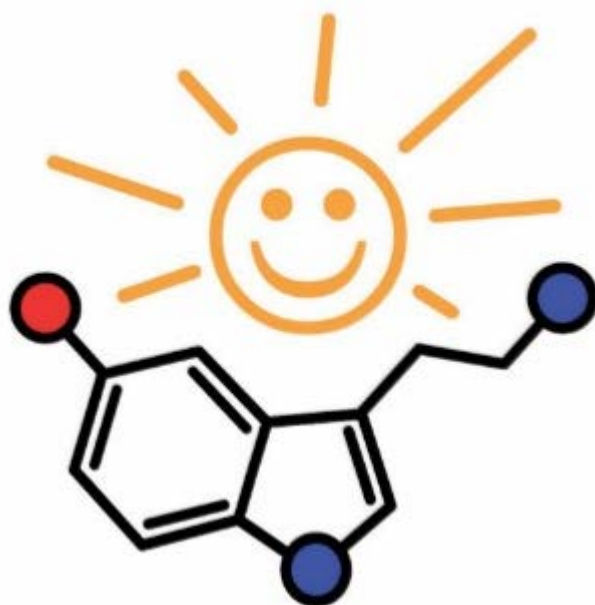


Student Name: _____

Class period: _____

RRHS AP Chemistry



Unit 6: Kinetics with Final Exam Review

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A Day: Text @APLestikA to 81010

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2nd Marking Period: October-December 2022

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
9 Oct.	10 Student Holiday/ Staff Development	11 A	12 PSAT	13 B	14 C End of 1st MP	15
16	17 A	18 B	19 A	20 B	21 A	22
23	24 Student Holiday/ Staff Development	25 B	26 A	27 B	28 A	29 2
30	31 B	1 Nov. A	2 B	3 A	4 B	5
6	7 A	8 B	9 A	10 B	11 A	12
13	14 B	15 A	16 B	17 A	18 B	19

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
20 Nov	21 FALL BREAK	22 FALL BREAK	23 FALL BREAK	24 FALL BREAK	25 FALL BREAK	26
27	28 A	29 B	30 A	1 Dec. B	2 A	3
4	5 B	6 A	7 B	8 A	9 B	10
11	12 Exams 2, 1	13 Exams 6, 5	14 Exams 3, 4	15 Exams 7, 8	16 BREAK BEGINS!	17
18	19 WINTER	20 BREAK	21 WINTER	22 BREAK	23 ☺	24
25	26 ☺	27 WINTER	28 BREAK	29 WINTER	30 BREAK	31

AP[®] CHEMISTRY EQUATIONS AND CONSTANTS

Throughout the exam the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)
 g = gram(s)
 nm = nanometer(s)
 atm = atmosphere(s)

mm Hg = millimeters of mercury
 J, kJ = joule(s), kilojoule(s)
 V = volt(s)
 mol = mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy
 ν = frequency
 λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^8$ m s⁻¹

Avogadro's number = 6.022×10^{23} mol⁻¹

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}, \text{ where } a A + b B \rightleftharpoons c C + d D$$

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$= K_a \times K_b$$

$$\text{pH} = -\log[H^+], \text{ pOH} = -\log[OH^-]$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_a (weak acid)

K_b (weak base)

K_w (water)

KINETICS

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

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

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure

V = volume

T = temperature

n = number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

a = molar absorptivity

b = path length

c = concentration

Gas constant, R = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr}$$

STP = 273.15 K and 1.0 atm

Ideal gas at STP = 22.4 L mol^{-1}

THERMODYNAMICS / ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

q = heat

m = mass

c = specific heat capacity

T = temperature

S° = standard entropy

H° = standard enthalpy

G° = standard Gibbs free energy

n = number of moles

E° = standard reduction potential

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

Faraday's constant, F = 96,485 coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$

AP Chem: Effective Study Skills Tips and Tricks!

Study smarter, not harder. ☺

What to Do	What NOT to Do
<p>Be ACTIVE in while learning/studying:</p> <ul style="list-style-type: none"> • Close your booklet and try problems on your own with just a periodic table and formula chart! Only check your answer/work when you've finished, or you can't go any farther. • Use flashcards (physical or digital) • Struggle with challenging problems and keep trying, even if you're stuck initially (or convinced you're doing it wrong) 	<p>Be passive while learning/studying:</p> <ul style="list-style-type: none"> • Re-read over your booklet and practice problems you've already completed • Ask your friend or look up the answer if you don't immediately know how to do the problem
<p>Focus when studying</p> <ul style="list-style-type: none"> • Decrease distractions while studying; don't read texts, check social media, or watch Netflix while studying. <u>Put your phone out of sight/hearing.</u> 	<p>Multitask</p> <ul style="list-style-type: none"> • Study while checking/writing texts, checking social media, and/or watching Netflix. • Keep your computer or tv on in the background
<p>Use Intensity when studying</p> <ul style="list-style-type: none"> • You control the effort that you apply in your work! 30 minutes of high focus, high intensity study can be better than 2 hours of unfocused, low energy multi-tasking. 	<p>Low intensity/low effort</p> <ul style="list-style-type: none"> • Look over problems and try them "in your head" but then just look up the answer • Use flashcards but don't try to recall the info on the other side before looking at the answer
<p>Space out studying over time</p> <ul style="list-style-type: none"> • Study a little bit of chemistry most days • Start long-term homework (like Mastering Chem or lab reports) the day they're assigned, and work a little bit every day or two • Less is more! Spaced practice studying is more effective than LONG hours of "studying" with multitasking and little focus. 	<p>Cram</p> <ul style="list-style-type: none"> • Only study for quizzes/tests the night before • Start Mastering Chem or your lab report only 1-2 days before it's due • Study for many hours at a time all at once
<p>Interleave your Studying</p> <ul style="list-style-type: none"> • Study more than just one type of problem; mix it up and jump between different concepts • Review and practice old units while studying (especially important since AP Chem assessments are cumulative!) 	<p>One Concept Studying</p> <ul style="list-style-type: none"> • Study only one type of problem, and practice those problems over and over • Don't review older content or units while studying
<p>Test Yourself!</p> <ul style="list-style-type: none"> • The best way to prepare for a test is to take a test! <ul style="list-style-type: none"> ○ Time yourself while trying practice problems ○ Access only the AP Periodic Table and Formula Chart when practicing problems 	<p>Open Notes Practice</p> <ul style="list-style-type: none"> • Use your notes, friends, and/or the internet while trying practice problems • Give yourself unlimited time for each problem

AP Chemistry Unit 5 Objectives

BIG IDEA 4 - Rates of chemical reactions are determined by the details of the molecular collisions.

- Enduring Understanding 4.A: Reaction rates that depend on temperature and other environmental factors are determined by measuring changes in concentrations of reactants or products over time.
- Enduring Understanding 4.B: Elementary reactions are mediated by collisions between molecules. Only collisions having sufficient energy and proper relative orientation of reactants lead to products.
- Enduring Understanding 4.C: Many reactions proceed via a series of elemental steps.
- Enduring Understanding 4.D: Reaction rates may be increased by the presence of a catalyst.

Kinetics Day 1: Zoom!

Chemical Kinetics: area of chemistry concerned with the _____ of chemical reactions.

- Simply because a reaction is considered spontaneous, implies NOTHING about the speed. *Spontaneous does not mean fast.*
- Thermodynamics says “_____.” Kinetics says “_____” and “how _____.”

The Rate of a Chemical Reaction: a measure of how _____ the reaction occurs.

- The reaction rate of a chemical reaction is defined as the change in concentration of a reactant or product per unit time.

$$\text{Rate} = \frac{-\Delta[\text{Reactant}]}{\Delta\text{time}} \text{ OR } \frac{\Delta[\text{Product}]}{\Delta\text{time}}$$

$$\text{Rate Unit: } \frac{\text{M}}{\text{time}}, \text{M time}^{-1}, \frac{\text{mol}}{\text{L time}}, \text{mol L}^{-1}\text{time}^{-1}$$

(Hint: all of these units are all the _____ thing!!)

For _____, a _____ sign is placed in front of the definition. Because reactant concentrations decrease as a reaction proceeds, the change in the concentration in the reactants is negative. The negative sign thus makes the overall rate positive.

Reaction Rate Changes Over Time

- As time goes on, the rate of a reaction generally _____ because the concentration of the reactants _____.
- At some point in time the reaction stops, either because the reactants run out or because the system has reached equilibrium.

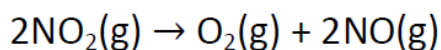
Reaction Rate and Stoichiometry: For reactions in which the coefficients of the balanced equation are not all the same, the change in the number of molecules of one substance is a multiple of the change in the number of molecules of another.

To be consistent, the change in the concentration of each substance is multiplied by _____.

Given the reaction: $A + 3 B \rightarrow 2 C$

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{3} \frac{\Delta[B]}{\Delta t} = \frac{1}{2} \frac{\Delta[C]}{\Delta t}$$

For example: given the following equation:



If we know, through experimentation, that the rate of production of NO is 8.57×10^{-6} M/s, what is:

1. What is the rate of NO₂ consumption?
2. What is the rate of O₂ production?

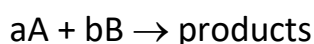
Four Factors Affecting Reaction Rate: MEMORIZE THESE!!!!

1. Increasing the _____ of a solid reactant can increase the rate by increasing the number of collisions between the reactant particles.
2. _____ increase the rate by lowering the activation energy of a reaction.
3. Increasing the _____ results in a faster reaction: _____ 'em up, _____ 'em up!
 → The rate constant is temperature dependent and a rise in temperature will increase the rate constant!
4. Increasing concentration of _____ increases the number of reactants colliding with each other, thus yielding more product.

The Rate Law: the mathematical relationship between the rate of the reaction and the concentrations of the reactants and homogeneous catalysts as well.

→ The rate law **must** be determined _____!

For the reaction

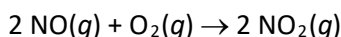


The rate law would have the form

$$\text{Rate} = k[A]^n[B]^m$$

1. The exponent on each reactant, n and m , are called the _____ with respect to that reactant.
2. k is called the _____: a larger k means a _____ reaction!
3. n and m are _____ necessarily the stoichiometric coefficients of A and B.
4. $n + m = p$, the _____ **rate order** (or the order of the _____).

Note: The concentrations of the products do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate.

Example

the experimentally determined rate law is

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2].$$

The reaction is said to be:

- _____ order with respect to NO,
- _____ order with respect to O₂,
- _____ order overall.

For example: given the following equation: $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$

If we know, through experimentation, rate law = $k[\text{NO}_2][\text{F}_2]^3$,

1. What the order of the reaction relative to NO₂?
2. What the order of the reaction relative to F₂?
3. What is the order of the reaction overall?

Overall Reaction Order

_____ order reaction rate: the rate of the reaction is always the _____.



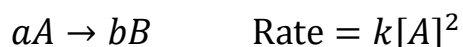
- Doubling [A] will have _____ effect on the reaction rate.
- Rate is _____ of time!

_____ order reaction rate: the rate of the reaction is directly proportional to the reactant concentration.

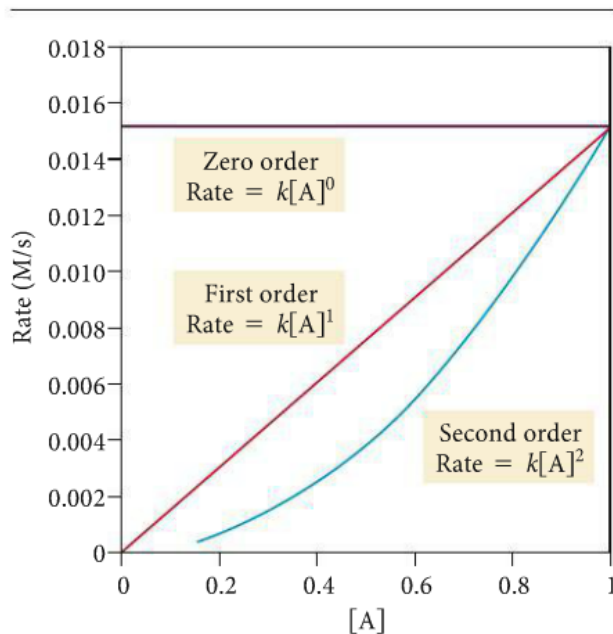


- Doubling [A] will _____ the reaction rate.

_____ order reaction rate: the rate is directly proportional to the _____ of reactant concentration.



- Doubling [A] will _____ the reaction rate.

Rate versus Reactant Concentration**How to determine orders:**

1. Order must be determined _____!
2. In reaction with multiple reactants, changing the concentration of _____ reactant will affect the overall rate of the reaction.
 - a. Change the initial concentration of _____ reactant at a time, while holding the initial concentration of the other reactants _____!
 - b. Conduct _____ trials with changing concentrations of each reactant and measure the rate each time to determine the effect of each change.

Example:

For example, for the following reaction, $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NOCl}(\text{g})$
 this data was collected:

Trial	[NO] mol/L	[Cl ₂] mol/L	Rate
1	0.200	0.200	1.20×10^{-6}
2	0.400	0.200	4.80×10^{-6}
3	0.200	0.400	2.40×10^{-6}
4	0.400	0.400	9.6×10^{-6}

a) Comparing Trial 1 and Trial 2:

→ the concentration of NO:

→ the concentration of Cl₂:

→ The reaction rate is increased ____ times,

Therefore, the rate of reaction with respect to NO is _____ order ($2^2 = 4$).

To justify your answer, you will need to explain this process. You could explain the above answer like this:

b) Comparing Trial 1 and Trial 3:

→ the concentration of NO:

→ the concentration of Cl₂:

→ The reaction rate is increased ____ times,

Therefore, the rate of reaction with respect to Cl₂ is _____ order ($2^1 = 2$).

Justify your answer here:

c) What is the rate law for the reaction?

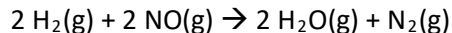
d) What is the value of the rate constant, k? (You can use any trial!)

e) For trial 3, calculate the concentration of Cl₂ remaining when 25% of the original amount of NO has been consumed.

You can use the same method for gaseous reactions with _____!

→ _____ is directly proportional to _____.

Example: The reaction between H_2 and NO occurs according to the equation



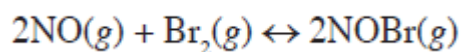
Six trials of the reaction were carried out. The initial rate of change of pressure for each trial was measured and recorded below.

Trial	Initial Pressure (atm)		Initial Rate $\Delta \text{atm min}^{-1}$
	P_{NO}	P_{H_2}	
I	0.50	0.09	0.025
II	0.50	0.18	0.050
III	0.50	0.27	0.075
IV	0.09	0.80	0.0063
V	0.18	0.80	0.025
VI	0.27	0.80	0.056

Based on these results, what is the rate law for this reaction? Justify your answer.

Multiple Choice Practice

- The reaction below was performed several times, and the following data was gathered. What is the rate law for this reaction?



Trial	$[\text{NO}]_{\text{init}}$ (M)	$[\text{Br}_2]_{\text{init}}$ (M)	Initial Rate of Reaction (M/min)
1	0.20 M	0.10 M	5.20×10^{-3}
2	0.20 M	0.20 M	1.04×10^{-2}
3	0.40 M	0.10 M	2.08×10^{-2}

- (A) Rate = $k[\text{NO}][\text{Br}_2]^2$ (C) Rate = $k[\text{NO}][\text{Br}_2]$
 (B) Rate = $k[\text{NO}]^2[\text{Br}_2]^2$ (D) Rate = $k[\text{NO}]^2[\text{Br}_2]$

2. A chemical reaction $A \rightarrow 2B + C$ performed with an initial $[A] = 5.25 \times 10^{-3}$ is found to have $[A] = 4.74 \times 10^{-3}$ M after 2.5 minutes. What is the concentration of B after 2.5 minutes?

(A) 5.10×10^{-4} M (B) 9.48×10^{-3} M (C) 1.02×10^{-3} M (D) $4. \times 10^{-4}$ M

3. $A(g) + B(g) \leftrightarrow 2 C(g)$

When the concentration of substance B in the reaction above is doubled, all other factors being held constant, it is found that the rate of the reaction remains unchanged. The most probable explanation for this observation is that

- the order of the reaction with respect to substance B is zero
- substance B is not involved in the reaction
- substance B is probably a catalyst, and as such, its effect on the rate of the reaction does not depend on its concentration
- the reactant with the smallest coefficient in the balanced equation generally has little or no effect on the rate of the reaction

More Practice!!!

1. Consider the reaction represented to the right and the experimental data below. $A(g) + B(g) \rightarrow C(g)$

<i>Experiment #</i>	<i>Initial [A]</i>	<i>Initial [B]</i>	<i>Initial Rate of Formation of C</i>
1	0.0030	0.0010	X
2	0.0060	0.0020	?

If the reaction is first order with respect to A and second order with respect to B, what is the initial rate of formation of C in experiment 2 (in terms of X)? Justify your answer.

2. A student wants to determine the rate law for the following reaction: $O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$. First, the student runs the reaction with a 0.50 M initial concentration of $O_3(g)$, and a 0.20 M initial concentration of $NO(g)$. They determine the rate of the reaction from these starting conditions is 0.0012 M/s.

What other data the student would need to collect to be able to determine the rate law of the reaction? Be specific!

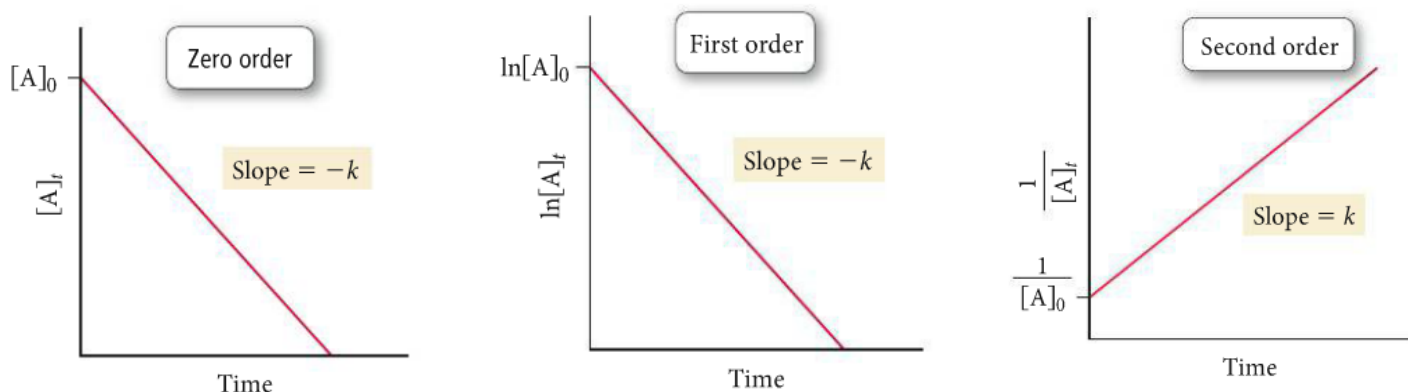
Integrated Rate Laws

Method #2: Go straight! Different orders require different plots to generate straight lines.

