

# CH 302 – Unit 3 Exam Review

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NUCLEAR, KINETICS, INORGANIC

# Learning Objectives - Nuclear

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- Explain the macroscopic observables associated with nuclear change and the microscopic or chemists view of nuclear change.
- Identify and define various types of nuclear transmutation including fission, fusion and decay reactions.
- Use proper isotopic notation to write down and balance a nuclear reaction.
- State and compare the differences and similarities between a nuclear change and a chemical change.
- Recall and properly use Einstein's theory of relativity equation,  $E = mc^2$ , to calculate the amount of energy released upon a nuclear change.
- Define binding energy and mass defect and be able to calculate each for a given nucleus.
- Understand and explain the concept of ionizing radiation and distinguish between the three different types of radiation.
- Understand and explain the concept of isotopic stability including the band of stability.
- Be familiar with the units used to quantify nuclear decay
- Understand the concept of rate of change and half life in the context of nuclear decay.
- Understand the basics of nuclear chemistry applications: nuclear power, medical treatment, isotopic labeling, and carbon dating.

# Learning Objectives - Kinetics

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- Understand the concept of rate of change associated with a given chemical reaction and how it can be measured
- Determine rate law of chemical change based on experimental data.
- Be able to identify the reaction order for a chemical change.
- Understand the concept of pseudo-first order kinetics and when they apply.
- Apply integrated rate equations to solve for the concentration of chemical species during a reaction of different orders.
- Understand the concept of mechanism and using rate law data predict whether or not a proposed mechanism is viable or not.
- Recall and explain why certain factors such as concentration, temperature, medium and the presence of a catalyst will affect the speed of a chemical change.
- Interpret a reaction coordinate diagram and determine if such a diagram supports a given single or multistep mechanism, including the concept and depiction of any transition states and reaction intermediates.
- Understand the concept of an activation energy in the context of the transition state and be able to calculate the activation energy given some experimental data.
- Recall, manipulate and properly employ the Arrhenius Law.
- Explain the function and purpose of a catalyst.

# Learning Objectives – Inorganic

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- Understand the fundamental differences between ionic, covalent and coordination bonds.
- Recall from CH301 general trends in reactivity and bonding and how these trends help organize elements in the periodic table.
- Understand trends in hydration energies and oxidation states of the transition metals.
- Be able to identify common organic ligands used to construct coordination complexes, and learn how certain ligands interact with transition metal ions.
- Understand basic substitution reactions involving ligands and transition metal ions.
- Be able to identify different coordination geometries in transition metal complexes, and use coordination geometry to predict the reactivity of coordination complexes.
- Understand the basics of crystal field theory and crystal field stabilization energy, and use these to predict the electronic configurations of transition metal coordination complexes.
- Relate electronic configurations to the basic spectroscopic properties of coordination complexes.
- Relate electronic configurations to the basic magnetic properties of coordination complexes.
- Calculate the "spin-only" magnetic moment of simple coordination complexes.

**Cross-outs apply to TTH classes ONLY**



# Inorganic Chemistry

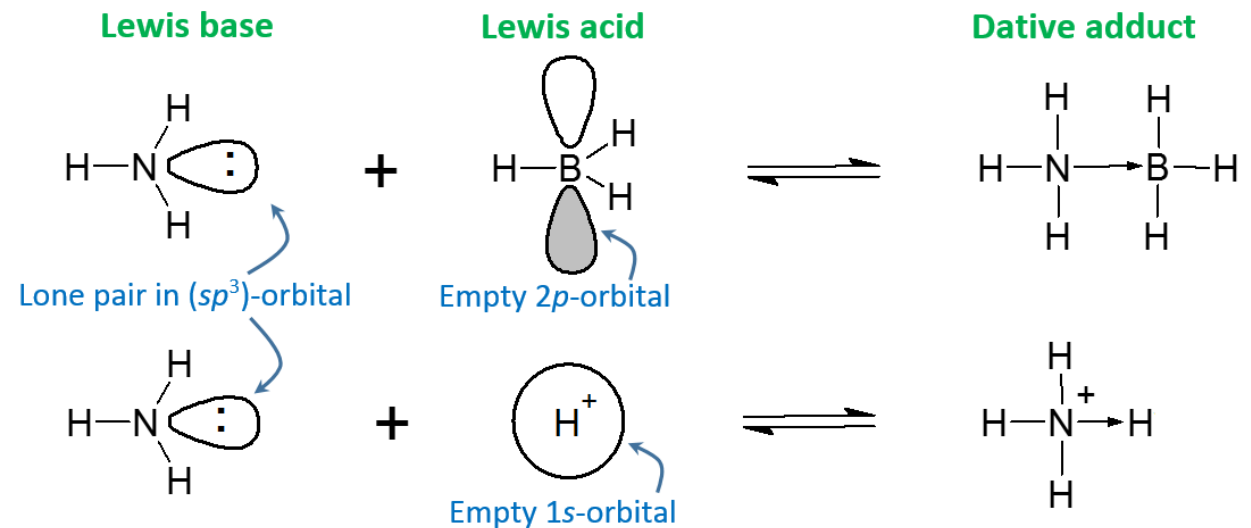
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FUNDAMENTALS OF COORDINATION COMPLEXES

# Fundamentals of Inorganic Chemistry

You will be responsible for being able to fully understand the formation and characteristics of coordination complexes:

1. **Lewis Base:** an electron pair donor ; identified as having lone pairs to share
2. **Lewis Acid:** an electron pair acceptor ; identified as having empty orbitals to accept electrons
3. **Dative Bond (Coordination Covalent Bond):** A bond formed when a lone pair from a **Lewis Base** is shared with a Lewis Acid ; the bond formed between a **ligand** and a **metal base** to form a coordination complex
4. **Denticity:** the number of dative bonds a single ligand can make with the metal center of a coordination complex

