TABLE III

HEATS OF SOLUTION AT INFINITE DILUTION AT 298.1°K. FROM SMOOTH CURVES, CAL./MOLE OF SOLUTE

Wt. % CH_3OH	Mole % CH_3OH	$-\Delta H°$ HCl	$-\Delta H°$ LiCl	$\Delta H°$ NaCl	$\Delta H°$ KCl	$\Delta H°$ KI	$-\Delta H°$ NaI	$\Delta H°$ KBr	$\Delta H°$ NaBr	$\Delta H°$ RbCl	$\Delta H°$ CsCl
0	0.00	17880	8900	920	4120	4870	1820	4780	−30	4000	4240
10	5.88	17550	8000	1400	4410	5200	1250	5050	450	4170	4400
20	12.32	17320	7600	1680	4610	5300	1000	5230	650	4290	4450
30	19.41	17200	7800	1750	4620	5200	1150	5150	660	4340	4420
40	27.25	17240	8050	1720	4540	5000	1400	4950	550	4350	4340
50	36.08	17440	8400	1590	4280	4620	1750	4550	300	4290	4160
60	45.74	17740	8800	1375	3870	4100	2150	4070	−40	4150	3920
70	56.73	18030	9350	1030	3400	3470	2800	3530	−600	3910	3600
80	69.41	18500	9950	500	2790	2700	3750	2820	−1320	3450	3150
90	83.50	19030	10650	−350	2060	1700	5050	2020	−2400	2630	2580
100	100.0	19700	11500	−2000	1080	175	7000	870	−4000	1280	1850

K. S. Pitzer. The difficult task of constructing the thermopile was carried out by Mr. G. F. Nelson and Mr. P. Fabricius.

Summary

The heats of solution at infinite dilution of the chlorides of lithium, sodium, potassium, rubidium, cesium and sodium bromide, potassium bromide, sodium iodide, potassium iodide and hydrogen chloride were determined in water–methyl alcohol solutions at 298.1°K. All of the compounds exhibited an appreciable maximum heat absorbed at around 15 mole per cent. methyl alcohol, and all of them evolved more heat upon solution in absolute methyl alcohol than in water.

BERKELEY, CALIFORNIA RECEIVED APRIL 2, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, AND THE DEPARTMENT OF SURGERY, CORNELL UNIVERSITY MEDICAL COLLEGE]

Oxidation–Reduction Potentials Measured with the Dropping Mercury Electrode. III. Polarographic Study of Quinhydrone in Buffered and Unbuffered Solutions[1]

BY OTTO H. MÜLLER[2]

In the first paper of this series,[3] it has been shown that a slowly dropping mercury electrode can function as a reliable indicator electrode for oxidation–reduction potentials. Under certain well defined conditions, this dropping mercury electrode was used in the presence of quinhydrone to determine the *p*H of solutions which were well buffered between *p*H 2 and *p*H 8. Even poorly buffered solutions were studied with this electrode and the *p*H values thus found agreed well with results obtained in different ways by others.

The latter investigations were carried out in potassium acid phthalate solutions which were diluted to different degrees. In spite of the fact that all were saturated with quinhydrone, the potentials were poorly poised in the more dilute solutions of potassium acid phthalate. One could notice marked oscillations of the galvanometer with each growing drop of mercury; also changes in the balancing e. m. f. produced relatively small changes in current. This is in contrast to well-buffered, well-poised systems, where oscillations of the galvanometer from its zero position during the growth of the mercury drops are negligible, and where slight changes in the balancing e. m. f. throw the galvanometer off scale. It seemed of interest to investigate this action of buffers further, using a polarograph for the automatic plotting of current–voltage curves.[4,5,6]

These experiments have brought out many peculiarities of polarographic curves which have hitherto not been observed. They also give new information about the processes at electrode–

---

[1] Presented in part before the Division of Physical and Inorganic Chemistry at the Ninety-sixth meeting of the American Chemical Society held at Milwaukee, Wisconsin, September 5–9, 1938. This work was supported at Stanford University by a fellowship from the Upjohn Company and at Cornell University Medical College by a grant from the John and Mary B. Markle Foundation.

[2] Present address: Cornell University Medical College, New York City.

[3] O. H. Müller and J. P. Baumberger, *Trans. Electrochem. Soc.*, **71**, 169 (1937).

[4] J. Heyrovský and M. Shikata, *Rec. trav. chim.*, **44**, 496 (1925).

