Announcement

CHEM 1001N quizzes

Surnames A - M: Stedman Lecture Hall D
Surnames N - Z: Accolade East 001

Those who will be writing in Accolade East 001 should go and find that room NOW because they will not be given extra time on the day of the quiz if they show up late.

Accolade East is still under construction and the only entrance that appears to be accessible is on the northeast corner. This building is across the street from Shulich, near the Student Services Centre. Room 001 is in the basement.

Announcements

Course format: the overall format of the course is similar to CHEM 1000

Textbook: Petrucci, Harwood and Herring (8th edition)

Section N specific material: www.chem.yorku.ca/profs/krylov/

Attending lectures and tutorial is mandatory

Questions will be addressed during and after lectures

Quizzes will be held during tutorial times on January 31, February 21, March 7, and March 21

Chemical Kinetics

Problem Set: Chapter 15 questions 29, 33, 35, 43a, 44, 53, 63, 80

Semantics

- Adjective “**kinetic**” **originates from** Greek “kinetikos” that, in turn, originates from Greek “kinetos’ which means “**moving**”.
- Noun “**kinetics**” **is** used in a **singular** form only.

Example: “The kinetics of this process is fast”

- In general, the word “**kinetics**” **is** used in physical and life sciences to represent the **dependence** of something **on time**. *Example:* “Kinetics of substance uptake by a cell was measured”
- **Chemical kinetics** is a branch of chemistry which **is concerned with the rates of change in the concentration** of reactants in a chemical reaction.

Kinetics versus Thermodynamics

- Thermodynamics tells us which direction a reaction will go (e.g. at room temperature and standard pressure, carbon is stable in a form of graphite)

- Kinetics can tell us how quickly it will get there (e.g. a diamond will not convert to graphite during your lifetime)

(Thermodynamics will be considered later in this course)

Aims of Chemical Kinetics

1) at the macroscopic level
- to define "rate of reaction", "order of reaction" and "rate law"
- to examine how "rates" and "orders" are determined

2) at the molecular (microscopic) level
- to predict plausible "reaction mechanisms" from experimental "rate laws"

Note: The macroscopic level operates with measurable parameters (e.g. T, P, V).

The microscopic level operates with parameters that are hard to measure directly (e.g. velocity of a molecule)

Knowing Balanced Chemical Reaction is Essential

- (i.e. the stoichiometry must be known for determining reaction rates)

Warm up example:

$2\ Fe^{3+} + Sn^{2+} \rightarrow 2\ Fe^{2+} + Sn^{4+}$

The rate of Fe^{3+} consumption is twice as high as that of Sn^{2+}

The rate of Fe^{3+} consumption has the same absolute value as the rate of Fe^{2+} production, but it is negative

General Reaction

$$aA + bB \rightarrow gG + hH$$

- The rates of loss of A and B and production G and H can be expressed through the rates of change in their concentrations (if the volume is constant):

$$\frac{d[A]}{dt}, \quad \frac{d[B]}{dt}, \quad \frac{d[G]}{dt}, \quad \frac{d[H]}{dt}$$

$$\frac{d[A]}{dt} = \frac{\Delta[A]}{\Delta t} \quad \textit{for} \quad \Delta t \rightarrow 0$$

Units: $\frac{\text{mol}}{\text{Ls}} = \frac{\text{M}}{\text{s}} = \text{Ms}^{-1}$

Relation Between the Rates of Loss and Production

- As reactants are consumed, their concentrations drop while those for products increase → the rates of production are positive and those of consumption are negative
- Rates of production and loss are related by the stoichiometry of the balanced reaction:

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{g}\frac{d[G]}{dt} = \frac{1}{h}\frac{d[H]}{dt}$$

- As usually: $\Delta[A] = [A]_{t_2} - [A]_{t_1}$, $\Delta t = t_2 - t_1$

Definition of the Rate of Reaction

$$\boxed{\begin{aligned}\text{rate of reaction} &= -\frac{1}{a}\frac{d[A]}{\Delta t} = -\frac{1}{b}\frac{d[B]}{dt}\\ &= \frac{1}{g}\frac{d[G]}{dt} = \frac{1}{h}\frac{d[H]}{dt}\end{aligned}}$$

- The rate of reaction may be expressed in terms of either the consumption of reactants, or the production of products.
- The rate of reaction is always positive (if you got it negative, it means the reaction proceeds in the opposite direction).

Example (similar to the warm-up one)

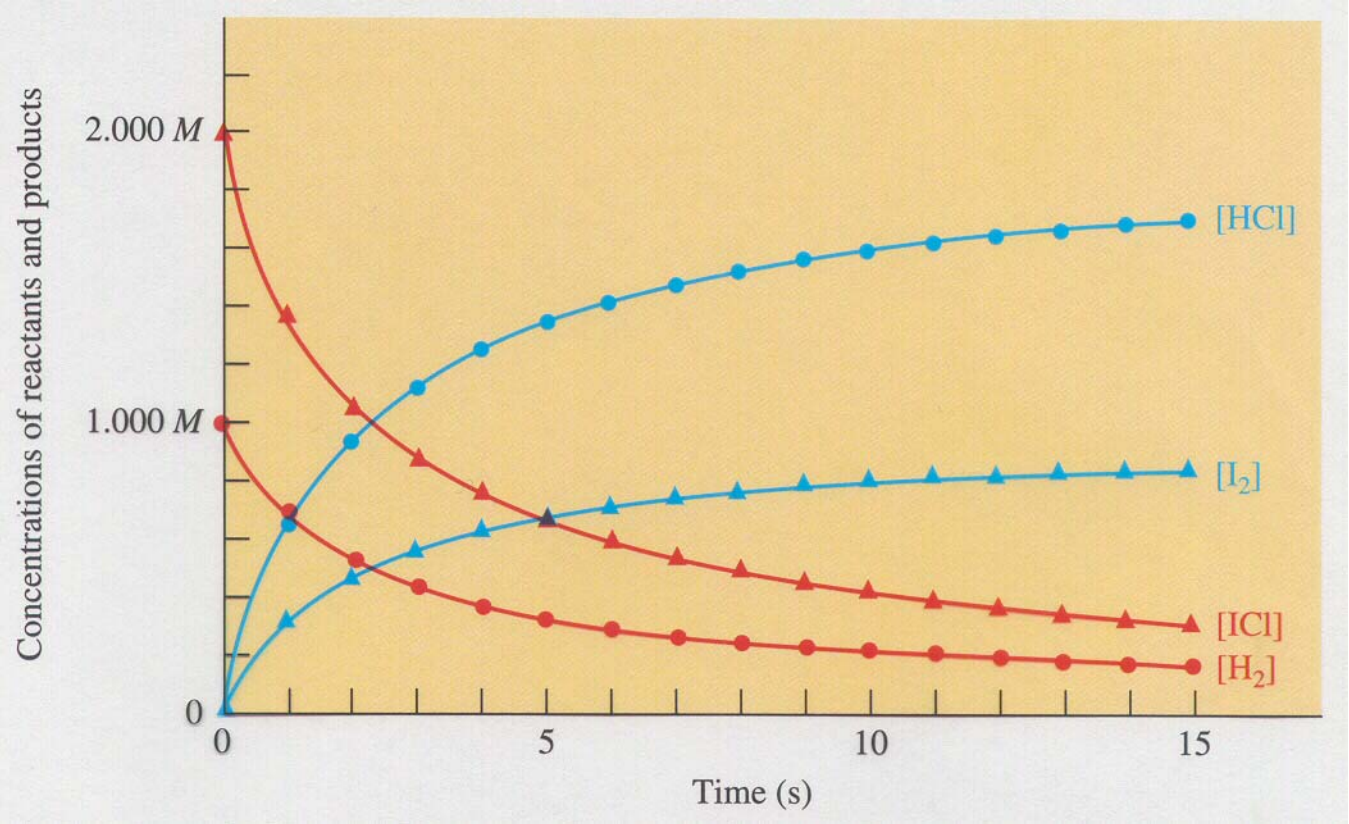
- $H_2(g) + 2\ ICl(g) \rightarrow I_2(g) + 2\ HCl(g)$

$$\text{rate of reaction} = -\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[ICl]}{dt}$$

$$= \frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[HCl]}{dt}$$

Real Kinetics! (for the same example)

$H_2(g) + 2\ ICl(g) \rightarrow I_2(g) + 2\ HCl(g)$



- rate slows as reaction approaches equilibrium

Measuring Reaction Rates is Generally Not Trivial

- Determining reaction rates requires measuring changes in concentration over time ($d[A]/dt$)
- Measuring time is simple; determining concentrations of products or reactants can be more difficult
- We could measure partial pressures of gases, pH of a solution, colour changes (spectroscopy), etc., to monitor the progress of the reaction (i.e. the change in concentration)

… the method for monitoring the reaction is dependent upon the properties of the substances in the reaction

Example (Experiment)

$H_2O_2(aq) \rightarrow H_2O(l) + ½\ O_2(g)$

- We could follow this reaction by measuring volume of $O_2(g)$ produced at different times, ***or***
- We could also follow this reaction by measuring remaining H_2O_2 in the following way. Titrate small samples of the reaction mixture with permanganate (MnO_4^-) from time to time. Permanganate reacts with H_2O_2:

  $$2\ MnO_4^- + 5\ H_2O_2 + 6\ H^+ \rightarrow 2\ Mn^{2+} + 8\ H_2O + O_2(g)$$

- Permanganate has color while its product (Mn^{2+}) does not. The amount of remaining H_2O_2 is measured by disappearance of color of permanganate:

\- Let’s follow the reaction by the latter method every 400 s

Experimental Data (Tabulated)

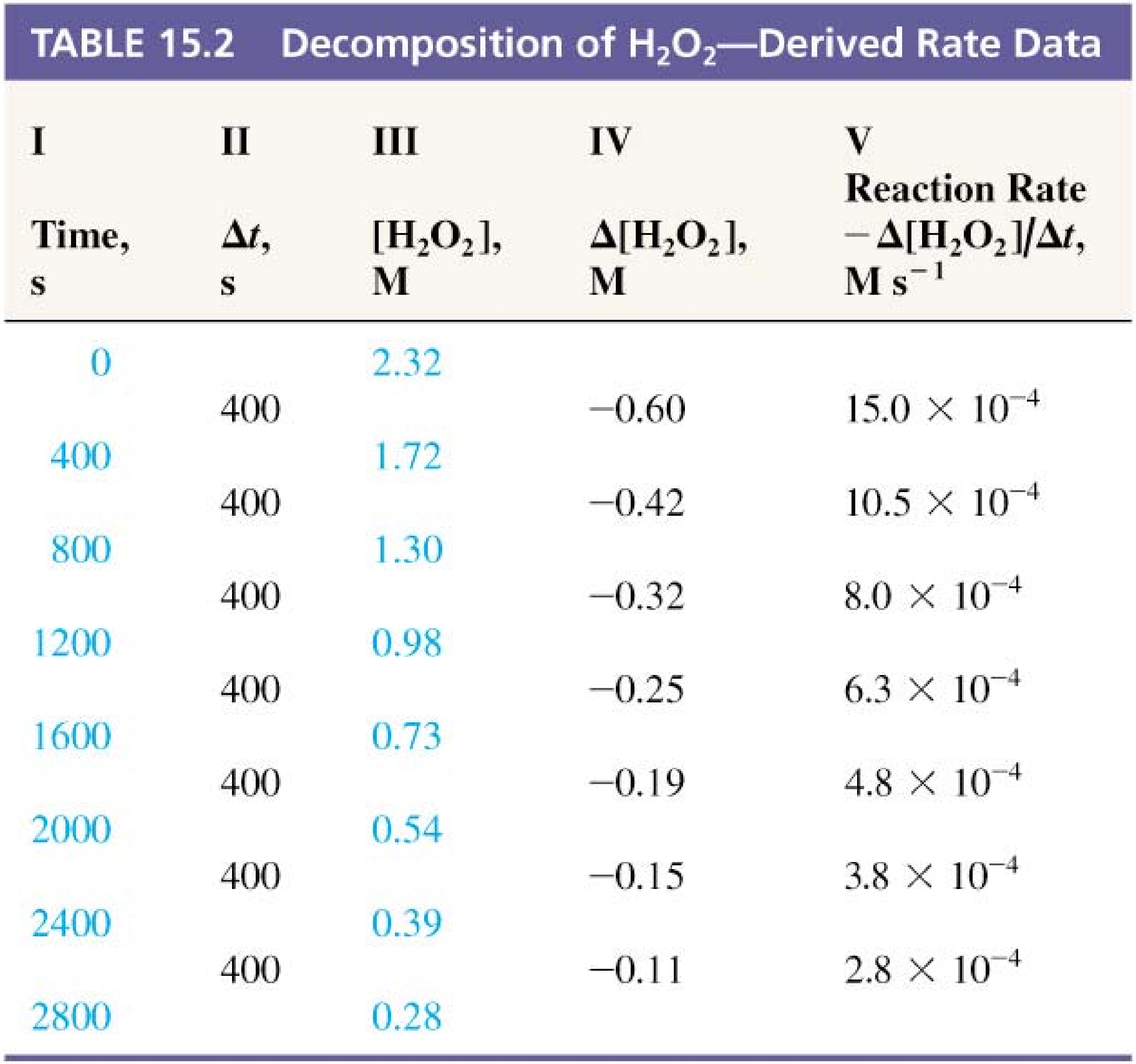
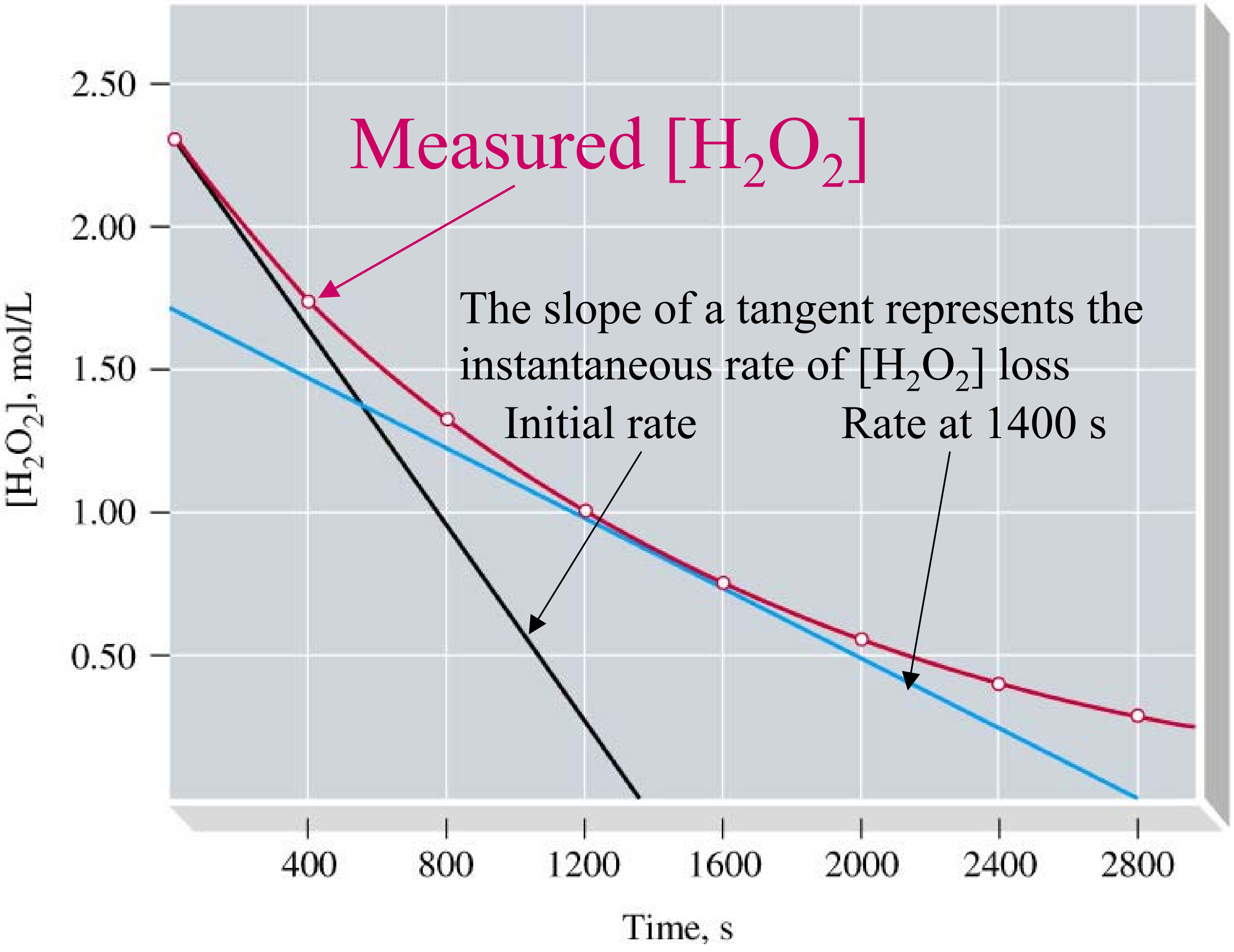


