The Solubilities and Heats of Crystallisation of Sucrose and Methyl α-D-Glucoside in Aqueous Solution.

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The solubilities and heats of crystallisation of sucrose and methyl α-D-glucoside have been determined over the temperature range 20—80° by a new method. The heats of crystallisation have been calculated from these results and activity data.

In a new method of determining the solubility of solids described by Dauncey and Still (*J. Appl. Chem.*, 1952, **2**, 399) the saturation temperature of a solution of fixed concentration is determined within only a few minutes. This is useful in determining the solubility of sucrose in water where decomposition becomes important at the higher temperatures if the experiments are too prolonged, and where equilibrium is reached only after many hours at lower temperatures. Previous determinations of the solubility of sucrose have given results which are not in complete agreement (*e.g.*, *Nat. Bur. Stand.*, Circular C440, 1942, p. 359).

Heats of crystallisation are readily calculated from solubility and activity data (Williamson, *Trans. Faraday Soc.*, 1944, **40**, 435). The heat of crystallisation of sucrose has therefore been calculated and, for comparison, that of methyl α-D-glucoside for which activity data exist. No solubility data appear to be available however, so that the solubility of methyl α-D-glucoside has been determined in the same way as that of sucrose.

Experimental

The sucrose used was selected granulated sugar of reducing sugar content less than 0·02% and ash content less than 0·01%. About 1 l. of a 50% solution of sucrose was concentrated at 60° at a water-pump, until a convenient concentration was reached as determined by a refractometer. The temperature of the solution was then quickly raised and the flask removed and fitted with a wash-bottle head. The contents were well shaken and then transferred through the tube of the head to the solubility cell.

This consisted of a 2″ T-piece pipe-fitting which had been machined smooth and silver-plated. Its capacity was about 100 ml. The end faces carried Perspex discs with a rubber gasket between them. The short upright arm of the T-piece carried a rubber stopper through which passed a stainless-steel stirrer, a thermometer graduated in 0·1°, and the entry tube for the solution. The last was joined to the tube of the wash-bottle head through a ground-glass joint which was normally closed with a stopper. The whole cell was contained in a Perspex box, about 4″ × 4″ × 6″, through which water was circulated by a centrifugal pump. Included in the system of circulating water was a conical flask which could be heated or cooled, thus adjusting the temperature of the sucross solution in the cell. There was very little lag between the temperature of the well-stirred sucrose solution and that of the circulating water.

On the outside of the Perspex box was a slit formed by two razor blades behind which was placed a 40-w. lamp. When the cell was assembled a sucrose crystal was clipped to the thermometer with a rubber band. By viewing the slit behind the crystal the saturation temperature of the sucrose solution could be determined as described by Dauncey and Still (*loc. cit.*). The solution was heated or cooled through the saturation temperature a number of times and the average value determined for each solution. Readings agreed to within 0·1—0·2°. The stem correction for the thermometer amounted to 0·5° at 90°.

After the saturation temperature had been determined, a sample of the solution was removed by a pipette from the solubility cell and transferred to a weighed 50-ml. flask through a glass sleeve to prevent sucrose solution from adhering to the neck of the flask. The flask was then quickly closed with a rubber stopper and allowed to cool. The weight of sucrose solution was determined by weighing and the contents of the flask were made up to volume. This was carried out in an air-conditioned room. The sucross concentration was then read in a Hilger polarimeter.

A sample of this diluted solution was taken for determination of reducing sugar by a modified ferricyanide method (J. H. Williams, unpublished work) which is insensitive to the presence of large amounts of sucrose.

In a separate series of experiments, no effect could be found due to rate of heating or cooling of the sucrose solution. The rates used in the experiments were less than 1·5° per min.

The experiments with methyl α-D-glucoside were carried out in the same way as those with sucrose. The material used had m. p. 165° and $[\alpha]_D^{20}$ +158·8° (cf. Rüber, *Ber.*, 1924, **57**, 1797: m. p. 166°, $[\alpha]_D^{20}$ +158·9°).

RESULTS

The results obtained with sucrose are shown in Table 1. These have been fitted by the method of least squares to a power series equation giving $C = 62{\cdot}77 + 0{\cdot}1706t + 0{\cdot}000344t^2$, where C is the saturation concentration (g. of sucrose per 100 g. of solution), and t is the saturation temperature.

TABLE 1. *Solubility of sucrose in water.*

Concn. (g./100 g. soln.)	Satn. temp.	Sucrose inverted (%)	Concn. (g./100 g. soln.)	Satn. temp.	Sucrose inverted (%)	Concn. (g./100 g. soln.)	Satn. temp.	Sucrose inverted (%)
66·09	18·5°	—	72·51	51·1°	0·020	75·80	66·4°	—
66·97	23·9	—	72·72	52·2	—	75·95	66·5	0·021
66·89	24·4	—	72·76	52·6	—	76·07	68·2	—
67·23	24·9	—	73·04	53·6	0·016	76·03	69·0	0·015
67·21	25·9	—	73·05	53·8	—	76·32	70·1	0·021
68·36	30·0	—	72·78	54·1	—	76·45	70·4	—
68·31	30·5	0·026	73·16	55·8	—	77·06	72·8	—
68·73	31·5	—	73·50	56·1	—	76·98	73·8	0·025
68·62	33·1	—	73·72	56·4	—	77·60	74·5	—
69·32	34·5	—	73·64	57·5	—	77·52	74·6	—
69·42	36·0	—	73·74	57·8	—	77·58	75·1	—
69·41	36·4	—	73·68	58·4	—	78·40	79·5	—
70·17	40·2	—	74·10	58·6	—	78·86	82·3	—
70·23	40·7	—	74·15	59·7	0·015	79·85	85·1	0·016
70·35	41·0	0·024	74·48	61·1	—	79·94	85·3	—
70·55	42·2	—	74·47	61·4	—	79·99	85·5	0·023
70·74	42·3	—	74·69	62·6	—	80·22	86·6	—
71·63	46·1	—	74·93	62·9	0·018	80·32	88·0	—
72·12	49·6	—	75·05	64·6	—	80·87	90·2	0·014
71·91	50·2	0·017	75·43	65·5	—			

