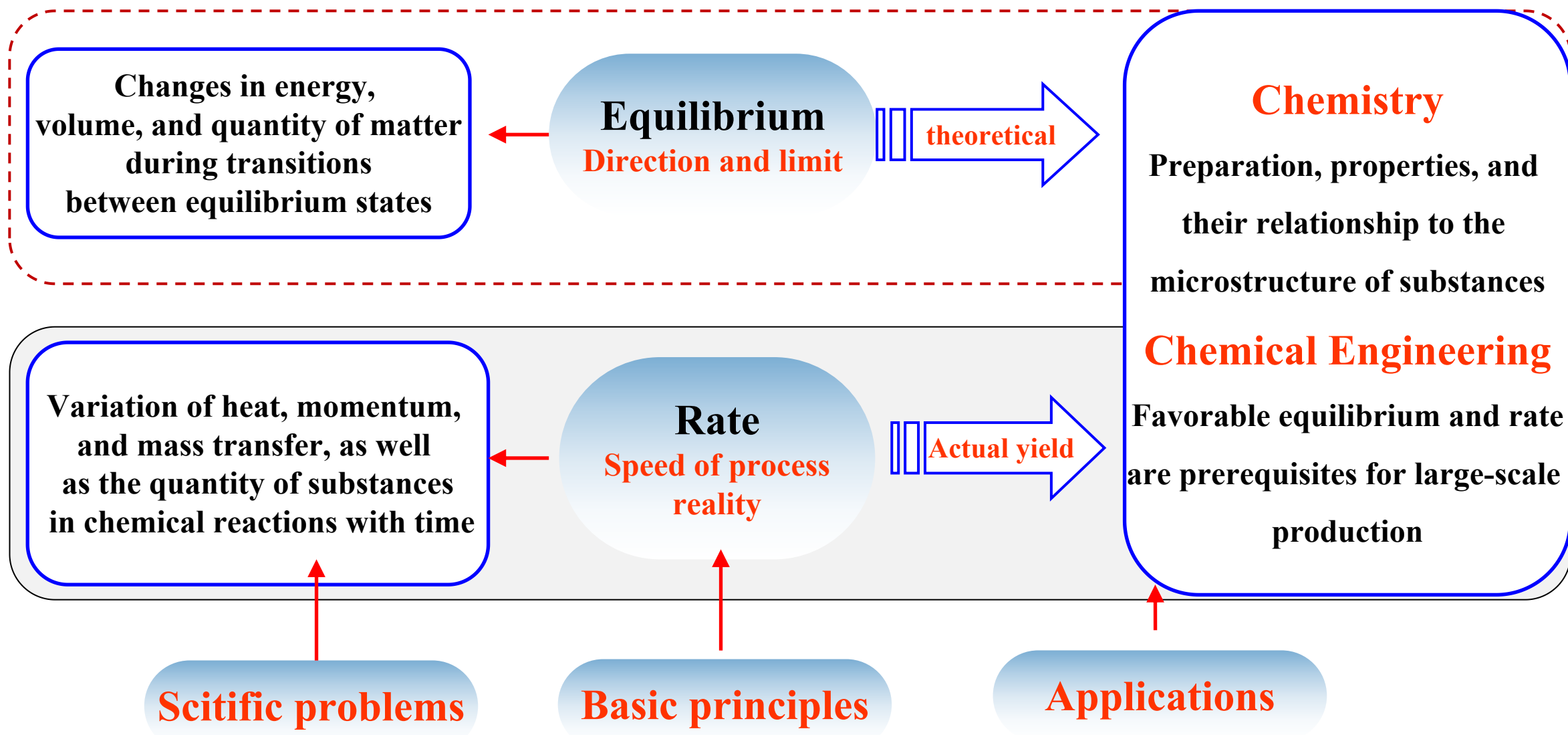


# Chemical Kinetics

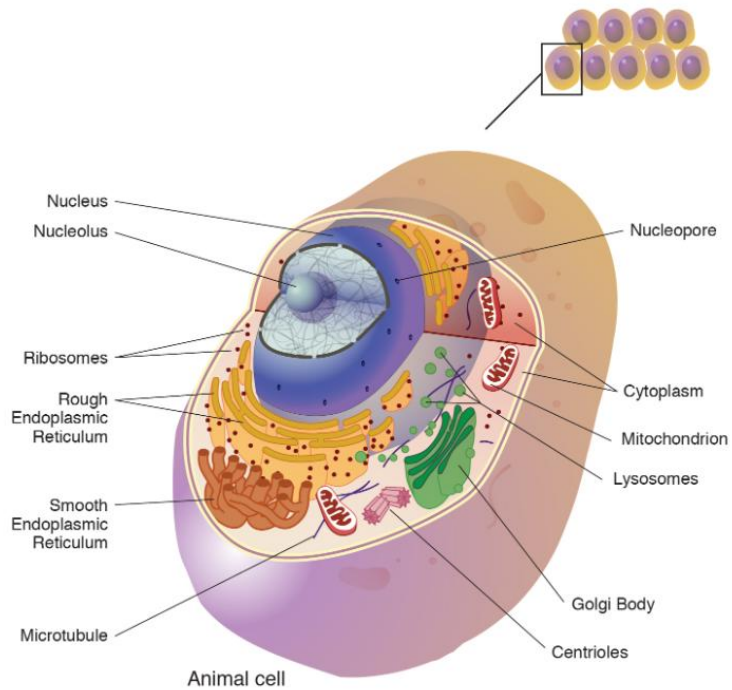


# Kinetics and thermodynamics——rate and equilibrium





# Chemical Kinetics—an all-embracing subject



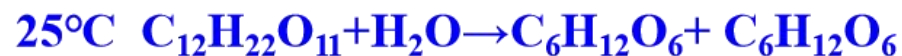


# Chemical Kinetics—an all-embracing subject

Chemical  
reaction

**Thermodynamics:** The direction, limit and equilibrium condition of spontaneous chemical reaction

**Necessity**



$$\Delta G_{T,p,W'=0} < 0$$

**Kinetics:** The rate and mechanism of chemical reaction and the factors affecting the rate.

**Adequacy**

$$v = f(T, p, c_B, \text{Cat.}, \text{solvent}, \text{light}, \text{electric}, \text{magnetic}, \dots)$$



**Three important factors:** space, time, and amount of substance



# Basic concepts

## Elementary Reactions

the products are formed from reactants by only one single step, and no intermediates can be detected by macroscopic experimental methods

- State-state reaction: the **quantum states** of the reactant molecules and product molecules are further assigned and clearly shown
- Complex Reactions: A reaction composed of two or more elementary reactions

## Reaction Mechanisms

The **pattern or sequence** of elementary reactions in composing a complex reaction



- If the reaction mechanism is known, **in principle**, we can predict the rate of a complex reaction by the rates of the corresponding elementary reactions.
- Kinetic **experiments** and other experiments such as separation and detection of intermediates, as well as **theoretical analysis** to make a synthetic judgment
- Most reaction mechanisms are only **reasonable hypotheses**



# Basic concepts

➤ **Macroscopic Chemical Kinetics**    **To establish reaction-rate equations on the macroscopic level**

