335. *The Solubility at High Temperatures of Pure Sucrose in Water.*

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A method of determining the solubility of sucrose at high temperatures has been devised which avoids the necessity of analysis of the solution. In its present form it has been found applicable only to temperatures between 64° and 82°. The relationship between saturation concentration and temperature is expressed by an equation which enables the results to be used in the determination of other thermodynamic properties of sucrose solutions.

THE method to be described was devised with the object of avoiding the filtration at high temperatures and the handling for analytical purposes of highly concentrated, viscous sucrose solutions. The behaviour of a crystal of sucrose in approximately saturated solution of accurately known concentration is observed microscopically during both falling and rising temperature, and the temperatures of incipient healing and erosion are noted. The mean of these two temperatures is taken as the saturation temperature of the solution. The first experiments on these lines were carried out by Dr. A. Wischin, but as she was unable to continue the work, the author undertook preliminary experiments which showed considerable deviation from the results of previous investigators (Herzfeld, *Z. ver. Rübenz.-Ind.*, 1892, 181, 232; Nuszbaum and Grube, *Z. Elektrochem.*, 1928, **34**, 91; Grut, *Z. Zuckerind. Czechoslovak*, 1937, **61**, 356). After some modification of the original apparatus and calibration of all precision instruments, the experiments described below were carried out.

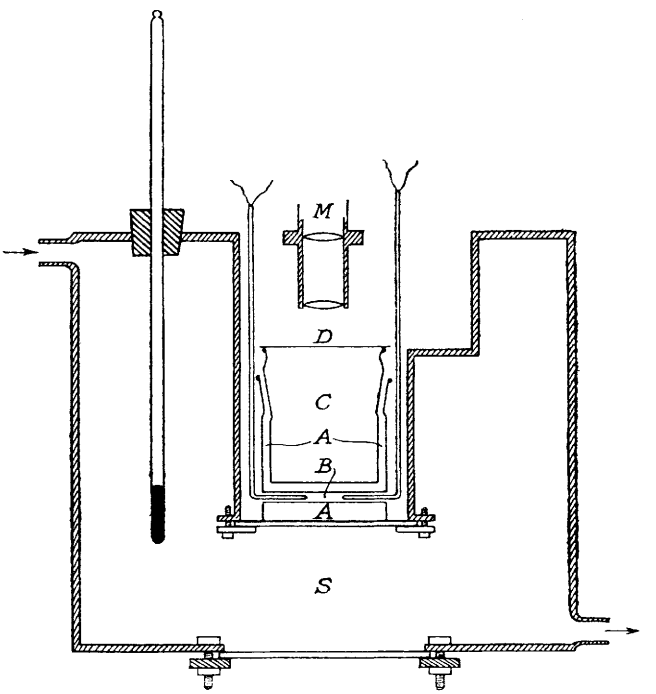
EXPERIMENTAL.

Apparatus.—A glass cell, *A* (Figs. 1 and 2), provided with a horizontal tubular observation shelf, *B*, is closed by a hollow stopper, *C*, the bottom of which is of plane optical glass. The cell slides into a cylindrical water-tight well in the cover of a small lagged thermostat, *S*, the temperature of which is controlled by water pumped from a large thermostat. The lower opening of the well and a corresponding circular opening in the bottom of the thermostat are closed by adaptable plane-glass plates, each held in position by a brass ring and rubber washer. The cell is illuminated through the glass plates by a reflected beam from a 100-watt lamp. A copper–constantan thermocouple consisting of two junctions in series passes into the tubular space under the shelf. The junctions and leads are enclosed for a length of about 8 cm. in very thin drawn-out glass tubing, which is bent at right angles to fit snugly against the side of the cell. A space is left between the junctions to allow of unobstructed microscopic observation of a crystal placed on the shelf between the two junctions. The plate *D*, also of plane optical glass, covering the hollow stopper, is required to prevent irregularities of temperature due to convection currents. Strips of tin foil, in all some 7 or 8 yards in length, are smoothly packed outside the cell and leads, and serve to prevent convection currents in, and to aid conduction of heat across, the annular space surrounding the cell. The latter is also provided with a copper collar carrying a rubber flange which

assists in closing any remaining air space. A mark inside the cell indicates the level at which the solution should stand before insertion of the stopper, which dips considerably under the surface of the solution. A Winkel–Zeiss camera microscope, *M*, which has a visual magnification of about 40 diameters, is used for observation of the crystal.

