Summary.

The authors highly recommend the basic nitrate method in the two forms herein outlined for the separation of erbium, holmium, dysprosium and the less basic earths from yttrium; and the crystallization of the chlorides from 1:1 hydrochloric acid for the separation of holmium and dysprosium from yttrium.

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OXIDATION AND REDUCTION OF HYDROQUINONE AND QUINONE FROM THE STANDPOINT OF ELECTROMOTIVE-FORCE MEASUREMENTS.

By F. S. Granger and J. M. Nelson.

Very little work has been done on the study of oxidation and reduction from the standpoint of potential measurements, in the field of organic chemistry, and nearly all of that has been of an empirical character. Bancroft[1] included in a study of a large number of more or less common oxidizing and reducing agents, alkaline solutions of hydroquinone and pyrogallol. The proportions used in making up these solutions were not given, but had they been, they would not have thrown much light upon the composition of the resulting mixtures, since both hydroquinone and pyrogallol are very unstable in alkaline solutions. Furthermore, the potentials were not measured against any standard electrodes, but against other oxidizing and reducing agents. Neumann[2] later put Bancroft's results on a more definite basis by comparing them with a calomel electrode. Baur[3] determined the potentials manifested by solutions made up of definite amounts of hydroquinone and formaldehyde, in aqueous sodium hydroxide. Slaboszewicz[4] made some admittedly rough measurements on aldehyde and alcohol in $2M$ sulfuric acid. Mathews and Barmeier[5] published some potentials of various photographic developers and Frary and Neitz[6] carried out a more elaborate study along the same lines as those of Mathews and Barmeier. All of these measurements were determinations of potentials of solutions, made up with definite concen-

[1] Bancroft, *Z. physik. Chem.*, **10**, 387 (1892).

[2] Neumann, *ibid.*, **14**, 193 (1894).

[3] Baur, *Ber.*, **34**, 3732 (1901).

[4] Slaboszewicz, *Z. physik. Chem.*, **42**, 343 (1902).

[5] Mathews and Barmeier, *Proc. 8th Intern. Congr. Appl. Chem.*, **20**, 189, 193, 179 (1912).

[6] Frary and Neitz, This Journal, **37**, 2246 (1915).

trations of the components but without any reference to the reaction taking place or the products formed, so that the results, while interesting in some cases from the technical side in showing the reducing powers of these particular solutions, are still of little scientific significance.

Haber and Russ[7] in a study of the electrolytic reduction of some organic compounds, such as nitrobenzene and quinone, observed that when the potential of a platinum electrode immersed in a quinone-hydroquinone solution was measured against a calomel electrode it behaved similarly to an ordinary metal electrode immersed in a solution of one of its salts. They considered the reaction which takes place in the quinone-hydroquinone solution to be

$$C_6H_6O_2 \rightleftharpoons C_6H_4O_2 + 2\,H^+ + 2\ominus \dots\dots\dots\dots\dots\dots(1)$$
$$\text{Hydroquinone} \qquad \text{Quinone}$$
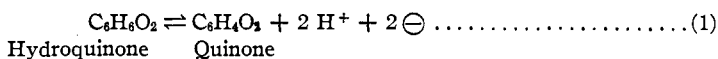
and compared the difference in the observed potentials of any two solutions with the corresponding difference in calculated values, obtained by means of Equation 3

$$\pi_1 - \pi_2 = \frac{RT}{2F}\left[ln\,\frac{(\text{Quinone})}{(\text{Hydroquinone})_1} - ln\,\frac{(\text{Quinone})_2}{(\text{Hydroquinone})_2}\right]. \qquad (3)$$

Equation 3 is the usual van't Hoff Equation 2

$$\pi = \frac{RT}{2F}\left[ln\,\frac{\text{Quinone}\times[H^+]^2}{\text{Hydroquinone}} - ln\,K\right] \qquad (2)$$

so modified as to avoid taking into account in the calculations the acidity of the solutions. This is of course possible by keeping the acidity the same in all the experiments. They found that the calculated and observed differences, obtained in this way, agreed quite well. Due to this agreement they concluded that the van't Hoff Equation 2 was applicable, and that this organic reaction was similar in character to oxidation-reduction reactions occurring in the case of electrolytes.

As is well known, quinone and hydroquinone combine, reversibly, in solution to form quinhydrone, and as no data as to the extent of this combination were at hand the actual or relative concentrations of quinone and hydroquinone in Haber and Russ's solutions, which were prepared by adding known excesses of either one of these substances to a solution of quinhydrone, were unknown and undetermined. There exists, therefore, one important assumption in their method of reasoning which requires additional experimental data before it can be considered as justified. Haber and Russ assumed on the one hand, that the van't Hoff equation was applicable and therefore the quinhydrone must have been practically completely dissociated, and on the other hand, that since the quin-

⁷ Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904).

hydrone was completely dissociated and therefore the concentrations of quinone and hydroquinone known, the van't Hoff equation was applicable.

