

Now, after 1 semester, we can do about half the problems, so my list will be like 100 pages. Due to this reason, I'll only list a few from the past 10 or 15 years as examples. You don't have to do all of these to do well on the test. You don't even have to do that many. Just do enough to get a good feel of what they're gonna throw at you

- a. **The longest wavelength of light with enough energy to break the Cl-Cl bond in Cl₂(g) is 495 nm.**
- Calculate the frequency, in s⁻¹, of the light.**
 - Calculate the energy, in J, of a photon of the light.**
 - Calculate the minimum energy, in kJ mol⁻¹, of the Cl-Cl bond.**
- b. **A certain line in the spectrum of atomic hydrogen is associated with the electronic transition in the H atom from the sixth energy level (n = 6) to the second energy level (n = 2).**
- Indicate whether the H atom emits energy or whether it absorbs energy during the transition. Justify your answer.**
 - Calculate the wavelength, in nm, of the radiation associated with the spectral line.**
 - Account for the observation that the amount of energy associated with the same electronic transition (n = 6 to n = 2) in the He⁺ ion is greater than that associated with the corresponding transition in the H atom.**

ANSWER:

9 points:

One point deduction for mathematical error (maximum once per question)

One point deduction for error in significant figures* (maximum once per question)

*number of significant figures must be correct within one digit.

- a.
- 1 point**

$$v = \frac{c}{\lambda} = \frac{3.00 \times 10^{17} \text{ nm/sec}}{495 \text{ nm}} \quad (\text{or, } = \frac{3.00 \times 10^8 \text{ m/sec}}{495 \times 10^{-9} \text{ m}}) = 6.06 \times 10^{14} \text{ sec}^{-1}$$

- 1 point**

$$E = hv = (6.626 \times 10^{-34} \text{ J sec})(6.06 \times 10^{14} \text{ sec}^{-1}) = 4.02 \times 10^{-19} \text{ J}$$

- 1 point**

$$(4.02 \times 10^{-19} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1})(0.00100 \text{ kJ/J}) = 242 \text{ kJ/mol}$$

Note: No units required if answers are numerically same as above. No penalty if answers are correct with different units and units are explicitly indicated (e.g., for part (ii), 4.02 x 10⁻²² kJ is acceptable)

b.

i. **1 point**

Energy is emitted.

1 point

The $n = 6$ state is at a higher energy than the $n = 2$ state. Going from a high energy state to a low energy state means that energy must be emitted.

Note: The key idea is that the energy of the $n = 6$ state is higher (more excited) than the lower (less excited) $n = 2$ state. The argument that " e^- is farther away" at the $n = 6$ level is not accepted.

ii. **1 point**

$$E_2 = \frac{-2.178 \times 10^{-18} \text{ J}}{2^2} = -5.45 \times 10^{-19} \text{ J}, \quad E_6 = \frac{-2.178 \times 10^{-18} \text{ J}}{6^2} = -6.05 \times 10^{-20} \text{ J}$$
$$\Delta E = E_6 - E_2 = -6.05 \times 10^{-20} \text{ J} - (-5.45 \times 10^{-19} \text{ J}) = 4.84 \times 10^{-19} \text{ J}$$

iii. **OR,**

$$\Delta E = 2.178 \times 10^{-18} (1/2^2 - 1/6^2) \text{ J} = 2.178 \times 10^{-18} (0.2222) \text{ J} = 4.84 \times 10^{-19} \text{ J}$$

iv. **Note:** Point earned for determining the energy of transition. Negative energies acceptable.

v. **1 point**

$$E = \frac{hc}{\lambda} \rightarrow \lambda = \frac{hc}{E}$$

vi. **OR,**

$$\nu = \frac{E}{h} = \frac{4.84 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J sec}} = 7.30 \times 10^{14} \text{ sec}^{-1}$$

vii. **Note:** Point earned for writing or using $E = hc/\lambda$, or for calculating the frequency, ν .

viii. **1 point**

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m sec}^{-1}}{7.30 \times 10^{14} \text{ sec}^{-1}} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 411 \text{ nm}$$

ix. **OR,**

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J sec})(3.00 \times 10^{17} \text{ nm sec}^{-1})}{4.84 \times 10^{-19} \text{ J}} = 411 \text{ nm}$$

x. **Note:** Point earned for correct wavelength; $\lambda = 4.11 \times 10^{-7} \text{ m}$ accepted. Negative wavelength not accepted.

xi. **1 point**

The positive charge holding the electron is greater for He, which has a 2 nucleus, than for H with its 1 nucleus. The stronger attraction means that it requires more energy for the electron to move to higher energy levels. Therefore, transitions from high energy states to lower states will be more energetic for He than for H.

Note: Other arguments accepted, such as, " E is proportional to Z^2 . Since $Z = 2$ for He and $Z = 1$ for H, all energy levels in He are raised (by a factor of 4)." Other accepted answers must refer to the increased **charge** on the He **nucleus**, and NOT the **mass**.

- a. Consider the carbon dioxide molecule, CO_2 , and the carbonate ion, CO_3^{2-} .
- Draw the complete Lewis electron-dot structure for each species.
 - Account for the fact that the carbon-oxygen bond length in CO_3^{2-} is greater than the carbon-oxygen bond length in CO_2 .
- b. Consider the molecules CF_4 and SF_4 .
- Draw the complete Lewis electron-dot structure for each molecule.
 - In terms of molecular geometry, account for the fact that the CF_4 molecule is nonpolar, whereas the SF_4 molecule is polar.

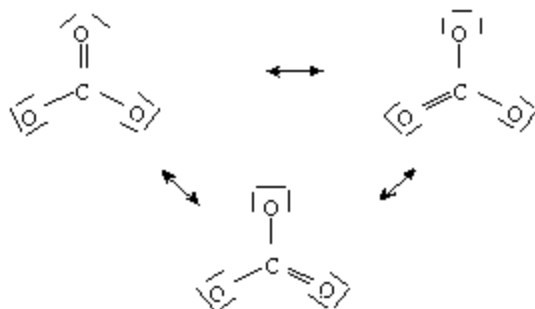
ANSWER:

8 points:

- a.
i. **2 point**



- One point earned for each Lewis electron-dot structure
 - Indication of lone pairs of electrons are required on each structure
 - Resonance forms of CO_3^{2-} are not required
- ii. In CO_2 , the C–O interactions are double bonds, **OR**, in CO_3^{2-} the C–O interactions 1 pt are resonance forms (or figures below.)



