Unit 2 – Day 6

Exam 2 - Review

KINETICS

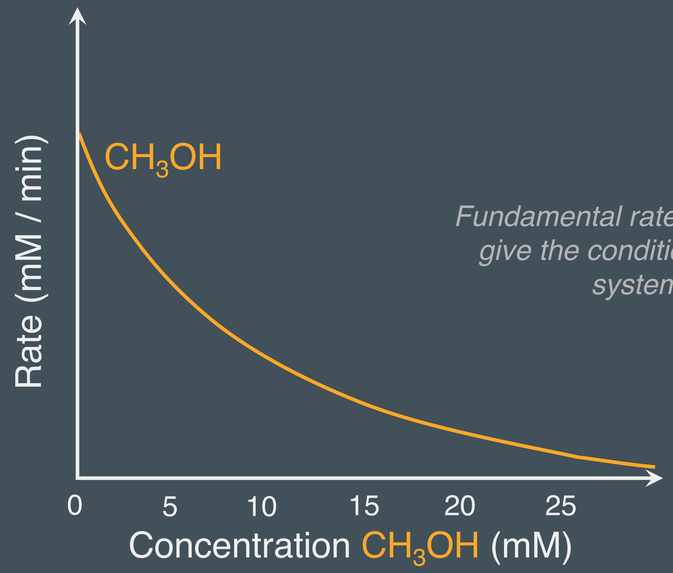
Kinetics

- Measuring rates of reaction, average, initial, instantenous, macroscopic (concentration), microscopic (k, molecular probabilities, molecularity)
- 4 factors that effect rate
- Engineering considerations
- Experimental rate laws from Initial rates
- Order of reaction
- Integrated rate laws and half lives
- Radioactivity
- Mechanism, elementary reactions, molecularity
- Rate laws from mechanisms (RDS and SSA)
- Mechanisms are models or “stories” we tell. We check to confirm they are consistent with experimental rate laws
- Arrhenius Law (Temperature dependance)
- Collision theory
- Sterics (complicated but we’ll leave it as very bulks compounds often react more slowly than smaller reactants
- Transition state theory
- Reaction coordinate diagrams (relations between ΔG, Ea forward, Ea reverse, kf, kr, Keq, reactants, products, reactive intermediates, RDS, would you need SSA to write the rate law?
- Catalysis: Heterogeneous, Homogenous, poisons, enzymes, true poisons, Michaelis-Menten Kinetics, rxn coordinate diagrams of catalytic reactions

Integrated Rate Laws

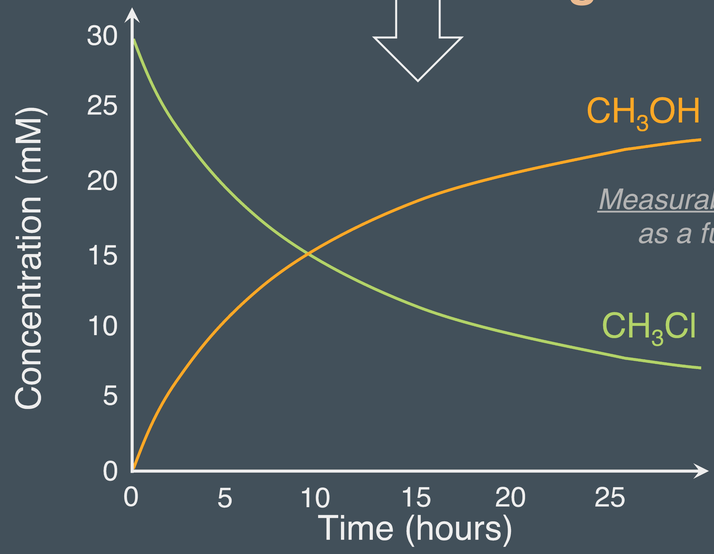
Rate law: relates the *rate* of reaction *to the concentration* of reactants, as in *rate* = $k[A]^x[B]^y$; A and B are reactants. Rate laws tell us the instantaneous rate given the current concentrations.

Integrated rate laws show *concentration as a function of time*. Calculate how much reactant is left after a time (t) has passed, or how much time (t) is required for a certain amount of reactant to react.

