forms is redissolved, and then sodium carbonate is added until the solution no longer effervesces; this requires about 13 g. of sodium carbonate monohydrate. After the mixture has cooled it is extracted with three 50cc. portions of amyl acetate, and the extracts are filtered. By adding sulfuric acid dropwise to the amyl acetate, the amino compounds are precipitated as sulfates which are filtered out and extracted very thoroughly several times with alcohol to remove impurities. After it has dried, 7 g. of crude *N*-methyl-*p*-amino-*o*-chlorophenol sulfate is obtained.

By recrystallization from water, using decolorizing carbon, this substance separates as fine white needles that dissolve in water forming a colorless solution that is acid to litmus. The aqueous solution when treated (a) with ferric chloride becomes red and then very deep purple, (b) with sodium nitrite gives a white precipitate, (c) with sodium carbonate becomes brown.

Analyses. Calc. for $(C_7H_8ONCl)_2H_2SO_4.H_2O$: Cl, 16.45; S, 7.45. Found: Cl, 16.55, 16.25; S, 7.49, 7.45.

I wish to acknowledge the assistance of Mr. Arthur J. Norton in some of the experimental work.

Summary

The preparation of *p*-amino-*o*-chlorophenol hydrochloride and N-methyl-*p*-amino-*o*-chlorophenol sulfate is described. Both of these substances are good photographic developing agents but the methylated compound is the better. The latter compound appears to be equal to but no better than Metol, from which it differs only in having a chlorine atom attached to the benzene ring.

BOSTON 17, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, HARVARD UNIVERSITY]

REDUCTION POTENTIALS OF QUINONES. I. THE EFFECT OF THE SOLVENT ON THE POTENTIALS OF CERTAIN BENZOQUINONES

BY JAMES B. CONANT AND LOUIS F. FIESER

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The measurement of reduction potentials affords a new method of studying quantitatively the free energy of an addition reaction which can be brought about with a series of related substances. By such quantitative studies the differences caused by substitution and by structural changes can be discovered and when sufficient data have been obtained it should be possible to make many interesting and important generalizations in regard to the driving force of a given organic reaction and the structure of the organic compound concerned.

The normal reduction potential of a quinone is a measure of the free energy of the reduction of that quinone in the solvent employed. It has been found that the normal potential for certain benzoquinones in aqueous solution is affected by the presence of salt[1] and that the potentials of a

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[1] S. P. L. Sörensen, M. Sörensen and Linderström-Lang, *Ann. chim.*, **16**, 283 (1921).

number of quinones in mixtures of alcohol and aqueous acid are somewhat different from the values obtained in aqueous solution.[2] This effect of the change of solvent on the potential is related to the ratio of the solubility of the quinone and hydroquinone as Sörensen has carefully proved. In the light of these results it is necessary to consider the following questions: to what extent are the reduction potentials of a series of organic compounds influenced by these solubility ratios and, further, in comparing the effects of substitution in quinones what solvent or solvents should be employed in measuring the potentials? To answer these questions we have determined the potentials of a series of benzoquinone derivatives (1) in alcoholic solution, (2) in aqueous solution and (3) under conditions in which the nature of the solvent does not influence the potential.

When we consider a cell composed of a hydrogen electrode immersed in a certain solvent connected with a half-cell containing an inert electrode immersed in the same solvent saturated with both the hydroquinone and quinone in question and containing both solid substances, it is obvious that on the passage of 2 faradays of electricity the following transformations would be realized: quinone (solid) + $H_2 \longrightarrow$ hydroquinone (solid). The potential of this combination thus enables us to calculate directly the free energy of reduction referred to the 2 solid states. This free energy change and the corresponding reduction potential are independent of the solvent employed. In the case of tetrachloro-benzoquinone such a cell can actually be constructed and the potential determined. If the quinone, however, forms a quinhydrone with the corresponding hydroquinone, a saturated solution of the two substances cannot usually be formed without the separation of solid quinhydrone. In this case it is experimentally necessary to measure two separate combinations: one, a half-cell containing a solution saturated with the quinone and quinhydrone, and another containing a saturated solution of the hydroquinone and quinhydrone. One-half the sum of these two potentials (π_q and π_h) is the reduction potential referred to the change from solid quinone to solid hydroquinone (π_s).

$$2 \text{ Quinone (solid)} + H_2 \longrightarrow \text{Quinhydrone (solid)} + 2\,F\pi_q \qquad (1)$$

$$\text{Quinhydrone (solid)} + H_2 \longrightarrow 2 \text{ Hydroquinone (solid)} + 2\,F\pi_h \qquad (2)$$

Adding (1) and (2),

$$\text{Quinone (solid)} + H_2 \longrightarrow \text{Hydroquinone (solid)} + \frac{2F(\pi_q + \pi_h)}{2} = 2\,F\pi_s$$

$$\text{or } \pi_s = \frac{\pi_q + \pi_h}{2} \qquad (3)$$

In two cases in which the quinhydrone formed only slowly in aqueous solution it was possible to measure π_s directly and also to calculate it from the quinhydrone cells; the agreement was very satisfactory.

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[2] Conant and Fieser, THIS JOURNAL, **44,** 2480 (1922).

A subtraction of (2) from (1), on the other hand, gives,

$$\text{2 Quinone (solid)} + \text{2 Hydroquinone (solid)} \longrightarrow \text{2 Quinhydrone (solid)} + 2F\,(\pi_q - \pi_h) \quad (4)$$

Thus, the difference between the potentials of the two combinations is a measure of the free energy of the formation of the solid quinhydrone from its solid components.

Such measurements are novel, in the case of benzoquinone itself, only in their application to the determination of the free energy of the reduction referred to the solid state. Granger and Nelson[3] saturated acid with hydroquinone and quinone in order to establish a definite ratio of quinone to hydroquinone in their verification of the logarithmic shape of the reduction curve. Sörensen[1] showed that solutions of sodium chloride saturated with quinhydrone and quinone, or quinhydrone and hydroquinone, gave constant potentials independent of the amount of salt present; these potentials were in close agreement with the values calculated from the solubility data which he experimentally determined. Biilmann and Lund[4] gave further evidence of this constancy and proposed the terms "quino-quinhydrone" and "hydro-quinhydrone" to describe the two electrodes that were free from the "salt error." They calculated the free energy of formation of quinhydrone at 18° but did not calculate the free energy of formation of solid hydroquinone from solid quinone.

Experimental Procedure

The normal potential in solution (π_0) was measured for all the quinones in alcoholic solution, and in aqueous solution when the solubility was sufficient, by electrometric titration with titanous chloride. This method has been thoroughly investigated[5] and has been recently applied to the determination of reduction potentials in mixtures of alcohol and aqueous acid.[2] The normal potential was found by interpolation of the titration curve to 50% reduction. As an indication of the slopes of these curves the difference between this potential and that at 20% and 80% reduction is given, in millivolts, under the headings $\Delta\pi_1$ and $\Delta\pi_2$. The theoretical value is 18 mv. All of these measurements were made at 25°.

We have previously shown that the normal potential is the same whether 50% or 95% alcohol is the solvent. Consequently, the one or the other concentration was used, according to the solubility of the quinone in question, the lower one being employed when possible in order to obtain better conductivity. Since π_0 often varies with the concentration of hydrochloric

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[3] Granger and Nelson, This Journal, **43,** 1401 (1921).

[4] Biilmann and Lund, *Ann. chim.*, **16,** 321 (1921).

[5] (a) Mansfield Clark, *J. Washington Acad. Sci.*, **10,** 255 (1920). (b) Conant, Kahn, Fieser and Kurtz, This Journal. **44,** 1382 (1922). (c) LaMer and Baker, *ibid.*, **44,** 1954 (1922).

acid, it was desirable to investigate this variation at least to the extent of using 2 different acid concentrations for the measurements. In aqueous solution the acid was 0.1 N and 1.0 N, but the presence of a large amount of alcohol so decreases the conductivity that the more dilute solution was replaced by 0.5 N hydrochloric acid. This variation in π_0 with relatively small changes in acid concentration gives an indication of the susceptibility to such changes of the quinone-hydroquinone solubility ratio.

