172. *The Vapour Pressure of Water over Aqueous Solutions of the Chlorides of the Alkaline-earth Metals. Part IV. Evaluation of Activity Coefficients.*

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THE adoption by Debye and Hückel, in the interionic theory of electrolytes, of Lewis's activity concept has given an impetus, particularly in America, to the determination of activity coefficients for electrolytes in aqueous solution. The available data are somewhat incomplete and fragmentary (see, *e.g.*, Lewis and Randall, "Thermodynamics," 1923, p. 362; Randall, *Trans. Faraday Soc.*, 1927, **23**, 502). Nevertheless, in order to make full use of the activity coefficient, it is important that this shall be known over the whole range of concentration, and not merely over the limited range hitherto studied in most cases.

The lack of experimental data for moderately concentrated solutions is occasioned by the methods which have been employed to determine activity coefficients. Of those enumerated by Randall (*loc. cit.*, p. 503), the freezing-point method has been most used, since this yields the most accurate results in dilute solutions; in addition, it appears to be the only satisfactory method permitting of extrapolation to infinite dilution. Troublesome corrections, however, involving a knowledge of thermal data, are necessary for more concentrated solutions. The final results relate to 0°, whereas most other figures for comparison are at 18° or 25°. It does not seem, therefore, that this method is well adapted for determining activity coefficients in more concentrated solutions.

The boiling-point method is very much less accurate; it is subject to corrections in the case of the more concentrated solutions, similar to those to be applied in the case of the freezing-point method; in addition, the results obtained are at the b. p. of the solvent.

The *E.M.F.* method is applicable to concentrated as well as to dilute solutions. It has yielded concordant results for the latter in the hands of different investigators, but these results do not always agree with those obtained by other methods. With more concentrated solutions, deviations occur between the results of different investigators using this method.

The method of determining activity coefficients from measurements of vapour pressure offers certain advantages over those previously mentioned. For instance, determinations may be made at any desired temperature, and, in addition, the results obtained are not subject to errors introduced through temperature corrections.

Lewis and Randall (*op. cit.*, p. 331) state that in relatively concentrated solutions vapour-pressure measurements furnish a very satisfactory means of determining the ratio of the activities of the solute between two concentrations. This method, however, does not appear to have been employed very widely hitherto for this purpose. Grollmann and Frazer (*J. Amer. Chem. Soc.*, 1925, **47**, 712) have calculated the activity coefficients for sulphuric acid in aqueous solution from their vapour-pressure data at 25°, and Randall and White (*ibid.*, 1926, **48**, 2514) utilised the data of Lovelace, Frazer, and Sease (*ibid.*, 1921, **43**, 102) in obtaining the activity coefficients for potassium chloride at 20°.

Method employed in computing Activity Coefficients.—According to the method employed in the present work, the activity, a_2, of the solute is obtained from that, a_1, of the solvent by employing the Gibbs–Duhem partial molal equation :

$$d \log_e a_2 = -(N_1/N_2) d \log_e a_1 . \quad . \quad . \quad . \quad (1)$$

where N_1 and N_2 represent the mol. fractions of the solvent and solute respectively. Integration between fixed temperature limits and conversion into common logarithms gives :

$$\log a_2'/a_2 = -\int_{a_1}^{a_1'} (N_1/N_2) d \log a_1 \quad . \quad . \quad . \quad (2)$$

Values of the expression on the right-hand side of equation (2) have been obtained by plotting N_1/N_2 against $\log a_1$ and determining the area enclosed by the curve between each pair of the given values of $\log a_1$. No experiments at sufficiently low concentrations are available from the present work to carry the curve to infinite dilution, and therefore an arbitrary value for a_2 must be assigned to the most dilute solution studied, from which relative values for the activities of the remaining solutions are derived. Putting $a_2 = 1$ and $\log a_2 = 0$ for the solution of lowest concentration (Table I), we obtain values of the relative activity ka_2 for the remaining solutions. Since each of the three electrolytes studied dissociates into three ions, the relative mean ionic activity coefficient will be given in each case by

$$k\gamma = \sqrt[3]{ka_2}/M \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where M is the molality.

Values of $k\gamma$ for each electrolyte at various concentrations are given in col. 5 of Table I. These are proportional to the absolute activity coefficients γ, which may be obtained from them by multiplication by a numerical factor.

