[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Heat Capacity of Glucose Glass[1]

BY EARL W. NELSON AND ROY F. NEWTON

Many investigators have measured the heat capacities of glassy substances by the Nernst method and have used such measurements in calculations of entropy and in discussions concerning the applicability of the third law of thermodynamics to glasses. An investigation of the heat capacity of supercooled liquid glycerol by Oblad and Newton[2] showed that the Nernst method of measurement of heat capacity did not give equilibrium values for glassy glycerol below its congealing temperature of about 190°K. In order to obtain equilibrium measurements, they stored samples of the glass at low temperatures for as long as seven days and measured the amounts of heat required to bring them to room temperature, where equilibrium was reached rather rapidly.

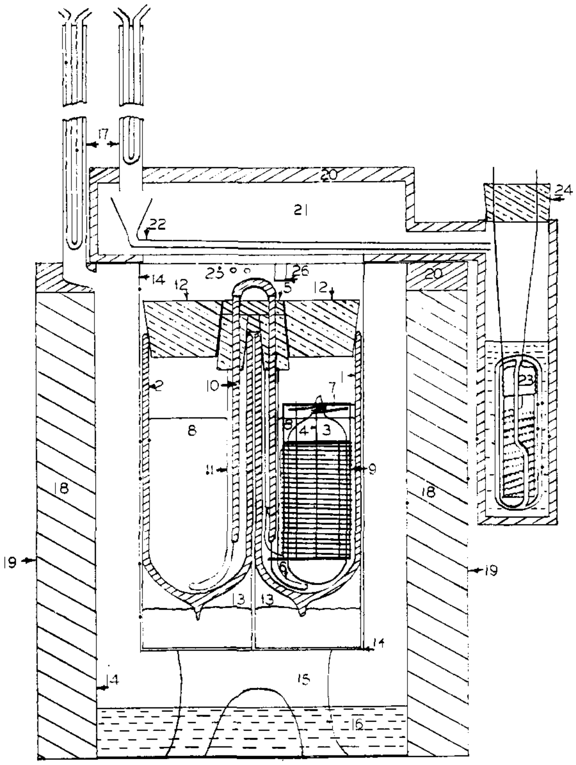

Fig. 1.—Calorimeter.

Since their work cast doubt upon the measurements by the Nernst method of the heat capacity of other glassy substances, a further investigation of glasses seemed desirable, and glucose glass was selected for a more detailed study because its congealing temperature of about 25° offered experimental advantages.

Experimental

Description of Apparatus.—A calorimeter (1 of Fig. 1) was designed to be used at 60° and was kept near that temperature by means of a copper jacket filled with the vapors of boiling chloroform. The lid (21) was removable and had its own chloroform boiler and condenser. Because the temperature of the vapor-bath changed with change of barometric pressure, a dummy calorimeter (2) was also placed inside the bath. A record of its temperature made it possible to calculate a correction for the change of bath temperature. The calorimeter and the dummy were made from wide-mouthed pint Dewar vessels which were held in position by a cork and wood frame (5). The neck of the Pyrex capsule (3) containing the glucose glass was fitted with a rubber collar around which an iron wire (7) was wrapped. When the capsule was rotated slightly, the wire caught under the edge of an iron cage (4) so that the capsule could be held submerged in the mercury (8). The cage also served as a support for an insulated manganin heating coil. Twenty-junction thermels were used to measure the temperature of the dummy, and the difference in temperature between the calorimeter and the dummy. The mercury was stirred by a stream of air which had been preheated to the temperature of the calorimeter by passing it through long copper tubes enclosed in the vapor-bath, using approximately the same volume of air for the dummy as for the calorimeter.

