alcohol, and benzene, slightly soluble in cold water. The molecular weight of the thiosemicarbazide was estimated by the Rast camphor method to be approximately 258. Element analyses proved the presence of C, H, N and S.

Anal. Calcd. for $C_{13}H_{14}N_4S$: C, 60.47; H, 5.43; N, 21.72. Found: C, 59.69; H, 5.41; N, 21.77.

The saturated solution of this reagent in 50% ethyl alcohol (0.05 g. per 100 cc.) added to normal nitrate solutions of the cations gave yellow precipitates with cadmium, zinc, and mercurous mercury, and brown precipitates with copper, nickel, cobalt, and silver. The presence of various anions (chloride, bromide, iodide, sulfate, cyanate, and thiocyanate) was found to affect the completeness of precipitation and the appearance of the precipitate to some extent. The most satisfactory test was secured in the presence of iodide ions, when a bright greenish-yellow precipitate was formed even with traces of cadmium ions. This precipitate contained cadmium, nitrogen, sulfur, potassium and iodine.

The sensitivity of the cadmium thiosemicarbazide iodide precipitation was tested by adding 1 cc. of 50% aqueous alcohol (saturated with the thiosemicarbazide and with potassium iodide) to 10 cc. each of solutions containing respectively, 1, 0.05 and 0.01 mg. of cadmium ion.

$Cd(NO_3)_2\cdot 4H_2O$, g./l.	Cd^{++}	Effect
0.278	1/10,000	Filterable precipitate
.0139	1/200,000	Filterable precipitate
.00278	1/1,000,000	Opalescence; precipitate after two minutes

The detection of cadmium ions in the presence of copper ions was accomplished by a modification of the above procedure, in the absence of the ions of zinc, nickel and cobalt. Interfering ammonia and sulfate, if present, were removed by boiling off ammonia and precipitating the sulfate with barium chloride. To this solution was added saturated potassium iodide solution and brown copper iodide precipitated. Without filtering, the addition of saturated thiosemicarbazide solution (50% alcohol) precipitated the yellow cadmium thiosemicarbazide iodide complex. Upon addition of ammonium hydroxide the copper salt dissolved but not the cadmium complex. Thus a blue solution indicated copper, while a yellow precipitate indicated cadimum.

Summary

1. N-Allyl-N′-2,6-dihydroxyphenyl thiourea and N-allyl-N-2-hydroxy-5-nitrophenyl thiourea were prepared and tested as analytical reagents.

2. 1-(2-Quinolyl)-4-allyl thiosemicarbazide was prepared. It is a sensitive precipitant for the cadmium ion, and a good qualitative reagent for cadmium in the presence of copper.

ATHENS, GA.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Activity Coefficients of Sulfuric Acid in Anhydrous Ethyl Alcohol from Electromotive Force Data

BY A. W. SCHOLL,[1] A. WITT HUTCHISON AND G. C. CHANDLEE

In continuation of the work in this Laboratory on the properties of non-aqueous solutions it was thought that a study of the activity coefficients of sulfuric acid in ethyl alcohol solutions would be of interest. Data were obtained by the electromotive force method using the cell H_2, H_2SO_4, Hg_2SO_4s, Hg. Activity coefficients were calculated from these data by the use of the Debye–Hückel first approximation and also by the use of the extended equation of Gronwall, La Mer and Sandved.

Experimental

All electromotive force measurements were made with a Leeds and Northrup type K potentiometer by the null method. A Weston standard cell was used as a reference. It was checked from time to time during the course of the experiments against several other cells of the same type recently calibrated at the Bureau of Standards. A type R galvanometer was used as an indicating instrument. All lead wires and the standard cell were shielded.

The thermostat was maintained at a temperature of 25 ± 0.01°. The cells were placed in a copper tank, filled with oil, suspended in the thermostat water.

The cells were of the H type and were made by connecting two Pyrex test-tubes by means of a short piece of Pyrex tubing. A piece of 7-mm. tubing was sealed to the bottom of each test-tube and bent so that it became parallel to the tube. One tube then became the mercury–mercurous sulfate half-cell, and connection was made to it by means of a platinum wire dipping into the mercury. The test-tubes were fitted with well ground, gas tight, glass stoppers. Through the one stopper two tubes were sealed into the ends of which platinum wires were sealed to serve as the platinum electrodes. Hydrogen was bubbled in through the bottom of the hydrogen half cell and escaped from the top through an alcohol trap. It was saturated with alcohol by bubbling it through a wash bottle, immersed in the thermostat, containing the solution being measured.

