ride, sodium carbonate, or sodium phosphate does not cause supersaturation with respect to sodium sulfate as long as this salt is the only solid phase.

2. If the solid phase deposited from these solutions is a double salt of sodium sulfate and sodium carbonate, or sodium sulfate and sodium phosphate marked supersaturation may be encountered.

3. Sodium sulfate and sodium chloride have formed heavy scales in the region in which the solubility increases with temperature.

4. The evaporation tests have furnished additional information concerning the solubility of sodium sulfate, and except where supersaturation results from the slow attainment of equilibrium with respect to double salts, results are in agreement.

COLLEGE PARK, MD. RECEIVED MAY 25, 1937

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

# The Kinetics of the Quinhydrone Electrode Reaction[1]

BY ROBERT ROSENTHAL, ARTHUR E. LORCH AND LOUIS P. HAMMETT

Before dependable kinetic measurements of an electrode process may be made it is necessary, first, that the catalytic properties of the electrode surface be fairly reproducible and be constant during the interval of measurement, and, second, that all materials be of such purity as to avoid complicating side reactions. To date, these requirements have been satisfied only in the recent work on the hydrogen electrode process.[2-4] In the present work, we have studied the kinetics of another reversible electrode process, to wit, the quinone–hydroquinone system, employing apparatus designed to allow fulfilment of the above requirements. Early measurements on this system were made by Haber and Russ[5] but this phase of their very important pioneer work on electrode processes was of low precision, complicated by the appearance of a "reststrom," and was carried out at only one acidity in an 80% ethanol solution.

## Experimental Method

**Apparatus.**—The reaction vessel, A, in Fig. 1 was constructed from a one-liter heavy-walled Pyrex bottle. Eight inner members of Bureau of Standards standard taper No. 15 ground glass joints were sealed in a ring close to the edge, and one inner No. 25 ground joint was sealed in the center of the top of the vessel. Through this latter runs a glass stirrer seated on a finely ground No. 15 joint, B, and water seal, C. This type of seating permits of stirring speeds in excess of 5000 r. p. m. without rattling or vibration, without ingress of air or overheating of the water seal. D is a thin strip of platinum foil of about three sq. cm. area, wrapped tightly around the glass tubing centering the stirrer. A fine platinum wire entering through a small hole (sealed over with Picein cement) in the stirrer adapter connects with this electrode.

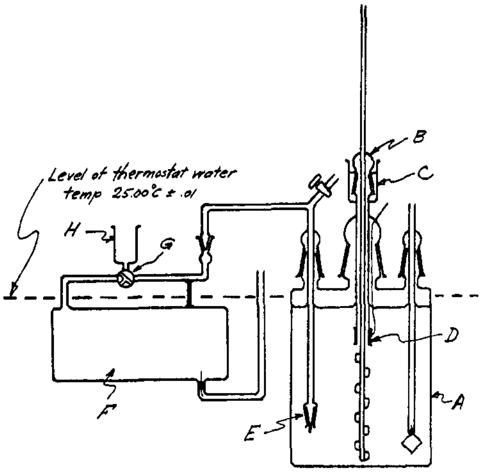

Fig. 1.

Through the eight peripheral ground joints were placed the following: (1) the salt bridge, provided with a ground-in plug, E, of the saturated calomel electrode, F (H is a reservoir of saturated potassium chloride solution used to flush the liquid junction at the beginning of each experiment); (2) a calibrated 10-ml. buret; (3) an addition tube (Fig. 2) for adding solids without ingress of air (a weighed amount of solid is placed in the tube, J, the stopcock, K, is closed and L and M are opened. Nitrogen gas which is bubbling through the solution is passed through these latter two stopcocks for about fifteen minutes, sweeping out J. Then L is closed and K opened, and the pressure of the nitrogen in the vessel forces solution up through N into J—then M is closed and L opened—

---

(1) Dissertation submitted by Robert Rosenthal in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(2) (a) Bowden and Rideal, *Proc. Roy. Soc.* (London), **A120**, 59, 80 (1928); (b) Bowden, *Trans. Faraday Soc.*, **24**, 473 (1928); (c) Bowden, *Proc. Roy. Soc.* (London), **A126**, 107 (1929); (d) Bowden and O'Connor, *ibid.*, **A128**, 317 (1930).

(3) Hammett, THIS JOURNAL, **46**, 7 (1924).

(4) (a) Erdey-Gruz and Volmer, *Z. physik. Chem.*, **A150**, 203 (1930); (b) Erdey-Gruz and Wick, *ibid.*, **A162**, 53 (1932); (c) Volmer and Wick, *ibid.*, **A172**, 429 (1935); (d) Butler and Armstrong, *Proc. Roy. Soc.* (London), **A137**, 604 (1932).

(5) Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904).

the liquid in J returns to the reaction vessel carrying dissolved solid with it. This process is repeated several times until all of the solid is washed down); (4) the outlet tube of a gas-washing bottle which usually contained 1.0 *M* sodium chloride solution (tank nitrogen (99.90%) was passed over thirty inches (76 cm.) of reduced cupric oxide wire in a quartz tube heated to dull redness in an electric furnace, through two small bubblers of concentrated potassium hydroxide solution, through a U-tube of precipitated silver and finally through several inches of tightly packed cotton wool, into the wash bottle and to the cell); (5, 6, 7, 8) four electrodes made of 0.25 inch (6.4 mm.) square platinum or gold foil welded to a fine platinum wire and sealed into a soft glass tube.