The direct current used for adding heat to the calorimeter was maintained constant to about one part in ten thousand by an arrangement of storage batteries and resistances as shown in Fig. 2. To keep the batteries in a steady state, the current was passed through an external resistance very nearly equal to that of the heating coil in the calorimeter, for about thirty minutes previous to use. A Leeds and Northrup type K potentiometer was used

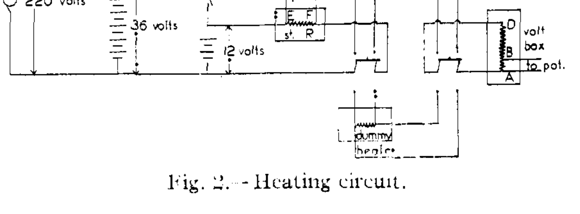

Fig. 2.—Heating circuit.

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[1] Based upon a thesis submitted by Earl W. Nelson to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1940. Presented before the Division of Physical and Inorganic Chemistry at the Detroit meeting of the American Chemical Society, September, 1940.

[2] A. G. Oblad and Roy F. Newton, THIS JOURNAL, **59**, 2495 (1937).

for all electrical measurements. The time of heating was measured by a stop watch reading to 0.01 second.

The thermostats in which the samples were held were maintained constant within 0.01°. The temperatures were measured by a mercury thermometer which had been calibrated to 0.01° by the U. S. Bureau of Standards.

Preparation of Samples.—Anhydrous C. P. dextrose from the Pfanstiehl Chemical Company was used. The glass was prepared by melting the crystals under vacuum, to remove any moisture present. The heating was continued until all of the crystals had melted, which took approximately one hour, under conditions such that the temperature did not rise much above the melting point of the crystals. Previous investigators have shown that such a treatment does not decompose the glucose to an appreciable extent.[3] Other samples were prepared which contained, respectively, 0.5, 1, 2 and 3% of water in order to determine the effect of small amounts of water on the heat capacity of the glass.

In the first three capsules which were made the glucose was in direct contact with the Pyrex, and because of difference in the coefficients of expansion, the capsules broke when cooled much below the congealing temperature of the glucose. In order to overcome this difficulty, a collodion bag was formed inside the Pyrex capsule, and after the collodion had been loosened from the Pyrex, it was filled with molten glucose. When the glass had cooled to room temperature, enough 1,2,3-trichloropropane was added to fill the space between the Pyrex and the collodion, and the capsule was then sealed. Trichloropropane was chosen as the heat transfer medium because it did not show any solvent action on either the glucose or the collodion.

One capsule was filled with crystalline glucose and heated under a vacuum to within a few degrees of the melting point for thirty minutes to remove moisture, the crystals were covered with the trichloropropane, and the capsule was then sealed. In order to obtain a check on the accuracy of the method, one capsule was filled with water. Measurements were also made on an empty capsule, and on one filled with 1,2,3-trichloropropane.

Experimental Procedure.—In making a measurement of heat capacity, the capsule was placed in a rubber-stoppered glass bottle and was submerged in the water thermostat until thermal equilibrium was attained. When the calorimeter and the dummy had reached an equilibrium temperature with the chloroform-bath, rubber tipped crucible tongs were used to transfer the capsule as rapidly as possible from the water thermostat to the calorimeter. In making this transfer, the cork stoppers for the calorimeter and dummy were removed and replaced simultaneously. As soon as the transfer was complete, electrical heat was added to compensate for the cooling effect of the capsule, and measurements were made as frequently as possible, of the difference in temperature between the calorimeter and the dummy, and of the potential difference across the resistances AB and EF. After the heat had been added, it was necessary to follow the temperature of the calorimeter occasionally for approximately one and one-half hours or until thermal equilibrium had been established within the calorimeter.

