AP Exam 2002

Question 1

$$HOBr \rightleftarrows H^+ + OBr^- \quad K_a = 2.3 \times 10^{-9}$$

Hypobromous acid, HOBr, is a weak acid that dissociates in water, as represented by the equation above.

    (a) Calculate the value of $[H^+]$ in a solution of HOBr that has a pH of 4.95.

pH = 4.95 pH = –log $[H^+]$ 4.95 = –log $[H^+]$ –4.95 = log $[H^+]$ $10^{-4.95} = 10^{\log [H^+]}$ 1.12×10^{-5} M = $[H^+]$	1 pt	What if the answer is left at $10^{-4.95}$ is that a point?

TL Feedback:

Votes: Calculate pH $\boxed{8}$ $10^{-4.95}$ $\boxed{2}$ *(willing to consider)*

    (b) Write the equilibrium constant expression for the ionization of HOBr in water, then calculate the concentration of HOBr$_{(aq)}$ in an HOBr solution that has $[H^+]$ equal to 1.8×10^{-5} M.

|	
$K_a = \dfrac{[H^+][OBr^-]}{[HOBr]}$ If the $[H^+] = 1.8 \times 10^{-5}$ M, then $[OBr^-] = 1.8 \times 10^{-5}$ M Substituting, $2.3 \times 10^{-9} = \dfrac{[H^+][OBr^-]}{[HOBr]} = \dfrac{[1.8 \times 10^{-5} \text{ M}][1.8 \times 10^{-5} \text{ M}]}{[HOBr]}$ $[HOBr] = \dfrac{[1.8 \times 10^{-5} \text{ M}][1.8 \times 10^{-5} \text{ M}]}{2.3 \times 10^{-9}} = 0.14$ M	1 pt K_a for expression 1 pt $[H^+] = [OBr^-]$ 1 pt.for [HOBr]

TL Feedback:

    Prefer only 2 points for part b) 1 pt for the equilibrium expression and 1 pt for the [HOBr]. Take the point saved here and use it in part c ii (see discussion below).

    Do the students need the unit M?

    Since the general equation for K_a is given in the exam, do not award a point for the expression. Shift the extra point to part a, award 1 point for $10^{-4.95}$ and the second point for the calculated pH or move the point to part c ii.

    Recommend only 2 points for the part. Move the extra point to part c ii.

    There is one TL who supports the 3 point distribution in this part.

(c) A solution of $Ba(OH)_2$ is titrated into a solution of HOBr.

(i) Calculate the volume of 0.115 M $Ba(OH)_{2(aq)}$ needed to reach the equivalence point when titrated into a 65.0 mL sample of 0.146 M $HOBr_{(aq)}$.

$Ba(OH)_{2(aq)}$ + $2HOBr_{(aq)}$ ---> $Ba(OBr)_{2(aq)}$ + $2H_2O_{(l)}$	1 pt for stoichiometry
$0.065 \text{ L} \left(\dfrac{0.146 \text{ mol HOBr}}{1 \text{ L}} \right) \left(\dfrac{1 \text{ mol Ba(OH)}_2}{2 \text{ mol HOBr}} \right) \left(\dfrac{1 \text{ L}}{0.115 \text{ mol Ba(OH)}_2} \right)$ $= 0.0413\text{L or } 41.3 \text{ mL}$	1 pt for calculation

TL Feedback:
If the student does not write the equation can they get the first point? (CR response…yes. The equation is there only to show the stoichiometry. Students do not have to write the reaction for the first point.)
Another possible solution;

$$\frac{V_b M_b}{V_a M_a} = \frac{1}{2} \qquad 2\,V_b M_b = V_a M_a$$

We will have to watch out for the units…L or mL.
Award the first point for an implied stoichiometry
We will be awarding a point for the correct calculation based on the wrong stoichiometry…right?
If the student misses the first point (wrong stoichiometry), can they get credit for the answer 82.6 mL? (the TL that asks this feels the student should not get the point.)

(ii) Indicate whether the pH at the equivalence point is less than 7, equal to 7, or greater than 7. Explain.

pH is greater than 7. At the equivalence point there is only OBr^- in solution. HOBr is a weak acid, OBr^- is a weak conjugate base; $K_b(OBr^-) = \left(\dfrac{K_w}{K_a(HOBr)} \right) = \left(\dfrac{1.0 \times 10^{-14}}{2.3 \times 10^{-9}} \right) = 4.3 \times 10^{-6}$ Such a solution is basic.	1 pt. For explanation

TL Feedback:
The pH should be worth a point and the explanation worth a point. Also except the equation $OBr^- + H_2O \rightleftarrows HOBr + OH^-$ for the explanation.
A second vote for a point for the pH and a point for the explanation.
Can the student say it is basic due to the hydrolysis? (just saying the word)
If the student calculates the pH with no explanation? How many points?
Do we give a point to the explanation: pH is greater than 7, because we are mixing a strong base with a weak acid?

Response showing the hydrolysis reaction OBr⁻ + H₂O ⇌ HOBr + OH⁻ would be a good explanation.

How about, 'at the equivalence point, equal moles of a WEAK acid and STRONG base have been added to the solution, so the solution will be basic (pH >7)?" Do we hold them to the identification of OBr⁻ as the conjugate base?

Keep this as is (no 2nd point, no credit for guessing an answer and having no valid explanation). Mentioning that OBr⁻ is basic should be sufficient. If they do calculate the pH (10.8) then they should certainly get the point even if they don't say it is greater than 7.

(d) Calculate the number of moles of NaOBr(s) that would have to be added to 125 mL of 0.160 M HOBr to produce a buffer solution with $[H^+] = 5.00$ x 10^{-9} M. Assume that volume change is negligible.

$K_a = \dfrac{[H^+][OBr^-]}{[HOBr]}$ Rearranged $[OBr^-] = \dfrac{[HOBr] \cdot K_a}{[H^+]} = \dfrac{0.160 \text{ M} \cdot 2.3 \text{ x } 10^{-9}}{5.00 \text{ x } 10^{-9} \text{ M}}$ $[OBr^-] = 0.074$ M $n_{NaOBr} = 0.125 \text{ L} \left(\dfrac{0.074 \text{ mol OBr}^-}{1 \text{ L}} \right) = 9.2 \text{ x } 10^{-3}$ mol	1 pt for [OBr⁻], the set-up or calculated value 1 pt for n_{NaOBr}

TL Feedback:

$pH = pKa + log\left(\dfrac{[OBr^-]}{[HOBr]}\right)$

$-log\ 5.00\ x\ 10^{-9} = -log\ 2.3\ x\ 10^{-9} + log\left(\dfrac{[OBr^-]}{[0.160]}\right)$

$8.30 = 8.64 + log\left(\dfrac{[OBr^-]}{[0.160]}\right)$

$10^{-0.34} = \left(\dfrac{[OBr^-]}{[0.160]}\right)$

$[OBr^-] = 0.073$ M

Do students have to find a value here? Or is the set up enough?
How do we distribute the points if the student uses the Henderson-Hasselbach equation
Need an answer here. Just setting up the calculation using HH is not enough. Students have a calculator and need to know how to use it.

