69. *The Vapour Pressure of Water over Aqueous Solutions of the Chlorides of the Alkaline-earth Metals. Part I. Experimental, with a Critical Discussion of Vapour-pressure Data.*

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MEASUREMENTS of vapour pressure have proved of considerable value, apart from their intrinsic interest, in testing and verifying current theories of solution, despite the fact that the experimental difficulties encountered in such measurements have limited their abundance and scope.

It appeared that the dew-point method previously described by the author (*Proc. Physical Soc.*, 1928, **40**, 256) was capable of experimental refinement so that it might be applied to the study of inorganic salts in aqueous solution to give results of a sufficiently high order of accuracy for the purpose intended. Further, this method possessed the advantage that it enabled determinations to be made over the whole concentration range from dilute to saturated solutions at the ordinary temperature.

Earlier workers in this field have generally employed aqueous solutions of uni-univalent salts which are neither hygroscopic in the solid state nor extensively hydrated in solution (*e.g.*, potassium and sodium chlorides, potassium nitrate). It appeared desirable to study a group of bi-univalent salts showing a progressive variation in hygroscopic character. The chlorides of the alkaline-earth metals have therefore been investigated, since they possess the additional advantages that they are well-characterised substances, readily obtained in a state of purity, and are not extensively subject in aqueous solution to such disturbing effects as hydrolysis, formation of complex ions, etc.

The present paper is limited to a discussion of the experimental data. Subsequent communications will deal with the application of the results to modern theories of solution, to the correlation of the vapour-pressure data with other physical properties of solutions, and particularly to the evaluation of activity coefficients.

Discussion of the Dew-point Method and of Standard Vapour-pressure Data employed in its Use.—In the experimental method employed in the present work, a glass tube, closed at one end by a metal thimble of high thermal conductivity, is enclosed in a bulb containing the given aqueous solution in equilibrium with its vapour. The bulb is evacuated and the vapour space is completely enclosed. The temperature of the metal thimble is continuously lowered by suitable means until dew forms on the surface. At this temperature the vapour pressure of the cooler water forming the layer of dew is equal to that of the water vapour above the solution, which is at 25°.

One of the great advantages of this method over tensimetric methods generally is the fact that the measurements may be made in the presence of air, whereas the accuracy of tensimetric methods is seriously affected in the presence of even traces of air. At the same time, experiment shows that the presence of air is prejudicial to accurate work with the dew-point method, since the accuracy with which the dew-point may be measured is determined by the sharpness of the formation and disappearance of dew; this is governed by the speed with which equilibrium is again set up after dew has been deposited on or evaporated from the silver thimble, which itself is controlled by (1) the rate of diffusion of water vapour in the vapour space and (2) the rate of evaporation or of condensation at the liquid surface.

It is evident that the rate of diffusion of water vapour will depend on the partial pressure of air, *i.e.*, it will be diminished through collisions with air molecules. Evidence of a rapid process of gaseous diffusion in the case of water vapour is provided by the work of Dieterici (*Ann. Physik*, 1893, **50**, 51) and of Smits (*Z. physikal. Chem.*, 1902, **39**, 393), who find that at 0°, even in an apparatus of relatively large volume, the pressure of water vapour reaches its normal value in less than 15 mins. It is probable that similar considerations apply equally to evaporation and condensation from the surface of the solution. The author has at no time found any difficulty in making measurements through sluggishness in the re-establishment of equilibrium, contrary to the observations of Goode. Bayliss, and Rivett (J., 1928, 1950). The difficulties encountered by Ormandy (*Trans. Inst. Chem. Eng.*, 1929, **7**, 78) in preliminary dew-point determinations with aqueous solutions of copper sulphate are probably to be attributed to inadequate cleaning of the thimble and to presence of air in the apparatus.

A second important source of error in all static methods for the measurement of vapour pressure is the liability to the formation of a surface layer on the solution through condensation or evaporation. Thus, if condensation occurs from the vapour space to the solution, *e.g.*, during disappearance of dew from the thimble, a more dilute surface layer will be formed, specifically lighter than the bulk of the solution, and the concentration will only be equalised by the relatively slow process of liquid diffusion. It is evident, therefore, that in any experiment the solution must be kept in movement throughout. This effect was confirmed in the present work; it was found to be most pronounced in the case of the more dilute solutions: results were inaccurate unless such solutions were shaken throughout each observation.

The temperature of observation (25°) was as a rule higher than that of the room; hence it was essential to prevent condensation of water upon the walls of the containing vessel. The dew-point apparatus was therefore designed so that the whole of the vapour space was completely immersed in water in the constant-temperature tank at 25°.

Since the accuracy of the vapour-pressure determinations is dependent upon that of the standard values for the vapour pressure of water, the most accurate data available should be employed. The vapour-pressure tables of Regnault (*Ann. Chim. Phys.*, 1844, **11**, 273), which were previously regarded as providing standard values, have been shown to be in error (Scheel and Heuse, *Ann. Physik*, 1910, **31**, 715; Holborn and Henning, *ibid.*, 1908, **26**, 833). Despite this fact, several recent workers have continued to employ these data, and in consequence their results are subject to a systematic error.