[5] J. Heyrovský, in W. Böttger, "Physikalische Methoden der analytischen Chemie," Akademische Verlagsgesellschaft, Leipzig, Vol. II, 1936, and Vol. III, 1939.

[6] I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

solution interfaces during electrochemical reactions.

Experimental

The polarograms were obtained in the usual way, using a Nejedlý Polarograph, Model VIII, and a galvanometer with a maximal sensitivity of 1.7×10^{-9} amp./mm./m. The same procedure was followed as in the previous publication.[7] Again, an external, saturated calomel half-cell with a large mercury surface was used instead of the customary mercury pool on the bottom of the vessel. All experiments were carried out at room temperature, which did not differ more than 1° for comparative runs. Due precautions were taken to avoid interfering ions.[3]

Experiments with Phosphate Buffers.—After preliminary experiments with different buffers, a Sørensen phosphate buffer of *p*H 6.9 was selected because, as will be shown, it serves best for the demonstration and study of the buffer effect on the quinhydrone potential. A 0.1 *M* solution of this buffer was prepared and diluted 10, 100, 1000, and 10,000 fold with 0.1 *N* potassium nitrate. To 9 cc. of each of these five solutions, 1 cc. of a 0.012 *M* solution of quinhydrone in 0.1 *N* potassium nitrate was added. The quinhydrone concentration was, therefore, constant, but its ratio to that of the buffer varied from approximately 1:100, characteristic of a well-buffered solution, to 100:1, which represents a very poorly buffered solution.

Polarograms obtained with these solutions are represented in Fig. 1. In every case two different sensitivities of the galvanometer have been used, namely, $^1/_{100}$ to bring the complete curve on to the polarogram, and $^1/_{10}$ in order to emphasize the change of current with change in voltage near galvanometer zero. It is obvious that the current must be zero wherever two such curves of different sensitivities cross. As indicated in this and subsequent figures, each interval between the automatically recorded vertical lines corresponds to 60 mv.; for each solution the abscissa corresponding to the E_h of the calomel half-cell (*i. e.*, when the *applied* voltage is zero) is marked by a circle. The applied voltage becomes more negative to the right and more positive to the left of these circles. The horizontal line on the polarograms indicates zero current ("galvanometer zero")[7]; above it a reduction, and below it an oxidation, takes place on the electrode surface.[8]

As is well known, the quinhydrone electrode is used for the determination of *p*H because, at constant temperature, its potential is a linear function of *p*H in the range of *p*H 1 to *p*H 8. This is usually expressed by the equation:

$$E = E_0 - \frac{RT}{2F} \ln \frac{[\text{hydroquinone}]}{[\text{quinone}]\,[\text{H}^+]^2}$$

which becomes $E = E_0 + RT/F \ln [\text{H}^+]$ in the case of quinhydrone, where hydroquinone (molecular plus ionic forms) and quinone concentrations are equal. It must be remembered, however, that this equation is based on two different equilibria. The first, the actual electrode equilibrium, deals with the addition of two electrons to the quinone molecule to form the hydroquinone ion

$$\text{Q} + 2\ominus \rightleftarrows \text{Q}^{--}$$

Therefore, the relative concentrations of the quinone molecules and the hydroquinone ions determine the potential. However, the concentration of the hydroquinone ions is dependent on the dissociation constants of the weak acid hydroquinone, so that the prevailing hydrogen ion concentration becomes important. Thus also the second, acid-base, equilibria:

$$\text{Q}^{--} + \text{H}^+ \rightleftarrows \text{HQ}^-$$

and

$$\text{HQ}^- + \text{H}^+ \rightleftarrows \text{H}_2\text{Q}$$

have their effect on the potential. From the known dissociation constants of hydroquinone one can calculate the concentration of free hydroquinone ions for any *p*H. One would obtain a concentration of the order of 10^{-11} *M* for a solution of *p*H 2 similar to the ones used above. This is such a small value that it would be considered insignificant by many who forget that this calculation gives a *limiting* value which as such is definitely significant. If, for instance, by electrochemical reduction of quinone, some hydroquinone ions are formed in the solution, they will at once react with the buffer to form hydroquinone molecules so as not to exceed the limiting concentration given by the above calculation. This will become obvious from the experiments presented in this paper. For the moment, it should be emphasized that all the equilibria shown above are perfectly reversible as indicated by the double arrows.

The equilibria must be established with extreme rapidity as is demonstrated by the smooth curve

---

(7) O. H. Müller and J. P. Baumberger, *Trans. Electrochem. Soc.*, **71**, 181 (1937).

(8) O. H. Müller, *Chem. Rev.*, **24**, 95 (1939).

