

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLORADO COLLEGE AND THE COASTAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

STUDIES ON ATMOSPHERIC OXIDATION. II. THE KINETICS OF THE OXIDATION WITH SODIUM FERRO-PYROPHOSPHATE

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In a recent publication Spoehr has shown that sodium ferro-pyrophosphate acts as a catalyst in the atmospheric oxidation of certain organic materials. In his discussion he has made no assumption as to the mechanism of the process. In the preceding article in *THIS JOURNAL* an outline¹ of the oxidation process is given, showing three possible ways in which the oxidation may take place. It is shown there that surface catalysis must be eliminated. It is the object of the present study to bring evidence bearing on the two remaining mechanisms, namely, electronic oxidation and reduction of the catalyst, and autoxidation.

These two possible ways in which the iron compound may oxidize any acceptor are as follows. 1. By oscillation between an oxidized and a reduced state in the presence of the acceptor, consecutive reactions: (a) $4\text{Fe}^{++} + \text{O}_2 = 4\text{Fe}^{+++} + 2\text{O}^{--}$; (b) $\text{Fe}^{+++} + \text{B} = \text{Fe}^{++} + \text{B}^+$. 2. By forming an intermediate compound with molecular oxygen and transmitting part of the oxygen to the acceptor by the process known as autoxidation, a coupled reaction: (a) $\text{Fe}^{++} + \text{O}_2 = \text{Fe}^{++}(\text{O}_2)$; (b) $2\text{Fe}^{++}(\text{O}_2) + \text{B} = \text{Fe}_2\text{O}_3 + \text{BO}$, where B represents the acceptor used in the oxidation.²

Two lines of reasoning upon which we may base our conclusions regarding the mechanism of the oxidation process are (1) the order of the reaction and (2) the amount of oxygen absorbed.

The Order of the Reaction

If the process is one of autoxidation, it will be readily seen that when the oxygen pressure remains constant the rate of the reaction should conform to that of the first order with respect to the ferrous compound. In first-order reactions the half period is constant, independent of the initial concentrations. By determining whether the half period remains constant, while varying the initial concentrations of sodium ferro-pyrophosphate over a considerable range, we can show what the order of the reaction is. Results obtained on the kinetics of the oxidation of the catalyst alone show that the half period is a constant for the reaction; therefore the reaction is one of the first order, indicating that we are dealing with a process of autoxidation.

¹ Spoehr, *THIS JOURNAL*, **46**, 1494 (1924).

² For a general discussion of this problem and bibliography see Baudisch and Welo, *J. Biol. Chem.*, **61**, 261 (1924).

To carry the oxidation on at constant pressure of oxygen and at the same time measure the rate of absorption, it was necessary to devise a special apparatus. This apparatus made it possible for the solution to be kept saturated with the gas throughout the duration of the experiment. Violent agitation of the absorption vessel D, Fig. 1, mounted on a mechanically driven shaker and shaken at 120 strokes per minute, threw the liquid onto the sides and into the interior of the flask, giving maximum interface between the liquid and the oxygen.

An actual experiment will be described to show the manipulation of the apparatus.

Two molecular equivalents of sodium pyrophosphate (4.82 g.) were dissolved in 100 cc. of water and the solution was poured into flask D. One molecular equivalent of ferrous sulfate (1.0 g.) dissolved in 50 cc. of water was introduced into the dropping funnel E and then the whole apparatus was evacuated through the tube I. Oxygen was then admitted to the apparatus from the oxygen tank G. The carbon dioxide contaminating the gas was removed by the soda-lime tube F. When the manometer C indicated that the oxygen pressure was slightly greater than atmospheric pressure, the oxygen was shut off and the whole system evacuated again. This was repeated at least twice so that the apparatus was filled with

