$$HC_3H_5O_2(aq) \rightarrow C_3H_5O_2^-(aq) + H^+(aq) \qquad K_a = 1.34 \times 10^{-5}$$

Propanoic acid, $HC_3H_5O_2$, ionizes in water according to the equation below

a) write the equilibrium-constant expression for the reaction

$K_a = \dfrac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]}$	1 pt equilibrium expression

Assume we will not hold students responsible for labeling the K_a.
Must have charges on ion formulas for the point?

b) calculate the pH of a 0.265 M solution of propanoic acid.

$\qquad HC_3H_5O_2(aq) \rightarrow H^+(aq) + C_3H_5O_2^-(aq)$ I $\quad$ 0.265 $\qquad\quad$ ~0 $\qquad\quad$ 0 C $\quad$ −x $\qquad\qquad$ +x $\qquad\quad$ +x E $\quad$ 0.265 − x $\qquad$ +x $\qquad\quad$ +x $K_a = \dfrac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]} = \dfrac{x \cdot x}{[0.265 - x]}$ Assume 0.265 − x ~ 0.265 $1.34 \times 10^{-5} = \dfrac{x^2}{[0.265]}$ $1.34 \times 10^{-5} \cdot 0.265 = x^2$ $3.55 \times 10^{-6} = x^2$ $x = [H^+] = 1.88 \times 10^{-3}$ M $pH = -\log[H^+] = -\log(1.88 \times 10^{-3})$ $pH = 2.725$	1 pt for substituting into the equilibrium expression $[H^+]$ $= [C_3H_5O_2^-])$ 1 pt calculating value of $[H^+]$ 1 pt for the pH

pH should have 3 sig figs. (fixed)
Award consistency points for pH consistent with wrong $[H^+]$.

c) A 0.496 g sample of sodium propanoate, $NaC_3H_5O_2$, is added to a 50.0 mL sample of a 0.265 M solution of propanoic acid. Assuming that no change in volume of the solution occurs, calculate each of the following.
   i. The concentration of the propanoate ion, $C_3H_5O_2^-(aq)$ in the solution

mol $NaC_3H_5O_2$ = 0.496 g $NaC_3H_5O_2$ $\left(\dfrac{1 \text{ mol } NaC_3H_5O_2}{96.0 \text{ g } NaC_3H_5O_2}\right)$ mol $NaC_3H_5O_2$ = 5.17 x 10^{-3} mol $NaC_3H_5O_2$ = mol $C_3H_5O_2^-$ $[C_3H_5O_2^-] = \dfrac{\text{mol } C_3H_5O_2^-}{\text{volume of solution}} = \dfrac{5.17 \times 10^{-3} \text{ mol } C_3H_5O_2^-}{0.050 \text{ L}} =$ 0.103 M	1 pt for concentration of $NaC_3H_5O_2$.

Award consistency points for $[H^+]$ consistent with $[C_3H_5O_2^-]$.

I would like to see 1 point moved here (perhaps from d). There is a lot here for just one point but that's the case with all this problem. Students have to find the molar mass and the number of moles. In the interest of front loading the question, it would be nice if we could reward those who do this correctly, even if they don't get the M right. There will probably be a lot of recalculating by the readers in ii with incorrect numbers from i.

I think that we should give credit for # moles sodium propanoate, since students may use a mole to mole rather than a M to M ratio in the Ka expression.

I can see moving another point here (from (d) (i))—and response to one of the comments that we should give credit for the no. moles---I vote no unless that is one of 2 points. They must have concentration.

ii. The concentration of the $H^+{}_{(aq)}$ ion in the solution

$HC_3H_5O_{2(aq)} \rightarrow H^+{}_{(aq)} + C_3H_5O_2^-{}_{(aq)}$ I 0.265 ~0 0.103 C −x +x +x E 0.265 − x +x 0.103 + x $K_a = \dfrac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]} = \dfrac{(x) \cdot (0.103 + x)}{[0.265 - x]}$ Assume $0.103 + x \sim 0.103$ $1.34 \times 10^{-5} = \dfrac{(x) \cdot (0.103)}{(0.265)}$ $x = [H^+] = 1.34 \times 10^{-5} \cdot \dfrac{(0.265)}{(0.103)} = 3.45 \times 10^{-5}$ M	1 pt calculating value of $[H^+]$

We should address the HH approach:- pH = pKa + log([base]/[acid]) = 4.873 + log (0.103/0.265)=4.463 hence, $[H^+] = 10^{-4.463} = 3.45 \times 10^{-5}$ mol/L.
Regarding the point distribution: I would suggest moving a point from (d) to here [rather than to c (i)]. c(ii) is much more detailed than c(i). We're looking at a buffer calculation versus a simple concentration of a basic salt calculation.
*I expect we will see just the line square root of (Ka * [HA])*

The methanoate ion, $HCO_2^-(aq)$ reacts with water to form methanoic acid and hydroxide ion, as shown in the following equation.

