LECTURE TOPICS:

TODAY'S CLASS: 15.5

NEXT CLASS: start equilibrium (Ch.16)

MIDTERM EXAM: Fri. Feb.29th (all including Ch.15)
                              in class

(1)

Factors that affect rxn rates:

1.) concentration

2.) temperature
      - reactions are
        faster at higher T   } related to rxn's energetics
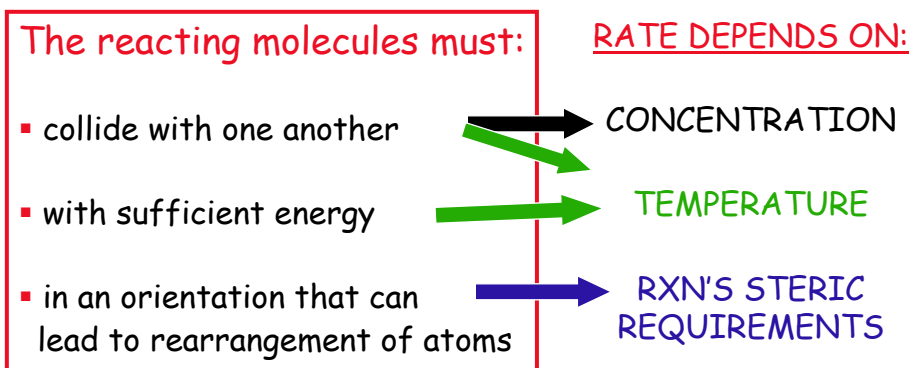   AND   reactant collisions

K&T Fig. 15.4: bleaching of a dye occurs faster at higher T

(2)

15.5 Particulate view of rxn rates: "Collision theory"

Only a small fraction of collisions leads to rxn...
Arrhenius: there is an "energy barrier" to rxn
   • AND: Molecules must be oriented correctly!

The reacting molecules must:

- collide with one another

- with sufficient energy

- in an orientation that can
  lead to rearrangement of atoms

RATE DEPENDS ON:

CONCENTRATION

TEMPERATURE

RXN'S STERIC
REQUIREMENTS

Rate = k [reactant]^n ⇐ T & steric info are inside k !
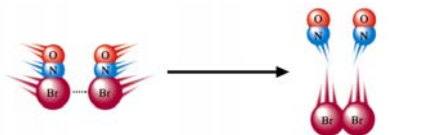
(3)

Molecules must be oriented properly to react

All reactions have geometric or "steric" requirements:
- the right atoms must interact with each other!
- sometimes a specific angle also required (see advanced courses)
- **lower probability of achieving correct orientation when collide**
            ⇨ **smaller rate constant k**
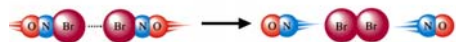   ⇨ **slower reaction...**

Which collisions can lead to...
  2 BrNO → 2 NO + Br$_2$

Zumdahl's Fig. 12.11 & 12.13
Similar: K&T Fig.15.15

Leads to rxn

Leads to rxn

(4)   No rxn results

Collision must impart sufficient energy for rxn

1 step: 2 BrNO $\rightarrow$ $\left[\begin{array}{c}\text{(structure)}\end{array}\right]^{\ddagger}$ $\rightarrow$ 2 NO + Br$_2$

Transition state (‡)
- **not an intermediate…**
- reactant bond mostly broken
- product bond starting to form

Activation energy (E$_a$)
= minimum E a collision must have
  to be able to form transition state
  i.e., to break necessary bond(s)…
= an enthalpic quantity

