

# **CHAPTER – II**

# **EXPERIMENTAL**

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The kinetics of oxidation of cyclohexanol and selenium dioxide ( $\text{SeO}_2$ ) by cerium (IV) catalysed by chromium (III) in  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  mixture ) has been studied. The experimental results obtained include :

- i) Effect of variation of oxidant  $\text{Ce(IV)}$  and alcohol concentration in one case and variation of oxidant  $\text{Ce(III)}$  and  $\text{SeO}_2$  concentration in the other case on the rate of reaction and determination of order of the reaction with respect to each reactant.
- ii) Effect of perchloric acid concentration on the reaction rate and determination of order with respect to  $\text{HClO}_4$ .
- iii) Effect of  $\text{Cr(III)}$  concentration on the reaction rate and determination of order with respect to  $\text{Cr(III)}$ .
- iv) Effect of temperature variation and to evaluate thermodynamic parameters for the reaction.
- v) Identification of end product and stoichiometry

### 2.1 Materials and Purity :

The double distilled water was used through out the work.

All the chemicals used for experiments were of BDH/ AR grade. Cyclohexanol (BDH) was first purified by fractional distillation and was used to prepare solutions.

Ferrous ammonium sulphate (BDH/AR) cerium ammonium sulphate (BDH/AR), potassium chromium (III) sulphate (BDH/AR), perchloric acid

(Analar) and sulphuric acid (Glaxo Excel R) SeO<sub>2</sub> selenium dioxide ( BDH ) were used directly as received.

## 2.2 Preparation and Standardization of Solutions

The double distilled water was used for preparation of stock solutions. The stock solutions were stored in air tight amber coloured bottles and kept in the dark.

The stock solutions used were of the following concentrations. :

1	Alcohol solution (Cyclohexanol)	0.1 mol dm <sup>-3</sup>
2.	Cerium (IV) Solution	0.1 mol dm <sup>-3</sup>
3	Chromium (III) Solution	0.02 mol dm <sup>-3</sup>
4.	Ferrous ammonium sulphate solution	0.1 mol dm <sup>-3</sup>
5.	Perchloric acid solution	BDH
6.	Sodium perchlorate solution	2.0 mol dm <sup>-3</sup>
7.	Sulphuric acid solution	2.0 mol dm <sup>-3</sup>
8.	Selenium dioxide solution	1.0 mol dm <sup>-3</sup>
9	Ferroin indicator solution	

The 0.1 mol dm<sup>-3</sup> stock solution of cyclohexanol and 1.0 mol dm<sup>-3</sup> stock solution of selenium dioxide was prepared by dissolving appropriate amounts of them in double distilled water.

The stock solution of cerium (IV) was prepared by dissolving a calculated quantity of cerium (IV) ammonium sulphate in  $2.00 \text{ mol dm}^{-3}$  sulphuric acid and allowed to stand overnight. The resulting solution was standardized against ferrous ammonium sulphate solution using ferroin as an indicator. The stock solution was diluted to the required concentration and then used.

Ferrous ammonium sulphate was prepared by dissolving calculated quantity of ferrous ammonium sulphate in  $2.00 \text{ mol dm}^{-3}$  sulphuric acid. It is standardised by using potassium dichromate using Barium diphenyl ammonium sulphonate. as an indicator solution of requisite concentration ( $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) was prepared by diluting stock solution.

Cr(III) solution was obtained by dissolving calculated quantity of potassium chromium sulphate, in double distilled water. The concentration of Cr(III) was confirmed by oxidising Cr(III) to Cr(VI) with excess persulphate in the presence of a drop of 0.01 M silver nitrate as follows :

To the Cr(III) solution excess persulphate was added followed by a drop of 0.01 M silver nitrate and the solution was boiled for five minutes. The excess persulphate remained after the oxidation was destroyed by further boiling the solution. The Cr(VI) thus obtained was titrated against ferrous ammonium sulphate solution using diphenyl ammonium sulphonate as indicator.

Sodium perchlorate solution was prepared by neutralization of perchloric acid with sodium carbonate.