TABLE 15.2 Decomposition of H_2O_2—Derived Rate Data

I Time, s	II Δt, s	III $[H_2O_2]$, M	IV $\Delta[H_2O_2]$, M	V Reaction Rate $-\Delta[H_2O_2]/\Delta t$, $M\ s^{-1}$
0		2.32		
	400		−0.60	15.0×10^{-4}
400		1.72		
	400		−0.42	10.5×10^{-4}
800		1.30		
	400		−0.32	8.0×10^{-4}
1200		0.98		
	400		−0.25	6.3×10^{-4}
1600		0.73		
	400		−0.19	4.8×10^{-4}
2000		0.54		
	400		−0.15	3.8×10^{-4}
2400		0.39		
	400		−0.11	2.8×10^{-4}
2800		0.28		

Same Experimental Data (Plotted)



- rate of reaction decreases as H_2O_2 is consumed

Average and Instantaneous Rates

- Calculating -Δ[H_2O_2]/Δt gives ***average*** rate of reaction over the time interval (e.g. between 1200 and 1600 s average rate of 6.3 × 10^{-4} M s^{-1} approximates the rate at the middle of the interval at about t = 1400 s)
- ***Instantaneous*** rate of reaction is best determined by tangent to the curve (blue line on previous diagram gives rate = 6.1 × 10^{-4} M s^{-1} at t = 1400 s)
- Using "Δt" to calculate rates give accurate values as Δt becomes very small (i.e. as it approaches zero) and Δ[A]/Δt becomes d[A]/dt
- A tangent to the concentration-time curve at t = 0 will provide the ***initial rate of reaction*** *(black line in the previous plot) which is very important in determining reaction orders*

The Rate Law

- One objective of chemical kinetics is to establish a relationship between the rate of reaction and the concentration of the reactants - this relationship is called the **rate law**, or **rate equation**
- For the general reaction, $aA + bB \rightarrow gG + hH$, we can write

$$\boxed{\textbf{rate of reaction} = k[A]^m[B]^n}$$

in which [A] and [B] represent reactant molar concentrations and the exponents **m** and **n** are generally small, positive integers, but may be zero, fractional and/or negative

Note: The product are not involved in the equation since the reaction is not reversible (forward arrow only in the balanced equation).

Differential Kinetic Equation

We have two definitions for the rate of reaction:

Definition 1:

$$\textbf{rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{g}\frac{\Delta[G]}{\Delta t} = \frac{1}{h}\frac{\Delta[H]}{\Delta t}$$

Definition 2: rate of reaction = $k[A]^m[B]^n$

From two definitions: $$\boxed{\frac{d[G]}{dt} = g \times k[A]^m[B]^n}$$

We will understand how to solve such equations later.

The goal of this lecture is to learn how to find “m”, “n” and “k”

The Meaning of m, n and k

Reaction: $aA + bB \rightarrow gG + hH$

rate of reaction = $k[A]^m[B]^n$

- The exponents are called **reaction orders**. We say **the reaction is of *order* m for reactant A**, ***order* n for reactant B, and the overall order of reaction is m + n**.
- The orders are generally ***not*** related to the stoichiometric coefficients in the balanced reaction (i.e. usually m≠a, n≠b). *Example:* the rate of reaction may depend on the concentration of a catalyst when the catalysts is not consumed or produced in the reaction: the reaction order with respect to the catalyst is not equal to 0 while the stoichiometric coefficient of the catalyst is 0
- *k* is a proportionality constant known as the **rate constant** - the faster the reaction, the larger the value for *k* (*k* is also temperature dependent)
- The units for *k* depend upon the order of reaction
- *k* is positive

Establishing the Rate Law means determining m, n, and k

The rate law can only be established by analysing experimental data - two methods will be considered

1) Method of Initial Rates

- At the start of an experiment (t = 0), the initial concentration of the reagents can be known
- A tangent to the concentration-time curve at t = 0 will provide the ***initial rate of reaction***

Based on this we will:

- Measure initial rates for two different concentrations of every reactant keeping concentrations of other reactants constant
- Compare relative rates and initial concentrations to find m, n and k

The simplest example

Reaction: aA → bB

- rate of reaction = $R = k[A]^m$
- Two unknowns: k and m. Two equations are needed to determine 2 unknowns.
- 2 experiments are needed to generate two equations
- Experiment 1: $R_1 = k[A]_1^m$
- Experiment 2: $R_2 = k[A]_2^m$

2 unknowns (“k” and “m”) can be found from 2 equations

- Solve the system for “m” and “k”

Solution, Step 1

- Step 1: To find “m”, exclude “k” from equations by dividing one by another. Instead of 2 equation with 2 unknown we will get 1 equation with 1 unknown:

$$\left.\frac{R_1}{R_2} = \frac{k[A]_1^m}{k[A]_2^m} = \frac{[A]_1^m}{[A]_2^m} = \left(\frac{[A]_1}{[A]_2}\right)^m \quad \right\}$$

1 unknown (m) can be easily found from 1 equations

$$\ln\left(\frac{R_1}{R_2}\right) = \ln\left\{\left(\frac{[A]_1}{[A]_2}\right)^m\right\} = m \times \ln\left(\frac{[A]_1}{[A]_2}\right)$$

$$m = \frac{\ln(R_1 / R_2)}{\ln([A]_1 / [A]_2)}$$

Solution, Step 1

- Step 2: To find “k”, use the rate expression for one of the two sets of experiments (e.g. experiment 1):

$$R_1 = k[A]_1^{\,m}$$

$$k = \frac{R_1}{[A]_1^{\,m}} = \frac{R_1}{[A]_1^{\frac{\ln(R_1/R_2)}{\ln([A]_1/[A]_2)}}}$$

More Complex Example

Reaction: $aA + bB \rightarrow cC + gG$

- rate of reaction = $R = k[A]^m[B]^n$
- 3 experiments are needed for 2 reagents (4 for 3 etc.)

$$\left.\begin{array}{l}\bullet\ \text{Experiment 1: } R_1 = k[A]_1^m[B]_1^n \\ \bullet\ \text{Experiment 2: } R_2 = k[A]_2^m[B]_2^n \\ \bullet\ \text{Experiment 3: } R_3 = k[A]_3^m[B]_3^n\end{array}\right\}$$

3 unknowns (k, m, n) can be found from 3 equations

Solve the system for “m”, “n”, and “k”

Reducing the System of Equations

Step 1: To find “m” and “n”, exclude “k” from equations by dividing pairs of equations one by another. Instead of three equation with three unknown we will get two equations with two unknowns:

$$\left.\begin{aligned}
\frac{R_1}{R_2} &= \frac{k[A]_1^m[B]_1^n}{k[A]_2^m[B]_2^n} = \frac{[A]_1^m[B]_1^n}{[A]_2^m[B]_2^n} = \left(\frac{[A]_1}{[A]_2}\right)^m\left(\frac{[B]_1}{[B]_2}\right)^n \\
\frac{R_2}{R_3} &= \frac{k[A]_2^m[B]_2^n}{k[A]_3^m[B]_3^n} = \frac{[A]_2^m[B]_2^n}{[A]_3^m[B]_3^n} = \left(\frac{[A]_2}{[A]_3}\right)^m\left(\frac{[B]_2}{[B]_3}\right)^n
\end{aligned}\right\}$$

2 unknowns (m, n)
can be found from
2 equations

$$\left.\begin{aligned}
\ln\left(\frac{R_1}{R_2}\right) &= \ln\left\{\left(\frac{[A]_1}{[A]_2}\right)^m\left(\frac{[B]_1}{[B]_2}\right)^n\right\} = m\times\ln\left(\frac{[A]_1}{[A]_2}\right) + n\times\ln\left(\frac{[B]_1}{[B]_2}\right) \\
\ln\left(\frac{R_2}{R_3}\right) &= \ln\left\{\left(\frac{[A]_2}{[A]_3}\right)^m\left(\frac{[B]_2}{[B]_3}\right)^n\right\} = m\times\ln\left(\frac{[A]_2}{[A]_3}\right) + n\times\ln\left(\frac{[B]_2}{[B]_3}\right)
\end{aligned}\right\}$$

Finding "m" and "n"

Solve the 1st equation for "m" and the 2nd for n:

$$m = \frac{\ln(R_1/R_2) - n \times \ln([B]_1/[B]_2)}{\ln([A]_1/[A]_2)}$$

$$n = \frac{\ln(R_2/R_3) - m \times \ln([A]_2/[A]_3)}{\ln([B]_2/[B]_3)}$$

Plug the 1st expression into the 2nd:

$$n = \frac{\ln(R_2/R_3) - \dfrac{\ln(R_1/R_2) - n \times \ln([B]_1/[B]_2)}{\ln([A]_1/[A]_2)} \times \ln([A]_2/[A]_3)}{\ln([B]_2/[B]_3)}$$

