[CONTRIBUTION FROM THE CHEMICAL LABORATORY, OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

The Effect of Ethylene Glycol upon the Activity of Sulfuric Acid in Aqueous Solutions

BY H. M. TRIMBLE AND P. F. EBERT

Numerous studies have been made of the activities of electrolytes in aqueous solutions. A few studies have also been made of the effect upon activity produced by adding to the solutions such solvents as ethyl alcohol,[1] methyl alcohol[2] and glycerol.[3] Such studies have importance in connection with the theory of solution, and they should aid also in gaining an understanding of the kinetics of reactions in mixed solvents. For example, it has recently been found[4] that the inversion of sucrose in the presence of sulfuric and hydrochloric acids as catalysts is promoted at some concentrations of glycol and retarded at others. Such behavior calls for further study. This paper presents the results of a study, by electrometric methods, of the activity of sulfuric acid in aqueous solutions in the presence of ethylene glycol.

Reagents.—Ethylene glycol was prepared for these experiments by the method which has been described previously.[5] The water which was used in making up the solutions was redistilled from alkaline permanganate solution in a still constructed throughout of Pyrex glass. C. P. sulfuric acid was used in making up stock solutions, whose acid content was then determined by precipitating the sulfate ion as barium sulfate and weighing as such. The hydrogen was a commercial electrolytic product. A small quantity of oxygen was removed from it by passing it over a glowing platinum wire. It was then passed through a washing bottle filled with water, next through a washing bottle immersed in the bath and filled with the liquid which was to be studied, and then to the hydrogen electrode vessel. Mercury was purified by distillation by the method of Hulett.[6] Mercurous sulfate was prepared by the method of Wolff and Waters.[7] Two samples from different preparations and a special "analyzed" commercial material were used to make up a number of mercurous sulfate electrodes, each with molar sulfuric acid as the electrolyte, and these electrodes were carefully compared. They were found to give the same potentials to one or two hundredths millivolt. Since the commercial material was satisfactory and more readily available it was used in nearly all of the experiments.

In preparing the solutions the desired quantities of stock sulfuric acid solution and of glycol were weighed out and washed into a calibrated volumetric flask, the flask was then filled very nearly to the mark, agitating to ensure thorough mixing, and brought to 25° in the thermostat. The meniscus was then brought exactly to the mark by adding water, also at 25°, and the solution was again thoroughly mixed.

Apparatus and Procedure.—The measurements were made using a calibrated po-

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(1) Among others: Harned and Fleysher, THIS JOURNAL, **47**, 92–95 (1925); Scatchard, *ibid.*, **47**, 2098–2111 (1925); **49**, 217–218 (1927); Brönsted and Williams, *ibid.*, **50**, 1338–1343 (1928).

(2) Åkerlöf, *ibid.*, **52**, 2353–2368 (1930).

(3) Lucasse, *ibid.*, **48**, 626–631 (1926).

(4) Young and Trimble, *J. Phys. Chem.*, **36**, 830–841 (1932).

(5) Trimble, *Ind. Eng. Chem.*, **23**, 165 (1931).

(6) Hulett, *Phys. Rev.*, **32**, 257 (1911).

(7) Wolff and Waters, Sci. Paper 70, U. S. Bureau of Standards, (1907).

tentiometer. A standard Weston cell of the unsaturated type, whose potential was certified by the manufacturers. was used as reference standard. Measurements were carried out in a thermostat filled with gas oil, and maintained at 25 ± 0.02°.

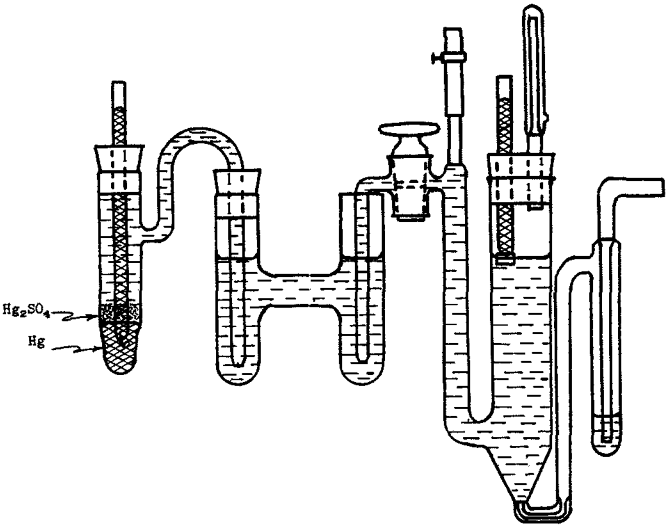

Fig. 1.—Cell assembly.

