REACTION KINETICS

Chemical Kinetics

Kinetics – how fast does a reaction proceed?

Will the reaction produce significant change within milliseconds or thousands of years?

Reaction rate is the change in the concentration of a reactant or a product with time (M/s).
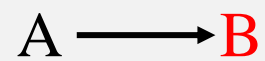
$$A \longrightarrow B$$

rate = $-\dfrac{\Delta[A]}{\Delta t}$ $\Delta[A]$ = change in concentration of A over time period Δt

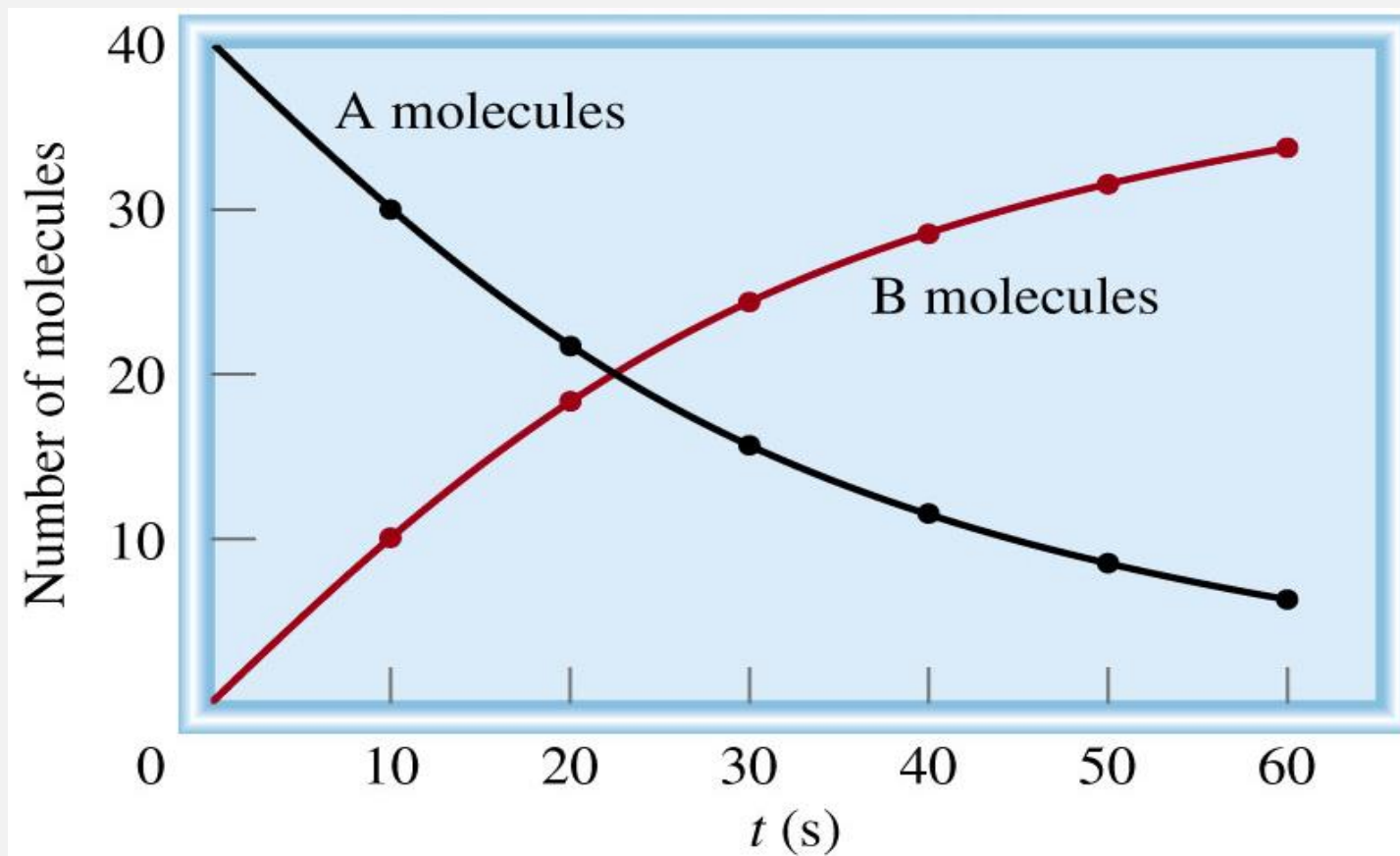rate = $\dfrac{\Delta[B]}{\Delta t}$ $\Delta[B]$ = change in concentration of B over time period Δt
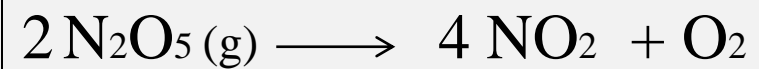
Because [A] decreases with time, $\Delta[A]$ is negative.

A ⟶ B
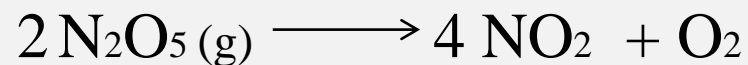

$$\text{rate} = -\ \frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

Reaction Rates and Stoichiometry

$$2\,N_2O_{5\,(g)} \longrightarrow 4\,NO_2 + O_2$$

Consider the decomposition of N_2O_5 to give NO_2 and O_2:

$$2\,N_2O_{5\,(g)} \longrightarrow 4\,NO_2 + O_2$$

Time	Concentration (M)		
(s)	N_2O_5	NO_2	O_2
0	0,02	0	0
100	0,0169	0,0063	0,0016
200	0,0142	0,0115	0,0029
300	0,0120	0,0160	0,0040
400	0,0101	0,0197	0,0049
500	0,0086	0,0229	0,0057
600	0,0072	0,0256	0,0064
700	0,0061	0,0278	0,0070

