

Chapter 12
Chemical Kinetics

Chemical Kinetics

- CHM 151: Studied what will happen in a chemical reaction (i.e., predicting products from reactants)
- Kinetics looks at the speed of chemical rxns.
- Kinetics is the study of rates (speed) of reactions and factors that affect rates:
 - Concentration (more moles = faster)
 - Temperature (higher temp = more kinetic energy)
 - Physical states of reactants (solid vs liquid vs gas)
 - Surface area (powder vs crystal)
 - Use of a catalyst (speeds up reaction)
 - Pressure, solvent, ionic environment, and others may affect rates

Reaction Rates

- Rates vary from very slow (rusting of iron) to very fast (combustion of H₂)
- Must be able to measure reaction rates to determine how to control them.
- Why do we care? Chemical industry, explosions, hazards, drug response, etc.
- Rate = change in conc. / change in time
- $\Delta M / \Delta t = (M_1 - M_2) / (t_1 - t_2)$

Reaction Rates

- $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
Colorless brown colorless
- The reaction rate can be defined in terms of the increase of [NO₂] or [O₂] or the decrease of [N₂O₅]. ([] = concentration)
- Reactants have negative rates (disappearing over time); products have positive rates (appearing over time)

Reaction Rates

- Overall reaction rates generally decrease over time (i.e., the reaction slows down).
- Rates are based on a specific substance. Rates of formation or consumption may differ depending on coefficients.
- Rate of formation of O₂ = 1/4(Rate of formation of NO₂) = 1/2(Rate of decomposition of N₂O₅)
- $$-\Delta [\text{N}_2\text{O}_5] / \Delta t = \frac{+\Delta [\text{NO}_2]}{4 \Delta t} = \frac{+\Delta [\text{O}_2]}{\Delta t}$$
 This is called the "rate expression".

Reaction Rates: Figure 12.1

General Rates of Reaction

- $5\text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
- If the rate of appearance of Br₂ is 1.2×10^{-3} M/s, what is the rate of disappearance of Br⁻?
- $+ \Delta[\text{Br}_2] / 3\Delta t = -\Delta[\text{Br}^-] / 5\Delta t \rightarrow$ solve for [Br⁻]
- $\text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{aq}) + 2\text{CO}_2(\text{g})$
- If the rate of appearance of ethanol is 4.2×10^{-2} M/s, what is the rate of disappearance of glucose?

Reaction Rates

- Since reaction rates change (decrease) over time, we can measure rates differently.
- Initial rate** is measured by the slope of the line when initial reactant concentrations are measured (tangent at time (t) = 0).
- Instantaneous rate** is measured at any particular time in a reaction (tangent at t).
- Average rate** is measured as the average between two times; similar to calculating slope: $[(y_2 - y_1) / (x_2 - x_1)]$.

Figure 12.2 – Different Rates

- Initial
- Instantaneous (pink)
- Average (blue and orange)

Rate Expressions

- Write rate expressions for the following:
- $C \rightarrow 2D$
 - $-\Delta[C] / \Delta t = +\Delta[D] / 2 \Delta t$
- $5F + 2G \rightarrow 2H + 4K$
- $SiO_3 + 3C \rightarrow SiC + 2CO$
- If the rate with respect to (wrt) CO is +0.78 M/s, what is the rate wrt C?
- Worked Example 12.1, Problems 12.1-2

Rate Laws/Reaction Order

- $aA + bB \rightarrow \text{products}$
- Rate = $-\Delta[A] / \Delta t = k[A]^m[B]^n$
- Rate = $k[A]^m[B]^n$ is the **rate law**
- The reaction rate's dependency on each reactant's concentration is given in this expression.
- Rate: units of M/s (concentration per time)
- [A], [B]: concentration(s) of **reactant(s)**
- k: rate constant (LOWER CASE), units are determined from exponents of m and n

Calculating Reaction Rates

- m, n: order of reaction with respect to reactant (NOT necessarily the stoichiometry coeff.)
- Exponents will be 0, 1, or 2 (in this class)
- Must be determined from experimental data

TABLE 12.2 Balanced Chemical Equations and Experimentally Determined Rate Laws for Some Reactions

