Worksheet 13: Thermodynamics 1 Key

1. The sign for $\Delta H$ in a spontaneous or product favored reaction is often **negative**

2. The sign for $\Delta S$ in a spontaneous or product favored reaction is often **positive**

3. The sign for $\Delta G$ in a spontaneous or product favored reaction is **often** or always **Always negative**

4. Calculate the sign of $\Delta G$ for reactions with the following $\Delta H$ and $\Delta S$ signs:

<table>
<thead>
<tr>
<th></th>
<th>Reaction 1</th>
<th>Reaction 2</th>
<th>Reaction 3</th>
<th>Reaction 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$</td>
<td>$-$</td>
<td>$+$</td>
<td>$+$</td>
<td>$-$</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>$+$</td>
<td>$-$</td>
<td>$+$</td>
<td>$-$</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>$-$</td>
<td>$+$</td>
<td>$-$ at high T, $+$ at low T</td>
<td>$+$ at high T, $-$ at low T</td>
</tr>
</tbody>
</table>

5. Reactions are always spontaneous when $\Delta S$ is $+$ and $\Delta H$ is $-$

6. Reactions are always non-spontaneous when $\Delta S$ is $-$ and $\Delta H$ is $+$

7. What is the equation used to determine $\Delta H^\circ$ from $\Delta H_f^\circ$?

$$\Delta H^\circ = \text{sum}(\Delta H_f^\circ_{\text{products}}) - \text{sum}(\Delta H_f^\circ_{\text{reactants}}) \quad \text{don’t forget to multiply by coefficients}$$

8. Write the formula for calculating the standard entropy change of a reaction or process.

$$\Delta S^\circ = \text{sum}(\Delta S^\circ_{\text{products}}) - \text{sum}(\Delta S^\circ_{\text{reactants}}) \quad \text{don’t forget to multiply by coefficients,} \quad S \text{ is in J/mol}\cdot K$$

9. In $\Delta H$ calculations, one ignores the $\Delta H_f$ of elements. Is this true for the standard entropy values?

The standard heat of formation of an element is zero (there is no heat change in making the standard state of an element from its elements. However, entropy is only zero for crystalline materials at 0 K (or for 1.0 M H+ ions in solution). Elements at 298 K will have some entropy.

10. Practice: Find the $\Delta H^\circ$ when 1 mole of ethane reacts with oxygen

$$\text{C}_2\text{H}_6(\text{g}) + \frac{7}{2} \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g})$$

$$\Delta H_f^\circ \text{values from Appendix} \quad -84.5 \quad 0 \quad -394 \quad -241.8 \quad \text{in kJ/mol}$$

$$\Delta H^\circ = [3 \text{ mol} \times (-241.8 \text{ kJ/mol}) + 2 \text{ mol} \times (-394 \text{ kJ/mol})] - [1 \text{ mol} \times -84.5 \text{ kJ/mol}] = -1428.9 \text{ kJ per mol of reaction}$$

*Continued...*
11. What is the standard entropy change when 1 mole of ethane reacts with oxygen? (standard entropy values are given below each substance)

\[
\text{C}_2\text{H}_6(\text{g}) + \frac{7}{2} \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g})
\]

<table>
<thead>
<tr>
<th>S° values from Appendix</th>
<th>229.5</th>
<th>205</th>
<th>214</th>
<th>189</th>
<th>in J/mol·K</th>
</tr>
</thead>
</table>

\[\Delta S° = [(3 \text{ mol} \times 189 \text{ J/mol} \cdot \text{K}) + (2 \text{ mol} \times 214 \text{ J/mol} \cdot \text{K})] - [(1 \text{ mol} \times 229.5 \text{ J/mol} \cdot \text{K}) + 3.5 \text{ mol} \times 205 \text{ J/mol} \cdot \text{K}] = 48 \text{ J/K per mol of reaction} \]