Solve it for n (ask students to solve) and plug it into

Example: Method of Initial Rates

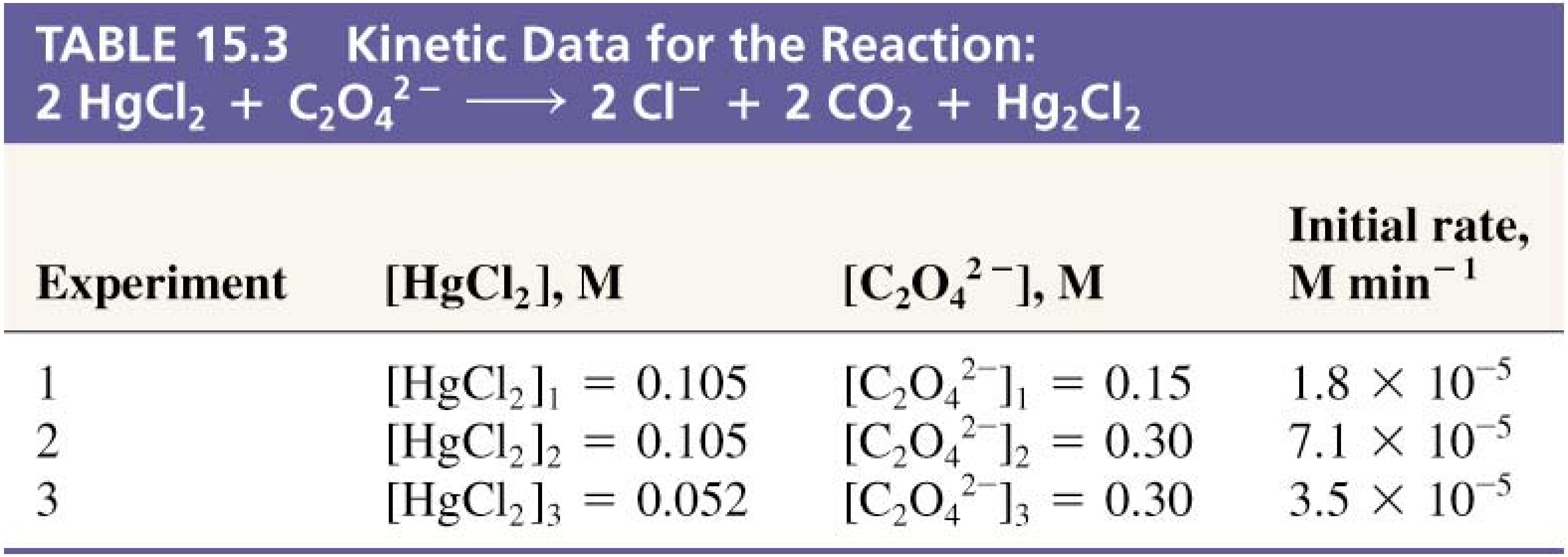


TABLE 15.3 Kinetic Data for the Reaction:
$2\,HgCl_2 + C_2O_4^{2-} \longrightarrow 2\,Cl^- + 2\,CO_2 + Hg_2Cl_2$

Experiment	$[HgCl_2]$, M	$[C_2O_4^{2-}]$, M	Initial rate, M min^{-1}
1	$[HgCl_2]_1 = 0.105$	$[C_2O_4^{2-}]_1 = 0.15$	1.8×10^{-5}
2	$[HgCl_2]_2 = 0.105$	$[C_2O_4^{2-}]_2 = 0.30$	7.1×10^{-5}
3	$[HgCl_2]_3 = 0.052$	$[C_2O_4^{2-}]_3 = 0.30$	3.5×10^{-5}

$$\text{rate of reaction} = k[HgCl_2]^m[C_2O_4^{2-}]^n$$

- consider experiments 2 & 3

  $[HgCl_2]$ approximately doubles, $[C_2O_4^{2-}]$ remains constant, and the initial rate doubles (approximately)

(from common sense $m = 1$)

Determination of “m”

We need to calculate Relative Rates and Relative Initial Concentration

From the rate law:

$$\frac{R_2}{R_3} = \frac{k(0.105)^m(0.3)^n}{k(0.052)^m(0.3)^n} = \left(\frac{0.105}{0.052}\right)^m = 2.0^m$$

From the initial rates:

$$\frac{R_2}{R_3} = \frac{7.1\times10^{-5}}{3.5\times10^{-5}} = 2.0$$

$2 = 2^m$, therefore **$m = 1$**

Determination of "n"

- still need to determine n, order of reaction for $[C_2O_4^{2-}]$
- consider experiments 1 & 2

  $[HgCl_2]$ remains constant, $[C_2O_4^{2-}]$ doubles, while the rate increased by a factor of ~4 (from common sense n = 2)

From the rate law

$$\frac{R_2}{R_1} = \frac{k(0.105)(0.30)^n}{k(0.105)(0.15)^n} = 2.0^n = \frac{7.1 \text{ X } 10^{-5}}{1.8 \text{ X } 10^{-5}} = 3.94$$

$2^n \approx 4$, $n = 2$ (by inspection)

or, take logs of both sides of the equation

$n \log(2.0) = \log(3.94)$

$n\,(0.30) = 0.595$, $\mathbf{n = 1.99 \approx 2}$

Determination of "k"

- The rate law thus far is

$$\text{rate of reaction} = k[HgCl_2][C_2O_4^{2-}]^2$$

- still need to determine the rate constant, k
- use data from any one of the experiments

$$k = \text{initial rate}/\{[HgCl_2][C_2O_4^{2-}]^2\}$$

in which concentrations are initial values, and solve for k:

k = 7.5 x 10^{-3} M^{-2} min^{-1} (from exp. 2)

- therefore **rate law** is

$$\mathbf{rate\ of\ reaction = 7.5 \times 10^{-3}\ [HgCl_2][C_2O_4^{2-}]^2}$$

(rate of reaction will be expressed in M min^{-1})

Units of the Rate Constant Depend on the Order of Reaction

Order of Reaction	Units of Rate Constant
0	$[\ ]\ \text{time}^{-1}$
1	time^{-1}
2	$[\ ]^{-1}\ \text{time}^{-1}$
3	$[\ ]^{-2}\ \text{time}^{-1}$

“[ ]” represents concentration, usually M, or mol L^{-1}

“time” represents s, min, h, etc.

What we learned up to this point

1. Definition 1:

$$\textbf{rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{g}\frac{\Delta[G]}{\Delta t} = \frac{1}{h}\frac{\Delta[H]}{\Delta t}$$

2. Definition 2:

   rate of reaction = $k[A]^m[B]^n$

3. Method of initial rates
4. Differential kinetic equation was obtained from the two definitions:

$$\boxed{\frac{d[A]}{dt} = -a \times k[A]^m[B]^n}$$

- The next goal is to understand how to solve such an equation for simple reaction aA → products

2) Method of Integrated Rate Laws

- The “Method of Initial Rate” uses data from the initial portion of multiple experiments
- The “Method of Integrated Rate Laws” uses the full concentration-time curve from one experiment
- The **integrated rate equation** relates concentration and time for a given order of reaction [A] = F(t). To find this function we will be integrating the differential kinetic equation (e.g. $d[A]/dt = -ak\,[A]^m[B]^n$)
- It can also be used to calculate the **half-life**, $\mathbf{t_{½}}$, of a reactant which is the time it takes for half of that reactant to be converted into product (constant for First-Order reactions only)

We Will Consider Three Types of Simple Reactions Whose Rates Depend on the Concentration of a Single Reactant Only

For the general reaction **aA → products** we can write

$$\textbf{rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = k[A]^n$$

in which “**n**” is the order of the reaction for the reactant “**A**”

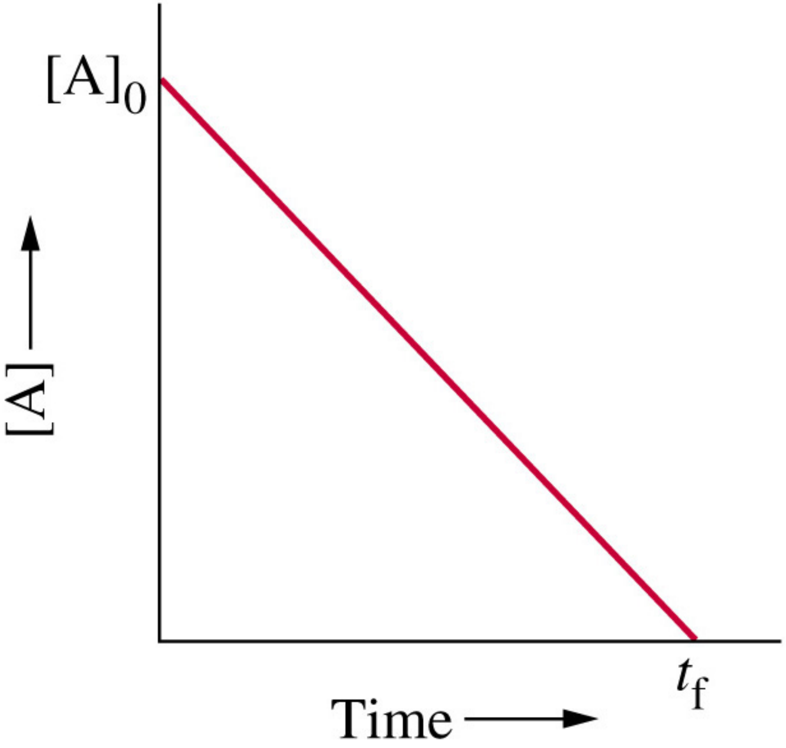
- the integration of this expression for different values of “n” gives the “integrated rate laws”

Note: Petrucci, Harwood & Herring do not include the “a” term but this approach is more general

Zero-Order Reactions: n = 0

rate of reaction $= \boxed{-\frac{1}{a}\frac{d[A]}{dt} = k[A]^0}$

$$-\frac{1}{a}\frac{d[A]}{dt} = k \quad \rightarrow \quad d[A] = -akdt \quad \rightarrow \quad [A] = [A]_0 - akt$$



Expression $[A] = [A]_0 - akt$

is called the integrated rate law for zero-order reactions

concentration-time graph is a straight line with a negative slope

rate of reaction = $k[A]^0$ = k = constant

Half-Life for Zero-Order Reactions

Integrated rate law for zero-order reactions:

$$[A] = [A]_0 - ak\mathit{t}$$

Definition: half-life, $\mathbf{t_{1/2}}$, is time required for the concentration of the reactant A to decrease to half its initial value

$A(t_{1/2}) = A_0/2$ by definition

$A(t_{1/2}) = A_0 - akt_{1/2}$ from the integrated rate law

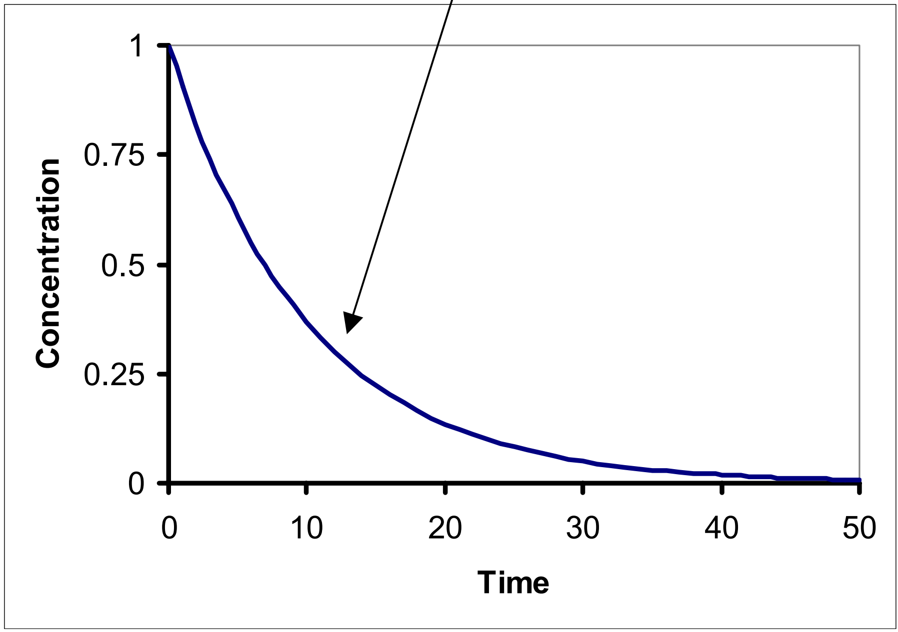
$A_0/2 = A_0 - akt_{1/2} \quad \rightarrow \quad \mathbf{t_{½} = [A]_0/2ak}$

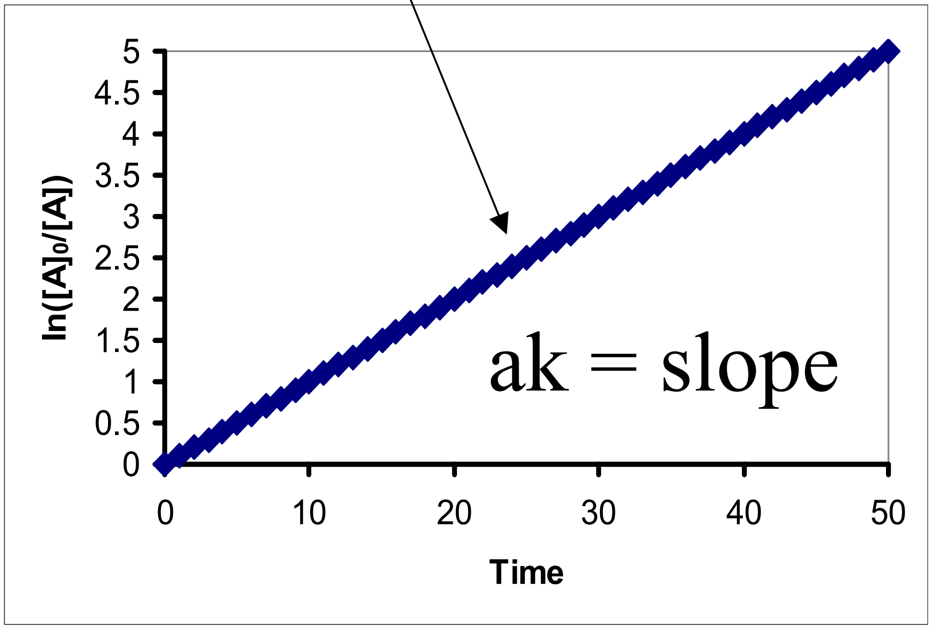
First-Order Reactions: n = 1

$$\text{rate of reaction} = \boxed{-\frac{1}{a}\frac{d[A]}{dt} = k[A]^1}$$

By integration of the differential equation we get integrated rate law: $\mathbf{[A] = [A]_0 e^{-akt}}$ (exponential decay)

Sometimes it is represented as $\ln[A]_0/[A] = akt$ to get a straight line





Half-Life for First-Order Reactions

- Integrated rate law in this form $$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]} = \mathrm{ak}t$$

can be used for easy calculation of half-life

From the integrated rate law: $$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]_{t_{1/2}}} = \mathrm{ak}t_{1/2}$$

From definition of $t_{1/2}$: $$\frac{[\mathrm{A}]_0}{[\mathrm{A}]_{t_{1/2}}} = \frac{[\mathrm{A}]_0}{[\mathrm{A}]/2} = 2 \quad \Rightarrow \ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]_{t_{1/2}}} = \ln 2$$

- $\mathrm{ak}t_{1/2} = \ln 2 \quad \Rightarrow \quad \mathbf{t_{1/2} = \ln 2/ak = 0.693/ak}$

$t_{½}$ is independent of $[\mathrm{A}]_0$ (it is constant for a first-order reaction)

What is the precision of 2 in ln2?

