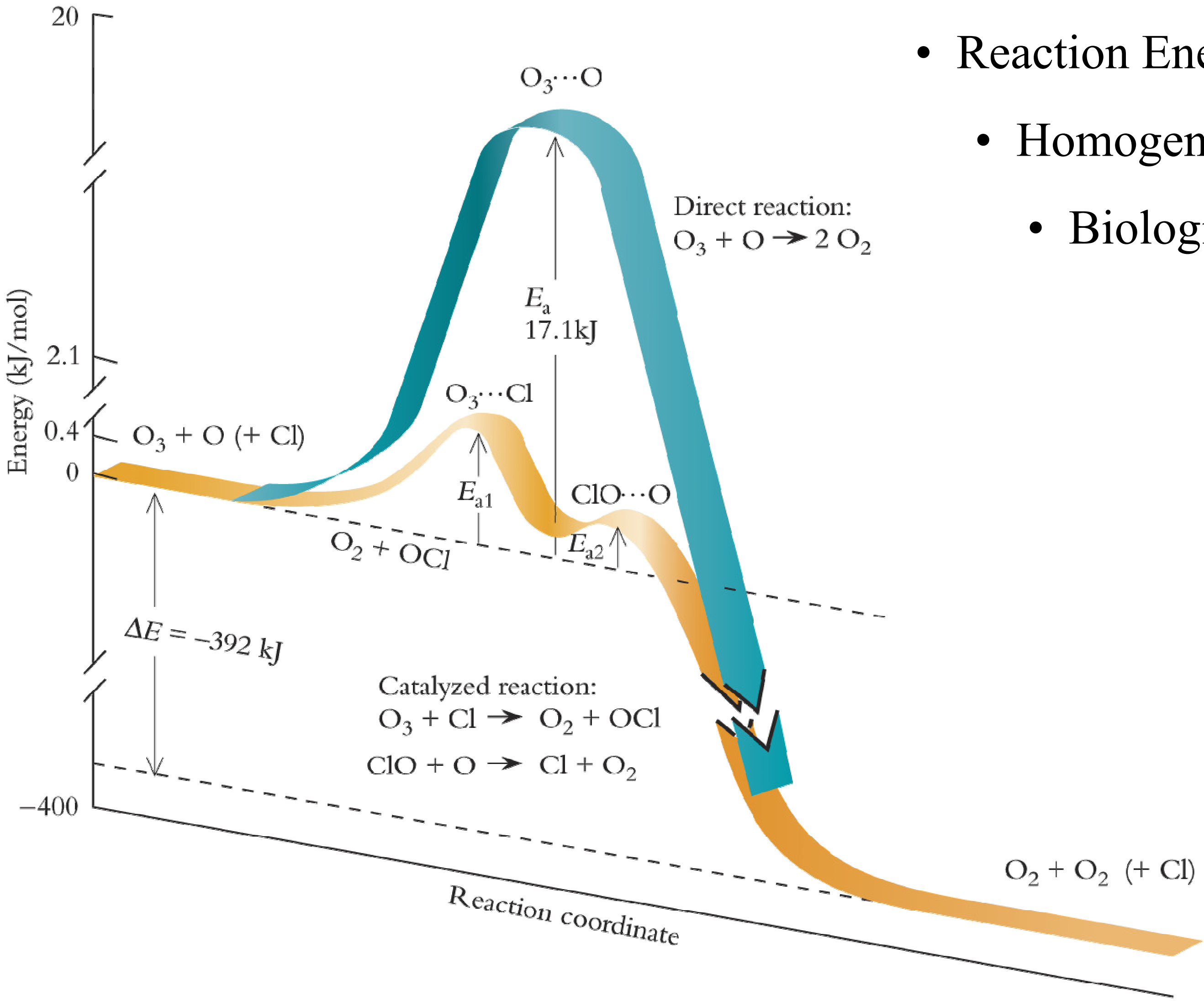
Lecture 12 – Chapter 15, Section 7
Catalysis

- Catalysis – definition and review
- Reaction Energy Profiles – modified
- Homogeneous vs. Heterogeneous
- Biological catalysts – enzymes



Catalyst

- A catalyst increases reaction rate without appearing in the OVERALL reaction

- Catalyst is still involved in the reaction
  - But, only with the transition state
  - Catalyst is does NOT affect reactants or products

If a catalyst does not affect reactants or products, what must be true?