Enthalpy

‡

E$_a$

products

reactants

ΔH_{rxn}

Rxn progress $\longrightarrow$

(5)
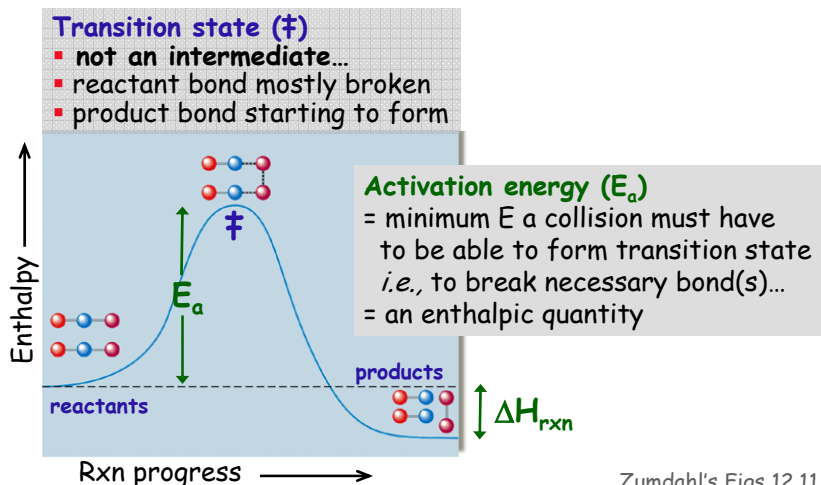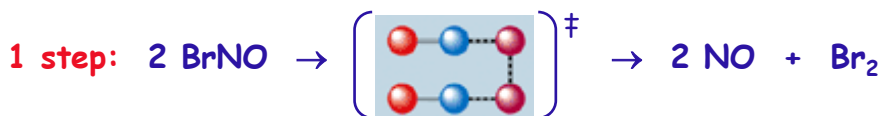
Zumdahl's Figs 12.11 & 13
See: Kotz Fig.15.13 & 15

Average kinetic energy increases with temperature…
When T ↑ $\Rightarrow$ # collisions with HIGHER ENERGY ↑!

Relative number of molecules with a given energy

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Lower temperature

Higher temperature

Minimum kinetic energy
required to react

T$_1$

T$_2$

Kinetic energy $\longrightarrow$
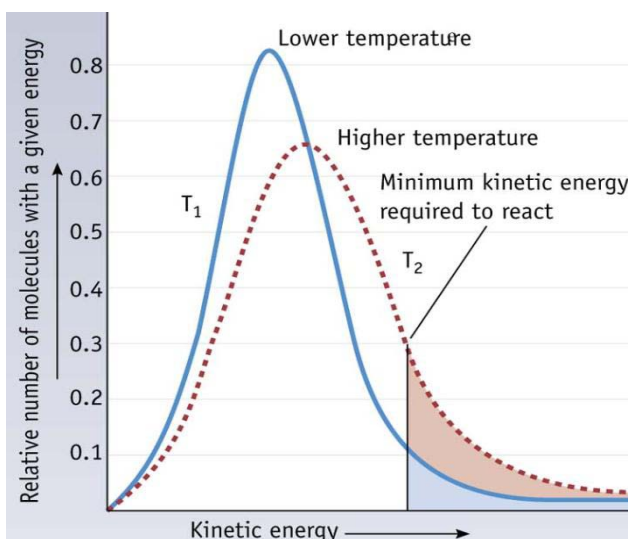
To perform a rxn
with a certain
activation
energy, E$_a$:

CHOOSE YOUR
TEMPERATURE
so that lots of
collisions will have
enough energy to
exceed E$_a$

(6)

K&T Fig. 15.12

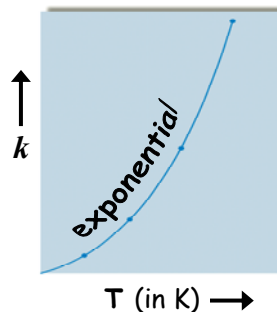## Looking inside a rate constant...

