[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ACTIVITY OF WEAK ACIDS IN AQUEOUS SULFATE SOLUTIONS

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It was shown in another place[1] that sulfates cause a marked rise in the activity coefficient of aqueous solutions of non-electrolytes. It was also shown in the previous article that the effect of salts was in general the same upon the activity coefficient of the undissociated part of weak acids and moderately strong acids as that upon non-electrolytes.

When we consider the total effect of sulfates upon the escaping tendency of acids of intermediate strength, the salting-out effect is greatly overshadowed by the removal of hydrogen ion to form hydrosulfate ion. Thus, in two solutions of a weak acid at a fixed activity, we have $(m_+'m_-')/(m_+m_-) = \gamma_\pm^2/\gamma_\pm'^2$, where m and m' are the molalities of the two solutions. If one of the solutions contains sulfate, there is formation of hydrosulfate ion with the removal of hydrogen ion from the solution. Consequently a larger molality of acid anion must be present to maintain equilibrium and the total molality will be increased.

Partially neutralizing this effect will be an increase in the activity coefficient of the undissociated molecules $m_u'/m_u = \gamma_u/\gamma_u'$. This effect will decrease the concentration of undissociated molecules, and the observed change in the molality of the acid, whose activity is held constant on adding sulfate, will be the algebraic sum of the change in the molality of acid anion and of undissociated molecules. The increase in total acid molality will be greater the larger the dissociation constant of the weak acid being studied.

Activity of Monochloro- and Dichloro-acetic Acids in Sulfate Solutions from Distribution Measurements

The same materials and methods were used as in the previous measurements.[1] The results are shown in Tables I, II and III. The first column gives the density of the aqueous phase, the second the ionic strength

TABLE I

DISTRIBUTION OF MONOCHLORO-ACETIC ACID BETWEEN MAGNESIUM SULFATE SOLUTIONS AND *n*-DIBUTYL ETHER AT 25°

$d\,\frac{25^\circ}{4^\circ}$	$\mu(MgSO_4)$	m	n	m°	m°/m
1.003	0.242	0.1012	0.004554	0.0960	0.949
1.010	.492	.1044	.004661	.0981	.940
1.023	.970	.1055	.004783	.1008	.956
1.049	1.880	.1035	.004992	.1050	1.014

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[1] Randall and Failey, *Chem. Rev.*, **4**, No. 3, (1927). The notation of that article will be used.

TABLE II

DISTRIBUTION OF MONOCHLORO-ACETIC ACID BETWEEN POTASSIUM SULFATE SOLUTIONS AND n-DIBUTYL ETHER AT 25°

$d\frac{25°}{4°}$	$\mu(K_2SO_4)$	m	n	$m°$	$m°/m$
1.008	0.300	0.1036	0.004356	0.0920	0.888
1.039	1.000	.1135	.004358	.0920	.811
1.058	1.500	.1128	.004298	.0910	.807
1.078	2.000	.1173	.004372	.0921	.785

TABLE III

DISTRIBUTION OF DICHLORO-ACETIC ACID BETWEEN MAGNESIUM SULFATE SOLUTIONS AND n-DIBUTYL ETHER AT 25°

$d\frac{25°}{4°}$	$\mu(MgSO_4)$	m	n	$m°$	$m°/m$
1.009	0.242	0.1925	0.04606	0.1535	0.797
1.017	.492	.1952	.04795	.1580	.809
1.029	.970	.1663	.03423	.1215	.731
1.054	1.880	.1871	.03883	.1340	.716

of the added sulfate, the third the molality of the chloro-acetic acid in the aqueous phase and the fourth the mole fraction of the acid in the normal dibutyl ether phase. The fifth column gives the molality of pure acid in equilibrium with the ether at the same mole fraction of acid in the ether and the sixth the quotient of this quantity by the molality of acid in the sulfate solution.

Solubility of Weak Acids in Sulfate Solutions.—We also present in Table IV the results of some measurements by Rördam[2] of the solubility of benzoic, *o*-toluylic and *o*-nitrobenzoic acids in magnesium sulfate solutions at 25°. Cols. 1, 4 and 7 give the ionic strength of the added sulfate, Cols. 2, 5 and 8, the solubility of the acid and Cols. 3, 6 and 9, the ratio of the solubility in pure water to the solubility in the salt solution.

TABLE IV

SOLUBILITY OF BENZOIC, *o*-TOLUYLIC AND *o*-NITROBENZOIC ACIDS IN AQUEOUS MAGNESIUM SULFATE AT 25°

Benzoic			*o*-Toluylic			*o*-Nitrobenzoic		
$\mu(MgSO_4)$	m(acid)	$m°/m$	$\mu(MgSO_4)$	m(acid)	$m°/m$	$\mu(MgSO_4)$	m(acid)	$m°/m$
0.00	0.02793	1.000	0.00	0.008783	1.000	0.00	0.04415	1.000
.02498	.02828	0.988	....	.....	...	.04792	.04783	0.923
.04910	.02837	.984	.04792	.009044	0.971	.1000	.05011	.881
.1018	.02818	.991	.1000	.009124	.963	.2000	.05241	.842
.2029	.02796	.999	.2000	.009126	.962	.4000	.05490	.804
.4008	.02723	1.026	.6400	.009015	.974	.6400	.05633	.784
.7580	.02578	1.083	.9836	.008653	1.015	.9836	.05679	.777

Discussion.—The values of $m°/m$ are plotted in Fig. 1 against the square root of the ionic strength of the added sulfate. Because of the number of variables and the complexity of the equilibria it is not practical to attempt to determine the activity coefficient of the various molecular

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[2] Rördam, *Thesis*, Copenhagen, 1925.

species in the solutions. If we define the activity as equal to the stoichiometric molality, m°, of a given solution of a weak acid in pure water, then m°/m will be analogous to the activity coefficient for a solution of the same activity in another solvent when the molality of the acid in equilibrium is m.

