The main aim of the present study was to know the rate of aqueous phase oxidation of S(IV) under atmospheric conditions. Keeping in view this objective, the whole study was divided into four parts. For assessment of the aerosol catalysed oxidation of S(IV), it was necessary to estimate the concentration of potential catalysts (trace metal ions) in the aerosols (dry deposition) and rain water (wet deposition). The rate of uncatalysed aqueous phase oxidation of S(IV) was the second important aspect, which was required to be investigated, so that its contribution to the total rate of atmospheric oxidation could be estimated. The third part incorporated the rate study in the medium of rain water. To use rain water as reaction medium was prompted by the fact that it would be closer to the atmospheric system carrying the soluble trace metal ions within itself. The fourth was the kinetics study catalysed by free fall atmospheric aerosols. The main reason behind choosing free fall aerosols was that the amount which was needed for the kinetics study would not be sufficient if it would have been collected by high volume samplers.

The chemical analysis of wet deposition (rain water) reveals three facts. Firstly, the concentrations of alkali and alkaline earth metals in wet deposition in Delhi are found to be high, which indicate towards alkaline nature of atmosphere. Secondly, the concentration of the sulphate acid radicals is also high that implies the high content of atmospheric SO₂. And, thirdly, the high concentrations of trace metal ions Fe³⁺, Mn²⁺ point towards higher rate of oxidation of SO₂ into sulphate. The rain water at I.T.O. has higher concentration of alkali and alkaline earth metal ions as well as sulphate ions than that at J.N.U. But J.N.U. has an appreciably high concentration of Fe³⁺. The major sources of these ions may be wind blown soil, vehicular traffic and nearby industries at I.T.O., where as at J.N.U. the source could be wind blown soil.

103
The chemical analysis of soluble components of dry deposition (aerosols) yields approximately similar levels of high concentration of trace metals at I.T.O. and J.N.U.. The other two sites (Hauz Khas and Janakpuri), show a lower concentration of trace metal ions than at I.T.O. and J.N.U. This may be due to lack of industrial units in the vicinity. But high concentration of these metal ions in aerosols at J.N.U. is quite surprising. It is supposed to be due to wind blown sources. The alkali and alkaline earth metals’ concentrations in aerosols at I.T.O. and J.N.U. show a similar trend as observed in rain water samples at these places. Hauz Khas and Janakpuri show a lower concentration of these metal ions. The high concentration of $\text{SO}_4^{2-}$ in aerosol samples at I.T.O. reveals the high rate of oxidation of $\text{SO}_2$ at I.T.O. due to its higher concentration from vehicular sources. The high concentration of $\text{SO}_2$ at J.N.U. are supposedly due to diffusion and transport from the neighbouring areas and wind blown dust.

The high concentrations of alkali and alkaline earth metals in rain water and aerosols indicate towards higher buffer capacity of the atmospheric environment of Delhi. But the high concentration of $\text{SO}_4^{2-}$ ($\text{SO}_2$ emission) indicates towards the problem of acidification. The high $\text{SO}_2$ emissions in along with high content of trace metals (especially Fe) increase the probability of acid rain due to the formation of $\text{H}_2\text{SO}_4$.

The uncatalysed kinetics study in aqueous phase shows that the uncatalysed oxidation of S(IV) does take place under atmospheric conditions, but the rate of reaction is too slow to account for the atmospheric conversion of $\text{SO}_2$ to $\text{SO}_4^{2-}$. The rate of reaction is found to vary significantly in different pH ranges. In pH range 4.00-6.00, the rate expression is,
\[
d[S(IV)]/dt = k [S(IV)]^n [H^+]^m
\]

Where, \( n = 0.3732, \quad m = -0.8781, \) and \( k = 1.85 \times 10^{-10} \text{ (M)}^{0.5049} \text{ s}^{-1} \)

and in pH range 6.00-7.00, it is given by,

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

Where, \( n' = 0.3732, \quad m' = 0.4277, \) and \( k' = 1.998 \times 10^{-5} \text{ (M)}^{0.1991} \text{ s}^{-1} \)

