Supplemental Activities

Module: Thermodynamics

Section: Second Law of Thermodynamics – Key

Spontaneity

ACTIVITY 1

The purpose of this activity is to practice your understanding of the concept of spontaneous change.

1. A spontaneous change is defined as one that happens in only one direction in isolation, which means on its own with no outside influences.

2. Give two examples of processes that are spontaneous at room temperature and pressure – provide one physical change and one chemical change.

   Physical processes: Dropping a book, dry ice subliming, ice melting

   Chemical processes: Iron rusting, some combustion reactions

3. Can spontaneous reactions ever be reversed? Does temperature ever play a role in the spontaneity of a reaction?

   Yes. Spontaneous reactions can be reversed by putting energy into the system. Sometimes by changing the conditions, you can make the reverse process spontaneous. This is where temperature can play a huge role in the spontaneity of a process. For example, you could pick up the book you dropped or you could place the ice in the freezer. In both cases the process would be occurring in the opposite direction – one you put energy into the system and in the other you changed the conditions by changing temperature.

ACTIVITY 2

The purpose of this activity is to consider again the law that governs spontaneous processes.

1. The second law of thermodynamics states that all spontaneous changes are accompanied by an increase in universal entropy.

2. The change in entropy of the universe takes into account the change in entropy of the system and the change in entropy of the surroundings.

3. Entropy is a state function that is a measure of the dispersal of energy.

4. In thermodynamics, the word "reversible" indicates a specifically defined path for some process.

5. Give an equation for the change in entropy using heat and absolute temperature. Explain the equation in words.

$$\boxed{\Delta S = \frac{q_{rev}}{T}}$$

   This equation states that the change in entropy, ΔS, equals the ratio of the reversible heat flow, q_{rev}, for the process over the absolute temperature, T, of the process.

ACTIVITY 3

The purpose of this activity is to practice thinking about the sign and magnitude of changes in entropy.

1. When dry ice sublimes, the sign of the change in entropy for the system must be **+**, the sign of the change in entropy of the surroundings must be **–**. The overall change in entropy of the universe must be **+**. Given this situation what must be the relationship of the magnitude of the values for the system and the surroundings?

   The change in entropy of the universe is the sum of the changes in entropy for the system and the surroundings. The change in entropy of the universe is greater than zero for a spontaneous process, such as dry ice subliming. When dry ice sublimes, the molecules move from a structured lattice to a greater dispersal of molecules and movement. Therefore, the change in entropy for the system when dry ice sublimes is positive. It is an endothermic process so q_{rev} is positive. Therefore, for the surroundings the q_{rev} is negative! The change in entropy for the surroundings is negative. However, we know that the net change in entropy for the universe (system + surroundings) is positive. Thus, the magnitude of the change in entropy for the surroundings must be smaller than the magnitude of the change in entropy for the system.

2. Consider the dissolution of a small amount of table salt into water at room temperature. Define the system and the surroundings. Is the $\Delta S_{sys} >$ or < 0 or is there no way to know? Is the $\Delta S_{sur} >$ or < 0 or is there no way to know? Please justify your answer.

   The system is the table salt. The surroundings are everything else – specifically the water!

   The system moves from being an ordered lattice to ions dispersed throughout a solution, so $\Delta S_{sys} > 0$.

   It's a little harder to predict the change in entropy of the surroundings without knowing the reversible heat associated with the process. Consider, however, that the water molecules will arrange themselves around the ions. This hydration process gives greater structure to the water molecules and therefore decreases the entropy of the surroundings slightly!

However, we know that the salt dissolves into the water meaning that the change in entropy of the system must be greater in magnitude than the change in entropy of the surroundings.

3. Consider a chemical reaction in which a solid metal is placed into a beaker of water. Upon mixing, a gas is released as well as light and heat. Define the system and the surroundings. Is the $\Delta S_{sys} >$ or < 0 or is there no way to know? Is the $\Delta S_{sur} >$ or < 0 or is there no way to know? Please justify your answer.

   The system is the solid metal and the water, which react together. The surroundings are everything else.

   We are informed that the process releases a gas, light and heat. The production of gas suggests that system increases in entropy while the exothermic release of energy indicates that there may be a decrease in entropy for the system. So we can't say for sure about the sign of the change of entropy of the system.

   For the surroundings, we know that the reaction was exothermic and released energy as light! Therefore, the entropy of the surroundings increased.

