Introducing an α-methyl group into vinyl chloride or bromide increases the moment by the predicted amount but a β-methyl group produces only about one-half the expected decrease in moment. Also, two chlorine atoms on the same carbon atom as in vinylidene chloride or 1,1-dichloropropene-1 fail to decrease the moment by the expected amount. These results have been interpreted in terms of resonance and hyperconjugation.

EAST LANSING, MICHIGAN RECEIVED JANUARY 24, 1947

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION, CHEMICAL ENGINEERING DEPARTMENT, TENNESSEE VALLEY AUTHORITY]

Activity of Orthophosphoric Acid in Aqueous Solutions at 25° from E.m.f. Measurements with the Lead Amalgam–Lead Phosphate Electrode

BY CHARLES M. MASON AND WINIFRED M. BLUM

In thermodynamic studies of phosphate systems involved in industrial and physiological processes, an electrode reversible with respect to phosphate ion would have many applications.

Several investigators[1,2,3] have studied galvanic cells involving the lead amalgam electrode. Bates, Edelstein and Acree[1] have shown that the lead and lead amalgam electrodes are reproducible within 0.02 mv. Fairhall[4] has shown that, of the possible lead phosphates, the secondary salt, $PbHPO_4$, is the only stable phase in equilibrium with phosphoric acid solutions containing up to 48% phosphorus pentoxide at 25°. Fairhall and Shaw[5] have found the solubility of secondary lead phosphate in water at 25° to be 0.000043 mole per liter.

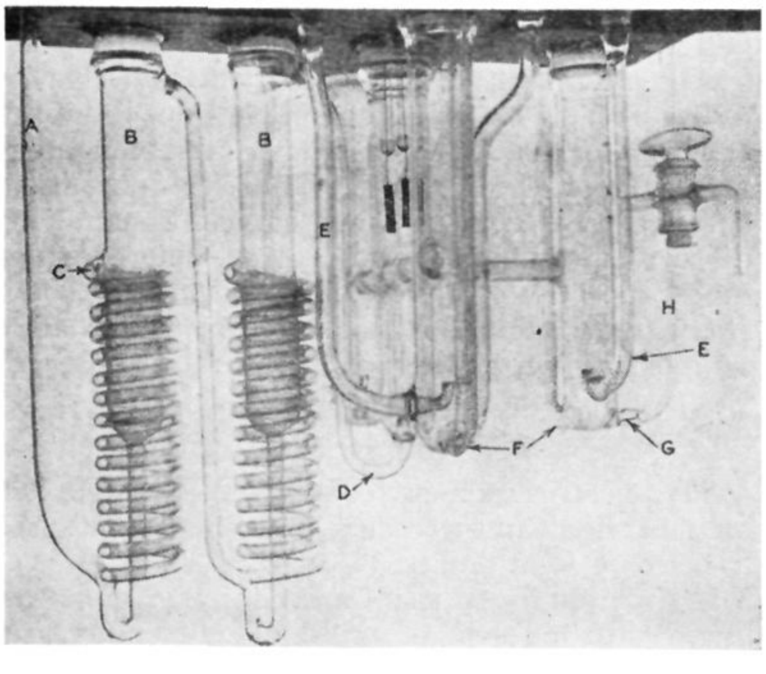

Fig. 1.—Cell.

The practicability of the lead amalgam electrode and the slight solubility of secondary lead phosphate indicated that the half-cell, Pb(2-phase amalgam), $PbHPO_4$, $H_2PO_4^-$, should be suitable for measurement of phosphate-ion activity.

The present paper describes an experimental study of the lead amalgam–lead phosphate electrode and the application of the electrode in measurement of the activity of aqueous orthophosphoric acid in concentrations up to 10 molal at 25°.

Experimental Methods

LaMer and Parks,[3] as well as Bray,[2] have reported that lead amalgam electrodes yield reproducible results only in the absence of oxygen. In the present work, therefore, care was taken to exclude oxygen from the system.