Examples of First-Order Reactions (mostly decays)

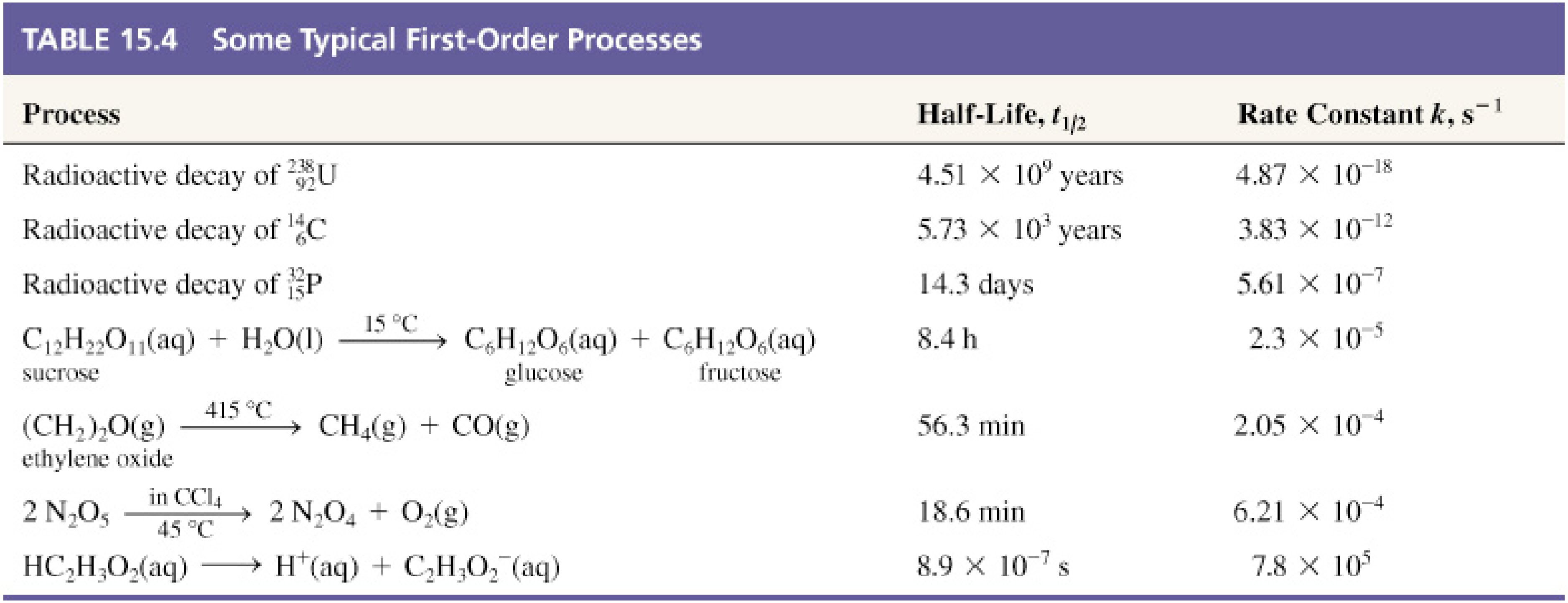


TABLE 15.4 Some Typical First-Order Processes

Process	Half-Life, $t_{1/2}$	Rate Constant k, s^{-1}
Radioactive decay of $^{238}_{92}U$	4.51×10^9 years	4.87×10^{-18}
Radioactive decay of $^{14}_{6}C$	5.73×10^3 years	3.83×10^{-12}
Radioactive decay of $^{32}_{15}P$	14.3 days	5.61×10^{-7}
$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{15\,^\circ C} \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{fructose}}{C_6H_{12}O_6(aq)}$	8.4 h	2.3×10^{-5}
$\underset{\text{ethylene oxide}}{(CH_2)_2O(g)} \xrightarrow{415\,^\circ C} CH_4(g) + CO(g)$	56.3 min	2.05×10^{-4}
$2\ N_2O_5 \xrightarrow[45\,^\circ C]{\text{in } CCl_4} 2\ N_2O_4 + O_2(g)$	18.6 min	6.21×10^{-4}
$HC_2H_3O_2(aq) \longrightarrow H^+(aq) + C_2H_3O_2^-(aq)$	8.9×10^{-7} s	7.8×10^5

The Goal of Kinetics

$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} P$ To find $\mathbf{[P] = F(t, [A]_0, [B]_0, [P]_0)}$

1. Study the chemical reaction and balance the equation
2. Write the rate law **Rate of reaction** $= k_1[A]^m[B]^n - k_2[P]^p$
3. Find k1, k2, m, n, and p using either the initial rates method or the method of integrated rate laws
4. Solve the differential kinetic equation:

$$d[P]/dt = k_1[A]^m[B]^n - k_2[P]^p$$

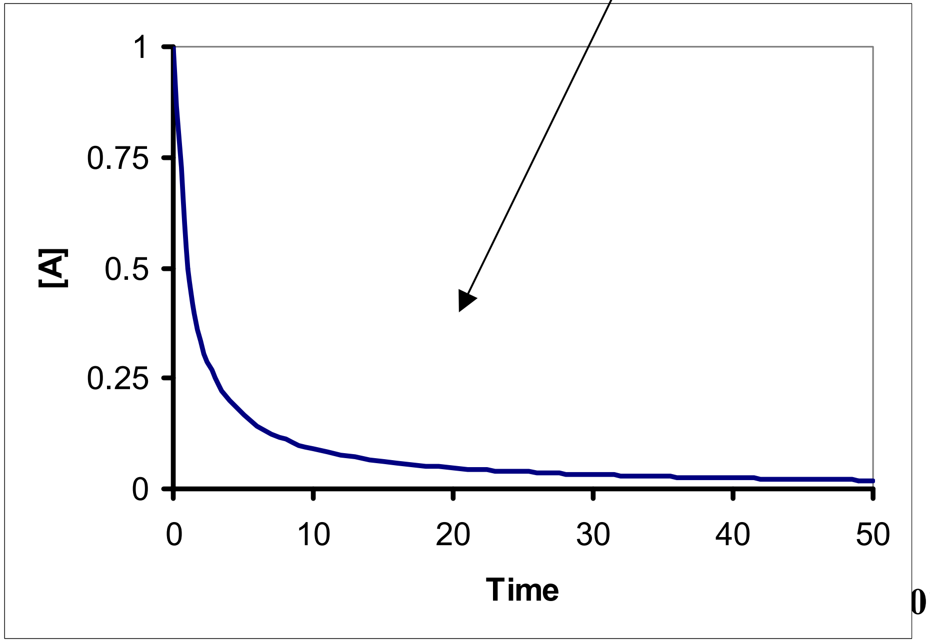
Its solution will be: $\mathbf{[P] = F(t, [A]_0, [B]_0, [P]_0)}$

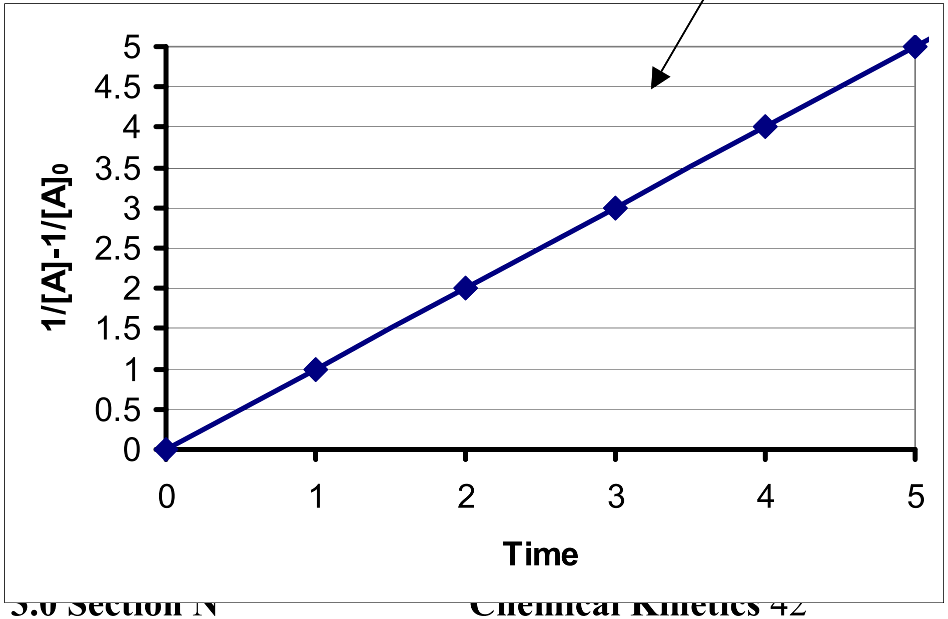
Second-Order Reactions: n = 2

$$\textbf{rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = k[A]^2$$

Integrated rate law: $[A] = \dfrac{[A]_0}{[A]_0 akt + 1}$

Integrated rate law in linearised form: $\dfrac{1}{[A]} - \dfrac{1}{[A]_0} = akt$





Half-Life for Second-Order Reactions

From the integrated rate law : $\frac{1}{[\mathrm{A}]_{t_{1/2}}} - \frac{1}{[\mathrm{A}]_0} = \mathrm{akt}_{1/2}$

From the definition of $\mathrm{t}_{1/2}$: $\frac{1}{[\mathrm{A}]_{t_{1/2}}} - \frac{1}{[\mathrm{A}]_0} = \frac{1}{[\mathrm{A}]_0}$

$$\mathrm{akt}_{1/2} = \frac{1}{[\mathrm{A}]_0} \longrightarrow \mathbf{t_{½} = \frac{1}{ak[A]_0}}$$

- $\mathrm{t}_{1/2}$ is not constant for second-order reactions

Method of Integrated Rate Laws – Comparing Different Reaction Orders

How can we use these integrated rate law equations to solve for reaction order? …make the appropriate plot!

	Order		
	Zero	***First***	***Second***
Plot	[A] vs. t	ln[A] vs. t	1/[A] vs. t
Slope	-ak	-ak	ak
Intercept	$[A]_0$	ln $[A]_0$	$1/[A]_0$

- or test for the consistency of the half-life

(***Note:*** only a first-order reaction has a constant $t_{1/2}$)

Integrated Rate Laws - more than one reactant

- so far we only considered integrated rate laws for simple reactions with only one reactant - how can we analyse reactions with more than one reactant?
- Consider the following rate law

$$\text{rate of reaction} = k[A]^m[B]^n$$

- control the experiment so that [A] » [B]
- very little "A" will be consumed so $[A] \approx [A]_0$ and rate law becomes

$$\text{rate of reaction} = k[A]_0^m[B]^n = k'[B]^n$$

- allows dependence on "B" to be isolated from dependence on "A"

Ex: More Than One Reactant

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(l) + 3H_2O(l)$

has the rate law

$$\text{Rate} = k[BrO_3^-][Br^-][H^+]^2$$

if $[Br^-]_0$=**1.0 M**, $[H^+]_0$=**1.0 M**, & $[BrO_3^-]_0$= 1.0×10^{-3} M,

then both $[Br^-]$ and $[H^+]$ » $[BrO_3^-]$ and relatively little of them will be consumed; rate law can be written as

$$\text{Rate} = k[Br^-]_0[H^+]_0^2\,[BrO_3^-] = k'[BrO_3^-]$$

where $k' = k[Br^-]_0[H^+]_0^2 \approx$ const

- a plot of $\ln[BrO_3^-]$ versus t would be a straight line with slope of k' (**pseudo-first-order reaction**)

Finding k' immediately allows to find k: $k = k'/[Br^-]_0[H^+]_0^2$

Theoretical Models for Chemical Kinetics - Introduction

- So far we’ve been busy with establishing rate laws
Rate = $k[A]^m[B]^n$

- We learned how to calculate rate constants, k, and reaction orders, m and n, based on experimental measurements of a single macroscopic parameter, concentration, as a function of time.

- We still do not know what k, n, and m depend on

- **Goal of today’s lecture is to understand what *k* depends on**

Two Important Facts to Be Explained

- **1) Experimental fact: Reaction rate, *k*, increases with temperature**
- **2) Only 1 of 10^{10} collisions leads to a reaction:**

To react molecules have to meet (collide). The ***collision frequency*** is typically 10^{30} collisions per second for molecules in gas phase

If each collision yielded a product molecule, the rate of reaction would be about 10^{6} M s^{-1}

Gas-phase reactions generally have a rate of reaction around only 10^{-4} M s^{-1}

Theoretical Models for Chemical Kinetics

Such models explain what reaction rates, k, depend on

1. Collision Theory

- In order for two molecules to react, old chemical bonds have to be broken. That requires energy!

