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## THE EFFECT OF SUBSTITUTION ON THE FREE ENERGY OF OXIDATION-REDUCTION REACTIONS. I. BENZOQUINONE DERIVATIVES

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### Introduction

This paper is an extension of the work on the oxidation-reduction potentials of quinone-hydroquinone mixtures initiated by Granger and Nelson<sup>2</sup> in this laboratory. The present authors have continued this study by measuring the potentials by another method and extending it to the derivatives of quinone to determine the effects of substitution on the free energy of reduction. A paper<sup>3</sup> has recently appeared dealing with the potentials of sulfonated anthraquinone salts, in which the authors state that they intend later to report upon the free energy of reduction of anthraquinone, naphthoquinone, and benzoquinone derivatives. We have accordingly considered it advisable to make a report of our observations and experiences at this time in order to avoid the possibility of future duplication of work and shall therefore limit ourselves in this paper to giving preliminary data regarding the effect of the substitution of methyl, *isopropyl*, dimethoxy, phenylene, bromo and chloro groups in the quinone nucleus, as well as data upon the validity, precision, and sources of error inherent in the titration method of measurement.

Quinone was chosen as a suitable nucleus for an investigation on the relation of structure to free energy<sup>4</sup> of reduction since such data would be most valuable for a systematic study and synthesis of dyestuffs for use as oxidation-reduction indicators<sup>5</sup> and also because some work<sup>6</sup> has indicated that data upon the oxidation potentials of hydroquinone derivatives may throw considerable light upon the nature and destruction of the anti-scorbutic vitamin, as previously intimated by one of us.<sup>7</sup>

The method of pure mixtures used by Granger and Nelson was aban-

<sup>1</sup> The data in this paper constitute a part of the data submitted by Miss Lillian E. Baker in a dissertation in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

<sup>2</sup> Granger and Nelson, *THIS JOURNAL*, **43**, 1401 (1921). For more details see Granger, *Dissertation*, Columbia University, March, 1920.

<sup>3</sup> Conant, Kahn, Fieser and Kurtz, *THIS JOURNAL*, **44**, 1382 (1922).

<sup>4</sup> At constant temperature and pressure as defined by G. N. Lewis, *ibid.*, **35**, 14 (1913).

<sup>5</sup> Clark, *J. Washington Acad. Sci.*, **10**, 255 (1920).

<sup>6</sup> Bezssonoff, *Compt. rend.*, **173**, 466 (1921).

<sup>7</sup> LaMer, *Dissertation*, Columbia University, May, 1921; *J. Ind. Eng. Chem.*, **13**, 1108 (1921); *THIS JOURNAL*, **44**, 172 (1922).

done, since their method requires a long period of time to reach equilibrium, and in that time appreciable chlorination from the hydrochloric acid in which the quinone and hydroquinone were dissolved often occurred as a side reaction, and furthermore because considerable unnecessary labor is involved in determining the concentrations existing at equilibrium. W. Mansfield Clark's<sup>5</sup> electrometric titration method was used instead, to avoid these difficulties.

The use of such a coupled reaction to hasten the attainment of the equilibrium of a slow reaction for potential measurements was first attempted by Haber and Russ<sup>8</sup> for the quinone-hydroquinone, and by Loimaranta and Abegg<sup>9</sup> for the arsenate-arsenite system. Luther<sup>10</sup> questioned the reliability of all methods that employ extraneous material to produce rapid equilibrium and outlined some of the criteria that must be met in order that potentials measured with inert electrodes, such as gold or platinum, may be considered to be those of the specific oxidation-reduction reaction under examination. These methods were, therefore, apparently abandoned until 1920, when Clark introduced the method of using the secondary material as a titrating agent and thereby measured the ratio of the concentrations of the reduced to those of the oxidized form from the volume of the titrating agent added and the end-point of the reaction. Clark infers that his potentials are the correct ones, since he obtains nearly constant values for different concentrations but offers no other proof<sup>11</sup> of the validity of his method of measurement. From the data which follow it will be seen that not only are all of Luther's criteria satisfied but that the still more rigorous test of reversing the direction of the reaction by oxidizing the hydroquinone with dichromate establishes the fact that the precision and validity of the titration method is of the same order as that of hydrogen-electrode measurements.

### Apparatus and Materials

The equipment consisted of a Leeds and Northrup Type K potentiometer, a galvanometer of high resistance with a sensitivity of 424 megohms, a period of 2.8 seconds and an external critical damping resistance of 2,000 ohms. The Weston cell was checked with other standardized cells in these laboratories and found to be 1.0187 volts as certified by the manufacturer. A Freas water-bath, constant to  $\pm 0.01^\circ$ , was used. Three saturated calomel cells were employed and checked daily with one another to 0.1 millivolt for all results herein recorded.