12. What is \(\Delta G°\) for the reaction of 1 mole of ethane? Is reaction spontaneous at 25 °C?

\[
\text{C}_2\text{H}_6(\text{g}) + \frac{7}{2} \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g})
\]

<table>
<thead>
<tr>
<th>(\Delta G_r°) values from Appendix</th>
<th>−32.9</th>
<th>−394.4</th>
<th>−228.6</th>
<th>in kJ/mol</th>
</tr>
</thead>
</table>

\[\Delta G° = [3 \text{ mol} \times (−228.6 \text{ kJ/mol}) + 2 \text{ mol} \times (−394.4 \text{ kJ/mol})] - [1 \text{ mol} \times −32.9 \text{ kJ/mol}] = -1441.79 \text{ kJ per mol of reaction} \]

13. At 25 °C, and using \(\Delta S°\) and \(\Delta H°\) (determined in previous problems) calculate \(\Delta G°\) for the combustion of 1 mole of ethane. \(\Delta G° = \Delta H° – T\Delta S°\)

\[\Delta G° = -1,428,900 \text{ J} - (298 \text{ K} \times 48 \text{ J/K}) = -1443 \text{ kJ per mol of reaction, very close to the other calculation} \]
Worksheet 14: Thermodynamics 2 Key

1. For the reaction given below, $\Delta G^\circ = -33.1$ kJ. What direction will the reaction proceed if $P_{N_2} = 0.040$ atm, $P_{H_2} = 0.060$ atm, and $P_{NH_3} = 0.35$ atm, at 298 K?

$$N_2(g) + 3 \; H_2(g) \rightleftharpoons 2 \; NH_3(g)$$

Calculate $Q = \frac{0.35^2}{[(0.060)^3 \times 0.04]} = 14180$

$\Delta G = \Delta^\circ G + RT\ln Q = (-33,100 \text{ J/mol reaction}) + [8.314 \text{ J/mol•K} \times 298 \text{ K} \times \ln 14180]$

$\Delta G = -9.4 \text{ kJ/mol reaction}$, spontaneous

2. For the reaction below, if $K_p = 9.55 \times 10^{-19}$ at 25 °C, what is $\Delta G^\circ$ in J/mol?

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

$\Delta G^\circ = -RT\ln K = 8.314 \text{ J/mol•K} \times 298 \text{ K} \times \ln 9.55 \times 10^{-19} = 103 \text{ kJ/mol}$ non-spontaneous in forward direction, and $K$ is really small that further shows the reaction doesn’t go to products (much)

3. Calculate $K_p$ for the reaction below using the $\Delta G^\circ_f$ values in kJ/mol: $CaCO_3 (-1129)$,

$$CaO \; (-604) \; CO_2 \; (-394) \; CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Calculate $\Delta G^\circ$ from $\Delta G^\circ_f$ values, $\Delta G^\circ = 1.31 \times 10^5 \text{ J/mol reaction}$

$\Delta G^\circ = -RT\ln K = 1.31 \times 10^5 \text{ J/mol} \div (-8.314 \text{ J/mol•K} \times 298 \text{ K}) \ln K = -52.83$

$K = e^{-52.83}$ $K = 1.1 \times 10^{-23}$ really small, corresponds to a positive $\Delta G^\circ$

4. Calculate $K_{sp}$ for Mg(OH)$_2$ using the $\Delta G^\circ_f$ values in kJ/mol: $Mg^{2+} (aq): -458$, $OH^- (aq): -157$, $Mg(OH)_2 (s): -834$

The reaction is $Mg(OH)_2 (s) \rightarrow Mg^{2+} (aq) + 2OH^- (aq)$

Calculate $\Delta G^\circ$ from $\Delta G^\circ_f$ values, $\Delta G^\circ = 6.2 \times 10^4 \text{ J/mol reaction}$

$\ln K = (6.2 \times 10^4 \text{ J/mol}) \div (-8.314 \text{ J/mol•K} \times 298 \text{ K}) \ln K = -25.02$

$K = e^{-25.02}$ $K = 1.4 \times 10^{-11}$ really small, corresponds to a positive $\Delta G^\circ$ and a substance that’s not very soluble

5. For the phase change of $Br_2(l) \rightarrow Br_2(g)$, $\Delta H^\circ = +31.0 \text{ kJ/mol}$ and $\Delta S^\circ = 92.9 \text{ J/mol K}$. Assuming $\Delta H^\circ$ and $\Delta S^\circ$ are temperature independent, calculate the approximate temperature where the following condition applies: $Br_2(l) \rightleftharpoons Br_2(g)$.

