1. (4 points each) Here are a few quick problems to get you going.
(a) Imagine formic acid, $HCOOH(g)$, decomposing into $CO_2(g)$ and $H_2(g)$ according to $HCOOH(g) \rightarrow CO_2(g) + H_2(g)$. The enthalpy change for this reaction is –30.5 kJ mol^{-1}, and the standard molar enthalpy of formation of $CO_2(g)$ is –393.5 kJ mol^{-1}. What is the standard molar enthalpy of formation, ΔH_f^o, of $HCOOH(g)$?

From the general relationship between enthalpies of formation and the reaction enthalpy change, we can write for this reaction

$$\Delta H_r^o = \Delta H_f^o(CO_2(g)) + \Delta H_f^o(H_2(g)) - \Delta H_f^o(HCOOH(g))$$

$$-30.5 \text{ kJ mol}^{-1} = -393.5 \text{ kJ mol}^{-1} + 0 - \Delta H_f^o(HCOOH(g))$$

which we solve for $\Delta H_f^o(HCOOH(g)) = -363$ kJ mol^{-1}.

(b) A saturated solution of lanthanum(III) iodate, $La(IO_3)_3$, in pure water has an iodate concentration, $[IO_3^-]$, equal to 2.0×10^{-3} M. What is K_{sp} for $La(IO_3)_3$?

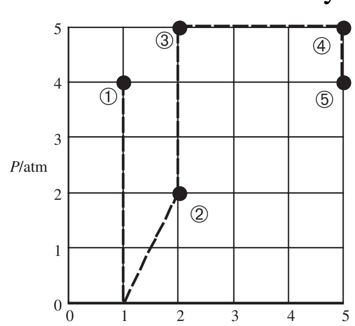
The net reaction here is $La(IO_3)_3(s) \rightarrow La^{3+}(aq) + 3\ IO_3^-(aq)$. Thus, if $[IO_3^-] = 2.0 \times 10^{-3}$ M, $[La^{3+}] = [IO_3^-]/3 = 6.7 \times 10^{-4}$ M because there is no other source for either of these ions except the $La(IO_3)_3$ solid. We now know the equilibrium concentrations that determine the solubility product:

$$K_{sp} = [La^{3+}]\,[IO_3^-]^3 = \left(6.7 \times 10^{-4}\right)\left(2.0 \times 10^{-3}\right)^3 = 5.3 \times 10^{-12}$$

(c) If 6.02 kJ is transferred as heat to 1 mol of ice, $H_2O(s)$ at a constant 1 atm pressure, all the ice melts to $H_2O(l)$. Thus, we can see that ΔH for the process $H_2O(s) \rightarrow H_2O(l)$ is 6.02 kJ because $\Delta H = q_P$. Why is ΔE for this process essentially the same number?

In general, ΔH and ΔE are related through $\Delta H = \Delta E + \Delta(PV)$. So if $\Delta H \approx \Delta E$, we need to consider why $\Delta(PV) \approx 0$. In this case, the pressure is constant, but that alone isn't enough to ensure $\Delta(PV) \approx 0$. Here, we write $\Delta(PV) = PV(H_2O(l)) - PV(H_2O(s)) = P[V(H_2O(l)) - V(H_2O(s))]$ and note that the volume of one mole of ice is almost the same as the volume of one more of liquid water, which makes $[V(H_2O(l)) - V(H_2O(s))] \approx 0$.

2. (4 + 6 + 6 + 4 points) A sample of a fixed amount of an ideal gas is subjected to a series of state changes as shown in the *P*, *V* diagram below. The gas starts in state ① at a temperature of 400 K, a pressure of 4 atm, and a volume of 1 L. The dashed lines in the diagram show how the external pressure varied as the gas was taken to a series of three intermediate equilibrium states, ② through ④, before ending at the final equilibrium state ⑤. The *P*, *V* coordinates of each state are indicated by a black dot.



(a) Calculate the *highest* and *lowest* temperatures experienced by the gas and indicate which equilibrium state (or states) have those temperatures.

highest T: <u>2500 K</u> at state(s) number <u>4</u>

lowest T: <u>400 K</u> at state(s) number <u>1 and 2</u>

We note that state 1 has T_1 = 400 K, and in general, $PV/T = nR$ = a constant. For state 1, P_1V_1 = 4 L atm, and for state 2, P_2V_2 also equals 4 L atm. Thus, T at state 2, T_2, is also 400 K. For state 3, P_3V_3 = 10 L atm, so T_3 must be $(P_3V_3/P_1V_1)T_1$ = (10/4)(400 K) = 1000 K; similarly for state 4, P_4V_4 = 25 L atm and T_4 = 2500 K; and at state 5, P_5V_5 = 20 L atm and T_5 = 2000 K.

(b) Calculate the work, w, associated with this *entire* process, ① → ⑤.