 d. Given the $[OH^-]$ is 4.18×10^{-6} M in a 0.309 M solution of sodium methanoate, calculate each of the following.
  i.   The value of K_b for methanoate ion, $HCO_2^-(aq)$

$$HCO_2^-(aq) + H_2O(l) \rightarrow OH^-(aq) + HCO_2H$$ I 0.309 – ~0 0 C –x – +x +x E 0.309 – x – +x +x $x = [OH^-] = 4.18 \times 10^{-6}$ M $$K_b = \frac{[OH^-][HCO_2H]}{[HCO_2^-]} = \frac{(x)\cdot(x)}{[0.309 - x]} = \frac{(4.18 \times 10^{-6})^2}{[0.309 - x]}$$ Assume $0.309 - x \sim 0.309$ $$K_b = \frac{(4.18 \times 10^{-6})^2}{[0.309 - x]} = 5.65 \times 10^{-11}$$	1 pt for substituting the $[OH^-] = [HCO_2H]$ 1 point for calculating K_b

Should be 0.309 – x, not 0.309 + x.
The term in the denominator is 0.309—this is not an assumption, since 'x' is given.

  (ii)   The value of K_a for methanoic acid, HCO_2H

$$K_w = K_a \cdot K_b$$ $$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{5.65 \times 10^{-11}}$$ $$K_a = 1.77 \times 10^{-4}$$	1 pt calculating value of K_a from the value of K_b in part i.

 e. which is stronger propanoic acid or methanoic acid? Justify your answer.

K_a for propanoic acid is 1.34×10^{-5}, K_a for methanoic acid is 1.77×10^{-4}. The larger the K_a the stronger the acid, therefore methanoic acid, since it has a larger K_a will be the stronger	1 pt for the explanation.

acid.	

Only 1 point here, so any statement consistent with (possibly erroneous) values of K_a.

2. Answer the following questions about a pure compound that contains carbon, hydrogen and oxygen.
   (a)   A 0.7549 g sample of the compound burns in $O_2(g)$ to produce 1.9061 g of $CO_2(g)$ and 0.3370 g $H_2O(g)$.
   (i)   Calculate the individual masses of C, H and O in the 0.7549 g sample.

$mass_C = 1.9061 \text{ g } CO_2 \left(\dfrac{1 \text{ mol } CO_2}{44.0 \text{ g } CO_2}\right)\left(\dfrac{1 \text{ mol C}}{1 \text{ mol } CO_2}\right)\left(\dfrac{12.0 \text{ g C}}{1 \text{ mol C}}\right)$ $mass_C = 0.51985 \text{ grams}$ $mass_H = 0.3370 \text{ g } H_2O \left(\dfrac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O}\right)\left(\dfrac{2 \text{ mol H}}{1 \text{ mol } H_2O}\right)\left(\dfrac{1.008 \text{ g H}}{1 \text{ mol H}}\right)$ $mass_H = 0.03777 \text{ grams}$ $mass_O = 0.7549 \text{ g} - 0.51985 \text{ g} - 0.03774 \text{ g} = 0.1973 \text{ g}$	1 point each for the mass of C, H and O.

How many significant figures? (perhaps we do not care?)
Mass of oxygen consistent with masses of carbon and hydrogen. I suspect there may be some papers with some stoichiometric calculations to determine oxygen. Calculations for each mass are slightly off since the number of sig figs in MM carbon dioxide and of C are only to three sig figs; and molar mass of water is to three sig figs. This has no impact on the empirical formula determined.

   (ii)   Determine the empirical formula for the compound.

$mol_C = 0.51985 \text{ g C} \left(\dfrac{1 \text{ mol C}}{12.0 \text{ g C}}\right) = 0.04332 \text{ mol}$ $mol_H = 0.\,03774 \text{ g H} \left(\dfrac{1 \text{ mol H}}{1.008 \text{ g H}}\right) = 0.03744 \text{ mol}$ $mol_O = 0.\,1973 \text{ g O} \left(\dfrac{1 \text{ mol O}}{16.0 \text{ g O}}\right) = 0.01233 \text{ mol}$ $\left(\dfrac{0.04332 \text{ mol C}}{0.01233}\right) : \left(\dfrac{0.03774 \text{ mol H}}{0.01233}\right) : \left(\dfrac{0.01233 \text{ mol O}}{0.01233}\right)$ 3.513 mol C : 3.061 mol H : 1 mol O empirical formula is $C_7H_6O_2$	1 point for the mol of C, H and O 1 point for the empirical formula

Many students may recognize that the moles of C and H have already been calculated above, so we may not see many explicit calculations here. We will have to watch for work shown in part(a).

Students who calculate incorrect moles will have variety of empirical formulas.
There may be fuzzy lines between credit/no-credit.
Calculations of moles are slightly different, again because of molar masses used;
in calculating mol H, the correct no. of grams has been brought down from part i.
I expect 1 point for the empirical formula must be consistent with molar ratio
calculated.

(b)   A 0.5246 g sample of the compound was dissolved in 10.0012 g of lauric
acid, and it was determined that the freezing point of the lauric acid was
lowered by 1.68 ˚C. The value of K_f of lauric acid is 3.90 ˚C m^{-1}. Assume
the compound does not dissociate in lauric acid.

(i)   Calculate the molality of the compound dissolved in the lauric
acid.

