POTENTIOMETRIC STUDIES OF OXIDATION REDUCTION

with special reference to

THE QUINHYDRONE ELECTRODE IN ALKALINE SOLUTION

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Edwin Thornton Rainier

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M. S. University of Cincinnati 1927

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OXIDATION - REDUCTION POTENTIALS

Introduction.

One of the oldest problems in theoretical chemistry has been that of measuring the "affinity" of substances. Closely related to this is the problem of measuring chemical energy. In 1894, Ostwald (45) gave the specifications for a "chemometer", and suggested that the galvanic cell might be such an instrument. He says (page 404 loc. cit.) :

> " Now since on the one hand the electrical energy is equal to the chemical energy and on the other hand the two capacity factors, the amount of substance and the quantity of electricity, are according to the Faraday law proportional, the intensity factors, the chemical potential and the electromotive force must be proportional to each other, and the electrometer serves as a "chemometer" in the sense as previously explained. And indeed, since electromotive forces can be distinguished from one another only through number and sign, we have a general measure of the chemical potential, or of the chemical affinity, as we may justly call the magnitude."

In the same year Victor Rothmund (53) set forth much the same idea. He mentions that J. Willard Gibbs and J. H. van't Hoff had previously come to the same conclusion.

With the idea in view of measuring chemical energy or chemical affinity by the potentials developed in galvanic cells, a great deal of work has been done on electromotive force measurements. Among the early work on oxidation-reduction reactions is that of W. D. Bancroft (1) in 1892. He simply made up cells consisting of two half-cells, one containing pure oxidising agent, the other pure reducing agent in contact with platinum foil electrodes. They were connected by means of a salt bridge and the E.M.F. was measured. An examination of his data shows that he got drifting potentials, although in some cases there is constancy to within .04 volt. He gave measurements on a large number of oxidising and reduction agents. In some cases there seems to be a relation between E. M. F. and "strength" of the reducing or oxidising agent. In regard to oxidation chains, Bancroft came to the following conclusions:

> "1. The electromotive force of oxidation chains is an additive property.
> 2. The electromotive force is within wide limits independent of the concentration.
> 3. The electromotive force in independent of the nature of the electrodes, so long as they are not attacked.
> 4. The electromotive force is independent of the salt bridge.
> 5. A free acid is a stronger oxidising agent than its salt, the opposite holds for a reducing agent.
> 6. Where 5 does not apply, the electromotive force is independent of the nature of indifferent ions."

R. Peters (46) was among the first to publish work on oxidation-reduction potentials of mixtures of oxidants and reductants. He worked with mixtures of ferric and ferrous salts and developed by means of thermodynamics the equation accepted even today:

$$\pi = A + \frac{R\ T}{F} \ln \frac{\text{conc. ferric ions}}{\text{conc. ferrous ions}}$$

where π is the electrode potential, R the gas constant, F the faraday, 96,500 couloumbs, and T the absolute temperature. Or in general, the equation known as the

Peter's equation may be written:

$$E = E_0 + \frac{R\,T}{n\,F} \ln \frac{(\text{Oxidant})}{(\text{Reductant})} \qquad \ldots\ldots\ldots\ldots \qquad (1)$$

Frary and Nietz (25) in 1915 attempted to measure the reducing power of photographic developers by measuring their "single potentials". They simply made up standard developers , sealed them in the electrode cells and allowed them to stand until they reached "equilibrium", and measured the single potential. This potential, substracted from the hydrogen electrode potential on the same solution, gave the partial pressure of hydrogen to which the developer is equivalent. They based their work on the Nernst theory of potentials (43). We read: (25)

> " Nernst stated that the reducing power is greater according as the gas evolution (H_2) takes place at a higher pressure. In order to determine the absolute pressure of hydrogen represented by a given single potential E_x of a developer, it is only necessary to also determine, in the same solution, the potential E_{H_2} of a platinized electrode saturated with hydrogen at atmospheric pressure. For two electrodes in the same solution but saturated with hydrogen at different pressures, the difference in potential is represented by the formula:
>
> $$E = .0001983\ T \log c/c'$$
>
> Since the pressure in one case is known to be atmospheric, c = 1, and at 25° the equation becomes:
>
> $$E = .05909 \quad \log 1/c',$$
>
> E being the difference between the hydrogen potential of the developer and its single potential ($E = E_{H_2} - E_x$). This partial pressure of hydrogen seems to be the only absolute standard to which the reducing power of the developer can be referred."

In many cases the cells never came to equilibrium but in four cases where equilibrium was attained, the values for the partial hydrogen pressure stand in the same order as the reducing power of the developers as otherwise measured.

Within the last decade a great deal of work has been done on oxidation-reduction potentials. We may mention here that of E. Biilmann on the oxidation-reduction of hydroquinone and similar compounds, the works of Conant on anthraquinones, LaMer, and Rideal on substituted quinones, and those of Mansfield Clark on indophenols. Direct references will be made to these later. Euler and Olander (24) have recently (1925) attempted to measure oxidation-reduction potentials on "pure" compounds. They failed to get definite potentials. Remington and Trimble (49) have very recently (1929) given measurements of electrode potentials of solutions of pure HClO in buffer solutions.

Theories of Oxidation-reduction Potentials.

Several theories have been advanced from time to time to account for the potential of an electrode in contact with electrolyte. Most of them are based on thermodynamics and they all lead to the same conclusions as regards the potential as a function of concentration of reagents. This is to be expected, since thermodynamics deals only with the end conditions and takes no cognizance of mechanism. It may be interesting however to examine briefly a few of the best theories in the light of the mechanisms postulated.

The first real theory of electrode potentials was set forth by Nernst about 1889. (See Nernst: Theoretical Chemistry, English Trans. 5th Ed. p. 856) He postulated "solution pressures" of the metals and developed thermodynamically the relations between solution pressures, osmotic pressures of the electrolytes, and the "maximum work", which is equal to the electrical energy. He considered oxidation-reduction electrodes to function like gas electrodes at low pressures On page 867 (loc. cit.) (43) we read:

> " Chemically an oxidising material is characterized by its power of giving off oxygen, a reducing material by its power of giving off hydrogen. Clearly the oxidising or reducing power is the greater the higher the pressure the evolution of gas can reach. If thus we bring platinum electrodes into solutions which contain an oxidising or reducing agent they will be charged with oxygen or hydrogen; by combination we get a cell according to the scheme:
>
> Pt/oxidising medium/ indifferent solution/ reducing medium/Pt
>
> We have, therefore, an oxyhydrogen cell, but with this difference that the oxygen or hydrogen charge can be, according to the nature of the oxidising or reducing medium, greater or smaller than if the charge were immediately produced by oxygen or hydrogen at atmospheric pressure, as in the primary gas cell.
>
> "In order to calculate the dependence of potential difference on the concentration of the various reagents we must write the reaction for the evolution of oxygen or hydrogen in each case. Thus, ferrous sulphate charges platinum according to the equation:
>
> $$Fe^{++} + H^{+} \rightleftharpoons Fe^{+++} + \tfrac{1}{2} H_2$$
>
> hence the hydrogen charge is proportional to the concentration of the ferrous and hydrogen ions directly, and inversely to that of the ferric ions."

The general Nernst equation may be written:

$$E = RT/nF \, . \ln P/p$$

where P is the pressure of ions, and the electrolytic solution tension of the electrode, n is the valence change and R, T, and F have the usual significance.

For the hydrogen electrode the reaction is:

$$\tfrac{1}{2}\,H_2 + \oplus \rightleftharpoons H^+$$

Here, $n = 1$, $p = \sqrt{P_{H_2}}$, and $P = [H^+]$

Hence: $E = RT/F \,.\, \ln[H^+]/\sqrt{P_{H_2}}$, where $\sqrt{P_{H_2}}$ = hydrogen pressure.

In the case of the ferric-ferrous electrode:

$$Fe^{++} + H^+ \rightleftharpoons Fe^{+++} + \tfrac{1}{2}\,H_2$$

$$\sqrt{P_{H_2}} = K \frac{[Fe^{++}] \cdot [H^+]}{[Fe^{+++}]}$$

Substituting in the hydrogen electrode equation:

$$E = \frac{R\,T}{F} \ln \frac{[H^+]\quad[Fe^{+++}]}{[H^+]\quad[Fe^{++}]\;K}$$

$$E = \frac{R\,T}{F} \ln \frac{[Fe^{+++}]}{[Fe^{++}]} - \frac{R\,T}{F} \ln K$$

$$E = E_0 + \frac{R\,T}{F} \ln \frac{[Fe^{+++}]}{[Fe^{++}]} \;..\; \ldots\ldots\ldots\ldots(2)$$

Equation (2) is identical with Peter's equation (see above).

In general, organic oxidation-reduction reactions may be written according to the Nernst theory:

$$H_n X \rightleftharpoons X + n/2\ H_2$$

where X represents the dehydrogenated substance or the oxidant and H_nX is the undissociated reductant. Here we assume that the reductant does not ionise.

Then: $$\sqrt{P_{H_2}} = K \frac{[H_nX]^{\frac{1}{n}}}{[X]^{\frac{1}{n}}}$$

Substituting in the hydrogen electrode equation:

$$E = E_0 + \frac{R\,T}{n\,F} \ln \frac{[X]}{[H_nX]} + \frac{R\,T}{F} \ln [H^+] \ldots\ldots \quad (3)$$

E. Biilmann (3) postulated this mechanism in arriving at equations for the oxidation-reduction potentials of quinhydrones. He arrived at the values of P_{φ}, the hydrogen pressure generated by benzo quinhydrone, of $10^{-24.40}$ atm. at 18° C and $10^{-23.69}$ atm. at 25° C.

As he says: (6)

> "These hydrogen pressures correspond to less than one single molecule of hydrogen in one liter, and as for free hydrogen in the solutions of quinhydrone there will not be one single molecule present in the quantity of the solution contained in the electrode vessel."

And as Clark (20) says in discussing the ferric-ferro electrode:

> "We find the hydrogen pressure to be about 10^{-27} atmospheres. If reduced to this pressure there would be but one molecule in about 37,000 litres. To assume any physical significance in such values is, of course, ridiculous."

Clark avoids solution tensions and these extremely low pressures by postulating an "electron pressure". See Clark: page 248, loc. cit. He states that this is only a makeshift similar to Nernst's solution tension, and probably does not represent the actual mechanism, yet the idea of electron pressures has some advantages. The following derivation is based on the discussion found in his book (loc.cit.) pages 248 to 254.

Oxidation-reduction may be regarded as an exchange of electrons. Thus in general, the equilibrium will be established:

$$X^{-n} \rightleftharpoons X + n\,e$$

where X is the total oxidant, X^{-n} the ionised reductant, and e is the electron. We may suppose that in this exchange, at any given instant, there will be a number of electrons balanced between the forces of the atoms and hence will be free electrons. This would give rise to an electron pressure. Now, let us suppose that these free electrons behave according to the perfect solute laws and hence may be regarded as ions of activity equal to their concentration. We may also suppose free electrons to exist in the metal of the electrode. Then the electrode reaction will consist simply of a transference of the electrons from the metal phase to the solution phase, or visa versa. Let $[e_m]$ and $[e_s]$ be the active concentrations of electron in metal and solution phases respectively. Then the change in free energy accompanying the isothermal transfer of one faraday of electrons from one phase to the other is:

$$-\Delta F = R\,T \ln \frac{[e_m]}{[e_s]}$$

If E is the difference of potential between metal and solution and F the faraday,

$$E\,F = -\Delta F$$

Hence

Hence: $$E = \frac{RT}{F} \ln [e_m] - \frac{RT}{F} \ln [e_s]$$

Now going back to our general equation for oxidation-reduction, we can get a value for $[e_s]$ in terms of concentrations.

$$[e_s] = K \frac{[X^{-n}]^{\frac{1}{n}}}{[X]^{\frac{1}{n}}}$$

Substituting this value in the E. M. F. equation:

$$E = \frac{RT}{F} \ln [e_m] - \frac{RT}{F} \ln \frac{K \, [X^{-n}]^{\frac{1}{n}}}{[X]^{\frac{1}{n}}}$$

Or, $$E = E_m - E_1 + \frac{RT}{nF} \ln \frac{[X]}{[X^{-n}]}$$

Writing $E_m - E_1 = E_0$,

$$E = E_0 + \frac{RT}{nF} \ln \frac{[X]}{[X^{-n}]} \quad \ldots\ldots\ldots \quad (4)$$

which is similar in form to that derived by the Nernst theory. It will be shown later how $[X^{-n}]$ depends upon the hydrogen ion concentration in the case of most organic compounds.

It should be noted here that the constant E_0 is made up of two terms $E_m - E_1$. The composite gives the same value for E_0 as is found in the other equations and is dependent in every case upon the standard of reference. Since approximately the same value for E_0 is obtained for any of the noble metals used as electrodes, it would seem that the term E_m, which is characteristic of the electrode, is the same for all metals. But we have not sufficient experimental data as yet to state this definitely.

J. A. V. Butler (12) has recently set forth a theory for potentials at inert electrodes, based upon surface attractions and adsorption. For the details of the theory the reader is referred to his paper. (loc. cit) In the case where the difference in charge between the ions of oxidant and reductant is unity, he arrives at the equation for equilibrium:

$$E = \frac{\phi_2 - \phi_1}{F} + \frac{R\,T}{F} \ln \frac{k_1}{k_2} - \frac{H_1 - H_2}{F} + \frac{R\,T}{F} \ln \frac{c_1}{c_2} \ldots\ldots (5)$$

Here, ϕ_1 is the work done by an electron in reaching the "balance point" against the surface attraction forces of the metal, ϕ_2 is the work done by an electron in reaching the balance point from its stable position in the ion of reductant. H_1 and H_2 are the energies of hydration of the ions of oxidant and reductant respectively, k_1 and k_2 are statistical constants, and c_1 and c_2 are the activities or effective concentrations of the respective ions of oxidant and reductant.

It is evident that for any given system, with a given electrode, the first three terms will be constant and may be replaced by the E_0 of the Peter's equation.

Butler shows that the term $\phi_2 - \phi_1 / F$ may be replaced by $V - \phi_0$, where V is the ionization potential of reductant ion and ϕ_0 is the thermionic work function of the metal. Hence we may write:

$$E_0 = V - \phi_0 - \frac{H_1 - H_2}{F} + \frac{R\,T}{F} \ln \frac{k_1}{k_2}$$

It is evident that V will vary from one substance to another and should be a measure of the "reducing power" of the reductant. ϕ_0 may or may not be the same for all electrode metals but would cancel out in the complete cell made up of two like electrodes. H_1 and H_2 likewise would be expected to vary from one system to another and may vary with solvent and with temperature. k_1 and k_2 are complex and probably depend upon many factors.

We may derive the general equation thermodynamically without regard to any mechanism. Assume the electrode reaction to be:

$$H_nX \text{ (conc. } c_1) + n \oplus \rightleftharpoons n\,H^+ \text{(conc. } c_2) + X \text{ (conc. } c_3)$$

(1) Change 1 mol of H_nX reversibly and isothermally from conc. c_1 to conc. 1 molar. $-\Delta F_1 = R\,T \ln c_1$

(2) By means of a reversible cell, change 1 mol of H_nX (1 mol.) to nH^+(1 mol) and X (1 mol.) $-\Delta F_2 = \tilde{E}\,n\,F$, where $\tilde{E}$ is the "molal potential".

(3) Change nH^+ reversibly and isothermally from conc. 1 mol. to conc. c_2. $-\Delta F_3 = R\,T \ln 1/c$

(4) Change nX reversibly and isothermally from conc. 1 mol.

to conc. c_3 $\qquad -\Delta F_4 = R\,T \ln 1/\,c_3$

$$\Sigma - \Delta F = \tilde{E}\, n\, F + RT \ln c_1 + RT \ln \frac{1}{c_2^{\,n}} + RT \ln \frac{1}{c_3} \;\ldots\ldots \qquad 6a$$

$$E = -\tilde{E} + \frac{R\,T}{n\,F} \ln \frac{[X]}{[H_nX]} + \frac{R\,T}{F} \ln [H^+] \;\ldots\ldots\ldots\ldots\ldots \qquad 6$$

which is of the same form as equation 3 (see above).

For the electrode reaction:

H_nX (conc. c_1) + n $\oplus \rightleftharpoons nH^+$ (conc. c_2) + X (conc. c_3),
the decrease in free energy when one mol. of H_nX changes reversibly and isothermally to H^+ and X is given by the van't Hoff isotherm:

$$-\Delta F = R\,T \left[\ln K - \ln \frac{c_2^{\,n} \cdot c_3}{c_1} \right]$$

where K is the equilibrium constant of the reversible reaction. But also,

$$-\Delta F = \tilde{E}\, n\, F + R\,T \ln \frac{c_2^{\,n} \cdot c_3}{c_1} \qquad \text{(see 6a above)}$$

Hence: $\qquad \tilde{E} = RT/nF.\ \ln K,$

and we may write the general electrode equation:

$$E = -\frac{R\,T}{n\,F} \ln K + \frac{R\,T}{n\,F} \ln \frac{[X]}{[H_nX]} + \frac{R\,T}{F} \ln [H^+] \;\ldots \qquad 7$$

It is obvious of course, that if the measured E. M. F. of the chain is to measure $-\Delta F$ of the given electrode reaction, $-\Delta F$ for the reaction at the standard electrode must be zero. Hence the above electrode equations must be referred to the normal hydrogen electrode as zero.

The reaction at the hydrogen electrode:

$$\frac{1}{2}\, H_2\,(1\ \text{atm.}) \rightleftharpoons H^+\ \ (1\ \text{mol.})$$

is arbitrarily assigned a free energy decrease of zero at all temperatures.

It will be noted that for the derivation of electrode equations we must always assume the presence of both oxidant and reductant. Nevertheless, as has been pointed out, there have been repeated attempts to measure the potentials of pure substances. On page 255 of his book (loc. cit.) Clark says:

> " It is of great practical importance for many studies to note that in any case where a definite potential difference is to be established at the electrodes there must be in the system two species, one of which is the direct or indirect reduction product of the other, and that the ratio of their concentrations or activities must be of finite magnitude. Neglect of this principle is not infrequent. There are not infrequently encountered in the literature attempts to measure electrode potential differences with a single oxidant or reductant. Were it possible to eliminate absolutely every trace of the oxidant, the potential difference obtained with the reductant alone would tend to become infinite. Wherever stable potentials have been reported as having been found with reductant alone it is doubtless due to the presence of the oxidant as an impurity.

But granted that this is so, is it not possible that measurements on pure reductants may give a better measure of reducing power than do the measurements on mixtures? It is very likely that any solution of pure reductant contains a finite amount of oxidant. And we may suppose that the ratio of oxidant to reductant will be fairly constant for any given method of purification.

Now, from the above equations, it will be noted that $-\Delta F$ for the reaction and E the electrode potential are both the same function of concentrations of reagents. Hence if our equations hold for the very small concentrations of oxidant in "pure" reductant, the measured E will always give us a true value for $-\Delta F$ of the reaction, and the unknown concentrations are automatically taken care of.

It is by no means certain, however, that the potentials which we get when one of the reagents is at a very low concentration, are measures of the free energy. In any given solution there are several things which may give rise to an electrode potential. In the case of mixtures of oxidant and reductant in finite ratios the oxidation-reduction potential seems to overshadow all others, but this may not be true if one reagent is very dilute.

Rideal, (50) in discussing the mechanism of reversible electrodes says:

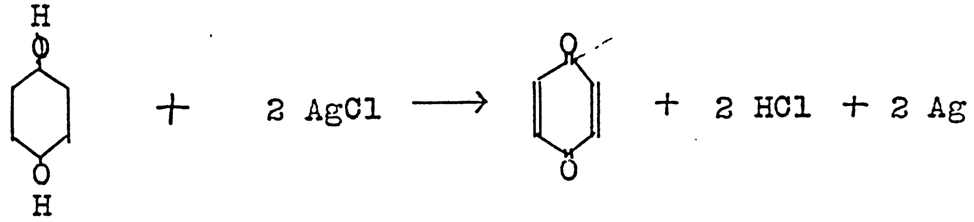
> "There is thus little doubt that there is a relationship between the electron affinity of a metal and its position in the electropotential series, but the method of ascribing the potential differences in a cell entirely to the contact potential between the electrodes suffers from the fundamental disadvantage that the E.M.F. of the cell should be independent of the concentration of the electrolyte which we know is not the case. The dependence of the E. M. F. of a cell on the ionic concentration of the electrolyte does, however, reach a limiting value for small concentrations, a fact not to be anticipated from the Nernst equation but one readily understandable from the conception of the Volta effect as the prime cause of the E. M. F. "

It is now well known that fairly definite potentials are obtained when inert electrodes are dipped into solutions of electrolytes, even though we can write no satisfactory equations for the reactions which undoubtly take place. The potentials are dependent upon the H - ion concentration, but seemingly independent of the concentrations of electrolytes. Kolthoff (35) noticed this for antimony and attributed the behavior to an oxide film. But Roberts and Fenwick (52) have studied very recently the antimony - antimony oxide electrode and give values quite different from those of Kolthoff. Evidently they are not working with the same electrode. The potentials of many inert metals in contact with electrolytes, are found to fluctuate with stirring of the solutions or with bubbling of various gases through the solutions. The E. M. F. in such cases has been attributed to gas films upon the electrodes.

Taking everything into consideration, it is not yet possible to state definitely that the E. M. F. measurements on "pure" substances are of no value. Yet the fact remains that constant, reproducible potentials are obtained only with finite ratios of concentrations of reagents. Such potentials give us accurate measures of the equilibrium constants and of the free energies of reactions taking place in the mixtures. As we shall see later, it is probable that these equilibrium constants are of more importance in measuring reducing powers than are the free energy values which take concentration into account.

Relation of Normal Reduction Potentials to Speed of Reduction.

The present work was begun with the end in view of obtaining a relationship between the oxidation-reduction potentials of photographic developers and their developing factors or the speed with they reduce silver halides, is such a relationship exists. The mechanism of photographic development is not definitely known, but it is generally believed to be a reduction of the silver halide by the developer. In the case of hydroquinone the equation may be written:



It is not known whether or not the reaction is strictly irreversible but it may be regarded as such, since it goes practically to completion.

J. B. Conant (18) has published a discussion on the electrochemical formulation of irreversible reactions. He states the problem as follows: (see page 4, loc. cit.)

"If we have a certain substance, for example an azo dye, which is irreversibly reduced by soluble reducing agents (with cleavage of the molecule) the general experience of organic chemists would lead us to believe that this process is in some way conditioned by the oxidation-reduction potential of the reducing agent. Qualitatively the idea of "powerful" reducing agents and "mild" reducing agents has long been in vogue. Is this concept sound? The problem is really this: Is the rate of an irreversible process governed by the free energy change involved? In other words, will the speed of reduction of a substance be a function of the oxidation-reduction potential of the reagent employed?"

In attempting to answer the question, Conant states: (page 5, loc. cit.)

"It is now generally recognized that there is in general no necessary relationship between the speed and the free energy change of a reaction. Thus in the process of racemization the free energy change from one antipode to another is zero; yet with many compounds racemization is very rapid, while with others it is very slow.

"There is obviously one set of conditions under which the speed of a reaction must be governed by a free energy change, -- that is, when some equilibrium process controls the amount of material undergoing a subsequent irreversible transformation. This can be expressed in general terms for the irreversible transfer of two hydrogen atoms as follows:

$$A + BH_2 \rightleftharpoons AH_2 + B$$
$$A + B'H_2 \rightleftharpoons AH_2 + B'$$
$$AH_2 \longrightarrow P$$

In the above scheme the total process with which we are concerned may be represented as an irreversible transformation of A into P. If this proceeds through the formation of AH_2 in a reaction which reaches equilibrium under the conditions of the experiment, the rate of the irreversible step will be a function of the amount of AH_2 in solution. This in turn will be different according as we use BH_2 or another substance of different potential $B'H_2$."

Conant has worked out the algebraic equations for such a reaction. See page 17 (loc.cit.)

If, as Conant has indicated, the speed of the reaction is connected up with equilibrium constants, which in turn are given by the oxidation-reduction potentials, measurements of these potentials should give us a measure of the relative speeds. Experiment shows that the speed of development is greatly accelerated by alkalies -- in fact does not usually take place in acid solution. The potentials are also greater in alkaline solutions. Hence we must measure our equilibrium constants in basic solutions and find how the constants vary with alkalinity.

Of the photographic developers upon which much work has been done, hydroquinone heads the list. It seems well, therefore, to take the system hydroquinone- quinone as the standard. An examination of the literature has shown that no measurements are reported for this system in alkaline solution. Moreover, some preliminary experiments have shown the system is quite unstable in alkaline buffers. The same is true of the other developers. Hence our present work has dealt almost wholly with the behavior of the quinhydrone electrode in alkaline solution. The study of other photographic developers must be left for future work.

THE QUINHYDRONE ELECTRODE IN ALKALINE SOLUTION

Historical

Considerable work has been done on the oxidation-reduction potential of hydroquinone. Bancroft (1) included alkaline hydroquinone among the reducing agents whose potentials he measured. Neumann (44) compared the potentials with a calomel electrode, and thus gave them a somewhat more definite value. Baur (2) measured the potentials of electrodes made up of definite amounts of hydroquinone and formaldehyde. But all of these measurements were made on "pure" reductants, hence they have little meaning from a theoretical standpoint.

Haber and Russ (30) were probably the first to study the potentials of mixtures of hydroquinone and quinone. Apparently they worked only in alcoholic sulphuric acid mixtures. They showed that the van't Hoff equation applies and gave values for the quinhydrone electrode against the hydrogen electrode as zero. Their values range from .7418 to .7435 volt at 25° C. They used various electrodes -- platinized platinum, gold, iridium, -- and got the same value within the limits of their experimental errors. Also they determined the temperature coefficient as -.00072 volt per degree.