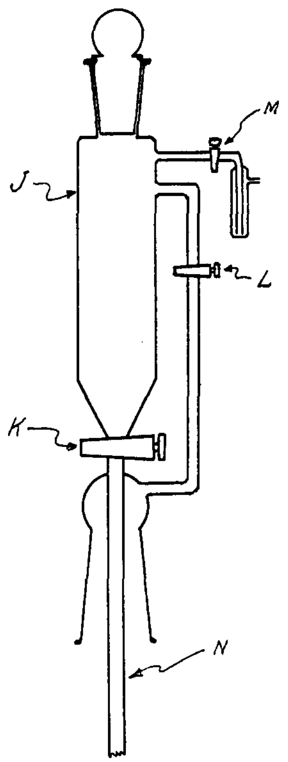

Fig. 2.

**Materials.**—Eastman practical grade quinone was sublimed at atmospheric pressure. The resulting product was very light yellow in color. Eastman hydroquinone was vacuum sublimed three times until the product was pure white. Eastman quinhydrone was recrystallized from 0.00001 *M* hydrochloric acid at 70°, filtered and washed with distilled water. This entire process was carried out in an atmosphere of purified nitrogen. The acids and salts were of high grade and in most cases were further purified.

The electrodes were cleaned in hot C. P. cleaning mixture as recommended by Morgan, Lammert and Campbell,[6] and then soaked in distilled water for several hours. To clean the reaction vessel, it was filled with distilled water and stirred very vigorously for several minutes and the wash water removed by suction. This was repeated a few times. After several runs, the cell was left filled with cleaning mixture overnight.

**Method.**—Solutions were made up directly in the cell. Sufficient sodium chloride to make the final solution 1.0 *M* was added, the electrodes set in place and the solution swept free of air by a rapid stream of nitrogen and stirring for about an hour. It is necessary that air be excluded in order to avoid the autoxidation of hydroquinone in the near-alkaline solutions,[7,8] and the possibility that molecular oxygen might enter into the electrode reactions. Also it was found that the presence of oxygen was always accompanied by unsteady behavior of the platinum electrodes. The cell was left in this condition for ten to fifteen hours before measurements were made. The lapse of time enables the electrodes, in contact with air-free solution, to come to a relatively steady catalytic state.

Weighed amounts of solid reactants and constituents of buffer mixtures were added in the absence of air by the addition tube; nitrogen-saturated acid or alkali solution by the microburet. The *p*H of the solution was directly calculated from the static potential of any of the platinum or gold electrodes measured against the saturated calomel electrode, the concentrations of quinone and hydroquinone being known. No account was taken of the effect of the presence of the high concentration of salt on the activities of the quinone and hydroquinone. In the solutions employed this "salt error"[9,10] never amounted to more than 0.05 *p*H unit, and furthermore the interest here centers less on the actual hydrogen ion activity than on the difference between hydrogen ion activities in two solutions. This difference is not affected by the salt error since the electrolyte concentration is sensibly constant—a relatively high concentration of swamping electrolyte being maintained to keep a constant ionic environment for the kinetic measurements.

By means of a slide wire rheostat and a 2-v. storage battery a variable voltage was impressed across the electrode under study and the much larger polarizing electrode. The current flowing was found by measuring the *IR* drop across a 1000-ohm resistance. The potential of the electrode under study, hereafter to be referred to merely as the electrode, was measured with a type K potentiometer and wall galvanometer against either a static platinum or gold electrode in the same vessel or the reference electrode. The former gives the polarization, while the latter gives the potential referred to the saturated calomel electrode. Both these values are in error by an amount equal to a potential drop in the solution between the electrode and the reference electrode. Lukens[11] has recently demonstrated that a potential drop exists between all parts of the conductor and the electrodes. It is not possible to eliminate completely this source of error; however, to exclude as much as possible of this fall of potential a fine capillary extension of the salt bridge was pressed lightly against the surface of the electrode. A direct comparison was made of the potential values obtained with and without this Haber–Luggin capillary. A maximum difference of 1.5% of the total polarization and an average of less than 1% was found. This deviation is well within the reproducibility of the measurements.[12] Anodic and cathodic polarization curves were obtained for a solution of known composition, and then further additions of reactants made through either the microburet or the addition tube. In this manner curves for six or eight different concentrations could be obtained in a few hours without at any time exposing the main body of solution or the electrodes to the atmosphere. Curves obtained with increasing and with decreasing current densities fall quite close together, generally within 2% of each other. The curves are linear for about 0.010 v. in either direction of the reversible potential, and then

---

[6] Morgan, Lammert and Campbell, THIS JOURNAL, **53**, 454 (1931).

[7] Reinders and Dingemans, *Rec. trav. chim.*, **53**, 209 (1934).

[8] Saint-Maxen, *J. chim. phys.*, **32**, 410 (1935).

[9] Hovorka and Dearing, THIS JOURNAL, **57**, 446 (1935).

[10] Kiss and Urmanczy, *Z. physik. Chem.*, **A169**, 31 (1934).

[11] Lukens, *Trans. Am. Electrochem. Soc.*, **67**, 29 (1935).

[12] A similar observation was made by Knorr and Schwartz, *Z. Elektrochem.*, **40**, 38 (1934).

bend logarithmically toward the current axis after a polarization of about 0.04 v. Residual currents never were detected.

The practical upper limit of the curves is reached when the galvanometer mirror starts to oscillate violently, making accurate reading impossible. Within the current density region employed (below 1 ma. per sq. cm.), the polarization is almost completely independent of stirring speeds above 2000 r. p. m., indicating that the best diffusion conditions possible with this type of stirring have been reached, but not proving concentration polarization to be eliminated completely.[13] However, the mere fact that a wide variation of catalytic activities exists points to the relative unimportance of diffusion as a rate controlling step. It must be emphasized that there is no net reaction in the cell—products are reformed at one electrode at the same rate as they are used up at the other.

