1. Enthalpy Change & Phase Transitions (10 points)

Break the process into five steps, all occurring at 1.00 atm.
(*3 points* for clearly stating these paths: picture/graph or words are OK, −1 per missing or incorrect path, max deduction −3)

State A→State B: heat ice from –30.0°C to 0.0°C
State B→State C: melt ice at 0.0°C
State C→State D: heat liquid water from 0.0°C to 100.0°C
State D→State E: vaporize water at 100.0°C
State E→State F: heat steam from 100.0°C to 140°C

Note that we are keeping more sigfigs than needed for these intermediate steps. Listed next to each value is the correct number of sigfigs.

A→B: heat ice from –30.0°C to 0.00°C

$$\Delta H_{AB} = nc_{p,ice}\Delta T$$

$$\Delta H_{AB} = (1.00 \text{ mol})(38 \text{ J mol}^{-1} \text{ K}^{-1})(0.00°C - (-30.0°C)) \text{ (}1 \text{ point)}$$

$$\Delta H_{AB} = 1140 \text{ J (2 sig figs)}$$

B→C: melt ice at 0.0°C

$$\Delta H_{BC} = n\Delta \widehat{H}_{\text{fusion}}$$

$$\Delta H_{BC} = (1.00 \text{ mol})(6.01 \text{ kJ mol}^{-1}) \quad \text{(1 point)}$$

$$\Delta H_{BC} = 6.01 \text{ kJ} = 6010 \text{ J (3 sig figs)}$$

C→D: heat liquid water from 0.0°C to 100.0°C

$$\Delta H_{CD} = nc_{p,liquid}\Delta T$$

$$\Delta H_{CD} = (1.00 \text{ mol})(75 \text{ J mol}^{-1} \text{ K}^{-1})(100.00°C - 0.00°C) \text{ (1 point)}$$

$$\Delta H_{CD} = 7500 \text{ J (2 sig figs)}$$

D→E: vaporize water at 100.0°C

$$\Delta H_{DE} = n\Delta \widehat{H}_{\text{vap}}$$

$$\Delta H_{DE} = (1.00 \text{ mol})(40.7 \text{ kJ mol}^{-1}) \quad \text{(1 point)}$$

$$\Delta H_{DE} = 40700 \text{ J (3 sig figs)}$$

E→F: heat steam from 100.0°C to 140°C

$$\Delta H_{EF} = nc_{p,steam}\Delta T$$

$$\Delta H_{EF} = (1.00 \text{ mol})(36 \text{ J mol}^{-1} \text{ K}^{-1})(140°C - 100.00°C) \text{ (1 point)}$$

$$\Delta H_{EF} = 1440 \text{ J (2 sig figs)}$$

Overall Process (A→F)

$$\Delta H = \Delta H_{A \to F} = \Delta H_{A \to B} + \Delta H_{B \to C} + \Delta H_{C \to D} + \Delta H_{D \to E} + \Delta H_{E \to F} \quad (\textbf{\textit{1 point}})$$

$$\Delta H = 1140 \text{ J} + 6010 \text{ J} + 7500 \text{ J} + 40{,}700 \text{ J} + 1440 \text{ J}$$

$$\Delta H = 56790 \text{ J}$$

$$\Delta H = 56.8 \text{ kJ} \quad \textbf{(2 points, no credit for incorrect sigfigs or units)}$$

A note about sig figs: We're adding values, so we are limited by the number of decimal places in our individual terms. This is the hundreds place in four of the processes.

$$\Delta H = \textbf{11}40 \text{ J} + \textbf{601}0 \text{ J} + \textbf{75}00 \text{ J} + \textbf{407}00 \text{ J} + \textbf{14}40 \text{ J}$$

Therefore, our final answer is significant to the hundreds place, which gives us THREE significant figures. Just because you started with values with only two sig figs doesn't necessarily mean that the final answer will have only two! (If you lost points for sig figs, review the worksheet on the course website for the mathematics of sig figs)

Note: We didn't need to convert temperature from Celsius to Kelvin even though the denominator for the heat capacity has units of Kelvin. As long as you deal with ***temperature differences***, you don't need to do the conversion since it simply subtracts out.

$$\Delta H_{A \to B} = n c_{P,ice} \Delta T$$

$$\Delta H_{A \to B} = (1.00 \text{ mol})(38 \text{ J mol}^{-1} \text{ K}^{-1})((0.0°\text{C}+273.15) - (-30.0°\text{C}+273.15))$$

$$\Delta H_{A \to B} = (1.00 \text{ mol})(38 \text{ J mol}^{-1} \text{ K}^{-1})((0.0°\text{C} - -30.0°\text{C}) + (273.15 - 273.15))$$

$$\Delta H_{A \to B} = (1.00 \text{ mol})(38 \text{ J mol}^{-1} \text{ K}^{-1})(0.0°\text{C} - -30.0°\text{C})$$

$$\Delta H_{A \to B} = 1140 \text{ J}$$

The same is true for Fahrenheit and Rankine. But you must convert from Celsius to Fahrenheit since the conversion is not simply adding a constant.