The titrations were performed with a calibrated buret in a deep 400cc. Pyrex beaker fitted with a carefully cleaned rubber stopper, through

<sup>8</sup> Haber and Russ, *Z. physik. Chem.*, **47**, 294 (1904).

<sup>9</sup> Loimaranta and Abegg, *Z. Elektrochem.*, **13**, 34 (1907).

<sup>10</sup> Luther, *ibid.*, **13**, 289 (1907).

<sup>11</sup> Conant *et al.* (Ref. 3, p. 1395) have compared the potentials of the sodium salt of *β*-anthraquinone sulfonic acid obtained by Clark's method with those obtained by the method of pure mixtures, but their results show differences of 11 and 15 mv.

which holes were bored to hold 3 electrodes, the buret tip, salt bridge, and nitrogen entrance and exit tubes. The hydrogen-electrode determinations were performed with the same apparatus, using platinized electrodes, hydrogen being exchanged for the nitrogen. Tank hydrogen was passed through mercuric chloride, acid permanganate, and twice through alkaline pyrogallate solutions, then through cotton wool before passing into the Fisher bottles containing some of the buffer solutions for saturating with water vapor. Barometric and vapor-pressure corrections were made in all cases. The nitrogen was passed through fresh pyrogallate solution and then through 30 cm. of tightly rolled copper gauze heated to 700–800°. Electrodes of pure gold, gold-plated platinum, and platinum were used, the same potentials being obtained in all cases. The first two types gave the sharpest potentials and the most rapid equilibrium.

The salt bridge consisted of a glass tube of 4mm. bore fitted with a glass stopper<sup>12</sup> ground sufficiently tight to prevent diffusion of the quinone substances and potassium chloride at the junction. Good conductivity was obtained through the joint. The salt bridge and calomel cells dipped into a beaker containing saturated potassium chloride solution.

The quinones were prepared by the oxidation of the corresponding amine or hydroxy compound with acidified dichromate in an ice-cooled solution, followed by distillation with steam wherever possible to separate the product. The materials were then recrystallized and sublimed as often as necessary until the melting points were constant and in agreement with those in the literature. No difficulty was experienced except in the case of the chloroquinone, where some dichloro compound is formed. Here 3 recrystallizations and 4 sublimations were necessary. Exposure to light is deleterious. Recrystallization or sublimation was always performed just before use. The melting points were: quinone, 115.7°; toluquinone, 67°; thymoquinone, 45.6°; chloroquinone, 57°; bromoquinone, 55°; hydroquinone, 169°; chlorohydroquinone, 102°; bromohydroquinone, 109–110°; dimethoxyquinone, 249°; *p*-xyloquinone, 123°; naphthoquinone, 124.5°. All were uncorrected for stem exposure.

The acidity of the titanous chloride solution used in making up the titrating solutions was determined by titration with sodium hydroxide in the presence of 0.05 *M* citric acid to prevent precipitation of titanous hydroxide. Sufficient 0.2 *M* hydrochloric acid and distilled water were then added to make a solution of *exactly* the same acidity as that of the buffer solution in the beaker, in order that there should be no change of acidity due to the addition of the titrating agent itself. The solutions were kept in the manner described by Thornton.<sup>13</sup>

<sup>12</sup> Suggested by Mr. L. Hammett of this Laboratory.

<sup>13</sup> Thornton, *THIS JOURNAL*, 43, 91 (1921).

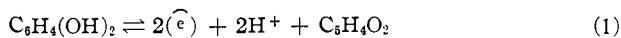
### Procedure

The apparatus being assembled the beaker was filled with 50, 75 or 100 cc. of buffer solution and the nitrogen bubbled through for at least an hour and a half to free the system from oxygen. The quinone compound, freshly resublimed, was then introduced through the buret-tip hole in quantity sufficient to make about a 0.001 to 0.003  $M$  solution, the buret replaced and the stopper sealed over with paraffin.

The flow of nitrogen was stopped after another half hour and the titration begun. The apparatus was so arranged that the solution in the beaker could be vigorously shaken by hand after each addition. Equilibrium was thus reached in 2 to 3 minutes with the gold electrodes. Readings were always continued for 6 to 10 minutes and recorded to the nearest 0.05 mv. within which limit the 3 separate electrodes checked. Moderate anodic or cathodic polarization did not affect the value of the potentials.