Calibration.—The thermocouple is calibrated up to 86° on a millivoltmeter reading up to 7 mv., against a standard thermometer (N.P.L.) graduated in 0·1° and correct to 0·02°. For calibration, the thermometer and the thermocouple are immersed to a depth of about 7 cm. in a narrow tube of mercury suspended in a thermostat. The temperature is regulated and read by means of a levelled telescope to about 0·02°. The millivoltmeter is graduated to 0·05 mv. and the reading can be estimated to about 0·005 mv., which corresponds on this instrument, using the two junctions, to approximately 0·05°. The accurate measurement of any temperature difference between the thermocouple under the shelf and the solution on the surface of the latter was initially found to be a matter of some difficulty. The problem was ultimately solved by calibrating the thermocouple *in situ* against the setting or melting points of highly purified samples of palmitic, stearic, and behenic acids, of which the respective setting points are 62·66°, 69·60°, and 80·02° (Professor F. E. Francis, unpublished work). *p*-Chloronitrobenzene, s. p. 83·04°, proves satisfactory at the somewhat higher temperature. The m. p.s were redetermined against

FIG. 1.



Solubility cell in thermostat.

the N.P.L. standard, which was used to calibrate the thermocouple. A sharp m. p. giving reliable results in the second decimal place could not, at first, be obtained. For example, in the case of stearic acid, which gave the least satisfactory value, the recorded m. p. lay between 69·48° and 69·60°. With palmitic acid and behenic acid, the corresponding range was almost negligible. The m. p.s so determined are 62·56°, 69·54° (mean), and 80·00°, respectively.

Two thermocouples, *X* and *Y*, have been used during these experiments. The former was in use during the period when it was impossible to obtain insulating sleeving, and short lengths of drawn-out glass tubing were slid over the leads as a somewhat inconvenient substitute. For the purpose of calibration a small quantity of the ground, purified compound was sealed into a very thin flattened glass tube, which replaced the sucrose crystal on the observation shelf. The cell was then filled up to the mark, in one case with sucrose solution of one of the experimental concentrations, and in another case with water. The change from water to sucrose solution did not affect the readings.

An example of the results obtained by the control calibration of thermocouple X is given in Table I.

The use of this mean takes into account the uncertainty in the m. p. of stearic acid and the fact that its m. p. lies between those of the other two acids. Subsequent checking of this calibration showed no significant change in the correction.

When thermocouple Y was prepared, insulating sleeving was available and a smoother and more compact tinfoil jacket was applied to the cell. Also, it was found possible to get a sharper comparison of the thermocouple and the standard thermometer by taking as identical in the melting point tube and in the solubility cell the temperature at which crystals shoot out from a partly molten mass, causing the smooth liquid meniscus to become irregular (setting point) or melting back to allow the smooth meniscus

TABLE I.

M. p.s of standards used for calibration of thermocouple X.

Acid.	In m. p. tube.	In solubility cell, read on milivoltmeter.	Correction on thermocouple.
Palmitic	62·56°	62·40°	+0·16°
Stearic	69·54 (mean)	69·45	+0·09
Behenic	80·00	79·84	+0·16
		Mean	+0·16

to re-form (melting point). The difference between the setting and melting points determined in this way lay within the accuracy of calibration of the standard thermometer.

For these reasons, the calibration of thermocouple Y is probably of higher accuracy than that of thermocouple X. The results of the calibration of thermocouple Y are given in Table II.

TABLE II.