Bousfield and Bousfield (*Proc. Roy. Soc.*, 1923, **103**, 429), in their investigation of the vapour pressure of water over aqueous solutions of sodium chloride, quote Regnault's value, *viz.*, 15·383 mm., for the vapour pressure of water at 18°; the figure given by Scheel and Heuse is 15·477 mm. There is therefore an error of 0·094 mm. in all the vapour pressures in Table I of their paper, which is considerably in excess of the estimated experimental error. Similarly, Goode, Bayliss, and Rivett (*loc. cit.*, p. 1954), in their measurements of the vapour pressure of water over aqueous solutions of magnesium acetate, use 23·52 mm. for 25° instead of 23·76 mm., and the resultant error is outside the estimated limit of ± 0·03 mm.

Measurements of vapour pressure prior to 1908 are necessarily subject to similar unavoidable errors. The data of Dieterici (*loc. cit.*) and of Smits (*loc. cit.*) need correction to the extent implied by their use of 4·62 mm. for the vapour pressure of water at 0° instead of 4·579 mm. Similarly, the figures of Roozeboom (*Z. physikal. Chem.*, 1889, **4**, 31) for the relative vapour pressure of water over saturated solutions of calcium chloride at various temperatures (see below) are based on the older incorrect data.

Experimental Standardisation of the Dew-point Method.—Since the dew-point determinations do not directly give absolute values for the vapour pressure, it seemed desirable to make a further independent comparison of the method with a direct method. Such a comparison was made for concentrated solutions in the previous work (*loc. cit.*, p. 258), saturated solutions of sodium chloride being used, but the experimental refinements now introduced, and the consequent greater accuracy, rendered a more thorough comparison necessary.

Recent accurate determinations of the vapour pressure of water over aqueous solutions of potassium chloride have been made by Lovelace, Frazer, and Sease (*J. Amer. Chem. Soc.*, 1921, **43**, 102), using the tensimetric method at 20°, and by Pearce and Snow (*J. Physical Chem.*, 1927, **31**, 231), using a dynamic gas-bubbling method at 25°. This salt, therefore, may be employed to provide convenient reference solutions at 25° for standardising the dew-point method. From the results of the first workers at 20°, values at 25° may readily be obtained on the assumption that the relative vapour pressure is independent of the temperature, an assumption which is justifiable over such a small temperature interval and in view of the fact that the differential heat of dilution for potassium chloride is small.

The author has determined by the dew-point method the vapour pressure of water over 8 solutions of potassium chloride at 25°, from 0·25*M* to saturation. The results are set out in Table I (col. 3), together with those of Pearce and Snow (col. 4) and the recalculated values of Lovelace, Frazer, and Sease (col. 5). The agreement appears to be satisfactory and within the limits of accuracy estimated by the author (*viz.*, 0·02° for the dew-point or 0·03 mm. for the vapour pressure).

TABLE I.

Vapour pressure of water over aqueous solutions of potassium chloride at 25°.

[H, Hepburn; PS, Pearce and Snow; LFS, Lovelace, Frazer, and Sease.]

Soln. No.	Conc., *M*.	Vapour pressure, mm.			Molecular lowering of vapour pressure.		
		H.	PS.	LFS.	H.	PS.	LFS.
1	0·250	23·56	23·56	23·57	0·80	0·80	0·77
2	0·375	23·46	23·47	23·47	0·80	0·77	—
3	0·750	23·20	23·19	23·20	0·75	0·76	0·75
4	1·000	23·03	23·02	23·01	0·730	0·739	0·749
5	2·027	22·27	22·22	22·24	0·735	0·756	0·750
6	3·001	21·53	21·50	21·48	0·743	0·753	0·760
7	4·015	20·72	20·69	20·68	0·759	0·765	0·770
8	4·81 (satd.)	20·04	20·02	—	0·773	0·777	—

In columns 6, 7, and 8 are given calculated values of the molecular lowering of vapour pressure. Here also the author's figures show a minimum value at the same concentration as that indicated by the other data, *viz.*, app. 1*M*, followed by a steady increase with fall in concentration. Special attention has been paid to the measurements in the more dilute solutions, *i.e.*, over the concentration range 0·25—1*M*, since the relative accuracy of the dew-point method progressively diminishes with fall in concentration, and it was desired to establish the fact that, despite this diminution in accuracy, the method was capable of detecting abnormal behaviour at these relatively low concentrations. The agreement with the other data for potassium chloride, therefore, confirms the view that the minima found in the molecular lowering of vapour pressure for the chlorides of the alkaline-earth metals over this concentration range are real.

The agreement in the figures for the saturated solution appears to indicate that the value of Edgar and Swan (*J. Amer. Chem. Soc.*, 1922, **44**, 570), *viz.*, 20·20 mm. at 25°, is in error.

EXPERIMENTAL.

