

5b. With halogens, phosphorus pentachloride and phenylarsenious chloride, products are obtained which would be expected, providing the original substances were mechanical mixtures of aldehyde and arsine. The compounds may be titrated quantitatively with a solution of iodine in ether.

5c. The compounds form unstable addition products with halogen acids, and stable addition compounds with chloroplatinic acid.

6a. The tetrahydro-dioxdiarsines formed according to Equation (1b), oxidize in the air to give aryl arsine oxides and aldehydes. This is particularly noticeable where the product is a derivative of formaldehyde.

6b. The compounds form double salts with chloroplatinic acid and cupric chloride.

6c. With iodine or phosphorus pentachloride, products are obtained which might be expected from a mixture of aryl arsine and aldehyde.

7. Aromatic primary arsines reduce aromatic aldehydes to alcohols with the formation of arsenobenzene, when a mixture is made at room temperature with no hydrochloric acid as a catalyst, or when a mixture is heated with or without hydrochloric acid.

8. A discussion of the structure of the various condensation products is given.

9. The probable mechanism for the condensation of aromatic primary arsines and aromatic arsine oxides, antimony tri-chloride, etc., is discussed.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

AN ELECTROCHEMICAL STUDY OF THE REVERSIBLE REDUCTION OF ORGANIC COMPOUNDS¹

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Introduction

Certain organic substances, such as anthraquinone, indigo and the vat dyes, have the rather unique property of being easily reduced in aqueous solutions by such reagents as sodium hydrosulfite and titanous chloride. The reaction is readily reversible, and the reduced material may be re-oxidized by almost any mild oxidizing agent, and even by oxygen itself. These reactions are very rapid, and take place at room temperature. They seem to involve a different kind of process from such irreversible reductions as the hydrogenation of ethylene derivatives, or the reduction of aldehydes, ketones, and nitriles. It is of interest to determine, if possible, the mecha-

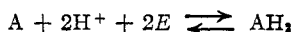
¹ The theoretical portions of this paper and an account of some preliminary experiments were presented to the Northeastern Section of the American Chemical Society, April 8, 1921.

nism of each of these two classes of reduction reactions and to discover what particular type of compound is essential for each.

The experiments described in this preliminary paper deal with the oxidation-reduction potentials of certain water-soluble substances related to the vat dyes, namely the salts of six anthraquinone sulfonic acids. The results show that the reduction of these substances is strictly reversible, and the oxidation-reduction potential may be readily measured. These reactions are, therefore, in every way comparable with such inorganic processes as the reduction of ferric salts. Such reactions appear to involve only the gain or loss of one or more electrons; the application of the principles of electrochemistry, therefore, seems justified, and leads to some interesting generalizations. On the other hand, many of the more usual cases of the reduction of organic substances do not seem to involve merely electron transfer. In the reduction of ethylene and its derivatives, for example, hydrogen atoms are actually added to the molecule; the reaction is not reversible. Such reductions are brought about not by reagents like hydrosulfite or titanous chloride, but by hydrogen and a catalyst, or by some metal capable of liberating "nascent" hydrogen. The conception of oxidation-reduction potentials does not seem applicable to such irreversible hydrogenations.

The conjugated system, $O=C-C=C-C=O$, is characteristic of many substances which undergo reversible reduction. The simplest case is that of quinone. Indigo and the indigoids, as well as anthraquinone and some of the vat dyes derived from it all contain this system. Haber and Russ² have carefully measured the potential of the system quinone-hydroquinone in acid solution. Recently Granger and Nelson³ have repeated Haber's work. Clark⁴ has studied the oxidation-reduction potential of indigo carmine and certain other dyestuffs and obtained reproducible and consistent results. All these investigations have shown that the reduction of certain organic compounds in acid solution can be expressed in terms of the general principles of electrochemistry.

In acid solution, the reaction may be represented thus: (A = oxidized form, AH_2 = reduced)



The potential of such a reaction is expressed by the well-known formula

$$\pi = \pi_0 + 0.059 \log [H^+] + 0.0295 \log [A]/[AH_2] \quad (1)$$

where $[A]$ is the concentration of oxidized form, and $[AH_2]$ is the concentration of the reduced form.

$$\pi = \pi_0, \text{ obviously, when } [H^+] = 1, \text{ and } [A]/[AH_2] = 1$$

² Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904).

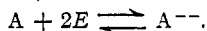
³ Granger and Nelson, *THIS JOURNAL*, **43**, 1401 (1921).

⁴ Clark, *J. Wash. Acad. Sci.*, **10**, 255 (1920); *Science*, **54**, 557 (1921).

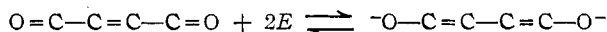
This formula was shown by Haber and Russ to express accurately all their experimental results with quinone.

While the system quinone:hydroquinone is reversible in acid solution, side reactions make it essentially irreversible in alkaline solutions, and no constant values could be obtained by Granger and Nelson. The reactions at present under investigation are reversible in both acid and alkaline solutions. Therefore, for the first time, it has been possible to measure the potential of an organic reduction process over a wide range of hydrogen-ion concentration.

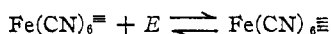
A consideration of the reaction in alkaline solution (the most usual condition for vat dye reduction) leads to a slightly different point of view from that represented in Equation 1. The reduction product, AH_2 , is an acid, and in alkaline solution is very largely present in the form of the ion A^{--} . The reduction, therefore, under these conditions is practically



Only the transfer of two electrons is involved. If the structure of the substances under investigation is examined, it will be observed that this process of reduction is essentially a 1,6 addition of two electrons to a conjugated system.



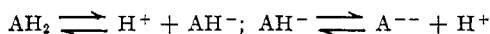
This reaction is in form exactly like those for such inorganic processes as



Considering the reaction from this point of view the equation for the single oxidation-reduction electrode at 25° would be

$$\pi = \pi'_0 + 0.0295 \log ([A]/[A^{--}]) \quad (2)$$

The reduced material is a weak dibasic acid, and dissociates according to the following equations.