A diagram of the complete cell as assembled is shown in Fig. 1; the device used for filling the mercurous sulfate half cell is shown in Fig. 2. Mercurous sulfate was first washed thoroughly with the solution to be used, and then the solution was saturated with it by rotating the two together for about twelve hours. The rubber stopper placed on the side tube of the electrode vessel was coated with Lubriseal to ensure an air-tight connection. Mercury was introduced into the vessel, the stopper bearing the tube with its platinum wire through which contact with the mercury was established was coated with Lubriseal and inserted, the small distilling flask was filled with the solution containing a suspension of mercurous sulfate, and then connected to the electrode vessel. Upon evacuation the solution was readily freed of its gases, and on releasing the suction the mercurous sulfate half cell was completely filled. Such electrodes were found to be practically at equilibrium at the start, and maintained constant and reproducible potentials, with a given solution, indefinitely. The hydrogen electrode vessel was a

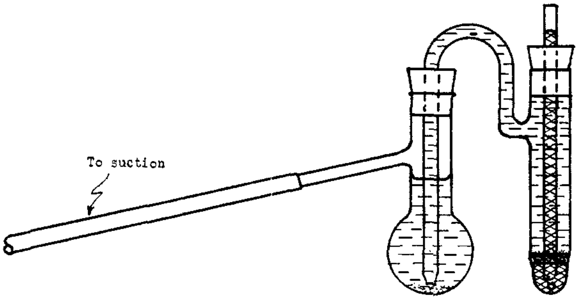

Fig. 2.—Device for filling mercurous sulfate electrodes.

modified form of the Walpole vessel. The gas outlet tube prevented back pressure by allowing the gas to escape upward through a very narrow annular space. The vessel was filled with the same solution as was the mercurous sulfate half cell, but, of course, containing no mercurous sulfate. An H tube filled with the same solution served to connect the two half cells.

After filling and assembling, the cell was placed in the bath and the liquid in the hydrogen half cell was thoroughly saturated with hydrogen, the cell being lightly stoppered. The platinum electrode was, meanwhile, saturated with hydrogen by making it the cathode in a dilute solution of sulfuric acid, passing only a small current. When ready to start, the electrode was quickly washed with conductivity water, then several times with more of the solution which had been put into the cell, and then it was brought into its place. Readings were started at once and continued for four to six hours. The potential generally became constant in twenty to thirty minutes. No results were accepted from experiments in which the potential failed to remain constant thence throughout the time of observation.

No variation in potential was at any time detected such as would indicate that glycol was combining with the acid. Special experiments were performed by one of us to determine whether glycol can combine either with sulfuric acid or hydrochloric acid. No reaction was ever found, since the titratable acidity remained constant for as long as five weeks. Acetic acid, on the other hand, showed a regular decrease in titratable acidity. The solutions contained as high as 3 moles of acid and 5 moles of glycol per liter. Glycol does not seem to poison platinized platinum electrodes; and the potentials are, if anything, more constant and reproducible in the presence of glycol than in its absence.

Experimental Results

The potentials as measured are set forth in Table I. Each value represents the mean of at least three very concordant determinations.

