On Osmotic Pressures Derived from Vapour-Pressure Measurements: Aqueous Solutions of Cane Sugar and Methyl Glucoside

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V. *On Osmotic Pressures Derived from Vapour-Pressure Measurements: Aqueous Solutions of Cane Sugar and Methyl Glucoside.*

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INTRODUCTORY.

SINCE our previous communications on cane sugar ('Roy. Soc. Proc.,' A, vol. 77, 1906) and on calcium ferrocyanide ('Phil. Trans.,' A, vol. 209) we have endeavoured to improve the apparatus and method therein described. In these endeavours, two objects, besides that of determining osmotic pressures, have been in view: (1) to find out what are the best conditions for making the method both accurate and of general applicability; (2) to obtain data for the construction of suitable apparatus for the determination of the absolute vapour density of liquids in air or other gas.

As far as accuracy is concerned, the close agreement between osmotic pressures observed directly, and those here calculated from the vapour pressures, shows that, for solutions at 0° C. the method is susceptible of considerable precision. The experiments at 30° C., however, are on the whole not quite so concordant; this is probably because the quantity of water vapour in the air stream is some six times the amount carried at 0° C., so that small variations in conditions which would be without effect at the lower temperature, now make themselves apparent. This, indeed, is shown clearly in the magnitude of the correction to be applied for the expansion of the air between the solution and water vessels (see p. 316). In the early stages of the work (at 0° C.) our results indicated that the successful application of the method depends largely on the control of the experimental conditions; accordingly we made as many changes as possible, but as each experiment takes several days to complete, a long time is required to determine the effect of any one change. The departure of Mr. HARTLEY for the front prevented a further investigation of the question but we think that no new changes will alter substantially the results now presented.

The importance of measurements of the absolute vapour density of water vapour in air has been realized generally for some time past; the differences between REGNAULT'S values for air and for a vacuum (at 0° C., especially) require

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re-determination, the more so in that his air values seem in themselves not very satisfactory, and it is just the air values which are wanted in the majority of researches. The experimental error of our results is now reduced sufficiently to warrant the belief that in absolute measurements the chief difficulty will lie in the determination of the quantity of air passed, rather than in the amount of water vapour it carries.

The research is divided into two parts. In Part I. are given the measurements of the compressibilities of the solutions; these were carried out with the aid of Dr. Burton. Part II. embodies the experiments on the vapour pressures of solutions of cane sugar and α-methyl glucoside at 0° C. and 30° C., also some determinations of the vapour pressures of dilute sulphuric acid. All the experiments, except a few dating later than January 22, 1916, were done in conjunction with Mr. Hartley.

As both these gentlemen have left the laboratory and are not within reach, the other author should be held responsible for all mistakes in presentation of fact or theory.

PART I.*

The Compressibilities. (Berkeley and Burton.)

In a previous communication we have given the results of our measurements on the compressibilities of calcium ferrocyanide solutions. These results were not very satisfactory because the experiments had to be carried out as rapidly as possible, otherwise the prolonged strain on the outer glass tube† (through which the readings on the piezometer stem were taken) soon caused it to collapse.

New Apparatus.—To obviate this, a new apparatus, A, was designed in which the glass tube was replaced by a metal casting pierced for windows. With this apparatus some of the experiments here recorded were made; but as the main features of A are embodied in yet another apparatus, B, the former will not be described.

Fig. 1 shows B in elevation. The apparatus is divided into two main pieces, A and B, which are joined "pressure tight" by means of a dermatine ring as shown; this method is similar to that described by us in 'Phil. Mag.,' vol. 32, 1916, p. 157. The upper part A (called the dome) is furnished with a pair of windows, C (the use of which will be described later), and is joined to the pressure system by a nut fitted with differential threads, by means of which the steel pressure tubing, E, can be forced home into its conical seating at D. The part B which is closed at the bottom by a nickel-steel plank (made "pressure tight" by dermatine), carries five pairs of windows, F, spaced at regular intervals for observing the level of the mercury in the stem of the

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* This part of the research was completed in 1911.

† See 'Phil. Trans.,' A, vol. 209, p. 192.

piezometer. The windows are tapered plugs cut from one-inch plate glass; they were inserted into dermatine washers moulded inside and outside to the same taper. The openings for the windows in the casting having been machined to this taper (large end inwards), the glass together with its dermatine wrappers was placed in position from the inside and pushed home as well as could be by means of wedges. On putting a high hydrostatic pressure on the apparatus a final "leak-tight" seating was secured.

The Bath.—The whole apparatus (about two feet high) is immersed in a water-bath, which is furnished with a thermostat and stirrer; submerged electric lamps supply heat, and two of the lamps are under the control of the thermostat. The front of the bath is fitted with a plate-glass window, so that the graduations on the piezometer stem are seen clearly when a small 4-volt lamp is placed behind the apparatus.

The same bath, divided into two compartments by a loosely fitting vertical partition, was used for the observations at 0° C. One of these compartments contained ice, and a constant stream of cold water was pumped from this compartment into the other. During an experiment, which took some hours, care was taken that the ice reached nearly to the bottom of the bath, and the supply was maintained by hand. The temperature variations were observed by means of a Beckmann thermometer reading to 0°·01 C. (estimating to 0°·001 C.) in the bath, and another reading to 0°·02 C. in the dome of the apparatus.

Piezometers.—Piezometers similar to those of our earlier research were used in apparatus A, but in the course of the work we found that there were two drawbacks to this form: (1) the somewhat large bulb took a very considerable time to return to the temperature of the bath after having been heated or cooled by the alterations in pressure (at 0° C. this effect is small); (2) it was found that for a given pressure on the

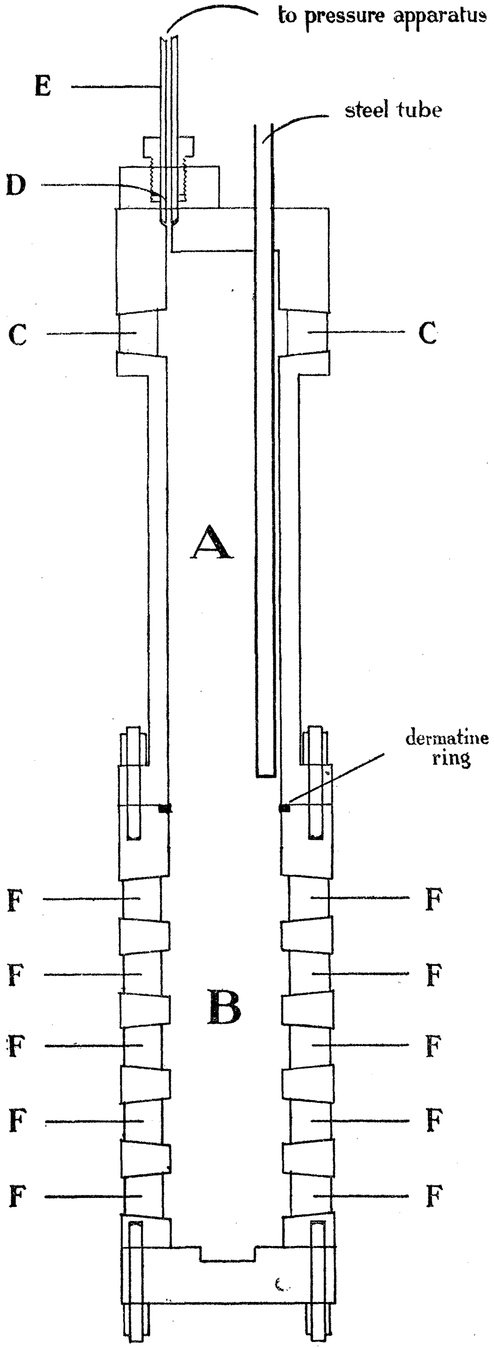

Fig. 1.

apparatus, there was a difference in the final* position of the mercury level in the stem according as the pressure had previously been rising or falling. In all cases the falling pressure gave the higher reading. The cause of this was eventually traced to the lubricant† surrounding the tap key at the top of the piezometer.

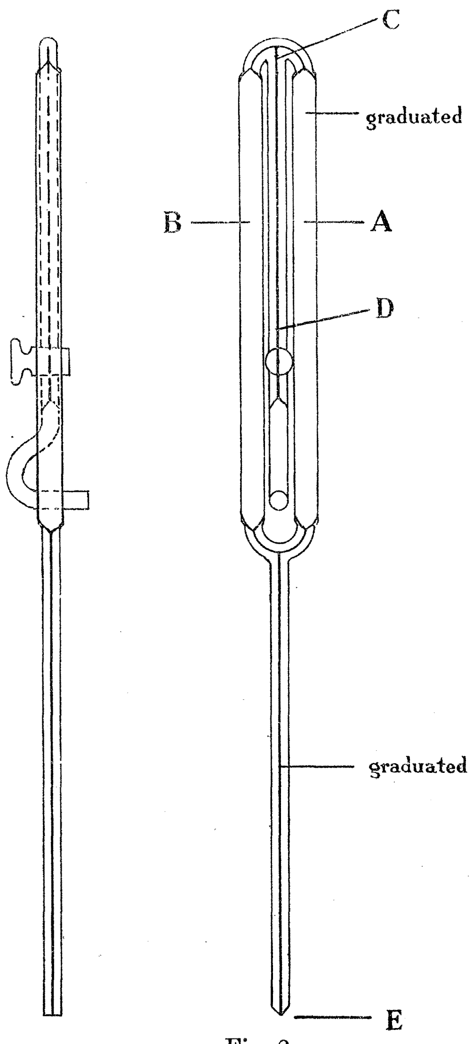

Fig. 2.

The piezometer shown in fig. 2 seems to meet both troubles. The bulb (total volume about 32 c.c.) is divided into two branches, A and B, thus giving a larger cooling surface. The tap is now placed at the end of a graduated capillary, CD, so that by careful manipulation the latter can be filled with mercury to a level which will be in the field of view of window C, of fig. 1.

The remainder of the piezometer contains the solution, except for a centimetre or two of mercury at the bottom of the stem. Thus the solution is confined between two surfaces of mercury, and although the mercury meniscus near the tap will move slightly, if this movement be noted the real change in volume of the solution can be calculated.

The Pressures.—The apparatus used is one of Schäffer and Budenberg's dead-weight gauges, delivering a maximum pressure of 140 atmospheres.‡ The pressure was transmitted by castor oil from the screw plunger to a mercury U-tube; and by water from the latter to the compressibility apparatus.

In the course of the research it was noticed that rapid changes of pressure, especially when on the up grade, caused some uncertainties in

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* That is when the temperature is constant again after the effects of changing the pressure have disappeared. Constancy of temperature is indicated by the fact that there is no further movement in the mercury; indeed, the piezometer is in effect a very sensitive thermometer.

† For, on increasing the pressure, the lubricant is compressed, and as there is a slight difference in pressure due to the unbalanced height of the mercury in the stem, the key may move slightly into its seating; this movement obviously is not reversible. Occasionally, another source of trouble was encountered, namely, that caused by a small bubble of air left in the key of the tap when filling the piezometer; this bubble could be seen easily, but it was found to be there sometimes even in the new form about to be described. The presence of this trace of air would give quite fallacious results for the lower measurements.

‡ The same apparatus as was used for the determination of direct osmotic pressure, see 'Phil. Trans.,' A, vol. 206, 1906, p. 485.

the reading of the mercury level in the piezometer. Direct observation showed that when a certain rate of increase of pressure was exceeded, the mercury thread might move rapidly enough to leave some of the solution behind clinging to the walls of the capillary, and this was the more marked the stronger the solution.* To decide the maximum rate of change of pressure that would be safe, experiments (which are not detailed) were made with the most viscous solution (960 gr. of cane sugar per litre) about to be examined. Judging by the information thus obtained, the method of changing the pressure described below seems free from objection.

A light metal cup was placed on the top of the floating weights of the Schäffer and Budenberg gauge. Above this was suspended a hollow cylinder with a conical end truncated so as to leave a horizontal opening of about 0·8 cm. in diameter. When it was desired to increase the pressure, a quantity of small lead shot equivalent in weight to one of the large weights supplied with the pressure apparatus was run into the cylinder. On opening the orifice the shot were delivered at a constant rate into the metal cup below.†

When all the shot had run through, a needle valve, situated so as to cut off the compressibility vessel from the pressure apparatus, was closed; and the metal cup with its contents was replaced rapidly by one of the weights, after which the needle valve was opened. This process was repeated until the mercury in the piezometer stem showed in the field of view of the adjacent window above. It was found that the pressure could be lowered slowly enough by means of two needle valves in series.

Method Followed in the Determinations of the Compressibilities.—In the present research no attempt was made to get air-free solution. In our work on calcium ferrocyanide we found that this precaution was unnecessary.

The method followed was to fill the piezometer by gentle suction, taking care that no visible bubbles of air were left behind. When full, the piezometer was inverted and some mercury run into the open tube above the tap, which, when cautiously opened, allowed a thread to flow downwards into the capillary (CD of fig. 2), the flow being stopped when the meniscus reached a part of the capillary known to be visible through the upper window (C of fig. 1).

If the determinations were to be made at 0° C., the piezometer when full was placed with its stem immersed in the solution, and the twin bulbs were then cooled by an ice pack until a temperature slightly above that of the bath had been reached;

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* This effect is partly dependent on viscosity; for where some solution has been left in the annular space between the mercury and the walls, this annular space is in effect a capillary tube through which the liquid has to be forced by the hydrostatic pressure of the mercury acting at the bottom of the enclosed solution.

† The rate at which the shot fall is independent of the head of shot and depends on the diameter of the orifice. The correct diameter was found by trial, and was such as to cause the mercury in the stem of the more sensitive piezometer to rise 1 mm. in 25 seconds.

further cooling with the stem in mercury, caused the latter to rise to a suitable level. The piezometer was then quickly transferred to its position in the lower half of the compressibility apparatus which was already in the bath, and, with luck, the mercury thread carried in the stem joined the mercury already in place at the bottom of the apparatus.

It was found that a satisfactory junction was greatly facilitated by chamfering off the bottom of the piezometer stem as shown at E in fig. 2.*

A very similar procedure was followed for the experiments at 30° C. The piezometer being in place, the upper half of the apparatus was passed over the projecting bulbs and secured both to the lower half and to the pressure system.

Supposing these operations to have been carried out successfully, the mercury meniscus should stand, when the bath temperature had been regained, slightly below the lowest window; then a small increase of pressure will bring it opposite the window.

On the other hand, should the meniscus be above this window, the apparatus has to be taken apart, the mercury driven out so as to replace some of it by solution, and after cooling, &c., replaced in the bath.

When a steady state had been reached, the pressure on the apparatus, the level of the meniscus showing in the lower window and that in the topmost window (C of fig. 1), and the temperature both of the bath and of the interior of the apparatus were noted. The pressure was then increased until the meniscus showed in the second window; this increase of pressure caused a development of heat which was dissipated in about three-quarters of an hour, as indicated by the constancy of the position of the meniscus; when steady, the five quantities were again noted, and so on.

Having taken the readings for the fifth window, the pressure was reduced and the process just described was precisely reversed until the initial phase was reached.

It is to be noted, on the assumption that there is no hysteresis in the glass of the piezometer,† that the same readings (corrected for small displacements of the upper meniscus and for any change in the temperature of the bath) should be obtained whether going up or going down the scale of pressures. When these readings are noticeably divergent we have generally found that a pellet of solution has formed across the mercury thread and therefore such experiments should be viewed with suspicion. On the other hand even if the readings are the same it is no proof of a

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* In later work this difficulty is overcome by fastening a small capsule containing mercury to the bottom of the stem.

† We would draw attention to a source of error which has been observed in one of the Jena-glass piezometers. This error lies in the fact that some of the air bubbles usually present in capillary tubing (as long hair-like lines) communicate with the bore of the tube; when under pressure minute threads of mercury can be seen to be moving in these capillaries.

good experiment; there may have been liquid left behind on the capillary walls which is picked up again when the meniscus reaches it on its downward journey, but we have reason to think that this seldom occurs when changing the pressure slowly as already described.

Example of Experiments.—The following experiments are selected from the laboratory note-book as a sample of our work with the twin bulb piezometer:—

EXPERIMENT with a Solution of α-Methyl Glucoside at 0° C.

(Wt. conc. = 54·692 gr. per 100 gr. water.)