M. p.s of standard substances.

Date.	Substance.	In m. p. tube.	In solubility cell, read on millivoltmeter.	Correction on thermocouple.
June, 1945	Palmitic acid	62·62°	62·57°	+0·05°
	Stearic acid	69·54	69·51	+0·03
	p-Chloronitrobenzene	83·04	83·00	+0·04
			Mean	+0·04
	Repeated after removal of tinfoil and repacking.			
Sept., 1945	Palmitic acid	62·56	62·57	−0·01
	Stearic acid	69·54	69·55	−0·01
	Behenic acid	79·91	79·94	−0·03
			Mean	−0·02

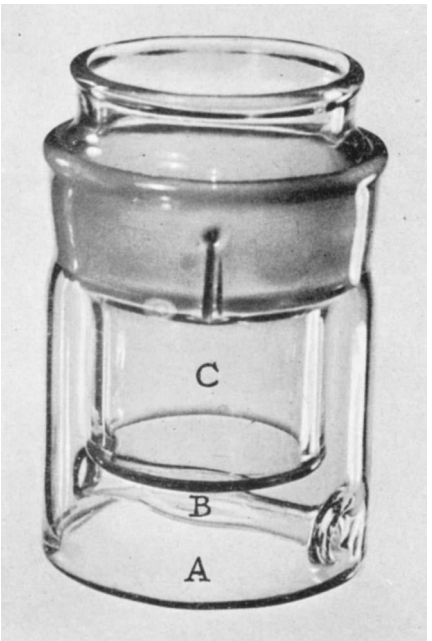
These corrections are within the limits of the error on the thermocouple readings, but they indicate that care must be taken in packing the cell and that frequent recalibration is advisable.

Procedure.—Tate and Lyle's purest sucrose containing on a dry basis 99·99% of sucrose and 0·001—0·003% of invert sugar is very finely ground and dried to constant weight in a vacuum oven under standard conditions (see International Commission for Uniform Methods of Sugar Analysis, London, 1936), *i.e.*, at a temperature not exceeding 60°, in a stream of dried air, the pressure not being allowed to exceed 5 cm. Hg. The air-drying agent used is an activated alumina, having a drying efficiency more than a 1000-fold that of calcium chloride. After being dried, the sucrose is transferred by means of a long, wide thistle funnel to a long-necked, weighed bulb of about 60 c.c. capacity. The lower part of the neck of the bulb has an internal diameter of at least ½″ to allow of unhindered outflow of the viscous solution. The calculated weight of conductivity water for any required concentration is added from a weight burette, provided with a long delivery tube. After thorough mixing at room temperature, the contents of the flask are rapidly frozen in solid carbon dioxide–methylated spirit and after constriction of the neck of the flask the latter is exhausted, the contents are allowed to warm up without admission of air, and the freezing and exhaustion are repeated. The flask is then sealed, subjected to violent automatic shaking for at least an hour at a temperature several degrees higher than the saturation point, and after rapid cooling in ice-water the solution is allowed to reach room temperature for a control weighing.

The seeding crystals, at least two in number and as small as can conveniently be handled, of linear dimensions 0·5—0·25 mm. or less, are placed in position on the shelf of the cell which, with its thermocouple in position, is now connected with the millivoltmeter and is ready to be put into the thermostat. All necessary regulation of the thermostats must be made before the bulb is opened. The cell must, of course, be cold, but the stopper should be slightly warm and greased with a mixture of apiezon grease plus 25% of aluminium stearate. The neck of the bulb, which is clean and dry inside, is then cut across the wide part, and a weighed rubber bung is inserted. After a final control weighing, the result of which has in no case differed by as much as 0·01% from the initial weight of the solution, the latter is cooled to the dew point as determined by a Casella whirling hygrometer, and is quickly poured into the cell. After being closed and before being transferred to the thermostat, the latter is put into a closely fitting, dry beaker and rapidly heated in an electrically controlled water-bath until the temperature indicated by the thermocouple approaches the saturation temperature. The object of this is to check the growth of the seeding crystals and of any centres of crystallisation which are liable to form as the cold solution is poured into the cell. The initial formation of a few such chance crystals may be advantageous as they are very small relatively to the original seeding crystals, are perfectly shaped, and while the smallest disappear rapidly when the saturation temperature is overstepped, a larger one can frequently be retained as a very sensitive temperature indicator. In solutions of higher concentration, 80% and upwards, the deposition of crystals becomes unmanageable, putting an upper limit to the range of concentrations to which this method has been found applicable.

