

due probably to its detection by a differential temperature curve. It should be pointed out that one temperature used in standardizing the thermocouple was 231.9° (m. p. of Bureau of Standards tin) which is quite close to the temperature of the transition in question.

Résumé

The liquidus curve of the binary system potas-

sium dichromate–sodium dichromate has been determined. It is of a simple eutectic type.

The melting point of sodium dichromate and the transition point of potassium dichromate have been redetermined.

The effect of the presence of sodium dichromate on the transition point of potassium dichromate has been noted.

NEW YORK, N. Y.

RECEIVED JUNE 18, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

A Study of the Heat Capacity of Aqueous Solutions of Barium Chloride

BY CHESTER M. WHITE

Thomsen¹ measured the specific heat of barium chloride solutions at 18° while some years later Marignac² reported values at 24.5°. More recently Urban³ has determined the specific heat at several temperatures for a number of solutions. Also Tippetts and Newton⁴ have made e. m. f. measurements on barium amalgam cells at several temperatures from which differences in partial molal heat capacities may be calculated. By an indirect method Richards and Dole⁵ have probably obtained the most precise data for barium chloride solutions, although the precision of their experiments is somewhat in doubt. Specific heats were redetermined for these solutions to provide precise results by the direct method. They will be useful as a test of recent theories of strong electrolytes for higher valence salts. The measurements were made with a twin adiabatic calorimeter.⁶ While the general design of the apparatus was similar to that of Gucker,⁷ the precision was of the order of 0.02%. This paper will stress the changes which were made in the construction and operation of the calorimeter to increase the precision to 0.01%.

Experimental

Modified Apparatus.—Figure 1 shows the construction of one of the calorimetric units. A threaded joint was used to secure the calorimeters in place. Internally threaded

collars (A) and externally threaded rings (B) were cast of brass. These were sweated to the original annular rings (C) which were secured permanently to the studs on the calorimeter cover by four special nuts (D). Originally the calorimeters were sealed to the annular rings, but the ground joint was not water tight after being in use two years. A coating of litharge and glycerol was placed between the calorimeter cover and the ring so that the joint would be water tight. A coating of de Khotinsky cement (E) was placed around the outside of the joint as a further protection. The Dewar jars (F), which served as calorimeters, were sealed to the rings by litharge and glycerol.

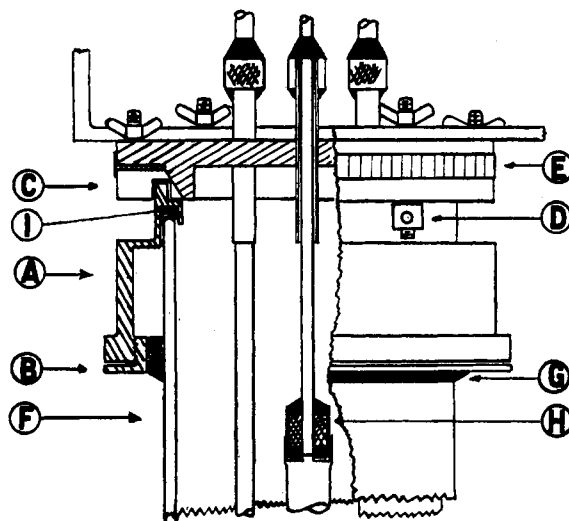


Fig. 1.—One unit of calorimeter.

(1) Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882.

(2) Marignac, "Oeuvres Complètes," Eggiman, Geneva, Vol. II, 1902, p. 624.

(3) Urban, *J. Phys. Chem.*, **36**, 1108 (1932).

(4) Tippetts and Newton, *THIS JOURNAL*, **56**, 1575 (1934).

(5) Richards and Dole, *ibid.*, **51**, 794 (1929).

(6) Unpublished work of Hess and Gramkee; see B. E. Gramkee, Master's Thesis, University of Rochester Library, 1930.

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

After this mixture was dry, a 3.2-mm. coating of Bakelite cement (G) was applied above and below the litharge seal. After baking for a week at 60°, several coatings of Bakelite varnish were applied. The threads were lubricated with a water-proof grease, since the entire unit was submerged in water. The joint was entirely water tight during the entire series of measurements. A flat gasket (I) of soft rubber was fitted into the top of the collar so that the vapor

space in the calorimeters was fairly tight. Thus the method of securing the calorimeters in place was modified without dismantling the apparatus.