Reactants decrease
with time

Products increase
with time
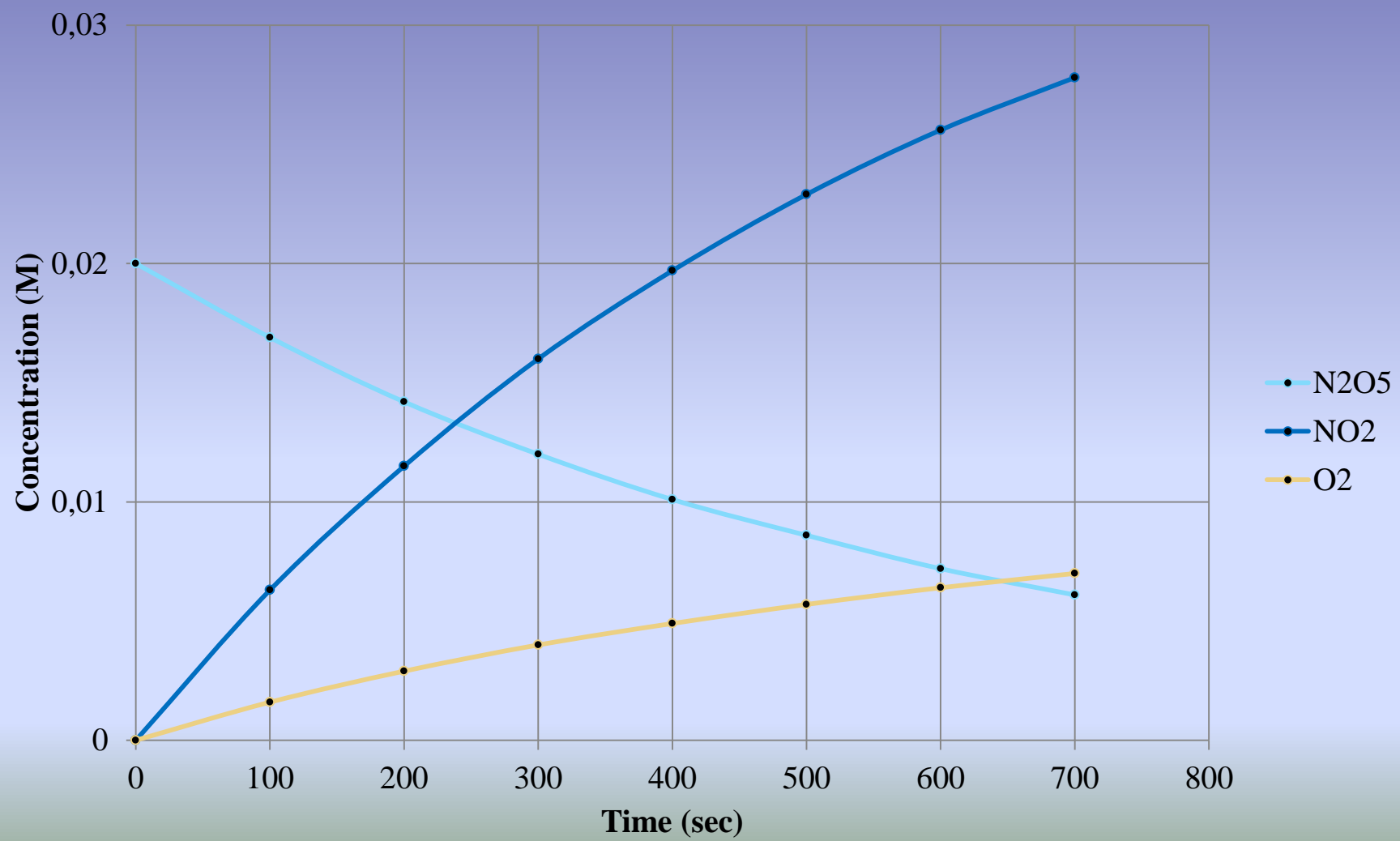
From the graph looking at t = 300 to 400 sec

Rate O_2 = $\dfrac{0.0009\ M}{100\ s}$ = 9 x 10^{-6} Ms^{-1}

Rate NO_2 = $\dfrac{0.0037\ M}{100\ s}$ = 3.7 x 10^{-5} Ms^{-1}

Rate N_2O_5 = $\dfrac{-0,0019\ M}{100\ s}$ = -1.9 x 10^{-5} Ms^{-1}

Why do they differ?

Recall :

$$2\ N_2O_{5\ (g)} \longrightarrow 4\ NO_2\ + O_2$$
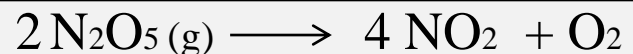
To compare the rates one must account for the **stoichiometry.**

Rate $O_2 = \dfrac{1}{1}$ x 9 x 10^{-6} Ms^{-1} = 9 x 10^{-6} Ms^{-1}

Rate $NO_2 = \dfrac{1}{4}$ x 3.7 x 10^{-5} Ms^{-1} = 9.2 x 10^{-6} Ms^{-1} **Now they agree !**

Rate $N_2O_5 = -\dfrac{1}{2}$ x 1.9 x 10^{-5} Ms^{-1} = 9.5 x 10^{-6} Ms^{-1}

Reaction Rates and Stoichiometry

$$2A \longrightarrow B$$
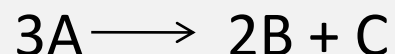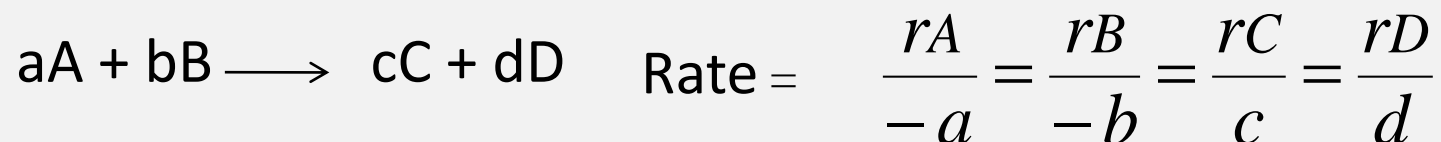
Two moles of A disappear for each mole of B that is formed.

$$\text{rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} \qquad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

$$aA + bB \longrightarrow cC + dD$$

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Example :

$$aA + bB \longrightarrow cC + dD \qquad Rate = \quad \frac{rA}{-a} = \frac{rB}{-b} = \frac{rC}{c} = \frac{rD}{d}$$

$$3A \longrightarrow 2B + C$$

If the overall rate of rxn is 1st order wrt to A , then r = k [A]

$$rate = \quad \frac{ra}{-3} = \frac{rb}{2} = \frac{rc}{1}$$

r_A = rxn. rate wrt to $\qquad r_A$ = -3 k [A]

r_B = rxn. rate wrt to $\qquad r_B$ = 2 k [A]

r_C = rxn. rate wrt to $\qquad r_C$ = k [A]

The Rate Law and Reaction Order

The *rate law* expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

$$aA + bB \longrightarrow cC + dD$$
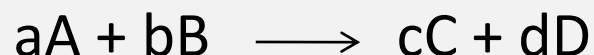
$$\text{Rate} = k\,[A]^x[B]^y$$

reaction is **xth order** with respect to reactant A

reaction is **yth order** with respect to reactant B

reaction is **(x +y)th order overall**

@ constant temperature,
the rate of rxn. (disappearance of a reactant or formation of a product) is some function of the concentration of the reactants

$$aA + bB \longrightarrow cC + dD$$
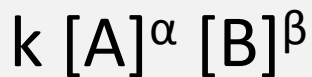
order of the rxn. respect to individual reactants A and B
(0, 1, 2 may be fractional)

