

TABLE XI

Reducing agent	Lowest acid concn. (N) necessary for reaction		Order of reaction concerning reducing agent		Temp. coeff. in H ₂ SO ₄ solutions
	H ₂ SO ₄	HCl	V ^V	reducing agent	
As ₂ O ₃	0.0	0.0	2	1	1.9
H ₂ C ₂ O ₄	0.0	0.0	1	2	3.2
H ₂ CO	7.8	4.6	2	1-0	1.6
C ₂ H ₅ OH	2.0	2.0	1	1	2.8

for the oxidation of oxalic acid. The catalytic effect of phosphoric acid seems to be connected with the arsenious oxide and not with the vanadium. Nitric acid is a peculiar and very sensi-

TABLE XII

Reducing agent	Accelerator Formula	Upper and lower final concn. (N)	<i>t</i> _{1/2} in minutes		Factor of acceleration
			Without accel.	With accel. in max. concn.	
As ₂ O ₃	H ₃ PO ₄	0.0225-0.3	182	23	7.9
H ₂ C ₂ O ₄	Mn ⁺⁺	.25 -1.0	86.25	18.25	4.7
H ₂ C ₂ O ₄	Fe ⁺⁺⁺	.05 -0.5	86.25	440	0.2
H ₂ CO	HNO ₃	.0025-0.02	186	46 ^a	4.0
C ₂ H ₅ OH	HNO ₃	.025 -0.25	485	32 ^a	15.1

^a The end of the induction period; from this point on the reaction passes very quickly.

tive inductor in presence of formaldehyde and ethyl alcohol.

JERUSALEM, PALESTINE

RECEIVED JANUARY 26, 1942

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

The Activity Coefficients of Some Bivalent Metal Nitrates in Aqueous Solution at 25° from Isopestic Vapor Pressure Measurements

BY R. A. ROBINSON, JEAN M. WILSON AND H. S. AYLING

In a recent communication¹ isopiestic measurements have been recorded from which the activity coefficient of calcium nitrate at 25° has been computed and found to be considerably lower than the activity coefficient of calcium chloride.² It is a matter of some interest, therefore, to obtain measurements on other nitrates of the alkaline earth metals and similar bivalent metals. We are now able to report results on magnesium, strontium, barium, cobalt, copper, cadmium and uranyl nitrate.

TABLE I

CONCENTRATIONS OF ISOPIESTIC SOLUTIONS OF POTASSIUM CHLORIDE AND BIVALENT METAL NITRATES AT 25°

Magnesium Nitrate					
Molality		Molality		Molality	
Mg(NO ₃) ₂	KCl	Mg(NO ₃) ₂	KCl	Mg(NO ₃) ₂	KCl
0.1322	0.1865	0.5498	0.8746	1.585	3.144
.1347	.1899	.5659	.9118	1.631	3.262
.1430	.2006	.6681	1.099	1.662	3.362
.1605	.2265	.8318	1.419	1.757	3.600
.1739	.2490	1.043	1.871	2.040	4.371
.2931	.4317	1.294	2.442	2.065	4.439
.3517	.5344	1.474	2.885	2.120	4.609
.4197	.6440	1.583	3.145	2.197	4.831
Strontium Nitrate					
Molality		Molality		Molality	
Sr(NO ₃) ₂	KCl	Sr(NO ₃) ₂	KCl	Sr(NO ₃) ₂	KCl
0.08822	0.1184	0.4522	0.5870	1.872	2.319
.09650	.1290	.7331	.9330	1.921	2.356
.09980	.1330	.7574	.9666	2.206	2.712
.1205	.1591	.9450	1.199	2.446	3.014
.1443	.1898	1.264	1.582	2.811	3.456
.2069	.2723	1.363	1.700	2.974	3.658
.3125	.4088	1.565	1.952	3.498	4.314
.4496	.5820	1.795	2.210	3.909	4.843