A weighing bottle of 25cc. capacity, fitted with a bright and a platinized platinum electrode, formed a convenient half-cell for carrying out the measurements which involved the use of saturated solutions. It was connected by a siphon plugged with filter paper to a Hildebrand hydrogen electrode vessel containing the same solvent as that used for making the saturated solution. The solids to be investigated were mixed with the solvent in this bottle which was then rotated in a thermostat at 25°. Potential measurements were made after the mixture had been shaken for different lengths of time; the constancy of repeated measurements was an indication that the solution was saturated with respect to both components.

Another method of insuring saturation was first to prepare a solution at 40–50° and after cooling it to the temperature of the bath, measure the potential. The latter was the more convenient method and always gave consistent results. All solutions measured at 0° were first saturated at 25°.

The choice of the solvent to be used in these cells containing solid substances depended on many factors. Aqueous solutions were employed when possible owing to the greater conductivity thus obtained. Even 0.1 N hydrochloric acid adds to quinone slowly,[6] and the reaction might occur with a velocity sufficient to vitiate the results if stronger acid were employed.

In solutions less concentrated than 0.1 N the hydrogen-ion concentration is perceptibly changed when the acid is saturated with hydroquinone.[4] Therefore, 0.1 N hydrochloric acid was used when possible. In the case of compounds that were too insoluble in water, aqueous alcoholic solutions were employed. It was found necessary to do this only with the tetra-substituted quinones; these substances do not add hydrogen chloride and, consequently, stronger hydrochloric acid could be used to insure better conductivity with no injurious effects.

In most cases, the potential was constant a few minutes after the cell was connected; a bright platinum, a gold plated and a platinized electrode gave identical readings. Several measurements were made with each cell after the potential had become constant. Each potential reported in the experimental portion of this paper represents the average value for each cell independently prepared. The reduction potential referred to the solid state (π_s) was calculated from the average of all the cells measured in the manner explained above.

The potential for each cell is reported to 0.1 mv. when the constancy of the electrodes permitted such a degree of accuracy. The final averages

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[6] Granger, *Dissertation*, Columbia University, March, 1920.

are reported to the nearest millivolt, as for most of the compounds the results are not significant beyond this figure and the potentiometer employed could not be relied on to more than 0.5 mv. The value of the hydrogen electrode was not corrected for dry hydrogen under standard conditions, as this correction is beyond the limit of accuracy of the present work. The accuracy of the measurements varies greatly with the substances investigated as can be seen by examining the concordance of the different determinations. The exact details of the experiments depended to such a great extent on the nature of the quinone in question that the results for each compound will be given separately.

Experimental Results

Benzoquinone.—The quinone and hydroquinone employed melted at 112–113° and 169°, respectively. Quinhydrone was prepared according to the method of Biilmann and Lund[4] by the partial oxidation of hydroquinone. Quino- and hydro-quinhydrone half-cells were prepared by saturating the 0.1 *N* acid with both components simultaneously.

BENZOQUINONE

0.1 *N* HCl Saturated with quinhydrone and

	Quinone	Hydroquinone	Quinone	Hydroquinone
	At 25°		At 0°	
	V.	V.	V.	V.
	0.7490	0.6129	0.7698	0.6270
	.7483	.6118	.7698	.6275
	.7490	.6132	.7700	....
	....	.6126	....	....
Av.	.7488	.6126	.7699	.6272
	$\pi_s = 0.681$		$\pi_s = 0.699$	

The potentials of the individual cells interpolated to 18° agree very well with the determinations of Sörensen and of Biilmann in the papers previously referred to. Thus the value of π_s at 18° is found to be 0.6867, while Sörensen's results give 0.6869, Biilmann's 0.6870. Granger and Nelson's measurements,[3] calculated to a suitable basis, give an average value for the hydro-quinhydrone electrode at 25°, of 0.6123, as compared with our number of 0.6126.

Toluquinone.—The quinone was prepared[7] by steam distillation of a mixture of *o*-toluidine, manganese dioxide and sulfuric acid (1:4); it was recrystallized from alcohol; m. p., 67–68°; yield 15%. Eastman's toluhydroquinone, (m. p., 124–125°) was employed. The quinhydrone was prepared either by shaking the components with water or by mixing their alcoholic solutions, adding a little water, and allowing the green crystals to form. When washed with water and dried it melted at 99–100° with decomposition. Siegmund[8] reports the melting point as 96–97°,

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[7] Clark, *Am. Chem. J.*, **14**, 565 (1892).

[8] Siegmund, *J. prakt. Chem.*, [2] **92**, 359 (1915).

while Nietzki[9] gives 52°. There are many such discrepancies in the literature, so that it appears likely that these melting points or points of decomposition are not characteristic of purity of quinhydrones.

TOLUQUINONE

0.1 *N* HCl Saturated with quinhydrone and

	Quinone	Hydroquinone	Quinone	Hydroquinone
	At 25°		At 0°	
	V.	V.	V.	V.
	0.6620	0.5840	0.6770	0.6094
	.6598	.5835	.6768	.6095
	.6617	.5857	.6776	.6098
Av.	.6612	.5844	.6771	.6096
	$\pi_s = 0.623$		$\pi_s = 0.643$	

***p*-Xyloquinone.**—Siegmund[8] states that *p*-xyloquinhydrone was not formed on applying the general method used in the preparation of other alkyl quinhydrones. Consequently, an electrode saturated with both quinone and hydroquinone was employed, and no evidence of the formation of a quinhydrone was observed in the potential measurements.

The *p*-xyloquinone used was Kahlbaum material and melted at 123.5°. For the preparation of the hydroquinone it was moistened with alcohol and a solution of stannous chloride containing hydrochloric acid was added. After the mixture had been thoroughly stirred, it was warmed on the steam-bath to complete the reduction. This caused the separation of a hard, black substance which, however, soon changed to the white hydroquinone and dissolved. The solution was boiled with animal charcoal and filtered, when *p*-xylohydroquinone separated in long, white needles; yield, 65%. It was completely pure, melting at 111.5°. This method of reduction is very convenient and is of general applicability.

Half-cells were prepared both by saturating the acid with a mixture of the solids and by mixing their saturated solutions and reading the potential immediately. Both methods gave the same result. In some cases the bright platinum and platinized electrodes were as much as 1 or 2 mv. apart, probably because of the slight solubility of the compounds. In these cases average values are reported.

p-XYLOQUINONE

0.1 *N* HCl Saturated with the quinone and the hydroquinone

Volts at 25° 0.5826 0.5820 0.5821 0.5801; $\pi_s = 0.582$
Volts at 0° 0.5988 0.6003 0.6000 ......; $\pi_s = 0.600$

MEASUREMENTS IN ALCOHOLIC SOLUTION BY THE TITRATION METHOD

HCl *N*	Alcohol %	$\Delta\pi_1$ Mv.	$\Delta\pi_2$ Mv.	$\Delta\pi_0$ V.	Av. V.
0.5	95	17	23	0.598	0.600
0.5	50	18	22	.601	
1.0	50	17	21	.597	.597
1.0	50	19	21	.596	

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[9] Nietzki, *Ber.*, **10**, 834 (1877).

Duroquinone (Tetramethylbenzoquinone).—The authors are greatly indebted to Dr. Lee I. Smith, of the University of Minnesota, for the sample of duroquinone (m. p., 110–111°) used in this work. It was reduced with stannous chloride in the manner previously described, except that a large volume of water (2 to 3 liters per g.) was required to dissolve the hydroquinone. Durohydroquinone crystallized from water in pure white, lustrous plates melting at 226–227°. This compound, prepared by reducing the quinone with zinc and sodium hydroxide, sodium amalgam and alcohol, zinc and glacial acetic acid, and aniline, is reported as melting at 210°,[10] 220°[11] and 210–224°,[12] and is said to be reoxidized by the air. No such oxidation was observed. The low reduction potential of the quinone (comparable with that of phenanthraquinone) would lead one to expect that the hydroquinone would be oxidized by the air but, since the reduction of the quinone is probably slow, the reverse process is probably also slow, presumably because of steric hindrance of the methyl groups.

