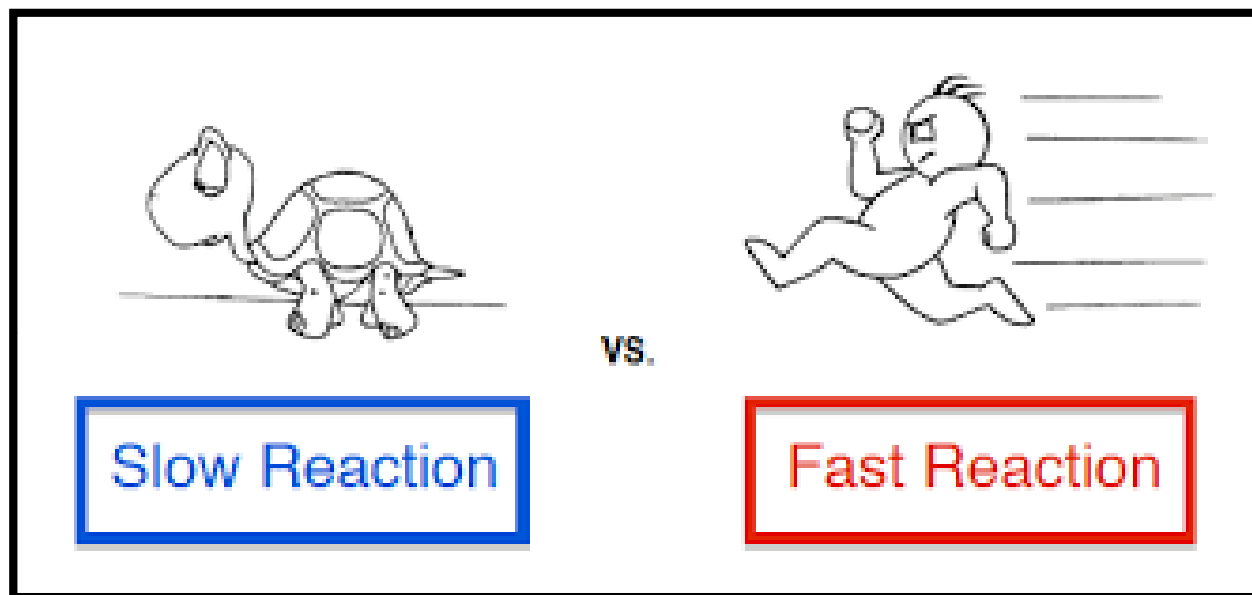


Total Marks is 100
Sessional Marks 50
ESE 50

Sessional Marks (50)
Mid term Exam 15
Lab exam 15
TA 20

ESE (50)
(Theory) $5 \times 8 = 40$
(Lab) $1 \times 10 = 10$

KINETICS OF CHEMICAL REACTIONS



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CHEMICAL KINETICS

The *branch of Physical chemistry* which *deals with the rate of reactions* or *the Kinetics of Chemical reactions* is called **Chemical Kinetics**.

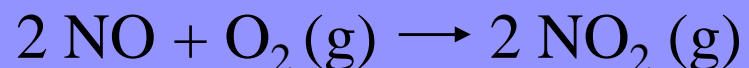
The Study of Kinetics of Chemical reactions includes:

- (1) The *rate of the reactions* and *rate laws*.
- (2) The *mechanism* or the sequence of steps by which a reaction occurs.
- (3) The *factors that influence the rate of a reaction*.
- (4) Proposes *theory of the reactions*.

Rate of a reaction

The **rate of reaction** is defined as the change in concentration of any of reactant or products per unit time.

For a chemical reaction, there are **many ways to express the reaction rate**. The relationships among expressions depend on the equation.



$$\text{Reaction rate} = -\frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t}$$

