

Chapter 19

Thermodynamics and Equilibrium

Concept Check 19.1

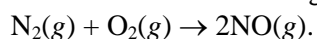
You have a sample of 1.0 mg of solid iodine at room temperature. Later, you notice that the iodine has sublimed (passed into the vapor state). What can you say about the change of entropy of the iodine?

Solution

The process is $I_2(s) \rightarrow I_2(g)$. The iodine atoms have gone from a state of some order (crystalline iodine) to one that is more disordered (gas). The entropy will have increased.

Concept Check 19.2

Consider the reaction of nitrogen, N_2 , and oxygen, O_2 , to form nitric oxide, NO :



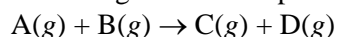
From the standard free energy of formation of NO , what can you say about this reaction?

Solution

The standard free energy of formation of $NO(g)$ is 86.60 kJ/mol. That this is a rather large positive value means that the equilibrium constant is small. At equilibrium, the NO concentration is low.

Concept Check 19.3

The following reaction is spontaneous in the direction given.



Suppose you are given a vessel containing an equilibrium mixture of A, B, C, and D, and you increase the concentration of C by increasing its partial pressure.

- How is the value of ΔG° affected by the addition of C to the vessel?
- How is the value of ΔG affected by the addition of C to the vessel?

Solution

- The standard free-energy change ΔG° is independent of concentration, so it will not change.
- The relationship between ΔG and ΔG° is given by $\Delta G = \Delta G^\circ + RT \ln Q$, where Q is the reaction quotient. If the concentration of C is increased, this causes the value of Q to increase, and in turn ΔG to increase.

Conceptual Problem 19.17

For each of the following statements, indicate whether it is true or false.

- A spontaneous reaction always releases heat.
- A spontaneous reaction is always a fast reaction.
- The entropy of a system always increases for a spontaneous change.
- The entropy of a system and its surroundings always increases for a spontaneous change.
- The energy of a system always increases for a spontaneous change.

Solution

- False. The enthalpy change (heat of reaction) has no direct relation to spontaneity.
- False. The rate of a reaction has nothing to do with the spontaneity (thermodynamics) of a reaction.
- False. The entropy may increase or decrease during a spontaneous reaction.
- True. The entropy of the system plus surroundings always increases during a spontaneous change.
- False. The energy may increase or decrease during a spontaneous reaction.

Conceptual Problem 19.18

Which of the following are spontaneous processes?

- A cube of sugar dissolves in a cup of hot tea.
- A rusty crowbar turns shiny.
- Butane from a lighter burns in air.
- A clock pendulum, initially stopped, begins swinging.
- Hydrogen and oxygen gases bubble out from a glass of pure water.

Solution

- Spontaneous. Sugar dissolves spontaneously in hot water.
- Nonspontaneous. Rust does not spontaneously change to iron; rather iron spontaneously rusts in air.
- Spontaneous. The burning of butane in air is a spontaneous reaction.
- Nonspontaneous. A pendulum once stopped will not spontaneously begin moving again.
- Nonspontaneous. Water will not spontaneously decompose into its elements.

Conceptual Problem 19.19

For each of the following series of pairs, indicate which one of each pair has the greater quantity of entropy.

- 1.0 mol of carbon dioxide gas at 20°C, 1 atm, or 2.0 mol of carbon dioxide gas at 20°C, 1 atm.
- 1.0 mol of butane liquid at 20°C, 10 atm, or 1.0 mol of butane gas at 20°C, 10 atm.
- 1.0 mol of solid carbon dioxide at -80°C, 1 atm, or 1.0 mol of solid carbon dioxide at -90°C, 1 atm.
- 25 g of solid bromine at -7°C, 1 atm, or 25 g of bromine vapor at -7°C, 1 atm.

Solution

- The 2.0 mol of CO₂ at 20°C and 1 atm has a greater entropy; two moles of substance has more entropy than one mole.
- The 1.0 mol of butane gas at 20°C and 10 atm has the higher entropy; the gaseous state has more entropy than the liquid state of the same substance under the same conditions.
- The 1.0 mol of CO₂(s) at -80°C and 1 atm has the higher entropy; a solid substance has more entropy at the higher temperature.
- The 25 g of bromine vapor at -7°C and 12 atm has the higher entropy; the gaseous (vapor) state has more entropy than the liquid state of the same substance under the same conditions.

Conceptual Problem 19.20

Predict the sign of the entropy change for each of the following processes.

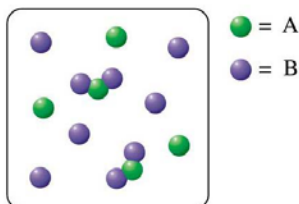
- A drop of food coloring diffuses throughout a glass of water.
- A tree leafs out in the spring.
- Flowers wilt and stems decompose in the fall.
- A lake freezes over in the winter.
- Rainwater on the pavement evaporates.

Solution

- Entropy increases; ΔS is positive; there is an increase of disorder when the food coloring disperses throughout the water.
- Entropy increases; ΔS is negative; as a tree leafs out, order increases, and entropy decreases.
- Entropy increases; ΔS is positive; as flowers wilt and stems decompose, order decreases and entropy increases.
- Entropy decreases; ΔS is negative; as a liquid changes to solid, there is an increase of order and a decrease of entropy.
- Entropy increases; ΔS is positive; as a liquid changes to vapor, there is a decrease of order and the entropy increases.

Conceptual Problem 19.21

Hypothetical elements A(g) and B(g) are introduced into a container and allowed to react according to the reaction $A(g) + 2B(g) \rightarrow AB_2(g)$. The container depicts the reaction mixture after equilibrium has been attained.



- Is the value of ΔS for the reaction positive, negative, or zero?
- Is the value of ΔH for the reaction positive, negative, or zero?
- Prior to equilibrium, is the value of ΔG for the reaction positive, negative, or zero?
- At equilibrium, is the value of ΔG for the reaction positive, negative, or zero?

Solution

- Since this is a gas phase reaction, calculate the change in the number of moles of gas molecules, $\Delta n = 1 - 3 = -2$. This corresponds to a decrease in entropy, so ΔS is negative for this reaction.
- Since this is an equilibrium state, $\Delta G = 0$, so $\Delta H - T\Delta S = 0$ also. This gives $\Delta H = T\Delta S$ and, since ΔS is positive, so is ΔH .
- The reaction spontaneously reestablishes equilibrium, so ΔG is negative prior to equilibrium.
- At equilibrium, $\Delta G = 0$.

Conceptual Problem 19.22

Here is a simple experiment. Take a rubber band and stretch it. (Is this a spontaneous process? How does the Gibbs free energy change?) Place the rubber band against your lips; note how warm the rubber band has become. (How does the enthalpy change?) According to polymer chemists, the rubber band consists of long, coiled molecules. On stretching the rubber band, these long molecules uncoil and align themselves in a more ordered state. Show how the experiment given here is in accord with this molecular view of the rubber band.

Solution

The process is not spontaneous; you have to stretch the rubber band (the opposite process, a stretched rubber band snapping to its normal shorter shape, is spontaneous). Thus, ΔG is positive. The fact that the stretched rubber band feels warm means that ΔH is negative (exothermic). Note that $\Delta G = \Delta H - T\Delta S$; so $\Delta S = -(\Delta G - \Delta H)/T$. This implies that ΔS is negative, which is consistent with an increase in order.