Supplemental Activities

Module: Thermodynamics

Section: Free Energy - Key

Gibb’s Free Energy

Activity 1

Gibb’s free energy is a thermodynamic state function. The purpose of this activity is to recall the origin of the function.

1. Both Gibb’s free energy, G, and the change in entropy of the universe, $\Delta S_{universe}$, can be used to predict the spontaneity of physical or chemical change.

2. The change in the Gibb’s free energy, ΔG, is actually derived from the change in entropy of the universe. What is the equation relating the change in Gibb’s free energy for a process and the change in enthalpy and entropy for the same process? Define the variables and provide units for each.

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

   ΔG is the change in Gibb’s free energy and it usually has units of kilojoules (kJ) or kilojoules per mole (kJ/mol). ΔH is the change in enthalpy and it usually has units of kilojoules (kJ) or kilojoules per mole (kJ/mol). T is absolute temperature in units of Kelvin (K). ΔS is the change in entropy and it usually has units of joules per Kelvin (J/K) or joules per mole per Kelvin (kJ/molK). Make sure to convert joules to kilojoules!

3. What is the sign of ΔG for a spontaneous process? For a nona spontaneous process?

   The sign of ΔG is negative when a process is spontaneous. The sign of ΔG is positive when a process is nona spontaneous.

4. What are the four possible combinations of ΔH and ΔS and what kind of change do they lead to – always spontaneous, always nona spontaneous or temperature dependent?
   - ΔH is negative and ΔS is negative – temperature dependent
   - ΔH is negative and ΔS is positive – always spontaneous
   - ΔH is positive and ΔS is negative – never spontaneous
   - ΔH is positive and ΔS is positive – temperature dependent

Activity 2

The purpose of this activity is to further develop your understanding of Gibb’s Free Energy by investigating Gibb’s free energy of formation and Gibb’s free energy of reaction.

1. How does the change in Gibb’s free energy of formation under standard conditions, ΔG_f°, inform us about the stability of a compound?

   ΔG_f° indicates whether or not that compound will form spontaneously under standard conditions. Very stable compounds under standard conditions will have large, negative values for ΔG_f° while unstable compounds under standard conditions will have more positive values for ΔG_f°.

2. Which compound would you expect to have the lowest ΔG_f° (under standard conditions) of the given pairs? Explain your choice.
    a. Br_2 (l) or Br_2 (g)?

       Molecular bromine at room temperature and pressure is a liquid. Therefore, it would be expected for Br_2 (l) to have the lower ΔG_f°.

    b. O (g) or O_2 (g)?

       Molecular oxygen at room temperature and pressure is a diatomic molecule. Therefore, it would be expected for O_2 (g) to have the lower ΔG_f°.

    c. Fe (s) or Fe_2O_3 (s)?

       Iron oxides are found all over the earth naturally! So it would be expected that iron oxides are more stable and therefore have lower ΔG_f° values than solid iron.

    d. O_2 (g) or Al_2O_3 (s)?

       This one is trickier to determine. It might be helpful to consider how reactive oxygen gas is. Oxygen gas reacts with metals easily to form metal oxides which indicates that the metal oxides are probably more stable under standard conditions. Therefore it would be expected that Al_2O_3 (s) would have a lower ΔG_f° value.

3. Explain the concept of thermodynamic stability. Explain how the temperature and pressure conditions of a given environment might change the stability of a compound.

   In the context of thermodynamics, stability is a measure of how low the free energy of the substance is under a given set of conditions. So substances with low free energies are often formed spontaneously. To cause that formation to run backward would be non-spontaneous. Therefore, for substances with low free energies they tend not to react "backwards" and we call such items stable. However, by changing the temperature and pressure conditions we can sometimes change stable compounds into unstable ones. Consider putting a glass of water into the freezer. It spontaneously changes into ice. The ice is more stable under the freezer conditions than the liquid water but the opposite is true on your kitchen counter.

4. Corrosion is a huge obstacle in industry. One of the most common and pervasive corrosion reactions is the formation of iron rust (iron oxides). Provide a thermodynamic explanation as to why the formation of iron oxides continues to present industrial challenges.

