Chapter V

KINETICS OF OXIDATION OF S(IV) IN RAIN WATER
The oxidation of sulphur dioxide in water droplets accounts for many atmospheric phenomena. The formation of sulphuric acid in urban fog and rain water by this process plays a significant role in acid rain and other forms of atmospheric pollution. The fact that the transition metal ions catalyse the aqueous phase oxidation of S(IV) (SO₂ in equilibrium with water) suggests that this may also happen in atmosphere in rain water. Jung and Ryan (1958) proposed the mechanism for the oxidation of SO₂ involving the metal ion catalyst. The studies on the oxidation of SO₂ in rain water reveal that the high concentration of metal ions (Fe and Mn) are responsible for the high rates of oxidation in the rain water of urban atmosphere. The laboratory studies at high pH disclose a limited role of transition metals in the oxidation of S(IV), due to decrease in their solubility (Martin, 1994). But whether the rate constants and rate of reactions obtained in laboratory can be applied to the atmospheric reactions with reliance is doubtful (Hegg and Hobbs, 1978).

This has led us to carry out experiments as much as possible study in pure rain water under atmospheric condition, so that the result (the rate constant and the reaction rate) may readily be applied to the atmospheric condition. Here, rain water has been taken as reaction medium as well as catalyst carrier. No buffer solution has been used in this study, as buffering would shift the reaction condition away from the atmospheric condition. For conducting experiments at a fixed pH dilute NaOH and HNO₃ solutions were used. The pH was fixed before the beginning of reaction because pH-electrode is also supposed to enhance the rate of reaction (Clarke and Redojevic, 1983). The pH change during the reaction was small to be neglected (Grgic et. al., 1993).
5.1. DEPENDENCE OF REACTION RATE ON S(IV) CONCENTRATION

The concentration-time profiles of the oxidation of S(IV) at different initial concentrations of S(IV) in the rain water have been given in Figures 5.1 and 5.2. From these figures it is clear that the initial rate of oxidation of S(IV) decreases as the initial concentration of it decreases. The rate of reaction is very slow when S(IV) concentration is $2 \times 10^{-3}$ mol/l and very high when it is $8 \times 10^{-3}$ mol/l. The pH was kept constant (4.00) throughout the reactions.

The log-log plot of initial concentration of S(IV) versus initial rate of reaction has been shown in figure 5.3. The slope of the best linear fit line gives the order of reaction and the intercept, the rate constant at the constant pH. The rate expression at 30°C ($\pm 0.5$) that has been obtained on the basis of this plot is

$$\frac{d[S(IV)]}{dt} = k_1 [S(IV)]^{n_1}$$  \hspace{1cm} (5.1)

Where, $n_1 = 1.217$

$$k_1 = 9.837 \times 10^{-4} \text{ (M)}^{-0.217} \text{ s}^{-1}$$

The order of reaction with respect to S(IV) concentration turns out to be 1.217. In the context of this study it may be mentioned that the first order reaction has been reported by Clarke and Radojevic (1987), whereas, Penkett et. al. (1979) have reported the reaction order 3/2 in S(IV) concentration. The first order reaction has been reported by Clarke and Redojevic (1987) and a 3/2 order by Penkett et. al. (1979).
Fig. 5.1: Concentration-time profiles for the oxidation of S(IV) in Rain water.

Fig. 5.2: Concentration-time profiles for the oxidation of S(IV) in Rain water.
Fig. 5.3: Log-log plot of rate vs. S(IV) Concentration for the oxidation of S(IV) in rain water

Fig. 5.4: Concentration-time profiles for the oxidation of S(IV) in Rain water at different pH
5.2. pH DEPENDENCE OF REACTION RATE

The concentration-time profiles obtained on the basis of experiments conducted at different pH and constant initial S(IV) concentration for oxidation of S(IV) have been shown in Figure 5.4. The highest initial rate of reaction has been observed at pH 4.00 and the lowest at pH 5.50 in the pH range 4.00-6.50.

Figure 5.5 is the plot between the negative log of the reaction rate versus pH fitted to straight line. The slope of the line gives the order of reaction and the intercept gives the negative log of rate constant with respect to [H\(^+\)] in the experimental pH range at constant S(IV) concentration. The rate expression at 30°C (±0.5) temp. and 5x10\(^{-3}\) S(IV) concentration is

\[
\frac{d[S(IV)]}{dt} = k_2[H^+]^{n_2} \tag{5.2}
\]

Where, \(n_2 = 0.1664\) and \(k_2 = 1.03 \times 10^{-5} (M)^{0.8336} \text{ s}^{-1}\)

The order of reaction in the pH range 4.00-6.50 is found to be 0.1842. It may be recalled that the orders of reaction in the pH ranges 4.00-6.00 and 6.00-7.00 were 0.8781 and 0.4277 respectively. The rate constants in the respective pH ranges were 1.85 \times 10^{-10} (M)^{0.5049} \text{ s}^{-1} and 1.998 \times 10^{-5} (M)^{0.1991} \text{ s}^{-1}, whereas, in case of rain water it is 1.03 \times 10^{-5} (M)^{0.8336} \text{ s}^{-1}.
Fig. 5.5: Log-log plot of rate of oxidation of $\text{S(IV)}$ vs. $[\text{H}^+]$ concentration in rain water

