

10.5 Ostwald Isolation Method

This method is used to find out the order of complex reactions. If n_A , n_B and n_C molecules of substance A, B and C, respectively are present in a reaction, then $n_A + n_B + n_C$ will be the order of reaction:

When B and C are in excess, the order of reaction will be n_A .

When A and B are in excess, the order of reaction will be n_C .

When A and C are in excess, the order of reaction will be n_B .

PROBLEM-SOLVING TACTICS

- (a) To determine the average rate for change in concentration over a time period.

Average rate of reaction is the change in concentration of reactants (or products) during large interval of time.

$$\text{Rate} = -\frac{[\text{reactant at } t_2] - [\text{reactant at } t_1]}{t_2 - t_1}$$

Square brackets denote concentration.

Negative sign in the above equation is used to make the rate of reaction positive. Minus sign can be ignored when calculating average rates from products.

$$\text{Rate} = -\frac{\Delta[\text{reactant}]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{\Delta[\text{product}]}{\Delta t}$$

- (b) To determine instantaneous rate from a plot of concentration versus time: Instantaneous rate at time t is determined as follows:

(i) Calculate the negative slope of the curve between concentration of a reactant and time at t .

(ii) Calculate the slope of the curve between concentration of a product and time at t .

- (c) Problem-solving tactics to determine the initial rate from a plot of concentration versus time: The initial rate of a reaction is the instantaneous rate at the start of the reaction (i.e., when $t = 0$).

Initial rate is equal to the negative slope of the curve between reactant concentration and time at $t = 0$.

- (d) To determining the order of a reaction from its rate law

Rate law of a reaction is used to determine:

- The order of the reaction with respect to one or more reactants.
- The overall order of the reaction.

$$\text{rate} = k[A]^n[B]^m[C]^p$$

For the rate law: Order with respect to A = n ; order with respect to B = m , order with respect to C = p

Reaction or overall order = $n + m + p$

Note: The stoichiometric coefficient in the balanced equation for a chemical reaction is usually different from the order.

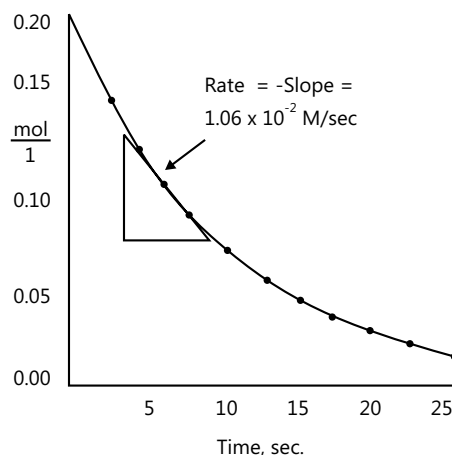


Figure 18.18: Plot of concentration versus time

Reaction	Experimental Rate Law	Order
$\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$	$\text{rate} = k[\text{NO}_2]^2$	2nd order reaction 2nd order in NO_2 0 order in CO
$\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$	$\text{rate} = k[\text{CH}_3\text{CHO}]^2$	2nd order reaction 2nd order in CH_3CHO

(e) To determining rate laws from graphs of concentration versus time (integrated rate laws).

To determine the rate law for a reaction for different concentration (or the values of some function of concentration) versus time, make three graphs.

[A] versus t (linear for a zero-order reaction)

$\ln [A]$ versus t (linear for a 1st order reaction)

$1 / [A]$ versus t (linear for a 2nd order reaction)

The graph that is linear indicates the order of the reaction with respect to A. Then, you can choose the correct rate equation:

For a zero-order reaction,	Rate = k	(k = -ve slope of line)
For a first order reaction,	rate = k[A]	(k = -ve slope of line)
For a second order reaction,	rate = k[A] ²	(k = slope of line)

(f) Regarding questions of half lives:

For a zero-order reaction $A \rightarrow \text{products}$, rate = k, $t_{1/2} = [A_0] / 2k$

For a first-order reaction $A \rightarrow \text{products}$, rate = k[A], $t_{1/2} = 0.693 / k$

For a second-order reaction $2A \rightarrow \text{products}$ or $A + B \rightarrow \text{products}$ (when $[A] = [B]$), rate = k[A]², $t_{1/2} = 1 / k [A_0]$

Graphical Relations and half-lives: Differences in half-lives for reactions of different orders (0, 1st, or 2nd) are determined by plotting graphs between reactant [A] and time (t). Change in time changes the concentration of a reactant to half.

(i) For a zero-order reaction, half-life decreases with decreasing concentration.

(ii) For a 1st order reaction, half-life is constant.

(iii) For a second-order reaction, half-life increases with decreasing concentration.

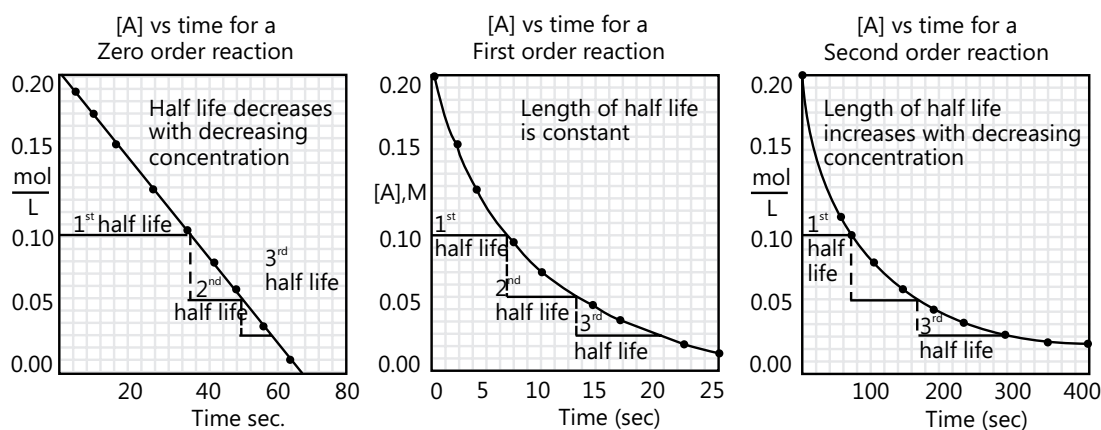


Figure 18.19: Plot of concentration versus change in time

For a first-order reaction:

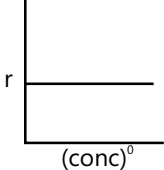
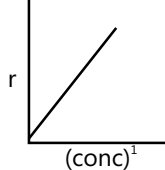
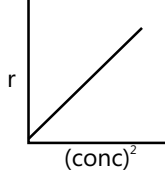
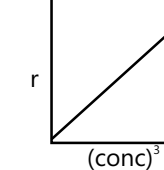
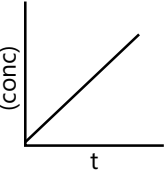
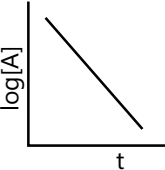
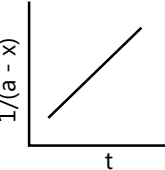
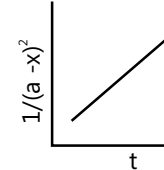
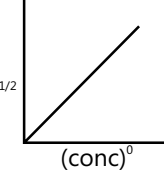
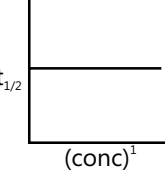
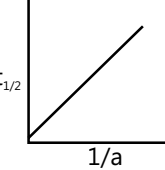
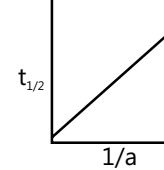
$A \rightarrow \text{products}$, rate = k A $\rightarrow \text{products}$, rate = k[A]

For a second-order reaction:

$2A \rightarrow \text{products}/A + B \rightarrow \text{products}$
(when $[A] = [B]$, rate = k[A]²)

POINTS TO REMEMBER

Topic	Formula				
Average rate of reaction	Average rate = $\frac{\text{Change in the concentration of reactants or(Products)}}{\text{Time}} = \pm \frac{\Delta C}{\Delta t} = \pm \frac{C_2 - C_1}{t_2 - t_1}$				
Instantaneous rate of reaction	Instantaneous rate = $\lim_{\Delta t \rightarrow 0} \frac{\Delta C}{\Delta t} = \frac{dC}{dt}$ For the reaction $n_1A + n_2B \rightarrow m_1C + m_2D$ Instantaneous Rate of reaction = $-\frac{1}{n_1} \frac{d[A]}{dT} = -\frac{1}{n_2} \frac{d[B]}{dT} = +\frac{1}{m_1} \frac{d[C]}{dT} = +\frac{1}{m_2} \frac{d[D]}{dT}$				
Factors affecting rate of reaction	<ul style="list-style-type: none"> • Nature of reactants and products • Effect of temperature • Concentration of Reactants • Presence of catalyst • Effect of Sunlight 				
Law of mass action and rate constant	The rate at which a substance is directly proportional to its active mass and the rate at which a reaction proceeds is proportional to the product of the active masses of the reacting substances For a reaction, $aA + bB \rightarrow \text{product}$ rate = $\left(\frac{dx}{dt}\right) \propto [A]^a[B]^b$; $\left(\frac{dx}{dt}\right) = k[A]^a[B]^b$ where k is rate constant or velocity constant. When $[A] = [B] = 1 \text{ mol/L}$, then $\frac{dx}{dt} = k$				
Unit of rate constant	Unit of rate constant = $\left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \text{sec}^{-1}$ When n = order of reaction.				
Various types of reactions	Type of reaction	Integrated rate equation	Unit of rate constant	$t_{1/2}$ Half-life period	$t_{3/4}$ period
	Zero-order reaction	$-\frac{d[A]}{dt} = k_0[A]^0$ Differential form $\frac{dx}{dt} = k$	Concentration time^{-1}	$\frac{A_0}{2k}$	

	First-order reaction	$k_1 = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$ Differential form $\frac{dx}{dt}$ $= k(a-x)$	Time ⁻¹	$\frac{0.693}{K_1}$	$2 \times \frac{0.693}{K_1} = \frac{1.382}{k_1}$
	Second-order reaction	$k_2 = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$ Differential form $\frac{dx}{dt}$ $= k(a-x)^2$	Mole ⁻¹ litre time ⁻¹	$\frac{1}{K_2 a}$	$\frac{3}{K_2 a}$
	Third-order reaction	$k_3 = \frac{1(2a-x)}{t2a^2(a-x)^2}$ Differential form $\frac{dx}{dt}$ $= k(a-x)^3$	Litre ² mole ⁻² time ⁻¹	$\frac{1}{2} \frac{3}{K_2 a}$	—
Relationship between Rate of reaction and rate constant	Zero Order 	First Order 	Second Order 	Third Order 	
					
					
Half-Life	$t_{1/2} \propto \frac{1}{a^{n-1}}$ where n = order of reaction				
Arrhenius theory	$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$ $k = A e^{-E_a/RT}$ where k_1 and k_2 are rate constant at temperatures T_1 and T_2 , respectively ($T_2 > T_1$).				