

Chapter 12

Chemical Kinetics

12.1 Kinetics

- ▶ The study of rates of reactions and reaction mechanisms (e.g., how fast a reaction will go and what steps it goes through)
- ▶ What is rate?
- ▶ Definition of reaction rate: the change in concentration of a reactant or product over change in time $\rightarrow \Delta[A] / \Delta t$

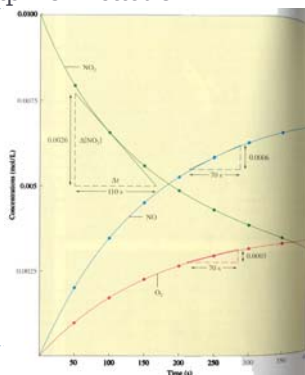
12.1 Factors that Affect Rate

- ▶ Concentrations
- ▶ Temperature
- ▶ Pressure
- ▶ Catalysts
- ▶ Surface area



- ▶ How can rate be represented on a graph?
- ▶ What happens to NO_2 over time? NO ? O_2 ?
- ▶ How can their rates be expressed relative to each other?

12.1 Graph of Reaction



12.1 Relative Rates

- ▶ Rate of NO_2 consumption =
- Rate of NO production =
- $2 \times$ Rate of O_2 production

$$-\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{NO}]}{\Delta t} = 2 \frac{\Delta[\text{O}_2]}{\Delta t}$$

- ▶ Then

$$-\frac{\Delta[\text{NO}_2]}{2\Delta t} = \frac{\Delta[\text{NO}]}{2\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

12.1 Relative Rates

- ▶ If NO_2 is disappearing at a rate of $4.2 \times 10^{-5} \text{ M/s}$, what is the rate of appearance of O_2 ?

$$-\left(\frac{1}{2}\right) \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

- ▶ Write the rates of the species in the following reaction:
 $5\text{Br}^- + \text{BrO}_3^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 2\text{H}_2\text{O}$

Group Quiz #1

- ▶ According to the following **unbalanced** reaction, if the rate of appearance of oxygen gas is $4.00 \times 10^{-2} \text{ M/s}$, what is the rate of disappearance of KClO_3 (g)?



12.2 Rate Laws & Reaction Order

- ▶ What happens to a chemical reaction over time?
- ▶ Over time, the change in concentration will depend on the forward and reverse reactions.
 - ▶ To simplify things, choose conditions before products become significant
 - ▶ This allows us to examine rates using **only** reactants

12.2 Rate Laws

- ▶ Reaction:
 - ▶ $a\text{A} + b\text{B} \rightarrow \text{Products}$
- ▶ Rate Law:

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

- ▶ **k is Rate Constant**
- ▶ **m & n are the order of reactants** (NOT the coefficient); **m & n must be determined experimentally!**
- ▶ **Reaction Order = sum of reactant orders**

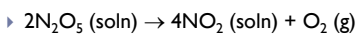
12.2 Rate Laws

- ▶ **Rate law** of the decomposition reaction of NO_2
 - ▶ $\text{Rate} = k[\text{NO}_2]^m$
 - ▶ **k = rate constant**
 - ▶ **m is order of reactant** (NOT the coefficient); **m must be determined experimentally**
- ▶ Why do we want to determine the rate of a reaction?

12.2 Types of Rate Laws

- ▶ **Differential Rate Law (or Rate Law)**
 - ▶ rate depends on concentration
$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2]^m$$
- ▶ **Integrated Rate Law**
 - ▶ rate depends on time

12.3 Determining the Rate Law



$[\text{N}_2\text{O}_5]$	Rate (M/s)
0.90 M	5.4×10^{-4}
0.45 M	2.7×10^{-4}

- ▶ What happens to rate as concentration is halved?
- ▶ What order is N_2O_5 ?

12.3 Initial Rates

- ▶ Initial rates are measured just after a reaction begins
- $$\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l})$$

TABLE 14.3 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

12.3 Initial Rates

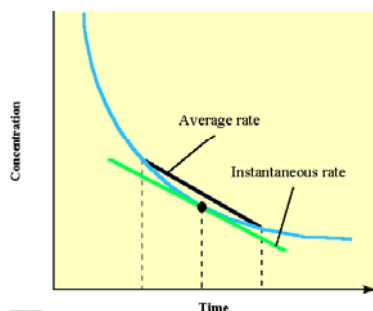
- ▶ The reaction is first order in NO_2^- .
- ▶ The reaction is first order in NH_4^+ .
- ▶ What is the overall order of the reaction?
 - ▶ Sum of exponents
 - ▶ Note: exponents can also be negative, fraction
- ▶ How can you find the value of the rate constant?
- ▶ What units will k have?