The more concentrated solutions were prepared by the addition of sulfuric acid from a weight pipet to a weighed

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[1] From a thesis presented by A. W. Scholl in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1934.

amount of the alcohol. The others were prepared by dilution of the stronger solutions. The electrodes were freshly platinized before each run. It was found that the cells reached a constant electromotive force (±0.2 mv.) after hydrogen had bubbled through them for about one hour. In the several cases studied the cells maintained this value for at least five or six hours. In general when the value had been constant for ninety minutes it was assumed that equilibrium had been reached.

Materials.—Ninety-five per cent. ethyl alcohol was purified by distilling from concentrated sulfuric acid (15 cc. of acid per liter of alcohol) to remove amines and most of the water. The distillate was next distilled from alkaline silver nitrate (5 g. per liter) to remove the aldehydes and similar oxidizing bodies. Finally, the last trace of water was removed by refluxing with fresh calcium oxide and then fractionated from aluminum ethoxide. The alcohol thus obtained had a specific conductivity of 1.5×10^{-7} mhos.

Anhydrous sulfuric acid was made by mixing concentrated acid with fuming acid of Baker's Analyzed Grade, as described by Kendall and Carpenter.[2] It had a freezing point of 10.46°.

Mercurous sulfate[3] was made electrolytically from redistilled mercury and dilute sulfuric acid. It gave results in good agreement with those obtained by using Baker's C. P. grade.

Mercury of C. P. grade was further purified by washing with dilute nitric acid, dilute alkali and water and then by vacuum distillation.

Electrolytic hydrogen was passed over finely divided platinum in a furnace at approximately 600° to remove the oxygen. The hydrogen was then dried with phosphorus pentoxide and passed into the cell through a saturating trap kept at the thermostat temperature.

Results and Discussion

The experimental values of the electromotive forces corrected to a partial pressure of hydrogen of one atmosphere together with the corresponding molalities are listed in Table I. In the third column are listed values of the square root of the ionic strength calculated from the volume concentration on the assumption that the sulfuric acid is completely dissociated. The concentrations were obtained from the molalities by use of the expression $C = M/(V_0 + K\text{M})$, where V_0 is the specific volume of pure alcohol and where K was given the value of 0.034 corresponding to its value in aqueous solutions of sulfuric acid.

TABLE I

EXPERIMENTAL DATA AND THE COMPUTATION BY THE DEBYE-HÜCKEL THEORY AS A 1,2-TYPE ELECTROLYTE. $N = 2$, AND "A" = 2.5 Å.

Soln. no.	Molality	$\mu^{1/2}$	E	Calcd. $-\log \gamma$	E_0
1	0.003562	0.0916	0.6478	0.4777	0.406
2	.007748	.1345	.6468	.6641	.419
3	.01143	.1641	.6457	.7815	.422
4	.01303	.1752	.6433	.8231	.421
5	.01820	.2071	.6426	.9381	.423
6	.02912	.2619	.6416	1.117	.426
7	.04154	.3128	.6344	1.266	.417
8	.04622	.3250	.6337	1.270	.420
9	.05462	.3670	.6327	1.405	.414
10	.07738	.4269	.6254	1.549	.407
11	.1170	.5241	.6192	1.747	.399
12	.1649	.6217	.6170	1.916	.396
13	.2245	.7248	.6104	2.070	.387
14	.2801	.8090	.6064	2.179	.382
15	.5854	1.165	.5900	2.531	.363
16	.6667	1.242	.5895	2.589	.357

In order to calculate the activity coefficient by the use of the well-known equation $E = E_0 - (3RT/2F) \ln \gamma M4^{1/3}$, it is necessary to evaluate E_0. This is ordinarily done by extrapolating to zero concentration a plot of E_0' against some function of the concentration where $E_0' = E + (3RT/2F) \ln M4^{1/3}$. Examination of the lower curve of Fig. 1 where the open circles represent experimental values of E_0' plotted against the square root of the ionic strength show that a simple extrapolation would yield an uncertain value

