

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF NORTHWESTERN UNIVERSITY]

A STUDY OF THE HEAT CAPACITY AND RELATED THERMODYNAMIC PROPERTIES OF AQUEOUS SOLUTIONS OF LITHIUM CHLORIDE, HYDROCHLORIC ACID AND POTASSIUM HYDROXIDE AT 25°¹

BY FRANK T. GUCKER, JR., AND KARL H. SCHMINKE

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Introduction

This work is a continuation of that begun several years ago by the senior author,² with the hope of throwing more light upon the nature of aqueous solutions of electrolytes, through careful determination of their heat capacities and comparison with modern theories of such solutions. The original apparatus was constructed in the Gates Chemical Laboratory of the California Institute of Technology, where the senior author was a National Research Fellow. Professor Arthur A. Noyes very kindly presented it to him to carry on the work begun there. It was then set up in the Wolcott Gibbs Memorial Laboratory, where the senior author was assistant to the late Professor Theodore W. Richards. A few changes and improvements were there made but the press of other work did not permit any additional measurements at that time. Further improvements in the apparatus will be discussed after the brief summary of the method given below.

It is a modification of the Joule-Pfaundler *twin calorimeter* method—a thermal balance. Two almost identical closed calorimeters of slightly over 250 ml. capacity are placed side by side in a *submarine* jacket surrounded by a water-bath. Each is well stirred and supplied with a quantitative heating coil of about 9.5 ohms resistance. The two coils are connected in series so that the same current flows through each and hence the same *relative* amount of heat is always liberated in each. The two calorimeters are brought to nearly the same initial temperature and then heated one degree. The temperature of the water-bath is raised simultaneously, making the process adiabatic. The small difference in temperature between the calorimeters before and after an experiment is measured by means of a multiple thermel connected directly to a sensitive galvanometer. The procedure is like weighing by substitution. In the *working* calorimeter weights, first of water and then of solution, are balanced against a fixed *tare* heat capacity in the second calorimeter. Thus thermally equivalent weights of water and of solution are determined directly and the *specific heat* is obtained by dividing the former by the latter.³

¹ Paper presented before the Buffalo meeting of the American Chemical Society, August 31, to September 3, 1931.

² Gucker, *THIS JOURNAL*, 50, 1005 (1928).

³ For a full description of the apparatus and experimental technique the reader is referred to the original article.² A somewhat similar apparatus and references to the

Apparatus

Three important changes deserve mention. The first was the substitution of spun gold linings for the original gold plating on the calorimeters, in order surely to protect them from any action of the solutions. The second was the use of a 25-ohm four-lead potential type platinum resistance thermometer and Mueller type Wheatstone bridge to measure the temperature of the water-bath before and after the experiment. This excellent apparatus, made by Leeds and Northrup and standardized by the Bureau of Standards, fixed the experimental temperature to 0.01° and is much more sensitive and convenient than the mercury thermometer used for the preliminary work. The third was an improvement in the quantitative heating coils which has further reduced their thermal lag and heat capacity. Each of these simple and satisfactory heaters, illustrated in Fig. 1, was made as follows. Slightly over 1 meter of thin gold tubing 1 mm. in outside diameter was bent into a loop and the two ends pushed through small holes in a threaded brass plug, *A*, protected with a spun gold covering, *B*. The tubing was fastened in place with a minimum amount of hard (silver) solder. A 95-cm. length of No. 30 B. and S. gage "salamander"⁴ coated "advance" (constantan) wire was then measured off for the resistance. The insulation was carefully pushed back from each end of the wire, which was filed at an angle of about 60° . A small brass bar served as a jig for this operation. A very small hole, through which the wire would just slip, was bored in one end, which was then ground off at the desired angle as shown. Two pieces of "salamander" coated copper wire of the same size which served as leads were filed in the same manner. The end of each of the wires was carefully tinned and they were joined together with soft solder, using a small iron. The joints were not

history of the method were described in an article by Richards and Gucker, *THIS JOURNAL*, 47, 1876 (1925). The method has also been used recently with great success by Randall and Ramage, *ibid.*, 49, 93 (1927), and especially by Randall and Rossini, *ibid.*, 51, 323 (1929).

In the present method the weight of solution is adjusted until the rise of temperature in the two calorimeters is the same ($\approx 0.0006^\circ$). Temperature measurements are then made under adiabatic conditions with high precision and great simplicity. Randall and his co-workers do not try to balance the temperature rise exactly, but determine the difference in temperature in the two calorimeters, which amounts to 0.01° in many cases. This requires the use of a special potentiometer with the thermel. Lamb and Fairhall (Thesis, Harvard University, 1918) used Richards' thermochemical heating in each calorimeter. This heating could be varied to make the temperature difference practically zero. Apparently no one has tried to vary the electrical energy input in one of the calorimeters, although then the rise in temperature could be balanced without changing the weight of solution. It does not seem practical to make one of the heaters variable in small known steps, still connecting the two in series so as to have the same current through each. However, it should be a simple matter to connect the two similar heaters in parallel and to vary the energy input into one by means of an external variable resistance in series with it. The current and voltage drop across the heater will both vary with this external resistance and the energy with the square of the total resistances. This will cause no serious difficulty in the experiments or calculations and will be tried at an early date in this Laboratory. It should be especially helpful in making measurements over a wide temperature range where, with our present method, any large change in the specific heat would require a different weight of solution.

⁴ The trade name for an excellent asbestos coating which can be applied to small wires by the York Insulated Wire Works of the General Electric Company, Bridgeport, Conn.

appreciably larger than the original wire (0.2 mm.). The insulation was carefully pushed back into place so that it completely covered the soldered joint. It was protected against subsequent dislocation by a piece of silk insulation wound over the joint and extending 15 mm. on either side.

