On the Osmotic Pressures of Aqueous Solutions of Calcium Ferrocyanide. Part I: Concentrated Solutions

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VIII. *On the Osmotic Pressures of Aqueous Solutions of Calcium Ferrocyanide. Part I. Concentrated Solutions.*

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In the following communication the experiments on the direct measurement of the osmotic pressures, on the vapour pressures, and on the densities have been carried out in conjunction with Mr. E. G. J. Hartley, those on the compressibilities with Dr. C. V. Burton.

In the 'Proceedings of the Royal Society,' Series A, vol. 77 (1906), pp. 156–169, Mr. Hartley and I gave a preliminary account of the determination of the osmotic pressures of strong aqueous solutions of cane sugar by means of measurements of the relative lowering of their vapour pressures as compared to that of water. We deduced a formula for the connection between the vapour and osmotic pressures of a solution, which, in view of the experimental errors, justified the neglect of corrections due to the compression of the solution and of the solvent. Since then Prof. A. W. Porter ('Proc. Roy. Soc.,' A, vol. 79, 1907) has put forward an exact equation in which the influence of these two factors can be taken into account; increased experience with, and further modifications of, the vapour-pressure apparatus apparently justified the belief that the experiments would be more accurate, and therefore it seemed advisable to endeavour to obtain complete data for the aqueous solutions of some one substance, so as to test the practical applicability of the new formula in its entirety.

The equation in question is

$$\int_{\pi_\pi}^{p} s\,dp = \int_{\pi_\pi}^{\pi_{00}} r\,dp + \int_{\pi_{00}}^{p-\mathrm{P}_p} u\,dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the notation is as follows:—

For the Solution:—

The hydrostatic pressure on the solution is . . . . p.
The vapour pressure when the solution is in contact with its own vapour alone . . . . π_π.
Reduction of volume when 1 gramme of solvent escapes at pressure p . . s_p.
Osmotic equilibrium pressure for a hydrostatic pressure p . . . . P_p.

For the Solvent :—

Specific volume at hydrostatic pressures p_0, π_{00} . . . . u_{p_0}.
Vapour pressure when the solvent is in contact with its own vapour alone π_{00}.
Specific volume of the vapour when under various pressures . . v_{π_0}, v_{π_π}, &c.

An examination of the equation will show that the following data are required :—

(1) The densities of solutions of different concentrations at the temperature at which the work was carried out, namely, 0° C.
(2) A series of measurements of the relative lowering of the vapour pressures of the solutions at 0° C.
(3) A corresponding series of measurements of the direct osmotic equilibrium pressures for the purpose of comparison with those to be deduced from the measurements of (2) by means of the equation.
(4) Measurements of the compressibilities of the solutions and of water.
(5) A knowledge of the change in the specific volume of water vapour with pressure—this knowledge we assume is given by REGNAULT'S work.

Choice of Solute.

Owing to the fact that, in the direct measurement of osmotic pressures, the copper ferrocyanide membrane is semipermeable to but few substances, the choice is strictly limited. In calcium ferrocyanide a substance was found which seemed likely to throw considerable light on osmotic phenomena.

Aqueous solutions of this substance have the following properties :—The copper ferrocyanide membrane is practically impermeable to the salt. The salt is very soluble, so that strong solutions can be obtained and hence high equilibrium pressures; the solutions at all strengths are apparently stable enough at 0° C. to allow the necessary data to be obtained. The solutions show a considerable shrinkage on dilution, and this fact makes it possible to determine experimentally the s of the equation.

In this part of the communication the work is limited to concentrations of from 30 to 50 gr. anhydrous salt to 100 gr. of water. These limits are imposed upon us by the fact that weaker solutions have vapour pressures differing little from that of pure water, and, consequently, measurements of the relative lowering of their vapour pressures would entail very lengthy experiments,[*] while the stronger solution has an osmotic equilibrium pressure of about 130 atmospheres, which is near the utmost pressure we can obtain with our apparatus.

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[*] Even for a solution of 30 gr. anhydrous salt in 100 gr. water it is necessary to pass the air current through the vessels for a period of seven days before the difference between the loss of weight of the solution and that of the water is sufficient to give accurate results.

General Scheme of Operations.

About 500 c.cm. of solution are necessary for a determination of equilibrium pressure and vapour pressure; as two independent measurements of these quantities are required at some five points in the total range of 40 to 130 atmospheres, it follows that a large amount of salt was necessary.

To save salt, and in order to have a direct comparison between the two methods ot measuring osmotic pressures, it was decided to use the same "make up" of solution for both these measurements and the densities. The procedure adopted was to make up the solution in the morning (a portion of salt being set apart for analysis) and weigh it, and determine its density in the evening. The vapour-pressure vessels were then filled and got ready for weighing; and at the same time the direct osmotic-pressure apparatus was set up for "guard-ring leak" (see 'Phil. Trans.,' A, vol. 206, p. 490). The next morning the vapour-pressure vessels were weighed, placed in the bath, and the air current started; meanwhile the direct determination of the equilibrium pressure was carried out and the tube set up for "solution leak" (*loc. cit.*, p. 493).

Purification of the Salt.

The calcium ferrocyanide was obtained from Messrs. Kahlbaum as their purest. The first lot of about 2 kgr. was found to contain some potassium, probably in the form of the double salt. This lot, and also all succeeding ones, some 10 kgr. in all, was dissolved to form as nearly a saturated solution at the laboratory temperature as possible (without warming), and then filtered through a Chamberland porcelain filter. The salt was then recovered by recrystallization. Various methods of recrystallization were tried, but the best was to pass, by means of a suction pump, a steady stream of filtered air over crystallizing dishes containing the solution, and at the same time maintain them at from 20° C. to 25° C.* The various crops were freed from mother liquor by means of a platinum centrifugalizing machine; they were then powdered and dried in the air current at the temperature of the laboratory.

Analyses of samples of the 1st and 2nd recrystallization showed no marked difference in composition, but it should be mentioned that sometimes the salt came out of solution slightly green instead of yellow, and although neither in analysis nor in the experiments (where want of the yellow salt compelled the use of the green) was there found to be any difference in the results, yet it was thought better to avoid the use of these crops as much as possible. It was found that, on prolonged standing, a trace of precipitate came out of solution—this we suspected to be $CaCO_3$, but tests failed to confirm this—the quantity was not enough for analysis.

The following table gives the analytical results:—

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* The solutions seem to decompose at higher temperatures.

	1st lot.		2nd lot.		Percentage composition calculated from $CaFe(CN)_6 11Aq$.
	1st recrystallization (yellow crystals).	2nd recrystallization (yellow crystals).	1st recrystallization (yellow crystals).	1st recrystallization (green crystals).	
	per cent.	per cent.	per cent.	per cent.	per cent.
$Fe(CN)_6$	43·41	43·24	43·35	43·27	43·27
Ca	Not determined	16·56	16·63	16·59	16·34
Water	39·97	39·92	39·81	39·93	40·39
		99·72	99·79	99·79	100·00

It is to be noted that ROSCOE and SCHORLEMMER (2nd ed., 'Treatise on Chemistry,' vol. ii., p. 1025), stated that the salt crystallizes with 12Aq; our results point, however, to 11Aq.

The foregoing results, considering the imperfection of analytical methods, seemed to justify the assumption that the salt is of unvarying composition as far as the metallic radical is concerned; but as it is a highly hydrated salt, with presumably a vapour pressure, it was considered necessary to determine the water content of a sample of the salt used in each "make up" of solution. These determinations are given in the table of the results of the direct osmotic-pressure measurements (p. 191), and were obtained by drying the salt to constant weight in an air oven.

DENSITIES.

A 400 c.cm. and a 500 c.cm. flask were obtained, with graduated necks, whose diameter was such that 1 cm. of neck corresponded to 1 c.cm. capacity, and the graduations were in millimetres. The back of the neck was of milk glass, with a blue line running down the middle (Prof. SCHELLBACH'S device for burettes). By this means, readings estimated to 0·01 mm. could be obtained with fair accuracy. The necks were calibrated by adding weighed quantities of water to the flask (already filled with water) when in a constant temperature bath at 0° C. and also at 30° C. The meniscus level was read through a telescope and care was taken to avoid parallax. The capacity of the flask was determined by weighing against a counterpoise on a large Oertling balance.

