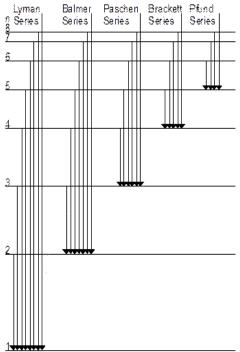
AP Chemistry First Semester Review

- 1. Answer the following questions regarding an arsenic atom.
 - (a) Write the ground state electron configuration for an arsenic atom, showing the number of electrons in each subshell.
 - (b) Give one permissible set of four quantum numbers for each of the outermost electrons in a single As atom when it is in its ground state.

- (c) Is an isolated arsenic atom in the ground state paramagnetic or diamagnetic? Explain briefly.
- (d) Explain how the electron configuration of the arsenic atom in the ground state is consistent with the existence of the following known compounds: Na₃As, AsCl₃, and AsF₅.

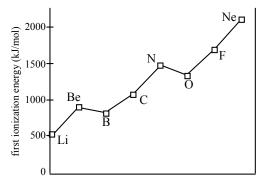
- 2. The emission spectrum of hydrogen consists of several series of sharp emission lines in the ultraviolet (Lyman series) in the visible (Balmer series) and in the infrared (Paschen series, Brackett series, etc.) regions of the spectrum.
 - (a) What feature of the electronic energies of the hydrogen atom explains why the emission spectrum consists of discrete wavelength rather than a continuum wavelength?
 - (b) Account for the existence of several series of lines in the spectrum. What quantity distinguishes one series of lines from another?

(c) Examine the electronic energy level diagram for the hydrogen atom and indicate on it the transition corresponding to the line of lowest frequency in the Balmer series.



(d) What is the difference between an emission spectrum and an absorption spectrum? Explain why the absorption spectrum of atomic hydrogen at room temperature has only the lines of the Lyman series.

- 3. Use the details of modern atomic theory to explain each of the following experimental observations.
 - (a) Within a family such as the alkali metals, the ionic radius increases as the atomic number increases.
 - (b) The radius of the chlorine atom is smaller than the radius of the chloride ion, Cl⁻. (Radii : Cl atom = 0.99Å; Cl⁻ ion = 1.81Å)
 - (c) The first ionization energy of aluminum is lower than the first ionization energy of magnesium. (First ionization energies: ${}_{12}Mg = 7.6 \text{ ev}; {}_{13}Al = 6.0 \text{ ev}$)
 - (d) For magnesium, the difference between the second and third ionization energies is much larger than the difference between the first and second ionization energies. (Ionization energies for Mg: $1^{st} = 7.6$ ev; $2^{nd} = 14$ ev; $3^{rd} = 80$ ev)



- 4. The diagram shows the first ionization energies for the elements from Li to Ne. Briefly (in one to three sentences) explain each of the following in terms of atomic structure.
 - (a) In general, there is an increase in the first ionization energy from Li to Ne.
 - (b) The first ionization energy of B is lower than that of Be.
 - (c) The first ionization energy of O is lower than that of N.
 - (d) Predict how the first ionization energy of Na compares to those of Li and of Ne. Explain.
- 5. Account for each of the following in terms of principles of atom structure, including the number, properties, and arrangements of subatomic particles.
 - (a) The second ionization energy of sodium is about three times greater than the second ionization energy of magnesium.

(b) The difference between the atomic radii of Na and K is relatively large compared to the difference between the atomic radii of Rb and Cs.

(c) A sample of nickel chloride is attracted into a magnetic field, whereas a sample of solid zinc chloride is not.

(d) Phosphorus forms the fluorides PF3 and PF5, whereas nitrogen forms only NF3.

6. Discuss briefly the relationship between the dipole moment of a molecule and the polar character of the bonds within it. With this as the basis, account for the difference between the dipole moments of CH_2F_2 and CF_4 .

 7. The boiling points of the following compounds increase in the order in which they are listed below: CH₄ < H₂S < NH₃

 Discuss the theoretical considerations involved and use them to account for this order.

8. Suppose that a molecule has the formula AB₃. Sketch and name two different shapes that this molecule may have. For each of the two shapes, give an example of a known molecule that has that shape. For one of the molecules you have named, interpret the shape in the context of a modern bonding theory.

9. Butane, chloroethane, acetone, and 1-propanol all have approximately the same molecular weights. Data on their boiling points and solubilities in water are listed in the table below.

		Boiling	Solubility in
Compound	Formula	Pt.(°C)	water
Butane	CH ₃ CH ₂ CH ₂ CH ₃	0	insoluble
Chloroethane	CH ₃ CH ₂ Cl	12	insoluble
Acetone	O ∥ CH3CCH3	56	completely miscible
1-Propanol	CH ₃ CH ₂ CH ₂ OH	97	completely miscible

On the basis of dipole moments (molecular polarities) and/or hydrogen bonding, explain in a qualitative way the differences in the

- (a) boiling points of butane and chloroethane.
- (b) water solubilities of chloroethane and acetone.
- (c) water solubilities of butane and 1-propanol.
- (d) boiling points of acetone and 1-propanol.
- 10. Answer the following questions:
 - (a) Draw the Lewis electron–dot structures for CO_3^{2-} , CO_2 , and CO, including resonance structures where appropriate.

