

Unit 3

???

3.1 Lecture 12: Intro to Catalysis

- 4/26:
- We're now moving from theoretical chemistry to some applications (namely catalysis) of the theory we've been learning.
 - History of defining catalysts:
 - Berzelius (in 1836) becomes interested in this behavior.
 - Ostwald (in 1894) defines a **catalyst**.
 - **Catalyst**: A substance that increases the rate of a chemical reaction without being consumed.
 - Energetically, this must happen by altering the transition state (this is a simplistic explanation).
 - The thermodynamics (ΔG , ΔS , and ΔH) are unaffected.
 - The kinetics (ΔG^\ddagger , ΔS^\ddagger , and ΔH^\ddagger) are reduced.
 - More realistically, a catalyst often substantially changes the reaction coordinate (one big hump in the energy diagram to many small humps).
 - The general set of intermediates during the reaction is the starting material plus the catalyst ($S + C$), the starting material-catalyst complex ($S \cdot C$), the product-catalyst complex ($P \cdot C$), and the product plus the catalyst ($P + C$).
 - Note that ΔG^\ddagger is the activation energy for the highest barrier step, as measured against the free energy of the reactants. This notably implies that ΔG^\ddagger is not necessarily the E_A of the *first* step; only the biggest. See Figure 3.2b.
 - Even though there are more steps, the rate increases because ΔG^\ddagger decreases.
 - If you get stuck at a low energy intermediate, this can reduce reaction rate, and the process is no longer being catalyzed.
 - Indeed, if your catalyst is a different structure at the end of the reaction, it's not a catalyst but a reagent.
 - Excessively stabilizing the starting materials can create a higher energy barrier to the products.
 - Example:

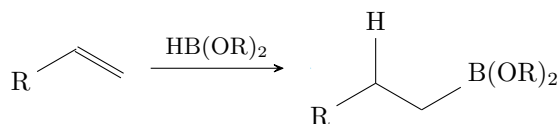


Figure 3.1: A process to be catalyzed.

