Sample Question 1   Time allotted: 25 minutes (plus 5 minutes to submit)

Common additives to drinking water include elemental chlorine, chloride ions, and phosphate ions. Recently, reports of elevated lead levels in drinking water have been reported in cities with pipes that contain lead, $Pb(s)$. When $Cl_2(aq)$ flows through a metal pipe containing $Pb(s)$, some of the lead atoms oxidize, losing two electrons each, and aqueous chloride ions form.

   a) Write a balanced, net-ionic equation for the reaction between $Pb(s)$, and $Cl_2(aq)$.

$$Pb + Cl_2 \rightarrow Pb^{2+} + 2Cl^-$$

Dissolution reactions and K_{sp} values for two lead compounds are given in the table.

Dissolution Reaction	Ksp
$PbCl_2(s) \leftrightarrows Pb^{2+}(aq) + 2Cl^-(aq)$	1.6×10^{-5}
$Pb_3(PO_4)_2(s) \leftrightarrows 3Pb^{2+}(aq) + 2PO_4^{3-}(aq)$	1.08×10^{-53}

   b) Write the K_{sp} expression for the dissolution of $Pb_3(PO_4)_2(s)$ in water.

$$K_{sp} = [Pb^{2+}]^3 [PO_4^{3-}]^2$$

   c) Calculate the molar solubility of $Pb_3(PO_4)_2(s)$.

$$1.08 \times 10^{-53} = (3x)^3 (2x)^2 = 108 x^5 \qquad x = 1 \times 10^{-11}$$

$\boxed{1 \times 10^{-11} \, mol/L}$

   d) Using the table of K_{sp} values above, explain why the addition of $PO_4^{3-}(aq)$ is more effective at reducing $[Pb^{2+}]$ in drinking water than $Cl^-(aq)$.

The goal is to get the lead ion to ppt out of sol'n, so you want the Rxn with the smaller Ksp so it ppts @ a lower [ ] so you can add less PO4³⁻ than Cl⁻ to get it to ppt

   e) Cities try to maintain a maximum dissolved lead concentration of $[Pb^{2+}] = 1.0 \times 10^{-9} M$. If a sample of water has $[Pb^{2+}] = 1.0 \times 10^{-9} M$ and enough phosphate is added such that $[PO_4^{3-}] = 3.0 \times 10^{-5} M$, would the concentration of $Pb^{2+}(aq)$ increase, decrease, or remain the same? Justify your answer with a comparison of Q and K_{sp}.

$$K_{sp} = [Pb^{2+}]^3 [PO_4^{3-}]^2 = 1.08 \times 10^{-53}$$
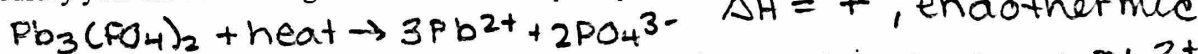$$Q = (1 \times 10^{-9})^3 (3 \times 10^{-5})^2 = 9 \times 10^{-37}$$

$K < Q$ so yes, it will ppt so $\boxed{[Pb^{2+}] \text{ will decrease}}$

   f) Higher concentrations of $Pb^{2+}(aq)$ are found in pipes carrying hot water than in pipes carrying cold water. Is this observation consistent with a negative enthalpy of dissolution, ΔH_{soln}? Justify your answer with regards to LeChâtelier's principle.

$\boxed{\text{not consistant}}$

$\Delta H = +$, endothermic

$$Pb_3(PO_4)_2 + heat \rightarrow 3Pb^{2+} + 2PO_4^{3-}$$

Incr. temp shifts Rxn to right, making more Pb^{2+}

A student researches the properties of the phosphate ion and finds the following Lewis electron-dot diagrams and table of bond lengths:

Bond type	Bond length (pm)
P–O	163
P=O	150

Diagram 1
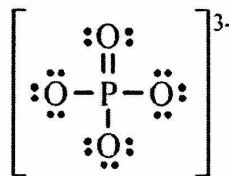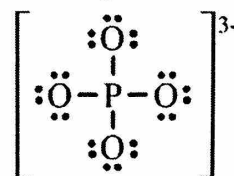
Diagram 2

   g) Using diagram 1, the student claims that the bond angles are 90°. Do you agree or disagree with the student's claim? Justify your answer in terms of VSEPR theory.

$\boxed{\text{Disagree}}$ 4 sp³ hybrid orbitals equally spaced to minimize e⁻ repulsions ∴ tetrahedral & 109.5°

   h) The student also finds that all four P—O bonds in phosphate have a bond length of 162.5 pm. Which diagram is consistent with this finding? Justify your answer.

