

# Key for Predict the Sign of Thermodynamic Parameters

If you open a bottle of concentrated HCl next to an open bottle of concentrated NH<sub>3</sub>, 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<sub>3</sub> are volatile), that produces particulate NH<sub>4</sub>Cl as the sole product:  $\text{HCl}(g) + \text{NH}_3(g) \rightarrow \text{NH}_4\text{Cl}(s)$ .

1. Predict the signs of  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  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  $\Delta G$  is negative. We also expect that  $\Delta S$  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  $\Delta S$  favors a positive  $\Delta G$ , the value of  $\Delta H$  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  $\Delta H^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  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.

$$\begin{aligned}\Delta H^\circ &= \left[ \Delta H_{f, \text{NH}_4\text{Cl}(s)}^\circ \right] - \left[ \Delta H_{f, \text{NH}_3(g)}^\circ + \Delta H_{f, \text{HCl}(g)}^\circ \right] \\ \Delta H^\circ &= [(-314.43)] - [(-46.3) + (-92.307)] = -175.82 \text{kJ/mol}_{\text{rxn}}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \left[ S_{f, \text{NH}_4\text{Cl}(s)}^\circ \right] - \left[ S_{f, \text{NH}_3(g)}^\circ + S_{f, \text{HCl}(g)}^\circ \right] \\ \Delta S^\circ &= [(94.6)] - [(193.0) + (186.908)] = -285.31 \text{J/mol}_{\text{K rxn}}\end{aligned}$$

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

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

$$\begin{aligned}\Delta G^\circ = 0 &= \Delta H^\circ - T\Delta S^\circ = -176.01 \text{kJ/mol}_{\text{rxn}} - T(-0.2848 \text{kJ/K} \cdot \text{mol}_{\text{rxn}}) \\ T_{crit} &= 617 \text{K}\end{aligned}$$

4. If you place a sample of NH<sub>4</sub>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 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<sub>4</sub>Cl(s) is unfavorable, but the reverse reaction in which NH<sub>4</sub>Cl(s) breaks apart to form NH<sub>3</sub>(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<sub>4</sub>Cl(s), which appears as a white powder on the walls of the test tube.