A similar process was followed for the determination of the densities. The flask was filled, weighed, and placed in ice, and the level read when the solution had ceased contracting—generally in about 5 hours' time.

Experimental Error.

It was found that the readings of the meniscus level could be relied on to ±0·01 mm.; this corresponds to a maximum error of 0·02 c.cm. on 400 c.cm., or

1 part in 20,000. It was not considered necessary to correct for the volume of liquid above the bottom of the meniscus as the error appertains to both the determination of capacities and of the density. One uncertainty remains, in that when making up the solution, the neck above the level has been wetted and an unknown, and possibly variable, quantity of liquid is left adhering. There is no means of correction for this, but the fact that the densities of slightly differing solutions generally follow the weight concentration indicates that this source of error is of no great importance.

In the following table all the results on the densities of the solutions are given. The first column gives the weight concentration, *i.e.*, the number of grammes of anhydrous salt in 100 gr. water, and the second gives the density.

TABLE I.

Weight concentration.	Density at 0° C.	Weight concentration.	Density at 0° C.
50·184	1·32145*	39·678	1·26953
49·913	1·32168	39·517	1·26914
49·875	1·32138	39·490	1·26872
49·827	1·32086	39·198	1·26692
47·292	1·30912	39·159	1·26728
47·146	1·30808	34·812	1·24315
44·167	1·29314	31·412	1·22330
44·114	1·29341	31·364	1·22364
42·900	1·28660	31·093	1·22149
42·878	1·28662		

TABLE IA.—Mean Values.

Weight concentration.	Density at 0° C.	Weight concentration.	Density at 0° C.
49·872	1·32131	42·889	1·28661
47·219	1·30860	39·408	1·26832
44·140	1·29327	31·290	1·22281

LOWERING OF THE VAPOUR PRESSURE.

During the progress of the research it was found that there was a disagreement of some two or three per cent. between the direct measurement of the equilibrium pressure and the same when calculated by means of PORTER'S equation from the lowering of the vapour pressure of the solutions.

The cause of this discrepancy is surmised to be due to the fact that the experiments were carried out in air at atmospheric pressure, while Prof. PORTER'S equation implies vacuum conditions; and although by modifying the equation to suit our requirements we obtain results (*infra*) which are in close agreement, yet the values for the vapour

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* This density was not used in the final computations—it is known to be wrong—sufficient time was not given for the temperature of the solution to become constant at 0° C.

pressure and density of water vapour in air, which are used in the reduction, may be somewhat in error.* It is, therefore, thought advisable to give somewhat full details of the various devices tried and of the test experiments made.

Improvement in the Apparatus† *and Test Experiments.*

Method of keeping the Bath at 0° C.—A large wooden tub was kept filled with ice and water; a small water pump, actuated by the laboratory shafting, pumped the water from the tub into the bath, and this water syphoned back into the tub. The temperature on a long run varied from about 0°·2 to 1°·0 C. It may be pointed out that the constancy of the temperature is not of so much importance as that there should be no difference between the temperatures of the various vessels in the bath. This was ensured by stirring the bath very vigorously and continuously. A thermometer placed in different positions in the bath showed no variation.

Limits of Accuracy of Weighing the Glass Vessels themselves.

One of the vessels was weighed four times, at intervals of a week or so, against the counterpoise, various operations having been performed on it between while, with the following results:—

> Weight of vessel before experiment, 37·7925 gr.; after, 37·7925, 37·7925, 37·7923 gr.

Another vessel, fitted with mercury cups (see *infra*, fig. 3, p. 186), was similarly weighed. The cups, after mercury had been poured into and out of them, were cleaned with nitric acid, dried with alcohol, &c.:—

> Weight of vessel before experiment, 29·2760 gr.; after various washings and leaving in the bath for a week, 29·2760, 29·2759, 29·2759, 29·2758, 29·2760, 29·2756, 29·2755 gr.

The change shown in the last two experiments is probably due to the balance wanting cleaning. From these numbers it will be seen that the maximum error is only 0·0005 gr.

New Form of Joint between Water and Sulphuric Acid Vessels.

The method adopted for measuring the relative lowering of the vapour pressure of the solution is that described in the 'Roy. Soc. Proc.' (BERKELEY and HARTLEY, vol. 77, A, 1906). The solution is contained in two vessels which are weighed separately. Dried air passes over the solution in these vessels in series; it then passes over water in a weighed vessel, and finally over sulphuric acid in a fourth weighed vessel. The assumption on which the method is based is that the air, on emerging

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[*] The values are derived from REGNAULT'S work, but he himself seems somewhat dissatisfied with them.

[†] Described 'Roy. Soc. Proc.,' vol. 77, A, 1906, pp. 156, 162.

from the 2nd solution vessel, is saturated with water vapour up to the vapour pressure of the solution, and on emerging from the water vessel it is then saturated up to the vapour pressure of the water. Hence the ratio of the loss of weight of the vessels containing the solution to the sum of the loss of weights of solution and water vessel equals the ratio of the density of the vapour over the solution to that over water. As pointed out in the communication mentioned above, it is evident that if the air on entering the train of vessels has been dried by sulphuric acid, and on emerging from the water vessel it is again dried in a similar manner, the gain in weight of the 4th vessel (the vessel containing the sulphuric acid) should equal the sum of the losses of weight of the solution and water vessels. In that paper it was shown that this did not obtain—there was a considerably greater loss of weight than there was gain by the 4th vessel. This discrepancy can be shown to be partly caused by the saturated air giving up some of its moisture* to the tube connecting the 3rd and 4th vessels.

As it was found to be impossible to weigh accurately the connecting tube, it was sought to bring the deposited moisture into the sulphuric acid by making the internal diameter of this tube only 1·5 mm., so that the velocity of the air current would sweep the moisture forward.

Fig. 1 (p. 184) shows the first form tried and is self-explanatory.

The use of the joint in this form, and other modifications of it which need not be further described, caused a considerable improvement, as shown by the following test experiments:—

Air was passed very rapidly for 24 hours through two vessels in series, joined by the above-mentioned form of joint. The 1st vessel contained water and the 2nd sulphuric acid. The temperature of the bath was constant at about 30° C.

The water lost 2·8425 gr.

The sulphuric acid gained 2·8393 gr.

The "dipping" tube (*i.e.*, the tube connecting the water and sulphuric acid vessels) was found to have gained 0·0048 gr.

The difference between the losses and gains being, therefore, +0·0016 gr.

A repetition of the experiment with a slow air current gave a difference of −0·0003 gr.

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* There are three plausible explanations of the phenomenon: (1) That there are eddy currents (possibly caused by inequalities of surface) in the junction tube and the consequent changes of temperature bring about deposition; in this connection it is noteworthy that more moisture is deposited on a dirty tube. (2) That the surface of any glass vessel is always slightly hydrated, and if the glass be soluble a solution of lower vapour pressure is formed, and, consequently, more moisture is deposited; evidence in favour of this view is afforded by the well-known fact that less moisture is deposited on lead glass, which is stated to be less soluble than soda glass; on the other hand, we find that we get the usual deposit on platinum-iridium tubes. (3) That the air, containing ions, is really supersaturated in as far as the ions may carry a watery envelope; the latter is deposited on the walls of the tube where the ions come in contact with it. We are at present engaged in experiments to test this hypothesis.

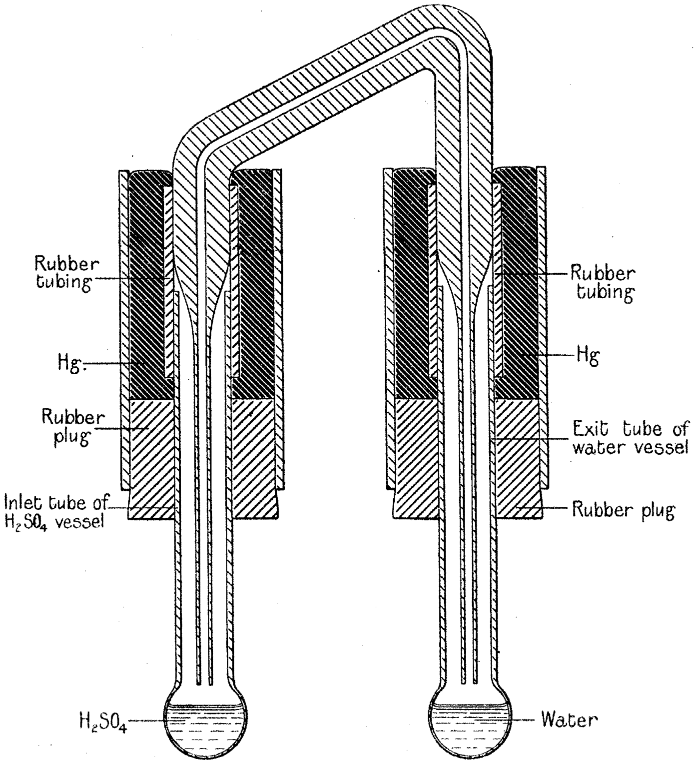

Fig. 1.

