If f_B were approximately constant over a range of acid concentrations a plot of $S/\log^{-1}(-H_0)$ against $1/\log^{-1}(-H_0)$ would be a straight line whose *x*-intercept equals $-1/K'$. In the case of the four acids studied, these plots do have this property and lead to the following values of the constant pK': benzoic -5.9, phenylacetic -5.8, *o*-nitrobenzoic -7.0, *p*-nitrobenzoic -6.9. Because of the behavior of nitrobenzene, and because the solubility increase with benzoyldiphenyl completely disagrees with this theory, it is quite improbable that the assumption of constant f_B is justified; and these figures are therefore devoid of any absolute significance. It is however possible that they do give a measure of some value of the base strengths relative to each other of these acids. In order for this to be true, it is only necessary that the variation with changing medium of the f_B coefficients should be the same for this group of closely related substances. Such a hypothesis is supported by the fact that the base strengths thus obtained are in the inverse order of the strengths of the acidic ionizations of the same substances, but its verification must await the determination by an independent method of the base strengths in question.

We wish to express our appreciation for the very helpful assistance in this work of Mr. Henry P. Treffers, who purified the organic compounds and made the solubility measurements on phenylacetic acid, and of Mr. Harry Parver.

Summary

The solubilities in a wide range of sulfuric acid-water mixtures of benzoic acid, phenylacetic acid, *o*-nitrobenzoic acid, *p*-nitrobenzoic acid, *p*-benzoyldiphenyl and nitrobenzene have been determined.

It has been shown that the sharp increase in solubility at high sulfuric acid concentrations may possibly be related in some cases to ionization or salt-formation arising from basic properties in the organic oxygen compound, but that this is not the sole cause of such solubility increases.

NEW YORK, N. Y. RECEIVED MARCH 3, 1934

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

The Conductivities of Dilute Sulfuric Acid Solutions in Anhydrous Acetic Acid

BY BRUCE V. WEIDNER, A. WITT HUTCHISON AND G. C. CHANDLEE

The conductivities of dilute sulfuric acid solutions in anhydrous acetic acid have been reported recently by several investigators.[1] Some variation in the specific conductances of the solvent used as well as in the molar conductances of the solutions is found in these results. This variation is presumably due to differences in the very small amount of water which may have been present.

In part of this work we have studied the conductances of solutions in acetic acid having essentially the same specific conductance for the solvent as that used by Hall and Voge[1b] and the results are in excellent agreement. In addition we have prepared acid with a somewhat lower specific conductance and data have been obtained for the conductance of the more dilute solutions prepared with it.

Experimental

The bridge assembly and thermostat described by Lasselle and Aston[2] was used in this work. The cell constants of the two type A Washburn cells were determined using Parker[3] solutions prepared from equilibrium water and purified potassium chloride.

Acetic acid was prepared by the method of Hutchison and Chandlee.[4] Acid with a specific conductivity of 0.56×10^{-8} mhos at 25° was obtained in quantity. The melting point determined with a thermometer calibrated against one certified by the Bureau of Standards was 16.60 ± 0.02°. No difference could be detected between the melting point of this acid and other samples with specific conductivities as great as 1.0×10^{-8} mhos. The more concentrated solutions were prepared by the use of weight pipets and the others by dilution. The volume concentrations were calculated using the densities of the solutions.[4]

Discussion of Results

In Table I are listed the data obtained for the conductivities of the sulfuric acid solutions.

---

(1) (a) Hantzsch and Langbein, *Z. anorg. allgem. Chem.*, **204**, 193 (1932); (b) Hall and Voge, THIS JOURNAL, **55**, 239 (1933); (c) Eichelberger and La Mer, *ibid.*, **55**, 3635 (1933).

(2) Lasselle and Aston, *ibid.*, **55**, 3067 (1933).

(3) Parker and Parker, *ibid.*, **46**, 332 (1924).

(4) Hutchison and Chandlee, *ibid.*, **53**, 2881 (1931).