$\boxed{\text{Diagram 1}}$ b/c single P-O bond = 163 and P=O = 150, a bond length of 162.5 implies resonance btwn the bonds so less than a single bond and more than a double bond

i) The student generates the following particulate diagram of an aqueous solution containing phosphate ions. The student uses dashed lines to show hydrogen bonding and omits lone pairs of electrons for clarity. Identify the letter corresponding to an incorrect hydrogen bonding interaction in the student's diagram, and indicate how the diagram should be changed to be correct.
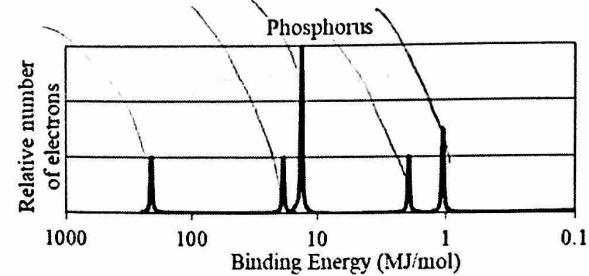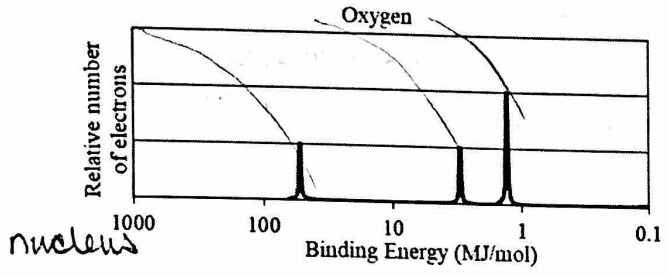
only N, O, F w/ lone pair

**A is incorrect** P is not electroneg. enough. The line should go to an oxygen
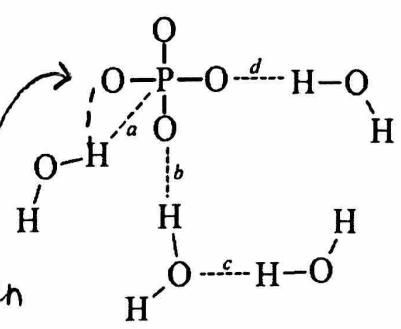
The complete photoelectron spectra of phosphorus and of oxygen are given in the following diagrams.

nucleus

j) The student notices that the rightmost peak of O is taller than the rightmost peak of P. The student claims that this is because O has fewer occupied electron shells, which means that the valence electrons are closer to the nucleus and experience greater attraction. Do you agree or disagree with the student's claim? Justify your answer based on the data and principles of atomic structure.

DISAGREE

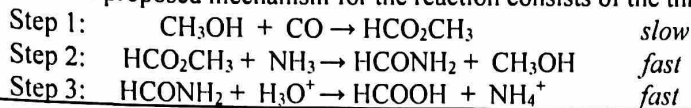$O: 1s^2 2s^2 \underline{2p^4}$

$P: 1s^2 2s^2 2p^6 3s^2 \underline{3p^3}$
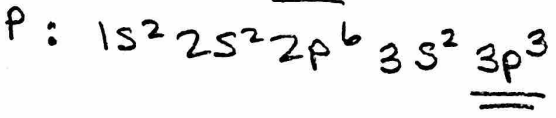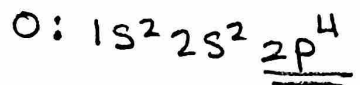
The height is a representation of the # e^- in that orbital. The far right hand peak represents 4 2p e^- for oxygen and 3 3p e^- for P. 4e^- vs 3e^- in the last orbital is why Oxygen's peak is taller.

Sample Question 2

Methanoic acid, $HCOOH_{(aq)}$, is a monoprotic acid that can be synthesized by the reaction between CO and NH_3 in the presence of hydronium ions. A proposed mechanism for the reaction consists of the three elementary steps shown below.

Time allotted: 15 minutes (plus 5 minutes to submit)

Step 1: $CH_3OH + CO \rightarrow HCO_2CH_3$ — *slow*

Step 2: $HCO_2CH_3 + NH_3 \rightarrow HCONH_2 + CH_3OH$ — *fast*

Step 3: $HCONH_2 + H_3O^+ \rightarrow HCOOH + NH_4^+$ — *fast*

Overall reaction: $CO + NH_3 + H_3O^+ \rightarrow HCOOH + NH_4^+$ $\quad \Delta H_{rxn} = -81 \text{ kJ/mol}_{rxn}$

a) Write the chemical formula of a species that behaves as a catalyst in the mechanism.

