The Mechanism of Oxidation of Ferrous Sulfate by γRays in Aerated Water

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The Mechanism of Oxidation of Ferrous Sulfate by γ-Rays in Aerated Water

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WE have studied the oxidation of ferrous ions by γ-rays absorbed in dilute aqueous solutions of ferrous ammonium sulfate saturated with air and in solutions from which the air was removed by exhaustive pumping. We have been particularly interested in establishing the role of oxygen in the mechanism of this oxidation.
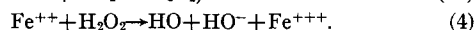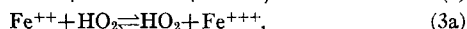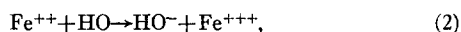
The most feasible primary process in both aerated and air-free solutions appears to be

$$H_2O \xrightarrow{\gamma\text{-rays}} HO+H, \tag{1a}$$
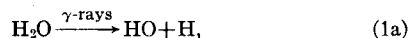
followed in aerated solutions by

$$H+O_2 \rightarrow HO_2. \tag{1b}$$

The oxidation of ferrous ions in solution then proceeds according to reactions originally proposed to account for the ferrous ion catalyzed decomposition of aqueous hydrogen peroxide.[1]

$$Fe^{++}+HO \rightarrow HO^-+Fe^{+++}, \tag{2}$$

$$Fe^{++}+HO_2 \rightleftharpoons HO_2+Fe^{+++}, \tag{3a}$$

$$H^++HO_2^- \rightleftharpoons H_2O_2, \tag{3b}$$

$$Fe^{++}+H_2O_2 \rightarrow HO+HO^-+Fe^{+++}. \tag{4}$$

Reactions (3a), (3b), and (4) combine to oxidize ferrous ions quantitatively in strongly acid solutions. We have found that in solutions 0.1 N or higher in sulfuric acid ferrous ions are oxidized quantitatively by sufficiently large doses of γ-radiation. In these studies we have made our solutions 0.8 N in sulfuric acid to conform to earlier work.[2-4] The solutions were irradiated with the γ-rays from a 2-curie radium source.

Our experimental results are summarized in Fig. 1. The yield of the oxidation is expressed in terms of the number of ferrous ions oxidized per 100 ev of γ-ray energy absorbed by the solution. Since the ferrous sulfate system has been accurately established by Miller[3b] as a dosimeter for x- and γ-radiation, it was possible to estimate the energy absorbed in our samples merely by determining the number of ferrous ions oxidized in a sample of suitable concentration.
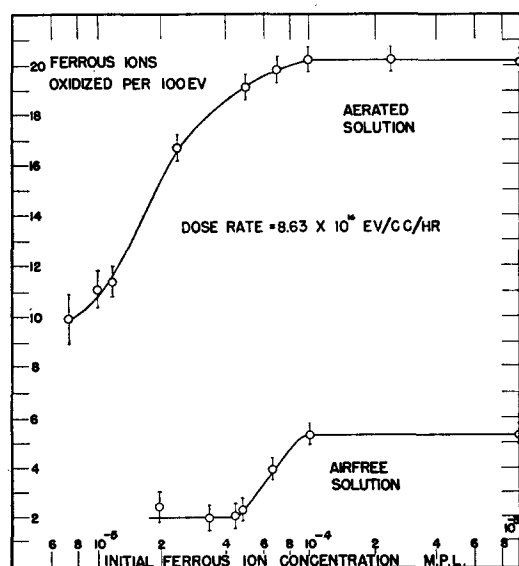

FIG. 1. The yield of ferrous ions oxidized per 100 ev of γ-ray energy absorbed in aqueous solutions 0.8 N in H_2SO_4 as a function of the initial ferrous ion concentration in (a) aerated solutions and (b) solutions from which the air had been removed by exhaustive pumping.

The yields were determined by plotting the amount of oxidation as a function of the energy absorbed in the solution and taking the tangent to this curve at the origin. Each point on Fig. 1 represents the average of a number of experiments.

Above a starting concentration of 10^{-4} m.p.l. the yield of oxidation was independent of the ferrous ion concentration as has been well established.[2-4] Below this concentration the yield falls off with concentration presumably because of the recombination of HO and HO$_2$. The kinetic consequences of recombination have been studied and will be reported elsewhere.