TABLE I

E. M. F. VALUES FOR THE CELL H_2^-, H_2SO_4 (GLYCOL), Hg_2SO_4, Hg^+

Mole H_2SO_4 per liter	Mole glycol per liter 0	1	5	10
0.005	0.8162	0.8130	0.7994	0.7834
.025	.7738	.7705	.7592	.7453
.050	.7546	.7529	.7422	.7290
.25	.7152	.7108	.7018	.6904
.50	.6952	.6933	.6844	.6730
1.00	.6744	.6730	.6633	.6505

TABLE II

DENSITIES OF H_2SO_4–GLYCOL–H_2O SOLUTIONS

Mole H_2SO_4 per liter	Moles of glycol per liter 0	1	2.5	5	10
0.0	0.9971	1.0049	1.0164	1.0364	1.0720
.005	.9975	1.0052	1.0167	1.0367	1.0723
.025	1.0001	1.0065	1.0179	1.0379	1.0735
.050	1.0008	1.0080	1.0194	1.0393	1.0748
.10	1.0038	1.0114	1.0229	1.0424	1.0774
.25	1.0131	1.0207	1.0319	1.0511	1.0858
.50	1.0285	1.0358	1.0470	1.0655	1.0995
1.00	1.0589	1.0660	1.0765	1.0943	1.1269

To evaluate the data properly it was essential to have, also, the densities of these solutions. These were determined at 25°, using Sprengel type pycnometers, with the results as set forth in Table II. Values for solutions containing 0.005, 0.025 and 0.050 mole of sulfuric acid per liter were secured by interpolation. Other values are as measured.

Method of Calculating Activities

The orthodox method for calculating the activities of electrolytes in solution from e. m. f. data using such cells as ours has been given by Lewis and Randall.[8] It involves the use of the equation, for sulfuric acid

$$0.08873 \log_{10} \frac{a_\pm}{m} = 0.08873 \log_{10} \gamma = E^0 - (E + 0.08873 \log_{10} m)$$

where $a_\pm$ is the geometric mean activity of the ions, γ is the activity coefficient, E is the electromotive force of the cell and E^0 is the value which is approached by the quantity in parentheses above, which is called $E^{0\prime}$, as the acid approaches infinite dilution in concentration. For our work it is necessary to take m as the number of moles of sulfuric acid in 1000 g. of solvent, whether this solvent be pure water or a mixture of water and glycol. This, in itself, is not particularly open to objection. It is the convention which is often adopted in connection with the equations of the Debye–Hückel theory.[9] Even with this convention, however, the handling of the data is difficult. Extrapolations to infinite dilution cannot be made with certainty because the electromotive forces of cells using very dilute solutions cannot be determined with sufficient accuracy. It happens that, in dilute solutions, in many cases the potentials of cells such as are here used are rectilinear functions of the logarithms of the mole fractions of the electrolytes in the solution. For sulfuric acid solutions, as will be shown, this is true up to concentrations of about 0.85 mole per liter. This permits the use of the equation, closely analogous to that of Lewis and Randall

$$0.08873 \log_{10} \frac{a_\pm}{N} = E_N - (E + 0.08873 \log_{10} N) \tag{1}$$

where N is the mole fraction of sulfuric acid in the solution, and E_N is the limiting value of the quantity in parentheses, here called E_N', which is found when the graph of E'_N against $\log_{10} N$ is extrapolated to zero. It must be emphasized that this equation describes the relations between the quantities represented for those solutions in which E is a rectilinear function of $\log N$. If this relation were to persist up to the point where pure sulfuric acid is reached, then we might reasonably take $a_\pm = N = 1$. E_N, then, would be the voltage of a cell such as ours, containing pure sulfuric acid. The graph of E_N' against $\log N$ up to a definite limit, as will be shown, is a straight line, which makes the extrapolated value, E_N very easy to arrive at and very certain.

[8] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, pp. 332–335.

[9] Lucasse, Ref. 3, p. 627.

