The solubility of anhydrous peroxide was measured in various organic solvents.

The solubility curves of sodium chloride, sodium nitrate, sodium sulfate and sugar were determined. It was shown that in hydrogen peroxide the dissociation is of the same order as in water. The tendency towards molecular compound formation is less than in the case of water, there being evidence of only one compound, $Na_2SO_4.2H_2O_2$.

The action of the halogen hydrides on pure hydrogen peroxide and its aqueous solutions was examined, and conditions were indicated under which the oxidation of the halogen hydride occurs. The halogens were found to be less soluble in hydrogen peroxide than in water.

Ammonia is soluble in pure hydrogen peroxide, a crystalline compound being formed which melts at 24.5°, and which is stable in the absence of water. This compound is slightly soluble in ether, and can be formed by passing ammonia into an anhydrous solution of peroxide in ether. It was shown that a compound corresponding to $2NH_3.H_2O_2$ does not form. The stability of the compound, $NH_3.H_2O_2$, shows that it is the hydroxyl ion which causes the decomposition of hydrogen peroxide. Water dissociates or possibly hydrolyzes it and, with the consequent formation of hydroxyl ions, the decomposition is cumulative. Whether this compound is an ammonium salt, NH_4O_2H, is not certain, but it is hoped that experiments with other alkalies will throw light on this point.

The vapor pressure and dielectric constant of hydrogen peroxide are being measured, as well as the conductivity of salts in anhydrous hydrogen peroxide.

MONTREAL, CANADA

FREE AND TOTAL ENERGY CHANGES IN THE REDUCTION OF QUINONES

By JAMES B. CONANT AND LOUIS F. FIESER

In a previous paper[1] we have dealt with the oxidation-reduction potentials of certain water-soluble anthraquinone derivatives and the change of these potentials with variations in the hydrogen-ion concentration. From the standpoint of the organic chemist one of the most interesting aspects of the subject of oxidation-reduction potentials is a comparison of the free energy of reduction of different classes of compounds and a study of the effects of substitution in a given class. We stated in our last paper that we should soon publish the results of our work on the oxidation-reduction potentials of certain derivatives of anthraquinone, naphthoquinone and benzoquinone together with the temperature coeffi-
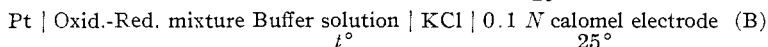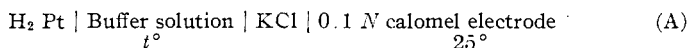
[1] THIS JOURNAL, **44**, 1382 (1922).

cients of these potentials. This paper presents these data and the free
and total energy changes calculated from them. Since the completion
of this work, the results of La Mer and Baker[2] have appeared. Their
data, like ours, were obtained by the titration method of Mansfield Clark
and consist of a careful study of the validity of this method, and a deter-
mination at 25° of the oxidation potentials of several derivatives of benzo-
quinone. Their work is of a considerably higher degree of accuracy than
ours. In the cases in which our work has overlapped, it is gratifying to
note that our results agree with theirs within 1 or 2 millivolts. This is
about the limit of accuracy we have attempted. The results presented
below, we feel, are sufficient to outline some important generalizations
in regard to the energy changes involved in the reduction of quinones.
There are, however, many unsolved problems which more accurate work
should elucidate. We, therefore, gladly leave further work along these
lines in aqueous solutions to La Mer and Baker who had already begun
such an investigation when our first paper appeared.

The number of substances which can be studied in aqueous solution
is limited. It was felt, therefore, that before the determination of the
free energy of reduction of quinones would be of much value to theoret-
ical organic chemistry, a method of more general applicability must
be found. We believe we have developed such a method by using alco-
holic solutions containing water and acid; some of the results obtained
with this method are given in this paper. We are at present engaged in
a determination of the oxidation-reduction potentials of many different
quinones in alcoholic solution and shall extend the method to include
solvents other than alcohol.

Potentials in Aqueous Solutions

The general method and apparatus were the same as those employed
in the study of the sulfonated anthraquinones.[1] Our first results were
obtained by measuring the electromotive force of the following combina-
tions.

$$H_2 \text{ Pt } | \text{ Buffer solution } | \text{ KCl } | 0.1 \text{ } N \text{ calomel electrode}$$
$$t° \qquad\qquad\qquad\qquad\qquad 25° \qquad\qquad\qquad\qquad (A)$$

$$\text{Pt } | \text{ Oxid.-Red. mixture Buffer solution } | \text{ KCl } | 0.1 \text{ } N \text{ calomel electrode } (B)$$
$$t° \qquad\qquad\qquad\qquad\qquad 25°$$