Overall order of rxn = r= $\quad k \, [A]^{\alpha} \, [B]^{\beta}$
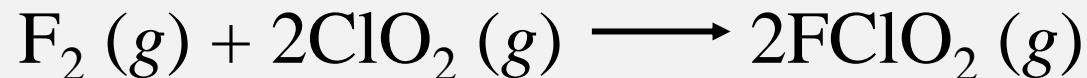
(mol/L.t)

molar concentrations of reactants (mol/ L)

reaction rate constant

Overall order of rxn = α+β
Order of rxn with respect to reactant A =α
Order of rxn with respect to reactant B = β

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

TABLE 13.2	Rate Data for the Reaction Between F_2 and ClO_2		
$[F_2]$ (M)	$[ClO_2]$ (M)	Initial Rate (M/s)	
1. 0.10	0.010	1.2×10^{-3}	
2. 0.10	0.040	4.8×10^{-3}	
3. 0.20	0.010	2.4×10^{-3}	

$$\text{rate} = k \, [F_2]^x[ClO_2]^y$$

Double $[F_2]$ with $[ClO_2]$ constant

Rate doubles

$x = 1$

Quadruple $[ClO_2]$ with $[F_2]$ constant

Rate quadruples

$y = 1$

$$\text{rate} = k \, [F_2][ClO_2]$$

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Rate Laws

- Rate laws are **always** determined experimentally.

- Reaction order is **always** defined in terms of reactant (not product) concentrations.

- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.

$$F_2\ (g) + 2ClO_2\ (g) \longrightarrow 2FClO_2\ (g)$$
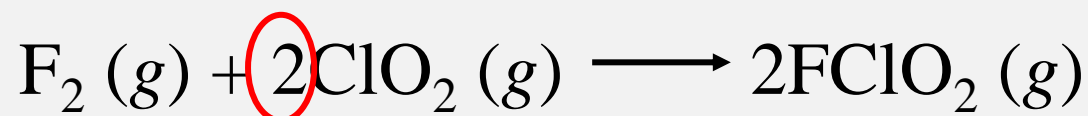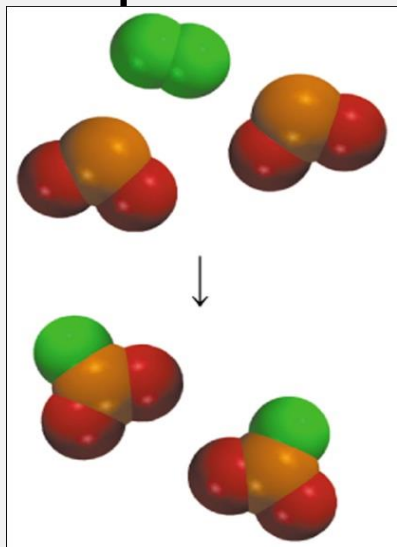
$$\text{rate} = k\ [F_2][ClO_2]^1$$

Unit of k (reaction rate constant)

$$k = M^{1-n} t^{-1}$$

For 0 order rxn. $\longrightarrow$ $k = \text{rate} = \dfrac{mol}{L.t}$

$r = k[A]^0$ $\longrightarrow$ $r = k$

For 1st order rxn. $\longrightarrow$ $k = \dfrac{rate}{\dfrac{mol}{L}} = \dfrac{\dfrac{mol}{L.t}}{\dfrac{mol}{L}} = \dfrac{1}{t}$

$r = k\,[A]$

For 2nd order rxn. $\longrightarrow$ $k = \dfrac{rate}{\left(\dfrac{mol}{L}\right)^2} = \dfrac{\dfrac{mol}{L.t}}{\left(\dfrac{mol}{L}\right)^2} = \dfrac{L}{mol.t}$

$r = k\,[A]^2$

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Example :

r = k [A]² [B]

Order of overall rxn. = 2 + 1 = 3

Order of rxn. with respect to reactant A = 2

Order of rxn. with respect to reactant B = 1

Unit of k = $M^{-2} t^{-1}$ = $\left(\dfrac{L}{mol}\right)^{2} \dfrac{1}{t}$

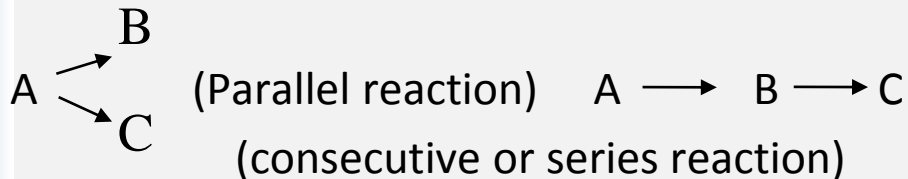# Classes of Reactions That Occur In Nature

Homogenous Reactions

Reactants and products are in the same phase. (i.e., liquid, solid or gas)

Reactants are distributed continuously(but not necessarily uniformly) throughout the fluid.

1a. Single irreversible reaction:

$A \longrightarrow B$ $A+A \longrightarrow B$ $aA + bB \longrightarrow C$

1b. Multiple irreversible reaction:

$A \begin{smallmatrix} \nearrow B \\ \searrow C \end{smallmatrix}$ (Parallel reaction) $A \longrightarrow B \longrightarrow C$

(consecutive or series reaction)

1c. Reversible reaction:

$A \rightleftarrows B$ $A+B \rightleftarrows C+D$

Heterogenous Reactions

Reactions that occur at surfaces between phases.

Examples:

Reactions on the surface of ion exchange resin

Reactions that require the presence of a solid phase catalyst
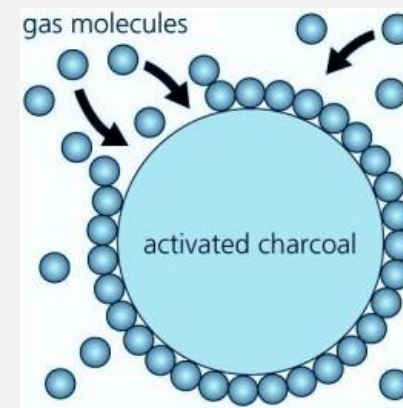
Types of Reactions and Reaction Rates

→ irreversible rxns

→ reversible rxns

→ saturation rxns

→ autocatalytic rxns

Irreversible Reactions

a)Single Irreversible Rxns:

$A \longrightarrow P$

$A + A \longrightarrow P$

$aA + bB \longrightarrow P$
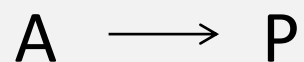
Irreversible Reactions

a)Single Irreversible Rxns:

$$r = \frac{r_A}{-a} = \frac{r_B}{-b} = r_P$$

Example:

aA $\longrightarrow$ pP   (Rxn. rate $\longrightarrow$ 1st order)

$$r = k\,[A]$$
$$r_A = r \times (-a)$$
$$r_A = -a\,k\,[A]$$
$$r_P = p\,k\,[A]$$

b)Multiple Irreversible Rxns:

b-1) Parallel rxns:

$$k_1 \quad bB$$

$$aA$$

$$k_2 \quad cC$$
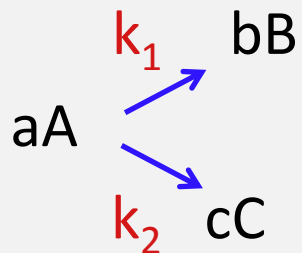
$$r_1 = -\frac{r_A}{a} = \frac{r_B}{b}$$

$$r_2 = -\frac{r_A}{a} = \frac{r_C}{c}$$

Overall rate of rxn: $\quad r_1 + r_2 \quad = -2\frac{r_A}{a} = \frac{r_B}{b} + \frac{r_C}{c}$

Rate of rxn with respect to $A = r_A = -ar_1 - ar_2$

Rate of rxn with respect to $B = r_B = b\,r_1$

Rate of rxn with respect to $C = r_C = cr_2$

k_1 bB

aA

k_2 cC
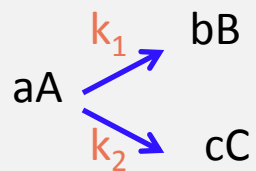
If both of the rates of rxn $\longrightarrow$ 1st order

$r_1 = k_1[A]$
$r_2 = k_2[A]$

$r_A = -ak_1[A] - ak_2[A]$
$r_B = bk_1[A]$
$r_C = ck_2[A]$

$$a\,A \xrightarrow{k_1} b\,B \xrightarrow{k_2} c\,C$$

Slowest step limits the overall rxn. rate
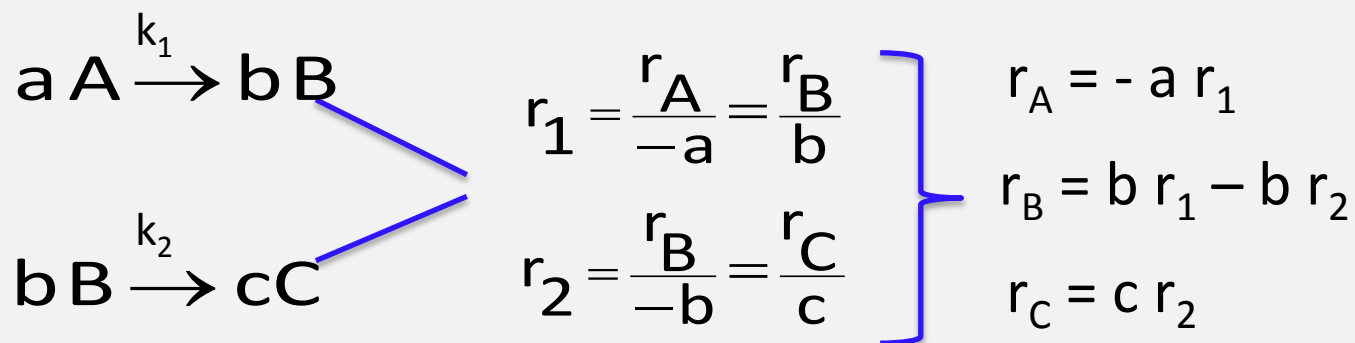
$$a\,A \xrightarrow{k_1} b\,B$$

$$b\,B \xrightarrow{k_2} c\,C$$

$$r_1 = \frac{r_A}{-a} = \frac{r_B}{b}$$

$$r_2 = \frac{r_B}{-b} = \frac{r_C}{c}$$

$$r_A = -a\,r_1$$

$$r_B = b\,r_1 - b\,r_2$$

$$r_C = c\,r_2$$

<u>If both of the rates of rxn $\longrightarrow$ 1st order</u>

$$r_1 = k_1[A]$$
$$r_2 = k_2[A]$$

$$r_A = -ak_1[A]$$

$$r_B = bk_1[A] - bk_2[B]$$

$$r_C = ck_2[A]$$

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Reversible Reactions

$$aA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} bB$$

$$aA \xrightarrow{k_1} bB$$
$$bB \xrightarrow[k_2]{} aA$$

$$\left.\begin{array}{l} r_1 = \dfrac{r_A}{a} = \dfrac{r_B}{b} \\[2em] r_2 = \dfrac{r_B}{b} = \dfrac{r_A}{a} \end{array}\right\}$$

$$r_A = ar_1 + ar_2$$
$$r_B = br_1 + br_2$$
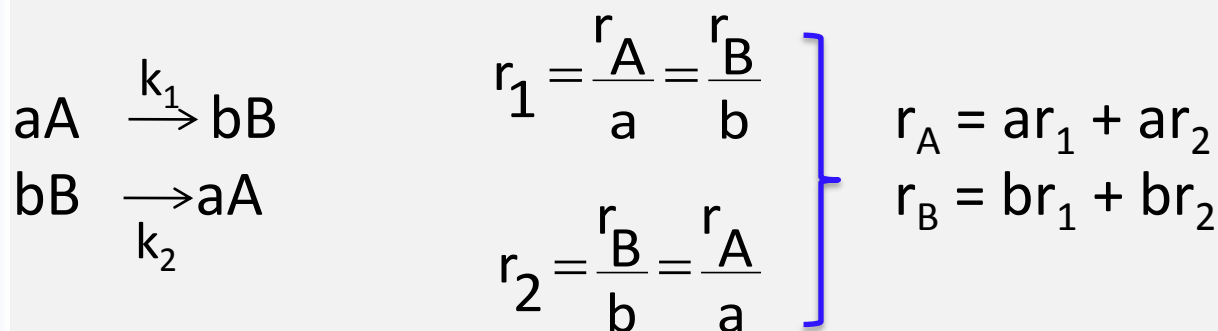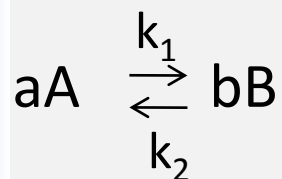
Note:

for reversible rxns →signs of stoichiometric coefficients
                    (both reactants & products) are always positive (+)

If both of the rates of rxn ⟶ 1st order

$$r_1 = k_1[A]$$
$$r_2 = k_2[A]$$

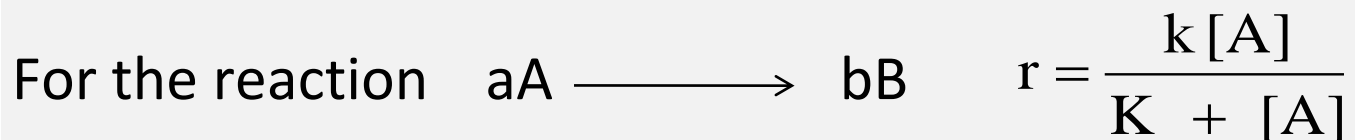$$r_a = ak_1[A] + ak_2[B]$$
$$r_b = bk_1[A] + bk_2[B]$$

Saturation Type Reactions

Saturation type reactions have a maximum rate that is a point at which the rate becomes independent of concentration A.