Reaction	Rate Law
$(CH_3)_3CBr(aq) + I_2(aq) \rightarrow (CH_3)_3COI(aq) + I^-(aq) + C_2H_6(g)$	Rate = $k[(CH_3)_3CBr]$
$HCl(aq) + Br_2(aq) \rightarrow H^+(aq) + Br^-(aq) + HBr(aq)$	Rate = $k[HCl]^2$
$NO_2^-(aq) + S_2O_8^{2-}(aq) \rightarrow NO_3^-(aq) + SO_4^{2-}(aq)$	Rate = $k[NO_2^-][S_2O_8^{2-}]^2$
$H_2(g) + I_2(g) \rightarrow 2HI(g)$	Rate = $k[H_2][I_2]$
$CH_3CO_2Cl(aq) \rightarrow CH_3CO_2H(aq)$	Rate = $k[CH_3CO_2Cl]$

Rate Laws

- The order of each reactant tells us how the rate depends on its concentration (orders must be determined experimentally)
- 1st order means that doubling reactant's concentration doubles the overall rxn rate
- 2nd order means doubling concentration quadruples rxn rate
- 0th order means doubling concentration has no effect on rxn rate.
- Units of k = $M^{-(n-1)}s^{-1}$ for an nth order reaction in solution

Rate Law

- $H_2(g) + I_2(g) \rightarrow 2HI(g)$
 - Rate = $k[H_2][I_2]$: 1st order wrt each reactant; 2nd order overall (add exponents together).
- $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$
 - Rate = $k[NO]^2[H_2]$: 2nd order wrt NO, 1st order wrt H_2 ; 3rd order overall.
- Group Work
- What is the order wrt each reactant and what is the overall order?
 - $5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2(aq) + 2H_2O(l)$
 - Rate = $k[Br^-][BrO_3^-][H^+]^2$
- Worked Example 12.2, Problem 12.3

Exp'l Determination of Rate Laws

- Example rate law data:
- $2NO + Cl_2 \rightarrow 2NOCl$

Experiment	[NO]	[Cl ₂]	Rate (M/s)
1	0.10 M	0.10 M	0.117
2	0.10 M	0.20 M	0.468
3	0.10 M	0.30 M	1.054
4	0.20 M	0.30 M	2.107
5	0.30 M	0.30 M	3.161

Exp'l Determination of Rate Laws

- Use experimental data and compare multiple trials.
- If [X] doubles and rate remains constant, the order of reaction wrt X is 0.
- If [X] doubles and the rate doubles, the order of reaction wrt X is 1.
- If [X] doubles and the rate quadruples, the order of reaction wrt X is 2.

Rate Law Calculations

- Rate = $k[NO]^x[Cl_2]^y$
- Find x and y depending on how rate changes when concentrations change.
- To find order wrt NO, use 2 trials where [Cl₂] is constant and [NO] changes.
- To find order wrt Cl₂, use 2 trials where [NO] is constant and [Cl₂] changes.

Rate Law Calculations

- Compare two rates $\frac{R_2}{R_1} = \frac{k[A]_2^x[B]_2^y}{k[A]_1^x[B]_1^y} = \left(\frac{[A]_2}{[A]_1}\right)^x \left(\frac{[B]_2}{[B]_1}\right)^y$
- NO:
 - Rate₂/Rate₃ = $([NO]_2/[NO]_3)^x ([Cl_2]_2/[Cl_2]_3)^y$
 - $(2.107 \text{ M/s} / 1.054 \text{ M/s}) = (0.20 \text{ M} / 0.10 \text{ M})^x$
 - Take log of both sides to solve for x.
- 1st order wrt NO
- Cl₂:
 - Rate₂/Rate₁ = $([NO]_2/[NO]_1)^x ([Cl_2]_2/[Cl_2]_1)^y$
 - $(0.468 \text{ M/s} / 0.117 \text{ M/s}) = (0.20 \text{ M} / 0.10 \text{ M})^y$
- 2nd order wrt Cl₂

