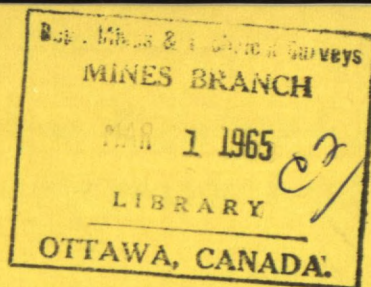




CANADA



**KINETICS OF THE CARBON  
CATALYZED AIR OXIDATION OF  
FERROUS ION IN SULPHURIC  
ACID SOLUTIONS**

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# Kinetics of the Carbon Catalyzed Air Oxidation of Ferrous Ion in Sulphuric Acid Solutions\*

G. THOMAS† and T. R. INGRAHAM‡

## Abstract

Air oxidation of acidic ferrous sulphate solutions is catalyzed by activated carbon. The oxidation rate during most of the reaction can be expressed by:

$$-d[\text{Fe}^{++}]/dt = k \cdot [\text{O}_2] \cdot [\text{C}] \cdot f[\text{H}_2\text{SO}_4] \cdot [\text{Fe}^{++}] / [\text{Fe}^{++} + \text{Fe}^{+++}]$$

For molar concentrations of each of the variables, the rate of oxidation ranges from 0.07 to 1.3 moles of ferrous ion oxidized per litre of solution per minute, for various types of 100-by-150-mesh activated carbon. The rate increases with increasing fineness of the carbon; it also increases almost linearly with increasing sulphuric acid concentration up to 2M, but thereafter decreases almost linearly to 10M H<sub>2</sub>SO<sub>4</sub>. The results are consistent with the hypothesis that the carbon surface is sparsely covered with adsorbed oxygen, ferrous ions, and ferric ions. The activation energy estimated for the process is 6 kilocalories per mole in the temperature range 1 to 24°C. At higher temperatures the activation energy is negligibly small. The activated carbon can be used repeatedly, with little loss in efficiency. Two types of apparatus were tested and found suitable for the continuous oxidation of flowing solutions.

## INTRODUCTION

Many uranium ores processed by acid leaching require oxidation before their tetravalent uranium can be extracted. This is generally done by ferric ions and the resulting ferrous ions can be reused after reoxidation. For continued leaching, the concentration of ferric ion must be maintained.

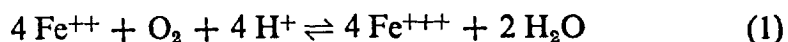
In industry, oxidation of ferrous ion for leaching may be done with chemical oxidants such as sodium chlorate or manganese

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dioxide.<sup>1-3</sup> However, most of the oxidation is done by oxygen from dissolved air:



Oxidation can be accelerated in autoclaves with elevated temperature and air pressure.<sup>4</sup> More rapid oxidation can also be obtained by the use of a soluble catalyst such as the cupric ion,<sup>5,6</sup> or a solid catalyst such as activated carbon.<sup>5,7</sup> At the Mines Branch, preliminary tests have shown that the rate of oxidation of ferrous ion in 0.5 molar sulphuric acid is increased 14-fold by the use of copper sulphate, or 2400-fold by the use of activated carbon.

In this paper, a description will be given of work done to resolve the effects of different variables on the rate of carbon-catalyzed air oxidation of ferrous ion in sulphuric acid solutions. Commercially-available activated carbons were used in most experiments. To eliminate the effects of extraneous impurities on the oxidation rate, synthetic leach liquors prepared from reagent-grade chemicals were used.

## APPARATUS AND PROCEDURE

The apparatus used for most of the oxidation experiments is shown in Figure 1.

The Pyrex-glass reaction cylinder was 5.5 cm in diameter and 60 cm in height. A 2-cm-diameter, porous Pyrex-glass frit was sealed into the tapered base of the reaction cylinder to support the carbon slurry and to disperse the air as fine bubbles. An air stream velocity of 200 ml/min was suitable for suspending the carbon and maintaining oxygen at its maximum solubility. To prevent plugging of the frit by the precipitation of salts, the incoming air was saturated with water. For experiments at temperatures other than ambient room temperature, an ice bath or a heating coil was used to regulate the temperature in the reaction cylinder. A water-cooled condenser was used to prevent losses of solution by evaporation.

In the continuous oxidation experiments, the Pyrex reaction cylinder was used with the settling tube attached. Solution was admitted continuously either at the top or, with inlet air, at the bottom of the reaction cylinder. The apparatus was tilted slightly to prevent air bubbles from entering the settling tube. When baffles were used to eliminate convection currents, and when the solution flow rate in the settling tube was less than the settling velocity of the carbon, the

oxidized effluent was clear. For the batch experiments, the settling tube was removed.

