be less suitable for our purpose (presence of hydrochloric acid as one of the constituents, total concentration too low to obtain significant departures from the old mixture rule, etc.).

Remarks.—(6) could also be written in terms of mobilities

$$u_{\text{Cl}} = xu^{\circ}_{\text{Cl.A}} + (1 - x)u^{\circ}_{\text{Cl.B}} \qquad (11)$$

From (1.2), (2.2) and (11) we deduce the interesting relations

$$u_{\text{A}} = [xu^{\circ}_{\text{Cl.A}} + (1 - x)u^{\circ}_{\text{Cl.B}}]\,(T^{\circ}_{\text{A}}/T^{\circ}_{\text{Cl.A}}) \qquad (12.1)$$

$$u_{\text{B}} = [xu^{\circ}_{\text{Cl.A}} + (1 - x)u^{\circ}_{\text{Cl.B}}]\,(T^{\circ}_{\text{B}}/T^{\circ}_{\text{Cl.B}}) \qquad (12.2)$$

and the limiting mobilities of ion A^+ at infinite dilution in BCl and of ion B^+ at infinite dilution in ACl

$$[\lim u_{\text{A}}]_{x=0} = u^{\circ}_{\text{Cl.B}} \cdot \frac{T^{\circ}_{\text{A}}}{T^{\circ}_{\text{Cl.A}}} = u^{\circ}_{\text{A}}\,\frac{u^{\circ}_{\text{Cl.B}}}{u^{\circ}_{\text{Cl.A}}} \qquad (13.1)$$

$$[\lim u_{\text{B}}]_{x=1} = u^{\circ}_{\text{Cl.A}} \cdot \frac{T^{\circ}_{\text{B}}}{T^{\circ}_{\text{Cl.B}}} = u^{\circ}_{\text{B}}\,\frac{u^{\circ}_{\text{Cl.A}}}{u^{\circ}_{\text{Cl.B}}} \qquad (13.2)$$

Figure 2 gives the ratios $u_{\text{K}}/u^{\circ}_{\text{K}}$ and $u_{\text{Na}}/u^{\circ}_{\text{Na}}$ in terms of x for mixtures of potassium chloride and sodium chloride of a total concentration of 2 moles per liter. We notice that in the mixture the potassium ion moves more slowly and the sodium ion more rapidly than in solutions of the pure salts. This is in qualitative agreement with the theoretical deductions of Onsager and Fuoss for very dilute solutions.[12]

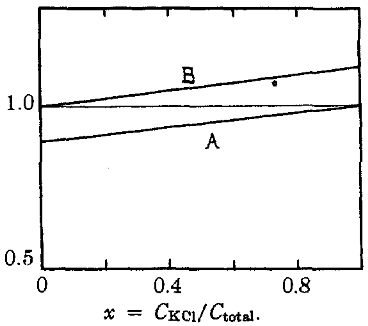

Fig. 2.—Mobility ratios $u_{\text{K}}/u^{\circ}_{\text{K}}$(A) and $u_{\text{Na}}/u^{\circ}_{\text{Na}}$ (B) in 2 M mixtures of KCl and NaCl.

Summary

1. A formula is obtained giving the equivalent conductivity of a mixture of alkali chlorides in terms of the conductivities and transport numbers of the pure salts at the same concentration as the total concentration of the mixture.

2. Measured and calculated conductivities of mixtures of potassium and sodium chloride agree remarkably well up to as high a total concentration as 4 moles per liter.

3. It is shown that at concentrations of the order of 0.1 mole per liter the new formula and the old mixture rule give the same results.

STANFORD UNIV., CALIF. RECEIVED DECEMBER 11, 1933

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[12] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Activity Coefficients of Sulfuric Acid in Aqueous Solutions of Ammonium Sulfate at 25°

BY H. D. CROCKFORD AND N. L. SIMMONS, JR.

Electromotive force data on solutions of various sulfates in sulfuric acid have been obtained by Harned and Sturgis[1] from a study of cells of the type

$$H_2 \mid H_2SO_4\ (m_1),\ M_2SO_4\ (m_2) \mid Hg_2SO_4 \mid Hg$$

wherein m_2 represents potassium or sodium and m_1 (H_2SO_4) = 0.1 and 0.01. Measurements were also made with magnesium sulfate. Åkerlöf[2] extended the measurements to m_1 (H_2SO_4) = 0.05 and 0.005, and included lithium sulfate as an added salt. Randall and Langford[3] have extended the data with sodium sulfate up to concentrations of 2 molal in various acid concentrations. All the above work was carried out at 25°.

In this paper are given data for the above cell with ammonium sulfate as the added salt and with m_1 (H_2SO_4) = 0.1 and 0.01 and at a temperature of 25°. These results are directly comparable to those obtained by Harned and Sturgis with sodium and potassium sulfates at these acid concentrations. From the results the activity coefficients of the acid have been calculated.

Experimental Procedure

All reagents employed were purified carefully and where necessary were analyzed according to the accepted methods. All electrical measuring instruments had been calibrated by the Bureau of Standards. The temperature was accurate to ±0.03°. The usual experimental procedure was followed.