### 2.3 Methods of Following Kinetics

The main features of the experimental method are as follow :

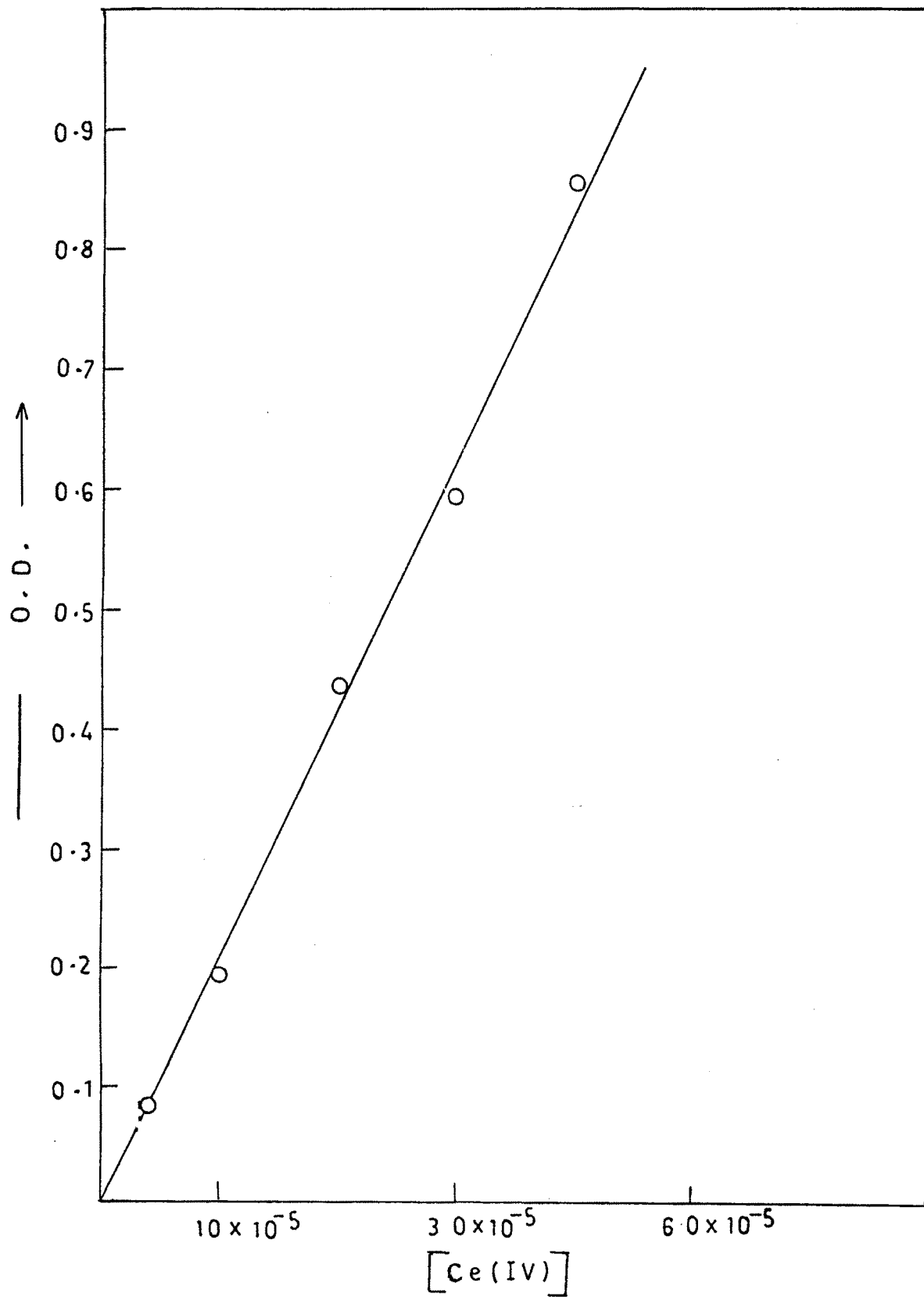
- i) The standard pyrex glassware was used through-out the experimental work.
- ii) The temperature of the reaction mixture was adjusted and maintained by using autothermostated water bath ( $\pm 0.1$  °C.)
- iii) The reactions were carried out in a stoppered conical flask (100 ml. ).
- iv) The reactions were carried out under pseudo-first order conditions with the cyclohexanol or selenium dioxide concentration much in excess to that of the cerium(IV).
- v) The reaction mixtures in all runs contained a constant amount of  $\text{H}_2\text{SO}_4$  (0.06 M) on account of  $\text{H}_2\text{SO}_4$  used in the dissolution of cerium (IV) ammonium sulphate to obtain the Ce(IV) stock solution.
- vi) Generally where the effect of acidity on the reaction rate was not under examination, a constant quantity of 2.0 M perchloric acid was used in addition to  $\text{H}_2\text{SO}_4$  in the reaction mixtures.
- vii) The ionic strength was maintained by the addition of a solution of sodium perchlorate.
- viii) Flask 1 : The calculated quantities of standard solution of cyclohexanol, chromium (III) and perchloric acid in one case and the calculated quantities of standard solution of selenium dioxide, Cr(III) and perchloric acid in the other case.