$\Delta T_f = K_f \cdot m$ $$molality = = \frac{\Delta T_f}{K_f} = \frac{1.68\ °C}{3.90\ °C\ m^{-1}} = 0.431\ molal$$	1 point for molality of the solution

(ii)   Calculate the molar mass of the compound from the information
provided.

$$0.431\ molal = \frac{0.431\ mol\ compound}{1\ kg\ lauric\ acid}$$ $$mol_{compound} = 10.0012\ g\ lauric\ acid \left(\frac{1\ kg}{1000\ g}\right)\frac{0.431\ mol\ compound}{1\ kg\ lauric\ acid}$$ $mol_{compound} = 0.00431\ mol$ $$molar\ mass_{compound} = \frac{0.5246\ g\ compound}{0.00431\ mol\ compound} = 122\ g\ mol^{-1}$$	1 point for molar mass of the compound

1 point for the molar mass not molality (fixed)

(c)   Without doing any calculations, explain how to determine the molecular
formula of the compound based on the answers to parts (a)(ii) and (b)(ii).

The empirical formula of the unknown compound is $C_7H_6O_2$ as determined in (a)(ii). The molar mass of the unknown compound as determined in (b)(ii) is 122 g mol^{-1}. To determine the molecular formula of the compound one must determine the empirical mass of the unknown compound by adding the atomic masses of 7 C, 6 H and 2 O. The empirical mass is then divided into the molecular mass of the compound to obtain a whole number. Each subscript in the empirical formula is multiplied by the whole number.	1 point the explanation

What happens when the student does this: 122/122 the empirical and molecular formula are the same? You are probably going to see this. Most chemistry students are analytical.

We may see many explanations of the sort '122/122 = 1, so empirical formula = molecular formula. I would vote to award credit here.

I agree that a simpler explanation should get the point. For example: MM/EM = 122/122 = 1 thus EF = MF. (2)

I am in favor of a point for MM/EM = ...etc, but NOT 122/122 = 1.... The student is specifically asked not to do the calculation for one thing, and secondly, how do we know they are not doing MM/MM or EM/EM =1?

The comments are specific to this compound (which is what the question asks), but by themselves do not constitute an explanation. My original answer went something like this: the molar mass of the molecular formula is the molar mass of the empirical formula multiplied by an integer. To determine the integer,....

(d)   Further tests indicate that a 0.10 M aqueous solution of the compound has a pH of 2.6. Identify the organic functional group that accounts for this pH.

The empirical formula of the unknown compound is $C_7H_6O_2$. Since the compound is acidic, the compound is an organic acid. The functional group is a carboxyl group –COOH.	1 point the correct functional group

Would we accept just 'carboxyl' or 'carboxylic acid'? Since the question doesn't ask for a structure, I would say yes.

I think carboxyl or carboxylic acid is sufficient.

3. Answer the following questions related to the kinetics of chemical reactions.

$$I^-(aq) + ClO^-(aq) \xrightarrow{-OH^-} IO^-(aq) + Cl^-(aq)$$

Iodide ion, I^-, is oxidized to hypoiodite ion, IO^-, by hypochlorite, ClO^-, in basic solution according to the equations above. Three initial-rate experiments were conducted; the results are shown in the following table.

Experiment	$[I^-]$ (mol L^{-1})	$[ClO^-]$ (mol L^{-1})	Initial Rare of Formation of IO^- (mol L^{-1} s^{-1})
1	0.017	0.015	0.156
2	0.052	0.015	0.476
3	0.016	0.061	0.596

(a) Determine the order of the reaction with respect to each reactant listed below. Show your work.

    (i) $I^-(aq)$

Experiments 1 and 2: $$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k_2[I^-]_2{}^x[ClO^-]_2{}^y}{k_1[I^-]_1{}^x[ClO^-]_1{}^y}$$ $$\frac{0.476}{0.156} = \frac{k_2(0.052)^x(0.015)^y}{k_1(0.017)^x(0.015)^y}$$ $$3.05 = \frac{(0.052)^x}{(0.017)^x} = 3.06^x$$ $$x = 1 \implies \text{first order}$$	1 point for correct order of the reaction with respect to I^-

Can do this without doing the math.(2)
    May be considerably more brief in their explanations,HOWEVER...they must at LEAST say: 3.05 = 3.06<x> thus x = 1 OR alternatively state...."the factor by which the rate increases is EQUAL to the factor by which the [iodide ion] increases, thus the order is FIRST". Something similar for (ii).
    No need for subscripts on k

    (ii) $ClO^-(aq)$

Experiments 1 and 3: $$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k_2[I^-]_2{}^x[ClO^-]_2{}^y}{k_1[I^-]_1{}^x[ClO^-]_1{}^y}$$ $$\frac{0.596}{0.156} = \frac{k_2(0.061)^x(0.016)^y}{k_1(0.017)^x(0.015)^y}$$	1 point for correct order of the reaction with respect to ClO^-

$3.82 = \dfrac{(0.061)^y}{(0.017)^y} = 3.59^y$ $y = 1 \quad \Rightarrow \quad$ first order	

Can do this without doing the math.(2)

(b) For the reaction,

      (i)   write the rate law that is consistent with the calculations in part (a);

|	
$\text{rate} = k[I^-]^1 [ClO^-]^1$	1 point for correct rate law based on exponents determined in part (a)

What if students omits 'rate =' and just gives the expression?

