03

CHEMICAL KINETICS

CONCENTRATION DEPENDENCE & REACTION ORDER

CHEMISTRY 136L // FALL 2019

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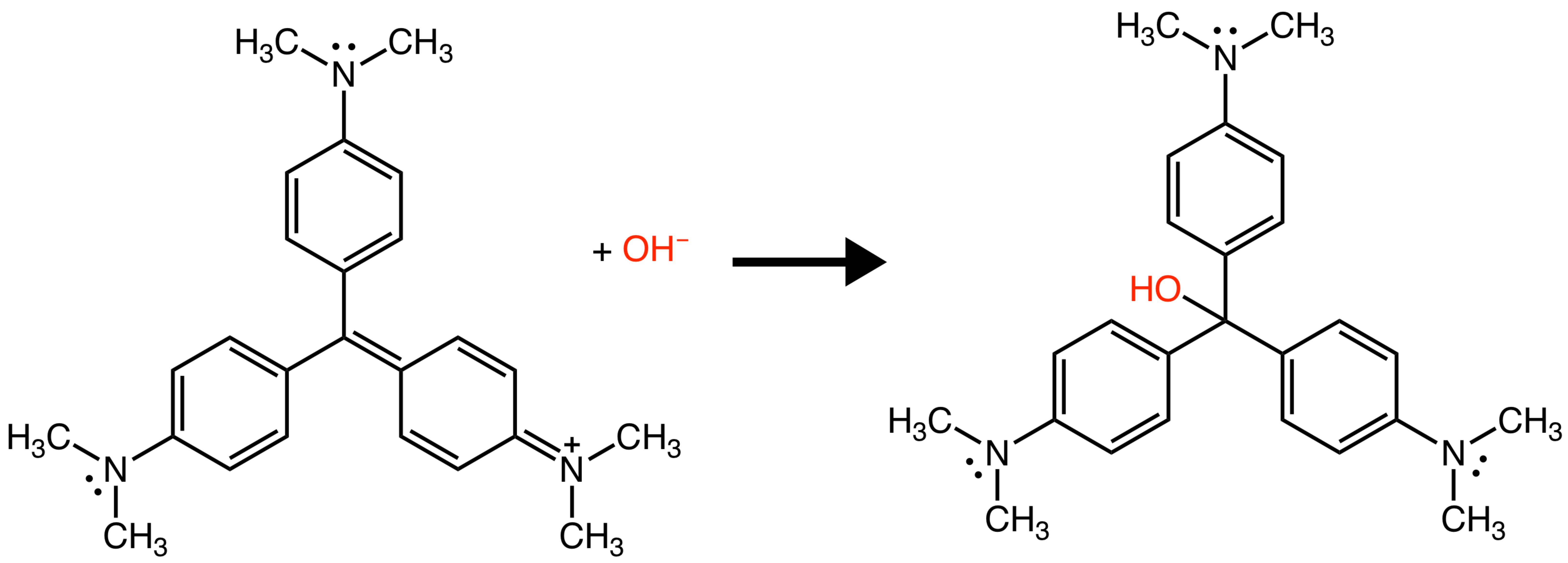
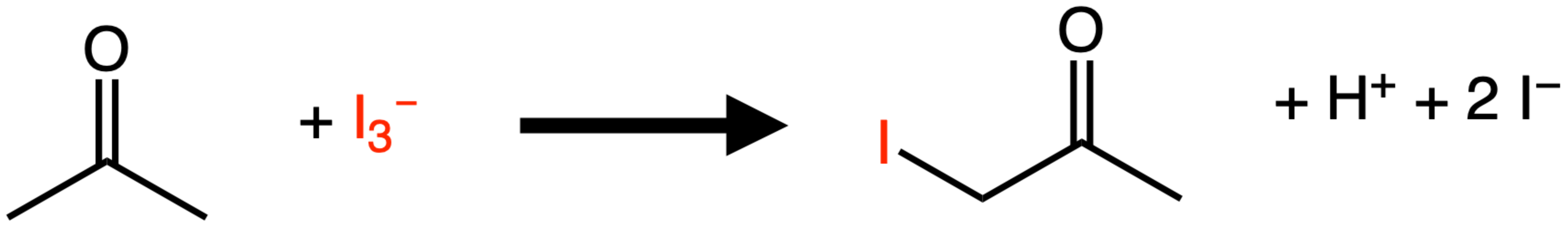
REACTIONS OF INTEREST

Decolorization of crystal violet



CRYSTAL VIOLET (CV)

COLORLESS



ACETONE TRIIODIDE

IODOACETONE

Iodination of acetone

PURPOSE

Reaction rates

We can express the reaction rate as

$$\text{Rate} = -\frac{d[\text{CV}]}{dt} = \frac{d[\text{OH}^-]}{dt} = +\frac{d[\text{product}]}{dt}$$

Purposes:

Study concentration dependence and rate order

Determine value of rate constant (k)