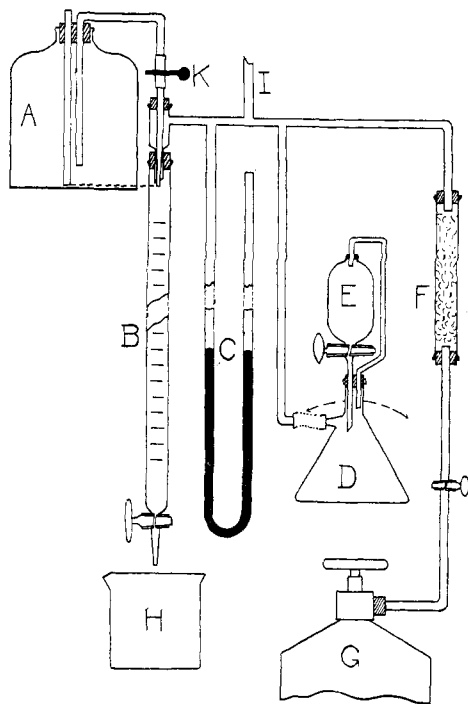


Fig. 1.

pure oxygen. During this process the pinch-clamp K was closed so that water from A would not be drawn into Buret B. To insure atmospheric pressure in the apparatus a slight excess of oxygen was admitted to the system and the excess of pressure relieved through a stopcock (not shown in the diagram) opening from the outside into D. When all was ready for the run, Pinch-cock K was opened, water adjusted in the buret so that it registered on the graduations, and the tube leading from A to the outside adjusted, so that the water in the siphon between A and B was just balanced at atmospheric pressure. A slight decrease in pressure on the inside of the apparatus would then cause water to flow into the buret until the original pressure was recovered, and the volume measured would be equal to that removed from the system. The ferrous sulfate solution was then run from E into D by opening the stopcock, the shaker was started and when the first drop of water fell from the siphon a stop watch set off. By taking the initial reading in the buret and the readings at definite time intervals, it was possible to follow the course of the reaction. From these data the order of the reaction could be computed. The accuracy of the set-up was demonstrated by removing known volumes of gas and determining the volume of water drawn into B necessary to equalize the pressure. The results obtained showed that the apparatus was entirely reliable.

No arrangement was made for temperature or pressure control, but the temperatures and pressures were recorded for each experiment. The variations were as follows: temperature $21 \pm 1^\circ$; barometer 607 ± 4 mm. In any given experiment the conditions were more nearly constant than this, but in comparing different experiments the maximum error should be based on these observations. This means that the amount of oxygen absorbed may vary by 1.5 cc., because the approximate volume of the apparatus was 400 cc.

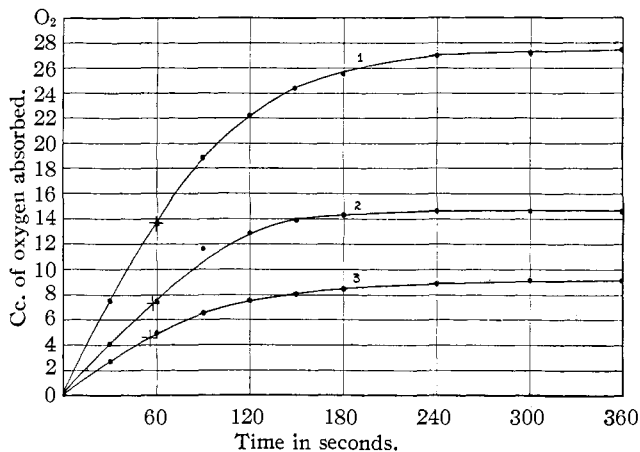


Fig. 2.—Curve 1. Rate of absorption for 1.0 g. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 4.82 g. of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$. Curve 2. Rate of absorption for 0.5 g. of the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 2.41 g. of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$. Curve 3. Rate of absorption for 0.3 g. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and the corresponding amount of the $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$. The crosses indicate the half periods of the reactions.

Three different concentrations of catalyst were used. The rate of absorption of oxygen is plotted in Fig. 2, and the half period is indicated by a cross. The values of the half period are taken from the graph and tabulated in Table I along with the concentrations used in each experiment.

TABLE I
THE HALF PERIOD OF THE REACTION

Curve	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, g.	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, g.	Half period, seconds
1	1.00	4.82	59.0
2	0.50	2.41	57.5
3	.30	1.45	56.0

The volume of the solution in every case was 150 cc. The fact that the half period remains so nearly constant, despite the factors militating against it, proves that the process is undoubtedly of the first order.

