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Isotonic Solutions. I. The Chemical Potential of Water in Aqueous Solutions of Sodium Chloride, Potassium Chloride, Sulfuric Acid, Sucrose, Urea and Glycerol at 25°[1]

BY GEORGE SCATCHARD, W. J. HAMER[2] AND S. E. WOOD

Sinclair and Robinson[3] have developed the isotonic or isopiestic method[4] so that it is more precise than any of the direct methods of measuring the chemical potential (or activity) of the solvent in which the temperature of measurement does not vary with the concentration. We have modified their method to give a still greater precision. We believe that our error is not greater than 0.1% of ϕ, the osmotic coefficient when the total molality, νm, is greater than one molal, and not greater than 0.001 in $\phi\nu m$ for smaller concentrations.

In order to determine the chemical potential of the solvent, or any related quantity, from isotonic measurements, however, it is necessary to know it as a function of the composition for one solute. On the other hand, the method gives a way of comparing the measurements with different solutes. We have, therefore, made such measurements on aqueous solutions of sodium chloride, potassium chloride, sulfuric acid, sucrose, urea and glycerol at 25° with a triple objective: to determine to what degree of precision we can extend the method, to obtain as accurate a standard as possible, and to make a comparison between the values of the chemical potential of water determined by a variety of the most accurate methods.

To understand the reasons for our modifications it is necessary to consider the attainment of equilibrium in some detail. The isotonic method is beautifully simple. A weighed amount of a solution of known composition is placed in a tared cup; a set of such cups are allowed to come to equilibrium through the vapor phase, and each cup is weighed again. Any change in weight must be due to a gain or loss of solvent. We compare six solutions simultaneously, but the discussion of the factors which must be taken into account is clearer if we consider but two. In our apparatus each solution weighs about a gram; each cup has a volume of about 15 cc. and the volume of the whole vapor space is about 300 cc. We may suppose that the solvent is water, that the solutions are about one molal in total solutes, that the initial concentration ratio is 1.01, and that we wish to reduce it to 1.001. This will require the distillation of about 0.05 g. of water from one cup to the other. At 25° the vapor pressure of water is about 25 mm., and that of a molal solution, about 0.5 mm. less. At the start the two vapor pressures differ by 0.005 mm. or 0.02%; at the end they should differ by 0.0005 mm. or 0.002%. The 0.05 g. of water would occupy about 2000 cc. as saturated vapor. Any air would doubtless be pumped from the cup losing water, and probably much of the air in the outer volume would be concentrated in the cup gaining water. However, the hydrostatic pressure of water vapor plus air is always equal throughout the vapor space. If the partial pressure of air in the cup gaining water exceeds 0.0005 mm. near the end of the reaction, the reaction will cease until the air diffuses out. Even smaller amounts of air will slow up the reaction considerably.

The final vapor pressure difference of 0.0005 mm. corresponds to a temperature difference of about 0.00035°. If the temperature fluctuates so that the solution with the lower vapor pressure is hotter than the other by more than this amount, the distillation will tend to go in the wrong direction. Moreover, the adiabatic distillation of 0.3×10^{-6} g. of water between one gram samples is sufficient to cause this temperature difference. This is only six millionths of the water which has to be distilled. It is a simple matter to calculate the effect upon each of these quantities of changes in the initial concentrations or concentration dif-

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Rochester, N. Y., September 6, 1937.

[2] Present address: National Bureau of Standards, Washington, D. C.

[3] (a) D. A. Sinclair, *J. Phys. Chem.*, **37**, 495 (1933): (b) R. A. Robinson and D. A. Sinclair, THIS JOURNAL, **56**, 1830 (1934).

[4] "Isotonic" was introduced by Hugo de Vries, who first used an isotonic method in 1882, to define solutions in equilibrium with respect to transfer of the solvent. "Isopiestic" was substituted by Bousefield in 1918 because he considered "isotonic" bound up with theories which he did not like. However, "isotonic" has the advantage of historical priority and the more important one that it stresses equilibrium, which is the important relation, while "isopiestic" overemphasizes the equality of pressure, which is no more important than the equality of several other properties.

ferences, the desired accuracy and the size of the sample.

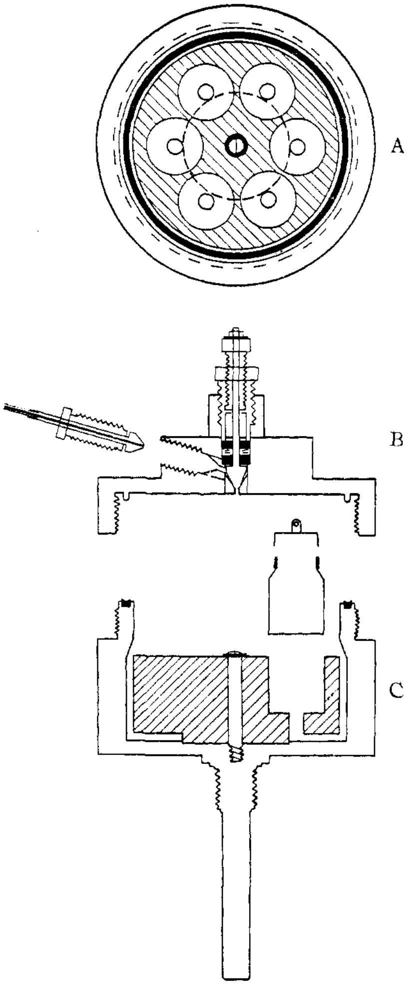

Fig. 1.—Apparatus. The left-hand side of the vertical section of the copper block is taken perpendicular to the other side.

Therefore, the essentials of the apparatus and procedure are: good heat conduction from one cup to another, a good thermal buffer to prevent fluctuations of temperature, efficient stirring to assure mixing and heat conduction without heating, evacuation adequate to remove the air, small samples to reduce the amount of distillation necessary and tight cups to permit accurate weighings. Sinclair[3a] discusses fully the heat and temperature effect, but states that thorough evacuation is unnecessary. His apparatus is as efficient as ours for the heat conduction, but we believe that our modifications give improvements in the other respects. To save space we will omit a detailed comparison and merely describe our apparatus and procedure.[5] The apparatus is illustrated in Fig. 1. The six cups are of platinum and are shaped like milk cans. Each is a cylinder 3.5 cm. high and 2.5 cm. in diameter. The top is constricted to 1.8 cm., and a nickel ring, 0.5 cm. high, is silver-soldered to the outside of the constriction. The outside of this ring is carefully ground with a 3° taper to fit a nickel lid. The bottom and lower 2 cm. of the side wall of the cup are lined with platinum gauze to increase the surface and aid the stirring and heat conduction.