In the observations on calcium chloride, the first dew-point apparatus, described in the earlier paper (*loc. cit.*, p. 256), was employed throughout. The accuracy of the temperature observations then was of the order 0·05°; this has now been increased to 0·01°. The two thermometers used—one for the constant-temperature tank, the other for the dew-point apparatus—were of Jena normal glass, graduated on the stem to 0·1°. They were compared with a thermometer standardised by the National Physical Laboratory, and subsequently checked against one another on three occasions, at intervals of about a year, during the progress of the work. A lens was attached to each thermometer to facilitate observations.

It was necessary to modify the method of raising and lowering the temperature of the dew-point tube for small lowering of dew-point, since when ether was employed with air bubbling, the initial temperature of the ether in the dew-point tube approximated to that of the room, the vacuous space in the bulb acting as an insulating jacket and so preventing the temperature of the tube from reaching 25°. Since the room temperature seldom exceeded 20°, some other method had to be employed to cool the tube if the dew-point was higher than 20°. A water-circulating method was therefore substituted for the ether-cooling method in cases where the latter was not available. A second tank of 8-litres capacity was fitted with an overflow device and supplied with a constant stream of water so that it always remained full. The water in this tank was thoroughly stirred mechanically, and the temperature could readily be adjusted by gas-heating or by increasing the flow of water. A glass tube, widened at the base and immersed in the water of the circulation tank, was connected to the inlet of the dew-point tube, and the outlet tube was connected to a water pump. By this arrangement, water at any desired temperature could be drawn through the dew-point tube.

The dew-point thimble was strongly illuminated by a screened, gas-filled, electric lamp, placed close to the window of the observation tank and in the same horizontal plane as the thimble; the dew was thereby rendered much more readily visible.

In the subsequent determinations (on strontium and barium chlorides) a modified dew-point apparatus was employed, in which the spherical glass bulb of the first apparatus was replaced by a somewhat larger cylindrical bulb (of 500 c.c. capacity). The silver thimble in this apparatus was soldered to a layer of copper deposited directly on the end of the glass dew-point tube, thus avoiding the use of a cement. Four glass beads were fused on the glass dew-point tube about 2 cm. above the point of attachment of the thimble; two of the beads served to hold a silver clip of slightly larger diameter than the silver thimble, in a way similar to the method used to attach an electric light bulb to its socket, except that the slots usually on the socket were in this case on the clip. This comparison clip was made of the same sample of fine silver as the dew-point thimble, and therefore took the same type of polish ; it was thermally insulated from the thimble by the four glass beads. When fitted to the dew-point tube, the clip overlapped the silver thimble, so that the two polished silver surfaces were alongside each other. In actual observations, when dew formed on the thimble, the clip remained bright. This comparison device proved to be of great value in observing the exact dew-point.

The general procedure followed in removing air from the solution was initially to lower the pressure to 2 cm. of mercury, and to leave the solution for 6—12 hours to allow bubbles of dissolved air to be evolved. During this process the silver thimble invariably became splashed with drops of the solution. At the end of this time, it was therefore removed, rinsed with water, dried, and replaced, before the pressure was lowered to the final value, as indicated by the small enclosed U-tube manometer. This value approximated closely to the vapour pressure of water over the given solution at 25°. Practically all the air present, whether previously in the gas space or dissolved, was removed by this process.

Both the calcium and the barium chloride were A.R. materials (British Drug Houses, Ltd.). Strontium chloride of this quality was not available, but the sample used consisted of 98·8% of the hexahydrate; it was free from barium and iron, and contained only traces of lead and arsenic, the chief impurity being alkali (0·44%), and it was further purified by two recrystallisations as the dihydrate above the transition temperature, *viz.*, 61·34° (Richards and Yngve, *J. Amer. Chem. Soc.*, 1918, **40**, 89).

In preparing the solutions used for the vapour-pressure determinations, a saturated solution was made at the ordinary temperature, which served as the standard solution; its composition was determined gravimetrically in duplicate by the chloride method. In the case of barium chloride, barium was also estimated as sulphate as a check; results were in agreement within 0·05%. The solutions employed in the actual vapour-pressure determinations were prepared in each case by admixture of weighed quantities of the standard solution and water; for solutions of higher concentration than the standard solution (including the saturated solution), however, the concentration was determined immediately after the dew-point determination by the gravimetric estimation of chlorine.

Full experimental details of the dew-point method are given in the earlier paper.

The experimental results for the three salts are given in Table II. Concentrations are given as (1) molalities (mols./1000 g. of water, col. 2), (2) weight percentages (g./100 g. of solution, col. 3), (3) normalities (col. 4), in order to facilitate comparison and reference. In computing the normalities, values for the densities of the solutions at 25° are required. For calcium chloride, these have been taken from the data of Pickering at 17·9°, corrected to 25° by assuming the known values for the coefficients of expansion. In the corresponding calculations for strontium and barium chlorides, the density data employed were those of Gerlach. All concentrations are expressed in terms of the anhydrous salt.