- ix) Flask 2 : The calculated quantities of Ce(IV), 2 M perchloric acid, sulphuric acid and water.
- x) Two conical flasks were thermostated for 30 minutes.
- xi) The reaction was initiated by adding the thermostated solution from flask 2 to flask 1. The time of initiation of reaction i.e. time of mixing the solutions was recorded as zero time.
- xii) After mixing, immediately the solution was transferred to one of the pair of matched cuvettes. The cuvette was then placed in cell compartment of Elico SL-159 UV-VIS spectrophotometer. The absorbance of Ce(IV) was measured as a function of time at 360 nm. The Beer's law plot for Ce(IV) was tested between the concentration range of  $4.0 \times 10^{-5}$  to  $4.0 \times 10^{-4} \text{ mol dm}^{-3}$  and the molar extinction coefficient was found to be  $2416 \text{ l mol}^{-1} \text{ cm}^{-1}$  [ Table II(i) and Figure II(i) ]

**Table II (i) : Beer's Law**

$[\text{Ce}^{\text{IV}}] \text{ mol dm}^{-3}$	O. D. (Absorbance) at 360 nm
$4.0 \times 10^{-5}$	0.085
$1.0 \times 10^{-4}$	0.245
$2.0 \times 10^{-4}$	0.437
$3.0 \times 10^{-4}$	0.697
$4.0 \times 10^{-4}$	0.855

FIG. II(i) - PLOT OF O.D. AGAINST Ce(IV).  
BEER'S LAW PLOT FOR Ce(IV).



## 2.4 Temperature Variation

In the preliminary work, experiments were carried out in order to decide the range of temperature, concentrations of cerium(IV), selenium dioxide, cyclohexanol and perchloric acid. It was observed that the reaction with measurable rate at ordinary temperatures (25°C to 40°C). So this temperature range was employed. The temperature was kept constant through out the kinetic study of the reaction by means of thermostat with  $\pm 0.1^\circ\text{C}$  accuracy.

## 2.5 Variation In Concentration

It was observed that satisfactory results were not obtained at higher concentration of Ce(IV) solution and rate of oxidation was found to be inversely proportional to the Ce(IV) concentration. Hence low concentrations of Ce(IV) in the range  $4.0 \times 10^{-5}$  to  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup> were employed. In case of cyclohexanol the rate of reaction was found to be very low at lower concentration hence, higher concentration of cyclohexanol was employed to get consistent results. The reactions were studied under pseudo first order conditions using concentration of cyclohexanol at least 5 to 10 times greater than that of Ce(IV). Hence cyclohexanol in the concentration range  $1.0 \times 10^{-3}$  to  $10.00 \times 10^{-3}$  mol dm<sup>-3</sup> was used. In case of HClO<sub>4</sub>, the rate of reaction was found to be very low at lower concentration range. Hence, HClO<sub>4</sub>, in the concentration range 1.0 to 2.0 M was employed to get consistent results. To study the effect of chromium(III) concentration on rate of the reaction, Cr(III) concentration was varied from  $2.0 \times 10^{-5}$  to  $20 \times 10^{-5}$  mol dm<sup>-3</sup>.



## 2.6 Stoichiometry

The stoichiometry was studied by keeping the oxidant in excess over that of the reactant. Several reaction mixtures containing the different concentrations of reactants Ce(IV) and Se(IV) in  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  were prepared and allowed to go for completion. The remaining oxidant Ce(IV) was analysed spectrophotometrically. The stoichiometry was studied by keeping Ce(IV) concentration excess over cyclohexanol or Se(IV) at  $60^\circ\text{C}$  for about 8 hours with a condenser. The concentration of unused cerium (IV) was determined by titrating against ferrous ammonium sulphate. The stoichiometry in both the case was found to be two moles of oxidant per mole of reductant indicating the product of oxidation are cyclohexanone and selenium (VI) respectively..

The catalyst Cr(III) remained unchanged at the end of reaction as found by measuring the absorbance at 580 nm, the molar absorptivity of Cr(III) at this wavelength being  $15.4 \pm 0.02$ .