Change in Weight of 2nd Solution Vessel.

It was mentioned that the 2nd solution vessel always lost weight (see p. 163 of vol. 77, A, 'Roy. Soc. Proc.'), and a possible explanation was suggested for this. Further work with the method seemed to point to the absorption of moisture by the rubber connecting piece as a possible cause of the difficulty. Fig. 2 (p. 185) shows the form of joint devised to get over this. A is the exit tube of one vessel, and B the entry tube of the next vessel. C is a rubber plug, cut on the lathe to the shape shown, and secured in place by the "umbrella rings" D. The inverted U-tube E is similarly held in place by F, and the space between the U-tube and the exit and entry tubes A and B is partially filled with mercury through the side tubes G, which are themselves closed by rubber plugs.

The following tests were made:—

Two vessels, containing sulphuric acid, were placed in series and dry air passed for 48 hours, with the result that each vessel gained 0·0006 gr.

This experiment was repeated and air passed for 116 hours, at the end of which the 1st vessel had gained 0·0022 gr., and the second 0·0032 gr.

The experiment was again repeated, but the precaution was taken to dry the rubber plugs in an air oven and keep them in a desiccator until use, as it might be that these plugs gave up moisture to the mercury which passed it on to the air current. A run of 70 hours resulted in a gain of weight in the 1st vessel of 0·0003 gr. The weight of the 2nd vessel was lost by an accident.

This experiment was again repeated with three vessels in series, the only change being the use of graphite as a lubricant for the rubber plugs. A run of 70 hours gave a gain in 1st vessel = 0·0045 gr., in 2nd 0·0034 gr., in 3rd 0·0010 gr.

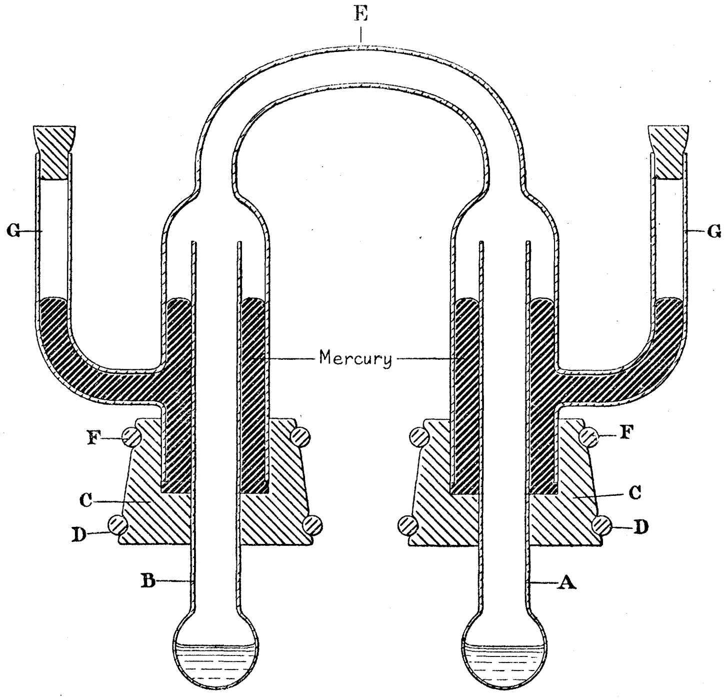

Fig. 2.

Another run of 70 hours resulted in a gain of 0·0032 gr., 0·0019 gr., and 0·0000 gr., respectively.

The rubber plugs were then given up and a plain mercury cup joint used, as in fig. 3 (p. 186).

A and B are the exit and entry tubes of the vessels, C C are the glass cups, fused to A and B, to contain the mercury. The inverted U-tube D is held in position by a clamp (not shown) supported from the oscillating platform.

The following tests of this joint were made :—

Three vessels, containing sulphuric acid, were placed in series, and air passed for 92 hours; 1st vessel gained 0·0035 gr., 2nd 0·0005, and 3rd 0·0025 gr.

It was thought that possibly the cups were not properly cleaned out before weighing, as it was found that the water of the bath had, during the experiment, become charged with rust from the clamps. A repetition of the experiment on a 116-hour run (using brass clamps) gave gains of 0·0045 gr., 0·0021 gr., and 0·0016 gr. respectively. In both these experiments the temperature of the bath was that of the laboratory.

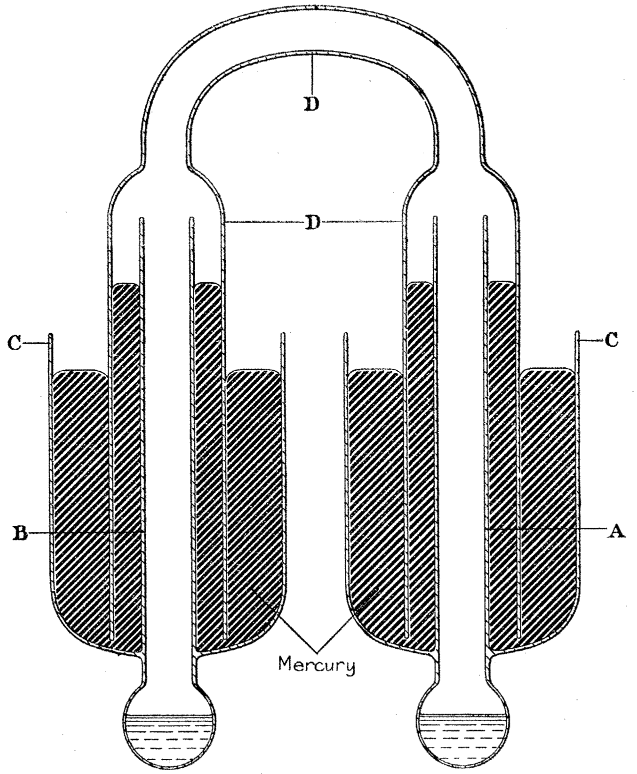

Fig. 3.

Pure Air.

It was now noticed that although the air passing through the train of vessels was filtered, yet a certain amount of reaction had taken place in the 1st sulphuric acid vessel (vessel D of original paper), for the acid had turned brown during the course of the experiments. This was completely remedied by drawing the air from outside the laboratory and by avoiding rubber tubing on the entry side. This latter modification was obtained by means of a mercury cup placed outside the bath, but in the axis of oscillation of the platform.

An experiment with four sulphuric acid vessels in series was then made, with the air current running for 92 hours, the temperature of the bath being constant at about 30° C. The 1st vessel gained 0·0021 gr., 2nd 0·0010 gr., 3rd 0·0012 gr., and 4th 0·0018 gr. It was now thought that possibly these changes in weight were due to the absorption of mercury vapour by the sulphuric acid. An attempt to test this was made by furnishing two out of the four vessels with gold sleeves suspended in the entry tubes. A run of 92 hours at 30° C. gave 0·0018 gr., 0·0013 gr., 0·0004 gr., and 0·0010 gr. respectively, and the gold sleeves were not found to have altered in weight.

Hitherto the vessels, while on the balance, had not been closed; in view of the fact that the errors now seemed to be considerably less than heretofore, it was thought better to have vessels made with their entry and exit tubes fitted with ground-glass stoppers. These vessels were then tested as before.

Run.				gr.	gr.	gr.		gr.	Average. gr.
43½	hours at	30° C.	gave	+0·0004	+0·0011	+0·0006	and	+0·0001,	0·0006.
67½	,,	30°	,,	+0·0005	+0·0007	+0·0008	,,	+0·0007,	0·0007.
90¾	,,	30°	,,	+0·0005	+0·0010	+0·0013	,,	+0·0007,	0·0009.
115½	,,	0°	,,	+0·0003	+0·0001	+0·0008	,,	0·0000,	0·0003.