The rate equations have various types connecting the rates of elementary reactions and complex reactions with the concentrations, the temperature and the pressure.

➤ **Microscopic Chemical Kinetics**    **To elucidate the microscopic essentials of the rate equations**

The microscopic characteristic properties of substances such as molecular sizes, geometric configurations, and translational, rotational, vibrational, electronic movements to study the state-state reactions

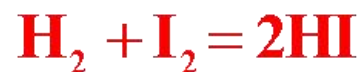
**the collision theory, the transition state theory and the molecular dynamics**



# Basic concepts

## Some commonly accepted rules in chemical stoichiometry

- ☑ If only the **balance** of the equation is concerned, we use equal sign



- ☑ If we stress that the reaction is in **equilibrium**, we use two half-arrows



- ☑ If we want to point out that the reaction happens in a **single direction**, we use a single arrow.  
If we are interested in **both the forward and the reverse reactions**, we use two arrows representing the two directions



- ☑ For an **elementary equation**, we use a single full arrow







# Reaction rate

**Reaction rate** — The variation of the amount of a reactant or a product in a unit time and in a unit space

**speed**

**scale**

$$\dot{\xi} \stackrel{\text{def}}{=} \frac{d\xi}{dt} = \frac{1}{\nu_B} \frac{dn_B}{dt}$$

$$d\xi = dn_B / \nu_B$$

$$\nu \stackrel{\text{def}}{=} \frac{\dot{\xi}}{V} = \frac{1}{\nu_B V} \frac{dn_B}{dt}$$

$$\nu = -\frac{\nu_A}{\nu_B} = \frac{\nu_P}{\nu_B} = \dot{\xi} / V$$

$$\nu \stackrel{\text{def}}{=} \frac{1}{\nu_B} \frac{dc_B}{dt} + \frac{c_B}{\nu_B V} \frac{dV}{dt}$$