For the reaction   aA $\longrightarrow$ bB $r = \dfrac{k\,[A]}{K\ +\ [A]}$

FIGURE 5.1

Graphical representation of saturation-type reaction rate as a function of concentration.

r = rate of rxn, mol /L.t

[A] = conc. of reactant, mol / L

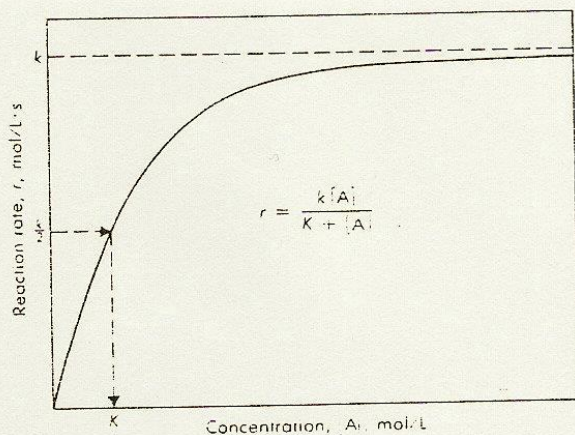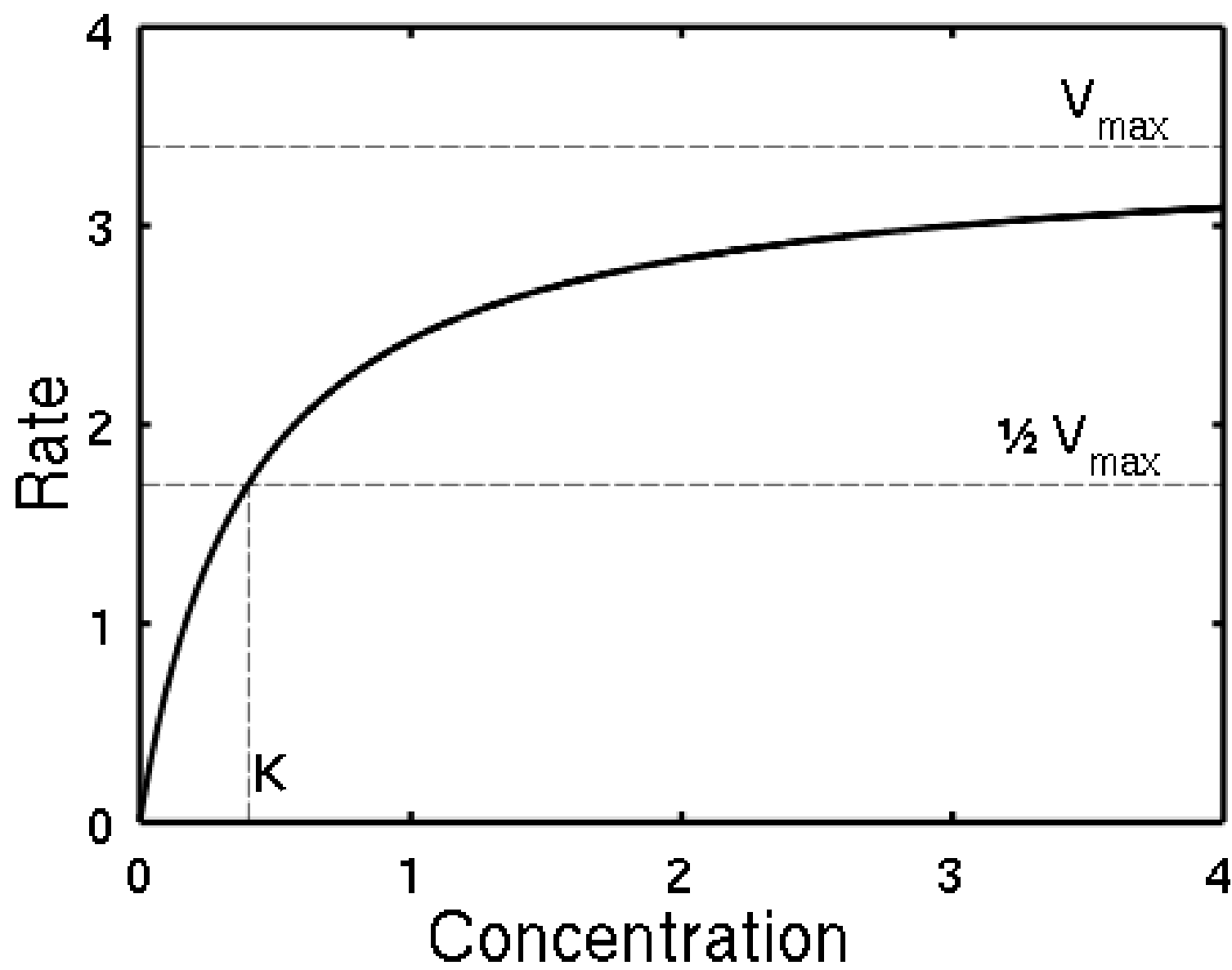k = rxn rate constant, mol/ L.t

K = half saturation constant, mol/ L

Fig.1. Graphical representation of Saturation –Type Reaction

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Saturation Type Reactions (continue)

$$r = \frac{k[A]}{K + [A]}$$

- When K << [A] $\longrightarrow$ r = $\dfrac{k\,[A]}{K + [A]}$ ≈ k (zero order)

  $\downarrow$

  Negligible

FIGURE 5.1
Graphical representation of saturation-type reaction rate as a function of concentration.

Ref: Tchobanoglous and Scroeder, 1985, Addison-Wesley Publishing Company
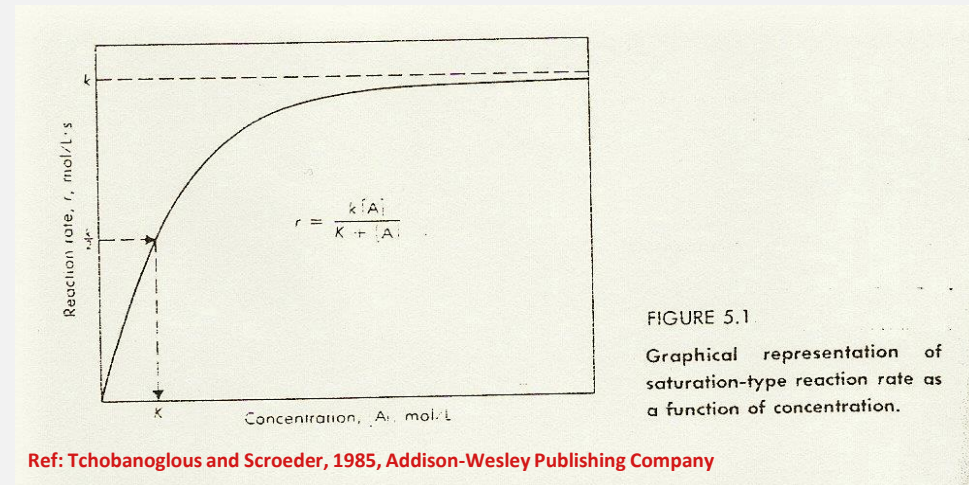
- When K >> [A] $\longrightarrow$ r = $\dfrac{k\;[A]}{K + [A]}$ ≈ $\dfrac{k\,[A]}{K}$ (first order)