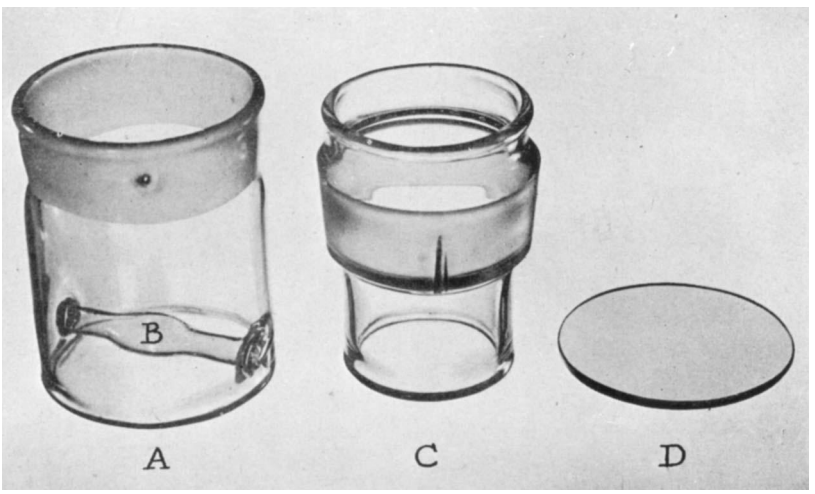
In the thermostat there is considerable time lag in the response of the cell temperature to the thermostat regulation. The lag is probably due to the residual air space in the well of the thermostat and is liable to lead to overstepping of the crucial temperature in either direction. This disadvantage has to some extent been overcome by changing the temperature very slowly. A rate of change of 0·02° per minute has been aimed at, and in most cases it has not been exceeded. A slow rate of change has disadvantages,

FIG. 2*a*.



Solubility cell. (*Actual size.*)

FIG. 2*b*.



Solubility cell. ($\frac{3}{4}$ *Actual size.*)

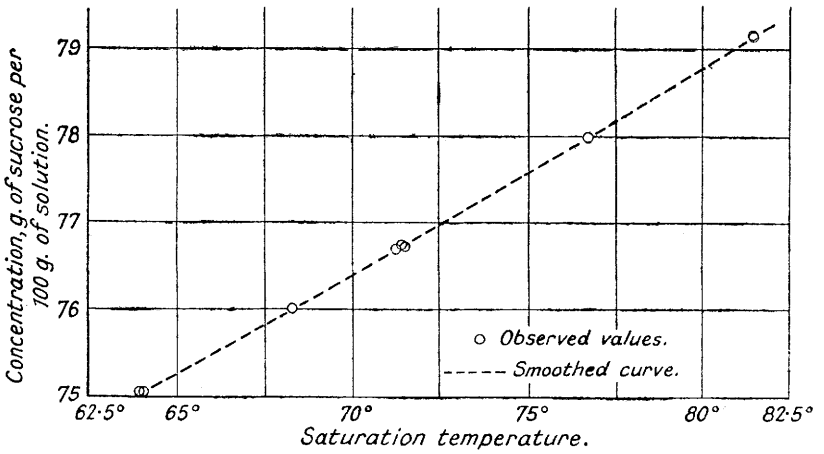
[*To face p.* 1680.

for example, the considerable inversion which is liable to take place, and the possibility of the formation of localities of different concentration either in layers or in the neighbourhood of the crystal. Cautious rocking of the whole thermostat is the limit of disturbance permissible on account of the liability of the crystal to escape from the field of vision, with consequent failure of the experiment. To detect possible errors due to the above-mentioned changes, two pairs of observations of incipient solution and healing temperatures have, when possible, been made with any one solution, and since the results have been found to agree within the limits of the experimental error, the mean of the two pairs of readings is taken as the saturation temperature.

Preliminary experiments were carried out with solutions having saturation temperatures lying between 59° and 62°, but owing to the slow rates of solution and growth at these temperatures, extremely long periods of watching were required, there was a wide interval between the observed incipient erosion and healing temperatures, and the results are somewhat irregular. It was, therefore, decided to limit the experiments to temperatures higher than 64°.