Discussion of Results.

In the discussion and comparison of data obtained at temperatures other than 25°, the thermodynamic relation between differential heat of dilution and temperature variation of the relative vapour pressure is verified, and in the case of barium chloride the comparison indicates that the (negative) differential heat of dilution should diminish in magnitude at concentrations approaching saturation, a result of some interest which is at present not capable of confirmation in the absence of experimental data for the differential heat of dilution at these concentrations.

1. *Calcium Chloride.—Data at* 25°, *or over a temperature range including* 25°. The only existing vapour-pressure data in this category are those of Biltz (*Z. physikal. Chem.*, 1902, **40**, 185), Paranjpe (*J. Indian Inst. Sci.*, 1918, **2**, 59), and Roozeboom (*Z. physikal. Chem.*, 1889, **4**, 31).

The results of Biltz at 25° include four observations only, limited to the concentration range 0·1—0·6M which is outside the scope of the present work; discussion of these data is deferred to Part II, but there is reason to believe that they do not attain a high degree of accuracy.

Paranjpe has carried out a large number of vapour-pressure

TABLE II.

Vapour pressure of water over aqueous solutions of the chlorides of the alkaline-earth metals at 25°.

Soln. No.	Molality, M.	Weight percentage, G.	Normality, N.	Dew point.	Vapour press., mm.	Relative vapour press., r.
			1. Calcium chloride.			
1	0·199	2·16	0·392	24·82°	23·50	0·9893
2	0·284	3·05	0·562	24·77	23·43	0·9863
3	0·344	3·68	0·682	24·77	23·43	0·9863
4	0·494	5·20	0·975	24·66	23·28	0·9800
5	0·635	6·59	1·250	24·54	23·12	0·9731
6	0·796	8·12	1·559	24·37	22·88	0·9629
7	1·000	9·99	1·949	24·17	22·61	0·9517
8	1·504	14·30	2·888	23·42	21·61	0·9097
9	1·985	18·06	3·764	22·52	20·47	0·8616
10	2·495	21·69	4·690	21·52	19·26	0·8106
11	2·990	24·91	5·497	20·30	17·86	0·7518
12	4·004	30·77	7·147	17·22	14·73	0·6200
13	5·826	37·25	9·133	10·44	9·48	0·3990
14	7·278 (satd.)	44·68	11·62	5·97	7·00	0·2946
			2. Strontium chloride.			
1	0·200	3·07	0·397	24·86	23·56	0·9917
2	0·301	4·56	0·597	24·85	23·55	0·9915
3	0·400	5·97	0·791	24·71	23·35	0·9828
4	0·600	8·69	1·180	24·56	23·14	0·9738
5	0·995	13·62	1·939	24·13	22·55	0·9493
6	1·495	19·17	2·880	23·45	21·65	0·9114
7	2·246	26·27	4·233	22·27	20·16	0·8486
8	2·872	31·29	5·315	21·01	18·66	0·7854
9	3·245	33·97	5·921	20·15	17·70	0·7450
10	3·403	35·05	6·175	19·75	17·27	0·7269
11	3·517 (satd.)	35·80	6·328	19·41	16·90	0·7114
			3. Barium chloride.			
1	0·199	3·98	0·395	24·86	23·56	0·9917
2	0·289	5·68	0·573	24·84	23·53	0·9906
3	0·406	7·80	0·802	24·83	23·52	0·9902
4	0·508	9·57	0·996	24·66	23·28	0·9800
5	0·606	11·21	1·183	24·60	23·20	0·9766
6	1·007	17·34	1·936	24·29	22·77	0·9583
7	1·285	21·11	2·446	24·03	22·42	0·9436
8	1·568	24·61	2·952	23·58	21·82	0·9185
9	1·655	25·64	3·111	23·47	21·68	0·9126
10	1·788 (satd.)	27·14	3·336	23·36	21·53	0·9061

observations, using the tensimetric method, with solutions of moderately high concentrations ($M = 1·352$) up to saturation, and at temperatures ranging from 0° to 40°. Vapour pressures interpolated from his results at 25° are quoted in Table III, together with the author's experimental figures. The former, except those for the highest concentrations, are low compared with the latter, but the values for the saturated solution are in agreement. The maximum difference is 0·7 mm., and diminishes with rising concentration. A

TABLE III.

