210. *The Dissociation of the Selenates of Zinc and Cadmium in Water.*

By William H. Banks.

The deviations which appear when the Debye–Hückel equation for a completely dissociated electrolyte is applied to solutions of salts have been studied mainly in two ways. Gronwall and LaMer and their co-workers (*Physikal. Z.*, 1928, **29**, 558; *J. Physical Chem.*, 1931, **35**, 2245) have developed extended equations which are free from the mathematical approximations involved in the Debye–Hückel derivation, and have sought to interpret deviations from the latter as due to interaction of ions of small size. Davies and his co-workers (*Trans. Faraday Soc.*, 1927, **23**, 351; Banks, Righellato, and Davies, *ibid.*, 1931, **27**, 621; Money and Davies, *ibid.*, 1932, **28**, 609) have shown that solutions in which such deviations occur can be treated as if incompletely dissociated, and the deviations expressed quantitatively by means of dissociation constants.

The two treatments are not necessarily incompatible, although the author in collaboration with others has shown (*ibid.*, 1931, **27**, 621) that the Gronwall–LaMer treatment can only have a limited application and must break down with many salts. LaMer, Cowperthwaite, and Barksdale (*J. Amer. Chem. Soc.*, 1934, **56**, 544) have recently accepted this view and expressed the deviations shown by thallous chloride in terms of a dissociation constant.

Zinc and cadmium sulphates have been treated in both ways. LaMer and Cowperthwaite (*ibid.*, 1931, **53**, 4333) and LaMer and Parks (*ibid.*, p. 2040) have shown that the activity data for these salts can be fully accounted for by the Gronwall–LaMer equations, plausible values being used for the ionic radii. Davies has calculated dissociation constants from the conductivities of these salts (*Trans. Faraday Soc.*, 1927, **23**, 354) and has pointed out that, as closely similar values are obtained for these two salts and for a number of other metal sulphates, there are grounds for attributing the deviations wholly to electrostatic interaction. It therefore seemed of interest to study the corresponding selenates.

The conductivities of these two salts have been measured at 25°, and the following values calculated: zinc selenate, $\Lambda_0 = 128{\cdot}8$, $K = 0{\cdot}0065$; cadmium selenate, $\Lambda_0 = 130{\cdot}0$,

$K = 0·0054$. For zinc and cadmium sulphates the dissociation constants are 0·0045 and 0·0038. The data are compatible with the view that for each of these four salts both cation and anion are too strongly hydrated for any mutual polarisation of the ions to exert an appreciable influence, and hence large variations in dissociation constant such as occur with oxalates and halides of the transitional metals are absent.

EXPERIMENTAL.

Apparatus.—The measurements were carried out in a conductivity cell of the Hartley and Barrett type, constructed in transparent silica. The electrodes were of platinum coated with grey platinum. Conductivity water was obtained from a still of a modified Bourdillon type.

The resistance measurements were made at 25·00° ± 0·003°, the cell during measurement being immersed in an electrically heated oil-thermostat. The bridge was of normal design, employing the Wheatstone circuit, with a reading accuracy of about 0·01%; this is to be described more fully in a future publication, together with details of the cell-constant determination.

The cell constant, based on the Kohlrausch and Maltby standards (equiv. wt. for potassium chloride = 74·60), at 18° as a mean of 18 determinations was $4·777_8 \times 10^{-2}$ with an average deviation from the mean of 0·03%.

Preparation of Zinc Selenate.—Pure zinc carbonate was added in small quantities, with continued stirring, to an equivalent quantity of selenic acid (*d* 1·4) at room temperature. The crystals which separated over-night were dissolved in the minimum quantity of cold water and recrystallised by allowing the water to evaporate slightly in an evacuated desiccator. Mellor ("Comprehensive Treatise, etc.," Vol. 10) states that crystals so obtained consist of the stable hexahydrate. After two crystallisations, however, the crystals effloresced on storage; this apparent instability of the hydrate necessitated storage under the saturated aqueous solution. When required for use, the crystals were drained by suction, dried by pressing between filter-paper, ground finely in an agate mortar, re-pressed, and re-ground (Found: Zn, 20·58, 20·90. Calc. for $ZnSeO_4,6H_2O$: Zn, 20·63%). The powder was weighed in a glass tube and dropped into a flask containing a known weight of conductivity water.

