ered, that on K_N' and on K. As far as K_N' is concerned, the firmer attachment of protons to the α-carbon may be expected to result again in a decrease in K_N' on passing from nitromethane to nitroethane to nitroisopropane. On the other hand, the stronger affinity for protons resulting from replacement of hydrogens with methyl groups is equivalent to a decrease in electron affinity of the carbon, and hence substitution should favor form B over A with a resultant increase in K. As the increase in K may well outweigh the decrease in K_N', K_N may increase appreciably with substitution, as has been observed here. This explanation would account also for the large increase in the tautomeric equilibrium constants K_T observed here on going from nitromethane through nitroethane to the isopropane.

Summary

1. Nitro ionization constants have been determined for nitromethane, nitroethane and nitroisopropane, and aci ionization constants for nitroethane and nitroisopropane at several temperatures.

2. From these constants have been calculated the nitro–aci tautomeric constants for nitromethane, nitroethane and nitroisopropane.

3. Values of ΔF^0 and ΔH for ionization and tautomerization as ascertained from these data are given.

4. The effect of substitution on the constants is discussed. It is shown that assumption of a common anion for the nitro and aci forms leads to inconsistencies in the influence of substitution on the nitro constants, and yields an anion with two basic strengths.

5. An alternate formulation of the nitro-aci relations in the nitroparaffins is presented which resolves these anomalies.

CLEVELAND, OHIO RECEIVED OCTOBER 13, 1942

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF TORONTO]

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

BY G. J. JANZ[1] AND A. R. GORDON

The investigation described here of the electromotive force of the cell with transference

$$\mathrm{Ag,\ AgCl/NaCl}(m_1)//\mathrm{NaCl}(m_2)/\mathrm{AgCl,\ Ag}$$

at temperatures from 15 to 45° was undertaken as a natural complement to that recently reported[2] from this Laboratory giving the corresponding data for potassium chloride solutions. Brown and MacInnes[3] in their classic investigation of this cell were restricted to measurements at 25°, but since transference numbers[4] are now available for the whole temperature range, it is now possible to compare the results of the e. m. f. measurements with the thermal data; fortunately, for sodium chloride solutions the latter are unusually complete. Finally, the accompanying paper[5] gives the results of an isopiestic comparison of sodium and potassium chloride solutions at concentrations less than tenth molal and thus provides an additional independent check on the accuracy of all the measurements.

Experimental

The cell, the electrodes and general experimental technique were the same as in the measurements with potassium chloride; the true reversible e. m. f. was determined both by the electrode reversal procedure of Brown and MacInnes and by static bias potential measurements before and after a run with both electrodes in the same solution (see ref. 2).

The sodium chloride was British Drug Houses Analar, twice recrystallized from conductivity water. The solutions were made up gravimetrically from the salt, which had been fused in platinum in an atmosphere of dry carbon dioxide-free nitrogen, and conductivity water (specific conductance 1.0–1.2 × 10^{-6}); after preparation, the solutions were swept out, immediately before being forced into the cell, with carbon dioxide-free air which after going through the potassium hydroxide bubblers had passed through a further bubbler containing conductivity water. In cal-

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(1) Canadian Industries Limited Fellow in Chemistry.

(2) W. J. Hornibrook, G. J. Janz and A. R. Gordon, THIS JOURNAL, **64**, 513 (1942).

(3) A. S. Brown and D. A. MacInnes, *ibid.*, **57**, 1356 (1935).

(4) R. W. Allgood and A. R. Gordon, *J. Chem. Phys.*, **10**, 124 (1942).

(5) A. R. Gordon, THIS JOURNAL, **65**, 221 (1943).

