titrated with 0.01 *m* ceric sulfate. The color change is from a faintly reddish-yellow to a clear yellow. In the presence of large amounts of iron, as in steel analysis, the addition of phosphoric acid to discharge the iron color becomes necessary. The indicator blank amounts to about 0.15 cc. of 0.01 *m* ceric sulfate in a volume of 200 cc. of 5 *m* sulfuric acid.

Table III contains the results of analyses which show the precision attainable on mixtures comparable to those obtained by solution of commercial steels. We have further analyzed the Bureau of Standards chrome–vanadium steel No. 30 c. A 2-g. sample was dissolved in 20 cc. of 5 *m* sulfuric acid, and after addition of 5 cc. of 8 *m* nitric acid, the solution was evaporated to fumes. After dilution and filtration the insoluble residue was ignited, treated with hydrofluoric and sulfuric acids, and fused with sodium carbonate. The dissolved melt was added to the main solution, and vanadium was then determined by the method given for the determination of small amounts. The results are

V (found), %	Detn.	Av. dev. pts. per 1000	V (certificate), %
0.2377	2	2.5	0.235 (range: 0.225–0.246)

Two determinations in which the recovery of vanadium from the silica residue was omitted led to values of 0.2349 and 0.2343, so that the amount of vanadium thus carried down is easily detected by this method. It is worthy of note that it is now possible to determine the vanadium content of a steel which carries only 0.2% of that element with a precision of about 3 parts per thousand.

Summary

Oxidation potentials relative to each other of the ferric–ferrous system, of the phenanthroline–ferrous indicator, and two stages of the vanadate reduction have been measured in 1, 3 and 5 *m* sulfuric acid.

From these the necessary conditions for the separate oxidimetric titration of iron and of vanadium have been predicted.

A rapid and precise method for the determination of vanadium in the presence of iron, chromium and molybdenum has been developed and tested.

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

Determination of Acidity in Ethyl Alcohol by Velocity of Acetal Formation

BY ALDEN J. DEYRUP[1]

The development of the theories of salt effects and general acid catalysis, due mainly to Brönsted, has placed reaction velocity measurement among the accurate methods of determination of acidity in aqueous solution.[2,3] A satisfactory application of the method to non-aqueous solutions depends on the selection of a reaction sufficiently sensitive to hydrogen ion to permit of measurements at low ionic strength. Adkins and Broderick[4] measured the rate of such a reaction, the formation of diethyl acetal from acetaldehyde in alcoholic solution with hydrogen chloride as catalyst. The decrease in velocity constants as the reaction proceeded was attributed to the effect of water produced in the reaction.[5]

This reaction has been investigated as a method of measurement of acidity in absolute ethyl alcoholic solutions. It was found convenient to follow the course of the reaction dilatometrically, the high sensitivity of this method making possible the use of dilute solutions of substrate.

Materials and Procedure

Ethyl Alcohol.—Commercial 95% ethanol was dehydrated by refluxing over several portions of calcium oxide and distilling in an apparatus designed to prevent access of moisture from the air. It was kept in a flask protected with calcium chloride tubes, and its water content was estimated at intervals from density determinations at 25°. The lowest density observed was 0.78505 g./ml., which is in good agreement with the density 0.78506 of Osborne, McKelvy and Bearce.[6] The density was found to vary linearly with the water content from 0 to 1%. The water content was therefore estimated from the density figures for 99 and 100% alcohol in the "International Critical Tables." It was not allowed to exceed 0.02%. No removal of aldehyde was necessary since the acetal formation is first order, and aldehyde increases the density of alcohol as does water.

Acetaldehyde.—Commercial acetaldehyde was distilled through a column of calcium chloride, the fraction boiling above 22° being rejected.

HCl, HBr, HI, $HClO_4$.—C. P. concentrated acids were used. Since the concentrations of these acids as catalysts did not exceed 0.001 molar, the amount of water introduced with the acid is negligible.

Picric acid, 2,4-dinitrophenol and oxalic acid were recrystallized from water, the last being dehydrated at

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[1] National Research Fellow in Chemistry.