REACTION ORDER

What is it?

$$\text{Rate} = -\frac{d[\text{CV}]}{dt} = k[\text{CV}]^a[\text{OH}^-]^b$$

where [ ] is the concentration ($mol \cdot L^{-1}$),

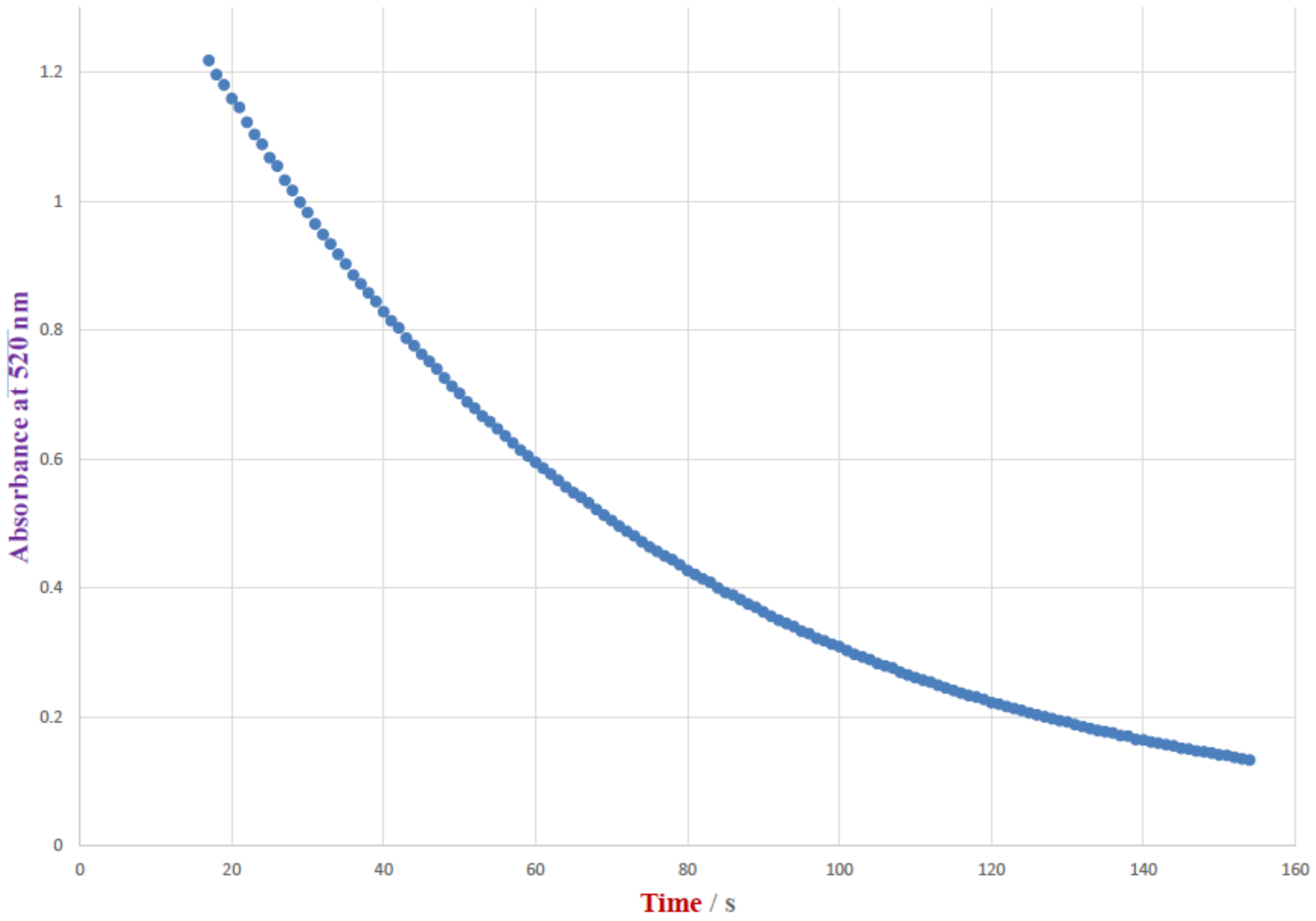
a is the order with respect to [CV], and

b is the order with respect to $[OH^-]$.

