short, single-point runs yield more realistic $\bar{D}$ values than those estimated by analogy or approximated through a modified Stokes–Einstein relation. A single previously-calibrated cell serves the purpose, but its constant should be redetermined at reasonable intervals. This cell need not include any provision for the mercury pool and contacts. Data from several polarograms at concentrations near 0.05 to 0.20 mM should be available, as well as that for the higher concentration to be used in compartment I. The cell is filled with equal volumes of nitrogen-saturated electrolyte in compartment II and of electrolyte plus 2 to 5 mM substance in I. Time and date of filling are noted, the cell is stoppered to prevent evaporation, and supported level and in as vibration-free a manner as possible in the laboratory thermostat-bath. After 24 (minimum) to 48 (preferable) hours, a portion of the solution in II is transferred to a polarograph cell, deaerated, and measured polarographically.

It is difficult to evaluate the absolute *accuracy* of the results here reported in any completely objective manner. Both the polarographic meas-

urements (statistically, at least, with reference to a number of points in the latter two-thirds of the runs) and the replicate runs on the cell constants are *precise* within about ±0.6%. The facts that data from at least 3 and up to 5 different cells are included in any given run, and that the final $\bar{D}$'s of duplicate runs using fresh solutions and new calibrations, checked within ±1.2% in the worst case and ±0.9% on an average, are reassuring. But all such criteria are more related to *precision* than to *accuracy*. As an estimate, however, it would appear that the technique as described yields $\bar{D}$ values with a precision of about ±1.0% and which should be accurate within about ±2%. The literature on diaphragm-cell measurements of conventional diffusion coefficients indicates that the technique may be improved to about ±0.5%.

Ann Arbor, Michigan

Polarographic Characteristics of +5 Vanadium in Phosphate, Borate and Carbonate Buffers

By I. Filipović, Z. Hahl, Z. Gašparac and V. Klemenčić

The polarographic behavior of +5 vanadium has been studied in phosphate, borate and carbonate buffers in the range from pH 2 to 12.5. The dependence of half-wave potential and height of polarographic waves on pH have been determined. In phosphate buffer at pH < 2, the two waves produced correspond to the reversible electrode reduction of +5 to +4 vanadium and to the irreversible electrode reduction of +4 vanadium to the +2 state, respectively. From pH 2 to 9 four waves are developed: the first two correspond to the adsorption–reduction of hydrogen polyvanadate ions; the third wave to the irreversible electrode reduction of +5 to - 4 vanadium; and the fourth to a reduction of +4 to +2 vanadium. With increasing pH the adsorption current falls and at pH 9 the adsorption wave disappears. From pH 9 to 12.5, in all three buffers, only two waves remain; the first, which corresponds to the reduction of +5 to +4 vanadium, decreases and the second, which partly corresponds to a reduction of +5 to +4 vanadium, increases with increasing pH. Above pH 12.5 a single wave is left, corresponding to a reduction of +5 to +2 vanadium. These results are attributable to the existence of five different kinds of +5 vanadium ions in equilibrium in the interval of pH examined. Two well developed waves arise about 0.5 v. apart in borate solution.

Solutions of vanadium have been frequently investigated by the polarographic method.[1] The reduction of +5 vanadium on the dropping mercury electrode in acid solutions (0.05 M sulfuric acid) produces two polarographic waves, one starting from zero, the other from −0.98 applied e.m.f. *vs.* S.C.E. In ammoniacal solutions containing 1 M ammonium chloride and less than 6 M ammonia, two very close waves arise in the interval −1 to −1.3 v. *vs.* S.C.E. With an increase of ammonia concentration the first wave shifts toward more negative, and the second toward more positive potentials, so that only one wave remains at concentrations above 6 M ammonia. In strongly basic solutions (0.1 M lithium hydroxide) a single wave develops, starting at about −1.7 v. *vs.* S.C.E. Hence it is evident that the polarographic behavior of +5 vanadium depends on pH. To elucidate the

chemical mechanism of the electrode process, a systematic polarographic investigation of +5 vanadium in buffer solutions has been carried out.

Experimental

Apparatus.—The current-voltage curves were recorded according to the usual technique with a Heyrovský photographically recording polarograph, Model V-301, manufactured by Československa Zbrojovka, Brno. The voltage on the bridge was controlled by a normal Weston standard cell from the Cambridge Instrument Co. With a head of 60 cm. of mercury, the capillary (thermometer capillary, Schott & Gen.) had a rate of flow, m, of 1.825 mg. sec.$^{-1}$ at short-circuited electrode and S.C.E. A modified polarographic cell from the Cambride Instrument Co. was used, which permitted the passage of an inert gas over the solution during measurement. The anode was either a saturated calomel, or a saturated mercurous sulfate electrode, type Cambridge Instrument Co. Before every measurement, oxygen was removed from the solution by bubbling through hydrogen obtained electrolytically and purified by means of alkaline pyrogallol solution. The polarographic cell was kept in a thermostat at 25.0°. Correction was made

(1) 1. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II. Interscience Publishers, Inc., New York, N. Y., pp. 447–452.

for residual currents in the determination of all diffusion current data. The height of the polarographic waves was measured by the exact method of Müller,[2] extrapolating the residual current