The calomel electrode was maintained at 25° ± 0.1° and was connected
by means of a saturated potassium chloride-agar bridge with the other
electrode cell which was kept in a hand-regulated thermostat so that its
temperature could be quickly adjusted to 40° ± 0.1° or 0°. The manipu-

[2] La Mer and Baker, THIS JOURNAL, **44**, 1954 (1922). Through the courtesy of the
Editor we had the opportunity of reading this paper in manuscript form. We should like
to note, in passing, that we cannot agree with the suggestions of these authors (p. 1959)
concerning the effect of their "correction for acidity" on the slopes of our titration curves,
since deviations from the theoretical curve were observed in well buffered solutions.

lation was exactly as described in our first paper. The electromotive force of A was first determined. The hydrogen electrode was of the Hildebrand type and dipped into the cell containing the buffer solution. The cell was then swept out with nitrogen, the material under investigation introduced, and titanous chloride run in from a buret, the potential being read after each increment was added. The value of the electromotive force of B at the midpoint of reduction was determined by a graphical interpolation of the titration curve. Table I summarizes the results obtained. The potential of the hydrogen electrode, π_h, was obtained by adding 0.337, the value of the calomel electrode, to the potential of Cell A. The oxidation-reduction electrode potential at the midpoint of reduction (π_n) was found by adding 0.337 to the potential of Cell B. Thus both π_h and π_n are expressed on the normal hydrogen electrode scale. The normal potential π_0 is equal to $\pi_n - \pi_h$. An error in the calomel electrode or the liquid junction is canceled in this method of determining the normal oxidation-reduction potential, π_0. The buffer solutions employed are indicated by letters in the first column as follows: A = 0.1 N hydrochloric acid; B = 1.0 N hydrochloric acid; C = sodium acetate and acetic acid; D = potassium dihydrogen phosphate and sodium hydroxide; E and F = glycocoll and sodium hydroxide; G = sodium citrate and sodium hydroxide.

The last 3 columns of Table 1 give the temperature coefficients in millivolts per degree as determined for 3 different temperature intervals. It is interesting to note that the temperature coefficients of Cell A (which may readily be calculated from Table I but which are not given) are very different with different buffers; in some cases they are positive and in some cases negative.

A more direct method of determining π_0 in acid solution where Equa-

$$\pi = \pi_0 + 0.059 \log [H^+] + 0.0295 \log \frac{[A]}{[AH_2]} \qquad (1)$$

tion 1 holds rigorously,[3] is to measure the e.m.f. of Combination C.

$$H_2 \text{ Pt} \mid \text{acid solution} \mid \text{acid solution} + \text{Oxid. Red. mixture} \mid \text{Pt} \qquad (C)$$
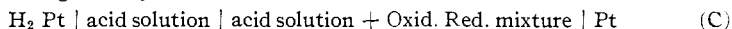
The e.m.f. of this cell when the reduced and oxidized material are present in equal amounts ([A] = [AH_2]) is obviously equal to the sum of $\pi_0 - \pi_H$ and π_h, or in other words π_0.

The apparatus consisted of a Hildebrand type hydrogen electrode dipping into the hydrochloric acid solution contained in a small bottle. The hydrogen was first passed through a similar bottle containing some of the same acid. The material under investigation was dissolved in the same solution and was contained in another bottle equipped in the usual way with a stirrer, nitrogen inlet and 2 platinum electrodes (1 bright, 1 platinized). The connection between the 2 half-cells was made by

[3] Ref. 1, p. 1383.