Method of Calculation.—The fundamental quantity required for the determination of the heat capacity is H_t, the quantity of heat required to raise the capsule and its contents from t to 60°. This was obtained from the equation

$$H_e + H_a = H_t + 0.00116\, C_t(\Delta e + k_1 \Delta e_D + k_2 A) \quad (1)$$

where H_e is the amount of electrical energy supplied and H_a is the quantity of heat required to raise the capsule from the initial temperature of the calorimeter to 60°. C_t is the total heat capacity of the calorimeter and its contents, and the factor 0.00116 is the change of temperature per microvolt change of e, the reading of the thermel between the calorimeter and the dummy. Δe is e (final) $-$ e (initial), and likewise Δe_D is e_D (final) $-$ e_D (initial), in which e_D is the reading of the thermel between the dummy and melting ice. The constant k_1 is calculated from the total heat capacities of the dummy and of the calorimeter and its contents, while k_2 is determined experimentally by adjusting the temperature of the calorimeter so that e is a few thousand microvolts, either positive or negative, and, after the approach to the steady state is fairly uniform, equating $\Delta e + k_1 \Delta e_D + k_2 A$ to zero and solving for k_2. A is the area above the steady state value of e minus the area below it, in a plot such as Fig. 3. The quantity of heat H_t may for convenience be subdivided into H_s, H_1, H_2, H_3 and H_4, which refer, respectively, to the contributions due to the glucose, the empty capsule, the collodion, the 1,2,3-trichloropropane and the water.

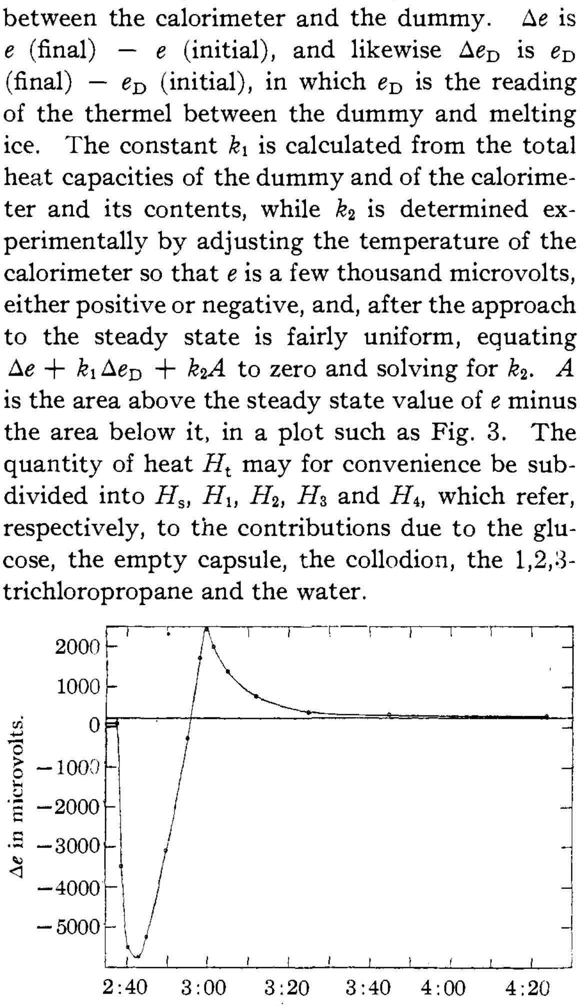

Fig. 3.—Typical determination.

During the transfer of a capsule from its container in the water thermostat to the calorimeter, heat was gained or lost by the capsule, depending on its temperature relative to that of the room. In the short time required for transfer, only the

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(3) Parks, Huffman and Cattoir, *J. Phys. Chem.*, **32**, 1366 (1928).

wall of the capsule will undergo appreciable change of temperature, and hence such gain or loss of heat should be the same for the empty capsule as for one containing a sample. Except for slight variations in the time required for transfer, subtraction of the experimentally observed heat capacity of the capsule from that of the capsule and contents should automatically compensate for this source of error.

Results

All quantities of heat here reported are in the defined calorie of 4.1833 int. joule in accordance with Rossini's usage in *Chem. Rev.*, **27** (1940). For convenience in combining the many observations with one another, the experimental results were fitted to equations by the method of least squares. The equation for a typical capsule is

$$H_1 = 10.85 + 12.587\ \Delta t - 0.01434(\Delta t)^2 \qquad (2)$$

where $\Delta t = 60° - t$. The average deviation from this equation of the 37 experimental values was 2 calories. It was found possible to calculate the value of H_1 for other capsules by the equation

$$H_1' = H_1 C_1'/C_1 \qquad (3)$$

where C_1 and C_1' are the total heat capacities of the two capsules calculated from the known weights of Pyrex, rubber and iron constituting the capsule, and the approximate specific heats of these materials.