[2] Brönsted and Grove, THIS JOURNAL, **52**, 1394 (1930).

[3] Kilpatrick and Chase, *ibid.*, **53**, 1732 (1931).

[4] Adkins and Broderick, *ibid.*, **50**, 178 (1928).

[5] De Leeuw, *Z. physik. Chem.*, **77**, 284 (1911).

[6] Osborne, McKelvy and Bearce, *Bur. Standards Bull.*, **9**, 327 (1913).

100°. **Trichloroacetic and monochloroacetic** acids were distilled *in vacuo*.

Aniline, *o*-toluidine, dimethylaniline, and pyridine were purified by distillation. Pyridine was dried over potassium hydroxide before distillation, and separate samples were titrated in a small volume with standard hydrochloric acid in the presence of thymol blue and of brom phenol blue as indicators. The mean result was 99.9% pyridine.

Procedure.—For fast reactions the dilatometer comprised a mixing bulb connected by a well ground stopcock to a reaction bulb of about 40 cc. capacity. A graduated capillary of about 0.4 sq. mm. cross section was sealed to the reaction bulb. The scale and capillary were calibrated by the mercury thread method. The leakage through the stopcock, which was lubricated with a small amount of vaseline, amounted to approximately 0.2 mm. on the scale per hour. The same stopcock with a mercury seal was found to leak more rapidly, presumably because the mercury does not immediately force the solution out of the interstices of the stopcock. For this reason a mercury seal was not used for the major portion of the work. The inhibition by mercury of the hydrogen chloride-catalyzed reaction noted by Adkins and Broderick[4] was not observed, however, in a series of experiments in which mercury in the dilatometer bulb was used to seal the stopcock.

For slow reactions a dilatometer was designed without stopcocks to eliminate leakage. To a 30-cc. reaction bulb were sealed two vertical tubes, one of which was a graduated capillary of 0.5 sq. mm. cross section; the other was a 2-mm. tube constricted to about 0.5 sq. mm. cross section and bent downward just above the constriction to minimize drainage. The bulb was filled through the constricted tube, and readings were taken on the graduated capillary after adjusting the level in the filling tube to a mark on the constricted portion.

The reaction was started by mixing a small definite volume of a 20% solution of acetaldehyde in absolute alcohol with the solution containing the catalyst (immediately after preparation of the latter) and transferring to the dilatometer by air pressure. Both solutions had previously been brought to temperature in a thermostat regulating to ±0.001°, and within five minutes after mixing the first reading was taken. The exact interval was not determined, since the reactions are of the first order. Time measurements were made with a calibrated stop watch.

It was not feasible to add pure aldehyde directly because of the large heat of solution in alcohol.

Since the water produced inhibits the reaction the concentration of aldehyde was kept below 0.02 molar. That this concentration affects neither the solvent properties nor the acidity was proved by the fact that variation of the initial concentration from 0.005 to 0.1 did not affect the velocity constant. The conclusion of de Leeuw[5] that the density of alcohol-acetaldehyde solutions increases with time was not corroborated. When acetaldehyde and ethyl alcohol were mixed at a temperature sufficiently below that of the thermostat to balance the heat of mixing, no volume change was observed from five minutes to three hours after mixing.

The first order reaction velocity constants were obtained graphically, and were reproducible to ±3% on separate runs. In Table I is part of a typical experiment with hydrochloric acid as catalyst (20 to 50 readings were taken usually). Δ represents the difference between the observed dilatometer reading, h_t, and that calculated from the graphically determined constant k and the initial and final readings, h_i and h_f, by the equation

$$kt = \ln \frac{h_i - h_f}{h_t - h_f}$$

All determinations were made at 25.00°.

TABLE I

DATA FOR TYPICAL REACTION

HCl 0.000217m k(graph.) 0.0318 min.$^{-1}$

t, min.	h_t (obs.), cm.	h_t (calcd.), cm.	Δ, cm.
0	7.25 (h_i)	....	....
1	7.18	7.17	−0.01
2	7.09	7.08	− .01
4	6.93	6.93	.00
8	6.64	6.66	.02
12	6.40	6.41	.01
16	6.18	6.19	.01
20	5.99	6.00	.01
32	5.57	5.56	− .01
40	5.37	5.34	− .03
50	5.17	5.14	− .03
(200)	4.60(h_f)	....	....

