Kinetics: The Rates of Reactions

– Chemical kinetics – studies the reaction rates and mechanisms

16.1 Factors Affecting the Reaction Rate

• **Chemical nature of the reactants** – each reaction has its own characteristic rate

• **Concentration** – the reaction rate increases with increasing the reactant concentrations (the collision frequency increases)

– The reactants must collide in order to react

Rate $\propto$ *Collision freq.* $\propto$ *Concentration*

• **Physical state** – the reaction rate increases with the degree of mixing (contact) between the reactants (depends on the reactant's phase)

• **Temperature** – the reaction rate increases with increasing the temperature (increases the collision frequency and the average kinetic energy of the molecules)

– The reactants must collide with sufficient energy in order to react

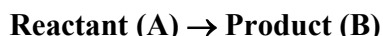*Rate* $\propto$ *Collision energy* $\propto$ *Temperature*

• **Catalyst** – increases (or decreases) the reaction rate by changing the reaction path (mechanism)

16.2 Expressing the Reaction Rate

• **Reaction rate** – change in the concentration (*C*) of reactants or products per unit time (*t*)

Rate = $\Delta C/\Delta t$

– Units $\rightarrow$ M/s or mol/L·s

Reactant (A) $\rightarrow$ Product (B)
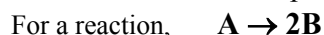$\Delta C < 0$ $\qquad\qquad$ $\Delta C > 0$

➤ The rate is positive by convention, but ΔC is (-) for the reactants and (+) for the products

$\Rightarrow$ **Rate = $-\Delta[A]/\Delta t$** $\qquad$ or $\qquad$ **Rate = $\Delta[B]/\Delta t$**

➤ Square brackets represent the concentrations of the reactant [A] and product [B] in mol/L

Reaction Rate and Stoichiometry

• ΔC is dependent on the stoichiometric coefficients of the reactants and products

For a reaction, $\qquad$ **A $\rightarrow$ 2B**

➤ The concentration of **B** changes twice faster than the concentration of **A**

$$\Delta[B]/\Delta t = 2(-\Delta[A]/\Delta t)$$

➤ To make the rate independent of the choice of a reactant or product, we use the convention:

For a reaction, $\qquad$ aA + bB $\rightarrow$ cC + dD

$$Rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Example:

For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of formation of NH_3 is **1.4 M/min**. Calculate the rate of disappearance of H_2 and the reaction rate.
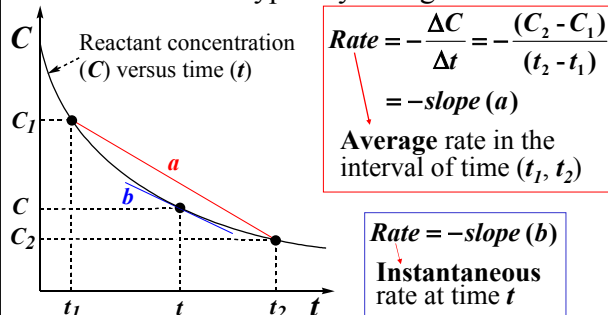
$$\frac{\Delta[NH_3]}{\Delta t} = 1.4\,\frac{M}{min} \quad \rightarrow \quad 1.4\,\frac{mol\ NH_3}{L\cdot min}$$

$$1.4\,\frac{mol\ NH_3}{L\cdot min} \times \frac{3\ mol\ H_2}{2\ mol\ NH_3} = \boxed{2.1\,\frac{mol\ H_2}{L\cdot min}}$$

$$Rate = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = \frac{1}{2}1.4\,\frac{mol\ NH_3}{L\cdot min} = \boxed{0.70\,\frac{mol\ NH_3}{L\cdot min}}$$

Average and Instantaneous Rates

• The reaction rate typically changes with time

$$Rate = -\frac{\Delta C}{\Delta t} = -\frac{(C_2 - C_1)}{(t_2 - t_1)}$$

$$= -slope\ (a)$$

Average rate in the interval of time (t_1, t_2)

$$Rate = -slope\ (b)$$

Instantaneous rate at time *t*

➤ The instantaneous rate at time *t* is given by the slope of the **tangent** (*b*) to the curve at this time

- As the interval of time (t_1, t_2) gets smaller, the slope of *a* approaches the slope of *b* and the average rate approaches the instantaneous rate
  - ⇒ The instantaneous rate can be estimated by measuring the average rate in a narrow time interval
- Normally the term reaction rate refers to the instantaneous rate
- **Initial rate** – the instantaneous rate at time, *t*=0 (the starting point of the reaction)
  - For most reactions the rate decreases gradually after the starting point so the slope of the tangents gets smaller with time
  - Initial rates are easier to measure and depend on the initial concentrations which are normally known