2. Entropy Changes & Phase Transitions (15 points)

Solution 2a

The change in entropy for an isothermal process is given by Eqn [13.8] in OGC6 (pg.543):

$$\Delta S = \frac{q_{rev}}{T}$$

You may also go directly to Eqn [13.10] in OGC6 for phase transitions,

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f}.$$

==(*1 points* for either of the equations above)==

Since the heat is removed from the system reversibly,

$$q_{rev} = q = -6.01 \text{ kJ mol}^{-1}.$$

==(*1 point* for equation or proper substitution for heat of fusion)==

Remember, the sign is negative since heat is removed. Before you continue, check the sign to see if it makes physical sense. Since $q_{rev} < 0$, then $\Delta S_{H_2O} < 0$. A decrease in entropy makes sense since a solid has fewer available configurations than a liquid. So far, so good. Substitute values,

$$\Delta S_{H_2O} = \frac{q}{T} = \left(\frac{-6.01 \text{ kJ mol}^{-1}}{273.15 \text{K}} \right) \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right)$$

$$\Delta S_{H_2O} = -22.0026 \text{ J mol}^{-1} \text{ K}^{-1}$$

Notice anything odd? Once again, OGC6 uses the same symbol for two similar thermodynamic properties that have different units. OGC6 use ΔS to represent the change in specific molar entropy (units: J/mol/K) *and* the change in entropy (units: J/K). Other texts use ΔS for the change in entropy and $\Delta \hat{S}$ for the change in specific molar entropy. Just like for enthalpy, sometimes you'll see the carat. Sometimes not. Always check units. So far we've calculated the change in specific molar entropy, but we want the change in entropy. Multiply by the number of moles (2.00 mol) to find that:

$$\Delta S_{H_2O} = (2.00 \text{ mol})(-22.0026 \text{ J mol}^{-1} \text{ K}^{-1}),$$

==$$\Delta S_{H_2O} = -44.0 \text{ J K}^{-1}.$$==

==(*3 points total*: 1 point for multiplying by 2.00 mol; 2 points for value, no credit for an answer with incorrect sigfigs or units)==

Solution 2b

The change in entropy for the surroundings can be calculated using Eqn [13.14] in OGC6 (pg.546),

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T} \cdot \text{(\textbf{1 point})}$$

If we apply the first law of thermodynamics to this (constant pressure) system, we know that the change in enthalpy of the system is simply equal to the heat added, q,

$$\Delta S_{surr} = \frac{-q_{sys}}{T} \cdot \text{(\textbf{1 point} for using } q\text{)}$$

Since $q_{sys} < 0$, the entropy of the surroundings will increase. This result makes sense.

From the second law of thermodynamics, we know that the total change in entropy must be at least zero. Since the entropy of the system decreased, then the entropy of the surroundings must increase by at least the same amount.

Substitute values, keeping in mind that the surroundings are maintained at -2.00°C,

$$\Delta S_{surroundings} = \left(\frac{6.01 \text{ kJ mol}^{-1}}{271.15 \text{ K}} \right)(2.00 \text{ mol})\left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right),$$

$$\Delta S_{surroundings} = 44.3 \text{ J K}^{-1}. \text{ (\textbf{2 points, no credit for incorrect sigfigs or units})}$$

Solution 2c

The total change in entropy (or, if you prefer, the change in entropy of the universe) is

$$\Delta S_{universe} = \Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = \Delta S_{H_2O} + \Delta S_{surroundings} \cdot \text{(\textbf{1 point})}$$

$$\Delta S_{universe} = -44.0052 \text{ J K}^{-1} + 44.3297 \text{ J K}^{-1}.$$

$$\Delta S_{universe} = 0.3 \text{ J K}^{-1}. \text{ (\textbf{2 points if consistent with parts a) and b), no credit for incorrect sigfigs or units})}$$

Solution 2d

ΔS_{total} is greater than zero whenever an irreversible process occurs. There are really two processes to consider in this problem. Although water freezes reversibly at these conditions, the transfer of thermal energy (heat) from the system to the surroundings is not reversible since there is a finite temperature difference between the system and the surroundings. **(3 points for anything related to irreversible heating of the surroundings)**

Note that ΔS_{total} would be identically zero only if the surroundings were at the same temperature as the system.