Results

Strong Acids. Catalytic Constant of Hydrogen Ion.—The catalytic constants k/C (where k is velocity constant in min.$^{-1}$ and C is concentration of acid in moles per liter) of HCl, HBr, HI and $HClO_4$ were determined in solutions from 0.00005 to 0.0005 molar. The mean values were: HCl, 143; HBr, 142; HI, 144; $HClO_4$, 144. They were independent of concentration and unaffected by addition of 0.001 molar salt with a common ion (LiCl, NaBr, KI, $NaClO_4$). These facts confirm the conclusion of Murray-Rust and Hartley[7] that these acids are completely ionized in dilute alcoholic solution. The contrary conclusion of Schreiner[8] with respect to HCl and HBr depends on catalytic esterification in relatively concentrated solutions of electrolytes. The average value 143 may therefore be taken as the catalytic constant, $k_{H^+(C_2H_5OH)}$, of solvated hydrogen ion in absolute alcohol at 25° for low concentrations of electrolyte.

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(7) Murray-Rust and Hartley, *Proc. Roy. Soc.*, **A126**, 84 (1929).

(8) Schreiner, *Z. physik. Chem.*, 111, 419 (1924).

The temperature coefficient and energy of activation for the reaction catalyzed by solvated hydrogen ions were obtained from the mean catalytic constant, 494, for HCl at 35°.

$$\frac{[k_{H^+(C_2H_5OH)}]_{35°}}{[k_{H^+(C_2H_5OH)}]_{25°}} = 3.45 \qquad E_{act.} = 22{,}600 \text{ cal.}$$

The reaction shows a linear primary salt effect (Fig. 1), the same for the different 1:1 electrolytes LiCl, KI, NaI, $NaClO_4$ up to ionic strength $\mu = 0.1$. The accuracy of the data from which this conclusion is drawn is probably not better than ±10% at the higher electrolyte concentrations since it depends on measurements in unbuffered solutions. The salts used, however, were carefully recrystallized. It is to be noted that this salt effect is considerably greater than known primary salt effects in aqueous solution.[9] It may be expressed by the equation

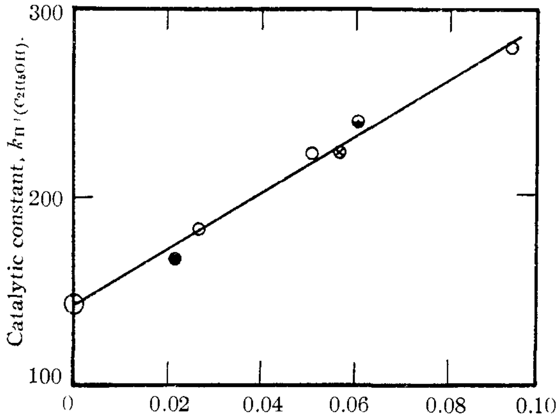

Fig. 1.—Primary salt effect. ○, $NaClO_4$; ⊗, LiCl; ●, KI; ⊖, NaI.

$$k_{H^+(C_2H_5OH)} = 143 + 1500\ \mu$$

For a measure of acidity in solutions containing more than a few thousandths molar electrolyte it is necessary to correct the catalytic constant by the above equation. This has been done where necessary in the work here reported.

Weak Acids. Change of Electrolyte Concentration.—The dissociation constants of some weak acids were determined by measurement of catalytic activity of their alcoholic solutions alone or with their salts. No measurable change in the velocity constant was obtained for nitric and picric acid buffers when the buffer concentration was changed from 0.0005 to 0.005 molar, keeping the buffer ratio and ionic strength constant. It may be concluded therefore that the reaction is not catalyzed by undissociated nitric and picric acids, and that it is not catalyzed by acids weaker than $H^+(C_2H_5OH)$ in alcoholic solution.