The current on first applying a potential, or after changing the potential, undergoes a rapid change for a period which varies from thirty seconds at low current densities to two minutes at higher current densities. This period of rapid change is followed by a very gradual downward drift which continues indefinitely. Readings were taken immediately after the first stage.

## Electrode Properties

The catalytic activity of the electrode, measured by the initial slope of the polarization curve,[14] undergoes a slow decrease with time for as long as thirty-six hours even under the most favorable conditions. This variation generally amounts to 2% per hour and is the same whether the electrode is being polarized anodically, cathodically or not at all. Various methods of pretreatment were tried in order to eliminate this downward drift, but without success. Cleaning the electrode in aqua regia or in hot alcoholic potassium hydroxide has no beneficial effect. Heating to 400° in an atmosphere of either air, nitrogen or hydrogen for one hour increases the activity initially by ten to twenty-fold. The activity then drops very rapidly for several hours, and in the course of one or two days comes again to a relatively steady state which however represents a level of catalytic activity considerably higher than that of the untreated electrode. It was found that platinum and gold electrodes may be activated in several other ways. Exposure of the wet electrode to air for ten to twenty minutes increases the activity by 70%; washing in running tap water for a half hour, by 60%; and immersion in equilibrium distilled water for two hours, by 40%. However, in all these cases the electrode returns to its former activity in a few hours.

In general, high cathodic polarization of the electrode (>0.15 v.) increases its activity to an extent roughly dependent upon the magnitude and the duration of this polarization. This effect was of the order of 10–20%. There is also some indication that this activation is affected by the nature of the electrolyte. A similar behavior toward cathodic pretreatment of a platinized platinum catalyst for the decomposition of hydrogen peroxide was noted by Spitalsky and Kagen.[15] It is known from the work of Beans and Hammett[16] that a platinum catalyst for the electrolytic evolution of hydrogen can be activated to almost any desired extent by proper control of anodic polarization. In the quinhydrone system, on the other hand, we have observed very little influence of anodic treatment, in fact it more frequently slightly inactivated the platinum electrode. It becomes evident that the activity of a platinum catalyst is conditioned by other factors as well as the available surface area, since here the same pretreatment leads to entirely divergent effects on the activities for different reactions.

Electrodes of various metals and surfaces differ considerably in their ability to catalyze the electrolytic oxidation and reduction of quinhydrone. While no extensive measurements of the relative activities have been made, there are summarized in Table I the approximate relative activities in 0.1 *N* sulfuric acid and saturated quinhydrone.

TABLE I

RELATIVE CATALYTIC ACTIVITIES

| | |
|---|---|
| Blank platinum | 1 |
| Gray platinum on gold | 10 |
| Bright platinum on gold | 80 |
| Bright gold on platinum | 3 |
| Blank gold | 0.5 |
| Mercury | .3 |
| Bright palladium on gold | 1 |

These values are very approximate and subject to wide variation with aging of the electrode and with the composition of the electrolyte.

We have used the slope of the polarization curve through the reversible potential to define the catalytic activity of the electrode. This initial slope, however, is dependent not only upon the electrode properties but also upon the constitution of the solution. It increases with increasing concentration of quinone and hydro-

---

[13] King and Schack, THIS JOURNAL, **57**, 1212 (1935).

[14] Hammett and Lorch, *ibid.*, **55**, 70 (1933).

[15] Spitalsky and Kagen, *Ber.*, **B59**, 2900 (1926).

[16] Beans and Hammett, THIS JOURNAL, **47**, 1215 (1925).

TABLE II

THE EFFECT OF ADDITION OF HYDROQUINONE ON THE ANODIC CURRENT

| Curve nos. | Concn. ratio | Current ratios 0.19 | 0.21 | 0.23 | 0.25 | 0.27 | 0.29 | 0.31 | 0.33 | 0.35 | 0.37 | 0.39 | 0.41 | Mean $I$ ratio | $n$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 and 2 | 1.87 | | | | | | | | 2.0 | 2.0 | 1.9 | 1.9 | 2.0 | 1.95 | 1.07 |
| 2 and 3 | 3.00 | | | | | | 4.3 | 3.3 | 3.0 | 2.9 | 3.1 | 3.5 | | 3.1 | 1.03 |
| 3 and 4 | 5.49 | | | | 5.3 | 5.0 | 4.7 | 4.8 | 5.2 | | | | | 4.9 | 0.94 |
| 4 and 5 | 5.5 | 5. | 5.4 | 4.8 | 4.2 | 4.1 | 4.6 | | | | | | | 4.6 | .89 |

quinone, with increasing acidity at $p$H's smaller than 4, and with increasing alkalinity at $p$H's greater than 4. Examination of the polarization curves shown further on will illustrate this characteristic behavior. Consequently, in comparing activities of various metals, it is necessary that the work be carried out in solutions of identical composition.

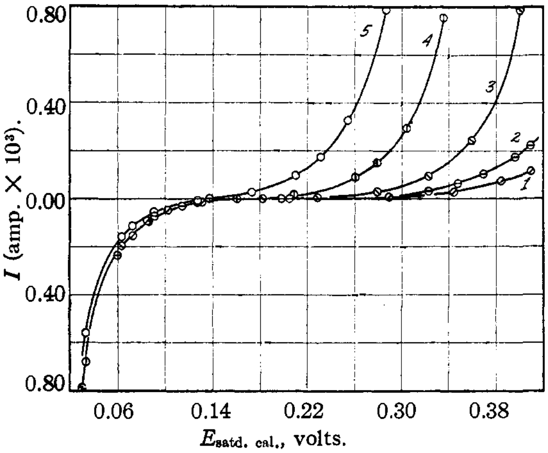

Fig. 3.—Addition of hydroquinone; acetate buffer, $p$H 4.7; quinone constant at 0.00360 m./l.; stirring rate, 3000 r. p. m.: to convert current to current density multiply by 1.24; (1) 0.000359 m./l. of hydroquinone; (2) 0.000665; (3) 0.00200; (4) 0.01097; (5) 0.0607.

