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.

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[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 $m_{\mathrm{KCl}}/m_{\mathrm{NaCl}}$ 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).

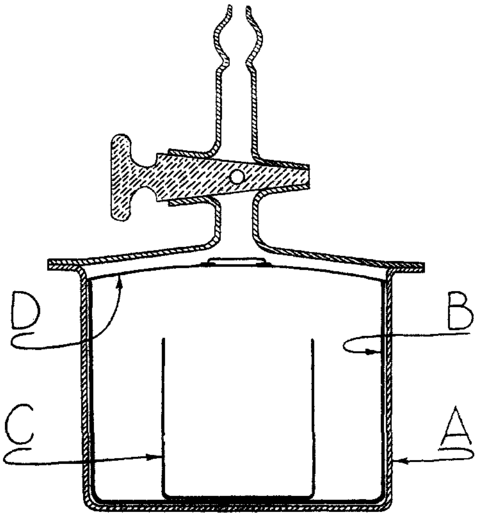

Fig. 1.

isopiestic ratio for two strong electrolytes of the same valence type must extrapolate to unity, it seems possible that there is some systematic error in their measurements.

The difficulty of carrying out measurements in dilute solutions comes from two sources. First, there is the necessity of shielding the apparatus from temperature fluctuations, or at any rate from fluctuations that are not slow in comparison with the rate at which thermal equilibrium is established in the system; second, there is the extremely slow rate at which equilibrium is attained under the slight vapor pressure head present. The factors governing the rate are now fairly well understood—diffusion in the solutions (this can be eliminated by any reasonably efficient system of stirring) diffusion of water vapor in the gaseous phase and finally the thermal resistance to the flow of heat from the one solution to the other.

After numerous trials, the apparatus described below was designed to satisfy as nearly as possible the conditions indicated above. A steady temperature was ensured by enclosing it in a Dewar flask, the thermal path was reduced to a minimum, and the rate of diffusion of the steam was favored by very careful removal of air. It must be confessed, however, that while the results show that values of the isopiestic ratio can be obtained for 1–1 electrolytes at concentrations as low as 0.03 molal, the performance as far as rate of attainment of equilibrium was concerned was distinctly disappointing. The apparent cause of this will be discussed below.

Experimental

The final form of the apparatus is shown in Fig. 1, which is largely self-explanatory. The glass vessel A, with a ground-glass lid, is 42 mm. internal diameter; fitting closely inside it is the silver dish B, and inside B in turn the silver dish C (22 mm. in diameter) held in position in B by means of a light frame of platinum wire (not shown in the figure); both B and C are heavily gold plated inside and out; inside C is a glass bead, 5 mm. in diameter, whose motion as the vessel is rocked stirs the inner solution; D is a loosely fitting silver lid resting on top of B. The glass vessel, enclosed in a copper box with removable lid, fits inside the Dewar flask, which is closed above the box with a heavy cork cylinder, fitting fairly closely, and a batten of tightly packed glass wool. The Dewars (two in this apparatus) are contained in a large glass vacuum desiccator, 25 cm. in diameter, the space about the Dewars being also packed with glass wool; the desiccator is held on a rocking table (total amplitude 45°, period of one complete oscillation six seconds) in a double-walled water-bath whose temperature is electrically controlled to ±0.003° as far as individual fluctuations are concerned, with a maximum drift over forty-eight hours of 0.01°.

The solutions were made up gravimetrically from the twice recrystallized salts which had been fused in platinum in an atmosphere of dry carbon dioxide-free nitrogen, and a good grade of conductivity water; in computing concentrations, all weights have been reduced to vacuum. Known amounts of solutions of known concentrations are introduced into the outer and inner vessels B and C from weight burets, usually about 0.7 g. in C and 6 g. in B. As a rule the initial concentrations were so chosen that the ratio $m_{\mathrm{KCl}}/m_{\mathrm{NaCl}}$ was about 10% different from the true isopiestic ratio corresponding to equilibrium; for example, the entries for 0.05 and 0.06 molal solutions in the table, resulted from an experiment where the "inner" solution in both experiments was 0.055 *m* KCl and the "outer" solutions were 0.049 *m* and 0.061 *m* NaCl, respectively. This precaution is essential when dealing with dilute solutions, since if the initial concentrations have been chosen near some preconceived idea of the isopiestic ratio and if air has not been completely removed (see below) the final concentrations will not have altered appreciably from the initial, and thus may suggest erroneously that equilibrium has been attained.