Molality, M		1·504	1·985	2·495	2·990	4·004	5·826	7·278
Vapour press. (mm.)	Paranjpe	20·94	20·00	18·64	17·28	14·50	9·68	7·04
	Hepburn	21·61	20·47	19·26	17·86	14·73	9·48	7·00

further discrepancy appears when the relative vapour pressures (r) are computed for any particular solution at various temperatures: those for solutions of concentration $G = 15$, 20, and 40% (taken from Paranjpe's table of interpolated figures; corresponding values of $M = 1·352$, 2·802, and 3·604 respectively) diminish with rise in temperature; thus, for solution $G = 15\%$, the following results are obtained :

Temp.	0°	10°	20°	25°
r	0·930	0·911	0·897	0·893

It is shown below that such a result is contrary to that to be anticipated from the fact that calcium chloride has a positive heat of dilution. Some error is therefore indicated in the interpolated figures. The author has repeated the process of interpolation employed by Paranjpe, and finds that in many cases the number of experimental points is not large enough to give accurate interpolated values, while in other cases extrapolation must be resorted to in order to obtain results at higher temperatures. Hence it appeared desirable to apply the heat of dilution criterion to the actual experimental figures, in testing their accuracy, instead of to the interpolated ones forming the final table. Choosing the solution $G = 37·32\%$ ($M = 3·362$), one finds :

Temp.	0°	9·1°	22·2°	30°
r	0·712	0·698	0·714	0·702

For a solution of this concentration the value of r at 0° obtained by Dieterici (see below) is 0·694; the author's value at 25° is 0·710. Similar results follow with other solutions.

Hence it appears that Paranjpe's experimental results are somewhat erratic, showing no definite trend with rise in temperature; the steady fall in the interpolated values is evidently introduced as a result of the interpolation. He states (*loc. cit.*, p. 63) that in the case of the lower concentrations and at higher temperatures, direct measurements of the vapour pressure could not be made, as water distilled from the solution and condensed in the manometer as soon as the vapour pressure of water over the solution rose above about 23 mm. The results obtained indicate that such effects were also operative at considerably lower temperatures.

Roozeboom, in determining the vapour pressure of water over the saturated solution at 25°, employed the tensimetric method of

Fröwein; he gives 6·70 mm., as compared with 7·00 mm. in the present work. The corresponding figures for the relative vapour pressure are 0·282 and 0·295 (Roozeboom's original value of 0·285 has been corrected from his data by using the modern figure for the vapour pressure of water at 25°, *viz.*, 23·76 mm., instead of 23·52 mm.). The discrepancy between these figures is possibly due to the fact that air may not have been completely removed from the apparatus in the experiments of Roozeboom, since such an effect is known to occur in this form of apparatus.

Data at temperatures other than 25°. (*a*) *Qualitative discussion.* It has been shown in the previous work that a study of the relative vapour pressure in conjunction with existing data on heats of dilution provides a convenient means of comparing results obtained in vapour-pressure determinations with those of other workers at different temperatures.

Measurements previous to the work of Roozeboom (*loc. cit.*) include those of Wüllner (*Ann. Physik*, 1858, **103**, 529) and of Emden (*ibid.*, 1887, **31**, 162). The fact that solutions of calcium chloride evolve heat on dilution should indicate from thermodynamic principles that the relative vapour pressure increases with rise in temperature; such a prediction was not confirmed by the results of either of these authors. A few experiments, mostly at relatively high temperatures, quoted by Roozeboom, however, agreed with the theory in indicating an increase in the relative vapour pressure with rise in temperature. These discrepancies were attributed by Roozeboom to the fact that the limits of temperature and concentration were not sufficiently widely spaced to obtain concordant results, and also to experimental error in the actual measurements.

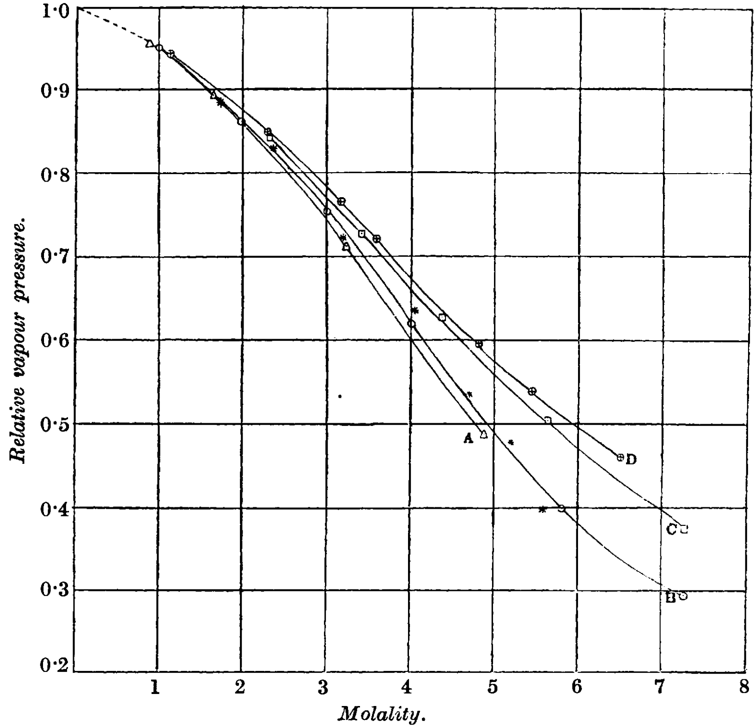
Similar considerations apply to the earlier vapour-pressure data of Tammann (*ibid.*, 1885, **24**, 530; 1888, **35**, 322) and of Perman and Price (*Trans. Faraday Soc.*, 1912, **8**, 74); their results are therefore not included here.