   Oxygen reacts with iron to form iron oxides spontaneously. It requires energy to run the formation backward! The iron oxide products have a lower free energy than the separated iron metal and oxygen gas therefore over time the iron oxides will form spontaneously unless energy is put into the system. A never-ending battle!

Activity 3

The purpose of this activity is to further develop your understanding of using Hess's Law to determine the change in Gibbs free energy for a reaction, ΔG_{rxn}.

1. Calculate the ΔG_{rxn} of the following reaction using the given standard free energy of formation data:
   $6CO_2\ (g) + 6H_2O\ (l) \rightarrow C_6H_{12}O_6\ (s) + 6O_2\ (6)$
   $\Delta G_f^\circ\ CO_2\ (g) = -394.36$ kJ/mol
   $\Delta G_f^\circ\ H_2O\ (l) = -237$ kJ/mol
   $\Delta G_f^\circ\ C_6H_{12}O_6\ (s) = -910$ kJ/mol

$$\boxed{\begin{aligned}
\Delta G_{rxn} &= \sum n\Delta G^\circ_{f,prod.} - \sum n\Delta G^\circ_{f,react.}\\
\Delta G_{rxn} &= \left[1\Delta G^\circ_{f,C_6H_{12}O_6} + 6\Delta G^\circ_{f,O_2}\right] - \left[6\Delta G^\circ_{f,H_2O} + 6\Delta G^\circ_{f,CO_2}\right]\\
\Delta G_{rxn} &= \left[1(-910\tfrac{kJ}{mol}) + 6(0\tfrac{kJ}{mol})\right] - \left[6(-237\tfrac{kJ}{mol}) + 6(-394.36\tfrac{kJ}{mol})\right]\\
\Delta G_{rxn} &= (-910\tfrac{kJ}{mol}) - (-3788.16\tfrac{kJ}{mol})\\
\Delta G_{rxn} &= -1183.08\tfrac{kJ}{mol} + 3788.16\tfrac{kJ}{mol}\\
\Delta G_{rxn} &= +2878.16\tfrac{kJ}{mol\ rxn}
\end{aligned}}$$

2. Here is a chemical reaction occurring under standard conditions:

   $C\ (s, graphite) + \frac{1}{2}\ O_2\ (g) + 2H_2\ (g) \rightarrow CH_3OH\ (l)$

   The associated thermodynamic data is:

   S° C (s, graphite) = 5.740 J/K mol
   S° O_2 (g) = 205 J/K mol
   S° H_2 (g) = 131 J/K mol
   S° CH_3OH (l) = 127 J/K mol
   ΔH_f° CH_3OH (l) = −239 kJ/mol

   Calculate the ΔG_{rxn} under standard conditions from this data.

$$\begin{aligned}
\Delta G_{rxn} &= \Delta H_{rxn} - T\Delta S_{rxn} \\
\Delta H_{rxn} &= \sum n\Delta H^{\circ}_{f,prod.} - \sum n\Delta H^{\circ}_{f,react.} \\
\Delta H_{rxn} &= \left[1\Delta H^{\circ}_{f,CH_3OH}\right] - \left[1\Delta H^{\circ}_{f,C,graphite} + \tfrac{1}{2}\Delta H^{\circ}_{f,O_2} + 2\Delta H^{\circ}_{f,H_2}\right] \\
\Delta H_{rxn} &= \left[1(-239\tfrac{kJ}{mol})\right] - \left[1(0\tfrac{kJ}{mol}) + \tfrac{1}{2}(0\tfrac{kJ}{mol}) + 2(0\tfrac{kJ}{mol})\right] \\
\Delta H_{rxn} &= (-239\tfrac{kJ}{mol}) - (0\tfrac{kJ}{mol}) \\
\Delta H_{rxn} &= -239\tfrac{kJ}{mol}
\end{aligned}$$