### Data and Discussion of Results

The reduction of quinone in acid solution may be expressed by the electrochemical equation<sup>14</sup>



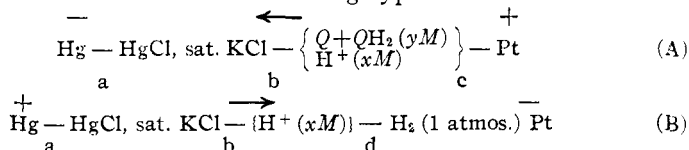
to which the familiar equation of Peters applies.

$$\pi = \pi_0 + 0.0591 \log \text{H}^+ + \frac{0.0591}{2} \log \frac{[Q]}{[QH_2]} \quad (2)$$

$$\pi_0 = \pi - 0.0591 \log \text{H}^+ - \frac{0.0591}{2} \log \frac{[Q]}{[QH_2]} \quad (2a)$$

where the normal potential  $\pi_0$  is a measure of the work necessary to transform one mole of quinone from the oxidized state to the reduced state by combining it with two atoms of hydrogen and is equal to  $\pi$  when the ratio of the activities of the reduced form to the oxidized form is unity, and when the activity of the hydrogen ion is likewise unity;  $[Q]$  and  $[QH_2]$  are, respectively, the concentrations of the oxidized and of the reduced forms.

The cells measured were of the following types



<sup>14</sup> Conant *et. al.*, have extended this equation to include the potentials for reactions in alkaline solutions. The reaction is different in alkaline solution since hydroquinone behaves as a very weak dibasic acid ( $K_1$  about  $10^{-10}$ ), and the reaction may be represented by  $\text{C}_6\text{H}_4\text{O}_2 + 2(\text{e}) \rightleftharpoons \text{C}_6\text{H}_4\text{O}_2^=$  in which case the potential is independent of the hydrogen-ion concentration. Conant's more general equation reduces to that of Peters' whenever the ionization of the hydroquinone becomes negligible, as is the case in all acid solutions, amounting to one part per thousand in a neutral solution or one part in  $10^{10}$  parts in our work.

where  $x$  varied between 0.1 and 0.2  $M$  hydrogen ion and  $y$  between 0.001 and 0.003  $M$ .

A minus B gives the value of the pole potentials of  $c$  against  $d$ , the pole of  $c$  being positive. This procedure is equivalent to converting the potential to that of a solution of hydrogen-ion activity 1  $M$  (that is, it is identical with performing the operation  $+0.0591 \log H^+$  in Equation 2), as well as eliminating the calomel cell and junction potential at the same time.

TABLE I  
ELECTROMETRIC TITRATION OF 20 MG. OF HYDROQUINONE IN 75 CC. OF 0.2  $M$  HYDROCHLORIC ACID BY POTASSIUM DICHROMATE OF THE SAME ACIDITY  
Potential of Combination B =  $-0.2907$ . Change of hydrogen-electrode potential due to the removal of  $H^+$  ion = 0.0009 for 100% oxidation. End-point = 17.70 cc.

Oxidizing Solution Cc.	Oxidized %	Observed potentials			A-B Corr.	$\frac{0.0591}{2} \log \frac{[O]}{[QH_2]}$	$\pi_0$ Normal Potentials
		Combination A	Combination B corrected for acidity change				
2.00	11.3	0.3812 <sub>5</sub>	-0.2908 <sub>0</sub>	0.6720 <sub>5</sub>	-0.0264	0.6984 <sub>5</sub>	
3.00	16.95	0.3875 <sub>5</sub>	-0.2908 <sub>5</sub>	0.6784 <sub>0</sub>	-0.0204	0.6988	
4.00	22.6	0.3923	-0.2909 <sub>0</sub>	0.6832 <sub>0</sub>	-0.0158	0.6990	
5.00	28.2	0.3961	-0.2909 <sub>5</sub>	0.6870 <sub>5</sub>	-0.0120	0.6990 <sub>5</sub>	
6.00	33.9	0.3992 <sub>5</sub>	-0.2910 <sub>0</sub>	0.6902 <sub>5</sub>	-0.0086	0.6988 <sub>5</sub>	
7.00	39.55	0.4024 <sub>5</sub>	-0.2910 <sub>5</sub>	0.6935	-0.0054 <sub>5</sub>	0.6989 <sub>5</sub>	
8.00	45.2	0.4055 <sub>5</sub>	-0.2911 <sub>0</sub>	0.6966 <sub>5</sub>	-0.0025	0.6991 <sub>5</sub>	
9.00	50.8	0.4083 <sub>5</sub>	-0.2911 <sub>5</sub>	0.6995	0.0004	0.6991	
10.00	56.5	0.4110 <sub>5</sub>	-0.2912 <sub>0</sub>	0.7022 <sub>5</sub>	0.0033 <sub>5</sub>	0.6989	
11.00	62.15	0.4140 <sub>5</sub>	-0.2912 <sub>5</sub>	0.7053	0.0064	0.6989	
12.00	67.8	0.4172 <sub>5</sub>	-0.2913 <sub>0</sub>	0.7085 <sub>5</sub>	0.0095 <sub>5</sub>	0.6990	
13.00	73.4	0.4206	-0.2913 <sub>5</sub>	0.7119 <sub>5</sub>	0.0130	0.6989 <sub>5</sub>	
14.00	79.1	0.4246 <sub>5</sub>	-0.2914 <sub>0</sub>	0.7160 <sub>5</sub>	0.0171	0.6989 <sub>5</sub>	
15.00	84.7	0.4295	-0.2914 <sub>5</sub>	0.7209 <sub>5</sub>	0.0220	0.6989 <sub>5</sub>	
16.00	90.4	0.4361	-0.2915 <sub>0</sub>	0.7276	0.0289	0.6987	
17.00	96.0	0.4477	-0.2915 <sub>5</sub>	0.7392 <sub>5</sub>	0.0408	0.6984 <sub>5</sub>	

