#### REACTION KINETICS AND REACTION MECHANISMS

Different levels of dealing with reaction rates:

I. REACTION KINETICS macroscopic level – mathematical description

II. REACTION MECHANISMS molecular level—interpretation

III. THEORIES OF REACTION RATES Arrhenius equation, collision and activated complex theories

### INTRODUCTION

#### History of reaction kinetics:

- 183X Berzelius: catalysis
- 1850 Wilhelmy: sugar inversion measurements
- 188X van't Hoff: rate equations
- 189X Arrhenius: a k = f(T) equation
- 1918 McLewis: collision theory
- 193X Eyring-Polányi: activated complex theory
- more than ten Nobel prizes awarded for achievements in reaction kinetics

#### I. REACTION KINETICS

- Before kinetic investigations, one should clarify:
  - the stoichiometric equation,
  - the identity of reactants (A, B, ...) and products (P, ...),
  - possibility of an intermediate (I) [vs. activated complex].
- After the investigation of reaction kinetics, taking the stoichiometry and the rate equation into account, a mechanism is postulated.

### **Concept of reaction rate**

- Change in concentration/time (closed system, constant V)
  - Generally:  $v = \frac{1}{v_J} \cdot \frac{d[J]}{dt}$ , where  $v_J$  is the stoichiometric coefficient of substance J
  - For reaction A + 2B  $\rightarrow$  P:  $v = -\frac{d[A]}{dt} = -\frac{1}{2} \cdot \frac{d[B]}{dt} = \frac{d[P]}{dt}$
  - Simplified formalism:  $v = d\xi/dt$ , where  $\xi$  is the extent of reaction:  $0 < \xi < 1$
  - Unit of rate (v): mol dm<sup>-3</sup> s<sup>-1</sup>

# Visualizing the reaction rate – graphical representation

• Rate equation: 
$$v = \frac{1}{v_J} \cdot \frac{d[J]}{dt}$$

- reactant: dc/dt negative
- product: dc/dt positive
   The rate of reaction at time t (or concentration c) is determined based on the slopes of the experimentally measured curves:



#### **Rate equation**

- $v = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}...$ 
  - v: rate of reaction
  - k: rate constant (or rate coefficient)
  - $\alpha, \beta, \gamma$ : order of reaction
  - $\alpha + \beta + \gamma$ : net order of the reaction
- Rate equation: v versus c connections

Integration of the differential equation (analytical or numerical) is needed for comparison

Measurement results: c versus t traces

### **First order kinetics**

- Stoichiometry: A → P (the reverse reaction is negligible)
- Rate equation:  $-\frac{d[A]}{dt} = k_1[A]$ or:  $\frac{d[P]}{dt} = k_1[A]$



• Integrated form:  $[A] = [A]_0 e^{-k_1 t}$ ;  $[P] = [A]_0 \left( \frac{k_{\text{smal}}}{1 - e^{-k_1 t}} \right)$ 

linearized: 
$$\ln \frac{[A]}{[A]_0} = -k_1 t$$

- Half-life:  $t_{1/2} = \ln 2/k_1$ 
  - t<sub>1/2</sub> is independent of the initial concentration in first order reactions.

#### Second order kinetics I.



#### Second order kinetics I.

Concentration vs time data for first and second order reactions



#### Second order kinetics II.

- Stoichiometry: A + B → P (the reverse reaction is negligible)
- Rate equation:  $-\frac{d[A]}{dt} = k_2[A][B]$ or:  $\frac{d[P]}{dt} = k_2[A][B]$  Integrated form:  $\frac{1}{[B]_0 [A]_0} \ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) = k_2 t$

#### Zeroth order kinetics

- Stoichiometry: A → P (the reverse reaction is negligible)
- Rate equation:  $-d[A]/dt = k_0$ or  $d[P]/dt = k_0$
- Integrated from:  $[A] = [A]_0 k_0 t$ 
  - the rate is independent of the reactant concentration (e.g. surface reactions)