Date.	Time.	Temperatures of		Pressure. Atmospheres.	Readings on		Remarks.
		Bath.	Apparatus.		Upper capillary.	Lower capillary.	
1911 July 7	6.30 p.m.	—	—	—	—	—	Filled Piezometer VIII. and filled up bath with ice.
„ 8	7.15 a.m.	—	—	—	—	—	Filled up with ice.
	7.45 „	—	—	—	—	—	
	8.0 „	—	—	—	—	—	Ran mercury thread into piezometer and placed in bath.
	9.0 „	—	—	—	—	—	Placed piezometer in apparatus (B) and joined up (the dome was previously cooled in ice).
	9.40 „	5·383	6·960	17·01	$26{\cdot}1_5$	410·8	
	9.55 „	5·381	6·920	17·01	—	408·1	Note that 5°·490 on the bath Beckmann = 0°·23 C.
	10.5 „	5·382	6·917	17·01	—	408·0	
	10.15 „	5·382	6·916	17·01	—	407·8	
	10.25 „	5·384	6·916	17·01	26·2	407·8	
	10.53 „	5·382	6·912	57·83	$26{\cdot}2_5$	251·0	
	11.3 „	5·382	6·912	57·83	$26{\cdot}2_5$	251·0	
	11.16 „	5·384	6·914	78·25	26·3	173·0	
	11.26 „	5·385	6·916	78·25	26·3	173·0	
	11.42 „	5·386	6·917	102·06	$26{\cdot}3_5$	83·0	
	11.52 „	5·385	6·916	102·06	$26{\cdot}3_5$	83·0	
	12.1 „	5·383	6·914	57·83	$26{\cdot}2_5$	251·0	
	12.11 „	5·385	6·915	57·83	—	251·2	
	12.21 „	5·385	6·915	57·83	26·25	251·2	
	12.31 „	5·388	6·919	17·01	26·2	408·0	
	12.41 „	5·388	6·919	17·01	26·2	408·0	
	12.51 „	5·388	6·919	17·01	26·2	408·0	

Experiment with a Solution of Cane Sugar at 30° C.

(Wt. conc. = 111·89 gr. per 100 gr. water.)

Date.	Time.	Temperatures of		Pressure. Atmospheres.	Readings on		Remarks.
		Bath.	Apparatus.		Upper capillary.	Lower capillary.	
1911							Filled Piezometer VII. with the solution on 10th, adjusted upper meniscus.
June 12	12.20 p.m.	—	—	—	—	—	Placed piezometer in position and screwed dome on.
	2.30 ,,	—	—	17·01	26·4	—	Joined up to pressure apparatus, and put pressure on till mercury showed in bottom window.
	11.40 ,,	3·444	7·344	17·01	27·2	209·5	
June 13	9.3 a.m.	3·444	7·344	17·01	27·2	209·5	Note that 3°·44 on Beckmann thermometer of bath = 29°·99 C.
	9.25 ,,	—	—	51·03	—	—	
	9.27 ,,	3·444	7·359	51·03	27·2	132·7	
	9.37 ,,	3·444	7·350	51·03	27·2	132·2	
	9.48 ,,	3·444	7·350	51·03	27·2	132·0	
	9.58 ,,	3·444	7·345	51·03	27·2	132·0	
	10.19 ,,	3·444	7·359	85·05	27·25	55·9	
	10.29 ,,	3·444	7·354	85·05	—	55·2	
	10.39 ,,	3·444	7·350	85·05	—	55·0	
	10.50 ,,	3·444	7·344	85·05	27·2	55·0	
	11.0 ,,	3·444	7·320	51·03	27·2	130·5	
	11.10 ,,	3·444	7·332	51·03	—	131·5	
	11.20 ,,	3·444	7·338	51·03	—	131·65	
	11.30 ,,	3·444	7·340	51·03	—	131·85	
	11.40 ,,	3·444	7·340	51·03	—	131·9	
	11.50 ,,	3·444	7·340	51·03	27·2	131·9	
	12.3 p.m.	3·444	7·323	17·01	27·15	208·0	
	12.18 ,,	3·444	7·336	17·01	—	209·1	
	12.35 ,,	3·444	7·340	17·01	—	209·2	
	12.48 ,,	3·444	7·340	17·01	27·2	209·25	
	1.1 ,,	3·444	7·340	17·01	—	209·3	
	2.25 ,,	—	—	—	—	—	Found temperature had fallen owing to failure in relay—adjusted.
	3.21 ,,	3·443	7·334	—	—	208·7	
	3.42 ,,	3·444	7·340	—	—	209·2	
	3.54 ,,	3·443	7·340	—	27·2	209·2	
	4.7 ,,	3·444	7·344	—	27·2	209·2	
	10.0 ,,	3·444	7·343	—	27·25	209·2	

Note.—The apparent constancy of the bath is partly fictitious. The thermometer ought to have been tapped before each reading.

The Corrections.—As already mentioned, a correction has to be applied to the observed pressure for the height of mercury in the stem, this correction (A of Table I.) is self-evident and need not detain us, but a further correction (B of Table I.) due to the same cause has to be applied to the volume of the piezometer, for it is evident that the higher the mercury in the stem, the more the walls of the bulb are caused to come in towards each other.

To obtain this correction a set of separate experiments was made with each piezometer, thus: the piezometer was inverted and filled (up to the graduations in the stem) with recently boiled water. The stem was then connected to a mercury manometer by means of a T-piece, so that by joining the T to an exhaust pump, the pressure on the water could be reduced and the amount of the reduction measured on the manometer. The change in volume caused by the change in pressure is given directly by the difference in readings of the water meniscus. These two corrections (together with others which will be understood readily) as applied to the experiment of June 12, are shown in Table I.

TABLE I.

Observed pressure.	Correction to pressure for excess of external pressure. A.	Corrected pressure.	Observed readings of mercury meniscus in stem.	Volume of solution uncorrected.	Correction to the volume for—			Volume of solution corrected.	Mean relative coefficient of compressibility.	Mean coefficient of compressibility of solution. *	Pressure range above atmospheric pressure.
					Temperature.	Reading of mercury meniscus in upper capillary.	Excess of external pressure B.				
atmospheres.				c.c.					$10^{-5}\times$	$10^{-5}\times$	atmospheres.
17·01	−0·00	17·01	209·5	32·42119	0·0	0·0	0·0	32·42119	2·550	2·773	17 to 51
51·03	−0·09	50·94	132·0	32·39319	−0·00001	0·0	−0·00004	32·39314	2. 528	2·751	51 ,, 85
85·05	−0·19	84·86	55·0	32·36541	0·0	0·0	−0·00008	32·36533	2·529	2·751	85 ,, 51
51·03	−0·09	50·94	131·9	32·39315	+0·00005	−0·00001	−0·00004	32·39315	2·550	2·773	51 ,, 17
17·01	−0	17·01	[209·4] estimated	32·42115	+0·00005	0·0	−0·0	32·42120			

* These values are obtained by adding the coefficient of compressibility of the glass of the piezometer ($= 0·223\times10^{-5}$) to the numbers in the preceding column.

THE RESULTS.

Compressibility of Mercury.—The following is a summary of our results with mercury. Five observations were made:—

With Piezometer 1A. The mean relative coefficient at 0° C. between 1 and 101 atmospheres was $0·169\times10^{-5}$.

With Piezometer 7. The mean relative coefficient at 1°·8 C. between 1 and 110 atmospheres was $0·171\times10^{-5}$.

With Piezometer 1A. The mean relative coefficient at 29°·5 C. between 8 and 150 atmospheres was $0·165\times10^{-5}$.

With Piezometer 3c. The mean relative coefficient at 29°·5 C. between 8 and 89 atmospheres was $0·163 \times 10^{-5}$.

With Piezometer 7. The mean relative coefficient at 30°·4 C. between 28 and 117 atmospheres was $0·169 \times 10^{-5}$.

All the piezometers, except 7 and 8 which are made of soda-glass, are of Jena No.16$^{\text{III}}$ glass, we may therefore mean the results for 1a and 3c at 30° C.

If we take Amagat's value for the coefficient compressibility of mercury at 0° C., namely $0·392 \times 10^{-5}$ and correct it to 30° C. by means of Carnazzi's ('Nuovo Cim.,' 5, 1903, pp. 73–89) temperature coefficient, we get

$$0·393 \times 10^{-5}.$$

Then the Jena-glass piezometer at 0° C. will have a coefficient of

$$0·392 \times 10^{-5} - 0·169 \times 10^{-5} = 0·223 \times 10^{-5};$$

and at 30° C. it will be

$$0·393 \times 10^{-5} - 0·164 \times 10^{-5} = 0·229 \times 10^{-5};$$

whilst the soda-glass piezometers, Nos. 7 and 8, may be taken to have, at 0° C. and 30° C., the coefficients

$$0·221 \times 10^{-5} \text{ and } 0·224 \times 10^{-5} \text{ respectively.}$$

The Compressibility of Water.—For purposes of comparison we give two observations at 0° C., which have already been published; these were obtained with piezometer 1a, and the mean relative coefficient was, between 15 and 76 atmospheres, $4·886 \times 10^{-5}$ in the one case, and in the other $4·904 \times 10^{-5}$ for a range of 1 to 61 atmospheres. On adding the coefficient of compressibility of the Jena-glass the mean coefficient for water becomes $5·109 \times 10^{-5}$ and $5·127 \times 10^{-5}$ respectively. These numbers agree with one another remarkably well and do not differ greatly from Amagat's values. The new results for water at 0° C. and 30° C. are given in Table II., where the columns tabulate the following:—

(1) Gives the number of the piezometer; (2) the mean temperature to which the results are reduced; (3) the pressure range—in the experiments with piezometers 7 and 8 the range is given both for a rising pressure and a falling one; (4) gives the mean relative coefficient of compressibility; (5) the coefficient for the glass of the particular piezometer in use, derived from the compressibility of mercury; (6) the coefficient of the liquid alone.

TABLE II.—Water at 0° C. and 30° C.

No. of piezometer.	Mean temperature of observation.	Pressure range in atmospheres above atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.	No. of piezometer.	Mean temperature of observation.	Pressure range in atmospheres above atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.
	° C.		$\times 10^{-5}$	$\times 10^{-5}$	$\times 10^{-5}$		° C.		$\times 10^{-5}$	$\times 10^{-5}$	$\times 10^{-5}$
7	0·12	10 to 27	4·864	0·221	5·085	8	0·18	14 to 41	4·850	0·221	5·071
		27 „ 48	4·858	—	5·079			41 „ 68	4·820	—	5·041
		48 „ 27	4·858	—	5·079			68 „ 41	4·819	—	5·040
		27 „ 10	4·869	—	5·090			41 „ 14	4·849	—	5·070
1A	29·52	0 to 14	4·382	0·229	4·611	3C	29·53	20 to 41	4·282	0·229	4·511
		14 „ 27	4·362	—	4·591			41 „ 54	4·225	—	4·454
		27 „ 41	4·316	—	4·545			54 „ 75	4·221	—	4·450
		41 „ 54	4·240	—	4·469			75 „ 95	4·180	—	4·409
7	29·6	10 to 51	4·263	0·224	4·487	7	30·19	20 to 32	4·262	0·224	4·486
		51 „ 10	4·261	—	4·485			32 „ 41	4·238	—	4·462
								41 „ 54	4·239	—	4·463
								54 „ 65	4·219	—	4·443
								65 „ 54	4·207	—	4·431
								54 „ 41	4·241	—	4·465
								41 „ 32	4·224	—	4·448
								32 „ 20	4·251	—	4·475
8	30·01	17 to 48	4·234	0·224	4·458						
		48 „ 78	4·210	—	4·434						
		78 „ 48	4·207	—	4·431						
		48 „ 17	4·234	—	4·458						

TABLE III.—Cane Sugar at 0° C.

No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of glass of piezometer.	True mean coefficient of solution.	No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of glass of piezometer.	True mean coefficient of solution.
	° C.		$\times 10^{-5}$	$\times 10^{-5}$	$\times 10^{-5}$		° C.		$\times 10^{-5}$	$\times 10^{-5}$	$\times 10^{-5}$
1A* 180 gr. of sugar per litre at laboratory temperature.	0·01	0 to 20	4·168	0·223	4·391	1A* 300 gr. of sugar per litre at laboratory temperature.	0·00	0 to 20	3·747	0·223	3·970
		20 ,, 41	4·178	—	4·401			20 ,, 41	3·730	—	3·953
		41 ,, 61	4·165	—	4·388			41 ,, 61	3·700	—	3·923
		61 ,, 82	4·135	—	4·358			61 ,, 82	3·673	—	3·896
1A* 420 gr. of sugar per litre of solution at laboratory temperature.	0·02	0 to 20	3·301	0·223	3·524	7 56·80 gr. of sugar to 100 gr. of water (420).	0·28	7 to 34	3·257	0·221	3·478
		20 ,, 37	3·303	—	3·526			34 ,, 61	3·241	—	3·462
		37 ,, 51	3·298	—	3·521			61 ,, 34	3·241	—	3·462
		51 ,, 81	3·270	—	3·493			34 ,, 7	3·257	—	3·478
1A* 540 gr. of sugar per litre at laboratory temperature.	0·01	0 to 20	2·973	0·223	3·196	3B* 660 gr. of sugar per litre at laboratory temperature.	0·21	0 to 20	2·611	0·223	2·834
		20 ,, 41	2·962	—	3·185			20 ,, 41	2·577	—	2·800
		41 ,, 61	2·925	—	3·148			41 ,, 61	2·567	—	2·790
		61 ,, 81	2·895	—	3·118			61 ,, 82	2·550	—	2·773
								82 ,, 102	2·509	—	2·732

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* These experiments were done with the old apparatus having a glass tube outside.

TABLE III—Cane Sugar at 0° C. (continued).

No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of glass of piezometer.	True mean coefficient of solution.	No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of glass of piezometer.	True mean coefficient of solution.
7 111·9 gr. of sugar to 100 gr. of water (660).	° C. 0·13	7 to 41 41 ,, 75 75 ,, 41 41 ,, 7	$\times 10^{-5}$ 2·575 2·556 2·563 2·576	$\times 10^{-5}$ 0·221 — — —	$\times 10^{-5}$ 2·796 2·777 2·784 2·797	3B* 750 gr. of sugar per litre at laboratory temperature.	° C. 0·03	0 to 20 20 ,, 41 41 ,, 61 61 ,, 82	$\times 10^{-5}$ 2·309 2·346 2·340 2·329	$\times 10^{-5}$ 0·223 — — —	$\times 10^{-5}$ 2·532 2·569 2·563 2·552
3B* 750 gr. of sugar per litre at laboratory temperature.	0·03	0 to 20 20 ,, 41 41 ,, 61 61 ,, 82	2·739 2·302 2·235 2·216	0·223 — — —	2·962 2·525 2·458 2·439	3C 750 gr. of sugar per litre at laboratory temperature.	0·00	14 to 48 48 ,, 82 82 ,, 122 122 ,, 14	2·347 2·323 2·292 2·322	0·223 — — —	2·570 2·546 2·515 2·545
7 141·4 gr. of sugar to 100 gr. of water (750).	0·10	7 to 44 44 ,, 82 82 ,, 44 44 ,, 7	2·343 2·324 2·322 2·341	0·221 — — —	2·564 2·545 2·543 2·562	1A 182·7 gr. of sugar to 100 gr. of water (850).	0·00	0 to 20 20 ,, 48 48 ,, 75 75 ,, 105	2·212 2·160 2·153 2·139	0·223 — — —	2·435 2·383 2·376 2·362
7 183·5 gr. of sugar to 100 gr. of water (850).	0·12	0 to 41 41 ,, 88 88 ,, 41 41 ,, 0	2·123 2·112 2·112 2·125	0·221 — — —	2·344 2·333 2·333 2·346	7 215·4 gr. of sugar to 100 gr. of water (920).	0·20	10 to 27 27 ,, 48 48 ,, 95 95 ,, 48 48 ,, 10	2·014 2·002 1·995 1·991 2·015	0·221 — — — —	2·235 2·223 2·216 2·212 2·236

* These experiments were done with the old apparatus having a glass tube inside.

TABLE IV.—Cane Sugar at 30° C.