The most work on the quinhydrone electrode seems to have been done by M. Einar Biilmann and his students. His first paper "Sur l'Hydrogenation des Quinhydrones", (3) appeared in 1920. He derived equations for E. M. F. as a function of concentrations, on the basis of the Nernst theory and showed that the quinhydrone electrode should function as a hydrogen electrode at reduced pressure. He gave the equation:

$$\pi = -0.0000992\ T \log P$$

π = 0.7044 v. at 18° C and π = 0.6990 v. at 25° C.

He worked in various buffer solutions and found that the electrode is quite stable in acid solution, is not affected by the presence of nitrate ions, and the potential is independent of the concentration of quinhydrone. Apparently, he worked only in acid buffers. He also worked with toluquinhydrone and xyloquinhydrone. A good summary of his work appeared in Trans. Farad. Soc. <u>19</u>, 676 (1924).

Billman, Jensen, and Pedersen (8) have worked out a method of obtaining the oxidation-reduction potentials of substituted quinhydrones without actually preparing them, making use of the potential of benzoquinhydrone.

Biilman and Blom (7) measured the oxidation-reduction potentials of azo and hydrazo compounds. They got regularly drifting potentials due to molecular rearrangements. By extrapolating to zero time they arrived at the true oxidation-reduction potentials. We have taken this as a precedent for our own extrapolations.

Other papers by Biilmann on the quinhydrone electrode have appeared from time to time. In 1927 (9) he published a summary of the theory and a fairly complete review of its applications. A list of references appears at the end of his paper.

Granger and Nelson (28) have made some very accurate determinations of the normal oxidation-reduction potential of quinhydrone in hydrochloric acid solutions. They determined the solubilities of hydroquinone, quinone, and quinhydrone in various concentrations of HCl, and the dissociation constant of quinhydrone. The hydrogen ion concentrations of their solutions were determined by conductivity measurements. In most cases they worked with saturated quinhydrone solutions in the presence of hydroquinone or of quinone.

LaMer and Baker (36) have determined the normal oxidation-reduction potentials of several derivatives of hydroquinone. Their method was to titrate dilute acid solutions of the hydroquinones with potassium dichromate of the same acidity, or to titrate dilute solutions of the quinones with titanous chloride. They arrived at practically the same values for the normal potentials in either case. They found that platinum, gold, and gold plated platinum electrodes all gave the same values.

For a salt bridge, they used a glass tube filled with saturated KCl and fitted with a ground glass stopper at either end. They give the following values for π_0 at 25° C.

Quinone reduced	0.6990
Hydroquinone oxidised	0.6991

At about the same time, but independently of the other workers, Conant and his associates began to publish a series of papers dealing with the reversible oxidation-reduction of quinone-like compounds. In their first paper (13) they discussed the theory of reversible organic oxidations and showed that in general the E. M. F. equation should be of the form:

$$\pi = \pi_0' + .0295 \log \frac{[A]}{[AH_2]_r} - 0.0295 \log K_1K_2$$

$$+ 0.0295 \log (K_1K_2 + [H^+]^2 + K_1 [H^+])$$

for the reaction represented by:

$$AH_2 \rightleftharpoons A + H_2 ,$$

in which AH_2 is a weak dibasic acid. They showed that this equation holds experimentally for the anthraquinones.

In a second paper (15) they have worked out the free and total energy changes in the reduction of quinones. For benzoquinone they give the following data:

Conc. HCl	π_0 at	0°	25°	40°
0.1		0.713	0.699	0.682
1.0		0.713	0.696	0.682

from which are calculated:

$$\Delta F = 134.7 \text{ Kj. and } \Delta H = 177.8 \text{ Kj at } 25^{\circ}\text{C.}$$

Also they give $\pi_0 = 0.711$ for benzoquinone in alcoholic solution at 25° C. In subsequent papers Conant and Fieser (16, 17) have given the potentials of various substituted quinones in aqueous and alcoholic acid solutions. In the conclusions to the latter paper they have attempted to correlate the reduction potentials and the structure. Conant has also referred the reduction potentials of various substituted quinones to the gaseous state and concludes that this gives a better relation between reduction potentials and constitution.

E. Scheiner (55) has worked out the thermodynamics of the quinhydrone electrode. He gives some very precise determinations in dilute acetic acid solutions. For the saturated quinhydrone electrode he gives:

$$E = 0.7175 - 0.00074\,t \quad (0^{\circ} \text{ to } 37^{\circ}).$$

J. N. Pring (47) has used the quinhydrone electrode to measure the hydrolysis constants of bases. He measured the E. M. F. of chains of the type:

$$\begin{array}{l|c|l} \text{Pt ,Quinhydrone} & \text{KCl} & \text{Pt , Quinhydrone} \\ & & 0.01\ \text{N HCl} \\ 0.01\ \text{N HCl} & \text{(sat.)} & 0.02\ \text{M base} \\ \multicolumn{3}{c}{\text{Water or acetone-water}} \end{array}$$

He found that definite potentials were obtained in either water or mixtures of acetone and water.

F. F. M. Cray and G. M. Westrip (21) have used the quinhydrone electrode to measure the hydrogen ion concentration of acetone-water buffer solutions. They find that the E. M. F. follows the same equation deduced for water solutions, except that the values for E_0 , K_1 and K_2 are different. They report that the upper limit of pH which can be measured in this solvent by the quinhydrone is pH 12.2 . The curve for E. M. F. as a function of pH is a straight line up to this point. However, it should be noted that pH 12.2 is only very weakly alkaline in this solvent. They give the neutral point as pH 9.7, hence there can be no direct comparison between the behavior of quinhydrone in acetone solutions and its behavior in water solutions of the same pH.

Within the last few years numerous papers have appeared on the applications of the quinhydrone electrode. No attempt will be made here to review all of this literature. The reader is referred to the bibliography compiled by Biilmann (loc. cit.) The quinhydrone electrode has been used recently by Schau-Kuang Liu (54) to study the hydrogen ion concentration of the blood. He discusses the limitations of the electrode in such solutions. Shirokichi Mori (41) discusses the applicability and the biological uses of the electrode. E. F. Snyder (57) has used the electrode on soils. The quinhydrone electrode has been used by Rabinovich and Kargin (48) and by A. Klit (34) in electrometric titrations. McKebben and Pugsley (40) have used it on colored fruit juices.

An examination of the literature shows that the quinhydrone electrode is stable only in acid or weakly alkaline solutions. LaMer and Parsons (37) report that reliable results are obtained in buffered solutions up to pH 8.0. They state:

> " In more alkaline solutions, autoxidation of the hydroquinone and the effect of the presence of hydroquinone on the actual pH in unbuffered alkaline solutions owing to its weak acid properties, are more important factors in yielding erroneous results than are the very small errors which are produced by the deviations from the simple Peter's oxidation-reduction potential equation owing to the partial ionization of hydroquinone."

Biilmann (10) discusses the applications of the electrode to alkaline solutions. He even calculates the deviations that would be expected, due to the ionization of hydroquinone. He reports that reliable results are obtained up to pH 8.5. Biilmann, Kilt, Swaetichin, (11) report reliable results with the quinhydrone electrode up to pH 7.73 in phosphate buffers. Shirokichi Mori (loc. cit.) reports reliable results up to pH 8.5 . E. F Snyder (57) used the electrode on soils of pH 4 to 9 . He got drifting potentials between pH 8 and 9. Felix Grossman (29) has used quinhydrone to measure the pH of buffers up to pH 8.91, for which value he gives andE. M. F. of - 0.056 v. against the saturated calomel electrode as zero.

It will be noted that while Conant and Clark have long ago worked out the equation of the quinhydrone electrode in alkaline solution and the theoretical values have been calculated, there seems to be no actual data on the E. M. F. above pH 9 in aqueous solutions. (1929). Practical photographic developers have a pH value of about 11.

Sorensen, Sorensen, and Lang (58) have found that there is a salt error for the quinhydrone electrode. They give the following values for E_o against the normal hydrogen electrode:

Electrolyte	E_o
0.01 n HCl	0.7044
0.01 n HCl, 0.09 n NaCl	0.7042
0.01 n HCl, 1.99 n NaCl	0.7042
0.01 n HCl, 3.99 n NaCl	0.6978
0.50 n HCl,	0.7029
0.50 n H_2SO_4	0.7039
0.50 n HCl, 0.50 n NaCl	0.7009

Jowett and Millet (33) have applied a correction for the pH as measured in buffers of ionic strength of 0.16. They give:

$$\Delta \text{pH} = -0.008 \text{ at } 25^\circ \text{ C.}$$

$$\Delta \text{pH} = -0.006 \text{ at } 37.5^\circ$$

Properties of Quinhydrone.

When quinone is partially reduced, or hydroquinone is partially oxidised (36) or equimolecular portions of quinone and hydroquinone are mixed in alcohol water solution, (54) greenish crystals of quinhydrone precipitate. They have the empirical formula $C_6H_4O_2 \cdot C_6H_4O_2H_2$

The exact structural formula is unknown. According to Beilstein the melting point is 171° C. Biilmann (3) gives the solubility of quinhydrone in water at room temperature as about 0.018 molar. Granger and Nelson give the value as 0.0178 molar. In water solution, quinhydrone dissociates into hydroquinone and quinone. Granger and Nelson give the dissociation constant in saturated solution as 0.289. Biilmann (4) gives the constant as 0.224. From these values it may be calculated that in .004 molar solution, quinhydrone will be about 98 per cent. dissociated. Hence we may regard a dilute solution of quinhydrone as a mixture of hydroquinone and quinone, and its properties will be those of its constituents.

Properties of hydroquinone: Hydroquinone or para dihydroxy benzene is a white crystalline solid whose melting point is 169° C. (36). It is soluble in water to the extent of 7.10 gms. per 100 cc. at room temperature. (28). It is a weak dibasic acid. Euler and Bolin (23) give 1.1×10^{-10} as the first dissociation constant, determined by conductivity methods. S. E. Sheppard (56) gives 1.75×10^{-10} as the first dissociation constant and 3.97×10^{-12} as the second, determined by titration with a hydrogen electrode. Frary and Nietz (26) have studied the reaction between alkalies and hydroquinone and metol in photographic developers. Their studies indicate that:

"Sodium hydroxide and hydroquinone can form either monO- or diquinolates, according to the conditions. With sodium carbonate and hydroquinone in the concentrations usually used for developers, most of the hydroquinone would unite with the alkali to form monoquinolate if the sulfite were not present. When sulfite and carbonate are both present, they appear to divide the hydroquinone between them."

In alkaline solutions hydroquinone takes up oxygen from the air and yields dark colored compounds. It is probable that quinone is the immediate oxidation product. LaMer and Rideal (38) have studied the absorption of oxygen by alkaline hydroquinone solutions. They found that the rate of oxidation does not become appreciable until the solution is more alkaline than about 7.3 or 7.8 for air. The rate of the reaction is highly sensitive to further increase of Sorensen value, being proportional to the three halves power of the hydroxyl ion concentration for the region investigated (up to pH 8.56). They write the reaction for the oxidation of hydroquinone:

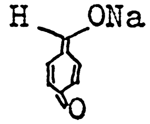
$$C_6H_4(OH)_2 + O_2 \longrightarrow C_6H_4O_2 + H_2O_2$$

They report that at pH 8.6 nearly twice the stoichiometrical quantity of oxygen was absorbed in two days. They have formulated the kinetic reactions, assuming a complex ion as an intermediate product.

$$2\ H_2C_6H_4O_2 - 3\ H^+ \rightleftharpoons HC_6H_4O_2^- \quad C_6H_4O_2^= \longrightarrow \text{Complex}$$

$$\text{Complex} + 2\ O_2 \longrightarrow 2\ C_6H_4O_2 + 2\ H_2O_2$$

They state that a red color is produced when hydroquinone solutions are made alkaline. They attribute this color to the formation of the complex. Euler and Bolin (23) also mention a coloration of the salts of hydroquinone and of pyrocatechin. They attribute it to the molecular structure:



for the salt.

In our present work, we have failed to observe any coloration of .008 molar hydroquinone in tenth molar sodium carbonate solution when oxygen was entirely excluded. On the contrary, the solutions remained colorless for several hours. It was observed that when pyrogallic acid is mixed with alkali in the air, the solutions are highly colored, but the color fades when the solutions are allowed to stand in an atmosphere of nitrogen.

M. A. Gordon (27) has studied the silver equivalent of hydroquinone in alkaline solutions. He found that:

> " In strongly alkaline solutions and with silver bromide in excess, the silver equivalent of hydroquinone is about 6 for short runs and about 8 for long runs, at room temperature. At 100° the silver equivalent is at least 9 for short runs.
>
> " With silver oxide and caustic alkali, the silver equivalent of hydroquinone is about 10.5 for five minute runs. The silver equivalent for quinone is about 2 less than for hydroquinone. Quinone is unquestionably an intermediate product when hydroquinone reacts with silver bromide in the absence of sodium sulfite."

<u>Properties of quinone</u>: Benzoquinone crystallizes in beautiful golden yellow needles, whose melting point is 115.7° C. (30). It is soluble in water to the extent of 1.37 gms per 100 cc. at room temperature. (28)

It is volatile with steam and sublimes. According to Euler and Bolin (23) quinone is a weak acid with a dissociation constant of 10^{-13}. As would be expected from its structure, quinone is quite active chemically. (See Beilstein VII, pages 609 - 622)

Quinone oxidizes in alkaline solutions in the air to a black substance. With concentrated nitric acid it oxidizes to oxalic acid. Hot ammoniacal silver solutions give mirrors with quinone, cold solutions give precipitates. When heated alone in a closed tube to 160° or with water to 100° , quinone yields hydroquinone, quinhydrone, and brown decomposition products. (31). Quinone may be reduced by hydrogen in the presence of nickel to hydroquinone -- in certain cases to phenol and benzene. Hydriodic acid reduces it quantitatively to hydroquinone. (60). Yellow ammonium sulfide also reduces it hydroquinone. In acid solution, SO_2 reduces quinone to hydroquinone.

J. W. Dodgson (22) has investigated the action of sulphites on p-benzoquinone. His summary (p. 2443 loc. cit.) reads:

> "(1) When p-benzoquinone is reduced by sulphurous acid, quinol, sulphuric acid, and quinolsulphonic acid are formed; the sulphonic acid to an extent equivalent to about 20 per cent. of the p-benzoquinone employed.
>
> "(2) The action is not affected by reasonable amounts of HCl, but is strongly inhibited by large quantities, owing to the formation of chloroquinol. It is also not materially affected by temperature.

"(3) When p-benzoquinone is reduced with alkaline sulphite the production of the sulphonate is greatly increased, whilst the sulphate formed sinks to a very small and almost constant quantity.

"(4) Further addition of alkali leads to a diminution in amount of sulphate produced. Prolonged action of the alkali almost completely prevents both reactions.

"(5) Dithionic acid, if formed at all, is produced in very minute quantities."

Sodium thiosulphate also reduces quinone to hydroquinone.

There is abundant evidence that in alkaline solutions quinone is spontaneously reduced to hydroquinone. Mees and Sheppard (61) got the usual blue color test with dichromate for the presence of H_2O_2 in alkaline solutions of quinone. They wrote the reaction:

$$C_6H_4O_2 + 2\ KOH \rightleftharpoons C_6H_4(OK)_2 + H_2O_2$$

But it is possible that quinone alone would give this test, and M. A. Gordon (27) in his paper on the silver equivalent of hydroquinone questioned this reaction in the case of actual photographic development. As he points out, such a reaction should lead to an infinite silver equivalent in the presence of excess alkali, which is not a fact. In his conclusions, Gordon says: (p. 82, loc. cit.)

"(21) When quinone reacts with alkali, one of the reaction products is unquestionably hydroquinone. Mees and Sheppard believe that the other product is hydrogen peroxide, but it is hard to reconcile this view with the fact of a definite silver equivalent. Luther and Leubner believe that the other product is oxyquinone; but they give no experimental evidence in support of this.

"(22) Luther and Leubner say that dioxyquinone is the final oxidation product when hydroquinone reacts with silver bromide in alkaline solution. They have not isolated the compound however.

"(23) The formation of dioxyquinone would account for a silver equivalent of 6 and consequently could not account for a value of 10.

"(24) The low values of the silver equivalent obtained by Luther and Leubner are due to their working for short times with solutions containing KBr and made alkaline with sodium carbonate.

"(25) The fact that the silver equivalent varies but slightly while the concentrations of sodium sulphite varies very largely shows that Mees and Sheppard are wrong in believing that sodium sulphite regenerates hydroquinone in the presence of a silver salt."

Gordon quotes largely from a paper by Luther and Leubner (39) on the chemistry of the hydroquinone developer. The following extract is illuminating. (See p. 711, loc. cit.)

"If equivalent quantities of quinone and hydroquinone are allowed to stand in aqueous solution for various times, if this solution is then added to an alkaline mixture of silver bromide and potassium carbonate, and if measurements are made of the reduction during one minute, it is found that the mixture of quinone and hydroquinone possesses no reducing properties, nor does it obtain them on long standing in aqueous solution. If, however, quinone and hydroquinone are left to stand for a considerable time with potassium carbonate, the solution acquired reducing properties. The disappearance of the retarding effect of quinone may depend on the one hand upon the slow formation of quinonate just as in the case of the hydroquinonate. On the other hand, quinone, by the action of alkali, may be split up into an oxidation and reduction product. Similar reactions are frequently met with in chemical literature.

"After long action of air-free potassium carbonate solution on quinone we obtained hydroquinone by extraction of the solution with ether. This experiment contradicts the view that the destruction of the retardation depends on the formation of a quinonate of reducing properties. At the same time it points to the decomposition of quinone by alkali. According to this view, quinone forms a quinonate with the alkali, this decomposes into hydroquinone and into a higher oxidation product of quinone, presumably oxyquinone. If this oxyquinone is likewise a dibasic acid, it follows that on the decomposition of the quinone, part of the alkali combined with the latter is liberated and increases the hydroxyl ion concentration."

Luther and Leubner conclude that the final product of the oxidation of hydroquinone is dioxyquinone. They suggest that the reactions are as follows:

1. $C_6H_4(OH)_2 + OH' \rightleftharpoons C_6H_4(OH)O' + H_2O$ Rapid
2. $C_6H_4(OH)O' + OH' \rightleftharpoons C_6H_4O_2'' + H_2O$ Rapid
3. $C_6H_4O_2'' + Ag^{\cdot} \longrightarrow C_6H_4O_2 + Ag$ Measurable
4. $C_6H_4O_2' + Ag^{\cdot} \longrightarrow C_6H_4O_2 + Ag$ Very rapid
5. $C_6H_4O_2 + 2OH \rightleftharpoons C_6H_2O_2''(?) + 2H_2O$ Very rapid
6. $2\ C_6H_4O_2 + H_2O \longrightarrow C_6H_2O_3''$(oxyquinone)(?)$+C_6H_2O_2''$
   $(\longrightarrow 3)$ Slow and measurable.
7. $2\ C_6H_2O_3'' \longrightarrow C_6H_2O_4'' + C_6H_2O_2''$
   $(\longrightarrow 6)$ Slow and measurable.

As far back as 1883, O. Hesse (32) found that when solutions of quinone are allowed to stand, they darken, and from the reaction mixture he was able to extract hydroquinone, or if the reaction was not complete, quinhydrone.

L. Meunier and M. Qeroix (42) have studied time changes in quinone solutions in various buffers. They say:

> "If one allows aqueous solutions of quinone, prepared with a definite pH to stand in diffused light, there are formed simultaneously, hydroquinone and dark colored oxidation products of quinone. In other words, there takes place simultaneously in the solution reduction and an oxidation. The hydrogen of the water goes to a part of the quinone to give hydroquinone, and the oxygen transforms another part of the quinone into oxidation products which are strongly colored but not defined."

They analyzed the solutions for hydroquinone by titrating with iodine in sodium bicarbonate solution and for quinone by titrating the iodine liberated by the solutions from acidified NaI. In solutions buffered with phosphates, they found that the rate of the reaction increases with the pH values. Marked decomposition begins at pH 6.5 The amount of hydroquinone formed is about half the amount of quinone used up. In acetate buffers, they found that the rate of decomposition is greater at first than in the case of phosphate buffers. Here the rate increases up to pH 5, falls to a minimum at pH 6.5 and thereafter increases. More than half the quinone is reduced to hydroquinone. They worked in buffers from pH 3 to pH 8, and allowed the solutions to stand six days. They report that the reaction "is strongly influenced by the action of light".

Euler and Bolin (23) in their work on the ionization constant of quinone got rapid drifts in the conductivity of alkaline quinone solutions. This indicated that quinone was undergoing a change into something more highly ionized. They arrived at the conductivity of the pure quinone solutions by extrapolating to zero time. In regard to the reaction they say (translating from the German.)

" The chemical investigation has given as the apparent result that quinone, in dilute aqueous solution and under the influence of an equivalent proportion of alkali, decomposes into hydroquinone and a higher acid oxidation product, difficultly soluble in ether. We have here an example of a reaction which is especially common with aromatic aldehydes -- the Cannizaro Reaction, the splitting up into a reduction and oxidation product. As with the aldehydes so with quinone, the reaction should proceed at a rate proportional to the concentration of the sodium salt."

Objects of the Investigation

From the proceeding review of the literature on quinhydrone, it is seen that the quinhydrone electrode is unstable in alkaline solutions. This is due to the spontaneous oxidation-reduction of quinone. Since the electrode potential is a function of concentrations of oxidant and reductant, the drift of potential should give us a measure of the rate of the reaction, and perhaps of the nature of the reaction. Moreover, it should be possible to extrapolate to zero time and get the true oxidation-reduction potential of quinhydrone in the given buffer, and thus extend the use of the quinhydrone electrode into the alkaline range. The investigation has been carried out with the following objects in view:

(a) To extend the use of the quinhydrone electrode to alkaline solutions.

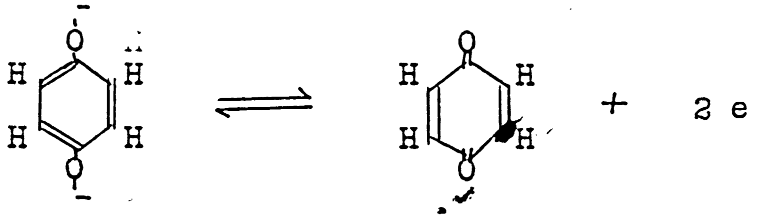
(b) To measure the oxidation-reduction potential of hydroquinone in alkaline solutions.

(c) To study the changes which quinone undergoes in solution.

Theoretical

Relation of E. M. F. to pH:

The electrode reaction of the quinhydrone electrode can be expressed as follows:



It is known that hydroquinone is a dibasic acid. Quinone is probably a dibasic acid also, but the second dissociation constant is unknown and is probably so small as to be negligible. Therefore, we will consider quinone to be monobasic.

We will let $[RED]$ be the concentration of the undissociated hydroquinone, $[R\bar{E}D]$ be the concentration of singly ionized hydroquinone, $[\bar{R}E\bar{D}]$ be the concentration of doubly ionized hydroquinone, $[OX]$ the concentration of undissociated quinone, $[\bar{O}X]$ the concentration of singly ionized quinone. Then the electrode potential may be expressed by the equation:

$$E = \tilde{E} + \frac{R\,T}{2\,F} \ln \frac{[OX]}{[\bar{R}E\bar{D}]}$$

Now in any actual solution, the following ionic equilibria will be set up:

$$\frac{[R\bar{E}D] \cdot [H^+]}{[RED]} = K_1 \quad , \quad \frac{[\bar{R}E\bar{D}] \cdot [H^+]}{[R\,\bar{E}\,D]} = K_2$$

$$\frac{[\bar{O}X] \cdot [H^+]}{[OX]} = K_3$$

Let $[\mathrm{Hydro}]$ be the total molar concentration of hydroquinone, ionized and unionized, and $[\mathrm{Quinone}]$ be the total concentration of quinone, ionized and unionized. Then:

$$[\mathrm{Hydro}] = [\mathrm{RED}] + [\mathrm{R\bar{E}D}] + [\mathrm{\bar{R}E\bar{D}}]$$

$$[\mathrm{Quinone}] = [\mathrm{OX}] + [\mathrm{O\bar{X}}]$$

From which:

$$[\mathrm{Hydro}] = \frac{[\mathrm{\bar{R}E\bar{D}}] \,.\, [H^+]^2}{K_1 K_2} + \frac{[\mathrm{\bar{R}E\bar{D}}] \,.\, [H^+]}{K_2} + [\mathrm{\bar{R}E\bar{D}}]$$

$$[\mathrm{R^{-}E^{-}D}] = \frac{[\mathrm{Hydro}] \,.\, K_1 K_2}{[H^+]^2 + K_1 [H^+] + K_1 K_2} \quad \dots\dots\dots\dots \quad 1$$

$$[\mathrm{Quinone}] = [\mathrm{OX}] \qquad \frac{K_3 [\mathrm{\bar{O}X}]}{[H^+]}$$

$$[\mathrm{OX}] = \frac{[H^+] \, [\mathrm{Quinone}]}{[H^+] + K_3} \quad \dots\dots\dots\dots\dots\dots \quad 2$$

And substituting the values found for $[\mathrm{\bar{R}E\bar{D}}]$ and for $[\mathrm{OX}]$ in the fundamental equation for the quinhydrone electrode, we get:

$$E = \tilde{E} + \frac{RT}{2F} \ln \frac{[H^+] \, [\mathrm{Quinone}] \, ([H^+]^2 + K_1 [H^+] + K_1 K_2)}{([H^+] + K_3) \, [\mathrm{Hydro}] \, K_1 K_2}$$

Collecting all the constants into one term E_o, we have:

$$\tilde{E} = \tilde{E}_o + \frac{RT}{2F} \ln \frac{[\mathrm{Quinone}]}{[\mathrm{Hydro}]} \quad \frac{RT}{2F} \ln \frac{[H^+]^3 + K_1 [H^+]^2 + K_1 K_2 [H^+]}{[H^+] + K_3} \quad \dots\dots \; 3.$$

If E is measured against the saturated calomel electrode, taken as +.2492 volt at 20°C. (59), then E_0 is +0.4535 (55). The values for the ionization constants as found in the literature are: Sheppard's values (56) $K_1 = 1.75 \times 10^{-10}$, $K_2 = 3.97 \times 10^{-12}$ and the values of Euler and Bolin (23) $K_1 = 1.1 \times 10^{-10}$ and $K_3 = 10^{-13}$ It is the value for K_1 which is most important in the range over which we were able to work.