The potential of this compound, which forms no quinhydrone, could not be measured in aqueous solution, apparently because of the very slight solubilities of the components. Consequently, measurements were carried out in aqueous alcohol containing 1.0 mole of hydrogen chloride per liter. The electrodes came rapidly to a definite equilibrium.

DUROQUINONE

50% Alcohol saturated with the quinone and the hydroquinone

Volts at 25° 0.4800 0.4796 0.4801; $\pi_s = 0.480$

Volts at 0° 0.4990 0.4988 0.4996; $\pi_s = 0.499$

Duroquinone is too insoluble to permit titrations in aqueous solution. Titrations in alcohol were rendered somewhat tedious by the tardiness with which equilibrium was established. After each increment of reducing agent was added the potential fell 100 or 200 mv. (towards the titanous-titanic potential level) and then rose slowly to a constant value. It should be noted that the results of this slow titration are entirely consistent with the potential of a saturated solution of the quinone and hydroquinone; there can be no doubt that the titration is valid even with such refractory substances as duroquinone.

MEASUREMENTS IN ALCOHOLIC SOLUTION BY THE TITRATION METHOD

HCl *N*	$\Delta\pi_1$ Mv.	$\Delta\pi_2$ Mv.	π_0 V.	Av. V.
0.5	15	25	0.468	0.466
0.5	15	19	.466	
1.0	16	14	.467	
1.0	17	19	.464	

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[10] Nef, *Ann.*, **237,** 6 (1887).

[11] v. Pechmann, *Ber.*, **21,** 1421 (1888).

[12] Rügheimer and Hankel, *ibid.*, **29,** 2174 (1896).

Thymoquinone.—Kahlbaum's thymoquinone, m. p., 45.5°, was reduced with stannous chloride in the usual way, giving long, white needles; m. p., 141.5°; yield, 88%. The usual procedure, using sulfur dioxide,[13] takes from 3 to 4 days and yields a dirty white product which, when purified, melts at 139.5°. Thymoquinhydrone was prepared by allowing a mixture of the ethereal solutions of equivalent weights of the components to evaporate very slowly. The lustrous, dark green crystals melted at 78° with decomposition.[8]

Electrode equilibrium was at times erratic in both cells, and both the bright and platinized types of electrodes often gave inconsistent, inconstant values. On the other hand, both types often became perfectly constant at the same point, so that there was no doubt when true equilibrium had been reached.

THYMOQUINONE

	0.1 *N* HCl Saturated with the quinhydrone and			
	Quinone	Hydroquinone	Quinone	Hydroquinone
	At 25°		At 0°	
	V.	V.	V.	V.
	0.5928	0.5660	0.6055	0.5922
	.5930	.5649	.6045	.5910
	.5927	.5661	.6050	.5920
Av.	.5928	.5657	.6050	.5917
	$\pi_s = 0.579$		$\pi_s = 0.598$	

MEASUREMENTS IN 50% ALCOHOLIC SOLUTION BY THE TITRATION METHOD

HCl *N*	$\Delta\pi_1$ Mv.	$\Delta\pi_2$ Mv.	π_0 V.	Av. V.
0.5	16	19	0.591	0.589
0.5	17	19	.589	
1.0	18	18	.589	
1.0	16	19	.587	

Monochloroquinone.—Monochlorohydroquinone was prepared[14] in a 74% yield by passing dry hydrogen chloride into a chloroformic solution of benzoquinone. When recrystallized from chloroform it melted at 101–102°. Oxidation by Clark's method proved convenient for small quantities and gave a 56% yield. By oxidation with potassium dichromate and extraction with benzene as in the method that has been developed for quinone,[15] an 84% yield was obtained, but the method was not as rapid. The compound was recrystallized from alcohol and melted at 57°. The quinhydrone was best prepared by the partial oxidation of the hydroquinone with ferric ammonium sulfate in aqueous solution. The bronze-green needles melted at 67°[16] with decomposition.

[13] Carstanjen, *J. prakt. Chem.*, [2] **3,** 54 (1871).

[14] Levy and Schultz, *Ann.*, **210,** 138 (1881).

[15] "Organic Syntheses," John Wiley and Sons, **1922,** Vol. II, p. 85.

[16] Ling and Baker [*J. Chem. Soc.*, **63,** 1314 (1893)] obtained a hydrate melting at 70–72°.

Difficulty was experienced in the measurement of the potentials of both this compound and 2,3-dichloroquinone because of the unusually great solubility of their hydroquinones. In 0.1 *N* hydrochloric acid at 25° the solubility of hydroquinone is 0.0696 g. per cc.[3] while that of monochlorohydroquinone is about 0.7 g. per cc. Even at 0° both the monochloro- and 2,3-dichlorohydroquinones are so soluble that they form deep red, sirupy solutions in which potential measurements would be very unreliable. This difficulty was to a large extent obviated by using 0.1 *N* hydrochloric acid saturated with sodium chloride as the solvent, thus depressing the solubilities of the organic compounds to a very considerable extent. In this way results were obtained which, though perfectly reliable, are not of the highest degree of accuracy since the bright and platinized electrodes gave measurements sometimes as much as 2 mv. apart. Averages are reported in the following tables.

MONOCHLOROQUINONE

0.1 *N* HCl Saturated with NaCl, the quinhydrone and

	Quinone	Hydroquinone	Quinone	Hydroquinone
	At 25°		At 0°	
	V.	V.	V.	V.
	0.722	0.635	0.740	0.651
	.721	.634	.740	.652
	.723	.634	.741	.651
Av.	.722	.634	.740	.651
	$\pi_s = 0.678$		$\pi_s = 0.696$	

MEASUREMENTS IN ALCOHOLIC SOLUTION BY THE TITRATION METHOD

HCl *N*	Alcohol %	$\Delta\pi_1$ Mv.	$\Delta\pi_2$ Mv.	π_0 V.	Av. V.
0.2	50	17	20	0.736	0.736
0.2	50	17	20	.736	
1.0	50	18	16	.735	
1.0	95	18	16	.737	

2,6-Dichloroquinone.—This compound, prepared[17] by oxidizing trichlorophenol with chromic acid (69% yield), was crystallized from alcohol and from glacial acetic acid. Both samples melted at 120.5°. It was reduced, with 80% yield, to the hydroquinone which was crystallized from benzene and melted at 161°.

All of the dichloroquinones form quinhydrones, but not as readily as does benzoquinone. The 2,5 and 2,6 derivatives, described by Ling and Baker,[16] are of such an ill-defined character that they are scarcely suited to potential measurements. The 2,5 derivative forms a violet hydrate which, on drying, changes into a pale yellow, anhydrous quinhydrone. The quinhydrone of the 2,6 isomer is variously described as brown powder, dark needles, and brown prisms with a reddish shimmer.

An anhydrous quinhydrone cannot be used in our half-cell if not in

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[17] Kehrmann, *J. prakt. Chem.*, [2] **40**, 481 (1889).

equilibrium with the solvent used. The best way to insure that such equilibrium is maintained is to prepare the quinhydrone in the solvent concerned, add an excess of the quinone or hydroquinone, and measure the potential when the solution is completely saturated. This method was used with 2,6-dichloroquinone, and the results are indicated below.

