A THERMODYNAMIC STUDY OF BIVALENT METAL HALIDES IN AQUEOUS SOLUTION. PART V. THE ACTIVITY COEFFICIENTS OF CADMIUM CHLORIDE AND BROMIDE AT 25°.

By R. A. Robinson.[1]

Received 30*th July*, 1940.

Four determinations of the activity coefficient of cadmium chloride have been made by e.m.f. methods; Horsch [2] made measurements over the range 0·0005 to 0·1 M. and a single measurement at 6·62 M.; Lucasse[3] covered the range 0·01 to 6 M. and Quintin[4] the range 0·001 to 0·05 M.; Harned and Fitzgerald,[5] who were concerned with the extrapolation of the standard potential of cadmium, made numerous measurements between 0·0005 and 0·1 M. and a few measurements up to 1 M. Whilst there is good agreement between the results of these four investigations in the concentration range up to 0·1 M., the data of Lucasse [3] and of Harned and Fitzgerald [5] do not agree between 0·1 and 1·0 M., the divergence increasing with the concentration. Isopiestic measurements have now been made on cadmium chloride solutions between 0·1 and 6 M. and the data of Lucasse have been confirmed with excellent agreement between his e.m.f. results and the present isopiestic data. Good agreement is also obtained with the determination of Horsch at the saturation point.

TABLE I.

Cadmium Chloride.

0·1060, 0·1054;	0·1085, 0·1092;	0·1184, 0·1180;	0·1596, 0·1531;
0·2002, 0·1870;	0·2055, 0·1925;	0·2908, 0·2597;	0·3487, 0·3062;
0·4285, 0·3680;	0·4738, 0·4021;	0·5778, 0·4758;	0·6643, 0·5366;
0·7262, 0·5836;	0·8772, 0·6815	0·9078, 0·7099;	0·9990, 0·7642;
1·218, 0·9120;	1·408, 1·033;	1·452, 1·065;	1·772, 1·282;
1·818, 1·308;	1·921, 1·371;	2·120, 1·509;	2·182, 1·551;
2·201, 1·564;	2·427, 1·723;	2·490, 1·771,	2·710, 1·925;
3·273, 2·334;	3·327, 2·383;	3·413, 2·449;	3·754, 2·714;
4·101, 3·009;	4·298, 3·162;	4·762, 3·554;	5·331, 4·068;
5·522, 4·241;	5·847, 4·541;	5·993, 4·688.	

Cadmium Bromide.

0·1065, 0·1017;	0·1261, 0·1187;	0·1457, 0·1338;	0·2205, 0·1903;
0·2965, 0·2459;	0·3897, 0·3112;	0·4563, 0·3583;	0·6634, 0·4975;
0·8097, 0·6037;	0·8924, 0·6615;	0·9710, 0·7122;	1·160, 0·8504;
1·437, 1·070;	1·558, 1·168;	1·884, 1·433;	2·097, 1·617;
2·192, 1·709;	2·285, 1·788;	2·306, 1·811;	2·515, 2·004;
2·792, 2·263;	2·984, 2·446;	3·261, 2·717;	3·418, 2·883;
3·639, 3·100;	3·758, 3·224;	3·844, 3·314;	4·062, 3·530;
4·064, 3·536.			

[1] Sterling Fellow, Yale University, 1940.
[2] *J. Amer. Chem. Soc.*, 1919, **41**, 1787.
[3] *Ibid.*, 1929, **51**, 2597. [4] *Compt. rend.*, 1935, **200**, 1754.
[5] *J. Amer. Chem. Soc.*, 1936, **58**, 2624.

Cadmium bromide has been investigated by Lucasse [3] and Bates,[6] using the e.m.f. method; the two sets of results are in reasonable agreement. Isopiestic measurements have been made on this salt but the method, which worked very well with cadmium chloride, proved more difficult to apply to the bromide at concentrations less than 0·5 M. The difficulty is probably due to hydrolysis of the salt, and is much more marked in the case of zinc bromide. Numerous attempts have been made to obtain the activity coefficient of the latter salt by the isopiestic method but without success. For this reason the present determination on cadmium bromide can only be presented as affording support for the data of Lucasse and Bates; on the other hand, the measurements on cadmium chloride are believed to be sufficiently good to rank as an independent determination.