The *magnitude* of the work, $|w|$, is equal to the area under the path line (the dashed lines). This area is (count squares under the lines: each square has an area of 1 L atm) 16 L atm. Next, we note that the overall process is an *expansion*, making the work *negative*: energy was transferred from the system to the surroundings. Thus, w = –16 L atm. (In joule units, this is about –1621 J. Either J or L atm units were accepted.)

(c) Calculate ΔE and ΔH for the *entire* process from state ① to state ⑤.

First, ΔE, for which $\Delta E = nC_V\Delta T$. We know $C_V = 3R/2$ for an ideal gas, we know $\Delta T = T_5 - T_1$ = 2000 K – 400 K = 1600 K, and we could find n from any equilibrium state, such as $n = P_1V_1/RT_1$. But if we substitute this expression into the expression for ΔE, we can write

$$\Delta E = \frac{3}{2}nR\Delta T = \frac{3}{2}\frac{P_1V_1}{RT_1}R\Delta T = \frac{3}{2}\frac{P_1V_1}{T_1}\Delta T = \frac{3}{2}\frac{4\text{ L atm}}{400\text{ K}}1600\text{ K} = 24\text{ L atm}$$

saving us the step of calculating n explicitly. Similarly, for ΔH, we start with $\Delta H = nC_P\Delta T$ and $C_P = 5R/2$ and find ΔH = 40 L atm.

(c) Calculate the heat, q, associated with *only the first step* in the process, ① → ②.

States 1 and 2 have the same temperature; so, for this first step, $\Delta T = 0$. Because the system is an ideal gas, ΔT tells us that $\Delta E = 0$: E can change only if T changes. If $\Delta E = 0 = q + w$, then $q = -w$. For this first step, w = – 1 L atm (the area under the dashed path line from state 1 to state 2, and again negative because this is an expansion). Thus, q = +1 L atm. Note that it is *incorrect* to say $q = C\Delta T = 0$ because $\Delta T = 0$. Why? The reason can be traced to the fact that q and thus C both depend on the nature of the path.

3. (6 + 10 points) A solution is prepared from pure water and Na_2CO_3 by adding 0.280 mol of Na_2CO_3 to 350 mL of water. Relevant equilibria and their equilibrium constants are:

$$H_2CO_3(aq) \rightleftarrows H^+(aq) + HCO_3^-(aq) \qquad K_{a_1} = 4.3\times 10^{-7}$$

$$HCO_3^-(aq) \rightleftarrows H^+(aq) + CO_3^{2-}(aq) \qquad K_{a_2} = 5.6\times 10^{-11}$$

(a) What is the pH of this solution?

When Na_2CO_3 dissolves in water, it dissociates completely into Na^+ and CO_3^{2-} ions. Thus, the dominant ion in this solution will be carbonate, CO_3^{2-}, and the dominant chemistry will be the *hydrolysis* of carbonate:

$$CO_3^{2-}(aq) + H_2O(l) \rightleftarrows HCO_3^-(aq) + OH^-(aq) \qquad K_b = \frac{K_w}{K_{a_2}} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.8 \times 10^{-4}$$

We also know that the initial concentration of carbonate is given by

$$[CO_3^{2-}]_0 = \frac{0.280 \text{ mol}}{0.350 \text{ L}} = 0.800 \text{ M}$$

and that the equilibrium concentration of carbonate will be essentially the same because the base hydrolysis constant, K_b, is << 1. Likewise, we expect $[OH^-] = [HCO_3^-]$ because the hydrolysis, while slight, is nevertheless the predominant source of these two ions. Writing $[OH^-] = x$ gives us the following equilibrium constant expression:

$$K_b = \frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]} = \frac{x^2}{0.800} = 1.8 \times 10^{-4} \quad \text{or} \quad x = 0.012 \text{ M} = [OH^-]$$

so that pH = 14.0 – pOH = 14.0 + $\log_{10}[OH^-]$ = 12.1.

(b) Next, 150 mL of a 1.00 M HCl solution is mixed into the Na_2CO_3 solution. Calculate the pH of this solution.

Before we figure out the chemistry that will happen following this addition, let's note two things: the total volume of the solution will become 0.150 L + 0.350 L = 0.500 L *and* we are adding, from the HCl, (0.150 L)×(1.00 M) = 0.15 mol H^+. Now for the chemistry. The predominant base in solution before HCl is added is carbonate ion. This is what H^+ goes after in the reaction $HCO_3^-(aq) \rightleftarrows H^+(aq) + CO_3^{2-}(aq)$ running in the reverse direction. There is significantly more carbonate ion (0.280 mol from part (a)) than there is H^+ added from the HCl solution. Thus, the amount of carbonate falls from 0.280 mol to (0.280 – 0.150) mol = 0.130 mol while hydrogen carbonate rises from essentially zero to 0.150 mol. We now can find the concentrations of carbonate and hydrogen carbonate:

$$[HCO_3^-] = \frac{0.150 \text{ mol}}{0.500 \text{ L}} = 0.300 \text{ M} \qquad [CO_3^{2-}] = \frac{0.130 \text{ mol}}{0.500 \text{ L}} = 0.260 \text{ M}$$

and we can write the second ionization equilibrium constant expression as

$$K_{a_2} = \frac{[H^+][HCO_3^-]}{[CO_3^{2-}]} = \frac{[H^+](0.300)}{0.260} = 5.6 \times 10^{-11} \quad \text{or} \quad [H^+] = 6.5 \times 10^{-11} \text{ M}$$

so that pH = $-\log_{10}(6.5 \times 10^{-11})$ = 10.2.

4. (2 points each) Fill in each blank with a short, succinct answer or expression.

(a) The molar solubility in pure water, *s*, of the simple binary salt MX (such as AgCl, AgBr, etc.) with solubility product K_{sp} is given by this function of K_{sp}:

$s = \sqrt{K_{sp}}$

The molar solubility of a binary salt equals the molar concentration of either of its ions, and for a pure water solution of MX, $[M^+] = [X^-] = s$. Moreover, $K_{sp} = [M^+][X^-] = s^2$.

(b) At the first equivalence point in the titration of a weak diprotic acid (such as H_2CO_3) with successive acid dissociation constants K_{a_1} and K_{a_2} the pH is given by the expression

$\mathrm{pH} = (\mathrm{p}K_{a_1} + K_{a_2})/2$

(c) In the isothermal reversible compression of an ideal gas, the external pressure, P_{ext}, is given by this function of the system's volume:

$P_{ext} = nRT/V$

If the path is reversible, then the external and system pressures are equal (or at most only infinitesimally different from each other). For an ideal gas, $P_{sys} = nRT/P$.

(d) When an endothermic reaction is carried out in an adiabatic container, the temperature of the reaction mixture must

decrease. (The energy needed to advance an endothermic reaction must come from the reaction mixture itself, and this loss of energy causes the temperature to decrease.)

(e) For the diprotic acid H_2A with successive acid dissociation constants K_{a_1} and K_{a_2}, the equilibrium constant K for the reaction $H_2A \rightarrow 2H^+ + A^{2-}$ is given by the expression

$K = K_{a_1}\ K_{a_2}$

The reaction in question is the sum of the two reactions represented by K_{a_1} and K_{a_2}; thus, K is the product of the equilibrium constants for these two reactions.
(f) The reaction for which the reaction enthalpy change equals the standard molar enthalpy of formation of the liquid compound acetic acid, $CH_3COOH(l)$, is

$2C(s) + 2H_2(g) + O_2(g) \rightarrow CH_3COOH(l)$

The formation reaction for a compound has one mole of that compound as its only product and sufficient amounts of *elements in their standard states* as reactants. (Note that the standard state of carbon should actually be specified as graphite, but simply saying "(*s*)" was acceptable here.)

(g) If a fixed amount of an ideal gas starts in the state described by P, V, T and ends in the state by P, $2V$, $2T$, the enthalpy change for the gas, ΔH, is given by the expression

$\Delta H = 5PV/2 = 5nRT/2$

Here's the reasoning:

$$\Delta H = nC_P\Delta T = \frac{5}{2}\,nR\Delta T. \quad \text{But here, } \Delta T = 2T - T = T \text{ and } nRT = PV.$$

(h) If 1 mol of slightly soluble $Ca(OH)_2(s)$ is in equilibrium with pure water, and then an additional 1 mol of $Ca(OH)_2(s)$ is added to the solution, the solution's pH will

not change!

This is *exactly* the same situation as appeared on Exam 1 in part 4 to problem 4, part b. In that problem, a solid dissociated into two gasses. The partial pressures of the gasses would not change if more solid was added: as long as *some* solid was present, no matter how much, the equilibrium was established and the pressures were fixed. Here, as long as *some* $Ca(OH)_2$ was present as a solid in equilibrium with the solution, $[Ca^{2+}]$ and $[OH^-]$ were fixed (and thus the pH was fixed as well), and adding more solid would not change that.

5. (8 + 8 points) Both silver chloride, AgCl, and silver chromate, Ag_2CrO_4, are rather insoluble:

$$AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 2.8 \times 10^{-10}$$
$$Ag_2CrO_4(s) \rightleftarrows 2Ag^+(aq) + CrO_4^{2-}(aq) \qquad K_{sp} = 1.9 \times 10^{-12}$$

Imagine a solution made from the completely soluble salts NaCl(*s*) and $Na_2CrO_4(s)$ so that $[Cl^-] = 0.100$ M and $[CrO_4^{2-}] = 0.010$ M. A highly concentrated solution of Ag^+ ion is now added in very small amounts to this solution. (We specify this solution to be "highly concentrated" so that we *do not* have to worry about dilution effects.)