The calorimeter heaters were made along the same general plan as before. The heating elements were made of No. 30 bare constantan wire. At the ends of this wire 3.2-cm. pieces of No. 28 copper wire were soldered, to which the lead wires (No. 18 bell wire) were soldered.⁸ The wire was wound bifilar on a slotted strip of mica. Thin protecting pieces of mica were tied with thread to the slotted strip and the whole was slipped into the case of the heater. The case was flattened and closed with a small amount of solder. The case⁹ was of thin copper chromium plated. A copper sleeve (H) was soldered to the neck of the heater. There was a shoulder inside the sleeve to support the Pyrex tube through which the lead wires ran. Asbestos fibers were packed around the bottom of the tube and a layer of litharge and glycerol poured over them. When this was dry, a layer of Bakelite cement was applied. The insulation resistance of the heaters was measured by the Meggar.¹⁰ Both heaters showed an infinite resistance between the case and either lead wire. The insulation resistances of the thermels were tested in the same way. The difference thermel (24 junctions) had an infinite resistance while the two adiabatic thermels (8 junctions each) showed resistance greater than 10 megohms.

In order to obtain an increased sensitivity without disturbing the thermels, Leeds and Northrup supplied a galvanometer with about five times the sensitivity of the original galvanometer but with the same damping resistance. The sensitivity with the difference thermel in series was 1.8 cm. μv (or 0.00006°/mm.). Since this galvanometer was more sensitive to vibrations, the simple Julius suspension was replaced by the improved type of Brevoort.¹¹ The entire suspension was enclosed by a double wall of shellacked paper to protect it from air currents.

It was found necessary to increase the speed of the calorimetric stirrers from 138 to 250 r. p. m. in order to establish thermal equilibrium in a relatively short time, fourteen minutes.

A large capacity Becker balance, which had a sensitivity of 3 mg. per scale division at 2000 g., was available for all but a few runs.

Materials, Constants, Molecular Weights, etc.—Baker c. p. barium chloride was used to make the solutions. The salt which was dehydrated at 120°¹² was always kept in the oven except when preparing the solutions. The usual precautions were taken in weighing the anhydrous material. A definite quantity of salt was added to a weighed amount of distilled water in the solution calorimeter. In some experiments a solution was weighed directly in the solution

calorimeter. Its molality was determined by weighing the silver chloride residues and also by weighing the anhydrous salt after evaporation of the water. The results of these two methods were in good agreement.

The lithium chloride was Baker c. p. material. It was recrystallized three times from distilled water but was not analyzed for alkali chlorides.¹³ The solution was made up and analyzed by weighing the silver chloride residues.

The molecular weight of barium chloride was calculated from the 1934 International Atomic Weight.¹⁴ The heat capacities are expressed in 15° calories. The specific heat of water at 25° in 15° calories is taken as 0.9979.

Experimental Procedure.—In these experiments a 1° temperature interval was employed. The Beckmann thermometer was used to measure the rise in temperature. As a result of a careful comparison with a thermometer standardized by the Bureau of Standards, suitable corrections were applied to the total rise in each determination. The fore and after drifts, which were followed for forty minutes, were plotted in the usual way and a straight line was fitted to the linear portion of each drift by the method of averages.¹⁶ The equations were used to extrapolate the drifts to the middle of the heating period. Equilibrium was usually established in 14 \pm 4 min. for the after drifts following the cessation of the input of electrical energy. The atmospheric conditions were recorded for the purpose of reducing the weight of water in the solution calorimeter to the vacuum basis.

Water standardization and heat capacity runs were made at 24.5 and 25.5°. The specific heat in 25° calories was obtained by averaging the specific heat at 24.5 and 25.5° (in 24.5 and 25.5° calories). The averaged value was translated to 15° calories. Thus in each run the specific heat at 25° depends on two separate determinations (24.5 and 25.5°) and more confidence may be placed on the extrapolation of the drifts.