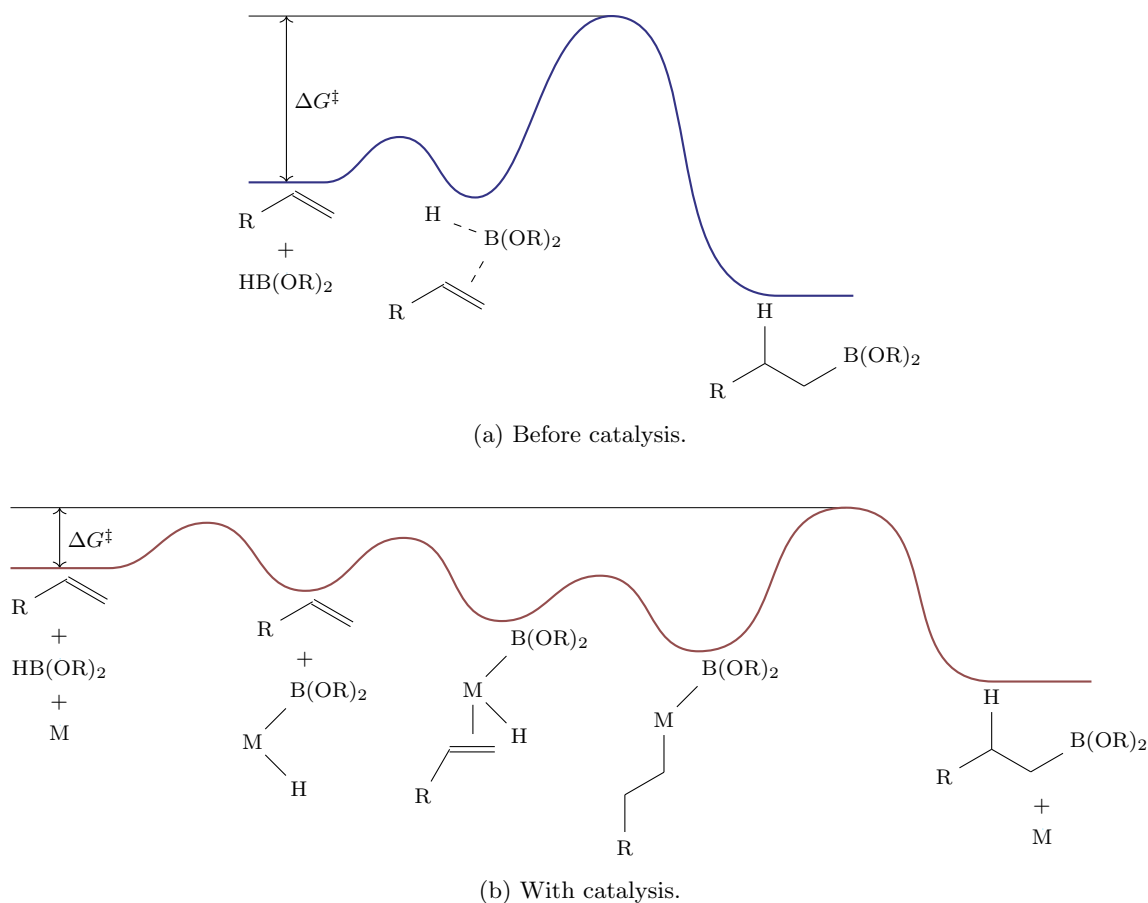


Figure 3.2: Catalysis energy diagrams.

- With transition metal catalysts, we have many more steps but potentially a lower ΔG^\ddagger .
- Anatomy/terminology of a catalytic cycle.

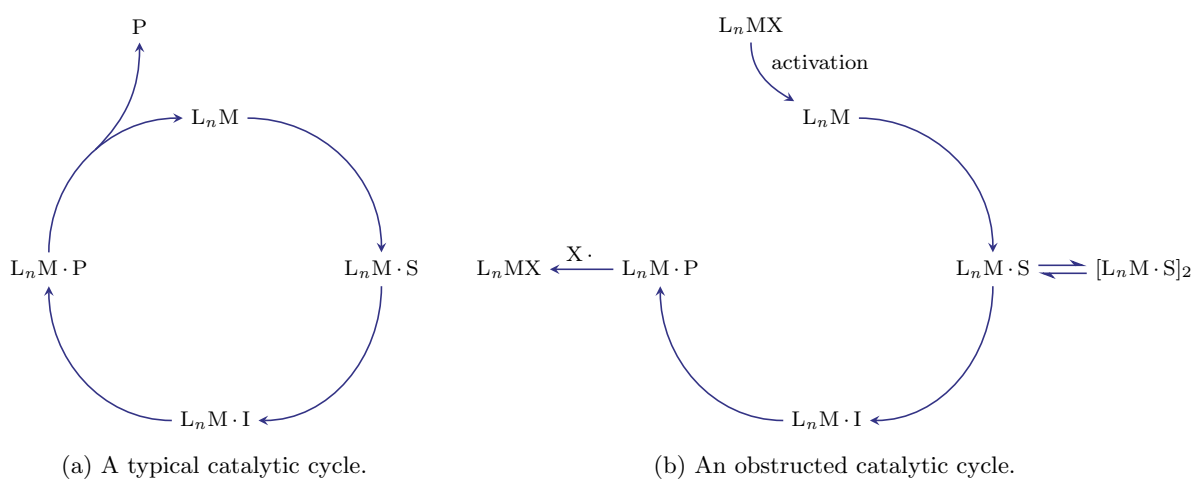


Figure 3.3: The anatomy of catalytic cycles.

- Simplistically, a catalytic cycle occurs as in Figure 3.3a.

- However, catalytic cycles can be complicated by **catalyst precursors**, **inactive off-cycles**, and **inactive poisoned states**.
- **Catalyst precursor:** A complex that must go through an activation step before it can be used as a catalyst.
 - See the reactant that becomes L_nM in Figure 3.3b.
- **Inactive off-cycle:** A reversible reaction that an intermediate participates in that is different from the intended reaction.
 - See the alternate pathway that $L_nM \cdot S$ participates in in Figure 3.3b.
- **Inactive poisoned state:** When an intermediate follows an alternate nonreversible reaction pathway.
 - See the alternate pathway that $L_nM \cdot P$ participates in in Figure 3.3b.
- Gives two examples of activating a catalyst (just a chemical reaction where one product is the catalyst).
 - A Pd^{2+} precursor must often be activated into a Pd^0 catalyst.
- **Turnover number:** The quotient of the moles of product and the moles of catalyst. *Also known as TON.*
- **Turnover frequency:** The quotient of the TON and time. *Also known as TOF.*
- Kinetics:
 - The rate constant for individual steps can vary, but at a steady state (where the catalyst is transforming the substrate as fast as possible), the rates must be identical.
- **Catalyst resting state:** The highest concentration form of the catalyst.
 - Can also be off-cycle or dormant.
 - The rate constant after it (i.e., the rate constant of the **turnover limiting step**) is the smallest among all rate constants for steps.
- **Turnover limiting step:** The step which proceeds from the catalyst resting state. *Also known as rate-determining step.*
- Heterogeneous vs. homogeneous catalysis:

Heterogeneous	Homogeneous
Solid state (2 phases).	Solution phase.
Robust (high pressures and temperatures are ok).	Selective.
Low-cost.	Tunable.
Easy separation.	Easy to study (comparatively).

- We distinguish between the two with **transmission-electron microscopy**, kinetics, a **filtration test**, a **mercury drop test**, and/or a **three-phase test**.
- **Transmission-electron microscopy:** Looks for nanoparticles. *Also known as TEM.*
- Kinetics: We need to observe soluble intermediates and show that they are **kinetically competent**.
- **Kinetically competent:** The step from the soluble intermediates to the products under another reagent must be at least as fast as the overall rate of catalysis.

- **Filtration test:** For heterogeneous catalysts. Do the reaction over the heterogeneous catalyst, filter out the solid heterogeneous catalyst, add in more substrate and see if the mother liquor or supernatant still catalyzes the reaction. If so, then something is leaching out of the catalyst.
- **Mercury drop test:** Mercury can typically block the pores of high-surface area catalysts or poison the cycle by forming TM alloys. *Also known as Hg-drop test.*
- **Three-phase test:** Attach a substrate to an insoluble support. If the catalyst is solid state, we see no reaction (poor phase mixing).
 - The gold standard.
- Asymmetric catalysis:
 - Propene is pro-chiral (it has a Re and a Si face) at the central carbon.
- **Dynamic kinetic resolution:** When a racemic mixture goes to an enantioenriched product.
 - Occurs when an achiral intermediate is accessed and selectively filtered into an enantioenriched product.
- **Kinetic resolution.** When a racemic mixture goes to an enantioenriched starting material and enantioenriched product.
 - Arises from selective reaction with one enantiomer over another.
- **Enantiomeric excess:** The quantity given by the following formula. *Also known as ee.*

$$\frac{[\text{major en.}] - [\text{minor en.}]}{[\text{major en.}] + [\text{minor en.}]} \times 100\%$$

- Enantiomeric ratio:

$$\frac{[\text{major en.}]}{[\text{minor en.}]} = e^{-\Delta\Delta G^\ddagger/RT}$$

- Note that $\Delta\Delta G^\ddagger$ is the difference in the ΔG^\ddagger values for the major and minor enantiomers.

- Ee is dependent on $\Delta\Delta G^\ddagger$ and T :

