THE ACTIVITY COEFFICIENT OF ZINC SULPHATE FROM ELECTROMOTIVE FORCE MEASUREMENTS.

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In the early days of the development of the activity coefficient few investigators⁽¹⁾ reported on the activity coefficient of zinc sulphate in the following cell

$$\text{Zn (amalgam)} \mid ZnSO_4(m),\ Hg_2SO_4(s) \mid Hg \ \ldots\ldots\ldots\ldots \quad (1)$$

but the results may be uncertain by the solubility of mercurous sulphate. Recently Cowperthwaite and LaMer⁽²⁾ had the excellent investigation upon the cell

$$\text{Zn (2 phase amalgam)} \mid ZnSO_4(m),\ PbSO_4(s) \mid \text{Pb(2 phase amalgam)} \ldots \quad (2)$$

and determined the activity coefficient of zinc sulphate in the various concentrations which is in good conformity with the predictions of the Gronwall, LaMer and Sandved's⁽³⁾ extension of the Debye-Hückel theory.⁽⁴⁾

In this investigation we measured the electromotive force of the cell (1) with a more concentrated range on which Cowperthwaite and LaMer made no investigation and we calculated the activity coefficient of zinc sulphate.

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(1) Lehfeldt, *Z. physik. Chem.*, **35** (1900), 257; Cohen, Chattaway and Tombrock, *Z. physik. Chem.*, **60** (1907), 706; **61** (1907), 384; **75** (1910), 1.

(2) *J. Am. Chem. Soc.*, **53** (1931), 4333.

(3) *Physik. Z.*, **29** (1928), 358.

(4) Ibid, **24** (1923), 185.

Theoretical.

Debye and Hückel introduced an approximate equation early in the development of their theory of strong electrolytes, solving the Poisson's equation by retaining only the linear term resulting from the expansion of the exponential in the Boltzmann's expression for the density of electricity for mathematical simplicity and they had many experimental investigations which demonstrated that the activity coefficients of strong electrolytes in aqueous solution agree fairly well with the predictions given by their equations. But even in regions of high dilution there are serious discrepancies between the calculated values from these equations and the experimental data. Gronwall, LaMer and Sandved obtained the following expression, solving the Poisson's equation by using the complete form of the Boltzmann's expression, for the activity coefficient of an electrolyte of symmetrical type, i.e. $Z_1 = - Z_2 = Z$.

$$\log f = -\frac{\epsilon^2 Z^2}{kTDa} \times \frac{1}{2} \times \frac{x}{1 \times x} + \sum_{m=1}^{\infty} \left(\frac{\epsilon^2 Z^2}{kTDa} \right)^{2m+1} \left[\frac{1}{2} X_{2m+1}(x) - 2m Y_{2m+1}(x) \right]. \quad (3)$$

In the above equation, $x = Ka$, and $K = \sqrt{\frac{8\pi N \epsilon^2 Z^2 c}{1000kTD}}$, D is the dielectric constant of water ($D = 78{,}54\,[1 - 0.0046\,(t - 25) + 0.0000088\,(t\text{-}25)^2]$)(1), Z is the valence of the cation and anion, ϵ is the charge of an electron ($\epsilon = 4.774 \times 10^{-10}$), k is Boltzmann's constant ($k = 1.372 \times 10^{-16}$), N is Avogadro's number ($N = 6.061 \times 10^{23}$), $\bar{a}$ is the distance of closest approach of the two ions, c is the concentration in moles per litre of solution, and $X(x)$ and $Y(x)$ are known functions of x.

Putting numerical values in (3) Gronwall, LaMer and Sandved got the following working equation

$$-\log_{10} f = 1.53636 \left(\frac{Z^2}{a} \right) \frac{x}{1+x} - 0.15382 \left(\frac{Z^2}{a} \right)^3 \cdot 10^3 \left[\frac{1}{2} X_3(x) - 2Y_3(x) \right]$$
$$-0.0770 \left(\frac{Z^2}{a} \right)^5 \cdot 10^5 \left[\frac{1}{2} X_5(x) - 4Y_5(x) \right] \;\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Numerical values for the functions $10^3[\frac{1}{2}X_3\,(x) - 2Y_3\,(x)]$ and $10^5[\frac{1}{2}X_5(x) - 4Y_5(x)]$ were tabulated by the Gronwall, LeMer and Sandved for various assigned values of x. Therefore the value for these functions at any desired x may be obtained from their tables by interpolation.