  $\downarrow$

  Negligible

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Saturation Type Reactions (continued)

For the reaction A + B $\xrightarrow{k}$ P

$$r = \frac{k\,[A]\,[B]}{K + [A]} = k\left(\frac{[A]}{K_1 + [A]}\right)\left(\frac{[B]}{K_2 + [B]}\right)$$

Autocatalytic Reactions

Autocatalytic reaction rates are functions of the product concentration.

Example: Bacterial growth

(rate of increase in bacterial number is proportional to the number present)

Autocatalytic rxns can be ⟶ 1st order

2nd order

Saturation Type

Partially Autocatalytic (function of

reactant & product)

1st order Autocatalytic Rxn.

$$aA \longrightarrow bB \qquad r = k\,[B] = \frac{r_A}{a} = \frac{r_B}{b}$$

$$r_A = a\,k\,[B]$$
$$r_B = b\,k\,[B]$$

2nd order Autocatalytic Rxn.

$$aA \longrightarrow Bb \qquad r = k\,[B]\,[A] = \frac{r_A}{a} = \frac{r_B}{b}$$
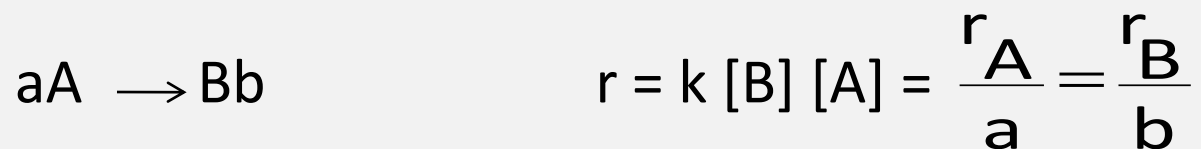
$$r_A = a\,k\,[A][B]$$
$$r_B = b\,k\,[A]\,[B]$$

Effect of Temperature On Reaction Rate Coefficients

The temperature dependence of the rate constant is given by

Van't Hoff- Arhenius relationship

$$\frac{k_2}{k_1} = \theta^{(T_2 - T_1)}$$

For BOD

$\theta = 1.047$ for temperatures between 20° - $30\,^oC$

Theta remains constant for only a small range of temperatures.

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

Subtracting $\ln k_2$ from $\ln k_1$ gives

$$\ln k_1 - \ln k_2 = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln k_1 - \ln k_2 = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

$$\frac{k_2}{k_1} = \theta^{(T_2 - T_1)}$$

EXAMPLE:

A first order reaction rate constant, k_1 at 20°C = 0.23/d.

If river temperature is 25°C, what will k_2 be in that environment?

$$\frac{k_2}{k_1} = \theta^{(T_2 - T_1)}$$

$k_2 = k_1(1.047)^{(T-20)} = 0.23(1.047)^{(T-20)} = 0.30/d$

Analysis of Experimental Data

Methods to determine the order of a reaction from experimental data

1-) Method of Integration

2-) Differential Method

           Most commonly used

3-) Time Reaction Method

4-) Isolation Method

I.Method of Integration

→ Integrated forms of the various rate expressions (0th order, 1st order, etc..)

→ Plotting the experimental data functionally based on the integrated form of the rate expression

If straight line plot is obtained ⟶ It is assumed that the order of the rxn corresponds to the rxn. plotted

→ Determine the reaction rate constant from the plot.

a) Irreversible Zero-Order Reaction $A \longrightarrow P$

$$\longrightarrow \quad rA = \frac{d[A]}{dt} = -k[A]^0 = -k$$

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

$$\longrightarrow \quad \int_{c_a(0)}^{c_a(t)} d[A] = \int_0^t -k.dt$$

$$\longrightarrow \quad \boxed{Ca_{(t)} = Ca_{(0)} - kt}$$

<u>To determine reaction rate constant (k)</u>

Plot $C_a(t)$ versus **t** $\longrightarrow$

(a)

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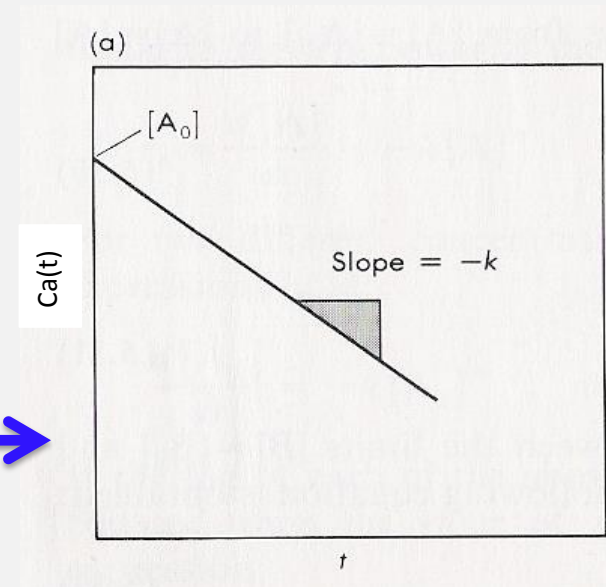
b) Irreversible First Order Reaction $A \longrightarrow P$

$\longrightarrow \quad r_A = \dfrac{d[A]}{dt} = -k[A]$

$\longrightarrow \quad \displaystyle\int_{C_{a(0)}}^{C_{a(t)}} \dfrac{d[A]}{[A]} = -k\int_0^t dt$

$\longrightarrow \quad LnCa_{(t)} - LnCa_{(0)} = -kt$

$\longrightarrow \quad Ln\dfrac{Ca_{(t)}}{Ca_{(0)}} = -kt$

$\longrightarrow \quad \boxed{C_{a(t)} = C_{a(0)}\, e^{-kt}}$

To determine reaction rate constant (k)

Plot $\quad -Ln\dfrac{Ca_{(t)}}{Ca_{(0)}} \quad$ versus **t** $\longrightarrow$

(b)

Slope = k

$-Ln\dfrac{Ca_{(t)}}{Ca_{(0)}}$

t

$$Ca_{(t)} = Ca_{(0)} - kt$$

$$C_{a(t)} = C_{a(0)} e^{-kt}$$

(a)

