quantity of the hydrogen liberated from any of the cathodically hydrogenated elements mentioned exercised this reducing action on roll sulfur. Moreover, this chemical action was not strong until after about five minutes had elapsed, indicating that the bulk of the hydrogen which was superficially held or easily liberated was practically inactive as compared with the more reluctantly released smaller portion of the hydrogen.

Summary

1. Practically all metals when heated in hydrogen, nitrogen, helium, argon, carbon dioxide or oxygen give off a peculiar, disagreeable, burnt nitrogenous odor which is due to impurities gathered on their surfaces from the air or objects with which they have been in contact. These impurities are dust particles laden with microorganisms, and the odor observed on heating is due to decomposition of the latter. When oxygen is used, the odor is slight and soon disappears, because complete oxidation to odorless products ensues. The presence of carbon in the odoriferous gas was established chemically. Hydrogen sulfide is also present in the gas, and the lead acetate test for it is positive as long as the odor lasts and for a very considerable time after the odor is gone.

2. When the metals are heated in hydrogen until all odor and hydrogen sulfide have disappeared, the hydrogen is unable to give hydrogen sulfide tests when passed over sulfur, or to reduce permanganate, ferric salts or blue starch iodide paper. The sulfur comes from sulfur compounds adsorbed by the metals from the air. Silver is especially able to take on sulfur.

3. Hydrogen passed over very pure hot silver was subjected to special study, chemically and spectroscopically. By this latter method it could not be distinguished from ordinary pure hydrogen. Observations were made in the visible and also in the ultraviolet. Quartz spectrograph and quartz vacuum tubes were employed in the latter case.

The hydrogen reduced permanganate, ferric chloride, blue starch iodide and yielded positive tests for hydrogen sulfide on the lead acetate paper as long as the odor persisted. The reductions also continued as long as did the hydrogen sulfide test, but no longer. The gas after that also gave no hydrogen sulfide test when passed over sulfur, even when the latter was at 65°.

The silver when cooled and kept in pure hydrogen, and then later heated again, never produced either the odor, the hydrogen sulfide test, or the reducing reactions. However, even momentary exposure to ordinary air at once resulted in the odor, the hydrogen sulfide test and the "activation."

4. Hydrogen released from cathodically hydrogenated Pd, Ni, Si or C in the form of Acheson graphite or coconut charcoal was found to be chemically active in that it reduced sulfur above 65°. Only a small fraction, namely, the more tightly held portion of the hydrogen, was found to be thus active.

MADISON, WISCONSIN RECEIVED MAY 10, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Activities of Ethylene and Ethanol in Sulfuric Acid

BY M. GALLAGHER AND D. B. KEYES

The purpose of this investigation was primarily to determine the activity of ethylene in concentrated sulfuric acid and the activity of ethanol in dilute sulfuric acid. These activities are involved in the calculation of the free energy change taking place in the formation of ethanol from ethylene and water by means of the reactions

$$C_2H_4(g) + H_2SO_4 = C_2H_5HSO_4 \tag{1}$$

$$C_2H_5HSO_4 + H_2O(l) = C_2H_5OH(l) + H_2SO_4 \tag{2}$$

whose sum is

$$C_2H_4(g) + H_2O(l) = C_2H_5OH(l) \tag{3}$$

An experimental value for the free energy from such equilibrium measurements is desirable in view of the discrepancies in the figures which have been published.

The values ΔF_{700} concern the reaction with all the compounds as gases; ΔF_{298} refer to the same reaction with ethanol and water as liquids.

The addition of reactions 1 and 2 seems more advisable than the direct hydration in reaction 3, since very small concentrations of alcohol are involved, the analysis of which is likely to result in large errors. Presuming the value of F_{700} = +14,070 calories published by Parks and Huffman to be correct, the conversion to ethanol would be only 0.005%, giving a concentration

TABLE I

FREE ENERGY OF HYDRATION OF ETHYLENE PUBLISHED IN THE LITERATURE[a]

		ΔF_{298}, cal.	ΔF_{700}, cal.
1928	Francis[1]	−4000	+ 5,650
1929	Francis and Kleinschmidt[2]	+1700	+ 7,660
1930	Frost[3]		+ 6,080
1932	Parks and Huffman[4]	+4060	+14,070

[a] A paper on this subject has appeared recently which is entitled "The Catalytic Vapor-Phase Hydration of Ethylene" by F. G. Sanders and B. F. Dodge.[5] The difficulties of low conversions and uncontrollable side reactions which are met with in the direct hydration of ethylene even at increased pressures, are shown by the authors. They conclude that their equation, $\log_{10} K_p = 1090/T - 4.71 \log_{10} T + 0.00235\, T + 7.05$ is at least the order of magnitude. From this equation at 427°, $K_p = 0.00072$, and $\Delta F_{700} = +10{,}000$ calories.

too small to be determined by existing analytical methods.

