XLI.—On the Osmotic Pressures of Salts in Solution.

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IN a paper in the *Zeit. physikal. Chem.*, **1**, 481, Van't Hoff discusses the analogy between the osmotic pressure of a salt in solution and the pressure exerted by a gas on the walls of its containing vessel.

The numbers upon which he bases the verification of his calculations were obtained by Pfeffer, in his *Osmotische Untersuchungen* (Leipzig, 1877), and only embrace the figures for a few salts, viz., potassium nitrate, potassium tartrate, and for the complex organic substances cane sugar, and gum arabic. These were the only independent measurements of osmotic pressures in absolute units, until A. Ladenburg published (*Ber.*, **22**, 1225) a few numbers for the osmotic pressures of solutions of dextrose, resorcinol, cane sugar, and "saccharin."

It is not easy to get actual measurements of osmotic pressures, but a number of comparisons of the osmotic pressures of different salts in solution were made by De Vries (*Pringsheim's Jahrb.*, **14**; *Zeit. physikal. Chem.*, **2**, 415; **3**, 103), who found the concentrations of isotonic solutions of these salts, by means of the exosmotic contractions which they bring about in the protoplasmic lining membrane of living cells.

In very dilute solutions, the substances examined appeared to obey the laws of Boyle, Gay-Lussac, and Avogadro, but in the case of strong solutions, the deviations were considerable.

At the suggestion of Professor J. J. Thomson, I took in hand the direct measurement of osmotic pressures by Pfeffer's method, but the length of time required by each experiment renders the accumulation of results very slow.

The method consists in depositing a membrane in the substance of a porous pot, which membrane must be continuous, and coarse-grained enough to allow the passage of water molecules through its interstices, but sufficiently fine-grained to prevent the passage of salt molecules, or the compound molecules of a salt, and water; a salt solution placed within such a pot gets up a pressure when placed in pure water. I have tried in various ways to form a membrane capable of withstanding a pressure of 3–4 atmos. without giving way, and have finally returned to the simple form of apparatus which is drawn in section in Fig. 1.

It consists of a porous pot, B, in which the membrane is deposited, connected with a simple manometer gauge, AC, which is connected with B by means of the glass adapter E.

I describe the parts in detail, as they are the product of considerable experimental work.

FIG. 1a.

FIG. 1.

The Pots.

The only porous pots found to give any consistent results are specially made of biscuit porcelain, 3 inches long, 1 inch external diameter, and $\frac{3}{16}$ -inch substance. Into the open end, a tightly fitting glass tube E (Fig. 1), drawn off at one end, is inserted and fixed for a length of about 1 inch, by sealing wax. No wax is put on the outside, for experience shows that, in this case, the membrane is formed irregularly between the two layers of wax. This is shown by Fig. 2,

which is a section of the wall of such a pot. As the membrane generally gives way at the top (perhaps the pores of the pot are coarser there, due to the method of manufacture), it is essential to give it a good connection with a solid wall of wax some way down the pot.

FIG. 2.

Some other methods were tried for getting the top secure: (i) supporting the upper end of the membrane by melting paraffin wax into the top of the pot, after a preliminary formation of the membrane and drying the pot; this did not give good results; (ii) having the upper ends of the pot glazed with porcelain glaze, but as the glaze could only be applied superficially inside and out, instead of throughout the mass of the biscuit, the membrane-forming solutions did not diffuse evenly, and the film was formed irregularly, and even locally, between the two layers of glaze, and when a high internal pressure was maintained for some time, it forced the solutions through minute cracks in the glaze. This is shown in section in Fig. 3. Messrs. Morlent Frères, Bayeux, kindly tried to glaze some throughout, but did not succeed.

The 1-inch long sealing wax joint withstands pressures of $3\frac{1}{2}$ to $4\frac{1}{2}$ atmos., depending on the temperature, and at the same time prevents the membrane from approaching the top of the pot, since the outer solution has diffused over $\frac{1}{2}$ inch downwards from the top, before it reaches the inner solution. This is shown in section in Fig. 4.

The dimensions of the pots allow all the connections and fittings to be made of glass.

Up to the present, sealing wax is the only cement with which I have been able to get any results, with one exception.

FIG. 3.

FIG. 4.

For temperature experiments it is necessary to use another cement. Portland cement is too porous to form a strong film, and the free alkali in it decomposes the copper sulphate solution used. The pressures obtained with this cement are only about one-half those got with sealing wax.

The double phosphate of zinc and sodium, and the oxychloride of zinc both make good cements, but only become hard when the zinc oxide used is prepared by heating the nitrate. This oxide is very hard, and requires careful and prolonged grinding before it is sufficiently fine to use. When made, the cement sets very quickly, and is difficult to manipulate. However, the only temperature experiment I have been able to complete was made with a pot fixed with the sodiophosphate cement.

The Membrane.

