524. *The Vapour Pressures of Concentrated Aqueous Sucrose Solutions up to the Pressure of* 760 *mm.*

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A method of determining the vapour pressure of pure sucrose solutions at relatively high temperatures is described. The design of the apparatus affords accurate control of the weight composition of the solution throughout the measurements and avoids errors inherent in earlier methods.

Systematic results covering a wide range of concentration and temperature are recorded. An empirical equation, relating vapour pressure to temperature, and enabling the elevation of the boiling point to be calculated, has been derived.

ALTHOUGH various investigators (Robinson and Sinclair, *J. Phys. Chem.*, 1933, **37**, 495; *J. Amer. Chem. Soc.*, 1934, **56**, 1830; Scatchard, Hamer, and Wood, *ibid.*, 1938, **60**, 3061) have used the isopiestic method for the determination of the activities of sucrose solutions at relatively low temperatures, the method has not been applied at higher temperatures. Attempts to determine systematically and accurately the vapour pressures of concentrated solutions at higher temperatures appear to be restricted to the work of Spengler, Böttger, and Werner (*Z. Wirtsch. Zückerind.*, 1938, **88**, 521). Neither the work of Perman and Saunders (*Trans. Faraday Soc.*, 1923, **19**, 112) nor that of Downs and Perman (*ibid.*, 1927, **23**, 95) covers concentrations higher than 76%, *i.e.*, 76 g. of sucrose in 100 g. of solution, nor does either supply data for any one solution over a comprehensive range of temperature. Spengler's interest is centred mainly on the technically important question of the relation between the elevation of the boiling point and the pressure as read on the manometer. He appears not to have made adequate allowance for the superheating and other sources of error in the modified Beckmann method employed by him. Notwithstanding this, his experiments give results which, in general, appear to be concordant among themselves.

We have endeavoured to determine the vapour pressures of sucrose solutions at various temperatures and concentrations by a method designed to be capable, in favourable conditions, of rigid measurement of these quantities. This method depends on the attainment of a true static equilibrium.

EXPERIMENTAL.

In the course of this work, we have several times had occasion to modify the apparatus. The present form is shown in Fig. 1. It consists essentially of a flask *A* containing the solution to be investigated, connected with one limb of the manometer *B*, the other limb of which is connected with the barometer. The pressure in the barometer can be adjusted to be equal to the vapour pressure in flask *A* by admitting or withdrawing air through the two-way tap *M* until the mercury is at the same level in the two arms of the manometer. To give freedom of movement, the manometer is connected through the train of tubes to the barometer by means of thick, water-jacketed pressure tubing, and is immersed in a rocking thermostat *C*. This is provided with a glass window *W* and is kept at a temperature about 1° higher than that of the main thermostat. By means of the air reservoir *L* under adjustable mercury pressure, the apparatus is adapted for use at pressures somewhat higher than atmospheric. The arrangement shown in Fig. 1*a*, consisting of a strong metal T-piece working in a glass socket, permits of free rotation of the tap attached to cork *D*, while the springs prevent leakage under excess internal pressure. For temperatures up to about 90°, the liquid used in the thermostats is water, covered, in the main thermostat, by crude heavy paraffin. For higher temperatures, dry crude paraffin is used in the main thermostat and refined paraffin in the rocking thermostat.

The Precision Apparatus.—The working thermometer, graduated in 0·1°, is calibrated at intervals of 5° against a National Physical Laboratory standard of which the limit of accuracy is ±0·02°. Besides being independently calibrated in the neighbourhood of 100° against the b. p. of water at known atmospheric pressure, its readings have been checked in the vapour-pressure apparatus by the determination of the vapour pressure of water at intervals of 5° from 60° upwards. The Reichsanstalt values for the temperatures corresponding to the different vapour pressures are taken as correct. Each thermometer reading in the apparatus is corrected for exposed stem. The barometer is enclosed in a water jacket, the temperature of which is read immediately after the pressure. Both the barometer and manometer readings are corrected for pressure towards the centres of curvature of the mercury menisci. A cathetometer is used for the reading of the mercury levels. The barometer readings are corrected for temperature and also for the effect of latitude on gravity. The glass barometer scale has been compared with a Zeiss scale over lengths of 100 mm. and the average divergence is found to be 0·07 mm.

In the earlier experiments, owing to the slight up and down temperature swing of 0·03—0·08°, causing a corresponding swing in the mercury levels in the manometer, the temperature was read at the instant that the mercury became level in the arms of the manometer. This necessitated two operators. In the later observations at higher temperatures, giving pressures approximately atmospheric, the use of an improved thermoregulator containing chlorobenzene greatly reduces this temperature variation and enables one operator (H. C. E.) to carry on the work. Increased accuracy is also attained by the use of a short-range N.P.L. calibrated thermometer, graduated in 0·05° and especially designed to afford satisfactory immersion in the thermostat.

Outline of Method.—Tate and Lyle's purest sucrose containing on a dry basis 99·99% of sucrose and 0·001—0·002% of invert sugar is used throughout. After very fine grinding to accelerate dissolution, the sucrose is dried at 60° under 5 cm. pressure in a stream of dry air. It is weighed into flask *A*, which is then sealed on to the manometer, and the requisite quantity of water is transferred from a weight burette into tube *G*, the whole of the mercury in the manometer being in reservoir *P*.

FIG. 1.

Apparatus for determination of the vapour pressure of solutions up to atmospheric pressure.

