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THE AQUEOUS OXIDATION OF
ATMOSPHERIC SULPHUR DIOXIDE

A Thesis Submitted to the
University of Auckland for the
Degree of Doctor of Philosophy

by

Peter Brimblecombe

May 1973



A distillery.

सर्वद्वेषु विद्यैव द्रव्यमाहुस्तमम् ।
अहार्थत्वादनर्थात्वाकक्षयत्वाच्च सर्वदा ॥४॥

हितोपदेशः २००

ABSTRACT

The work has been divided and abstracted under three headings :

(1) The Absorption of Sulphur Dioxide by Aqueous Solution.

The rate of absorption of low concentrations of SO_2 ($\sim 500 \mu g.m^{-3}$) was examined, varying a number of parameters. The results were expressed as deposition velocities ($V_g = \text{flux} / \text{gas concentration}$). V_g did not vary with relative humidity. Deposition into acid solutions ($pH < 3$) was controlled by diffusion processes in the liquid film while under more alkaline conditions ($pH > 4$) the process was governed by the rate at which SO_2 could diffuse to the interface through the gas boundary layer. Oxidizing agents (e.g. H_2O_2) were found to increase the rate of diffusion in the liquid boundary layer. Salts generally exerted a more complex effect on liquid phase diffusion. V_g for SO_2 deposition into aqueous solution under calm conditions and at pH values expected in the atmosphere was calculated to be about 0.7 cm.s^{-1} from these experiments. Efflux of SO_2 from solution was examined at low pH values under boundary conditions similar to the deposition work. At high S(IV) concentrations in solution ($\sim 10^{-3} M$) the half lives for SO_2 desorption from solution were 600, 1020, 2200 s for pH values 2.0, 2.5, 3.0 respectively. The consequences of the experimental results are discussed with respect to the atmosphere at large and to scrubbing of flue gases. Poor absorption rates for SO_2 at low pH values suggested that sea water with its high pH would be an excellent scrubbing agent

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and its buffering ability was investigated. Experiments showed $10^{-3} M$ S(IV) could be absorbed with the pH dropping only as far as pH 5.5.

(2) The Oxidation of Sulphur Dioxide in Aqueous Solution

The rate of oxidation in $10^{-5} M$ of SO_2 solutions was examined. The results showed the reaction to be very sensitive to traces of metallic ions, which made it impossible to determine the uncatalysed rate. The half life for oxidation of S(IV) in ($10^{-5} M$) in triply distilled water was 36, 8, 5 hours at pH 4.6, 5.2 and 6 respectively. The rate increased upon addition of traces ($10^{-6} M$) of Fe(III) and Mn(II) ions (pH 4 - 5) while Cu(II) seemed to act as an inhibitor.

In solutions of ammonium sulphate Fe(III) was found to be an excellent catalyst. The reaction appeared to have a variable order with respect to S(IV) being 1st order at pH < 4 and 2nd order at pH > 5 . Results in potassium sulphate were similar, but the reactions somewhat slower. At pH > 5 the reaction was sensitive to the alkali used for neutralization, the oxidation rate being much greater if ammonium hydroxide was used rather than sodium hydroxide. Solutions of ammonium chloride and sodium bicarbonate showed a second order dependence on S(IV) concentration at high pH values. The Fe(III) catalysed oxidation was faster in 'chloride' solutions than in 'sulphate' solutions at pH < 4 .

A radical mechanism previously proposed by a number of workers was found to give considerable insight into the complex

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experimental results.

(3) The Dissolution of Iron from Ferric Oxide and Pulverized Fuel Ash

The aqueous oxidation of SO_2 requires the presence of a catalytic metal ion. The most abundant catalyst in the atmosphere would appear to be iron. However, it would have to be present in solution to be an effective homogeneous catalyst. The rates of dissolution of iron from Fe_2O_3 were investigated and found to be extremely slow even in the presence of H_2SO_4 or H_2SO_3 . The dissolution of iron from pulverised fuel ash (a possible atmospheric source of iron in polluted areas) is quite rapid even under only moderately acid conditions (pH 3.5) where solutions $1.9 \times 10^{-4} M$ in Fe(III) can be reached in a matter of 20 minutes. The high rate of dissolution is thought to arise from the fusing of iron oxides with other alkaline oxides in the furnace.

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