$[A_0]$

$Ca(t)$

Slope $= -k$

t

(b)

$-\text{Ln}\dfrac{Ca_{(t)}}{Ca_{(0)}}$

Slope $= k$

t

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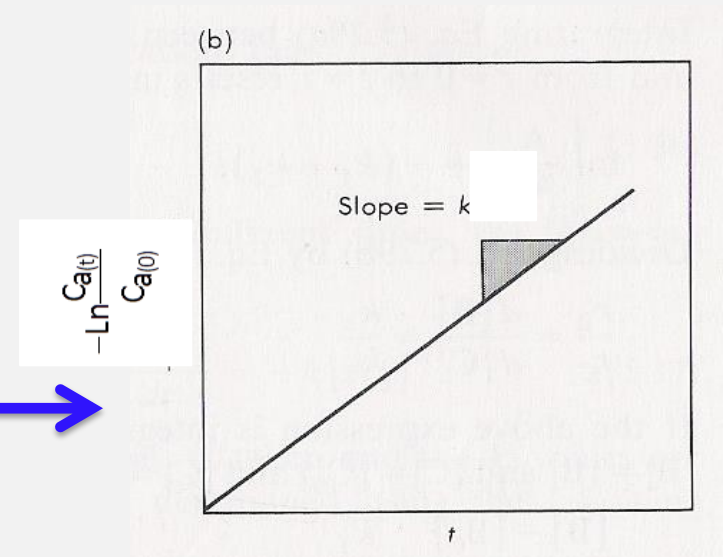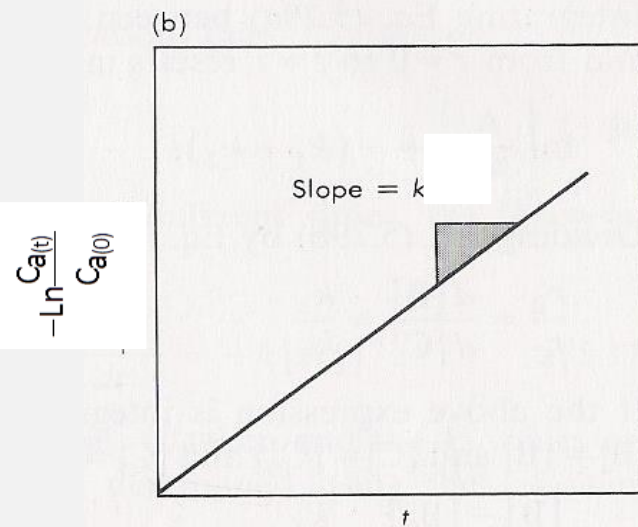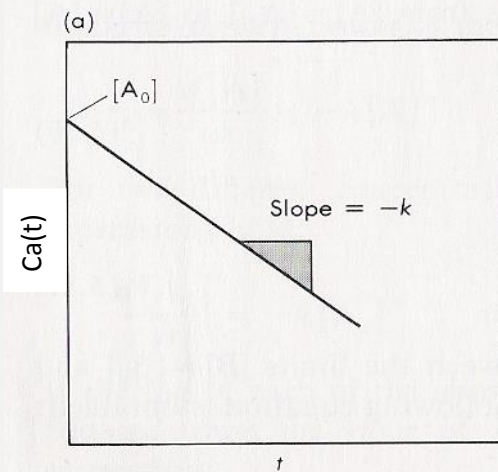
Half Life

Time required for the amount of substance to decrease to half its initial value

$$Ca_{(t_{1/2})} = \frac{Ca_{(0)}}{2}$$

For 1st order rxn :

$$\longrightarrow \quad Ca_{(t)} = Ca_{(0)} \cdot e^{-kt}$$

$$\longrightarrow \quad Ca_{(t_{1/2})} = Ca_{(0)} \cdot e^{-k \cdot t_{1/2}}$$

$$\longrightarrow \quad \frac{Ca_{(0)}}{2} = Ca_{(0)} \cdot e^{-k \cdot t_{1/2}}$$

$$\longrightarrow \quad 1/2 = e^{-k \cdot t_{1/2}}$$

$$\longrightarrow \quad Ln\frac{1}{2} = Ln \cdot e^{-k \cdot t_{1/2}} \quad \longrightarrow \quad Ln\frac{1}{2} = -k \cdot t_{1/2} \quad \longrightarrow \quad \boxed{t_{1/2} = \frac{Ln2}{k} = \frac{0.693}{k}}$$

c) Irreversible Second Order Reaction $\quad A+A \longrightarrow P$

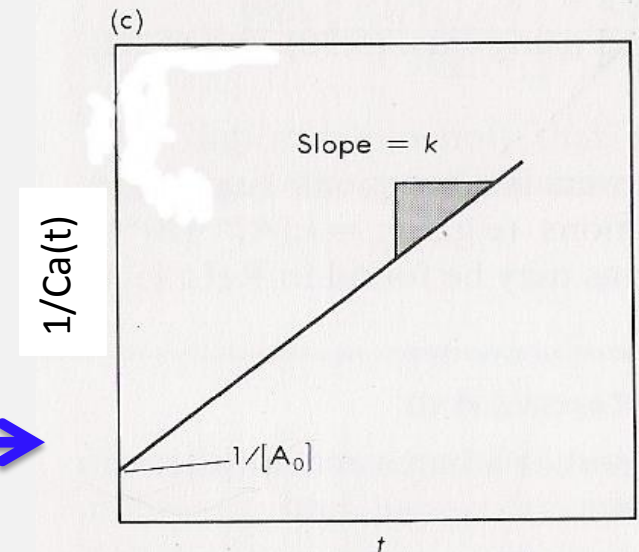$$\longrightarrow \quad r_A = \frac{d[A]}{dt} = -k[A]^2$$

$$\longrightarrow \quad \int_{Ca(0)}^{Ca(t)} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

$$\longrightarrow \quad -\frac{1}{[A]} \Big|_{Ca_{(0)}}^{Ca_{(t)}} = -kt$$
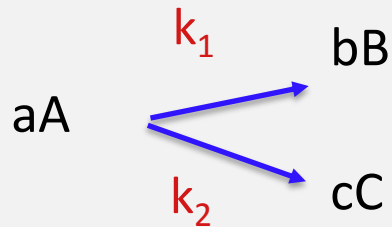
$$\longrightarrow \quad \boxed{-\frac{1}{C_a(t)} = kt + \left(\frac{1}{C_a(t)} \right)}$$

<u>To determine reaction rate constant (k)</u>

Plot $\dfrac{1}{C_a(t)}$ versus **t** $\longrightarrow$

(c)

Slope = k

1/Ca(t)

