

1. Which of the following processes are spontaneous?

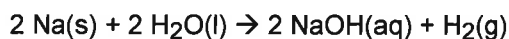
- (a) dissolving salt in water
- (b) dissolving NaCl in NaCl(sat'd)
- (c) paper burning
- (d) iron rusting
- (e) ice melting in a freezer
- (f) a reaction at equilibrium shifting right or left
- (g) water evaporating at 25 °C in a container in which the relative humidity is 50%. (The vapor pressure of water is 24.0 mmHg at 25 °C. If the partial pressure of water is 24.0 mmHg, that would be 100% humidity. A 50% humidity at 25 °C corresponds to a partial pressure of water = 12.0 mmHg.)

This just says the air is unsat'd - so more can dissolve

2. Which of the following processes are associated with an increase in entropy?

- (a) $\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{CO}_2\text{(g)}$ *3 mol → 2 mol*
- (b) $2 \text{NO}_2\text{(g)} \rightarrow \text{N}_2\text{O}_4\text{(g)}$
- (c) $2 \text{Na(s)} + 2 \text{H}_2\text{O(l)} \rightarrow 2 \text{NaOH(aq)} + \text{H}_2\text{(g)}$
- (d) iron rusting *this consumes O₂(g)*
- (e) water freezing in a freezer
- (f) water evaporating

3. Sodium reacts violently with water according to the equation:



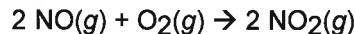
The resulting solution has a higher temperature than the water prior to the addition of sodium. What are the signs of ΔH° and ΔS° ?

$$\Delta H^\circ < 0 \quad \Delta S^\circ > 0$$

4. Phase changes always have the same signs for ΔH° and ΔS° . What are the signs for ΔH° and ΔS° for these phase changes?

2a. vaporization	+
2b. freezing	-
2c. condensation	-
2d. fusion (melting)	+
2e. sublimation	+
2f. deposition	-

5a. Calculate ΔS° for the following reaction.



	ΔH_f° kJ/mol	ΔG_f° kJ/mol	S° J/mol K
NO(g)	91.3	87.6	210.7
O ₂ (g)	0	0	205.0
NO ₂ (g)	33.2	51.3	240.0

$$\begin{array}{r}
 2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \\
 S^\circ \quad 210.7 \quad 205.0 \quad 240.0 \\
 \quad \quad \times -2 \quad \quad \times -1 \quad \quad \times 2 \\
 \hline
 \Delta S^\circ = -421.4 \quad -205 \quad + 480 = -146.4 \text{ J/K}
 \end{array}$$

5b. Calculate ΔH° for the reaction above.

$$\begin{array}{r}
 2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \\
 \Delta H_f^\circ \quad 91.3 \text{ kJ/mol} \quad \quad \quad 33.2 \text{ kJ/mol} \\
 \quad \quad \times -2 \text{ mol} \quad \quad \quad \times 2 \text{ mol} \\
 \hline
 \Delta H^\circ = -182.6 \text{ kJ} + 66.4 \text{ kJ} = -116.2 \text{ kJ}
 \end{array}$$

5c. Calculate ΔG° for the reaction using the data.

$$\begin{array}{r}
 2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \\
 \Delta G_f^\circ \quad 87.6 \text{ kJ/mol} \quad \quad \quad 51.3 \\
 \quad \quad \times -2 \text{ mol} \quad \quad \quad \times 2 \\
 \hline
 \Delta G_{rxn}^\circ = -175.2 + 102.6 = -72.6 \text{ kJ}
 \end{array}$$

5d. Calculate ΔG° for the reaction using the Gibbs-Helmholtz equation: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

$$\begin{array}{r}
 \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \\
 = -116.2 - (298)(-0.1464 \text{ kJ/K}) \\
 = -72.6 \text{ kJ}
 \end{array}$$

5d. Estimate ΔG for the reaction at 350 K using the Gibbs-Helmholtz equation: $\Delta G = \Delta H^\circ - T\Delta S^\circ$.

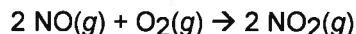
$$\begin{array}{r}
 \Delta G = -116.2 - (350)(-0.1464) \\
 = -64.96 \text{ kJ}
 \end{array}$$

Now try these problems from the book:

Section 17.1, 17.2, 17.4, 17.5. Problems 1 – 3, 7, 8, 28, 30, 40, 42, 46, 48, 64, and 66.

Chapter 17 Number 2 (17.6 – 17.9)

1. In the previous worksheet, you calculated $\Delta H^\circ = -116.2 \text{ kJ}$, $\Delta S^\circ = -146.4 \text{ J/K}$ and $\Delta G^\circ = -72.6 \text{ kJ}$ for the reaction.