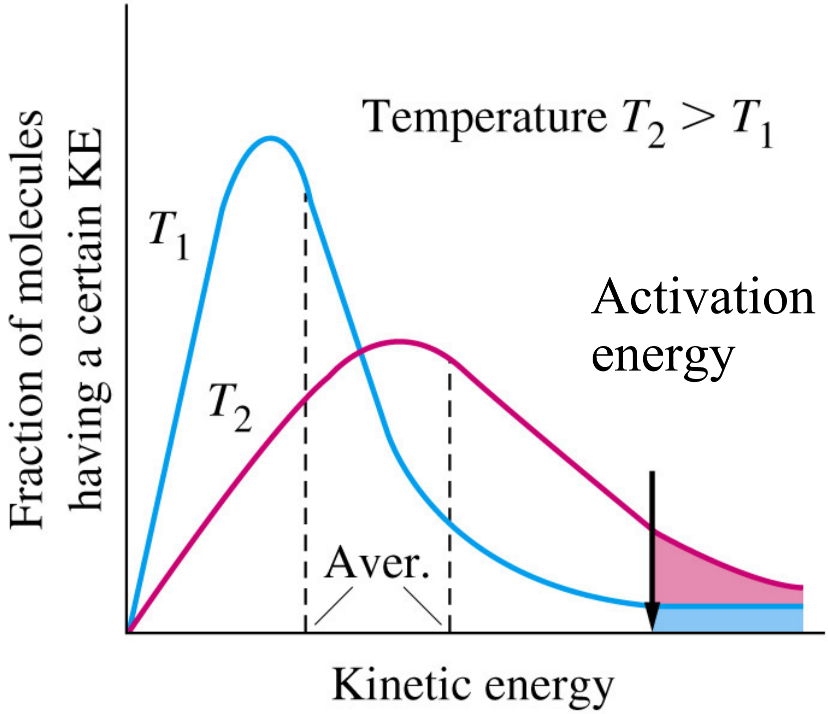
- *Collision theory considers that such energy is provided by kinetic energies of molecules upon their collisions.*

- Collision theory can qualitatively explain: 1) why the reaction rate, *k*, increases with increasing temperature and 2) why only 1 of 10^{10} collisions results in reaction

Collision Theory Considers Distribution of Kinetic Energies of Molecules

- If the minimum energy required for a reaction to occur (activation energy) is indicated by the arrow in the accompanying figure, then the fraction of molecules possessing this energy will be greater at T_2 than at T_1

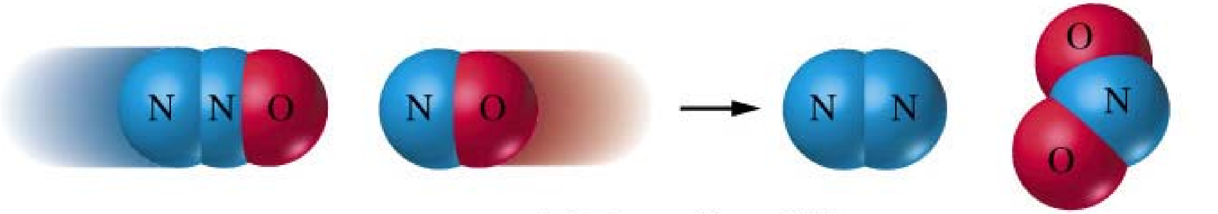
- Regardless of T, the fraction of molecules possessing enough energy will be small and thus the rate of reaction will be much less than the collision frequency



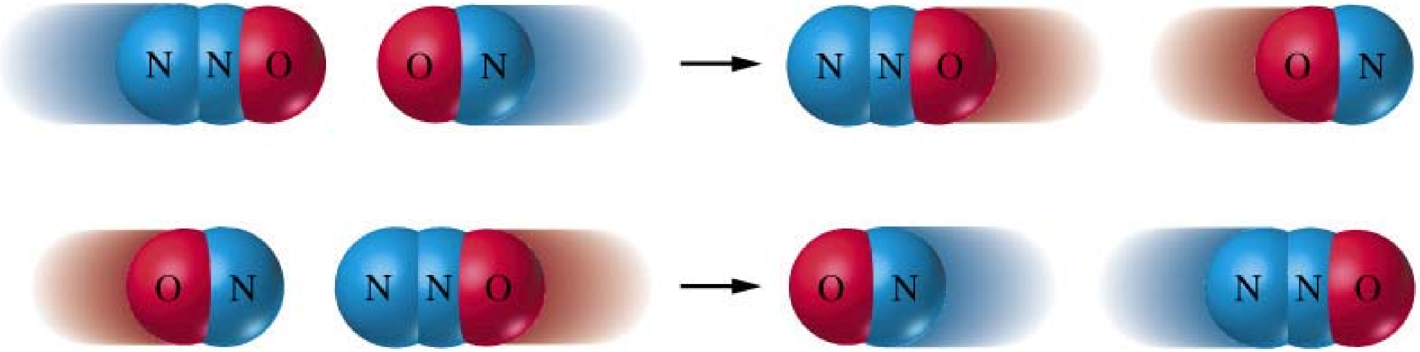
Collision Theory – Importance of Orientation of Molecules

- rate of reaction is also be limited by the orientation of molecules at the time of their collision

Example: $N_2O(g) + NO(g) \rightarrow N_2(g) + NO_2(g)$



(a) Favorable collision

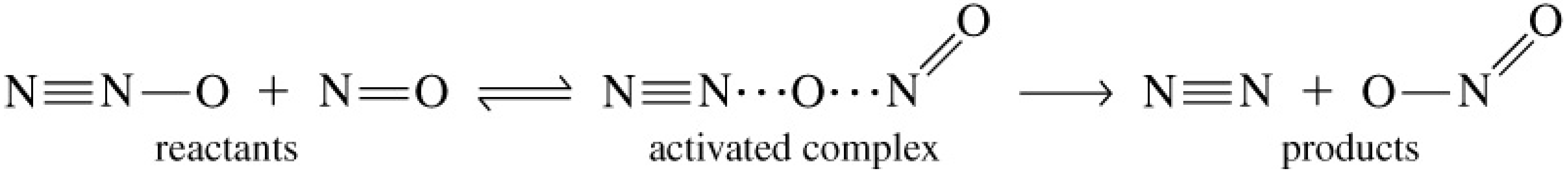


(b) Unfavorable collisions

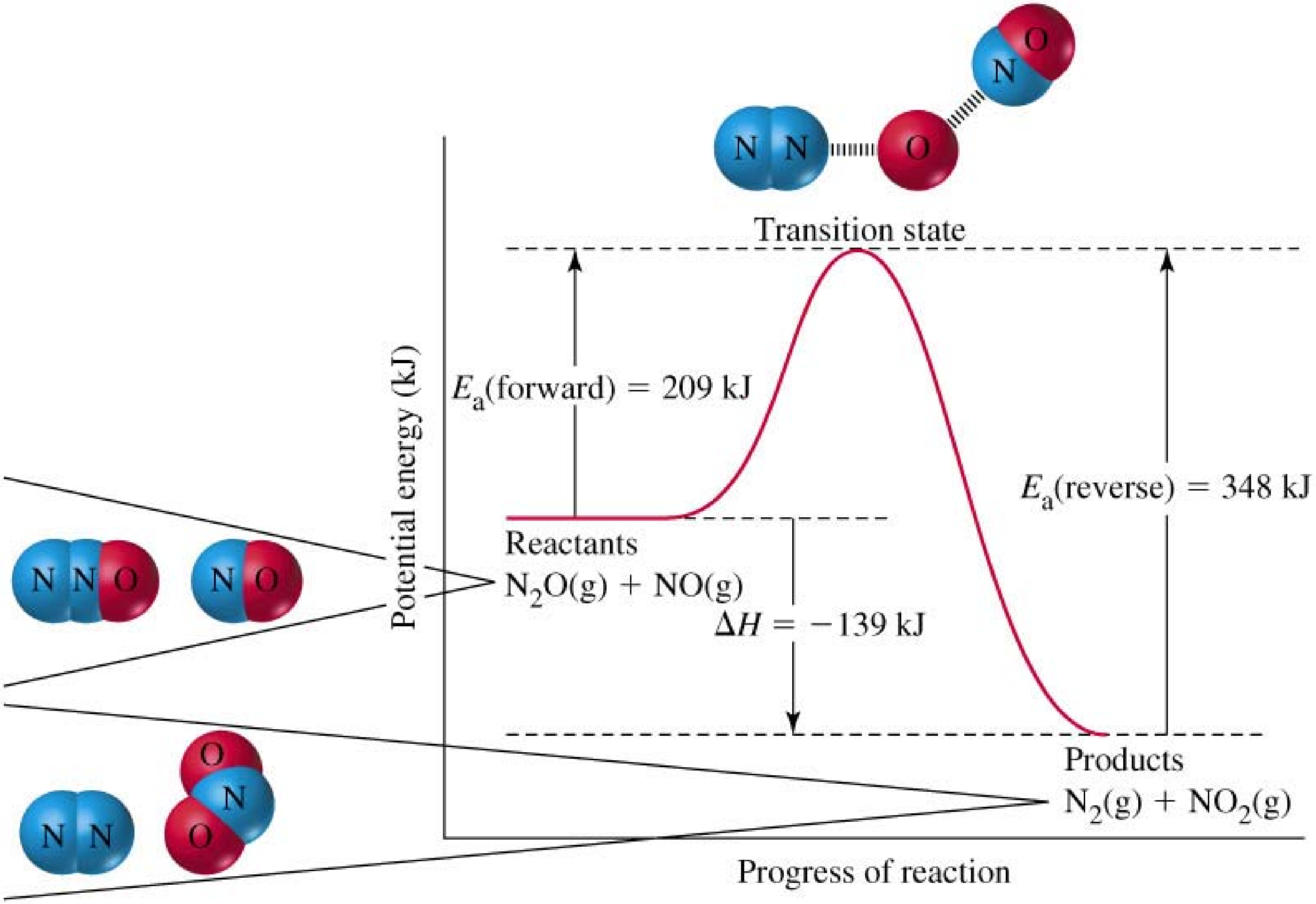
2. Transition State Theory

- An unobserved, **activated complex** is proposed to exist as a transition state between reactants and products
- The activated complex is short-lived because it is highly reactive (may break apart to form products or revert to reactants)

Example: $N_2O(g) + NO(g) \rightarrow N_2(g) + NO_2(g)$



Reaction Profile



The enthalpy change for the reaction is the difference in the activation energies of the forward and reverse reaction

Collision Theory vs Transition State Theory

- Very similar
- Using slightly different considerations both theories explain 1) why k depends on T and 2) why k may be very low
- Both can be used to get a very important formula for the dependence of k on T.

Effect of Temperature on Reaction Rates

- Experimental observation: Rate of a reaction generally increases with temperature (roughly doubles every 10 ºC)
- Arrehenius expression illustrates this for rate constants

$$k = A\mathrm{e}^{-E_a/RT}$$

or, taking logarithms,

$$\ln k = -\frac{E_a}{RT} + \ln A$$

E_a is the activation energy (J/mol) and *A* is the frequency or pre-exponential factor (same units as *k*)

The Meaning of "A" and "E_a"

A - (frequency of collisions or pre-exponential factor)

factor related to the collision frequency of a molecule; represents the limit to how fast two molecules can react (molecules cannot react unless they have enough energy)

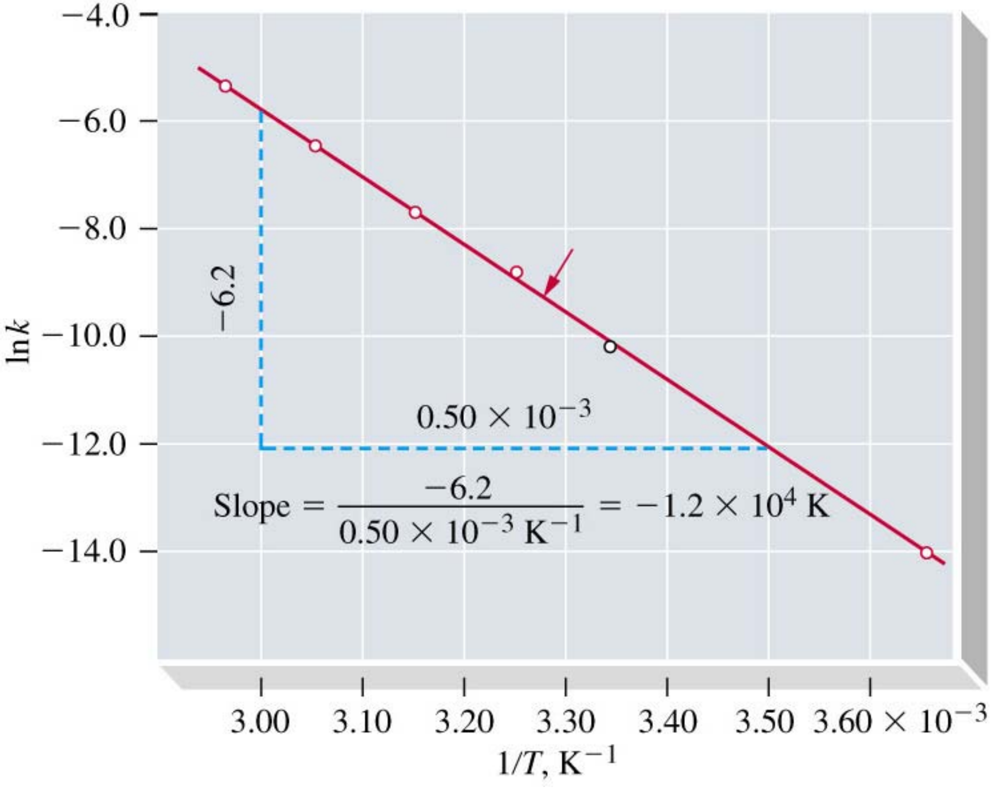
E_a - (activation energy)

even when molecules collide they cannot react unless they possess enough energy; E_a is the minimum energy the reactants must possess in order to react