   We know that the reaction occurred spontaneously. So the sum of the change in entropy of the system and the change in entropy of the surroundings must be positive. We know with certainty that the change in entropy of the surroundings is positive.

Change in Entropy

ACTIVITY 1

The purpose of this activity is to recall your conceptual understanding of the change in Entropy of a system, ΔS_{sys}.

1. What are the five things that will lead to a change in entropy of the system.
   - Temperature
   - Volume
   - Phase
   - Mixing
   - Composition (Chemical Reaction)

2. Describe how each of the five things you listed above could change to result in a decrease in entropy for a system.
   - Decreasing temperature
   - Decreasing volume
   - Phase Transitions – Freezing, Condensation, Deposition (Solidification)
   - Separating a mixture

- Changing the composition to result in a more organized system (often reducing the number of moles of substances)

3. How could a sample increase in positional disorder without increasing in thermal disorder?

   Positional disorder is related to the ways a substance can orient itself in a sample. Whereas, thermal disorder is related to the amount kinetic energy as sample has in its molecules. So let's take a gas at 298 K in a small container, then we release the gas into a larger container at the same temperature. The thermal disorder of the gas sample hasn't changed but there are more positions for the gas particles to assume. Therefore, the positional disorder of the sample has increased without an increase in thermal disorder.

ACTIVITY 2

The purpose of this activity is to practice your ability to quantify the change in entropy of a physical system.

1. Write three equations for the change in entropy of a system when it experiences a change in temperature, a change in volume and or a change in phase. Define each of the variables and give the units for each.

   For a change in temperature:

$$\boxed{\begin{array}{l} \Delta S_{sys} = nC_m \ln\left(\dfrac{T_{final}}{T_{initial}}\right) \\ \\ \textit{Also Acceptable}: \\ \\ \Delta S_{sys} = mC_s \ln\left(\dfrac{T_{final}}{T_{initial}}\right) \end{array}}$$

   ΔS is the change in entropy for the process usually given units of joules per Kelvin (J/K). n or m is moles or mass respectively with units moles (mol) or mass (g) respectively. C_m or C_s is molar heat capacity or specific heat capacity respectively with units joules per mol per Kelvin (J/molK) or joules per gram per Kelvin (J/gK) respectively. T_{finail} is the final temperature in Kelvin (K) and $T_{initial}$ is the initial temperature in Kelvin (K).

   For a change in volume:

$$\boxed{\Delta S_{sys} = nR \ln\left(\dfrac{V_{final}}{V_{initial}}\right)}$$

   ΔS is the change in entropy for the process usually given units of joules per Kelvin (J/K). n is moles with units moles (mol). R is the universal gas constant in units of joules per mole per

Kelvin (J/molK). V_{finail} is the final volume and $V_{initial}$ is the initial volume. The volume units can be any volume unit as long as they are the same for the two volume values.

For a change in phase:

$$\boxed{\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}}}$$

ΔS is the change in entropy for the process usually given units of joules per Kelvin (J/K). ΔH is the change in enthalpy for the transition in units of joules (J). T is the temperature of the transition in Kelvin (K).

2. Calculate the change in entropy for 4.8 moles of H_2O gas when it increases in temperature from 400 K to 500 K. The heat capacity for H_2O gas is 36.57 J/molK.

$$\boxed{\begin{aligned}
&\Delta S_{sys} = nC_m \ln\left(\frac{T_{final}}{T_{initial}}\right)\\
&n = 4.8mol\\
&C_m = 36.57\tfrac{J}{molK}\\
&T_{final} = 500K\\
&T_{initial} = 400K\\
&\\
&\Delta S_{sys} = (4.8mol)(36.57\tfrac{J}{molK})\ln\left(\frac{500K}{400K}\right)\\
&\Delta S_{sys} = (4.8mol)(36.57\tfrac{J}{molK})\ln(1.25)\\
&\Delta S_{sys} = 39.17\tfrac{J}{K} \approx 39\tfrac{J}{K}
\end{aligned}}$$

3. Calculate the change in entropy of fusion for one mole of mercury. The melting point of mercury is –37.9˚C.

Fusion occurs at the melting point of mercury, which is –37.9˚C at atmospheric pressure.