Average of normal potentials between 15 and 70% = 0.6990

TABLE II  
ELECTROMETRIC TITRATION OF 20.5 MG. OF HYDROQUINONE IN 75 CC. OF 0.2  $M$  HYDROCHLORIC ACID BY POTASSIUM DICHROMATE OF THE SAME ACIDITY  
Potential of Combination B =  $-0.2907$ . Change of hydrogen-electrode potential due to removal of  $H^+$  ion = 0.0009 for 100% of oxidation. End-point = 18.15 cc.

2.00	11.0	0.3811	-0.2908	0.6719	-0.0268	0.6987
3.00	16.5	0.3873 <sub>5</sub>	-0.2908 <sub>5</sub>	0.6782	-0.0208	0.6990
4.00	22.0	0.3919 <sub>5</sub>	-0.2909	0.6828 <sub>5</sub>	-0.0162	0.6990 <sub>5</sub>
5.00	27.5 <sub>5</sub>	0.3957 <sub>5</sub>	-0.2909 <sub>5</sub>	0.6867	-0.0124 <sub>5</sub>	0.6991 <sub>5</sub>
6.00	33.0 <sub>5</sub>	0.3990 <sub>5</sub>	-0.2910	0.6900 <sub>5</sub>	-0.0090 <sub>5</sub>	0.6991
7.00	38.4 <sub>5</sub>	0.4020 <sub>5</sub>	-0.2910 <sub>5</sub>	0.6931	-0.0059 <sub>5</sub>	0.6990 <sub>5</sub>
8.00	44.1	0.4047 <sub>5</sub>	-0.2911	0.6958 <sub>5</sub>	-0.0030	0.6988 <sub>5</sub>
9.00	49.6	0.4076	-0.2911 <sub>5</sub>	0.6987 <sub>5</sub>	-0.0002	0.6989 <sub>5</sub>
10.00	55.1	0.4104 <sub>5</sub>	-0.2912	0.7016 <sub>5</sub>	+0.0026	0.6990 <sub>5</sub>
11.00	60.6	0.4133	-0.2912 <sub>5</sub>	0.7045 <sub>5</sub>	+0.0055	0.6990 <sub>5</sub>
12.00	66.1	0.4163	-0.2913	0.7076	+0.0086	0.6990
13.00	71.6	0.4196	-0.2913 <sub>5</sub>	0.7109 <sub>5</sub>	+0.0119	0.6990 <sub>5</sub>
14.00	77.1	0.4233	-0.2914	0.7147	+0.0156	0.6991
15.00	82.6 <sub>5</sub>	0.4279	-0.2914 <sub>5</sub>	0.7193 <sub>5</sub>	+0.0200	0.6993 <sub>5</sub>
16.00	88.1 <sub>5</sub>	0.4334 <sub>5</sub>	-0.2915	0.7249 <sub>5</sub>	+0.0257	0.6992 <sub>5</sub>
17.00	93.6 <sub>5</sub>	0.4421	-0.2915 <sub>5</sub>	0.7336 <sub>5</sub>	+0.0344 <sub>5</sub>	0.6992

Average of normal potentials between 15 and 70% = 0.6990

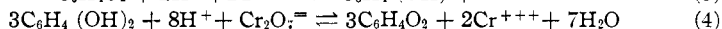
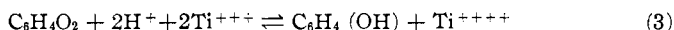
TABLE III

ELECTROMETRIC TITRATION OF 15 MG. OF BROMOQUINONE IN 75 CC. OF 0.2 *M* HYDROCHLORIC ACID BY TITANIUM CHLORIDE OF THE SAME ACIDITYPotential of Combination B = -0.2907. Change of hydrogen-electrode potential due to removal of H<sup>+</sup> ion = 0.0003 for 100% reduction. End-point = 17.53 cc.

