Problems Chapter 18 (Entropy and Free Energy)

1. Compare the compounds in each set below and decide which is expected to have the higher entropy. Assume all are at the same temperature.
    a. HF (g), HCl (g) or HBr (g)
    b. $NH_4Cl$ (s) or $NH_4Cl$ (aq)
    c. $C_2H_4$ (g) or $N_2$ (g)
    d. NaCl (s) or NaCl (g)

a. **HBr (g)** because it is the largest molecule.
b. **$NH_4Cl$ (aq)** – more disorder in the aqueous state
c. **$C_2H_4$ (g)** – more complex structure
d. **NaCl (g)** – more disorder in the gaseous state

2. When water vapors from hydrochloric acid and aqueous ammonia come in contact, they react, producing a white cloud of solid $NH_4Cl$.

$$HCl\ (g) + NH_3\ (g) \Leftrightarrow NH_4Cl\ (s)$$

Defining the reactants and products as the system under study:
    a. Predict whether $\Delta S^\circ_{system}$, $\Delta S^\circ_{surroundings}$, $\Delta S^\circ_{universe}$, $\Delta H^\circ_{rxn}$ and $\Delta G^\circ_{rxn}$ (at 298 K) are greater than zero, equal to zero or less than zero and explain your prediction. Verify your predictions by calculating values for each of these quantities.
    b. Calculate the value of K for this reaction at 298 K.

a. **$\Delta S^\circ_{sys} < 0$** (from 2 moles of gas to 1 mole of solid – decrease in entropy
**$\Delta S_{sur} > 0$** ($=-\Delta H^\circ/T$ and $\Delta H^\circ < 0$)
**$\Delta S_{universe} > 0$** (this process is spontaneous product-favored, so based on the second law of thermodynamics, $\Delta S_{universe}$ must be positive)
**$\Delta H^\circ < 0$** (since this process is product-favored and not entropically driven, it must be enthalpically driven. Also stronger IMFs are associated with the solid state and formation of IMFs is exothermic)
**$\Delta G^\circ < 0$** (this process is product-favored)

Calculations to verify:

| **Substance** | **$\Delta H^\circ_f$ (kJ mol$^{-1}$)** | **$S^\circ$ (J K$^{-1}$ mol$^{-1}$)** | **$\Delta G^\circ_f$ (kJ mol$^{-1}$)** |
|---|---|---|---|
| HCl (g) | –92.31 | 186.2 | –95.09 |
| $NH_3$ (g) | –45.90 | 192.77 | –16.37 |
| $NH_4Cl$ (s) | –314.55 | 94.85 | –203.08 |

**$\Delta S^\circ_{sys}$** = 94.85 J K$^{-1}$ mol$^{-1}$ – (186.2 J K$^{-1}$ mol$^{-1}$ + 192.77 J K$^{-1}$ mol$^{-1}$) =
**–284.1 J K$^{-1}$ mol$^{-1}$**
**$\Delta S^\circ_{sur}$** = (176340 J mol$^{-1}$)/(298.15 K) = **+591.45 J K$^{-1}$ mol$^{-1}$**
**$\Delta S^\circ_{universe}$** = $\Delta S_{sys} + \Delta S_{sur}$ = –284.1 J K$^{-1}$ mol$^{-1}$ + 591.45 J K$^{-1}$ mol$^{-1}$ =
**+307.3 J K$^{-1}$ mol$^{-1}$**
**$\Delta H^\circ$** = –314.55 kJ mol$^{-1}$ – [–92.31 kJ mol$^{-1}$ + (–45.90 kJ mol$^{-1}$)] = **–176.34 kJ mol$^{-1}$**
**$\Delta G^\circ$** = –203.08 kJ mol$^{-1}$ – [–95.09 kJ mol$^{-1}$ + (–16.37 kJ mol$^{-1}$)] = **–91.62 kJ mol$^{-1}$**

b. $\Delta G^\circ = -RT\ln K \rightarrow -91620\ \text{J mol}^{-1} = -(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298.15\ \text{K})\ln K \rightarrow$
**$K = 1.1 \times 10^{16}$**