We wish to point out here that the reduction of the yield above 10^{-4} m.p.l. by a factor of approximately 4 when the oxidation is performed in air-free water can be predicted from Eqs. (1)–(4). Inspection of these equations will show that for every free radical pair formed in aerated solution 4 ferrous ions are oxidized. In air-free water no HO$_2$ could be formed by (1b) and the oxidation should be described by reaction (2). Only one ferrous ion would then be oxidized per free radical pair formed.

A summary by Miller[3a] of previous work on this subject shows that attempts to remove oxygen from ferrous sulfate solutions have reduced the oxidation yield by no more than a factor of 2.6. We attribute this to incomplete removal of oxygen. We have found great difficulty in removing oxygen from these solutions, and have noticed that the difficulty appears to increase with increasing ferrous ion concentration.

A detailed account of this work will be submitted to the Canadian Journal of Research. We are very much indebted to Dr. Miller for discussions and for access to his unpublished results.

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[2] H. Fricke and S. Morse, (a) Am. J. Roentgenology and Radium Therapy **18**, 430 (1927); (b) Phil. Mag. **7**, 129 (1929).
[3] N. Miller, (a) Nature **162**, 448 (1948); (b) J. Chem. Phys. (to be published).
[4] N. A. Shishacow, Phil. Mag. **14**, 198 (1932).

Surface Tension of Small Droplets from Volmer and Flood's Nucleation Data

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CURRENT theoretical work on the effect of droplet size on surface tension predicts that the surface tension of a droplet smaller than about 200A in diameter should be appreciably different from the value obtained by measurements on the bulk phase. Using a quasi-thermodynamic approach, Tolman[1] predicted a decrease in surface tension at small droplet sizes, and this result is supported by a statistical mechanical treatment due to Kirkwood and Buff.[2] Martynov,[3] on the other hand, takes the view that surface tension should increase with droplet curvature.

As yet, there seems to be no direct experimental method for confirmation of these theoretical results, but the authors suggest that insight into this problem might be gained by a consideration of nucleation phenomena. Volmer and Flood[4] have measured the critical supersaturation pressure necessary for spontaneous production of fog at a given temperature for a series of vapors by an adiabatic expansion method. Their data are well described in terms of directly measured properties of the substance by means of the kinetic treatment of Becker and Döring.[5,6] According to their treatment, the critical size for a stable droplet is about 20A in diameter. This means that an embryo droplet that has attained this size through a series of statistical fluctuations will, in general, grow to become a macroscopic drop of liquid. Further, the exponential function expressing nucleation rate is such that critical pressure necessary for spontaneous nucleation of droplets from

TABLE I.

Vapor	Number of molecules in stable nucleus	Nucleus radius r in angstroms	σ^* / σ_0	P/P_∞ calculated using σ	P/P_∞ calculated using σ_0	P/P_∞ measured
Water, 275.2°K	80.0	8.9	0.82	2.9	4.2	4.2 ±0.1
Water, 261.0°K	72.0	8.0	0.80	3.2	5.0	5.0
Methanol, 270.0°K	32.0	7.9	0.80	1.5	1.8	3.0
Ethanol, 273.0°K	128.0	14.2	0.88	2.0	2.3	2.3
n-propanol, 270.0°K	115.0	15.0	0.88	2.6	3.2	3.0
Isopropyl alcohol, 265.0°K	119.0	15.2	0.88	2.4	2.9	2.8
n-butyl alcohol, 270.0°K	72.0	13.6	0.88	3.5	4.5	4.6
Nitromethane, 252.0°K	66.0	11.0	0.85	4.2	6.2	6.0
Ethyl acetate, 242.0°K	40.0	11.4	0.85	6.4	10.4	8.6 to 12.3**

* Ratio of surface tension predicted from Tolman's results to the surface tension measured in the bulk liquid phase.
** The higher value is assumed to be more nearly correct.

supersaturated vapor is strongly dependent on the surface tension. This is illustrated by Fig. 1 where calculated values of the ratio of critical supersaturation pressure to equilibrium vapor pressure of the bulk liquid phase, P/P_∞, are plotted as a function of assumed values of surface tension, σ, for the case of condensing water vapor at 275.2°K. The surface tension values are assumed for the purpose of calculating P/P_∞ as a function of σ by means of the Becker and Döring[5] treatment. It is seen that a value of surface tension very close to that measured for the bulk liquid phase is required if calculated and experimental values of P/P_∞ are to agree.