No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above the atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.	No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above the atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.
	° C.		× 10⁻⁵	× 10⁻⁵	× 10⁻⁵		° C.		× 10⁻⁵	× 10⁻⁵	× 10⁻⁵
3c 420 gr. sugar per litre at laboratory temperature.	29·52	0 to 27	3·106	0·229	3·335	7 56·7 gr. sugar to 100 gr. of water (540).	29·84	17 to 41	3·111	0·224	3·335
		27 ,, 54	3·076	—	3·305			41 ,, 71	3·087	—	3·311
		54 ,, 82	3·061	—	3·290			71 ,, 41	3·091	—	3·315
		82 ,, 109	3·025	—	3·254			41 ,, 17	3·104	—	3·328
		0 ,, 82	3·079	—	3·308						
3c 540 gr. sugar per litre at laboratory temperature.	29·53	0 to 27	2·824	0·229	3·053	3c 660 gr. sugar per litre at laboratory temperature.	29·83	0 to 27	2·552	0·229	3·781
		27 ,, 61	2·794	—	3·023			27 ,, 61	2·559	—	3·788
		61 ,, 88	2·769	—	2·998			61 ,, 95	2·504	—	3·733
		88 ,, 116	2·783	—	3·012			95 ,, 122	2·485	—	3·714
7 660 gr. sugar per litre at laboratory temperature.	29·55	17 to 34	2·562	0·224	2·786	7 111·9 gr. sugar to 100 gr. of water (660).	29·87	17 to 51	2·550	0·224	2·774
		34 ,, 51	2·547	—	2·771			51 ,, 85	2·528	—	2·752
		51 ,, 68	2·527	—	2·751			85 ,, 51	2·529	—	2·753
		68 ,, 88	2·509	—	2·733			51 ,, 17	2·550	—	2·774
3c 142·1 gr. sugar to 100 gr. of water (750).	29·52	0 to 34	2·370	0·229	2·599	3c 850 gr. sugar per litre at laboratory temperature.	29·52	0 to 34	2·176	0·229	2·405
		34 ,, 68	2·350	—	2·579			34 ,, 75	2·163	—	2·392
		68 ,, 102	2·332	—	2·561			75 ,, 109	2·132	—	2·361
		102 ,, 136	2·302	—	2·531			109 ,, 149	2·115	—	2·344

TABLE IV.—Cane Sugar at 30° C. (continued).

No. of piezometer and concentration.	Mean temperature of observation.	Pressure range in atmospheres above the atmospheric pressure.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.
	° C.		× 10⁻⁵	× 10⁻⁵	× 10⁻⁵
3C 185·3 gr. sugar to 100 gr. water (850).	29·53	0 to 34	2·165	0·229	2·394
		34 „ 75	2·144	—	2·373
		75 „ 109	2·130	—	2·359
		109 „ 147	2·117	—	2·346
7 183·6 gr. sugar to 100 gr. of water (850).	29·90	20 to 61	2·189	0·224	2·413
		61 „ 102	2·138	—	2·362
		102 „ 61	2·140	—	2·364
		61 „ 20	2·186	—	2·410
1A 920 gr. sugar per litre at laboratory temperature.	29·53	17 to 44	2·130	0·229	2·359
		44 „ 71	2·055	—	2·284
7 238·3 gr. sugar to 100 gr. water (960).	29·54	27 to 71	1·974	0·224	2·198
		71 „ 116	1·919	—	2·143
		116 „ 71	1·920	—	2·144
		71 „ 27	1·975	—	2·199
	29·72	27 „ 71	1·983	—	2·207
	° C.		× 10⁻⁵	× 10⁻⁵	× 10⁻⁵
1A 185·3 gr. sugar to 100 gr. water (850).	29·53	0 to 27	2·202	0·229	2·431
		27 „ 54	2·166	—	2·395
		54 „ 75	2·168	—	2·395
		75 „ 102	2·143	—	2·372
1A 218·5 gr. sugar to 100 gr. water (920).	29·52	0 to 27	2·089	0·229	2·318
		27 „ 54	2·071	—	2·300
		54 „ 82	2·053	—	2·282
		82 „ 109	2·043	—	2·272
1A 243·0 gr. sugar to 100 gr. of water (960).	29·53	0 to 27	2·019	0·229	2·248
		27 „ 61	2·004	—	2·233
		61 „ 88	1·984	—	2·213
		88 „ 116	1·976	—	2·205

TABLE V.—α-Methyl Glucoside at 0° C. and 30° C.

No. of piezometer and weight concentration.	Mean temperature of observation.	Pressure range above the atmospheric pressure in atmospheres.	Mean relative coefficient of compressibility.	Coefficient of compressibility of the glass.	True mean coefficient of compressibility.
	° C.		$\times 10^{-5}$	$\times 10^{-5}$	$\times 10^{-5}$
8 23·0 gr. to 100 gr. of water.	0·12	17 to 48	3·857	0·221	4·078
		48 ,, 82	3·843	—	4·064
		82 ,, 48	3·834	—	4·055
		48 ,, 17	3·866	—	4·087
8 54·7 gr. to 100 gr. of water.	0·13	17 to 58	3·110	0·221	3·331
		58 ,, 78	3·081	—	3·302
		78 ,, 102	3·069	—	3·290
		102 ,, 58	3·076	—	3·297
		58 ,, 17	3·109	—	3·330
8 75·3 gr. to 100 gr. of water.	0·21	20 to 48	2·817	0·221	3·038
		48 ,, 92	2·798	—	3·019
		92 ,, 48	2·800	—	3·021
		48 ,, 20	2·817	—	3·038
		[20 ,, 0	2·812	—	3·033]
8 90·2 gr. to 100 gr. of water.	0·13	0 to 44	2·672	0·221	2·893
		44 ,, 95	2·649	—	2·870
		95 ,, 44	2·649	—	2·870
		44 ,, 0	2·671	—	2·892
	° C.		$\times 10^{-5}$	$\times 10^{-5}$	$\times 10^{-5}$
7 23·0 gr. to 100 gr. of water.	29·98	20 to 31	3·624	0·224	3·848
		31 ,, 44	3·635	—	3·859
		44 ,, 58	3·605	—	3·829
		58 ,, 68	3·512	—	3·736
		68 ,, 58	3·567	—	3·791
		58 ,, 44	3·601	—	3·825
		44 ,, 31	3·637	—	3·861
		31 ,, 20	3·609	—	3·833
7 54·5 gr. to 100 gr. of water.	29·98	20 to 37	3·101	0·224	3·325
		37 ,, 51	3·107	—	3·331
		51 ,, 64	3·062	—	3·286
		64 ,, 78	3·103	—	3·327
		78 ,, 64	3·071	—	3·301
		64 ,, 51	3·094	—	3·318
		51 ,, 37	3·112	—	3·335
		37 ,, 20	3·105	—	3·329
7 75·2 gr. to 100 gr. of water.	29·99	14 to 27	2·931	0·224	3·155
		27 ,, 41	2·895	—	3·119
		41 ,, 58	2·883	—	3·107
		58 ,, 71	2·876	—	3·100
		71 ,, 58	2·876	—	3·100
		58 ,, 41	2·883	—	3·107
		41 ,, 27	2·890	—	3·114
		27 ,, 14	2·922	—	3·146
8 90·2 gr. to 100 gr. of water.	29·86	24 to 75	2·755	0·224	2·979
		75 ,, 95	2·740	—	2·964
		95 ,, 119	2·719	—	2·943
		119 ,, 95	2·719	—	2·943
		95 ,, 75	2·738	—	2·962
		75 ,, 24	2·757	—	2·981

On looking at the tables it will be seen that the values for piezometers 7 and 8 at 0° C., although agreeing among themselves, are considerably lower than our previous results. We are, however, inclined to attach more weight to these experiments, for as may be seen by comparing the numbers for rising and for falling pressures, they are very concordant. In the experiments at 30° C., the earlier values with the Jena-glass piezometer are again higher. It is evident that the experiment with No. 7 at 30°·19 C. is somewhat faulty; we are unable to give a reason for this.

The Results for Cane Sugar.—The experiments at 0° C. are gathered together in Table III. where the columns have the same meaning as for water, except that the concentration of the solution is put under the number of the piezometer in column (1), and when the solution had been made up by weight, its approximate volume concentration (number of grammes per litre) is given in brackets. The numbers in column (4) for the experiments with the Jena-glass piezometers are generally the mean values obtained with a rising and a falling pressure; these, as already mentioned, are by no means concordant. In one or two cases even with No. 7 there were failures due to temperature troubles or to the mercury thread breaking. These remarks apply generally to all our observations.

Again it will be noticed that the No. 7 results are lower on the whole than those for the other piezometers.

The experiments at 30° C. are tabulated in the same way in Table IV., and again the values for piezometer 7 are lower.

The Results for α-methyl Glucoside.—These, both for 0° C. and 30° C., are given in Table V. All the observations are made with either piezometers 7 or 8 and they seem, except in one case, to be good.

Final Values for the Compressibilities.—In this communication the compressibilities are only required for the purpose of calculating the s of PORTER's equation.* The solutions themselves are very incompressible, so that even over the range of the highest osmotic pressure the effect on the volume is but small, and therefore the pressure effect on s will be that of a small correcting term. In these circumstances it will suffice to give the mean coefficients (over the range from one atmosphere to the osmotic pressure of each solution) that we will use later on. In the set of mean values entered in Table VI. greater importance was given to the best experiment with piezometers 7 and 8.

The Calculation of s.—Although it is common knowledge that the quantity s, for the solutions with which we are concerned, differs but little from unity, yet it seems worth while to give the following analysis (due to Mr. G. W. WALKER), as there are numerous cases in which a detailed statement may be important.

Prof. PORTER† defines s_1 as "the reduction in a practically infinite volume of

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* 'Roy. Soc. Proc.,' A, vol. 80, 1908, p. 460.

† *Loc. cit.*

TABLE VI.—Cane Sugar.

Approximate volume concentration.	Weight concentration.	At 0° C.		At 30° C.	
		$k \times 10^{-5}$.	Pressure range. 1 to osmotic pressure.	$k \times 10^{-5}$.	Pressure range. 1 to osmotic pressure.
—	34·0	—	—	3·62	1 to 27
420	56·5	3·46	1 to 44	3·31	1 ,, 47
540	81·2	—	—	3·00	1 ,, 73
660	112·0	2·78	1 to 100	2·73	1 ,, 108
750	141·0	2·53	1 ,, 135	2·56	1 ,, 143
850	183·0	2·33	1 ,, 187	2·36	1 ,, 199
920	217·5	2·20	1 ,, 230	2·28	1 ,, 249
960	243·0	—	—	2·15	1 ,, 264

α-Methyl Glucoside.

Approximate volume concentration.	Weight concentration.	At 0° C.		At 30° C.	
		$k \times 10^{-5}$.	Atmospheres.	$k \times 10^{-5}$.	Atmospheres.
—	23·0	4·096	1 to 30	3·860	1 to 32
—	54·7	3·327	1 ,, 81	3·326	1 ,, 82
—	73·3	3·027	1 ,, 113	3·104	1 ,, 114
—	90·2	2·869	1 ,, 141	2·971	1 ,, 141

solution when one gramme of solvent escapes"; the pressure being maintained constant. The corresponding quantity for the solute is s_2.

Hence if w is the specific volume of the solution at any pressure p, and c_1 and c_2 are the concentrations (grammes per gramme of solution) of the two constituents, we deduce that

$$s_1 = w - c_2\,\partial w/\partial c_2,^*$$

where w is a function of c_2 and p, and

$$s_2 = w - c_1\,\partial w/\partial c_1,$$

where w is a function of c_1 and p.

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* CALLENDAR, 'Roy. Soc. Proc.,' A, vol. 80, 1908, p. 470, gives this equation without proof. It may be obtained thus: Let m_1 and m_2 be the masses of the two components present in a volume V of solution, then $m_1/(m_1+m_2) = c_1$ and $m_2/(m_1+m_2) = c_2$ and $w = \mathrm{V}/(m_1+m_2)$. Now add a mass δm_1 of solvent, and let the increase in volume be $\delta\mathrm{V}$, we have $m_2/(m_1+m_2+\delta m_1) = c_2+\delta c_2$ and $w+\delta w = (\mathrm{V}+\delta\mathrm{V})/(m_1+m_2+\delta m_1)$, from which $w - c_2\,\partial w/\partial c_2 = \delta\mathrm{V}/\delta m_1$, which is s_1.

From this it follows, since $c_1+c_2 = 1$, that

$$w = s_1c_1+s_2c_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$c_1\,\partial s_1/\partial c_2 = c_2\,\partial s_2/\partial c_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The form of (1) at first suggests that s_1 and s_2 are the specific volumes in the solution of the two components. This is not necessarily so. For calling the true specific volumes $s_1{}^1$ and $s_2{}^1$, then we have $w = s_1{}^1c_1+s_2{}^1c_2$, which on differentiating gives

$$s_1{}^1 = w-c_2\,\partial w/\partial c_2+c_2\,(c_1\,\partial s_1{}^1/\partial c_2-c_2\,\partial s_2{}^1/\partial c_1),$$

and

$$s_2{}^1 = w-c_1\,\partial w/\partial c_1-c_1\,(c_1\,\partial s_1{}^1/\partial c_2-c_2\,\partial s_2{}^1/\partial c_1),$$

thus

$$s_1{}^1 = s_1 \text{ and } s_2{}^1 = s_2 \text{ only if } c_1\,\partial s_1{}^1/\partial c_2 = c_2\,\partial s_2{}^1/\partial c_1.$$

There does not appear to be any adequate ground for supposing this condition is in general satisfied. If it is not, we have $s_1{}^1 = s_1+kc_2$ and $s_2{}^1 = s_2-kc_1$ where $k = (c_1\,\partial s_1{}^1/\partial c_2-c_2\,\partial s_2{}^1/\partial c_1)$ is in general a function of the pressure and concentration.

Returning now to the calculation of s_1. Some of the densities given in LANDHOLT and BÖRNSTEIN for cane sugar solutions having been verified experimentally, the remainder of their table was taken as correct; the densities of the α-methyl glucoside solutions were determined by us and the mean values are tabulated in Table VII.

TABLE VII.—Cane Sugar.

Weight concentration.	$\bar{s}_1$ at	
	0° C.	30° C.
34·00	0·99768	1·00287
56·50	0·99515	1·00103
81·20	0·98157	0·99873
112·0	0·98690	0·99554
141·0	0·98321	0·99176
183·0	0·97842	0·98653
217·5	0·97399	0·97360
243·0	0·97117	0·98176

α-Methyl Glucoside.

Weight concentration.	Densities at		$\bar{s}_1$ at	
	0° C.	30° C.	0° C.	30° C.
25·0	—	—	—	—
35·0	1·09319	1·08399	0·99810	1·00260
45·0	1·11341	1·10308	0·99709	1·00186
55·0	1·13149	1·12017	0·99597	1·00087
64·0	1·14619	1·13407	0·99491	0·99996
75·0	1·16243	1·14942	0·99354	0·99881
90·0	1·18195	1·16788	0·99166	0·99721
105·0	1·19896	1·18399	0·98974	0·99507

Empirical formulæ were then obtained which represented the experimental values of the densities and the compressibilities (Table VI.) for different concentrations, and from these formulæ the values s_1 were computed as a function of c_2 and p_0. In PORTER'S equation* s_1 has to be integrated over a range of pressure from one atmosphere to the osmotic pressure of the particular solution; it was considered sufficiently accurate to regard it as a linear function of the pressure and the mean value, $\bar{s}_1$ (equals half the sum of the value at the limits) is given in Table VII.

PART II.

THE VAPOUR-PRESSURE MEASUREMENTS.

Description of Apparatus and Method.—Although the method employed has already been described it may not be out of place to recall it to mind.

Dry air is led through a number of vessels containing the solution, then through a vessel containing the solvent (water), and finally over sulphuric acid in the end vessel of the train. The air is supposed to flow slowly enough to be saturated up to the vapour pressures of the liquids. In these circumstances, if we call the sum of the losses of weight of solution and solvent l_0, and the loss in the solution alone l_1, then the observed ratio of the vapour density of the solvent to the vapour density of the solution is l_0/l_1.

This statement is however subject to various corrections; but, before considering these, it will be convenient to describe the complete installation.

Fig. 3 represents in diagram form the arrangement for passing the air stream over the vessels, as finally modified so as to eliminate the various sources of error, which several years' experience has shown to be possible.

Filtered air, drawn from outside the laboratory, is passed through soda-lime, and then over the surface of sulphuric acid in vessel A, where it is deprived of almost all its moisture. (It may here be mentioned that the chief aim of this final arrangement has been to avoid, as far as possible, any sudden alteration of pressure; the air passages are therefore made as wide as may be and at no point does the air bubble through any liquid.) On leaving A the air passes through another sulphuric acid vessel B which is in, and at the constant temperature of, the bath; it then enters the train of weighed vessels 1, 2, 3, 4, and 5, which contain the various liquids under examination; the last of these, No. 5, is again a sulphuric acid vessel.

From 5 it goes to the regulating valve C. This valve, which was designed by BERKELEY and THOMAS for another research, consists of a biscuit-porcelain filter (f) surrounded to a variable height by mercury. It will be seen that the volume of

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* See p. 343.