TABLE I

CONDUCTIVITY OF SULFURIC ACID IN ANHYDROUS ACETIC ACID AT 25°

Concn. mole/liter	$\sqrt{\text{Concn.}}$	Sp. cond. $k \times 10^7$	Molar cond.
Series A			
Spring 1932		$k_{\text{solvent}} = 3.69 \times 10^{-8}$	
0.3510	0.5925	977.8	0.2785
.1541	.3925	128.7	.08352
.06368	.2523	29.65	.04656
.02696	.1642	11.91	.04420
.01411	.1188	7.157	.05072
.01135	.1065	6.224	.05483
.006493	.08058	4.330	.06668
.004423	.06652	3.518	.07952
.002859	.05346	2.933	.1026
.001456	.03815	1.939	.1332
.000678	.02603	1.520	.2242
.000104	.01020	0.727	.699
Series B			
Spring 1933		$k_{\text{solvent}} = 0.66 \times 10^{-8}$	
0.01479	0.1216	7.104	0.0483
.006794	.08240	4.317	.0635
.001135	.03368	1.585	.1397
$.0_34221$	.02055	0.9440	.2236
$.0_33297$	.01816	.8580	.2602
$.0_31473$	.01214	.5563	.3776
$.0_31441$	.01200	.5612	.3896
$.0_45783$	.00760	.3487	.6028
$.0_44281$	.006543	.326	.762
$.0_42553$	.005053	.233	.913
$.0_5917$	.003029	.151	1.64
$.0_5292$	.00171	.096	3.26
Series C			
Fall 1933		$k_{\text{solvent}} = 0.56 \times 10^{-8}$	
0.03286	0.1813	12.39	0.03770
.009590	.09793	4.912	.05122
$.0_38614$	.02935	1.273	.1477
$.0_32471$	.01572	0.6892	.2789
$.0_46814$	.008256	.3909	.5737
$.0_42176$	.004664	.237	1.09
$.0_5492$	.00222	.115	2.34

In calculating the molar conductances no solvent correction was applied.

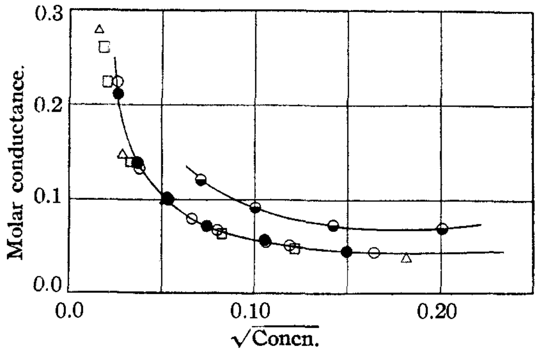

Fig. 1.—●, Hall and Voge, $k_{\text{solvent}} = 3.0 \times 10^{-8}$; ◒, Hall and Voge, $k_{\text{solvent}} = 8.2 \times 10^{-8}$; ○, Series A; □, Series B; △, Series C.

In Fig. 1 the data obtained in the range of concentrations studied by Hall and Voge[1b] have been represented. The curve with black circles represents the results of these authors obtained with a solvent of 3.0×10^{-8} mhos specific conductivity. The open circles are the experimental values of Series A ($k_{\text{solvent}} = 3.69 \times 10^{-8}$). The agreement between these two sets of data is striking when the difficulties encountered in working with such highly resistant solutions are considered. The half closed circles represent the data of Hall and Voge[1b] using moist acetic acid, 0.08% water and $k_{\text{solvent}} = 8.2 \times 10^{-8}$, as a solvent. The squares and triangles, respectively, show the results listed in Series B and C of Table I ($k_{\text{solvent}} = 0.66$ and 0.56×10^{-8}). It is interesting to see that the displacement of these points below the curve is small despite the large percentage change in the specific conductivity of the solvent. As would be expected the displacement is more pronounced in the very dilute solutions.

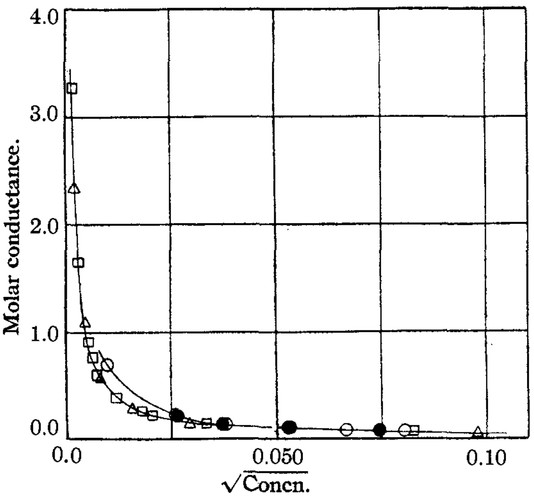

Fig. 2.—●, Hall and Voge, $k_{\text{solvent}} = 3.0 \times 10^{-8}$; ○, Series A; □, Series B; △, Series C.