TABLE II.

ACTIVITY COEFFICIENTS OF CADMIUM HALIDES AT 25°.

m.	$CdCl_2$.	$CdBr_2$.	CdI_2.
0·1	(0·228)	0·190	0·1074
0·2	0·1632	(0·132)	(0·0685)
0·3	0·1324	0·105	0·0523
0·4	0·1133	0·0895	0·0433
0·5	0·1001	0·0784	0·0377
0·6	0·0902	0·0702	0·0337
0·7	0·0825	0·0640	0·0307
0·8	0·0758	0·0594	0·0284
0·9	0·0708	0·0553	0·0266
1	0·0664	0·0521	0·0251
1·5	0·0523	0·0418	0·0205
2	0·0439	0·0363	0·0181
2·5	0·0384	0·0329	—
3	0·0351	0·0307	—
3·5	0·0322	0·0292	—
4	0·0304	0·0280	—
4·5	0·0290	—	—
5	0·0278	—	—
5·5	0·0269	—	—
6	0·0263	—	—

Experimental.

Table I records the molalities of isopiestic solutions, that of the reference solution, potassium chloride, being given by the second of each pair of figures. The activity coefficients, calculated relative to those of potassium chloride previously recorded,[7] are given in Table II, together with the data for cadmium iodide.[8]

The activity coefficients are very low compared with those more normal bivalent metal halides which can probably be classified as strong electrolytes; of this group barium chloride exhibits the lowest activity coefficient with a minimum value of 0·384 at 0·7 M. Complex ion formation appears to be established in the case of cadmium iodide and from the nature of the activity coefficient curves this must be almost equally operative in the case of the chloride and bromide. The three activity coefficient curves place themselves regularly in the order $CdCl_2 > CdBr_2 > CdI_2$, but the corresponding osmotic coefficient curves are more complex, the order being $CdCl_2 > CdBr_2 > CdI_2$ below 1·4 M. and the reverse of this order above 2 M.

Summary.

The activity coefficients of cadmium chloride and bromide have been determined at 25°.

Yale University,
New Haven, Conn.

[6] *J. Amer. Chem. Soc.*, 1939, **61**, 308.
[7] Robinson, *Trans. Faraday Soc.*, 1939, **35**, 1217.
[8] Robinson and Wilson, *ibid.*, 1940, **36**, 738.

PART VI. THE ACTIVITY COEFFICIENTS OF MANGANESE, COBALT, NICKEL AND COPPER CHLORIDE IN AQUEOUS SOLUTION AT 25°.

By R. A. Robinson [1] and R. H. Stokes.

The activity coefficient of cobalt chloride [2] is intermediate between that of calcium chloride and magnesium chloride, indicating that it belongs to the class of highly dissociated bivalent metal chlorides; in contrast to this salt zinc chloride [3] has a very low activity coefficient in concentrated solution consistent with intermediate and possibly complex ion formation. It is therefore of interest to examine some other chlorides of metals in this transition group.

Experimental.

The solutions recorded in Table I were found to be isopiestic, the second of each pair of figures indicating the molality of the reference salt, potassium chloride. The copper chloride solutions were contained in platinum dishes, the other solutions in silver dishes.

TABLE I.

Manganese Chloride.

0·1148, 0·1596;	0·1463, 0·2044;	0·2276, 0·3248;	0·2937, 0·4251;
0·4537, 0·6801;	0·6091, 0·9450;	0·9826, 1·660;	1·259, 2·236;
1·329, 2·396;	1·539, 2·868;	1·601, 3·000;	1·966, 3·860;
2·306, 4·662;	2·353, 4·782.		

Nickel Chloride.

0·1188, 0·1662;	0·1975, 0·2820;	0·2158, 0·3113;	0·5380, 0·8482;
0·7864, 1·328;	0·9430, 1·661;	1·212, 2·284;	1·443, 2·872;
1·831, 3·942;	2·123, 4·81.		

Cupric Chloride.

