321
$D$	-0.0140	-0.0075	-0.0055	-0.0040

thus from Table IV,  $\gamma$  for 0.05  $m$  and 0.10  $m$  is 0.8172 and 0.7697, respectively; their correspond-

TABLE III  
 $k \int_0^m t_2 d \log \gamma m$ 

$m^{1/2}$	15°	25°	35°	45°
0.08	-0.022	-0.027	-0.033	-0.040
.16	.040	.051	.059	.067
.24	.057	.070	.076	.082
.32	.074	.083	.084	.086

 TABLE IV  
 1 + log  $\gamma$ 

$m^{1/2}$	15°	25°	35°	45°
0.04	0.9810	0.9808	0.9805	0.9801
.08	.9639 (-1)	.9634	.9627 (0)	.9620 (0)
.12	.9482	.9475	.9466	.9456
.16	.9339 (+1)	.9330	.9319 (0)	.9306 (-1)
.20	.9206	.9197	.9183	.9169
.24	.9083 (0)	.9073	.9059 (-1)	.9042 (-2)
.28	.8969	.8959	.8943	.8925
.32	.8863 (+1)	.8853	.8836 (-3)	.8818 (-3)

ing values<sup>7</sup> are 0.817<sub>2</sub> and 0.770<sub>1</sub>. Harned and Cook<sup>8</sup> from measurements on cells without transference give  $\gamma_{\text{obs}}$  for 0.1  $m$  at 20, 25 and 40° as 0.770, 0.769 and 0.765, respectively; the values obtained by interpolation in Table IV are 0.770<sub>7</sub>, 0.769<sub>7</sub> and 0.765<sub>2</sub>. For 0.05  $m$  the agreement is not as close; for the same three temperatures they find 0.816, 0.815 and 0.811, while our values are 0.818<sub>1</sub>, 0.817<sub>2</sub> and 0.813<sub>5</sub>. When it is remembered that their results were obtained by extrapolation from higher concentrations, and that their cells employed flowing amalgam electrodes which are notoriously difficult to handle in dilute solution, the agreement is all that can be expected.

From our values of log  $\gamma$  at 25°, Rossini's values<sup>9</sup> of  $L_2$  at 18°, and White's values<sup>10</sup> of  $C_{P_2} - C_{P_1}^0$ , it is possible to compute the entries for 15, 35 and 45° by integration of the identity

$$\partial \ln \gamma / \partial T = -L_2 / 2RT^2 \quad (5)$$

The result of such a calculation is indicated by the numbers in parentheses after the entries in

(7) Shedlovsky and MacInnes' observed e. m. f. for the 11 cells involving concentrations up to 0.1  $N$  which they report is compared with the e. m. f. calculated from our Tables III and IV in the accompanying table:

$E_{\text{obs.}}$	70.765	54.025	53.895	37.489	37.483	
$E_{\text{calcd.}}$	70.765	54.020	53.895	37.475	37.470	
$E_{\text{obs.}}$	27.890	27.688	21.170	15.905	11.731	5.113
$E_{\text{calcd.}}$	27.905	27.685	21.165	15.920	11.750	5.115

(8) H. S. Harned and M. A. Cook, *THIS JOURNAL*, **59**, 1290 (1937).

(9) F. D. Rossini, *National Bureau of Standards J. Research*, **6**, 791 (1931).

(10) C. M. White, *J. Phys. Chem.*, **44**, 494 (1940).

Table IV; these give in units in the fourth decimal place of log  $\gamma$ , the difference log  $\gamma$  of Table IV—log  $\gamma$  calculated by Eq. 5, e. g., the entry for 0.0064  $m$  at 15° indicates that the value of 1 + log  $\gamma$  computed from the 25° entry and the thermal data is 0.9640. The agreement on the whole is excellent, the most serious discrepancy (amounting to 0.07% in the activity coefficient) being for the strongest solution at 35 and 45°. It might be added that had Rossini's<sup>11</sup> value of  $C_{P_2} - C_{P_1}^0$  for the temperature range 18–25° been assumed valid up to 45°, these discrepancies would have been reduced to 0.0001.

The agreement of our results with those of Shedlovsky and MacInnes and of Harned and Cook and their consistency with the thermal data indicate (we believe) that Tables IV and V cannot be seriously in error, and that osmotic and activity coefficients obtained from them are probably reliable to a tenth of a per cent. or better.

TABLE V

$m^{1/2}$	THE OSMOTIC COEFFICIENT $\phi$			
	15°	25°	35°	45°
0.08	0.9736	0.9733	0.9728	0.9723
.16	.9538	.9533	.9526	.9517
.24	.9385	.9381	.9372	.9362
.32	.9266	.9264	.9255	.9243

### Summary

1. The e. m. f. of the cell with transference Ag, AgCl/KCl( $m_1$ )/KCl( $m_2$ )/AgCl, Ag has been measured for concentrations up to 0.1  $M$  at temperatures from 15–45°. Employing transference data obtained in this Laboratory, activity and osmotic coefficients have been obtained for this range of temperature and concentration.

2. The results are in excellent agreement with those of Shedlovsky and MacInnes for 25°, and are in satisfactory agreement with those of Harned and Cook. The change of the activity coefficient with temperature is in reasonable agreement with the thermal data.

3. Activity and osmotic coefficients at round values of the square root of the molality are tabulated to provide isotonic standards for this range of temperatures.

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(11) F. D. Rossini, *National Bureau of Standards J. Research*, **7**, 47 (1931).