Class period: _____

RRHS AP Chemistry



<u>Unit 12</u>: Gases

8

Epic AP Chem Test Review

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1 AP Chem: Effective Study Skills Tips and Tricks! Study smarter, not harder. ⁽²⁾

What to Do	What NOT to Do
 Be <u>ACTIVE</u> in while learning/studying: 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) 	 Be passive while learning/studying: 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
 Focus when studying Decrease distractions while studying; don't read texts, check social media, or watch Netflix while studying. Put your phone out of sight/hearing. 	 Multitask Study while checking/writing texts, checking social media, and/or watching Netflix. Keep your computer or tv on in the background
 Use <u>Intensity</u> when studying 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. 	 Low intensity/low effort 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
 Space out studying over time 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. 	Cram 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
 Interleave your Studying 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!) 	 One Concept Studying Study only one type of problem, and practice those problems over and over Don't review older content or units while studying
 The best way to prepare for a test is to take a test! Time yourself while trying practice problems Access only the AP Periodic Table and Formula Chart when practicing problems 	 Use your notes, friends, and/or the internet while trying practice problems Give yourself unlimited time for each problem

	4 th M	arking Pe	riod: Mare	ch – May :	2023	
Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
26	27 A	28 B	1 Mar. A SAT (11 ^{th only)}	8	3 A	4
D	6 B	7 A	8	9 A	10 B	
					MP3 ENDS	
12	13 SPRING	14 BREAK	15 SPRING	16 BREAK	1. (3)	2 ©
19	20 A	21 B	22 A	23 B	24 A	25
26	27 B	28 A	29 B	30 A	31 B	1 Apr.
2	А 8	4 B	A	9	7 Student & Staff Holiday	ω

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
9 Apr	10 A	11 B	12 A	13 B	14 A	15
16	17 B	18 A STAAR English I Exam	19 B	20 A STAAR English II Exam	21 Student Holiday/ Staff Development	22
23	24 B	25 STAAR Biology EOC	26 B	27 A STAAR US Hist EOC	28 B	29
30	1 May A AP Chem Exam! ;D	2 STAAR AIg I EOC	3 A	4 B	5 A	3 • 9
7	8	6 V	10 B	11 WHAP Exam: some 10 th	12 B	13
14	15 A	16 B	17 A Seniors: 3 rd & 4 th Exams in class	18 B Seniors: 7 th and 8 th Exams in class	19 C Last day for obligations MP4 ENDS	20
21	22 Exams 2, 1	23 Exams 6, 5	24 Exams 3, 4	25 Exams 7, 8	26	27

4 Unit 12 Objectives

BIG IDEA 2 - Chemical and physical properties of materials can be explained by the structure and arrangement of atoms, ions, molecules and the forces between them.

- <u>Enduring Understanding 2.A</u>: Matter can be described by its physical properties. The physical properties of a substance generally depend on the spacing between the particles (atoms, molecules, ions) that make up the substance and the forces of attraction among them.
- <u>Enduring Understanding 2.B</u>: Forces of attraction between particles (including the noble gases and also different parts of large molecules) are important in determining many macroscopic properties of a substance, including how observable physical state changes with temperature.

BIG IDEA 3 - Changes in matter involve the rearrangement and/or the reorganization of atoms and /or the transfer of electrons.

- <u>Enduring Understanding 3.A</u>: Chemical changes are represented by a balanced chemical equation that identifies the ratios with which reactants react and products form.
- <u>Enduring Understanding 3.B</u>: Chemical reactions can be classified by considering what the reactants are, what the products are, or how they change from one into the other. Classes of chemical reactions include synthesis, decomposition, acid-base, and oxidation-reduction reactions.
- <u>Enduring Understanding 3.C</u>: Chemical and physical transformation may be observed in several ways and typically involve a change in energy.

Intro to Gases

Pressure (____): the _____ per unit area on a surface.

→ The pressure of a gas is the force that the gas exerts on the ______ of its container.

- 1. A _______ is used to measure atmospheric pressure. When you see the word "barometric" or "barometer", it's telling you the pressure.
- 2. Units for pressure:

1 atm = 760 mmHg = 760 torr

*note: mmHg = torr! (same exact unit, two names)

Temperature (_____): a measure of the average ______ energy of the particles in a sample of matter.

- Kinetic energy (_____) is the energy of ______
- Kinetic energy is given by the following equation: $KE = \frac{1}{2}mv^2$

Temperature \propto Kinetic Energy \therefore Same Temp \rightarrow Same (average) KE (!!)

Particle diagrams with _____ can be used to illustrate differing kinetic energies at differing temperatures: the _____ the vector, the

______ the kinetic energy.

There are two temperature scales to be familiar with:

- 1. <u>Celsius</u> (°C) scale: the temperature based on water
 - a. H₂O: freezes at ____°C and boils at _____°C
- 2. <u>Kelvin</u> (K) scale: the absolute temperature scale used in the scientific community.
 - a. There are no negative values on the Kelvin scale!!
 - **b.** H₂O: freezes at _____K and boils at _____K.
 - c. ______ is the theoretical lowest temperature possible at which all molecular motion stops.
 - **d.** To convert between °C and K use the formula:





Standard Temperature and Pressure: (_____) standard conditions of 1.0 atm, 273.15 K

STP = **1**. **0** atm (pressure), **273**. **15** K (temperature)





Low Temperature

High Temperature

<u>Two factors</u> affect the speed (velocity) of gas particles: <u>molar mass</u> and <u>temperature</u>!



In summary,

- 1. At the same temperature (i.e. same kinetic energy), heavier gas particles are ______ than light particles.
- 2. The same gas particle will move ______ at low temperatures and ______ at high temperatures.

Kinetic Molecular Theory (____): In Five Postulates

Ideal gases are assumed to behave according to these postulates!

٦

 Gas particles, space between them Gas particles = negligible volume Gas are compressible because of large spaces between particles 	
 Gas particles bounce off walls (and each other) with loss of energy → "" collisions Force of particles hitting wall = gas! 	• • • • • • • • • • • • • • • • • • •
3. Gases particles are in constant, rapid, random	
 4. Gas particles do attract or repel each other! Gas particles can easily past each other because attractive forces (IMFs) are insignificant 	__(ש)_/_
 AVERAGE kinetic energy of a gas is to the velocity of its particles. 	

Ideal vs. Real Gases

- 1. <u>Ideal Gas</u>: an ______ gas that perfectly fits all the assumptions of the kinetic-molecular theory.
- 2. <u>Real Gas</u>: a gas that does _____ behave completely according to the assumptions of the kinetic-molecular theory.
 - The more ______ (more _____) the gas molecules = greater the deviation from ideal behavior.
 Pressure will be ______ than predicted because of intermolecular attractions.
 - At ______ temperatures, gas particles have insufficient kinetic energy to overcome attractions (IMFs).
 o Pressure will be ______ than predicted because of intermolecular attractions.
 - At _____ pressures, distance between particles in likely to be small relative to the size of the particles.
 O Volume will be _____ than predicted because of non-negligible particle size.







Gases behave most like ideal gases when they have:

- 1. High Temperature because _____ overcomes IMFs
- 2. Low Pressure because gas particles are relatively _____ apart (molecular volume is low relative to container volume)
- 3. Small Intermolecular Forces (IMFs):
 - a. Small particles (low London dispersion forces)
 - b. Non-polar (no dipole-dipole IMFs)

Data	What happened?	Because Ideal Gas doesn't account for:
\downarrow P (than predicted by KMT)	T orIMFs (or both!)	Attractive forces between particles
ightarrow V (than predicted by KMT)	T orIMFs (or both!)	Attractive forces between particles
个V (than predicted by KMT)	P or tiny container	Size of particles

Interpreting Data from Non-Ideal Gases

Graham's Law of Diffusion and Effusion

Diffusion: the ______ of gases. The rate of diffusion is the rate of the mixing.

<u>Effusion</u>: the passage of gas through a tiny _____ into an evacuated chamber (as shown below). The rate of effusion measures the speed at which the gas is transferred into the chamber.



- The rates of diffusion and effusion of a gas are related to the average ______ of its particles.
- For gases at the same temperature, this means the rate of gas movement is inversely proportional to the square root of its molar mass.

rate of gas movement
$$\propto \frac{1}{\sqrt{MM}}$$

→ ______ gases (lower molar mass) diffuse and effuse more rapidly.

Note: "heavier" ≠ "bigger". Be very careful about word choice when answering FR problems!

Let's Practice!

- 1. Consider two 1.0 L balloons at STP: one is filled with helium gas and the other with carbon dioxide gas.
 - a. Do the atoms in the helium sample have the same average kinetic energy as the atoms in the carbon dioxide sample? Justify your answer.
 - b. Do the atoms in the helium sample have the same average velocity as the atoms in the carbon dioxide sample? Justify.
 - c. Which balloon will deflate faster? Explain.



1. A sample of gas at constant pressure is graphed at two different temperatures. Which of the following must be true?

- A) T₁ is a higher temperature.
- B) T₂ is a higher temperature.
- C) The gas becomes lighter.
- D) The gas becomes heavier.



2. The Maxwell-Boltmann distribution above analyzes a sample of a mixture of carbon dioxide, methane (CH₄), sulfur hexafluoride, and hydrogen gases. The analysis was performed at a constant temperature and pressure. Which answer correctly assigns each curve to its appropriate gas?

A) hydrogen-A; methane-B; carbon dioxide-C; sulfur hexafluoride-D

B) hydrogen-A; carbon dioxide-B; methane-C; sulfur hexafluoride-D

C) sulfur hexafluoride-A; methane-B; carbon dioxide-C; hydrogen-D

D) sulfur hexafluoride-A; carbon dioxide-B; methane-C; hydrogen-D

3. The kinetic molecular theory predicts that pressure rises as the temperature of a gas increases because:

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- a. the gas molecules collide more frequently with the wall
- b. the gas molecules collide less frequently with the wall
- c. the gas molecules collide more energetically with the wall
- d. the gas molecules collide more frequently <u>and</u> more energetically with the wall
- 4. A sealed flask contains O₂(g), SO₂(g), and SO₃(g) at 25°C. Which gas molecules will have the highest velocity and why?
 - a. The O_2 molecules, because they have the least mass.
 - b. The O₂ molecules, because they are the smallest.
 - c. The SO₃ molecules, because they have the most mass.
 - d. Molecules of all three gases will have the same speed because they are at the same temperature.
- 5. Under which of the following conditions will gases in a sealed container most deviate from ideal conditions, and why?
 - a. Low pressure, because the gas molecules would be spread far apart.
 - b. High pressure, because the gas molecules will be colliding frequently.
 - c. Low temperature, because the attractive forces between the gas molecules would be more significant.
 - d. High temperature, because the gas molecules are moving too fast to interact with each other.

- 6. Because the ideal gas law doesn't include a factor for the volume of gas particles, actual gas volume is ______ the volume predicted by kinetic molecular theory.
 - a. larger than c. equal to
 - b. smaller than d. unable to be compared to
- Because the ideal gas law doesn't include a factor for the attraction between gas particles, actual gas pressure is
 _________ the pressure predicted by kinetic molecular theory.
 - a. larger than c. equal to
 - b. smaller than d. unable to be compared to

More Practice!

СО	H ₂ O	CO ₂				
Lewis dot structure:	Lewis dot structure:	Lewis dot structure:				
Molecular geometry:	Molecular geometry:	Molecular geometry:				
Molecular polarity:	Molecular polarity:	Molecular polarity:				
Which of the molecules above shows the most significant deviation from ideal gas behavior and why?						

Хе	F ₂	Не				
Lewis dot structure:	Lewis dot structure:	Lewis dot structure:				
Molecular geometry:	Molecular geometry:	Molecular geometry:				
Molecular polarity:	Molecular polarity:	Molecular polarity:				
Which of the species above shows the	Which of the species above shows the most significant deviation from ideal gas behavior and why?					

Ideal Gas Law

$$PV = nRT$$

P = pressure (variable units) V = volume (MUST be in)

T = temperature (MUST be in , of course) n = quantity (MUST be in _____)

R = universal gas constant **>** the value for **R** depends on the units for pressure! (on formula chart)

(R relates the energy scale in physics to the temperature scale: super important!)

The value for R is provided on the formula chart!

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

= 0.08206 L atm mol $^{-1} \text{K}^{-1}$
= 62.36 L torr mol $^{-1} \text{K}^{-1}$
1 atm = 760 mm Hg = 760 torr

GAS CONSTANT MUST MATCH ALL THE UNITS!!!!!!!!!

Guided Practice

1. What is the pressure in atmospheres exerted by a 0.500 mol sample of nitrogen gas in a 10.0 L container at 298 K?

2. What is the volume, in liters, of 8.00 g of oxygen gas at 20.0°C and 740.24 mmHg pressure?

3. What mass of chlorine gas, Cl₂, in grams, is contained in a 10.0 L tank at 27.0°C and 3.50 atm of pressure?

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Standard Molar Volume

Volume-Mass Relationships of Gases

The volume occupied by one mole of a gas at STP is known as the standard volume of a gas. Let's solve the ideal gas equation for the volume of 1.00 mol of gas at **<u>STP</u>** (273.15 K, 1.00 atm):

$$PV = nRT$$

1. The following conversion factors can be written for the standard molar volume of a gas @ STP:

1 mol GAS	0.0	22.4 <i>L GAS</i>
22.4 L GAS	ÛŔ	1 mol GAS

!

2. At STP, 1 mole of ANY gas is equal to 22.4 L of gas but has different ______



Let's Practice!

- 1. A chemical reaction produces 0.0680 mol of oxygen gas. What volume (in L) is occupied by this gas at STP?
- 2. A chemical reaction produced 98.0 mL of sulfur dioxide gas, SO₂, at STP. What mass in grams of the gas was produced?

Equations You can Derive from the Ideal Gas Law: Yum!

Note: ONLY the ideal gas law is given on the AP Chem formula chart, so...

You must either be able to derive or memorize the following formulas!

1. The Other Gas Laws:

Rearranging the ideal gas law for R gives the following equation $R = \frac{PV}{nT}$

Because R is a _____, we can derive the combined gas, which can be used to compare changing conditions for a sample of gas:

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

Luckily, we are often only focused on one or two variables. All of the following gas laws can be derived from the combined gas law by holding two of the four variables constant:

	Boyle's Law		Charles' Law		Avogadro's Law
	$P_1V_1 = P_2V_2$	$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad \qquad \frac{V_1}{n_1} = \frac{V_2}{n_2}$		$\frac{V_1}{n_1} = \frac{V_2}{n_2}$	
•	Temperature, moles constant	•	Pressure, moles constant	•	Temperature, pressure constant
•	If P then V =	•	If T then V =	•	If n then V =
	relationship		relationship		relationship

Key vocab words:

• <u>rigid</u> container: ______ volume (for example, a sealed glass container)

• <u>flexible</u> container: volume can ______ (for example, a balloon)

2. Density/ Molar Mass:

Moles (the variable n), can be calculated by the mass of a sample divided by the molar mass of the substance.

Molar mass (*MM*) =
$$\frac{mass(m)}{moles(n)}$$
 therefore $n = \frac{m}{MM}$

Substituting this into the ideal gas law allows to solve for density! Remember, density (D) = $\frac{mass}{volume} = \frac{m}{V}$

PV = nRT therefore $PV = \frac{m}{MM}RT$ therefore $\frac{MMP}{RT} = \frac{m}{V} = D$ or (if you know density): $MM = \frac{DRT}{P} = \frac{mRT}{PV}$

3. Density related to Standard Molar Volume: since density is the ______ of mass to volume,

$$Density = \frac{molar \ mass}{molar \ volume} \ \text{at STP}$$

Examples: $density_{He} = \frac{4.00 \ g/mol}{22.4 \ L/mol} = 0.179 \frac{g}{L}, \qquad density_{N_2} = \frac{28.02 \ g/mol}{22.4 \ L/mol} = 1.25 \ g/L$

1. If we lower the temperature of a gaseous system by a factor of 4 and increase the volume by a factor of 2, what will happen to the pressure of the system (if all other variables remain constant)?

2. Calculate the density of nitrogen gas at 125°C and a pressure of 755 mmHg.

3. A helium-filled balloon has a volume of 50.0 L at STP. What volume will it have at 0.855 atm and 10.°C?

4. A sample of gas has a mass of 0.311 g. Its volume is 0.225 L at a temperature of 55°C and a pressure of 886 torr. Find its molar mass.

5. A sample of nitrogen gas is contained in a cylinder with a freely moving piston. At 0.00°C, the volume of the gas is 375 mL. To what temperature must the gas be heated to occupy a volume of 0.500 L?

A Brief Note about "R" and MC Problems: Use R = $\frac{8}{100}$ when doing multiple choice calculation approximations!

- 1. A sample of nitrogen gas has a volume of 1.80 L at 25°C and 1.00 atm. How many moles of N₂ are present?
 - a. 0.014 mol N₂
 - b. 0.072 mol N₂
 - c. 0.72 mol N₂
 - d. 3.6 mol N₂
- 2. At constant volume, decreasing the temperature of a gas (in Kelvin) by half would result in:
 - a. the pressure decreasing by half c. the pressure doubling
 - b. no change in the pressure d. a ½ increase in pressure
- 3. A gas sample with a mass of 10 grams occupies 6.0 liters and exerts a pressure of 2.0 atm at a temperature of 26°C. Which of the following expressions is equal to the molecular mass of the gas?

a.	(10)(0.08206)(299) (2.0)(6.0) g/mol	C.	(299)(2.0)(6.0) (10)(0.08206) g/mol
b.	$\frac{(10)(0.08206)(26)}{(2.0)(6.0)}\text{g/mol}$	d.	$\frac{(2.0)(6.0)}{(10)(0.08206)(26)}g/mol$

4. If 2.0 moles of gas in a sealed glass flask is heated from 25°C to 50°C, which of the following conditions are true?

К	inetic energy	Pressure	Number of moles	Distance between particles
a.	increases	increases	stays the same	stays the same
b.	stays the same	increases	stays the same	increases
c.	increases	stays the same	stays the same	increases
d.	increases	increases	increases	stays the same

- 5. A sample of oxygen gas (47.1 g) occupies _____ L at 22°C and 4.5 atm.
 - a. 0.079
 - b. 0.12
 - c. 13
 - d. 7.9
- 6. A sample of oxygen gas at 50°C is heated, reaching a final temperature of 100°C. Which statement best describes the behavior of the gas molecules?
 - a. Their velocity increases by a factor of two.
 - b. Their velocity increases by a factor of four.
 - c. Their kinetic energy increases by a factor of two.
 - d. Their kinetic energy increases by a factor of less than two.

Sample	02	Не	SO ₂	CH_4
Molar Mass	32 g/mol	4 g/mol	64 g/mol	16 g/mol
Volume	2 L	4 L	3 L	2 L
Temperature	400 K	400 K	400 K	400 K
Pressure	1 atm	1 atm	0.5 atm	0.5 atm
7. Which gaseous s	sample has the largest n	umber of moles?	d	CH
a. O ₂ 8. Which gaseous s	b. He sample has the largest m	c. SO ₂	α.	CH4
a. O ₂	b. He	c. SO ₂	d.	CH₄
9. Which gaseous s	sample has the smallest	density?		
a. O ₂	b. He	c. SO ₂	d.	CH₄
	1 atm Flask 1	2 atm Flask 2 Flask 3	4 atm Flask 4	

10. Each of these flasks is the same size and at the same temperature. Which one contains the most molecules?

- a. Flask 1 b. Flask 2 c. Flask 3 d. Flask 4
- 11. An ideal gas is contained in a 5.0 L chamber at a temperature of 37°C. If the gas exerts a pressure of 2.0 atm on the walls of the chamber, which of the following expressions is equal to the number of moles of the gas?

a.
$$\frac{(2.0)(5.0)}{(0.08206)(37)}$$
 molc. $\frac{(2.0)(310)}{(0.08206)(5.0)}$ molb. $\frac{(2.0)(0.08206)}{(5.0)(37)}$ mold. $\frac{(2.0)(5.0)}{(0.08206)(310)}$ mol

Questions 7–9 below refer to the information in table below.



12. Each of the flasks above contains the same number of molecules. In which container is the pressure the lowest? a. Flask 1 b. Flask 2 c. Flask 3 d. Flask 4

13. The density of an unknown gas is 2.00 grams per liter at 3.00 atmospheres pressure and 127°C. What is the molecular mass of this gas?

a.
$$\frac{254}{3}R$$
 c. $\frac{800}{3}R$
b. 188 R d. 800 R

- 14. According to the kinetic molecular theory, gases are compressible because:
 - a. their particles are in constant, random motion
 - b. collisions between particles are elastic
 - c. attractive forces between particles are insignificant
 - d. the volume of their particles is very small compared to the total volume of the container



- 15. The unlabeled graph shown above is a correct representation of the relationship between each pair of variables below <u>except</u>:
 - **a.** temperature and pressure
- c. temperature and volume
- **b.** pressure and volume
- d. number of moles and volume

18 Dalton's Law

Dalton's Law of Partial Pressures: the total pressure of a mixture of gases is equal to the ______ of the partial pressures of the component gases.

$$P_{total} = P_{gas A} + P_{gas B} + P_{gas C} + \cdots$$

→ The pressure of each gas in a mixture is called the _____ pressure of that gas.

Example #1: A sealed container of helium, hydrogen, and nitrogen gases is measured to have a pressure of 288 kPa. If the partial pressures of the helium and the hydrogen are 112 kPa and 83 kPa respectively, what would be the partial pressure of the nitrogen?



- 1. Gases collected in this way are not pure but always mixed with ______ vapor.
- 2. Like other gases, water vapor exerts a ______.
- To find the "_____" gas pressure, use Dalton's Law to subtract the vapor pressure of water from the atmospheric (or ______) pressure.

$$P_{atm} = P_{gas} + P_{H_2O}$$

19 **Table 1: Water-Vapor Pressure**

Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)
0.0	4.6	18.5	16.0	23.5	21.7	40.0	55.3
5.0	6.5	19.0	16.5	24.0	22.4	50.0	92.5
10.0	9.2	19.5	17.0	24.5	23.1	60.0	149.4
15.0	12.8	20.0	17.5	25.0	23.8	70.0	233.7
15.5	13.2	20.5	18.1	26.0	25.2	80.0	355.1
16.0	13.6	21.0	18.6	27.0	26.7	90.0	525.8
16.5	14.1	21.5	19.2	28.0	28.3	95.0	633.9
17.0	14.5	22.0	19.8	29.0	30.0	100.0	760.0
17.5	15.0	22.5	20.4	30.0	31.8		
18.0	15.5	23.0	21.1	35.0	42.2		

Now you try!

1. A sample of solid potassium chlorate (KClO₃) was heated in a test tube (see the figure to the right) and decomposed by the following reaction:

 $2 \text{ KClO}_3(s) \rightarrow 2 \text{ KCl}(s) + 3 \text{ O}_2(g)$

The oxygen produced was collected by displacement of water at 22°C at a barometric pressure of 754 torr. The volume of the gas collected was 0.650 L.

a. Calculate the partial pressure of O_2 in the gas collected (the dry pressure of O_2).

b. What mass of KClO₃ was decomposed in this experiment?

c. What would the volume of the dry O_2 be at STP?



20 Mixtures of Gases: Mathy Math

Many gas samples are not pure, but instead are ______ of different gases.

- In certain applications, the gas mixture can be treated as _____ gas.
 - We can calculate the ______ number of moles of ALL gases, and use the ideal gas law to calculate other properties of the mixture.

$$P_{total} = P_{gas A} + P_{gas B} + P_{gas C} + \cdots$$
$$= n_A \frac{RT}{V} + n_B \frac{RT}{V} + n_C \frac{RT}{V} + \cdots$$
$$= (n_A + n_B + n_C + \cdots) \frac{RT}{V}$$
$$= (n_{total}) \frac{RT}{V}$$

Mole Fractions

Mole fraction (X_A): number of moles of a component in a mixture, divided by the total number of moles in the mixture

$$X_{\rm A} = \frac{\text{moles A}}{\text{total moles}}$$

The mole fraction can be used to determine the _____ pressure of a component in a gaseous mixture $P_A = P_{\rm total} \times X_A$

Let's Practice!

1. The mole fraction of nitrogen in the air is 0.7808. Calculate the partial pressure of N₂ in the air when the atmospheric pressure is 760. torr.



Two one-liter flasks (Flask A and Flask B, shown above) are sealed at 25°C. Flask A contains helium gas, and Flask B contains argon gas. If the contents of both flasks are combined into a previously evacuated four-liter flask (Flask C), what would be the total pressure in Flask C at 25°C?

```
a. 4.0 atm b. 3.0 atm c. 2.0 atm d. 1.0 atm
```

- A reaction produces a gaseous mixture of carbon dioxide, carbon monoxide, and water vapor. After one reaction, the mixture was analyzed and found to contain 0.60 mol of CO₂, 0.30 mol of CO, and 0.10 mol of H₂O. If the total pressure of the mixture was 0.80 atm, what was the partial pressure of the CO?
 - a. 0.080 atm c. 0.24 atm
 - b. 0.13 atm d. 0.48 atm
- 4. A sealed, rigid canister contains three gases: 28.0 g of nitrogen, 40.0 g of argon, and 36.0 g of water vapor. If the total pressure exerted by the gases is 2.0 atm, what is the partial pressure of the nitrogen?
 - a. 0.33 atm b. 0.40 atm c. 0.50 atm d. 2.0 atm

Use the following information to answer questions 5–6.

An evacuated rigid container is filled with exactly 2.00 g of hydrogen gas and 10.00 g of neon. The temperature of the gas is held at 0°C and the pressure inside the container is a constant 1.0 atm.

- 5. What is the mole fraction of neon in the container?
 - a. 0.17 b. 0.33 c. 0.67 d. 0.83
- 6. What is the volume of the container?
 - a. 11.2 L b. 22.4 L c. 33.5 L d. 48.8 L



- 7. Two one-liter flasks (Flask A and Flask B, shown above) are sealed at 22°C. Flask A contains nitrogen gas, and Flask B contains oxygen gas. If the contents of both flasks are combined into a previously evacuated two-liter flask (Flask C), what would be the total pressure in Flask C at 22°C?
 - a. 6.0 atm b. 4.0 atm c. 3.0 atm d. 2.0 atm
- 8. Nitrogen gas was collected over water at 25°C. If the vapor pressure of water at 25°C is 23 mmHg, and the total pressure in the container is measured at 781 mmHg, what is the partial pressure of the nitrogen gas?
 - a. 46 mmHg b. 551 mmHg c. 735 mmHg d. 758 mmHg

Gas Stoichiometry!

Two Types of Gas Stoich

1. Gas Stoich at STP: use ______=____. Follow normal stoichiometry process!

Example #1: Propane, C₃H₈, is a gas that is sometimes used as fuel for cooking and heating. The complete combustion of propane occurs according to the following equation.

 $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

- a. What will be the volume, in liters, of oxygen required for the complete combustion of 0.250 L of propane? Assume that all volume measurements are made at STP.
- b. What will be the volume of gaseous products created in the reaction? Assume that all volume measurements are made at STP.

*Note: this shortcut works when the volume of ALL gases is measured at the T and P, not just STP!

- 2. <u>Gas Stoich NOT at STP</u>: OR not at the same ____ and ____ (when calculating volume \rightarrow volume)
 - → you must use the Ideal Gas Law to:
 - a. Calculate the number of moles from the provided volume of gas (if needed)
 - b. Calculate the final volume of gas produced from the number of moles (if needed)

A cheer to help you remember!

When you're **NOT** at , Use ______ !

Go chemistry!!

Example #2: Tungsten, W, a metal used in light-bulb filaments, is produced industrially by the reaction of tungsten oxide with hydrogen according to the reaction below. How many liters of hydrogen gas at 35°C and 0.980 atm are needed to react completely with 875 g of tungsten oxide?

 $WO_3(s) + 3 H_2(g) \rightarrow W(s) + 3 H_2O(g)$

Example #3: If 34 grams of propane gas, C_3H_8 , reacts with 18 grams of oxygen gas in a 0.75 L sealed bomb calorimeter, what is the pressure inside the container after the reaction is complete? Assume the reaction happens at 25°C.

 $C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(g) + heat$

Let's Practice!

1. Solid calcium carbonate, also known as limestone, will decompose upon heating to produce solid calcium oxide, also known as lime (an industrial chemical with a wide variety of uses), and carbon dioxide gas. How many grams of calcium carbonate must be decomposed to produce 5.00 L of carbon dioxide gas at 273 K and 760 torr?

2. How many liters of gaseous carbon monoxide at 27°C and 0.247 atm can be produced from the burning of 65.5 g of carbon according to the following equation?

$$2 C(s) + O_2(g) \rightarrow 2 CO(g)$$

3. How many milliliters of 2.5 molar hydrochloric acid, HCl, would be required to produce 1.25 L of carbon dioxide gas, assuming sufficient calcium carbonate? Assume the reaction takes place at STP.

2 HCl(aq) + CaCO₃(aq) \rightarrow CaCl₂(aq) + CO₂(g) + H₂O(I)

4. Assuming all volume measurements are made at the same temperature and pressure, what volume of hydrogen gas is needed to react completely with 4.55 L of oxygen gas to produce water vapor?

5. Air bags in cars are inflated by the sudden decomposition of sodium azide, NaN₃, by the following reaction.

$$2 \text{ NaN}_3(s) \rightarrow 3 \text{ N}_2(g) + 2 \text{ Na}(s)$$

What volume of N₂ gas, measured at 1.30 atm and 87°C, would be produced by the reaction of 70.0 g of NaN₃?

25 Gas Equilibrium

At a constant volume and temperature, ______ can be substituted for M in a RICE table!

• This is because pressure is directly proportional to moles, and moles are directly proportional to M

<u>Example</u>: The noble gas krypton reacts with chlorine gas in a rigid, sealed container at constant temperature. Initially, the partial pressure of krypton is 0.85 atm and the partial pressure of Cl_2 is 1.35 atm. When the reaction goes to completion, the partial pressure of the remaining krypton is 0.40 atm. What is formula of the compound produced?

The Equilibrium Constant, K (the Law of Mass Action): relates the concentrations of reactants and products at equilibrium at a given temperature.

$K_c \& K_p - Not the same!$

For the general reaction: $aA + bB \Leftrightarrow cC + dD$

 $K_{p} = \frac{(P_{C})^{c}(P_{D})^{d}}{(P_{A})^{a}(P_{B})^{b}} = \frac{(P_{products})^{coefficient}}{(P_{reactants})^{coefficient}} \quad \text{where P is the partial pressure of the gas}$

Le Châtelier's Principle

If a "stress" (_____) is applied to a system at equilibrium,

processes will occur to counteract (_____) that change.

*****Note:** The equilibrium shift will move toward returning the concentration to where it was before you applied the stress, but the concentration never quite gets back to the original value before a new equilibrium is established.

Examples of Counteracting

1. Heat:

- a. If you add heat to a system, it will shift in a way that it tends to ______ the added heat.
- b. If you remove heat from a system, it will shift in a way that it tends to ______ heat.
- 2. Adding or removing a reagent:
 - a. If you remove a reagent, the reaction shifts to ______ it. (NOT solids and liquids!)
 - b. If you add a reagent, the reaction shifts to get _____ of it. (NOT solids and liquids!)
- 3. Pressure/ Volume: Depends on number of _____ of gas!
 - a. ____ pressure (or ____ volume) favors a shift to the side with the ______ # of moles of gas.
 - b. ____ pressure (or ____ volume) favors a shift to the side with the ______ # of moles of gas.
- 4. Catalysts: ______ effect on K; just gets to equilibrium faster (Kinetics moment)!

REMEMBER – nothing but a change in temperature will change the VALUE of K

Let's practice!

1. Consider the following reaction: $2 H_2(g) + O_2(g) \rightleftharpoons 2 H_2O(I)$ Write the equilibrium expression, K_p , for this equation. At equilibrium, the partial pressure of hydrogen gas is 0.9968 atm and the partial pressure of oxygen gas is 1.105 atm. Calculate K_p . Does this reaction favor reactants, products, or neither? Explain.

2.

 $2 \operatorname{Cl}_2 \operatorname{O}_5(g) \rightleftharpoons 2 \operatorname{Cl}_2(g) + 5 \operatorname{O}_2(g)$

If the mole fractions in this system at equilibrium are Cl_2 : 0.243, O_2 : 0.274, Cl_2O_5 : 0.483, and the total pressure of the system is 3.00 atm, what is K_p ?

3. Consider the following reaction at equilibrium:			uilibrium:	2 KClO₃(s) ≓ 2 KCl(s) + 3 O₂(g)	∆H = −391.2 kJ/mol
Disturbance	After equili what will b the follow	brium is <u>re-e</u> e the effect o ving? (same,	<u>stablished</u> , on each of ↑, or ↓?)	Why?	
	<i>n</i> ₀₂	<i>P</i> ₀₂	K _P		
个V of container					
↓V of container					
Add inert gas					
Add more KCl					
个Temperature					
↓Temperature					
Add more O ₂					

Free Response Practice

1.

 $NH_4HS(s) \leftrightarrow NH_3(g) + H_2S(g)$

 Δ H $^{\circ}$ = +93 kilojoules

The equilibrium above is established by placing solid NH₄HS in an evacuated container at 25°C. At equilibrium, some solid NH₄HS remains in the container. Predict and explain each of the following.