A piece of small bare copper wire was now threaded through the gold tubing. One end of the copper lead wire was soldered to it, and the resistance wire was gently pulled inside the gold tubing. The somewhat sticky surface of the "salamander" coating was lubricated with talc, preventing any undue strain on the soldered joints. When in place, the ends of the resistance wire were at *C*, 3 cm. below the ends of the gold tubing. Thus no appreciable amount of the heat generated in the coil escaped from the calorimeter. The tubing was now bent into a loose bifilar coil about 3 cm. in diameter and 6 cm. long,

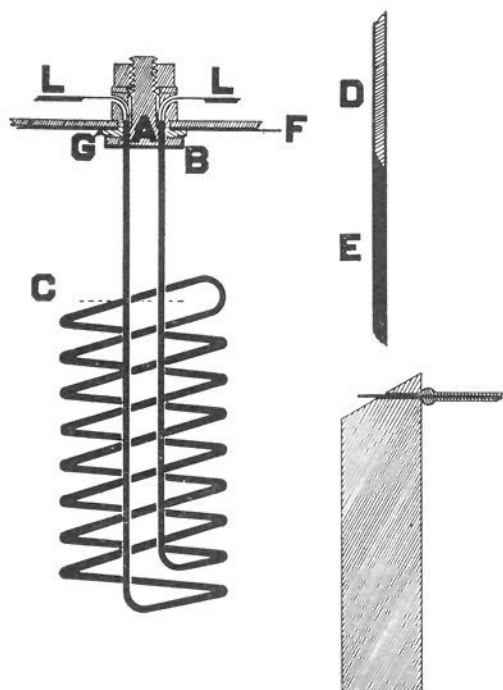


Fig. 1.—Left, heating coil; right top, detail of joint; right bottom, jig for filing fine wires.

mounted on the calorimeter lid as shown (Fig. 1). A rubber gasket *G* ensured an air-tight joint between the gold casing of the plug *B* and the gold lining *F* of the lid. The No. 30 copper wires⁵ were cut off 5 mm. above the lid of the calorimeter and soldered to No. 20 copper leads *L*, *L* of uniform length (6.5 cm.).⁶

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A three-stage propeller stirrer occupied the space inside the heater and, run at 216 r. p. m., provided an efficient heat dissipation. A higher stirring rate (270 r. p. m.) gave no more rapid thermal equilibrium but caused a 60% increase in the heat of stirring, which was found to increase approximately as the cube of the stirring speed.

The 18-junction thermel originally used to measure the difference in temperature between the calorimeters was replaced by a new 12-junction one, made in two opposable halves. Each

junction was insulated from the metal case by means of a small glass capillary tube, which proved to be more satisfactory than the cellulose acetate varnish originally used. The thermel, connected directly as before to a Leeds and Northrup HS galvanometer by means of a simple reversing switch, gave a deflection of 1 mm. on the scale for a difference in temperature of 0.00008°.

Materials and Solutions

The substances were all prepared, and the solutions made up, analyzed and handled with the care necessary to take full advantage of the calorimetric precision. Fortunately

⁵ The "salamander" coating is omitted from the drawing to avoid confusion.

⁶ This construction is similar to that used by Randall and Rossini, *THIS JOURNAL*, 51, 326 (1929). Decreasing the lead resistance reduces the heat liberated in the leads to 0.04% of that liberated in the calorimeter. Appreciable error due to increased heat conduction is prevented by the careful adiabatic control and the compensation of the twin calorimeters.

extreme care in purification and analysis is not required, since the effect of impurities and the change of specific heat with concentration are both small. Water from the laboratory still, distributed through block tin pipes and containing no known impurity except dissolved air, was used throughout the work. It was freshly boiled (to drive out this air) before use in the calorimeters or in making up solutions.

The best commercial grade of lithium chloride was dissolved in hot water, filtered and twice recrystallized with centrifugal drainage. Probably the most persistent impurity is sodium, for small traces of which a test is very difficult. The method of analysis recommended by Noyes and Bray⁷ gave no test for sodium or potassium in a quantity of solution containing 200 mg. of Li^+ . A comparison test showed that 0.5 mg. of either constituent could easily be detected. The solution therefore contained less than 0.07 mole per cent. of Na^+ and 0.05% of K^+ . Assuming that the change of specific heat is proportional to the mole per cent., the corresponding error in the specific heat of the *two molal* solution is less than 0.004%. The solutions, made up and stored in glass-stoppered Pyrex flasks, were analyzed by means of silver chloride residues.

The hydrochloric acid was made by diluting the best commercial acid to the concentration of the constant boiling mixture. This was slowly distilled from a hard glass flask with constricted neck (like the Richards water still) to which was fitted a Pyrex condenser tube. The middle third of the distillate was collected in a Pyrex or Jena hard glass flask and diluted to the required concentration. Most of the solutions were analyzed by silver chloride residue, although some of the most concentrated ones were titrated against sodium carbonate, made by heating the recrystallized bicarbonate to constant weight in a platinum dish. Titrations were made with weight burets, using methyl orange as an indicator.

The potassium hydroxide was carefully purified by a modification of the method described by Knobel.⁸ Two round-bottomed Pyrex flasks, of one and two liter capacity, respectively, were joined by a 15-mm. U-shaped tube, one end of which was sealed to the bottom of each. The inside of flasks and tube was heavily coated with paraffin. Enough purified mercury was put into the apparatus to fill the U-tube and the bottom of each flask. The device was mounted on a rocking table, by which the mercury could be made to flow slowly from one flask to the other. A saturated solution of purest obtainable potassium hydroxide was put into the smaller flask, whence it was slowly electrolyzed into the mercury, which served as cathode. When the resulting amalgam was rocked under the freshly boiled water in the second flask, it reacted to make a very pure solution. A piece of platinized platinum connected to the mercury allowed easy evolution of hydrogen. Once started, the operation was slow but easily controlled and very satisfactory. Using a current of 0.15 ampere, a 2.5 m. solution of potassium hydroxide was produced in two weeks. A higher current gives a more concentrated, viscous amalgam which will not flow properly. The solution was siphoned out of the flask, diluted as desired with freshly boiled water and stored in paraffin-lined bottles, fitted with appropriate siphon tubes and with gas-washing bottles containing some of the solution, to remove carbon dioxide from the entering air. Each concentration of alkali was standardized against a suitable concentration of the hydrochloric acid described above, using weight burets and methyl red as indicator. Inter-comparisons of the different acid and alkali solutions were made to check the concentration of each. The potassium hydroxide solution showed no trace of silica, only 0.01 to 0.02% carbonate and about 0.74 mole per cent. of sodium. This would cause a small error in the most concentrated solutions (0.041% at 2.6 m.) for which due correction was made.