$$\boxed{\begin{aligned}
&\Delta S_{sys} = \frac{\Delta H_{phase\ \ change}}{T}\\
&T_{fusion} = -37.9^{\circ}C = 235.25K\\
&\Delta H_{fus} = 2.33\tfrac{kJ}{mol}\\
&\Delta H_{phase\ \ change} = n\Delta H_{fus} = (1mol)(2.33\tfrac{kJ}{mol}) = 2.33kJ = 2{,}330J\\
&\Delta S_{sys} = \frac{2{,}330J}{235.25K} = 9.90\tfrac{J}{K}
\end{aligned}}$$

4. Calculate the change in entropy of fusion for 63 grams of mercury.

We either need to look up the specific ΔH_{fus} for mercury first or convert 63 grams to moles and use the molar ΔH_{fus} for mercury. Since we already have the molar heat of fusion, let's convert 63 grams to moles. Fusion occurs at the melting point of mercury, which is –37.9°C at atmospheric pressure.

$$\boxed{\begin{aligned}
&\Delta S_{sys} = \frac{\Delta H_{phase\ change}}{T} \\
&T_{boiling} = -37.9^{\circ}C = 235.25K \\
&\Delta H_{fus} = 2.33\tfrac{kJ}{mol} \\
&n = 63g\ Hg \times \frac{1mol\ Hg}{200.59g\ Hg} = 0.314mol\ Hg \\
&\Delta H_{phase\ change} = n\Delta H_{fus} = (0.314mol)(2.33\tfrac{kJ}{mol}) = 0.73162kJ = 731.62J \\
&\Delta S_{sys} = \frac{731.62J}{235.25K} = 3.11\tfrac{J}{K}
\end{aligned}}$$

ACTIVITY 3

The purpose of this activity is to recall your conceptual and quantitative understanding of the change in Entropy of the surroundings, ΔS_{sur}.

1. Write the equation for the change in entropy of the surroundings. Define each of the variables and give the units for each.

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

ΔS_{surr} is the change in entropy for the surroundings during a process usually given units of joules per Kelvin (J/K). ΔH_{sys} is the change in enthalpy for the ***system*** in units of joules (J). T_{surr} is the temperature of the surroundings in Kelvin (K).

2. If you know the heat flow in or out of the system at constant pressure, could you calculate the change in entropy of the surroundings (given the temperature of the surroundings)?

As we can see from the equation above the change in entropy for the surroundings is directly related to the change in enthalpy for the system. The change in enthalpy for the system is equivalent to the heat flow in or out of the system at constant pressure. So if you know the heat flow in or out of the system at constant pressure, you just need to change the sign of this ΔH_{sys} value and divide by the temperature of the surroundings.

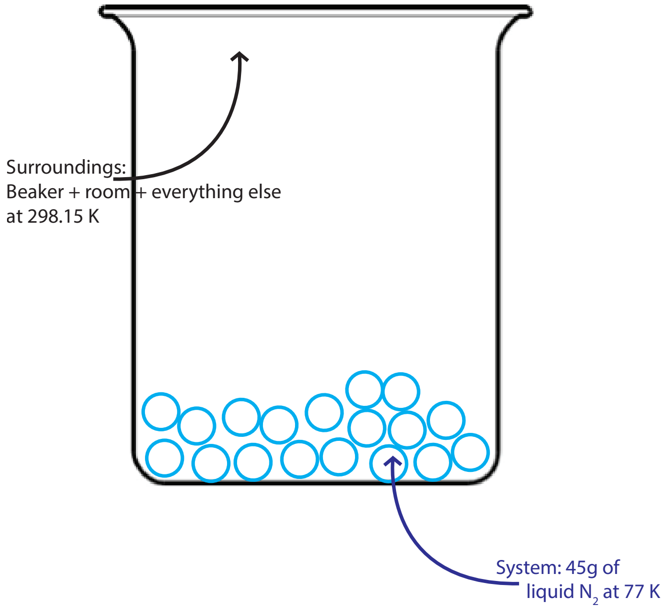
3. Calculate the ΔS_{sur} for the vaporization of 216 g of benzene (C_6H_6) if the surrounding temperature is 25.0 °C.