A second type of apparatus used for some batch experiments consisted of a flat hollow stainless steel disc, 28 cm in diameter and 1 cm

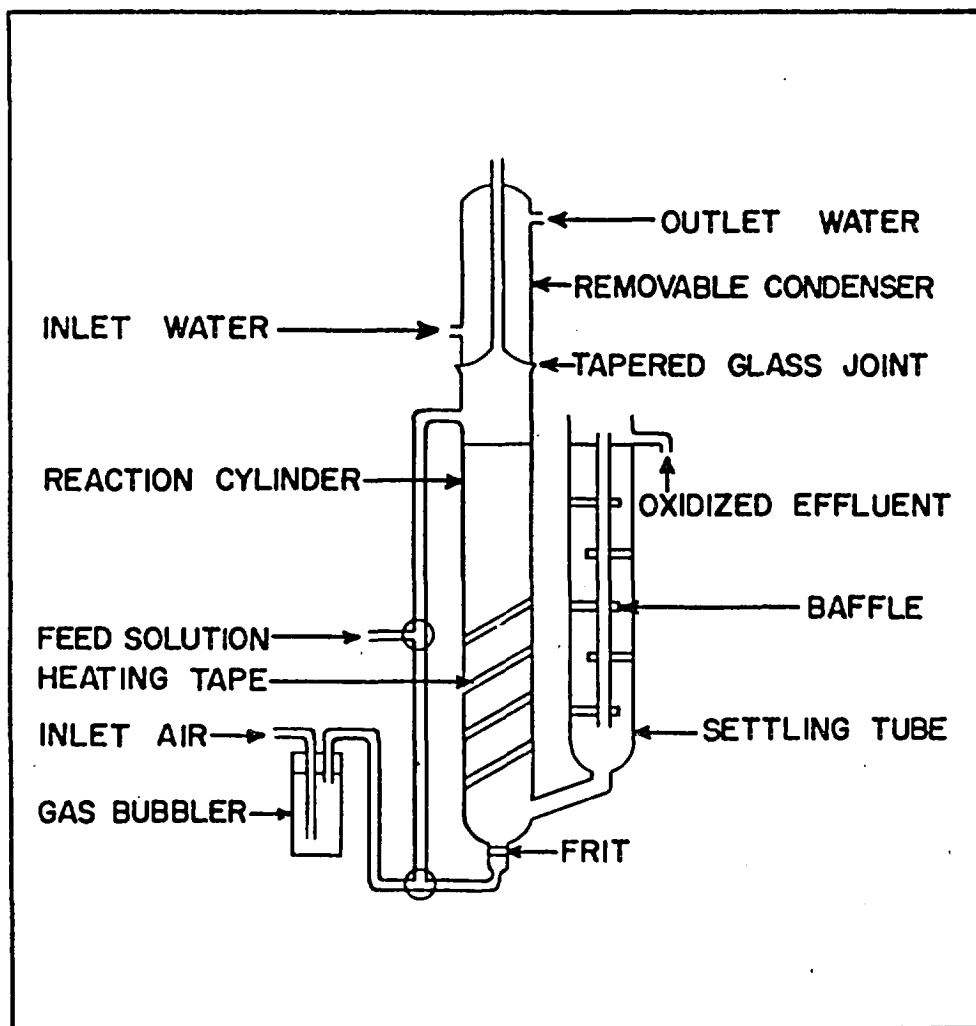


Fig. 1. Oxidation apparatus.

thick at its centre. 60-mesh screen was used to construct the disc, which contained 100 g of 28-by-48-mesh activated carbon. It was rotated vertically with about 40 per cent of its surface immersed in a narrow rectangular lucite box containing the solution.

A coarse-tipped pipet was used to withdraw samples of slurries which were filtered rapidly to separate the carbon and thus quench



the oxidation. The extent of oxidation was determined by titration to the diphenylamine sulphonate end-point with a standard dichromate solution.

## RESULTS

In the first group of batch experiments done at room temperature with aerated 0.5M sulphuric acid solutions, carbon samples from different sources and with different histories of activation were used to oxidize samples which were 0.018M in total iron and 1.1M in carbon.

TABLE I  
Effect of Type of Carbon on Relative Rate of Oxidation  
(1.1M carbon, 0.018M total iron, 0.5M acid, room temperature)

Type of carbon	Relative reaction rate
Household wood charcoal	1.0
Activated wood carbon, brand A	1.0
Activated coconut carbon, brand B	4.4
Activated sugar carbon <sup>a</sup>	6.9
Activated lignite carbon, brand A	8.4
Activated pecan carbon, brand C, grade 1	10.4
Activated coconut carbon, brand C	19.5
Activated pecan carbon, brand C, grade 2	19.7

<sup>a</sup> Prepared from sugar, FeCl<sub>3</sub> and urea.<sup>7</sup>

The results in Table I show that the carbon samples have a wide range of activity and that both the source material and the history of activation are important in selecting the most effective catalyst.