In quinhydrone the ratio of quinone to hydroquinone is unity, providing the activities of the two components are the same. Substituting these values we get for the quinhydrone electrode against the saturated calomel electrode as zero, at 20° C the equations:

Using Sheppard's values:

$$E = +.4535 + .02906 \log \frac{[H^+]^3 + 1.75\text{x}10^{-10}[H^+]^2 + 7 \times 10^{-22}[H^+]}{[H^+] + 10^{-13}} \quad (4)$$

And using the value for K_1 as given by Euler and Bolin:

$$E = +.4535 + .02906 \log \frac{[H^+]^3 + 1.1\text{x}10^{-10}[H^+]^2 + 4.37\text{x}10^{-22}[H^+]}{[H^+] + 10^{-13}} \quad (5)$$

In either case, it is seen that for values of pH of 7 or less, the equation simplifies to:

$$E = .4535 - .05812 \text{ pH} \quad .... (6)$$

and the dissociation affects the E. M. F. only in basic solutions.

From these equations, we may calculate the values of E in basic solutions. These values are given in the following table.

Table A.

pH	Using Sheppard's Values	Using Euler's Values
7.00	-.04668	-.04668
8.00	-.01124	-.01124
8.50	-.03985	
9.00	-.06755	-.0683
9.50	-.09304	-.0949
10.00	-.11464	-.1183
10.50	-.13180	-.1367
11.00	-.14510	-.1507
11.500	-.15383	-.1602
12.00	-.15965	-.1655
13.00	-.1698	
14.00	-.1915	

The plots of these equations are shown in Plate II.

On the same plate are shown the experimental points obtained by extrapolating E. M. F. data. See experimental data and curves. It will be noted that the experimental points do not fit the curves closely in the more strongly alkaline range. This may be due to errors in extrapolation, or in calculation of the pH values. It may be due to the electrode not reaching equilibrium sufficiently rapidly to actually measure concentrations. Or it may be due to errors in the values of the equilibrium constants used.

There is some evidence, as will be explained later, that quinone is an acid with an ionization constant of about 10^{-11}. If we use this value for K_3 the equation is:

$$E = +.4535 + .02906 \log \frac{[H^+]^3 + 1.1 \times 10^{-10}[H^+]^2 + 4.37 \times 10^{-22}[H^+]}{[H^+] + 10^{-11}} \qquad (7)$$

The calculated values for E according to this equation are:

Table B

pH value	E. M. F.
10.00	-.1193
10.50	-.1416
11.00	-.1538
11.20	-.1668
11.40	-.1742
11.50-	-.1776
12.00	-.1945

It will be observed that this curve, which is plotted as curve C in Plate II, fits the experimental points very closely, well within the experimental errors of the method.

Change in pH due to the presence of quinhydrone:

Since hydroquinone is a weak acid, in alkaline solutions of quinhydrone, the hydroquinone should combine with a portion of the alkali and lower the pH value. This has already been pointed out by LaMer and Parsons (37) and by Frary and Nietz (26) . J. B. Conant (13) has the following to say about the control of the hydrogen ion concentration in his work on anthraquinone derivatives:

> "The concentration of the hydrogen-ion could not be determined in the presence of the anthraquinone derivative. It was thus necessary to keep the hydrogen-ion concentration at a constant value by means of a buffer solution during the addition of the reducing agent. Except in 0.1 N acid and alkali, buffer solutions such as those described by Clark were employed. Since the concentration of organic substance was very low (o.003 M.) it seemed that such buffer solutions would keep the hydrogen ion constant throughout the reduction. The solutions were not made up determinate but were adjusted by the hydrogen electrode just before the anthraquinone derivative was added."

In the case of hydroquinone, however, it is found that the pH of alkaline buffers is actually lowered by the presence of the organin substance in concentrations of .004 M. This may easily be shown colorimetrically for sodium carbonate buffers. The determination of the actual pH by means of indicators is not sufficiently accurate, however, especially in the presence of quinone, which acts as an oxidising agent. It was found that the hydrogen electrode is very unstable in the presence of quinone, hence can not be used for the determination of the pH of alkaline solutions of quinhydrone. Moreover, as will be pointed out later, it is quite likely that the pH of alkaline quinhydrone solutions changes with time, and the hydrogen electrode is not sufficiently rapid. The antimony electrode was tried, but no definite potentials could be obtained. Since no means of measuring the pH of the solutions directly seemed to be available, the pH was calculated. The buffer solutions were made up indeterminate and their pH values were accurately determined with a hydrogen electrode. The correction to be applied for the presence of quinhydrone was arrived at as follows.

We may consider the acidity of quinhydrone to be due only to the hydroquinone portion, although this is probably not true in the stronger alkalies. On this assumption we may arrive at the initial pH values of the quinhydrone solutions. It seems impossible to calculate the variation of the pH with time, so in our calculations we have assumed it to remain constant.

Let the symbol $\underline{A}$ be the acid or alkaline equivalent of the dissociated hydroquinone in the buffer at equilibrium, that is the number of equivalents of completely dissociated alkali, that are neutralized by the dissociated hydroquinone. Let the symbols $[\mathrm{Hydro}]$, $[\mathrm{RED}]$ $[\mathrm{R\bar{E}D}]$, $[\mathrm{R\bar{E}\bar{D}}]$, K_1, K_2, and $[\mathrm{H}^+]$ have the meanings given to them in the last section. Then at equilibrium, the following simultaneous equations should hold.

$$[\mathrm{Hydro}] = [\mathrm{RED}] + [\mathrm{R\bar{E}D}] + [\mathrm{R\bar{E}\bar{D}}]$$

$$\underline{A} = [\mathrm{R\bar{E}D}] + 2[\mathrm{R\bar{E}\bar{D}}]$$

Expressing concentrations in terms of ionization constants:

$$[\mathrm{Hydro}] = [\mathrm{RED}] + \frac{K_1[\mathrm{RED}]}{[\mathrm{H}^+]} \qquad \frac{K_1 K_2[\mathrm{RED}]}{[\mathrm{H}^+]^2} .$$

$$\underline{A} = \frac{K_1[\mathrm{RED}]}{[\mathrm{H}^+]} + \frac{2 K_1 K_2[\mathrm{RED}]}{[\mathrm{H}^+]^2}$$

Eliminating $[\mathrm{RED}]$ and simplifying,

$$\underline{A} = \frac{[\mathrm{Hydro}] \; (K_1[\mathrm{H}^+] + 2 K_1 K_2)}{([\mathrm{H}^+]^2 + K_1[\mathrm{H}^+] + K_1 K_2)}$$

We will let x be the number of cc. of N/5 acid or alkali to which 200 cc. of .004 M quinhydrone are equivalent, as explained above. And using the values $K_1 = 1.1 \times 10^{-10}$ and $K_2 = 3.97 \times 10^{-12}$, the equation becomes:

$$x \text{ cc.} = \frac{4.4 \times 10^{-10}[\mathrm{H}^+] + 3.52 \times 10^{-21}}{[\mathrm{H}^+]^2 + 1.1 \times 10^{-10}[\mathrm{H}^+] + 4.4 \times 10^{-22}} \quad \ldots\ldots\ldots (8)$$

The calculated values from this equation are:

Table C.

pH	x cc.
8	.0435
9	.397
10	2.26
11	4.83
12	7.20
13	7.90

The graph of the equation is shown in Plate XVIII. The curves for the buffer mixtures showing the number of cc. of acid or alkali added to a definite volume of salt solution to give buffers of definite pH values, were also plotted. See Plates XIX, XX, and XXI.

The corrected pH values were determined as follows. The value of x in the buffer of pH value as determined with the hydrogen electrode, was read from Plate XVIII. This value was added or substracted (depending upon whether HCl or NaOH is added to the buffer salt) along the buffer curves, and a new value of pH was determined. Then using this new value a new value of x was obtained from Plate XVIII and another approximation was made. This was continued until two sucessive approximations agreed to within .01 pH.

The pH values of alkaline solutions and the corrected values as determined above, are shown in columns 2, and 3 of Table 2. It is to be noted that the corrections were made on the assumption that quinone does not affect the pH. It is likely that the corrections for the buffers above pH 11.0 are too small.

Changes of E. M. F. with Time:

Experimentally it is observed that at about pH 8.0 or above and in the absence of air, the potential of the quinhydrone electrode varies with time. This drift is always negative, that is more basic, or the reduction potential tends to increase. Moreover, the rate of drift increases with the alkalinity. The general shape of the curves is the same in every case; the rate of change decreasing at first and then becoming essentially linear with time.

We may suppose that the electrode reaction is sufficiently rapid that at any instant, the E. M. F. is an equilibrium value. We have no absolute proof that this is the case, except that in solutions where equilibrium is attained, i.e. acid solutions, the equilibrium is attained almost instaneously. Moreover, alternate readings on two electrodes always fell on the same smoothe curve. Initial values for the E.M.F. are probably somewhat in error, however, due to incomplete mixing of the solutions. Hence they are less trustworthy than the later values.

If we assume then, that at any instant, the general electrode equation holds, the change in the observed value of E must be due to a change in the ratio (Quinone)/(Hydro), and the drift of potential will be a measure of the rate of change of the logarithm of this ratio.

As a first approximation, we may assume that:

Quinone $\longrightarrow$ Hydroquinone (Monomolecular reaction)

Initially, the rate of change of the ratio will be much greater than the rate of the reaction. After a large portion of the quinone has changed into hydroquinone, the rate of change will be porportional to the rate of the reaction, since the concentration of hydroquinone has become nearly constant.

At constant hydrogen ion concentration the general electrode equation becomes:

$$E = E_0' + \frac{RT}{nf} \ln(\text{Quinone}) - \frac{RT}{nF} \ln(\text{Hydro})$$

and if (Hydro) has become constant, we have:

$$\frac{dE}{dt} = \frac{RT}{nF} \frac{d \ln(\text{Quinone})}{dt}$$

And if the reaction is monomolecular, we may write:

$$\frac{d(\text{Quinone})}{dt} = -k(\text{Quinone}) \quad \text{or} \quad d \ln(\text{Quinone}) = -k\,dt$$

Whence: $$\frac{dE}{dt} = \frac{RT}{nF}(-k)$$

which means that after most of the quinone has disappeared the curve of E. M. F. plotted against time should approach a straight line, the slope of which will be proportional to the rate of the disappearance of quinone. It is an experimental fact that the curves do approach ~~a~~ straight lines.

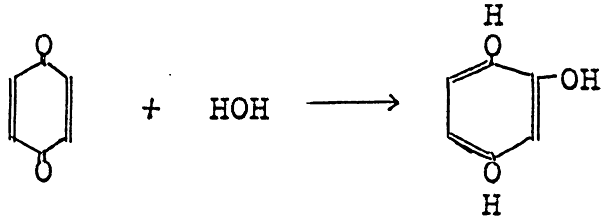
We have determined the rate of change of E.M.F. as follows. For the initial rate of change, a straightedge was laid tangent to the curves at $t = 0$ and the slope taken as the rate of change. These values are given in Table 18 column 3. It is quite certain that the values are only approximate, since a very small displacement of initial points, would make a large error in the slope, especially in the case of small slopes, i.e. the lower pH values. In column 4 of the same table are given values of the slopes of the straight portions of the curves, taken as the average slope of the curve between $E = E'_0 - .025$ and $E = E'_0 - .045$. This is the rate of change of quinone between concentrations of about .00096 molar and .00001 molar and of hydroquinone between .00704 molar and .00790 molar. It is true that the concentration of hydroquinone does not remain constant in this range, so the above assumptions will not hold rigidly, but beyond this range the curves deviate considerably from a straight line, due probably to side reactions. Hence this seems to be the best range for comparison. In the case of the curves for lower pH values, the curves were extrapolated, and the values for slope may be somewhat in error.

It will be observed that the initial slopes are from twice to three times the values for the constant slope. This fact tends to substantiate the assumptions made in regard to the reaction.

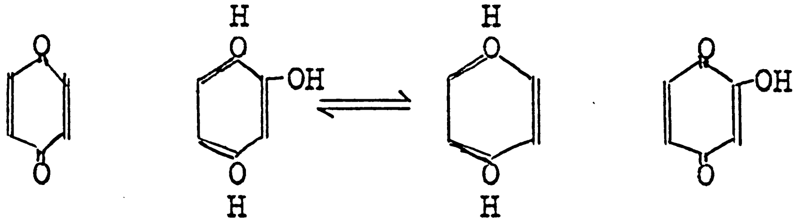
Time Changes in the Quinhydrone Solutions.

Let us suppose the reactions of quinone in aqueous solution to be represented by:

(I)



(slow)



In reaction I, water is adding to quinone to form hydroxy-hydroquinone, by a monomolecular reaction. Hydroxyhydroquinone may have an oxidation-reduction potential less than, equal to, or greater than hydroquinone. In any case, the reaction II will take place -- probably rapidly -- until an equilibrium is reached such that the potential generated by hydroxyhydroquinone - hydroxyquinone is equal to that generated by hydroquinone - quinone, and the measured E.M.F. will measure either ratio if the reaction is reversible, and the ratio hydroquinone to quinone even if the reactions are irreversible. We will consider the three possible cases in the limits.

Case 1. Hydroxyhydroquinone is a much weaker reducing agent is hydroquinone. Then reaction II will not go at all, and the change in E.M.F. will be due entirely to reaction I.

Let c = initial conc, of quinone or of hydroquinone.
x = moles of quinone changed into hydroxyhydroquinone up to time t.
$c - x$ = conc. of quinone at time t.
c = concentration of hydroquinone.

$$dx/dt = k\,(c - x) \qquad \ln \frac{(c - x)}{c} = -\,k\,t.$$

$$E = E_0' + RT/2F . \ln(c - x)/\,c \qquad \text{(at constant pH)}$$

$$E = E_0' - RT/2F \,.\, k\,t$$

The plot of equation 1 would give straight lines for all values of k. Moreover the formation of hydroquinone is unaccounted for. This does not fit the facts.

Case 2. Hydroxyhydroquinone has an oxidation reduction potential equal to that of hydroquinone. Then the equilibrium reaction II will adjust the concentrations so that the ratio (hydroxyquinone)/(hydroxyhydroquinone) is equal to the ratio (quinone)/(hydroquinone). But since the oxidation-reduction potentials are the same, the effective ratios for E. M. F. will be the same as if quinone were being removed from the mixture and an equal amount of hydroquinone were being added, and the final products will be hydroquinone and hydroxyhydroquinone in equal proportions, if the reaction is complete as outlined. If the reaction is not complete, the mixture of products will contain hydroxyquinone. This might undergo a reaction similar to that postulated for quinone. All of these assumptions lead to results not contrary to those which have been found by other investigators.

Let the symbols c and x have the meanings as defined above. Then:

$c - x$ = conc. of quinone at time t. (or of oxyquinone)

$c + x$ = conc. of hydroquinone or other reductant at time t.

$$dx/dt = k\,(c - x) \qquad \text{whence;} \quad \ln\,(c - x)/c = -k\,t$$

$$x = c(1 - e^{-kt})$$

$$c - x = c\,e^{-kt}$$

$$c + x = c(2 - e^{-kt})$$

Whence:

$$E = E_0' + RT/2F \,.\, \ln c\,e^{-kt} - RT/2F \,.\, \ln\,(2 - e^{-kt}).$$

$$E = E_0' + RT/2F.\ kt - RT/2F.\ \ln(2 - e^{-kt})$$

Which at 20° C. becomes:

$$E = E_0' - .01262\,k\,t - .02906 \log\,(2 - e^{-kt}). \;\ldots\ldots\; 2$$

$$dE/dt = -.01262\,k - \frac{.02906\ e^{-kt}}{2 - e^{-kt}}\,k$$

At $t = 0$, $dE/dt = -.04168\,k$

At $t = \infty$ $dE/dt = -.01262\,k$

Initial rate / Final rate = 3.3

It will be noted that the ratio of initial to final rate is greater than that found by experiment, still the method of measuring initial rates is probably not justifiable, so the ratio of 3.3 may not be contrary to the facts.

Equation 2 was plotted for various values of k as deduced from the experimental curves. The curves are shown in Plates XXII and XXIII. The values from which these curves were plotted are as follows:

Table D

Time in Minutes	1 k = .024	2 k = .0368	3 k = .0935	4 k = .088	5 k = .1078	6 k = .317
1	-.00006	-.00084		-.00226		-.0074
5			-.0099		-.0109	-.0273
10	-.0054	-.0081	-.0178	-.0169	-.0210	-.0485
20	-.0101	-.0147	-.0313	-.0293	-.0359	-.0887
40	-.0182	-.0259	-.0558	-.0530	-.0631	-.1687
60		-.0361	-.0797	-.0753	-.0903	
100	-.03845	-.0550	-.1267	-.1197	-.1447	
150	-.0540	-.0784				

The values of k were obtained from the curves as follows; (1) is from borate buffer pH 9.709. (2) is from borate buffer pH 9.872. (3) is from borax buffer pH 10.33. (4) is from carbonate buffer pH 10.23. (5) is from carbonate buffer pH 10.41. (6) is from phosphate buffer pH 11.14.

A comparison of these curves with the experimental curves shows a fair agreement in the initial portions. The experimental curves deviate from the theoretical in the direction of greater curvature after a change of about 40 millivolts. This is especially pronounced for the borate buffers. The carbonate buffers show a better agreement.

This increase in curvature may be due in part to a change in the pH of the buffers, brought about by increasing hydroquinone concentration. An increase in hydrogen ion concentration would decrease the rate of the reaction and cause a greater curvature in the e.m.f. - time curves. The greater curvature may also be due to side reactions or to subsequent reactions which we have not taken into account.

<u>Case 3.</u> Hydroxyhydroquinone is a much stronger reducing agent than is hydroquinone. Then reaction II will go nearly to completion towards the right and the final products of the reaction will be hydroquinone and hydroxyquinone. Moreover, the hydroxyquinone will have very little effect upon the electrode potential and so may be neglected in the calculations. It is possible, however, that the hydroxyquinone formed would likewise undergo a transformation similiar to that of quinone. This would complicate the reaction. For purposes of the present analysis, we must suppose that the hydroxyquinone remains unchanged.

Let the symbols c and x have the meanings already given to them. Then:

$c - 2x$ = conc. of quinone at time t.

$c + x$ = conc. of hydroquinone at time t.

$$dx/dt = k\,(c - 2x)$$

$$x = c/2 \,.\, (1 - e^{-2kt})$$

From which:

$$E = E_0' - RT/nF.2kt - RT/nF.\ \ln(3 - e^{-2kt}) + R\ T/nF\ .\ \ln 2$$

$$E = E_0 - .02524\ k\ t - .02906 \log (3 - e^{-2kt}) + .02906 \log 2 \quad ...(3)$$

The curves for equation (3) with various values of k would be similar in shape to those of equation (2), but would have even less curvature. Hence this equation does not fit the facts so well.

$$dE/dt = -.02524\ k - \frac{.05812\ e^{-2kt}}{3 - e^{-2kt}}\ k$$

At $t = 0$, $dE/dt = -.0543\ k$

At $t = \infty$ $dE/dt = -.02524\ k$

Initial rate / Final rate = 2.1

This ratio of initial rate to final rate is in better agreement with the facts than is the ratio derived for case 2.

From the above analysis, it is evident that we do not have sufficient data to reach any definite conclusions in regard to the mechanism of the reaction. Starting with the reactions postulated, we can arrive at equations which approximate the facts, but it is quite possible that other assumptions would lead to equations which were just as good. The most that can be said, is that initially the electrode behaves as if quinone were changing by a monomolecular reaction into a reductant which has an oxidation-reduction potential somewhere near that of hydroquinone. By an equilibrium reaction, this reductant reacts with quinone to yield hydroquinone and a higher oxidation product.

Be fore we can explain completely the drift in e. m. f. of the quinhydrone electrode, it will be necessary to isolate and identify the oxidation and reduction products and to measure their oxidation-reduction potentials directly.

<u>Rate of change as a function of the hydroxyl ion concentration</u>:

In columns 6, 7, and 8 of Table 18 are given the ratios between the constant slopes and hydroxyl ion concentration, the square root of the concentration and two-thirds power of the concentration. It is apparent that in the weakly alkaline buffers, the rate of change is nearly proportional to the first power of the hydroxyl ion concentration, but this is not true for the higher hydroxyl ion concentrations. Likewise no other simple power of hydroxyl ion concentration will express the function by which the rate of change varies with hydroxyl ion. In column 9 and 10 of Table 18 are given values of dE/dt divided by the function $\frac{[OH^-]}{K_3+[OH^+]}$. It is noted that the value for $K_3 = 10^{-13}$ gives a fair constant for the ratio. See column 9. This function is arrived at as follows:

Suppose quinone to be a weak acid with ionization constant K_3. If $[\overline{O}X]$ is the concentration of these ions,

$$[O\overline{X}]\,[H^+] = K_3\,[OX]$$

and $$[\text{Quinone}] = [OX] + [\overline{OX}]$$

whence $$[O\overline{X}] = [\text{Quinone}]\,\frac{K_3}{[H^+] + K_3}$$

or $$x = z\,y$$

Suppose the reaction to be:

$$\text{Quinone} \rightleftharpoons O\overline{X} \longrightarrow \text{RED}$$

Let m = moles of RED formed up to time t

c = initial conc. of Quinone (total)

yc = initial conc. of $\overline{OX}$

$c - m$ = conc. of Quinone at time t, $= z$

$y\,(c - m)$ conc. of $\overline{OX}$ at time t, $= x$

$$dm/dt = k'\,x = k'y(c - m) = k'yz$$

$$d(c - z)/dt = k'yz$$

$$d(\ln z)/dt = -k'y$$

But as we have already seen,

$dE/dt = RT/nF.d(\ln z)/dt$ for certain conditions.

Whence:

$dE/dt = -RT/nF \,.\, k'y$, where y is a function of the hydrogen ion concentration as defined.

If K_3 is 10^{-11} the function y becomes:

$$\frac{[OH^-]}{10^{-3} + [OH^-]}$$

It has already been pointed that the slopes of the straight portions of the curves seem to be this function of the hydroxyl ion concentration. Also the initial values for the e.m.f. indicate that quinone is an acid with a dissociation constant of about 10^{-11}. Thus the dissociation of quinone shows up in two ways quite independent of each other, which is a strong indication that the dissociation is an actual fact. Nevertheless this is not conclusive proof, for in the range where the dissociation becomes appreciable the errors of extrapolation are necessarily very great, so the initial values of e.m.f. may be in error somewhat. Also it is quite probable that some of our assumptions regarding the rate of the reaction are not justifiable. In the strongly alkaline buffers, the curves deviate considerably from a straight line, indicating that the reaction is not strictly monomolecular. Moreover the "constant" we get by dividing dE/dt by y is not strictly a constant. Indeed, dE/dt divided by OH gives about as good a "constant", so it is possible that the rate of change is some other function of hydroxyl ion concentration. The rate seems to depend somewhat upon the nature of the buffer. The rate is greater in carbonate buffers that in borate buffers of the same pH.

EXPERIMENTAL

Apparatus:

A saturated calomel electrode was used as the reference electrode. A diagram of the cell is shown in *A*, figure I. The reservoir is an ordinary dropping funnel fused on to a test-tube *N*. The tube *o* is filled with mercury and ends in a platinum seal at *p*. The wire to the potentiometer dips into mercury in contact with this platinum wire.

A diagram of the working cell is shown in *C*, figure I. It consists of an adapter of about 60 cc. capacity, with the stem fused off. It is closed by a rubber stopper with six holes through which glass tubes lead. The syphon tube *q* reaches nearly to the bottom of the cell and makes contact through the flowing junction. *r* is a bulbed tube through which exhaust gas can pass, and it passes just through the rubber stopper. It is connected by a rubber tube with another glass tube which dips into the oil bath and serves as a liquid seal. *s* is a syphon tube through which the cell can be emptied. It reaches to the bottom of the cell. The cell is filled through tube *u*, bent as shown in the diagram. Two tubes are fused on the sides of tube *u*. Through one, distilled water can be forced into the cell for washing. Through the other, *h*, oxygen free air is forced. The tube is connected with the dropping funnel T, which holds the solutions prior to mixing. The funnel is fitted with a rubber stopper carrying a T-tube through which the funnel may be evacuated or filled with nitrogen. In order to shut out light, the whole cell and the funnel T, are covered with tin foil.

The electrode is shown as v, figure I, C. Two of these passiinto the cell. Gold wire electrodes are used A length of gold wire is fused on to platinium which in turn is fused through the glass tube. Copper wire is fused on to the inner end of the platinum and makes contact with the potentiometer. The exposed platinum is gold plated. For added strength the gold wire is wrapped around the glass tube. Gold wire about 0.6 m.m in diameter is used. For one electrode about 5 cm. of wire was used; for the other about 10 cm. The larger electrode seemed to give the better results.

The flowing junction is shown as B, figure I, and is a slight modification of that described by Roberts and Fenwick (51). It is made from an ordinary test-tube. A syphon tube is fused on at the bottom and leads up and out of the water bath. Through this the bulb w is automatically emptied.

A diagram of the hydrogen electrode cell is shown in figure II. The Hildebrand type electrode a passes through a rubber stopper fitted into the outter cell b. This is made from an eight inch by one inch pyrex test-tube. It is fitted with the liquid seal c and the syphon tube d. The syphon tube is closed by means of a ground glass cap e, and dips into a test tube filled with saturated KCl. LaMer and Baker (36) report that such a junction gives constant liquid junction potentials and that there is a minimum of diffusion.

As reference electrodes for the hydrogen electrode, ordinary saturated KCl - calomel electrodes were used. Several of these dipped into the salt bridge and could be compared from time to time.

The electrode proper, was of gold wire, and plated with platinum black. It was made similar to the gold electrodes already described, except that the wire was not coiled around the glass tube, but was made into a helix. It was found necessary to use fairly large electrodes -- about a foot or more of gold wire. Smaller electrodes were too easily polarized. It was found that a thin gray plate, obtained with a low current density and concentrated platinum solution, gave the best results.