3. Elemental boron, in the form of thin fibers, can be made by reducing a boron halide with $H_2$.

$$BCl_3\ (g) + 3/2\ H_2\ (g) \rightarrow B\ (s) + 3\ HCl\ (g)$$

Calculate $\Delta H^\circ_{rxn}$, $\Delta S^\circ_{rxn}$ and $\Delta G^\circ_{rxn}$ at 25 ˚C for this reaction. Is this reaction predicted to be product-favored at equilibrium at 25 ˚C? If so, is it enthalpy- or entropy-driven? S˚ for B (s) is 5.86 J $K^{-1}$ $mol^{-1}$.

| **Substance** | **$\Delta H^\circ_f$ (kJ mol$^{-1}$)** | **S˚ (J K$^{-1}$ mol$^{-1}$)** | **$\Delta G^\circ_f$ (kJ mol$^{-1}$)** |
|---|---|---|---|
| $BCl_3$ (g) | –402.96 | 290.17 | –387.95 |
| $H_2$ (g) | 0 | 130.7 | 0 |
| B (s) | 0 | 5.86 | 0 |
| HCl (g) | –92.31 | 186.2 | –95.09 |

**$\Delta H^\circ$** = 3(–92.31 kJ mol$^{-1}$) – (–402.96 kJ mol$^{-1}$) = **+126.03 kJ mol$^{-1}$**
**$\Delta S^\circ$** = 5.86 J K$^{-1}$ mol$^{-1}$ + 3(186.2 J K$^{-1}$ mol$^{-1}$) – (290.17 J K$^{-1}$ mol$^{-1}$) – 1.5(130.7 J K$^{-1}$ mol$^{-1}$) =
**+78.2 J K$^{-1}$ mol$^{-1}$**
**$\Delta G^\circ$** = 3(–95.09 kJ mol$^{-1}$) – (–387.95 kJ mol$^{-1}$) = **+102.68 kJ mol$^{-1}$**
**Reactant-favored**

4. Sulfur undergoes a phase transition between 80 and 100 ˚C.

$$S_8\ (\text{rhombic}) \rightarrow S_8\ (\text{monoclinic})$$
$$\Delta H^\circ_{rxn} = 3.213\ \text{kJ mol}^{-1}$$
$$\Delta S^\circ_{rxn} = 8.7\ \text{J K}^{-1}\ \text{mol}^{-1}$$

   a. Estimate $\Delta G^\circ_{rxn}$ for the transition at 80.0 ˚C and 110.0 ˚C. What do these results tell you about the stability of the two forms of sulfur at each of these temperatures?
   b. Calculate the temperature at which $\Delta G^\circ_{rxn} = 0$. What is the significance of this temperature?

**$\Delta G^\circ_{rxn,\ 80.0\ ^\circ C}$** = $\Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$ = (3.213 kJ mol$^{-1}$) – (353 K)(0.0087 kJ K$^{-1}$ mol$^{-1}$) =
**+0.14 kJ mol$^{-1}$**

Based on the positive $\Delta G^\circ_{rxn}$, the reaction is reactant-favored at 80.0 ˚C – therefore, **rhombic sulfur is more stable at 80.0 ˚C.**

**$\Delta G^\circ_{rxn,\ 110.0\ ^\circ C}$** = $\Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$ = (3.213 kJ mol$^{-1}$) – (383 K)(0.0087 kJ K$^{-1}$ mol$^{-1}$) =
**–0.12 kJ mol$^{-1}$**

Based on the negative $\Delta G^\circ_{rxn}$, the reaction is product-favored at 110.0 ˚C – therefore, **monoclinic sulfur is more stable at 110.0 ˚C.**

$\Delta G^\circ_{rxn} = 0 \rightarrow \Delta H^\circ_{rxn} = T\Delta S^\circ_{rxn} \rightarrow 3.213\ \text{kJ mol}^{-1} = T(0.0087\ \text{kJ K}^{-1}\ \text{mol}^{-1}) \rightarrow$
**T = 370 K = 96 ˚C**
This is the exact temperature at which the rhombic-monoclinic phase transition takes place (two phases coexist at equilibrium)