To create the needed graphs, set time as your x-axis, and graph three different y-axes (in alphabetical order!)

- **C:** Concentration of the reactant, $[A]$ vs time
- **L:** Natural log of the concentration, $\ln[A]$ vs time
- **R:** Reciprocal of the concentration, $1/[A]$ vs time

The graph which is **most linear** is the one you want!



Note: for each rate order, the absolute value of the slope is equal to the rate constant \rightarrow IF you pick the correct graph!

$$k = |\text{slope}|$$

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate = $k[A]^0$	$M \cdot s^{-1}$	$[A]_t = -kt + [A]_0$		$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k} \frac{[A]_0}{2}$
1	Rate = $k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$ $\ln \frac{[A]_t}{[A]_0} = -kt$		$t_{1/2} = \frac{0.693}{k} = \frac{1}{k} (0.693)$
2	Rate = $k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$		$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k} \frac{1}{[A]_0}$

Units for the Rate Constant (k): different depending of your overall reaction order! The AP Test loves to ask you about the correct units for k given a specific rate law.

Remember: the units of rate are always M/time (often, M/sec; be sure to notice which _____ of time is used).

To determine the unit of k for a given rate law, you can use dimensional analysis (yum!) or the following handy equation:

If $p = \text{overall rate order}$ (_____ of the rate order of each reactant), then:

$$\text{Units for } k = M^{1-p} \text{ time}^{-1}$$

Now you try! Determine the units of k for each of the following rate laws.

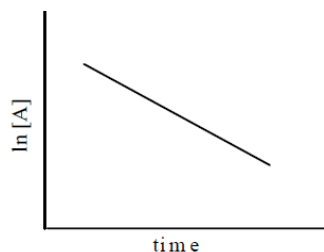
1. Rate = $k[\text{NO}_2]$, overall order of reaction: _____ units of k = _____
2. Rate = $k[\text{H}_2][\text{NO}]^2$, overall order of reaction: _____ units of k = _____
3. Rate = $k[\text{H}_2\text{O}]^0$, overall order of reaction: _____ units of k = _____
4. Rate = $k[\text{O}_3]^2$, overall order of reaction: _____ units of k = _____

Multiple Choice Practice!

Questions 1-3 refer to the following reaction and rate laws. $\text{A} + \text{B} \rightarrow \text{C}$

- (A) Rate = $k[\text{A}]$
- (B) Rate = $k[\text{A}]^2$
- (C) Rate = $k[\text{A}][\text{B}]^2$
- (D) Rate = $k[\text{A}]^2[\text{B}]$
- (E) Rate = $k[\text{B}]$

1. Which represents a reaction that is zero order with respect to reactant A? _____
2. Which represents a reaction that is second order with respect to reactant A and is third order overall? _____
3. Which represents a reaction that is zero order with respect to reactant B and is second order overall? _____
4. For the reaction whose rate law expression is rate = $k[\text{X}]^2$, a plot of which of the following is a straight line?
 - a) $[\text{X}]$ versus time
 - b) $[\text{X}]$ versus 1/time
 - c) $1/[\text{X}]$ versus time
 - d) $\ln[\text{X}]$ versus time
 - e) $\ln[\text{X}]$ versus 1/time
5. Each of the following factors can affect the rate of a chemical reaction EXCEPT
 - a) increasing temperature
 - b) decreasing reactant concentration
 - c) adding a catalyst
 - d) removing products
 - e) breaking up solid reactants



6. Which of the following statements best describe this graph?

- I. The graph represents a reactant that is second order.
- II. The absolute value of the slope for the graph is equal to the rate constant, k .
- III. The units for the rate constant, k will be $M^{-1} \text{time}^{-1}$

- | | |
|------------------|--------------------|
| a) I only | d) II and III only |
| b) II only | e) I, II and III |
| c) I and II only | |

7. As the reaction $A + 2B \rightarrow C$ proceeds at constant temperature, the reaction rate

- a) remains the same since there is no catalyst present
- b) remains the same since the temperature is constant
- c) increases because the rate constant is a large number
- d) increases because the rate of effective collisions increases over time
- e) decreases because the concentrations of the reactants decrease as the reaction progresses

8. For the reaction whose rate law is given below, a plot of which of the following is a straight line?

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

- | | |
|--------------------|--------------------------------|
| a) $[X]$ vs time | c) $\ln[X]$ vs $1/\text{time}$ |
| b) $1/[X]$ vs time | d) $\ln[X]$ vs time |

9. What are the potential units for the rate constant for the reaction below?



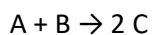
- | | | | |
|-------------|--------------------|--------------------|--------------------|
| a) s^{-1} | b) $s^{-1} M^{-1}$ | c) $s^{-1} M^{-2}$ | d) $s^{-1} M^{-3}$ |
|-------------|--------------------|--------------------|--------------------|

10. $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$

Which of the following is true of the relative rates of disappearance of the reactants and appearance of the products?

- a) O_2 appears at twice the rate that H_2O disappears.
- b) H_2 appears at half the rate that H_2O disappears.
- c) H_2 appears at twice the rate that H_2O disappears.
- d) O_2 appears at half the rate that H_2O disappears.

Free Response Practice Part 1



1. An experiment was performed to determine the rate law for the reaction above. The data below was collected.

Trial	[A] (M)	[B] (M)	rate (M h ⁻¹)
1	0.50	0.50	1.20 x 10 ⁻³
2	1.0	0.50	4.80 x 10 ⁻³
3	2.0	1.0	3.84 x 10 ⁻²
4	1.0	1.0	9.60 x 10 ⁻³

a. What is the order of this reaction with respect to A? Justify your answer.

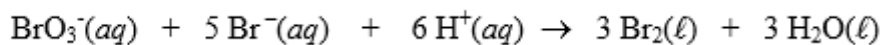
b. What is the order of this reaction with respect to B? Justify your answer.

c. What is the rate law for this reaction?

d. What is the value of the rate constant, k? Include units.

Free Response Practice Part 2

The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the equation:



The table below gives the results of four experiments.

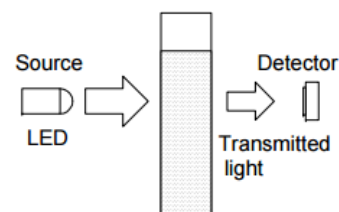
Experiment	Initial [BrO ₃ ⁻]	Initial [Br ⁻]	Initial [H ⁺]	Measured initial rate (mol/L•s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

- Using the data above, determine the order for all three reactants and the overall reaction order. Justify.
- Write the rate law for the reaction.
- What is the value of k , and what are the units of k ?
- For experiment 4, calculate the amount of BrO₃⁻ remaining when 75% of the H⁺ has reacted.
- What is the rate of formation of Br₂ in experiment 1?

Colorimetry: An Experimental Method to Measure Reaction Rate

Colorimetry: an experimental method to measure reaction rate by using a _____ (or spectrophotometer) to determine the _____ of solution by analyzing its color intensity.

- Light from an LED light source passes through a _____ (tiny container) filled with a solution sample, as shown in the figure to the right.
- Some of the incoming light is _____ by the solution. As a result, light of a _____ intensity strikes a photodiode.
- The colorimeter is set to a wavelength the solution being studied absorbs the most, based on the color of the solution: of course, colorimetry only works if one of your reactants or products is _____.



Beer's Law

$$A = abc$$

A: absorbance

a: molar absorptivity (a proportionality constant that's different for every solution)

b: path length (usually 1.00 cm)

c: concentration (measured in molarity)

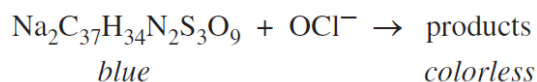
- Beer's Law is important because it demonstrates that absorbance is _____ proportional to concentration (providing the absorbing substance, wavelength, and path length are fixed).
- By measuring the change in absorbance over _____, you can use Beer's law to convert absorbance to _____.
- Graphing [reactant] vs. time, \ln [reactant] vs. time, and $1/[\text{reactant}]$ vs time will allow you to determine if the reaction being studied is zero, first, or second order with respect to that reactant:
 - If **[reactant] vs. time** is most linear, the reaction is _____ order with respect to that reactant.
 - If **\ln [reactant] vs. time** is most linear, the reaction is _____ order with respect to that reactant.
 - If **$1/[\text{reactant}]$ vs. time** is most linear, the reaction is _____ order with respect to that reactant.

Swamping

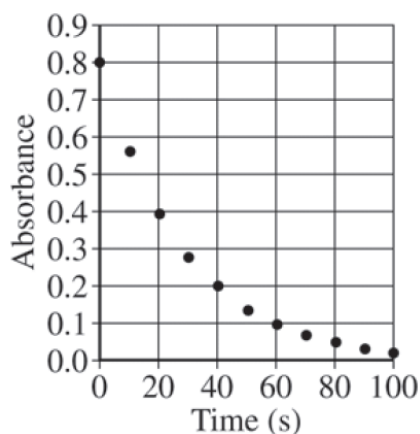
In order to focus on the order of a reaction with respect to a single reactant, a technique called _____ is used.

- All but one of the reactants will start at extremely _____ concentrations (1000X or more in excess)
- The reactants that are in excess won't change significantly during the experiment, so their concentrations can be considered effectively _____; thus, any change in the measured rate of the reaction must be due to the limiting reactant being studied.
- A rate constant determined using the swamping technique is called a _____ rate constant (since you will only know the order with respect to a single reactant).

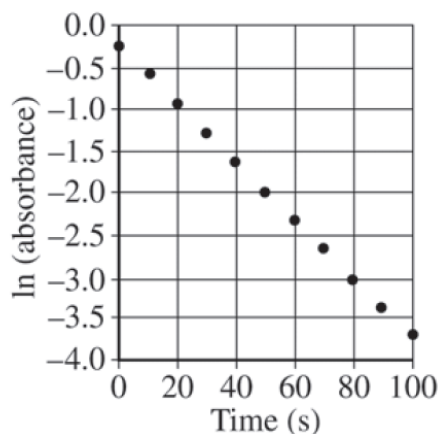
AP Free Response Practice, yum! (2015 FR, modified)



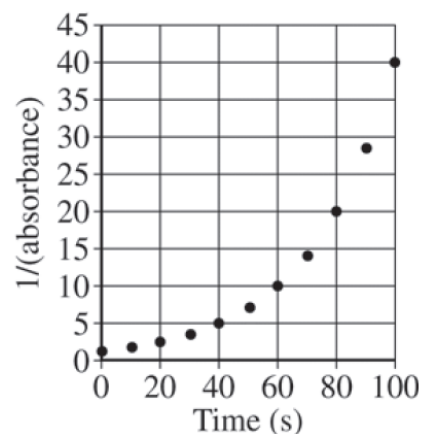
1. Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the study, bleach is present in large excess so that the concentration of OCl^- is essentially constant throughout the reaction. The student used data from the study to generate the graphs below.



Graph I



Graph II



Graph III

- a. Based on the graphs above, what is the order of the reaction with respect to the blue food coloring? Justify your answer.
- b. What would the units be for the rate constant, k ?
- c. In a second experiment, the student prepares solutions of food coloring and bleach with concentrations that differ from those used in the first experiment. When the solutions are combined, the student observes that the reaction mixture reaches an absorbance near zero too rapidly. In order to correct the problem, the student proposes the following three possible modifications to the experiment.
- Increasing the temperature
 - Increasing the concentration of the food coloring
 - Increasing the concentration of the bleach

Circle the one proposed modification above that could correct the problem and explain how that modification increases the time for the reaction mixture to reach an absorbance near zero.

- d. In another experiment, a student wishes to study the oxidation of red food coloring with bleach. How would the student need to modify the original experimental procedure to determine the order of the reaction with respect to the red food coloring?

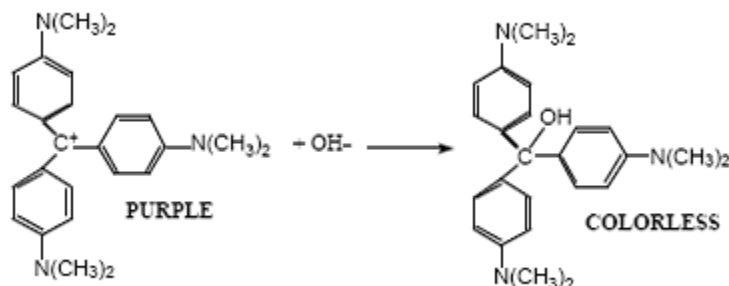
Crystal Violet Lab:

Determination of the Rate of a Reaction, Its Order, and the Effect of Temperature

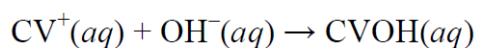
Introduction

In this experiment you will investigate the reaction of crystal violet with sodium hydroxide using a colorimeter. Crystal violet, in aqueous solution, is often used as an indicator in biochemical testing.

We see crystal violet as purple, since it is reflecting a mixture of red and blue light, thus absorbing green light.



The reaction of this organic molecule with sodium hydroxide can be simplified by abbreviating the chemical formula for crystal violet as CV.



As the reaction proceeds, the violet-colored CV⁺ reactant will slowly change to a colorless product. The color change will be precisely measured by a colorimeter set at 565 nm (green) wavelength. You can assume that absorbance is directly proportional to the molar concentration of crystal violet according to Beer's law:

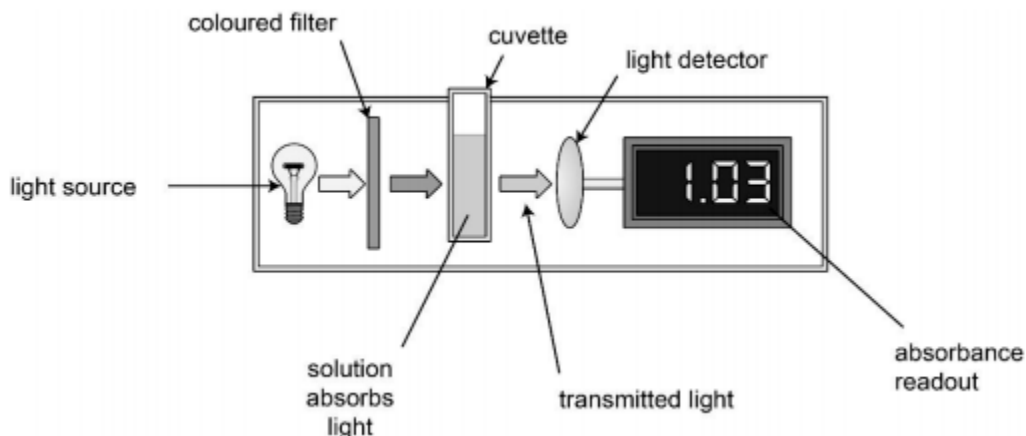
$$A = abc$$

A: absorbance

a: molar absorptivity (a proportionality constant that's different for every solution)

b: path length (usually 1.00 cm)

c: concentration (measured in molarity)



- Beer's Law demonstrates that absorbance is directly proportional to concentration.
- By measuring the change in absorbance over time, you can use Beer's law to convert absorbance to concentration.

Swamping: Determining a Pseudo Rate Constant

The rate law for this reaction is in the form: $\text{rate} = k[\text{CV}^+]^m[\text{OH}^-]^n$, where k is the rate constant for the reaction, m is the order with respect to crystal violet (CV^+), and n is the order with respect to the hydroxide ion. Since the hydroxide ion concentration is *much* more than the concentration of crystal violet, $[\text{OH}^-]$ will not change appreciably during this experiment. This technique is often referred to as “swamping”. Thus, you will find the order with respect to crystal violet (m), but not the order with respect to hydroxide (n). Therefore, the rate constant you will determine is a *pseudo rate constant*.

Objectives: In this experiment, you will

- React solutions of crystal violet and sodium hydroxide at different temperatures.
- Graph the concentration-time data and use the integrated rate law methods to determine the order of CV and the value of a pseudo rate constant, k , for the reaction.
- Measure and record the effect of temperature on the reaction rate and rate constant.

Materials

Data collection device	0.20 M NaOH solution, 10 mL
colorimeter, cuvette	5.0×10^{-3} M crystal violet ($\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$), 10 mL
test tubes	distilled water for calibration, about 10 mL
temperature probe	Kimwipes
cups or beakers	ice bath

Procedure: Someone will need to download the “Sparkvue” app on their phone. It’s free!

1. Turn on the Sparklink Air using the button on the back, and then open Bluetooth settings on your phone, and connect to the Sparklink Air.
2. Open Sparkvue on your phone.
 - a. Choose Sensor path, then choose Table and Graph. (It should already be connected to the Sparklink Air.)
 - b. In the lower left, choose “Periodic” and change the following:
 - i. Sample interval: click left until it reaches **10 seconds**.
 - ii. Autostop: click “no conditions” and change to “**stop after duration**” and set the time to **180 seconds**.
 - iii. Click okay.
 - c. On the graph AND the data table, choose where it says “Red Transmittance” and change to “**Green (565 nm) Absorb**”.
3. Remove blank, and collect materials to start your crystal violet data collection!

Read all steps in #4 completely before you begin.

You will need to MOVE QUICKLY in order to get good results.

4. The first trial will be performed at room temperature. You have been provided with a pipette of 0.20 M NaOH (colorless solution) and a pipette containing an equal quantity of 5.0×10^{-3} M crystal violet (purple solution) in a room temperature water bath.
 - a. Record the temperature of the water bath in your data table.
 - b. Simultaneously squirt both solutions into a cup. Use the tip of one of the pipettes to stir the mixture.
 - b. Quickly fill the cuvette about $\frac{3}{4}$ full with solution and cap it. Wipe exterior of cuvette with a Kimwipe.
 - c. Place the cuvette in the colorimeter and start data collection. (Hit the green start button on the Sparkvue screen, NOT the colorimeter.)
 - d. Once data collection is finished, record your data in the table below, and discard the reaction mixture into the sink.
5. Repeat step #4 using solutions of crystal violet and sodium hydroxide that have been sitting in an ice bath.
6. Clean all apparatus and your lab station: empty pipettes go in the trash, the solution can go down the drain. Rinse all glassware (but NOT the blank cuvette). Return equipment to its proper place.