Pfeffer in his researches used a membrane of copper ferrocyanide formed by precipitation from 3 per cent. solutions of copper sulphate, and potassium ferrocyanide, when these were allowed to diffuse from each side of a porous pot which had been immersed in the copper sulphate solution, and partially dried. He also experimented with membranes of calcium phosphate, ferric hydroxide, ferrous carbonate, and ferric ferrocyanide, and found that they did not prevent the passage of salts so completely as the copper compound. I also tried the same membrane and, in addition, aluminium hydroxide, and silicic, and tungstic acids, but could not get satisfactory results with the commercial pots, except with ferric ferrocyanide. The specially manufactured pots gave excellent results with the copper salt, and so saved further experiment.

The chief objection to the ferrocyanide film is that the solutions which surround it must be neutral, or at any rate not dissociated* in solution. On the other hand, the destruction of the film is an excellent, but trying proof that a salt is dissociated in solution.

The Gauge.

A simple form of manometer was found to give good results, since it could be attached to the pot by the help of a blowpipe, after the film was made (Fig. 1, p. 345). C is a capillary tube of uniform bore about 45 cm. long. The rest of the tubing is about $\frac{3}{16}$ inch bore. The heights were read sufficiently accurately by the millimetre scale D.

Mode of Preparing the Membranes and Setting up the Apparatus.

At first I tried Pfeffer's method of depositing the membranes, but could not get a strong film by it. The following, based on a suggestion of Professor J. J. Thomson's assistant, Mr. E. Everett, was, however, found to give excellent results:—

The clean and dry pot with its glass tube attached is gradually lowered into the copper sulphate solution, while the ferrocyanide solution is being poured into the inside. The pots are then placed under the air pump and kept in a vacuum for some days till all the air is drawn out of their pores. They are then allowed to stand about three weeks in more dilute solutions, to thicken up any weak places in the film. Too long standing in a vacuum is apt to cause a precipitation of copper oxide on the outside of the pot, and this seems to interfere with the free passage of water.

The film thus formed at the first contact of the two liquids is right in the middle of the pot walls, and stands pressures up to $4\frac{1}{2}$ atmos.

When ready for use, the pots are attached to their gauges by the blowpipe.

It is easy to empty the pots through the drawn-out tube A, by means of a piece of tube drawn out into a long capillary (Fig. 1a), and a suction pump. They are filled by a wash-bottle, or pipette with a capillary delivery tube.

In order to select the pots which can be used, they are filled with a salt solution which will get up a pressure of about 1 atmo. A solution of potassium nitrate $\frac{1}{20}$ gram mol. per litre does for this purpose, but solutions of $\frac{1}{40}$ gram mol. of potassium sulphate per litre or of $\frac{1}{80}$ gram mol. of potash alum per litre are better, as they

* Throughout this paper the term "dissociation" is used in its ordinary acceptance of dissociation into constituents. When dissociation into ions is meant, the words "into ions" have been inserted in the text.

keep their maximum pressures constant for a longer time than the nitrate. If a stronger solution is used at first, the film very often bursts.

Only about 25—30 per cent. of the pots set up give satisfactory results.

Pots which gave results nearly a maximum on their trials were used for testing Boyle's law in solutions. but only those which gave the maximum were used for observations which had to be compared with those from other pots.

When not in use, the pots were filled with, and stood in, distilled water. That this does not affect the film was shown by the fact that a pot (ϵ and ξ_3) which was kept standing in water for about a year gave practically the same results after this interval as it did before.

The Observations.

Owing to the thickness of the pot and the distance of the membrane from the inner surface, washing, &c., which requires the help of diffusion, takes a long time.

As the solutions used are very dilute (about 0.5—3 per cent.), it is necessary to remove any excess of salt left in the pot walls by the last solution. The pot is first thoroughly washed with distilled water, in order to remove any salt solution adhering to the sides of the pot and tubes, but to extract the salt contained in the pores it is necessary to fill the pot with distilled water and allow it to stand in distilled water for 24 hours.

The small percentage of salt in the pores causes a current of water through the film from the outside, which assists the washing as well as the diffusion. This treatment is generally sufficient to remove traces of the last occupant, though it is advisable to wash for 2—3 days, when time allows, and the consecutive solutions are not isotonic. (For examples see I.)

The pot is now filled with the new solution, allowed to stand for 24 hours, and then refilled. When the temperature is constant, readings are taken of the top of the air column of gauge, a ; the level of mercury, b and c , in both limbs of the U-tube; the upper level of the solution, d , in A (p. 345); the barometric height, e ; and the temperature, f . These give us the initial values for the volume and pressure of the air in the manometer gauge, v_0 and p_0 .

The top of A is now sealed, and these readings taken daily till the pressure is constant. For a good pot it does not seem necessary, though advisable in some cases, to take readings oftener than once a day, as the final pressure keeps constant for 1—3 days, according to the solution.

When constant, the diminished volume of the air, v , in the gauge is read, and the pressure calculated by Boyle's law.

p_0 is obtained by correcting the atmospheric pressure for the difference of level of the mercury in the two limbs of the U-tube, and also for the column of solution in A. p_1 is corrected for the difference of the mercury levels, for the atmospheric pressure on the water surrounding the pot, and for the difference of level between this water and the mercury column in communication with the pot. The last correction may be obviated by making the water-level of the vessel in which the pot is immersed the same as that of the mercury column.