TABLE II  
Effect of Particle Size of Carbon on Rate of Oxidation  
(1.1M carbon, 0.018M total iron, 0.5M acid, room temperature)

Mesh size	14-by-28	28-by-48	60-by-80	115-by-170
Relative particle size	8	4	2	1
Relative external area	1	2	4	8
Relative reaction rate	1.0	1.5	2.3	2.8

In Table II, the results of experiments using different sizes of carbon particles show that the rate of oxidation increases with the state of subdivision of the carbon but is not directly proportional to the screen size of the particles. This lack of direct proportionality is probably

caused by the large internal surface area of the carbon, much of which is available for adsorption.

The next group of batch experiments was done using 750 ml of 0.5M sulphuric acid containing carbon and iron in a variety of ratios.

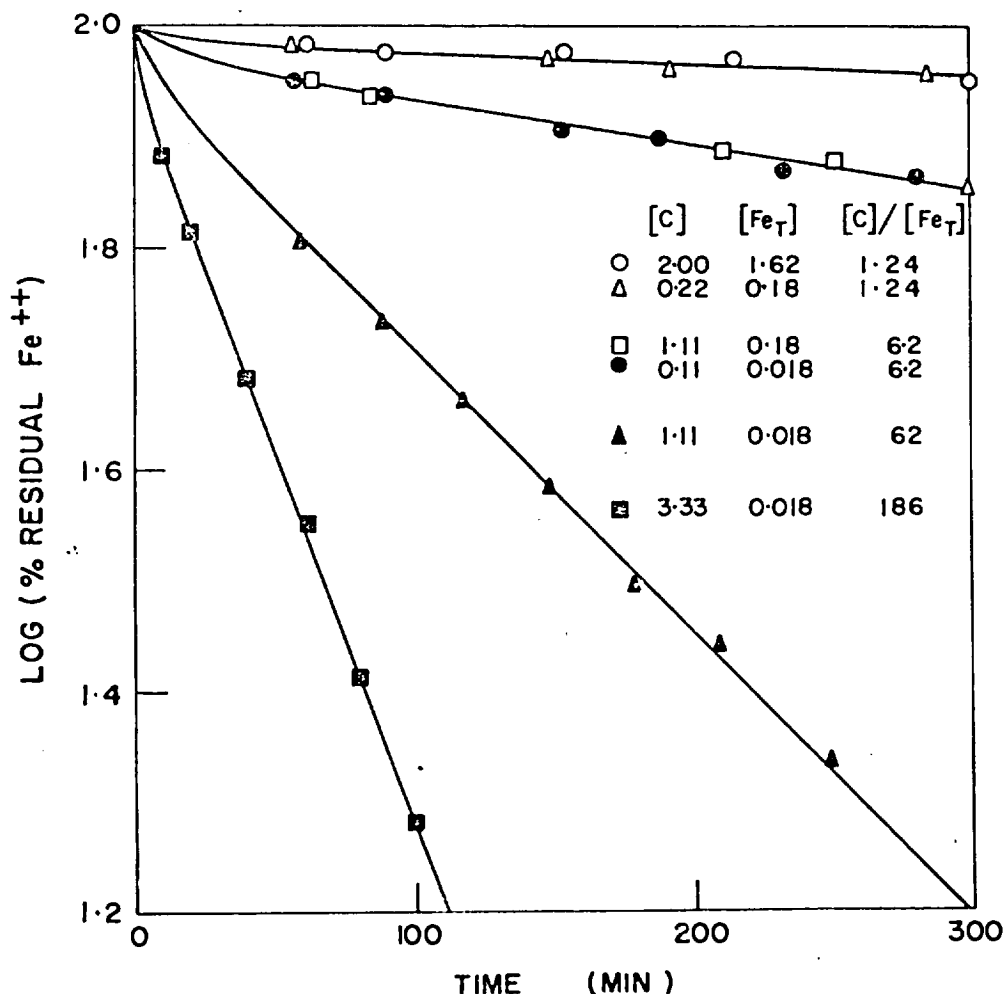


Fig. 2. Effect of carbon/iron ratio on reaction rate.

The results in Fig. 2 show that except for a brief initial period, the reaction is first order with respect to ferrous ion concentration and the rate is determined by the ratio of the concentrations of carbon to total iron, rather than by either concentration alone. The first order reaction rate constant,  $k_{exp}$ , was calculated by multiplying the slope of the linear portion of the curves by  $-2.303$ .