⁷ Noyes and Bray, "Qualitative Analysis for the Rarer Elements," The Macmillan Company, New York, 1927, pp. 254 *et seq.*

⁸ Knobel, *THIS JOURNAL*, 45, 70 (1923).

Experimental Technique

The only change made here was to reduce the temperature interval from 2 to 1°. This made no apparent decrease in the accuracy of the method, partly because the experimental time was reduced and partly because the correction necessary for the slight difference in temperature trend in the two calorimeters was made in a more precise manner. The galvanometer deflection was plotted at one-minute intervals for five minutes before the experiment (which was not started until the trend was uniform) and afterward, until a uniform trend was again obtained for the same length of time.⁹ By drawing straight lines through these two *series of points* and extrapolating to the middle of the heating time, the corrected galvanometer change was found more accurately than if only four points had been used.¹⁰ The plot of a typical experiment is given in Fig. 2. As

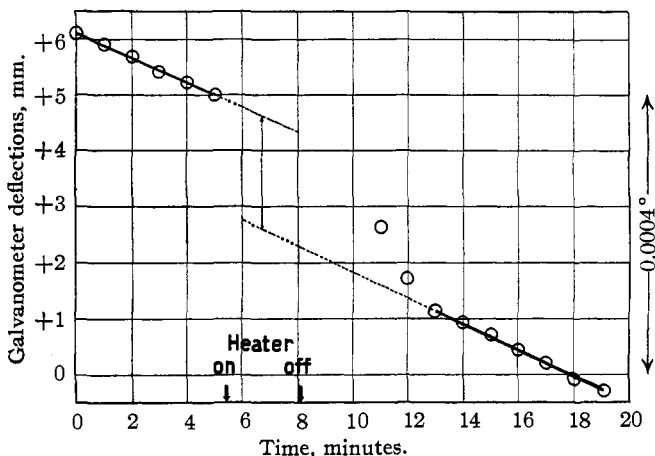


Fig. 2.—A typical experiment (LiCl, Experiment 1a).

can be seen, the deviations of the observed points from the straight lines are only of the order of 1 or 2 one hundred thousandths of a degree, and the lines before and after the experiment are nearly parallel. These facts make it possible to determine the actual temperature change during the experiment to better than one ten thousandth of a degree.

Two series of water standardizations were carried out in the manner previously described.¹¹ In the first series, 250.00 g. of water in the *tare*

⁹ With the new type of heaters, a constant trend was reached about *five minutes* after the current was turned off, instead of *ten minutes* afterward as with the old coils (cf. Ref. 2, p. 1013).

¹⁰ The advantage of this method, which has been used by a number of investigators, was pointed out to us by Dr. Malcolm Dole, who was able to obtain better agreement in measuring heats of dilution in this way. Cf. Richards and Dole, *THIS JOURNAL*, 51, 799 (1929).

¹¹ Cf. Ref. 2, p. 1011.

calorimeter was balanced against weights of water in the *working* calorimeter which were varied from 250.40 to 250.66 g. (*in vacuo*). In order to accommodate the thermally equivalent weight of the concentrated solutions of low specific heat, a second series of standardization experiments was made with 15 g. less water in each calorimeter. The two series are plotted in Fig. 3.¹² The radius of the circle marking each point will be

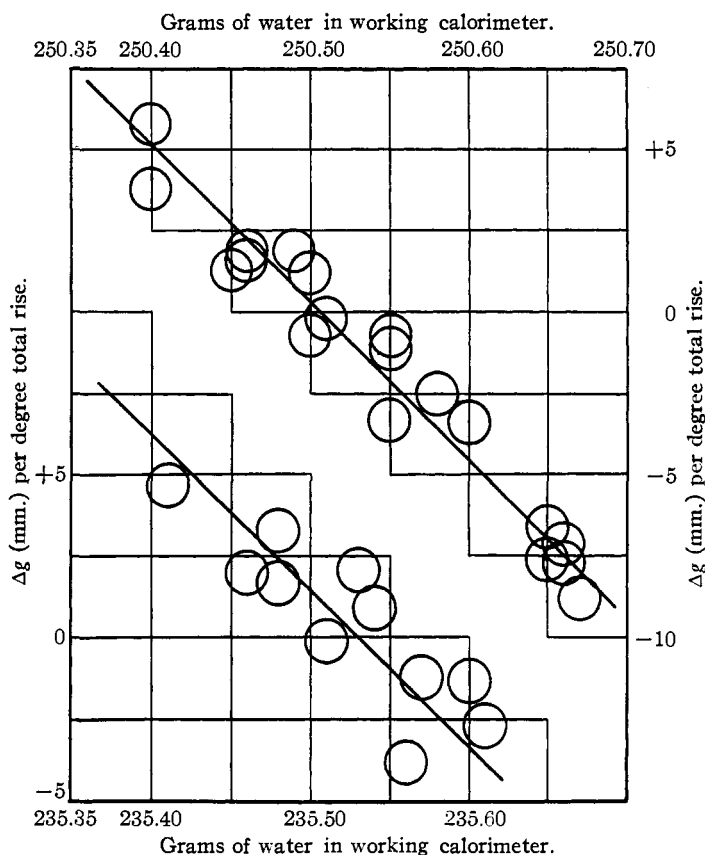


Fig. 3.—Calibration curves.