A correction for dilution of the original solution by the entry of water to take the place of the mercury in the gauge has been avoided by making the capacity of the apparatus considerable, with respect to the bore of the gauge-tube C, and by making the amount of air enclosed in A very small also.

The time taken by the salt to get up its maximum pressure depends partly on the pot and partly on the character of each salt. A slow rate of rise is usually the characteristic of a strong and lasting film, but I have had a few exceptions.

Neutral salts do not in general attack the membrane, but some curious exceptions were noted. Ordinary potash alum and ammonia alum are not dissociated in solution; chrome alum gradually attacks the film. Potassium nitrate and many others (see below, V) are not dissociated; sodium nitrate gradually attacks the film. Potassium, calcium, ammonium, and aluminium sulphates are not dissociated; sodium, magnesium, and copper sulphates are dissociated. Potassium ferricyanide is dissociated, whilst the cobalticyanide is not. Potassium hydrogen carbonate gradually weakens the film, and trisodium phosphate, as might be expected, destroys it at once. In fact, it appears that the potassium salts of the strong acids are the least dissociated, whilst the sodium salts of these acids are much more generally dissociated.

This might almost be expected from the position of sodium in the periodic arrangement of the elements, in the same section of the first group as hydrogen, and from the behaviour of acids towards the film, but at the same time it is possible that the action is not due to simple dissociation, but to a specific action of the sodium salts, caused by their being relatively less completely saturated than the corresponding potassium salts. If this be the case, there ought to be some difference between the two in their action as solvents of more complex compounds. The only case which suggests itself is the incomplete precipitation of the paraglobulins from solution by means of sodium salts as compared with other neutral salts, though I am not aware of any comparative trials of the potassium salts.

The phenomena of dissociation of simple, and of double salts in solution has been investigated by F. Rüdorff (*Ber.*, **21**, 4, 3044). He shows that many of these are dissociated, and may be separated into their constituents by diffusion through a porous cell into water.

The quotient P/π , which is the same numerically as Arrhenius' coefficient of dissociation, i , is the number of times the observed pressure, P , is greater than that π , calculated on the assumption that the ultimate osmotic pressure is the same as would be exerted by the compression of a gram-molecule of hydrogen into the same space as the solution occupies. The values of π are for

and for $n \times \frac{1}{169}$ „ „ = $n \times 0.14$ atmo.

It may also be convenient to remember that at 15° a pressure of 1 atmo. would be produced by 0.424 gram-molecule per litre.

In the following tables column I is the strength of the solution in gram formula weights per litre; column II the osmotic pressure in atmospheres; column III the quotient P/π , or i , the dissociation coefficient.

The results will be found plotted out in Figs. 5 and 10.

1. *Simple Salts.*a. Solution of KNO_3 in different pots. Fig. 5.

I.	II.	III.
$\frac{1}{5}$ (nearly)	4.50	1.04
$\frac{1}{7.5}$	2.87	0.96
$\frac{1}{10}$	2.39 ¹	1.07
$\frac{1}{20}$	1.56 ²	1.39
$\frac{1}{40}$	0.89 ³	1.59
$\frac{1}{80}$	0.466	1.66

¹ Mean of 2.39, 2.41, 2.37.² Mean of 1.76, 1.48, 1.38, 1.61, 1.49, 1.64.*³ Mean of 0.96, 0.82.

* These figures were obtained for the nitrate when used as the first solution, for trying the pots. Hence they differ more than the others.

b Solution of NaNO_3 in different pots. Fig. 6.

I.	II.	III.
$\frac{1}{10}$	3.11	1.39
$\frac{1}{20}$	1.69 ⁴	1.51
$\frac{1}{40}$	0.60	1.07

⁴ Mean of 1.79, 1.59.

c. Solution of K_2SO_4 . Fig. 7 (p. 354).

Series (i) in one pot ρ_2 . In order starting with strongest.

I.	II.	III.
$\frac{5}{80}$	1.895	1.35
$\frac{4}{80}$	1.68	1.50
$\frac{3}{80}$	1.38	1.65
$\frac{2}{80}$	1.02 ¹	1.82
$\frac{1}{80}$	0.505	1.81

¹ Mean of 1.05, 0.99.

Series (ii) in one pot ξ_3 , in following order : 2, 4, 1, 3, 5 $\times \frac{1}{80}$.

I.	II.	III.
$\frac{5}{80}$	2.82	2.01
$\frac{4}{80}$	2.19	1.96
$\frac{3}{80}$	1.705	2.03
$\frac{2}{80}$	1.01	1.81
$\frac{1}{80}$	0.66	2.36

d. Solution of (NH₄)₂SO₄ in one pot τ .

I.	II.	III.
$\frac{1}{20}$	2.64	2.36
$\frac{1}{40}$	1.30	2.33

e. Solution of CaSO₄ in one pot σ_2 .

I.	II.	III.
$\frac{1.148^2}{80}$	0.467	1.59
$\frac{0.574}{80}$	0.245	1.67

² This is a saturated solution.

f. Solution of KI in one pot σ_2 . Fig. 8.

