

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.

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

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

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Several investigators have studied the specific heat of solutions of electrolytes in a precise manner. Richards and his co-workers<sup>1,2</sup> 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.<sup>3</sup> The determinations reported in this paper were made with a view to supplying specific heats for such solutions with a precision of  $\pm 0.01\%$ . The present work will be concerned with aqueous solutions of urea and mannite from 0.01 to 1.0 molal. Many years ago Magie<sup>4,5</sup> 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 Haas<sup>6</sup> reported heat capacities at several temperatures for urea solutions from heats of dilution. Their precision was placed at  $\pm 0.1\%$ . Apparently no other workers have reported measurements for urea or mannite solutions.

The experiments were performed with a pre-

viously described twin calorimeter.<sup>7,8</sup> 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,<sup>9</sup> 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).

solutions had to be prepared in a flask and a portion of this solution was weighed in the solution calorimeter.

### Experimental Results

In Tables I and II the results are summarized for the urea and mannite solutions. The deviations from 25.00° were such that no corrections to the specific heat were necessary. The experiments are numbered in chronological order. All weights are on the vacuum basis. The 1935 atomic weights were used. The molality is expressed in moles per 1000.0 g. of water.  $\Delta G$  is the galvanometer deflection which corresponds to a 1° rise. The average of  $\Delta G_{24.5}$  and  $\Delta G_{25.5}$  is given in the table. These two values differed by 1.4 mm. on the average. The maximum difference amounted to 6.6 mm. in one run. The equivalent weights of water were calculated from the empirical equations given in the previous paper.<sup>7</sup> Water standardizations were made frequently during the course of the experiments. These runs did not show deviations greater than  $\pm 0.01\%$  from the linear equations. The specific heats are given in 15° calories. The specific heat of water was taken as 0.9979 at 25°. The apparent molal heat capacity  $\Phi$  was calculated in the manner described by Randall and Rossini.<sup>10</sup> The

TABLE I  
SUMMARY OF RESULTS FOR UREA SOLUTIONS

| Expt. no. | Molality | Solution, g. | Av. $\Delta G_{25}$ , cm. | Sp. heat, cal. <sub>15</sub> deg. <sup>-1</sup> g. <sup>-1</sup> | $\Phi$ |
|-----------|----------|--------------|---------------------------|--|--------|
| 6A        | 0.0100   | 705.635      | -1.24                     | 0.99745  | +14.8  |
| B         | .0100    | 705.635      | -1.38                     | .99735   | + 4.8  |
| 5A        | .0300    | 706.186      | -0.90                     | .99691   | +26.8  |
| B         | .0300    | 706.186      | - .93                     | .99688   | +25.8  |
| 1A        | .0500    | 706.819      | - .85                     | .99604   | +22.6  |
| B         | .0500    | 706.819      | - .78                     | .99609   | +23.6  |
| 2A        | .1000    | 707.928      | -1.26                     | .99420   | +21.2  |
| B         | .1000    | 707.928      | -1.29                     | .99420   | +21.2  |
| 11A       | .1250    | 708.990      | -0.90                     | .99296   | +20.0  |
| B         | .1250    | 708.997      | - .82                     | .99301   | +20.4  |
| 3A        | .1522    | 709.626      | - .80                     | .99214   | +21.7  |
| B         | .1522    | 709.640      | - .68                     | .99221   | +22.2  |
| 4A        | .1998    | 711.147      | - .40                     | .99029   | +21.3  |
| B         | .1998    | 711.140      | - .31                     | .99037   | +21.7  |
| 7A        | .2997    | 714.333      | + .81                     | .98669   | +21.8  |
| B         | .2997    | 714.340      | + .61                     | .98654   | +21.3  |
| 8B        | .5000    | 719.659      | + .57                     | .97923   | +21.4  |
| B         | .4995    | 719.652      | + .69                     | .97933   | +21.6  |
| 9A        | .6993    | 724.885      | +1.07                     | .97250   | +22.0  |
| B         | .6993    | 724.899      | +1.06                     | .97248   | +22.0  |
| 10A       | .9990    | 731.573      | -0.64                     | .96248   | +22.25 |
| B         | .9990    | 731.573      | - .69                     | .96245   | +22.26 |

(10) Randall and Rossini, THIS JOURNAL, 51, 326 (1929).