Arrhenius' Equation:

k = rate constant
A = frequency factor
E_a = activation energy
T = temperature
R = gas constant

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

fraction of collisions (< 1)
with sufficient energy (> E_a)
to reach transition state (‡)

k

exponential

T (in K) →

A = "frequency factor" :
how many potentially successful collisions?
relates to: fraction of total collisions (depends on T)
with correct geometry (specific to rxn)

$$\text{Rate} = k\,[\text{reactant}]^n = (A\, e^{-E_a/RT}) \cdot [\text{reactant}]^n$$

(7)

USING THE ARRHENIUS EQUATION:

Z.'s Fig. 12.14: T-dependence for
$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

Temperature dependence
of a reaction's rate constant
(found via ways discussed earlier)
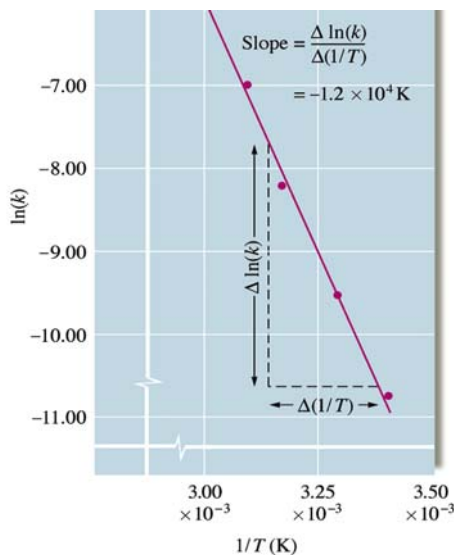lets us determine the
rxn's activation energy

$$k = A\, e^{-E_a/RT}$$
$$\Rightarrow \ln k = \ln A - (E_a/RT)$$

Plot: $\ln k$ vs. 1/T
Slope: $-(E_a/R)$

$\text{Slope} = \dfrac{\Delta \ln(k)}{\Delta (1/T)}$
$= -1.2 \times 10^4\,K$

ln(k)

−7.00

−8.00

−9.00

−10.00

−11.00

$\Delta \ln(k)$

$\leftarrow \Delta(1/T) \rightarrow$

3.00
×10⁻³

3.25
×10⁻³

3.50
×10⁻³

1/T (K)

If a reaction occurs three times as quickly at 50°C as it does at 20°C, what is the reaction's activation energy?

- Assume: rxn performed using same [reactant]$_o$ at both Ts
  - Implies: the RATE CONSTANT k is only thing that changes

  THUS: at T_1 = (273 + 20) = 293 K: rate constant = k_1
  at T_2 = (273 + 50) = 323 K: rate constant = $3k_1$

  To use T-dependence data: Arrhenius' eqn $\quad k = A\, e^{-Ea/RT}$

  Easiest to use in 'log' form: $\qquad\qquad \ln k = \ln A - E_a/RT$
  Same rxn $\Rightarrow$ E_a & A assumed constant

To compare the two temperatures:
- 2 equations, 2 unknowns (k & E_a)

$$\ln k_1 = \ln A - E_a/RT_1$$
$$\ln(3k_1) = \ln A - E_a/RT_2$$

- if subtract them, lnA disappears: $\quad \ln k_1 - \ln(3k_1) = -E_a/RT_1 - (-E_a/RT_2)$

(9)

If a reaction occurs three times as quickly at 50°C as it does at 20°C, what is the reaction's activation energy? ...continued...

$$\ln k_1 - \ln(3k_1) = -E_a/RT_1 + E_a/RT_2$$

Simplify: $\quad \ln\left(\dfrac{k_1}{3k_1}\right) = \dfrac{-E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$ 　　*review the rules for manipulating logs!*

Solve for E_a: $\quad E_a = \dfrac{-R\,\ln(1/3)}{(1/T_1 - 1/T_2)}$

$$E_a = \dfrac{-(8.314\ \text{J/mol}\cdot\text{K})\,\ln(1/3)}{(1/293K - 1/323K)}$$

$$= 28800\ \text{J/mol}$$

$\Longrightarrow \quad E_a = 30\ \text{kJ/mol} \quad$ *(1 SF)*

(10)

WATER is more stable
THERMODYNAMICALLY
i.e., $\Delta G_{rxn} < 0$ to form H_2O...

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

but: O_2 & H_2 are quite
     KINETICALLY stable
i.e., E_a is fairly large (SLOW!)
→ rxn doesn't occur at RT
→ a spark (high E) will initiate rxn...
→ energy evolved from the
   exergonic rxn provides energy
   required to keep rxn going...

