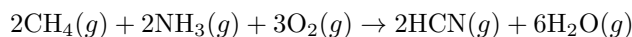


Key for Review Problems for Thermodynamics Unit

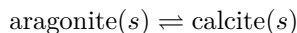
Problem 1. Hydrogen cyanide, which is used industrially in the manufacture of Plexiglas (and which is highly toxic), is produced by the following reaction



Is this reaction spontaneous at all temperatures, at only low temperatures, at only high temperatures, or is it unfavorable at all temperatures? The industrial preparation of HCN usually is carried out at 1100°C. Given your answer to the effect of temperature on the reaction's favorability, why is such a high temperature used? Keep in mind that heating a reaction mixture is costly and that industries generally aren't interested in spending more money than is necessary.

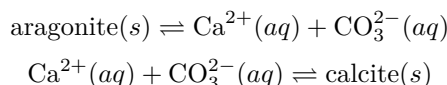
Answer. Using standard state heats of formation and entropy values you should be able to show that ΔH is -938.9 kJ/molrxn and that ΔS is $+160.2$ J/molrxn \cdot K (*note: your values may differ slightly from those listed here due to small differences between textbooks when reporting thermodynamic values*). Because ΔH is less than zero and ΔS is greater than zero, this reaction is favorable at all temperatures. So why not run the reaction at room temperature and save lots of money? The only logical reason is that the reaction must not occur at lower temperatures because of kinetic difficulties. Remember that thermodynamics tells you what is possible but not whether it will in fact happen.

Problem 2. The hard shells of starfish, sea urchins, and sand dollars are made from calcium carbonate. There are two forms of calcium carbonate found in nature: aragonite and calcite. When the shells first form, they are made from aragonite. Over time, however, the shells slowly convert to calcite. We can represent this transition by the following equilibrium reaction



The K_{sp} for calcite is 5.0×10^{-9} , while that for aragonite is 7.0×10^{-9} . What is the equilibrium constant for the conversion of aragonite to calcite? What is ΔG° for the equilibrium between aragonite and calcite? Why do you think the shells initially form as aragonite and why do they change to calcite over time?

Answer. We can think of this reaction as a combination of the following two equilibrium reactions:



The equilibrium constant for the first reaction is 7.0×10^{-9} and the equilibrium constant for the second reaction is $(K_{sp})^{-1} = 2.0 \times 10^8$. The equilibrium constant for the conversion of aragonite to calcite, therefore, is $(7.0 \times 10^{-9}) \times (2.0 \times 10^8) = 1.4$. This gives $\Delta G^\circ = -RT \ln K_{sp} = -0.833$ kJ/mol_{rxn} at 298 K. When the thermodynamically stable product does not form initially then there must be a kinetic effect. Apparently the formation of aragonite occurs more quickly. Over time, however, the shells convert to their thermodynamically most stable form.