The tare always contained 700 g. of water (uncorr.). It would be better theoretically to correct the weight of water in the tare, but since the correction factor presented some difficulty, no account was taken of the change in the weight with atmospheric conditions. The maximum effect on the specific heat amounted to less than 0.003% in one experiment. The results at 24.5 and 25.5° are plotted in Fig. 2. The radius of the circle for each point represents a deviation of 0.005%. The weight of water in the solution calorimeter varied from 704 to 706 g. (uncorr.). The data at each temperature were fitted to a linear equation by the method of least squares. The equation was of the form

$$W = A + B\Delta G$$

where W is the weight of water and ΔG is the deflection of the galvanometer in cm. No runs were omitted at 24.5° while one run was cast out at 25.5° since its deviation was greater than four times the average deviation. The constants and the probable error at each temperature are given in Table I. The curves shown in Fig. 2 were determined by least squares.

(13) Gucker and Schminke stated that this procedure diminishes the quantity of sodium and potassium chlorides to such amounts that they have a negligible effect on the specific heat.

(14) THIS JOURNAL, 56, 753 (1934).

(15) Daniels, "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., Inc., New York, 1928.

(8) This procedure, which has been used previously by (a) Randall and Rossini, THIS JOURNAL, 51, 326 (1929), and (b) Gucker and Schminke, *ibid.*, 54, 1358 (1932), simplifies the construction of these heaters.

(9) The cases were those used in the construction of the Cenco Lagless Knife Heaters and were supplied by the Central Scientific Company. Their length was cut to about 12.7 cm.

(10) The author is indebted to the Physics Department of the University of Rochester for the loan of this instrument.

(11) Brevoort, U. S. Bureau of Mines, Report of Investigations No. 3086.

(12) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928.

TABLE I
WATER STANDARDIZATION SUMMARY

Temperature, °C.	24.5	25.5
No. of runs	32	33
Water equivalent (A), g.	705.901	705.933
Sensitivity (B/10), g./mm.	0.048	0.049
Probable error, %	.007	.006

During the salt measurements a standardization run was made occasionally to test the integrity of the apparatus.

The apparatus in its original form had checked some of Randall and Rossini's data to 0.01%. Since several changes had been made in the construction and the operation of the calorimeter, it seemed advisable to compare the results of the modified apparatus with the recent precise results of Gucker and Schminke on lithium chloride solutions. The results in 25° calories are recorded in Table II.

TABLE II
SUMMARY OF RESULTS FOR LiCl SOLUTIONS AT 25°, MOLALITY 0.0492

Expt.	Soln., g.	$\Delta G(24.5)$ cm.	$\Delta G(25.5)$ cm.	Sp. heat, cal. ₂₅ deg. ⁻¹ g. ⁻¹	Φ	Φ (calcd.)
R 2	707.735	-0.36	-0.39	0.99717	-14.8	-14.5
R 3	707.735	-.06	-.70	.99717	-14.8	
R 4	707.735	-.40	-.20	.99722	-13.8	
R 5	707.742	-.40	-.14	.99724	-13.3	

The average deviation for these runs is 0.003% and they check the curve of Gucker and Schminke to 0.003%, which is about half of his precision. Thus the results are in good agreement with Gucker's precise measurements. These determinations were performed after the work on barium chloride was completed so that they constitute an added check on their reliability.

Experimental Results

The specific heats for barium chloride solutions are summarized in Table III. The experiments are numbered in chronological order. All weights are *in vacuo*. The averaged value of ΔG_{25} is recorded in Table III for a one degree rise. The average difference between $\Delta G_{24.5}$ and $\Delta G_{25.5}$ is 1.5 mm. The maximum difference amounts to 6.9 mm. in one run. The empirical equations were used to calculate the equivalent weight from ΔG . The apparent molal heat capacity as well as the specific heat is tabulated. The maximum deviations from the nominal temperature of 25.00° change the specific heat by $\pm 0.001\%$ in three runs. One run was discarded from each of the series D (out of 3), K (out of 4) and M (out of 4), while three were discarded from series N (out of 6). In each case the average deviation was greater than four times the average with the questionable run omitted. As far as was known, nothing went wrong during these determinations but it was felt that they should be discarded for

the above reason. The concentration of all these runs except D was below 0.01 molal.