Wyman, *Phys. Rev.*, **35** (1930), 623.

The electromotive force of the cell (1), corresponding to the following process.

$$\mathrm{Zn(solid)+Hg_2SO_4(solid) = Hg(liquid)+ZnSO_4}(m) \quad \ldots\ldots\ldots \quad (5),$$

is given by the equation

$$\begin{aligned} E &= E_0-\frac{RT}{2F}\ln m_{\mathrm{Zn}^{++}}\cdot f_{\mathrm{Zn}^{++}}-\frac{RT}{2F}\ln m_{\mathrm{SO}_4^{--}}\cdot f_{\mathrm{SO}_4^{--}} \\ &= E_0-\frac{RT}{2F}\ln m_{\mathrm{Zn}^{++}}-\frac{RT}{2F}\ln m_{\mathrm{SO}_4^{--}}-\frac{RT}{2F}\ln f_{\mathrm{Zn}^{++}}\cdot f_{\mathrm{SO}_4^{--}} \\ &= E_0-\frac{RT}{2F}\ln m_{\mathrm{Zn}^{++}}-\frac{RT}{2F}\ln m_{\mathrm{SO}_4^{--}}-\frac{RT}{F}\ln f\pm \quad \ldots\ldots\ldots\ldots \quad (6) \end{aligned}$$

For 25°C., this equation (6) takes the following form

$$E = E_0-0.05915\log m-0.05915\log f \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

For convenience in plotting and calculating the mean activity coefficient $f_{\mathrm{ZnSO}_4} = \sqrt{f_{\mathrm{Zn}^{++}}\cdot f_{\mathrm{SO}_4^{--}}}$, we calculate the quantity E_0', where

$$E_0' = E+0.02957\log m+0.02957\log m \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

$$E_0' = E_0-0.05915\log f \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

and the intercept of extrapolated E_0' at zero concentration gives the value of E_0.

Experimental.

Preparation of Materials. Mercurous sulphate: Kahlbaum's "for analysis" was employed and kept in the dark room.

Zinc sulphate: Kahlbaum's "for analysis" was employed without recrystallization. The salt was dissolved in conductivity water and stored in a steamed-out hard glass flask equipped with a stopper which was deviced to make the evaporation least possible.

Mercury: Purified mercury was washed ten times with a mixture of dilute mercurous nitrate and nitric acid and distilled thrice in a reduced pressure with a current of air.

Zinc: A purest profitable zinc stick was employed.

Zinc amalgam: The zinc stick stated above was attached to a nip of a Pt wire which was sealed into a glass tube at the end. Then the joint and Pt part was covered with highest grade sealing wax, and the zinc was amalgamated after being scraped clean from oxide.

Analysis of Zinc Sulphate Solution. Kahlbaum's zinc sulphate was dissolved in conductivity water to form a stock solution from which dilutions were made by weight. Besides, a weighed salt was dissolved in a weighed quantity of conductivity water to prove the accuracy of the analytical method employed. The determinations of the concentration was performed as described by Cowperthwaite and LaMer. A weighed sample of the solution was carefully evaporated to dryness in a steam oven and then the residue was heated in an air oven at 300°C. for several hours after treated with a small quantity of strong sulphuric acid. Then the bottle was cooled in a desiccator and weighed. Then treating with sulphuric acid, heating at 300°C. and weighing were repeated till the weight of the dried mass became constant. The residue was the weight of anhydrous zinc sulphate. This method is quite satisfactory. The reference solution which was made to be 1.03955 mol was determined by this method as 1.03967 mol. The error was only 0.02% and in a region of the experimental error. The stock solution was determined as 1.16994 mol.