In the next group of experiments, the rate of oxidation was studied

as a function of acidity. The samples were 0.018 molar in total iron and 1.1 molar in carbon. The results are shown in Fig. 3 in which an adjusted reaction rate constant is plotted against the concentration of

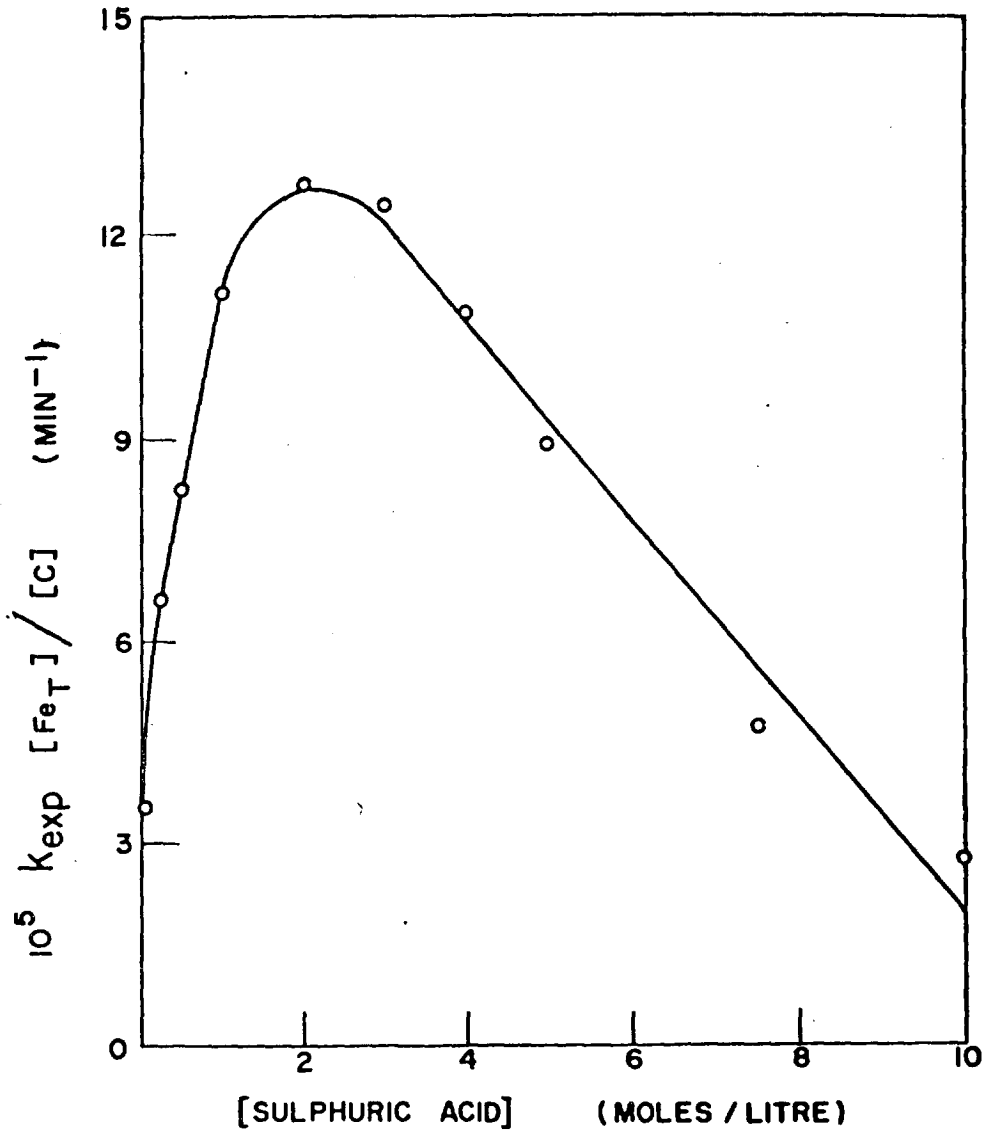


Fig. 3. Effect of acid concentration on reaction rate adjusted to 1 molar carbon and 1 molar total iron.

sulphuric acid. The adjusted rate constant,  $k_{\text{exp}}[\text{Fe}_T]/[\text{C}]$ , was calculated to express the first order rate constant,  $k_{\text{exp}}$ , on the basis of one mole of total iron and one mole of carbon per litre of solution. It is evident from Fig. 3 that the adjusted reaction rate increases almost



linearly with increasing acidity in the range 0.1 to 1 molar. The oxidation rate reaches a maximum at about 2 molar, and then decreases almost linearly from 3 to 10 molar acid.