seen to represent a deviation of 0.005%, and the concordance of the results can be judged from the figure. Enough experiments were made, at in-

¹² After a few preliminary water experiments were made to develop the experimental technique, no experiments with water or solution were rejected except those affected by some known cause of error and two early standardizations made June 10, 1930. In these, 250.41 g. of water (*in vacuo*) gave corrected galvanometer deflections of +0.8 and +0.5 mm. These results differed by about 0.03% from the calibration curve based on all other results and hence were rejected, on the assumption that some large error (such as 0.1 g. in weighing) was responsible for the discrepancy. Even if these results were included, however, the curve would not be greatly affected.

tervals during the course of the work, to reduce the probable error in the water value to about $\approx 0.005\%$ —half that desired in the case of any individual solution. The exact cause of the small residual uncertainty is not known, but further repetition would have served no useful purpose.

Results

The results are summarized in the accompanying Tables I–III.

Beside the values of the specific heats are tabulated those of the apparent molal heat capacity of the solute, defined as

$$\Phi = \left[\frac{1000}{m} + M_2 \right] s - \frac{1000}{m}$$

where M_2 is the molecular weight of the solute. Φ is given in 25° -calories/degree, the unit in which the specific heats are measured. This quantity, which was shown by Randall and Rossini¹³ to vary directly with \sqrt{m} over a wide range of concentrations and for a large number of salts, is extremely useful in tabulating specific heat data. As was pointed out by Rossini,¹⁴

TABLE I^a

SUMMARY OF RESULTS FOR LITHIUM CHLORIDE SOLUTIONS

The quantities of water and of solution were weighed out to even centigrams (≈ 2 mg.). All weights are *in vacuo*. Δg is the corrected galvanometer deflection for 1° total rise. The specific heat, s , is referred to water at the same temperature as unity, hence values of Φ are in 25° -calorie units.

Expt.	m	Solution, g.	Δg , mm.	Equiv. wt. of water	Specific heat, s	Mean temp., $^\circ\text{C}$.	Φ	\sqrt{m}
5a	0.0400	251.080	+0.6	250.494	0.99767	25.02	-15.9	0.200
b		251.110	-	250.508	.99760	24.96	-17.7	
8a	.0625	251.390	-1.4	250.535	.99660	25.00	-13.3	.250
b		251.340	+0.2	250.503	.99667	25.01	-12.2	
4a	.0897	251.780	+1.0	250.486	.99486	25.01	-15.1	.299
b		251.810	-0.1	250.508	.99483	25.01	-15.5	
7a	.1600	252.770	- .7	250.521	.99110	25.01	-13.6	.400
b		237.610	+1.7	235.494	.99109	25.01	-13.7	
3a	.2504	254.020	-0.4	250.514	.98620	24.99	-13.3	.500
b		253.970	+ .5	250.496	.98632	25.01	-12.8	
2a	.4904	257.360	-6.0	250.629	.97385	24.98	-12.0	.700
b		257.190	+1.1	250.483	.97392	25.02	-11.9	
1a	1.0000	263.910	-2.0	250.548	.94937	25.00	-10.38	1.000
b		263.840	+0.4	250.498	.94943	25.00	-10.31	
c		263.820	+ .8	250.490	.94947	25.02	-10.27	
6a	2.4614	264.940	\approx .0	235.530	.88899	25.03	- 7.41	1.569
b		264.970	-1.0	235.552	.88898	25.01	- 7.41	

^a The experiments are numbered in chronological order. m is moles of solute per 1000.0 g. of water. The atomic weights are those of the 1930 report, *THIS JOURNAL*, **52**, 861 (1930).

¹³ Randall and Rossini, *THIS JOURNAL*, **51**, 323 (1929).

¹⁴ F. D. Rossini, "Heat Capacities in Some Aqueous Solutions," Research Paper No. 151, reprinted from *Bur. Standards J. Research*, **4**, 315 (1930).

TABLE II
 SUMMARY OF RESULTS FOR HYDROCHLORIC ACID SOLUTIONS

Expt.	<i>m</i>	Solution, g.	Δg , mm.	Equiv. wt. of water	Specific heat, <i>s</i>	Mean temp., °C.	Φ	\sqrt{m}
5a	0.0100	250.670	-3.8	250.584	0.99966	24.99	+ 2.5	0.100
b		250.570	+2.8	250.448	.99951	25.00	-12.5	
c		250.620	+0.6	250.494	.99950	25.00	-13.5	
d		250.600	+1.6	250.473	.99949	25.00	-14.5	
4a	.0400	251.150	-2.5	250.557	.99764	25.00	-22.6	.200
b		251.030	+3.8	250.427	.99760	24.99	-23.6	
8a	.0626	251.490	-0.3	250.513	.99612	25.00	-25.7	.250
b		251.460	+ .8	250.492	.99615	25.00	-25.2	
3a	.0900	251.960	- .6	250.518	.99428	24.99	-27.3	.300
b		252.040	-3.7	250.582	.99422	24.99	-27.9	
2a	.1629	253.140	-0.8	250.523	.98966	24.98	-27.4	.404
b		253.250	-3.7	250.582	.98946	24.96	-28.6	
c		253.060	+3.3	250.438	.98964	24.99	-27.5	
1a	.2552	254.530	+1.7	250.472	.98406	25.08	-26.5	.505
b		254.630	-4.9	250.607	.98420	25.00	-26.0	
c		254.580	-2.8	250.564	.98422	24.99	-25.9	
7a	.8100	247.430	-0.5	235.508	.95182	25.00	-24.77	.900
b		247.390	+1.4	235.474	.95183	24.99	-24.76	
6a	2.0112	264.480	+3.5	235.437	.89019	24.98	-22.13	1.418
b		264.580	-2.6	235.545	.89026	25.01	-22.10	