**(V cons.)**

$$\nu = \frac{1}{\nu_B} \frac{dc_B}{dt}$$

**Rate of Consumption (Reactant)**

$$\nu_A \stackrel{\text{def}}{=} -\frac{1}{V} \frac{dn_A}{dt} \xrightarrow{\text{(V cons.)}} \nu_A = -\frac{dc_A}{dt}$$

**Rate of Formation (product)**

$$\nu_P \stackrel{\text{def}}{=} \frac{1}{V} \frac{dn_P}{dt} \xrightarrow{\text{(V cons.)}} \nu_P = \frac{dc_P}{dt}$$



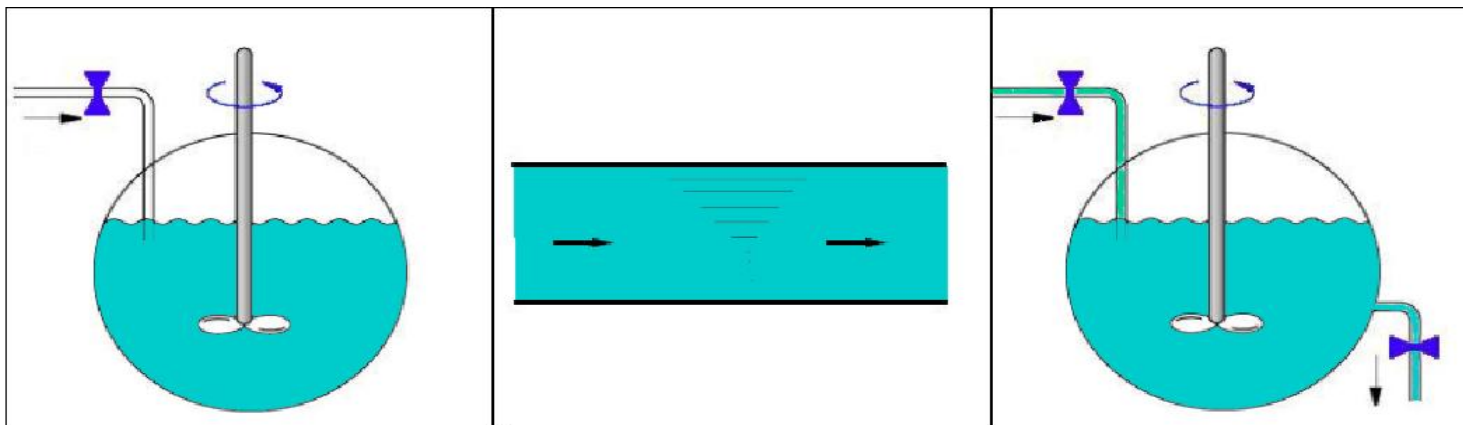


# Rate equations

## Reaction-Rate Equations (Kinetic Equations)

Mathematical equations quantitatively describing the effect of concentrations of various substances on reaction rates when fixing the other factors

**Reaction-rate equations are irrelevant to the types and the sizes of the reactors**



**Batch Tank Reactor**

*Concentrations* vary with the time only, irrelevant to the space

**Continuous Tubular Reactor**

*Concentrations* vary with the space only, irrelevant to the time

**Continuous Tank Reactor**

*Concentrations* vary neither with the time nor with the space.



# Rate equations

## □ Elementary Reactions——Mass action law

Reaction rate is proportional to the power product of concentrations of various reactants.

**Molecularity of Reaction**



**Unimolecular Reactions**,  $A \rightarrow P$

$$v = kc_A$$

**Rate Constant ( $f(T)$ )**

$$(\text{mol} \cdot \text{m}^{-3})^{1-n} \cdot \text{s}^{-1}$$

or  $(\text{mol} \cdot \text{dm}^{-3})^{1-n} \cdot \text{s}^{-1}$

**Bimolecular Reactions**,  $2A \rightarrow P$ ,  $A + B \rightarrow P$

$$v = kc_A^2, \quad v = kc_A c_B$$

**Trimolecular Reactions**,  $3A \rightarrow P$ ,  $2A + B \rightarrow P$ ,  $A + B + C \rightarrow P$

$$v = kc_A^3, \quad v = kc_A^2 c_B, \quad v = kc_A c_B c_C$$

The molecularity with a symbol  $n$  of an elementary reaction is the number of reactant molecules in the corresponding chemical equation.