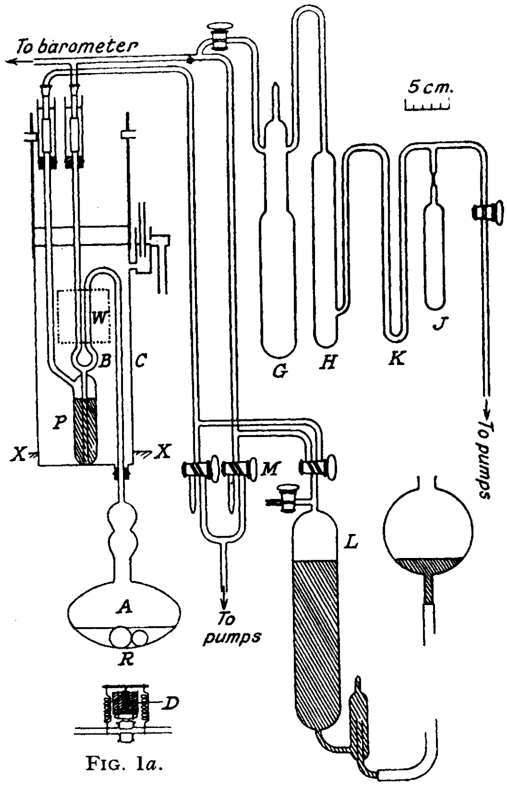


FIG. 1*a*.

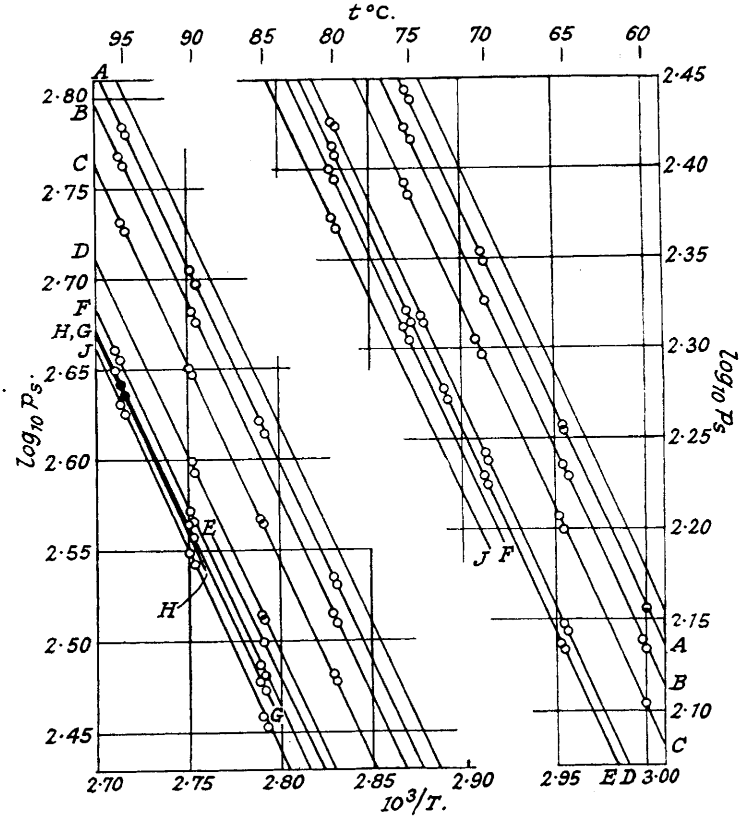
XX = Water level in thermostat.

After tube *G* has been sealed, the water is immediately frozen by means of liquid air, and the apparatus exhausted by a Cenco Hyvac and a mercury-vapour pump, till no air can be detected by the McLeod gauge. During the pumping out of the air, tube *H* must be immersed in liquid air to detect and prevent any loss of water.

After complete evacuation, the mercury is pushed up into the manometer, thus isolating flask *A* from the water tubes. By repeated distillation from tube *G* to tube *H* and *vice versa*, and subsequent exhaustion when the water is frozen, the air can be removed from the water, which should be as free as possible from carbon dioxide before being put into the apparatus. Conductivity water is used, but as a final precaution, a few c.c. of water may be distilled over into tube *J*, which is then sealed off, and the water discarded after its weight has been determined. The mercury in the manometer is drawn down, the flask *A* immersed in carbon dioxide and methylated spirit, and the water is distilled into the sucrose. The flask is again closed by pushing the mercury up into the manometer, and the sugar is dissolved by rocking the thermostat *C*. With solutions of high concentration, it is preferable to obtain the requisite high temperature for solution by rapidly heating the flask in a large beaker, containing, *e.g.*, calcium chloride solution, and then replacing the beaker by the heated main thermostat. The thermostat *C* is continually rocked until equilibrium is attained, effective disturbance of the solution being ensured by the marbles *R*, which project through the surface. The mercury in the manometer is levelled, and the shaking stopped only for the time required to take the temperature reading. At least ten such readings are rapidly taken and the mean is the equilibrium temperature. The variation in the mean reading for duplicate sets of observations at any one temperature is not more than 0·02°. Any drift in the readings is taken to indicate that equilibrium has not been attained, and the process is repeated after further shaking.

FIG. 2.

Graphic relationship between $\log_{10} p_s$ *and* $10^3/T$.