In the present investigation the determination of the actual concentrations of the reactants was undertaken and the study was extended to varying hydrogen-ion concentration as well. By the use of the data obtained it has been possible to show, without resorting to any assumption as to the degree of the dissociation of the quinhydrone as Haber and Russ did, that the calculated values, using Equation 3, for the differences in the electromotive-force measurements of any two solutions of different concentrations of quinone and hydroquinone, agree with the corresponding experimental values. Furthermore, having determined the actual concentrations of the reactants, quinone, hydroquinone and hydrogen ion, it has been possible to calculate also, by means of Equation 2, the potential of each solution and to show that this calculated value agrees with the experimental value, when the difficulties in determining the exact concentrations of the reactants and resultants of the reaction are taken into consideration and when it is borne in mind that the van't Hoff equation is based on the ideal gas laws and osmotic pressure rather than upon concentration. This method is therefore more satisfactory and direct for ascertaining the applicability of the van't Hoff equation than that of only comparing the differences between the potentials of two solutions with the corresponding calculated values.

Determination of the Concentrations of the Reactants and Resultants.

Solubility of Hydroquinone.—Since no data on the solubility of hydroquinone at 25° could be found in the literature, solubility determinations were made.

TABLE I.

Solvent.	G. per 100 cc. of Solution.						Moles per liter.
	1.	2.	3.	4.	5.	Av.	
Water...............	7.094	7.091	7.112	7.086	...	7.10	0.645
0.01 M HCl..........	7.060	7.128	7.136	7.028	7.146	7.10	0.645
0.1 M HCl..........	6.978	6.944	...	...	...	6.96	0.633
1.0 M HCl..........	5.436	5.442	...	...	...	5.44	0.494

Because the hydrogen ion is considered as one of the resultants in the reaction, Equation 1, various amounts of hydrochloric acid were added. The hydrochloric acid also served to make the solutions good conductors, which of course is necessary. It will be noticed in the table that the hydrochloric acid decreased the solubility of the hydroquinone.

Solubility of Quinone.—The solubility of quinone in water at 25° had been determined previously by Luther and Leubner[8] using the analytical method of Valeur[9] which consisted in titrating the liberated iodine with thiosulfate. In this way they found the solubility of quinone to be 1.265 moles per liter, a value in which there is evidently an

[8] Luther and Leubner, *J. prakt. Chem.*, **85,** 314 (1912).

[9] Valeur, *Compt. rend.*, **129,** 552 (1899).

TABLE II.

Solvent.	Moles per liter.		G. per 100 cc.
	1.	2.	
Water........................	0.1266	0.1266	1.37
0.1M HCl....................	0.1275	0.1275	1.38
1.0M HCl....................	0.1332	0.1332	1.44

error in the placing of the decimal, since the value we obtained by repeating the determination is just one-tenth of theirs.

Here again it is to be noticed that the hydrochloric acid influences the solubility, but in the opposite direction from that observed in the case of hydroquinone.

Solubility of Hydroquinone and Quinone in the Presence of Each Other. Solubility of Quinhydrone.—It was not possible to make up solutions containing known concentrations of both hydroquinone and quinone by simply dissolving weighed quantities of these substances in a measured volume, because they combine immediately in equimolar proportions to form quinhydrone. Furthermore, since in solution the quinhydrone exists in mobile equilibrium with them their concentrations cannot be determined directly, by analytical means. For the series of solutions (see below), in which only the hydrogen-ion concentration varied, the concentrations of either hydroquinone or quinone were fixed by saturating the solutions with one of them and quinhydrone. A solution saturated with both was not possible owing to the slight solubility of the quinhydrone, which separated out when only a small quantity of quinone was added.

In order to prepare solutions containing known concentrations of the reactants it was necessary to know not only their solubilities and that of quinhydrone but also the degree of dissociation of the latter into its components, hydroquinone and quinone.

Luther and Leubner determined the solubility, in water, of the undissociated quinhydrone and also its dissociation constant by a method similar to that used by von Behrend[10] for the phenanthrene picrates. They saturated water and aqueous hydroquinone solutions of known concentrations with quinhydrone at 25°, and determined the total quinone, combined and free, present in the filtrate by Valeur's method, which is applicable owing to the complete dissociation of the quinhydrone as the quinone is removed by the iodide. This total quinone represents (formula-weight for formula-weight) the total quinhydrone, dissociated and undissociated, which was dissolved in saturating the solution. If s is the solubility of the undissociated quinhydrone, a the solubility of the undissociated and dissociated quinhydrone, b the known excess of hydroquinone added, h the actual concentration of hydroquinone, q the actual concentration of quinone, all in formula-weights per liter, then the free and combined hydroquinone in the solution, which is the same in moles as the total quinhydrone (dissociated and undissociated) or a, plus the added excess of hydroquinone, b, is equal to the hydroquinone combined in the undissociated quinhydrone, s, plus the free hydroquinone, h, in the solution; or

$$a + b = s + h; \text{ or } h = a + b - s \qquad \text{(4) and (5)}$$

The total quinone (free and combined in the form of quinhydrone) in the solution, a, determined by titration, is equal to the undissociated quinhydrone, s, plus the free quinone, q; or

$$a = s + q; \text{ or } q = a - s \qquad \text{(6) and (7)}$$

[10] von Behrend, Z. physik. Chem., **15**, 183 (1894).

