

Glow-discharge Electrolysis. Part II. The Anodic Oxidation of Ferrous Sulphate.*

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The electrolysis of ferrous sulphate solutions in dilute sulphuric acid has been investigated by use of a glow-discharge anode. Oxidation of the ferrous salt occurs, accompanied by marked evolution of hydrogen from the solution, and it appears that much of the oxidation arises from the dissociation of water molecules owing to bombardment of the solution by positive gaseous ions. The phenomena are closely similar to the effects produced by ionising radiations in solution, particularly α -rays, although in the present work comparatively low-energy particles at high dose rates are involved. The oxidation yield (G , in equivalents per faraday) depends upon the concentration of ferrous sulphate, the nature of the electrolyte, the temperature, and the presence of oxygen, but is otherwise independent of most experimental variables; it can be represented by an equation, which has been deduced theoretically, of the form

$$G = 1 + n([\text{Fe}^{++}] + A)/([\text{Fe}^{++}] + A + B)$$

where n is the number of equivalents of oxidising agent formed per faraday by the dissociation of water, and A and B are constants, which can be evaluated, for any given set of experimental conditions. Most of the experimental results can be simply explained on the assumption that the OH radical is the primary oxidising species, but the action of inert salts in raising the oxidation yield suggests that the H_2O^+ ion may possibly play a direct part in the oxidation.

THE present investigation was undertaken to ascertain the nature of the anodic process in the glow-discharge electrolysis of an easily oxidisable ion. The results show, however, that the oxidation brought about electrolytically is overshadowed by that arising from the ionisation and dissociation of water molecules. This is brought about apparently by the entry of positively charged gaseous ions into the aqueous solution in carrying the current, and the chemical effects produced have many features in common with those observed in the study of the effect of ionising radiations on ferrous salt solutions. (See, e.g., for X- and γ -rays: Fricke, *Phys. Review*, 1928, **31**, 1117; Fricke and Morse, *Phil. Mag.*, 1929, **7**, 129; Shishacow, *ibid.*, 1932, **14**, 198; Fricke and Hart, *J. Chem. Phys.*, 1935, **3**, 60; Krenz and Dewhurst, *ibid.*, 1949, **17**, 1337; Miller, *ibid.*, 1950, **18**, 79; Rigg, Stein, and Weiss, *Proc. Roy. Soc.*, 1952, *A*, **211**, 375; Amphlett, *Discuss. Faraday Soc.*, 1952, **12**, 144; Hardwick, *ibid.*, p. 203; Miller and Wilkinson, *ibid.*, p. 50. For α -rays: Nurnberger, *J. Phys. Chem.*, 1934, **38**, 47; Miller and Wilkinson, *Discuss. Faraday Soc.*, 1952, **12**, 110. For neutrons: Wright, *ibid.*, p. 60. For β -rays: Hardwick, *Canadian J. Chem.*, 1952, **30**, 39.) In glow-discharge electrolysis the energy of the particles entering the solution is relatively very low, but they can be supplied at very high and accurately controlled rates, and the present

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technique thus affords an easy method of studying the chemical behaviour of radicals derived from water molecules.

EXPERIMENTAL

An H-shaped cell was used as shown in Fig. 1. It consisted of two cylindrical glass vessels, which formed the anode and cathode compartments, joined by short side tubes near the bottom. The anolyte and catholyte were prevented from mixing by a filter-paper plug in the side tube of the anode compartment, and the two halves of the cell were connected by a short length of rubber tubing. The height of the cell was about 13 cm., and except where otherwise stated an anode compartment with a cross-sectional area of 10 sq. cm. was used. The compartments were closed by rubber bungs which carried the cell components. The anode, from which the discharge occurred, was of platinum wire connected to a tungsten rod sealed into a glass holder; the cathode was a small sheet of platinum foil of approximately 1 sq. cm. area. The anode and the cathode compartment were separately connected to the vacuum line through small ground-glass joints, which permitted easy removal of the cell. In most cases the anolyte was stirred during electrolysis by a small rotor magnet enclosed in a plastic case; this was rotated from beneath by means of a strong bar magnet mounted on an electric motor. To remove the

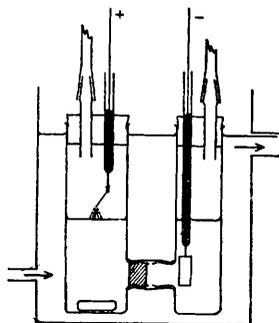


FIG. 1. *Cell for glow-discharge oxidation.*

considerable heat dissipated in the discharge, the cell was almost completely immersed in a bath through which a rapid stream of tap water was passed; under usual conditions the bulk temperature could be kept fairly steady at 18° by this means.