**The Dependence of the Reaction Rate on the Composition of the Solution and on the Potential.**—By keeping all factors constant except the concentration of one of the reactants, and obtaining polarization curves for each concentration of that reactant, it is possible to determine directly the effect of this variable upon the rate of the electrochemical reaction. Under these conditions the ratio of the currents at a given potential for two solutions is practically independent of potential provided that the polarization is greater than 0.05 v. The failure of this relationship at lower polarizations is no doubt due to the fact that the measured current is in every case the difference between a current equivalent to the rate of oxidation of hydroquinone and one equivalent to the rate of reduction of quinone. These opposing currents are equal at the reversible potential and comparable in magnitude at low polarizations. Because of the generally exponential nature of the relation between rate and potential,[3] one of the current terms becomes negligible compared with the other at larger polarizations. Consequently the current at large positive polarizations is a measure of the rate of oxidation of hydroquinone to quinone uncomplicated by a significant reverse reaction, while the current at large negative polarizations is an equally definite measure of the rate of reduction of quinone to hydroquinone.

**The Effect of Hydroquinone Concentration.**—In Fig. 3 is plotted a typical set of polarization curves obtained by successive additions of hydroquinone to an acetate buffer. From these curves the data in Table II were obtained.

The hydroquinone exponent, $n$, is defined by the equation

$$(I''_a/I'_a) = (C''_{H_2Q}/C'_{H_2Q})^n \qquad (1)$$

where $C''$ and $C'$ are the concentrations of hydroquinone in the two solutions, and $I''_a$ and $I'_a$ are the respective anodic currents at fixed potential. $n$ is the order of reaction with respect to the hydroquinone. In a total of twelve experiments, the acidities varying from $p$H 2.2 to 6.6, the mean value of this exponent has been found to be 0.94 ± 5% with no apparent trend with acidity. The direction of the deviation of this value from unity is to be anticipated on the basis of the incomplete dissociation of quinhydrone. Luther and Leubner[17a] and Nelson and Granger[17b] give the value of this dissociation constant as 0.27. The electrochemical oxidation of hydroquinone is thus first order with respect to hydroquinone, while the rate of reduction of quinone is independent of the concentration of hydroquinone, as the coincidence of the various curves at high cathodic polarizations shows. The slight decrease in reduction rate with addition of hydroquinone is roughly quantitatively attributable to

---

[17] (a) Luther and Leubner, *Z. prakt. Chem.*, **193**, 314 (1912); (b) Nelson and Granger, THIS JOURNAL, **43**, 1401 (1921).

the effect of the latter on the incomplete dissociation of quinhydrone.

**Addition of Quinone.**—At constant *p*H and fixed hydroquinone concentration, addition of quinone gives rise to a completely analogous set of polarization curves (Fig. 4). The data obtained from these curves are treated in the same manner as in the previous section. The quinone exponent may be defined by an entirely similar equation involving the cathodic currents. In a total of eight experiments over the *p*H range 0.0 to 5.8, the average value of the quinone exponent was found to be 0.96 ± 4%. These results show the electrochemical reduction of quinone to be first order with respect to quinone. The oxidation rate of hydroquinone is affected only to a very slight extent, generally less than 5% for a threefold increase in quinone concentration, accountable for in terms of decay of catalytic activity and repression of the hydroquinone concentration by quinone.

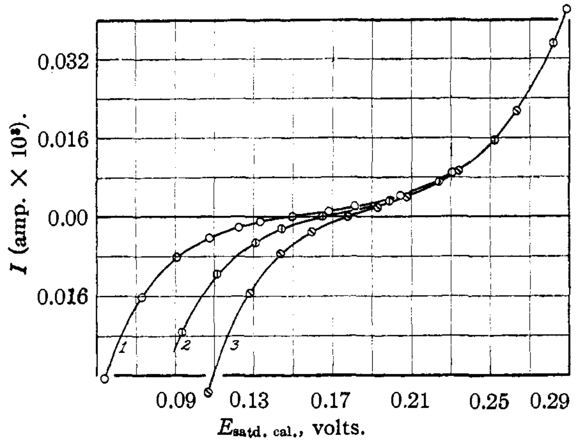

Fig. 4.—Addition of quinone; phosphate buffer at *p*H 4.7; hydroquinone constant at 0.00863 m./l.; (1) 0.000962 m./l. of quinone; (2) 0.00313; (3) 0.00848.

**Addition of Quinhydrone.**—By addition of quinhydrone, at fixed acidity, to an equimolar solution of quinone and hydroquinone, the concentration of each of these constituents is increased to the same extent without affecting the reversible potential, and consequently both oxidation and reduction rates would be expected to increase as the first power of the quinhydrone concentration. The results of a typical experiment are plotted in Fig. 5. From these data both quinone and hydroquinone exponents are calculated as previously described, using cathodic and anodic current ratios, respectively. On the assumption of complete dissociation of quinhydrone, these values are: 0.84 ± 11% for the oxidation, and 0.88 ± 10% for the reduction process. These values are the averages of eleven experiments in several buffers over the *p*H range 0.0 to 6.6.