1 point

The carbon-oxygen bond length is greater in the resonance forms than in the double bonds

- 1st point earned for indicating double bonds are present in CO_2 **OR** resonance occurs in CO_3^{2-}
- 2nd point earned for **BOTH** of the above **AND** indicating the relative lengths of the bond types

b.

○ 2 point



- One point earned for each Lewis electron-dot structure
- Lone pairs of electrons are required on each structure

○ 1 point

CF_4 has a tetrahedral geometry, so the bond dipoles cancel, leading to a nonpolar molecule.

1 point

With five pairs of electrons around the central S atom, SF_4 exhibits a trigonal bipyramidal electronic geometry, with the lone pair of electrons. In this configuration, the bond dipoles do not cancel, and the molecule is polar.



- One point earned for each molecule for proper geometry and explanation

2) An unknown compound contains only the three elements C,H, and O. A pure sample of the compound is analyzed and found to be 65.60 percent C and 9.44 percent H by mass.

(a) Determine the empirical formula of the compound.

(b) A solution of 1.570 grams of the compound in 16.08 grams of camphor is observed to freeze at a temperature 15.2 Celsius degrees below the normal freezing point of pure camphor. Determine the molar mass and apparent molecular formula of the compound. (The molal freezing-point depression constant, K_f , for camphor is $40.0 \text{ kg}\cdot\text{K}\cdot\text{mol}^{-1}$.)

(c) When 1.570 grams of the compound is vaporized at $300 \text{ }^\circ\text{C}$ and 1.00 atmosphere, the gas occupies a volume of 577 milliliters. What is the molar mass of the compound based on this result?

(d) Briefly describe what occurs in solution that accounts for the difference between the results obtained in parts (b) and (c).

ANSWER:

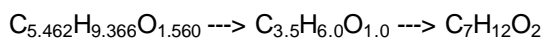
a) Assume a 100 gram sample (not necessary for credit):

$$65.60\text{g C} \times (1 \text{ mol C} / 12.01 \text{ g C}) = 5.462 \text{ mol C}$$

$$9.44\text{g H} \times (1 \text{ mol H} / 1.0079 \text{ g H}) = 9.366 \text{ mol H}$$

$$\text{mass O} = [100 - (65.60 + 9.44)] = 24.96 \text{ g O}$$

$$24.96 \text{ g O} \times (1 \text{ mol O} / 15.9994 \text{ g O}) = 1.560 \text{ mol O}$$



One point earned for determining moles of C and moles of H

One point earned for determining moles of O

One point earned for correct empirical formula

$$(b) m = ? T / K_f = 15.2 \text{ }^\circ\text{C} / 40.0 \text{ K kg mol}^{-1} = 0.380 \text{ mol / kg}$$

$$0.01608 \text{ kg} \times (0.380 \text{ mol} / 1 \text{ kg}) = 0.00611 \text{ mol}$$

$$\text{molar mass} = 1.570 \text{ g} / 0.00611 \text{ mol} = 257 \text{ g / mol}$$

One point earned for determination of molarity

One point earned for conversion of molarity to molar mass

OR,

$$\text{moles solute} = (? T \times \text{kg solvent}) / K_f = 0.00611 \text{ mol (one point)}$$

$$\text{molar mass} = 1.570 \text{ g} / 0.00611 \text{ mol} = 257 \text{ g / mol (one point)}$$

OR,

$$\text{molar mass} = (\text{mass} \times K_f) / (? T \times \text{kg solvent}) = 257 \text{ g / mol (two points)}$$

$$\text{empirical mass of } \text{C}_7\text{H}_{12}\text{O}_2 = 7(12) + 12(1) + 2(16) = 128 \text{ g/mol}$$

$$128 \text{ g/mol} = 1/2 \text{ molar mass} \rightarrow \text{molecular formula} = 2x (\text{empirical formula}) \rightarrow \text{molecular formula} = \text{C}_{14}\text{H}_{24}\text{O}_4 \text{ (one point)}$$

One point earned if molecular formula is wrong but is consistent with empirical formula and molar mass

No penalty for simply ignoring the van't Hoff factor

Only one point earned for part (b) if response indicates that $? T = (15.2 + 273) = 288 \text{ K}$ and molar mass = 13.6 g / mol

$$(c) n = (pV) / (RT) = [(1 \text{ atm}) (0.577 \text{ L})] / [(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) (573 \text{ K})] = 0.0123 \text{ mol (one point)}$$

$$\text{molar mass} = \text{mass of sample} / \text{moles in sample} = 1.570 \text{ g} / 0.0123 \text{ mol} = 128 \text{ g/mol (one point)}$$

Only one point can be earned for part (c) if wrong value for R is used and/or T is not converted from C to K

(d) The compound must form a dimer in solution, because the molar mass in solution is twice that it is in the gas phase,

OR,

the compound must dissociate in the gas phase ($A(g) \rightarrow 2B(g)$) because the molar mass in the gas phase is half that it is in solution.

One point earned for a reference to either or both the ideas of dimerization and dissociation, but no point earned for a "non-ideal behavior" argument

5) Consider the molecules PF_3 and PF_5 .

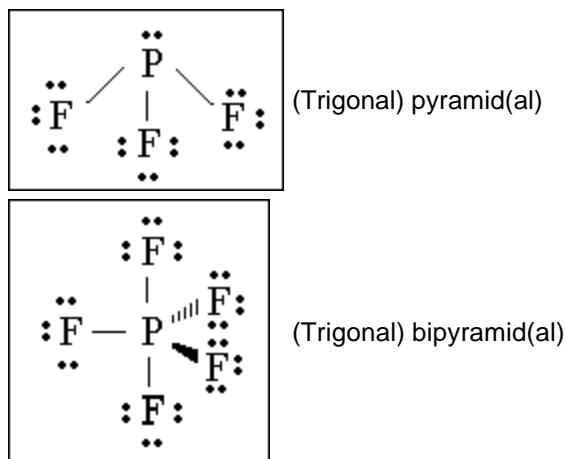
a) Draw the Lewis electron-dot structures for PF_3 and PF_5 and predict the molecular geometry of each.

b) Is the PF_3 molecule polar, or is it nonpolar? Explain.

c) On the basis of bonding principles, predict whether each of the following compounds exists. In each case, explain your prediction.