The results for methyl α-D-glucoside are shown in Table 2. These were fitted to the equation $C = 44{\cdot}86 + 0{\cdot}2495t + 0{\cdot}00120t^2$.

TABLE 2. *Solubility of methyl* α-D-*glucoside.*

Concn.	70·90	68·78	66·70	66·08	65·25	64·71	64·02	62·40	61·48	60·79	59·78
Temp.	78·0°	73·2	67·8	66·2	64·2	62·7	60·6	57·3	54·4	51·8	49·6
Concn.	59·42	57·31	55·33	54·48	53·42	52·41	52·36	51·59	51·20	49·38	
Temp.	49·0°	43·2	37·2	33·9	31·8	27·3	26·6	25·5	22·5	17·8	

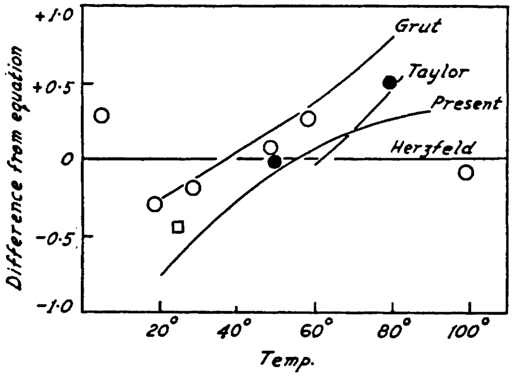
DISCUSSION

Solubility Results.—The present results for sucrose are compared with those of other workers in the Figure, where the difference between the saturation concentrations and those given by the equation $C = 64{\cdot}18 + 0{\cdot}1348t + 0{\cdot}000531t^2$ is plotted as a function of temperature. This equation is the smoothed curve through Herzfeld's results (*Z. ver. Rübenz.-Ind.*, 1892, **42**, 181). It will be seen that the present results deviate fairly considerably from this equation, especially at the lower temperatures. Herzfeld's experimental results, also plotted, do not fit the smoothed equation very well. The four results at intermediate temperatures fall on a curve lying parallel to and slightly above the present results. At 5·2° the determined saturation concentration, which was approached from supersaturated solution, is apparently too high.

Grut (*Z. Zuckerind. cechoslovak. Rep.*, 1937, **61**, 356) determined the solubility of sucrose at 10° intervals from 20° to 80°. The general trend of his results is in agreement with the present results and Herzfeld's experimental results at intermediate temperatures, although the saturation concentrations are all higher than those we have found.

There are isolated determinations at 25° by Scatchard, Hamer, and Wood (*J. Amer. Chem. Soc.*, 1938, **60**, 3061) and at 50° and 80° by Hruby and Kasjanov (*Intern. Sugar J.*, 1940, **42**, 21), the latter being the average of ten determinations. These agree fairly well with the present results.

Probably the best solubility results for sucrose are those of Taylor (*J.*, 1947, 1678). They cover a rather narrow temperature range, but within this are in good agreement with ours. There is a slight deviation above 75°, probably due to the fact that for the two experiments which Taylor carried out above 80° inversion was more serious than at the lower temperatures. Inversion is not significant for the present results, however, as the concentrated sucrose solutions were prepared by vacuum-distillation at moderate temperatures and not by dissolving solid sucrose at temperatures about 10° above the saturation temperatures, the method used by Taylor. Moreover, the determination of the saturation temperature required only a short time by the present method.



Comparison of various determinations of sucrose solubility.

The full lines represent smoothed values. Experimental results are expressed as follows :

○ Herzfeld ; ● Hruby and Kasjanov ; ☐ Scatchard, Hamer, and Wood.

Heats of Crystallisation of Sucrose and Methyl α-D-*Glucoside*.—Williamson (*loc. cit.*) has given a convenient summary of the formulæ for combining solubility and activity data to give heats of crystallisation. For activity data the following have been used. For sucrose at 25° the isopiestic data quoted by Harned and Owen ("Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1950, p. 289), for methyl α D-glucoside at 30° the vapour pressure data given by Berkeley *et al.* (*Phil. Trans.*, 1919, **218**, *A*, 295), and at 60° and 90° unpublished vapour-pressure data of R. W. Jackson (sucrose) and W. J. Read (methyl α-D-glucoside) provided by Dr. W. J. Dunning.

The calculated heats of crystallisation are shown below in Table 3. The heats of crystallisation of the two sugars are approximately equal and increase markedly with temperature. (cf. Davies and Griffiths, *Trans. Faraday Soc.*, 1953, **49**, 1405).

TABLE. 3. *Calculated heats of crystallisation.*

Temp.	25°	30°	60°	90°
Sucrose (kJ/mole)	12·2	—	18·8	31·8
Methyl α-D-glucoside (kJ/mole)	—	15·5	18·5	31·0

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