The cell, shown in Fig. 1, was so arranged that either of two hydrogen half-cells could be measured against any of three lead amalgam–lead phosphate half-cells. Oxygen-free hydrogen entered at A and passed through two saturators, B, before entering the bottom of the hydrogen electrode chamber at D. The saturators, B, contained air-free solution of the same concentration as that in the cell and were adapted from the conductivity cells described by Brown and Felger.[6]

To prevent fouling of the surface of the amalgam electrodes, the amalgam half-cells were filled in an atmosphere of oxygen-free nitrogen. Lead amalgam at 90° was run from a pipet down tube F against a stream of nitrogen. The pool of amalgam thus formed from underneath exhibited a bright surface for contact with the solution. Any scum resulting from the transfer remained in tube F. When enough amalgam had been added to cover the opening of tube F into the cell chamber, the amalgam was allowed to solidify. Nitrogen was then passed in through side tube E, and enough dried secondary lead phosphate was added through the top of the cell to make a 1-mm. layer on the amalgam.

Phosphoric acid solution, previously degassed by boiling under reduced pressure and saturated with secondary lead phosphate, was introduced, by nitrogen pressure, through tube E to fill the cell to the center of the hydrogen electrodes.

---

[1] R. G. Bates, M. Edelstein and S. F. Acree, *J. Research Natl. Bur. Standards*, **36**, 159–170 (1946).

[2] U. B. Bray, THIS JOURNAL, **49**, 2372–2380 (1927).

[3] V. K. LaMer and W. G. Parks, *ibid.*, **53**, 2040–2061 (1931).

[4] L. T. Fairhall, *ibid.*, **46**, 1593–1598 (1924).

[5] L. T. Fairhall and C. P. Shaw, *J. Ind. Hyg.*, **6**, 159–168 (1924).

[6] E. H. Brown and M. M. Felger, *Ind. Eng. Chem., Anal. Ed.*, **17**, 277–280 (1945).

Finally, the saturators were filled to point C and flushed with hydrogen. At the top of the cell (not shown) all the stoppers were equipped with stopcocks to facilitate flushing the cell. The hydrogen escaped through an S-shaped trap which prevented back diffusion of oxygen. Electrical contact with the amalgam half-cell was made through platinum wire G to mercury in tube H. The lead amalgam electrodes usually checked each other within 0.1 mv. in the same solution.

Hydrogen electrodes were prepared in the usual manner. Pairs usually checked within 0.02 mv.; if not, they were replaced. All the readings were corrected to 1 atmosphere hydrogen pressure.

Measurements of electromotive force were made with a Leeds & Northrup type K-2 potentiometer. All measurements were made with the cells immersed in a water thermostat at 25 ± 0.01°. The Eppley standard cell and thermometers were calibrated frequently against standards calibrated by the National Bureau of Standards.

Phosphoric acid of reagent grade was used without further treatment. Tests showed the absence of phosphorus acids of lower oxidation states. Mercury, hydrogen and nitrogen were purified by standard procedures.

Secondary lead phosphate, $PbHPO_4$, was prepared by the method of Millet and Jowett[7] from C. P. lead nitrate that had been recrystallized, washed and dried at 110°. Repeated analyses of batches prepared at different times checked the theoretical composition within the limits of accuracy of the analytical methods.

The 2-phase lead amalgam contained about 5% lead and consisted of the compound Pb_2Hg in equilibrium with a saturated solution of lead in liquid mercury.[8] The amalgam was prepared electrolytically by the method of LaMer and Parks.[3] The amalgam was stored under nitrogen in a round-bottomed flask fitted with side tubes. Samples of amalgam were obtained for introduction into the cells by heating the flask to 90° in a water-bath and withdrawing the resulting single-phase amalgam with a pipet. The flask was flushed with nitrogen during withdrawal of the sample.