(e) HOBr is a weaker acid than HBrO$_3$. Account for this fact in terms of molecular structure.

According to the formula for HOBr and HOBrO$_2$ there are two additional terminal, electronegative oxygen atoms attached to the central bromine atom. The additional terminal oxygen atoms distribute the negative charge on the anion BrO$_3^-$ compared to BrO$^-$. The result is to reduce the electrostatic attraction between the H$^+$ and BrO$_x^-$. Or The formal positive charge of bromine in HOBr is 0 and is +2 on HOBrO$_2$. The higher formal charge on the central atom further polarizes and weakens the O-H bondThe weaker the H-O bond, the stronger the acid. Or The two additional terminal electronegative O atoms on the central bromine atom pull electron density from the central bromine atom. The net result is to weaken the H-O bond in H-O-Br. Since HOBr has no additional terminal O atoms the H-O bond is stronger. The weaker the H-O bond, the stronger the acid. Or In HOBr there is a Br attached to OH in HOBrO$_2$ there is a BrO$_2$ attached to the OH.	1 pt

TL Feedback:
I would have trouble giving a point to the third explanation.
For HBrO$_x$: As additional oxygen atoms are bonded to the central atom and the electron density is withdrawn from the Br the bond is weakened and polarized. To what extent will polarity explanations suffice?
The most likely answer will be the third response, the last response is not worth a point (2 TLs). The last response just re-stated the structure, and does not explain how the structure works. Could also move the point from part b to here, 1 point for structure and 2nd point for connection to strength.
No credit for the 2nd response. With regards to the 3rd response: is the bond energy for O-H that different in the two acids? Isn't the polarity of the O-H bond that makes the IMF stronger between water and the O-H that breaks the bond?
Do they shoot themselves in the foot if the imply that the acidic proton is attached directly to the bromine atom?
Keep this 1 pt, for the explanation. I would list the 3rd response first. You are going to see this the most, and I think it is the most valid answer.

List the 1st response second. I feel the use of the term "stabilize" here is awkward. The last sentence of this might read better as: "The additional terminal oxygen

atoms spread out the negative charge on BrO3-, compared to BrO-. The result is to reduce..."

Question 2:

Answer parts (a) through (e) below, which relate to reactions involving silver ion, Ag^+.

The reaction between silver ion and solid zinc is represented by the following equation.

$$2Ag^+{}_{(aq)} \ + \ Zn_{(s)} \ \rightarrow \ Zn^{2+}{}_{(aq)} \ + \ 2\,Ag_{(s)}$$
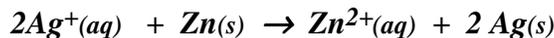
(a) A 1.50 g sample of Zn is combined with 250.0 mL of 0.110 M AgNO$_3$ at 25 ˙C.

(i) Identify the limiting reactant. Show calculations to support your answer.

$n_{Zn} = 1.50 \text{ g Zn} \left(\dfrac{1 \text{ mol Zn}}{65.4 \text{ g Zn}}\right) = 2.29 \times 10^{-2} \text{ mol Zn}$ $n_{Ag^+} = 0.250 \text{ L} \left(\dfrac{0.110 \text{ mol Ag}^+}{1 \text{ L}}\right) = 2.75 \times 10^{-2} \text{ mol Ag}^+$ $n_{Ag^+} = 1.50 \text{ g Zn} \left(\dfrac{1 \text{ mol Zn}}{65.4 \text{ g Zn}}\right)\left(\dfrac{2 \text{ mol Ag}^+}{1 \text{ mol Zn}}\right) = 4.59 \times 10^{-2} \text{ mol Ag}^+$ required and 2.75×10^{-2} mol Ag$^+$ available more required than is available so Ag$^+$ is the limiting reactant. Or $n_{Ag^+} = 0.250 \text{ L} \left(\dfrac{0.110 \text{ mol Ag}^+}{1 \text{ L}}\right) = 2.75 \times 10^{-2} \text{ mol Ag}^+$ $n_{Zn} = 2.75 \times 10^{-2} \text{ mol Ag}^+\left(\dfrac{1 \text{ mol Zn}}{2 \text{ mol Ag}^+}\right) = 1.38 \times 10^{-2} \text{ mol Zn}$ required 2.29×10^{-2} mol Zn are available more available than required so Zn is in excess and Ag$^+$ is limiting. Or $n_{Ag^+} = 0.250 \text{ L} \left(\dfrac{0.110 \text{ mol Ag}^+}{1 \text{ L}}\right) = 2.75 \times 10^{-2} \text{ mol Ag}^+ \text{ available}$ $\text{grams}_{Zn} = 2.75 \times 10^{-2} \text{ mol Ag}^+\left(\dfrac{1 \text{ mol Zn}}{2 \text{ mol Ag}^+}\right)\left(\dfrac{65.4 \text{ g Zn}}{1 \text{ mol Zn}}\right) = 0.899 \text{ g}$ Zn required. 1.50 g Zn available so Zn is in excess and Ag$^+$ is the limiting reactant.	1 pt for the moles of each reactant 1 pt for the limiting reagent and the supporting calculation or explanation

TL Feedback:

$$1.50 \text{ g } Zn\left(\frac{1 \text{ mol } Zn}{65.4 \text{ g } Zn}\right)\left(\frac{1 \text{ mol } Zn^{2+}}{1 \text{ mol } Zn}\right) = 2.29 \text{ x } 10^{-2} \text{ mol } Zn^{2+} \text{ formed}$$

$$0.250 \text{ L}\left(\frac{0.110 \text{ mol } Ag^+}{1 \text{ L}}\right)\left(\frac{1 \text{ mol } Zn^{2+}}{2 \text{ mol } Ag^+}\right) = 1.38 \text{ x } 10^{-2} \text{ mol } Zn^{2+} \text{ formed}$$

Ag^+ is the limiting reagent since fewer moles of product are formed. Two TLs feels this is worth full credit.

Another possible solution:

$$\left(\frac{0.110 \text{ mol } Ag^+}{1 \text{ L}}\right) \cdot 0.250 \text{ L} \qquad \qquad 1.5 \text{ grams}$$

$2 Ag^+$	Zn
0.0275 mol	0.0229 mol

divide each by coefficient

0.0137 mol	0.0229 mol

$$1.50 \text{ g } Zn\left(\frac{1 \text{ mol } Zn}{65.4 \text{ g } Zn}\right)\left(\frac{2 \text{ mol } Ag^+}{1 \text{ mol } Zn}\right)\left(\frac{1 \text{ L}}{0.110 \text{ mol } Ag^+}\right) = 0.417 \text{ L}$$

only have 0.250 L so Ag^+ is the limiting reagent.

Award the points: 1 point for the calculation and then 1 point for the correct conclusion. My guess is that we'll see a lot of calculations beginning with the each reactant to calculate grams of Zn^{2+} produced. The smaller amount is the LR. We give a point for the calculation and then a point for the correct conclusion. It could be an easy 1st point and a hard 2nd point.