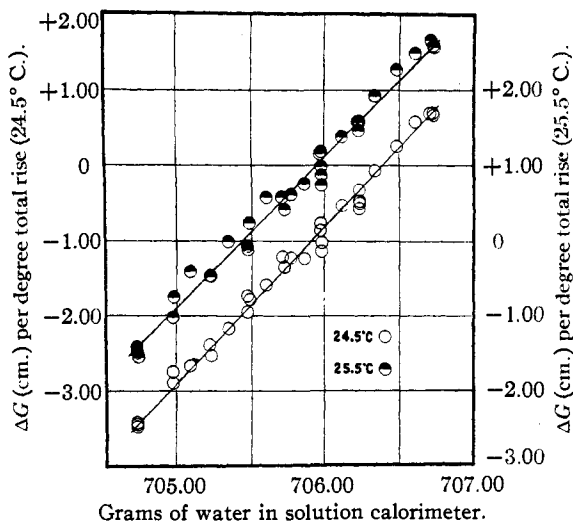


Fig. 2.—Calibration curves.

The so-called "evaporation error," which results from the substitution of a salt solution for the water in the solution calorimeter, depends on the lower vapor pressure and greater density of the salt solution. Because of the lack of vapor pressure measurements over a temperature range, it is difficult to correct for this effect in the case of barium chloride solutions. For an approximate calculation the vapor pressure lowering and density data in the "International Critical Tables" were used. The volume of the air space above the liquid level in the calorimeter was estimated at 265 cc. This error influenced the specific heats by about 0.003% at 0.5 molal. Thus, the above heat capacities need not be corrected for this effect.

The temperature difference for the two calorimeters was noted just before the heating current was stopped. It was usually about 0.007°, which compares favorably with Gucker's value of 0.005°.⁷

Two series of measurements were made at 0.12 molal (P and Q). The Q series was made by direct weighing of the salt in the usual manner, while in the P series an analyzed solution was weighed out directly in the solution calorimeter. While the Φ values differ by slightly more than 0.01% the average deviations are about large enough to account for this difference. Thus, it makes no difference by which method the solution is prepared.

TABLE III

SUMMARY OF RESULTS FOR BARIUM CHLORIDE SOLUTIONS

Expt.	Molality	Soln., g.	Av. ΔG_{25} , cm.	Sp. heat, cal. ₁₅ , deg. ⁻¹ g. ⁻¹	Φ
N3	0.0030	706.668	+0.49	0.99717	-35.8
N4	.0030	706.668	+ .37	.99709	-62.5
N5	.0030	706.675	+ .46	.99714	-45.8
M1	.0050	706.965	+ .06	.99646	-76.8
M2	.0050	706.986	+ .11	.99649	-70.8
M3	.0050	706.979	+ .18	.99652	-65.0
L1	.0072	707.272	- .07	.99593	-60.0
L2	.0072	707.272	+ .01	.99599	-57.9
L3	.0072	707.272	- .06	.99594	-64.8
K1	.0080	707.403	+ .02	.99581	-54.0
K2	.0080	707.403	- .19	.99571	-66.5
K3	.0080	707.410	- .02	.99572	-65.3
K4	.0080	707.410	- .07	.99579	-57.8
J1	.0090	707.556	- .12	.99552	-57.4
J2	.0090	707.557	- .10	.99552	-57.4
J3	.0090	707.550	- .25	.99543	-67.4
J4	.0090	707.543	- .10	.99554	-55.2
I1	.0100	708.184	+ .56	.99509	-73.9
I2	.0100	708.198	+ .60	.99510	-72.9
I3	.0100	708.198	+ .50	.99503	-79.9
I4	.0100	708.205	+ .77	.99521	-61.7
H1	.0200	708.670	-2.40	.99237	-70.1
H2	.0200	708.677	-2.22	.99250	-63.5
H3	.0200	708.677	-2.27	.99246	-65.6
H4	.0200	708.670	-2.10	.99258	-59.5
O1	.0200	708.670	-2.49	.99232	-72.6
O2	.0200	708.670	-2.53	.99229	-74.1
A1	.0300	711.143	-1.25	.98971	-67.3
A2	.0300	711.122	-1.19	.98979	-64.6
A3	.0300	711.115	-1.22	.98979	-64.6
B1	.0500	715.087	-0.92	.98449	-63.3
B2	.0500	715.087	-1.07	.98438	-63.5
C1	.0700	719.056	-0.65	.97923	-62.9
C2	.0700	719.049	- .79	.97914	-64.2
D1	.1000	725.524	+ .85	.97150	-61.8
D3	.1000	725.524	+ .81	.97148	-62.0
P1	.1200	729.520	- .92	.96630	-62.1
P2	.1200	729.521	-1.09	.96634	-61.7
P3	.1200	729.528	-0.96	.96625	-62.5
P4	.1200	729.506	-1.18	.96642	-61.1
Q1	.1196	729.512	+1.24	.96645	-61.6
Q2	.1199	729.505	+1.19	.96643	-61.2
Q3	.1199	729.512	+1.28	.96648	-60.8
Q4	.1199	729.512	+1.43	.96658	-59.9
E1	.1499	734.987	+0.81	.95896	-60.0
E2	.1499	734.980	+ .91	.95904	-59.5
F1	.1999	744.498	+1.32	.94705	-57.2
F2	.1999	744.483	+1.40	.94712	-56.8
G1	.2998	762.558	+0.47	.92585	-53.8
G2	.2998	762.565	+ .59	.92559	-53.5