The vapour-pressure results in the more dilute solutions (*viz.*, at concentrations less than $0{\cdot}5M$; compare Part I this vol., p. 557)

TABLE I.

Activity coefficients for the chlorides of the alkaline-earth metals in aqueous solution at 25°, calculated from vapour-pressure data.

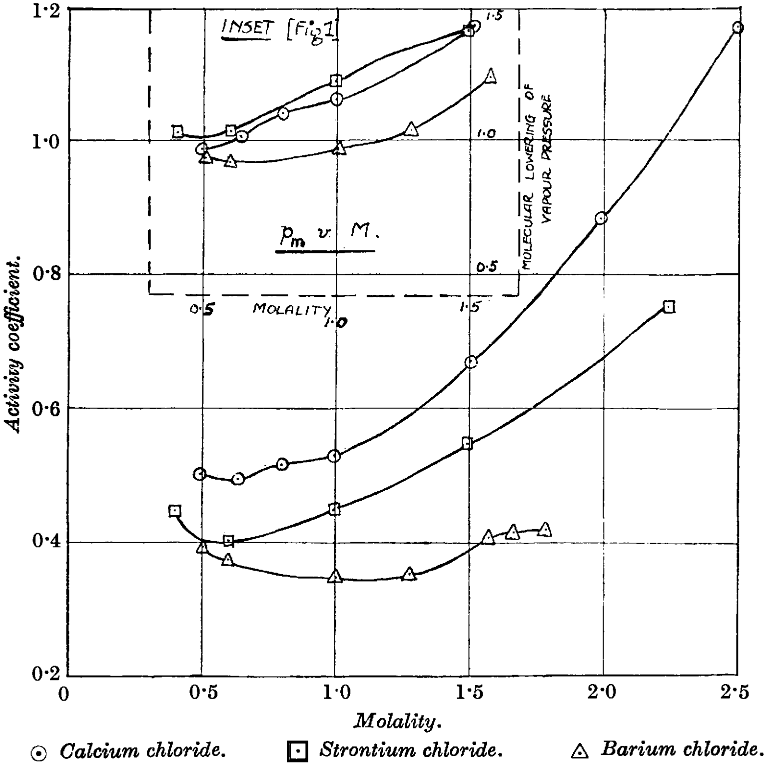
M.	N_1/N_2.	$\log a_1$ $= \log p/p_0$.	$\log a_2'/a_2$.	$k\gamma$.	γ.
1. Calcium chloride.					
0·494	112·4	−0·0088	—	2·02	(0·502)
0·635	87·4	0·0120	0·317	2·01	0·498
0·796	69·7	0·0164	0·341	2·08	0·517
1·000	55·5	0·0217	0·329	2·13	0·528
1·504	36·9	0·0413	0·841	2·71	0·671
1·985	28·0	0·0649	0·722	3·57	0·884
2·495	22·25	0·0916	0·659	4·71	1·17
2·990	18·57	0·1242	0·662	6·53	1·62
2. Strontium chloride.					
0·400	138·9	−0·0075	—	2·50	(0·427)
0·600	92·6	0·0115	0·449	2·35	0·401
0·995	55·8	0·0226	0·796	2·61	0·446
1·495	37·15	0·0403	0·800	3·21	0·549
2·246	24·74	0·0713	0·940	4·40	0·752
2·872	19·34	0·1049	0·733	6·04	1·031
3·245	17·12	0·1278	0·415	7·35	1·256
3·403	16·32	0·1385	0·190	8·11	1·386
3·517	15·80	0·1479	0·151	8·81	1·504
3. Barium chloride.					
0·508	109·0	−0·0088	—	1·97	(0·394)
0·606	91·6	0·0105	0·170	1·88	0·376
1·007	55·1	0·0184	0·559	1·74	0·348
1·285	43·2	0·0254	0·336	1·76	0·352
1·568	35·4	0·0371	0·448	2·04	0·408
1·655	33·6	0·0397	0·091	2·07	0·414
1·788	31·1	0·0430	0·108	2·09	0·418

have not been employed in the graphical evaluation of the relative activity coefficients, since, owing to the slope of the curve at these concentrations, it was impracticable to carry out the integration over this range.

The variation in the activity coefficients with concentration is shown graphically in Fig. 1. The figures for all three salts pass through minimum values, following the normal behaviour of electrolytes, as described by Harned (*J. Amer. Chem. Soc.*, 1920, **42**, 1808). Further, the curves are arranged in the order to be expected from the general behaviour of the three electrolytes considered, calcium chloride showing the highest relative activity coefficient throughout the whole range of concentration, and barium chloride the least.