A, 44·85% *soln.*
◒ A′, 44·87 „
B, 58·90 „
C, 69·91 „
D, 78·39 „

E, 79·97% *soln.*
F, 81·10 „
G, 82·05 „
H, 82·22 „
J, 83·22 „

◒ *With the exception of this point, the values of* A′ *coincide too closely with those of* A *to permit insertion in the graph.*

As an additional precaution, at least two independent readings are taken at each round temperature, and in the one case equilibrium is attained by lowering, and in the other by raising the temperature, thus lessening the possibility of unrecognised errors caused by the presence of condensed drops of solvent or of surface layers differing in concentration from the main liquid. Since inversion of sucrose is known to occur in aqueous solution at a rate depending on the temperature as well as on other factors, the readings are taken at temperatures which are not consecutive. Appreciable and gradually increasing inversion would, therefore, produce irregularities in the pressure–temperature curve, rather than a steady drift which might escape observation.

At the completion of the vapour-pressure measurements with any one solution, the total weight is redetermined to ensure that no loss of water has occurred. Any change in weight has, in every case, been found to be negligible, being of the order of 0·01% of the total weight of the solution. In calculating the coucentration of the solutions no correction for buoyancy of air is applied. The weight of water forming the vapour phase is subtracted from the total weight of water. This correction is equivalent to an addition of 0·03—0·07 to the percentage of sucrose in solution, depending on the temperature, pressure, and dimensions of the apparatus, as well as on the concentration and total volume of the solution. At the end of every series of experiments with any one solution, the latter is examined by the polarimeter to determine the percentage of sucrose inverted. Also, in cases in which the solution has been subjected to higher temperatures, such as those reached in the determination of vapour pressures of the order of one atmosphere, the percentage of invert present is determined by Lane and Eynon's method to detect possible further breakdown of invert sugar. In some such cases, Clerget's method has also been used.

The experimental work falls into two parts. The first deals with solutions examined over a wide range of pressure, at temperatures in no case exceeding 95°; the second part is mainly concerned with the temperatures required to produce a vapour pressure of 760 mm., *i.e.*, with the elevation of the b. p. under normal atmospheric pressure.

RESULTS.

Part I.

Table I records the observed temperatures, t°, and the corresponding vapour pressures, p_s (in mm.), for sucrose solutions, in which the weight concentration ranges from about 45 to 83%, and the mole-fraction of the sucrose, N_2, from about 0·04 to 0·20. The table also gives the elevation of the boiling points, $E_{\text{exp.}}$, calculated from these pressures and temperatures, the requisite b. p.s of water being taken from the Reichsanstalt Tables (Landolt–Börnstein, 1931, Erg. IIb, 1329 *et seq.*). $E_{\text{calc.}}$ refers to values of E smoothed by means of equation (2) (see below). At the foot of the column for each solution is recorded the percentage of the initial sucrose found to be inverted at the end of the experiment. These symbols are retained throughout the paper.

Fig. 2 shows, for the different solutions, the relationship between $\log_{10} p_s$ and $10^3/T$, where T is the absolute temperature (0° C = 273·16° K.), corresponding to the observed vapour pressure p_s. The left-hand portion of the diagram is the continuation upwards of the right-hand portion and, for reading, should be superimposed on the latter as indicated by the marginal temperatures and pressures. The vapour pressure curve for water is on the extreme right of each portion of the diagram. On the scale of the original drawing (21″ × 17″), these curves do not deviate appreciably from straight lines and are very nearly parallel to each other. The slopes of the lines give the heats of vaporization of water from the solutions. Any deviation from exact parallelism indicates that there is a heat of dilution.

For each solution, values of $\log_{10} p_s/p_w$ (p_w is the vapour pressure of water at the temperature T) have been calculated for each temperature and plotted against T^{-1}. It is quite clear from these curves that $\log_{10} p_s/p_w$ depends on the temperature and hence that there is a heat of dilution, $\Delta\overline{H}_1$, *i.e.*,

$$\frac{\partial \log_{10} p_s/p_w}{\partial(T^{-1})} = \frac{-\Delta\overline{H}_1}{2{\cdot}303\boldsymbol{R}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In order to smooth the results and obtain an empirical equation for them, the following procedure was adopted. For each of the solutions, mean squares were used to obtain a relation between $\log p_s/p_w$ and T^{-1} of the form

$$\log p_s/p_w = A(N_2) + B(N_2)/T$$

where A and B are taken as independent of the temperature, but functions of N_2, the mole-fraction of the sucrose. Then the values of $\log p_s/p_w$ were calculated for the respective solutions at 80° (approximately the median temperature for all solutions). These values at 80° were smoothed by applying mean squares to find the constants a and b in the equation

$$\frac{1}{N_2}\left(\log_{10}\frac{p_w}{p_s}\right)_{80} - 0{\cdot}4343 = aN_2 + bN_2^2$$

The values of $B(N_2)$ were plotted against N_2 and it was found that, within the limits of the experimental accuracy, they were proportional to N_2^2. Finally, the results were assembled into an empirical relation

$$\log_{10} p_w/p_s = 0{\cdot}4343N_2 + (0{\cdot}4721 + 713/T)N_2^2 - 1{\cdot}32N_2^3 \quad . \quad . \quad . \quad . \quad (2)$$

which may be considered to represent our results for the vapour pressures of sucrose solutions from 45 to 85% concentration between the temperatures of 60° and 95°.

Calculations from this equation of p_s, for comparison with the experimental results, show close agreement. The degree to which it represents the experimental data may be judged from the values of $E_{calc.}$, the calculated elevation of the b. p., which are given in Table I.

TABLE I.

The vapour pressures of pure sucrose solutions at various temperatures.