ENERGY CHANGES IN THE REDUCTION OF QUINONES

TABLE I
TEMPERATURE COEFFICIENTS IN ACID SOLUTION
Indirect Method

	Solution	$[H^+]^a$	0° π_h	π_n	π_0	40° π_h	π_n	π_0	Temperature Coefficient 0–25°	0–40°	25–40°
			Volts	Volts	Volts	Volts	Volts	Volts	Mv. per deg.	Mv. per deg.	Mv. per deg.
Sodium anthraquinone-2-sulfonate	A	7.94×10^{-2}	-0.079	$+0.120$	$+0.199$	-0.056	$+0.115$	-0.171	-0.47	-0.70	-1.07
	C	5.62×10^{-6}	-0.304	-0.106	$+0.198$	-0.313	-0.140	$+0.173$	-0.44	-0.63	-0.93
	D	1.41×10^{-7}	-0.397	-0.199	$+0.198$	-0.408	-0.236	$+0.172$	-0.44	-0.65	-1.00
								Av.	-0.45	-0.66	-1.00
Disodium anthraquinone-2,6-disulfonate	A	7.94×10^{-2}	-0.079	$+0.163$	$+0.242$	-0.056	$+0.155$	$+0.211$	-0.56	-0.78	-1.23
	D	1.41×10^{-7}	-0.397	-0.157	$+0.240$	-0.408	-0.200	$+0.208$	-0.48	-0.80	-1.33
								Av.	-0.52	-0.79	-1.28
Disodium anthraquinone-2,7-disulfonate	A	7.94×10^{-2}	-0.079	$+0.163$	$+0.242$	-0.056	$+0.155$	$+0.211$	-0.52	-0.78	-1.20
	D	1.41×10^{-7}	-0.397	-0.153	$+0.244$	-0.408	-0.191	$+0.217$	-0.60	-0.68	-0.80
								Av.	-0.56	-0.73	-1.00
Sodium[b] anthraquinone-1,5-disulfonate	A	7.08×10^{-2}	-0.084	$+0.167$	$+0.251$	-0.058	$+0.169$	$+0.227$	-0.48	-0.60	-0.80
	B	5.01×10^{-4}	-0.204	$+0.047$	$+0.251$	-0.190	$+0.041$	$+0.231$	-0.48	-0.50	-0.53
	G	1.18×10^{-6}	-0.341	-0.089	$+0.252$	-0.356	-0.127	$+0.229$	-0.52	-0.57	-0.67
								Av.	-0.49	-0.56	-0.67
Potassium[b] anthraquinone-1-sulfonate	A	8.91×10^{-2}	-0.078	$+0.131$	$+0.209$	-0.052	$+0.134$	$+0.186$	-0.56	-0.57	-0.60
	B	5.01×10^{-4}	-0.204	$+0.004$	$+0.208$	-0.190	$+0.007$	$+0.183$	-0.52	-0.63	-0.80
								Av.	-0.54	-0.60	-0.70
Potassium-1,4-naphthoquinone-3-sulfonate	A	7.94×10^{-2}	-0.079	$+0.469$	$+0.548$	-0.056	$+0.466$	$+0.522$	-0.60	-0.65	-0.73
	A	7.94×10^{-2}	-0.079	$+0.470$	$+0.549$	-0.056	$+0.470$	$+0.526$	-0.64	-0.58	-0.53
								Av.	-0.62	-0.61	-0.63
Benzoquinone	A	7.94×10^{-2}	-0.079	$+0.631$	$+0.710$	-0.056	$+0.626$	$+0.682$	-0.44	-0.70	-1.13

[a] Calculated from hydrogen-electrode potential interpolated to 25°.

[b] The authors are indebted to Mr. S. S. Kurtz, Jr., for making these measurements.

a siphon filled with the acid of the same concentration and plugged with filter paper to prevent diffusion. Since essentially identical ionic concentrations existed on both sides of these plugs (the organic material is present in low concentration) the liquid junction correction must be negligible. The whole apparatus including the siphon was immersed in water at the desired temperature. The materials used were prepared and purified in this Laboratory with the exception of certain anthraquinone sulfonic acids described in the previous paper which we neglected to state had been identified by conversion into the chloro-anthraquinones and by solubility measurements.

The e.m.f. of such a combination was measured after different increments of titanous chloride had been run into the oxidation-reduction half-cell. From the titration curve a value for π_0 was obtained in the usual way. The results[4] are summarized in Table II. This method seems to

TABLE II

TEMPERATURE COEFFICIENTS IN ACID SOLUTION

Direct Method

	Conc. of HCl	$\pi_0^{0°}$	$\pi_0^{25°}$	$\pi_0^{40°}$	Temperature Coefficients		
					$0-25°$	$0-40°$	$25-40°$
					Mv. per deg.	Mv. per deg.	Mv. per deg.
	N	Volts	Volts	Volts			
Toluquinone	0.1	0.660	0.644	0.630	−0.64	−0.75	−0.93
	0.1	0.660	0.643	0.630	−0.68	−0.75	−0.87
	1.0	0.657	0.641	0.628	−0.64	−0.72	−0.87
	1.0	0.655	0.641	0.628	−0.56	−0.70	−0.87
				Av.	−0.64	−0.73	−0.88
Monochloroquinone	0.1	0.729	0.713	0.697	−0.64	−0.80	−1.07
	0.1	0.730	0.713	0.701	−0.68	−0.72	−0.80
	1.0	0.726	0.710	0.699	−0.64	−0.68	−0.73
				Av.	−0.65	−0.73	−0.87
1,2-Naphthoquinone[a]	0.1	0.565	0.545	0.540	−0.80	−0.62	−0.33
	0.1	0.568	0.546	0.535	−0.88	−0.83	−0.73
	0.1	0.560	0.549	0.538	−0.44	−0.55	−0.73
				Av.	−0.71	−0.67	−0.60
Potassium 1,4-naph-thoquinone-3-sulfo-nate	0.1	0.553	0.534	0.523	−0.76	−0.75	−0.73
	1.0	0.547	0.532	0.520	−0.60	−0.68	−0.80
				Av.	−0.68	−0.71	−0.76
Benzoquinone	0.1	0.713	0.699	0.682	−0.56	−0.77	−1.15
	1.0	0.713	0.696	0.682	−0.68	−0.77	−0.93
				Av.	−0.62	−0.77	−1.03

[a] This compound was so insoluble in aqueous solution that measurements could not be made with much accuracy.