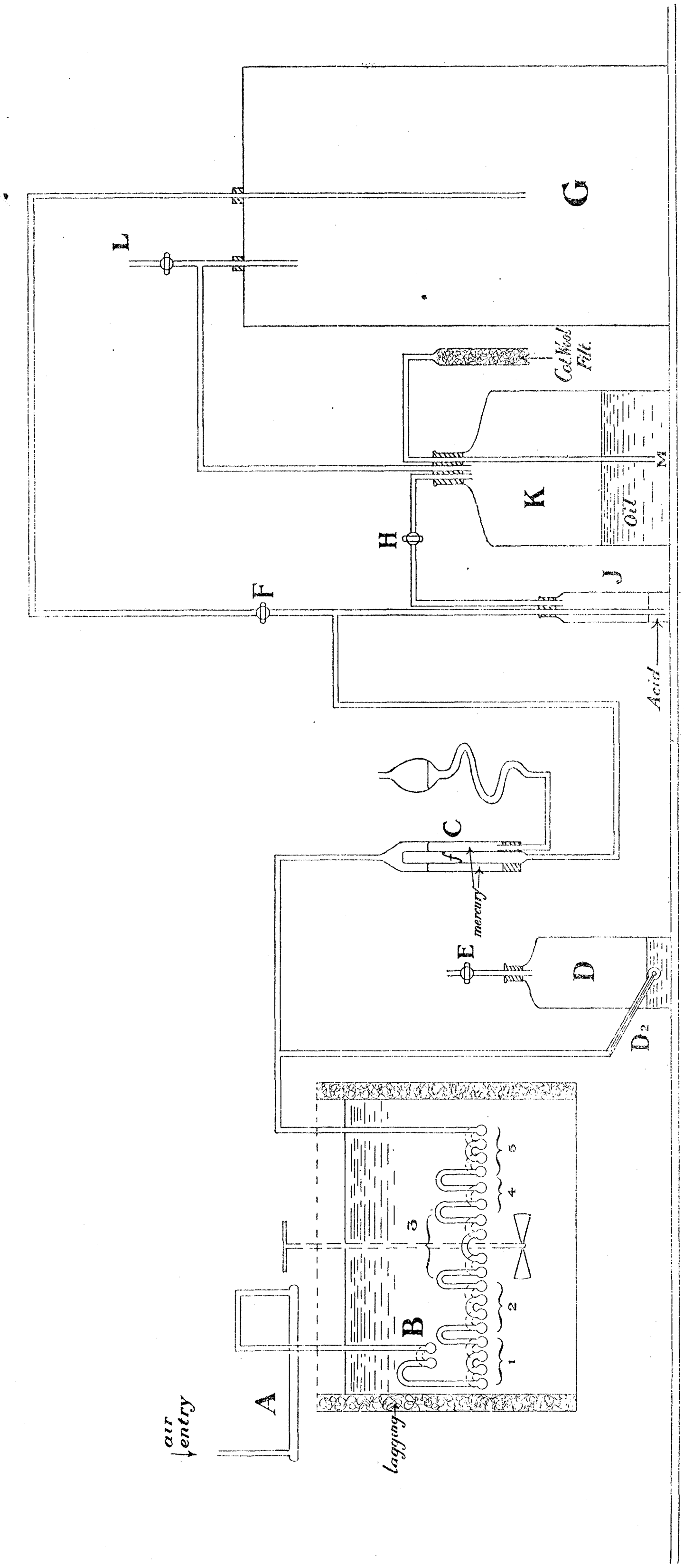
air entry
lagging
A
B
1
2
3
4
5
C
f
mercury
D
D2
E
F
G
H
J
K
L
M
Oil
Acid
Cot. Wool Filt.

Fig. 3.

air passing through the whole apparatus is approximately proportional to the area of the filter not covered by mercury, and it may be stated that we have found this device most useful, especially when it is provided with a graduated scale to enable one to set the mercury level to a definite height.

Before reaching C, the air has passed a side-tube which connects with the vessel D. This vessel (of 5 litres capacity), containing a small quantity of water, the level of which is observed (telescopically) in the graduated capillary tube D_2, serves three purposes. With the tap E closed, and the mercury in C adjusted to the proper level, the rise of the water in D_2 is a measure of the rate at which the air is passing; thus any obstruction in the air stream will at once be indicated, while the amplitude of the oscillations (if any) of the water meniscus affords a means of detecting outside atmospheric pulses. Again, with the tap E open (and this is the normal position during an experiment) the outside air pulses are practically eliminated, and any oscillations that may then be apparent are the result of changes in pressure on the exhaust side. It was found that when the iron tank G was added to the apparatus the pulses were so reduced as to be scarcely perceptible.

The air normally passes through tap F into G (200 litres capacity), and tap H is kept closed; this latter tap is only used in conjunction with vessel J when testing the various joints for leaks. A partial vacuum is maintained both in G and in the 15-litre jar K by a Fleuss pump (not shown) which is joined on at L. In the main, the degree of vacuum is determined by the height of oil in K, above the air inlet M.

We will now consider the various corrections that have to be applied to the experimentally determined vapour pressures.

BURTON'S *Correction.*—The most important of these is that which we will call "BURTON'S correction," for it was he who showed that the effect is not negligible as we had erroneously assumed. The correction is inherent in the method itself, and will be apparent at once when it is realized that the air stream (which has been saturated up to the vapour-pressure of the solution) on entering the water vessel is expanded slightly by the vapour it takes up there; consequently the volume of air when leaving the water vessel is slightly greater than when it left the solution.

This correction, together with the effect due to changes in barometric pressure, was briefly outlined in 'Nature' (March 11, 1915, p. 34); there are, however, other factors involved which make a more general discussion desirable.

If we make the assumptions that the temperature of both solution and solvent is the same and remains constant, and that the air space between them is negligibly small, and further, that the air stream flows slowly enough for complete saturation and freedom from turbulent motion, then the following analysis (for which we have to thank Mr. G. W. WALKER) will be applicable.

Let p be the pressure of the air at any point in the train of vessels and r its rate of passage in cubic centimetres per second. Let π_π and π_0 be the vapour pressures of solution and solvent respectively and ρ_1 and ρ_0 the corresponding vapour densities.

If p_1 and r_1 be the values of p and r when the air enters the solution vessel, then the volume of air that passes through this vessel in time δt is

$$\frac{r_1 p_1}{p_1 - \pi_\pi}\,\delta t,$$

and the mass of vapour carried off is

$$\frac{\rho_1 r_1 p_1}{p_1 - \pi_\pi}\,\delta t,$$

and the loss of weight will be

$$l_1 = \int_0^t \frac{\rho_1 r_1 p_1}{p_1 - \pi_\pi}\,dt,$$

where t is the whole time of the experiment.

In a similar way, if the dry air were passed through the solvent vessel the loss of weight would be

$$l_0 = \int_0^t \frac{\rho_0 r_0 p_0}{p_0 - \pi_0}\,dt.$$

But in the actual experiment the moist air passes from the solution to the solvent, so that the loss of weight in the solvent vessel is

$$l_0 - l_1 = \int_0^t \left(\frac{\rho_0 r_0 p_0}{p_0 - \pi_0} - \frac{\rho_1 r_1 p_1}{p_1 - \pi_\pi}\right) dt.$$

Since the mass of air passing through is the same at all points, $r_1 p_1 = r_0 p_0$. Also as r is proportional to the effective driving pressure through the whole train of vessels (and to a factor depending on the dimensions of the apparatus), if we assume this pressure and the barometer to be constant, we have

$$\frac{l_0}{l_1} = \frac{\rho_0}{\rho_1} = \frac{p_1 - \pi_\pi}{p_0 - \pi_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

but p_1 and p_0 are of the order of 0·1 mm. Hg below atmospheric pressure, whilst the difference between them is of order 0·004 mm. Hg ; and further, the barometric pressure, B, is of the order 760 and π_0 of 30 mm. mercury ; we may, therefore, as a first approximation write

$$\frac{l_0}{l_1} = \frac{\rho_0}{\rho_1} = \frac{\mathrm{B} - \pi_\pi}{\mathrm{B} - \pi_0},$$

and assuming

$$\frac{\pi_\pi}{\pi_0} = \frac{\rho_1}{\rho_0}$$

we get

$$\frac{\rho_0}{\rho_1} = \frac{l_0}{l_1}\,\frac{\pi_0}{\mathrm{B}}\left(\frac{l_0}{l_1} - 1\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If either the barometer or the driving pressure varies, this formula is not strictly correct, and in general we should have to evaluate the integral numerically from a record of the pressures ; we may still, however, write

$$l_1 = t\left(\frac{\rho_1 r_1 p_1}{p_1 - \pi_{\pi}}\right)_{\text{mean}} \quad \text{and} \quad l_0 = t\left(\frac{\rho_0 r_0 p_0}{p_0 - \pi_0}\right)_{\text{mean}},$$

where the quantities involved must now be given some mean value, which is not necessarily the arithmetic mean.

But in the experiments the magnitude of the quantities makes it clear that the arithmetic mean is a very close approximation to the true value, and hence equation (4) is sufficiently accurate if B is the mean barometer.

To make quite sure that this is correct we have verified it in an extreme case, where during the experiment the barometer varied irregularly by some 30 mm., but no sensible error was introduced. Nevertheless cases may arise in which the error might be important, and attention is therefore drawn to it so that the correction may not be overlooked. For instance, during high winds the barometer fluctuates rapidly, and it is conceivable that equilibrium is not established throughout the apparatus instantaneously. In this case the assumptions made in the formula are not valid, and indeed we have some experimental evidence that the results are affected by rapid air pulses.

As regards a change in the temperature of the bath, obviously the quantities involved in the calculation are also affected, but equation (4), in which the values appropriate to the mean temperature are used, is still a close approximation provided the temperature changes are sufficiently small.

In our experiments l_0/l_1 is always less than 1·22, hence the osmotic pressure, which is proportional to $\log_e l_0/l_1$, is approximately proportional to $(l_0 - l_1)/l_0$; thus it is only with the loss of weight of the water vessel that the highest accuracy is required.

We will now endeavour to estimate the errors involved should the assumptions made at the beginning of the preceding analysis not be strictly accurate.

*Solution and Solvent not at same Temperature.**—Although the effect of a difference between the temperatures of the solution and solvent could be investigated fully from the equations already established, yet it is thought that the following simple method of considering the matter is sufficient. Take the case of a weight normal solution of cane sugar at 30° C. This solution is the most dilute that we have investigated, and it is here that the error due to a temperature difference has the largest effect. Suppose $l_0 = 20$ gr. (*i.e.*, 20 gr. of water are evaporated from the whole system during the run) and $l_0 - l_1 = 0·5$ gr. Now assume a persistent difference in temperature during the whole run of 0°·001 C ; this is equivalent to a change of 0·006 per cent. in the vapour density of water ; so that the loss in the water vessel will differ from the

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* See note at end of paper.

true value by $20 \times 0{\cdot}006/100 = 0{\cdot}0012$ gr., entailing a per cent. error of 0·2 both in the loss in this vessel and on the calculated osmotic pressure.

Several attempts to explore the distribution of temperature throughout the bath were made with Beckman thermometers and with thermocouples, but, except within about 3 cm. of the surface, no certain indication of a difference approaching to 0°·001 C. could be detected; further, as a check to this, vapour pressure experiments in which the bath was stirred 50 per cent. faster than the normal rate (in the normal rate, the surface of the water immediately over the stirrer is raised about 1 cm. above the general level) resulted in no change.

Similarly, should the pressure p_1 (see equation (3)) over the solution differ from p_0 over the solvent by as much as 0·015 mm. Hg, an amount which represents a change of 0·02 per cent. on the volume of air passed, we get an error on the loss of weight of the solvent of 0·0004 gr., and this is nearly 0·1 per cent. on the osmotic pressure derived from experiments on a weight normal solution at 30° C. Direct observations (by means of a sensitive oil manometer) of the difference between p_1 and p_0 show that in no case is this quantity greater than 0·004* mm. Hg, and the consequent correction will be, for the most dilute solutions, about 1 part in 5000. It should be pointed out, however, that the magnitude of the correction is proportional to the vapour pressure of the pure solvent, so that for very volatile liquids or water at a higher temperature the air passages must be wide so as to offer as little resistance to flow as possible.

Air Space between Solution and Solvent.—An error, due to the air space between the two vessels, may arise thus. When the barometer is varying no steady state is reached, and it is easy to see that as it takes a finite time for the air to travel from one vessel to the other, $r_1\ p_1$ and $r_0\ p_0$ are no longer equal, and a time lag results.

An estimate of the maximum error due to this cause is the following.

From the dimensions of the apparatus it is computed that, supposing 500 litres of air to pass in 125 hours, it will take 25 seconds to pass from one vessel to the other. If the barometer rises 30 mm. during the run, it is readily found that the solvent vessel will have lost 0·00005 gr. in excess of the amount given by the approximate formula (4).

Slowness of Air Stream and Turbulent Motion.—There seems to be no means of subjecting these two factors to mathematical analysis; but in both cases we may safely assume that any effect there may be will be enhanced when we increase the rate at which water vapour is taken from the system. Experiments, the details of which need not be given, were made in this direction, but without any variation in the result; also a further safeguard is provided by the fact that in experiments where there were two or more vessels (containing the solution) in series, the last vessel scarcely changes in weight. It is as well however to point out that owing to the irregular contours of the air passages some turbulent motion must set up,

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* This is for Apparatus A; for Apparatus D the fall of pressure is about 0·001 mm. Hg.

and possibly fluctuations in this may help to cause the slight variations which seem to occur in high winds.

Weighing Corrections.—In applying the usual buoyancy corrections there are two special circumstances to be considered. In the earlier part of our research we had been content to regard the loss of weight in the solution as a measure of the change in the volume of displaced air for which the buoyancy correction should be calculated. Having improved the manipulation and consequently the accuracy of the experiments, it was seen that this rough estimate could be bettered if we knew the specific volume of the solution remaining in the vessel at the end of the run. The data required are obtained approximately if we know the initial quantity of solution in each branch and how far crystallization has proceeded.

The magnitude of the correction thus deduced is in no case greater than 0·0015 gr. and may in the calculations of osmotic pressure be neglected; it however is of importance when we balance the losses against the gain by the sulphuric acid in the end vessel.

Similarly, but only since November 5, 1915, have we applied the corresponding correction to the change in the specific volume of the sulphuric acid when it absorbs water. In this case we have succeeded in making the correction more precise, for knowing that practically all the water is absorbed in the first two branches* of the vessel, it is an easy matter (especially in the new quartz apparatus) to cause their contents to mix, so that having noted the original amount of acid present the specific volume of this new solution can be calculated. The correction obviously depends on the relative quantities of acid and water; it has never risen to a higher figure than 0·0045 gr.

From a series of blank weighings with vessels treated as in an actual experiment it was deduced that the probable weighing error is ±·0005 gr., a quantity which is about the millionth part of the total weight on the pans.

Other Sources of Error.—A few other sources of error have been investigated, but as, in the apparatus used, their effect is never large enough to alter the results, they will only be mentioned briefly. There is a small weighing error due to the fact that the air contained in the water vessel† is saturated, and its density is therefore less than that of the air in the balance case. The usual buoyancy correction might have to be modified were it not that the vessels are weighed before and after the experiment under practically the same circumstances. It is found that even two or three degrees difference in the temperature of the balance case, although it causes a change in the vapour pressure, does not affect the weighings.

It was thought that plunging the vessels straight from the laboratory temperature into the bath at 30° C. might bring about some uncertainties; these, if any, are

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[*] See BERKELEY and HARTLEY, "On a New Form of Sulphuric Acid Drying Vessel," 'Phil. Mag.,' vol. 29, 1915.

[†] Care is taken that the pressure inside the vessel is the same as that in the balance case.

reduced to small dimensions if care be taken that the full air stream is not turned on before the apparatus has come to the bath temperature; on the other hand, we found that taking the apparatus out of the bath without any preliminary treatment* caused a large error owing to the fact that the connecting tubes (and other air spaces) cooled more rapidly than the liquids, and so acted as condensers on which moisture was deposited; this trouble was eventually overcome by running cold water into the bottom of the bath (so as to displace the hot water) until it just reached the level of the vessels. In this manner the liquids were caused to cool earlier than the connecting tubes.

Another Possible Source of Error is that Due to Diffusion.—A small amount of diffusion of water vapour from the solvent to the sulphuric acid takes place during the time the apparatus is being set up and taken down; the total time taken for these operations is roughly about four hours, and calculation shows that at 12° C. not more than 0·0002 gr. of water would come over.

The Vessels.—Four different sets of vessels have been used in this research, and for a proper understanding of the objects for which they were made, a brief description follows.

In the earlier part we used the set of vessels (with their platinum joining tubes, &c.) and the method of oscillating the platform on which they stand in the bath described in 'Phil. Trans.,' A, vol. 209, pp. 177–203. In the same communication it will be noticed that one experiment (p. 188), where there had been no oscillation, gives a result that scarcely differs from the others. This led to a number of test experiments (details need not be given) which satisfied us that oscillation, anyhow under certain circumstances, was not essential.

We will call this set, when oscillated, Apparatus Aa; and without oscillation, Apparatus Ab. It is to be noted that from now onwards oscillation was given up.