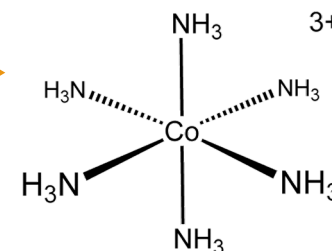


# The Octahedral Complex

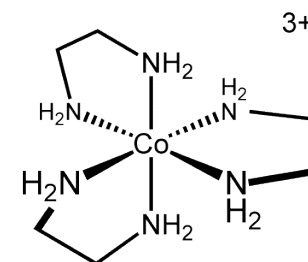
M = Metal  
L = Ligand

The most common complex geometry is octahedral. This is a total of six dative bonding regions (12 total electrons) – NOT 6 total ligands necessarily. The following are the complexes corresponding to different common ligands:

## 1. Monodentate Ligand



## 2. Bidentate Ligand



## 3. Tridentate Ligand



## 4. Mix-and-Match: make sure your total dative bonds equals 6

# Inorganic Complexes

- **Determine the charge on the metal center:**

charge on complex = **(charge of the metal)** + (total charge of all ligands)

(Always neutral or positive)

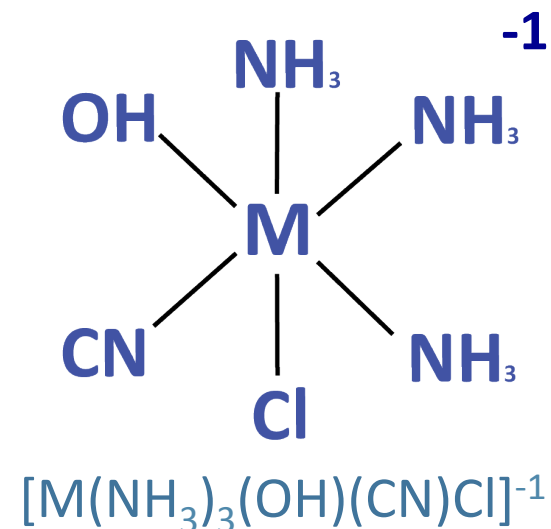
(Usually neutral or negative)

- **Determine the total electrons of the complex:**

**total complex e<sup>-</sup>** = (ligand e<sup>-</sup>) + (valence e<sup>-</sup> of metal base)

(# of dative bonds \* 2)  
\*Always 12 for octahedral complexes

(4s and 3d orbital electrons  
[accounting for charge on the metal])



\*\*\*Remember you can further apply all this information!

# Inorganic Complexes

- **Determine the charge on the metal center:**

charge on complex = **(charge of the metal)** + (total charge of all ligands)

(Always neutral or positive)

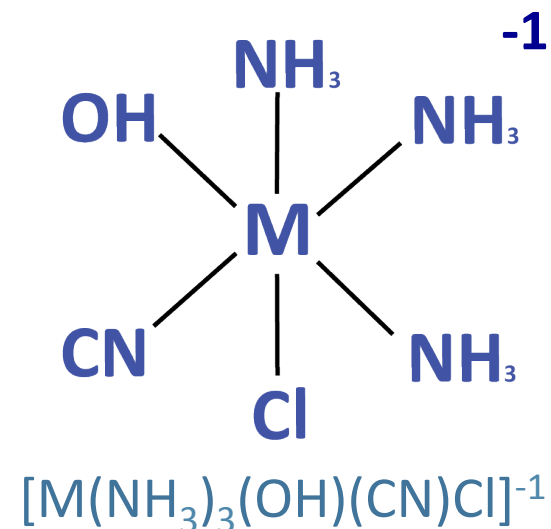
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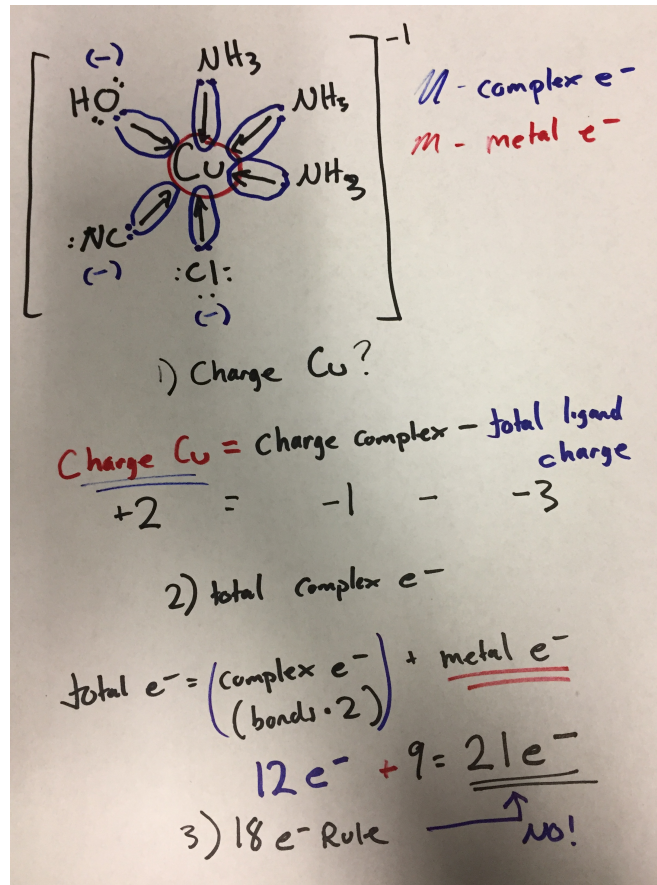
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\*\*\*Remember you can further apply all this information!