N_2 = mole-fraction of sucrose; p_s = vapour pressure of the solution in mm. Hg at temperature t° C; $E_{exp.}$ = elevation of b. p. calculated from p_s and t° and the b. p. of water under pressure p_s: $E_{calc.}$ = elevation of b. p. calculated from equation (2).

	A				A′				B			
g. of sucrose per 100 g. of solution.	44·85				44·87				58·90			
N_2	0·041043				0.041077				0·070135			
			E,				*E*,				*E*,	
Temp. region	t, °c	p_s	exp.	calc.	t, °c	p_s	exp.	calc.	t,° c	p_s	exp.	calc.
60°	—	—	—	—	60·20	143·145	1·12	$1{\cdot}10_6$	60·17	136·02	2·18	2·12
	—	—	—	—	—	—	—	—	60·40	137·63	—	—
65	65·09	179·38	1·08	—	64·89	177·75	1·08	—	64·88	169·37	2·14	—
	65·26	180·68	1·09	$1{\cdot}13_4$	65·21	180·06	1·12	—	65·24	171·73	2·20	2·18
70	70·08	222·77	1·18	$1{\cdot}16_5$	70·07	222·95	1·15	—	70·10	213·00	2·23	2·25
	70·39	226·16	1·14	—	70·46	227·05	1·12	—	70·21	213·57	2·27	—
75	74·98	274·70	1·19	$1{\cdot}20_4$	74·98	274·18	1·24	—	74·89	260·86	2·32	—
	75·29	277·76	1·24	—	75·34	278·61	1·22	—	75·30	265·02	2·36	2·31
80	80·08	338·90	1·23	—	79·49	338·35	1·18	—	80·07	323·25	2·37	2·38
	80·29	341·61	1·24	$1{\cdot}24_6$	80·21	340·90	1·22	—	80·36	327·18	2·37	—
85	84·97	412·38	1·24	—	84·73	407·99	1·27	—	84·77	389·45	2·47	2·47
	85·37	417·80	1·31	$1{\cdot}27_6$	85·07	413·09	1·30	—	85·04	394·21	2·44	—
90	89·86	498·28	1·27	—	89·85	497·70	1·29	—	89·84	474·15	2·54	—
	90·28	505·56	1·31	$1{\cdot}32_6$	90·27	505·67	1·29	—	90·18	480·69	2·54	2·53
95	94·89	601·29	1·32	1·36	94·47	592·83	1·28	—	95·10	578·59	2·56	2·60
	95·14	607·33	1·30	—	95·36	612·96	1·29	—	95·46	586·97	2·53	—
		1·17 *				2·21				1·07		

	C				D				E			
g. of sucrose per 100 g. of solution.	69·91				78·39				79·74			
N_2	0·108957				0·160312				0·171601			
			E,				*E*,				*E*,	
Temp. region	t, °c	p	exp.	calc.	t, °c	p_s	exp.	calc.	t, °c	p_s	exp.	calc.
60°	60·29	126·97	3·76	$3{\cdot}76_1$	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—
65	65·20	158·30	3·87	3·88	65·00	139·22	6·51	6·57	65·16	135·86	7·20	$7{\cdot}23_1$
	65·49	160·87	3·88	—	65·21	140·30	6·55	—	65·41	137·00	7·27	—
70	70·29	198·00	4·07	—	69·95	172·81	6·76	—	69·95	167·58	7·45	—
	70·70	201·79	4·05	4·00	70·07	174·37	6·69	6·75	70·20	169·58	7·43	$7{\cdot}43_0$
									72·52	186·86	7·60	$7{\cdot}52_4$
									72·76	189·49	7·53	—
75	75·10	243·12	4·18	—	74·07	206·34	6·92	6·90	74·91	207·47	7·64	—
	75·38	246·64	4·12	4·10	74·28	208·19	6·93	—	75·25	210·68	7·63	$7{\cdot}62_7$
80	80·14	300·09	4·25	—	79·96	264·47	7·17	7·12	80·00	255·94	7·88	$7{\cdot}82_4$
	80·33	302·03	4·29	4·23	80·27	267·16	7·13	—	80·19	258·92	7·80	—
85	85·14	366·54	4·36	4·33	85·10	324·65	7·30	7·31	85·14	315·57	8·03	$8{\cdot}02_6$
	85·34	369·00	4·39	—	85·26	326·93	7·29	—	85·16	315·16	8·08	—
90	90·10	443·61	4·52	4·47	89·98	391·67	7·54	7·50	—	—	—	—
	90·39	448·65	4·52	—	90·14	395·28	7·47	—	—	—	—	—
95	94·99	532·44	4·66	—	—	—	—	—	—	—	—	—
	95·30	538·47	4·67	4·58	—	—	—	—	—	—	—	—
		0·68				0·36				See p. 2370.		

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* Data in the last line of each section record the sucrose inverted as g. per 100 g. of original.

TABLE I—*continued*.