Reagents.—All reagents were analytical grade. The buffered solutions of +5 vanadium were prepared from a 0.01 M stock solution of ammonium metavanadate (C. Erba, Milano) or from a 0.01 M solution of +5 vanadium prepared by dissolving the calculated amount of vanadium pentoxide in sodium hydroxide solution. The concentrations of phosphate, borate and carbonate, and of the total salt (*i.e.*, sodium ion) were constant for all pH values. 0.4 M phosphate or borate solutions with a pH of about 12.5 were prepared by mixing 1000 ml. of 0.4 M phosphoric acid, or boric acid, and 500 ml. of 2.4 M sodium hydroxide. For a 0.2 M phosphate (or borate) buffered solution of +5 vanadium, 25 ml. of the buffer was placed in a 50-ml. volumetric flask and the pH adjusted approximately by the addition of 2 N sulfuric or hydrochloric acid; the 0.01 M vanadate solution was then added and the volume made up to the mark. Before measurement the pH was determined accurately by means of a Doran Model 4981 pH meter with an "alkacid" glass electrode, linear 0–13 pH. Buffer solutions with different concentrations of phosphate or borate were prepared analogously from the 0.4 M solutions; the ionic strength was controlled by addition of the calculated amount of potassium chloride or sodium sulfate. The solutions of +5 vanadium in carbonate buffer were prepared analogously from 0.4 M sodium hydrogen carbonate; the pH was adjusted approximately with sodium hydroxide solution and the total sodium ion concentration with 3 M sodium chloride. Acetate buffers were prepared according to Walpole.[3] As preliminary investigations had shown that freshly prepared buffered solutions of +5 vanadium did not develop well-defined polarographic waves, all solutions were examined polarographically after standing for at least two days. The orange color of +5 vanadium in acetate buffer did not change with aging. The color of the phosphate and borate solutions disappeared completely after two days when the pH was between 5 and 9; it changed to pale yellow when the pH was less than 3; and between pH 3 and 5 it remained unchanged.

Results

Phosphate Buffer.—Figure 1 shows typical polarograms with 0.2 M phosphate buffer and 10^{-3} M ammonium metavanadate. Below pH 3 and above pH 9 only two waves are produced; three waves are obtained between pH 3 and 5; and four waves between pH 5 and 9 which will be referred to as waves 1, 2, 3 and 4. Figure 2a shows polarograms recorded with a more sensitive galvanometer up to wave 4. Above pH 3 the first wave begins to split into two waves (1 and 2). Between pH 5 and 9 a third wave (3) appears. Above pH 5 wave 2 has a "maximum," because the current, having reached the limiting value, falls to a minimum and then, rising again, passes over into wave 3. Figure 3 shows the dependence of the heights of all four waves on pH.

In the presence of potassium chloride (Fig. 2b) wave 2 does not appear; the other waves are unaltered. Likewise, in phosphate buffers containing less than 5×10^{-4} M ammonium metavanadate (Fig. 2c), wave 2 is not developed, but a minimum still exists behind the first wave.

Borate Buffer.—In the pH range examined, 7.5 to 12.5, two well-defined waves (3 and 4) are obtained in borate buffer (Fig. 4). As with phosphate buffer above pH 7, the height of wave 3 is approximately constant to about pH 9 (Fig. 3); it then decreases and simultaneously that of wave 4
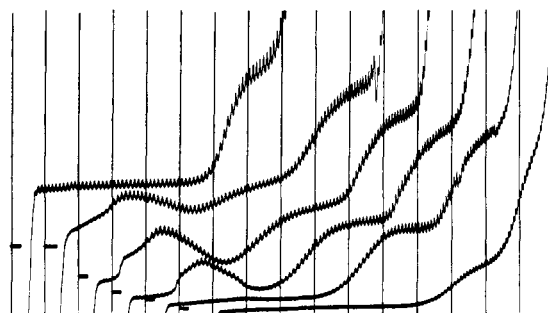
(2) O. M. Müller, *J. Chem. Education*, **18**, 320 (1941).

(3) A. I. Vogel, "A Text-book of Quantitative Inorganic Analysis," Longmans, Green & Co., London, 1951, p. 869.

Fig. 1.—Polarograms of 0.001 M ammonium metavanadate in 0.2 M phosphate buffers: pH, 2.04, 5.66, 6.64, 7.52, 9.92, 11.53. Short horizontal lines indicate the galvanometer zero of each polarogram. Each curve starts at +0.2 v. *vs.* S.C.E., and each voltage increment corresponds to 0.2 v.

increases, so that only wave 4 remains at pH values greater than 12.5.

Carbonate and Acetate Buffers.—With carbonate buffer in the pH range examined (9 to 12.5), the current–voltage curves are similar to those obtained with borate buffer, but wave 4 is poorly defined. In the pH range examined (3 to 6) only ill-defined waves could be obtained with acetate-buffered solutions with or without potassium chloride.

Influence of pH on Half-wave Potentials.—Figure 5 shows the influence of pH on the half-wave potentials of waves 1, 3 and 4 in 0.2 M phosphate buffer. The values of the half-wave potentials of wave 1 plotted against the pH give a straight line with the slope $\Delta E_{1/2}/\Delta p$H $= 0.148$ v./ pH which coincides fairly well with the theoretical line for a reversible electrode reduction of +5 to +4 vanadium.[4] As $E_{d.e.}$ *vs.* log $i/(i_d - i)$ gives a straight line with a slope of 0.041 v., wave 1 is steeper than a wave corresponding to a reversible reduction of +5 to +4 vanadium. The height of mercury in the dropping electrode has no influence on the half-wave potential of wave 1, but increasing concentration of vanadate causes a shift toward more positive values.