Crystal Violet Lab Data Table

Room Temperature (_____)		Ice Bath (_____)	
Time (sec)	Green Absorbance	Time (sec)	Green Absorbance
0		0	
10		10	
20		20	
30		30	
40		40	
50		50	
60		60	
70		70	
80		80	
90		90	
100		100	
110		110	
120		120	
130		130	
140		140	
150		150	
160		160	
170		170	
180		180	

Feeling Trendy? Data Analysis with Google Sheets

1. Download a copy of the "Crystal Violet Data Analysis Spreadsheet" from your teacher's website. (The molar absorptivity constant for crystal violet is $5.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and the path length of the cuvette is 1.0 cm.)
2. Add both sets of data: there is one tab at the bottom for ice bath data, and another for room temperature data.

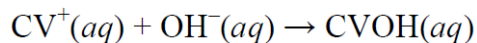
Note 1: The trendline which shows an R^2 value closest to 1.00 is your most linear graph! (Yum, stats.)

Note 2: when looking at graphs, if the first couple of points are clearly erratic, remove from data set!

3. Use the graphs produced to answer the analysis questions below!

Analysis

1. Compare the three graphs created from your room temperature data: what is the order of the reaction with respect to crystal violet? How do you know?
2. Compare the three graphs created from your ice bath temperature data: what is the order of the reaction with respect to crystal violet? How do you know?
3. Are your answers to #1 and #2 the same, or different? *Should* they be the same or different?
4. In another experiment, the reaction is determined to be zeroth order with respect to hydroxide, OH^- . Using this information and your experimental results, write the rate law for the following reaction:



5. Which temperature produced the greatest slope in the [CV] vs time graph? _____
6. How does the slope of a graph relate to the rate constant of this reaction? Which graph will you use?

A Brief Summary of Rate Laws

There are _____ types of rate laws!

- ❖ **Differential rate law:** data table contains _____ and _____ data. Compare change in rate when one reactant is held constant but another doubles to determine the order of the reactants and the value of the rate constant, k .
- ❖ **Integrated rate law:** data table contains _____ and _____ data. (BE CAREFUL: the Tro textbook calls this the 'differential rate law'!!) Use graphical methods determine the order of a given reactant and the value of the rate constant k .

Integrated Rate Laws Review: set time as your x-axis, and graph three different y-axes (in alphabetical order!)

Order	Rate Law	Linear Plot	Straight Line Equation	Half-life
0 th	Rate = $k[A]^0 = k$	Concentration, $[A]$ vs time	$[A]_t - [A]_0 = -kt$	totally exists. (but not AP tested)
1 st	Rate = $k[A]^1$	Natural log, $\ln[A]$ vs time	$\ln[A]_t - \ln[A]_0 = -kt$	$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k}$
2 nd	Rate = $k[A]^2$	Reciprocal, $1/[A]$ vs time	$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$	totally exists. (but not AP tested)

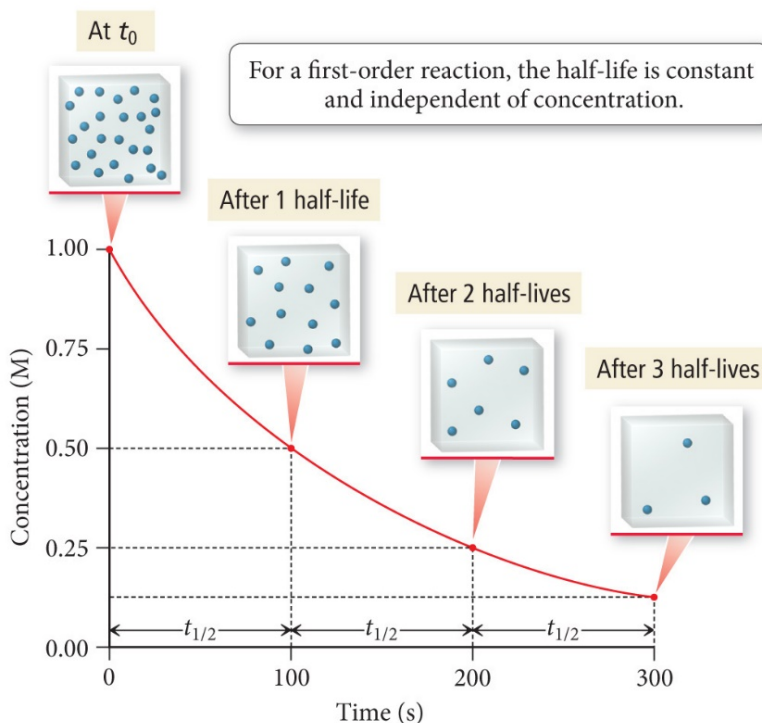
Half-life (_____): time required for _____ of the original reactant sample to disappear.

- ➔ The AP test focuses on the half-life of _____ order reactions only!! They are the only types of reactions for which the length of a half-life is _____.

In a first order reaction, the half-life equation is as follows:

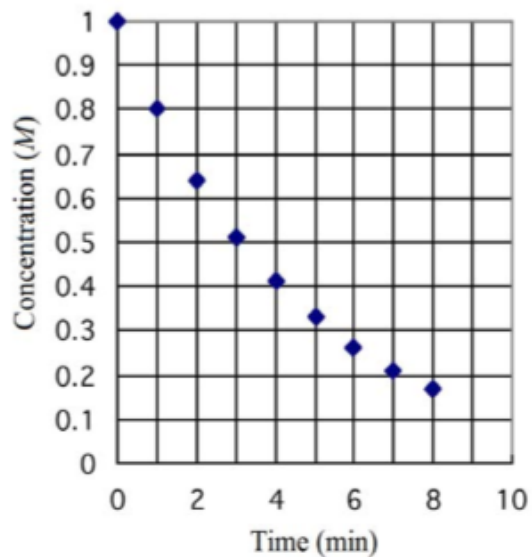
$$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k}$$

Half-Life for a First-Order Reaction

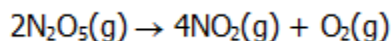


Half-Life Multiple-Choice Practice

- Which reaction order is *not* the reaction order of this reaction?
 - 0th order
 - 1st order
 - 2nd order
 - 3rd order
- What is the half-life of the element shown?
 - 2.05 minutes
 - 3.13 minutes
 - 4.18 minutes
 - 5.22 minutes
- What is the molar concentration of this element after a second half-life has elapsed?
 - 0.75 M
 - 0.50 M
 - 0.25 M
 - 0.13 M
- At what time has 75% of the sample decayed?
 - 4.17 minutes
 - 5.33 minutes
 - 6.08 minutes
 - 7.51 minutes



- The following data was collected at 25°C and 1 atmosphere of pressure for the reaction shown below. Which of the following best represents the half-life for this reaction?



Time (minutes)	[N ₂ O ₅] (mol/L)
0	1.24×10^{-2}
10.	0.92×10^{-2}
20.	0.68×10^{-2}
30.	0.50×10^{-2}
40.	0.37×10^{-2}
50.	0.28×10^{-2}
70.	0.15×10^{-2}

- 15 minutes
 - 18 minutes
 - 23 minutes
 - 36 minutes
- After 44 minutes, a sample of ⁴⁴K is found to have decayed to 25% of the original amount present. What is the half-life of ⁴⁴K?
 - 11 minutes
 - 22 minutes
 - 44 minutes
 - 66 minutes

Collision Theory: A Model that Explains Reaction Rates

Collision Theory is based on the reality that, for a given reaction to occur, molecules **MUST** _____!

****The rate of a reaction is directly proportional to the rate of reactant collisions.****

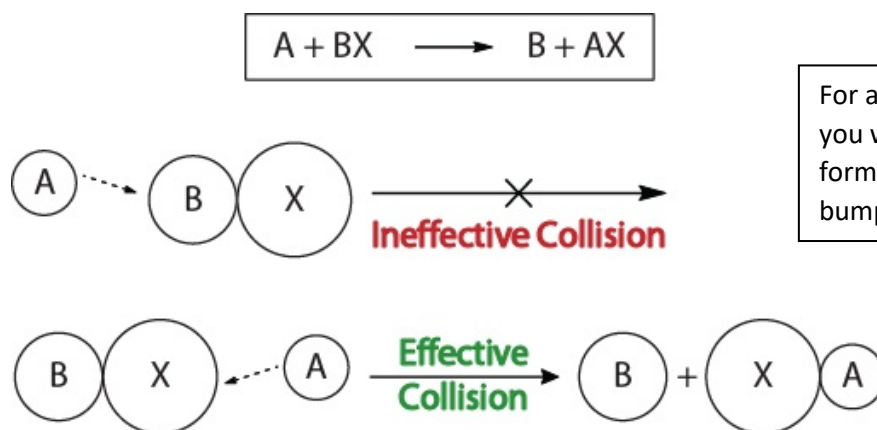
Two conditions must be met for an effective collision: (i.e., collisions of reactants that result in products 😊)

1. Correct orientation: atoms that will form new bonds must _____ into each other.
2. Sufficient energy: atoms that will form new bonds must collide with enough energy to _____ the activation energy of the reaction.

Let's take a look at both of these conditions.

Correct orientation: The reacting species must collide in an orientation that allows _____ between the atoms that will become _____ together in the product.

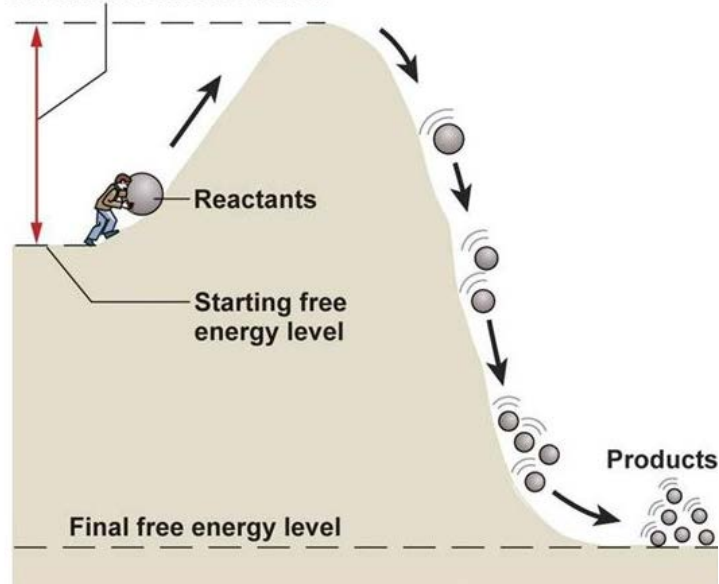
- Sometimes known as the orientation _____: represents the fraction of collisions that occur with an orientation that allows the reaction to occur.
- _____ orientation factor = _____ probability of an effective collision



Sufficient energy: The collision must occur with enough energy to overcome the _____ attractions in the reactant molecules between each bonded atom and their shared electrons, breaking the preexisting bonds and forming new bonds.

- Must overcome the _____ energy!

Activation energy is the "push" needed to start a reaction

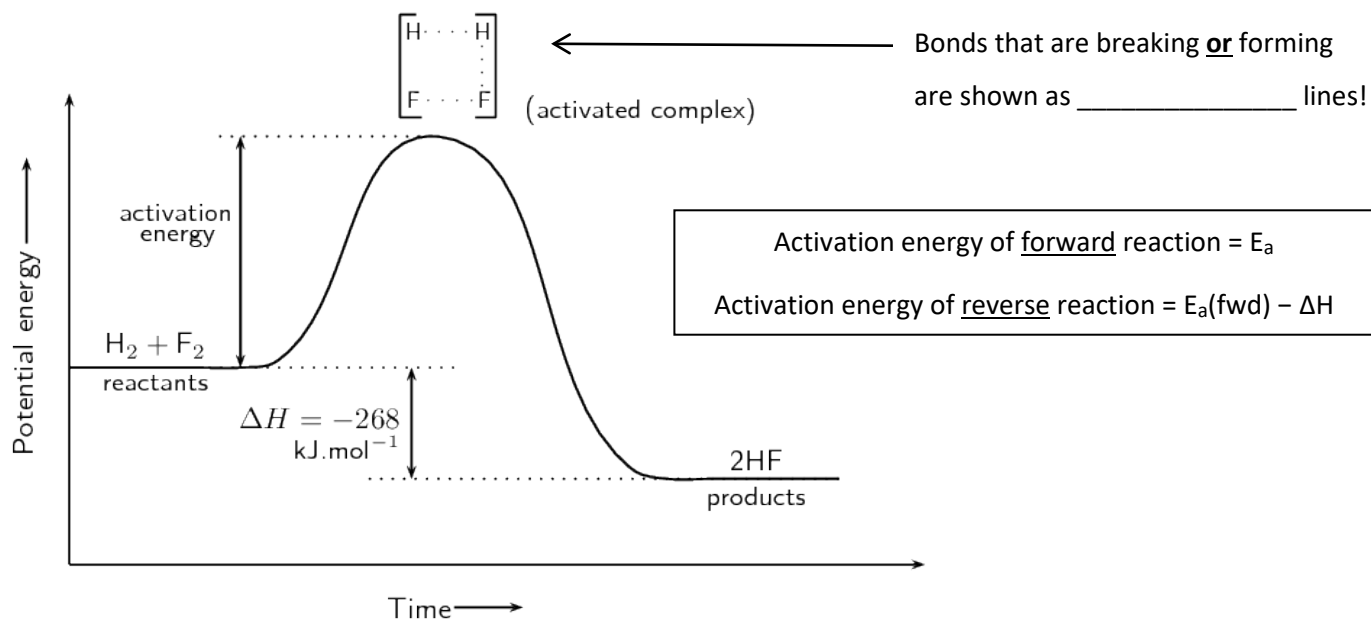


The Reaction Pathway

Activation energy (_____): the energy barrier (or hump) that must be overcome for reactants to convert into products.

IMPORTANT: _____ activation energy = _____ reaction rate!

Activated complex (or transition state): the high energy _____ state that is the collision product of the reactants, with some bonds partially broken and some bonds partially formed. The activated complex can either revert to reactants or proceed to products.



Effect of Temperature on Effective Collisions

As temperature increases, by definition the average _____ energy of the particles also increases.

_____ 'em up = _____ 'em up!

Higher temperature = _____ (faster) reaction rate because:

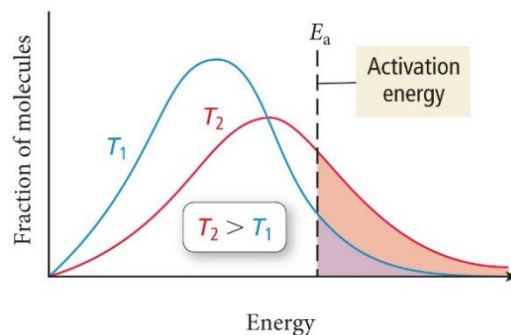
Faster particles =

1. More total collisions
2. Higher energy collisions: a greater fraction of collisions will have enough energy to overcome the activation energy

As you can see in the graph,

- At a lower temperature (T_1), fewer particles have enough energy to overcome activation energy
- At a higher temperature (T_2), _____ particles have enough energy to collide and overcome the activation energy (shaded part of graph)

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.



Please note:

_____ Temperature does _____ decrease activation energy!!
 (Only a catalyst can decrease activation energy: more on that shortly!)

Which is changing: the rate of reaction, or the rate constant, k ?

Only _____ changes will actually affect the rate constant, k , but lots of things can affect the rate of reaction!

- The **rate constant**, k , is the proportionality constant related to the rate of a particular reaction.

Conditions that can change the Rate Constant, k	
Increase k	Decrease k
High temperature	Low temperature
Lower activation energy (catalyst)	Higher activation energy (no catalyst)

- The **rate of a reaction** is the change in concentration of reactants or products per unit time.

Conditions that can change the Reaction Rate	
High Reaction Rates	Low Reaction Rates
High temperature	Low temperature
Low activation energy	High activation energy
Weak reactant bonds	Strong reactant bonds
High orientation factor	Low orientation factor
High reactant concentration	Low reactant concentration

Collision Theory in a Nutshell

Collision theory states that:

1. Particles must collide
2. with sufficient energy
3. in the correct orientation

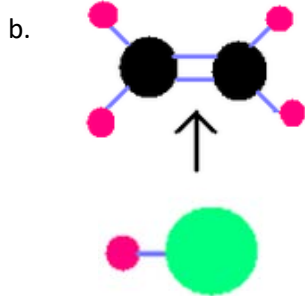
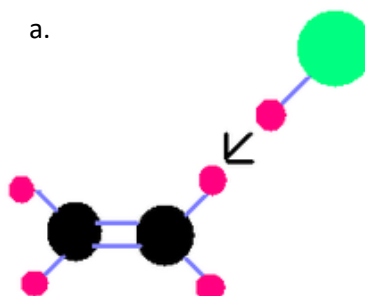
→ for an **effective collision** to occur (where reactants actually turn into products)

Collision theory explains why certain conditions increase the rate of reaction:

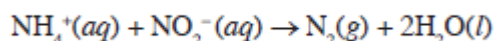
1. **Increased concentration of reactant particles:** More particles means _____ collisions, and thus more opportunity to collide with correct orientation → faster reaction rate!
2. **Increased temperature (i.e. increased kinetic energy):** Particles move faster and collide more _____, which means greater chance of colliding with effective orientation AND they move faster and collide with greater _____, thus having a better chance of overcoming the activation energy → faster reaction rate!
3. **Increased pressure for gases:** Particles are _____ together and therefore _____ likely to collide, and thus more opportunity to collide with correct orientation → faster reaction rate!

Let's Practice! Mmm, delicious multiple choice.

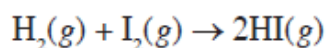
1. In the synthesis reaction between ethene, CH_2CH_2 and HCl , the molecule $\text{CH}_3\text{CH}_2\text{Cl}$ is formed. Which of the following options indicates a viable orientation of both reactant molecules prior to the collision? (Note: the arrow indicates the direction the HCl molecule is moving prior to the collision.)



2. Which of the following reasons correctly explains one reason that increasing the temperature of a reaction increases its speed?
- All the reactant molecules will have more kinetic energy.
 - A larger percentage of reactant molecules will exceed the activation energy barrier.
 - A higher percentage of molecular collisions will have the correct orientation to cause a reaction.
 - The order of each reactant will increase.



3. Increasing the temperature of the above reaction will increase the rate of reaction. Which of the following is NOT a reason that increased temperature increases reaction rate?
- The reactants will be more likely to overcome the activation energy.
 - The number of collisions between reactant molecules will increase.
 - A greater distribution of reactant molecules will have high velocities.
 - The decreased activation energy is easier for reactant molecules to overcome.