Cc. reducing solution	Reduction %	Combination A	Observed potentials Combination B corrected for acidity change		A - B Corr.	$\frac{0.0591}{2} \log \frac{[Q]}{[QH_2]}$	$\pi_0$ Normal potentials
2.08	11.9	0.4503 <sub>5</sub>	-0.2907 <sub>5</sub>	0.7411	0.0257	0.7154	
3.08	17.6	0.4443	-0.2907 <sub>6</sub>	0.7350 <sub>5</sub>	0.0198	0.7152 <sub>5</sub>	
4.08	23.3	0.4397 <sub>5</sub>	-0.2908	0.7305 <sub>5</sub>	0.0153	0.7152 <sub>5</sub>	
5.08	29.0	0.4360 <sub>5</sub>	-0.2908	0.7268 <sub>5</sub>	0.0115	0.7153 <sub>5</sub>	
6.08	34.7	0.4325 <sub>5</sub>	-0.2908	0.7233 <sub>5</sub>	0.0081	0.7152 <sub>5</sub>	
7.08	40.4	0.4294 <sub>5</sub>	-0.2908	0.7202 <sub>5</sub>	0.0050	0.7152 <sub>5</sub>	
8.08	46.1	0.4264 <sub>5</sub>	-0.2908 <sub>5</sub>	0.7173	0.0020	0.7153	
9.08	51.8	0.4233	-0.2908 <sub>5</sub>	0.7141 <sub>5</sub>	-0.0009	0.7150 <sub>5</sub>	
10.08	57.5	0.4203 <sub>5</sub>	-0.2909	0.7112 <sub>5</sub>	-0.0039	0.7151 <sub>5</sub>	
11.08	63.2	0.4171	-0.2909	0.7080	-0.0069	0.7149 <sub>5</sub>	
12.08	68.9	0.4139 <sub>5</sub>	-0.2909	0.7048 <sub>5</sub>	-0.0102	0.7150 <sub>5</sub>	
13.08	74.6	0.4100 <sub>5</sub>	-0.2909 <sub>5</sub>	0.7010	-0.0138	0.7148	
14.08	80.3	0.4059 <sub>5</sub>	-0.2909 <sub>5</sub>	0.6969	-0.0181	0.7150	
15.08	86.0	0.4004 <sub>5</sub>	-0.2910	0.6914 <sub>5</sub>	-0.0233	0.7147 <sub>5</sub>	
15.58	88.9	0.3974 <sub>5</sub>	-0.2910 <sub>5</sub>	0.6885	-0.0267	0.7152	
16.08	91.6	0.3930 <sub>5</sub>	-0.2910	0.6840 <sub>5</sub>	-0.0307	0.7147 <sub>5</sub>	
17.08	97.3	0.3776	-0.2910	0.6686	-0.0460	0.7146	
Average of normal potentials between 15 and 70% = 0.7152							

Tables I, II and III give the results of typical titrations and show (Col. 7) the constancy of  $\pi_0$  when measured for different concentrations. Table IV summarizes the results on 8 different compounds at varying acidities and also shows the close concordance obtained when the equilibrium is approached from both sides in the cases of quinone, chloroquinone and bromoquinone.

In Tables I, II and III the values of B in Col. 4 are given a plus correction which has not been taken account of by any previous investigator, namely, for the removal of hydrogen ion during the course of the reaction, as indicated by the equations



$2^{2/3}$  moles of hydrogen ion being removed per mole of hydroquinone when dichromate is used and 2 moles when titanous chloride is used. We shall call this correction that of acidity change to distinguish it from the other larger correction of acidity represented by B. It is positive for Equations 3 and 4 and amounts in some of our data to 1 mv. for 100% reduction or oxidation; it is distributed proportionally in Col. 4. In Conant's titrations<sup>15</sup> for 0.0407 *M* hydrogen ion it amounts to as much as 4.1 millivolts, and we think it may be one of the causes for the variation of the

<sup>15</sup> Ref. 3, p. 1391.