	F				G				J*			
g. of sucrose per 100 g. of solution.	81·10				82·05				83·22			
N_2	0·184232				0·193924				0·20699			
			E,				E,				E,	
Temp. region	t, °c	p_s	exp.	calc.	t, °c	p_s	exp.	calc.	t, °c	p_s	exp.	calc.
75°	75·02	201·80	8·37	8·41$_3$	—	—	—	—	—	—	—	—
	75·43	205·32	8·39	—	—	—	—	—	—	—	—	—
80	80·05	248·24	8·68	8·63$_5$	—	—	—	—	79·95[2]	232·96	10·02	10·10
	80·43	251·58	8·69	—	—	—	—	—	80·27[2]	236·25	10·01$_5$	—
85	85·08	303·40	8·92	8·86	85·08	296·96	9·44	—	84·94[2]	283·68	10·39	10·41$_8$
	85·40	306·74	8·98	—	85·45	300·31	9·54	9·53$_5$	85·27[2]	287·17	10·43	—
90	90·06	368·42	9·15	9·00$_4$	90·12	360·52	9·75	9·66$_3$	89·96[2]	347·32	10·51	10·68$_7$
	90·33	372·84	9·11	—	90·45	365·50	9·74	—	90·42[2]	353·59	10·53	10·75
95	95·39	452·24	9·30	9·34$_5$	—	—	—	—	95·00[1]	422·36	10·66	10·95$_8$
	95·73	457·37	9·34	—	95·71	446·31	9·98	10·05	95·37[1]	427·17	10·75	—
	0·41				1·61				[1] 0·6, see p. 2370. [2] 1·01			

* For solution H, data are as follows: 82·22 g./100 g. of solution, N_2 = 0·193741, sucrose inverted 0·39.

t, °c	p_s	$E_{\text{exp.}}$	$E_{\text{calc.}}$	t, °c	p_s	$E_{\text{exp.}}$
95·00	432·10	10·09	10·19$_4$	95·35°	437·76	10·11

By means of this equation, the smoothed values of p_s, E, and $\log_{10} p_w/p_s$ have been calculated for 45—90% concentrations at 5% intervals and for 60—95° at 5° intervals. These values are listed in Table II.

TABLE II.

Values of $\log_{10}\mathrm{p_w/p_s}$, $\mathrm{p_s}$, *and* E, *calculated by means of equation* (2), *in which* $\mathrm{p_w}$ *and* $\mathrm{p_s}$ *represent the vapour pressure of water and of the solution, respectively, at the temperature* $\mathrm{t_0}$, *and* E *represents the elevation of the boiling point at the same temperature.*

g. sucrose/ 100 g. soln.	45	60	65	70	75	80	85	90
$10^7 N_2$	412,839	731,698	890,396	1,093,737	1,363,621	1,739,111	2,297,273	3,214,257
t_0				$10^7 \times \log_{10} p_w/p_s$				
60°	222,887	452,454	584,477	770,222	1,044,493	1,475,920	2,216,244	3,656,379
65	222,348	450,761	581,969	766,436	1,038,609	1,466,350	2,199,546	3,623,690
70	221,813	449,116	579,533	762,761	1,032,907	1,457,058	2,183,333	3,591,949
75	221,300	447,571	577,165	759,192	1,027,348	1,448,033	2,167,585	3,561,121
80	220,821	445,966	574,876	755,723	1,021,957	1,439,264	2,152,283	3,531,167
85	220,340	444,457	572,634	752,352	1,016,716	1,430,757	2,137,409	3,502,047
90	219,774	442,990	570,417	749,073	1,011,620	1,422,450	2,122,946	3,473,731
95	219,419	441,563	568,347	745,883	1,006,662	1,414,386	2,108,873	3,446,183
				p_s, mm.				
60	141·907	134·601	130·570	125·104	117·447	106·349	89·674	64·366
65	178·180	169·051	164·020	157·199	147·649	133·801	113·016	81·419
70	220·636	210·740	204·506	196·057	184·232	167·091	141·360	102·203
75	274·738	260·790	253·123	242·733	228·199	207·131	175·505	127·332
80	337·496	320·445	311·074	298·386	280·644	254·932	216·332	157·483
85	412·154	391·421	380·037	364·631	343·098	311·899	265·063	193·591
90	499·816	474·766	461·048	442·466	416·510	378·916	322·473	236·273
95	602·668	572·674	556·143	533·866	502·753	457·701	390·062	286·683
				E°, c				
60	1·10$_5$	2·23$_3$	2·88$_0$	3·78$_1$	5·10$_8$	7·16$_4$	10·62$_4$	17·12$_8$
65	1·14$_0$	2·30$_3$	2·96$_7$	3·89$_3$	5·25$_2$	7·36$_0$	10·90$_6$	17·55$_4$
70	1·17$_2$	2·36$_9$	3·05$_1$	4·00$_4$	5·39$_6$	7·55$_9$	11·18$_8$	17·97$_7$
75	1·21$_4$	2·43$_7$	3·13$_4$	4·11$_7$	5·54$_6$	7·76$_1$	11·47$_5$	18·40$_8$
80	1·25$_0$	2·51$_8$	3·24$_0$	4·24$_4$	5·70$_5$	7·97$_0$	11·77$_1$	18·85$_4$
85	1·28$_4$	2·58$_0$	3·31$_8$	4·34$_5$	5·85$_0$	8·17$_7$	12·06$_2$	19·28$_8$
90	1·32$_6$	2·66$_3$	3·42$_5$	4·48$_4$	6·01$_8$	8·39$_2$	12·36$_4$	19·74$_3$
95	1·36$_6$	2·73$_4$	3·51$_2$	4·59$_7$	6·17$_8$	8·61$_7$	12·66$_8$	20·20$_1$

Also, by a method of approximations, equation (2) has been employed to calculate at the above regular intervals of concentration, the elevations of the b. p. under fixed pressures. Table III records these elevations for 760 mm. and the stated fractions of 760 mm. pressure.

TABLE III.

