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* ∝ *Collision freq.* ∝ *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* ∝ *Collision energy* ∝ *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***)

$$\textbf{Rate} = \Delta C/\Delta t$$

– **Units → M/s** or **mol/L·s**

Reactant (A) → Product (B)

$\Delta C < 0$ $\quad$ $\Delta C > 0$

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

$\Rightarrow$ $\textbf{Rate} = -\Delta[A]/\Delta t$ or $\textbf{Rate} = \Delta[B]/\Delta t$

➢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, $\mathbf{A \rightarrow 2B}$

➢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, $a\mathbf{A} + b\mathbf{B} \rightarrow c\mathbf{C} + d\mathbf{D}$

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

Example:

For the reaction $\mathbf{N_2 + 3H_2 \rightarrow 2NH_3}$, the rate of formation of NH_3 is **1.4 M/min**. Calculate the rate of disappearance of H_2 and the reaction rate.

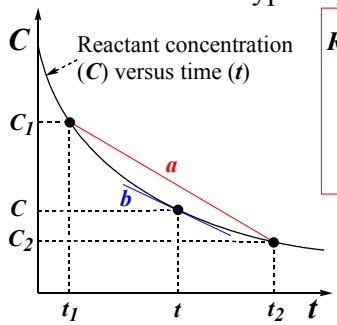
$$\frac{\Delta[NH_3]}{\Delta t} = 1.4\frac{M}{min} \rightarrow 1.4\frac{mol\ NH_3}{L \cdot min}$$

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

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

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

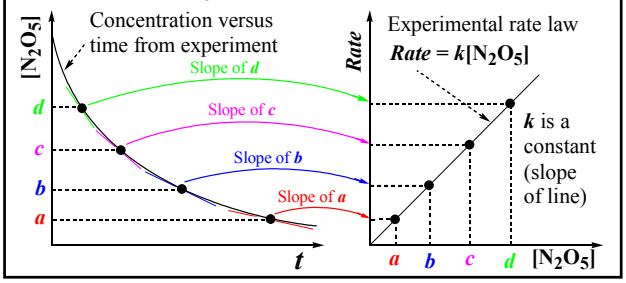
➢ Normally the term reaction rate refers to the instantaneous rate

- **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

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

$$aA + bB + \ldots \rightarrow \text{Products}$$

the rate law can be expressed in the form:

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

→ ***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* + … = 1 → first order overall**

Some Examples of Experimental Rate Laws

– General rate law expression:

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

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 $\rightarrow$ $Rate = k[NO]^m[H_2]^n$

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

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

$\Rightarrow 9 = 3^m \rightarrow m = 2 \rightarrow 2^{nd}$ **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 $\quad Rate_o = k[A]_o^m[B]_o^n$

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

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

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

$\Rightarrow$ 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. $\times10^{-2}$ (mol/L)		Initial Rate $\times10^{-3}$ (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

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

$\rightarrow$ Calculate the relative concentrations and rates by dividing with the smallest number in a column

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

$\Rightarrow$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**

$\Rightarrow$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. $\times10^{-2}$ (mol/L)		Initial Rate $\times10^{-3}$ (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

$\rightarrow Rate = k[O_2]^m[NO]^n$

#1 $3.2\times10^{-3} = k(1.1\times10^{-2})^m(1.3\times10^{-2})^n$

#2 $5.8\times10^{-3} = k(2.0\times10^{-2})^m(1.3\times10^{-2})^n$

#3 $17.0\times10^{-3} = k(1.1\times10^{-2})^m(3.0\times10^{-2})^n$

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

$$\frac{5.8}{3.2} = \frac{k\times2.0^m\times1.3^n}{k\times1.1^m\times1.3^n} \Rightarrow \frac{5.8}{3.2} = \left(\frac{2.0}{1.1}\right)^m \Rightarrow 1.8 = 1.8^m \quad (1)$$

$$\frac{17.0}{3.2} = \frac{k\times1.1^m\times3.0^n}{k\times1.1^m\times1.3^n} \Rightarrow \frac{17.0}{3.2} = \left(\frac{3.0}{1.3}\right)^n \Rightarrow 5.3 = 2.3^m \quad (2)$$