1a. Is this reaction spontaneous at...

- (a) all temperatures
- (b) never
- (c) spontaneous at high temperatures; non-spontaneous at low temperatures
- (d) spontaneous at low temperatures; non-spontaneous at high temperatures

1b. At what temperature does this reaction become spontaneous?

$$\text{when } \Delta G = 0 \\ T = \frac{\Delta H}{\Delta S} = \frac{-116.2 \text{ kJ}}{-0.1464 \text{ kJ/K}} = 793 \text{ K}$$

1c. Estimate ΔG at a temperature of 25 degrees lower than the temperature calculated in the previous problem. Is the reaction spontaneous at this temperature?

$$\Delta G = \Delta H - T\Delta S \\ = -116.2 \text{ kJ} - 769 \text{ K} \times (-0.1464) \text{ kJ/K} \\ = -3.62 \text{ kJ}$$

1d. Estimate ΔG at a temperature of 25 degrees higher than the temperature calculated in Problem 1b. Is the reaction spontaneous at this temperature?

$$\Delta G = \Delta H - T\Delta S \\ = -116.2 \text{ kJ} - 818 \text{ K} \times (-0.1464) \\ = +3.56 \text{ kJ}$$

1e. In our next lecture we will tie ΔG° to the equilibrium constant, K_p . From what you know already, how does ΔG , Q_p , and K_p relate to one another? In each case, circle one: $<$, $=$, or $>$

If $\Delta G < 0$ then Q_p ($\textcircled{<} = >$) K_p

If $\Delta G = 0$ then Q_p ($\textcircled{=} = >$) K_p

If $\Delta G > 0$ then Q_p ($\textcircled{>} = >$) K_p

1f. A reaction that is spontaneous at certain temperatures, but not at others can be described as either **entropy-driven** or **enthalpy-driven**. Is the reaction described in this problem either one of these? If so, which one?

enthalpy-driven

(Unit 3) 19 March 2018

2. Determine ΔH° and ΔS° for the vaporization of mercury and then estimate the boiling point.

	ΔH_f° kJ/mol	ΔG_f° kJ/mol	S° J/mol K
Hg(l)	0	0	76.0
Hg(g)	61.3	31.9	174.8

$$\text{Hg}(l) \rightarrow \text{Hg}(g) \quad \Delta H_{\text{vap}}^\circ = 61.3 \text{ kJ} \\ \Delta S_{\text{vap}}^\circ = 98.8 \text{ J/K} \\ \text{when } \Delta G = 0 \\ T = \frac{\Delta H}{\Delta S} = \frac{61.3 \text{ kJ}}{0.0988 \text{ kJ/K}} \\ = 620 \text{ K}$$

3. Predict ΔH° , ΔS° and ΔG° for these processes and classify each as

- (a) spontaneous at all temperatures,
- (b) never spontaneous,
- (c) spontaneous at high temperatures; non-spontaneous at low temperatures, or
- (d) spontaneous at low temperatures; non-spontaneous at high temperatures

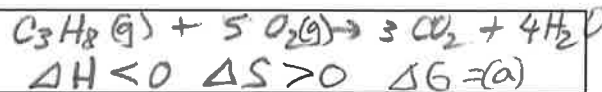
4a. $\text{O}_2(g) \rightarrow 2 \text{ O}(g)$

$$\Delta H > 0 \quad \Delta G \text{ is (c)} \\ \Delta S > 0$$

4b. $2 \text{ NO}(g) + \text{O}_2(g) \rightarrow 2 \text{ NO}_2(g)$ (exothermic)

$$\Delta H < 0 \quad \Delta G = \text{(d)} \\ \Delta S < 0$$

4c. combustion of propane (bp = -42°C) to form $\text{H}_2\text{O}(g)$



4d. $\text{H}_2\text{O}_2(l) \rightarrow \text{H}_2\text{O}(l) + \text{O}_2(g)$ (exothermic)

$$\Delta H < 0 \quad \Delta G \text{ is (a)} \\ \Delta S > 0$$

4e. Which of these reactions is/are **entropy-driven** or **enthalpy-driven**?

enthalpy driven: 4b, 4c, 4d
entropy-driven: 4a

Now try these problems from the book:

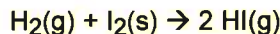
Section 17.6 – 17.9. Problems 9 – 16, 80 – 102, even

Chapter 17 Number 3 (17.10 – 17.11)

$$\Delta G = \Delta G^\circ + R T \ln(Q_p) \quad \Delta G^\circ = -R T \ln(K_p)$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

- 1a. Calculate ΔG for this reaction at 298 K given $\Delta G^\circ = +3.4 \text{ kJ}$, $P_{\text{H}_2} = 1.0 \text{ atm}$, and $P_{\text{HI}} = 5.0 \text{ atm}$.



