

**70.** *The Vapour Pressure of Water over Aqueous Solutions of the Chlorides of the Alkaline-earth Metals. Part II. Deviations from Raoult's Law, as indicated by the Molecular Lowering of Vapour Pressure and van 't Hoff Coefficients ; with Theoretical Discussion.*

By JACK REGINALD IRONS HEPBURN.

IN the study of the vapour pressure of water over aqueous solutions of electrolytes, deviations from normal behaviour as expressed by Raoult's law have generally been studied by means of either the so-called molecular lowering of vapour pressure or the van 't Hoff coefficient. The former is given by the expression

$$p_m = (p_0 - p)/M \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $p_0$  = vapour pressure of pure water at the given temperature,  $p$  = vapour pressure of water over the given solution, and  $M$  = molality. The van 't Hoff coefficient has been variously expressed as either (2) or (3),  $N_1$  and  $N_2$  being mols. of solvent and solute respectively :

$$i_1 = (p_0 - p)N_1/p_0N_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$i_2 = (p_0 - p)(N_1 + N_2)/p_0N_2 \quad . \quad . \quad . \quad . \quad (3)$$

$N_2/N_1$  is the mol. ratio, and  $N_2/(N_1 + N_2)$  the mol. fraction of the solute. Opinions differ as to which of these relations more truly represents the fundamental principle underlying Raoult's law. Formula (2) is that employed by van 't Hoff, but Raoult, in his original paper on this subject (*Z. physikal. Chem.*, 1888, **2**, 353), implicitly used the mol. fraction. Formula (2) cannot be correct at high concentrations, since it tends to the value 0, whereas formula (3) approaches the limiting value 1, in agreement with experience. Smits, in experiments on the vapour pressure of water over aqueous solutions (*ibid.*, 1902, **39**, 396), employed the van 't Hoff formula, but in later calculations (*loc. cit.*, p. 421) he points out that this method of computing concentrations (*i.e.*, the mol. ratio) could not portray the whole of the curve, for according to this the curve is infinite. He therefore recalculates the concentrations on the basis :

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mols. of salt per 100 mols. of water + salt, which is equivalent to that used in calculating the mol. fraction.

The difference between the values of  $i_1$  and  $i_2$  is not important at low concentrations, but at higher concentrations it becomes much more notable, as shown in cols. 8 and 9 of Table I. Here,  $M$  = molality,  $N_2/N_1 = M/55.5$ ,  $N_2/(N_1 + N_2) = M/(55.5 + M)$ ,  $dp = p_0 - p$ , and  $dp/p_0 = 1 - p/p_0 = 1 - r$ .

TABLE I.

Molecular lowering of vapour pressure and values of  $i$  for aqueous solutions of the chlorides of the alkaline-earth metals at 25°.