Discussion

An equation was fitted to the heat capacities by the method of least squares. In dilute solu-

tion a given error in the specific heat produces a large percentage error in Φ , but the error rapidly diminishes as the concentration increases. It was felt that this difficulty would be largely eliminated if the curve was fitted to the ΔC_p values, since ΔC_p is defined as $m \Phi$.¹⁶ The following equation was obtained

$$\Phi = -73.46 + 36.1 m^{1/2}$$

with a probable error of 0.007%. An inspection of Fig. 3 will show the magnitude of the deviations of the experimental points from the empirical equation. The average value at each concentration and the empirical equation are plotted in Fig. 3. The dotted lines indicate an error of 0.01% from the straight line. The apparent molal heat capacities are adequately represented by the linear equation. The dotted lines indicate that large percentage errors in Φ occur below 0.01 molal. Several determinations were made at the same concentration for these very dilute solutions in the hope that the average value would yield some information as to the shape of the curve in this region. Since the results fall within the 0.01% band in a fairly random manner, they are in agreement with the linear equation.

It is a simple matter to calculate the partial molal heat capacity of the solvent and the solute from the empirical equation for Φ . The necessary thermodynamic equations which connect with \bar{C}_{p_2} and \bar{C}_{p_1} are given by Randall and Rossini. \bar{C}_{p_2} curve is also plotted in Fig. 3.

The results of Richards and Dole (recalculated to cal.₁₅) are plotted in Fig. 3. This calculation was unnecessary for comparison with the present data, since the correction amounts to 0.003% at 0.3 molal. It reaches 0.007% at 1.0 molal. Their heat capacities were calculated from heats of dilution and specific heat measurements at two temperatures by the Person-Kirchoff relation. The curve for these results as drawn by Rossini¹⁷ has a definite curvature at the higher concentrations. Richards and Dole pointed out in their paper that the specific heats of the $\text{BaCl}_2 \cdot 100\text{H}_2\text{O}$ might be in error by 0.05 to 0.1%. An error of 0.1% in the heat capacity of this solution would cause an error of 0.05% in the calculated specific heat at $\text{BaCl}_2 \cdot 200\text{H}_2\text{O}$. Therefore as the solutions become more dilute the original error decreases. If the procedure is reversed, an error of

(16) This method of treatment was developed several years ago in connection with an unpublished research on the specific heat of sodium chloride solutions.

(17) Rossini, *Bur. Standards J. Research*, **4**, 313 (1930).

0.1% in BaCl₂·100H₂O will cause an error of 0.2% in BaCl₂·50H₂O. This is their most concentrated solution. The curvature is established by the results at BaCl₂·50H₂O and BaCl₂·100H₂O, which are the least precise. Therefore their data were fitted to a linear instead of a parabolic equation by the same procedure as mentioned above. The following equation was obtained

$$\Phi = -74.36 + 35.5m^{1/2}$$

with a probable error of 0.013%. This equation as well as the individual runs of Richards and Dole in dilute solution are in good agreement with the present data. The results of Marignac check the equations to about 0.1%, while the data of Urban show differences of the order of 0.5%.