### Multiterm rate equations: <u>consecutive</u> first-order reactions

- Stoichiometry:  $A \xrightarrow{k_a} B \xrightarrow{k_b} P$
- Classical examples: radioactive decay series  $^{239}U \xrightarrow{23,5 \text{ minutes}} ^{239}Np \xrightarrow{2,35 \text{ days}} ^{239}Pu$
- The rate equation can be stated for each component:  $-\frac{d[A]}{dt} = k_a[A]$

$$\frac{d[B]}{dt} = k_a[A] - k_b[B]$$

### Multiterm rate equations: <u>consecutive</u> first-order reactions

- Integrated form:
  - reactant: exponential decay,  $[A] = [A]_0 e^{-k_a t}$

intermediate: maximum,

$$[B] = \frac{k_{a}}{k_{b} - k_{a}} \left( e^{-k_{a}t} - e^{-k_{b}t} \right) [A]_{0}$$

product: S shaped curve (a.k.a. induction period),

$$[P] = \left\{ 1 + \frac{k_{a}e^{-k_{b}t} - k_{b}e^{-k_{a}t}}{k_{b} - k_{a}} \right\} [A]_{0}$$



### Multiterm rate equations: parallel first-order reactions

Relatively simple (close to obvious)Stoichiometry:

$$A \xrightarrow{k_{1}} P_{1} \qquad d[P_{1}]/dt = k_{1}[A] \quad [P_{1}] = \frac{k_{1}}{k_{1} + k_{2} + \dots + k_{i}}[A]_{0}(1 - e^{-(k_{1} + k_{2} + \dots + k_{i})t})$$

$$A \xrightarrow{k_{2}} P_{2} \qquad d[P_{2}]/dt = k_{2}[A] \quad [P_{2}] = \frac{k_{2}}{k_{1} + k_{2} + \dots + k_{i}}[A]_{0}(1 - e^{-(k_{1} + k_{2} + \dots + k_{i})t})$$

 $A \xrightarrow{k_{i}} P_{i} \quad d[P_{i}]/dt = k_{i}[A]$ -d[A]/dt =  $(k_{1} + k_{2} + ... + k_{i})[A] \quad [A] = [A]_{0}e^{-(k_{1} + k_{2} + ... + k_{i})t}$ 

 Integration gives exponential (first order) formulas.

### Multiterm rate equations: <u>reversible</u> first-order reactions

#### **Reversible first order reaction:**

- Stoichiometry: A ⇒ B
- Rate equation:

 $d[A]/dt = -k_1[A] + k_{-1}[B]$ 

- Integration: [A] =  $\frac{k_{-1} + k_1 e^{-(k_1 + k_{-1})t}}{k_1 + k_{-1}}$ [A]<sub>0 0.4</sub>
- These concentration time traces are exponential.



### Multiterm rate equations: reversible 2<sup>nd</sup>-order reactions

#### **Reversible second order reaction:**

- Stoichiometry: A + B  $\rightleftharpoons$  C + D
- Rate equation:
  - $d[A]/dt = -k_2[A][B] + k_{-2}[C][D]$
- Integration: ...
- Message: in equilibrium d[A]/dt = 0, so the  $\rightleftharpoons$ rates are identical:  $k_2[A][B] = k_{-2}[C][D]$ .

Therefore: 
$$\frac{k_2}{k_{-2}} = \frac{[C][D]}{[A][B]} = K_2$$

- Rate equation:  $v = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$
- Determination of all orders of reaction ( $\alpha$ ,  $\beta$ ,  $\gamma$ , ...) Summing the individual orders gives the **net order of reaction**.
- 2. Calculation of rate constant k

#### Rate equation: $v = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$

- Determination of all orders of reaction ( $\alpha$ ,  $\beta$ ,  $\gamma$ , ...)
  - A. "trial-and-error" based on individual c t traces. Plot the c t pairs of points:
    - if first order:  $\ln c t$  (semilogarithmic formula)
    - if second order: 1/c t (reciprocal formula) gives a straight line.
    - Simple first and second order are common cases, but by no means exclusive, a "more certain" method is needed.