Soln. No.	$M$ .	$N_2/N_1$ .	$\frac{N_2}{N_1 + N_2}$ .	$dp$ .	$\frac{dp}{p_0} = 1 - r$ .	$p_m$ .	$i_1$ .	$i_2$ .
1. Calcium chloride.								
1	0.199	0.00358	0.00357	0.26	0.0107	1.3	3.0	3.0
2	0.284	0.00511	0.00509	0.33	0.0137	1.2	2.7	2.7
3	0.344	0.00619	0.00616	0.33	0.0137	0.96	2.2	2.2
4	0.494	0.00889	0.00881	0.48	0.0200	0.97	2.25	2.27
5	0.635	0.01143	0.01130	0.64	0.0269	1.01	2.35	2.38
6	0.796	0.01433	0.01413	0.88	0.0371	1.10	2.59	2.63
7	1.000	0.01800	0.01768	1.15	0.0483	1.15	2.68	2.73
8	1.504	0.02707	0.02635	2.15	0.0903	1.43	3.34	3.43
9	1.985	0.03574	0.03448	3.29	0.1384	1.658	3.87	4.01
10	2.495	0.04491	0.04298	4.50	0.1894	1.803	4.22	4.41
11	2.990	0.05383	0.05106	5.90	0.2482	1.973	4.61	4.86
12	4.004	0.07207	0.06723	9.03	0.3800	2.255	5.273	5.652
13	5.826	0.1048	0.09488	14.28	0.6010	2.451	5.735	6.334
14	7.278	0.1310	0.1158	16.76	0.7054	2.302	5.384	6.092
2. Strontium chloride.								
1	0.200	0.00360	0.00359	0.20	0.0083	1.0	2.3	2.3
2	0.301	0.00542	0.00539	0.21	0.0085	0.70	1.6	1.6
3	0.400	0.00720	0.00715	0.41	0.0172	1.03	2.4	2.4
4	0.600	0.01080	0.01069	0.62	0.0262	1.03	2.43	2.45
5	0.995	0.01791	0.01760	1.21	0.0507	1.215	2.83	2.88
6	1.495	0.02692	0.02620	2.11	0.0886	1.411	3.29	3.38
7	2.246	0.04042	0.03886	3.60	0.1514	1.603	3.74	3.90
8	2.872	0.05170	0.04917	5.10	0.2146	1.776	4.15	4.36
9	3.245	0.05841	0.05518	6.06	0.2550	1.867	4.37	4.62
10	3.403	0.06127	0.05773	6.49	0.2731	1.906	4.46	4.73
11	3.517	0.06330	0.05954	6.86	0.2886	1.948	4.56	4.85
3. Barium chloride.								
1	0.199	0.00358	0.00357	0.20	0.0083	1.0	2.3	2.3
2	0.289	0.00520	0.00518	0.23	0.0094	0.80	1.8	1.8
3	0.406	0.00731	0.00725	0.24	0.0098	0.60	1.3	1.35
4	0.508	0.00915	0.00906	0.48	0.0200	0.94	2.19	2.21
5	0.606	0.01091	0.01079	0.56	0.0234	0.92	2.15	2.17
6	1.007	0.01812	0.01780	0.99	0.0417	0.98	2.30	2.34
7	1.285	0.02313	0.02261	1.34	0.0564	1.04	2.44	2.50
8	1.568	0.02822	0.02745	1.94	0.0815	1.237	2.89	2.97
9	1.655	0.02980	0.02893	2.08	0.0874	1.257	2.93	3.02
10	1.788	0.03218	0.03118	2.23	0.0939	1.247	2.92	3.01

The molecular lowering of vapour pressure is chiefly of value in comparing results for different electrolytes obtained at a standard

temperature. Values of  $p_m$  obtained at different temperatures, however, are not comparable (*e.g.*,  $p_m$  for 1*M*-calcium chloride at  $25^\circ = 1.15$ , at  $0^\circ = 0.204$ ). For a normal solute, *e.g.*, sucrose,  $p_m$  should be constant at constant temperature, and independent of the concentration.

On the other hand, the van 't Hoff coefficient is practically independent of temperature, and therefore is of considerable value in comparing results obtained at temperatures far removed from one another. Departures from this rule are occasioned in cases where the heat of dilution becomes appreciable. This point will be elaborated later.

*Values of  $p_m$  and  $i$ .*—(1) *At low concentrations.* Considering first the results in moderately dilute solution (*i.e.*, 0.2—1*M*), one finds that for all three electrolytes the values of  $p_m$  as also of  $i_1$  and  $i_2$  pass through a minimum with increasing concentration, and thereafter increase. Further, the positions of the minima, although these are situated close to each other, are not identical for all three electrolytes, being at 0.34, 0.30, and 0.4*M* respectively.

The accuracy with which  $p_m$  may be determined is limited by that of the vapour-pressure data: in the present work (Part I), this is of the order of 0.03 mm., and the error in the value of  $p_m$  is therefore 12% at 0.2*M* and 6% at 0.5*M*. Although the determinations at these relatively low concentrations are necessarily less accurate than those at higher concentrations, they are believed to establish, not only the existence of the minimum in each case, but also the concentration at which it occurs. Nevertheless, the course of the curve is not accurately represented by the data given over this concentration range, and more accurate data would probably show a less pronounced curvature.