The potentiometer was a new Leeds and Northrup student's potentiometer, catalog No. 7651. Galvanometers were used as null point instruments; for approximate adjustment an L & N. portable galvanometer and for the final adjustment an L. & N. mirror galvanometer. This had a resistance of 1300 ohms, a sensitivity of 1448 megs, and a period of 14.5 sec. The deflections were read by a telescope and scale. As standard cells, Clark cadmium cells were used. Three of these gave the same value 1.0183 volts and were compared from time to time. The apparatuse was connected by means of switches so that any combination of the electrodes or of the galvanometers could be connected with the potentiometer.

The temperature was held constant at 20°C by means of a water thermostat, heated electrically. The cells were set in baths of parafin oil, set in the water bath. Since the room temperature was near twenty degrees, the temperature of the bath would remain constant for long periods without attention. When working below room temperature, the bath was kept cool by adding cold water or smallpieces of ice from time to time. The temperature was measured on a short range, calibrated thermometer. The maximum variation during a run was about 0.1 degree, and it is probable that the temperature of the solutions in the cells varied much less than this.

Materials:

The quinhydrone used was an Eastman Kodak Co. product. It appeared to be quite pure and no attempts at further purification were made. It was kept in a well-stoppered brown bottle.

The Clark buffer solutions were prepared according to the directions given in Clark's "Determination of Hydrogen Ions" page 99. The salts were all purified according to directions.

$Na_2 HPO_4 . 2 H_2O$ was prepared according to the method of Clark. (loc. Cit.)

Borax used was a well crystallized commercial C. P. product, and since direct measurements of the pH of the borax solutions were made, the salt was not further purified.

Calomel for the reference electrodes was prepared electrolytically, by electrolysing a dilute HCl solution, using a layer of Hg as the anode.

Water was redistilled from alkaline permanganate and was collected warm and kept in pyrex flasks.

The nitrogen supply was obtained under pressure by allowing water under pressure to run into a large bottle filled with air. The displaced air was forced through five half-gallon bottles three-fourths filled with a mixture of strong ammonium hydroxide, cuprous chloride, ammonium chloride and copper wire. It was then passed over copper gauze heated to about 500 °C, then through a copper cooling coil, two wash bottles containing dilute sulphuric acid, two bottles containing alkaline pyrogallic acid, and finally through a lead coil immersed in the thermostat.

The hydrogen was generated from zinc and sulphuric acid in a Kipp generator. It was purified by passing it through five bead columns moistened with sodium hydroxide, potassium permanganate, saturated silver nitrate and two with water. It was then passed through a tube containing reduced copper and heated electrically to 350° C; and then through a copper coil immersed in water kept at the temperature of the thermostat.

Method of Operation:

The method finally adopted was as follows: 100 cc. of double strength buffer is made up. 25 cc. is taken out with a pipette and is diluted to 50 cc. The hydrogen electrode cell is washed out with a portion of this solution and is then filled. The cell is put into the thermostat and the air space above the solution evacuated through f (See figure II.) By opening a screw clamp on the hydrogen chain the space is filled with hydrogen. This is repeated three times. Then a fairly rapid stream of hydrogen is allowed to pass into the cell, washing past the electrode and stirring the solution. As a rule, equilibrium is reached in from one to three hours.

To make up an .008 molar quinhydrone solution, .0436 gm. of quinhydrone is carefully weighed out and brushed into a large, dry test-tube covered with tin foil to shut out light. From a pipette, 25 cc. of water is added and the mixture is stirred until the quinhydrone is all dissolved. This usually takes considerable time.

The cell is filled as follows. (See figure I.) At the start, stop-cocks *a*, *b*, *c*, and *d*, the pinch clamps *e*? *f*, and *h*, the clamps on the water tube and the stop-cock on the nitrogen chain are closed. Pinch clamp *g* is open. The tube *d* is filled with distilled water. The syphon tubes on the reference electrode and on the flowing junction are both filled with liquid. The cell *C* is filled with nitrogen and empty of liquid. The stopper in *T* is removed and 20 cc. of double strength buffer is run into the funnel from a pipette. The stopper is replaced, pinch clamp *e* is opened and the funnel is evacuated. Pinch clamp *e* is closed and *f* is opened. Then the stop-cock on the nitrogen chain is opened and the evacuated apparatus is filled with nitrogen. This is repeated three times. With pinch-clamp *f* open, stop-cock *d* is opened and the nitrogen under pressure forces the buffer solution down into the cell *C*. Stop-cock *d* is then closed, *f* is closed and the pinch clamp *h* is opened allowing a slow stream of nitrogen to bubble through the solution.

The stopper in *T* is now removed and the funnel is filled with distilled water, which is then removed with a pipette. This is to wash out the funnel. Now, 20 cc. of the quinhydrone solution is put into the funnel. Pinch clamps *f* and *h* are closed and the funnel is evacuated and filled with nitrogen as described above. The evacuation serves to remove dissolved air from the solution. Everything is now ready to start the run.

The temperature of the bath is checked, the potentiometer adjustment is checked, and dials are set at the estimated reading. Stop-cock b is opened wide, and stop-cock a just a little, so that saturated KCl - calomel solution flows very slowly through the reference electrode and out through the syphon tube of the flowing junction. Now with everything ready and a nitrogen pressure of about 2 cm. of Hg, stop-cock d is opened and the quinhydrone solution flows into the buffer solution in the cell C. When about half the solution has flowed in (after about 15 seconds) the stop watch is started. As soon as all the solution has run out of the funnel T and the tube u, stop-cock d is closed and pinch clamp h is opened allowing nitrogen to bubble through the cell and stir the solution. Immediately, stop-cock c is opened wide allowing solution to flow out of the cell and displace the water. Now the initial reading is made on the potentiometer. This reading can usually be made within about one to three minutes after the start. The stop-cock c is then adjusted so that solution flows very slowly-- just enough to prevent diffusion. The nitrogen supply is adjusted so that a slow stream of bubbles passes through the apparatus and this flow of nitrogen is kept up during the entire run.

Readings are taken on alternate electrodes at intervals of from ½ to 30 minutes, depending upon the rapidity of the change. For the fast reactions, the potentiometer dials are set just ahead of the null point and the time is noted when the galvanometer gives no deflection upon closing the tap key. The time can be noted within about ten seconds. For the slower reactions the readings are taken in the usual way. The readings are taken over periods of from one to six hours, depending upon the speed of the reaction.

When the run is complete, the cell is emptied and washed as follows: Pinch clamp *g* is closed and with *h* open, nitrogen forces the solution out through the tube *s*. When all the solution has been displaced, pinch-clamps *h* is closed, and with pinch-clamp *f* closed, the stopper in *t* is removed and the funnel is filled with water which is allowed to run down into the cell. When the cell is filled, stop-cock *d* is closed and *c* is opened wide, allowing water to displace the solution in the syphon tube, Stop-cock *c* is then closed and pinch clamp *g* is closed. Pinch clamp *h* is opened, allowing nitrogen to displace the water as before. This is repeated. Finally the cell is washed out by forcing pure water through tube *u* from a flask (not shown). The cell is then emptied as before and the apparatuse is ready for another run.

Data and Tables:

The quinhydrone electrode is stable below pH 8.00. For measurements in the acid range, no particular concentration of quinhydrone was used, but the quinhydrone was simply dissolved in the buffer and the solutions run into the cell. Values for E. M. F. in the acid range are shown in Table 1.

In the alkaline range, more or less rapid drifts of potential are encountered, so the readings were taken against time as explained. Preliminary experiments showed that the rate of change is apparently independent of the concentration of quinhydrone, and is influenced very slightly by the temperature. But since the concentration of quinhydrone affects the pH value, concentrations of .004 molar were used for the data reported. And since E. M. F. is a function of temperature, the runs were all carried out at 20° C.

Duplicate runs were made with fresh quinhydrone solutions, using a portion of the same buffer solution used in the first run. The values of E. M. F. were plotted against time, and thus two or more curves were obtained. In case the curves were irregular, or in case the points obtained from the duplicate electrodes did not fall on the same smoothe curve, the curve was discarded. When two or more curves, seemingly free from errors were obtained for a given buffer mixture, smoothe lines were drawn through the points and from these curves were read the values of E. M. F. at various time intervals. These values were averaged to get the "mean values". Each value was subtracted from the mean to get the deviations, and deviations were averaged to get the mean deviation. The mean values were plotted as the curves for E. M. F. in the given buffers. The values for fifteen average curves are given in Tables 3 to 17.

The values are given as values of potential difference between the quinhydrone electrode and the saturated calomel electrode as zero. The sign of potential is that of solution to electrode.

Table 1

Quinhydrone in Acid Buffers. (Equilibrium values).

Run No.	Buffer solution	pH	E.M.F	Exp.error estimate)	Deviation f.theory.
30	KCl - HCl	1.60	.3598	.0002	-.0010
71	KCl - HCL	1.835	.3445	.0005	-.0026
1	KCl - HCl	2.0	.3332	.0002	-.0040
67	KHphthalate, HCl	2.635	.2987	.0002	-.0018
2	KHphthalate, HCl	3.0	.2765	.0000	-.0030
28	KHphthalate, HCl	3.0	.2796	.0004	-.0001
3	KHphthalate, NaOH	4.0	.2205	.0005	-.0005
32	KHphthalate, NaOH	4.0	.2195	.0005	-.0010
4	KHphthalate, NaOH	5.0	.1625	.0005	-.0003
68	KHphthalate, NaOH	5.55	.1307	.0003	-.0003
66	KHphthalate, NaOH	5.65	.1262	.0002	.0011
5	KHphthalate, NaOH	6.0	.1050	.0003	.0001
6	KH_2PO_4, NaOH	6.0	.1053	.0002	.0004
69	KH_2PO_4, NaOH	6.021	.1018	.0002	-.0016
70	KH_2PO_4, NaOH	6.81	.0572	.0002	-.0010
7	KH_2PO_4, NaOH	7.0	.0465	.0003	-.0001
37	KH_2PO_4, NaOH	7.0	.0465	.0002	-.0001
61	KH_2PO_4, NaOH	7.6	.0125	.0003	.0015
72	KH_2PO_4, NaOH	7.77	.0014	.0001	.0004
13	Boric acid, NaOH	8.00	-.0105	.0005	.0035
8	KH_2PO_4, NaOH	8.00	-.0107	.0005	.0033

Table 2

Quinhydrone in Alkaline Buffers (Extrapolated data)

Nature of Buffer	pH H_2 electrode	pH corrected	E. M. F. Initial	Deviation f. theory
Boric acid, KCl, NaOH	8.4	8.396	-.0287	.005
Boric acid, KCl, NaOH	8.59	8.580	-.0464	-.001
Boric acid, KCl, NaOH	9.000	8.985	-.0640	.001
Boric acid, KCl, NaOH	9.22	9.20	-.0793	.000
Boric acid, KCl, NaOH	9.795	9.709	-.1082	+.003
Boric acid, KCl, NaOH	10.00	9.872	-.1111	.004
Na_2CO_3 - HCl	9.85	9.801	-.1079	.002
Na_2CO_3 - HCl	10.33	10.23	-.1296	.0001
Na_2CO_3 - HCl	10.58	10.41	-.1380	-.0005
Na_2CO_3 (M/20)	11.28	10.85	-.1486	.0005
Na_2HPO_4 , NaOH	11.00	10.86	-.1510	-.0001
Na_2HPO_4 , NaOH	11.27	11.14	-.1683	-.005
Na_2HPO_4 , NaOH	11.775	11.663	-.1833	.002
Borax, Na_2CO_3, NaOH		10.33	-.1348	-.0005
Borax, Na_2CO_3, NaOH		11.00	-.1537	.0002

Table 3.

.004 M quinhydrone in boric acid- KCl- NaOH buffer
pH 8.396 (Corrected)

Time in Minutes	Run No. 62	Run NO. 63	Run No. 64	Mean Value	Mean Deviation
0	-.0294	-.0285	-.0282	-.0287	.0005
5	-.0298	-.0289-	-.0284	-.0290	.0005
10	-.0303	-.0290	-.0286	-.0293	.0006
20	-.0307	-.0291	-.0290	-.0296	.0007
40	-.0313	-.0298	-.0297	-.0303	.0007
80	-.0327	-.0310	-.0311	-.0316	.0011
120	-.0340	-.0320	-.0325	-.0328	.0008
180	-.0362	-.0350	-.0360	-.0357	.0005

Table 4.

.004 M quinhydrone in boric acid - KCl - NaOH buffer
pH 8.580 (Corrected)

Time in Minutes	Run No. 73	Run No. 110	Run No. 111	Mean Value	Mean Deviation
0	-.0433	-.0480	-.0480	-.0464	.0021
5	-.0450	-.0483	-.0482	-.0472	.0014
10	-.0460	-.0486	-.0486	-.0478	.0009
20	-.0476	-.0493	-.0491	-.0487	.0007
40	-.0490	-.0505	-.0500	-.0498	.0006
60	-.0498	-.0516	-.0510	-.0508	.0007
80	-.0510	-.0530	-.0520	-.0520	.0007
100	-.0520	-.0540	-.0528	-.0529	.0007
120	-.0528	-.0550	-.0535	-.0538	.0008
140	-.0538	-.0562	-.0542	-.0547	.0010
160	-.0546	-.0573	-.0550	-.0556	.0010
180	-.0555	-.0583	-.0560	-.0566	.0011

Table 5.

.004 M. quinhydrone in borate buffer pH 8.985 (Corrected)

Time in Minutes	Run No. 39	Run No. 40	Mean Value	Mean Deviation
0	-.0650	-.0630	-.0640	.0010
5	-.0663	-.0643	-.0653	.0010
10	-.0675	-.0652	-.0663	.0011
15	-.0686	-.0665	-.0675	.0010
25	-.0702	-.0680	-.0691	.0011
40	-.0718	-.0695	-.0706	.0011
60	-.0733	-.0718	-.0725	.0007
100	-.0765	-.0752	-.0758	.0006
140	-.0798	-.0785	-.0791	.0006
180	-.0830	-.0820	-.0825	.0005
240	-.0903	-.0873	-.0888	.0015
300	-.0960	-.0922	-.0941	.0019
360	-.1013	-.0970	-.0991	.0021

Table 6.

.004 M. quinhydrone in borate buffer pH 9.20 (Corrected)

Time in Minutes	Run No. 76	Run No. 113	Mean Value	Mean Deviation
0	-.0797	-.0790	-.0793	.0003
5	-.0817	-.0810	-.0813	.0003
10	-.0830	-.0827	-.0828	.0001
20	-.0854	-.0851	-.0852	.0001
30	-.0870	-.0870	-.0870	.0000
40	-.0886	-.0889	-.0887	.0002
60	-.0917	-.0917	-.0917	.0000
80	-.0945	-.0943	-.0944	.0001
120	-.1000	-.0993	-.0996	.0003
140	-.1030	-.1018	-.1024	.0006
180	-.1081	-.1068	-.1074	.0006
240	-.1165	-.1147	-.1156	.0009
280	-.1217	-.1198	-.1207	.0010
320	-.1266	-.1250	-.1258	.0008
360	-.1320	-.1300	-.1310	.0010

Table 7.

.004 M. quinhydrone in borate buffer pH 9.709 (Corrected)

Time in Minutes	Run No. 115	Run No. 116	Mean Value	Mean Deviation
0	-.1088	-.1076	-.1082	.0006
5	-.1115	-.1110	-.1112	.0002
10	-.1142	-.1140	-.1141	.0001
15	-.1168	-.1168	-.1168	.0006
20	-.1193	-.1193	-.1193	.0000
30	-.1237	-.1236	-.1236	.00005
40	-.1276	-.1274	-.1275	.0001
50	-.1310	-.1307	-.1308	.0001
60	-.1342	-.1340	-.1341	.0001
80	-.1401	-.1408	-.1404	.0003
100	-.1462	-.1470	-.1466	.0004
120	-.1524	-.1530	-.1527	.0003
140	-.1583	-.1586	-.1584	.0001
160	-.1640	-.1643	-.1641	.0001
180	-.1700	-.1700	-.1700	.0000

Table 8.

.004 M. quinhydrone in borate buffer pH 9.872 (Corrected)

Time in Minuted	Run No. 42	Run No. 43	Run No. 44	Run No. 45	Mean Value	Mean Deviation
0	-.1118	-.1090	-.1103	-.1135	-.1111	.0012
2	-.1136	-.1110	-.1143	-.1154	-.1136	.0013
5	-.1160	-.1138	-.1168	-.1180	-.1161	.0012
10	-.1198	-.1180	-.1208	-.1215	-.1200	.0011
15	-.1230	-.1204	-.1245	-.1250	-.1232	.0015
20	-.1258	-.1248	-.1280	-.1280	-.1266	.0010
30	-.1307	-.1308	-.1341	-.1340	-.1324	.0015
40	-.1350	-.1356	-.1400	-.1392	-.1375	.0021
60	-.1432	-.1440	-.1502	-.1490	-.1466	.0030
80	-.1510	-.1522	-.1580	-.1570	-.1545	.0042
100	-.1583	-.1600	-.1650	-.1648	-.1620	.0035
120	-.1643	-.1678	-.1720	-.1716	-.1694	.0035
140	-.1700	-.1740	-.1790	-.1784	-.1754	.0034
160	-.1755	-.1808	-.1860	-.1851	-.1819	.0030
180	-.1810	-.1870	-.1930	-.1920	-.1883	.0045

Table 9.

.004 M. quinhydrone in carbonate buffer pH 9.801 (Corrected)

Time in Minutes	Run No. 124	Run No. 125	Mean Value	Mean Deviation
0	-.1080	-.1078	-.1079	.0001
5	-.1114	-.1117	-.1115	-.0001
10	-.1148	-.1152	-.1150	.0002
20	-.1210	-.1222	-.1216	.0006
30	-.1274	-.1288	-.1281	.0007
60	-.1463	-.1480	-.1471	.0008
80	-.1592	-.1610	-.1601	.0009
100	-.1718	-.1740	-.1729	.0011
120	-.1850	-.1870	-.1860	.0010

Table 10.

.004 M. quinhydrone in carbonate buffer pH 10.23 (Corrected)

Time in Minutes	Run No. 84	Run No. 119	Run No. 118	Mean Value	Mean Deviation
0	-.1280	-.1300	-.1310	-.1296	.0011
5	-.1360	-.1388	-.1397	-.1381	.0013
10	-.1435	-.1462	-.1462	-.1453	.0012
15	-.1506	-.1530	-.1530	-.1522	.0010
20	-.1572	-.1597	-.1591	-.1586	.0010
30	-.1700	-.1721	-.1707	-.1709	.0007
40	-.1820	-.1832	-.1814	-.1822	.0007
50	-.1932	-.1938	-.1912	-.1927	.0010
60	-.2042	-.2035	-.2000	-.2036	.0014
80	-.2256	-.2228	-.2170	-.2218	.0032
100	-.2450	-.2405	-.2332	-.2396	.0043
120	-.2615	-.2583	-.2480	-.2559	.0049

Table 11.

.004 M. quinhydrone in carbonate buffer pH 10.41 (Corrected)

Time in Minutes	Run No. 121	Run No. 122	Run No. 123	Mean Value	Mean Deviation
0	-.1375	-.1375	-.1390	-.1380	.0007
2	-.1418	-.1450	-.1453	-.1440	.0015
5	-.1480	-.1530	-.1515	-.1512	.0018
10	-.1578	-.1620	-.1606	-.1601	.0016
20	-.1750	-.1765	-.1760	-.1760	.0005
30	-.1895	-.1896	-.1880	-.1891	.0006
40	-.2023	-.2020	-.1990	-.2011	.0014
60	-.2260	-.2227	-.2180	-.2233	.0029
70	-.2360	-.2320	-.2267	-.2316	.0033
80	-.2470	-.2410	-.2354	-.2411	.0036
90	-.2578	-.2504	-.2440	-.2504	.0039
100	-.2686	-.2600	-.2525	-.2603	.0054
110	-.2780	-.2690	-.2610	-.2693	.0057
120	-.2870	-.2780	-.2695	-.2782	.0059

Table 13

.004 M. quinhydrone in phosphate buffer pH 10.86 (Corrected)

Time in Minutes	Run No. 133	Run No. 134	Run No. 135	Mean Value	Mean Deviation
0	-.1510	-.1500	-.1520	-.1510	.0007
3	-.1680	-.1660	-.1640	-.1660	.0013
5	-.1770	-.1740	-.1705	-.1738	.0022
10	-.1910	-.1890	-.1850	-.1883	.0022
20	-.2095	-.2080	-.2085	-.2087	.0006
30	-.2235	-.2223	-.2228	-.2229	.0004
40	-.2348	-.2340	-.2335	-.2341	.0005
45	-.2405	-.2393	-.2385	-.2391	.0007
50	-.2457	-.2446	-.2428	-.2444	.0010
60	-.2575	-.2552	-.2524	-.2550	.0017
70	-.2696	-.2657	-.2648	-.2667	.0023
80	-.2830	-.2775	-.2780	-.2795	.0023
90	-.2960	-.2900	-.2903	-.2921	.0025
100	-.3100	-.3023	-.3030	-.3051	.0033
110	-.3220	-.3130	-.3160	-.3170	.0033
120	-.3300	-.3220	-.3245	-.3255	.0030

Table 12.

.004 M quinhydrone in M/20 sodium carbonate. pH 10.85 (Corr.)

Time in Minutes	Run No. 18	Run No. 46	Run No. 47	Run No. 49	Run No. 90
0	-.1500	-.1490	-.1480	-.1490	-.1470
2	-.1650	-.1583	-.1550	-.1615	-.1580
5	-.1770	-.1685	-.1670	-.1695	-.1700
10	-.1888	-.1822	-.1823	-.1820	-.1830
20	-.2060	-.2040	-.2010	-.2070	-.2034
30	-.2200	-.2190	-.2155	-.2210	-.2190
40	-.2320	-.2336	-.2275	-.2335	-.2320
50	-.2428	-.2485	-.2383	-.2465	-.2450
60	-.2530	-.2630	-.2485	-.2600	-.2580
70	-.2658	-.2780	-.2595	-.2730	-.2710
80	-.2800	-.2930	-.2695	-.2860	-.2854
90	-.2960	-.3075	-.2810	-.2990	-.2996
100	-.3135	-.3220	-.2920	-.3120	-.3130

Time in Minutes	Mean Value	Mean Deviation
0	-.1486	.0011
2	-.1596	.0028
5	-.1702	.0025
10	-.1834	.0019
20	-.2043	.0018
30	-.2189	.0014
40	-.2317	.0017
50	-.2453	.0020
60	-.2565	.0046
70	-.2694	.0058
80	-.2826	.0063
90	-.2966	.0064
100	-.3105	.0074

Table 14.

.004 M. quinhydrone in phosphate buffer pH 11.27

Time in Minutes	Run No. 98	Run No. 129	Run No. 130	Mean Value	Mean Deviation
0	-.1690	-.1770	-.1650	-.1685	.0057
2	-.1840	-.1920	-.1800	-.1853	.0041
4	-.1940	-.2005	-.1950	-.1965	.0027
6	-.2020	-.2080	-.2090	-.2063	.0029
10	-.2143	-.2180	-.2210	-.2178	.0023
15	-.2255	-.2290	-.2310	-.2285	.0023
20	-.2358	-.2390	-.2392	-.2380	.0015
25	-.2460	-.2480	-.2470	-.2470	.0007
30	-.2565	-.2570	-.2543	-.2559	.0017
40	-.2790	-.2755	-.2715	-.2753	.0026
45	-.2913	-.2860	-.2815	-.2863	.0034
50	-.3070	-.2980	-.2915	-.2988	.0057
55	-.3220	-.3100	-.3025	-.3115	.0070
60	-.3400	-.3230	-.3160	-.3263	.0091
65	-.3555	-.3400	-.3290	-.3415	.0093
70	-.3655	-.3510	-.3430	-.3532	.0082
80	-.3768	-.3665	-.3600	-.3677	.0060
90	-.3846	-.3760	-.3720	-.3775	.0047
100	-.3923	-.3820	-.3810	-.3851	.0049
120	-.4020	-.3930	-.3920	-.3957	.0042

Table 15.

.004 M quinhydrone in phosphate buffer pH 11.663 (Corr.)

Time in Minutes	Run No. 96	Run No. 94	Run No. 95	Mean Value	Mean Deviation
0	-.1800	-.1870	-.1830	-.1833	.0024
1	-.1950	-.1990	-.1970	-.1970	.0013
3	-.2100	-.2120	-.2100	-.2107	.0009
6	-.2240	-.2250	-.2230	-.2240	.0007
10	-.2373	-.2395	-.2370	-.2379	.0010
15	-.2510	-.2550	-.2500	-.2520	.0020
20	-.2650	-.2720	-.2700	-.2690	.0027
25	-.2810	-.2900	-.2840	-.2850	.0033
28	-.2920	-.3040	-.3000	-.2987	.0044
30	-.3015	-.3150	-.3100	-.3088	.0049
35	-.3280	-.3440	-.3370	-.3363	.0056
40	-.3540	-.3720	-.3620	-.3627	.0062
45	-.3804	-.3980	-.3900	-.3893	.0060
48	-.3920	-.4060	-.4010	-.3997	.0051
50	-.3985	-.4100	-.4060	-.4048	.0047
55	-.4086	-.4175	-.4150	-.4137	.0034
60	-.4140	-.4230	-.4225	-.4198	.0039

Table 16.