3. Adiabatic Flame Temperature (20 points)

Solution 3a

$$\Delta H^{\mathrm{O}} = \sum_{i=1}^{prod} n_i \Delta H_i^{\mathrm{O}} - \sum_{j=1}^{react} n_j \Delta H_j^{\mathrm{O}} \quad (\textbf{\textit{1 points}})$$

$$\Delta H^{\mathrm{O}} = \left(2\Delta H_{CO_2}^{\mathrm{O}} + \Delta H_{H_2O}^{\mathrm{O}} \right) - \left(\Delta H_{C_2H_2}^{\mathrm{O}} + \frac{5}{2}\Delta H_{O_2}^{\mathrm{O}} \right), \ (\textbf{\textit{2 points}})$$

$$\Delta H^{\mathrm{O}} = \left[2\left(-393.51 \ \text{kJ mol}^{-1}\right) + \left(-241.82 \ \text{kJ mol}^{-1}\right) \right] - \left[\left(226.73 \ \text{kJ mol}^{-1}\right) + \frac{5}{2}(0) \right]$$

$$\Delta H^{\mathrm{O}} = -1255.57 \ \text{kJ mol}^{-1}. \ (\textbf{\textit{2 points, no credit for incorrect sigfigs or units}})$$

Note: ΔH^{O} (or sometimes $-\Delta H^{\mathrm{O}}$) is often called the standard heat of combustion for these types of problems. You'll find most people use $\left|\Delta H^{\mathrm{O}}\right| \sim 1300 \ \text{kJ mol}^{-1}$ as a reasonable approximation for acetylene.

Solution 3b
For ideal gases with a temperature independent heat capacity, the change in enthalpy of the products between the initial state and the final state can be written,

$$\Delta H = n_{prod} c_{P,prod} \Delta T . \ (\textbf{\textit{3 points}})$$

Since the reactants are at standard temperature and pressure (298 K, 1 atm) and the reaction goes to completion, all heat generated by the exothermic reaction is used to heat the products.

Note: You don't need to include the heat of vaporization for water since $H_2O(g)$ *is shown as a product and it's listed in Appendix D. If* $H_2O(\ell)$ *is shown in the reaction instead, you would need to include the heat of vaporization. If the reaction doesn't go to completion, you would have to include a fraction of the reactants on the right-hand side.*

Since all energy generated by the <u>exothermic</u> reaction is used to raise the temperature of the products, and since the reaction goes to completion,

$$\Delta H^{\mathrm{O}} = -n_{prod} c_{P,prod} \Delta T_{max} . \ (\textbf{\textit{2 points}} \text{ for reasonable justification})$$

Before we go any further, take a closer look at this equation and why you have to be careful with units when dealing with energies.

   (a) The right-hand side has units of energy (Joules). $c_{P,prod}$ has units of J mol^{-1} K^{-1}.

     n_{prod} has units of moles. ΔT_{max} has units of Kelvin.

   (b) The left-hand side has units of specific energy (kJ/mol).
Now you see the potential issues when books (or problem sets, lectures, etc.) don't use different symbols – such as a carat over the regular symbol – to differentiate specific

energy from energy. For this problem you get the correct answer if you don't notice this subtlety and if you just ignore the extra unit of moles in your calculation.

Always check for consistency of units in your equations before you start solving or substituting values!

You can multiply the left side by the number of moles of acetylene since that is the basis for your answer in part (a) so that both sides of the equation have units of energy,

$$n_{C_2H_2} \Delta H^O = -n_{prod} c_{p,prod} \Delta T_{max} \text{,}$$ **(2 points** for multiplying LHS by # of moles)

(You'll still get the right numerical answer if you don't multiply by # of moles of C_2H_2 by virtue of cancelation of mistakes)

$$n_{C_2H_2} \Delta H^O = -\sum_{i=1}^{prod} n_i c_{P,i} \Delta T_{max} \text{,}$$ **(2 points** for summation or average values)

$$n_{C_2H_2} \Delta H^O = -\Delta T_{max} \sum_{i=1}^{prod} n_i c_{P,i} \text{,}$$

GRADERS: students can perform this summation anywhere in the solution. Some may find it easier to do at the beginning.

$$n_{C_2H_2} \Delta H^O = -\Delta T_{max} \sum_{i=1}^{prod} n_i c_{P,i} \text{,}$$

$$\Delta T_{max} = -\frac{n_{C_2H_2} \Delta H^O}{\sum_{i=1}^{prod} n_i c_{P,i}} \text{,}$$

$$T_{final,max} = T_{initial} - \frac{n_{C_2H_2} \Delta H^O}{\sum_{i=1}^{prod} n_i c_{P,i}} \text{.}$$

