

# CHEM355 EXPERIMENT 8

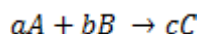
## Experimental Determination of the Reaction Rate

### Chemical Kinetics

A reaction rate is the change in concentration per unit time, either the decrease of concentration per unit time of a reactant or the increase of concentration per unit time of a product. In this case, the rate is expressed in  $\text{mol.L}^{-1} \cdot \text{sec}^{-1}$ .

$$\text{Rate} = \frac{\text{concentration change of a reactant or product}}{\text{time interval}}$$

For example, if we consider the reaction



A has a stoichiometric coefficient of ' $a$ ', B has a coefficient of ' $b$ ', and the product C has a coefficient of ' $c$ '. The rate of this reaction can be determined by monitoring the concentration change of the reactants or products. It can be seen from the reaction equation that when  $ax$  mol of A and  $bx$  mol of B are consumed,  $cx$  mol of C is produced so the reaction rate is the change in concentration of these species divided by its stoichiometric coefficient. Therefore the rate of the reaction in terms of concentration change of the species is:

$$v = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt}$$

When we define the rate using concentration of any of the reactants, a negative sign should be used as the concentrations of reactants decrease.

Reaction	Order	Differential form	Integrated form	Graph	Slope
$A \rightarrow P$	Zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$	$[A] \text{ vs } t$	$-k$
$A \rightarrow P$	First	$\frac{d[A]}{dt} = -k[A]$	$\ln[A] = \ln[A]_0 - kt$	$\ln[A] \text{ vs } t$	$-k$
$2A \rightarrow P$	Second	$\frac{1}{2} \frac{d[A]}{dt} = -k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$\frac{1}{[A]} \text{ vs } t$	$k$

## Half lifes

The half-life,  $t_{1/2}$ , of a substance is defined as the time it takes for the concentration of the substance to fall to half of its initial value. We can obtain equations for the half-lives for reactions of various orders by substituting the values  $t = t_{1/2}$  and  $[A] = \frac{1}{2} [A]_0$  into the integrated rate laws. We obtain:

Order	Half-life
Zeroth order reaction	$t_{1/2} = \frac{[A]_0}{2k}$
First order reaction	$t_{1/2} = \frac{\ln 2}{k}$
Second order reaction	$t_{1/2} = \frac{1}{k [A]_0}$

## Rate Laws

The rate law is an expression relating the rate of a reaction to the concentrations of the chemical species present, for example, if the above reaction is an elementary reaction, a simple rate law can be written as:

$$\vartheta = -k[A]^a[B]^b$$

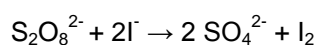
i.e. the rate is proportional to the concentrations of the reactants each raised to some power. The constant of proportionality, ***k***, is called ***the rate constant***. The power a particular concentration is raised to is *the order of the reaction with respect to that reactant*. Note that the orders do not have to be integers. The sum of the powers is called ***the overall order***.

For the above reaction, if B is in great excess so the concentration of B does not change during the reaction. Therefore, it can be assumed as constant and combined with the rate constant as

$$\vartheta = -k'[A]^a \text{ where } k' = k[B]^b$$

This type of reactions is called as '**pseudo first order**' reaction.

The reaction that is going to be examined in this experiment is the oxidation of iodide by persulfate in neutral solution and it is a pseudo first order reaction as  $I^-$  concentration is in excess amount.



## Apparatus and chemicals

Apparatus: Erlenmeyer, pipette, stopper, water bath, watch.

Chemicals: 0.036 M  $K_2S_2O_8$ , 0.4 M KI, 0.4 M KCl, 0.02M  $Na_2S_2O_3$ , starch.

## Procedure

### First part of the experiment

1. Put 50 mL of **0.036 M  $K_2S_2O_8$**  into an erlenmeyer (close it with stopper) placed in a 50 °C water bath.
2. To a second erlenmeyer, put 50 mL of 0.4 M KI and immerse it into a 50 °C water bath.
3. Wait 10 minutes to reach thermal equilibrium.
4. Then pour KI solution to  $K_2S_2O_8$  solution.
5. Leave this mixture 60 minutes at this constant temperature water bath.
6. At the end of the 60 minutes, take 10 mL from this solution and put it into another flask containing 200 mL cold water (tap water).
7. Add starch as an indicator (1-2 mL).
8. Titrate with 0.02 M  $Na_2S_2O_3$ .

### Second part of the experiment (with two sets)

#### Set I

1. Put 50 mL of **0.036 M  $K_2S_2O_8$**  into an erlenmeyer (close it with stopper) placed in a 25°C water bath.
2. To a second erlenmeyer, put 50 mL of 0.4 M KI and immerse it into a 25°C water bath.
3. Wait 10 minutes to reach thermal equilibrium.
4. Then pour KI solution to  $K_2S_2O_8$  solution.
5. Start the chronometer.
6. After 3 minutes, take 10 mL from this solution and put it into another flask containing 200 mL cold water (tap water).
7. Add starch as an indicator (1-2 mL).
8. Titrate with 0.02 M  $Na_2S_2O_3$ .
9. Do the same procedure (step 6 to 8) by the time intervals: 7, 10, 15, 20, 30, 42, 60 minutes.

#### Set II

1. Put 50 mL of **0.036 M  $K_2S_2O_8$**  and 25 mL of 0.4 M KCl into an erlenmeyer (closed it with stopper) placed in a 25°C water bath.
2. To a second erlenmeyer, put 50 mL of 0.4 M KI and immerse it into a 25 °C water bath.
3. Perform the same procedure as mentioned above.

**(Waste container of experiment: SINK waste container)**

## Treatment of data

1. Find the concentration of  $\text{S}_2\text{O}_8^{2-}$  at the time that you take sample (from titration data).
2. Plot  $[\text{S}_2\text{O}_8]_{\text{unreacted}}$  vs time graph in the polynomial order of **five**.
3. Take the derivative of the equation to find  $dc/dt$ .
4. Plot  $dc/dt$  vs  $[\text{S}_2\text{O}_8]_{\text{unreacted}}$  to find  $k$  (rate constant).

$$\frac{d[A]}{dt} = -k[A]$$

5. Plot  $\ln[\text{S}_2\text{O}_8]_{\text{unreacted}}$  vs time to find  $k$ .

$$\ln[A] = \ln[A]_0 - kt$$

6. Find  $k_{\text{av}}$ .
7. Find half-life of the reaction.

## Questions

1. Discuss the effect of temperature on reaction rate.
2. Why is KCl added in the second part? Discuss the effect of KCl on reaction rate.
3. How can you determine the order of a reaction?

Date:.....Assistant name and Signature:.....

$$V_{S_2O_3^{2-}} =$$

**Set I.**

[illegible][illegible]