

available oxygen than is demanded by the equation in (f); and (h) the results obtained are best explained on the assumption that a continuous series of double salts of manganese or double oxides of the alkali metal and manganese were formed in the strongly alkaline solutions.

4. The initial presence of precipitated manganese dioxide in a reaction mixture brings about an ultimate decomposition of the permanganate to the dioxide in a relatively short time when compared with the time for the reactions summarized in 3 (a).

5. Slow stirring of a reaction mixture increases the speed slightly without appreciably influencing the point of apparent rest in the reaction.

6. A new method for the preparation of manganese dioxide gel is described.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ELECTROMOTIVE ACTIVATION OF OXYGEN

BY ARTHUR B. LAMB AND LUCIUS W. ELDER, JR.

RECEIVED DECEMBER 1, 1930

PUBLISHED JANUARY 12, 1931

The achievement of a fuel cell, in which the free energy of combination of hydrogen or some comparable gaseous fuel with oxygen is converted directly into electric energy, has encountered its most serious difficulties at the oxygen electrode. Gaseous oxygen establishes its potential sluggishly and imperfectly on inert electrodes at ordinary temperatures, even on open circuit, and an oxygen electrode on closed circuit polarizes at once if any appreciable current is withdrawn.

These difficulties have been overcome to some extent by operating the electrodes in suitable electrolytes at elevated temperatures.¹ Similarly progress has been made in the electromotive activation of oxygen by the use of catalysts. These catalysts have been of two types. In the one type, the catalytic action is confined to the surface of the electrode, the catalyst being either a part of the electrode itself or a reaction product formed upon its surface, which enhances the electromotive activity of the gaseous oxygen. Electrodes where catalysts of this type are effective are the familiar platinized platinum and similar electrodes, and the electrode of copper immersed in a solution of potassium hydroxide described by K. A. Hofmann.² In the second type the catalytic action takes place throughout the bulk of the electrolyte. This type of catalyst must be susceptible of rapid oxidation by gaseous oxygen under the conditions in the cell, and its oxidation product must be a rapid depolarizer.

¹ Haber and Bruner, *Z. Elektrochem.*, **10**, 712 (1904); Taitelbaum, *ibid.*, **16**, 286 (1910); Baur, Treadwell and Trümpler, *ibid.*, **27**, 199 (1921); *Helv. Chim. Acta*, **4**, 325 (1921); Rideal and Evans, *Trans. Faraday Soc.*, **17**, 466 (1921).

² Hofmann, *Ber.*, **51**, 1526 (1918); **52**, 1185 (1919); **53**, 914 (1920).

This second type of catalyst, or bulk catalyst, as one may call it, has the marked advantage over the first type, or surface catalyst, in that with it the chemical oxidation of the catalyst by the gaseous oxygen, which in general is a relatively slow step in the process as a whole, can take place far more abundantly, and with adequate stirring the oxidized catalyst can be brought into effective contact with the electrode. Nernst³ patented this method some time ago, and suggested a variety of catalysts for its execution, but apparently it has not as yet been put into successful operation. Nevertheless, the method has seemed to us to be of considerable promise, and the experiments which we shall describe below have been directed toward its further development.

The catalyst to be used in such a method of overcoming the easy polarizability of the oxygen electrode should meet several requirements. As pointed out above, it should be susceptible of rapid oxidation by gaseous oxygen under the conditions in the cell, and its oxidation product should be a rapid depolarizer. But it is also desirable that the normal potential of the catalyst system approximate that of the reversible oxygen electrode in the electrolyte used. Other things being equal, this will afford the highest working potential for the electrode.

There are a number of catalyst systems which give rapidly adjusting and reversible potentials, but unfortunately they absorb oxygen very slowly. Conversely, there are several such systems which absorb oxygen rapidly, but their potentials are very low. Examples of the former group are the thallos-thallic and vanadyl-vanadic acid systems; of the latter are the vanadous-vanadic and the chromous-chromic systems. The ferrous-ferric system occupies a somewhat favorable intermediate position; it establishes its potential with great rapidity on various electrodes; it has a fairly high normal potential; but it reacts with gaseous oxygen with only slight (though measurable) rapidity. However, the kinetics of this reaction have been studied to some extent, and a variety of factors which increase its velocity, particularly secondary catalysts, such as copper salts, platinum black and charcoal, have been recognized.

We have, therefore, undertaken a further study of the velocity of oxidation of ferrous solutions by gaseous oxygen, since this is the limiting factor in the utility of the ferrous-ferric system as a bulk catalyst. For this study we have perfected a method of determining the rate of oxidation of ferrous solutions by means of electromotive force measurements. Using this method we have ascertained the effects of a variety of factors on the velocity of the reaction. Finally, we have tested the actual depolarizing efficiency of certain of the systems which had shown the maximum velocity of reaction with gaseous oxygen.

³ Nernst, German Patents 260,426 and 265,424 (1912). See also Grube and Hermann, *Z. Elektrochem.*, 26, 291 (1920).

Procedure and Apparatus

Velocity of Oxidation of Ferrous Sulfate Solutions by Gaseous Oxygen.—Oxygen in air was bubbled through the solution to be studied and the progress of the oxidation was followed by measurements of the potential of a bright platinum electrode immersed in the solution.

The apparatus (see Fig. 1), constructed chiefly of pyrex glass, comprised a short, wide test-tube (A) containing the solution of iron salt (50.2 cc.); a tubular stirrer (S), with four slightly re-curved tips (C) at its base at right angles to its axis; a baffle (D) to prevent undue swirling of the liquid; an electrode (K); and a saturated potassium chloride bridge (F), connecting the ferrous salt solution with a reservoir (H), filled also with saturated potassium chloride solution and connected in turn with the tip (N) of the calomel electrode. The whole was immersed to within a few millimeters of its top in a thermostat bath (P) maintained at a temperature of $30.0 \pm 0.1^\circ$.

The stirrer was rotated by means of an induction motor at constant speed and rapidly enough to force air through the solution in a fine, white foam. The standard rate of stirring was 1250 r. p. m.

The electrode was of bright platinum wire 2–3 cm. in length. It and the salt bridge (F) were lowered into the solution only at the time of reading. When not in use it was kept short-circuited with several duplicate electrodes in a ferrous–ferric salt mixture, and was washed and ignited to a red heat before each run. In this way constant and reproducible potentials could be secured. Preliminary measurements showed that the potential of the electrode in any given solution was independent of the presence of the gaseous oxygen.

The calomel electrode was of the saturated type prepared according to the method of Fales and Mudge,⁴ using all the customary precautions in purifying the materials. Three such electrodes were prepared. Their potentials checked against each other from time to time showed an average agreement to within ± 0.0005 v. Fales and Mudge give the absolute potential of this electrode as $E_0 = 0.5266$ v., which corresponds to E_{H}

⁴ Fales and Mudge, *THIS JOURNAL*, 42, 2453 (1920).

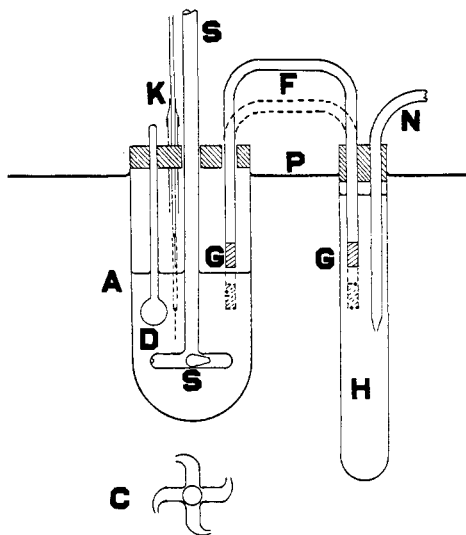


Fig. 1.—Apparatus for kinetic measurements.

= +0.253 v. on the hydrogen scale. The potentiometer was of the compensating type, using an Eppley-Weston standard cell.

Materials.—The ferrous sulfate used was recrystallized from one to two per cent. sulfuric acid and dried to incipient efflorescence in air. Prepared in this way we found that it could be kept for months without appreciable oxidation. The solutions were made up by weight from the above material, and their composition checked by analysis. Ferrous iron was determined in the usual manner by titration with potassium permanganate. Ferric iron was titrated in partially oxidized solutions containing 0.005 to 0.01 *N* Fe⁺⁺⁺ by iodimetry under carbon dioxide, using specially prepared reagents.⁵ The initial ferric-ion concentration of the "unoxidized" stock solution was calculated from this by applying Equation 3 (see below) to the corresponding potentials. This equation holds fairly accurately over this small range at such low concentrations. For subsequent runs it was only necessary to weigh out a sample of equal weight to make the same volume of solution and compare its initial potential with that of the calibration, as outlined above.