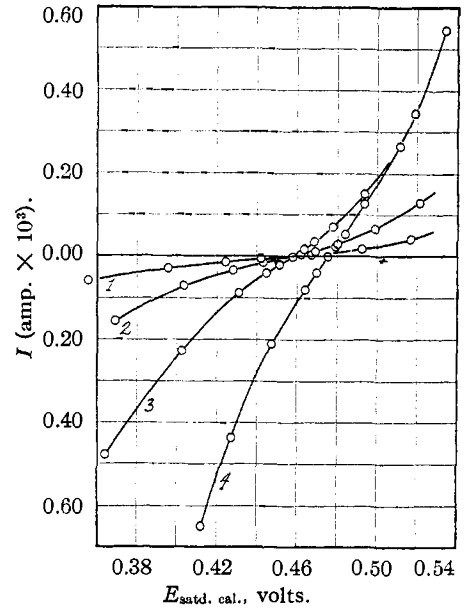

Fig. 5.—Addition of quinhydrone; sulfuric acid solution, *p*H 0.0; (1) 0.0001295 m./l. of quinhydrone; (2) 0.000378; (3) 0.001174; (4) added 0.00330 m./l. of quinone.

The fact that these values are considerably lower than those obtained through the addition of single components is quite puzzling. The high average deviation may be connected with the recognized difficulty of purifying quinhydrone.[18] Of course we must expect a somewhat smaller exponent because addition of quinhydrone will repress its own dissociation more than will either quinone or hydroquinone alone; however, simple calculation shows that an effect of only 2 or 3% is to be expected in most of these experiments.

It is interesting to note that with additions of quinhydrone, the current ratio remains constant even at potentials very close to the reversible potential. This point will be discussed further in the section on the kinetic equation.

**Effect of Acidity.**—In Figs. 6 and 7 are shown two groups of polarization curves taken at various acidities. Together they cover the *p*H range 1.0 to 8.2.[19]

---

(18) Clark, "The Determination of Hydrogen Ions," 3d ed., Williams and Wilkins, Baltimore, 1928, p. 411.

(19) In all these experiments in which the acid concentration was varied, as in all other experiments, 1.0 *M* sodium chloride was

These curves present several interesting features. (1) Addition of acid accelerates the reduction of quinone but retards the oxidation of hydroquinone. (2) The nature of the curve changes decidedly above *p*H 6, giving rise to an inflection point above the no-current axis. (3) The initial slope of these curves varies in a regular manner with *p*H. A plot of initial slope against *p*H has the shape of a catenary. (4) The anodic and cathodic halves of all the polarization curves except those obtained at acidities very close to *p*H 3.0 in equimolar solution of quinone and hydroquinone are unsymmetrical. As the *p*H increases above 3.0, the anodic curve exhibits regularly increasing polarization, while as the *p*H decreases below this value, the cathodic curve shows regular increase of polarization. (5) In contradistinction to the hydrogen system, in which Bowden[2b] and others found that the cathodic polarization (also called overvoltage and overpotential[20]) was independent of *p*H over a wide range of current density and acidity, it is immediately evident from these curves that in the quinhydrone system the same relationship does not apply, at least on blank platinum electrodes. However, in the single case in which a series of polarization curves at different acidities were obtained for a gold electrode, it was found that for the cathodic but not the anodic process, in the range of *p*H from 1.65 to 4.0, the polarization was independent of *p*H, *i. e.*, plots of current against polarization fell on the same curve.

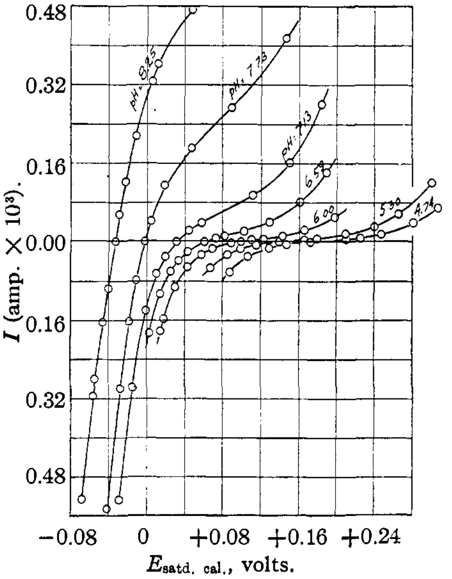

Fig. 6.—Effect of acidity; phosphate buffer; quinhydrone constant at 0.00588 m./l.; hydrochloric acid added, *p*H's indicated on curves.

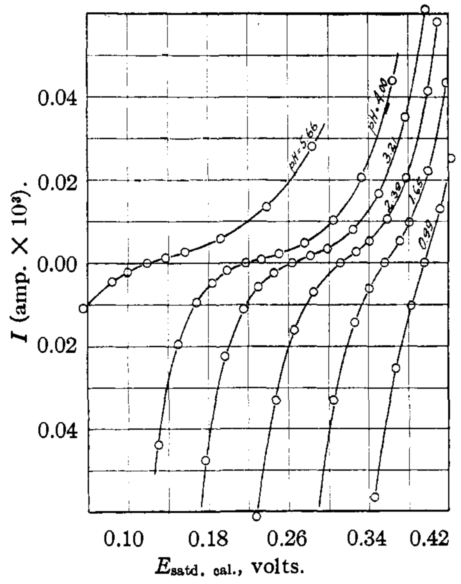

Fig. 7.—Effect of acidity; sulfuric acid; quinhydrone constant at 0.001267 m./l.; acid added, *p*H's indicated on curves.

Anodic and cathodic hydrogen ion exponents, *p* and *q*, respectively, are defined by the equations

$$I_a''/I_a' = 1/(C''_{H^+}/C'_{H^+})^p \qquad (2)$$

$$\text{and } I_c''/I_c' = (C''_{H^+}/C'_{H^+})^q \qquad (3)$$

where the other symbols have the same significance as in equation (1). Values of these exponents have been calculated from the results of twenty-seven experiments in solutions whose acidities and ratios of quinone–hydroquinone concentrations varied widely, and are plotted against *p*H in Figs. 8 and 9.