It will be noticed that the gains are greater for the higher temperatures than for the lower, and, further, the average gain shows a tendency to increase with increased length of run. Both facts are explicable on the assumption that the gains are due to mercury vapour, and it is noteworthy that, calculating from the approximately known vapour pressure of mercury (LANDOLT and BÖRNSTEIN'S tables) and estimating the amount of air passed (from previous work), the gains are found to be of the order of the number given from these data. Exact concordance cannot be expected, because in all experiments the inverted U-tubes (fig. 3, p. 186) were brought down as close to the exit and entry tubes as was practicable.

It was therefore decided to test this question by using a form of joint which avoided the use of mercury. For this purpose Messrs. Johnson and Matthey made inverted U-tubes of platinum-iridium (see fig. 4) in such a way that they were not rigid and, consequently, allowed the unavoidable expansion and contraction, when the whole train of vessels was put into and taken out of the bath, to take place without risk of breaking the glass vessels or unduly straining the joints.

A and B are the exit and inlet tubes, and the inverted platinum-iridium U-tube C is ground into these at D and E. The internally conical parts E and F are for the ground-glass stoppers (not shown) used when weighing the vessels. The upper part of the U-tube is of thin tubing and is flexible. This joint was tested, after some preliminary experiments, as follows :—

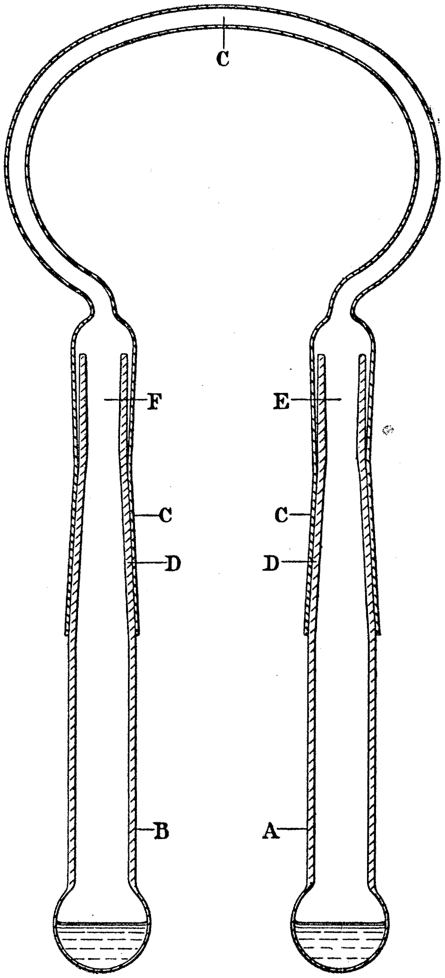

Fig. 4.

Two sulphuric acid vessels in series were joined by one platinum-iridium joint and air passed for 63 hours at 30° C. (rubber lubricant in ground joint). There was a gain in the 2nd vessel of 0·0004 gr. Another run of 72 hours at 30° C. gave a gain of 0·0001 gr. Three vessels in series, run of 116 hours at 30° C., with a dry-air current, gave losses 0·0001 gr., 0·0001 gr., 0·0004 gr.

This seems to show conclusively that some of the previous gains in weight were due to mercury vapour.

As the gain at 0° C. (see p. 187) was only 0·0003 gr. for 116 hours' run, it was decided to use this form of vessel (*i.e.*, mercury cups) for work at 0° C., and to reserve the platinum-iridium U-tubes for work at 30° C.

Test of Fall of Air Pressure.

In connection with the change of weight in the 2nd solution vessel it was thought possible that the loss might be due to a difference of pressure in the air current, caused by "wire-drawing" the air when passing over and through the platinum rolls.

The total difference in the pressure of the air when entering and when leaving the train of vessels at a rate of 50 bubbles in 11 seconds was determined and was found to be about 1 mm. of water. This number, even if the whole difference of pressure were supposed to take place between the two solution vessels, is inadequate to account for the loss of weight observed.

Test to see whether the Oscillation of the Vessels causes any Change.

It was thought that the oscillation of the train of vessels might affect the results; for J. J. Thomson and others have pointed out that the surface layer of a solution is at a different concentration to that of the bulk of the liquid. Now, in the method of operation adopted, the air is caused to pass over platinum rolls recently wetted by the solution, and from which the solution is slowly draining off. It might be that a layer of solution thus left in contact with the air has a different concentration to that of the ordinary surface,* and this effect was looked for by setting up a vapour-pressure experiment without oscillating the apparatus nor using the platinum rolls, but passing the air over at a slower rate. No appreciable difference resulted (see experiment marked * on next page).

In the following table *all* vapour-pressure results with $Ca_2Fe(CN)_6$ solutions are given.

The 1st column gives the date of the beginning of the experiment; the 2nd gives the weight concentration of the solution used, *i.e.*, the number of grammes of anhydrous salt to 100 grammes of water, and is calculated from the analyses given in the table on p. 191, column 3; the 3rd gives the mean temperature of the bath; the 4th gives the number of hours the air was passing; the 5th gives the rate of bubbling, *i.e.*, the time taken for 50 bubbles to pass; the 6th, 7th, 8th and 9th give the changes in weight in the several vessels. It is to be noted that the algebraic sum of the

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* Another disturbing factor is that the small radius of curvature of the surface of the solution clinging to the thin edges of the platinum rolls raises the vapour pressure; the experiment without the platinum rolls shows that the joint influence of this together with that indicated in the text is of no practical importance.

TABLE II.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)
Date.	Weight concentration. Number of grammes of anhydrous salt to 100 gr. Aq.	Mean temperature of bath.	Number of hours' run.	Time in seconds for 50 bubbles to pass.	Change in weight of 1st solution vessel, in grammes, (sum $= l_1$.)	Change in weight of 2nd solution vessel, in grammes, (sum $= l_1$.)	Change in weight of water vessel, in grammes.	Change in weight of sulphuric acid vessel, in grammes.	Total loss of weight of solution and water, in grammes, l_0.	Total gain of weight of H_2SO_4 and U-tube, in grammes.	Ratio, l_0/l_1.
		° C.									
November 6, 1907 . .	50·184	0·7	116½	29	−1·5588	+0·0004	−0·1673	+1·7237	1·7261	1·7248	1·10735
*February 19, 1908 . .	49·913	0·4	140	37	−1·5355	0·0000	−0·1645	+1·6999	1·7000	1·7007	1·10713
March 2, 1908	49·800	0·3	92	25	−1·7470	+0·0006	−0·1866	+1·9326	1·9336	1·9345	1·10681
†January 14, 1907 . . .	49·8	0·5	116	21	−1·2173	−0·0003	−0·1306	+1·3467	1·3482	1·3471	1·10726
February 6, 1908 . . .	47·292	1·1	92	19	−2·3905	+0·0004	−0·2207	+2·6095	2·6112	2·6112	1·09230
November 28, 1907 . .	47·146	0·6	92	22	−1·7729	+0·0002	−0·1614	+1·9323	1·9343	1·9338	1·09104
†December 8, 1906 . . .	44·6	0·6	164	28	−1·1721	−0·0006	−0·0900	+1·2606	1·2627	1·2611	1·07675
November 21, 1907 . .	42·900	0·5	116	22	−2·3657	+0·0003	−0·1660	+2·5306	2·5317	2·5318	1·07017
November 13, 1907 . .	42·878	0·9	116	20	−2·7719	0·0000	−0·1945	+2·9645	2·9664	2·9652	1·07017
January 28, 1908 . . .	39·490	0·4	140	20	−3·6699	+0·0006	−0·2095	+3·8785	3·8794	3·8809	1·05709
December 7, 1907 . . .	39·517	0·6	116	23	−2·3622	0·0000	−0·1349	+2·4980	2·4981	2·4998	1·05708
December 31, 1907 . .	31·413	0·2	164	20	−4·2789	+0·0008	−0·1421	+4·4196	4·4210	4·4220	1·03322
December 13, 1907 . .	31·364	0·7	164	22	−3·9868	+0·0007	−0·1312	+4·1188	4·1180	4·1197	1·03311

* Experiment with no oscillation (see preceding page).

† Old form of apparatus. These two observations were in the nature of preliminary experiments, and the weight concentration and densities were not accurately determined.