.004 M. quinhydrone in borax buffer pH 10.33 (Corrected)

Time in Minutes	Run No. 141	Run No. 142	Run No. 144	Mean Value	Mean Deviation
0	-.1380	-.1335	-.1330	-.1348	.0021
2	-.1435	-.1390	-.1375	-.1400	.0023
5	-.1495	-.1450	-.1445	-.1467	.0019
10	-.1575	-.1533	-.1546	-.1551	.0016
15	-.1640	-.1605	-.1627	-.1624	.0013
20	-.1700	-.1665	θ.1665	-.1677	.0016
30	-.1795	-.1770	-.1772	-.1779	.0011
40	-.1878	-.1855	-.1858	-.1864	.0010
50	-.1950	-.1930	-.1932	-.1937	.0008
60	-.2010	-.2003	-.1997	-.2003	.0004
70	-.2067	-.2070	-.2060	-.2066	.0004
80	-.2123	-.2128	-.2118	-.2123	.0003
90	-.2178	-.2183	-.2176	-.2179	.0003
100	-.2235	-.2238	-.2235	-.2236	.0001
110	-.2291	-.2292	-.2292	-.2292	.0000
120	-.2349	-.2348	-.2352	-.2350	.0002

Table No. 17

.004 molar quinhydrone in borax buffer pH 11.00 (Corrected)

Time in Minutes	Run No. 137	Run No. 138	Run No. 139	Mean Value	Mean Deviation
0	-.1580	-.1530	-.1500	-.1537	.0029
2	-.1645	-.1650	-.1645	-.1647	.0002
5	-.1800	-.1830	-.1790	-.1807	.0016
10	-.1951	-.1970	-.1970	-.1951	.0028
20	-.2073	-.2140	-.2163	-.2125	.0038
30	-.2205	-.2280	-.2285	-.2257	.0034
40	-.2325	-.2407	-.2397	-.2376	.0028
50	-.2450	-.2530	-.2518	-.2499	.0033
60	-.2570	-.2656	-.2638	-.2621	.0034
70	-.2700	-.2800	-.2755	-.2752	.0034
80	-.2832	-.2960	-.2887	-.2893	.0045
90	-.2980	-.3120	-.3035	-.3045	.0050
100	-.3130	-.3250	-.3180	-.3187	.0042
110	-.3250	-.3350	-.3283	-.3294	.0037
120	-.3330	-.3410	-.3360	-.3367	.0029

Table 18

pH of buffer (Corr.)	dE/dt k' (m.v/min.) Initial	dE/dt k' (m.V./min.) Constant	k'/OH x 10^{-6}	k'/ OH x 10^{-3}	k'/ OH $^{\frac{1}{2}}$
A 8.396	.070	.026	2.49	10.4	16.55
A 8.58	.170	.045	3.80	11.8	23.0
A 8.985	.230	.087	9.66	9.0	28.
A 9.20	.310	.129	15.85	8.2	32.
A 9.709	.640	.303	51.17	5.9	42.
B 9.801	.780	.555	63.24	8.8	70.
A 9.872	.900	.465	74.47	6.3	54.
B 10.23	1.80	1.11	169.8	6.5	85.
D 10.33	2.68	1.18	213.8	5.52	81.
B 10.41	3.00	1.36	257.0	5.3	85.
B 10.85	5.50	2.56	707.9	3.6	96
C 10.86	4.00	2.50	724.4	3.4	93.
D 11.00	6.50	2.86	1000.	2.9	89.
C 11.14	10.0	4.00	1380.	2.9	108
C 11.66	11.0	5.70	4571.	1.3	266.

pH of buffer (Corr.)	$\frac{k'}{[OH^-]}$ x 10^{-1}	k' / $\frac{[OH^-]}{10^{-3} + [OH^-]}$	k'/ $\frac{[OH^-]}{10^{-4} + [OH^-]}$
A 8.396	16.	10.4	1.2
A 8.58	18.	11.9	1.2
A 8.985	19.	9.1	1.0
A 9.20	20.	8.3	0.9
A 9.709	22.	6.2	.9
B 9.801	35.	9.3	1.4
A 9.872	26.	6.8	1.1
B 10.23	36.	7.6	1.8
D 10.33	33.	6.8	1.2
B 10.41	34.	6.6	1.9
B 10.85	32.	6.2	2.9
C 10.86	31.	5.9	2.8
D 11.00	29	5.7	3.8
C 11.14	32	6.8	4.3
C 11.66	21	6.9	6.9

Conclusions

1. In the entire pH range from 1.0 to 11.7, the oxidation-reduction potential of hydroquinone - quinone may be expressed by the equation:

$$E = E_0 + \frac{R\,T}{2\,F} \ln \frac{[\text{Quinone}]}{[\text{Hydroquinone}]} + \frac{R\,T}{2\,F} \ln \frac{[H^+]^3 + K_1[H^+]^2 + K_1 K_2 [H^+]}{[H^+] + K_3}$$

At 20° C. against the saturated calomel electrode as zero, $E_0 = .4530$ $K_1 = 1.1 \times 10^{-10}$, $K_2 = 3.97 \times 10^{-12}$ and $K_3 = 10^{-11}$.

2. The presence of quinhydrone lowers the pH value of alkaline buffers. For .004 molar quinhydrone solutions in the ordinary buffer solutions, the lowering is not appreciable below pH 9.0, but may be as much as 0.3 pH in sodium carbonate buffers. In the alkaline phosphate and borax mixtures, the effect is about 0.15 pH.

3. Beyond about pH 8.0 the quinhydrone electrode is unstable. In the absence of oxygen, the potential becomes more basic with time. This drift is highly sensitive to increasing hydroxyl ion concentration. The curves for e. m. f. against time approach straight lines after a change of about 30 millivolts. The slope of these straight portions is approximately $6.55 \times [OH^-]/\ 10^{-3}+[OH^-]$ millivolts per minute. The initial portions of the curves follow the equation:

$$E = E_0' - .01262\,k\,t - .02906 \log (2 - e^{-kt}).$$

4. The drift in potential is due to the spontaneous oxidation-reduction of quinone. It appears that in alkaline solutions, quinone adds water to form hydroxyhydroquinone, which has an oxidation-reduction potential nearly equal to that of hydroquinone. This reacts with quinone to form hydroquinone and hydroxyquinone. This last may undergo changes also.

5. The reaction:

$$\text{Quinone} + \text{HOH} \longrightarrow \text{Hydroxyhydroquinone}$$

appears to be a monomolecular reaction, conditioned by the concentration of quinonate ions. The reaction constant k' appears to be about .52 mols per liter per minute.

6. It appears that quinone functions as an acid with an ionization constant of about 10^{-11}.

7. With special apparatus for mixing the solutions and for working in the absence of air, it seems possible to extend the use of the quinhydrone electrode to about pH 10 without serious error in well buffered solutions. Beyond this range the effect of hydroquinone on the actual pH of the solutions and the uncertainties of extrapolated data, would introduce large errors in the determination of pH.

Summary

The general theory of oxidation-reduction potentials has been reviewed.

The behavior of the quinhydrone electrode in alkaline solutions has been studied. It was found that the potential can be expressed by an equation which is in accord with the general theory. The drift in potential has been studied as a function of concentrations, and the kinetics of the reactions have been deduced theoretically.

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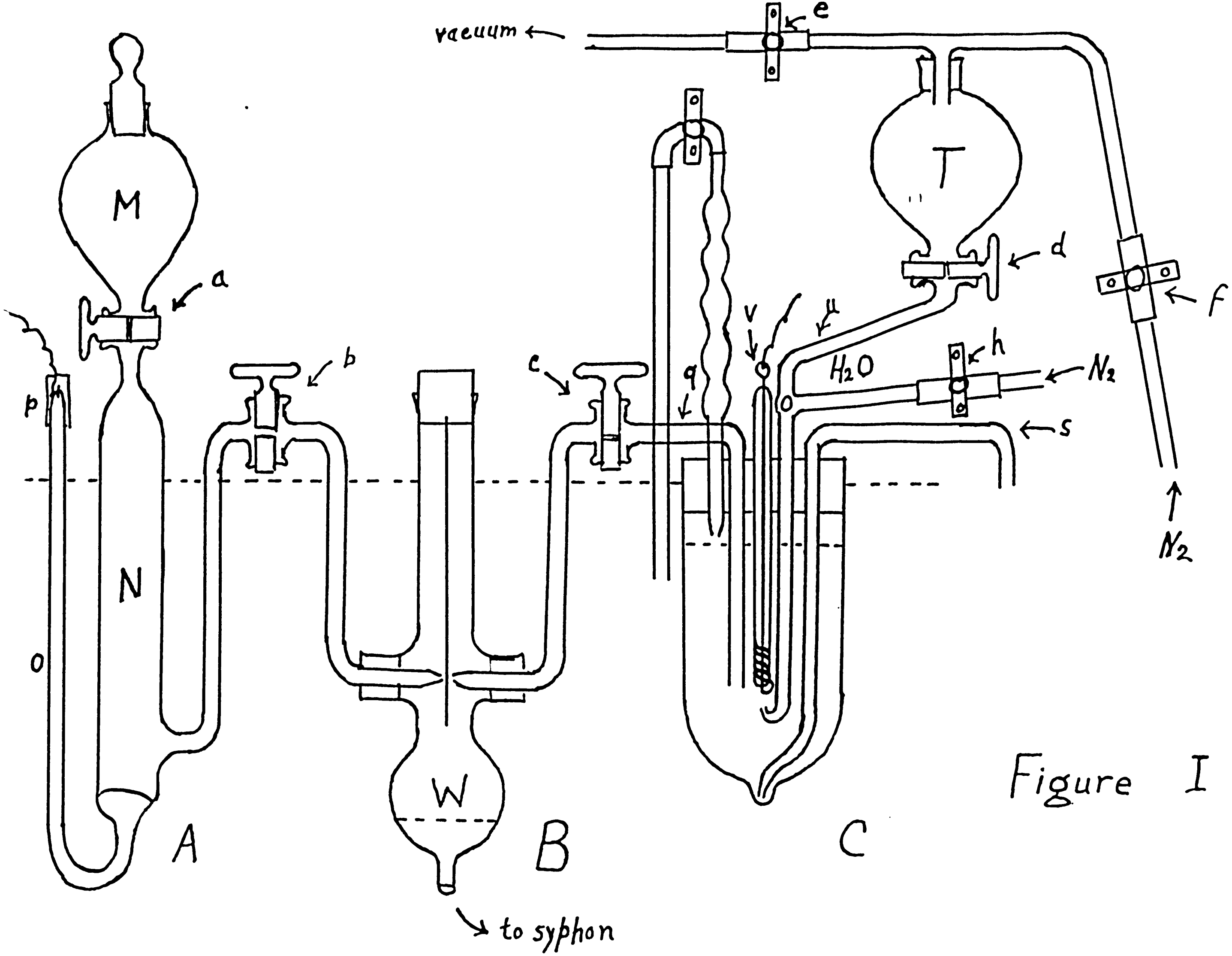


Figure I

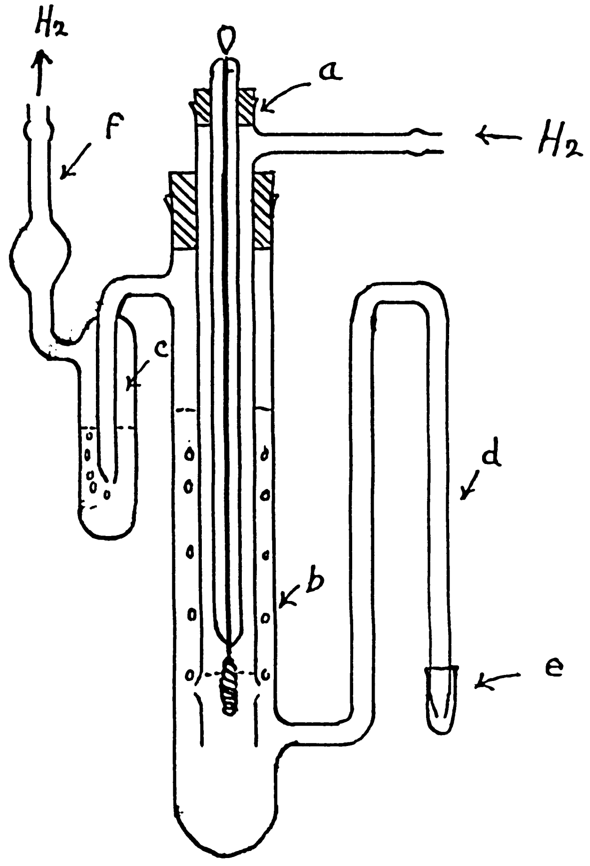


Figure II.

Plate 1.

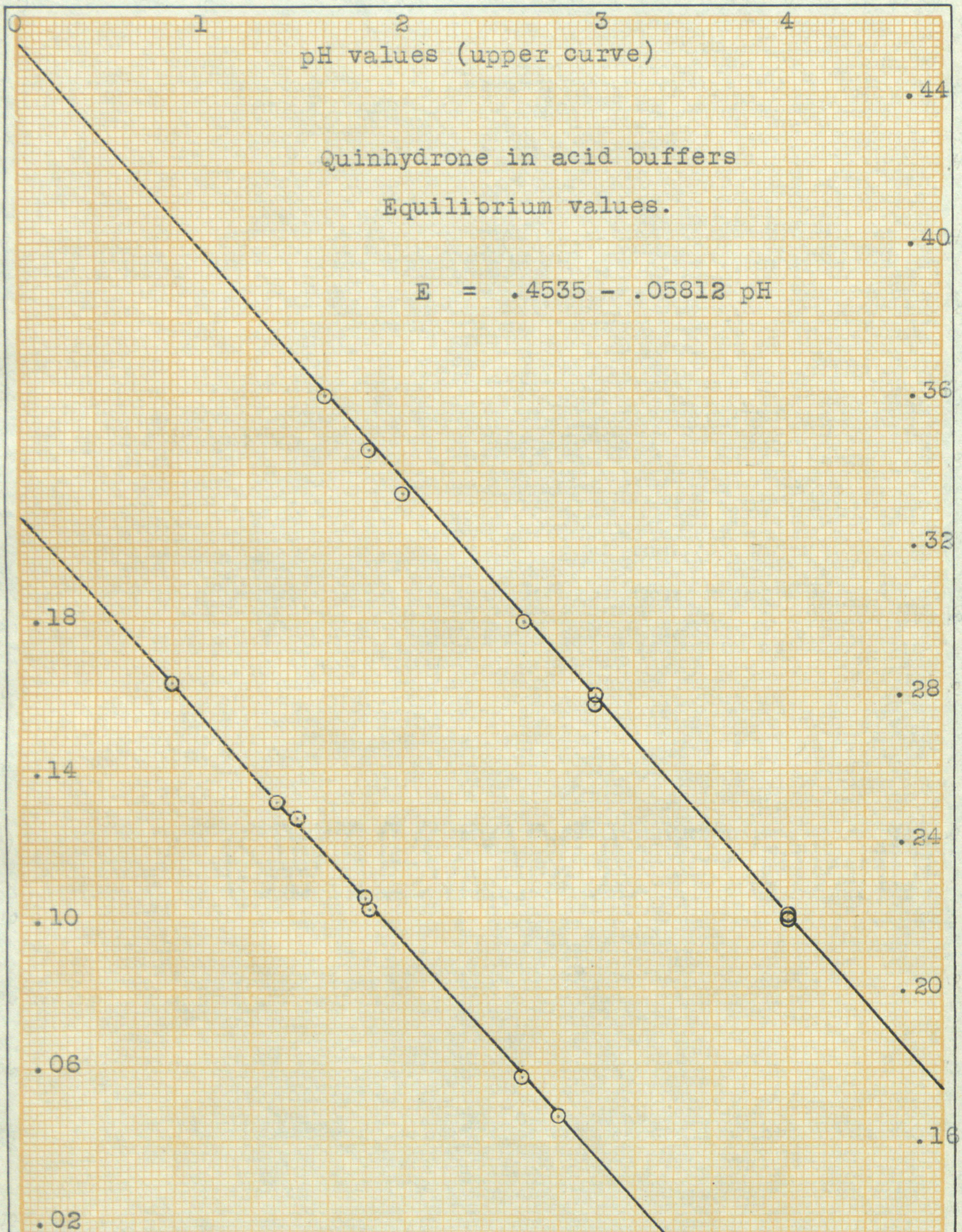
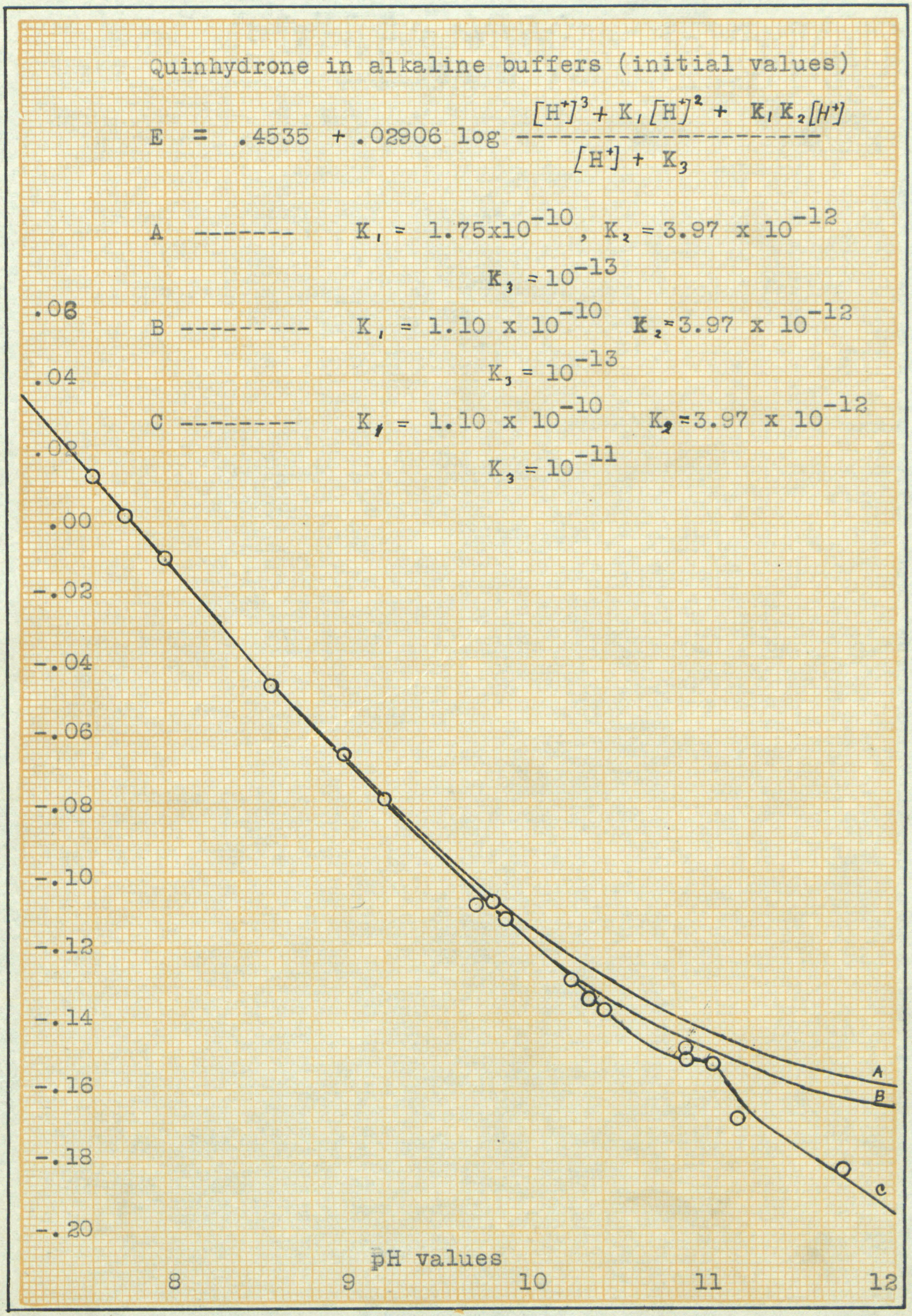

0
1
2
3
4
pH values (upper curve)
.44
Quinhydrone in acid buffers
Equilibrium values.
.40
E = .4535 - .05812 pH
.36
.32
.18
.28
.14
.24
.10
.20
.06
.16
.02
pH values (lower curve)
-.10
5
6
7
8

Plate 2



Quinhydrone in alkaline buffers (initial values)

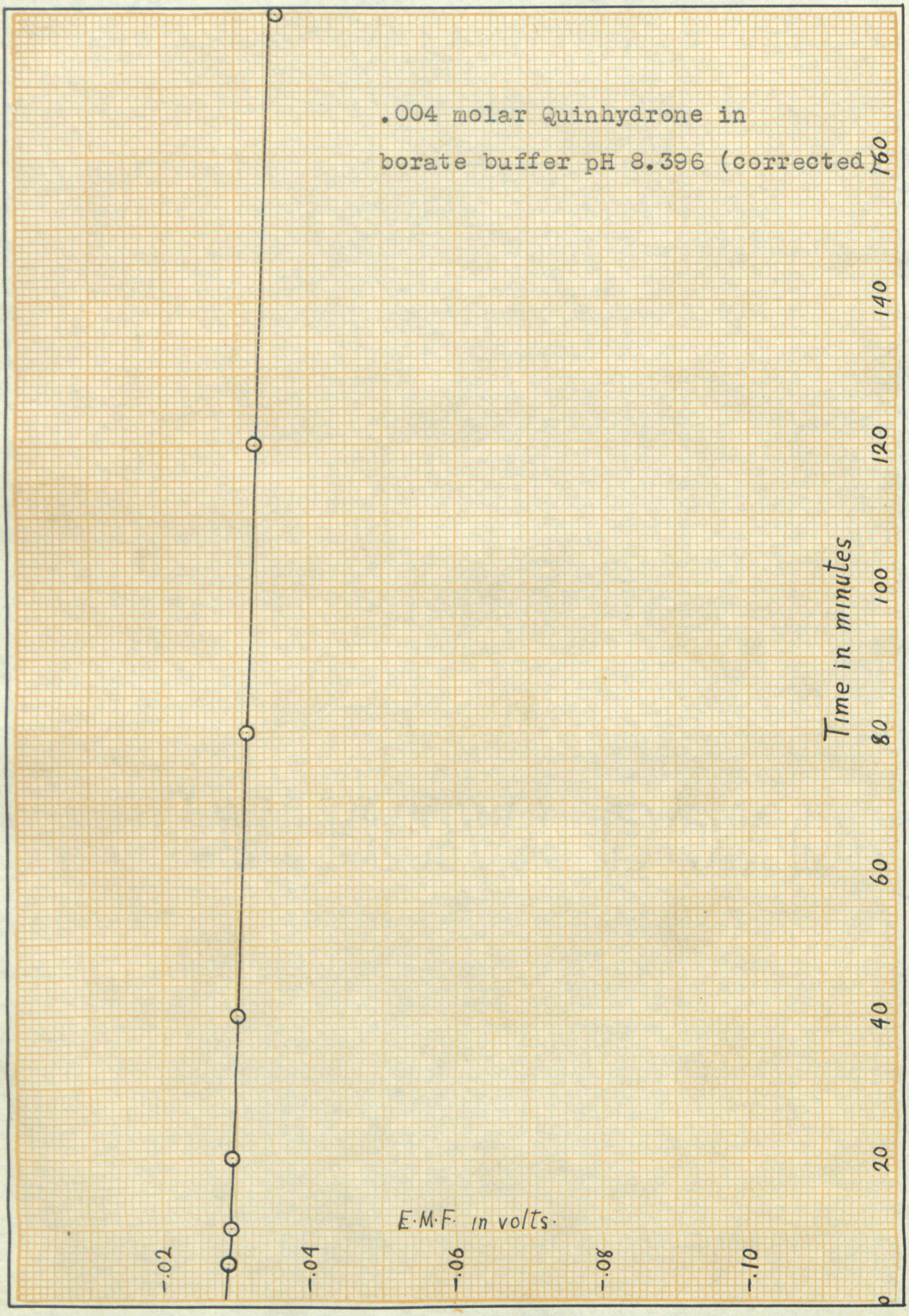
$$E = .4535 + .02906 \log \frac{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+]}{[H^+] + K_3}$$

A ------- $K_1 = 1.75 \times 10^{-10}$, $K_2 = 3.97 \times 10^{-12}$
$K_3 = 10^{-13}$

B --------- $K_1 = 1.10 \times 10^{-10}$ $K_2 = 3.97 \times 10^{-12}$
$K_3 = 10^{-13}$

C -------- $K_1 = 1.10 \times 10^{-10}$ $K_2 = 3.97 \times 10^{-12}$
$K_3 = 10^{-11}$

Plate 3.



.004 molar Quinhydrone in
borate buffer pH 8.396 (corrected)

Plate 4.