I.	II.	III.
$\frac{8}{80}$	3.37 ¹	1.50
$\frac{7}{80}$	3.05	1.56
$\frac{6}{80}$	2.56 ²	1.52
$\frac{5}{80}$	2.21	1.57
$\frac{4}{80}$	1.775 ³	1.58
$\frac{3}{80}$	1.35	1.61
$\frac{2}{80}$	0.92	1.64
$\frac{1}{80}$	0.496	1.77

$$^1 \zeta_3 = 3.31.$$

$$^2 \zeta_3 = 2.22.$$

$$^3 \sigma_2 = 1.81.$$

KI.

FIG. 8.

2. *Hydrogen Salts.*a. Solution of KHCO_3 in one pot ρ_2 . Fig. 9.

I.	II.	III.
$\frac{8}{80}$	2.03	0.91
$\frac{4}{80}$	1.01 ¹	0.90
$\frac{2}{80}$	0.59 ²	1.05

¹ Mean of 0.95, 1.07.Duplicate from $\delta = 1.32$.² Duplicate from $\delta = 0.655$.

FIG. 9.

b. Solution of Na_2HPO_4 in one pot ν . Fig. 10 (p. 357).

I.	II.	III.
$\frac{4}{80}$	1.82	1.62
$\frac{2}{80}$	1.50	2.68
$\frac{1}{80}$	0.51	1.40

Na_2HPO_4 . FIG. 10. c. Solution of Na_2HCl in one pot π_2 . FIG. 11.

I.	II.	III.
$\frac{1}{20}$	4.32	3.86
$\frac{1}{40}$	2.12	3.79
$\frac{1}{80}$	1.23	4.40

 Na_2HCl . FIG. 11.

3. *Salts of Compound Acids.*

a. Solutions of $K_4FeC_6N_6$. ξ_3 working down from strong to weak.
Fig. 12.

I.	II.				III. For mean.
	ξ_1	α_2	ξ_3	Mean.	
$\frac{8}{160}$	3.49	—	3.38	3.44	3.07
$\frac{6}{160}$	2.49	—	2.65	2.57	3.30
$\frac{4}{160}$	2.05	—	1.78	1.92	3.42
$\frac{3.3}{160}$	—	1.68	—	1.68	3.64
$\frac{2.6}{160} = \frac{1}{60}$	1.49	—	—	1.49	3.99
$\frac{2.5}{160}$	—	1.27	—	1.27	3.64
$\frac{2}{160}$	0.90	—	0.99	0.95	3.40
$\frac{1}{160}$	0.50	0.48	0.53	0.50	3.58

 $K_4FeC_6N_6$.

FIG. 12.

b. Solutions of $K_6Co_2C_{12}N_{12}$. In two pots, π_2 working down from strong to weak. Fig. 13.

I.	II.		Mean.	III.	
	δ .	π_2 .		δ .	π_2 .
$\frac{4}{160}$	3.46	3.28	3.37	6.19	5.85
$\frac{3}{160}$	--	2.49	2.49	—	5.95
$\frac{2.6}{160} = \frac{1}{60}$	2.17	—	2.17	5.82	—
$\frac{2}{160}$	1.77	1.70	1.74	6.35	6.08
$\frac{1}{160}$	0.91	0.90	0.91	6.50	6.43
$\frac{0.5}{160}$	0.512	0.515	0.514	7.31	7.36

$K_6Co_2C_{12}N_{12}$.

FIG. 13.

c. Solutions of $K(SbO)C_4H_4O_6$. In one pot π_2 , working up from dilute to strong. Fig. 14.

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I.	II.	III.
$\frac{8^1}{160}$	1.35	1.20
$\frac{6}{160}$	1.03	1.23
$\frac{4}{160}$	0.747	1.33
$\frac{2}{160}$	0.32	1.14

¹ This solution is nearly saturated.

FIG. 14.

4. Double Salts.

a. Solutions of $K_2Al_2(SO_4)_4 \cdot 24H_2O$. In two pots, γ and ξ_3 , working from strong to dilute in ξ_3 . Fig. 15.

I.	II.		III.	
$\frac{6.023^1}{160}$	γ .	ξ_3 .		
	2.70	—	3.20	—
$\frac{6}{160}$	—	3.36	—	4.00
$\frac{5}{160}$	—	2.695	—	3.85

I.	II.		III.	
	γ .	ξ_3 .		
$\frac{4.82}{160}$	2.32	—	3.44	—
$\frac{4}{160}$	—	2.04	—	3.65
$\frac{3.616}{160}$	1.84	—	3.64	—
$\frac{3}{160}$	—	1.56	—	3.72
$\frac{2.41}{160}$	1.18	—	3.50	—
$\frac{2}{160}$	—	1.08	—	3.86
$\frac{1.205}{160}$	0.61	—	3.63	—
$\frac{1}{160}$	—	—	—	—
$\frac{0.602}{160}$	0.37	—	4.39	—

¹ This is a nearly saturated solution.

FIG. 15.

$K_2Al_2(SO_4)_4 \cdot 24Aq.$

b. Solutions of $K_2Cr_2(SO_4)_4, 24Aq$ in two pots. Fig. 16.