Wave 3, which starts above pH 5, corresponds to the reduction of +5 to +4 vanadium since it disappears upon reduction of vanadate by sulfur dioxide. The buffer has no influence on the half-wave potential of wave 3, providing the pH and ionic strength remain unchanged, but wave 4 is considerably affected. An increase in ionic strength causes a shift of the half-wave potentials of waves 3 and 4 toward more positive values. For wave 3 the plot of $E_{1/2}$ *vs.* pH gives a straight line with a slope of 0.120 v./pH. $E_{d.e.}$ *vs.* log $i/(i_d - i)$ gives a straight line with a slope of 0.170 v. With increasing height of mercury, the half-wave potential shifts to the negative side. Accordingly, wave 3 corresponds to an irreversible electrode reduction of +5 to +4 vanadium with an overpotential of approximately 0.8 v. which decreases with increasing ionic strength. Wave 3, unlike wave 1, shows no change of the half-wave potential with vanadate concentration.

The change of the half-wave potential of wave 4

(4) J. E. Carpenter, THIS JOURNAL, **56**, 1847 (1934); A. B. Hart and J. R. Partington, *J. Chem. Soc.*, 1532 (1940).
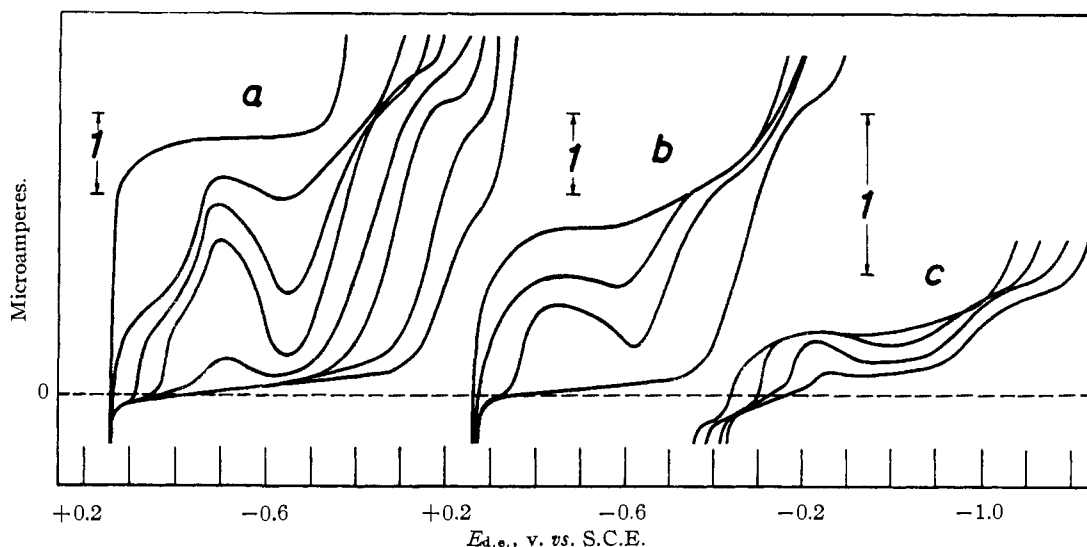
Fig. 2.—Polarograms of ammonium metavanadate in phosphate buffers: (a) 10^{-3} M NH$_4$VO$_3$ at pH 2.50, 5.55, 6.41, 7.16, 8.42, 9.71, 10.93 and 11.47; (b) 10^{-3} M NH$_4$VO$_3$ and 1 M KCl at pH 5.10, 6.18, 7.24 and 9.66; (c) 10^{-4} M NH$_4$VO$_3$ at pH 4.97, 5.96, 6.84 and 7.56.
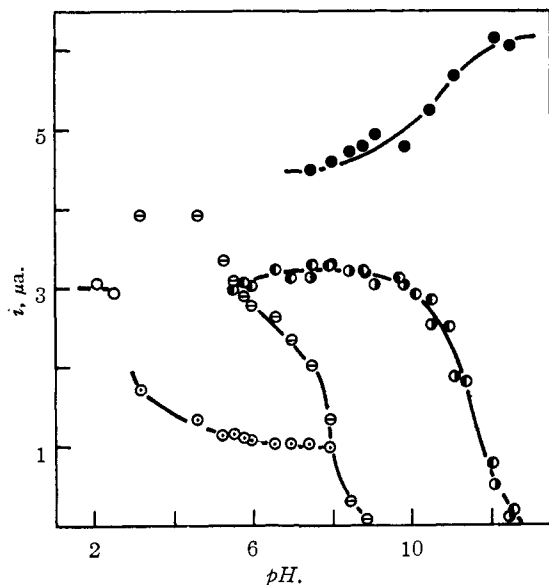

Fig. 3.—Variation of diffusion current with pH in 0.2 M phosphate and borate buffers: O, reversible wave (phosphate); ⊙, wave 1 (phosphate); ⊖, sum of heights of waves 1 and 2 (phosphate); ◐, wave 3 (phosphate); ◑, wave 3 (borate); ●, wave 4 (borate).