 TABLE III
 SUMMARY OF RESULTS FOR POTASSIUM HYDROXIDE SOLUTIONS

Expt.	<i>m</i>	Solution, g.	Δg , mm.	Equiv. wt. of water	Specific heat, <i>s</i> ^b	Mean temp., °C.	Φ	\sqrt{m}
5a	0.0399	236.310	-2.1	235.574	0.99687	25.02	-23	0.200
b		251.290	-1.8	250.543	.99697	24.97	-21	
8a	.0622	251.760	+0.2	250.502	.99500	24.99	-25	.249
b		236.680	+1.4	235.500	.99501	25.02	-25	
6a	.0894	252.390	-1.4	250.536	.99268	25.00	-27	.299
b		252.800	-3.4	250.574	.99272	25.04	-26	
7a	.1602	253.800	+1.7	250.472	.98690	25.00	-27.0	.399
b		253.760	+3.4	250.436	.98692	25.02	-27.0	
2a	.2497	240.370	-0.4	235.516	.97978 ¹	25.02	-25.9	.500
b		255.640	+ .8	250.490	.97982	25.01	-25.7	
3a	.4931	244.830	+ .5	235.496	.96183 ²	25.02	-23.4	.702
b		260.280	+5.7	250.429	.96190	25.01	-22.7	
1a	.8484	250.930	+5.6	235.411	.93803 ³	25.01	-20.4	.921
b		267.070	-1.2	250.534	.93799	25.04	-20.4	
4a	2.5873	277.200	-11.8 ^a	235.286	.84845 ⁴	25.02	-11.00	1.609
b		277.500	+1.1	235.512	.84837	25.02	-11.03	

^a Calibration curve extends only to -6.7 mm. The equivalent weight of water in this case was obtained by linear extrapolation.

^b Correction was made for 0.74 mole per cent. Na⁺ from the data of Richards and Rowe.¹⁵ Assuming linear change of *s* with mole per cent. at any one concentration of OH⁻ the corrections were: ¹ 3×10^{-4} calorie/degree; ² 7×10^{-4} calorie/degree; ³ 12×10^{-4} calorie/degree; ⁴ 35×10^{-4} calorie/degree.

¹⁵ Richards and Rowe, THIS JOURNAL, 43, 770 (1921).

it "gives directly the relatively small difference between the heat capacity of a given amount of solution and the heat capacity of an amount of pure water equivalent to that in the given solution." The convenience of Φ is shown by the following illustration: Wanting to know the specific heat of 1 m lithium chloride when starting our series of experiments, we plotted the values of Φ against \sqrt{m} for lithium chloride solutions at 18° from the data of Richards and Rowe¹⁵ and thus determined the best smoothed value of Φ when $m = 1$. This value, -12.3 , was corrected to 25° by the temperature coefficient of Φ between 18 and 25°, found by combining the data of Richards and Rowe for sodium chloride and potassium chloride with those of Randall and Rossini for the same salts. This gave $\Phi = -10.6$ and $s = 0.94916$. Our direct experiments gave $s = 0.94942$ (slightly less than 0.03% different) and $\Phi = -10.3$.

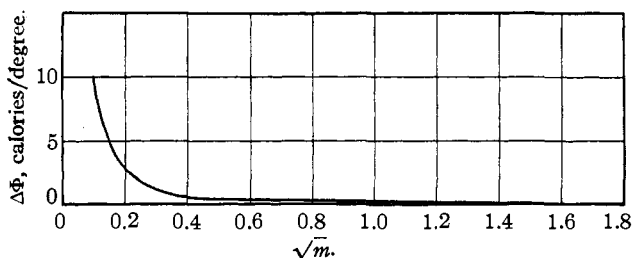


Fig. 4.—Error in Φ for 0.01% error in s .

The usual method of differentiating for errors shows how the values of Φ are affected by errors in m and in s .

$$\Delta\Phi = \frac{1000}{m} (1-s) \frac{\Delta m}{m}$$

$$\Delta\Phi = \left[\frac{1000}{m} + M_2 \right] \Delta s \simeq \frac{1000}{m} \frac{\Delta s}{s}$$

Since over a wide range $(1-s)$ decreases almost exactly as fast as $(1000/m)$ increases, their *product* has a constant value of about 50. An error of 0.1% in m therefore only causes an error of 0.05 calorie per degree in Φ . On the other hand, the error in Φ caused by any error in s is *inversely proportional* to m . An error of 0.01% in s changes the value of Φ by only 0.04 in a 2.5 m solution but by 10 in a 0.01 m solution. This makes it useless to go below 0.04 or 0.01 m in these experiments. In Fig. 4 is shown the effect upon Φ of a 0.01% error in s . The error is plotted against \sqrt{m} so as to be comparable with the other curves. In all but the most concentrated solutions, the limiting factor is the error in s , if that in m is 0.1%. Even at 2.25 m an error of 0.01% in s is three times as serious as one of 0.03% in m .

Figures 5 and 6 show graphically the results for Φ plotted against \sqrt{m} . Experimental values are indicated by separate circles or triangles. Several concentric marks indicate coincident results. Three series of experiments

are distinguished in the lithium chloride results by means of signs within the circles. The more dilute solutions in each series were made by quanti-

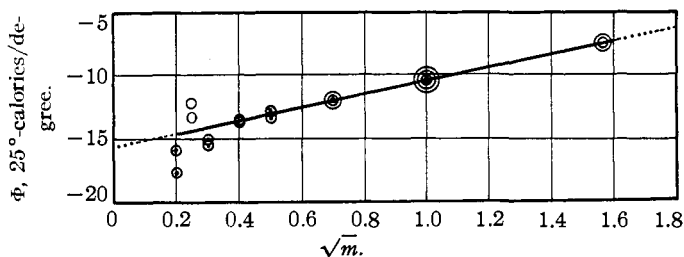


Fig. 5.—Apparent molal heat capacity of lithium chloride.

tative dilution of the most concentrated, which was analyzed as previously described.