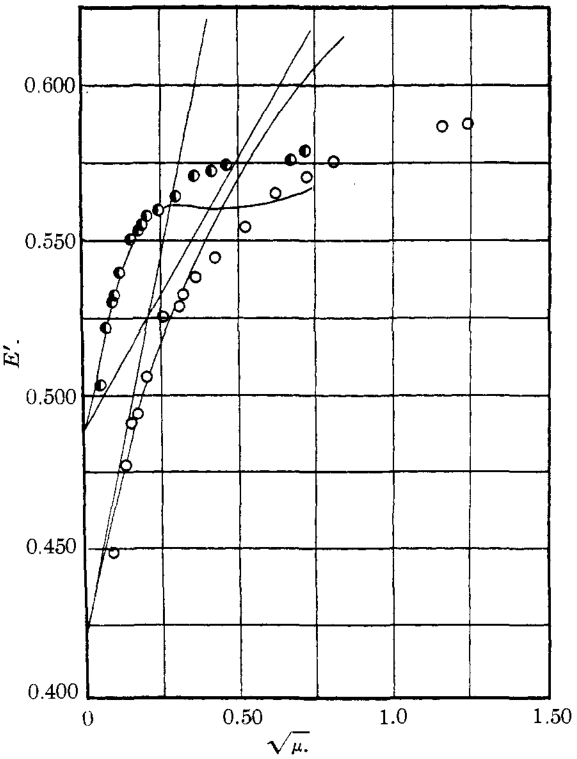

Fig. 1.—Open circles represent experimental data as a 1,-2 type electrolyte. Shaded circles represent experimental data as a 1,-1 type electrolyte. Straight lines are the limiting law in each case.

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[2] Kendall and Carpenter, THIS JOURNAL, **36**, 2498 (1914).

[3] Carhart and Hulett, *Chem. News*, **90**, 226 (1904).

of E_0 in this case. If it is assumed that the Debye–Hückel equation[4]

$$-\log \gamma = \frac{2.96\, Z_1 Z_2 \sqrt{\mu}}{1 + .592 \times 10^8\, a \sqrt{\mu}}$$

with a reasonable value of the ion diameter is applicable to these solutions a value of E_0 may be calculated from each experimental measurement. The constancy of these values indicates the validity of the assumptions made. In columns five and six of Table I values of $-\log \gamma$ and of the corresponding E_0 are listed. These calculations were made with a value of 2.5×10^{-8} cm. for the ion diameter. In the figure the solid curve represents a plot of E_0' calculated from the values of $-\log \gamma$ and the value of 0.420 for E_0. The slope of the limiting law is also indicated on the figure. As may be seen from the figure and also from Table I the calculated and experimental values are in reasonably good agreement in the dilute solutions except for the first point.

Since the dissociation of the second hydrogen ion from sulfuric acid is not complete even in water solutions it might reasonably be assumed to be even less so in the solutions of alcohol. The limiting case would of course be one in which only the primary dissociation would be considered. The equation for the electromotive force, from this point of view, becomes $E = E_0 - (2RT/2F) \ln \gamma M$ and the ionic strength is equal to the concentration. Calculations from this point of view were made using the extended equation of Gronwall, La Mer and Sandved,[5] and an assumed ion diameter of 1.7×10^{-8} cm. The shaded circles of the figure represent the experimental points, the full curve the calculated values and the straight line the limiting law on this basis. Results of these calculations showed that the equation is not convergent for this small ion diameter in alcohol. However, a larger value for the ion diameter would not be in agreement with the experimental values.

Since the experimental curve lies above the limiting law in dilute solutions it is obvious that the application of the first approximation of Debye and Hückel will not account for the experimental curve. Although the extended equation does give constant values for E_0 on this basis the significance of this is perhaps questionable in view of the non-convergence of the series.

Summary

Activity coefficients of sulfuric acid solutions in ethyl alcohol have been determined by measurement of the cell H_2, H_2SO_4, $Hg_2SO_4(s)$, Hg. The data have been treated by the Debye–Hückel equation and by the extended equation of Gronwall, La Mer and Sandved.

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(4) The constants in this equation were evaluated using for the dielectric constant of ethyl alcohol the value of 24.20 as given by Åkerlöf [THIS JOURNAL, **54**, 4126 (1932)].

(5) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928). For alcohol solutions at 25° the constants become, +5.00, −5.30 and −28.11.

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

The Nature of the Surface of Copper Catalysts

BY W. WALKER RUSSELL AND LEONARD G. GHERING[1]

Experimental evidence concerning the nature of catalytic surfaces is conflicting. Kinetic measurements are in general consistent with the concept of a uniformly active catalytic surface, while adsorption phenomena for the most part require a surface of non-uniform nature. This apparent conflict would largely disappear were it found that the reaction catalyzed proceeded predominantly on a relatively few surface types out of many existing on a surface. It is well recognized that a knowledge of the different qualities of catalytic surface present and their distribution is vital to any theory of the catalytic surface or mechanism of catalysis.

By studying the changes in catalytic activity produced by controlled, selective poisoning, much can be learned about the nature of a catalyst surface. Studies have been made of synthetic ammonia catalysts[2] using oxygen and water as poisons; of thoria as a catalyst using water and acetaldehyde to poison the decomposition of

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(1) Metcalf Fellow in Chemistry at Brown University.

(2) J. A. Almquist and C. A. Black, THIS JOURNAL, **48**, 2814 (1926); J. A. Almquist, *ibid.*, **48**, 2820 (1926); P. H. Emmett and S. Brunauer, *ibid.*, **52**, 2682 (1930).