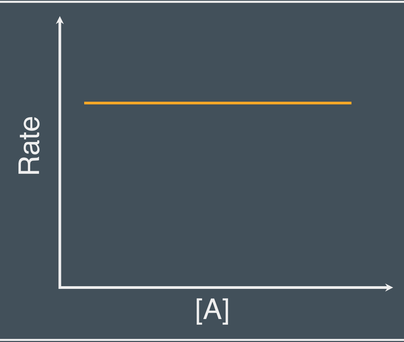
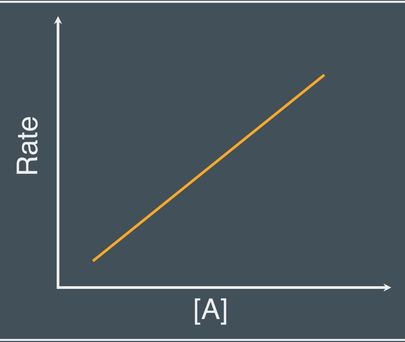
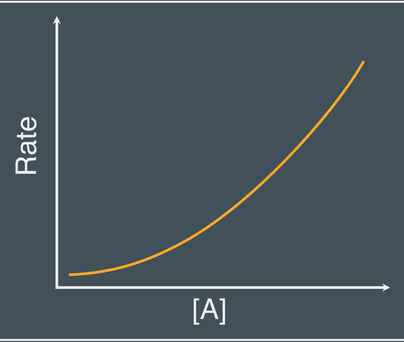
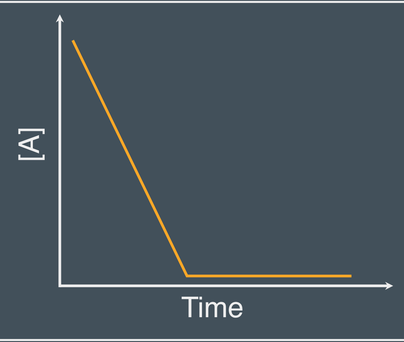
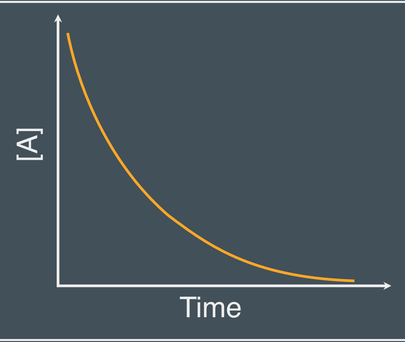
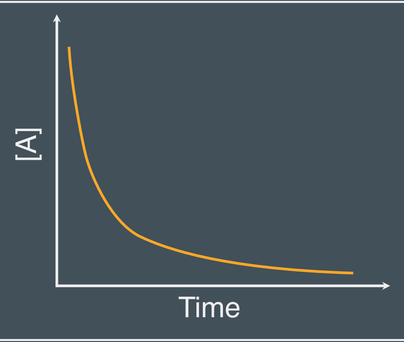
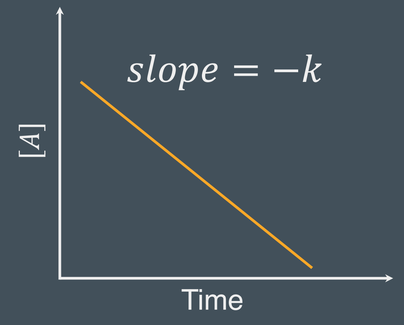
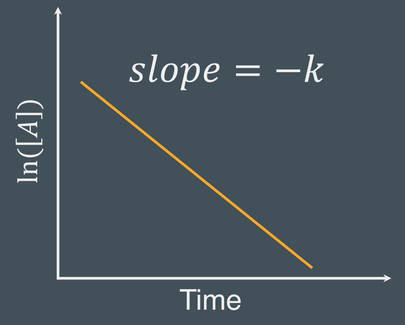
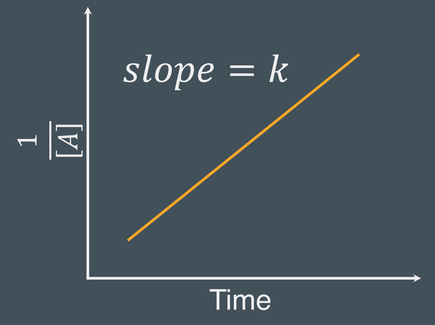


