[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Heats of Solution of Sugars in Water*

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Standard references such as the "International Critical Tables" and Landolt and Beilstein do not give heats of solution for sugars. Because of the low precision of the apparatus and the uncertain purity of the sugars used, the results of early workers[1] in this field are not acceptable to modern students of calorimetry. More recent work[2] is of higher precision and has indicated greater care for the purity of solutes used.

Method, Apparatus and Sugars Used

The technique of the work here reported has been previously[3] described. The control of conditions for the experiments was improved by a modification of the equipment as indicated in a later paper.[4] The sugars studied were *d*-galactose, β-*d*-glucose, *d*-glucose, *d*-glucose hydrate, α-methyl *d*-glucoside, and α-methyl-*d*-mannoside. The *d*-galactose was Pfanstiehl C. P. special grade with a specific rotation of $(\alpha)^{20}_{\mathrm{D}}$ 80°. The beta glucose was prepared in this Laboratory from Mallinckrodt C. P. anhydrous dextrose using the method of Hudson and Dale[5] and after purification gave the specific rotation $(\alpha)^{0}_{\mathrm{D}}$ 18.2°. The *d*-glucose was Mallinckrodt C. P. sugar with a specific rotation of $(\alpha)^{20}_{\mathrm{D}}$ 52.5°. *d*-Glucose hydrate was prepared by crystallizing it from a concentrated solution of *d*-glucose in water at 2°. The product used had an initial specific rotation $(\alpha)^{20}_{\mathrm{D}}$ 103.1° and melted at 93–94°. The α-methyl-*d*-mannoside was a C. P. chemical from Eastman Kodak Laboratories with a rotation constant of $(\alpha)^{20}_{\mathrm{D}}$ 80.8° and a melting point of 188–189°. The α-methyl-*d*-glucoside was prepared in this Laboratory following a standard method.[6] Its constants were rotation $(\alpha)^{20}_{\mathrm{D}}$ 157° and melting point 164.9°.

Experimental Work

All heats of solution were determined in a calorimeter, the heat capacities of whose inner vessels were found as indicated previously[3] to be a water equivalent of 84.1 for Tables I and II; 53.9 for Table IV and 78.79 for other tables. The last value was checked by an alternative method using heat of neutralization[7] of sodium hydroxide by hydrochloric acid. The 53.9 for the Dewar used for Table IV was checked by use of the heat of solution value,[8] 1019 gram calories per mole, of sodium chloride in water solution. The agreement of the two results in both checks was within the range of experimental error. It will be noted that the first two heats of solution were determined at 21 ± °, while the others were determined at 25 ± °.

In the following tables of results, *W* is the weight of the sugar sample, *T* is the temperature of the calorimeter and contents at the time the sample was introduced and T_f was the minimum temperature attained during the solution of the sugar. T_c is the temperature change corrected for heat of stirring, and by the Bureau of Standards correction chart and stem immersion. H. S. is the heat of solution per gram of solute. The water equivalent for the calorimeter plus its charge of water for the first two tables was 1077.4

TABLE I

HEAT OF SOLUTION OF *d*-GALACTOSE DILUTED TO 0.0004 MOLE OF SUGAR TO ONE MOLE WATER

Expt.	*W*	*T*	T_f	T_c	H. S.
1	3.608	21.7475	21.6775	0.0700	−21.0
2	4.082	21.5610	21.4800	.0810	−21.4
3	3.749	21.6940	21.6180	.0760	−21.8
4	5.228	21.6670	21.5635	.1035	−21.3
			Average value at 21.7 ± °		−21.4

TABLE II

HEAT OF SOLUTION OF β-*d*-GLUCOSE DILUTED TO 0.0004 MOLE OF SUGAR PER MOLE WATER

Expt.	*W*	*T*	T_f	T_c	H. S.
1	3.838	21.5545	21.5345	0.0200	−5.64
2	5.818	21.6550	21.6280	.0270	−5.76
3	2.428	21.7200	21.7075	.0125	−5.54
			Average value at 21.6 ± °		−5.65

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(1) Berthelot and Matignon, *Compt. rend.*, **111**, 11 (1890); M. Berthelot, *Ann. chim. phys.*, [VII] **7**, 51 (1890); Brown and Pickering, *J. Chem. Soc.*, **71**, 756 (1897); Magie, *Phys. Rev.*, **17**, 107, 115 (1903).

(2) Hudson and Brown, THIS JOURNAL, **30**, 960–971 (1908). Barry, *ibid.*, **42**, 1927–1928 (1920).

(3) Hendricks, Dorsey, LeRoy and Moseley, *J. Phys. Chem.*, **34**, 418–426 (1930).

(4) Hendricks and Steinbach, *J. Phys. Chem.*, **36**, 1279–1281 (1932).