$\Rightarrow Rate = k[O_2][NO]^2$

$\rightarrow$The reaction is **3rd-overall order**

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

$\rightarrow$From Exp. #1:

$$k = \frac{Rate}{[O_2][NO]^2} = \frac{3.2\times10^{-3}\ \text{mol/L}\cdot\text{s}}{1.1\times10^{-2}\text{mol/L}\times\left(1.3\times10^{-2}\text{mol/L}\right)^2}$$

$$k = 1.7\times10^3\ \text{L}^2/\text{mol}^2\cdot\text{s}$$

➢ 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*** **= -Δ[A]/Δ*t***

-Δ[A]/Δ*t* = *k* → **Differential** rate law (zero-order)

– Integration of the differential equation leads to:

$[A] = [A]_0 - kt$ → **Integrated** rate law (zero-order)

– Gives the concentration of the reactant **[A]** at time ***t*** during the reaction

– **$[A]_0$** is the initial concentration at time ***t*** **= 0**

- **First order reactions**

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

→ ***Rate*** **= *k*[A]** and ***Rate*** **= -Δ[A]/Δ*t***

-Δ[A]/Δ*t* = *k*[A] → **Differential** rate law (1st order)

– Integration of the differential equation leads to:

$[A] = [A]_0 e^{-kt}$ → **Integrated** rate law (1st order)

→ Exponential form

– Take a natural logarithm of both sides:

$\ln[A] = \ln[A]_0 - kt$ → Logarithmic form

– Gives the concentration of the reactant **[A]** at time ***t*** during the reaction

– **$[A]_0$** is the initial concentration at time ***t*** **= 0**

- **Second order reactions**

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

→ ***Rate*** **= *k*[A]²** and ***Rate*** **= -Δ[A]/Δ*t***

-Δ[A]/Δ*t* = *k*[A]² → **Differential** rate law (2^{nd} order)

– Integration of the differential equation leads to:

$1/[A] = 1/[A]_0 + kt$ → **Integrated** rate law (2^{nd} 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**?

$[A] = [A]_0 - kt = 1.4\ M - 0.011\ M/s \times 90\ s = 0.4\ M$

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** → 2^{nd} order

➢ 30% HI reacted ↔ 70% HI remaining

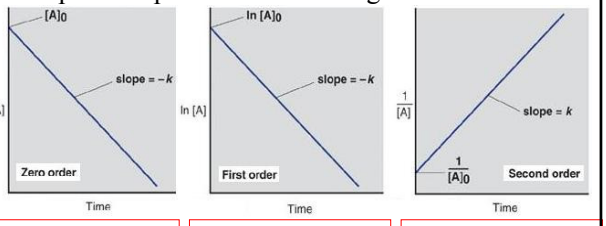
⇒ $[HI]_0 = 0.050\ M$ $[HI] = 0.70\times0.050 = 0.035\ M$

→ $1/[HI] = 1/[HI]_0 + kt$ → $1/[HI] - 1/[HI]_0 = kt$

→ $t = (1/[HI] - 1/[HI]_0)/k$

$$t = \frac{\left(\frac{1}{0.035\ mol/L} - \frac{1}{0.050\ mol/L}\right)}{2.4\times10^{-21}\ L/mol\cdot s} = 3.6\times10^{21}\ s = 1.1\times10^{14}\ yr$$

- Graphical representation of integrated rate laws



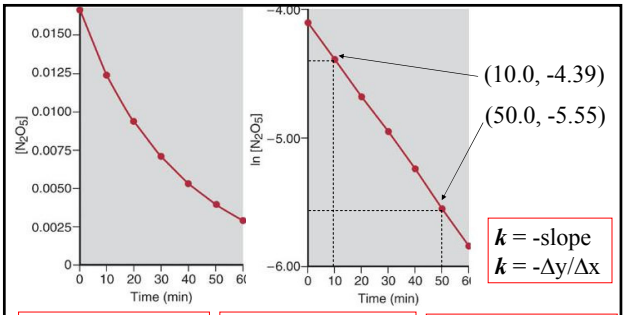
$[A] = [A]_0 - kt$	**$\ln[A] = \ln[A]_0 - kt$**	**$1/[A] = 1/[A]_0 + kt$**
y = b + mx	***y = b + mx***	***y = b + mx***
⇒ If a plot of **[A] versus time** gives a straight line, the reaction is **zero-order** in A	⇒ If a plot of **ln[A] versus time** gives a straight line, the reaction is **1st order** 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



k = -slope
k = -Δy/Δx

→ A plot of $[N_2O_5]$ versus t is not a straight line ⇒ reaction is not zero-order