Elevations of the boiling point, E°, *calculated by means of equation* (2) *for sucrose solutions of concentration* C (*mole-fraction of sucrose* = N_2) *under pressure* p_s (*mm.*).

p_s, mm.		190	380	570	760
Concn. *C* (g. sucrose/100 g. soln.)	N_2	Elevation of boiling point, *E*°, under pressure p_s (mm.)			
45	0·0412839	$1{\cdot}15_0$	$1{\cdot}27_0$	$1{\cdot}35_4$	$1{\cdot}41_6$
60	0·0731698	$2{\cdot}33_8$	$2{\cdot}57_2$	$2{\cdot}73_5$	$2{\cdot}85_8$
65	0·0890396	$3{\cdot}02_3$	$3{\cdot}31_8$	$3{\cdot}52_6$	$3{\cdot}68_2$
70	0·1093737	$3{\cdot}99_1$	$4{\cdot}36_5$	$4{\cdot}63_9$	$4{\cdot}84_1$
75	0·1363621	$5{\cdot}41_4$	$5{\cdot}92_8$	$6{\cdot}28_0$	$6{\cdot}54_9$
80	0·1739111	$7{\cdot}68_1$	$8{\cdot}39_5$	$8{\cdot}86_4$	$9{\cdot}23_3$
85	0·2297273	$11{\cdot}58_1$	$12{\cdot}62_5$	$13{\cdot}30_7$	$13{\cdot}84_8$
90	0·3214257	$19{\cdot}24_9$	$20{\cdot}88_8$	$21{\cdot}97_3$	$22{\cdot}81_2$

Table III enables the calculated results to be compared with those of earlier investigators and with the results of the actual determinations in Tables I and V.

Further, with regard to the application of equation (2), it should be pointed out that the heat of dilution ΔH can be obtained from the coefficient of T^{-1}. This corresponds to the relation

$$\Delta\overline{H}_1 = -3{\cdot}3 \times 10^3 N_2^{\,2} \text{ cals./mol.} \qquad (3)$$

and indicates that the heat of dilution is small. Direct measurements of the heat of dilution of sucrose have been made previously (Stackelberg, *Z. physikal. Chem.*, 1898, **26**, 533; Wood, *Trans. Faraday Soc.*, 1917, **13**, 123; Hunter, *ibid.*, 1926, **22**, 194; Vallender and Perman, *ibid.*, 1931, **27**, 126; Gucker, Pickard, and Planck, *J. Amer. Chem. Soc.*, 1939, **61**, 459), the results of Vallender and Perman being the most extensive. Although our relation (3) should be considered only as a term in an empirical expression for our vapour pressures, yet it is interesting to compare the value which Vallender and Perman obtained for the heat of dilution of 68·79% sucrose at 80° with the value obtained for (3). As regards temperature and concentration, this lies close to the median of our ranges of concentration and temperature. For a 68·79% solution (N_2 = 0·10394) equation (3) gives −1·98 cals./g.; direct determination by Vallender and Perman gave −2·02 cals./g. This close agreement must be regarded as merely fortuitous.

Inversion.—The sucrose used throughout these investigations contains, initially, not more than 0·002% of invert sugar. During use in the vapour-pressure apparatus, this proportion increased to not more than 2·21% of the original weight of sucrose (see Table I). The extent of inversion depends on many factors, such as concentration, temperature, pH, and time of heating, and, in the case of pure sucrose solutions, it may be complicated by the presence of an induction period. The detailed investigation of inversion is outside the scope of the present work, but the following experiments provide some information on the condition of the solutions at various times during the consecutive vapour-pressure measurements.

A 44·92% solution, made up with water of conductivity 1×10^{-6} mho, is heated *in vacuo* for successive periods of 2 hours at 60°, 65°, 70°, 75°, and 80°. In the course of the experiment, the solution is left to cool overnight several times. The polarimeter reading is the same at the end as at the beginning, indicating that no change in concentration and no inversion measurable by this method has taken place. However, after subsequent consecutive two-hour periods of heating at 90°, 95°, and 100°, the percentages of sucrose inverted are 0·32, 0·76, and 3·0, respectively. After further heating for 13 hours at 100°, 99% of the sucrose present is found to be inverted.

In the case of solution " E," after the vapour pressure readings given in Table I had been taken up to 85°, the solution was kept at about 85° for a further 30 hours. After this prolonged heating, in all about 50 hours, vapour-pressure readings were taken at intervals of 1—2 hours, as shown in Table IV.

Owing to this inversion, N_1, the mole-fraction of the water in the solution, is reduced from 0·8284 to 0·8075, and N_2, the mole-fraction of the solute (sucrose and invert sugar) is increased to 0·1925. By calculation from equation (2), it is found that at this mole-fraction, an unin-

TABLE IV.

Solution E. Concentration : 79·74 g. of sucrose per 100 g. of solution : $N_2 = 0{\cdot}171610$.
h = total hours of heating before the readings are taken.
t_0° = temperature of the solution under vapour pressure p_s.
$E_{\text{exp.}}$ = observed elevation of b. p.
$E_{\text{calc.}}$ = elevation calculated from equation (2), inversion being assumed not to have occurred.

h	t_0	p_s	$E_{\text{exp.}}$	$E_{\text{calc.}}$
54	82·40°	274·44	8·64	7·925
53	82·58	276·64	8·63	
48	87·46	339·33	8·58	8·28
49	87·64	340·98	8·64	
51	92·40	408·89	8·89	8·50
50	92·82	416·12	8·87	

Percentage of initial sucrose inverted after 54 hours = 12·2.