- (i) NF_5
- (ii) AsF_5

ANSWER:



1 point for each structure

Note ; One point (total) deducted if lone pairs not shown on F atoms in either molecule.

(b) The PF_3 molecule is polar

The three P-F dipoles do not cancel, or,

the lone pair on P leads to asymmetrical distribution of charge.

Note; "Molecule is not symmetrical" does not earn point. Both points can be earned if answer is consistent with incorrect (a).

(c) NF_5 does not exist because no 2d orbitals exist for use in bonding, or,

N is too small to accommodate 5 bonding pairs

AsF₅ does exist because 4d orbitals are available for use in bonding, or,

As can accommodate an expanded octet using d orbitals

Note; Response with two correct predictions with no explanations earns one point. Also, argument of "no expanded octet" vs. "expanded octet" alone does not earn explanation point.

6) Explain each of the following observations using principles of atomic structure and/or bonding.

d) Potassium has a lower first-ionization energy than lithium.

b) The ionic radius of N³⁻ is larger than that of O²⁻.

c) A calcium atom is larger than a zinc atom.

d) Boron has a lower first-ionization energy than beryllium.

ANSWER:

No points earned for "K electron is easier to remove" (or some other restatement).

b) Nitrogen has one less proton than oxygen 1 point

Nitride and oxide ions are isoelectronic 1 point

or,

In nitride ion the electron/proton ratio is greater, causing more repulsion; thus, nitride is the larger ion. 2 points

c) A Zn atom has more protons (10 more) than an atom of Ca 1 point

Electrons in d orbitals of Zn have a lower principal quantum number; thus, they are not in orbitals that are farther from the nucleus. 1 point

d) Correct identification of the orbitals involved (2s versus 2p) 1 point

Clear statement that the two orbitals have different energies 1 point

Note: Arguments that "the 2p orbital is farther out than the 2s orbital", or that "the Be atom has a filled subshell, which is a more stable configuration" earn no explanation point.

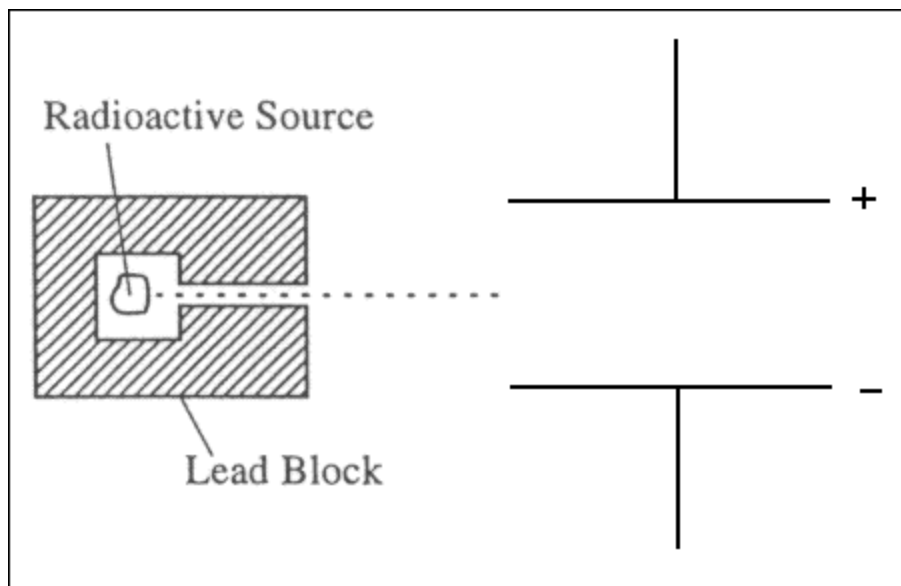
General note: For all parts (a) through (d), discussions of position in the periodic table earn no points.

8) Answer each of the following questions regarding radioactivity.

a) Write the nuclear equation for decay of 94-Pu-234 by alpha emission.

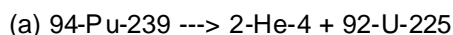
b) Account for the fact that the total mass of the products of the reaction in part (a) is slightly less than that of the original 94-Pu-234.

c) Describe how α , β , and γ rays each behave when they pass through an electric field. Use the diagram below to illustrate your answer.



d) Why is it not possible to eliminate the hazard of nuclear waste by the process of incineration?

ANSWER:



Notes; One point is earned for [He] (or α), one point for correct total mass number in products, and one point for consistent atomic numbers and symbols. Full credit is also earned for correct decay starting with Pu-234 (as was printed on the green insert)

(b) Missing mass is converted to energy (or " $E=mc^2$ ")

Notes; No point earned for just mentioning "mass defect".

(c) In words, or drawn on diagram:

path of α particle bends toward negative (-) plate, 1 point
 path of β particle bends toward positive (+) plate, 1 point
 path of γ ray is undeflected. 1 point

(d) Incineration (combustion, oxidation) is a *chemical* process AND as such it has no effect on a nuclear process (decay).
 1 point

Notes; No point for thermodynamic, kinetic, or equilibrium arguments. No point earned for "dispersion of material is bad for the environment" or similar statements.

4) Concentrated sulfuric acid (18.4-molar H_2SO_4) has a density of 1.84 grams per milliliter. After dilution with water to 5.20-molar, the solution has a density of 1.38 grams per milliliter and can be used as an electrolyte in lead storage batteries for automobiles.

(a) Calculate the volume of concentrated acid required to prepare 1.00 liter of 5.20-molar H_2SO_4 .

(b) Determine the mass percent of H_2SO_4 in the original concentrated solution.

(c) Calculate the volume of 5.20-molar H₂SO₄ that can be completely neutralized with 10.5 grams of sodium bicarbonate NaHCO₃.

(d) What is the molality of the 5.20-molar H₂SO₄ ?