Fundamental rate of reaction give the conditions of the system

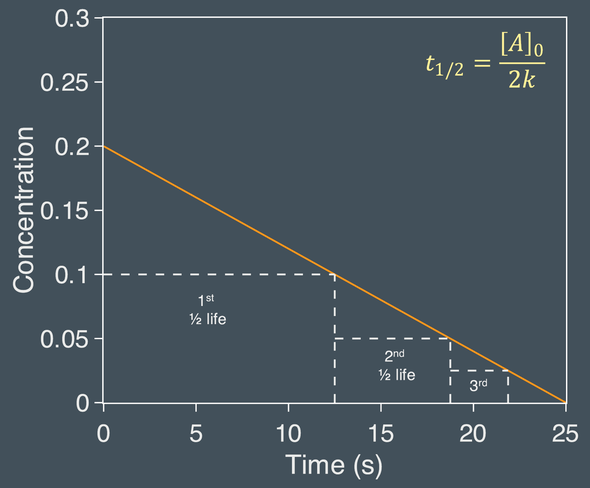
Integration

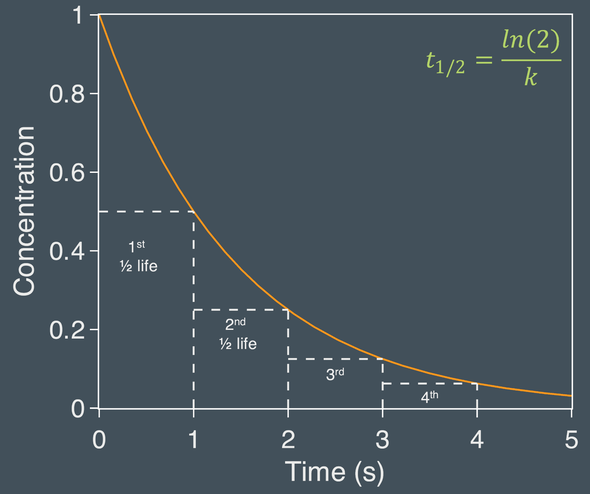


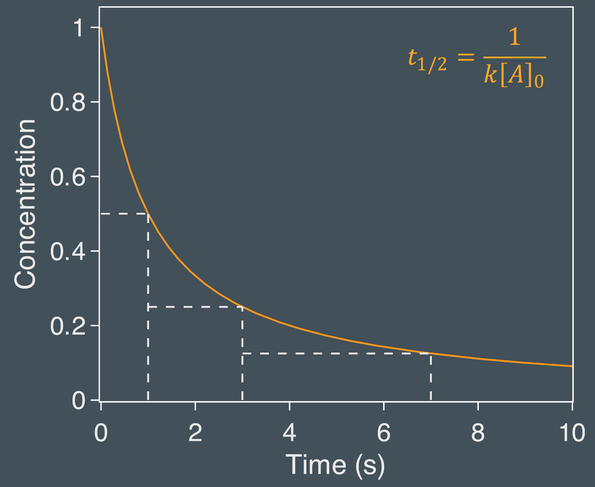
Measurable concentrations as a function of time

Order	Zeroth order	First order	Second order
Rate law	$rate = k[A]^0 = k$	$rate = k[A]^1$	$rate = k[A]^2$
Rate vs [A]			
[A] vs time			
Integrated rate law	$[A] = [A]_0 - kt$	$\ln([A]) = \ln([A]_0) - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Linearized integrated rate law plot			

Order and Half-lives







Zero order: As [A] ↓, $t_{1/2}$ ↑

First order:

As [A] ↓, $t_{1/2}$ **remains constant**

Second order:

As [A] ↓, $t_{1/2}$ ↑

Radioactivity

	Zeroth order	**First order**	**Second order**
Rate law	$rate = k[A]^0 = k$	$rate = k[A]^1$	$rate = k[A]^2$
Integrated rate law	$[A] = [A]_0 - kt$	$\ln([A]) = \ln([A]_0) - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Units of k	$\frac{M}{s}$	$\frac{1}{s}$	$\frac{1}{M \cdot s}$
First half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln(2)}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

K_{eq} can be defined using rates of reaction

At equilibrium, the rates of of the forward and reverse overall reactions are equal

$$@\ K_{eq} \rightarrow \frac{rate_{forward}}{rate_{reverse}} = 1$$

For an elementary reaction: $K_{eq} = \frac{k_{forward}}{k_{reverse}}$

With multiple elementary steps:

$$K_{eq} = \frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}} \frac{k_3}{k_{-3}} \ldots$$

When $K \gg 1$, the rate constant for the forward reaction is much larger than the rate constant for the reverse reaction. The rates are equal at equilibrium. This is a product favored reaction.