Calculations of $k\gamma$ have been made by the author from the vapour-pressure data of Dieterici (*Ann. Physik*, 1897, **62**, 616) at 0° and Harrison and Perman at 80° (*Trans. Faraday Soc.*, 1927, **23**, 1) for aqueous solutions of calcium chloride. In neither case did the results indicate any minimum value in $k\gamma$. It appears from a study of the data that the degree of accuracy attained by these investigators is not sufficiently high for the purpose (compare also, Part I, p. 563). Similar remarks apply to the results of Tammann (*Mem. Acad. Pet.*, 1887, **35**, 7) on barium chloride at 100°, where a computation of $k\gamma$ did not lead to reasonable results. It therefore appears that none of the previous data on the salts studied in the present work is sufficiently accurate to permit of the evaluation of activity coefficients.

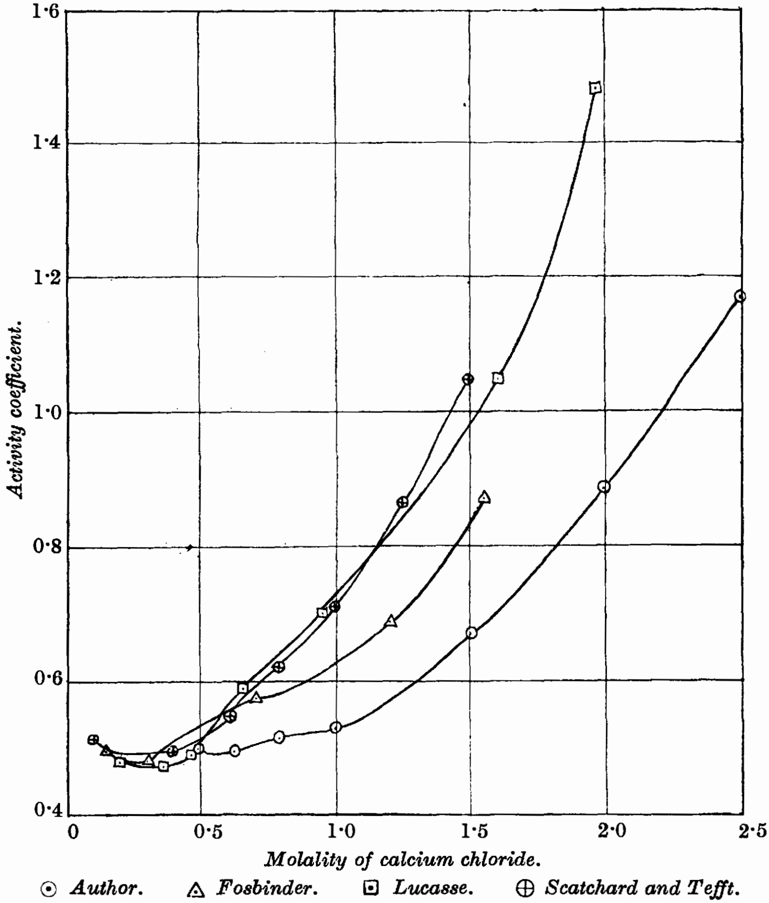
FIG. 1.



Comparison of the Results with those obtained from E.M.F. *Data.*—1. *Calcium chloride.* For this salt, activity coefficients derived from accurate freezing-point data over the concentration range studied by the author are not available, and therefore direct comparison to obtain absolute values of the activity coefficients is not possible. Figures derived from measurements of *E.M.F.* are, however, directly comparable with those of the present work.

Lucasse (*J. Amer. Chem. Soc.*, 1925, **47**, 745) obtained values for the activity coefficient at 25° over the concentration range 0·01—4·98*M*, from a study of the *E.M.F.* of concentration cells with calcium amalgam electrodes. Fosbinder (*ibid.*, 1929, **51**, 1345) independently obtained values over the range 0·01—3·27M in connexion with a study of the calcium amalgam electrode in dilute aqueous solution, and Scatchard and Tefft (*ibid.*, 1930, **52**, 2265), employing similar methods, obtained a third set of values over the range 0·01—1·5M during the compilation of comparative data for the chlorides of the bivalent metals. Each of these investigators obtained values of γ by equating the observed relative value (*i.e.*, $k\gamma$) for a concentration of 0·01M to that obtained at this concentration by the accurate freezing-point method (*viz.*, $M = 0{\cdot}01$, $\gamma = 0{\cdot}716$). The value of $k\gamma$ at 0·5M in the present work has been equated to that obtained by Lucasse at this concentration for γ. By multi-