Recently Tippett and Newton reported relative partial molal heat contents which compared favorably with the values of Richards and Dole. Their $\bar{C}_{p_2} - \bar{C}_{p_2}^0$ values, however, did not agree with those calculated from Richards and Dole's or the present empirical equation. In Table IV values at several concentrations are compared for the three methods. It is evident that the e. m. f. measurements merely indicate the order of magnitude of the results—a fact which Tippett and Newton recognized.

TABLE IV
A COMPARISON OF $\bar{C}_{p_2} - \bar{C}_{p_2}^0$ VALUES FROM THREE SOURCES

Molality	Heat capacities	Heat capacities and heats of dilution	E. m. f.
0.1	17.1	16.8	74
.3	29.7	29.2	96
.5	..	37.7	100
1.0	..	53.3	91

The e. m. f. measurements usually agree more closely with the calorimetric values than in this case.¹⁸ The extrapolation of the e. m. f.'s to infinite dilution is eliminated when the results are expressed as $(\bar{C}_{p_2} - \bar{C}_{p_2}^0)_m = 0.05$. While somewhat better agreement is obtained by this proce-

(18) Harned and Hecker, THIS JOURNAL, 55, 4838 (1933).

dure, the e. m. f. values still differ by a factor of 2.

In Table V the slope of \bar{C}_{p_2} curve for barium chloride is compared with the limiting value as predicted by the Debye-Hückel theory^{8a} and the modified form which was put forth by La Mer and Cowperthwaite.¹⁹ It is also interesting to compare the slopes of bivalent and univalent salts. Present theories predict the same slope for both valence types. The values of sodium and potassium sulfate in the table were determined by Randall and Rossini.

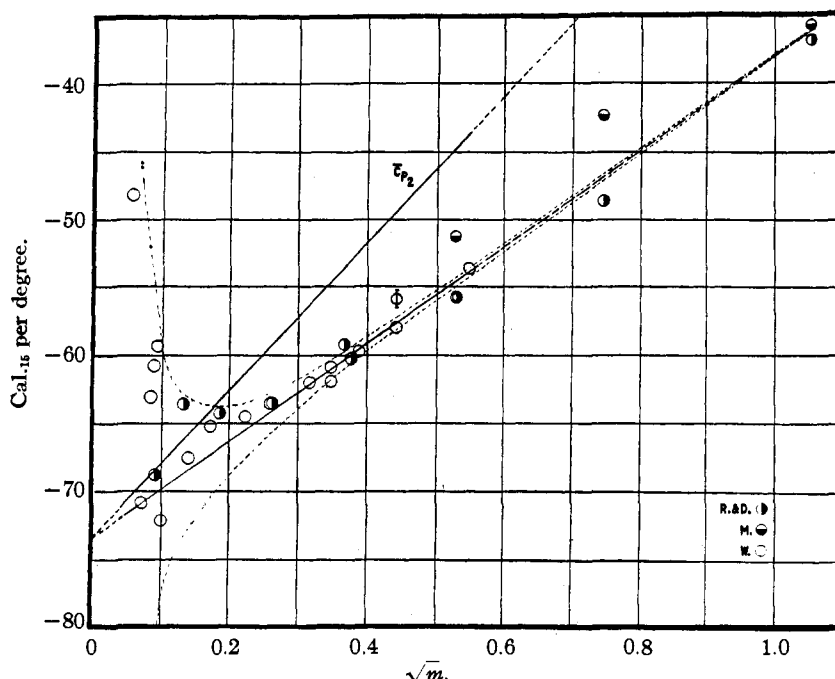


Fig. 3.—Apparent molal heat capacity (Φ) and partial molal heat capacity (\bar{C}_{p_2}) of barium chloride solutions.

TABLE V
COMPARISON OF THE SLOPE OF THE PARTIAL MOLAL HEAT CAPACITY CURVES WITH THE LIMITING VALUES

BaCl ₂	Na ₂ SO ₄	K ₂ SO ₄	Debye-Hückel	La Mer and Cowperthwaite
54	76	62	31	69

The slopes of the three salts merely show the same order of magnitude, since the differences greatly exceed the precision of measurement. The barium chloride slope seems to agree with limiting value somewhat closer than the 1-2 salts and other uniunivalent electrolytes where the slopes are about three times the limiting value. Gulbransen and Robinson²⁰ have suggested that the

(19) La Mer and Cowperthwaite, *ibid.*, 55, 1004 (1933).