with pH is linear as far as pH 7.5; the slope of the straight line is 0.133 v./pH. Above pH 7.5 the rate of the change is reduced and the distance between waves 3 and 4 becomes progressively smaller. The ratio $\Delta E_{d.e.}/\Delta \log [i/(i_d - i)]$ has the value 0.064 v., and with increasing height of the mercury column the half-wave potential shifts to more negative values. Increasing vanadate concentration causes a shift in the opposite direction. Hence, up to pH 7.5, wave 4 corresponds to an irreversible electrode reduction of +4 to +2 vanadium with an overpotential of about 0.5 v.[5] Since above pH 9 wave 4 increases with the decrease of wave 3, here

(5) F. Förster and F. Böttcher. Z. physik. Chem., **151A**, 321 (1930).

wave 4 partly corresponds to the reduction of +5 to +2 vanadium as well. This was confirmed by a polarogram of a 5.5 × 10^{-4} M solution of +4 vanadium in borate buffer at pH 10.46. The height of wave 3 was 0.31, that of wave 4, 2.62 μa.; hence about 30% of the height of wave 4 at pH 10.46 is due to the reduction of +5 vanadium.

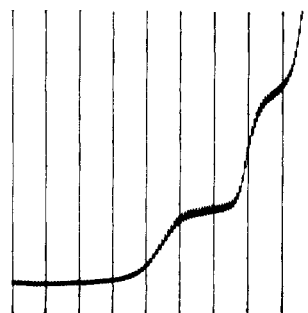Fig. 4.—Polarogram of 0.001 M ammonium metavanadate in 0.05 M Na$_2$B$_4$O$_7$, pH 9.26. The polarogram starts at −0.4 v. applied e.m.f., and each voltage increment corresponds to 0.2 v.

Influence of the Height of Mercury Column and Temperature.

For waves 3 and 4, the ratio $i_d/h^{1/2}$ (where h is the height of mercury above the tip of the capillary) was constant within 3% from $h = 50$ to 80 cm. Thus, the currents corresponding to waves 3 and 4 are controlled by diffusion; this is confirmed by the values for the temperature coefficients of the diffusion current, which are 1.7% and 1.5%, respectively. The ratio $i_1/h^{0.8}$ for wave 1, as well as for the total limiting current corresponding to the sum of the heights of waves 1 and 2, is constant. This is in accord with an adsorption diffusion process. The temperature coefficient of the limiting current of wave 1 is 1.7% and that of the sum of waves 1 and 2 is 1.6%.

The change of the half-wave potentials of waves 3 and 4 is negligible (the temperature coefficient is
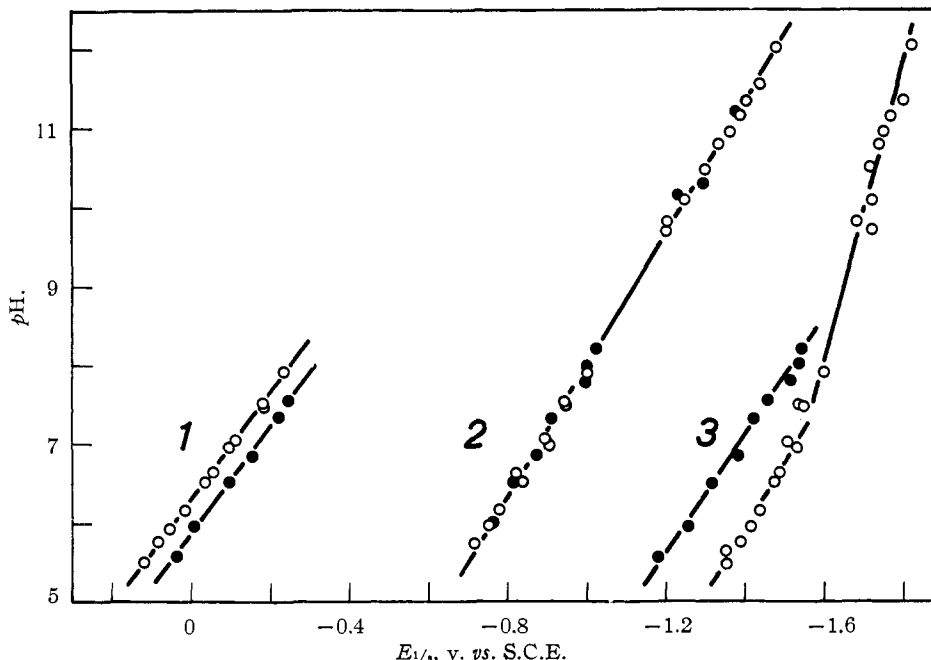
Fig. 5.—Variation of $E_{1/2}$ with pH in 0.2 M phosphate buffer: (1) wave 1, (2) wave 3, (3) wave 4. The open circles correspond to 10^{-3} M vanadate and the solid ones to 10^{-4} M vanadate.

positive), but the temperature coefficient of the half-wave potential of wave 1 is -0.003 v. per degree.

Influence of Capillary-active Substances.—The influence of several capillary-active substances on wave 1 and the sum of waves 1 and 2 is shown in Table I; 0.01% gelatin, which is the usual concentration for suppressing polarographic maxima, reduces the height of wave 1 by about 30%, and the sum of the heights of waves 1 and 2 by 38%. Saturated solutions of the exceedingly capillary-active agents, amyl alcohol and camphor, totally eliminate wave 2 and reduce wave 1 to about 60–66%; the height of wave 2 is reduced by concentrations considerably below saturation. The half-wave potential of wave 1 is practically unaffected by capillary-active agents.