# Rate equations

## □ Complex Reactions

- Empirical Rate Equations
- Theoretical Rate Equations

### ☑ Power-Function Type

$$\nu = k c_A^\alpha c_B^\beta c_C^\gamma \dots$$

**$k$  —Rate Coefficient**



➤ Partial Orders  $\alpha, \beta, \gamma, \dots$

※ Positive or negative integers or non-integers

➤ Reaction Order  $n = \alpha + \beta + \gamma + \dots$

※ **Irrelevant to the stoichiometric coefficients**

➤ Rate Equations Using Rate of Consumption or Rate of Formation

$$\nu_A = k_A c_A^\alpha c_B^\beta c_C^\gamma \dots \quad \nu_P = k_P c_A^\alpha c_B^\beta c_C^\gamma \dots$$

$$k = -\frac{k_A}{\nu_A} = \frac{k_P}{\nu_P}$$

### ☑ Non-Power-Function Type $\nu = \frac{k c_A^\alpha c_B^\beta \dots}{1 + k' c_A^{\alpha'} c_B^{\beta'} \dots}$

**Meaningless to talk about partial orders and the reaction order**  
 $k$  or  $k'$  — rate equation coefficient



# Rate equations

Rate of consumption  $v_A = -\frac{dc_A}{dt}$

Rate of reaction  $v = \frac{1}{\nu_B} \frac{dc_B}{dt}$

Rate of formation  $v_P = \frac{dc_P}{dt}$

Differential form



Integrated form

relations for the change of concentrations with time

depends on the type of the reactor

✓  $V$  is constant

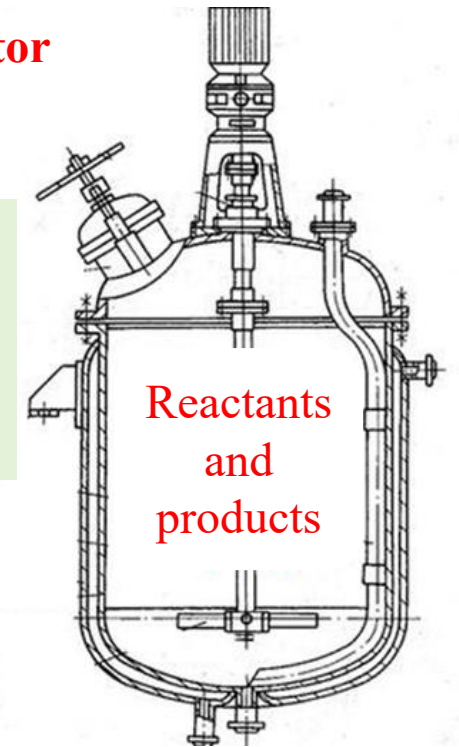
✓ To feed reactants only once then to obtain products after reaction

Concentration of A at initial time ( $t=0$ )  $C_{A0}$

Concentration of A at time  $t$   $C_A$

Concentration of Reactant A Consumed at time  $t$   $x = C_{A0} - C_A$

Half Life  $t_{1/2}$  : Time needed to consume one half of the reactant A



Batch Tank Reactor



# Zeroth order reactions $aA + bB \rightarrow pP$

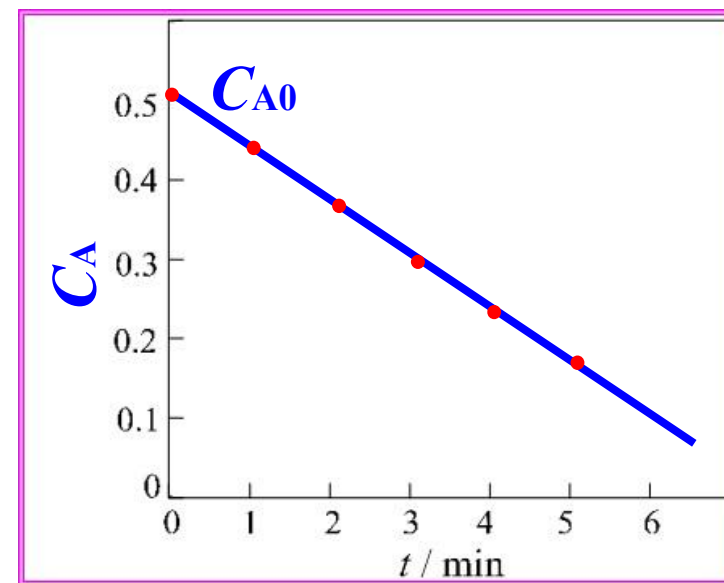
✓ **Differential form**  $v_A = -\frac{dc_A}{dt} = -\frac{d(c_{A0} - x)}{dt} = \frac{dx}{dt} = k_A$

$$-\int_{c_{A0}}^{c_A} dc_A = \int_0^t k_A dt$$

✓ **Integrated form**  $c_{A0} - c_A = x = k_A t$

(1) Plotting  $c_A$  against  $t$ , a straight line is obtained;  $k_A$  is the negative value of the slope of the line.