ANSWER:

(a) one point

$$V_1M_1 = V_2M_2$$

$$(1.00\text{L}) (5.20 \text{ mol/L}) = (x) (18.4 \text{ mol/L})$$

$$x = 5.2 \text{ mol} / (18.4 \text{ mol/L}) = 0.283 \text{ L (or 283 mL)}$$

(b) two points

$$\text{mass 1 liter of concentrated H}_2\text{SO}_4 = 1 \text{ L} \times (1.84 \text{ g/mL}) \times (1,000 \text{ mL/L}) = 1,840 \text{ g H}_2\text{SO}_4$$

$$18.4 \text{ mol H}_2\text{SO}_4 \times 98.1 \text{ g/mol} = 1,805 \text{ g H}_2\text{SO}_4$$

$$\text{mass percent H}_2\text{SO}_4 = (1,805 \text{ g} / 1,840 \text{ g}) \times 100 = 98.1\%$$

(c) three points

$$\text{Stoichiometric ratio of NaHCO}_3 \text{ to H}_2\text{SO}_4 = 2:1$$

$$10.5 \text{ g NaHCO}_3 \times (1 \text{ mol NaHCO}_3 / 84.0 \text{ g NaHCO}_3) = 0.125 \text{ mol NaHCO}_3$$

$$\text{Since 1 mol H}_2\text{SO}_4 \text{ reacts with 2 mol NaHCO}_3, 0.125 \text{ mol NaHCO}_3 \text{ reacts with } 0.0625 \text{ mol H}_2\text{SO}_4$$

$$0.0625 \text{ mol H}_2\text{SO}_4 = V \times M = (V) (5.20 \text{ M})$$

$$V = 0.0625 \text{ mol} / (5.20 \text{ mol/L}) = 0.0120 \text{ L (or 12.0 mL)}$$

(d) three points

$$\text{molality} = \text{moles solute} / 1,000 \text{ g solvent} = \text{moles solute} / 1 \text{ kg solvent}$$

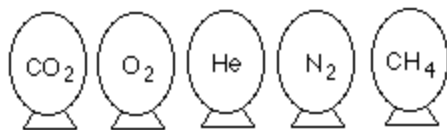
$$\text{mass of 1 L of 5.20 M H}_2\text{SO}_4 = 1 \text{ L} \times (1,000 \text{ mL} / 1 \text{ L}) \times (1.38 \text{ g 1 mL}) = 1,380 \text{ g}$$

$$\text{mass of H}_2\text{SO}_4 \text{ in 1 L} = (5.20 \text{ mol/L}) (98.1 \text{ g.mol}) = 510 \text{ g}$$

$$\text{mass of H}_2\text{O in 1 L} = 1,380 - 510 = 870 \text{ g}$$

$$\text{molality} = (5.20 \text{ mol H}_2\text{SO}_4 / 870 \text{ g}) \times (1,000 \text{ g} / 1 \text{ kg}) = 5.98 \text{ m}$$

Note: no credit earned for $5.20 \text{ mol} / 1.38 \text{ kg} = 5.77 \text{ m}$



Represented above are five identical balloons, each filled to the same volume at 25°C and 1.0 atmosphere pressure with the pure gas indicated.

- Which balloon contains the greatest mass of gas? Explain.
- Compare the average kinetic energies of the gas molecules in the balloons. Explain.
- Which balloon contains the gas that would be expected to deviate most from the behavior of an ideal gas? Explain.
- Twelve hours after being filled, all the balloons have decreased in size. Predict which balloon will be the smallest. Explain your reasoning.

ANSWER:

(a) two points

CO₂

because all contain same number of molecules (moles), and CO₂ molecules are the heaviest

Note: total of 1 point earned if CO₂ not chosen but same number of molecules (moles) is specified

(b) two points

All are equal

because same temperature, therefore same average kinetic energy

Note: just restatement of "same conditions, etc." does not earn second point

(c) two points

CO₂

either one:

it has the most electrons, hence is the most polarizable
it has the strongest intermolecular (London) forces

Note: also allowable are "polar bonds", "inelastic collisions"; claiming larger size or larger molecular volume does not earn second point

(d) two points

He

Any one:

greatest movement through the balloon wall
smallest size
greatest molecular speed
most rapid effusion (Graham's law)

9) Explain each of the following in terms of the electronic structure and/or bonding of the compounds involved.

(a) At ordinary conditions, HF (normal boiling point = 20°C) is a liquid, whereas HCl (normal boiling point = -114°C) is a gas.

(b) Molecules of AsF₃ are polar, whereas molecules of AsF₅ are nonpolar.

(c) The N-O bonds in the NO₂⁻ ion are equal in length, whereas they are unequal in HNO₂.

(d) For sulfur, the fluorides SF₂, SF₄, and SF₆ are known to exist, whereas for oxygen only OF₂ is known to exist.

ANSWER:

(a) two points

Hydrogen bonding (or dipole-dipole attraction) in HF is greater than it is in HCl

Note: only one point earned if simply stated that HF has greater intermolecular forces than HCl

(b) two points

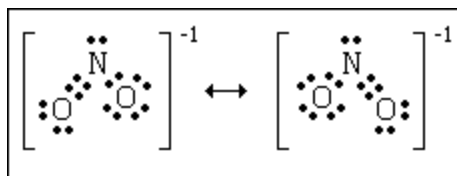
AsF₃ has a trigonal pyramid shape and bond dipoles do NOT cancel (or asymmetric molecule)

AsF₅ has a trigonal bipyramid shape and bond dipoles cancel (or symmetric shape)

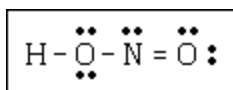
Notes: explanation must refer to shape in order to earn point; one point earned if only correct Lewis structures are given.

(c) two points

NO₂⁻ has resonance structures



HNO₂ has no resonance structures



OR

one N-O single bond, one N=O double bond

Note: one point earned if only correct Lewis structures, including resonance for NO_2^- given.

(d) two points

Sulfur uses d orbitals (or expanded octet), oxygen has no d orbitals in its valence shell

OR

Sulfur is a larger atom, can accommodate more bonds.

3) A sample of dolomitic limestone containing only CaCO_3 and MgCO_3 was analyzed.

(a) When a 0.2800 gram sample of this limestone was decomposed by heating, 75.0 milliliters of CO_2 at 750 mm Hg, and 20°C were evolved. How many grams of CO_2 were produced?