The vacuum system was of a conventional type but included a float manostat so that the pressure in the apparatus could be kept constant over long periods. Before each electrolysis the pressure was reduced until the anolyte boiled, and the cell was then filled with nitrogen from a reservoir bulb; the pressure was then again reduced and maintained at any desired value throughout electrolysis. Where it was desired to estimate the gaseous anode products, the anode compartment was isolated from the vacuum line and connected to a Toepler pump; after initial evacuation, the pressure was allowed to rise to the desired value and was then kept steady by pumping off the anode gases as formed and collecting them over mercury in a glass hood. At the end of electrolysis the cell was again evacuated and the total volume of gas was measured in a gas burette; samples were then analysed in a Bone-Newitt apparatus.

The electrical circuit was essentially as previously described and consisted of a Leland rectifier unit of adjustable voltage (0—1500 v) connected to the cell through a calibrated milliammeter and suitable ballast resistance (2000—10,000 ohms). The discharge was initiated by a pulse from an induction coil, and took the form of a sharply defined cone between the tip of the anode and the electrolyte surface; once started, the discharge required about 600 v, and the current could be kept steady at any desired value in the range 0.025—0.10 A.

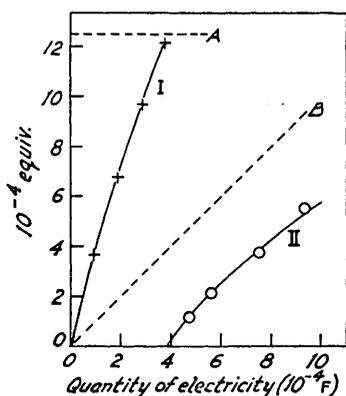
The anolyte was a solution of ferrous sulphate in a sulphuric acid medium; the catholyte was sulphuric acid alone. As preliminary experiments showed that the glow-discharge oxidation was in many respects similar to that produced by ionising radiations, a 0.8N-sulphuric acid solution was used in most cases to conform with the majority of work in the radiation field. "AnalaR" reagents were employed in preparing the electrolyte, which was gassed out with nitrogen before use. The amount of ferrous ion oxidised was determined by titration with 0.025N-potassium permanganate before and after electrolysis. In the absence of ferrous ions or after their complete oxidation, hydrogen peroxide was formed in the anolyte as indicated by reaction with titanous sulphate; the hydrogen peroxide was also estimated by permanganate titration.

The experimental conditions usually employed were: Anolyte, 50 ml. of stirred 0.025M-ferrous sulphate in 0.8N-sulphuric acid; anode, platinum wire with its tip 0.75 cm. from the electrolyte surface; current, 0.075 amp.; pressure of nitrogen in cell, 50 mm.; temp., ca. 18°. These are referred to as the "standard conditions" and are to be taken to apply when the experimental variables are not otherwise specified.

RESULTS

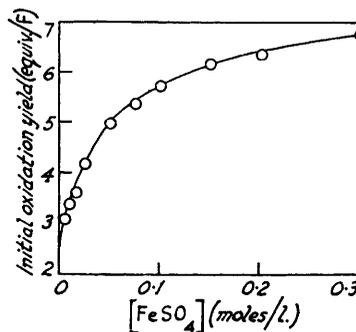
Influence of General Factors.—Quantity of electricity. In Fig. 2 are shown the results of a series of experiments in which 0.025M-ferrous sulphate in 0.8N-sulphuric acid was electrolysed under standard conditions for various times; the number of equivs. of ferrous ion oxidised and hydrogen peroxide produced are plotted against the quantity of electricity passed expressed in faradays. It is seen that oxidation of ferrous ion takes place from the start of electrolysis but the amount oxidised is much greater than the yield of 1 equiv./faraday expected from Faraday's laws. The initial instantaneous or differential yield, as given by a tangent to the curve, is 4.2 equivs./faraday, and this decreases during electrolysis to a final value of 2.5 as the last of the ferrous sulphate is used up. At this point formation of hydrogen peroxide begins and it proceeds exactly as for the sulphuric acid medium alone, ultimately attaining a stationary concentration when it is being decomposed as fast as it is formed (see Part I).