(2) The unit of  $k_A$  is  $\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$  or  $\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$ .



✓ **Half time**  $t_{1/2} = \frac{c_{A0}}{2k_A}$

Zeroth order reactions are observed mostly in catalytic reactions and in reactions subject to external fields.



# First order reactions $aA + bB \rightarrow pP$

✓ **Differential form**  $v_A = -\frac{dc_A}{dt} = k_A c_A = \frac{dx}{dt} = k_A (c_{A0} - x)$

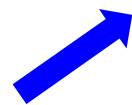


$$-\int_{c_{A0}}^{c_A} \frac{1}{c_A} dc_A = \int_0^t k_A dt$$

**conversion ratio**  $\alpha = \frac{x}{c_{A0}}$

$$k_A = \frac{1}{t} \ln \frac{1}{1 - \alpha}$$

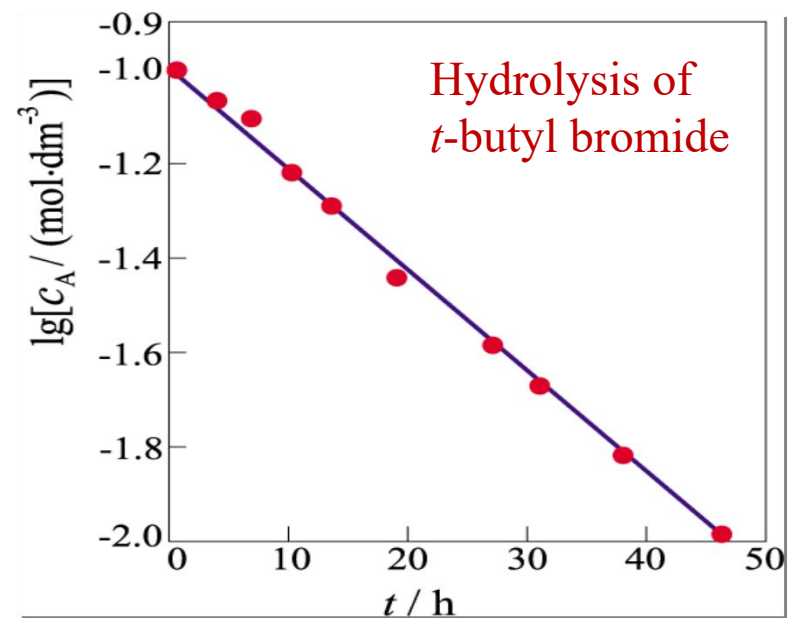
✓ **Integrated form**  $k_A = \frac{1}{t} \ln \frac{c_{A0}}{c_A} = \frac{1}{t} \ln \frac{c_{A0}}{c_{A0} - x}$



- (1) Plotting  $\ln\{c_A\}$  against  $t$ , a straight line is obtained;  $k_A$  is the negative value of the slope of the line.
- (2) Dimension and unit of  $k_A$  are  $T^{-1}$  and  $s^{-1}$ , respectively. The value of  $k_A$  is independent of the unit of concentration.

✓ **Half time**  $t_{1/2} = \frac{\ln 2}{k_A}$

**Irrelevant to initial concentration!**





# Second order reactions $aA + bB \rightarrow pP$

Type I  $v_A = -\frac{dc_A}{dt} = k_A c_A^2 = \frac{dx}{dt} = k_A (c_{A0} - x)^2$  (A)

Type II  $v_A = -\frac{dc_A}{dt} = k_A c_A c_B = \frac{dx}{dt} = k_A (c_{A0} - x) \left( c_{B0} - \frac{b}{a} x \right)$

$\left\{ \begin{array}{ll} a = b, c_{A0} = c_{B0} & \text{(B)} \\ a \neq b, c_{A0} / c_{B0} = a / b & \text{(C)} \\ a = b, c_{A0} \neq c_{B0} & \text{(D)} \\ a \neq b, c_{A0} \neq c_{B0} & \text{(E)} \end{array} \right.$