In this qualitative discussion of data the experimental results of the various investigators are not quoted; values of the vapour pressure obtained in each case are converted into the corresponding values of r and plotted against the molality, which in certain cases is recalculated from the original data.

Dieterici (*Ann. Physik*, 1893, **50**, 47; 1897, **62**, 616) has determined directly by a differential tensimetric method the vapour pressure of water over aqueous solutions of calcium chloride at 0°. His experiments are in two groups: the first four are concerned with concentrated solutions ($M = 1$—5), and the last five with more dilute solutions ($M = 0{\cdot}05$—1). His results are shown by curve A (Fig. 1) and curve B shows the author's results. Harrison and

Perman (*Trans. Faraday Soc.*, 1927, **23**, 1) have determined the vapour pressure of water over aqueous solutions of calcium chloride at 40°, 50°, 60°, 70°, and 80°, using a statical method. Only the curve for 40° is represented in Fig. 1 (curve C). The remaining curves reproducing their data lie between this curve and that (curve D) of Tammann (*Mem. Acad. St. Petersburg*, 1887, **35**, 7), who determined the vapour pressure at 100° over a wide range of concentration.

FIG. 1.



Curve B : Author at 25°, ⊙. *Curve D : Tammann at* 100°, ⊕.
Curve A : Dieterici at 0°, △. *Curve C : Harrison and Perman at* 40°, ⊡.
Sidgwick and Ewbank at 5·179°, *.

Sidgwick and Ewbank obtained data at 5·179° (J., 1924, **125**, 2268) by an indirect method, measuring the depression of the freezing point of nitrobenzene after it had been brought into equilibrium with the given solution. Although such a method would not be expected to give very exact results, the figures obtained fit reasonably well into position in the graph (see Fig. 1; the actual curve is not drawn since it intersects the others at certain points). Sidgwick and Ewbank were apparently unaware of the existence of

Dieterici's data at 0° : in considering the accuracy of their own data they refer only to Tammann's results.

A survey of the curves in Fig. 1 indicates that in every case and at every concentration r increases with rise in temperature, in agreement with the theory. Harrison and Perman's data for 80° (not shown) are practically superimposed upon those of Tammann for 100°, a result which, taken in conjunction with the arrangement of the other curves, appears to indicate that the results of the former workers at 80° are high.

(*b*) *Quantitative discussion.* The thermodynamic relation between the relative vapour pressure and the differential heat of dilution is given by Kirchhoff's equation (*Ann. Physik*, 1858, **103**, 200) :

$$d \log r/dT = \bar{L}/RT^2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where L is the differential heat of dilution.

The available data on this property for calcium chloride include those of Tucker at 14—17° (*Phil. Trans.*, 1915, **215**, *A*, 340) and of Harrison and Perman (*loc. cit.*, p. 13) at 40—80°. Other thermal data for dilution changes are due to Pickering, who gives the integral heats of dilution, and Pratt (*J. Franklin Inst.*, 1918, **185**, 663), who gives the heat developed on the addition of relatively large quantities of water to a given quantity of solution. The results of neither of these investigators appeared to be in a form suitable for computing the differential heats of dilution with sufficient accuracy for the present purpose.

In general, the heat of dilution–concentration and heat of dilution–temperature curves approximate to straight lines. Equation (1) may be integrated, following Kirchhoff, between fixed temperature limits on the assumption that $\bar{L}$ is independent of temperature; if one assumes a value for $\bar{L}$ midway between the two temperatures considered, this will lead to no serious error, particularly in view of the linear relation between $\bar{L}$ and T, mentioned above. The integration gives :

$$\log r_1/r_2 = \bar{L}(T_2 - T_1)/2{\cdot}303RT_1T_2 \quad . \quad . \quad . \quad (2)$$

According to Porter (see Harrison and Perman, *loc. cit.*, p. 18), the assumption that water vapour obeys the gas laws is not strictly justified, and Callendar's gas equation (*Proc. Roy. Soc.*, 1900, **67**, 191) should strictly be substituted for the ordinary gas law. However, in the use of equation (2) as a check on experimental data, such a refinement does not appear to be essential, and has been ignored here as in the earlier work (*loc. cit.*).

In employing equation (2) for comparing the vapour-pressure data, values of r have been read off from Fig. 1 at round concentrations from the data of Dieterici at 0°, Tammann at 100°, and

Harrison and Perman at 80° and 40°. The required values of $\bar{L}$ have been obtained by interpolation from the data of Harrison and Perman at round concentrations, those of Tucker at 14—17° also being used. The actual figures employed are quoted in Table IV.

TABLE IV.

Recalculated values of r_{25° from data of other workers, compared with the author's observed values.