TABLE IV  
NORMAL POTENTIALS OF SOME QUINONE DERIVATIVES, SHOWING EFFECT OF  
SUBSTITUTION

Substance	B			average $\pi_0$	Log $K_0$	— $F\Delta$ of reduction Kilojoules
	A	Corrected for acidity change at mid- point	$\pi_0$			
Bromoquinone re- duced	0.4241	-0.2909	0.7150	0.7151	24.19	138.0
	0.4243 <sub>s</sub>	-0.2909	0.7152 <sub>s</sub>			
Bromohydroquinone oxidized	0.4240 <sub>s</sub>	-0.2909 <sub>s</sub>	0.7150	0.7125	24.10	137.5
Chloroquinone re- duced	0.4199 <sub>s</sub>	-0.2921 <sub>s</sub>	0.7121			
	0.4148	-0.2978	0.7126			
Chlorohydroquinone oxidized	0.4155(?)	-0.2978	0.7133(?)	0.6990	23.65	134.9
	0.4212 <sub>s</sub>	-0.2909 <sub>s</sub>	0.7122			
Quinone reduced	0.3978	-0.3017	0.6995	0.6991	23.65	134.9
	0.4009 <sub>s</sub>	-0.2978 <sub>s</sub>	0.6988			
	0.4079	-0.2908 <sub>s</sub>	0.6987 <sub>s</sub>			
Hydroquinone oxi- dized	0.4078 <sub>s</sub>	-0.2911 <sub>s</sub>	0.6990	0.6454	21.84	124.6
	0.4014	-0.2980	0.6994			
Toluquinone reduced	0.3438 <sub>s</sub>	-0.3017 <sub>s</sub>	0.6456	0.5900	19.96	113.9
	0.3437 <sub>s</sub>	-0.3017 <sub>s</sub>	0.6455			
	0.3471	-0.2978	0.6449			
<i>p</i> -Xyloquinone re- duced	0.3546 <sub>s</sub>	-0.2908 <sub>s</sub>	0.6455	0.5875 <sub>s</sub>	19.87	113.4
	0.2991 <sub>s</sub>	-0.2908	0.5899 <sub>s</sub>			
	0.2992	-0.2908	0.5900	0.5139	17.39	99.2
<i>p</i> -Thymoquinone re- duced	0.2860	-0.3016	0.5876			
	0.2859	-0.3016	0.5875	0.4698	15.90	90.7
Dimethoxyquinone reduced	0.2232	-0.2908	0.5140			
	0.2230	-0.2908	0.5138	0.4698	15.90	90.7
Naphthoquinone re- duced	0.1789	-0.2908 <sub>s</sub>	0.4697 <sub>s</sub>			
	0.1790 <sub>s</sub>	-0.2908 <sub>s</sub>	0.4699			

slopes of their curves (the  $\pi_0$  drifts) which they attribute to the formation of quinhydrone.

Calculation of the degree of association of quinone and hydroquinone into quinhydrone using 0.263 as the value of the constant, determined independently by Granger and Nelson<sup>16</sup> and by Sörensen<sup>17</sup> and his collaborators, shows that the error from this source is negligible (only 0.05 mv. at 20% change) in the dilute solutions that we have used, except perhaps in those ranges of oxidation in which other errors to be discussed further on, can assume a more important role. The concordance of the results of Col. 7, which gives the value of the normal potential  $\pi_0$  by cor-

<sup>16</sup> Ref. 2, p. 1406.

<sup>17</sup> S. P. L. Sörensen, M. Sörensen and K. Linderström-Lang, *Compt. rend. Lab. Carlsberg*, 14, No. 14 (1921).

recting for the concentration ratio in Col. 6 shows that this is true. The Danish investigators<sup>18</sup> have also determined the activities of quinone and of hydroquinone in hydrochloric acid solutions with various additions of sodium chloride to determine the effect of salt on the potential of the quinhydrone electrode.

Their data show that the substitution of concentrations for activities is justified in this paper, since the correction amounts to only 0.3 mv. at 0.2 *M* (acid + salt) and zero at 0.1 *M*, but this would not necessarily be true for other concentrations or for other acids and salts. We have postponed our work with other buffers until we are able to obtain data on the respective activities of quinone and hydroquinone in such solutions.

Fortunately, we need not concern ourselves with the magnitude of the contact potential (b) except to show that it is constant and reproducible with our technique.<sup>19</sup> Preliminary experiments using 0.1 *N* acid in Combination B have shown us that any of the published results<sup>20</sup> may be obtained depending largely upon the size of the contact opening and the compactness with which it is plugged with cotton, as well as with the manner of making the junction. We are thoroughly convinced from a number of experiments that the ground-glass stopper form of junction is strictly reproducible, in addition to being the best means that has been used so far for the prevention of the interdiffusion of quinone substances and saturated potassium chloride<sup>21</sup>. For example, the following results were obtained with 0.2000 *N* hydrochloric acid in Combination B over a period of 10 hours.