This difficulty has probably limited earlier data. However, Dieterici (*Ann. Physik*, 1897, **62**, 616), studying the vapour pressure of water over moderately dilute (0.05—1.0*M*) solutions of calcium chloride at  $0^\circ$ , concluded that the molecular lowering of vapour pressure at  $0^\circ$  passed through a minimum between 0.1*M* and 0.2*M*, although his results were not sufficiently accurate to establish the point with certainty. Although his results at  $0^\circ$  agree with those of the author at  $25^\circ$ , in that in both cases a minimum in  $p_m$  is found, yet the minimum in the latter case is at a different concentration (0.34*M*). Such a result may well be in accordance with a temperature effect in the phenomena observed (see p. 569).

Biltz (*Z. physikal. Chem.*, 1902, **40**, 185) has carried out a few observations at  $25^\circ$  on aqueous solutions of calcium, strontium, and barium chlorides, using the air-bubbling method of Walker, slightly modified by carrying out the experiment at constant temperature.

Such a method leaves much to be desired for accurate work, and even with elaborate experimental arrangements, such as those of Perman and Price (*Trans. Faraday Soc.*, 1912, **8**, 74), is liable to serious error, particularly in dilute solution. Little weight is therefore attached to Biltz's determinations, particularly in view of his statement (*loc. cit.*, p. 189) that certain of his results were irregular. His values of  $i_1$ , calculated as described above from the experimental determinations at 25°, pass through flat minima at almost the same concentrations as those for the molecular lowering of freezing point, as found by Jones and Chambers (see Part III). Moreover, he did not attempt any thermodynamic correlation of the vapour-pressure and freezing-point data.

Allmand (*Trans. Faraday Soc.*, 1927, **23**, 477) has drawn attention to the existence of minima in recent vapour-pressure data, including those of Frazer and his collaborators on potassium and lithium chlorides, and of Bousfield and Bousfield on sodium chloride. His suggestions in reference to activity coefficients are more fully discussed in Part IV. It is noteworthy that Harned (*ibid.*, p. 541) has expressed doubt as to the reality of these minima, since no corresponding minima have been found in the data for lowering of freezing point or raising of boiling point, which one would expect to find in such a case.

Neither Allmand nor Harned appears to have been aware of the investigation of Smits (*Z. physikal. Chem.*, 1902, **39**, 385) on aqueous solutions of sodium chloride. He showed that not only is there a minimum in the  $p_m$ - $M$  curve for this salt at 0° (at 0.5*M*), but that a corresponding minimum occurs at the same concentration in the curve connecting molecular raising of boiling point with concentration (*i.e.*, at temperatures near 100°).

(2) *At high concentrations.* When comparing the results of different investigators over the higher concentration range, the temperature variation of  $i$  has to be taken into account. This occurs if  $(p_0 - p)/p_0 = (1 - r)$  varies with temperature. The latter changes have already been treated in Part I (preceding paper), where it is shown that, in cases where the heat of dilution is appreciable, the variation of  $r$  with temperature is given by formula (2).

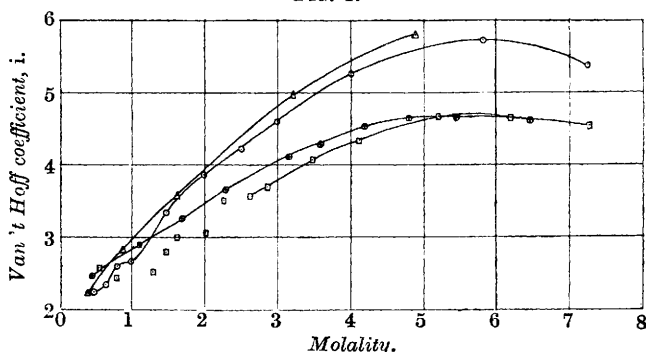
With this reservation, the results of Dieterici at 0° (*loc. cit.*; *Ann. Physik*, 1893, **50**, 47), the author at 25°, Harrison and Perman at 80° (*Trans. Faraday Soc.*, 1927, **23**, 1), and Tammann at 100° (*Mem. Acad. Pet.*, 1887, **35**, 7) may be compared. The calculated values of  $i_1$  for calcium chloride are shown in Fig. 1, which demonstrates that the results of Harrison and Perman are erratic at the lower concentrations; they agree fairly well with the other data at higher concentrations. The temperature effect mentioned above is

also shown by the graph; the relatively large numerical differences between the values of  $i$  are seen in the table:

$M.$	Values of $i_1$ .		
	Dieterici, 0°.	Author, 25°.	Tammann, 100°.
2	3.94	3.90	3.45
3	4.81	4.62	4.04
4	5.43	5.27	4.47
6	—	5.70	4.70

Fig. 1 shows that in each case, for calcium chloride,  $i$  increases with concentration up to a limiting value and thereafter decreases. The effect appears to be practically independent of temperature; the maximum value, however, is displaced towards higher concentrations

FIG. 1.