20%	1. It makes ΔH_{rxn} more negative
20%	2. It makes ΔH_{rxn} more positive
20%	3. It makes ΔS_{rxn} more negative
20%	4. It makes ΔS_{rxn} more positive
20%	5. It has no effect on ΔH_{rxn} or ΔS_{rxn}

1	2	3	4	5

Catalyst – new mechanism

- A catalyst changes the reaction mechanism
- New mechanism will have a completely different transition state (but identical reactants and products)
- Thus, new mechanism has a different activation energy
- If catalyst is good, E_a will be much lower

$$k = Ae^{-\frac{E_a}{RT}}$$

- Catalyst also affects Arrhenius prefactor, A
  - But, this is much less important than E_a, so usually ignore this

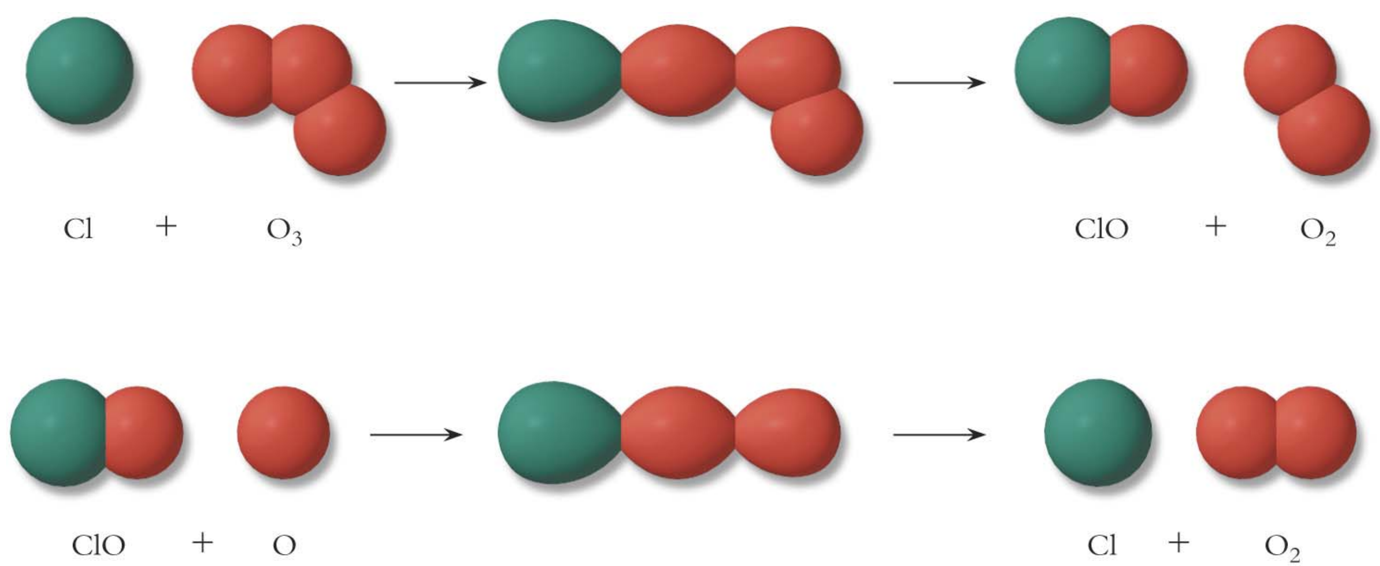
Example – Ozone

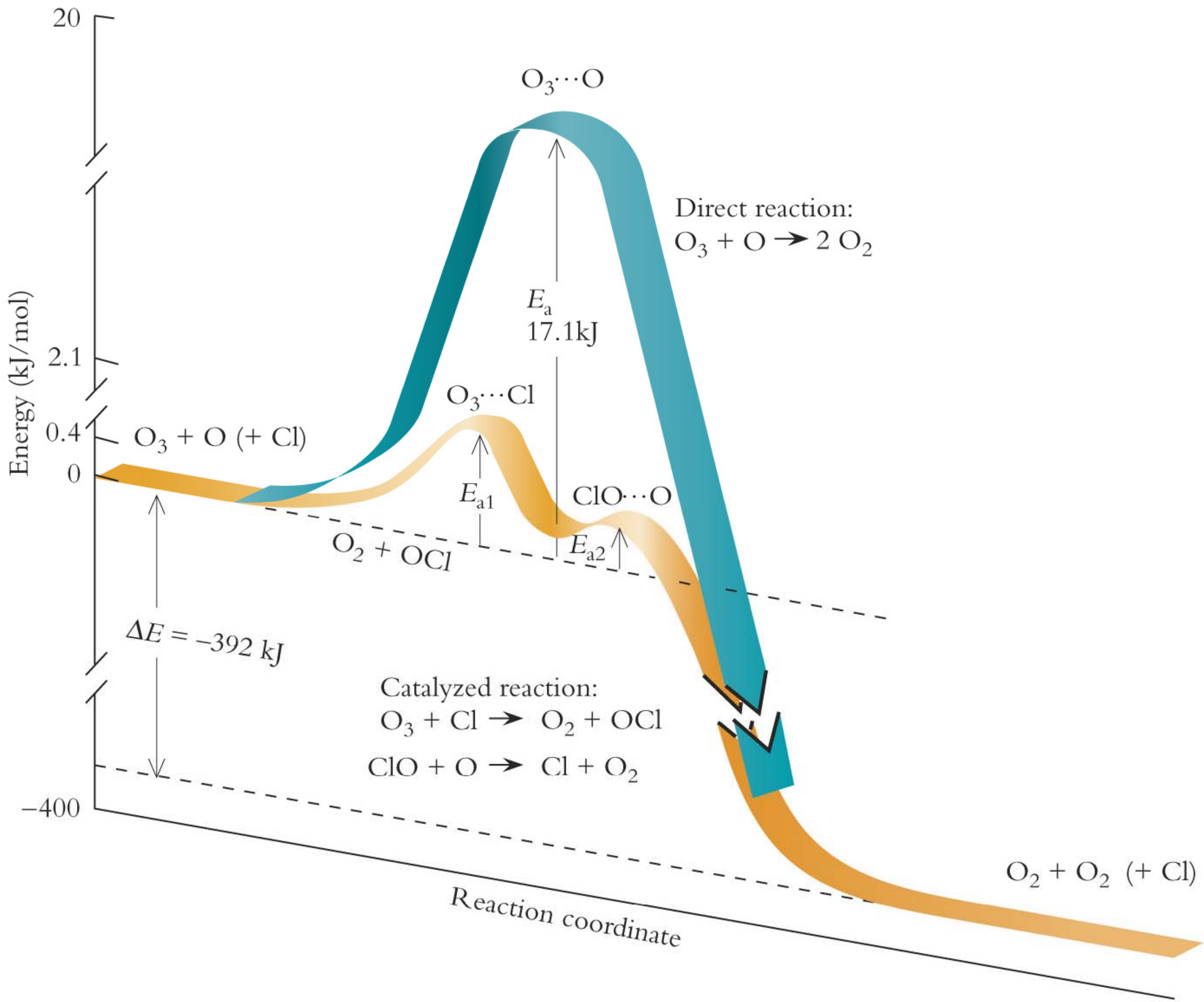
- Recall CFC's have big effect on atmospheric ozone levels