Nowhere in the problem are we given the number of moles of acetylene that are initially present, but we know that the reactants are fed in stoichiometric proportions, that the reaction goes to completion, and we know the stoichiometic proportions for products and reactants in the chemical reaction; so divide by n_{C2H2} and use the ratio of stoichiometric coefficients,

$$T_{final,max} = T_{initial} - \frac{\Delta H^O}{\left(\dfrac{\sum_{i=1}^{prod} n_i c_{P,i}}{n_{C_2H_2}} \right)} \text{,}$$

$$T_{final,max} = T_{initial} - \frac{\Delta H^O}{\sum_{i=1}^{prod} \dfrac{n_i}{n_{C_2H_2}} c_{P,i}} \text{,}$$

$$T_{final,max} = T_{initial} - \frac{\Delta H^O}{\dfrac{n_{CO_2}}{n_{C_2H_2}} c_{P,CO_2} + \dfrac{n_{H_2O}}{n_{C_2H_2}} c_{P,H_2O}} \text{.}$$

GRADERS: If students don't convert J to kJ, then they will get an incorrect answer of 3.10×10^2 K if they do everything else correctly.

Substitute values,

$$T_{final,max} = (25 + 273.15)\,K - \frac{(-1255.57 \text{ kJ mol}^{-1})\left(\dfrac{1000 \text{ J}}{1 \text{ kJ}}\right)}{\dfrac{2}{1}\left(37.11\text{J mol}^{-1}\text{ K}^{-1}\right) + \dfrac{1}{1}\left(35.58\text{J mol}^{-1}\text{ K}^{-1}\right)}.$$

$$T_{final,max} = 1.173 \times 10^4 \text{ K}.$$

(3 pts algebra, 3 pts answer, no credit for answer if incorrect sigfigs or units. −2 if J were not converted to kJ)

Yes, there are four sig figs. (25+273.15) K is significant to the ones place. The fraction is significant to the tens place since it has four sig figs for a value that is in the ten thousands. When these two values are added, the sum should then be significant to the tens place.

This estimate is much too large. A typical flame temperature for acetylene is ~3000K. Why the difference? If you find a difference this large, you should evaluate whether you made a calculation error or if any of your assumptions are incorrect. The heat capacity of acetylene actually varies dramatically with temperature over this range.

This temperature ($T_{final,max}$) is called the adiabatic flame temperature (or theoretical flame temperature) since we assumed there were no heat losses. The adiabatic flame temperature is the highest attainable temperature. It is greatest when the fuel and air are fed in approximately stoichiometric proportions and is much greater when pure oxygen is used instead of air – why?

Note: To properly calculate the adiabatic flame temperature you must use temperature-dependent heat capacities. Here's what happens if you account for this:

$$\Delta H^O = -\sum_{i=1}^{prod} \int_{T_1}^{T_2} \frac{n_i}{n_{C_2H_2}} c_{P,i} dT,$$

$$c_{P,CO2} = 36.11 + 4.233 \times 10^{-2} T - 2.887 \times 10^{-5} T^2 + 7.464 \times 10^{-9} T^3,$$

$$c_{P,H_2O_{(g)}} = 33.46 + 0.688 \times 10^{-2} T + 0.7604 \times 10^{-5} T^2 - 3.593 \times 10^{-9} T^3,$$

where temperature has units of °C and heat capacity has units of J/mol/°C.

$$\Delta H^O = \left[-\int_{T_1}^{T_2} \left(105.68 + 9.154 \times 10^{-2} T - 4.9936 \times 10^{-5} T^2 + 11.335 \times 10^{-9} T^3\right) dT \right] \left[\frac{1 \text{ kJ}}{1000 \text{ J}} \right]$$

$$-\Delta H^O = 0.10568(T_2 - T_1) + 4.577 \times 10^{-5}\left(T_2^2 - T_1^2\right) - 1.665 \times 10^{-8}\left(T_2^3 - T_1^3\right) + 2.83375 \times 10^{-12}\left(T_2^4 - T_1^4\right)$$

with $\Delta H^O = -1255.57$ kJ mol^{-1} and $T_1 = T_{initial} = 25°C$.

Solve for $T_2 = T_{final,max}$ iteratively to find $T_{final,max} \approx 5100K$.

This value for adiabatic temperature is *still* too high. Now what? Unfortunately, the equations for heat capacity are only valid from 0–1500°C; so we've introduced a bit of a calculation error. We would need to find a second set of equations that are valid at higher temperatures to properly solve this problem. Regardless, you can still see the dramatic effect of our poor assumption about constant heat capacity.

4. Equilibrium Constant (11 points)

This problem is very similar to Example 14.9 in OGC6 (pg.592).

Since the reactant is a solid material, the equilibrium constant, K, is written as a product of only the partial pressures of the products:

$$K = \left(\frac{P_{\mathrm{NH_3}}}{P_{ref}}\right)\left(\frac{P_{\mathrm{H_2S}}}{P_{ref}}\right), \; \textbf{\textit{(2 points)}}$$

where $P_{\mathrm{NH_3}}$ is the partial pressure of ammonia, $P_{\mathrm{H_2S}}$ is the partial pressure of hydrogen sulfide, and P_{ref} is the reference pressure (standard pressure: 1 atm).

