are a measure of atomic volume, and that the volume of the carbon atom is that of a sphere of radius 0.77 Å., it is found that *one parachor unit* = 0.210 Å.[3]

3. By adopting simple atomic models, this relation is then used to calculate bond radii for quadrivalent atoms and packing radii for univalent atoms that are in good agreement with existing data.

MELBOURNE, AUSTRALIA RECEIVED DECEMBER 30, 1936

[CONTRIBUTION FROM THE NORTHWESTERN UNIVERSITY CHEMICAL LABORATORY]

The Specific Heats of Aqueous Sucrose Solutions at 20 and 25° and the Apparent Molal Heat Capacity of Non-electrolytes[1]

BY FRANK T. GUCKER, JR., AND FRED D. AYRES

Introduction

The specific heats of aqueous solutions of electrolytes have been studied recently by a number of investigators. The behavior of such solutions is summarized conveniently in terms of the apparent molal heat capacity. Randall and Rossini[2] first showed that over a wide range the apparent molal heat capacity is a linear function of the square root of the concentration and that the slopes of the curves increase with the valence type of the electrolyte, in qualitative agreement with the Debye–Hückel limiting law. The extrapolated value of the apparent molal heat capacity at infinite dilution is usually negative for strong electrolytes, and increasingly more negative for electrolytes of higher valence type.[3]

The apparent molal heat capacity of non-electrolytes is usually assumed to be a constant independent of concentration and nearly equal to the heat capacity of the pure solute in the liquid state. The present investigation is the beginning of a systematic study of the thermochemistry of non-electrolytic aqueous solutions, undertaken to find out how ideal these solutions are and what light they may throw on the general properties of solutions. Sucrose was chosen as the first solute because it could be obtained pure and because other thermodynamic properties of its solutions already had been investigated carefully.

Preparation of the Sucrose Solutions.—The sucrose used in these experiments was the best material obtainable, purified by the Bureau of Standards as a standard for polarimetry[4] and supplied to us through the courtesy of Dr. F. D. Rossini and Dr. F. J. Bates. Following the procedure recommended by the Bureau of Standards, the sucrose was pulverized in an agate mortar and dried for four hours at 65–70° in a vacuum of about 0.01 mm. This procedure is found to reduce the moisture content to less than 0.01%. The solutions were made up determinate, with distilled water freshly boiled to remove air. In the concentrated solutions, the sucrose and water were weighed successively into the same flask in which the solution was made up. In the dilute solutions, the smaller amounts of sucrose were determined with sufficient accuracy by weighing from a weighing bottle. All weights were reduced to the vacuum basis. In order to conserve material, the most concentrated solution (Expt. 4, Table I) was diluted quantitatively in two successive steps (Expts. $4a_1$, $4a_2$) while solution 3 was divided into two portions, each of which was diluted quantitatively to form solutions 3a and 3b.

Experimental Results.—The specific heats were determined by means of the differential twin calorimeter apparatus previously described.[5] Each value represents the average of at least two experiments with heating ratios on either side of the exact balancing ratio. The dilute sucrose solutions were handled as easily as the salt solutions, and their specific heats are probably accurate to ±0.01% as in our previous work. The great viscosity of the concentrated solutions introduced two complications which seem unavoidable in any calorimetric apparatus. First, the heat of stirring was increased enormously (amounting to about 0.001° per minute in the 5.8 *m* solution). This large temperature trend increased the uncertainty in determining the balancing resistance ratio to about 0.02% error in the specific heat. A second effect of the high viscosity of the solution was a lag in the distribution of heat from the coil in the working calorimeter. Heat may be lost from the working calorimeter by increased conduction up the heater lead wires, if the temperature of the heater in this calorimeter is greater than that in the tare. On the other hand, heat may be gained by the working calorimeter, because the temperature of the rest of its surface is lower than that of the tare. Fortunately these errors tend to

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[1] Parts of this paper were presented at the Midwest Sectional Meeting of the American Chemical Society at Louisville, November, 1935, and at the Group Symposium on "The Electrochemistry of Solutions" at the Kansas City Meeting of the American Chemical Society, April, 1936.