Once the student correctly calculates the n (in moles) of each reactant (the 1st point), there are many ways to identify the limiting reagent and I don't think you need to list them all. One might say: "You need twice as much Ag^+ as Zn to run the reaction. Since you have less than twice as much, Ag^+ must be limiting." This should do.

(ii) On the basis of the limiting reactant that you identified in part (i), determine the $[Zn^{2+}]$ after the reaction is complete. Assume that volume change is negligible.

$n_{Zn^{2+}} = 2.75 \times 10^{-2}$ mol $Ag^+ \left(\dfrac{1 \text{ mol } Zn^{2+}}{2 \text{ mol } Ag^+}\right) = 1.38 \times 10^{-2}$ mol Zn^{2+}	1 pt for mol Zn^{2+}
$\left(\dfrac{1.38 \times 10^{-2} \text{ mol } Zn^{2+}}{0.250 \text{ L}}\right) = 0.0550$ M Zn^{2+}	1 pt for $[Zn^{2+}]$

TL Feedback:

Need to watch out for student who use the moles of unreacted Zn in their calculation here.

1.5 g Zn - 0.902 g Zn reacted = 0.598 g Zn unreacted (remaining in solution)

$$0.598 \text{ g Zn} \left(\frac{1 \text{ mol Zn}}{65.4 \text{ g}}\right)\left(\frac{1 \text{ mol } Zn^{2+}}{1 \text{ mol Zn}}\right) = 9.14 \times 10^{-3} \text{ mol } Zn^{2+}$$

$$\left(\frac{9.14 \times 10^{-3} \text{ mol } Zn^{2+}}{0.250 \text{ L}}\right) = 0.0366 \text{ M } Zn^{2+}$$

I think this should be worth 1 point, the concentration/divide by 0.250 L point.

If the student concludes Zn is the limiting reagent than,

$$1.50 \text{ g Zn} \left(\frac{1 \text{ mol Zn}}{65.4 \text{ g}}\right)\left(\frac{1 \text{ mol } Zn^{2+}}{1 \text{ mol Zn}}\right) = 2.29 \times 10^{-2} \text{ mol } Zn^{2+} \text{ formed}$$

$$\left(\frac{2.29 \times 10^{-2} \text{ mol } Zn^{2+}}{0.250 \text{ L}}\right) = 0.0916 \text{ M } Zn^{2+}$$

I assume consistent answers from i will receive full credit in ii.

The moles of Zn^{2+} may be found in part a).

No credit for using moles of unreacted Zn. If the student had Zn as LR, then the 0.0916 M Zn^{2+} should get full credit here.

(b) Determine the value of the standard potential, E˙, for a galvanic cell based on the reaction between $AgNO_3(aq)$ and solid Zn at 25 ˙C.

	E°	
$Ag^+(aq)$ $+ e^- \rightarrow$ $Ag(s)$	+0.80 v	
$Zn(s) \rightarrow Zn^{2+}(aq)$ + $2e^-$	+0.76 v	1 pt for E°
$2Ag^+(aq)$ + $Zn(s) \rightarrow Zn^{2+}(aq)$ + $2 Ag(s)$	+1.56 v	

My analytical colleagues are very vocal about not changing the sign of E° when reversing a half reaction. These are properly electrode potentials. I don't object to student answers like what is shown, but the modern way to do this should be shown as the correct answer.

$E°_{cell} = E°(reduction) - E°(oxidation)$ $= (0.80\ V) - (-0.76\ V)$ $= 1.56\ V$ $2Ag^+(aq)$ + $Zn(s) \rightarrow Zn^{2+}(aq)$ + $2\ Ag(s)$ +1.56 v	1 pt for E°

Another galvanic cell is based on the reaction between $Ag^+(aq)$ and $Cu(s)$, represented by the equation below. At 25 ˙, the standard potential, E˙, for the cell is 0.46 V.

$$2Ag^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$$

(c) Determine the value of the standard free-energy change, ΔG˙, for the reaction between $Ag^+(aq)$ and $Cu(s)$,at 25 ˙C.

$\Delta G° = -nFE°$ $\Delta G° = -2$ mol electrons $\cdot$ 96,500 $\frac{J}{V \cdot mol}$ +0.46 V $\Delta G° = -$ 89 kJ	1 pt for n in the correct equation 1 pt for value of ΔG°

TL Feedback:

$\Delta G° = -\ 88,800\ J$

$\log K= \dfrac{nE°}{0.592} = \dfrac{2\ mol\ e^- \cdot +0.46\ V}{0.592} = 15.54$ $K = 10^{15.54} = 3.47\ x\ 10^{15}$

$\Delta G° = -RT\ \ln K = -\ 8.314\ \dfrac{J}{mol \cdot K} \cdot 298\ K\ \ln 3.47\ x\ 10^{15} = -\ 88,700\ J\ (89\ kJ)$

     Does the student get the first point for the substitution or will the student get it for writing the number 2 (for the number of electrons)?

     Units HAVE to be in the answer.

     Students need a meaningful relationship that shows the 2 electrons for the first point, the second point for the correct calculation.

Many students will miss units and significant figures. Should this be worth 1 point?

I hope we will hold them to units.
The answer should have units & 2 or 3 SF (for 2nd point).

(d)   The cell is constructed so that $[Cu^{2+}]$ is 0.045 M and the $[Ag^+]$ is 0.010 M. Calculate the value of the potential, E, for the cell

$$E_{cell} = E° - \frac{RT}{nF} \ln Q = E° - \frac{RT}{nF} \ln \frac{[Cu^{2+}]}{[Ag^+]^2}$$	1 pt for correct substitution
$$E_{cell} = +0.46\ V - \frac{8.314\ \frac{J}{mol \cdot K} \cdot 298\ K}{2\ mol\ e^- \cdot 96500\ \frac{J}{V \cdot mol}} \ln \frac{[0.045]}{[0.010]^2}$$ $$E_{cell} = +0.46\ V - 0.0128\ V \ln 450$$	1 pt for correct answer
$$E_{cell} = +0.46\ V - 0.0128\ V \cdot 6.11$$ $$E_{cell} = +0.46\ V - 0.0782\ V$$ $$E_{cell} = +0.38\ V$$	

TL Feedback:
  1 point for $[Ag^+]^2$
  1 point for the ratio and 1 point for the answer.
  Would a student get a point for writing the K(Q) expression that shows the concentration relationship but not using it in the correct E_{cell} equation?I vote to award the 1ˢᵗ point here. The 2ⁿᵈ point comes from a calculation done correctly.
  If the square is omitted from the $[Ag^+]$, but everything is consistent, I hope we award one point.

(e)   Under the conditions specified in part (d), is the reaction in the cell spontaneous? Justify your answer.

$E_{cell} = +0.38\ V$ The cell potential under the non-standard conditions in part (d) is positive. Therefore the reaction is spontaneous under the conditions stated in part (d).	1 pt for correct answer, with correct explanation

TL Feedback:
  Is just the statement that includes the word positive enough for the point?

We may see answers relating ΔG rather than E, if connection to E is made then they get the points.

Any reference to a positive E_{cell} should get the point.

Will we accept an argument based on the relative standard reduction potentials of silver and copper? A justification based on the negative sign of ΔG should be OK.