Determining the orders:

1. Initial rate method
2. Integrated equation method
3. Half-life method

CV/OH⁻ Reaction



METHOD OF FLOODING

Isolating effects of concentrations

$$\text{Rate} = -\frac{d[\text{CV}]}{dt} = k[\text{CV}]^1[\text{OH}^-]^1$$

Make $[\text{OH}^-]_0 \gg [\text{CV}]_0$

Today:

$[\text{CV}]_0 \approx 3\times10^{-5}$ M

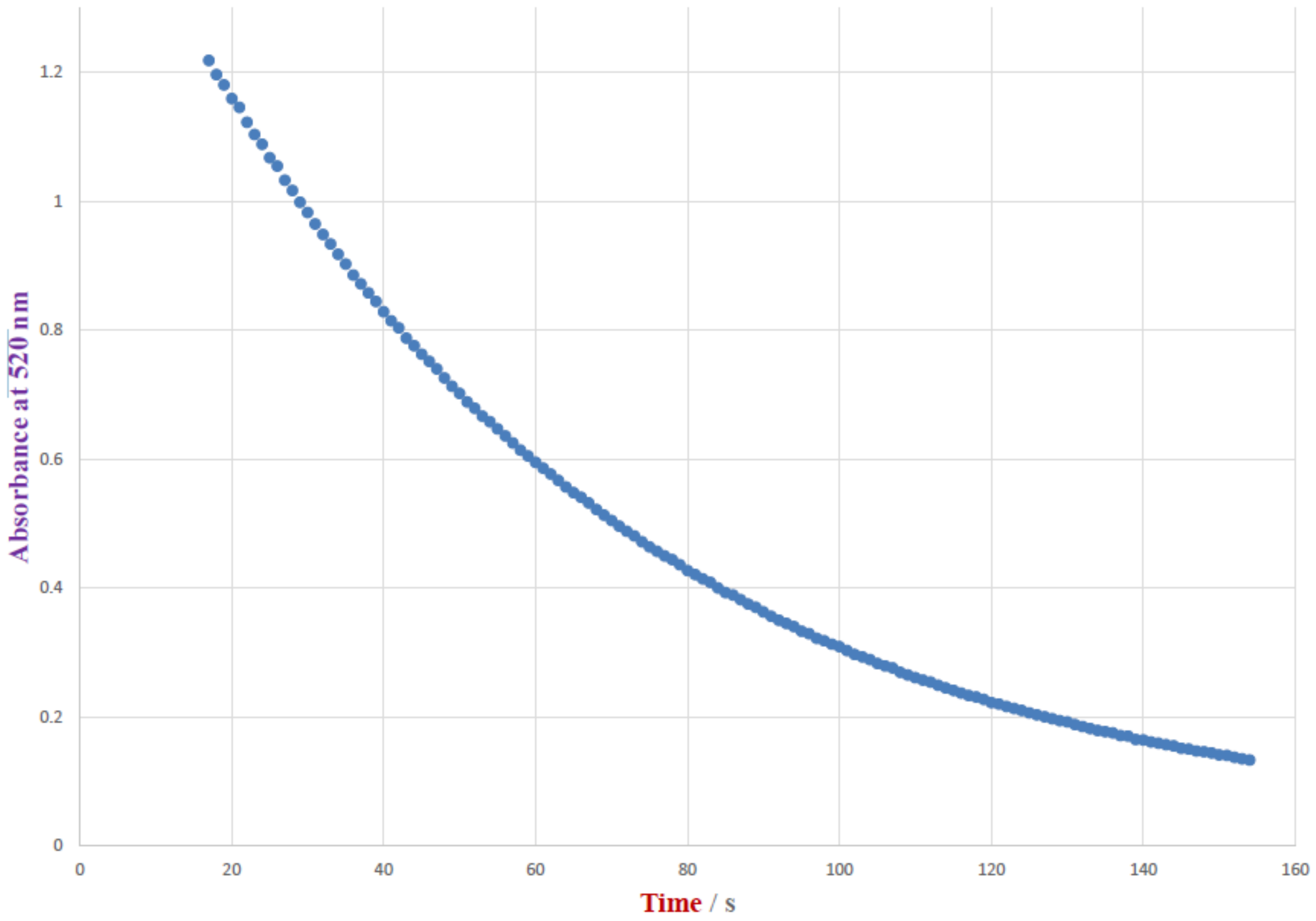
$[\text{OH}^-]_0 \approx 0.05 \rightarrow 0.2$ M

Therefore:

$$\text{Rate} = -\frac{d[\text{CV}]}{dt} \approx k'[\text{CV}]^1$$

$$k' = k[\text{OH}^-]_0$$

CV/OH⁻ Reaction



INTEGRATED EQUATION METHOD

Extracting rate orders

$$\text{Rate} = -\frac{d[\text{CV}]}{dt} \approx k'[\text{CV}]^1$$

Integrating the above differential rate equation gives:

$$\ln[\text{CV}]_t = \ln[\text{CV}]_0 - k't$$

$$\ln A_t = \ln A_0 - k't$$

$$y = b + mx$$

Logic:

If a plot of $\ln A$ vs. t is linear,

then order with respect to $[\text{CV}]$ is 1

and the slope is $-k'$.

ORDER WITH RESPECT TO $[OH^-]_0$

Overview of procedure

Determine k' for various $[\mathrm{OH}^-]_0$

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If a plot of k' vs. $[\mathrm{OH}^-]_0$ is linear,

then order with respect to $[\mathrm{OH}^-]$ is 1

and the slope is k.