The values for 1,2,3-trichloropropane are represented by the equation

$$H_2 = 37.625\ \Delta t - 0.01345(\Delta t)^2 \qquad (4)$$

with an average deviation of 2 calories for the eighteen measurements. By differentiation with respect to t and division of the result by 123.4, the weight of the trichloropropane, the specific heat of 1,2,3-trichloropropane was found to be

$$c_p = 0.292 + 0.000218t \qquad (5)$$

for the temperature interval from 0 to 60°.

Similarly the specific heat of crystalline glucose was found to be

$$c_p = 0.265 + 0.000975t \qquad (6)$$

between 0 and 60°. Parks and Thomas[4] report $0.270 + 0.00092t$, for about the same temperature range.

To check the accuracy of our experimental procedure, measurements were made with a capsule containing 97.88 g. of water. The average observed specific heat was calculated by subtracting the heat absorbed in heating from t_2 to 60 from that absorbed in heating from t_1 to 60, and dividing the result by the weight of water and by $t_2 - t_1$. In Table I these results are shown in comparison with similar calculations made on the data of Osborne, Stimson and Ginnings.[5] It would appear from the table that our measurements of heat capacity may be in error by about 0.5%.

TABLE I

HEAT CAPACITY MEASUREMENTS ON CAPSULE CONTAINING WATER

Δt	No. of detns.	Av. H_t, cal.	Av. deviation, cal.
60–35	4	2438.8	4.0
60–15	3	4385.5	1.5
60– 5	5	5360.8	3.4

Δt	Av. obsd. sp. ht., cal./g. deg.	Av. accepted sp. ht., cal./g. deg.	% Error
60–35	0.997	0.999	−0.2
35–15	.994	.999	− .5
15– 5	.996	1.002	− .6

All of the measurements which have been listed thus far are equilibrium ones, and the values of specific heat are not dependent upon the time of storage at the low temperatures. In Fig. 4 are shown a few examples of how, for some of the samples of glassy glucose, the measured values of specific heat are dependent upon the time of storage. Because these values were dependent not only upon the time of storage, but also upon the rate of cooling, a somewhat standard procedure was followed in cooling the capsules to low temperatures. The warm capsule was cooled in air and was allowed to remain at room temperature for approximately one day. Then it was slowly cooled in water during a period of about one hour, to the temperature at which it was to be stored.

In selecting non-equilibrium values of H_t to be used in calculating metastable specific heats of glucose glass, longer storage times were taken for the lower temperatures, because the same internal rearrangements in the glass which resulted from a given storage time at one temperature required a longer time when stored at some lower temperature. In order to show the changes in these metastable values with small variations in temperature and in water content, it was assumed that the activation energies for the transitions in the glass were such that a 10° rise in temperature approximately doubled the speed of the transition.

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(4) Parks and Thomas, THIS JOURNAL, **56**, 1423 (1934).

(5) Osborne, Stimson and Ginnings, *J. Research Natl. Bur. Standards*, **23**, 197 (1939).

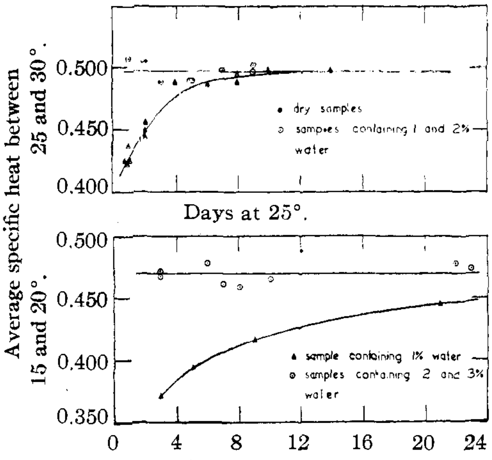

Fig. 4.