TABLE IIA.—Mean Values.

Weight concentration.	l_0/l_1.
49·966	1·10710
47·219	1·09167
42·889	1·07017
39·503	1·05708
31·388	1·03316

numbers in the horizontal row included in columns 6 and 7 gives l_1; the 10th gives the total loss of weight of solution and water, $= l_0$; the 11th gives the total gain, including the amount of moisture found in the "dipping tube," while the 12th gives the ratio of the vapour pressure of water to that of the solution and is obtained by dividing the total loss by the loss of weight of the solution, $= l_0/l_1$.

Remarks on the Table.

It will be noticed that the ratios of l_0 to l_1 for experiments with similar concentrations are in very close agreement.

It should be mentioned that at first, in these experiments at 0° C., a difficulty was experienced in that the sulphuric acid in the first branch of the last vessel crystallized out during the run. Now, the freezing-point of the hydrate $H_2SO_4 1Aq$ is higher than 0° C., hence when the pure acid in the first branch takes up enough water to form a liquid of that concentration it solidifies, but the addition of more water will lower the freezing-point. The difficulty, therefore, was overcome by filling this first branch, at the start, with an 85-per cent. solution of sulphuric acid, *i.e.*, a solution slightly weaker than $H_2SO_4 1Aq$.

OSMOTIC EQUILIBRIUM PRESSURES.

The equilibrium pressures were determined in exactly the same way as described in 'Phil. Trans.,' A, vol. 206, pp. 481–507.

It is only necessary, before giving a table of the results, to call attention to the fact that in all cases the "solution-leak correction," that is, the amount of calcium ferrocyanide which came through the membrane during the experiment, is practically negligible. The amount coming through was determined by evaporating the water contents of the tubes together with 100 c.c. washing water passed through the tube after an interval of four days, down to a small bulk, and determining the calcium in it by the oxalate method.

It should be mentioned that the solutions act on the gunmetal of the osmotic apparatus; this was prevented by coating the metal with a varnish.

In Table III., Column (1) gives the date of the experiment; (2) the weight concentration (*i.e.*, the number of grammes of anhydrous salt to 100 grammes of

TABLE III.

(1.) Date.	(2.) Weight concentration.	(3.) Water content of the salt.	(4.) Tube used.	(5.) Apparent turning point.	(6.) Guard-ring leak.	(7.) Time.	(8.) Solution leak. [gr. $Ca_2Fe(CN)_6$].	(9.) Rate of movement of water gauge per increment of pressure.	(10.) Osmotic equilibrium pressure.
		per cent.		atmospheres		hours	gr.	mm.	atmospheres
November 6, 1907 . .	50·184	39·81	X	131·11	−0·7	2¼	Nil	4·0	131·04
February 19, 1908 . .	49·913	Not determined	X	131·42	−0·3	3	Nil	2·75	131·38
*January 14, 1907 . .	49·8	Not determined	N	130·59	−0·9	2¾	0·0009	2·2	130·45
February 6, 1908 . .	47·292	39·99	N	113·42	+0·6	3	Nil	3·6	113·48
November 28, 1907 . .	47·146	39·98	X	112·20	0·0	2¾	0·0010	3·4	112·20
*December 8, 1906 . .	44·6	39·97	X	95·63	−0·4	5	0·0014	3·0	95·61
November 21, 1907 . .	42·900	39·91	N	87·03	−1·2	2½	0·0005	2·7	86·88
November 13, 1907 . .	42·878	39·93	N	87·43	−0·9	3	0·0010	2·6	87·30
December 7, 1907 . .	39·517	39·97	X	70·92	−0·3	3½	Nil	4·0	70·89
January 28, 1908 . .	39·490	39·98	N	70·86	−0·3	2¼	Nil	3·6	70·80
December 31, 1907 . .	31·413	39·99	X	41·29	−0·75	4	0·0010	2·85	41·20
December 15, 1907 . .	31·364	39·92	X	41·30	−0·75	2¾	0·0005	3·05	41·24

The two experiments marked * were preliminary, and the weight concentration and solution leak were only determined approximately.

TABLE IIIA.—Mean Values.

Weight concentration.	Osmotic equilibrium pressure.
	atmospheres
50·048	131·21
47·219	112·84
42·889	87·09
39·503	70·84
31·388	41·22

water) of the solution; (3) the water content of the hydrated salt used in the "make up" of the solution; (4) the name of the tube used; (5) the apparent turning-point, *i.e.*, the pressure at which no movement of the water gauge takes place; (6) the movement of the water level, in millimetres, in 15 minutes, caused by the "guard-ring leak"; (7) the time the pressure was on the solution; (8) the solution leak, *i.e.*, the total amount of $Ca_2Fe(CN)_6$ come through the membrane during the time in Column (7); (9) the movement of the water level, in millimetres, in 15 minutes, caused by an increment of pressure of 0·34 atmosphere; (10) the apparent turning-point [Column (5)], corrected for "guard-ring leak"; as there is practically no correction for "solution leak," the numbers in column (10) can be taken as the osmotic equilibrium pressure of the solution when there is a pressure of 1 atmosphere on the solvent.

COMPRESSIBILITY OF THE SOLUTIONS.

An attempt was made, in view of other work with more compressible solutions, to design the apparatus so that accurate results might be obtained. The piezometer is represented by fig. 5. The gunmetal vessel A is filled with water and connected by B and C to a Schaffer and Budenberg dead-weight pressure apparatus.

The "Robax"* Jena glass tube D, 19 mm. external and 12 mm. internal diameter, is made pressure-tight with the gunmetal piece E by means of a dermatine ring F, which is compressed between a shoulder and a metal sleeve actuated by a nut, J. The lower end of the tube is closed pressure-tight in a similar manner and the tube is prevented from slipping out by four distance stays such as G G. The compressibility vessel H, which is filled with the solution to be examined, is of No. 16^{III} Jena glass. This glass was selected as its compressibility has been carefully determined by SCHOTT and STRAUBEL.† The bulb is of about 15 c.cm. capacity and the stem, open at the lower end, is graduated into millimetres (1 mm. of the bore has a capacity of 0·0002 c.cm.). The whole tube, bulb, and stem were carefully calibrated in the usual

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* The Robax tubes were found to withstand pressure fairly well, but after considerable use they burst at a lower pressure than that originally reached; hence, after using a tube for four or five observations at 100 atmospheres, it must be replaced by a new one.

† SCHOTT and STRAUBEL—see references in LANDOLT and BÖRNSTEIN'S tables, 3rd ed.

way by means of mercury. The stem was made 40 cm. long, and its bore such that an appreciable change in reading could be observed even when caused by only a change of pressure of a few atmospheres.

The bottom of the Robax tube is filled for some few centimetres with mercury and matters are so arranged that the mercury rises in the stem of the compressibility tube H a centimetre or two above the level of the mercury outside when the whole apparatus has been brought to a constant temperature at atmospheric pressure.

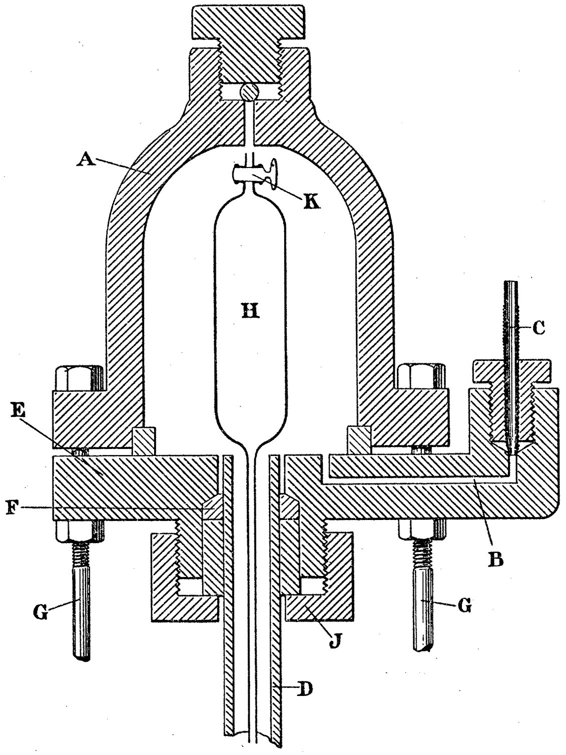

Fig. 5.