5. At 298 K, 1.00 mol BrCl (g) is introduced into a 10.0 L vessel, and equilibrium is established in the reaction BrCl (g) ⇔ ½ $Br_2$ (g) + ½ $Cl_2$ (g). Calculate the amounts of each of the three gases present when equilibrium is established.

| **Substance** | **$\Delta G^\circ_f$ (kJ mol$^{-1}$)** |
|---|---|
| BrCl (g) | –0.98 |
| $Br_2$ (g) | 3.12 |
| $Cl_2$ (g) | 0 |

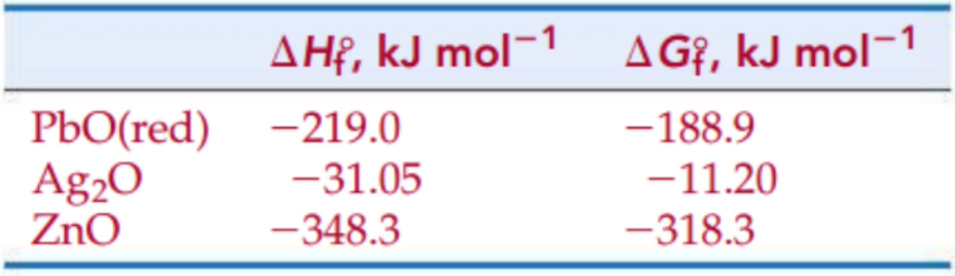
$\Delta G^\circ_{rxn}$ = ½(3.12 kJ mol$^{-1}$) + 0 – (–0.98 kJ mol$^{-1}$) = +2.54 kJ mol$^{-1}$
$\Delta G^\circ_{rxn}$ = –RTlnK → 2540 J mol$^{-1}$ = –(8.314 J K$^{-1}$ mol$^{-1}$)(298 K)lnK → K = 0.359

| | BrCl (g) ⇔ | ½ $Br_2$ (g) + | ½ $Cl_2$ (g) |
|---|---|---|---|
| I | 0.100 M | 0 | 0 |
| C | -x | +0.5x | +0.5x |
| E | 0.100 - x | 0.5x | 0.5x |

$$K = \frac{[Br_2]^{1/2}[Cl_2]^{1/2}}{[BrCl]} \rightarrow 0.359 = \frac{0.5x}{0.100 - x} \rightarrow x = 0.0418\ M$$

**[$Cl_2$] = [$Br_2$]** = 0.5(0.0418 M) = **0.0209 M → 0.209 mol**
**[BrCl]** = 0.100 M – 0.0418 M = **0.0582 M → 0.582 mol**

6. The following table shows the enthalpies and Gibbs free energies of formation of three metal oxides at 25 ˚C.



| | $\Delta H^\circ_f$, kJ mol$^{-1}$ | $\Delta G^\circ_f$, kJ mol$^{-1}$ |
|---|---|---|
| PbO(red) | −219.0 | −188.9 |
| $Ag_2O$ | −31.05 | −11.20 |
| ZnO | −348.3 | −318.3 |

   a. Which of these oxides can be most readily decomposed to the free metal and $O_2$ (g)?

b. For the oxide that is most easily decomposed, to what temperature must it be heated to produce $O_2$ (g) at 1.00 atm pressure?

$\Delta G^\circ_f$ for elements in their standard states - $O_2$ (g), Pb (s), Ag (s) and Zn (s) – is 0. Therefore:

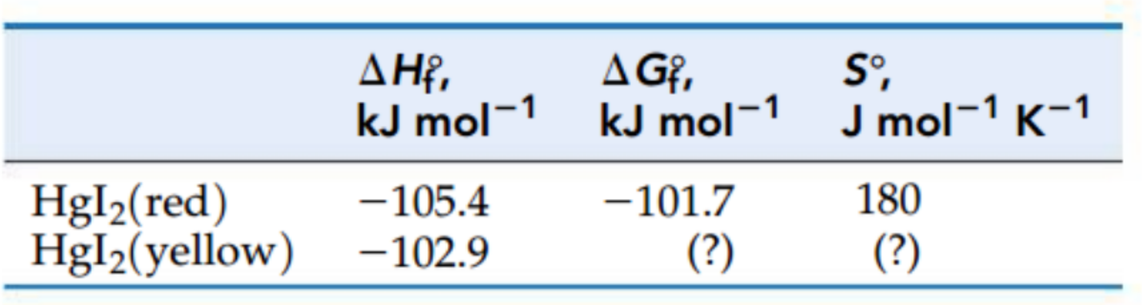
a. $PbO (s) \rightarrow Pb (s) + \frac{1}{2} O_2 (g)$ $\Delta G^\circ = +188.9$ kJ mol$^{-1}$ (298 K)
$Ag_2O (s) \rightarrow 2 Ag (s) + \frac{1}{2} O_2 (g)$ $\Delta G^\circ = +11.20$ kJ mol$^{-1}$ (298 K)
$ZnO (s) \rightarrow Zn (s) + \frac{1}{2} O_2 (g)$ $\Delta G^\circ = +318.3$ kJ mol$^{-1}$ (298 K)

**$\Delta G^\circ$ is smallest/least positive for $Ag_2O$ (s), so this oxide can be most readily decomposed to free metal and $O_2$ (g).**

b. At 298 K: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \rightarrow 11.20$ kJ mol$^{-1}$ = 31.05 kJ mol$^{-1}$ –(298 K)$\Delta S^\circ \rightarrow$
$\Delta S^\circ = 0.0666$ kJ K$^{-1}$ mol$^{-1}$

$\Delta H^\circ = T\Delta S^\circ \rightarrow 31.05$ kJ mol$^{-1}$ = T(0.0666 kJ K$^{-1}$ mol$^{-1}$) $\rightarrow$ **T = 466 K (193 °C)**

7. The following data are given for the two solid forms of $HgI_2$ at 298 K.



| | $\Delta H^\circ_f$, kJ mol$^{-1}$ | $\Delta G^\circ_f$, kJ mol$^{-1}$ | $S^\circ$, J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| $HgI_2$(red) | −105.4 | −101.7 | 180 |
| $HgI_2$(yellow) | −102.9 | (?) | (?) |

Estimate values for the two missing entries. To do that, assume that for the transition $HgI_2$ (red) → $HgI_2$ (yellow), the values of $\Delta H^\circ_{rxn}$ and $\Delta S^\circ_{rxn}$ at 25 °C have the same values that they do at the equilibrium temperature of 127 °C.

$HgI_2 (red) \Leftrightarrow HgI_2 (yellow)$

$\Delta H^\circ = -102.9$ kJ mol$^{-1}$ – (-105.4 kJ mol$^{-1}$) = +2.5 kJ mol$^{-1}$

At 127 °C: $\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ \rightarrow +2.5$ kJ mol$^{-1}$ = (400. K)$\Delta S^\circ \rightarrow \Delta S^\circ = 6.3$ J K$^{-1}$ mol$^{-1}$

At 25 °C: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ = (+2.5 kJ mol$^{-1}$) – (298 K)(0.0063 kJ K$^{-1}$ mol$^{-1}$) = +0.64 kJ mol$^{-1}$

$\Delta G^\circ = \Delta G^\circ_f$ (yellow) – $\Delta G^\circ_f$ (red) $\rightarrow$ 0.64 kJ mol$^{-1}$ = x + 101.7 kJ mol$^{-1}$ $\rightarrow$
x = **$\Delta G^\circ_f$ (yellow) = –101.1 kJ mol$^{-1}$**

$\Delta S^\circ = S^\circ$ (yellow) – $S^\circ$ (red) $\rightarrow$ 6.3 J K$^{-1}$ mol$^{-1}$ = x – 180 J K$^{-1}$ mol$^{-1}$ $\rightarrow$
x = **$S^\circ$ (yellow) = 186 J K$^{-1}$ mol$^{-1}$**