Group Quiz #2

- ▶ The following experimental data was collected for this reaction. $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$. What is the rate law? Show your work and circle your final answer.

Trial	$[\text{NO}]$ (M)	$[\text{H}_2]$ (M)	Rate (M/s)
1	0.60	0.15	0.076
2	0.60	0.30	0.15
3	0.60	0.60	0.30
4	1.20	0.60	1.21

12.3 Instantaneous vs. Average Rates



12.3 Initial Rates

- ▶ What is the overall order of the reaction of the following?
 - ▶ Rate = $k[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2$
 - ▶ Rate = $k[\text{I}^-][\text{OCl}^-]/[\text{OH}^-]$

12.4 Integrated Rate Law

- ▶ Only look at 0th, 1st, and 2nd order reactions
- ▶ What do these orders mean (how does a change in concentration affect the rate)?

▶ Ex: $\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2]^n$

- ▶ Integrate w.r.t. time to get 1st order IRL (calculus ☺)

$$\ln \frac{[\text{NO}_2]_t}{[\text{NO}_2]_0} = -kt$$

$$\ln[\text{NO}_2]_0 - \ln[\text{NO}_2]_t = kt$$

12.4 Integrated Rate Law

- ▶ Can modify to get linear form: (refer to Appendix A, p.A5-6 for log functions)
- ▶ Reaction A → products
 - ▶ $\ln [A]_t = -kt + \ln [A]_0$
 - ▶ $y = \ln [A]$
 - ▶ $m = -k$
 - ▶ $x = t$
 - ▶ $b = \ln [A]_0$

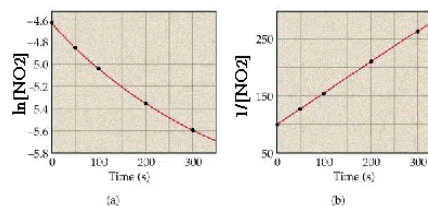
12.4 Integrated Rate Law

Table A.1 in Appendix A

Eqn ($y=mx+b$)	y vs. x	m	b
$[A] = -kt + [A]_0$	$[A]$ vs. t	-k	$[A]_0$
$\ln [A] = -kt + \ln [A]_0$	$\ln[A]$ vs. t	-k	$\ln[A]_0$
$1/[A] = kt + 1/[A]_0$	$1/[A]$ vs. t	k	$1/[A]_0$

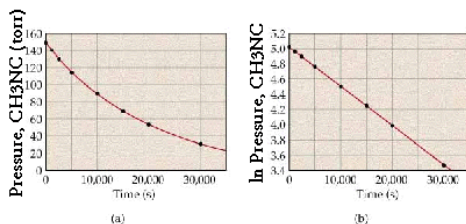
12.4 IRL

- ▶ What order is this reaction?



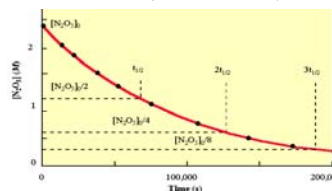
12.4 IRL

- ▶ What order is this reaction?



12.5 IRL & Half-lives

- ▶ By definition, $[A] = [A]_0/2$, when $t = t_{1/2}$



- ▶ 0th order: $t_{1/2} = [A]_0/2k$
- ▶ 1st order: $t_{1/2} = 0.693/k$
- ▶ 2nd order: $t_{1/2} = 1/k[A]_0$
- ▶ Table 12.6 gives summary of equations

12.5 IRL & Half-lives

- ▶ Example: Determine the half life of a substance that has a rate constant of $1.7 \times 10^{-3} \text{ s}^{-1}$ (1st order)

Rate Laws Summary

- ▶ Be able to find the orders of reactants given table of rate and concentration data
- ▶ Know what it means to say a reactant is a certain order
- ▶ Given a rate law, know how changing concentration changes rate
- ▶ Know the graphs of the orders of reactions
- ▶ Be able to interpret the order of reaction from a graph

12.8 Reaction Mechanisms

- ▶ Mechanisms outline the steps in a reaction that will convert the reactant(s) into product(s)
- ▶ May be one or many steps involved
- ▶ Chemical equation **may or may not** describe the mechanism

