curve of the form required by Equations 6 and 7. From this curve and the third and fifth columns of Table I, we find the following expression for the dissociation of pure monochloro-acetic acid in the concentration range 0.003 to 0.300 molar

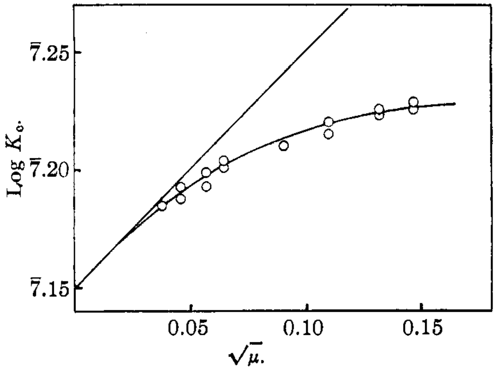

Fig. 2.—The relation of log K_c to $\sqrt{\mu}$.

$$\log K_c = (7.150 - 10) + \sqrt{\mu} - 3.2\mu$$

Summary

1. The H_3O^+ concentrations of solutions of monochloro-acetic acid from 0.003 to 0.300 molar have been determined.

2. From these measurements, the dissociation constant of monochloro-acetic acid has been determined. It has been shown to vary with the ionic strength in the manner required by theory.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

A MERCURY-BASIC MERCURIC SULFATE VOLTAIC CELL[1]

BY WARREN C. VOSBURGH AND OSCAR N. LACKEY

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The lead storage cell can be considered as a modification of the cell

$$\mathrm{M} \mid \mathrm{M^{I}X}\text{ (sat.)} \mid \mathrm{M^{I}X}\text{ (sat.)}, \mathrm{M^{II}X_2}\text{ (sat.)} \mid \text{(Pt)} \qquad (1)$$

where M^{I} and M^{II} stand for a metallic element in two states of oxidation and $M^{I}X_2$ has a small solubility. In the storage cell $M^{I}X$ is lead sulfate, but $M^{II}X_2$ is replaced by the higher oxide. Sulfuric acid must then be present in the electrolyte, and the electromotive force depends upon the concentration of the acid.

It has been found in this investigation that a cell analogous to the lead storage cell, namely

$$\mathrm{Hg} \mid \mathrm{Hg_2SO_4},\ xM\ \mathrm{H_2SO_4} \mid xM\ \mathrm{H_2SO_4},\ \mathrm{Hg_2SO_4},\ \mathrm{3HgO{\cdot}SO_3} \mid \text{(Au)} \qquad (2)$$

is reproducible and constant over short periods of time.

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[1] Taken from a thesis presented by Oscar N. Lackey in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Duke University in June, 1929.

Preparation of Materials

Mercurous sulfate was prepared by precipitation from recrystallized mercurous nitrate and c. p. sulfuric acid solution.

Basic mercuric sulfate was prepared by slowly adding mercuric oxide to 5 *M* sulfuric acid, diluting with ten times its volume of water, and boiling until no more yellow precipitate was obtained. According to Hoitsema[2] the substance obtained under such conditions is the yellow compound $3HgO \cdot SO_3$.

Mercury was purified by washing with mercurous nitrate solution and distilling under reduced pressure in a current of air.

Sulfuric acid solutions were prepared from c. p. acid and were standardized by titration with standard sodium hydroxide solution.

Experimental

Preparation of the Cells.—The cells were set up in vessels of the type used by Vosburgh and Craig,[3] an H-shaped vessel with a side-arm for the introduction of materials. The mercurous sulfate electrode was set up in the plain leg of the vessel. In the other leg a gold-plated platinum wire[4] was fixed in place and enough of a mixture of mercurous sulfate, basic mercuric sulfate and the sulfuric acid electrolyte was poured in to completely cover the wire. The vessel was then filled to a point above the cross-arm with the sulfuric acid solution. No precautions were taken to protect from air.[5]

Electromotive Force Measurements.—The cells were immersed in an oil thermostat at 25 ± 0.02° and electromotive force measurements were made daily until constancy over a period of several days was assured. The final values differed from the values obtained at the end of the first day less than 1 mv. Constancy within two or three hundredths of a millivolt was obtained within from three to seven days and the cells were observed for from four to seven days longer. All cells had been made in duplicate (triplicate in the case of the 0.0954 *M* electrolyte) and duplicates agreed within 0.2 mv., except in the case of the cells with the most dilute electrolytes, in which case it was within 0.3 mv. When constancy at 25° was attained, the temperature of the thermostat was changed successively to 20, 30, 35, 30 and 25° and measurements were made at each temperature, after allowing thirty to thirty-six hours for the attainment of constancy.

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[2] Hoitsema, *Z. physik. Chem.*, 17, 656 (1895).

[3] Vosburgh and Craig, This Journal, 51, 2012 (1929).

[4] No. 28 platinum wire was sealed into a glass tube with about 4 cm. projecting. The wire was wound in the form of a helix and gold-plated. Preliminary experiments had shown that gold-plated electrodes gave greater sensitivity than plain platinum electrodes. Platinized platinum electrodes gave somewhat erratic results when the cells were first set up.