#### Rate equation: $v = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$

- Determination of all orders of reaction ( $\alpha$ ,  $\beta$ ,  $\gamma$ , ...)
  - B. van't Hoff method (initial rate method):
    - Logarithm of the rate equation with initial values:  $lgv_0 = lgk + \alpha lg[A]_0 + \beta lg[B]_0 + \gamma lg[C]_0$
    - Set [B]<sub>0</sub> and [C]<sub>0</sub> so that [B] = constant and
       [C] = constant (pseudo-zeroth order).
    - Rate  $v_0$  is measured at different [A]<sub>0</sub>, then the data pairs  $\lg v_0 \lg[A]_0$  are plotted.
    - The slope of the straight line is the  $\alpha$  (order of reaction with respect to reactant A). <sup>19</sup>

- Rate equation:  $v = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$
- Determination of all orders of reaction ( $\alpha$ ,  $\beta$ ,  $\gamma$ , ...)
  - B. van't Hoff method (initial rate method):

 Then change [B]<sub>0</sub> and keep [A]<sub>0</sub> and [C]<sub>0</sub> constant, so order β with respect to B is obtained.

#### Rate equation: $v = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$

- **Determination of all orders of reaction (** $\alpha$ **,**  $\beta$ **,**  $\gamma$ **, ...)** The individual orders of reactions may be:
  - small positive integers (1, 2, 3)
    - no explanation needed, a natural case
  - small negative integers (-1, -2, -3)
    - e.g. interpretation by rapid pre-equilibrium (deprotonation)
  - small positive/negative fractional numbers (1/2, 3/2)
    - e.g. dimer dissociation as a pre-equilibrium
    - e.g. chain reactions
  - O (this can be directly seen from the data, no plot needed)
    - e.g. certain surface reactions, drug intake processes

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Rate equation:  $v = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$ 

- **Determination of all orders of reaction (** $\alpha$ ,  $\beta$ ,  $\gamma$ , ...)
- 2. Calculation of the rate constant k
- Numerical calculations from measured v rates (mol dm<sup>-3</sup> s<sup>-1</sup>) and the known form of the rate equation.
- dimension of k:  $[k_1] = s^{-1}$ ,  $[k_2] = mol^{-1} dm^3 s^{-1}$  etc.
- Equilibrium constant K is the ratio of the rate constants k<sub>+</sub> and k<sub>-</sub> both numerically and dimensionally:

$$K = k_+ / k_-$$

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macroscopic level – mathematical description

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#### **II. REACTION MECHANISMS**

- Mechanism and its role: elementary reaction that interpret...
  - a) the net stoichiometry of the process (observed intermediates if there are any) and
  - b) The kinetic observations (the rate equation).
- rate equation ↔ mechanism

### **Concept and properties of elementary reactions:**

- Elementary reaction: consumption of a few reactant molecules, the dissociation and formation of maximum 1–2 bonds through a single activated complex.
- Elementary reactions are reversible!
- types of elementary reactions and their rate equations:
   unimolecular
  - $A \rightarrow product(s)$
  - bimolecular (most common)
    - $A + B \rightarrow product(s)$  or  $2A \rightarrow product(s)$
- Order of reaction and molecularity are the same for elementary reactions!

#### Law of kinetic mass action:

- For elementary reactions, the rate equation can be deduced from the stoichiometry. For example:
  - $A \rightarrow \text{product(s)}$
  - $A \rightleftharpoons B$  C
  - $A + B \rightarrow \text{product(s)}$
  - $2A \rightarrow \text{product(s)}$

- $d[A]/dt = k_1[A]$
- $d[A]/dt = k_1[A] k_1[B]$
- $d[A]/dt = k_2[A][B]$
- $d[A]/dt = k_2[A]^2$
- An elementary reaction is always reversible, but the rate of the reverse reaction is often negligible.

- Enzymes: efficient, specific biocatalysts
- Stoichiometry:  $S \xrightarrow{E} P$
- Kinetics: initial rates are measured (because...):



- Two more observations:
  - Maximum in the *T*-dependence. Arrhenius equation and denaturing.
     37°C Enzymes denaturing



The pH-dependence also often shows a maximum. Amphoteric amino acids!