To illustrate and justify the application of this equation, we have employed the data for the cell (H_2, H_2SO_4 (m), Hg_2SO_4, Hg) as given in "International Critical Tables."(10) Table III will be self-explanatory. Values of N, the mole fraction, are readily found from the molalities of the solutions, using the equation

$$N = \frac{m}{m + 55.51}$$

TABLE III

DATA FOR CALCULATION OF E_N FOR CELLS

m H_2SO_4	N	E	E'_N	m H_2SO_4	N	E	E'_N
0.005	0.000090	0.8160	0.4570	0.8453	0.0150	0.6812	0.5193
.05	.00090	.7546	.4843	1.133	.0200	.6720	.5212
.1112	.00198	.7343	.4944	2.922	.0500	.6315	.5160
.2789	.0050	.7114	.5073	4.827	.0800	.5915	.5002
.5607	.0100	.6929	.5154				

Values of E'_N are plotted against log N in curve I of Fig. 3. The points from this table are indicated by means of circles. The data are adequately represented by the equation

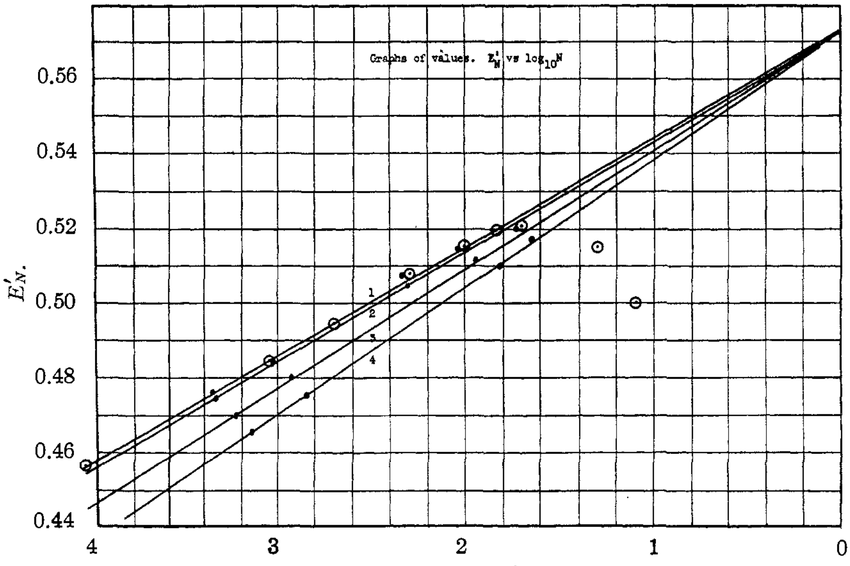

Fig. 3.—Graphs of values of E'_N vs. $\log_{10} N$.

$$E'_N = 0.5724 + 0.0287 \log_{10} N \qquad (2)$$

whence it follows that $E'_N = 0.5724$. Obviously equation (2) ceases to hold for solutions in which $\log_{10} N$ is less than -1.825. This corresponds to a concentration of approximately 0.85 molal. Since, by definition,

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(10) "International Critical Tables," Vol. VI, p. 323.

$E'_N = E + 0.08873 \log_{10} N$, we may substitute in this equation the equivalent of E'_N from equation (2), and get

$$E = 0.5724 - 0.0600 \log_{10} N \tag{3}$$

Using equation (3) and the proper values for N we have calculated E for the cells involved. Column 2 of Table IV gives these values; and, for comparison, column 3 gives the values of E from "International Critical Tables." Perhaps the best test of the essential correctness of the method lies in the fact that, as shown here, the potentials of galvanic cells using the various solutions of sulfuric acid can be calculated by means of equation (3) with an average error of ± 0.00065 volt, an accuracy which is of the same order of magnitude as the accuracy of the potentials given, which is, according to "International Critical Tables," about ± 0.0002 volt. The potential calculated for 1.133 molal sulfuric acid has been omitted from this analysis of errors, as it lies outside the range within which these equations hold accurately. The errors of prediction, moreover, are consistent, since three potentials as calculated are slightly too high and three are slightly too low, and the average positive and negative errors are very nearly the same.