E_a

H_2, O_2

ΔG

ΔE
H_2O

read as ΔG_{rxn}
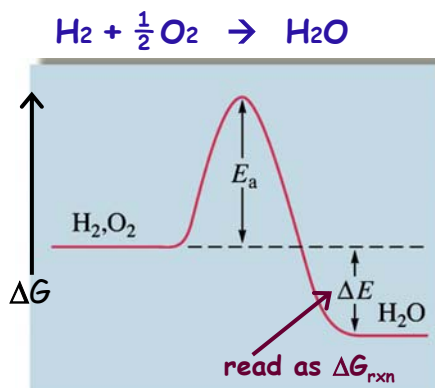
A physical analogy →

H

A

Zumdahl's
Figure 13.7

B
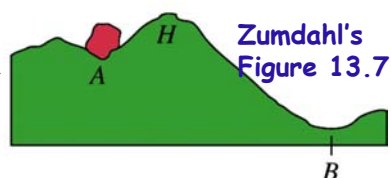
Factors that affect rxn rates:

1.) concentration
2.) temperature

3.) catalysts: "catalyze rxn" ⇨ increase rxn's rate
              work by changing the rxn's mechanism...
              ...such that ↑ reactant's kinetic instability

K&T Fig.15.5: metals can act as catalysts...
Solid MnO_2 catalyzes the exothermic
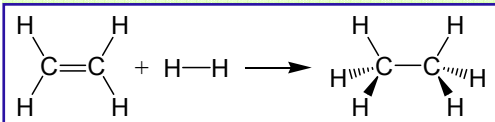decomposition of H_2O_2 into H_2O and O_2

$MnO_2(s)$

Bombardier beetle:
This rxn provides
hot, irritating spray
for defense

Catalytic hydrogenation of ethylene
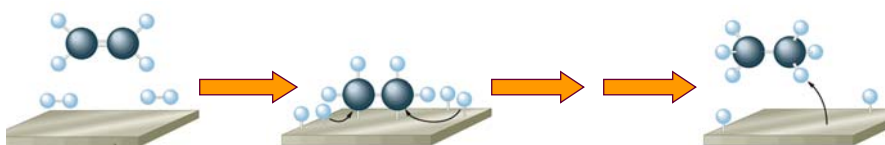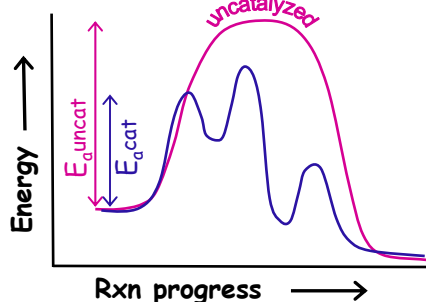(an example of heterogeneous catalysis)

Uncatalyzed rxn: one-step process
large E_a ⇨ <u>very</u> slow

When catalyzed by a metal surface:
⇨ rxn broken into several steps
⇨ **even slowest step has E_a < $E_{a}uncat$**
⇨ **rxn is <u>much</u> faster**

1. Adsorption & activation of reactants on surface of metal particles.
2. Rxn of adsorbed substances.
3. Desorption of products (leave catalyst).

Z's Fig. 12.17…same ideas Kotz Fig.15.15-16

Catalysis: increasing rxn rates, by "cheating" !
(*i.e.,* increasing kinetic instability of reactants)

A catalyst speeds up a reaction without being consumed overall.

<u>WHAT IS GOING ON??</u>   **Catalyst changes rxn's mechanism!**

Catalysts INTERACT with reactant molecules: (∴ rxn-specific…)

- push/pull on e^- density in molecules ⇨ ↑ polarity…*or other properties*
- catalyst-bound reactants react more EASILY
- AFTER RXN: products DISSOCIATE FROM catalyst
- catalyst is REGENERATED!

