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 μm in diameter (compared to 100 μm 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), that produces particulate NH_4Cl as the sole product: $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$.

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 the reaction happen, we know that ΔG is negative. We also expect that ΔS is negative as the reaction combines two gases into a solid and the entropy of a gas generally is greater than the entropy of a solid. Because a negative ΔS favors a postive ΔG, the value of 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 ΔG^o, ΔH^o, and ΔS^o at 25°C. If there is a discrepancy between the actual signs and your predictions, then explain why the calculated signs makes sense and identify your error when answering question 1.

$$\Delta H^o = \left[\Delta H^o_{f,NH_4Cl(s)}\right] - \left[\Delta H^o_{f,NH_3(g)} + \Delta H^o_{f,HCl(g)}\right]$$
$$\Delta H^o = [(-314.43)] - [(-46.3) + (-92.307)] = -175.82\text{kJ/mol}_{\text{rxn}}$$

$$\Delta S^o = \left[S^o_{f,NH_4Cl(s)}\right] - \left[S^o_{f,NH_3(g)} + S^o_{f,HCl(g)}\right]$$
$$\Delta S^o = [(94.6)] - [(193.0) + (186.908)] = -285.31\text{J/mol}_{K\text{Ĺrxn}}$$

$$\Delta G^o = \left[\Delta G^o_{f,NH_4Cl(s)}\right] - \left[\Delta G^o_{f,NH_3(g)} + \Delta G^o_{f,HCl(g)}\right]$$
$$\Delta G^o = [(-203.87)] - [(-16.45) + (-95.299)] = -92.12\text{kJ/mol}_{\text{rxn}}$$

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 ΔH^o and a negative ΔS^o, the reaction is less favorable at higher temperatures because the $-T\Delta S^o$ term becomes more positive than the negative value for ΔH^o, making ΔG^o a positive value. The critical temperature, T_{crit} is

$$\Delta G^o = 0 = \Delta H^o - T\Delta S^o = -176.01\text{kJ/mol}_{\text{rxn}} - T(-0.2848\text{kJ/K} \bullet \text{mol}_{\text{rxn}})$$
$$T_{crit} = 617K$$

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 2-3 sentences, clearly explain, using a thermodynamic argument, what is happening in the test tube.

   Heating the test tube must raise its temperature above T_{crit}. At this temperature, the formation of $NH_4Cl(s)$ is unfavorable, but the reverse reaction in which $NH_4Cl(s)$ breaks apart to form $NH_3(g)$ and $HCl(g)$ is favorable. As the gases rise up through the tube, they cool to a temperature below T_{crit} and recombine to make $NH_4Cl(s)$, which appears as a white powder on the walls of the test tube.