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16.3 Rate Laws

- **Rate law** – the dependence of the instantaneous rate on the concentrations of the different species in the reaction → **determined experimentally**
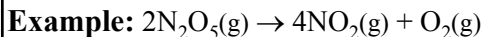
Example: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$
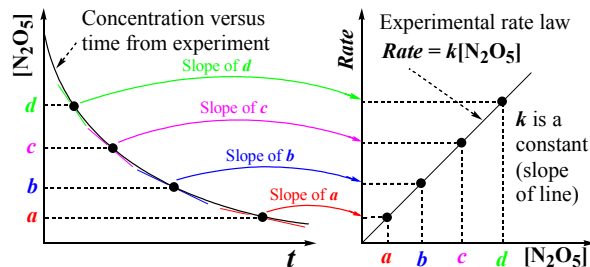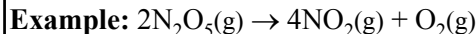
- For most reactions of the type

$$a\text{A} + b\text{B} + \ldots \rightarrow \textbf{Products}$$

the rate law can be expressed in the form:

$$Rate = k[\text{A}]^m[\text{B}]^n \ldots$$

- → *k* – **rate constant** (depends on the nature of A, B, … and the temperature)
- → *m, n, …* – **reaction orders** with respect to A, B, …
- → *m + n + …* – **overall order** of the rate law

Example: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

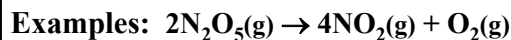Rate law → *Rate* = $k[N_2O_5]$

$m = 1$ → **first order in N_2O_5**

$m + n + \ldots = 1$ → **first order overall**

Some Examples of Experimental Rate Laws

- General rate law expression:

$$Rate = k[\text{A}]^m[\text{B}]^n \ldots$$

Examples: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

Rate law → *Rate* = $k[N_2O_5]$

$m = 1$ → **first order in N_2O_5**

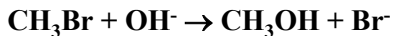$m + n + \ldots = 1$ → **first order overall**

$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

Rate law → *Rate* = $k[NO_2]^2$

$m = 2$ → **second order in NO_2**

$m + n + \ldots = 2$ → **second order overall**
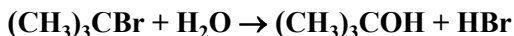

Examples:

$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$

Rate law → *Rate* = $k[CH_3Br][OH^-]$

$m = 1$ → **first order in CH_3Br**

$n = 1$ → **first order in OH^-**

$m + n + \ldots = 2$ → **second order overall**

$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$

Rate law → *Rate* = $k[(CH_3)_3CBr]$
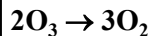
same as → *Rate* = $k[(CH_3)_3CBr]^1[H_2O]^0$

$m = 1$ → **first order in $(CH_3)_3CBr$**
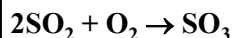
$n = 0$ → **zero order in H_2O**

$m + n + \ldots = 1$ → **first order overall**

- The reactions orders are not related to the stoichiometric coefficients of the reactants
- The reaction orders can sometimes be fractional or negative numbers
- The rate law can include concentrations of products
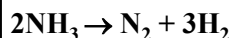
Examples:

$2O_3 \rightarrow 3O_2$

Rate law → *Rate* = $k[O_3]^2[O_2]^{-1}$

$2SO_2 + O_2 \rightarrow SO_3$

Rate law → *Rate* = $k[SO_2][SO_3]^{-1/2}$

$2NH_3 \rightarrow N_2 + 3H_2$

Rate law → *Rate* = k → zero overall order

➢The reactions orders can be determined by measuring the changes in the reaction rate upon changing the reactant concentrations

Example:

For the reaction $2NO + 2H_2 \rightarrow N_2 + 2H_2O$, the rate increases by a **factor of nine** when the concentration of **NO** is **tripled** while the concentration of H_2 is kept constant. What is the order of the reaction with respect to **NO**?

Rate law → $Rate = k[NO]^m[H_2]^n$

$9 \times Rate = k(3 \times [NO])^m[H_2]^n = 3^m \times k[NO]^m[H_2]^n$

$9 \times Rate = 3^m \times Rate$

$\Rightarrow 9 = 3^m \rightarrow m = 2 \rightarrow$ **2nd order in NO**

Experimental Determination of Rate Laws

• Determination of reaction orders and rate constants

  – **The initial rate method** – the initial rate ($Rate_o$) of the reaction is measured at various initial concentrations ($[X]_o$) of the reactants

$aA + bB \rightarrow$ **Products**　　$Rate_o = k[A]_o^m[B]_o^n$

  → If $[A]_o$ is increased by a factor, f, while $[B]_o$ is kept constant:

$new\ Rate_o = k(f \times [A]_o)^m[B]_o^n = f^m \times k[A]_o^m[B]_o^n$

$new\ Rate_o = f^m \times Rate_o$

  ⇒ The initial rate increases by a factor of f^m

Example: Determine the rate law for the reaction $O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$ from the following data:

Exp. #	Initial Conc. $\times 10^{-2}$ (mol/L)		Initial Rate $\times 10^{-3}$ (mol/L.s)
	O_2	NO	
1	1.1	1.3	3.2
2	2.0	1.3	5.8
3	1.1	3.0	17.0

→ Select experiments with the same concentrations of one of the reactants → (1, 2) and (1, 3)

→ Calculate the relative concentrations and rates by dividing with the smallest number in a column

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Exp #	Relative Conc.		Relative Rate
	O_2	NO	
1	1.1/1.1=1.0	1.0	3.2/3.2=1.0
2	2.0/1.1=1.8 ×1.8	1.0	5.8/3.2=1.8 ×1.8[1]

Exp #	Relative Conc.		Relative Rate
	O_2	NO	
1	1.0	1.3/1.3=1.0	3.2/3.2=1.0
3	1.0	3.0/1.3=2.3 ×2.3	17.0/3.2=5.3 ×2.3[2]