Theoretical Discussion

The conventions employed in the following discussion are those established by Lewis and Randall.[9]

The cell is represented by Pb(2-phase amalgam), $PbHPO_4(s)$, $H_3PO_4(m)$, H_2. The corresponding cell reaction is

$$\text{Pb(2-phase amalgam)} + H_3PO_4 = PbHPO_4 + H_2 \qquad (1)$$

With the cell reaction written in the direction indicated, the cell potential is positive in sign, and the substance of variable activity occurs to the left of the equality sign. If secondary and tertiary ionization are assumed to be negligible at finite concentrations, the equation for the cell potential becomes

$$E = E^0 + \frac{RT}{2F}\ln a_{H^+}\,a_{H_2PO_4^-} \qquad (2)$$

If the concentration of hydrogen ion is designated as m_1, the concentration of dihydrogen phosphate ion as m_2, and the mean ion activity coefficient of phosphoric acid as $\gamma_\pm$, equation 2 becomes

$$E = E^0 + \frac{RT}{2F}\ln \gamma_\pm^2 + \frac{RT}{2F}\ln m_1 + \frac{RT}{2F}\ln m_2 \qquad (3)$$

which, on rearrangement, gives

$$E - \frac{RT}{2F}\ln m_1 - \frac{RT}{2F}\ln m_2 = E^0 + \frac{RT}{2F}\ln \gamma_\pm^2 \qquad (4)$$

Elmore, Mason and Christensen[10] have demonstrated the reasonableness of using the Debye–Hückel limiting law for the mean ion activity coefficient of phosphoric acid up to an ionic strength of 0.03. Hence, if the left-hand side of equation 4 be represented by $E^{0\prime}$, the equation becomes

$$E^{0\prime} = E^0 - \frac{2.30259RT}{F}(A'\sqrt{\mu}) \qquad (5)$$

It is apparent that a plot of $E^{0\prime}$ against the square root of the ionic strength should approach a straight line intersecting the zero axis of ionic strength at E^0 with a limiting slope to be calculated from the constant terms in the equation. Values of A' and of $2.30259RT/F$ were taken from the compilation of Manov, Bates, Hamer and Acree[11] and were 0.5085 and 0.059138, respectively.

To calculate the value of $E^{0\prime}$, it was necessary to determine the values of m_1 and m_2 over a range of concentration sufficiently low to enable an extrapolation to zero ionic strength. If it is assumed that the slightly soluble lead salt, $PbHPO_4$, does not alter the extent of ionization of phosphoric acid, m_1 may be taken as equivalent to αm, where α is the degree of dissociation and m the molality of the phosphoric acid.

The degree of dissociation, α, on the assumption that phosphoric acid is a one–one electrolyte, was determined for the concentration range from 0.01 to 0.1 molal phosphoric acid from conductance data. The limiting conductance, Λ_0, was first calculated by the method of Shedlovsky[12] from the data of Noyes and Eastman[13] for the conductivity of phosphoric acid.

Activity coefficients for the calculation were derived from the Debye–Hückel limiting law. Since there was a deficiency of experimental data in the very dilute region, the value obtained for

---

[7] H. Millet and M. Jowett, THIS JOURNAL, **51**, 997–1004 (1929).

[8] R. H. Gerke, *ibid.*, **44**, 1684–1704 (1922).

[9] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923.

[10] K. L. Elmore, C. M. Mason and J. H. Christensen, THIS JOURNAL, **68**, 2528–2532 (1946).

[11] G. G. Manov, R. G. Bates, W. J. Hamer and S. F. Acree, *ibid.*, **65**, 1765–1767 (1943).

[12] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739–743 (1938).

[13] A. A. Noyes and G. W. Eastman, *Carnegie Inst. Wash. Pub.*, **63**, 262 (1907).

Λ_0 by the method of Shedlovsky[12] (Λ_0 = 378.3) was adjusted until a plot of functions calculated from the conductance data[13] by the method described by Lugg[14] extrapolated to the value reported by Nims[15] for the first ionization constant for phosphoric acid (pK = 2.124). The final value, Λ_0 = 379.48, was used to calculate α, the degree of dissociation, by the method of Banks[16]; identical results, within experimental error, were obtained by Shedlovsky's[12] method. These values of α, reported in Table I, were used to calculate the value of m_1.