(b) Write equations for the decomposition of both carbonates described above.

(c) It was also determined that the initial sample contained 0.0448 gram of calcium. What percent of the limestone by mass was CaCO_3 ?

(d) How many grams of the magnesium-containing product were present in the sample in (a) after it had been heated?

ANSWER:

a) three points

$$75.0 \text{ mL} = 0.0750 \text{ L} = V$$

$$n = PV / RT = [(750/760) \text{ atm} \times 0.0750 \text{ L}] / [(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) (20^\circ\text{C} + 273)] = 0.00308 \text{ mol CO}_2$$

$$= 3.08 \times 10^{-3} \text{ mol CO}_2$$

$$3.08 \times 10^{-3} \text{ mol CO}_2 \times (44.0 \text{ g CO}_2 / 1 \text{ mol CO}_2) = 0.136 \text{ g CO}_2 = 1.36 \times 10^{-1} \text{ g CO}_2$$

b) two points



c) two points

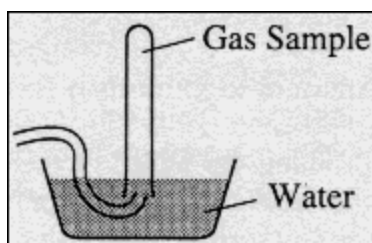
$$0.0448 \text{ g Ca} \times (1 \text{ mol Ca} / 40.08 \text{ gCa}) \times (1 \text{ mol CaCO}_3 / 1 \text{ mol Ca}) \times (100.0 \text{ g CaCO}_3 / 1 \text{ mol CaCO}_3) = 0.112 \text{ g CaCO}_3$$

$$(0.112 \text{ g CaCO}_3 / 0.2800 \text{ g sample}) \times 100\% = 40.0\%$$

d) two points

$$0.2800 \text{ g sample} \times 60\% = 0.168 \text{ g MgCO}_3$$

$$0.168 \text{ g MgCO}_3 \times (1 \text{ mol MgCO}_3 / 84.31 \text{ g MgCO}_3) \times (1 \text{ mol MgO} / 1 \text{ mol MgCO}_3) \times (40.30 \text{ g MgO} / 1 \text{ mol MgO}) = 0.0802 \text{ g MgO}$$



A student collected a sample of hydrogen gas by the displacement of water as shown by the diagram above. The relevant data are given in the following table.

GAS SAMPLE DATA	
Volume of sample	90.0 mL
Temperature	25° C
Atmospheric Pressure	745 mm Hg
Equilibrium Vapor Pressure of H ₂ O (25° C)	23.8 mm Hg

(a) Calculate the number of moles of hydrogen gas collected.

(b) Calculate the number of molecules of water vapor in the sample of gas.

(c) Calculate the ratio of the average speed of the hydrogen molecules to the average speed of the water vapor molecules in the sample.

(d) Which of the two gases, H₂ or H₂O, deviates more from ideal behavior? Explain your answer.

ANSWER:

a) three points

$$n = PV \div RT = [(721) (0.090)] \div [(62.4) (298)] = 3.49 \times 10^{-3} \text{ mol H}_2$$

Each worth one point:

25°C to 298 K
745 - 24 = 721 mm Hg
calculation of moles H₂

Note: 62.4 is R in units of L torr per mol K

b) two points

$$[(23.8) (0.090)] \div [(62.4) (298)] = 1.15 \times 10^{-4} \text{ mol H}_2\text{O}$$

$$(1.15 \times 10^{-4}) (6.02 \times 10^{23}) = 6.92 \times 10^{19} \text{ molecules H}_2\text{O}$$

c) two points (one for formula, one for calculation)

The average kinetic energies are equal, so:

$$(1/2 m v^2)_{\text{H}_2\text{O}} = (1/2 m v^2)_{\text{H}_2}$$

$$v_{\text{H}_2} / v_{\text{H}_2\text{O}} = \text{square root} [MM_{\text{H}_2\text{O}} / MM_{\text{H}_2}]$$

$$= \text{square root} (18 / 2) = 3$$

Note: credit also given for correct use of $v_{\text{rms}} = \text{square root} (3RT / M)$

d) two points

H₂O deviates more from ideal behavior.

Explanation:

1) The volume of the H₂O molecule is larger than that of the H₂ molecule

OR

2) The intermolecular forces among the H₂O molecules are stronger than those among H₂ molecules.

9) Use principle of atomic structure and/or chemical bonding to answer of each of the following.

(a) The radius of the Ca atom is 0.197 nanometer; the radius of the Ca²⁺ ion is 0.099 nanometer. Account for this difference.

(b) The lattice energy of CaO(s) is -3,460 kilojoules per mole; the lattice energy for K₂O(s) is -2,240 kilojoules per mole. Account for this difference.

	Ionization Energy (kJ/mole)	
	First	Second
K	419	3,050
Ca	590	1,140

(c) Explain the difference between Ca and K in regard to:

- (i) their first ionization energies.**
- (ii) their second ionization energies.**

(d) The first ionization energy of Mg is 738 kilojoules per mole and that of Al is 578 kilojoules per mole. Account for this difference.

ANSWER:

a) two points

Ca^{2+} has fewer electrons, thus it is smaller than Ca.

The outermost electron in Ca is in a 4s orbital, whereas the outermost electron in Ca^{2+} is in a 3p orbital.

Note: The first point is earned for indicating the loss of electrons, the second point for indicating the outermost electrons are in different shells -- must account for the magnitude of the size difference between Ca and Ca^{2+} .

b) two points

U for CaO is more negative than U for K_2O , so it is more difficult to break up the CaO lattices (stronger bonds in CaO). Ca^{2+} is smaller than K^+ , so internuclear separations (between cations and O^{2-}) are less.

OR

Ca^{2+} is more highly charged than K^+ , thus cation- O^{2-} bonds are stronger

Note: understanding what "lattice energy" is earns 1 point; size or charge explanation needed for the second point. Responses that use Lewis structures or otherwise indicate molecules rather than ionic lattice earn no points.

c) two points

i) Ca has more protons and is smaller. The outermost electrons are more strongly held by the nuclear charge of Ca.

ii) The outermost electrons in Ca are in the 4s, which is a higher energy orbital (more shielded) than the 3p electrons in K.