A reference to E° is not sufficient.

Question 3:

Consider the hydrocarbon pentane, C_5H_{12} (molar mass 72.15 g).

    (a)   Write the balanced equation for the combustion of pentane to yield carbon dioxide and water.

C_5H_{12} + 8 O_2 → 5 CO_2 + 6 H_2O	1 point for having O_2 as a reactant 1 point for the correct balance.

TL Feedback:

    Only give 1 point for part (a). (move the second point to part (b) and assign it to the units in the answer.)

    If part (a) is 2 points, will the 2ⁿᵈ point be given for any balanced equation? Maybe this is a 1 point equation. (make part (b) worth 3 points.)

    Any points for using O and not O_2?Will they get the 2ⁿᵈ point and no 1ˢᵗ point using O?

    My preference is: the 1ˢᵗ point should require the chemical formulas for all R & P. No credit for "O". Then give the 2ⁿᵈ point for correct balancing, as suggested. Allow credit for balancing (2ⁿᵈ pt only) if using "O" or a wrong formula for pentane (as C_5H_{10}).

    (b)   What volume of dry carbon dioxide, measured at 25 ˚C and 785 mm Hg, will result from the complete combustion of 2.50 g pentane?

$n_{C_5H_{12}} = 2.50$ g $C_5H_{12}\left(\dfrac{1 \text{ mol } C_5H_{12}}{72.15 \text{ g } C_5H_{12}}\right) = 0.0347$ mol C_5H_{12} $n_{CO_2} = 0.0347$ mol $C_5H_{12}\left(\dfrac{5 \text{ mol } CO_2}{1 \text{ mol } C_5H_{12}}\right) = 0.173$ mol CO_2 $V = \left(\dfrac{nRT}{P}\right) = \dfrac{0.173 \text{ mol} \cdot 0.0821 \frac{\text{L atm}}{\text{mol K}} \cdot 298 \text{ K}}{\dfrac{785 \text{ mm Hg}}{760 \text{ mm Hg}}} = 4.10$ L	1 point for correct mol of CO_2 1 point for the correct substitution and calculation of V.

TL Feedback:

Depending on rounding the answer is between 4.11 and 4.13.

The volume does not need to be calculated does it? So the second point can be for just the substitution?

Should there be a point for the units.

Some students will show a complete dimensional analysis set up using 22.4 and temperature and pressure conversions.

I want to see an answer. I know the student can go back and work on these questions if time permits, and they will not have a calculator. Need to establish the policy.

Need to watch significant figures here.

the 2ⁿᵈ point should require a calculated answer, with units.

Some are going to calculate V at STP. For this I would allow the 1st point only, even if n_{CO_2} is not calculated separately:

$$V = 2.50 \text{ g } C_5H_{12}\left(\frac{1 \text{ mol } C_5H_{12}}{72.15 \text{ g } C_5H_{12}}\right)\left(\frac{5 \text{ mol } CO_2}{1 \text{ mol } C_5H_{12}}\right)\left(\frac{22.4 \text{ L } CO_2}{1 \text{ mol } CO_2}\right) = 3.88 \text{ L } CO_2$$

(c)   The complete combustion of 5.00 g of pentane releases 243 kJ of heat. On the basis of this information, calculate the value of ΔH for the complete combustion of one mole of pentane.

$5.00 \text{ g } C_5H_{12}\left(\dfrac{1 \text{ mol } C_5H_{12}}{72.15 \text{ g } C_5H_{12}}\right) = 0.0693 \text{ mol } C_5H_{12}$ $\left(\dfrac{243 \text{ kJ}}{0.0693 \text{ mol } C_5H_{12}}\right) = 3.51 \times 10^3 \text{ kJ mol}^{-1}$ $\Delta H = -3.51 \times 10^3 \text{ kJ mol}^{-1}$	1 point for correct mol of C_5H_{12} 1 point for the correct substitution and calculation of ΔH.

TL Feedback:

$$\left(\frac{243 \text{ kJ}}{5.00 \text{ g } C_5H_{12}}\right) = \left(\frac{x \text{ kJ}}{72.0 \text{ g } C_5H_{12}}\right) \qquad x = 3.50 \times 10^3 \text{ kJ mol}^{-1}$$

Does the word value in the statement of the question get around the sign of ΔH? What the significant figures.
The answer should show the correct sign and units, for the 2nd point. Accept kJ as the units, as many texts use this as the units of ΔH_{rxn}.

(d)   Under identical conditions, a sample of an unknown gas effuses into a vacuum at twice the rate that a sample of pentane gas effuses. Calculate the molar mass of the unknown gas.

$\text{rate}_{\text{unknown}} = 2 \cdot \text{rate}_{C_5H_{12}}$ $, 2 \cdot \text{rate}_{C_5H_{12}}$ $\dfrac{\text{rate}_{\text{unknown}}}{\text{rate}_{C_5H_{12}}} = \sqrt{\dfrac{72 \text{ g mol}^{-1}}{MM_{\text{unk}}}}$ $\dfrac{2 \cdot \cancel{\text{rate}_{C_5H_{12}}}}{\text{rate}_{\cancel{C_5H_{12}}}} = \sqrt{\dfrac{72 \text{ g mol}^{-1}}{MM_{\text{unk}}}}$ $2 = \sqrt{\dfrac{72 \text{ g mol}^{-1}}{MM_{\text{unk}}}}$ $4 = \dfrac{72 \text{ g mol}^{-1}}{MM_{\text{unk}}}$ $MM_{\text{unk}} = \dfrac{72 \text{ g mol}^{-1}}{4} = 18 \text{ g mol}^{-1}$	Option 1: 1 point for recognizing the relationship between rate and velocity 1 point for the correct substitution and calculation of MM. Option 2: Or should it be 1 point for the magnitude and 1 point for the correct units on the molar mass?

TL Feedback:

What if the student says..'Since the unknown effuses twice as fast its mass must be four times lighter.' Therefore the molar mass of the unknown is $\left(\dfrac{72.0 \text{ g mol}^{-1}}{4}\right)$ or 18 g mol^{-1} 2 points?

Three vote for the first option #1 point distribution.

Another TL feels a point should not be given for the units on the MM. "Many individuals will leave them off."

1 point for the correct 1:2 ratio and 1 point for the answer.

One TL prefers Option #2

The mathematical equation is given and the question says 'twice the rate'. The main insight is how to express twice the rate (having no numerical value for tae.) Giving the point for substitution would be possible here. If the C_5H_{12} molar mass is used in the problem, the student would have to know the value is for one mol. Maybe the last point is for calculation alone. I would like to see g mol^{-1} or g somewhere in the set-up and response.

Prefer Option 1..does not molar mass imply units?

I would vote for one point for recognizing the relationship between effusion rate and molar mass, and a second point for a correct answer.

Chalk up one more vote for Option 1. Require units for the second point. Accept simply "g" as the units of MM, as this was used (unfortunately) in the statement of the problem. Two points, yes, for the first TL "what if."

(e)   The structural formula of one isomer of pentane is shown below. Draw the structural formulas for the other two isomers of pentane. Be sure to include all atoms of hydrogen and carbon in your structures.