# Inorganic Complexes



# Nuclear Chemistry

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NUCLEAR REACTIONS, DECAY, MASS & ENERGY

# Nuclear Fundamentals

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There are four types of nuclear reactions that we discuss in this class:

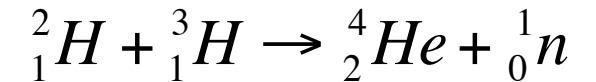
1. Fission: a large atom splits into medium nuclei

- Fission reactions are exothermic with atoms larger than iron
- Common with large, unstable nuclei such as uranium

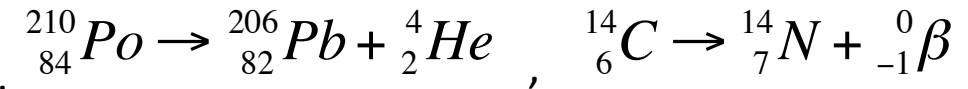


2. Fusion: small nuclei join to form larger nuclei

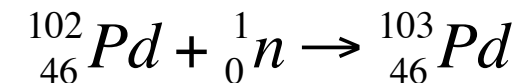
- Fusion reactions are exothermic with atoms smaller than iron
- Common with hydrogen isotopes (tritium, deuterium) and helium in extreme conditions (such as in stars)



3. Nuclear Decay: an unstable nucleus reaches a lower energy state by spontaneously releasing ionizing radiation (beta decay, positron decay, alpha decay, electron capture)

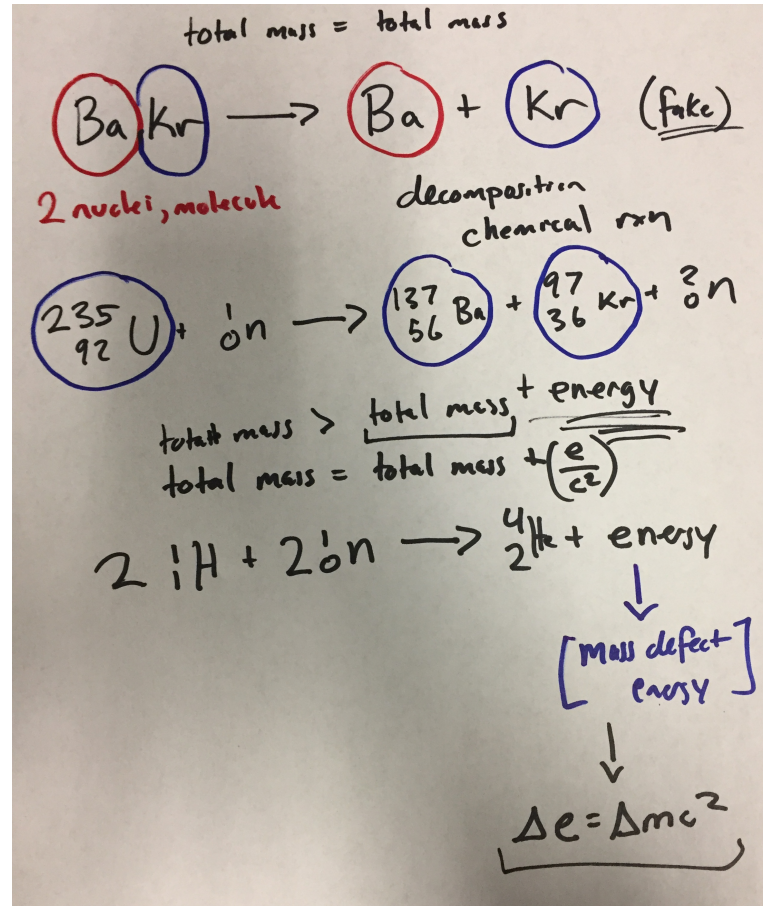


4. Transmutation: a less stable nucleus is created by **non-spontaneously** bombarding it with ionizing radiation (opposite of nuclear decay)