- a) The effect on the equilibrium partial pressure of NH₃ gas when additional solid NH₄HS is introduced into the container.
- b) The effect on the equilibrium partial pressure of NH₃ gas when additional solid H₂S is introduced into the container. (Hint: H₂S(s) readily sublimes into H₂S(g).)
- c) The effect on the mass of solid NH₄HS present and the value of the equilibrium constant when the volume of the container is decreased.
- d) The effect on the mass of solid NH₄HS present and the value of the equilibrium constant when the temperature is increased.



Multiple Choice Practice

- Chlorine gas and fluorine gas will combine to form one gaseous product. 1.0 liter of Cl₂ reacts with 3.0 liters of F₂ to produce 2.0 liters of product. Assuming constant temperature and pressure conditions, what is the formula of the product?
 - a. Cl_2F_2 b. ClF_2 c. Cl_2F d. ClF_3

2. Some students are invited to a barbeque. The food is cooked with propane burning in excess oxygen to produce heat, as shown in this equation.

$$C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(g) + heat$$

If 22 grams of propane are consumed, what volume of gaseous products is produced at 1.0 atm and 37°C? (The molar mass of propane is 44 g/mol).

a. 130 L b. 89 L c. 74 L d. 11 L

 $\mathsf{N}_2(g) + 2 \mathsf{O}_2(g) \rightarrow \mathsf{N}_2\mathsf{O}_4(g)$

3. The reaction above takes place in a closed, rigid vessel. The initial pressure of $N_2(g)$ is 1.0 atm, and that of $O_2(g)$ is 1.5 atm. No N_2O_4 is initially present. The experiment is carried out at a constant temperature. What is the total pressure in the container when the partial pressure of N_2O_4 reaches 0.75 atm?

a. 0.25 atm b. 0.75 atm c. 1.0 atm	d.	2.0 atm
------------------------------------	----	---------

- 4. A sample of 18.0 g of aluminum metal is added to excess hydrochloric acid. The volume of hydrogen gas produced at 0.0°C and 1.0 atm pressure is approximately:
 - a. 67 L b. 45 L c. 22 L d. 11 L

29

Use the following information to answer questions 5–8.

$$2 \text{ SO}_2(g) + O_2(g) \rightarrow 2 \text{ SO}_3(g)$$

4.0 mol of gaseous SO_2 and 6.0 mol of O_2 are allowed to react in a sealed container.

5. Which particulate drawing below best represents the contents of the flask after the reaction goes to completion?



6. If the temperature remains constant, what percentage of the original pressure will the final pressure in the container be equal to?

a. 67%	b. 80%	c. 100%	d. 133%
--------	--------	---------	---------

- 7. At a given point in the reaction, all three gases are present at the same temperature. Which gas molecules will have the highest velocity and why?
 - a. The O_2 molecules, because they have the least mass.
 - b. The O₂ molecules, because they are the smallest.
 - c. The SO_3 molecules, because they are products in the reaction.
 - d. Molecules of all three gases will have the same speed because they are at the same temperature.
- 8. Under which of the following conditions would the gases in the container most deviate from ideal conditions, and why?
 - a. Low pressure, because the gas molecules would be spread far apart.
 - b. High pressure, because the gas molecules will be colliding frequently.
 - c. Low temperature, because the attractive forces between the gas molecules would be more significant.
 - d. High temperature, because the gas molecules are moving too fast to interact with each other.

9. Consider the decomposition of ammonium nitrite, in which 6 atm of ammonium nitrite is added to an evacuated flask with a catalyst and then heated.

 $NH_4NO_2(g) \rightarrow N_2(g) + 2 H_2O(g)$

At equilibrium, the total pressure is 14 atm. Calculate the partial pressure of the water vapor at equilibrium.

- a. 2.0 atm b. 4.0 atm c. 6.0 atm d. 8.0 atm
- 10. Nitrogen gas reacts with chlorine gas in a rigid, sealed container at constant temperature. Initially, P_{N_2} = 6.0 atm and P_{Cl_2} = 3.6 atm. When the reaction is done, all of the chlorine gas has reacted, and the partial pressure of the remaining krypton is 4.8 atm. What is formula of the compound produced?
 - a. N_2Cl_3 b. NCl_2 c. N_2Cl d. NCl_3

$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$

- 11. When 1.0 mole of H_2 is combined with 1.0 mol of O_2 in a sealed flask, the reaction above occurs to completion at a constant temperature. After the reaction, the pressure in the container will have:
 - a. increased by 25% c. decreased by 25%
 - b. increased by 50% d. decreased by 50%

Use the following information to answer questions 12-14.

The following reaction is found at equilibrium at 25°C: $2 SO_3(g) \rightleftharpoons O_2(g) + 2 SO_2(g)$ $\Delta H = -198 \text{ kJ/mol}$

12. Which of the following would cause the reverse reaction to speed up?

- a. Adding more SO₃ c. Raising the pressure
- b. Lowering the temperature d. Removing some SO₂
- 13. Which of the following would cause a reduction in the value for the equilibrium constant?
 - a. Increasing the amount of SO_3 c. Reducing the amount of O_2
 - b. Raising the temperature d. Lowering the temperature
- 14. If initially only SO₃ was added to the reaction vessel, what is true about the following values as the system approached equilibrium?
 - a. $\Delta G > 0$ and Q > K b. $\Delta G < 0$ and Q > K c. $\Delta G > 0$ and Q < K d. $\Delta G < 0$ and Q < K

³¹ Lab: Molar Mass of Butane

Introduction

Butane, C₄H₁₀, is a hydrocarbon and a highly flammable, colorless, odorless, easily liquefied gas. It is typically used for cigarette lighters and portable stoves, a propellant in aerosols, a heating fuel, a refrigerant, and in the manufacture of a wide range of products. Butane is also found in Liquefied Petroleum Gas (LPG).

Background

In this lab, we are going to determine the molar mass of butane, C₄H₁₀, experimentally. A simple calculation using a periodic table would give us the correct answer for the molar mass of butane. However, you are going to conduct an experiment in the lab to see how close you can come to the accepted value.

We are trying to find the molar mass, which is expressed in units of grams per mole (g/mol). We will measure the mass of the butane released from the pressurized container, and we will measure the volume of the gas that we collect. You can use the method of water displacement at room conditions and then substitute the measurements of volume, temperature, and pressure into the ideal gas law equation in order to find n, the number of moles of butane. Once we know the mass and the number of moles, we will divide the mass by the number of moles to calculate the molar mass (g/mol).

Procedure

Determination of the Molar Mass of Butane

- 1. Fill the trough (giant tub) with water.
- 2. Weigh the disposable butane lighter to the nearest 0.01 g and record the mass. <u>Be careful not to discharge any</u> <u>butane after measuring the initial mass of the lighter!</u>
- 3. Record the water temperature in the trough using a temperature probe.
- 4. Record the barometric pressure posted at the front of the room.
- Submerge the graduated cylinder in the trough and fill it completely with water. Have a group member hold the inverted graduated cylinder (filled with water) in the trough. <u>There should be no air bubbles in the cylinder at</u> <u>the start of the experiment.</u>
- 6. Place the tube connected to the lighter underneath the opening of the graduated cylinder and fill the cylinder with butane by holding down the trigger on the butane lighter. The tube should be long enough that the butane holder is not itself under water. Be careful not to let any of the gas escape around the graduated cylinder.
- 7. Displace about 90 mL of water from the graduated cylinder. As you collect the last 10 mL of butane, fill the graduated cylinder to the 100 mL mark with butane, but be careful: be sure to adjust the graduated cylinder up or down until <u>the 100 mL mark lines up **EXACTLY** with the level of the water inside the cylinder AND in the trough outside.</u>
 - a. This ensures that the pressure of the gas inside the graduated cylinder will be the same as the atmospheric pressure.
- 8. Dry off the butane lighter tube and weigh it again. Record the mass.

Initial mass of butane container	
Water temperature	
Barometric pressure	
Volume of gas collected	
Final mass of butane lighter	

Calculations

- 1. Calculate the mass of butane collected.
- 2. Convert the volume of butane to liters.
- 3. Convert the water temperature to Kelvin.
- 4. Determine the vapor pressure of the water in the graduated cylinder. (Hint: this is not something you can calculate.)
- 5. Use Dalton's Law of Partial Pressures to determine the pressure of the dry butane.
- 6. Using the values found above for P, V, and T, calculate the number of moles of butane collected.

- 7. Using the calculated mass and number of moles of butane collected, calculate the experimental molar mass of butane.
- 8. Using a periodic table, calculate the accepted molar mass of butane, C_4H_{10} .
- 9. Calculate your percent error.

Analysis (& More Calculations ©)

10. Why is it essential to make sure the water level inside the graduated cylinder is even with the water level in trough when making your final volume measurement of butane collected?

11. Calculate the density of dry butane collected in the graduated cylinder (in g/L).

- 12. Calculate the mole fraction of water and the mole fraction of butane in the graduated cylinder.
- 13. If all of the butane, C₄H₁₀, that you collected was combusted, what total volume of products would be produced? (Hint: you will need to write a balanced reaction!)

Gas Laws Math Summary

Ideal Gas Law	Combined Gas Law	Dalton's Law and Mole Fractions	Molar Volume	Molar Mass Kitty Cat	Gas Stoich
PV = nRT	$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$	$P_{total} = P_1 + P_2 + \cdots$ $P_A = P_{total} \times X_A$ where $X_A = \frac{\text{moles } A}{\text{total moles}}$	1 mol = 22.4 L at STP	$MM = \frac{DRT}{P} = \frac{mRT}{PV}$	One chemical (g, mol, L) → another chemical (g, mol, or L)
Use when you have <u>only one</u> of each variable	Use when conditions have <u>changed</u>	Use when you have a mixture of gases	Use to convert between quantity and volume of a gas	Use to calculate gas density	Use to convert from one chemical to a different chemical
 Things to watch for: Temp: need K Choose R based on unit for pressure Volume: need L 	 Things to watch for: Temp: need K Units for each variable need to be the same on both sides 	 Things to watch for: Gas collection over water (or collection by water displacement): pure gas is mixed with water vapor 	Only true at STP!!! (273 K, 1.0 atm)	Potential shortcut When at STP: $D = \frac{molar \ mass}{22.4 \ L}$	Two types: • L → L (at same T and P) • Non-STP (or NOT at same T and P): use stoich for mol → mol, and use PV=nRT for L ↔ mol

Gas Laws Conceptual Summary

1. <u>Temperature is directly proportional to average kinetic energy</u>, which means:

- a. Same temperature = same average kinetic energy!
- b. Same temperature, different gases? High molar mass = slower, low molar mass = faster
- c. Same gas, different temperature? Higher temperature = faster, lower temperature = slower
- 2. <u>Kinetic Molecular Theory</u> (5 postulates): gas particles are vert small and very far apart; are in constant, rapid, random motion; bounce off things with no energy loss (elastic collisions); do not attract or repel (negligible IMFs), kinetic energy directly proportional to velocity

3. Ideal vs Real Gases

- a. Ideal gases: follow KMT postulates (most ideal at high T, low P)
- b. Real gases: have actual volume or attractive forces (most real at low T, high P)
35 Unit 12 Multiple Choice Practice

- 1. Which of the following has an average atomic or molecular speed closest to that of N₂ molecules at 0°C and 1 atm?
 - a. Ne b. Xe c. O_2 d. CO
- 2. A gas sample is confined in a rigid 5-L container. Which of the following will occur if the temperature of the container is increased?
 - I. The pressure of the gas will increase.
 - II. The density of the gas will increase.
 - III. The distance between the gas particles will increase.
 - a. I only b. I and III only
 - b. III only d. I, II, and III
- 3. At standard temperature and pressure, a 0.50 mol sample of H₂ gas and a separate 1.0 mol sample of O₂ gas have the same:
 - a. average molecular kinetic energy c. effusion rate
 - b. average molecular speed d. density
- 4. Equal numbers of moles of He(g), Ar(g), and Ne(g) are placed in a glass vessel at room temperature. If the vessel has a pinhole-sized leak, which of the following will be true regarding the relative values of the partial pressures of the gases remaining in the vessel after some of the gas mixture has effused?
 - a. $P_{He} < P_{Ne} < P_{Ar}$ c. $P_{Ne} < P_{Ar} < P_{He}$
 - b. $P_{He} < P_{Ar} < P_{Ne}$ d. $P_{Ar} < P_{He} < P_{Ne}$
- 5. Consider the combustion of 6.0 g of ethane, C₂H₆. What volume of carbon dioxide will be formed at STP?
 a. 0.20 L
 b. 2.2 L
 c. 9.0 L
 d. 22.4 L

$$\begin{array}{r} 36\\ \text{CO}_2(g) + \text{H}_2(g) \ \rightleftharpoons \ \text{H}_2\text{O}(g) + \text{CO}(g) \end{array}$$

- 6. Which two stresses, separately, will each cause the equilibrium to shift to the left?
 - a. increase [H₂], increase [CO] c. decrease [H₂], increase [H₂O]
 - b. increase [CO₂], decrease [CO] d. decrease [CO₂], decrease [H₂O]
- 7. A mixture of helium and neon gases has a total pressure of 1.2 atm. If the mixture contains twice as many moles of helium as neon, what is the partial pressure due to neon?
 - a. 0.2 atm b. 0.3 atm c. 0.4 atm d. 0.8 atm
- 8. A 22.0 gram sample of an unknown gas occupies 11.2 L at STP. Which of the following could be the identity of the gas?
 - a. CO_2 b. SO_3 c. O_2 d. He
- 9. In an experiment, 2 moles of $H_2(g)$ and 1 mole of $O_2(g)$ were completely reacted according to the following equation in a sealed container of constant volume and temperature:

$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$$

If the initial pressure in the container before the reaction is denoted as P_i, which of the following expressions gives the final pressure, assuming ideal gas behavior?

a. P_i b. 2 P_i c. (3/2) P_i d. (2/3) P_i

A gas sample with a mass of 10 grams occupies 5.0 liters and exerts a pressure of 2.0 atm at a temperature of 26°C. Which of the following expressions is equal to the molecular mass of the gas? The gas constant, R, is 0.08 (L atm)/(mol K).

a.
$$\frac{(10.0)(0.08)(299)}{(2.0)(5.0)}$$
 g/molc. $\frac{(2.0)(5.0)}{(10.0)(0.08)(26)}$ g/molb. $\frac{(10.0)(0.08)(26)}{(2.0)(5.0)}$ g/mold. $\frac{(2.0)(5.0)}{(10.0)(0.08)(299)}$ g/mol

11. The following reaction is found at equilibrium: $Ni(s) + 4 CO(g) \rightleftharpoons Ni(CO)_4(I)$ $\Delta H = -160.8 \text{ kJ/mol}$ Which of the following will cause this equilibrium to shift to the left?

- a. add some CO c. decrease the volume
- b. remove some Ni(CO)₄ d. increase the temperature
- 12. A gaseous mixture of oxygen and nitrogen is maintained at a constant temperature. Which of the following MUST be true regarding the two gases?
 - a. Their average molecular speeds will be the same.
 - b. Their average kinetic energies will be the same.
 - c. Their partial pressures will be the same.
 - d. Their densities will be the same.
- 13. Assume the amount of gas is constant. If the temperature increases and the pressure stays the same, then what will happen to the volume of a non-rigid container?
 - a. stay the same b. increase c. decrease



- 14. Each of these flasks is the same size and at the same temperature. Which one contains the most molecules?
 - a. Flask 1 b. Flask 2 c. Flask 3 d. Flask 4
- 15. Because ideal gases have elastic collisions, when two gas particles collide:
 - a. They bounce off each other with no loss in energy.
 - b. They bounce off each other with a small loss in energy.
 - c. They bounce off each other with a large loss in energy.
 - d. They bounce off each other with a small increase in energy.

Use the following information to answer questions 17–21.

The diagram below shows three identical 1.0 L containers filled with the indicated amounts of gas. The stopcocks connecting the containers are originally closed and the gases are all at 25°C.



- a. Increasing the volume at constant temperature
- b. Decreasing the volume at constant temperature
- c. Increasing the temperature at constant volume
- d. Decreasing the temperature at constant volume

- 22. Which of the following has the most molecules?
 - a. 1.00 L of CH_4 at 0°C and 1.00 atm
 - b. 1.00 L of N_2 at 0°C and 1.00 atm
- c. $1.00 \text{ L of } \text{CO}_2 \text{ at } 20^{\circ}\text{C} \text{ and } 1.00 \text{ atm}$
- d. 1.00 L of CO at 0°C and 1.25 atm
- 23. A sealed container with 8.0 g of O_2 and 7.0 g of N_2 is kept at a constant temperature and pressure. Which of the following is true?
 - a. The volume occupied by O_2 is greater than the volume occupied by N_2 .
 - b. The volume occupied by O_2 is equal to the volume occupied by N_2 .
 - c. The volume occupied by O_2 is less than the volume occupied by N_2 .
 - d. The density of O_2 is less than the density of N_2 .
- 24. In an ideal gas, the Kelvin temperature:
 - a. fluctuates widely when the gas is in a sealed container.
 - b. is inversely proportional to the kinetic energy of the gas
 - c. is directly proportional to the kinetic energy of the gas
 - d. is a measure of the potential energy of the gas

Use the following information to answer questions 26–28.

10.0 g each of three different gases are present in three glass containers of identical volume, as shown below. The temperature of all three gases is held constant at 298 K.



25. The container with which gas would have the greatest pressure?

a. SO_2 b. CH_4 c. NCI_3 d. All three containers would have the same pressure.

26. Which of the gases would have the greatest density?

a. SO₂ b. CH₄ c. NCl₃ d. All three gases would have the same density.

- 27. If a small, pinhole-sized leak were to be drilled into each container, the container with which gas would experience the fastest pressure decrease?
 - a. SO₂ b. CH₄ c. NCl₃ d. All gases would decrease pressure at the same rate.

- 28. Which of the following assumption(s) is (are) valid based on kinetic molecular theory?
 - I. Gas molecules have negligible volume.
 - II. Gas molecules exert no attractive forces on each other
 - III. The temperature of a gas is directly proportional to its kinetic energy.
 - a. I only b. II and III only
 - b. III only d. I, II, and III
- 29. A 0.33 mole sample of CaCO₃(s) is placed in a 1 L evacuated flask, which is then sealed and heated. The CaCO₃(s) decomposes completely according to the balanced equation below. The total pressure in the flask, measured at 300 K, is closest to which of the following?

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

a. 2.0 atm b. 4.1 atm c. 8.1 atm d. 16 atm

30. Identify the three gases represented on the Maxwell-Boltzmann diagram below. Assume all gases are at the same temperature.





31. Each of the flasks above contains the same number of molecules. In which container is the pressure the lowest?

Flask 1 b.	Flask 2	c. Flask 3	d.	Flask 4
------------	---------	------------	----	---------

a.

32. A sample of 0.010 mole of nitrogen dioxide gas is confined at 127°C and 2.5 atm. What would be the pressure of this sample at 27°C and the same volume?

a.	0.033 atm	b.	0.33 atm	с.	1.25 atm	d.	1.88 atm

33. Nitrogen gas was collected over water at 25°C. If the vapor pressure of water at 25°C is 23 mmHg, and the total pressure in the container is measured at 781 mmHg, what is the partial pressure of the nitrogen gas?

a.	23 mmHg	b.	46 mmHg	с.	551 mmHg	d.	758 mmHg
••••				•.	<u> </u>		

- 34. A mixture of gases contains 1.5 moles of oxygen, 3.0 moles of nitrogen, and 0.5 mole of water vapor. If the total pressure is 700 mmHg, what is the partial pressure of the nitrogen gas?
 - a. 210 mmHg b. 280 mmHg c. 350 mmHg d. 420 mmHg



35. If all of these flask are the same size, at the same temperature, and contain the same number of molecules, in which flask will the pressure be the highest?

a. Flask 1 b. Flask 2 c. Flask 3 d. All have the same pressure.

42 FR Practice #1 (2011B #2, 9 points)

1. An 8.55 mol sample of methanol, CH₃OH, is placed in a 15.0 L evacuated rigid tank and heated to 327°C. At that temperature, all of the methanol is vaporized and some of the methanol decomposes to form carbon monoxide gas and hydrogen gas, as represented in the equation below.

 $CH_3OH(g) \rightleftharpoons CO(g) + 2 H_2(g)$

- a. The reaction mixture contains 6.30 mol of CO(g) at equilibrium at 327°C.
 - i. Calculate the number of moles of $H_2(g)$ in the tank. (1 point)

ii. Calculate the number of grams of $CH_3OH(g)$ remaining in the tank. (1 point)

iii. Calculate the mole fraction of $H_2(g)$ in the tank. (2 points)

iv. Calculate the total pressure, in atm, in the tank at 327°C. (2 points)

- b. Consider the three gases in the tank at 327° C: CH₃OH(g), CO(g), and H₂(g).
 - i. How do the average kinetic energies of the molecules of the gases compare? Explain. (1 point)

ii. Which gas has the highest average molecular speed? Explain. (1 point)

c. The tank is cooled to 25°C, which is well below the boiling point of methanol. It is found that small amounts of H₂(g) and CO(g) have dissolved in the liquid CH₃OH. Which of the two gases would you expect to be more soluble in methanol at 25°C? Justify your answer. (1 point)

- 2. A rigid 8.20 L flask contains a mixture of 2.50 moles of H₂, 0.500 mole of O₂, and sufficient Ar so that the partial pressure of Ar in the flask in 2.00 atm. The temperature is 127°C.
 - a. Calculate the total pressure in the flask. (3 points)

b. Calculate the mole fraction of H_2 in the flask. (2 points)

c. Calculate the density (in g L^{-1}) of the mixture in the flask. (2 points)

The mixture is ignited by a spark, and the reaction represented below occurs until one of the reactants is entirely consumed.

$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$$

d. Give the mole fraction of all species present in the flask at the end of the reaction. (3 points)

46 FR Practice #3 (2005B #6, 8 points)



- 3. Consider two containers of volume 1.0 L at 298 K, as shown above. One container holds 0.10 mol $N_2(g)$ and the other holds 0.10 mol $H_2(g)$. The average kinetic energy of the $N_2(g)$ molecules is 6.2 x 10^{-21} J. Assume that the $N_2(g)$ and the $H_2(g)$ exhibit ideal behavior.
 - a. Is the pressure in the container holding the $H_2(g)$ less than, greater than, or equal to the pressure in the container holding the $N_2(g)$? Justify your answer. (2 points)

b. What is the average kinetic energy of the $H_2(g)$ molecules? (1 point)

c. The molecules of which gas, N₂ or H₂, have the greater average speed? Justify your answer. (1 point)

 d. What change could be made that would decrease the average kinetic energy of the molecules in the container? (1 point)

- e. If the volume of the container holding the H₂(g) was decreased to 0.50 L at 298 K, what would be the change in each of the following variables? In each case, justify your answer.
 - i. The pressure within the container (2 points)

ii. The average speed of the $H_2(g)$ molecules (1 point)

 $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

4. When heated, calcium carbonate decomposes according to the equation above. In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of powdered $CaCO_3(s)$ to a 1.00 L rigid container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100 K. As the container was heated, the total pressure of the $CO_2(g)$ in the container was measured over time. The data are plotted in the graph below.



The student repeated the experiment, but this time the student used a 100.0 g sample of powdered $CaCO_3(s)$. In this experiment, the final pressure in the container was 1.04 atm, which was the same final pressure as in the first experiment.

a. Calculate the number of moles of $CO_2(g)$ present in the container after 20 minutes of heating. (1 point)

b. The student claimed that the final pressure in the container in each experiment became constant because all of the CaCO₃(s) had decomposed. Based on the data in the experiments, do you agree with this claim? Explain. (1 point)

c. After 20 minutes some CO₂(g) was injected into the container, initially raising the pressure to 1.5 atm. Would the final pressure inside the container be less than, greater than, or equal to 1.04 atm? Explain your reasoning. (1 point)

d. Are there sufficient data obtained in the experiments to determine the value of the equilibrium constant, K_P , for the decomposition of CaCO₃(*s*) at 1100 K? Justify your answer. (1 point)

Epic AP Chem Test Review



AP Chemistry FTW!

...Not That! Write This... Rationale Generally The language used in the question Other words that may mean the Make it easy to give you points, and be sure the reader can when asked to make a choice (ex: same thing but are likely more understand what you saying "increases", "decreases", etc.) ambiguous (ex: "goes up", "goes down", etc.) Make it easy to give you points Answer the specific question first, Burying the answer in the text of then "justify", "explain" etc. the response names of specific elements and "it" Ambiguous compounds, "reactants", "products", etc. Be formal in language "Species" "It", "stuff", etc. A justification or explanation when it Only the answer without Justification/explanation required to earn point is part of the question supporting it "mass", "volume", etc. Be specific "size" References to specific data or graphs Required to earn point Make generalizations about the when prompted to "explain how the data without specifically citing data..." or something similar provided data or trials Including these is not a net ionic, Net ionic equations only containing Aqueous ionic compounds in their it's a molecular or complete ionic species that change undissociated form, spectator ions Particle view diagrams with ions and Incorrectly oriented dipoles Drawings must demonstrate understanding of interactions at polar molecules orientated in the the molecular level correct direction relative to each (ref. 2015 #4) other If "include units" is written in the An answer with units if "include An answer without units prompt, a unit is required to earn units" is stated in the problem full points Show all work used to derive an Work is often what earns some/all An answer without supporting of the points work shown answer Answers with an incorrect number 1 pt traditionally is assessed Answers expressed to the correct somewhere in the FR for number of significant figures of significant figures significant figures. Gases arguments based on PV = nRT are Components of the Kinetic Ideal gas law for molecular level at the bulk level and not the Molecular Theory as justifications justification molecular level for changes at the molecular level (ref. 2013 #5) Thermodynamics Necessary for correct calculations Values with correct signs Values with incorrect signs and determinations – watch signs based on bonds breaking/forming, heat flow in calorimetry indicated by temperature changes, signs that may change in application of Hess' Law, etc. **Kinetics** Value of k without units Units required to earn point Value of k with units Specific parts of the molecules that AP wants more specific answer "Collision must occur in the must collide in order for the reaction correct orientation" to occur A rate law that includes the rate Incomplete rate law if k is not A rate law without k being included constant k as part of it included Rate laws are based only on A rate law based only on reactants A rate law that includes products

reactants

When Responding to the AP Chemistry Free Response Questions:

Equilibrium		
Discussion of Q vs. K	"reduce the stress", or "due to Le	Preferred AP language
	Châtelier's Principle"	
"Proceeds"	"Shift" – if equilibrium has not yet	If equilibrium is not yet
	been established (i.e. a precipitate	- rxn will proceed in a certain
	has not yet been formed when	direction until equilibrium is
	evaluating K _{sp})	established
K_{sp} expressions that only contain the	K _{sp} expressions that contain or	Solids and liquids are not included
ions	imply a species in the denominator	in equinorium expressions
Correct formulas (including	Substitutions, abbreviations,	Equilibrium expressions must be
charges!) for all species in	chargeless ions, other shorthand	written formally when requested
equilibrium expressions	that may work out in calculations	
	but does not represent the correct	
In K averagional D	species	Concentration is not used in K
In K _p expressions: P _{species}	In K _p expressions: [species]	partial pressures are
"x has been assumed to be so small	Nothing about why you ignore x to	Show you understand why you are
relative to the original concentrations	avoid quadratics	making the decision
that it can be ignored		
Acids and Bases "The $p_{\rm H} > 7$ because the solt	"The pU > 7 because it's a battle	State the actual reason not the
The $pH > 7$ because the salt produced in the neutralization	I he pH $>$ / because it s a battle	memory aid
	and strong base wins "	
behaves as a base: $A + H_2O^{\times}$ HA + OH ⁻ "	and strong base whis.	
"The solution is neutral when $[H_3O^+]$	"The solution is neutral when	True definition of neutral – neutral
= [OH ⁻]."	pH=7."	is only pH of 7 when $K_w = 1.0 \text{ x}$ 10^{-14} (at 298 K)
$K_w = K_a \times K_b$ for a conjugate pair	$K_w = K_a \times K_b$ for an unrelated	This equation only holds true for
	acid/base pair	conjugate acid-base pairs
$pH = pKa$ because it is at $\frac{1}{2}$ the	pH = pKa	Explains the reason behind this,
equivalence point of a titration of a		only true at this point
weak acid with a strong base		
Atomic Structure	"It monto to have a full a stat", "t'a	State the actual reason not the
Effective nuclear charge increases	close to having a full octet"	memory aid
"It has a more polarizable cloud of	"It has more electrons". "it has	This is the shortest way to show
electrons"	more mass", "it has more surface	the reason – simply mentioning
	area", "it is bigger", "it has more	"more" of something is probably
	protons"	without further explanation of
		why that is the case
"period"	"shell" when referring to elements	Elements are in a period, electrons
	and their location on the Periodic	are in a snell
	Table	
Reterence reasons for periodic trends	Stating the trend as the reason	State the actual reason not the memory aid
(1.e. effective nuclear charge,	("because it is to the left",	memory and
coulomb's law, polarizability, etc.)	because it is further down the	
"Electrong in history and the level	(More electrone/more energy)	Explanation of reason not just
farther from the nucleus, resulting in	iviore electrons/more energy	statement of fact, required for
a larger atom/ion "	ievers make the atom/ton bigger.	point
		(Ref 2016 #1)

Bonding and Intermolecular Forces		
"Overcome intermolecular forces"	"break up" a solid/liquid	IMFs should be used to justify
Ion interactions	LDF's when discussing ionic compounds	Ionic compounds have ions with whole charges, which dominate interactions
"Coulombic attraction"	"Opposites attract"	State the actual reason not the memory aid
Describe the process of overcoming intermolecular forces/polarity	"Like dissolves like"	State the actual reason not the memory aid
"Has hydrogen bonds between the molecules"	"Has hydrogen bonds"	Shows that you understand hydrogen bonds are not actually bonds
"ionic compound"	"molecule" when discussing an ionic compound	A molecule is a covalent compound
"ions"	"atoms" when discussing ionic compounds	Ionic compounds contain ions
"atoms"	"ions" when discussing covalent compounds	Covalent compounds do not contain ions
Lewis structures that are complete with necessary lone pairs and/or resonance	Lewis structures that are missing lone pairs and/or resonance (if needed for correct structures)	Lewis structures are incorrect without necessary lone pairs
Identify specific intermolecular forces at play	"stronger intermolecular forces"	Shows your understanding of the chemistry at play
"dissolve" when discussing interactions between molecular substances in solution	"ionize", "dissociate", "bond", "react", "attack", "break up", etc.	Molecular substances do not dissociate into ions, dissolving is not reacting, and otherwise be formal in usage
Electrochemistry		
Loss of mass of electrode is due to atoms of electrode going into solution as ions	Loss of mass of electrode is due to loss of electrons	Electrons have extremely small (negligible in this case) mass (ref. 2014 #3)
Discussion of Q vs. K for changes in cell potential after a change, or qualitative discussion of Nernst Equation	Discussion of Le Châtelier's principle	Preferred AP language (ref. 2014 #3)

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 Sources:
 Review of Released Free-Response Questions with Samples and Commentary

 Adrian Dingle's Blog Posts on Writing Good Answers (<u>https://www.adriandingleschemistrypages.com/</u>)

 AACT Webinar: Teaching Students How to Better Answer Non-Calculator Problems

 AP Teacher Community

 AP Teachers in the National AP Chemistry Teachers Facebook Group

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Essential Things You MOST CERTAINLY SHOULD Know for the AP Chem Test

(Is this everything? Of course not! But it's a good place to start. $\textcircled{\sc 0}$)

General

1. Solubility Rules you must know!!!

Always soluble: alkali metal (Group 1) cations, NH4⁺, and NO3⁻

- 2. Before weighing on electronic balances, allow heated items to cool.
- 3. Beakers and Erlenmeyer flasks are NOT measuring instruments.
- 4. <u>Empirical formula</u>: simplified formula, shows the smallest whole-number mole ratio of the different atoms; find using the empirical poem: Percent to mass, Mass to mole, Divide by small, Multiply til whole
- 5. Percent composition: the percent by mass of each element in a compound

% composition of an element = $\frac{total \text{ mass of element in compound}}{total \text{ mass of compound}} \times 100$

Electrochemistry

- 1. Reduction (gain of e-), Oxidation (loss of e-). Helpful mnemonics: OIL RIG, LEO goes GER.
- 2. How to balance by half-reaction:
 - **a.** Balance charge: Add e^- to the side with more positive charge (or less negative).
 - **b.** Equalize number of electrons: Multiply half-reactions if needed.
 - c. Combine half-reactions: Cancel species that are the same on both sides.

Thermochemistry

- 1. ENDing (breaking) a bond is END-othermic!
- 2. Heat is a transfer of energy from a high energy system, to a low energy system, in order to ultimately achieve thermal equilibrium. The heat transfer (J) is equal, but the temperature change is not! The temp change depends on the specific heat capacity (C) which is the energy in J required to change the temp of 1 gram of a substance by 1°C. Lower C = bigger temp change with same energy and vice versa.
- 3. Thermo Units: q = J, $\Delta H = kJ/mol_{rxn}$
- **4.** $\Delta H_{rxn}^{\circ} = \Sigma \left[n \Delta H_{f}^{\circ}(products) \right] \Sigma \left[n \Delta H_{f}^{\circ}(reactants) \right]$ works only if you use heats of FORMATION!