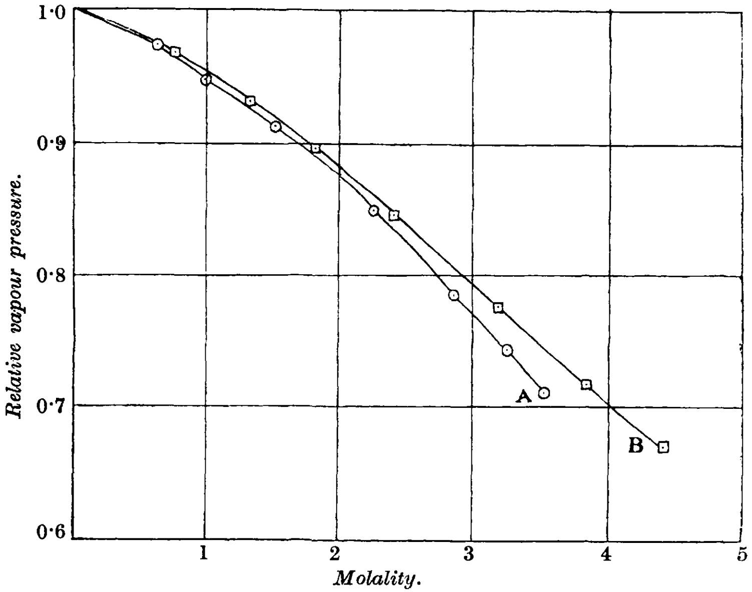
$M =$	6.	5.	4.	3.	2.
			Dieterici, 0°.		
r_{0°	—	0·474	0·605	0·740	0·857
$\bar{L}_{12\cdot5^\circ}$	—	263	121	49	14
$\log r_{25^\circ}/r_{0^\circ}$	—	0·0177	0·0081	0·0033	0·0010
r_{25° (calc.)	—	0·494	0·617	0·746	0·859
			Tammann, 100°.		
r_{100°	0·497	0·580	0·678	0·778	0·874
$\bar{L}_{62\cdot5^\circ}$	715	459	252	117	50
$\log r_{100^\circ}/r_{25^\circ}$	0·1054	0·0678	0·0372	0·0173	0·0074
r_{25° (calc.)	0·390	0·496	0·622	0·748	0·859
			Harrison and Perman, 80°.		
r_{80°	0·493	0·581	0·690	0·796	0·888
$\bar{L}_{52\cdot5^\circ}$	652	407	220	101	47
$\log r_{80^\circ}/r_{25^\circ}$	0·0745	0·0465	0·0351	0·0115	0·0054
r_{25° (calc.)	0·415	0·522	0·652	0·775	0·877
			Harrison and Perman, 40°.		
r_{40°	0·466	0·564	0·670	0·790	0·885
$\bar{L}_{32\cdot5^\circ}$	518	301	153	68	36
$\log r_{40^\circ}/r_{25^\circ}$	0·0182	0·0106	0·0054	0·0024	0·0013
r_{25° (calc.)	0·447	0·550	0·662	0·786	0·882
r_{25° (obs. by author)	0·397	0·491	0·619	0·751	0·861

Summarised results for comparison.

	Relative vapour pressure at 25°,				
		recalculated from data of			
Molality.	obs. by author.	Dieterici at 0°.	Tammann at 100°.	Harrison and Perman at 80°.	Harrison and Perman at 40°.
6	0·397	—	0·390	0·415	0·447
5	0·491	0·494	0·496	0·522	0·550
4	0·619	0·617	0·622	0·652	0·662
3	0·751	0·746	0·748	0·775	0·786
2	0·861	0·859	0·859	0·877	0·882

The value of r at 25° has been calculated in each case by means of equation (2) and the appropriate value of $\bar{L}$; these values of r are then compared with those obtained from the author's experiments. The recalculated data of Dieterici and of Tammann are in agreement with the author's, whereas those of Harrison and Perman both at 80° and at 40° give results which are consistently high. The last authors have calculated values of $\bar{L}$ from their own vapour-pressure data at various temperatures by an approximate method involving measurements of the slope of the curve representing Porter's modification of equation (1), which cannot be integrated directly. They state from these calculations that their vapour-pressure determinations may be considered to be accurate to within 0·2 mm., but it seems that the accuracy of their observations is not so high as they claim. This view is confirmed by a consideration of the results for the van 't Hoff coefficients (see Part II).

FIG. 2.