TABLE I

m_1	m_2	$E_{obs.}$	$E_{calcd.}$	m_1	m_2	$E_{obs.}$	$E_{calcd.}$
15°							
0.050170	0.010004	+29.140	+29.145	0.050841	0.059771	− 2.850	− 2.860
.050002	.019968	+16.443	+16.445	.050073	.070216	− 5.986	− 5.975
.049765	.029809	+ 9.140	+ 9.130	.049816	.080035	− 8.345	− 8.345
.049765	.039878	+ 3.922	+ 3.930	.050029	.089888	−10.295	−10.290
				.050010	.099841	−12.120	−12.130
25°							
.049903	.009963	+30.391	+30.400	.050375	.029878	+ 9.717	+ 9.725
.049896	.009962	+30.391	+30.395	.049794	.029980	+ 9.440	+ 9.435
.049741	.010021	+30.220	+30.215	.049984	.040050	+ 4.103	+ 4.105
.049819	.019955	+17.112	+17.110	.049915	.059944	− 3.373	− 3.370
.049826	.019978	+17.112	+17.090	.049741	.079333	− 8.581	− 8.570
				.049846	.099872	−12.720	−12.720
35°							
.050032	.010011	+31.650	+31.660	.050032	.040010	+ 4.338	+ 4.320
.050023	.019987	+17.867	+17.890	.050218	.066805	− 5.486	− 5.480
.050976	.030096	+10.228	+10.220	.050032	.079883	− 8.968	− 8.970
				.050976	.099455	−12.759	−12.770
45°							
.050030	.010955	+31.080	+31.085	.050071	.039772	+ 4.643	+ 4.630
.050071	.020030	+18.565	+18.600	.049986	.070081	− 6.753	− 6.750
.050030	.030723	+ 9.843	+ 9.845	.050115	.090239	−11.728	−11.715
				.050024	.10068	−13.899	−13.910

culating molalities, all weights have been reduced to vacuum.

The results are given in Table I; here m_1 and m_2 are the molalities, and $E_{obs.}$ the e. m. f. in millivolts, corrected for bias potential (see above and ref. 2). In almost all cases, several runs, each with a different set of electrodes, were carried out on the same pair of solutions; to save space in the table, these have been averaged, *e. g.*, the first 15° entry is the mean of three independent results 29.145, 29.137 and 29.138 mv.; this agreement is typical of that obtaining between the individual measurements.

The e. m. f. is related to the activity coefficients by the familiar relation[2,3]

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

$$= kt^0_+ \, \Delta\log\gamma m + k\int_{m_2}^{m_1} t_\delta \, d\log\gamma m \qquad (2)$$

where $k = 2.3026 \times 2\,RT/F$, F is Faraday's constant, t_+ and t^0_+ are the transference numbers of the cation at molality m and at infinite dilution, respectively, and $t_\delta = t_+ - t^0_+$. The usual procedure[2,3] of successive approximations yields values of $\Delta \log \gamma$ and from these in turn the coefficients b and D in the expression for the activity coefficient

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

Here a and b are the theoretical Debye–Hückel coefficients multiplied by the square root of the density of water; this form, valid for dilute solutions, has the advantage that the activity coefficient is expressed explicitly as a function of the molality rather than of the volume concentration. Table II gives the numerical values of the constants, those for b corresponding to a distance of closest approach of 4.12 Å. Table III gives for round values of $m^{1/2}$ the integral of Eq. 2 to the nearest 5 microvolts. It should be noted that owing to the considerable variation of the transference number for sodium chloride with concentration, this term is much more important here than it was in the case of potassium chloride solutions.

TABLE II

	15°	25°	35°	45°
k, mv.	114.32	118.29	122.26	126.23
t^0_+	0.3929	0.3962	0.4002	0.4039
a	0.4966	0.5049	0.5141	0.5244
b	1.343	1.350	1.357	1.364
D	+0.022	+0.031	+0.034	+0.033

TABLE III

$$-k\int_0^m t_\delta \, d\log\gamma m$$

$m^{1/2}$	15°	25°	35°	45°
0.08	0.370	0.380	0.390	0.405
.16	0.690	0.715	0.735	0.750
.24	0.975	1.010	1.040	1.060
.32	1.230	1.270	1.310	1.330

Tables IV and V give for round values of $m^{1/2}$ values of the activity and osmotic coefficients computed from the data of Table II. The last column of Table I, headed $E_{\text{calcd.}}$, gives for purposes of comparison the value of the e. m. f. calculated from Tables III and IV. The agreement is in general satisfactory; in only three instances is the difference between the observed and calculated e. m. f. as great as 0.02 mv. The striking discrepancy for the cell involving 0.02 molal solution at 45° (which was only noted after the work was completed) is probably due to a mistake in the concentration since the individual measurements with different pairs of electrodes were in excellent agreement.