The ΔF expressions for the above reactions are

$$\Delta F_1 = -RT \ln \frac{A'\mathrm{C_2H_5HSO_4}}{A\mathrm{C_2H_4}} + RT \ln A'\mathrm{H_2SO_4} \qquad (4)$$

$$\Delta F_2 = -RT \ln \frac{A\mathrm{C_2H_5OH}}{A''\mathrm{C_2H_5HSO_4} \times A\mathrm{H_2O}} - RT \ln A''\mathrm{H_2SO_4} \qquad (5)$$

adding (4) and (5)

$$\Delta F_3 = -RT \ln \frac{A'\mathrm{C_2H_5HSO_4} \times A\mathrm{C_2H_5OH}}{A\mathrm{C_2H_4} \times A''\mathrm{C_2H_5HSO_4} \times A\mathrm{H_2O}} + RT \ln \frac{A'\mathrm{H_2SO_4}}{A''\mathrm{H_2SO_4}} \qquad (6)$$

The prime (′) states refer to reaction 1, the seconds (″) to reaction 2. Hence the ΔF for reaction (3) can be determined from the knowledge of the activities indicated. The quantity $RT \ln A'\mathrm{H_2SO_4}/A''\mathrm{H_2SO_4}$ can be determined from the potential E of the concentration cell: Pt, H_2, H_2SO_4', Hg_2SO_4, Hg.... Hg, Hg_2SO_4, H_2SO_4'', H_2, Pt. H_2SO_4' is H_2SO_4 in the environment of reaction 1; H_2SO_4'' is in the environment of reaction (2)

$$\Delta F = -nFE = -RT \ln A'\mathrm{H_2SO_4}/A''\mathrm{H_2SO_4} \qquad (7)$$

Combining the second and third terms with (6)

$$\Delta F_3 = -RT \ln \frac{A'\mathrm{C_2H_5HSO_4} \times A\mathrm{C_2H_5OH}}{A\mathrm{C_2H_4} \times A''\mathrm{C_2H_5HSO_4} \times A\mathrm{H_2O}} + nFE \qquad (8)$$

The present paper makes available the partial pressure data for ethylene and ethanol, from which are calculated the respective activities.

Aqueous solutions of sulfuric acid, 95.4 and 62.81%, were considered as solvents for ethylene gas and liquid ethanol, respectively. In this case the activities a_2 of a solute can be determined from the partial pressures p_2 above the solution, as shown by Lewis and Randall.[6]

$$a_2 = p_2/K = p_2 N_2'/p_2'$$

N_2' and p_2' are the mole fraction and the partial pressure at infinite dilution.

The partial pressures involved were determined by the dynamic method perfected by Pearce and Snow.[7] The following form of Dalton's law was used to calculate the partial pressures

$$p = \frac{n_1}{n_1 + n_2} P$$

P is the total pressure on the saturators, n_1 is the number of moles of the constituent which has a partial pressure p, and n_2 is the number of moles of electrolytic gas used during the experiment. The apparatus and the experimental details were essentially the same as used by Pearce and Snow.

Materials and Apparatus

Ethylene gas containing 99.2% unsaturateds, 0.63% carbon dioxide and 0.16% residue, was used from a cylinder of ethylene from the U. S. Industrial Chemical Company. It was purified by passing it first through three scrubbers containing concentrated sulfuric acid, 95%, to remove any higher olefins, then through a trap cooled with carbon dioxide and acetone, to remove any condensable gases, and finally through a column of activated charcoal.

Sulfuric acid 95.4%, manufactured by the Grasselli Chemical Company, was used without further purification.

The alcohol was a commercial grade absolute, purified by drying it for two weeks over lime and finally distilled in anhydrous condition over metallic sodium as suggested by Gibson, Parks and Latimer.[8]

The water used was doubly distilled, approaching the purity of conductivity water.

The silver coulometer consisted of a platinum dish supported by a short brass cylinder. The anode was built up from electrolytic silver deposited on a platinum wire from pure metallic silver in a bath of $KAg(CN)_2$. During an experiment the electrolysis removed only the outer layer of silver which had been deposited electrolytically as crystalline silver from silver nitrate solution. The anode and the porous cup surrounding it were supported from the neck of a liter and a half bottle, the bottom of which was removed, allowing the bottle to protect the coulometer from dust. The electrolyte was made just before using it, from Mallinckrodt C. P. grade silver nitrate. The operation of the coulometer was the same as that suggested by Roosa and Vinal[9] consistent with an accuracy of 0.1%.

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(1) Francis, *Ind. Eng. Chem.*, **20**, 277 (1928).