FIG. 2. Glow-discharge oxidation of ferrous ion.



A, Total Fe⁺⁺ present.
B, Theoretical electrolytic yield.
I, Fe⁺⁺ oxidised.
II, H₂O₂ formed.

FIG. 3. Influence of ferrous-ion concentration upon oxidation yield.



Current. In Table I are shown the amounts of ferrous ion oxidised for increasing quantities of electricity at each of four currents (0.10, 0.075, 0.05, and 0.025 A) severally; a pressure

TABLE I. Influence of current on oxidation of ferrous ion.

Quantity of electricity (10 ⁻⁴ F)	Fe ⁺⁺ oxidised (10 ⁻⁴ equiv.)			
	0.10 A	0.075 A	0.05 A	0.025 A
0.93	3.57	3.60	3.77	3.77
1.86	7.12	6.90	6.90	6.90
2.80	10.17	9.92	10.00	9.67
3.73	12.77	12.23	12.35	11.75

of 25 mm. was used, as the discharge at the lowest current was more stable at low pressures. In spite of the very different electrical power dissipated at the different currents, and the different times of electrolysis involved, the oxidation yields are practically the same for equal quantities of electricity passed. This indicates very clearly that whatever is the mechanism of the oxidation it is primarily dependent upon the quantity of electricity passed.

Volume, surface area, and stirring of anolyte. A selection of the results obtained by variation of these factors is given in Table 2. The amount of ferrous ion oxidised appears to be independent of the volume of the anolyte in the early stages of electrolysis; for the passage of greater quantities of electricity, it increases slightly the larger the volume of the anolyte, but this is simply

due to the higher ferrous-ion concentration then existing, and at comparable concentrations no volume effect could be detected. Similarly, variation of the surface area of the anolyte has no marked effect upon the course of the oxidation; experiments carried out with surface areas of 10 and 19 sq. cm. show that for equal quantities of electricity the amount of ferrous ion oxidised is substantially the same. Stirring has little influence upon the oxidation in its early stages, but as it nears completion the unstirred solution gives lower yields. This was found to be due to the premature build-up of a stationary concentration of hydrogen peroxide in the surface of the anolyte before all the ferrous ion in the bulk of the solution had been oxidised; hence in the later stages of electrolysis a solution of hydrogen peroxide is being electrolysed and undergoing its usual decomposition.

Influence of Factors affecting the Discharge.—Electrode distance. In Table 3 are shown the results of a series of experiments in which the distance of the anode from the electrolyte surface

TABLE 2. *Influence of volume, surface area, and stirring.*

Quantity of electricity (10^{-4} F)	Fe ⁺⁺ oxidised (10^{-4} equiv.)				
	Area, sq. cm. : Vol., ml. :	Stirred		Stirred	Unstirred
		30	10	75	19
0.93	3.59	3.64	3.65	3.73	3.69
1.86	6.77	6.78	6.97	7.30	6.60
2.80	—	9.62	10.37	10.40	8.78
3.73	—	12.10	13.10	13.50	10.55

TABLE 3. *Influence of electrode distance.*

Quantity of electricity (10^{-4} F)	Fe ⁺⁺ oxidised (10^{-4} equiv.)				
	Distance of anode from solution surface, in cm.				
	0.15	0.38	0.77	1.30	1.95
0.93	3.87	3.77	3.64	3.77	3.82
1.86	7.75	7.07	6.78	6.92	7.07
2.80	10.47	10.17	9.62	9.95	10.07
3.50	12.25	12.10	11.60	11.85	11.95

was varied, standard conditions being otherwise employed. Apart from a trivial increase in yield when the anode is very close to the surface and the discharge is probably somewhat distorted, the electrode distance seems to have remarkably little influence.

Pressure. Experiments were carried out under the usual standard conditions at different pressures of nitrogen, and the results are summarised in Table 4. At the highest pressure the oxidation yields are somewhat increased, but apart from this the effect of pressure appears to be very slight.