Substituting (2) in (1), we may write

$$\begin{aligned} 0.08873 \log k'a_{\pm} &= E_N - E'_N + 0.08873 \log_{10} N \qquad (4) \\ &= (-0.0287 + 0.0887) \log_{10} N = 0.0600 \log_{10} N \end{aligned}$$

and

$$\log_{10} k' a_{\pm} = \frac{0.0600}{0.08873} \log_{10} N = 0.6766 \log_{10} N \tag{5}$$

Using equation (5) we have calculated values of activity for these same solutions. They may be found in column 4 of Table IV. The activities of sulfuric acid in its solutions, as calculated from the data of Lewis and Randall[11] are given in column 6. The γ values given by Lewis and Randall were plotted against the corresponding molalities. From the curve drawn through the points, values of γ corresponding to the molalities of Table IV were read off and multiplied by the molalities to get $a_{\pm}$. From the comparative values it is obvious, however, that equation (5) gives, not activi-

TABLE IV

CHECK UPON THE METHOD OF CALCULATION

Values of E and of $a_{\pm}$, calculated

m H_2SO_4	E calcd.	E found	$k' a_{\pm} c$	$a_{\pm}$ calcd.	$a_{\pm}$ from L. and R.
0.005	0.8153	0.8160	0.00183	0.0041	0.0035
.05	.7553	.7546	.00869	.0194	.0199
.1112	.7345	.7343	.01481	.0332	.0334
.2789	.7105	.7114	.02779	.0622	.0600
.5607	.6925	.6929	.04434	.0993	.0953
.8453	.6820	.6812	.05828	.1305	.1345
1.133	.6744	.6720	.07088	.1588	.1700

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[11] Lewis and Randall, Ref. 8, pp. 344 and 357.

ties, but simply quantities proportional to them, namely, values of $k' a_\pm$. On the average $k' a_\pm$ multiplied by the factor 2.240 gives values of activity. These are given in column 5 of the table.

The agreement between these values of $a_\pm$ and those calculated by means of equation (5) is fairly good. So far as the authors are aware, this method of calculating the activities of electrolytes in dilute solutions from electromotive force data has not previously been employed.

This method of calculating activities has been applied to the data of our experiments. The essential data for the drawing of the curves and values of E calcd. are given in Table V. In this table N was calculated from the densities of the solutions and the weights of glycol and sulfuric acid known to be present.

TABLE V

H_2SO_4–H_2O (GLYCOL) SOLUTIONS, ESSENTIAL DATA FOR CURVES

Part 1. No glycol

Mole H_2SO_4 per liter	N	E'_N	E found	E calcd.
0.005	0.00009	0.4572	0.8162	0.8153
.025	.00045	.4768	.7738	.7731
.050	.00090	.4843	.7546	.7549
.25	.0045	.5070	.7152	.7133
.50	.0091	.5141	.6952	.6949
.85	.0156			.6808
1.00	.0184	.5205	.6744	.6766

Part 2. 1 Mole of glycol per liter

Mole H_2SO_4 per liter	N	E'_N	E found	E calcd.
0.005	0.000094	0.4557	0.8130	0.8121
.025	.00047	.4752	.7705	.7705
.050	.00094	.4843	.7529	.7526
.25	.00471	.5043	.7108	.7110
.50	.00946	.5137	.6933	.6929
.85	.0162			.6790
1.00	.0191	.5205	.6730	.6747

Part 3. 5 Moles of glycol per liter

Mole H_2SO_4 per liter	N	E'_N	E found	E calcd.
0.005	0.00011	0.4481	0.7994	0.7992
.025	.00055	.4700	.7592	.7592
.050	.00110	.4796	.7422	.7419
.25	.00550	.5013	.7018	.7019
.50	.01118	.5112	.6844	.6842
.85	.0192			.6708
1.00	.0227	.5174	.6633	.6666

Part 4. 10 Moles of glycol per liter

Mole H_2SO_4 per liter	N	E'_N	E found	E calcd.
0.005	0.000143	0.4422	0.7834	0.7835
.025	.000714	.4660	.7453	.7452
.050	.00143	.4766	.7290	.7286
.25	.00714	.4998	.6904	.6903
.50	.0145	.5098	.6730	.6733
.85	.0251			.6603
1.00	.0297	.5150	.6505	.6562