I.		II.		III.	
$\frac{5}{160}$		2.70^2	—	3.85	—
$\frac{4}{160}$		2.46	—	4.40	—
„ Green ¹		—	2.08^3	—	3.72
$\frac{3}{160}$		1.62	—	3.86	—
„ Green		—	1.33	—	3.17
$\frac{2}{160}$		1.10	—	3.96	—
$\frac{1}{160}$		0.47	—	3.36	—

¹ The green solution is prepared by boiling the ordinary blue-green solution, and is in a condition of dissociation, since it attacks the film.

² This observation may be too low, since it followed (3), which weakened the film.

The examination of these curves leads to the observation that they are nearly continuous, and take the form OABCD, Fig. 17.

This may be divided into four parts; starting with a saturated

solution at D, dilution diminishes the osmotic pressure until the point C is reached. From C to B, the curve produced passes through O, and may represent the duration of existence of some complex

FIG. 17.

molecule of the salt, or of a definite hydrate. The part CB may be long or short, and above or below the line of gaseous pressure of an undissociated molecule. At B, the specific action of the solvent may be supposed to begin dissociating this complex molecule of the salt. This goes on increasing through A towards O, but does not pass beyond the line of complete dissociation into ions. In many cases, dilution does not appear to make this part of the pressure curve approach the line of complete dissociation into ions.

The portion OABC may be well seen in the KNO_3 curve, but in the K_2SO_4 and the KI curves, only the portion OA, and a little beyond A towards B.

The portion CD is well seen at the more concentrated end of the alum, and better in the tartar emetic curve, both of which are nearly saturated.

OABC is nearly straight for KI, for the double salts, and for the salts of the compound acids.

In the case of alum, the change of direction at C takes place at the concentration $\frac{4}{100}$ gram form. wt. per litre. Where the part OA is straight, it cuts the complete dissociation line when produced backwards, at a point between $\frac{2}{500}$ and $\frac{3}{500}$ concentrations.

The presence of hydrogen in the acid salts does not appear to have any specific effect on the form of the curves.

As the curves are so nearly continuous, we cannot infer the existence of definite hydrates in the solutions of the salts examined. For this purpose, one must get a larger range of observations, which can only be procured by some less lengthy method, such as the lowering of the freezing point.

The part DC shows a loss of kinetic energy on dilution; this may be due to the retardation of the molecules in the state in which they

exist in solution, being greater than that of those which are just entering the solid state.

II. Charles' Law applied to Salts in Solution.

In this case the difficulty is to procure a cement which will allow the formation of a film, but which will neither crack, nor melt. I found that sealing-wax joints will not allow the use of a temperature above 30°.

Using the sodiophosphate of zinc, I have got one observation. Unfortunately, the solution used, potassium ferrocyanide, attacked the film at a temperature of 70°, and I have not been able to get another film.

At 17°, $\frac{2.5}{160}$ $K_4FeC_6N_6$ gave a pressure of 0.77 atmo.

54° " " " " 1.13 "

Assuming Charles' law applies to salts in solution, and that $K_4FeC_6N_6$ behaves as a single unit, the pressure should have been

$$\frac{0.77 \times 327}{290} = 0.87 \text{ atmo.}$$

That is, the calculated rise on this assumption

$$= 0.87 - 0.77 = 0.10 \text{ atmo.}$$

But the observed rise

$$= 1.13 - 0.77 = 0.36 \text{ atmo.}$$

Now, on reference to the preceding results, I, 3, *a*, we find that the ratio of observed osmotic pressure to that calculated on the undissociated molecule hypothesis is about 3.65* for the above solution. Therefore, the calculated rise, instead of being 0.10 atmo., should be $0.10 \times 3.65 = 0.365$ atmo., which is the value found.

That is, so far as a single experiment can uphold the point, Charles' law does appear to apply to salts in solution.

It must be noted that the factor *i*, whatever be its interpretation, appears here as well as in the application of Boyle's law.

III. Dalton's Law of Partial Pressures applied to Salts in Solution.

I have arranged the values obtained under three heads:—

* The factor, 3.65 is that found for the above solution at 17°. De Vries has shown (*loc. cit.*) that the ratios of *i* are nearly independent of temperature.

a. Salts which combine to form well-marked double salts:—

Salt solution.	In pot κ .		In pot τ .	
	Osmotic pressure.	Sum of components.	Osmotic pressure.	Sum of components.
$\frac{1}{40}$ $(\text{NH}_4)_2\text{SO}_4$	1·264	—	1·295	—
$\frac{1}{40}$ $\text{Al}_2(\text{SO}_4)_3$	1·265	—	1·22	—
$\frac{1}{40}$ K_2SO_4	1·29	—	1·40	—
$\frac{1}{40}$ $(\text{NH}_4)_2\text{Al}_2(\text{SO}_4)_4, 24\text{Aq}$	2·37	2·53	1·98	2·515
$\frac{1}{40}$ $\text{K}_2\text{Al}_2(\text{SO}_4)_4, 24\text{Aq}$	2·39	2·56	1·96	2·32