[4] The values found by La Mer and Baker[2] at 25° in 0.1 N HCl for quinone, toluquinone and chloroquinone are 0.6991, 0.6453, 0.7127, as compared with our values of 0.699, 0.644, 0.713. Biilman, *Ann. chim.*, 15, 109 (1921) and 16, 321 (1921), in his recent works on the quinhydrone electrode obtained the same values for quinone and toluquinone; his value for the temperature coefficient (18-25°) was —0.78 as compared with our values of —0.75 and —0.73.

us a more convenient and reliable procedure for obtaining values of π_0 in acid solutions than the more indirect method given above and used by other investigators.

A comparison of Tables I and II shows that both the indirect and direct methods yielded results of about the same degree of accuracy. The maximum error in the temperature coefficients (calculated from a 40° range) is about 13% and most of the results agree much more closely than this. An inspection of the temperature coefficients calculated from 3 different temperature intervals (0–25°, 25–40°, 0–40°) shows that the temperature coefficient is a function of the temperature and increases with rise in temperature in the case of the benzoquinone derivatives and certain of the anthraquinone derivatives. With the naphthoquinone compounds the temperature coefficient is nearly the same over the range measured. This phase of the subject should be a profitable one for further work. It should be noted (Table I) that the temperature coefficient is constant within the experimental error over a wide range of hydrogen-ion concentration.

Energy Changes in Aqueous Solution

Table III summarizes the energy changes at 25° calculated from the data given in Tables I and II and the Gibbs-Helmholtz equation.

$$\Delta H = 2F\pi_0 - 2FT \cdot \frac{d\pi_0}{dT} \tag{2}$$

The temperature coefficient calculated over the range 0–40° was taken as being the most accurate and representing an average value for 20° which

TABLE III

FREE, LATENT AND TOTAL ENERGY OF REDUCTION IN AQUEOUS SOLUTION AT 25°

	$\pi_0^{25°}$	Temperature Coefficient 0−40°	ΔF	$-T\frac{d(\Delta F)}{dT}$	ΔH
	Volts	Volts per deg.	Kj.	Kj.	Kj.
Sodium anthraquinone-2-sulfonate.....	0.187	−0.00066	36.1	38.0	74.1
Sodium anthraquinone-2,6-disulfonate..	0.228	−0.00079	44.0	45.4	89.4
Sodium anthraquinone-2,7-disulfonate	0.229	−0.00073	44.2	42.0	86.2
Potassium anthraquinone-1-sulfonate..	0.195	−0.00060	37.6	34.5	72.1
Sodium anthraquinone-1,5-disulfonate..	0.239	−0.00056	46.1	32.2	78.3
Benzoquinone......................	0.698	−0.00075	134.7	43.1	177.8
Toluquinone......................	0.642	−0.00073	123.9	42.0	165.9
Monochloroquinone.................	0.712	−0.00073	137.4	42.0	179.4
1,2-Naphthoquinone................	0.547	−0.00067	105.6	38.5	144.1
Potassium 1, 4-naphthoquinone-3-sulfonate...........................	0.533	−0.00066	102.9	38.0	140.9

would not be very different from the true value at 25° which should be employed in the calculations. The third column gives the values for the free energy change (ΔF), the fourth the latent heat of the reversible reduction and the last the total energy change (ΔH) for the following process

(in aqueous solution); $A + H_2 \rightleftarrows AH_2$. It is very striking that while the free energy changes and total energy changes are very different for different types of quinones, the latent heat of the reversible reduction is approximately constant for all the substances investigated; thus, the latent heat of the reduction of anthraquinone, naphthoquinone and benzo-quinone derivatives does not vary by more than 7 kj., while the free energy of reduction of an anthraquinone derivative is nearly 100 kj. less than that of benzoquinone. It is, perhaps, particularly surprising that the latent heat of reduction of an *ortho*quinone (1,2-naphthoquinone) is essentially the same as of the *para*quinones. This constancy of the latent heat of reduction probably means, in the light of the Nernst heat theorem, that the difference in the heat capacities of the oxidized and reduced compounds (in solution) is the same for many different types of quinones. In other words the difference between the heat capacities of a given quinone and a given hydroquinone is almost independent of the rest of the molecule. From our present results it seems as if the qualtity most characteristic of all substances generally classed as quinones is this latent heat of reduction.

