

Chapter 3 - Answer Key

Page 183, Quick Check

1. a) a mole of liquid water has more disorder, or, entropy, and will occur spontaneously.
b) the solution has more entropy and will occur spontaneously.
c) the collection of pieces will occur spontaneously.
d) the raw rubber has more entropy and will occur spontaneously.
e) The randomly shuffled deck therefore has higher entropy and will occur spontaneously.

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1. $\Delta S = 109 \text{ J/(K}\cdot\text{mol)}$
2. a) Cl_2 has more layers of electrons (ie. more "shells") in which the electrons can position themselves than F_2 . Therefore, there are more microstates and thus more entropy in Cl_2 .
b) CO_2 has more places where electrons can exist due to the bigger electron cloud and more total electron shells in CO_2 than CO . Therefore, there are more microstates and more entropy in CO_2 .
c) The right picture (pile of bricks) has more entropy since there is more disorder while the left brick wall is organized, thus low on entropy.

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1. a) the gas particles have far more microstates than the liquid particles (the entropy change will be positive), and thus the entropy change is going to be positive and evaporation will be spontaneous.
b) ΔS is going to be negative. The reaction will be non-spontaneous.
c) ΔS is positive and the change is likely spontaneous.
d) the entropy change is going to be positive and the dilution will be spontaneous.
2. a) $\Delta S = 174.51 - 413.61 = \frac{-239.1 \text{ J}}{\text{mol rxn}\cdot\text{K}}$
The reaction is non-spontaneous (not thermodynamically favourable) as $\Delta S < 0$. [This makes sense as the moles of gas have decreased.]
b) The reaction is non-spontaneous as $\Delta S < 0$.

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1. a) ΔS is positive
b) ΔS is negative
c) ΔS is positive
d) ΔS is negative
e) ΔS is negative
f) ΔS is negative
2. a) ΔS is negative
b) ΔS is negative
c) ΔS is positive
d) ΔS is negative
e) ΔS is positive
f) ΔS is negative
3. $S = 93.8 \text{ J/mol}\cdot\text{K}$
4. $T = \frac{\Delta H^\circ}{\Delta S^\circ} = 373.8 \text{ K} = 100.6^\circ\text{C}$. At room temperature is 25°C , formic acid is in liquid state at room temperature.
5. $\Delta S = -238 \text{ J/K}$
6. $T = 150^\circ\text{C}$
7. a) $229.6 \text{ J/mol}_{\text{rxn}} \text{ K}$
b) $-311.4 \text{ kJ/mol}_{\text{rxn}}$
c) 1065°C
8. a) Sign of ΔS° will be negative as the reaction goes from 3 moles of gas to 2 moles of gas, and gases have much higher entropy than solids that the 3 moles of solid's entropy is negligible.
b) $-186.74 \text{ J/mol}_{\text{rxn}} \text{ K}$
9. $205 \text{ J/mol O}_2\cdot\text{K}$
10. a) $-44.42 \text{ J/mol}_{\text{rxn}} \text{ K}$
b) $-137.56 \text{ J/mol}_{\text{rxn}} \text{ K}$
c) $-5.14 \text{ J/mol}_{\text{rxn}} \text{ K}$
d) $-206.16 \text{ J/mol}_{\text{rxn}} \text{ K}$
e) $974 \text{ J/mol}_{\text{rxn}} \text{ K}$

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1. a) Vapourizing any substance requires heat energy. Therefore, it is logical that this is an endothermic process (thus ΔH is positive).
b) Gases have more microstates (occupy far more positions in space) than liquids, so a transition from liquid to gas results in an increase in entropy.
c) 60°C
d) This temperature represents the boiling point for bromine.

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1. $-1325.33 \text{ kJ/mol rxn}$

2. -5296.9 kJ of work is available from oxidation of 1 mol of octane.

3. Method 1:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 180.50 \text{ kJ/mol} - 298$$

$$\text{K}(24.77 \text{ J/K}\cdot\text{mol}) = 173.12 \text{ kJ/mol}_{\text{rxn}}$$

Method 2:

$$\Delta G^\circ = 2\Delta G^\circ_f \text{ NO} = 2(86.55 \text{ kJ/mol}) = 173.10$$

$$\text{kJ/mol}_{\text{rxn}}$$

The values are very close.

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1. a) $\Delta G^\circ = 14.0 \text{ kJ/mol rxn}$
b) $\Delta G^\circ = -18.1 \text{ kJ/mol rxn}$
c) The reaction becomes more favorable as temperature increases as ΔG° decreases as temperature increases.

