Objectives:

- Define rate law and reaction order
- Determine the reaction order with respect to each reactant
- Write the rate equations
- Specify the overall order of a reaction
- Find the values and the units of rate constants

Rate Law / Rate Equation

The ***RATE LAW***: expresses the relationship of the **rate** of a reaction to the **rate constant** and **concentrations** of reactants raised to some powers that appear in the rate equation.

$$aP + bQ \longrightarrow cS + dT$$

$$\text{Rate, } r = k\,[P]^{m}\,[Q]^{n}$$

k: rate constant

[*P*] , **[*Q*]**: concentrations of *P* and *Q*

m: reaction order with respect to reactant *P*

n: reaction order with respect to reactant *Q*

(*m* + *n*): overall reaction order

Rate Law / Rate Equation

$$\text{Rate} = k\,[P]^m\,[Q]^n$$

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

$$\text{Rate} = A\,e^{-E_a/RT}\,[P]^m\,[Q]^n$$

Reaction **rate** depends on:

a) **Concentration** of reactants

b) **Temperature**

c) Catalyst

Reaction Order

$$\text{Rate} = k\,[A]^{m}\,[B]^{n}$$

- The sum of the **powers** to which all reactant concentrations in the rate law are raised.
- Can only be determined **experimentally**
- May be **integral** (i.e., 1, 2, 3,…), **zero, fractional, deimal** or /and **negative**
- Reaction orders are **NOT** the stoichiometric coefficients in a balance chemical equation.

$$F_2\,(g) + 2ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

$$\text{Rate} = k\,[F_2][ClO_2]^1$$

Reaction Order

Example:

(a) Rate = $k\,[H_2]\,[Br_2]^{0.5}$

(b) $r = k\,[CH_3CHO]^{3/2}$

Solution:

a) The reaction order with respect to H_2 =

The reaction order with respect to Br_2 =

The overall reaction order =

b) The reaction order with respect to CH_3CHO =

The overall reaction order =

Reaction Order

Example:

The decomposition of N_2O_5 at 45°C is first order.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

i. Write an expression for the rate equation.

$$\text{Rate, } r = k\,[N_2O_5] \quad or \quad -\frac{d[N_2O_5]}{dt} = k\,[N_2O_5]$$

ii. Calculate the rate constant if the concentration of N_2O_5 is 1.5×10^{-3} M at a dissociation rate of 8.6×10^{-7} M s^{-1}.

$$8.6 \times 10^{-7} = \boldsymbol{k}\,(1.5 \times 10^{-3})$$

$$\text{Rate constant, } \boldsymbol{k} = 5.7 \times 10^{-4}\ s^{-1}$$

Determining Reaction Order

5 methods:

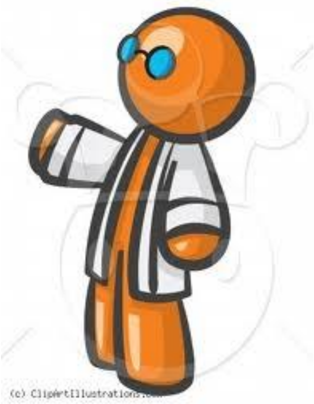
A) Initial Rate Method

B) Unit of rate constant

C) Statement

D) Half-life Method

E) Linear Graph Method (**Integrated rate equation**)



Initial Rate Method

is used when the data is reaction rate at several initial concentrations of reactant

Example:

Based on the data given below:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

Exp.	Initial [NO]/M	Initial [Cl_2]/M	Initial rate, M s^{-1}
1	0.10	0.025	2.0×10^{-5}
2	0.10	0.050	4.0×10^{-5}
3	0.20	0.025	8.0×10^{-5}

a) Deduce the reaction orders with respect to NO and Cl_2.

b) Write the rate law of the reaction.

c) Calculate the rate constant.

Initial Rate Method

Compare 2 experiments in which the concentration of one reactant varies and the concentration of the other reactant(s) remains constant.

Compare exp. 1 with exp.2; [NO] is constant

Initial Rate Method

Using rate equation, Eq(1) ÷ Eq(2)

Initial Rate Method

Compare exp. 1 with exp.3; [Cl_2] is constant

Using rate equation, Eq(1) ÷ Eq(3)

Initial Rate Method

SUMMARY

- rate law = rate equation: rate, $\boldsymbol{r} = \boldsymbol{k}\,[A]^m\,[B]^n$

- Determining reaction order
  ~ initial rate method

$$\frac{r_1}{r_2} = \left(\frac{c_{A1}}{c_{A2}}\right)^m \left(\frac{c_{B1}}{c_{B2}}\right)^n$$