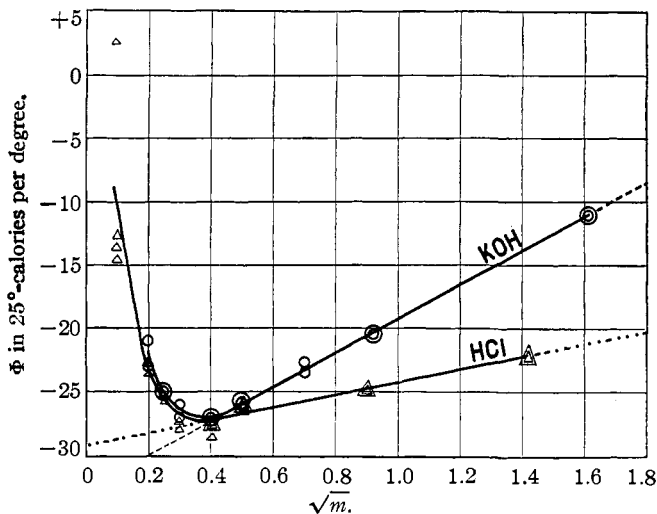


Fig. 6.—Apparent molal heat capacity of solute.

From the values of Φ it is a simple matter to calculate the partial molal heat capacity of the solute (\bar{C}_{p_2}) and the relative partial molal heat capacity of the solvent ($\bar{C}_{p_1} - \bar{C}_{p_1}^\circ$) by the method used by Randall and Rossini,¹⁶ using the equations

$$\bar{C}_{p_2} = \Phi + \frac{1}{2} m^{1/2} \left(\frac{d\Phi}{dm^{1/2}} \right) \quad \text{and}$$

$$\bar{C}_{p_1} - \bar{C}_{p_1}^\circ = -\frac{m}{55.507} \left(\frac{1}{2} m^{1/2} \frac{d\Phi}{dm^{1/2}} \right)$$

The values of these quantities are shown graphically in Figs. 7 and 8. In Table IV are given values of Φ , \bar{C}_{p_2} and $\bar{C}_{p_1} - \bar{C}_{p_1}^\circ$ for rounded values of the concentration.

¹⁶ Randall and Rossini, THIS JOURNAL, 51, 323 (1929).

TABLE IV
SUMMARY OF RESULTS FOR ALL SOLUTIONS AT ROUNDED CONCENTRATIONS

(Figures in parentheses are extrapolated)

	Molality, m	0.01	0.04	0.10	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00	2.25
LiCl	$-\Phi = 15.63 - 5.25 m^{1/2}$	(15.1)	14.6	14.0	13.0	11.9	11.1	10.38	9.76	9.20	8.69	8.21	7.76
	$-\bar{C}_{v_2} = 15.63 - 7.88 m^{1/2}$	(14.8)	14.1	13.1	11.7	10.1	8.8	7.75	6.82	6.09	5.23	4.50	3.81
	$-100(\bar{C}_{v_1} - \bar{C}_{v_1}^0) = 4.68 m^{3/2}$	(0.005)	0.04	0.15	0.58	1.65	3.04	4.68	6.53	8.59	10.82	13.23	15.78
HCl	$-\Phi = 29.20 - 5.00 m^{1/2}^a$	9	23	27.0	26.7	25.7	24.9	24.20	23.62	23.08	22.59	22.13	(21.70)
	$-\bar{C}_{v_2} = 29.20 - 7.50 m^{1/2}^a$	17	30	29	25.5	23.9	22.7	21.70	20.82	20.02	19.26	18.60	(17.95)
	$-100(\bar{C}_{v_1} - \bar{C}_{v_1}^0) = 4.50 m^{3/2}^a$	-0.13	-0.50	-0.36	0.56	1.59	2.93	4.50	6.29	8.25	10.40	12.73	(15.20)
KOH	$-\Phi = 32.10 - 13.25 m^{1/2}^a$	(9)	22	26.1	25.5	22.7	20.6	18.75	17.29	15.87	14.57	13.34	12.21
	$-\bar{C}_{v_2} = 32.10 - 19.88 m^{1/2}^a$	(17)	29	30.2	22.3	18.0	14.9	12.22	10.90	7.75	5.79	3.96	2.30
	$-100(\bar{C}_{v_1} - \bar{C}_{v_1}^0) = 11.99 m^{3/2}^a$ (-0.13)	-0.47	-0.73	1.49	4.25	7.73	11.89	16.65	21.86	27.62	34.22	40.25	

^a These expressions are valid above $m = 0.2$. The entries in the table are the best values, corresponding to the curves of Figs. 5, 6, 7 and 8.

Discussion

The results obtained for the lithium chloride solutions are about what would be predicted. Over the whole range from 2.46 m to 0.04 m the values of Φ plotted against \sqrt{m} fall along a straight line, from which they deviate only in the very dilute range. In no case does this deviation correspond to one in s appreciably greater than 0.01%. When correction is made for the difference in temperature, as previously explained, our results are in excellent agreement with those of Richards and Rowe and of Jauch (both at 18°) which have been plotted by Rossini.¹⁷

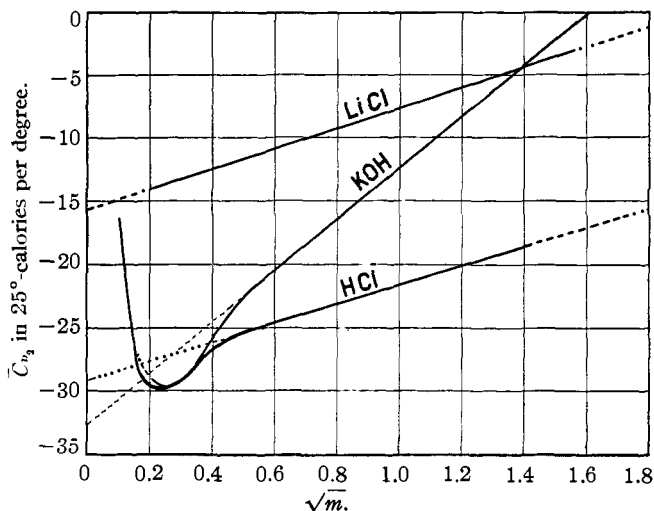


Fig. 7.—Partial molal heat capacity of solute.