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$$

$$Cl + O_3 \rightarrow ClO + O_2 \qquad \text{(chlorine consumed)}$$

$$ClO + O \rightarrow Cl + O_2 \qquad \text{(chlorine regenerated)}$$





20
2.1
0.4
0
−400
Energy (kJ/mol)
O3···O
Direct reaction:
O3 + O → 2 O2
Ea
17.1kJ
O3···Cl
O3 + O (+ Cl)
Ea1
ClO···O
Ea2
O2 + OCl
ΔE = −392 kJ
Catalyzed reaction:
O3 + Cl → O2 + OCl
ClO + O → Cl + O2
O2 + O2 (+ Cl)
Reaction coordinate

Compare rates

- Uncatalyzed reaction:

$O_3 + O \rightarrow 2O_2$ $E_a = 17.1$ kJ/mol $k = 4.1 \times 10^5\ (Ms)^{-1}$

(rate per O_2) $k = 8.2 \times 10^5\ (Ms)^{-1}$

- Catalyzed reaction:

$O_3 + Cl \rightarrow O_2 + OCl$ $E_{a1} = 2.1$ kJ/mol $k = 5.2 \times 10^9\ (Ms)^{-1}$

$ClO + O \rightarrow Cl + O_2$ $E_{a2} = 0.4$ kJ/mol $k = 2.2 \times 10^{10}\ (Ms)^{-1}$

- Note that uncatalyzed reaction still occurs
  - Presence of catalyst provides a faster pathway, doesn't prohibit anything

Suppose a reaction (at STP) has a rate of 4.6×10^4 $(Ms)^{-1}$ and an activation energy of 15 kJ/mol.

If a catalyst speeds the reaction up to 7.5×10^6 $(Ms)^{-1}$, what must the new activation energy be? (Assume that *A* does not change.)

20%	1. -13 kJ/mol
20%	2. 2.4 kJ/mol
20%	3. 3.4 kJ/mol
20%	4. 15 kJ/mol
20%	5. 16 kJ/mol

1	2	3	4	5

Heterogeneous vs. Homogeneous

- In ozone example, the catalyst was same phase as reactants and products (all gasses)
  - Homogeneous
- Often catalyst is a different phase
  - For example, car catalytic converter is solid phase catalyzing gas phase reactions
  - Haber process involved solid phase catalyst with gas phase reaction
  - Heterogeneous

Example 2 – catalytic converter

- Nifty engineering catalyzes several reactions in one device

$$2\ CO + O_2 \rightarrow 2\ CO_2$$
$$\text{various hydrocarbons} + O_2 \rightarrow CO_2 + H_2O$$
$$2\ NO \rightarrow N_2 + O_2$$

- All gas phase reactions, catalyzed by several different solid phase catalysts
  - Mostly platinum
  - Also CuO, Cr_2O_3, palladium, rhodium

Heterogeneous mechanism

Separation of phases makes mechanism of heterogeneous catalysts slightly more complicated

1. Reactants bind to surface of catalyst (**adsorption**)
   a. Interaction with surface weakens bonds in reactants
2. Bound reactants wander over 2-D catalyst surface
3. Bound reactants collide and react
4. Products escape from surface of catalyst (**desorption**)