8. Oxides of nitrogen are produced at high-temperature combustion processes. The essential reaction is $N_2$ (g) + $O_2$ (g) ⇔ 2 NO (g). At what approximate temperature will an equimolar mixture of $N_2$ (g) and $O_2$ (g) be 1.0% converted to NO (g)?

| **Substance** | **$\Delta H^\circ_f$ (kJ mol$^{-1}$)** | **$S^\circ$ (J K$^{-1}$ mol$^{-1}$)** |
|---|---|---|
| $N_2$ (g) | 0 | 191.56 |
| $O_2$ (g) | 0 | 205.07 |
| NO (g) | 90.29 | 210.76 |

| | $N_2$ (g) + | $O_2$ (g) ⇔ | 2 NO (g) |
|---|---|---|---|
| I | A | A | 0 |
| C | –x | –x | +2x |
| E | A – x | A – x | 2x |

1.0% conversion → x = 0.010A

[NO] = 2(0.010A) = 0.020 A
[$N_2$] = [$O_2$] = A – 0.010 A = 0.99 A

$$K = \frac{[NO]^2}{[N_2][O_2]} = \frac{(0.020\,A)^2}{(0.99\,A)^2} = 4.1 \times 10^{-4}$$

$\Delta H^\circ$ = 2(90.29 kJ mol$^{-1}$) = +180.6 kJ mol$^{-1}$
$\Delta S^\circ$ = 2(210.76 J K$^{-1}$ mol$^{-1}$) – 191.56 J K$^{-1}$ mol$^{-1}$ – 205.07 J K$^{-1}$ mol$^{-1}$ = +24.89 J K$^{-1}$ mol$^{-1}$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K$ →
(180600 J mol$^{-1}$) – T(24.89 J K$^{-1}$ mol$^{-1}$) = –(8.314 J K$^{-1}$ mol$^{-1}$)(T)ln(4.1 x 10$^{-4}$)
**T = 2010 K**

9. For the majority of compounds, the value of $\Delta G^\circ_f$ is more positive (or less negative) than the value of $\Delta H^\circ_f$.
    a. Explain this observation using $NH_3$ (g) and $CCl_4$ (l) as examples.
    b. An exception to this observation is CO (g). Explain the trend in the $\Delta H^\circ_f$ and $\Delta G^\circ_f$ values for this molecule.

a. $\Delta S^\circ_f$ is usually a negative value (creating a single mole of compound from multiple elements creates "order") – so $\Delta G^\circ_f = \Delta H^\circ_f - T\Delta S^\circ_f$ ends up being more positive/less negative than $\Delta H^\circ_f$ (a subtraction of a negative number is like an addition of a positive number – so a positive number is added to $\Delta H^\circ_f$ to get $\Delta G^\circ_f$).

Example: $NH_3$ (g)

| **Substance** | **S˚ (J K$^{-1}$ mol$^{-1}$)** |
|---|---|
| $N_2$ (g) | 191.56 |
| $H_2$ (g) | 130.7 |
| $NH_3$ (g) | 192.77 |

½ $N_2$ (g) + 3/2 $H_2$ (g) → $NH_3$ (g)
$\Delta H^\circ_f = -45.90$ kJ mol$^{-1}$
$\Delta S^\circ_f = 192.77$ J K$^{-1}$ mol$^{-1}$ – 0.5(191.56 J K$^{-1}$ mol$^{-1}$) – 1.5(130.7 J K$^{-1}$ mol$^{-1}$) =
–99.06 J K$^{-1}$ mol$^{-1}$ = –0.09906 kJ K$^{-1}$ mol$^{-1}$ ($\Delta S^\circ_f$ negative because the number of moles of gas is reduced from 2 to 1)
$\Delta G^\circ_f = \Delta H^\circ_f - T\Delta S^\circ_f$ = -45.90 kJ mol$^{-1}$ –(298.15 K)(–0.09906 kJ K$^{-1}$ mol$^{-1}$) = –16.36 kJ mol$^{-1}$ (value matches Appendix L)