12.8 Reaction Mechanisms

- ▶ $\text{NO}_2 (\text{g}) + \text{CO} (\text{g}) \rightarrow \text{NO} (\text{g}) + \text{CO}_2 (\text{g})$
- ▶ Rate = $k[\text{NO}_2]^2$
- ▶ Does the rate match the equation?
- ▶ Divide reaction into elementary steps:
 - ▶ $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ Slow
 - ▶ $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ Fast

12.9 Rate Laws for Elementary Steps

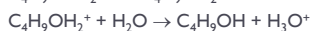
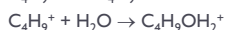
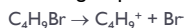
- ▶ Elementary steps are defined by their **molecularity** - the number of molecules that have to collide to give the defined products.
 - ▶ **Unimolecular** - 1 reactant = Rate = $k[\text{A}]$
 - ▶ **Bimolecular** - 2 reactants = Rate = $k[\text{A}]^2$
or Rate = $k[\text{A}][\text{B}]$
 - ▶ **Termolecular** - 3 reactants = Rate = $k[\text{A}]^3$
or Rate = $k[\text{A}]^2[\text{B}]$
or Rate = $k[\text{A}][\text{B}][\text{C}]$
- ▶ See Table 12.5, p. 466

12.8 Reaction Mechanisms

- ▶ $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ Slow
- ▶ $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ Fast
- ▶ NO_3 is an intermediate (produced in 1st step, consumed in last)
- ▶ NO_2 is a catalyst (consumed in 1st step, produced in last)
- ▶ Elementary steps sum to give overall equation (Hess's Law)

12.8 Reaction Mechanisms

- ▶ Identify the intermediate(s) and catalyst(s) in the following steps:



- ▶ What is the overall equation?
- ▶ Write the rate law for each step.

12.10 Rate Law for Overall Reactions

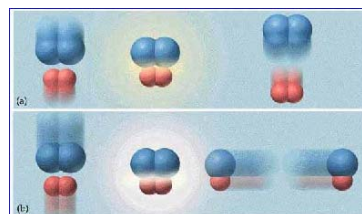
- ▶ Analogy: Running Errands
- ▶ Overall reaction can only occur as fast as the slowest step (**R**ate **D**etermining **S**tep - rds)
- ▶ If rds is the first step, rate law is easy
- ▶ If rds is second or later, more mathematically involved (we won't do this ☺)

12.10 Rate Law for Overall Reactions

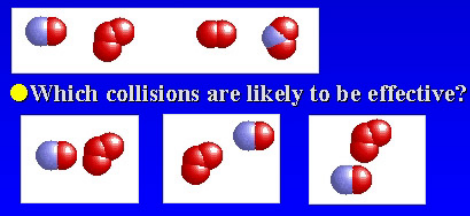
- ▶ Mechanisms must agree with the rate law:
- ▶ Example
 - ▶ $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$
 - ▶ Rate = $k[\text{NO}_2][\text{F}_2]$ → determined experimentally
 - ▶ Suggested mechanism:
 - ▶ $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$ slow
 - ▶ $\text{F} + \text{NO}_2 \rightarrow \text{NO}_2\text{F}$ fast
- ▶ Is this an acceptable mechanism?
- ▶ What's the intermediate? Catalyst?

12.11 Model for Kinetics

- ▶ What makes molecules react and form new species?
- ▶ What would result in no reaction?