b. Salts of the same acids, which do not form double salts:—

i. Iodides in pot σ_2 :—

Salt solution.	Osmotic pressure.	Sum of components.
$\frac{1}{40}$ KI	0·92	—
$\frac{1}{80}$ CaI_2	0·65	—
$\frac{1}{40}$ $\text{KI} + \frac{1}{80}$ CaI_2	1·83	1·57

ii. Sulphates in pot σ_2 :—

Salt solution.	Osmotic pressure.	Sum of components.
$\frac{0·574}{40}$ CaSO_4	0·467	—
$\frac{1}{40}$ K_2SO_4	1·43	—
$\frac{0·574}{40}$ $\text{CaSO}_4 + \frac{1}{40}$ K_2SO_4	1·88	1·897

c. Salts of different acids which do not form double salts:—

Salt solution.	In pot τ .		In pot σ_2 .	
	Osmotic pressure.	Sum of components.	Osmotic pressure.	Sum of components.
$\frac{1}{40}$ K_2SO_4	1.40	—	1.43	—
$\frac{1}{40}$ KNO_3	0.814	—	0.96	—
$\frac{1}{160}$ $\text{K}_4\text{Fe}(\text{CN})_6$	0.50	—	0.48	—
$\frac{1}{40}$ K_2SO_4 + $\frac{1}{40}$ KNO_3	2.05	2.21	2.37	2.39
$\frac{1}{40}$ K_2SO_4 + $\frac{1}{160}$ $\text{K}_4\text{Fe}(\text{CN})_6$.	1.80	1.90	1.935	1.91
$\frac{1}{40}$ KNO_3 + $\frac{1}{160}$ $\text{K}_4\text{Fe}(\text{CN})_6$	1.23	1.31	1.495	1.44

As a whole, these results show that when the two components can combine to form a double salt, Dalton's law does not hold accurately, and that the observed pressure for the compound is less than the sum of the pressures of the constituents.

In the cases when the components do not combine to form a double salt which may be crystallised out, the observed pressure of the mixture of the two salts is about equal to the sum of the pressures of the constituents. In the case of the iodides, *b*, *i*, the observed pressure is even considerably greater than the sum. In the results of pot τ in *c*, as in those of pot σ_2 in the same class, the deviations, when in the same direction, are smaller than those in class *a*.

IV. Influence of the Acid.

a. Solutions of potassium salts of different strengths, mostly in one pot δ :—

	$\frac{1}{20}$		$\frac{1}{40}$		$\frac{1}{60}$		$\frac{1}{80}$	
	<i>o. p.</i>	<i>i.</i>	<i>o. p.</i>	<i>i.</i>	<i>o. p.</i>	<i>i.</i>	<i>o. p.</i>	<i>i.</i>
KNO_3	1.64	1.47	0.96	1.72	—	—	0.47	1.66
KI	1.81	1.62	0.92	1.64	—	—	0.496	1.77
KClO_3	1.73	1.55	—	—	—	—	—	—
$\text{KC}_2\text{H}_3\text{O}_2$	1.26	1.13	—	—	—	—	—	—
K_2SO_4	2.16	1.93	1.25	2.24	—	—	—	—
$\text{K}_2\text{C}_2\text{O}_4$	2.26	2.02	1.31	2.34	—	—	—	—
KHCO_3	1.32	1.18	0.66	1.17	—	—	—	—
KHSO_3	—	—	0.79	1.41	—	—	—	—
$\text{K}_2\text{C}_4\text{H}_4\text{O}_6$	2.30	2.50	1.17	2.10	—	—	—	—
$\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$	1.35	1.21	0.75	1.34	—	—	0.32	1.14
$\text{K}_4\text{Fe}(\text{CN})_6$	3.49	3.12	2.05	3.67	1.49	4.11	6.90	3.14
$\text{K}_6\text{Co}_2(\text{CN})_{12}$..	—	—	3.46	6.18	2.17	5.98	1.77	6.35

b. Solutions of sodium salts of different strengths, mostly in δ :—

	$\frac{1}{20}$		$\frac{1}{40}$		$\frac{1}{60}$	
	o. p.	i.	o. p.	i.	o. p.	i.
NaNO_3	1.59	1.42	—	—	—	—
$\text{Na}_2\text{S}_2\text{O}_3$	2.21	1.95	1.30	2.33	—	—
Na_2HPO_4 ..	1.82	1.63	1.50	2.68	0.51	1.42
Na_3Ci	—	—	—	—	0.97	2.68

c. Solutions of potassium salts of organic acids. Two series in pots ρ_2 and τ for $\frac{1}{20}$ form. wt. per litre :—

	ρ_2		τ	
	o. p.	i.	o. p.	i.
KFO.....	1.09	0.975	1.43	1.28
KAc	1.42	1.27	1.66	1.48
KPr.....	1.46	1.33	1.78	1.59
KBz	1.95	1.74	—	—
K ₂ Ox	2.26 (δ)	2.02	—	—
$\frac{1}{40}$ K ₂ Ox.....			$\left. \begin{array}{l} 1.41 \\ 1.41 \\ 1.31 \end{array} \right\} 2.52$	

These results are discussed after the next series.