The concentration of the divalent ion A^{--} can, therefore, be expressed in terms of the total concentration of the reduced material, $([AH_2]_T)$, (which is what is really measured) in accordance with the following considerations.

$$K_1 = \frac{[H^+][AH^-]}{[AH_2]}; K_2 = \frac{[H^+][A^{--}]}{[AH^-]}$$

$$[AH_2]_T = [A^{--}] + [AH^-] + [AH_2]$$

From this it follows that

$$[A^{--}] = K_1 K_2 [AH_2]_T / (K_1 K_2 + [H^+]^2 + K_1 [H^+])$$

Substituting this value in Equation 2 we have

$$\pi = \pi'_0 + 0.0295 \log ([A]/[AH_2]_T) - 0.0295 \log K_1 K_2 \\ + 0.0295 \log (K_1 K_2 + [H^+]^2 + K_1 [H^+])$$

The last term can be expressed more conveniently by multiplying and dividing by $[H^+]^2$ which gives:

$$\pi = \pi'_0 + 0.0295 \log ([A]/[AH_2]_T) - 0.0295 \log K_1K_2 + 0.059 \log [H^+] + 0.0295 \log \{K_1(K_2 + [H^+]/[H^+]^2) + 1\} \quad (3)$$

Equation 3 is thus a general expression for the oxidation-reduction potential in both acid and alkaline solutions. Since the reduced compounds are very weak acids, Equation 3 can be simplified when applied to the potentials measured in acid solutions. The last term is, under these conditions, negligible and $[AH_2] = [AH_2]_T$, therefore

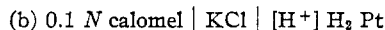
$$\pi = \pi'_0 + 0.0295 \log ([A]/[AH_2]) - 0.0295 \log K_1K_2 + 0.059 \log [H^+]$$

Comparing this modified Equation 3 with Equation 1, which also expresses the potential in acid solution, we see that

$$\pi_0 = \pi'_0 - 0.0295 \log K_1K_2. \quad (4)$$

This relationship is obviously correct since π_0 is a measure of the free energy of the formation of AH_2 from A , π'_0 a measure of the free energy of formation of A^{--} from A , and $0.0295 \log K_1K_2$ corresponds to the free energy change in the dissociation of AH_2 into A^{--} .

In order to test the applicability of Equation 3 the electromotive force of the following two types of cells was measured.



The mixture of oxidized and reduced material was obtained by adding definite increments of a reducing agent to a solution of the oxidized form. The hydrogen-ion concentration was controlled by means of "buffer" solutions. The observed value of the potential of the hydrogen electrode (Cell b) supplied the necessary information in regard to the hydrogen-ion concentration; the potential of Cell a was the required oxidation-reduction potential, and a knowledge of the amount of reducing agent added enabled one to calculate the value for the ratio of $[A]/[AH_2]_T$.⁵ As will be shown below, the results thus obtained were in accord with Equation 3.

Apparatus and Materials

The oxidation-reduction potentials were measured on 2 platinum electrodes (one bright, the other platinized) immersed in the solution which was contained in a glass cell of 400 cc. capacity. The contents of the cell were agitated by a glass stirrer working through a mercury seal and driven by an electric motor by means of a flexible shaft. An agar-agar bridge saturated with potassium chloride made connection with a 0.1 *N* calomel electrode. The cell could be swept free from air by the introduction of nitrogen free from oxygen. The reducing agent was contained in a buret the tip of which was fitted to a tube leading to the bottom of the cell; this served also as the inlet tube for the nitrogen.

It was found convenient to have the cell also equipped with a hydrogen

⁵ Clark first used this method in his studies (Ref. 4); his paper, however, did not come to our attention until after we had developed a similar procedure.

electrode of the Hildebrand type through which hydrogen was bubbled when desired. By this arrangement the potential of the hydrogen electrode was determined in the same apparatus as the oxidation-reduction potential. As will be evident later, any errors due to liquid junctions or to the calomel cell were thus canceled in the final calculations.

The electromotive force was measured on a Leeds and Northrup student potentiometer accurate to about 0.5 mv. The temperature of the cells was kept at 25° within a degree.

The organic compounds used in this work were the salts of 6 anthraquinone sulfonic acids.⁶ As shown by the titration curves, they contained considerable amounts of inert material which, however, did not interfere with the determination of the oxidation-reduction potentials by the present method. It might be noted that two samples of the β salt from different laboratories yielded identical results. The purities of the sodium salts of the α -, β -, the 2,6-, the 2,7- and the 1,5-sulfonic acids were 96, 95, 94, 87 and 92%, respectively. The 1,5- and the 1,8-calcium salts were 83 and 56% pure, respectively. Two reducing agents were employed; titanous chloride in 0.1 *N* acid solutions, and sodium hydrosulfite in all other solutions. Difficulties were encountered with titanous chloride in both citrate and acetate buffer solutions in the range of Sørensen value P_H 2 to P_H 7, complex precipitates being formed. Hydrosulfite is decomposed by even dil. acids, but it was found that it could be used in acid solutions because the speed of its oxidation by the anthraquinone derivative is much greater than that of its decomposition by the acid.

Control of the Hydrogen-ion Concentration

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 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 Clark⁷ were employed. Since the concentration of organic substance was very low (0.003 *M*) it seemed that such buffer solutions would keep the hydrogen-ion concentration constant throughout the reduction. The solutions were not made up determinate but were adjusted to the desired hydrogen-ion concentration which was determined by the hydrogen electrode just before the anthraquinone derivative was added. For the range P_H 10 to 12, a sodium phenolate solution was used with good results. It was not stable, however, for longer than a day.

Certain of the compounds investigated are rapidly decomposed by solu-

⁶ With one exception kindly furnished by E. I. Du Pont de Nemours and Company.

⁷ "The Determination of Hydrogen Ions," by W. M. Clark, Williams and Wilkins, 1920.

tions of sodium hydroxide 0.1 *N* or stronger. In citrate buffer solutions of the same hydrogen-ion concentration, however, the substances are stable. The use of buffer solutions, therefore, enabled us to measure the potentials of these compounds in the range P_H 11 to 13.