The *pK* (negative logarithm of the dissociation constant K_c) of nitric acid is plotted in Fig. 2 against the square root of the ionic strength. The slope, 5.9, of the experimental curve up to $\sqrt{\mu} = 0.06$ is approximately that calculated from the Debye–Hückel limiting law, 5.6. The variation of *pK* with $\sqrt{\mu}$ for picric acid determined by Larsson[10] (conductivity) and by Gross and Goldstern[11] (spectrophotometric) are shown in the same figure for comparison. The slopes are, respectively, 7.6 and 7.7.

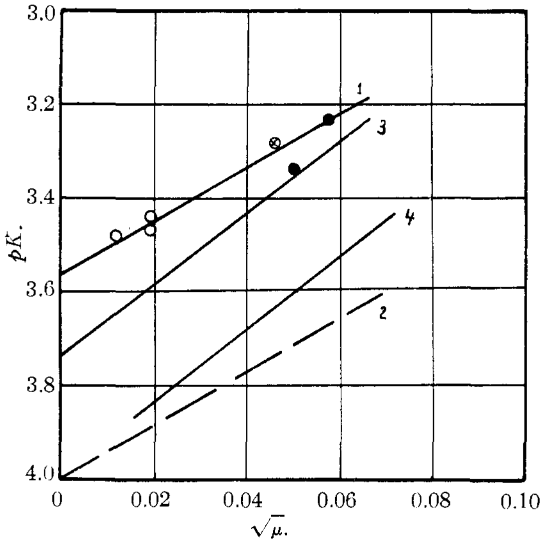

Fig. 2.—*pK* of weak acids as function of electrolyte concentration: Curve 1, nitric acid at 25°; added electrolyte: ○, none; ⊗, sodium nitrate; ●, silver nitrate. Curve 2, theoretical slope calculated from Debye–Hückel limiting law. Curve 3, picric acid at 20° (Gross and Goldstern). Curve 4, picric acid at 25° (Larsson).

In Table II, column 2, are given the mean calculated dissociation constants K_0 of three carboxylic acids, two phenolic acids, and nitric acid. For intercomparison they have been extrapolated to zero ionic strength by the equation

$$\log K_c = \log K_0 + 5.9\sqrt{\mu}$$

As a check the dissociation constants of picric acid and 2,4-dinitrophenol were determined colorimetrically, using a Bausch and Lomb colorimeter, and are given in the table in paren-

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[9] Brönsted and Grove (Ref. 2) and Kilpatrick and Chase (Ref. 3) found an unusually large primary salt effect on the reverse reaction (acetal hydrolysis) in aqueous solution.

[10] Larsson, Thesis, Kopenhagen, 1924.

[11] Gross and Goldstern, *Monatsh.*, **55**, 316 (1930).

theses. The discrepancy in the case of 2,4-dinitrophenol is probably due to the necessity of determinations in unbuffered solutions with this weak acid. For the same reason the dissociation constant of monochloroacetic acid is not as precise as those of the less weak acids.

TABLE II

DISSOCIATION CONSTANTS OF WEAK ACIDS

Acid	K_0 Et. alc.	pK_0 Et. alc.	pK Water	ΔpK
Nitric	2.7×10^{-4}	3.57	...	...
Picric	1.0×10^{-4}	4.0	0.8	3.2
	(1.0×10^{-4})			
Trichloroacetic	3.5×10^{-6}	5.46	.7	4.8
Oxalic	2.6×10^{-7}	6.58	1.3	5.3
Monochloroacetic	1.8×10^{-8}	7.74	2.9	4.8
2,4-Dinitrophenol	1.8×10^{-8}	7.74	3.9	3.8
	(4.2×10^{-8})	(7.38)		(3.5)

The dissociation constant found for nitric acid agrees in order of magnitude with the figure 0.9×10^{-4} of Murray-Rust and Hartley[7] from conductivity measurements. The constant for picric acid is in good agreement with the constants of Larsson[10] (0.8×10^{-4}) and of Gross and Goldstern[11] (1.8×10^{-4}, 20°).