Barium Nitrate					
Molality		Molality		Molality	
Ba(NO ₃) ₂	KCl	Ba(NO ₃) ₂	KCl	Ba(NO ₃) ₂	KCl
0.09144	0.1151	0.1450	0.1775	0.3316	0.3743
.09208	.1155	.2184	.2591	.3598	.4030
.1194	.1489	.2240	.2664	.3961	.4358
.1413	.1735	.2899	.3322	.4022	.4434
Cobalt Nitrate					
Molality		Molality		Molality	
Co(NO ₃) ₂	KCl	Co(NO ₃) ₂	KCl	Co(NO ₃) ₂	KCl
0.1022	0.1419	1.137	2.009	1.760	3.454
.2297	.3293	1.155	2.038	1.815	3.587
.2932	.4263	1.214	2.177	1.886	3.772
.3715	.5498	1.223	2.203	1.935	3.898
.5798	.9028	1.362	2.499	1.990	4.033
.5962	.9322	1.421	2.640	2.198	4.578
.8645	1.445	1.477	2.767	2.244	4.678
.8881	1.490	1.487	2.810	2.261	4.738
1.109	1.948	1.650	3.178		
Copper Nitrate					
Molality		Molality		Molality	
Cu(NO ₃) ₂	KCl	Cu(NO ₃) ₂	KCl	Cu(NO ₃) ₂	KCl
0.1091	0.1514	0.4241	0.6132	1.618	2.936
.1211	.1820	.5389	.8181	1.701	3.136
.1921	.2691	.7310	1.150	1.915	3.633
.2333	.3300	1.000	1.668	2.158	4.178
.2382	.3383	1.183	2.032	2.283	4.501
.2585	.3684	1.390	2.442	2.415	4.828
.3060	.4411	1.529	2.766		
Cadmium Nitrate					
Molality		Molality		Molality	
Cd(NO ₃) ₂	KCl	Cd(NO ₃) ₂	KCl	Cd(NO ₃) ₂	KCl
0.1134	0.1571	0.6730	1.031	1.841	3.201
.1217	.1707	0.6863	1.048	1.873	3.255
.1559	.2190	1.041	1.672	1.989	3.497
.1975	.2778	1.138	1.848	2.162	3.824
.3309	.4766	1.206	1.974	2.315	4.150
.4141	.5061	1.267	2.082	2.381	4.269
.5345	.8012	1.531	2.597	2.638	4.810
.6409	.9786	1.681	2.888		

(1) R. A. Robinson, *THIS JOURNAL*, **62**, 3130 (1940).

(2) R. A. Robinson, *Trans. Faraday Soc.*, **36**, 735 (1940).

TABLE I (Concluded)

Molality UO ₂ (NO ₃) ₂	Uranyl Nitrate		Molality UO ₂ (NO ₃) ₂	Molality KCl	Molality UO ₂ (NO ₃) ₂	Molality KCl
	Molality KCl	Molality UO ₂ (NO ₃) ₂				
0.0930	0.1344	0.7557	1.378	1.493	3.248	
.1156	.1681	0.8650	1.626	1.505	3.281	
.2492	.3833	1.020	1.999	1.545	3.400	
.2865	.4441	1.116	2.251	1.654	3.715	
.2982	.4627	1.219	2.525	1.697	3.844	
.4797	.7929	1.252	2.599	1.759	4.012	
.5510	.8370	1.453	3.139	1.887	4.381	
.6632	1.173	1.457	3.165	2.035	4.801	

brought into equilibrium with solutions of potassium chloride by the method previously described,³ the concentrations of the isopiestic solutions being recorded in Table I.

Table II contains values of the osmotic and activity coefficients calculated from the experimental results in Table I. The selection of reference values for the activity coefficients at 0.1 *M* was a matter of some difficulty; provisional values were obtained by plotting the osmotic

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF BIVALENT METAL NITRATES AT 25°

<i>m</i>	Mg(NO ₃) ₂		Sr(NO ₃) ₂		Ba(NO ₃) ₂		Co(NO ₃) ₂		Cu(NO ₃) ₂		Cd(NO ₃) ₂		UO ₂ (NO ₃) ₂	
	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ
0.1	0.858	0.532	0.816	0.470	0.769	0.430								
.2	.871	.490	.797	.403	.726	.346								
.3	.893	.478	.787	.367	.691	.298								
.4	.918	.478	.780	.342	.663	.263								
.5	.946	.483	.774	.324								
.6	.973	.492	.770	.309								
.7	.999	.504	.767	.298								
.8	1.026	.519	.764	.288								
.9	1.053	.536	.761	.279								
1.0	1.080	.554	.758	.271								
1.2	1.137	.598	.756	.259								
1.4	1.195	.650	.754	.249								
1.6	1.258	.714	.755	.241								
1.8	1.323	.788	.757	.234								
2.0	1.389	.874	.759	.229								
2.5771	.220								
3.0788	.215								
3.5807	.212								
4.0827	.211								
0.1	0.850	0.519	0.848	0.516	0.851	0.520	0.888	0.599						
.2	.859	.473	.852	.467	.855	.472	.909	.570						
.3	.874	.455	.864	.445	.866	.450	.935	.566						
.4	.893	.448	.882	.437	.879	.440	.966	.575						
.5	.915	.448	.900	.435	.893	.436	1.001	.594						
.6	.939	.453	.921	.436	.909	.434	1.039	.619						
.7	.964	.461	.942	.441	.923	.434	1.076	.648						
.8	.991	.472	.963	.448	.939	.437	1.114	.682						
.9	1.016	.485	.985	.455	.955	.441	1.153	.719						
1.0	1.041	.498	1.007	.466	.969	.446	1.193	.762						
1.2	1.094	.532	1.049	.488	.997	.457	1.269	.859						
1.4	1.149	.573	1.092	.515	1.027	.472	1.344	.970						
1.6	1.206	.620	1.137	.546	1.058	.491	1.419	1.099						
1.8	1.261	.674	1.182	.582	1.090	.510	1.487	1.244						
2.0	1.316	.734	1.228	.624	1.120	.531	1.552	1.400						
2.2	1.370	.800	1.275	.671	1.149	.554						
2.4578						
2.6602						

Each of these salts was purified by a three-fold recrystallization from water and used in the form of stock solutions whose concentrations were determined by gravimetric analysis of the cation constituent. The solutions of the nitrates were

coefficient at 0.1 *M* against the activity coefficient at this concentration for a number of 1-2 electrolytes and interpolating a value of the ac-

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

tivity coefficient corresponding to the osmotic coefficient of each of these nitrates at 0.1 *M*.