	2 points 1 pt for each correct structural formula

	2 points 1 pt for each correct structural formula
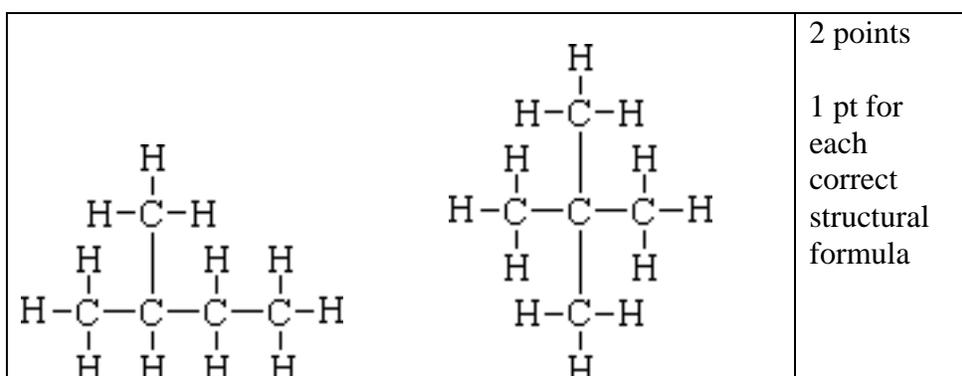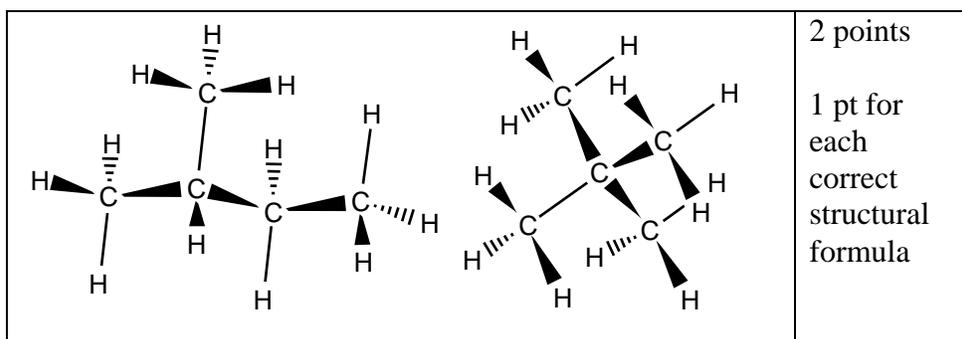
TL Feedback:

Do students need to show 3-dimensional structure? (CR response…No, I used Chem3D/ChemDraw to draw the structure)

Can the student lose a point for including redundant or incorrect formulae?

Accept structures indicated as:

$CH_3\text{-}CH\text{-}CH_2\text{-}CH_3$
|
CH_3
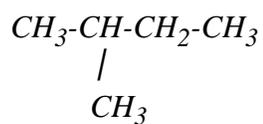
Question 4:

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 solutions as ions if the substances are extensively ionized. Omit formula for any ions or molecules that are unchanged by the reaction. You need not balance the equations.

(a)   A solution of sodium iodide is added to a solution of lead(II) acetate.

$$\boxed{I^- \ + \ Pb^{2+} \ \rightarrow \ PbI_2}$$
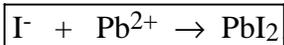
(I think this is the only product that is acceptable.)

(b)   Pure solid phosphorus (white form) is burned in air.

$$\boxed{P_4 \ + \ O_2 \ \rightarrow \ P_4O_{10}}$$
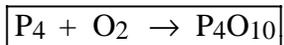
(P_4O_6, is an acceptable product. P_4O_7 - P_4O_9 is formed when P_4O_6 is heated so those are not acceptable, PO and P_2O_6 are obtained through other reactions. P_2O_3 or P_2O_5 should not be accepted.)

TL Feedback:
$P + O_2$ should be worth a point. Students should not be working with white phosphorus and the reactions should be things they have done.

P_2O_3 or P_2O_5 should be worth a point because the student knows that there is an oxidation of phopshorus occurring. (2 other TLs agrees with a point)

Agree with P alone, and any oxidation product that they contrive that is sensible.

Will we award a point for an incorrect formula for phosphorus oxide.

Accept P for P4, and P4O6 or P4O10, but no other variations, for full credit. I can be talked into 1 pt for P2O3 and P2O5.

(c)   Solid cesium oxide is added to water.

$$\boxed{Cs_2O \ + \ H_2O \ \rightarrow \ Cs^+ \ + \ OH^-}$$
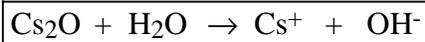
TL Feedback:
We might accept CsOH since excess water was not specified.

(d)   Excess concentrated hydrochloric acid is added to a 1.0 M solution of cobalt(II) chloride.

$$\boxed{Cl^- \ + \ Co^{2+} \ \rightarrow \ CoCl_4^{2-}}$$
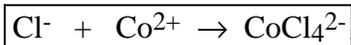
(other possible complex ions that are probably acceptable are $CoCl_3^-$, $CoCl_5^{3-}$, or $CoCl_6^{4-}$)

TL Feedback:
$H^+ \ + \ Co^{2+} \ \rightarrow H_2 \ + \ Co^{3+}$ Is this worth 1 point? I know the reaction does not occur but the student realizes the reaction is a redox.

How about Cl⁻ + Co(H₂O)₆²⁺ → H₂O + CoCl₄²⁻
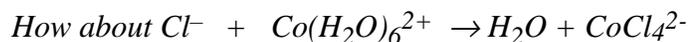
Fine, for any of the range of product complex ions indicated. Also fine for $Co(H_2O)_6^{2+}$ as a reactant.

(e)   Solid sodium hydrogen carbonate (sodium bicarbonate) is strongly heated.

$$\boxed{NaHCO_3 \rightarrow \ Na_2CO_3 + H_2O + CO_2}$$

TL Feedback:
How about $Na_2O + H_2O + CO_2$?

How about $Na_2CO_3 + H_2O + CO_2$?(this reaction is found in Moeller, Bailar, et al 3ʳᵈ edition, 1989. p. 668)

Do we accept Na⁺ and OH⁻?

Variations involving Na_2O and Na_2CO_3 should be allowed for full credit. Indeed, I suspect Na_2CO_3 is produced under most conditions. No credit for Na⁺ & OH⁻.

(f)   An excess of hydrochloric acid is added to solid zinc sulfide.

$$\boxed{H^+ \ + \ ZnS \ \rightarrow \ Zn^{2+} \ + \ H_2S}$$
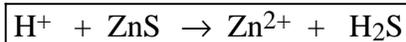
TL Feedback:
Do we accept H⁺ and HS⁻?

No credit for H⁺ & HS⁻, not with excess conc. HCl.

(g)   Acidified solutions of potassium permanganate and iron(II) nitrate are mixed together.

$$\boxed{MnO_4^- \ + \ H^+ \ + \ Fe^{2+} \ \rightarrow \ H_2O + \ Fe^{3+} \ + \ Mn^{2+}}$$
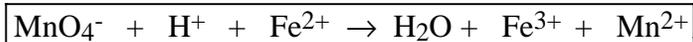
(Fe does not really have any higher oxidation states than III, MnO_2 is fomed in basic solution.)

