Summary

The magnetic susceptibilities of europium and ytterbium in the form of the di- and trivalent sulfates have been determined. The values obtained check well with known values except in the case of ytterbic sulfate. The low value recorded is thought to be due to the absence of thulium in the material used.

The susceptibility of an earth in the divalent state is found to approach that of the earth of next higher atomic number in the trivalent state.

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The Activity Coefficient of Potassium Chloride in Aqueous Solutions at 0° from Electromotive Force and Freezing Point Data

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Since the electromotive forces of cells with flowing amalgams have been used extensively to determine activity coefficients, and since some question as to their applicability has arisen, it is of importance to have a direct comparison between such results and those obtained by some other accurate method. The recent values of the activity coefficients of potassium chloride calculated by Spencer[1] from freezing point measurements should serve as a good standard for comparison. While the activity coefficients of potassium chloride at 25° determined by Harned[2] from electromotive force measurements are in close agreement with those obtained from vapor pressure measurements, they are not in good agreement with the values obtained from freezing point measurements, corrected to 25° by the use of available calorimetric data. To make a fair comparison between the two methods, both determinations should be made at nearly the same temperature so that the temperature correction is either negligible or a very small quantity.

For this purpose the electromotive force of the cell

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{KCl}\ (m) \mid \mathrm{KxHg} \mid \mathrm{KCl}\ (0.1) \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

has been measured at 0°. The cells and the procedure were similar to those described by Harned[2] for type 2 electrodes. The temperature was maintained at less than 0.1° by a stirred ice-bath with a capacity of 300 lb. of cracked ice.

The relation between the electromotive force and the activity coefficient for this cell at 0° is given by the equation[3]

$$E = 0.10844 \log (\gamma \times m)/(\gamma_{0.1} \times 0.1) \qquad (1)$$

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(1) Spencer, THIS JOURNAL, **54**, 4490 (1932).

(2) Harned, *ibid.*, **51**, 416 (1929).

(3) The constants used are those given by Birge, *Phys. Rev. Suppl.*, I, 1, 1929.

Since the activity coefficients calculated from this equation not only depend upon the value of E, but also on the value of the activity coefficient at the reference concentration, it is important to have a reliable method of determining $\gamma_{0.1}$. The usual practice has been to determine the constants for a Debye–Hückel equation of the type

$$\log \gamma = \frac{-k\sqrt{2c}}{1 + A\sqrt{2c}} + B \times 2c - \log(1 + 0.036m) \qquad (2)$$

by combining this equation with equation 1, using values of E at relatively high concentrations. Since it is known that an equation of this type holds, in most cases, only over a limited range of concentration, the value of $\gamma_{0.1}$ may depend to some extent on the concentration range chosen for the determination of the constants of the equation. For this reason two methods have been used to determine the activity coefficient at the reference concentration.

Method 1.—Assuming the above equation may be made to fit the experimental results in the concentration range from 0.1 m to 1.0 m the constants A and B may be computed and the value of $\gamma_{0.1}$ calculated. Since

$$\frac{E}{0.10844} = \log\frac{\gamma \times m}{\gamma_0 \times m_0} = \log\frac{m}{m_0} - \frac{k\sqrt{2c}}{1 + A\sqrt{2c}} + \frac{k\sqrt{2c_0}}{1 + A\sqrt{2c_0}} + 2\mathrm{B}(c - c_0) - \log\frac{(1 + 0.036m)}{(1 + 0.0036)} \qquad (3)$$

where $k = 0.3443$,[4] the values of A and B may be obtained from two experimental values of E, or by using four experimental values of E the terms relating to the reference concentration may be eliminated, leaving two equations of the type

$$\frac{E_1 - E_2}{0.10844} + \log\frac{m_2}{m_1} + \frac{k\sqrt{2c_1}}{1 + A\sqrt{2c_1}} - \frac{k\sqrt{2c_2}}{1 + A\sqrt{2c_2}} + \log\frac{(1 + 0.036m_1)}{(1 + 0.036m_2)} = 2B(c_1 - c_2) \qquad (4)$$

which may be solved for A and B. Using the latter method with values of E at 0.1 m, 0.7 m, 0.2 m and 1.0 m, the following equation is obtained

$$\log \gamma = \frac{-0.3443\sqrt{2c}}{1 + 0.788\sqrt{2c}} + 0.00672 \times 2c - \log(1 + 0.036m) \qquad (5)$$

This equation gives a value for the activity coefficient at 0.1 m of 0.769. A similar method has been used by Saxton and Smith.[5]

Method 2.—If equation 2 be written in the form

$$\frac{E}{0.10844} - \log\frac{m}{m_0} + \frac{k\sqrt{2c}}{1 + A\sqrt{2c}} - \frac{k\sqrt{2c_0}}{1 + A\sqrt{2c_0}} + \log\frac{(1 + 0.036m)}{(1 + 0.036m_0)} = B(c - c_0) \qquad (6)$$

it is clear that the left-hand side plotted against $c - c_0$ should be a straight line if the equation fits the data. Choosing a reasonable value of A it is

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[4] The dielectric constant used is that given by Wyman, *Phys. Rev.*, **35**, 623 (1930).