TABLE II  
SUMMARY OF RESULTS FOR MANNITE SOLUTIONS AT 25°

| Expt. no. | Molality | Solution, g. | Av. $\Delta G_{25}$ , cm. | Sp. heat, cal. <sub>15</sub> deg. <sup>-1</sup> g. <sup>-1</sup> | $\Phi$ |
|-----------|----------|--------------|---------------------------|--|--------|
| 9A        | 0.0100   | 706.014      | -1.13                     | 0.99699  | +90.5  |
| B         | .0100    | 706.014      | -1.13                     | .99699   | +90.5  |
| 10A       | .0200    | 706.794      | -0.53                     | .99630   | +101.4 |
| B         | .0200    | 706.794      | - .60                     | .99625   | +98.9  |
| 1A        | .0300    | 707.558      | - .05                     | .99555   | +102.9 |
| B         | .0300    | 707.558      | - .06                     | .99555   | +102.9 |
| 2A        | .0500    | 709.101      | + .96                     | .99408   | +104.6 |
| B         | .0500    | 709.101      | +1.16                     | .99422   | +105.4 |
| 3A        | .0699    | 709.630      | +0.16                     | .99273   | +106.9 |
| B         | .0699    | 709.630      | + .19                     | .99281   | +108.0 |
| 4A        | .1000    | 710.900      | - .52                     | .99056   | +106.9 |
| B         | .1000    | 710.906      | - .77                     | .99044   | +105.7 |
| C         | .1000    | 710.957      | - .51                     | .99049   | +106.2 |
| 5A        | .1500    | 713.662      | - .32                     | .98685   | +106.0 |
| B         | .1500    | 713.683      | - .34                     | .98681   | +105.7 |
| 6A        | .1998    | 716.360      | + .22                     | .98350   | +107.0 |
| B         | .1998    | 716.367      | + .21                     | .98354   | +107.2 |
| 7A        | .2997    | 721.553      | + .57                     | .97665   | +107.0 |
| B         | .2997    | 721.553      | + .46                     | .97658   | +106.7 |
| 8A        | .5002    | 730.946      | - .16                     | .96362   | +107.2 |
| B         | .5002    | 730.946      | - .19                     | .96357   | +107.1 |
| 11A       | .6997    | 740.355      | +1.05                     | .95218   | +108.1 |
| B         | .6997    | 740.343      | +1.05                     | .95219   | +108.1 |
| 12A       | .9995    | 753.107      | +0.78                     | .93588   | +108.4 |
| B         | .9995    | 753.107      | + .67                     | .93581   | +108.3 |

magnitude of the "evaporation error" is less than 0.001% at 1.0 molal with a vapor space of 265 cc. Thus, no correction is necessary for this effect.

The heat capacities, expressed as  $\Delta C_p$ , were fitted to an empirical equation by least squares. The constants and the probable error of an individual run from the equation are given in Table III for the two non-electrolytes.

TABLE III  
CONSTANTS AND PROBABLE ERRORS FOR LINEAR EQUATIONS

| Solute                | Urea        | Mannite     |
|-----------------------|-------------|-------------|
| Intercept (A)         | 20.52       | 105.16      |
| Slope (B)             | 1.72        | 3.23        |
| Probable error (cal.) | $\pm 0.065$ | $\pm 0.069$ |

The individual determinations of  $\Phi$  are plotted against the  $\sqrt{m}$  for urea and mannite solutions in Figs. 1 and 2, respectively. The least square curves are also plotted and the dotted lines indicate an error of  $\pm 0.01\%$  from the linear equation. An inspection of Figs. 1 and 2 will indicate the magnitude of the deviations of the experimental points from the empirical equations.

The relation between the partial molal heat

capacity of the solute (or the solvent) and the apparent molal heat capacity has been derived by Randall and Rossini. It is only necessary to differentiate the empirical equation for  $\Phi$  and substitute in their equation to obtain an expression for the variations of  $\bar{C}_{p2}$  (or  $\bar{C}_{p1}$ ) with  $m$ . The following empirical expressions were obtained for the partial molal quantities.

$$\begin{aligned} & \text{UREA} \\ \bar{C}_{p2} &= 20.52 + 2.58 m^{1/2} \\ \bar{C}_{p1} - \bar{C}_{p1}^0 &= -0.0154 m^{3/2} \\ & \text{MANNITE} \\ \bar{C}_{p2} &= 105.16 + 4.85 m^{1/2} \\ \bar{C}_{p1} - \bar{C}_{p1}^0 &= -0.0291 m^{3/2} \end{aligned}$$

The  $\bar{C}_{p2}$  curves for urea and mannite are also plotted in Figs. 1 and 2, respectively.