The results obtained with hydrochloric acid and potassium hydroxide above about 0.2 m also show the expected absolute linearity of Φ against \sqrt{m} . In the very dilute range, however, they are more interesting. Both curves show sudden breaks and a decided *increase* in the apparent molal heat capacity as the dilution is increased. There seems to be no indication of such a change in any previous work, with the possible exception of lithium hydroxide at 18° as plotted by Rossini from the data of Richards and Rowe. Their data are not sufficiently precise to be conclusive and we are now studying solutions of lithium hydroxide and sodium hydroxide in this Laboratory to see if they behave like potassium hydroxide. Although the deviation we find is only about twice the probable experimental error, fourteen experiments show this deviation, while none deviates in the

¹⁷ F. D. Rossini, "Apparent and Partial Molal Heat Capacities in Aqueous Solutions of Nineteen Uni-univalent Strong Electrolytes," Research Paper No. 331, reprinted from *Bur. Standards J. Research*, 7, 47 (1931).

other direction. Moreover, nearly the same curve is followed by the two solutions, which seem to behave very similarly. Most of the results with hydrochloric acid were obtained consecutively by the senior author. After this, the perfectly linear ones for lithium chloride were found and then those for potassium hydroxide by the junior author. Finally a new solution of 0.0626 *m* hydrochloric acid was made up, standardized and investigated. The results (Experiments 8a and b) are seen to fall exactly on the curve previously plotted. This self-consistency and agreement with the results obtained five months or more before seems to indicate that the

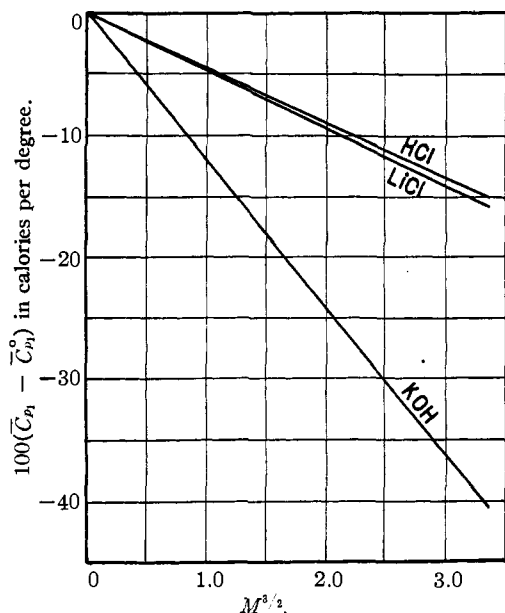


Fig. 8.—Relative partial molal heat capacity of solvent.

effect is not due to experimental error. Moreover, as the apparatus is standardized with water and is strictly differential, we should expect any systematic error to disappear at great dilution. That due to the different cooling by evaporation from the surface of the water and from that of the solution,¹⁸ into the small air space above the liquid, is known to be negligible even at the highest concentrations. The volume of the air space was only 42 cc. and the evaporation from the water, due to the increased vapor pressure during an experiment, was found to amount to only 1.3×10^{-4} degree per degree total rise.

The difference in the case of the solution is therefore entirely negligible.

It is impossible to follow the course of the apparent molal heat capacity curves to any lower concentration by specific heat measurements with our present apparatus; nor does it seem promising to try to push the accuracy of these measurements beyond the limit of 0.01% in our experiments and those of Randall and Rossini. However, it should be possible to determine apparent molal heat capacities in even more dilute solutions from the heats of dilution at two different temperatures.¹⁹ The very small temperature changes due to dilution can be measured with extreme calorimetric

¹⁸ Ref. 2, p. 1014.

¹⁹ This method has been used frequently; recently with great success by Richards and his co-workers, *THIS JOURNAL*, 51, 707 *et seq.* (1929).

sensitivity without requiring a high *percentage* accuracy. We are now setting up an apparatus to measure the heats of dilution of such solutions with a sensitivity of 10^{-6} degree, as Lange and his co-workers have done, mostly at one temperature, for the last few years.²⁰

Our results for hydrochloric acid agree well with those of Richards, Mair and Hall,²¹ corrected from 18 to 25° as before. Their results for the most concentrated solutions were obtained directly, while those for the more dilute ones were calculated from the temperature coefficient of the heats of dilution. They are appreciably *higher* than those of Randall and Ramage²² who obtain an extrapolated value of -42 calories per degree for \bar{C}_{ps}° , compared with our value of -28 , from linear extrapolation of the values for Φ from $0.09 m$ and higher. The much greater scattering of their experimental points for \bar{C}_{ps} over the whole range of \sqrt{m} is doubtless due in great measure to the use of a method of calculating the partial molal heat capacity which is inferior to that used by Randall and Rossini; but their data seem less accurate than those of the latter.

