

Here's a little guidance on the old exam problems...

General hint. Probably the *worst* thing you can do in working problems like these is to screw up the conversion between J and kJ. *kilo* means 1000, so 1 kJ = 1000 J. !!! Making this mistake usually produces such numerically ridiculous results that it's very hard to feel much sympathy when grading.

8. from Ex1 (b) Plug 'n' chug. Don't forget that ΔH°_f of molecular oxygen is zero, by definition. $\Delta H^\circ_{\text{rxn}} = -3140$ kJ/mol. (c) That's 0.0641 mol, so 200 kJ of energy, i.e. heat, is released. (d) final temp = 61°C

1. $\text{Na (s)} + \text{H}_2\text{O (l)} \rightarrow 1/2 \text{H}_2 \text{(g)} + \text{NaOH (aq)}$. (b) Combine oxidation of Na and reduction of water (to H_2 and hydroxide) — $\mathcal{E}^\circ = +1.88$ V. (c) $\Delta G^\circ = -nF\mathcal{E}^\circ = -181$ kJ/mol (this is per mole of Na, appropriate to the reaction as written. If you double the coefficients in the reaction, there are 2 electrons transferred, so ΔG° is -362 kJ, but this would be *per 2 mol* of Na.) (d,e) The table values give $\Delta H^\circ = -184$ kJ/mol and $\Delta S^\circ = -5.5$ J/molK, so $\Delta G^\circ = -182$ kJ/mol at room temp. Should those two numbers be about the same?

2. (b) + 0.53V. (e) If the two reactants, Ag metal (electrode) and chromate, CrO_4^{2-} , are allowed to come in contact, they will just react directly.

3. (a) + 0.421 V. (c) + 0.239 V. (d) -81.2 kJ/mol. (e) 1.74×10^{-14} . (f) Reverse the reaction and invert the K from part e to get $K_{\text{sp}} = 5.75 \times 10^{-15}$. (g) this part would have been more appropriate on our first midterm (or the final), 1.13×10^{-5} M.

4. (a) Aluminum's *oxidation* potential is +1.66 V, so anything whose *reduction* potential is greater than -1.66 V will give a positive overall potential. (b) Cupric ion would be reduced in this process, either to cuprous ion (+0.16 V) or to Cu metal (+0.34 V). The oxidation potential of iodide is -0.54 V, so no, this would not fly. (c) Reduction of nitrate ion under acidic conditions (i.e. aqueous nitric acid) has a potential of +0.96 V, so we're looking for someone with an oxidation potential greater than -0.96 V. Metallic silver is the only one that can be oxidized by nitric acid. Notice that Cd *metal* would work, but the species in the list is Cd^{2+} — that's not oxidizable!

5. Use the heat capacity to calculate the change in enthalpy (negative) for cooling the liquid to its freezing point, then the "enthalpy of fusion" to calculate the enthalpy change (negative) for freezing of the liquid. The entropy changes (also both negative, right?) can be determined from $nC_p \ln(T_2/T_1)$ and $\Delta H_{\text{fusion}}/T$. $\Delta H = -7.40 - 9.87 = -17.3$ kJ, and $\Delta S = -24.25 - 35.4 = -59.7$ J/K. Note that these are for a specified quantity of benzene (1 mol) so units are kJ and J/K.

6. (a) 0. (b) 354 J (heat flows into system). (c) 14.5 J/K (note that T is not 298K here. You can divide q by T to get the entropy change only if you calculated the T (24K), otherwise just use $nR \ln(V_2/V_1)$). (d) Entropy change depends only on initial and final volumes, so that would be the same, but the corresponding heat flow would be larger.

7. (a) $2 \times 5 = 10$. (b) 19.1 J/molK. (c) -1.9 kJ/mol — note that this is favorable ("downhill"), even though the ΔH° is positive! Even though each of the "one-kink" conformations is 3.8 kJ/mol higher in enthalpy, there are 10 ways for the chain to have one kink, so this *set* of conformations is overall lower in free energy than the one zig-zag! (d) $K = 2.16$. 32% A, 68% B. (e) -74°C . Brrrr.

8. First, let's see if we can estimate ΔH° and ΔS° ... The reaction trades two σ -bonds (H–H and C–O) for two different σ -bonds (H–O and C–H). These are all pretty ordinary, and they're all roughly the same strength. But, once again, we have a strained 3-membered ring involved — relief of that ring strain should make the reaction exothermic — if you remember the previous problems, that's worth around 120 kJ/mol, so we expect ΔH° to be negative by a considerable amount. Two molecules come together to make one, so there should be a substantial decrease in "disorder" or "degrees of freedom", and we'd expect ΔS° to be negative as well.

(a) Before we break out the calculators, let's think about how to get ΔH°_f and ΔS° for ethanol *gas* from the values given for the *liquid*. ΔH°_f for gas-phase ethanol is just ΔH°_f for the liquid + $\Delta H^\circ_{\text{vaporization}}$, right? And keep in mind that it takes heat input to vaporize a liquid, so the ΔH°_f we calculate for the gas had better be *higher* than that for the liquid. ΔH°_f for ethanol gas is -236 kJ/mol. Same procedure for the entropy change — keep in mind that entropy must *increase* upon going from liquid to gas. You know how to calculate ΔS° for the phase transition. ΔS° for ethanol gas is 281 J/molK.

The enthalpy and entropy changes for the reaction with everything in the gas phase, are -183 kJ/mol and -92 J/molK, respectively, and (b) ΔG° at 373K is -149 kJ/mol.