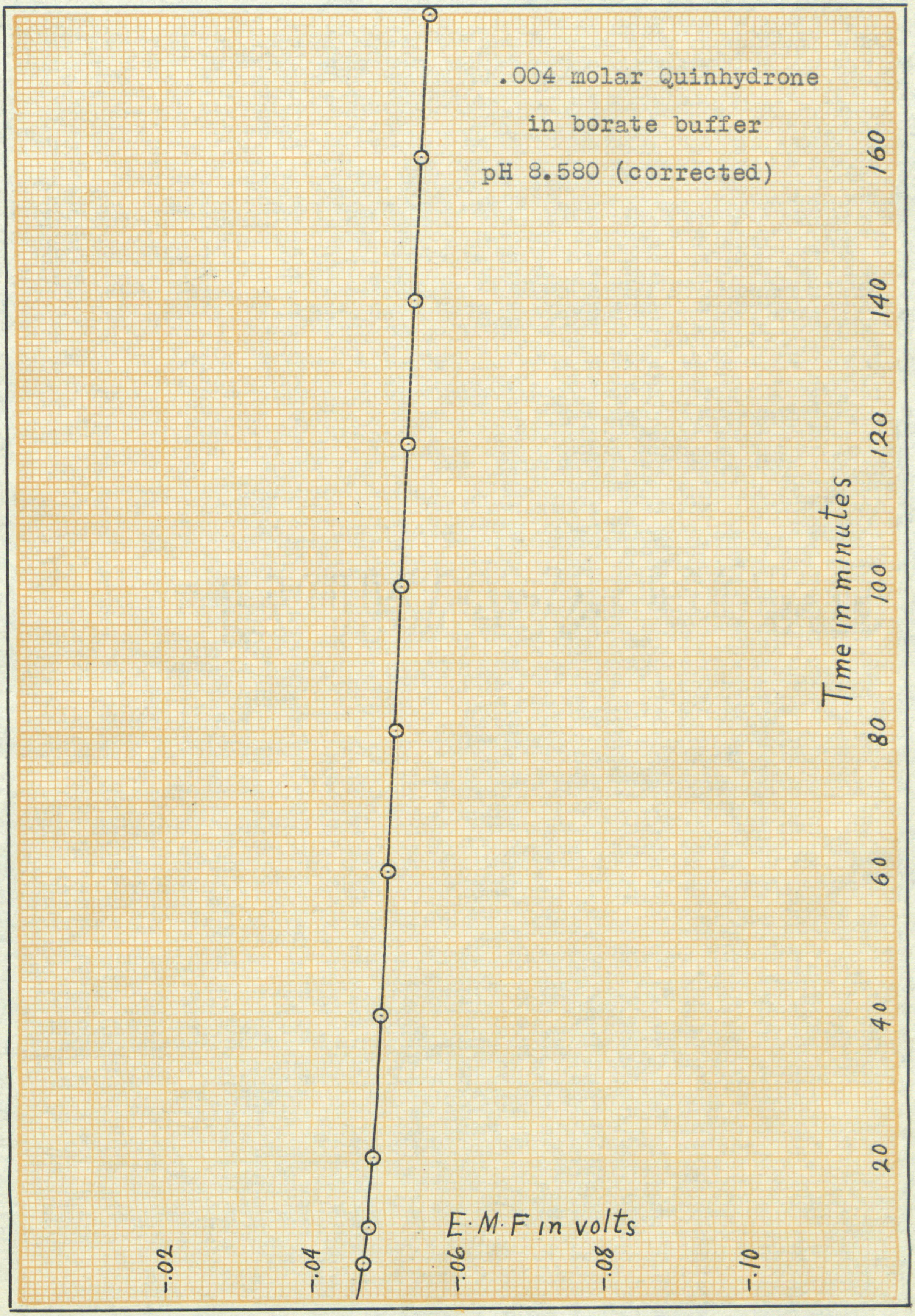
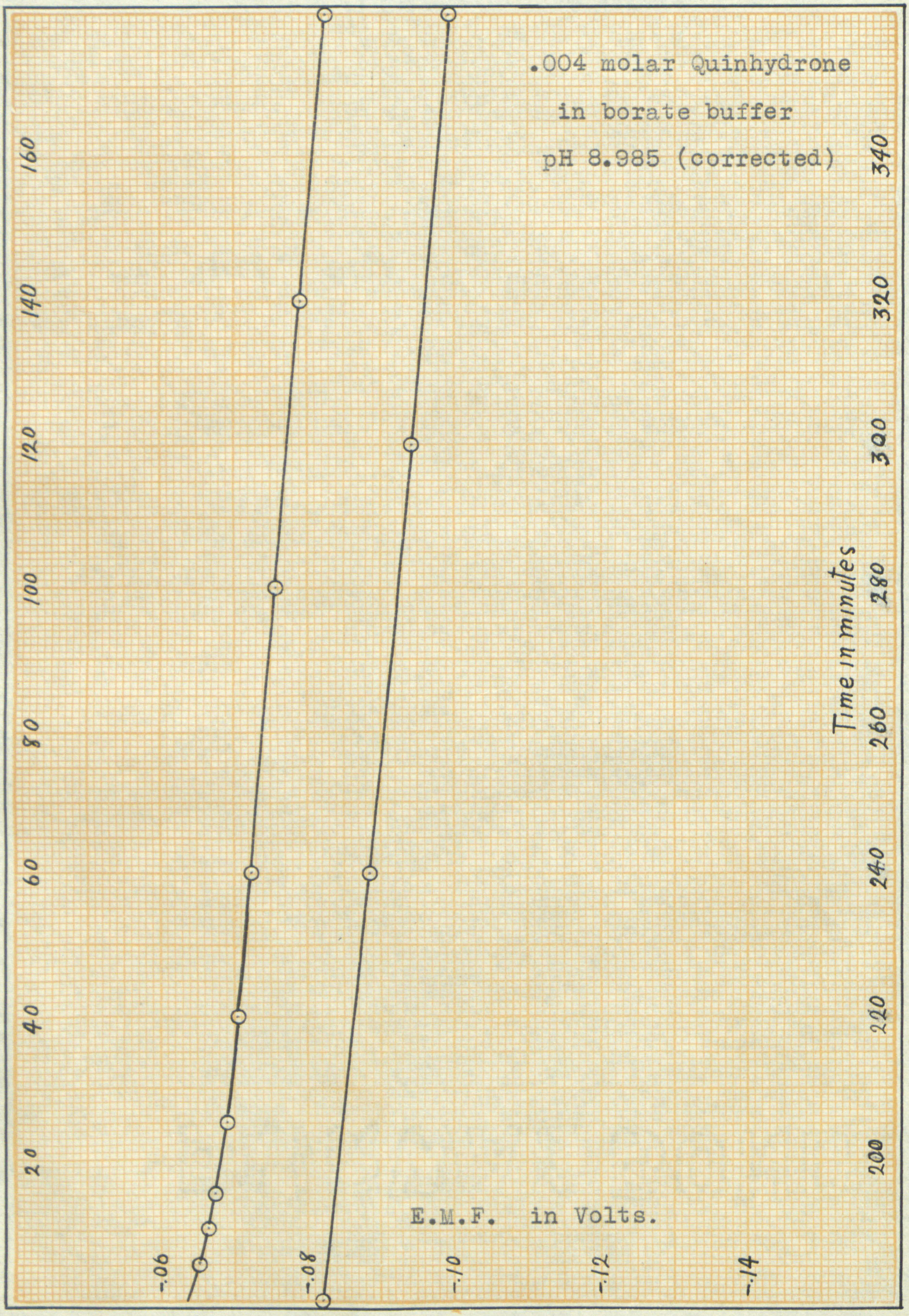

.004 molar Quinhydrone
in borate buffer
pH 8.580 (corrected)
Time in minutes
20
40
60
80
100
120
140
160
E·M·F in volts
-.02
-.04
-.06
-.08
-.10

Plate 5.



.004 molar Quinhydrone
in borate buffer
pH 8.985 (corrected)

Plate 6.

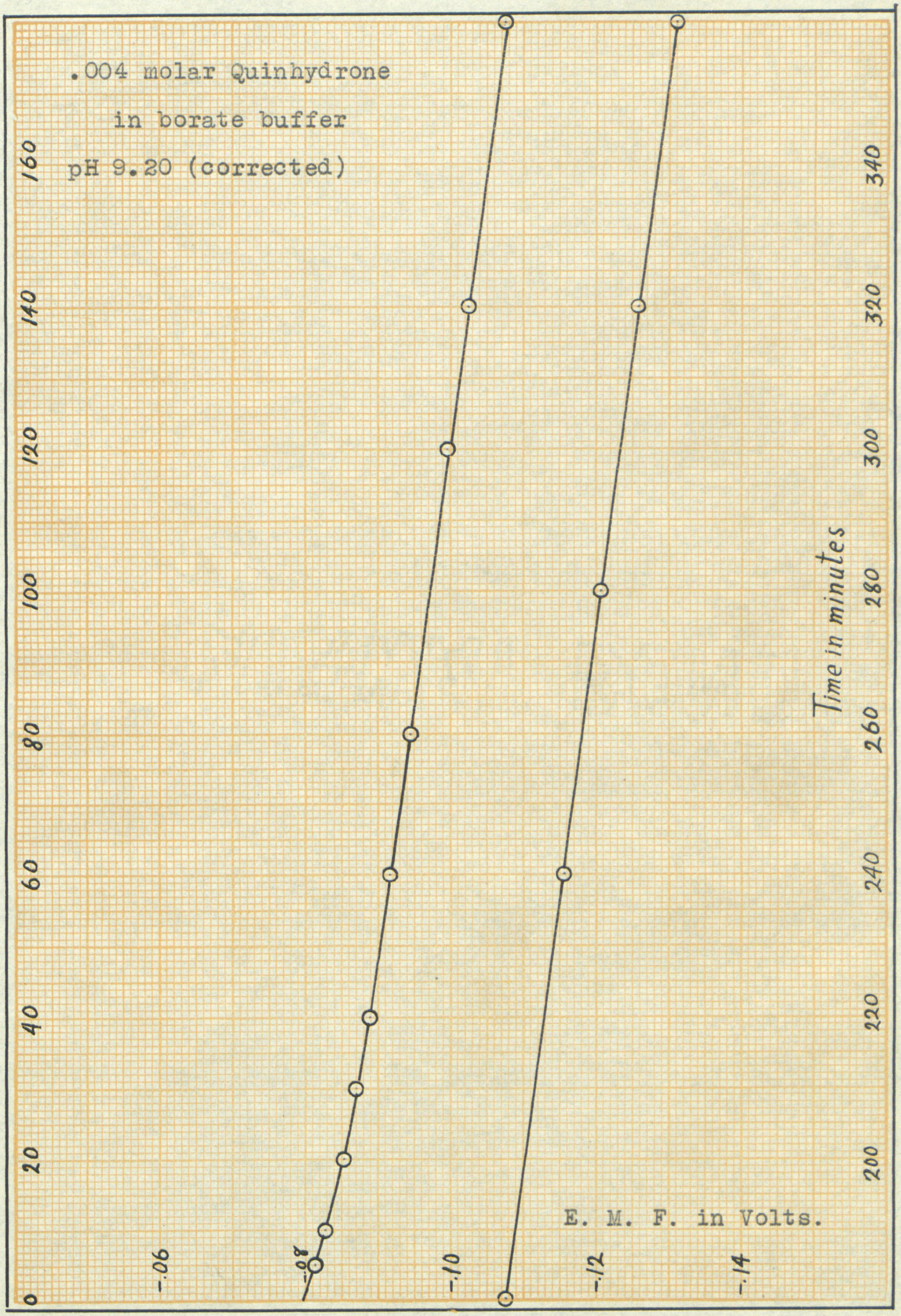

.004 molar Quinhydrone
in borate buffer
pH 9.20 (corrected)
E. M. F. in Volts.
Time in minutes
0
20
40
60
80
100
120
140
160
200
220
240
260
280
300
320
340
-.06
-.08
-.10
-.12
-.14

Plate 7.

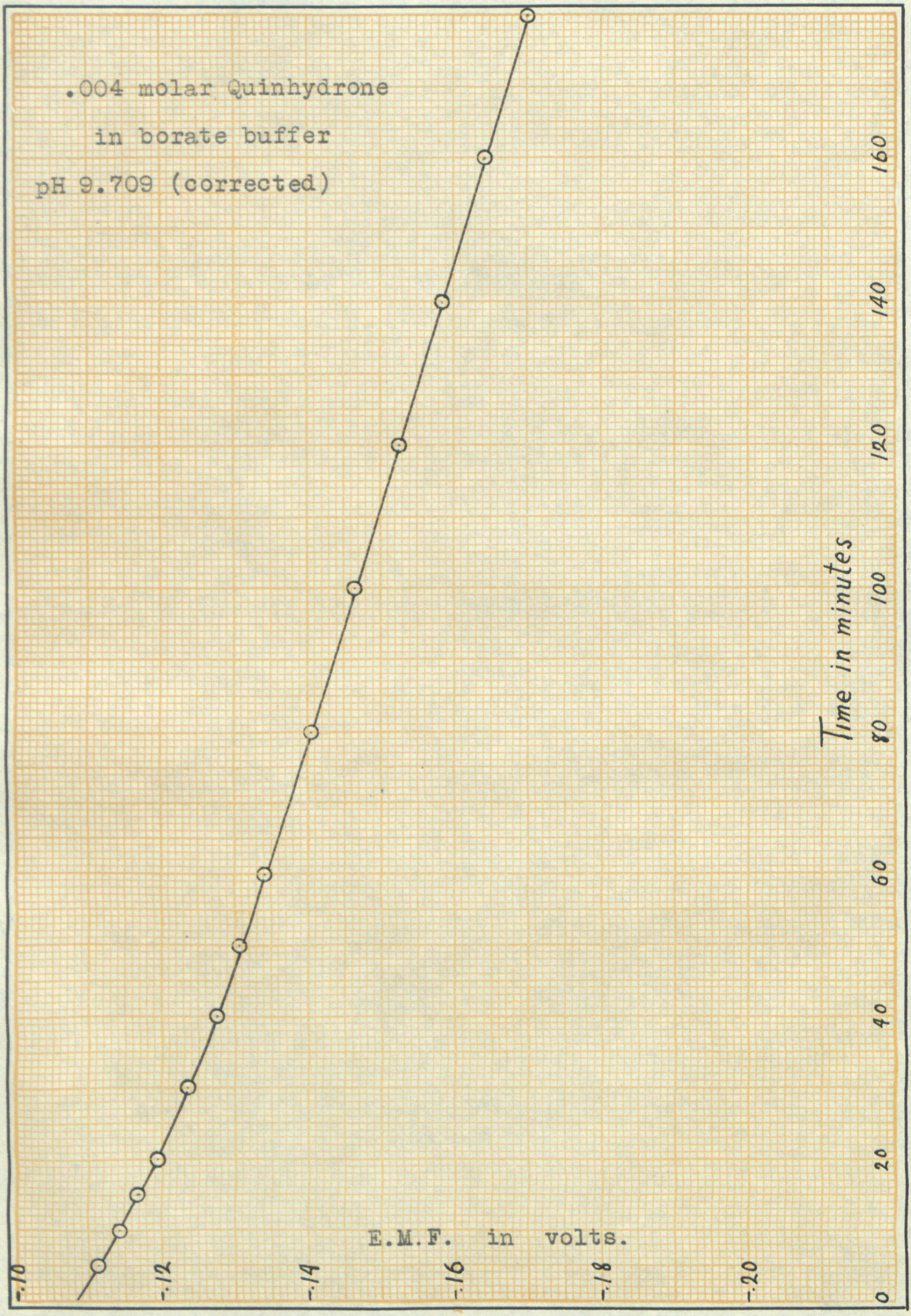

.004 molar Quinhydrone
in borate buffer
pH 9.709 (corrected)
Time in minutes
0
20
40
60
80
100
120
140
160
E.M.F. in volts.
-.10
-.12
-.14
-.16
-.18
-.20

Plate 8

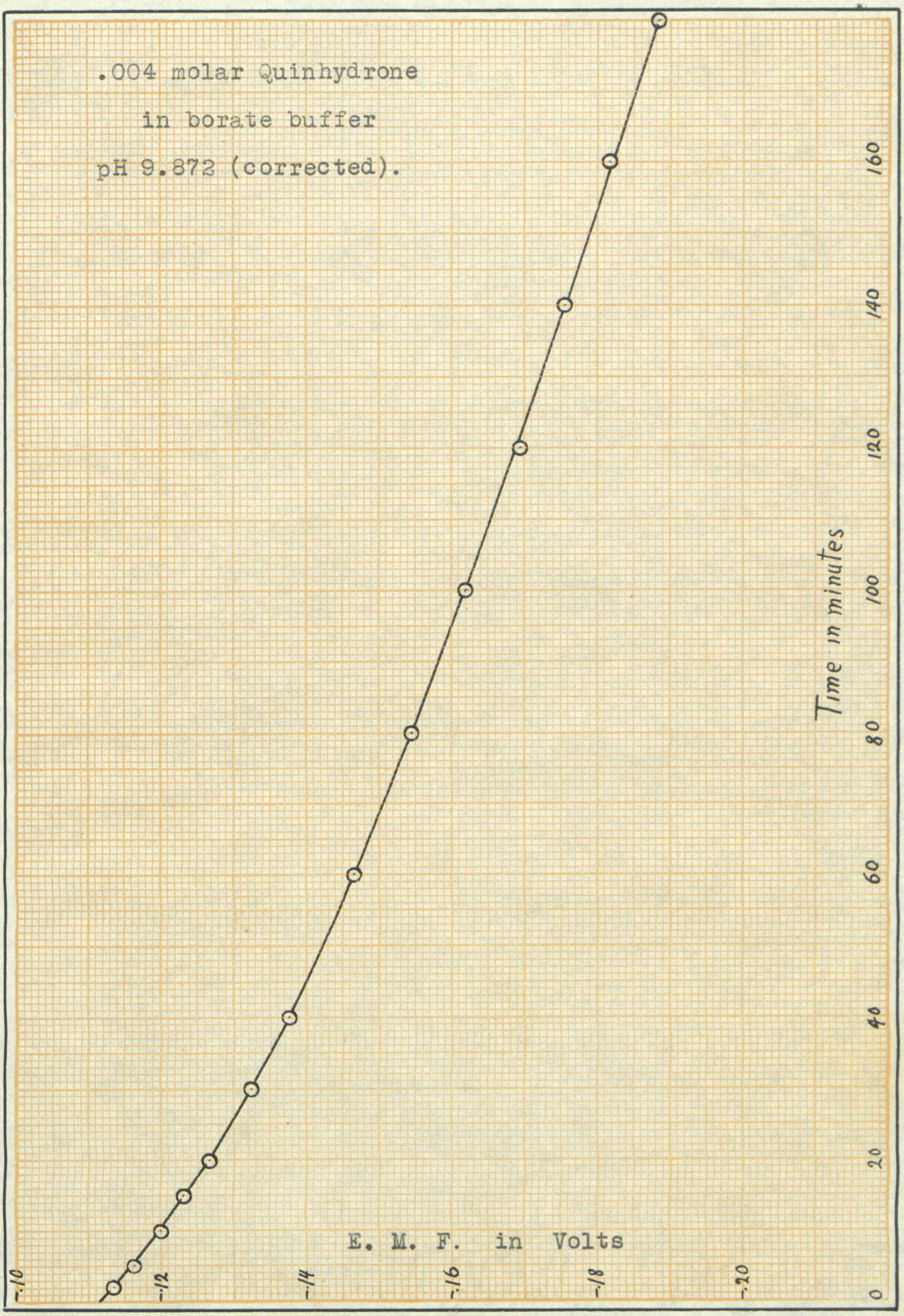

.004 molar Quinhydrone
in borate buffer
pH 9.872 (corrected).
E. M. F. in Volts
-.10
-.12
-.14
-.16
-.18
-.20
Time in minutes
0
20
40
60
80
100
120
140
160

Plate 9.

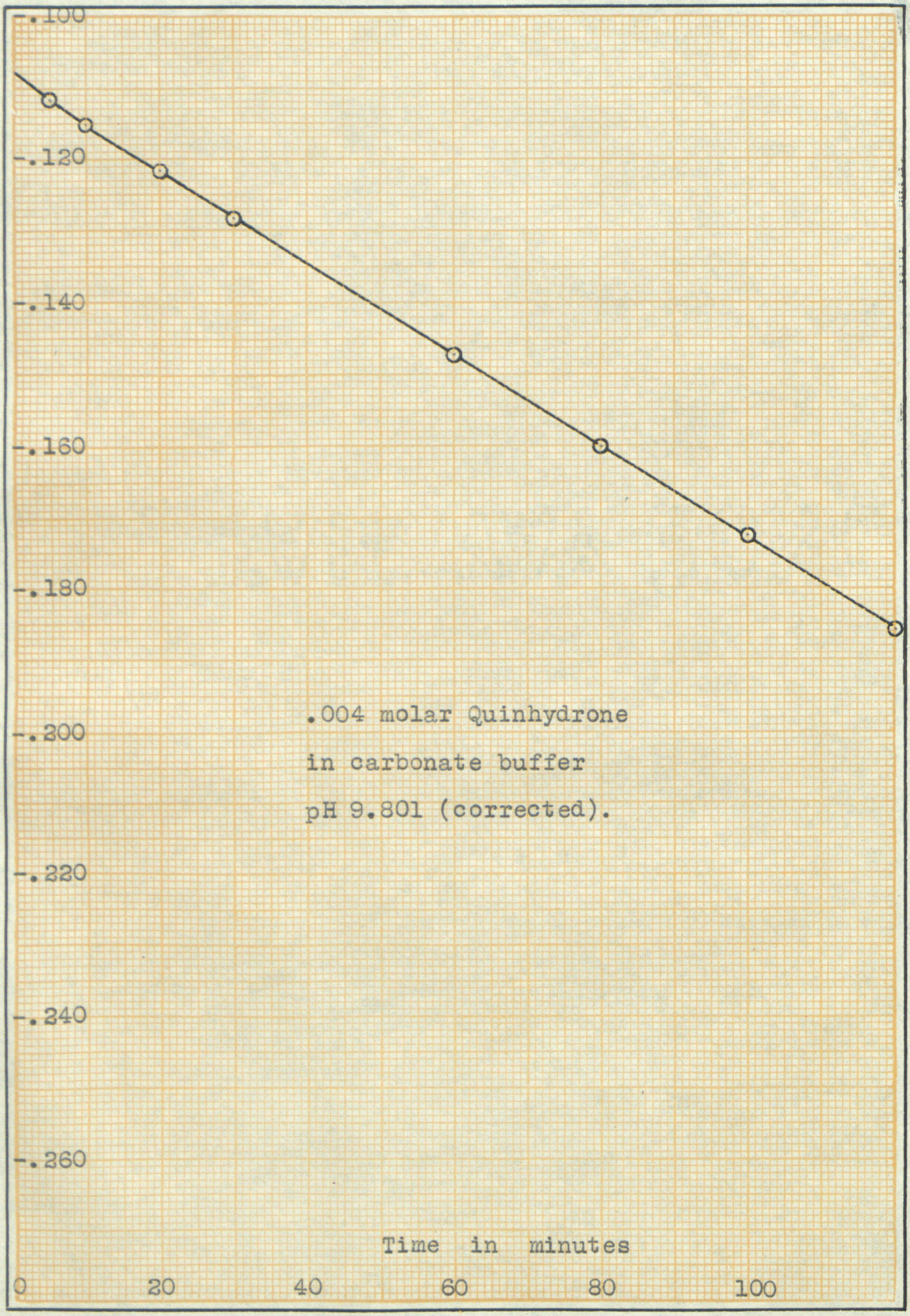

-.100
-.120
-.140
-.160
-.180
-.200
-.220
-.240
-.260
.004 molar Quinhydrone
in carbonate buffer
pH 9.801 (corrected).
Time in minutes
0
20
40
60
80
100

Plate 10

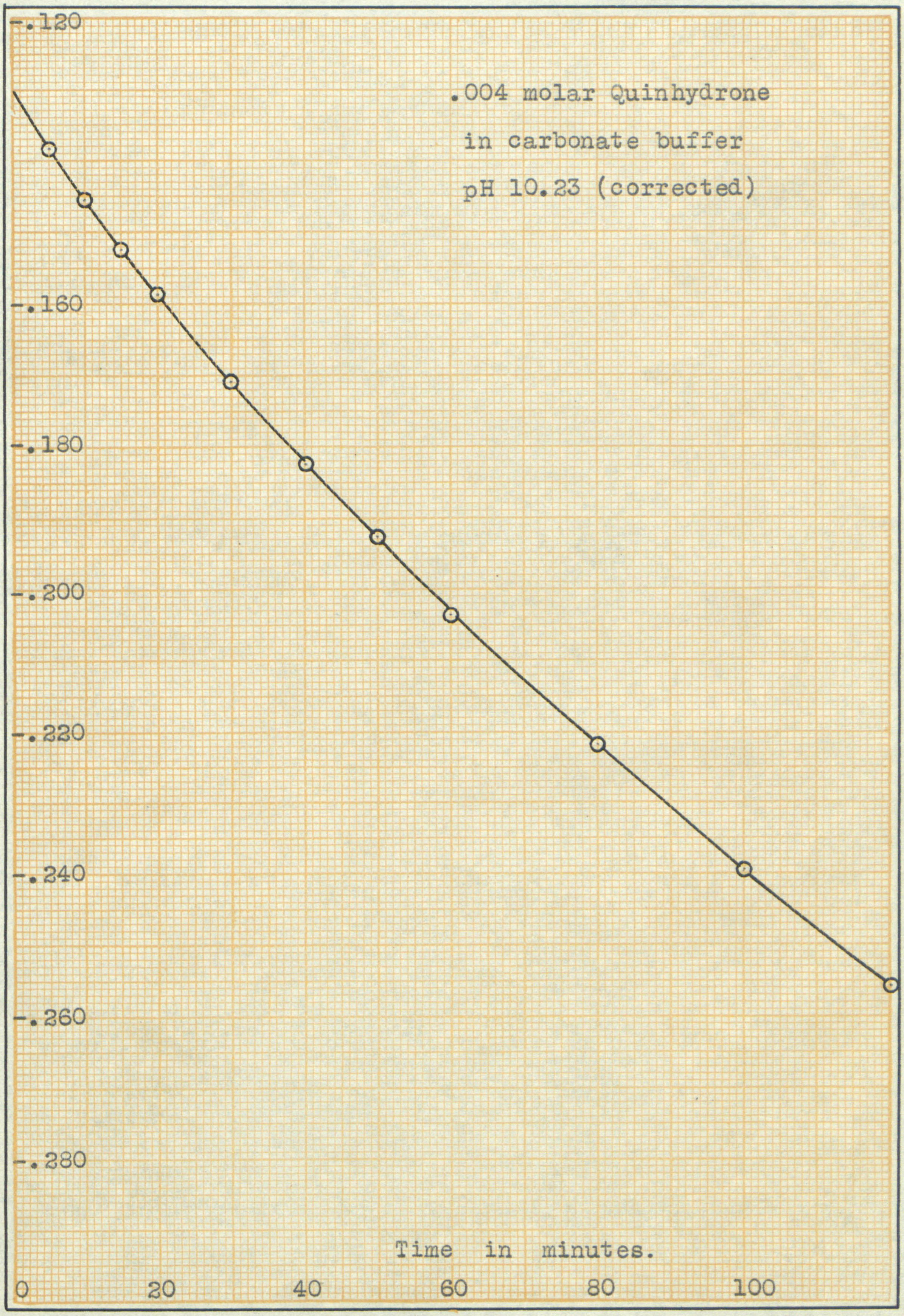

.004 molar Quinhydrone
in carbonate buffer
pH 10.23 (corrected)
-.120
-.160
-.180
-.200
-.220
-.240
-.260
-.280
Time in minutes.
0
20
40
60
80
100

