

19.7a) The point at which ΔH and $T\Delta S$ are equal represents the conditions at which the reaction is at equilibrium.

b) Since ΔH and ΔS are positive, the entropy term will favor spontaneity at higher temperatures. As such, the reaction will be spontaneous at temperatures above 300K

19.8

a) A system is at equilibrium when $\Delta G = 0$. This occurs at $T=250\text{K}$

b) The reaction will be spontaneous at temperatures above 250K.

Negative ΔG values indicate spontaneous reactions. From the graph, ΔG is negative at temperatures above 250K.

c) This reaction is spontaneous at high temperatures, meaning the enthalpy change must not favor spontaneity and must therefore be positive.

d) This reaction is spontaneous at high temperatures, meaning the entropy change must favor spontaneity and must therefore be positive.

19.43

- a) This statement is false. The entropy change associated with a solid becoming a liquid is less than a liquid becoming a gas.
- b) This statement is true. When ice melts at 0°C , the temperature does not change until all the ice melts. During this time, the entropy of the ice increases.
- c) This statement is true. For water at temperatures above 100°C , as the temperature increases the entropy increases.

19.45

- a) The bromine gas will have higher entropy, because gases tend to have higher entropies than liquids.
- b) $\text{C}_2\text{H}_5\text{OH}$ will have higher entropy because entropy varies directly with molecular mass.
- c) SiCl_4 will have a higher entropy because it has a greater mass than similarly shaped CCl_4 .
- d) Iron will have a higher entropy at higher temperature because entropy varies directly with temperature.

19.47

a) $\text{Sc}_{(s)}$, 34.6 J/mol·K and $\text{Sc}_{(g)}$, 174.7 J/mol·K.

Generally, gases have greater S° than solids because they have greater volume and positional freedom.

b) $\text{NH}_3_{(g)}$, 192.5 J/mol·K and $\text{NH}_3_{(aq)}$, 111.3 J/mol·K.

Generally, gases have greater S° than solutions because they have greater volume and positional freedom.

c) 1 mol $\text{O}_2_{(g)}$, 205.15 J/K and 1 mol $\text{O}_3_{(g)}$, 237.6 J/K

While both sample contain 1 mole of gaseous molecules, the O_3 has a greater mass and therefore a greater entropy.

d) $\text{C}_{\text{graphite}(s)}$, 5.69 J/mol·K and $\text{C}_{\text{diamond}(s)}$, 2.43 J/mol·K.

As solids, both have relatively low entropies. Diamond is a covalent network solid with little freedom of movement. Graphite have sheets of carbon atoms bound by IMF's, which allow more movement.

19.51a)

$$\Delta S^\circ_{\text{rxn}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta S^\circ_{\text{rxn}} = S^\circ_{\text{C}_2\text{H}_6} - (S^\circ_{\text{C}_2\text{H}_4} + S^\circ_{\text{H}_2})$$

$$\Delta S^\circ_{\text{rxn}} = 229.5 \text{ J/K} - (219.4 \text{ J/K} + 130.38 \text{ J/K})$$

$$\Delta S^\circ_{\text{rxn}} = -120.5 \text{ J/K}$$

$\Delta S^\circ_{\text{rxn}}$ is negative because there are fewer moles of gas in the products

19.51b

$$\Delta S^\circ_{\text{rxn}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta S^\circ_{\text{rxn}} = 2 \cdot S^\circ_{\text{NO}_2} - S^\circ_{\text{N}_2\text{O}_4}$$

$$\Delta S^\circ_{\text{rxn}} = 2 \cdot 240.45 \text{ J/K} - 304.3 \text{ J/K}$$

$$\Delta S^\circ_{\text{rxn}} = +176.6 \text{ J/K}$$

$\Delta S^\circ_{\text{rxn}}$ is positive because there are more moles of gas in the products

19.53

- a) A change in Gibb's free energy can be the result of a change in entropy or a change in enthalpy.
- b) If ΔG is positive, the process is not spontaneous, but the reverse process is spontaneous.
- c) There is **no relationship** between ΔG and reaction rate.

19.55

- a) Based on the negative value for ΔH , this reaction is exothermic.
- b) Based on the negative value for ΔS , this reaction leads to a decrease in the disorder of the system.
- c) $\Delta G = \Delta H - T\Delta S = -35.4 \text{ kJ} - 298\text{K}(-0.0855\text{kJ/K}) = -9.92\text{kJ}$
- d) Based on the negative value for ΔG calculated in part (c), this reaction is spontaneous at these conditions.

