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Studies on Glass.

XVIII. The Heats of Solution of Crystalline and Glassy Glucose;
the Heat of Mutarotation of α -Glucose

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A calorimeter has been developed for the rapid solution of a powdered solid in a suitable solvent and the accurate determination of the heat of solution during the process. This calorimeter has now been used to determine the heats of solution of two preparations of crystalline α -D-glucose in water, both with and without mutarotation, and also the heats of solution of two preparations of glucose glass. Relatively accurate thermodynamic data for the crystal-to-glass transformation have been computed from these solution heats. Also small, but significant, differences per mole in enthalpy ($\Delta H_{298} = 102 \pm 18$ cal.), in entropy ($\Delta S_{298} = 0.24 \pm 0.06$ cal./deg.), and in free energy ($\Delta F_{298}^\circ = 31 \pm 10$ cal.) have been found for these two glass preparations. A value of $\Delta H_{298} = -175 (\pm 5)$ calories has been obtained for the mutarotation of a mole of α -glucose, dissolved in water, to yield the equilibrium mixture of the alpha- and beta-forms.

INTRODUCTION

THE measurements here described were carried out during 1937–38 in order to provide as accurate data as possible concerning the relative heat contents of crystalline α -glucose and glassy glucose. The present results supersede the earlier, essentially preliminary, values of Parks, Snyder, and Cattoir.¹ Consequently, their thermodynamic calculations for the crystal-to-glass transformation are now revised in the light of these newer data.

When this investigation was started, it was also considered likely that the heat of solution of a sample of glucose glass would show variations with the history of its annealing, i.e., the time and temperature of storage, prior to the solution process itself, as previous measurements of the optical rotatory power² and the viscosity³ of this material had disclosed rather appreciable changes with aging. No such effect was discernible, however, in the present study, probably because of the character of these solution experiments and the time requirements here involved.

Incidentally, the data for the heat of solution of the crystalline α -glucose in water, both with

and without mutarotation, provide a new and relatively accurate value for the heat of mutarotation.

METHOD AND APPARATUS

After considerable preliminary experimentation, the "ordinary" method of calorimetry was adopted for measuring the heats of solution of the various glucose samples in water at approximately 25°C. With our final apparatus the actual solution process of the glucose, properly powdered, took place in about twenty seconds and complete thermal equilibrium was then attained two or three minutes later. The corrected temperature changes were readily computed by the Regnault-Pfaundler method from

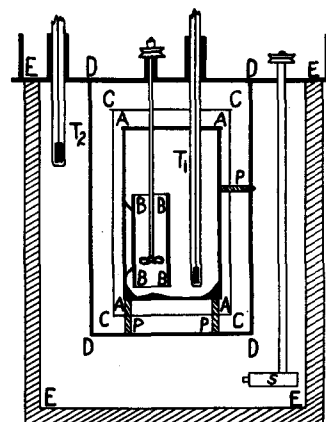


FIG. 1. A schematic diagram of the calorimetric assembly.

¹ G. S. Parks, L. J. Snyder, and F. R. Cattoir, *J. Chem. Phys.* **2**, 595 (1934).

² C. J. Jacobs and G. S. Parks, an unpublished study at Stanford University.

³ G. S. Parks and J. D. Reagh, *J. Chem. Phys.* **5**, 364 (1937).

two series of temperature readings, taken for periods of twenty to thirty minutes prior to and immediately following each solution process.

Our calorimetric assembly, as finally developed, is represented schematically in Fig. 1. The calorimeter proper, designated by the lettering *AAAA*, was a cylindrical copper container of about 450-ml capacity, which had been given a number of coats of Bakelite varnish both inside and outside to protect the metal from alkaline reagents. It had a specially shaped, streamlined bottom and a tightly fitting lid. The stirrer was a four-bladed propeller of monel metal, operating in a small copper cylinder (*BBBB*) immersed in the solvent liquid and set off center in such a way as to circulate all of the liquid around the calorimeter thermometer (T_1) and the walls of the container. Evaporation was prevented by the tightly fitting lid, the special grease-filled seal on the stirrer shaft, and a rubber gasket about the thermometer. This container, the calorimeter, was surrounded by a silver shield (*CCCC*), in the form of a cylindrical can with a removable lid, to reduce radiation and convection effects and thus insure a small, uniform rate of heat transfer to or from the jacket, which in turn was a large copper can (*DDDD*) with a removable top. Six Bakelite pegs (only three are indicated in Fig. 1) supported both the convection shield and the calorimeter firmly, but in such a way that the latter could be easily removed. A special doorway, not shown in this figure, was provided through all three lids so that samples could be added with a minimum of heat transfer. These holes were closed by a removable, hollow outside door which supported covers for the convection shield and the inner calorimeter lid. A small spring on the support held the cover of this hole in the calorimeter lid tightly in place so as to prevent evaporation of the solvent.