******* Bond energy is backwards!**

 $\Delta H^{\circ}_{rxn} = \Sigma H^{\circ}_{(bonds \ broken)} - \Sigma H^{\circ}_{(bonds \ formed)} \ \mathsf{OR} \ \ \Delta H^{\circ}_{rxn} = \Sigma \mathsf{BE}_{(reactants)} - \Sigma \mathsf{BE}_{(products)}$

5. The ΔH for the formation of an element in its standard state is zero.

- 1. Changing temperature does NOT change the activation energy!
- 2. Catalysts increase the rate of the forward and the backward reaction. Catalysts provide alternative reaction mechanism with lower activation energy.
- 3. Increasing the temperature will always increase the rate of a chemical reaction, because the increased kinetic energy means that:
 - a. particles are colliding more often, and
 - b. particles are colliding with more FORCE, making it more likely they'll collide with enough energy to overcome the activation energy
- 4. The order of a reaction/reactant must always be determined experimentally!
- 5. The most linear graph can give order of a reactant. The |slope| of said linear line = k (rate constant).
 - a. If [] vs time is linear = 0 order
 - b. If In[] vs time is linear = 1st order
 - c. If 1/[] vs time is linear = 2^{nd} order

General Equilibrium

- 1. The speed of a chemical reaction is NOT related to the equilibrium position (K value).
- 2. The equilibrium position (K value) is NOT related to the rate of the reaction or the rate constant (k)
- 3. When a system is at equilibrium, the forward and backward reactions do not stop, they just occur at the same rate. This keeps all concentrations of reactant and products constant.
- 4. Only changing temperature will change the value of K (equilibrium constant) for any given reaction!
- 5. Le Chatelier's Principle: a system at equilibrium will respond to stress so as to reduce the stress
 - a. Increase concentration? Shift to use up that chemical.
 - b. Increase temperature? Shift away from heat (consider if reaction is exo or endothermic)
 - c. Increase pressure/ decrease volume? Shift towards fewer moles of gas particles.

Solubility

Solubility Language	Normal Equilibrium Language
solubility product constant (K _{sp})	equilibrium constant (K)
molar solubility	x (from RICE table)
saturated solution	system at equilibrium

- 1. Acid/base reactions involve the transfer of one or more protons (H⁺) between chemical species.
- 2. A Brønsted-Lowry acid is a proton donor (loses H⁺); a Brønsted-Lowry base is a proton acceptor (gains H⁺).
- 3. Brønsted-Lowry conjugate acid and base pairs differ in their formula only by one single H^+ . (i.e. H_3PO_4 and $H_2PO_4^-$ are a conjugate pair, but H_3PO_4 and PO_4^{3-} are NOT a conjugate pair).
- 4. The equivalence point in a titration occurs when the analyte has completely reacted with the titrant (the amounts of analyte and titrant are stoichiometrically equal).
- 5. Memorize STRONG acids and bases (100% dissociation):
 - a. Strong Acids: HCl, HBr, HI, HNO₃, HClO₄, H₂SO₄
 - b. Strong Bases: Groups IA and IIA metal hydroxides
- 6. If it's not a strong acid/base, it's weak:

a. Weak Acids:
$$K_a = \frac{[x][x]}{[HA]_o - x} \approx \frac{[x][x]}{[HA]_o}$$
 where $[H_3O^+] = x << [HA]_o$

- b. <u>Weak Bases</u>: $K_b = \frac{[x][x]}{[B]_o x} \approx \frac{[x][x]}{[B]_o}$ where $[OH^-] = x << [B]_o$
- 7. <u>Salts</u>: to know if a salt will affect pH, ask: will the salt ions hydrolyze water?
 - a. Conjugates of Strong Acids/Bases: do NOT hydrolyze water, and thus don't affect pH
 - b. Conjugates of <u>Weak</u> Acids/Bases: <u>DO</u> hydrolyze water, and thus do affect pH!
- 9. <u>Buffer</u>: Whenever a weak acid or base is present with its conjugate salt. Four ways to get a buffer:
 - a. Weak acid and its conjugate base (HA and A⁻ **OR** HA and *Na*A) **1:1 mole ratio**
 - b. Weak base and its conjugate acid (B and BH⁺ **OR** B and BHCl) 1:1 mole ratio
 - c. Weak base with strong acid (titration) **1 WB : 0.5 SA mole ratio** (strong acid reacts with weak base, producing conjugate acid)
 - d. Weak acid with strong base (titration) **1 WA : 0.5 SB mole ratio** (strong base reacts with weak acid, producing conjugate base
- 10. <u>Best buffer</u>: 1) High capacity (lots of acid and base), 2) [HA] = $[A^-]$, 3) pH (of buffer) = pK_a (of acid form)



- a. <u>Best Indicator</u>: Choose indicator with pK_a (of indicator) $\approx pH$ (at equivalence point of titration). This means that K_a of the indicator $\approx 1 \times 10^{-pH} @ eq pt$)
- b. If $pH \le pK_a$ the acid form (HA) predominates, if $pH > pK_a$ the conjugate base form (A⁻) predominates

- 1. Coulomb's Law states the energy of attraction/repulsion increases as magnitude of charges increases and decreases as the distance between the particles increases.
- 2. When considering valence electrons of p block elements, remember to include the outer s electrons as well (e.g., Al has 3 valence electrons, s² and p¹)
- 3. Transition metal lose their valence electrons first (these are the s electrons; NOT the d)
- 4. The first ionization energy of an atom corresponds to the lowest energy peak on a PES spectrum. No other ionization energies match any PES peaks. More nuclear charge (more protons) results in higher binding energies when comparing elements in the same period.
- 5. Writing the full electronic configuration of an atom can help to explain differences in ionization energies.
- 6. A Mass Spectrum has a peak for each particle of a different mass. Typically used to measure relative abundance of isotopes. Isotope = same element (same # of protons), but different mass (different # of neutrons).



- 7. Justifying all of the trends on the periodic table can be simplified using these two generalizations:
 - a. Use number of protons to justify trends across a period.
 - b. Use *increased distance* (greater value of *n*) to justify trends <u>down a group</u>.
- 8. Comparisons between isoelectronic species (same # of e^{-}): explain with their p^{+}/e^{-} ratio.
- 9. Comparisons between an atom and its ion/ions of the same atom, <u>same n</u>: explain with e⁻/e⁻ repulsion.
- 10. Comparisons between an atom and its ion/ions of the same atom, <u>different n</u>: explain with distance.

Bonding and IMFs

- 1. General bond strength order: Covalent Network Solid > Metallic > Ionic >> Covalent
- Coulomb's Law governs ionic bond strength. Greater ion charges = greater attraction = stronger bond. Smaller ions = smaller distance = stronger attraction = stronger bond. Ion charges are generally more important. (Stronger bonds have higher melting points).
- 3. Two types of Alloys: Substitutional (two metals of relatively same size, alloy retains similar properties) and Interstitial (smaller atoms put in spaces between larger metal atoms, alloy is more brittle/less malleable).

	What holds them together?	Characteristic Properties	Conductivity
Ionic	Strong electrostatic attraction between ions (lattice energy)	 High melting and boiling points; Usually found in the solid state because the electrostatic attraction is SO strong 	 Conductors of electricity only in (aq) or (I) states (mobile ions) Electrolytes when aqueous
Covalent	Electrons are shared by nuclei; <u>however</u> , sharing is rarely equal!	 Can be solids, liquids or gases (depending on IMFs); Low melting and boiling points 	 Poor conductors of electricity (no mobile charges) Not electrolytes when aqueous
Metallic	Attraction between "sea" of mobile or delocalized electrons and positive metal ions	 Solids with a crystalline structure at room temp; Range of melting points 	• Excellent conductors of electricity since electrons in the "sea" are free to move

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- 5. Since C and H have a similar electronegativity, hydrocarbons are non-polar (the C-H bond is non-polar).
- 6. Only the first bond of a double or triple bond is counted in hybridization. The others are pi bonds formed by the overlap of unhybridized p orbitals.
- 7. Hybridization

# of Electron Domains	# of Hybrid Orbitals	Electron Geometry	Hybridization
2	2	Linear	sp
3	3	Trigonal planar	sp²
4	4	Tetrahedral	sp³

8. Bond Types/ Sigma (σ) and Pi (π) bonds

Bond Type	Bond Order	Made of	Length / Strength
single bond	1	1 sigma bond	longest/ weakest
double bond	2	1 sigma bond + 1 pi bond	medium length/ strength
triple bond	3	1 sigma bond + 2 pi bonds	shortest/ strongest

- 9. When predicting shape, a double or triple bond counts as one area of electron density.
- 10. VSEPR Shapes and Angles

Electron Groups	Bonding Groups	Lone Pairs	Electron Geometry	Molecular Geometry (VSEPR Shape)	Approximate Bond Angle
2	2	0	linear	linear	180 ⁰
_	3	0		trigonal planar	(2.2)
3	2	1	trigonal planar	bent	120°
	4	0		tetrahedral	
4	3	1	tetrahedral	trigonal pyramidal	109.5°
	2	2		bent	
	5	0		trigonal bipyramidal	
_	4	1	tuidenel hin wensidel	seesaw	120º (equatorial),
5	3	2	trigonal dipyramidai	T-shaped	90° (axial)
	2	3		linear	
	6	0		octahedral	
6	5	1	octahedral	square pyramidal	90°
	4	2		square planar	

11. IMFs

IMFs present	Non-polar molecules (C–H only, diatomic or completely symmetric molecules)	Polar molecules (without H – FON)	Polar H – FON molecules
London dispersion forces (LDFs) Induced dipole – induced dipole	yes	yes	yes
Dipole – dipole attractive forces	no	yes	yes
Hydrogen "bonding" attractive forces (strongest dipole-dipole force)	no	no	yes

Mixed IMFs! Attractive forces between two different compounds

IMFs present	Compound types present
Dipole – induced dipole attractive forces	Polar + non-polar molecules
Ion – dipole attractive forces	lons + polar molecules

12. When comparing similarly-sized particles: Ion – Dipole > Hydrogen bonding > Dipole – dipole > Dipole – Induced Dipole > Dispersion

- 13. LDFs are stronger with a more polarizable electron cloud (more electrons/higher molar mass = more polarizable = stronger LDFs)
- 14. Higher melting points, boiling points, solubility, viscosity = stronger IMFs. Higher vapor pressure, volatility = weaker IMFs.

- 15. Alcohols (hydrocarbon with an –OH group) are soluble because they can hydrogen bond with water, NOT because they have a hydroxide group (OH⁻) they DON'T!
- 16. Capillary action and surface tension can be explained in terms of intermolecular forces. More capillary action, suface tension = stronger IMFs.
- 17. Hydrogen bonding is an INTERmolecular force (IMF), not an INTRAmolecular bond. The name is misleading!
- 18. Changing phase (state) in molecular substance involves overcoming IMF's, NOT breaking covalent bonds.
- 19. Temperature (KE) is constant during a phase change; PE changes. Two phases exist on the horizontal part of a cooling or heating curve.

Gases

- 1. Temperature is directly proportional to average kinetic energy of gases: same temp = same KE!
- 2. At the same temperature (i.e. same kinetic energy), heavier gas particles are slower than light particles.
- 3. Gases will be less ideal and more real at higher pressures, lower temperatures, and higher IMFs.
- 4. The same gas particle will move slower at low temperatures and faster at high temperatures.
- 5. Kelvin temperature must be used for all gas calculations.
- 6. If using R (the gas constant), all other variables' units must match the units of R.
- 7. Molar Mass Kitty Cat = DiRT over Pee: $MM = \frac{DRT}{P} = \frac{mRT}{PV}$
- 8. People Vomit over Nasty Toilets $\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$

Electrochem Equilibrium Summary

Given on formula chart:

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

$$n = e^{-} \text{ transferred, F = Faraday's constant}$$

$$\Delta G^{o} = -RT \ln K$$

$$R = 8.314 \text{ J/(mol K), T = temp (K), ln(k) = natural log of K}$$

Not given on formula chart:

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



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 >> 1
K >>> Q	K >> Q	K > Q	K = Q
[reactants] > [products]	[reactants] = [products]	[reactants] < [products]	[reactants] << [products]
Higher voltage (than standard E°cell)Ecell > E°cell	Equal voltage (to standard E ^o cell) Ecell = E ^o cell	Lower voltage (than standard E ^o cell) Ecell < E ^o cell	No voltage! (dead battery) E _{cell} = 0 V
 <u>How Does this Happen</u>? Increase reactants Decrease products Increase both, but increase REACTANTS more Decrease both, but decrease PRODUCTS more 	 <u>How Does this Happen</u>? 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>? Increase products Decrease reactants Increase both, but increase PRODUCTS more Decrease both, but decrease REACTANTS more 	 <u>How Does this Happen</u>? Cell runs for a very long time All reactants used up

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!

Oxidat	ion Rules:	Nonmetal	Oxidation State	Example
1.	Free elements = 0	Fluorine	-1	MgF ₂
2.	All atoms in a <u>neutral</u> compound <u>add up</u> to 0.	Hydrogen	+1	H ₂ 0
3. 4.	The rules below apply to bonded elements:	Oxygen	-2	CO ₂
	a. Group 1A metals = +1	Group 7A	-1	CCl ₄ -1 ox state
	 b. Group 2A = +2 Non-metals usually follow the short to the right in order: 	Group 6A	-2	H ₂ S -2 ox state
	 d. Note: the carbon family (4A) isn't mentioned – you will ALWAYS have to 	Group 5A	-3	NH ₃ -3 ox state



Electrochemistry Involves TWO MAIN TYPES Of Electrochemical Cells:

- 1. <u>Galvanic (voltaic) cells</u> thermodynamically favorable \rightarrow <u>battery</u> (+E_{cell}, – Δ G, K > 1)
- 2. <u>Electrolytic cells</u> –thermodynamically unfavorable and require external power source ($-E_{cell}$, $+\Delta G$, K < 1)

GALVANIC or VOLTAIC CELL "ANATOMY"

- <u>Anode</u> (An Ox) the electrode where oxidation occurs, loses mass into solution as the cell runs ("anode"-rexic)
- <u>Cathode</u> (Red Cat) the electrode where reduction occurs, gains mass from solution as the cell runs (fat cat)
- <u>Inert electrodes</u> used when a gas is involved OR ion to ion; Pt (expensive) or graphite (cheap)
- <u>Salt bridge</u> used to maintain electrical neutrality in a galvanic cell: <u>anions to anode, cations to cathode</u>
- <u>Electron flow</u> 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^ocell

- 1. The Metal with the MORE POSITIVE REDUCTION POTENITAL 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^o_{ox}.

$$E_{cell}^o = E_{ox}^o + E_{red}^o$$

DEPENDENCE OF CELL POTENTIAL ON CONCENTRATION

- <u>Voltaic cells at NONstandard conditions</u>: 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]: $E_{cell} > E^{\circ}_{cell}$, \uparrow voltage
 - \downarrow [reactants] or \uparrow [products]: $E_{cell} < E^{\circ}_{cell}$, \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 + ΔG^0 and ΔE^0
- 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).

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

Are you SAFe? MMM.



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Study Guide or: How I Learned to Stop Worrying and Love Thermochem \heartsuit

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:
 A lot of bond energies A reaction <u>without</u> ΔH_{rxn} 	ΔH_{rxn}	 Draw the Lewis structures. Use the following: ΔH_{rxn} = Σ(BE_{reactants})- Σ(BE_{products})
1. A lot of heats of formation (ΔH_f) 2. A reaction <u>without</u> ΔH_{rxn}	ΔH_{rxn}	$\Delta H_{rxn} = \Sigma \Delta H_f (products) - \Sigma \Delta H_f (reactants)$
 Multiple reactions with ΔH 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 !)
 info to calculate q (using mCΔT or nCΔT) Moles/grams of a chemical 	ΔH_{rxn}	$\Delta H_{\rm rxn} = \frac{\rm q}{\rm mol}_{\rm rxn}$

2. Asked to find something else? 3 Options!

	Given?	Asked to find?	Use:
1. 2.	 A reaction with ΔH_{rxn} Either: a. g or mol of a substance b. energy change (J or kJ) 	 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. 2.	A phase change (vaporizing, condensing, freezing or melting) ΔH _{vap} or ΔH _{fus}	Energy change (heat absorbed or released)	$q = n\Delta H$
1. 2. 3.	A temperature change Mass or moles of a substance Heat capacity $\left(\frac{J}{g^{\circ}C} \text{ or } \frac{J}{mol^{\circ}C}\right)$	Energy change (heat absorbed or released)	q=mC∆T



Calorimetry:

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

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

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

b. Aqueous/reacting things

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

Usually C = 4.18 J/g°C = C_{water} , but not always! Be careful.

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

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

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 $\Delta H!$

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 **<u>1 mole</u>** of a substance.

 $\Delta H_{rxn} = \sum \Delta H_f \text{ products} - \sum \Delta H_f \text{ reactants}$ *Don't forget to multiply by coefficients!

PROBLEM SQLVING IN THERMODYNAMICS

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.

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

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

> Determining ΔS = Entropy

Qualitative:

 $S_{solid} < S_{liquid} << S_{gas}$

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:

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

Determining ΔG = Free Energy

<u>Using ΔH and ΔS</u>: 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.):

 $\Delta G^{\circ} = -RTIn(K)$

R = 8.314 x 10⁻³ kJ/mol*K

 $\Delta G^{\circ} = 0$ only if K = 1

If K < Q, the rxn is LESS spontaneous (less negative or more positive)

If K > Q, the rxn is MORE spontaneous (more negative or less positive)

<u>Related to E[°]_{cell} (Electro)</u>: $\Delta G^{\circ} = -nF(E^{\circ}_{cell})$

F = 96,485 C/mol e-

n = number of electrons transferred

Free Energy of Formation:

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

If ΔG is <u>negative</u>, the reaction IS thermodynamically favorable. If ΔG is <u>positive</u>, the reaction is NOT thermodynamically favorable.

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

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Thermochemistry/Thermodynamics Study Guide

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

Elements ARE zero for: _____

Elements are NOT zero for: _____

Nature favors:

1. _____ (increasing entropy, greater disorder)

2. _____ (exothermic, release of energy)

- **Driven by enthalpy:** a very exothermic reaction (_____) overcomes a decrease in entropy
- **Driven by entropy:** an endothermic reaction occurs spontaneously because of a highly _____ 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. (3))

E ^o cell	ΔG^{o}	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):

$$\Delta G^o = -nFE^o_{cell}$$

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):
$$\Delta G^o = -RT \ln K$$

 $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ T = temperature (in Kelvin) K = equilibrium constant

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

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

67 A Visual Summary of Le Châtelier's Principle



68 Solubility Summary Sheet

Solubility Language	Normal Equilibrium Language	
solubility product constant (K _{sp})	equilibrium constant (K)	
molar solubility	x (from RICE table)	
saturated solution	system at equilibrium	

When you need to solve for molar solubility

Given?	Asked to find?	Strategy
K _{sp}	molar solubility	 Write K_{sp} expression using ions produced when solid dissolves. Substitute x values from mini-RICE table Solve for x
 K_{sp} OR Concentration of all ions in a saturated solution 	# of grams that can dissolve	 Write K_{sp} expression using ions produced when solid dissolves. Substitute x values from mini-RICE table Solve for x (in M = mol / L) Use the volume of solution to calculate moles that can dissolve Use molar mass to convert to grams

When you don't need to solve for molar solubility

Given?	Asked to find?	Use:
Concentration of all ions in a saturated solution	K _{sp}	 Write K_{sp} expression using ions produced when solid dissolves. Substitute given concentrations and solve for K_{sp}.
other ion concentrations at equilibrium <u>and</u> K _{sp}	Concentration of ONE ion in a saturated solution	 Write K_{sp} expression using ions produced when solid dissolves. Plug in known values, solve for unknown concentration.
ion concentrations when solutions are added or mixed <u>and</u> K _{sp}	If a precipitate will form	 Write Q_{sp} expression using ions produced when solid dissolves. Substitute given concentrations and solve for Q_{sp}. Compare K and Q: K > Q = no precipitate K < Q = yes precipitate

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Acids, Bases & Buffers Cheat Sheet: The 6 Ways to Determine pH

1) Strong Acids/ Strong Bases

You MUST memorize:

Strong Acids: HBr, HI, HCl, H₂SO₄, HNO₃, HClO₄

Hint: BrICl – SO NO ClO

Strong Bases: Groups IA and IIA metal hydroxides

100% Dissociation! Easy life:

$$pH = -\log[H^+] = -\log[HA]_o$$

$$pOH = -\log[OH^{-}] = -\log[B]_{o}$$

$$pH + pOH = 14$$

2) Weak Acids/ Weak Bases

If it's not strong, it's weak!

< 1% Dissociation \rightarrow Equilibrium!

Time saver!! Since acids ionize 1 H⁺ at a time, $[H_3O^+] = [A^-]$, and $[OH^-] = [BH^+]$. For weak acids and bases, make the assumption $[HA]_0 - x \approx [HA]_0$ and $[B]_0 - x \approx [B]_0$.

Weak Acids:

$$K_a = \frac{[x][x]}{[HA]_o - x} \approx \frac{[x][x]}{[HA]_o}$$
 where $[H_3O^+] = x << [HA]_o$

Weak Bases:

$$K_b = \frac{[x][x]}{[B]_o - x} \approx \frac{[x][x]}{[B]_o}$$
 where $[OH^-] = x << [B]_o$

3) Salty Salts

<u>To know if a salt will affect pH, determine</u>: \rightarrow Will the salt ions will <u>hydrolyze</u> (or split) water?

Conjugates of Strong Acids/Bases: do NOT hydrolyze water, and thus don't affect pH

Conjugates of <u>Weak</u> Acids/Bases: <u>DO</u> hydrolyze water, and thus do affect pH!

How to Determine the pH of a Salt

- Dissociate your salt.
 Make the cation into a base: is it strong or weak?
- 2. Make the anion into an acid: is it strong or weak?
- 3. Strong wins!
- 4. If either is weak, write the hydrolysis reaction:
 - Conjugate base of WA: $A^- + H_2O \rightleftharpoons OH^- + HA$
 - Conjugate acid of WB: $BH^+ + H_2O \rightleftharpoons H_3O^+ + B$

Example

CaSO₃→ Ca²⁺ + SO₃²⁻ Ca²⁺ + 2 OH⁻→ Ca(OH)₂ Strong base H⁺ + SO₃⁻ → HSO₃⁻ Weak acid SB + WA, so this salt is basic! SO₃⁻ + H₂O \rightleftharpoons OH⁻ + HSO₃⁻

- 5. Use your hydrolysis equation to calculate the pH using the <u>Weak Acids/Bases</u> method.
- 6. **Be careful**. Did the problem give you K_a , or K_b instead? Do you need to convert based on your hydrolysis reaction? Remember: $K_w = K_a \times K_b = 1.0 \times 10^{-14}$

4) Adding Strong Acids + Strong Bases (Yes, this includes titrations!)

These are really just stoichiometry problems with a limiting reagent! $\textcircled{\sc 0}$

- What is "excess" determines the pH (since all strong/strong combos neutralize)
- <u>Beware the change in volume</u> if multiple solutions are being <u>added</u>! (calculate moles of either H⁺ or OH⁻ in excess, and divide by <u>total</u> volume to determine concentration of [H⁺] or [OH⁻], and go from there)

5) Buffers

Whenever a weak acid or base is present with its conjugate salt – YOU HAVE A BUFFER!!! Four ways to get a buffer:

- 1. Weak acid and its conjugate base (HA and A⁻ **OR** HA and *Na*A) **1:1 mole ratio**
- 2. Weak base and its conjugate acid (B and BH⁺ OR B and BHC/) 1:1 mole ratio
- 3. Weak base with strong acid (titration) 1 WB : 0.5 SA mole ratio
 - \rightarrow strong acid reacts with weak base, producing conjugate acid
- 4. Weak acid with strong base (titration) 1 WA : 0.5 SB mole ratio

 \rightarrow strong base reacts with weak acid, producing conjugate base

The <u>best buffer</u> has: 1) High capacity (lots of acid and base), 2) [HA] = [A⁻], 3) pH (of buffer) = pK_a (of acid form)

Two calculation options:

 $[H_3 0^+] = K_a \frac{[HA]}{[A^-]}$ or $pH = pKa + \log(\frac{[A^-]}{[HA]})$

[HA] = Weak acid or salt of conjugate base or added strong base (in a WB/SA titration)

[A⁻] = Weak base **or** salt of conjugate acid **or** added strong acid (in a WA/SB titration)

Shortcut!!! Since $\frac{[Acid]}{[Base]}$ is a ratio in the equations, the <u>amount of moles may be substituted in place of concentration</u> because the final volumes will be the same, and thus cancel out.

6) Adding Strong Acids/Bases + Weak Bases/Acids (Yes, this includes titrations!)

Buffers make the titration curve "flat" at the region where buffering occurs. On a titration curve, this is the point of inflection (buffer arrow) = maximum buffering capacity!

Weak Acid Titrated with Strong Base

Weak Base Titrated with Strong Acid



There are 4 zones of interest along a titration curve for a Weak Acid/Base and Strong Base/Acid:

- 1. <u>Initial pH</u>: simply a weak acid or weak base problem!
- 2. <u>During titration, before equivalence point</u>: BUFFER! The amount of conjugate formed = the amount of strong acid or base added. (Amount of weak left = HA_o strong added)
- 3. Equivalence point: only salt and water are left; salt is either a weak base (if a weak acid was titrated) or a weak acid (if a weak base was titrated); remember to convert K_a to K_b or vice versa! (Use M_AV_A = M_BV_B)
- 4. <u>Beyond the equivalence point</u>: Stoichiometry! Calculate how much STRONG (acid or base) is left after equivalence, recalculate its molarity (remember, volume increased during titration), and calculate using the strong acid/base method.

<u>Best Indicator</u>: Choose indicator with pK_a (of indicator) $\approx pH$ (at equivalence point of titration). This means that K_a of the indicator $\approx 1 \times 10^{-pH} @ eq pt$)

<u>Remember</u>: if $pH \le pK_a$ the acid form (HA) predominates, if $pH > pK_a$ the conjugate base form (A⁻) predominates


72 Bonding and IMFS Free Response Study Guide

- 1. Draw the dang Lewis dot structure!
- 2. Reference the chart below depending on the question type.

Question Type	Example Question(s)	What to consider/talk about:
Expanded octet exceptions	• Which atoms can be stable with more than 8 bonded valence electrons and why?	 Must have access to <u>empty d sublevel</u> Only available to elements in rows 3-7
Comparing bond length and/or strength	 Which bond is shorter, X₂ or Y₂? Which bond is stronger, X₂ or Y₂? 	 More shared electron pairs means: Stronger/shorter bond Greater attractive force between e⁻ and nuclei Nuclei pulled closer together/ harder to separate
Comparing bond angles	 Which bond angle is larger/smaller, H – X – H or H – Y – H? 	 Count number of lone pairs vs bonding pairs on central atom Lone pairs are more repulsive than bonding pairs More lone pairs = smaller bond angle
Comparing VSEPR geometry	 Why does XH₂ have bent geometry, but YH₂ is linear? Why does XH₃ have trigonal planar geometry, but YH₃ is trigonal pyramidal? 	 Count number of lone pairs vs bonding pairs on central atom Lone pairs distort the symmetry, pushing bonded atoms away
Comparing polar vs non-polar <u>bonds</u>	 Which bond is more polar, HX or HY? The X₂ bond is non-polar. Explain. 	 Greater electronegativity difference between bonded atoms = <u>more uneven distribution of e⁻</u> <u>density</u> = more polar Non-polar = equally distributed e⁻ density
Comparing polar vs non-polar <u>molecules</u>	 Why is XH₃ a polar molecule, but YH₃ is non- polar? 	 Lone pair on central atom distorts symmetry = <u>uneven distribution of e⁻ density</u> = polar No lone pair on central atom = symmetrical e⁻ density = non-polar
Comparing vapor pressures, boiling points, or melting points	 Why does XH₂ have a lower vapor pressure than YH₂? Which has a higher melting point, XH₃ or YH₃? Explain. 	 Identify IMFS Non-polar = LDFs Polar = dipole to dipole H - FON = hydrogen bonding Connect IMF strength to vocab ↑ IMFs = ↓ VP, because molecules are more attracted to each other, less in gaseous state ↑ IMFs = ↑ BP/MP, because molecules are more attracted to each other and require more energy to separate

But WAIT! How can I tell if I molecule is polar?

Lone pairs on the central atom?	Yes	Polar molecule		
		Look at terminal (non-central atoms)		
	No	Same?	Different?	
		Non-polar molecule	Polar molecule	

Gas Laws Math Summary

Ideal Gas Law	Combined Gas Law	Dalton's Law and Mole Fractions	Molar Volume	Molar Mass Kitty Cat	Gas Stoich
PV = nRT	$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$	$P_{total} = P_1 + P_2 + \cdots$ $P_A = P_{total} \times X_A$ where $X_A = \frac{\text{moles } A}{\text{total moles}}$	1 mol = 22.4 L at STP	$MM = \frac{DRT}{P} = \frac{mRT}{PV}$	One chemical (g, mol, L) → another chemical (g, mol, or L)
Use when you have <u>only one</u> of each variable	Use when conditions have <u>changed</u>	Use when you have a mixture of gases	Use to convert between quantity and volume of a gas	Use to calculate gas density	Use to convert from one chemical to a different chemical
 Things to watch for: Temp: need K Choose R based on unit for pressure Volume: need L 	 Things to watch for: Temp: need K Units for each variable need to be the same on both sides 	 Things to watch for: Gas collection over water (or collection by water displacement): pure gas is mixed with water vapor 	Only true at STP!!! (273 K, 1.0 atm)	Potential shortcut When at STP: $D = \frac{molar \ mass}{22.4 \ L}$	Two types: • L → L (at same T and P) • Non-STP (or NOT at same T and P): use stoich for mol → mol, and use PV=nRT for L ↔ mol

Gas Laws Conceptual Summary

1. <u>Temperature is directly proportional to average kinetic energy</u>, which means:

- a. Same temperature = same average kinetic energy!
- b. Same temperature, different gases? High molar mass = slower, low molar mass = faster
- c. Same gas, different temperature? Higher temperature = faster, lower temperature = slower
- 2. <u>Kinetic Molecular Theory</u> (5 postulates): gas particles are vert small and very far apart; are in constant, rapid, random motion; bounce off things with no energy loss (elastic collisions); do not attract or repel (negligible IMFs), kinetic energy directly proportional to velocity

3. Ideal vs Real Gases

- a. Ideal gases: follow KMT postulates (most ideal at high T, low P)
- b. Real gases: have actual volume or attractive forces (most real at low T, high P)

Totally Epic AP Chem Review: Empirical and Molecular Formulas!

Percent Composition: the percent by mass of each element in a compound.

According to the law of <u>Definite Proportions</u>, the molar ratio of elements in a specific compound is constant, regardless of the compound's source or method of preparation.

```
% composition of an element = \frac{total mass of element in compound}{total mass of compound} \times 100 **NOT on F.C.
```

Example: As some salts crystallize from a water solution, they bind water molecules in their crystal structure. Sodium carbonate forms such a hydrate: find the mass percentage of water in sodium carbonate decahydrate.

2. Qualitative analysis shows that a compound contains 32.28% sodium, 22.65% sulfur, and 44.99% oxygen. Find the empirical formula and name of this compound.

How to Get the Molecular Formula

- 1. Find the mass of the empirical formula.
- 2. Take the molecular mass and divide it by empirical mass (this will always give you a whole number).
- 3. Multiply the whole # by the empirical formula's subscripts to determine the molecular formula.

Let's Practice!

1. What is the molecular formula for a compound with the empirical formula H_2O and a molecular mass of 54 g/mol?

- 2. The analysis of a rocket fuel showed that it contained 87.4% nitrogen and 12.6% hydrogen by weight. Mass spectral analysis showed the fuel to have a molar mass of 32.06 g/mol.
 - a. What is the empirical formula of the fuel?

b. What is the molecular formula of the fuel?

Empirical Formula: the symbols for the **elements** combined in a compound, with **subscripts** showing the smallest whole-number mole ratio of the different atoms in the compound.

Molecular Formula: the actual formula of a compound which shows the total number of each atom in the molecule.

*** It is possible for the empirical formula and the molecular formula to be the same! ***

For example:

Molecular	Simplify by dividing	Empirical
P ₄ O ₁₀		
	3	C ₃ HON ₄
NaCl		

The Empirical Song! (sung with the melody from Twinkle, Twinkle Little Star)

Percent to mass and mass to mole, Divide by small then multiply til whole. That's how you find the empirical Smallest whole-number ratio.

Let's Practice!

1. Analysis of a sample of a compound known to contain only phosphorus and oxygen indicates that it contains 43.67% phosphorus by mass. What is the empirical formula and name of this compound?

Totally Epic AP Chem Review: <u>Hydrates and Combustion Analysis</u>!

Combustion Analysis: Technique used to obtain the empirical formula of a hydrocarbon

→ Remember a standard (unbalanced) combustion reaction? (This formula is unbalanced!)