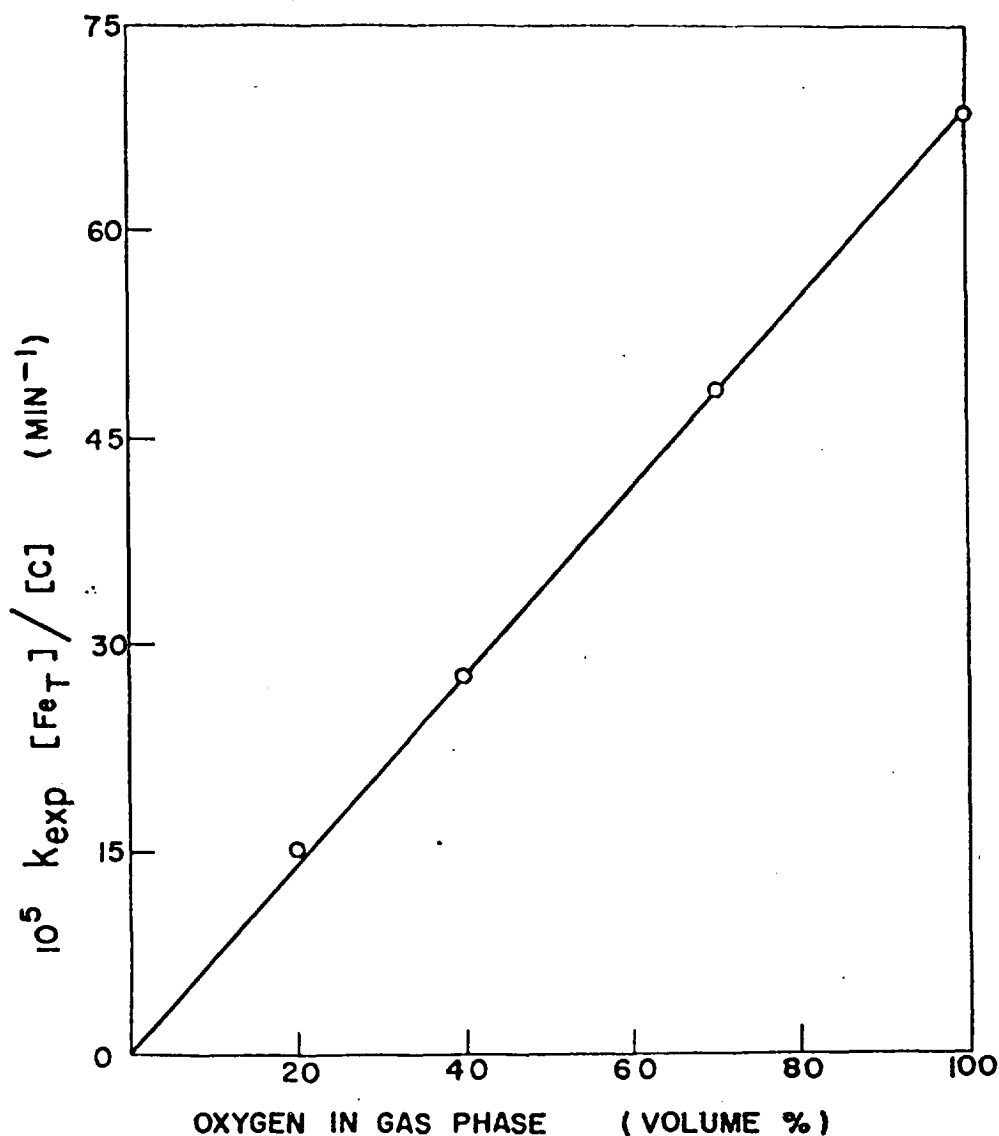


Fig. 4. Effect of oxygen concentration on reaction rate adjusted to 1 molar carbon and 1 molar total iron.

In the next group of batch experiments, samples 0.9M in total iron and 1.1M in carbon were oxidized at room temperature using a 200 ml/min flow of oxygen-enriched air. Figure 4 shows that the rate of oxidation is directly proportional to the volume percentage of oxygen in the gas phase. Since, at constant temperature, oxygen solubility is

proportional to its partial pressure in the gas phase, it follows that the rate of oxidation is directly proportional to the amount of oxygen dissolved in the solution.

In another group of experiments, the rate of oxidation reaction was studied as a function of solution temperature, using samples