Instantaneous Rate of Reaction

If the time interval be infinitesimally small (*i.e.*, Δt approaches zero), the rate is referred to as the **instantaneous rate** and is written in calculus as

$$\text{rate} = \frac{d[]_t}{dt}$$

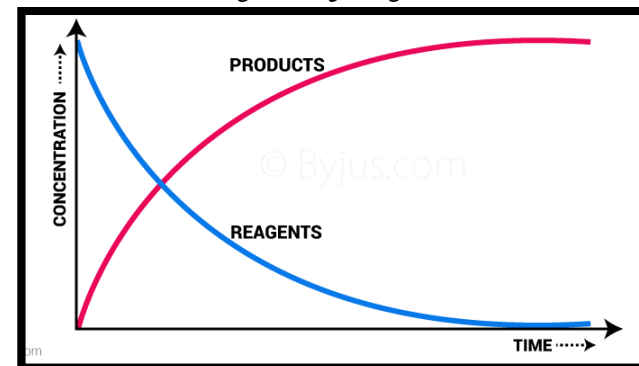
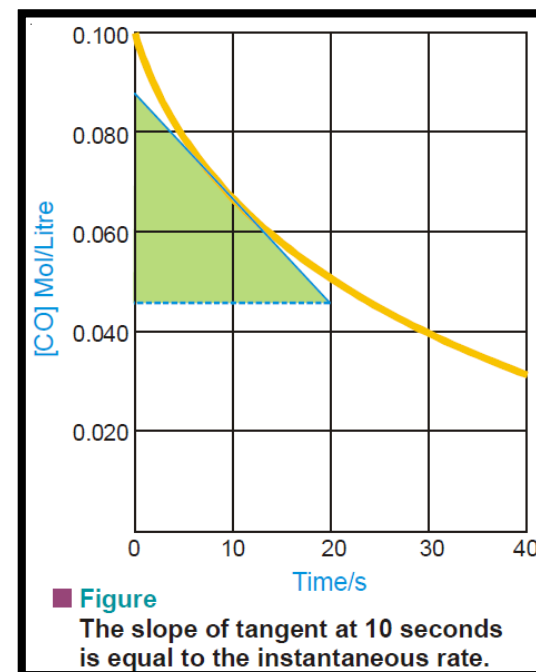


Fig.- Variation of conc. of reactant and products with time.



Rate law

Let us consider the example of a reaction $2A + B \rightarrow \text{products}$ which has the **rate law** can be expressed as:

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

*An expression which shows how the reaction rate is related to concentrations is called the **rate law** or **rate equation**.*

Order of a reaction

The order of a reaction is defined as the sum of the powers of concentrations in the rate law. The order of such a reaction is $(m + n)$.

In general for a reaction of order n , the **unit of rate constant**, $k = (\text{mol l}^{-1})^{n-1} \text{ s}^{-1}$

Methods for the determination of order of a reaction:

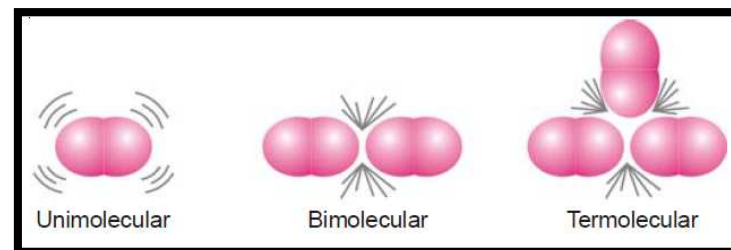
- 1) *Using integrated rate equations (Devised by van't Hoff)*
- 2) *Graphical method*
- 3) *Using half-life period (Suggested by Ostwald): $n = 1 + (\ln t_{1/2})_1 / \ln(t_{1/2})_2 / \ln(a_2/a_1)$*
- 4) *The differential method: $(r = k_n c^n)$*
- 5) *Ostwald's isolation method*

Molecularity of a reaction

Chemical reactions may be classed into two types :

(a) *Elementary reactions* and (b) *Complex reactions*

(a) *The molecularity of an elementary reaction is defined as : the number of reactant molecules involved in a reaction.*



High Molecularity Reactions are Rare

(b) *The molecularity of a complex reaction is defined as : the number of molecules or atoms taking part in the rate-determining step (i.e., the slowest step).*

Order of a Reaction

1. It is the **sum of powers** of the concentration terms in the rate law expression.
2. It is an **experimentally** determined value.
3. It can have **fractional** value.
4. It can assume **zero value**.
5. Order of a reaction **can change** with the conditions such as pressure, temperature, concentration.

Molecularity of a Reaction

1. It is number of **reacting species** undergoing simultaneous collision in the elementary or simple reaction.
2. It is a **theoretical** concept.
3. It is always a **whole number**.
4. It **can not have zero value**.
5. Molecularity is **invariant** for a chemical equation.