 $C_xH_yO_z + O_2 \rightarrow \underline{CO_2} + \underline{H_2O}$

How to Solve a Combustion Analysis Problem

- 1. Convert mass of CO_2 and mass of H_2O to **moles** of each compound.
- 2. Convert moles of CO₂ to moles of carbon, and moles of H₂O to moles of hydrogen.
- 3. If compound contains something which is <u>NOT</u> C or H, find its mass by subtraction, and convert the mass to moles.
- Now you have mole numbers! Complete the <u>empirical</u> formula calculation (divide by small, multiply til whole).

Practice:

1. Combustion analysis determined that a compound containing only carbon and hydrogen produces 1.83 g CO_2 and 0.901 g H_2O . Find the empirical formula of the compound.

2. Upon combustion, a 0.8233 g sample of a compound containing only carbon, hydrogen, and oxygen produces 2.445 g CO₂ and 0.6003 g H₂O. What is the empirical formula of the compound?

Hydrates: Salty salts with a hidden surprise!

A hydrate is a pure substance (often ionic) that contains a fixed composition of water molecules (known as "waters of hydration") embedded in its crystal structure.

→ Heating a hydrate <u>"drives off"</u> the water molecules, and the solid that remains behind is called anhydrous, meaning "without water." By measuring the mass of water removed when dehydrating a hydrate, we can determine the <u>ratio</u> of water molecules to anhydrous salt for a given hydrate, which allows us to find the formula of the hydrate!

Notes about Language: Taiking about nyurates can be tricksy: here's a quick guide to the terminology

Word/ Phrase	Meaning/ Context
Waters of hydration	The embedded water molecules within the hydrate
Heating to "constant mass"	The process where the hydrate is heated multiple times and the mass measured each time until the mass stops changing, to ensure all of the water molecules have been driven off.

Steps to gravimetrically (by mass) determine the formula of a hydrate:

- 1. Determine the **mass** of the water that has left the compound.
- 2. Convert the mass of water to moles.
- 3. Convert the mass of anhydrate that is left over to moles.
- 4. Find the water-to-anhydrate mole <u>ratio</u> (just like finding an <u>empirical</u> formula, but be careful: you can't multiply til whole! The mole ratio of the anhydrous salt must always be <u>1</u>; only the number of waters can be a whole number greater than 1)
- 5. Use the mole ratio to write the formula.

Example: A student attempts to experimentally determine the number of moles of water in one mole of BeC_2O_4 . $3 H_2O$. The student collects the data shown in the table below.

Mass of empty crucible	36.48 g
Initial mass of sample and crucible	39.69 g
Mass of sample and crucible after first	38.82 g
heating	-

- a. Calculate the total number of moles of water lost when the sample was heated.
- b. Determine the formula of the hydrated compound.

Common Lab Errors when Determine the Formula of a Hydrate

Error	Effect on Calculated % H₂O
Crucible (container) not heated "to <u>constant</u> mass" • You didn't heat the crucible to remove extra	• Water from the crucible will be lost as well as the expected water loss from heating the hydrate.
water molecules before getting the mass of the container and hydrate sample	 The calculated % H₂O will be <u>larger</u> than the actual % H₂O in the hydrate.
Excess heating caused the dehydrated sample to decompose.	• Gas from the decomposition will be lost as well as the expected water loss from heating the hydrate.
 Often times, a gas will be released during the decomposition 	 The calculated % H₂O will be <u>larger</u> than the actual % H₂O in the hydrate.
Strong initial heating caused some of the hydrate	 Hydrated salt will be lost as well as the expected water loss from heating the hydrate.
sample to spatter out of the crucible.	 The calculated % H₂O will be <u>larger</u> than the actual % H₂O in the hydrate.
The dehydrated sample absorbed moisture from the air after heating (but before the mass is measured).	 Not all of the waters of hydration will be removed. The calculated % H₂O will be <u>smaller</u> than the actual % H₂O in the hydrate.
 The hydrate is not heated to "constant mass" The hydrate should be heated multiple times and the mass measured each time, to ensure all 	 Not all of the water molecules will have been driven off, so the remaining salt is not completely anhydrous. The calculated % H₂O will be smaller than the
of the water molecules have been driven off.	actual % H_2O in the hydrate.

Practice with Combustion Analysis and Hydrates: Fiery yet Thirst-Quenching!

1. When the <u>unbalanced</u> reaction below occurs at STP, 1.5 L of CO₂ and 1.0 L of H₂O are created. What is the empirical formula of the hydrocarbon?

$$C_x H_y(g) + O_2 \rightarrow CO_2(g) + H_2O(g)$$

a. CH_2 b. C_2H_3 c. C_2H_5 d. C_3H_4

A sample of a hydrate of CuSO₄ with a mass of 250 grams was heated until all the water was removed. The sample was then weighed and found to have a mass of 160 grams. What is the formula for the hydrate?

b. $CuSO_4 \cdot 10 H_2O$ b. $CuSO_4 \cdot 7 H_2O$ c. $CuSO_4 \cdot 5 H_2O$ d. $CuSO_4 \cdot 2 H_2O$

Epic AP Chem Review: Types of Chemical Reactions

There are three subsets of <u>double replacement reactions</u> that you will need to know and be able to identify!

1. Precipitation Reaction: two aqueous solutions mix to form a precipitate (solid)

 $AB(aq) + CD(aq) \rightarrow AD(s) + CB(aq)$

2. <u>Neutralization (Acid-Base) Reaction</u>: an Arrhenius acid and base react to produce a salt and water.

 $HB + C(OH) \rightarrow H_2O + CB$

- 3. <u>Oxidation-reduction (redox) reactions</u>: where electrons are transferred from one atom to another.
 - If a substance accepts an electron, it is <u>reduced</u>.
 - If a substance loses an electron, it is <u>oxidized</u>.
 - Electrons are always transferred from the species that is oxidized to the species that is reduced.

Two great mnemonics!

- 1. OIL RIG: <u>O</u>xidation <u>Is</u> <u>L</u>oss (OIL) and <u>R</u>eduction <u>Is</u> <u>G</u>ain (RIG)
- 2. LEO goes GER: A species loses electrons when oxidized, and gains electrons when reduced.

Almost all reaction types (except double replacement) are redox. We will learn soooooooo much more about oxidation-reduction reactions in the next video!!

Don't Overreact: More Reactions Practice!

Part I: Complete the following chart. (Balance the reactions if you want more practice!)

Reaction	Type of Reaction A/B, PPT, Redox?
1Ca(s) +H ₂ O(I) \rightarrow Ca(OH) ₂ (aq) +H ₂ (g)	
2NH ₄ F(aq) +Sr(ClO ₃) ₂ \rightarrow NH ₄ ClO ₃ (aq) +SrF ₂ (aq)	
3HNO ₃ (aq) +LiOH(aq) \rightarrow LiNO ₃ (aq) + H ₂ O(I)	
4. $_LiI(aq) + \Pb(NO_3)_2(aq) \rightarrow \LiNO_3(aq) + \PbI_2(s)$	
5. $\C_6H_{14}(g) + \O_2(g) \rightarrow \H_2O(I) + \CO_2(g)$	

Part II: Multiple Choice Practice



- b. Oxidation/reduction d. Decomposition
- 2. Consider the following three equations for chemical reactions:

$$2 \operatorname{Na}(s) + \operatorname{Cl}_2(g) \to 2 \operatorname{NaCl}(s)$$
$$2 \operatorname{NaCl}(aq) + \operatorname{Pb}(\operatorname{NO}_3)_2(aq) \to \operatorname{PbCl}_2(s) + 2 \operatorname{NaNO}_3(aq)$$
$$\operatorname{NaOH}(aq) + \operatorname{HBr}(aq) \to \operatorname{H}_2\operatorname{O}(l) + \operatorname{NaBr}(aq)$$

These are examples of:

- a. three redox reactions c. a redox reaction, a precipitation reaction, and an acid-base reaction
- b. three acid-base reactions d. a neutralization reaction, then two precipitation reactions

Totally Epic AP Chem Review: Limiting and Excess!

Limiting reactant: will be completely used up during the chemical reaction \rightarrow determines all other amounts Excess reactant: will <u>NOT</u> be completely used up during the chemical reaction \rightarrow has some left over at the end Percent Yield: a method to calculate the effectiveness of a chemical reaction.

- Actual yield: what you produce from actually doing the reaction in a lab setting.
- Theoretical yield: what "should have been" produced from the chemical reaction. This is calculated with stoichiometry!

Percent Yield =
$$\frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$

How do I know if a problem is a limiting reactant problem?

→ Check if you are given a mass or mole value for <u>MORE THAN ONE reactant</u> AND the reaction goes to completion (very large K, acid/base neutralization, etc.). If so, this is a limiting problem.

How to Solve a Limiting Problem: Let's Count the Ways

- <u>Straight-up</u>: Do math! Twice! Convert from given quantity of reactants to a chosen product: whichever
 product amount is SMALLER is the product amount actually produced.
- 2. <u>Shortcuts</u>:
 - a. RICE table (aka BCA table): use a mol RICE table or BCA –before, change, after table (same process as a M or atm RICE table)
 - b. Find your limiting: convert all givens to moles, then divide each by their stoichiometric coefficient from the balance equation. Whichever reactant gives you the SMALLER final number is your limiting!

Types of Limiting/ Excess Calculations: Be prepared to answer questions for each of the following types.

- 1. What is the limiting reactant?
- 2. What is the excess reactant, and how much is left over at the end of the reaction?
- 3. How much product is produced during this reaction?

Guided Practice

1. Silicon dioxide is usually quite unreactive but reacts readily with hydrogen fluoride according to the following balanced equation:

$$SiO_2(s) + 4 HF(g) \rightarrow SiF_4(g) + 2 H_2O(l)$$

If 6.0 mol of HF taking up a volume of 850. mL are exposed to 4.0 mol of SiO_2 , how many grams of the excess reactant are left over once the reaction stops?

2. A gaseous mixture at 25°C contained 3.0 mole of CH_4 and 2.0 moles of O_2 and the pressure was measured to be 2.0 atm. The gases then underwent the reaction shown below.

$\operatorname{CH}_4(g) + 2\operatorname{O}_2(g) \rightarrow 2\operatorname{H}_2\operatorname{O}(l) + \operatorname{CO}_2(g)$

What was the pressure in the container after the reaction had gone to completion and the temperature was allowed to return to 25° C?

a. 0.40 atm b. 1.2 atm c. 2.0 atm d. 2.4 atm

5. The percentage yield for the reaction $PCI_3 + CI_2 \rightarrow PCI_5$ is 83.2%. What mass is PCI_5 is expected from the reaction of 73.7 g of PCI_3 with excess chlorine?

6. Which of the following particulate diagrams best shows the formation of water vapor from hydrogen gas and oxygen gas in a rigid container at 125°C?



3. Nitrogen and hydrogen gas react to form ammonia according to the following reaction:

$$N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$$

- If a flask contains the mixture of reactants represented in the image to the left,
- a. Which reactant is limiting?
- b. Which reactant is in excess?
- c. How much of the excess reactant will remain once the reaction stops?
- d. How much NH₃ was produced in this reaction?

4. The reaction of silver metal and dilute nitric acid proceeds according to the equation below. If 0.10 mol of powdered silver is added to 100. mL of 0.40 M of HNO₃, how many grams of the excess reactant remain? (The molar mass of HNO₃ is 63.018 g/mol.)

 $3 \operatorname{Ag}(s) + 4 \operatorname{HNO}_3(aq) \rightarrow 4 \operatorname{AgNO}_3(aq) + \operatorname{NO}(g) + 2 \operatorname{H}_2\operatorname{O}(l)$

a. 3.8 g b. 6.2 g c. 7.6 g d. 9.7 g

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Totally Epic AP Chem Review: Gravimetric Analysis!

Gravimetric Analysis: analytical technique used to find the percent mass of an ion in an impure substance.

Method:

- 1. Reactant impure material with a known compound, forming a precipitate that contains the ion of interest.
- 2. Filter and dry precipitate, then measure its mass.
- Use stoichiometry calculations to determine the <u>mass</u> of the ion of interest, using the balanced reaction to work backwards from the mass of the precipitate measured in the lab.

Steps in Gravimetric Analysis (Lab Technique)

- 1. Dry and weigh impure sample.
- 2. Dissolve sample in water.
- 3. Add precipitating reagent in excess.
- 4. Filter precipitate from solution.
- 5. <u>Wash</u> precipitate to remove soluble impurities.
- 6. Dry and weigh to constant mass



component of the mixture)

Steps in Gravimetric Analysis (Math-y Math)

- 1. Write the balanced precipitation reaction.
- 2. Use stoichiometry to convert from the mass of your precipitate to the mass of the ion of interest.

3. Calculate % by mass: % mass of ion = $\frac{mass of ion (calculated in step 2)}{mass of original sample} \times 100$

____ NOT precipitate mass!!!

Example: The following data were obtained when a sample of unknown chloride was analyzed:

Mass of watch glass	8.2030 g
Mass of unknown chloride sample + watch glass	8.3014 g
Mass of AgCl(s) + watch glass (after drying)	8.432 g

a. Calculate the mass of the precipitate.

b. Calculate the mass of chloride ions in the original sample.

c. Calculate the percent mass of chloride ions in the sample.

Error	Effect on Calculated % by Mass of Ion
Failure to add precipitating reagent in excess.	 Not all of the ion of interest will precipitate, thus some of the ion will be lost in the filtrate. The calculated ion % will be <u>lower</u> than the actual ion % by mass.
Failure to wash the precipitate to remove soluble impurities.	 Some impurities will be left in the precipitate, so measured mass includes both the precipitate and these contaminants. The calculated ion % will be higher than the actual ion % by mass.
The precipitate is excessively washed or washed with warm water.	 Although the precipitate is "insoluble", small amounts of precipitate will dissolve into the wash water and be carried into the filtrate. The calculated ion % will be <u>lower</u> than the actual ion % by mass.
The precipitate is not dried to "constant mass".	 Not all of the water molecules will have been removed, so measured mass includes both the precipitate and remaining water molecules. The calculated ion % will be <u>higher</u> than the actual ion % by mass.

Let's practice!

- A 3.187 g impure sample containing sulfur and an inert material was to be analyzed for sulfur. As part of the
 procedure, the sample is dissolved, and the sulfur is converted to sulfate ion, SO₄²⁻. Barium nitrate is added,
 which causes the sulfate to precipitate out as BaSO₄. The dried BaSO₄ has a mass of 2.005 g.
 - a. Write the balanced net ionic equation for the precipitation reaction.

b. What mass of sulfur was in the original sample?

c. What is the percent of sulfur in the original ore?

Common Lab Errors in Gravimetric Analysis

Totally Epic AP Chem Review: Oxidation Numbers and Redox Balancing!

Oxidation-Reduction (Redox) Review

Oxidation-reduction (redox) reactions: where electrons are transferred from one atom to another.

- If a substance accepts an electron, it is <u>reduced</u>.
- If a substance loses an electron, it is <u>oxidized</u>.

Two great mnemonics!

- 1. OIL RIG: Oxidation Is Loss (OIL) and Reduction Is Gain (RIG)
- 2. LEO goes GER: A species loses electrons when oxidized, and gains electrons when reduced.

If a chemical reaction has two species which change oxidation number: yes, it's redox!

Oxidation Numbers/States: Oxidation states are imaginary charges assigned based on a set of rules simply used to determine electron flow. Even though they look like them, oxidation states are NOT ionic charges!

Rules for Assigning Oxidation Numbers (in order of priority)

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

Oxidation Ru	ules:
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xidat	ion Rules:		Oxidation	
1.	Free elements = 0	Nonmetal	State	Example
2.	All atoms in a <u>neutral</u> compound <u>add up</u> to o.	Fluorine	-1	MgF ₂ -1 ox state
3.	All atoms in a polyatomic ion add up to the ion's charge.	Hydrogen	+1	H ₂ 0 +1 ox state
	The rules below apply to bonded elements:	Oxygen	-2	CO ₂
4.	Group 1A metals = +1			-2 ox state
5.	Group 2A = +2	Group 7A	-1	CCI ₄ -1 ox state
6.	Non-metals usually follow the chart to the right, in order:	Group 6A	-2	H ₂ S
	 Note: the carbon family (4A) isn't mentioned – you will ALWAYS have to solve for the oxidation number of 	Group 5A	-3	NH ₃ -3 ox state
	group 4A elements in a compound.			

Oxidation State Practice: Give the oxidation number of each element for the chemical species listed below.

1. SO3 ²⁻ (aq) 3. H2O2(I) 5. NaH(s)	1.	l. S	O ₃ ²⁻ (aq)	3.	H ₂ O ₂ (I)	5.	NaH(s)
------------------------------------------------------------	----	------	-----------------------------------	----	-----------------------------------	----	--------

2. KMnO₄(aq)

Fe(ClO₄)₃(s)

6. C₂H₄O₂(aq)

How to Identify What is Oxidized or Reduced in a Reaction

A substance that has the element that has been oxidized (LOST electrons) will have an oxidation number that becomes more **positive** (or less negative).

A substance that has the element that has been reduced (GAINED electrons) will have an oxidation number that becomes more negative (or less positive).

$\operatorname{Zn}(s) + \operatorname{Fe}^{2+}(aq) \to \operatorname{Zn}^{2+}(aq) + \operatorname{Fe}(s)$		
Oxidation states:		
What was oxidized?	What was reduced?	
$2\operatorname{C}_2\operatorname{H}_2(g)+5\operatorname{O}_2(g)\to 4\operatorname{CO}_2(g)+2\operatorname{H}_2\operatorname{O}(g)$ Oxidation states:		
What was oxidized? What was reduced?		

Steps to Balance Redox Reactions using the Half-Reaction Method

- 1. Write the oxidation and reduction half-reactions (without electrons).
- 2. Balance all atoms other than H and O.
- 3. Balance O by adding H_2O , and balance H by adding H^+ .
- 4. Balance charge in each half reaction using electrons.
- 5. Equalize electron transfer by multiplying so both half-reactions have the same # of electrons exchanged.
- 6. Add the two half-reactions, cancelling anything that appears on both sides of the equation.
- 7. In a basic solution: add equal OH⁻ ions to both sides of the equation to neutralize H⁺ ions. Combine H⁺ and OH⁻ to form H₂O, and cancel if needed.

Practice:

1. Balance the following redox reaction: $Ag^+(aq) + Cu(s) \rightarrow Ag(s) + Cu^{2+}(aq)$

2. Balance the following redox reaction: $H^+ + Cr_2O_7^{-2} + S^2 \rightarrow Cr^{3+} + S + H_2O$

3. Balance the following redox reaction: $H_2O + MnO_4 + I \rightarrow I_2 + MnO_2 + OH$

 $2 \operatorname{H}_2 O(l) + 4 \operatorname{MnO}_4^-(aq) + 3 \operatorname{ClO}_2^-(aq) \rightarrow 4 \operatorname{MnO}_2(aq) + 3 \operatorname{ClO}_4^-(aq) + 4 \operatorname{OH}^-(aq)$

- 4. Which species is reduced in the reaction represented above?
 - a. MnO₂ b. ClO_2 c. MnO₄ d. ClO_{4}

5. In the reaction below, a piece of solid nickel is added to a solution of potassium dichromate.

 $14 \text{ H}^+(aq) + \text{Cr}_2 0_7^{2-}(aq) + 3 \text{ Ni}(s) \rightarrow 2 \text{ Cr}^{3+}(aq) + 3 \text{ Ni}^{2+}(aq) + 7 \text{ H}_2 0(l)$

Which species is being oxidized and which is being reduced?

	Oxidized	<u>Reduced</u>
a.	$Cr_2 0_7^{2-}(aq)$	Ni(s)
b.	$\operatorname{Cr}^{3+}(aq)$	$Ni^{2+}(aq)$
c.	Ni(s)	$\operatorname{Cr}_2O_7^2(aq)$
d.	$Ni^{2+}(aq)$	$Cr^{3+}(aq)$

- 6. Which net ionic equation below represents a possible reaction that takes place when a strip of magnesium metal is oxidized by a solution of chromium (III) nitrate?
 - a. $Mg(s) + Cr(NO_3)_3(aq) \rightarrow Mg^{2+}(aq) + Cr^{3+}(aq) + 3NO_3(aq)$
 - b. $3 \text{ Mg}(s) + 2 \text{ Cr}^{3+}(aq) \rightarrow 3 \text{ Mg}^{2+}(aq) + 2 \text{ Cr}(s)$
 - c. $Mg(s) + Cr^{3+}(aq) \rightarrow Mg^{2+}(aq) + Cr(s)$
 - d. $3 \text{ Mg}(s) + 2 \text{ Cr}(\text{NO}_3)_3(aq) \rightarrow 3 \text{ Mg}^{2+}(aq) + 2 \text{ Cr}(s) + \text{NO}_3^-(aq)$

Totally Epic AP Chem Review: Cell Potential!

Electrochemistry: a study of the interchange of electrical and chemical energy

- There are two types of electrochemical cells: galvanic (voltaic) and electrolytic.
 - Voltaic or Galvanic Cell (Battery): a thermodynamically favorable (i.e. spontaneous) redox reaction which generates useful electrical energy in the form of an electric current
 - Electrolytic Cell: requires electrical energy (direct current or DC power source) to drive a thermodynamically unfavorable (i.e. non-spontaneous) redox reaction.
- In short: galvanic (voltaic) cells produce current, while electrolytic cells use current!

Cell Potential (Ecel): a measure of the potential difference (how much voltage exists) between two half cells an electrochemical cell. The potential difference is caused by the ability of electrons to flow from one half-cell to the other.

→ The cell potential is a quantitative description of the driving force behind an electrochemical reaction that pushes electrons through the wire (or external circuit).

Standard Cell Potential (E° cell): cell potential measured at standard conditions: 1 atm, 1 M solution, and 25°C. A 'naught' sign (°) is used to show standard conditions. Usually measured in Volts (1 V = 1 Joule/Colomb = 1 J/C)

The cell potential can be easily calculated by adding the oxidation and reduction potentials.

$$E_{cell}^{o} = E_{ox}^{o} + E_{red}^{o}$$

- E_{cell}^{o} is the standard cell potential.
- E_{ox}^{o} is the standard oxidation cell potential for the oxidation half-reaction.
- E_{red}^{o} is the standard reduction cell potential for the reduction half-reaction.
- \rightarrow The more <u>positive</u> the value of E[°]_{cell} the greater the driving force of electrons through the system (under standard conditions), thus the more likely the reaction will proceed \rightarrow more spontaneous/more thermodynamically favorable.

When you balance a redox reaction, don't change the cell potential!

Cell potential is an intensive property and thus does not depend on how many times a reaction occurs.

Because the values come from a chart of standard reduction potentials, you MUST REVERSE the sign of the E° of the oxidized species before adding to the E° of the reduced species.

- 1. For a spontaneous redox reaction to occur, the overall cell potential must be positive.
 - a) The metal with the greater (more positive) reduction potential will be reduced!
- 2. For a non-spontaneous redox reaction to occur, the overall cell potential must be negative.
 - a) The metal with the greater (more positive) reduction potential will be oxidized!

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Example 1: Consider the half reactions shown below and the standard electrode reduction potentials that follow.

$$\begin{array}{ll} Al^{3+}(aq) + 3 e^{-} & \rightarrow Al(s) \\ Zn^{2+}(aq) + 2 e^{-} & \rightarrow Zn(s) \end{array} \qquad E^{\circ} = -0.76 \ V \\ \end{array}$$

- a. Write the balanced redox reaction for copper and aluminum that is thermodynamically favorable (i.e. spontaneous). Calculate the standard cell potential of this reaction.
- b. Write the balanced redox reaction for copper and aluminum that is not thermodynamically favorable (i.e. non-spontaneous). Calculate the standard cell potential of this reaction.

Totally Epic AP Chem Review: Galvanic/Voltaic Cells!

Galvanic/ Voltaic Cells

Redox reactions involve the transfer of electrons from one substance to another, and thus have the potential to generate an electric current (i.e. flow of electrons). To use that current, we need to separate the place where oxidation is occurring from the place where reduction is occurring.

- \circ $\;$ Current is the number of electrons that flow through the system per second.
- \circ Current is measured in amperes, or <u>Amp</u> (A) = 1 coulomb of charge per second.

This known as a <u>voltaic</u> (or <u>galvanic</u>) cell: the most common form of which is a <u>battery</u>! Galvanic (voltaic) cells are always thermodynamically favorable (spontaneous) and thus have a <u>positive (+)</u> E°_{cell} .



Parts of the Galvanic Cell

- 1. <u>Anode (-)</u>: electrode where <u>oxidation</u> occurs (loses mass as reaction progresses)
- 2. Cathode (+): electrode where reduction occurs (gains mass as reaction progresses, metal 'plated')
- 3. Salt bridge (or disk): provides ions to balance the charge build-up in each cell
 - Anions (-) flow to the anode; cations (+) flow to the cathode
 - If the salt bridge is removed, current will slow and then stop (V = 0) as charge builds up in half-cells.
- 4. <u>Voltmeter</u>: measures the cell potential (emf or E°) in volts
 - Over time, voltage in the galvanic cell will decrease as [reactants] \downarrow and [products] \uparrow

Electron Flow: ALWAYS through the wire from anode to cathode (alpha order)

Ion-ion or Ion-Gas Redox: a voltaic cell can be constructed where the underlying redox reaction involves a gas or the conversion from one ion to another; requires an <u>inert</u> electrode: doesn't take part in the redox reaction but provides surface on which electrons can transfer; commonly made of platinum (expensive) or graphite (cheap)

Example 2: use the provided information to find the reduction potential of the missing half-reaction

$Al^{3+}(aq) + 3 e^- \rightarrow Al(s)$	$\mathbf{E}_{red}^{\circ} = -1.66 \mathrm{V}$
$3 \operatorname{Cu}^+(aq) + 3 \operatorname{e}^- \rightarrow 3 \operatorname{Cu}(s)$	$\mathbf{E}_{red}^{\circ} = ???$
$Al^{3+}(aq) + 3Cu(s) \rightarrow Al(s) + 3Cu^{+}(aq)$	$E_{call}^{\circ} = -2.18 V$

$\operatorname{Cu}^{2+}(aq) + 2 e^{-} \rightarrow \operatorname{Cu}(s)$	$E_{red} = + 0.34 V$
$\operatorname{Zn}^{2+}(aq) + 2 e^{-} \rightarrow \operatorname{Zn}(s)$	$\mathbf{E}_{red}^{\circ}=-0.76\mathbf{V}$
$Mn^{2+}(aq) + 2 e^- \rightarrow Mn(s)$	$\mathbf{E}_{red}^{\circ} = -1.18 \mathrm{V}$

Example 3: Based on the reduction potentials given above, which of the following reactions will be thermodynamically favored?

a.
$$\operatorname{Mn}^{2+}(aq) + \operatorname{Cu}(s) \to \operatorname{Mn}(s) + \operatorname{Cu}^{2+}(aq)$$

b.
$$\operatorname{Mn}^{2+}(aq) + \operatorname{Zn}(s) \to \operatorname{Mn}(s) + \operatorname{Zn}^{2+}(aq)$$

c.
$$\operatorname{Zn}^{2+}(aq) + \operatorname{Cu}(s) \to \operatorname{Zn}(s) + \operatorname{Cu}^{2+}(aq)$$

d. $\operatorname{Zn}^{2+}(aq) + \operatorname{Mn}(s) \to \operatorname{Zn}(s) + \operatorname{Mn}^{2+}(aq)$

1. The diagram below shows the experimental setup for a typical electrochemical cell that contains two standard half-cells. The cell operates according to the reaction represented by the following equation.



- a. Identify M and M²⁺ in the diagram and specify the initial concentration for M²⁺ in solution.
- b. Indicate which of the metal electrodes is the anode and which the cathode.
- c. Write the balanced equation for the reaction that occurs in the half-cell containing the

i. cathode. ii. anode

- d. Circle the electrode that loses mass as the reaction progresses. As mass is "lost", where does it go?
- e. Put a rectangle around the electrode that gains mass as the reaction progresses. Where does the mass come from?
- f. If the salt bridge is made of NaCl(s), describe the ion flow that would occur in the salt bridge as the cell operates. Add the correct ions to each half-cell in the diagram above.
- g. Describe what would happen if the salt bridge was removed. Justify your answer.

Totally Epic AP Chem Review: Electrochem Equilibrium!

Gibb's Free Energy (ΔG): the energy associated with a chemical reaction that can be used to do work.

Because of the following equation, the sign of ΔG will always be the <u>opposite</u> of cell potential, E°

(this does NOT mean they are inversely proportional!!)

$$\Delta G^o = -nFE^o_{cel}$$

The variables are: 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)

Remember: E° is measured in volts, and V = J/C

 ΔG and K are related by the following equation at standard conditions (1 M, 1 atm, 298 K)

K = equilibrium constant

The variables are: T = temperature (in Kelvin)



 $K = e^{-\Delta G^o/RT}$ • This equation can be rewritten to give:

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

• The units for
$$\Delta G^o = \frac{\text{joules}}{\text{moles}_{\text{reaction}}} = \frac{J}{\text{mol}_{\text{rxn}}}$$

Summary

E ^o cell	ΔG^o	К	K & Q Relationship	Reaction Direction	Spontaneity in the Forward Direction
+	-	K > 1	K > Q	Forward	Spontaneous
-	+	K < 1	K < Q	Reverse	Non-spontaneous
= 0	= 0	K = 1	K = Q	No reaction	n/a

Example: At 25° C, H_2O_2 decomposes according to the following equation.

 $2 H_2O_2(aq) \rightarrow 2 H_2O(l) + O_2(g)$ E° = 0.55 V

a. Determine the value of the standard free energy change, ΔG° , for the reaction at 25°C.

b. Determine the value of the equilibrium constant, Keq, for the reaction at 25°C.

How to Determine Cell Potential under Non-standard Conditions

- > \uparrow [reactants] OR \downarrow [products]:
 - Make the reaction more thermodynamically favorable (more spontaneous)
 - Treaction driving force, thus:
 - $\uparrow E_{cell}$, \uparrow voltage
- \downarrow [reactants] OR \uparrow [products]:
 - Make the reaction less thermodynamically favorable (less spontaneous)
 - \downarrow reaction driving force, thus:
 - $\circ \downarrow E_{cell}, \downarrow voltage$

As a voltaic cell discharges, reactants are consumed and products are generated.

Therefore, as the cell operates, the conditions become non-standard and the voltage drops!

 \rightarrow But if you <u>decrease</u> <u>both</u> reactant AND product concentration <u>by the same factor</u>:

- Spontaneity is unaffected!
- $E_{cell} = E_{cell}^{o}$
- However, fewer reactants means that the electrochemical cell will operate for a shorter <u>time</u> before running out of reactants! The reverse is true if you increase both by the same factor.

Practice:

1. In the reaction below, a piece of solid nickel is added to a solution of potassium dichromate.

14 H⁺(aq) + Cr₂0^{2−}(aq) + 3 Ni(s) → 2 Cr³⁺(aq) + 3 Ni²⁺(aq) + 7 H₂O(l)

How many moles of electrons are transferred when 1 mole of potassium dichromate is mixed with 3 mol of nickel?

- a. 2 moles of electrons c. 5 moles of electrons
- b. 3 moles of electrons d. 6 moles of electrons

2. Calculate the standard free energy of the following reaction at 25°C.

Fe ²⁺ (aq) + Mg(s) →	Fe(s) + Mg ²⁺ (aq)
---------------------------------	-------------------------------

a.	-1.6	x 10 ⁵	kJ/mol	rxn

c. -3.7 x 10⁵ kJ/mol_{rxn}

 $E^{o}_{cell} = 1.92 V$

b. –160 kJ/mol_{rxn} c. –370 kJ/mol_{rxn}





so

a. Complete the chart below.

SO,2

 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-1}$

Conditions	Effect on Rxn Driving Force	E _{cell} vs. E ^o cell	Effect on voltage	Effect on time cell can run
Addition of Cu(s)				
[ZnSO ₄] = 1.0 M, [CuSO ₄] = 0.3 M				
Removal of salt bridge				
[ZnSO ₄] = 0.5 M, [CuSO ₄] = 1.0 M				
Removal of all Zn(s)				
[ZnSO ₄] = 2.0 M, [CuSO ₄] = 2.0 M				
The cell has been running for 2 hours.				
[ZnSO ₄] = 1.0 M, [CuSO ₄] = 1.7 M				

b. A student accidentally adds additional ZnSO₄ to the Zn(s)/Zn²⁺(aq) half-cell. What happens to the magnitude of the cell voltage (relative to the standard cell)? Justify your answer.

c. Is the value of the equilibrium constant for the cell reaction greater than 1, less than 1, or equal to 1? Explain.

d. What must be true about the standard free energy change of this reaction, ΔG° ? Justify.

Totally Epic AP Chem Review: Electrolytic Cells!

Electrolytic Cells: You have the power!

Electrolytic cells: thermodynamically unfavorable, therefore + ΔG° and - E°

• Since an electrolytic cell is NOT spontaneous, it will undergo a redox reaction only if current is applied!

Electrolysis: using electrical energy to break a compound apart (separate elements from compounds)

Electrorefining: Purification of metals through electrolysis

- The <u>anode</u> is the <u>impure metal</u> (ore) to be purified.
- The cathode is where the pure metal will be deposited (made of a thin sheet of the pure metal).
- The electrolyte (solution) contains the cation of the metal to be purified.

