

Homogeneous Kinetics

5. Elementary Reactions

⟨Rate Equation⟩

Rate of reaction: $m\text{A} + n\text{B} + \dots \rightarrow i\text{X} + j\text{Y} + \dots$

$$v = -\frac{1}{m} \frac{d[\text{A}]}{dt} = -\frac{1}{n} \frac{d[\text{B}]}{dt} = \dots = \frac{1}{i} \frac{d[\text{X}]}{dt} = \frac{1}{j} \frac{d[\text{Y}]}{dt} = \dots \quad (5.1)$$

[A], [B], ...: concentrations of A, B, ...

Rate equation

$$v = k[\text{A}]^m[\text{B}]^n \dots \quad (5.2)$$

k : rate constant

Exercise 5.1

- 1) Write the rate equation for an irreversible reaction, $\text{A} \rightarrow \text{B}$ (rate const. = k_1), with respect to A, and solve the differential equation (rate equation) for the initial condition, $[\text{A}] = [\text{A}]_0$ at $t = 0$.
- 2) Write the rate equation for an irreversible reaction, $2\text{A} \rightarrow \text{B}$ (rate const. = k_2), with respect to A, and solve it for the initial condition, $[\text{A}] = [\text{A}]_0$ at $t = 0$.

Solution to exercise 5.1

1) rate equation: $(v =) -\frac{d[\text{A}]}{dt} = k_1[\text{A}]$. solution: $[\text{A}] = [\text{A}]_0 \exp(-k_1 t)$.

2) rate equation: $(v =) -\frac{1}{2} \frac{d[\text{A}]}{dt} = k_2[\text{A}]^2$. solution: $\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + 2k_2 t$ or $[\text{A}] = \frac{[\text{A}]_0}{1 + 2k_2 t [\text{A}]_0}$.

⟨Elementary Reaction⟩

≡ Minimum step of reaction that obeys eq. (5.2)

Examples:

1) $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$: $v = \frac{1}{2} \frac{d[\text{HBr}]}{dt} \propto \frac{[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + c[\text{HBr}]}$ elementary reaction?
NO

· complex sequence of reactions: $\text{Br}_2 \rightarrow 2\text{Br}$, $\text{Br} + \text{H}_2 \rightleftharpoons \text{HBr} + \text{H}$,
 $\text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br}$, etc.

2) $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$: $v = \frac{d[\text{H}_2\text{O}]}{dt} = k[\text{OH}][\text{H}_2]$ YES

Exercise 5.2

Argue whether the reaction, $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$, is an elementary reaction or not, from the following measurements for the initial rate of formation at 600 K.

exp. #	$[\text{H}_2]$ / mol m ⁻³	$[\text{I}_2]$ / mol m ⁻³	$d[\text{HI}]/dt _{t=0}$ / mol m ⁻³ s ⁻¹
#1	0.72	0.51	0.175
#2	0.72	1.02	0.350
#3	1.44	1.02	0.700

Solution to exercise 5.2

from #1 & #2, $d[\text{HI}]/dt \propto [\text{I}_2]$; from #2 & #3, $d[\text{HI}]/dt \propto [\text{H}_2]$. So, $v \propto [\text{H}_2][\text{I}_2]$ and this reaction CAN to be an elementary reaction.

* Eq. (5.2) may be accidentally satisfied. (but this is really an elementary reaction.)

Consecutive Reactions

Rate equations for consecutive reactions, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, with respect to [A] and [B]

$$\frac{d[A]}{dt} = -k_1[A], \quad \frac{d[B]}{dt} = k_1[A] - k_2[B], \quad \frac{d[C]}{dt} = k_2[B] \quad (5.3)$$

Solutions for $k_1 \neq k_2$ and for the initial conditions, $[A] = [A]_0$ and $[B] = [C] = 0$ at $t = 0$

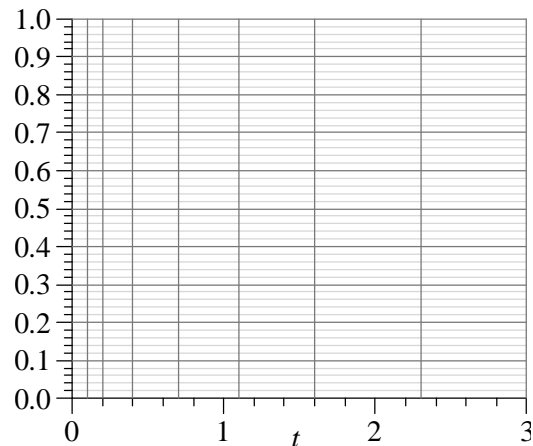
$$[A] = [A]_0 \exp(-k_1 t), \quad [B] = \frac{k_1 [A]_0}{k_1 - k_2} \{ \exp(-k_2 t) - \exp(-k_1 t) \},$$

$$[C] = [A]_0 - [A] - [B] \quad (5.4)$$

Exercise 5.3

1) Fill the following table of solution (5.4) for $k_1 = 5$, $k_2 = 1$ and $[A]_0 = 1$ and plot [A], [B] and [C].

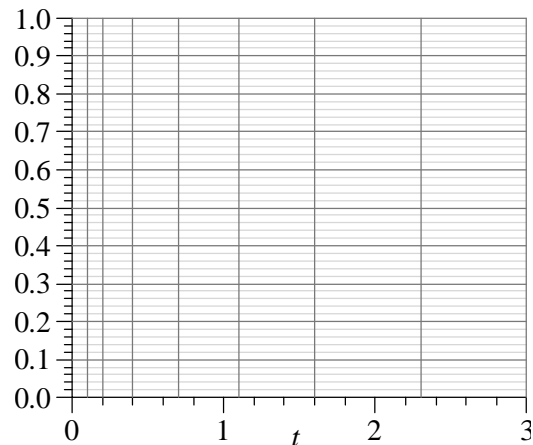
t	[A]	[B]	[C]
0	1	0	0
0.1	0.61	0.37	0.02
0.2	0.37	0.56	0.07
0.4	0.14	0.67	0.19
0.7	0.03	0.58	0.39
1.1	0	0.41	0.59
1.6	0	0.25	0.75
2.3	0	0.13	0.87
3	0	0.06	0.94



2) Describe which parts of the time-profile of [B] represent k_1 and k_2 .

3) Fill the following table of solution (5.4) for $k_1 = 1$, $k_2 = 5$ and $[A]_0 = 1$ and plot.

t	[A]	[B]	[C]
0	1	0	0
0.1	0.90	0.07	0.03
0.2	0.82	0.11	0.07
0.4	0.67	0.13	0.20
0.7	0.50	0.12	0.38
1.1	0.33	0.08	0.59
1.6	0.20	0.05	0.75
2.3	0.10	0.03	0.87
3	0.05	0.01	0.94



4) Describe which parts of the time-profile of [B] represent k_1 and k_2 .

Solution to exercise 5.3

- As shown in the figure to the right.
- [B] rises with k_1 ($\tau_1 = k_1^{-1} = 0.2$) and decays with k_2 ($\tau_2 = k_2^{-1} = 1$).
- As shown in the figure to the right.
- [B] rises with k_2 ($\tau_2 = k_2^{-1} = 0.2$) and decays with k_1 ($\tau_1 = k_1^{-1} = 1$).

* Exactly the same solution for [C]!

* Similar (same except for the height) solution for [B]!

* For [B], k_1 & k_2 look reversed when $k_2 > k_1$.