TABLE IV

$1 + \log \gamma$

$m^{1/2}$	15°	25°	35°	45°
0.04	0.9812	0.9809	0.9806	0.9802
.08	.9643 (+1)	.9637	.9631 (+1)	.9624 (+1)
.12	.9490	.9483	.9474	.9464
.16	.9352 (0)	.9344	.9333 (0)	.9320 (+1)
.20	.9226	.9218	.9205	.9189
.24	.9111 (−2)	.9103	.9089 (0)	.9071 (0)
.28	.9007	.8998	.8984	.8963
.32	.8911 (−1)	.8903	.8888 (0)	.8866 (−1)

TABLE V

$$\varphi = 1 + (1/m) \int_0^m m \, \mathrm{d} \ln \gamma m$$

$m^{1/2}$	15°	25°	35°	45°
0.08	0.9740	0.9737	0.9732	0.9727
.16	.9552	.9548	.9541	.9532
.24	.9416	.9414	.9406	.9395
.32	.9319	.9320	.9312	.9298

Brown and MacInnes[3] tabulated not γ but the activity coefficient on a volume concentration basis; a calculation[6] of γ from their f for 0.1 m gives 0.7784, exactly the result obtained by interpolation in the 25° column of Table IV. A calculation of the e. m. f. of the cells in their Table III, however, from our Tables III and IV predicts values[7] which are slightly greater than those they obtained. The reason for this apparent contradiction is that the smoothed transference numbers listed in their Table III and used in their calculation are slightly less for concentrations from 0.04 N to 0.08 N than those used in computing our Table III, which are based on the actual results of Longsworth[8] and of Allgood and Gordon[4] (see Table II of ref. 4). A recalculation of Brown and MacInnes' data using our Table III leads (for b = 1.350) to D = 0.027, *i. e.*, γ for 0.1 molal will be 0.7777 as compared with our value 0.7784. While this discrepancy is not serious, being only slightly greater than the precision of the measurements, it is nevertheless puzzling in view of the phenomenally close agreement of our results for potassium chloride with those of Shedlovsky and MacInnes.[9] The only suggestion we can make, and we do so very tentatively, is that Brown and MacInnes used wire electrodes, while Shedlovsky and MacInnes and ourselves used electrodes of large area rigidly fixed in the cell; the latter are much more rugged and less easily polarized than the former.

The e. m. f. measurements of Harned and Nims[10] on cells without transference have been recalculated by Harned and Cook[11] in the light of Brown and MacInnes' results. For 25°, Eq. 3 with the constants of our Table II gives Harned and Cook's revised values of γ up to 0.5 molar almost exactly[12]; the results on the cells with transference up to tenth molal are thus entirely consistent with the results on the cells without transference above this concentration.

By integration of the identity $\partial \ln \gamma / \partial T = -L_2/2RT^2$, it is possible to check the e. m. f. measurements against the thermal data. Gulbransen and Robinson[13] give values of L_2 for 15, 20 and 25° while White [14] gives data for 35 and 45° based on the 25° numbers and his values of $C_{P_2} - C^0_{P_2}$. The result of the calculation, effected by tabular integration, is shown by the numbers in brackets after the 15, 35 and 45° entries of Table IV; these give in units in the fourth decimal place of log γ the difference log γ of Table IV minus log γ computed from the 25° entry and the thermal data; the agreement is satisfactory; in only one instance is the difference as great as 0.05% in the activity coefficient.

There is yet another test that may be applied to the data. This is discussed in the accompanying paper which gives the results of the isopiestic

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(6) H. S. Harned, *J. Franklin Inst.*, **225**, 623 (1938).

(7) The comparison between Brown and MacInnes' nine cells in their Table III and our Tables III and IV is summarized

$E_{\text{obs.}}$ (B. and MacI.)	56.450	49.907	43.029	29.804	22.181
$E_{\text{calcd.}}$	56.475	49.935	43.045	29.820	22.190
$E_{\text{obs.}}$ (B. and MacI.)	16.818	12.695	9.317	4.056	
$E_{\text{calcd.}}$	16.820	12.685	9.330	4.060	

(8) L. G. Longsworth, THIS JOURNAL, **54**, 2741 (1932).

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

(10) H. S. Harned and L. F. Nims, *ibid.*, **54**, 423 (1932).

(11) H. S. Harned and M. A. Cook, *ibid.*, **61**, 495 (1939).

(12) Eq. 3 predicts 0.7784, 0.733, 0.680 and 0.655 for γ at 0.1, 0.2, 0.5 and 1.0 m, respectively; Harned and Cook's corresponding values are 0.779, 0.733, 0.681 and 0.658.

(13) E. A. Gulbransen and A. L. Robinson, THIS JOURNAL, **56**, 2637 (1934).