Plate 11

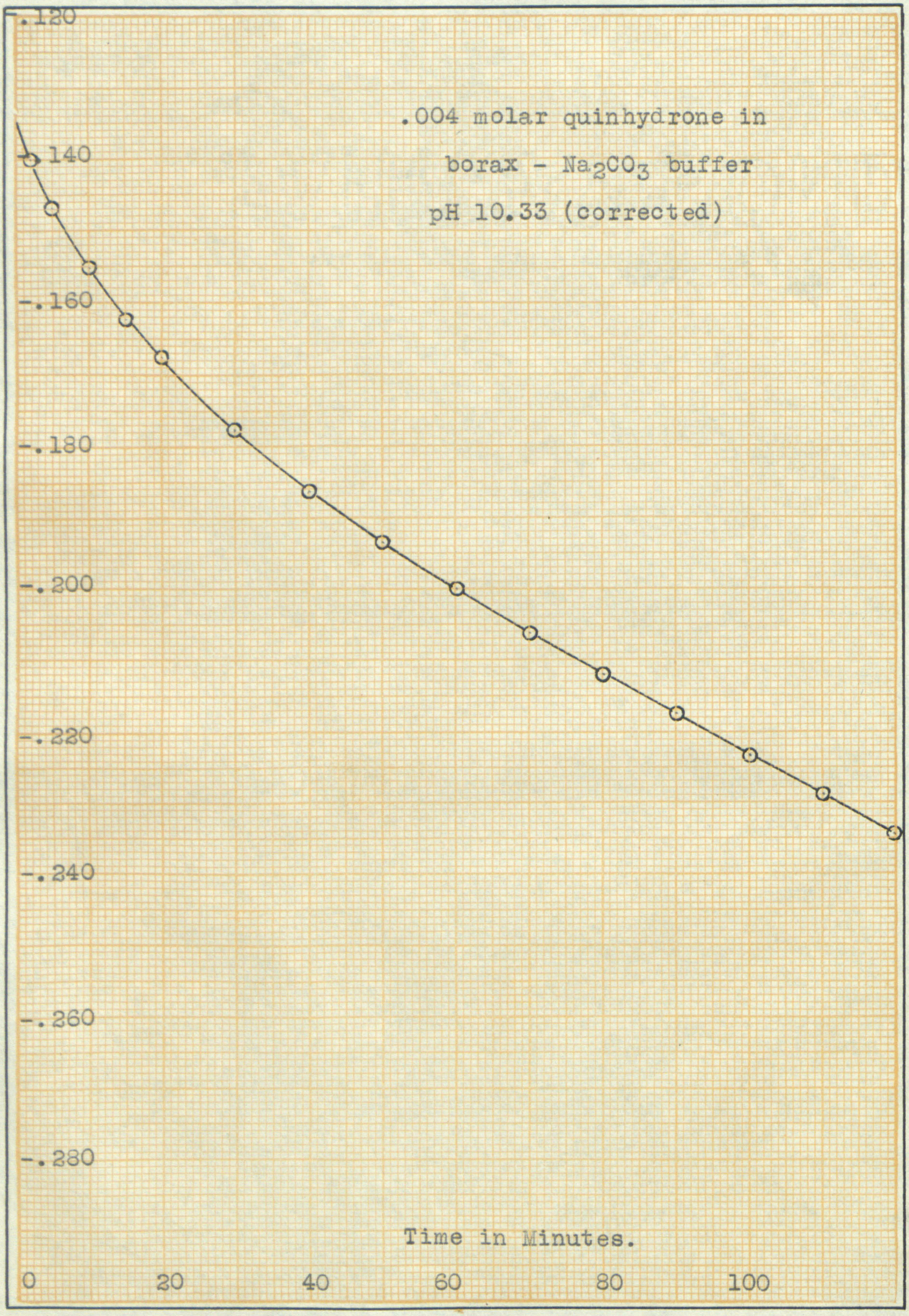

.004 molar quinhydrone in
borax - Na_2CO_3 buffer
pH 10.33 (corrected)
.120
.140
-.160
-.180
-.200
-.220
-.240
-.260
-.280
Time in Minutes.
0
20
40
60
80
100

Plate 12

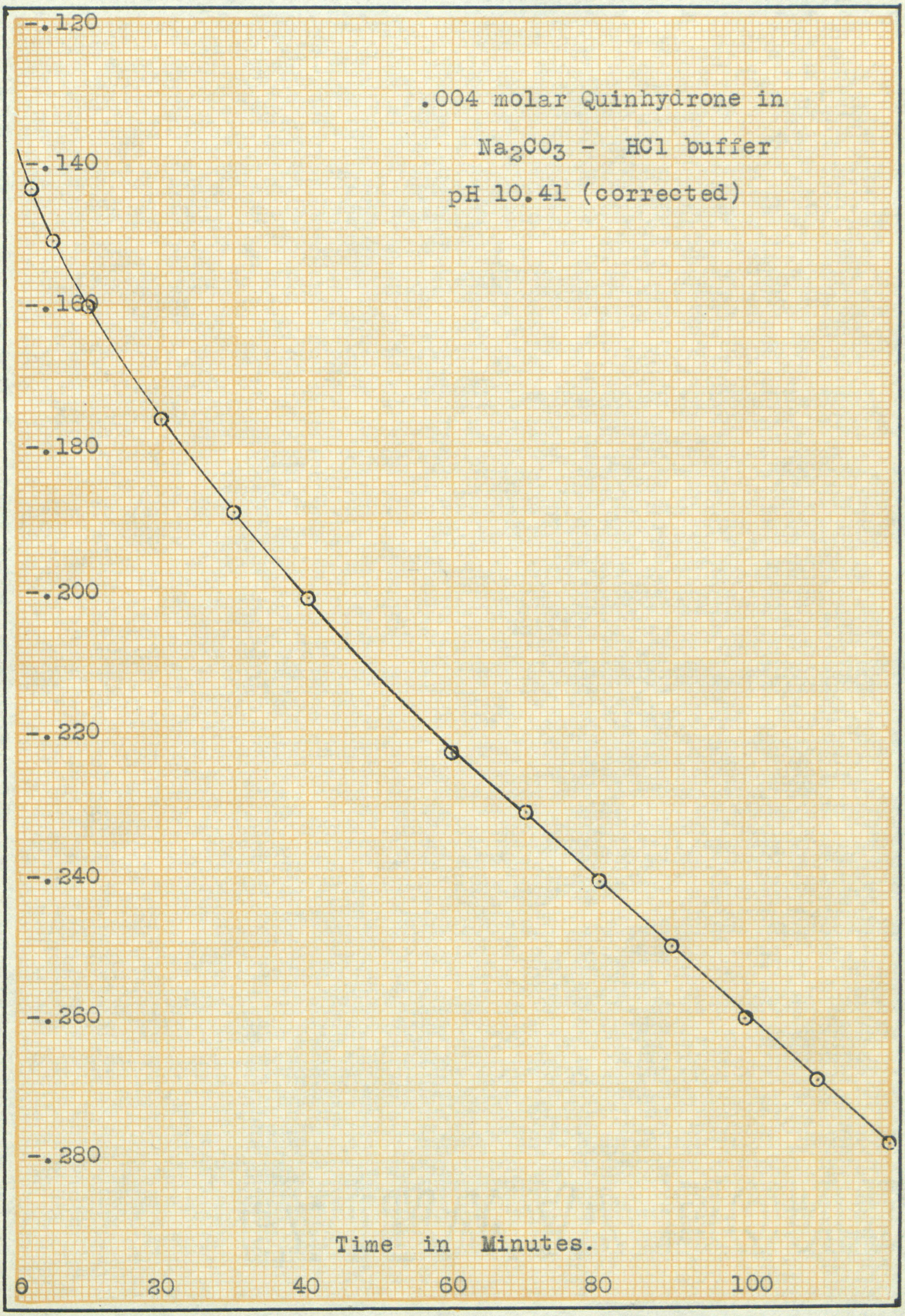

.004 molar Quinhydrone in
Na_2CO_3 - HCl buffer
pH 10.41 (corrected)
-.120
-.140
-.160
-.180
-.200
-.220
-.240
-.260
-.280
Time in Minutes.
0
20
40
60
80
100

Plate 13

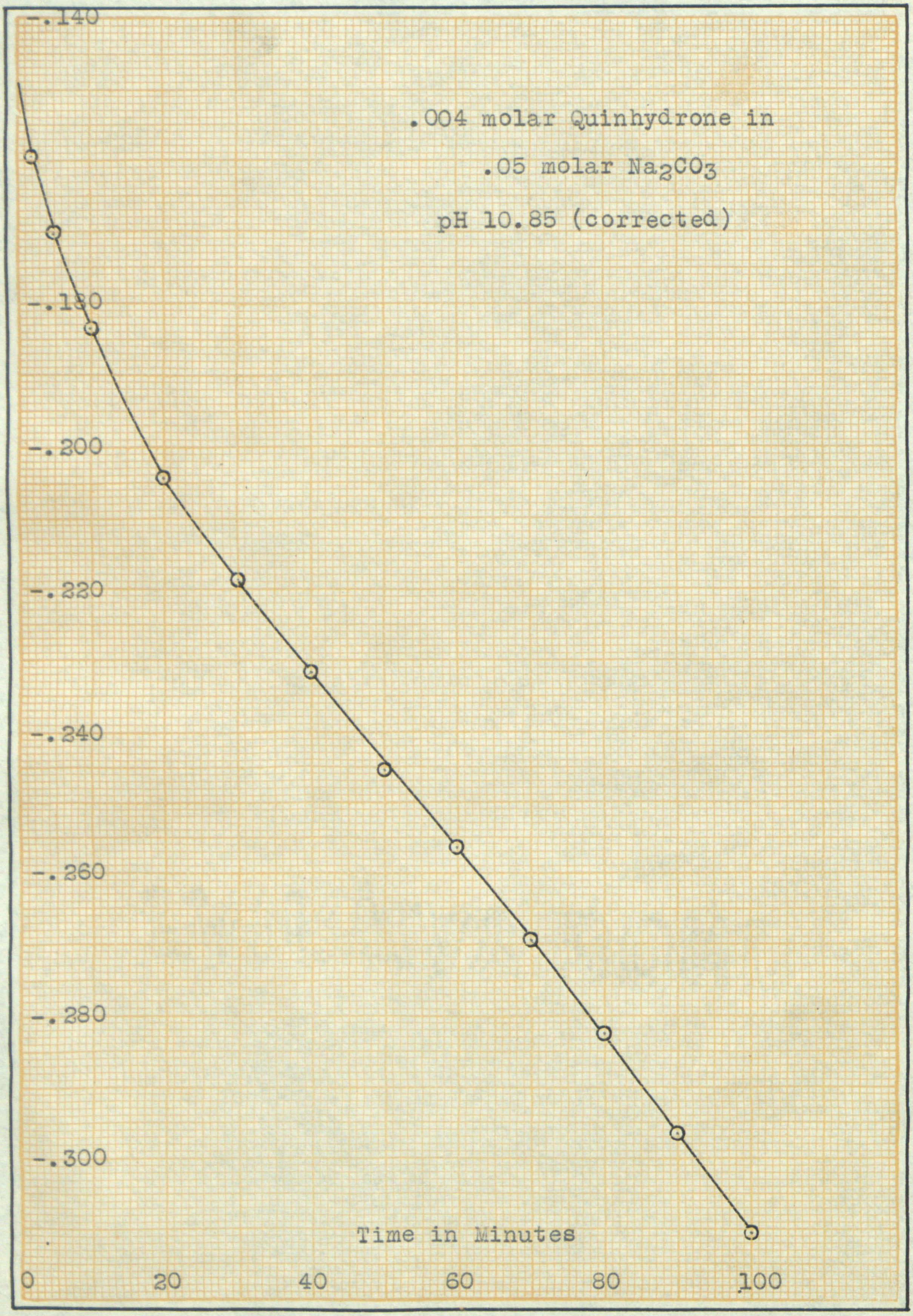
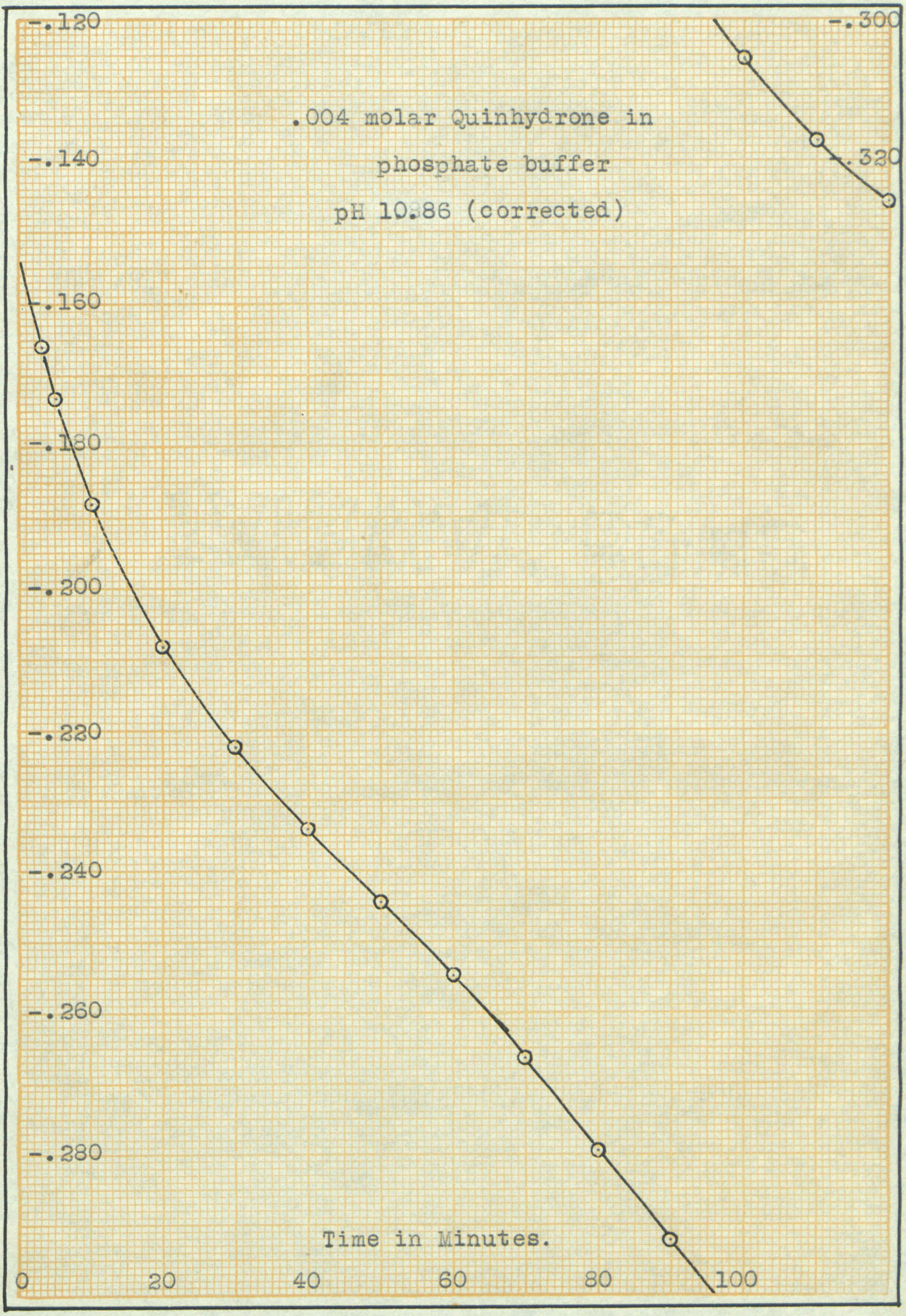
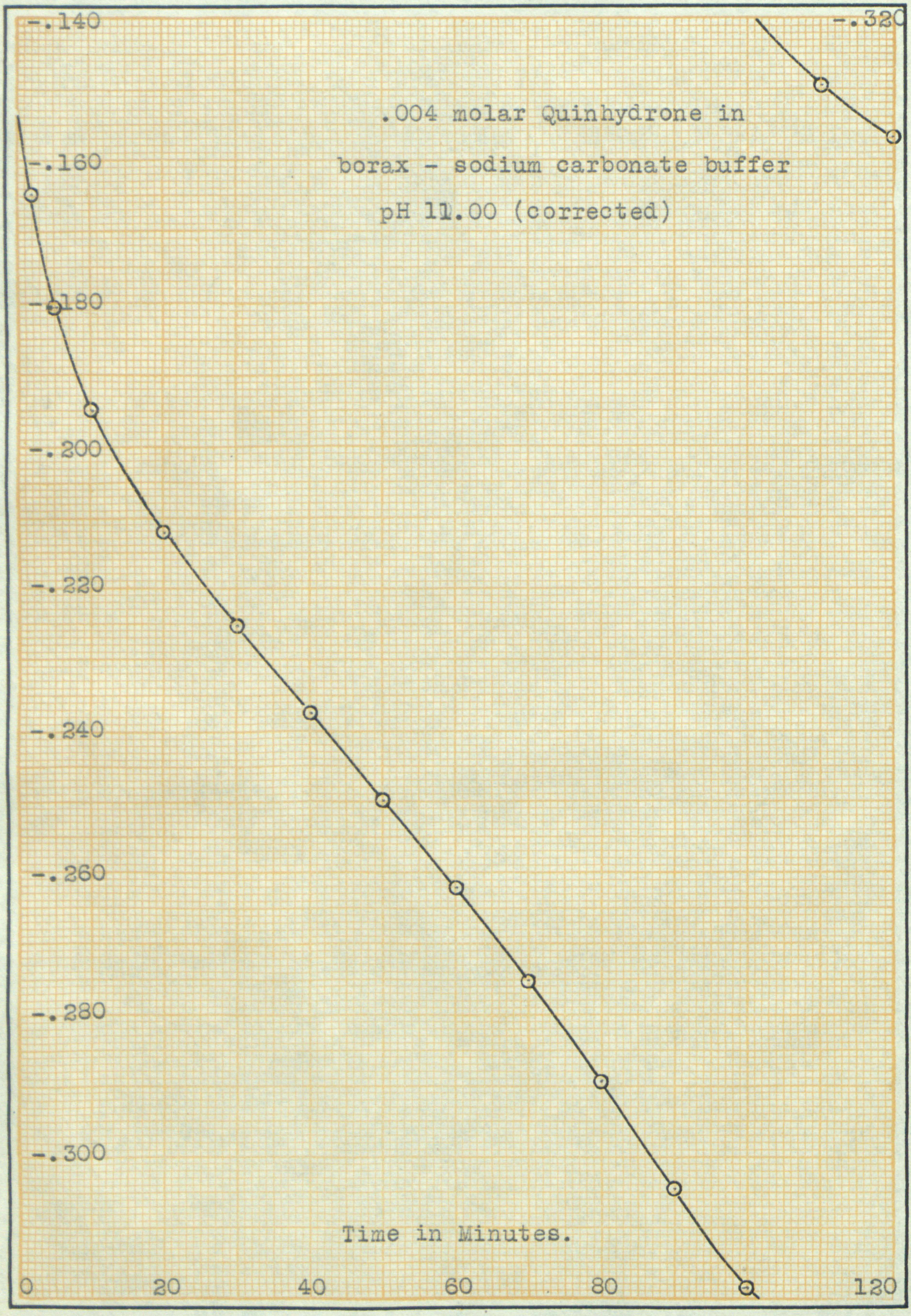

-.140
-.180
-.200
-.220
-.240
-.260
-.280
-.300
.004 molar Quinhydrone in
.05 molar Na_2CO_3
pH 10.85 (corrected)
Time in Minutes
0
20
40
60
80
100

Plate 14



.004 molar Quinhydrone in
phosphate buffer
pH 10.86 (corrected)
-.120
-.140
-.160
-.180
-.200
-.220
-.240
-.260
-.280
-.300
-.320
Time in Minutes.
0
20
40
60
80
100

Plate 15



.004 molar Quinhydrone in
borax - sodium carbonate buffer
pH 11.00 (corrected)

Plate 16

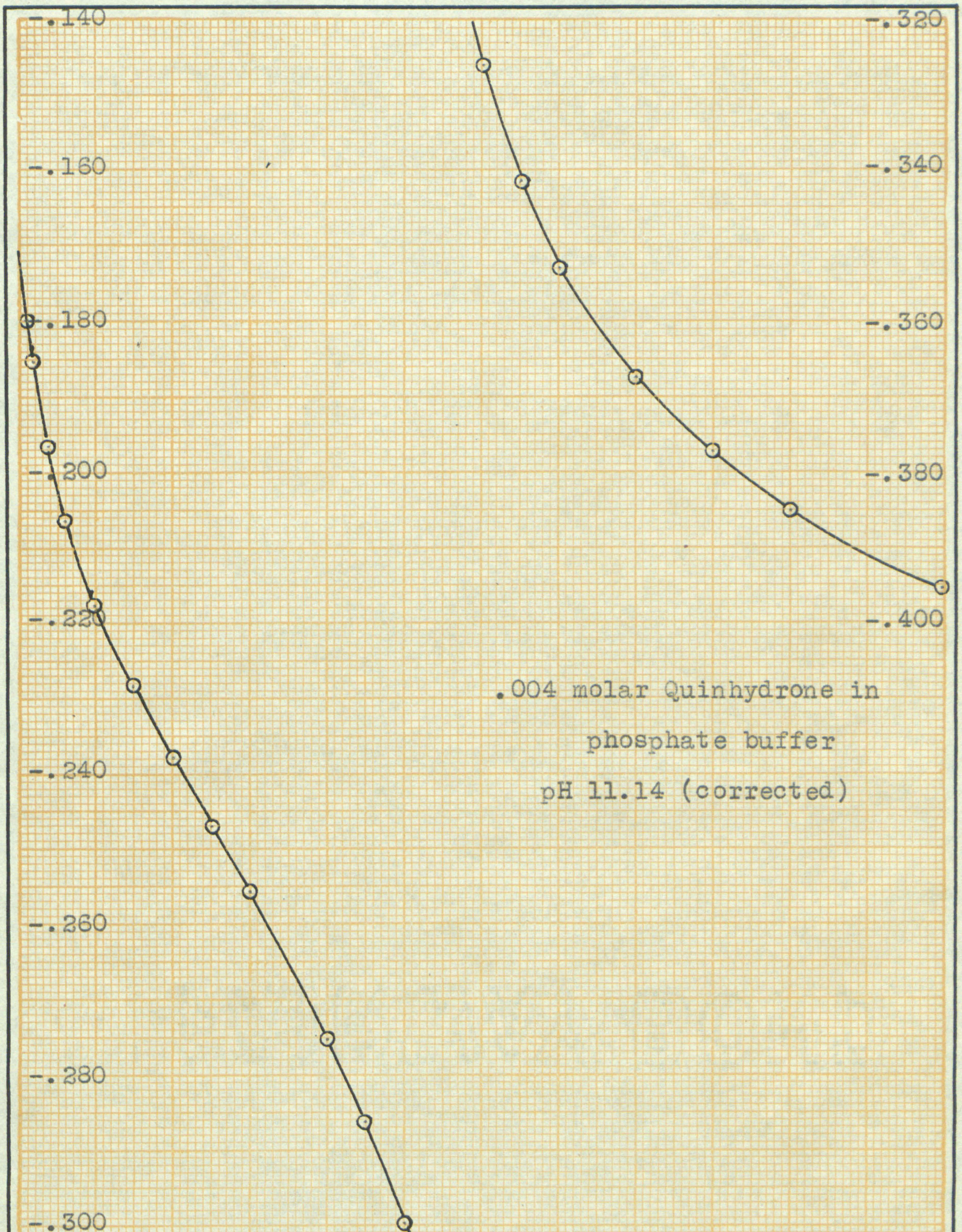
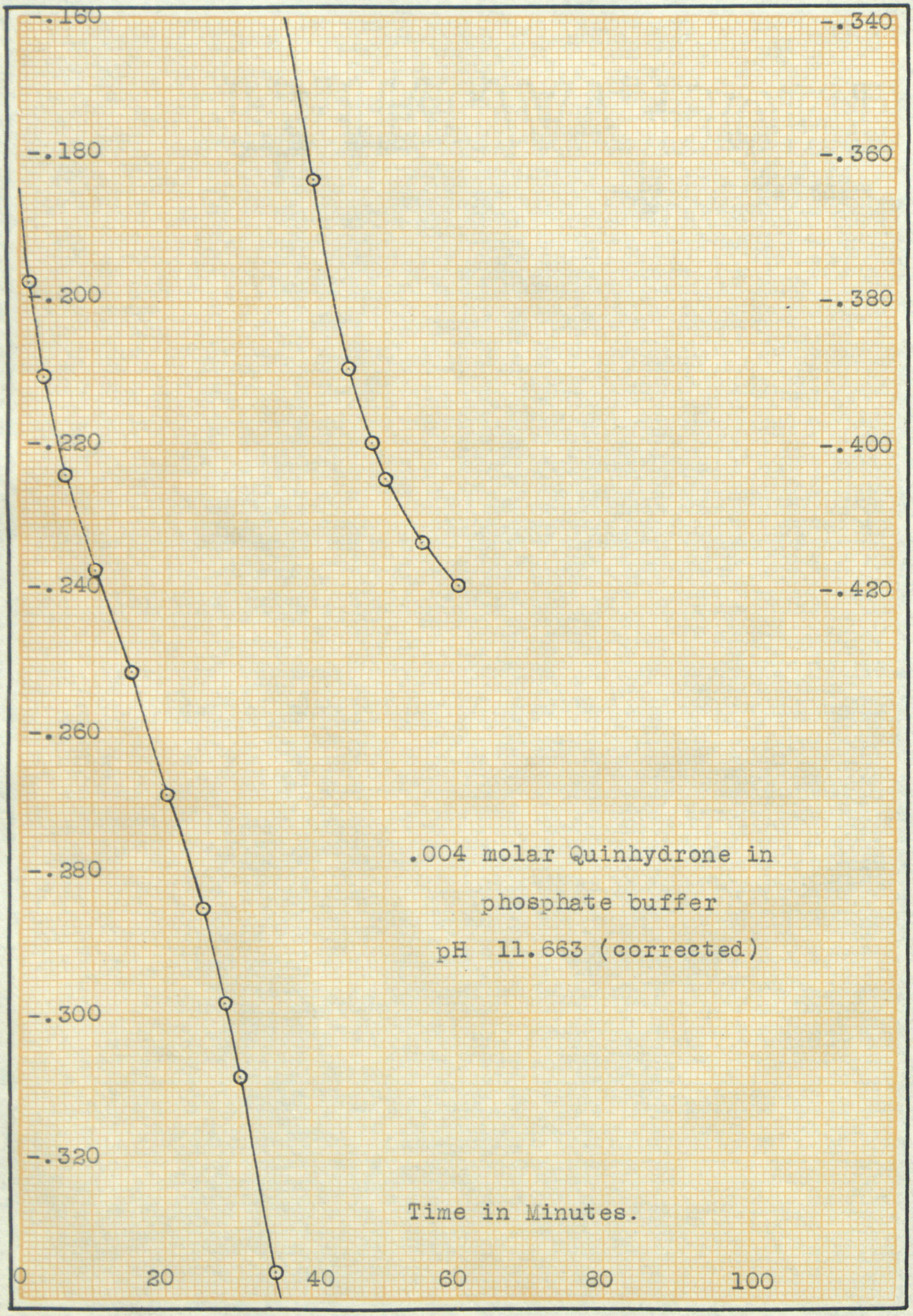

-.140
-.160
-.180
-.200
-.220
-.240
-.260
-.280
-.300
-.320
-.340
-.360
-.380
-.400
.004 molar Quinhydrone in
phosphate buffer
pH 11.14 (corrected)
Time in Minutes.
0
20
40
60
80
100

Plate 17



.004 molar Quinhydrone in
phosphate buffer
pH 11.663 (corrected)

Time in Minutes.