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[1] Harned and Sturgis, THIS JOURNAL, **47**, 945 (1925).

[2] Åkerlöf, *ibid.*, **48**, 1160 (1926); *Physik. Z.*, **27**, 411 (1926).

[3] Randall and Langford, THIS JOURNAL, **49**, 1445 (1927).

The cell employed was so constructed that two hydrogen electrodes could be used with the same mercurous sulfate electrode. Equilibrium was realized in approximately ten minutes. Potentials would then remain constant until poisoning from the mercury ions resulted. The potentials given are an average of at least four readings with different hydrogen electrodes. In many cases two mercurous sulfate electrodes were employed. All voltage readings are corrected to a pressure of 1 atmosphere of hydrogen.

Data and Conclusions

In Table I are given the corrected electromotive force values for the various molalities of ammonium sulfate in the two acid concentrations. The ionic strengths of the solutions and the activity coefficients of the acid are included. Potential values are accurate to at least 0.1 mv. Average deviations were smaller than this figure.

For the calculations of γ the following thermodynamic equations were employed

$$\Delta E = \frac{RT}{2F} \ln \frac{a^2{}_{\mathrm{H}}(\mathrm{s})\, a_{\mathrm{SO_4}}(\mathrm{s})}{a^2{}_{\mathrm{H}}\, a_{\mathrm{SO_4}}} = \frac{3}{2}\,\frac{RT}{F}\, \frac{\sqrt[3]{a^2{}_{\mathrm{H}}(\mathrm{s})\, a_{\mathrm{SO_4}}(\mathrm{s})}}{\sqrt[3]{a^2{}_{\mathrm{H}}\, a_{\mathrm{SO_4}}}}$$

$$= \frac{3}{2}\,\frac{RT}{F} \ln \frac{a_{\pm}(\mathrm{s})}{a_{\pm}} = 0.08872 \log \frac{a_{\pm}(\mathrm{s})}{a_{\pm}}$$

S refers to the solution of the salt. $a_{\pm}(\mathrm{s})$ is the cube root of the activity product of the acid in the solution which contains the salt and $a_{\pm}$ is the cube root of the activity product in the acid solution without the salt. Therefore if $a_{\pm}$ is known, $a_{\pm}(\mathrm{s})$ can be calculated. The activity coefficient can be calculated from the equation

$$y = a_{\pm}(\mathrm{s})/(m^2{}_{\mathrm{H}} m_{\mathrm{SO_4}})^{1/3}$$

To employ these equations the electromotive force of the cell without added salt must be known accurately. The difference between this value and the measured E, that is ΔE, is the potential characteristic of the work involved in the process of transferring the acid from the salt solution to that of the pure acid.

There is poor agreement between the various sources as to the activity coefficient of sulfuric acid in aqueous solutions. However, since we wished to compare our data with those of Harned and Sturgis on sodium and potassium sulfate, we employed the values used by them. For 0.1 molal solutions they used for γ a value of 0.313; for 0.01 molal solutions a value of 0.662.

TABLE I

Molality of $(NH_4)_2SO_4$	H_2SO_4, $m = 0.1$			H_2SO_4, $m = 0.01$		
	E_{298}	μ	γ	E_{298}	μ	γ
0	0.7372	0.30	0.313	0.7971	0.03	0.662
0.01	.7375	.33	.301	.7952	.06	.552
.04	.7382	.42	.273	.7964	.15	.395
.10	.7397	.60	.233	.7997	.33	.278
.20	.7430	.90	.187	.8037	.63	.202
.30	.7456	1.20	.159	.8065	.93	.165
.50	.7497	1.80	.125	.8102	1.53	.127
1.0	.7558	3.30	.087	.8153	3.03	.089
2.0	.7616	6.30	.060	.8215	6.03	.060

If the electromotive force is plotted against the concentration of added salt a minimum is found in the case of the 0.01 molal acid and is indicated in the case of the 0.1 molal acid. This is in accord with the work of the other investigators cited and as explained by Åkerlöf is due to the solubility of the mercurous sulfate in the more dilute solutions. As the change in these minima is small the plot of γ against μ does not show them. In the γ against μ plots it is found that the values obtained in this investigation fall on a curve between the values for sodium and potassium sulfate solutions. The values are nearer the sodium sulfate curve. Consequently the effect of the ammonium sulfate on the activity coefficient of the sulfuric acid is between that of sodium sulfate and potassium sulfate.

Acknowledgment is made to the Rockefeller Fund for the original purchase of part of the equipment used in the investigation.

Summary

1. Measurements have been made of the electromotive force of the cells

$H_2 \mid (NH_4)_2SO_4\ (m)\ H_2SO_4\ (m = 0.1 \text{ and } 0.01) \mid Hg_2SO_4 \mid Hg$

2. From the measurements the activity coefficients of the sulfuric acid have been calculated.

CHAPEL HILL, N. C. RECEIVED FEBRUARY 5, 1934