Procedure

The buffer solution (350 cc.) was introduced into the cell and the potential of the hydrogen electrode determined. One thousandth of a mole of the anthraquinone sulfonic acid in the form of its sodium or calcium salt was then added. The cell was swept free from air, the stirrer started and the reducing agent added in suitable increments from a buret. Fresh solutions of the hydrosulfite (1.25 g. in 100 cc.) were prepared for each run; the titanous chloride was also diluted to a 1% solution just before the beginning of the run in which it was to be used. The solution in the buret was protected by a layer of benzene.

After the addition of each increment of reducing agent, the potentials of both the bright and platinized electrodes were determined. No more reducing agent was added until both electrodes came to the same value which was then recorded. In a few cases (at about P_H 3), the potential of the platinized electrode gave consistent and reproducible values which were considered correct, although the bright electrode gave lower and variable potentials. The electrodes soon came to equilibrium when the solutions were rapidly stirred; without stirring it would be necessary to wait about 30 min. after the addition of each increment. The course of the reduction was followed by plotting the potential against the increments of reducing agent. Fig. 1 shows some typical titration curves thus obtained (the variations in the slope are discussed below). By an inspection of these curves it is possible to determine the end-point of the titration with considerable accuracy. Taking this value as 100% reduction, the increments of the reducing agent may now be expressed in terms of percentage

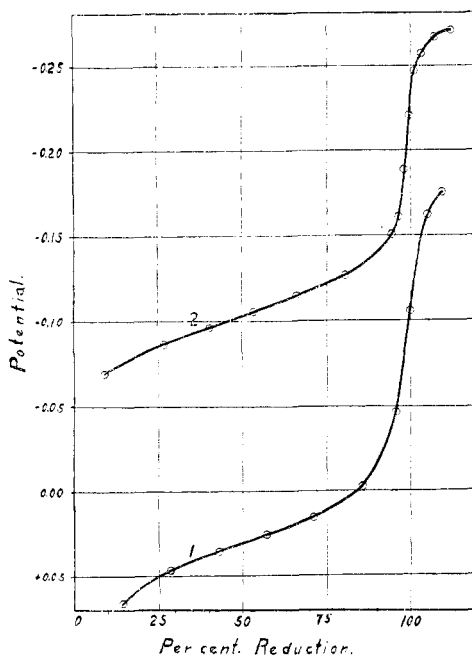


Fig. 1.—Typical titration curves.

Curve 1: disodium salt of anthraquinone-2,7-disulfonic acid; P_H 3.44. Curve 2: sodium salt of anthraquinone- β -sulfonic acid P_H 3.83.

reduction as in Fig. 1. The value for the potential at the mid-point (50% reduction) can now be determined by graphical interpolation of the curve.

Such a procedure as the one just outlined might be found useful for determining the purity of anthraquinone derivatives and similar compounds. The details of such an analytical method have not yet been elaborated.

Experimental Results

Table I summarizes the results obtained in this investigation. All the electromotive force measurements are given as single potentials in *volts* referred to the normal hydrogen electrode as zero. Thus the values for the hydrogen electrode (π_h) and the oxidation-reduction electrode at the

TABLE I
SODIUM SALT OF ANTHRAQUINONE BETA SULFONIC ACID

Hydrogen-ion conc. [H ⁺]	Hydrogen electrode π_h v.	Oxidation-reduction electrode π_n v.	$\Delta\pi_1$ ($m=0.2$) v.	$\Delta\pi_2$ ($m=0.8$) v.	$\pi_n - \pi_h$ $= \pi_o$ v.	$\pi_n - \pi_h$ $= \pi_o$ v.	Calc. dissociation constants	Nature of buffer solution
6.03×10^{-2}	-0.072	+0.117	0.022	0.024	0.189	HCl
4.07×10^{-2}	-0.082	+0.105	0.022	0.024	0.187	KCl + HCl
1.41×10^{-4}	-0.227	-0.085	0.031	0.023	0.192	NaAc + HAc
1.86×10^{-5}	-0.279	-0.096	0.024	0.027	0.183	NaAc + HAc
5.79×10^{-6}	-0.309	-0.129	0.022	0.023	0.180	NaAc + HAc
1.41×10^{-6}	-0.345	-0.154	0.024	0.025	0.191	NaAc + HAc
6.52×10^{-7}	-0.365	-0.176	0.020	0.022	0.189	KH ₂ PO ₄ + NaOH
1.86×10^{-7}	-0.397	-0.214	0.022	0.020	0.183	KH ₂ PO ₄ + NaOH
1.26×10^{-7}	-0.407	-0.223	0.024	0.022	0.184	KH ₂ PO ₄ + NaOH
8.55×10^{-8}	-0.417	-0.232	0.021	0.023	0.185	KH ₂ PO ₄ + NaOH
2.27×10^{-8}	-0.451	-0.258	0.019	0.020	0.193	KH ₂ PO ₄ + NaOH
				Av.	0.187	
7.31×10^{-9}	-0.480	-0.277	0.015	0.018	...	0.016	2×10^{-8}	KH ₂ PO ₄ + NaOH
6.03×10^{-9}	-0.485	-0.278	0.014	0.017	...	0.020	2×10^{-8}	KH ₂ PO ₄ + NaOH
2.45×10^{-9}	-0.508	-0.304	0.025	0.019	...	0.017	0.7×10^{-8}	Borax + H ₂ BO ₃
1.41×10^{-9}	-0.522	-0.319	0.022	0.017	...	0.016	0.4×10^{-8}	Borax + H ₂ BO ₃
6.26×10^{-10}	-0.543	-0.323	0.018	0.015	...	0.033	0.8×10^{-8}	H ₂ BO ₃ + NaOH
2.45×10^{-10}	-0.567	-0.335	0.014	0.017	...	0.045	0.8×10^{-8}	H ₂ BO ₃ + NaOH
7.59×10^{-11}	-0.597	-0.350	0.014	0.014	...	0.060	0.7×10^{-8}	H ₂ BO ₃ + NaOH
2.45×10^{-11}	-0.626	-0.370	0.037	0.023	...	0.069	0.3×10^{-8}	Phenol + NaOH
7.03×10^{-12}	-0.658	-0.383	0.034	0.022	...	0.088	5×10^{-9}	Phenol + NaOH
1.38×10^{-12}	-0.700	-0.381	0.044	0.025	...	0.132	5×10^{-9}	Phenol + NaOH
1.38×10^{-12}	-0.700	-0.380	0.028	0.018	...	0.133	6×10^{-9}	Glycocoll + NaOH
6.27×10^{-13}	-0.720	-0.381	0.058	0.014	...	0.152	5×10^{-9}	Citrate + NaOH
1.88×10^{-13}	-0.751	-0.384	0.039	0.033	...	0.180	4×10^{-9}	Citrate + NaOH
1.55×10^{-13}	-0.756	-0.379	0.034	0.032	...	0.190	7×10^{-9}	Glycocoll + NaOH
8.89×10^{-14}	-0.770	-0.393	0.027	0.034	...	0.190	2×10^{-9}	KOH