- (b) Which of the three species has the shortest C-O bond length? Explain the reason for your answer.
- (c) Predict the molecular shapes for the three species. Explain how you arrived at your predictions.

11. The values of the first three ionization energies (I_1, I_2, I_3) for magnesium and argon are as follows:

		I ₁ (kJ/mol)	I ₂ (kJ/mol)	I ₃ (kJ/mol)
Μ	g	735	1443	7730
A	[1525	2665	3945

- (a) Give the electronic configurations of Mg and Ar.
- (b) In terms of these configurations, explain why the values of the first and second ionization energies of Mg are significantly lower than the values for Ar, whereas the third ionization energy of Mg is much larger than the third ionization energy of Ar.
- (c) If a sample of Ar in one container and a sample of Mg in another container are each heated and chlorine is passed into each container, what compounds, if any, will be formed? Explain in terms of the electronic configurations given in part (a).
- (d) Element Q has the following first three ionization energies:

	I ₁ (kJ/mol)	I ₂ (kJ/mol)	I ₃ (kJ/mol)
Q	496	4568	6920

What is the formula for the most likely compound of element Q with chlorine? Explain the choice of formula on the basis of the ionization energies.

12. Use the following table to answer the following questions:

Substance	Melting Point, °C
Н2	-259
C ₃ H ₈	-190
HF	-92
CsI	621
LiF	870
SiC	>2,000

- (a) Discuss how the trend in the melting points of the substances tabulated above can be explained in terms of the types of attractive forces and/or bonds in these substances.
- (b) For any pairs of substances that have the same kind(s) of attractive forces and/or bonds, discuss the factors that cause variations in the strengths of the forces and/or bonds.

13. Nitrogen is the central atom in each of the species given below.

$$NO_2$$
 $NO_2^ NO_2^+$

(a) Draw the Lewis electron-dot structure for each of the three species.

- (b) List the species in order of increasing bond angle. Justify your answer.
- (c) Select one of the species and give the hybridization of the nitrogen atom in it.
- (d) Identify the only one of the species that dimerizes and explain what causes it to do so.
- 14. A 0.964 gram sample of a mixture of sodium formate and sodium chloride is analyzed by adding sulfuric acid. The equation for the reaction for sodium formate with sulfuric acid is shown below. The carbon monoxide formed measures 242 milliliters when collected over water at 752 torr and 22.0°C. Calculate the percentage of sodium formate in the original mixture.

 $2 \text{ HCOONa} + \text{H}_2\text{SO}_4 \rightarrow 2 \text{ CO} + 2 \text{ H}_2\text{O} + \text{Na}_2\text{SO}_4$

15. Three volatile compounds X, Y, and Z each contain element Q. The percent by weight of element Q in each compound was determined. Some of the data obtained are given below.

Compound	Percent by Weight of Element Q	Molecular Weight
Х	64.8%	?
Y	73.0%	104.
Ζ	59.3%	64.0

- (a) The vapor density of compound X at 27 degrees Celsius and 750. mm Hg was determined to be 3.53 grams per liter. Calculate the molecular weight of compound X.
- (b) Determine the mass of element Q contained in 1.00 mole of each of the three compounds.
- (c) Calculate the most probable value of the atomic weight of element Q.
- (d) Compound Z contains carbon, hydrogen, and element Q. When 1.00 gram of compound Z is oxidized and all of the carbon and hydrogen are converted to oxides, 1.37 grams of CO₂ and 0.281 gram of water are produced. Determine the most probable molecular formula.
- 16. A mixture of H₂(g), O₂(g), and 2 millilitres of H₂O(l) is present in a 0.500 litre rigid container at 25°C. The number of moles of H₂ and the number of moles of O₂ are equal. The total pressure is 1,146 millimetres mercury. (The equilibrium vapor pressure of pure water at 25°C is 24 millimetres mercury.) The mixture is sparked, and H₂ and O₂ react until one reactant is completely consumed.
 - (a) Identify the reactant remaining and calculate the number of moles of the reactant remaining.
 - (b) Calculate the total pressure in the container at the conclusion of the reaction if the final temperature is 90°C. (The equilibrium vapor pressure of water at 90°C is 526 millimetres mercury.)

- (c) Calculate the number of moles of water present <u>as vapor</u> in the container at 90°C.
- 17. An experiment is performed to determine the empirical formula of a copper iodide formed by direct combination of elements. A clean strip of copper metal is weighed accurately. It is suspended in a test tube containing iodine vapor generated by heating solid iodine. A white compound forms on the strip of copper, coating it uniformly. The strip with the adhering compound is weighed. Finally, the compound is washed completely from the surface of the metal and the clean strip is dried and reweighed.