Comparison of Results with Thermochemical Data

It is interesting to compare our results with the total energy of reduction of the solid substances as determined by the usual calorimetric method. Valeur[5] determined the heats of combustion of a number of quinones and hydroquinones and thus the total heat of reduction referred to the two solid substances. The difference between this total energy change (ΔH_s) and the total energy change in solution (ΔH) is the difference between the heats of solution of the oxidized and reduced form. This has been measured in aqueous solution for quinone and hydroquinone by Valeur and found to be only 1.7 kj. If benzoquinone derivatives show similar small differences in aqueous solution, we should expect a close agree-ment between Valeur's value for ΔH_s and our values for ΔH in aqueous solution. For benzoquinone, toluquinone and chloroquinone, Valeur's values were 175, 156 and 166 kj., respectively. We have found the total energy change in solution (ΔH) for the same substances to be 178, 166, and 179 kj. (Table III) . The maximum difference, 13 kj., is not more than can be accounted for by the experimental errors in both methods.

It is hardly necessary to point out that a knowledge of the total energy change reveals little concerning the power of a given quinone as an oxidiz-ing agent. This is, however, measured by the free energy of reduction. This free energy is 49% of the total energy with the weakest and 76% of the total energy with the strongest oxidizing agent of the series measured. Such differences show the impossibility of successfully solving the prob-lems of organic chemistry from a knowledge of only the total energy changes

[5] Valeur, *Ann. chim. phys.*, [7] **21**, 470 (1900).

involved. Calorimetric results obtained with this series of quinones would lead to quite erroneous results in regard to their relative reducing and oxidizing action.

Reduction in Alkaline Solution

It was shown in the last paper that with certain derivatives of anthraquinone, it was possible to measure the potential of the process represented by the equation; $A + 2E \rightleftharpoons A^{--}$. In those cases in which the reduced form is completely dissociated in alkaline solution a value (π_0') was obtained which, when referred to the normal hydrogen electrode, represents the free energy of the process; $A + H_2 \rightleftharpoons A^{--} + 2H^+$. Table IV summarizes the results obtained in those cases in which π_0' could be measured. The energy changes have been calculated from the Gibbs-Helmholtz equation and the temperature coefficients.

TABLE IV

ENERGY CHANGES IN ALKALINE SOLUTION

Buffer[a] solution	[H+] × 10^{+13}	0° π_0' Volts	40° π_0' Volts	Temp. coeff. 0-40° Mv. per deg.	25° π_0' Volts	$\Delta F' - T \dfrac{d(\Delta F')}{dT}$ Kj.	Kj.	ΔH Kj.
Sodium anthraquinone-2-sulfonate								
E	13.2	−0.359	−0.389	−0.75	−0.383	−73.9	49.5	−24.4
G	3.98	−0.348	−0.387	−0.98				
Sodium anthraquinone-2,6-disulfonate								
G	3.98	−0.287	−0.331	−1.10	−0.325	−62.7	62.1	−0.6
F	2.82	−0.291	−0.334	−1.07				
Sodium anthraquinone-2,7-disulfonate								
G	3.98	−0.283	−0.329	−1.15	−0.313	−60.4	61.5	1.1
G	3.98	−0.281	−0.320	−0.98				

[a] Letters refer to nature of buffer solution as in Table I.

It will be noted that the latent heat is of the same order of magnitude as found for the reduction in acid solution. The free energy change is of the opposite sign, on the other hand, and the total energy change is small. The free energy of this process ($\Delta F'$) is related to the free energy of the reduction in acid solution (ΔF) as follows.

$$\Delta F' = \Delta F - RT \ln K_1 K_2 \tag{3}$$

The last term of this equation is the free energy of complete dissociation of the reduced form and $K_1 K_2$ the dissociation constants of the 2 phenolic hydrogen atoms. It should be pointed out in this connection that the value of $\Delta F'$ does not show the same constancy for all the anthraquinones investigated as does ΔF. The free energy of reduction in acid solution (ΔF) varies by small and definite increments throughout the series of anthraquinone sulfonic acids. The value of $\Delta F'$, on the other hand, in certain cases undergoes great changes. Thus, it was found[6] that the

[6] Ref. 1, p. 1395.

value of K_1K_2 was so small for the 1,5- and 1,8- disulfonic acids that π_0' and consequently $\Delta F'$ could not be measured directly. Obviously, in these cases $\Delta F'$ must be much more negative than for the substances given in Table IV; judging from the potentials found in the most alkaline solutions the difference must be at least 30 kj. The free energy of formation of the undissociated hydroquinone from the quinone is thus characteristic of a given series of compounds; the free energy of formation of the hydroquinone ion from the quinone is not so characteristic.