0·1085, 0·1495;	0·1128, 0·1558;	0·2048, 0·2838;	0·2474, 0·3462;
0·2516, 0·3521;	0·3998, 0·5750;	0·5334, 0·7856;	0·6555, 0·9860;
0·7236, 1·107;	0·8388, 1·300;	0·9378, 1·472;	1·054, 1·677;
1·206, 1·945;	1·259, 2·035;	1·297, 2·105;	1·328, 2·157;
1·481, 2·430;	1·553, 2·574;	1·847, 3·106;	1·996, 3·366;
2·111, 3·577;	2·415, 4·121;	2·530, 4·314;	2·652, 4·522;
2·769, 4·729.			

From these measurements activity coefficients were evaluated with reference to the activity coefficients of potassium chloride recorded previously.[4] In an earlier paper [2] activity coefficients for cobalt chloride were given relative to $\gamma = 0{\cdot}570$ at 0·05 M. Now that isopiestic results are available for more salts of this type, it appears from a comparison of the isopiestic ratios at low concentrations that a more probable reference value would be $\gamma = 0{\cdot}526$ at 0·1 M. In Table II are given the activity coefficients of cobalt chloride recomputed on this basis.

[1] Sterling Fellow, Yale University, 1940.
[2] Robinson, *Trans. Faraday Soc.*, 1938, **34**, 1142.
[3] Robinson and Stokes, *ibid.*, 1940, **36**, 733.
[4] Robinson, *ibid.*, 1939, **35**, 1217.

No data are available with which to compare the results for manganese, cobalt and nickel chloride. Redlich and Rosenfeld [5] have made an estimate of the activity coefficient of cupric chloride which agrees with the values now obtained within 0·005 up to 1 M., but shows considerable divergence at 2 and 3 M.

The three salts, manganese, cobalt and nickel chloride have activity coefficients of the magnitude of calcium chloride, decreasing in the order : $NiCl_2 > CoCl_2 > MnCl_2$. Copper chloride is out of place in this series, its activity coefficient being comparable with that of barium chloride. Since magnesium, calcium, strontium, manganese, nickel and cobalt chloride form hexahydrates in the solid state, whereas copper and barium chloride form dihydrates, the low values of the activity coefficient of copper chloride may be associated with the lower amount of water co-ordinated with the ion in solution, and hence with a lower "ionic diameter." The next member of the series, zinc chloride, has a somewhat larger "ionic diameter" of 5 A., according to e.m.f. data at high dilutions,[3] and in the solid state can accommodate a maximum of four molecules of water of crystallisation. In dilute solution (< 0·4 M.) its activity coefficient is intermediate between copper chloride and strontium chloride but at higher concentrations its behaviour is complicated by the formation of intermediate or complex ions.

TABLE II.

ACTIVITY COEFFICIENTS OF MANGANESE, COBALT, NICKEL AND CUPRIC CHLORIDE AT 25°.

m.	MnC'_2.	$CoCl_2$.	$NiCl_2$.	$CuCl_2$.
0·1	0·522	0·526	0·526	0·501
0·2	0·474	0·482	0·483	0·447
0·3	0·454	0·466	0·468	0·423
0·4	0·446	0·463	0·465	0·409
0·5	0·446	0·465	0·468	0·405
0·6	0·448	0·473	0·476	0·403
0·7	0·455	0·483	0·489	0·403
0·8	0·463	0·496	0·504	0·405
0·9	0·474	0·514	0·522	0·408
1·0	0·486	0·533	0·542	0·411
1·2	0·516	0·578	0·595	0·419
1·4	0·554	0·635	0·660	0·430
1·6	0·596	0·706	0·737	0·442
1·8	0·637	0·785	0·826	0·454
2·0	0·682	0·884	0·935	0·466
2·2	0·732	—	—	0·478
2·4	—	—	—	0·489
2·6	—	—	—	0·500
2·8	—	—	—	0·512

Summary.

Data are presented for the activity coefficients of manganese, nickel, cobalt and copper chloride in aqueous solution at 25°.

Yale University,
New Haven, Conn.

Auckland University College,
New Zealand.

[5] Landolt-Bornstein, "*Tabellen*," 3^er^ *Ergänz.*, 2143.