Computation of the Progress of the Oxidation from the Potentials.—We had hoped to be able to compute the progress of the oxidation directly from the observed change in potential ΔE , since

$$\Delta E = \frac{RT}{F} \ln \left[\frac{\gamma_2^{+++} \text{Fe}_2^{+++}}{\gamma_1^{+++} \text{Fe}_1^{+++}} \times \frac{\gamma_1^{++} \text{Fe}_1^{++}}{\gamma_2^{++} \text{Fe}_2^{++}} \right] \quad (1)$$

where γ^{++} and γ^{+++} represent the activity coefficients of the ferrous and ferric ions and the subscripts 1 and 2 refer to the initial and final concentrations, respectively. This equation becomes

$$\Delta E = \frac{RT}{F} \ln \left[\frac{(\text{Fe}_1^{+++} + \Delta C)}{\text{Fe}_1^{+++}} \times \frac{\text{Fe}_1^{++}}{(\text{Fe}_1^{++} - \Delta C)} \right] + \frac{RT}{F} \ln \left[\frac{\gamma_2^{+++} \gamma_1^{++}}{\gamma_1^{+++} \gamma_2^{++}} \right] \quad (2)$$

where ΔC represents the change in the concentration of the ferric ion corresponding to the change in potential ΔE .

From Equation 2 it is clear that to compute ΔC in this way for any value of Fe⁺⁺ and Fe⁺⁺⁺ we must know, in addition to ΔE , either the activity coefficients of the ferrous and ferric ions under the conditions of our experiments (which unfortunately we do not), or we must be able to consider the last term on the right of the equation as equal to zero. In this case Equation 2 can easily be rewritten as

$$\Delta C = \text{Fe}_1^{+++} \text{Fe}_1^{++} \left[\frac{e^{(F\Delta E/RT)} - 1}{\text{Fe}_1^{++} + \text{Fe}_1^{+++} e^{F\Delta E/RT}} \right] \quad (3)$$

which gives ΔC directly in terms of known or measured quantities.

We have conducted numerous experiments to test this latter alternative, measuring the changes of potential produced by the addition of known amounts of potassium permanganate to solutions of ferrous sulfate. Corrections were applied for the disturbing effects of the reaction

⁵ Morse and Burton, *Am. Chem. J.*, 10, 321 (1888).

products from the potassium permanganate which will be explained later in another connection. We found that the change in concentration of the ferric ion could be calculated accurately by means of the simplified Equation 3 only when the concentrations lay within certain narrow limits, namely, when the ferric ion was less than about 0.001 *M* and the sulfuric acid was between 1.0 *M* and 0.01 *M*. When the concentrations departed from these limits, the divergence of the observed potentials from the calculated values became considerable and in extreme cases the discrepancy was as much as 500%. This is shown by the typical results collected in Table I.

TABLE I
COMPARISON OF CALCULATED AND ACTUAL CONCENTRATIONS

Solution, m. mol.	ΔE obs. (corr.), mv.	ΔC		Solution m. mol.	ΔE obs. (corr.), mv.	ΔC	
		Calcd. from ΔE , m. mol.	Actual from KMnO ₄ , m. mol.			Calcd. from ΔE , m. mol.	Actual from KMnO ₄ , m. mol.
Fe ⁺⁺⁺ =0.405 Fe ₂ SO ₄ =183 H ₂ SO ₄ =11.0	33.0	1.03	0.98	Fe ⁺⁺⁺ =0.172 FeSO ₄ =150 H ₂ SO ₄ =3000	32.5	0.422	1.94
	46.0	1.94	1.95		46.7	.855	3.87
	54.8	2.87	2.93		54.1	1.18	5.80
	60.3	3.61	3.90		62.2	1.68	7.74
Fe ⁺⁺⁺ =3.98 FeSO ₄ =178 H ₂ SO ₄ =12.0	5.4	0.90	0.98	Fe ⁺⁺⁺ =5.35 FeSO ₄ =131 H ₂ SO ₄ =500	3.9	0.82	0.84
	10.1	1.83	1.95		4.5	.95	.98
	12.8	2.44	2.93		4.6	.98	1.00
	15.3	3.05	3.90		8.1	1.82	1.84

The explanation of these discrepancies probably is that at high concentrations of sulfuric acid or of ferric ions the activity coefficients are markedly different from unity; at low concentrations of sulfuric acid, on the other hand, the hydrolysis of the ferric salt becomes of importance. Whatever the explanation, it is clear that this direct method of computation cannot be used successfully.

Failing then an accurate method of calculating the amount of oxidation from the corresponding potential change, resort was taken to a purely empirical method of calibration. Blank experiments were run in the solutions whose rates of oxidation were to be measured, where a known amount of oxidation was secured by the addition of measured quantities of potassium permanganate. The observed potential changes thus obtained were then corrected for the dilution produced by the introduction of the permanganate solution and for the effect of the potassium and manganous ions. These correction terms were ascertained by adding to a control solution equal volumes of a solution of potassium and manganous sulfates to approximately the same concentration as that resulting from the reduction of the standard potassium permanganate. The resulting potential change is the desired correction term. This procedure affords a measure of the change in potential due solely to the introduction of oxygen.

The following data for a particular solution will serve as an illustration (Table II).

TABLE II
CALIBRATION DATA FOR FeSO_4 0.148 *M*; H_2SO_4 1.0 *M*
Initial $E_C = +0.3614$

KMnO_4 , 0.002528 <i>N</i> , cc.	ΔC equiv. concn. of oxygen per liter of original FeSO_4	ΔE observed, mv.	Correction term, mv.	ΔE corrected, mv.
9.85	0.000495	13.8	-1.5	15.3
19.70	.000991	22.9	-3.7	26.6
29.55	.001487	30.1	-8.5	38.6
39.40	.001982	36.3	-9.5	45.8

The corrected values of ΔE were plotted against the corresponding values of ΔC and the resulting curve served as a calibration curve (Fig. 2). In using it, the initial potential of the system being observed was compared with the initial potential of the calibration curve and the value of ΔC corresponding to this difference was subtracted from each subsequent value of ΔC read from the curve. In other words, the curve applied to each run was referred to the initial potential of that run as origin. An example follows, using the calibration data given above.

TABLE III
RUN No. 325

DATA			
Without aeration		With aeration	
t	E_C	t	E_C
3.45 P. M.	+0.3614	7.35 P. M.	+0.3712
		8.52	+ .3737
		9.39	+ .3756
		9.20 A. M.	+ .3896
		10.47	+ .3920

TABLE IV
CALCULATION

t , hrs.	ΔE ($E_C - 0.3614$) mv.	ΔC from curve m. mol.	ΔC (from initial t) m. mol.	2d order constant, $K_2 \times 10^6$
...	9.8	0.000320
1.28	12.3	.000405	0.000085	295
2.07	14.1	.000465	.000145	311
13.75	28.2	.001030	.000710	230
15.20	30.6	.001130	.000810	237

($\Delta C = 0.000810 \approx 0.22$ cc. O_2 at N. T. P.)

Av. = 268 ± 35

In order to facilitate comparison of the velocities under varying conditions, we have computed velocity constants from corresponding values of t and ΔC , both assuming a first- and a second-order reaction. In most

cases reasonably constant values (average deviation from the mean = $\pm 10\%$) were obtained on *both* assumptions. This result is readily understood when it is appreciated that in most of our experiments only about one per cent. of the ferrous salt present was oxidized, so that experimental and other variations would mask the relatively small differences in the trend of the constants calculated on the two different assumptions. In a later section experiments to ascertain more definitely the order of the reaction are described. Since our aim here was primarily to secure a means of comparison, we have, in general, used the constant for a second order reaction

$$K_2 = 1/t \frac{\Delta C}{\text{Fe}_{e^{++}}(\text{Fe}_{e^{++}} - \Delta C)}$$

as easier to compute arithmetically. Occasionally the velocity measurements have given constants with a drift or trend, sometimes in the one direction and sometimes in the other, for no assignable reason. Duplicate measurements have often eliminated this uncertainty, so that it has apparently been due to some accidental effect. Where such drifting constants have been obtained, the average value is relatively uncertain and we have indicated this by enclosing such values in parentheses.

The usual average deviation of the constants in any one run was, as stated above, $\pm 10\%$. The usual reproducibility of our results for a given solution is shown, for instance, by the average values of the constant (K_2) obtained in seven duplicate runs on the solution FeSO_4 0.169 *M*, H_2SO_4 0.50 *M*, as follows: 313, 338, 265, 263, 307, 261, 259 $\times 10^{-5}$; grand average $287 \times 10^{-5} \pm 9\%$.

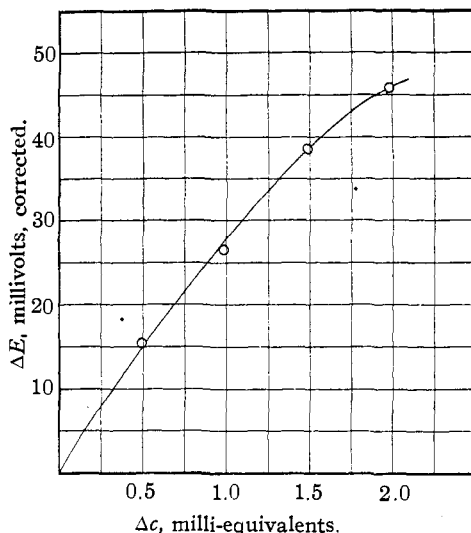


Fig. 2.—Calibration curve.