Then by selecting a 20-day storage time at 5°, the storage times at the other temperatures were fixed. On the basis of these two arbitrary choices, metastable values for the specific heat of glucose glass have been plotted, together with the equilibrium ones, in Fig. 5. Wherever the values of H_t were found to be still changing after one day of storage, the values of specific heat which were calculated from those measurements are designated by a check mark. Each point on the graph represents the average of several measurements.

In calculating the specific heat of the glucose in the samples containing water, it is assumed that the heat capacities of the glucose and water are additive. Since by this method of calculation, all of the samples of the glass give the same value for the specific heat of glucose above 30°, where equilibrium measurements could be made on all of the glasses, and very nearly the same values at temperatures so low that even those containing water did not reach equilibrium, this assumption seems quite sound. Some additional evidence for assuming approximate additivity of heat capacities in these calculations is found in the work of Bennewitz and Kratz[6] in which they obtained the apparent molal heat capacity of glucose in water solutions by extrapolation to zero concentration. Considering the large difference in the concentration of solutions investigated, their value of 0.456 cal./g. deg. at 20° is in good agreement with the value of 0.477 obtained from Fig. 5.

It can also be seen from Fig. 5 that the effect of water in lowering the congealing temperature of glucose glass is essentially the same when detected by heat capacity measurements as when found from the viscosity measurements of Parks and Gilkey.[7] They reported a lowering of the congealing temperature of approximately 8° for each 1% of water in the glass. According to the data shown in Fig. 5, in the temperature interval from 20 to 30° the change in the equilibrium values for the specific heat is larger than usual. If this effect is genuine, it may indicate some transition in the glucose which may also be responsible for the sudden change of viscosity characteristic of this range of temperature.

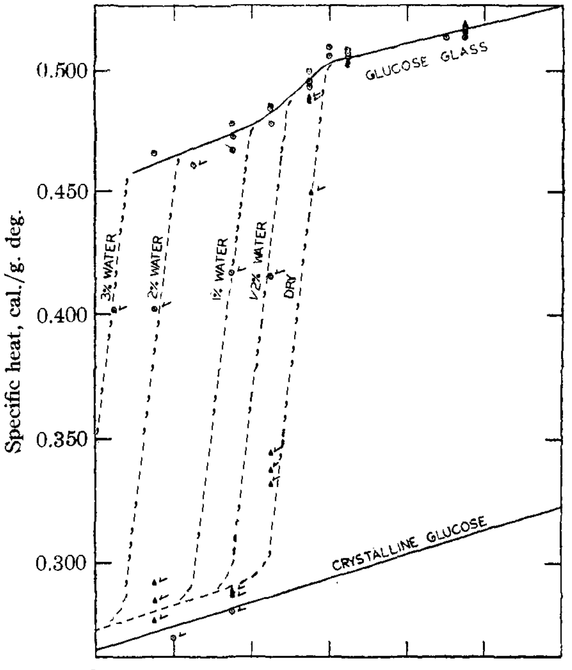

Fig. 5.

Because this method of determining specific heat requires high absolute precision in the measurement of H_t, the total heat absorbed, it becomes less satisfactory for very low temperatures, when this quantity is relatively large. A more serious objection is the excessively long time required to reach equilibrium. If this difficulty is circumvented by decreasing the viscosity of the glass, as, in the case of these measurements, by the addition of water, it becomes increasingly more difficult to avoid crystallization. While samples of dry glucose have been known to remain as glass for years, measurements on a sample containing 3% of water had to be discontinued after four and one-half months because it had begun to crystallize.

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(6) Bennewitz and Kratz, *Physik. Z.*, **37**, 496–511 (1936).

(7) Parks and Gilkey, *J. Phys. Chem.*, **33**, 1428 (1929).