TABLE I

INFLUENCE OF CAPILLARY-ACTIVE SUBSTANCES

0.1 M Phosphate Buffer, pH 6.73, and 10^{-3} M NH$_4$VO$_3$

Adsorbent added	$E_{1/2}$ of wave 1 vs. S.C.E.	$E^d_{1/2}$ vs. S.C.E.	i_1 of wave 1 amp.	i_1 of sum of waves 1 and 2, amp.
None	-0.048	-0.586	1.08	2.46
0.01% gelatin	$-$ .051	$-$ .594	0.76	1.52
0.01% camphor	$-$ .050	$-$ .236	1.08	1.13
Satd. camphor	$-$ .042	$-$ .088	0.71	0.71
25 ml. satd. amyl alc. soln. in 50 ml. soln.	$-$ .050	$-$ .294	1.08	1.25
Satd. amyl alc.	$-$ .046	$-$ .102	0.64	0.64

Relation between Diffusion Current and Vanadium Concentration.—As the best-defined waves were obtained with 0.05 M sodium tetraborate (Fig. 4), the relation between the diffusion current and concentration of vanadium was examined in this solution. If the concentration of vanadate is not greater than 10^{-3} M, this relation is linear for

both waves. The values of the diffusion current constant $I = i_d/Cm^{1/2}t^{1/6}$ are: $I_3 = 1.60$ and $I_4 = 3.00$ for the first (3) and the second (4) waves, respectively. Obviously wave 4 corresponds to a two-electron transfer process, i.e., a reduction of $+4$ to $+2$ vanadium. Foreign salts influence the height as well as the shape of both waves. Thus, the diffusion current constant of wave 3 is practically invariable in solutions with ionic strengths below 0.6; however, the square of the diffusion current constant falls almost linearly with the square root of the ionic strength when $\mu > 0.6$, although this value is considerably outside the range of Onsager's limiting law.[6]

The limiting current of wave 1 in phosphate buffer at pH 6.5 has tendency to level off as the vanadate concentration increases (Fig. 6). Thus, wave 1 is due to adsorption, a conclusion which was indicated above by the constancy of $i_1/h^{0.8}$.
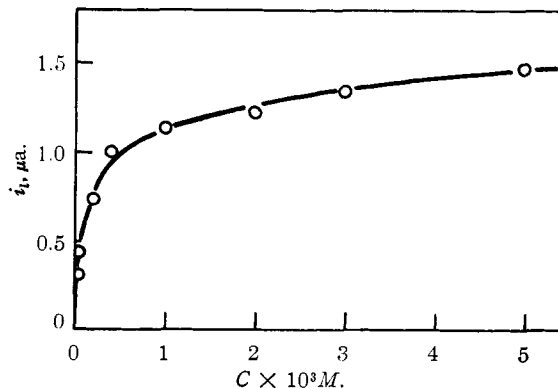

Fig. 6.—Relation between concentration of ammonium metavanadate and limiting current of wave 1.

(6) G. Kortüm, "Elektrolytlösungen," Becker & Erler, Leipzig, 1941, pp. 140, 147, 192.

Reduction of Vanadate in Presence of Nitrate.— As little as 0.01 M potassium nitrate causes an increase in the height and limiting current of wave 4. At higher concentrations wave 4 rises constantly, so that only wave 3 is left on the polarogram. Accordingly, the process in question is a continuous oxidation of +2 vanadium (produced by electroreduction) by nitrate.

Discussion

The polarographic behavior of +5 vanadium is possibly caused by the existence of various kinds of +5 vanadium ions in the buffered solutions.[7-9]
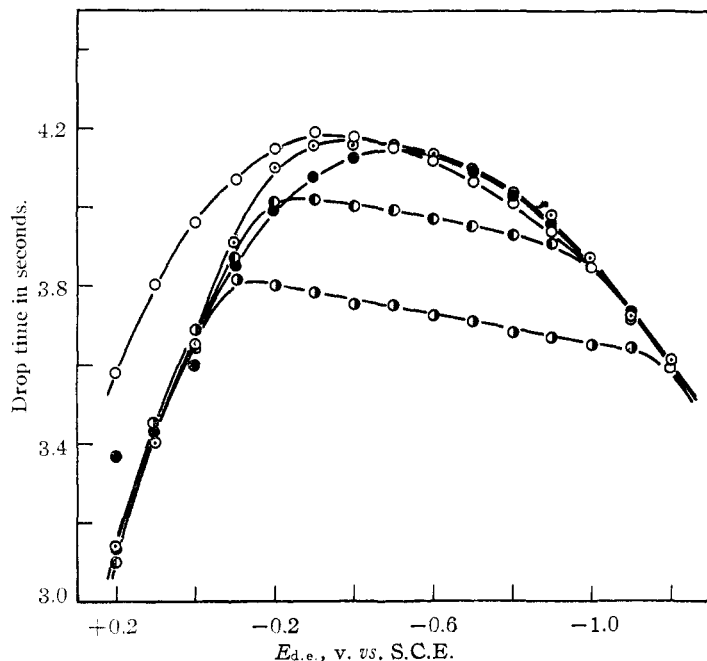

Fig 7.—Electrocapillary curves of: O, 0.1 M phosphate buffer, pH 6.73; ⊙, 0.1 M phosphate buffer and 10^{-3} M NH₄VO₃; ●, 0.1 M phosphate buffer, 10^{-3} M NH₄VO₃ and 1 M KCl; ◉, 0.01 M phosphate buffer, 10^{-3} M NH₄VO₃ and 5 ml. saturated solution of amyl alcohol per 50 ml. buffer solution; ◑, 0.1 M phosphate buffer and 10^{-3} M NH₄VO₃ saturated with amyl alcohol.