$$\begin{aligned}
\Delta S_{rxn} &= \sum nS^{\circ}_{prod.} - \sum nS^{\circ}_{react.} \\
\Delta S_{rxn} &= \left[1S^{\circ}_{CH_3OH}\right] - \left[1S^{\circ}_{C,graphite} + \tfrac{1}{2}S^{\circ}_{O_2}\right] \\
\Delta S_{rxn} &= \left[1(127\tfrac{J}{K\cdot mol})\right] - \left[1(5.740\tfrac{J}{K\cdot mol}) + \tfrac{1}{2}(205\tfrac{J}{K\cdot mol}) + 2(131\tfrac{J}{K\cdot mol})\right] \\
\Delta S_{rxn} &= (127\tfrac{J}{K\cdot mol}) - (370.24\tfrac{J}{K\cdot mol}) \\
\Delta S_{rxn} &= -243.24\tfrac{J}{K\cdot mol} \\
\Delta S_{rxn} &= -0.24324\tfrac{kJ}{K\cdot mol} < --Units!
\end{aligned}$$

$$\begin{aligned}
\Delta G_{rxn} &= \Delta H_{rxn} - T\Delta S_{rxn} \\
\Delta G_{rxn} &= -239\tfrac{kJ}{mol} - (298.15K)(-0.24324\tfrac{kJ}{K\cdot mol}) \\
\Delta G_{rxn} &= -239\tfrac{kJ}{mol} + 72.522\tfrac{kJ}{mol} \\
\Delta G_{rxn} &\approx -166\tfrac{kJ}{mol}
\end{aligned}$$

3. Is the above equation a formation equation? Explain. Look up $\Delta G^{\circ}_{f\ CH_3OH\ (l)}$, and compare that tabulated value to the value you calculated here.

   Yes! This reaction shows the formation of one mole of a compound from its elements in their standard states. Furthermore, the value for $\Delta G^{\circ}_{f\ CH_3OH\ (l)}$ is –166 kJ/mol, which is identical to the calculated value for this reaction at standard conditions.

Predicting Spontaneity

ACTIVITY 1

The purpose of this activity is to use ΔG_{rxn} to predict change.

1. Dry ice (solid CO_2) spontaneously sublimes in room temperature. What can you conclude about the *ΔH* of this system: CO_2 (s) → CO_2 (g)

   Sublimation is an endothermic process. Therefore *ΔH* for the process would be positive.

2. What can we conclude about the magnitude of the ΔH term in the dry ice example?

   A spontaneous process has a negative value for ΔG. However, a positive value for ΔH would contradict a negative ΔG value. So in order for an endothermic process to be spontaneous the magnitude of $T\Delta S$ must be larger than the magnitude of ΔH.

3. What can we conclude about changing the temperature and its effect on the spontaneity of this reaction? That is do you predict that decreasing the temperature will help the dry ice not sublime?

   The ΔS term scales with temperature. If the temperature is decreased too far the ΔS term has less influence. If it is decreased too far the magnitude of the positive ΔH term would overcome the magnitude of the $T\Delta S$ term and the process would become non-spontaneous.

4. The equation for the formation of 2 moles of NH_3 under standard conditions is:

   $$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

   The associated thermodynamic data is:

   $S°_{N_2\,(g)}$ = 192 J/K mol $S°_{H_2\,(g)}$ = 131 J/K mol $S°_{NH_3\,(g)}$ = 193 J/K mol
   $\Delta H_f^\circ\ NH_3\,(g)$ = −46 kJ/mol

   a. Given this information calculate the ΔS_{univ}. Based on the ΔS_{univ} for this example would you predict that this reaction spontaneous? Why or Why not?

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys}$$

$$\Delta S_{surr} = \frac{-q}{T} = \frac{-\Delta H_{sys}}{T}$$

$$\Delta H_{sys} = \left[2\Delta H^{\circ}_{f,NH_3}\right] - \left[1\Delta H^{\circ}_{f,N_2} + 3\Delta H^{\circ}_{f,H_2}\right]$$

$$\Delta H_{sys} = \left[2(-46\tfrac{kJ}{mol})\right] - \left[1(0\tfrac{kJ}{mol}) + 3(0\tfrac{kJ}{mol})\right]$$

$$\Delta H_{sys} = (-92\tfrac{kJ}{mol}) - (0\tfrac{kJ}{mol})$$

$$\Delta H_{sys} = -92\tfrac{kJ}{mol}$$

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T}$$

$$Assume\ T\ of\ surroundings = Room\ Temp = 298.15K$$

$$\Delta S_{surr} = \frac{-(-92\tfrac{kJ}{mol})}{298.15K} = \frac{92\tfrac{kJ}{mol}}{298.15K} = 0.30857\tfrac{kJ}{K\cdot mol}$$