(5) Hudson and Dale, THIS JOURNAL, **39**, 323 (1917).

(6) Helferich and Schäfer, "Organic Syntheses," John Wiley and Sons, New York, 1926, Vol. VI, p. 64.

(7) Mathews and Germann, *J. Phys. Chem.*, **15**, 78–80 (1911).

(8) Randall and Bisson, THIS JOURNAL, **42**, 364 (1920).

g., for Tables III, V and VI it was 1073.2 g., while in Table IV it is included under heading C_p.

TABLE III

HEAT OF SOLUTION OF *d*-GLUCOSE DILUTED TO 0.0003 MOLE OF SUGAR PER MOLE OF WATER

Expt.	W	T	T_f	T_c	H. S.
1	2.941	25.0906	25.0525	0.0381	−14.5
2	3.319	25.2503	25.2074	.0419	−14.5
3	3.441	25.3239	25.2793	.0447	−14.5
			Average value at 25.2 ± °		−14.5

TABLE IV

HEAT OF SOLUTION OF *d*-GLUCOSE HYDRATE DILUTED TO 0.0003 MOLE SUGAR PER MOLE WATER

Expt.	W	C_p	T	T_f	T_c	H. S.
1	3.257	1047.0	25.0678	24.9893	0.0785	−25.2
2	3.092	1047.1	25.0678	24.9933	.0745	−25.2
3	3.085	1047.0	25.1003	25.0258	.0745	−25.3
				Average value at 25.07 ± °		−25.2

TABLE V

HEAT OF SOLUTION FOR α-METHYL-*d*-GLUCOSIDE DILUTED TO 0.0003 MOLE OF HEXOSIDE PER MOLE OF WATER

Expt.	W	T	T_f	T_c	H. S.
1	2.913	25.4237	25.4156	0.0081	−3.10
2	4.152	24.3847	25.3727	.0120	−3.15
3	4.566	25.2868	25.2739	.0129	−3.15
			Average value at 25.4 ± °		−3.13

TABLE VI

HEAT OF SOLUTION FOR α-METHYL-*d*-MANNOSIDE DILUTED TO 0.0004 MOLE OF HEXOSIDE PER MOLE OF WATER

Expt	W	T	T_f	T_c	H. S.
1	4.149	24.8541	24.8128	0.0413	−11.1
2	4.128	25.0784	25.0379	.0405	−11.0
3	4.242	25.0485	25.0066	.0419	−11.0
4	4.129	25.1099	25.0692	.0407	−11.0
			Average value at 25.0 ± °		−11.0

Discussion

All solutes reported in this paper, except the two hexosides, are mutarotating sugars. If heat is a factor in the mutarotation of the sugar that heat is an element of the heat of solution as determined in these experiments. An examination of each sugar for such a possibility is pertinent.

Hudson and Dale[5] have shown that the velocity coefficients for alpha and beta glucoses are the same, within the limits of experimental error, from 0–40°. This indicates that the heat of mutarotation of the two forms of *d*-glucose is zero.

Mackenzie and Ghosh[9] report the same optical rotation for *d*-galactose at 12.5° as at 20°. Otherwise stated, an increase in temperature does not alter the proportions of the alpha and beta forms of the *d*-galactose. From this it is inferred that *d*-galactose is another sugar with a zero heat of mutarotation.

From exploratory studies made in this Laboratory, the time–temperature curve for dissolving β-*d*-mannose first drops in temperature, then rises slowly. A plausible explanation of this fact is that the heat of solution is negative while that of the mutarotation of this sugar into α-*d*-mannose is positive. Further work is planned to determine the precise time–temperature curve for the solution of this sugar, from which both its heat of solution and mutarotation may be computed.

From work[10] previously done the optical rotation of β-*d*-fructose at 0° is −161.0 and −123.6° for the equilibrium mixture, while for 14° the rotation for beta is −155°, and for *d*-fructose it is −115.7°. Another paper[11] reports these values for 20° as −133.5° for beta and −92.0° for *d*-fructose. From these facts it is evident that increased temperature decreases the percentage of β-*d*-fructose in the equilibrium mixture. This is just what would result if heat were absorbed by β-*d*-fructose in its transformation into its epimer.

Heat of solution values for *d*-fructose reported[12] as −10.5 calories per gram at 16°, −10.6 calories per gram at 18.7°,[13] and −12.0 calories per gram at 25°[14] even though they may include both a heat of mutarotation and a heat of solution, still these values support the inference drawn in the preceding paragraph that there is a measurable heat of mutarotation for this sugar. To measure this heat of mutarotation, however, requires a careful determination of the time–temperature curve for α-*d*-fructose as it dissolves in water. By use of the data so collected and the constant[15] for the rate of mutatransformation, its heat of mutarotation and true heat of solution may be calculated.