After removal of air, the apparatus was left in the water-bath for from seven days for the most concentrated solutions to eighteen days for the most dilute; these times were selected after a lengthy preliminary series of measurements in which sodium chloride solutions of different strengths were run against one another; they are on the liberal side but give reasonable assurance that sufficient time has been allowed for equilibrium to be attained. On completion of the run dry air was cautiously admitted to the vessel, the glass lid and the silver cover were removed, and the inner dish C was closed with a close-fitting tapered ground glass stopper; the outer dish B was then quickly transferred with forceps to a light glass container with ground glass lid, and weighed; the inner dish C with its stopper still in place was then removed, dried externally with filter paper, and weighed; these two weighings serve to fix the final weights and thus the final concentrations of the two solutions.

Blank experiments showed that with reasonable care and speed the loss in weight of the inner solution during these operations was not more than 0.2 mg. and of the outer 2 mg.; since these errors tend to cancel in the isopiestic ratio, the resultant error in the ratio is not more than 0.03%.

The most serious experimental difficulty is the removal of air from the system. The procedure finally adopted was to pump the vessel A initially down only to 60 mm. pressure and then allow it to rock for six hours; it was then pumped to 30 mm. and left overnight; in the morning, a further pumping reduced the pressure to the vapor pressure of water. It was then allowed to rock for three periods of twenty-four hours, at the end of each of which the vapor above the solutions was pumped off. In this way it was possible as a rule to effect a fairly complete outgassing of the solutions without risk of spray and consequent risk of transfer of liquid from one dish to the other. To eliminate the chance of air leaking into A from the large desiccator during the run, the glass wool packing was kept moistened with water, and the desiccator was always thoroughly exhausted so that the atmosphere surrounding A during the run was saturated steam.

The necessity for as complete a removal of air as possible became evident in the course of the preliminary measurements on sodium chloride solutions; for example, two solutions (0.080 and 0.086 *m*) with approximately 1 mm. partial pressure of air present, still differed by 1% in concentration after one week in the bath. Since the thermal path in this apparatus can only be a small fraction of that encountered in the more conventional types, it would seem that the governing factor at low concentrations is not necessarily rate of heat flow, but that rate of diffusion in the vapor phase may be predominant. Dr. H. Sheffer of this department has supplied some qualitative evidence in support of this; using the apparatus of Janis and Ferguson[3] but with a hinged copper paddle suspended in the space above the dishes, he finds near 0.1 *m* a definite increase in the rate of attainment of equilibrium as a result of the turbulence induced in the vapor. In view of the extreme slowness of the experiments, it would therefore seem that tenth molal is still the practical lower limit for isopiestic measurements; however, if the unknown and reference salt are of the same valence type, the uncertainty involved in a linear extrapolation of the isopiestic ratio to infinite dilution from this concentration would not seem to be too serious.

TABLE I

Dist.	m_{KCl}	m_{NaCl}	φ_{KCl}	φ_{NaCl}	Q
a	0.03172_0	0.03163_0	0.9495	0.9514	1.0009
b	$.03575_0$	$.03571_5$	.9473	.9494	0.9988
b	$.03726_5$	$.03717_0$	.9465	.9487	1.0002
b	.04563	.04573	.9427	.9452	0.9951*
a	.05041	.05028	.9407	.9437	.9994
b	.06075	.06051	.9370	.9406	1.0001
a	.06833	.06764	.9347	.9387	1.0059*
a	.07201	.07142	.9336	.9378	1.0037*
a	.07312	.07279	.9333	.9375	1.0000
b	.08749	.08703	.9296	.9346	0.9999
a	.09022	.08942	.9292	.9342	1.0036*
b	.09735	.09690	.9274	.9328	0.9988
b	.09980	.09916	.9269	.9325	1.0005
a	.10062	.09983	.9267	.9324	1.0018

If the performance of the apparatus was disappointing, the results obtained are none the less of interest. They are summarized in the table; the first column gives the direction of distillation in the experiments, *a* indicating transport of solvent from the sodium chloride solution to the potassium and *b* the reverse; the next two columns give the observed isopiestic molalities, while the fourth and fifth give the corresponding osmotic coefficients obtained by interpolation in the tables of Hornibrook, Janz and Gordon[9] and of Janz and Gordon[10]; the last column gives the quantity $Q = (m\varphi)_{\mathrm{KCl}}/(m\varphi)_{\mathrm{NaCl}}$, which for equilibrium should be unity. It should be noted that in case *a* Q will approach unity from the side of greater values and in case *b* from lesser. The table contains the results of all the runs carried out with the technique described above except those rejected for some definite experimental reason, *e. g.*, condensation of water on the walls of the glass vessel indicating a fluctuating bath temperature at some stage of the run, evidence of gross spray during the out-gassing indicated by droplets on the walls of the silver dishes, etc. A glance at the table shows that the results fall roughly into two groups; in those indicated by a star, Q deviates markedly from unity, in the remainder, it differs only by an amount comparable with the precision of the data. In the starred results, the sign of the deviation can be correlated with the direction in which the distillation is taking place, and is what would be expected if the experiment were interrupted before equilibrium was attained; it would, therefore, seem reasonable to assume that the solutions had not been successfully out-gassed. In the unstarred results on the other hand, the sign of the deviation is related to the direction of distillation in an apparently random manner; it would, therefore, seem that these correspond to true isopiestic