In calculating the hydrogen ion exponents current ratios were employed at only such potentials as were removed from either reversible potential by a value of more than 0.05 but less than 0.10 v. This restriction is necessitated by the deviation from linearity of the plot of log $I$ against potential, and the further variation of the slope of this semilogarithmic plot with *p*H. This variation of slope with *p*H appears in the current-potential curves as an inconstancy in the current ratios at different potentials. The implications of this disturbance are referred to in the discussion of results.

present in order to minimize change in the electrostatic environment with addition of electrolytes. In several cases sodium sulfate was used in place of sodium chloride for obvious reasons.

(20) Blum and Vinal, *Trans. Am. Electrochem. Soc.*, **66**, 359 (1934).

For the cathodic process the hydrogen ion exponent in solutions more acid than $pH$ 6.0 is 0.99 ± 10%. At higher $pH$ the curve shows decreasing dependence of the rate upon the hydrogen ion concentration (Fig. 9), and presumably complete independence around $pH$ 8.5. In acid solutions, then, the cathodic current

$$I_c = k_c'(Q)(H^+) \tag{4}$$

On the other hand, from the curve in Fig. 8, it may be seen that the rate of anodic reaction becomes independent of hydrogen ion concentration in very acid solutions ($pH < 0$). As the $pH$ increases, the order of reaction of hydrogen ion changes to unity at about $pH$ 7. The anodic current

$$I_a = k_a'(H_2Q)/(H^+)^p \tag{5}$$

where $p$ varies with $pH$ as in Fig. 8.

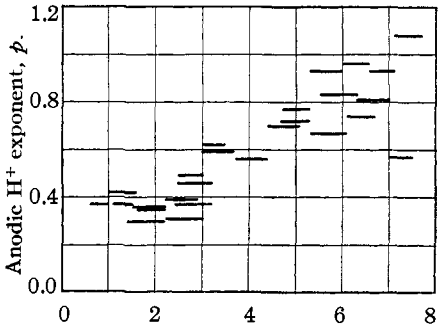

Fig. 8.—Variation of anodic hydrogen ion exponent, $p$, with $pH$.

**Effect of Potential.**—In the above sections there have been described the effects of concentration changes on the current at fixed potential. The individual polarization curve represents the variation of current with potential, the concentration of reactants remaining unchanged. A plot of log $I$ against $E$ shows that the potential, as a first approximation, follows the Tafel equation,[21] $E = a + b \log I$. Deviations from linearity of this semilogarithmic plot are to be anticipated at both very low polarizations (<0.05 v.) and high polarizations: the former arising from the significant contribution of the reverse reaction to the net current at potentials not far removed from the reversible potential, and the latter caused by concentration polarization and irreversible effects of the high polarization on the catalytic properties of the electrode. This leaves an estimated polarization region of about 0.1 v. in which we may be certain that the reaction under study is the sole electrode process. However, examination of over two hundred such semilogarithmic curves has indicated that a truly linear region does not exist here. This observation is by no means without parallel in other electrochemical reactions. Hammett[3] noted that an empirical equation of the type $E = a + b \log I + cI$ fitted his data on the hydrogen electrode system better than did the Tafel equation. Recently, Volmer and Wick[4c] and Chang and Wick[22] have set up similar equations to represent their data on both the hydrogen and halogen systems. Although they were unable to explain the origin of this linear term, they proved it was not due to concentration polarization or to a "transfer resistance." In the present work, too, it was found that the data for both anodic and cathodic reactions are better fitted by the addition of a linear term to the Tafel equation than by the latter alone. That it does not arise from concentration polarization is evidenced, among other points, by the fact that the coefficient of this term sometimes increases, sometimes decreases, with increase in concentration of reactant.

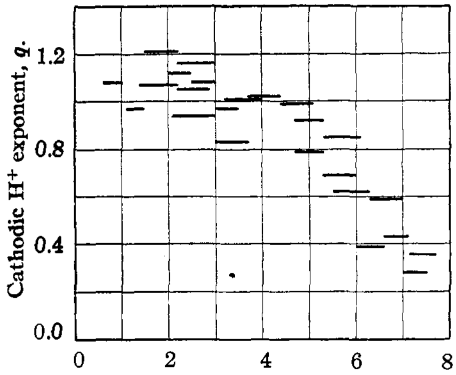

Fig. 9.—Variation of cathodic hydrogen ion exponent, $q$, with $pH$.

There being no completely linear region of the semilogarithmic curve, the slope at some intermediate polarization (generally 0.07 v.) was recorded as typical of that curve. It was observed that this slope is markedly dependent upon the acidity of the solution, but not upon the concentrations of the other reactants. All of the data on the variation of the slope of the semilogarithmic curves with $pH$ are plotted in Figs. 10 and 11.

**A General Approximate Equation.**—By introducing into equations (4) and (5) factors to rep-

---

(21) Tafel, *Z. physik. Chem.*, **34**, 200 (1900); **50**, 649 (1905).

(22) Chang and Wick, *ibid.*, **172A**, 448 (1935).

resent the variation of the current with potential for each of the two processes, but neglecting the above-described deviations from the Tafel equation, we arrive at the following approximate expression

$$I = k_a \frac{[H_2Q]}{[H^+]^p} e^{E/a} - k_c[Q][H^+]e^{-E/c} \qquad (6)$$

where $a = \frac{1}{2.3} \frac{dE}{d \log I}$ for the anodic reaction, and $c$ is the corresponding value for the cathodic process. The two rate constants may be evaluated separately, each under such conditions of polarization (>0.05 v.) that the other term becomes negligible. At the reversible potential the two terms become equal, and $I$, as required, becomes zero.