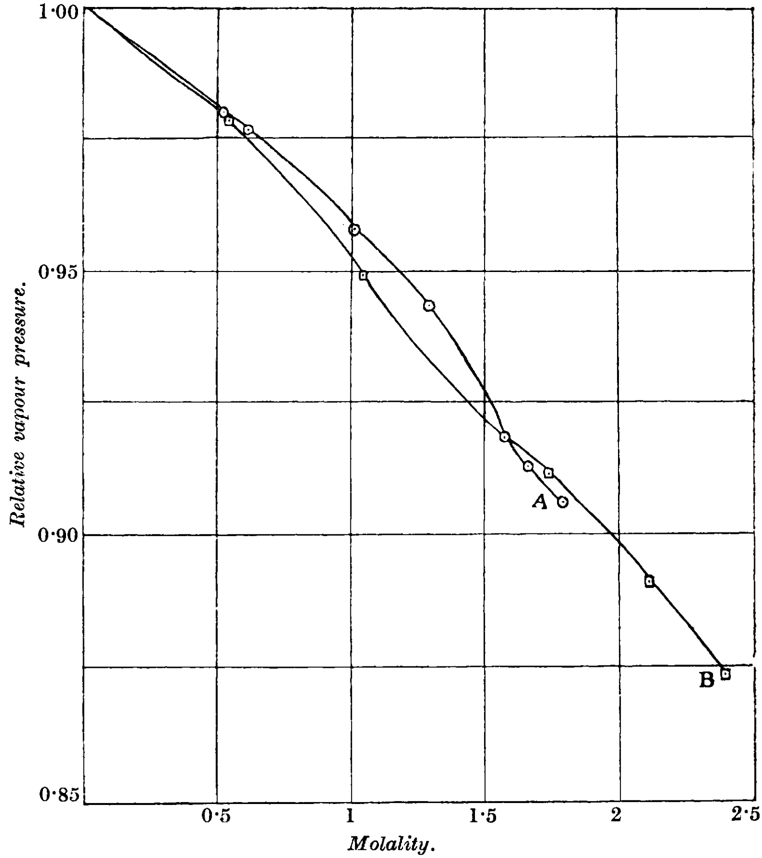
Curve A : Author at 25°, ⊙. *Curve B : Tammann at* 100°, ⊡.

2. *Strontium Chloride.*—No data appear to exist on the vapour pressure of water over aqueous solutions of strontium chloride at 25° apart from 4 determinations by Biltz over the very limited concentration range 0·1—0·6*M*, which will be discussed later (see Part II).

Tammann (*loc. cit.*) has determined the vapour pressure of water over aqueous solutions of strontium chloride at 100°. The values of *r* computed from these data are shown (curve B) in Fig. 2, together with those of the author (curve A). At low concentrations, up to 1*M*, *i.e.*, at concentrations where the heat of dilution is inappreciable, the two curves coincide; but at higher concentrations they diverge increasingly. Further, it follows from the relative position of the two curves that the value of $r_{100°}$ is always greater than that of $r_{25°}$, as in the case of calcium chloride. It should therefore follow that strontium chloride possesses a positive heat of dilution, increasing with concentration.

Results on heats of dilution for strontium chloride are scanty, but the differential heat of dilution has been determined at 25° by Stearn and Smith for 4 solutions (*J. Amer. Chem. Soc.*, 1920, **42**, 18). That at 25° was positive and increased with the concentration; this result is evidently in qualitative accord with the vapour-pressure data quoted above. Nevertheless, the values for the positive heat of dilution were considerably smaller than for calcium chloride, at corresponding concentrations, and this agrees with the degree of

FIG. 3.



Curve A : Author at 25°, ⊙. *Curve B : Tammann at* 100°, ⊡.

separation of the r curves compared with those for calcium chloride.

In order to make a quantitative comparison of the present results with those of Tammann, it would be necessary to know the mean heats of dilution over the temperature range 25—100°, and these are not directly available.

3. *Barium Chloride.*—Apart from three observations by Biltz over the concentration range 0·1—0·6M, no vapour-pressure data exist at 25°. However, the results of Tammann at 100° may be compared with those of the author. This worker gives values for 5 solutions over the concentration range 0·5—2M, and these are shown by curve B (Fig. 3), curve A representing those of the author at 25°. The results in this case at higher concentrations are opposed to those for calcium and strontium chlorides. Up to 0·5M, the two curves are practically coincident; at higher concentrations, the curve for 25° lies above that for 100°, indicating that up to a concentration of 1·5M the value of $r_{100°}$ at any particular concentration is less than that of $r_{25°}$. Above this concentration, curve A shows a point of inflexion and becomes practically superimposed on curve B. This result indicates that the mean differential heat of dilution over the temperature range 25—100° should be negative up to 1·5M, and that above this concentration it should become less negative and approach zero.

The recorded data for the differential heats of dilution are again due to Stearn and Smith at 25° and at concentrations between 0·2M and 1·5M; data at higher temperatures are not available. However, their results show that, in the case of barium chloride up to 1·5M, the differential heat of dilution is negative, in qualitative accord with the result indicated by the vapour-pressure data. Here, too, a direct quantitative comparison cannot be instituted owing to lack of data for the mean differential heat of dilution at 25—100°.

Summary.

The vapour pressure of water over aqueous solutions of the chlorides of the alkaline-earth metals has been measured at 25° and for concentrations from 0·2M to saturation by a dew-point method. The existing data for these salts in aqueous solution are critically examined. For determinations at temperatures other than 25°, comparison is effected by the use of the thermodynamic relation between the differential heat of dilution and the temperature variation of the relative vapour pressure. Attention is drawn to the fact that systematic errors exist in recent vapour-pressure data, introduced through the use of Regnault's values for water instead of the more recent standard data of Scheel and Heuse.

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