[2] Randall and Rossini, THIS JOURNAL, **51**, 323 (1929).

[3] For a discussion of this and related thermodynamic properties of electrolytes see (a) Gucker, *Chem. Rev.*, **13**, 111 (1933). For a discussion of the limiting slope, see (b) Young and Machin, THIS JOURNAL, **58**, 2254 (1936).

[4] Standard Sample No. 17. For the method of purification and specifications see "Polarimetry," Circular No. 44 of the Bureau of Standards.

[5] Gucker, Ayres and Rubin, THIS JOURNAL, **58**, 2118 (1936).

TABLE I

THE SPECIFIC HEATS AND APPARENT MOLAL HEAT CAPACITIES OF SUCROSE SOLUTIONS AT 20 AND 25°

				20°C. (in cal.$_{20}$ per degree)				25°C. (in cal.$_{25}$ per degree)			
Expt.	Wt., %	m	$c(20°)$	s	Φ(obsd.)	Φ(calcd.)	Δs (in 0.01 %)	s	Φ(obsd.)	Φ(calcd.)	Δs (in 0.01 %)
5	0.350	0.0103	0.0103	0.99793	140	146	−0.6	0.99793	140	151	−1.1
9	.4285	.0126	.0125	.99757	148	146	.3	.99757	148	151	−0.4
7	.6783	.0200	.0199	.99605	143	146	− .6	.99617	149	151	− .4
8	1.1184	.0331	.0328	.99343	141	146	−1.6	.99376	151	151	.0
1	1.3598	.0403	.0399	.99219	145	146	−0.4	.99240	151	151	.0
6	3.2338	.0977	.0956	.98149	146.3	146.1	.2				
2	8.3061	.2647	.2503	.95251	146.6	146.4	.5	.95376	151.7	151.5	.5
3a	19.087	.6894	.6007	.89137	147.4	147.2	1.1	.89409	152.3	152.1	1.1
3b	29.660	1.2323	.9754	.83190	148.25	148.09	1.4	.83593	152.90	152.73	1.5
3	45.275	2.4178	1.5931	.74567	149.92	149.89	0.4	.75102	153.97	153.99	−0.3
4a$_2$	52.267	3.2001	1.8973	.70769	150.81	150.90	−1.4	.71354	154.64	154.72	−1.2
4a$_1$	58.229	4.0739	2.1716	.67612	151.85	151.85	0.0	.68228	155.47	155.43	0.7
4	66.548	5.8137	2.5784	.63251	153.22	153.21	.2	.63895	156.53	156.52	.2

TABLE II

SPECIFIC HEATS, APPARENT AND PARTIAL MOLAL HEAT CAPACITIES OF SUCROSE SOLUTIONS AT EVEN MOLALITIES

	20°C. (in cal.$_{20}$ per degree)				25°C. (in cal.$_{25}$ per degree)			
m	s	$\Phi(C_{p_2})$	$\bar{C}_{p_2}$	$\bar{C}^{\circ}_{p_1} - \bar{C}_{p_1}$	s	$\Phi(C_{p_2})$	$\bar{C}_{p_2}$	$\bar{C}^{\circ}_{p_1} - \bar{C}_{p_1}$
0	1.0000	146	146	0.0	1.0000	151	151	0.0
0.5	0.9166	146.8	147.7	.0083	0.9187	151.8	152.5	.0057
1	.8551	147.70	149.42	.0309	.8586	152.45	153.64	.0213
1.5	.8081	148.53	150.92	.0647	.8125	153.03	154.70	.0451
2	.7710	149.30	152.25	.1064	.7761	153.57	155.66	.0752
3	.7165	150.66	154.38	.2012	.7222	154.54	157.25	.1463
4	.6785	151.78	155.80	.2894	.6845	155.37	158.42	.2196
5	.6505	152.67	156.50	.3459	.6567	156.07	159.17	.2797
6	.6288	153.31	156.50	.3450	.6353	156.62	159.50	.3114

cancel each other, but we have no method of measuring or calculating the resultant systematic error.