Rate Law Calculations

- **Rate = $k[\text{NO}][\text{Cl}_2]^2$**
- 3rd order overall (1 + 2)
- Now we can calculate the rate constant.
- Pick any experiment and plug in concentrations.
- Exp 1: $0.117 \text{ M/s} = k(0.10\text{M})(0.10\text{M})^2$
- Worked example 12.3-4, Problems 12.4-5

Group Work

- Determine the rate law and calculate the rate constant for: $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$
- | $[\text{O}_3] \text{ (M)}$ | Rate (M/s) |
|----------------------------|-----------------------|
| 0.00600 | 5.03×10^{-7} |
| 0.00300 | 1.28×10^{-7} |
| 0.00150 | 3.08×10^{-8} |
- What is the rate if $[\text{O}_3] = 0.00500 \text{ M}$?
 - Hint: Find the rate constant first.

Extra Credit (5 pts): Rate Laws

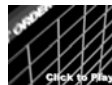
- Compose a table of experimental data (minimum of 3 experiments) to coincide with the rate law and equation below:
- $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$
- **Rate = $k[\text{A}]^2[\text{B}]^2$**
- Also calculate the rate constant for each experimental trial. They should all be close to each other.

Integrated Rate Laws: 1st Order

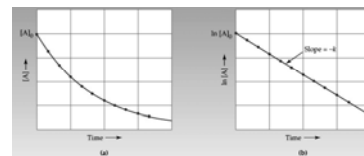
- Example reaction equation: $\text{A} \rightarrow \text{B}$
- If an **overall** reaction is 1st order, the rate law is $\text{rate} = k[\text{A}]$
- We also know from section 12.1 that $\text{Rate} = -\Delta[\text{A}]/\Delta t$
- Setting rates equal: $k[\text{A}] = -\Delta[\text{A}]/\Delta t$
- Integrate: $\ln ([\text{A}]_t / [\text{A}]_0) = -kt$
- This is the First Order Integrated Rate Law (IRL).

Calculations and Rate law

- Math note: $\ln (5/7)$ does NOT equal $\ln 5 / \ln 7$
- **$\ln (5/7) = \ln 5 - \ln 7$**
- Rearrange 1st order Integrated Rate Law:
 - **$\ln [\text{A}]_t = -kt + \ln [\text{A}]_0$**
 - Linear graph ($y = mx + b$)
 - **$y = \ln [\text{A}]_t$**
 - **$m = -k$** (rate constant)
 - **$x = \text{time}$**
 - **$b = \ln [\text{A}]_0$**



First Order Graphs



Using the Integrated Rate Law

- Example: What is the rate constant if the initial concentration of a first order reactant is 2.4 M and after 7.5 minutes, the reactant concentration is 1.8 M?
 - $k = 0.038 \text{ min}^{-1}$
- If a first order reaction has a rate constant of $4.73 \times 10^2 \text{ s}^{-1}$, how long would it take for 75% to react?
 - $t = 2.93 \times 10^{-3} \text{ s}$

1st Order Integrated Rate Law

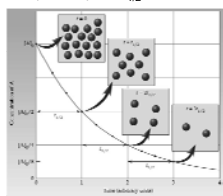
- Note: we can also use pressures of gases instead of concentrations of solutions.
- Worked Examples 12.5-6, Problems 12.7-8

Half-Life of 1st Order Reactions

- Half-life ($t_{1/2}$): time it takes for half (50%) of a reactant to disappear. 50% of the reactant also remains unreacted.
- How much of a sample remains after 3 half-lives?
 - Start with 100%, 50% left after 1 half-life, 25% left after 2 half-lives, 12.5% left after 3 half-lives.

Half-Life of 1st Order Reactions

- Half-life using IRL: $\ln(50/100) = -kt_{1/2}$
- $\ln(1/2) = -kt_{1/2}$
- $t_{1/2} = -\ln 1/2 / k$
- $t_{1/2} = \ln 2 / k$
- $t_{1/2} = 0.693 / k$
- A longer half-life means a smaller rate constant.



