

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF NEW HAMPSHIRE]

The Osmotic and Activity Coefficients of Trivalent Chlorides in Aqueous Solution at 25°

BY CHARLES M. MASON

As a part of the general study of the rare earths now being carried on at New Hampshire, it has been of interest to investigate some of the thermodynamic properties of the aqueous solutions of the rare earth chlorides. In order to make the study more complete other 3:1 electrolytes also have been included in the program of experimental investigation, as this allows a comparison of the thermodynamic properties of the rare earths in aqueous solution with those substances with similar chemical properties. The present investigation includes new data for the osmotic coefficients of samarium and europium chlorides determined by the isotonic (or isopiestic) method of Robinson and Sinclair.¹

In connection with the report of the osmotic data on these salts the opportunity has been taken to reinterpret the previous data² on the osmotic coefficients of a number of 3:1 electrolytes for which the activity coefficients were computed by the method of Randall and White.³ It was found, as explained therein, that when this computation was undertaken it unavoidably involved a large error in the graphical integration used to obtain the activity coefficients and consequently an attempt was made to use the extended Debye-Hückel equation to correct for the error in the extrapolation to infinite dilution. Recently the experimental results of Shedlovsky and MacInnes⁴ and Longworth and MacInnes⁵ have cast some doubt on the advisability of the application of the extended Debye-Hückel equation to dilute solutions. Since the results which were obtained by the use of this equation now appear to have been too low and not as accurate as those obtained directly from the Randall and White integration, a new method of calculation of the activity coefficients from the osmotic coefficients has been developed and all of the osmotic data obtained in the whole series of investigations have been converted to activity coefficients by the use of this method.

(1) R. A. Robinson and D. A. Sinclair, *THIS JOURNAL*, **56**, 1830 (1934).

(2) C. M. Mason, *ibid.*, **60**, 1638 (1938).

(3) M. Randall and A. M. White, *ibid.*, **48**, 2514 (1926).

(4) T. Shedlovsky and D. A. MacInnes, *ibid.*, **61**, 200 (1939).

(5) L. G. Longworth and D. A. MacInnes, *ibid.*, **60**, 3070 (1938).

Experimental Details

The experimental details of the isotonic measurements were identical with those which have been described previously² for the other rare earths and the preparation of the salts used in this investigation has been described by Mason, Hickey and Wilson⁶ in their report on some magnetic properties of the rare earths.

The isotonic ratios which were obtained experimentally are given in Table I. The accuracy for φ_2 was in general about 0.3% in the concentrated solutions and 0.5% in the dilute ones. The values of φ_2 were obtained as before from the equation

$$\varphi_2 = m_1/2m_2 \quad (1)$$

and are given in Table I. The values of φ_1 used for this equation were obtained from a large-scale plot of the osmotic coefficients for sodium and potassium chloride obtained by Scatchard, Hamer and Wood.⁷

In the use of the isotonic method it is not possible to secure the osmotic coefficients at round concentrations and all of the osmotic data must, therefore, be smoothed by some suitable procedure. This was done previously by graphical smoothing from a large-scale plot of the experimental osmotic coefficients against the square root of the molality but in the present report a new method of smoothing has been devised, based on the use of the Debye theory, which gives more reliable results for the dilute solutions than the graphical method and coincides with it in the concentrated solutions. This method involves the use of the equation for the osmotic coefficient devised by Scatchard⁸ which has been altered at his suggestion to include a factor a' giving for the value of φ_D

$$\varphi_D = 1 + \frac{A}{(a')^3(6m)} \left[1 + a'\sqrt{6m} - \frac{1}{1 + a'\sqrt{6m}} - 2 \ln(1 + a'\sqrt{6m}) \right] + Bm \quad (2)$$

In order to use this equation for smoothing, the

(6) C. M. Mason, J. W. Hickey and W. K. Wilson, *ibid.*, **62**, 95 (1940).

(7) G. Scatchard, W. J. Hamer and S. E. Wood, *ibid.*, **60**, 3061 (1938).

(8) G. Scatchard, *Chem. Rev.*, **19**, 309 (1936).