Av. (first eight), $K_1 = 1 \times 10^{-8}$

Av. (last seven), $K_1 K_2 = 5 \times 10^{-20}$

DISODIUM SALT OF ANTHRAQUINONE-2,6-DISULFONIC ACID

3.63×10^{-2}	-0.085	+0.143	0.023	0.033	0.228	HCl
1.41×10^{-4}	-0.227	+0.001	0.030	0.031	0.228	NaAc + HAc
1.41×10^{-5}	-0.345	-0.120	0.024	0.033	0.225	NaAc + HAc
1.26×10^{-7}	-0.407	-0.181	0.024	0.032	0.226	KH ₂ PO ₄ + NaOH
2.27×10^{-8}	-0.451	-0.220	0.019	0.027	0.231	KH ₂ PO ₄ + NaOH
				Av.	0.228	
9.62×10^{-10}	-0.532	-0.275	0.024	0.032	...	0.029	0.8×10^{-8}	Borax + H ₂ BO ₃
2.36×10^{-10}	-0.568	-0.292	0.021	0.027	...	0.048	0.9×10^{-8}	H ₂ BO ₃ + NaOH

3.24×10^{-11}	-0.619	-0.811	0.040	0.036	...	0.080	1×10^{-8}	Phenol + NaOH
7.91×10^{-12}	-0.655	-0.321	0.042	0.041	...	0.106	0.6×10^{-8}	Phenol + NaOH
5.37×10^{-12}	-0.665	-0.324	0.035	0.035	...	0.113	2×10^{-10}	Phenol + NaOH
1.32×10^{-12}	-0.701	-0.326	0.038	0.040	...	0.147	2×10^{-10}	Phenol + NaOH
6.26×10^{-13}	-0.720	-0.326	0.043	0.042	...	0.166	2×10^{-10}	Citrate + NaOH
8.89×10^{-14}	-0.770	-0.325	0.037	0.046	...	0.217	2×10^{-10}	KOH

Av. (first four) $K_1 = 8 \times 10^{-9}$ Av. (last four) $K_1 K_2 = 2 \times 10^{-10}$

DICALCIUM SALT OF ANTHRAQUINONE-1,8-DISULFONIC ACID

7.32×10^{-2}	-0.067	+0.135	0.035	0.024	0.202	HCl
7.59×10^{-4}	-0.184	+0.012	0.045	0.026	0.196	Citrate + HCl
1.17×10^{-4}	-0.232	-0.035	0.045	0.026	0.197	NaAc + HAc
1.86×10^{-5}	-0.279	-0.069	0.022	0.030	0.210	NaAc + HAc
1.05×10^{-5}	-0.353	-0.144	0.047	0.027	0.209	KH_2PO_4 + NaOH
8.55×10^{-8}	-0.417	-0.206	0.044	0.027	0.211	KH_2PO_4 + NaOH
1.26×10^{-8}	-0.466	-0.252	0.045	0.030	0.214	KH_2PO_4 + NaOH

Av. 0.206

6.76×10^{-10}	-0.541	-0.303	0.038	0.037	...	0.032	0.7×10^{-8}	Borax + H_3BO_3
8.89×10^{-11}	-0.593	-0.332	0.034	0.025	...	0.055	0.7×10^{-8}	H_3BO_3 + NaOH
1.17×10^{-11}	-0.645	-0.351	0.050	0.033	...	0.088	1×10^{-8}	Phenol + NaOH
3.63×10^{-12}	-0.675	-0.371	0.040	0.030	...	0.098	0.7×10^{-8}	Phenol + NaOH
1.23×10^{-12}	-0.703	-0.383	0.043	0.041	...	0.114	0.7×10^{-8}	Phenol + NaOH
4.58×10^{-13}	-0.728	-0.405	0.042	0.039	...	0.117	0.4×10^{-8}	Phenol + NaOH
4.25×10^{-13}	-0.730	-0.407	0.040	0.032	...	0.117	0.4×10^{-8}	Citrate + NaOH
3.22×10^{-13}	-0.737	-0.419	0.040	0.036	...	0.112	0.2×10^{-8}	Citrate + NaOH
1.87×10^{-13}	-0.751	-0.413	0.046	0.036	...	0.132	0.6×10^{-8}	Citrate + NaOH
4.77×10^{-14}	-0.786	-0.413	0.049	0.035	...	0.167	2×10^{-8}	KOH

Av. $K_1 = 7 \times 10^{-9}$ $K_1 K_2$ is negligible

DISODIUM SALT OF ANTHRAQUINONE-2,7-DISULFONIC ACID

3.63×10^{-2}	-0.085	+0.132	0.025	0.025	0.217	HCl
2.55×10^{-3}	-0.138	+0.070	0.024	0.025	0.223	Citrate + HCl
1.41×10^{-4}	-0.227	+0.005	0.025	0.026	0.232	NaAc + HAc
1.95×10^{-5}	-0.278	-0.049	0.021	0.025	0.229	NaAc + HAc
3.63×10^{-6}	-0.321	-0.092	0.026	0.026	0.229	NaAc + HAc
1.86×10^{-7}	-0.397	-0.167	0.023	0.020	0.230	KH_2PO_4 + NaOH
2.27×10^{-8}	-0.451	-0.205	0.021	0.024	0.246	KH_2PO_4 + NaOH