Experimental Method. According to Landolt's "Physikalisch-chemische Tabellen" the system of zinc-mercury forms no compound nor solid solution and the composition of the liquid phase is definite at a given temperature when the solid phase coexists. Hence an amalgamated zinc can be employed as a reversible and reproducible zinc electrode. We made pairs of electrodes mentioned above and each of them was proved to be identical within 0.02 mv. They were kept in the nitrogen atmosphere to prevent the oxidation. But in its practical employment at the temperature 25°C. the presence of air is considered to give a little effect on it. The cells gave a constant electromotive force within two or six hours even in air. A slight scum on the surface of the cathode was found after four days.

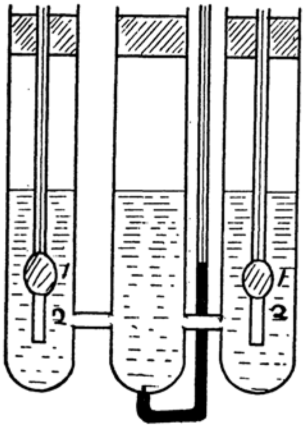

Fig. 1.

The zinc sulphate solutions which were made by weight from the stock solution were saturated with mercurous sulphate in a thermostat maintained at 25°+0.05°C. for two days with frequent shaking. The cells used had the special form as Fig. 1. In this figure, 1: the red wax, 2: zinc amalgam. The electromotive forces of the cell were measured after being kept in the thermostat at

25°C. for one hour and the average values of two or three cells were described in the table.

Experimental Data. The experimental values of the electromotive force and the computed function E are given in Table 1. The observed electromotive force given in column 3 is the average value of two or three cells, each of the cell being nearly idential with a little difference of 0.05 mv. A correction for the solubility of mercurous sulphate is

Table 1.

E.M.F. of the Cell Zn-Hg (sat. amalgam) | $ZnSO_4(m)$, $Hg_2SO_4(s)$ | Hg at 25°C.

No.	Molality of $ZnSO_4$	E (obs.)	Molality of total SO_4^{--}	0.02957 log m Zn^{++}	0.02957 log m SO_4^{--}	E_0'
1	3.000	1.43048	3.000	+0.01411	+0.01411	1.45870
2	2.500	1.43646	2.500	.01177	.01177	1.46000
3	2.000	1.44375	2.000	.00891	.00891	1.46156
4	1.800	1.44648	1.800	.00755	.00755	1.46158
5	1.600	1.44803	1.600	.00604	.00604	1.46010
6	1.400	1.45094	1.400	.00432	.00432	1.45958
7	1.000	1.45595	1.000	.00000	.00000	1.45595
8	1.16994	1.45415	1.17014	.00202	.00202	1.45819
9	0.934504	1.45736	0.934676	− .00087	− .00087	1.45562
10	.699756	1.46240	.699959	.00458	.00458	1.45108
11	.465742	1.46547	.465939	.00981	.00981	1.44585
12	.387925	1.46708	.388101	.01216	.01216	1.44276
13	.232547	1.47292	.232736	.01874	.01873	1.43535
14	.165698	1.47736	.165909	.02309	.02308	1.43119
15	.128833	1.48073	.129053	.02632	.02630	1.42811
16	.105386	1.48301	.105639	.02890	.02887	1.42524
17	.0891541	1.48498	.0893737	.03104	.03101	1.42293
18	.0772633	1.48663	.0774078	.03288	.03285	1.42090
19	.0681679	1.48832	.0684336	.03449	.03444	1.41939
20	.0609883	1.48973	.0612565	.03592	.03586	1.41795
21	.0441321	1.49295	.0444176	.04008	.04001	1.41286
22	.0101087	1.51370	.0105397	0.5901	.05847	1.39622
23	.0039726	1.52326	.0045819	.07101	.06916	1.38303
24	.0020793	1.52808	.0028429	.07932	.07529	1.37347
25	.0008558	1.53310	.0018150	.09072	.08106	1.36132
26	.0004321	1.53465	.0015055	.09950	.08346	1.35169

necessary at the concentration of 0.232547 molal solution or less. This was made by calculating the increase of concentration of sulphate ion in the solution which is due to the slight solubility of the mercurous sulphate, and calculating the potential resulting therefrom.