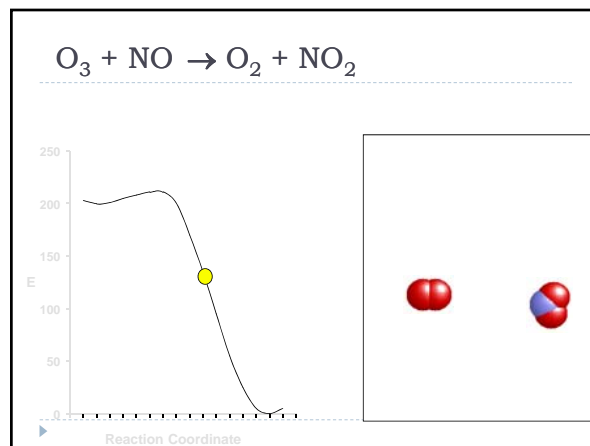
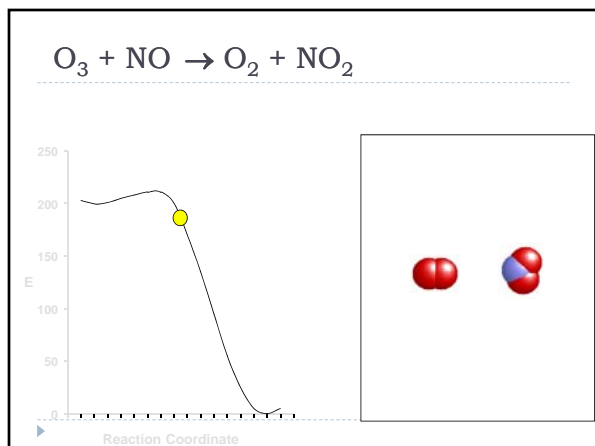
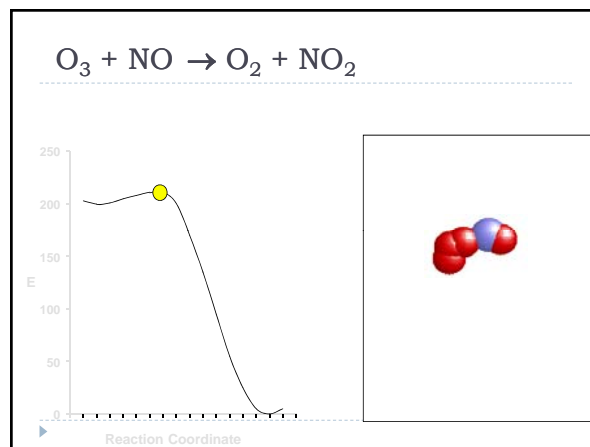
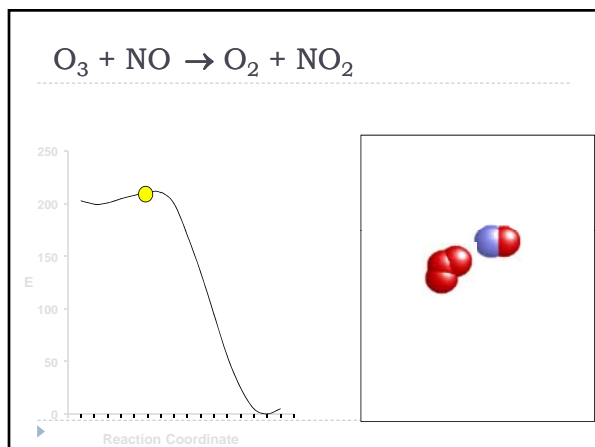
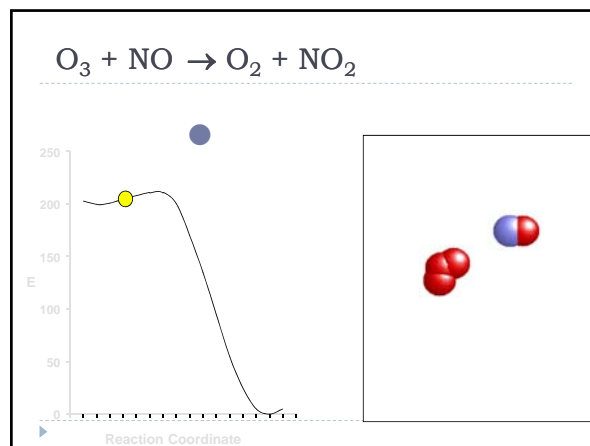
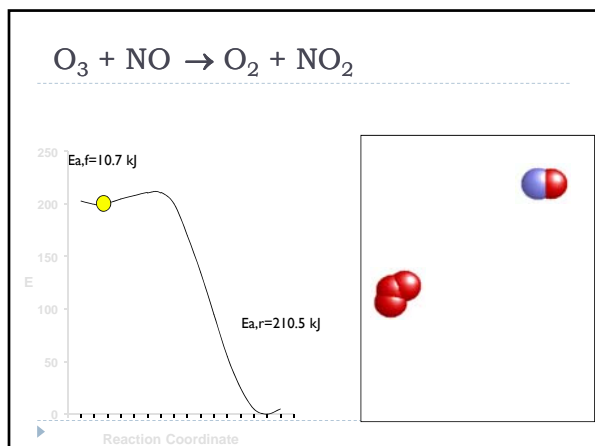
12.11 Model for Kinetics

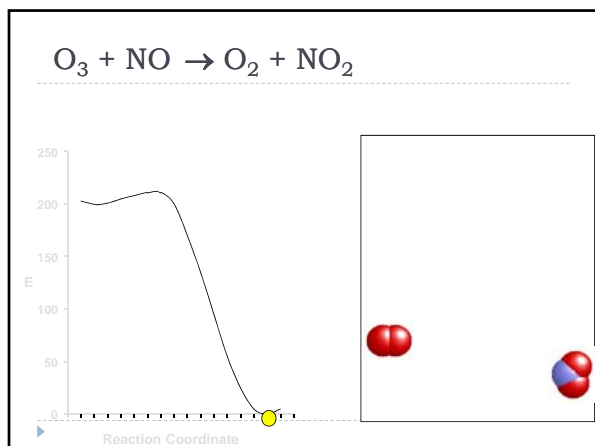


- ▶ Draw pictures of some effective and ineffective collisions.