⇒As $[O_2]_o$ increases by a factor of 1.8, the initial rate increases by a factor of $1.8=1.8^1 \rightarrow$ **1st order** in O_2

⇒As $[NO]_o$ increases by a factor of 2.3, the initial rate increases by a factor of $5.3=2.3^2 \rightarrow$ **2nd order** in **NO**

Alternative method:

Exp.#	Initial Conc. $\times 10^{-2}$ (mol/L)		Initial Rate $\times 10^{-3}$ (mol/L.s)
	O_2	NO	
1	1.1	1.3	3.2
2	2.0	1.3	5.8
3	1.1	3.0	17.0

→$Rate = k[O_2]^m[NO]^n$

#1　$3.2 \times 10^{-3} = k(1.1 \times 10^{-2})^m (1.3 \times 10^{-2})^n$

#2　$5.8 \times 10^{-3} = k(2.0 \times 10^{-2})^m (1.3 \times 10^{-2})^n$

#3　$17.0 \times 10^{-3} = k(1.1 \times 10^{-2})^m (3.0 \times 10^{-2})^n$

Divide eq.2 by eq.1 and eq.3 by eq.1 :

$\dfrac{5.8}{3.2} = \dfrac{k \times 2.0^m \times 1.3^n}{k \times 1.1^m \times 1.3^n} \Rightarrow \dfrac{5.8}{3.2} = \left(\dfrac{2.0}{1.1}\right)^m \Rightarrow 1.8 = 1.8^m$ 　[1]

$\dfrac{17.0}{3.2} = \dfrac{k \times 1.1^m \times 3.0^n}{k \times 1.1^m \times 1.3^n} \Rightarrow \dfrac{17.0}{3.2} = \left(\dfrac{3.0}{1.3}\right)^n \Rightarrow 5.3 = 2.3^m$ 　[2]

⇒ $Rate = k[O_2][NO]^2$

→The reaction is **3rd-overall order**

→Determine the rate constant by substituting the initial concentrations and initial rate from one of the experiments and solve the equation for k

  →From Exp. #1:

$$k = \frac{Rate}{[O_2][NO]^2} = \frac{3.2 \times 10^{-3}\ mol/L \cdot s}{1.1 \times 10^{-2}\ mol/L \times \left(1.3 \times 10^{-2}\ mol/L\right)^2}$$

$$k = 1.7 \times 10^3\ L^2/mol^2 \cdot s$$

➢Note that the units of k depend on the overall order of the reaction and are different for different rate laws

16.4 Integrated Rate Laws
  – Give the concentration of the reactants as a function of time
- **Zero order reactions**

General reaction: **A → Products** (Zero-order)

→ **Rate** = k and   **Rate** = $-\Delta[A]/\Delta t$

$-\Delta[A]/\Delta t = k$ → **Differential** rate law (zero-order)
  – Integration of the differential equation leads to:

$\boxed{[A] = [A]_o - kt}$ → **Integrated** rate law (zero-order)
  – Gives the concentration of the reactant **[A]** at time t during the reaction
  – $[A]_o$ is the initial concentration at time $t = 0$

- **First order reactions**

General reaction: **A → Products** (1st order)

→ **Rate** = $k[A]$ and   **Rate** = $-\Delta[A]/\Delta t$

$-\Delta[A]/\Delta t = k[A]$ → **Differential** rate law (1st order)
  – Integration of the differential equation leads to:

$\boxed{[A] = [A]_o e^{-kt}}$ → **Integrated** rate law (1st order)
                    → Exponential form
  – Take a natural logarithm of both sides:

$\boxed{\ln[A] = \ln[A]_o - kt}$ → Logarithmic form
  – Gives the concentration of the reactant **[A]** at time t during the reaction
  – $[A]_o$ is the initial concentration at time $t = 0$

- **Second order reactions**

General reaction: **A → Products** (2nd order)

→ **Rate** = $k[A]^2$ and   **Rate** = $-\Delta[A]/\Delta t$

$-\Delta[A]/\Delta t = k[A]^2$ → **Differential** rate law (2nd order)
  – Integration of the differential equation leads to:

$\boxed{1/[A] = 1/[A]_o + kt}$ → **Integrated** rate law
                    (2nd order)

Example: For a given **zero-order** reaction the rate constant is **0.011 M/s** at 25°C. If the initial concentration of the reactant is **1.4 M**, what is its concentration after **1.5 minutes**?

$[A] = [A]_o - kt = 1.4 \text{ M} - 0.011 \text{ M/s} \times 90 \text{ s} = 0.4 \text{ M}$

Example: The decomposition of HI at 25°C is a **2nd order** reaction with a rate constant of **2.4×10^{-21} L/mol·s**. If the initial concentration of HI is **0.050 M**, how long would it take for **30%** of it **to react**?