19.57a)

$$\Delta H_f^\circ \text{ rxn} = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta H_f^\circ \text{ rxn} = 2 \cdot \Delta H_f^\circ \text{ HF} - (\Delta H_f^\circ \text{ H}_2 + \Delta H_f^\circ \text{ F}_2)$$

$$\Delta H_f^\circ \text{ rxn} = 2 \cdot -273.3 \text{ kJ} - (0 + 0)$$

$$\Delta H_f^\circ \text{ rxn} = -546.6 \text{ kJ}$$

$$\Delta S^\circ \text{ rxn} = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta S^\circ \text{ rxn} = 2 \cdot S^\circ \text{ HF} - (S^\circ \text{ H}_2 + S^\circ \text{ F}_2)$$

$$\Delta S^\circ \text{ rxn} = 2 \cdot 173.78 \text{ J/K} - (130.58 \text{ J/K} + 202.7 \text{ J/K})$$

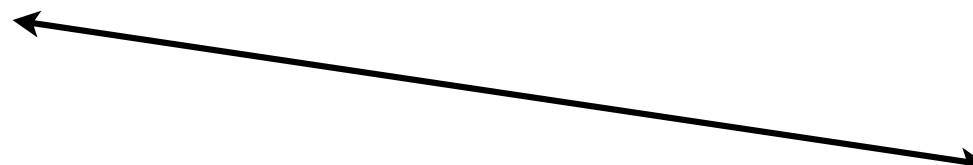
$$\Delta S^\circ \text{ rxn} = 14.3 \text{ J/K}$$

$$\Delta G_f^\circ \text{ rxn} = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G_f^\circ \text{ rxn} = 2 \cdot \Delta G_f^\circ \text{ HF} - (\Delta G_f^\circ \text{ H}_2 + \Delta G_f^\circ \text{ F}_2)$$

$$\Delta G_f^\circ \text{ rxn} = 2 \cdot -275.4 \text{ kJ} - (0 + 0)$$

$$\Delta G_f^\circ \text{ rxn} = -550.5 \text{ kJ}$$

$$\Delta G = \Delta H - T\Delta S = -546.6 \text{ kJ} - 298 \text{ K} \cdot 0.0143 \text{ kJ/K} = -550.91 \text{ J}$$


19.59a)

$$\Delta G_f^\circ \text{ rxn} = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G_f^\circ \text{ rxn} = 2 \cdot \Delta G_f^\circ \text{ SO}_3 - (2 \cdot \Delta G_f^\circ \text{ SO}_2 + \Delta G_f^\circ \text{ O}_2)$$

$$\Delta G_f^\circ \text{ rxn} = 2 \cdot (-370.4 \text{ kJ}) - (2 \cdot (-300.4 \text{ kJ}) + 0)$$

$$\Delta G_f^\circ \text{ rxn} = -140.0 \text{ kJ}$$

Based on negative ΔG , this reaction is spontaneous

19.59b

$$\Delta G_f^\circ \text{ rxn} = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G_f^\circ \text{ rxn} = 3 \cdot \Delta G_f^\circ \text{ NO} - (\Delta G_f^\circ \text{ NO}_2 + \Delta G_f^\circ \text{ N}_2\text{O})$$

$$\Delta G_f^\circ \text{ rxn} = 3 \cdot 86.71 \text{ kJ} - (51.84 \text{ kJ} + 103.59 \text{ kJ})$$

$$\Delta G_f^\circ \text{ rxn} = 104.70 \text{ kJ}$$

Based on positive ΔG , this reaction is not spontaneous

19.63

a) This reaction has a ΔH that favors spontaneity and a ΔS that doesn't favor spontaneity.

b) This reaction has a ΔH that doesn't favor spontaneity and a ΔS that doesn't favor spontaneity.

c) This reaction has a ΔH that does not favor spontaneity and a ΔS that does favor spontaneity.

19.67a)

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

$$0 = -32\text{kJ} - T(-0.098\text{kJ/K})$$

$$T = 330\text{K}$$

b) If the reaction is increased from this temperature, the reaction will be nonspontaneous. The sign of ΔS is negative. As temperature increases, ΔG becomes more positive.