      (ii)   calculate the value of the specific rate constant, k, and specify units.

$\text{rate} = k[I^-]^1[ClO^-]^1$ $k = \dfrac{\text{rate}}{[I^-]^1 [ClO^-]^1}$ Use data from any Experiment – using Experiment #1: $k = \dfrac{0.156 \text{ mol L}^{-1} \text{ s}^{-1}}{(0.017 \text{ mol L}^{-1})^1(0.015 \text{ mol L}^{-1})^1}$ $k = 612 \text{ L mol}^{-1} \text{ s}^{-1}$ (units M^{-1} s^{-1} also acceptable)	1 point for value of rate constant 1 point for correct units

Two sig figs in the answer…610 L mol⁻¹ s⁻¹

The catalyzed decomposition reaction of hydrogen peroxide, H_2O_2, is represented by the following equation,

$$2\ H_2O_2(aq) \xrightarrow{\ -\text{catalyst}\ } 2H_2O(l) + O_2(g)$$
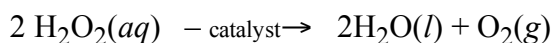
The kinetics of the decomposition reaction were studied and the analysis of the results show that it is a first-order reaction. Some of the experimental data are shown in the table below.

$[H_2O_2]$ (mol L^{-1})	Time (minutes)
1.00	0.0
0.78	5.0
0.61	10.0

(c) During the analysis of the data, the graph below was produced

      (i)   Label the vertical axis of the graph.

$\ln[H_2O_2]$	1 point for y-axis label

      (ii)   What are the units of the rate constant, k, for the decomposition of $H_2O_2(aq)$?

minutes^{-1}	1 point for correct units on k

Why ask for units twice in the same question?
Would we accept sec^{-1}? I vote yes.
I agree that sec^{-1} is worth a point.

If k is determined from the graph's slope, units are sec^{-1}; if we accept inverse seconds, then we must accept all inverse time units.

      (iii)   On the graph, draw the line that represents the plot of the uncatalyzed first-order decomposition of 1.00 M $H_2O_2(aq)$.

The graph should have a straight line originating from the same starting point, with a negative slope. However, the magnitude of the slope will be smaller so the line for the uncatalyzed reaction will be above the catalyzed reaction	1 point for any two features (origin, negative slope, smaller slope) 2 points for all three features

4. Write the formulas to show the reactants and the products for any FIVE of the laboratory situations described below. Answers to more than five choices will not be graded. In all cases, a reaction occurs. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solution as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You need not balance the equations.

General Scoring: 3 points each: 1 point for correct reactant(s) and 2 points for correct product(s)

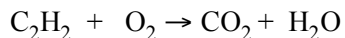(a) A strip of zinc is placed in a solution of nickel(II) nitrate.

$$Zn + Ni^{2+} \rightarrow Zn^{2+} + Ni$$
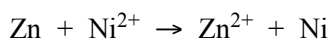
(b) Solid aluminum hydroxide is added to a concentrated solution of potassium hydroxide.

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$$

what about Al(OH)$_6^{3-}$ as a product.

(c) Ethyne (acetylene) is burned in air.

$$C_2H_2 + O_2 \rightarrow CO_2 + H_2O$$

What about CO + CO$_2$ + H$_2$O
Accept the structural diagram for ethyne.

(d) Solid calcium carbonate is added to a solution of ethanoic (acetic) acid.

$$CaCO_3 + HC_2H_3O_2 \rightarrow Ca^{2+} + C_2H_3O_2^- + CO_2 + H_2O$$
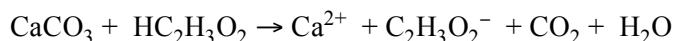
Get this answer if acetic acid is in excess. Since no mole relationship, could get HCO$_3^-$ or
probably a combination.
Since acetic acid is a weak acid will we accept HCO$_3^-$ on the product side?

(e) Lithium metal is strongly heated in nitrogen gas.

$$Li + N_2 \rightarrow Li_3N$$
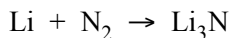
(f) Boron trifluoride gas is added to ammonia gas.

$$BF_3 + NH_3 \rightarrow BF_3NH_3$$
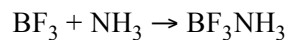
Change H to F in reactants and products. Boron TRIFLUORIDE rather than hydride. (fixed)

(g) Sulfur trioxide gas is bubbled into a solution of sodium hyroxide.

$$SO_3 + OH^- \rightarrow SO_4^{2-} + H_2O$$
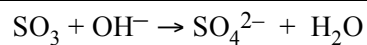
May see some HSO_4^- here.
since no molar data – we will see HSO_4^-

(h) Equal volumes of 0.1 M solutions of lead(II) nitrate and magnesium iodide are combined.

$$Pb^{2+} + I^- \rightarrow PbI_2$$
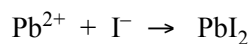
5.   Answer the following questions that relate to laboratory observations and procedures.