Drucker⁽¹⁾ reported the solubility of mercurous sulphate at 25°C. to be 11.71×10^{-4} mol per litre. LaMer and Parks⁽²⁾ studied the parameter of $CdSO_4$ and reached to the conclusion that the value is larger than 3.6 Å but less than 3.7 Å. Also Cowperthwaite and LaMer got the value 3.64 Å for zinc sulphate. Hereupon we assumed that for mercurous sulphate the parameter $\bar{a}$ is 3.7 Å. Then by the Gronwall, LaMer and Sandved's equation we can find the activity coefficient f as 0.704. In order to calculate the increase in sulphate ion we used the equation

$$m_{Hg_2^{++}} \cdot f_\pm \cdot m_{SO_4^{--}} \cdot f_\pm = a_{Hg_2^{++}} \cdot a_{SO_4^{--}} = k = 6.80 \times 10^{-7}$$

Then an approximation was performed as

$$x(fm+x) = k \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (10)$$

where x is the mean activity resulting from the mercurous sulphate dissolved, and the mean activity coefficient was calculated by (4) at concentration m. The solubility was obtained by x/f. Accurately saying, f is the mean activity coefficient at $m+f/x$, and repeated calculations are necessary for dilute solutions. The procedure is as follows.

The solubility m_1 obtained by the first calculation was added to m and f_2 was calculated at $(m+m_1)$ and x_2 was obtained by (10). This procedure was repeated to get a practically constant solubility. For instance for No. 26.

By 1st calculation	2nd	3rd	4th	5th	6th
$m_{Hg_2SO_4} = 0.000842$	0.0010276	0.0010659	0.0010720	0.0010734	0.0010734

The values of E_0' are shown graphically in Fig. 2. The values for dilute solutions, where the solubility of mercurous sulphate amounts to some 4% or more of the total concentration, abnormally decreases with increasing dilution.

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(1) *Z. anorg. Chem.*, **28** (1901), 362.

(2) *J. Am. Chem. Soc.*, **53** (1931), 2040.

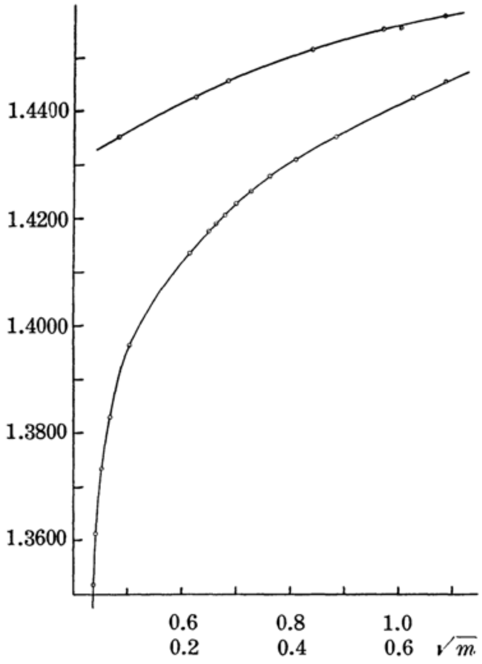

Fig. 2.

Discussion of Results. The abnormal decrease of E_0' in highly dilute solutions prevents us from the interesting application of the Gronwall, LaMer and Sandved's extension of the Debye-Hückel's theory. Because the extension is expected to be valid in the concentration range up to 0.01 molal solution. The cause of the anomaly can be attributed to either the self discharge effect or the absurd assumption that the parameter $\bar{a}$ of mercurous sulphate is 3.7 Å. Upon these problems we will render the same discussion in a following paper. Cowperthwaite and LaMer determined the activity coefficient of zinc sulphate in dilute solution at 25°C. as follows.

Molality	0.0005	0.001	0.002	0.005	0.01	0.02	0.05
Calc.	0.780	0.701	0.608	0.478	0.386		
Obs.	0.780	0.700	0.608	0.477	0.387	0.297	0.206

We used these data for the determination of E_0 and the activity coefficient in more concentrated parts. For by the equation

$$E_0' = E_0 - 0.05915 \log f$$

we can polt $E_0' - E_0$ against the square root of the molality to which the activity coefficient is assigned, and the extrapolation of our data to higher dilutions was carried out strictly parallel to the curve $E_0'-E_0$. This is shown in Fig. 3.