Let x = the amount of NH_3 injected into the container, y = the partial pressure of H_2S at equilibrium after the NH_3 is added.

	$P_{\mathrm{NH_3}}$ (atm)	$P_{\mathrm{H_2S}}$ (atm)	Note	State
Initial	0.0	0.0	1	A
Equilibrium after adding solid	$\frac{1}{2}(0.659)$	$\frac{1}{2}(0.659)$	2	B
Immediately after injecting ammonia	$\frac{1}{2}(0.659)+x$	$\frac{1}{2}(0.659)$	3	C
Equilibrium after adding ammonia	0.750	y	4	D

(**6 points total**: 1 pt per highlighted entry. No credit for not putting in tabular form, since we told you to, and we gave you the table to use! No need for the notes below, they're for elaboration of this solution)

Note 1: Initially the chamber is evacuated and there is no ammonia or hydrogen sulfide present in the chamber.

Note 2: After adding the solid and reaching equilibrium, the total pressure in the chamber is 0.659 atm. Since ammonia and hydrogen sulfide have the same stoichiometric coefficients, an equal number of moles of each chemical species are produced. Since an equal number of moles are produced, the mole fraction of each chemical species is one-half. (Recall Dalton's law of partial pressure.)

Note 3: An unknown amount of ammonia is added. This additional ammonia only affects the partial pressure of ammonia. The partial pressure of hydrogen sulfide initially stays the same.

Note 4: We are given the final value of the partial pressure for ammonia. The partial pressure for hydrogen sulfide is unknown.

Use the equation for the equilibrium constant and the conditions for States B and D,

$$K = \left(\frac{P_{NH3,B}}{P_{ref}}\right)\left(\frac{P_{H2S,B}}{P_{ref}}\right) \text{ and } K = \left(\frac{P_{NH_3,D}}{P_{ref}}\right)\left(\frac{P_{H_2S,D}}{P_{ref}}\right).$$

Eliminate the equilibrium constant, rearrange and substitute,

$$\left(\frac{P_{NH_3,D}}{P_{ref}}\right)\left(\frac{P_{H_2S,D}}{P_{ref}}\right) = \left(\frac{P_{NH_3,B}}{P_{ref}}\right)\left(\frac{P_{H_2S,B}}{P_{ref}}\right),$$

$$y = P_{H_2S,D} = P_{H_2S,B}\left(\frac{P_{NH_3,B}}{P_{NH_3,D}}\right),$$

$$y = P_{H_2S,D} = \left(\frac{1}{2}\times0.659\text{atm}\right)\left(\frac{\frac{1}{2}\times0.659\text{atm}}{0.750\text{atm}}\right),$$

$$y = P_{H2S,D} = 0.145 \text{ atm}.$$

(*3 points, no credit for incorrect units or sigfigs*)

5. Ion Concentrations for Various Household Products (9 points)

Solution
Start with the definition of pH,

$$pH = -\log_{10}\left[H_3O^+\right],$$ **(1 point)** (OGC6 pg.631)

and solve for the concentrations of H_3O^+,

$$10^{-pH} = \left[H_3O^+\right].$$ **(1 point)**

Use the relationship for autoionization of water,

$$\left[H_3O^+\right]\left[OH^-\right] = K_w.$$ **(1 point)** (OGC6 pg.630)

At 25°C,

$$K_w = 1.01\times10^{-14},$$ **(1 point)** (Table 15.1, OGC6 pg.630)

so

$$\left[OH^-\right] = \frac{1.01\times10^{-14}}{\left[H_3O^+\right]}.$$

(Note: Students may also state pH + pOH = 14 and calculate [OH⁻] from this expression for full credit)

	pH	[H₃O⁺] (M)	[OH⁻] (M)
Orange Juice	2.8	2×10^{-3}	6×10^{-12}
Tomato Juice	3.9	1×10^{-4}	8×10^{-11}
Milk	4.1	8×10^{-5}	1×10^{-10}
Borax solution	8.5	3×10^{-9}	3×10^{-6}
Household ammonia	11.9	1×10^{-12}	8×10^{-3}

(5 points total: 0.5 point per value, no credit for incorrect sigfigs or units. No need to put into tabular form)**

6. Buffer Solutions (15 points)
Solution 6a
Write the acid-base equilibrium and generate a table,

$$NH_2C_6H_4SO_3H_{(aq)} + H_2O_{(l)} \rightleftharpoons (NH_2C_6H_4SO_3)^-_{(aq)} + H_3O^+_{(aq)}$$
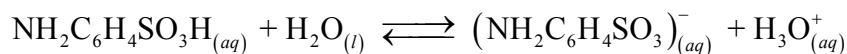
Initial concentration (M)	0.20		0.13	≈ 0
Change	-x		+x	+x
Equilibrium concentration (M)	0.20-x		0.13+x	x

Note: Since the initial concentrations of the acid and its conjugate base are so large, we can ignore the concentration of hydronium ions caused by the autoionization of water. This approximation is usually valid for buffer solutions, but this approximation is not always valid when adding a small amount of a weak base to water.