Integrated rate equations and The differential method for rate of a reaction:

One reactant A decomposes in 0^{th} or 1^{st} or 2^{nd} order rate law.

Differential rate law

$$-d[A] / dt = k[A]^0$$

$$d[A]$$

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

$$dt$$

$$d[A]$$

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

$$dt$$

Integrated rate law

$$[A] = [A]_0 - k t$$

$$[A] = [A]_0 e^{-k t}$$

$$\text{or } \ln [A] = \ln [A]_0 - k t$$

$$1$$

$$1$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k t$$

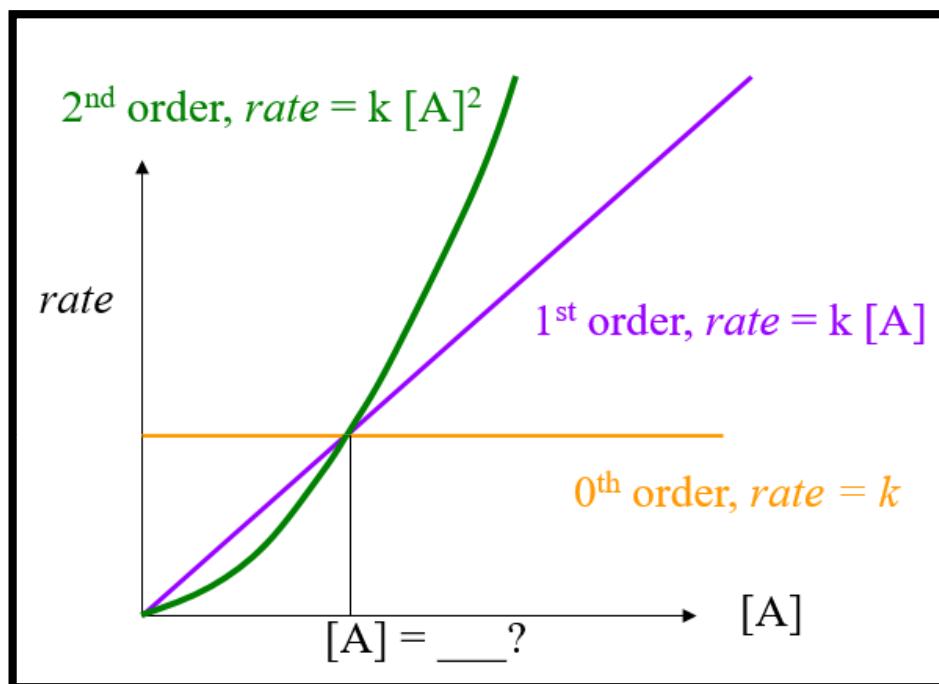
$$[A]$$

$$[A]_0$$

$[A]$ is conc. at any time, t and $[A]_0$ is conc. at time, $t = 0$

PSEUDO-ORDER REACTIONS: A reaction in which one of the reactants is present in a large excess shows an order different from the actual order.

Graphical analysis of Variation of *Reaction rates* vs Concentration of reactants with respect to the Order of a reaction