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1. a) Change in enthalpy (ΔH) and change in entropy (ΔS) affect the spontaneity of a process
b) ΔH is the change in potential energy available to be converted to heat and ΔS is the change in the number of microstates the matter can occupy.
c) negative ΔH and positive ΔS are associated with spontaneity

2.

Sign of ΔH°	Sign of ΔS°	Temp	Sign of ΔG°	Spontaneous/ Non-spontaneous
-	+	Low	-	Spontaneous
-	+	High	-	Spontaneous
+	-	Low	+	Non-spontaneous
+	-	High	+	Non-spontaneous
-	-	Low	-	Spontaneous
+	+	High	-	Spontaneous
-	-	High	+	Non-spontaneous
+	+	Low	+	Non-spontaneous

3. Circle A:

- i) ΔH is positive, ΔS is also positive
- ii) spontaneous only at high temperatures as ΔG is negative only when $T\Delta S$ is bigger than ΔH .

Circle B:

- i) ΔH is negative, ΔS is also negative
- ii) spontaneous only at low temperatures as ΔG is negative only when $T\Delta S$ is smaller than ΔH .

4. a) ΔS° is positive as there are more gas molecules (and thus more microstates) on the product side. ΔG° is negative as $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and ΔH° is negative while ΔS° is positive, hence $\Delta G^\circ = (-) - T(+)$ gives a negative value.

b) This process is spontaneous at all temperatures - $\Delta G^\circ = (-) - T(+)$ gives a negative answer no matter what the T value.

5. a) $3 \text{ H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2 \text{ NH}_3(\text{g})$

$$\text{b) } -92.22 \text{ kJ/mol}_{\text{rxn}}$$

c) $\Delta S^\circ_{\text{rxn}}$ is negative.

d) As $\Delta H^\circ_{\text{rxn}}$ is negative and $\Delta S^\circ_{\text{rxn}}$ is also negative, and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, this process will be spontaneous only if temperature is low.

Otherwise, $-T\Delta S^\circ$ will make ΔG° positive.

e) The spontaneity of this reaction changes when $\Delta G^\circ = 0$, so $\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$, or, when $T = \Delta H^\circ / \Delta S^\circ$.

$$\Delta S^\circ = -198.75 \text{ J/K}\cdot\text{mol}_{\text{rxn}}$$

$$T = 191.0^\circ\text{C}$$

6. a) $\text{I}_2(\text{g}) \rightarrow \text{I}_2(\text{s})$

$$\text{b) } T = 159.0^\circ\text{C}$$

7. a) $\Delta S^\circ_{\text{rxn}}$ will be positive

$$\text{b) } \Delta S^\circ_{\text{rxn}} = 137.56 \text{ J/K}\cdot\text{mol}$$

$$\Delta G^\circ_{\text{rxn}} = -326.4 \text{ kJ/mol}$$

The predicted signs match the calculated signs, hence the predictions were accurate.

8. a) $-91.12 \text{ kJ/mol}_{\text{rxn}}$

$$\text{b) } -91.73 \text{ kJ/mol}_{\text{rxn}}$$

$$\text{c) } 13374.0 \text{ kJ/mol}_{\text{rxn}}$$

9. a) $-74 \text{ kJ/mol}_{\text{rxn}}$

$$\text{b) } 537 \text{ J/mol}_{\text{rxn}}$$

$$\text{c) } -228 \text{ kJ/mol}_{\text{rxn}}$$

d) Since the enthalpy change is negative and the entropy change is positive, the free energy change will be negative (and hence the reaction will be thermodynamically favourable - that is spontaneous) under all temperature conditions.

e) The ability to produce fuel over a wide range of temperature conditions improves the economic feasibility. It is particularly expensive to maintain high temperatures during a chemical process, so being able to produce fuels without this necessity makes the process very attractive to a company trying to make money.

10. a) $-47 \text{ J/K}\cdot\text{mol}_{\text{rxn}}$

b) As ΔS° is negative and ΔH° is also negative, ΔG° will be negative only when the temperature is low enough.

c) $-187 \text{ kJ/mol}_{\text{rxn}}$. The reaction is *still* spontaneous at this high temperature (though as expected, it is less spontaneous).

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$$1. -36.31 \text{ kJ/mol}_{\text{rxn}}$$

$$2. 1.26 \text{ kJ/mol}_{\text{rxn}}$$

3. $-33.38 \text{ kJ/mol}_{\text{rxn}}$

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- $110 \text{ kJ/mol}_{\text{rxn}}$
- 1×10^6
 - 7×10^{-7}
 - The K value for a) is much bigger than K value for b). This means the reaction in a) is very spontaneous in the forward direction while the reaction in b) is very spontaneous in the reverse direction. This is well supported by the values of ΔG° , as negative value of ΔG° in a) indicates that the reaction is spontaneous while the positive value of ΔG° in b) indicates that the reaction is non-spontaneous or spontaneous in the reverse reaction.