Use the definition of acid ionization constant,

$$K_a = \frac{[H_3O^+][NH_2C_6H_4SO_3^-]}{[NH_2C_6H_4SO_3H]}, \textbf{\textit{(2 points)}}$$

and substitute the equilibrium concentrations,

$$K_a = \frac{(x)(0.13 + x)}{(0.20 - x)} \cdot \textbf{\textit{(2 points)}}$$

For buffer solutions, we can usually make the approximation that the change in concentration (x) is small compared to the initial concentrations. We'll make this assumption, then use our final answer to check this assumption.

$$K_a \approx \frac{(x)(0.13)}{(0.20)}, x \ll 0.13.$$

$$\frac{0.20}{0.13}K_a \approx x, x \ll 0.13.$$

Use the definition of pH,

$$pH = -\log_{10}[H_3O^+], \textbf{\textit{(1 point)}}$$

(OGC6 p. 631)

and substitute the equilibrium concentration of the hydronium ion (x),

$$pH = -\log_{10}\left[\frac{0.20}{0.13}K_a\right], \qquad [1]$$

$$pH = 3.04.$$

(*2 points, no credit for an answer with incorrect sigfigs*)

Note that $x \approx 1 \times 10^{-3}$, which is much smaller than 0.13. Thus, our approximation is valid.

NOTE TO GRADERS: If students do not make the approximation that $x << 0.13$, then there should be no penalty. The answer will be *pH=3.05* if no approximation is made.

NOTE TO STUDENTS: If you didn't make this approximation, you might consider it for quizzes, exams and real-life – especially if you don't solve quadratic equations quickly. It's a trick that's a good time saver and has only a small effect on the answer, but you should always check to make sure that the assumption is valid.

Solution 6b
There are two ways to solve this problem

Method 1:
Since HCl is a strong acid, it completely dissociates. All hydrogen ions are taken up by the conjugate base; thus, increasing the concentration of the acid from 0.20M to 0.24M and decreasing the concentration of the conjugate base from 0.13M to 0.09M. (*2 points for using this statement properly to solve the problem. The statement itself is not required.*).

$$NH_2C_6H_4SO_3H_{(aq)} + H_2O_{(l)} \rightleftharpoons \left(NH_2C_6H_4SO_3\right)^-_{(aq)} + H_3O^+_{(aq)}$$
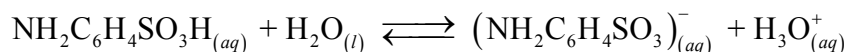
	NH₂C₆H₄SO₃H		(NH₂C₆H₄SO₃)⁻	H₃O⁺
Initial concentration (M)	0.24		0.09	≈ 0
Change	-x		+x	+x
Equilibrium concentration (M)	0.24-x		0.09+x	x

Using the new initial concentrations in Equation [1] from part (a),

$$pH = -\log_{10}\left[\frac{0.24}{0.09}K_a\right], \qquad [1]$$
$$pH = 2.8.$$
(*2 points for answer, no credit for incorrect sigfigs*)

Note that $x \approx 1.6 \times 10^{-3}$, which is much smaller than 0.09; so our approximation was valid.

GRADERS: Students do not need to make the approximation to receive full credit. They may solve the quadratic equation.

Method 2

Define x as the change in concentrations relative to the solution after HCl dissociates, but before the H^+ has bonded to the sulfanilate anion. Then,

$$K_a = \frac{\left[H^+\right]\left[A^-\right]}{[HA]} = \frac{(0.040-x)(0.13-x)}{(0.20+x)} \quad \textbf{\textit{(2 points)}}$$

Using the given K_a, we can solve for x and calculate [H+] and the pH:

$$x = 0.038463 \text{ M} \left(\text{reject the second solution, } 0.132127 \text{ M}\right)$$

$$\left[H^+\right] = \left(0.040 \text{ M} - x\right) = 0.001537 \text{ M (one sigfig)}$$

$$pH = 2.8$$

(*2 points for answer, no credit for incorrect sigfigs*)

Solution 6c

Change #1: Increase the number of moles (or concentration) of both the acid and base. **(*1 point*)** This change will allow more acid/base to be added before changing the pH.)