In columns 3 and 4 are given the values of pK in alcohol and water,[12] respectively. $\Delta\ pK$, the difference in logarithmic units between the constants in water and in alcohol, is given in the last column. The decreases in ionization constants of the carboxylic acids in passing from water to absolute alcohol appear to be the same (5.0 pK units) within the probable experimental error involved in a comparison with ionization constants determined by miscellaneous methods in aqueous solution. The decrease in strength of the two phenolic acids appears to be less than that for carboxylic acids by about 1.3 units, although the aqueous dissociation constant of picric acid is not known with certainty. For carboxylic acids the mean decrease in pK has been reported as: 5.6, Larsson[10]; 5.5, Goldschmidt[13]; 3.0, Bright and Briscoe.[14] The last estimate is based on extrapolation from measurements in 95% alcohol. According to Halford[15] the variation in the relative strength of benzoic and salicylic acids is as great as 0.5 unit in passing from water to 93.8% alcohol. This conclusion has been confirmed by colorimetric measurements made in this Laboratory with 2,4-dinitrophenol as indicator.

Weak Bases.—The dissociation constants of the cations of aniline, *o*-toluidine, dimethylaniline, and pyridine were determined from the acidity of buffer solutions of the base B and its hydrochloride. The constants did not vary with concentration, nor with addition of 0.03 molar LiCl (corrections having been made for primary salt effect). The concentrations of the two primary amines were kept less than 0.001 molar because otherwise a reaction between amine and acetaldehyde occurs at an appreciable velocity. In Table III, column 2, are given the cation dissociation constants, $K_a = C_B \cdot C_{H^+(C_2H_5OH)}/C_{BH^+}$. In columns 3 and 4 are the values of pK' ($-\log K_a$) in alcohol and water,[12] respectively. The differences, $\Delta pK'$ (column 5), are constant within experimental error. The discrepancy between the mean value (0.8) of $\Delta pK'$ and that found by Goldschmidt[13] (−0.2) for the same bases may be due to the effect of electrolyte on the dissociation constants of the weak acids used by Goldschmidt for determining base strength.

TABLE III

DISSOCIATION CONSTANTS OF WEAK BASE CATIONS

Base	K_a Et. alc.	pK' Et. alc.	pK' Water	$\Delta pK'$
Aniline	1.9×10^{-4}	3.73	4.6	0.9
o-Toluidine	1.0×10^{-4}	4.00	4.4	.4
Dimethylaniline	0.74×10^{-4}	4.13	5.0	.9
Pyridine	$.47 \times 10^{-4}$	4.33	5.3	1.0

Inhibition by Water.—In Table IV are given the catalytic constants k/C for hydrochloric acid in solutions containing water. The decrease in velocity may be attributed either to a medium effect,[16] or to the basic action of water:

$$H_2O + H^+(C_2H_5OH) \rightleftharpoons H_3O^+ + C_2H_5OH$$

On the basis of the latter assumption the pK' of water in alcoholic solution was calculated from the concentration of water and the ratio $C_{H_3O^+}/C_{H^+(C_2H_5OH)} = (143 - k/C)/k/C$, and is given in the last column. The values are in good agreement with calculations of the pK' from the extent of ionization, measured colorimetri-

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[12] The aqueous dissociation constants of the acids and bases in Tables II and III are the most probable values from Landolt-Börnstein. The figure for picric acid is taken from von Halban and Ebert, *Z. physik. Chem.*, **112**, 359 (1924). The figure for monochloroacetic acid is that given by Saxton and Langer, THIS JOURNAL, **55**, 3638 (1933).

[13] Goldschmidt and co-workers, *Z. physik. Chem.*, **89**, 129 (1914); **91**, 46 (1916); **99**, 116 (1921); **119**, 439 (1926).

[14] Bright and Briscoe, *J. Phys. Chem*., **37**, 787 (1933).

[15] Halford, THIS JOURNAL, **55**, 2272 (1933).

