Chapter 6 - Kinetics

Rate of Reaction \[\text{must be positive}\]

\[\text{Def: change in concentration of products/reactants per unit time} = \text{mol dm}^{-3} \text{s}^{-1}\]

- can be monitored through volume of gas evolved, mass change, colour change (clock experiment)
- pH changes, colour change (use of spectrophotometer to measure colour absorption)

Finding Rate of Reaction at given point on a graph

1. Plot data onto graph
2. \(\frac{\Delta x}{\Delta t}\) of graph = rate of reaction
3. Draw tangent to curve at given point (e.g. A)
4. \(\frac{\Delta C}{\Delta t}\) = rate at \(x = A\) (instantaneous Rate R)

Note: initial Rate R is at \(x = 0\)

\(E_a\) = minimum amount of energy that particles need to collide successfully leading to reaction

Note that \(E_a\) (activation energy) of particles is directly proportional to temperature (Kelvin)

Collision Theory
- For reaction to occur
  1. Particles must collide
  2. Particles must collide with \(E \geq E\alpha\)
  3. Particles must collide with appropriate geometry

Maxwell-Boltzmann Distribution (MBD)
- Representation of distribution of energy amongst reactant particles
- Area under graph \((\int_{0}^{\infty} f(E) dE)\) = total number of particles (Never changes)

At 298 K

\[f(E) = E^2 \exp(-E/E_a)\]

At 398 K

\[f(E) = E^2 \exp(-E/E_a)\]

\(S_{y dE}\) is the same for both, but \(E_{\text{max}}\) is higher at 398 and more particles have \(E \geq E_a\)

All MBDs have horizontal asymptote = 0

All have no particles at 0 energy hence moves through origin

No of particles at \(E_{\text{max}}\) (398 K) lower to accommodate more particles at \(E \geq E_a\)
**Collisions Per Unit Time**

- **Temperature**
  - $T \uparrow\Rightarrow R (\uparrow \frac{dy}{dx})$, reaches end faster.
  - More important reasons: $\uparrow KE$ of particles, more successful collisions, $\uparrow R_{0R}$
  - Other: more particles move faster $\Rightarrow$ more collisions, more successful collisions, $\uparrow R_{0R}$

- **Surface Area**
  - More S.A., more particles that can come into contact with surrounding reactant.
  - More collisions $\Rightarrow$ more successful collisions $\Rightarrow \uparrow R_{0R}$

- **Pressure/Concentration**
  - $\uparrow$ conc./pressure, more collisions per unit time, per unit vol.
  - More successful collisions, $\uparrow R_{0R}$

- **However**, $R_{0R}$ gets smaller as reaction proceeds as $\downarrow$ conc. of reactants, hence $\downarrow$ collisions.

**Catalysts**

- **Substance that $\uparrow R_{0R}$ without being chemically changed.**
- Bring reactant molecules closer together, hence reducing $E_a$, by providing alternative reaction pathway.

- More particles with $E > E_a \Rightarrow \uparrow$ rate because $\uparrow$ successful collisions.

**Rate**

- **Note**: If reactants have same charge, they repel each other, hence few collisions, $\uparrow E_a$.

**Rate Expressions**

- If $A = \text{reactants}$ and $[C] \text{ represents conc.}$
  - Rate of reaction $= K \cdot [A]$
  - $K = \text{rate constant}$

  - If you double the $[A]$, and the rate doubles, $\Rightarrow R = K[A]$
  - If you double the $[A]$, and rate $\times 4$, $\Rightarrow R = K[A]^2$
  - You can have $[C] \text{ influence reaction as well.}$
  - If no change in $R$ when $[A]$ is doubled, $R = K[C]A^0 \Rightarrow R = \$K$
Orders \( = \) sum of exponents

1\(^{st}\) \( R = k[A] \) where \( k = \text{s}^{-1} \) (sum of exponents = 1)

2\(^{nd}\) \( R = k[A]^2 \) or \( k[A][B] \), where \( k = \text{mole} \cdot \text{m}^{-2} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \)

3\(^{rd}\) \( R = k[A][B][C] \) or \( k[B]^2[A] \) or \( k[B][C][A][C] \), where \( k = \text{mole}^2 \cdot \text{m}^{-2} \cdot \text{s}^{-1} \)

Reaction Mechanisms (construct of how overall reaction occurs)
- comprise all the elementary steps that lead to the occur in the reaction

Elementary steps outline overall reaction mechanism

Molecularity
- No. of species (inclusive as it involves A, 1st, bi and ternolecular process.
- Uni = 1 reactant, Bi = 2 x, Tern = 3
- Ternolecular reactions are rare and unlikely because 3 molecule are needed to collide with sufficient energy and correct orientation, very unlikely for this to occur
- Statistically unlikely

Note: Rate equations can only be determined experimentally

Intermediate = substance produced and consumed during elementary steps

\[ \text{e.g. } \begin{align*}
2\text{NO}_2(\text{g}) & \rightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \quad \text{(Overall)} \\
\text{N}_2(\text{g}) + \text{O}_2(\text{g}) & \rightarrow 2\text{NO}_2(\text{g}) \quad \text{f. elementary} \\
\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) & \rightarrow \text{2NO}_2(\text{g}) \quad \text{f. elementary}
\end{align*} \]

Determine the expression by number of molecules involved in the steps

State what are the reactants in rate determining step.
- Say if overall equation matches stoichiometric too. Rate of slow step with respect to intermediate, then replace.
The rate determining step is the slowest elementary step (usually low or high \( E_a \)).

- The rate expression includes species in the rate determining step or any species that lead to the formation of the species in the step.

Note: Rate expression cannot contain intermediates because they have no role in overall reaction mechanism and its concentration cannot be used to assess change in rate because it is produced and consumed in elementary step.

Rate expression would include whatever molecule component used in slow step.

**Arrhenius**

As the temperature increases, so does the rate constant.

\[
k = A e^{-\frac{E_a}{RT}}
\]

**Arrhenius constant**

\[
\ln k = \ln A - \frac{E_a}{R} \cdot \text{Temp}
\]

**Activation energy**

\[
\text{Gradient} = -\frac{E_a}{RT}
\]

A also represents the frequency of collisions with correct orientation for the reaction to occur and relates to energy requirements of collisions.

\[
\ln A = y \text{ intercept} - \frac{E_a}{RT} = \text{gradient}
\]

**Dependence on temperature**

- If \( E_a \) low, then \( \Delta \text{temp} \) would have a small increase on \( k \) as \( \Delta \text{small increase in particles with } E \geq E_a \), small change in rate.
- If \( E_a \) is high, \( \Delta \text{temp} \), big \( \Delta k \) because large increase in particles with \( E \geq E_a \), hence large change in rate.

**Simultaneous Arrhenius**

\[
\ln \left( \frac{k_1}{k_2} \right) = -\frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

\( E_a \) is in J mol\(^{-1} \).