TABLE I
ISOTONIC RATIOS AND OSMOTIC COEFFICIENTS OF SALT
SOLUTIONS

m_1	m_2	φ_1	m_1	m_2	φ_2
Samarium Chloride (m_2) against Sodium Chloride (m_1)					
6.1367	2.0836	1.9115	5.0944	1.8056	1.7043
6.0908	2.0730	1.9010	4.5167	1.6462	1.5904
5.3298	1.8687	1.7474	4.0650	1.5171	1.5032

Samarium Chloride (m_2) against Potassium Chloride (m_1)					
4.5837	1.5035	1.4978	1.1217	0.5308	0.9499
4.4211	1.4702	1.4705	0.9925	.4861	.9172
3.8692	1.3390	1.3856	.9572	.4740	.9069
3.1832	1.1687	1.2781	.8800	.4393	.8984
2.8316	1.0726	1.2251	.8505	.4303	.8875
2.6462	1.0279	1.1883	.8355	.4241	.8846
2.5870	1.0019	1.1901	.7821	.3960	.8869
2.2732	0.9169	1.1327	.7437	.3918	.8744
2.2417	.9042	1.1319	.6960	.3627	.8616
2.1879	.8946	1.1151	.6486	.3402	.8564
1.8028	.7692	1.0603	.5933	.3138	.8497
1.7435	.7565	1.0419	.5912	.3137	.8465
1.5929	.7015	1.0245	.5336	.2884	.8322
1.4176	.6454	0.9894	.4374	.2416	.8160
1.2279	.5777	.9560	.3873	.2132	.8200
1.2087	.5662	.9601	.3573	.1979	.8159
1.1634	.5524	.9469			

Europium Chloride (m_2) against Sodium Chloride (m_1)

6.1367	2.0803	1.9145	5.0944	1.7974	1.7116
6.0908	2.0653	1.9080	4.5167	1.6312	1.6050
5.3298	1.8574	1.7619	4.0650	1.5097	1.5105

Europium Chloride (m_2) against Potassium Chloride (m_1)

4.5837	1.4963	1.5042	0.9925	0.4845	0.9202
4.4211	1.4642	1.4765	.9572	.4711	.9125
3.8692	1.3324	1.3924	.8505	.4272	.8939
3.1832	1.1636	1.2837	.8355	.4215	.8900
2.8316	1.0699	1.2283	.6960	.3606	.8666
2.6462	1.0233	1.1937	.5933	.3121	.8543
2.5870	0.9933	1.9998	.5336	.2870	.8363
2.2417	.8965	1.1416	.4374	.2408	.8187
1.8028	.7633	1.0685	.3873	.2123	.8235
1.5929	.6967	1.0316	.3573	.1969	.8200
1.2279	.5740	0.9622			
1.2087	.5624	.9666			

deviations, $\Delta\varphi$, were computed from the equation

$$\Delta\varphi = \varphi_2 - \varphi_D \quad (3)$$

In these equations A is -3.495 for 3-1 electrolytes and B is a constant so defined that $\Delta\varphi$ is equal to zero for some concentrated solution, usually 2.0 molal.

These values of φ_D will differ from those of Scatchard⁸ and Scatchard, Hamer and Wood⁷ only in the introduction of the term a' , which was taken as unity by these authors. The value of a' was adjusted so that the values of $\Delta\varphi$ would not pass through an inflection point as they approached zero in the plot of $\Delta\varphi$ against m . To

show this effect, $\Delta\varphi$ for lanthanum chloride has been plotted in Fig. 1 for those values of $\Delta\varphi$ obtained when a' was fixed at 2.40 and it will be noted that any inflection point below 0.1 molal, such as was shown in the previous report,² has been eliminated.

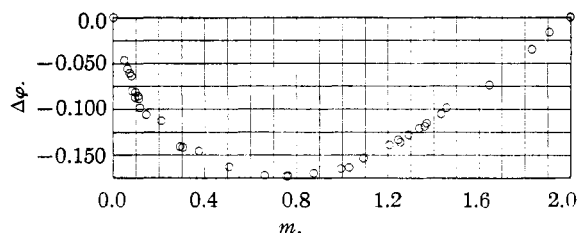


Fig. 1.— $\Delta\varphi$ for LaCl_3 , $a' = 2.40$.

When the proper value of a' had been found and a smooth curve obtained for $\Delta\varphi$ against m for this value of a' , the smoothed values of $\Delta\varphi$ at round concentrations were read back from the curve. From these the smooth values of φ were calculated at round concentrations by equation (3) for all the 3-1 salts which have been studied and these values of the osmotic coefficients are given in Table II, together with the values of a' used.

Activity Coefficients.—As explained in the previous report,² activity coefficients were computed from the osmotic coefficients by the method of Randall and White.³ In the present report a different method has been devised and employed for this calculation. The osmotic coefficient is related to the activity coefficient by the equation

$$1 + m \frac{d \ln \gamma}{dm} = \varphi + m \frac{d\varphi}{dm} \quad (4)$$

If one substitutes in this equation the values of φ obtained from equations (2) and (3) one obtains for the activity coefficient the equation

$$\ln \gamma = \frac{A\sqrt{6m}}{1 + a'\sqrt{6m}} + 2Bm + \Delta\varphi + \int_0^m \Delta\varphi/mdm \quad (5)$$

The activity coefficients of all the salts studied in the series have been calculated by means of this equation using the smoothed values of the deviations $\Delta\varphi$, read back from the large-scale plots of $\Delta\varphi$ against m .