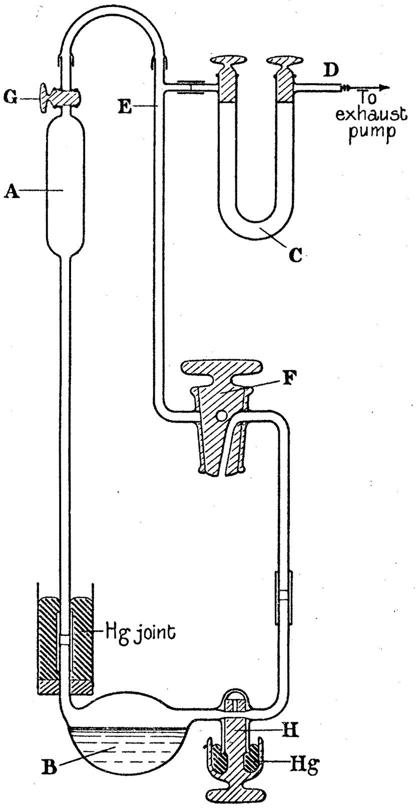

Fig. 6.

General Method of Experiment.

The compressibility tube is filled as shown in fig. 6, which represents the method adopted to fill with air-free liquid. The compressibility tube A is joined at its lower end to a bulb, B, containing the liquid, and at its upper end to the U-tube C containing pumice moistened with sulphuric acid; this U-tube is weighed before and after the experiment. The U-tube is connected at D to a Fleuss exhaust pump by flexible pressure tubing; the T-piece E serves to connect it to the other end of the bulb containing the solution through the three-way tap F. By closing tap G, turning F so as to have through communication, and opening tap H, the liquid in B can be caused to boil. Care, however, must be taken only to create a vacuum above B sufficient to get rid of the air (shown by air bubbles coming off), otherwise an unnecessary increase of concentration of the solution in B will take place. When it is judged that practically all dissolved air has been removed, tap H is closed and G opened; the aim is to sweep out any air adhering to the sides of A by a current of moisture. Tap G is then closed, and the whole apparatus tilted to the left, so that the liquid in B closes the left-hand orifice; the tap H is then opened and F is cautiously turned so as to admit air above the solution. In this manner the compressibility tube is filled up to the tap without any air bubbles being apparent, as a rule. The key of tap G must also be filled, otherwise deformation may take place when the vessel is placed under compression. The compressibility tube is then taken down and placed in the piezometer.

Now, if the bulb B has been filled with a known volume of solution whose density and concentration are known, and the change in weight in C is known, then the concentration of the solution filling the compressibility tube is known.

All the experiments on compressibility here given were those obtained at 0° C. For this temperature, after the introduction of the compressibility tube, the whole apparatus was filled with ice-cold water and the upper part, down to 3 or 4 cm. below the coupling J of fig. 5, was surrounded by ice. A period of some four or five hours, the ice being rammed down at intervals, was allowed to elapse so that a constant temperature approximating to 0° C. might be attained. The constancy of the temperature was judged by readings of the mercury level in the compressibility tube,* the readings being taken by means of a telescope.

A pressure of some 20 atmospheres was then gradually put on the water in the apparatus and when the level of the mercury in the compressibility tube was constant it was noted. Another gradual increase of pressure of the same amount was then put on and the level read, and so on till the maximum pressure of about 100 atmospheres was attained, after which the reverse process was carried out.

The intention had been to reach a pressure of 150 atmospheres, but, although at times the "Robax" tubing stood this, one or two serious breakages (causing in one case the fracture of the compressibility tube) made it desirable to limit the experiment to 100 atmospheres.

Sources of Error.

There seem to be two main sources of error:—

(1) Variation of temperature during the experiment. There are two causes for a change of temperature. One is that the ice in melting round the apparatus causes a small quantity of warm air to come into contact with the gunmetal casting. This was obviated by ramming the ice down at intervals of about 15 minutes. The second cause of a change of temperature is unavoidable and is due to the development of heat by the compression of the liquid itself. This thermodynamic change of temperature was found to disappear in about 10 minutes.

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* In later work the piezometer was altered so that a mercury thermometer could be placed close to the compressibility tube.

(2) A possible source of error is the presence of lubricant in the tap at the top of the compressibility tube and also any unobserved air bubbles in the solution.

It was considered that these errors were overcome when the same reading of the mercury level in the compressibility tube was obtained for the same pressure reading, whether when increasing the pressure or when decreasing it. On the other hand, it was noticed that on increasing the pressure somewhat quickly the rapid rise of the mercury in the stem of the compressibility tube caused it to enclose small globules of liquid which further increase of pressure did not seem to move, hence the apparent constancy of the change in volume for a given change in pressure may be no indication that the true change in volume has been obtained.

It was found, however, that the enclosed globules of liquid were avoided when the rate of change of pressure was slow.

The following is from the laboratory book and gives the details of one of the experiments with calcium ferrocyanide solution.

The solution was made up by weight in the 400 c.c. flask and its density determined as on p. 180.

Date.	Time.	Weight of H_2SO_4 U-tube.	Remarks.
March 18			Made up solution.
March 19		70·584 gr.	Used No. II. compressibility tube.
	9.0 A.M.		Filled bulb and connected up as before (*i.e.*, as in fig. 6).
	10.45		Started pumping.
	11.5		Opened bulb to pump for 5 seconds.
	11.15		" " "
	11.35		" " "
	?		Closed taps and opened compressibility tube to pump.
	?		Closed compressibility tube and filled.
	12.40 P.M.	70·612 gr.	Withdrew compressibility tube and placed its bulb in ice for 2 minutes while lower end dipped in solution and then placed in apparatus which was immediately filled with ice-cold water and covered with ice.

During the afternoon the ice was rammed down at intervals of one hour, and at intervals of a quarter of an hour between 4 and 5 P.M.

Date.	Time.	Pressure in atmospheres.	Reading of stem.	Difference of pressure.	Difference of reading.	Remarks.
	P.M.		mm.		mm.	
March 19	5.5	1	63·3			
	5.9	21·4	102·2			Rammed down ice.
	5.14	21·4	102·8			
	5.19	21·4	102·85	20·412	32·55	
	5.22	41·8	140·4			Rammed down ice.
	5.27	41·8	141·1			
	5.32	41·8	141·15	20·412	38·3	
	5.34	62·2	177·9			Rammed down ice.
	5.39	62·2	179·0			
	5.45	62·2	179·05	20·412	37·9	

Date.	Time.	Pressure in atmospheres.	Reading of stem.	Difference of pressure.	Difference of reading.	Remarks.
	P.M.		mm.		mm.	
March 19	5.46	82·6	215·0			Rammed down ice.
	5.51	82·6	215·7			
	5.56	82·6	215·8	20·412	36·75	
	5.59	103·1	251·0			
	6.4	103·1	252·0			
	6.9	103·1	252·0	20·412	36·2	
	6.10	82·6	216·6			Rammed down ice.
	6.15	82·6	216·0			
	6.20	82·6	215·95	20·412	36·05	
	6.22	62·2	180·1			Rammed down ice.
	6.27	62·2	179·2			
	6.32	62·2	179·1	20·412	36·85	
	6.33	41·8	142·0			Rammed down ice.
	6.38	41·8	141·2			
	6.43	41·8	141·15	20·412	37·95	
	6.44	21·4	103·4			Rammed down ice.
	6.49	21·4	102·7			
	6.54	21·4	102·7	20·412	38·45	
	6.58	1	64·4			Rammed down ice.
	7.3	1	64·1			
	7.8	1	64·05	20·412	38·65	

The weight concentration of the solution before filling the compressibility tube was 38·812 gr. of anhydrous salt to 100 gr. of Aq and its density 1·2432 at 0° C. 50 c.cm. of this solution were pipetted into the bulb and, during filling, gave up to the H_2SO_4 U-tube a weight of 0·028 gr. of water, from which it is deduced that the concentration of the solution filling the compressibility tube was 38·834 gr.

Reduction of Observations of Compressibilities.

(1) *Determination of Compression of Compressibility Tube.*—The observed change in volume of the liquid filling the compressibility tube is the algebraic sum of two terms—the actual change of the liquid less that due to the glass itself.