Hours	Volts	Hours	Volts
1	0.29068	4	0.29070
2	0.29069	6	0.29070
3	0.29070	10	0.29067

<sup>18</sup> Ref. 17, p. 10.

<sup>19</sup> It is true that b differs in Combination A by having 0.003 *M* quinone on one side, but the current carried by such a weak electrolyte as hydroquinone in acid solution is entirely negligible in hydrochloric acid solutions.

<sup>20</sup> Values for 0.1 *N* HCl in Combination B (Col. 1) and the values of the saturated calomel cell derived therefrom using 0.0612 as the pole potential for 0.1 *N* HCl ( $\alpha = 92\%$ ). (Col. 2).

1	2	Source
0.3100	0.2488	Fales and Mudge, <i>THIS JOURNAL</i> , <b>40</b> , 2443 (1920).
0.3094	0.2482	Nelson and Beegle, <i>ibid.</i> , <b>42</b> , 2226 (1920), quoted.
0.3111	0.2499	Beans and Oakes, <i>ibid.</i> , <b>42</b> , 2226 (1920).
0.3083	0.2471	Our results with ground-glass junction.
....	0.2464	Clark, "Determination of Hydrogen Ions," Williams and Wilkins, Baltimore, 1920, p. 306.
....	0.2458	Michaelis, 1914, quoted by Clark, <i>op. cit.</i> , p. 140.

<sup>21</sup> Fales and Vosburgh, **40**, 1306 (1918), for the variations in contact potential with agar bridge.



These values check within 0.1 mv. of those obtained on 4 previous dates. The 4 other buffers used in this paper gave equally good results when determined on separate occasions. Also 8 determinations made on 4 different dates, have yielded  $0.30825 \pm 0.00005$  volts for 0.1 *N* hydrochloric acid.

Curve A, Fig. 1 shows the effect of a combined error of 0.05 cc. due to a hanging drop (0.03 cc.) on the tip of the buret and the error in reading

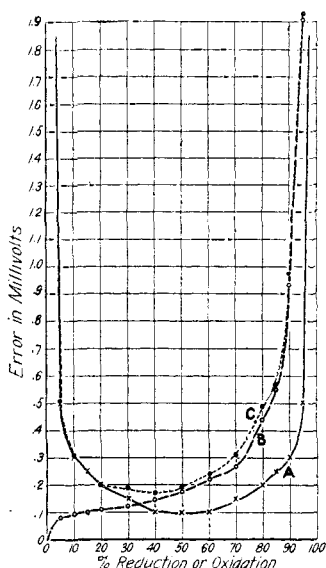


Fig. 1.

the buret (0.02 cc.) on the concentration correction at any stage of the titration. Curve B shows the same for the most likely error (0.10 cc.) in determining the end-point when the volume of titrating solution used is 20 cc. Curve C is the probable error, that is, the square root of the sum of the squares of each error, from both of these sources. Since the effect of the end-point error may become very pronounced in the later stages of the titration we have included only those values that correspond to a range of 15 to 70% oxidation or reduction, or an error limit of  $\pm 0.3$  mv. in determining the average values of  $\pi_0$ . For example, in the last 7 titrations on quinone derivatives the maximum deviations from the mean between 15 and 70% change were as follows: 0.10; 0.13; 0.23; 0.23; 0.20; 0.10; 0.40 mv. In the

last titration the values for  $\pi_0$  fell regularly, and the average of these values did not check with the values obtained in other experiments on thymoquinone, indicating an erroneous end-point. This experiment was the only one discarded for being outside the limit of error set above.

In Table IV we have given the value of the equilibrium constant  $K_0$  for the reactions involved when Equation 2 is written in the manner

$$\pi = \frac{0.0591}{2} \log \frac{[Q][H^+]^2}{[QH_2]} K_0 \quad (5)$$

The value of this thermodynamic constant shows the ratio of the concentrations of the reduced to the oxidized forms existing in equilibrium with a molal hydrogen electrode, that is,

$$\frac{[QH_2]}{[Q][H^+]^2} = K_0; \text{ or when } [H^+] = 1; \frac{[Q]}{[QH_2]} = K_0$$

The positive value of the exponent of  $K_0$  (or  $+\log K_0$ ) then becomes identical in sign and value with Clark and Zoller's<sup>22</sup>  $r_H$  which is the negative

<sup>22</sup> Clark and Zoller, *Science*, N. S., **44**, 557 (1921). See also Clark, Ref. 20, Chap. 14, and Ref. 5, p. 260 for a discussion of the meaning of  $r_H$ .