The dissociation constant, K, of the quinhydrone, assuming that the mass law holds in this case, can be represented as

$$K = (q \times h)/s; \text{ or } Ks = q \times h \qquad (8)$$

Substituting in (8) the values for q and h, from Equations 7 and 5 respectively, then

$$Ks = (a - s)(a + b - s) \qquad (9)$$

If the experimental precision were fine enough, s, and K, in Equation 9, could be calculated from any pair of determinations by means of simultaneous equations, since a and b are measured quantities. But comparatively slight deviations from these ideal conditions render this method of calculation inapplicable, so that recourse must be had to a method of trial and approximation which Luther and Leubner carried out in the following way.

By trying different values for s in Equation 9, they found K to approach the nearest to constancy when s was assigned the value 0.0013.

TABLE III. (Luther and Leubner.)

Added hydro-quinone b.	Solubility of quinhydrone a (Av.)	a — b.	K(s = 0.0013).
0.0	0.01827	0.01827	0.221
0.01	0.01421	0.02421	0.227
0.02	0.01150	0.03150	0.236
0.05	0.00664	0.05664	0.227

Luther and Leubner's determinations were repeated in this work and the range extended up to the saturation point for hydroquinone in water, and also in 0.1 molar and molar hydrochloric acid. The results are given in Table IV.

TABLE IV.

	Moles per liter.			Solvent, water and no hydrochloric acid. Dissociation constant, $K \times 10^3$, for quinhydrone when s (moles per liter of undissociated quinhydrone) has the following values.					
Added hydro-quinone b.	Quinhydrone (dissoc. and undissoc.) a.	Total hydro quinone a + b.	$s =$	0.0013	0.00125	0.00100	0.00098	0.00096	0.00095
0.0	0.0178	0.0178		209	219	282	289	296	299
0.01	0.0135	0.0235		208	218	282	289	295	298
0.02	0.0106	0.0306		210	219	284	291	298	301
0.05	0.00625	0.05625		210	220	290	297	304	308
0.1	0.00374	0.10374		192	204	282	290	298	302
0.2	0.00244	0.20244		176	192	290	300	310	316
0.3	0.00189	0.30189		136	154	268	280	292	298
0.4	0.00179	0.40179		152	178	316	332	347	355
0.5	0.00172	0.50172		162	189	361	378	397	405
Sat'd	0.001815	0.645 − s		255	291	526	550	574	587
Mean of the first 7 values.				192	204	283	291	299	303
Sum of deviations from mean.				141	122	33	31	32	35

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TABLE IV (Continued).

Solvent, 0.1 M hydrochloric acid.

b.	a.	a + b	s = 0.00103	0.00102.	0.00101
0.000	0.0173	0.0173	256	260	263
0.01	0.0131	0.0231	259	262	264
0.02	0.0102	0.0302	259	263	265
0.05	0.00593	0.05593	261	264	267
0.1	0.00363	0.10363	259	263	265
0.2	0.00237	0.20237	262	267	271
0.3	0.00190	0.30190	254	260	265
0.4	0.00172	0.40172	268	274	281
0.5	0.00170	0.50170	326	334	342
Sat'd	0.00181	0.633 + s	478	490	501
Mean of first 7 values.			289	263	264
Sum of deviation from mean.			13	12	14

Solvent, Molar hydrochloric acid.

b.	a.	a + b	s = 0.00088.	0.00087.	0.00086.
0.0	0.0162	0.0162	267	270	274
0.01	0.0118	0.0218	260	263	267
0.02	0.0091	0.0291	264	267	270
0.05	0.0052	0.0552	267	270	274
0.1	0.0031	0.1031	258	262	266
0.2	0.00202	0.20202	261	267	272
0.3	0.00164	0.30164	260	267	273
0.4	0.00152	0.40152	291	299	307
Sat'd	0.00159	0.494 + s	399	409	419
Mean of first 7 values.			262	266	271
Sum of deviations from mean.			21	18	19

On comparing the values obtained in the case of the water solution with those of Luther and Leubner, it will be seen that the values for a, the solubility of quinhydrone (dissociated and undissociated), are lower than theirs by about 5%. The reason for this latter difference has not been ascertained. The selected value for s, the solubility of the undissociated quinhydrone, which gives the minimum sum of deviations for the dissociation constant, K, from its mean, for the range comprising the first four solutions, which was as far as the determinations of Luther and Leubner were carried, is 0.00125 formula-weights per liter, which is a very close agreement with theirs. If, however, the entire range, up to the saturation point of hydroquinone, is considered it will be seen that in the column under $s = 0.00125$, there is a decided but continuous decrease in the value for K, until the added hydroquinone amount to $b = 0.3$ mole per liter, and after that a gradual increase occurs which becomes suddenly abrupt at the saturation point of the hydroquinone.