The last term of equation (5) was evaluated by graphical integration of $\Delta\varphi/m$ against m . This latter plot has much less extrapolation error than that used in the method of Randall and White³ and the intercept was easily calculated on the assumption that the curve followed a simple quadratic in m below 0.1 molal.

TABLE II
 OSMOTIC COEFFICIENTS SMOOTHED FROM DEVIATIONS, $\Delta\phi$

m	AlCl ₃	ScCl ₃	YCl ₃	LaCl ₃	CeCl ₃	PrCl ₃	NdCl ₃	SmCl ₃	EuCl ₃
Osmotic Coefficients									
0.05	0.823	0.799	0.801	0.806	0.783	0.778	0.794	0.796	0.800
.1	.819	.797	.789	.788	.782	.784	.783	.789	.794
.2	.841	.827	.810	.800	.805	.801	.801	.809	.812
.3	.890	.869	.848	.833	.836	.831	.833	.842	.843
.4	.948	.918	.893	.871	.873	.867	.872	.880	.883
.5	1.009	.970	.940	.912	.915	.906	.914	.922	.927
.6	1.073	1.027	.989	.950	.955	.945	.954	.964	.971
.7	1.141	1.087	1.040	.998	1.005	.994	1.004	1.017	1.025
.8	1.214	1.150	1.095	1.044	1.053	1.042	1.052	1.069	1.077
.9	1.292	1.216	1.155	1.096	1.101	1.094	1.104	1.122	1.131
1.0	1.376	1.285	1.217	1.149	1.152	1.148	1.159	1.180	1.187
1.1	1.469	1.355	1.281	1.205	1.204	1.206	1.217	1.238	1.245
1.2	1.558	1.427	1.350	1.263	1.260	1.267	1.278	1.298	1.306
1.3	1.653	1.499	1.420	1.322	1.318	1.326	1.340	1.360	1.371
1.4	1.754	1.573	1.491	1.383	1.379	1.387	1.403	1.426	1.437
1.5	1.855	1.650	1.564	1.444	1.442	1.449	1.466	1.492	1.506
1.6	1.966	1.727	1.638	1.506	1.508	1.512	1.531	1.559	1.575
1.7	2.081	1.807	1.715	1.569	1.577	1.577	1.597	1.627	1.646
1.8	2.203	1.886	1.795	1.633	1.649	1.642	1.667	1.698	1.719
1.9	...	1.965	1.879	1.699	1.719	1.709	1.738	1.770	1.795
2.0	1.965	1.766	1.796	1.777	1.809	1.845	1.875
Constants									
a'	2.60	2.60	2.60	2.40	2.40	2.40	2.40	2.40	2.40
B	0.71872	0.55484	0.52615	0.43295	0.44795	0.43845	0.45450	0.47247	0.48715

The resulting activity coefficients, given in Table III, therefore, will be in error, if at all, only by a constant deviation in $\ln \gamma$. The constants used in equations (2) and (5) have also been included in Table II.

Discussion

An examination of the literature reveals that of the salts studied, there have been a number of determinations of the activity coefficient of lanthanum chloride in solution in recent years.⁹

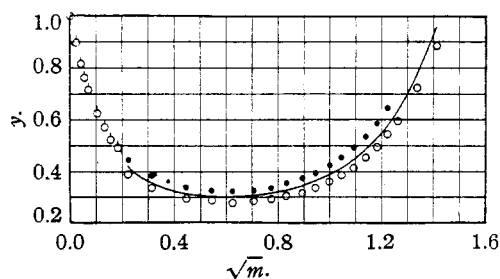


Fig. 2.—Activity coefficients of LaCl₃. Solid line, present paper; O, Mason, 1938; ●, Robinson, 1939; ○, Shedlovsky and MacInnes, 1938.

(9) (a) E. Proskauer, Dissertation, Leipzig, 1933; (b) C. M. Mason and G. L. Ernst, *THIS JOURNAL*, **58**, 2032 (1936); (c) R. A. Robinson, *ibid.*, **59**, 84 (1937); (d) C. M. Mason, *ibid.*, **60**, 1638 (1938); (e) T. Shedlovsky and D. A. MacInnes, *ibid.*, **61**, 200 (1939); (f) J. Kielland, *J. Phys. Chem.*, **43**, 797 (1939); (g) R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1229 (1939).

In order to make a comparison of the different results, the more recent determinations have been plotted against the square root of the molality in Fig. 2. The results so compared include those of Mason,^{9d} obtained by the method of Randall and White,³ those of Shedlovsky and MacInnes,^{9e} those of Robinson^{9g} corrected to coincide with Shedlovsky and MacInnes and the results of the present calculation shown as a solid line.

