

### Problem Set 7 (For March 3)

**Recommended Text Problems:** 10.28, 10.40, 10.50, 10.60, 10.64, 10.71, 10.87

1. The standard molar free energies of formation at 298 K,  $\Delta G_f^\circ$ , the standard molar entropies,  $S^\circ$ , and the standard molar enthalpies of formation,  $\Delta H_f^\circ$ , for the species in an “interhalogen scrambling reaction” are shown below:

	ICl(g)	+	BrF(g)	$\rightleftharpoons$	IBr(g)	+	ClF(g)
$\Delta G_f^\circ/\text{kJ mol}^{-1}$	-5.44		-73.80		3.71		-51.78
$S^\circ/\text{J mol}^{-1}\text{K}^{-1}$	247.56		228.93		258.95		217.91
$\Delta H_f^\circ/\text{kJ mol}^{-1}$	17.51		-58.46		40.88		-50.29

Calculate the entropy change for this reaction and explain why it is so small. Calculate the equilibrium constant for this reaction. Will  $K$  increase or decrease with increasing  $T$ ? Suppose 1 mol ICl(g) is mixed with 1 mol BrF(g) at 298 K. What amount of ClF will be present at equilibrium? (Hint: ideas we used to discuss weak acid dissociation equilibria will be useful here!)

2. The reason ant bites sting and the French word for ant is “fourmi” is traceable to the compound formic acid, HCOOH, a monoprotic acid we met in the second exam. (It’s the last H in the formula, bonded to an oxygen atom, that is acidic.) Use the free energy of formation data below (for 298 K) to calculate  $K_a$  for HCOOH. (Note, by the way, that the free energy of formation of  $\text{H}^+(\text{aq})$  is zero. So is its enthalpy of formation. It forms the reference state for ions in solution.)

	HCOOH(aq)	HCOO <sup>-</sup> (aq)	H <sup>+</sup> (aq)
$\Delta G_f^\circ/\text{kJ mol}^{-1}$	-372.3	-351.0	0

Now consider our favorite strong acid, HCl.  $\Delta G_f^\circ$  for  $\text{Cl}^-(\text{aq})$  is  $-131.3 \text{ kJ mol}^{-1}$ . What can you say about the free energy of formation of  $\text{HCl}(\text{aq})$ ? (You can’t calculate it, but you can place some reasonable limits on it!)

3. Consider two reactions with equal  $\Delta H_f^\circ$  values, both run at the same temperature. Reaction 1 produces two moles of gaseous products per mole of gaseous reactants. Reaction 2 produces only one mole of gaseous products per mole of gaseous reactants. Which reaction, 1 or 2, will have the larger equilibrium constant, and why?

4. When xenon difluoride,  $\text{XeF}_2$ , was first synthesized in the early 1960’s, there was a great rush to characterize its physical properties. (It was one of the first compounds synthesized containing any of the rare gas elements.) Near room temperature  $\text{XeF}_2$  is a fairly volatile solid, and light absorption methods could measure the concentration of  $\text{XeF}_2(\text{g})$  via its absorbance, which is directly proportional to the  $\text{XeF}_2$  pressure. In 1963, the first such measurements found the absorbance to be 10 at 294 K and 1.2 at 267 K in a particular experiment. What is the molar enthalpy of sublimation of  $\text{XeF}_2$ , i.e., the enthalpy change for the sublimation process  $\text{XeF}_2(\text{s}) \rightarrow \text{XeF}_2(\text{g})$ ?

5. Your first job is with a small mining company that plans to recover trace gold from spent iron ore by a new process. In your analysis of this process, you find that you need to know the standard molar free energies of formation ( $\Delta G_f^\circ$ ) of the gold and iron oxides  $\text{Au}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . You rush to the library, look them up, write them down, return to your office, and find to your initial horror that all you wrote were the values,  $-742 \text{ kJ mol}^{-1}$  and  $126 \text{ kJ mol}^{-1}$ , without an indication of which is which. How can a little basic chemical knowledge coupled with the meaning of  $\Delta G_f^\circ$  makes it clear which number goes with which compound?