The six cups fit snugly in cylindrical holes arranged symmetrically in a gold-plated copper block, 9.5 cm. in diameter and 3.5 cm. deep. This block fits into a stainless steel vessel of 12.5 cm. outside diameter and 7.5 cm. high. The cover screws on against a lead gasket and has a conical valve through which the vessel is evacuated. The male fitting for the evacuating tube is replaced by a dummy while the vessel is in the thermostat. This vessel fits on a table in the thermostat which rotates around an axis inclined at 45°. Each cup rotates about its own axis also inclined at 45°, as it revolves around the central axis.

The copper block weighs 1.6 kg. and the steel of the vessel weighs 4.6 kg. The only contact between them is over a circular area 5 cm. in diameter at the center of the bottom. They should give an effective thermal buffer. The fact that the thermostat oil must circulate around the lead counterweight and the massive steel rotating table just before it reaches the vessel increases the buffer action so that short-time temperature fluctuations must be much smaller in the vessel than in the recording thermometer. Slow changes of temperature of moderate magnitude are not troublesome.

The oil thermostat bath and thyratron regulator are similar to those described by Beattie[6] except that the plate circuit of the thyratron is connected directly to the main a. c. line instead of to the transformer, and that a mercury regulator in the bath is inserted in the galvanometer circuit to protect the galvanometer if the bath cools. This regulator maintains its temperature constant within 0.001° over an interval of a few hours and within 0.005° over a twenty-four hour period.

The composition of the most concentrated sulfuric acid solution in each series was determined

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(5) Certain of these modifications which were adopted by us in 1935 and used in this work have been previously reported by C. M. Mason, THIS JOURNAL, **60**, 1638 (1938).

(6) J. A. Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389 (1934).

by a weight titration of sodium carbonate with methyl orange as indicator. All other solutions were made up by weight. All weights were corrected to vacuum. For solutions in which the total concentration, νm,[7] was greater than 0.4, about 1 g. of solution was weighed into each of the six cups. For more dilute solutions about 0.5 g. was used. For solutions in which νm was greater than one, six drops of water was placed at the bottom of the vessel so that their evaporation might sweep out the air from below the copper block and might reduce the evaporation from the cups. To control the evacuation and prevent splattering the vessel was not connected directly to the vacuum line but to a bulb of about the same volume as the vessel itself. The bulb could be connected to an oil pump or to the vessel. The latter connection was always made so that the passage of gas was very slow. After the pressure had reached the vapor pressure of water, the vessel was evacuated ten times more. For solutions in which νm was less than one, 20 cc. of the sodium chloride solution was put directly into the steel vessel. When the vessel tipped, this rose around the lower cups and gave better thermal contact between them and the copper block. Since it also made necessary washing and drying the cups before they were weighed, this procedure was used only for the more dilute solutions for which it was needed. The vessel was evacuated as for the more concentrated solutions and, after three hours' rotation in the thermostat, it was evacuated ten times more and then replaced in the bath.

Solutions with νm greater than one were rotated in the bath for twenty-four hours; those with νm less than 0.6 were rotated seventy-two hours, and the intermediate solutions were rotated forty-eight hours. The vessel was then removed from the bath, dry air was allowed to enter, the top was removed and the lids were placed on the cups as soon as possible, which was usually less than half a minute after the opening of the vessel. In most of the runs each cup contained a different solute. For runs 7, 9, 11, 13, 15, 17, 19 and 21, the cups were returned to the vessel after the previous run, so that each of these depended upon the same initial weighings as the previous run.

The success with which equilibrium is attained in concentrated solutions is illustrated by two preliminary experiments which are not included in our final results. The first shows how closely equilibrium is attained even when the amount of water distilled is large. The initial concentrations of urea and of sulfuric acid were adjusted so poorly that the urea lost 0.58 of its 0.92 g. of water and the sulfuric acid gained about the same amount. In spite of this huge change, the largest difference from the equilibrium value is only four-tenths of one per cent. The initial, final and equilibrium concentrations are

	Initial	Final	Equilibrium
NaCl	3.237	2.670	2.671
KCl	2.693	2.931	2.926
H_2SO_4	3.510	2.111	2.114
Sucrose	3.592	3.985	3.982
Urea	2.382	6.429	6.427
α-Met. gluc.	4.063	4.509	4.523

The other experiment illustrates the reproducibility of the equilibrium concentrations because the drops of water added before evacuating in the second of two runs with the same solutes compensated so exactly for the loss during evacuation that the average loss was only 0.05 mg., and the concentrations are almost the same for the two runs. We list the concentrations before the first run, the equilibrium concentrations after each run and the milligrams gained during the second run.

	Initial concn.	Equilibrium concn.		Second gain, mg.
		First	Second	
NaCl	1.5730	1.5483	1.5479	+0.25
KCl	1.6585	1.6432	1.6429	+ .17
H_2SO_4	1.3391	1.3081	1.3080	+ .03
Sucrose	2.4177	2.4186	2.4188	− .04
Urea	3.2026	3.2920	3.2925	− .15
α-Met. gluc.	2.5716	2.6083	2.6082	+ .03

The discrepancy between the two determinations of ϕ for any solute from ϕ for any other is measured in parts per thousand by the difference between the corresponding entries in the last column. The maximum discrepancy is 0.04% and the average is only 0.02%.

The isotonic method was also adapted to the simultaneous measurement of solubility and the chemical potential of water from the saturated solution. A stock solution was made up which was almost saturated. In one or two of the cups an unweighed quantity of this solution was added to about a gram of the solid. The other cups each contained a weighed quantity of the same solution or of a comparison solution. At equilibrium the concentration of the solution without excess solid must be the same as that in the solu-

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(7) ν is the number of particles from one molecule of solute, and m is the concentration in moles per kg. of water.

tion directly in equilibrium with the solid phase. So the solubility may be determined conveniently without any need of separating from the solid phase. The composition of the comparison solutions gives at the same time the potential of the solvent. This method is particularly convenient for cases of high solubility varying rapidly with the temperature, and with viscous saturated solutions. The solubility of each solid used was determined in this way. These measurements were made with cups without the nickel rings and with light platinum covers which leaked enough at this stage so that it was necessary to make two weighings and extrapolate back to the time of closing.