Finding Ea from the Arrehenius Eq-n

$$\ln k = -\frac{E_a}{RT} + \ln A$$

A plot of ln k versus 1/T will yield a straight line with a slope of $-E_a/R$ (studied in first lab for this course)



Temperature Effects - Arrehenius equation

the Arrehenius equation can relate rate constants at two temperatures

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

(temperature in Kelvin and R in standard SI units)

It allows finding E_a by measuring k at two different T

Or it allows finding k for any T if E_a is known and k for one specific T is known

Next question: the nature of reaction orders

- We understood what k depends on.
- The next goal is to understand what reaction orders depend on

$$\text{rate of reaction} = k[A]^{m}[B]^{n}$$

Reaction Mechanisms

- Most reactions will not proceed in a single step
- The step-by-step pathway by which a reaction occurs is called the **reaction mechanism**
- A plausible reaction mechanism must be consistent with the:

  1) stoichiometry of the overall reaction

  2) experimentally determined rate law
- Each step in the mechanism is called an **elementary reaction (or process)**

Characteristics of Elementary Reactions

- Elementary processes are either **unimolecular** (a single molecule dissociates) or **bimolecular** (two molecules collide); termolecular reactions (simultaneous collision of three molecules) are rare
- Orders of reaction in the rate law for the elementary reaction are the same as the stoichiometric coefficients in the balanced equation for the process - ***not*** true for the overall rate law and the overall balanced equation
- Elementary processes can be reversible reactions; sometimes rates of forward and reverse reactions are equal (we say that the two reactions are et equilibrium)

Characteristics of Elementary Reactions

- **Intermediate species** can be produced in an elementary reaction which do not appear in either the overall chemical reaction or the overall rate law; such species produced by one elementary reaction must be consumed by another
- Sometimes the rate of the overall reaction depends on a single elementary step (a single rate constant); such a step is called the **rate-determining step**. Often the reaction mechanism does not have a rate determining step, that is the rate of the overall reaction depends on more than 1 step (more than 1 rate constant)

Intermediate Species in Elementary Processes

1. **Intermediate species (I)** can be produced in an elementary reaction. They do not appear in either the overall chemical reaction or the overall rate law; such species produced by one elementary reaction must be consumed by another.
2. **An intermediate is a highly reactive species (often free radicals);** its production is usually slower than that of its consumption
3. **Due to its high reactivity an intermediate very rapidly reaches its "steady-state" concentration** which is much lower than the concentrations of reactants and products during the steady-state period: $[I]_{ss} << [A]_{ss}, [B]_{ss}, [C]_{ss}$, …It may be hard to observe intermediates experimentally.
4. **The last allows us to use so-called steady-state approximation**

Steady state of reaction

Reaction

$$aA + bB \rightarrow gG + hH$$

is in the steady state if the rates of loss of all reactants and the rates of production of all products which appear in the balanced reaction equation are equal:

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{g}\frac{d[G]}{dt} = \frac{1}{h}\frac{d[H]}{dt}$$

In the other words it means that intermediates are present at very low concentrations and the rates of their productions and loss are equal

The consequence of $[\mathrm{I}]_{ss} << [\mathrm{A}]_{ss}, [\mathrm{B}]_{ss}, [\mathrm{C}]_{ss}$ is

$$\left(\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}\right)_{\mathrm{prod}} = -\left(\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}\right)_{\mathrm{cons}}$$

Indeed, lets consider the overall reaction A + B + C → D

Possible reaction mechanism

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{I} \qquad \left(\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}\right)_{\mathrm{prod}} = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_1[\mathrm{A}][\mathrm{B}]$$

$$\mathrm{I} + \mathrm{C} \xrightarrow{k_2} \mathrm{D} \qquad \left(\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}\right)_{\mathrm{cons}} = -\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = -k_2[\mathrm{I}][\mathrm{B}]$$

$$[\mathbf{I}]_{ss} << [\mathbf{A}]_{ss}, [\mathbf{B}]_{ss}, [\mathbf{C}]_{ss}, [\mathbf{D}]_{ss} \Rightarrow \left|\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}\right| = \left|\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}\right| = \left|\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t}\right| \approx \left|\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t}\right|$$

$$\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = \left(\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}\right)_{\mathrm{prod}} + \underbrace{\left(\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}\right)_{\mathrm{cons}}}_{\text{Negative}} = \left|\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}\right| - \left|\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t}\right| \approx 0 \quad \Longrightarrow \quad \left(\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}\right)_{prod} = -\left(\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}\right)_{cons}$$

Steady-State Approximation

- The assumption that

$(d[I]/dt)_{prod} = - (d[I]/dt)_{cons}$

is called **steady-state approximation**.

- The steady-state approximation is the most common approach to the analysis of Reaction Mechanisms.
- In the steady state the rate of all elementary processes are equal (find the way to prove it).

General Approach to the Analysis of *Simple* Reaction Mechanisms Using the Steady-State Approximation

- 1. Check the proposed mechanism for agreement with experimentally found balanced chemical equation
- 2. Write the expression for the reaction rate using the last elementary process in the reaction mechanism, which does not produce intermediates at the right-hand side. It there is a reverse process for this step, include it in the reaction rate.
- 3. Determine the steady state concentration of the intermediate using $(d[I]/dt)_{prod} = - (d[I]/dt)_{cons}$ as a function of the concentrations of reagents
- 4. Substitute [I] in the reaction rate found in 2) with [I] determined in 3. Compare the theoretical and experimental rates of reaction.

Check the proposed mechanism for agreement with experimental rate law

Examples of Steady-State Approximation

Example 1

We know from the experiment that:

1) $A + 2B \rightarrow C$ and

2) Experimental rate of reaction = $k[A][B]$

Q: Is the following proposed mechanism plausible:

(1) $A + B \xrightarrow{k1} I$

(2) $I + B \xrightarrow{k2} C$

1. Examine whether the proposed mechanism satisfies the balanced chemical equation

- *Experiment:* $A + 2B \xrightarrow{k} C$

- *Mechanism:* $A + B \xrightarrow{k1} I$

  $I + B \xrightarrow{k2} C$

- *Overall:* $A + B + \cancel{I} + B \xrightarrow{k} \cancel{I} + C$

  $A + 2B \xrightarrow{k} C$

- <u>Thus, the proposed mechanism satisfies the balanced chemical equation</u>

2. Write the expression for the reaction rate using the last elementary process in the reaction mechanism.

The rate of the second reaction is:

$$\mathbf{Rate} = \boldsymbol{k_2}\mathbf{[I][B]}$$

The concentration of the intermediate has to be eliminated

3. Determine the steady state concentration of the intermediate using the steady-state approximation:

$$(d[I]/dt)_{prod} = -\ (d[I]/dt)_{cons}$$

$$k_1[A][B] = -\ (-k_2[I][B])$$

$$k_1[A][B] = k_2[I][B]$$

$$\mathbf{[I] = k_1[A]\cancel{[B]}/k_2\cancel{[B]} = k_1[A]/k_2}$$

4. Substitute [I] in the reaction rate with [I] determined using steady-state approximation. Compare the theoretical and experimental rates of reaction.

$$\textbf{Rate} = k_2[\mathrm{I}][\mathrm{B}]$$

$$[\mathrm{I}] = k_1[\mathrm{A}]/k_2$$

$$\mathrm{Rate} = k_1[\mathrm{A}][\mathrm{B}]$$

It is the same as the experimental rate so that the proposed mechanism is plausible

- **NOTE: The rate of the overall reaction does not depend on k_2 and depends only on k_1. In such a case the first reaction is called a rate-determining step.**

Rate-Determining Step is a Slow Reaction

- Rate determining elementary *process* is a bottle-neck in the overall process. It is often called a rate-determining *step*
- In general, finding whether or not there is a rate-determining step requires the analysis that we have just done.
- Note: In the previous example the steady-state approximation **requires** that the intermediate-producing reaction is a rate-determining step and that the second process must be fast:

$$A + B \xrightarrow{k1} I$$

$$I + B \xrightarrow{k2} C$$

- Note also that the rates of the two elementary processes are identical, which ensures that I does not accumulate

Distinguish Reaction Intermediates And Transition States (Activated Complexes)

$$A + B \xrightarrow{k1} I$$

$$I + B \xrightarrow{k2} C$$

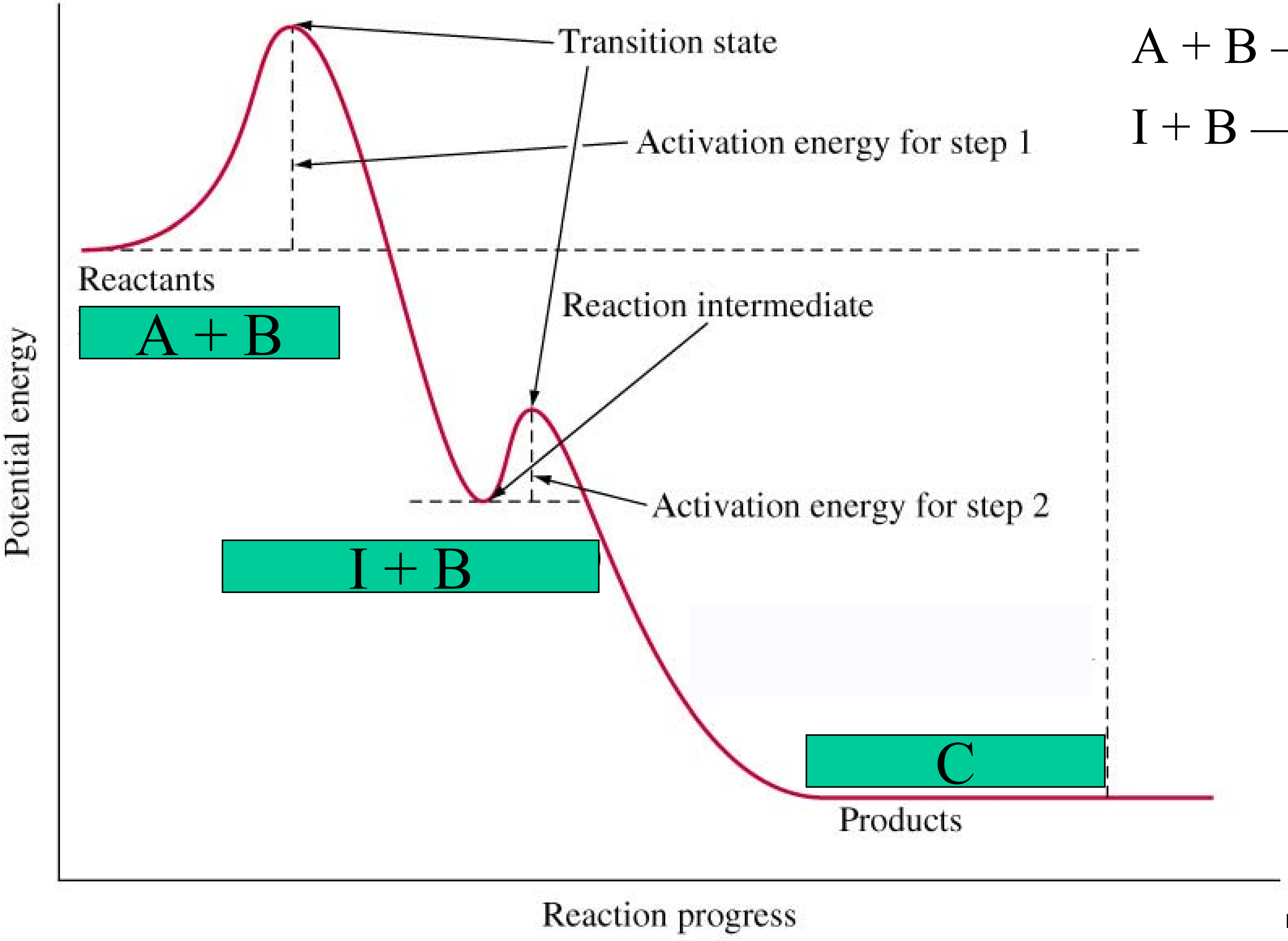


Illustration of a two-step mechanism

$H_2(g) + 2\ ICl(g) \rightarrow I_2(g) + 2\ HCl(g)$

rate of reaction = $k[H_2][ICl]$ (from experiment)

Let's propose the following mechanism:

(1) $H_2 + ICl \rightarrow HI + \cancel{HCl}$ (*rate-determining)*

(2) $HI + \cancel{ICl} \rightarrow I_2 + HCl$

Overall: $H_2 + 2\ ICl \rightarrow I_2 + 2\ HCl$

Note: sum of steps in mechanism yields the correct overall reaction

Example of two-step mechanism continued

- each step in the mechanism is an elementary step (also bimolecular in this example) and rate law can be written directly

$$\text{rate of } (1) = k_1[\mathrm{H_2}][\mathrm{ICl}]$$

$$\text{rate of } (2) = k_2[\mathrm{HI}][\mathrm{ICl}]$$

- step *(1)* was assumed to be slow relative to step *(2)* (i.e. step *(1)* is the **rate-determining step**) so the overall reaction rate is linked to the rate of step *(1)*
- recall, from experiment,