Experimental Results

Effect of Variations in the Rate of Stirring.—The normal rate of stirring, as pointed out above, was 1250 r. p. m. Although the "atomization" of the injected air was excellent, it was necessary to find out whether the observed rate of oxidation was limited by the rate of solution of the oxygen, or by the rate of reaction of the dissolved oxygen. To accomplish

this we have varied the rate of stirring under various conditions over relatively wide ranges. The results are shown in the following table (Table V) where the average values of the constants obtained in the various runs are recorded, computed on the assumption of a second-order reaction.

TABLE V
EFFECT OF RATE OF STIRRING ON VELOCITY OF REACTION

FeSO ₄ 0.15 M; H ₂ SO ₄ 1.0 M;			FeSO ₄ 0.15 M; H ₂ SO ₄ 0.5 M;			FeSO ₄ 0.15 M; H ₂ SO ₄ 1.0 M			
			1 g. of charcoal per 50 cc.			10 g. of charcoal per 50 cc.			
Expt.	$K_2 \times 10^5$			Expt.	$K_2 \times 10^5$		Expt.	$K_2 \times 10^5$	
	720 r. p. m.	1250 r. p. m.	1640 r. p. m.		1250 r. p. m.	1640 r. p. m.		1250 r. p. m.	1920 r. p. m.
1	290	253	349	1	81300	75000	1	305000	713000
2	271	289	268	2	65400	84100	2	311000	408000
3	...	295	267	3	79500
4	...	(309)	...	4	67500
5	...	(211)	...	5	66400
...	6	66900
Mean	280	279	295	Mean	71200	79500	Mean	308000	560000
K_2 at 1250 r. p. m. = 6.36 $\times 10^{-6}$ eq. of O ₂ per liter per hr.			K_2 at 1250 r. p. m. = 0.0115 eq. of O ₂ per liter per hr.			K_2 at 1250 r. p. m. = 0.0328 eq. of O ₂ per liter per hr.			

It is obvious from the above results that only those reactions which proceed at a rate greater than about 0.0115 equivalent of O₂ per liter per hour, corresponding to a second-order constant K_2 of about 0.7 (*i. e.*, 70,000 $\times 10^{-5}$), are affected appreciably by the rate of stirring at a rate of 1250 r. p. m.

Effect of the Variation of Concentration of the Oxygen.—The times required for 0.5% oxidation by means of air and pure (commercial) oxygen, in different portions of the same solution, are given in the following table (Table VI).

TABLE VI
EFFECT OF THE CONCENTRATION OF THE OXYGEN
Times to 0.5% oxidation: FeSO₄ 0.15 M; H₂SO₄ 0.50 M

Expt.	Air, hrs.	Oxygen, hrs.
1	14.5	3.10
2	14.4	2.50
3	10.3	..
4	11.2	..
5	13	..
	12.7 = 1.6	2.80 = 0.3

The ratio of the times is 1:4.54, or substantially what would be expected (1:5.0) on the assumption that the reaction is unimolecular with respect to the oxygen.

Effect of Variation in the Concentration of the Ferrous Sulfate.—As

pointed out above, the percentage oxidation of the ferrous sulfate in these experiments was relatively so inconsiderable that the constancy of any particular "velocity constant" based on a single initial concentration affords no certain evidence as to the order of the reaction with respect to the ferrous sulfate. To obtain more conclusive evidence on this point we have carried out two sets of comparative experiments where there were marked differences in the initial concentration of the ferrous sulfate, and have compared the times required to produce 1% oxidation. The data are presented in Table VII.

TABLE VII
EFFECT OF THE CONCENTRATION OF FERROUS SULFATE
Time in hours for 1% oxidation

Expt.	Set 1		Set 2	
	FeSO ₄ 0.169 M H ₂ SO ₄ 0.23 M	FeSO ₄ 1.36 M H ₂ SO ₄ 0.18 M	FeSO ₄ 0.170 M H ₂ SO ₄ 2.0 M	FeSO ₄ 1.24 M H ₂ SO ₄ 2.0 M
1	21.2	4.52	30.5	4.31
2	(16.7)	4.09	25.6	4.32
3	22.1
4	25.2
5	22.9
Mean	22.8 ± 1.2	4.31 ± 0.2	28.1 ± 2.6	4.32 ± 0.01

Ratio of total ferrous

concentrations.....1:8.0.....1:7.3

Ratio of velocities.....1:5.3.....1:6.5

One can see from the above results that the initial velocities are approximately proportional to total ferrous salt concentrations in the two pairs of comparable solutions. This indicates, since the oxygen concentration was kept constant throughout the runs, that the reaction is approximately bimolecular with respect to the ferrous salt. The deviations are about what one would expect if the velocity were directly proportional to the activity of the ferrous ion rather than to the total ferrous salt concentration, but the data are hardly accurate enough to justify any numerical calculation.

Effect of Variation in the Concentration of the Acid.—The data obtained bearing on this point are collected in Table VIII.

TABLE VIII
EFFECT OF VARIATION IN THE CONCENTRATION OF THE ACID

FeSO ₄ M	0.146	0.176	0.146	0.169	0.17	0.181	0.170	0.15
H ₂ SO ₄ M	0.008	0.012	0.055	0.23	0.50	1.0	2.0	3.0
Expt.	$K_2 \times 10^3$							
1	(1280)	528	453	289	338	253	(213)	294
2	(1250)	580	377	357	265	289	(245)	234
3	281	263	295
4	236	307
5	269	261
Mean	(1265)	554	415	286	287	279	(229)	264

These mean values of K_2 are also plotted in Fig. 3. It is evident that change of acid concentration between the limits of 3.0 M and 0.23 M produces scarcely any change in reaction velocity; indeed, the change is scarcely beyond the limits of error. A decrease in acid concentration below 0.23 M , however, increases the velocity, the rate of increase rising rapidly as the acid becomes more dilute. This relation is in accord with the fact that acid solutions of ferrous sulfate are relatively stable in air, whereas ferrous hydroxide absorbs oxygen from air with great rapidity.

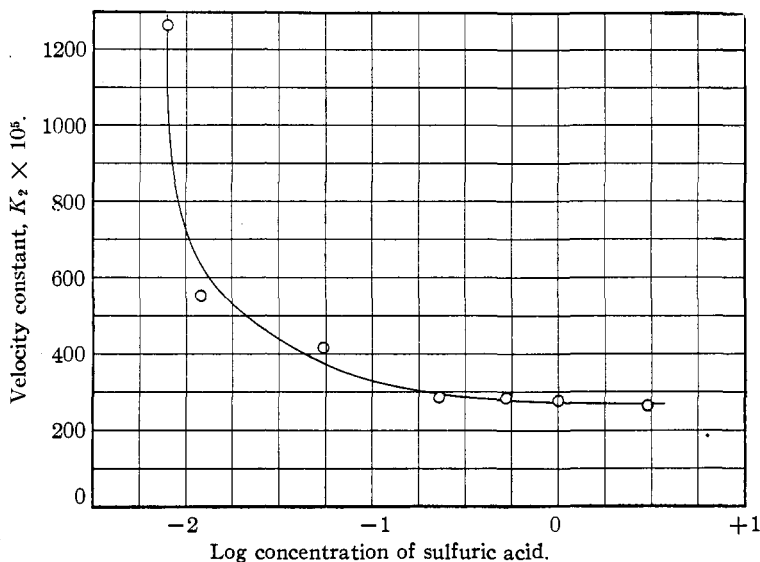


Fig. 3.—Variation of the velocity with the concentration of the sulfuric acid. FeSO_4 , 0.15–0.18 M .

Effect of Neutral Salts.—Sufficient of each of a variety of salts was added to portions of a stock solution to be 0.1 M . The velocity constants obtained are collected in Table IX.

TABLE IX

EFFECT OF SALTS
 FeSO_4 0.15 M ; H_2SO_4 0.52 M

Salt Expt.	Na_2SO_4	K_2SO_4^a	MgSO_4^a	ZnSO_4	MnSO_4	$\text{Cr}_2(\text{SO}_4)_3$	NaAc	Na_2PO_4	NiSO_4^a	None
					$K_2 \times 10^5$					
1	300	240	357	239	301	192	266	290	340	
2	263	221	290	423	213	195	295	286	381	
3	372	291	283	
Mean	312	251	323	331	257	194	281	288	360	287

^a These solutions contained 0.23 M H_2SO_4 .

Similar experiments were made with Ag_2SO_4 0.1 M and Hg_2SO_4 0.001 M , and except for the fact that they were in whole or in part reduced by

the ferrous sulfate, the results were substantially identical with those obtained with the solutions already cited.

It follows from the data that these salts are practically without effect on the velocity of oxidation of the ferrous sulfate by the gaseous oxygen.⁶

The Effect of Copper Sulfate.—It has long been known that copper salts accelerate the oxidation of ferrous salt solutions by oxidizing agents⁷ and by gaseous oxygen.⁸ The results of our measurements are given in Table X.