Fig. 5.6: Concentration-time profiles for oxidation of $\text{S(IV)}$ in different rain waters ($\text{pH}=4.00$)
Fig. 6.7: Concentration-time profiles for the oxidation of S(IV) in different rain waters (pH=4.00)

Fig. 6.8: Concentration-time profiles for the oxidation of S(IV) in different rain waters at (pH=4.00)
4.3. GENERAL RATE EXPRESSION

On including [H⁺] dependence in the pH range 4.00-6.50 the rate law (5.1) becomes

\[
\frac{d[S(IV)]}{dt} = k [S(IV)]^n[H^+]^m
\]  
(5.3)

Where, \( n = 1.217 \),
\( m = 0.1664 \), and
\( k = 6.59 \times 10^{-3} (M)^{-0.3834} \text{ s}^{-1} \)

Clarke and Radojevic (1987) have reported a first order reaction in S(IV) concentration and a reaction order of -.514 in [H⁺] concentration for the oxidization of S(IV) in rain water.

5.3. REACTION RATE IN DIFFERENT RAIN WATERS

The experiments for obtaining the rate of oxidation of S(IV) in different rain water have been conducted at constant S(IV) concentration (5x10⁻³ mol/l) and pH 4.00. The concentration versus time profiles of these experiments has been plotted in Figures 5.6, 5.7 and 5.8. The initial rates of these reactions have determined with the help of best fit regression lines. The concentrations of the trace metals in rain waters important from the view point of reaction kinetics have also been determined. The rate and the concentrations of these trace metals have given in Table 5.1. From this table the dependence of the rate of reaction on the trace metals concentrations can be found.
Table 5.1: Rate of oxidation of S(IV) in different rain water along with the concentration of trace metals at S(IV) concentration $5 \times 10^{-3}$ mol/l, pH 4.00 and tempt. 30°C ($\pm 0.5$).

<table>
<thead>
<tr>
<th>Rain Water No.</th>
<th>Rate $\times 10^{-3}$ (mol/l/min)</th>
<th>Fe $\times 10^{-6}$ (mol/l)</th>
<th>Mn $\times 10^{-6}$ (mol/l)</th>
<th>Co $\times 10^{-6}$ (mol/l)</th>
<th>Cu $\times 10^{-6}$ (mol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>16.12</td>
<td>15.04</td>
<td>6.92</td>
<td>3.22</td>
<td>4.56</td>
</tr>
<tr>
<td>7</td>
<td>10.90</td>
<td>4.48</td>
<td>9.10</td>
<td>4.24</td>
<td>6.45</td>
</tr>
<tr>
<td>9</td>
<td>6.36</td>
<td>4.11</td>
<td>7.10</td>
<td>3.90</td>
<td>3.46</td>
</tr>
<tr>
<td>12</td>
<td>15.04</td>
<td>7.52</td>
<td>6.55</td>
<td>3.22</td>
<td>4.72</td>
</tr>
<tr>
<td>14</td>
<td>10.12</td>
<td>11.10</td>
<td>5.83</td>
<td>10.52</td>
<td>5.04</td>
</tr>
<tr>
<td>18</td>
<td>11.39</td>
<td>5.19</td>
<td>6.55</td>
<td>7.47</td>
<td>2.99</td>
</tr>
<tr>
<td>20</td>
<td>13.82</td>
<td>5.19</td>
<td>4.01</td>
<td>5.43</td>
<td>9.92</td>
</tr>
<tr>
<td>25</td>
<td>10.40</td>
<td>6.44</td>
<td>5.10</td>
<td>5.94</td>
<td>6.92</td>
</tr>
<tr>
<td>28</td>
<td>8.41</td>
<td>3.22</td>
<td>6.01</td>
<td>3.73</td>
<td>10.54</td>
</tr>
<tr>
<td>33</td>
<td>12.49</td>
<td>4.83</td>
<td>4.73</td>
<td>5.77</td>
<td>5.82</td>
</tr>
<tr>
<td>Mixed</td>
<td>12.84</td>
<td>6.27</td>
<td>4.92</td>
<td>5.94</td>
<td>4.28</td>
</tr>
</tbody>
</table>

A correlation analysis of the rate and the trace metal concentrations shows good correlation between the rate and Fe concentration (correlation coefficient 0.55638). Surprisingly enough, the correlation coefficient for Mn was negative. This implies that Fe play catalytic role oxidation of S(IV) rather than of Mn. Earlier studies on the catalytic role of trace metals in the oxidation process have yielded different results. For example, Penkett et. al. (1979) have observed an opposite trend, i.e., a good correlation with Mn but poor with Fe, Clarke and Redojevic (1987) have shown a good correlation with Fe and Mn, both. However, Martin and Good (1991) have reported a zero order reaction in Mn$^{2+}$ concentration.
The study of oxidation of S(IV) in rain water confirms the catalytic role of dissolved metal ions in rain water, which is evident from the (i) rate expression of the uncatalysed oxidation (equation 4.4 and 4.5) and oxidation in rain water (equation 5.3) and (ii) from the correlation between the rate and Fe concentration. In case of uncatalysed oxidation the order of reaction in S(IV) concentration was 0.3731, whereas in rain water it is 1.217.