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 $\delta$ 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.

TABLE I

| $m$ | $a_1$ | $m$ | $a_1$ |
|---|---|---|---|
| | 20° | | |
| 2.442 | 0.9156 | 4.028 | 0.8510 |
| 3.089 | .8900 | 4.471 | .8312 |
| 3.261 | .8831 | 4.913 | .8114 |
| 3.522 | .8726 | 5.783 | .7706 |
| 3.543 | .8718 | 6.125[a] | .7546 |
| | 25° | | |
| 2.294 | .9210 | 3.973 | .8530 |
| 2.755 | .9027 | 4.028 | .8506 |
| 2.764 | .9023 | 4.471 | .8305 |
| 3.089 | .8896 | 4.673 | .8217 |
| 3.261 | .8827 | 4.913 | .8110 |
| 3.286 | .8815 | 5.368 | .7901 |
| 3.664 | .8660 | 5.783 | .7704 |
| | | 6.145[a] | .7532 |
| | 30° | | |
| 2.442 | .9149 | 4.471 | .8296 |
| 3.089 | .8892 | 4.659 | .8217 |
| 3.261 | .8822 | 4.913 | .8108 |
| 3.286 | .8810 | 4.966 | .8082 |
| 4.028 | .8500 | 5.783 | .7701 |
| | | 6.165[a] | .7522 |

[a] Saturated solution.

integration of the identity $\partial \ln a_1/\partial T = -L_1/RT^2$. For this purpose, Robinson's 25° $L_1$ values[4] were employed since for the small temperature range involved heat capacity terms make only a negligible contribution. A glance at the figure shows that the observed change in $a_1$ with temperature is in satisfactory agreement with the heat of dilution data. Our results for the three temperatures and those of Negus for 25° differ in only nine instances by more than 0.0002 in the activity from the curves as drawn, and in the majority of cases by less than this amount.

TABLE II

| $m$ | $a_1$ 20° | $a_1$ 25° | $a_1$ 30° | $m$ | $a_1$ 20° | $a_1$ 25° | $a_1$ 30° |
|---|---|---|---|---|---|---|---|
| 2.0 | 0.9321 | 0.9318 | 0.9315 | 4.0 | 0.8521 | 0.8516 | 0.8511 |
| 2.5 | .9134 | .9130 | .9126 | 4.5 | .8299 | .8295 | .8290 |
| 3.0 | .8936 | .8932 | .8928 | 5.0 | .8073 | .8069 | .8065 |
| 3.5 | .8734 | .8729 | .8724 | 5.5 | .7841 | .7838 | .7836 |
| | | | | 6.0 | .7603 | .7600 | .7598 |

There is a good deal of additional experimental information that may be compared with ours. Norris[5] 20° activities scatter somewhat from ours, two of his points lying below our curve, and the third above. Gibson and Adams' 25° activities,[2] determined dynamically, however, are in definite disagreement with our measurements and those of Negus, although their averaged 20° static result for saturated solution is almost exactly the same as ours. Integration by means of the Gibbs–Duhem equation of Harned and Nims' 25° e. m .f. data,[6] as recalculated by Harned and Cook,[7] gives the dotted curve of the figure; it corresponds almost exactly to Robinson and Harned's recently published "best" values[8] of the osmotic coefficient. It lies from 0.0003 at 2 $m$ to 0.0010 at 4 $m$ below our curve, and would extrapolate roughly through Gibson and Adams' dynamic values.

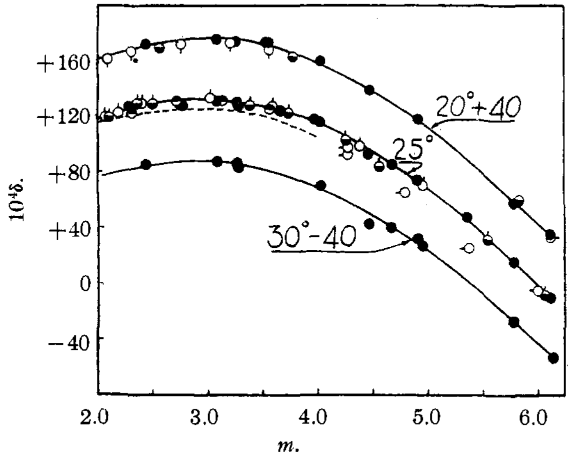

Fig. 1.—●, O. & G.; ȯ, Negus; ọ, L. F. & S. + R.; ◒, Norris; ◓, H. & C. + R.; ◒, S. & G. + S. H. & W.; -O, G. & A. (dyn.); O-, G. & A. (static); ---, H. & N.

Thanks to the development of the isopiestic method, however, there is additional evidence available. The Lovelace, Frazer and Sease vapor pressure measurements[9] on potassium chloride solutions at 20° may be compared with our 20° results by means of Robinson's data.[10] The resulting $a_1$ lie slightly below our curve as drawn[11] on the average by 0.0002. Similarly, Harned and Cook's KCl e. m. f. measurements[12] at 25° plus Robinson's most recent values of the isopiestic ratio[13] at this temperature yield a further

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(4) A. L. Robinson, THIS JOURNAL, **54**, 1311 (1932).