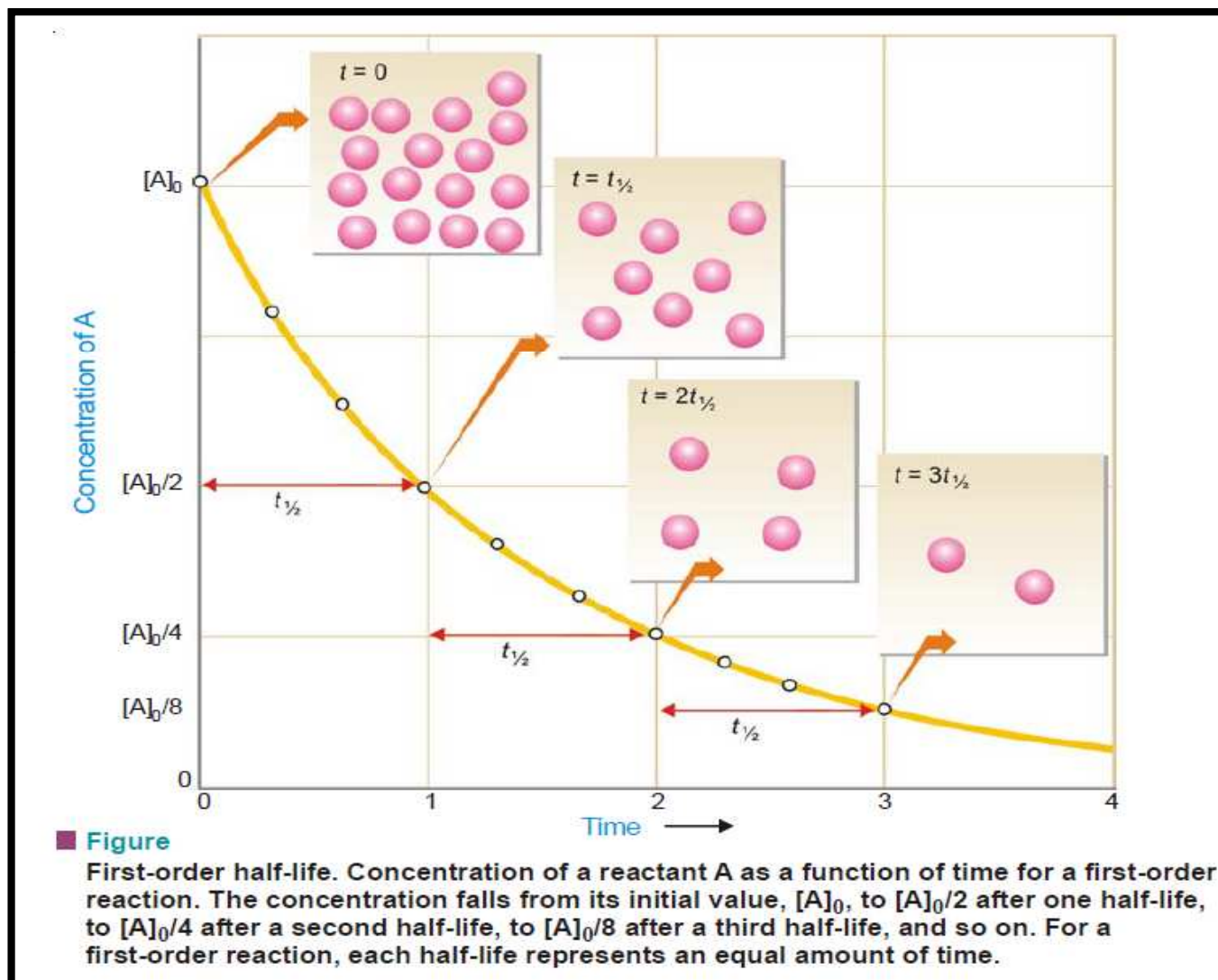


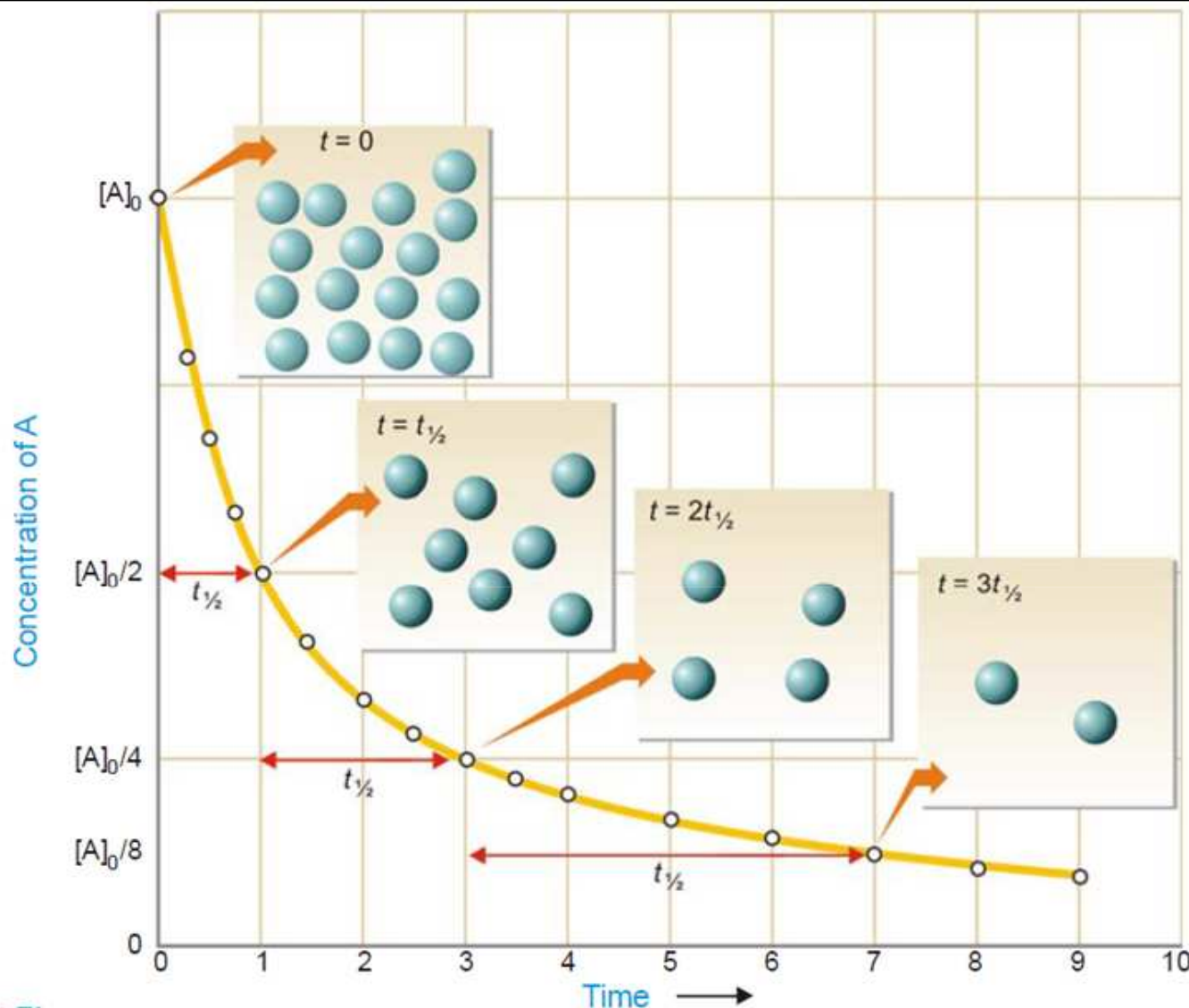
The variation of *reaction rates as functions of concentration* for various order is interesting.

Radioactive decay usually follow ***1st order kinetics***, and half life of an isotope is used to indicate its stability.

Half-life: *It is defined as the time required for the concentration of a reactant to decrease to half its initial value.*

Half-life, $t_{1/2} \propto 1/[A]^{n-1}$, where 'n' is the order of the reaction.