(a)   An unknown gas is one of three possible gases: nitrogen, hydrogen or oxygen. For each of the three possibilities, describe the result expected when the gas is tested using a glowing splint (a wooden stick with one end that has been ignited and extinguished, but still contains hot, glowing, partially burned wood.)

|	

Nitrogen:
        When the glowing splint is inserted into the gas sample the glowing splint will be extinguished.
 	
Hydrogen:
        When the glowing splint is inserted into the gas sample a popping sound (explosion) can be heard.
 	
Oxygen:
        When the glowing splint is inserted into the gas sample the splint will glow brighter.
	1 point for each description

Should accept oxygen gas causes splint to RE_IGNITE.
*   The popping sound presumed the accessibility of oxygen, which is not explicit in the directions. What to do if a student claims that the splint will be extinguished? I would give the credit. Also, would accept 're-ignite' for oxygen.*
*   I have a problem with the hydrogen gas because you have to assume that hydrogen gas escapes and oxygen gas comes in to get a pop. If students have seen the demonstration where you take a balloon filled with hydrogen and take a candle to it, the balloon burst due to the heat and no reaction with hydrogen. Good students could assume you are placing splint into pure hydrogen. The question should have stated that the splint is inserted into the balloon. When we read the answers before grading starts, might indicate no problem with the question.*
*   Hydrogen – we may get no reaction with the glowing splint if the hydrogen/oxygen mixture is not within range – I have not achieved a reaction ALL the time this way.*
*   Oxygen – it may also relight or flame up.*
*   One comment on the glowing splint controversy - it wouldn't be glowing if there weren't already oxygen around somewhere, just try to make a splint with "hot glowing partially burned wood" in pure hydrogen! Those good students shouldn't think the experiment is done in an atmosphere of pure hydrogen or they are not that good! No mention of a balloon in my text, so where did that notion come from? "Burns" may be enough for the point without an explosion pop, though. I bet most will "pop".*

(b)   The following three mixtures have been prepared: CaO plus water, SiO_2 plus water, and CO_2 plus water. For each mixture, predict whether the pH is less than 7, equal to 7, or greater than 7. Justify your answers.

CaO plus water:
      The pH of the solution will be greater than 7. CaO in water forms the base $Ca(OH)_2$.
 	
 SiO_2 plus water:
      The pH of the solution will be equal to 7. SiO_2 (sand) is insoluble in water, so expect no change in the pH of the mixture.
 	
 CO_2 plus water:
      The pH of the solution will be less than 7. CO_2 in water forms the acid H_2CO_3.
	1 point for each description

The rubic omits justification, without these it is a three sided coin. (fixed)
See http://www.pqcorp.com/msds/britesorb_C930.pdf - certain forms of SiO_2 are
highly activated and this shows slightly alkaline! Debate on whether we accept either answer? Students may be confused anyway with "mixture in water" = suspension?, or if they state - no reaction, or "insoluble" do we give them any credit. The question doesn't even say pure distillied unaerated water, so in their own lab experience, all water would probably be acidic to start with and unchanged by SiO_2 .
Carbon dioxide plus water gives hydronium ion and bicarbonate ion.

(c)   Each of three beakers contains a 0.1 M solution of one of the following solutes: potassium chloride, silver nitrate, or sodium sulfide. The three beakers are labeled randomly as solution 1, solution 2, and solution 3. Shown below is a partially completed table of observations made of the results of combining small amounts of different pairs of solution.

	Solution 1	Solution 2	Solution 3
Solution 1		black precipitate	
Solution 2			no reaction
Solution 3			

(i)   Write the chemical formula of the black precipitate.

The black precipitate is Ag_2S.	1 point for the correct formula.

(ii)   Describe the expected results of mixing solution 1 with solution 3.

A white precipitate will be produced when the two solutions are mixed.	1 point for the correct observation.

AgCl forms should be good since the question doesn't ask for OBSERVATIONS only a result! (and all the other combinations you have described. Readers will want to avoid this one!
Does the student have to say white could they say a ppt is formed.

(iii)   Identify each of the solutions 1, 2 and 3.

Solution 1 is silver nitrate. Solution 2 is sodium sulfide. Solution 3 is potassium chloride.	1 point for the correct assignments of all three solutions.

NOTE: In part (c) consistency will be important when (c) (i) is wrong. Consistency points will hinge on not only the answer in part (c) (i) but also correct chemistry.

If the student indicates in part (c) (i) the formula is K_2S. Then Solution 1 and 2 can be either KCl or Na_2S. If the student answers part (c) (ii) is a white ppt (because the student has concluded that silver nitrate and sodium sulfide do not react, the student should receive the point in part (c) (ii). If the student answers part (c) (ii) is a black ppt (because the student has concluded that silver nitrate and potassium chloride do not react, the student should receive the point in part (c) (ii). In the first case in part (c) (ii) Solution 1 is sodium sulfide, Solution 2 is potassium chloride and Solution 3 is silver nitrate should receive a point, or in the first case in part (c) (ii) Solution 1 is potassium chloride, Solution 2 is sodium sulfide and Solution 3 is silver nitrate should receive a point.