TABLE X
EFFECT OF COPPER SULFATE

	0.15	0.170	0.171	0.16	0.169	0.161	0.176
FeSO ₄ M	0.15	0.170	0.171	0.16	0.169	0.161	0.176
H ₂ SO ₄ M	3.0	2.0	1.0	.52	.23	.055	.012
CuSO ₄ M	0.1	0.1	0.1	.1	.1	.1	.1
Expt.	$K_2 \times 10^3$						
1	38700	(18860)	20242	13265	(8810)	(5087)	(2630)
2	43900	(19500)	22902	12024	10873	(5897)	(2748)
3	43200	...	(23440)	...	(9820)
4	67266
Mean	48300	(19200)	21600	12644	9800	(5500)	(2700)
FeSO ₄ M	0.146	0.169	0.169	0.169	0.161	0.176	0.146
H ₂ SO ₄ M	.008	.23	.23	.23	.055	.012	.008
CuSO ₄ M	.1	.05	.01	.001	.001	.001	.001
Expt.	$K_2 \times 10^3$						
1	2580	9109	(7134)	1960	2336	684	2860
2	2430	8213	6440	1701	(2175)	955	(2600)
3	(2360)	(1253)	...
Mean	2500	8700	6500	1830	2300	960	2730

The mean values in 0.23 M acid with varying concentrations of copper sulfate are plotted in Fig. 4; those obtained with 0.1 copper sulfate in varying concentrations of acid are plotted in Fig. 5.

These results show that copper sulfate has a pronounced effect on the oxidation of the ferrous salt solutions, and that, in sharp contrast with solutions containing no copper sulfate, the rate of oxidation increases rapidly with increasing acid concentration. It also appears that in 0.23 M sulfuric acid the accelerating effect of the copper sulfate increases markedly with its concentration, following quite accurately a logarithmic relationship. In lower concentrations of acid the increase with concentration is less marked, and at the lowest concentration there appears to be no well-defined change with the concentration.

Potassium Ferrocyanide Solutions.—It was of interest to measure the rate of oxidation of potassium ferrocyanide by gaseous oxygen be-

⁶ Chromic sulfate showed a slight depressing effect.

⁷ Hess, Supplee and Bellis, *J. Biol. Chem.*, **57**, 725 (1923); Quartaroli, *Gazz. chim. ital.*, **55**, 252 (1925).

⁸ Warynski, *Ann. chim. anal.*, **14**, 45 (1909); Boselli, *Compt. rend.*, **152**, 602 (1911); Meyerhof, "Chemical Dynamics of Life Phenomena," J. B. Lippincott Co., Philadelphia, 1924, p. 39; Reinders and Vles, *Rec. trav. chim.*, **44**, 29 (1925).

cause, in contrast to the simple ferrous salts, it can be studied in neutral solution.

Potassium ferrocyanide can be titrated against permanganate in very dilute solution, when acidified, by the method of de Haën.⁹ Solutions more concentrated than about 0.05 *M*, and especially solutions free from acid, deposit a precipitate of potassium manganese ferrocyanide.

We have, therefore, tried iodine for this titration. A 0.10013 *M* solution of freshly recrystallized and air-dried $K_4Fe(CN)_6 \cdot 3H_2O$ was prepared, and portions of it were shaken with an excess of a 0.0766 *N* solution of iodine under carbon dioxide. After fifteen minutes the excess

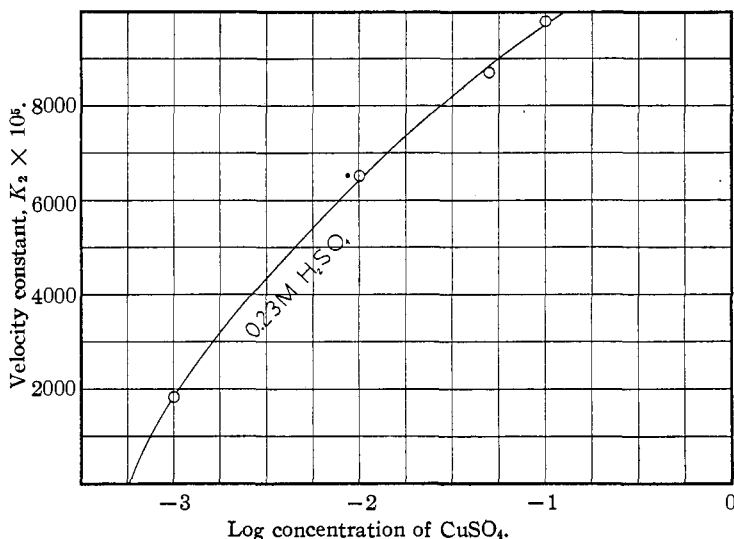


Fig. 4.—Variation of the velocity with the concentration of copper sulfate. $FeSO_4$, 0.15–0.18 *M*.

iodine was titrated back with a 0.0985 *N* solution of thiosulfate. Two analyses of the stock solution by this method gave its normality as 0.09982 *M* and 0.10002 *M*, or on the average 0.09992, agreeing with the calculated value of 0.10013 to within two-tenths of one per cent.

A calibration of the potential was carried out against known mixtures of ferro- and ferricyanide, using potassium iodide 0.5 *M* as a blank solution, by the method as outlined under the similar calibration of the ferrous-ferric potential. The results are given in Table XI.

Two oxygen absorption experiments were now run with a neutral solution of 0.150 *M* ferrocyanide, and identical values of $K_2 = 111 \times 10^{-5}$ were obtained. This shows that in neutral solution the ferrocyanide

⁹ De Haën, *Ann. Chem. Pharm.*, 90, 160; also Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1919, Vol. II, 5th ed., p. 632.

TABLE XI

FERRO-FERRICYANIDE POTENTIAL IN $K_4Fe(CN)_6$ 0.150 M			
ΔC as I_2	ΔE obs., mv.	$\Delta E'$ blank, mv.	ΔE corr., mv.
0.00742	114.4	10.7	103.7
.01484	131.6	12.3	119.3
.02968	151.4	14.1	137.3
.03940	152.9	13.7	139.2

is oxidized about one-half as fast as is ferrous sulfate in solutions from 3 M to 0.01 M in sulfuric acid.

Two similar experiments were then made with portions of this same stock solution to which copper sulfate 0.001 M had been added. Values

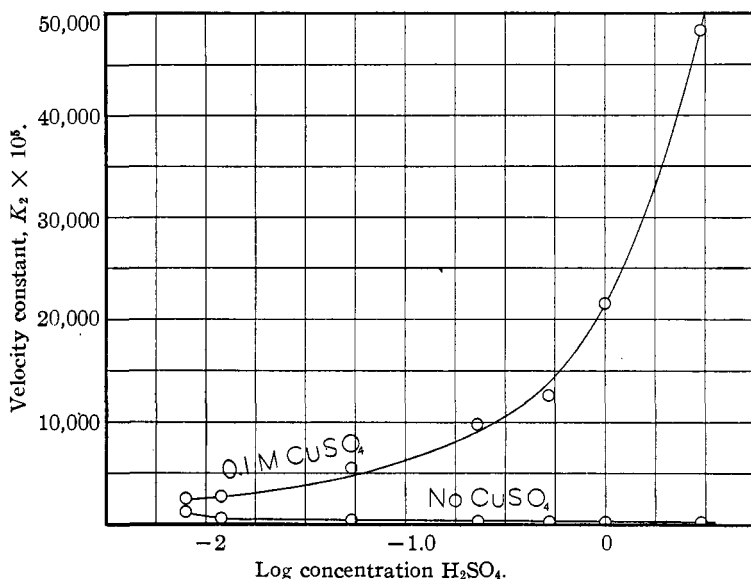


Fig. 5.—Effect of copper sulfate at various concentrations of sulfuric acid.

of $K_2 = 121$ and 151×10^{-5} , averaging 136×10^{-5} were obtained. It is evident that the copper sulfate produces no significant change in the velocity. This may be due to the fact that a precipitate of copper ferro- and ferricyanide is formed in the solution to which it is added, so that the copper ion may be present only in very minute amounts. It is of interest that the velocity of oxidation of the neutral ferrocyanide solution is substantially equal to that of the acid solutions of the ferrous sulfate. Either the ferrocyanide ion is directly oxidized by the gaseous oxygen, or the rapidity of oxidation of the ferrous ion in the neutral solution, in spite of its infinitesimal concentration, is tremendously greater than in the acid solution of the simple ferrous salts.

Solutions Containing Pyrophosphates.—Solutions of ferrous sulfate

containing sodium pyrophosphate were found by Spoehr¹⁰ to absorb oxygen rapidly, the originally green solution becoming deep red. Later Smith and Spoehr¹¹ measured the rate of the oxidation in order to ascertain the order of the reaction. These measurements were made by shaking 150 cc. of the solution with oxygen at constant pressure in a mechanically operated shaker making 120 strokes per minute. They found that the half-period of the reaction averaged about 57.5 seconds, irrespective of the concentration of the reactants. They concluded from this that the reaction was of the first order.