The equilibrium concentrations as moles per kilogram of water are given in Table I for the 32 runs which are used in the computations. About a hundred other runs were made and not used. A few were discarded because of obvious spattering, or leakage with the old platinum covers, or insufficient purification of one of the materials. However, most of these runs were made in developing the technique, particularly with dilute solutions. In some of the more concentrated solutions two cups contained the same initial solution. Both final values are given in the table, and their agreement gives another check on the accuracy of the method. The saturated solutions are indicated in the table.

TABLE I

ISOTONIC CONCENTRATIONS AT 25°

Run	NaCl	KCl	H_2SO_4	Sucrose	Urea	Glycerol
1	6.1430[a]		4.3740			
	6.1451[a]		4.3756			
2	6.1429[a]		4.3725			
	6.1461[a]		4.3742			
4	6.0781		4.3145		20.007[a]	14.572
22	5.4593		3.9289		17.078	12.583
			3.9294			12.589
23	4.6013		3.3890		13.332	10.036
			3.3895			10.036
24	4.2585		3.1668		11.957	9.0887
			3.1658			9.0889
3	4.1983	4.8029[a]			11.750	
		4.8051[a]				
5[b]				6.0526[a]	11.239	8.5959
				6.0533[a]		
25	3.7390	4.2210	2.8298	5.5266	9.9882	7.7240
26	3.3911	3.7916	2.6023	5.0110	8.7450	6.8614
27	2.5022	2.7273	1.9998	3.7462	5.8919	4.8294
29	2.4135	2.6232	1.9351	3.6210	5.6262	4.6455
28	2.0845	2.2460	1.7065	3.1646	4.6999	3.9427
30	1.6220	1.7228	1.3651	2.5172	3.4728	3.0233
31	1.1614		1.0109	1.8578	2.3669	2.1334
7	1.0010	1.0427	0.88920	1.6277	2.0088	1.8332
6	0.99954	1.0399	.88666	1.6260	2.0033	1.8318
32	.68788	0.70998	.62219		1.3375	1.2558
13	.51709	.53045	.47046	0.88639	0.99133	0.94213
12	.50593	.51923	.46089	.86829	.96818	.92265
15	.40846	.41783	.37419	.70940	.77579	.74537
14	.40034	.40838	.36619	.69549	.75828	.72942
17	.30922	.31486	.28463	.54621	.58361	.56589
16	.30303	.30896	.27916	.53546	.57270	.55533
9	.21275	.21584	.19654	.38066	.40016	.39170
19	.20603	.20893	.19006	.37043	.38766	.37918
8	.20432	.20715	.18892	.36611	.38563	.37694
18	.20120	.20444	.18577	.36229	.37746	.37002
21	.10288	.10380	.09405	.18917	.19448	.19089
10	.10014	.10059	.09079	.19297	.18866	.18587
20	.09930	.10027	.09082	.19257	.18764	.18477
11	.09918	.10098	.09095	.18303	.18845	.18766

[a] Saturated solution. [b] Compared with the standard through urea.

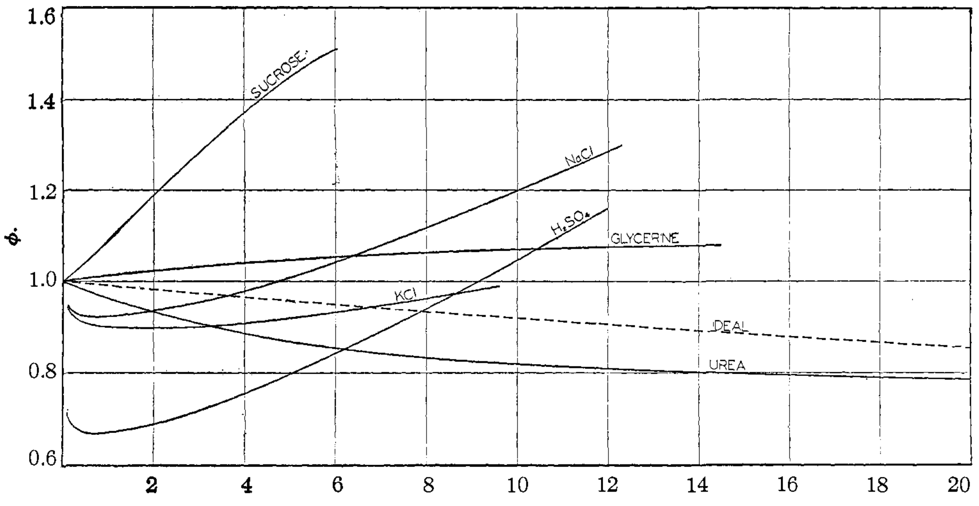

Fig. 2.—Osmotic coefficients.

A convenient way of comparing the results is in terms of the osmotic coefficient, ϕ

$$\phi = (\mu_{00} - \mu_0)/w_0RT\nu m = -(\ln a_0)/w_0\nu m \quad (1)$$

in which μ_{00} is the chemical potential of the pure solvent, μ_0 is the potential of the solvent in the solution, w_0 is one thousandth of the molecular weight of the solvent, R and T have their usual significance, ν and m have been defined above, and a_0 is the activity of the solvent. In Fig. 2 our values of ϕ are plotted against νm. The curve labeled ideal is $[\ln (1 + w_0\nu m)]/w_0\nu m$ and is the osmotic coefficient of an ideal solution, for which the activity of the solvent is equal to its mole fraction. For solutions which are isotonic, $(\mu_{00} - \mu_0)$ is the same in each solution, and therefore $\nu m\phi$ is also the same. In this diagram the isotonic lines are rectangular hyperbolas with the equations $\phi = k/\nu m$. For some purposes it is convenient to plot ϕ against $\nu m\phi$ so that the isotonic lines are all perpendicular.

In determining the best standard curve from measurements on several substances, it is convenient to assume a curve for one substance as standard and to compute each value for another solution from this curve and the concentrations of the standard and of the other solution. Then the standard curve is altered as often as necessary to give the best fit for all the measurements. We have chosen sodium chloride as the standard since it was used in almost every run; it is easily purified, and its curve is much simpler than that of sulfuric acid which is the only other substance used in all the most concentrated solutions.