If the student indicates in part (c) (i) the formula is AgCl. Then Solution 1 and 2 can be either KCl or $AgNO_3$. If the student answers part (c) (ii) is a black ppt (because the student has concluded that silver nitrate and sodium sulfide react, the student should receive the point in part (c) (ii). If the student answers part (c) (ii) is no reaction (because the student has concluded that sodium sulfide nitrate and potassium chloride do not react, the student should receive the point in part (c) (ii). In the first case in part (c) (ii) Solution 1 is silver nitrate sulfide, Solution 2 is potassium chloride and Solution 3 is sodium sulfide should receive a point, or in the first case in part (c) (ii) Solution 1 is potassium chloride, Solution 2 is silver nitrate and Solution 3 is sodium sulfide should receive a point.

I think this will actually grade cleaner than it looks. Many students will get the colors wrong and claim that the black ppt. is AgCl. I think that these students should still be able to earn two of three points (as written in the rubric).

6.   Answer the following questions that relate to chemical bonding.

(a)   In the boxes provided, draw the complete Lewis structure (electron-dot diagram) for each of the three molecules represented below.
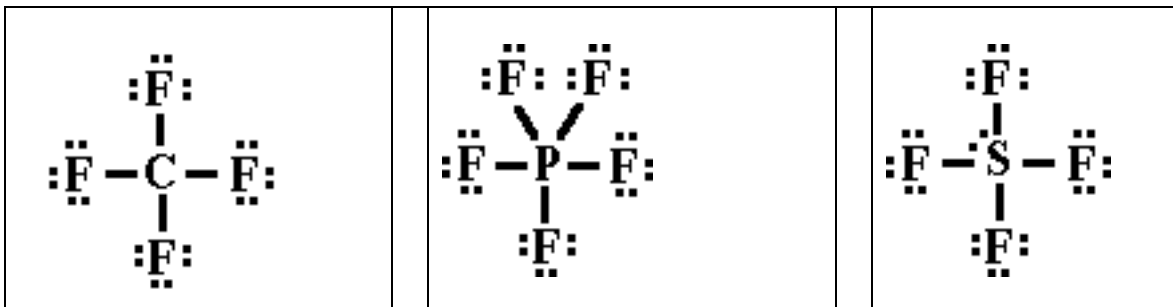
	1 point each for the correct (complete) Lewis structure. NOTE: The Lewis structures draw for the student in part (c) are complete.

Do we dock all three points if a student consistently fails to place unshared electrons around the fluorine atoms? I would dock the student only one point if the rest of the structure is correct.
sketches can get awfully ambiguous.

(b)   On the basis of the Lewis structures drawn above, answer the following questions about the particular molecule indicated.
        (i)   What is the F–C–F angle in CF_4?

	1 point for the correct bond angle.
109.5˚	The bond angle in this part must be consistent with the Lewis structure drawn in (a).

What range is acceptable? 109˚ (yes)? Really almost anything between 90˚ and 120˚ should indicate that the student knows it is neither square (planar) nor trigonal.

        (ii)   What is the hybridization of the valence orbitals of P in PF_5?

	1 point for the correct hybridization.
dsp^3	The hybridization in this part must be consistent with the Lewis structure drawn in (a).

Accept sp^3d. (2)

        (iii)   What is the geometric shape formed by the atoms in SF_4?

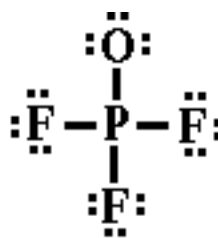|	
seesaw	1 point for the correct molecular geometry. The molecular geometry in this part must be consistent with the Lewis structure drawn in (a).

Accept 'distorted tetrahedron' or a sketch.
Do we take "asymmetrical tetrahedron"?
Do not accept saw horse – we did not in past years
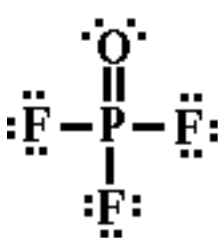
Structure 1   Structure 2

(c)   Two Lewis structures can be drawn for the OPF$_3$ molecule, as shown below.
    (i)   How many sigma bonds and how many pi bonds are in structure 1?

4 sigma bonds and 1 pi bond.	1 point for the correct # of sigma bonds. 1 point for the correct # of pi bonds.

    (ii)   Which one of the structures best represents a molecule of OPF$_3$ molecule, as shown below? Justify your answer in terms of formal charge.

Structure 1 is the best structure. It has all atoms with formal charge of 0. P: 5 – 5 – 0 = 0 F: 7 – 1 – 6 = 0 O: 6 – 2 – 4 = 0	1 point for the correct structure and either showing the calculation for formal charge or indicating that the formal charge is 0 on all atoms.

I would not hold students to explicitly calculate each of the formal charges.

7.   Use principles of atomic structure, bonding, and/or intermolecular forces to respond to each of the following. Your responses must include specific information about all substances referred to in each question.
(a)   At a pressure of 1 atm, the boiling point of $NH_3(l)$ is 240 K, whereas the boiling point of $NF_3(l)$ is 144 K.
(i)   Identify the intermolecular forces(s) in each substance.

NH_3 has dispersion forces and hydrogen bonding forces. NF_3 has dispersion forces and dipole-dipole forces.	1 point for the correct intermolecular attractive forces for both NH_3 and NF_3.

I would recommend not insisting that dispersion forces be mentioned explicitly in either case.