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

comparison of potassium chloride and sodium chloride solutions at concentrations from 0.03 *m* to 0.10 *m;* it is sufficient to say here that the vapor pressure measurements provide strong independent evidence for the accuracy of the e. m. f. data for both salts.

Added Nov. 16, 1942.—Stonehill and Berry [THIS JOURNAL, **64**, 2724 (1942)] have recently pointed out that the theoretical coefficients of the Debye–Hückel theory should be revised in the light of the currently accepted values of the universal constants *e*, *k* and *N;* they give for 25° $\alpha = 0.5103$, corresponding to a value of *a* of Table II of 0.5096. While this causes considerable changes in the values of *b* and *D* demanded by the extrapolation to infinite dilution, it is of no significance from the practical point of view of obtaining a satisfactory analytic representation of the data. For example, a calculation of the 25° column of Table IV with $a = 0.5096$, $b = 1.500$ and $D = 0.005_0$, leads to values identical with those in the table except that $(1 + \log \gamma)$ for 0.04 and 0.08 is 0.0001 less than the entries as printed and for 0.28 is 0.0001 greater. A similar calculation of the 25° potassium chloride data (see Table IV of ref. 2) with $b = 1.453$, $D = -0.033$, leads to similar agreement. These changes correspond at most to 5 microvolts in the e. m. f., which is less than the accuracy of the measurements.

In conclusion, we wish to express our thanks to Canadian Industries Limited for the grant to one of us (G. J. J.) of a fellowship.

Summary

1. The e. m. f. of the cell with transference Ag, AgCl/NaCl(m_1)//NaCl(m_2)/AgCl, Ag has been measured for concentrations up to 0.1 molal at temperatures from 15 to 45°. Activity and osmotic coefficients have been obtained for this range of temperature and concentration.

2. The results are in good agreement with those of Brown and MacInnes for 25°, and are consistent with those obtained by Harned and Nims from cells without transference for concentration stronger than tenth molal.

3. The variation of the activity coefficient with temperature is in excellent agreement with the heat of dilution and heat capacity data.

TORONTO, CANADA RECEIVED OCTOBER 13, 1942

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF TORONTO]

Isopiestic Measurements in Dilute Solutions; the System Potassium Chloride–Sodium Chloride at 25° at Concentrations from 0.03 to 0.10 Molal

BY A. R. GORDON

Of the various techniques that have been developed for the thermodynamic investigation of solutions, unquestionably one of the most useful and widely applicable has been the isopiestic vapor pressure method.[1] Since the work of Robinson and Sinclair[2] it has yielded a mass of valuable information in the hands of numerous investigators. It has suffered under the disability, however, that the measurements become progressively more difficult the more dilute the solutions. In practice, for 1–1 electrolytes, the lower limit of concentration for which the isopiestic ratio may be determined with reasonable accuracy (say to 0.1%) seems to have been in the neighborhood of tenth molal. Thus Robinson and Sinclair[2] at 25° found 1.011 for the isopiestic ratio m_{KCl}/m_{NaCl} at this concentration; Janis and Ferguson[3] report 0.999 although the smoothed value they use in their calculations is 1.005; Scatchard, Hamer and Wood[4] in the three experiments they report near 0.1 *m* found 1.018, 1.010 and 1.004_5; later Robinson[5] gave as a best value 1.006 for tenth molal while as a result of a recent careful reinvestigation,[6] he selects 1.0070.

Measurements at still lower concentrations have as a rule given somewhat erratic results. For example, Phillips, Watson and Felsing[7] have recently reported isopiestic ratios for the system strontium chloride–barium chloride down to 0.033 molal (corresponding to about 0.05 molal for 1–1 salts); their data for the more concentrated solutions differ considerably from those obtainable from Robinson's measurements[8] and moreover appear to extrapolate at infinite dilution to a value between 1.03 and 1.04. Since the

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[1] For a review of the literature up to 1941, see R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

[2] R. A. Robinson and D. A. Sinclair, THIS JOURNAL, **56**, 1830 (1934).

[3] A. A. Janis and J. B. Ferguson, *Can. J. Research*, **B17**, 215 (1939).

[4] G. Scatchard, W. J. Hamer and S. E. Wood, THIS JOURNAL, **60**, 3061 (1938).

[5] R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1217 (1939).

[6] R. A. Robinson, private communication.

[7] B. A. Phillips, G. M. Watson and W. A. Felsing, THIS JOURNAL, **64**, 244 (1942).

[8] R. A. Robinson, *Trans. Faraday Soc.*, **36**, 735 (1940).