TABLE I

CALCULATED VALUES OF α, m_1, m_2, μ AND $E^{0\prime}$ USED TO DETERMINE E^0 FROM SMOOTHED ELECTROMOTIVE FORCE MEASUREMENTS

m	α	m_1	m_2	μ	$E^{0\prime}$
0.01	0.6027	0.006027	0.006157	0.006417	0.24234
.02	.4946	.009892	.01010	.01052	.24170
.03	.4359	.01308	.01338	.01398	.24121
.04	.3970	.01588	.01625	.01699	.24085
.05	.3688	.01844	.01890	.01982	.24055
.06	.3473	.02084	.02138	.02210	.24030
.07	.3301	.02311	.02374	.02500	.24001
.08	.3162	.02530	.02601	.02743	.23976
.09	.3040	.02736	.02815	.02973	.23960
.10	.2938	.02938	.03026	.03202	.23944

The total concentration of phosphate ion, m_2, is the sum of the concentration of dihydrogen phosphate ion from the dissociation of the phosphoric acid, αm, and the concentration of dihydrogen phosphate ion resultant from hydrolysis of the dissolved secondary lead phosphate.

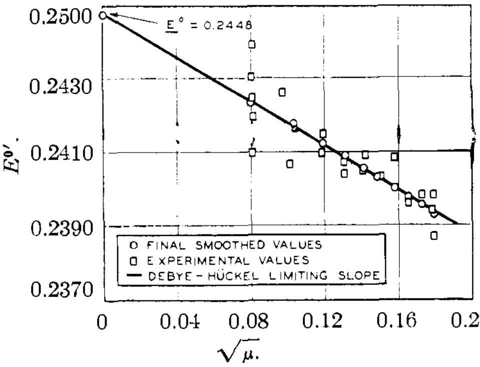

Fig. 2.—Determination of E^0 by graphical extrapolation.

Nims[17] gives the second ionization constant of phosphoric acid as 6.226 × 10^{-8}, which means that the ratio, $a_{H_2PO_4^-}/a_{HPO_4^=}$, is of the order of 10^6. Hence, the $HPO_4^=$ ion may be neglected, and the $H_2PO_4^-$ ion derived from the lead salt may be considered equivalent to the concentration of the salt on the assumption that the salt is ionized completely. These relationships are

$$\begin{aligned} m_1 &= \alpha m \\ m_2 &= \alpha m + m_{Pb^{++}} \\ \mu &= m_1 + 3m_{Pb^{++}} \end{aligned} \qquad (6)$$

Numerical values of these quantities are given in Table I. The solubility of secondary lead phosphate was obtained from the data of Fairhall.[4]

Experimental Data and Calculations

Determination of E^0.—It was not practical to obtain the electromotive force of the cells at round values of concentration of phosphoric acid. In addition, when values of $E^{0\prime}$ were calculated from the original data in dilute solutions the points, as shown by the squares in Fig. 2, were unsatisfactory for an accurate extrapolation to determine E^0. To obtain a better extrapolation, the data were smoothed. The original readings were plotted on a large scale with observed electromotive force as a function of the logarithm of the molality. The plot was nearly linear. Below 0.1 m the points tended to scatter with a deviation from the smooth curve of as much as ±0.3 mv. for some cells. Above 0.1 m the deviation decreased rapidly to about ±0.1 mv.

Equation 2 was rearranged to

$$\frac{(E - E^0)F}{2.30259RT} - \log m = \log \alpha\gamma \qquad (7)$$

A plot of the left-hand side of equation 7 as some function of m will intersect both axes at zero. Using an approximate value of E^0 obtained by extrapolation of the actual data and values of E obtained from the logarithmic plot mentioned above, values were calculated for the left-hand side of equation 7 at various round molalities. These values for the left-hand side of equation 7 were then plotted on a large scale as a function of the square root of m as shown in Fig. 3. A smooth curve through these points permitted a determination of the final values of E by interpolation.