In the next set (Apparatus B) which followed the general lines of Apparatus A, but was unfortunately constructed of soft Jena-glass, three changes were made: (1) the capacity of the vessels was largely increased (the diameter of the tubing forming the horizontal branches is now 1·7 cm.) to ensure that, for a dilute solution such as weight-normal sugar, the loss of the water vessels would be large enough to reduce the probable weighing error to 1 part in a 1,000; (2) the dipping tube, that is the tube joining the water and sulphuric acid vessels, was now increased in diameter from 1 mm. to 6 mm; (3) the platinum joining tubes were replaced by glass ones as shown in fig 4, which is a vertical cross-section through the centre of the vessels; A, B, and C are ground and lubricated joints, drowned in mercury; whilst D is a silver sleeve which was added when constructing the quartz-glass apparatus to be described. The object of this new form of joint is to enable the observer to weigh the inverted U-tubes E so as to find out whether water has been deposited in them. We would state here that normally water is only found in the U-tube joining the

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* The precautions to be taken when working at 0° C. will be obvious.

water vessel to the sulphuric acid; when it occurs in the other tubes there has always been some faulty manipulation or a rapid change in the temperature of the bath.

Apparatus C. It was soon noticed that the soft Jena-glass seemed particularly liable to deposition of moisture (possibly this glass is more soluble than others?) and also that cracks were developed in it. Hitherto, it will be recalled, the vessels are constructed so that the air enters at the middle of the first branch and leaves at the middle of the last branch; the stream is thus divided, re-united, divided again and then re-united.

It was thought that possibly better results would be obtained if the air were to enter at one end of the first branch, and, travelling along each branch in succession, were to leave the vessel at the end of the fourth and last branch. Apparatus C was so constructed of ordinary soda-glass, but no apparent gain resulted.

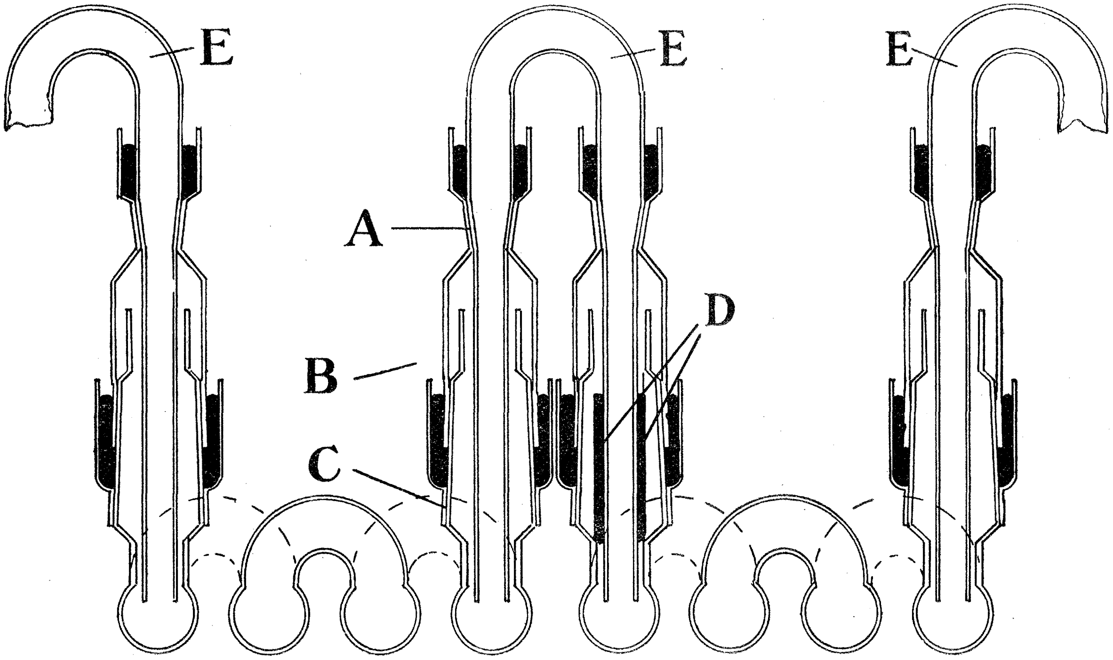

Fig. 4.

Apparatus D. Meanwhile a number of experiments were made with a view to preventing the deposition of moisture mentioned above. A quartz vessel was substituted for the water vessel in Apparatus B and was found to be an improvement, so it was decided to make all the vessels of silica glass, the joints being similar to fig. 4, with the addition of a silver sleeve D resting on the cone as shown in that figure; this sleeve helps to prevent diffusion into the space surrounding the lower ends of the inverted U-tubes.

Even now water was occasionally deposited where it had no business to be. The cause of this was finally traced to the method we had hitherto employed in cleaning the vessels and their joining tubes. We had made a point of always cleaning out everything with "chromic" acid, and washing this acid out with distilled water (six washings in all) and then drying the parts in a current of air. It was noticed that dew formed at the places where the last drops of water evaporated off. This at once suggested that on evaporation the water left behind it some soluble substance, which, during the subsequent passage of saturated air, formed a solution having a smaller vapour pressure than pure water, hence the deposits. That the water actually did contain soluble matter was easily shown by evaporating off 100 c.c. in a platinum dish.

Efforts to obtain water free from this soluble matter failed completely, even though it was redistilled four times with all the usual precautions for obtaining "conductivity" water. That the deposit shown on the platinum dish did not come from the atmosphere was proved by evaporating off the samples in a desiccator over sulphuric acid. Eventually the vessels were cleaned by giving them a final washing with pure alcohol* and drying in a current of warm air. Although this procedure was successful in reducing the trouble, yet the platinum tube (bore 6·5 mm.) which joined vessels 4 and 5 (the water to the sulphuric acid) generally contained about 0·0030 gr. of water.

No valid explanation of this phenomenon has yet been found,† and it is the more inexplicable in that three experiments have lately been carried out in which both the third and fourth vessels were reserved for water, with the result that the quartz tube between 3 and 4 contained less than 0·0010 gr., while the platinum tube retained the usual quantity. One of these experiments was arranged so that hydrogen was passed through the train of vessels instead of air.

We would draw particular attention to this question of the deposition of moisture, for there seems to be no doubt that it may have been a source of error in previous determinations of the absolute vapour density of water in air.

The Experiments at 0° C.—These experiments were all made with Apparatus Aa. The cane sugar and the α-methyl together with the method of estimating the water content are described in 'Roy. Soc. Proc.' A, vol. 92, 1916, p. 479. The following is an example experiment.

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* The alcohol used was KAHLBAUM'S purest, re-distilled twice. Samples from the first distillation left deposits on the platinum dish, which were partially soluble in water, but the second distillation was found to be pure.

† If the conclusion come to in the note added at the end of the paper be correct, namely, that the last branch of vessel 4 is at a higher temperature than the remainder of the bath, then condensation in the platinum tube is to be expected.

EXPERIMENT with Cane Sugar at 0° C. Apparatus Aa. (Weight concentration = 182·805.)

Date.	Time.	Temperature.		Barometer.	Weight of vessels.				Remarks.
		Bath.	Balance.		(1.)	(2.)	(3.)	(4.)	
1911. Dec. 12	9.50 a.m.	° C.	° C. 9·0	741·5	L. 78·6211				Solution made up on December 11 and vessels filled same evening.
	10.10 „		9·0		R. 78·6228 78·6219				No. (1) contained in first half 20 c.c. and in second half 20 c.c. solution. No. (2) contained in first half 20 c.c. and in second half 15 c.c. solution. No. (3) contained in first half 14 c.c. and in second half 14 c.c. of water. No. (4) contained in first half 10 c.c. and in second half 14 c.c. of H_2SO_4.
	10.40 „		9·1		− 0·1098 78·5121	L. 75·7152			
	11.0 „		9·2			R. 75·7167 75·7159			
	11.30 „		9·4			− 0·1059 75·6100	L. 54·3377		
	11.50 „		9·6				R. 54·3388 54·3382		
	12.20 p.m.		9·8				− 0·0988 54·2394	L. 81·2685	
	12.40 „		9·8	742·0				R. 81·2700 81·2692	
	1.0 „	(0·55)						− 0·1095 81·1597	Started air current.
	5.0 „	0·35							
„ 13	9.0 a.m.	0·39							NOTES. True mean temperature = 0°·51 C. Losses = 3·8872. Gains = 3·8886, including 0·0034 in "dipping" tube. Difference = +0·0014. ("Tot up.") l_0/l_1 = 1·15901.
	5.0 p.m.	0·35							
„ 14	9.0 a.m.	0·40							
	6.0 p.m.	0·41							
„ 15	9.0 a.m.	0·51							
	5.0 p.m.	0·45							

EXPERIMENT with Cane Sugar at 0° C. Apparatus Aa. (Weight concentration = 182·805) (continued).

Date.	Time.	Temperature.		Barometer.	Weight of vessels.				Remarks.
		Bath.	Balance.		(1.)	(2.)	(3.)	(4.)	
1911.		° C.	° C.						
Dec. 16	9.0 a.m.	0·42							
	5.0 p.m.	0·40							
„ 17	10.0 a.m.	0·51							
	5.0 p.m.	0·41							
„ 18	9.0 a.m.	0·44							
	5.0 p.m.	0·51							
„ 19	9.0 a.m.	0·59							Stopped and took down.
	10.15 a.m.		11·0	744·0	L. 75·2704				
	10.35 „		11·1		R. 75·2724 75·2714 − 0·1130 75·1584				
	11.5 „		11·2			L. 75·7143			
	11.25 „		11·3			R. 75·7161 75·7152 − 0·1054 75·6098			
	11.55 „		11·4				L. 53·8043		
	12.15 p.m.		11·6				R. 53·8057 53·8050 − 0·0989 53·7061		
	12.45 „		11·8					L. 85·1489	
	1.5 „		11·9	744·2				R. 85·1508 85·1498 − 0·1049 85·0449	

A word of explanation is necessary; all weighings are made against a sealed counterpoise which is constructed of the same material as the vessels, and has approximately the same area exposed to the air. The counterpoise and vessels are, before weighing, treated with "chromic" acid, washed carefully with distilled water, and finally with pure alcohol. The alcohol is wiped off with linen dusters. It is hoped that this procedure results in leaving the surfaces in the same condition. The letters R and L mean that the counterpoise is on the right or left pan respectively, and the small correcting terms are those due to buoyancy.

The results obtained for these two substances are given in Tables VIII. and IX., and it should be mentioned that in all the tables relating to vapour pressure, columns, which are numbered the same, tabulate corresponding quantities.

Column (1) gives the date of setting the apparatus up in the bath and starting the air current.

Column (2) gives the weight concentration of the solutions, that is the ratio of number of grammes of anhydrous substance to 100 gr. of water.

Column (3) gives the mean temperature* of the bath during the experiment; and

Column (4) the mean barometer. It was only after the experiments at 0° C. were finished that the importance of BURTON's correction was discovered. Although the height of the barometer had not been noted we were able to estimate the mean barometric pressure to an accuracy of 1 mm., from the records of a large-size aneroid barograph which is part of the laboratory equipment. Where by some mischance the barograph has failed, the barometer readings were kindly supplied by the Director of the Radcliffe Observatory at Oxford, to whom our best thanks are due.

Column (5). The numbers in this column are the total loss of weight of solution and solvent vessels; in the earlier part of the research we filled all solution vessels with the same solution; later work showed that two different solutions in series might be used, and the numbers marked thus † indicate these experiments. The numbers are the observed values corrected for buoyancy.

Column (6) gives the sum of the observed losses of weight of the solution and water vessels divided by the loss in the solution vessels, *i.e.*, the ratio l_0/l_1.

Column (7) gives the change in weight in the inverted U-tube ("dipping" tube) connecting the water and sulphuric acid vessels. This tube was always weighed as soon as possible after disconnecting the vessels; in most experiments with Apparatus Aa a trace of dew,‡ which quickly disappeared, was noticed on the outer surface of the part of the tube next to the water. A *minus* sign means that the tube lost weight on passing warm air through it; a positive sign can only be the result of

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[*] In the cases where this quantity is enclosed in brackets it is to be understood that owing to some slight mishap the experiment is not as trustworthy as others.

[‡] Probably the dew (it was seldom observed with the other apparatus) is caused by the cooling of the air stream, when throttled by having to pass through this tube, which is slightly less than 1 mm. in internal diameter.

TABLE VIII.—Cane Sugar at 0° C.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)
Date.	Weight concentration.	Mean value of		Total loss of weight. l_0.	Observed ratio. l_0/l_1.	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 0° C.	"Jump."	Sugar used in experiment.
		Temperature of bath.	Barometer during experiment.									
		° C.	mm.									
Standard Weight Concentration = 56·50 gr. Sugar to 100 gr. Water.												
Mar. 11, 1911	56·631	(0·76)	744	7·2437	1·03612	−0·0004	−0·0004	116	1·03587	0·03516	Not determined.	Pure cane.
Standard Weight Concentration = 81·20 gr. Sugar to 100 gr. Water.												
Feb. 17, 1911	81·269	0·58	748	5·7198	1·05566	+0·0009	+0·0006	116	1·05530	0·05380	Not determined.	Pure cane.
Standard Weight Concentration = 112·00 gr. Sugar to 100 gr. Water.												
Feb. 2, 1911	111·637	0·37	767	5·2181	1·08379	+0·0001	+0·0007	92	1·08328	‡0·08034	Not determined.	Pure cane.
,, 8, 1912	111·494	0·42	734	4·2419†	1·08264	−0·0003	−0·0007	92	1·08211	‡0·07939	,,	KAHLBAUM'S 1st sample.
,, 20, 1912	112·273	0·61	743	4·2227†	1·08388	−0·0026	+0·0015	92	1·08334	0·07985	,,	M.W.C.
Mar. 23, 1912	112·120	0·48	746	3·4719†	1·08321	−0·0010	−0·0015	116	1·08268	‡0·07936	,,	KAHLBAUM'S 2nd sample.
June 14, 1912	111·906	0·60	749	3·9729†	1·08348	−0·0008	−0·0002	140	1·08295	0·07981	,,	M.W.C.
Standard Weight Concentration = 141·00 gr. Sugar to 100 gr. Water.												
Jan. 20, 1911	141·182	0·37	761	3·4378	1·11342	+0·0002	−0·0002	68	1·11272	0·10669	Not determined.	Pure cane.

† In these experiments two different solutions were placed in series.

‡ When taking the mean values (given in Table XIII.) these results have not been used.

TABLE VIII.—Cane Sugar at 0° C. (continued).

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)
Date.	Weight concentration.	Mean value of		Total loss of weight. l_0.	Observed ratio. l_0/l_1.	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 0° C.	"Jump."	Sugar used in experiment.
		Temperature of bath.	Barometer during experiment.									
		° C.	mm.									
Standard Weight Concentration = 183·00 gr. Sugar to 100 gr. Water.												
Jan. 14, 1911	182·649	0·32	763	2·4094	1·15915	+0·0001	−0·0004	68	1·15817	0·14724	Not determined.	Pure cane.
Dec. 12, 1911	182·805	0·51	742	3·8872	1·15901	−0·0034	+0·0014	164	1·15799	0·14697	,,	Pure cane.
Standard Weight Concentration = 217·50 gr. Sugar to 100 gr. Water.												
Mar. 6, 1912	217·599	0·43	745	3·5276[†]	1·19970	−0·0007	−0·0001	116	1·19843	0·18084	Not determined.	M.W.C.
,, 23, 1912	217·296	0·48	746	3·4719[†]	1·19890	−0·0010	−0·0015	116	1·19764	0·18063	,,	M.W.C.
Oct. 5, 1912	218·148	0·40	759	3·1745[†]	1·20028	−0·0002	−0·0010	116	1·19903	0·18094	,,	M.W.C.
Standard Weight Concentration = 243·00 gr. Sugar to 100 gr. Water.												
July 17, 1912	242·280	0·74	(750)	3·0638[†]	1·22960	+0·0006	+0·0001	116	1·22812	0·20632	Not determined.	M.W.C.
Oct. 16, 1912	243·192	0·46	741	3·1641[†]	1·23160	0·0000	−0·0003	116	1·23012	0·20700	,,	M.W.C.

[†] In these experiments two different solutions were placed in series.