Av. 0.229

1.32×10^{-9}	-0.524	-0.268	0.013	0.016	...	0.027	1×10^{-8}	Borax + H_3BO_3
9.62×10^{-10}	-0.532	-0.263	0.028	0.024	...	0.040	2×10^{-8}	Borax + H_3BO_3
4.57×10^{-10}	-0.551	-0.274	0.021	0.027	...	0.048	2×10^{-8}	H_3BO_3 + NaOH
2.36×10^{-10}	-0.568	-0.278	0.023	0.019	...	0.061	3×10^{-8}	H_3BO_3 + NaOH
7.03×10^{-11}	-0.599	-0.292	0.025	0.028	...	0.078	3×10^{-8}	Glycocoll + NaOH
1.58×10^{-11}	-0.637	-0.312	0.031	0.031	...	0.096	5×10^{-10}	Phenol + NaOH
1.17×10^{-11}	-0.645	-0.311	0.034	0.035	...	0.105	5×10^{-10}	Phenol + NaOH
7.91×10^{-12}	-0.655	-0.319	0.036	0.036	...	0.107	3×10^{-10}	Phenol + NaOH
1.38×10^{-12}	-0.700	-0.319	0.032	0.031	...	0.152	3×10^{-10}	Phenol + NaOH
1.38×10^{-12}	-0.700	-0.314	0.030	0.030	...	0.157	4×10^{-10}	Glycocoll + NaOH
4.25×10^{-13}	-0.730	-0.311	0.028	0.032	...	0.190	5×10^{-10}	Citrate + NaOH
3.35×10^{-13}	-0.736	-0.315	0.037	0.046	...	0.192	4×10^{-10}	Citrate + NaOH
1.95×10^{-13}	-0.750	-0.319	0.046	0.043	...	0.202	3×10^{-10}	KOH
2.02×10^{-14}	-0.808	-0.298	0.040	0.044	...	0.281	1×10^{-10}	KOH

Av. (first five), $K_1 = 2 \times 10^{-8}$ Av. (last nine), $K_1 K_2 = 5 \times 10^{-10}$

POTASSIUM SALT OF ANTHRAQUINONE ALPHA SULFONIC ACID

1.86×10^{-1}	-0.046	+0.150	0.020	0.020	0.196	HCl
7.93×10^{-2}	-0.065	+0.134	0.020	0.019	0.199	HCl
4.07×10^{-4}	-0.200	-0.007	0.022	0.021	0.193	NaAc + HAc
7.03×10^{-5}	-0.245	-0.056	0.023	0.018	0.189	Citrate + HCl
5.86×10^{-6}	-0.311	-0.111	0.025	0.019	0.200	NaAc + HAc
2.19×10^{-6}	-0.334	-0.138	0.027	0.022	0.198	Citrate + NaOH
1.95×10^{-7}	-0.396	-0.210	0.020	0.018	0.186	KH_2PO_4 + NaOH
2.55×10^{-8}	-0.448	-0.247	0.018	0.016	0.201	Borax + H_3BO_3

Av. 0.195

TABLE I (continued)

Hydrogen-ion conc. [H ⁺]	Hydrogen electrode π_h v.	Oxidation-reduction electrode		$\pi_{n-\pi_h}$ $=\pi_o$ v.	$\pi_{n-\pi_h}$ $-\pi_o$ v.	Calc. dissociation constants	Nature of buffer solution
		$\Delta\pi_1$ ($m=0.2$) v.	$\Delta\pi_2$ ($m=0.8$) v.				
1.36×10^{-9}	-0.523	-0.311	0.019	0.017	...	3×10^{-9}	Borax + H ₂ BO ₃
9.25×10^{-11}	-0.592	-0.355	0.018	0.018	...	2×10^{-9}	Phenol + NaOH
4.76×10^{-11}	-0.609	-0.364	0.018	0.014	...	2×10^{-9}	Phenol + NaOH
4.41×10^{-12}	-0.670	-0.387	0.016	0.013	...	3×10^{-9}	Phenol + NaOH
2.45×10^{-12}	-0.685	-0.395	0.013	0.014	...	4×10^{-9}	Phenol + NaOH
4.99×10^{-13}	-0.726	-0.414	0.020	0.019	...	5×10^{-9}	Citrate + NaOH
3.89×10^{-13}	-0.732	-0.420	0.015	0.015	...	4×10^{-9}	Phenol + NaOH
2.63×10^{-13}	-0.742	-0.423	0.019	0.020	...	4×10^{-9}	Citrate + NaOH
8.59×10^{-14}	-0.771	-0.436	0.021	0.019	...	5×10^{-9}	Citrate + NaOH
5.67×10^{-14}	-0.782	-0.444	0.022	0.020	...	4×10^{-9}	Citrate + NaOH
Av. $K_1 = 4 \times 10^{-9}$							
K_1K_2 is negligible							
DISODIUM SALT OF ANTHRAQUINONE-1,5-DISULFONIC ACID							
2.36×10^{-1}	-0.037	+0.199	0.017	0.019	0.236	...	HCl
9.61×10^{-2}	-0.060	+0.176	0.018	0.019	0.236	...	HCl
3.77×10^{-2}	-0.084	+0.154	0.017	0.018	0.238	...	HCl
1.37×10^{-2}	-0.228	+0.011	0.022	0.023	0.239	...	NaAc + HAc
3.63×10^{-3}	-0.321	-0.081	0.024	0.025	0.240	...	NaAc + HAc
5.57×10^{-3}	-0.428	-0.191	0.036	0.028	0.237	...	NaAc + HAc
9.62×10^{-10}	-0.532	-0.290	0.018	0.019	0.242	...	KH ₂ PO ₄ + NaOH
4.57×10^{-10}	-0.551	-0.307	...	0.019	0.243	...	H ₂ BO ₃ + NaOH
4.24×10^{-11}	-0.612	-0.372	0.017	0.016	0.240	...	Phenol + NaOH
3.35×10^{-11}	-0.618	-0.379	0.015	0.016	0.239	...	Phenol + NaOH
Av. 0.239							
3.92×10^{-12}	-0.673	-0.422	0.015	0.016	...	4×10^{-12}	Phenol + NaOH
9.60×10^{-13}	-0.709	-0.454	0.013	0.014	...	2×10^{-12}	Phenol + NaOH
4.58×10^{-13}	-0.728	-0.468	0.019	0.018	...	2×10^{-12}	Glycocoll + NaOH
1.87×10^{-13}	-0.751	-0.485	0.022	0.021	...	2×10^{-12}	Glycocoll + NaOH
1.73×10^{-13}	-0.753	-0.494	0.029	0.020	...	0.6×10^{-12}	NaOH
1.26×10^{-13}	-0.761	-0.489	0.025	0.022	...	2×10^{-12}	Citrate + NaOH
8.89×10^{-14}	-0.770	-0.499	0.025	0.022	...	1×10^{-12}	KOH
3.77×10^{-14}	-0.792	-0.498	0.033	0.031	...	4×10^{-12}	NaOH
3.35×10^{-14}	-0.795	-0.502	0.035	0.028	...	2×10^{-12}	NaOH
2.75×10^{-14}	-0.800	-0.500	0.040	0.031	...	3×10^{-12}	NaOH
Av. $K_1 = 3 \times 10^{-12}$							
K_1K_2 is negligible							
DICALCIUM SALT OF ANTHRAQUINONE-1,5-DISULFONIC ACID							
2.36×10^{-1}	-0.037	+0.199	0.020	0.018	0.236	...	HCl
9.61×10^{-2}	-0.060	+0.178	0.020	0.022	0.238	...	HCl
1.12×10^{-2}	-0.233	+0.002	0.029	0.024	0.235	...	NaAc + HAc
4.96×10^{-3}	-0.313	-0.080	0.020	0.022	0.233	...	NaAc + HAc
1.05×10^{-3}	-0.412	-0.175	0.020	0.024	0.237	...	KH ₂ PO ₄ + NaOH
3.48×10^{-10}	-0.558	-0.313	0.020	0.019	0.245	...	Phenol + NaOH
3.35×10^{-11}	-0.618	-0.374	0.027	0.020	0.244	...	Phenol + NaOH
Av. 0.238							
4.58×10^{-12}	-0.669	-0.407	0.028	0.026	...	3×10^{-11}	Phenol + NaOH
1.41×10^{-12}	-0.699	-0.433	0.034	0.019	...	1×10^{-11}	Phenol + NaOH
2.09×10^{-13}	-0.748	-0.475	0.043	0.024	...	3×10^{-12}	Citrate + NaOH
1.12×10^{-13}	-0.764	-0.483	0.048	0.031	...	3×10^{-12}	Citrate + NaOH