Dieterici at 0°,  $\Delta$ .

Author at 25°,  $\circ$ .

Harrison and Perman at 80°,  $\square$ .

Tammann at 100°,  $\oplus$ .

at higher temperatures. This point is important, since it indicates that the effect is not altogether connected with the fact that the solution is approaching saturation; for instance, at 100° the position of the maximum is far removed from saturation.

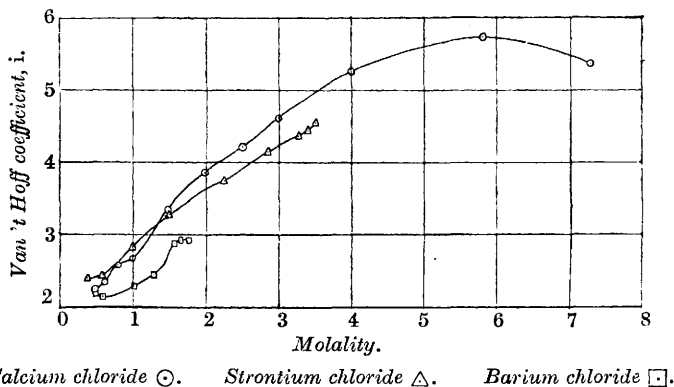
The author has calculated values of  $i_1$  and  $i_2$  in view of the fact that according to Smits (*loc. cit.*, p. 422) the two magnitudes do not follow the same course in certain cases. However, in the present instance they follow closely parallel lines, the maximum value occurring at the same concentration in each case. The fall in the values of  $i$  for calcium chloride appears to be characteristic of this salt; such a pronounced action is not shown by electrolytes studied by other authors, *viz.*, potassium chloride, potassium nitrate, or sodium chloride.

The variation of  $i_1$  with concentration over the higher concentration range is shown graphically for all three salts in Fig. 2. It is of interest that the curve for strontium chloride intersects that for

calcium chloride, and up to  $1.5M$  the values of  $i_1$  are actually higher than for calcium chloride. Above this concentration, however, the two curves follow the normal behaviour, that for strontium chloride being below that for calcium and above that for barium chloride. Attention is directed to the large variation in the values of  $p_m$  shown by these electrolytes, more particularly calcium chloride, for which the smallest figure is 0.96 and the largest 2.26. The corresponding figures for sulphuric acid (Grollmann and Frazer, *J. Amer. Chem. Soc.*, 1925, **47**, 712), which is also a bi-univalent electrolyte, are 0.8 and 1.2 at  $25^\circ$ , while for potassium chloride the variation in  $p_m$  at  $25^\circ$  is very much smaller, the maximum value from the author's measurements (see Part I, p. 553) being 0.80, and the minimum 0.73.

With strontium chloride, corresponding with the fact that the heat of dilution is considerably smaller than for calcium chloride,

FIG. 2.



the variation between the values of  $i_1$  at  $100^\circ$  (from the data of Tammann, *loc. cit.*) and at  $25^\circ$  is not so large:  $i_1$  does not pass through a maximum value in this case; nevertheless, a distinct falling off occurs at higher concentrations (see Fig. 2).

The author's results for barium chloride at higher concentrations show a noteworthy decline in the value of  $p_m$  and also of  $i_1$  and  $i_2$  at a concentration approaching saturation, a maximum value occurring at approximately  $1.7M$  (Fig. 2). This effect is not indicated by the results of Tammann at  $100^\circ$ ; these are, however, very limited in scope, only 5 observations being recorded over the whole concentration range.