As stated, the compressibility tube was made of Jena glass $16^{\rm III}$ and the compressibility of this glass has been worked out by STRAUBEL* and others (see LANDOLT and BÖRNSTEIN's tables, 3rd ed., for references) to be ·00000228 per atmosphere at ordinary laboratory temperature.

There seems to be good reason for believing that AMAGAT's value for the compression of mercury is accurate (see JAMIN, 'Cours de Physique'), so that by using this value and observing the apparent change in volume of the compressibility tube when filled with mercury a check on the above coefficient of the glass can be obtained.

An experiment in which the compressibility tube was exhausted by means of a Gaede pump and then filled by recently redistilled mercury gave $0_4 0169$ as its apparent coefficient of compression in the compressibility tube between 1 and 101

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* The value in LANDOLT and BÖRNSTEIN's tables seems to have been derived from torsion and bending experiments.

atmospheres at 0° C. AMAGAT's value for the true coefficient is $0{\cdot}0_4 0392$; hence that of the glass is $0{\cdot}0_4 0223$ at 0° C.

The agreement between this result and STRAUBEL's value seems to prove that no serious experimental error has been incurred.

(2) *Corrections to be Applied to the Volume Reading.*—The method used is based on the assumption that the pressure inside and outside the compressibility tube is the same, but it must be remembered that this can only be the case at the beginning of the experiment (*i.e.*, when the level of the mercury is the same inside and outside of the compressibility tube), for when the mercury has been caused to rise in the stem, there is an excess of pressure on the outside of the compressibility tube due to the amount of the rise of the mercury above the level outside. The change in volume of the compressibility tube due to this was determined by special experiments, and a correction has been applied to both the volume and the pressure. The latter correction, in view of the nature of the results required in this paper, is of no importance.

Results.

The following tables give the corrected results obtained :—

EXPERIMENTS on the Compressibility of Water at 0° C.

The 1st column gives the range of pressure in atmospheres; the 2nd column gives the coefficient of compression per atmosphere in that range; the 3rd column gives AMAGAT's results for the same range.

Pressure range, in atmospheres.	Observed coefficient of compression.	AMAGAT's coefficient.	Remarks.
1·0 to 62·2	0·00005117	0·0000518	Air-free water (¾ hour "boiling").
13·6 ,, 74·8	0·00005114	0·0000515	,, ,, (,, ,,).
1·0 ,, 62·2	0·00005132	0·0000518	Water not quite free of air.

The compressibility of the calcium ferrocyanide solution is only required for the purpose of calculating the osmotic equilibrium pressure from vapour-pressure measurements, and as the latter were only made on solutions whose weight concentration varied from 50 to 31 gr. of anhydrous salt per 100 gr. of Aq, the compressibility measurements recorded here were restricted to this range.

The following table gives the results obtained for the solutions at 0° C. Column 1 gives the weight concentration in grammes of anhydrous salt per 100 grammes of water of the solution; column 2 gives the range of pressure; column 3 gives the corresponding coefficient per atmosphere :—

Concentration before filling.	Pressure range, in atmospheres.	Coefficient per atmosphere.
39·7	1·0 to 14·6	$0\cdot 0_4265$
	14·6 „ 28·2	0_4262
	28·2 „ 41·7	0_4260
	41·7 „ 55·3	0_4253
	55·3 „ 68·9	0_4259
	68·9 „ 82·5	0_4255
47·3	1·0 to 21·4	$0\cdot 0_4238$
	21·4 „ 48·6	0_4234
	48·6 „ 75·8	0_4234
	75·8 „ 103·1	0_4232
	103·1 „ 116·7	0_4229

These two experiments were of the nature of preliminary experiments; the data for calculating the density of the solution filling the compressibility tube were not obtained, nor was great care taken to avoid concentrating the solutions while "boiling" off the dissolved air.

TABLE IV.

Weight concentration.	Pressure range, in atmospheres.	Coefficient per atmosphere.
50·9*	1 to 140	$0\cdot 0_4235$
49·95	1·0 to 21·4	0_4233
	21·4 „ 41·8	0_4225
	41·8 „ 62·1	0_4229
	62·1 „ 82·4	0_4227
	82·4 „ 102·8	0_4220
Mean coefficient =		0_4227
44·21	1·0 to 41·8	0_4251
	41·8 „ 62·1	0_4245
	62·1 „ 82·4	0_4245
	82·4 „ 102·8	0_4245
Mean coefficient =		0_4247
39·28	1·0 to 21·4	0_4255
	21·4 „ 41·8	0_4263
	41·8 „ 62·1	0_4264
	62·1 „ 82·4	0_4260
	82·4 „ 102·8	0_4268
Mean coefficient =		0_4262
34·83	1·0 to 21·4	$0\cdot 0_4287$
	21·4 „ 41·8	0_4280
	41·8 „ 62·1	0_4280
	62·1 „ 82·4	0_4278
	82·4 „ 102·8	0_4276
Mean coefficient =		0_4280
31·09†	1·0 to 21·4	0_4305
	21·4 „ 41·8	0_4295
	41·8 „ 62·1	0_4299
	62·1 „ 82·4	0_4296
	82·4 „ 102·8	0_4290
Mean coefficient =		0_4297

* This experiment was not finished owing to breakage.

† This experiment was made on a solution which was not freed from air at all, and, on plotting the several results, it appears to come on the curve, from which it would seem that dissolved air has no appreciable influence on the coefficient.

Modification of Porter's Equation.

The experiments on vapour pressures and on the equilibrium pressure were done in air, but Prof. Porter's equation is derived from the consideration of somewhat ideal conditions approximating to that of a vacuum, and it is therefore necessary to obtain an expression suitable to the conditions of the actual experiments.

This may be derived in the following manner :—

Assume that the pistons in the ideal apparatus are permeable to air but not to the liquids or their vapour, then no work can be done on or by the atmosphere.

Using the notation on p. 177 with the additional symbols

A = pressure of the atmosphere ;

π_{a0} = vapour pressure of the solvent in air when it is under a total pressure of $\mathrm{A}+\pi_{a0}$;

$\pi_{a\pi}$ = vapour pressure of the solution in air when it is under a total pressure of $\mathrm{A}+\pi_{a\pi}$;

and performing the thermo-dynamic cycle, as in Prof. Porter's paper, it is easily seen that the work done in the various operations is :—

1st operation. $\mathrm{P}_{(\mathrm{A}+p)}s_{(\mathrm{A}+p)}-(p_0+\mathrm{A})\,(u_{(\mathrm{A}+p_0)}-s_{(\mathrm{A}+p)})$.

2nd operation. $-\int_{u_{(\mathrm{A}+p_0)}}^{u_{(\mathrm{A}+\pi_{a0})}} p\,du-\pi_{a0}v_{\pi_{a0}}+(\mathrm{A}+\pi_{a0})\,u_{(\mathrm{A}+\pi_{a0})}$.

3rd operation. $-\int_{\pi_{a0}}^{\pi_{a\pi}} p\,dv$.

4th operation. $-\int_{\mathrm{A}+p}^{\mathrm{A}+\pi_{a\pi}} p\,d\mathrm{V}+\pi_{a\pi}v_{a\pi}-(\mathrm{A}+\pi_{a\pi})\,s_{(\mathrm{A}+\pi_{a\pi})}+\int_{\mathrm{A}+p}^{\mathrm{A}+\pi_{a\pi}} p\,d\,(\mathrm{V}+s)$.

Summing up, equating to zero, and integrating by parts, we get*

$$\int_{\mathrm{A}+\pi_{a\pi}}^{\mathrm{A}+p} s\,dp=\int_{\pi_{a\pi}}^{\pi_{a0}} v\,dp+\int_{\mathrm{A}+\pi_{a0}}^{\mathrm{A}+p_0} u\,dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

This equation is, in appearance, the same as Prof. Porter's, with the limits slightly altered ; yet if we carefully consider what assumptions underlie the various operations, it will appear that the quantities involved are different.

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* Since this was written, Prof. Porter has published the second part of his paper "On the Osmotic Pressure of Compressible Solutions of any Degree of Concentration" ('Proc. Roy. Soc.,' A, vol. 80) ; he points out, in a private communication, that equation (2) may be directly obtained, as in Section 5 of that paper, by estimating (throughout the cycle) the changes in $\int v\,dp$, which must vanish also because this integral is the same as $|pv| - \int p\,dv$.