Electroplating: Applying a thin layer of an expensive metal onto a less expensive one for structural or cosmetic reasons

- The <u>object to be plated</u> is the <u>cathode</u>. (*fat cat)
- The electrolyte (solution) contains the cation of the metal to be plated on the object.
- The best anode is made of the metal to be plated onto the object

Differences between Galvanic/Voltaic Cells and Electrolytic Cells

Galvanic/ Voltaic Cells	Electrolytic Cells
$-\Delta G$, + E^{o}_{cell} , K > 1	+ ∆G, −E° _{cell} , K < 1
Thermodynamically favorable	Thermodynamically Unfavorable
spontaneous in the <u>forward</u> direction	spontaneous in the reverse direction
Separated into two half cells to generate electricity	Usually occurs in a <u>single</u> container (but can be set up in two containers)
<u>Is</u> a battery (turns chemical energy into electrical energy)	<u>Needs</u> a battery (turns electrical energy into chemical energy)
Often electrodes made of metal used in half-reactions	Usually use <u>inert</u> electrodes (such as Pt or graphite)
Electrons supplied by species being oxidized	Electrons supplied by external battery at cathode
Cathode + , Anode –	Anode + , Cathode – (*EPA: Electrolytic = positive anode)

Note: In electrolytic cells, An Ox and Red Cat still work (yay!)

<u>Quantitative Electrolysis</u>: In an electrolytic cell, the amount of product made is related to the number of electrons transferred. Essentially, the electrons are a reactant. To solve, use the formula for current from the periodic table and follow the following steps:



Example: Gold can be plated out of a solution containing Au³⁺ according to the half-reaction:

$Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$

What mass of gold (in grams) is plated by a 25-minute flow of 5.5 A current?

Solution:
$$25 \min \times \frac{60 \text{ s}}{1 \min} \times \frac{5.5 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mote}^{-}}{96,485 \text{ C}} \times \frac{1 \text{ motAu}}{3 \text{ mote}} \times \frac{196.97 \text{ gAu}}{1 \text{ motAu}} = 5.6 \text{ gAu}$$

 $time(se) \times \frac{cwllent}{(Amp)} \times \frac{1}{9} \times \frac{solid \text{ metal}}{molee} \times \text{ molar mass}(3/mol)$

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).

Of course, there are endless variaties of these two calculation types we can give you! 🕲

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

Are you **SAF**e? **MMM.**

Practice:

1. How long must a current of 5.00 A be applied to a solution of Ag⁺ to produce 10.5 g silver metal?

- If a current of 10.0 amp is applied to a Cu²⁺ solution for 60.0 minutes, what mass of copper will be plated out?
- b. How many moles of electrons must be transferred in this reaction to produce 5.16 g of copper metal?

3. In an electrolytic cell, Cu(s) is produced by the electrolysis of $CuSO_4(aq)$. Calculate the maximum mass of Cu(s) that can be deposited by a direct current of 100. amperes passed through 1.50 L of 2.00 M CuSO $_4(aq)$

Totally Epic AP Chem Review: Thermochem Basics!

Thermochemistry: deals with the energy changes that occur during chemical reactions.

Temperature: measure of the average kinetic energy of the particles of a substance

- → Temperature is an *intensive* property: amount of matter doesn't affect it!
- → The Kelvin temperature is directly proportional to the average kinetic energy. For example, doubling the Kelvin temperature doubles the average kinetic energy.
- \rightarrow As absolute zero is approached (o K), the particles approach zero kinetic energy.

A Maxwell-Boltzmann distribution shows how the particles at a high temperature have greater kinetic energies than those at a low temperature.



Thermal energy: internal energy of an object due to the kinetic energy of its particles

Heat (q): amount of thermal energy capable of being transferred from one object to another

- \rightarrow heat is an <u>extensive</u> property (depends on how much of a substance you have), unlike temperature.
- → Heat always flows from a **warmer** object to a **cooler** object.

In thermochemistry, the universe is divided into two parts:

- a. the **system**: the substance of interest
- b. the surroundings: whatever is outside the system

Specific Heat Capacity (C): amount of heat (energy) required to raise temperature of 1 g of a substance by 1 K (1°C)

→ Units are
$$\frac{J}{g^{\circ}C}$$
 or $\frac{J}{gK}$

- \rightarrow Metals have relatively low specific heats relatively less energy is required to raise their temperatures.
- \rightarrow Water has a relatively <u>high</u> specific heat requires much more energy to achieve a similar temp change.

Specific Heat Capacity $(C_p) = \frac{\text{quantity of heat supplied}}{(\text{mass of object})(\text{temperature change})}$

Substance	Specific Heat (J/g · K)	
Al	0.902	
H ₂ O (l)	4.184	
Glass	0.84	

- Gold ore, when discovered in nature, often contains impurities. If a sample of gold ore contains some silver impurity, the ore can be purified by electrolysis. (Assume Au(s) will form a Au³⁺(aq) cation.)
 - a. On the diagram below, identify the anode (and what it's made of), the cathode (and what it's made of), and the direction of electron flow.



for a period of 1.00 hour.

- b. Where will the purified gold be found?
- c. What might be a possible electrolyte for use in this solution?

How to calculate heat transferred: mCAT!

 $q = mC\Delta T$



 $\Delta T = T_{\text{final}} - T_{\text{initial}} = \text{change in temperature}$

∆T Object	Sign of ∆T	Sign of q	Direction of Heat Transfer
Increase	+	+	Heat transferred into object
Decrease	-	-	Heat transferred out of object

 $\label{eq:change} \textbf{Enthalpy Change} \ (\Delta H) \textbf{:} amount of energy \textbf{absorbed} or \textbf{released} as heat by a system when the pressure is constant$

(per 1 mol_{rxn}); measured in units of J/mol_{rxn}

$$\Delta H_{rxn} = \frac{q}{mol_{rxn}}$$

- → Enthalpy change can be applied to physical or chemical changes
- → The magnitude of heat change is directly proportional to the <u>moles</u> of reactants and products involved in the change (but NOT enthalpy! b/c it is per mole!)
- → the sign of enthalpy change (+ or -) indicates direction of energy flow

Standard Enthalpy Change: (ΔH^{o}): enthalpy changed measured at <u>standard</u> conditions

- Thermochemistry standard conditions are **<u>NOT</u>** the same as gas laws STP
- Thermochemistry standard conditions are: 25°C and 1 atm

Enthalpy Changes of Different Types of Reactions

You will encounter a variety of **subscripts** following the ΔH , however, they are simply indicating a **specific** type of reaction or change of state.

Examples

 $\begin{array}{l} \Delta H^{*}_{comb} = \mbox{Enthalpy of Combustion} \\ \Delta H^{*}_{neut} = \mbox{Enthalpy of Neutralization} \\ \Delta H^{*}_{soln} = \mbox{Enthalpy of Solution} \\ \Delta H^{*}_{vap} = \mbox{Enthalpy of Vaporization} \\ \Delta H^{*}_{fus} = \mbox{Enthalpy of Fusion} \\ \Delta H^{*}_{e} = \mbox{Enthalpy of Formation} \end{array}$

(Heat Energy Released during Combustion Reactions)
(Heat Energy Released during Acid-Base Neutralization Reactions)
(Heat Energy Released/Absorbed Dissolving a Solute in Water)
(Heat Energy Absorbed to Convert from Liquid to Gas Phase)

- (Heat Energy Absorbed to Convert from Solid to Liquid Phase)
- ation (Heat Energy Released during Formation of 1 Mole of a Substance)

Two	Thermochemical Reaction Types
-----	-------------------------------

Endothermic <u>(+∆H)</u>	Exothermic <u>(-ΔH)</u>	
Energy is absorbed (by system)	Energy is released (by system)	
$+q/mol_{rxn} = +\Delta H_{rxn}$	$-q/mol_{rxn} = -\Delta H_{rxn}$	
Break "end" bonds/IMFs	Form new bonds/attractions	
Energy appears in <u>reactants</u>	Energy appears in products	
The energy added to a reaction (for endo AND exo) will always be positive value !		

Endothermic Reaction







Thermochemical equation: chemical equation that includes the enthalpy change

Let's Try! Complete the chart below.

Equation with Separate ΔH^o_{rxn}	Thermochemical Equation	Endo- or exothermic?
	$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O + 890 kJ$	
$H_2O(I) \rightarrow H_2O(g) \Delta H_{vap} = 44 \text{ kJ/mol}_{cxn}$		
$2 C_2 H_6 + 7 O_2 \rightarrow 4 CO_2 + 6 H_2 O \Delta H^o_{rxn} = -3120$ kJ/mol _{rxn}		

Energy Stoichiometry! 😳

Enthalpy is commonly measured in kJ/mol_{rxn}, but what is a mole of reaction?

 $1 \text{ mol}_{rxn} = 1 \text{ mole of reaction} = \text{stoichiometric } \# \text{ of reactants} / \text{ products}$

For the combustion of ethane: $2 C_2H_6 + 7 O_2 \rightarrow 4 CO_2 + 6 H_2O + 3120 \text{ kJ}$

When **1** mole of reaction has occurred,

- <u>2</u> mol of C₂H₆ reacted <u>4</u> mol of CO₂ were produced
- **7** mol of O₂ reacted **6** mol of H₂O were produced
 - <u>3120 kJ</u> heat released!

Luckily for us, the enthalpy of a reaction, when measured in kJ/mol_{rxn}, can act as a <u>conversion</u> factor between the amount of chemicals which react and the energy that is absorbed or released by the reaction!

Example 1: Give the following reaction, $2 Fe + 3 CO_2 \rightarrow 3 CO + Fe_2O_3$ ($\Delta H = +25 \text{ kJ/mol}_{rxn}$) what energy change occurs when 6.00 moles of carbon dioxide react?

Example 2: Give the following reaction, $N_2 + 3 H_2 \rightarrow 2 NH_3$ ($\Delta H = -324 \text{ kJ/mol}_{rxn}$) what mass of hydrogen must have reacted if 525 kJ of heat energy were released?

Totally Epic AP Chem Review: Enthalpy Calculations!

You Must Know: 6 Ways to Calculate Enthalpy (Δ H)

1.	Calorimetry	4.	Stoichiometry
2.	Heat of formation, ΔH_f°	5.	Bond energies

- **3.** Heat of reaction, ΔH_{rxn}° **6.** Hess's Law
- 1. **Calorimetry:** technique used to experimentally determine the change in **energy** of a chemical reaction or phase change by putting it in contact surroundings of known heat capacity (e.g. H2O)
 - → The heat change in the water is **equal** and **opposite** to the energy change by the system!
 - The system can be an object, a phase change, or a chemical reaction.

$$+q_{H_20} = -q_{system}$$

$$+[mC\Delta T]_{H_2O} = -[mC\Delta T]_{system}$$

- → If <u>water bath increases in temperature</u>, it gained energy → chemical reaction or phase change lost energy (exo, $-\Delta$ H).
- → If <u>water bath decreases in temperature</u>, it lost energy → chemical reaction or phase change gained energy (endo, +∆H).

To calculate the enthalpy of reaction (or phase change), you will need to divide q_{system} by the moles of reaction.

For example,

For the dissolution of a salt (your solute):

$$\Delta H_{soln} = \frac{q_{soln}}{mol_{solute}}$$

For the enthalpy of neutralization for the following reaction: $3 \operatorname{NaOH}(aq) + H_3 \operatorname{PO}_4(aq) \rightarrow 3 H_2 O(l) + \operatorname{Na_3PO}_4(aq)$

$$\Delta H_{neut} = \frac{q_{rxn}}{mol_{acid}} = \frac{q_{rxn}}{\frac{1}{2}mol_{base}}$$
 (assuming neither reactant is in excess)

Warning: Experimental Error with Calorimetry!

- We assume in the above equation that **ALL** energy lost by the system is gained only by the water, but that's not true! The calorimeter can also absorb heat, or heat can be lost to the surrounding air.
- Both of these errors would lead to a calculated heat (q) that was SMALLER than the actual heat exchange, and thus the calculated ΔH would be <u>lower</u> (in magnitude) than the actual ΔH.

<u>Coffee cup calorimeter</u>: Styrofoam cups are commonly used as insulators in the high school chemistry lab to measure temperature changes without a loss of energy to the surroundings.



2. Standard enthalpy (heat) of formation (ΔH°_{f}) : change in enthalpy that accompanies the formation

of <u>1</u> mole of the compound in its standard state from its component <u>elements</u> their standard states.

Example $S(s) + 3/2 O_2(g) \rightarrow SO_3(g)$

 $\Delta H_f^\circ = -396 \text{ kJ/mol}_{rxn}$

Note: you will see **fractional** coefficients to ensure only **1** mole of compound is formed.

The ΔH_f° for elements (in their standard state) is always **O** kJ/mol_{rxn}!

3. <u>Heat of reaction</u>: ΔH[°]_{rxn} (aka Big Momma's Equation)

You can use the heat of formation of the reactants and products to find the total enthalpy change in a reaction, according to the following equation:

$$\Delta H_{rxn}^{o} = \sum \left[\Delta H_{f}^{o} \left(products \right) \right] - \sum \left[\Delta H_{f}^{o} \left(reactants \right) \right]$$

- 4. <u>Stoichiometry</u>: heat is an extensive property. Amount matters!
- 5. **Bond energies:** Breaking chemical bonds requires an input of energy to overcome the attractive forces. When new bonds are formed, energy is released. The difference between input and output determines whether a process is endothermic or exothermic. This can be quantified in the following reaction:

 $\Delta H = \Sigma$ Energy to break bonds – Σ Energy released forming new bonds $\Delta H = \Sigma \text{ E (bonds in reactants)} - \Sigma \text{ E (bonds in products)}$

There are three steps to calculating enthalpy change through use of bond energies.

- 1. Draw the Lewis dot structures for the reactants and products.
- 2. Identify the type and number of bonds being broken and bonds being formed.
- 3. Subtract the sum of bond energies formed from the sum of bond energies broken.

Endo thermic: + ΔH° (system gains energy)	Exo thermic: - ΔH°(system loses energy)
 Breaking a chemical bond is always endothermic 	 Forming a chemical bond is always exothermic (more stable)
Hint: "end-ing a bond is end othermic"	

6. <u>Hess's Law</u>: the overall enthalpy change in a reaction is the sum of all the reactions (and is independent of the route taken)

Rule 1: If you <u>reverse</u> the reaction, then change the <u>sign</u> of ΔH .

Rule 2: If you <u>multiply</u> the reaction by a coefficient, then <u>multiply</u> ΔH by same coefficient.

<u>Strategy</u>: Find things in your goal equation that appear in only one of the available reactions and make them match by flipping equations or multiplying/dividing coefficients. Then arrange equations to cancel out things that don't appear in the "goal." Whatever you do to the equation, you must do to Δ H!

Let's Practice!

 The specific heat (in J/(g °C)) of solid aluminum is 0.89, of solid iron is 0.45, of liquid mercury is 0.14, and of carbon graphite is 0.71. When the same amount of heat is applied to one gram of these substances, which one will reach the highest temperature? Explain.

2. Use the data regarding the standard enthalpies of formation to calculate ΔH°_{rxn} for the following reaction: 2 $C_3H_6(g) + 9 O_2(g) \rightarrow 6 CO_2(g) + 6 H_2O(I)$

Substance	∆H° _f (kJ/mol)
$C_3H_6(g)$	20.9 kJ/mol _{rxn}
$CO_2(g)$	-393.5 kJ/mol _{rxn}
$H_2O(l)$	-286 kJ/mol _{rxn}

- 3. When 1.095 g of NaOH is dissolved in 150.0 g of water initially at 23.50°C in a coffee-cup calorimeter, the final temperature is found to be 25.32°C. Assume the specific heat of the solution is the same as that of water $(4.184 J/g^{\circ}C)$ and no heat is absorbed by the calorimeter.
 - a. What is the enthalpy of dissolution, ΔH_{soln} ?

b. If heat was absorbed by the calorimeter, what effect would it have on the calculated heat of reaction? Justify your answer.

- 4. The heat of formation of copper(I) chloride is –137 kJ/mol_{rxn}.
 - a. Write the balanced chemical equation. [Hint: use the definition of a heat of formation!]
 - b. How many joules are released when 4.46 grams of copper react with excess chlorine to produce copper(I) chloride?

Totally Epic AP Chem Review: Thermodynamics!

Entropy: Let the chaos begin!

<u>Entropy</u> can be considered the extent of randomness or <u>disorder</u> in a chemical or physical system. The more <u>positions</u> available (the more space, or more places something can move) the greater the entropy.

The entropy change for a system (Δ) is calculated from the absolute entropies of the products and reactants.

$$\Delta S_{system}^{\circ} = \sum [S^{\circ}(\text{products})] - \sum [S^{\circ}(\text{reactants})]$$

Units of Entropy:
$$\frac{J}{mol \cdot K} = J \cdot mol^{-1} \cdot K^{-1}$$

*Note: Entropy of element in most stable form is NOT zero!!

 \rightarrow The entropy of a perfect, pure crystal at <u>o K</u> is given a value of zero,

 \rightarrow All absolute entropies for individual substances in the real world, are <u>positive, +</u> \rightarrow even elements!

Two biggest factors for evaluating ∆S_{rxn}

1) Change in <u>state</u> of matter (gas >> aqueous > liquid > solid)

2) Change in <u>number</u> of particles $(\uparrow particles = \uparrow places for particles to be = \uparrow entropy)$

In order of lowest to highest entropy:

Solids < Liquids < Aqueous solutions << Gases < More moles of Gas

Thermodynamically Favorable Processes

Neither entropy (Δ S) nor enthalpy (Δ H) can tell us if a reaction is thermodynamically favored \rightarrow must use some combination of the two: <u>Gibb's</u> Free Energy!

 ΔG (Gibb's free energy) represents the amount of useful work that can be obtained from a process at constant temperature and pressure. "Free" energy refers to the amount of energy available to do work once you have "paid your price" to entropy.

$$\Delta G^{\circ}_{reaction} = \Delta H^{\circ} - T\Delta S^{\circ}$$

T = temperature in Kelvin

 Δ H = enthalpy change (usually has units of kJ/mol or kJ mol⁻¹) Δ S = entropy change (usually has units of J/(mol K) or J mol⁻¹ K⁻¹) Notice difference in units! You must make both units the same (J or kJ) before you calculate ΔG .

The sign of ΔG tells if any given process is thermodynamically favored:

If ΔG is	The Process Is	Term
Negative (-)	Thermodynamically favored (spontaneous)	Exergonic
Positive (+)	Not thermodynamically favored (reverse reaction is spontaneous)	Endergonic
Zero (o)	At equilibrium	

5. Given the following information, find the heat of formation for methane:
$$C(s) + 2H_2(g) \rightarrow CH_4(g)$$

$\mathrm{CH}_4(g) + 2\mathrm{O}_2(g) \mathrel{\Rightarrow} \mathrm{CO}_2(g) + 2\mathrm{H}_2\mathrm{O}(l)$	$\Delta H^{\circ}_{comb} = -891 \text{ kJ mol}^{-1}$
$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H^{\rm o}_f = -394 \text{ kJ mol}^{-1}$
$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$	$\Delta H^{\circ}_{f} = -286 \text{ kJ mol}^{-1}$

6. The flammable gas ethene, C_2H_4 , combusts as such: $C_2H_4(g) + 3 O_2 \rightarrow 2 CO_2(g) + 2 H_2O(I)$ 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 = 0	799
C - C	347	H - O	467
C = C	614	H - H	432
C-0	358	O = O	495

 $\Delta G_{\text{reaction}}^{0} = \sum [G_{f}^{0}(\text{products})] - \sum [G_{f}^{0}(\text{reactants})]$

Note: <u>Elements DO have a value of zero for ΔG° </u>, because forming an element from itself results in no change.

Elements ARE zero for:
$$\Delta H$$
, ΔG
Elements are NOT zero for: ΔS

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

What does it mean when a reaction is "driven" by enthalpy, entropy, or both?

Nature favors:

- 1. $\pm \Delta S$ (increasing entropy, greater disorder)
- 2. $-\Delta H$ (exothermic, release of energy)
- **Driven by enthalpy:** a very exothermic reaction $(-\Delta H)$ overcomes a decrease in entropy $(-\Delta S)$
- Driven by entropy: an endothermic reaction ($\pm \Delta H$) occurs spontaneously because of a very $\pm \Delta S$

You can use the signs of ΔS and ΔH (together with the reaction $\Delta G = \Delta H - T\Delta S$) to predict qualitatively 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. (3))



Connections to Electrochem and Equilibrium

	ΔG^{o}	K	E°
$\Lambda G^{\circ} = -n \Im F^{\circ}$	0	at equilibrium	0
$\Delta G^{\circ} = -RT \ln K$	negative	>1, products favored	+
	positive	<1, reactants	

favored

Let's Practice!

- 1. Predict the sign of the entropy change for each of the following reactions:
 - a. $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
 - b. $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$
 - c. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
- 2. Which of the following is true concerning the reaction where two chlorine atoms form one chlorine molecule, as shown in the following equation: $2 Cl(g) \rightarrow Cl_2(g)$?
 - a. This reaction is driven by enthalpy: the large negative ΔH overcomes a positive ΔS .
 - b. This reaction is driven by enthalpy: the large negative ΔH overcomes a negative ΔS .
 - c. This reaction is driven by entropy: the large positive ΔS overcomes a positive $\Delta H.$
 - d. This reaction is driven by entropy: the large positive ΔS overcomes a negative ΔH .
- 3. Which of the following correctly describes the standard voltage, E°, and the standard free energy change, ΔG°, for the reaction represented below?

 $X(s) + Y^{+}(aq) \rightleftharpoons X^{+}(aq) + Y(s), K_{eq} = 5 \times 10^{-5}$

a. E° and ΔG° are both positive.

d. E° is negative and ΔG° is positive.
e. E° and ΔG° are both zero.

- b. E° and ΔG° are both negative.
- c. E° is positive and ΔG° is negative.
- 4. A given reaction, $X_2(g) + Y_2(g) \rightarrow 2 XY(g)$, is not thermodynamically favorable at 298 K. However, at higher temperatures the reaction becomes spontaneous. Which of the following is true at 298 K?

ΔН	ΔS	ΔG
a. +	+	+
o. –	-	-
. +	-	+
1. +	+	-

 $H_2O(l) \rightarrow H_2O(s)$

- 5. Which of the following is true for the above reaction?
 - a. The value of ΔS is positive.
 b. The value of ΔG is positive.
 d.
- c. The value of ΔH is positive. d. The reaction is favored at 1.0 atm and 298 K.

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Totally Epic AP Chem Review: Rate Laws

The Rate of a Chemical Reaction: defined as change in concentration of a reactant or product per unit time.

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

Rate Unit: M/time, M time⁻¹, mol/(L = time), or mol L⁻¹ time⁻¹ (<u>Hint</u>: these are all the <u>same</u> thing!!)

As time goes on, the rate of a reaction slows down because concentration of the reactants decreases.

Reaction Rate and Stoichiometry: In most reactions, the coefficients of the balanced equation are not all the same.

To be consistent, the change in the concentration of each substance is multiplied by <u>coefficient</u>⁻¹.

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

Data -	$\Delta[A]$	$1\Delta[B]$	$1\Delta[C]$
Rate -	Δt –	$\overline{3} \Delta t$	$\frac{1}{2}\Delta t$

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

- Increasing the <u>surface area</u> of a solid reactant can increase the rate by increasing the number of collisions between the reactant particles.
- 2. <u>Catalysts</u> increase the rate by lowering the activation energy of a reaction.
- 3. Increasing the temperature results in a faster reaction: heat 'em up, speed 'em up!
 - → The rate constant is temperature dependent and a rise in temperature will increase the rate constant!
- Increasing concentration of <u>reactants</u> increases the number of reactants colliding with each other, thus yielding more product.

The Rate Law: the mathematical relationship between rate of the reaction and the concentrations of the reactants

→ The rate law *must* be determined <u>experimentally</u>!

For the reaction

Example

aA + bB → products Rate = k[A]ⁿ[B]^m

The rate law would have the form

- 1. The exponent on each reactant, *n* and *m*, are called the <u>orders</u> with respect to that reactant.
- 2. *k* is called the <u>rate constant</u>: a larger k means a <u>faster</u> reaction!
- 3. *n* and *m* are <u>NOT</u> necessarily the stoichiometric coefficients of A and B.
- **4.** *n* + *m* = p, the <u>overall</u> **reaction** order (or the order of the <u>reaction</u>).

$2 \operatorname{NO}(g) + O_2(g) \rightarrow 2 \operatorname{NO}_2(g)$

the experimentally determined rate law is Rate = $k[NO]^2[O_2]$.

The reaction is said to be:

- <u>2</u>nd order with respect to NO,
- 1^{st} order with respect to O_2 ,
- 3rd order overall.

Overall Reaction Order

A. Zero order reaction rate: rate of reaction is independent of the concentration of the reactant(s).

B. First order reaction rate: rate of reaction is directly proportional to concentration of one of the reactants.

 \rightarrow Radioactive decay is a very common example of a first-order process. They have a constant half-life.

$$k = \frac{0.693}{\text{half-life}}$$

C. Second <u>order reaction rate</u>: the rate of the reaction is directly proportional to the <u>square</u> of the concentration of one of the reactants.

How to Determine Orders

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

Strategy #: Chart-tabulous! Compare trials in which the concentration of one of the reactants stays the same to determine how changing the concentration of a single reactant affects the rate of reaction.

For example, for the following reaction, this data was collected.

 $2NO(q) + Cl_2(q) \rightarrow 2NOCl(q)$

Trial	[NO] mol/L	[Cl ₂] mol/L	Rate
1	0.200	0.200	$1.20 imes 10^{-6}$
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 <u>doubled</u>, while the concentration of Cl₂ remains constant, and the reaction rate increases by a factor of <u>four</u>.

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

- b) Comparing Trial 1 and Trial 3:
 - → The concentration of NO remains constant, while the concentration of Cl₂ <u>doubled</u>, and the reaction rate increases by a factor of <u>two</u>.

Therefore, the rate of reaction with respect to Cl_2 is <u>first</u> order ($2^1 = 2$).

c) Thus, the rate law for the reaction is:

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

→ <u>Pressure</u> is directly proportional to <u>concentration</u>.

<u>Strategy #2</u>: 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!)

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

Graph vs time	If this is most linear, the reaction is	Units of k
Concentration of the reactant, [A]	Zero order (k = - slope)	M ⋅ sec ⁻¹
Natural log of the concentration, In[A]	First order (k = - slope)	sec ⁻¹
Reciprocal of the concentration, 1/[A]	Second order (k = slope)	M ⁻¹ ⋅ sec ⁻¹

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



<u>Note</u>: for each rate order, the absolute value of the slope equals the rate constant \rightarrow IF you pick the correct graph!

k = |slope|







Colorimetry: An Experimental Method to Measure Reaction Rate

Colorimetry: an experimental method to measure reaction rate by using a colorimeter (or spectrophotometer) to

determine the concentration of solution by analyzing its color intensity.

- Light from an LED light source passes through a <u>cuvette</u> (tiny container) filled with a solution sample, as shown in the figure to the right.
- Some of the incoming light is <u>absorbed</u> by the solution. As a result, light of a <u>lower</u> 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 <u>colored</u>. (3)

Source

LED

Detector

Transmitted

light

Beer's Law

A = abcA: 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 <u>directly</u> proportional to concentration (providing the absorbing substance, wavelength, and path length are fixed).
- By measuring the change in absorbance over <u>time</u>, you can use Beer's law to convert absorbance to <u>concentration</u>.
- Graphing [reactant] vs. time, ln[reactant] vs. time, and 1/[reactant] vs time will allow you to determine if the reaction being studied is zero, first, or second order with respect to that reactant:
 - o If [reactant] vs. time is most linear, the reaction is <u>zeroth</u> order with respect to that reactant.
 - $\circ~$ If ln[reactant] vs. time is most linear, the reaction is \underline{first} order with respect to that reactant.
 - o If **1/[reactant] vs. time** is most linear, the reaction is <u>second</u> 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 <u>swamping</u> is used.

- All but one of the reactants will start at extremely high 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 <u>constant</u>; 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 <u>pseudo</u> rate constant (since you will only know the order with respect to a single reactant).

Multiple Choice Practice!



- 1. 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} time⁻¹

a. I only b. II only c. I and II only d. II and III only e. I, II, and III

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

 $2NO(g) + Br_2(g) \leftrightarrow 2NOBr(g)$

Trial	[NO] _{init} (M)	$\begin{bmatrix} Br_2 \end{bmatrix}_{init} \\ (M)$	Initial Rate of Reaction (<i>M</i> /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 = $k[NO][Br_2]^2$	(C)	Rate = $k[NO][Br_2]$
(B)	Rate = $k[NO]^2[Br_2]^2$	(D)	Rate = $k[NO]^2[Br_2]$

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

(A) 5.10 x 10 ⁻⁴ min	(B) 9.48 x 10 ⁻³ min	(C) 1.02 x 10 ⁻³ min	(D) 4. x 10 ⁻⁴ min
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4. What are the potential units for the rate constant for the reaction below?

		A + B	\rightarrow C + D	rate = $k[A][B]^2$
a) s ⁻¹	b)	s ⁻¹ M ⁻¹	c) $s^{-1} M^{-2}$	d) s ⁻¹ M ⁻³

Totally Epic AP Chem Review: Collision Theory and Reaction Mechanisms

Collision Theory: A Model that Explains Reaction Rates

For a given reaction to occur, molecules that collide must meet two conditions before an <u>effective collision</u> will occur (and the reaction takes place):

1. Correct <u>orientation</u> 2. Suff

Sufficient <u>energy</u> (i.e. <u>activation energy</u>)

For example:



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

IMPORTANT: The higher the activation energy, the slower the reaction rate!!!!!



Activated complex (or transition state): the high energy transient 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 <u>kinetic</u> energy of the particles also increases.

- <u>Heat</u> 'em up = <u>speed</u> 'em up!
- More speed = more collisions with greater energy
- Thus, more chances of an effective collision.

<u>Note</u>: As temperature <u>increases</u> (from $T_1 \rightarrow T_2$) the fraction of molecules of particles energetic enough to achieve E_a <u>increases</u>, thus more particles react and the reaction rate <u>increases</u>.

re particles react and the reaction rate <u>increases</u>. Two very important concepts: 1. Only changing <u>activation energy</u> or <u>temperature</u> can change the rate constant! 2. Sooooo important: ↑ Temperature does <u>NOT</u> decrease activation energy!!!!!!

of

(only a catalyst can decrease activation energy!)

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 <u>reaction mechanism</u>.

<u>Elementary steps</u>: each single step in the mechanism \rightarrow must <u>add</u> up to overall balanced equation for mechanism!

Molecularity: Number of molecules participating in an elementary step

To be correct, the reaction mechanism:

- 1. Must be determined by experiment.
- 2. Must agree with overall stoichiometry.
- 3. Must agree with the experimentally determined rate law.

Rate Laws for Elementary Steps

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

Example

Overall reaction

 $2NO_2(g) + F_2(g) \rightleftharpoons 2NO_2F(g)$ $rate = k_0[NO_2]^{\text{from exp.data}}[F_2]^{\text{from exp.data}}$

Reaction Mechanism

Step 1: NO ₂ (g) + $F_2(g) \rightleftharpoons$ NO ₂ $F(g) + F(g)$	$rate = k_1[NO_2]^1[F_2]^1$ from step 1 coefficients
Step 2: NO ₂ (g) + F(g) \rightleftharpoons NO ₂ F(g)	$rate = k_1 [NO_2]^1 [F]^1$ from step 2 coefficients

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As temperature increases, the fraction

of molecules with enough energy to surmount

the activation energy barrier also increases.

TABLE 13.3 Rate Laws for Elementary Steps				
Elementary Step	Molecularity	Rate Law		
$A \longrightarrow \text{products}$	1	Rate = $k[A]$		
$A + A \longrightarrow products$	2	Rate = $k[A]^2$		
$A + B \longrightarrow products$	2	Rate = $k[A][B]$		
$A + A + A \longrightarrow products$	3 (rare)	$Rate = k[A]^3$		
$A + A + B \longrightarrow products$	3 (rare)	Rate = $k[A]^2[B]$		
$A + B + C \longrightarrow products$	3 (rare)	Rate = $k[A][B][C]$		

Energy Diagram for a Two-Step Mechanism

Reaction Mechanisms and Rate Expressions:

- The <u>rate determining step</u> (RDS) is always the slowest step (with the <u>highest</u> activation energy)
- Rate of overall reaction = combined rates of <u>all</u> elementary steps up to and including slowest step in mechanism.



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

- 1. Elementary steps must sum to overall reaction.
- Rate law predicted by the <u>mechanism</u> (the combined rates of all elementary steps up to and including slowest step (RDS) in the mechanism) must be consistent with the <u>experimentally</u> observed rate law.

To get credit for free response: you MUST relate the <u>coefficients</u> from the balanced RDS (<u>slow</u> step) to the <u>exponents</u> of the rate law (the order with respect to each reactant) to justify the mechanism!

Example: Consider the following two step mechanism:

Reaction Mechanism			
Step 1:	$2\:A\to A_2$	slow	
Step 2:	$A_2 \ + B \ \rightarrow \ A_2 B$	fast	

- a. Determine the overall reaction.
- b. Predict the rate law for the overall reaction. Justify your answer.