DATA TABLE	
Mass of clean copper strip	1.2789 grams
Mass of copper strip and compound	1.2874 grams
Mass of copper strip after washing	1.2748 grams

- (a) State how you would use the data above to determine each of the following. (<u>Calculations not required</u>.)
 (1) The number of moles of iodine that reacted
 - (2) The number of moles of copper that reacted
- (b) Explain how you would determine the empirical formula for the copper iodide.
- (c) Explain how each of the following would affect the empirical formula that could be calculated.
 (1) Some unreacted iodine condensed on the strip.
 - (2) A small amount of the white compound flaked off before weighing.
- 18. Four bottles, each containing about 5 grams of finely powdered white substance, are found in a laboratory. Near the bottles are four labels specifying high purity and indicating that the substances are glucose ($C_6H_{12}O_6$), sodium chloride (NaCl), aluminum oxide (Al_2O_3), and zinc sulfate (ZnSO₄). Assume that these labels belong to the bottles and that each bottle contains a single substance. Describe the tests that you could conduct to determine which label belongs to which bottle. Give the results you would expect for each test.

- 19. Answer the following questions:
 - (a) A solution containing 3.23 grams of an unknown compound dissolved in 100.0 grams of water freezes at -0.97°C. The solution does not conduct electricity. Calculate the molecular weight of the compound. (The molal freezing point depression constant for water is 1.86°C kg mole⁻¹)

(b) Elemental analysis of this unknown compound yields the following percentages by weight H=9.74%; C=38.70%; O=51.56%. Determine the molecular formula for the compound.

(c) Complete combustion of a 1.05 gram sample of the compound with the stoichiometric amount of oxygen gas produces a mixture of H₂O(g) and CO₂(g). What is the pressure of this gas mixture when it is contained in a 3.00 liter flask at 127°C?

- 20. The molecular formula of a hydrocarbon is to be determined by analyzing its combustion products and investigating its colligative properties.
 - (a) The hydrocarbon burns completely, producing 7.2 grams of water and 7.2 liters of CO₂ at standard conditions. What is the empirical formula of the hydrocarbon?
 - (b) Calculate the mass in grams of O_2 required for the complete combustion of the sample of the hydrocarbon described in (a).

- (c) The hydrocarbon dissolves readily in CHCl₃. The freezing point of a solution prepared by mixing 100. grams of CHCl₃ and 0.600 gram of the hydrocarbon is -64.0°C. The molal freezing-point depression constant of CHCl₃ is 4.68°C/molal and its normal freezing point is -63.5°C. Calculate the molecular weight of the hydrocarbon.
- (d) What is the molecular formula of the hydrocarbon?

21. The data in the table below were determined at 25°C.

 $CO(g) + 2 H_2(g) / CH_3OH(l) \quad \Delta H^\circ = -128.1 \text{ kJ}$

	ΔH_{f}° (kJ mol ⁻¹)	ΔG_{f}° (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)
CO(g)	-110.5	-137.3	+197.9
CH ₃ OH(l)	-238.6	-166.2	+126.8

(a) Calculate ΔG° for the reaction above at 25°C.

- (b) Calculate K_{eq} for the reaction above at 25°C.
- (c) Calculate ΔS° for the reaction above at 25°C.

(d) In the table above, there are no data for H₂. What are the values of ΔH_{f}° , ΔG_{f}° , and of the absolute entropy, S°, for H₂ at 25°C?

Substance	Standard Heat of Formation, ΔH_{f}° , in kJ mol ⁻¹	Absolute Entropy, S°, in J mol ⁻¹ K ⁻¹
C(s)	0.00	5.69
$CO_2(g)$	-393.5	213.6
H ₂ (g)	0.00	130.6
H ₂ O(l)	-285.85	69.91
O ₂ (g)	0.00	205.0
C ₃ H ₇ COOH(l)	?	226.3

22. The enthalpy change for the combustion of butyric acid at 25°C, ΔH°_{comb} , is -2,183.5 kilojoules per mole. The combustion reaction is $C_3H_7COOH(l) + 5 O_2(g) \rightarrow 4 CO_2(g) + 4 H_2O(l)$

(a) From the above data, calculate the standard heat of formation, ΔH_{f}° , for butyric acid.

(b) Write a correctly balanced equation for the formation of butyric acid from its elements.

(c) Calculate the standard entropy change, ΔS_{f}° , for the formation of butyric acid at 25°C. The entropy change, ΔS° , for the combustion reaction above is -117.1 J K⁻¹ at 25°C.

(d) Calculate the standard free energy of formation, $\Delta G^{\circ}f$, for butyric acid at 25°C.