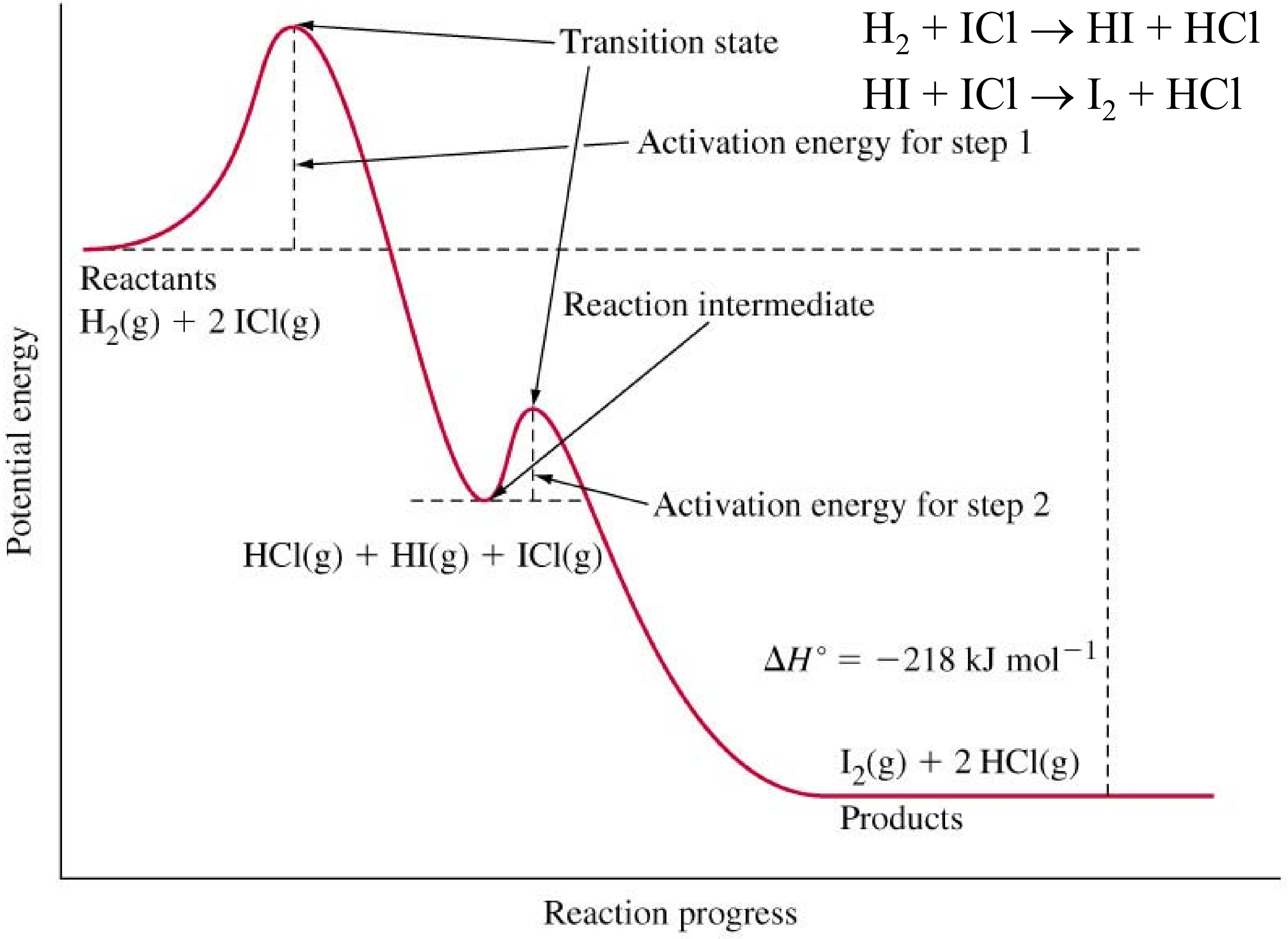
$$\text{rate of reaction} = k[\mathrm{H_2}][\mathrm{ICl}]$$

- proposed mechanism is plausible

Slow Step - Fast Step Mechanism Example continued

$$H_2 + ICl \rightarrow HI + HCl$$

$$HI + ICl \rightarrow I_2 + HCl$$



Reaction Mechanism with a Reversible Reaction

Example 2

Experiment:

$2\,A + B \xrightarrow{k} 2\,C$

rate of reaction = $k[A]^2[B]$

Proposed Mechanism:

$A + A \xrightarrow{k1} I$

$I \xrightarrow{k\text{-}1} A + A$ (k_{-1} since it is reverse to the first)

$I + B \xrightarrow{k2} 2C$

How should rate constants relate to make the proposed mechanism plausible?

General Approach to the Analysis of *Simple* Reaction Mechanisms Using Steady-State Approximation

- 1. Check the proposed mechanism for agreement with experimentally found balanced chemical equation
- 2. Write the expression for the reaction rate using the last elementary process in the reaction mechanism, which does not produce intermediates at the right-hand side. It there is a reverse process for this step, include it in the reaction rate.
- 3. Determine the steady state concentration of the intermediate using $(d[I]/dt)_{prod} = -(d[I]/dt)_{cons}$ as a function of the concentrations of reagents
- 4. Substitute [I] in the reaction rate found in 2) with [I] determined in 3. Compare the theoretical and experimental rates of reaction.

1. Examine whether the proposed mechanism satisfies the balanced chemical equation

- *Experiment:* $2A + B \xrightarrow{k} 2C$
- *Mechanism:* $A + A \xrightarrow{k1} I$ (1)

  $I \xrightarrow{k-1} A + A$ (2)

  $I + B \xrightarrow{k2} 2C$ (3)

- *Overall:* $A + A + I + B \xrightarrow{k} I + 2C$

  $2A + B \xrightarrow{k} 2C$
- Note that reverse process is excluded from the sum
- <u>The proposed mechanism satisfies the balanced chemical equation</u>

2. Write the expression for the reaction rate using the last elementary process in the reaction mechanism.

The rate of the second reaction is:

$$\textbf{Rate} = k_2[\mathrm{I}][\mathrm{B}]$$

The concentration of intermediate has to be eliminated

3. Determine the steady state concentration of the intermediate using the steady-state approximation:

$$(\mathrm{d}[\mathrm{I}]/\mathrm{d}t)_{\mathrm{prod}} = -\,(\mathrm{d}[\mathrm{I}]/\mathrm{d}t)_{\mathrm{cons}}$$

$$k_1[\mathrm{A}][\mathrm{A}] = -\,(-k_{-1}[\mathrm{I}] - k_2[\mathrm{I}][\mathrm{B}])$$

$$k_1[\mathrm{A}]^2 = k_{-1}[\mathrm{I}] + k_2[\mathrm{I}][\mathrm{B}] = [\mathrm{I}]\,(k_{-1} + k_2[\mathrm{B}])$$

$$[\mathrm{I}] = k_1[\mathrm{A}]^2/(k_{-1} + k_2[\mathrm{B}])$$

4. Substitute [I] in the reaction rate with [I] determined using steady-state approximation. Compare the theoretical and experimental rates of reaction.

Rate = $\boldsymbol{k_2}$**[I][B]**

[I] = $\boldsymbol{k_1}$**[A]**$^2/(k_{-1} + k_2[\mathrm{B}])$

Rate = $\boldsymbol{k_2\, k_1}$**[A]**^{2}**[B]**$/(k_{-1} + k_2[\mathrm{B}])$

This rate appears different from the experimental one (*k*[A]^2[B]). Does this imply that the proposed mechanism is not plausible?

Do not hurry with conclusions!

Assumptions About the Relations of Rate Constants

Note that this rate: Rate = $\mathbf{k_2\, k_1[A]^2[B]/(}k_{-1} - k_2[B])$ was derived with no assumption on rate constants and concentrations

However, if we assume that $k_{-1} \gg k_2[B]$ (it is called rapid equilibrium as we will see below) then we can neglect term $k_2[B]$ with respect to k_{-1} in the denominator. Then, for the rate we will have:

$$\text{Rate} = \boldsymbol{k_2\, k_1[\mathrm{A}]^2[\mathrm{B}]}/k_{-1}$$

If we assume that $k = \boldsymbol{k_2\, k_1}/k_{-1}$ then the theoretical rate is the same as the experimental one:

$$\text{Rate} = \boldsymbol{k[\mathrm{A}]^2[\mathrm{B}]}$$

One More Requirement for the Relative Rates

Thus the proposed mechanism implies that $k_{-1} >> k_2[\mathrm{B}]$

(1) $\mathrm{A} + \mathrm{A} \xrightarrow{k1} \mathrm{I}$

(2) $\mathrm{I} \xrightarrow{k-1} \mathrm{A} + \mathrm{A}$

(3) $\mathrm{I} + \mathrm{B} \xrightarrow{k2} 2\mathrm{C}$

Always slower than 2

What about k_1?

$k_1[\mathrm{A}]$ should be always much less than k_{-1} ($k_1[\mathrm{A}] << k_{-1}$) otherwise the intermediate will accumulate forcing the process out of the steady-state (remember that in the steady-state $\mathrm{d}[\mathrm{I}]/\mathrm{d}t = 0$).

Rapid Equilibrium

(1) $A + A \xrightarrow{k1} I$

(2) $I \xrightarrow{k-1} A + A$

(3) $I + B \xrightarrow{k2} 2C$

$k_1[A] << k_{-1}$ always

If $k_2[B] << k_{-1}$ then, the first two reactions are said to establish **rapid equilibrium**

That can be written as:

(1) Rapid equilibrium $A + A \underset{k_{-1}}{\overset{k1}{\rightleftarrows}} I$

(2) Rate-determining step $I + B \xrightarrow{k2} 2C$

Illustration of the Rapid Equilibrium Mechanism

Consider the reaction

$$2\ \mathrm{NO(g)} + \mathrm{O_2(g)} \rightarrow 2\ \mathrm{NO_2(g)}$$

with the experimentally determined rate law

$$\text{rate of reaction} = k[\mathrm{NO}]^2[\mathrm{O_2}]$$

Note: Although the rate law is consistent with the reaction proceeding as a one-step, termolecular process, this is highly unlikely - we will consider another mechanism.

Fast Reversible Step, Slow Step Mechanism continued

Consider this:

Rapid equilibrium: $2\ NO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_2$

Rate determining step: $N_2O_2 + O_2 \xrightarrow{k_3} 2\ NO_2$

Overall: $2\ NO + O_2 \longrightarrow 2\ NO_2$

- a rapid equilibrium is established in the first step; the reaction intermediate, N_2O_2, is then slowly consumed in the second, rate-determining step
- the rate law is given by

$$\text{rate of reaction} = k_3[N_2O_2][O_2]$$

Fast Reversible Step, Slow Step Mechanism continued

- the rate law cannot include a reaction intermediate, so $[N_2O_2]$ must be eliminated
- if the first, reversible step is established quickly, then

rate of forward reaction = rate of reverse reaction

$$k_1[NO]^2 = k_2[N_2O_2]$$

or $$[N_2O_2] = (k_1/\ k_2)[NO]^2$$

- substitute into rate law

$$\text{rate of reaction} = (k_1k_3/\ k_2)[NO]^2[O_2]$$

which is consistent the experimental rate law if

$$k = k_1k_3/\ k_2$$

Generalization of the Reaction Mechanisms

- Balanced reaction: A + B → C may be described by many reaction mechanisms involving intermediates. Intermediate (I) is always a highly reactive species that is its production is slower than at least one of the ways of its consumption. In the steady-state approximation the following mechanisms have to be distinguished

1)

$$\begin{aligned} A &\xrightarrow{k_1} I \\ I &\xrightarrow{k_2} B \end{aligned}$$

$\xcancel{k_1 \gg k_2}$

2)

$$\begin{aligned} A &\xrightarrow{k_1} I \\ I &\xrightarrow{k_2} B \end{aligned}$$

$k_1 \ll k_2$

Rate of Process = $k_1[A]$

Generalization of the Reaction Mechanisms - Continued

3) $k_1\,[\mathrm{A}] \ll k_2$, k_3 is anything

$$\begin{aligned} &\mathrm{A} + \mathrm{A} \xrightarrow{k_1} \mathrm{I} \\ &\mathrm{I} \xrightarrow{k_2} \mathrm{A} + \mathrm{A} \\ &\mathrm{I} \xrightarrow{k_3} \mathrm{C} \end{aligned} \qquad \text{Rate of Process} = \frac{k_1 k_3 [\mathrm{A}]^2}{k_2 + k_3}$$