V. Influence of Base.

a. Solutions of nitrates of different bases in two pots, η and β :—

	$\frac{1}{20}$			$\frac{1}{40}$		
	η .	β .	i.	η .	β .	i.
KNO_3	1.61	1.76	1.50 (Mean)	0.89 (Mean)	—	1.59
NaNO_3	—	1.79	1.60	0.60	—	1.07
NH_4NO_3 ...	—	1.48	1.32	0.66	—	1.18
$\text{Mg}(\text{NO}_3)_2$..	2.12	—	1.89	0.96	—	1.72
$\text{Ca}(\text{NO}_3)_2$...	1.67	—	1.49	1.07	1.08	1.92 (Mean)
$\text{Sr}(\text{NO}_3)_2$...	1.58	—	1.41	—	1.38	2.47
$\text{Ba}(\text{NO}_3)_2$..	—	2.04	1.82	—	1.33	2.38
$\text{Co}(\text{NO}_3)_2$..	2.14	—	1.91	1.35	—	2.42
$\text{Cu}(\text{NO}_3)_2$..	2.14	—	1.93	0.93	—	1.66

b. Solutions of sulphates of different bases in two pots, κ and τ , with O.P. for $\frac{1}{20}$ in different pots :—

	$\frac{1}{20}$		$\frac{1}{40}$		
	o.p.	<i>i</i> .	κ .	τ .	<i>i</i> for mean.
K ₂ SO ₄	2.19	1.97	1.29	1.40	2.40
Na ₂ SO ₄	3.13	2.79	—	—	—
(NH ₄) ₂ SO ₄	2.64	2.38	1.26	1.295	2.29
MgSO ₄	0.78 ¹	0.70	—	—	—
CaSO ₄	—	—	0.79 ²		1.41
Al ₂ (SO ₄) ₃	—	—	1.265	1.22	2.23

¹ Probably due to destruction of film by the salt.

² Extrapolation value beyond saturated solution, and has no interpretation. Inserted to show different order of O.P. for an undissociated solution.

c. Solutions of alums of different composition of $\frac{1}{40}$ gram form. wt. per litre; κ at 16°, τ at 14°:—

	O. p.		<i>i</i> .	
	κ .	τ .	κ .	τ .
K ₂ Al ₂ (SO ₄) ₄ .24H ₂ O	2.39	1.96	4.27	3.50
K ₂ Cr ₂ (SO ₄) ₄ .24H ₂ O	2.46	—	4.40	—
(NH ₄) ₂ Al ₂ (SO ₄) ₄ .24H ₂ O .	2.37	1.98	2.25	3.54

d. Solutions of normal and hydrogen salts:—

$\frac{1}{40}$ Na ₃ Cl.....	[1.46 calcd.] $\frac{1}{60} = 0.97$.
$\frac{1}{40}$ Na ₂ HCl	2.12
$\frac{1}{40}$ K ₂ Ox	1.41
$\frac{1}{40}$ KHOx	0.77

Na₃PO₄, KHSO₄, and K₂SO₃ are decomposed by water, and dissolve the film.

Magnesium, copper, ammonium and sodium nitrates, and ammonium sulphate have smaller values of *i* for dilute solutions than for concentrated. This may be explained by the existence of a hydrate, but it is not practicable to define them, by this method.

In examining these results, it must be remembered that they are taken at any points in the curve OABCD, § I. In order to be strictly comparable they should be taken from OA, or from BC; this is con-

firmed by the fact that the values of i are more nearly constant for $\frac{1}{20}$ than for $\frac{1}{40}$ solutions in the case of the bases, and that this point is in BC.

It must be noted that sodium salts generally are more dissociated than potassium salts, particularly when the acids have high affinity. This is also borne out by the fact that sodium salts generally destroy the film, sooner or later, whilst potassium salts do not. The sulphates also are much more dissociated in watery solution than the nitrates, except when they form double salts, such as the alums.

The base values do not appear to be periodic, but rather to be connected with the acidity of the base.

No general principle governs the action of hydrogen in acid salts; in some cases it lowers the O.P., in others it raises it.

Taking the salts of the organic acids first, we see that an increase in the molecular weight of the acids is accompanied by an increase of the O.P., and also that the O.P. seems to depend on the basicity of the acid.

This may be interpreted that the carboxyl group gradually loses its unsaturated condition with increase of molecular weight of the attached carbon group, so that the retardation which occurs from the action of the water on the carboxyl group gradually loses its prominence.

In order to compare my values of osmotic pressures with those of the electric conductivities, I append the following values of Kohlrausch's (*B.A. Reports*) for the molecular conductivities of solutions of $\frac{1}{10}$ gram form. wt. per litre ($= 10^8 k/m$, where k = the conductivity and m = the molecule in grams). The osmotic pressures are those determined for $\frac{1}{20}$ gram form. wt. per litre.

