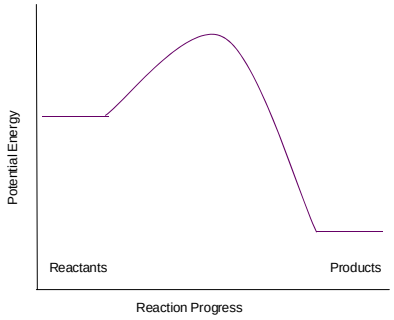
Chemical Kinetics

Predictions of likelihood for a reaction to occur have been based on difference in energy between products and reactants:

Thermodynamics only compares reactants to products, says nothing about how fast the reaction gets from reactants to products (if at all)!

Kinetics focuses on ***how*** the reactants get to products: the ***mechanism*** of the reaction



1

What Influences Kinetics?

What determines the *rate* of a chemical reaction?

Rate: change in concentration of a reactant (or product) per unit time.

Average Rate:

Instantaneous Rate:

Contributors to Kinetics

$$A + B \rightarrow C$$

1.

2.

3.

2

Quantifying Reaction Kinetics

Rate Law: Describes the relationship between rate and concentration of species

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

Exponents like *m, n, p* are usually positive integers

BUT: Can be negative, fractions, zero

k: rate constant

3

Determining Rate Laws from Experiment

Look at effect of changing concentration on initial rates

Example: The initial rate for the reaction of nitrogen monoxide and oxygen was measured at 25°C for various concentrations of NO and O_2. Determine the rate equation from these data. What is the value of the rate constant, *k*?

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

	Initial Concentrations (M)		Initial Rate
Experiment	[NO]	$[O_2]$	(mol/Ls)
1	0.020	0.010	0.028
2	0.020	0.020	0.057
3	0.020	0.040	0.114
4	0.040	0.020	0.227
5	0.010	0.020	0.014

4

Integrated Rate Laws:

Predict concentration/time relationships throughout reaction.

Reaction Order	Rate Law	Integrated Rate Law
0	Rate = k	$[R]_0 - [R]_t = kt$
1	Rate = $k[R]$	$\ln[R]_0 - \ln[R]_t = kt$
2	Rate = $k[R]^2$	$\frac{1}{[R]_t} - \frac{1}{[R]_0} = kt$

If you monitor [R] as a function of time and treat the data properly, it is possible to determine reaction order and k for R.

5

Integrated Rate Laws…"Linearized"

GOAL: Rearrange Integrated Rate Laws to y = kt + b form. (y is related to $[R]_t$, b is related to $[R]_0$)

Reaction Order	Integrated Rate Law	y = kt + b Form
0	$[R]_0 - [R]_t = kt$	$[R]_t = -kt + [R]_0$
1	$\ln[R]_0 - \ln[R]_t = kt$	$\ln[R]_t = -kt + \ln[R]_0$
2	$\frac{1}{[R]_t} - \frac{1}{[R]_0} = kt$	$\frac{1}{[R]_t} = kt + \frac{1}{[R]_0}$

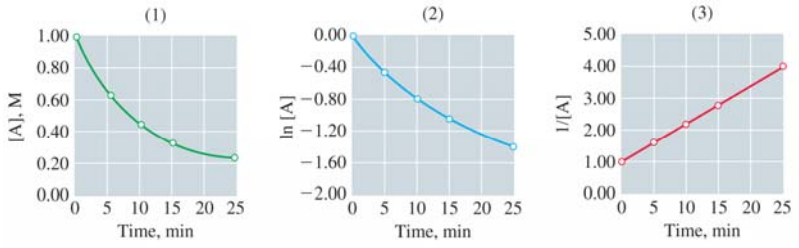
"Linearizing" makes it easier to determine reaction order at a glance.

6

Graphical Treatment of Data

TABLE 14.5 Reaction Kinetics: A Summary for the Hypothetical Reaction A ⟶ Products

Order	Rate Law	Integrated Rate Equation	Straight Line	k =	Units of k	Half-life
0	Rate = k	$[A]_t = -kt + [A]_0$	[A] v. time	−slope	mol L^{-1} s^{-1}	$[A]_0/2k$
1	Rate = $k[A]$	$\ln[A]_t = -kt + \ln[A]_0$	ln [A] v. time	−slope	s^{-1}	$0.693/k$
2	Rate = $k[A]^2$v	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]}$. time	slope	L mol^{-1} s^{-1}	$\frac{1}{k[A]_0}$

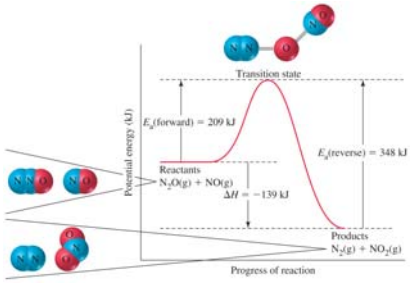


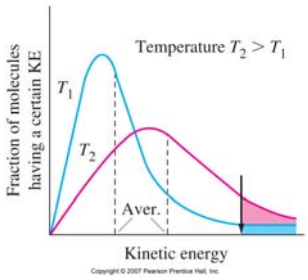
Dealing with Reactions of Multiple Reactants

- Pseudo-nth-order rates

7

Temperature-Dependence of *k*





As T changes, the # of molecules with sufficient energy to react (overcome activation barrier) also changes.