(20) Gulbransen and Robinson, *ibid.*, 56, 2637 (1934). The dilution measurements of these authors for sodium chloride have been recalculated recently by Young and Groenier, *ibid.*, 58, 187 (1936). Their values of the slope differ from the theory by 5%.

rather good agreement for sodium chloride solutions with the La Mer and Cowperthwaite modification is "largely fortuitous." Because of the uncertainty in $f(DT)$ there is probably an error of 15 calories or more in the limiting value for a 2-1 salt. Although the present results were extended to 0.003 molar, the slope as given by the least squares is determined by runs in relatively concentrated solutions, where the theory is not applicable. As far as these theories are concerned specific heat measurements apparently cannot be used to verify the limiting law. When a theory is proposed for relatively concentrated solutions, the heat capacity data should be of value.

The author wishes to express his appreciation to Dr. A. A. Sunier for many helpful suggestions during the course of this work.

Summary

1. A twin adiabatic calorimeter was used to measure the heat capacity of barium chloride solutions from 0.003 to 0.3 molal at 25° with a precision of better than 0.01%.

2. The apparent molal heat capacity of the salt plotted against the square root of the molality follows the usual linear relationship. An empirical equation is given from which the apparent heat capacity and partial molal heat capacity of the solute, and the partial molal heat capacity of the solvent may be computed.

3. The present data have been shown to be in satisfactory agreement with the results of indirect determinations.

ROCHESTER, N. Y.

RECEIVED MAY 18, 1936

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

A Study of the Heat Capacity of Aqueous Solutions of Urea and Mannite

BY CHESTER M. WHITE

Several investigators have studied the specific heat of solutions of electrolytes in a precise manner. Richards and his co-workers^{1,2} have presented precise values for some weak electrolytes, but substances which are strictly non-electrolytic have been largely neglected in recent years. Some semi-precision results on amino acids were reported recently by Zittle and Schmidt.³ The determinations reported in this paper were made with a view to supplying specific heats for such solutions with a precision of $\approx 0.01\%$. The present work will be concerned with aqueous solutions of urea and mannite from 0.01 to 1.0 molal. Many years ago Magie^{4,5} determined specific heats for both of these solutions at several concentrations. The precision of his experiments was believed to be about 0.05%. Recently Funzel, Burian and Haas⁶ reported heat capacities at several temperatures for urea solutions from heats of dilution. Their precision was placed at $\approx 0.1\%$. Apparently no other workers have reported measurements for urea or mannite solutions.

The experiments were performed with a pre-

viously described twin calorimeter.^{7,8} No changes were made in the construction or method of operation of the calorimeter. The reader is referred to the previous paper for a complete description of the apparatus and the experimental technique.

Materials

Merck and E. K. Co. urea was used. It was twice recrystallized from methanol. After pulverizing, it was dried for two weeks at a temperature which was always maintained below 55° so that ammonium cyanate would not be formed. Shnidman and Sunier,⁹ who had highly purified some urea for solubility determinations, kindly supplied the author with some of this material. The runs at 0.125 molal were made with this urea. Since these experiments were in satisfactory agreement with the other determinations, the above method of purification was sufficient for specific heat work.

The mannite, which was Pfanstiehl product, was thoroughly dried for all the runs. For some of the experiments it was recrystallized from distilled water and dried to constant weight at 130°. The experiments in which the purified mannite was used showed no substantial deviations from the other runs. The urea solutions were prepared by adding a known amount of solute to the solution calorimeter, which contained a weighed quantity of distilled water. Since a noticeable cooling effect takes place on the solution of mannite above 0.2 molal, the concentrated

(1) Richards and Gucker, *THIS JOURNAL*, **51**, 712 (1929).

(2) Richards and Mair, *ibid.*, **51**, 740 (1929).

(3) Zittle and Schmidt, *J. Biol. Chem.*, **108**, 161 (1935).

(4) Magie, *Phys. Rev.*, **9**, 65 (1899).

(5) Magie, *ibid.*, **13**, 91 (1901).

(6) Funzel, Burian and Haas, *Z. Elektrochem.*, **41**, 419 (1935).

(7) White, *THIS JOURNAL*, **58**, 1615 (1936).

(8) Unpublished work of Hess and Gramke.

(9) Shnidman and Sunier, *J. Phys. Chem.*, **36**, 1232 (1932).