The experimental results are collected in Table I, from which no experiments are omitted. The specific heat of the 0.1 *m* solution (Expt. 6) was not determined at 25° because one of the heaters was burned out after the experiment at 20°. The experiments are numbered chronologically. Each number refers to a solution made up from weighed quantities of sucrose and water, while the letters and subscripts refer to those made by quantitative dilution in the manner already described. We have listed the weight % and molality, *m* (moles of sucrose per 1000 g. of water) taking the molecular weight of sucrose as $M_2 = 342.18$. The molarity *c* (moles of sucrose per liter of solution) at 20° was calculated with the aid of the accurate density data of the "International Critical Tables."[6] The specific heat, *s*, is relative to water at the temperature of the experiment. The values of the apparent molal heat capacity, $\Phi(C_{p_2})$, calculated by means of the usual equation

$$\Phi(C_{p_2}) = \left[\frac{1000}{m} + M_2\right] s - \frac{1000}{m}$$

are also expressed in calories at the temperature of the experiment. The calculated values of Φ were obtained from equations which will be described subsequently. Δ*s* is the difference, in 0.01%, between the observed values of *s* and those corresponding to the calculated values of Φ.

These results show that the apparent molal heat capacity of sucrose is not constant, but changes appreciably with concentration, although the change from 0 to 1 *m* is only about a third as great as in the case of hydrochloric acid, which has the least change of any uni-univalent electrolyte. A plot of the apparent molal heat capacity against $c^{1/2}$ shows, however, no linear relationship over any appreciable concentration range, such as that which characterizes electrolytic solutions. Instead, the apparent molal heat capacity is much more nearly a linear function of the *first* power of the concentration, although appreciable curvature appears above 1.6 molar. Figure 1 is a plot of all the values of Φ at 20°, above a concentration of 0.1 molar, comparing the two abscissas. The values at 25° are similar.

These results are almost exactly like those which Redlich and Klinger[7] found when they calculated

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[6] "I. C. T.," Vol. II, p. 343.

[7] Redlich and Klinger, *Sitzb. Akad. Wiss. Wien.*, Abt. IIb, **143**, 489 (1934); *Monatsh.*, **65**, 137 (1934).

the apparent molal volume of this same solute. Using the best density data available, they showed that the apparent molal volume is much more nearly a linear function of the first power than of the square root of the concentration, but that there is a slight concavity upward such as we find for the apparent molal heat capacity. If this functional relationship is general, it would show a clear-cut difference between the behavior of electrolytes and of non-electrolytes in solution. Very little attention has been devoted to the theory of non-electrolytic solutes, but recently Fuoss[8] has published a brief article in which he derives certain thermodynamic properties of solute molecules which may be regarded as spheres with point dipoles at the center. He finds that, in very dilute solutions, the partial molal heat capacity of such a solute should be a linear function of the first power of the concentration.

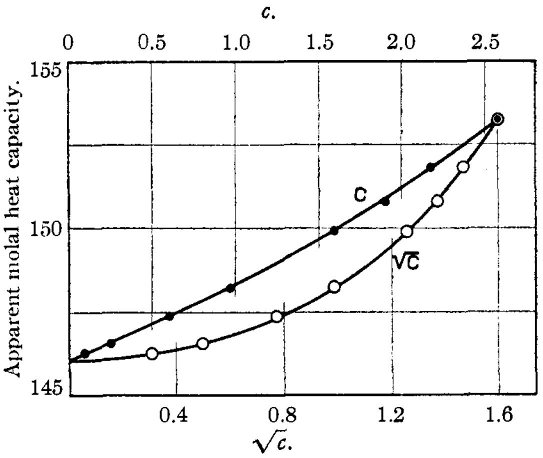

Fig. 1.—A comparison of square root and first power of concentration.