➤ $2HI \rightarrow H_2 + I_2$ → $Rate = k[HI]^2$ → 2nd order

➤ 30% HI reacted ↔ 70% HI remaining

⇒ $[HI]_o = 0.050$ M $[HI] = 0.70 \times 0.050 = 0.035$ M

→ $1/[HI] = 1/[HI]_o + kt$ → $1/[HI] - 1/[HI]_o = kt$

→ $t = (1/[HI] - 1/[HI]_o)/k$

$$t = \frac{\left(\dfrac{1}{0.035\,mol/L} - \dfrac{1}{0.050\,mol/L}\right)}{2.4 \times 10^{-21}\,L/mol\cdot s} = 3.6 \times 10^{21}\,s = 1.1 \times 10^{14}\,yr$$

- Graphical representation of integrated rate laws
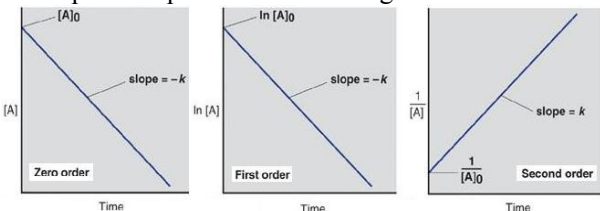
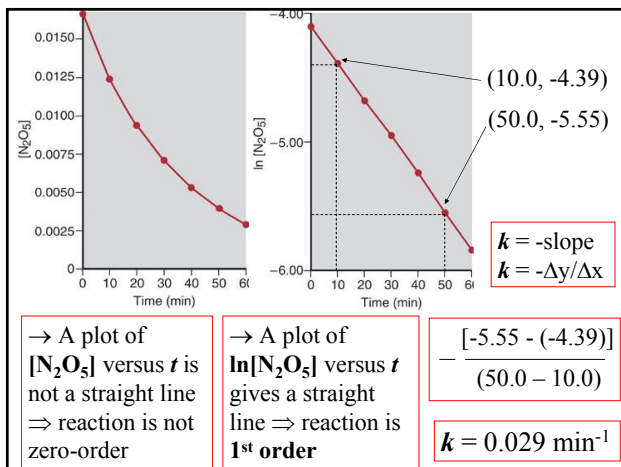| $[A] = [A]_o - kt$	$\ln[A] = \ln[A]_o - kt$	$1/[A] = 1/[A]_o + kt$
$y = b + mx$	$y = b + mx$	$y = b + mx$
⇒ If a plot of **[A] versus time** gives a straight line, the reaction is **zero-order** in A	⇒ If a plot of **ln[A] versus time** gives a straight line, the reaction is **1st order** in A	⇒ If a plot of **1/[A] versus time** gives a straight line, the reaction is **2nd order** in A

Example: Determine the reaction order and the rate constant for the decomposition of N_2O_5 from the following data: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

Time (min)	$[N_2O_5]$	$\ln[N_2O_5]$	$1/[N_2O_5]$
0	0.0165	−4.104	60.6
10	0.0124	−4.390	80.6
20	0.0093	−4.68	1.1×10^2
30	0.0071	−4.95	1.4×10^2
40	0.0053	−5.24	1.9×10^2
50	0.0039	−5.55	2.6×10^2
60	0.0029	−5.84	3.4×10^2

← Calculate $\ln[N_2O_5]$ and $1/[N_2O_5]$

→ Using a trail-and-error approach, plot $[N_2O_5]$, $\ln[N_2O_5]$, and $1/[N_2O_5]$ versus time until a straight line is obtained

→ A plot of $[N_2O_5]$ versus t is not a straight line $\Rightarrow$ reaction is not zero-order	→ A plot of $\ln[N_2O_5]$ versus t gives a straight line $\Rightarrow$ reaction is **1st order**	$-\dfrac{[-5.55 - (-4.39)]}{(50.0 - 10.0)}$
		$k = 0.029$ min^{-1}

k = -slope
$k = -\Delta y/\Delta x$

Reaction Half-Life

- **Half-life** ($t_{1/2}$) – the time needed to reduce the reactant concentration to ½ of its initial value
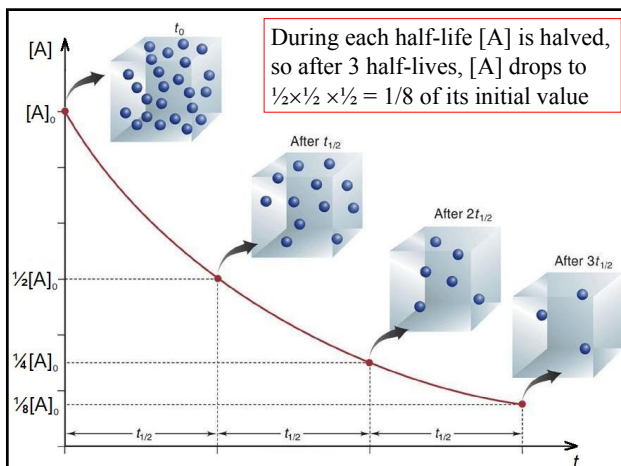
➤ $t_{1/2}$ for **1st order** reactions

→ $[A] = [A]_o e^{-kt}$ → ½$[A]_o$ = $[A]_o e^{-kt_{1/2}}$

→ $\ln(½) = -kt_{1/2}$ → $\ln(2) = kt_{1/2}$

$$t_{1/2} = \ln(2)/k = 0.693/k$$

$\Rightarrow t_{1/2}$ is independent of the initial concentration $[A]_o$

$\Rightarrow$ During the course of the reaction, $t_{1/2}$ remains the same, so it always takes the same time to half $[A]$

During each half-life [A] is halved, so after 3 half-lives, [A] drops to ½×½×½ = 1/8 of its initial value

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➤ $t_{1/2}$ for **zero-order** reactions