TABLE IX.—α-Methyl Glucoside at 0° C.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)
Date.	Weight concentration.	Mean value of Temperature of bath.	Mean value of Barometer during experiment.	Total loss of weight. l_0.	Observed ratio. l_0/l_1.	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 0° C.
		° C.	mm.							
Standard Weight Concentration = 35·00 gr. per 100 Water.										
Mar. 29, 1911	34·767	0·65	749	6·8485	1·03943	−0·0008	+0·0023	116	1·03921	0·03881
April 13, 1911	34·817	0·54	752	6·1123	1·03949	−0·0003	−0·0001	116	1·03922	0·03875
Standard Weight Concentration = 45·00 gr. per 100 Water.										
Mar. 21, 1911	44·980	0·62	750	5·5954	1·05315	−0·0001	0·0000	92	1·05281	0·05158
April 6, 1911	44·928	0·29	756	6·7285	1·05301	−0·0003	−0·0010	92	1·05268	0·05147
Standard Weight Concentration = 55·00 gr. per 100 Water.										
Feb. 25, 1911	54·758	0·61	744	6·0562	1·06663	+0·0004	+0·0017	92	1·06620	0·06453
Mar. 4, 1911	54·735	0·54	752	5·8768	1·06655	−0·0001	+0·0018	92	1·06613	0·06449
Standard Weight Concentration = 64·00 gr. per 100 Water.										
Dec. 10, 1910	63·701	0·54	730	5·8291	1·07984	+0·0004	+0·0001	92	1·07932	0·07686
Jan. 7, 1911	63·765	0·25	(755)	5·6167	1·08026	+0·0004	−0·0008	92	1·07976	0·07712
Standard Weight Concentration = 75·00 gr. per 100 Water.										
Jan. 26, 1911	74·888*	0·52	761	4·8511	1·09729	+0·0006	+0·0008	92	1·09668	0·09261
Feb. 9, 1911	75·477	0·46	755	5·4195	1·09804	0·0000	+0·0012	92	1·09743	0·09244
Standard Weight Concentration = 90·00 gr. per 100 Water.										
May 1, 1912	90·085	(0·70)	752	3·4898†	1·12100	−0·0004	−0·0013	116	1·12023	0·11367
" 10, 1912	89·949	(0·59)	748	3·5090†	1·12084	−0·0005	+0·0001	116	1·12007	0·11368
Standard Weight Concentration = 105·00 gr. per 100 Water.										
May 24, 1912	104·714	0·45	755	3·3429†	1·14538	0·0000	−0·0028	116	1·14447	0·13556
June 5, 1912	104·684	(0·60)	745	3·9269†	1·14520	−0·0002	−0·0024	140	1·14427	0·13550

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* The determination of the water content in this experiment showed that the glucoside crystals had picked up water and were slightly decomposed.

† In these experiments two different solutions were placed in series.

faulty manipulation. It must be remembered that the tube has to be weighed as quickly as possible.

Column (8). This column is headed "tot up"; by this we mean that the tabulated numbers are the difference in weight between the gain in the last vessel of the train (which contains sulphuric acid) and the sum of the losses of solution and water; the weight of water found in the "dipping" tube is added to that of the sulphuric acid, and a negative sign means that the losses are the greater, whilst the positive sign means that they are the smaller. It has been pointed out in a previous communication that the closer these numbers approach to zero the greater the probability that the experiment is a good one.

Column (9) gives the number of hours during which the air has passed through the vessels.

Column (10) gives ρ_0/ρ_1 the value of the ratio l_0/l_1 corrected for "BURTON'S" correction (see p. 316) on the assumption that p_1 and p_0 of equation (3) are equal to one another.

Column (11) gives log ρ_0/ρ_1 corrected to the standard weight concentration* printed across the page, and also corrected to the standard temperature of 0° C. or 30° C., as the case may be.

The Experiments at 30° C.—Before proceeding to enumerate the experiments on sulphuric acid solutions it may be mentioned that since the completion of the work on calcium ferrocyanide we have made over 60 special test experiments (they are in addition to such as are detailed here) which have taken 287 days to complete. For the most part these were directed to testing alterations both in the vessels and in the speed of the air stream; a number were devoted to investigating the influence of ions in the air current (for this purpose a special set of vessels furnished with electrodes was constructed), but with no definite result; others on "tot up," and fall of pressure along the vessels were also made. The changes thus suggested are embodied in Apparatus D, whilst the final method of causing the air to flow is given on p. 316.

We give an example of what we consider to be a satisfactory experiment at this temperature.

The experiments on sulphuric acid solutions we made more for the purpose of testing the experimental conditions than for the determination of vapour pressures. But as they have turned out to be sufficiently concordant we give the details in Table X.

From a study of these figures the following remarks seem justified.

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[*] This correction is obtained from the equation $\log_e \rho_0/\rho_1 = bc + dc^2 - ec^3$, where c is the weight concentration and b, d and e are constants. For cane sugar $b = 4{\cdot}881 \times 10^{-4}$, $d = 2{\cdot}4655 \times 10^{-6}$, and $e = 4{\cdot}041 \times 10^{-9}$; and for glucoside $b = 9{\cdot}54 \times 10^{-4}$, $d = 4{\cdot}921 \times 10^{-6}$, and $e = 1{\cdot}668 \times 10^{-8}$. There is a maximum at $c = 489$ for cane sugar and one at $c = 204$ for the glucoside.

EXPERIMENT on Dilute Sulphuric Acid. Apparatus B.

Date.	Time.	Temperature of		Barometer.	Weight of vessels.					Remarks.
		Bath.	Balance.		(1.)	(2.)	(3.)	(4.)	(5.)	
1915 Feb. 13	9.5 a.m.		° C. 9·6	722·2					L. 58·0795	Filled vessels on Feb. 12. Vessel (1) contained 80 c.c. of the acid.
	9.25 "		9·7						R. 58·0869 58·0822	Vessel (2) contained 80 c.c. of the acid.
	9.55 "		9·8		R. 23·9223				− 0·1245 57·9577	Vessel (3) contained 80 c.c. of the acid.
	10.15 "		9·7		L. 23·9152 23·9188					Vessel (4) contained 80 c.c. of water.
	10.45 "		9·6		− 0·0929 23·8254	L. 25·6163				Vessel (5) contained 20 c.c. H_2SO_4 in first half and 40 c.c. in second half.
	11.5 "		9·6			R. 25·6237 25·6200				
	11.35 "		9·5			− 0·0938 25·5262	R. 27·7765			
	11.55 "		9·5				L. 27·7703 27·7734			
	12.25 "		9·6				− 0·0917 27·6817	L. 14·8985		
	12.45 "		9·6	718·5				R. 14·9061 14·9023		Started air current at 1 p.m.
" 14	9.30 a.m.	30·01						− 0·0955 14·8068		
	7.0 p.m.	30·01								NOTES. True mean temperature is 29°·90 C.
" 15	9.0 a.m.	30·01								Losses = 15·4847.
	5.0 p.m.	30·02								Gains = 15·4779 + 0·0038 in "dipping" tube.
" 16	9.0 a.m.	30·02								Diff. = −0·0030. ("Tot up.")
	5.0 p.m.	30·02								l_0/l_1 = 1·02671.

Experiment on Dilute Sulphuric Acid. Apparatus B (continued).

Date.	Time.	Temperature of		Barometer.	Weight of vessels.					Remarks.
		Bath.	Balance.		(1.)	(2.)	(3.)	(4.)	(5.)	
1915 Feb. 17	9.0 a.m.	30·02	° C.							
	5.0 p.m.	30·02								
,, 18	9.0 a.m.	30·02								
	4.0 p.m.	30·02								
,, 19	8.0 a.m.	30·02								Stopped and took down at 9 a.m.
	9.55 ,,		10·4	726·4					L. 73·5402	
	10.15 ,,		10·5						R. 73·5481 73·5442 − 0·1086 73·4356	
	10.45 ,,		10·7		R. 8·8572					
	11.5 ,,		10·8		L. 8·8511 8·8542 − 0·1092 8·7450					
	11.35 ,,		10·9			L. 25·6150				
	11.55 ,,		10·9			R. 25·6227 25·6189 − 0·0941 25·5248				
	12.25 ,,		11·0				R. 27·7766			
	12.45 ,,		11·1	726·5			L. 27·7708 27·7737 − 0·0921 27·6816			
	2.5 ,,		11·3					L. 14·4971		
	2.25 ,,		11·3	726·5				R. 14·5039 14·5005 − 0·0965 14·4040		

Experiments with Sulphuric Acid.—These are given in Table X. The headings of the columns are the same as before. Column (11) gives the $\log_e \rho_0/\rho_1$ corrected for temperature only, and column (12) headed "jump" is concerned with fluctuations in the flow of air consequent on oscillating the vessels.

TABLE X.—Solutions of Sulphuric Acid at 30° C.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)	(14.)	
Date.	Per cent. H_2SO_4.	Mean value of		Total loss of weight $= l_0$.	Observed ratio l_0/l_1.	Change in weight of "dipping" tube.	"Tot up."	Number of hours air passed.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$.	$\log_e \rho_0/\rho_1$ reduced to 30°·00 C. †	"Jump."	Apparatus used.	Remarks.
		Temperature of bath.	Barometer during experiment.											
		° C.												
Mar. 8, '13	24·871	30·13	756	6·0151	1·22084	−0·0011	−0·0019	67	1·21147	0·19183	0·19171	not determined	Aa	
,, 14, '13	24·871	30·20	737	6·1286	1·22118	−0·0003	−0·0021	67	1·21151	0·19186	0·19168	,,	,,	
,, 25, '13	24·871	30·06	746	5·9615	1·22087	−0·0003	−0·0015	67	1·21141	0·19178	0·19173	,,	,,	
Nov. 22, '13	22·446	30·01	752	8·4426	1·17772	−0·0017	−0·0002	91	1·17019	0·15716	0·15716		Ab	
Dec. 6, '13	22·446	30·09	747	6·9805	1·17763	−0·0032	+0·0022	68	1·17003	0·15703	0·15695	none	Aa	
,, 11, '13	22·446	30·07	755	6·8753	1·17768	−0·0015	+0·0013	91	1·17016	0·15714	0·15708	,,	,,	
Jan. 8, '14	22·446	30·09	753	5·7385	1·17790	−0·0012	−0·0011	91	1·17034	0·15729	0·15721		Ab	
Oct. 26, '14	6·192	30·06	742	17·6036	1·02681	−0·0111	−0·0051*	115	1·02566	0·02534			B	Glass "dipping" tube.
Nov. 11, '14	6·192	29·94	744	18·3545	1·02699	−0·0119	−0·0102*	115	1·02584	0·02551			,,	Glass "dipping" tube.
,, 25, '14	6·192	29·99	745	18·7375	1·02681	−0·0446	−0·0103*	115	1·02567	0·02535			,,	Glass "dipping" tube.
Jan. 8, '15	6·192	30·02	734	7·4370	1·02673	−0·0009	−0·0035	67	1·02557	0·02525			,,	Quartz "dipping" tube.
,, 13, '15	6·192	29·98	747	15·4526	1·02674	−0·0061	−0·0020	139	1·02560	0·02528			,,	Quartz "dipping" tube.
Feb. 13, '15	6·192	29·90	730	15·4847	1·02671	−0·0038	−0·0030	139	1·02555	0·02523			,,	Platinum "dipping" tube.

* In these experiments water was lost to the system by condensing on parts that could not be weighed (actually observed).

† The numbers in column (10) lead to values for the vapour pressures of the solutions which differ as much as 1 per cent. from REGNAULT'S experiments (see LANDHOLT and BÖRNSTEIN, 'Tabellen'), but from REGNAULT'S results (which are for different temperatures) a temperature coefficient was calculated by means of which the numbers in column (11) were reduced to 30° C.; unfortunately there seem to be no data for carrying out a similar reduction for the two very dilute solutions.

TABLE X.—Solutions of Sulphuric Acid at 30° C. (continued).

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)	(14.)	
Date.	Per cent. H_2SO_4.	Mean value of		Total loss of weight $= l_0$.	Observed ratio l_0/l_1.	Change in weight of "dipping" tube.	"Tot up."	Number of hours air passed.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$.	$\log_e \rho_0/\rho_1$ reduced to 30°·00 C.	"Jump."	Apparatus used.	Remarks.
		Temperature of bath.	Barometer during experiment.											
		° C.												
Oct. 9, '15‡	6·157	30·00	747	17·5641	1·02637	−0·0049	−0·0003	115	1·02525	0·02494			D	"Dipping" tube 0·5 cm. from water.
,, 20, '15‡	6·157	30·01	751	18·2298	1·02627	−0·0054	−0·0065*	115	1·02516	0·02485			,,	"Dipping" tube 0·5 cm. from water.
,, 28, '15‡	6·157	29·96	740	17·9249	1·02627	−0·0031	−0·0024	115	1·02514	0·02483			,,	"Dipping" tube 0·5 cm. from water.
Nov. 5, '15†	6·157	29·99	745	18·3081	1·02632	−0·0036	−0·0017	115	1·02520	0·02489			,,	"Dipping" tube 0·3 cm. from water.
,, 13, '15†	6·157	30·04	749	18·5168	1·02615	−0·0018	+0·0011	115	1·02504	0·02473			,,	"Dipping" tube 0·8 cm. from water.
,, 24, '15†	6·157	29·95	754	18·7143	1·02632	−0·0034	−0·0005	115	1·02521	0·02490			,,	"Dipping" tube 1·0 cm. from water.

* In these experiments water was lost to the system by condensing on parts that could not be weighed (actually observed).

† These three experiments are the first in which a true buoyancy correction could be made, *i.e.*, it was possible to compute the specific volume of the sulphuric acid in the last vessel after it had absorbed the water.

‡ Approximate buoyancy correction applied for specific volume of sulphuric acid.

If we neglect the experiment of November 22, 1913, where the soda-lime tube was found to be nearly blocked up, the first two sets of experiments, as judged by the figures in column (11), show very good agreement. It is probable that the experiment of January 8, 1914, is slightly too high, on account of air pulses, a gale blowing during the run.

The experiments of October 26, November 11 and 25, in 1914, are only included to show the kind of results obtained when moisture condenses on the connecting tubes and in other parts, the magnitude of this is seen from the numbers in columns (7) and (8); but the last three experiments are in excellent agreement. In the first three of the next set, approximate buoyancy corrections for the specific volume of the sulphuric acid are applied, whilst the last three are properly corrected.

Two important deductions may be drawn:—

(1) The method, even with a liquid having a vapour pressure as high as 31 mm. mercury, is susceptible of considerable accuracy. (2) Confirmation is obtained of the view that the losses on the solution and solvent should be equal to the gain of the sulphuric acid.

Experiments with Cane Sugar and α-Methyl Glucoside.—These are given in Tables (XI.) and (XII.) and the columns have the same signification as before. The numbers in column (12) for both cane sugar and α-methyl glucoside are derived from the equation $\log_e \rho_0/\rho_1 = bc+dc^2-ec^3$ where, for cane sugar, $b = 5{\cdot}136\times10^{-4}$, $d = 1{\cdot}866\times10^{-6}$, $e = 2{\cdot}335\times10^{-9}$, with a maximum at $c = 647$; and for α-methyl glucoside $b = 9{\cdot}088\times10^{-4}$, $d = 3{\cdot}891\times10^{-6}$, and $e = 1{\cdot}511\times10^{-8}$, with a maximum at $c = 252$. The correction for temperature, which in all cases is very small, is assumed to be proportional to the temperature interval.

The numbers in the column headed "jump" (the jump was not determined for the α-methyl glucoside solution) were obtained as follows:—When the vessels had been weighed at the end of the experiment they were again set up in the bath and a Threlfall oil manometer was connected to the air-stream, so that the fall in the pressure along the vessels could be measured. It was found that at a certain point in the oscillation, there was frequently a distinct and rapid throttling action; the numbers in the column record the change of pressure due to this.* We would point out that a "jump" taking place at the end of an experiment, when water has already been transferred from one vessel to another, is no proof that the obstruction has been there during the whole run, and conversely, no "jump" does not necessarily mean that there has not been one during part of the run.

The "new sugar" mentioned in the sugar column is some specially pure, which Messrs. Tate, to whom our thanks are due, kindly gave us.

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* The "jump" seems to be connected with the great viscosity of sugar solutions.

TABLE XI.—Cane Sugar at 30° C.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)	(14.)	
Date.	Weight-concentration.	Mean value of		Total loss of weight. l_0.	Observed ratio. l_0/l_1.	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 30° C.	"Jump."	Sugar used.	Apparatus used.	Remarks.
		Temperature of bath.	Barometer.											
		° C.												
Standard Weight Concentration = 34·00 gr. Sugar to 100 gr. Water.														
Oct. 16, '13	33·937	30·03	750	11·0599	1·02047	−0·0010	Not determined.	91	1·01960	§0·01945	0·5 mm. oil.	M.W.C.	Aa	
,, 24, '13	33·944	30·13	745	10·8036*	1·02061	Not determined.	,,	91	1·01973	§0·01958	0·8 mm. oil.	,,	,,	
Nov. 12, '13	33·945	30·03	745	12·1405	1·02047	−0·0010	−0·0001	163	1·01960	0·01944	0·05 mm. oil.	,,	,,	
Feb. 24, '15	33·939	30·05	751	18·6185	1·02054	−0·0056	−0·0048	115	1·01967	0·01952		,,	B	
Jan. 25, '16†	33·941	29·95	758	20·7327*	1·02056	−0·0044	−0·0064	139	1·01970	0·01955		New sugar.	D	
June 24, '16‡	33·965	30·02	745	25·3141*	1·02053	−0·0037	−0·0084	138	1·01965	0·01948		,,	,,	
July 13, '16‡	33·980	(30·02)	751	22·6611*	1·02055	−0·0046	−0·0056	138	1·01968	0·01950		,,	,,	
Standard Weight Concentration = 56·50 gr. Sugar to 100 gr. Water.														
June 23, '11	56·713	30·10	741	6·5507	1·03673	−0·0009	+0·0015	67	1·03514	§0·03439	Not determined.	Pure cane.	Aa	
Nov. 1, '13	56·721	30·02	748	9·5373*	1·03665	−0·0006	−0·0007	67	1·03509	§0·03433	Large.	M.W.C.	,,	
,, 7, '13	56·687	30·12	741	9·6735*	1·03667	−0·0006	−0·0002	67	1·03506	0·03433	0·15 mm. oil.	,,	,,	
Mar. 26, '14	56·712	30·03	746	10·0051	1·03656	−0·0023	+0·0018	115	1·03500	0·03425		,,	Ab	

* In these experiments two different solutions were placed in series.