As the first wave, which appears when pH < 2, disappears upon reduction with sulfur dioxide, it obviously corresponds to a reversible electrode process

$$VO_2^+ + 2H^+ + e^- \rightleftarrows VO^{+2} + H_2O$$
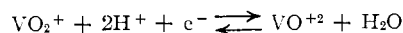
for which

$$E_{1/2} = 0.764 - 0.059 \log \left(\frac{D_{ox}}{D_{red}}\right)^{1/2} - 0.118\,p\text{H}$$

and $\Delta E_{1/2}/\Delta p\text{H} = 0.118$ v./pH.

From pH 2 to 9 waves 1 and 2 are due to adsorp-

(7) J. Meyer and A. Pawleta, Z. angew. Chem., **39**, 1284 (1926); reference 5; Ch. D. Coryell and D. M. Yost, This Journal, **55**, 1909 (1933); G. Jander and K. Jahr, Z. anorg. allgem. Chem., **211**, 49 (1933); G. Jander, K. Jahr and H. Witzmann, ibid., **217**, 65 (1934); H. T. S. Britton, J. Chem. Soc., 1842 (1934); J. E. Carpenter, This Journal, **56**, 1847 (1934); H. T. S. Britton and G. Welford. J. Chem. Soc., 764 (1940); A. B. Hart and J. R. Partington. ibid., 1532 (1940); P. Souchay and G. Carpeni, Bull. soc. chim., France, 160 (1946).

(8) G. Charlot, "Theorie et methode nouvelle d'analyse qualitative." Masson et Cie, Paris, 1949, pp. 225–228.

(9) F. Hein. "Chemische Koordinationslehre." Hirzel Verlag. Zürich, 1950, pp. 579–581.

tion. The reduction of tetrachloroplatinate(II) on the dropping mercury electrode is a similar case.[10] The electrocapillary curves (Fig. 7) show that negative vanadate ions are adsorbed on the electrode surface at potentials more positive than −0.5 v. vs. S.C.E., due to the positive charge of the electrode at these potentials. Chloride ions are adsorbed more readily than vanadate ions at potentials more negative than −0.2 v. vs. S.C.E.; therefore, wave 2, which otherwise appears at potentials more negative than −0.2 v., cannot be developed in a solution containing chloride. Amyl alcohol is strongly adsorbed from a saturated solution at −0.1 to −1.2 v. vs. S.C.E., and thus displaces the weakly adsorbed vanadate ions, with the result that wave 2 and the upper part of wave 1 disappear. At the lower concentration of amyl alcohol the adsorption occurs between −0.2 and −1 v.; therefore only wave 2 is partly suppressed, while wave 1 remains unaffected. With the desorption of vanadate ions which begins at potentials more negative than −0.5 v. vs. S.C.E., the adsorption current falls and a desorption reduction wave is produced. According to Laitinen and Onstott's[10] equation for a reversible desorption wave, the plot of $E_{d.e.}$ vs. log $(i_d - i)/i$, for the reduction of +5 to +4 vanadium, should give a straight line with a slope of 0.059 v. As the slope found experimentally was 0.100 v., the desorption reduction process is irreversible. The dependence of the half-wave potential of the desorption wave $(E_{1/2}^d)$ on the concentration of vanadate supports this interpretation. A change in concentration of vanadate from 10^{-4} to 5×10^{-3} M causes a shift of $E_{1/2}^d$ by 0.2 v. to more negative potentials. $E_{1/2}^d$ also shifts in the same direction with increasing height of the mercury column. Thus, the tendency of vanadate ions to be adsorbed increases with increasing concentration and decreasing drop time.

An increase of temperature, however, has an opposite effect; the temperature coefficient of $E_{1/2}^d$ is +2 millivolts. Thus, the energy of adsorption decreases with increasing temperature,[11] and the desorption wave shifts to more positive potentials. The influence of strong capillary-active substances, on $E_{1/2}^d$ agrees with Laitinen and Onstott's equation[10]; as the average area available for adsorption of reducible vanadate ions is reduced by more adsorbed material, the desorption wave shifts to more positive potentials.

Accordingly, the adsorption of vanadate between pH 2 and 9 makes possible its reduction to the +4 state at potentials considerably more positive than would be expected with an irreversible electrode reduction of vanadate. Below pH 5, where the irreversible electrode reduction of +5 vanadium proceeds at potentials more positive than −0.6 v.

(10) H. A. Laitinen and R. I. Onstott, This Journal, **72**. 4565 (1950).