→ A plot of $\ln[N_2O_5]$ versus t gives a straight line ⇒ reaction is **1st order**

$$-\frac{[-5.55 - (-4.39)]}{(50.0 - 10.0)}$$

$k = 0.029\ \text{min}^{-1}$

Reaction Half-Life

- **Half-life** ($t_{½}$) – the time needed to reduce the reactant concentration to ½ of its initial value

➢ $t_{1/2}$ for **1st order** reactions

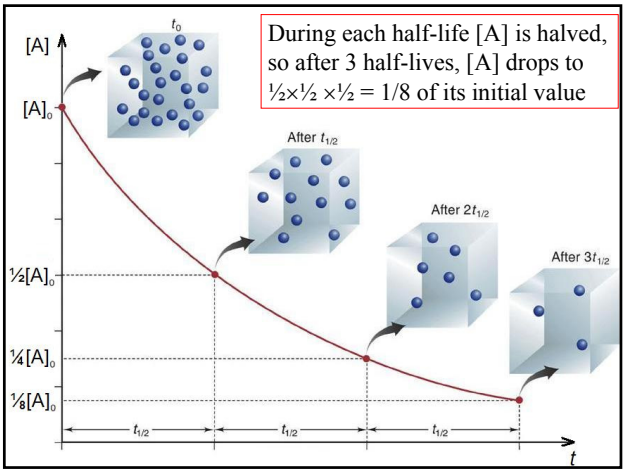
→ $[A] = [A]_0e^{-kt}$ → $½[A]_0 = [A]_0e^{-kt_{½}}$

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

$$t_{½} = \ln(2)/k = 0.693/k$$

⇒ $t_{½}$ is independent of the initial concentration $[A]_0$

⇒ During the course of the reaction, $t_{½}$ 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

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

→ $[A] = [A]_0 - kt$ → $½[A]_0 = [A]_0 - kt_{½}$

→ $kt_{½} = [A]_0 - ½[A]_0$ → $kt_{½} = ½[A]_0$

$$t_{½} = [A]_0/2k$$

⇒ $t_{½}$ is directly proportional to $[A]_0$

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

→ $1/[A] = 1/[A]_0 + kt$ → $1/½[A]_0 = 1/[A]_0 + kt_{½}$

→ $2/[A]_0 - 1/[A]_0 = kt_{½}$ → $1/[A]_0 = kt_{½}$

$$t_{½} = 1/k[A]_0$$

⇒ $t_{½}$ is inversely proportional to $[A]_0$

➢ Radioactive decay is a 1st order process

Example: $t_{½}$ 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?

→ $t_{½} = 0.693/k$ → $k = 0.693/t_{½} = 0.693/5700\ \text{yr}$

→ $k = 1.21\times10^{-4}\ \text{yr}^{-1}$

→ $[^{14}C] = [^{14}C]_0e^{-kt}$ → $[^{14}C] = 0.25[^{14}C]_0$

→ $0.25[^{14}C]_0 = [^{14}C]_0e^{-kt}$ → $0.25 = e^{-kt}$

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

→ $t = -\ln(0.25)\ /\ 1.21\times10^{-4}\ \text{yr}^{-1} =$ **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

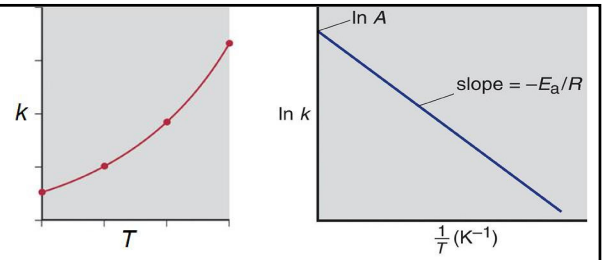
- **Arrhenius equation** – gives the temperature dependence of k