mid-point of reduction (π_n) are the observed electromotive forces of Cells b and a referred to above, subtracted from +0.337, the value assigned to the 0.1 N calomel electrode.

Under the heading "oxidation-reduction electrode" are given, first, π_n the the potential at the mid-point where $[A]/[AH_2]_T=1$, determined for

the titration curves as described above; second, $\Delta\pi_1$ the difference between the potential at the mid-point and at 20% reduction; and third, $\Delta\pi_2$ the corresponding difference to 80% reduction. These two values thus give the approximate slopes of the titration curves. It will be noted that the slopes vary greatly. This is probably due to combination between the reduced and oxidized material with the formation of a substance similar to quinhydrone. Similar difficulties were encountered and corrected for by Granger and Nelson in their work on quinone. If we let m equal the fractional moles of reducing agent added and x the degree of association of the supposed complex then the value for $\Delta\pi$ is

$$\Delta\pi = \pm 0.0295 \log \frac{1-m-mx}{m-mx}$$

The following table gives values for $\Delta\pi$ for varying values of x when $m=0.2$ ($\Delta\pi_1$ in Table I).

x	0.0	0.2	0.4	0.6	0.8	0.9
$\Delta\pi_1$	0.018	0.020	0.023	0.027	0.035	0.044

A comparison of these numbers with the values for $\Delta\pi$, given in Table I,

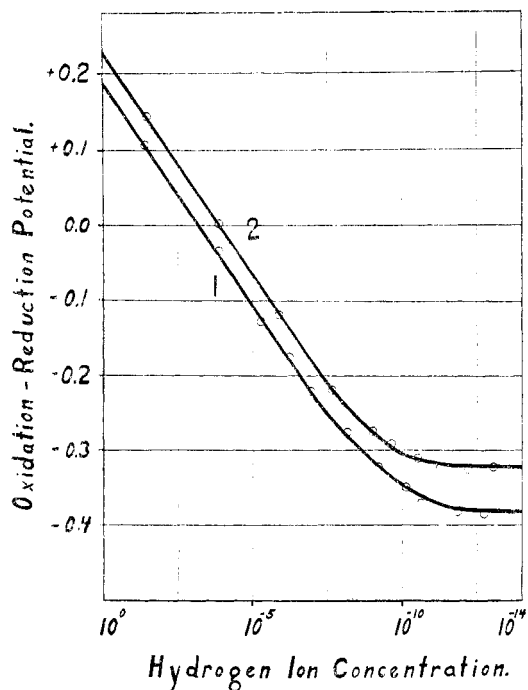


Fig. 2.

Curve 1: sodium salt of anthraquinone- β -sulfonic acid. Curve 2: disodium salt of anthraquinone-2,6-disulfonic acid.

shows that with certain compounds, particularly in alkaline solution, the complex must be highly associated. The errors of the present method, which seem to be about 5 millivolts, make the values for $\Delta\pi$ much less reliable than those for π_n . Moreover, the potential at the mid-point would not be affected by complex formation so that π_n is the most significant potential for theoretical discussion.

The Potential in Acid and Alkaline Solutions

The curves shown in Figs. 2, 3, and 4 are graphical representations of the results given in Table I. The points show typical experimentally determined values of π_n plotted against the hydrogen-ion concentration. The smooth curve was drawn through points calculated from Equation 3.

