

CHAPTER - II
EXPERIMENTAL TECHNIQUE

The reactions of peroxydisulphate are known to be greatly influenced by traces of impurities, hence, all possible precautions were taken to avoid the impurities in the reaction system from reagents to reaction vessels.

Potassium peroxydisulphate of AnalaR quality (E. Merck) was used after recrystallisation (in conductivity water) and drying at room temperature under vacuum, below 40°C.

Standard solution of peroxydisulphate was always prepared by the exactly weighed quantity of the recrystallised peroxydisulphate in conductivity water using measuring flasks of pyrex glass. The aqueous solution of $S_2O_8^{2-}$ decomposes slowly on standing, hence a freshly prepared solution of peroxydisulphate was used. The strength of $S_2O_8^{2-}$ solution was always checked by Eckardt's¹⁸⁵ method or iodometric method as described in detail later in this chapter.

The catalyst (silver nitrate) use was of B.D.H., AnalaR quality. The standard solution of silver nitrate was prepared by dissolving exact quantity of silver nitrate and was kept in a stoppered pyrex glass flask coated on outside with black Japan and further wrapped with black cloth to avoid photochemical effects.

B.D.H. or E. Merck quality of amides were used. The purity of compounds was checked by their melting points. The solutions were prepared in 80 % (v/v) acetic acid, and kept in a pyrex flask.

B.D.H., AnalaR quality of starch indicator was prepared by dissolving (approximately weighed) soluble starch in boiling distilled water. A pinch of mercurous iodide was added for greater stability of starch solution.

All the reactions were carried out in glass stoppered vessels of pyrex glass or in iodine flasks. The flasks were coated on the outside with black Japan and wrapped in black cloth to avoid any possibility of photochemical effect.

Calculated amounts of the reactants were kept separately in a thermostatic water bath (accuracy $\pm 0.1^{\circ}\text{C}$) maintained at the desired temperature of the experiment. Solutions were kept 15 minutes in order to attain the temperature of the bath.

The three solutions were rapidly mixed and aliquot of the reaction mixture was withdrawn at suitable intervals of time. This aliquot was added to a mixture of KI, FeSO_4 and CuSO_4 (KI \rightarrow 10 %, 10 ml, $\text{FeSO}_4 \rightarrow$ 1 %, 1 ml and $\text{CuSO}_4 \rightarrow$ 1 %, 1 ml) in iodine flask. The iodine flask was stoppered



and allowed to stand for about ten minutes for complete liberation of iodine and the equivalent iodine liberated was titrated against a standard sodium thiosulphate using starch as an indicator.

Various iodimetric methods for estimating unreacted peroxydisulphate were suggested from time to time, but in this kinetic study the method of Szabo,¹⁸⁶ Csanyi and Galiba (further modified by Khulbe⁶⁴ and Srivastava) as given above was used for kinetic study.

The blank titrations were carried out by taking 10 ml of 10 % KI, 1 ml of 1 % CuSO_4 and 1 ml of 1 % FeSO_4 , in order to evaluate the quantity of sodium thiosulphate, corresponding to the iodine liberated by CuSO_4 and FeSO_4 mixture alone. The volume of sodium thiosulphate equivalent to unreacted peroxydisulphate was determined by subtracting the titre value of blank titration from the titre value for the reaction mixture.

The amides used did not interfere with this method of estimation of peroxydisulphate. Throughout the kinetic study, a simultaneous study of the silver catalysed self decomposition of peroxydisulphate alone, under exactly similar conditions has been carried out in each case.

In recording the observations for different kinetic runs, the following notations are used :

- (1) 'C' denotes the volume in ml. of the standard $\text{Na}_2\text{S}_2\text{O}_3$ solution equivalent to the unreacted $\text{K}_2\text{S}_2\text{O}_8$ at any time interval.
- (2) ' k_1 ' represents the first order rate constant for the total reaction.
- (3) ' k_2 ' represents the first order rate constant for the Ag^+ catalysed self decomposition of $\text{S}_2\text{O}_8^{2-}$ under exactly similar conditions.
- (4) ' k ' denotes the rate constant for the oxidation of substrate alone. It has been evaluated by subtracting k_2 from k_1 . Thus the net $k = (k_1 - k_2)$.
- (5) 'min' denoted minutes and conc. denotes the concentration.

The data for different kinetic runs for self decomposition although carried out in each case, has not been given for all cases. Only for the first compound the self decomposition of peroxydisulphate has been shown. Similarly for the second compound the self decomposition was also carried out and only k_2 values are shown directly at the end of each table.