$$\Delta G = \Delta G^\circ + R T \ln Q$$

$$= +3.4 \text{ kJ} + 0.008314 \times 298 \times \ln \frac{5.0^2}{1.0}$$

$$= +11.4 \text{ kJ}$$

- 1b. Repeat the calculation at 298 K if $P_{\text{H}_2} = 5.0 \text{ atm}$, and $P_{\text{HI}} = 1.0 \text{ atm}$.

$$\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightleftharpoons 2 \text{HI} \quad Q_p = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})} = \frac{1}{5} = 0.20$$

$$\Delta G = +3.4 \text{ kJ} + 0.008314 \times 298 \times \ln(0.20)$$

$$= -0.59 \text{ kJ}$$

- 1c. What is the equilibrium constant, K_p , for this reaction at 298 K?

$$\Delta G^\circ = -R T \ln K_p$$

$$3.4 \text{ kJ} = -0.008314 \times 298 \times \ln K_p$$

$$K_p = 0.254$$

2. Is this reaction spontaneous at 298 K?

$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ if $P_{\text{H}_2} = P_{\text{N}_2} = 0.10 \text{ atm}$ and $P_{\text{NH}_3} = 10. \text{ atm}$, and $K_p = 4 \times 10^5$ at 298 K

$$Q_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \cdot P_{\text{H}_2}^3} = \frac{10^2}{0.1 \times 0.1^3} = 1.0 \times 10^6$$

$$Q_p > K_c \therefore \text{shift L}$$

3. What is the relationship between ΔG° and the equilibrium constant, K_p ?

If $\Delta G^\circ < 0$ then $K_p (< = >) 1$

If $\Delta G^\circ = 0$ then $K_p (< = >) 1$

If $\Delta G^\circ > 0$ then $K_p (< = >) 1$

4. What is the vapor pressure of water at 298 K? Express your answer in mmHg. Given: $\Delta G_f^\circ = -237.2 \text{ kJ}$ for $\text{H}_2\text{O}(\text{l})$ and -228.6 kJ $\text{H}_2\text{O}(\text{g})$

$$\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) \quad \Delta G^\circ = +8.6 \text{ kJ}$$

$$\begin{array}{ccc} -237.2 & -228.6 & K_p = P_{\text{H}_2\text{O}(\text{g})} \\ \times -1 & \times 1 & \end{array}$$

$$\Delta G^\circ = -R T \ln K_p$$

$$K_p = 0.0311 \text{ atm} = 23.62 \text{ mmHg}$$

(Unit 3) 21 March 2018

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

for which $\Delta H^\circ = -92.2 \text{ kJ}$, $\Delta S^\circ = -198.9 \text{ J/K}$, and $\Delta G^\circ = -33.0 \text{ kJ}$.

- 5a. At what temperature does this reaction become spontaneous?

$$T = \frac{\Delta H}{\Delta S} = \frac{-92.2 \text{ kJ}}{-0.1989} = 461 \text{ K}$$

- 5b. What is the equilibrium constant, K_p , at 298 K?

$$\Delta G^\circ = -R T \ln K_p$$

$$-33.0 \text{ kJ} = -0.008314 \times 298 \ln K_p$$

$$K_p = 6.1 \times 10^5$$

- 5c. The reaction is kinetically too slow at 298 K. Increasing the temperature increases the rates of every reaction. What is the trade-off in terms of kinetics vs. thermodynamics if we increase the temperature?

rate constant \uparrow but
equilibrium constant \downarrow

- 5d. Does the LeChatelier principle support reducing the volume (increasing the pressure) to shift the mixture towards more ammonia? Circle: Yes or No

6. As a reaction proceeds undisturbed, which of these things happen? Circle all that apply.

$\Delta G^\circ \rightarrow 0$

$\Delta G \rightarrow 0$

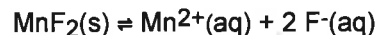
$Q_p \rightarrow K_p$

$Q_p \rightarrow 0$

$K_p \rightarrow 1$

$\Delta G \rightarrow \Delta G^\circ$

7. The solubility of manganese(II) fluoride in water is 6.6 g/mL at 40 °C and 4.8 g/L at 100 °C. Based on these data, what is the sign of ΔH° and ΔS° for the process below?



A. ΔH° is negative but the sign of ΔS° cannot be determined from this information.

B. ΔH° is negative and ΔS° is definitely negative.

C. ΔH° is positive but the sign of ΔS° cannot be determined from this information.

D. ΔH° is positive and ΔS° is definitely negative.

Now try these problems from the book:

Section 17.10 – 17.11. Problems 17 – 22, 104 – 118, even.