Predicting the Sign of Thermodynamic Parameters

If you open a bottle of concentrated HCl next to an open bottle of concentrated NH_3, a white smoke immediately forms in the space above the bottles. Smoke is nothing more than very small particulates, typically about 2.5 mm in diameter (compared to 100 mm for the diameter of a human hair). The reaction taking place is a gas-phase acid-base reaction (both HCl and NH_3 are volatile), producing particulate NH_4Cl

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

1. Predict the signs of ΔG, ΔH, and ΔS for this reaction and clearly explain your reasoning. If you have insufficient information to assign a sign to any or all of these thermodynamic parameters, then clearly explain why. Do not use published heats of formation, free energies of formation, or enthalpies to answer this question!

   Because we see that the reaction happens, we know that ΔG is negative. We also can predict that ΔS is negative as the reaction combines two gases to make a solid and the entropy of a gas is greater than that for a solid. Because a negative value for ΔS favors a positive value for ΔG, the value for ΔH must be negative if the reaction is to be favorable.

2. Using published heats of formation, free energies of formation, and enthalpies, determine the values for $\Delta G°$, $\Delta H°$ and $\Delta S°$ at 25°C. If there is a discrepancy between the actual signs and your predictions, then explain why the calculated sign makes sense and identify your error when answering question 1.

$$\Delta H° = [\Delta H°_{f,NH_4Cl(s)}] - [\Delta H°_{f,NH_3(g)} + \Delta H°_{f,HCl(g)}]$$

$$= [(-314.43)] - [(-46.11) + (--92.307)] = -176.01 \text{ kJ/mol}_{rxn}$$

$$\Delta S° = [S°_{NH_4Cl(s)}] - [S°_{NH_3(g)} + S°_{HCl(g)}]$$

$$= [(94.6)] - [(192.45) + (186.908)] = -284.8 \text{ J/mol}_{rxn}\text{•K}$$

$$\Delta G° = [\Delta G°_{f,NH_4Cl(s)}] - [\Delta G°_{f,NH_3(g)} + \Delta G°_{f,HCl(g)}]$$

$$= [(-203.87)] - [(-16.45) + (-95.299)] = -92.12 \text{ kJ/mol}_{rxn}$$

3. How do you expect the favorability of this reaction to change with temperature? If the reaction is not favorable at all temperatures, determine the temperature at which the reaction changes from favorable to unfavorable.

   With a negative $\Delta H°$ and a negative $\Delta S°$, the reaction is less favorable at higher temperatures because the $-T\Delta S°$ term becomes more positive than the negative value for $\Delta H°$, making $\Delta G°$ a positive value. This critical temperature is

$$\Delta G° = 0 = -176.01 \text{ kJ/mol}_{rxn} - T\times(-0.2848 \text{ kJ/mol}_{rxn}\text{•K})$$

$$T = 618 \text{ K}$$

4. If you place a sample of $NH_4Cl(s)$ in a test tube and gently heat the test tube's bottom with a Bunsen burner, a white powder forms near the top of the test tube. In a few sen-

tences, clearly explain, using a thermodynamic argument, what is happening in the test tube.

Heating the test tube must raise its temperature above the critical T of 618 K. At this temperature the reaction

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

is unfavorable; however, the reverse reaction

$$NH_4Cl(s) \rightarrow HCl(g) + NH_3(g)$$

is now favorable and $NH_4Cl(s)$ decomposes into $HCl(g)$ and $NH_3(g)$. The gases cool as they rise toward the top of the test tube. When the temperature falls below 618 K the gases recombine to make $NH_4Cl(s)$, which appears as a white powder on the walls of the test tube.