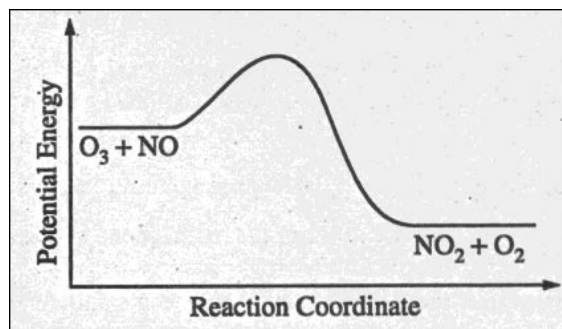


4. When the reaction given above takes place in a sealed isothermal container, the rate law is: $\text{rate} = k[\text{H}_2][\text{I}_2]$. If a mole of H_2 gas is added to the reaction chamber and the temperature remains constant, which of the following will be true?
- The rate of reaction and the rate constant will increase.
 - The rate of reaction and the rate constant will not change.
 - The rate of reaction will increase, and the rate constant will decrease.
 - The rate of reaction will increase, and the rate constant will not change.

More Practice!

1. The diagram to the right shows the energy pathway for the reaction $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$. Clearly label the following directly on the diagram.

- The activation energy for the forward reaction.
- The activation energy for the reverse reaction.
- The enthalpy change (ΔH) for the reaction.
- The point where the activated complex is present.



b. The Lewis dot structures for O_3 and NO are shown below. Use these and your knowledge of chemistry to draw a structure for a possible activated complex of this reaction given the incomplete structure below. Use solid lines to represent unchanged bonds and dotted lines to represent any bonds that are broken or formed in the reaction.

Reactants:

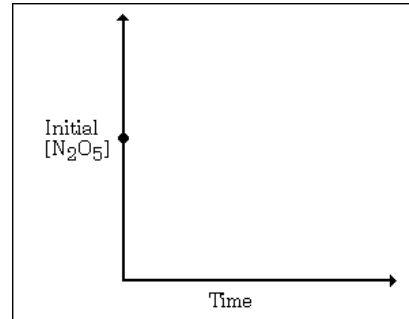


Activated Complex:



2. The reaction $2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2$ is first order with respect to N_2O_5 .

- Using the axes to the right, complete the graph that represents the change in $[\text{N}_2\text{O}_5]$ over time as the reaction proceeds.
- Considering the rate law and the graph in (a), describe how the value of the rate constant, k , could be determined. (Hint: there are two ways!)



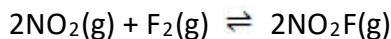
c. If more N_2O_5 were added to the reaction mixture at constant temperature, what would be the effect on the rate constant, k ? Explain.

Reaction Mechanisms: Elementary, my dear Watson!

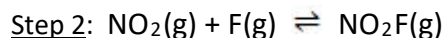
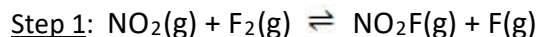
Collision theory assumes that most reactions occur in a series of steps where one or more reactant particles collide, known as the _____.

Example

Overall reaction



Reaction Mechanism



Elementary steps: each single _____ in the mechanism: cannot be broken down into simpler steps

- Elementary steps occur exactly as written: they represent the chemical species that are _____ interacting.
- Because F(g) is made and then consumed, F(g) does _____ show up in the overall reaction: species that are products in an earlier step but then used up as reactants in a later step are called _____.
- When all elementary steps are _____ together, they must add up to be the _____ balanced reaction.

Molecularity (number of molecules participating in an elementary step)

- **Unimolecular:** _____ reactant particle is involved in an elementary step (it may collide with a solvent molecule or other non-reactive particle that is present)
- **Bimolecular reaction:** _____ reactant particles are involved in an elementary step
- **Termolecular reaction:** _____ reactant particles are involved in an elementary step (*very _____*, since three particles would need to simultaneously collide with correct orientation and sufficient energy)

Rate Laws for Elementary Steps

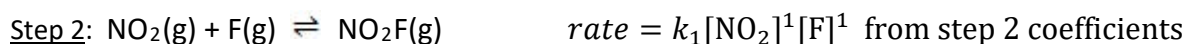
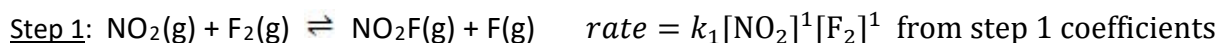
- Each elementary step in the mechanism has its _____ activation energy and its _____ rate law.
- Although the rate law and orders for an overall reaction MUST be determined _____, the rate laws and orders of an elementary step can be derived from the _____ of that specific elementary _____.

Example

Overall reaction



Reaction Mechanism



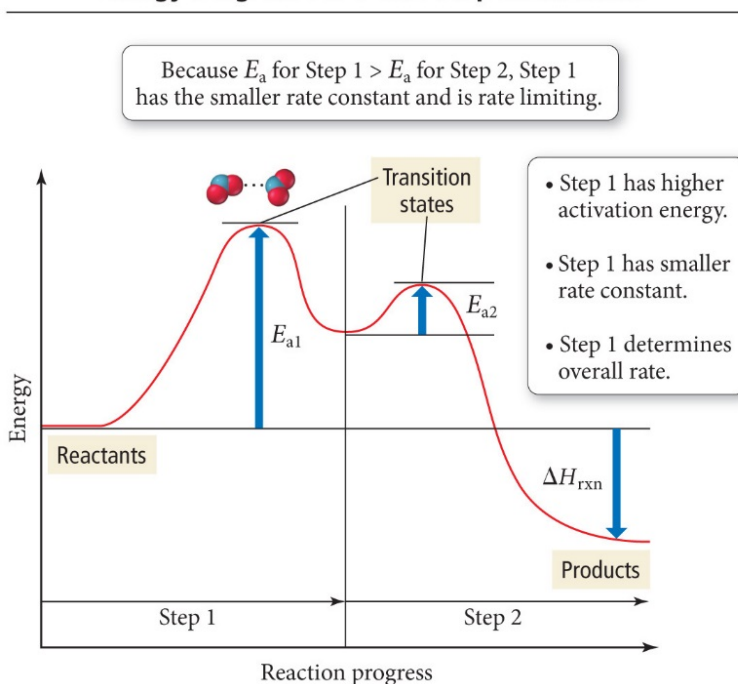
In Summary:

Elementary Step	Molecularity	Rate Law
$A \longrightarrow \text{products}$	1	Rate = $k[A]$
$A + A \longrightarrow \text{products}$	2	Rate = $k[A]^2$
$A + B \longrightarrow \text{products}$	2	Rate = $k[A][B]$
$A + A + A \longrightarrow \text{products}$	3 (rare)	Rate = $k[A]^3$
$A + A + B \longrightarrow \text{products}$	3 (rare)	Rate = $k[A]^2[B]$
$A + B + C \longrightarrow \text{products}$	3 (rare)	Rate = $k[A][B][C]$

Rate-Determining Step (_____): the _____ elementary step in the reaction mechanism

- In a reaction mechanism, product production cannot occur any faster than the _____ step, so this step determines the rate of the overall reaction.
- The slowest, or _____ determining step, has the largest activation energy.
- To determine the rate of the overall reaction, you must combine the rates of _____ elementary steps _____ to and _____ the slowest step in the mechanism.

Energy Diagram for a Two-Step Mechanism



To validate a reaction mechanism, two conditions must be met:

1. Elementary steps must _____ to overall reaction.
2. Rate law predicted by the _____ (the combined rates of all elementary steps up to and including slowest step (RDS) in the mechanism) must be consistent with the _____ observed rate law.

To get credit for free response:

You MUST relate the _____ from the balanced RDS (_____ step) to the _____ of the rate law to justify the mechanism!

Mechanisms with a Fast Initial Step

1. When a mechanism contains a fast initial step, the rate limiting step may contain _____.
2. When a previous step is rapid and reaches _____, the forward and reverse reaction rates are _____, so the concentrations of reactants and products of that step are related – the product is an intermediate.
3. Substituting into the rate law of RDS will produce a rate law in terms of just _____.

Example: Nitrogen oxide is reduced to hydrogen gas to give water and nitrogen: $2 \text{H}_2(\text{g}) + 2 \text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$

The experimentally determined rate law for this reaction is: $\text{rate} = k[\text{H}_2][\text{NO}]^2$

One possible mechanism to account for this reaction is:

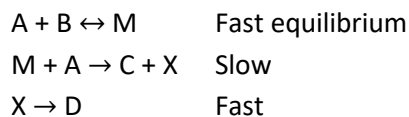
		Rate Law
Step 1:	$2 \text{NO}(\text{g}) \rightleftharpoons \text{N}_2\text{O}_2(\text{g})$	Fast equilibrium
Step 2:	$\text{N}_2\text{O}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g})$	Slow
Step 3:	$\text{N}_2\text{O}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$	Fast

To determine the rate law,

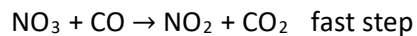
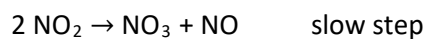
1. Write the rate law for the slow step:
2. Substitute reactants from the equilibrium step to replace any intermediates in the rate law:

Let's Practice!

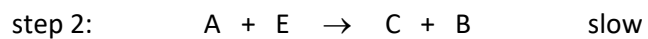
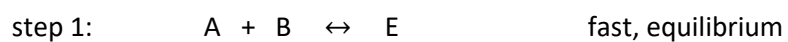
1. Write the rate law for the mechanism shown below. What is the overall reaction?



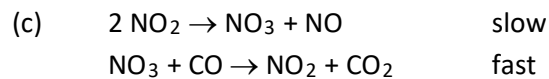
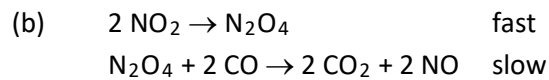
2. Write the rate law for the mechanism shown below. What is the overall reaction?



3. The reaction $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$, obeys the rate law expression $\text{Rate} = k[\text{A}][\text{B}]$. Is the following mechanism consistent with this information? Justify your answer.



4. The rate law for $\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$ is $\text{rate} = k [\text{NO}_2]^2$. Which of the following mechanisms is consistent with the data? Justify your choice.

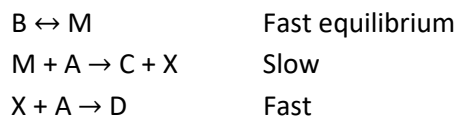


Released AP Free Response Practice – Wheel

1. The following results were obtained when the following reaction was studied at 25°C: $2A + B \rightarrow C + D$

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of C (mol L ⁻¹ min ⁻¹)
1	0.25	0.75	4.3×10^{-4}
2	0.75	0.75	1.3×10^{-3}
3	1.50	1.50	5.3×10^{-3}

- a. Determine the order of the reaction with respect to A and to B. Justify your answer.
- b. Write the rate law for the reaction.
- c. Calculate the value of the rate constant, k , for the reaction, specifying units.
- d. Predict the initial rate of the disappearance of A if $[A]_{\text{init}} = 0.75 \text{ mol L}^{-1}$ and $[B]_{\text{init}} = 1.50 \text{ mol L}^{-1}$.
- e. Is the reaction mechanism represented below consistent with the rate law developed in part (b)? Justify your answer.

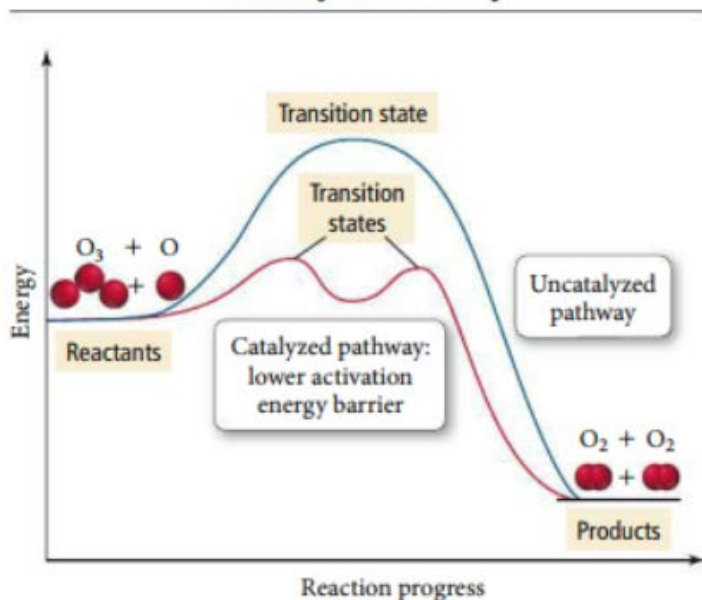


Catalysts

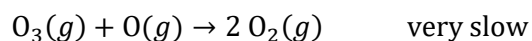
Catalyst: something that _____ the rate of a reaction _____ being consumed in the reaction.

- Provides a surface or better orientation (an alternate pathway) for reaction, increasing _____ of effective collisions
- Usually replaces _____ activation energy step with _____ or more _____ activation energy steps (you need to draw a new energy diagram for catalyzed reaction)
- Is _____ in an early mechanism step and then _____ in a later step.
- Does not change thermodynamics, only kinetics! (can speed up a reaction, but _____ is the same)

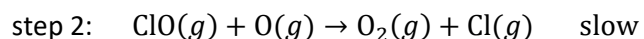
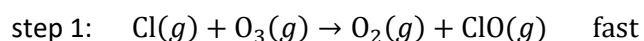
Energy Diagram for Catalyzed and Uncatalyzed Pathways



Mechanism without catalyst:



Mechanism with catalyst:

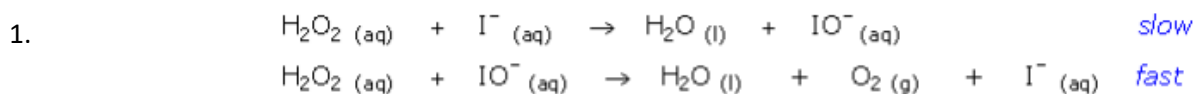


Catalysts vs. Intermediates: two species that can appear in a reaction mechanism, but NOT in the overall reaction!

→ Both are species crossed off when summing a reaction mechanism into overall reaction

- If a species forms as a _____ in an earlier step and is used up as a _____ in a later step (and cancels out), it's an **intermediate**.
- If a species is used as a _____ in an earlier step and is re-formed as a _____ in a later step (and cancels out), it's a **catalyst**.

Let's Practice!

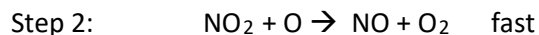


Does this reaction mechanism have an intermediate and/or catalyst? Identify and explain your classification.

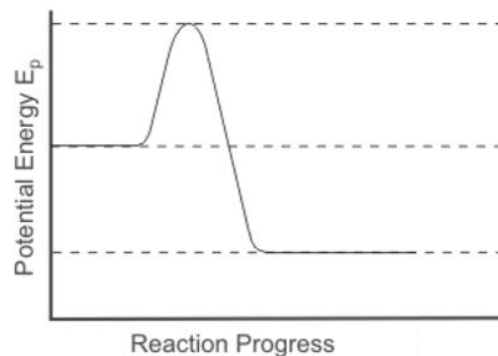
2. Monoxygen reacts with ozone to produce dioxygen molecules in the upper atmosphere: $O + O_3 \rightarrow 2O_2$

The potential energy diagram for this reaction is shown to the right.

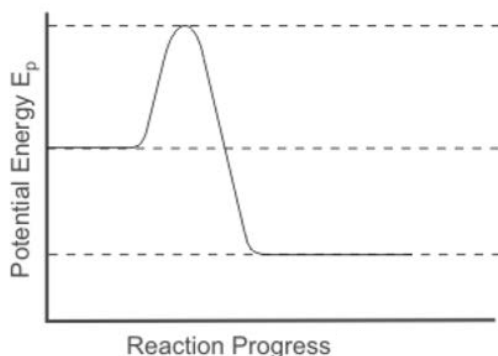
- a. Modify the diagram to the right to show any changes to the reaction pathway that would result for the catalyzed reaction involving these steps:



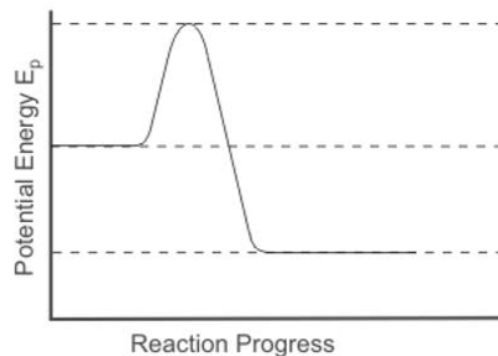
Explain your reasoning.



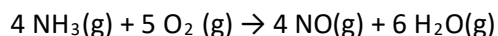
- b. Modify the diagram to the right to show any changes to the reaction pathway that would result when the starting temperature of the reaction was doubled. Explain your reasoning.



- c. Modify the diagram to the right to show any changes to the reaction pathway that would result when the concentration of ozone, O_3 , was decreased by a factor of 3. Explain your reasoning.



Multiple Choice Practice FTW!



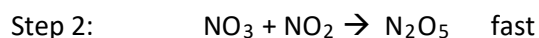
1. The above reaction will experience a rate increase by the addition of a catalyst such as platinum. Which of the following best explains why?
- The catalyst causes the value for ΔG to become more negative.
 - The catalyst increases the percentage of collisions that occur at the proper orientation in the reactant molecules.
 - The catalyst introduces a new reaction mechanism for the reaction.
 - The catalyst increases the activation energy for the reaction.

Use the following information to answer questions 2 – 5.

A multi-step reaction takes place with the following elementary steps:



2. What is the overall balanced equation for this reaction?
- a. $2A + B + 2C + D \rightarrow C + D + B + E$ c. $A + 2C \rightarrow D + E$
 b. $A + B \rightarrow D + E$ d. $2A + C \rightarrow E$
3. What is the function of species B in this reaction?
- a. Without it, no reaction would take place.
 b. It is a reaction intermediate which facilitates the progress of the reaction.
 c. It is a catalyst which lowers the activation energy of the reaction.
 d. It increases the temperature, thus increasing the rate of the reaction.
4. If step II is the slow step for the reaction, what is the overall rate law?
- a. $\text{rate} = k[A]^2[B]$ c. $\text{rate} = k[A][B]$
 b. $\text{rate} = k[A][C]$ d. $\text{rate} = k[A]/[D]$
5. Why would increasing the temperature make the reaction rate go up?
- a. It is an endothermic reaction that needs an outside energy source to function.
 b. The various molecules in the reactions will move faster and collide more often.
 c. The overall activation energy of the reaction will be lowered.
 d. A higher fraction of molecules will have the same activation energy.