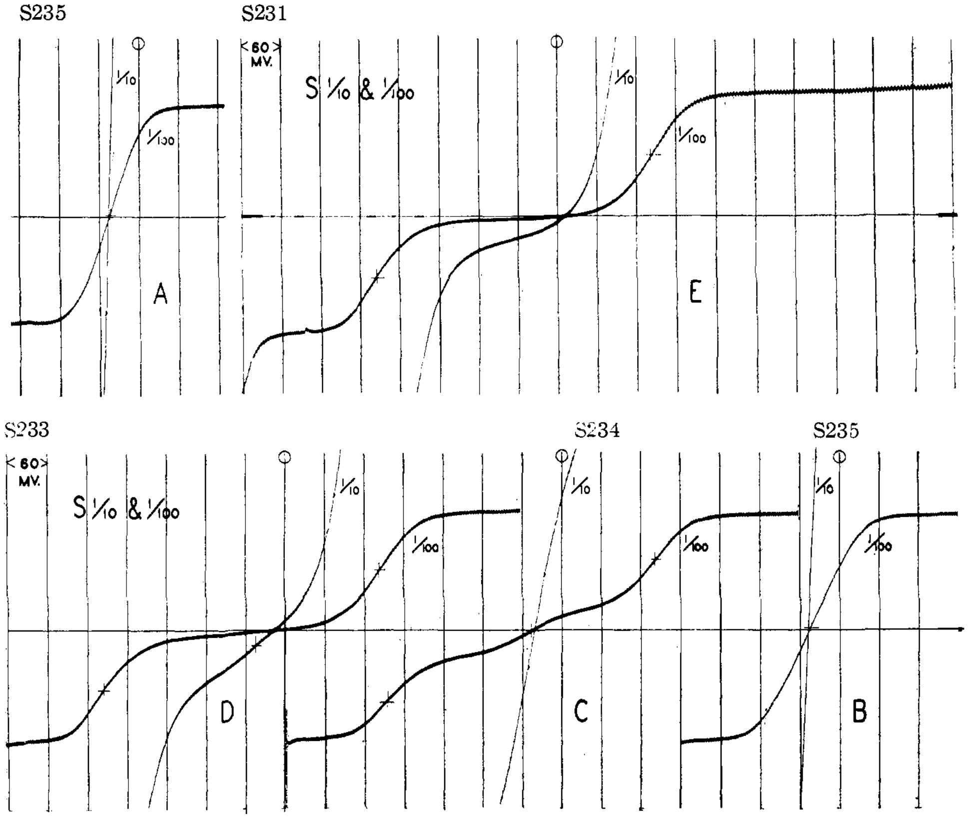

Fig. 1.—Polarograms of 0.0012 *M* solutions of quinhydrone in phosphate buffer of *p*H 6.9: (A) 0.1 *M*, (B) 0.01 *M*, (C) 0.001 *M*, (D) 0.0001 *M*, (E) 0.00001 *M*. The indifferent electrolyte is 0.1 *N* potassium nitrate.

of Fig. 1A, which is a typical representative of well-buffered and well-poised reversible systems,[7] and which is strictly analogous to a potentiometric titration curve[9] where always sufficient time is allowed for the establishment of the potential. Additional evidence for the rapidity with which these equilibria are established is the identity of the half-wave potentials of quinone reduction and hydroquinone oxidation in buffered solutions.[7] The latter implies, furthermore, a similarly rapid dissociation or association of the buffer molecules and ions present. (That this is not always rapid enough will be shown later on in this paper.)

If no buffer is present and sufficient energy is available to cause a reaction that either produces or consumes hydrogen ions, one would expect a change of *p*H at the electrode surface and, accordingly, a change in the electrode potential. This is indeed the case when a 0.001 *M* solution of quinone is reduced in a neutral, unbuffered solution such as 0.1 *N* potassium nitrate. The half-wave potential here corresponds to an E'_0 for *p*H 10 instead of *p*H 7. Also in the oxidation of hydroquinone, erroneous values for the *p*H *of the solution* would be calculated if the half-wave potential in unbuffered solutions were used. Here the error is in the opposite direction, the half-wave potential indicating *p*H 3 instead of the *p*H of the body of the solution, *viz.*, *p*H 7.