The scale of Fig. 2 is much too small for comparison of our smooth curves with the experimental results. We have therefore plotted the deviation function $\Delta\phi$ which is defined for each solute under the corresponding figure. The last term for the electrolytes is the Debye–Hückel square root correction in very dilute solutions and becomes very nearly constant in more concentrated solutions.[8] The constants in the other terms are empirical. The graphs for the individual solutes all have the same scale of ordinates in which each division is 1%.

Sodium Chloride (Fig. 3).—An analytical reagent was dissolved in conductivity water and precipitated by hydrogen chloride gas. The precipitate was dried at 300° and then at room temperature by passing through the finely powdered material in a Gooch crucible a current of air which had been dried by calcium chloride. The solubility of 6.144 *M* may be compared with 6.145 *M* of the "I. C. T." (vol. IV, p. 235).

The vapor pressures of sodium chloride solutions have been measured at 25° by Frazer and S. S. Negus,[9] and by Pearce and F. Fordemwalt,[10] and at 20° by Frazer and W. R. Norris.[9] The latter were corrected to 25° through the use of the heat of dilution measurements of Gulbransen and Robinson[11] and of Lipsett, Johnson and Maass.[12] Osmotic coefficients at 25° were calculated from the freezing point measurements of Scatchard and Prentiss[13] and the first of these heat measurements. The treatment of dilute solutions will be discussed elsewhere. The os-

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[8] George Scatchard, *Chem. Rev.*, **19**, 309 (1936).

[9] J. C. W. Frazer, "The Direct Measurement of Osmotic Pressure. Contemporary Developments in Chemistry," Columbia University Press, New York, N. Y., 1927.

[10] J. N. Pearce and A. F. Nelson, THIS JOURNAL, **54**, 3544 (1932).

[11] E. A. Gulbransen and A. L. Robinson, *ibid.*, **56**, 2637 (1934).

[12] S. G. Lipsett, F. M. G. Johnson and O. Maass, *ibid.*, **49**, 1940 (1927).

[13] G. Scatchard and S. S. Prentiss, *ibid.*, **55**, 4355 (1933); **56**, 2314 (1934).

motic coefficients were also calculated from Harned's measurements of the electromotive force of cells with sodium amalgam and silver chloride electrodes[14] with the use of activity coefficients up to 0.1 M determined by Brown and MacInnes[15] from cells with transference and the transference numbers. Since sodium chloride was chosen as our standard, no experimental points appear in Fig. 3 for our own measurements. The freezing point values agree with the standard curve almost exactly. Below one molal the vapor pressure measurements scatter too widely to be of use. At higher concentrations those of Pearce and Fordemwalt check the curve within their fluctuations from any smooth curve. Those of Frazer and Negus agree even better except for the last two points which were measured in two steps. The measurements at 20° give values about 1% high. The electromotive force measurements agree with the standard up to 0.1 M; they yield osmotic coefficients lower than the standard below 1 M and higher above that concentration, with a maximum deviation of almost 1%.

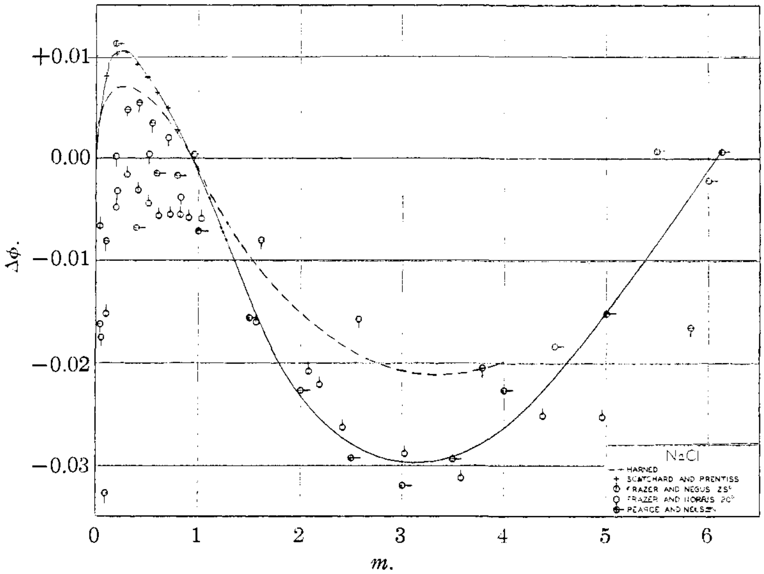

Fig. 3.—Sodium chloride deviations: $\Delta\phi = \phi - 1 - 0.07m + 1.165[1 + \sqrt{m} - 1/(1 + \sqrt{m}) - 2 \ln (1 + \sqrt{m})]/m$.

Potassium Chloride (Fig. 4).—An analytical reagent was crystallized three times from conductivity water and dried at 300° and then in a current of dry air as described for sodium chloride. The solubility of 4.804 M may be compared with 4.81 M ± 0.5% of the "I. C. T." (vol. IV, p. 239). The vapor pressure measurements of Pearce and Snow[16] are much less consistent than those from the same laboratory with sodium chloride, and the average deviation is almost one per cent. and negative. The measurements of Lovelace, Frazer and Sease[17] at 20°, computed to 25° with the use of the heat of dilution measurements of Lange and his collaborators,[18] are about 1% higher than the standard curve. The electromotive force measurements of Harned and Cook,[19,14] yield high values of the osmotic coefficient throughout the range of their measurements. The measurements of Shedlovsky and MacInnes[20] with cells with transference combined with transference numbers lead to very exact agreement up to half molal. We did not integrate their results further because the measurements are sparse and there seems to be some question of the accuracy of their measurement at 0.5 M. Figure 4 shows how precisely the standard curve for potassium chloride is fixed by the isotonic measurements once the curve for sodium chloride is determined.

We may also compare our measurements with Robinson and Sinclair's measurements of the isotonic ratios of sodium chloride to potassium chloride.[5b] For concentrations above one molal their ratio of sodium chloride concentration to potassium chloride concentration averages 0.1% smaller than ours. This difference is smaller than the fluctuations of their results or the accuracy they claim. Below one molal, where our fluctuations are also larger, their ratio is about 0.1% larger than ours.