[5] See Randall and Stone, This Journal 51, 1752 (1929).

The results are given in Table I, the successive columns of electromotive force values being given in the order in which the measurements were made.

TABLE I

ELECTROMOTIVE FORCES AT VARIOUS TEMPERATURES

H_2SO_4 M/l.	Electromotive force, v. 25°	20°	30°	35°	30°	25°	$\Delta E/\Delta T$ v./degree
0.1450	0.2113	0.2129	0.2098	0.2082	0.2097	0.2113	−0.00031
.0954	.1975	.1992	.1957	.1940	.1957	.1974	− .00034
.04724	.1744	.1764	.1724	.1704	.1724	.1744	− .00040
.02385	.1505	.1527	.1482	.1460	.1482	.1504	− .00044
.01194	.1258	.1281	.1234	.1211	.1234	.1257	− .00046

Comparison of the first and second sets of measurements at 25 and at 30° indicates that no change in electromotive force other than that caused by the temperature took place. The electromotive force is a linear function of the temperature within the limits of error.

Over a period of about six months, the cells showed a decrease in electromotive force of from 0.7 to 15.5 mv. The cells with the more dilute electrolytes decreased considerably less than those with the more concentrated electrolytes. A decrease is to be expected because diffusion of mercuric ion to the mercury electrode and its reaction with mercury would involve using up some of the sulfuric acid of the electrolyte.

$$3HgO\cdot SO_3 + 3Hg + 2H_2SO_4 \longrightarrow 3Hg_2SO_4 + 2H_2O$$

Solubility of Basic Mercuric Sulfate.—The rate of diffusion of mercuric ion to the mercury electrode must depend on the solubility of basic mercuric sulfate, which increases with the sulfuric acid concentration. For a concentration of 0.0127 *M* at 25° Cox[6] found a mercuric oxide concentration of 0.0007 *M*. Data for concentrations in the vicinity of the more concentrated solutions used in the present work seemed to be lacking, so a few determinations were made. The sulfuric acid solutions were saturated with basic mercuric sulfate at room temperature, 25 to 30°. Mercury was determined in samples by titration with standard thiocyanate solution. The results are given in Table II.

TABLE II

SOLUBILITY OF BASIC MERCURIC SULFATE

H_2SO_4 concn., *M/l*	Sample, cc.	0.0977 *M* NH_4CNS, cc.[a]	Concentration, *M/l* HgO	SO_3
0.1450	100	40.81	0.0203	0.1518
.0954	100	26.31	.0131	.0998
.01194	100	2.07	.00103	.01228

[a] Each value is the average of three closely agreeing results.

The appreciable solubility of the basic mercuric sulfate makes energy data calculated from the results in Table I uncertain.

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[6] Cox, *Z. anorg. Chem.*, **40**, 146 (1904).

Summary

The cell Hg | Hg_2SO_4, xMH_2SO_4 | xMH_2SO_4, $Hg_2SO_4,3HgO{\cdot}SO_3$ | (Au) has been set up and its electromotive force measured. It is fairly reproducible, and constant in electromotive force for a short period soon after it is set up, but the e. m. f. decreases slowly over a period of several months.

The solubility of basic mercuric sulfate in some of the sulfuric acid electrolytes was measured.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

CATALYSIS IN THE HYDRATION OF PROPIONIC ANHYDRIDE[1]

BY MARTIN KILPATRICK, JR.

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In a recent investigation of catalysis in the hydration of acetic anhydride[2] it was shown that while bases other than hydroxyl ion exert a catalytic effect, the magnitude of the effect is not in the order of increasing basic strength of the catalyst as it is in other cases.[3] Thus it was found that the formate ion accelerates the reaction to a marked degree, the acetate ion to a lesser extent, while in the presence of propionate ion the reaction is slower than in water alone. From the theory the reverse order was to be expected. The possibility of mixed anhydride formation was offered in explanation of the experimental results.

The question may be raised as to whether the hydration of acetic anhydride is an exception to the general theory, or a chemical process which may not be classed as a catalytic reaction at all. It remains, however, that a study of the facts is far more useful than debating the catalytic or non-catalytic nature of the reaction.[4]

The experimental results obtained in the case of acetic anhydride suggest that when the reaction is retarded there is partial formation of the mixed anhydride, or some other intermediate compound formed from the anhydride and the ion in question, which has the same order of stability as the mixed anhydride. It is therefore desirable to know the relationships which exist in the hydration of propionic and acetopropionic anhydrides. The present paper deals with the effect on the hydration of propionic

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[1] Paper presented at the Minneapolis Meeting of the American Chemical Society, September, 1929.

[2] Kilpatrick, THIS JOURNAL, **50**, 2891 (1928).

[3] Brönsted and Pedersen, *Z. physik. Chem.*, **113**, 389 (1924); Brönsted and Guggenheim, THIS JOURNAL, **49**, 2554 (1927); Brönsted, *Trans. Faraday Soc.*, **24**, 630 (1928).

[4] In this connection see Hinshelwood, *ibid.*, **24**, 552 (1928).