Catalysts vs. Intermediates

Intermediate: formed in an early step and consumed in a later step.

Catalyst: something that increases the rate of a reaction without being consumed in the reaction.

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



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

- ightarrow Both are species crossed off when summing a reaction mechanism into overall reaction
- If a species forms as a <u>product</u> in an earlier step and is used up as a <u>reactant</u> in a later step (and cancels out), it's an <u>intermediate</u>.
- If a species is used as a <u>reactant</u> in an earlier step and is re-formed as a <u>product</u> in a later step (and cancels out), it's a <u>catalyst</u>.

$$H_2O_2(aq) + I^-(aq) \rightarrow H_2O_{(1)} + IO^-(aq)$$
 slow
 $H_2O_2(aq) + IO^-(aq) \rightarrow H_2O_{(1)} + O_2(q) + I^-(aq)$ fast

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

Totally Epic AP Chem Review: Equilibrium in a Day!

EQUILIBRIUM CONSTANT EXPRESSIONS: The product concentrations appear in the numerator and the reactant concentrations in the denominator. Each concentration is raised to the power of its stoichiometric coefficient in the balanced equation.

• K_c is for concentration (aqueous)

• Pure solids and pure liquids do not appear in

- K_p is for partial pressure (gases)
- expression
- "K" values are written without units

Practice: Write the expressions for K_c and K_p for the following process:

1. $PCI_5(s) \rightleftharpoons PCI_3(l) + CI_2(g)$

THE REACTION QUOTIENT, Q: When you need to know the answer to the question, "Is the system at equilibrium?"

A: The answer can be yes or no!

For the general reaction: $aA + bB \Leftrightarrow cC + dD$

$$Q = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \text{ or } \frac{(P_{C})^{c}(P_{D})^{d}}{(P_{A})^{a}(P_{B})^{b}}$$

 \rightarrow <u>Reminder</u>: Q has the appearance of K but the concentrations are not *necessarily* at equilibrium!

What does Q mean?

1. If **K > Q**, system not at equilibrium: forward reaction is favored (shift right) to make Q = K.

- 2. If **K** = **Q**, the system is at equilibrium.
- 3. If K < Q, system not at equilibrium: reverse reaction is favored (shift left) to make Q = K.

Practice:

- 1. The value of the equilibrium constant, K_c, at 25°C is 8.1 for the following reaction: $2 SO_3(g) \rightleftharpoons 2 SO_2(g) + O_2(g)$. What must happen for the reaction to reach equilibrium if the initial concentrations of all three species was 2.0 M?
 - a. The rate of the forward reaction would increase, and [SO₃] would decrease.
 - b. The rate of the reverse reaction would increase, and [SO₂] would decrease.
 - c. Both the rate of the forward and reverse reactions would increase, and the value for the equilibrium constant would also increase.
 - d. No change would occur in either the rate of reaction or the concentrations of any of the species.

2. Consider the following reaction:

 $CH_4(g) + 2 H_2S(g) \leftrightarrow CS_2(g) + 4 H_2(g)$

1.00 M CH₄, 1.00 M CS₂, 2.00 M H₂S and 2.00 M H₂ are mixed in a reaction vessel at 960°C. At this temperature, the reaction will make more methane and hydrogen sulfide gases. What is a possible K for this reaction?

а.	K = 16	с.	K = 4
b.	K = 8	d.	K = 1

2. $2 SO_3(g) \rightleftharpoons 2 SO_2(g) + O_2(g)$

for the following reaction:

a. 2.5 x 10⁻⁵

Manipulating Reactions

- Stoichiometric Coefficients: If you multiply the coefficients in the equation by a factor, the K is raised to the power of the multiplication factor. 2x is K², 3x is K³, etc
- <u>Reversing Equations</u>: take the <u>reciprocal</u> of K (1/K)
- Adding Equations: multiply respective Ks (K1 × K2 × K3 ...)

b. 2.5 x 10⁻⁴

Practice:

1. Calculate the value of K_c for the reaction 2 NO(g) + Br₂(g) \rightleftharpoons 2 NOBr(g) using the following information.

2. For the reaction 2 X(g) + Y(g) \leftrightarrow 2 Z(g), K_c = 4.0 x 10⁴. Determine the value of the equilibrium constant, K_c,

 $2 Z(g) \leftrightarrow 2 X(g) + Y(g)$ $K_c = ??$

c. 4.0 x 10⁻⁵

d. 4.0 x 10⁻⁴

 $2 \operatorname{NO}(g) \rightleftharpoons \operatorname{N}_2(g) + \operatorname{O}_2(g) \qquad K_{c1} = 1 \times 10^{30}$

 $N_2(g) + Br_2(g) \rightleftharpoons 2 \text{ NOBr}(g)$ $K_{c2} = 2 \times 10^{-27}$

Calculating with the Equilibrium Expression:

You MUST have a balanced equation.

If the amounts are given in moles BE WARY – you must convert to M (molarity).

- 1. Write the Equilibrium Constant Expression for $K_c \mbox{ or } K_p$
- 2. Set up RICE TABLE
 - **R** = Balanced Reaction
 - I = Initial concentrations
 - C = Change in concentration Remember: Everything changes stoichiometrically!
 - E = Equilibrium concentrations These are the concentrations (pressures) of all species at equilibrium

Hint: If none of the initial concentrations are zero, then Q must be calculated first to determine the direction of the shift (who gains and loses) before calculating the equilibrium concentrations.

Practice:

1. Ammonia and oxygen react according to the following equilibrium: $4 \text{ NH}_3(g) + 3 \text{ O}_2(g) \rightleftharpoons 2 \text{ N}_2 + 6 \text{ H}_2O(g)$. A 1.0 liter flask is initially filled with 4.0 mol of oxygen and 3.0 mol of ammonia, and 1.0 mol of N₂ is present at equilibrium. How much oxygen is present at equilibrium?

a. $1.0 \text{ mol } O_2$ b. $1.5 \text{ mol } O_2$ c. $2.5 \text{ mol } O_2$ d. $3.0 \text{ mol } O_2$

- 2. Here is a general reaction with a K value of 16: $A(aq) + B(aq) \rightleftharpoons 2 C(aq)$.
- Initially, [A] = [B] = 2.0 M. Solve for the equilibrium concentration of each substance.
- a. [A] = [B] = 0.67 M, [C] = 1.3 M c. [A] = [B] = 0.67 M, [C] = 2.7 M
- b. [A] = [B] = 1.6 M, [C] = 0.88 M d. [A] = [B] = 0.50 M, [C] = 3.0 M

3. The reaction below came to equilibrium at a temperature of 100°C. At equilibrium the partial pressure due to NOBr was 4 atm, the partial pressure due to NO was 4 atm, and the partial pressure due to Br_2 was 2 atm. What is the equilibrium constant, K_p , for this reaction at 100°C?

$$2 \operatorname{NOBr}(g) \rightleftharpoons 2 \operatorname{NO}(g) + \operatorname{Br}_2(g)$$

Le Châtelier's Principle: If a "stress" (change) is applied to a system at equilibrium, processes will occur to counteract (undo) that change.

- <u>Temperature</u> exothermic think of heat is a product; endothermic think of heat is a reactant.
- <u>Adding or removing a reagent</u> shift tries to reestablish K. If you remove it the reaction shifts to replace it; if
 you add it, the reaction shifts to get rid of it
 - UNLESS: you are adding or subtracting a solid or pure liquid: this will <u>NOT</u> change the concentration, and therefore this will not shift the position of equilibrium!
- <u>Pressure</u> Increasing pressure favors a shift to side with the <u>fewest</u> # of moles of gas and vice versa.
 - UNLESS: you increase pressure by adding an <u>inert</u> (unreactive) gas: this will <u>not</u> increase the number of effective collisions, and therefore will not affect equilibrium position.
- Volume same effect as pressure; remember Boyle's Law... Pressure and volume are inversely related, thus
 increasing the volume is the same as decreasing the pressure and vice versa.
- <u>Catalysts</u> NO EFFECT on K; just gets to equilibrium faster (kinetics moment)!
- REMEMBER nothing but a change in temperature will change the VALUE of K
- Increasing the temperature causes equilibrium to be reached faster (regardless of shift!)

Practice:

1. Liquid phosphorus trichloride is produced by the exothermic reaction: $P_4(s) + 6 \operatorname{Cl}_2(g) \rightleftharpoons 4 \operatorname{PCl}_3(I)$

Change	Direction of shift	Effect on K?
Addition of phosphorus trichloride		
Reduction of container volume		
Increase in temperature		
Increase in partial pressure of chlorine gas		
Decrease in temperature		

2. The endothermic reaction: $2 \text{ COF}_2(g) \rightleftharpoons \text{CO}_2(g) + \text{CF}_4(g)$

Change	Direction of shift	Effect on K?
Increase in temperature		
Decrease in temperature		
Addition of argon gas		
Increase in pressure		
Decrease in pressure		
Addition of catalyst		

3. Consider the following reaction at chemical equilibrium: $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$. At time t_1 , heat is applied to the system. Which of the following best describes the equilibrium reaction and the change in K_c ?



Totally Epic AP Chem Review: <u>Solubility in a Day</u>!

K_{sp}: Solubility product constant

- Equilibrium expression for the dissolution of a solid.
- Like all K values, this is constant (at a constant temperature).
- Because solids are not included in an equilibrium expression, this will have only products.

Write the Ksp expression for each of the following dissolutions:

Salt	Dissociation reaction	K _{sp} Expression
K ₂ CO ₃		
Al ₂ S ₃		

Remember, there are some basic solubility rules you MUST know!

Always soluble: Alkali metal cations, NH4⁺, and NO3⁻

<u>Solubility</u> "S" (aka <u>Molar Solubility</u>) = "x" in your K_{sp} RICE Table

How much of a <u>solid</u> will dissolve per <u>1.0</u> L of solution (Units: M = mol/L)

Solubility is an equilibrium position and therefore <u>CAN</u> change (for example, if you change the number of ions in solution, this will shift the equilibrium position and thus, the solubility).

- Larger molar solubility values suggest more dissociation into ions and more solid dissolves.
- Smaller molar solubility values suggest <u>less</u> dissociation into ions and <u>less</u> solid dissolves.
- 1. The molar solubility of barium fluoride is at 25° C is 2.45 x 10^{-5} . Calculate K_{sp} .

Precipitation: Will it or won't it?

Determining if Precipitation Will Occur: A Task for K vs Q!

Precipitation occurs when the concentrations of ions is greater than the solubility of the ionic compound.

- $K_{sp} < Q$ more ions than the system can dissolve; precipitate will form!
- $K_{sp} = Q$ exactly as many ions in solution as the system can dissolve; <u>no</u> precipitate
- **K**_{sp} > **Q** more of the solid will dissolve, and more ions will form; <u>no</u> precipitate forms

Important Ideas to Note:

- 1. If any solid is present, the solution is at equilibrium (a saturated solution)
- 2. Ion concentration, [ions], is **independent** of volume when at equilibrium (for instance, in a <u>saturated</u> solution).
- 3. If ions are present that could form $\underline{multiple}$ salts, the solid with the $\underline{smallest}\ K_{sp}$ will form.

Let's Practice!

- 1. A chemist makes a 2.0 L saturated solution of $Ba_3(PO_4)_2$ solution, which has a $K_{sp} = 6.0 \times 10^{-39}$.
 - a. What is the concentration of Ba^{2+} ions in solution?

b. After two days of sitting on the counter, some liquid has evaporated from the solution. Did [Ba²⁺] increase, decrease, or remain the same? Justify your answer.

2. Calculate the molar solubility of nickel (II) carbonate, which has a K_{sp} of 1.4 × 10⁻⁷ at 25°C.

c. The chemist adds 3.00 g of solid (NH₄)₃PO₄ to the original saturated solution of Ba₃(PO₄)₂. Did [Ba²⁺] increase, decrease, or remain the same? Justify your answer.

The Common Ion Effect

Remember: solubility can change if you change reaction conditions!

- Le Châtelier's principle predicts that a salt will become less soluble in a solution that already contains one of its own ions already dissolved: what's known as a common ion.
- The presence of a common ion acts like increasing the concentration of a <u>product</u> ion in the salt dissolution, causing the system to shift <u>left</u> to establish equilibrium (towards the <u>solid</u> side).

Example:

1. Circle any of the following compounds that contain a common ion to MgCl₂:

AgF₂ NaCl Mg(OH)₂ AlCl₃ Al₂S₃

2. Which of the compounds above, if present in solution in equimolar amounts, would reduce the solubility of

MgCl₂:

- a. the most? Why?
- b. the least? Why?

The Effect of pH on Solubility

The common ion effect predicts that when a salt contains ions that can act as an acid or a base, the solubility of that salt will be affected by changes in ______.

Example:

Fe(OH)₃ ≓ Fe³⁺(aq) + 3 OH⁻(aq)

- Will iron (III) hydroxide be more, less, or equally soluble in a <u>basic</u> solution (when compared to its solubility in pure water)? Explain.
- 2. Will iron (III) hydroxide be more, less, or equally soluble in an <u>acidic</u> solution (when compared to its solubility in pure water)? Explain.

The sign of ΔH can be predicted for each step in the overall dissolution process. In order to dissolve a substance, you must:

- 1. <u>Overcoming attractions (requires energy = endothermic)</u> "endo-ing" an attraction is endothermic!
 - a. Solute-solute IMFs (or ion-ion electrostatic attraction, if ionic) Step 2
 - b. Solvent-solvent IMFs Step 1
- 2. Form solute-solvent attractive forces upon mixing (releases energy = exothermic) Step 3









Totally Epic AP Chem Review: Intro to Acids and Bases!

Acid/Base Definitions

Arrhenius acid: hydrogen ion (H*) or proton donor	Arrhenius base: hydroxide ion (OH ⁻) donor
Examples: HCl, H ₂ SO ₄ , H ₂ O	Examples: NaOH, Ca(OH) ₂ , H ₂ O
$HCl_{(aq)} \to H^{*}_{(aq)} + Cl^{-}_{(aq)}$	$NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$

Note: H⁺ ions are so reactive they cannot exist in water <u>alone</u>. Instead, they react with water molecules to
produce complex ions, mainly hydronium ion, H₃O⁺. Be careful: H⁺ and H₃O⁺ are often used interchangeably!

$$\mathrm{H}^{+} + : \overset{\mathrm{H}}{\odot} : \mathrm{H} \longrightarrow \begin{bmatrix} \mathrm{H} \\ \mathrm{H} : \overset{\mathrm{H}}{\odot} : \mathrm{H} \end{bmatrix}^{+}$$

$\underline{\mathbf{H}}^{\pm} = \underline{\mathbf{H}}_{3} \underline{\mathbf{O}}^{\pm} (!!!)$

• Because of hydronium, acid dissociation reactions can be written in two, equivalent ways!

Shortcut Dissociation More Accurate Dissociation Reaction	
$HBr \rightarrow H^+ + Br^-$	$HBr + H_2O \rightarrow H_3O^+ + Br^-$
$HClO_2 \rightarrow H^+ + ClO_2^-$	$\text{HClO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{ClO}_2^-$

Brønsted-Lowry Acids and Bases

• Defined by relationship to protons

	Arrhenius	BrønstedLowry	Notes
Acids	<u>H</u> * donor	<u>H</u> ⁺ donor	<u>*SAME</u>
Bases	<u>H</u> ⁺ donor	<u>H</u> * acceptor	*DIFFERENT

• Chemists prefer the **Brønsted-Lowry** definition, because it Illustrates the <u>reversibility</u> of acid/base reactions as a proton exchange. To examine why, let's look at how the Bronsted-Lowry base, NH₃ (ammonia) reacts with water:

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH$$

 Note: when a Bronsted-Lowry base reacts with water, <u>OH</u>⁼, is still produced! But it comes from what's left of the water molecule *after* NH₃ removes a proton (H[±]).

→ You MUST know (i.e. memorize) that NH₃ is a <u>weak</u> (Brønsted-Lowry) base! ←

Conjugate Acid-Base Pairs

In a Brønsted—Lowry acid–base reaction, the original base becomes an acid in the reverse reaction, and the
original acid becomes a base in the reverse process.

 \circ ~ Each reactant and the product it becomes is called a ${\bf conjugate \ pair}.$



→ By definition, the <u>acid</u> and <u>base</u> are reactants, and the <u>conjugate</u> of each are products ←

Practice:

- 1) Identify each of the following as Arrhenius or Brønsted-Lowry acids or bases (mark all that apply).
- 2) In each box that you mark, write the formula for conjugate.

	Arrhenius		Brønsted-Lowry	
	Acid	Base	Acid	Base
HSO4 ⁻				
H ₃ O ⁺				
H_3PO_4				
Al(OH)₃				
NH_3				

Part 3:

1. In the following reactions, identify the acid, base, conjugate acid (CA) and conjugate base (CB). a) HBr(aq) + NH₃(aq) \rightarrow NH₄^{*}(aq) + Br⁻(aq)

b) $HPO_4^{2-}(aq) + H_2SO_4(aq) \rightarrow HSO_4^{-}(aq) + H_2PO_4^{-}(aq)$

c) CO_3^2 -(aq) + NH_4^+ (aq) \rightleftharpoons NH_3 (aq) + HCO_3^- (aq)

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- What is the conjugate base of H₂S?
- What is the conjugate acid of HCO₃⁻?
- 4. Which of the following represent a Bronsted-Lowry conjugate acid-base pair?
 - a. $H_2CrO_4(aq)$ and $CrO_4^2(aq)$ c. $HCrO_4^-(aq)$ and $H_2O(I)$
 - b. $HCrO_4^-$ (aq) and CrO_4^{2-} (aq) d. H_3O^+ (aq) and OH^- (aq)

Memorize the following strong acids and bases!

- <u>Strong acids</u>:
 - Hydrohalic acids: HCl, HBr, HI (note: HF is NOT a strong acid! The H F bond is too strong.)
 - Sulfuric acid: H₂SO₄
 - Nitric acid: HNO₃
 - Perchloric acid: HClO₄

→ BriCI-SO-NO-CIO (pronounced "Brickle-So-No-Clo; all long "oh" sounds) ←

• <u>Strong bases</u>: **Group IA and IIA metal hydroxides** (i.e. LiOH, NaOH, Ca(OH)₂, etc)

→ Everything else is weak! ←

Totally Epic AP Chem Review: Acids and Bases in a Day!

Various Ways to Describe Acid Strength					
Property Strong Acid Weak Acid					
Ionization constant (K _a) value	K _a is large	K _a is small			
Percent Ionization	% Ionization = 100%	% Ionization << 100%			
Position of the dissociation (ionization) equilibrium	Far to the <u>right</u> (product-favored)	Far to the <u>left</u> (reactant-favored)			
Equilibrium concentration of H ⁺ when compared to original [HA]	[H ⁺] ≈ [HA] ₀	[H ⁺] << [HA]₀			

<u>Generic Acid</u>: $HA + H_2O \rightarrow H_3O^+ + A^-$

$$K_a = \frac{[x][x]}{[HA]_i - x} \approx \frac{[x][x]}{[HA]_i} \text{ where } [\mathsf{H}_3\mathsf{O}^+] = \mathsf{x} << [\mathsf{HA}]_i$$

Conjugate Base (of Generic Acid): $A^- + H_2O \rightarrow HA + OH^-$

$$K_b = \frac{[x][x]}{[A^-]_i - x} \approx \frac{[x][x]}{[A^-]_i}$$
 where [OH⁻] = x << [A⁻]_i

Self-Ionization of Water: About 2 out of 1 billion water molecules self-ionize!

 $H_2O(l) + H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$

 $K_w = [H_3O^+][OH^-] = K_a \times K_b = 1.0 \times 10^{-14}$ (at 25°C)

1) Strong Acids/ Strong Bases 2) Weak Acids/ Weak Bases If it's not strong, it's weak! You MUST memorize: < 1% Dissociation \rightarrow Equilibrium! Strong Acids: HBr, HI, HCl, H2SO4, HNO3, HClO4 Time saver: Hint: BriCl-SO-NO-ClO ("Brickle-So-No-Clo") Since acids ionize 1 H⁺ at a time, [H₃O⁺] = [A⁻], and $[OH^-] = [BH^+]$. Strong Bases: Groups IA and IIA metal hydroxides • For weak acids and bases, make the assumption $[HA]_{\circ} - x \approx [HA]_{\circ} \text{ and } [B]_{\circ} - x \approx [B]_{\circ}.$ 100% Dissociation! Easy life: Weak Acids: $pH = -\log[H^+] = -\log[HA]_o$ $K_a = \frac{[x][x]}{[HA]_i - x} \approx \frac{[x][x]}{[HA]_i}$ where $[H_3O^+] = x << [HA]_i$ $pOH = -\log[OH^-] = -\log[B]_o$ Weak Bases: pH + pOH = 14 $K_b = \frac{[x][x]}{[B]_i - x} \approx \frac{[x][x]}{[B]_i}$ where [OH⁻] = x << [B]_i

Percent Ionization

Percent Ionization: percentage of acid molecules that dissociate (ionize) when dissolved in water

% **Ionization** =
$$\frac{\text{molarity of ionized acid}}{\text{initial molarity of acid}} \times 100 = \frac{[H_3O^+]_{equil}}{[HA]_0} \times 100$$

Important Notes

- The **favored direction of the reaction** is the one in which the <u>weaker</u> acid/base are produced.
- The stronger an acid is, the weaker its conjugate base (and vice versa).
- Diluting an acid (decreasing concentration) will increase pH and increase percent ionization.

Practice, practice, practice!

1. Calculate the pH of a 0.020 M solution of hydrochloric acid.

2. Calculate the pH and percent ionization of a 0.020 M solution of acetic acid ($K_a = 1.8 \times 10^{-5}$).

3. Calculate the pH for a 1.7 x 10⁻² M solution of KOH.

4. Calculate the pH and percent ionization for a 1.7×10^{-2} M solution of NH₃ (K_b = 1.8×10^{-5}).

Salty Salts

<u>To know if a salt will affect pH, determine</u>: \rightarrow Will the salt ions will <u>hydrolyze</u> (or split) water?

Conjugates of <u>Strong</u> Acids/Bases: do <u>NOT</u> hydrolyze water, and thus do <u>NOT</u> affect pH Conjugates of <u>Weak</u> Acids/Bases: do hydrolyze water, and thus <u>do</u> affect pH!

	How to Determine t	he pH of a Salt	Examp	le
1.	. Dissociate your salt.		$CaSO_3 \rightarrow Ca^{2+} + SO_3^{2-}$	
	Make the cation into a <u>bas</u>	e: is it strong or weak?	Ca ²⁺ + 2 OH −→ Ca(O	H) ₂ Strong base
	Make the anion into an <u>aci</u>	d: is it strong or weak?	$\rm H^{+} + \rm SO_{3}^{-} \rightarrow \rm HSO_{3}^{-}$	Weak acid
2.	. Strong wins!		SB + WA, so	this salt is basic!
3.	. If either is weak, write the hydrolysis reaction:		SO ₃ + H ₂ O	≓ OH - + HSO ₃ -
	Conjugate base of WA:	$A^- + H_2O \rightleftharpoons OH^- + HA$		
	Conjugate acid of WB:	$BH^{*} + H_{2}O \ \rightleftharpoons H_{3}O^{*} + B$		

4. Use your hydrolysis equation to calculate the pH using the Weak Acids/Bases method.

Practice: Identify the salt solutions below as acidic, basic, or neutral and justify your answer.

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pH vs pK_a: Which form dominates?

Given the generic weak acid reaction: $HA(aq) + H_2O(I) \rightleftharpoons A^-(aq) + H_3O^+$

- $pH \le pK_a$ the acid form (HA) predominates (plenty of H⁺ present in solution)
- $pH > pK_a$ the conjugate base form (<u>A</u>) predominates (not enough H⁺ present in solution)

Let's Practice! (2016 #4, 4 points)

 $C_6H_5OH(aq) + H_2O(l) \rightleftharpoons C_6H_5O^-(aq) + H_3O^+(aq)$ $K_a = 1.12 \times 10^{-10}$

Phenol is a weak acid that partially dissociates in water according to the equation above.

- a. What is the pH of a 0.75 M $C_6H_5OH(aq)$ solution?
- b. For a certain reaction involving $C_6H_5OH(aq)$ to proceed at a significant rate, the phenol must be primarily in its deprotonated form, $C_6H_5O^-(aq)$. In order to ensure that the $C_6H_5OH(aq)$ is deprotonated, the reaction must be conducted in a buffered solution. On the number scale below, circle <u>each</u> pH for which more than 50 percent of the phenol molecules are in the deprotonated form ($C_6H_5O^-(aq)$). Justify your answer.

Totally Epic AP Chem Review: Buffers and Titrations in a Day!

Buffer: solutions that resist change in pH

Whenever a weak acid or base is present with its conjugate salt - YOU HAVE A BUFFER !!!

4 Ways to Make a Buffer			
Components	Ideal Buffer Ratio		
weak acid and its conjugate base	HA and A [−] or HA and <i>Nα</i> A	<u>1:1</u> mole ratio	
weak base and its conjugate acid B and BH ⁺ or B and BHCI		<u>1:1</u> mole ratio	
weak acid + strong base (titration)	$HA + NaOH \rightarrow H_2O + NaA$	<u>1</u> weak acid: <u>0.5</u> strong base mole ratio	
weak base + strong acid (titration)	$B + HCI \rightarrow BH^+ + CI^-$	<u>1</u> weak base: <u>0.5</u> strong acid mole ratio	

How does a buffer work?

The acidic species donates protons to resist increases in pH, and the basic species will accept protons to resist decreases in pH.

When preparing a buffer solution, you want:

- $[HA] = [A^2]$ (acid/base ratio \approx 1:1)
- <u>pH</u> of buffer $\approx pK_a$ (of acid form)
 - → weak acid K_a with an exponent \approx buffer pH.
- High <u>capacity</u> (lots of acid and base)

Calculating the pH of a Buffer Solution: Henderson-Hasselbach Equation

We can derive an equation that relates the pH of a buffer solution to the initial concentration of the buffer components by rearranging the acid ionization constant expression. This can be written in two different formats:

$$[H_30^+] = K_a \frac{[HA]}{[A^-]} \qquad \text{or} \qquad pH = pKa + \log \left(\frac{[A^-]}{[HA]}\right)$$

[HA] = Weak acid **or** salt of conjugate base [A⁻] = Weak base **or** salt of conjugate acid

- WARNING: If concentrations of separate solutions are given with volumes and then the two are added together, you must recalculate the "new concentrations" due to dilution.
- Shortcut!!! Since [Acid] is a ratio in the equations, the amount of moles may be substituted in place of <u>concentration</u> because the final volumes will be the same, and thus cancel out.

Let's Practice!

1. Calculate the pH of a solution containing 0.75 M lactic acid, $HC_3H_5O_3$ ($K_a = 1.4 \times 10^{-4}$) and 0.25 M sodium lactate, $NaC_3H_5O_3$.

2. Calculate the pH of a solution prepared by mixing 30.0 mL of 0.300 M acetic acid, HC₂H₃O₂, with 20.0 mL of

Net Ionic Equations for Weak + Strong Acid/Base Reactions

Remember, strong acids and bases dissociate 100%, but weak acids and bases do not!

• In a strong/ weak net ionic, the only spectator ion that will be removed is the conjugate of the strong acid or base!

Example:

molecular equation:	HNO₂(aq) + Na	¦OH(aq) → H₂O(l)) + NaNO₂(aq)
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net ionic equation:

 $HNO_2(aq) + OH(aq) \rightarrow H_2O(l) + NO_2(aq)$

Let's Practice!

1. Write the balanced net ionic equation for the reaction that occurs between HCl and NH₃.

2. Write the balanced net ionic equation for the reaction that occurs between KOH and $HC_2H_3O_2$.

How Does a Buffer Work? Explaining with Reactions.

Example Buffer #1: HBrO3 and LiBrO3

- 1. Write the net ionic equation that represents that reaction that explains why adding a few drops of HBr will not significantly change the pH of the buffer solution:
- 2. Write the net ionic equation that represents that reaction that explains why adding a few drops of NaOH will not significantly change the pH of the buffer solution:

Example Buffer #2: NH₄Cl and NH₃

- 1. Write the net ionic equation that represents that reaction that explains why adding a few drops of HBr will not significantly change the pH of the buffer solution:
- 2. Write the net ionic equation that represents that reaction that explains why adding a few drops of KOH will not significantly change the pH of the buffer solution:

Acid	Acid Dissociation Constant, K _a		
H_3PO_4	7×10^{-3}		
H ₂ PO ₄ -	8×10^{-8}		
HPO42-	5×10^{-13}		

1. On the basis of the information above, a buffer with a pH = 9 can best be made by using

a. $H_3PO_4 + H_2PO_4^$ c. H₂PO₄⁻ + PO₄³⁻

0.350 M NaC₂H₃O₂. The K_a for acetic acid is 1.80 x 10⁻⁵.

b. $H_2PO_4^- + HPO_4^{2-}$ d $HPO_{2}^{2-} + PO_{3}^{3-}$

- 2. Which of the following changes would affect the pH of a buffer solution?
 - ed.

 - III. Adding a small amount of strong acid or strong base.
 - a. Ill only b. I and II only c. II and III only d. I, II, and III
- 3. A buffer solution can be formed by dissolving equal moles of:

b.	HF and NaOH	с.	CH ₃ COOH and NaCl
c.	KBr and Na_3PO_4	d.	HF and NaF

4. Which of the following acids would be the best choice to create a buffered solution with a pH of 5?

a.	$H_2C_2O_4$	$K_a = 5.9 \times 10^{-2}$	c.	$HC_2H_3O_2$	$K_a = 1.8 \times 10^{-5}$
b.	H ₃ AsO ₄	$K_a = 5.6 \times 10^{-3}$	d.	HOCI	$K_a = 3.0 \times 10^{-8}$

11104	u.	111 04	1104		
llowing changes w	ould -	offoct the	on Hofah	uffor coluti	on2

I.	Doubling the amount	of acid and	conjugate	base used
	boubing the uniount	or acia aria	conjugate	buse used

II. Doubling the amount of water in the solution.



Titrations: Quick Summary

A substance in a solution of <u>known</u> concentration (the <u>titrant</u>, usually in a buret) is reacted with another substance in a solution of <u>unknown</u> concentration (the <u>analyte</u>, usually in a flask or beaker)

- Equivalence point: the point at which the moles of each reactant are stoichiometrically equal to each other in solution: moles(H⁺) = moles(OH⁻) because the acid and base have completely neutralized.
- End point: the point of the titration where an indicator changes color

Equivalence point and end point are NOT the same thing!

How to Choose the Best Indicator: An indicator is a weak acid where HA and A⁻ are different colors!

• If $pH \le pK_a$ mostly \underline{HA} (one color), if $pH > pK_a$ mostly $\underline{A^{=}}$ (different color) Choose an indicator that:

- > $pK_a \approx pH$ equivalence point of titration (moles acid = moles base).
- > Has $\underline{K}_a \approx 1 \times 10^{-pH}$ (that is, the pH of the solution at equivalence point)

Titration Curves



Strong Base Titrated with Strong Acid



- At equivalence point, $\underline{pH} = 7$ (only neutral salt and water present)
- Net ionic will always be: $\underline{H^+(aq) + OH^-(aq)} \rightarrow \underline{H_2O(l)}$
- Use $M_a V_a = M_b V_b$ to calculate volume needed to reach equivalence point
 - Moles acid = moles base at equivalence point!



pH at Equivalence point

<u>Weak acid + strong base</u>: pH > 7 <u>Weak base + strong acid</u>: pH < 7

Buffers and the ½ Equivalence point (midpoint). A perfect buffer!

- Buffers make the titration curve <u>flat</u> at the region where buffering occurs. On a titration curve, this is the point of inflection (buffer arrow).
 - At point of inflection (1/2 equivalence point), solution has maxiumum buffering capacity, and:
 - [acid] = [conjugate base] or [base] = [conjugate acid]

pH = pK_a (or pH = 14 – pK_b)

[titrant] = ½ [weak acid] or [titrant] = ½ [weak base]

Note: We can still use $M_a V_a = M_b V_b$ to calculate volume needed to reach equivalence point!

How to Determine pK_a/pK_b of Weak Acid or Base from Titration Data

- 1. Calculate location of half-equivalence point by dividing volume at equivalence point in half!
- 2. Use titration curve to determine the <u>pH</u> at the half-equivalence point.
 - **a.** Analyte a weak acid? $pH = pK_a$, $K_a = 1 \times 10^{-pH}$
 - **b.** Analyte a weak base? $pH = pK_a$ (of BH^+), so $pK_b = 14 pH$, $K_b = 1 \times 10^{-(14-pH)}$

How to Sketch a Titration Curve - the following characteristics must be considered

- 1. General Shape of Curve: see above curves
- 2. Starting pH: if acid titrated with base \rightarrow pH < 7; if base titrated with acid \rightarrow pH > 7
- 3. Equivalence Point: steepest part (inflection point)
 - a. Volume: use M_aV_a=M_bV_b
 - **b.** pH: SA + SB \rightarrow pH = 7; SA + WB \rightarrow pH > 7; WA + SB \rightarrow pH < 7
- 4. Ending pH: if acid titrated with base \rightarrow pH > 7; if base titrated with acid \rightarrow pH < 7
Let's Practice!