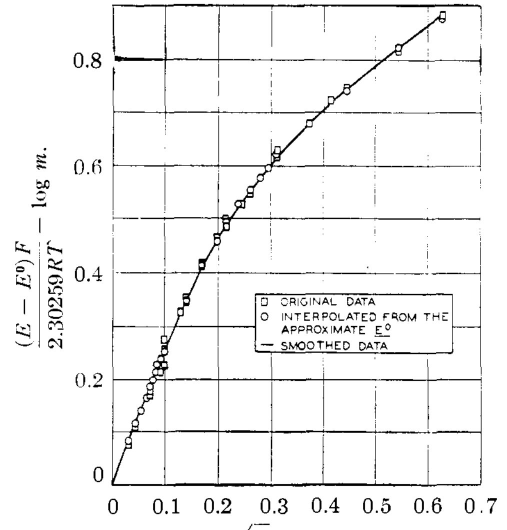

Fig. 3.—Deviation function used to smooth electromotive force data.

---

[14] J. W. H. Lugg, THIS JOURNAL, **53**, 1-8 (1931).

[15] L. F. Nims, *ibid.*, **56**, 1110-1112 (1934).

[16] W. H. Banks, *J. Chem. Soc.*, 3341-3342 (1931).

[17] L. F. Nims, THIS JOURNAL, **55**, 1946-1951 (1933).

Smoothed values of E are given in Table II. These values of E were used in the calculation of the final values in Table I for $E^{0\prime}$. A plot of $E^{0\prime}$ as a function of the square root of the ionic strength yielded, by the method of least squares, a value of 0.2448 volt for E^0. Fig. 2 shows the final plot. In Fig. 3 the curvature for concentrations below 0.04 molal is so slight that the curve is readily extended to the axis of ordinates in a manner that will give values of E in the dilute concentrations within ±0.1 mv. E, then, should yield values of $E^{0\prime}$ that will extrapolate to within ±0.1 mv. of the true standard potential, E^0.

TABLE II

SMOOTHED VALUES OF E FOR THE CELL Pb(2-PHASE AMALGAM), $PbHPO_4$ (s), H_3PO_4 (m), H_2

m	E	m	E	m	E
0.001	0.06229	0.05	0.13831	0.9	0.18112
.002	.07814	.06	.14121	1.0	.18275
.003	.08707	.07	.14360	2.0	.19419
.004	.09305	.08	.14568	3.0	.20184
.005	.09775	.09	.14755	4.0	.20804
.006	.10140	.10	.14920	5.0	.21336
.007	.10432	.2	.15930	6.0	.21819
.008	.10705	.3	.16506	7.0	.22285
.009	.10931	.4	.16911	8.0	.22704
.01	.11133	.5	.17235	9.0	.23094
.02	.12342	.6	.17502	10.0	.23428
.03	.13010	.7	.17738		
.04	.13475	.8	.17934		

Calculation of Activity of Phosphoric Acid.—The free energy, F, of a solution of m moles of electrolyte in 1000 g. of solvent is

$$F = M\mu_1 + m\mu_2 \tag{8}$$

where μ_1 and μ_2 are the chemical potentials of the solvent and solute, respectively. If the solute is dissociated to a degree, α, into simple ions, the molality of the positive ion is $\nu_+\alpha m$, that of the negative ion is $\nu_-\alpha m$, and that of the undissociated solute is $(1-\alpha)m$, where ν_+ and ν_- represent the respective numbers of positive and negative ions.