Potential Measurements in Alcoholic Solution

The normal oxidation-reduction potential of a number of substances was determined by measuring the e.m.f. of the following combination.

H_2 Pt Aq. alcohol + HCl | Aq. alcohol + HCl + Oxid.-Red. mixture | Pt
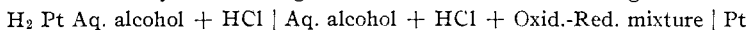
When the midpoint of reduction is reached ($[A] = [AH_2]_T$) the e.m.f. of this cell is equal to π_0, since the hydrogen electrode potential cancels as in the corresponding aqueous combination. Thus, although the single potential of the hydrogen electrode in alcoholic solutions has not yet been determined[7] and the activities of the hydrogen chloride are not known, the normal oxidation-reduction potential can be measured. This potential is a measure of the free energy of reduction in the alcoholic solutions under consideration.

The alcoholic solutions were made up from ethyl alcohol and water to the desired percentages (determined by an hydrometer) and dry hydrogen chloride was passed in until the concentration was 0.2 N as determined by titration with sodium carbonate solution. The resulting mixture was used as the solvent for the material in the oxidation-reduction half-cell, filled the siphon and the hydrogen electrode cell and served as the diluent for the titanous chloride. All the potentials were read on both the bright and platinized electrodes. The two readings did not always check. With quinone and toluquinone the platinized electrode gave higher and more constant values than the bright; with the sulfonated anthraquinones and sulfonated naphthoquinone, on the other hand, the bright electrode gave steadier and higher readings. Of these values the higher more constant potential has alone been reported. Equilibrium was attained somewhat more slowly in alcoholic than in aqueous solution and the resistance of the cell was appreciably greater, particularly at 0°. With the galvanometer we were employing, this resistance somewhat increased the probable error of our measurements. This can, of course, be overcome by using a more sensitive instrument.

Table V summarizes the results obtained with 4 different compounds in alcoholic solutions of different strengths. A comparison between the oxidation-reduction potential in aqueous solution and alcoholic solutions is given in Table VI. From the data in these two tables certain conclu-

[7] Hildebrand, THIS JOURNAL, **44**, 135 (1922).

sions can be drawn. The oxidation-reduction potential of a given quinone is the same in 50, 75 and 95% alcoholic solutions. The potential in alcoholic solutions is a little higher than in aqueous solutions; the difference, in the case of the substances so far investigated, varies from 10 to 30 millivolts. Two quinones do not show the same relationship in water

TABLE V

OXIDATION-REDUCTION POTENTIALS IN ALCOHOLIC SOLUTION

	Solvent: % alcohol containing 0.2 mole HCl	$\pi_0^{0°}$	$\pi_0^{25°}$	$\pi_0^{40°}$	Temperature coefficient $0-40°$
		Volts	Volts	Volts	Mv. per deg.
Benzoquinone...............	50	0.734	0.712	0.691	−1.08
	75	0.737	0.713	0.693	−1.10
	95	...	0.709	...	....
Toluquinone.................	50	0.682	0.657	0.637	−1.12
	75	0.676	0.656	0.637	−0.98
	95	...	0.653	...	....
1,2-Naphthoquinone..........	50	0.591	0.576	0.554	−0.93
	75	0.604	0.582	0.552	−1.30
	95	...	0.579	...	....
Potassium 1,4-naphthoquinone-3-sulfonate...............	50	0.573	0.558	0.543	−0.75
	75	0.568	0.550	0.535	−0.82
	95	...	0.552	...	....

and in alcohol; thus chloroquinone is 24 mv. higher than quinone in alcohol, and only 14 higher than in water. The temperature coefficient in alcoholic solution seems to be somewhat greater than in aqueous solutions, although our present results for the coefficients in alcohol are only preliminary. The free energy and latent energy changes are thus somewhat greater in solutions containing over 50% of alcohol than they are in water.

TABLE VI

COMPARISON OF SOLVENTS

	Normal potential at 25°		
	In alcoholic solution	In aqueous solution	Difference
	Volts	Volts	Mv.
Benzoquinone..............................	0.711	0.698	13
Toluquinone...............................	0.655	0.642	13
Monochloroquinone.........................	0.736[a]	0.712	24
1,2-Naphthoquinone........................	0.579	0.547	32
Potassium 1,4-naphthoquinone-3-sulfonate......	0.553	0.533	20
Sodium anthraquinone-2-sulfonate.............	0.197[a]	0.187	10

[a] Details to be published later.