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

→A – preexponential factor; E_a – activation energy

→Take a natural logarithm (ln) of both sides

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



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

$\uparrow T \Rightarrow \uparrow k \Rightarrow \uparrow Rate$

$\ln k = \ln A - (E_a/R)(1/T)$

$y = b + m\,x$

– 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

$\rightarrow \quad \ln k_2 = \ln A - E_a/RT_2$

$\rightarrow \quad \ln k_1 = \ln A - E_a/RT_1 \quad \Big| \ominus$

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

→ 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 $\qquad k_1 = 2.6\times10^{-10}$ s^{-1}

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

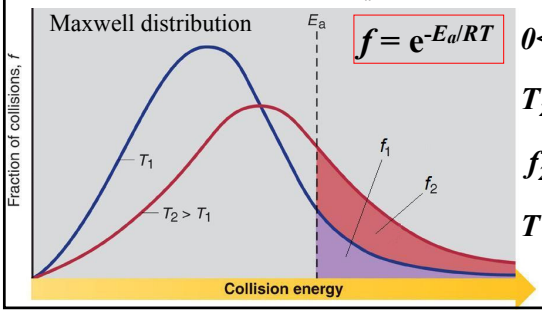
→ For a 2nd order reaction (A + B → Products)

$$Z = Z_o[A][B]$$

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)



$f = e^{-E_a/RT}$

$0 < f < 1$

$T_2 > T_1$

$f_2 > f_1$

$T\uparrow \Rightarrow f\uparrow$

→ The reaction rate is proportional to f

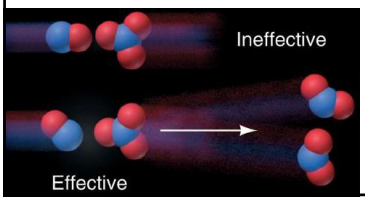
$\Rightarrow \uparrow T \Rightarrow \uparrow f \Rightarrow \uparrow Rate$

$\Rightarrow \uparrow E_a \Rightarrow \downarrow f \Rightarrow \downarrow Rate$

$f = e^{-E_a/RT}$

➢ **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 ($0 < p < 1$)



→ 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

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

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

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

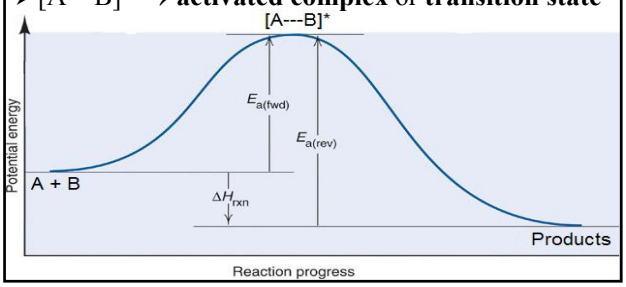
→ The equation is the same as the Arrhenius equation

→ 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 ↔ **[A---B]*** ↔ Products

➢ [A---B]* → **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

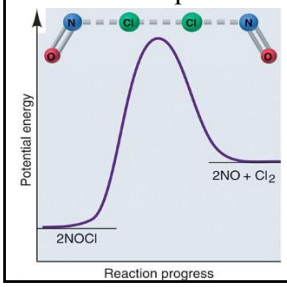
➢ Reaction **energy diagrams** – show the energy profile of the reaction ($E_{a(fwd)}$, $E_{a(rev)}$, and ΔH_{rxn})

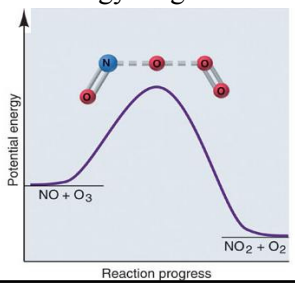
Example: For a given reaction $E_{a(fwd)}$ is 55 kJ/mol and $E_{a(rev)}$ is 28 kJ/mol. Calculate ΔH_{rxn}.