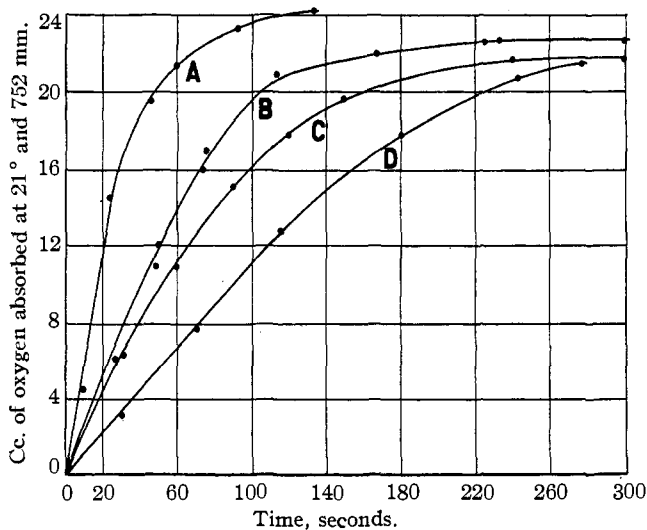


Fig. 6.—Velocity of oxidation of solutions containing pyrophosphate at different rates of stirring. A—170 r. p. m.; B—130 r. p. m.; C—120 r. p. m. (Smith and Spoehr); D—90 r. p. m.

We have repeated the measurements of Smith and Spoehr, adhering as closely as possible to the exact dimensions of their apparatus and to all the details of their procedure. With 150 cc. of a solution containing one gram of ferrous sulfate and 4.82 g. of sodium pyrophosphate, identical with that employed by them, and shaken at a rate of 130 strokes per minute, a half-period of about fifty seconds was obtained, confirming the numerical results of Smith and Spoehr as closely as could be expected.

However, we then repeated this experiment *at other rates of stirring*. Our results, together with the corresponding ones of Smith and Spoehr, are shown in Fig. 6.

It can be seen from these results that the velocity is largely a matter of the rate of stirring. Indeed, the half-period plotted against the rate of

¹⁰ Spoehr, *THIS JOURNAL*, **46**, 1499 (1924).

¹¹ Smith and Spoehr, *ibid.*, **48**, 107 (1926).

stirring gives a nearly linear curve. What is being measured is, therefore, not the rate of the chemical reaction itself, but a *rate of diffusion*. It is well known that this, in general, follows a logarithmic course and, therefore, simulates a first order reaction. The conclusion of Smith and Spoehr as to the order of the chemical reaction, based on these measurements, is, we believe, unwarranted.

In order to compare their results in ferro-pyrophosphate solution with our results in solutions of other iron salts, we have measured the rate of oxidation in this solution by our usual electrometric method. The potential change was calibrated in terms of oxygen by fitting to the apparatus of Smith and Spoehr an electrode, a salt bridge and a calomel electrode. The solutions were mixed under purified nitrogen, and the potentials observed before and after successive additions of pure oxygen, measured under known conditions of temperature and pressure in the calibrated buret included in the apparatus. A leveling bulb was attached to the buret for pumping and measuring the gas at atmospheric pressure. The oxygen introduced was not always completely absorbed, but the volume of gas absorbed was measured after ten minutes' shaking, after which no appreciable change in volume was observed. Under these conditions the potential measured before and after the volume measurement was the same to within ± 0.2 millivolt. The results obtained, compared with those on a corresponding solution of ferrous sulfate and a similar solution of ferrous sulfate containing charcoal (to be described later), are shown in Table XII.

TABLE XII

	COMPARISON OF RESULTS		
	FeSO ₄ 0.15 M Na ₂ P ₂ O ₇ .023 M	FeSO ₄ 0.15 M H ₂ SO ₄ 1.0 M	FeSO ₄ 0.18 M H ₂ SO ₄ 1.0 M Charcoal 10 g.
E_C , v.....	-0.114	+0.361	+0.500
$K_2 \times 10^5$	322000	279	318000
Eq. O ₂ /1 hr....	0.049	0.000053	0.038

It can be seen that the velocity of oxidation is indeed high, about 1000 times greater than in the ferrous sulfate solution. However, the potential is so very much lower that the solution is of little interest to us in the present investigation; indeed, it is scarcely more practical than such systems as the vanadate-vanadic, etc., previously referred to.

Heterogeneous Systems

The Effect of Coconut Charcoal.—A sample of granular, commercial, steam-activated coconut charcoal of the variety used in gas masks was ground in a mill and screened. Two lots were prepared, one of fineness between 60 and 100 mesh, and one finer than 100 mesh. Introduction of 1 g. of the 60–100 mesh material into 50 cc. of a 0.150 M FeSO₄–0.50 M

H₂SO₄ solution gave in duplicate experiments velocity constants ($\times 10^5$) of 81,300 and 65,400, respectively. This is an increase of about 200 times, as compared with the velocity in the solution in the absence of the charcoal.

A series of experiments in duplicate was then made, using this same electrolyte, to find out the variation of the velocity with the amount of the charcoal. The average values of the velocity constant are given in Table XIII and are plotted in Fig. 7.

TABLE XIII
VARIATION OF THE VELOCITY WITH THE AMOUNT OF CHARCOAL
Solution: 0.150 M FeSO₄; 0.50 M H₂SO₄

Charcoal, g.	0.05	0.10	0.20	0.50	0.90	1.0	1.1	10.0
	$K_2 \times 10^5$							
Expt. 1.....	(9380)	(18000)	26600	62400	79000	81300	88000	319000
Expt. 2.....	(5230)	(14600)	24500	50800	58600	65400	79400	173000
Mean.....	(7305)	(16300)	25500	56600	68800	71200 ^a	83700	246000
Mean $K_2 \times 10^5$ /wt.	(146100)	(163000)	127500	113200	76444	73300	76100	246000

^a Average of six experiments whose average deviation was ≈ 6000 .

These results show that the accelerating effect of the charcoal is approximately proportional to its amount. The slight decrease with amounts

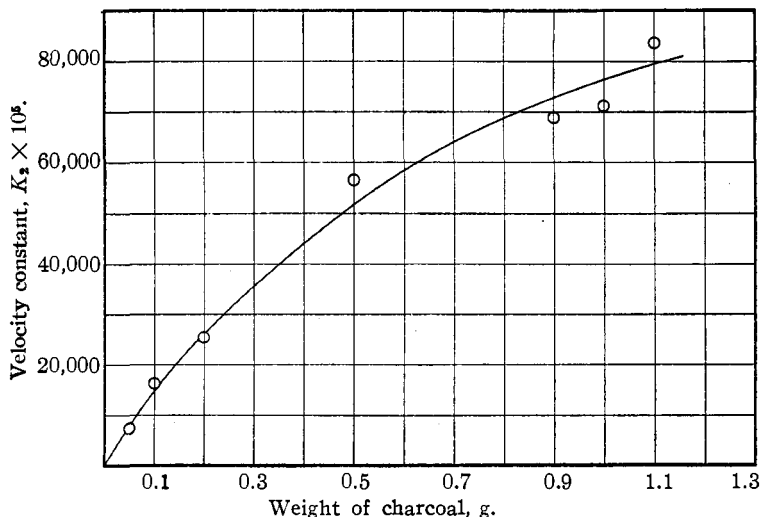


Fig. 7.—Variation of the velocity with the weight of the charcoal.

up to 1 g. and the considerable decrease with 10 g. may well be due to the less efficient stirring under these conditions.

Two series of experiments were then made to find out the variation, if any, of this effect with the acidity of the ferrous sulfate solution. In one series 1 g. and in the other 10 g. of charcoal were used. The results are collected in Table XIV, and are plotted in Fig. 8.

TABLE XIV
 VARIATION OF THE EFFECT OF THE CHARCOAL WITH THE ACIDITY
 Solution: 0.150 M FeSO₄

Charcoal	Concn. H ₂ SO ₄	$K_2 \times 10^5$			
		0.05	0.50	1.00	3.0
1 g. per 50 cc.	Series No. 1	(26600)	81300	45900
	Series No. 2	(27800)	65400	37600
	Mean	(27200)	73300	41800
10 g. per 50 cc.		$K_2 \times 10^5$			
	Series No. 3	21000	(319000)	305000	167000
	Series No. 4	20900	(173000)	311000	149000
	Mean	20900	(246000)	308000	158000

It can be seen that with a constant amount of charcoal the velocity varies considerably with change in the concentration of the acid, a maximum velocity being reached in each case at 0.50 to 1.0 M acid.