Change #2: Change the ratio of acid and conjugate base to a 1:1 ratio. **(*1 point*)** Since the buffer solution is imbalanced, it cannot withstand the same number of moles of acid and base.

Solution 6d

The implication is that the [HA]:[A⁻] ratio should be between 10:1 and 1:10. **(*1 points*)**

Justification: **(1 pt** for work below, or any other reasonable derivation/mathematical logic)

$$pH = \log_{10}\left[K_a \frac{[HA]}{[A^-]}\right]$$

$$pH = pK_a + \log_{10}\left[\frac{[HA]}{[A^-]}\right]$$

since $pH = pK_a \pm 1$, $\log_{10}\left[\frac{[HA]}{[A^-]}\right] = \pm 1$

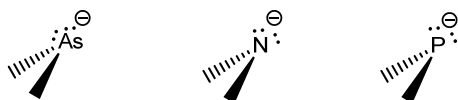$$\frac{[HA]}{[A^-]} = 10^{\pm 1}$$

7. Acidity of Organic Molecules (20 points)
1 pt per conjugate base, −0.5 if one resonance structure is missing, −1 if two or more are missing, or if the base is drawn wrong. No credit for responses missing lone pairs or formal charges.
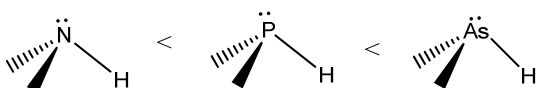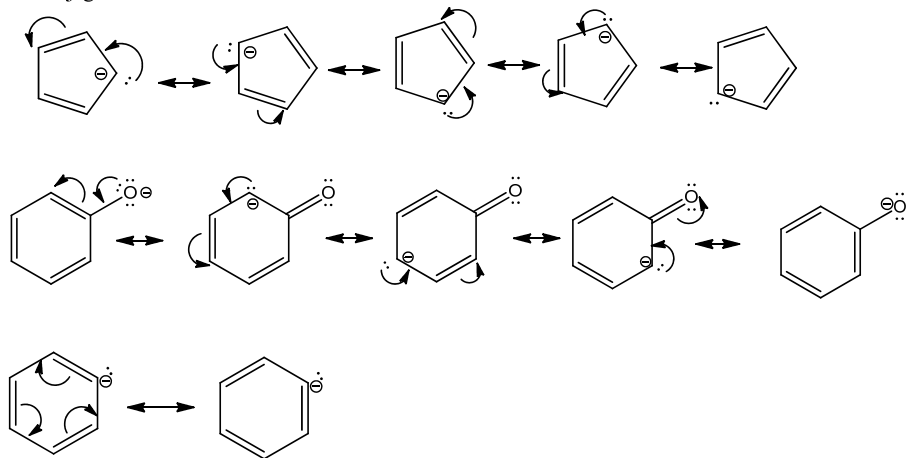0.5 pts for correct order, 0.5 pts for correct explanation
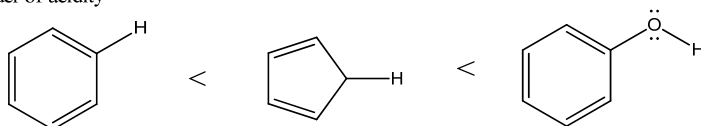
a)
Conjugate Bases

Order of acidity

Atomic radius increases going down a column on the periodic table. Since the same amount of charge occupies more volume in the As conjugate base, the As compound most easily stabilizes the negative charge.

b)
Conjugate bases and resonance structures

Order of acidity

Deprotonation of phenol results in a conjugate base with the major contributing resonance structure having a negative charge on the oxygen, so this conjugate base most effectively stabilizes the negative charge. The cyclopentadienyl anion stabilizes the negative charge over five resonance structures (three drawn) with the anion on carbon. Finally, deprotonated benzene can make no resonance structures that delocalize the anion.
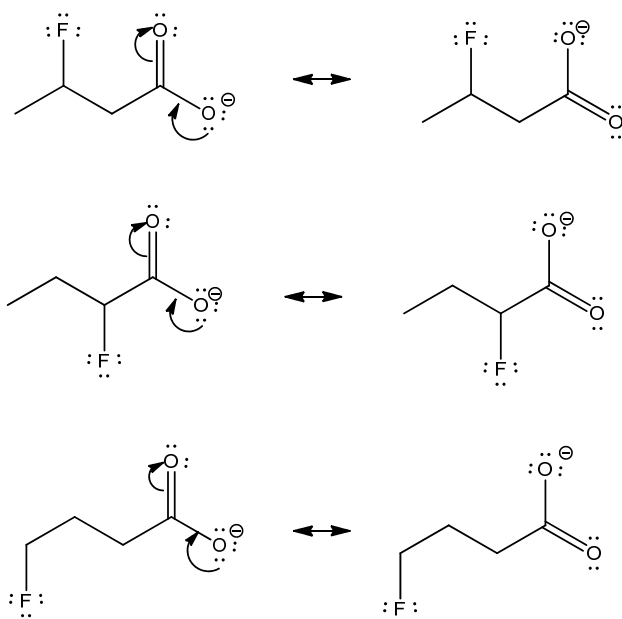
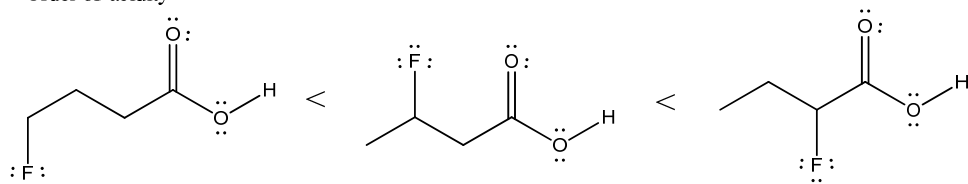c)