(a) Figure out which solid precipitates first, and calculate the silver concentration at which this precipitate first appears.

The solid to precipitate first is the one for which the silver concentration that established the solubility equilibrium is the *lowest*. We calculate the two possibilities:

For AgCl:

$$K_{sp} = 2.8 \times 10^{-10} = [Ag^+][Cl^-]$$
$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{2.8 \times 10^{-10}}{0.100} = 2.8 \times 10^{-9}\text{ M}$$

For Ag_2CrO_4:

$$K_{sp} = 1.9 \times 10^{-12} = [Ag^+]^2[CrO_4^{2-}]$$
$$[Ag^+] = \sqrt{\frac{K_{sp}}{[CrO_4^{2-}]}} = \sqrt{\frac{1.9 \times 10^{-12}}{0.010}} = 1.3 \times 10^{-5}\text{ M}$$

The smaller $[Ag^+]$ is for AgCl; thus, the first solid to precipitate is AgCl. (Note that simply comparing K_{sp} values is *not* the correct thing to do—*ever*!)

(b) As more Ag^+ is added, that first solid continues to precipitate until its anion is nearly all removed from the solution and the other solid begins to precipitate. Calculate the concentration of the first anion to precipitate at the point when the second anion starts to precipitate.

As AgCl precipitates, the chloride concentration in solution will fall, and as it does, the silver concentration will slowly rise. But Ag_2CrO_4 will not precipitate until $[Ag^+]$ has risen to 1.3×10^{-5} M, as we found in part (a). Once enough Cl^- has left the solution in the form of solid AgCl so that $[Ag^+]$ can rise to this value, Ag_2CrO_4 can precipitate. The Cl^- concentration at that point is given by solving the AgCl K_{sp} expression for $[Cl^-]$ and using the desired $[Ag^+]$ value:

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{2.8 \times 10^{-10}}{1.3 \times 10^{-5}} = 2.2 \times 10^{-5}\ \text{M}$$

6. (10 + 10 points each) Consider the weak monoprotic acid formic acid (which was also featured in question 1a, but nothing in that question applies to this one). It dissociates into formate ion, $HCOO^-$, and hydrogen ion, H^+, according to

$$HCOOH(aq) \rightleftarrows H^+(aq) + HCOO^-(aq) \qquad K_a = 1.8 \times 10^{-4}$$

(a) How many *grams* of sodium formate, NaHCOO, (of molar mass 68.01 g mol^{-1}) must be added to 400 L of a 0.15 M HCOOH solution to produce a buffer at pH = 3.5?

A confession: I intended the volume to be 400 ***mL*** *instead of 400 L, but it makes no difference to how the problem is solved. We're just making one huge bucket-full of buffer!*
Think about what's going on here. We want to know how many grams of NaHCOO to add, which suggests we find how many moles we should add, and furthermore, we recognize that NaHCOO is producing one mole of formate ion, $HCOO^-$, per mole of NaHCOO added. We know how many moles of formic acid, HCOOH, are there initially: (400 L)×(0.15 M) = 60 mol (and we expect very little HCOOH dissociation, because K_a is so small, ensuring that the equilibrium [HCOOH] is the analytical amount, 0.15 M. Because these species, HCOOH and $HCOO^-$, are in the same volume, we can consider amounts in moles rather than concentrations. The Henderson-Hasselbalch equation is called for (but not absolutely necessary):

$$\text{pH} = \text{p}K_a + \log\frac{[HCOO^-]}{[HCOOH]}$$

where pH = 3.5, $\text{p}K_a = -\log(1.8 \times 10^{-4}) = 3.74$, and the concentration ratio becomes the mole ratio x/(60 mol) where x is the number of moles of NaHCOO we need to add. We find x = 34.15 mol, and at 68.01 g mol^{-1}, the mass of NaHCOO we need is 2.32 kg. (In case you wondered, that much NaHCOO costs about $80 these days.)

(b) How many moles of NaOH(s) can be added to this buffer before the pH rises to 4.0?

Here's the thing about buffers: *every mole of OH^- added to a buffer destroys one mole of the buffer acid and produces one mole of that acid's conjugate base*. Here, let y be the number of moles of OH^- we add. The amount of $HCOO^-$ will thus rise from 34.15 mol to 34.15 mol + y, and the amount of HCOOH will fall from 60 mol to 60 mol – y. The Henderson-Hasselbalch equation becomes, for pH = 4.0,

$$\text{pH} = \text{p}K_a + \log\frac{[HCOO^-]}{[HCOOH]} = 4.0 = 3.74 + \log\frac{34.15 + y}{60.0 - y}$$

and we solve this, finding y = moles of NaOH to add = 26.4 mol.