verted sucrose solution would show elevations of 9·39°, 9·54°, and 9·85° respectively at the mean temperature of each pair of readings. The elevations $E_{\text{exp.}}$ found for the partly inverted solute (Table IV, col. 4) are considerably less, indicating that the osmotic properties of sucrose solutions containing some invert sugar are not simply a function of the mole-fraction of the water, but depend also on the sizes of the molecules present. In the present case, it is fortunate that the invert sugar has not such a marked effect on the osmotic properties as one might expect from the reduction produced in the water mole-fraction, and we may assume that the vapour pressures recorded in Table I are not appreciably affected by the small amounts of inversion which have occurred. Nevertheless, in all work on sucrose solutions, it is obviously important to keep a strict check on inversion, to reduce as much as possible the time of exposure to high temperature, and to ensure the purity of the water. There is, however, some indication that the presence of even a small percentage of invert sugar tends to prevent the crystallisation of supersaturated solutions, thereby facilitating the determination of their vapour pressures. For example, several attempts to obtain an approximately 83% solution which was stable enough to give satisfactory vapour-pressure readings below 95°, were unsuccessful. In each of these cases, the times of heating (at 105—108°) to effect solution had been curtailed as much as possible, and the final inversion was found to be less than 1% (see Table I, solution *J*, concentration 83·22%, final inversion, 0·6% of the sucrose). Solution J_2, of appreciably the same composition as J_1, was then prepared by maintaining the high temperature of solution for a considerably longer period. By this means, consistent readings were obtained at 5° intervals to the 80° region. The solubility of sucrose at 80° is 78·805 g. per 100 g. of solution (Taylor, *J.*, 1947, 1682). The final inversion was, in this case, found to be 1·01% of the total sucrose.

Since temperature is one of the more important factors influencing the rate of inversion, the vapour-pressure determinations in the foregoing experiments have been limited to temperatures not exceeding 95°. In concentrated solutions, temperatures considerably higher than 95° are required to produce a vapour pressure of 760 mm. The determination of these higher temperatures (*i.e.*, the b. p.s of concentrated sucrose solutions under 760 mm.) by the vapour-pressure method has been carried out independently by one of us (H. C. E). The experimental work and results are described in Part II.

Part II.

A preliminary experiment showed that, after being heated for 6 hours under a vapour pressure of approximately 760 mm., a 60% sucrose solution had undergone inversion to the extent of 20%. Therefore, in order to reduce the time of exposure at high temperatures, the vapour pressure of each solution is determined at only two temperatures, one slightly above and the other slightly below that required to give a vapour pressure of 760 mm. The b. p. under 760 mm. is then determined by interpolation in the logarithmic curve connecting the experimental points (Fig. 2). By this means, the total time of heating is reduced to about 3 hours, and the percentage, in the different solutions, of sucrose inverted, as determined by the polarimeter, is found to lie between 3·71 and 0·82%. The direct determination of invert sugar by Lane and Eynon's method gives the corresponding percentages as 3·61 and 0·87%, respectively, showing that no significant molecular breakdown other than inversion has occurred.

Table V records, for each of the solutions, the concentration, the actual vapour pressure data, and the interpolated temperature, $t_{\text{int.}}$, at which $p_s = 760$ mm. Cols. 5 and 6 give the resulting elevation of the b. p. at 760 mm., $E_{\text{exp.}}$, and the elevation, $E_{\text{calc.}}$, as calculated from equation (2) and the vapour pressure tables for water given in Landolt–Börnstein's " Tabellen " (1936, Vol. IIIc, p. 2415). The complete inversion data are collected in cols. 7 and 8.

TABLE V.

Elevation of boiling point of pure sucrose solutions at 760 *mm. pressure.*

p_s = vapour pressure in mm. at t_0°.
$t_{\text{int.}}$ = interpolated temperature at 760 mm.
$E_{\text{exp.}}$ = elevation of b. p. at 760 mm.
$E_{\text{calc.}}$ = elevation of b. p. at 760 mm. calculated from eqn. (2).

Concn., %	p_s	t_0, °C	$t_{\text{int.}}$	$E_{\text{exp.}}$, 760 mm.	$E_{\text{calc.}}$, 760 mm.	I_1*	I_2*
43·23	747·22	100·77	101·25	1·25	1·30$_2$	1·29	1·62
	763·31	101·38					
60·12	758·29	102·77	102·83	2·83	2·88$_8$	1·60	—
	770·59	103·22					
69·27	756·39	104·69	104·79	4·79	4·66$_6$	3·71	3·61
	767·97	105·06					
75·08	751·75	106·45	106·75	6·75	6·60$_7$	2·23	2·25
	763·90	106·89					
79·08	755·19	108·68	108·84	8·84	8·66$_2$	2·78	2·29
	763·05	108·94					
82·74	750·17	111·06	111·45	11·45	11·44$_9$	1·04	1·03
	772·45	111·95					
84·72	748·07	112·96	113·41	13·41	13·52$_9$	1·36	1·43
	766·22	113·65					
86·36	749·28	114·94	115·33	15·33	15·70$_0$	1·56	1·35
	763·92	115·46					
87·87	756·28	117·51	117·62	17·62	18·18$_4$	0·82	0·87
	778·13	118·24					

* I_1 = g. of invert sugar produced per 100 g. of sucrose (by polarimeter).
I_2 = ,, ,, ,, (by Lane and Eynon's method).