**A**

$$v_A = -\frac{dc_A}{dt} = k_A c_A^2$$

**B**

$$a = b, c_{A0} = c_{B0} \Rightarrow c_A = c_B$$

$$v_A = k_A c_A c_B = k_A c_A^2$$

**C**

$$a \neq b \quad \frac{c_{A0}}{c_{B0}} = \frac{a}{b} \Rightarrow \frac{c_A}{c_B} = \frac{a}{b}$$

$$v_A = k_A c_A c_B = k'_A c_A^2 \quad k'_A = \frac{b}{a} k_A$$

$$v_A = -\frac{dc_A}{dt} = k_A c_A^2$$





# Second order reactions $aA + bB \rightarrow pP$

✓ **Differential form**

$$v_A = -\frac{dc_A}{dt} = k_A c_A^2$$



$$-\int_{c_{A0}}^{c_A} \frac{1}{c_A^2} dc_A = \int_0^t k_A dt$$

✓ **Integrated form**

$$\frac{1}{c_A} - \frac{1}{c_{A0}} = \frac{1}{c_{A0} - x} - \frac{1}{c_{A0}} = k_A t$$

(1) Plotting  $1/c_A$  against  $t$ , a straight line is obtained.

(2) Unit of  $k_A$  is  $\text{mol}^{-1} \cdot \text{m}^3 \cdot \text{s}^{-1}$  or  $\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ .

✓ **Half time**

$$t_{1/2} = \frac{1}{k_A c_{A0}}$$



# Second order reactions $aA + bB \rightarrow pP$

$$(D) \quad v_A = k_A c_A c_B \xrightarrow{a=b, c_{A0} \neq c_{B0}} v_A = \frac{dx}{dt} = k_A (c_{A0} - x)(c_{B0} - x)$$

$$\frac{1}{c_{A0} - c_{B0}} \ln \frac{c_{B0}(c_{A0} - x)}{c_{A0}(c_{B0} - x)} = k_A t \quad \leftarrow \quad \frac{dx}{(c_{A0} - x)(c_{B0} - x)} = k_A dt$$

(1) Plotting  $\ln(c_A/c_B)$  or  $\ln(c_{B0}c_A/c_{A0}c_B)/(c_{A0} - c_{B0})$  against  $t$ , a straight line is obtained. ↵

(2) Dimension and unit of  $k_A$  are the same as those of the case (A). ↵

$$(E) \quad v_A = k_A c_A c_B \xrightarrow{a \neq b, c_{A0} \neq c_{B0}} k_A = \frac{a}{t(bc_{A0} - ac_{B0})} \ln \frac{c_{B0}c_A}{c_{A0}c_B}$$



# $n$ -th order reactions ( $n \neq 1$ )

✓ **Differential form**  $v_A = -\frac{dc_A}{dt} = k_A c_A^n = \frac{dx}{dt} = k_A (c_{A0} - x)^n$

✓ **Integrated form**  $k_A = \frac{1}{t(n-1)} \left[ \frac{1}{(c_{A0} - x)^{n-1}} - \frac{1}{c_{A0}^{n-1}} \right]$

(1) Plotting  $c_A^{1-n}$  or  $(c_{A0} - x)^{1-n}$  against  $t$ , a straight line is obtained.

(2) Dimension of  $k_A$  is  $L^{3(n-1)}N^{(1-n)}T^{-1}$ .

✓ **Half time**  $t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k_A c_{A0}^{n-1}}$



# Extended——rate expressed by pressure

Ideal Gas  $p_A V = n_A RT \rightarrow p_A = c_A RT$

**Zeroth**

$$-\frac{dc_A}{dt} = k_A$$

$$-\frac{dp_A}{dt} = k_p$$

$$k_p = k_A RT$$

$$p_{A0} - p_A = k_p t$$

**First**

$$-\frac{dc_A}{dt} = k_A c_A$$

$$-\frac{dp_A}{dt} = k_p p_A$$

$$k_A = k_p$$

$$k_A = \frac{1}{t} \ln \frac{p_{A0}}{p_A} = \frac{1}{t} \ln \frac{1}{1-\alpha}$$

**Second  
(A,B,C)**

$$-\frac{dc_A}{dt} = k_A c_A^2$$

$$-\frac{dp_A}{dt} = k_p p_A^2$$

$$k_A = k_p RT$$

$$\frac{1}{p_A} - \frac{1}{p_{A0}} = k_p t$$