TABLE 4. *Influence of pressure.*

Quantity of electricity (10^{-4} F)	Fe ⁺⁺ oxidised (10^{-4} equiv.)			
	Pressure of N ₂ above the solution, in mm.			
	25	50	78	126
0.93	3.60	3.64	3.64	4.26
1.86	6.90	6.78	6.84	7.44
2.80	9.92	9.62	9.70	10.45
3.50	11.80	11.60	11.60	12.27

Influence of Factors affecting the Solution.—Temperature. The heat liberated in the glow-discharge electrolysis is so great that it is impossible to keep the temperature of the cell constant, but some experiments were carried out in which the average bulk temperature of the electrolyte was maintained at different values by varying the rate of flow of the cooling water; the results are given in Table 5. It is apparent that increase of temperature markedly increases the amount of oxidation corresponding to a given quantity of electricity.

Ferrous sulphate concentration. Preliminary experiments showed that variation of ferrous sulphate concentration had a significant effect upon the oxidation yield, and a comprehensive investigation of this factor was therefore made over the concentration range 0.005—0.935M-ferrous sulphate in 0.8N-sulphuric acid. With each solution, a graph of the amount of ferrous ion oxidised plotted against quantity of electricity passed was obtained, from which, by con-

structing tangents, the initial and final differential yields in equiv./faraday could be obtained. These are summarised in Table 6. The initial yields have been plotted against concentration in Fig. 3, and it may be noted that the initial yield increases rapidly at first with rise of ferrous sulphate concentration but ultimately approaches a value of about 7 equivs./faraday in the most concentrated solution. The final yield in each case (*i.e.*, the yield when the ferrous sul-

TABLE 5. *Influence of temperature.*

Quantity of electricity (10^{-4} F)	Fe ⁺⁺ oxidised (10^{-4} equiv.)		
	Average temperature of electrolyte (approx.)		
	18°	27°	36°
0.93	3.64	4.26	5.28
1.40	5.20	6.00	7.96
1.86	6.78	7.62	9.81
2.33	8.24	9.26	12.05
2.80	9.62	10.83	—
3.27	10.90	12.19	—
3.73	12.10	—	—

TABLE 6. *Influence of ferrous sulphate concentration.*

FeSO ₄ , mole/l.	Differential yield, equiv. Fe ⁺⁺ oxidised/faraday		FeSO ₄ , mole/l.	Differential yield, equiv. Fe ⁺⁺ oxidised/faraday	
	Initial	Final		Initial	Final
0.005	3.1	1.6	0.10	5.8	2.5
0.01	3.4	1.8	0.15	6.2	2.4
0.015	3.6	2.4	0.20	6.4	2.6
0.025	4.2	2.5	0.30	6.8	2.7
0.05	5.0	2.5	0.935	7.0	—
0.075	5.4	2.6			

phate has been almost completely oxidised) increases initially with rise of concentration but then approaches a limiting value of *ca.* 2.5 equivs./faraday. The variation in yield during the course of any one electrolysis is apparently solely due to the decrease of ferrous-ion concentration as oxidation takes place; hence at any stage in one electrolysis the differential yield is the same as that obtained initially in a solution of corresponding ferrous-ion concentration. Thus the presence of ferric ions in the solution as oxidation proceeds appears to have very little effect. This was confirmed by comparing directly the results of the electrolysis of a mixture of ferrous and ferric sulphates with that of ferrous sulphate alone; no significant difference was observed.

The fact that the oxidation yield in all cases is much higher than the 1 equiv./faraday expected for electrolysis implies that some reduction product must also be formed in the anode compartment, and the most likely product appeared to be hydrogen arising from the water. To check this, a series of electrolyses were carried out with 0.075M-ferrous sulphate in 0.8N-sulphuric acid in which the gaseous products formed at the anode were estimated as well as the amount of oxidation in solution. The anode gas was found to contain considerable amounts of hydrogen together with small amounts of oxygen, and in Table 7 a comparison is made between the

TABLE 7. *Total products formed.*

Quantity of electricity (10^{-4} F)	Amounts of products (10^{-4} equiv.)				
	Fe ⁺⁺ oxidised	H ₂	O ₂	H ₂ - O ₂	Excess Fe ⁺⁺ oxidised
1.86	9.50	7.48	0.23	7.25	7.64
3.73	18.00	13.86	0.41	13.45	14.27
5.60	25.80	19.95	0.41	19.54	20.20
7.46	32.60	25.13	0.25	24.88	25.14
9.32	37.75	28.25	0.57	27.68	28.43

excess of oxidation in solution and the excess of hydrogen in the gas liberated. The last two columns agree well, showing that the excess of oxidation above that expected electrolytically is to be accounted for by simultaneous reduction of water to hydrogen.