Both phenomena are easily demonstrated with quinhydrone, where oxidant and reductant are in equal concentrations. The curves of solution E (Fig. 1) are typical representatives of polarograms obtained in unbuffered solutions, since under the given conditions of galvanometer sensitivity and quinhydrone concentration the 10^{-5} *M* phosphate solution gives a polarogram identical with that obtained in pure 0.1 *N* potassium nitrate solution. Two widely separated waves of equal height may be noticed, one due to the reduction of quinone, the other due to the oxidation of hydroquinone. The effect of buffering consists thus of bringing the two waves of Fig. 1E together until they overlap to form the one continuous wave with a total height equal to their sum, as in Fig. 1A. To

(9) O. H. Müller, *Cold Spring Harbor Symposia Quant. Biol.*, **7**, 59 (1939).

study this further, curves B, C, and D of Fig. 1 were prepared. For convenience in describing the results, the two waves due to *un*buffered anodic and cathodic reactions will be designated by subscripts "a" and "c," while the middle wave which goes continuously from oxidation to reduction due to the added buffer will be designated by subscript "b."

In curve D the phosphate concentration is about 10^{-4} M and a small wave (D_b) is barely noticeable between D_a and D_c. As the buffer concentration in the solution increases, this middle wave also increases at the expense of the unbuffered waves. For curve C a condition exists in which the concentration of quinone, hydroquinone, and phosphate are of the same order. Here we find that the middle wave (C_b) has reached almost the same height as C_a and C_c. When the buffer concentration is about ten times that of the oxidation–reduction system, as in curve B, the three waves can no longer be distinguished. However, in this case, too, the curve is still complex as may be seen by a comparison of the slope of curve B with that of curve A where the buffer concentration is a hundred times that of the oxidation–reduction system.

The fact that the sum total of all the waves is independent of the concentration of the buffer indicates that the action of the buffer is only secondary in that it removes or furnishes hydrogen ions during a reaction at the electrode surface, preventing a change of *p*H. In the absence of a buffer, the hydrogen ion concentration at the mercury–solution interface may be increased over or decreased below that in the body of the solution during an electrode reaction. When the solution has only little buffer capacity, a fraction of the reaction at the electrode will go on at a *p*H which is approximately the same as that in the body of the solution, but the main reaction will produce profound changes in acidity at the interface. This means that whenever the necessary potential energy is not available to continue the reaction at a different *p*H, the reaction will be slowed down or stopped when the buffer is exhausted, or, in other words, the reaction will be governed by the buffer present. The significance of this observation for the interpretation of reactions in biological systems is discussed elsewhere.[9]

The observation that the action of the buffer produces a measurable wave when its concentration is of the same order as that of the reacting material has led to the discovery of a new kind of polarographic determination that depends on the buffering action of compounds which are not directly oxidized or reduced at the dropping mercury electrode. Examples and the principles involved will be given in a subsequent paper.

TABLE I

Curve	Half-wave potential $E_{cal.}$	E_h	*p*H, uncor.	*p*H, cor.
A	+0.044	+0.287	6.9	6.9
B	+ .044	+ .287	6.9	6.9
C_a	+ .266	+ .509	3.2	3.8
C_b	+ .046	+ .289	6.8	6.8
C_c	− .141	+ .102	10.0	9.3
D_a	+ .275	+ .518	3.0	3.5
D_b	+ .046	+ .289	6.8	6.8
D_c	− .143	+ .100	10.0	9.5
E_a	+ .275	+ .518	3.0	3.5
E_c	− .143	+ .100	10.0	9.5

In Table I the observed half-wave potentials of the different waves of Fig. 1 have been listed in column 2. These values were measured against the standard calomel electrode. They are referred to the standard hydrogen electrode in column 3. If, for a first approximation, these potentials are assumed as reliable E'_0 values for the conditions at the interface, the uncorrected *p*H shown in column 4 can be calculated. This column brings out a surprisingly good agreement of the *p*H at the half-wave potentials of the different groups of waves, which led to some interesting conclusions. The fact that all the E'_0 values obtained in the unbuffered oxidations gave a *p*H around 3 suggested that the hydroquinone which was in a concentration of 10^{-3} M was liberating its hydrogen ions *at the interface* as it was oxidized to quinone. An analogous reasoning would give *p*H 11 for the reduction of 10^{-3} M quinone to *associated* hydroquinone, whereby the hydrogen ions would have to come from water, liberating hydroxyl ions. Actually a *p*H 10 is observed, but hydroquinone is a weak acid so that not all hydroquinone ions would be associated with hydrogen ions, permitting therefore a lower *p*H. These conclusions were verified by studying quinhydrone at varying concentrations in the same unbuffered solutions, as will be shown later on.