Summary

A calorimeter which operates near 60° has been devised and used to measure the heat taken up by a sample when transferred to the calorimeter from a thermostat at some lower temperature. Measurements of the changes in heat content have been made on dry glucose glass, and on samples containing up to 3% of water. When the glass is cooled only a few degrees below its congealing temperature, which is between 25 and 30° for the dry glass, it was found that equilibrium heat content was not reached even after three weeks of storage. For equilibrium heat capacity measurements, the contribution of any water present in the glass was found to be additive. One per cent. of water in the glass lowered the congealing temperature about 8°. Equilibrium heat capacity values have been obtained for glucose glass between 5 and 60°.

The heat capacities of crystalline glucose and of 1,2,3-trichloropropane were also measured between 0 and 60°.

Since glassy substances are so extremely slow to reach equilibrium with respect to heat content, it is not permissible to use the heat capacity of glasses obtained by the Nernst method in entropy calculations or in discussions concerning the third law of thermodynamics.

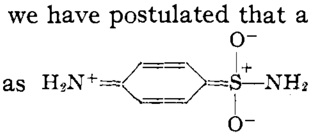
LAFAYETTE, INDIANA RECEIVED APRIL 26, 1941

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

The Dipole Moment of Sulfanilamide and Related Compounds[1,2]

BY W. D. KUMLER AND I. F. HALVERSTADT[3]

In a previous paper[4] we have postulated that a resonance form such as



may contribute somewhat to the structure of sulfanilamide. Although it has been stated[5] that forms of this same type are not possible with a sulfonic acid we see no reason for such an assumption since sulfur is a second row element and is not necessarily limited to a maximum of four covalent bonds as is the case with first row elements like nitrogen or oxygen.[6,7] In this paper we have measured the dipole moment of sulfanilamide and some related compounds to obtain evidence on the possible existence of such resonance forms.

Results

The symbols used in the equations and tables are: ω, the weight fraction of solute; d, the density of the solution; ϵ, the dielectric constant; P_2, the polarization of the solute; P_{2_0}, the polarization of the solute at infinite dilution; P_{E_2}, the electronic polarization of the solute; μ, the dipole moment; T, the absolute temperature; p_1, the specific polarization of the solvent; p_2, the specific polarization of the solute; and p_{12}, the specific polarization of the solution. The P_{E_2} values were calculated from the refractive indices of the solutions using the D sodium line. The P_{2_0} values were obtained by plotting P_2 against ω and extrapolating to zero concentration. The polarization and dipole moments were calculated by means of the equations

$$p_1 = \frac{\epsilon - 1}{\epsilon + 2}\frac{1}{d}$$

$$p_{12} = \frac{\epsilon - 1}{\epsilon + 2}\frac{1}{d} = (1 - \omega)\, p_1 + \omega p_2$$

$$P_2 = M_2\left(p_1 + \frac{p_{12} - p_1}{\omega}\right)$$

$$\mu = 0.0127\sqrt{(P_{2_0} - P_{E_2})T}$$

TABLE I

MEASUREMENTS IN DIOXANE AT 25°

ω	d	ϵ	P_2
	Aniline		
0.004758	1.0269	2.2332	102
.007211	1.0269	2.2434	98
.012450	1.0270	2.2670	95
	Xenylamine		
.004209	1.0272	2.2268	147
.008937	1.0277	2.2443	150
.012436	1.0280	2.2565	147
.017020	1.0284	2.2755	149

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[1] Supported in part by a grant from the Research Board of the University of California.

[2] Presented at the meeting of the American Chemical Society held in conjunction with the A. A. A. S. meeting at Pasadena, June 20, 1941.

[3] James M. Goewey Fellow in Pharmaceutical Chemistry, 1940–41.

[4] Halverstadt and Kumler, THIS JOURNAL, **63**, 624 (1941).

[5] Armstrong, James and Weissberger, *ibid.*, **63**, 182 (1941).

[6] Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941.

[7] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 221.