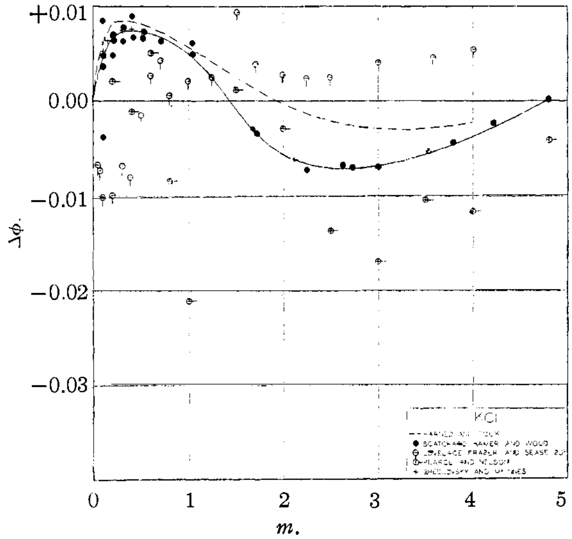

Fig. 4.—Potassium chloride deviations: $\Delta\phi = \phi - 1 - 0.026m + 1.165[1 + \sqrt{m} - 1/(1 + \sqrt{m}) - 2 \ln (1 + \sqrt{m})]/m$.

Sulfuric Acid (Fig. 5).—Chemically pure sulfuric acid was distilled very slowly in an all-glass still into conductivity water to give a solution of density 1.8. The vapor

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[14] H. S. Harned, THIS JOURNAL, **51**, 416 (1929); H. S. Harned and L. F. Nims, *ibid.*, **54**, 423 (1932).

[15] A. S. Brown and D. A. MacInnes, *ibid.*, **57**, 1356 (1935).

[16] J. N. Pearce and R. D. Snow, *J. Phys. Chem.*, **31**, 231 (1927).

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

[18] J. Wüst and E. Lange, *Z. physik. Chem.*, **116**, 161 (1925); E. Lange and J. Monheim, *ibid.*, **A150**, 349 (1930).

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

[20] T. Shedlovsky and D. A. MacInnes, *ibid.*, **59**, 503 (1937).

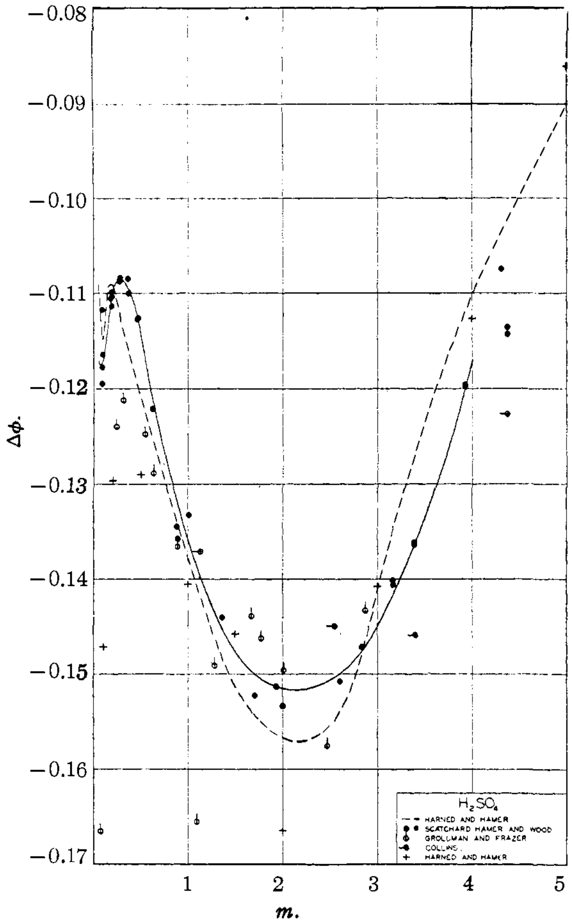

Fig. 5.—Sulfuric acid deviations: $\Delta\phi = \phi - 1 - 0.13m + 2.330[1 + \sqrt{3m} - 1/(1 + \sqrt{3m}) - 2 \ln (1 + \sqrt{3m})]/3m$.

pressure measurements of Grollman and Frazer[21] scatter about our standard curve with a small average difference. Those of Collins[22] lie slightly above it below 3 *M* and below it above 3 *M*. Harned and Hamer's measurements[23] of the cells

$$H_2,\ H_2SO_4\ (m),\ PbSO_4,\ PbO_2,\ Pt \qquad (I)$$

and

$$H_2,\ H_2SO_4\ (m),\ Hg_2SO_4,\ Hg \qquad (II)$$

may be combined to give

$$E_{\rm I} + E_{\rm II} - E_{\rm I_0} - E_{\rm II_0} = (RT/F) \ln a_0 \qquad (2)$$

However, 0.01 mv. corresponds to 1% at 1 *M* and to 0.1% at 5 *M*. The largest deviation from our standard curve corresponds to 0.03 mv. at 2 *M*. The values of ϕ determined by integration from the chemical potential of the acid measured by one of these cells singly lie below our standard curve below about 3 *M*, and above at higher concentrations, with a maximum deviation of about 0.5%. The integrated deviation curve has a minimum at about 0.1 *M*, and a maximum at about 0.2 *M* which cannot be avoided without attributing to the experiments an error much larger than appears probable. We have drawn our standard curve with a similar maximum and minimum to correspond to our measurements although these measurements are probably not precise enough to establish independently that there is such an irregularity.

Sucrose (Fig. 6).—From a nearly saturated cane sugar solution prepared by percolation the sucrose was precipitated by adding ethyl alcohol at 0°. It was dried over calcium chloride and then in a current of dried air as described for sodium chloride. To avoid errors due to hydrolysis no solution of sucrose was used which had been in contact with water more than a week. Our solubility of 6.053 *M* corresponds to 67.44% sucrose, which may be compared with the 67.89% of "I. C. T." (vol. II, p. 344). We have not found the measurements of osmotic pressure to be accurate enough for our purposes. The vapor pressures of sucrose solutions have been measured at 25° by Frazer and L. C. Beard,[9] at 20° by Frazer and H. K. Parker,[9] and at 0° and 30° by Berkeley, Hartley and Burton.[24] We have interpolated these last measurements linearly in $1/T$, which corresponds to a heat of dilution independent of the temperature, and have used the same temperature coefficient to calculate ϕ at 25° from the measurements of Frazer and Parker. Above two molal the measurements of Frazer and his collaborators are in good agreement with our standard curve. Those of Berkeley and collaborators are about 1.5% higher.