Before going further, it will be necessary to consider a few points which have been neglected in the foregoing approximations. First of all, corrections for the drop of potential in the solution during the flow of current, *IR*, which are essential for accurate work,[7,8] have been neglected.

Second, it must be remembered that in the present case the concentrations of quinone and hydroquinone at the electrode interface are only equal (as they are in the body of the solution) at galvanometer zero. As soon as current flows, the ratio of quinone to hydroquinone deviates from unity. Therefore, an additional correction (obtained from the height of the waves) becomes necessary in the calculation of the *p*H corresponding to the above half-wave potentials. If these corrections are made, the *p*H values shown in column 5 of Table I are obtained. These may be considered accurate to 0.1 *p*H unit. It may be seen that the actual *p*H at the interface differs somewhat from that anticipated on the basis of the quinhydrone concentration. More will be said about this discrepancy later on.

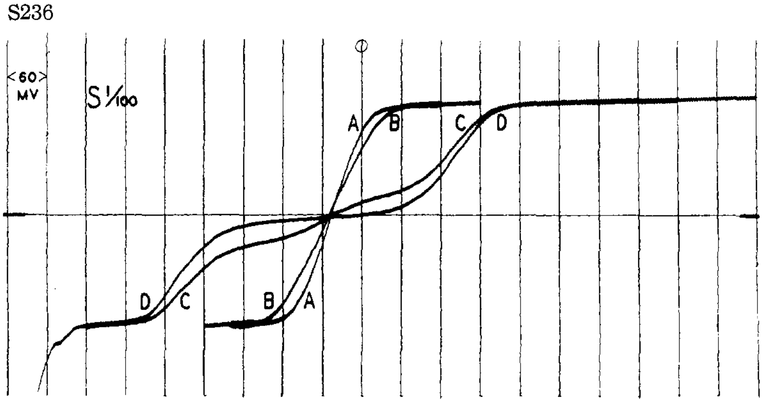

Fig. 2.—Curves from Fig. 1 drawn on a single polarogram.

Another point has to be brought out with regard to Fig. 1. As has been shown elsewhere,[3] the galvanometer can be used as a nullpoint instrument and the polarograph as a potentiometer to determine the potential of a solution with the dropping mercury electrode, which in this case serves as indicator electrode. Such potentials can also be read directly from the polarograms of Fig. 1 by taking the points where the curves of different galvanometer sensitivities cross each other or cross the galvanometer zero line. The potentials can then be used to calculate the *p*H of the *body* of the solution. The values thus obtained for different concentrations of buffer are given in Table II; they correlate well with similar determinations made in other ways.[3] As might be expected, the potentials are poorly poised in unbuffered solutions. This is illustrated by the curves taken at sensitivity $^1/_{10}$. We observe that for curve E a current of 10^{-7} amp. in either direction is sufficient to polarize the electrode about ±25 mv., while for curve A the polarization at a similar current intensity is only about 1 mv.

TABLE II

Curve	Potentiometric potential $E_{cal.}$	E_h	*p*H
A	+0.044	+0.287	6.9
B	+ .044	+ .287	6.9
C	+ .043	+ .286	6.9
D	+ .016	+ .259	7.2
E	− .008	+ .235	7.7

In order to facilitate discussion, Müller[9] proposed the terms *potentiometric potentials* to represent the electrode potential with respect to the body of the solution and *polarographic potentials* to represent the electrode potential with respect to the mercury–solution interface. Both potentials will be equal when no current flows, that is, when no reaction takes place at the interface which would make its composition different from that of the body of the solution. A simple demonstration of these conditions may be given polarographically by superimposing the curves of Fig. 1, as has been done in Fig. 2. Because they represent the *p*H in the body of the solution which has changed but little with dilution of the buffer, the potentiometric potentials are relatively constant, while the polarographic potentials vary widely whenever current flows since they indicate the changed conditions during reactions at the electrode interface.

Changing Concentration of Quinhydrone in Unbuffered Solutions.—As has been stated before, the half-wave potentials of quinhydrone in unbuffered solutions should be dependent on the concentration of the quinhydrone if our interpretation of the processes at the interface are correct. This hypothesis has been tested and some typical results are presented in Fig. 3.

Curve a has been obtained with pure 0.1 *N* potassium nitrate solution. The other curves (b-e) are due to solutions of 0.1 *N* potassium nitrate with varying concentrations of quinhydrone as shown in Table III, column 2. This table also gives data from an additional polarogram (not reproduced) where the quinhydrone concentration was 0.01 *M*. To be able to measure the half-wave potentials at the smallest concentration of quinhydrone, the top set of curves has been prepared at galvanometer sensitivity $^1/_{10}$, while for the higher concentrations sensitivity $^1/_{70}$, as used in the lower set of curves, was satisfactory.