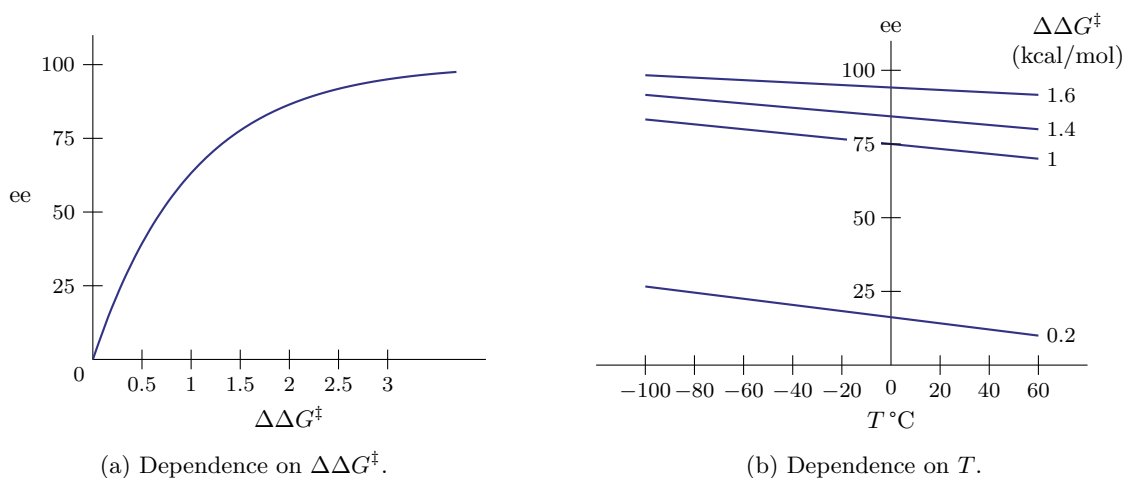


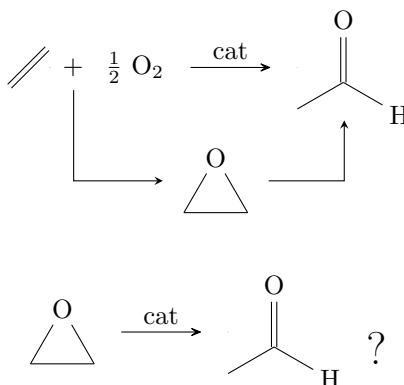
Figure 3.4: Dependence of ee on $\Delta\Delta G^\ddagger$ and T .

- Some enantiomers have differing catalytic properties.

- Furthermore, chirality is not necessarily set at the RDS.
- If A and B are two enantiomers, then it is possible that ΔG^\ddagger will differ for the formation of $M \cdot A + B$ vs. $M \cdot B + A$ (remember that this difference is $\Delta\Delta G^\ddagger$).
- If the activation energy required to form $M \cdot A + B$ (for example) is greater than that required to get from $M \cdot A + B$ to the products, formation of the $M \cdot A + B$ intermediate will be irreversible.
 - In this case, the kinetic product will be favored.
- If the activation energy required to form $M \cdot A + B$ (for example) is less than that required to get from $M \cdot A + B$ to the products, formation of the $M \cdot A + B$ intermediate will be reversible.
 - In this case, the thermodynamic product will be favored (we may see more of the intermediate that forms quickly, but in time, more of the other product will be formed because formation of the other product is irreversible^[1]).

3.2 Office Hours (Anderson)

- What does kinetically competent mean?



- Consider the reaction of ethylene and $\frac{1}{2} O_2$ with a catalyst to make acetaldehyde.
- We propose that the intermediate is an epoxide.
- To test this hypothesis, we take ethylene oxide and react it with the catalyst to see if it makes acetaldehyde.
- If it does, that's a good first step. If it reacts with a rate at least as fast or faster than the overall catalyzed reaction, then we know that this intermediate *is* an intermediate in a catalytic cycle.
- Essentially, this test confirms that an intermediate is one. If the rate of epoxide to product is at least as fast as the overall rate, then we're good.
- What do all of those tests test for? I.e., if we find nanoparticles with TEM, what does this mean?
 - We need all of these tests because none of them are definitive.
 - You can never prove a mechanism; you can only disprove it.
 - If you see nanoparticles with TEM, it might make you ask if a heterogeneous pathway is present.
 - You go through these experiments to try to determine that it's *not* homogeneous or *not* heterogeneous.
- Resources for synthesis?
 - Inorganic is not like organic where we're pushing electrons and stuff.

¹Think the Mrs. Meer pens example.

- Don't worry about step efficiency.
- Don't worry about reactive fragments.
- For syntheses, completely ignore mechanism. Just balance the reaction.
 - Balance in terms of electrons and atoms.
 - Just focus on stoichiometry to start.
 - 99% of the time, this will get you to the right conclusion.
- If you have methyl iodide and you want to methylate the metal center, you want to make the metal nucleophilic and then react it.
- If you want to be really lazy, just show the reagents that will give you the products and be done.
 - You'll probs lose a few points for this, but that's ok.
 - Try and show the intermediates.
- Time crunch?
 - Skip a question.
 - Go through the easiest questions first.
 - You can probably get 80% of the points on the first question without writing a single synthesis.
 - Do the easy things fast and then move on.
 - View it as a scavenger hunt for points.