

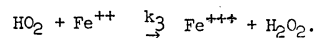
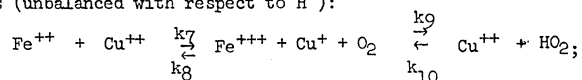
At a given pH, the rate of reaction decreases in the series pyrophosphate, phosphate, chloride, sulfate, and perchlorate.

Cher and Davidson, 1955 (24) examined the kinetics of the $\text{Fe}^{+2} - \text{O}_2$ system in phosphoric acid solution. They observed that the rate law for the Fe^{+2} , O_2 reaction in H_3PO_4 , NaH_2PO_4 solutions (1.0 - 1.1 M) is:

$$-d(\text{Fe}^{++})/dt = k(\text{Fe}^{++})\text{Po}_2 (\text{H}_2\text{PO}_4^-)^2, \text{ where}$$

$$k = 4.5 (\pm 0.3) \text{ atm}^{-1} \text{ mole}^{-2} \text{ liter}^2 \text{ hr}^{-1} \text{ at } 30^\circ.$$

The activation energy is 20 (± 2) kcal. There is some heterogeneous reaction on a glass wool surface, but it is believed that the above rate data apply to the homogeneous reaction. There is no inhibition by added Fe^{+++} . A one-electron reaction mechanism with the rate-determining step, $\text{Fe}^{++} + \text{O}_2 \rightarrow \text{Fe}^{+++} + \text{HO}_2$, is consistent with the results. The marked catalytic effect of added Cu^{++} can be explained by the reactions (unbalanced with respect to H^+):



At 30° , $\mu = 1 \text{ M}$, $(\text{H}_2\text{PO}_4) = 0.434 \text{ F}$, $(\text{H}_2\text{PO}_4^-) = 0.302 \text{ F}$, $\text{Po}_2 = 150 \text{ mm}$,

$k_7 = 1.0 \times 10^3 \text{ M}^{-1} \text{ hr}^{-1}$, $k_9/k_8 = 5.1 \times 10^{-2} \text{ M atm}^{-1}$, and $k_{10}/k_3 = 23$.

Stumm and Lee, 1961 (25) report that the rate of ferrous iron in bicarbonate solutions follows the law $-d[\text{FeII}]/dt = k[\text{FeII}]\text{Po}_2[\text{OH}^-]^2$.

Thus, the oxidation of ferrous iron is directly related to the available oxygen, the presence of complexing anions, and the concentration of various catalytic materials, such as Cu^{+2} .

Lamb and Elder, 1931 (26) also report catalytic activity due to platinum black and charcoal.