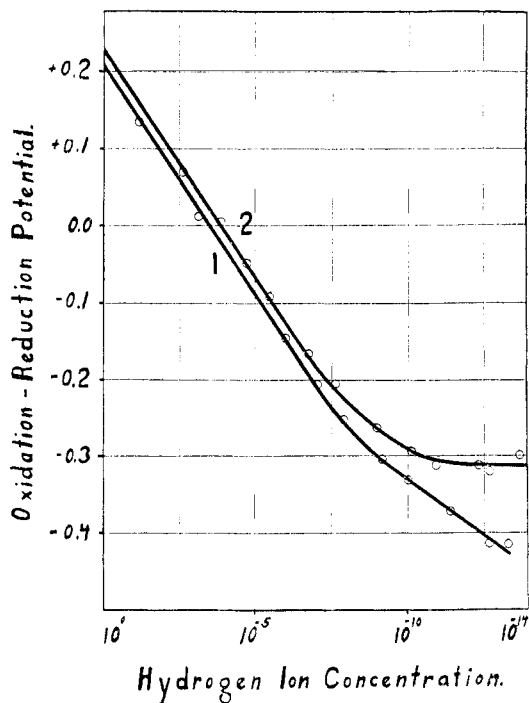


Fig. 3.

Curve 1: dicalcium salt of anthraquinone-1,8-disulfonic acid. Curve 2: disodium salt of anthraquinone-2,7-disulfonic acid.

In acid solution, $\pi_n - \pi_h$ is obviously equal to π_0 since, from Equations 3 and 4, $\pi_n = \pi_0 + 0.059 \log [H^+]$ and $\pi_h = 0.059 \log [H^+]$. The values thus obtained for π_0 are essentially constant (Col. 6, Table I). The last term of Equation 3 is equal to $\pi_n - \pi_h - \pi_0$ from similar considerations; it is negligible in acid solutions.

In alkaline solution this last term of Equation 3 (Col. 7, Table I) becomes appreciable and the curve bends. In some cases the curve becomes flat showing that the term has now reduced to $+0.0295 \log K_1 K_2 / [H^+]^2$ since $K_2 > [H^+]$ and Equation 3 is therefore now: $\pi_n = \pi'_0$, the reduced form being present entirely as the divalent ion. In such cases the value for $K_1 K_2$ can be directly calculated from Equation 4. Values for K_1 may now be obtained by solving Equation 3 for each point on the bend of the graph. The values for $K_1 K_2$ and K_1 calculated in this manner are given in Col. 8 of Table I. In those instances in which the normal potential did not reach a limiting value in strongly alkaline solutions, K_2 was apparently too small to be measured by this method. Its effect on the oxidation-reduction potential is obviously negligible and K_1 can be directly calculated. The values of K_1 and K_2 thus calculated were used in drawing the curves shown in Figs. 2, 3 and 4.

The correspondence between the experimentally determined points and the curves thus drawn shows that all the results of this investigation can be expressed by Equation 3.

The reproducibility of the results and the accuracy of the method can be seen either from the points shown in the figures or by examining Table I. It is obvious that π_0 for each substance should be constant; with a few exceptions the values agree within 10 millivolts. The values for K_1 calculated from the results obtained in alkaline solutions should agree; they are given in the next to the last column; some divergence will be noted. Finally, with those compounds in which the curves become flat, the last few values of π_n (π'_0) should be constant; they agree within the experimental error of the present method.

Validity of the Method

It was important to show that the reactions under investigation were strictly reversible and that the potential measured by the reduction method was the same as would be obtained from a mixture of the pure components. That the reaction is reversible is shown by the fact that the reduced vat may be oxidized by air or by ferric chloride and then reduced again to give the same potentials.

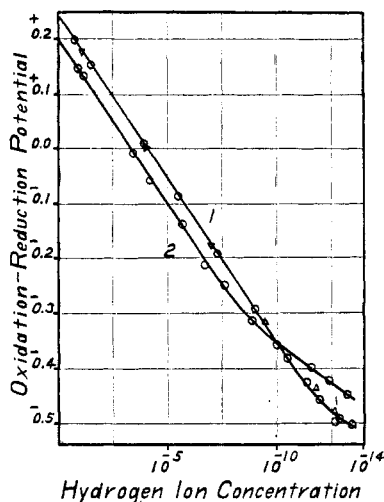


Fig. 4.

Curve 1: the 1,5-anthraquinone disulfonic acid, O = sodium salt; Δ = calcium salt. Curve 2: potassium salt of anthraquinone α -sulfonic acid.

That the potential of the system is not affected by the presence of the reducing agent and its oxidation product was shown by the results of another method. This consisted in preparing a diacetyl-anthrahydroquinone-sulfonic acid which was stable in the air, hydrolyzing it to the anthrahydroquinone derivative, and measuring the potential of mixtures of this with the anthraquinone compound.

Preparation of the Sodium Salt of Diacetyl-anthrahydroquinone- β -sulfonic Acid

The method of preparation was similar to that used by Liebermann in preparing diacetyl-anthrahydroquinone⁸ in which the compound was reduced and acetylated at the same time.

A mixture of 15 g. of sodium anthraquinone- β -sulfonate, 30 g. of sodium acetate, 45 g. of zinc dust and 180 g. of acetic anhydride was heated under a reflux condenser for a few minutes, poured into 500 cc. of water and allowed to stand for 4 hours. The solution was filtered and evaporated until crystals separated out of the sirup. These crystals were filtered, washed and recrystallized from glacial acetic acid.

Analyses. Calc. for $C_{18}H_{13}O_7SNa$: Na, 5.8. Found: 5.7, 5.6. Equivalents of NaOH required for hydrolysis: 2.0. Found: 2.1, 2.1.

The potential measurement was carried out as follows. The hydrogen-ion concentration of a mixture of 250 cc. of a phosphate buffer and 100 cc. of 0.1 *N* potassium hydroxide solution was determined. Two hundred and fifty cc. of the same buffer solution was placed in the cell and 0.2 g. of the diacetyl compound was weighed into a flask so arranged that it could be swept free from oxygen and its contents later blown over into the cell with the stream of nitrogen. One hundred cc. of oxygen-free 0.1 *N* potassium hydroxide solution was run into the flask through a dropping funnel and the solution heated to boiling to effect complete hydrolysis. The solution was cooled and blown over into the cell. Successive portions of a solution containing 0.004 g. of the sodium salt of β -anthraquinone-sulfonic acid per cc. were run into the cell and the potential measured after each addition.