Note: for (i), the idea of attraction between nucleus and electrons must be present; for (ii), a "noble-gas configuration" argument must be tied to an energy argument in order to earn credit.

d) two points

the highest energy (outermost) electrons in Al is in a 3p orbital, whereas that electron in Mg is in a 3s orbital.

The 3p electron in Al is of higher energy (is more shielded) than is the 3s electron in Mg.

Note: noting that different orbitals are involved earns the first point; a correct energy argument earns the second point.

Responses that attribute the greater stability of Ca over K (or K^+ over Ca^+ , or Mg over Al) to the stability of a completely filled (vs. half or partially filled) orbital earn NO credit.

2) Elemental analysis of an unknown pure substance indicates that the percent composition by mass is as follows:

Carbon - 49.02%

Hydrogen - 2.743%

Chlorine - 48.23%

A solution that is prepared by dissolving 3.150 grams of the substance in 25.00 grams of benzene, C_6H_6 , has a freezing point of $1.12^\circ C$. (The normal freezing point of benzene is $5.50^\circ C$ and the molal freezing-point depression constant, K_f , for benzene is $5.12\ C^\circ/molal$.)

(a) Determine the empirical formula of the unknown substance.

(b) Using the data gathered from the freezing point depression method, calculate the molar mass of the unknown substance.

(c) Calculate the mole fraction of benzene in the solution described above.

(d) The vapor pressure of pure benzene at $35^\circ C$ is 150. millimeters of Hg. Calculate the vapor pressure of benzene over the solution described above at $35^\circ C$.

ANSWEr:

2) average score = 4.5

a) two points

carbon: $49.02 / 12.01 = 4.081\ g$

hydrogen: $2.743 / 1.008 = 2.722\ g$

chlorine: $48.23 / 35.453 = 1.360\ g$

mole ratios: $C/Cl = 3$; $H/Cl = 2$; $Cl/Cl = 1$

empirical formula = C_3H_2Cl

b) three points

$$[\Delta]T_f = K_f m$$

$$4.38 \text{ }^\circ\text{C} = (5.12) (x / 0.025)$$

$$x = 0.0214 \text{ mol}$$

$$3.150 \text{ g} / 0.0214 \text{ mol} = 147 \text{ g} / \text{mol}$$

Note: the scoring standards has this equation rather than the above three lines:

$$4.38 = 5.12 \times \left(\frac{\left(\frac{3.150}{\text{MM}} \right)}{25 / 1000} \right) = 147 \text{ g/mol}$$

The standards then show:

$$\text{MM} = [(5.12) (3.150) (1000)] / [(4.38) (25)] = 147$$

c) two points

mole fraction = moles benzene / total moles

$$\text{C}_6\text{H}_6 = 78.108$$

$$25.00 \text{ g} / 78.108 = 0.32 \text{ mol}$$

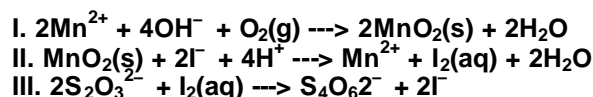
$$0.32 / (0.32 + 0.0214) = 0.94$$

d) two points

$$P_{\text{soln}} = P_{\text{pure}} \times \text{mole fraction}$$

$$P_{\text{soln}} = (150) (0.94) = 141 \text{ mm Hg}$$

3)



The amount of oxygen, O_2 , dissolved in water can be determined by titration. First, MnSO_4 and NaOH are added to a sample of water to convert all of the dissolved O_2 to MnO_2 , as shown in equation I above. Then H_2SO_4 and KI are added and the reaction represented by equation II proceeds. Finally, the I_2 that is formed is titrated with standard sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, according to equation III.

(a) According to the equations above, how many moles of $\text{S}_2\text{O}_3^{2-}$ are required for analyzing 1.00 mole of O_2 dissolved in water?

(b) A student found that a 50.0 milliliter sample of water required 4.86 milliliters of 0.0112 molar $\text{Na}_2\text{S}_2\text{O}_3$ to reach the equivalence point. Calculate the number of moles of O_2 dissolved in this sample.

(c) How would the results in (b) be affected if some I_2 were lost before the $\text{S}_2\text{O}_3^{2-}$ was added? Explain.

(d) Name an appropriate indicator for the reaction shown in equation III and describe the change you would observe at the end point of the titration.

ANSWER:

a) one point

$$(1.00 \text{ mol O}_2) (2 \text{ mol MnO}_2 / 1 \text{ mol O}_2) (1 \text{ mol I}_2 / 1 \text{ mol MnO}_2) (2 \text{ mol S}_2\text{O}_3^{2-} / 1 \text{ mol I}_2) = 4 \text{ mol S}_2\text{O}_3^{2-}$$

Note: answer only is sufficient.

b) two points

$$\text{mol S}_2\text{O}_3^{2-} = (0.00486) (0.0112) = 5.44 \times 10^{-5} \text{ mol S}_2\text{O}_3^{2-}$$

$$\text{mol O}_2 = 5.44 \times 10^{-5} / 4 = 1.36 \times 10^{-5} \text{ mol}$$

c) one point

less I_2 therefore less $\text{S}_2\text{O}_3^{2-}$ required therefore lower amount of O_2 (both direction and reason required)

d) two points

starch indicator

color disappears or blue disappears (violet or purple OK)

color change alone is not sufficient for 2nd pt

any other color with starch is not sufficient for 2nd pt

6) Account for each of the following in terms of principles of atomic 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 solid nickel chloride is attracted into a magnetic field, whereas a sample of solid zinc chloride is not.

(d) Phosphorus forms the fluorides PF_3 and PF_5 , whereas nitrogen forms only NF_3 .

ANSWER:

a) three points

Electron configuration of Na and Mg (1 pt)

Any one earns a point:

Octet / Noble gas stability comparison of Na and Mg
Energy difference explanation between Na and Mg
Size difference explanation between Na and Mg

Note: If only Na or Mg is used 1 point can be earned by showing the respective electron configuration and using one of the other explanations

Shielding/effective nuclear charge discussion earns the third point.

b) one point

Correct direction and explanation of any one of the following:

shielding differences
energy differences
of proton/ # of electron differences

c) two points

Any one set earns one point:

(i) Ni unpaired electrons. paramagnetic
(ii) Zn paired electrons/ diamagnetic
(iii) Ni unpaired electrons/ Zn paired electrons
(iiii) Ni paramagnetic/ Zn diamagnetic

Orbital discussion/ Hund's Rule/ Diagrams earns the second point.

d) two points

Expanded octet or sp^3d hybrid of phosphorous (1 pt)

Lack of d orbitals in nitrogen (1 pt)

OR

nitrogen is too small to accomodate (or bond) 5 Fluorines or 5 bonding sites (2 pts)

8) Explain each of the following in terms of atomic and molecular structures and/or intermolecular forces.