Enzymes

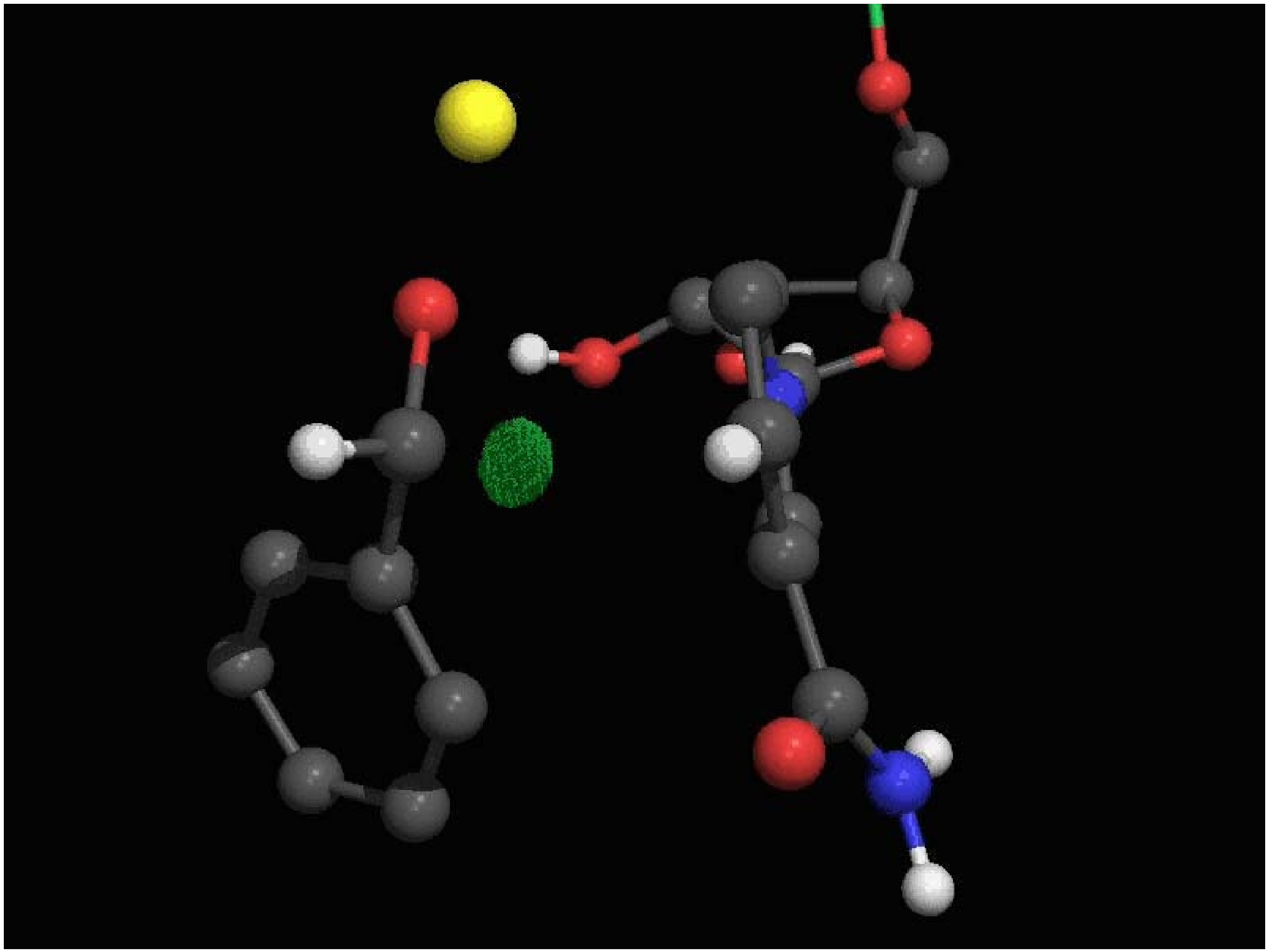
- Simply biological catalysts
- Almost always heterogeneous catalyst
  - Reactants and products are dissolved in solution
  - Catalyst acts as a solid (though also usually dissolved in solution)
- Reactant that **binds** (absorbs) to enzyme is called the **substrate**
- Particular way the enzyme interacts with substrate stabilizes the transition state – lowers activation energy

Enzyme mechanism

- Called the Michaelis-Menten mechanism
- Looks just like general heterogeneous mechanism we had before
  1. Substrate binds to enzyme   E + S → ES
  2. E-S interactions change shape   ES → E···S
  3. React to form products   E···S (+ R) → E···P
  4. Product is released   E···P → E + P

- Overall reaction is either E + S → E + P
  or E + S + R → E + P
  – So, enzyme does not 'take part' – catalyst

Enzyme example - LADH



Today

- Finish CAPA #7 (due tomorrow)
- Get extremely serious about exam review

Wednesday

- We'll review together
- Please work lots and lots of problems