General Chemistry

Kinetics

Author:
Aini Norhidayah Mohamed
ainin@ump.edu.my
Faculty of Industrial Sciences & Technology,
Universiti Malaysia Pahang

Chapter Description

- Expected Outcome:
- At the end of the lecture, the students should be able to understand and solve the problems regarding on the Reaction rate, Kinetic Reaction Theory, Rate Law and Reaction Order, Methods of Determining Rate of Reaction & Factors Affecting Reaction Rate.

- References:

1) Stephen B. Barone. Introduction to general chemistry. Blackwell Science.
2) James E. Bradry General Chemistry: Principles & Structure. John Wiley.

Contents

- Reaction rate
- Kinetic Reaction Theory
- Rate Law and Reaction Order
- Methods of Determining Rate of Reaction
- Factors Affecting Reaction Rate

Reaction rate

changes in the concentration of a reactant or a product with time.

- **Unit: mol L^{-1} s^{-1} @ mol dm^{-3} s^{-1} @ M s^{-1}**

Example; $A \longrightarrow B$

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

d[A] = change in concentration of A

dt = period of time

$$\text{Rate} = +\frac{d[B]}{dt}$$

d[B] = change in concentration of B

Since [A] decreases with time, so d[A] is negative.

Rate of reaction

Average rate: rate over a period of time

Instantaneous rate - rate of reaction at a given time

Initial rate : instantaneous rate at the beginning of a reaction

Differential rate equation

- Relates the rate of disappearance of a reactants and the rate of appearance (formation) of products.

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

- a, b, c and d are the stoichiometric coefficients.
- negative sign (-) indicate that the concentration of reactants decrease with time.
- positive sign (+) indicate that the concentration of products increase with time.

Rate law

Rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

$$aM + bN \longrightarrow cP + dQ$$

Rate α [reactant]

$$\text{Rate} = k\,[M]^{x}\,[N]^{y}$$

k **is called** ***rate constant***

reaction **order is:**

x with respect to M

y **with respect** to N

Overall reaction order is **(x + y)**

Kinetics
by Aini Norhidayah
http://ocw.ump.edu.my/course/view.php?id=479

Order of reaction

Defining how the rate is affected by reactant concentration.

$$A \longrightarrow \text{Products}$$

$$\text{Rate} = k\,[A]^{x}$$

If x= 0

Rate = k $[A]^0$

Therefore, Rate = k

Rate is not depend on [A]

Therefore this reaction is *zero order* with respect to A

Kinetics
by Aini Norhidayah
http://ocw.ump.edu.my/course/view.php?id=479

Half life

The time required for concentration of a reactant to decrease to half of its initial value.

Kinetics
by Aini Norhidayah
http://ocw.ump.edu.my/course/view.php?id=479

Zero order reaction

Reaction which is independent to the concentration of reactant.

$A \rightarrow$ product

The rate law of zero order is given by:

Rate = $k\,[A]^0$

$\boxed{\text{Rate} = k}$

Kinetics
by Aini Norhidayah
http://ocw.ump.edu.my/course/view.php?id=479

Half life of zero order reaction

Substituting $t = t_{1/2}$, and $[A] = \frac{[A]_0}{2}$ into the zero order reaction, gives:

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

$$[A]_0 - \frac{[A]_0}{2} = kt$$

Therefore,

$$\boxed{t_{\frac{1}{2}} = \frac{[A]_0}{2k}}$$

Kinetics
by Aini Norhidayah
http://ocw.ump.edu.my/course/view.php?id=479

First order reaction

A first order reaction is a reaction whereby its rate depends on the concentration of reactant raised to the first power.