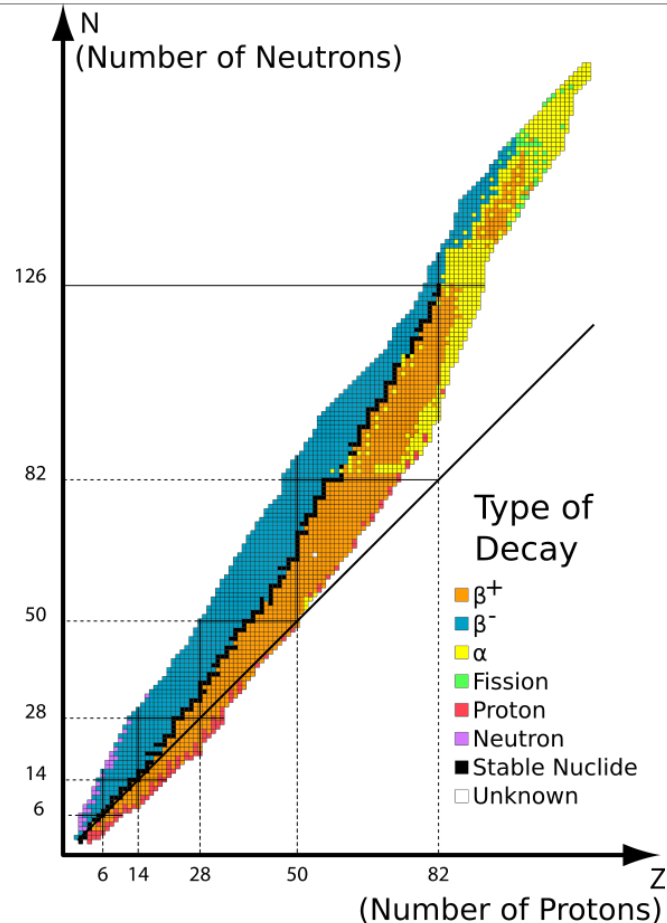




# Nuclear Fundamentals



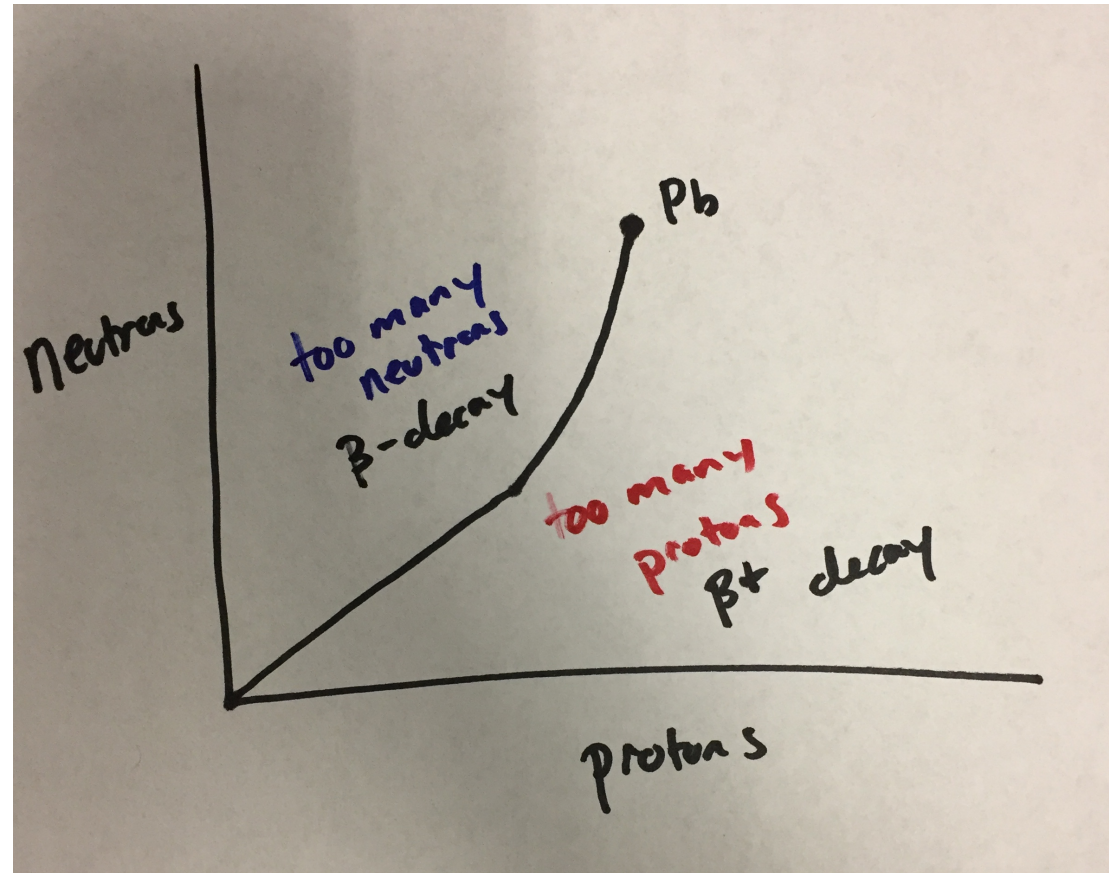
# The Band of Stability



- The band of stability tells us the stable ratio of protons : neutrons for each element.
- Additional isotopes exist outside of the band of stability
- Where you are in relationship to the stable isotope dictates the type of decay necessary to get to the lowest energy state
- **Above the line: too many neutrons**
- Beta emission converts a neutron into proton to get back to the line of stability
- **Below the line: too many protons**
- Positron emission converts a proton into a neutron to get back to the line of stability
- *Notice how the band of stability ends at lead – everything after lead is radioactive*

# The Band of Stability

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# Nuclear Fundamentals

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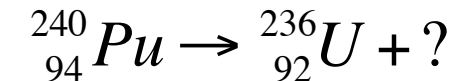
## Nuclear Decay Summary:

- $\alpha$  decay: emission of an  $\alpha$ -particle
  - The result is a new atomic species (z-2, m-4) and a new mass
- $\beta$  decay: emission of an electron
  - The result is a new atomic species (z+1) with the same mass
  - Neutron becomes a proton
- $\beta^+$  decay: emission of a positron
  - The result is a new atomic species (z-1) with the same mass
  - Proton becomes a neutron
- Electron capture: the **addition** of an electron
  - The result is a new atomic species (z-1) with the same mass
  - Proton becomes a neutron (same effect as positron decay)

*Note: z = atomic number ; m = atomic mass*

Questions:

1. What is the unknown in the following equation? What type of nuclear decay is this? (Alpha particle, alpha decay)



2. Suppose you create an antimony isotope with a weight of 124 via transmutation. What type of decay will most likely restore the most stable isotope? (beta decay)

# Nuclear Rate of Decay: Half-Life

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- The rate at which an unstable isotope decays is measured by its half-life. **Half-life is defined as the amount of time it takes for ½ of your material to decay.**

$$\frac{\ln(2)}{k} = t_{1/2}$$

$$\frac{\ln(2)}{t_{1/2}} = k$$

- Radioactive decay follows first order kinetics. **This means the rate of decay is dependent on the amount of the decaying material.**

$$[A] = [A]_0 e^{-kt}$$

$$\ln \frac{[A]_0}{[A]} = kt$$

# Kinetics

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RATES, INTEGRATED RATES, MECHANISMS, COLLISION THEORY


# Introduction to Kinetics

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There are four types of kinetics questions types that we have discussed in this class:

1. **Overall rate of a reaction (think stoichiometry):** If you can measure the rate of formation for a product, you can use stoichiometry to determine the rates for all other products and reactants
2. **Rate Laws:** The rate law is a fundamental equation used to calculate the rate of a reaction from the rate constant,  $k$ , and the concentrations of the reactants raised to the power of their "order". The overall reaction order is the sum of the orders of the reactants. **This question type also includes deriving the rate law from a mechanism.**
3. **Empirical Rate Law:** Because the order of reactants are not necessarily based on stoichiometry, you must run an experiment to measure this value based on the initial rate of reaction at different starting concentrations
4. **Integrated Rate Law:** Knowing the order of a reaction, you can determine the rate or concentrations of a reactant at any given point in time (calculus is necessary here because if the rate is dependent on concentration, the rate is changes as the reaction proceeds)

Work well for initial rates



Takes into account the fact that the rate can change over time



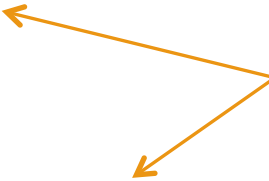
# The Four Factors that Affect Rates

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## 1. Nature of reactants/ Availability of the molecules

- Larger surface area = faster rate
- Ex: this is the reason why we chew our food (mechanical digestion)

Increase the rate without changing the rate constant



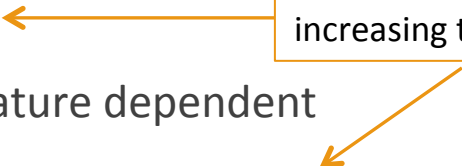
## 2. Concentration (and pressure)

- Higher concentration, higher rate **if your reaction is first order or higher**
- Increases the rate based on the fact that the rate law is concentration dependent

## 3. Temperature

- Higher temperature, higher rate **always** (in this class)
- Increases the rate based on the fact that the **rate constant** is temperature dependent

Increase the rate by increasing the rate constant



## 4. Catalysts

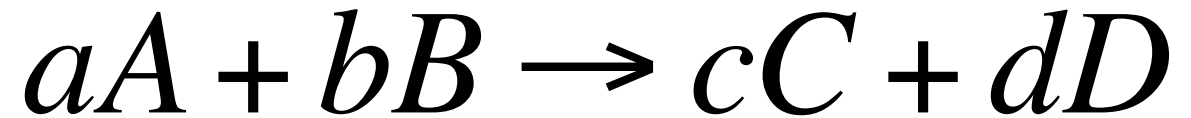
- Catalysts decrease the **activation energy**, which increases the rate based on the Arrhenius Equation
- Increases the rate based on the fact that the rate constant is proportional to the **negative activation energy**



# Question Type 1: Overall Rate of a Reaction

The fundamental rate of a reaction can be described by the rate of change of any reactant or product of the reaction. A few important notes:

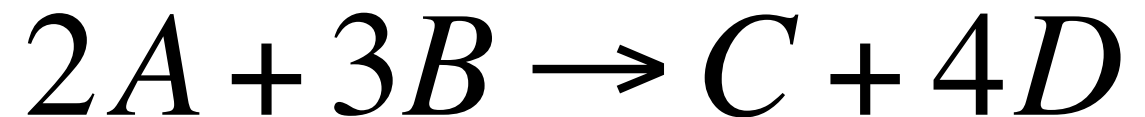
1. **Coefficients play an important role:** if  $b = 3$ , the rate of consumption for B is 3 times the overall reaction rate; if  $d = 4$ , the rate of formation for D is 4 times the overall reaction rate
2. **The rate of change for different species can be interconverted:** based on the information above, we can say that the rate of formation for D is  $4/3$  the rate of consumption of B
3. The rate of change for reactants and products are always opposite in sign



$$rate = \frac{-\Delta[A]}{a\Delta t} = \frac{-\Delta[B]}{b\Delta t} = \frac{+\Delta[C]}{c\Delta t} = \frac{+\Delta[D]}{d\Delta t}$$

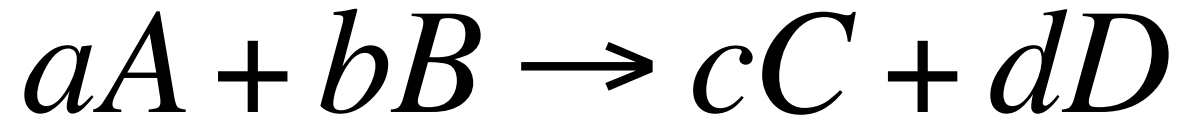
$$\frac{-d\Delta[B]}{b\Delta t} = \frac{\Delta[D]}{\Delta t}$$

Example:



## Question Type 2: Introduction to Rate Laws

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$$rate = k[A]^x[B]^y$$

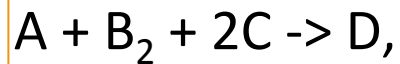
Rate of reaction in the units of M/s

Rate constant (measured value). Units depend on the order of reaction; must cancel units of  $[A]^x$ ,  $[B]^y$  to get rate = M/s

x = order of A  
y = order of B  
x + y = overall order of the reaction  
Order is usually positive integers, but can be fractional or negative in rare cases

# Question Type 3: Exam Question (do on your own)

For the reaction:



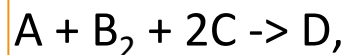
You run an experiment to determine the initial rates of the reaction under 4 different starting conditions. Write the complete rate law for the reaction. What is the value of  $k$ ?