When the smaller values for the solubility of the undissociated quinhydrone, s, are considered, it is seen that the first 7 values of the dissociation constant, K, in their respective columns become more uniform, giving a minimum deviation sum of 31 for $s = 0.00098$. This latter value for s was selected as the solubility, formula weight per liter, in preference to the value, $s = 0.0013$, originally put forth by Luther and Leubner.

Parallel results were obtained with 0.1 and 1 M hydrochloric acid solutions. The calculated solubilities and the dissociation constants for the quinhydrone are recapitulated in Table V. The basis of the last column is given in the subsequent part of the paper.

TABLE V.

Solvent.	Mole of quinhydrone per liter.		Dissociation constant, K for quinhydrone.	
	Sol. of quinhydrone (dissoc. and undissoc.).	Sol. of quinhydrone (undissociated).	(Av. first 7).	When solution was satur. with hydroquinone.
	a.	s.		
Water............	0.0178	0.00098	0.289	0.550
0.1 M HCl........	0.0173	0.00102	0.263	0.490
1.0 M HCl........	0.0162	0.00087	0.267	0.409

Determination of the Hydrogen-Ion Concentration, or the Acidity of the Solutions.

One of the difficulties encountered in this work was the determination of the hydrogen-ion concentration of the various solutions studied. In the case of the acid solutions conductivity data were used for this purpose. This involved, of course, the tentative assumption that the condition of the acid, or hydrogen-ion concentration, was the same as in a pure solution of hydrochloric acid. The question naturally arises, why not determine the hydrogen-ion concentration by the electromotive-force method with a hydrogen electrode This method was not used at all (although it was realized that the assumption upon which the use of the conductivity values was based, might be the source of considerable error), because it was believed that, even if a constant potential could be obtained with a hydrogen electrode, in the presence of another active electrochemical system this potential still might be very different from the true hydrogen-ion potential because of the influence of the other system. It was felt that this was too big a question to take up in the time at our disposal.

For this reason, the values for the hydrogen-ion concentrations were obtained as follows. Bray and Hunt[11] by the conductivity method, found for the degree of ionization (α) of hydrochloric acid at 25°, 92.1% in 0.1M solution, and 97.1% in 0.091M solution. But no direct data could be found in the literature for 0.1M hydrochloric acid at 25°. Kohlrausch,[12] however, gives the following for the equivalent conductivity (Λ) at 18°:

Moles per liter.	Λ.
0.01	370
0.1	351
1.0	301

From these figures $\Lambda_1/\Lambda_{.01}$ is found to be 0.948 at 18°, while from Bray and Hunt's data $\alpha_{0.1}/\alpha_{0.01}$ is found to be 0.948 at 25°. Moreover, according to Kohlrausch,[13] the temperature coefficient of conductivity of

[11] Bray and Hunt, THIS JOURNAL, 33, 781 (1911).
[12] Landolt-Börnstein, "Tabellen," 1912, p. 1104.
[13] Op. cit. p. 1115.

hydrochloric acid solutions varies less and less with increasing concentration, approaching constancy as molar concentration is reached. Thus:

Concentration	0.001	0.01	0.1	0.5
Coefficient	0.0163	0.0158	0.0153	0.0152

The coefficient for molar hydrochloric acid was not given.

In the absence of definite date, therefore, it has been assumed that

$$\left(\frac{\Lambda_1}{\Lambda_{.1}}\right)_{25^\circ} \text{or} \left(\frac{\alpha_1}{\alpha_{.1}}\right)_{25^\circ} = \left(\frac{\Lambda_1}{\Lambda_{.1}}\right)_{18^\circ} = 0.858 \text{ (from Kohlrausch's figures)}.$$

$$\alpha_1 = \alpha_{.1}\left(\frac{\Lambda_1}{\Lambda_{.1}}\right)_{18^\circ} = 0.921 \times 0.858 = 0.790.$$

Therefore 0.790 has been taken as the concentration for the hydrogen ion in a molar hydrochloric acid solution at 25° (Solution A).

Measurements of Potentials.—Mixtures were made up as described below, and their potentials measured at 25° in a half-element vessel against a saturated potassium chloride calomel electrode, by means of an e.m.f. combination of the type Hg | HgCl sat. KCl | sat. KCl Solution A | Pt.