(11) R. Brdička. Z. Elektrochem., **48**. 278 (1942).

vs. S.C.E., the adsorption–reduction and diffusion–reduction processes overlap and the corresponding waves are not separated. Above pH 5, a minimum is produced on the current–voltage curve due to desorption of vanadate at potentials more negative than -0.5 v. *vs.* S.C.E.; this is followed by the diffusion current of the irreversible reduction process, which, with increasing pH, proceeds at more and more negative potentials. Thus, between pH 5 and 9 the adsorption and reduction waves become more and more separated.

Above a pH of about 5.5 the total adsorption current decreases progressively to zero at about pH 9, while the height of the reduction wave (3) remains constant (Fig. 3); obviously the concentration of a definite species of vanadate ions which is adsorbed on the electrode surface, decreases with increasing pH to zero at pH 9. According to the literature[7–9] various polyvanadate ions exist between pH 2 and 9. Although the results have varied with the method, certainly the hydrolysis products of VO_2^+ (vanadate ions $H_2VO_4^-$, HVO_4^{-2} and VO_4^{-3}) are in equilibrium above pH 5. These ions, in turn, are in equilibrium with their condensation products, the polyvanadate ions, the formation of which increases with increasing acidity as far as pH 2. Since our solutions were orange below pH 5 and colorless above pH 5, probably the orange penta- or hexavanadate ions ($H_3V_5O_{16}^{-4}$ and $HV_6O_{17}^{-3}$, respectively) exist below pH 5, and the colorless di- and tetravanadate ions ($H_2V_4O_{13}^{-4}$ and $V_2O_7^{-4}$) between pH 5 and 9. The large, highly charged hydrogen polyvanadate ions are probably capillary active.[12] Furthermore, it is possible that ions of the corresponding heteropoly acids are formed, which are stable in acid media only.[13]

The twofold adsorption wave (waves 1 and 2) can be attributed to an additional adsorption layer of the reduced form of $+5$ vanadium. Below pH 5 the reduction should yield $VO(OH)_2$ or vanadyl vanadate,[8] sparingly soluble products, which are adsorbed only by a strongly positively charged mercury drop, at potentials more positive than -0.2 v. *vs.* S.C.E. Above a vanadate concentration of 5×10^{-4} M, the adsorption layer of $VO(OH)_2$ reaches a definite thickness, due probably to the formation of a monomolecular layer,[14] thus limiting the value of the adsorption current to about 1 μa. (Fig. 3). Accordingly, the mercury drop becomes polarized, and wave 1 appears. But at potentials more negative than -0.2 v. *vs.* S.C.E., desorption of $VO(OH)_2$ sets in and the adsorption current reaches its full limiting value, giving rise to wave 2. Below 5×10^{-4} M vanadate the time required for the formation of a compact adsorption layer of $VO(OH)_2$ is so long that only one adsorption wave appears. This is true with more concentrated vanadate solutions at higher pH values (*e.g.*, pH 8 and 10^{-3} M vanadate), because the concentration of adsorbable polyvanadate ion decreases with increasing pH; also an increase of pH causes a shift of the adsorption wave of vanadate to more negative potentials. Therefore, beyond the ad-

sorption range of $VO(OH)_2$, *i.e.*, at potentials more negative than -0.2 v. *vs.* S.C.E., wave 1 must disappear. Below pH 5 wave 1 has a height greater than 1 microampere, probably because of the greater porosity of the $VO(OH)_2$ layer.

The ratio $\Delta E_{1/2}/\Delta p\mathrm{H} = 0.120$ v./pH for the irreversible reduction wave (3) agrees excellently with the value (0.118 v./pH) for the reversible electrode reduction of $+5$ vanadium to the $+4$ state. 0.120 v./pH corresponds to the electrode reductions

$$H_2VO_4^- + 2H^+ + e^- \longrightarrow VO(OH)_2 + H_2O$$
$$2HVO_4^{-2} + 4H^+ + 2e^- \longrightarrow V_2O_5^{-2} + 3H_2O$$
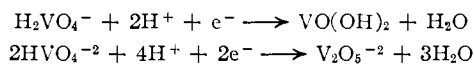
reactions requiring the presence of $H_2VO_4^-$ and HVO_4^{-2}, which are known to exist between pH 5 and 9 and 9 and 12.5, respectively.[8] Although wave 3 corresponds to an irreversible process, the half-wave potential is independent of the vanadate concentration, so that

$$E_{d.e.} = E_{1/2} + \frac{0.059}{\alpha} \log \frac{i}{i_d - i}$$

can be applied[15]; α equals 0.35, since the slope of the line $E_{d.e.}$ *vs.* $\log i/(i_d - i)$ is 0.170 v. The shift of the half-wave potential to more positive values with increasing concentration of supporting electrolyte is certainly connected with the action of these factors upon the overpotential, *i.e.*, the rate of the electrode process, as it has been repeatedly found with irreversible waves.[10,16]

The decrease in the height of wave 3 with the simultaneous increase in that of wave 4 above pH 9 means that above pH 9, HVO_4^{-2} ion is transformed into a vanadate ion which requires a still greater overpotential for its reduction. Since this ion can only be the orthovanadate ion,[7–9] its hydration may be the cause of the increase of overpotential.