2,6-DICHLOROQUINONE

0.1 *N* HCl Saturated with the quinhydrone and

	Quinone	Hydroquinone	Quinone	Hydroquinone
	At 25°		At 0°	
	V.	V.	V.	V.
	0.730	0.667	0.744	0.687
	.720	.669	.735	.692
	.726	.670	.744	.691
	.727	...	.747	...
Av.	.726	.669	.743	.690
	$\pi_s = 0.698$		$\pi_s = 0.717$	

These results are decidedly irregular but π_s, being an average value, is probably correct within a few millivolts, and it is certainly accurate enough for purposes of comparison. That the results obtained in saturated solution for all of the dichloroquinones are thus less accurate than those for the other compounds studied seems to be due wholly to the character of the quinhydrones which they form. It soon appeared that even the method employed above could not be used for the other isomers, since the quino- and hydro-quinhydrone electrodes gave quite varying potentials, indicating that the quinhydrone or its hydrate was not of constant composition. But since these quinhydrones do not form as readily as does the 2,6-derivative, it was found possible to mix saturated solutions of the quinone and hydroquinone and obtain reproducible readings before any quinhydrone separated. This method was proved valid in the measurements of trichloroquinone, when both this procedure and the one using the quinhydrone gave the same value for π_s. For further confirmation and for purposes of verifying the above results obtained with

2,6-DICHLOROQUINONE

MEASUREMENTS IN 95% ALCOHOLIC SOLUTION BY THE TITRATION METHOD

HCl *N*	$\Delta\pi_1$ Mv.	$\Delta\pi_2$ Mv.	π_0 V.	Av. V.
0.5	14	23	0.746	
0.5	14	20	.748	0.748
1.0	12	22	.752	
1.0	15	22	.748	

MEASUREMENTS IN AQUEOUS SOLUTION BY THE TITRATION METHOD

HCl *N*	$\Delta\pi_1$ Mv.	$\Delta\pi_2$ Mv.	π_0 V.	Av. V.
0.1	17	19	0.722	0.722
0.1	17	18	.723	
1.0	18	19	.719	0.719
1.0	18	17	.719	

2,6-dichloroquinone, measurements were made on half-cells prepared by mixing saturated solutions of the two components. The values found for π_s were, at 25°, 0.697, 0.699, 0.692 (compare 0.698), and at 0°, 0.715, 0.714 (0.717). Because of the rapidity of precipitation of quinhydrone, the first values reported are considered to be more nearly correct.

These results are in good agreement with determinations made by Baker[18] which gave the value 0.7210 for 0.2 *N* hydrochloric acid. Her sample was prepared from 2,6-dichloro-*p*-aminophenol.

2,3-Dichloroquinone.—2,3-Dichloro-hydroquinone was obtained by Peratoner and Genco by the action of sulfuryl chloride on hydroquinone[19a] and by the reduction of quinone dichloride with sulfur dioxide.[19b] They also observed that this compound was a by-product in the preparation of 2,5-dichloro-hydroquinone from monochloroquinone and hydrochloric acid. Oliveri-Tortorici[20] obtained a 12% yield by the last-named method and pointed out that the other two processes are not only troublesome but give rise to a variety of by-products. Den Hollander[21] recently repeated the experiments of the Italians but was unable to obtain any of the desired compound. On saturating a cooled ethereal solution of monochloroquinone with dry hydrogen chloride he obtained a mixture that he could not separate by fractional crystallization from benzene but which he identified by oxidation and separation of the quinones as a mixture of the 2,5 and the 2,6 isomers.

Under apparently identical conditions we obtained, after fractional crystallization from benzene, 2,3-dichloro-hydroquinone (melting at 137°) and monochlorohydroquinone. The products of the reaction are thus difficult to control.

A satisfactory method, however, has recently developed in the work of Eckert and Endler[22] on the chlorination of hydroquinone in glacial acetic acid. Since their interest lay in finding a suitable method for the preparation of the 2,5-isomer, their directions were examined and modified as follows.

Forty g. of hydroquinone was suspended in 200 cc. of glacial acetic acid and treated with chlorine at 40–50° until the solution had gained 33 g. of chlorine (30% excess). Only a small amount of crystals formed on cooling and the liquid was concentrated in a vacuum. The crystalline paste was dissolved in water and filtered hot to remove a small amount of insoluble tetrachloro-hydroquinone. The filtrate was boiled with animal charcoal and filtered hot. As the solution cooled, 28 g. of rose-colored

[18] Baker, *Dissertation*, Columbia University, August, **1922**.

[19] (a) Peratoner and Genco, *Gazz. chim. ital.*, [2] **24,** 376 (1894); (b) p. 388.

[20] Oliveri-Tortorici, *ibid.*, [2] **27,** 584 (1897).

[21] Den Hollander, *Rec. trav. chim.*, **39,** 481 (1920).

[22] Eckert and Endler, *J. prakt. Chem.*, [2] **104,** 81 (1922).

crystals separated which lost water at 100° and melted at 138–139°. When these were dried in benzene and crystallized, 19.5 g. of white crystals was obtained that melted at 143°; 9 g. was recovered from the various filtrates but was not purified; total yield, 43%; yield of pure product, 30%.

Oxidation to the quinone was accomplished by Clark's method with an 88% yield. The product crystallized from alcohol in long needles melting at 100–101° (the melting point given is 96–98°).

Measurements with this compound were made in 0.1 *N* hydrochloric acid saturated with sodium chloride as in the case of monochloroquinone, because of the extreme solubility of the hydroquinone. Cells containing the red quinhydrone (probably a hydrate), which is formed on shaking the components with the solvent, were variable and inconstant, but a mixture of the saturated solutions of the components was sufficiently stable to permit measurements to be made. The length of time during which the potential remains constant (before the quinhydrone starts to separate) is, of course, dependent on the many factors that initiate the crystallization of a supersaturated solution. Inoculation by minute crystals adhering to the apparatus used in a previous experiment invariably caused the potential to drop and the red quinhydrone hydrate to separate in 1 to 2 minutes. But even when all precautions in regard to cleaning the apparatus were taken, crystallization often began before a large number of readings could be made, especially at 0°, and especially when the half-cell had to be shaken to obtain true equilibrium at the platinum surfaces.

2,3-Dichloroquinone

0.1 *N* HCl Saturated with NaCl, the quinone and the hydroquinone

Volts at 25°	0.675	0.676	0.675; $\pi_s = 0.675$
Volts at 0°	0.691	0.693	0.692; $\pi_s = 0.692$

Measurements in 95% Alcoholic Solution by the Titration Method

HCl *N*	$\Delta\pi_1$ Mv.	$\Delta\pi_2$ Mv.	π_0 V.	Av. V.
0.5	16	18	0.740	0.739
0.5	14	15	.738	
1.0	8	16	.711	.711
1.0	10	16	.710	

Measurements in Aqueous Solution by the Titration Method

0.1	17	19	.708	.708
0.1	17	17	.708	
1.0	17	21	.703	.704
1.0	18	17	.705	

2,5-Dichloroquinone.—The crude hydroquinone (m. p., 156–159°) was obtained from hydroquinone and potassium chlorate in 68% yield by the directions of Ling.[23] Monochlorohydroquinone (m. p., 100–105°) was

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[23] Ling, *J. Chem. Soc.*, **61**, 558 (1892).

obtained from the filtrate as a by-product. The dichloro-hydroquinone was recrystallized from benzene and melted at 166°.

It was oxidized in the cold with dichromate and sulfuric acid, and the quinone, recrystallized from alcohol and washed with ether, melted at 158.5°. It is necessary to wash with ether and dry rapidly, for otherwise the surfaces of the crystals become darkened with the formation of the quinhydrone.

Potential measurements were carried out on mixtures of the saturated solutions of the quinone and hydroquinone. Quinhydrone formation was so slow that concordant results were also obtained by stirring the acid with the two solids at 25°.