Plate 18

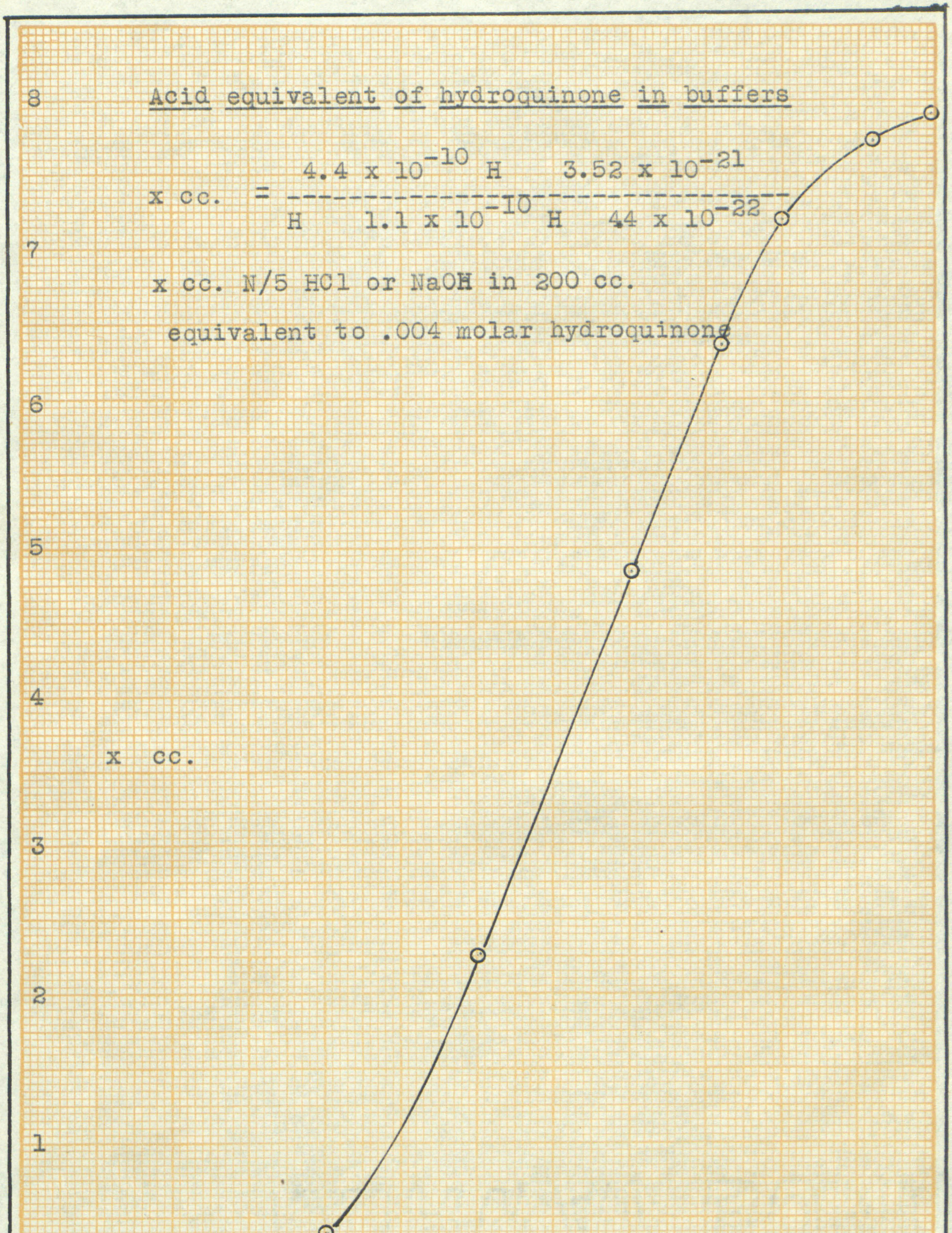

Acid equivalent of hydroquinone in buffers
x cc. = 4.4 x 10^-10 H   3.52 x 10^-21 / H   1.1 x 10^-10 H   44 x 10^-22
x cc. N/5 HCl or NaOH in 200 cc.
equivalent to .004 molar hydroquinone
x cc.
8
7
6
5
4
3
2
1
pH value
7
8
9
10
11
12
13

Plate 19.

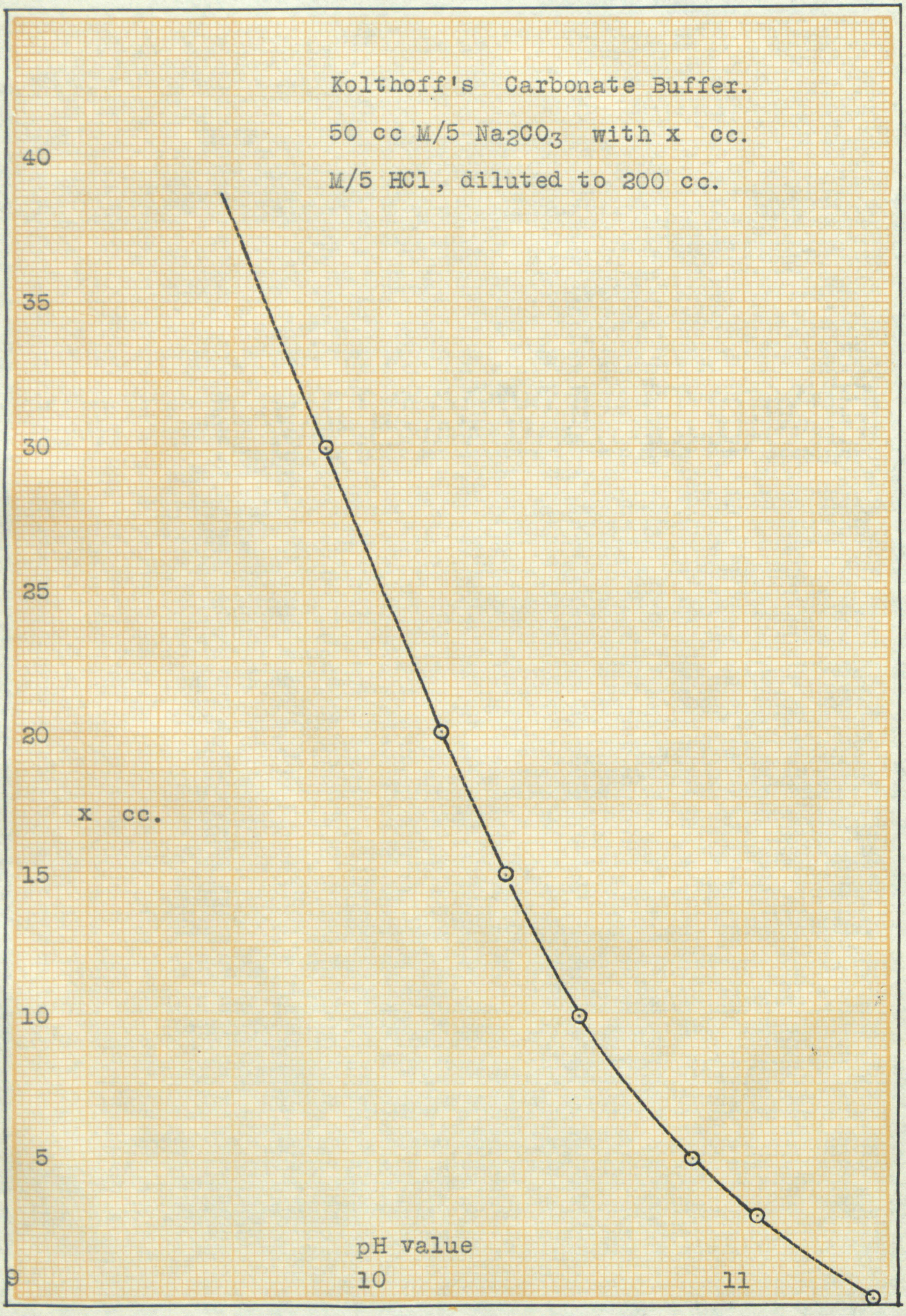

Kolthoff's Carbonate Buffer.
50 cc M/5 Na_2CO_3 with x cc.
M/5 HCl, diluted to 200 cc.
40
35
30
25
20
x cc.
15
10
5
pH value
9
10
11

Plate 20

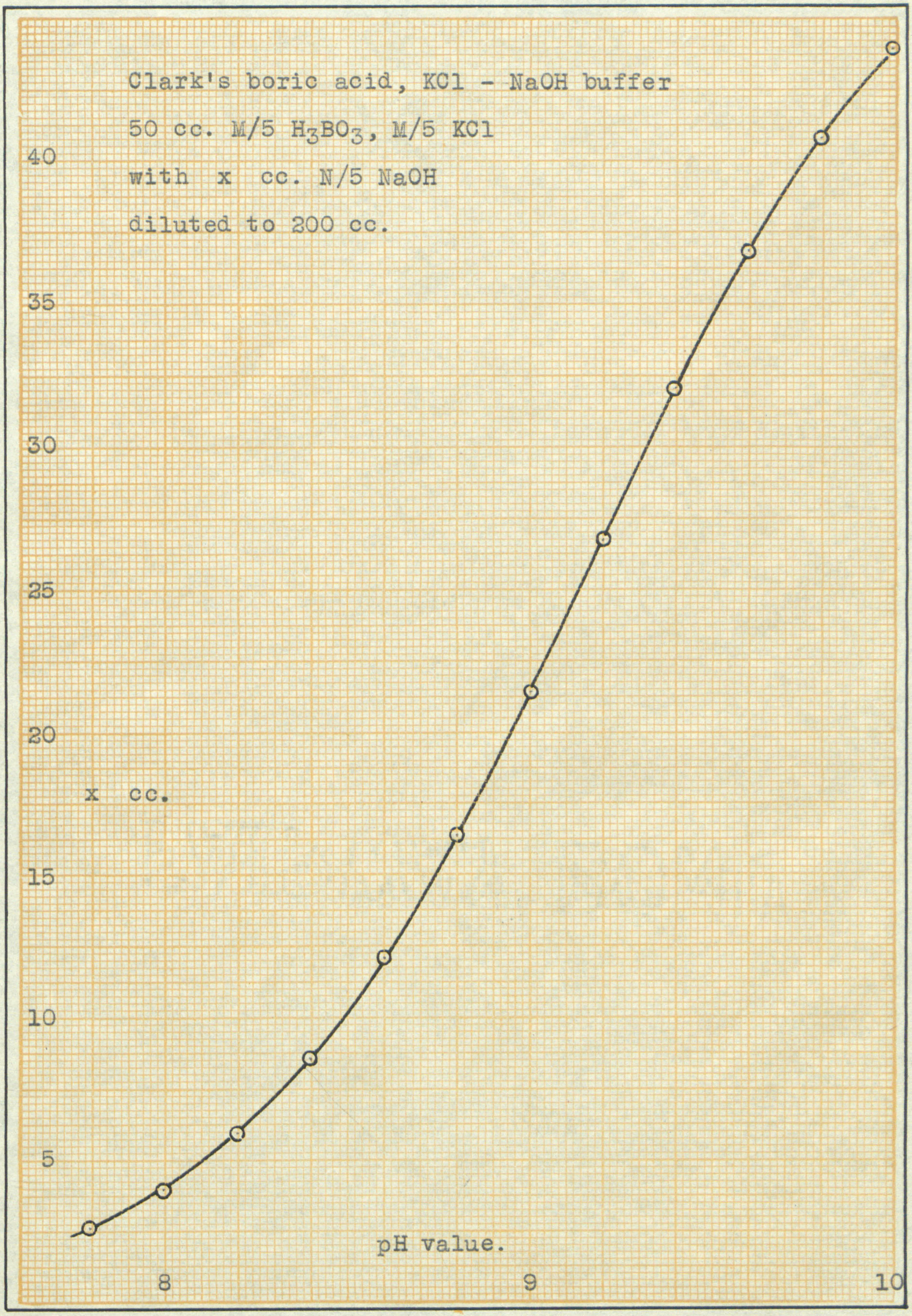

Clark's boric acid, KCl - NaOH buffer
50 cc. M/5 H_3BO_3, M/5 KCl
with x cc. N/5 NaOH
diluted to 200 cc.
40
35
30
25
20
x cc.
15
10
5
pH value.
8
9
10

Plate 21.

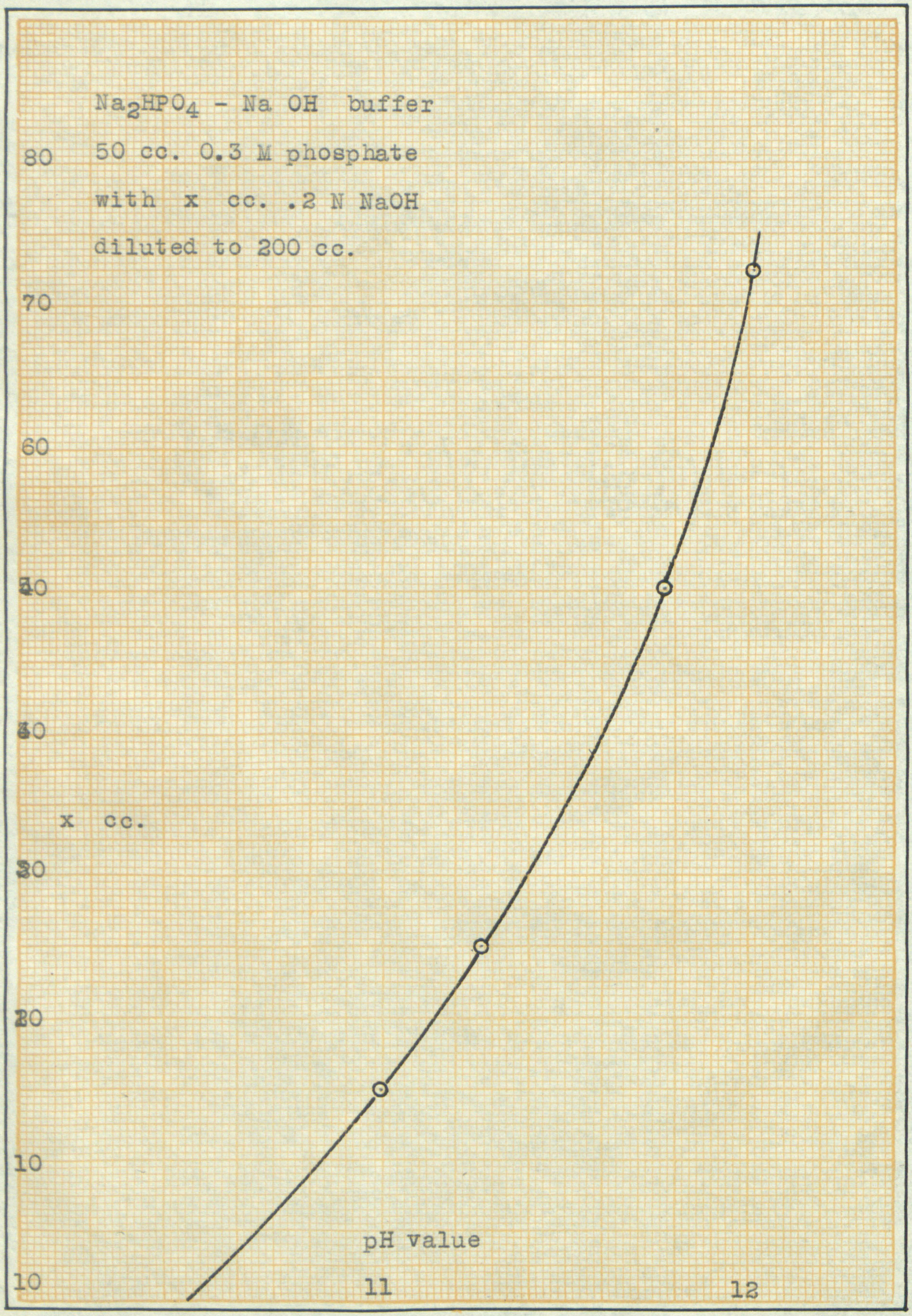

Na_2HPO_4 - Na OH buffer
50 cc. 0.3 M phosphate
with x cc. .2 N NaOH
diluted to 200 cc.
80
70
60
50
40
x cc.
30
20
10
pH value
10
11
12

Plate 22.

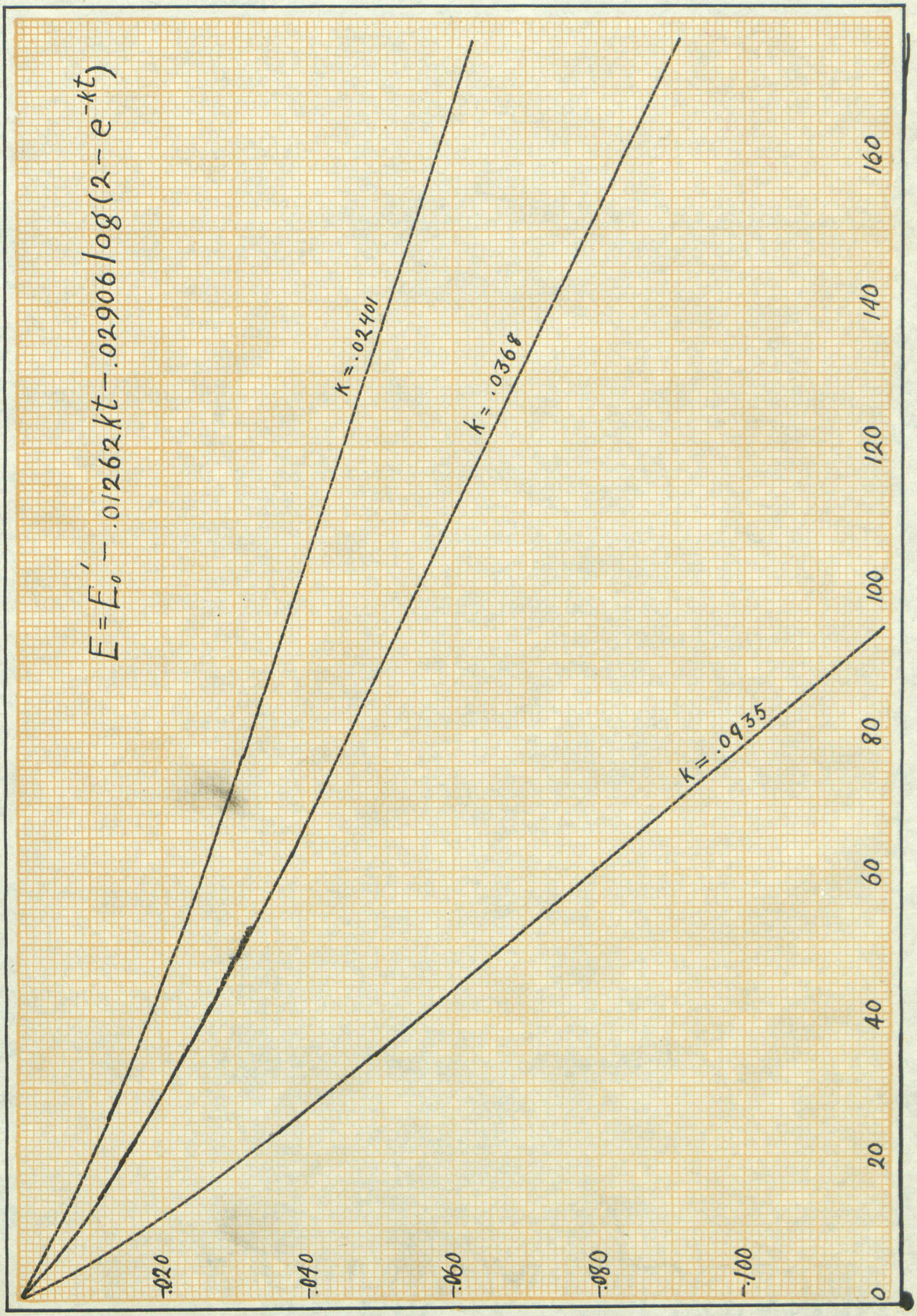
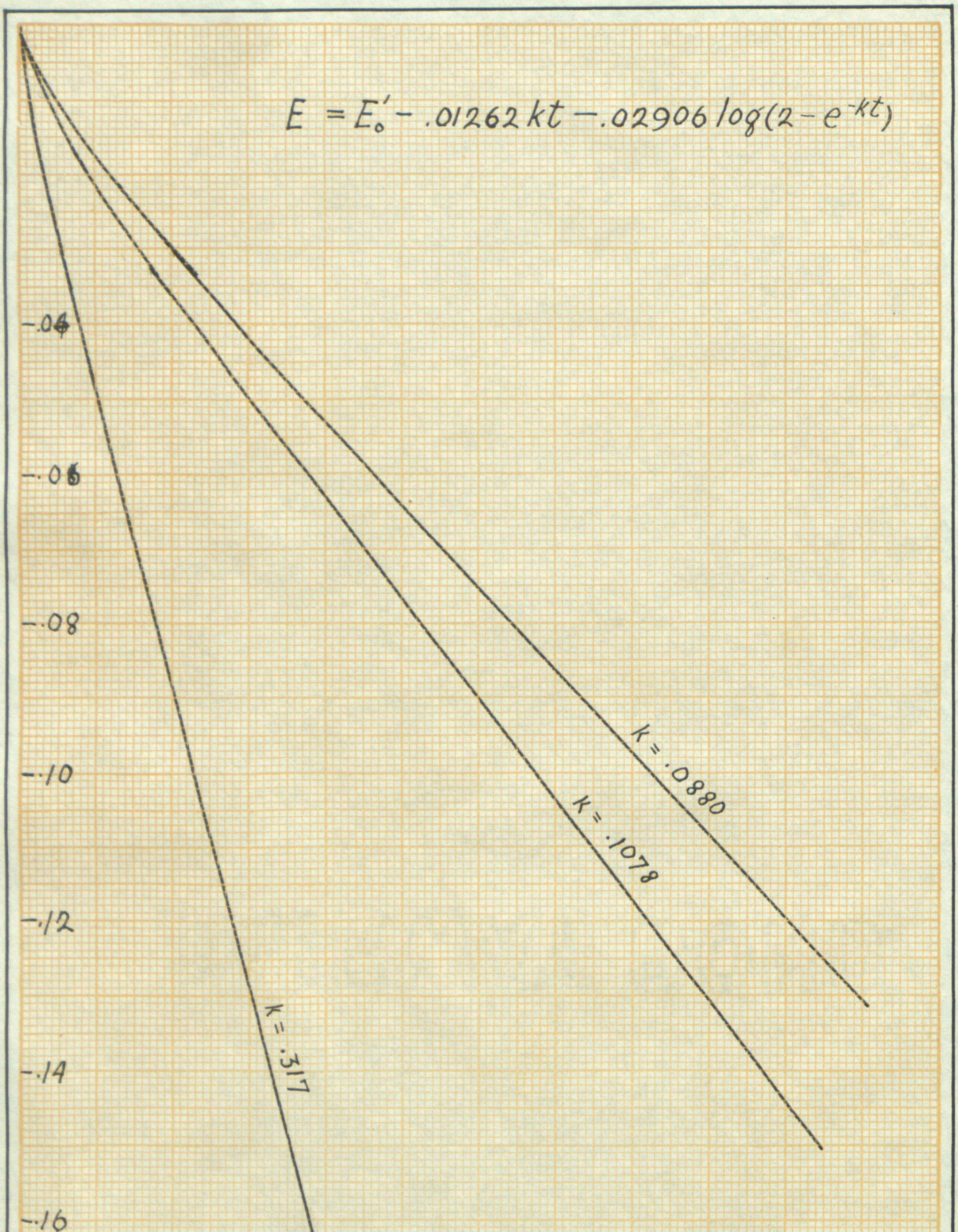

$E = E_0' - .01262kt - .02906 \log(2 - e^{-kt})$
k = .02401
k = .0368
k = .0935
0
20
40
60
80
100
120
140
160
-.020
-.040
-.060
-.080
-.100

Plate 23.


$E = E_0' - .01262\,kt - .02906 \log(2 - e^{-kt})$
-.04
-.06
-.08
-.10
-.12
-.14
-.16
0
20
40
60
80
100
120
k = .0880
k = .1078
k = .317