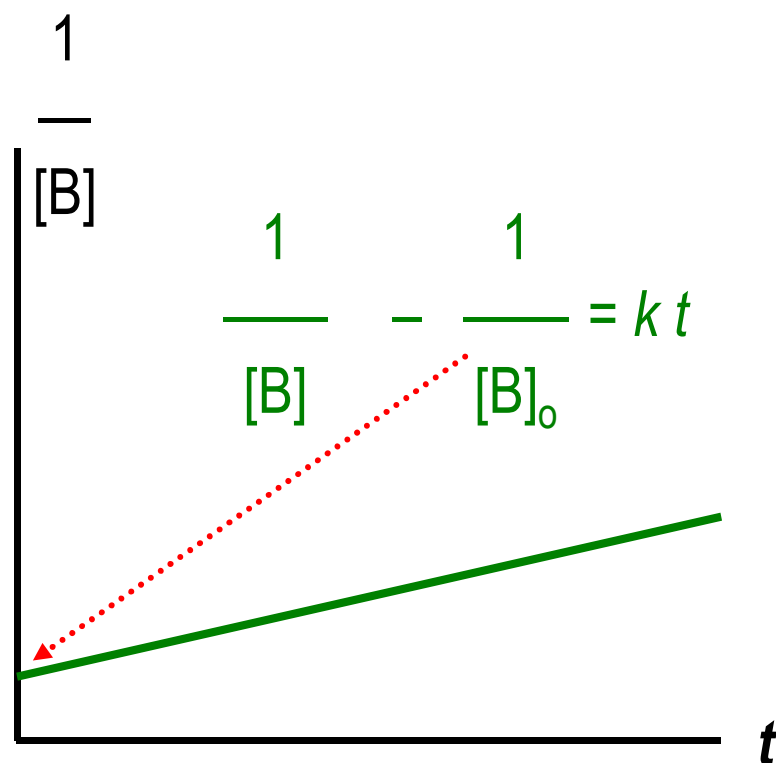
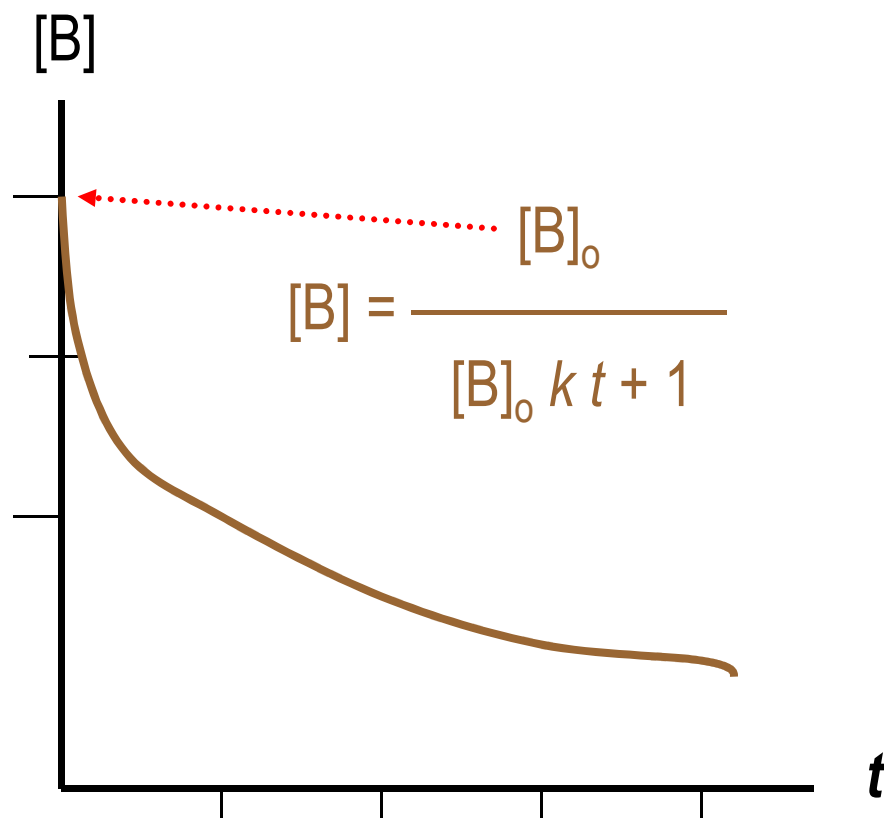


■ **Figure**

Second-order half-life. Concentration of a reactant A as a function of time for a second-order reaction. Note that each half-life is twice as long as the preceding one because $t_{1/2} = 1/k[A]_0$ and the concentration of A at the beginning of each successive half-life is smaller by a factor of 2.

Plot of [B] vs. t & $1/[B]$ vs. t for 2nd Order Reactions

$t =$	1	5	10	15	30	35
$[B] =$	1.67	1.0	0.67	0.50	0.29	0.25



What kind of plot is linear for 1st and 2nd reactions?

Factors influencing the rate of a reaction:

- 1) Nature of reactants (*Defines the activation energy*)
- 2) Concentrations of reactants (*Increases the number of collisions*)
- 3) Temperature (*Increases in the energy, hence the number of effective collisions*).

EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE

It has been found that generally an increase of temperature increases the rate of reaction. As a rule, an increase of temperature by 10°C doubles the reaction rate. Thus the ratio of rate constants of a reaction at two different temperatures differing by 10 degree is known as **Temperature Coefficient**.

$$\text{i.e., Temperature Coefficient} = \frac{k_{35^\circ}}{k_{25^\circ}} = \frac{k_{308}}{k_{298}}$$

- 4) Catalyst (*Lowers the activation energy*)
- 5) Pressure (*increase in the number of collisions and hence probability to get preferred orientation also increases*)
- 6) Surface area of solid reactants (*Increases the probability of have preferred orientations for collisions and lowers the activation energy*)