The following mixtures were investigated

A. 1.0 M hydrochloric acid solution, saturated with hydroquinone and quin-hydrone.

B. 0.1 M hydrochloric acid solution, saturated with hydroquinone and quin-hydrone.

C. 0.01 M hydrochloric acid solution, saturated with hydroquinone and quin-hydrone.

F. 0.1 M hydrochloric acid solution, saturated with quinhydrone and containing 0.1 M hydroquinone.

G. 0.1 M hydrochloric acid solution, saturated with quinhydrone and containing 0.05 M hydroquinone. .

H. 0.1 M hydrochloric acid solution, saturated with quinhydrone and containing 0.02 M hydroquinone.

I. 0.1 M hydrochloric acid solution, saturated with quinhydrone and containing 0.01 M hydroquinone.

J. 0.1 M hydrochloric acid solution, saturated with quinhydrone.

The pole potential differences for the respective solutions were derived from the electromotive-force measurements, adding the latter to 0.5265 (value provisionally adopted by Professor H. A. Fales of this laboratory, for the saturated calomel electrode at 25°) when the electrode in the solution was the positive pole, and subtracting when the electrode was the negative pole. Possible contact potential differences at the boundaries of the solutions were not taken into consideration. The constancy and reproducibility of the values obtained for the respective mixtures can be seen in Figs. 1 and 2, in which the pole potential differences are plotted against the age of the cell as indicated.

In Fig. 1 each pair of curves, consisting of a light and a heavy line, represents a duplicate cells of the solution, indicated by the letter at the right-hand end of the pair of lines. The heavy lines connect the points representing the readings of Cell 1, and the light lines those of Cell 2 of the solution in question. The dotted lines represent the theoretically calculated potentials as shown below.
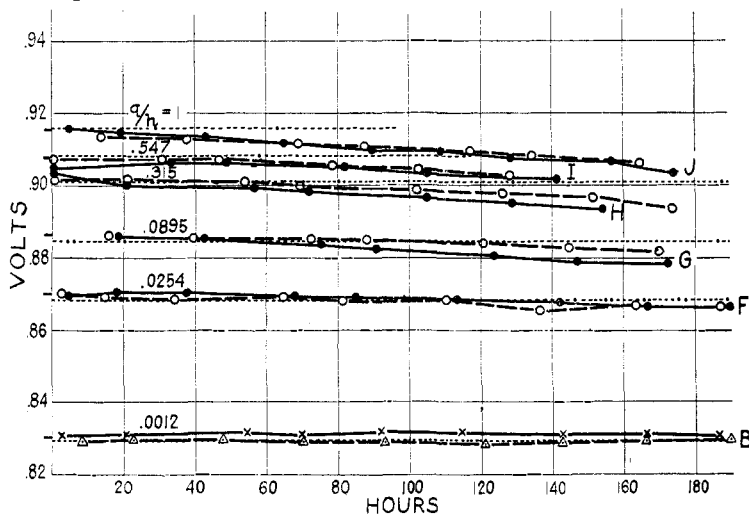

Fig. 1.

It will be observed in the graphs, that in the case of the solutions not saturated with hydroquinone there is a well defined and quite regular sloping off of the potentials which becomes more marked as the ratio of quinone to hydroquinone q/h, increases. This indicates one or more side reactions involving quinone associated very likely with the increasing brown color which solutions of quinone acquire on standing, and consistent with its general instability or reactivity. The true initial potential for each of the mixtures was therefore obtained from the above curves by inspection. Ignoring the irregularities of the first day or two, the value, which seemed to be most consistent with the contours of the curves for the particular mixture and with those of the neighboring curves, was selected and marked on the chart by the short lines extending to the left from the left border of the diagram. The fairness of this method of approximation and its precision of half a millivolt, which is sufficient for the purpose, may be seen on inspection of the curves. The method is not as crude as it might seem, at first glance, and is the only one suitable for the purpose. These values are given as π (observed) in Table IX.

In Fig. 2 are plotted, by the same method as employed in Fig. 1, the readings obtained from mixtures indicated by the different letters. In these solutions the ratio of quinone to hydroquinone, q/h, has been kept

comparatively constant by saturating the solutions with either hydroquinone or quinone, and with quinhydrone, while the hydrogen ion or acidity varied. The values for the observed potentials of the solutions A, B and C, were obtained by averaging all of the measurements taken on a given mixture during the period in which the readings produced practically a horizontal line. These values are given in Table IX.
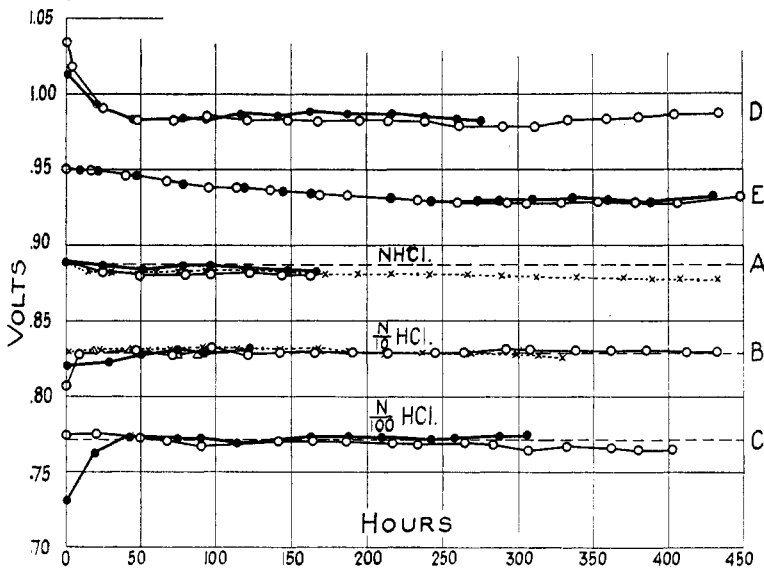