$$\Delta S_{sys} = \sum nS^{\circ}_{prod.} - \sum nS^{\circ}_{react.}$$

$$\Delta S_{sys} = \left[2\Delta S^{\circ}_{NH_3}\right] - \left[1\Delta S^{\circ}_{N_2} + 3\Delta S^{\circ}_{H_2}\right]$$

$$\Delta S_{sys} = \left[2(193\tfrac{J}{K\cdot mol})\right] - \left[1(192\tfrac{J}{K\cdot mol}) + 3(131\tfrac{J}{K\cdot mol})\right]$$

$$\Delta S_{sys} = (386\tfrac{J}{K\cdot mol}) - (585\tfrac{J}{K\cdot mol})$$

$$\Delta S_{sys} = -199\tfrac{J}{K\cdot mol}$$

$$\Delta S_{sys} = -0.199\tfrac{kJ}{K\cdot mol} <--Units!$$

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys}$$

$$\Delta S_{univ} = 0.30857\tfrac{kJ}{K\cdot mol} + (-0.199\tfrac{kJ}{K\cdot mol})$$

$$\Delta S_{univ} \approx 0.110\tfrac{kJ}{K\cdot mol}$$

ΔS_{univ} is positive. Therefore, the reaction is spontaneous.

b. Using the given thermodynamic data calculate ΔG_{rxn} at 298K.

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$$

$$\Delta H_{rxn} = \sum n\Delta H^{\circ}_{f,prod.} - \sum n\Delta H^{\circ}_{f,react.}$$

$$\Delta H_{rxn} = \left[2\Delta H^{\circ}_{f,NH_3}\right] - \left[1\Delta H^{\circ}_{f,N_2} + 3\Delta H^{\circ}_{f,H_2}\right]$$

$$\Delta H_{rxn} = \left[2(-46\tfrac{kJ}{mol})\right] - \left[1(0\tfrac{kJ}{mol}) + 3(0\tfrac{kJ}{mol})\right]$$

$$\Delta H_{rxn} = (-92\tfrac{kJ}{mol}) - (0\tfrac{kJ}{mol})$$

$$\Delta H_{rxn} = -92\tfrac{kJ}{mol}$$

$$\Delta S_{rxn} = \sum nS^{\circ}_{prod.} - \sum nS^{\circ}_{react.}$$

$$\Delta S_{rxn} = \left[2\Delta S^{\circ}_{NH_3}\right] - \left[1\Delta S^{\circ}_{N_2} + 3\Delta S^{\circ}_{H_2}\right]$$

$$\Delta S_{rxn} = \left[2(193\tfrac{J}{K\cdot mol})\right] - \left[1(192\tfrac{J}{K\cdot mol}) + 3(131\tfrac{J}{K\cdot mol})\right]$$

$$\Delta S_{rxn} = (386\tfrac{J}{K\cdot mol}) - (585\tfrac{J}{K\cdot mol})$$

$$\Delta S_{rxn} = -199\tfrac{J}{K\cdot mol}$$

$$\Delta S_{rxn} = -0.199\tfrac{kJ}{K\cdot mol} <-- Units!$$

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$$

$$\Delta G_{rxn} = -92\tfrac{kJ}{mol} - (298.15K)(-0.199\tfrac{kJ}{K\cdot mol})$$

$$\Delta G_{rxn} = -92\tfrac{kJ}{mol} + 32.67\tfrac{kJ}{mol}$$

$$\Delta G_{rxn} = -59.33\tfrac{kJ}{mol}$$

c. Based on your calculated value of ΔG_{rxn} is the formation of 2 moles of NH_3 under these conditions spontaneous?

ΔG_{rxn} is negative. Therefore, the reaction is spontaneous.

d. Is there a temperature at which point this reaction would become nonspontaneous? If so what is that temperature?

$$\begin{aligned}
&\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}\\
&\Delta H_{rxn} = -92\tfrac{kJ}{mol}\\
&\Delta S_{rxn} = -0.199\tfrac{kJ}{K\cdot mol}\\
&T = ?\\
&0 = -92\tfrac{kJ}{mol} - (T)(-0.199\tfrac{kJ}{K\cdot mol})\\
&92\tfrac{kJ}{mol} = (T)(0.199\tfrac{kJ}{K\cdot mol})\\
&\frac{92\tfrac{kJ}{mol}}{0.199\tfrac{kJ}{K\cdot mol}} = T\\
&462K = T\\
&\\
&Nonspont\ when\ T > 462K
\end{aligned}$$

Yes, the reaction would become non spontaneous at temperatures above 462 K.