Description of v–[S] curves:  $v = \frac{a}{h}$  or  $v = \frac{a[S]}{h+[S]}$ 



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- The equation is interpreted by the following mechanism:
  - $E + S \rightleftharpoons ES$

 $ES \rightarrow P + E$ 

- $k_1$  and  $k_1$
- $k_{2}$ , rate determining step



- A common evaluation method:
  - Experimental rate equation Lineweaver–Burk plot





- It is quite instructive t compare the formation of HBr and other HX. The same stoichiometry, but ...
  - HBr formation:
    - measurements: Bodenstein, Lind (1907)
    - explanation: Christiansen, Herzfeld, Polányi (1919)
  - a classic example used in reaction kinetics
  - Stoichiometry:  $H_2 + Br_2 \rightleftharpoons 2 HBr$
  - Kinetics:  $v = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} = \frac{k[H_2][Br_2]^{1/2}}{1 + \frac{k'[HBr]}{[Br_2]}}$
  - A suitable mechanism was necessary.
     Finding it took a decade!



Mechanism: five (irreversible) elementary steps.

 $Br_{2} \rightarrow 2 Br_{1}$   $Br_{1} + H_{2} \rightarrow HBr + H_{2}$   $H_{1} + Br_{2} \rightarrow HBr + Br_{2}$   $H_{1} + HBr \rightarrow Br_{1} + H_{2}$   $2 Br_{1} + M \rightarrow Br_{2} + M$ 

 $v_a = k_a[Br_2]$   $v_b = k_b[Br \cdot ][H_2]$   $v_c = k_c[H \cdot ][Br_2]$   $v_d = k_d[H \cdot ][HBr]$  $v_e = k_e[Br \cdot ]^2$ 



Mechanism: five (irreversible) elementary steps.

 $Br_2 \rightarrow 2 Br_2$  $v_a = k_a [Br_2]$  $v_b = k_b [Br \cdot ][H_2]$  $Br \cdot + H_{2} \rightarrow HBr + H \cdot$  $H \cdot + Br_{2} \rightarrow HBr + Br \cdot$  $v_c = k_c [\text{H} \cdot ] [\text{Br}_2]$  $H \cdot + HBr \rightarrow Br \cdot + H_{2}$  $v_d = k_d [\text{H} \cdot ] [\text{HBr}]$  $2 \text{ Br} + \text{M} \rightarrow \text{Br}_{2} + \text{M}$  $v_{\rho} = k_{\rho} [\text{Br} \cdot]^2$ Notice: reversible  $Br_{2} \rightleftharpoons 2 Br_{2}$ reversible  $Br + H_{\gamma} \rightleftharpoons HBr + H_{\gamma}$  $H_{\cdot} + Br_{2} \rightarrow HBr + Br_{\cdot}$  irreversible

 A typical chain reaction: a reaction of a reactive intermediate produces another reactive intermediate and these form a chain (cycle).

HBr

#### Visualization of the mechanism for the chain reaction:

Chain length =



HI

- Stoichiometry:  $H_2 + I_2 \rightleftharpoons 2 HI$
- Kinetics:

 $v = k_2[H_2][I_2] - k_2[HI]^2$ 

- Mechanism:
  - A. if  $H_2 + I_2 \rightleftharpoons 2HI$  is an elementary reaction, kinetic mass action gives:  $v = k_2[H_2][I_2] - k_2[HI]^2$ 
    - this agrees with the experimental rate equation.
    - Note: the  $H_2 + I_2 \rightarrow 2$  HI reaction played an important role in setting up the collision theory.

### Catalysis

#### Properties of catalytic phenomena:

- a catalyst accelerates a reaction by reacting and then re-producing (no apparent consumption),
- a catalyst is often written on both sides of the stoichiometric equation, but its order of reaction is positive,
- a catalyst opens a new path for the reaction: the rate of this catalyzed process is typically larger then the rate of the reaction without the catalyst,
- a catalyst never influences the position of the equilibrium (thermodynamic neutrality), it accelerates both the forward and reverse reactions.

### Catalysis



### Catalysis

Stoichiometric scheme:  $A + \{B\} + K \rightarrow P + Q + K$ 