2,5-DICHLOROQUINONE

0.1 *N* HCl Saturated with the quinone and the hydroquinone

Volts at 25°	0.686	0.692	0.693	0.689	0.688	0.689;	$\pi_s = 0.689$
Volts at 0°	0.708	0.711	0.711	0.709	0.709	.....;	$\pi_s = 0.710$

MEASUREMENTS IN 95% ALCOHOLIC SOLUTION BY THE TITRATION METHOD

HCl *N*	$\Delta\pi_1$ Mv.	$\Delta\pi_2$ Mv.	π_0 V.	Av. V.
0.5	10	20	0.740	0.740
0.5	10	17	.740	
1.0	11	23	.735	.734
1.0	10	20	.733	
MEASUREMENTS IN AQUEOUS SOLUTION BY THE TITRATION METHOD				
0.1	19	21	.719	.719
0.1	18	18	.722	
1.0	18	20	.718	
1.0	17	19	.718	

Trichloroquinone.—Kahlbaum's trichloroquinone (m. p., 162–163°) was reduced with stannous chloride and the hydroquinone crystallized from glacial acetic acid. After removal of the acetic acid of crystallization in a vacuum desiccator the compound melted at 136°. By the spontaneous evaporation of a chloroformic solution of the components, trichloroquinhydrone was obtained in well-formed clusters of green-black crystals melting[24] at 114–115°.

Half-cells were prepared by stirring a suspension of the quinone and hydroquinone in 0.1 *N* hydrochloric acid at 25° for as long as 15 hours and by cooling from a higher temperature; no quinhydrone formation was observed. On cooling to 0°, however, small amounts of this compound separated, so that when working at this temperature the solids were dissolved separately and the solutions mixed. Such a half-cell was stable for 1 to 2 hours. Though the quinhydrone is formed with difficulty in

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[24] Ling and Baker (Ref. 16) obtained by this method a compound melting at 103°. Of their other preparations, the highest-melting compound (115–117°) analyzed for $^1/_2$ H_2O but did not lose water over concd. sulfuric acid.

the presence of water, electrodes containing previously prepared quinhydrone were stable at 25°. The potentials of a quino- and a hydroquinhydrone half-cell were 0.6811 and 0.6612, from which π_s = 0.671, in good agreement with the following results.

TRICHLOROQUINONE

0.1 *N* HCl Saturated with the quinone and the hydroquinone

Volts at 25° 0.6695 0.6698 0.6696; $\pi_s = 0.670$
Volts at 0° 0.6904 0.6905 0.6902; $\pi_s = 0.690$

MEASUREMENTS IN 95% ALCOHOLIC SOLUTION BY THE TITRATION METHOD

HCl *N*	$\Delta\pi_1$ Mv.	$\Delta\pi_2$ Mv.	π_0 V.	Av. V.
0.5	12	18	0.733	0.731
0.5	13	20	.730	
1.0	11	16	.724	.726
1.0	11	14	.728	

Tetrachloro-benzoquinone.—Tetrachloroquinone (m. p., 283–284°) was reduced with stannous chloride in the usual way. The hydroquinone was repeatedly crystallized from glacial acetic acid, dissolved in this solvent, and precipitated with alcohol. It melted constantly at 230–231°.

Half-cells saturated with the quinone and the hydroquinone were employed. Though both components are almost insoluble in water, measurements in 0.1 *N* acid could be carried out, although equilibrium was established with some difficulty, especially at 0°.

Thus, at 0° one cell, on long standing, reached a potential about 4 mv. above the recorded value, while the other cell under similar conditions was 4 mv. below this value. When the cell was shaken, the potential of each came to about the same (the recorded) value. Slight polarization apparently causes appreciable concentration changes in these dilute solu-

TETRACHLORO-BENZOQUINONE

SATURATED SOLUTIONS OF THE QUINONE AND THE HYDROQUINONE

25° V.		0° V.
0.6641	0.1 *N* HCl	0.6830
0.6638		0.6838
0.6640	50% alcohol, 1.0 *N* HCl	0.6830
0.6622		0.6825
$\pi_s = 0.664$		$\pi_s = 0.683$

MEASUREMENTS IN 95% ALCOHOLIC SOLUTION BY THE TITRATION METHOD

HCl *N*	$\Delta\pi_1$ Mv.	$\Delta\pi_2$ Mv.	π_0 V.	Av. V.
0.5	11	16	0.694	
0.5	14	24	.696	0.695
0.5	14	25	.695	
1.0	15	25	.704	
1.0	15	21	.703	.703
1.0	13	27	.703	

tions. It was more convenient to use aqueous alcohol as the solvent, although even in this case, electrode equilibrium was not of the best and both types of electrode were occasionally erratic. The agreement of the results in aqueous and in aqueous-alcoholic solution constitutes a good proof of the constancy of this quinone-hydroquinone electrode.

The Potentials Referred to the Solid and Dissolved States

A summary of the results obtained is given in Table I. A few values, the details of which do not appear above, are taken from a previous paper.[2] The potentials of benzoquinone, toluquinone, monochloroquinone and 2,6-dichloroquinone in dil. acid have also been determined by other investigators and our results agree with theirs within 1 mv. except in the case of toluquinone; for this compound the more accurate value of Biilmann[25] is given preference to our number of 0.6435. The two starred figures are taken from the results of LaMer and Baker[5c] who used 0.2 *N* hydrochloric acid as solvent. In the two columns under the normal potential for each of the solvents two values are given when π_0 varied with the acid concentration beyond the limits of experimental error. When but one figure is given under the heading "1.0 *N* HCl," it indicates that such variation was not observed.

Table I

Reduction Potentials at 25°

	Solid state		In solution			
			π_0 (water)		π_0 (alcohol)	
	π_s V.	$\Delta\pi_s 0° - 25°$ Mv.	0.1 *N* HCl V.	1.0 *N* HCl V.	0.5 *N* HCl V.	1.0 *N* HCl V.
Benzoquinone	0.681	−18	0.699	0.696	...	0.711
Toluquinone	.623	−20	.645	.641	...	.656
p-Xyloquinone	.582	−18	.590*	...	.600	.597
Duroquinone	.480	−19	...	...	...	.466
Thymoquinone	.579	−19	.588*	...	...	.589
Monochloroquinone	.678	−18	.713	.710	...	.736
2,3-Dichloroquinone	.675	−17	.708	.704	.739	.711
2,5-Dichloroquinone	.689	−21	...	.719	.740	.734
2,6-Dichloroquinone	.698	−19	.722	.719	...	.748
Trichloroquinone	.670	−20	...	...	.731	.726
Tetrachloroquinone	.664	−19	...	...	.695	.703

It will be observed from the table that the potentials for the three conditions exhibit a certain parallelism. This is shown more clearly in Fig. 1 in which the potentials are plotted against the number of substituents. For the dichloroquinone the *para* isomer was arbitrarily selected for plotting since its potential is always intermediate between those of the other two. In those cases in which π_0 varied with the acid concentration an average value was used for the purpose of characterizing each compound as completely as possible.

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[25] Biilmann, *Ann. chim.*, **15**, 109 (1921).

The three lines for both the chlorine and methyl series are roughly parallel. In every case but one, the order of the potentials is: alcoholic solution > aqueous solution > solid state. With the tetramethyl compound this order is reversed for the alcoholic solution and the solid state (the substance was not soluble in aqueous solution). It is evident from Fig. 1 that from the results obtained either in solution or referred to the solid state one would conclude: (a) that the introduction of methyl groups progressively and regularly decreases the potential, and (b) that the introduction of chlorine atoms first *raises* the potential and then *lowers* it even