(a) Solid K conducts an electric current, whereas solid KNO_3 does not.

(b) SbCl_3 has a measurable dipole moment, whereas SbCl_5 does not.

(c) The normal boiling point of CCl_4 is 77°C , whereas that of CBr_4 is 190°C .

(d) $\text{NaI}(\text{s})$ is very soluble in water whereas $\text{I}_2(\text{s})$ has a solubility of only 0.03 gram per 100 grams of water.

ANSWER:

8) average score = 3.0

a) two points

K conducts because of its metallic bonding or "sea" of mobile e's (or "free" e's)

KNO_3 does not conduct because it is ionically bonded and has immobile ions (or imm. e's)

b) two points

SbCl_3 has a measurable dipole moment because it has a lone pair of e's which causes a dipole

or its dipoles do not cancel

or it has a trigonal pyramidal structure

or clear diagram illustrating any of the above

SbCl_5 has no dipole moment because its dipoles cancel

or it has a trigonal bipyramidal structure

or clear diagram illustrating either of the above

c) two points

CBr_4 boils at a higher T than CCl_4 because it has stronger intermolecular forces (or van der Waals or London dispersion). These stronger forces occur because CBr_4 is larger and/or has more electrons than CCl_4 . (Note added to scoring standard: student misconception of inter-, with "inter-" double underlined.)

d) two points

NaI has greater aqueous solubility than I_2 because NaI is ionic (or polar) whereas I_2 is nonpolar (or covalent). H_2O , being polar, interacts with the ions of NaI but not with I_2 . (Like dissolves like accepted if polarity of H_2O clearly indicated.)

2) 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.

(b) Calculate the mass in grams of O₂ 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?

ANSWER:

$$0.5 \text{ }^{\circ}\text{C} = ((4.68 \text{ }^{\circ}\text{C mol}^{-1}) \times (0.60 \text{ g} / \text{MM})) / 0.1 \text{ kg}$$

$$\text{MM} = (4.68 \times 0.60) / (0.5 \times 0.1) = 56 \text{ or } 6 \times 10^1$$

an alternate solution for (c)

$$\text{molality} = 0.5 \text{ }^{\circ}\text{C} / (4.68 \text{ }^{\circ}\text{C}/m) = 0.107 \text{ } m$$

$$\text{mol solute} = (0.107 \text{ mol} / \text{kg solvent}) \times 0.100 \text{ kg solvent} = 0.0107 \text{ mol}$$

$$\text{MM} = 0.60 \text{ g} / 0.0107 \text{ mol} = 56 \text{ or } 6 \times 10^1$$

d) one point

$$(56 \text{ g/mol of cmpd}) / (29 \text{ g/mol of empirical formula}) = 1.9 \text{ empirical formula per mol}$$

OR

$$6 \times 10^1 / 29 = 2.1$$

empirical formula times 2 equals molecular formula = C₄H₁₀

9) Explain each of the following in terms of nuclear models.

(a) The mass of an atom of ⁴He is less than the sum of the masses of 2 protons, 2 neutrons, and 2 electrons.

(b) Alpha radiation penetrates a much shorter distance into a piece of material than does beta radiation of the same energy.

(c) Products from a nuclear fission of a uranium atom such as ⁹⁰Sr and ¹³⁷Ce are highly radioactive and decay by emission of beta particles.

(d) Nuclear fusion requires large amounts of energy to get started, whereas nuclear fission can occur spontaneously, although both processes release energy.

ANSWER:

a) two points

When nucleons are combined in nuclei, some of their mass is converted to energy (binding energy) which is released and stabilizes the nucleus. (Key concepts: mass defect; binding energy)

b) two points

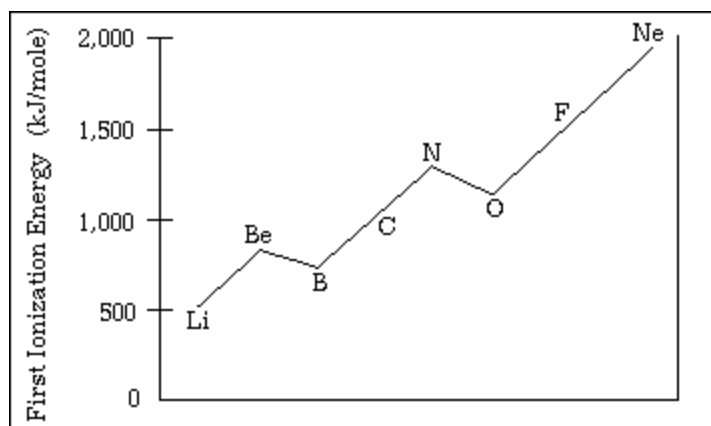
Alpha particles have a greater mass than beta particles. Thus their speed (penetrating potential) is less. (Alternate explanation could be based on charge.)

c) two points

The neutron/proton ratio in Sr-90 and Cs-137 is too large and they emit beta particles (converting neutrons to protons) to lower this ratio.

d) two points

Large amounts of energy are needed to initiate fusion reactions in order to overcome the repulsive forces between the positively charged nuclei. Large amounts of energy are not required to cause large nuclei to split.



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.

ANSWER:

a) two points

Across the period from Li to Ne the number of protons is increasing in the nucleus hence the nuclear charge is increasing with a consequently stronger attraction for electrons and an increase in I.E.

b) two points

The electron ionized in the case of Be is a 2s electron whereas in the case of B it is a 2p electron. 2p electrons are higher in energy than 2s electrons because 2p electrons penetrate the core to a lesser degree.

c) two points

The electron ionized in O is paired with another electron in the same orbital, whereas in N the electron comes from a singly-occupied orbital. The ionization energy of the O electron is less because of the repulsion between two electrons in the same orbital.

d) two points

The ionization energy of Na will be less than those of both Li and Ne because the electron removed comes from an orbital which is farther from the nucleus, therefore less tightly held.