Table III contains a complete record of all the results except those of the above-mentioned tentative experiments and those that gave no reliable result on account of breakdown of the thermocouple or other obvious accident.

FIG. 3.



Solubility of sucrose in water.

The solutions are arranged in order of concentration. The letters in the first column give the order in which the solutions were prepared and investigated. The missing letters refer to solutions which gave no result for one or other of the reasons stated above. The numerals in brackets beside the actual temperature readings record the length of time in hours for which the solution had been in the cell when the reading was taken. The final percentage of sucrose inverted, estimated as described later, is recorded in the last column. The remainder of the table is self-explanatory.

TABLE III.

Saturation temperatures of sucrose solutions varying in concentration from 75 to 79 g. of sucrose per 100 g. of solution.

Soln.	Concn., g./100 g. solution.	Thermo-couple.	t_1. Incipient erosion.	t_2. Incipient healing.	Saturation temp., $\frac{t_1 + t_2}{2}$.	Total time in cell (hrs.).	% inverted
F	75·036	X	64·21° (4)	64·04° (2½)	64·13°	8	0·07
D	75·047	X	64·45 (3)	63·50 (4)	63·98	6	0·22
E	75·050	X	(i) 64·26 (2½)	—	—	—	—
			(ii) 64·26 (5)	64·03 (5½)	64·15	6½	0·18
Q	76·010	Y	68·33 (4½)	68·23 (2)	68·28	5¾	0·13
N	76·699	Y	(i) 71·28 (2¼)	71·18 (1¼)	71·23	—	—
			(ii) 71·28 (3¼)	71·18 (4)	71·23	7½	0·20
J	76·730	X	(i) 71·57 (½)	71·46 (1¼)	71·52	—	—
			(ii) 71·65 (3)	71·35 (3¼)	71·50	3½	0·07
G	76·740	X	(i) 71·50 (1¾)	71·32 (1)	71·41	—	—
			(ii) 71·55 (5½)	71·32 (6)	71·44	7	0·31
H	76·747	X	71·58 (2¾)	71·22 (3¼)	71·40	8	0·10
R	77·994	Y	76·80 (4½)	76·65 (3¼)	76·72	7½	0·17
O	79·144	Y	81·44 (5½)	81·40 (2)	81·42	7¾	0·50
M	79·172	Y	81·44 (3¼)	81·34 (1¼)	81·39	7½	1·0

Fig. 3 is a graphic record of the results collected in Table III. The broken line represents the smoothed curve of best fit, calculated by the method of least mean squares, on the assumption that the

concentrations are correct to the third decimal place. The mean of two determinations of saturation temperature for one and the same solution is given the same weight in the calculation as the single determination in the case of the other solutions.

The equation for the curve is $C = 63{\cdot}608 + 0{\cdot}1322t + 0{\cdot}00722t^2$, where C is the concentration in g. of sucrose per 100 g. of solution and t is the saturation temperature (°C.). The calculated probable error of observation is $\pm 0{\cdot}053°$ in the sense that the chances that the error is greater or less than the true value are even. This error is of the same order as the observed uncertainty in the reading of the millivoltmeter.

The readings in Table III, recording saturation temperatures at different times for any one solution, show that any progressive change such as inversion or possible evaporation during the observations has had no appreciable effect on the saturation temperature. Also, different solutions of approximately the same initial concentration give closely concordant values.

TABLE IV.

Saturation concentrations of aqueous solutions of pure sucrose from 64° *to* 82°, *in g. per* 100 *g. of solution.*

Temp.	Herzfeld.	Grut.	Taylor.	Temp.	Herzfeld.	Grut.	Taylor.
64°	74·98	75·41	75·026	74°	77·06	77·71	77·345
65	75·18	75·64	75·251	75	77·27	77·95	77·584
66	75·38	75·86	75·478	76	77·48	78·18	77·825
67	75·59	76·09	75·706	77	77·70	78·42	78·068
68	75·80	76·31	75·936	78	77·92	78·66	78·312
69	76·01	76·54	76·168	79	78·14	78·90	78·558
70	76·22	76·78	76·400	80	78·36	79·15	78·805
71	76·43	77·01	76·634	81	78·58	—	79·053
72	76·64	77·24	76·869	82	78·80	—	79·305
73	76·85	77·47	77·106				

A final control determination of the concentration is impracticable on account of the small size of the cell, the fact that the stopper dips deeply into the viscous solution, and the necessity of removing the stopper before the solution is uniformly cold. Nevertheless, the percentage of sucrose inverted is not affected by evaporation occurring after opening the cell and is determined, after suitable dilution, by refractometer and polarimeter readings. Where inversion is very small the result has been checked by means of de Whalley's colorimetric method (*Intern. Sugar J.*, 1937, **39**, 300; 1944, **46**, 211).