† Approximate buoyancy correction applied for specific volume of sulphuric acid at end of experiment.

‡ True buoyancy correction applied for specific volume of sulphuric acid at end of experiment.

§ Not used in table of mean values.

TABLE XI.—Cane Sugar at 30° C. (continued).

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)	(14.)	
Date.	Weight concentration.	Mean value of Temperature of bath.	Mean value of Barometer.	Total loss of weight. l_0.	Observed ratio. l_0/l_1.	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 30° C.	"Jump."	Sugar used.	Apparatus used.	Remarks.
		° C.												
Standard Weight Concentration = 81·20 gr. Sugar to 100 gr. Water.														
June 9, '11	81·262	30·06	747	7·1025	1·05651	−0·0001	+0·0002	68	1·05409	§0·05263	Not determined.	Pure cane, M.W.C.	Aa	
Sept. 24, '13	81·209	30·11	748	6·6490*	1·05640	−0·0002	−0·0019	67	1·05399	0·05257	0·27 mm. oil.		,,	
Oct. 8, '13	81·209	30·01	745	5·9518*	1·05631	−0·0004	−0·0007	67	1·05390	0·05249	0·15 mm. oil.	,,	,,	
Jan. 16, '14	81·262	30·04	748	5·3660*	1·05595	−0·0001	0·0000	67	1·05356	§0·05212	0·5 mm. oil.	,,	,,	
Mar. 19, '14	81·251	(30·11)	729	8·0183	1·05651	−0·0024	+0·0003	91	1·05403	0·05258		,,	Ab	
Jan. 25, '16†	81·198	29·95	758	20·7327*	1·05639	−0·0044	−0·0064	139	1·05403	0·05262		,,	D	
Standard Weight Concentration = 112·00 gr. Sugar to 100 gr. Water.														
Jan. 17, '13	111·814	30·07	742	8·0082	1·08418	−0·0008	−0·0012	67	1·08058	0·07763	Not determined.	M.W.C.	Aa	
Feb. 1, '13	111·864	30·04	747	7·8742	1·08427	−0·0006	+0·0013	67	1·08067	0·07764	,,	,,	,,	
,, 7, '13	111·886	30·00	751	8·1202	1·08415	−0·0009	−0·0009	67	1·08058	0·07760	,,	,,	,,	
Standard Weight Concentration = 141·00 gr. Sugar to 100 gr. Water.														
Feb. 14, '13	141·095	30·03	755	6·4649*	1·11335	+0·0007	−0·0006	67	1·10856	0·10297	Not determined.	M.W.C.	Aa	
Oct. 24, '13	141·096	30·13	743	10·8036*	1·11338	Not determined.	Not determined.	91	1·10849	§0·10293	0·8 mm. oil.	,,	,,	
July 13, '16	141·257	30·03	751	22·6611*	1·11372	−0·0056	−0·0046	138	1·10889	0·10313		New sugar.	D	

* In these experiments two different solutions were placed in series.
† Approximate buoyancy correction applied for specific volume of sulphuric acid at end of experiment.
§ Not used in table of mean values.

TABLE XI.—Cane Sugar at 30° C. (continued).

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)	(14.)	
Date.	Weight concentration.	Mean value of		Total loss of weight. l_0.	Observed ratio. l_0/l_1.	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 30° C.	"Jump."	Sugar used.	Apparatus used.	Remarks.
		Temperature of bath.	Barometer.											
		° C.												
Standard Weight Concentration = 183·00 gr. Sugar to 100 gr. Water.														
May 12, '11	183·213	29·91	741	4·3940	1·16035	−0·0006	+0·0003	67	1·15350	§0·14262	Not determined.	Pure cane.	Aa	
Feb. 21, '13	183·560	29·95	755	6·4314	1·16071	−0·0007	−0·0007	67	1·15395	§0·14266	,,	,,	,,	
June 7, '13	182·963	30·01	749	6·0778	1·15969	−0·0006	+0·0005	67	1·15290	0·14232	,,	M.W.C.	,,	
,, 13, '13	182·927	30·10	754	5·9142	1·15958	−0·0009	−0·0005	67	1·15280	§0·14228	Large.	,,	,,	
,, 20, '13	182·944	30·10	751	5·7285	1·15983	−0·0001	−0·0007	67	1·15302	0·14245	Not determined.	,,	,,	
,, 27, '13	183·013	30·01	757	5·6330	1·15967	−0·0003	−0·0022	67	1·15295	0·14231	0·15 mm. oil	,,	,,	
July 8, '13	182·996	30·06	746	5·6438	1·15984	−0·0014	−0·0009	67	1·15300	§0·14238	0·8 mm. oil	,,	,,	
,, 15, '13	182·899	30·03	748	6·2847	1·15984	0·0000	+0·0007	67	1·15303	§0·14250	0·5 mm. oil	,,	,,	
Sept. 24, '13	182·843	30·11	748	6·6490*	1·15953	−0·0002	−0·0019	67	1·15270	0·14228	0·27 mm. oil	,,	,,	
Oct. 8, '13	182·683	30·01	745	5·9518*	1·15938	−0·0004	−0·0007	67	1·15255	0·14224	0·15 mm. oil	,,	,,	
Apr. 21, '14	183·066	30·13	756	7·5503	1·15978	−0·0009	−0·0011	91	1·15300	0·14233		,,	Ab	
May 28, '14	183·079	29·94	754	12·2725	1·15845	−0·0020	−0·0014	91	1·15178	§0·14123		,,	C	"Dipping" tube 2·4 cm. from water surface.

* In these experiments two different solutions were placed in series.

§ Not used in table of mean values.

TABLE XI.—Cane Sugar at 30° C. (continued).

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)	(14.)	
Date.	Weight concentration.	Mean value of		Total loss of weight. l_0.	Observed ratio. l_0/l_1.	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 30° C.	"Jump."	Sugar used.	Apparatus used.	Remarks.
		Temperature of bath.	Barometer.											
		° C.												
Standard Weight Concentration = 183·00 gr. Sugar to 100 gr. Water (continued).														
June 6, '14	183·071	30·01	743	11·5499	1·15940	−0·0005	−0·0018	91	1·15257	§0·14192		M.W.C.	C	"Dipping" tube 1·1 cm. from water surface.
,, 12, '14	183·071	30·01	752	11·4518	1·15840	+0·0002	−0·0015	91	1·15169	§0·14116		,,	,,	"Dipping" tube 2·3 cm. from water surface.
,, 19, '14	183·071	29·99	748	8·5645	1·15746	0·0000	−0·0015	68	1·15077	§0·14036		,,	,,	4th branch of water vessel empty.
,, 24, '14	183·071	29·99	756	9·2148	1·15958	−0·0004	−0·0042	67	1·15286	§0·14217		,,	,,	4th branch coated with paraffin wax.
July 10, '14	183·088	29·92	752	8·4568	1·15959	−0·0077	−0·0034	67	1·15287	§0·14216		,,	,,	4th branch bakelized.
Oct. 7, '14	182·920	30·01	757	9·1733	1·15962	−0·0046	Lost.	67	1·15290	0·14235		,,	B	"Dipping" tube bakelized.
Jan. 19, '16†	182·737	29·92	750	10·6833	1·15937	−0·0021	−0·0042	67	1·15264	0·14229		New sugar.	D	
June 24, '16‡	183·160	30·02	745	25·3141*	1·15986	−0·0037	−0·0084	138	1·15302	0·14223		,,	,,	
Standard Weight Concentration = 217·50 gr. Sugar to 100 gr. Water.														
July 6, '11	218·264	29·95	756	3·9771	1·20150	−0·0003	+0·0017	43	1·19304	§0·17576	Not determined.	Pure cane.	Aa	
Feb. 14, '13	217·632	30·03	755	6·4649*	1·20092	−0·0006	+0·0007	67	1·19243	0·17586	,,	M.W.C.	,,	
Nov. 1, '13	217·217	30·02	748	9·5373*	1·20029	−0·0006	−0·0007	67	1·19176	§0·17571	Large	,,	,,	

* In these experiments two different solutions were placed in series.

† Approximate buoyancy correction applied for specific volume of sulphuric acid at end of experiment.

‡ True buoyancy correction applied for specific volume of sulphuric acid at end of experiment.

§ Not used in table of mean values.

TABLE XII.—α-Methyl Glucoside at 30° C.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)
Date.	Weight concentration.	Mean value of		Total loss of weight $= l_0$.	Observed ratio. l_0/l_1.	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 30° C.	"Jump."	Apparatus used.
		Temperature.	Barometer.									
		° C.										
Standard Weight Concentration = 35·00 gr. to 100 gr. of Water.												
June 30, 1911	34·779	30·18	746	6·6027	1·03795	+0·0002	+0·0015	67	1·03631	0·03592	Not determined	Aa
Standard Weight Concentration = 45·00 gr. to 100 gr. of Water.												
July 22, 1911	44·938	29·91	753	5·8846	1·05050	−0·0005	+0·0020	67	1·04838	0·04731	Not determined	Aa
Standard Weight Concentration = 55·00 gr. to 100 gr. of Water.												
July 12, 1911	54·869	30·01	760	7·4075	1·06358	0·0000	+0·0007	67	1·06092	0·05930	Not determined	Aa
Standard Weight Concentration = 64·00 gr. to 100 gr. of Water.												
June 16, 1911	63·845	30·04	742	5·8225	1·07573	−0·0010	−0·0003	67	1·07247	0·07016	Not determined	Aa
May 12, 1916†	63·810	30·04	748	17·7474*	1·07555	−0·0028	−0·0025	115	1·07233	0·07007		D
,, 19, 1916†	63·810	30·08	754	17·4767*	1·07567	−0·0026	−0·0057	114	1·07246	0·07021		,,
June 9, 1916‡	63·818	(30·04)	750	12·1437*	1·07546	−0·0011	+0·0030	90	1·07225	0·06999		,,

* In these experiments two different solutions were placed in series.

† Approximate buoyancy correction applied for specific volume of sulphuric acid at end of experiment.

‡ True buoyancy correction applied for specific volume of sulphuric acid at end of experiment.

TABLE XII.—α-Methyl Glucoside at 30° C. (continued).

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)	(13.)
Date.	Weight concentration.	Mean value of		Total loss of weight $= l_0$.	Observed ratio. l_0/l_1.	Change in weight of "dipping" tube.	"Tot up."	No. of hours air passed.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$ reduced to standard weight concentration and 30° C.	"Jump."	Apparatus used.
		Temperature.	Barometer.									
		° C.										
Standard Weight Concentration = 75·00 gr. to 100 gr. of Water.												
June 3, 1911	75·708	29·98	754	6·3093	1·09208	−0·0004	+0·0002	66	1·08819	0·08363	Not determined	Aa
Oct. 14, 1911	75·904	(30·07)	753	3·0798*	1·09208	−0·0009	+0·0004	67*	1·08817	0·08340	”	”
June 5, 1915	75·287	30·01	751	6·2789	1·09137	−0·0006	−0·0024	66	1·08749	0·08352		Ab
Standard Weight Concentration = 90·00 gr. to 100 gr. of Water.												
July 10, 1915	90·005	30·16	746	6·9694	1·11277	+0·0001	−0·0014	67	1·10791	0·10253		Ab
Dec. 4, 1915†	90·049	29·99	732	14·7591	1·11265	−0·0008	−0·0063	91	1·10777	0·10229		D
Standard Weight Concentration = 105·00 gr. to 100 gr. of Water.												
Oct. 9, 1911	105·075	(30·05)	758	2·6210	1·13488	Not determined	+0·0008	45	1·12920	0·12144	Not determined	Aa

* In these experiments two different solutions were placed in series.

† Approximate buoyancy correction applied for specific volume of sulphuric acid at end of experiment.

We would draw particular attention to the results noted in the long series of experiments with a weight concentration of 183·000 gr. to 100 of water. It would seem, judging from the numbers in column (11) with apparatus Aa (*i.e.*, when oscillating) and apparatus Ab (no oscillation), that the results are more consistent when the "jump" is small.

Coming now to the experiments with apparatus C, it will be noticed at once from the three experiments of May 28, June 6, and June 12, 1914, that the further the bottom of the dipping tube is from the water level (these experiments, unlike a similar set with sulphuric acid, were varied by keeping the water-level constant and altering the length of the dipping tube) the smaller $\log_e \rho_0/\rho_1$ becomes. In other words, the quantity of water taken away from the water vessel is a function of the vertical distance between the water and the tube.

Obviously one way of explaining this is by supposing that some of the water which was originally in the air-stream condenses on the sides of the vessel before it reaches the dipping tube. That this explanation is probably correct is shown by the next three experiments; in the first of these, the last branch of the water vessels was empty and consequently a large proportion of the water condensed in it; in the next two this branch was coated with either paraffin wax or "bakelite," with the result that the normal values were regained. That these results are normal is shown by the two experiments with apparatus D, where the vessel is of quartz and the dipping tube is some 0·3 cm. away from the surface.

Thus we have conclusively proved that no accurate results can be obtained with these glass vessels, unless the bottom of the exit tube is very close to the surface of the water; incidentally it may be remarked that such is actually the case with apparatus Aa and Ab.

Air Pulses.—It will be seen that the deviations in $\log_e \rho_0/\rho_1$ are larger than can be accounted for by the known probable error of weighing. During the search for an explanation of this, it was noticed that the results, when all other conditions were constant, seemed higher during the prevalence of gales. Unfortunately, this connection (if any) cannot be put on firm ground, because, as already stated, we have made as many alterations in the conditions as possible and consequently there are but few suitable experiments for comparison.

Mr. J. W. WALKER suggested that the anomalies might be due to the greater number and amplitude of the air pulses in high winds.*

To reduce this source of trouble as much as possible the air current was altered so that there were no pulses of any kind either from the atmosphere or from the Fleuss pump, and the two experiments of June 24 and July 13, 1916, were carried out on the most dilute solution. The results show a satisfactory agreement and differ but little from previous experiments. One interesting fact requires mention. It was noticed

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* We were unable to test this hypothesis as the only suitable records of air pulses, those of Mr. DINES, are kept at the Meteorological Office and Sir N. SHAW would not let us have them for reference.

that in the experiments at 30° C. with dilute sulphuric acid the second vessel scarcely changes in weight, but with both cane sugar and α-methyl glucoside there is a small but persistent loss; this effect may indicate that the latter two substances suffer a slight decomposition, but experiments designed to elucidate this point are now in progress.

The Calculation of the Osmotic Pressures.—The osmotic pressures are connected with the vapour pressures by PORTER's equation ('Roy. Soc. Proc.' A, vol. 79, p. 521),

$$\int_{\pi_\pi}^{p} s_1\,dp = \int_{\pi_\pi}^{\pi_0} v\,dp + \int_{\pi_0}^{p-\mathrm{P}} u\,dp, \quad \ldots \ldots \ldots \quad (5)$$

where P is the osmotic pressure, and p the pressure on the solution; π_π and π_0 are, as before, the vapour pressures of the solution and solvent respectively; v and u are the specific volumes of the solvent vapour and pure liquid solvent respectively.

In our paper on calcium ferrocyanide solutions we give reasons for thinking that equation (5) should be modified so as to be applicable to the vapour densities when measured in air. From the following discussion, which is contributed by Mr. G. W. WALKER, it would seem that we were mistaken, and that the air values may be used without change.

In the experiments the pressure on the pure solvent is one atmosphere. Hence (5) becomes

$$\int_{\pi_\pi}^{\mathrm{P}+1} s_1\,dp = \int_{\pi_\pi}^{\pi_0} v\,dp + \int_{\pi_0}^{1} u\,dp,$$

but $\partial\pi/\partial p = u/v_\pi$ for vapour over the pure solvent. (*Cf.* PORTER, *loc. cit.*)

Therefore

$$\int_{\pi_0}^{1} u\,dp = \int_{\pi_0}^{\pi'_0} v\,dp$$

where $\pi_0{}^1$ is the vapour pressure observed. Again, $\partial\pi/\partial p = s_1 v\pi$ for the vapour over the solution.