value of the exponent of the hypothetical pressure in atmospheres of gaseous hydrogen in equilibrium with an equimolecular mixture of the oxidized and reduced forms in a molal hydrogen-ion solution. They have proposed that we use the symbol  $r_H$  in a manner analogous to Sørensen's  $P_H$  as a convenient index in biological work for the oxidizing or reducing properties of a material. We prefer the thermodynamic constant  $\log K_0$  to  $r_H$  largely because, as we have written it in this paper, it avoids the troublesome change from negative to positive values, and also because it does not involve the assumption of a hydrogen-gas pressure so minute that in many cases its existence is merely hypothetical. Thus, for the quinone equilibrium this gas pressure ( $10^{-23.65}$  atmospheres) would represent a concentration of only 1.4 molecules of hydrogen in 22.4 liters of gas around the electrode. High values for  $\log K_0$  mean a better oxidizing (weaker reducing) agent or condition and *vice versa*, just as  $P_H$  indicates higher alkalinity or lower acidity.

Granger and Nelson did not refer their results to the molal hydrogen electrode, but taking Nelson and Beegle's value of 0.3094 as the most likely value for Combination B, in their work we get  $0.6989 \pm 0.0014$  as the normal potential of quinone-hydroquinone, which is in excellent agreement with our result  $0.6990_5 \pm 0.00025$  given in Table V. Haber and Russ' work cannot be compared, for they assumed complete dissociation of quinhydrone in a saturated solution, which is incorrect. Sørensen<sup>17</sup> obtains 7048 volts at 18° which yields a temperature coefficient of  $-0.00082$  volts per degree when taken in conjunction with our value at 25°.

The order of influence of the substituent on the free energy of reduction is as follows: bromo > chloro > none > methyl > dimethyl > *p*-methyl > *iso*-propyl > *m*-dimethoxy > phenylene (naphthoquinone), a result in general accord with the positive-negative rule of Michael. That is, it requires a higher (hypothetical) pressure of hydrogen to reduce the quinone nucleus with an alkyl group in it than without it, and the reverse is true for a halide group. A similar transposed order for the bromo and the chloro groups when substituted in the *ortho* position was pointed out by Derick<sup>23</sup> from the ionization constants of the chloro- and bromobenzoic acids. Other work in this Laboratory indicates that the atomic volumes of the atom or group of atoms may require consideration in addition to their electro character. Kehrman's<sup>24</sup> work on oxime formation in the substituted quinones offers support for this contention. It is interesting to note that the influence of a second methyl group in the *para* position is almost exactly twice that of the single group. It will be important to see how far the relationships given for the quinone nucleus hold for other similar nuclei such as naphtho- and anthraquinone. The part isomerism plays

<sup>23</sup> Derick, *THIS JOURNAL*, **33**, 1173 (1911).

<sup>24</sup> Cohen, "Organic Chemistry," Arnold, London 3rd. ed., 1920, vol. I, p. 332.

in the influence of these and other groups must be postponed for a later paper in which we expect to calculate the entropy changes from the temperature coefficients.

We wish to express our indebtedness to Professor H. A. Fales for elucidating at the commencement of this investigation certain phases of the electrochemical theory involved and to Professor James Kendall for reading the manuscript and offering suggestions upon it.

### Summary and Conclusions<sup>25</sup>

1. Data showing the effect of substituting methyl, *isopropyl*, methoxy, phenylene, chloro and bromo groups in the quinone nucleus are given and discussed in the light of the positive-negative rule of Michael.

2. A type of junction especially adapted for precise electrometric titrations is described.

3. The validity of the electrometric-titration method of measuring the oxidation-reduction potentials of organic compounds has been established by meeting the criteria of; (a) constancy and reproducibility of the potentials under widely varying concentrations, and following anodic or cathodic polarization; (b) use of different electrode materials; (c) agreement of the e.m.f. with values obtained by the method of pure mixtures; and (d) approach of the equilibrium from both sides.

4. The technique described has been shown to yield results precise to  $\pm 0.2$  mv.

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<sup>25</sup> We regret that the original article containing Professor Biilmann's work "Sur L'hydrogénation des quinhydrone," referred to by Sørensen (Ref. 17, p. 1) as "dans l'écrit de fête Universitetes Festskrift (Copenhagen)" did not come to our attention through its subsequent publication in the *Ann. Chim.*, 15, 109 (1921) until after this article had gone to press. We wish to note that he obtains average values identical with ours for quinone and toluquinone by the use of his electrodes of quinhydrone; namely, 0.6990 and 0.6454, respectively. Evidently the preparation which he calls xyloquinhydrone is one or the other of the 2 possible isomers of our *para* xyloquinone, for he obtains 0.5960 against our value of 0.5900, a difference well outside the limit of error for either of us—*Note added to proof, August 14.*