Example: $CCl_4$ (l)

| **Substance** | **S˚ (J K$^{-1}$ mol$^{-1}$)** |
|---|---|
| C (s) | 5.6 |
| $Cl_2$ (g) | 223.08 |
| CCl4 (l) | 214.39 |

C (s) +2 $Cl_2$ (g) → $CCl_4$ (l)
$\Delta H^\circ_f = -128.4$ kJ mol$^{-1}$
$\Delta S^\circ_f = 214.39$ J K$^{-1}$ mol$^{-1}$ – 5.6 J K$^{-1}$ mol$^{-1}$) – 2(223.08 J K$^{-1}$ mol$^{-1}$) =
–237.37 J K$^{-1}$ mol$^{-1}$ = –0.23737 kJ K$^{-1}$ mol$^{-1}$ ($\Delta S^\circ_f$ negative because the number of moles of gas is reduced from 2 to 0)
$\Delta G^\circ_f = \Delta H^\circ_f - T\Delta S^\circ_f$ = –128.4 kJ mol$^{-1}$ –(298.15 K)(–0.23737 kJ K$^{-1}$ mol$^{-1}$) = –57.63 kJ mol$^{-1}$ (value matches Appendix L)

b. $\Delta S^\circ_f$ for CO happens to be positive because the number of moles of gas is increased from 0.5 to 1. As a result, $\Delta G^\circ_f$ is more negative than $\Delta H^\circ_f$.

| **Substance** | **S˚ (J K$^{-1}$ mol$^{-1}$)** |
|---|---|
| C (s) | 5.6 |
| $O_2$ (g) | 205.07 |
| CO (g) | 197.674 |

C (s) + ½ $O_2$ (g) → CO (g)
$\Delta H^\circ_f = -110.525$ kJ mol$^{-1}$
$\Delta S^\circ_f = 197.674$ J K$^{-1}$ mol$^{-1}$ – 5.6 J K$^{-1}$ mol$^{-1}$ –0.5(205.07 J K$^{-1}$ mol$^{-1}$) = +89.539 J K$^{-1}$ mol$^{-1}$ = 0.089539 kJ K$^{-1}$ mol$^{-1}$
$\Delta G^\circ_f = \Delta H^\circ_f - T\Delta S^\circ_f$ = –110.525 kJ mol$^{-1}$ –(298.15 K)(+0.089539 kJ K$^{-1}$ mol$^{-1}$) = –137.22 kJ mol$^{-1}$ (value matches Appendix L)

10. Use the following data, as appropriate, to estimate the molarity of a saturated aqueous solution of $Sr(IO_3)_2$ at 298 K.

| | **$\Delta H^\circ_f$ (kJ $mol^{-1}$)** | **$S^\circ$ (J $mol^{-1}$ $K^{-1}$)** |
|---|---|---|
| $Sr(IO_3)_2$ (s) | –1019.2 | 234 |
| $Sr^{2+}$ (aq) | –545.8 | –32.6 |
| $IO_3^-$ (aq) | –221.3 | 118.4 |

$Sr(IO_3)_2$ (s) $\Leftrightarrow$ $Sr^{2+}$ (aq) + 2 $IO_3^-$ (aq)
$\Delta H^\circ = -545.8 \text{ kJ mol}^{-1} + 2(-221.3 \text{ kJ mol}^{-1}) + 1019.2 \text{ kJ mol}^{-1} = +30.8 \text{ kJ mol}^{-1}$
$\Delta S^\circ = -32.6 \text{ J K}^{-1} \text{ mol}^{-1} + 2(118.4 \text{ J K}^{-1} \text{ mol}^{-1}) - 234 \text{ J K}^{-1} \text{ mol}^{-1} = -29.8 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = +30800 \text{ J mol}^{-1} - (298 \text{ K})(-29.8 \text{ J K}^{-1} \text{ mol}^{-1}) = +39700 \text{ J mol}^{-1}$
$\Delta G^\circ = -RT\ln K \rightarrow +39700 \text{ J mol}^{-1} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})\ln K \rightarrow K = 1.11 \times 10^{-7}$

| | $Sr(IO_3)_2$ (s) $\Leftrightarrow$ | $Sr^{2+}$ (aq) + | 2 $IO_3^-$ (aq) |
|---|---|---|---|
| I | | 0 | 0 |
| C | | +x | +2x |
| E | | x | 2x |

