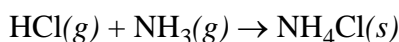


Predicting the Sign of Thermodynamic Parameters

If you open a bottle of concentrated HCl next to an open bottle of concentrated NH₃, 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 human hair). The reaction taking place is a gas-phase acid-base reaction (both HCl and NH₃ are volatile), producing particulate NH₄Cl



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 you cannot do so. Do not use the tables in your textbook to answer this question!

Because we see that the reaction happens, we know that ΔG must be negative. We also can predict that ΔS must be 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 data from Appendix B.16, determine the actual values for ΔG° , ΔH° and ΔS° 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 the error in your reasoning when answering question 1.

$$\begin{aligned}\Delta H^\circ &= [\Delta H^\circ_{f,\text{NH}_4\text{Cl}(s)}] - [\Delta H^\circ_{f,\text{NH}_3(g)} + \Delta H^\circ_{f,\text{HCl}(g)}] \\ &= [(-314.43)] - [(-46.11) + (-92.307)] = -176.01 \text{ kJ/mol}_{\text{rxn}}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= [S^\circ_{\text{NH}_4\text{Cl}(s)}] - [S^\circ_{\text{NH}_3(g)} + S^\circ_{\text{HCl}(g)}] \\ &= [(94.6)] - [(192.45) + (186.908)] = -284.8 \text{ J/mol}_{\text{rxn}} \cdot \text{K}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= [\Delta G^\circ_{f,\text{NH}_4\text{Cl}(s)}] - [\Delta G^\circ_{f,\text{NH}_3(g)} + \Delta G^\circ_{f,\text{HCl}(g)}] \\ &= [(-203.87)] - [(-16.45) + (-95.299)] = -92.12 \text{ kJ/mol}_{\text{rxn}}\end{aligned}$$

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.

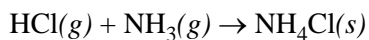
With a negative ΔH° and ΔS° the reaction will become less favorable at higher temperatures because the $-T\Delta S^\circ$ term becomes more positive than the negative value for ΔH° , making ΔG° a positive value. This critical temperature is

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

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

4. If you place a sample of $\text{NH}_4\text{Cl}(s)$ 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 sentences, 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



is unfavorable; however, the reverse reaction



is now favorable and $\text{NH}_4\text{Cl}(s)$ decomposes into $\text{HCl}(g)$ and $\text{NH}_3(g)$. 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 $\text{NH}_4\text{Cl}(s)$, which appears as a white powder on the walls of the test tube.