TL Feedback:
We might also consider oxidation by H⁺ & NO₃⁻.

$NO_3^- \ + \ H^+ \ + \ Fe^{2+} \ \rightarrow \ H_2O + \ Fe^{3+} \ + \ NO \ (NO_2)$
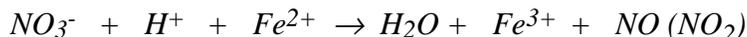
(h)   A solution of potassium hydroxide is added to solid ammonium chloride.

$$\boxed{NH_4Cl \ + \ OH^- \ \rightarrow \ NH_3 \ + \ Cl^- \ + \ H_2O}$$

TL Feedback:
I think we are going to see lots of NH₄OH!! Is that worth points?
One vote for a point for NH₄OH.

.   *No credit for NH₄OH, but if they use this correctly they still get one pt for Cl⁻.*

Question 5:

$$H^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow H_2O_{(l)}$$
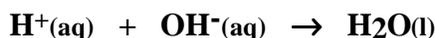
A student is asked to determine the molar enthalpy of neutralization, ΔH_{neut}, for the reaction represented above. The student combines equal volumes of 1.0 M HCl and 1.0 M NaOH in an open polystyrene cup calorimeter. The heat released by the reaction is determined by using the equation $q = mc\Delta T$.

Assume the following.

- **Both solutions are at the same temperature before they are combined.**
- **The densities of all solutions are the same as that of water.**
- **Any heat lost to the calorimeter or to the air is negligible.**
- **The specific heat capacity of the combined solutions is the same as that of water.**

       (a) Give the appropriate units for each of the terms in the equation $q = mc\Delta T$.

q has units of joules (kilojoules or calories/kilocalories) m has units of grams or kilograms c has units of J g^{-1} $^\circ$C^{-1} or J g^{-1} $^\circ$K^{-1} (cal) T has units of $^\circ$C or K	1 point for any two OR 2 points for all four

TL Feedback:
Students might use kg as a unit in c.
What about $^\circ$K?

       (b) List the measurements that must be made in order to obtain the value of q.

volume or mass of the HCl and NaOH solutions initial temperature of HCl and NaOH before mixing final temperature of HCl and NaOH after mixing	1 point for any volume (mass) 1 point for initial and final temperature (ΔT is not a measurement)

TL Feedback:
     If the students says find the change in temperature of the mixture…is that sufficient for the second point?
     A response using mass of the HCl and NaOH probably indicates the student who has not done the lab, but then again may just forgot how the lab was done. Since the problem says the initial temperature of HCl and NaOH are stated as the same, does the student only have to mention the initial temperature of either HCl or NaOH?
     The problem also says the volume of HCl and NaOH are the same so the student only has to mention mass or volume of HCL or NaOH, not both.

I would accept ΔT as a measurement. Otherwise, use the terminology "final temperature of the combined solution after mixing."

(c) Explain how to calculate each of the following.

(i) The number of moles of water formed during the experiment

Since we are mixing equal volumes of the same concentration and the reaction has 1:1 stoichiometry the moles of water are equal to the moles of HCl and NaOH. To determine moles of HCl; $$\text{volume HCl}\left(\frac{\text{mol HCl}}{1 \text{ L}}\right)\left(\frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol HCl}}\right) = \text{mol H}_2\text{O}$$ or $$\text{volume NaOH}\left(\frac{1.0 \text{ mol NaOH}}{1 \text{ L}}\right)\left(\frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol NaOH}}\right) = \text{mol H}_2\text{O}$$ or $$n_w = n_{HCl} = n_{NaOH} = V_{HCl} \times 1 \text{ M} = V_{NaOH} \times 1 \text{ M}$$	(i) 1 point for determining the moles of HCl or NaOH 1 point for the stoichiometric relationship between HCl and H_2O, or between NaOH and H_2O.

TL Feedback:
I do not think many students will give the stoichiometric relationship explicitly.
Could we consider giving one point to c i and 2 points to c ii?
This can be stated more simply as: 1 pt for $n_w = n_{HCl} = n_{NaOH}$ and then
1 pt for relating n(any) to V(any).

(ii) The value of the molar enthalpy of neutralization, ΔH_{neut}, for the reaction between HCl(aq) and NaOH(aq).

determine the quotient of the heat produced, q, from $q = mc\Delta T$ and divide by the mol H_2O determined in (c i). $$\Delta H_{neut} = \frac{-q}{\text{mol H}_2\text{O}} \text{ or } \frac{q}{\text{mol H}_2\text{O}}$$	1 point for $\dfrac{q}{\text{mol H}_2\text{O}}$

TL Feedback:
Should the sign of the change in enthalpy be negative?
The qualifying statement that mol H^+ = mol OH^- = mol H_2O would suggest that q could be divided by any of these terms.
If students divide by mol of HCl or NaOH reacted, award the point.
The left box suggests that one must explain from where comes the values of q and nw. The right side suggests only q and n_w are needed, without explanation as to source. Some clarification here is needed. Do we disregard the sign of ΔH?

Some students may figure out that one doesn't actually need to measure V or calculate q or n_w. For the conditions stated, the equations can be reduced to:
  $\Delta H = - (1000 \text{ g}) c \Delta T$. We should be prepared to accept this as the answer.

(d) **The student repeats the experiment with the same equal volumes as before, but this time uses 2.0 M HCl and 2.0 M NaOH.**

  (i) **Indicate whether the value of *q* increases, decreases, or stays the same, compared to the first experiment. Justify your prediction.**

q increases because the ΔT will be greater. There are more moles of HCl and NaOH reacting so the final temperature of the mixture will be higher.	1 point for direction and explanation

TL Feedback:
  How about 'q increases because there is a greater number of moles of reactants present, and the $\Delta H°_{rxn}$ does not change?' I suspect that a few papers may have parts (i) and (II) answered together.

  (ii) **Indicate whether the value of the molar enthalpy of neutralization, ΔH_{neut}, increases, decreases, or stays the same, compared to the first experiment. Justify your prediction.**

Both *q* and the moles of H_2O increase proportionately. However when the quotient is determined there is no change in ΔH_{neut}.	(ii) 1 point for direction and explanation

TL Feedback:
Comments for d i and ii and part e: Is this becoming a trend?? One point split two ways to evaluate which is more important...the direction or the explanation?

Since the kJ mol^{-1} are known, this prediction could be justified stoichiometrically.

An explanation based on units as kJ/mol is acceptable.

(e) **Suppose that a significant amount of heat were lost to the air during the experiment. What effect would this have on the calculated value of the molar heat of enthalpy of neutralization, ΔH_{neut}, ? Justify your answer.**

Heat lost to the air will produce a smaller ΔT. In the equation; $$q = mc\Delta T$$ a smaller ΔT well produce a smaller q (heat released). In the equation; $$\Delta H_{neut}, = \frac{-q}{\text{mol } H_2O}$$ the smaller magnitude of q, and the constant number of moles of H_2O means ΔH_{neut} will be less negative (more positive).	1 point for direction and explanation

TL Feedback:

      This problem has so many parts! Giving 1 point for direction and explanation is going to be hard---no longer the coin toss points! Will kids survive?