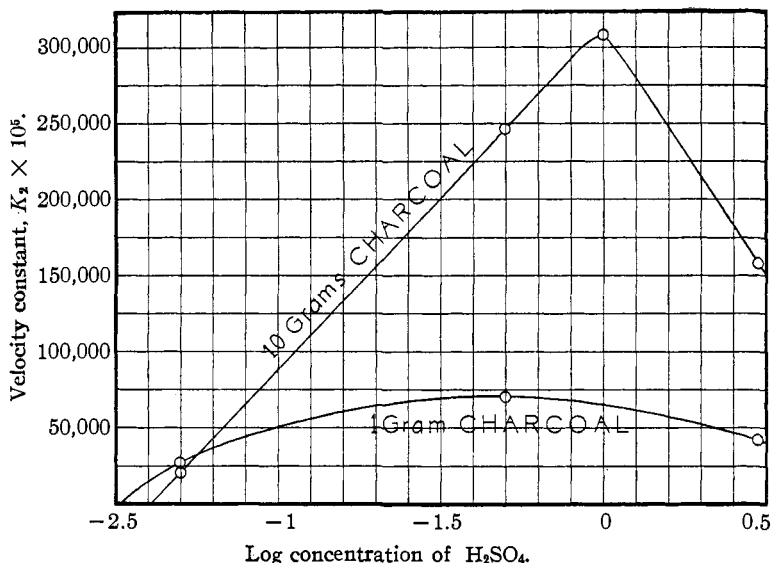


Fig. 8.—Variation of the velocity in the presence of charcoal with the concentration of the sulfuric acid. FeSO₄, 0.15 M.

Experiments were also made on the effect of charcoal on the rate of oxidation of solutions containing copper sulfate. The results of these experiments and of the corresponding blank experiments are collected in Table XV.

These results show that the velocities of oxidation with and without the copper sulfate are substantially the same, indicating that the action of the copper sulfate in the presence of the charcoal is either suppressed, or at most is only arithmetically additive.

To ascertain whether these data were significantly affected by the

TABLE XV
SIMULTANEOUS EFFECT OF CHARCOAL AND COPPER SULFATE
Solution: 0.150 *M* FeSO₄; 0.50 *M* H₂SO₄

Catalysts added	{ 263 307	0.10 <i>M</i> CuSO ₄ ... 13300 12000 1 g. charcoal 79500 67500	0.10 <i>M</i> CuSO ₄ 1 g. charcoal (77000) (66000)
$K_2 \times 10^5$				
$K_2 \times 10^5$ (Mean)	285	12600	73500	(72000)

alkaline ash of the charcoal (or by a possible preferential adsorption of sulfuric acid) 1-g. samples of charcoal of different degrees of fineness were each shaken with 50 cc. of 0.5 *M* sulfuric acid, filtered off by suction and the concentration of the filtrates determined by titration. It was found that the concentration had changed by about 2%, corresponding to a removal of about 0.0005 mole of sulfuric acid from the solutions by the charcoal. No significant variation of this percentage was observed with the different mesh sizes of the charcoal. This change in concentration is too small to have been of any significance in the above measurements.

Similar experiments were made with a solution 0.5 *M* in sulfuric acid and 0.01 *M* in copper sulfate. Here again about 2% of the acid was removed and about 1% of the copper sulfate. This latter result indicates that the apparent inactivity of the copper sulfate in the solution with charcoal could not have been due to its removal from solution by adsorption.

The Effect of Platinum Black.—Two grams of scrap platinum was converted into platinum black by the method of Willstätter and Jaquet¹² and this was dried overnight over sulfuric acid in a vacuum desiccator. Suspensions of 0.5 g. of this material in 50 cc. of a 0.15 *M* FeSO₄–0.5 *M* H₂SO₄ solution were subjected to oxidation with air, and velocity constants of (341,000) and (347,000), averaging (344,000) $\times 10^{-5}$ were obtained. Suspensions of only 0.25 g. of this material in the same volumes of the same solution gave a velocity constant of only 75,800 $\times 10^{-5}$. This more than proportional decrease in the velocity with the smaller amount of catalyst suggested a possible progressive poisoning of the catalyst.

To test this, the platinum black catalysts were removed from the solution, thoroughly washed, then replaced in the cells with fresh 50-cc. portions of the original solution, and the velocity of oxidation of each suspension was again measured. The 0.5-g. sample gave a constant of (19,900); the 0.25-g. sample in two experiments gave constants of (17,400) and (17,600), averaging (17,500) $\times 10^{-5}$. These low values show that the catalyst had indeed become much less active with use.

The Effect of Silica Gel.—A sample of a commercial silica gel was powdered to pass a 60-mesh (per inch) screen. A suspension of one gram of this material in 50 cc. of a 0.15 *M* FeSO₄–0.5 *M* H₂SO₄ solution gave an oxidation velocity constant of 865, corresponding to about a three-

¹² Willstätter and Jaquet, *Ber.*, 51, 767 (1918).

fold increase as compared with the velocity constant given by the same solution without the silica gel. This increase, while a decided one, is scarcely one one-hundredth of that produced by charcoal in this same solution, and is only one three-hundredth of that produced by half as much platinum black.

Discussion of the Kinetic Results

The unimolecular behavior of the gaseous oxygen in the oxidation of these solutions of ferrous salts agrees with the observations of McBain¹³ made with solutions of ferrous sulfate and with those of Just¹⁴ made in his study of the autoxidation of solutions of ferrous bicarbonate. Similarly, the bimolecular behavior of the ferrous sulfate agrees with the observations of McBain,¹³ Ennos¹⁵ and Boselli,¹⁶ made with the same substance but not with those of Just made with ferrous bicarbonate. On the other hand, the relatively slight retarding effect of acid on the velocity of oxidation in the absence of catalysts (a decrease of only four times in passing from 0.008 to 0.23 *M* acid) is not compatible with McBain's hypothesis that the rate of oxidation of the solution is primarily determined by the rate of oxidation of the relatively minute hydrolyzed portion of the ferrous sulfate.¹⁷ Even less compatible with this hypothesis are our measurements showing that in the presence of catalysts (copper sulfate or charcoal) the velocity of oxidation *increases* with increasing concentration of acid.

Our finding of the outstanding activity of copper sulfate in accelerating the oxidation of ferrous sulfate solutions by gaseous oxygen confirms the observations of Boselli¹⁶ upon this substance, as contrasted with those of Banerjee,¹⁸ and is in agreement with the work of Meyerhof,¹⁹ Reinders and Vles²⁰ and others on the autoxidation of numerous other substances.

The outstanding fact established by our experiments is that the very substances, namely, charcoal, platinum and cupric salts, which hasten markedly the decomposition of hydrogen peroxide, particularly in the presence of ferrous salt solution,²¹ also greatly accelerate the oxidation of ferrous salt solutions by gaseous oxygen. This parallelism at once suggests that the two phenomena may be intimately related.

¹³ McBain, *J. Phys. Chem.*, **5**, 623 (1901).

¹⁴ Just, *Z. physik. Chem.*, **63**, 385 (1908); *Ber.*, **40**, 3695 (1907).

¹⁵ Ennos, *Proc. Cambridge Phil. Soc.*, **17**, 182 (1913).

¹⁶ Boselli, *Compt. rend.*, **152**, 602 (1911).

¹⁷ For the degree of hydrolysis of ferrous sulfate, see A. Krause, *Z. anorg. Chem.*, **174**, 148 (1928).

¹⁸ Banerjee, *ibid.*, **128**, 343 (1923).

¹⁹ Meyerhof, *Arch. ges. Physiol. (Pflügers)*, **200**, 1 (1923).

²⁰ Reinders and Vles, *Rec. trav. chim.*, **44**, 1 (1925).

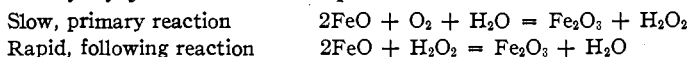
²¹ See Lemoine, *Compt. rend.*, **162**, 657, 702 and 725 (1916); Bohanson and Robertson, *THIS JOURNAL*, **45**, 2493, 2512 (1923); Warburg, *Biochem. Z.*, **113**, 257 (1921); **119**, 134 (1921).

An alluring hypothesis to explain this parallelism would be as follows. Hydrogen peroxide might conceivably be formed slowly from oxygen and water. Once formed it would react relatively rapidly with the ferrous salt. The slowness of the oxidation of the ferrous salt solutions would then be due to the slow rate of formation of the hydrogen peroxide. Catalysts which accelerate the oxidation of the solutions would then do this by virtue of the acceleration of the formation of hydrogen peroxide. But, by the fundamental principles of catalysis, the very catalysts which hasten this formation of hydrogen peroxide from oxygen and water will correspondingly hasten the decomposition of hydrogen peroxide into these substances. On this hypothesis, then, the above-mentioned parallelism would be expected.

A difficulty with this attractive hypothesis is that from energetic considerations it appears that even the maximum possible partial pressure, that is, the equilibrium partial pressure, of hydrogen peroxide in a 1:1 gaseous mixture of oxygen and water vapor at room temperature is only of the order of 10^{-22} atmospheres.²² The equilibrium concentration of hydrogen peroxide in a saturated aqueous solution of oxygen at room temperature would be correspondingly infinitesimal²³ and, therefore, apparently quite inadequate to bring about the relatively rapid oxidation of ferrous salt solutions by gaseous oxygen which does, indeed, take place when catalysts are present.

There are still other objections to this explanation. Goard and Rideal²⁴ found that copper salts do not catalyze the oxidation of ferrous salts by hydrogen peroxide in *acid* solutions. Again, while Bohnsen and Robertson did find a marked accelerating effect of copper salts on the decomposition of hydrogen peroxide, a maximum effect was observed at very low concentrations of copper salt, while in our experiments the catalytic effect increased progressively with the concentration of the copper salt.