→ $[A] = [A]_o - kt$ → ½$[A]_o$ = $[A]_o - kt_{1/2}$

→ $kt_{1/2} = [A]_o - ½[A]_o$ → $kt_{1/2} = ½[A]_o$

$$t_{1/2} = [A]_o/2k$$

$\Rightarrow t_{1/2}$ is directly proportional to $[A]_o$

➤ $t_{1/2}$ for **2nd order** reactions

→ $1/[A] = 1/[A]_o + kt$ → $1/½[A]_o = 1/[A]_o + kt_{1/2}$

→ $2/[A]_o - 1/[A]_o = kt_{1/2}$ → $1/[A]_o = kt_{1/2}$

$$t_{1/2} = 1/k[A]_o$$

$\Rightarrow t_{1/2}$ is inversely proportional to $[A]_o$

➤ Radioactive decay is a 1st order process

Example: $t_{1/2}$ is **5700 yr** for the radioactive isotope of carbon, **^{14}C**. **C**-dating shows that the concentration of ^{14}C in an object has decreased to **25%** of its original value. How old is the object?

→ $t_{1/2} = 0.693/k$ → $k = 0.693/t_{1/2} = 0.693/5700$ yr

→ $k = 1.21×10^{-4}$ yr^{-1}

→ $[^{14}C] = [^{14}C]_o e^{-kt}$ → $[^{14}C] = 0.25[^{14}C]_o$

→ $0.25[^{14}C]_o = [^{14}C]_o e^{-kt}$ → $0.25 = e^{-kt}$

→ $\ln(0.25) = -kt$ → $t = -\ln(0.25) / k$

→ $t = -\ln(0.25) / 1.21×10^{-4}$ yr^{-1} = **11,000 yr**

16.5 Theories of Chemical Kinetics

The Effect of Temperature

- For most reactions, the reaction rate increases almost exponentially with T (rate ~ doubles for every 10°C of T↑)

- T affects the rate through the rate constant, k
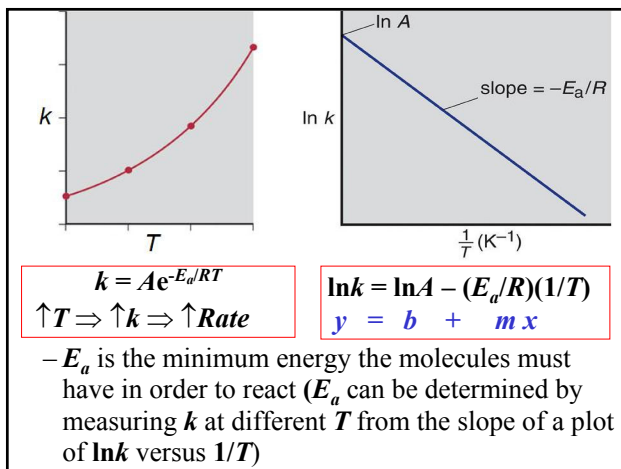
- **Arrhenius equation** – gives the temperature dependence of k

$$k = Ae^{-E_a/RT}$$

→ A – preexponential factor; E_a – activation energy

→ Take a natural logarithm (ln) of both sides

$$\ln k = \ln A - E_a/RT$$

$$k = Ae^{-E_a/RT}$$
$$\uparrow T \Rightarrow \uparrow k \Rightarrow \uparrow Rate$$

$$\ln k = \ln A - (E_a/R)(1/T)$$
$$y = b + mx$$

– E_a is the minimum energy the molecules must have in order to react (E_a can be determined by measuring k at different T from the slope of a plot of $\ln k$ versus $1/T$)

➤ For two different temperatures, T_1 and T_2

→ $\ln k_2 = \ln A - E_a/RT_2$ $\ominus$

→ $\ln k_1 = \ln A - E_a/RT_1$

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

→ Allows the determination of E_a by measuring k at two different Ts

→ Allows the calculation of k at a given T, if k is known at another T (E_a must be known too)

Example: For a given 1st order reaction, k is **2.6×10⁻¹⁰ s⁻¹** at **300°C** and **6.7×10⁻⁴ s⁻¹** at **500°C**. Calculate the activation energy.

$T_1 = 300°C = 573$ K $k_1 = 2.6\times10^{-10}$ s⁻¹

$T_2 = 500°C = 773$ K $k_2 = 6.7\times10^{-4}$ s⁻¹

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

$$E_a = -8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}}\left(\ln\frac{6.7\times10^{-4}\,\text{s}^{-1}}{2.6\times10^{-10}\,\text{s}^{-1}}\right)\left(\frac{1}{773\,\text{K}} - \frac{1}{573\,\text{K}}\right)^{-1}$$

$$E_a = 2.72\times10^5 \text{ J/mol} = 272 \text{ kJ/mol}$$

Explaining the Effects of Concentration and Temperature

– The Arrhenius equation is empirical and it does not explain the T dependence of k

• **Collision theory** – molecules must collide in order to react

➤ **Collision frequency** (Z) – number of collisions per unit time per unit volume (the reaction rate is proportional to Z)

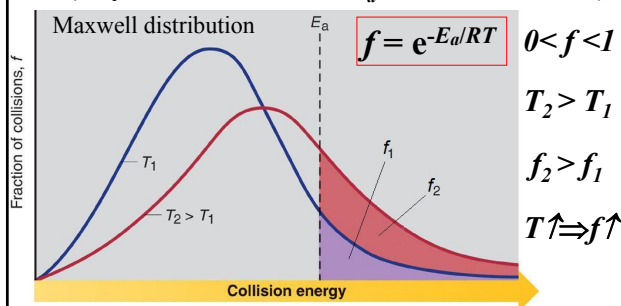→ Z is proportional to the concentration of the reactants