The potentials read were plotted against $\log [A]/[AH_2]_T$ and the value of π_n found by interpolation. The results obtained in this and a second similar determination are

Phosphate buffer: $\pi_n = -0.231$, $\pi_h = -0.433$, $\pi_o = +0.202$

Citrate buffer: $\pi_n = -0.051$, $\pi_h = -0.249$, $\pi_o = +0.198$

Determined by the titration method (Table I) $\pi_o = +0.187$

The constant errors, namely, impurity of the sample, incomplete hydrolysis, and oxidation, would all tend to increase π_o , and a correction for them would bring the determination into closer agreement with the average value of the other method. This clearly indicates that the method of measuring oxidation-reduction potentials chosen in this investigation gives

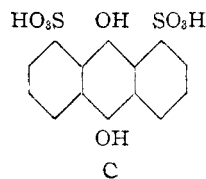
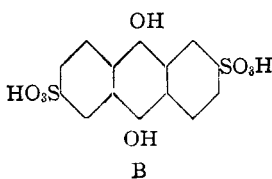
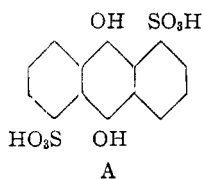
⁸ Liebermann, *Ber.*, **21**, 1172 (1888).

results comparable to those obtainable by more direct methods and that the presence of the reducing agent in no way affects the results.

Discussion

There is nothing to indicate that the two constants used in Equation 3 are the real dissociation constants of the reduced form except that Equation 3 can be developed on this basis. It would be very desirable to obtain independent evidence of the value of K_1K_2 , but this cannot be easily done.⁹ Unquestionably anthrahydroquinone and its derivatives are very weak acids but anthrahydroquinone itself is strong enough to form a disodium salt.¹⁰ The only related substance whose dissociation constants have been measured is hydroquinone; for this compound $K_1 = 10^{-10}$, K_2 is probably less and, therefore, K_1K_2 is somewhat less¹¹ than 10^{-20} . These values are of the same order of magnitude as those found for the anthrahydroquinone derivatives here investigated.

Table II summarizes the average values of the normal potentials and dissociation constants as determined by the results given in Table I. An examination of the values for K_1 and K_2 will show that they are entirely consistent with the structures of the compounds in question, and several regularities can be pointed out. Substitution of sulfonic acid groups in the β position does not markedly affect the degree of dissociation of either of the phenolic groups in the anthrahydroquinones. The values of K_1 and K_2 are approximately constant for the three β compounds; K_2 is somewhat less than K_1 , as would be expected. Substitution in the α position, however, has a marked effect on the adjacent phenolic group, lowering its dissociation constant by about 10^{-4} . Thus, in the 1,5 compound (A) which has a sulfonic acid group α to both phenolic groups, $K_1 = 10^{-12}$ and K_2 is probably less than 10^{-15} in contrast to the 2,6 compound (B) where $K_1 = 10^{-8}$ and $K_2 = 10^{-11}$.



On the other hand, in the α monosulfonic acid and the 1,8-disulfonic acid (C) the dissociation of the phenolic group farthest away from the substituent is not affected ($K_1 = 10^{-8}$) but the dissociation of the hydroxyl group

⁹ We are, of course, dealing throughout this article with the dissociation of the weak phenolic groups of the reduced compound. The sulfonic acid groups in the molecule are so strongly acidic that they can be neglected in this discussion.

¹⁰ *Ann.*, **379**, 37 (1911).

¹¹ *Z. physik. Chem.*, **66**, 71 (1909).

which has the adjacent substituents is lowered so that it is negligible in this work (less than 10^{-15}).

The oxidation-reduction potential (π_0) is made more positive by about 40 millivolts by the introduction of a second sulfonic acid group in either the α or β position. The 1,8 compound is, however, an exception to this rule, as here the increase is only about 10 millivolts. As would be expected from the properties of anthraquinone all these potentials are much lower than that recorded by Granger and Nelson for quinone, +0.695. A further discussion of the relationship between the structure of related compounds and their oxidation-reduction potentials will be deferred until the next paper, which will deal with the free and total energy changes in the reduction of anthraquinone, naphthoquinone and benzoquinone derivatives. The measurement of the temperature coefficients of the oxidation-reduction potentials of a series of such compounds is now in progress.

TABLE II
OXIDATION POTENTIALS OF ANTHRAQUINONE SULFONIC ACIDS AND THE DISSOCIATION
CONSTANTS OF THE PHENOLIC GROUP OF ANTHRAHYDROQUINONE SULFONIC ACID

Position of substituent	Normal potential of $AH_2(\pi_0)$ Volts	Normal potential of $A^{--}(\pi'_0)$ Volts	Dissociation constants	
			K_1	K_2
β	0.187	-0.383	1×10^{-8}	5×10^{-12}
2,6	0.228	-0.325	0.8×10^{-8}	3×10^{-11}
2,7	0.229	-0.313	2×10^{-8}	3×10^{-11}
α	0.195	0.4×10^{-8}	Too
1,5	0.239	3×10^{-12}	small to
1,8	0.206	0.7×10^{-8}	measure

The authors wish to express their indebtedness to Dr. E. K. Bolton and to E. I. Du Pont de Nemours and Company for supplying them with materials and to the Cyrus M. Warren Fund of the American Academy for a grant of money for the purchase of the potentiometer.

Summary

1. A general equation has been developed which expresses the oxidation-reduction potentials of compounds of the type of quinone in both acid and alkaline solutions.

2. The potentials of 6 anthraquinone sulfonic acids have been measured by a titration method using titanous chloride and sodium hydrosulfite. The results obtained over a wide range of hydrogen-ion concentration have been found to be in accord with the general equation as developed.

3. The validity of the experimental method has been shown by determining the potentials of mixtures of the reduced and oxidized compounds.

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