      Since ΔH is negative less heat is produced (q is more positive) so ΔH will become more positive.

      Could the student argue the ΔT will be too small in terms of the calculations?

      I dislike coin toss credit so would require some explanation. I like to be generous as to how good that explanation must be.

Question 6:

Use the principles of atomic structure and/or chemical bonding to explain each of the following. In each part, your answer must include references to <u>both</u> substances.

(a)   The atomic radius of Li is larger than that of Be.

(a) Both Li and Be have the same number of inner core electrons shielding the valence electrons from the nucleus. But Be has 4 protons and Li has only three protons. So the effective nuclear charge experienced (attraction experienced) by the valence electrons is greater in Be compared to Li and Be has a smaller atomic radius.	1 point for indicating Be has more protons compared to Li. 1 point for indicating the effective nuclear charge experienced by the valence electrons in Be is greater compared to Li.
What ifs; Student response: Going across a period the effective nuclear charge experienced by the outer electrons increases, therefore Be is smaller than Li. Be has 4 protons and Li has three protons. The electrons feel a greater attraction to the Be nucleus because of the greater number of protons. The electrons in Li where the nucleus has only 3 protons experience a smaller attraction.	*TL Feedback:* *2 points....4 TL* *1 point....4 TL* *0 points...1 TL* *2 points....5 TLs* *1 point.....4 TL* *The student knows the attraction to the nucleus part.*

TL Feedback:

I do not like giving credit to a discussion related to the periodic table. What if the student says that electrons are going into the same shell?

1 point for recognizing the atoms have the same sublevels, but Be hhas one more proton than Li or that Be has a higher effective nuclear charge than Li.

Do not hold students to using the phrase 'effective nuclear charge' as long as they can describe the relationship between the increasing number of protons and the attractive force on the electrons in a correct manner.

I vote for holding them to state WHY the trend exists (number of protons) rather than memorize the trend (IE's increase across a period).

We have any easy 1 pt here, which raises the bar on the 2nd point.

Arguments based on ENC are more valid than discussions involving Z. A theory based on Z only would suggest that Na would be much smaller than Li.

(b) The second ionization energy K is greater than the second ionization energy of Ca.

(b) The second electron removed from a potassium atom comes from the 3rd level. The second electron removed from a calcium atom comes from the 4th level. The attraction to the nucleus of electrons in the 3rd level is much greater than the attraction of an electron in the 4th level. Or The second electron removed from a potassium atom comes from an inner core level where the effective nuclear is much larger. In Ca both the electrons are removed from the valence shell (outer most level) and the effective nuclear charge is low for both electrons.	1 point for indicating electrons are removed from an inner core/3rd level in potassium 1 point for indicating electrons are removed from an valence/outer most level in calcium.

TL Feedback:

What if: The student says, 'The second electron removed from K is a noble gas core electron which is harder to remove than Ca's second electron which is just getting to the noble gas core.'

This question was asked in 1994 what were the standards then? (CF Notes: From the Draft version of the 94 Rubric: The 2nd IE of K is much larger than the 2nd IE of Ca because in the 2nd ionization of K a 3p electron is being removed, while in the 2nd ionization of Ca a 4s electron is being removed. A 3p electron is; 1) much closer to the nucleus; 2) less effectively shielded.

Is nonpolar a requirement for the point? Or if they just discuss dispersion forces as long as they do not mention other forces. What if they use 'increasing molar mass implies stronger dispersion forces, but do not discuss polarizability?

Need a reference to core electrons, inner shell, etc. versus valence electrons for these points.

Fine as stated, but I would also accept "filled outer subshell" in place of "inner core." I also like the historic standard.

(c) **The carbon-to-carbon bond energy in C_2H_4 is greater than it is in C_2H_6.**

C_2H_4 has a double bond between the two carbon atoms, while C_2H_6 has a carbon-carbon single bond. More energy is required to break a sigma and a pi-bond in C_2H_4 compared to only a sigma bond in C_2H_6.	1 point for indicating C_2H_4 has a double bond and C_2H_6 has a single bond. 1 point for indicating the additional bond in C_2H_4 requires more energy to break compared to C_2H_6.

TL Feedback:

    Would not recommend requiring discussion of a sigma and pi bond.

    I assume that we will not hold them to identfying the seond bond as a pi-bond. What about structural formulae that show single and double bonds?

    State the 2nd point as indicating that the double bond is stronger than the single bond. This permits but does not require discussion of sigma and pi bonds.

(d) **The boiling point of Cl_2 is lower than the boiling point of Br_2.**

(d) Both of Cl_2 and Br_2 are nonpolar and the only intermolecular attractive forces are London Dispersion type. Since Br_2 has more electrons compared to Cl_2, the valence electrons in Br_2 are more polarizable. The more polarizable the valence electrons the greater the dispersion forces and the higher the boiling point.	1 point for indicating Cl_2 and Br_2 are both nonpolar and have London Dispersion forces only. 1 point for indicating more electrons, more polarizable, greater the dispersion forces and the higher the boiling point.

TL Feedback:

    Will any points be given for the following? The increased molecular weight causes average speed to be lower therefore higher chance of attractive forces capturing the molecules.

    How about a size (not mass) explanation of larger LDFs in bromine?

    Is it necessary to state the more electrons and polarizability are associated with increased boiling point?

    Are we going to hold the students to the concept of polarizability?

    I would answer "no" to all 3 TL questions. The point here is to identify <u>LDF</u> as what is relevant (1st point) and that these are stronger for molecules with more electrons, or more shells of electrons (2nd point).

Question 7:

An environmental concern is the depletion of O_3 in Earth's upper atmosphere, where O_3 is normally in equilibrium with O_2 and O. A proposed mechanism for the depletion of O_3 in the upper atmosphere is shown below.

$$\text{Step I } O_3 + Cl \rightarrow O_2 + ClO$$

$$\text{Step II } ClO + O \rightarrow Cl + O_2$$
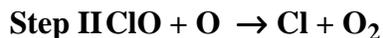
(a) Write a balanced equation for the overall reaction represented by Step I and Step II above.

$O_3 + O \rightarrow 2O_2$	1 point for the correct overall reaction

(b) Clearly identify the catalyst in the mechanism above. Justify your answer.

Cl is the catalyst in the reaction. It is a reactant in Step I and re-appears as a product in Step II.	1 point for identifying Cl as the catalyst. 1 point for the justification

TL Feedback:

Is it possible to get the second point and not the first?

(c) Clearly identify the intermediate in the mechanism above. Justify your answer.

ClO is the intermediate in the reaction. It is a product in Step I and re-appears as a reactant in Step II.	1 point for identifying ClO as the intermediate. 1 point for the justification

(d) If the rate law for the overall reaction if found to be *rate* = $k[O_3][Cl]$, determine the following.
      (i) The overall order of the reaction.
      (ii) Appropriate units for the rate constant, k.
      (iii) The rate-determining step of the reaction, along with justification for your answer.