A study of these data shows no fundamental deviation which cannot be corrected by a small difference in the value of $\ln \gamma$.

It is interesting to observe that the values now presented on the basis of a new method of calculation are entirely consistent with the experimental results of Shedlovsky and MacInnes which were obtained by an entirely different experimental technique.

The effect of the choice of the numerical value of a' on the activity and osmotic coefficients finally obtained is not great. It was found that a shift of 0.4 in the value of a' made a change of about 2% in the activity coefficient.

In conclusion I wish to thank Dr. H. N. McCoy for the loan of the sample of europium oxide and Professor George Scatchard for suggesting the method used in the computation of the results.

TABLE III
 ACTIVITY COEFFICIENTS RECALCULATED FROM $\Delta\phi$

<i>m</i>	AlCl ₃	ScCl ₃	YCl ₃	LaCl ₃	CeCl ₃	PrCl ₃	NdCl ₃	SmCl ₃	EuCl ₃
	Activity Coefficients								
0.05	0.436	0.412	0.417	0.417	0.394	0.402	0.403	0.408	0.412
.1	.384	.357	.357	.356	.338	.343	.344	.351	.355
.2	.348	.322	.317	.312	.299	.302	.302	.310	.315
.3	.338	.315	.307	.298	.286	.289	.290	.300	.303
.4	.357	.321	.309	.295	.285	.286	.289	.299	.303
.5	.378	.334	.318	.303	.290	.290	.294	.304	.308
.6	.406	.353	.332	.312	.300	.298	.303	.316	.322
.7	.442	.378	.350	.324	.313	.300	.316	.331	.338
.8	.487	.409	.373	.340	.330	.327	.334	.351	.359
.9	.542	.447	.402	.362	.349	.347	.354	.375	.384
1.0	.610	.492	.436	.387	.372	.371	.380	.403	.413
1.1	.689	.544	.476	.416	.399	.399	.410	.436	.447
1.2	.815	.604	.524	.449	.430	.433	.445	.475	.486
1.3	.918	.674	.580	.488	.467	.471	.485	.518	.533
1.4	.935	.755	.644	.533	.509	.514	.531	.569	.587
1.5	1.253	.850	.718	.583	.558	.562	.570	.628	.649
1.6	1.610	.961	.804	.639	.614	.618	.642	.695	.720
1.7	1.773	1.089	.904	.703	.681	.681	.710	.771	.802
1.8	2.131	1.238	1.023	.776	.758	.753	.790	.859	.897
1.9	...	1.408	1.164	.859	.846	.836	.881	.961	1.009
2.0	1.330	.954	.946	.929	.984	1.079	1.140

Summary

1. The osmotic coefficients of samarium and europium chlorides have been determined in aqueous solution at 25° by the isotonic method.

2. A new method is described for the smoothing of osmotic coefficients and the calculation of activity coefficients.

3. The activity coefficients of aluminum, scandium, yttrium, lanthanum, cerous, praseodymium, neodymium, europium and samarium chlorides have been calculated by a new method.

4. The activity coefficients of lanthanum chloride have been compared with existing data.

DURHAM, NEW HAMPSHIRE

RECEIVED JULY 17, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF HAWAII]

The Relation between the Oxidizing Action and Catalytic Decomposition of Concentrated Hydrogen Peroxide. I. Osmium Tetroxide as a Catalyst in the Oxidation of Acetic and Propionic Acids

BY LUTHER M. FOSTER AND JOHN H. PAYNE

The apparent relationship between the rate of decomposition and the oxidizing action of hydrogen peroxide has generally been explained by assuming that atomic oxygen liberated in the decomposition is the active oxidizing agent. The unique action of hydrogen peroxide upon many organic compounds has shown that such is not the case.^{1,2,3}

In many instances, for example in the addition of hydroxyl groups to double bonds, the hydrogen peroxide molecule enters into the reaction. It is possible, nevertheless, that the same catalyst

may increase the speed of both the oxidation reaction as well as the decomposition of the hydrogen peroxide.

In order to study this problem, the oxidation of acetic and propionic acids by 60% hydrogen peroxide in the presence of varying amounts of osmium tetroxide as a catalyst was investigated. The method used made possible the simultaneous quantitative determination of the extent of the oxidation, as indicated by the amount of carbon dioxide formed, and the decomposition of the peroxide, as shown by the evolution of oxygen. Osmium tetroxide was chosen for study because it is one of the most active catalysts for the de-

(1) Fry and Payne, *THIS JOURNAL*, **53**, 1973 (1931).

(2) Milas and Sussman, *ibid.*, **58**, 1302 (1936).

(3) Milas and Sussman, *ibid.*, **59**, 2345 (1937).