$K = 1.11 \times 10^{-7} = [Sr^{2+}][IO_3^-]^2 = 4x^3 \rightarrow$ **$x = 3.02 \times 10^{-3}$ M**

11. Indicate whether each of the following statements is true or false. If it is false, correct it.
    a. The feasibility of manufacturing $NH_3$ from $N_2$ and $H_2$ depends entirely on the value of $\Delta H$ for the process $N_2$ (g) + 3 $H_2$ (g) $\rightarrow$ 2 $NH_3$ (g).
    b. The reaction of Na (s) with $Cl_2$ (g) to form NaCl (s) is a product-favored process.
    c. Spontaneous processes in general require that work is done to force them to proceed.
    d. Spontaneous processes are those that are exothermic and that lead to a higher degree of order in the system.

    a. **False** – it also depends on the $\Delta S$ value of that process.
    b. **True** – $\Delta G^\circ_f$ of NaCl (s) is $-384.04 \text{ kJ mol}^{-1}$
    c. **False** – spontaneous processes proceed without outside intervention.
    d. **False** – spontaneous processes lead to higher degree of disorder in the universe ($\Delta S_{universe} > 0$)

12. For each of the following processes, indicate whether the signs of $\Delta S$ and $\Delta H$ are expected to be positive, negative or about zero.
    a. A solid sublimes.
    b. The temperature of a sample of Co (s) is lowered from 60 ˚C to 25 ˚C.
    c. Ethyl alcohol evaporates from a beaker.
    d. A diatomic molecule dissociates into atoms.
    e. A piece of charcoal is combusted to form $CO_2$ (g) and $H_2O$ (g).

a. Gas has higher S than solid → **$\Delta S > 0$**. Heat needs to be added for sublimation to happen → **$\Delta H > 0$**.
b. Temperature is lowered → **$\Delta S < 0$**. Heat is removed as T is lowered → **$\Delta H < 0$**.
c. Gas has higher S than liquid → **$\Delta S > 0$**. Heat needs to be added for evaporation to happen (to break IMFs in ethyl alcohol) → **$\Delta H > 0$.**
d. More "disorder" associated with breaking a molecule into atoms → **$\Delta S > 0$**. Heat needs to be added to break a bond → **$\Delta H > 0$**.
e. Solid charcoal is converted to gaseous species → **$\Delta S > 0$**. Combustions are exothermic → **$\Delta H < 0$**.

13. Consider the reaction occurring at 298 K:
$N_2O\,(g) + NO_2\,(g) \Leftrightarrow 3\,NO\,(g)$
a. Show that this reaction is not product-favored under standard conditions by calculating $\Delta G^\circ_{rxn}$.
b. If a reaction mixture contains only $N_2O$ and $NO_2$ at partial pressures of 1.0 atm each, the reaction will be spontaneous until some NO forms in the mixture. What maximum partial pressure of NO builds up before the reaction ceases to be spontaneous?
c. Can the reaction be made more product-favored by an increase or decrease in temperature? If so, what temperature is required to make the reaction product-favored?

| **Substance** | **$\Delta G^\circ$ (kJ mol$^{-1}$)** | **$\Delta H^\circ_f$ (kJ mol$^{-1}$)** | **$S^\circ$ (J K$^{-1}$ mol$^{-1}$)** |
|---|---|---|---|
| $N_2O$ (g) | 104.20 | 82.05 | 219.85 |
| $NO_2$ (g) | 51.23 | 33.1 | 240.04 |
| NO (g) | 86.58 | 90.29 | 210.76 |

a. **$\Delta G^\circ_{rxn}$** = 3(86.58 kJ mol$^{-1}$) – 104.20 kJ mol$^{-1}$ – 51.23 kJ mol$^{-1}$ = **+104.31**
$\Delta G^\circ > 0$ → reactant-favored.