TABLE III

Curve	Quinhydrone concn.	pH of the interface at the half-wave potential (see text) Obsd.	Calcd.	Difference in pH units
Fig. 3b	0.0000333 *M*	5.0	4.5	0.5
		8.6	9.5	1.1
Fig. 3c	.00011 *M*	4.5	4.0	.5
		9.0	10.0	1.0
Fig. 3d	.000323 *M*	4.0	3.5	.5
		9.4	10.4	1.0
Fig. 3e	.001 *M*	3.5	3.0	.5
		9.6	10.7	1.1
Not shown	.01 *M*	2.6	2.0	.6
		10.2	11.3	1.1

From the half-wave potentials indicated in Fig. 3, the observed pH of the interface (Table III, column 3) was calculated. For each quinhydrone concentration two different values are given; the upper pH refers to the anodic wave, and the lower one to the cathodic wave. As for Table I, corrections were made in these calculations for *IR* and for the fact that the hydroquinone–quinone ratio at the half-wave potential is 1:3 for the anodic wave and 3:1 for the cathodic wave. The last correction becomes clear if one remembers that in a solution of quinhydrone the hydroquinone–quinone ratio at the electrode interface is unity only when no current flows. Considering then the anodic wave, one must take into account that both components of the solution, the hydroquinone as well as the quinone, diffuse to the electrode surface. The quinone remains unchanged, but the hydroquinone is oxidized to quinone, so that at the half-wave potential the concentration of hydroquinone at the interface is one-half that which diffused, while the concentration of quinone is three-halves times as much as that which diffused. An analogous consideration of the processes at the cathodic half-wave potential will give the inverse ratio.

In column 4 of Table III are listed pH values which have been calculated from the quinhydrone concentration on the following hypothesis. If, for each hydroquinone molecule oxidized, two hydrogen ions are liberated at the electrode interface, then at the half-wave potential, where one-half of all the hydroquinone molecules is oxidized, the hydrogen ion concentration will be equal to the original hydroquinone concentration. Similarly, if all the hydroquinone ions which are formed during the reduction of quinone were fully associated with hydrogen ions, the hydroxyl ion concentration at the half-wave potential of the quinone reduction should be equal to the original concentration of quinone. However, at higher concentrations of quinone, the latter assumption is not justified since hydroquinone has a pKa_1 of 9.76 and a pKa_2 of 11.40. Suitable approximations were therefore made in the calculation of the pH at the cathode interface.

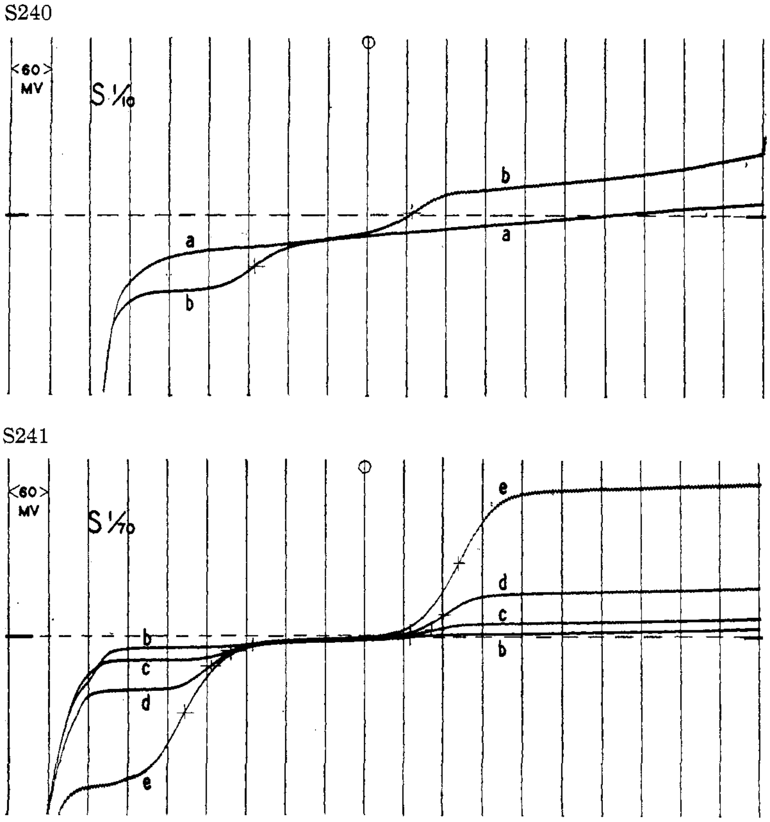

Fig. 3.—Polarograms of 0.1 *N* potassium nitrate solutions containing quinhydrone in the following concentrations: (a) 0, (b) 0.0000333 *M*, (c) 0.00011 *M*, (d) 0.000323 *M*, (e) 0.001 *M*.