For ammonia LDF, dipole-dipole and hydrogen bonding   Do you want student to have dipole-dipole for ammonia?

I think that not mentioning dispersion forces is OK.

Perhaps indicate that in addition to "London" dispersion forces, BOTH ammonia and nitrogen trifluoride have dipole-dipole forces, however, ammonia has the EXCEPTIONALLY STRONG dipole-dipole force called HYDROGEN BONDING???

(ii)   Account for the difference in the boiling points of the two substances.

The magnitude of the dispersion forces are not significantly different in NH_3 and NF_3. The higher boiling point for NH_3 is due to the strong hydrogen-bonding intermolecular attractive forces between adjacent NH_3 molecules. NF_3 does not exhibit hydrogen-bonding.	1 point for the correctly identifying hydrogen-bonding forces as present in NH_3 but not in NF_3.

I sense the impending footsteps of a 'Demmin Diagram'.
comment--what's a Demmin Diagram?

(b)   The melting point of KCl(s) is 776 ˚C, whereas the melting point of NaCl(s) is 801 ˚C.
(i)   Identify the type of bonding in each substance.

Both KCl and NaCl are ionic compounds so the type of bonds are ionic bonds.	1 point for saying ionic bonding for the bonds in KCl and NaCl.

(ii)   Account for the difference in the melting point of the substances.

The strength of the ionic bond is a measure of the relative melting points for ionic compounds. The lattice energy is a measure of the strength of the ionic bond; $$LE \, \alpha \, \frac{Q_1 Q_2}{d}$$ In this case the charge on cation and anion are the same in both compounds, so the relative size of the ions is the determining factor. Since Na^+ has a smaller ionic radius compared to K^+, the lattice energy for NaCl is higher compared to KCl. Therefore NaCl will have the higher melting point compared to KCl.	1 point for the correct discussion regarding the difference between KCl and NaCl.

Ah, comparing the values of quantities that are inherently negative! This will have to be read carefully, the LE[NaCl] is less than (more negative than) the LE[KCl]. I think that any statement that refers to equal charge magnitudes and smaller ions (or smaller distance) in NaCl should be OK. (2)

The point portion of the rubric should reference the size differences relative to the LE (it is a repeat of a.ii. now)

(c)   As shown in the table below, the first ionization energies of Si, P and Cl show a trend.

Element	First Ionization Energy (kJ mol^{-1})
Si	786
P	1,012
Cl	1,251

(i)   For each of the three elements, identify the quantum level (e.g., $n = 1$, $n = 2$, etc.) of the valence electrons in the atom.

The electron configuration for each element is; Si: $1s^2 2s^2 2p^6 3s^2 3p^2$ P: $1s^2 2s^2 2p^6 3s^2 3p^3$ Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$ The valence electron is located in the n = 3 level for all three atoms.	1 point for the principle quantum level for all three elements.

Since no mention is made of electron configuration or justification, I think we will have to take the briefest of responses.

It should be enough to simply state that n = 3 for all three species. (Read the question stated.)

Is just the configuration of all three sufficient – I think so – give em a break!

(ii)   Explain the reasons for the trend in first ionization energies.

The electron configuration for each element is; Si: $1s^2 2s^2 2p^6 3s^2 3p^2$ P: $1s^2 2s^2 2p^6 3s^2 3p^3$ Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$ The valence electron is located in the n = 3 level for all three atoms. Since the valence electrons in all three elements are shielded by the same number of inner core electrons, and the nuclear charge increases going from Si to P to Cl, the valence electrons feel a greater attraction to the nucleus going from Si to P to Cl. Valence electrons that feel a greater attraction to the nucleus (Cl) will be more difficult to remove so Cl has the highest ionization energy. P has the second highest followed by Si.	1 point for arguing the greater ionization energy is determined by the nuclear charge since the valence electrons for the three elements are shielded by the same number of IC electrons. Students can also argue the trend on the basis of effective nuclear charge.

This will be a more difficult point to earn. Obviously we will not, should not, can not accept arguments based on the position of the elements on the periodic table (which might be erroneous in the Southern Hemisphere!).
    How would we handle a response dealing with atomic radii (trends) decrease from left to right across a row in the PT. Cl with the smallest radius will therefore have a larger IE?
    The answer to 7.(c).(ii) is very reminiscent of the Sherdian-Miller axis of years ago. The trend in radii is an EFFECT, NOT a cause - let's be consistent on that.

(d)   A certain element has two stable isotopes. The mass of one of the isotopes is 62.93 amu and the mass of the other isotope is 64.93 amu.
   (i)   Identify the element. Justify your answer.

The element must have an relative weighted average atomic mass between the two isotopic masses, therefore the element must be Cu, copper.	1 point for the element.

(ii)   Which isotope is more abundant? Justify your answer.

Since the relative weighted average atomic mass for copper is 63.55 amu the isotope with the lower isotopic mass must have the greater abundance. If the two isotopes were equally abundant the atomic mass would be 63.93 amu, since the actual mass is less the isotope with a mass of 62.93 amu has a greater abundance.	1 point the correct choice and correct explanation.

$$AgNO_3(s) \rightarrow Ag^+(aq) + NO_3^-(aq)$$
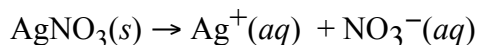
8.   The dissolving of $AgNO_3(s)$ in pure water is represented by the equation above.