$A \rightarrow$ product

The rate law of first order is given by:

$\text{Rate} = k[A]^1$

$$\boxed{\text{Rate} = k[A]}$$

Kinetics
by Aini Norhidayah
http://ocw.ump.edu.my/course/view.php?id=479

Half life of first order reaction

$$t = \frac{\ln \frac{[A]_0}{[A]}}{k}$$

$$\boxed{\ln \frac{[A]_0}{[A]} = kt}$$

When $t = t_{\frac{1}{2}}$, $[A] = \frac{[A]_0}{2}$

$$\boxed{t_{\frac{1}{2}} = \frac{\ln 2}{k}}$$

$$t_{\frac{1}{2}} = \frac{\ln \frac{[A]_0}{\frac{[A]_0}{2}}}{k} = \frac{\ln 2}{k}$$

Second order reaction

Rate that depends on the concentration of one reactant raised to the second power or on the concentration of two different reactants each raised to the first power.

$A \rightarrow$ product

The rate law of second order is given by:

Rate = $k[A]^2$

$$\boxed{\text{Rate} = k[A]^2}$$

Half life of second order reaction

$$\boxed{\frac{1}{[A]} = \frac{1}{[A]_0} + kt}$$

By substituting $t = t_{\frac{1}{2}}$, $[A] = \frac{[A]_0}{2}$

$$\frac{1}{\frac{[A]_0}{2}} = \frac{1}{[A]_0} + kt_{\frac{1}{2}}$$

$$\boxed{t_{\frac{1}{2}} = \frac{1}{k[A]_0}}$$

Collision theory

To explain the rate of chemical reactions.

$$\text{Rate} \propto \frac{\text{Number of effective collisions}}{\text{time}}$$

The ideas:

1. molecule must collide to react
2. The collision involved is an effective collision.

Kinetics
by Aini Norhidayah
http://ocw.ump.edu.my/course/view.php?id=479

Minimum energy

Aka activation energy, E_a

The energy required to initiate a chemical reaction.

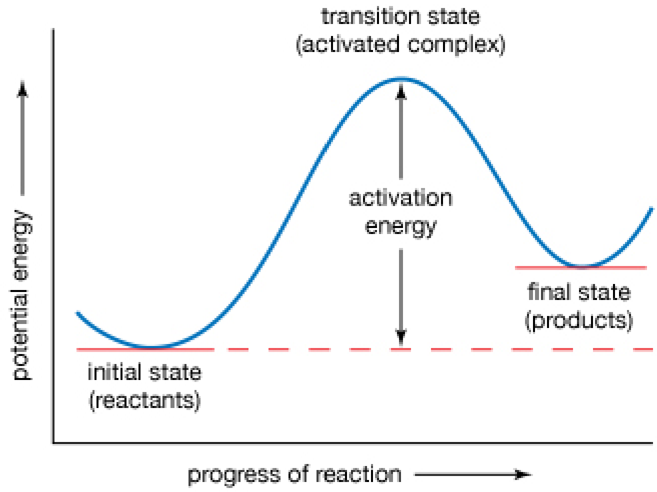
Molecules must possess a minimum energy for a chemical reaction to occur.

Kinetics
by Aini Norhidayah
http://ocw.ump.edu.my/course/view.php?id=479

Transition state theory

the configuration of the atoms of the colliding species at the time of the collision

Picture source: https://www.britannica.com/science/transition-state-theory



Energy profile diagram

potential energy plotted as a against the progress of the reaction.

The differences in the potential energies between the products and the reactants is ΔH for the reaction.

Reactant molecules must have enough energy to overcome an energy barrier to separate products from reactants, E_a.

Concentration of reactants

- A concentration of reactants increases, the frequency of collision increases.

Collision α Concentration

- This would also result in the increase in the quantity of effective collision. Thus the reaction rate increases.

Reaction rate $\propto$ concentration of reactants (depending on its rate order)

Kinetics
by Aini Norhidayah
http://ocw.ump.edu.my/course/view.php?id=479

Pressure

When pressure increases, volume will be decreased. Number of molecules per unit volume increases which result in more collisions per second.

Number of effective collision increases, therefore the rate of reaction also increases.