→ For a 2nd order reaction (A + B → Products)

$$Z = Z_o[\text{A}][\text{B}]$$

Z_o – proportionality constant (depends on $\sqrt{T}$)

➤ **Activation energy** (E_a) – the minimum collision energy required for the reaction to occur (not all collisions result in reaction)

→ f – fraction of collisions with energy $E > E_a$ (only collisions with $E > E_a$ can lead to reaction)

Maxwell distribution

$$f = e^{-E_a/RT} \quad 0 < f < 1$$

$$T_2 > T_1$$

$$f_2 > f_1$$

$$T\uparrow \Rightarrow f\uparrow$$
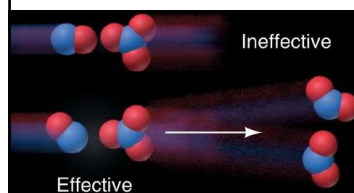

→ The reaction rate is proportional to f

$\Rightarrow \uparrow T \Rightarrow \uparrow f \Rightarrow \uparrow Rate$

$\Rightarrow \uparrow E_a \Rightarrow \downarrow f \Rightarrow \downarrow Rate$ $f = e^{-E_a/RT}$

➤ **Steric factor** (p) – the colliding molecules must have proper orientation with respect to each other in order to react

→ p – fraction of the total # of collisions having proper orientations ($0 < p < 1$)

Ineffective

Effective

→ The reaction rate is proportional to p

→ **Effective collisions** – having $E > E_a$ and proper orientation

> The reaction rate is proportional to the collision frequency (Z), the fraction of collisions (f) with $E > E_a$, and the fraction of collisions (p) with proper orientations

$\rightarrow$ For a 2nd order reaction (A + B $\rightarrow$ Products)

$Rate = p \times f \times Z = p \times e^{-E_a/RT} \times Z_o[A][B]$ (From theory)

$Rate = k[A][B]$ (From exper.)

$\Rightarrow k = p \times Z_o \times e^{-E_a/RT}$ ($p \times Z_o = A$)

$$\Rightarrow \quad k = A \times e^{-E_a/RT}$$

$\rightarrow$ The equation is the same as the Arrhenius equation

$\rightarrow A$ contains the steric factor, p, and part of the collision frequency, Z_o (Z_o depends weakly on $\sqrt{T}$)

• **Activated complex theory** – the reacting molecules form a high energy complex which is unstable and breaks down to form either the products or the original reactants

$$A + B \leftrightarrow [A\text{---}B]^* \leftrightarrow Products$$

> $[A\text{---}B]^* \rightarrow$ **activated complex** or **transition state**
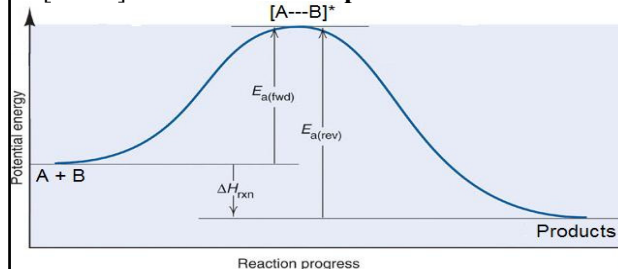
– E_a is the height of the barrier between the reactants and the transition state

– E_a is needed to weaken the bonds in the reactants so that the new bonds in the products can be formed

– Every reaction (every step in a reaction) goes through its own transition state

– Theoretically all reactions are reversible since once reached the transition state can go forward to products or back to reactants
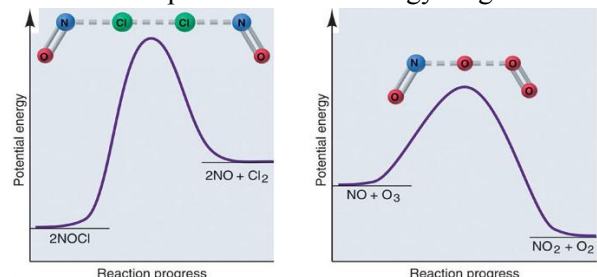
> Reaction **energy diagrams** – show the energy profile of the reaction ($E_{a(fwd)}$, $E_{a(rev)}$, and ΔH_{rxn})

Example: For a given reaction $E_{a(fwd)}$ is 55 kJ/mol and $E_{a(rev)}$ is 28 kJ/mol. Calculate ΔH_{rxn}.