When $K \ll 1$, the rate constant for the reverse reaction is much larger than the rate constant for the forward reaction. This is a reactant favored reaction.

Chain reaction

A highly reactive intermediate reacts to produce another highly reactive intermediate, which reacts to produce another, and so on.

In this context, the intermediate is referred to as the chain carrier

Examples:

- Radical chain reaction (chain carrier = radical)
- Radical polymerizations
- Nuclear Bomb (chain carrier = neutron)

Initiation	$H_2 \xrightarrow{\Delta} H\bullet + H\bullet$	(might be fast, might be slow)
Branching	$H\bullet + O_2 \rightarrow HO\bullet + \bullet O\bullet$	
Branching	$\bullet O\bullet + H_2 \rightarrow HO\bullet + H\bullet$	

The nature of explosions

Type 0: Over-pressurization

$$2\,H_2O_2\,(aq) \longrightarrow H_2O\,(l) + O_2\,(g)$$

A gas evolving reaction in a sealed container

Type 1: Thermal explosion

$$CH_4 + 2O_2 \longrightarrow 2H_2O + CO_2 + \Delta$$

A reaction generates heat. Heat speeds up the reaction in a positive feedback loop.

Type 2: Branched-chain explosion

$$H_2 + O_2 \longrightarrow H_2O + \Delta$$

$$H_2 \rightarrow H\bullet + H\bullet \qquad \text{(initiation)}$$

$$H\bullet + O_2 \rightarrow HO\bullet + \bullet O\bullet \qquad \text{(branching)}$$

$$\bullet O\bullet + H_2 \rightarrow HO\bullet + H\bullet \qquad \text{(branching)}$$

1 reactive intermediate in, 2 reactive intermediates out

Rate of Reaction

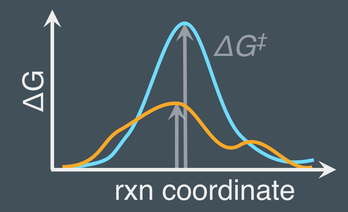
There are *4 chemical factors* that affect the speed of a reaction:

1. **Concentration –** Concentration increases, # collisions increase, reaction rate increases.

2. **Medium –** diffusion: gas > liquid > solid. Reaction rates between phases increase as the surface area of their interface increases (*e.g.* fine powder dissolve faster than large crystals).

3. **Temperature –** reactant molecules have more energy at higher temperatures, therefore a larger number of reactant molecules can get over the activation energy hump.

4. **Catalysis –** some species can speed up the rate of a reaction but are not used up in the reaction. How does this happen?
(We'll talk about catalysts later.)

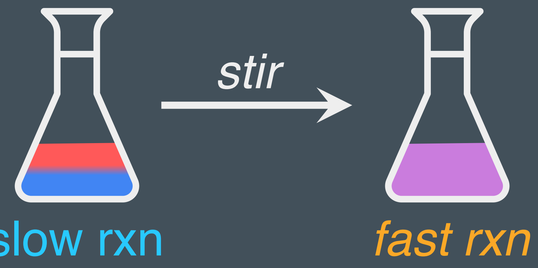


Rate of Reaction

There are *2 engineering factors* that affect the speed of a reaction:

1. **Thermal Transport** – when you heat a pot of water the water at the top is colder than the water at the bottom.

2. **Mass Transport –** stirring makes inhomogeneous solution homogenous. Homogenous solutions of reactants usually react faster.