12.11 Model for Kinetics

- ▶ Only a small fraction of collisions will produce a reaction. Why?
- ▶ The *threshold energy*, or activation energy, must be overcome for a reaction to occur.
- ▶ It takes energy to break and make bonds;





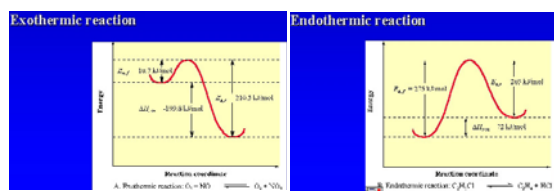
12.11 Reaction Mechanisms

- At maximum energy, energy barrier, the atoms form a transition state



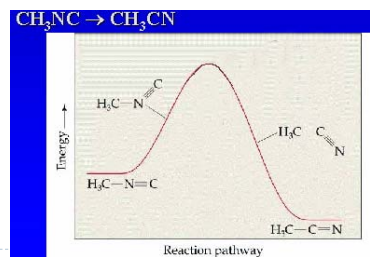
12.11 Reaction Mechanisms

- Why does the rate depend on E_a and not on ΔE ?



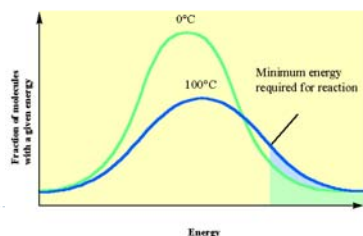
12.11 Reaction Mechanisms

- Identify $E_{a,f}$, $E_{a,r}$, ΔE , transition state, and exo- or endothermicity for the reaction below.



12.11 Model for Kinetics

- Only the collisions with energy $> E_a$ will react to give products
- What can increase the number of collisions?



12.11/12.12 Arrhenius

- The fraction of collisions increases exponentially with temperature.
- Arrhenius: $k = Ae^{-E_a/RT}$
 - k = # of collisions at E_a (rate constant predicted by collision theory)
 - A = frequency factor
 - E_a = activation energy
 - R = gas constant (8.3145 J/mol · K)
 - T = temperature in K
- Linear form: $\ln k = -E_a/RT + \ln A$

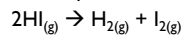
12.12 Arrhenius

- ▶ Can find E_a from 2 reactions: subtract 2nd equation from the first to give

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

12.12 Arrhenius

- ▶ Example:

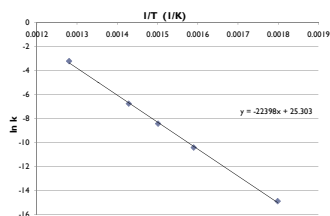


Temperature (°C)	$k(\text{M}^{-1}\text{s}^{-1})$
283	3.52×10^{-7}
356	3.02×10^{-5}
393	2.19×10^{-4}
427	1.16×10^{-3}
508	3.95×10^{-2}

- Find E_a using all five data points
- Calculate E_a from rate constants at 283°C and 508°C
- Given rate constant at 283°C and E_a from b), what is the rate constant at 293°C

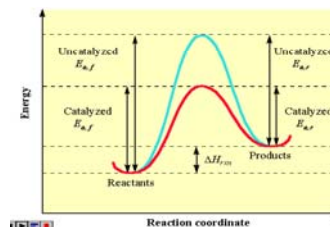
12.12 Arrhenius

a)



12.13 Catalysis

- ▶ Catalysts speed up a reaction without being consumed
- ▶ Gives reactions a new (lower) activation energy and larger percent of successful collisions



12.14 Catalysis

- ▶ Homogeneous catalysis - catalyst is in the same phase as the reacting molecules
- ▶ Heterogeneous catalysis - catalyst is in a different phase (usually a solid)

12.14 Catalysis

- ▶ Homogeneous catalysts - nitric oxide toward ozone
 - $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$ (in lower atmosphere)
 - $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$
 - $\text{NO}_2 \rightarrow \text{NO} + \text{O}$ (NO_2 absorbs light)
 - $\text{O}_2 + \text{O} \rightarrow \text{O}_3$ (ozone is toxic, reacts with other pollutants to form irritating substances)