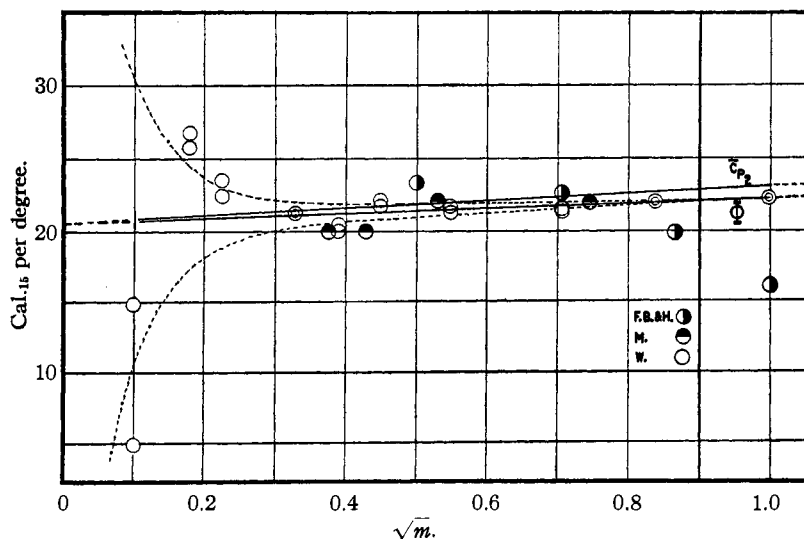


Fig. 1.—Apparent molal heat capacity ( $\Phi$ ) and partial molal heat capacity ( $\bar{C}_{p2}$ ) of urea solutions.

The data of Magie<sup>4</sup> for urea solutions are also plotted in Fig. 1. These values are in excellent agreement with the present results since the average deviation of the points from the empirical equation is about 0.02%. The recent results of Fuznel, Burian and Haas, which were determined with a precision of  $\pm 0.01\%$ , are shown in Fig. 1. The plotted values of  $\Phi$  were calculated from the specific heats at 24° (without converting to 25°) and the specific heat of water which they used. The average deviation of the  $\Phi$  values from the empirical equation is 0.2%. In view of their precision of measurement the agreement with the present data is satisfactory.

Magie<sup>4,5</sup> is apparently the only worker who has

studied mannite solutions. His results are plotted in Fig. 2. They appear to be in good agreement with the present data except for three points which differ from the empirical equation by 0.1 to 0.3%. Magie pointed out in the first paper that these three determinations were probably in error. The points, which show deviations of only 0.05% from the equation, were published in the second paper. While Magie does not record the temperature of his experiments he gives a quantity which is equivalent to  $\Phi$ . This uncertainty in the temperature introduces an insignificant error in the  $\Phi$  values.

It is apparent from the plots that the  $\Phi$  values for urea are equally distributed about the linear equations in dilute solution. The mannite solutions show a break at 0.06  $m$  below which the apparent molal heat capacities decrease. However, it is evident that the deviations are equal to the probable experimental error so that no importance may be attached to them. If the lowest points had been discarded in the least square calculation, the slope of the equation would not be substantially altered.

It is interesting to compare the extrapolated intercept of the  $\bar{C}_{p2}$  (or  $\Phi$ ) curve with the molal heat capacity of the solute in the pure state ( $c_p$ ).  $c_p$  for crystalline urea and mannite at 25° are 19.2 and 58.3 cal., respectively.  $\bar{C}_{p2}^0$  for urea is in very close agreement with  $c_p$ . In the case of mannite there is an appreciable difference. It is interesting to note that this deviation is positive while all electrolytes show negative deviations from  $c_p$ . Presumably the intercepts for the two types of compounds are equally uncertain because of the extrapolation from 0.01  $m$  to zero concentration which has been shown for electrolytes, at least, to be a questionable procedure. Edsall<sup>11</sup> has suggested that non-electrolytes which possess polar groups have  $\Phi$  values which approximate rather closely the heat capacity of the pure solid while a single polar group attached to a long hydrocarbon chain yields  $\Phi$  values which show positive deviations from  $c_p$ .

(11) Edsall, THIS JOURNAL, 57, 1506 (1935).