Preparation of Cadmium Selenate.—13 C.c. of selenic acid were added to a suspension of 10 g. of cadmium carbonate in water. The mixture was warmed on a steam-bath and, after action had ceased, filtered through glass-wool and concentrated in a silica dish. The crystals formed on cooling were drained free of mother-liquor and recrystallised. This second crop of crystals was redissolved, and the solution concentrated (but not sufficiently to cause crystallisation). The cool solution was then treated with absolute alcohol, and the salt thus precipitated as a fine white powder was filtered off, dried gently at first and finally to constant weight at 105°. The salt was analysed by Daubney's method (*Analyst*, 1932, **57**, 22) (Found: Se, 28·87. Calc. for $CdSeO_4,H_2O$: Se, 28·95%); it was therefore the monohydrate, as stated by van Hauer (*J. pr. Chem.*, 1860, **40**, 214) and Daubney (*loc. cit.*).

Results.—The results obtained for two runs in each case are summarised in the tables, where the concentrations in cols. 1 are expressed in g.-equivs. per 1000 c.c. of solution, all weights being calculated on vacuum basis (density of $ZnSeO_4,6H_2O$ = 2·33; of $CdSeO_4,H_2O$ = 3·63). The equiv. wts. for the cadmium and zinc salts were taken as 136·82 and 158·34 respectively.

Cols. 2 show the specific conductivity (κ) of the solvent water, which was in each case subtracted from that of the solution. The final equivalent conductivities are given in cols. 3.

$ZnSeO_4$; $K_{mean} = 0·00651$.

$C \times 10^4$.	$\kappa \times 10^6$.	Λ.	$10^3/\Lambda_a$.	$\Lambda_a m f_{\pm}^2 \times 10^3$.	$K \times 10^5$.
2·0091	1·182	123·22	7·811	1·070	1162
4·9089	,,	118·57	7·934	2·328	729
7·6513	,,	115·29	8·032	3·348	661
10·409	,,	112·85	8·093	4·265	695
1·6739	0·431	123·15	7·841	0·904	595
3·1640	,,	120·54	7·903	1·592	630
5·6924	,,	117·12	7·993	2·625	613
7·6460	,,	115·13	8·042	3·340	637
9·3459	,,	113·50	8·085	3·915	648

$CdSeO_4$; $K_{mean} = 0·00542$.

$C \times 10^4$.	$\kappa \times 10^6$.	Λ.	$10^3/\Lambda_a$.	$\Lambda_a m f_{\pm}^2 \times 10^3$.	$K \times 10^5$.
2·6445	0·762	122·33	7·823	1·369	560
5·0764	,,	118·33	7·943	2·393	506
6·6907	,,	116·37	7·998	3·002	526
8·3719	,,	114·48	8·052	3·592	517
11·127	,,	111·83	8·137	4·477	525
3·3670	0·912	121·42	7·836	1·695	633
5·5239	,,	118·03	7·943	2·570	542
7·7998	,,	115·24	8·026	3·400	527
11·525	,,	111·76	8·127	4·607	547

Calculation of Dissociation Constants.—Since the value of Λ_0, the sum of the ionic mobilities at infinite dilution, is unknown, and it is also impossible to employ the " squareroot " rule, resort has been made to Davies's method (J., 1933, 645) in which Λ_0 is obtained graphically from the relation $1/\Lambda_a - 1/\Lambda_0 = \Lambda_a m f_{\pm}^2 / K \Lambda_0^2$, Λ_a being defined by $\Lambda_a = \alpha \Lambda_0$. The symbols have their usual significance. Λ_a is calculated by a series of approximations, and $f_{\pm}$ from $\log f_{\pm} = -0{\cdot}505 \times 4\sqrt{2C_i}$. The plotting data are shown in cols. 4 and 5 of the tables.

From the values of Λ_0 so obtained (see p. 1010) the sum of the ionic mobilities was calculated, for each concentration, from the Onsager equation, $\Lambda_x = \Lambda_0 - b\sqrt{C_i}$, and hence the degree of dissociation. The mass-action constants so obtained are shown under K in the last columns of the tables.

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