$-1/[A_0]$

t

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d) Irreversible Parallel Reaction (1st order)

$$aA \quad\begin{matrix} \xrightarrow{k_1} & bB \\ \xrightarrow{k_2} & cC \end{matrix}$$

$$r_1 = k_1[A] = \frac{r_a}{-a} = \frac{r_b}{b}$$

$$r_2 = k_2[A] = \frac{r_a}{-a} = \frac{r_c}{c}$$
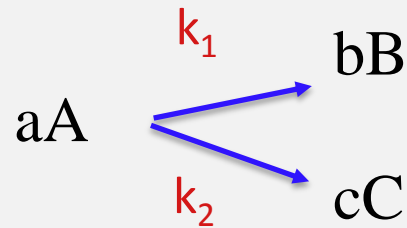
a, b, c = 1

$$r_a = \frac{d[A]}{dt} = -k_1[A] - k_2[A]$$

$$r_b = \frac{d[B]}{dt} = k_1.[A]$$

$$r_c = \frac{d[C]}{dt} = k_2[A]$$

d) Irreversible Parallel Reaction (1st order-continue)

$$aA \overset{k_1}{\underset{k_2}{\Large <}} \begin{array}{c} bB \\ \\ cC \end{array}$$

$$r_a = \frac{d[A]}{dt} = -k_1[A] - k_2[A]$$

$$\frac{-d[A]}{dt} = (k_1 + k_2).[A]$$

$$-\int_{Ca_{(0)}}^{Ca_{(t)}} \frac{d[A]}{[A]} = (k_1 + k_2).\int_0^t dt$$

$$-(LnCa_{(t)} - LnCa_{(0)}) = (k_1 + k_2).t$$

$$LnCa_{(t)} - LnCa_{(0)} = -(k_1 + k_2).t$$

$$Ln\frac{Ca_{(t)}}{Ca_{(0)}} = -(k_1 + k_2).T$$

$$\boxed{Ca_{(t)} = Ca_{(0)} \cdot e^{-(k_1 + k_2)..t}}$$

d) Irreversible Parallel Reaction (1st order-continue)

$$aA \xrightarrow{k_1} bB$$
$$aA \xrightarrow{k_2} cC$$
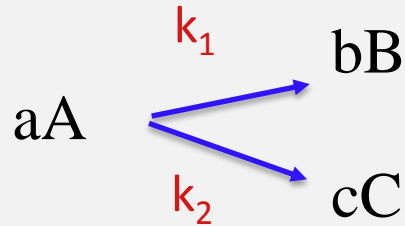
1st order reaction $\longrightarrow$ $C_{a(t)} = C_{a(0)} e^{-kt}$

1st order irreversible parallel reaction $\longrightarrow$ $Ca_{(t)} = Ca_{(0)} \cdot e^{-(k_1+k_2) \cdot t}$

$$aA \underset{k_2}{\overset{k_1}{\Longrightarrow}} \begin{matrix} bB \\ cC \end{matrix}$$

$$\frac{r_b}{r_c} = \frac{d[B]/dt}{d[C]/dt} = \frac{k_1 \cdot [A]}{k_2 \cdot [A]}$$

$$\frac{r_b}{r_c} = \frac{d[B]}{d[C]} = \frac{k_1}{k_2} \longrightarrow k_2 \int_{Cb_{(0)}}^{Cb_{(t)}} d[B] = k_1 \int_{Cc_{(0)}}^{Cc_{(t)}} [C]$$
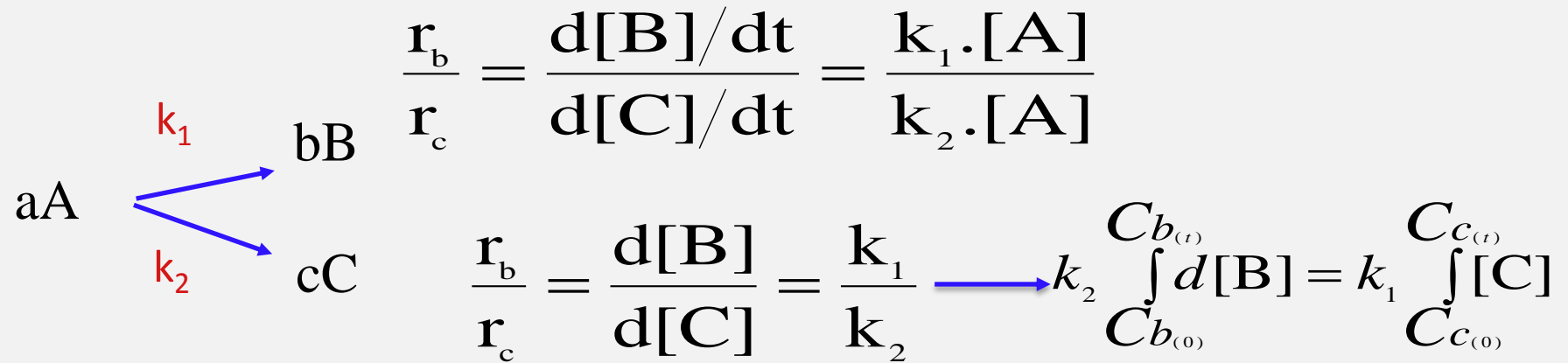
$$k_2 \cdot [Cb_{(t)} - Cb_{(0)}] = k_1 \cdot [Cc_{(t)} - Cc_{(0)}]$$

$$\boxed{k_1 = \frac{k_2 [Cb_{(t)} - Cb_{(0)}]}{[Cc_{(t)} - Cc_{(0)}]}}$$

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II.Differential Method

Assumption: The rate of rxn is proportional to the nth power of concentration.

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

For 2 different concentrations at 2 different times;

$$t = t_1, \qquad A = A_1 \qquad \longrightarrow \qquad \frac{d[A_1]}{dt} = -k[A_1]^n$$

$$t = t_2, \qquad A = A_2 \qquad \longrightarrow \qquad \frac{d[A_2]}{dt} = -k[A_2]^n$$

If logarithm of each of the above equation is taken and the k values are equated:

$$\frac{d[A_1]}{dt} = -k[A_1]^n \longrightarrow \log\left(\frac{-d[A_1]}{dt}\right) = \log k + n\log[A_1]$$

$$\frac{d[A_2]}{dt} = -k[A_2]^n \longrightarrow \log\left(\frac{-d[A_2]}{dt}\right) = \log k + n\log[A_2]$$

$$n = \frac{\log(-d[A_1]/dt) - \log(-d[A_2]/dt)}{\log[A_1] - \log[A_2]}$$

Example:

Determine the order of the reaction and the reaction rate constant for the following data derived from on experiment carried out in a batch reactor.

Solve the problem

a)Using Integration Method
b)Using Differential Method

Time (min)	[A] mol/L
0	100
1	50
2	37
3	286
4	23.3
5	19.6
6	16.9
7	15.2
8	13.3
9	12.2
10	11.1