The copper jacket, with the silver shield and calorimeter therein, was finally suspended within a fifteen-liter crock, which was filled with water at a temperature of about 24°C. A small rotary pump circulated the water in this crock, and both the jacket lid and hollow door were also filled with water. The entire apparatus was then placed in a thick-walled Celotex box with a removable Celotex cover. A 1/15 hp synchronous

motor, connected by means of a system of belts and pulleys, drove the calorimeter stirrer and jacket circulating pump at constant speed, the former at 505 r.p.m. and the latter at 600 r.p.m.

The temperature changes within the calorimeter were measured to 0.0005° with a very fine Beckmann thermometer, manufactured specially for us by Max Tischler and Company (Ilmenau, Germany) and calibrated at 0.2° intervals by the Physikalisch-Technische Reichsanstalt. The jacket temperature was observed with an ordinary Beckmann thermometer (T_2). These thermometers were set at proper temperatures against a 0°–50° thermometer which had been calibrated to 0.01° by the National Bureau of Standards. This latter thermometer was also used to obtain the temperature of the samples and of the room during the experimental runs. Lens magnifiers were used in reading all thermometers.

The calibration of the calorimeter in the 22°–25° range was effectuated by a method of mixtures. In this calibration procedure a weighed sample of distilled water, initially at about 20°, was added to the calorimeter, which had been previously prepared by a partial filling with water and a temperature adjustment to 24° or 25°. By means of a copper-constantan thermocouple in conjunction with a White potentiometer, the temperature of this added water was measured to within 0.001° as it entered the calorimeter proper from a pipette. The final temperature of the calorimeter was then determined on its own Beckmann thermometer, against which the thermocouple had been standardized. Six such calibration experiments yielded a mean result of 62.0 calories per degree with a mean deviation of only ± 0.3 calorie. This result checked roughly with a prior estimate of 59.2 calories per degree, exclusive of the heat capacity of the Beckmann thermometer, which had been made from the weights and known specific heats of the materials used in the construction of the calorimeter.

MATERIALS

Crystalline Glucose

Two preparations of crystalline α -D-glucose were employed in the present study.

The first material was a C. P. Pfanstiehl product, which was dried in a vacuum desiccator

over P_2O_5 for six weeks before use. It was then estimated to contain around 0.01 percent moisture in view of Jackson's observations.⁴ An analysis by the polarimeter, based on the rotation data of Isbell and Pigman,⁵ indicated that it was about 96 percent alpha- and 4 percent beta-glucose. This dried material was used in our initial measurements of the heat of solution of crystalline glucose and also in preparing the first sample of our glucose glass. Some of the undried crystals were likewise used in preparing the second sample of glass.

Our second crystalline material was some of Standard Sample No. 41, "Dextrose," as prepared by the National Bureau of Standards. It was a fine powder and was guaranteed to contain not over 0.01 percent moisture. Its initial rotation indicated that it was 100 percent α -glucose within the limits of error of our polarimetric measurements. This material was used in our final measurements of the heat of solution of crystalline α -D-glucose and its heat of mutarotation.

Glassy Glucose

As in other studies,⁶ the preparations of glassy glucose were obtained by heating the crystalline Pfanstiehl glucose in a flask in a paraffin bath. The crystals melted at approximately 146°C and were then maintained under a vacuum at 155–160° for about five minutes, in order to eliminate bubbles of air or water vapor. When the liquid had become fairly clear, air was admitted and the material was allowed to cool to the glassy condition. To facilitate use in the solution experiments, the glass so prepared was next reduced to a powder by passing it through an old-fashioned, home meat grinder. This powder was then stored in vacuum desiccators over P_2O_5 until used.