In order to obtain a convenient analytical expression for apparent molal heat capacity, which could be used to calculate values of the specific heat and partial molal heat capacities at various concentrations, we investigated plots of Φ against the molality, m, and also against $(1000\ N_2/M_1)$ where M_1 is the molecular weight of the solvent and N_2 is the mole fraction of solute. N_2 is multiplied by the factor $(1000/M_1)$ in order to make it equal to m in the dilute range and comparable at all concentrations. Figure 2, from which the results at concentrations below 0.1 m have been omitted to avoid confusion, shows that there is little difference between kN_2 and m, although the molarity, c, differs greatly from them both. The plot against m exhibits a curvature opposite to that against c, and about 50% greater.[9] Since the molality is a more convenient abscissa than the molarity, we employed it in subsequent calculations. A power series of the type

$$\Phi = \Phi^\circ + am + bm^2 \qquad (1)$$

proved adequate to reproduce the data over the whole range of concentration. We evaluated the coefficients by the method of least squares. Since the same error in the heat capacity makes a large change in the apparent molal heat capacity in dilute solutions and only a small change in concentrated ones, we weighted the values of Φ suitably in carrying out the calculations. The results were

$$(20^\circ)\quad \Phi = 145.87 + 1.950m - 0.1182m^2$$
$$(25^\circ)\quad \Phi = 151.20 + 1.325m - 0.0704m^2$$

From these equations we obtained the calculated values of Φ which are compared with the observed in Table I. As this tabulation shows, the agreement is quite satisfactory, with an average deviation in the specific heat of ±0.006% and a maximum deviation of 0.016%.

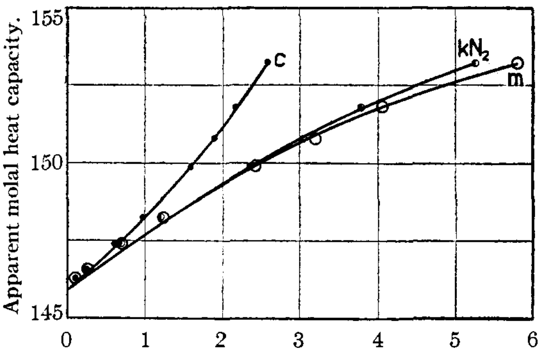

Fig. 2.—A comparison of volume and weight concentration (abscissas).

The partial molal heat capacities of solute and solvent may be calculated from equation (1) by means of the equations

$$\bar{C}_{p2} = \Phi^\circ + 2am + 3bm^2 \qquad (2)$$
$$\bar{C}^\circ_{p1} - \bar{C}_{p1} = 10^{-3}M_1(am^2 + 2bm^3) \qquad (3)$$

which are analogous to those derived by Randall and Rossini[2] when Φ is a linear function of $m^{1/2}$. For sucrose the equations are

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[8] Fuoss, This Journal, 58, 982 (1936).

[9] The graph of Φ against $m^{1/2}$ was also plotted. It is like an elongated S. In the dilute region it shows a curvature about midway between that of the graphs against $c^{1/2}$ and c. It nearly coincides with the latter in solutions more concentrated than 1.5 molar, although it exhibits a slight concavity downward. This curve was omitted from Fig. 1 to avoid confusion.

(at 20° in cal$_{20}$/deg.) $\begin{cases} \bar{C}_{p_2} = 145.87 + 3.900m - 0.3546m^2 \\ \bar{C}^\circ_{p_1} - \bar{C}_{p_1} = 0.018016\,(1.950m^2 - 0.2364m^3) \end{cases}$

(at 25° in cal$_{25}$/deg.) $\begin{cases} \bar{C}_{p_2} = 151.20 + 2.650m - 0.2112m^2 \\ \bar{C}^\circ_{p_1} - \bar{C}_{p_1} = 0.018016\,(1.325m^2 - 0.1408m^3) \end{cases}$

In Fig. 3 we have plotted the values of the apparent and partial molal heat capacities of sucrose at 20 and 25°. The experimental values of Φ at 20° are designated by open circles; those at 25° by dots. The values at every point agree within the limits of 0.016% in the specific heat, as we mentioned above. In the very dilute region (below 0.04 *m*) seven of the eight points lie *below* their respective lines. Although the differences appear large on the graph, only two of them actually correspond to more than 0.01% difference in *s*, as Table I shows. We hesitate to attribute any particular significance to this trend, although we hope that a study of heats of dilution of very dilute solutions, now under way in this Laboratory, may settle this question unequivocally.