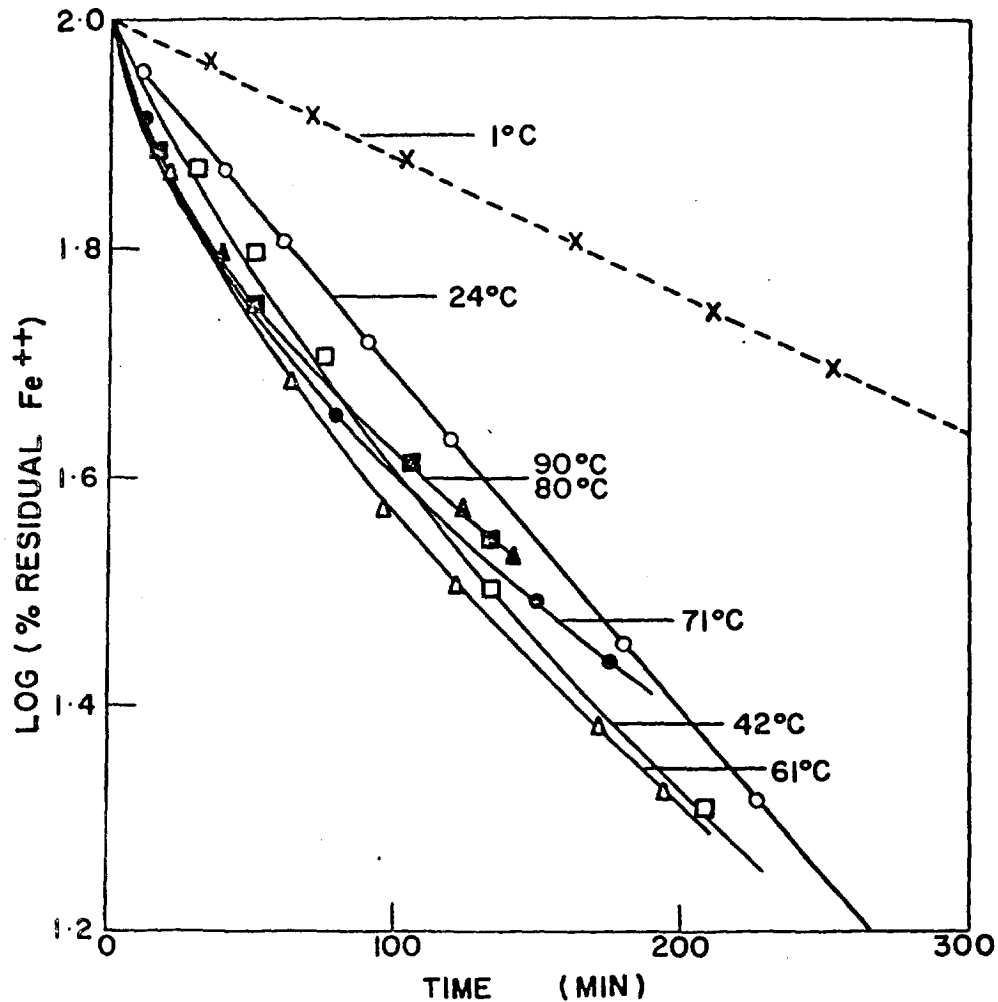


Fig. 5. Effect of temperature on reaction rate.

0.018M in total iron and 1.1M in carbon, with 200 ml/min of air. Using the oxygen solubility versus temperature data of Seidell,<sup>8</sup> the reaction rates were normalized to correspond with air-saturation at 24°C. The results in Fig. 5 show that the rate increases with increasing temperature. The rate of increase is greatest at the lower temperatures, for which an activation energy of about 6 kilocalories per mole was estimated between 1 and 24°C. At temperatures above 60°C, there is

no detectable increase in rate with additional increases in temperature.

Experiments done with a variety of anions and cations as contaminants have shown that the ferric, thiocyanate and chloride ions reduced the rate of oxidation. The sodium, calcium, magnesium, manganous, cupric, aluminum, uranyl and silicate ions did not influence the rate.

In the next group of experiments, a 2-gram sample of activated carbon was used repeatedly, over a 6-week period, to oxidize successive samples of solution containing one mole per litre of total iron. The efficiency of the carbon as a catalyst for oxidation was ascertained at the end of each test by determining the rate at which it was capable of oxidizing fresh 150-ml samples of solution 0.018 molar in total iron. The decrease in activity of the carbon is shown in Fig. 6, in which the rate is plotted against the time in days. It is evident, that although the rate of deterioration of the catalyst is quite rapid for the first few days, after about five days the rate of decrease is very slow. The decrease in activity tends to a logarithmic form, so it would seem reasonable to predict that, after use for one year, the carbon would still have about fifty per cent of its original activity.

Continuous oxidation tests were done with a 200-gram sample of activated carbon which was aerated in a reaction cylinder containing 750 ml of solution. Feed solution was pumped into the reaction cylinder continuously, and clear oxidized solution was collected from the settling tube. Changes were made successively in the iron concentration, in the flow rate, and in the temperature of the solution. The results of these tests are given in Table III.