Sulphuric acid concentration. The oxidation yield was found to increase as the concentration of sulphuric acid was raised. This is shown by the figures in Table 8 which refer to a 0.025M-ferrous sulphate solution and standard conditions.

Salt effects. In Part I it was noted that the anodic yield of hydrogen peroxide was increased by raising the concentration of the electrolyte in the medium used. This same tendency is apparent in the oxidation yield with ferrous sulphate solutions when inert salts are added to

the solution. A selection of results is given in Table 9. These were obtained with 0.025M-ferrous sulphate in 0.1N-sulphuric acid in the presence of various salts and are expressed as initial and final differential oxidation yields; for comparison the initial yields of hydrogen peroxide in the absence of ferrous sulphate are also given. It is seen that the oxidation yield

TABLE 8. *Influence of sulphuric acid concentration.*

H ₂ SO ₄ , equiv./l.	Differential yield, equiv. Fe ⁺⁺ oxidised/faraday		H ₂ SO ₄ , equiv./l.	Differential yield, equiv. Fe ⁺⁺ oxidised/faraday	
	Initial	Final		Initial	Final
0.02	3.4	1.6	0.80	4.2	2.5
0.10	3.6	1.8	3.6	4.8	2.5

with ferrous sulphate can be increased from 3.6 to 5.4 equivs./faraday by addition of inert salts, while the yield of hydrogen peroxide when ferrous sulphate is not present is raised from 1.1 to 2.3 equivs./faraday under comparable conditions. The effect appears to be largely independent of the chemical nature of the salt added and runs very roughly parallel to the ionic strength of the medium; it is noteworthy that the addition of a weak electrolyte such as boric acid did not influence the yields appreciably.

TABLE 9. *Influence of added salts.*

Salt added	Fe ⁺⁺ oxidised, equiv./faraday		H ₂ O ₂ formed, equiv./faraday
	Initial	Final	
None	3.6	1.8	1.1
0.02M-K ₂ SO ₄	4.0	2.0	1.5
0.075M-K ₂ SO ₄	4.5	2.5	1.7
0.10M-K ₂ SO ₄	4.8	2.6	1.7
0.20M-K ₂ SO ₄	5.4	2.6	2.3
0.10M-Na ₂ SO ₄	4.8	2.6	1.7
0.10M-(NH ₄) ₂ SO ₄	4.8	2.6	1.7
0.075M-MgSO ₄	4.4	2.4	1.5
0.075M-ZnSO ₄	4.4	2.4	1.4
0.02M-Al ₂ (SO ₄) ₃	4.4	2.3	1.5
0.10M-Al ₂ (SO ₄) ₃	4.8	2.6	1.9

Oxygen. In the oxidation of ferrous sulphate solutions by ionising radiations the presence of dissolved oxygen often has a marked effect. In the present work it was found that pre-saturation of the solution with oxygen had no significant effect, probably because the solution is effectively degassed before electrolysis. If, however, the electrolysis was carried out in an atmosphere of oxygen instead of nitrogen, the oxidation yields were markedly increased, as the results in Table 10 show; replacing the nitrogen atmosphere by one of hydrogen did not

TABLE 10. *Influence of oxygen.*

Quantity of electricity (10 ⁻⁴ F)	Fe ⁺⁺ oxidised (10 ⁻⁴ equiv.) in atmosphere of :			Quantity of electricity (10 ⁻⁴ F)	Fe ⁺⁺ oxidised (10 ⁻⁴ equiv.) in atmosphere of :		
	N ₂	O ₂	H ₂		N ₂	O ₂	H ₂
0.47	1.90	2.97	—	2.33	8.20	11.73	—
0.93	3.64	5.54	3.58	2.56	8.84	12.40	—
1.40	5.30	7.98	—	2.80	9.62	—	10.10
1.86	6.78	10.05	6.95	3.73	12.10	—	12.30