$E_{a(fwd)} > E_{a(rev)} \Rightarrow$ the reaction is endothermic

$\Delta H_{rxn} = E_{a(fwd)} - E_{a(rev)} = 55 - 28 = 27$ kJ/mol

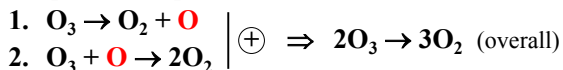> Some examples of reaction energy diagrams:

16.6 Reaction Mechanisms

– Sequences of molecular level steps (called elementary reactions) that sum up to the overall reaction

• **Elementary reactions (steps)** – describe individual molecular events (collisions)

Example: $2O_3(g) \rightarrow 3O_2(g)$

$\rightarrow$ Proposed 2 step mechanism:

1. $O_3 \rightarrow O_2 + O$
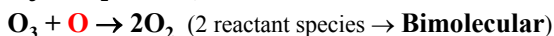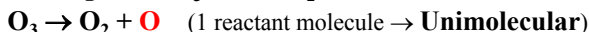2. $O_3 + O \rightarrow 2O_2$ $\boxed{+} \Rightarrow 2O_3 \rightarrow 3O_2$ (overall)

> **Reaction intermediate** – formed in one step and used up in another (does not appear in the overall reaction) $\rightarrow O$ is an intermediate

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$\rightarrow$ Reaction intermediates are usually unstable species, but some are stable enough to be isolated

• **Molecularity** – the number of reactant species involved in an elementary reaction (the number of colliding species)

Example: $2O_3(g) \rightarrow 3O_2(g)$

$O_3 \rightarrow O_2 + O$ (1 reactant molecule $\rightarrow$ **Unimolecular**)

$O_3 + O \rightarrow 2O_2$ (2 reactant species $\rightarrow$ **Bimolecular**)

$\rightarrow$ **Termolecular** reactions are very rare – very low probability for a three-particle collision with enough energy and proper orientation

$\rightarrow$ Higher order molecularities are not known

- **Rate laws for elementary reactions** – can be derived from the reaction stoichiometry
  - The reaction orders are equal to the stoichiometric coefficients of the reactants
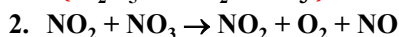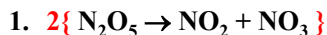
  $$iA + jB \rightarrow Products$$
  $$Rate = k[A]^i[B]^j$$
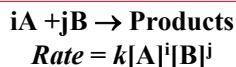
  →**Applies only to elementary reactions!**
  $\Rightarrow$ Overall reaction order $(i + j)$ = Molecularity

Table 16.6 Rate Laws for General Elementary Steps		
Elementary Step	**Molecularity**	**Rate Law**
$A \longrightarrow$ product	Unimolecular	Rate = $k[A]$
$2A \longrightarrow$ product	Bimolecular	Rate = $k[A]^2$
$A + B \longrightarrow$ product	Bimolecular	Rate = $k[A][B]$
$2A + B \longrightarrow$ product	Termolecular	Rate = $k[A]^2[B]$

Example: For the following three-step mechanism, determine the rate law and molecularity of each step, identify the intermediate and write the overall balanced equation.
1. $2\{ N_2O_5 \rightarrow NO_2 + NO_3 \}$
2. $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$
3. $NO + NO_3 \rightarrow 2NO_2$

$\rightarrow 2\{...\}$ – the 1st equation is taken twice

1. $Rate_1 = k_1[N_2O_5]$ $\rightarrow$ **unimolecular**
2. $Rate_2 = k_2[NO_2][NO_3]$ $\rightarrow$ **bimolecular**
3. $Rate_3 = k_3[NO][NO_3]$ $\rightarrow$ **bimolecular**

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1. $2\{ N_2O_5 \rightarrow NO_2 + NO_3 \}$
2. $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$ $\quad \oplus \quad \Rightarrow$
3. $NO + NO_3 \rightarrow 2NO_2$

$2N_2O_5 + \cancel{NO_2} + \cancel{NO_3} + \cancel{NO} + \cancel{NO_3} \rightarrow$
$\qquad 2NO_2 + \cancel{2NO_3} + \cancel{NO_2} + O_2 + \cancel{NO} + 2NO_2$

$\Rightarrow 2N_2O_5 \rightarrow 4NO_2 + O_2$ (**overall reaction**)
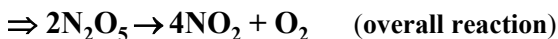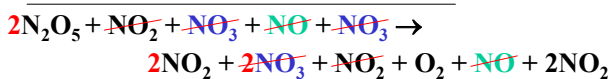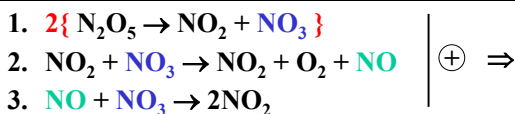
  → NO_3 and NO are produced in the 1st and 2nd steps and consumed in the 2nd and 3rd steps (not present in the overall reaction) $\Rightarrow$ **intermediates**
➤ The rate law of the overall reaction can be deduced from the rate laws of the elementary reactions

- **Rate-determining step (*RDS*)** – the slowest step in a mechanism (limits the rate of the overall reaction)

  $$Rate = Rate\ of\ RDS$$

Correlating Mechanisms and Rate Laws

- The validity of a mechanism can be tested by correlating it with the experimental rate law
  - The elementary steps must add up to the overall reaction
  - The elementary steps must be physically reasonable (uni- or bi-molecular)
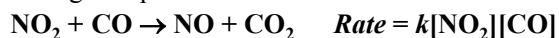 - The rate law of the *RDS* must agree with the experimental rate law

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➤ Mechanisms with a **slow initial step**

Example: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Experimental rate law: $Rate = k[NO_2]^2$

→ Three proposed mechanisms:

I. A single step mechanism:
$NO_2 + CO \rightarrow NO + CO_2$ $\quad Rate = k[NO_2][CO]$
→ **Inconsistent** with the exp. rate law $\Rightarrow$ **reject**