### Theoretical Discussion.

It is necessary to emphasise, in considering the anomalous behaviour of the solutions studied in the present work, that there

is no comprehensive theory of solution applicable to aqueous solutions of moderate concentration. Any attempt to explain these anomalies must therefore be incomplete (compare Brönsted, *Trans. Faraday Soc.*, 1927, **23**, 430). The interionic attraction theory of Debye and Hückel (*Physikal. Z.*, 1923, **21**, 185) applies rigidly only up to a concentration of  $0.01M$ ; beyond this, arbitrary assumptions are necessary, and the formulation of the original theory is replaced by empirical expressions, such as those of Hückel (*ibid.*, 1926, **26**, 93) or Harned (*J. Amer. Chem. Soc.*, 1920, **42**, 1808). Nevertheless, it is probable that there are certain contributory factors, the combined effect of which leads to the observed results, although it is unknown to what extent each factor participates in the combined effect.

In recent years the idea has been gaining ground that greater attention should be directed towards the rôle of the solvent in the study of aqueous solutions. In the original electrolytic dissociation theory, as also in the more recent interionic attraction theory, the solvent has been disregarded as an inert medium, except in so far as its dielectric properties are concerned. Such an assumption does not seem justifiable, and from time to time the idea of the molecular complexity of water has been emphasised, notably by Armstrong (*e.g.*, *Proc. Roy. Soc.*, 1923, *A*, **103**, 610), Sutherland (*Phil. Mag.*, 1900, **50**, 481), Blanchard (*J. Amer. Chem. Soc.*, 1904, **26**, 1318), and Bancroft (*J. Physical Chem.*, 1926, **30**, 1194). Although views differ in detail, the consensus of opinion is that liquid water is aggregated, and contains double and triple molecules in addition to the normal single molecules. Sutherland (*loc. cit.*) assumes that only double and triple molecules are present in liquid water, Applebey (*J.*, 1910, **97**, 2000) that only triple and single molecules are present. Blanchard (*loc. cit.*) and also Lewis and Randall ("Thermodynamics," 1923, p. 86) assign no particular state of aggregation. Sidgwick ("Electronic Theory of Valency," 1927), arguing by analogy from the structure of ice, suggests three as the maximum aggregation number.

When an electrolyte (*e.g.*, calcium chloride) is dissolved in water, at least two effects may be produced: (i) the state of equilibrium between the molecular species of water will be disturbed by this addition in such a direction as to increase the number of single at the expense of the associated molecules; (ii) owing to the dipole nature of the water, each ion tends to co-ordinate water molecules, *i.e.*, a hydration effect will also occur. A third effect due to ionic association may also be envisaged at higher concentrations of electrolyte.

One may assume that in liquid water, as in any given solution, the vapour pressure equilibrium is set up by dynamic exchange of



single water molecules leaving and returning to the liquid surface (compare Dieterici, *Ann. Physik*, 1893, **50**, 80), since water vapour is known not to be associated to any large extent: according to Callendar it contains a small proportion of double molecules at temperatures below  $100^{\circ}$ . However, the proportion of such molecules at the temperatures now considered (*viz.*,  $0-25^{\circ}$ ) is probably so small as to be neglected in the argument given. Such a conclusion is supported by the recent investigation of the density of water vapour by Berkeley and Stenhouse (*Phil. Trans.*, 1930, **A**, **229**, 255). In any case, it is exceedingly difficult to appreciate how such a vapour pressure exchange could occur if liquid water consisted solely of double and triple molecules, as assumed by Sutherland, and also by van Laar (see below).

On addition of a solute to the water, the dissociating effect will increase the proportion of monomeric water molecules present at equilibrium in the liquid phase, so that the lowering of vapour pressure produced by the addition of the solute will be less than it would otherwise be; on the other hand, the hydration effect will tend to lower the vapour pressure by decreasing the number of free monomeric molecules.