(i) overall order is $1 + 1 = 2$	1 point for the overall order
(ii) $k = \dfrac{rate}{[O_3][Cl]} = \dfrac{M \text{ time}^{-1}}{M^{-2}} = M^{-1} \text{ time}^{-1}$	1 point for the correct units
(iii) Step I in the mechanism is the rate determining step. The coefficients of the reactants in Step I correspond to the exponents of the species concentrations in the rate law equation.	1 point for the correct Step and justification

TL Feedback:

Acceptable units could be $L \cdot mol^{-1} \text{ time}^{-1}$ ·
Accept $M^{-1} \text{ time}^{-1}$, $M^{-1} s^{-1}$, $M^{-1} min^{-1}$
Will we accept '1st order in each reactant' rather than 2nd order overall?

Watch out for Liters per mol sec

Question 8:

$$C_{(s)} + CO_{2(g)} \rightleftarrows 2CO_{(g)}$$
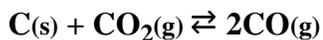
Carbon (graphite), carbon dioxide, and carbon monoxide form an equilibrium mixture, as represented by the equation above.

(a)   Predict the sign for the change in entropy, ΔS, for the reaction. Justify your prediction.

ΔS = + : There is more disorder in a gas compared to a solid so the products are more disordered compared to the reactant and the change in entropy is positive. Saying there is 1 mol of gas in the reactants yield 2 moles of gas in the products is not enough to get the second point. Must indicate that a mol of solid and a mol of gas form two mol of gas.	1 point for ΔS positive 1 point for indicating more moles of gas in products compared to reactants

TL Feedback:

Do students have to say a solid reactant and gaseous products? What if they simply say a solid reactant and gaseous products?

I disagree with you idea of distinguishing between 1 mol of solid and 1 mol of gas to 2 mol of gas AND 1 mol of gas gives 2.

Student could say from solid to a gas is positive ΔS, without mentioning more moles of gas.

Just saying one mole of gas to 2 mol of gas should not get credit. If they also say that there is more disorder then I would give them credit. Do not need to say solid.

I think saying 1 mol of gas to two mol of gas should be OK

The discussion (left box) seems inconsistent with the standard (right box) as to whether solid and gas entropies must be compared. I would (and the right box seems to) argue for "1 mol gas in R yields 2 mol gas in P" as being sufficient. The TL quoted seem to be saying the same.

(b) In the table below are data that show the percent of CO in the equilibrium mixture at two different temperatures. Predict the sign for the change in enthalpy, ΔH, for the reaction. Justify your prediction.

Temperature	% CO
700 ˙C	60
850 ˙C	94

|	
ΔH = + : more CO at the higher temperature indicates that the reaction shifts right with increasing temperature. For this to occur heat must be a reactant, so that increasing the temperature (adding heat) shifts the reaction from left to right to form more product.	1 point for ΔH positive 1 point for the explanation

TL Feedback:

An argument based on increased products could relate increased K_c to endothermic reaction. If the reaction produces more products, its K_c lies increasingly to the right with the increase in temperature.

Could say increasing T favors the endothermic process, in this case the forward direction since CO increases, therefore the change in enthalpy is positive (2 TLs agree this statement should receive full credit.)

The statement of the problem is unfortunate. "… the % CO in the equilibrium mixture…" should have read ".. the % CO in the gas phase…". The total mixture would include the C(s), and the % CO2 cannot be determined. Fortunately no calculations are required.

In the left box, the explanation might better read "… higher temperature indicates that the reaction shifts right with increasing…".

(c) **Appropriately complete the potential energy diagram for the reaction by finishing the curve on the graph below. Also, clearly indicate ΔH for the reaction on the graph.**

	1 point for completing the graph 1 point for the correct label off ΔH_{rxn} If the student has a differnet sign for ΔH from part b, be consistent here.
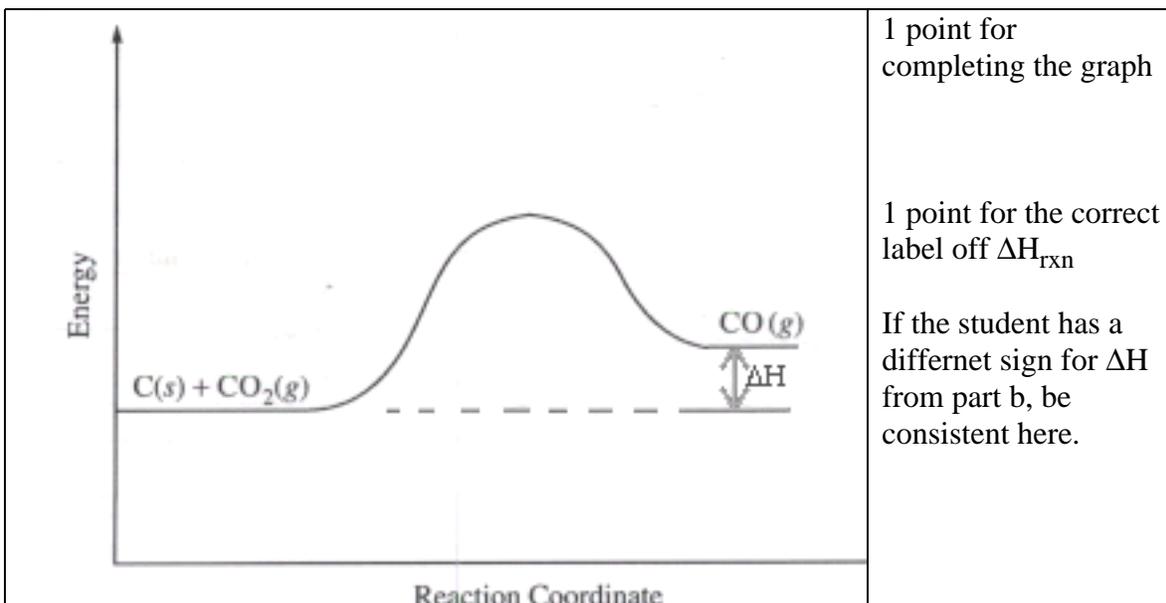
(d) **If the initial amount of C(s) were doubled, what would be the effect on the percent of CO in the equilibrium mixture? Justify your answer.**

No effect with the increase in C(s). Solids do not appear in the equilibrium expression so adding more C(s) will not effect the % of CO in the equilibrium mixture.	1 point for no effect. 1 point for explanation

TL Feedback:

What if a student says adding more carbon solid changes the volume available for the gases and then gives a correct explanation due to volume change? I think the student should get full credit. No indication in the question that volume remains constant.

Also be prepared to accept a kinetic argument.

Here is where "equilibrium mixture" instead of "gas phase" can get one into real trouble. We should be prepared to give full credit for the following:

"Adding a solid will not shift an equilibrium, so P_{CO} and P_{CO2} stay the same. The % CO decreases, however, because now there are more total moles.

$$\% \, CO = n_{CO}/(n_{CO} + n_{CO_2} + n_C)$$

As n_C is raised, the denominator increases, and % CO decreases."