Two batches of glassy glucose were prepared for the present measurements. Glass I was made from the remaining Pfanstiehl crystals which had been previously dried over P_2O_5 for six

weeks. Glass II was made from similar undried material, which, however, should become completely freed of its water when heated above 150°C. Half of this latter glass preparation was kept at room temperature; the remainder was kept in the laboratory "cold room" at about 3°C.

THE HEATS OF SOLUTION

A uniform procedure was followed in measuring the heats of solution of these several glucose samples in water. Exactly 250 g of distilled water were first placed in the calorimeter and subsequently a portion of powdered glucose of 45.0 (± 0.2) g mass was dissolved therein. Thus the resulting solution was always 1.00 molal.

The initial temperature of the calorimeter and solvent water in these experiments was about 24°C. The solution process for the crystals, being distinctly endothermic, resulted then in a temperature drop of 1.8 to 2.0°. On the other hand, the solution process of the glass was somewhat exothermic and yielded temperature rises of 0.8 to 1.0°. In the computations of the corresponding heat effects, the necessary values for the specific heat of water were taken from the International Critical Tables⁷; those for the glucose crystals and glass were derived from the preceding studies of Parks and co-workers.⁸ In order to put all results on a truly comparable basis, the value for the changes in enthalpy (ΔH) in the solution process were finally adjusted to the standard temperature of 25° (i.e., 298°K) by taking $\Delta C_p = 0.20$ cal./g for the solution of the crystals and $\Delta C_p = 0$ for the solution of the glass. These ΔC_p values were based on the plausible assumption that the glucose in water constituted an almost ideal solution. The former value has also received excellent corroboration, subsequent to the completion of our work, from the measurements of Sturtevant,⁹ who has shown that for the solution of alpha-crystals to a final concentration of approximately 0.2 molal $\Delta C_p = 0.200$ cal./g between 25° and 35°C. Our second value of $\Delta C_p = 0$ for the solution of the glass is of less importance, as the temperature adjustment to

⁴ R. F. Jackson, Bureau of Standards Scientific Paper No. 293 (1916).

⁵ H. S. Isbell and W. W. Pigman, J. Research Nat. Bur. Stand. 18, 141 (1937).

⁶ G. S. Parks and W. A. Gilkey, J. Phys. Chem. 33, 1430 (1929); G. S. Parks, L. E. Barton, M. E. Spaght, and J. W. Richardson, Physics 5, 193 (1934).

⁷ International Critical Tables (McGraw-Hill Book Company, Inc., New York), Vol. VII, p. 232.

⁸ G. S. Parks, H. M. Huffman, and F. R. Cattoir, J. Phys. Chem. 32, 1366 (1928); G. S. Parks and S. B. Thomas, J. Am. Chem. Soc. 56, 1423 (1934).

⁹ J. M. Sturtevant, J. Phys. Chem. 45, 127 (1941).

TABLE I. Heat of solution of Pfanstiehl *d*-glucose crystals at 25°C.

Experiment No.	Solvent	ΔH_{298} for solution (cal./g)
P-1	Pure water	14.63
P-2	Pure water	14.63
Mean without mutarotation	Pure water	14.63 (± 0.02)
P-3	0.025N HCl	14.64
P-4	0.025N HCl	14.63
Mean	0.025N HCl	14.63 (± 0.02)
P-5	0.0025N NH_4OH	13.99
P-6	0.0025N NH_4OH	13.97
P-7	0.0025N NH_4OH	13.96
P-8	0.0025N NH_4OH	13.91
Mean, incomplete mutarotation	0.0025N NH_4OH	13.96 (± 0.03)
P-9	0.0050N NH_4OH	13.70
P-10	0.010N NH_4OH	13.74
P-11	0.020N NH_4OH	13.67
Mean with mutarotation		13.70 (± 0.03)
Enthalpy change of mutarotation	$\Delta H_{298} = -0.93$ (± 0.04)	

25° in these cases involved an average interval of considerably less than one degree.