On plotting the values of E'_N against $\log_{10} N$ in each case the following equations, analogous to equation (3), are found to represent the data very satisfactorily

$$E'_N = 0.5724 + 0.0287 \log_{10} N \qquad (2)_0$$

$$E'_N = 0.5724 + 0.0292 \log_{10} N \qquad (2)_1$$

$$E'_N = 0.5724 + 0.0314 \log_{10} N \qquad (2)_5$$

$$E'_N = 0.5724 + 0.0338 \log_{10} N \qquad (2)_{10}$$

The subscripts of the equation numbers in each case refer to the number of moles of glycol present per liter of solution. The curves are numbers 2, 3 and 4 of Fig. 3. The curve for solutions containing no glycol falls upon that found from the data from "International Critical Tables," discussed above. Since the constant term of the linear equation comes out the same in each case, it is unnecessary in this method of calculation to derive a relation between limiting values of E'_N for different concentrations of glycol in order to be able to calculate activities in solutions containing glycol in relation to those which contain no glycol.[12] The activities, then, are functions only of the mole fraction of the sulfuric acid and the concentration of glycol in the solution. Proceeding just as before (equation 3) it may be shown that the following equations hold for the voltages of the cells at different concentrations of glycol.

$$E = 0.5724 - 0.0600 \log_{10} N \quad (3)_0$$
$$E = 0.5724 - 0.0595 \log_{10} N \quad (3)_1$$
$$E = 0.5724 - 0.0573 \log_{10} N \quad (3)_5$$
$$E = 0.5724 - 0.0549 \log_{10} N \quad (3)_{10}$$

A comparison of the values of "E calculated" with those found, as set forth in Table V, shows the validity of our method of calculation. It appears, again, that the range over which it holds does not quite extend to one mole of sulfuric acid per liter. It seems reasonable, in view of the agreement shown in Table IV, to assume that it holds, within the limits of experimental error, to concentrations as great as 0.85 mole per liter. Experiments just completed give for 5 moles of glycol and 0.85 mole of sulfuric acid per liter, a voltage of 0.6707, in excellent agreement with the calculated value which is 0.6708. Partial data for this concentration of sulfuric acid have, therefore, been inserted in Table V.

Proceeding as in the derivation of equation (5) we have for calculation of values of $k'a_{\pm}$

$$\log_{10} k'\, a_{\pm} = 0.6766 \log_{10} N \quad (5)_0$$
$$\log_{10} k'\, a_{\pm} = 0.6706 \log_{10} N \quad (5)_1$$
$$\log_{10} k'\, a_{\pm} = 0.6461 \log_{10} N \quad (5)_5$$
$$\log_{10} k'\, a_{\pm} = 0.6191 \log_{10} N \quad (5)_{10}$$

$k'\, a_{\pm}$ is here used, since, as has been shown, the calculated value is only proportional to, not equal to $a_{\pm}$. This latter value is found in each case by multiplying $k'\, a_{\pm}$ by the factor 2.240. The values of $a_{\pm}$ as calculated are shown in column 3 of Table VI.

The equations developed above by means of which E and $k'\, a_{\pm}$ may be calculated from our data involve, in the coefficients of the variable terms, the slope of the straight line which is obtained when E'_N is plotted against $\log_{10} N$ for each number of moles of glycol per liter. This slope is a rectilinear function of the number of moles of glycol per liter in the solutions. The relation is $k = 0.0287 + 0.00052\, G$ where k is the multiplying factor in the equation $E'_N = 0.5724 + k \log_{10} N$ for any given number of moles of glycol per liter, and G is the number of moles of glycol. We may now write the following general equations, which give E and $k'\, a_{\pm}$ in terms of moles of glycol per liter and mole fraction of sulfuric acid for any such solutions as these

$$\begin{aligned} E &= 0.5724 - [0.0887 - (0.0287 + 0.00052\, G)] \log_{10} N && (6) \\ &= 0.5724 - [0.0600 - 0.00052\, G] \log_{10} N && \text{general} \end{aligned}$$

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[12] See Scatchard, THIS JOURNAL, 47, 2105 (1925).

and

$$\log k'\, a_{\pm} = \left[\frac{0.0600 + 0.00052\, G}{0.08873}\right] \log_{10} N \qquad \begin{matrix}(5)\\ \text{general}\end{matrix}$$