The dissociating effect would not become appreciable at low concentrations (of the order  $0.01-0.1M$ ) and therefore at such concentrations one has to take into account the normal increase in the activity of the solute as provided for by the Debye-Hückel theory; this increase will tend to a high value for the molecular lowering of vapour pressure. At higher concentrations of solute (of the order  $0.1-0.5M$ ), where, however, the number of water molecules co-ordinated with the ions of the solute is still small, the dissociating effect on the water should predominate. It is shown in Part IV that, although the activity coefficient for the solute at such concentrations is approaching a minimum value, the actual minimum is not attained until a higher concentration is reached, which suggests that the observed minimum in  $p_m$  cannot be solely due to changes in the solute.

As a result of the above-mentioned effect, the value of  $p_m$  should progressively decrease with increasing concentration up to a point such that the hydration effect, which is itself steadily increasing, becomes larger than the dissociating effect of the solute upon the solvent. The position of this point will depend upon the dissociating effect of the solute upon the solvent and its tendency to hydration; it is, of course, quite possible that these two properties of the solute may be themselves inter-related. Such an argument provides an explanation of the observed minima in the molecular lowering of vapour pressure for the chlorides of the alkaline-earth metals.



At high concentrations, where the solution approaches saturation, the number of water molecules available for co-ordination to produce the hydration effect will be very largely diminished, so that the maximum in the molecular lowering of vapour pressure found with calcium and barium chlorides, and the decrease with strontium chloride, may conceivably be attributed to this cause. Ionic association may also be a factor in such solutions.

The characteristic differences in the behaviour of the individual salts at high concentrations are probably attributable mainly to the kation, the anion being the same in each case; in addition, following Sidgwick (*op. cit.*), it is to be expected that the kation will co-ordinate water molecules much more readily than the anion.

The fact that with fall in temperature the minima observed appear to occur at lower concentrations is not opposed to the idea of the molecular complexity of water, since at lower temperatures one would expect the number of associated water molecules to be greater, and therefore the dissociating effect of the added solute correspondingly larger at any given concentration.

Since the foregoing ideas were adumbrated, van Laar (*Proc. K. Akad. Wetensch. Amsterdam*, 1930, **33**, 1140) has published a theoretical derivation of the lowering of the vapour pressure of water by dissolved uni-univalent electrolytes, assuming that liquid water is associated and consists only of dimeric molecules at ordinary temperatures. The formula connecting  $x$ , the mol. fraction of the solute, with the lowering of vapour pressure, is derived directly from the thermodynamic potential of the solvent and solute, the Debye-Hückel theory as applied to concentrated solutions being taken into account, but hydration effects being ignored. The final expression takes the form

$$(p_0 - p)/p_0x = i - \phi x^{\frac{1}{2}} + \epsilon x + \sigma x\sqrt{x} \quad . \quad . \quad . \quad (4)$$

where, for strong binary electrolytes,  $i = 2$ , even at high concentrations;  $\phi$  is the Debye-Hückel coefficient for  $x^{\frac{1}{2}}$ , and the remaining constants refer to the physical inter-influence of the two components of the solution. It immediately follows from this formula (*ibid.*, p. 1146) that the molecular lowering of vapour pressure should pass through a minimum and a maximum respectively at relatively low and high concentrations. The theoretical conclusions from the formula given are thus in general agreement with those reached in the present work from the experimental data.

Although the data employed by van Laar in verifying the conclusions were for binary electrolytes only, the deductions should apply equally to bi-univalent electrolytes, the necessary modifications being made in the first two terms of the formula quoted.

This therefore provides further confirmation of the views expressed by the author, although the assumptions made by van Laar cannot be regarded as covering all the facts.

*Summary.*

Departures from the laws of the ideal solution are studied for the chlorides of the alkaline-earth metals. It is shown that the molecular lowering of vapour pressure and also the van 't Hoff coefficient for each of the three salts pass through minimum values at moderate concentrations, and in the case of the chlorides of calcium and barium, pass also through maximum values at concentrations approaching saturation.

These results are compared with those of earlier workers, including data on other electrolytes.

It is shown that there is evidence for the existence of a displacement of the observed minima in the direction of lower concentration with fall in temperature.

In the theoretical interpretation of the phenomena it is suggested that a depolymerising or dissociating effect of the electrolyte upon the solvent—regarded as an equilibrium mixture of single, double, and triple molecules—is the primary cause of the observed minima.

NORTHERN POLYTECHNIC,  
LONDON, N. 7.

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