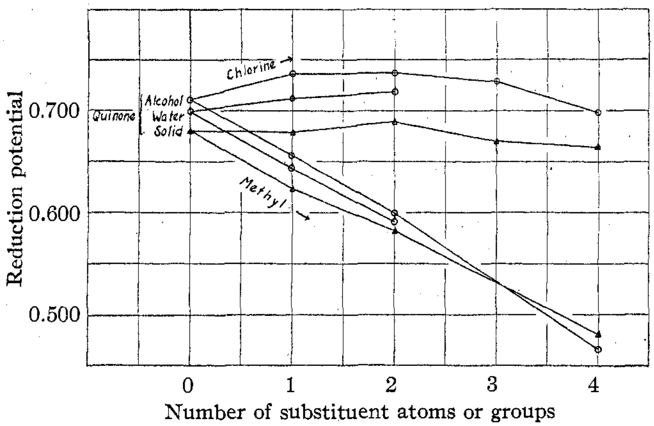

Fig. 1.—Effect of substituent groups

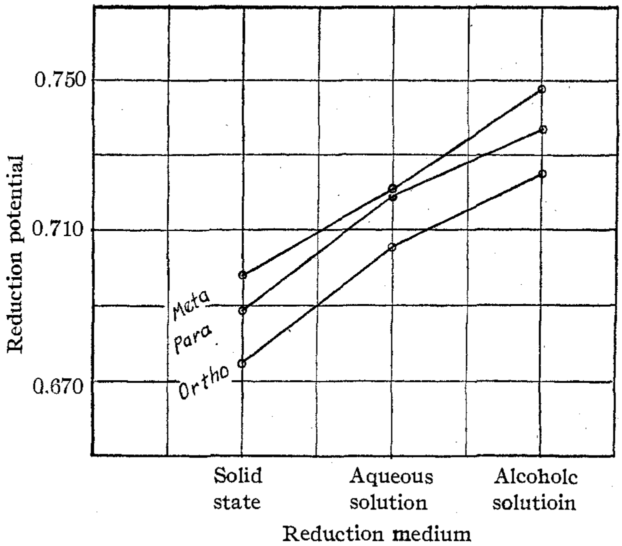

Fig. 2.—Dichloroquinones

below that of the parent substance. In Fig. 2, in which the potentials are plotted on an arbitrary scale, it is seen that even the subtle differences between the positional isomers are reflected in a nearly parallel manner by the potentials referred to the solid state, an aqueous solution or an alcoholic solution.

It will be further observed from Table I that all of the temperature coefficients of the potentials referred to the solid state have the same sign and are very nearly identical. It was shown in a previous paper[2] that this is also true of the temperature coefficients in aqueous and alcoholic solution. Therefore, relations based upon either π_s or π_0 can reasonably be expected to hold at any temperature at which the comparisons may be made.

Thus, a definite answer has been obtained to the questions raised at the beginning of this article. The lines in Fig. 1 are so nearly parallel that one may safely say that the *relation between the potentials of a series of compounds* is very nearly the same whether the experiments are performed in aqueous solution, alcoholic solution or in saturated solutions.

We have been particularly anxious to settle this point in connection with our studies on the potentials of many naphthoquinone and anthraquinone derivatives which are too insoluble to be measured in aqueous solution either by the titration method or in saturated solutions. If the relationship in a series of quinones is essentially independent of the nature of the solvent we can safely proceed with our measurements of these insoluble substances in alcoholic solution. There is every reason to believe that the divergences from this simple generalization are greatest in the case of such benzoquinone derivatives as we have examined. The introduction of a substituent into the naphthoquinone or anthraquinone nucleus would certainly change the ratio of the solubility of the quinone to the hydroquinone much less than the introduction of the same substituent into benzoquinone. In fact, evidence in regard to this point is already at hand; we have measured some 20 naphthoquinone and anthraquinone derivatives in alcoholic solutions containing 1.0 N and 0.5 N hydrochloric acid and the potential (π_0) was found to be the same in both solvents; this is in contrast to such benzoquinone derivatives as xyloquinone and the dichloroquinones. Another example of the relatively great susceptibility of the potential of benzoquinone derivatives to changes in the solvent is found by comparing the varying potential of benzoquinone in salt solutions[1] with the consistency of the potentials of certain anthraquinone sulfonic acids in buffer solutions.[5b]

In considering those cases in which the relationship of the potentials of a series of compounds varies somewhat with the nature of the solvent, the problem arises as to which set of measurements is most significant. For example, in developing a general theory of the relation between constitution and reduction potential, are the potentials of the chloroquinones in alcoholic solution (top line, Fig. 1) to be considered, or the potentials referred to the solid compounds (lowest line, Fig. 1)? In discussing the potentials of the isomeric dichloroquinones (Fig. 2), should one employ the results in alcoholic solutions or aqueous solution or those referred to the solid state? The potentials that are referred to the solid state (π_s) represent the algebraic sum of the free energy of three distinct processes, thus: $nF\pi_s = \Delta F$ (formation of dilute solution of quinone) $+ nF\pi_0 +$ ΔF (precipitation of the hydroquinone from dilute solution).

The introduction of a substituent into a quinone affects the value of all three terms on the right-hand side of this equation. We are concerned with the effects of substitution on the affinity of the quinone for hydrogen; since π_s includes not only this term but also the energy changes involved in passing from the two solid states into dilute solution, it is not an accurate measure of the relationship we are investigating. The ideal potential would be measured in a solvent in which both the quinone and the hydroquinone molecules are completely free from association or solvation of any sort; in other words, in a solvent in which the conditions of a perfect gas are realized. Under such conditions where the *absolute activity*[26] was equal to the concentration, the potentials of a series of quinones would give a true measure of the effect of substitution on the affinity of the quinone for hydrogen. The values of π_0 obtained in aqueous or alcoholic solution are at present our best approximation to this ideal potential and probably give relationships which are only slightly in error. As the results in both solutions are almost parallel, one cannot go far wrong in deducing generalizations from either of them. For the present purpose it would be misleading to assign arbitrarily an activity coefficient of unity to the compounds in pure aqueous solution and refer our results to this standard; for all that we know at present, the *absolute* activity coefficient may be more nearly unity in alcoholic than in aqueous solution.

An examination of the experimental results obtained with the chloroquinones shows the general consistency of the series of potentials in alcoholic solution (π_0) whereas the potentials referred to the solid state form an irregular series and they are related to the irregular solubility relationships of certain of the chlorohydroquinones. The potentials of the first 4-chloro compounds, both in alcohol and in water, are all higher than that of quinone itself; the relation is not additive, however, and the potential gradually falls with the presence of 3, then 4, chlorine atoms. In the experimental portion of this paper attention was called to the abnormal solubility of mono- and of 2,3-dichloro-hydroquinone. The potential of the latter compound in alcohol changes greatly with the acid concentration, an indication of a susceptible solubility ratio. But, al-

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[26] Lewis, *Proc. Am. Acad. Arts Sci.*, **43**, 259 (1907).

though the ratios for these two compounds are anomalous, the relative positions of their potentials in solution fall in line with those of the other chloroquinones. This is not the case with π_s. Again the potential is low with 3 or 4 chlorine atoms present, and again the 2,5- and 2,6-dichloroquinones occupy a position above that of quinone. But mono- and 2,3-dichloroquinone, whose solubility ratios are abnormal, fall below the position of the parent compound. Thus, from the above data it appears that π_0 is more significant for the purposes of studying structure than π_s.

The main points of interest in connection with the problem of the relation between reduction potential and chemical constitution have already been pointed out in this discussion. It should be further noted that thymoquinone (Table I) has the same potential as *p*-xyloquinone and is very different from its structural isomer duroquinone. This disposes of the idea that the lowering of the reduction potential is a simple function of the molecular weight.[27] The data at present available are not sufficient for any wide generalizations in regard to even benzoquinone derivatives; nevertheless the striking difference between the effects of methyl groups and chlorine atoms deserves special comment. Whereas the effect of the methyl group is progressively accumulative in lowering the potential, the introduction of chlorine atoms first raises then lowers the potential. The usual distinction between a "positive" methyl group and a "negative" chlorine atom harmonizes well with the decreasing potential of the methyl homologs and the increased potential of monochloroquinone. However, some other factor must be considered in explaining the potentials of the other chloroquinones. It will be very interesting to determine whether or not other "negative" groups or atoms behave in the same manner as the chlorine atom.