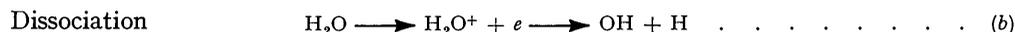
influence the yields appreciably. The presence of oxygen raises the initial yield under standard conditions from 4.2 to 6.6 equivs./faraday, but the final yield remains unaffected at 2.5 equivs./faraday. The same tendency was found with ferrous sulphate solutions over the whole range of concentrations, and with 0.78M-ferrous sulphate in 0.8N-sulphuric acid the very high initial yield of 11.6 equivs./faraday was found as compared with a maximum yield of about 7 equivs./faraday observed in electrolysis under nitrogen. It is noteworthy that no oxidation of ferrous sulphate solution was brought about by passing a discharge between platinum electrodes just above the liquid surface in an oxygen atmosphere; this suggests that the effect of oxygen in the glow-discharge electrolysis must be a fundamental one.

DISCUSSION

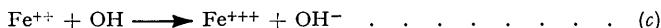
In Part I (*loc. cit.*), arguments were presented which suggested that with a glow-discharge anode the current is conveyed across the gas-liquid interface by positive gaseous ions derived from water vapour; these, it was supposed, are driven into the liquid from the gas phase under the high potential gradient which exists near the cathode (*i.e.*, liquid) surface

and are subsequently discharged. In these circumstances in addition to any purely electrolytic action it is possible that entry of positive gaseous ions into the solution may bring about dissociation of water molecules in the general way now attributed to ionising radiations of many types (cf. Dainton, *Ann. Reports*, 1948, 45, 5). In the earlier work the yields of hydrogen peroxide obtained were not usually very much greater than 1 equiv. per faraday, and it was possible to regard this product as arising mainly by electrolytic action although the possibility of some direct dissociation of water molecules was not excluded. The present investigation of the oxidation of ferrous sulphate shows that oxidation yields vastly in excess of that expected from electrolysis occur accompanied by evolution of hydrogen from the solution, and it is at once apparent that in this case electrolysis is of minor importance and the oxidation occurs mainly *via* the dissociation of water molecules. Quantity of electricity is still the experimental factor of prime importance, but it now serves to measure the number of charged particles which have entered the solution, and the chemical effects they produce are much greater than is to be expected simply by a transference of charge.

The primary result of the passage of current across the gas-water interface can be represented quite generally in conventional terms as follows :



Thus the oxidising species arising either from electrolysis or from dissociation will be the same, but the electrolytic reaction (a) yields only 1 equiv. of OH per faraday, while the dissociation reaction (b) may produce several equivalents of OH per faraday, depending upon the energy available, but these will be accompanied necessarily by a corresponding number of equivalents of hydrogen. In the absence of a depolariser, dimerisation of the OH radicals to give hydrogen peroxide may then occur in the way previously discussed (Part I). In the presence of a ferrous salt, the ferrous ion may be oxidised by the OH radical either directly



or *via* the formation of hydrogen peroxide



followed by



and these reactions will compete with the back reaction



Thus if n equivalents of OH are formed per faraday by the dissociation reaction (b), and if v_1 , v_2 , and v_3 are the velocities of reactions (c), (d), and (e) in the stationary state, then the oxidation yield (G) in equivalents per faraday will be given by the equation

$$G = 1 + n \frac{v_1 + v_2}{v_1 + v_2 + v_3} \quad \dots \quad (1)$$

The velocities being expressed in terms of the concentrations of the reacting species, this becomes

$$G = 1 + n \frac{k_1[\text{OH}][\text{Fe}^{++}] + k_2[\text{OH}]^2}{k_1[\text{OH}][\text{Fe}^{++}] + k_2[\text{OH}]^2 + k_3[\text{OH}][\text{H}]} \quad \dots \quad (2)$$

which simplifies to

$$G = 1 + n \frac{[\text{Fe}^{++}] + k_2[\text{OH}]/k_1}{[\text{Fe}^{++}] + k_2[\text{OH}]/k_1 + k_3[\text{H}]/k_1} \quad \dots \quad (3)$$