Consider the titration of a 20.0 mL sample of 0.105 M HCN (K_a = 4.9 x 10⁻¹⁰) with 0.125 M NaOH.
 a. What is the initial pH?

2.	The c	omplete neut	raliza	ation of 15.0 n	nL of KOH r	requires	0.025 mol H	₂SO₄. 1	he [KOH] was:	
	a. 1	.50 M	b.	1.67 M	с.	3.33 M		d.	6.67 M		
3.	What	t is the pH of t	he so	olution formed	d when 0.0	40 moles	of NaOH(s)	is add	ed to 1.0	0 L of 0.050	M HCI?
		a. 1.00		b. 2.00		с.	7.00		d.	12.00	

4. Which of the following indicators would be most suitable for the titration of 0.10 M lactic acid (pK_a = 3.08) with 0.10 M KOH(aq)?

a.	phenol red (pK _a = 6.9)	с.	thymol blue (pK _a = 1.7)
b.	alizarin red (pKa = 4.5)	d.	methyl orange (pK _a = 3.4)

Use the following information to answer 5-7.

A student titrates some 1.0 M HCl into 20.0 mL of methylamine (CH_3NH_2), a weak base which only accepts a single proton. The following titration curve results:



- b. What volume of base, in mL, must be added to reach equivalence point?
- c. Sketch the curve that would result from this titration experiment on the grid below.



- 2. For the following graphs, answer these questions:
 - a. What type of titration was performed? (That is, what vs what?)
 - b. What is the approximate pH at the equivalence points?
 - c. For relevant graphs, what is the pK_a or pK_b of the analyte?



1) Strong Acids/ Strong Bases	2) Weak Acids/ Weak Bases				
You MUST memorize:	If it's not strong, it's weak!				
Strong Acids: HBr, HI, HCl, H ₂ SO ₄ , HNO ₃ , HClO ₄	< 1% Dissociation \rightarrow Equilibrium!				
Hint: BrICl – SO NO ClO	Time saver!! Since acids ionize 1 H ⁺ at a time, $[H_3O^+] =$				
Strong Bases: Groups IA and IIA metal hydroxides	$[A^-]$, and $[OH^-] = [BH^+]$. For weak acids and bases, make				
100% Dissociation! Easy life:	Weak Acids:				
$pH = -\log[H^+] = -\log[HA]_o$	$K_a = \frac{[x][x]}{[HA]_o - x} \approx \frac{[x][x]}{[HA]_o} \text{ where } [H_3O^+] = x << [HA]_o$				
$pOH = -\log[OH^-] = -\log[B]_o$	Weak Bases:				
pH + pOH = 14	$K_b = \frac{[x][x]}{[B]_o - x} \approx \frac{[x][x]}{[B]_o} \text{ where } [\text{OH}^-] = x << [\text{B}]_o$				
3) Salty Salts					

<u>To know if a salt will affect pH, determine</u>: \rightarrow Will the salt ions will <u>hydrolyze</u> (or split) water?

Conjugates of <u>Strong</u> Acids/Bases: do <u>NOT</u> hydrolyze water, and thus don't affect pH

Conjugates of weak Acius/Ba	ases. <u>DO</u> fiyuroiyze water, and th		
How to Determi	ne the pH of a Salt	Example	
1. Dissociate your salt.		$CaSO_3 \rightarrow Ca^{2+} + SO_3^{2-}$	
Make the cation into a	base: is it strong or weak?	$Ca^{2+} + 2 OH^{-} \rightarrow Ca(OH)_2$	Strong base

3.	Strong wins!	SB + WA, so this salt is basic!
4.	If either is weak, write the hydrolysis reaction:	$SO_3^- + H_2O \rightleftharpoons OH^- + HSO_3^-$

Conjugate acid of WB: $BH^+ + H_2O \rightleftharpoons H_3O^+ + B$

5. Use your hydrolysis equation to calculate the pH using the <u>Weak Acids/Bases</u> method.

 $A^- + H_2O \rightleftharpoons OH^- + HA$

4) Adding Strong Acids + Strong Bases (Yes, this includes titrations!)

 $H^+ + SO_3^- \rightarrow HSO_3^-$

Weak acid

These are really just stoichiometry problems with a limiting reagent!

2. Make the anion into an acid: is it strong or weak?

Conjugate base of WA:

- What is "excess" determines the pH (since all strong/strong combos neutralize)
- <u>Beware the change in volume</u> if multiple solutions are being <u>added</u>! (calculate moles of either H⁺ or OH⁻ in excess, and divide by <u>total</u> volume to determine concentration of [H⁺] or [OH⁻], and go from there)



Totally Epic AP Chem Review: <u>Atomic Structure & Periodicity in a Day</u>!

Average Atomic Mass: weighted average mass of an element's isotopes and is the mass found on the periodic table.

 $\label{eq:average} \textit{Average atomic mass} = \textit{mass}_1 \Bigl(\frac{\%\textit{Abundance}}{100} \Bigr) + \textit{mass}_2 \Bigl(\frac{\%\textit{Abundance}}{100} \Bigr) + \cdots$

- The average atomic mass will be <u>between</u> the masses of the largest and smallest isotopes.
- The average atomic mass will generally be <u>closest</u> to the most abundant isotope.

Mass Spectrometry: Measuring the Mass of Atoms and Molecules: The masses of elements and their percent abundances of isotopes of elements are measured using mass spectrophotometry, a technique that separates particles according to their mass.

Result: The ionized material is separated according to their mass, the result of which produces a mass spectrum.

a. The $\underline{\text{position}}$ (location) of each $\underline{\text{peak}}$ on the x-axis indicates the $\underline{\text{mass}}$ of the

isotope.



abundance (how common that isotope is in nature).

Rules Governing How Electrons Fill Orbitals

A. The <u>Aufbau principle</u> states that an electron will occupy the lowest-energy orbital that can receive it. (This principle only applies to atoms and ions in the ground state.)



B. The <u>Pauli Exclusion principle</u> states that no two electrons can have the same set of four quantum numbers. For the new AP CHEM exam, you do NOT have to answer questions about quantum numbers. So, basically, recognize that no two electrons can exist in the exact same orbital having the exact same spin.



C. <u>Hund's rule</u> states that orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron, and all electrons in singly occupied orbitals must have the same spin.



Electron Configurations

1. Orbital Notation/Orbital Diagram: uses arrows to represent electrons.



- 2. Standard Notation: Standard electron configurations eliminate the lines and arrows of orbital notation.
 - → The number of electrons in a sublevel is shown by adding a <u>superscript</u>.

1s²2s²2p²

 Noble Gas Electron Configurations: A noble gas configuration is an electron configuration that utilizes a noble gas which has its valence level fully occupied.

[Ne]2s²2p²

TIMESAVER:

Any question on the AP FR which asks for the electron configuration will accept EITHER standard or noble gas notation (<u>unless it asks for "complete electron configuration</u>") but NEVER orbital notation.

Noble gas notation takes less time to write!!!

Adding Electrons

The periodic table holds the answer for the order in which electrons FILL orbitals.

IA				<u>VIII</u> A
1 1s IIA		П		A 1s
2 2 <i>s</i>			2p	
3 3 <i>s</i>			3р	
4 4s	3d		4p	
5 55	4d		5p	
6 6s	5d		6p	\square
7 75	6d			_

		4 <i>f</i>			
		5f			

The Order in Which Electrons FILL Energy Levels 1s²2s²2p⁶3s²3p⁶4s²3d¹⁰4p⁶5s²4d¹⁰5p⁶6s²4f¹⁴5d¹⁰6p⁶7s²5f¹⁴6d¹⁰

100%

50%

107 109 Mass (amu)

Removing electrons: Those pesky transition metals!

→ When REMOVING electrons from transition metals, remove valence <u>s</u> electrons <u>before</u> removing electrons from a d sublevel!



Isoelectronic atoms and ions: the "iso" in "isoelectronic" means "same", so isoelectronic atoms and ions have the same number of <u>electrons</u>.

Quantitative Atomic Structure: Mmm, math!

• Electromagnetic radiation (including light) can behave like a <u>wave</u>, characterized by measurable properties of wavelength and frequency, or like a stream of particles (<u>photons</u>).

$$E = h\nu$$

$$c = \lambda\nu$$
Where: E = energy and: Planck's constant, h = 6.626 \times 10^{-34} \text{ J s}
$$\nu = \text{ frequency}$$

$$\lambda = \text{ wavelength}$$
Speed of light, c = 2.998 × 10⁸ m s⁻¹

Note: This energy represents the energy of a **single photon.** Be prepared to convert to energies absorbed or emitted to kJ/mol instead of joules (J/photon).

Spectroscopy

Spectroscopy: a study of the interaction between matter and electromagnetic radiation

- Can be used to determine the atoms, molecules, or structure of a given substance
- So many kinds!!

Types of	Spectroscopy
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Name of Spectroscopy	Type of Radiation Used	Relative energy	What does it do to the atom/molecule?	What does it tell us?
Photoelectron spectroscopy (PES)	X-ray	very high	Removes electrons (valence and core).	 Identity of element How tightly electrons are held by the nucleus
UV-Visible spectroscopy (UV-Vis)	Ultraviolet (UV)	high	Excites electrons to	Identity of element or molecule
UV-Visible spectroscopy (Colorimetry)	Visible	medium	jump between energy levels.	 Identity of element or molecule Concentration of solution
IR (vibrational) spectroscopy	Infrared (IR)	low	Changes vibrations within bonds.	 Types of atoms, bonds, and functional groups within a molecule
Microwave (rotational) spectroscopy	Microwave	very low	Changes the rotation of atoms in bonds.	 Location of hydrogen atoms within a molecule

Photoelectron Spectroscopy (PES)

Photoelectron Spectroscopy (PES): a technique to determine the ionization (or binding) energy of EVERY electron in an atom

- <u>lonization energy</u> (for PES, more commonly referred to as the <u>binding energy</u>): the energy required to remove (<u>ionize</u>) an electron from an atom
- Binding energy is plotted on the horizontal axis, with energy <u>decreasing</u> (!!) from left to right (although sometimes this is flipped, so always check)

How to Interpret PES Spectra

- Peak height corresponds to the relative number of electrons in each sublevel of an atom
- Peak location corresponds to the relative amount of energy required to remove each electron
 - Higher energies = sublevels found <u>closer</u> to the nucleus (1s, 2s, etc)
 - Lower energies = sublevels found <u>farther</u> from the nucleus
- When comparing PES from different atoms:
 - As the number of <u>protons</u> in the nucleus increases, the binding energy will <u>increase</u> for electrons in comprable sublevels
 - As the number of <u>electrons</u> in a specific sublevel increases, the peak height will <u>increase</u> for electrons in comprable sublevels

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Photoelectron Spectrum of Neon



Interpretation of Spectrum:

- Electrons in 1s subshell (peak A) have a much higher binding energy than electrons in 2s (peak B), because the core electrons experience a much higher effective nuclear charge than valence electrons.
- The 2p signal (peak C) is three times higher than the 1s (peak A) and 2s (peak B) signals, indicating it contains triple the number of electrons (2p⁶ vs 1s², 2s²).

Photoelectron Spectrum of Element Z



- a. Boron b. Carbon c. Neon d. Magnesium
- 2. Label the identity of each peak with principal quantum number, n (energy level), subshell (s, p, d, or f) and a superscript representing the number of electrons found in the subshell.
- 3. If the PES spectrum above had actually represented the element sodium, what would be different? List at least two differences you would expect to see:

How to Answer Periodic Trends Free Response Questions

Justifying all of the trends on the periodic table can be simplified using these two generalizations:

- 1. Use number of protons (or Z_{eff}) to justify trends across a period.
- 2. Use increased distance (greater value of n) to justify trends down a group.

How to Earn Full Points on Periodic Trends Problems

Follow these three steps EVERY time you answer a periodicity question!

- Locate both elements on the periodic table and <u>state</u> the principal energy level (n) and the sublevel containing the valence electrons for *each* element.
- 2) Do they have the same or different <u>n</u> values?
- If same n: argue with number of protons; if different n: argue with n vs. n (distance between nucleus and valance electrons).

REMEMBER: a trend is not an explanation!

Simply identifying a trend (atomic radius decreases as you move from left to right across a period, electronegativity decreases as you move down a column, etc) earns <u>zero</u> points!

Avoid Losing Easy Points

- When explaining, you <u>must</u> refer to <u>ALL</u> species (atoms, ions) referenced in the question, or you will not get full credit.
- 2. Read the question: justify with "principles of atomic structure" or "Coulomb's Law" (it will always be one or the other (3)).

Specific Question Types

- 1. Comparisons between $\underline{isoelectronic}$ species: explain with number of \mathbf{p}^{\star}
 - Isoelectronic species with more protons are SMALLER because the valence electrons are MORE attracted to and thus CLOSER to the nucleus.
 - b. Isoelectronic species with <u>less</u> protons are LARGER because the valence electrons are LESS attracted to and thus FARTHER from the nucleus.
- 2. Comparisons between an atom and its ion/ions of the same atom, same n: explain with e⁻/e⁻ repulsion
 - Positively charged cations are SMALLER than the neutral atom because of <u>decreased</u> e⁻/e⁻ repulsion, thus valence electrons are CLOSER to the nucleus.
 - b. Negatively charged anions are LARGER than the neutral atom because of <u>increased</u> e⁻/e⁻ repulsion, thus valence electrons are FARTHER from the nucleus.
- 3. Comparisons between an atom and its ion/ions of the same atom, different n: explain with distance
 - If a species has their outermost electrons on a lower energy level (n), their valence electrons are <u>closer</u> to and thus <u>more</u> attracted to the nucleus.



- <u>Atomic radius</u> (size of atom): distance between the <u>nucleus</u> and valence electrons.
- Ionic radius: distance from the nucleus to valence electrons in a charged ion.
- Metallic character can be defined as how easily an atom loses an electron. This is exactly the opposite of the trend for first ionization energy: <u>higher IE = lower</u> metallic character.
- Reactivity depends on whether the element reacts by losing electrons (metals) or gaining electrons (nonmetals).
 - Metals are MORE reactive as you move down a column: because metals lose electrons as they react,
 LESS attraction between valence electrons and nucleus results in a more reactive metal.
 - <u>Non-metals are LESS reactive as you move down a column</u>: because non-metals gain electrons as they
 react, LESS attraction between valence electrons and nucleus results in a less reactive non-metal.
- Electronegativity: attraction of an atom for pair of <u>valence</u> level electrons in a <u>covalent bond</u> with another atom. Think of the atoms as playing "tug of war" with their <u>valence</u> shell electrons!
- **Ionization Energy (IE):** energy required to <u>remove</u> an electron from a gaseous atom or ion. **Higher** attraction between nucleus and electron = **harder** to remove electron = <u>higher</u> ionization energy
 - \circ 1st Ionization Energy: (IE₁) energy required to remove the first (highest energy level) electron
 - \circ 2nd Ionization Energy: (IE₂) energy required to remove the second highest energy electron
 - \circ Each additional electron requires **MORE** energy to remove than the previous one, so: $IE_1 < IE_2 < IE_3$ etc.

Note: You can identify an element by being given a table showing the pattern of successive ionization energies.

Successive Ionization Energies (kJ/mol)							
First	Second	Third	Fourth	Fifth			
801	2,426	3,660	24,682	32,508			

Totally Epic AP Chem Review: Bonding and IMFs in a Day!

<u>Chemical bonds</u>: forces of attraction that hold groups of atoms together <u>within</u> a molecule or crystal lattice and make them function as a unit

Remember, nature is striving for a lower energy state!

lonic

Characteristics of ionic substance usually include:

- Electrons are transferred between atoms having large differences in electronegativity
- Often contain a metal and a non-metal
- Strong Coulombic attractions between positive (+) and negative (-) ions
- Formulas are given in the simplest ratios of elements (empirical formula; NaCl, MgCl₂)
- <u>Solids</u> at room temperature
- Form a crystal lattice structure as pictured to the right
- Melt at <u>high</u> temperatures
- Good conductors of electricity in the molten (I) or dissolved (aq) state

Covalent

Characteristics of covalent substance usually include:

- Electrons are shared between atoms having small differences in electronegativity
- Non-metals attracted to other non-metals
- Formulas are given in the true ratios of elements (molecular formula; C₆H₁₂O₆)
- May exist in <u>any</u> state of matter at room temperature (solid, liquid, or gas)
- Melt at low temperatures (separate molecules held together by IMFs)
- Do <u>NOT</u> conduct electricity in any state (EXCEPT strong acids, when aqueous)

Metallic

Characteristics of metallic substance usually include:

- Substances that are metals
- A sea of delocalized, mobile electrons surrounding a positively charged metal center
- An attraction between metal ions and surrounding electrons
- Formulas are written as a neutral atom (Mg, Pb)
- <u>Solid</u> with a crystalline structure at room temperature
- Range of melting points usually depending on the number of valence electrons
- Excellent conductors of electricity since electrons in the "sea" are free to move

Most chemical bonds are in fact somewhere between purely ionic and purely covalent.

DRAW THE DANG LEWIS DOT STRUCTURE

when answering bonding multiple choice or free response questions.





Alloys: similar in structure to pure metal solids, but contain more than one type of element.

There are two types of alloys that are AP tested!

Substitutional Alloys	Interstitial Alloys
 Form between atoms of <u>similar</u> size, where one atom substitutes for the other in the lattice. Similar properties to component atoms <u>Still</u> malleable and ductile 	Form between atoms of <u>different</u> size, where the smaller atoms fill the interstitial spaces (lattice holes) between the larger atoms. • Properties change!! • More <u>brittle</u> , harder • <u>Less</u> malleable and ductile
$(\circ \circ \circ \circ \circ \circ \circ$	



IONIC BONDS: All about Coulomb's Law

When answering questions about ionic bond strength, justify your response using Coulomb's Law:

Lattice Energy = $k(\frac{Q_1Q_2}{d})$

Use Coulomb's Law to justify melting point, solubility, and lattice energy differences between two ionic compounds.

→ The more highly <u>charged</u> the ions OR the <u>smaller</u> the ions, the **GREATER** the attraction!

Lattice energy: energy released when the solid crystal forms from separate ions in the gas phase

- Directly dependent on size of charges
- Inversely dependent on distance between ions
- Ion charge is generally more important than ion size

Greater lattice energy = <u>more</u> energy required to separate ions

- \rightarrow <u>Stronger</u> ionic bond
- $\rightarrow \uparrow$ melting point
- → ↓ solubility (ions must separate/dissociate from one another and attach to water to dissolve)





Percent Ionic Character:

- The greater the difference in <u>electronegativity</u> between two bonded atoms, the greater the <u>ionic character</u> of the bond.
- The more <u>similar</u> in electronegativity, the greater the <u>covalent character</u> of the bond.

<u>Dipole moment</u>: a measure of bond polarity; \uparrow dipole moment means \uparrow ionic character!

$$\stackrel{\longrightarrow}{H \longrightarrow} P or \stackrel{\delta^+}{H \longrightarrow} Or \stackrel{\delta^$$

→ Represented by an arrow pointing in the direction of greater electron density

COVALENT BONDS

Bond length: the distance two covalently bonded atoms at their lowest potential energy. It is a balance between opposing forces:

- Attractive electrostatic forces between the nucleus of one atom and the electrons of another
- Repulsive forces between the two positively charged nuclei



Bond Order: the number of chemical bonds between a pair of atoms; indicates the stability of a bond.

Bond Type	Bond Order	Bond Length	Bond Strength
Single bond	1	longer	weaker
Double bond	2	medium	medium
Triple bond	3	shorter	stronger

Higher Bond Order: \uparrow electron density, \downarrow nucleus-nucleus repulsion, \uparrow electron-nuclei attraction \rightarrow multiple bonds \uparrow bond strength and \downarrow bond length!

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Helpful Hints for Drawing Covalent Lewis Dot Structures

1 sigma bond + 2 pi bonds

shortest/ strongest

triple bond

VSEPR: Memorize Shapes and Bond Angles!

4 L i	s always a terminal atom 🗎	ALWAYS connected to only 1 other stom									
2 10		antral atom in molecule		Electron Groups*	Bonding Groups	Lone Pairs	Electron Geometry	Molecular Geometry	Approximate Bond Angles	E	xample
2. <u>Lo</u>	west electronegativity is co	e for a polyatomic ion		2	2	0	Linear	Linear	180°	:;; = c = ;;	
j. ne	- For positive ions	subtract electron(s) from the central atom									•
	b. For pegative ions	add electron(s) to the central atom		3	3	0	Trigonal planar	Trigonal planar	120°	····	
	c Enclose the dot st	ructure in square brackets and include the	ion's charge outside the brackets								~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
	at all elements can form	double or triple bonds: only C N O P a	nd SI (Think (NOP-S)	3	2	1	Trigonal planar	Bent	≈118°	:0 = S - 0	
4. NO										H	0
		Free attended the ended with		4	4	0	Tetrahedral	Tetrahedral	109.5°	н — с — н	
		Exceptions to the octet rule								H H	-0 -0
1.	Elements that will have <u>le</u>	ess than 8 valence electrons and are stable.		4	3	1	Tetrahedral	Trigonal	≈107°	н <u>н</u> н 	20
	a. <u>Hydrogen</u> , 2 elect	rons (<u>1</u> bond)			0	2	*	Dent	-1059	н 	
	b. <u>Beryllium</u> , 4 elect	rons (<u>2</u> bonds)		4	2	2	Tetrahedral	Bent	≈105°	н—й—н	000
	c. <u>Boron</u> , 6 electror	ns (<u>3</u> bonds)								·· :ci:	•
				5	5	0	Trigonal	Trigonal	120° (equatorial)	·ci / P-ci:	20-0
2.	2. Elements that will have more than 8 valence electrons and are stable \rightarrow expanded octet!		$e \rightarrow$ expanded octet!				upytamidai	Dipyrainiuai	90 (axiai)	:;;; : · · · ·	T .
a. Elements in period (row) 3 through 7 can often expand their octet and can form more than 4 bonds			octet and can form more than 4 bonds								
(can have up to 12 electrons, 6 bonds)				5	5 4	1	1 Trigonal bipyramidal	Seesaw	≈118º (equatorial) ≈88º (axial)	:F: :F:→S→F: :F:	Lo
1. This is only possible between periods 3 through 7 because they can hold electrons in their			cause they can hold electrons in their	5		4 1					T.
empty <u>d subleve</u> l.										·::-	
	 If you are 	unsure where to put extra lone pairs, check	k to see if the <u>central atom</u> can have an	5	5 3	3 2	Trigonal bipyramidal	T-shaped	≈86°	·r	
	expanded	l octet (check to see if the element is in per	loas 3 through /)	5	2	2	Trigonal	Hener	1000		0 0 0
				5	2	3	bipyramidal	Linear	180°	·r- xe -r.	
		Sigma (σ) and Pi (π) Bonding	Ś							:F: :F. F:	
Sigma	(σ) bond: covalent bond fo	ormed by orbitals overlapping end to end. T	he electron density is concentrated	6	6	0	Octahedral	Octahedral	90°	S F	
between the nuclei of the two atoms involved in a bond.											6
Pi (π) bond: covalent bond formed by orbitals overlapping side by side. The electron density is concentrated above		electron density is concentrated above					Square		:F:	9	
and <u>be</u>	and <u>below</u> the nuclei of the two atoms involved in a bond.			6	5	1	1 Octahedral	pyramidal	≈88°	F - Br - F:	
	Bond Type	Made of	Length / Strength							·E: ·E: :F:	
	single bond	<u>1</u> sigma bond	longest/ weakest	6	4	2	Octahedral	Square	90°	:F-Xe-F:	· · · ·
	double bond	<u>1</u> sigma bond + <u>1</u> pi bond	medium length/ strength					planai		: <u>F</u> :	00

Hybridization

Hybrid Orbitals: orbitals of equal energy created by blending two or more valence orbitals on the same atom

• Hybridization can be determined by counting regions of <u>electron</u> density: electron domains!

# of Electron Domains	# of Hybrid Orbitals	Electron Geometry	Hybridization
2	2	Linear	sp
3	3	Trigonal planar	sp ²
4	4	Tetrahedral	sp ³
5	5	Trigonal bipyramidal	sp³d **
6	6	Octahedral	sp ³ d ² **Not AP Tested

Isomers vs Resonance Hybrids

Isomers: molecules with the same molecular formula but different spatial arrangement of atoms

- Same <u>number</u> of atoms of each element
- Different arrangement of their atoms in space
- Different physical properties (boiling point, viscosity, etc) depending on their IMFs!

Resonance structures: when two or more Lewis structures can validly represent a molecule (or ion)

- Same position of atoms in space (and same number of each atom)
- Different electron arrangement
- The actual structure, the resonance hybrid, is intermediate between the two or more resonance structures.
 - All possible dot structures contribute to the real structure, BUT more stable ones (↓ formal charge) contribute more.
 - Resonance often occurs in structures with a <u>double</u> or <u>triple</u> bond.

Formal Charge

Formal Charge: a way to identify the best Lewis dot structure when more than one valid dot structure exists

• Formal charges are hypothetical charges assigned to each <u>element</u> in the dot structure

Formal Charge = # of valence electrons – # non-bonding electrons (lone) – $\frac{1}{2}$ # bonding electrons

You do NOT need to show work for formal charge calculations!!! 🛞

Formal Charge Rules (Which dot structure is best?)

- 1) Small (or even better, <u>o</u>) formal charges are more stable.
- 2) formal charge on the more electronegative atoms.
- 3) + formal charge on the <u>less</u> electronegative atoms.
- 4) Sum of all formal charges must <u>equal</u> the charge of the molecule.

Bonding vs. Attractions: IntRA vs IntER

2 Basic Types of Intramolecular forces: attraction when electrons are given, taken, or shared to form a bond.

- 1. <u>Electrostatic attraction</u>: ion-ion (ionic) or sea of electrons to positive metal cores (metallic)
- 2. Covalent bonds: mutual sharing of electrons

4 Basic Types of Intermolecular forces (IMFs): attraction between two or more distinct molecules or particles.

- 1. Ion dipole: ion is attracted to a polar molecule (strongest of all IMFs)
- 2. Dipole dipole: polar molecules are attracted to each other
 - a. Hydrogen bonding: strongest type of dipole dipole attraction; only when molecules contain an H bonded to an F, O, or N
- 3. Dipole induced dipole: polar molecules attracted to non-polar molecules
- Induced dipole induced dipole (London dispersion forces, LDFs): attraction of ALL atoms and molecules to each other due to temporary dipoles caused by the polarizability of the electron cloud (↑ surface area and/or ↑ # of electrons = ↑ LDFs)
 - **Intramolecular bonds are much, MUCH stronger than intermolecular forces!**

Note on language:



How do IMFs affect physical properties?

- → More IMFs means the more energy (heat) needed to put into the solution to overcome the IMFs.
- → Greater IMFS = \uparrow melting, boiling points
- \rightarrow Greater IMFS = $\frac{1}{2}$ vapor pressure (fewer molecules are in the gaseous state at a given temperature)

Chromatography: Lab Application of IMFs!

<u>Chromatography</u>: a technique used to separate mixtures of materials based on differences in migration rates among mixture components.

Paper chromatography: a common analytical technique used for separating and identifying mixtures that are (or can be) colored.

- A small, concentrated spot of the sample is applied to a strip of chromatography paper near the bottom.
- The paper is dipped into a suitable solvent, such as alcohol or water, and placed into a sealed container.
- The solvent moves <u>up</u> the paper by capillary action, which occurs as a result of the attraction of the solvent molecules to the paper.
- As the solvent rises through the paper it meets and dissolves the sample mixture, which will then <u>travel</u> up the paper with the solvent.
- Different compounds in the sample mixture travel at different <u>speeds</u> due to differences in solubility in the solvent and due to differences in their attraction to the fibers in the paper.
- The more soluble the component the further up it goes.



In short:

- Polar substances will travel FARTHEST in polar solvents
- Non-polar substances will travel FARTHEST in non-polar solvents

Why? Intermolecular attractions, of course!

Polar solute + polar solvent OR non-polar solute + non-polar solvent attractive forces are most energetically favorable, increasing solubility and thus mobility.

Totally Epic AP Chem Review: Gases FTW!

Math Based on the Ideal Gas Law

Ideal Gas Law	Combined Gas Law	Molar Mass/ Density
PV = nRT	$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$	$MM = \frac{DRT}{P} = \frac{mRT}{PV}$
On the formula chart	NOT on the formula chart	NOT on the formula chart
Use when you have only <u>1</u> of each variable	Use when conditions have changed	Use to calculate molar mass or density of a gas
Things to watch out for:	Things to watch out for:	Time-saver.
• Temp: convert to <u>K</u>	• Temp: convert to <u>K</u>	• At <u>STP</u> ,
• Choose R based on unit for P	Units for each variable need to	$Density = \frac{molar mass}{molar molume}$
 Torr = mmHg 	be the <u>same</u> on both sides	motar votume
• Volume: convert to L		• Molar volume = 22.4 L/mol

Other Math

Dalton's Law and Mole Fractions	Molar Volume	Gas Stoich
$P_{total} = P_1 + P_2 + \cdots$ $P_A = P_{total} \times X_A$ where $X_A = \frac{\text{moles } A}{\text{total moles}}$	1 mol = 22.4 L at STP	One chemical (g, mol, L) → another chemical (g, mol, or L)
On the formula chart	On the formula chart	NOT on the formula chart
Use when you have a mixture of gases	Use to convert between quantity and volume of a gas	Use to convert from one chemical to a different chemical
 Things to watch out for: Gas collection over water (or collection by water displacement): pure gas is mixed with <u>H20</u> vapor 	Only true at STP!!! (273.15 K, 1.0 atm)	Two types: • L→L (at same T and P) • Non-STP (or NOT at same T and P): When you're not at STP, Use <u>PV=nRT!</u>

Conceptual Summary

- 1. Temperature is directly proportional to average kinetic energy, which means:
 - a. Same temperature = same average kinetic energy!
 - b. Same temperature, different gases? Higher molar mass = slower, lower molar mass = faster (b/c KE = ½ mv²)
 - c. Same gas, different temperature? Heat 'em up, speed 'em up!

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2. Kinetic Molecular Theory (5 postulates)

- a. Gas particles are very **small** and very **far** apart (so gases are very compressible)
- b. Gas particles bounce off walls and each other with no loss of energy (elastic collisions)
- c. Gas particles are in constant, rapid, random motion (can't stop, won't stop!)
- d. Gas particles do NOT attract or repel each other (no IMFs!)
- e. Average kinetic energy of a gas particle is directly proportional to its velocity: $KE = \frac{1}{2} mv^2$

3. Ideal vs Real Gases

- a. Ideal gases: follow KMT postulates (most ideal at high I, low P)
- b. Real gases: have actual volume or attractive forces (most real at low T, high P)

Let's Practice!

- 1. A 22.0 gram sample of an unknown gas occupies 11.2 L at STP. Which of the following could be the identity of the gas?
 - a. CO₂ b. SO3 c. 0₂ d. He
- 2. A sample of oxygen gas at 50°C is heated, reaching a final temperature of 100°C. Which statement best describes the behavior of the gas molecules?
 - a. Their velocity increases by a factor of two.
 - b. Their velocity increases by a factor of four.
 - c. Their kinetic energy increases by a factor of two.
 - d. Their kinetic energy increases by a factor of less than two.
- 3. A mixture of gases contains 1.5 moles of oxygen, 3.0 moles of nitrogen, and 0.5 mole of water vapor. If the total pressure is 700 mmHg, what is the partial pressure of the nitrogen gas?
 - d. 420 mmHg a. 210 mmHg b. 280 mmHg c. 350 mmHg

- 4. If all of these flask are the same size, at the same temperature, and contain the same number of molecules, in which flask will the pressure be the highest? c. Flask 3
 - b. Flask 2 a. Flask 1
- d. All have the same pressure.

Totally Epic AP Chem Review: Lab Review!

Even if you haven't done the exact experiment being described in a question, you can use your knowledge and skills to account for the observations described.

Lab Question Hints

- 1. Materials: If they give you a list of equipment, you do NOT have to use all of it!
- 2. Procedure: Be sure to include important techniques like heating to constant mass, rinsing a precipitate, or rinsing the buret with solution before a titration.
- 3. Data needed: The data needed are values that can be measured like initial and final temperature. Writing all the mathematical equations needed to do the calculations will help you determine what data is needed.
- 4. Calculations: A calculation is made using what was measured, like temperature change. Show the set up of mathematical equations required for the calculations. Use sample data when appropriate.
- 5. Graphs: Be sure to label the axes and other important points on your graph.
- 6. Error analysis: State whether the quantity will be too high, too low, or no change. Use equations to help you determine what change will occur and to support your answer.

Common Lab Procedure: Colorimetry

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

 Light from an LED light source passes through a cuvette (tiny container) filled with a solution sample, as shown in the figure to the right.



Source

- · Some of the incoming light is absorbed by the solution. As a result, light of a lower 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 **colored**. 🙂

Beer's Law

A = abcA: 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 directly proportional to concentration (providing the absorbing substance, wavelength, and path length are fixed).
- By measuring the change in absorbance over time, you can use Beer's law to convert absorbance to concentration.
- Graphing [reactant] vs. time, In[reactant] vs. time, and 1/[reactant] vs time will allow you to determine if the reaction being studied is zero, first, or second order with respect to that reactant.