TABLE VI

H_2SO_4–H_2O–GLYCOL SOLUTIONS. VALUES OF m, $a_{\pm}$ FOR H_2SO_4 AND F OF THE REACTION

Mole H_2SO_4 per liter	m	$a_{\pm}$	ΔF reaction	γ	Mole H_2SO_4 per liter	m	$a_{\pm}$	ΔF reaction	γ
Part 1. No glycol					Part 3. 5 Moles of glycol per liter				
0.005	0.005	0.0041	−37,625	0.820	0.005	0.005	0.0062	−36,882	1.240
.025	.025	.0122	−35,678	.488	.025	.025	.0175	−35,037	0.700
.050	.050	.0195	−34,838	.390	.050	.049	.0274	−34,238	.559
.25	.253	.0579	−32,918	.227	.25	.244	.0777	−32,392	.319
.50	.511	.0934	−32,069	.183	.50	.492	.1227	−31,575	.249
.85	.879	.1342	−31,418	.153	.85	.848	.1741	−30,956	.205
1.00	1.041	.1500	−31,225	.150	1.00	1.004	.1942	−30,763	.193
Part 2. 1 Mole of glycol per liter					Part 4. 10 Moles of glycol per liter				
0.005	0.005	0.0045	−37,478	0.900	0.005	0.005	0.0094	−36,157	1.880
.025	.025	.0131	−35,553	.524	.025	.023	.0253	−34,390	1.109
.050	.050	.0209	−34,728	.418	.050	.047	.0388	−33,624	0.826
.25	.251	.0617	−32,811	.246	.25	.236	.1048	−31,856	.444
.50	.507	.0984	−31,972	.194	.50	.476	.1628	−31,072	.342
.85	.873	.1401	−31,335	.161	.85	.821	.2286	−30,472	.272
1.00	1.031	.1577	−31,136	.153	1.00	.972	.2540	−30,283	.261

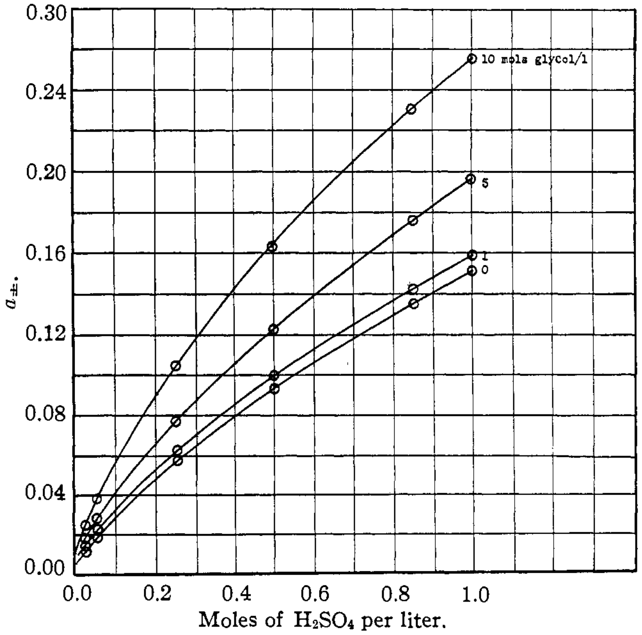

Fig. 4.—Variation of activity with sulfuric acid concentration.

Since $\Delta F = -NFE$, the free energy of the reaction

$$H_2 + Hg_2SO_4 \rightleftharpoons 2Hg + H_2SO_4$$

in the presence of glycol may be calculated by the equation

$$\Delta F = -2 \times 23{,}074\ [0.5724 - (0.0600 - 0.00052\ G) \log_{10} N] \qquad (7)$$

These free energy values are set forth in column 5 of Table VI. The calculated values of $a_\pm$ and ΔF for solutions containing 1 mole of sulfuric acid per liter are somewhat in error since the equations apply only up to about a concentration of 0.85 mole of sulfuric acid per liter. The trend of the free energy of the reaction as glycol is substituted for water may be seen from these values. For the sake of completeness, values of γ are set forth in the last column of Table VI.