Another mechanism involving hydrogen peroxide which has been proposed recently by Jander²⁵ can be represented as follows



This mechanism obviates the thermodynamic difficulties of the former explanation. However, the activity of copper salts in catalyzing this reaction, in view of the above-mentioned observation of Goard and Rideal, would appear to exclude it.

²² Computed from the free energy data for this reaction given by Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1923, p. 496. See also Lewis and Randall, *THIS JOURNAL*, 26, 1916 (1914).

²³ This same conclusion follows from computations by Baur based on data of Nernst, given in Abegg, "Handbuch," Leipzig, 1908, Vol. II, 1, p. 99.

²⁴ Goard and Rideal, *Proc. Roy. Soc. (London)*, 105A, 163 (1924).

²⁵ Abegg's "Handbuch" Leipzig, 1930, Vol. IV, 3d. Section, 2d part, pp. B13-14.

It appears, therefore, to be unlikely that these explanations, in spite of their simplicity, can be correct. Apparently, hydrogen peroxide is not the effective actor in all of these oxidations. Instead, it is probable that specific intermediate compounds, presumably peroxides of the several catalysts themselves, are primarily formed, which either oxidize directly the ferrous salt more rapidly, or accomplish this same result by hastening the formation or decomposition of a peroxide of iron which many authors consider to be involved in the oxidation of ferrous salts.

Peroxide in the Charcoal.—In view of this likelihood that a specific peroxide is involved in the case of each catalyst, we tested for a peroxide in or on the charcoal. For this purpose we stirred a suspension of 2 g. of the previously mentioned 100 mesh charcoal in 100 cc. of distilled water for five minutes with a current of air. This charcoal was then filtered off and successive small portions were shaken with pure water, or with solutions of sulfuric acid of various concentrations. The charcoal was again filtered off and the filtrates added to separate portions of acidified starch-iodide solution. No color developed in the filtrates from the suspensions in water, but a deep and nearly constant color, indicating the presence of a peroxide, appeared in a few seconds with the filtrates from the suspensions in 0.5, 1.0 and 1.5 molar sulfuric acid. The color was considerably less intense with the filtrate from the suspensions in 2.0 *M* acid, so that there was an evident maximum of color development at about 1.0 *M* acid.

These observations indicate that a peroxide is present in this charcoal, which is either insoluble or inactive in pure water, and has its maximum solubility or activity in solutions of sulfuric acid at an acid concentration of about 1 *M*. The location of this maximum activity is in striking agreement with that of the maximum velocity of oxidation observed in our kinetic measurements, using this charcoal as a catalyst in solutions of sulfuric acid of various concentrations.

A rough titration indicated that 1 g. of the 100 mesh charcoal in 50 cc. of water produces in dilute sulfuric acid about 0.0001 equivalent of active oxygen.

Further tests using 0.1 *M* sulfuric acid showed (1) that a positive test for a peroxide is obtained when fresh, dry charcoal without any deliberate aeration is acidified under an atmosphere of carbon dioxide (in the absence of air); (2) that charcoal once extracted with acid gives no further test for peroxide when shaken with fresh acid in an atmosphere of carbon dioxide; (3) that the same sample of charcoal once extracted with acid can again be made to give an equally positive test for peroxide by shaking the residual charcoal with more water and air, and repeating the extraction with acid; (4) that this successive aeration and extraction by acid can be repeated at least twice, and usually several times, with the

same sample of charcoal; (5) that no difference in behavior is observed if the suspension of charcoal is aerated first and then acidified immediately before filtration, or if it is first acidified and then aerated.

These observations indicate that this charcoal acquired a charge of the peroxide in the process of manufacture; that this can be removed by shaking with dilute sulfuric acid; that a fresh charge can be rapidly added by exposure to air; that this process can be repeated at least twice and that the re-oxidation will take place equally well in neutral or acid solutions.²⁶

All of these conclusions and, in particular, the parallelism in acid solutions of various concentrations between the activity of the charcoal as a catalyst and its activity in liberating indirectly iodine from starch-iodide solutions harmonize with our above conclusions drawn from the kinetic measurements.

Narcotics.—To obtain further information as to the presence of a peroxide in the charcoal, we have made tests similar to those of Warburg²⁷ on the oxidation of cystine by charcoal and air. He found that minute amounts of certain substances markedly retarded on this oxidation. We have tested the effect of two of his substances, phenyl urea and amyl alcohol, and in addition acetanilide, on the oxidation of ferrous sulfate solutions by charcoal and air.

The phenyl urea was made from aniline hydrochloride and potassium cyanate;²⁸ the other two were commercial preparations and were used without further purification.

The kinetic results obtained, both in uncatalyzed and catalyzed systems, are shown in the following table (Table XVI).

It can be seen from these results that, while no effect is produced on the uncatalyzed reaction, a marked depression of the velocity results when even small amounts of these "narcotics" are added to the catalyzed reaction mixtures. A plausible explanation of these results is that the "narcotics" combine with or, in any case, render less active relatively minute active ingredients or products, presumably peroxides of the catalysts.

Direct Measurement of the Efficiency of Depolarization.—The above

²⁶ De Saussure [*Thomson's Ann. Phil.*, **6**, 243 (1815)] and particularly Stenhouse [*Pharmaceutical Journal*, **13**, 454-457 and **14**, 328-330 (1854)] recognized the enhanced oxidizing power of oxygen adsorbed on charcoal. Calvert [*J. Chem. Soc.*, **20**, 293 (1867)] showed that oxygen adsorbed on charcoal oxidizes ethyl alcohol to acetic acid, and ethylene to carbon dioxide and water. Degener and Lach [*Dinglers polytech. J.*, **256**, 519 (1885)] observed that freshly calcined animal charcoal, if thoroughly moistened and then exposed to the air and light, formed hydrogen peroxide and ozone. Hulett and Lowry [*THIS JOURNAL*, **42**, 1408 (1920)] found that a slow reaction takes place at room temperature between coconut charcoal and oxygen, with the formation of a non-volatile oxide.

²⁷ Warburg, *Biochem. Z.*, **113**, 257 (1921); **119**, 134 (1921); *Naturwissenschaften* **112**, 862 (1923).

²⁸ Weith, *Ber.*, **9**, 820 (1876).

TABLE XVI
EFFECT OF NARCOTICS
FeSO₄ 0.150 M; H₂SO₄ 0.5 M

Narcotic	Uncatalyzed			Catalyzed			Catalyzed		
	Blank	$K_2 \times 10^5$ Nar- cotized	Relative narcosis	Blank	CuSO ₄ 0.1 M Narcotized	Relative narcosis	Blank	1 g. Charcoal Narcotized	Relative narcosis
Phenyl urea satd. 0.02 M	287	12644	1857	0.147	71200	19900	0.280
Amyl alcohol 0.10 M	287	12644	2626	0.208	71200	16680	0.234
Acetanilide 0.04 M	287	303	1.05	12644	1426	0.113	71200	18925	0.268

kinetic measurements permit us, as we have seen, to evaluate the activity of the various catalysts studied in accelerating the oxidation of the ferrous sulfate solution. The greater the activity of the catalyst in this respect, the greater should be the activity of the system as a depolarizer. We have measured the efficiency of depolarization of certain of these systems directly by bubbling oxygen through them, surrounding an electrode through which a current was passed in such a direction as would tend to evolve hydrogen upon it. The single potential of this electrode when the oxygen is absorbed at a constant rate, that is, when a steady current is maintained, compared with the single potential of this electrode immersed in the same solution when no current is passing, is a measure of the efficiency of the particular system.

The apparatus used for these measurements is shown diagrammatically in Fig. 9. A hollow stirrer from the previously described apparatus (Fig. 1)

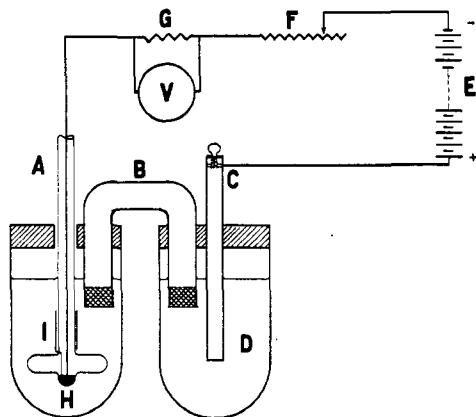


Fig. 9.—Apparatus for measuring the efficiency of depolarization.

was provided with a sealed-in electrode (I) of polished platinum foil, connected by means of a mercury cup (H) at the bottom of the stirrer (A) with a copper wire leading through the hollow shaft of the stirrer to the battery (E). This arrangement provides a compact rotating air electrode on which concentration polarization is reduced to a minimum. The other pole, selected for its relatively slight tendency to polarize, consisted of a zinc bar (C) immersed in a saturated zinc sulfate solution (D) in a similar half-cell. The internal circuit between the two half-cells was completed by means of a saturated potassium chloride salt-bridge (B)

in a pyrex glass tube of 8-mm. bore, plugged at each end with cotton wool. The external circuit, containing a 40-volt battery (E), a variable resistance (F) for current control and a milliammeter (G-V), is shown in the diagram. The external e. m. f. is imposed in such a way as to make the platinum electrode negative, *i. e.*, to impress reducing conditions upon the air electrode. The relatively high potential of the battery was necessary to overcome particularly the resistance of the bridge. The milliammeter circuit contained a Weston millivoltmeter with a calibrated shunt resistance. The left-hand cell contained in addition a movable platinum electrode which could be immersed in the solution in order to determine its composition with respect to oxidizing and reducing ions. The single electrode potentials of this extra electrode and of the working (rotating) electrode were measured through a separate salt-bridge against the saturated calomel reference electrode in the usual way.