TABLE III  
Continuous Oxidation of Acidic Ferrous Sulphate Solutions  
(22 molar carbon, varying iron concentrations)

Test conditions	Test number			
	(1)	(2)	(3)	(4)
Feed solution, Fe <sup>++</sup> , (g/l.)	25.5	8.64	25.6	19.9
Feed solution flow rate, (ml/hr)	152	151	52.7	44.4
Reaction temperature, (°C)	25	25	25	63
Test duration, (days)	4	3	5	6
Reaction cylinder residence time, (hr)	4.17	4.20	12.0	14.3
Oxidized overflow, Fe <sup>++</sup> , (g/l.)	14.2	1.59	5.95	2.37
Fe <sup>++</sup> oxidation, (%)	44.4	81.6	76.8	88.1
Fe <sup>++</sup> oxidation, (g/hr)	1.7	1.1	1.0	0.8
10 <sup>5</sup> k <sub>exp</sub> [Fe <sub>T</sub> ]/[C], (min <sup>-1</sup> )	4.7	4.6	4.1	4.0

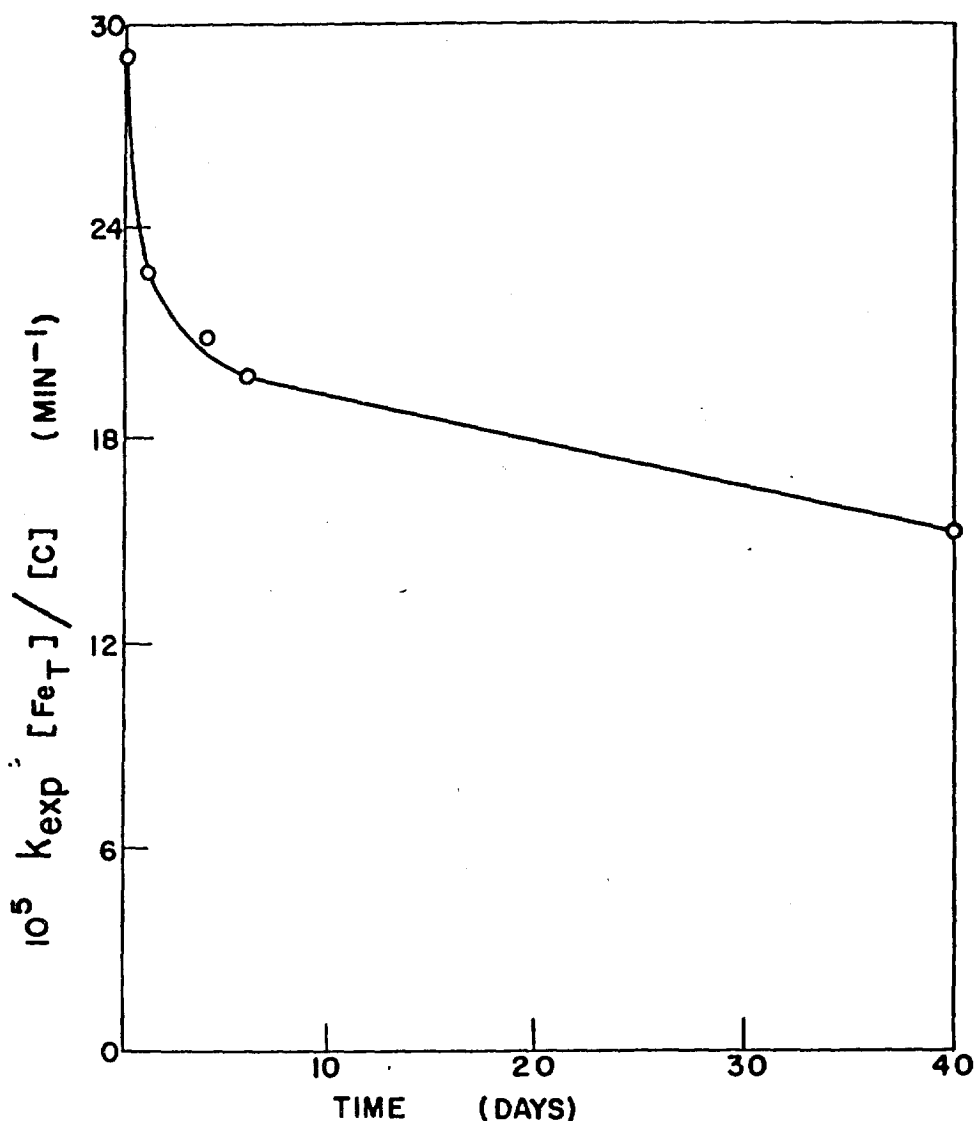


Fig. 6. Effect of continuous use of carbon on reaction rate adjusted to 1 molar carbon and 1 molar total iron.

From Table III it is evident that high percentage oxidations were obtained by using slow flow rates or dilute feed solutions, whereas, on a weight basis, more iron was oxidized when a faster solution flow rate was used. The rate constant for 1 molar concentrations of carbon and total iron, was similar for all tests.