A comparison of these pH values shows that there is a constant difference between the observed and the calculated pH of the two groups of waves (column 5 Table III). One of the most likely causes for the apparent loss in acidity and basicity seemed to be the diffusion of the hydrogen and hydroxyl ions away from the electrode, since both have mobilities which exceed all other ions. It cannot account for the observed facts, however, because the expected discrepancies would be just in the inverse ratio from what they really are; the loss of hydrogen ions would be almost twice as much as the loss of hydroxyl ions. Another possible cause was the drop-time of the mercury electrode since it changes with potential and since two different potentials are involved in the two unbuffered waves. This seems the best explanation so far, as some preliminary experiments have shown indeed that the unbuffered half-wave potentials vary with the drop-time of the mercury electrode. When these potentials, obtained at different drop-times, were extrapolated to an infinitely large drop-time, values were obtained approaching those corresponding to the calculated *p*H. This would indicate that the stirring effect of the growing drop or the removal of the established interface is responsible for the observed discrepancies. However, further studies will be necessary to verify this point.

As additional proof for the correctness of the above interpretations of the polarographic waves in unbuffered solutions may be mentioned the fact that well-established electrochemical equations are found to fit these waves if the hydrogen ion concentration is expressed as a function of the current.[9] This will be discussed in detail in a subsequent paper.

One thing becomes perfectly clear from the foregoing, namely, that one can get a kind of polarographic wave in which the half-wave potential obtained with a perfectly reversible system is *not* independent either of the concentration, or of drop-time, merely because the solution is inadequately buffered. In addition to other reasons which have been pointed out elsewhere,[8] this must be considered of greatest importance in the interpretation of so much of the published polarographic work where no adequate buffering has been provided. It should also be kept in mind whenever the constancy of a half-wave potential during changing concentration of the reacting material or changing drop-time is doubted.

This brings up the question what is meant by adequate buffering. As may be seen from Fig. 1B, a buffer concentration which is tenfold that of the reacting material is not yet adequate; the curve is still not steep enough, and *p*H changes obviously must occur at the electrode surface during the reaction. It has been our observation that fifty-fold, or better yet a hundred-fold, concentration of buffer over that of the reacting material is satisfactory.[9] However, it is essential that the buffer used has the additional feature that its acid dissociate hydrogen ions and its salt associate with hydrogen ions without an added energy of activation. Most buffers fortunately are of this type, but there are exceptions as will be shown presently. Another and very important point is that the ratio acid-salt of the buffer used is near unity, or, in other words, that the *p*H for which the buffer is used is near the *pKa* of the buffer.

Experiments with Other Buffers.—The discussion so far has dealt only with phosphate buffers because they are most satisfactory for a demonstration of the phenomenon. Other buffers, of course, act similarly as long as they meet the above requirements. Phthalate, citrate, and acetate buffers were tested and showed perfect buffer action when in proper concentration. However, the effect of dilution could not be so clearly demonstrated in these instances because the *pKa* of these buffers was too close to the *p*H obtained in the unbuffered curves so that the waves began to overlap. As will be shown in detail in a subsequent publication, the middle or buffer wave obtained on the polarogram of Fig. 1 corresponds to the familiar equation

$$pH = pKa - \log (\text{Acid}/\text{Salt})$$

upon which a minor change of the ratio oxidant–reductant is superimposed. Thus the point of inflection of the middle wave indicates the *pKa* of the buffer used.