Our procedure was as follows. The solution of iron salt containing the catalyst was introduced into the left-hand cell and the air supply turned on. After a few preliminary readings on open circuit, the circuit was closed and the rheostat adjusted so that from 60 to 100 milliamperes flowed through the cell with the stirrer operating at 1250 r. p. m. Readings were then taken at intervals of the potential of the working electrode and that of the extra electrode. The difference between the two gives directly the polarization potential. Readings were continued until the potentials became constant or until it was evident that the potentials were not going to become constant.

Using this apparatus and procedure the efficiency of depolarization by gaseous oxygen was measured in the solution which had been found to exhibit the highest velocity of oxidation by gaseous oxygen. In making these measurements the circuit through the apparatus was closed at a predetermined instant and the current of air was then started. The observed values of the polarizing current and the potentials of the working and of the accessory electrodes are given in Table XVII.

It can be seen from these data that the initial closing of the circuit before the air supply and stirring had been started lowered considerably the potential of the working electrode. This potential rose slowly as the air supply was continued, reaching a nearly steady state at a potential of $E_h = +0.250 + 0.253 = 0.503$. When the current was now cut off and the air supply continued, the potential rose rapidly to that of the accessory electrode, $E_h = +0.410 + 0.253 = 0.663$. When the same current drain was again started after this preliminary aeration with no current flowing, the potential of the working electrode dropped only to $E_h = +0.353 + 0.253 = 0.606$ volt, indicating a polarization of only $+0.400 - 0.353 = 0.047$ volt. The measurements on the accessory electrode showed that no significant change occurred in the composition of the solution.

TABLE XVII
 EFFICIENCY OF DEPOLARIZATION
50 cc. of solution: 1.1 M FeSO₄; 0.9 M H₂SO₄ + 10 g. of charcoal

Time, Hrs. min.	Current, m. a.	Potential	
		Working electrode, $E_C = 0,$ v.	Accessory electrode, $E_C = 0,$ v.
12:15	85.9	+0.199
12:35	85.9	+ .213
1:56	85.9	+ .241
2:05	85.9	+ .247
2:20	85.9	+ .247
2:35	85.9	+ .250
2:45	85.9	+ .250
2:56	0.0	+0.4060
3:00	.0	+ .4059
3:08	.0	+ .4092
3:11	.0	+ .4103
3:15	85.9	+ .400
3:20	85.9	+ .400
3:25	85.9	+ .352
3:40	85.9	+ .354
3:45	85.9	+ .352
3:55	85.9	+ .353

From these data the rate of oxygen absorption per liter of solution per hour can be calculated. It evidently equals $(0.0859 \times 3600 \times 1000) / (96,500 \times 50) = 0.0641$ eq. of oxygen per liter per hour at an open circuit potential of +0.406 volt.

This rate of absorption can be compared with that found in the direct experiments on the velocity of oxidation. The data obtained in our experiments on solutions of this same composition at the same stirring rate of 1250 r. p. m. are collected in the following table.

 TABLE XVIII
 FeSO₄ 1.1 M; H₂SO₄ 0.9 M; charcoal 10 g.

Expt.	Time, hrs.	$\Delta C,$ M	$E_C,$ v.	Oxygen, eq./liter-hr.
1	1.88	0.118	+0.4147	0.0627
2	1.88	.102	+ .4104	.0543
3	3.80	.240	+ .4446	.0632
		Average	+ .423	.0601

It can be seen that the average rate of absorption of oxygen (0.0601) agrees closely with that found in the depolarization experiments (0.0641) being slightly less, as would be expected, at the somewhat higher potential (+0.423 as compared with 0.406). The agreement of these two results derived from such fundamentally different data affords very satisfactory evidence of their individual correctness.

In the following table the performance of one of these oxygen electrodes is compared with that of previous oxygen electrodes operating at room

temperature, namely, the copper-cuprous oxide electrode of Hofmann²⁹ and the platinized carbon electrode of St. v. Náray-Szabó.³⁰

TABLE XIX
EFFICIENCY OF SEVERAL OXYGEN ELECTRODES

Cell		Potential O ₂ electrode, v.	Current, ma. Total	Density 100 cm. ²	Working potential O ₂ elect., v.	Work, watts	Polariza- tion, v.	Temp., °C.	
Air	Cu CuO 5% KOH Cu CO	0.92 ^a	..	(80) ^b	0.2	0.016	0.72	20	Hofmann
O ₂	Plat.-Pt H ₂ SO ₄ ZnSO ₄ Zn	0.963	..	80	0.376	0.03	0.587	20	St. v. Náray-Szabó
Air	Pt C FeSO ₄ H ₂ SO ₄ ZnSO ₄ Zn	0.659	86	2150	0.606	1.30	0.053	30	Lamb and Elder

^a Potential of cell. ^b Estimated.

It can be seen that the present electrode, although it exhibits a lower open circuit potential, shows at a much higher current density a higher working potential, a much higher energy output and a much lower polarization. Indeed, it appears not to have been equaled in these respects except by the oxygen electrode of Baur operating at elevated temperatures.³¹ The relatively considerable activity of this electrode is to be ascribed not only to the intrinsic effectiveness of the catalyst, but also to the fact that it operates as a "bulk" as contrasted with a "surface" type of catalyst, as set forth in our introductory paragraphs.

These results were obtained with electrodes of 4 sq. cm. area immersed in 50 cc. of electrolyte. Assuming that a proportionate increase in these dimensions would be without effect on the efficiency of this electrode and that the normal hydrogen electrode with which it is in series is unpolarized and of negligible internal resistance, the cell would have an energy output of 0.94 watt per liter, or 0.94 kilowatt per cubic meter of electrolyte. These assumptions as to the hydrogen electrode are obviously ideal; but it does not appear improbable that a much more favorable ratio between the area of the electrode and the volume of the electrolyte than that used in our experiments might be secured, so that an even higher energy output per unit of volume might well be realized. A discussion of these matters, however, lies outside the scope of this article.

Summary

1. In an attempt to overcome by means of catalysts the well-known sluggishness of the oxygen electrode, the kinetics of the reaction between solutions of ferrous sulfate and gaseous oxygen has been re-investigated, particularly with reference to the accelerating effect of various secondary

²⁹ Hofmann, *Ber.*, **51**, 1531 (1918).

³⁰ St. v. Náray-Szabó, *Z. Elektrochem.*, **33**, 18 (1927).

³¹ Baur, *Helv. Chim. Acta*, **4**, 325 (1921).

or accessory catalysts. For this purpose an electrometric method was perfected for ascertaining the progress of the oxidation, which is independent of the, at present, unknown activity coefficients of the ferrous and ferric ions in these solutions.

It has been found from the measurements thus made (a) that the reaction is unimolecular with respect to the oxygen, and bimolecular with respect to the ferrous sulfate; (b) that the velocity of the reaction is independent of the concentration of the sulfuric acid at concentrations of 0.1 molar and higher, but increases progressively at lower acidities; (c) that a large number of metallic ions are without noticeable effect but copper ions have a pronounced accelerating effect; (d) that coconut charcoal and platinum black have pronounced accelerating effects, while silica gel is inactive; (e) that the accelerating effect of the charcoal reaches a maximum in 1 molar acid.

The conclusion is drawn that specific peroxides are presumably responsible for the accelerating action. Confirming this, a peroxide-like substance has been extracted in minute amounts from the aerated coconut charcoal, while several so-called narcotics have been found to have a pronounced depressing effect on the velocity of the reaction when catalyzed either by charcoal or by copper salts.

2. Neutral solutions of potassium ferrocyanide have been found by similar measurements to oxidize about half as rapidly as do corresponding solutions of ferrous sulfate in 0.01 to 3.0 molar sulfuric acid. Copper salts are here without significant effect.

3. Solutions of ferrous sulfate containing sodium pyrophosphates have been found to oxidize about 1000 times faster than ferrous sulfate in 0.1 to 3.0 molar sulfuric acid. Their oxidizing potential is, however, nearly half a volt lower. The conclusion previously reached by others that this is a reaction of the first order with respect to the ferrous salt has been shown to be based on an error of interpretation.

4. Direct measurements of the depolarizing activity of ferrous sulfate solutions containing certain of these accessory catalysts have been made. Electrodes utilizing these solutions exhibit, as compared with previously studied oxygen electrodes at room temperature, at a higher current density, a higher working potential, a higher energy output and a much lower polarization.

5. The rates of absorption of the oxygen in these direct measurements of depolarization have been found to check closely the rates of absorption determined in a very different way in the kinetic measurements.