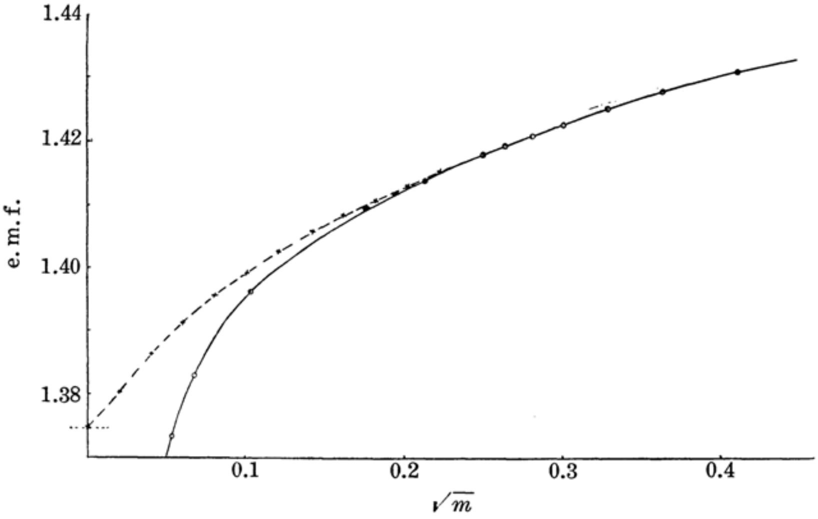

Fig. 3.

Table 2.
The Activity Coefficient of Zinc Sulphate at 25°C.

No.	Molality of total SO_4^{--}	Activity Coef. $E_0=1.37375$	$E_0=1.37470$	$E_0=1.37480$
1	3.000	0.0381		
2	2.500	0.0362		
3	2.000	0.0341		
4	1.800	0.0340		
5	1.600	0.0361		
6	1.400	0.0368		
7	1.000	0.0422		
8	1.17014	0.0389	0.0388	0.0389
9	0.934676	0.0429	0.0429	0.0430
10	0.699959	0.0493	0.0492	0.0494
11	0.465939	0.0628	0.0627	0.0629
12	0.388101	0.0708	0.0707	0.0710
13	0.232736	0.0945	0.0943	0.0947
14	0.165909	0.1111	0.1107	0.1113
15	0.129053	0.1253	0.1251	0.1255
16	0.105639	0.1401	0.1400	0.1403
17	0.0893737	0.1533	0.1530	0.1536
18	0.0774078	0.1659	0.1656	0.1662
19	0.0684336	0.1759	0.1756	0.1762
20	0.0612565	0.1860	0.1856	0.1864

We find graphically joint of the E'_0—E_0 curve and the experimental E'_0 curve where the dissolved mercurous sulphate is so little as to give no effect on the study of E_0. Thus we find E_0 as 1.37475. The activity coefficient calculated by this value for E_0 is tabulated in Table 2. The most possible value for E_0 is 1.37475, but two slightly different values are used to the calculation of the activity coefficient. These results are given in columns 2 and 3.

Using the values measured by Cowperthwaite and LaMer, we tabulated the activity coefficient of zinc sulphate for round concentration in Table 3. The third column was compiled from the data of LaMer and Parks for cadmium sulphate at 25°C.

Table 3.

Mean Activity Coefficient for Round Concentration.

Molality	$ZnSO_4$	$CdSO_4$
1.000	0.0422	0.0418
0.500	0.0596	0.0605
0.200	0.101	—
0.100	0.144	0.137
0.050	—	0.199
0.010	0.387	0.383
0.005	0.477	0.476
0.002	0.608	—
0.001	0.700	0.699
0.0005	0.780	0.774

Summary.

1. Electromotive forces of the cell, Zn-Hg (sat amalgam) | $ZnSO_4(m)$, $Hg_2SO_4(s)$ | Hg, were measured at 25°C. in the range of the concentrations of 0.0004321 to 3 molål.

2. The electromotive force of higher dilutions is quite abnormal owing to the solubility of mercurous sulphate.

3. The mean activity coefficients of zinc sulphate for more concentrated parts were calculated by using the Cowperthwaite and LaMer's data about dilute solutions. The potential E_0 of the cell, when ion activities of zinc sulphate are hypothetically one molal, was found to be 1.37475 volt at 25°C.

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