6. A proposed reaction mechanism for the reaction of nitrogen dioxide and ozone is detailed above. Which of the following is the rate law for the reaction?
- a. $\text{rate} = k[NO_2][O_3]$ c. $\text{rate} = k[NO_2]^2[O_3]$
 b. $\text{rate} = k[NO_3][NO_2]$ d. $\text{rate} = k[NO_3][O_2]$

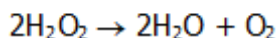
Unit 5 MC Practice

Use the following information to answer questions 1–3.

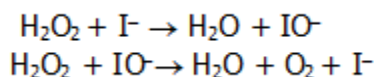
The following experimental data was collected for the hypothetical decomposition reaction $2A \rightarrow B + C$.

Experiment	[A] (M)	T (K)	$t_{1/2}$ (min)
1	0.200	298	0.270
2	0.400	298	0.270
3	0.200	273	0.350
4	0.400	273	0.350

- Based on the information above, what is the order of the reaction?
 - The reaction is second order, because the stoichiometric coefficient of the reactant is 2.
 - The reaction is first order, because half-life is independent of reactant concentration.
 - The reaction is zero order, because changing the reactant concentration did not affect the half-life.
 - The reaction is second order, because decreasing the temperature of the reaction increased the half-life.
- For which experiment is the initial rate of the reaction highest?
 - Experiment 1, because fewer reactant molecules will need to be converted into product.
 - Experiment 2, because both the temperature and reactant concentration are maximized.
 - Experiment 3, because a lower temperature will decompose A most efficiently.
 - Experiment 4, because a lower temperature and higher [reactant] maximizes reaction rate.
- Calculate the rate constant, k , for this reaction at 273 K.
 - 2.86 min^{-1}
 - $2.86 \text{ min}^{-1} \text{ M}^{-1}$
 - 1.98 min^{-1}
 - $1.98 \text{ min}^{-1} \text{ M}^{-1}$



4. The decomposition of hydrogen peroxide is shown above and has the following proposed mechanism:



Which of the following substances serves as a catalyst for this reaction?

- H_2O_2
 - I^-
 - H_2O
 - IO^-
5. For the reaction whose rate law is given below, a plot of which of the following is a straight line?
- $$\text{rate} = k[\text{X}]$$
- [X] vs time
 - $1/[\text{X}]$ vs time
 - $\ln[\text{X}]$ vs 1/time
 - $\ln[\text{X}]$ vs time

6. $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ $\text{rate} = k[\text{A}][\text{B}]^2$

What are the potential units for the rate constant for the above reaction?

- s^{-1}
- $\text{s}^{-1} \text{ M}^{-1}$
- $\text{s}^{-1} \text{ M}^{-2}$
- $\text{s}^{-1} \text{ M}^{-3}$

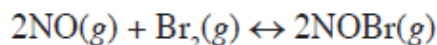
Use the following information to answer questions 7–8.

Reactant A underwent a decomposition reaction: $A \rightarrow 2B + C$. The concentration of A was measured periodically and recorded in the chart below.

Time (Hours)	[A] M
0	0.40
1	0.20
2	0.10
3	0.05

7. Based on the data in the chart, which of the following is the rate law for the reaction?
- a. $\text{rate} = k[A]$ b. $\text{rate} = k[A]^2$ c. $\text{rate} = 2k[A]$ d. $\text{rate} = \frac{1}{2} k[A]$
8. What would be the concentration of B after two hours?
- a. 0.15 M b. 0.20 M c. 0.30 M d. 0.60 M

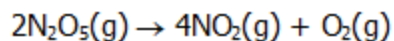
Use the following information to answer questions 9–10.



The above experiment was performed several times, and the following data was gathered:

Trial	$[\text{NO}]_{\text{init}}$ (M)	$[\text{Br}_2]_{\text{init}}$ (M)	Initial Rate of Reaction (M/min)
1	0.20 M	0.10 M	5.20×10^{-3}
2	0.20 M	0.20 M	1.04×10^{-2}
3	0.40 M	0.10 M	2.08×10^{-2}

9. What is the rate law for this reaction?
- a. $\text{rate} = k[\text{NO}][\text{Br}_2]^2$ b. $\text{rate} = k[\text{NO}]^2[\text{Br}_2]^2$ c. $\text{rate} = k[\text{NO}][\text{Br}_2]$ d. $\text{rate} = k[\text{NO}]^2[\text{Br}_2]$
10. What would be the initial rate of the reaction if $[\text{NO}]_{\text{init}} = 0.40 \text{ M}$ and $[\text{Br}_2]_{\text{init}} = 0.20 \text{ M}$?
- a. $2.08 \times 10^{-2} \text{ M/min}$ b. $4.16 \times 10^{-2} \text{ M/min}$ c. $6.24 \times 10^{-2} \text{ M/min}$ d. $8.32 \times 10^{-2} \text{ M/min}$
11. A proposed mechanism for a reaction is as follows:
- $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$ slow step
- $\text{F} + \text{NO}_2 \rightarrow \text{NO}_2\text{F}$ fast step
- What is the order of the overall reaction?
- a. zero order b. first order c. second order d. third order



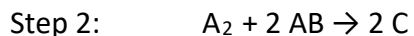
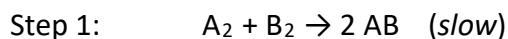
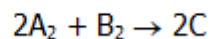
12. The following data was collected at 25°C and 1 atm of pressure for the reaction shown above.

Time (minutes)	[N ₂ O ₅] (mol/L)
0	1.24×10^{-2}
10.	0.92×10^{-2}
20.	0.68×10^{-2}
30.	0.50×10^{-2}
40.	0.37×10^{-2}
50.	0.28×10^{-2}
70.	0.15×10^{-2}

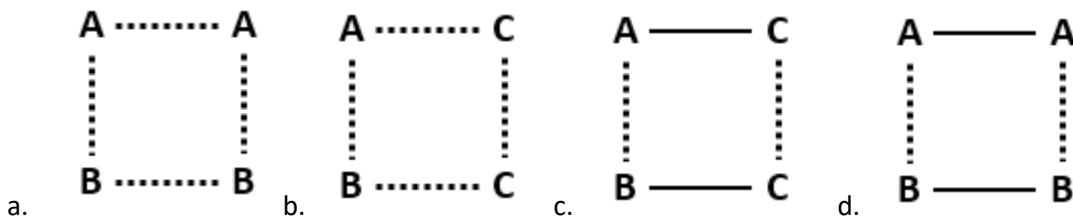
Which of the following best represents the half-life for this reaction?

- a. 15 min b. 18 min c. 23 min d. 36 min

Use the following information to answer questions 13–14.

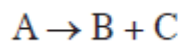


13. The activated complex that forms in Step 1 of the mechanism shown above could have which of the following structures? (The dotted lines represent partial bonds.)



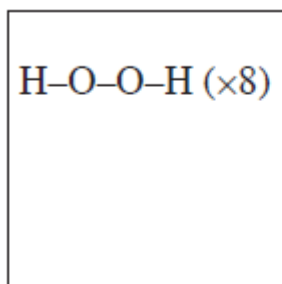
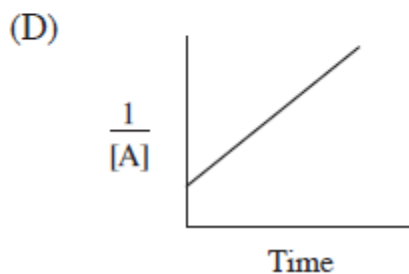
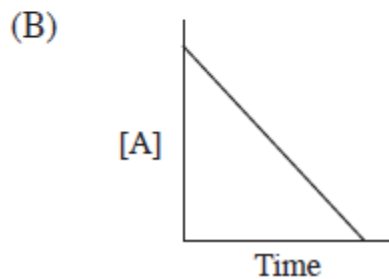
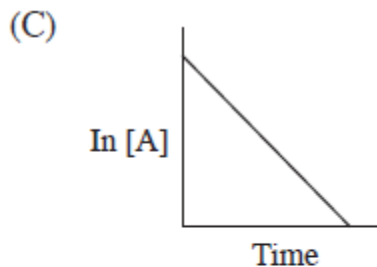
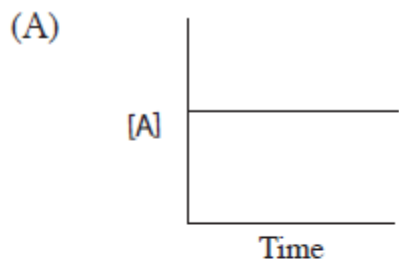
14. Which of the following rate law expressions best agrees with the proposed mechanism?

- a. rate = $k[\text{A}_2]$ b. rate = $k[\text{A}_2]^2$ c. rate = $k[\text{A}_2][\text{R}]$ d. rate = $k[\text{A}_2][\text{B}_2]$

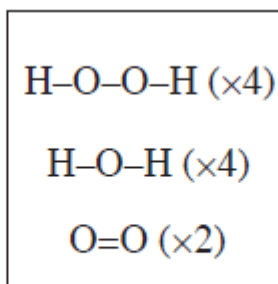


$$\text{rate} = k[A]^2$$

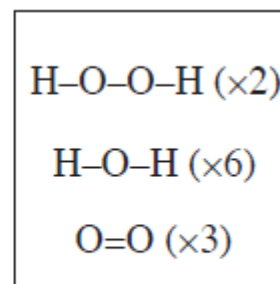
15. Which of the following graphs may have been created using data gathered from the above reaction?



$t = 0\text{s}$



$t = 200\text{s}$



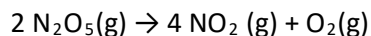
$t = 400\text{s}$

16. The above diagrams show the decomposition of hydrogen peroxide in a sealed container in the presence of a catalyst. What is the overall order for the reaction?

- a. zero order b. first order c. second order d. third order

Unit 5: AP Free Response Practice #1 [2022 #5, 4 points]

1. The following equation represents the decomposition of N_2O_5 , for which the rate law is $\text{rate} = k[\text{N}_2\text{O}_5]$.

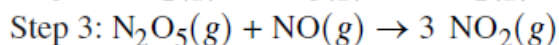
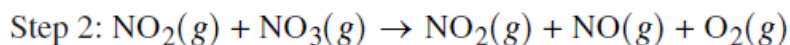
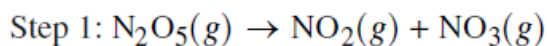


A sample of pure $\text{N}_2\text{O}_5(\text{g})$ is placed in an evacuated container and allowed to decompose at a constant temperature of 300 K. The concentration of $\text{N}_2\text{O}_5(\text{g})$ in the container is measured over a period of time, and the measurements are recorded in the following table.

Time (hr)	$[\text{N}_2\text{O}_5](M)$
0	0.160
1.67	0.0800
3.33	0.0400
5.00	0.0200

- a. Determine the value of the rate constant, k , for the reaction. Include units in your answer. [2 points]

- b. The following mechanism is proposed for the decomposition of $\text{N}_2\text{O}_5(\text{g})$.



Identify which step of the proposed mechanism (1, 2, or 3) is the rate-determining step. Justify your answer in terms of the rate law given. [1 point]

- c. If this experiment was repeated at the same temperature but with twice the initial concentration of N_2O_5 , would the value of k increase, decrease, or remain the same? Explain your reasoning. [1 point]

Unit 5: AP Free Response Practice #2 [4 points]

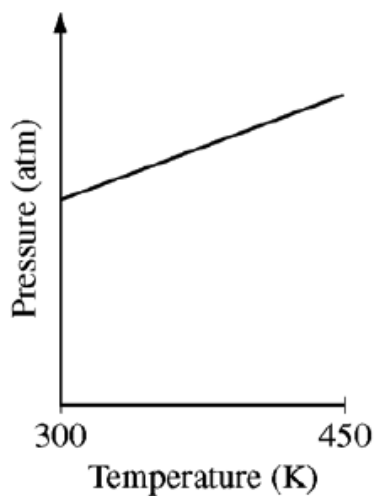
2. The rate of decomposition of azomethane ($C_2H_6N_2$) was studied by monitoring the partial pressure of the reactant as a function of time, and the data below was collected.

Time (s)	P (mmHg)	ln(P)
0	284	5.65
100	220	5.39
150	193	5.26
200	170	5.14
250	150	5.01

- a. Determine if the data above support a first order reaction. Justify your answer. [1 point]
- b. Calculate the rate constant for the reaction, including units. [2 points]
- c. In a second trial, the initial pressure of azomethane was doubled. Does the rate constant, k , for the reaction increase, decrease, or stay the same? Justify your answer. [1 point]

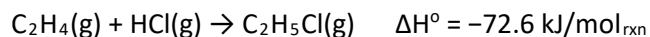
Unit 5: AP Free Response Practice #3 [2013 #5, 8 points]

3. A sample of $\text{C}_2\text{H}_4(g)$ is placed in a previously evacuated, rigid 2.0 L container and heated from 300 K to 450 K. The pressure of the sample is measured and plotted in the graph below.



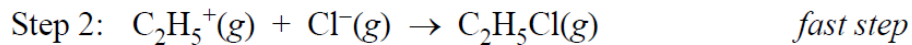
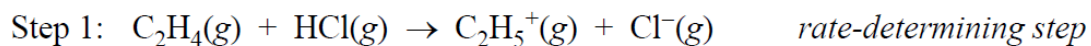
- a. Describe TWO reasons why the pressure changes as the temperature of the $\text{C}_2\text{H}_4(g)$ increases. Your descriptions must be in terms of what occurs at the molecular level. [2 points]

$\text{C}_2\text{H}_4(g)$ reacts readily with $\text{HCl}(g)$ to produce $\text{C}_2\text{H}_5\text{Cl}(g)$, as represented by the following equation.



- b. When $\text{HCl}(g)$ is injected into the container of $\text{C}_2\text{H}_4(g)$ at 450 K, the total pressure increases. Then, as the reaction proceeds at 450 K, the total pressure decreases. Explain this decrease in total pressure in terms of what occurs at the molecular level. [1 point]

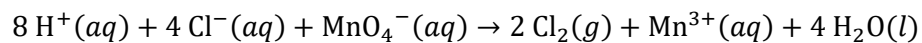
It is proposed that the formation of $\text{C}_2\text{H}_5\text{Cl}(\text{g})$ proceeds via the following two-step reaction mechanism.



- c. Write the rate law for the reaction that is consistent with the reaction mechanism above. [1 point]
- d. Identify an intermediate in the reaction mechanism above. [1 point]
- e. Using the axes provided below, draw a curve that shows the energy changes that occur during the progress of the reaction. The curve should illustrate both the proposed two-step mechanism and the enthalpy change of the reaction. [2 points]



- f. On the diagram above, clearly indicate the activation energy, E_a , for the rate-determining step in the reaction. [1 point]

Unit 5: AP Free Response Practice #4 [2010 #4, 8 points, modified]

1. $\text{Cl}_2(g)$ can be generated in the laboratory by reacting potassium permanganate with an acidified solution of sodium chloride. The net ionic equation for the reaction is given above. An initial rate study was performed on the reaction system. Data for the experiment are given in the table below.

Trial	$[\text{Cl}^-]$	$[\text{MnO}_4^-]$	$[\text{H}^+]$	Rate of Disappearance of MnO_4^- in $M s^{-1}$
1	0.0104	0.00400	3.00	2.25×10^{-8}
2	0.0312	0.00400	3.00	2.03×10^{-7}
3	0.0312	0.00200	3.00	2.03×10^{-7}

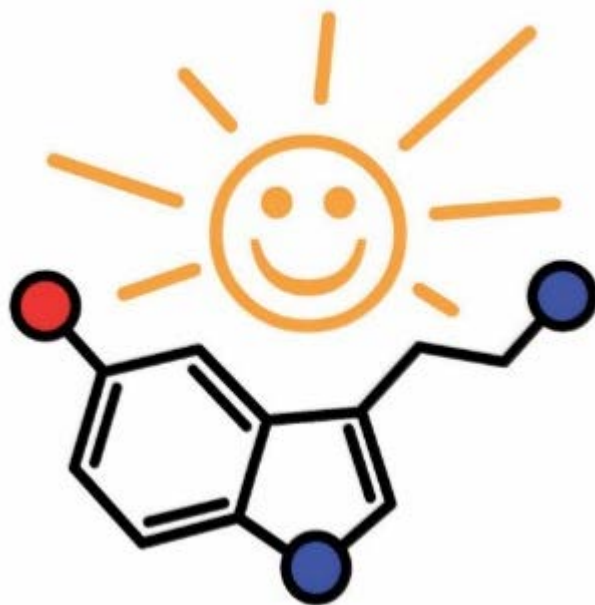
- a. Using the information in the table, determine the order of the reaction with respect to each of the following. Be sure to justify your answers.

i. Cl^- [1 point]

ii. MnO_4^- [1 point]

- b. What other experiments would need to be run in order to determine the reaction order with respect to H^+ ? [1 point]

AP Chemistry FTW!



Fall Final Exam:

Study Guides and Practice

Electrochem Equilibrium Summary

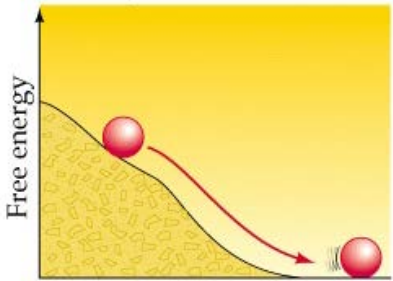
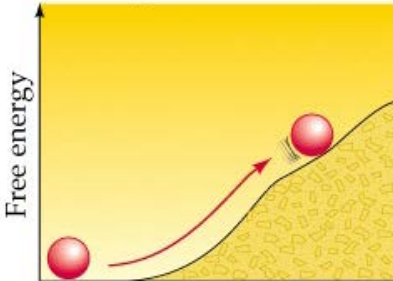
Given on formula chart:

$$\Delta G^{\circ} = -nFE_{cell}^{\circ} \quad n = e^{-} \text{ transferred, } F = \text{Faraday's constant}$$

$$\Delta G^{\circ} = -RT \ln K \quad R = 8.314 \text{ J/(mol K), } T = \text{temp (K), } \ln(k) = \text{natural log of } K$$

Not given on formula chart:

$$K = e^{-\Delta G^{\circ}/RT} \quad e = 2.718, R = 8.314 \text{ J/(mol K), } T = \text{temp (K), } \Delta G \text{ must be in J/mol}$$

Exergonic Reaction ($-\Delta G$)	Endergonic Reaction ($+\Delta G$)
Spontaneous (Thermodynamically Favorable)	<u>Not</u> Spontaneous (Thermodynamically <u>Un</u> favorable)
$+E^{\circ}_{cell} =$ voltage created (battery)	$-E^{\circ}_{cell} =$ external power source needed
$K > 1$	$K < 1$
	

For Spontaneous Reactions: What if it's not at standard conditions?