The velocity constants $k_a$ and $k_c$ are functions of the catalytic properties of the electrode surface on which the reactions occur. For this reason it must not be expected that their values be constant for different electrodes or for the same electrode over a long period of time or after treatment. These constants were calculated using values of $p$, $a$ and $c$ interpolated from Figs. 8, 10 and 11. The averages of a large number of such values of $k_a$ and $k_c$ are, respectively, $7 \times 10^{-10}$ and $3 \times 10^{+4}$ (a. d. for each = 70%). This deviation although many times the value usually found for homogeneous reaction constants, is surprisingly small considering the limitation mentioned above. The physical meanings of the constants are the currents in amperes/sq. cm. of apparent electrode surface obtained at $E_{\text{satd. cal.}} = 0.00$ v. from a solution whose constituents are at fixed concentrations of 1 m./l.

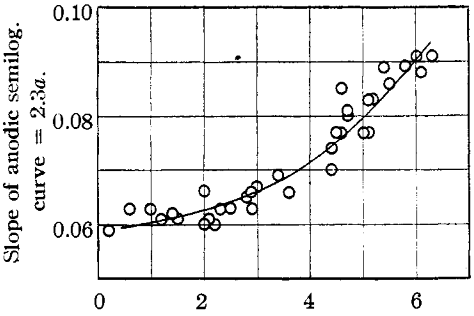

Fig. 10.—Variation of slope of anodic semilogarithmic curve with $p$H.

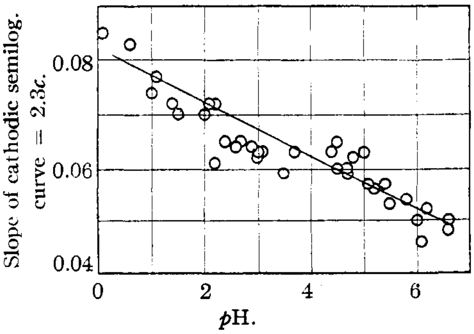

Fig. 11.—Variation of slope of cathodic semilogarithmic curve with $p$H.

Equation (6) is plotted as the curve in Fig. 12 while the points represent experimental data.

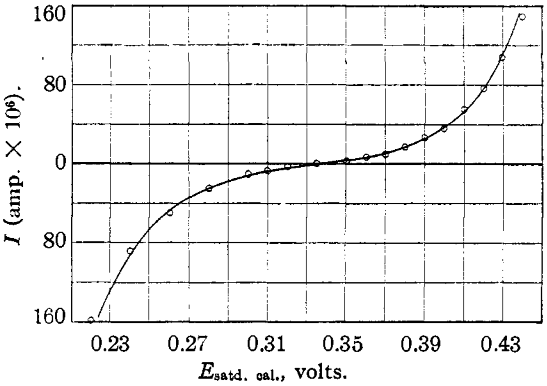

Fig. 12.—A comparison of equation 6 (curve) and experimental data (points): $p$H = 2.00; $H_2Q$ = 0.00374 m/l.; Q = 0.00374 m/l.; $k_a = 7.0 \times 10^{-10}$; $k_c = 0.75 \times 10^4$.

Values of the rate constants were chosen to fit the data at the higher polarizations, and the portion of the curve closer to the reversible potential was calculated on the basis of this best set of values, namely, $k_a = 7.0 \times 10^{-10}$ and $k_c = 0.75 \times 10^{+4}$. The agreement is very good at the lower polarizations but becomes poorer necessarily as the deviations from the simple exponential path mount. In very acid solutions in particular, it has been observed that the Tafel equation is incapable of representing the data, and consequently equation (6) does not fit the experimental points.

It has been shown experimentally that the current ratio upon addition of quinone, hydroquinone or acid, does not remain constant if the potential approaches closer than 0.05 v. to either reversible potential. Calculation of the two separate current terms in equation (6) indicates very clearly that it is only at polarization greater than this value that the contribution of the opposing reaction sinks below 3 or 4%. On addition of quinhydrone, on the other hand, the reversible potential is unaffected and therefore the exponential factors are unaffected, consequently, provided that both curent terms increase in the same proportion with this increase of concentration of both quinone and hydroquinone, the current ratio will remain constant all the way to the reversible potential. This behavior has already been noted, and in view of the fact that the quinone and the hydroquinone exponents have both been shown to be equal to unity, the equation offers a satisfactory explanation.

## Discussion

At the present time there is no satisfactory theoretical basis on which the important question of the number of electrons participating in the rate-determining step may be answered. For the cathodic reduction of hydrogen ions on a large variety of metals and even at temperatures as high as 80°, Bowden has shown that the use of an empirical value of 0.50 as the order of reaction of electrons gives precisely the correct experimental value of the coefficient $b$ in the Tafel equation. This same value has been found to hold also for the oxygen[2c] and the chlorine[22] electrode reactions (the latter, only on platinum). On the other hand, in the quinhydrone system the slope of the log $I$–$E$ curves (equal to the $b$-value referred to) is not constant but varies very considerably with $p$H (Figs. 10 and 11). It is significant that the slope is independent of the concentration of quinone or hydroquinone. From this and evidence previously discussed, it becomes clear that the electrical effects and the hydrogen ion effects are closely interwoven; thus, while the kinetics of quinone and hydroquinone are independent of $p$H and potential, the kinetics of hydrogen ion is strongly affected by both.