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- 163 kJ/mol
- $48.3 \text{ kJ/mol}_{\text{rxn}} > 0$
Therefore, the forward reaction is not spontaneous at room temperature.
b) $\Delta S^\circ = 175.0 \text{ J/K} \cdot \text{mol}_{\text{rxn}} > 0$
Entropy drives the reaction forward.
 $\Delta H^\circ = 100.6 \text{ kJ/mol}_{\text{rxn}} > 0$
Enthalpy drives the reaction in the reverse direction. Therefore, only entropy drives the reaction forward.
c) 3×10^{-9}
 - 301.9°C
 - $\Delta G = \Delta H^\circ - T \cdot \Delta S^\circ$ thus (+) - T(+) only becomes negative when T exceeds 299.9. As T increases further, ΔG becomes more negative and the reaction becomes more spontaneous.
- When the barrel is wide open, $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$.
 $\Delta G^\circ = -800.78 \text{ kJ/mol}_{\text{rxn}}$
When the barrel is nearly closed, $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$.
 $\Delta G^\circ = -817.90 \text{ kJ/mol}_{\text{rxn}}$
b) When the barrel is wide open,
 $K = 2 \times 10^{140}$
When the barrel is nearly closed,
 $K = 2 \times 10^{143}$
c) As evidenced by larger K value and more negative ΔG° , the combustion of methane is more spontaneous when the barrel is nearly closed.
d) Opening barrel allows more O_2 gas to react to force reaction right.
- $\Delta H^\circ = -41.16 \text{ kJ/mol}_{\text{rxn}}$
 - $\Delta S^\circ = -42.08 \text{ J/K} \cdot \text{mol}_{\text{rxn}}$
 - $\Delta G^\circ = -28.62 \text{ kJ/mol}_{\text{rxn}}$
 - $K = 1 \times 10^5$
 - $K = 1.0 \times 10^3$

f) As temperature increased, the K value decreased. This means the reaction was exothermic - as temperature increases, the reaction shifts left to offset the additional heat energy, decreasing the K value.
This agrees with the answer to part (a) as $\Delta H^\circ = -41.16 \text{ kJ/mol}_{\text{rxn}} < 0$

- The graphs are similar in that they show potential energy changes as reactants convert to products. Also both graphs represent reactions in which the products have less available energy than the reactants ("exo").
 - The graphs are different in that the first graph shows changes in free energy as the reaction proceeds while the second graph shows changes in enthalpy. The second graph shows the activated complex while the first graph shows equilibrium point.
- The sign of ΔH° is positive, as ice melts into water by absorbing heat from its surroundings.
 - The sign of ΔS° is positive, as the state of water changes from solid to liquid (which has more microstates).
 - Both ΔH° and ΔS° are positive, so at high temperatures, ΔG° is negative while at low temperatures it is positive.
- The sign of ΔH° is positive as the reverse reaction, the combustion of hydrogen, is exothermic.
 - The sign of ΔS° is positive, as the reaction goes from 2 moles of gas to 3 moles of gas.
 - ΔH° and ΔS° are both positive, so ΔG° will be negative at high temperatures and positive at low temperatures.
- $\Delta G^\circ = 4.73 \text{ kJ/mol}_{\text{rxn}}$
 - $\Delta G = -1.53 \text{ kJ/mol}_{\text{rxn}}$
 - As $\Delta G < 0$, the equilibrium will shift right, producing more NO_2 from N_2O_4 . Therefore, the representation will have more NO_2 molecules and less N_2O_4 molecules.
- $-60.3 \text{ kJ/mol}_{\text{rxn}}$
 - The reaction is less spontaneous under these pressure conditions as $\Delta G^\circ = -71.2 \text{ kJ/mol}_{\text{rxn}} < -60.3 \text{ kJ/mol}_{\text{rxn}} = \Delta G$
- $-4.0 \text{ kJ/mol}_{\text{rxn}}$
 - The reaction is more spontaneous under these conditions than under standard conditions as $\Delta G = -14.02 \text{ kJ/mol}_{\text{rxn}} < 20.21 \text{ kJ/mol}_{\text{rxn}} = \Delta G^\circ$
- $27 \text{ kJ/mol}_{\text{rxn}}$
 - $-13. \text{ kJ/mol}_{\text{rxn}}$
 - The ionization is more spontaneous under the conditions in part (b) as:
 $\Delta G = -13 \text{ kJ/mol}_{\text{rxn}} < 27.1 \text{ kJ/mol}_{\text{rxn}}$