    (a)   Is ΔG for the dissolving of $AgNO_3(s)$ positive, negative, or zero? Justify your answer.

ΔG for the dissolving of $AgNO_3(s)$ is –. Since $AgNO_3(s)$ is known to be soluble in water, the solution process must be spontaneous, so ΔG is negative.	1 point the correct sign of ΔG and correct explanation.

    (b)   Is ΔS for the dissolving of $AgNO_3(s)$ positive, negative, or zero? Justify your answer.

ΔS for the dissolving of $AgNO_3(s)$ is +. Since the reactants are more ordered compared to the products $Ag^+(aq) + NO_3^-(aq)$ ΔS is positive. In the balanced chemical equation 1 mol of solid is more ordered compared to 2 moles of aqueous ions.	1 point the correct sign of ΔS and correct explanation.

I think we should insist on a mention of phases and not accept simply "1 mole to 2 moles," but I am willing to be overruled here.

Does the argument for increasing disorder on dissolution consider solvent ordering due to solvation effects? In this problem, delta S must be positive, based on solubility and the fact that dissolution is an endothermic process. I wish parts b and c had been asked in reverse order.

    (c)   The solubility of $AgNO_3(s)$ increases with increasing temperature.
        (i)   What is the sign of ΔH for the dissolving process? Justify your answer.

ΔH must be positive for its solubility to increase with increasing temperature. Solubility is an equilibrium process, since increasing temperature is accomplished by adding heat and the reaction is shifting towards the products in the chemical equation, heat must be on the reactants side of the equation and the solution process is endothermic.	1 point the correct sign of ΔH and correct explanation.

Yes. Here, Le Chatelier will undoubtedly rear his hoary head, but a good case can be made using Le Chatelier's Principle.

(ii)   Is the answer you gave in part (a) consistent with your answers to parts (b) and c(i) ? Explain.

Since ΔS is + and ΔH is +, for ΔG to be − the relative magnitude of the ΔS term must be more positive compared to the ΔH term. Since $\Delta G = \Delta H - T\Delta S$, for solution process to be spontaneous the entropy term must be more important compared to the enthalpy term.	1 point the correct sign correct explanation.

NOTE: Consistency will be an issue on this part. Depending on the sign of ΔG, ΔS and ΔH that the student assigns their argument in part (c) (ii) must focus on the equation $\Delta G = \Delta H - T\Delta S$ for the points.

Is it important that the relative magnitude of the ΔH and $T\Delta S$ terms be discussed? I would say not. Also, credit may again be awarded for incorrect responses that are consistent with previous answers.
Agree that the MAGNITUDE of "delta H" and the "TdeltaS" term need NOT be addressed in this question.
The magnitude of the relative terms is important in all but two cases (1) delta S is pos. and delta H is negative, making delta G negative at all temps; (2) delta S is neg. and delta H is pos, making delta G positive at all temps. Neither of these cases corresponds to the correct set of answers, so I would argue that magnitude of the terms must at least be alluded to.

The compound NaI dissolves in pure water according to the equation $NaI(s) \rightarrow Na^+(aq) + I^-(aq)$. Some of the information in the table of standard reduction potentials given below may be useful in answering the questions that follow.

Half-reaction	E˚ (V)
$O_2(g) + 4\ H^+ + 4\ e^- \rightarrow 2H_2O(l)$	1.23
$I_2(s) + 2\ e^- \rightarrow 2I^-$	0.53
$2H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2OH^-$	0.83
$Na^+ + 1\ e^- \rightarrow Na(s)$	−2.71

(d)   An electric current is applied to a 1.0 M NaI solution.
    (i)   Write the balanced oxidation half-reaction for the reaction that takes place.

$2I^- \rightarrow I_2(s) + 2\ e^-$ Since E˚ for this oxidation is more positive compared to -1.23 v for the oxidation of water.	1 point the correct half-reaction.

| When an aqueous solution is electrolyzed the more positive half-reaction occurs at each electrode. | |

The question does not call for an explanation. The ½ Rxn equation should be enough for credit.(4)

(ii)   Write the balanced reduction half-reaction for the reaction that takes place.

$2H_2O(l) + 2\ e^- \rightarrow H_2(g)\ + OH^-$ Since E˚ for this reduction is more positive compared to -2.71 v for the reduction of Na^+. When an aqueous solution is electrolyzed the more positive half-reaction occurs at each electrode.	1 point the correct half-reaction.

The question does not call for an explanation. The ½ Rxn equation should be enough for credit.(2)

(iii)   Which reaction takes place at the anode, the oxidation reaction or the reduction reaction?

The oxidation half-reaction occurs at the anode.	1 point the correct choice.

(iv)   All electrolysis reactions have the same sign of ΔG˚. Is the sign positive or negative? Justify your answer.

The sign of ΔG for all electrolysis reactions is +. Since electrolysis reactions are non-spontaneous energy (electrical current) must be added before the reaction can occur, therefore ΔG is positive.	1 point the correct sign of ΔG and correct explanation.

FULL JUSTIFICATION would be required for the mark.