[16] The constancy of the velocity constant throughout the reaction indicates that the reverse reaction is negligible in these solutions, as does also an approximate calculation of the rate of the reverse reaction from the equilibrium constant data of Adkins and Broderick.[4]

cally, of picric acid in alcohol, assuming the pK' of picric acid to be unchanged by the water added (Table V). The deviation of pK' (Table V) from the estimates of Larsson[10] (1.3, electrometric) and of Goldschmidt[13] (1.2, reaction velocity) is in the opposite sense to that which a medium effect on the dissociation of picric acid would be expected to produce. The causes for the wide deviation between the most probable pK' of water as base referred to water as solvent, measured in different solvents: alcohol, +1.6; water,[17] −1.8; and formic acid,[18] −3.4, have been discussed in an earlier paper.[18]

TABLE IV

INHIBITION OF HCl CATALYSIS BY WATER

HCl 0.0002 to 0.0004m		
C_{H_2O}, m	k/C	pK'_{H_2O}
0	143	...
0.1	87	0.8
.2	62	.8
.5	30	.9

TABLE V

COLORIMETRIC DETERMINATION OF BASE STRENGTH OF WATER

Picric acid, m	Water, m	$C_{\text{Picrate ion}}/(C_{\text{Picric acid}} + C_{\text{Picrate ion}})$ (colorimetric)	pK'_{H_2O}
0.00171	0	0.25	...
.00179	0.12	.32	0.9
.00186	.51	.39	.6

Catalysis of Acetal Formation by Metallic Salts.—Salts have been used as catalysts in the synthesis of some acetals. According to Adkins and Nissen and Adams and Adkins[19] the most effective salt catalysts for the formation of diethyl acetal are calcium chloride, calcium nitrate and lithium chloride. They point out that salts which catalyze the reaction give acidic solutions in water, but that the converse is not true.

Since there was no direct connection between the hydrolysis of these salts in water and their order of efficiency, it was of interest to examine these salts in acid-free solutions. The extent of reaction was determined by titration by the Seyewetz–Bardin method as modified by Adams and Adkins.[19,20] Lithium chloride purified by recrystallization from alcohol has no detectable catalytic effect in saturated solution at 25° for twenty-four hours. It is not practicable to free calcium chloride and calcium nitrate from acid impurities by recrystallization from water because of hydrolysis on dehydration and the fact that calcium hydroxide causes a side-reaction (probably aldol condensation). No measurable reaction could be detected, however, after twenty-four hours at 35° in 3 molar solutions of these salts to which 0.01 molar benzoic acid–calcium benzoate buffer had been added. It appears that use of these salts in acetal synthesis depends not on a catalytic effect of the salts themselves but on traces of strong acids which they contain as impurities, together with the large salt effects on the acid catalysis. The shift in equilibrium produced by the removal of water as salt hydrate is also of advantage for the synthesis.

The author wishes to thank Professor Farrington Daniels for many valuable suggestions.

Summary

1. The rate of formation of diethyl acetal is suitable as a measure of acidity in absolute alcoholic solution at relatively high or low ionic strength. The reaction is not catalyzed by acids weaker than hydrogen ion, and a correction may be applied for the large primary salt effect.

2. Hydrochloric, hydrobromic, hydriodic and perchloric acids are completely ionized strong acids. Nitric and picric acids are weak acids of about the same strength in this solvent.

3. The effect of change of electrolyte concentration and solvent on the dissociation constants of a number of weak acids and bases has been determined.

4. The inhibition of the reaction by traces of water may be ascribed to its basic character. The base strength of water in alcohol has been estimated.

5. Catalysis of the reaction in the presence of calcium chloride, calcium nitrate and lithium chloride is due to traces of strong acids.

MADISON, WISCONSIN RECEIVED SEPTEMBER 7, 1933

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(17) Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

(18) Hammett and Deyrup, This Journal, **54**, 4239 (1932).

(19) Adkins and Nissen, *ibid.*, **44**, 2749 (1922); Adams and Adkins, *ibid.*, **47**, 1358 (1925).

(20) Thymolphthalein was found more satisfactory than phenolphthalein as indicator. Its color change corresponds more closely with the P_H of stoichiometrically neutral sodium sulfite solutions, thus making unnecessary the use of comparison solutions of indicator.