CH 223 Chapter Sixteen Concept Guide

1. Enthalpy

Question

$\Delta H°$ for the following reaction is positive. What does this mean in terms of the relative strengths of the bonds in the reactants and products?

$CH_3OH(\ell) + NH_3(g) \rightarrow CH_3NH_2(g) + H_2O(g)$

Solution

The fact that $\Delta H°$ is positive indicates that the bonds broken in the reactants are stronger than the bonds formed in the products. The reactants are thus more stable than the products, explaining why the reaction requires an input of thermal energy to occur.

2. Entropy

Problem

For each of the following processes, predict whether you would expect entropy to be greater for the reactants or for the products.

(a) $CO_2(g) \rightarrow CO_2(s)$

(b) $KCl(s) \rightarrow KCl(aq)$

(c) $MgCO_3(s) + \text{heat} \rightarrow MgO(s) + CO_2(g)$

Solution

(a) For a given compound, molecules in the vapor state have higher entropy because the vapor state is more disorder than is the solid state. The entropy of solid carbon dioxide is, therefore, less than of CO_2 vapor.

(b) Solid KCl is a more ordered state than KCl dissolved in water. Thus, the entropy of the dissolved KCl is greater than that of the solid KCl.

(c) One mole of solid $MgCO_3$ yields one mole of solid MgO and one mole of gaseous CO_2. As the number of moles increases from the reactant to the product side of the equation, the entropy also increases. This is particularly true when one of the products is a gas. The products, therefore, have a greater entropy than do the reactants.

3. Entropy in Physical Changes

Question

Would you predict an increase or decrease in the entropy for the system that undergoes the change described below?

(a) Making rock candy (crystalline sugar) from a saturated sugar solution. (System = candy + solution)

(b) Putting cream in your coffee (System = cream + coffee)

Solution

(a) The crystallization of the sugar would involve a decrease in entropy. The molecules are more ordered in a crystal than in a solution.

(b) Mixing the cream and the coffee would cause entropy to increase. The randomness of the combined liquids is greater than that of the liquids in separate containers.

4. Entropy in Physical Changes

Question

Calculate the standard state entropy change for the vaporization of one mole of argon at the normal boiling point. $\Delta H°$ is 6519 J/mol for argon at 87.5 K. Is this an increase or decrease in entropy?

Solution

The entropy change for this change of state is

$$\Delta S°(87.5)(\text{vaporization}) = \frac{\Delta H°(87.5)(\text{vaporization})}{T}$$

$\Delta S°$ is positive, indicating that the entropy of argon has increased by 74.5 J/(K mol).

5. Entropy in Chemical Reactions

Problem

Predict whether the entropy change for each of the following reactions will be large and negative, large and positive, or small:

(a) $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$

(b) $2\ N_2O(g) \rightarrow 2\ N_2(g) + O_2(g)$

(c) $2\ ZnS(s) + 3\ O_2(g) + \text{heat} \rightarrow 2\ ZnO(s) + 2\ SO_2(g)$

Solution

(a) Two moles of gas react to form two moles of gaseous product. Since the number of moles does not change, we would expect only a small change in randomness for this reaction. (The actual value is 20.07 J/K.)

(a) Two moles of gas react to form three moles of gaseous product. This net gain of one mole indicates that a large, positive value for $\Delta S°$ is likely. (The actual value is 148.54 J/K.)

(a) Two moles of a solid react with three moles of gas to produce two moles of a solid and two moles of gas. This is a net loss of one mole of gas, which represents a decrease in randomness. Thus, a large, negative value of $\Delta S°$ is expected. (The actual value is -147.1 J/K.)

6. ΔG° of Reaction

Problem

Calculate $\Delta G°$ for the following reaction and determine if it is spontaneous at 25 °C under standard state conditions. At this temperature, $\Delta H° = -91.34$ kJ and $\Delta S° = 41.5$ J/K for this reaction.

$CCl_4(\ell) + H_2(g) \rightarrow HCl(g) + CHCl_3(\ell)$

Solution

The value of $\Delta G°$ is

$$\Delta G° = \Delta H° - T\,\Delta S°$$

$$\Delta G° = (-91.34\ \text{kJ}) - (298.15)(41.5\ \text{J/K})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

$$\Delta G° = -103.7\ \text{kJ}$$

The negative value of $\Delta G°$ indicates that the reaction will be spontaneous at this temperature under standard state conditions.

7. ΔG° of Reaction

Problem

Calculate $\Delta G°$ for the following reaction and determine if it is spontaneous at 25 °C. At this temperature, $\Delta H° = -391.9$ kJ and $\Delta S° = 10.29$ J/K for this reaction.

$O_3(g) + O(g) \rightarrow 2\ O_2(g)$

Solution

$\Delta G° = \Delta H° - T\,\Delta S°$

$$\Delta G° = (-391.9\ \text{kJ}) - (298.15)(10.29\ \text{J/K})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

$$\Delta G° = -395.0\ \text{kJ}$$

The negative value of $\Delta G°$ indicates that the reaction will be spontaneous at this temperature.

8. Free Energy and Equilibrium

Problem

Calculate the equilibrium constant for the reaction shown in problem 1.

$CCl_4(\ell) + H_2(g) \rightarrow HCl(g) + CHCl_3(\ell)$

$\Delta G°$ is -103.7 kJ at 25 °C for this reaction.

Solution

The following equation shows the relationship between $\Delta G°$ and the equilibrium constant, K.

$\Delta G° = -RT \ln K$, where R = 8.314 J/(K mol)

$$\ln K = -\frac{\Delta G°}{RT} = -\frac{(-103.7\ \text{kJ})\left(\frac{1000\ \text{J}}{1\ \text{kJ}}\right)}{(8.314\ \text{J/K·mol})(298\ \text{K})} = 41.86$$

$K = 1.5 \times 10^{18}$

Under standard state conditions at 25 °C, this reaction is spontaneous and the products are highly favored over the reactants at equilibrium.