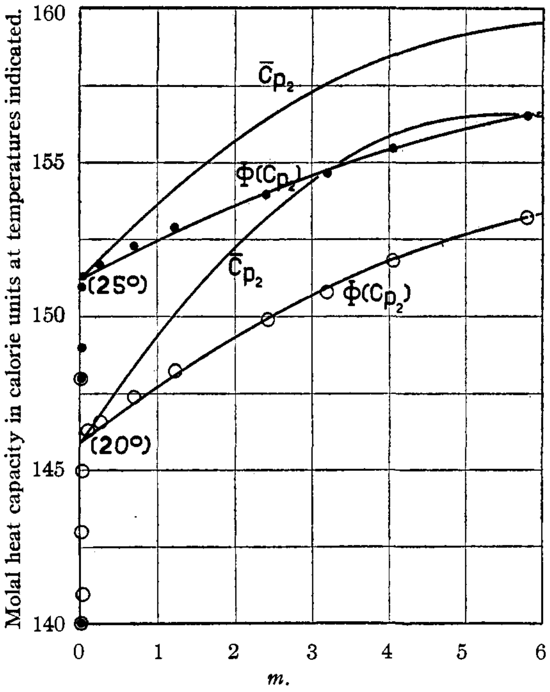

Fig. 3.—Apparent and partial molal heat capacities of sucrose at 20 and 25°.

In comparing the results at 20 and at 25°, the large change of the apparent molal heat capacity with temperature is a striking fact. The value of Φ° changes by 5.3 calorie units—over 1 unit per degree. This is much larger than the change[10] of a 1–1 electrolyte, which averages only about 0.3, and even a 2–1 electrolyte, which averages about 0.8. The initial slope of the curve is appreciably larger at 20 than at 25°. If the slope decreased at the same rate it would be 0 at about 40°—and at this temperature we might have a solute with a nearly constant apparent molal heat capacity, such as has usually been postulated for all orthodox non-electrolytes.

Comparison with Previous Results.—There are two recent series of measurements of the heat capacities of sucrose solutions. Frenzel, Burian and Haas[11] determined the heat capacities by measuring with a Beckmann thermometer the rise of temperature in the solution contained in a Dewar flask, in which a known amount of electrical energy was dissipated. They record in 15°-calories their results for solutions from 0.1 to 1 *m* at 16, 24, 32 and 39°. We have calculated the corresponding values at 20 and 25° by graphical interpolation and have converted them into 20- and 25°-calories by multiplying by the factors 1.0010 and 1.0017. These factors are obtained from Jaeger and von Steinwehr's[12] equation for the heat capacity of water at different temperatures, which Frenzel, Burian and Haas employed in their calculations. The results at 20° are given in column 3 of Table III, while the corresponding values calculated from our equation are given in the final column. Their values at 20° agree with ours to about ±0.06%, which is within their es-

TABLE III

SPECIFIC HEATS OF SUCROSE SOLUTIONS AT 20° FOUND BY DIFFERENT INVESTIGATORS

Weight, %	*m*	*s*(F., B. and H.)	*s*(Y. and A.)	*s*(I. C. T.)	*s*(G. and A.)
0	0.0	1.0000	1.0000	1.000	1.0000
	.1	0.9830			0.9810
5	.1538			0.966	.9714
	.2	.9633			.9633
	.3	.9452			.9467
10	.3247		0.9436	.930	.9428
	.4	.9305			.9312
15	.5157		.9162	.902	.9144
	.6	.9032			.9029
20	.7306			.870	.8861
	.8	.8791			.8776
	1.0	.8579			.8551
30	1.2525		.832	.811	.8299
40	1.9483		.777	.751	.7744
50	2.9224		.711	.703	.7213
60	4.3838			.677	.6668
65	5.4274		.633		.6406

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[10] Rossini, *B. S. J. Research*, **4**, 327 (1930); Gucker and Schminke, THIS JOURNAL, **55**, 1018 (1933).

[11] Frenzel, Burian and Haas, *Z. Elektrochem.*, **41**, 419 (1935).

[12] Jaeger and von Steinwehr, *Ann. Physik*, 4F, **64**, 365 (1921).

timated uncertainty of ±0.1%. Their values at 25°, on the other hand, are all ***higher*** than ours, on an average about 0.3%. We have no explanation for this discrepancy.