	Initial [A] M	Initial [B <sub>2</sub> ] M	Initial [C] M	Initial rate M/s
1	0.01	0.01	0.10	$1.20 \times 10^3$
2	0.02	0.01	0.10	$4.80 \times 10^3$
3	0.03	0.01	0.20	$2.16 \times 10^4$
4	0.04	0.02	0.10	$3.84 \times 10^4$

$$\frac{Rate_2}{Rate_1} = \frac{k[A]_2^x [B_2]_2^y [C]_2^z}{k[A]_1^x [B_2]_1^y [C]_1^z}$$

# Exam Question

For the reaction:



You run an experiment to determine the initial rates of the reaction under 4 different starting conditions. Write the complete rate law for the reaction. What is the value of  $k$ ?

$$\text{Rate} = 1.2 \times 10^{10} [A]^2 [B_2] [C]$$

(units of  $k$  omitted)

	Initial [A] M	Initial [B <sub>2</sub> ] M	Initial [C] M	Initial rate M/s
1	0.01	0.01	0.10	$1.20 \times 10^3$
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$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[A]_2^x [B_2]_2^y [C]_2^z}{k[A]_1^x [B_2]_1^y [C]_1^z}$$

# Question Type 4: Integrated Rate Laws

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- **First Order: general formula, slope-intercept formula, half life**

$$\text{rate} = k[A]$$

$$\ln \frac{[A]_0}{[A]} = kt$$

$$\ln[A] = -kt + \ln[A]_0$$

$$\frac{\ln(2)}{k} = t_{1/2}$$

- **0<sup>th</sup> Order: general formula, slope-intercept formula, half life**

$$\text{rate} = k$$

$$[A]_0 - [A] = kt$$

$$[A] = -kt + [A]_0$$

$$\frac{[A]_0}{2k} = t_{1/2}$$

- **2<sup>nd</sup> Order: general formula, slope-intercept formula, half life**

$$\text{rate} = k[A]^2$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{k[A]_0} = t_{1/2}$$

# Half-Lives of Integrated Rate Laws

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- **First Order Half-Life: Independent of concentration**

$$\frac{\ln(2)}{k} = t_{1/2}$$

- **0<sup>th</sup> Order Half-Life: Directly related to concentration**

$$\frac{[A]_0}{2k} = t_{1/2}$$

- **2<sup>nd</sup> Order Half-Life: Inversely related to concentration**

$$\frac{1}{k[A]_0} = t_{1/2}$$

# Applying Integrated Rate Laws

The integrated rate laws can be written to yield straight lines on the curves.  
The main difference between them is the axes:

- All graphs have time as the x axis
- 0<sup>th</sup> order: y-axis is **concentration**
- 1<sup>st</sup> order: y-axis is the **natural log of the concentration**
- 2<sup>nd</sup> order: y-axis is the **inverse of the concentration**

The other difference is the slope

- 0<sup>th</sup> and 1<sup>st</sup> order have a negative slope (**slope = -k**)
- 2<sup>nd</sup> order has a positive slope (**slope = k**)

$$[A] = -kt + [A]_0$$

$$\ln[A] = -kt + \ln[A]_0$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

# Conceptual Note: Integrated Rate Laws

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- **Integrated rate laws take into account a single reactant that has 0<sup>th</sup> order, 1<sup>st</sup> order, or 2<sup>nd</sup> order kinetics.** These equations fail when:
  - The reaction has any significant backward rate
  - The reaction is at equilibrium (backwards rate equals the forward rate)
  - When the overall rate depends on the concentration of another reactant
    - We get around this by setting up Pseudo-first Order conditions:

$$rate = k[A][B]$$

- We can “mimic” first order conditions by using disproportionate starting conditions. Suppose we start with 2M A and 0.05M B. We get a new expression with a new “k” value that is equal to the product of the original k and the relatively consistent concentration [A]:

$$rate = k \cdot 2 \cdot [B] = k'[B]$$



# Fundamentals of Mechanisms

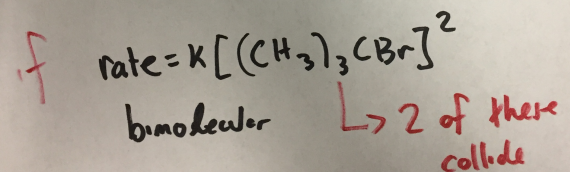
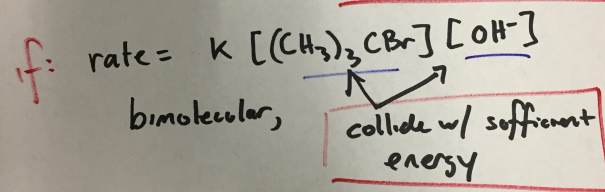
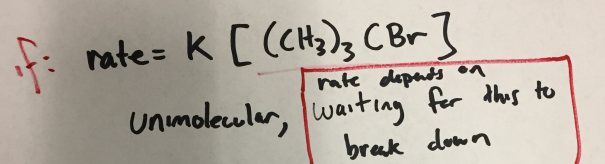
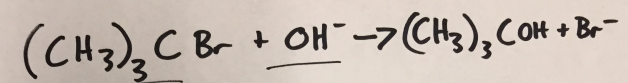
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We can propose a mechanism that dictates the kinetics of the reaction. This helps us define the following terms:

- 1. Rate-limiting step:** the slow step of a mechanism; dictates the rate of the reaction and activation energy
- 2. Molecularity:** the number of species involved in the rate-limiting step
  - Unimolecular: the rate-limiting step involves a single mole of a single species ; the rate law for this step is first order
  - Bimolecular: the rate-limiting step involves the collision of 2 species ; the rate law for this step is second order
  - Note: we do not often propose elementary steps that are trimolecular and beyond. This is because it is very improbable for 3 species to collide with the correct energy / orientation
- 3. The Overall Rate Law:** the rate law properly expressed in terms of only reactants
  - If the rate-limiting step involves an intermediate, you will need to substitute to in to express your rate in terms of only the reactants of the overall reaction

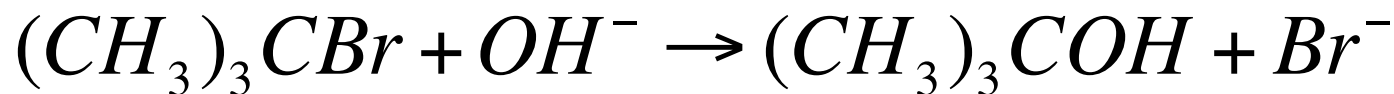
# Mechanisms Conceptual

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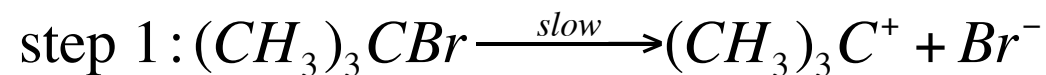


# Reaction Mechanisms: Elementary Steps

- At first we said that we cannot simply look at an overall equation and use stoichiometry to determine the rate law.
- However, we can determine the rate law if we can determine **the elementary steps**, or the steps that make up the overall reaction. **If you identify the correct elementary step, you will use stoichiometry to determine the rate law.**
- Most elementary steps are “fast.” The elementary step we use to determine the rate law is the one labeled as “slow” or “rate limiting.”
- **Collision theory** states that the reaction rate is proportional to the number of successful collisions divided by time. **Therefore, it should make sense that the rate law can be determined by the slowest elementary step.**



Mechanism:



$$\text{rate} = k_1 [(CH_3)_3CBr]$$

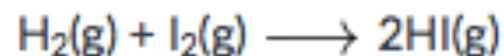
The rate of this reaction depends only on step 1. This elementary step involves a tert-butyl bromide decomposing in solution to form bromide and a carbocation. Because it involves only one reactant, we call this a unimolecular elementary step.

# Mechanisms: Example

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- In the previous examples, our rate limiting step was the first step. If this is the case, your rate law is very easy to determine.
- However, a rate law must always be written in terms of the species that show up in the overall reaction. **In other words, intermediates cannot be written in the rate law.**
- We will need to do a few additional steps for an example where the slow step is not the first step.
- **If the slow step is the third step, you will have to repeat this process**

Consider the reaction below:

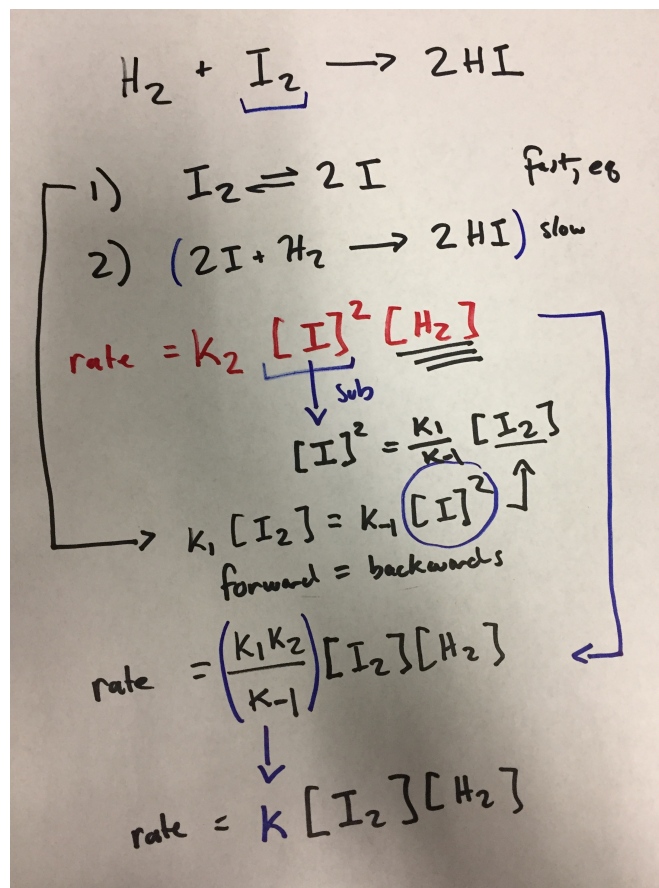


The proposed mechanism of this reaction is:



What is the rate of the overall reaction?

# Mechanisms Problem



# Reaction Coordinate Diagrams

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Be able to identify/explain the following on a graph:

**1.** The number of steps

- The number of “humps” on a diagram; each representing a high energy transition state

**2.** The intermediates

- Found in the number of valleys between humps

**3.** The transition states

- High energy, transient states
- Always represent a higher energy state than the previously existing intermediate/reactant
- Found on the peaks of the humps

**4.** Rate-limiting step (slow step vs. fast step)

- The hump with the greatest change in energy (not always the highest energy maxima on the diagram)

**5.** Activation Energy of the reaction

- The energy difference between the reactant/intermediate and the transition state of the rate-limiting step