To determine whether the results of batch experiments could be used to predict the results of continuous experiments, a batch experiment was done with amounts of carbon and solution comparable with

those used in test 2 in Table III. The time for 82 per cent oxidation was 3.6 hours in the batch test versus 4.2 hours in the continuous oxidation test. This agreement showed that batch tests should be useful in predicting the amount of oxidation obtainable in a continuous experiment.

To determine the effectiveness of a simple apparatus design which would be applicable to large-scale, multi-unit equipment, batch experiments were done with a stainless steel mesh disc containing granular activated carbon. The disc was partly immersed in solutions of 0.018 molar total iron and was rotated at various speeds for 30-minute

TABLE IV  
Effect of Disc Rotation Speed on Oxidation Rate  
(12.7 molar carbon, 0.018 molar total iron, 0.5M acid, room temperature)

Disc rotation speed, (rpm)	1.6	40	21	30	53
Per cent of Fe <sup>++</sup> oxidized/30 min	36	70	78	78	52
10 <sup>5</sup> $k_{exp}[Fe_T]/[C]$ , (min <sup>-1</sup> )	2.1	5.6	7.1	7.1	3.4

periods. The rates of oxidation for various speeds are given in Table IV which shows that there is a wide range of rotation speeds at which a high degree of oxidation can be achieved. This type of apparatus would be suitable for on-stream continuous oxidation of acidic ferrous sulphate solutions

## DISCUSSION AND CONCLUSIONS

The foregoing experiments have shown that the rate of oxidation of ferrous ion in sulphuric acid solutions varies directly with the concentration of dissolved oxygen, the amount, fineness and activity of carbon catalyst and the concentration of ferrous ion, and inversely with the sum of the concentrations of ferrous and ferric ions. At acidities between 0.1 and 1 molar, the reaction rate changes almost linearly with changes in acidity. However in the range of acidity from 3 to 10 molar, the rate decreases almost linearly with additional increases in acidity. The rate of oxidation has a small temperature coefficient in the range 1 to 24°C. At temperatures between 40 and 90°C, the rate is almost unaffected by temperature changes.

Neglecting this small but complex influence of changes in temperature, the rate of disappearance of ferrous ion by oxidation may be

expressed by the equation:

$$\frac{-d[\text{Fe}^{++}]}{dt} = \frac{k \cdot [\text{O}_2] \cdot [\text{C}] \cdot f[\text{H}_2\text{SO}_4] \cdot [\text{Fe}^{++}]}{[\text{Fe}^{++} + \text{Fe}^{+++}]} \dots \quad (2)$$

Except for a difference in the acid dependency of the reaction rate, this equation is identical with the one postulated by Posner<sup>7</sup> for the catalytic oxidation of ferrous ion in aqueous hydrochloric acid solutions in the presence of activated sugar charcoal.

Except for a brief initial reaction period, the experimental results are consistent with the expected behaviour for a surface reaction in which the surface is sparsely covered with oxygen, acid, and ferrous and ferric ions.<sup>9</sup> It is assumed that ferrous ions are adsorbed in small amounts on selected sites for which ferric ions compete equally. The extent of ferrous ion adsorption is controlled by the fraction of total dissolved iron in the ferrous state. Hydrogen ions are adsorbed also, but more strongly than the other reactants. It is reasonable to expect that when the concentration of sulphuric acid exceeds some critical value, the increased adsorption of acid decreases the adsorption of the other reactants and, consequently, decreases the rate of oxidation.

The activity of the carbon as a catalyst is retained for long periods. None of the substances occurring normally in uranium leach liquors acts as poison to the carbon activity. Oxygen, which is adsorbed in amounts proportional to the amount in solution, probably reacts as a diradical  $-\text{O}-\text{O}-$ ,<sup>10</sup> in conjunction with hydrogen ions, to extract electrons from the adsorbed ferrous ions. Because carbon is a good electrical conductor, it is probably not essential that the electron exchange occur at adjacent adsorption sites.

#### Acknowledgement

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### Discussion

**I. H. Warren:**\* Have the authors considered the possible role of residual quinoid structures, remaining or present in the various carbon samples, in the oxidation process?

**G. Thomas and T. R. Ingraham:** According to the literature, the surface of activated carbon has a variety of organic functional groups containing oxygen and hydrogen. The activated carbon has been described as a disordered agglomerate of layers of large polynuclear benzenoid hydrocarbons. It is also known that hydroquinone-type compounds are useful in the production of hydrogen peroxide, which, in turn, can oxidize ferrous ion. Consequently, hydroquinone was added in concentrations from 0.01 to 1 g/l. to aerated acidic ferrous sulphate solutions. Hydroquinone by itself was of little use as a catalyst and it was found to interfere with the catalytic action of activated carbon. Further experiments to identify the exact functional groups which may be responsible for the catalytic action of activated carbon were considered to be outside the scope of the main investigation.

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