The results for potassium hydroxide are in good agreement with those of Richards and Rowe and Richards and Hall, as plotted by Rossini.²³

Our results at low concentrations show that the extrapolation of the apparent molal heat capacity curves to infinite dilution is a much more dubious procedure than was formerly realized, at least in the case of *strong* electrolytes. Rossini²⁴ postulated abrupt changes in the apparent molal heat capacity of *weak* electrolytes in the range below $0.04 m$, in order to account for the discrepancy between the extrapolated curve for such a substance as citric acid (which he concludes represents nearly the apparent molal heat capacity of the *undissociated* substance) and the value calculated from the sum of the values for the individual ions. These values for individual ions are obtained and combined in a manner similar to that used to determine the value of Λ_{∞} for a weak electrolyte by Kohlrausch's law. We have no criticism of the conception that in very dilute solutions the apparent molal heat capacity of the ions must be additive, but we doubt if it is possible to extrapolate safely even from a concentration as low as $0.04 m$, in order to obtain the limiting values. La Mer and Cowperthwaite²⁵ have reached the same conclusion. From a study of the e. m. f. of suitable cells over a wide range of temperature, they have calculated \bar{C}_{ps} for zinc sulfate below $0.01 m$ and find that, even as low as $0.0005 m$, it is not a linear

²⁰ Lange and Robinson, *Chem. Rev.*, 9, 89 (1931), summarizes this excellent work.

²¹ Richards, Mair and Hall, *THIS JOURNAL*, 51, 727 (1929).

²² Randall and Ramage, *ibid.*, 49, 93 (1927).

²³ Ref. 17, p. 50.

²⁴ F. D. Rossini, Ref. 14, p. 323.

²⁵ Paper presented before the Buffalo meeting of the American Chemical Society by La Mer. The experimental work has been published in Cowperthwaite's Thesis, Columbia University, 1930.

function of \sqrt{m} . "This shows how misleading it is to extrapolate calorimetric data linearly from 0.01 or 0.02 m to zero concentration."

The incorrectness of such a procedure in the case of heats of dilution has been shown by Lange's work in the very dilute range. Even such a salt as potassium nitrate, which *absorbs* a great deal of heat on dilution to 0.04 m , is found to *give out* heat on dilution below 0.01 m . This is strikingly shown by a comparison of the heats of dilution of many strong electrolytes down to moderate dilution, measured by Richards and Rowe, with those of similar electrolytes in the extremely dilute range, measured by Lange and his co-workers. Such a graphical comparison has been made by one of us.²⁶

Moreover, it seems impossible to account for the linear change of the apparent and partial molal heat capacities with \sqrt{m} up to a concentration of several molal by an application of the Debye-Hückel limiting law, as did Randall and Rossini. This would mean that the *second derivative* of the partial molal electrical free energy was correct at a concentration where the function and first derivative (measured by the logarithm of the activity coefficient and the partial molal heat content) no longer were applicable. The experimental curves have appreciably different slopes over the range studied and all are about *three times* that predicted by the theory. Also, if they are actually linear in the dilute range, there is no chance for them to approach a *common* limiting tangent. Finally, as Randall and Rossini observe, a negative value for the partial molal heat capacity at *infinite dilution* is inexplicable on the Debye-Hückel theory, since charged ions, infinitely far apart, have no effect on each other. Such a negative value, if it really is the limiting one, must seek an explanation in the effect of the ions upon the solvent molecules, such as has been postulated by Zwicky.²⁷ His calculation of the apparent molal heat capacity in dilute solutions, however, gives a negative value which is about four times that actually observed.

Further study of the heat capacity of solutions of strong electrolytes in very dilute solutions, such as we are preparing to carry out, should at least provide experimental data by which any theoretical explanation must finally be gaged.

It is a pleasure to acknowledge once again our indebtedness to Professor A. A. Noyes for the kind gift of the apparatus built at the California Institute of Technology, and to an anonymous benefactor of the Wolcott Gibbs Memorial Laboratory of Harvard University for financial aid in the improvements in the apparatus made at that time.

Summary

The adiabatic twin calorimeter method of determining specific heats of aqueous solutions has been further improved and used to determine the

²⁶ Gucker, *School Science and Mathematics*, 29, 929, 930 (1929).

²⁷ F. Zwicky, *Physik. Z.*, 27, 271 (1926), summarized in *Physik. Z.*, 26, 664 (1925); and *Proc. Nat. Acad. Sci.*, 12, 86 (1926).

heat capacities of aqueous solutions of lithium chloride, hydrogen chloride and potassium hydroxide at 25°. The solutions have been investigated from a concentration of 0.01 or 0.04 *m* to a concentration of 2 to 2.5 *m*, with a precision of about 0.01%.

The apparent molal heat capacity of the solutes plotted against the square root of the molality shows the important linear relation announced by Randall and Ramage and confirmed by Randall and Rossini: in the case of lithium chloride solutions over the whole concentration range and in the case of the other solutions *above* about 0.2 *m*. In the range *below* this concentration, however, the apparent molal heat capacity shows a sudden *increase* which has not been noted before. This throws some doubt on the validity of extrapolation to infinite dilution. Work is now in progress in this Laboratory to see if this behavior is shown by other solutions.

The partial molal heat capacities of the solute and those of the solvent have been calculated and are presented in graphs and tables.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA,
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THE SORPTION OF GASES BY COPPER

BY ARTHUR F. BENTON AND T. A. WHITE¹

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Introduction

The numerous researches of recent years on the adsorption of gases by solids possessing catalytic activity have brought to light many cases in which gas is extensively and strongly adsorbed at relatively high temperatures and low pressures, where the older idea of adsorption as merely an increased concentration of ordinary molecules at the solid surface would predict that little or no gas would be taken up. These anomalous adsorptions were variously described as "selective," "irreversible," "chemical," etc. Nevertheless the idea persisted that such processes differed only in degree from "physical" adsorption,² and that no sharp distinction could be drawn.

As a result of an extensive investigation of the adsorption of gases by oxide catalysts, Benton³ proposed the view that the two kinds of adsorption could be sharply differentiated, and that the total adsorption by active solids was the sum of the amounts of gas taken up in the two different ways.

¹ Du Pont Fellow in Chemistry.

² See, for example, Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 2d ed., p. 193 (1929).

³ Benton, *THIS JOURNAL*, **45**, 887, 900 (1923). This work was carried out in the Princeton Laboratory, with the cooperation and advice of Professor H. S. Taylor.