2) A mixture of H₂(g), O₂(g), and 2 milliliters of H₂O(l) is present in 0.500-liter 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 millimeters of mercury. (The equilibrium vapor pressure of pure water is 24 millimeters mercury.)

The mixture is sparked, and H₂ and O₂ react until one reactant is completely consumed.

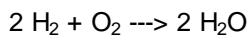
(a) Identify the reactant remaining and calculate the number of moles of the reactant remaining.

(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 millimeters mercury.)

(c) Calculate the number of moles of water present as vapor in the container at 90 °C.

ANSWER

a) six points



moles H₂ = moles O₂ initially but 2 moles of H₂ react for every mole of O₂. O₂ is left.

$$P_{\text{tot}} = P_{\text{H}_2} + P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$

$$1146 = P_{\text{H}_2} + P_{\text{O}_2} + 24 \text{ (v.p. of H}_2\text{O} = 24 \text{ mmHg)}$$

$$P_{\text{H}_2} + P_{\text{O}_2} = 1122 \text{ mm Hg}$$

$$1122 \text{ mm} / 4 = P_{\text{O}_2} \text{ left (1/2 of initial O}_2 \text{ which is 1/2 total)}$$

$$P_{\text{O}_2} = 280.5 \text{ mm}$$

$$P_1 V_1 / T_1 = P_2 V_2 / T_2$$

$$((280.5) (0.5 \text{ L})) / (298) = ((760 \text{ mm})V_2) / (273)$$

$$V_2 = 0.169 \text{ L therefore}$$

$$n = 0.169 \text{ L} / 22.4 \text{ L mol}^{-1} = 7.55 \times 10^{-3} \text{ mol}$$

OR

$$PV = nRT$$

$$((280.5 / 760)\text{atm} (0.5 \text{ L})) / ((0.0821 \text{ L atm/mol K}) (298 \text{ K})) = n = 7.55 \times 10^{-3} \text{ mol}$$

b) two points

$$P_{\text{O}_2} \text{ (@ } 90^\circ\text{C)} / 363 = 280.5 / 298 = 342 \text{ mm Hg}$$

OR

$$P = ((7.55 \times 10^{-3} \text{ mol}) (0.0821) (363)) / 0.5 = 0.45 \text{ atm} = 342 \text{ mm Hg}$$

therefore

$$P_{\text{tot}} = P_{\text{O}_2} + P_{\text{H}_2\text{O}} = 342 + 526 = 868 \text{ mm Hg}$$

c) one point

$$V_{\text{H}_2\text{O}} \text{ (@ STP)} = ((526 \text{ mm Hg}) (0.5) (273)) / ((760) (363)) = 0.260 \text{ L}$$

$$\text{mol. of H}_2\text{O} = 0.260 \text{ L} / 22.4 \text{ L mol}^{-1} = 0.0116 \text{ mol}$$

OR

$$n = ((526 / 750)\text{atm} (0.50)) / ((0.0821) (363)) = 0.0116 \text{ mol}$$

5) Use simple structure and bonding models to account for each of the following.

(a) The bond length between the two carbon atoms is shorter in C₂H₄ than in C₂H₆.

(b) The H - N - H bond angle is 107.5° in NH₃.

(c) The bond lengths in SO_3 are all identical and are shorter than a sulfur-oxygen single bond.

(d) The I_3^- ion is linear.

ANSWER:

a) two points

C_2H_4 has a multiple bond; C_2H_6 has a single bond.

Multiple bonds are stronger and therefore shorter than single bonds.

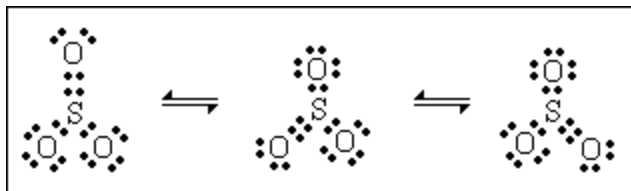
b) two points

NH_3 has 3 bonding pairs and 1 lone pair of electrons.

Bond pairs are forced together because the repulsion between the lone pair and the bond pairs is greater than that between bond pairs.

c) two points

The bonding in SO_3 can be described as a combination of 3 resonance forms of 1 double and single bonds.

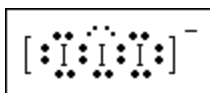


The actual structure is intermediate between the 3 resonance forms, having 3 bonds which are equal and stronger (therefore shorter) than a S-O single bond.

(Credit is given for three sulfur-oxygen double bonds @ 120° with explanation.)

d) two points

The central I atom has 3 lone pairs and 2 bond pairs around it. To minimize repulsion, the 3 lone pairs are arranged in a trigonal plane at right angles to the I-I-I axis.



8) Give a brief explanation for each of the following.

(a) For the diprotic acid H_2S , the first dissociation constant is larger than the second dissociation constant by about 10^5 ($K_1 = 10^5 K_2$).

(b) In water, NaOH is a base, but HOCl is an acid.

(c) HCl and HI are equally strong acids in water but, in pure acetic acid, HI is a stronger acid than HCl.

(d) When each is dissolved in water, HCl is a much stronger acid than HF.

ANSWER:

a) two points

After the first H^+ is lost from H_2S , the remaining species, HS^- , has a negative charge. This increases the attraction of the S atom for the bonding electrons in HS^- . The bond is therefore stronger, H^+ is harder to remove, and K_2 is lower.

b) two points

Polar H_2O can separate ionic NaOH into Na^+ (aq) and OH^- (aq) giving a basic solution. In HOCl, chlorine has a high attraction for electrons due to its greater charge density. This draws electrons in the H-O bond towards it and weakens the bond. H^+ can be removed, making an acid solution.

c) two points

Water is a more basic solvent (greater attraction for H^+) and removes H^+ from Cl^- and I^- equally.

Acetic acid has little attraction for H^+ but the H^+ separates from the larger I^- easier than from the smaller Cl^- .

d) two points

The bond between H and Cl is weaker than the bond between H and F. HCl is therefore a stronger acid.

9) 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	