Conjugate Bases
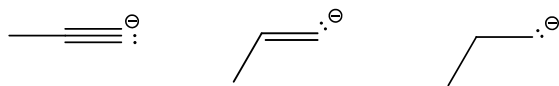
Order of acidity
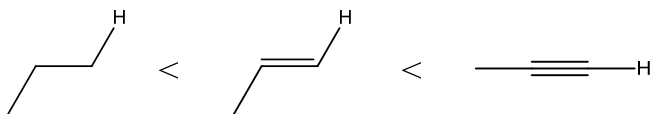
The greater the s character of an orbital, the more easily it can accommodate an additional negative charge. Since the ethyne proton is bound to an sp orbital, the conjugate base of ethyne is the most stable, followed by ethene, then ethane.

d)

Conjugate bases and resonance structures

Order of acidity

Upon loss of the carboxylic acid proton, each of these species forms a carboxylate anionic group stabilized by two resonance structures. The closer the fluorine is to the carboxylate group, the more effectively it can stabilize the anion through induction. Therefore, the species with the fluorine in the alpha position (adjacent to the carbonyl) is the strongest acid, that with the fluorine in the beta position (next to alpha position) is the second strongest, and that with the fluorine in the gamma position is weakest.

e)

Conjugate Bases (X=F, Cl, I)
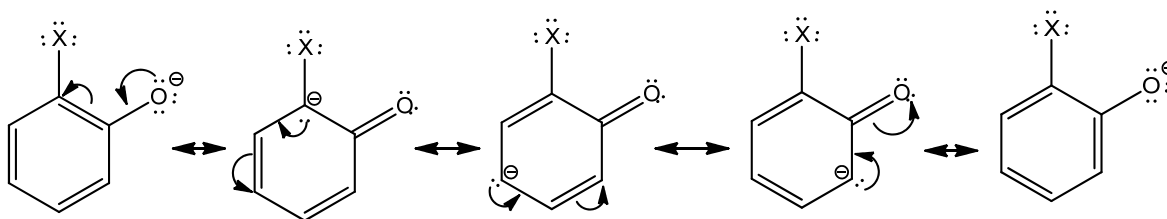
Order of acidity
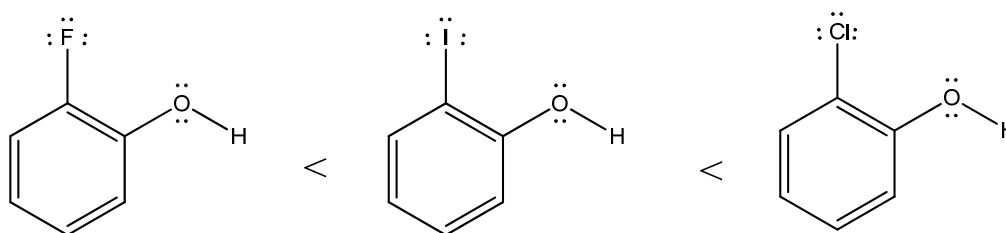
Here, resonance forms will move the negative charge onto the carbon with the halogen substitution. Cl has a higher electronegativity than I, so it is a stronger acid since it can better stabilize the negative charge by delocalization through inductive effects. Although F is the most electronegative, one has to also think about the lone pairs on F. Because these lone pairs are in sp^3 orbitals derived from 2p orbitals, and the lone pair on carbon will be in a 2p orbital, these electrons can better interact, destabilizing the molecule. Cl and I's lone pairs are in 3p and 4p derived orbitals. These will not interact as well with the 2p lone pair on the anionic carbon. This destabilizing interaction of the F lone pairs washes out the inductive effect of F, making it the worst acid of the three (measured pK_a values: Cl: 8.49, I: 8.52, F: 8.81).