This effect of a change of solvent on the free energy of reduction in solution (the normal oxidation-reduction potential) is related to the change in solubility of the oxidized and reduced compound as the following con-

siderations show. The free energy of reduction referred to the 2 solids (ΔF_s) is

$$\Delta F_s = 2F\pi_0 + RT \, ln \, \frac{a}{b} \tag{4}$$

where π_0 is the potential in a given solvent, and a and b are the solubilities of the quinone and, the hydroquinone in the same solvent at temperature T. This follows from a consideration of a cell composed of a hydrogen electrode and an oxidation-reduction electrode in a half-cell containing the solid quinone and hydroquinone in contact with their saturated solution. The work done by such a cell is, obviously the free energy of reduction of the solid quinone to the solid hydroquinone. If π_0'' and a', b' are the potentials and solubilities respectively in some other solvent then we can write a similar equation for ΔF_s and combining the two equations we have

$$\pi_0'' - \pi_0 = \frac{RT}{2F}\left(ln \, \frac{a}{b} - ln \, \frac{a'}{b'}\right) \text{ or } \pi_0'' - \pi_0 = \frac{RT}{2F}\left(ln \, \frac{a}{a'} - ln \, \frac{b}{b'}\right) \tag{5}$$

This equation also follows from a calculation of the work done in transferring one mole of oxidized and reduced material from one saturated solution to another; it must, of course, be slightly modified if there is any change in molecular weight in either solvent.

The equation (4) for the free energy change referred to the solid state, and its temperature differential enables one to calculate the free and latent energy changes referred to the solid state from the e.m.f. measurements in any solvent and a knowledge of the solubilities of the reduced and oxidized material. The total energy change referred to the solid can be calculated with the aid of the heats of solution of the quinone and hydroquinone which in turn follow from the solubilities at two different temperatures according to the equation, $Q = RT^2 \, dln \, a/dT$. We intend to present the necessary solubility data in another paper together with more accurate determinations of the temperature coefficients in solvents other than water. We will, therefore, postpone a further consideration of the energy changes in alcoholic solutions and a comparison with calorimetric determinations until experiments along these lines have been completed.[8]

It might be well to point out that our general equation for the potential of a mixture of a quinone and a hydroquinone in solutions of varying hydrogen-ion concentration[9] should include another term representing variations in solubility of the oxidized and reduced form. In most instances this correction is very slight but with certain compounds, which we will consider in another paper, this solubility term is very appreciable. As La Mer and Baker have pointed out, Sörensen[10] has recently applied the conception of the varying "activity" of dissolved molecules to the ap-

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[8] Preliminary results indicate that the difference between ΔH_s and ΔH is much greater than in aqueous solution.

[9] Ref. 1, p. 1385.

[10] Sörensen, *Ann. chim. phys.*, **16**, 283 (1921); see also Biilmann, *ibid.*, **16**, 321 (1921).

parently abnormal behavior of the quinhydrone electrode in strong salt solutions. Sörensen has developed an equation similar to the one above from this different point of view and has verified it experimentally by solubility and potential measurements on the system, quinone-hydroquinone, in aqueous salt solutions.

The Work of Haber and Russ[11]

Haber and Russ found a value for the potential of quinone in aqueous alcohol of 0.743 volts, whereas that found by the above method was 0.711. This difference has been traced to an invalid assumption made by the pioneer investigators. They measured the e.m.f. of the cell: H_2 Pt aq. H_2SO_4 (conductivity = x)|quinhydrone, alc. H_2SO_4 (conductivity = x)Pt. Obviously the e.m.f. of such a cell gives the true quinone potential only when the hydrogen-ion activities in both half-cells are identical, and when there is no junction potential between the liquids in the two compartments. Haber and Russ assumed that both of these conditions were fulfilled in their cell because the conductivity of the aqueous acid and of the alcoholic acid were identical. This assumption can be easily tested for, if true, there should be no potential between hydrogen electrodes dipping into these two solutions.

Such a potential, whether it be due to an actual difference in hydrogen-ion activity or to a liquid-junction potential, has been found to exist. Two solutions were prepared to correspond to those used by Haber and Russ. An aqueous solution of sulfuric acid was 0.138 N (Haber, 0.1386 N) and had a conductivity of 0.0163 mho (Haber, 0.0162 mho). Its hydrogen electrode potential against a 0.1 N calomel electrode was 0.432 volts (Haber, 0.434). Two hundred cc. of aqueous sulfuric acid, 7.87 N (Haber, 7.872 N) was diluted to 1 liter with 95% alcohol. The conductivity of the solution, slightly diluted, was 0.163 mho (Haber, 0.162 mho).

On placing these solutions in hydrogen-electrode vessels and making connection by a siphon containing either one solution or the other, the potential difference was found to be 0.025 volts (the alcoholic solution being the more positive). When a siphon filled with saturated potassium chloride was used the potential difference was 0.064 volts. These values representing averages for the potentials fluctuated as much as 10 mv., indicating the experimental difficulties in any attempt to use different solvents in the 2 electrode compartments.