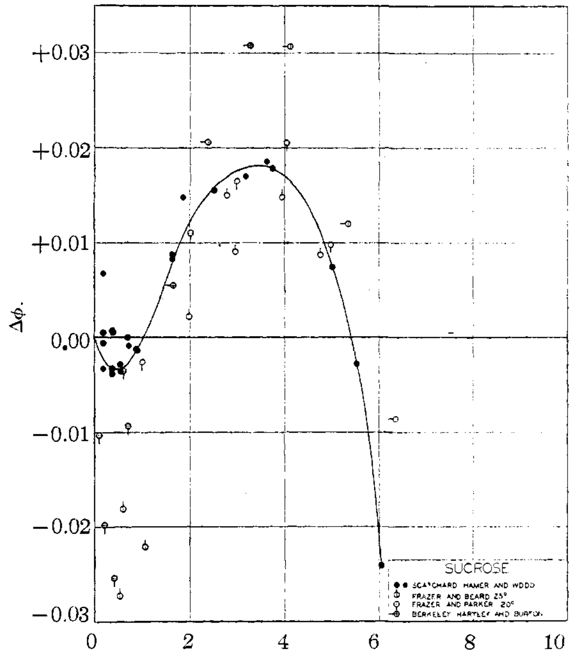

Fig. 6.—Sucrose deviations: $\Delta\phi = \phi - 1 - 0.088m$.

Urea (Fig. 7).—Synthetic urea was crystallized from conductivity water and then from ethyl alcohol, both without heating above 60°. It was dried over calcium chlo-

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

(22) E. M. Collins, *J. Phys. Chem.*, **37**, 1191 (1933).

(23) H. S. Harned and W. J. Hamer, THIS JOURNAL, **57**, 27 (1935).

(24) Earl of Berkeley, E. G. C. Hartley and C. V. Burton, *Phil. Trans.*, **218A**, 295 (1919); G. Scatchard, THIS JOURNAL, **43**, 2406 (1921).

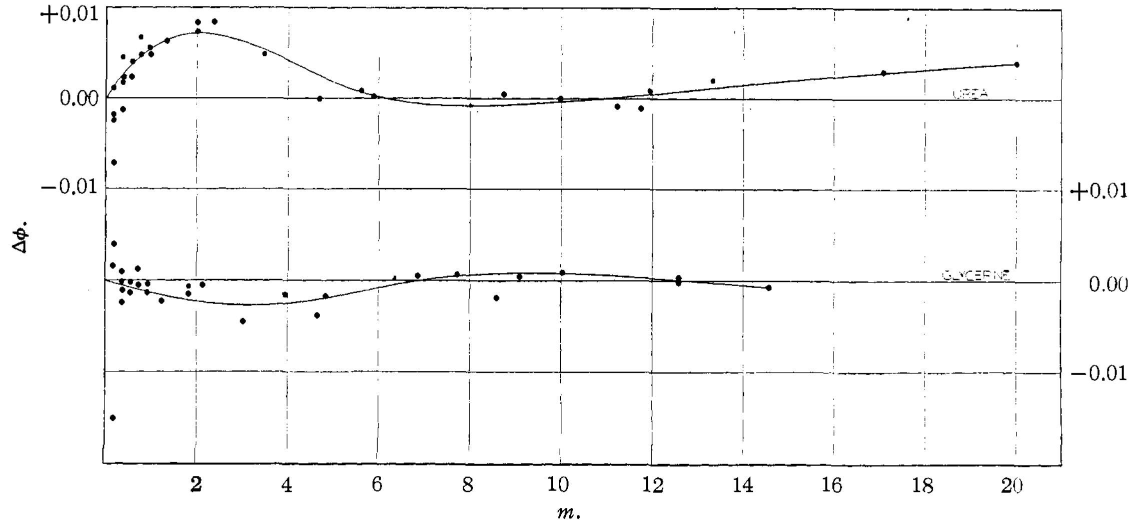

Fig. 7.—Urea and glycerol deviations: Urea, $\Delta\phi = \phi - 1 + 00.05m/(1 + 0.179m)$; Glycerol, $\Delta\phi = \phi - 1 - 0.016m/(1 + 0.1333m)$.

ride and then in a current of dry air as described for sodium chloride. To avoid errors due to hydrolysis or to rearrangement to ammonium cyanate, no urea was used which had been in contact with water more than a week. A study of 0.01, 0.1 and 1.0 *M* urea solutions showed that at room temperature it requires a month for the conductance of a urea solution to reach 0.1% of that of a sodium chloride solution of the same molality. The solubility of 20.007 *M* was confirmed by two determinations in each of which four cups contained urea solutions. These gave an average of 20.006 with an average deviation of 0.006. This checks the measurements of Pinck and Kelly[25] as closely as they can be interpolated to 25°. Values of 17, 18 and 19 *M* are also found in the literature. The vapor pressures of urea solutions have been measured at 25° by Lewis and Burrows.[26] We confirm their statement that a saturated solution is nearly ideal, but find that their measurements are otherwise not sufficiently accurate for our purposes. Urea was included in our study in the hope that the deviations from ideality would be so much smaller in dilute solutions that a simple interpolation would be justified. Figures 2 and 7 show that the difference from ideality does not decrease rapidly with decreasing concentration until the solutions are quite dilute and that the deviations from our analytical function are little, if any, simpler than for the other substances.

The measurements of Chadwell and Politi[27] yield values of ϕ at the freezing point which are very slightly higher than ours at 25° in dilute solutions but decrease more nearly linearly to 0.7646 at 8.083 *M* (the eutectic) where the value at 25° is 0.8333. This difference would correspond to a partial heat content of water 0.65 cal./mole more positive than that of pure water if this heat content difference were independent of the temperature. However, the heat capacity measurements of Gucker and Ayres[28] show that this difference is becoming more positive with decreasing temperature, and is changing more rapidly the lower the temperature. This variation together with the decrease of freezing point with increasing concentration may explain the fact that the average value of $(d\phi/dT)/m$ between the freezing point and 25° appears to increase rapidly with increasing concentration although ϕ/m decreases slightly. However, the value of $(d\phi/dT)/m$ at 8.08 molal is only about half as large as the value calculated for concentrations below one molal from Naudé's heat of dilution measurements at 18°.[29]

Glycerol (Fig. 7).—To 300 cc. of C. P. glycerol was added 25 cc. of concentrated hydrochloric acid and the mixture was heated on the water-bath for twelve hours. It was then distilled *in vacuo* and the middle portion collected and stored in small glass containers in which it was protected from the atmosphere. The vapor pressures of aqueous glycerol solutions have been measured by Drucker and Moles.[30] Their results correspond to our curve for sucrose much more closely than they do to our results for glycerol. This means a discrepancy of 40-50% in ϕ at 5 and 11 *M*. Glycerol, like urea, was chosen in the hope that the deviations from ideality would be small enough to justify a simple interpolation. The deviations of our smooth standard curve from the analytical expression are never greater than 0.3% so that our hopes appear to be realized. However, glycerol is a hygroscopic liquid and therefore it is not a convenient standard.