That it is possible to interpret an electrode process in terms of usual reaction kinetics is shown by Hammett's picture[23] of the two consecutive reactions involved in the cathodic polarization of the hydrogen electrode. Several possibilities present themselves as mechanisms of the processes reported on in the present work. (1) The reaction, $Q + 2H^0 = H_2Q$, and its reverse may be rate determining. This intermediate hydrogen mechanism was early proposed by Haber and Russ[5] and recently revived by Glasstone and Hickling.[24] Against it, however, several arguments strongly militate. If there be any truth at all in the currently accepted pictures of the hydrogen electrode reactions in which the process $OH_3^+ + e = H^0 + H_2O$, is rate determining, then at such high positive potentials as $E_H = 0.65$ v., at which the reduction of quinhydrone is observed to proceed with great rapidity even on blank platinum electrodes, the electrochemical reduction rate of hydrogen ion is completely negligible even on extremely active electrodes. Further, the very fact that so marked a difference in the catalytic properties of blank platinum for the hydrogen ion and the quinhydrone reduction exists, speaks strongly against this mechanism. Completely analogous arguments prevail against the theory of an intermediate active oxygen in the anodic process. Glasstone and Hickling have suggested in their intermediate hydrogen mechanism that the slow step in the oxidation and reduction of quinhydrone is the reaction, $H^0 = H^+ + e$, and its reverse. In addition to the above failings, this suffers further in being incompatible with the observed dependence of the rate upon the concentrations of quinone and hydroquinone.

(2) The direct oxidation and reduction of molecular quinhydrone suggests itself as another possibility. If this were the case, then addition of quinone, in so far as it increases the concentration of quinhydrone, should strongly increase the anodic current (at constant potential), and addition of hydroquinone should similarly increase the cathodic current. Neither effect was ever observed.

(3) A third possibility is the direct electrochemical oxidation of hydroquinone and the direct electrochemical reduction of quinone. However, no single reaction path can account for all of the involved relationships. The retardation of the oxidation by hydrogen ion may be attributed to its effect on the concentrations of molecular hydroquinone and its ionization products, HQ′ and Q″, all three of which are assumed to be capable of direct loss of electrons to the anode. The number of electrons lost in the rate-determining step may be either one or two: if one, there is formed a molecule of Michaelis' semiquinone[25] (which then rapidly disproportionates to quinone and hydroquinone) and the proper number of hydrogen ions are liberated; if two, a molecule of quinone is formed, together with hydrogen ions. That the number of electrons lost does vary is evinced by the

---

[23] Hammett, *Trans. Faraday Soc.*, **29**, 770 (1933).

[24] Glasstone and Hickling, "Electrolytic Oxidation and Reduction," D. Van Nostrand Co., New York, N. Y., 1936, p. 90.

[25] Michaelis, *Chem. Rev.*, **16**, 243 (1935).

change in the slope factors to which reference was made in the preceding section. Thus, for the complete oxidation process, we may picture as many as six parallel reaction paths. Under certain conditions one or another of these may predominate—in very acid solutions, for example, molecular hydroquinone is the only component present in kinetically significant concentration. That this is the only reactant is shown by the fact that hydrogen ion under these conditions exerts practically no retardation on the oxidation process. At the high positive potentials encountered in such a solution, it is probable that two electrons will be lost directly.

In a similar manner the reduction process may be viewed as being a composite of several parallel reactions. The molecule of quinone may react with either two, one or no hydrogen ions, taking up in each case either one or two electrons from the cathode. Examination of Fig. 9 indicates that the reduction becomes zero order with respect to hydrogen ion in slightly alkaline solutions, is close to first order in the range *p*H 6 to 0, and shows a trend to higher order at greater acidities.

## Summary

1. An apparatus is described for measuring polarizations under conditions of rapid agitation and the exclusion of oxygen.

2. The catalytic properties of blank platinum for the oxidation and reduction of quinhydrone were investigated, and the optimum conditions for reproducibility determined.

3. The kinetics of the anodic and cathodic processes were ascertained by determining the current at fixed potential as a function of the concentrations of quinone, hydroquinone and hydrogen ion; and a general approximate equation was set up.

4. Several possible mechanisms were examined with the conclusion that the reaction mechanism is a complicated one involving several parallel reaction paths.

NEW YORK, N. Y. RECEIVED MAY 3, 1937

---

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 615]

# The Structure of the Hydrides of Boron. III.[1] Borine Carbonyl and Borine Trimethylammine

BY S. H. BAUER

## Introduction

For many years the chemistry of the boron hydrides and their derivatives has provided a very interesting puzzle which has strongly resisted attempts at solution. A new method of attack on the problem is that of determining the structure of the molecules of these substances by electron diffraction or similar methods. The direct result of such an investigation is the determination of the nuclear configuration of the molecule. From the proximity of certain nuclei straightforward conclusions can be drawn regarding the distribution of valence bonds; it is possible also to make some statements regarding the nature of these bonds by the study of the experimentally determined values of the interatomic distances. However, the general interpretation of chemical properties in terms of molecular structures cannot be made without the aid of some relationship connecting them, and very few correlations of this nature have been discovered.[2] As a working hypothesis to be used in the interpretation of the results communicated in the present paper, the author has adopted the program of assuming the relationship to be a simple one and interpreting the facts as far as possible from this viewpoint. It is very likely that as more data become available it may be necessary to refine or even alter the hypothesis.

In this paper an electron diffraction investigation of two derivatives of diborane,[3] borine carbonyl and borine trimethylammine, is described leading to unique assignments of structures to

---

(1) Papers which have appeared previously will be designated as follows: 1, "The Pentaborane $B_5H_9$," S. H. Bauer and L. Pauling, THIS JOURNAL, **58**, 2403 (1936). II, "Diborane," S. H. Bauer, *ibid.*, **59**, 1096 (1937).

(2) For an application to the case of the fluoromethanes see L. O. Brockway, *J. Phys. Chem.*, **41**, 185 (1937), and discussion on page 317 of the same issue.

(3) Drs. Schlesinger and Burg suggested that these substances may be suitable for an electron diffraction investigation. A description of the methods of preparation and of some interesting chemical properties has recently been published [A. B. Burg and H. I Schlesinger, THIS JOURNAL, **59**, 780 (1937)].