**6.** The overall change in enthalpy

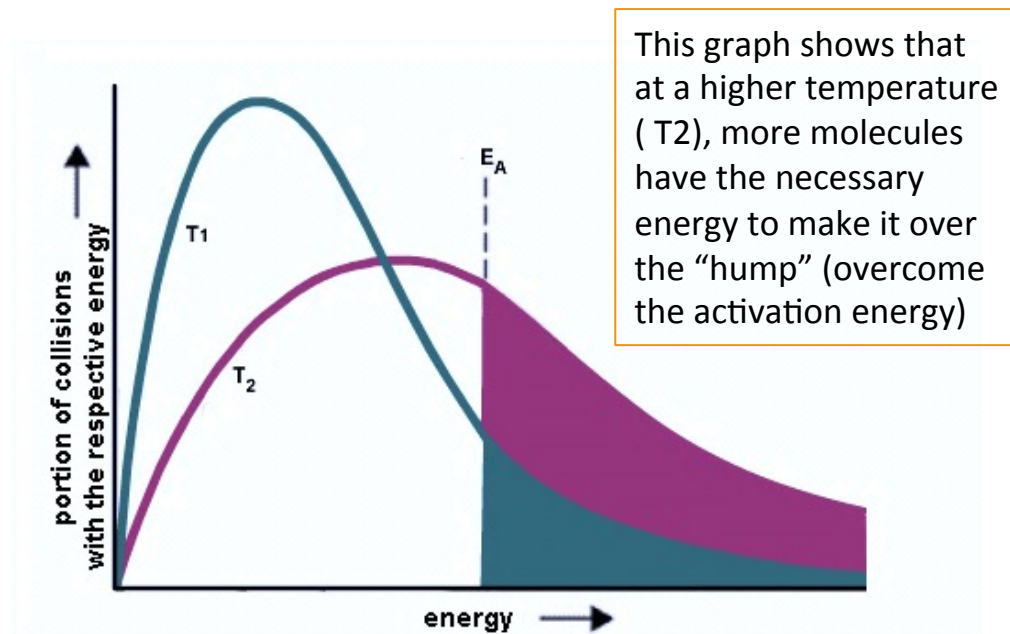
- The energy difference between the reactants and the products (think thermodynamic state functions)

# Collision Theory: Activation Energy

Earlier, I mentioned that **Collision Theory** states that the reaction rate is proportional to the number of successful collisions divided by time.

- We can define a “successful collision” as one that has sufficient energy to break or form the bonds in the elementary step.
- **The energy required for a successful elementary step is called the Activation Energy.**
- Remember: you can increase the probability of collisions by increasing the surface area or increasing the concentration.
- Taking it one step further, the Arrhenius Equation give us two very helpful ways of increasing the rate of a reaction:
  1. **You can increase the temperature**
  2. **You can add a catalyst (lower  $E_a$ )**

Increase the rate constant



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



# Collision Theory: Temperature and Catalysts

How does temperature affect the rate of reaction?

- By increasing the temperature, you are increasing the number of particles that have enough energy to collide successfully. In other words, **you are increasing the number of particles with the ability to overcome the activation energy.**
- **Based on the Arrhenius Equation, you will get a higher rate constant that will give you a faster rate of reaction.**

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{Ea}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

How does adding a catalyst affect the rate of reaction?

- Catalysts lower the activation energy **by stabilizing the transition state.**
- Like temperature, **this mathematically results in a higher rate constant**
- Catalysts are not consumed in the reaction. They will show up on the reactant and product side of the reaction mechanism
- Enzymes are biological catalysts

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



# Excess Stuff

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What is the order? You have to use experimental data to figure it out.

# Introduction to Rate Laws

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$$\text{rate} = k[A]^x$$

0<sup>th</sup> Order: rate is independent of [A]

$$\text{rate} = k$$

$$k = M / s$$

First Order: rate is directly proportional to [A]

$$\text{rate} = k[A]$$

$$k = 1 / s$$

Second Order: rate is proportional to [A]<sup>2</sup>

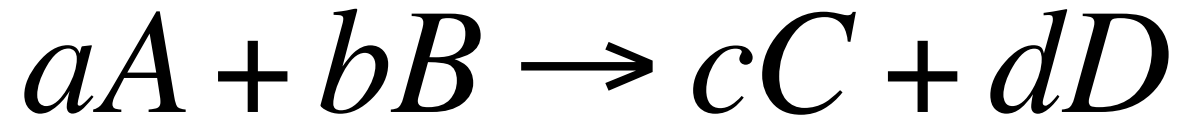
$$\text{rate} = k[A]^2$$

$$k = 1 / Ms$$

You must determine the rate law based on experimental data OR based on a provided mechanism

# Introduction to Rate Laws

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$$\text{rate} = k[A]^x[B]^y$$

0<sup>th</sup> Order:

$$\text{rate} = k$$

$$k = M / s$$

First Order:

$$\text{rate} = k[A] \text{ or } \text{rate} = k[B]$$

$$k = 1 / s$$

Second Order:

$$\text{rate} = k[A][B] \text{ or } \text{rate} = k[A]^2 \text{ or } \text{rate} = k[B]^2$$

$$k = 1 / Ms$$

# Overall Reaction Order

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Order can be applied to the total reaction:

- In this case, the order of the reaction is the sum of the exponents in the rate law.
- Our units of  $k$  are dependent on the order of the total reaction:
  - 0<sup>th</sup> order:  $k = \text{Ms}^{-1}$
  - 1<sup>st</sup> order:  $k = \text{s}^{-1}$
  - 2<sup>nd</sup> order:  $k = \text{M}^{-1}\text{s}^{-1}$
  - 3<sup>rd</sup> order:  $k = \text{M}^{-2}\text{s}^{-1}$

*These are all based on the fact that the rate must be in  $\text{Ms}^{-1}$ , and you are cancelling out the concentration terms on the rate law*