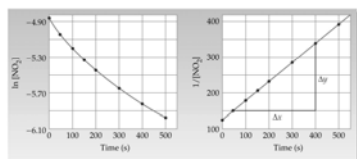
Half-life calculations

- If the half-life for a first order reaction is 144 seconds, how long would it take for the starting 3.50 M reactant to reach a concentration of 2.75 M?
 - $k = 4.8125 \times 10^{-3} \text{ s}^{-1}$
 - Use IRL to solve for t.
 - $t = 50.1 \text{ s}$
- Worked Example 12.7, Problems 12.9-10

Second Order Reactions

- Two options:
 - Rate = $k[A]^2$ OR Rate = $k[A][B]$
 - 2nd option is too complex, we'll only work with the first example.
- What are units of k?
 - Rate = M/s M/s = k·M² **k = M⁻¹s⁻¹**
 - Rate = $k[A]^2 = -\Delta[A]/\Delta t = k$
 - Integrate: **$1/[A]_t = kt + 1/[A]_0$** (linear graph)

Second-Order Reactions



Second Order Reactions

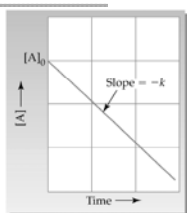
- I.R.L.: **$1/[A]_t = kt + 1/[A]_0$** (linear graph)
- $y = 1/[A]_t$, $m = +k$, $x = \text{time}$, $b = 1/[A]_0$
- Half-life equation: $t_{1/2} = 1/k[A]_0$
- Example: A second order reaction has a half life of 699 seconds. If the initial reaction concentration is 0.0355 M, what will the reactant concentration be after 855 seconds?
- Worked Example 12.8, Problem 12.11

Zero Order Reactions

- They do exist, but are rare (i.e., we won't do examples of these).
- Rate = $-\Delta[A]/\Delta t = k[A]^0 = k$
- $[A] = -kt + [A]_0$**
- Plot: $y = [A]$, $m = -k$, $x = \text{time}$, $b = [A]_0$
- When the reactant concentration changes, the rate remains the same and equals the rate constant.

Zero Order Plot

- $[A] = -kt + [A]_0$**



Summary: Table 12.4

	First-Order	Second-Order	Zero Order
Rate law	$-\frac{\Delta[A]}{\Delta t} = k[A]$	$-\frac{\Delta[A]}{\Delta t} = k[A]^2$	$-\frac{\Delta[A]}{\Delta t} = k$
Concentration-time equation	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$[A]_t = -kt + [A]_0$
Linear graph	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t	$[A]$ versus t
Graphical determination of k	$k = -(\text{slope})$	$k = \text{slope}$	$-k = \text{slope}$
Half-life	$t_{1/2} = \frac{0.693}{k}$ (constant)	$t_{1/2} = \frac{1}{k[A]_0}$ (not constant)	$t_{1/2} = [A]_0 / 2k$

Reaction Mechanisms

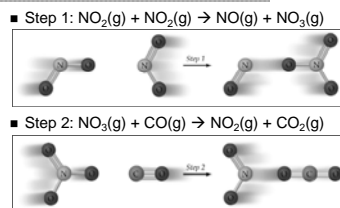
- Sequence of steps that defines the pathway from reactants to products.
- Elementary reactions (or steps) are the sequences that add up to give the overall reaction equation.

Reaction Mechanisms



- Usually one of the steps will be slower than the others. This is the rate-determining step. (Like a slow driver on a two-lane road.)
- The overall reaction rate depends on the rate-determining step.
- The rate law will be written for the slow step.

2-Step Reaction Mechanism



2-Step Reaction Mechanism

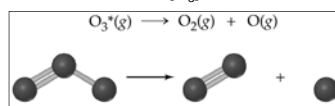
- Step 1: $\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{NO}_3(\text{g})$
- Step 2: $\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$
- What is the overall equation? (Hint: Think Hess's Law - adding equations)
- Each step is called an **elementary step**; they are defined in terms of their molecularity (number of molecules on the reactant side).

