E2-07: Spectrophotometric determination of rate laws and rate constants of the iodide ion catalyzed reaction between ammonium ceric sulphate and sodium arsenite.

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The kinetic method using the catalytic effect of iodide ions on the reaction of Ce(IV) and As(III) has been used extensively for the determination of iodide and iodine, although the kinetics of this reaction has not been studied well and there are no reported values for the rate constants.

In this study an attempt was made to determine the rate laws for this reaction under different experimental conditions. The progress of the reaction was followed by monitoring the absorbance of Ce(IV) at 420 nm. Experimental results were fitted to appropriate theoretical models to arrive at rate laws.

Experiments carried out with low concentrations of As(III) revealed that the reaction was first order in both Ce(IV) and As(III) and zero th order in I^- when the ratio of concentrations of As(III) to Ce(IV), ([As(III)]/[Ce(IV)]), was below 0.5 at a Ce(IV)) concentration of 3.0×10^{-3} mol dm^{-3}.

At higher concentrations of As(III), the reaction was found to be zero th order in As(III) and first order in both Ce(IV) and I^- when the ratio, [As(III)]/[Ce(IV)], was above 2 and the rate law was of the form: rate = $(k + k_{cat}[I^-])$ [Ce(IV)]. The values of k and k_{cat} were found to be $1.90 \times 10^{-4} s^{-1}$ and 1.70×10^4 dm^3 mol^{-1} at 29°C.

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