From the rate constants in the two pH ranges it is clear that the uncatalysed oxidation of S(IV) is not very important from the atmospheric environment point of view, because the most prevalent atmospheric pH lies in the former pH range. In the pH range 4.00-6.00 the rate of reaction increases on increasing pH, i.e., decreasing [H+] concentration, but in the pH range 6.00-7.00 the rate of reaction increases with decreasing pH. Experiments were conducted at constant pH using buffer solutions (Na-acetate/acetic acid). The influence of increasing buffer concentrations (but keeping the ratio of Na-acetate and acetic acid constant, so that the pH remain constant) on the reaction rates was studied. The increase in buffer concentration decreases the rate of reaction. The buffer concentration of \( 1.5 \times 10^{-2} \text{ mol/l (Na-acetate)}, \) which was used in our experiments, does not have significant effect on the reaction rate. Some experiments were conducted using EDTA, which is strong ligand and readily forms complexes with trace metal ions. The rate of reaction is influenced
by EDTA, and the rate decreases on increasing its concentration to a considerable extent and follows approximately exponential trend. Here, one point is noteworthy, that though, the rate of reaction is low at high EDTA concentration, but it does not become zero. This confirms uncatalysed oxidation of S(IV) in aqueous phase even in absence of trace amount of catalysts.

The oxidation of S(IV) conducted in the rain water medium reveals that dissolved trace metals ions play a significant catalytic role in the oxidation reaction. The order of reaction in S(IV) concentration is more than 1 and the rate constant is also higher than that of uncatalysed oxidation. The correlation analysis between the rate of reaction in different rain waters and the water soluble trace metal concentrations shows a significant correlation between the rate and Fe ion concentration. But no significant correlation was observed between the rate of oxidation and other metal ion concentrations. The rate expression for the oxidation in the pH range 4.00-6.00 in rain water is found to be,

\[
d[S(IV)]/dt = k [S(IV)]^n [H^+]^m
\]

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

The aqueous phase oxidation of S(IV) catalysed by atmospheric aerosols reinforces the assertion that the presence of trace metal ions in aerosols act as catalyst in the reaction process. The order of reaction in S(IV) concentration is approximately 1, which is significantly higher than that of uncatalysed oxidation. The order of reaction in \([H^+]\) concentration is -0.1683 and in aerosols concentration is 0.1633. The
correlation analysis between the reaction rates of the oxidation catalysed by different aerosols and the water soluble trace metal ions concentrations reveal that only Fe ions are capable of acting as catalyst in the oxidation process. No significant correlation was observed with other metal ions concentrations. The reaction rate increases on increasing concentration of aerosols. The rate expression of the oxidation catalysed by aerosols is

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

Where, \( n = 1 \), \( m = -0.1683 \), \( p = 0.1633 \) and
\[ k = 4.533 \times 10^{-3} (M)^{0.1683} (g/l)^{-0.1633} \text{ s}^{-1} \]

The order of rate constants has been the same in the two cases, i.e., the oxidation of S(IV) in rain water (catalysed by dissolved metal ions) and that in distilled water catalysed by aerosols. This indicates that the chemical nature and concentrations of the catalysts in the two cases are similar. This is further confirmed by the order of reaction in the two cases in respect of S(IV) concentration. The significant correlation coefficients in two cases are associated with only Fe ions concentrations.

The undissolved suspensions and also the organic fraction of the aerosols were found to have negligible effect on the reaction rates. The increasing buffer concentration decreases the rate of oxidation catalysed by aerosols. But the unbuffered reactions were slower than those in moderately buffered (Na-acetate concentration \( 1.5 \times 10^{-2} \) mol/l) solution due to increase in pH on the advancement of reaction. The presence of EDTA decreases the rate of aerosol catalysed reactions and the decrease is
approximately exponential with increasing concentration of EDTA. Initially, this decrease was sharp but on further increase in EDTA concentration the decrease in reaction rate reduces slowly.

To summarise, the present study shows that the aqueous phase oxidation of S(IV) plays a significant role in the acidification of atmosphere. The presence of trace metals in aerosols of atmosphere acts as catalyst in this oxidation process.