In Fig. 2 the experimental points are indicated as before but the ordinate now has a value ten times and the abscissa one-half as large as in Fig. 1 so that the trend in the very dilute region may be shown. The region of concentration below 0.0006 molar had not been investigated previously. As may be seen in the figure the marked change of slope in the dilute range suggested in Fig. 1 is still more pronounced in the very dilute solutions.

As to the specific conductivity of anhydrous acetic acid a value of 1.4×10^{-8} mhos has been reported by Eichelberger and La Mer.[1c] Hall and Voge[1b] state that they have obtained samples with a specific conductivity of 1.05×10^{-8} mhos. We have found that acid of specific conductivity of about 0.60×10^{-8} mhos may be prepared in quantity without undue difficulty. Recently acid with a specific conductivity as low as 0.40×10^{-8} mhos has been prepared in this Laboratory. Our work would indicate that the influence of small amounts of moisture, responsible for the slight variations in the specific conductivity of the solvent, is without appreciable effect on the conductivities of solutions except possibly in the very dilute range.

Summary

1. Anhydrous acetic acid has been prepared in quantity with a specific conductivity at 25° of 0.60×10^{-8} mhos.

2. The specific conductances of dilute sulfuric acid solutions in this acid as well as in acid of somewhat higher specific conductivity have been determined.

STATE COLLEGE, PENN. RECEIVED MARCH 5, 1934

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, YALE UNIVERSITY]

The Equilibrium between Carbon Monoxide, Hydrogen, Formaldehyde and Methanol.[1] II. The Reaction $CO + 2H_2 \rightleftharpoons CH_3OH$

BY ROGER H. NEWTON AND BARNETT F. DODGE

Introduction

In the course of some experiments undertaken primarily to determine the conditions of equilibrium in the synthesis of formaldehyde from carbon monoxide and hydrogen, it was possible at the same time and by some additional experiments in the same apparatus to secure further data on the equilibrium conditions in the methanol synthesis reaction. Although the equilibrium constants for this reaction have been measured by a number of investigators, the results are not very concordant and further work was desirable. Part of the lack of agreement may be attributed to (1) the use of different thermal data for the interpolation and extrapolation of the equilibrium constant with respect to temperature and (2) the difficulties involved in reducing the measurements to a common pressure. The publication of some new thermal data and an increase in our knowledge of the effect of pressure on the equilibrium constant was a further justification for a paper on this subject.

This equilibrium constant may be calculated from those obtained for two other reactions, namely, $CO + H_2 \rightleftharpoons HCHO$, and $HCHO + H_2 \rightleftharpoons CH_3OH$, which have been measured by the authors.[2] However, the measurements for these two reactions were not made at the same temperature, and the thermal data for formaldehyde are so doubtful that the equations given in the earlier paper can only be considered as order of magnitude results and the values of the Kp for this reaction derived from them would be far less accurate than actually measured data for the reaction in question. It seemed therefore desirable to continue the earlier work at 3 atmospheres total pressure and over a temperature range of 225 to 275° to measure directly the equilibrium constant in the methanol equilibrium.

Review of Previous Work

The previous work on the methanol equilibrium has been very well summarized by Parks and Huffman[3] and a table of the values observed at the various temperatures and pressures and the calculated values of Kp_0 (equilibrium constant at low pressure) is all that will be given here. In Table I, the factor given for the conversion of Kp at the measured temperature and pressure, to Kp_0, at the same temperature, is derived by a method (to be published shortly) based on the assumptions that the partial fugacity rule of Lewis and Randall[4] holds for this case, and that the activity coefficient (ratio of fugacity to pressure) for any gas is a function of the reduced pressure and reduced temperature only. These assumptions appear to be justified for the ammonia equilibrium, for which accurate data are available.

---

(1) This paper is based on a Dissertation presented by R. H. Newton in June, 1933, to the Faculty of the Graduate School of Yale University, in candidacy for the degree of Doctor of Philosophy.

(2) Newton and Dodge, THIS JOURNAL, **55**, 4747 (1933).

(3) "Free Energies of Some Organic Compounds," A. C. S. Monograph No. 60.

(4) Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Co., Inc., New York, 1923.