Under a given set of experimental conditions it is reasonable to suppose that in the stationary state $[\text{OH}]$ and $[\text{H}]$ are constant and the equation may then be written

$$G = 1 + n \frac{[\text{Fe}^{++}] + A}{[\text{Fe}^{++}] + A + B} \quad \dots \quad (4)$$

where A and B are constants. The numerical values of A , B , and n can be determined by reference to the experimental data in the following way. On rearranging equation (4) and inverting it, we have

$$\frac{1}{G-1} = \frac{1}{n} \cdot \frac{B}{A + [\text{Fe}^{++}]} + \frac{1}{n} \quad \dots \quad (5)$$

At substantial concentrations of ferrous sulphate $A + [\text{Fe}^{++}] \rightleftharpoons [\text{Fe}^{++}]$ and hence the plot of $1/(G - 1)$ against $1/[\text{Fe}^{++}]$ should be a straight line of slope B/n and intercept $1/n$. Furthermore, at very low ferrous-ion concentrations the oxidation yield should be constant and have the value

$$G = 1 + nA/(A + B) \dots \dots \dots (6)$$

from which A can be found. On treating the data in Table 6 in this way, we obtain the values $n = 6.2$, $B = 0.030$, and $A = 0.0096$, and hence the dependence of the initial differential yield upon the ferrous-ion concentration should be given by the equation

$$G = 1 + 6.2([\text{Fe}^{++}] + 0.0096)/([\text{Fe}^{++}] + 0.0396) \dots \dots \dots (7)$$

This relation has been tested by calculating G for different ferrous sulphate concentrations and in Table 11 these calculated values are compared with those found experimentally.

TABLE 11. *Experimental and calculated oxidation yields.*

FeSO ₄ , mole/l.	0.005	0.010	0.015	0.025	0.05	0.075	0.10	0.15	0.20	0.30	0.935
$G_{\text{exptl.}}$	3.1	3.4	3.6	4.2	5.0	5.4	5.8	6.2	6.4	6.8	7.0
$G_{\text{calc.}}$	3.0	3.4	3.8	4.3	5.1	5.6	5.9	6.2	6.4	6.7	7.0

The agreement between the experimental and calculated values is very satisfactory, which suggests that the method of deriving the equation is sound in principle. It is noteworthy that according to equation (7) the oxidation yield is practically independent of ferrous sulphate concentration at concentrations below 10^{-3} mole/l.; in the oxidation of ferrous sulphate by α -rays a similar change to a concentration-independent region is found at low concentrations (cf. Nurnberger, *J. Phys. Chem.*, 1934, **38**, 47).

In the reaction scheme which has been postulated, no reduction of the ferric salt produced by the hydrogen formed in the dissociation of water has been suggested. All the experimental evidence in the present work indicates that no reduction of this type takes place. Thus the oxidation of the ferrous salt proceeds to completion independently of the concentration of ferric ions present, and even when a glow-discharge cathode was used with a ferric sulphate solution very little reduction could be brought about. This absence of reducing power in a system in which the existence of hydrogen atoms is postulated has frequently been noted in the radiation field, and much ingenuity has been directed to explaining it (see, e.g., Haissinsky, *Discuss. Faraday Soc.*, 1952, **12**, 133).

Estimates of the cathode fall of potential have been made in the present work from observations on the variation of anode-cathode voltage with anode-surface distance, the ohmic drop in the solution being negligible. These indicate that it is approximately 470 v, and it appears to be independent of current, pressure, and nature of the solution, and to be confined to a layer less than 1 mm. thick near the liquid surface. Thus the energy of the positive ions reaching the solution is independent of most experimental variables and hence n will be constant. Since n has normally a value of 6.2, it follows that the maximum energy required on the present scheme to form an ion-pair cannot exceed about 76 ev; the actual energy may be much less than this, since some will undoubtedly be lost in collision processes. If n is constant, it follows from equation (3) that, apart from the ferrous-ion concentration, the oxidation yield will only be affected by variation in the stationary concentrations of the radicals or in the velocity coefficients. The concentrations of the radicals would be expected to be directly connected with the current density in the reaction zone, and hence measurements have been made of the area of the glow-spot in the water surface under different experimental conditions. These show that the current density (I) is independent of the actual current used (the spot expanding proportionately as the current is increased) and of the nature of the electrolyte, but varies as the square root of the pressure (p), the average of a large number of determinations giving $I p^{1/2} = 0.018$ A/sq. cm./mm.^{1/2}, and is only slightly affected by change in the anode-surface distance. The yield should thus be independent of current and practically independent of pressure and anode-surface distance, as was found experimentally. It should be emphasised that all the reactions considered are regarded as being confined to a localised reaction zone beneath the glow-spot in the liquid surface.