The chemical potential of the solute is

$$\mu_2 = \alpha(\nu_+\mu_+ + \nu_-\mu_-) + (1 - \alpha)\mu_u \tag{9}$$

where μ_u is the chemical potential of the undissociated portion of the solute. At ionic equilibrium

$$\mu_u = \nu_+\mu_+ + \nu_-\mu_- \tag{10}$$

Substitution of equation 10 into equation 9 yields

$$\mu_2 = \mu_u \tag{11}$$

which, by virtue of the equation of definition

$$\mu_u = \mu_u^0 + RT \ln a_u \tag{12}$$

identifies a_u, the activity of the undissociated portion of a weak electrolyte, as equivalent to the activity of the electrolyte in solution. The foregoing treatment is based on the derivations of Van Rysselberghe.[18]

Since

$$K_1 = \frac{a_+a_-}{a_u} \tag{13}$$

equation 2 becomes

$$E = E^0 + \frac{RT}{2F} \ln K_1a_u \tag{14}$$

for any weak electrolyte. With the aid of the value reported by Nims[15] for K_1, 7.516 × 10^{-3}, values of a_u were computed from the smooth values of E in Table II. In Table III the results are compared with values of a_u obtained previously from vapor pressure measurements.[10] The agreement between the two sets of data is good in the range 0.01 to 0.1 molal acid; any discrepancy in this range is attributable to experimental error. The continuous divergence at concentrations above 0.1 m may result from the increase in the solubility of the lead salt with increase in the concentration of the acid.

Standard Potential of the Lead–Lead Phosphate Electrode.—The potential between stick lead and lead amalgam was established recently by Bates, Edelstein and Acree[1] as being 0.0059 volt at 25°. Hence, for the electrode, Pb, $PbHPO_4$, $H_2PO_4^-$, E^0_{25} = 0.2507 volt.

TABLE III

ACTIVITY OF PHOSPHORIC ACID IN AQUEOUS SOLUTION AT 25°

m	a_u (e. m. f.)	a_u (e. m. f.)/a_u (vapor pressure)	m	a_u (e. m. f.)	a_u (e. m. f.)/a_u (vapor pressure)
0.001	0.00008947	...	0.2	0.1708	1.064
.002	.0003074	...	.3	.2675	1.073
.003	.0006162	...	.4	.3666	1.073
.004	.0009816	...	.5	.4718	1.078
.005	.001415	...	.6	.5809	1.084
.006	.001881	...	.7	.6981	1.095
.007	.002361	...	.8	.8132	1.095
.008	.002920	...	.9	.9341	1.098
.009	.003482	...	1.0	1.060	1.102
.01	.004075	1.027	2	2.585	1.136
.02	.01045	1.014	3	4.690	1.158
.03	.01758	1.012	4	7.600	1.176
.04	.02525	1.012	5	11.50	1.183
.05	.03331	1.012	6	16.75	1.186
.06	.04175	1.013	7	24.08	1.202
.07	.05029	1.011	8	33.37	1.193
.08	.05913	1.011	9	45.21	1.196
.09	.06841	1.013	10	58.64	1.197
.10	.07779	1.012			

Summary

The activity of orthophosphoric acid in concentrations up to 10 molal has been derived from electromotive force measurements with the lead amalgam–lead phosphate electrode. At concentrations of acid from 0.01 to 0.1 molal, the results are in good agreement with those of a previous study in which the activity was derived from

---

(18) P Van Rysselberghe, *J. Phys. Chem.*, **39**, 403–414 (1935).

vapor pressure measurements. At higher concentrations, the progressive divergence between the two sets of data may be attributed to the increased solubility of the lead phosphate in the more concentrated acid.

The standard potentials of the lead amalgam–lead phosphate and lead–lead phosphate electrodes are as follows:

Pb(2-phase amalgam), $PbHPO_4$, $H_2PO_4^-$; $E^0_{25} = 0.2448$ volt

Pb, $PbHPO_4$, $H_2PO_4^-$; $E^0_{25} = 0.2507$ volt.