2-Step Reaction Mechanism

- Step 1: $\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{NO}_3(\text{g})$
- Step 2: $\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$
- Rate laws of elementary steps are written from equations using coefficients
- Step 1: rate = $k[\text{NO}_2][\text{NO}_2]$ (bimolecular)
- Step 2: rate = $k[\text{NO}_3][\text{CO}]$ (bimolecular)
- Intermediates: substance produced in one step and consumed in a later step
- Catalyst: reactant in one step, product in next

Unimolecular Reaction

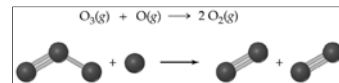
- $\text{O}_3^*(\text{g}) \rightarrow \text{O}_2(\text{g}) + \text{O}(\text{g})$
- (* = energetically excited state)
- Rate Law: rate = $k[\text{O}_3^*]$



Bimolecular Reaction

- $\text{O}_3(\text{g}) + \text{O}(\text{g}) \rightarrow \text{O}_2(\text{g})$
- Rate Law: rate = $k[\text{O}_3][\text{O}]$

Bimolecular Reactions



Molecularity: Table 12.5

TABLE 12.5 Rate Laws for Elementary Reactions

Elementary Reaction	Molecularity	Rate Law
$A \rightarrow \text{Products}$	Unimolecular	Rate = $k[A]$
$A + A \rightarrow \text{Products}$	Bimolecular	Rate = $k[A]^2$
$A + B \rightarrow \text{Products}$	Bimolecular	Rate = $k[A][B]$
$A + A + B \rightarrow \text{Products}$	Termolecular	Rate = $k[A]^2[B]$
$A + B + C \rightarrow \text{Products}$	Termolecular	Rate = $k[A][B][C]$

Multistep Mechanisms

- Many rate laws are more complex, so the overall reaction cannot be an elementary reaction. These have multistep mechanisms.
- One step in multistep mechanism will be slower than the others. The slow step is the **rate-determining step**.
- Step 1 (slow): $A + B \rightarrow D$ Rate = $k[A][B]$
- Step 2 (fast): $A + D \rightarrow 2C$ Rate = $k[A][D]$
- Write the rate law for each step. Write the overall equation. What is the intermediate?
- Rate = $k[A][B]$

Multistep Mechanisms

- $\text{Ti}^{3+} + 2\text{Fe}^{2+} \rightarrow \text{Ti}^{4+} + 2\text{Fe}^{3+}$
- Elementary steps:
 - $\text{Ti}^{3+} + \text{Fe}^{2+} \rightarrow \text{Ti}^{2+} + \text{Fe}^{3+}$ fast
 - $\text{Ti}^{2+} + \text{Fe}^{2+} \rightarrow \text{Ti}^{4+} + \text{Fe}^{3+}$ slow (RDS)
 - Rate = $k[\text{Ti}^{3+}][\text{Fe}^{2+}]^2 / [\text{Fe}^{3+}]$
- Intermediate: Ti^{2+}
- If the 1st step is slow, rates are easy to predict. If the 2nd step is slow, rates are more difficult (we will not do these).

Rate Laws/Reaction Mechanisms

- **Group Work:**
- $S_2O_8^{2-} + I^- \rightarrow 2SO_4^{2-} + I^*$ slow
- $I^* + I^- \rightarrow I_2$ fast
- Which step is rate determining?
- What is the intermediate?
- What is the rate law for each step? What is the overall rate law?
- Worked Example 12.9; Problem 12.12

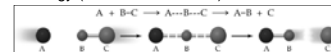
Rate Laws/Reaction Mechanisms

- Step 1 (slow): $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$
- Step 2 (fast): $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$
- What is the rate law for this 2-step reaction?
- What is the intermediate?
- Worked Example 12.10, Problem 12.13 - 15

Collision Theory

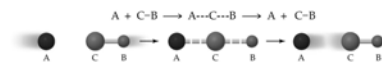
[Collision Theory Movie](#)

- In order for a reaction to occur, molecules must not only collide, they must collide in the correct orientation and with enough energy to create the products.
- Ex: $A + BC \rightarrow AB + C$
- The middle state (transition state) is higher in energy (unstable substance).



Collision Theory

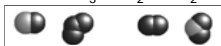
- Non-effective collisions; wrong orientation means no reaction can occur.



- We can increase the probability of successful collisions by increasing concentrations, temperature, or adding a catalyst.