Yanovski and Archangelski[13] measured the heat capacities of solutions at approximately even weight percentages up to 65%, and at temperatures of 20.6, 51.2 and 80.8°. We have made the slight changes necessary to interpolate their results to even weight percentages at 20°, and have changed them from 15- to 20°-calories and tabulated them in column 4 of Table III. These results differ from ours on an average by ±0.4%, which is slightly more than their estimated error of 0.2 or 0.3%. Their experiments were not precise enough to detect the change of the apparent molal heat capacity with concentration and they concluded it was constant at any temperature. However, they noted its linear increase with temperature from an average value of 148.2 at 20° to 185.9 at 80°. This change is in qualitative agreement with the change in Φ° from 20 to 25°, which we have observed. The change in the *average* value is smaller because the change of the apparent molal heat capacity with temperature is less at higher concentrations.

In the fifth column of Table III we have tabulated the values of the specific heats calculated from the heat capacities given in the "International Critical Tables."[14] These represent a weighted mean of the early results. They differ from our results by ±1.5%, and are *lower* for every concentration except the last.

Other Non-electrolytes.—Unfortunately we have not been able to find in the literature any values of the heat capacities of non-electrolytes which allow us to draw further conclusions as to the functional relationship between the apparent molal heat capacity and the concentration. Such data must be accurate and they must include a series of results extending over a wide concentration range and including dilute solutions. The recent excellent study of the heat capacities of solutions of urea and mannite, made by C. M. White,[15] unfortunately does not extend above 1 *m*. White finds that "The apparent molal heat capacities seem to follow a linear equation when plotted against the $\sqrt{m}$." However, even his results, precise to ±0.01%, are not adequate to decide unequivocally between the square root and first power of the concentration over so short a range, when the change with concentration is so small.

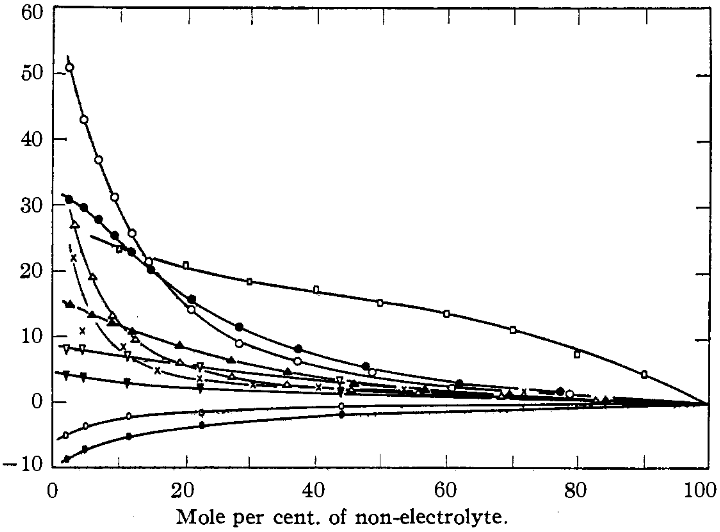

Fig. 4.—Apparent molal heat capacities of some non-electrolytes: △, methyl alcohol 5°; ▲, methyl alcohol 20°; ○, ethyl alcohol 3°; ●, ethyl alcohol 41°; 0, *n*-propyl alcohol 15°; ●, *n*-propyl alcohol 32°; ×, glycol 20°; ▽, glycerine 15°; ▼, glycerine 32°; □, acetone 20°.

Among the older determinations there are several series of results for liquids miscible with water, covering the whole range of concentration. We have taken the specific heat values from the "International Critical Tables" and calculated the corresponding apparent molal heat capacities of the solutes. This may introduce some errors, depending upon the way the original data were smoothed in tabulation, but it does not affect our discussion. In this case, so as to minimize the confusion of intersecting curves, we have taken the mole per cent. as abscissa and have plotted as ordinate the difference between the apparent molal heat capacity of the solute and the molal heat capacity of the pure solute (C_{p_2}). The results are shown in Fig. 4, and several interesting conclusions can be drawn. In the first place, acetone alone shows an appreciable deviation in the very concentrated solution. Most of the others lie within 10 calorie units until the solution contains 70 or more mole % water. The large deviations occur beyond this dilution, in a region which is still, how-

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(13) Yanovski and Archangelski, *Zhur. Sakharnoi Prom.*, **2**, 614 (1928).