α-Methyl Glucoside.—Berkeley, Hartley and Burton[24] also measured the vapor pressures of aqueous solutions of α-methyl glucoside at 0 and at 30°. Therefore this substance was used in some of the preliminary runs. Eastman "Eastman Grade" product was crystallized once from synthetic methyl alcohol, and dried in a current of air as described for sodium chloride. The melting point was raised thereby from 157.5 to 164.0°. Since the small sample could not be purified further and since the vapor pressure measurements appeared to be less useful than

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(25) L. A. Pinck and M. A. Kelly, This Journal, **47**, 2170 (1925).

(26) G. N. Lewis and G. H. Burrows, *ibid.*, **34**, 1515 (1912).

(27) H. M. Chadwell and F. W. Politi, *ibid.*, **60**, 1291 (1938).

(28) F. T. Gucker, Jr., and F. D. Ayres, *ibid.*, **59**, 2152 (1937).

(29) S. M. Naudé, *Z. physik. Chem.*, **135**, 209 (1928).

(30) K. Drucker and E. Moles, *ibid.*, **75**, 405 (1911).

those with sucrose, glycerol was substituted in the later runs. Our measurements may be represented approximately by $\Phi = 1 + 0.0785m/(1 + 0.163m)$, and a solubility of 5.55 M.

Table II contains the osmotic coefficients and one plus the logarithms of the activity coefficients at rounded molalities. The one is added to the logarithms of the activity coefficients to avoid negative values and to make this column, like that for ϕ, approach unity at zero concentration. We do not consider our measurements at low concentrations sufficiently accurate for the extrapolation of the activity coefficients of the electrolytes to zero concentration. We have therefore accepted the value for sodium chloride at 0.2 M from heat of dilution and freezing point measurements,[13,11] the value for potassium chloride at 0.1 M of Shedlovsky and MacInnes,[20] and the value for sulfuric acid at 0.2 M of Harned and Hamer.[23] The differences at other concentrations correspond, of course, to the differences in osmotic coefficients discussed above.

Robinson and Sinclair[3b] and Robinson in his later papers based their standard largely on the electromotive force measurements of Harned with potassium chloride[14] and it corresponds very closely to the dotted curve we have drawn from these measurements, agreeing with our standard within 0.1% up to 1 M and giving a maximum deviation of 0.66% at 3 M. Smith and Smith[31] use as standards sucrose solutions, for which they use the equation $\phi = 1 + 0.095m + 0.0013m^2$ up to 3 M based on the vapor pressure measurements of Berkeley, Hartley and Burton[24] and measurements of osmotic pressure. Above 0.5 M their values are about 0.8% higher than our standard. Our measurements permit the comparison of sixteen of the most precise series of measurements of the chemical potential of water in aqueous solutions made with four different solutes in six laboratories by six distinct methods. Although any choice of the best curve through such a mass of data must involve some subjective judgment, we believe that the uncertainty in our curve is not more than 0.2%. With the osmotic coefficient

TABLE IIa

OSMOTIC COEFFICIENTS AND LOGARITHMS OF ACTIVITY COEFFICIENTS

	NaCl		KCl		H_2SO_4	
m	ϕ	1 + $\log\gamma$	ϕ	1 + $\log\gamma$	ϕ	1 + $\log\gamma$
0.1	0.9342	0.8928	0.9264	0.8865	0.6784	0.4239
.2	.9255	.8678	.9131	.8566	.6675	.3202
.3	.9224	.8531	.9063	.8377	.6685	.2620
.4	.9217	.8430	.9023	.8240	.6723	.2225
.5	.9224	.8358	.9000	.8134	.6773	.1931
.6	.9242	.8304	.8987	.8048	.6824	.1700
.7	.9266	.8265	.8980	.7978	.6895	.1521
.8	.9295	.8236	.8980	.7918	.6980	.1380
.9	.9329	.8214	.8982	.7867	.7075	.1269
1.0	.9363	.8199	.8985	.7822	.7176	.1181
1.2	.9434	.8135	.8996	.7751	.7396	.1061
1.4	.9509	.8179	.9008	.7685	.7634	.0997
1.6	.9589	.8188	.9024	.7635	.7888	.0977
1.8	.9681	.8209	.9048	.7596	.8154	.0992
2.0	.9786	.8243	.9081	.7568	.8431	.1034
2.5	1.0096	.8366	.9194	.7532	.9152	.1229
3.0	1.0421	.8530	.9330	.7532	.9922	.1525
3.5	1.0783	.8727	.9478	.7557	1.0740	.1902
4.0	1.1168	.8951	.9635	.7599	1.1606	.2346
4.5	1.1578	.9199	.9799	.7655		
5.0	1.2000	.9464	(.9900	.7695)[a]		
5.5	1.2423	.9742				
6.0	1.2861	1.0029				
	(1.2987	1.0114)[a]				

[a] Saturated solution. See Table I for composition.