II. 1. $NO_2 + NO_2 \rightarrow NO_3 + NO$ $\qquad$ [Slow, *RDS*]
$\qquad$ 2. $NO_3 + CO \rightarrow NO_2 + CO_2$ $\qquad$ [Fast]
$\oplus \rightarrow$ $\quad NO_2 + CO \rightarrow NO + CO_2$ $\qquad$ (overall)
$Rate = Rate_1 = k_1[NO_2][NO_2] = k_1[NO_2]^2$
$\rightarrow$ **Consistent** with the exp. rate law ($k = k_1$)

III. 1. $NO_2 + NO_2 \rightarrow N_2O_4$ $\qquad\qquad$ [Slow, *RDS*]
$\qquad$ 2. $N_2O_4 + CO \rightarrow NO + NO_2 + CO_2$ [Fast]
$\oplus \rightarrow$ $\quad NO_2 + CO \rightarrow NO + CO_2$ $\qquad$ (overall)
$Rate = Rate_1 = k_1[NO_2][NO_2] = k_1[NO_2]^2$
$\rightarrow$ **Consistent** with the exp. rate law ($k = k_1$)

$\Rightarrow$ Both (II) and (III) are physically reasonable (involve bimolecular steps) and consistent with the experimental rate law $\rightarrow$ more data are needed to give preference to one of them

➤ Mechanisms *can never be proved* by kinetics data alone; we can only *reject* a mechanism or state that a mechanism is *consistent* with the kinetics data

> Mechanisms with a **fast initial step**

A $\xrightarrow{k_1}$ **Int**	[Slow]	[Fast]
Int $\xrightarrow{k_2}$ **B**	[Fast]	[Slow]
$\oplus \rightarrow$ A $\rightarrow$ B	*Rate = k_1[A]*	*Rate = k_2[Int]*

→ **[Int]** can not be in the rate law (intermediate) and must be expressed through the concentrations of the reactants (or products) in the overall reaction

→ If the first reaction is **fast and reversible**, it quickly reaches equilibrium and the rate of formation of the intermediate is equal to the rate of its consumption (steady state approximation)

→ The **steady state approximation** allows the calculation of [Int]

Example: $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$

Experimental rate law: *Rate = $k[NO]^2[Br_2]$*

→ Proposed mechanism:

1. $NO + Br_2 \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} NOBr_2$ [Fast, *revers.*]

2. $NOBr_2 + NO \xrightarrow{k_2} 2NOBr$ [Slow, *RDS*]

$\oplus \rightarrow$ $2NO + Br_2 \rightarrow 2NOBr$ (overall)

$\Rightarrow Rate = Rate_2 = k_2[NO][NOBr_2]$

→ **$NOBr_2$** is an intermediate and must be expressed through the reactants

→ The 1st step reaches equilibrium so the rates of the forward (***$Rate_1$***) and reverse (***$Rate_{-1}$***) reactions are equal

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1. $NO + Br_2 \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} NOBr_2$ [Fast, *revers.*]

2. $NOBr_2 + NO \xrightarrow{k_2} 2NOBr$ [Slow, *RDS*]

$\Rightarrow Rate = Rate_2 = k_2[NO][NOBr_2]$

→ $Rate_1 = Rate_{-1}$ → $k_1[NO][Br_2] = k_{-1}[NOBr_2]$

→ $[NOBr_2] = (k_1/k_{-1})[NO][Br_2]$

$\Rightarrow Rate = k_2[NO][NOBr_2] = k_2[NO](k_1/k_{-1})[NO][Br_2]$

$\Rightarrow Rate = (k_2k_1/k_{-1})[NO]^2[Br_2] = k[NO]^2[Br_2]$

→ Experimental rate law: *Rate = $k[NO]^2[Br_2]$*

→ **Consistent** with the exp. rate law ($k = k_2k_1/k_{-1}$)

16.7 Catalysis

• **Catalyst** – a substance that increases the reaction rate without being consumed in it

– In general catalysts increase the rate by **lowering the activation energy (E_a)** of the reaction

– Catalysts provide a different mechanism for the reaction
– Catalysts speedup both the forward and reverse reactions
– Catalysts don't change the ΔH_r

• **Homogeneous catalysis** – the catalyst is in the same phase as the reactants

Example: Decomposition of H_2O_2

$$2H_2O_2(aq) \xrightarrow{Br_2(aq)} 2H_2O(l) + O_2(g)$$

→ **$Br_2(aq)$** is in the same phase as **$H_2O_2(aq)$**

→ **Br_2** catalyses the reaction by providing a two step mechanism with lower E_a

1. $H_2O_2(aq) + Br_2(aq) \rightarrow 2Br^- + 2H^+ + O_2(g)$

2. $H_2O_2(aq) + 2Br^- + 2H^+ \rightarrow Br_2(aq) + 2H_2O(l)$

→ **Br_2** is not consumed in the reaction

• **Heterogeneous catalysis** – the catalyst is in a phase different from that of the reactants

Example: Hydrogenation of ethylene

$$H_2C=CH_2(g) + H_2(g) \xrightarrow{Pt(s)} H_3C-CH_3(g)$$

→ **Pt(s)** is in a different phase (solid)

→ The reactants are adsorbed over the Pt and their bonds are weakened (**H_2** splits into 2**H**)