At the boiling point, the liquid is in equilibrium with its vapor at 1.0 atm. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$

Rearrange: $\Delta H^\circ = T\Delta S^\circ$ and then $T = \Delta H^\circ/\Delta S^\circ$ $T = 31,000 \text{ J/mol} \div 92.9 \text{ J/mol•K} = 333.7 \text{ K}$, which is very close (0.5%) to the actual b.p. of 332 K.

6. At 25°C, the value of $\Delta G^\circ$ is $+5.40 \text{ kJ/mol}$ for the decomposition of $N_2O_4$ to nitrogen dioxide. If $\Delta H^\circ$ and $\Delta S^\circ$ are both positive, under what temperature conditions might this reaction be spontaneous? If $\Delta H^\circ$ and $\Delta S^\circ$ are both positive, then the reaction is entropy-driven and higher temperatures are needed to force the reaction to be spontaneous. One can calculate the temperature where $\Delta G$ becomes zero, and that is at about 325 K. Above 325 K, the reaction would have a negative $\Delta G$ and be spontaneous.
7. The equilibrium that exists between $2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ gases has $\Delta G^\circ = -5.40 \text{kJ/mol}$. In a reaction mixture that contains 0.25 atm of NO$_2$ and 0.60 atm of N$_2$O$_4$, which way does the reaction shift to restore equilibrium?

Calculate $Q = 0.60 \div (0.25^2) = 9.6$ use $\Delta G = \Delta^\circ G + RT \ln Q$ so $\Delta G = (-5400 \text{ J/mol reaction}) + [8.314 \text{ J/mol} \cdot \text{K} \times 298 \text{ K} \times \ln 9.6] = 204 \text{ J/mol}$ If $\Delta G = 204 \text{ J/mol}$, then the reaction is spontaneous in the reverse direction.

OR Calculate $K$ from $\Delta G^\circ = -RT \ln K$

$\ln K = (-5400 \text{ J/mol reaction}) \div (-8.314 \text{ J/mol} \cdot \text{K} \times 298 \text{ K})$ so $K = 0.11$

Analyze $K$ vs. $Q$ (from above) 0.11 < 9.6 so $K < Q$ and reaction is spontaneous in reverse direction

8. In the gas phase equilibrium of $2 \text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$, the value of $K_p$ is $1.7 \times 10^{12}$ at 25.0 °C. What is the value of $\Delta G^\circ$ in kJ/mol?

$\Delta G^\circ = -RT \ln K$  $\Delta G = -[8.314 \text{ J/mol} \cdot \text{K} \times 298 \text{ K} \times \ln 1.7 \times 10^{12}] = -7.0 \times 10^4 \text{ J/mol}$ spontaneous as seen by a negative $\Delta G^\circ$ and product favored as seen by $K$ being large

9. Sulfur dioxide gas is present in polluted air, especially near coal fired industrial sites. It oxidizes in air to make sulfur trioxide. $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ The value of $\Delta G^\circ$ for this reaction is $-1.4 \times 10^2 \text{ kJ/mol}$. What is the value of $K_p$?

$\Delta G^\circ = -RT \ln K$ or $\ln K = (-140,000 \text{ J/mol reaction}) \div (-8.314 \text{ J/mol} \cdot \text{K} \times 298 \text{ K})$

so $K = 3 \times 10^{24}$ really big, meaning reaction is product favored