Because of the lack of data for these solutions, his conclusions were based on results at various concentrations. Since these rules are expected to apply in concentrated solution, it is suggested that the apparent value of  $\bar{C}_{p_2}^0$  be used. On this basis the present results for urea follow his rule while those for mannite do not. Edsall found that the available data for glycerol, which is also a polyhydric alcohol, are in satisfactory agreement with the theory at 1 *m*. Obviously more data must be obtained before the validity of these rules may be tested.<sup>12</sup>

In the derivation of the theoretical slope of the  $C_{p_2}$  curves for electrolytes from the Debye-Hückel theory, Randall and Rossini considered that the free energy change, on passing from a definite concentration to the infinitely dilute solution, was composed of the part due to the ions taken as ideal solutes and the part due to the effect of the charged ions. For non-electrolytes the second term is zero and the total free energy is given by  $RL \ln c$ . The second derivative of this expression with respect to the temperature is zero. Thus  $\Phi$  or  $\bar{C}_{p_2}$  would be independent of the concentration. Zwicky<sup>13</sup> is led to the same conclusion on the basis of his theory. The present results for urea and mannite show small but appreciable slopes. Gucker<sup>14</sup> has shown that the apparent molal volume and compressibility for urea solutions also have small slopes when plotted against the  $\sqrt{c}$ . Apparently these properties have not been studied for mannite solutions. It should not be implied that all non-electrolytes have small slopes because Gucker has shown that  $\Phi$  (V) and  $\Phi$  (K) for sucrose solutions have slopes equal to a 2-1 electrolyte. These properties have been studied

(12) The reviewer of the paper suggested that  $\bar{C}_{p_2}^0$  for an ideal solution would be more nearly equal to the heat capacity of the pure liquid.

(13) Zwicky, *Physik. Z.*, **27**, 271 (1926).

(14) Gucker, *Chem. Rev.*, **13**, 111 (1933).

over a wide range of concentration and very definitely follow a linear equation when plotted against  $\sqrt{c}$ . Since the apparent molal heat capacities in the present paper cover a relatively limited range of concentration and change only slightly with *m*, it is difficult to determine whether the  $\Phi$  values for urea and mannite are strictly proportional to  $\sqrt{m}$  or to *m* itself. On the basis of these results it may be said that they seem to cluster more closely about a straight line when plotted against  $\sqrt{m}$ .

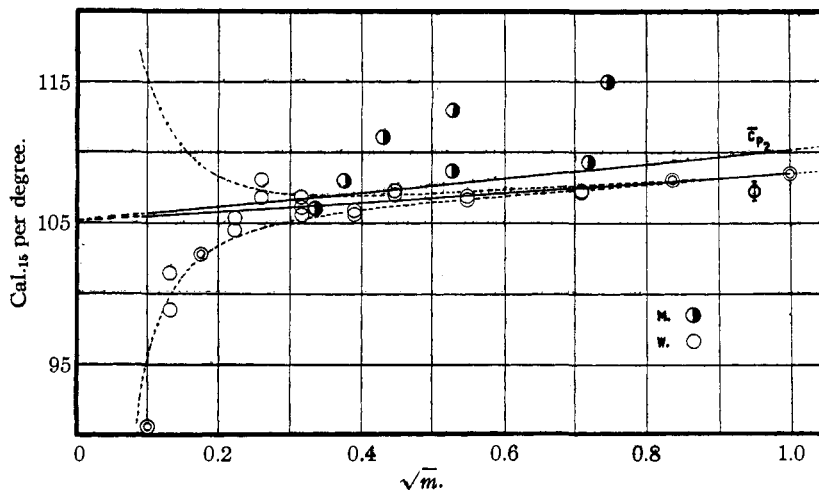


Fig. 2.—Apparent molal heat capacity ( $\Phi$ ) and partial molal heat capacity ( $\bar{C}_{p_2}$ ) of mannite solutions.

The author wishes to thank Professor A. A. Sunier for suggesting the problem and for his helpful suggestions in the preparation of the manuscript.

### Summary

1. The twin adiabatic calorimeter method was used to determine the specific heats of aqueous solutions of urea and mannite at 25° from 0.01 to 1.0 *m* with a precision of  $\pm 0.01\%$ .

2. The apparent molal heat capacities were calculated and they seem to follow a linear equation when plotted against the  $\sqrt{m}$ . The intercepts are positive and the slopes are small for these solutes. Empirical equations are given for the apparent and the partial molal heat capacities of the solutes and the relative partial molal heat capacity of the solvent.

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