The solution experiments with the Pfanstiehl crystals were essentially preliminary and exploratory in character. These results are summarized in Table I. Experiments 1 and 2, carried out with pure water as solvent, yielded a value of $\Delta H_{298} = 14.63$ cal./g; and this result may be ascribed to the heat of solution of the material without mutarotation, as the crystals dissolved in less than twenty seconds and any subsequent, relatively slow mutarotation was automatically provided for in the derivation of the small, post-solution heating correction. The following pair of experiments with 0.025 normal HCl as solvent were expected to show at least some mutarotation effects, but apparently such a weak solution of hydrochloric acid is not an effective catalyst for the mutarotation process. Next, one to eight drops of concentrated ammonium hydroxide were added to the 250 g of solvent water to yield solutions ranging from 0.0025 up to 0.020 normal. The tabulated results show that in these cases the mutarotation process is apparently complete for our measurements with concentrations of, or above, 0.0050 normal.

Following these exploratory experiments, the heat of solution of the high grade α -*d*-glucose, prepared at the National Bureau of Standards, was measured in a first pair of determinations with pure water as solvent and in a second pair with 0.0125N NH_4OH as solvent. The results, representing the solution process both without and with mutarotation, are summarized in Table II.

A comparison of these values for the heat of solution of α -glucose with most of the earlier data in the literature is fraught with uncertainty, as several of these earlier investigators either overlooked the mutarotation problem or, at least, made inadequate allowance for its effect. Thus Barry's results,¹⁰ adjusted by us to 25°C, are, respectively, $\Delta H_{298} = 15.04$ (± 0.09) for solution of one gram of glucose in pure water to yield 0.2 molal concentration and $\Delta H_{298} = 14.90$ (± 0.16) for corresponding solution in 1.64 normal hydrochloric acid, but he assumed that the heat of mutarotation was zero. Hendricks and co-workers¹¹ have also reported, without reference to possible mutarotation, 13.85 cal./g for the heat of solution of α -glucose in water at 21.6° to yield a 0.017 molal concentration; this result adjusts to $\Delta H_{298} = 14.53$ cal./g. The result of Parks, Snyder, and Cattoir,¹ which corresponds to $\Delta H_{298} = 14.72$ cal./g, probably involved very incomplete mutarotation, although these workers recognized the possible importance of this effect. The best published work to the present date appears to be that of Sturtevant⁹ who has reported $\Delta H_{298} = 14.22$ (± 0.02) cal./g for the solution of α -glucose, presumably without the mutarotation effect, in water to yield an approximately 0.2 molal concentration. His result is thus about 0.84 calorie below our present average for the non-mutarotated sugar. While his concentration differs considerably from ours, it is really hard to explain such a large difference in heat of solution.

Next, the heats of solution of preparations I and II of the glassy glucose were measured with 0.0125N NH_4OH as the solvent. This solvent was employed because the work of Jacobs and

TABLE II. Heat of solution of pure α -*d*-glucose crystals at 25°C.

Experiment No.	Solvent	ΔH_{298} for solution (cal./g)
BS-1	Pure water	15.090
BS-2	Pure water	15.041
Mean without mutarotation	Pure water	15.065 (± 0.025)
BS-3	0.0125N NH_4OH	14.085
BS-4	0.0125N NH_4OH	14.116
Mean with mutarotation	0.0125N NH_4OH	14.100 (± 0.015)
Enthalpy change of mutarotation	$\Delta H_{298} = -0.965$ (± 0.030)	

¹⁰ F. Barry, J. Am. Chem. Soc. **42**, 1912 (1920).

¹¹ C. B. Hendricks, J. H. Dorsey, R. H. LeRoy, and A. G. Moseley, Jr., J. Phys. Chem. **34**, 418 (1930).

Parks² had indicated that such glucose glass preparations represent a mixture of the alpha- and beta-forms, and hence it seemed desirable to ensure here a final solution of mutarotated product comparable to that obtained when the crystals of α -glucose were previously dissolved in a mutarotating solvent. Our various results with the two glasses, as these were subjected to an aging treatment of from one to sixteen days, have been summarized in Table III. From these data it is noticeable that the heats of solution of Glass I averaged about 10 percent greater (numerically) than those of Glass II.