When the velocity constant is calculated over the whole reaction period, it is found that there is a considerable variation in the value. This can

be accounted for by the fact that we have here a series of consecutive reactions, the first of which is the formation of the "moloxide,"³ a ferrous-oxygen compound, and the second which is an oxidation by the "moloxide" of a portion of the remaining ferrous compound. Not enough facts are available for the evaluation of the separate velocity constants. It may be of significance in this connection that stoichiometrically the moloxide, FeO-O_2 , is equivalent to a ferrate.

The Amount of Oxygen Absorbed

If the process is one of catalytic nature, the amount of oxygen absorbed will be controlled by the amount of acceptor present, rather than by the initial concentration of the catalyst. If, however, it is based on autoxidation alone, the amount of oxygen absorbed will be approximately double that absorbed by the oxidator alone. Two acceptors were used, sodium sulfite and potassium arsenite, and the amount of oxygen absorbed was measured in each case. It will be observed that while the oxidation of sodium sulfite is catalytic, because with either the ferri or ferro compound the reaction proceeds, yet the actual process is probably one of autoxidation. The potassium arsenite, on the other hand, is oxidized only by autoxidation, because the ferro compound alone is effective.

The procedure was essentially that used in the absorption experiments with the catalyst itself, except that the sodium sulfite or potassium arsenite was dissolved in the same solution as the sodium pyrophosphate.

The experiments with sodium sulfite showed that the iron compound acted as a catalyst, because the amount of oxygen absorbed, in excess of that necessary to oxidize the catalyst itself, was dependent on the sulfite present. The catalytic effect was further verified by starting with the ferri derivative, which would not absorb oxygen of itself, and getting the same oxygen absorption that was observed in the case of the ferro derivative. The experimental results are given in Table II.

TABLE II

THE VALENCE OF OXYGEN ABSORBED				
Sodium sulfite, g.	Iron salt, g.	O ₂ absorbed, cc.	Calcd. for sulfite	Obs. for sulfite
0.210	0.50 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	40.0	24.9	26.4
.210	.30 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	29.5	24.9	21.3
.210	.30 $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	23.3	24.9	23.3

From these observations we can conclude that the oxidation is a catalytic phenomenon. Sodium sulfite is oxidized very slowly by oxygen as shown by Curve 6, Fig. 3. The hastening action of the ferric salt is seen in Curve 5 of the same figure, and of the ferrous derivative in Curve 4.

³ "Moloxide" is the term applied to a compound between molecular oxygen and the reduced form of the iron compound.

Since Curve 4 follows the autoxidation curve, Curve 1, more closely than does Curve 5, it seems probable that actually the oxidation of the sulfite in the presence of the ferrous salt is an autoxidation process, at least in the initial stages.

In the study of the potassium arsenite oxidation, however, we find quite a different relationship. The results obtained corroborate the findings of Manchot, that the arsenite was oxidized in the presence of ferrous hydroxide as the autoxydator.⁴ Here we find that the amount of oxygen is not proportional to the amount of arsenite present, but is twice that used by

