Homogeneous Kinetics

5. Elementary Reactions

⟨Rate Equation⟩

Rate of reaction: mA + nB + ... → iX + jY + ...

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

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

Rate equation

$$\upsilon = k[A]^m[B]^n \cdots \quad (5.2)$$

k: rate constant

Exercise 5.1

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

Solution to exercise 5.1

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

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

⟨Elementary Reaction⟩

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

Examples: elementary reaction?

1) $H_2 + Br_2 \rightarrow 2HBr$: $\upsilon = \frac{1}{2}\frac{d[HBr]}{dt} \propto \frac{[H_2][Br_2]^{3/2}}{[Br_2] + c[HBr]}$ — NO

· complex sequence of reactions: $Br_2 \rightarrow 2Br$, $Br + H_2 \rightleftarrows HBr + H$, $H + Br_2 \rightarrow HBr + Br$, etc.

2) $OH + H_2 \rightarrow H_2O + H$: $\upsilon = \frac{d[H_2O]}{dt} = k[OH][H_2]$ — YES

Exercise 5.2

Argue whether the reaction, $H_2 + I_2 \rightarrow 2HI$, is an elementary reaction or not, from the following measurements for the initial rate of formation at 600 K.

exp. #	$[H_2]$ / mol m^{-3}	$[I_2]$ / mol m^{-3}	$d[HI]/dt\|_{t=0}$ / 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[HI]/d$t \propto [I_2]$; from #2 & #3, d[HI]d$t \propto [H_2]$. So, $\upsilon \propto [H_2][I_2]$ and this reaction CAN be an elementary reaction.

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

〈Consecutive Reactions〉

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

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

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

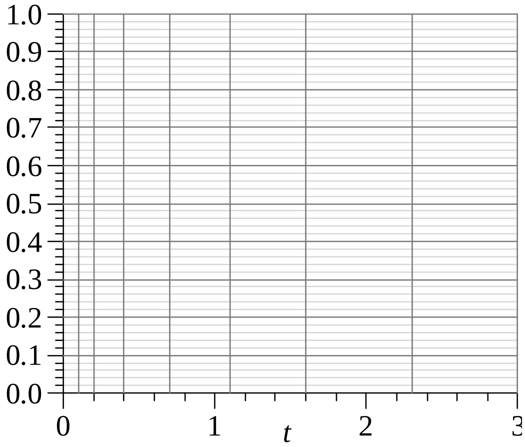
$$[\mathrm{A}] = [\mathrm{A}]_0 \exp(-k_1 t), \quad [\mathrm{B}] = \frac{k_1[\mathrm{A}]_0}{k_1 - k_2}\{\exp(-k_2 t) - \exp(-k_1 t)\},$$

$$[\mathrm{C}] = [\mathrm{A}]_0 - [\mathrm{A}] - [\mathrm{B}] \qquad (5.4)$$

Exercise 5.3

1) Complete the following table of solution (5.4) for $k_1 = 5$, $k_2 = 1$ and $[\mathrm{A}]_0 = 1$ and plot concentrations [A], [B] and [C].

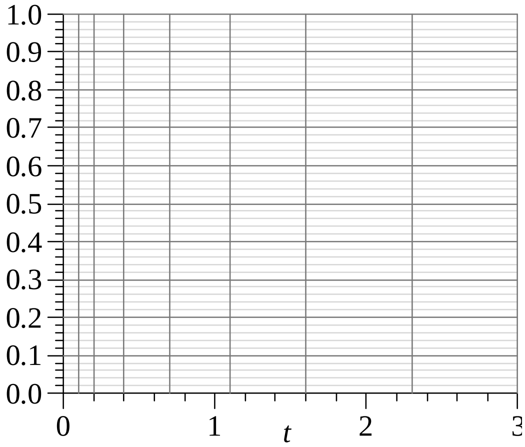
t	[A]	[B]	[C]
0	1	0	0
0.1	0.61	0.37	0.02
0.2	0.37	0.56	0.07
0.4	0.14	0.67	0.19
0.7	0.03	0.58	0.39
1.1	0	0.41	0.59
1.6	0	0.25	0.75
2.3	0	0.13	0.87
3	0	0.06	0.94



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

3) Complete the following table of solution (5.4) for $k_1 = 1$, $k_2 = 5$ and $[\mathrm{A}]_0 = 1$ and plot concentrations.

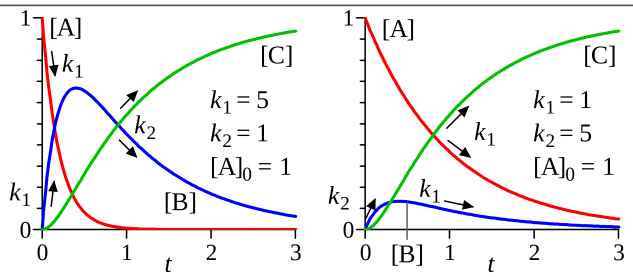
t	[A]	[B]	[C]
0	1	0	0
0.1	0.90	0.07	0.03
0.2	0.82	0.11	0.07
0.4	0.67	0.13	0.20
0.7	0.50	0.12	0.38
1.1	0.33	0.08	0.59
1.6	0.20	0.05	0.75
2.3	0.10	0.03	0.87
3	0.05	0.01	0.94



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

Solution to exercise 5.3

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