$\boxed{CH_3OH}$ – used & then reformed

b) According to the proposed mechanism, if additional NH_3 is added to the reaction mixture, will the rate of the overall reaction increase, decrease, or remain the same? Justify your answer.

$\boxed{\text{remain same}}$ NH_3 is not a reactant in the slow, rate determining step so changing it wont change rate

A student generates the following potential energy diagram for the overall reaction.

c) Is the student's diagram consistent with the enthalpy of the overall reaction? Justify your answer.

$\boxed{NO}$ exothermic, $\Delta H = -81 \text{ kJ/mol}$ so energy released, products lower than reactants. ∴ the arrow should point down
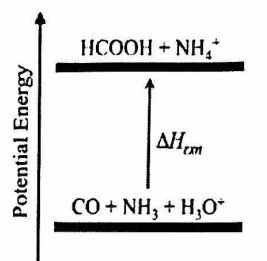
At the end of the reaction, HCOOH is separated from CH_3OH by distillation. The chemical structures and vapor pressures at 50°C for the two substances are given.

Substance	HCOOH	CH₃OH
Structure	H—C—Ö—H (with =O above C)	H—C—Ö—H (with H above and below C)
Vapor Pressure at 50°C	17.3 kPa	55.6 kPa

d) Identify the types of intermolecular forces in HCOOH and CH_3OH.

HCOOH → LDF, DP DP, H-bonding

CH3OH → LDF, H-bonding

e) When an equimolar mixture of the two compounds is heated to 50°C in the distillation, the vapor phase contains a higher mole fraction of CH_3OH molecules. Explain this result in terms of the types and relative strengths of intermolecular forces in both substances.

IMFs HCOOH > IMFs CH3OH b/c HCOOH also has DP-DP. ↑ IMFs = ↓ vapor press, it takes more energy to separate HCOOH molecules into gas phase than CH3OH, so at 50°C there will be more CH3OH molecules present than HCOOH molecules

$$HCOOH(aq) + NaOH(aq) \rightarrow NaHCOO(aq) + H_2O(l)$$
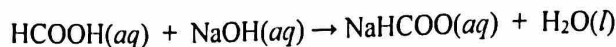
The student uses NaOH(aq) to titrate a methanoic acid solution of unknown concentration. A balanced chemical equation for the reaction appears above. The student places 20.00 mL of the HCOOH solution into a flask and uses a buret filled with 0.300 M NaOH to deliver just enough NaOH(aq) to reach the endpoint. The incomplete data from the student's three trials are summarized in the following table.

Trial	Volume of HCOOH	Initial Buret Reading	Final Buret Reading	Volume of NaOH Dispensed
1	20.00 mL	10.94 mL	27.61 mL	16.67 mL
2	20.00 mL	27.61 mL	48.84 mL	?
3	20.00 mL	1.12 mL	?	?

f) Calculate the molarity of HCOOH from the student's data for Trial 1.

$$\frac{16.67 \text{ mL}}{} \cdot \frac{1 \text{ L}}{1000 \text{ mL}} \cdot \frac{0.3 \text{ mol}}{1 \text{ L}} = 5.001 \times 10^{-3}$$

mol OH$^-$ = mol used H$^+$

$$\frac{5.001 \times 10^{-3} \text{ mol}}{(0.02 \text{ L})} = \boxed{0.250 \text{ M}}$$

g) The final buret reading for Trial 3 is shown in the experimental setup below. What should the student report as the volume of NaOH(aq) dispensed for Trial 3 in the data table?
Clearly show the final reading from the buret and the calculation of the volume dispensed.

*Buret's use 2 decimal points, read bottom of meniscus

18.20
↑
uncertain digit

18.20 − 1.12 = $\boxed{17.08 \text{ mL}}$ dispenced

h) The student calculates a value of [HCOOH(aq)] for Trial 2 that is significantly higher than the value for the other two trials. The student claims that the reason for the higher calculated concentration is that water remained in the flask to which the HCOOH(aq) was added, which meant more NaOH(aq) was needed to reach the endpoint. Do you agree or disagree with the student's claim? Justify your answer.

DISAGREE adding extra water will not change the moles of Acid present so the moles base needed to reach end point wont change