Comparison with Thermochemical Data

In 1900 Valeur[28] made an extensive study of the thermochemistry of quinones in which he measured the heats of combustion of the quinones and their hydroquinones and thus calculated the heats of reduction. Comparison of his values with the total energy of reduction in solution as found electrometrically has already been shown by Biilmann[25] and by the authors[2] to yield fairly concordant results in a few cases. From the above data ($\pi_s^{25°}$ and $d\pi_s/dt$) it is now possible to compare Valeur's figures for the solid state (ΔH_s) with the same quantities calculated from potentials. Such a comparison is given in Table II. Two values are inclosed in brackets to indicate that they are of a lower degree of accuracy than the others, because of the difficulties referred to in the experimental portion of this paper.

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[27] First advanced by Kehrmann, *Ber.*, **31**, 979 (1898).

[28] Valeur, *Ann. chim.*, **21**, 470 (1900).

TABLE II

COMPARISON OF THERMOCHEMICAL AND ELECTROCHEMICAL DATA

	Total energy change of reduction referred to the solid state (ΔH_s)	
	Thermochem. (Valeur) *Kj.*	Electrochemically *Kj.*
Benzoquinone	175.1	172.8
Toluquinone	156.3	166.2
Thymoquinone	146.3	155.4
Monochloroquinone	165.5	(172.3)
2,6-Dichloroquinone	140.9	(178.4)
Trichloroquinone	93.2	175.3
Tetrachloroquinone	99.1	171.9

Since potential measurements are so likely to be free from large accidental or systematic errors, we are convinced that the great discrepancy which is evident from the table is due to both the great experimental difficulties in thermochemical work and the errors inherent in the calculations of the total energy change from the heats of combustion of the quinone and the hydroquinone. The heat of reduction is the small difference between the large heats of formation of quinone and of hydroquinone. Furthermore, an error in the heats of combustion of each substance is multiplied by the molecular weight and the two errors are additive. The accuracy of the thermochemical measurements is in most cases not very great. Thus for benzoquinone, which has been investigated by others[29] besides Valeur, the mean of all the determinations shows a probable error of 8.7%. With other quinones, for each of which Valeur made 2 or 3 determinations, the error is always greater owing to the increased molecular weight. Valeur's two values for benzoquinone agree within less than 2%; and for the alkyl derivatives within 7%. Now, while these compounds were easily burned, great difficulties were experienced with the polychloro compounds; a correction for unoxidized chlorine had to be made and auxiliary combustible material evolving as much as 76% of the total heat had to be employed. Valeur's value for tetrachloroquinone is 42% lower than ours; while the difference is 47% for trichloroquinone, for which potential measurements show a high degree of accuracy. The other chloro derivatives show similar, though smaller, deviations. The thermochemical data must be considered to be greatly in error for these quinones.

Unfortunately, while Valeur was fully aware of the errors of his method and expressly stated that his results were but approximations, he made them the basis of conclusions as to the oxidizing power of quinones, which also involved the tacit assumptions of equal solubility ratios and of the truth of the Berthelot principle. Needless to say, these conclusions are

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[29] Berthelot and Recoura, *Ann. chim.*, [6] **13**, 311 (1888). Berthelot and Longuinine, *ibid.*, [6] **13**, 333 (1888). Stohmann, *J. prakt. Chem.*, [2] **45**, 335 (1892).

at variance with the results of potential measurements and must be discarded.

Energy of Quinhydrone Formation

The total energy of formation of solid benzoquinhydrone from solid quinone and hydroquinone was calculated by Berthelot[30] from the heat of formation in solution and the heats of solution of the factors and the product. This same value may be calculated from the potentials and temperature coefficients of the quino- and hydro-quinhydrone electrodes. The potential (π_{qh}) corresponding to the free energy of the reaction, Quinone (solid) + Hydroquinone (solid) ⟶ Quinhydrone (solid), is calculated, as explained above, (Eq. 4) from the simpler relation, $\pi_{qh} = \pi_q - \pi_h$. From the data on p. 2198, the total energy change at 13° is found as follows.

$$\frac{d\pi_{qh}}{dt} = \frac{(0.749 - 0.613) - (0.770 - 0.627)}{25} = -0.00028 \text{ v.}$$

$$\Delta H = 96.5 \times 0.139 + 96.5 \times 286 \times 0.00028 = 21.1 \text{ kj.}$$

This is quite different from Berthelot's value of 37.1 kj. for the same temperature. In view of the general concordance of our electrochemical results with those of Sörensen and of Biilmann, it is not unlikely that the discrepancy is due to an error in the thermochemical measurements.

It has been pointed out [31] that the free energy of the reaction, Quinone (solid) + H_2 ⟶ Hydroquinone (solid), is given by the expression,

$$\Delta F_s = 2F\pi_0 + RT ln \frac{a}{b}, \tag{5}$$

in which π_0 is the reduction potential referred to the *dissolved state; a* and *b* are the solubilities of quinone and hydroquinone, respectively, in a solution saturated with them both. This stipulation, that the solubilities employed be those of each compound in the presence of the other and not in solution by itself, was shown by Smits[32] to be necessary in the application[33] of the van't Hoff equation for the shift in equilibrium constant with a change in solvent. Equation 5 simply states that to obtain the free energy of reduction in the solid state one must add to the free energy of reduction in solution ($2F\pi_0 = RT\,ln\,K$) the free energy of bringing quinone from a saturated to a dilute solution ($R\,T\,ln\,a$) and of concentrating the dilute solution of hydroquinone ($-RT\,ln\,b$). The free energy of passing from the solid phase to a saturated solution is, of course, zero.

We may now expand this equation to include those cases in which simultaneous saturation of a solution with quinone and hydroquinone is not realizable. If *k* is the dissociation constant of quinhydrone and *c* its solubility, it is seen that, in any solution saturated with quinhydrone and

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[30] Berthelot, *Ann. chim.*, [6] 7, 203 (1886).

[31] Ref. 2, p. 2490.

[32] Smits, *Z. physik. Chem.*, **92,** 35 (1918).

[33] Dimroth, *Ann.*, **377,** 127 (1910).

one of its components, $k = \frac{a \times b}{c}$; $a = \frac{kc}{b}$; $b = \frac{kc}{a}$. These values for a and b may now be substituted in Equation 5 for a solution saturated with quinone in the first case and with hydroquinone in the second. An electrode dipping in the first solution records the potential corresponding to the free energy of reduction of quinone to quinhydrone (ΔF_q); in the second, the free energy of reduction of quinhydrone to hydroquinone (ΔF_h) (all solids). Thus:

$$\text{Quinone} + H \longrightarrow {}^1/_2\ \text{Quinhydrone:}\quad \Delta F_q = \frac{1}{2}RT\,ln\,K + \frac{1}{2}RT\,ln\frac{a^2}{k_1c} \qquad (6)$$

$$^1/_2\ \text{Quinhydrone} + H \longrightarrow \text{Hydroquinone:}\quad \Delta F_h = \frac{1}{2}RT\,ln\,K + \frac{1}{2}RT\,ln\frac{k_2c}{b^2} \qquad (7)$$

Subtracting (quinone + hydroquinone ⟶ quinhydrone)

$$\Delta F_{qh} = \Delta F_q - \Delta F_h = RT\,ln\,\frac{a \times b}{c} - \frac{1}{2}RT\,ln\,k_1k_2 \qquad (8)$$

In Equations 6 and 7 the dissociation constants used are the actual constants (k_1 and k_2) for quinhydrone when in the presence of a saturated solution of quinone and of hydroquinone, respectively. Granger and Nelson[3] have shown that k_2 differs from k, the normal dissociation constant. Using their solubility data and their value for k_2 at 25° for 0.1 *N* hydrochloric acid and assuming at first that $k_1 = k$, ΔF_{qh} is found to have a value of 13.37 kj. This is higher than the value of 13.14 kj., found from the potential measurements and recorded in Table III. But, using the normal potential of quinone and the solubilities, in 0.1 *N* hydrochloric acid, with the same assumption concerning k_1, ΔF_q and ΔF_h are found to be equal to 72.54 kj. and 59.16 kj. From our potential measurements these quantities are found to be 72.28 kj. and 59.16 kj., respectively. The lack of exact agreement in the values for ΔF_q indicates that the dissociation constant of quinhydrone is inconstant not only in the presence of an excess of hydroquinone but also in the presence of an excess of quinone.