The fact that a considerable potential was apparent proves the assump-

[11] Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904). Strangely enough, Granger and Nelson [THIS JOURNAL, **43**, 1401 (1921)] did not compare their actual values for the potential of quinone with Haber's earlier determination. La Mer and Baker (Ref. 2) likewise fail to consider adequately Haber's measurements; their reference to his failure to take into account quinhydrone formation is quite beside the point, as this complication does not affect appreciably the value for π_0.

tion of Haber and Russ to have been unjustified.   Our measurements were not intended to give an exact correction to their work but it can be seen that the subtraction of 25 mv. lowers their value to 0.718, in fair agreement with our value of 0.711.   As the potential between the solutions was quite different when a salt bridge was used, it is probable that the potential is due partly to the liquid junction.   Since, however, the salt bridge does not eliminate the total potential there is, probably, an actual difference in hydrogen-ion activity in the 2 solutions even though they have the same conductivity.   If the salt bridge completely eliminates the liquid junction potential, the remaining potential must be due to the differences in activities of the hydrogen ion in the 2 half-cells.   If the activity coefficient of the hydrogen ion is the same in the aqueous and alcoholic solutions, this potential can be directly calculated from the known total concentrations of acid in both solutions and the usual concentration equation.   Such a calculation for the two solutions under consideration (0.138 N aqueous acid and 1.57 N alcoholic-aqueous) gives a value of 62 mv. The observed value was 64 mv; this agreement seems to indicate that the activity coefficients of the hydrogen ion are nearly the same in these aqueous and aqueous-alcoholic solutions.

Summary

    1.   The temperature coefficients of the oxidation-reduction potentials of a number of derivatives of benzoquinone, naphthoquinone and anthraquinone have been measured by two slightly different methods.

    2.   The free energy, total energy and latent heat of reduction in aqueous solution have been calculated from the potentials and temperature coefficients.   The free and total energy changes vary greatly with different types of quinones.   The latent heat of reduction is approximately the same for all the quinones measured.   The total energy change (in aqueous solution) agrees with the total heat change for the solids as measured calorimetrically, since the heats of solution are slight.

    3.   A method has been developed for measuring the free energy of reduction of quinones in alcoholic solutions.   By means of this method a number of substances have been investigated which are too insoluble to be measured in aqueous solution.

    4.   The oxidation-reduction potential of a given quinone is slightly greater in alcoholic than in aqueous solution.   It is practically identical in 50, 75 and 95% alcoholic solutions.   Preliminary measurements indicate that the temperature coefficient is greater than in aqueous solution.

5.   An equation has been developed relating the free energy change referred to the solids to the potential in a given solution and the solubilities of the quinone and hydroquinone.   The differences in the oxidation potential as measured in 2 different solvents can be thus calculated from the solubilities.

6.   The discrepancy between our value for quinone and the one obtained by Haber and Russ has been traced to an invalid assumption made by these investigators.

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A NEW METHOD FOR THE GRAVIMETRIC DETERMINATION OF GERMANIUM

By JOHN HUGHES MÜLLER

Analytical procedure for the quantitative determination of germanium has not changed since the early investigations of Winkler[1] immediately following his discovery of the element in 1886; that is to say, germanium has always been weighed as sulfide or dioxide and no other compound has been reported which admits of direct application to quantitative estimation.

Weighing of the disulfide yields excellent results but is usually avoided on account of the required washing for the removal of free sulfur, as well as the inability of this salt to withstand ordinary ignition.   In consequence, the sulfide is nearly always converted to dioxide by frequent evaporation with nitric acid and ignition to constant weight.

In many determinations it has been the writer's experience that the conversion of sulfide to oxide, aside from being time consuming, is subject to serious conflicting errors.   First, the sulfide is violently attacked by even dil. nitric acid and yet must be thoroughly decomposed by this acid before much heat is applied to the residue.   Second, after complete oxidation the removal of all of the sulfuric acid is very difficult, if indeed possible.

A slight loss of germanium through volatility of the unoxidized sulfide plus the mechanical loss in the escaping oxides of nitrogen tends to give low results, but on the other hand the tightly held sulfuric acid which clings to the ignited residue causes error in the other direction.   These conflicting or balancing errors are practically beyond control of the analyst and have suggested to the writer the search for an altogether different method for the estimation of germanium.

The purpose of this communication is to describe a new method for the gravimetric determination of germanium, which is based upon the action

[1] Winkler, *J. prakt. Chem.*, [2] **34**, 177 (1886); **36**, 177 (1887).