Further from equilibrium	At standard conditions (1.0 M, 1.0 atm, 298K)	Closer to equilibrium	At equilibrium
$Q < 1$	$Q = 1$	$Q > 1$	$Q \gg 1$
$K \gg \gg Q$	$K \gg Q$	$K > Q$	$K = Q$
[reactants] > [products]	[reactants] = [products]	[reactants] < [products]	[reactants] \ll [products]
Higher voltage (than standard E°_{cell})	Equal voltage (to standard E°_{cell})	Lower voltage (than standard E°_{cell})	No voltage! (dead battery)
$E_{cell} > E^{\circ}_{cell}$	$E_{cell} = E^{\circ}_{cell}$	$E_{cell} < E^{\circ}_{cell}$	$E_{cell} = 0 \text{ V}$
<u>How Does this Happen?</u> <ul style="list-style-type: none"> • Increase reactants • Decrease products • Increase both, but increase REACTANTS more • Decrease both, but decrease PRODUCTS more 	<u>How Does this Happen?</u> <ul style="list-style-type: none"> • Set [reactants] = 1.0 M • Set [products] = 1.0 M • Increase both, but increase BOTH the same • Decrease both, but decrease BOTH the same 	<u>How Does this Happen?</u> <ul style="list-style-type: none"> • Increase products • Decrease reactants • Increase both, but increase PRODUCTS more • Decrease both, but decrease REACTANTS more 	<u>How Does this Happen?</u> <ul style="list-style-type: none"> • Cell runs for a very long time • All reactants used up

AP Fall Final Electrochem Review

OIL RIG – oxidation is loss, reduction is gain (of electrons)

Rules for Assigning Oxidation Numbers (in order of priority)

If any rules are in conflict, follow the rule that is _____ on the list!

Oxidation Rules:

1. Free elements = 0
2. All atoms in a neutral compound add up to 0.
3. All atoms in a polyatomic ion add up to the ion's charge.
4. *The rules below apply to bonded elements:*
 - a. Group 1A metals = +1
 - b. Group 2A = +2
 - c. Non-metals usually follow the chart to the right, in order:
 - d. Note: the carbon family (4A) isn't mentioned – you will ALWAYS have to solve for the oxidation number of group 4A elements in a compound.

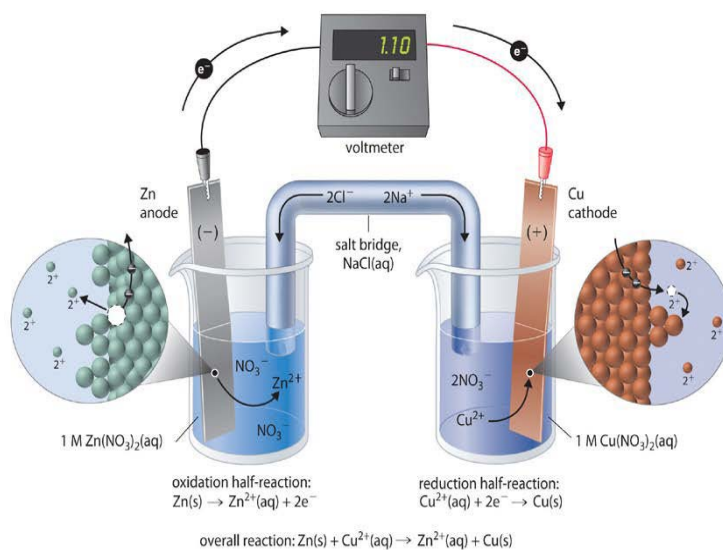
Nonmetal	Oxidation State	Example
Fluorine	-1	MgF ₂ -1 ox state
Hydrogen	+1	H ₂ O +1 ox state
Oxygen	-2	CO ₂ -2 ox state
Group 7A	-1	CCl ₄ -1 ox state
Group 6A	-2	H ₂ S -2 ox state
Group 5A	-3	NH ₃ -3 ox state

Electrochemistry Involves TWO MAIN TYPES Of Electrochemical Cells:

1. Galvanic (voltaic) cells – thermodynamically favorable → **battery** (+E_{cell}, -ΔG, K > 1)
2. Electrolytic cells – thermodynamically unfavorable and require external power source (-E_{cell}, +ΔG, K < 1)

GALVANIC or VOLTAIC CELL “ANATOMY”

- Anode – (An Ox) the electrode where oxidation occurs, loses mass into solution as the cell runs (“anode”-rexic)
- Cathode – (Red Cat) the electrode where reduction occurs, gains mass from solution as the cell runs (fat cat)
- Inert electrodes – used when a gas is involved OR ion to ion; Pt (expensive) or graphite (cheap)
- Salt bridge – used to maintain electrical neutrality in a galvanic cell: **anions to anode, cations to cathode**
- Electron flow – ALWAYS through the wire from anode to cathode (alphabetical order) **FAT CAT



CELL POTENTIAL, E_{cell}

- it is a measure of the electromotive force or the “pull” of the electrons as they travel from the anode to the cathode, measured in Volts (V)
- E_{cell} becomes E^o_{cell} when measurements are taken at standard conditions (1 atm, 1.0 M, and 25°C)

Standard Electrode Potentials (will be given as needed for each problem!)

- Galvanic/voltaic cells: **The MORE POSITIVE reduction potential is reduced**

Calculating Standard Cell Potential Symbolized by E°_{cell}

1. The Metal with the MORE POSITIVE REDUCTION POTENTIAL is be REDUCED, so the other is oxidized.
2. Reverse the equation that will be oxidized and change the sign of its voltage: this is now E°_{ox} .

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{ox}} + E^{\circ}_{\text{red}}$$

DEPENDENCE OF CELL POTENTIAL ON CONCENTRATION

- **Voltaic cells at NONstandard conditions:** Le Chatlier's principle can be applied. An increase in the concentration of a reactant will favor the forward reaction and the cell potential will increase. The converse is also true!
 - \uparrow [reactants] or \downarrow [products]: $E_{\text{cell}} > E^{\circ}_{\text{cell}}$, \uparrow voltage
 - \downarrow [reactants] or \uparrow [products]: $E_{\text{cell}} < E^{\circ}_{\text{cell}}$, \downarrow voltage
- For free response, write out how you calculate the value of the reaction quotient, Q , and compare that value to when $Q = 1$ (standard conditions).
 - **$Q > 1$:** As the concentration of the products of a redox reaction increases, the value of the reaction quotient, Q , increases and therefore the voltage decreases as the reaction shifts to the left decreasing the driving force.
 - **$Q < 1$:** As the concentration of the reactants of a redox reaction increases, the value of the reaction quotient, Q , decreases and therefore the voltage increases as the reaction shifts to the right increasing the driving force.

ELECTROLYTIC CELLS

- Thermodynamically unfavorable, therefore $+\Delta G^{\circ}$ and $-\Delta E^{\circ}$
- Since an electrolytic cell is NOT spontaneous, it will undergo a redox reaction only if an outside power source is applied!
- AN OX and RED CAT still work
- Used to separate ores or plate out metals.

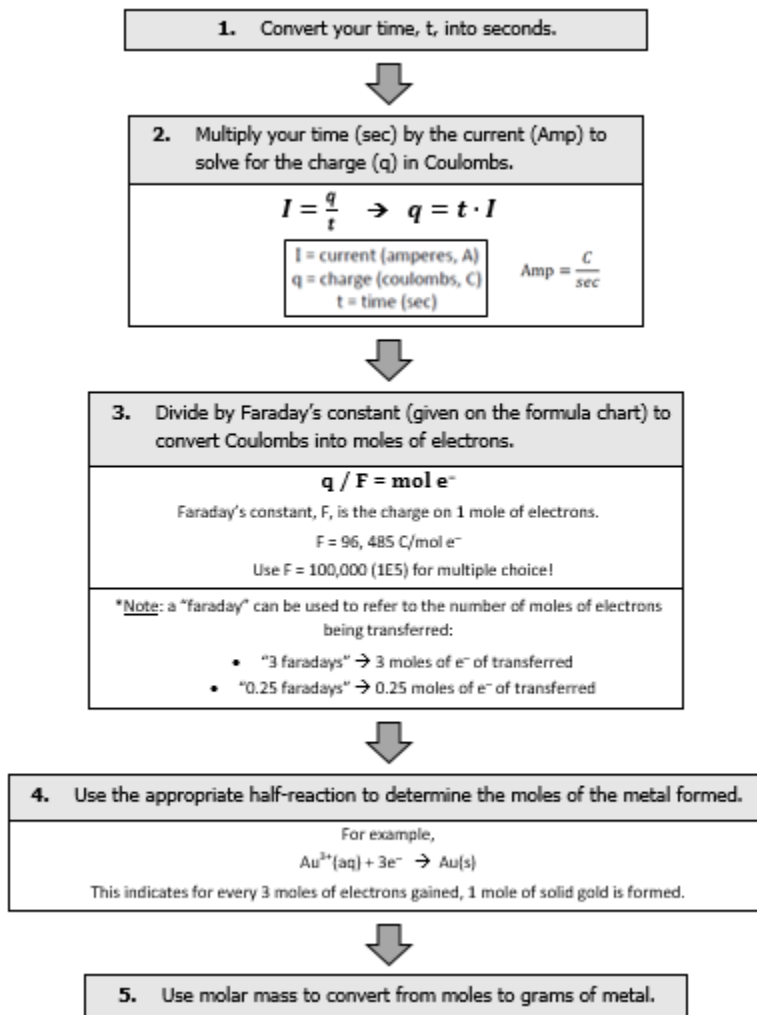
In an electrolytic cell, the amount of product made is related to the number of electrons transferred. Essentially, the electrons are a reactant.

You will need to be able to do two basic calculations for quantitative electrolysis:

1. Given time (sec) and current (A), calculate mass (g).
2. Given mass (g) and current (A), calculate time required (sec).

Quick Trick to remember the order of steps to calculate mass of a metal produced (given time and current):

Are you **SAFE? MMM.**





First: determine what you're being asked to find: ΔH_{rxn} or something else?

1. Asked to find ΔH_{rxn} ? 3 Options!

Given?	Asked to find?	Use:
1. A lot of bond energies 2. A reaction without ΔH_{rxn}	ΔH_{rxn}	1. Draw the Lewis structures. 2. Use the following: $\Delta H_{rxn} = \Sigma(BE_{reactants}) - \Sigma(BE_{products})$
1. A lot of heats of formation (ΔH_f) 2. A reaction without ΔH_{rxn}	ΔH_{rxn}	$\Delta H_{rxn} = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$
1. Multiple reactions with ΔH 2. A goal reaction without ΔH_{rxn}	ΔH_{rxn}	Hess's Law! Rearrange the equations to make the goal equation, then combine your new ΔH 's (remember, what you do to an equation you must do to ΔH !)
1. info to calculate q (using $mC\Delta T$ or $nC\Delta T$) 2. Moles/grams of a chemical	ΔH_{rxn}	$\Delta H_{rxn} = \frac{q}{\text{mol}_{rxn}}$

2. Asked to find something else? 3 Options!

Given?	Asked to find?	Use:
1. A reaction with ΔH_{rxn} 2. Either: a. g or mol of a substance b. energy change (J or kJ)	1. Either: a. g or mol of a substance b. energy change (J or kJ)	Stoich! Don't forget to convert between moles of your substance and moles_{rxn}
1. A phase change (vaporizing, condensing, freezing or melting) 2. ΔH_{vap} or ΔH_{fus}	Energy change (heat absorbed or released)	$q = n\Delta H$
1. A temperature change 2. Mass or moles of a substance 3. Heat capacity ($\frac{J}{g\text{ }^\circ\text{C}}$ or $\frac{J}{\text{mol }^\circ\text{C}}$)	Energy change (heat absorbed or released)	$q = mC\Delta T$

Thermodynamics Study Guide

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

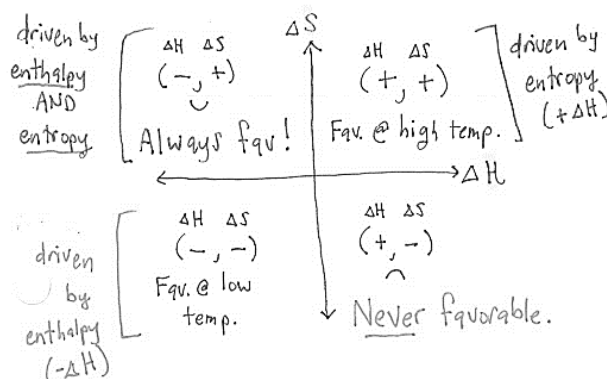
Elements ARE zero for: $\Delta H^\circ, \Delta G^\circ$

Elements are NOT zero for: ΔS°

Nature favors:

1. $+\Delta S^\circ$ (increasing entropy, greater disorder)
2. $-\Delta H^\circ$ (exothermic, release of energy)

- **Driven by enthalpy:** a very exothermic reaction ($-\Delta H$) overcomes a decrease in entropy
- **Driven by entropy:** an endothermic reaction occurs spontaneously because of a highly positive ΔS
- You can use the signs of ΔS and ΔH (together with the reaction $\Delta G = \Delta H - T\Delta S$) to qualitatively predict the spontaneity of a given reaction. You can show this graphically, which leads to the best graph of all time (but SHHHH! It's a secret. 😊)



E_{cell}°	ΔG°	K	K & Q Relationship	Reaction Direction	Spontaneity in the Forward Direction (as written)
+	-	$K > 1$	$K > Q$	Forward	thermodynamically favorable
-	+	$K < 1$	$K < Q$	Reverse	NOT thermodynamically favorable
= 0	= 0	$K = 1$	$K = Q$	No reaction	n/a

At standard conditions (1 M, 1 atm, 298 K):

$$\Delta G^\circ = -nFE_{cell}^\circ$$

n = number of moles of electrons transferred in a **BALANCED** redox reaction

F = faraday's constant = 96,485 C/mol e^- (charge on one mole of electrons)

At standard conditions (1 M, 1 atm, 298 K):

$$\Delta G^\circ = -RT \ln K$$

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

T = temperature (in Kelvin)

K = equilibrium constant

For both reactions, the units for $\Delta G^\circ = \frac{\text{joules}}{\text{moles}_{\text{reaction}}} = \frac{\text{J}}{\text{mol}_{\text{rxn}}}$

END-ing a bond (or IMF/attraction) is always END-othermic! ($+\Delta H$)

Determining
 $\Delta H =$ Enthalpy

PROBLEM SOLVING IN THERMODYNAMICS

Determining
 $\Delta G =$ Free Energy

Calorimetry:

$$q_{\text{gained}} = -q_{\text{lost}}$$

Assess everything losing and gaining heat in the system.
Determine energy change (J) associated with each.

Types of Calorimetry:

1. Things in water:

a. Solid, non-reacting metal

$$[mC\Delta T]_{\text{water}} = -[mC\Delta T]_{\text{metal}}$$

b. Aqueous/reacting things

$$q_{\text{rxn}} = -m_{\text{total}}C\Delta T$$

Usually $C = 4.18 \text{ J/g}^\circ\text{C} = C_{\text{water}}$, but not always! Be careful.

2. Things separate from each other (often this means using a rxn to heat something up):

$$q_{\text{gained}} = -q_{\text{lost}}$$

$$[mC\Delta T]_{\text{gained}} = -[mC\Delta T]_{\text{lost}}$$

Hess's Law:

Using the ΔH 's from equations that were added to get the "goal" equation.

Whatever you do to the equation, you must do to ΔH !

Ex. Flipping an equation $\Delta H * (-1)$
Multiply by two = $\Delta H * 2$
Divide by two = $\Delta H / 2$

Standard Heats of Formation:

Amount of energy involved in the formation of **1 mole** of a substance.

$$\Delta H_{\text{rxn}} = \sum \Delta H_f \text{ products} - \sum \Delta H_f \text{ reactants}$$

*Don't forget to multiply by coefficients!

The Question to answer: **Is the reaction thermodynamically favorable?**

Bond Energy:

The energy it takes to break a bond.
Higher BE implies stronger bonds. Higher bond orders have higher BE's.

$$\Delta H_{\text{rxn}} = \sum \Delta H_{\text{BE}} \text{ reactants} - \sum \Delta H_{\text{BE}} \text{ products}$$

$$\Delta H_{\text{rxn}} = \sum \Delta H_{\text{BE}} \text{ broken} - \sum \Delta H_{\text{BE}} \text{ formed}$$

*Be sure to draw structures to see exactly how many of each bond type are broken and formed!

Determining
 $\Delta S =$ Entropy

Qualitative:

$$S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$$

Compare products to reactants to judge if entropy is increasing/decreasing. Entropy is greater on the side with more moles of gas... etc. Entropy is higher for molecules of higher structural complexity.

Quantitative:

$$\Delta S_{\text{rxn}} = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

Using ΔH and ΔS :

When gas pressures all equal 1 atm.

$$\Delta G = \Delta H - T\Delta S$$

**Units of enthalpy are often kJ/mol while entropy is in J/mol K. Make them match!

Related to Q and K (Equil.):

$$\Delta G^\circ = -RT \ln(K)$$

$$R = 8.314 \times 10^{-3} \text{ kJ/mol}^\circ\text{K}$$

Write in alpha order to predict shift.
 $K > Q$, shift right, $\Delta G = -$ (favorable)
 $K = Q$, at equilibrium, $\Delta G = 0$
 $K < Q$, shift left, $\Delta G = +$ (not favorable)

Le Châtelier's Principle:

Endo (heat as reactant): $\uparrow T$, $\uparrow K$

Exo (heat as product): $\uparrow T$, $\downarrow K$

Related to E°_{cell} (Electro):

$$\Delta G^\circ = -nF (E^\circ_{\text{cell}})$$

$$F = 96,485 \text{ C/mol e}^-$$

n = number of electrons transferred

Free Energy of Formation:

$$\Delta G_{\text{rxn}} = \sum \Delta G_f \text{ products} - \sum \Delta G_f \text{ reactants}$$

If ΔG is **negative**, the reaction **IS** thermodynamically favorable.

If ΔG is **positive**, the reaction is **NOT** thermodynamically favorable.

*Be able to predict spontaneity based on enthalpy, entropy, temperature, voltage, and equilibrium quotients.

General Chemistry**1. [5 POINTS]**

A sample of an unknown hydrocarbon was burned in air.