Fig. 2.

Agreement Between the Calculated and Observed Potentials of the Solutions, Containing Known Concentrations of Quinone, Hydroquinone and Acid.—In Table VI is given a comparison between the calculated and observed differences in potentials, $\pi_1 - \pi_2$, manifested by different

TABLE VI.

Solution.	b.	$q = a - s$.	$h = a + b - s$.	$\pi_1 - \pi_2$ Calc.	$\pi_1 - \pi_2$ Obs.
J	0.0	0.01628	0.01628		
				0.00781	0.0075
I	0.01	0.01208	0.02208		
				0.00741	0.0065
H	0.02	0.00918	0.02918		
				0.0162	0.0155
G	0.05	0.00491	0.05491		
				0.0163	0.0165
F	0.10	0.00261	0.10261		

pairs of the solutions, F, G, H, I and J. All of these measurements were done at 25° and in 0.1M hydrochloric acid solutions and therefore Equation 3 above can be written

$$\pi_1 - \pi_2 = 0.0298 \log q_1/h_1 - 0.0298 \log q_2/h_2. \tag{3}$$

The values for h, the concentration of hydroquinone, q, the concentration of quinone, in the above solutions, were obtained from the values of a, the concentration of quinhydrone (dissociated and undissociated) present in the solutions, s, the concentration of the undissociated quinhydrone, and b, the amount of added hydroquinone, all of which are given in Table IV. The values of b are given also in the description of the solutions.

As can be seen in Table VI, the calculated values for the differences in potentials, $\pi_1 - \pi_2$, agree quite well with the observed values, and therefore are like those obtained by Haber and Russ. They have, however, the additional weight over the values of Haber and Russ in that they are based on determined concentrations of quinone and hydroquinone instead of assumed values.

The Solubility of the Undissociated Quinhydrone is Independent of the Presence of an Excess of Hydroquinone.—It was pointed out in the discussion following Table IV that there is an abrupt increase in the values of the dissociation constant, K, of the quinhydrone as the solutions become saturated with respect to hydroquinone. Due to the method of trial and Equation 9 used in obtaining the values of K in Table IV, the assumption was made that the solubility of the quinhydrone, s, was not affected by the varying concentration of hydroquinone present in the solutions. Some evidence for the justification of this assumption can be had by comparing the potentials of Solutions F to J, which were not saturated with hydroquinone, with the potentials of Solutions A, B and C, which were. It is not extravagant to assume that Solutions A, B and C obey the van't Hoff equation just as Solutions F to J do, since when compared with the latter in this respect (see Table IX below) their potentials appear to be normal.

Solution B has the same acidity as Solutions F to J, and therefore it is possible by means of Equation 3

$$\pi_1 - \pi_2 = 0.0298 \log (q/h)_1 - 0.0298 \log (q/h)_2 \quad . \quad . \quad . \quad . \tag{3}$$

to obtain an expression involving only the one unknown $(q/h)_2$, since $(q/h)_1$ is given in Table VI and the potentials, π, can be obtained from the graphs. Inspection of Fig. 1 shows that Solution F gives a very stable potential. Therefore the data for this solution were selected as the basis of this calculation, taking for π_F, the initial reading, 0.8695 volt, obtained as explained above, and which is also the average of the readings up to the point at which the falling off commences. Similarly Solution B, Fig. 2, has an average value for π_B of 0.8300 volt. Introducing these values and also —0.0475 for $0.0298 \log(q/h)_F$, from Table VI, in Equation 3

$$0.8695 - 0.8300 = -0.0475 - 0.0298 \log (q/h)_B \text{ or } (q/h)_B = 0.001202.$$

But h_B, the concentration of hydroquinone in $0.1M$ hydrochloric acid

is 0.633 mole per liter (Table I) and therefore q_B, the concentration of the quinone in Solution B is 0.00076 mole.