[5] Saxton and Smith, THIS JOURNAL, **54**, 2626 (1932).

found that the resulting plot is not a straight line. To make the equation fit the experimental results another term $D(c^2 - c_0^2)$ may be added to the right-hand side of the equation.[6] Having taken a value for A the constants B and D may be found graphically or by solving two simultaneous equations. The latter method has been used, with values of E at 1.0 m and 3.0 m concentrations. Within certain limits the choice of "a" is arbitrary, in this case a value of a = 3.5 Å., 3.6 Å. or 3.7 Å. will give an equation reproducing the experimental results with an accuracy within the experimental error. Using a value of a = 3.6 Å. the following equation is obtained

$$\log \gamma = \frac{-0.3443\sqrt{2c}}{1 + 0.826\sqrt{2c}} + 0.00302\,c + 0.00574\,c^2 - \log(1 + 0.036\,m) \qquad (7)$$

which gives a value for the activity coefficient at 0.1 m of 0.770.

Table I, column 2, gives the values of the electromotive force read from a curve drawn through the experimental points; the maximum deviation from the curve was about 0.2 mv., column 3, the values of γ determined from equation (1) using $\gamma_{0.1}$ = 0.770, column 4, the values of γ from freezing point data reported by Spencer corrected to 0°, column 5, the values of γ from equation 7, column 6, the values of γ from equation 5, and column 7, the concentration in mols per liter. The densities used are those given in the "International Critical Tables."

TABLE I

m	E	γ exp.	γ f. p.	γ Eq. 7	γ Eq. 5	
0.001			0.966	0.966	0.966	
.002			.953	.953	.953	
.005			.929	.929	.929	
.01			.903	.904	.904	
.02			.872	.873	.873	0.01998
.05			.818	.820	.818	.04993
.10		(0.770)	.771	.770	.769	.09973
.20	0.02926	.717	.719[a]	.716	.715	.19899
.35	.05271	.674	.674	.671	.670	.34691
.50	.06723	.642	.645	.642	.641	.49367
.70	.08109	.615		.615	.615	.68753
.75			.612	.610	.610	.73567
1.00	.09579	.589	.590	.589	.588	.97436
1.25			.573	.574	.571	1.20914
1.50	.11274	.562	.561	.563	.558	1.44169
2.00	.12508	.548		.548	.539	1.89560
2.50	.13499	.541		.542		2.33610
3.00	.14348	.540		.540		2.76342
3.50	.15092	.542		.543		3.17775

[a] The value of 0.737 was originally published. In a private communication Dr. H. M. Spencer has pointed out that a numerical error had been made and that the correct value is 0.719.

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(6) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

The agreement between the results obtained from the freezing point data and those obtained from the electromotive force measurements is seen to be within the experimental accuracy of our method. Consequently there is every reason to believe that the amalgam cell reaction represents the postulated transfer in the range of concentration from 0.1 *m* to 3.5 *m*, and that the flowing amalgam electrode is reversible.

The measurements are to be extended to other temperatures.

Since this paper was submitted for publication Dr. George Scatchard has kindly sent me some recent results obtained by himself and Dr. Prentiss on the activity coefficient of potassium chloride in aqueous solutions obtained from freezing point measurements. He gives the value of $\gamma_{0.1}$ as 0.773, which differs slightly from the value given by our results. We do not consider this small discrepancy as serious since one would expect that a method which allowed measurements in the dilute range would give more accurate values than our method where the results must be determined by the extrapolation of measurements at high concentrations. On the other hand, if we take 0.773 as the reference point at 0.1 *M*, our values of γ agree with those of Scatchard and Prentiss to within one in the third decimal place of activity coefficient.

Summary

1. The electromotive force of the cell Ag | AgCl | KCl (1 *m*) | K_xHg | KCl (0.1 *m*) | AgCl | Ag has been measured at 0°.

2. The activity coefficient at the reference concentration has been determined by two methods.

3. The activity coefficient of potassium chloride has been calculated from 0.1 *m* to 3.5 *m*, at 0°, and shown to be in good agreement with the values obtained from freezing point measurements.

4. An extended Debye–Hückel equation is given which reproduces the activity coefficient of potassium chloride at 0° over the entire concentration range.

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