Group Work

- $NO + O_3 \rightarrow O_2 + NO_2$



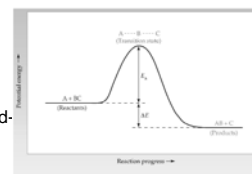
- Which collisions are likely to be effective?



Reaction Energy Profile

- Energy profile of an exothermic reaction.

- E_a is the **activation energy** (amount of energy needed for a rxn to occur).

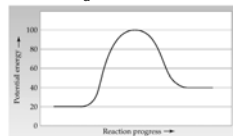


Transition State Theory

- Same basic requirements as collision theory, but it examines energy in more detail.
- Reactants \rightarrow (activated complex or transition state) \rightarrow products
- Activated complex or transition state is the highest energy (E_a) configuration through which the system must go to convert reactants to products. It is a very short-lived configuration. It represents an energy barrier to reaction.

Reaction Energy Profile

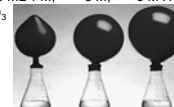
- $AB + CD \rightarrow AC + BD$ (one-step rxn)
- Is this reaction endo- or exothermic?
- What is the value of E_a ?



Effect of Concentration on Rates

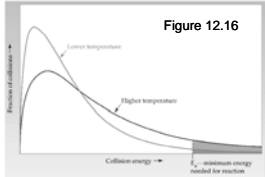
- Rates usually vary with concentrations of some or all reactants, possibly products, and possibly other substances (catalysts) that might be present.

- Example: 50 mL 1 M, 3 M, 6 M HCl in balloons + 2g Na_2CO_3



Effect of Temperature on Rates

- The number of molecules with sufficient kinetic energy to react increases as the temperature increases



Arrhenius Equation and Plot

- Activation Energy can be found graphically (rate constant, temperature, $R = 8.314 \text{ J/K}\cdot\text{mol}$, and "frequency factor" (given))

$$m = -E_a / R \rightarrow E_a = -R \cdot m$$

$$\ln k = \left(\frac{-E_a}{R} \right) \left(\frac{1}{T} \right) + \ln A$$

\uparrow \uparrow \uparrow \uparrow
 y m x b

Arrhenius Equation and Plot

- E_a can also be found from rate constants at two temperatures:
 - Derived on p. 475 (don't need to know)

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

- Worked Example 12.12, Problem 12.17

Arrhenius Equation Practice

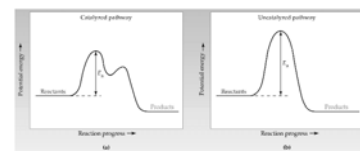
- A certain first-order reaction has a rate constant of $1.0 \times 10^{-3} \text{ s}^{-1}$ at 25°C .
- If the reaction rate doubles when the temperature is increased to 35°C , what is the activation energy for this reaction in kJ/mol ?

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

Catalysis

- Concentrations, temperatures, and catalysts affect reaction rates.
- Catalysts are substances that increase the rate of reaction without being consumed. They lower the activation energy and are reusable.

Catalysis

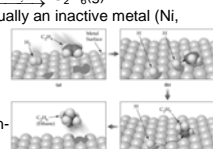


Homogeneous Catalyst

- A homogeneous catalyst is one that is in the same phase as the reactants.
- $\frac{1}{2} \text{O}_2(\text{g}) + \text{NO}(\text{g}) \rightarrow \text{NO}_2(\text{g})$
- $\text{NO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{O}(\text{g})$
- $\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$
- Net rxn:** $\frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$
- $\text{NO}(\text{g})$ (nitric oxide) is the catalyst

Heterogeneous Catalyst

- A heterogeneous catalyst is in a different phase than the reactants:
 - $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \xrightarrow{\text{catalyst}} \text{C}_2\text{H}_6(\text{g})$
 - The catalyst is usually an inactive metal (Ni, Pd, or Pt).
 - Figure 12.19
 - Biology: enzymes are catalysts (amylase helps break down starches into glucose)



Catalytic Converters

- Convert pollutants (hydrocarbons, carbon monoxide, and nitric oxide) into CO_2 , H_2O , N_2 , and O_2 using a heterogeneous catalyst (Pt, Pd, Rh).