Since Solution B was saturated with hydroquinone and quinhydrone, the total quinhydrone (dissociated and undissociated), present in the solution, and a_B is 0.00181 mole (Table IV), is equal to the undissociated quinhydrone s_B plus the concentration of the free quinone q_B is 0.00076 mole, because the number of moles of the latter is equivalent to that of the dissociated quinhydrone in this case since no quinone had been added to the solution. Then from

$$a_B = s_B + q_B \quad \cdots \cdots \cdots \cdots \quad (6)$$

the solubility s_B of the undissociated quinhydrone in Solution B is 0.00105 mole per liter. This value is so close to 0.00102, the value assumed in Table IV, that the assumption mentioned above appears to be justified.

Instead of using Solution F for this purpose, the other solutions, G, H, I and J, were tried also and gave the following results:

Basis.	s_B.
F	0.00105
G	0.00105
H	0.00101
I	0.00094
J	0.00092

The values obtained when Solutions I and J were used as the basis for the calculations of the concentration of the undissociated quinhydrone, s_B, are slightly lower. The higher values from Solutions F, G and H are to be preferred because these solutions manifested more stable and definite potentials, as is evident from our examination of the corresponding curves, especially those of F and G in Figs. 1 and 2.

Calculation of Potentials of Solutions, Saturated with Hydroquinone and of Various Acidities.—Adopting, for the reasons just stated above the values for s, the solubility of the undissociated quinhydrone showing the smallest deviation from the mean, and given in Table IV, it becomes possible to calculate the potentials of Solutions A, B and C. The procedure followed in these calculations differs from that in the case of Solutions F to J, in that the acidity of the solutions varied and therefore had to be taken into account in Equation 3, or

$$\pi_1 - \pi_2 = 0.0298 \ \log(q/h)_1 + 0.0596 \ \log[H^+]_1 - 0.0298 \ \log(q/h)_2 -$$
$$0.0596 \ \log H^+]_2 \quad\quad (10)$$

The values of the hydrogen-ion concentrations are given in the section dealing with the concentration of hydrogen ion. The values of q, the concentration of the free quinone, are obtained by means of Equation 6, and since the solutions were saturated with respect to hydroquinone, the value of h is given in Table I. The values for a, the total concentration

of quinhydrone (dissociated and undissociated) and s, the concentration of the undissociated quinhydrone, are given in Table IV. The value of s for Solution C, which was 0.001 M with respect to hydrochloric acid, is considered to be the same as that for pure water. No solubility experiments for 0.01 M hydrochloric acid solutions were run because the results obtained for 0.1 M hydrochloric acid and water were so nearly the same that these determinations for 0.01 M hydrochloric acid seemed unnecessary. The results obtained are given in Table VII.

TABLE VII.

Solution.	$q = a - s.$	$h.$	$H^+.$	$\pi_1 - \pi_2$ Calc.	π Obs.	$\pi_1 - \pi_2$ Obs.
A	0.00072	0.494	0.790		0.883	
				0.0579		0.053
B	0.00079	0.633	0.0921		0.830	
				0.0576		0.060
C	0.000835	0.645	0.00971		0.770	

In like manner, $\pi_A - \pi_C = 0.1155$ (calc.) and 0.113 (observed). Thus the observed potentials are found to agree quite well with the theoretical, just as was found to be the case for Solutions F to J, even though in these solutions the concentration of the hydrogen ion was varied.

The Equilibrium Constant of the Oxidation-Reduction Reaction between Quinone and Hydroquinone.—The value of the equilibrium constant, for the oxidation-reduction reaction (1) between quinone and hydroquinone, K, was obtained by means of Equation 2.

$$\pi = 0.0298 \log(q/h) + 0.0596 \log[H^+] - 0.0298 \log K \ . \ . \ . \ . \ . \ . \ (2)$$

The concentrations of the free quinone and hydroquinone, q and h, were taken from Tables VI and VII. The hydrogen-ion concentration can be found in the section dealing with the concentration of hydrogen ion. In Table VIII are given the values for K, obtained in the form $0.0298 \log K$.

TABLE VIII.

Solution.	A.	B.	C.	F.	G.	H.	I.	J.
$-0.0596 \log H^+$	0.0061	0.0618	0.1200	0.0618	0.0618	0.0618	0.0618	0.0618
π	0.8830	0.8300	0.7700	0.8695	0.8860	0.9015	0.9075	0.9150
$-0.0298 \log(qh)$	0.0845	0.0867	0.0861	0.0475	0.0312	0.0149	0.0078	0.0000
$0.0298 \log K$	0.9736	0.9785	0.9761	0.9788	0.9790	0.9782	0.9771	0.9768
Deviation	-0.0037	+0.0012	-0.0012	+0.0015	+0.0017	+0.0009	-0.0002	-0.0005

The mean value for $0.0298 \log K$ is 0.9773, and hence the equilibrium constant for Reaction 1 is $K = 1.6 \times 10^{-23}$.

The average deviation in the values for $0.0298 \log K$, as can be seen in Table VIII, is 0.0014 volt or 1.4 millivolts. This compares favorably with the closest agreement that has been obtained in parallel work in inorganic chemistry, as can be seen from the following summary.