Quantify this dependence using Arrhenius Equation:

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

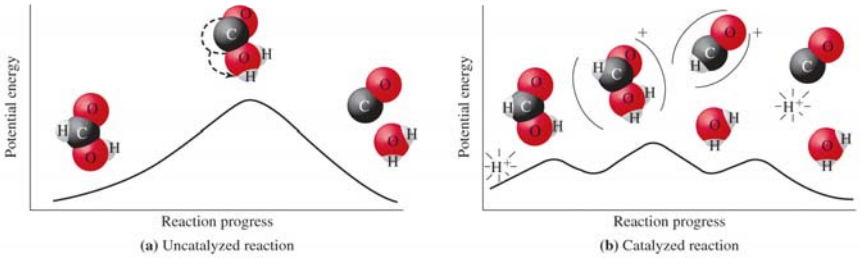
A = frequency factor

Arrhenius Equation is especially useful for determining activation energy (E_a)

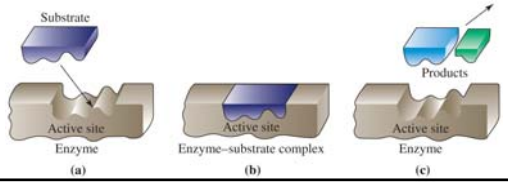
8

Catalysts and Catalysis

- Effect rate of reaction, but are not consumed in the reaction
- Provide alternate mechanism with lower activation barrier.



- Homogeneous vs Heterogeneous



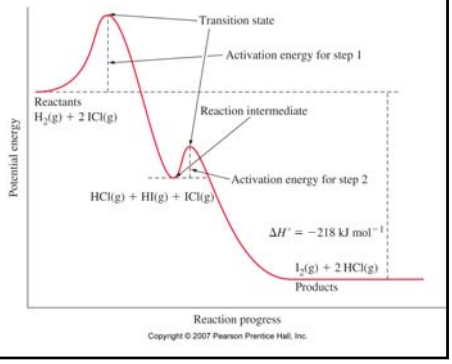
9

Determining Reaction Mechanism

- All reactions are a sequence of <u>elementary steps</u>
  - Single molecular event, with its own rate law and kinetics
- Defined by <u>molecularity</u>: # of molecules that come together

  1 molecule =
  2 molecules =
  3 molecules =

- The sum of all elementary steps <u>must</u> add up to the overall reaction.
- **Rate Determining Step:** Slowest elementary step in a reaction sequence.



Determining Reaction Mechanism

- Rate law for *elementary step* is based on stoichiometry

A $\rightarrow$ product	Rate = k[A]
A + B $\rightarrow$ product	Rate = k[A][B]
A + A $\rightarrow$ product	Rate = k[A]^2
2A + B $\rightarrow$ product	Rate = k[A]^2[B]

Example:

$$NO_2 + CO \rightarrow NO + CO_2$$

Predict that this is an O-transfer reaction b/w one NO_2 and one CO
(1 elementary step)

Rate =

11

Determining Reaction Mechanism

BUT experiments show a different rate law:

$$\text{Rate} = k[NO_2]^2$$

Mechanism must fit this rate law. Here's a proposed mechanism:

Step	Elem. Step	Rate
1	$NO_2 + NO_2 \rightarrow NO_3 + NO$	
2	$NO_3 + CO \rightarrow NO_2 + CO_2$	

12

Mechanisms involving equilibria

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C + D$$

At equilibrium rate forward rxn. = rate reverse rxn

$A + B \rightarrow C + D$	Rate = $k_1[A][B]$
$C + D \rightarrow A + B$	Rate = $k_{-1}[C][D]$

One More Example:

What is the overall reaction for this combination of elementary steps?

What is the rate law for this process?

Step 1	Fast, Equilibrium	$NO_2Cl \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NO_2 + Cl^-$
Step 2	Slow	$NO_2Cl + Cl^- \xrightarrow{k_2} NO_2 + Cl_2$

13

Steady-State Approximation:

- What if there is no single, rate determining step in a reaction? Consider the previous reaction mechanism. What if the rates of all reactions are comparable?
- The solution is more complex, but it becomes doable if we utilize the **steady-state approximation:**

14