Therefore

$$\int_{\pi_\pi}^{1} s_1\,dp = \int_{\pi_\pi}^{\pi'_\pi} v\,dp,$$

where π'_π is the observed vapour pressure of the solution.

Therefore

$$\int_{1}^{\mathrm{P}+1} s_1\,dp = \int_{\pi'_\pi}^{\pi'_0} v\,dp,^*$$

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[*] This result might have been anticipated had it been noticed that Sir J. J. THOMSON, in articles 90 and 91 of "Applications of Dynamics," shows that the increase in vapour pressure of a pure liquid caused by the pressure of the atmosphere upon it, precisely balances the lowering brought about by the dissolved air in it.

hence

$$\bar{s}\mathrm{P} = \int_{\pi'_\pi}^{\pi'_0} v\,dp,$$

where $\bar{s}$ is the mean value of s over the range of 1 to 1+P. If BOYLE's law is true for the vapour in air we get

$$\mathrm{P} = \log_e \pi'_0/\pi'_\pi \times \mathrm{RT}/\bar{s}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and modifying this in conformity with (4) we get

$$\mathrm{P} = \log_e [l_0/l_1 - (l_0/l_1 - 1)\,\pi_0/\mathrm{B}] \times \mathrm{RT}/\bar{s}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $[l_0/l_1-(l_0/l_1-1)\pi_0/\mathrm{B}] = \rho_0/\rho_1 = \pi'_0/\pi'_\pi$.

The osmotic pressures calculated by means of (7) are given in Tables XIII. and XIV., in which column (1) gives the weight concentrate. Columns (2) and (5) the values of $\log_e \rho_0/\rho_1$ obtained as a weighted mean value of the numbers in column (11) of the previous tables. Columns (3) and (6) the values of $\bar{s}$ used in the calculation, and (4) and (7) the resulting osmotic pressures. Column (8) gives such osmotic pressures as have been observed directly; these are the results tabulated in 'Roy. Soc. Proc.,' A, vol. 92, 1916, pp. 483–484, reduced to the new concentrations. Unfortunately, in that paper, by an oversight, the following two "direct" osmotic pressures were omitted:—A solution of cane sugar of weight concentration 56·631 gave an osmotic pressure of 43·95 atmospheres, another of weight concentration

TABLE XIII.—Cane Sugar.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)
	At 30° C.			At 0° C.			
Weight concentration.	$\log_e \rho_0/\rho_1$.	$\bar{s}$.	Calculated osmotic pressure.	$\log_e \rho_0/\rho_1$.	$\bar{s}$.	Calculated osmotic pressure.	Direct osmotic pressure.
			atmospheres.				
34·00	0·01950	1·00287	26·82	—	—	—	—
56·50	0·03429	1·00103	47·25	0·03516	0·99515	43·91	43·84
81·20	0·05256	0·99873	72·59	0·05380	0·99157	67·43	67·68
112·00	0·07762	0·99554	107·55	0·07983	0·98690	100·53	100·43
141·00	0·10305	0·99176	143·33	0·10669	0·98321	134·86	134·71
183·00	0·14231	0·98653	198·98	0·14711	0·97842	186·86	—
217·50	0·17586	0·97360	249·16	0·18080	0·97399	230·70	—
243·00	—	—	—	0·20666	0·97117	264·46	—

TABLE XIV.—α-Methyl Glucoside.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)
	At 30° C.			At 0° C.			
Weight concentration.	$\log_e \rho_0/\rho_1$.	$\bar{s}$.	Calculated osmotic pressure.	$\log_e \rho_0/\rho_1$.	$\bar{s}$.	Calculated osmotic pressure.	Direct osmotic pressure.
			atmospheres.				
35·00	0·03592	1·00260	49·42	0·03878	0·99810	48·29	48·11
45·00	0·04731	1·00186	65·14	0·05153	0·99709	64·22	63·96
55·00	0·05930	1·00087	81·73	0·06451	0·99597	80·50	81·00
64·00	0·07011	0·99956	96·75	0·07699	0·99491	96·17	96·24
75·00	0·08352	0·99881	115·34	0·09253	0·99354	115·74	115·92
90·00	0·10241	0·99721	141·66	0·11368	0·99166	142·46	—
105·00	0·12144	0·99507	168·34	0·13553	0·98974	170·18	—

56·713 gave an osmotic pressure of 44·05 atmospheres; in neither case was there any "solution leak." Table XV. gives our calcium ferrocyanide results after applying BURTON's correction.

TABLE XV.—Calcium Ferrocyanide at 0° C.

Weight concentration.	Calculated osmotic pressure.	Direct osmotic pressure.
31·389	41·10	41·22
39·504	70·59	70·84
42·889	86·62	87·09
47·219	112·97	112·84
49·857	131·33	131·00

The results for cane sugar and α-methyl glucoside are plotted against weight concentration in Diagrams I. and II. It is interesting to observe that the curves at 0° C. and 30° C. for α-methyl glucoside intersect.

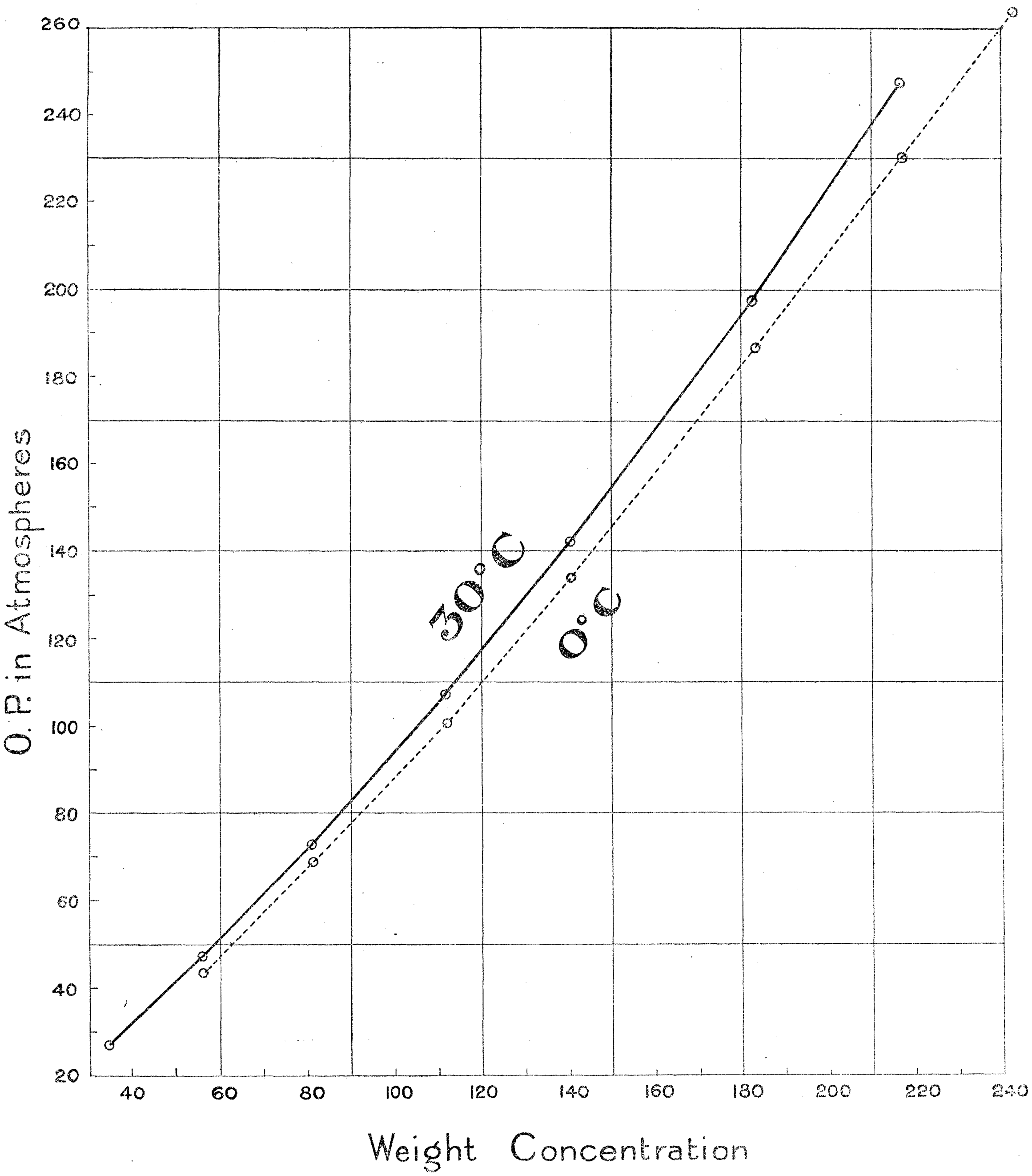

Diagram I. Cane sugar.

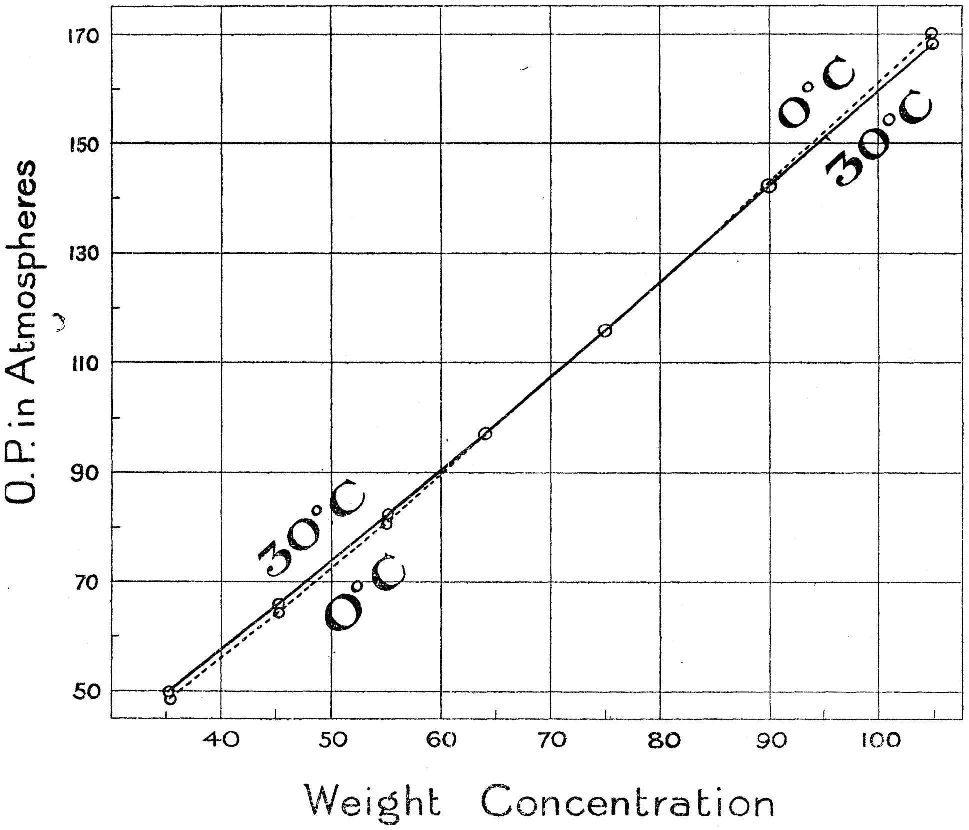

Diagram II. α-methyl glucoside.

Note added by Lord Berkeley, *April* 5, 1919.

[During the course of further work on vapour pressures at 30° C., Mr. E. Stenhouse and I have found that with apparatus D when the 3rd and 4th vessels each contain water,* the latter always gives up a measurable quantity of vapour to the air stream. A number of experiments, which need not be detailed, have proved that the air on leaving 3 is saturated; yet 4 loses, on the average 0·000235 gr. of water per gramme of total vapour carried to, and absorbed by, the sulphuric acid in vessel 5.

Three explanations seem to me to be possible:

(1) The current of air may not be fast enough to prevent an extra loss caused by diffusion to the sulphuric acid. (It is to be noted that when no air passes, about 0·03 gr. of water diffuses in the time usually taken for an experiment.) This hypothesis is ruled out by the fact that in an experiment with water in 3, 4 and the first two branches at 5 (the other two containing sulphuric acid), 4 still showed the usual loss in weight.

(2) Remembering that the vapour is practically all absorbed in the first branch of 5, it seemed possible that the sudden drop in pressure caused by this absorption

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* It is only with apparatus D, where the deposition of water in the quartz joining tubes is very small, that we have been able to put two water vessels in series.

might disturb the air stream over the adjacent water sufficiently to upset the steady conditions of flow demanded by theory. Testing this hypothesis by an experiment in which the sulphuric acid was absent, there was the usual loss in 4. Incidentally this experiment strengthens the conclusion come to under (1), and it also shows that the heat generated in 5 by the absorption of the water is not the cause of the trouble.

(3) Nevertheless I am driven to the assumption that a permanent inequality of temperature between vessels 3 and 4 is maintained. Unfortunately, when exploring the bath by means of thermocouples, as mentioned on p. 318, it was not realized that the presence of the train of vessels might make a difference to the free circulation of the bath water. A further examination with a Beckman thermometer (reading to 0°·02 C. and estimating to 0°·002 C.), placed alternately over the last branches of 3 and 4 respectively (it is only the exit branches that matter), seems to show that the latter is 0°·002 C. higher than the former. No stress should be laid on this result, for its magnitude only became apparent when the readings had been averaged and disentangled from the oscillations in the temperature of the bath as a whole. It is noteworthy, however, that a difference of 0°·003 C. between the two vessels is sufficient to account for the observed loss.

Whatever be the cause of the loss of water in vessel 4 of apparatus D, it is obvious that a correction should be applied to the experiments with that set of vessels. It seems probable that a correction should also be applied to the experiments with the other apparatus, but as the method of heating the bath, and the original position of the heaters cannot be recovered exactly, I am unable to determine what the correction should be.

The accompanying table gives, for the experiments with D, the corrected values together with the osmotic pressure calculated from the mean $\log_e \rho_0/\rho_1$.

It will be seen that the percentage difference between the new and old values of $\log_e \rho_0/\rho_1$ diminishes as the concentration increases. Taking the values for cane sugar, the difference for the weight concentration of 34 gr. per 100 water is about 1 per cent., while at 183 it is only 0·14 per cent.; we may therefore feel confident that for higher concentrations the values given in the body of this communication would not be modified appreciably even if we were in a position to apply the correction under discussion.]

SULPHURIC Acid at 30° C.

Date.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$.
Oct. 9, 1915	1·02502	0·02472
„ 20, 1915	1·02493	0·02462
„ 28, 1915	1·02491	0·02460
Nov. 5, 1915	1·02497	0·02466
„ 13, 1915	1·02482	0·02451
„ 24, 1915	1·02498	0·02467

CANE Sugar at 30° C.

Date.	Weight concentration.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$ corrected to standard weight concentration and 30° C.	Osmotic pressure. Atmospheres.	Mean osmotic pressure. Atmospheres.
Standard weight concentration = 34·00 gr. sugar to 100 gr. of water.					
Jan. 25, 1916	33·941	1·01947	0·01931	26·56	26·52
June 24, 1916	33·965	1·01942	0·01926	26·49	
July 13, 1916	33·980	1·01945	0·01927	26·50	
Standard weight concentration = 81·20 gr. sugar to 100 gr. water.					
Jan. 25, 1916	81·198	1·05379	0·05239	72·36	
Standard weight concentration = 141·00 gr. sugar to 100 gr. water.					
July 13, 1916	141·257	1·10865	0·10289	143·11	
Standard weight concentration = 183·0 gr. sugar to 100 gr. water.					
Jan. 19, 1916	182·737	1·15240	0·14211	198·70	198·63
June 24, 1916	183·160	1·15277	0·14201	198·56	

α-METHYL Glucoside at 30° C.

Date.	Weight concentration.	ρ_0/ρ_1.	$\log_e \rho_0/\rho_1$. corrected to standard weight concentration and 30° C.	Osmotic pressure. Atmospheres.	Mean osmotic pressure. Atmospheres.
Standard weight concentration = 64·00 gr. α-methyl glucoside to 100 gr. water.					
May 12, 1916	63·810	1·07210	0·06986	96·37	96·38
,, 19, 1916	63·810	1·07222	0·06997	96·53	
June 9, 1916	63·818	1·07203	0·06977	96·24	
Standard weight concentration = 90·00 gr. to 100 gr. water.					
Dec. 4, 1915	90·049	1·10748	0·10203	141·13	