The heat of solution −5.63 for β-*d*-glucose taken from Table II when put with the reported[3] value, −14.0 for α-*d*-glucose, would give a heat of solution of an equilibrium mixture of these sugars, or *d*-glucose, less than −5.63 and more than −14.0. But Table III does not give such an intermediate value for *d*-glucose. At different periods in the course of this investigation, three of us have repeatedly failed to get such an intermediate heat of solution for *d*-glucose. We have, on the other hand, checked these values to within

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[9] Mackenzie and Ghosh, *Proc. Roy. Soc. Edin.*, **36**, 204 (1916).

[10] Patterson, *J. Chem. Soc.*, **109**, 1204 (1916).

[11] Hudson and Yanovsky, THIS JOURNAL, **39**, 1015 (1917).

[12] Brown and Pickering, *J. Chem. Soc.*, **71**, 756 (1897).

[13] Magie, *Phys. Rev.*, **17**, 107 (1903).

[14] Steinbach, unpublished data from this Laboratory.

[15] Hudson and Sawyer, THIS JOURNAL, **39**, 475 (1917).

experimental error for the heats of solution for each of the three glucose sugars. When the heats of solution were measured for samples prepared by mixing solid alpha and beta *d*-glucose in measured proportions approximating the composition of the equilibrium mixture at 20–25°, the experimental results check the calculated heats of solution in a very satisfactory manner.

A comparison of the heat of solution of hydrated glucose with that of *d*-glucose suggests that a small percentage of the hydrate in a sample of *d*-glucose would account for the discrepancy just noted. Preliminary experimental studies made in this Laboratory seem to support this explanation, that commercial dextrose, commonly considered as *d*-glucose, is not strictly anhydrous.

Summary

1. The heats of solution to a dilution of 0.00035 ± mole of solute per mole of water are here reported for the first time as: −21.4 for *d*-galactose, −3.13 for α-methyl-*d*-glucoside, and −11.0 calories per gram of sugar for α-methyl-*d*-mannoside.

2. Redeterminations of heats of solution to the same dilution are presented for *d*-glucose, −14.5; β-*d*-glucose, −5.65, and *d*-glucose hydrate, −25.2 calories per gram of sugar.

3. Heats of mutarotation are shown to be zero for *d*-galactose and *d*-glucose.

4. Heats of mutarotation are proposed as positive for β-*d*-mannose and α-*d*-fructose, and a procedure is suggested for their experimental determination.

5. The inconsistent heat of solution for samples of *d*-glucose is considered and the inconsistency attributed to traces of hydrated glucose in the samples used.

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NOTE

The Reaction of Nitrous Oxide with Hydrogen Atoms

BY J. K. DIXON[1]

The reaction of nitrous oxide with hydrogen atoms has been studied at low pressures. The hydrogen atoms were produced in a discharge at low pressures and the concentration of the atoms measured by means of a calorimetric method. The type of apparatus and the procedure used has been described in detail,[2] so that only certain modifications of the same need be mentioned. Since water was added to the hydrogen which was admitted to the discharge, it was necessary to make blank runs without adding nitrous oxide. Water was expected to form as a result of reaction. The difference between the water collected in the blank experiments and the amount found in experiments with added nitrous oxide, under identical conditions, gave the quantity of water formed in the reaction. The water was collected in a trap by cooling with dry ice and in some cases with liquid air. At the end of an experiment dry air was admitted to the apparatus slowly, the cooling mixture surrounding the trap removed and the water which had been collected was blown through a tared tube containing phosphorus pentoxide. Experiments showed that the air and nitrous oxide were free from water.

Careful tests for oxygen and hydrogen peroxide showed that these substances were not formed to any measurable extent. Table I gives the results of a few typical experiments in which the amount of water formed by reaction was determined. The temperature of the reaction tube was in each case 25°. Owing to the difficulty of obtaining results in the blank experiments reproducible to better than about 2 mg., it is difficult to draw any conclusions with regard to the effects of the hydrogen atom concentration, the nitrous oxide pressure and the amount of water added to the hydrogen upon the amount of water formed. The addition of nitrous oxide always gave a small increase in the amount of water above that in the blank experiment. The maximum increase observed was 5 mg. in thirty minutes. Table I shows that when the water was collected by cooling with liquid air the increase was about the same. There was no appreciable change when the temperature of the reaction tube was changed from 2 to 45°. For example, in certain experiments the quantities of water formed were 2.8, 3.5 and 0.3 mg. at 2, 24.5 and 45°, respectively. Table I

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[1] Sterling Research Fellow in Chemistry, Sterling Chemistry Laboratory, Yale University. Present address, Calco Chemical Company, Inc., Bound Brook, N. J.

[2] Dixon, THIS JOURNAL, **54**, 4262 (1932).