- (a) When the hydrocarbon sample was burned in a reaction that went to completion, 2.2 grams of water and 3.6 liters of carbon dioxide were produced under standard conditions. What is the empirical formula of the hydrocarbon? **[2 POINTS]**
- (b) If the molar mass of the compound was determined to be 28.1 g/mol, what is the molecular formula of the hydrocarbon? **[2 POINTS]**
- (c) Write the balanced equation for the combustion reaction that took place in (a). **[1 POINT]**

UNIT 3 FREE RESPONSE REVIEW

Electrochemistry

2. [9 POINTS]

A strip of Ni metal is placed in a 1.0 M solution of $\text{Ni}(\text{NO}_3)_2$ and a strip of Ag metal is placed in a 1.0 M solution of AgNO_3 . An electrochemical cell is created when the two solutions are connected by a salt bridge and the two metal strips are connected by wires to a voltmeter.

Standard Reduction Potentials at 25°C	
Reduction Half-Reaction	$E^\circ(\text{V})$
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	+ 1.50
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+ 0.80
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	- 0.25
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}(\text{s})$	- 2.71

- (a) Write the balanced chemical equation for the overall reaction that occurs in the cell, and calculate the cell potential, E° . [2 POINTS]
- (b) Calculate how many grams of metal will be deposited on the cathode if the cell is allowed to run at constant current of 1.5 amperes for 8.00 minutes. [2 POINTS]
- (c) Calculate the value of the standard free energy change, ΔG° , for the cell reaction. [2 POINTS]

UNIT 3 FREE RESPONSE REVIEW

Electrochemistry

- (d) Predict: will the cell potential, E_{cell} , at 25°C for the cell shown above be higher, lower, or equal to the standard cell potential E°_{cell} , if the initial concentration of $\text{Ni}(\text{NO}_3)_2$ is 0.100 M and the initial concentration of AgNO_3 is 1.20 M . **[2 POINTS]**
- (e) Is the reaction in the cell thermodynamically favorable under conditions described in part (d)? Justify your answer. **[1 POINT]**

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UNITS 4 and 5 FREE RESPONSE REVIEW
Thermochemistry and Thermodynamics

3. [8 POINTS]



The above reaction for the combustion of methane gas has a standard entropy change, ΔS° , with a value of 242.7 J/mol•K. The following data are also available.

Compound	ΔH°_f (kJ/mol)
CH ₄ (g)	-74.8
H ₂ O(l)	-285.9
CO ₂ (g)	-393.5

- (a) What are the values of ΔH°_f and ΔG°_f for O₂(g)? **[1 POINT]**
- (b) Calculate the standard change in enthalpy, ΔH° , for the combustion of methane. **[2 POINTS]**
- (c) Calculate the standard free energy change, ΔG° , for the combustion of methane. **[2 POINTS]**
- (d) How would the value of ΔS° for the reaction be affected if the water produced in the combustion remained in the gas phase? **[1 POINT]**
- (e) A 20.0 g sample of CH₄(g) underwent combustion in a bomb calorimeter with excess oxygen gas.
- (i) Calculate the mass of carbon dioxide produced. **[1 POINT]**
- (ii) Calculate the heat released by the reaction. **[1 POINT]**

Kinetics

4. [8 POINTS]



The following results were obtained in experiments designed to study the rate of the reaction above:

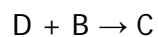
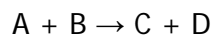
Experiment	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial rate of disappearance of A (M/sec)
1	0.05	0.05	3.0×10^{-3}
2	0.05	0.10	6.0×10^{-3}
3	0.10	0.10	1.2×10^{-2}
4	0.20	0.10	2.4×10^{-2}

- (a) Determine the order of the reaction with respect to A. Justify your response. **[1 POINT]**
- (b) Determine the order of the reaction with respect to B. Justify your response. **[1 POINT]**
- (c) Write the rate law for the reaction. **[1 POINT]**
- (d) Calculate the value of the rate constant, k , for the reaction. Include the units. **[2 POINTS]**
- (e) If another experiment is attempted with [A] and [B], both 0.020-molar, what would be the initial rate of disappearance of A? **[1 POINT]**

UNIT 6 FREE RESPONSE REVIEW

Kinetics

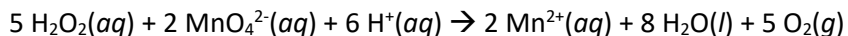
- (f) The following reaction mechanism was proposed for the reaction above:



- (i) Show the mechanism is consistent with the balanced reaction. **[1 POINT]**
- (ii) Show which step is the rate-determining step, and explain your choice. **[1 POINT]**
- (iii) In the mechanism, would D be classified as a catalyst or an intermediate? Justify your response. **[1 POINT]**

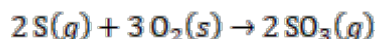
MMM, Delicious MC Practice for the AP Chem Fall Final!

1. Dark purple KMnO_4 solution is added from a buret to a colorless, acidified solution of $\text{H}_2\text{O}_2(\text{aq})$ in an Erlenmeyer flask. (Note: At the end point of the titration, the solution is a pale pink color.)

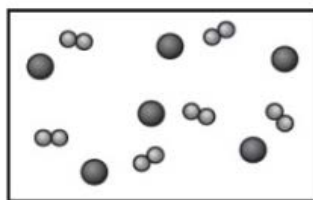


Which element is being oxidized, and what is the element's change in oxidation number?

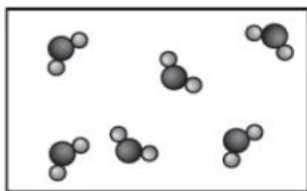
- A Oxygen, which changes from -1 to 0
 B Oxygen, which changes from 0 to -2
 C Manganese, which changes from -1 to +2
 D Manganese, which changes from +7 to +2
2. The equation for the reaction is:



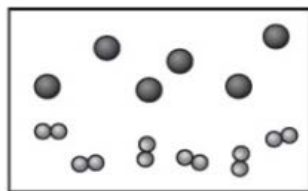
Consider a mixture of sulfur atoms and dioxygen molecules in a closed container below:



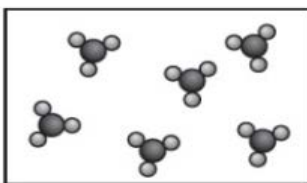
Which of the following best represents what's in the container after the reaction goes to completion?



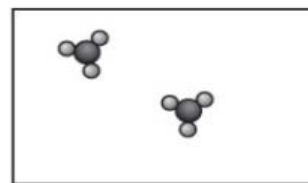
A



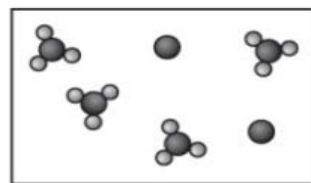
B



C



D

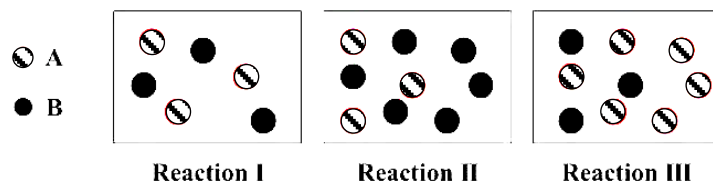


E

3. What is the net ionic equation for the acid-base reaction that occurs when nitric acid is added to solid copper (II) hydroxide?

- a. $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$
 b. $2 \text{H}^+(\text{aq}) + \text{Cu}(\text{OH})_2(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$
 c. $2 \text{H}^+(\text{aq}) + 2 \text{NO}_3^-(\text{aq}) + \text{Cu}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq}) \rightarrow \text{Cu}(\text{NO}_3)_2(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$
 d. $2 \text{H}^+(\text{aq}) + 2 \text{NO}_3^-(\text{aq}) + \text{Cu}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2 \text{NO}_3^-(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$

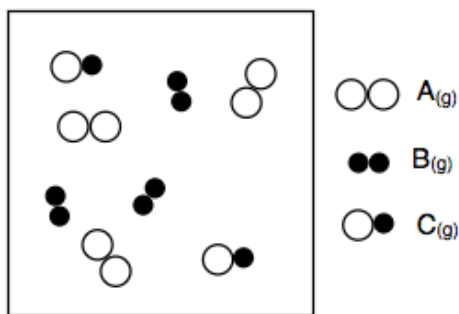
4. When 2.00 g of H_2 reacts with 32.0 g of O_2 in an explosion, the final gas mixture will contain:
- a. H_2 , H_2O , and O_2 b. H_2 and H_2O only c. O_2 and H_2O only d. H_2O only



5. The following boxes represent reactions of $\text{A} \rightleftharpoons \text{B}$ at equilibrium.
- For which reaction shown above is K smallest?
- a. Reaction I
 b. Reaction II
 c. Reaction III
 d. Cannot be determined.
6. Under equilibrium conditions, 0.60 moles of A, 0.60 moles of B and 0.60 moles of C are present in a 3.1 L solution for the reaction shown below. Determine the value of the equilibrium constant, K .



- a. $K = 17$ b. $K = 5.2$ c. $K = 1.7$ d. $K = 0.52$



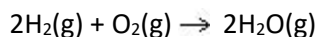
7. The picture above shows the species initially present in a 1.0 L container. The chemical reaction shown below takes place.



Which of the following statements is true?

- a. The reaction shifts towards the products to reach equilibrium.
 b. The reaction shifts towards the reactants to reach equilibrium.
 c. The reaction mixture is at equilibrium.
 d. The direction of shift cannot be determined from the information given.

8. If the temperature at which a reaction takes place is increased, the rate of the reaction will
- A increase if the reaction is endothermic and decrease if the reaction is exothermic.
 - B decrease if the reaction is endothermic and increase if the reaction is exothermic.
 - C increase if the reaction is endothermic and increase if the reaction is exothermic.
 - D decrease if the reaction is endothermic and decrease if the reaction is exothermic.

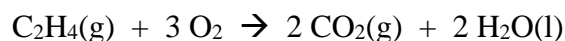


9. Based on the information given in the table below, what is the ΔH° for the above reaction?

Bond	Average Bond Energy (kJ/mol)
H-H	500
O=O	500
O-H	500

- A +1000kJ B -500kJ C +1000kJ D -1500kJ

10. The equation for the combustion of the flammable gas ethene, C_2H_4 , is shown below.

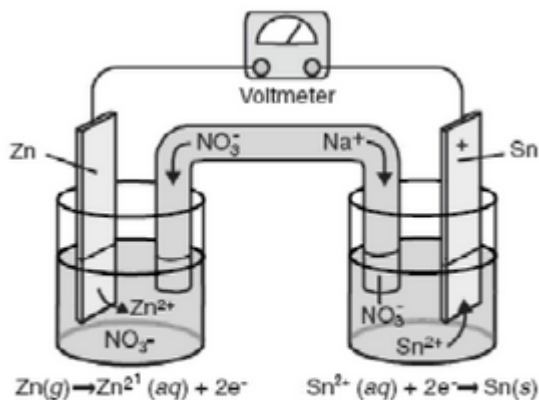


Given the table of bond energies below, what is the enthalpy change for this reaction?

Bond	Average Bond Energy (kJ/mol)	Bond	Average Bond Energy (kJ/mol)
C - H	413	C = O	799
C - C	347	H - O	467
C = C	614	H - H	432
C - O	358	O = O	495

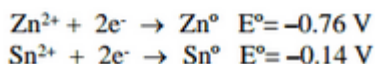
- A -1,313 kJ/mol B +1,313 kJ/mol C -952 kJ/mol_{rxn} D +952 kJ/mol_{rxn}

11.

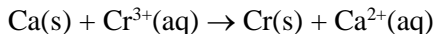


If the half-cell containing 1.00 M $\text{Zn}^{2+}(\text{aq})$ to the left is replaced with a half-cell containing 2.00M $\text{Zn}^{2+}(\text{aq})$, what will be the effect on the cell potential and voltage of the galvanic cell?

- A The voltage will decrease and the cell potential will increase.
- B The voltage will increase and the cell potential will decrease.
- C The voltage will decrease and the cell potential will decrease.
- D The voltage will increase and the cell potential will increase.

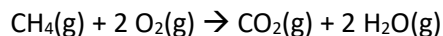


12. How many electrons are transferred in the following reaction? (The reaction is unbalanced.)



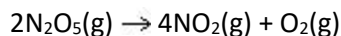
- A 2 B 4 C 3 D 6

13. What element is undergoing oxidation (if any) in the following reaction?



- A O B H C C D both C and H

14.



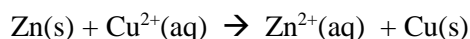
A sample of N_2O_5 was placed in an evacuated container, and the reaction represented above occurred. The value of $P_{\text{N}_2\text{O}_5}$, the partial pressure of $\text{N}_2\text{O}_5(\text{g})$, was measured during the reaction and recorded in the table below.

Time (min)	$P_{\text{N}_2\text{O}_5}$ (atm)	$\ln(P_{\text{N}_2\text{O}_5})$	$\frac{1}{P_{\text{N}_2\text{O}_5}}$ (atm^{-1})
0	150	5.0	0.0067
100	75	4.3	0.013
200	38	3.6	0.027
300	19	2.9	0.053

Which of the following correctly describes the reaction?

- A The decomposition of N_2O_5 is a zero-order reaction.
 B The decomposition of N_2O_5 is a first-order reaction.
 C The decomposition of N_2O_5 is a second-order reaction.
 D The overall reaction order is 3.

15.



Based on the reaction represented above, an electrolytic cell was constructed from zinc and copper half-cells. The observed voltage was found to be 1.30 volt. However, the standard cell potential, E° , is 1.05 volts. Which of the following could correctly account for this observation?

- A The copper electrode was larger than the zinc electrode.
 B The Cu^{2+} solution was more concentrated than the Zn^{2+} solution.
 C The Zn^{2+} solution was more concentrated than the Cu^{2+} solution.
 D The solutions in the half-cells had different volumes.

16. Which of the following sets of conditions must be true for a reaction that is thermodynamically favorable at low temperatures?

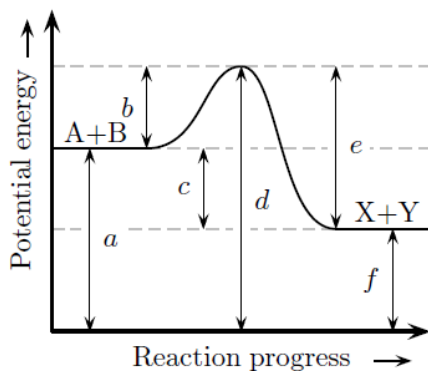
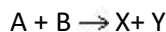
A $\Delta H > 0, \Delta S > 0$

C $\Delta H < 0, \Delta S > 0$

B $\Delta H > 0, \Delta S < 0$

D $\Delta H < 0, \Delta S < 0$

Consider the following potential energy diagram and the statements that follow for the general reaction



17. Which of the following statements are true?

I. The reaction represents an endothermic reaction.

II. Arrow *d* represents the enthalpy change for the reaction.

III. The reaction releases heat energy to the surroundings.

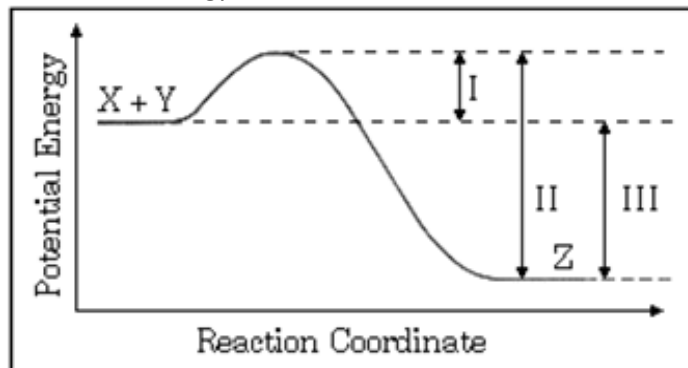
A II and III only

B III only

C I only

D I and II only

18. The energy diagram for the reaction $X + Y \rightarrow Z$ is shown below. The addition of a catalyst to this reaction would cause a change in which of the indicated energy differences?



A I only

B II only

C III only

D I and II only

19. Consider the following equilibrium: $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$

The proper K_{eq} expression is:

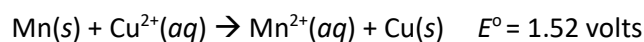
A $\frac{\sqrt{[H_2][I_2]}}{[HI]^2}$

B $\frac{[H_2][I_2]}{[HI]}$

C $\frac{[HI]^2}{[H_2][I_2]}$

D $\frac{[HI]^2}{[H_2]}$

Refer to the following equation for the following two questions.



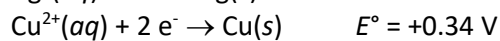
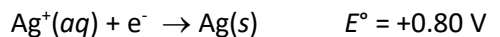
20. Which expression shows the calculations of ΔG° in **kJ/mol** for this reaction?

- | | |
|---|---|
| <p>A $-2 \times 8.31 \times 1.52 \times 1000$</p> <p>B $\frac{-2 \times 96500 \times 1.52}{1000}$</p> | <p>C $\frac{-2 \times 96500 \times 1.52}{8.31}$</p> <p>D $\frac{-2 \times 96500}{8.31 \times 1.52}$</p> |
|---|---|

21. Which of the following statements about the above reaction are correct?

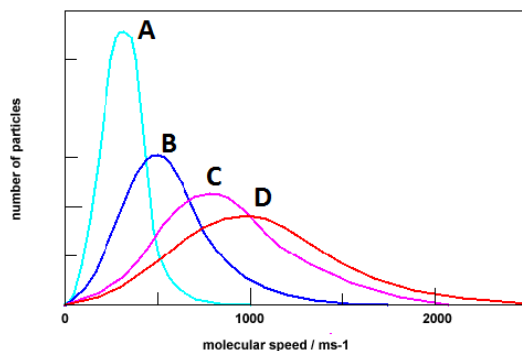
- | | |
|---|--|
| <p>I. $\text{Mn}(s)$ is oxidized.</p> <p>II. The $\text{Cu}(s)$ acts as the anode.</p> <p>III. The equilibrium constant, K_{eq}, is less than 1.</p> <p>A I only</p> <p>B II only</p> | <p>C I and II only</p> <p>D I, II, and III</p> |
|---|--|

22. A galvanic cell consists of one half-cell that contains $\text{Ag}(s)$ and $\text{Ag}^+(aq)$, and one half-cell that contains $\text{Cu}(s)$ and $\text{Cu}^{2+}(aq)$. What species are produced at the electrodes under standard conditions?