HOW TO FIND A CATALYST FOR YOUR RXN:

Trial & error…   followed by rational attempts to improve
- If understand rxn's mechanism: can predict what might help

- **Catalyst candidates:**
  - metal ions   → good at pulling on electrons
  - native metal surfaces → good at pulling on e^-s, breaking bonds…
  - protons   → good at attaching to lone pairs!
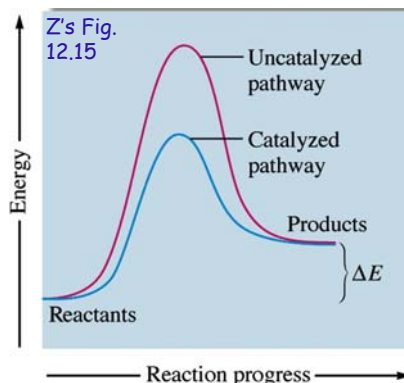 - species with lone pairs → good at pulling off H's…

(14)

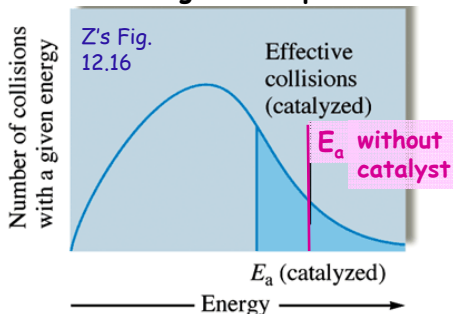## WHY CATALYSTS WORK...

RXN'S MECHANISM CHANGES!

A catalyst provides an
ALTERNATE RXN PATHWAY
with a **lower E_a**

⇨ ↑ rate constant ⇨ rxn goes faster...

*We would not call a substance a
catalyst if it did not do this.*

Z's Fig. 12.15

THUS: at a given temperature...

Z's Fig. 12.16

E_a **without catalyst**

E_a (catalyzed)

Catalyzed *vs.* **uncatalyzed** :
- the reactants are more *kinetically
unstable* due to interactions with
the catalyst
  ⇨ E_a is lower
- at a given temp., more collisions
  (blue shading, *vs.* right of pink line)
  have sufficient E to lead to rxn

Terms used to describe catalysts

Heterogeneous catalyst: in different phase than reactants
- *e.g.,* **Solid-supported metal catalysts in car exhaust systems
         (Pt compounds in catalytic converters)**
- Easily recovered to be used again!

Homogeneous catalyst: in same phase as reactants
- *e.g.,* **Digestive enzymes in stomach**
- Catalyst in solution with reactants
- Hard to separate from products afterwards...

Enzyme: Large molecule, usually a protein, that catalyzes
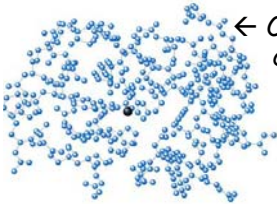   a specific <u>biological</u> reaction (or type of rxn)
- *e.g.,* **Alcohol dehydrogenase; α-galactosidase ("Beano!")**
- Substrate = molecule whose rxn the enzyme catalyzes

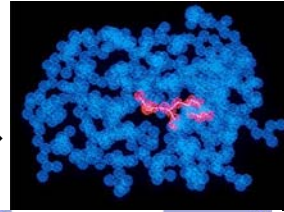*See Kotz 6th p.732 "A Closer Look" at Enzyme's, Nature's Catalysts*

(16)

ENZYMES = Proteins that act as specialized catalysts

← Carboxypeptidase-A
consists of 307 amino acids
& a Zn^{2+} ion

Enzyme with substrate →
(pink)

What carboxypeptidase-A
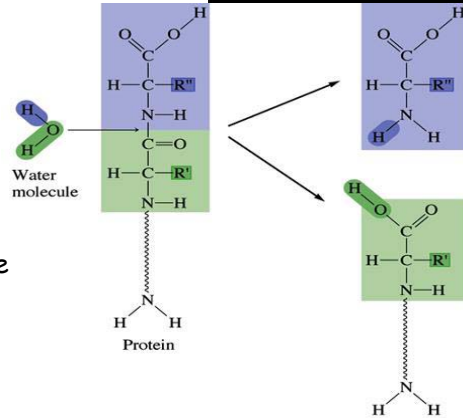catalyzes:

Rxn: removal of the terminal
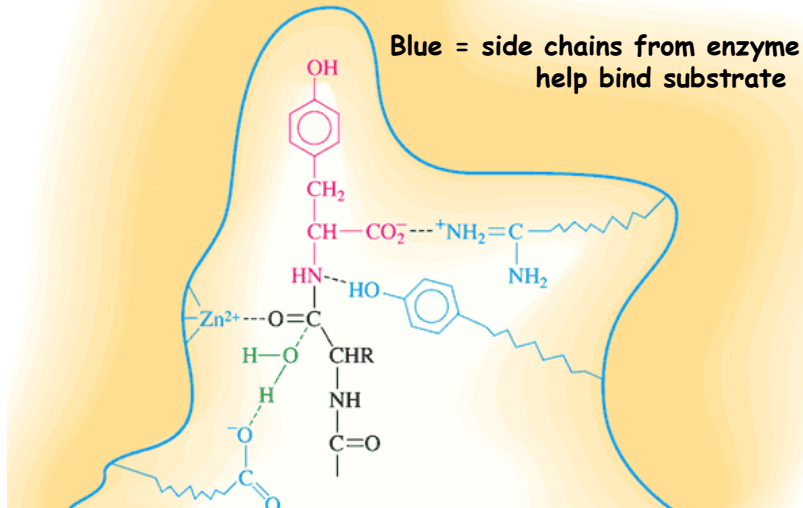(end) amino acid from a protein
by reaction with a H_2O molecule

Products = a free amino acid
and a new, smaller protein.

(17)

**Enzyme-substrate interaction
inside the "active site"**

**Substrate: black & red
red = terminal amino acid.**

**Blue = side chains from enzyme
help bind substrate**

COMBINING ALL KINETICS CONCEPTS...

Consider the reaction: $H_2(g) + I_2(g) \rightarrow 2HI(g)$
Its exp'tal rate law is: rate $= k[H_2][I_2]$

Which of the following statements are true?
If a statement is false, explain why it is incorrect.

(a) This is a second-order reaction overall.

(b) Raising the temperature will cause the value of k to decrease.

(c) Raising the temperature lowers the activation energy for the rxn.

(d) The reaction must occur in a single step.

(e) Adding a catalyst will cause the initial rate to increase.

(f) Adding a catalyst will increase the yield of HI.

(19)

ASSIGNED READINGS:

BEFORE NEXT CLASS:

Read: Ch.15 (all)

  + WORK ON Problems from Ch.15

MIDTERM EXAM: Fri. Feb.29th
covers: Ch. 6 (all), 9.8, 19.1-6, 13.1-5,
          14 (all), 15 (all)
practice general Qs, & midterms on website

(20)

Extra Ex.1: What about with a catalyst? *(from earlier)*

If a reaction (E_a = 30 kJ/mol) occurs 10x faster at 20°C when a catalyst is used, what is the catalyzed reaction's E_a?

- **Assume: rxn performed using same [reactant]$_o$. T is same.**
  - **Implies: k changes, new (lower) E_a...**
    BUT: rxn totally different with catalyst, so A changes too

  Phrased this way, we don't have enough information.
  - Known: relative k's, Temp., $E_a$uncat
  - Unknown: both A's, E_a(cat) (thus: 3 unknowns!)
  - Only have 2 equations, so can only solve 2 unknowns.
  - If had a real value for k(uncat), could solve A(uncat)
    ...and then all else would be solvable too.

NOTE: it's best to build your E_a-related problem-solving formulas
        from the ground up, using ln$k$ = lnA – E_a/RT
        & derive whatever you need from it via algebra...

        → don't memorize unnecessary formulas
        → be sure to think through knowns/unknowns
(21)   before blindly plugging into formulas!