WILSON DAM, ALABAMA RECEIVED NOVEMBER 4, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

High Pressure Hydrogenations with Adams Catalyst

BY ROBERT H. BAKER AND ROBERT D. SCHUETZ[1]

Extensive application of Adams platinum oxide has proved its value as a catalyst for low pressure hydrogenation,[2] but little is known of its utility at high hydrogen pressure. Some indication that it may be useful at high pressure is found in the reduction of L-mannonic lactone to L-mannitol,[3] and in the reduction in this laboratory of phenacylpyridinium bromide to the alcohol.[4] This paper reports an extension of the high pressure method to some simple aromatic compounds.

It was found that the simple benzenoid hydrocarbons may be reduced at room temperature on a preparative scale in a practical period of time. As a specific example 21 g. of toluene dissolved in 25 ml. of glacial acetic acid was completely hydrogenated at 2000 lb. over 0.67 g. of platinum oxide within twenty minutes at 25°. Benzene and *m*-xylene were hydrogenated even more rapidly, and phenol, *o*-cresol and 2-naphthol were only slightly slower. Thus the method was more rapid than the low pressure method of Adams and Marshall[5] in which hours were required for many aromatic nuclei. In addition it should be useful in the reduction of acids and other compounds which poison nickel but not platinum or of other compounds in acid medium.

It was hoped that the great increase in rate occasioned by high pressure would allow a practical rate of hydrogenation of the aromatic nucleus even in the absence of the acidic solvent. Experience has shown, however, that benzene was not reduced over platinum in the absence of solvent or when dissolved in ethanol or dioxane and heated to 180° at 2000 lb. This was in sharp contrast to the rapidity of reduction in glacial acetic acid solution at 25° and clearly demonstrated that the well-known promoting effect of acids on Adams catalyst applies at high as well as at low pressure.

Recent investigations of Smith and coworkers[6,7] with this catalyst at low pressure revealed the facts that the rate was first order with respect to hydrogen pressure, zero order with respect to acceptor and directly proportional to the amount of catalyst. They found that the phenyl-substituted aliphatic acids and the alkylated benzenes followed the rate equation

$$\log p_0/p = kt/2.303$$

When the constant, k, was referred to a constant quantity of catalyst, one gram, its magnitude was dependent only upon temperature and the nature of the compound under investigation and it was designated as k^0_t.

Although the evaluation of k^0_t at high pressure was more difficult than at low pressure the data presented in Table I indicated that for benzene it was independent of pressure in the range of 1000–2980 lb. of hydrogen.

TABLE I

HYDROGENATION OF BENZENE, 0.0226 MOLE, IN GLACIAL ACETIC ACID, 4 ML., OVER PLATINUM OXIDE IN THE 43-ML. BOMB

Initial pressure, lb./sq. in.	Catalyst, mg.	t, °C.	Time, min.	$k^0_t \times 10^2$
1000	64	27	41	66
1050	127	26	18	67
1380	63	25	35	47
1470	67	28	21	64[a]
1670	62	30	21	73[a]
1990	66	27	15	57
2480	64	26	15	51
2980	63	26	12	51
				Average 60

[a] These reactions were run at a shaking rate of 24 cycles per minute in order to show that the usual 40 cycles was sufficient to make the hydrogenation rate independent of rate of shaking.

Although the k^0_t values were not comparable unless the experiments were made with a constant hydrogen void, they had more significance than such measurements as total time of hydrogenation, time required for the reduction of the middle third, etc. With the k^0_t values it was possible to study either the activity of the catalyst or the reactivity of the hydrogen acceptor. Thus in the preparative scale in reductions of the compounds

---

[1] Abstracted from the Ph.D. Thesis of Robert D. Schuetz.

[2] For a general review of this and other catalysts see Adkins and Shriner in Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 779.

[3] Baer and Fischer, THIS JOURNAL, **61**, 761 (1939).

[4] Riegel and Wittcoff, *ibid.*, **68**, 1805, 1913 (1946).

[5] Adams and Marshall, *ibid.*, **50**, 1970 (1928).

[6] Smith, Alderman and Nadig, *ibid.*, **67**, 272 (1945).

[7] Smith and Pennekamp, *ibid.*, **67**, 276, 279 (1945).