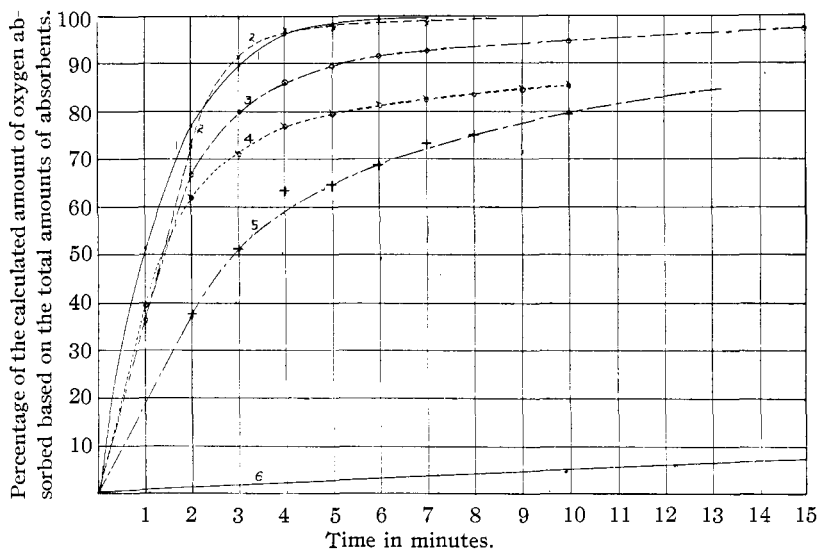


Fig. 3.—Curve 1. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 1.0 g.; and $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, 4.82 g. Curve 2.^a $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 g.; $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, 2.41 g.; KAsO_2 , 0.490 g. Curve 3. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 g.; $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, 2.41 g.; Na_2SO_3 , 0.210 g. Curve 4. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.3 g.; $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, 1.44 g.; Na_2SO_3 , 0.210 g. Curve 5. $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, 0.3 g.; $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, 1.44 g.; Na_2SO_3 , 0.210 g. Curve 6. Na_2SO_3 , 0.202 g.

^a In this reaction the theoretical amount was taken to be twice that which the catalyst itself would absorb.

the ferro derivative itself. Furthermore, no oxygen absorption takes place when the ferri compound is substituted for the ferrous salt. Both of these results point to the fact that autoxidation is taking place.

First we must determine the amount of oxygen absorbed by the sodium ferro-pyrophosphate. One g. of ferrous sulfate heptahydrate, in two experiments, absorbed 27.5 cc. and 27.6 cc. of oxygen, respectively, as compared with 27.4 cc. calculated. The calculated value was based on the equation $4\text{Fe}^{++} + \text{O}_2 = 4\text{Fe}^{+++} + 2\text{O}^{--}$.

Now we are in a position to discuss the oxygen absorbed by the arsenite.

⁴ Manchot, *Z. anorg. Chem.*, 27, 420 (1901).

KAsO ₂ , g.	FeSO ₄ ·7H ₂ O, g.	O ₂ abs., cc.	Calcd. for 2FeSO ₄ ·7H ₂ O, cc.
0.490	0.50	26.7	27.4
.490	.30	17.2	16.4

From these values it is readily seen that those calculated on the basis that autoxidation was taking place are in very good agreement with those actually found. Curve 2, Fig. 3, shows the rate at which absorption takes place. From the figure it is evident that this absorption curve follows very closely that of the catalyst itself, showing that we are dealing again with an autoxidation.

Summary

The present investigation was carried out to show, if possible, what the mechanism of the oxidation process is, using ferro-pyrophosphate as catalyst. The conclusion has been reached that in the oxidation of potassium arsenite and sodium ferro-pyrophosphate there is an intermediate "mol-oxide" formed, which is the active oxidizing agent. In the case of the oxidation of sodium sulfite, the mechanism can be explained either on this hypothesis or by assuming the oscillation of the iron salt between its two valences. From the shape of the absorption curve in the initial stages, however, it seems likely that here too the oxidation is by the iron "mol-oxide." These views are substantiated by quantitative measurements, and by the order of the reaction.

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TEMPERATURE-CONDUCTANCE CURVES OF SOLID SALTS I. THE HALIDES OF SODIUM

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Temperature-conductance curves of fused salts and of solutions are difficult to interpret since both the number of ions and the ion mobilities change simultaneously with temperature. On the other hand the electrolytic conductance of a solid salt at a given temperature depends only upon the number of free ions present in the lattice at that temperature; the mobility of these ions may be assumed to be constant, at least for temperatures remote from the melting point.

The first important generalization relating temperature to the conductance of solids was made by Rasch and Hinrichsen¹ and independently by J. Königsberger.² It was observed that a linear relation resulted in all cases when $\log \kappa$ (specific conductance) was plotted against $1/T$ (the

¹ Rasch and Hinrichsen, *Z. Elektrochem.*, **14**, 41 (1908).

² Königsberger, *Physik. Z.*, **8**, 833 (1907).