The relation between $E_{1/2}$ and pH indicates that up to pH 7.5 wave 4 corresponds to the electrode process

$$VO^{+2} + 2H^+ + 2e^- \longrightarrow V^{+2} + H_2O$$
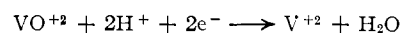
although this process is irreversible. It is evident that the reduction of $+4$ vanadium on the dropping mercury electrode proceeds to the $+2$ state, not only from the relation between the diffusion current constants of waves 3 and 4, but also from the catalytic reduction of nitrate in the range of potentials of wave 4, for it is known[8] that nitrates can be reduced by $+2$ vanadium in alkaline solution.

Wave 3, developed in borate, phosphate and carbonate solutions between pH 8.5 and 9.5, might be utilized in polarographic analysis as it is well defined and has a maximum height which is constant within 2–3%; the concentration of vanadium should not exceed 10^{-3} M. Wave 4 might be used in polarographic analysis only in borate buffer, because it is badly defined in the other solutions. The distance of more than 0.5 v. between waves 3 and 4 in borate solution could be utilized for the determination of vanadium in the presence of elements whose

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polarographic waves fall within the range of one of the vanadium waves; this possibility is being investigated.

[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES]

Alkaline-catalyzed Reaction of Formaldehyde and the Methylols of Phenol; A Kinetic Study[1]

BY JAMES H. FREEMAN AND C. W. LEWIS

Previous attempts to analyze the kinetics of the phenol–formaldehyde reaction have been limited to determination of a cumulative over-all reaction rate. By means of paper chromatography it is now possible to follow quantitatively the appearance and disappearance of each individual methylolphenol in the reaction system. Mathematical analysis of the data from separate experiments involving phenol, p-hydroxybenzyl alcohol, saligenin, 2,4-dimethylol- and 2,6-dimethylolphenol, respectively, with formaldehyde at 30°, has provided individual rate constants for the reaction of each phenolic compound. Reactivities of individual positions in various phenolic nuclei may also be compared. The reactions are of second kinetic order. Significant differences in both positional and molecular reactivity were found. An ortho position in phenol is slightly less reactive than the para. In saligenin the reverse is true. Introduction of an o-methylol group enhances the reactivity of the remaining active nuclear positions. The same group in the para position retards further activity. These effects are multiplied in the dimethylol analogs. 2,6-Dimethylolphenol is, by far, the most reactive molecule present in the system. The observed differences in reactivity are attributed to the effect of hydrogen bonds in the o-methylol compounds. It was further observed that, under alkaline conditions, the formation of diphenylmethane bridges occurred only between methylol groups with loss of formaldehyde and water, not between methylol groups and free nuclear positions. The reaction appears to be first order and considerably slower than the reaction of methylolphenol formation. Deterioration of polymethylolphenols by loss of methylol groups from the ortho position also has been observed under certain conditions.

Over a period of many years, a number of investigators have attempted to determine the course of the phenol–formaldehyde reaction by means of a variety of kinetic studies. Most frequently these studies have involved determination of unreacted formaldehyde, or the observation of some rather indefinite factor such as the appearance of turbidity as an indication of the degree of reaction with time. In the particular case of reaction with phenol, the formaldehyde is consumed by five competing primary reactions (formation of the five methylolphenols) as well as several possible secondary reactions (self condensation,[2] Cannizzaro, etc.). Hence, such determinations, at best, can only serve to furnish an over-all kinetic rate constant. This leads to conclusions such as that of Jones[3] that the reaction obeys the first-order rate law for the first 45% of reaction. Likewise those of Debing,

Fig. 1.

Murray and Schatz,[4] that the reaction follows second-order kinetics if sufficient correction factors are included to account for presumed differences in over-all reactivities of the formaldehyde and phenol, and for an unduly reduced reactivity of methylol substituted phenols. The latter paper may be consulted for further references to the earlier literature.

The preferred method of approach to this problem is by examination of the reaction of formaldehyde with each separate methylolphenol. Such an experiment has not been feasible hitherto because of lack of the necessary model compounds, and the inadequacy of available analytical methods for examination of this necessarily complex system. Syntheses of the three polymethylolphenols and successful application of the technique of paper chromatography to their separation and quantitative determination have been reported by one of the authors in the past year.[5–6] Thus it is now possible to study the reaction by starting with phenol, or any particular methylolphenol, and observing the appearance and disappearance, in turn, of each subsequent intermediate phenolic compound. One such study is described here.

The system of reactions to be considered is shown in Fig. 1, together with their individual rate constants (k).

In the experiments reported, the following conditions pertain throughout. (1) All reactions were carried out at 30°. (2) The amount of formaldehyde used was equivalent to the total number of available reactive phenolic nuclear positions, providing for complete conversion to trimethylolphenol in each case. (3) In order to preclude
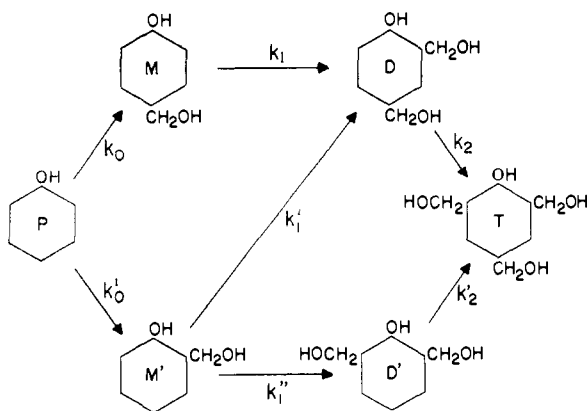
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