(2) Francis and Kleinschmidt, *Oil Gas J.*, **28**, No. 29, 117 (1929).

(3) Frost, *Zhur. Prikladnoi Khim.*, **3**, 1069 (1930).

(4) Parks and Huffman, "Free Energies of Some Organic Compounds," Chemical Catalog Company, New York, 1932.

(5) Sanders and Dodge, *Ind. Eng. Chem.*, **26**, 208 (1934).

(6) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, New York, 1923.

(7) Pearce and Snow, *J. Phys. Chem.*, **31**, 231 (1927).

(8) Gibson, Parks and Latimer, THIS JOURNAL, **42**, 1542 (1920).

(9) Roosa and Vinal, *Bull. Bur. Stand.*, **13**, 497 (1916).

The electrolytic cells were slightly different from those of Pearce and Snow, who employed chlorine-free sodium hydroxide between nickel electrodes to generate the hydrogen and oxygen. Instead, platinum electrodes were used in a 12 to 15% solution of sodium sulfate as suggested by Lehfeldt.[10] Reisenfeld[11] found that small amounts of nickel peroxide formed on the nickel anode in chlorine-free sodium hydroxide solution.

The saturators were of the type described by Bichowsky and Storch.[12]

Experimental

I. The Partial Pressure of Ethylene in Equilibrium with Concentrated Sulfuric Acid.—The solutions of ethylene were prepared by allowing ethylene to pass through concentrated sulfuric acid, 95.4%, until the desired increase in weight was obtained. Good contact was established by allowing the ethylene to pass through a sintered glass plate in contact with the sulfuric acid.

The equilibrium content of ethylene in the electrolytic gas was determined by passing it through a series of five traps containing a known volume of standard solution of bromine, 0.05 *N*, in dry carbon tetrachloride, as suggested by Allen[13] Davis,[14] Williams,[15] and Morrell and Levine.[16] The excess bromine was determined with standard solutions of sodium thiosulfate and iodine. The contents of the fifth trap were treated as a control blank and titrated separately. The method was shown to be sufficiently accurate by checking it against a known volume of ethylene.[17]

These traps were protected from light and kept at approximately 0° in ice-baths. Just preceding these traps was a small tube containing soda and lime to remove any sulfur dioxide or ethyl sulfuric acid from the gas.

It was demonstrated that equilibrium conditions were being maintained by running two experiments on the same solution; for one experiment the first saturator was at a temperature higher than the thermostat and for the second experiment it was lower than the thermostat temperature. Under the conditions used, temperature 54.4° (measured on thermometer number B 11, made in Germany, graduated in tenths of a degree in the range 40 to 80°), with a gas flow of one cubic centimeter per minute, no difficulty was experienced in maintaining equilibrium. The check results of these experiments were always well within the experimental error of about 0.5%.

The results are listed in Table II. In column 1 are the mole fractions of the solutions, expressed in moles[18] of ethylene per mole of solution. Column 2 contains the partial pressures of ethylene. Column 3 contains the Henry's law constants p/N and column 4, the activities of ethylene in the six solutions calculated from equation 4 above.

TABLE II

THE ACTIVITY OF ETHYLENE IN CONCENTRATED SULFURIC ACID

1 N, mole fraction of C_2H_4	2 p, partial pressure of C_2H_4, mm.	3 p/N	4 a, activity of C_2H_4
0.3122	9.541	30.56	0.7376
.2674	6.037	22.57	.4662
.2307	4.294	18.61	.3318
.2039	3.339	16.38	.2578
.1561	2.160	13.84	.1668
.1280	1.658	12.95	.1280

Henry's law constant was taken as the value in the most dilute solution, the last entry in column 3.

$$K = p'/N' = 12.95$$

Figure 1 shows the results graphically; the partial pressures are plotted against the mole fraction of ethylene. Although there is some question whether Henry's law holds up to 13 mole per cent., the shape of the curve, since it must go through the origin, indicates this to be approximately true.

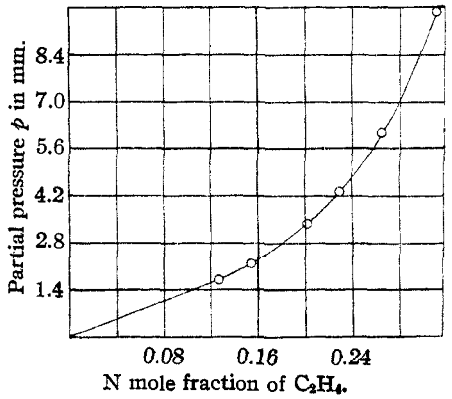

Fig. 1.

II. The Partial Pressures of Ethanol in Equilibrium with Diluted Sulfuric Acid.—The equilibrium solutions of ethanol and dilute sulfuric acid, 62.81%, were prepared by direct

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(10) Lehfeldt, *Phil. Mag.*, **15**, 614 (1908).