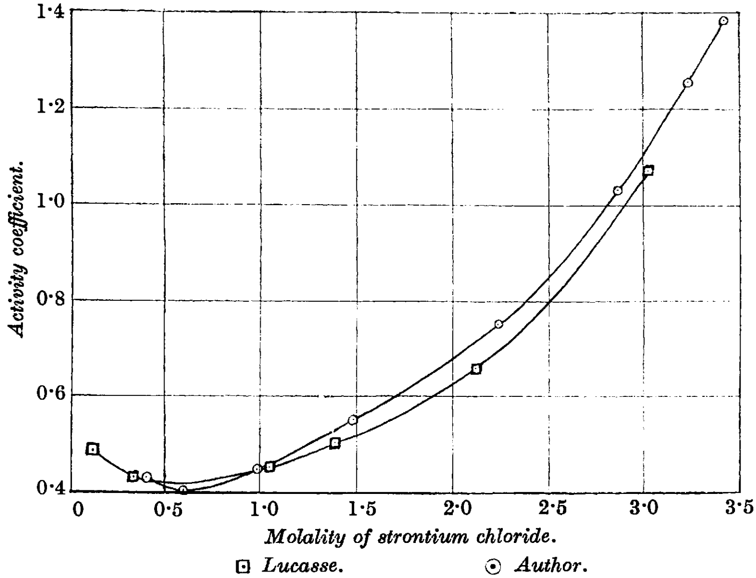
FIG. 2.



plication by the appropriate factor, this provides a series of values of γ; these are plotted in Fig. 2, together with those obtained by the various investigators using the *E.M.F.* method.

The figure shows that the minimum in γ does not occur in the same position in each case: it is at 0·37, 0·3, and 0·24*M* according to Lucasse, Fosbinder, and Scatchard and Tefft respectively. The author's figures show a minimum at 0·6*M*. Differences at higher concentrations are also shown in the figure, where the author's results give the lowest curve. However, it will be observed that each curve, including that derived from the vapour-pressure data, shows a distinct point of inflexion at a concentration between 0·8 and 1*M*, which is presumably not due to experimental error. The origin of this effect is somewhat obscure; it was apparently attributed by Lucasse to experimental error. Reference to Fig. 1 (inset) shows that a corresponding point of inflexion occurs at the same concentration in the curve connecting molality with molecular lowering of vapour pressure.

FIG. 3.



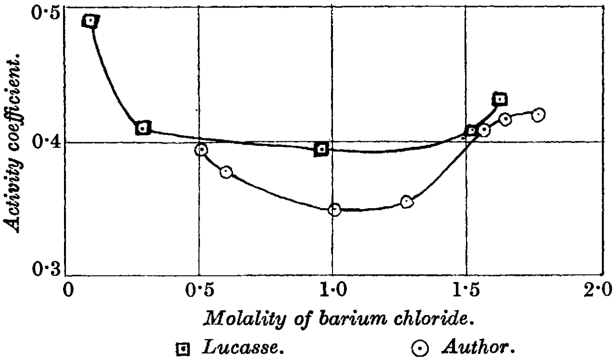
The comparison therefore shows that the results studied are in general qualitative agreement, in that each of the curves of Fig. 2 shows a minimum value for γ, and also is of the same form. Exact quantitative agreement is, however, lacking.

2. *Strontium chloride.* Comparative data for this salt are

available from the *E.M.F.* results of Lucasse (*loc. cit.*) over the concentration range 0·01—3·015*M*. The plots of γ against *M* (Lucasse) and $k\gamma$ against *M* (author) are very similar in form, the minima occurring at 0·55*M* on each curve. On the assumption that the two values ($k\gamma$ and γ) are identical at a concentration of 0·4*M*, the curve shown in Fig. 3 is obtained. The agreement is satisfactory. It will be noted that the results are in considerably better agreement than those for calcium chloride, including the figures at higher concentrations.