In the case of the Sørensen buffer of *p*H 6.9, the middle wave is very easily seen because that *p*H is near the pKa_2 of phosphoric acid, so that the point of inflection of the middle wave is almost at galvanometer zero. When *p*H is equal to the *pKa* of the buffer, the acid and salt components of the buffer are in equal concentration and therefore the buffer is best suited to accept as well as furnish hydrogen ions. Whenever *p*H becomes smaller than *pKa*, the oxidative processes which produce hydrogen ions are less buffered than the cathodic processes which require a supply of hydrogen ions, and *vice versa*. In some polarographic studies, ammonium chloride has been used as buffer. Obviously the ammonium ion is not capable of neutralizing any hydrogen ions formed as the result of a reaction, although the formation of free hydroxyl ions during a reaction would undoubtedly be suppressed by ammonium ions because of the formation of the weak base ammonium hydroxide. Experiments have verified this conclusion. It was found that the hydroquinone oxidation in a solution of ammonium chloride proceeds as if it were entirely unbuffered, while at least some buffering action was observed in the quinone reduction.[8] A better buffer is obtained if ammonium hydroxide is added to the ammonium chloride solution because then also the hydrogen ions formed during anodic oxidations could be neutralized.[10]

The outstanding example of an acid which requires energy of activation for its dissociation is carbonic acid.[11] Also the reactions of carbon dioxide with water and the liberation of carbon dioxide from carbonic acid by the addition of a strong acid are not instantaneous and require an energy of activation. In biological systems, where this association and dissociation of carbon dioxide and carbonic acid is of prime importance, an enzyme, carbonic anhydrase, is therefore present to catalyze the reaction. It seemed worth while to study the behavior of a carbonate buffer at the dropping mercury electrode, and Fig. 4 is an example of the results obtained. Figure 4A represents an unbuffered quinhydrone solution (0.001 *M)* in 0.1 *N* potassium nitrate. Figure 4B shows the same solution when a mixture of carbonic acid and carbonate which had been adjusted to *p*H 7.5 was added so that its final concentration was 0.01 *M*. While this would not represent a perfectly buffered solution according to our above standard, we would at least expect a steep curve through galvanometer zero without any visible steps, similar to Fig. 1B. Obviously no such direct action occurred; the anodic and cathodic waves are still separated. However, as may be seen by comparing Fig. 4A, which is superimposed on Fig. 4B, the curves obtained with the carbonate buffer differ definitely from the unbuffered curves. It does not seem unlikely that with more data of this sort plus a knowledge of the temperature coefficient of the reactions, the necessary activation energies involved may be calculated from such curves.

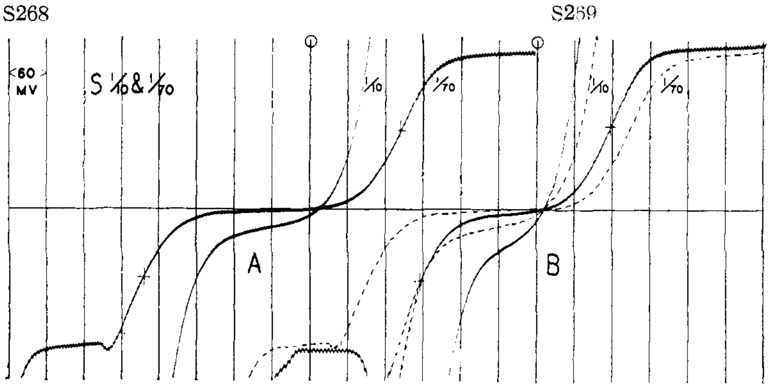

Fig. 4.—Polarograms of 0.001 *M* solutions of quinhydrone in: (A) 0.1 *N* potassium nitrate solution, (B) 0.01 *M* carbonate buffer of *p*H 7.5. Dash line is curve A superimposed on curve B.

Summary

Polarograms obtained with quinhydrone in unbuffered solutions and solutions containing varying amounts of buffer are described and discussed. It is shown that the oxidation of hydroquinone and the reduction of quinone at the dropping mercury electrode in unbuffered solutions produce marked changes in the *p*H of the interface which are a function of the concentration of the reacting material. Most buffers prevent these changes to a degree depending on the relative concentrations of the buffer and the reacting material; carbonate buffer is an outstanding exception.

To be adequately buffered a solution must contain: (1) a buffer at a concentration which is hundred-fold that of the reacting material; (2) a buffer whose acid and salt components dissociate and associate without an added energy of activation; and (3) a buffer in which the concentration of acid and salt are nearly equal.

Of particular interest for polarographic work is the observation that if solutions are not adequately buffered, the half-wave potential cannot be used for the determination of the E'_0 of an unknown system because the *p*H at the interface is not known. Furthermore, under these conditions the half-wave potential fails to remain constant with changing concentration of the reacting material or with changing drop-time.

NEW YORK, N. Y. RECEIVED JUNE 17, 1940

---

[10] R. Brdička, *Collection Czechoslov. Chem. Commun.*, **8**, 366 (1936).

[11] G. N. Lewis and G. T. Seaborg, THIS JOURNAL, **61**, 1886 (1939).