b.

| | $N_2O$ (g) + | $NO_2$ (g) ⇔ | 3 NO (g) |
|---|---|---|---|
| I | 1.0 atm | 1.0 atm | 0 |
| C | ~0 | ~0 | +3x |
| E | 1.0 | 1.0 | 3x |

$\Delta G^\circ = -RT\ln K$ → 104310 J mol$^{-1}$ = –(8.314 J K$^{-1}$ mol$^{-1}$)(298 K)lnK → K = 5.2 x 10$^{-19}$

$$K = 5.2 \times 10^{-19} = \frac{(P_{NO})^3}{P_{NO_2}P_{N_2O}} = \frac{(3x)^3}{(1.0)^2} \rightarrow x = 2.7 \times 10^{-7}$$

**$P_{NO} = 3x = 8.0 \times 10^{-7}$ atm**

c. $\Delta H^\circ$ = 3(90.29 kJ mol$^{-1}$) – 33.1 kJ mol$^{-1}$ – 82.05 kJ mol$^{-1}$ = +155.72 kJ mol$^{-1}$

$\Delta S^\circ = 3(210.76\ \text{J K}^{-1}\ \text{mol}^{-1}) - 240.04\ \text{J K}^{-1}\ \text{mol}^{-1} - 219.85\ \text{J K}^{-1}\ \text{mol}^{-1} = +172.39$

**This is an entropically driven process, so it can be made more spontaneous by an increase in T.**

$\Delta H = T\Delta S \rightarrow 155.72\ \text{kJ mol}^{-1} = T(0.17239\ \text{kJ K}^{-1}\ \text{mol}^{-1}) \rightarrow$ **T = 903 K**

14. Living organisms use energy from the metabolism of food to create an energy-rich molecule called adenosine triphosphate (ATP). ATP acts as an energy source for a variety of reactions that the living organisms must carry out to survive. ATP provides energy through its hydrolysis, which can be symbolized as follows:

    ATP (aq) + $H_2O$ (l) → ADP (aq) + $P_i$ (aq) $\Delta G^\circ_{rxn} = -30.5$ kJ

    where ADP represents adenosine diphosphate and $P_i$ represents an inorganic phosphate group (such as $HPO_4^{2-}$).

    a. Calculate the equilibrium constant, K, for the given reaction at 298 K.
    b. The free energy obtained from the oxidation (reaction with oxygen) of glucose ($C_6H_{12}O_6$) to form carbon dioxide and water can be used to re-form ATP by driving the given reaction in reverse. Calculate the standard Gibbs free energy change for the oxidation of glucose and estimate the maximum number of moles of ATP that can be formed by the oxidation of one mole of glucose. For $C_6H_{12}O_6$ (s), $\Delta G^\circ_f = -910.4\ \text{kJ mol}^{-1}$.

a. $\Delta G^\circ = -RT\ln K \rightarrow -30500\ \text{J mol}^{-1} = -(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298\ \text{K})\ln K \rightarrow$ **K = 2.22 x 10$^5$**

b. $C_6H_{12}O_6$ (s) + 6 $O_2$ (g) → 6 $CO_2$ (g) + 6 $H_2O$ (l)

| **Substance** | **$\Delta G^\circ$ (kJ mol$^{-1}$)** |
|---|---|
| $H_2O$ (l) | –237.15 |
| $CO_2$ (g) | –394.359 |

$\Delta G^\circ_{rxn} = 6(-394.359\ \text{kJ mol}^{-1}) + 6(-237.15\ \text{kJ mol}^{-1}) - (-910.4\ \text{kJ mol}^{-1}) = -2878.6\ \text{kJ mol}^{-1}$

$$1\ mol\ C_6H_{12}O_6 \times \frac{2878.6\ kJ}{1\ mol\ C_6H_{12}O_6} \times \frac{1\ mol\ ATP}{30.5\ kJ} = \mathbf{94.4\ mol\ ATP}$$