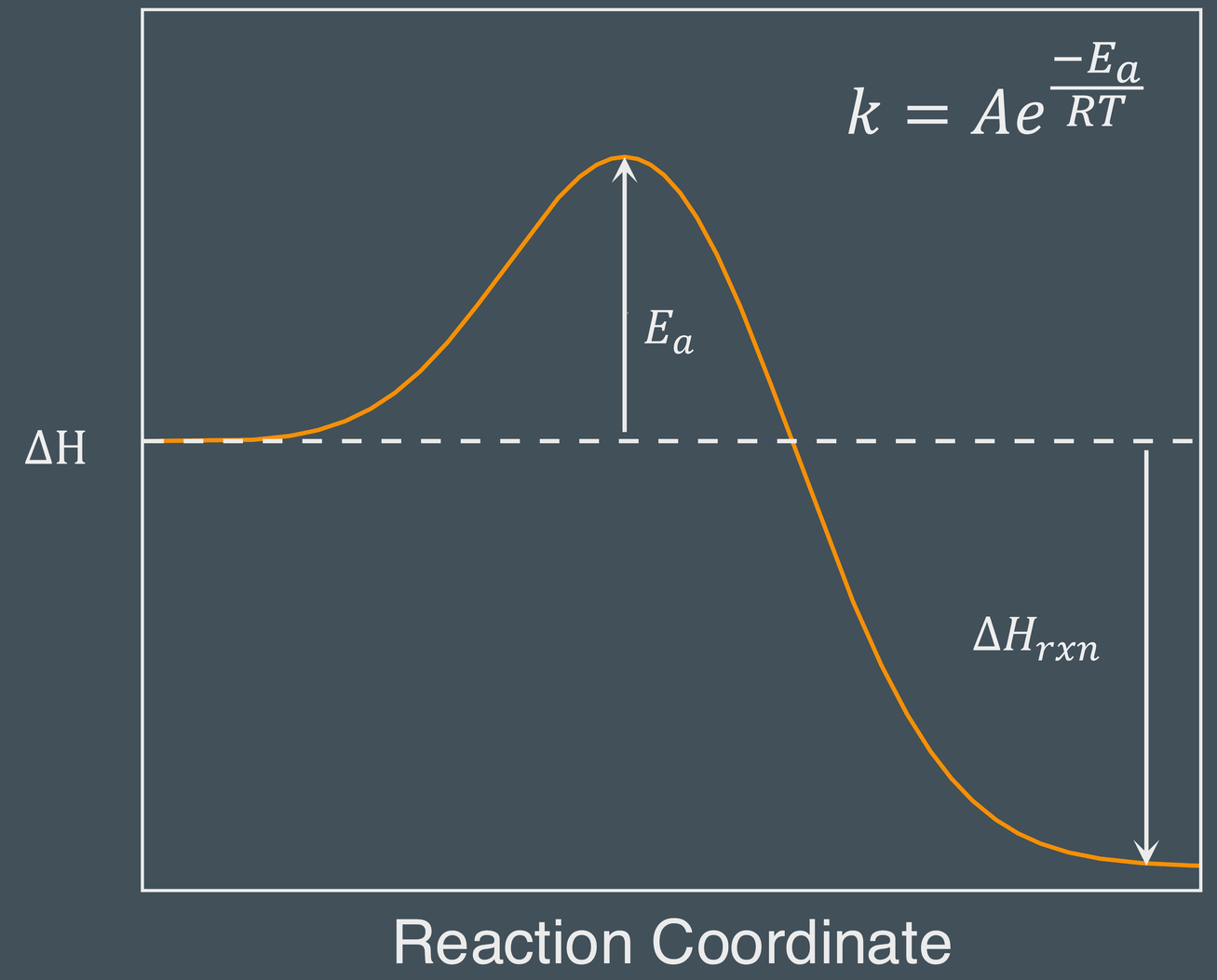


Definitions – Components of Arrhenius relation

DEF pre-exponential factor ***A*** : the rate constant at infinite temperature, or the theoretical maximum reaction rate possible.

DEF Activation Energy $\mathbf{E_a}$: the minimum amount of energy that the reactants need in order to undergo a chemical reaction

DEF Reaction Coordinate : Progress of a reaction describe at each point as a particular arrangement and trajectory of atoms and molecules in space