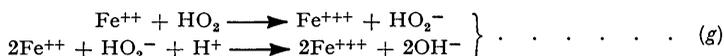
Increase of temperature has been found markedly to increase the oxidation yield with

the stock ferrous sulphate electrolyte, and it also increases the yield of hydrogen peroxide when no oxidisable substance is present (see Part I). It was found by experiments with concentrated ferrous sulphate solutions that there is an increase in n with rise of temperature; by substituting the values obtained in equation (7), however, it appears that this alone is insufficient to account for the increase of yield observed at lower concentrations. This would imply, therefore, that the overall velocities of the oxidation reactions are increased by rise of temperature; this could arise by there being an energy of activation both for the interaction of the OH radical with the ferrous ion [reaction (c)] and for the dimerisation reaction (d), or possibly by the acceleration of diffusion processes in the reaction zone. It is not yet feasible to distinguish clearly between these possibilities.

The marked effect of oxygen in increasing the initial yield in the oxidation of ferrous sulphate can be simply explained on the supposition, frequently made in radiation chemistry, that oxygen reacts with hydrogen atoms as follows :



The HO₂ radicals produced might then themselves bring about oxidation by an initial reaction of the type



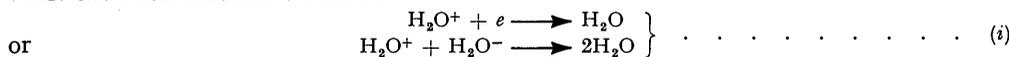
followed by

Thus there would be an increase in the number of oxidising radicals formed and a decrease in the concentration of hydrogen atoms leading to a reduction in the speed of the back reaction (e). In practice, the experimental results show that n in equation (4) is raised from 6.2 to 11.1 by the presence of oxygen, and since the energy expended in the discharge remains the same, this can only be attributed to the formation of new oxidising species by chemical reaction as suggested.

The theory which has been outlined so far has assumed that the OH radical is in general the primary effective oxidising agent, and it has provided a plausible explanation of most of the experimental observations. The very marked effect of inert salts in raising the oxidation yields with ferrous sulphate, and in the formation of hydrogen peroxide, receives no obvious interpretation on this theory, however, and it suggests another possibility. The effect, which has also been observed in radiation chemistry, is of so general a nature that it appears to be unmistakably due to the change of ionic environment on addition of an electrolyte, *i.e.*, to arise by a primary salt effect on the velocities of the reactions involved. This would imply that charged species are concerned in the reactions. Now it has been suggested that H₂O⁺ is a precursor of the OH radical, and this might then react directly with the ferrous ion



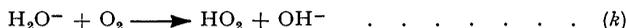
while the back reaction would be



Reaction (h) would then be accelerated and reaction (i) retarded by addition of electrolytes, giving the enhanced oxidation yields as found; in the absence of ferrous sulphate, the retardation of the back reaction would lead to an increased yield of hydrogen peroxide as observed. A further attractive feature of this scheme is that in acid solution there is a possibility of the reaction of H₂O⁻ with a hydrogen ion leading to the direct elimination of molecular hydrogen rather than the formation of hydrogen atoms, thus :



This would account for the absence of reducing properties in the solution, each initial act of dissociation leading to the formation of 2 oxidising radicals and 1 molecule of hydrogen. In the presence of oxygen a possible reaction is



and in view of the stoichiometry of reaction (g) where one HO₂ radical oxidises 3 ferrous ions, the value of n should be increased.

The postulation of these ionic reactions in addition to or in place of the free-radical

reactions of the more conventional scheme would not change fundamentally the previous treatment of the system, but it appears to satisfy certain requirements where the free-radical reaction scheme is inadequate. It must, however, be noted that the participation of H_2O^+ and H_2O^- in the reactions is not in conformity with the generally accepted view of the instability of these ions in solution, and while the hypothesis advanced has many attractive features it must be regarded as speculative.

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