TABLE IIb

OSMOTIC COEFFICIENTS AND LOGARITHMS OF ACTIVITY COEFFICIENTS

	Sucrose		Urea		Glycerol	
m	ϕ	1 + $\log\gamma$	ϕ	1 + $\log\gamma$	ϕ	1 + $\log\gamma$
0.1	1.0073	1.0063	0.9959	0.9964	1.0014	1.0012
.2	1.0151	1.0130	.9918	.9929	1.0028	1.0025
.3	1.0234	1.0198	.9879	.9894	1.0042	1.0037
.4	1.0319	1.0270	.9841	.9860	1.0055	1.0049
.5	1.0407	1.0343	.9804	.9827	1.0068	1.0060
.6	1.0497	1.0418	.9768	.9794	1.0081	1.0072
.7	1.0590	1.0494	.9732	.9762	1.0093	1.0083
.8	1.0684	1.0572	.9698	.9731	1.0105	1.0094
.9	1.0781	1.0652	.9664	.9700	1.0117	1.0104
1.0	1.0878	1.0732	.9631	.9669	1.0128	1.0115
1.2	1.1076	1.0895	.9567	.9610	1.0150	1.0136
1.4	1.1280	1.1062	.9506	.9552	1.0171	1.0155
1.6	1.1484	1.1231	.9447	.9496	1.0192	1.0175
1.8	1.1686	1.1400	.9390	.9442	1.0211	1.0193
2.0	1.1884	1.1567	.9346	.9389	1.0230	1.0212
2.5	1.2359	1.1978	.9206	.9262	1.0274	1.0255
3.0	1.2817	1.2382	.9087	.9143	1.0316	1.0297
3.5	1.3262	1.2778	.8976	.9031	1.0355	1.0336
4.0	1.3691	1.3166	.8877	.8925	1.0393	1.0374
4.5	1.4100	1.3542	.8783	.8824	1.0428	1.0411
5.0	1.4477	1.3902	.8700	.8730	1.0462	1.0446
5.5	1.4820	1.4244	.8612	.8641	1.0494	1.0480
6.0	1.5070	1.4540	.8555	.8559	1.0525	1.0512
6.5	(1.5090	1.4568)[a]	.8494	.8481	1.0554	1.0543
7.0			.8440	.8408	1.0580	1.0573
7.5			.8391	.8340	1.0604	1.0601
8.0			.8347	.8275	1.0626	1.0628
8.5			.8307	.8213	1.0645	1.0653
9.0			.8270	.8155	1.0663	1.0677
9.5			.8236	.8099	1.0679	1.0700
10.0			.8205	.8046	1.0694	1.0721
11.0			.8148	.7946	1.0720	1.0762
12.0			.8099	.7853	1.0741	1.0799
13.0			.8056	.7768	1.0760	1.0833
14.0			.8019	.7689	1.0777	1.0865
15.0			.7985	.7614		
16.0			.7954	.7544		
17.0			.7926	.7478		
18.0			.7901	.7415		
19.0			.7878	.7355		
20.0			.7856	.7298		
			(.7855	.7297)[a]		

[a] Saturated solutions. See Table I for compositions.

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(31) E. R. B. Smith and P. K. Smith, *J. Biol. Chem.*, **117**, 209 (1937); **121**, 607 (1937).

in Table II any one of the five solutes may be used as standard.

Summary

A modification for precision work of the isotonic apparatus and method of Sinclair and Robinson is described.

The isotonic concentrations at 25° of aqueous solutions of sodium chloride, potassium chloride, sulfuric acid, sucrose, urea and glycerol have been determined from 0.1 *M* sodium chloride to the saturated solution or to a saturated solution of sodium chloride.

The solubilities in water at 25° of sodium chloride, potassium chloride, sucrose and urea have been determined in the same apparatus by a new and convenient method.

The most precise determinations of the chemical potential of water in solutions of non-volatile solutes have been compared critically by means of these isotonic measurements, and a standard curve for the osmotic coefficients of each substance has been based on all the measurements with any of these substances.

CAMBRIDGE, MASS. RECEIVED AUGUST 4, 1938

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

Transference Numbers of Lanthanum Chloride at 25° by the Moving Boundary Method

BY L. G. LONGSWORTH AND D. A. MACINNES

Introduction

In recent publications from this Laboratory Brown and MacInnes[1] and Shedlovsky and MacInnes[2] have shown that transference numbers, and electromotive forces of concentration cells, may be used in determining activity coefficients of salt solutions. The salts studied in this manner have been the chlorides of hydrogen, sodium, potassium and calcium. The results were found to be in close accord with the Debye–Hückel theory. In addition transference numbers are of utility in interpreting the results of conductance measurements according to the recent developments of the interionic attraction theory. The extension of the studies to solutions of lanthanum chloride appeared to be of interest. Since this salt is of a highly unsymmetric valence type, the data obtained should afford a severe test of the interionic attraction theory in relation to both activity coefficients and conductances. This paper describes the determination of the transference numbers of lanthanum chloride by the moving boundary method and gives data on these numbers at 25° in the concentration range 0.0075 to 0.5 normal.

Description of the Apparatus

Of the apparatus used in determining transference numbers by the moving boundary method the cell was the same as that used in recent investigations in this Laboratory and has been described fully.[3] The constant current device has, however, been much simplified, as shown in Fig. 1. In this figure a portion, B, of the storage battery, A-B, furnishing current to the moving boundary cell, C, is shunted by a potential divider, the point of contact, T, being shifted by winding resistance wire from one of the insulated cylinders, DD′, to the other. In series with this and the cell C is a decade resistance box, R, with the range 10 to 11,110 ohms, which is shunted by the galvanometer, G, and the Hulett cell, X, which is, essentially, a heavy-duty Weston unsaturated standard cell. The needle of the galvanometer carries a vane, V, of aluminum foil which serves to intercept the light to the photo-tube, PJ 23. The photoelectric current operates a thyratron, FG 57, whose plate circuit includes the electromagnet E which controls the addition of potential by the divider, DD′, by drawing the pulley P_1 against the constantly rotating disk F. On release the pulley P_2 causes an adjustment in the reverse direction. For use with continuously increasing resistance, as in the present case, P_2 may be removed.

In operation the resistance R is set at such a value that a drop of 1.0189 v., the potential of the Hulett cell, results from the passage of the current. The advantages of this arrangement over that previously described[3] are: (1) a thyratron has replaced a vacuum tube and two mechanical relays and (2) a Hulett cell and a resistance box have replaced a Weston standard cell, standard resistances, potentiometer and storage battery. The precision and convenience of the apparatus have been increased since it is no longer necessary to adjust the potentiometer current at intervals during a transference number determination. As a matter of fact, the device will operate for an indefinitely long period with an accuracy of 0.01% or better.

The frequency control of the local a. c. power supply is

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[1] Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).

[2] Shedlovsky and MacInnes, *ibid.*, **58**, 1970 (1936); **59**, 503 (1937).

[3] MacInnes and Longsworth, *Chem. Rev.*, **11**, 171 (1932).