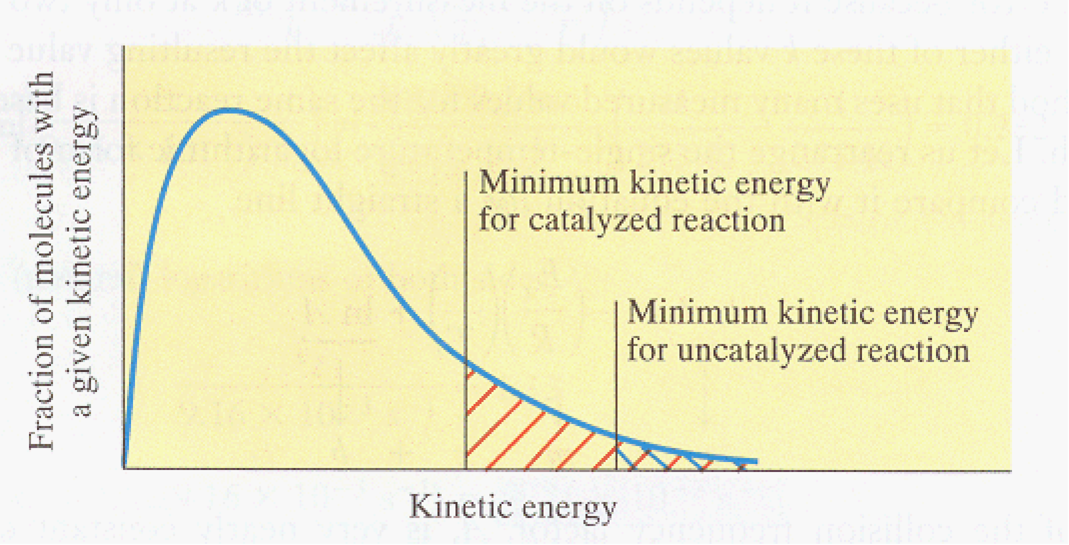
4) Rapid equilibrium in the first step ($k_1\,[\mathrm{A}] \ll k_2$, $k_3 \ll k_2$) which means that the second step is rate-determining:

$$\left.\begin{aligned} &\mathrm{A} + \mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{I} \quad \text{rapid equil.} \\ &\mathrm{I} \xrightarrow{k_3} \mathrm{C} \qquad\qquad\quad \text{rate-determ.} \end{aligned}\right\} \equiv \left\{\begin{aligned} &\mathrm{A} + \mathrm{A} \xrightarrow{k_1} \mathrm{I} \\ &\mathrm{I} \xrightarrow{k_2} \mathrm{A} + \mathrm{B} \\ &\mathrm{I} \xrightarrow{k_3} \mathrm{C} \end{aligned}\right.$$

$$\text{Rate of Process} = \frac{k_1 k_3 [\mathrm{A}]^2}{k_2}$$

Catalysis

- We saw previously that increasing the temperature generally increases the rate of of reaction (some molecules gain enough energy to exceed the activation energy).
- A catalyst can also speed up a reaction by providing an alternate reaction pathway with a lower activation energy



Two Types of Catalysis

- A catalyst participates in a chemical reaction, but does not undergo a permanent change - overall, the catalyst is neither generated nor consumed
- two basic types of catalysis

Homogeneous Catalysis

- catalysts exists in same phase, or homogeneous mixture, as reacting molecules (usually in gas or liquid phase)

Heterogeneous Catalysis

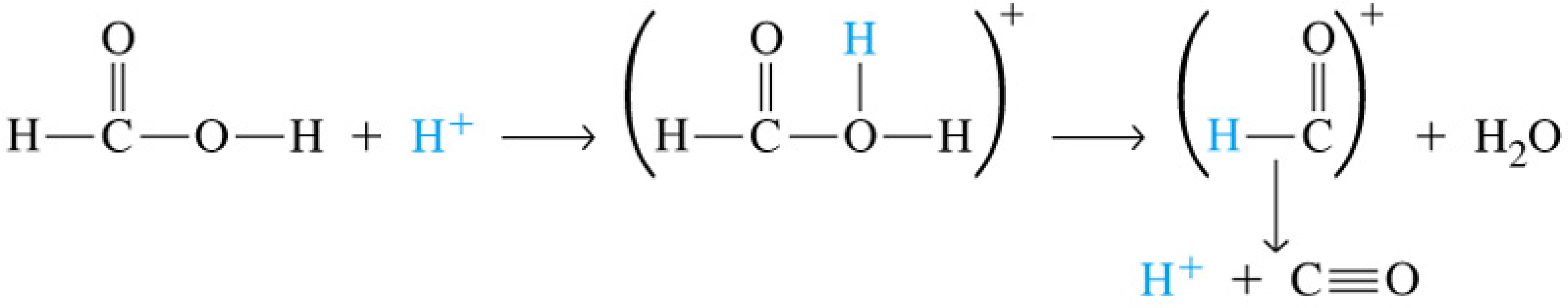
- catalyst and reacting molecules in different phases (often gaseous reactants are adsorbed on to the surface of a solid catalyst)

Homogeneous Catalysis example

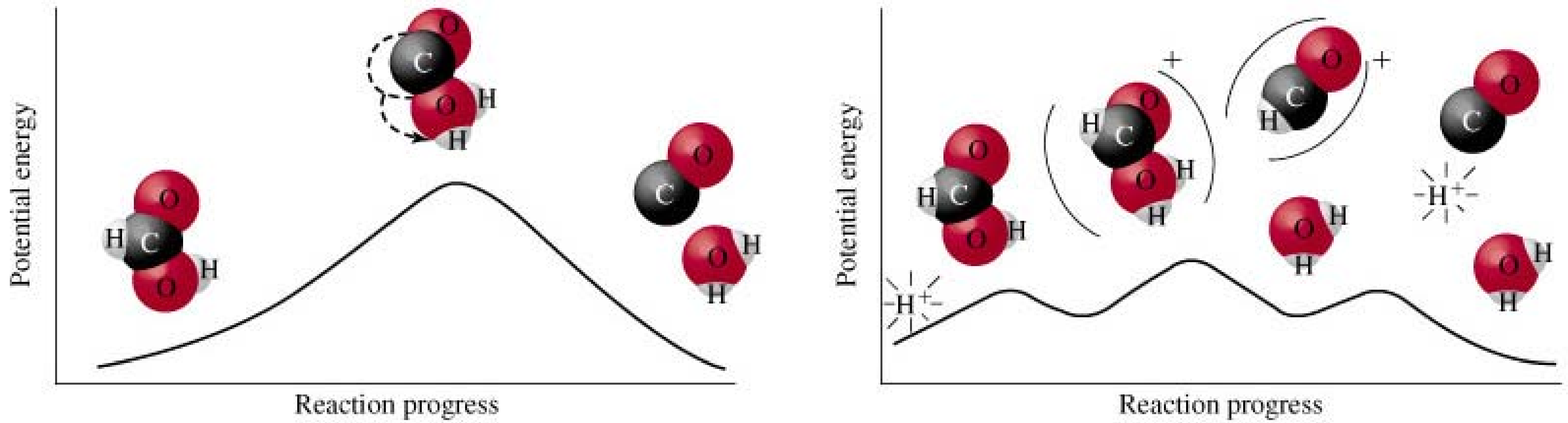
Acid-Catalyzed Decomposition of Formic Acid

$$HCOOH(aq) \rightarrow H_2O(l) + CO(g)$$

- in uncatalyzed reaction, H atom must move from one part of the HCOOH molecule to another before the C-O bond can break - high activation energy for this atom transfer
- in the catalyzed reaction, H^+ from solution can add directly to this position - lower activation energy



Catalysts Influences the Energy Profile



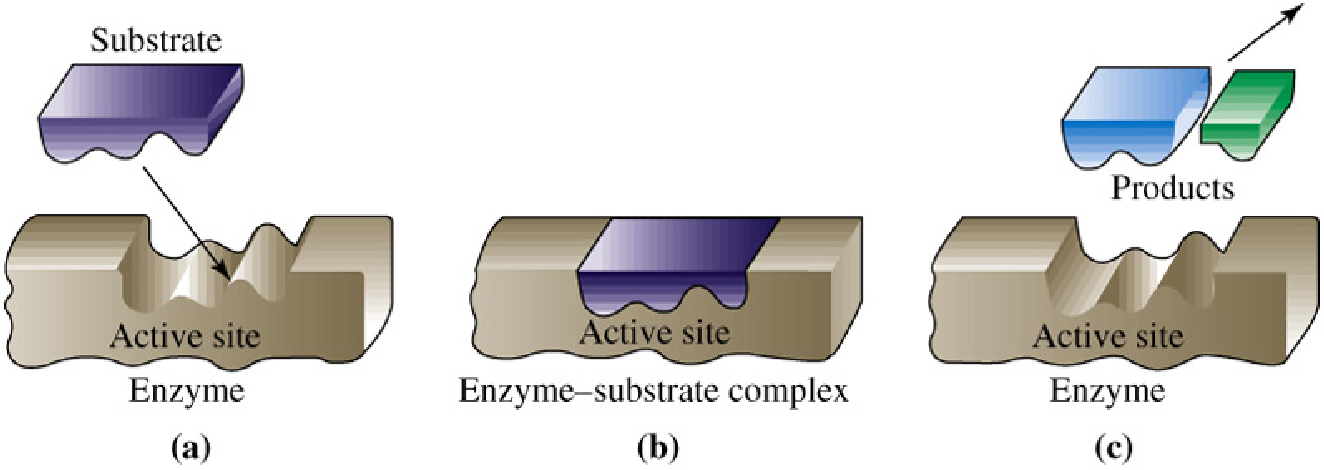
(a) Uncatalyzed reaction

(b) Catalyzed reaction

- Protonation of formic acid produces $(HCOOH_2)^+$
- The protonation reaction could simply be reversed, or the C-O could break to release water
- If C-O bond breaks, intermediate species $(HCO)^+$ produced will release H^+ back into solution … not the same H^+ that was absorbed, but no net change in $[H^+]$

Enzymes as Catalysts

- The most impressive examples of homogeneous catalysis occur in nature where complex reactions are made possible by high molar mass molecules known as enzymes
- Catalytic action of enzymes is extremely **specific**
- Enzyme activity often described by a **lock-and key model**; only a reacting substance, the **substrate** (the key), that fits into an active site on the enzyme (the lock), will undergo a reaction



Kinetics of Enzymatic Reactions

- the following mechanism is common to virtually all enzyme-catalyzed reactions:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} E + P$$

E - enzyme, S - substrate, P - product

- the steady-state approximations yields the following rate law:

$$\text{Rate of Reaction} = \frac{\boldsymbol{k}_2[\mathrm{E}]_0[\mathrm{S}]}{\boldsymbol{K}_\mathrm{M} + [\mathrm{S}]}$$

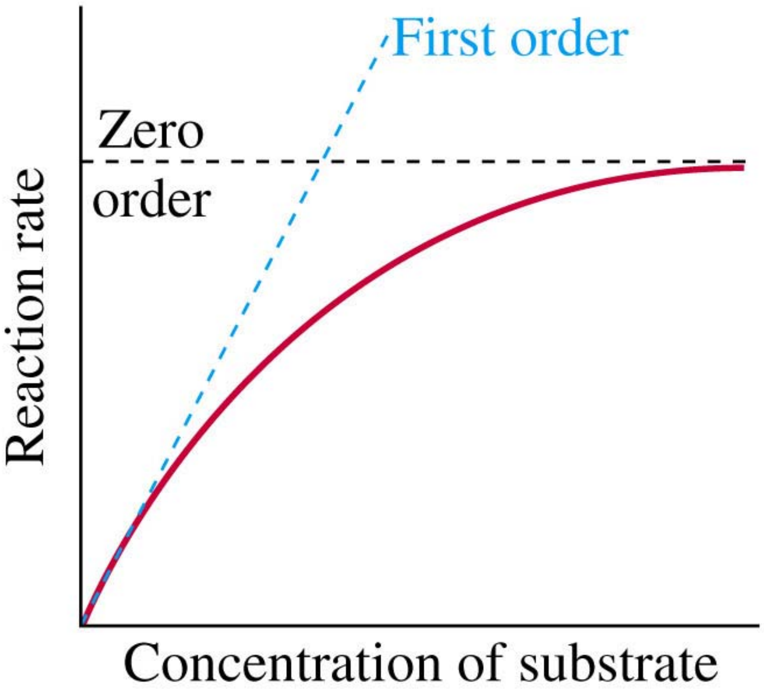
$[E_0]$ is total enzyme concentration and $K_\mathrm{M} = (k_{-1} + k_2)/k_1$

Enzymes as Catalysts continued

- At low substrate concentrations, K_M >> [S] and the rate of reaction is first order for [S] (i.e. rate of reaction = k[S], where $k = (k_2/k_1)(k_{-1}+k_2)[E_0]$)
- At high substrate concentrations,

[S] >> K_M and the rate of reaction is zero order with respect to [S]

(i.e. rate of reaction = k', $k' = k_2[E_0]$)



Heterogeneous Catalysis

- Many gaseous or solution phase reactions can be catalysed on an appropriate solid surface - many transition metals, or their compounds, are effective catalysis
- Not all surface atoms are effective for catalysis; those that are effective are called **active sites**

Proceeds by four basic steps

1) *adsorption* of reactants
2) *diffusion* of reactants along the surface to reach the active site
3) *reaction* at an active site to form adsorbed product
4) *desorption* of product

Heterogeneous Catalysis example

- carbon monoxide, CO, and nitric oxide, NO, found in automobile emissions, are partially responsible for the formation of photochemical smog (see Petrucci, pp. 275-6)
- automobiles are now equipped with *catalytic converters* containing a mixture of catalysts to reduce these emissions though the reaction

$$2\ CO(g) + 2\ NO(g) \rightarrow 2\ CO_2(g) + N_2(g)$$

- the method by which this process is believed to occur on a rhodium surface is illustrated on the next slide

Mechanism of Heterogeneous Catalysis

a) *adsorption* of CO and NO

b) *diffusion* and dissociation of NO

c) combination of CO and O to form CO_2, N atoms to form N_2, along with *desorption* of products

(dissociation & combination processes are equivalent to *reaction* step)