We note that the "activity coefficient" of the acid is lowered by a larger amount the larger the dissociation constant of the acid. This is in agreement with the assumption of a larger amount of hydrosulfate ion formed with the stronger acid. The salting-out effect is more noticeable with the weaker acids. The order of the effect of the potassium sulfate and magnesium sulfate upon dichloro-acetic acid is the same as the order of the effect of these salts on the activity coefficient of sulfuric acid,[3] which must be considered a moderately weak acid. The activity coefficient of hydrobromic acid, a typical strong electrolyte, is greatly lowered by sulfates.[4] This effect is almost wholly due to the formation of hydrosulfate ion. If we were to draw a curve for hydrobromic acid similar to that of Fig. 1, we should find that it lies lower than that of dichloroacetic acid for the same added sulfate.

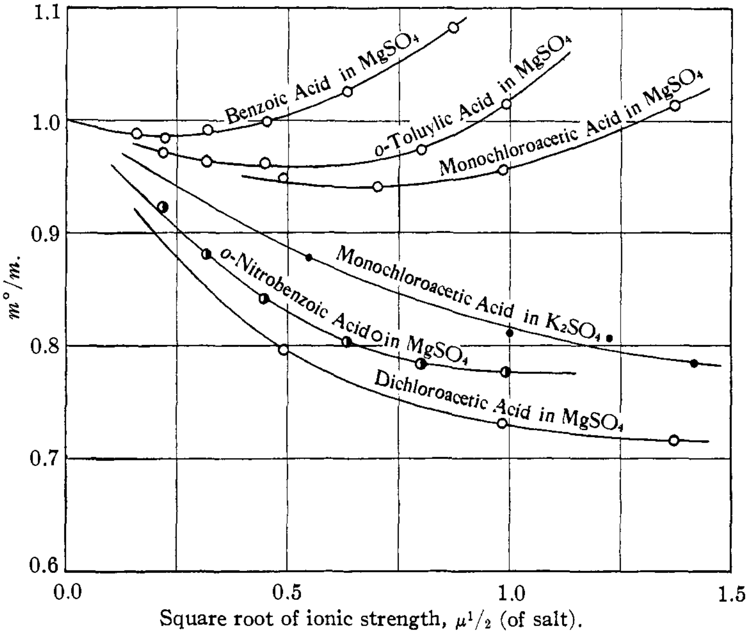

Fig. 1.—"Activity coefficients" at constant activity of weak acids in aqueous sulfate solutions at 25°.

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[3] See (a) Harned and Sturgis, THIS JOURNAL, **47**, 945 (1925). (b) Randall and Langford, *ibid.*, **49**, 1445 (1927).

[4] See Livingston, *ibid.*, **48**, 45 (1926).

Summary

The distribution of monochloro- and dichloro-acetic acids between aqueous sulfate solutions and normal dibutyl ether has been measured.

The "activity coefficient" as measured by the ratio of the molality in pure water to that in a salt solution at a constant activity is determined by the salting-out effect of the sulfate on the undissociated part of a weak acid, and the amount of formation of hydrosulfate ion.

At constant ionic strength the "activity coefficient" is lower the greater the dissociation constant of the weak acid.

The "activity coefficient" is lowered to a greater extent by potassium sulfate than by magnesium sulfate.

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THE EFFECT OF SHAKING ON THE EVOLUTION OF GASES FROM SUPERSATURATED SOLUTIONS AND ITS IMPORTANCE FOR THE MEASUREMENT OF THE VELOCITY OF CERTAIN CHEMICAL REACTIONS

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Introduction

During the examination of the rate of decomposition of nitro-acetic acid in aqueous solution

$$NO_2CH_2COOH \longrightarrow NO_2CH_3 + CO_2$$

by means of an apparatus described by J. N. Brönsted[1,2] in which the pressure of the gas is measured during the reaction, it was found necessary to examine whether the gas was evolved sufficiently quickly to prevent a supersaturation effect. In order to get a quick evolution of the carbon dioxide the reaction flask was shaken horizontally. It was found that the supersaturation is very much less at a certain rate of shaking than with slower or quicker shaking. When the rate of shaking is not kept very constant, the supersaturation may, even when it is only small, as a consequence of this variability, cause a considerable error. The author thinks that this examination of the influence of the supersaturation may have some interest for other investigators who study the velocity of chemical reactions by measurement of the rate of gas evolution. Part 1 of this paper is an examination of the velocity of the evolution of carbon dioxide from supersaturated solution and its dependence upon the length and number per minute of the horizontal shakings of the reaction vessel. Part

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[1] Brönsted and King, THIS JOURNAL, **47,** 2523 (1925).

[2] Brönsted and Duus, *Z. phyiks. Chem.*, **117,** 299 (1925).