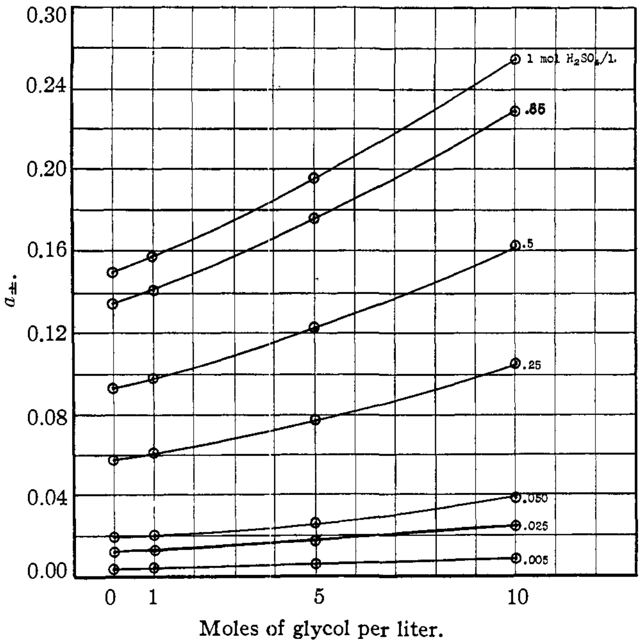

Fig. 5.—Variation of activity with added glycol.

In Fig. 4 the variation of activity with concentration of sulfuric acid for each of the concentrations of glycol is shown. In Fig. 5 the variation of activity with concentration of glycol for each of the concentrations of acid is shown. As will be seen, the variation of activity of the acid which is brought about by substituting glycol for water is normal and regular in every way.

Summary

The activity of sulfuric acid in the system H_2SO_4–H_2O–$C_2H_4(OH)_2$ has been studied up to 1 mole of acid and 10 moles of glycol per liter. A new method for calculating activities in such solutions has been presented. The activity of sulfuric acid has been found to vary regularly with change in the concentration of glycol present. Abnormalities in the inversion of sucrose in the presence of ethylene glycol, as catalyzed by sulfuric acid, cannot be attributed to abnormal variations in the activity of the acid in the presence of glycol.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGY, SCHOOL OF PUBLIC HEALTH, HARVARD UNIVERSITY]

A Rapid Micro Method for the Determination of Chlorides in Fluids

BY LAWRENCE T. FAIRHALL AND J. WILLIAM HEIM

The following method of chloride determination was devised especially for the analysis of very small amounts of fluids and in particular those of biological importance. Certain body fluids, such as peripheral lymph, or the blood of very small animals, or of insects, can be obtained only in such small quantities that analyses hitherto have been very difficult or out of the question.

A necessary step in the volumetric determination of chlorides by means of silver nitrate is that of exactly estimating the excess of silver used in precipitation. Field[1] in 1860 employed iodine dissolved in potassium iodide solution using starch for the end-point, having first neutralized the excess of nitric acid in the solution. King[2] reduced the amount of nitric acid (which interferes with the starch end-point), filtered the silver chloride suspension and titrated the filtrate with potassium iodide solution, using sodium nitrite to oxidize the excess of iodide. McLean and Van Slyke[3] using the same procedure considerably sharpened the end-point by the introduction of a buffer salt—sodium citrate. In the iodimetric method, as in the Volhard method, it is necessary to filter the excess of silver nitrate from the precipitated silver chloride, before completing the titration with potassium iodide; otherwise the latter reacts with the solid silver chloride. For very exact work it has also been shown[4] that it is necessary to remove the precipitated silver iodide just before the end-point is reached, as otherwise the latter is obscured.

The filtration and washing are not only time-consuming but so dilute the sample that for very small amounts of chloride the accuracy is diminished. This step has been eliminated in the following method by carrying out the

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(1) Field, *Chem. News*, **2**, 17 (1860).

(2) King, *Merck's Rept.*, **18**, 57 (1909).

(3) McLean and Van Slyke, THIS JOURNAL, **37**, 1128 (1915).

(4) Lamb and Fairhall, *ibid.*, **45**, 390 (1923).