3. *Barium chloride.* The results for barium chloride may also be compared with data obtained from *E.M.F.* measurements by Lucasse (*loc. cit.*), covering the concentration range 0·01—1·65*M* (see Fig. 4). The author has equated his value for $k\gamma$ at a concentration of 0·5*M* to that of Lucasse for γ. The minimum in γ occurs at approximately the same concentration as that found by Lucasse, but the author's curve is steeper than Lucasse's. The two curves do not agree so well as in the case of strontium chloride.

FIG. 4.



It is unfortunate that Lucasse did not obtain values at concentrations higher than 1·6*M*, since, as shown by the author's curve (Fig. 4), there appears to be an abrupt falling off in the value of γ as the solution approaches saturation. This result corresponds with the maximum value of p_m (the molecular lowering of vapour pressure) mentioned in Part II (this vol., p. 571), which occurs at the same concentration. It is of interest, therefore, that Foxton and Shutt (*Trans. Faraday Soc.*, 1927, **23**, 487) found a distinct falling off in the activity coefficient of zinc chloride at concentrations approaching saturation. Although the concentration ranges over which the effect occurs are far removed from each other in the two cases (*viz.*, 1·6—1·78*M* for barium chloride; 20—25*M* for zinc chloride), it is possible that the effect may be connected with the fact that both solutions are in the neighbourhood of saturation at these concentrations.

Correlation of Data on Activity Coefficients with those on Molecular Lowering of Vapour Pressure.—The results now obtained may be considered in relation to the suggestions of Allmand (*Trans. Faraday Soc.*, 1927, **23**, 477) in a study of earlier work on vapour pressure and activity coefficients. These are based on the Gibbs–Duhem partial molal equation (p. 1285). He finds that for electrolytes (where the curve connecting activity coefficients with molality passes through a minimum value) the curve connecting vapour pressure and molality should show a point of inflexion, and that connecting the molecular lowering of vapour pressure and molality should show a minimum; these minima need not necessarily occur at the same concentration as the activity coefficient minima.

These conclusions may be directly tested by comparing the values for γ in the case of calcium, strontium, and barium chlorides with those for p_m recorded in Part II for the same solutions. The change in the slope of the curve connecting vapour pressure and molality with increasing concentration is so small that it is impossible to make a satisfactory comparison by using these magnitudes. No functional relation has to be assumed or derived between the values of γ and M, since a graphical method of integration has been employed in evaluating γ from the vapour-pressure data.

Values of p_m for the three electrolytes were recorded in Part II, Table I. For convenience, the values over the concentration range 0·5—1·5M are shown graphically in Fig. 1 (inset) of the present paper, together with the activity coefficients. The graph shows that in the case of barium chloride, p_m passes through a minimum value at a concentration slightly greater than 0·6M. For strontium chloride a minimum value also occurs, at approximately 0·5M. For calcium chloride no actual minimum is found, the value of p_m in this case appearing, however, to approach a minimum value.

The p_m minima at a concentration below 0·5M for each of the electrolytes studied in the present work (compare Part II, p. 568) have not been included in the previous discussion, as already indicated (p. 1285). However, a provisional computation of γ, including in the graphical integration the vapour-pressure data over the concentration range 0·2—0·5M, indicated that this p_m minimum gives rise to a point of inflexion in the curve connecting γ with M for calcium chloride, and to a secondary minimum in this curve for strontium and barium chloride. These γ minima also appeared to occur at almost the same concentration as the p_m minima.

No evidence is provided by the *E.M.F.* data discussed above as to the existence of these effects. In any case, the point of inflexion in the curve connecting γ and M for calcium chloride is not pronounced, and any experimental determination indicating such a point of inflexion might well be overlooked in the attempt to obtain a smoothed curve from the *E.M.F.* data.

In the case of strontium and of barium chloride, the only available *E.M.F.* data for comparison—those of Lucasse—are restricted to a limited number of observations. Thus, over the range 0·1—1M, they include observations at 0·1, 0·3, and 1M only. The position of the secondary minimum suggested by the author's figures is such that it might be completely overlooked under these conditions.

Summary.

Activity coefficients have been evaluated from the vapour-pressure data at 25° for the chlorides of the alkaline-earth metals in aqueous solution. The values obtained are in general agreement with those derived from *E.M.F.* measurements by other workers, passing through minima at approximately the same concentration. A correlation of the molecular lowering of vapour pressure with the activity coefficients computed in the present work showed agreement with the suggestion of Allmand, in that a minimum in the activity coefficient corresponded with a minimum in the molecular lowering of vapour pressure.

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