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

(10) G. J. Janz and A. R. Gordon, *ibid.*, **65**, 218 (1943).

equilibrium. If so, they argue very strongly in favor of the accuracy of the e. m. f. data for both salts from which the osmotic coefficients were computed, and indicate that isopiestic standards for 1–1 electrolytes in dilute solution are settled within rather narrow limits.

In conclusion, I wish to express my thanks to Dr. R. A. Robinson for many interesting and illuminating discussions of this problem.

Summary

1. An isopiestic apparatus is described which will yield values of the isopiestic ratio for 1–1 electrolytes to concentrations as low as 0.03 *m*.

2. Evidence is adduced that the extreme slowness with which equilibrium is attained in such dilute solutions is primarily due to the rate of transport of solvent in the vapor phase, and not to the rate of heat transfer from the one solution to the other.

3. Results for the system potassium chloride–sodium chloride at concentrations from 0.03 *m* to 0.10 *m* are in highly satisfactory agreement with the e. m. f. data for both salts.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF TORONTO]

The Vapor Pressure of Aqueous Solutions of Sodium Chloride at 20, 25 and 30° for Concentrations from 2 Molal to Saturation

BY P. OLYNYK AND A. R. GORDON

A few years ago results were presented from this Laboratory giving the vapor pressures of sulfuric acid solutions[1] at 25°; the work reported here was undertaken to supplement these in the hope that it would serve to fix within somewhat narrower limits isopiestic standards for strong solutions.

Experimental

The apparatus was of the Gibson and Adams static type[2] previously used by Shankman and Gordon.[1] The experimental procedure, in particular the method of outgassing the solutions, was the same as that previously described except that a mercury diffusion pump was used ahead of the Hyvac. The air thermostat enclosing the manometer and leads from the water-bath was held at a temperature 3.0 ± 0.1° above the temperature of the water-bath. Bath temperatures were read on standard thermometers which had been calibrated against a platinum resistance thermometer with National Bureau of Standards certificate. In all experiments, Hyvac pump oil, outgassed as described in ref. 1, served as the manometer liquid. In some cases measurements were carried out on the same solution at the three temperatures in succession, an additional final set of readings being made at the temperature at which the initial readings had been taken; no significant change in solution or solvent vapor pressure or in the differential vapor pressure lowering was observed. In general, values of the activity of the water resulting from repeated measurements on the same solution showed a mean absolute deviation from the mean of 0.0002 or less—in the majority of cases of 0.0001.

The solutions were made up from British Drug Houses Analar sodium chloride, twice recrystallized from water, and a good grade of conductivity water. At the end of an experiment, the solution was analyzed gravimetrically by evaporation to dryness in a platinum crucible at 120° with a subsequent rapid heating to 600° in a small electric furnace with the crucible covered; check analysis on solutions of known concentration showed that the method gave results accurate to 0.03% or better.

Table I presents the results, the first column giving the molality and the second the activity. The results are shown graphically on the deviation plots of Fig. 1; here δ is defined by

$$a_1 = 1 - 0.0400m + \delta$$

The results for 20° have been displaced 0.0040 upward in the figure, and those for 30° downward by the same amount.

The most extensive series of vapor pressure measurements on sodium chloride solutions in the literature are those of Negus,[3] who used a Rayleigh gage; his measurements at 25° for solutions stronger than 2 *m* are also shown on the figure, and it is at once apparent that there is very satisfactory agreement between his results and ours. Accordingly, the smooth curve, corresponding to the 25° column in Table II, has been drawn through both sets of results. From the 25° entries of Table II, the 20 and 30° values in the table (and the corresponding smooth curves of the figure) have been computed by

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[1] S. Shankman and A. R. Gordon, THIS JOURNAL, **61**, 2370 (1939).

[2] R. E. Gibson and L. H. Adams, *ibid.*, **55**, 2679 (1933).

[3] J. C. W. Frazer, "The Direct Measurement of Osmotic Pressure," Columbia University Press, 1927, p. 19.