	Kohlrausch.		o. p.
KNO ₃	983		1·64
KI	1069		1·81
KClO ₃	927		1·73
KAc	784		1·26
$\frac{1}{2}$ K ₂ SO ₄	897	$\frac{1}{40}$	1·25
KNO ₃	983		1·76
NaNO ₃	817		1·79
$\frac{1}{2}$ Ba(NO ₃) ₂	755	$\frac{1}{40}$	1·33
$\frac{1}{2}$ K ₂ SO ₄	897	$\frac{1}{20}$	2·19
$\frac{1}{2}$ Na ₂ SO ₄	734	$\frac{1}{20}$	3·13

The values in the two cases appear to take a similar direction, though in the case of sodium, my values are always higher than the corresponding values for potassium.

Kohlrausch also gives the relative velocities of the ions :—

K.	NH ₄ .	Na.	H.	$\frac{1}{2}$ Ba.	$\frac{1}{2}$ Mg.
62	50	32	274	30	26
	I.	NO ₃ .	ClO ₃ .	Ac.	
	55	48	44	26	

These velocities take the same direction as the osmotic pressure values, except in the case of sodium. This might be expected if osmotic pressure and electric conductivity are due to the same cause, since the O.P. must depend on the velocity as well as the mass of the molecule.

I append the values of the relative affinities of the acids used, from Ostwald.

HCl	1.00
HI	0.97
HNO ₃	0.96
HClO ₃	0.96
H ₂ SO ₄	0.73
HF	0.016
HAc	0.004
HPr	0.003
H ₂ Ox	0.18
H ₂ T	0.023
H ₃ Ci	0.017

He states that no base affinity tables have been constructed which have any value.

It will be seen that for the inorganic acids a high relative affinity is accompanied by a high O.P. of their salts, whilst in the case of the organic acids, the reverse holds. I think this must conclusively prove that there is some other factor entering into the problem of solution besides simple dissociation into ions.

VI. *Avogadro's Law applied to Salts in Solution.*

In comparing the results obtained, and looking at the values of P/π or i , it will be seen that it is always greater than unity or approximately equal to it. Its excess above unity tends, except for nearly saturated solutions, to increase with increasing dilution. (See remarks on I.)

In the table in IV, the values of i vary much. For $\frac{1}{20}$ form. wt.

per litre the limits are 1.13 to 2.02 for simple salts, and for $\frac{1}{40}$ form. wt. 1.17 to 2.34.

In the table in V, the values of i do not differ so much: 1.33—1.93 for $\frac{1}{20}$ form. wt. per litre, and 1.66—2.47 for $\frac{1}{40}$.

This confirms the fact that the osmotic pressures do not furnish any guide to the determination of the molecular weights of inorganic salts in solution in water, at least for comparison with gaseous molecular weights. It is possible that the results may be more consistent with organic than with metallic bases.

In the case of the acids, the osmotic pressures of the solutions which contain $\frac{1}{40}$ equivalent of potassium, or sodium per litre agree much better than the corresponding proportion of the formula weight.

The sulphates are more consistent than the nitrates, though they dissociate more easily; the latter may be connected with the formation of water compounds of the acid formed by dissociation, giving as result a basic salt in solution, mixed with dilute sulphuric acid.

The limiting value of i , as found by Arrhenius' hypothesis into ions is as follows—

$$\begin{array}{ll} \text{For} & \text{M}'\text{X}' \dots\dots\dots = 2 \\ & \text{M}''\text{X}'_2 \text{ or } \text{M}'_2\text{X}'' \dots\dots = 3 \\ & \left\{ \text{M}''' \text{X}'_3 \text{ or } \text{M}'_3\text{X}''' \right\} \dots\dots = 4 \\ & \text{or } \text{M}''_2\text{X}'_2 \end{array}$$

where

M = any metal,
X = any acid radicle.

These values are not exceeded in my observations, and it is only the stronger acids and bases which approach this limit. On the other hand, for the organic acids, the stronger are less dissociated.

If dissociation into ions takes place, why do they not get through the film rather than the water molecules? As a matter of fact, the dissociations which can be observed are those of the salt into an acid and a basic portion, of which the acid part gets through, and destroys the film. This passage of the ions through the film should be more distinctly noticeable in the case of the acid salts, where, according to Kohlrausch's numbers, the velocity of H is 274; while that of K is only 62. However we do not find the O.P. of these salts less than it ought to be, from this cause, V, d .

On the other hand, the value of i may be conditioned by the amount of dissociation of the molecules of the salt, produced by the action of the solvent, as described above. On this hypothesis, the value of i at its limit represents the maximum amount of dissociation of each molecule of the solid in the state in which it exists in solution, produced by the action of the solvent.

There is no doubt that the values of i , obtained by any of the

various methods in use, agree with one another, are fairly definite, and have a meaning, but I incline to the explanation that the action of the solvent is twofold, and may be expressed as—

i. Combination of the molecules of the dissolved substance with the solvent to form complex molecules.

ii. Separation of the complex molecules of the dissolved substance, under the action of the solvent, into simpler molecules, not necessarily as small as the limiting gaseous molecule.

In conclusion, I have great pleasure in thanking Professor J. J. Thomson for the use of the Cavendish Laboratory, Cambridge, where this research was conducted, and for his kind assistance, and advice during the progress of the work.