- A** $\text{Cu}(s)$ is formed at the cathode, and $\text{Ag}^+(aq)$ is formed at the anode.
- B** $\text{Cu}^{2+}(aq)$ is formed at the cathode, and $\text{Cu}(s)$ is formed at the anode.
- C** $\text{Ag}(aq)$ is formed at the cathode and, $\text{Cu}(s)$ is formed at the anode.
- D** $\text{Ag}(s)$ is formed at the cathode, and $\text{Cu}^{2+}(aq)$ is formed at the anode.

23.



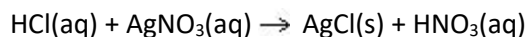
The Maxwell-Boltzmann distribution above represents four different temperature samples of the same gas collected under constant pressure conditions. Which plot in the graph represents the sample at the highest temperature?

- A** A **B** B **C** C **D** D

24. How many Na^+ ions are in 500. mL of 0.20 M NaF solution?

- A 3.01×10^{22} ions C 6.02×10^{20} ions
 B 3.01×10^{20} ions D 6.02×10^{22} ions

25.



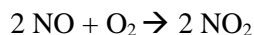
One-half liter of a 0.20 molar HCl solution is mixed with one-half-liter of a 0.40-molar solution of AgNO_3 . A reaction occurs forming a precipitate as shown above. If the reaction goes to completion, what is the mass of AgCl produced?

- A 14 grams B 70 grams C 84 grams D 28 grams

26.

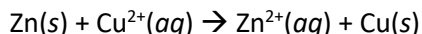
Experiment	Initial [NO] (mol L ⁻¹)	Initial [O ₂] (mol L ⁻¹)	Initial Rate of Formation of NO ₂ (mol L ⁻¹ s ⁻¹)
1	0.10	0.10	2.5×10^{-4}
2	0.20	0.10	5.0×10^{-4}
3	0.20	0.40	8.0×10^{-3}

The initial-rate data in the table above were obtained for the reaction represented below. What is the experimental rate law for the reaction?



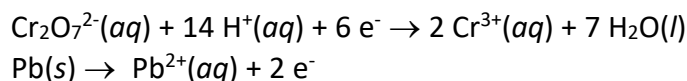
- A rate = $k[\text{NO}][\text{O}_2]$ C rate = $k[\text{NO}]^2[\text{O}_2]$
 B rate = $k[\text{NO}][\text{O}_2]^2$ D rate = $k[\text{NO}]^2[\text{O}_2]^2$

27. The equilibrium constant, K , for the reaction below is greater than 1×10^{10} . Which of the following correctly describes the standard voltage, E° , and the standard free energy change, ΔG° , for this reaction?



- A E° is positive and ΔG° is negative. C E° and ΔG° are both positive.
 B E° is negative and ΔG° is positive. D E° and ΔG° are both negative.

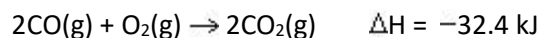
28. For a galvanic cell that uses the following two half-reactions,



how many moles of Pb(s) are oxidized by three moles of $\text{Cr}_2\text{O}_7^{2-}$?

- A 3 B 6 C 18 D 9

29. Carbon monoxide reacts with oxygen to form carbon dioxide by the following reaction:



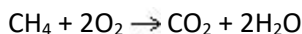
How much heat would be released if 336 g of carbon monoxide reacted with sufficient oxygen to produce carbon dioxide?

- A** 389 kJ **B** 672 kJ **C** 777 kJ **D** 194 kJ

30. How long must a constant current of 50.0 A be passed through an electrolytic cell containing aqueous Cu^{2+} ions to produce 5.00 moles of copper metal?

- A** 5.4 hours **B** 0.37 hours **C** 1.7 hours **D** 0.19 hours

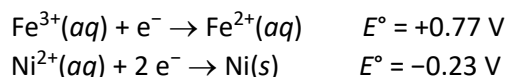
31.



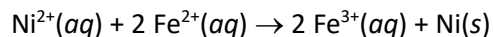
If 16 grams of CH_4 reacts with 16 grams of O_2 in the reaction shown above, which of the following will be true?

- A** Equal number of moles of CO_2 and H_2O will be formed. **C** The limiting reagent will be O_2 .
B The limiting reagent will be CH_4 . **D** Equal masses of CO_2 and H_2O will be formed.

32. Using the following standard reduction potentials,



Calculate the standard cell potential for the galvanic cell reaction given below, and determine whether or not this reaction is spontaneous under standard conditions.



- A** $E^\circ = +1.00 \text{ V}$, spontaneous **C** $E^\circ = +1.00 \text{ V}$, nonspontaneous
B $E^\circ = -1.00 \text{ V}$, spontaneous **D** $E^\circ = -1.00 \text{ V}$, nonspontaneous

33. The electrolysis of molten AlCl_3 for 3.25 hr with an electrical current of 15.0 A produces _____ g of aluminum metal.

- A** 147 **B** 16.4 **C** 4.55×10^{-3} **D** 0.606

Multiple Choice Key

1. A
2. E
3. B
4. C
5. C
6. B
7. B
8. C
9. B
10. A
11. C
12. D
13. C
14. B
15. B
16. D
17. B
18. D
19. D
20. B
21. A
22. D
23. D
24. D
25. A
26. B
27. A
28. D
29. D
30. A
31. C
32. D
33. B

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction		$E^\circ(\text{V})$
$\text{F}_2(\text{g}) + 2 e^-$	$\rightarrow 2 \text{F}^-$	2.87
$\text{Co}^{3+} + e^-$	$\rightarrow \text{Co}^{2+}$	1.82
$\text{Au}^{3+} + 3 e^-$	$\rightarrow \text{Au}(\text{s})$	1.50
$\text{Cl}_2(\text{g}) + 2 e^-$	$\rightarrow 2 \text{Cl}^-$	1.36
$\text{O}_2(\text{g}) + 4 \text{H}^+ + 4 e^-$	$\rightarrow 2 \text{H}_2\text{O}(\text{l})$	1.23
$\text{Br}_2(\text{l}) + 2 e^-$	$\rightarrow 2 \text{Br}^-$	1.07
$2 \text{Hg}^{2+} + 2 e^-$	$\rightarrow \text{Hg}_2^{2+}$	0.92
$\text{Hg}^{2+} + 2 e^-$	$\rightarrow \text{Hg}(\text{l})$	0.85
$\text{Ag}^+ + e^-$	$\rightarrow \text{Ag}(\text{s})$	0.80
$\text{Hg}_2^{2+} + 2 e^-$	$\rightarrow 2 \text{Hg}(\text{l})$	0.79
$\text{Fe}^{3+} + e^-$	$\rightarrow \text{Fe}^{2+}$	0.77
$\text{I}_2(\text{s}) + 2 e^-$	$\rightarrow 2 \text{I}^-$	0.53
$\text{Cu}^+ + e^-$	$\rightarrow \text{Cu}(\text{s})$	0.52
$\text{Cu}^{2+} + 2 e^-$	$\rightarrow \text{Cu}(\text{s})$	0.34
$\text{Cu}^{2+} + e^-$	$\rightarrow \text{Cu}^+$	0.15
$\text{Sn}^{4+} + 2 e^-$	$\rightarrow \text{Sn}^{2+}$	0.15
$\text{S}(\text{s}) + 2 \text{H}^+ + 2 e^-$	$\rightarrow \text{H}_2\text{S}(\text{g})$	0.14
$2 \text{H}^+ + 2 e^-$	$\rightarrow \text{H}_2(\text{g})$	0.00
$\text{Pb}^{2+} + 2 e^-$	$\rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+} + 2 e^-$	$\rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+} + 2 e^-$	$\rightarrow \text{Ni}(\text{s})$	-0.25
$\text{Co}^{2+} + 2 e^-$	$\rightarrow \text{Co}(\text{s})$	-0.28
$\text{Cd}^{2+} + 2 e^-$	$\rightarrow \text{Cd}(\text{s})$	-0.40
$\text{Cr}^{3+} + e^-$	$\rightarrow \text{Cr}^{2+}$	-0.41
$\text{Fe}^{2+} + 2 e^-$	$\rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+} + 3 e^-$	$\rightarrow \text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+} + 2 e^-$	$\rightarrow \text{Zn}(\text{s})$	-0.76
$2 \text{H}_2\text{O}(\text{l}) + 2 e^-$	$\rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-$	-0.83
$\text{Mn}^{2+} + 2 e^-$	$\rightarrow \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+} + 3 e^-$	$\rightarrow \text{Al}(\text{s})$	-1.66
$\text{Be}^{2+} + 2 e^-$	$\rightarrow \text{Be}(\text{s})$	-1.70
$\text{Mg}^{2+} + 2 e^-$	$\rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+ + e^-$	$\rightarrow \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+} + 2 e^-$	$\rightarrow \text{Ca}(\text{s})$	-2.87
$\text{Sr}^{2+} + 2 e^-$	$\rightarrow \text{Sr}(\text{s})$	-2.89
$\text{Ba}^{2+} + 2 e^-$	$\rightarrow \text{Ba}(\text{s})$	-2.90
$\text{Rb}^+ + e^-$	$\rightarrow \text{Rb}(\text{s})$	-2.92
$\text{K}^+ + e^-$	$\rightarrow \text{K}(\text{s})$	-2.92
$\text{Cs}^+ + e^-$	$\rightarrow \text{Cs}(\text{s})$	-2.92
$\text{Li}^+ + e^-$	$\rightarrow \text{Li}(\text{s})$	-3.05

Polyatomic Ions

1st six-weeks

Nick the Camel **ate** an Icky Clam for Supper in Phoenix with his Bros

NO_3^- nitrate	ClO_3^- chlorate	PO_3^{3-} phosphite
NO_2^- nitrite	ClO_2^- chlorite	BrO_3^- bromate
CO_3^{2-} carbonate	SO_4^{2-} sulfate	BrO_2^- bromite
IO_3^- iodate	SO_3^{2-} sulfite	Consonants = # of Oxygen Vowels = Charge
IO_2^- iodite	PO_4^{3-} phosphate	

2nd six-weeks

ClO_4^- perchlorate	IO^- hypoiodite
ClO^- hypochlorite	BrO_4^- perbromate
IO_4^- periodate	BrO^- hypobromite

	Difference in Oxygen from ATE
Per____ate	+1
Ate	0
Ite	-1
Hypo____ite	-2

3rd six-weeks

H_2PO_4^- dihydrogen phosphate	HCO_3^- hydrogen carbonate <i>or</i> bicarbonate
HPO_4^{2-} hydrogen phosphate	HSO_4^- hydrogen sulfate

4th six-weeks

NH_4^+ ammonium	OH^- hydroxide
$\text{C}_2\text{H}_3\text{O}_2^-$ <i>or</i> CH_3COO^- acetate	H_3O^+ hydronium

5th six-weeks

MnO_4^- permanganate	CrO_4^{2-} chromate
CN^- cyanide	$\text{Cr}_2\text{O}_7^{2-}$ dichromate

6th six-weeks

O_2^{2-} peroxide	$\text{C}_4\text{H}_4\text{O}_6^{2-}$ tartrate
$\text{S}_2\text{O}_3^{2-}$ thiosulfate	$\text{C}_2\text{O}_4^{2-}$ oxalate

Acid Nomenclature	
Binary	Hydro____ic
ate	ic
ite	ous

Polyatomic Ions**Br-Based Ions**

BrO^-	hypobromite
BrO_2^-	bromite
BrO_3^-	bromate
BrO_4^-	perbromate

Cr-Based Ions

CrO_4^{2-}	chromate
$\text{Cr}_2\text{O}_7^{2-}$	dichromate

I-Based Ions

IO^-	hypoiodite
IO_2^-	iodite
IO_3^-	iodate
IO_4^-	periodate

P-Based Ions

PO_3^{3-}	phosphite
PO_4^{3-}	phosphate
HPO_4^{2-}	hydrogen phosphate
H_2PO_4^-	dihydrogen phosphate

Other Ions

CN^-	cyanide
O_2^{2-}	peroxide
MnO_4^-	permanganate

C-Based Ions

CO_3^{2-}	carbonate
HCO_3^-	hydrogen carbonate or bicarbonate
$\text{C}_2\text{H}_3\text{O}_2^-$ or CH_3COO^-	acetate
$\text{C}_4\text{H}_4\text{O}_6^{2-}$	tartrate
$\text{C}_2\text{O}_4^{2-}$	oxalate

Cl-Based Ions

ClO^-	hypochlorite
ClO_2^-	chlorite
ClO_3^-	chlorate
ClO_4^-	perchlorate

N-Based Ions

NO_2^-	nitrite
NO_3^-	nitrate
NH_4^+	ammonium

S-Based Ions

SO_3^{2-}	sulfite
SO_4^{2-}	sulfate
HSO_4^-	hydrogen sulfate
$\text{S}_2\text{O}_3^{2-}$	thiosulfate

Acid & Base Ions

H_3O^+	hydronium
OH^-	hydroxide

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8																																													
1 H 1.008 Hydrogen	2 He 4.00 Helium	3 B 10.81 Boron	4 C 12.01 Carbon	5 N 14.01 Nitrogen	6 O 16.00 Oxygen	7 F 19.00 Fluorine	8 Ne 20.18 Neon																																													
9 Li 6.94 Lithium	10 Ne 20.18 Neon	11 Na 22.99 Sodium	12 Mg 24.30 Magnesium	13 Al 26.98 Aluminum	14 Si 28.09 Silicon	15 P 30.97 Phosphorus	16 S 32.06 Sulfur	17 Cl 35.45 Chlorine	18 Ar 39.95 Argon																																											
19 K 39.10 Potassium	20 Ca 40.08 Calcium	21 Sc 44.96 Scandium	22 Ti 47.90 Titanium	23 V 50.94 Vanadium	24 Cr 52.00 Chromium	25 Mn 54.94 Manganese	26 Fe 55.85 Iron	27 Co 58.93 Cobalt	28 Ni 58.69 Nickel	29 Cu 63.55 Copper	30 Zn 65.39 Zinc	31 Ga 69.72 Gallium	32 Ge 72.59 Germanium	33 As 74.92 Arsenic	34 Se 78.96 Selenium	35 Br 79.90 Bromine	36 Kr 83.80 Krypton	37 Rb 85.47 Rubidium	38 Sr 87.62 Strontium	39 Y 88.91 Yttrium	40 Zr 91.22 Zirconium	41 Nb 92.91 Niobium	42 Mo 95.94 Molybdenum	43 Tc (98) Technetium	44 Ru 101.10 Ruthenium	45 Rh 102.91 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.87 Silver	48 Cd 112.41 Cadmium	49 In 114.82 Indium	50 Sn 118.71 Tin	51 Sb 121.75 Antimony	52 Te 127.60 Tellurium	53 I 126.91 Iodine	54 Xe 131.29 Xenon	55 Cs 132.91 Cesium	56 Ba 137.33 Barium	57 *La 138.91 Lanthanum	58 Ce 140.12 Cerium	59 Pr 140.91 Praseodymium	60 Nd 144.24 Neodymium	61 Pm (145) Promethium	62 Sm 150.4 Samarium	63 Eu 151.97 Europium	64 Gd 157.25 Gadolinium	65 Tb 158.93 Terbium	66 Dy 162.5 Dysprosium	67 Ho 164.93 Holmium	68 Er 167.26 Erbium	69 Tm 168.93 Thulium	70 Yb 173.04 Ytterbium	71 Lu 174.97 Lutetium
87 Fr (223) Francium	88 Ra 226.02 Radium	89 *Ac 227.03 Actinium	90 Th 232.04 Thorium	91 Pa 231.04 Protactinium	92 U 238.03 Uranium	93 Np (237) Neptunium	94 Pu (244) Plutonium	95 Am (243) Americium	96 Cm (247) Curium	97 Bk (247) Berkelium	98 Cf (251) Californium	99 Es (252) Einsteinium	100 Fm (257) Fermium	101 Md (258) Mendelevium	102 No (259) Nobelium	103 Lr (262) Lawrencium	104 Rf (261) Rutherfordium	105 Db (262) Dubnium	106 Sg (266) Seaborgium	107 Bh (264) Bohrium	108 Hs (277) Hassium	109 Mt (268) Meitnerium	110 Ds (271) Darmstadtium	111 Rg (272) Roentgenium	112 Cn (285) Copernicium	113 Nh (286) Nihonium	114 Fl (289) Flerovium	115 Mc (288) Moscovium	116 Lv (293) Livermorium	117 Ts (294) Tennessine	118 Og (294) Oganesson																					

Atomic number	14
Symbol	Si
Atomic mass	28.09
Name	Silicon

58 Ce 140.12 Cerium	59 Pr 140.91 Praseodymium	60 Nd 144.24 Neodymium	61 Pm (145) Promethium	62 Sm 150.4 Samarium	63 Eu 151.97 Europium	64 Gd 157.25 Gadolinium	65 Tb 158.93 Terbium	66 Dy 162.5 Dysprosium	67 Ho 164.93 Holmium	68 Er 167.26 Erbium	69 Tm 168.93 Thulium	70 Yb 173.04 Ytterbium	71 Lu 174.97 Lutetium
90 Th 232.04 Thorium	91 Pa 231.04 Protactinium	92 U 238.03 Uranium	93 Np (237) Neptunium	94 Pu (244) Plutonium	95 Am (243) Americium	96 Cm (247) Curium	97 Bk (247) Berkelium	98 Cf (251) Californium	99 Es (252) Einsteinium	100 Fm (257) Fermium	101 Md (258) Mendelevium	102 No (259) Nobelium	103 Lr (262) Lawrencium

*Lanthanide Series

†Actinide Series

AP[®] CHEMISTRY EQUATIONS AND CONSTANTS

Throughout the exam the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)
 g = gram(s)
 nm = nanometer(s)
 atm = atmosphere(s)

mm Hg = millimeters of mercury
 J, kJ = joule(s), kilojoule(s)
 V = volt(s)
 mol = mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy
 ν = frequency
 λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^8$ m s⁻¹

Avogadro's number = 6.022×10^{23} mol⁻¹

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}, \text{ where } aA + bB \rightleftharpoons cC + dD$$

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$= K_a \times K_b$$

$$\text{pH} = -\log[H^+], \text{ pOH} = -\log[OH^-]$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_a (weak acid)

K_b (weak base)

K_w (water)

KINETICS

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

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

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure

V = volume

T = temperature

n = number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

a = molar absorptivity

b = path length

c = concentration

Gas constant, R = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr}$$

STP = 273.15 K and 1.0 atm

Ideal gas at STP = 22.4 L mol^{-1}

THERMODYNAMICS / ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

q = heat

m = mass

c = specific heat capacity

T = temperature

S° = standard entropy

H° = standard enthalpy

G° = standard Gibbs free energy

n = number of moles

E° = standard reduction potential

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

Faraday's constant, F = 96,485 coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$