I ED

Errors Associated with Colorimetry				
Error	Effect on Data			
Cuvette (container) is smudged, cracked or otherwise unclear	Absorbance is too high (transmittance too low); some of the source light is blocked from passing through the solution $\rightarrow []$ too high			
Solution is accidently diluted (by extra water present, etc)	Absorbance is too low (transmittance is too high) [] too low			
Moved wavelength away from maximum absorption setting	Absorbance is too low (transmittance is too high) [] too low			

Common Lab Procedure: Calorimetry

Calorimetry: technique used to experimentally determine the change in energy of a chemical reaction or phase change by putting it in contact surroundings of known heat capacity.

- → The heat change in the water is **equal** and **opposite** to the energy change by the system!
 - The system can be an object, a phase change, or a chemical reaction.

 $+q_{H_2O} = -q_{system}$

 $+[mC\Delta T]_{H_2O} = -[mC\Delta T]_{system}$

- \rightarrow If water bath increases in temperature, it gained energy \rightarrow chemical reaction or phase change lost energy (- Δ H).
- \rightarrow If water bath decreases in temperature, it lost energy \rightarrow chemical reaction or phase change gained energy (+ Δ H).

Coffee cup calorimeter: Styrofoam cups are commonly used as insulators in the high school chemistry lab to measure temperature changes without a loss of energy to the surroundings.

 $q_{calorimeter} = -q_{reaction (or change)}$ (at constant pressure)

$$\Delta H_{rxn} = \frac{-q_{calorimeter}}{mol_{rxn}}$$

 \rightarrow Here $q_{calorimeter}$ is assumed to be the water in the coffee cup.

Errors Associated with Calorimetry				
Error	Effect on Data			
Heat is lost to the environment (container not perfectly insulated)	Calculated ΔH_{rxn} is too <u>low</u> , because ΔT (calculated from measurements) does not account for all of heat transferred			
Calorimeter (coffee cup) or thermometer absorbs heat	Calculated $\Delta H_{\rm rxn}$ is too low , because ΔT (calculated from measurements) does not account for all of heat transferred			

Watch out for masses in calorimetry!

• If there is an object: (for example, a steel cube), use separate masses of object and water!

=-[m(AT]

-1

-10

If there is a reaction or phase change: (for example, a salt dissolving in ٠ water), combine masses of water and reactants!

Common Lab Procedure: Titrations

A substance in a solution of known concentration (the titrant, usually in a buret) is reacted with another substance in a solution of **unknown** concentration (the **analyte**, usually in a flask or beaker)

- Equivalence point: the point at which the moles of each reactant are stoichiometrically equal to each other in solution: moles(titrant) = moles(analyte)
- End point: the point of the titration where an indicator changes color

How to Choose an Indicator

- Choose an indicator with **pK**_a of indicator = pH at the equivalence point of titration
- \circ K_a of the indicator \approx 1 x 10^{-pH @ eq pt}
- Indicator is a weak acid where HA and A⁻ are different colors!
- If $pH \le pK_a$ mostly HA (one color), if $pH > pK_a$ mostly A⁻ (different color)

Quick Reminder: How to Read a Buret

Burets, unlike most glassware, are read from the top down, not the bottom up!

Calculation Hints: Moles of titrant = moles of substance at equivalence point

- If substance analyzed is a solution/liquid:
 - \circ M₁V₁ = M₂V₂ @ equivalence point
 - Volume of titrant used to reach end point = difference between initial and final volumes
 - M_{titrant}V_{titrant added} = moles of titrant = moles of unknown
- If substance analyzed is a solid:
 - M_{titrant}V_{titrant added} = moles of titrant = moles of unknown @ equivalence point
 - Molecular weight of unknown = mass of solid dissolved

Potential Titration Lab Errors

	Error	Cause	Effect
1.	Over-titration	Going <u>past</u> equivalence point by adding too much titrant	Calculated moles of titrant and thus calculated moles of analyte are too large.
2.	Under-titration	Not reaching equivalence point by adding too little titrant	Calculated moles of titrant and thus calculated moles of analyte are too small.
3.	Water added to titrant (buret)	<u>Buret</u> still wet from rinsing when it is filled with titrant	Actual concentration of titrant is lower than marked, so more volume was added, thus calculated moles of analyte are too <u>large.</u>
4.	Water added to analyte (flask)	Flask or beaker is still wet from rinsing when analyte is added	Moles of analyte don't change, so <u>no effect</u> on calculated moles of analyte.

Random Lab Questions!

- 1. A 50 g sample of a metal is heated to 100°C and then placed in a calorimeter containing 100.0 g of water (c = 4.18 $J/g^{\circ}C$) at 20°C. The final temperature of the water is 24°C. Which metal was used?
 - a. Lead (c = 0.14 J/g°C) c. Iron (c = 0.45 J/g°C)
 - b. Copper (c = $0.20 \text{ J/g}^{\circ}\text{C}$) d. Aluminum (c = $0.89 \text{ J/g}^{\circ}\text{C}$)
- 2. Why are solutions of sodium chloride and magnesium nitrate unsuitable for analysis via colorimeter in a Beer-Lambert experiment?
 - a. Alkali metals and nitrates are always soluble and thus cannot be precipitated for analysis.
 - b. Both solutions are colorless, and as a result their absorbance will not vary with the concentration of solution.
 - c. Both sodium ions and magnesium ions are too corrosive when dissolved in water.
 - d. Neither chloride nor nitrate anions absorb wavelengths in the UV-VIS region of the electromagnetic spectrum.
- 3. Which of the following indicators would be most suitable for the titration of 0.10 M lactic acid (pKa = 3.08) with 0.10 M KOH(aq)?
 - a. phenol red (pK_a = 6.9) c. thymol blue (pK_a = 1.7)
 - **b.** alizarin blue ($pK_a = 10.2$) **d.** methyl orange ($pK_a = 3.4$)

Questions 4 – 5 refer to the following.

Inside a calorimeter, 100.0 mL of 1.0 M hydrocyanic acid (HCN), a weak acid, and 100.0 mL of 0.50 M sodium hydroxide are mixed. The temperature of the mixture rises from 21.5° C to 28.5° C. The specific heat of the mixture is approximately 4.2 J/g °C, and the density is identical to that of water.

4. What is the approximate amount of heat released during the reaction?

a. 1.5 kJ b. 2.9 kJ c. 5.9 kJ d. 11.8 kJ

5. If the experiment is repeated for a second time with 100.0 mL of 1.0 M HCN and 100.0 mL of 1.0 M NaOH, what would happen to the values for ΔT and ΔH_{rxn} (relative to the original experimental results)?

	ΔΤ	ΔH _{rxn}
(A)	Increase	Stay the same
(B)	Increase	Increase
(C)	Decrease	Stay the same
(D)	Stay the same	Increase

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Free Response Practice #1

2008 #2, shortened (5 points)

A student is given 2.94 g of a mixture containing anhydrous $MgCl_2$ and KNO_3 . To determine the percentage by mass of $MgCl_2$ in the mixture, the student uses excess $AgNO_3(aq)$ to precipitate the chloride ion as AgCl(s).

a. Starting with the 2.94 g sample of the mixture dissolved in water, briefly describe the steps necessary to quantitatively determine the mass of the AgCl precipitate.

- b. The student determines the mass of the AgCl precipitate to be 5.48 g. On the basis of this information, calculate each of the following.
 - i. The number of moles of $MgCl_2$ in the original mixture.

ii. The number of percent by mass of $MgCl_2$ in the original mixture.

AP Chemistly Exam Review

Free Response Practice #2



A student sets up a galvanic cell at 298 K that has an electrode of Ag(s) immersed in a 1.0 M solution of $Ag^+(aq)$ and an electrode of Cr(s) immersed in a 1.0 M solution of $Cr^{3+}(aq)$, as shown in the diagram above.

a. The student measures the voltage of the cell shown above and discovers that it is zero. Identify the missing component of the cell, and explain its importance for obtaining a nonzero voltage.

Half-Reaction	$E^{\circ}(\mathbf{V})$
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+ 0.80
$\operatorname{Cr}^{3+}(aq) + 3 e^{-} \rightarrow \operatorname{Cr}(s)$?

- b. The student adds the missing component to the cell and measures E^{o}_{cell} to be +1.54 V. As the cell operates, Ag⁺ ions are reduced. Use this information and the information in the table above to do the following.
 - i. Calculate the value of E° for the half-reaction $Cr^{3^+} + 3e^- \rightarrow Cr(s)$.
 - ii. Write the balanced net-ionic equation for the overall reaction that occurs as the cell operates.
 - iii. Calculate the value of ΔG° for the overall cell reaction in J/mol_{rxn}.

AP Chemistry Exam Review Free Response Practice #3

2017 #5 (4 points)

$2 \operatorname{C_3H_7OH}(l) + 9 \operatorname{O_2}(g) \rightarrow 6 \operatorname{CO_2}(g) + 8 \operatorname{H_2O}(g)$

A student performs an experiment to determine the enthalpy of combustion of 2-propanol, $C_3H_7OH(I)$, which combusts in oxygen according to the equation above. The student heats a sample of water by burning some of the $C_3H_7OH(I)$ that is in an alcohol burner, as represented below. The alcohol burner uses a wick to draw liquid up into the flame. The mass of $C_3H_7OH(I)$ combusted is determined by weighing the alcohol burner before and after combustion.



Initial

Final

Data from the experiment are given in the table below.

Mass of $C_3H_7OH(l)$ combusted	0.55 g
Mass of water heated	125.00 g
Initial temperature of water	22.0°C
Final temperature of water	51.1°C
Specific heat of water	4.18 J/(g·°C)

a. Calculate the magnitude of the heat energy, in kJ, absorbed by the water. (Assume that the energy released from the combustion is completely transferred to the water.)

b. Based on the experimental data, if one mole of $C_3H_7OH(I)$ is combusted, how much heat, in kJ, is released? Report your answer with the correct number of significant figures. c. A second student performs the experiment using the same mass of water at the same initial temperature. However, the student uses an alcohol burner containing C₃H₇OH(I) that is contaminated with water, which is miscible with C₃H₇OH(I). The difference in mass of the alcohol burner before and after the combustion in this experiment is also 0.55 g. Would the final temperature of the water in the beaker heated by the alcohol burner in this experiment be greater than, less than, or equal to the final temperature of the water in the beaker in the first student's experiment? Justify your answer.

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Free Response Practice #4

2016 #2, shortened (5 points)

 $NaHCO_3(s) + HC_2H_3O_2(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$

A student designs an experiment to study the reaction between NaHCO₃ and HC₂H₃O₂. The reaction is represented by the equation above. The student places 2.24 g of NaHCO₃ in a flask and adds 60.0 mL of 0.875 M HC₂H₃O₂. The student observes the formation of bubbles and the flask gets cooler as the reaction proceeds.

a. Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.

b. The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

- c. In thermodynamics terms, a reaction can be driven by enthalpy, entropy, or both.
 - i. Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between NaHCO₃(s) and HC₂H₃O₂(aq)? Answer by drawing a circle around one of the choices below.

Enthalpy only

Entropy only

Both enthalpy and entropy

ii. Justify your selection is part (d)(i) in terms of ΔG° .

AP Chemistry₂Exam Review Free Response Practice #5

$2 \text{ NO(g)} + \text{Br}_2(g) \rightarrow 2 \text{ NOBr(g)}$

	Initial Concentration (mol/L)		Initial Rate of Appearance
Experiment	[NO]	[Br ₂]	of NOBr (M/sec)
1	0.02	0.02	9.6 × 10-2
2	0.04	0.02	3.8 × 10 ⁻¹
3	0.02	0.04	$1.9 imes 10^{-1}$

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

a. Write the rate law for the reaction. Justify. [3 points]

b. Calculate the value of the rate constant, k, for the reaction. Include units. [2 points]

- c. Determine the initial rate of the reaction in experiment 1. [1 point]
- d. Which sof the following reaction mechanisms is consistent with the rate law established in (a)? Explain your choice. [2 points]

I. NO + NO
$$\rightleftharpoons$$
 N₂O₂ (fast)
N₂O₂ + Br₂ \rightarrow 2NOBr (slow)
II. Br₂ \rightarrow Br + Br (slow)

 $2(NO + Br \rightarrow NOBr)$ (fast)

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Free Response Practice #6

1.

 $NH_4HS(s) \leftrightarrow NH_3(g) + H_2S(g)$ $\Delta H^\circ = +93$ kilojoules

The equilibrium above is established by placing solid NH₄HS in an evacuated container at 25°C. At equilibrium, some solid NH₄HS remains in the container. Predict and explain each of the following.

a) The effect on the equilibrium partial pressure of NH₃ gas when additional solid NH₄HS is introduced into the container.

b) The effect on the equilibrium partial pressure of NH₃ gas when additional solid H₂S is introduced into the container. (Hint: H₂S(s) readily sublimes into H₂S(g).)

c) The effect on the mass of solid NH₄HS present and the value of the equilibrium constant when the volume of the container is decreased.

d) The effect on the mass of solid NH₄HS present and the value of the equilibrium constant when the temperature is increased.

AP Chemistr<u>w</u> **F**xam Review

Free Response Practice #7

2015 #4 (4 points)

Answer the following questions about the solubility of Ca(OH)₂ ($K_{sp} = 1.3 \times 10^{-6}$).

a. Write a balanced chemical equation for the dissolution of $Ca(OH)_2$ in pure water.

b. Calculate the molar solubility of Ca(OH)₂ in 0.10 M Ca(NO₃)₂.

c. In the box below, complete a particle representation diagram that includes <u>four</u> water molecules with proper orientation around the Ca²⁺ ion.

Represent water molecules as

Ca ²⁺	

AP Chemistry Exam Review

Free Response Practice #8

2017 #3, shortened, 5 points

Nitrogen monoxide, NO(g), can undergo reactions to produce acids such as HNO₂, a weak acid with a K_a of 4.0 x 10⁻⁴ and a pK_a of 3.40.

- a. A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M HNO₂(aq) and 0.100 M NaOH(aq).
 - i. Explain why the addition of 0.100 M NaOH(aq) to 0.100 M HNO₂(aq) can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the NaOH(aq) to the HNO₂(aq).

ii. Determine the volume, in mL, of 0.100 M NaOH(aq) the student should add to 100. mL of 0.100 M HNO₂(aq). to make a buffer solution with a pH of 3.40. Justify your answer.

b. A second student makes a buffer by dissolving 0.100 mol of NaNO₂(s) in 100. mL of 1.00 M HNO₂(aq). Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c)? Justify your answer.

AP Chemiztry Exam Review Free Response Practice #9

2018 #3, shortened, (4 points)

Answer the following questions relating to Fe and its ions, Fe²⁺ and Fe³⁺.

a. Write the ground-state electron configuration of the Fe²⁺ ion.

Ion	Ionic Radius (pm)
Fe ²⁺	92
Fe ³⁺	79

b. The radii of the ions are given in the table above. Using principles of atomic structure, explain why the radius of the Fe²⁺ ion is larger than the radius of the Fe³⁺ ion.

c. Fe³⁺ ions interact more strongly with water molecules in aqueous solution than Fe²⁺ ions do. Give one reason for this stronger interaction, and justify your answer using Coulomb's law.

A student obtains a solution that contains an unknown concentration of $Fe^{2+}(aq)$. To determine the concentration of $Fe^{2+}(aq)$ in the solution, the student titrates a sample of the solution with $MnO_4^{-}(aq)$, which converts $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$, as represented by the following equation.

 $5 \text{ Fe}^{2+}(aq) + \text{MnO}_4^{-}(aq) + 8 \text{ H}^+(aq) \rightarrow 5 \text{ Fe}^{3+}(aq) + \text{Mn}^{2+}(aq) + 4 \text{ H}_2\text{O}(l)$

d. Write the balanced equation for the half-reaction for the oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$.

AP Chemistry Exam Review Free Response Practice #10

2017 #4 (4 points)



A student investigates various dyes using paper chromatography. The student has samples of three pure dyes, labeled A, B, and C, and an unknown sample that contains one of the three dyes. The student prepares the chromatography chambers shown above on the left by putting a drop of each dye at the indicated position on the chromatography paper (a polar material) and standing the paper in a nonpolar solvent. The developed chromatograms are shown above on the right.

a. Which dye (A, B, or C) is the least polar? Justify your answer in terms of the interactions between the dyes and the solvent or between the dyes and the paper.

b. Which dye is present in the unknown sample? Justify your answer.

AP Chemistry Exam Review

Free Response Practice #11

2018 #4 (4 points)

Sulfur atom = \bigcirc Carbon atom = \bigcirc Oxygen atom = \bigcirc				
Compound	Molecular Structure	Boiling Point at 1 atm (K)		
CS ₂		319		
COS		223		

The table above gives the molecular structure and boiling points for the compounds CS₂ and COS.

a. In terms of the types and relative strengths of all the intermolecular forces in each compound, explain why the boiling point of $CS_2(I)$ is higher than that of COS(I).

A 10.0 g sample of CS₂(*I*) is put in an evacuated 5.0 L rigid container. The container is sealed and heated to 325 K, at which temperature all of the CS₂(*I*) has vaporized. What is the pressure in the container once all of the CS₂(*I*) has vaporized?

Begin your response to **QUESTION 1** on this page.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

For each question, show your work for each part in the space provided after that part. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

$$\text{HCOOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCOO}^-(aq) \qquad K_a = 1.8 \times 10^{-4}$$

1. Methanoic acid, HCOOH, ionizes according to the equation above.

(a) Write the expression for the equilibrium constant, K_a , for the reaction.

(b) Calculate the pH of a 0.25 *M* solution of HCOOH.

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Continue your response to **QUESTION 1** on this page.

(c) In the box below, complete the Lewis electron-dot diagram for HCOOH. Show all bonding and nonbonding valence electrons.



$$H_2NNH_2(aq) + H_2O(l) \rightleftharpoons H_2NNH_3^+(aq) + OH^-(aq)$$
 $K_b = 1.3 \times 10^{-6}$

(d) In aqueous solution, the compound H_2NNH_2 reacts according to the equation above. A 50.0 mL sample of 0.25 *M* $H_2NNH_2(aq)$ is combined with a 50.0 mL sample of 0.25 *M* HCOOH(aq).

(i) Write the balanced net ionic equation for the reaction that occurs when H_2NNH_2 is combined with HCOOH.

(ii) Is the resulting solution acidic, basic, or neutral? Justify your answer.

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Continue your response to **QUESTION 1** on this page.

When a catalyst is added to a solution of HCOOH(aq), the reaction represented by the following equation occurs. $HCOOH(aq) \rightarrow H_2(g) + CO_2(g)$

(e) Is the reaction a redox reaction? Justify your answer.



(f) The reaction occurs in a rigid 4.3 L vessel at 25°C, and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of $CO_2(g)$ produced in the reaction. (Assume that the amount of $CO_2(g)$ dissolved in the solution is negligible.)

(g) After the reaction has proceeded for several minutes, does the amount of catalyst increase, decrease, or remain the same? Justify your answer.

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Begin your response to **QUESTION 2** on this page.

- 2. Answer the following questions about the element Si and some of its compounds.
 - (a) The mass spectrum of a pure sample of Si is shown below.



- (i) How many protons and how many neutrons are in the nucleus of an atom of the most abundant isotope of Si ?
- (ii) Write the ground-state electron configuration of Si.

Two compounds that contain Si are SiO₂ and SiH₄.

(b) At 161 K, SiH₄ boils but SiO₂ remains as a solid. Using principles of interparticle forces, explain the difference in boiling points.

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At high temperatures, SiH₄ decomposes to form solid silicon and hydrogen gas.

(c) Write a balanced equation for the reaction.

A table of absolute entropies of some substances is given below.

Substance	$S^{\circ} (J/(mol \cdot K))$
$H_2(g)$	131
Si(s)	18
$SiH_4(g)$	205

(d) Explain why the absolute molar entropy of Si(s) is less than that of $H_2(g)$.

(e) Calculate the value, in $J/(\text{mol} \cdot K)$, of ΔS° for the reaction.

(f) The reaction is thermodynamically favorable at all temperatures. Explain why the reaction occurs only at high temperatures.

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(g) A partial photoelectron spectrum of pure Si is shown below. On the spectrum, draw the missing peak that corresponds to the electrons in the 3p sublevel.



(h) Using principles of atomic structure, explain why the first ionization energy of Ge is lower than that of Si.

(i) A single photon with a wavelength of 4.00×10^{-7} m is absorbed by the Si sample. Calculate the energy of the photon in joules.

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3. A student is given the task of determining the molar concentration of a CuSO₄ solution using two different procedures, precipitation and spectrophotometry.

For the precipitation experiment, the student adds 20.0 mL of $0.200 M \text{ Ba}(\text{NO}_3)_2$ to 50.0 mL of the $\text{CuSO}_4(aq)$. The reaction goes to completion, and a white precipitate forms. The student filters the precipitate and dries it overnight. The data are given in the following table.

Mass of dry filter paper	0.764 g
Volume of $CuSO_4(aq)$	50.0 mL
Volume of 0.200 M Ba(NO ₃) ₂	20.0 mL
Mass of filter paper and dried precipitate	1.136 g

- (a) Write a balanced net ionic equation for the precipitation reaction.
- (b) Calculate the number of moles of precipitate formed.

(c) Calculate the molarity of the original $CuSO_4$ solution.

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For the spectrophotometry experiment, the student first makes a standard curve. The student uses a 0.1000 M solution of CuSO₄(aq) to make three more solutions of known concentration (0.0500 M, 0.0300 M, and 0.0100 M) in 50.00 mL volumetric flasks.

(d) Calculate the volume of 0.1000 M CuSO₄(aq) needed to make 50.00 mL of 0.0500 M CuSO₄(aq).

(e) Briefly describe the procedure the student should follow to make 50.00 mL of 0.0500 *M* CuSO₄(*aq*) using 0.1000 *M* CuSO₄(*aq*), a 50.00 mL volumetric flask, and other standard laboratory equipment. Assume that all appropriate safety precautions will be taken.

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The standard curve is given below.



(f) The absorbance of the $CuSO_4$ solution of unknown concentration is 0.219. Determine the molarity of the solution.

(g) A second student performs the same experiment. There are a few drops of water in the cuvette before the second student adds the $CuSO_4(aq)$ solution of unknown concentration. Will this result in a $CuSO_4(aq)$ concentration for the unknown that is greater than, less than, or equal to the concentration determined in part (f) ? Justify your answer.

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Begin your response to **QUESTION 4** on this page.

$$4 \operatorname{Fe}(s) + 3 \operatorname{O}_2(g) \rightarrow 2 \operatorname{Fe}_2 \operatorname{O}_3(s) \quad \Delta H^\circ = -1650 \,\mathrm{kJ} \,/ \,\mathrm{mol}_{rxn}$$

4. A student investigates a reaction used in hand warmers, represented above. The student mixes Fe(s) with a catalyst and sand in a small open container. The student measures the temperature of the mixture as the reaction proceeds. The data are given in the following table.

Time (min)	Temperature of Mixture (°C)
0	22.0
1	25.1
2	34.6
3	37.3
4	39.7
5	39.4

(a) The mixture (Fe(s), catalyst, and sand) has a total mass of 15.0 g and a specific heat capacity of 0.72 J/(g.°C). Calculate the amount of heat absorbed by the mixture from 0 minutes to 4 minutes.

(b) Calculate the mass of Fe(s), in grams, that reacted to generate the amount of heat calculated in part (a).

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(c) In a second experiment, the student uses twice the mass of iron as that calculated in part (b) but the same mass of sand as in the first experiment. Would the maximum temperature reached in the second experiment be greater than, less than, or equal to the maximum temperature in the first experiment? Justify your answer.

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5. Molten $MgCl_2$ can be decomposed into its elements if a sufficient voltage is applied using inert electrodes. The products of the reaction are liquid Mg (at the cathode) and Cl_2 gas (at the anode). A simplified representation of the cell is shown above. The reduction half-reactions related to the overall reaction in the cell are given in the table.

(a) Draw an arrow on the diagram to show the direction of electron flow through the external circuit as the cell operates.

(b) Would an applied voltage of 2.0 V be sufficient for the reaction to occur? Support your claim with a calculation as part of your answer.

(c) If the current in the cell is kept at a constant 5.00 amps, how many seconds does it take to produce 2.00 g of Mg(l) at the cathode?

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Begin your response to **QUESTION 6** on this page.

6. A student is studying the properties of $CaSO_4$ and $PbSO_4$. The student has samples of both compounds, which are white powders.

(a) The student tests the electrical conductivity of each solid and observes that neither solid conducts electricity. Describe the structures of the solids that account for their inability to conduct electricity.

The student places excess $CaSO_4(s)$ in a beaker containing 100 mL of water and places excess $PbSO_4(s)$ in another beaker containing 100 mL of water. The student stirs the contents of the beakers and then measures the electrical conductivity of the solution in each beaker. The student observes that the conductivity of the solution in the beaker containing the $CaSO_4(s)$ is higher than the conductivity of the solution in the beaker containing the $PbSO_4(s)$.

(b) Which compound is more soluble in water, $CaSO_4(s)$ or $PbSO_4(s)$? Justify your answer based on the results of the conductivity test.

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The left side of the diagram below shows a particulate representation of the contents of the beaker containing the $CaSO_4(s)$ from the solution conductivity experiment.



(c) Draw a particulate representation of $PbSO_4(s)$ and the ions dissolved in the solution in the beaker on the right in the diagram. Draw the particles to look like those shown to the right of the beaker. Draw an appropriate number of dissolved ions relative to the number of dissolved ions in the beaker on the left.

(d) The student attempts to increase the solubility of $CaSO_4(s)$ by adding 10.0 mL of 2 M H₂SO₄(aq) to the beaker, and observes that additional precipitate forms in the beaker. Explain this observation.

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7. A student investigates gas behavior using a rigid cylinder with a movable piston of negligible mass, as shown in the diagram above. The cylinder contains 0.325 mol of $O_2(g)$.

(a) The cylinder has a volume of 7.95 L at 25°C and 1.00 atm. Calculate the density of the $O_2(g)$, in g/L, under these conditions.

(b) Attempting to change the density of the $O_2(g)$, the student opens the valve on the side of the cylinder, pushes down on the piston to release some of the gas, and closes the valve again. The temperature of the gas remains constant at 25°C. Will this action change the density of the gas remaining in the cylinder? Justify your answer.

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(c) The student tries to change the density of the $O_2(g)$ by cooling the cylinder to $-55^{\circ}C$, which causes the volume of the gas to decrease. Using principles of kinetic molecular theory, explain why the volume of the $O_2(g)$ decreases when the temperature decreases to $-55^{\circ}C$.

(d) The student further cools the cylinder to -180° C and observes that the measured volume of the $O_2(g)$ is substantially smaller than the volume that is calculated using the ideal gas law. Assume all equipment is functioning properly. Explain why the measured volume of the $O_2(g)$ is smaller than the calculated volume. (The boiling point of $O_2(l)$ is -183° C.)

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150 Polyatomic Ions

1st six-weeks

<u>N</u>ick the <u>C</u>amel <u>ate</u> an <u>I</u>cky <u>Cl</u>am for <u>S</u>upper in <u>P</u>hoenix with his <u>Br</u>os

NO_3^-	nitrate	ClO ₃ ⁻ chlorate		PO ₃ ³⁻ pho	osphite
NO_2^-	nitrite	ClO ₂ ⁻ chlorite		BrO ₃ ⁻ bro	mate
CO_{3}^{2-}	carbonate	SO ₄ ^{2–} sulfate		BrO ₂ ⁻ bro	mite
IO_3^-	iodate	SO ₃ ^{2–} sulfite		Consonants	= # of Oxygen
IO ₂ -	iodite	PO ₄ ^{3–} phosphate		Vowels = Ch	arge
2 nd six	-weeks				Difference in
ClO ₄ ⁻	perchlorate	IO ⁻ hypoiodite			Oxygen from ATE
ClO-	hypochlorite	BrO ₄ ⁻ perbromate		Perate	+1
10	neriodate	BrO^- hypohromite		Ate	0
104	periodate	bio hypobronnice		Hypoite	-2
3 rd six	weeks				
H ₂ PO ₄ -	dihydrogen phosphate		HCO ₃ -	hydrogen carbonate	or bicarbonate
HPO ₄ ²⁻	hydrogen phosphate		HSO ₄ -	hydrogen sulfate	
4 th six-	weeks				
NH ₄ +	ammonium		OH-	hydroxide	
C ₂ H ₃ O ₂	[−] or CH ₃ COO [−] acetate		H_3O^+	hydronium	
5 th six-	weeks				
MnO ₄ -	permanganate	CrO ₄ ^{2–} chromate			
CN-	cyanide	$Cr_2O_7^{2-}$ dichromate			
6 th six	weeks				
				Acid Nome	nclature
O_2^{2-}	peroxide	$C_4H_4O_6^{2-}$ tartrate		Binary	Hydroic
$S_2O_3^{2-}$	thiosulfate	$C_2O_4^{2-}$ oxalate		ite	OUS

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PERIODIC TABLE OF THE ELEMENTS

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)	$\begin{array}{rcl}mm \ Hg &=& millimeters \ of \ mercury\\ J, \ kJ &=& joule(s), \ kilojoule(s)\\ V &=& volt(s)\\ mol &=& mole(s)\end{array}$
ATOMIC STRUCTURE $E = hv$ $c = \lambda v$	$E = \text{energy}$ $\nu = \text{frequency}$ $\lambda = \text{wavelength}$ Planck's constant, $h = 6.626 \times 10^{-34} \text{ J s}$ Speed of light, $c = 2.998 \times 10^8 \text{ m s}^{-1}$ Avogadro's number = $6.022 \times 10^{23} \text{ mol}^{-1}$ Electron charge, $e = -1.602 \times 10^{-19}$ coulomb
EQUILIBRIUM $K_{c} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}, \text{ where } a \text{ A} + b \text{ B} \rightleftharpoons c \text{ C} + d \text{ D}$ $K_{p} = \frac{(P_{C})^{c}(P_{D})^{d}}{(P_{A})^{a}(P_{B})^{b}}$ $K_{a} = \frac{[H^{+}][A^{-}]}{[HA]}$ $K_{b} = \frac{[OH^{-}][HB^{+}]}{[B]}$ $K_{w} = [H^{+}][OH^{-}] = 1.0 \times 10^{-14} \text{ at } 25^{\circ}\text{C}$ $= K_{a} \times K_{b}$ $p\text{H} = -\log[H^{+}], \text{ pOH} = -\log[OH^{-}]$ $14 = p\text{H} + p\text{OH}$ $p\text{H} = pK_{a} + \log\frac{[A^{-}]}{[HA]}$ $pK_{a} = -\log K_{a}, \text{ p}K_{b} = -\log K_{b}$	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 $t_{1/2} = \text{half-life}$

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GASES, LIQUIDS, AND SOLUTIONS	P = pressure
	V = volume
PV = nRT	T = temperature
$P_A = P_{\text{total}} \times X_A$, where $X_A = \frac{\text{moles } A}{1 + 1 + 1 + 1}$	n = number of moles
A total moles	m = mass
$P_{total} = P_{\rm A} + P_{\rm B} + P_{\rm C} + \dots$	M = molar mass
m	D = density
$n = \frac{m}{M}$	KE = kinetic energy
$K = {}^{\circ}C + 273$	v = velocity
	A = absorbance
$D = \frac{m}{V}$	a = molar absorptivity
	b = path length
KE per molecule = $\frac{1}{2}mv^2$	c = concentration
Molarity, $M =$ moles of solute per liter of solution	Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{K}^{-1}$
A = abc	$= 0.08206 \text{ L} \text{ atm mol}^{-1} \text{ K}^{-1}$
$m = u \sigma c$	$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$
	1 atm = 760 mm Hg = 760 torr
	STP = 273.15 K and 1.0 atm
	Ideal gas at STP = 22.4 L mol^{-1}
THERMODYNAMICS/ELECTROCHEMISTRY	- heet
	q = heat
$q = mc\Delta T$	m = mass
$\Delta S^{\circ} = \sum S^{\circ}$ products $-\sum S^{\circ}$ reactants	T = temperature
	$S^{\circ} = \text{standard entropy}$
$\Delta H^{\circ} = \sum \Delta H_f^{\circ} \text{ products} - \sum \Delta H_f^{\circ} \text{ reactants}$	$H^{\circ} = \text{standard entropy}$
	G° = standard Gibbs free energy
$\Delta G^{\circ} = \sum \Delta G_f^{\circ}$ products $-\sum \Delta G_f^{\circ}$ reactants	n = number of moles
	E° = standard reduction potential
$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$	I = current (amperes)
$= -RT \ln K$	q = charge (coulombs)
$= -nFE^{\circ}$	t = time (seconds)
$I = \frac{q}{t}$	Faraday's constant, $F = 96,485$ coulombs per mole
	$1 \text{ volt} = \frac{1 \text{ joure}}{1 \text{ coulomb}}$

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		17	, - ,	6	Н	19.00	17	CI	35.45	35	Br	79.90	53	Ι	126.91	85	At	(210)				ī	/1	Lu	174.97	103	Lr	(262)
		16		∞	0	16.00	16	S	32.06	34	Se	78.96	52	Te	127.60	84	Po	(209)				C T	/0	Чh	173.04	102	No	(229)
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		13		S	В	10.81	13	AI	26.98	31	Ga	69.72	49	In	114.82	81	T	204.38				ŗ	9/	Ho	164.93	66	Es	(252)
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