(5) Ref. 3, p. 18.

(6) H. S. Harned and L. F. Nims, THIS JOURNAL, **54**, 423 (1932).

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

(8) R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

(9) B. F. Lovelace, J. C. W. Frazer and V. B. Sease, THIS JOURNAL, **43**, 102 (1921).

(10) R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1222 (1939).

(11) The molality of Lovelace, Frazer and Sease' five strongest solutions, their observed activity of the water in the solutions, and the corresponding molality of the isopiestic sodium chloride solution are

| | | | | | |
|---|---|---|---|---|---|
| $m_{\text{KCl}}$ | 2.2450 | 2.4916 | 3.0017 | 3.5783 | 4.0070 |
| $a_1$ | 0.9288 | 0.9208 | 0.9039 | 0.8848 | 0.8703 |
| $m_{\text{NaCl}}$ | 2.087 | 2.301 | 2.736 | 3.215 | 3.564 |

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

(13) R. A. Robinson, private communication. The activity of the water in the potassium chloride solutions, computed from Harned and Cook's data, and the corresponding isopiestic molality for sodium chloride are

| | | | | |
|---|---|---|---|---|
| $m_{\text{KCl}}$ | 2.5 | 3.0 | 3.5 | 4.0 |
| $a_1$ | 0.9200 | 0.9038 | 0.8870 | 0.8702 |
| $m_{\text{NaCl}}$ | 2.307 | 2.734 | 3.152 | 3.561 |

set of points which are in good agreement with ours.

Finally, there are the vapor pressure data of Grollman and Frazer[14] and of Shankman and Gordon[1] on sulfuric acid solutions; these are in agreement with Harned and Hamer's e. m. f. measurements[15] up to 3 *m*, corresponding as far as the activity of the water in the solutions is concerned to about 4 *m* for sodium chloride. The isopiestic ratio has been determined by Scatchard, Hamer and Wood[16] and by Sheffer, Janis and Ferguson;[17] there are minor discrepancies between the two sets of results for the concentrations of interest here. We have been informed by Professor Ferguson, however, that further measurements in his Laboratory are in substantial agreement with Scatchard, Hamer and Wood's measurements, and we shall therefore use the latter. Ignoring their ratio for saturated solution, the nine results they give for sodium chloride solutions stronger than twice molal, when used in conjunction with Shankman and Gordon's Table II, yield with one exception points within 0.0002 of the curve as drawn.

The measurements thus fall into two groups. In the first are five independent sets of vapor pressure measurements carried out by two different methods (those of Negus, of Lovelace, Frazer and Sease, of Grollman and Frazer, of Shankman and Gordon, and our own) supported by the e. m. f. measurements of Harned and Cook, and for the more dilute range, by those of Harned and Hamer. The second group comprises the e. m. f. measurements of Harned and Nims and the dynamic vapor pressure results of Gibson and Adams. The question of a choice between the two is somewhat subjective, and we are naturally not unprejudiced in the matter, but we feel that the preponderance of evidence is in favor of the former.

If the $a_1$ values of Table II are adopted, integration of the Gibbs–Duhem equation

$$d \ln \gamma m = -(55.51/2m)\, d \ln a_1$$

from 1.5 *m* (where the vapor pressure data of Negus and the e. m. f. data of Harned and Nims are in substantial agreement) leads to the activity coefficients[18] listed in Table III.

TABLE III

25°

| $m$ | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 |
|---|---|---|---|---|---|
| $\gamma$ | (0.659) | 0.666 | 0.685 | 0.713 | 0.744 |
| $m$ | 4.0 | 4.5 | 5.0 | 5.5 | 6.0 |
| $\gamma$ | 0.781 | 0.824 | 0.873 | 0.925 | 0.984 |

## Summary

1. The vapor pressure of aqueous solutions of sodium chloride at concentrations from 2 *m* to saturation has been determined by the static method at 20, 25 and 30°.

2. The results are in excellent agreement with the vapor pressure measurements of Negus and, when used in conjunction with isopiestic data, with the measurements of Lovelace, Frazer and Sease on potassium chloride solutions and of Grollman and Frazer and of Shankman and Gordon on sulfuric acid solutions. They are consistent with the e. m. f. measurements of Harned and Cook on potassium chloride and up to 3 *m*, with those of Harned and Hamer on sulfuric acid. The temperature variation of the activity of the water is in agreement with the heat of dilution data. The results are in disagreement with the dynamic vapor pressure measurements of Gibson and Adams and with the e. m. f. measurements of Harned and Nims.

3. Values of the activity of the water and of the activity coefficient of the salt are tabulated at round values of the concentration.

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[14] A. Grollman and J. C. W. Frazer, THIS JOURNAL, **47**, 712 (1925).

[15] H. S. Harned and W. J. Hamer, *ibid.*, **57**, 27 (1935).

[16] G. Scatchard, W. J. Hamer and S. E. Wood, *ibid.*, **60**, 3061 (1938).

[17] H. Sheffer, A. A. Janis and J. B. Ferguson, *Can. J. Research*, **B17**, 336 (1939).

[18] The value in parentheses for 1.5 molar, used as the lower limit of the integration, is that of Robinson and Harned, Table VIII, ref. 8.