The generally accepted values of E at 760 mm. pressure are those of Claassen (*Z. Ver. Deutsch. Zückerind.*, Techn. T., 1904, **54**, 1159) and of Spengler, Böttger, and Werner (*loc. cit.*, p. 601). In 1941, Tressler, Zimmerman, and Willits (*J. Physical Chem.*, **45**, 1242) carried out a series of boiling-point determinations under atmospheric pressure, designed to give values for the elevation of the boiling point as accurate as are obtainable by a differential modification of the original Beckmann method. The work of all these investigators suffers from the drawback that, although the total weight concentration of the solution purported to be determined at the end of each experiment, no attempt was made to determine the final composition—sucrose and invert sugar—of the solute. Claassen, making determinations of E under atmospheric pressure, reached, in the case of the highest concentrations, temperatures between 120° and 130°, and assuming no inversion, he relied on the polarimeter to give the total concentration. Owing to the opposing effects of the sucrose and invert sugar on the polarimeter reading, the unsuspected presence of even a small percentage of invert sugar would cause a relatively large error in the result. Spengler and Tressler each relied solely upon the refractometer for the same purpose; at lower and medium temperatures, the consequent error might be inconsiderable, since the correction for the presence of invert sugar in the determination of the total solid in a sucrose solution by this method is small. Also, we have demonstrated above that the effect on the vapour pressure of the conversion of sucrose into invert sugar is smaller than would be calculated from the decrease in the mole-fraction of the water in the solution.

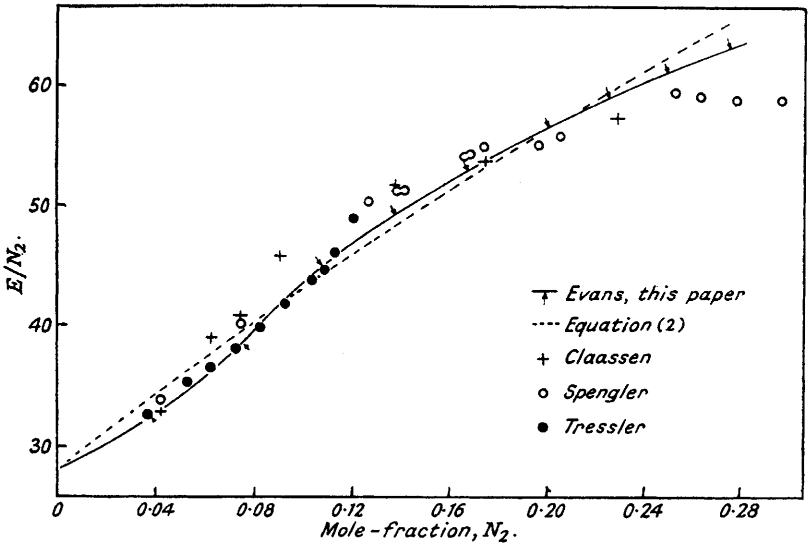
The experiments of Tressler *et al.* were not carried out at 760 mm., but under the prevailing atmospheric pressure. However, the b. p.s of the solution and of the water were determined at the same time and, since the altitude of their laboratory appears to be about 600 feet, the divergence of their values of E from the values at 760 mm. might not be large.

In Spengler's experiments, the pressures were accurately measured and the values of t_0 at 760 mm. were obtained by interpolation, but, in addition to the uncertainty regarding the final percentage of invert sugar, there are well-known errors inherent in the original Beckmann method which Spengler's calibration of his apparatus with pure water (*loc. cit.*, p. 554) would not enable him to estimate. Also, his method of establishing high pressures with solutions of high concentration is open to criticism (*loc. cit.*, p. 552). A great advantage of the method now recorded is that it enables the solutions to be made up very accurately to a known concentration, which not only is maintained throughout the experiment, but also can be checked at the end. Then, as shown above, any one or more of the methods for the estimation of invert can be applied.

To obtain a comparison of the relative consistency of the results of the various methods described, the values of the ratio E/N_2, calculated from the results at 760 mm. of each of the authors concerned, have been plotted against the corresponding mole-fractions of the sucrose (N_2), and the results are illustrated in Fig. 3. The continuous line has been drawn smoothly through all the results (indicated by arrows) from Table V, and the broken line corresponds to the values of E calculated by means of equation (2). The agreement between these lines is quite good, especially when the extent to which the equation has been extrapolated is considered. Not only has it been extrapolated with regard to temperature, but also to some extent with regard to concentration, the equation having been derived from results obtained with solutions ranging in concentration from about 45 to 85% (mole-fraction 0·04—0·20) and over this range it is seen that the values of E/N_2 obtained from the equation and from direct experiment agree closely. The deviation between the two appears to be due to a sigmoid tendency in the experimental curve and, naturally, the simple algebraic relation assumed for the equation cannot reflect this. The results of Tressler *et al.* are in good agreement with the present values except at their highest concentration—about 72% of sucrose—at which they had obviously reached the limit of concentration for which their apparatus was suited. The values given by Claassen and Spengler produce curves of a more pronounced sigmoid tendency. It is difficult to compare the results of these two authors with the present results. The relatively low values of N_2 indicated in the larger proportion of Claassen's results may be referred, as already indicated, to the use of the polarimeter alone for the final determination of concentration. On the other hand, in the case of Spengler's highest concentration, the failure of E to increase consistently with N_2 may be due to the introduction of nitrogen into his apparatus.

FIG. 3.

Comparison of E/N_2 *against* N_2 *calculated from equation* (2) *and from the results of different investigators.*



Further work on the problems raised by the foregoing results is now in progress in this laboratory.

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