However, the aging process at 24°C had no appreciable effect on the character of our results, nor did the storage of samples of Glass II for thirteen days at 3° produce any significant change in its heat content as we measured this quantity. Previously, Parks and Reagh³ had observed very appreciable changes in the viscosity of glucose threads when these were aged in the neighborhood of 20° to 30°; and more recently Nelson and Newton¹² have found that the average specific heat between 25° and 30° for a sample of glucose glass increased about 15 percent when stored at 25° for seven days. In view of our present results, it would seem that any appreciable changes in the enthalpy of these glasses with aging must have developed largely within the first twenty-four hours. Moreover, our experimental method, which involved maintaining the glucose glass samples for one or two hours around 24° prior to a solution determination but following the storage for thirteen days at 3°, apparently precluded the observation of such a change of heat content as was noted by Nelson and Newton in their specific heat study.

THERMODYNAMIC CALCULATIONS FOR THE CRYSTAL-TO-GLASS TRANSFORMATION

The thermodynamics of the crystal-to-glass transformation have been previously considered by Parks, Snyder, and Cattoir,¹ but our new data now provide a more accurate basis for such a study with two somewhat different glass preparations.

From the mean results for Glass I in Table III and for the crystals with mutarotation in Table II

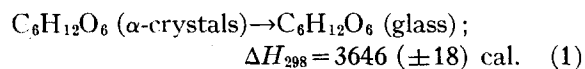
¹² E. W. Nelson and R. F. Newton, J. Am. Chem. Soc. 63, 2178 (1941).

TABLE III. Heat of solution of glassy glucose samples in 0.0125*N* NH₄OH at 25°C.

Experiment No.	Age of sample in days*	ΔH_{298} for solution Glass I	(cal./g) Glass II
GG-1	1	-6.15	—
GG-2	1	-6.22	—
GG-3 and 6	2	-6.07	-5.62
GG-7	2	—	-5.62
GG-8	2	—	-5.58
GG-4	3	-6.27	—
GG-5	3	-6.21	—
GG-9	11	-6.25	—
GG-10	11	-5.98	—
GG-11 and 13	15	-6.00	-5.56*
GG-12 and 14	15	-6.08	-5.62*
GG-15	16	—	-5.61
GG-16	16	—	-5.51
Mean result		-6.14 (± 0.09)	-5.57 (± 0.05)

* The aging of samples was carried out at a temperature of 24°C except in Experiments GG-13 and 14. These two samples of Glass II were aged for 13 days at 3° prior to the solution experiments.

the enthalpy difference is 20.24 (± 0.10) cal./g at 25°C. This yields for the molal process



Above 25°C the glass softens and in the neighborhood of 40° the product in this process becomes obviously a very viscous liquid. An examination of the available specific heat data^{8,12} for crystalline and undercooled liquid glucose indicates that the difference between the heat capacity of the undercooled liquid and the crystalline form is almost independent of the temperature; and accordingly we shall now take the value $\Delta C_p = 35$ cal. per mole between 25° and 146° (the melting point of pure α -glucose crystals). Hence, by Kirchhoff's law, we can calculate for the conversion of a mole of α -crystals into liquid glucose at 146°C

$$\Delta H_{419} = 3646 + 35 (146 - 25)$$

$$= 7881 (\pm 100) \text{ cal.} \quad (2)$$

This result for the heat of fusion of α -glucose crystals is in fairly good agreement with the experimental one obtained by Thomas and Parks⁸ with their radiation calorimeter. Their value for a glucose sample, somewhat contaminated with decomposition products, was 41.7 cal. per gram at 141°, which corresponds to about 7685 cal. per mole at 146°C.

The entropy increase on fusion of the α -crystals

TABLE IV. Thermodynamic data for the transformation α -glucose crystals \rightarrow glassy glucose, per mole.