(14) "I. C. T.," Vol. V, p. 125.

(15) C. M. White, THIS JOURNAL, **58**, 1620 (1936).

ever, considered concentrated—8 or 10 molar. In contradiction to the behavior of all electrolytes and of sucrose, urea and mannite the apparent molal heat capacities of all these solutes except *n*-propyl alcohol *decrease* with increasing concentration. The highest value in the dilute region and the steepest slope occurs at low temperature. In other words, in almost every case when the temperature is raised, the solute shows a closer approximation to the behavior of an ideal non-electrolyte, where the apparent molal heat capacity is constant.

Acknowledgments.—It is a pleasure to express our thanks to Dr. Rossini and Dr. Bates of the Bureau of Standards for supplying us with the sucrose used in these experiments.

Summary

We have determined the specific heats of solutions of sucrose at 20 and 25° by means of a differential apparatus employing adjustable heaters.

The apparent molal heat capacity of sucrose is not constant, although it increases with concentration considerably less than a uni-univalent strong electrolyte. It is much more nearly a linear function of the first power than of the square root of the concentration. Its change with concentration decreases with rising temperature. Its limiting value at low concentration increases more rapidly with temperature than the same property of most electrolytes. The apparent molal heat capacity can be expressed satisfactorily as a second degree power series in the molality, and values of the apparent and partial molal heat capacities and the specific heats calculated by these equations are tabulated.

A review of other available specific heat data for non-electrolytes shows a general *decrease* of apparent molal heat capacity with concentration. with greater deviations at *low* temperatures.

EVANSTON, ILLINOIS RECEIVED NOVEMBER 27. 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Reactivity of Zinc Amalgams

BY HERMAN A. LIEBHAFSKY

The stability of zinc amalgams, and perhaps of most amalgams, depends in a curious way upon their concentrations. The great inertness of the concentrated (say, 1%) amalgams has been observed by all investigators who have tried to make them react with hydrochloric acid: hydrogen evolution, even when fairly strong acid is employed, does not proceed rapidly with a cold amalgam although the reaction mixture is shaken; this inertness has usually been attributed, in part at least, to the overvoltage of these amalgams for hydrogen gas. On the other hand, dilute (say, 0.001%) amalgams become increasingly unstable as their concentrations decrease, so that the electromotive forces of cells containing these amalgams vary with time and cannot be measured accurately even when the amalgams are in contact with oxygen-free zinc salt solutions.[1] That these two sets of experimental facts constitute a paradox well worth investigating appears to have escaped previous notice.

Accordingly, exploratory experiments were undertaken and the following experimental method was adopted. (1) With oxidizing agents in aqueous solution, approximately 25 cc. of amalgam and 40 cc. of solution were shaken vigorously by hand at a constant rate (240 times a minute) in a 125-cc. separatory funnel. From time to time 3-cc. samples of amalgam were withdrawn into one side of a cell containing a similar portion of the original amalgam as reference electrode in the other. The electromotive force of this concentration cell was then measured, a 1 *M* zinc sulfate–0.05 *M* sulfuric acid solution serving as electrolyte. (The acid was added in order to prevent the formation of an oxidized film on the amalgam surface; concentrations as high as 0.1 *M* have been employed without sensibly disturbing the measurements except in the case of amalgams containing less than about 10^{-4} % zinc, which are so unstable anyhow that an accurate measurement is impossible.) Beyond stirring the amalgams several times during the measurements, which were made as rapidly as possible and without excluding air, no precautions were taken. The electromo-

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[1] (a) Liebhafsky, THIS JOURNAL, 57, 2657 (1935), recently has correlated and re-interpreted the accurate electromotive force data for zinc amalgams. See also (b) Crenshaw, *J. Phys. Chem.*, 14, 158 (1910), and the other work cited in Ref. 1a.