ACTIVITY 2

The purpose of this activity is to check your understanding of the temperature effects of spontaneity across change.

1. Choose the correct word to complete the statement and then give an example of that kind of reaction:
   a. An endothermic reaction for which the entropy of the system is increasing the reaction will be (choose one: always/never/sometimes) spontaneous. Give an example of such a reaction.

      Melting is an endothermic process in which the entropy of the system is increasing.

   b. An endothermic reaction for which the entropy of the system is decreasing the reaction will be (choose one: always/never/sometimes) spontaneous.

   c. An exothermic reaction for which the entropy of the system is increasing the reaction will be (choose one: always/never/sometimes) spontaneous. Give an example of such a reaction.

      Combustion is an exothermic process in which the entropy of the system is often increasing (if more gases are being made than consumed)

   d. An exothermic reaction for which the entropy of the system is decreasing the reaction will be (choose one: always/never/sometimes) spontaneous. Give an example of such a reaction.

Freezing is an exothermic process in which the entropy of the system is decreasing.

2. What is the value of ΔG_{rxn} when a system is at equilibrium?

   The value ΔG_{rxn} at equilibrium is zero.

3. What is true about the forward process and the backward process of a system at equilibrium?

   At equilibrium the forward and the backward process are happening at the same rate.

4. The condensation of CH_3OH gas to CH_3OH liquid is spontaneous when ΔG is negative. Using the data below, predict at what temperature is this process first spontaneous at 1 bar.

$S°$ CH_3OH (g) = 240 J/K mol	$S°$ CH_3OH (l) = 127 J/K mol
ΔH_f° CH_3OH (g) = −201 kJ/mol	ΔH_f° CH_3OH (l) = −239 kJ/mol

$$CH_3OH(g) \rightarrow CH_3OH(l)$$

$$\Delta H_{rxn} = \sum n\Delta H^{\circ}_{f,prod.} - \sum n\Delta H^{\circ}_{f,react.}$$

$$\Delta H_{rxn} = \left[2\left(\Delta H^{\circ}_{f,CH_3OH(l)}\right)\right] - \left[1\left(\Delta H^{\circ}_{f,CH_3OH(g)}\right)\right]$$

$$\Delta H_{rxn} = \left[1\left(-239\tfrac{kJ}{mol}\right)\right] - \left[1\left(-201\tfrac{kJ}{mol}\right)\right]$$

$$\Delta H_{rxn} = -39\tfrac{kJ}{mol}$$

$$\Delta S_{rxn} = \sum nS^{\circ}_{prod.} - \sum nS^{\circ}_{react.}$$

$$\Delta S_{rxn} = \left[1\left(S^{\circ}_{CH_3OH(l)}\right)\right] - \left[1\left(S^{\circ}_{CH_3OH(g)}\right)\right]$$

$$\Delta S_{rxn} = \left[1(127\tfrac{J}{K\cdot mol})\right] - \left[1\left(240\tfrac{J}{K\cdot mol}\right)\right]$$

$$\Delta S_{rxn} = -113\tfrac{J}{K\cdot mol}$$

$$\Delta S_{rxn} = -0.113\tfrac{kJ}{K\cdot mol} < - - Units!$$

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$$

$$\Delta H_{rxn} = -39\tfrac{kJ}{mol}$$

$$\Delta S_{rxn} = -0.113\tfrac{kJ}{K\cdot mol}$$

$$0 = -39\tfrac{kJ}{mol} - (T)(-0.113\tfrac{kJ}{K\cdot mol})$$

$$39\tfrac{kJ}{mol} = (T)(0.113\tfrac{kJ}{K\cdot mol})$$

$$\frac{39\tfrac{kJ}{mol}}{0.113\tfrac{kJ}{K\cdot mol}} = T_{Condensation}$$

$$345K = T_{Condensation} \ldots \text{ Spont when } T < 345K$$