	Glass I	Glass II	Glass P-S-C
ΔH_{298} in calories	3646	3544	3893
ΔS_{298} in cal./°K	6.87	6.63	7.46
ΔF_{298}° in calories	1598 (± 15)	1567 (± 15)	1669 (± 50)
ΔH_{419} in calories	7881	7779	8128
ΔS_{419} in cal./°K	18.80	18.56	19.39
ΔF_{419}° in calories	0	0	0

at 146° follows directly from the data of Eq. (2):

$$\Delta S_{419} = 7881/419 = 18.80 \text{ e.u.} \quad (3)$$

The entropy change for the hypothetical conversion of a mole of the crystals into glucose glass at 25°C can be evaluated next with the aid of the ΔC_p value used previously:

$$\begin{aligned} \Delta S_{298} &= 18.80 - 35 \ln (419/298) \\ &= 6.87 (\pm 0.07) \text{ e.u.} \end{aligned} \quad (4)$$

By means of the fundamental thermodynamic equation $\Delta F = \Delta H - T\Delta S$, and the data of Eqs. (1) and (4), we can then obtain the molal free energy change for the crystal-to-glass transformation at 25°C:

$$\Delta F_{298}^\circ = 1598 (\pm 15) \text{ cal.} \quad (5)$$

It may be noted that the relatively small uncertainty in this final free energy value is a consequence of a compensative effect in the corresponding uncertainties for the ΔH_{298} and ΔS_{298} values.

Similar data have also been worked out for the case of Glass II, and the preliminary results of Parks, Snyder, and Cattoir have now been revised with 35 for ΔC_p instead of the value of 33 calories per degree, which was originally used. The thermodynamic values for the three glasses are here summarized in Table IV to facilitate comparisons.

From these tabulated data we obtain for the hypothetical transformation, per mole,

$$\begin{aligned} &\text{Glass I} \rightarrow \text{Glass II,} \\ \Delta H_{298} &= -102 (\pm 18) \text{ cal.;} \\ \Delta S_{298} &= -0.24 (\pm 0.06) \text{ e.u;} \end{aligned}$$

and

$$\Delta F_{298}^\circ = -31 (\pm 10) \text{ cal.}$$

Here the uncertainties are those which exist

after the elimination of possible systematic errors, common to the data for both glasses and canceling in a transformation of this type.

Such results strongly support the concept of a *series of glassy states* for a substance, with appreciably different enthalpy and free energy contents, as previously suggested by Parks and Reagh.³

THE HEAT OF MUTAROTATION OF ALPHA-GLUCOSE

Our data in Tables I and II provide new values for the enthalpy change when a mole of α -D-glucose, dissolved in water, is transformed into an equilibrium mixture of the alpha- and beta-forms. By use of the optical rotation values of Isbell and Pigman⁵ we estimate that such an equilibrium solution contains 63.6 percent beta- and 36.4 percent alpha-glucose at 25°C. As our Pfanstiehl crystals initially appeared to be only about 96.0 (± 1.0) percent α -glucose, we now calculate from Table I, for the mutarotation effect starting with a mole of pure α -glucose,

$$\begin{aligned} \Delta H_{298} &= -(0.93)(180.156)(63.6/59.6) \\ &= -178 (\pm 8) \text{ cal.} \end{aligned}$$

Likewise, from the solution data for the pure alpha-crystals of Table II we obtain a somewhat more reliable value of

$$\Delta H_{298} = -(0.965)(180.156) = -174 (\pm 5) \text{ cal.}$$

Accordingly, as a final, weighted mean we shall take $\Delta H_{298} = -175 (\pm 5)$ calories per mole.

As noted in the previous discussion of the heats of solution of glucose crystals, several of the earlier investigators either overlooked this heat effect in mutarotation or assumed that it was zero. Brown and Pickering,¹³ however, obtained a value of 106 cal. per mole in 1897 and Sturtevant¹⁴ reported 162 (± 4) cal. in 1937. More recently, in a second paper⁹ dealing with precise calorimetry, he has found a result of 174.2 (± 0.9) cal., which agrees excellently with our final value of 175 (± 5) calories for this mutarotation process.

¹³ H. T. Brown and S. Pickering, J. Chem. Soc. **71**, 756 (1897).

¹⁴ J. M. Sturtevant, J. Am. Chem. Soc. **59**, 1528 (1937).