$E_{a(fwd)} > E_{a(rev)} \Rightarrow$ 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: $2O_3(g) \rightarrow 3O_2(g)$

→ Proposed 2 step mechanism:

1. $O_3 \rightarrow O_2 + O$
2. $O_3 + O \rightarrow 2O_2$

$\oplus \Rightarrow 2O_3 \rightarrow 3O_2$ (overall)

➢ **Reaction intermediate** – formed in one step and used up in another (does not appear in the overall reaction) → O is an intermediate

→ 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 → **Unimolecular**)

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

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

→ 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

$$\mathbf{iA + jB \rightarrow Products}$$
$$\boldsymbol{Rate = k[A]^i[B]^j}$$

→ **Applies only to elementary reactions!**

⇒ Overall reaction order (i + j) = Molecularity

Table 16.6 Rate Laws for General Elementary Steps

Elementary Step	Molecularity	Rate Law
A ⟶ product	Unimolecular	Rate = k[A]
2A ⟶ product	Bimolecular	Rate = k[A]^2
A + B ⟶ product	Bimolecular	Rate = k[A][B]
2A + B ⟶ 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. $NO + NO_3 \rightarrow 2NO_2$

→ $2\{\ldots\}$ – the 1st equation is taken twice

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

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

⊕ ⇒

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

$$\Rightarrow 2N_2O_5 \rightarrow 4NO_2 + O_2 \quad \textbf{(overall reaction)}$$

→ 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) ⇒ **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)

$$\boldsymbol{Rate = Rate\ of\ RDS}$$

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- and rarely termolecular)
  - The rate law of the ***RDS*** must agree with the experimental rate law

➢ 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 ⇒ **reject**

II. 1. $NO_2 + NO_2 \rightarrow NO_3 + NO$ **[Slow, *RDS*]**

2. $NO_3 + CO \rightarrow NO_2 + CO_2$ **[Fast]**

⊕ → $NO_2 + CO \rightarrow NO + CO_2$ (overall)

$Rate = Rate_1 = k_1[NO_2][NO_2] = k_1[NO_2]^2$

→ **Consistent** with the exp. rate law ($k = k_1$)

III. 1. $NO_2 + NO_2 \rightarrow N_2O_4$ **[Slow,*RDS*]**

2. $N_2O_4 + CO \rightarrow NO + NO_2 + CO_2$ **[Fast]**

⊕ → $NO_2 + CO \rightarrow NO + CO_2$ (overall)

$Rate = Rate_1 = k_1[NO_2][NO_2] = k_1[NO_2]^2$

→ **Consistent** with the exp. rate law ($k = k_1$)

⇒ Both (II) and (III) are physically reasonable (involve bimolecular steps) and consistent with the experimental rate law → 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]
⊕ → $A \rightarrow B$	$Rate = k_1[A]$	$Rate = k_2[Int]$

→ [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. $NO + Br_2 \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} NOBr_2$ [Fast, *revers.*]
2. $NOBr_2 + NO \xrightarrow{k_2} 2NOBr$ [Slow, *RDS*]

⊕ → $2NO + Br_2 \rightarrow 2NOBr$ (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

1. $NO + Br_2 \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} NOBr_2$ [Fast, *revers.*]
2. $NOBr_2 + NO \xrightarrow{k_2} 2NOBr$ [Slow, *RDS*]

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

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

→ $[NOBr_2] = (k_1/k_{-1})[NO][Br_2]$

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

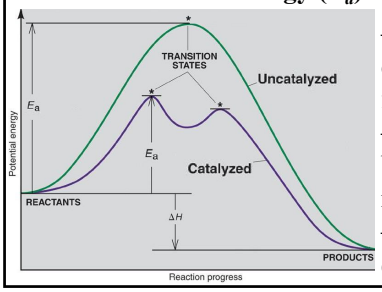
$\Rightarrow Rate = (k_2k_1/k_{-1})[NO]^2[Br_2] = k[NO]^2[Br_2]$

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

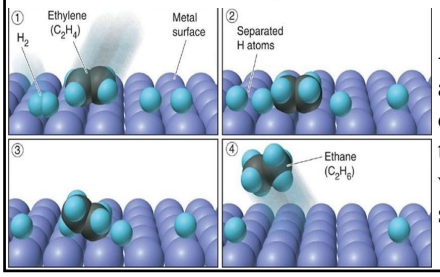
→ Br_2 is not consumed in the reaction

- **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 2H)