Kinetics
by Aini Norhidayah
http://ocw.ump.edu.my/course/view.php?id=479

Temperature

- **When temperature increases, kinetic energy of molecules will increase, thus, more collision**
- **The higher the kinetic energy, the higher the energy of the effective collisions, so, more molecule will have energy greater than activation energy. Thus, rate of reaction increases**

Particle size

Size of reacting particles decrease, the total surface area exposed for reaction will increase, thus reaction rate will increase.

Catalyst

- **A *catalyst* is a substance that provides an alternative pathway by lowering the activation energy to increases the rate of a chemical reaction without itself being consumed.**
- **A catalyst increases the rate by increasing the frequency of effective collision. That is by decreasing the E_a and with correct orientation.**
- **Catalyst will not affect the enthalpy of reactant or product.**

Arrhenius Equation

$$k = A\, e^{-E_a/RT}$$

Where…

k = rate constant

A = constant known as the *frequency factor*

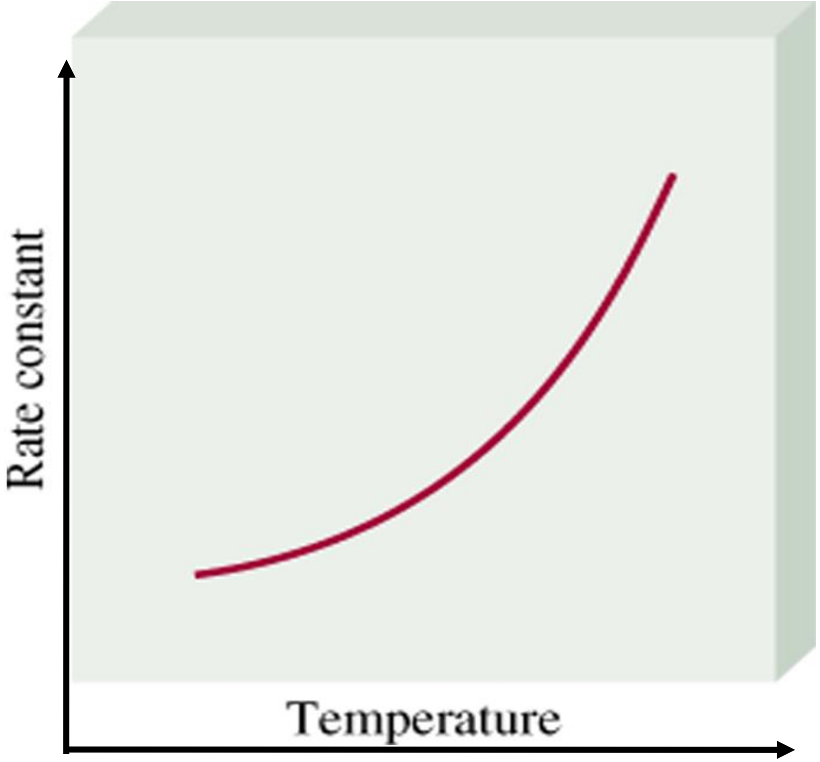
e = natural log exponent

E_a = activation energy for the reaction

R = universal gas constant (8.314 J mol^{-1} K^{-1})

T = absolute temperature

Rate constant (k) and Temperature (t)



$$k = A\,e^{-E_a/RT}$$

Rate constant

The rate constants for decomposition of hydrogen iodide, HI

$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$

Using the data below, plot ln *k* versus 1/T, and determine the activation energy (in kJ/mol) for the reaction.

k ($M^{-1}s^{-1}$)	T (K)
3.52×10^{-7}	555
3.02×10^{-5}	629
2.19×10^{-4}	666
1.16×10^{-3}	699
3.95×10^{-2}	781

Kinetics
by Aini Norhidayah
http://ocw.ump.edu.my/course/view.php?id=479

Author Information

Aini Hidayah Mohamed is a lecturer from Faculty of Industrial Sciences & Technology Industry, Universiti Malaysia Pahang, Malaysia. She is also a chemist who is expert in general chemistry, industrial chemistry and natural product.