System.	Investigators.	Average dev. millivolts.
Ferrous/ferric	Peters(Tab. 1)	3.9
" "	" "	2.7
Ferrocyanide/ferricyanide	Friedenhagen	1.0
Manganate/permanganate	"	4.0
Uranous/uranyl	Luther and Michie	1.2
Iodine/iodate	Luther and Sammet	0.8
Bromine/bromate	" "	1.0
Bromide/bromine	" "	0.5
Iodide/iodine	" "	1.0
Hydroquinone/quinone	This work	1.4

Comparison of the Theoretical and Observed Potentials.

By using the mean value, obtained above for $0.0298 \log K = 0.9773$ the theoretical values for the potentials of the various solutions have been calculated and arranged together with the observed values in Table IX for the sake of comparison.

TABLE IX.

Solution	π (Calculated).	π (Observed).
A	0.8867	0.8830
B	0.8288	0.8300
C	0.7712	0.7700
F	0.8680	0.8695
G	0.8843	0.8860
H	0.9006	0.9015
I	0.9077	0.9075
J	0.9155	0.9150

The theoretical potentials are represented in the figures by the straight dotted lines.

Potential Measurements on Unstable Solutions.—Seven cells saturated with quinone and a great number of neutral and alkaline solutions, in which potassium chloride and sodium hydroxide were used as electrolytes, were run also. Full details on these measurements are given in the original dissertation.[14] They are omitted here, for the reason that on account of the extreme instability of these solutions they could not be made the basis of any quantitative calculations.

Qualitatively, however, they were perfectly in accord with the theory. The solutions saturated with quinone, as already shown, gave higher oxidizing potentials than solutions of the same acidity, but of lower ratio between the quinone and the hydroquinone, q/h. The neutral solutions gave lower potentials than the acid solutions, and the alkaline gave still lower potentials, decreasing as the alkalinity was increased.

[14] "Oxidation and Reduction in Organic Chemistry from the Standpoint of Potential Differences," by F. S. Granger. Columbia University Press, New York, N. Y., 1920.

Experimental Part.

Hydroquinone.—The hydroquinone used was partly Merck's and partly Eimer and Amend's. Only one grade was obtainable and it was claimed to be very pure. No accurate method for determining its purity could be found. It all melted at 169° (uncorrected), the same value as given by Hlasiwetz,[15] or 173.0° (corrected). The solubility determinations of the hydroquinone were made by evaporating 5 cc. of a saturated solution to constant weight in weighed flasks, at room temperature and about 25 mm. pressure.

Quinone.—The quinone was Kahlbaum's. Some of it was recrystallized from gasoline (which was found to be an excellent solvent for this purpose). Both methods gave clean, bright yellow products, titrating, by the method already described, 99.4% of the theoretical requirement, and melting sharply at 115.7° (corrected), the melting point given in Beilstein.

Quinhydrone.—The quinhydrone was prepared in two ways: by treating an aqueous solution of hydroquinone with ferric chloride, and then acidifying with hydrochloric acid; and by mixing equivalent amounts of hydroquinone and quinone in water. The product, in each case, was filtered off and washed with water. That by the first process titrated 99.2% of the theoretical amount by the method previously described. Some was recrystallized from alcohol followed by ether, and some from glacial acetic acid. Acetic acid proved to be a very good solvent for the purpose, being by far the best of the three. All of the recrystallized products titrated 99.4%. Only the samples giving this titration were used. Quinhydrone decomposes upon heating, so its purity can not be checked in this way.

In determining the solubility of the quinhydrone, solutions containing an excess of the material were placed in a large test-tube fitted with a spiral mechanical stirrer, immersed in the thermostat, and vigorously and continuously stirred. Samples were taken out every 15 to 30 minutes, by means of a pipet fitted with a filter, until two successive titrations gave the same value, which was usually the case with the first two samples. In a number of cases, fresh mixtures were made up and tested as checks, and all the results were almost identical with the original, so it was not deemed necessary to verify all the solutions in this way, the regularity of the results and the parallelism between the aqueous and acid solutions also serving as a check.

Potential Measurements.—Sensitive Leeds and Northrup potentiometer and galvanometer were used. Saturated potassium chloride solution was used as the connecting medium. The cells were kept immersed in a constant temperature bath at 25°, the temperature remaining constant to 0.01°. Nitrogen was bubbled through the solution in the cell, for the first few hours, to insure complete removal of the air and to provide agitation at the start. The gas inlet and outlet tubes were closed then to prevent access of air. The potential of each cell was measured at least once a day over a period of from one to three weeks. Two or more cells of each solution were made up and examined, usually at different times and sometimes with different lots of materials, in order to determine the reproducibility of the potentials measured. No marked difference was observed, whether the electrodes were platinized or not.

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[15] Hlasiwetz, *Ann.*, 177, 336 (1875).