The present authors have computed the critical droplet size for a number of vapors by the Becker and Döring[5] method, using the measured critical supersaturation ratio and the value for surface tension measured on the bulk liquid phase. Then, using Tolman's[1] theoretical results for decrease in surface tension with droplet radius, a value for surface tension at the critical droplet size was obtained. This new value of σ was used to calculate P/P_∞ for comparison with the experimental quantity. The results are summarized in Table I. It is seen that in most of the cases fair agreement is obtained between measured values of P/P_∞ and values calculated using the surface tension σ_0 as measured on the bulk liquid phase. On the other hand, values of P/P_∞ calculated
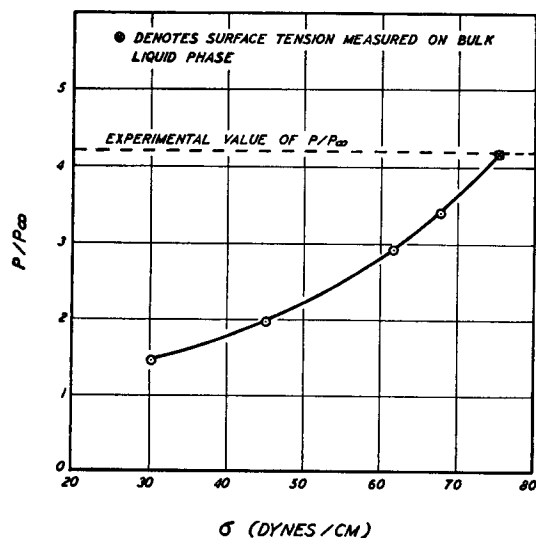

FIG. 1. Calculated values of critical supersaturation pressure ratio *versus* assumed values of surface tension for the case of condensing water vapor at 275.2°K.

using the surface tension σ, as predicted from Tolman's results, are in poor agreement with the data. The inconsistency between the work on nucleation and the current theoretical studies on surface tension of droplets is evident. It may be that some revision of the present theoretical approach is in order.

It is interesting to note that in the two anomalous cases, methanol and ethyl acetate, the number of molecules per stable nucleus is considerably smaller than in the other cases. Further, these anomalies could be resolved by employing a value for surface tension somewhat higher than that measured on the bulk liquid phase.

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[6] M. Volmer, *Kinetik der Phasenbildung* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1945), Chapter 4.

A Theoretical Calculation of the Parameters α and β Used in the Molecular Orbital Method

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THE molecular orbital method in the usual L.C.A.O. approximation enables us to express the energy of the r-electrons in two parameters: the Coulomb integral

$$\alpha \equiv \int \varphi_1 H \varphi_1 d\tau$$

and the exchange integral

$$\beta_{12}' \equiv \int \varphi_1 H \varphi_2 d\tau - S_{12}\alpha', \quad S_{12} = \int \varphi_1 \varphi_2 d\tau.$$

φ_1 and φ_2 are the P_z-orbitals of adjacent C atoms.

Hitherto β_{12}' (and α) were empirical parameters. There is, however, a large discrepancy between the values calculated for β_{12}' from resonance energies and from electronic-transition processes. We have therefore tried to calculate α and β_{12}' theoretically to get some insight into the nature of this discrepancy.

For benzene we put for the Hamilton operator:

$$H = -\frac{h^2}{\delta r^2 m}\nabla^2 + \sum_k H_k + V_r.$$

For the part

$$-\frac{h^2}{\delta r^2 m}\nabla^2 + \sum_k H_k,$$

we refer to Goeppert-Mayer and Sklar;[2] V_r is the potential energy of one r-electron (ν) in the field of the other five r-electrons (μ) which are supposed to be distributed among the six P_z-orbitals of the C atoms. The electron is also supposed to be equally distributed, which is numerically equivalent to a localization on one carbon atom. This gives

$$V_r = \tfrac{5}{6}e^2 \sum_\mu \frac{1}{r_{\nu\mu}} \quad \text{and} \quad \int \varphi_1(\nu) V_r \varphi_2(\nu) d\tau = V_r \cdot S_{12}.$$

For this calculation of α and β_{12}' we further need integrals as

$$\int \varphi_i(\nu) \varphi_j(\nu) H_k(\nu) d\tau$$

and

$$\int \varphi_i(\nu) \varphi_j(\nu) \frac{e^2}{r_{\nu\mu}} \varphi_k^2(\nu) d\tau.$$

They are reduced to known integrals by substituting

$$S_{ij} \int \varphi_m^2(\nu) \cdots \quad \text{for} \quad \int \varphi_i(\nu) \varphi_j(\nu) \cdots.$$

$\varphi_m(\nu)$ is a virtual P_z function located midway between the original i and j functions.[3,4]