We have tacitly assumed that the actual semi-permeable membrane is impermeable to the air dissolved in both solution and solvent; so that the s of the equation is the actual change in volume under the conditions of the experiment. This element will be given by the density measurements in conjunction with the measurements of the compressibility of the solutions and of water, which in all cases contain dissolved air.

The u term is similarly obtained; although this term, as will be seen later on, is of no importance in this work, it may be so when dealing with liquids that are more volatile than water; then the compressibility of air-containing solvents will have to be obtained with considerable accuracy. It should be noted that the P of the limit represents the actual osmotic equilibrium pressure due both to the dissolved salt and the dissolved air in the solution measured against the back osmotic pressure of the air dissolved in the otherwise pure solvent.

On the other hand, the v term is, in one respect, different from the actual conditions; it is vapour pressure *in air* when both solution and solvent are under the sum of the pressures of the atmosphere and their own vapour pressures, while the actual experiments are made when the two liquids are under the pressure of the atmosphere alone. It is thought that this slight difference may be neglected.

Evaluation of the Integrals.

(1) *The term* $\int_{A+\pi_{a\pi}}^{A+p} s\,dp$.—It will be seen on p. 198 (Table IV.) that the coefficient of compression of any one solution varies but little at different pressures; it was, therefore, thought that its mean value would be accurate enough for the purpose in view, and the following table gives the resulting volumes of the several solutions when under compression. Columns (1) and (2) are a repetition of those on p. 181 (Table 1A.); (3) gives the number of grammes of water to one gram-molecular weight of anhydrous salt; (4) gives the observed equilibrium pressure, taken from a graph when necessary; (5) gives the mean coefficient of compression per atmosphere, also taken from a graph when necessary; (6) to (12) give the volumes of the respective solutions which contain one gram-molecule of salt when under the pressure given at the head of the respective columns.

The numbers in the horizontal line between the brackets have not been used in the reduction—it was considered that the changes in volume were too small to give reliable results.

On plotting the volumes in any one of the columns (6) to (12) against the figures in column (3), it will be seen that the resulting curve is practically a straight line, hence we may take the change in volume (at any given pressure) caused by a change in concentration due to the loss of one gramme of water as constant, and this volume change will be given by the ratio of the difference in volume divided by the

TABLE V.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)
Weight concentration. Number of grammes of anhydrous salt to 100 grammes of Aq.	Density at 0° C.	Number of grammes of Aq to 290·22 grammes of salt.	Observed equilibrium pressure, in atmospheres.	Coefficient of compression per atmosphere.	Volume in litres containing one gram-molecular weight when compressed to 131 atmospheres.	Volume in litres containing one gram-molecular weight when compressed to 113 atmospheres.	Volume in litres containing one gram-molecular weight when compressed to 96 atmospheres.	Volume in litres containing one gram-molecular weight when compressed to 87 atmospheres.	Volume in litres containing one gram-molecular weight when compressed to 71 atmospheres.	Volume in litres containing one gram-molecular weight when compressed to 41 atmospheres.	Volume in litres containing one gram-molecular weight when compressed to 1 atmosphere.
49·872	1·32131	872·15	131	$0\cdot0_4227$	0·65811	0·65837	0·65863	0·65877	0·65900	0·65945	0·66006
47·219	1·30860	904·85	113	$0\cdot0_4235$	0·68934	0·68963	0·68990	0·69006	0·69031	0·69080	0·69146
44·140	1·29327	947·72	96	$0\cdot0_4246$	0·73046	0·73077	0·73108	0·73124	0·73153	0·73207	0·73281
(42·889	1·28661	966·90	87	$0\cdot0_4250$	0·74905	0·74939	0·74971	0·74988	0·75017	0·75073	0·75151)
39·408	1·26832	1026·67	71	$0\cdot0_4262$	0·80670	0·80708	0·80743	0·80763	0·80797	0·80860	0·80947
31·290	1·22281	1217·74	41	$0\cdot0_4297$	0·99199	0·99252	0 99302	0·99329	0·99376	0·99464	0·99585

corresponding difference in column (3). This ratio is practically the s of the term. Further, it will be seen that the s for any given solution varies but slightly with the pressure. The maximum difference is only 0·5 per cent. It was, therefore, considered that for the purpose of evaluating the integral, sufficient accuracy would be attained if we put

$$\int_{A+\pi_{a\pi}}^{A+p} s\,dp = \bar{s}\int_{A+\pi_{a\pi}}^{A+p} dp\,. = \bar{s}\,(p-\pi_{a\pi}),$$

where the mean value of s between the limits is $\bar{s}$, obtained in the manner just indicated.

These mean values are given in the following table* :—

Weight concentration.	$\bar{s}$.	Weight concentration.	$\bar{s}$.	Weight concentration.	$\bar{s}$.
49·966*	0·956	42·889	0·967	31·388	0·977
47·219	0·959	39·503	0·971		

In Prof. PORTER'S ideal apparatus, it will be remembered that there is supposed to be a pressure p_0 on the pure solvent piston. In our actual experiments this p_0 vanishes; hence $p = \mathrm{P}$, so that the term under discussion becomes $\bar{s}\mathrm{P}$.

(2) *The term* $\int_{A+\pi_{a0}}^{A+p_0} u\,dp$.—As the specific volume of water at 0° C. does not differ appreciably from unity, even over a pressure range of one atmosphere, this term, remembering that $p_0 = 0$, reduces to $-\pi_{a0}$, which is a negligibly small quantity.

(3) *The term* $\int_{\pi_{a\pi}}^{\pi_{a0}} v\,dp$.—There seem to be no data for the exact evaluation of this integral, but if we assume that both BOYLE'S law and the partial-pressure law apply to the vapour pressure of water in air, we may put

$$\int_{\pi_{a\pi}}^{\pi_{a0}} v\,dp = \frac{\pi_{a0}}{\rho_{a0}}\log_e\frac{\pi_{a0}}{\pi_{a\pi}} = \frac{\pi_{a0}}{\rho_{a0}}\log_e\frac{l_0}{l_1},$$

where

ρ_{a0} = vapour density of water vapour in air when the water is under the pressure $A+\pi_{a0}$,
l_0 = observed loss of weight of the solution and water vessels,
l_1 = observed loss of weight of the solution alone.

The original equation thus reduces to

$$\bar{s}\mathrm{P} = \frac{\pi_{a0}}{760\rho_{a0}}\log_e\frac{l_0}{l_1}.$$

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* The solution of weight concentration 49·966 is taken because it is the solution for which we have the lowering of vapour pressure. See p. 190, Table IIA.

On p. 341 of CASTELL EVANS' 'Phys. Chem. Tables,' the value of π_{a0} derived from REGNAULT'S measurements is given, together with the value of ρ_{a0}, which he has calculated from REGNAULT'S work on the assumption that the partial-pressure law holds.* Using these two values, the results tabulated below are obtained.

By a similar process of evaluation of the integrals in Prof. PORTER'S equation [equation (1) on p. 177] it is easily seen that it reduces to

$$\bar{s}\,(\mathrm{P}+1) = \frac{\pi_0}{760\rho_0}\log_e\frac{l_0}{l_1}+1,$$

where π_0 is the vacuum vapour pressure of water and ρ_0 its vacuum vapour density, and taking BROCH'S recalculation of REGNAULT'S work on these two quantities in a vacuum, and assuming that they are applicable to the experiments, we obtain the results given below under the head of "unmodified" equation.

TABLE VI.

(1.) Weight concentration.	(2.) "Unmodified" equation.	(3.) "Modified" equation.	(4.) Observed equilibrium pressure.
	atmospheres.	atmospheres.	atmospheres.
49·966	135·04	131·45	130·66†
47·219	116·05	112·96	112·84
42·889	88·99	86·61	87·09
39·503	72·54	70·61	70·84
31·388	42·38	41·24	41·22

The concordance of these numbers seems to indicate a satisfactory agreement between experiment and thermodynamic theory.

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* Private communication.

† On turning to Table III., p. 191, it will be seen that a solution of weight concentration 50·184 gave an equilibrium pressure of 131·04 atmospheres, while one of 49·913 gave 131·38 atmospheres. One of these two observations must evidently be in error. As the value for equilibrium pressure of the strongest solution given in the table is derived from the graph of this pressure against concentration, using the mean of these two observations as the ultimate point, it may be that the value given is 0·5 atmosphere too low.