This method has the advantage over methods hitherto described (see below) that the concentration is accurately known and, as the results show, is maintained appreciably constant till the readings are complete. Exposure to the atmosphere occurs only on transfer of the solution to the experimental cell, after accurate cooling to the dew point which, in the absence of crystals, presents no difficulty.

Table IV records saturation concentrations for whole degrees calculated from the equation of the smoothed curve. For purposes of comparison the corresponding saturation concentrations given by Herzfeld and by Grut (*locc. cit.*) are also included. All weights are uncorrected for buoyancy. Herzfeld's equation was $C = 64{\cdot}1835 + 0{\cdot}13477t + 0{\cdot}0005307t^2$ (no probable error given), and calculation shows that his curve would cut ours at 62°. Grut did not suggest an equation.

Discussion.—Herzfeld's equation is undoubtedly distorted by the fact that after a solution had been heated for a long period at 90—100°, he determined the saturation concentration of the solution at *ca.* 100° solely by a polarimeter reading. Also, he took no measurements between that temperature and 60°. Experiments in this laboratory have shown that at temperatures exceeding 85° inversion becomes rapid even in a vacuum, and the process is hastened by the presence of air. Consequently, the actual concentration in the above experiments of Herzfeld must have been considerably higher than that indicated by the polarimeter on the assumption that the percentage of invert present was negligible. Grut (*loc. cit.*), on the other hand, gives no satisfactory indication as to how he attacked the problem of loss of water by evaporation. It is, therefore, probable that Herzfeld's saturation concentrations above 60° are too low and Grut's too high. Our values fall between the two. Inspection of Table IV shows that in the concentration region of 78·80%, Herzfeld's saturation temperatures are about 2° higher than ours and Grut's about $1\frac{1}{2}°$ lower.

There is some confirmation of the validity of our equation in a determination of the solubility of sucrose at 25° by Scatchard, Hamer, and Wood (*J. Amer. Chem. Soc.*, 1938, **60**, 3061), who used an isopiestic method which appears to be extremely accurate as far as temperature measurement is concerned, though the method of drying otherwise pure sucrose is less reliable than the standard method used by us. Nevertheless, the recorded solubility of 67·44 g. of sucrose per 100 g. of solution (corrected for buoyancy) is probably more accurate than any other practically determined value, and it agrees remarkably with the extrapolated value of 67·357% at 25° calculated from our equation, and corrected in this example for buoyancy. If there were error appreciably greater than the calculated probable error in our results, extrapolation should expose it.

In conclusion, it may be pointed out that any method which tends to increase the accuracy of the determination of saturation concentrations is important for the calculation of other thermodynamic relationships. For example, Williamson (*Trans. Faraday Soc.*, 1944, **40**, 435, eqn. 34) has introduced the quantity $(dm/dt)_{sat.}$, where m = mols. of sucrose/1000 g. of water, into an exact equation for the calculation of heats of solution. This quantity is immediately obtained, for any given value of t, from our equation by substitution for C in terms of m and differentiation.

My thanks are due to Mr. Philip Lyle, of Messrs. Tate and Lyle, Ltd., for arranging that this work shall be submitted for publication, to Professor W. E. Garner, C.B.E., F.R.S., for suggesting the method and for helpful advice, and also to Miss Marjorie J. Littleton, B.A., for calculating the equation for the smoothed curve and the probable mean error of the experiment.

This work has been carried out by arrangement with the Ministry of Food, Sugar Division.

THE UNIVERSITY, BRISTOL. [*Received, February 7th*, 1947.]