A detailed quantitative investigation of these results does not seem to be profitable at this stage. Nevertheless, the results do present some interesting features, some of which are illustrated in Fig. 1, which is a plot of the activity coefficients of eight bivalent metal nitrates and four chlorides of the alkaline earth metals, together with the curve corresponding to the limiting Debye-Hückel equation for 1-2 electrolytes. More extensive plots for 1-2 salts have been given by Robinson and Harned.⁴

The highest curve of Fig. 1 is that of uranyl nitrate; such high values of the activity coefficient are also found for the magnesium halides and for zinc iodide, the latter salt having an \AA . value of 6 according to Bates.⁵ This is close to the critical Bjerrum distance of 7 \AA . for 1-2 salts and therefore it is unlikely that any appreciable intermediate ion formation occurs with these salts. This is probably true also for the nitrates of cobalt, copper and cadmium, their activity coefficient curves being comparable with that of strontium chloride. The activity coefficients of cadmium nitrate are in marked contrast to those of the cadmium halides.⁶ Cadmium chloride, bromide and iodide yield activity coefficient curves lying below the curve predicted by the limiting Debye-Hückel equation even at the lowest concentrations measured; this behavior is probably due to complex ion formation and is not evidenced in the case of cadmium nitrate. Finally the curve for magnesium nitrate lies comparatively high in the plot, whilst those of calcium, strontium and barium nitrate, although above the curve predicted by the limiting law, occupy a low position in the plot comparable with the curve for sodium sulfate for which Harned and Hecker⁷ found an \AA . value of 3.4. Magnesium nitrate should therefore closely approximate a completely dissociated electrolyte whilst considerable intermediate ion

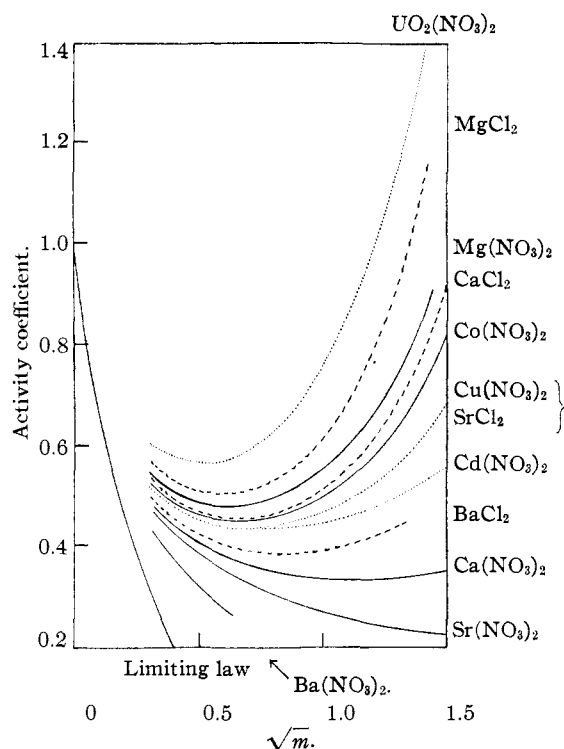


Fig. 1.—Activity coefficients of bivalent metal nitrates and chlorides: ———, nitrates of alkaline earth metals; - - - - - , chlorides of alkaline earth metals; , nitrates of other bivalent radicals. The curve on the left corresponds to the limiting Debye-Hückel equation for ions of \AA . = 0.

formation would be expected in the case of the other three nitrates.

We wish to thank the Chemical Society (London) for a grant from their Research Fund.

Summary

Osmotic and activity coefficients have been determined from isopiestic measurements on the following nitrates: magnesium, strontium, barium, uranyl, cobalt, copper and cadmium.

It is likely that in an extended treatment intermediate ion formation will prove to be an important factor in the case of calcium, strontium and barium nitrate and that the other nitrates, especially magnesium and uranyl nitrate, can be treated as completely dissociated electrolytes. Cadmium nitrate does not offer evidence of the complex ion formation which is so marked in the case of the cadmium halides.

AUCKLAND, NEW ZEALAND RECEIVED OCTOBER 28, 1941

(4) R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 463 (1941).

(5) R. G. Bates, *THIS JOURNAL*, **60**, 2983 (1938).

(6) H. S. Harned and M. E. Fitzgerald, *ibid.*, **58**, 2624 (1936); R. G. Bates, *ibid.*, **61**, 308 (1939); **63**, 399 (1941); R. A. Robinson, *Trans. Faraday Soc.*, **36**, 1135 (1940); R. A. Robinson and J. M. Wilson, *ibid.*, **36**, 738 (1940).

(7) H. S. Harned and J. C. Hecker, *THIS JOURNAL*, **55**, 4838 (1933).