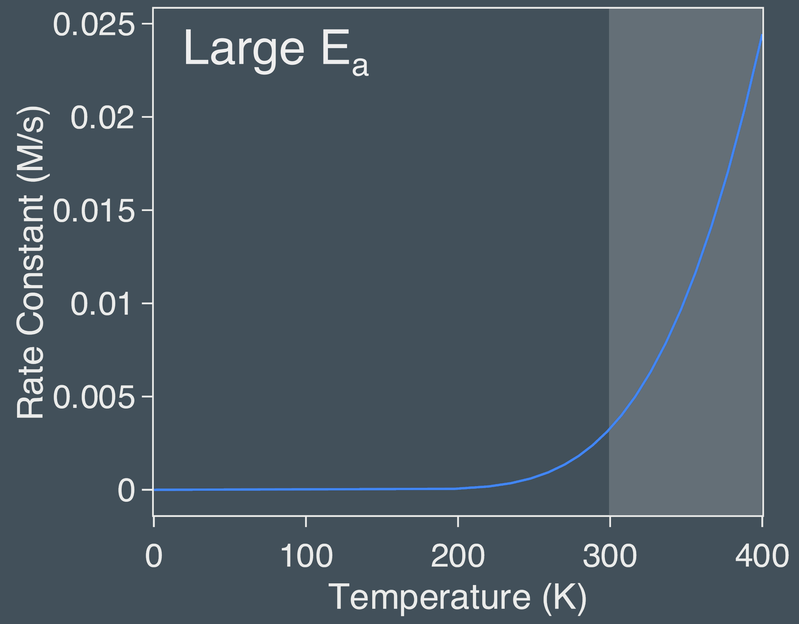
E_a vs. rate constants

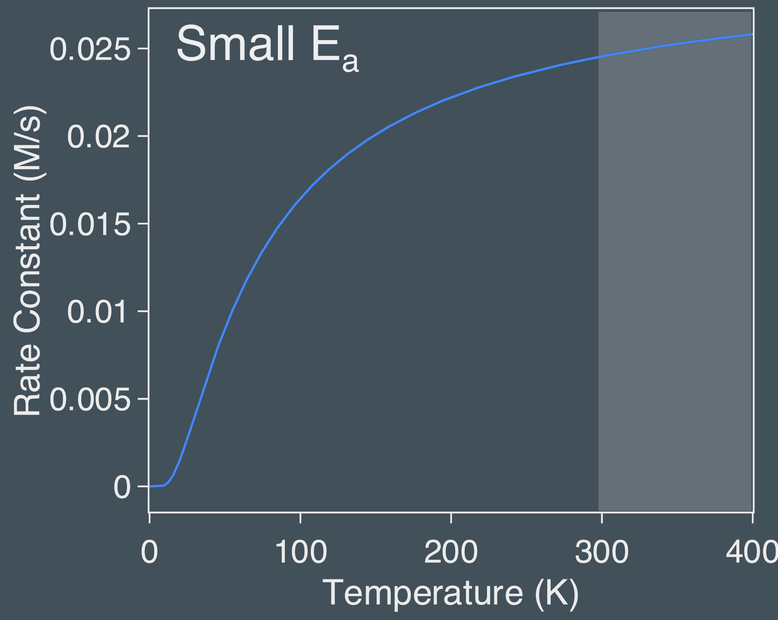
The higher the activation energy, the stronger the temperature dependence of the rate constant

- Low activation energies ≈ 10 kJ/mol — temperature “independent”
- High activation energies ≈ 60 kJ/mol — temperature “dependent”

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

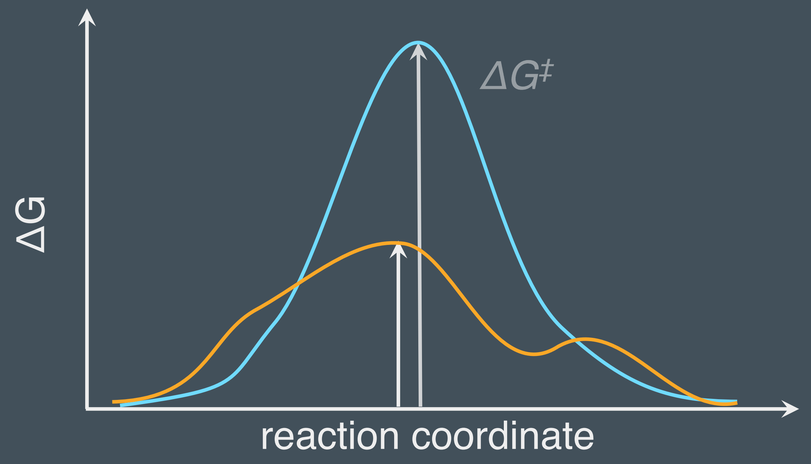
We can use the relationship between activation energy and temperature to predict rate constants





Rate of Reaction

There are 4 factors that affect the speed of a reaction:

#4 Catalysts

speed up the rate of a reaction by providing an alternate mechanism for the reaction. They are not used up in the reaction.