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 mol.L^{-1}. sec^{-1}.

concentration change of a reactant or product
Rate = ---
time interval

For example, if we consider the reaction

$$aA + bB \rightarrow cC$$

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:

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

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*	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$	$[A]\ vs\ t$	$-k$
$A \rightarrow P$	*First*	$\frac{d[A]}{dt} = -k[A]$	$ln[A] = ln[A]_0 - kt$	$ln[A]\ vs\ t$	$-k$
$2A \rightarrow P$	*Second*	$\frac{1}{2}\frac{d[A]}{dt} = -k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$\frac{1}{[A]}\ vs\ t$	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 $[A] = ½ [A]_0$ into the integrated rate laws. We obtain:

Order	Half-life
Zeroth order reaction	$t_{1/2} = \frac{[A]_0}{2k}$
First order reaction	$t_{1/2} = \frac{ln2}{k}$
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

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

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.

$$S_2O_8^{2-} + 2I^- \rightarrow 2\ SO_4^{2-} + I_2$$

Apparatus and chemicals

Apparatus: Erlenmayer, 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 erlenmayer (close it with stopper) placed in a 50 ˚C water bath.
2. To a second erlenmayer, 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 erlenmayer (close it with stopper) placed in a 25˚C water bath.
2. To a second erlenmayer, 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 erlenmayer (closed it with stopper) placed in a 25˚C water bath.
2. To a second erlenmayer, 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 $S_2O_8^{2-}$ at the time that you take sample (from titration data).
2. Plot $[S_2O_8]_{unreacted}$ 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 $[S_2O_8]_{unreacted}$ to find k(rate constant).

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

5. Plot $\ln[S_2O_8]_{unreacted}$ vs time to find k.

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

6. Find k_{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?

Group Number:………Group Members:……………………………………………………….

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

Part I.

$V_{S2O3}{}^{2-}$ =

Part II.

Set I.

Time(sec)	$V_{S2O3}{}^{2-}$

Set II.

Time(sec)	$V_{S2O3}{}^{2-}$