

Problem Set 7 Solutions (For March 3)

1. Using the usual “products – reactants” expression, we find the following standard reaction changes:

$$\Delta S_r^\circ = (258.95 + 217.91 - 247.56 - 228.93) \text{ J mol}^{-1} \text{ K}^{-1} = 0.37 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H_r^\circ = [40.88 + (-50.29) - 17.51 - (-58.46)] \text{ kJ mol}^{-1} = 31.54 \text{ kJ mol}^{-1}$$

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ = 31,540 \text{ J mol}^{-1} - (298.15 \text{ K})(0.37 \text{ J mol}^{-1} \text{ K}^{-1}) = 31.43 \text{ kJ mol}^{-1}$$

$$\text{or } \Delta G_r^\circ = [3.71 + (-51.78) - (-5.44) - (-73.80)] \text{ kJ mol}^{-1} = 31.17 \text{ kJ mol}^{-1}$$

The entropy change is so small because (a) both reactant molecules and both product molecules are gases, (b) all the gases have the same complexity (all are diatomic molecules), and (c) the total mass of the reactant molecules equals the total mass of the product molecules. Note that the reaction is *endothermic* (positive ΔH_r°), which tells us that K will increase with increasing T . Note as well that the two values for ΔG_r° are quite close: less than 0.5 kJ mol^{-1} apart, or about 1% different. If we calculate K with each of these values, we can see that the calculated value for K reflects the difference in these two values rather substantially. The 1% difference in ΔG_r° values leads to about a 10% difference in K values:

$$K = e^{-\Delta G_r^\circ/RT} = e^{-(31430 \text{ J mol}^{-1})/(8.315 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = 3.12 \times 10^{-6}$$

$$\text{or } K = e^{-\Delta G_r^\circ/RT} = e^{-(31170 \text{ J mol}^{-1})/(8.315 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = 3.46 \times 10^{-6}$$

Let's settle on $K = 3 \times 10^{-6}$ for the rest of this problem. The small value for K tells us that at equilibrium, not very much of the reactants will have turned into products. If we start with 1 mol of each reactant, then at equilibrium, the amounts of each product will be equal, and we can write, in analogy with the approximation we used for weak acids, where K is also $\ll 1$,

$$K = \frac{P_{\text{IBr}}P_{\text{ClF}}}{P_{\text{ICl}}P_{\text{BrF}}} = \frac{n_{\text{IBr}}n_{\text{ClF}}}{n_{\text{ICl}}n_{\text{BrF}}} = \frac{x^2}{(1-x)(1-x)} \approx x^2 \quad \text{or} \quad x = \sqrt{K} = 0.0017 \text{ mol}$$

We conclude that the equilibrium amounts of everything will be $1.7 \times 10^{-3} \text{ mol}$ for both ClF and IBr, with essentially 1 mole of ICl and BrF.

2. The net formic acid dissociation reaction is $\text{HCOOH}(aq) \rightleftharpoons \text{HCOO}^-(aq) + \text{H}^+(aq)$, and if it is a weak acid, K_a will be small compared to 1. We find K_a from the free energy of formation values:

$$\Delta G_r^\circ = [0 + (-351.0) - (-372.3)] \text{ kJ mol}^{-1} = 21.3 \text{ kJ mol}^{-1}$$

$$K_a = e^{-\Delta G_r^\circ/RT} = e^{-(21300 \text{ J mol}^{-1})/(8.315 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = 1.86 \times 10^{-4}$$

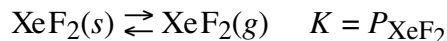
Sure enough, $K_a \ll 1$, and formic acid is a weak acid. For HCl, we know $K_a \gg 1$. For its dissociation reaction, $\text{HCl}(aq) \rightleftharpoons \text{H}^+(aq) + \text{Cl}^-(aq)$, we can calculate ΔG_r° formally through

$$\Delta G_r^\circ = \Delta G_f^\circ(\text{H}^+) + \Delta G_f^\circ(\text{Cl}^-) - \Delta G_f^\circ(\text{HCl}) = 0 - 131.3 \text{ kJ mol}^{-1} - \Delta G_f^\circ(\text{HCl})$$

If $K \gg 1$, then $\Delta G_r^\circ \ll 0$. We see that our ΔG_r° equals zero if $\Delta G_f^\circ(\text{HCl}) = \Delta G_f^\circ(\text{Cl}^-)$. Thus, if $\Delta G_f^\circ(\text{HCl}) > -131.3 \text{ kJ mol}^{-1}$, ΔG_r° will be negative. As an aside, if you look in thermodynamic tables for the ΔG_f° value of $\text{HCl}(aq)$, you will find $-131.3 \text{ kJ mol}^{-1}$, the $\text{Cl}^-(aq)$ value.

3. In Reaction 1, the number of moles of gaseous products is greater than the number of moles of gaseous reactants. In Reaction 2, these are equal. Thus, Reaction 1 has a *positive* (and probably large) ΔS_r° . If ΔH_r° is the same, then Reaction 1, with the *higher* entropy change, will have the *lower* free energy change: $G = H - TS$. Reaction 1 will have the larger K .

4. Sublimation, the conversion of a solid to the gas phase, is a physical transformation rather than a real chemical reaction, but all such transformations have their equilibrium properties governed by the same physical laws as do “real” reactions. Here, the reaction and its equilibrium constant are

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where P_{XeF_2} is the solid's vapor pressure. We are told that the absorbance measurements, 10 at 294 K and 1.2 at 267 K, are directly proportional to vapor pressures. Thus, we use the van't Hoff equation relating temperature changes to equilibrium constant changes and write

$$\ln\left(\frac{K_2}{K_1}\right) = \ln\left(\frac{10}{1.2}\right) = -\frac{\Delta H_{\text{r}}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) = -\frac{\Delta H_{\text{r}}^{\circ}}{R} \left(\frac{1}{294 \text{ K}} - \frac{1}{267 \text{ K}}\right)$$

Solving for $\Delta H_{\text{r}}^{\circ}$, which here is also called the (standard molar) enthalpy of sublimation, $\Delta H_{\text{sub}}^{\circ}$, we find

$$\Delta H_{\text{r}}^{\circ} = \Delta H_{\text{sub}}^{\circ} = \frac{R \ln(10/1.2)}{\left(\frac{1}{267 \text{ K}} - \frac{1}{294 \text{ K}}\right)} = 51.3 \text{ kJ mol}^{-1}$$

5. Here, the free energies of formation are the *reaction* free energies for the elemental metal reacting with oxygen. If the reaction free energy is negative, the reaction is spontaneous. Iron “rusts” spontaneously, but gold does not react with oxygen. Thus, the Fe_2O_3 value is -742 kJ mol^{-1} , and the Au_2O_3 value is 126 kJ mol^{-1} . It's interesting to note (see Example 10.14 on page 440 as well) that the Fe_2O_3 formation reaction (which produces only one mole of Fe_2O_3 whereas the example in the book writes a reaction producing two moles) has an equilibrium constant at 298 K equal to about 10^{130} ! This really is a “reaction that goes to completion,” as the relentless formation of rust attests.