TABLE III

FREE ENERGY OF FORMATION OF SOLID QUINHYDRONE FROM SOLID COMPONENTS

	25°		0°		
Quinhydrone of	π_{qh} V.	ΔF_{qh} Kj.	π_{qh} V.	ΔF_{qh} Kj.	$\left(\Delta F^{0°}_{qh} - \Delta F^{25°}_{qh}\right)$ Kj.
Benzoquinone	0.136	13.1	0.143	13.8	−0.7
Toluquinone	.077	7.4	.068	6.6	+0.8
Thymoquinone	.027	2.6	.013	1.3	+1.3
Monochloroquinone	.088	8.5	.089	8.6	−0.1
2,6-Dichloroquinone	.057	5.5	.053	5.1	+0.4
Trichloroquinone	.020	1.9	....	...	.....

Before examining Table III it should be pointed out that any conclusions based on the values given are rendered somewhat doubtful by the fact that the chloroquinhydrones undoubtedly exist in contact with aqueous solution in the form of hydrates. Consequently ΔF_{qh} represents the free energy of formation and of hydration of the compounds in these cases. However, in relation to the above comparison of the affinity of reactions occurring in solution and in the solid state, it is perhaps significant that temperature coefficients indicated in the table vary so greatly as even to be of opposite sign. For benzoquinhydrone ΔF_{qh} decreases slightly with temperature while for thymoquinhydrone it is doubled in the same temperature interval and there is no indication of hydrate formation in either case.

Whether or not this is true of the free energy of formation of quinhydrones in solution cannot, at present, be decided. The latter quantity, calculated from the dissociation constants in water, is 3.3 kj. (25°) for benzoquinhydrone[3,25] and 5.8 kj. for toluquinhydrone. The affinity of formation of the complex in solution is increased by the substitution of a methyl group while, when the total process involving the solids is considered, this group lowers the affinity. The first term in Eq. 8, $RT\, ln\, \frac{a \times b}{c}$, is found by subtraction to be 10.1 kj. for benzoquinhydrone and 1.6 kj. for toluquinhydrone. The small value of this term indicates that the solubility of toluquinhydrone is very nearly equal to the product of the solubilities of its components. This rather surprising relationship is easily demonstrated by the fact that no toluquinhydrone precipitates when saturated solutions of its components are mixed. Benzoquinhydrone precipitates at once under these conditions, as the relatively large value of the "solubility term" indicates.

Since ΔF_{qh}, the free energy of formation of solid quinhydrone, is subject to wide variations in its temperature coefficient and because of the different solubility relations of a series of closely related compounds, it cannot be considered to be of much significance in the study of the structures of these complexes. It does give an indication of the "ease" with which the various quinhydrones are obtained. In order that a quinhydrone be obtained from a given solution of the components it is necessary that (1) they associate and that (2) the quinhydrone, being less soluble than its factors, precipitate. The total free energy, ΔF_{qh}, will be the same regardless of the solvent, so that if a solvent is chosen in which relatively great association takes place, the quinhydrone will not be so insoluble relative to its components in that solvent as in one in which association is less. Thus, one may prepare a quinhydrone by precipitation, by mixing the components in a solvent which favors precipitation, or by evaporation, if the solvent chosen favors association but not precipitation. Of course the quinhydrone may be made more insoluble by adding an excess of one of the components, according to the law of mass action, unless the quinhydrone is of the toluquinone type, when addition of a component precipitates the quinhydrone contaminated with that component.

It is interesting to notice that other investigators have observed the effect of these two factors, solubility and dissociation, in determining the course of the reaction, though the precise relationship was not seen. Torrey and Hunter[34] believed that the stability of the halogenated quinhydrones depends "on the number of halogens present only as this affects the solubility of the factors and of the quinhydrone itself." Jackson and Bolton,[35] finding that the quinhydrone of iodanil but not of chloranil could be prepared, and believing the solubility relations to be about identical in the two cases, held that the solubility relations play no part in the formation or non-formation of quinhydrones, but that the determining factor is the negativity of the substituent groups. Since this factor, the negativity, must determine dissociation, the two opposing views are now fused into one which maintains that both solubility and dissociation constants are important.

It will be observed that the figures in the table agree well with the known behavior of these quinhydrones. The free energy of formation of benzoquinhydrone is the greatest of all and is decreased by the introduction of substituents, whether these are positive or negative. Tendency of formation vanishes with the introduction of 2 methyl groups or 4 chlorine atoms. It is well known that the stability of quinhydrones decreases with the number of halogen substituents, and that neither chloranil nor *p*-xyloquinone forms a quinhydrone with its hydroquinone.[36]

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Summary

1. The question has been raised as to the relationship of the reduction potentials of a series of quinones in different solvents and referred to the solid state.

2. The reduction potentials of 4 alkyl derivatives and 6 chloro derivatives of benzoquinone have been measured in alcoholic solution, in aqueous solution (with three exceptions) and referred to the solid state.

3. Essentially the same relationships have been found whether the potentials measured in aqueous or alcoholic solutions were compared. The potentials referred to the solid state are not entirely parallel to those measured in solution. From these facts and general considerations it has been shown that in comparing the reduction potentials of a series of quinones the substances should ideally be measured in a solvent in which the absolute activity coefficient of the organic substances is unity; alcoholic

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[34] Torrey and Hunter, THIS JOURNAL, **34,** 702 (1912).

[35] Jackson and Bolton, *Ber.*, **45,** 871 (1912); THIS JOURNAL, **36,** 304 (1914).

[36] Ref. 16. Schlenk, *Ann.*, **368,** 287 (1909).

or aqueous solutions seem to be sufficiently close to this ideal condition to make the measurements in these solvents significant.

4. The introduction of alkyl groups progressively lowers the reduction potential in the case of the 4 alkyl compounds investigated. The introduction of chlorine, on the other hand, first raises and then lowers the potential.

5. In order to measure the reduction potential referred to the solid state of those quinones that form quinhydrones, it was necessary to measure the potential of cells containing quinone-quinhydrone and hydroquinone-quinhydrone. The validity of this procedure has been demonstrated. Data concerning the energy of quinhydrone formation have been thus obtained.

6. The temperature coefficient of the reduction potential referred to the solid state has been measured for all of the quinones investigated and the total energy of reduction thus calculated. A comparison with previous thermochemical measurements shows great discrepancies in the case of the polychloroquinones; the cause for this discrepancy seems to lie in the errors inherent in the thermochemical measurements.

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NEW BOOKS

A Course of Laboratory Experiments on Physico-chemical Principles. By MILES S. SHERRILL, Associate Professor of Theoretical Chemistry in the Massachusetts Institute of Technology. The Macmillan Co., New York, 1923. x + 125 pp. Illustrated. 22.5 × 14.5 cm. Price $2.00.

The 27 experiments contained in this book are divided into 12 groups of from 1 to 5 experiments, under the following headings: Molecular Weight from Vapor Density; Vapor Pressure and its Lowering by Solutes; Distillation in Relation to Vapor Pressure; Distribution of Solutes between Phases; Freezing-Point Lowering and Molal Composition; Electrolysis, Transference and Conductance; Rate of Chemical Change; The Equilibrium of Chemical Changes at Constant Temperature; Equilibrium of Chemical Systems in Relation to the Phases Present; Heat Effects Attending Chemical Change; Electromotive Force of Cells; Effect of Temperature on Chemical Equilibrium. Each experiment is carefully organized according to a uniform plan, in which the Principles Involved are first listed, followed in order by an Outline, a description of Apparatus, the detailed Procedure, the required Treatment of Results, and a Discussion of the broader aspects of the experiment and the sources of error.

The individual experiments are, in general, good. This is particularly true, for example, of the study of the equilibrium of hydrogen and iodine at high temperatures, and of several of the experiments on electromotive force. The use of conductivity measurements in following the rate of a