(11) Reisenfeld, *Z. Elektrochem.*, **12**, 621 (1906).

(12) Bichowsky and Storch, THIS JOURNAL, **37**, 2696 (1915).

(13) Allen, "Commercial Organic Analysis," J. and A. Churchill, London, 1924, fifth edition, Vol. III, p. 15.

(14) Davis, THIS JOURNAL, **50**, 2769 (1928).

(15) Williams, *J. Chem. Soc.*, [3] 2911 (1932).

(16) Morrell and Levine, *Ind. Eng. Chem., Anal. Ed.*, **4**, 319 (1932).

(17) It is very doubtful that alcohol interfered with this ethylene determination. Early investigators were unable to detect any alcohol formed from ethylene and concentrated sulfuric acid. Furthermore, in order to interfere in this determination, the alcohol would have to react with bromine in dry carbon tetrachloride at 0° in the dark and leave no compounds after the reaction which would liberate iodine from potassium iodide solution.

(18) The mole fractions of the solutions were calculated by the following expression

$$\frac{n_1}{n_1 + n_2 + n_3}$$

n_1 = number of moles of C_2H_4, or later C_2H_5OH.

n_2 = number of moles of H_2SO_4 determined by titration of the original H_2SO_4 with standard alkali.

n_3 = number of moles of H_2O in the H_2SO_4 by difference.

weight. The partial pressure experiments, including the check on maintaining equilibrium conditions, were essentially the same as the preceding ones. The soda and lime tube was replaced by one containing barium carbonate to remove any sulfur dioxide or ethyl sulfuric acid. It was first shown that barium carbonate did not retain any ethanol vapors which could not be blown out later with dry air.

The ethanol in the electrolytic gas was condensed in a trap surrounded by liquid air and then analyzed for alcohol by an oxidation method with excess standard potassium dichromate solution, 0.1 N, in the presence of perchloric acid.[19] Ether was not formed at 54.4° in any appreciable amount. This was shown by checking the analysis for alcohol by an acetylation method specific for alcohol based on one developed by Verley.[20]

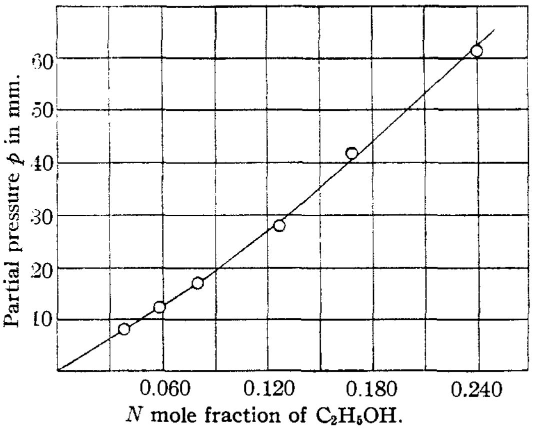

Fig. 2.

These results are listed in Table III. In column 1 are the mole fractions of ethanol; in column 2, the partial pressures; in column 3, the Henry's law constants; and in column 4 are the activities of ethanol in the solutions. The partial pressures are the averages of four determinations, in some cases eight, all within the experimental accuracy of approximately two per cent.

TABLE III

THE ACTIVITY OF ETHANOL IN DILUTED SULFURIC ACID

1 N mole fraction of C_2H_4	2 p, partial pressure of C_2H_4, mm.	3 p/N	4 a activity of C_2H_4
0.2400	60.85	254	0.2953
.1685	41.77	248	.2027
.1274	27.65	217	.1342
.08051	16.76	208	.08135
.05837	12.11	207	.05878
.03820	7.84	205	.03805

Henry's law constant was taken from the values in the most dilute solutions, the average of the last two entries in column 3

$$K = p'/N' = 206$$

Figure 2 shows the results plotted graphically, partial pressures against mole fraction.

Summary

1. The partial pressures of ethylene, from dilute solutions to mole fraction 0.3122, in concentrated sulfuric acid, and the partial pressures of ethanol, from dilute solutions to mole fraction 0.2400, in dilute sulfuric acid, were determined.

2. The activities for ethylene and ethanol in the same range of concentrations were calculated.

URBANA, ILL. RECEIVED JUNE 4, 1934

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[19] Bobtelsky and Radovensky-Cholatnikow, *Z. anorg. allgem. Chem.*, **199**, 241 (1931). No ethylene present was determined as alcohol since check analysis were obtained by two methods, one by oxidation of the alcohol with standard potassium dichromate and one by esterification of the alcohol with acetyl chloride.

[20] Verley, *Bull. soc. chim.*, **43**, 469 (1928).