$$\begin{aligned}
&\Delta S_{surr} = \frac{-\Delta H_{sys}}{T_{surr}}\\
&T_{surr} = 25^{\circ}C = 298.15K\\
&m = 216g\ C_6H_6\\
&\Delta H_{sys} = m\Delta H_{vap}\\
&\Delta H_{vap} = 390\tfrac{J}{g}\\
&\Delta H_{sys} = (216g)(390\tfrac{J}{g}) = 84{,}240J\\
&\Delta S_{surr} = \frac{-\Delta H_{sys}}{T_{surr}} = \frac{-(84{,}240J)}{298.15K} \approx -282\tfrac{J}{K}
\end{aligned}$$

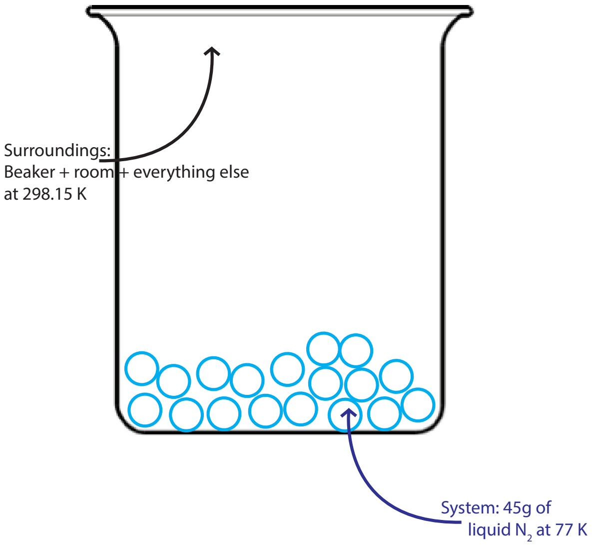
ACTIVITY 4

The purpose of this activity is to recall your conceptual and quantitative understanding of the change in Entropy of the universe for a common physical change.

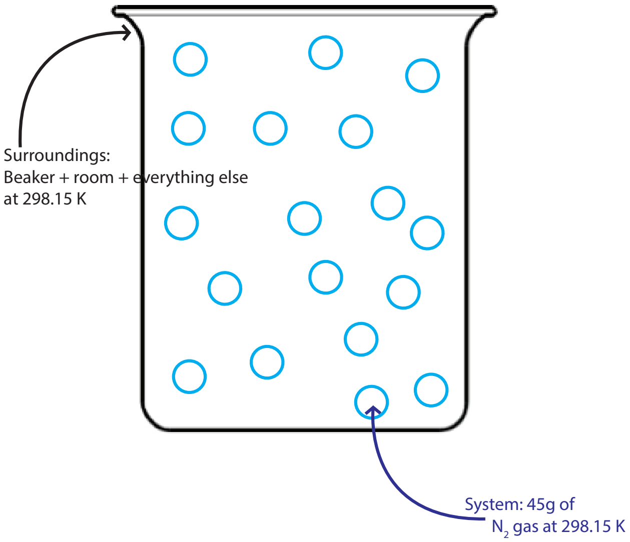
1. Imagine you start with a beaker that has **45 g** of liquid nitrogen. The initial temperature of the liquid nitrogen is 77 K. If you leave this beaker in a room that has a constant temperature of 25 °C, the liquid nitrogen will *spontaneously* boil and you will end up with all gaseous nitrogen at 25 °C. Here we will calculate the entropy change for the process of the liquid nitrogen boiling and increasing in temperature to 25 °C.
    a. First identify what the system and surroundings are. (what are they composed of, what is their temperature, etc…) Often it is helpful to make a sketch or diagram.



b. Now identify what the initial and final states of the system are. Again a diagram, equation, or sketch can be helpful. You should break this down into two steps: liquid nitrogen boiling, then the nitrogen gas warming up.



Initial



Final

c. Now look at the energy change for this process. Does energy flow into or out of the system? If so, as heat or work?

Energy flows into the system as heat.

d. Given that ΔH°_{vap}=5.92 kJmol^{-1} and that the heat capacity for nitrogen gas is 1.04 Jg^{-1}°K^{-1}. How much heat flows into the system for this process (in kJ)?

There are two steps in the overall process: boiling the liquid nitrogen and warming the gas. We need to calculate *q* for each of these steps and sum them to find the total amount of heat energy required to complete this process.

$$Boiling:$$

$$q_1 = n\Delta H^\circ_{vap}$$

$$\Delta H^\circ_{vap} = 5.92\,\tfrac{kJ}{mol}$$

$$n = 45g\ N_2 \times \frac{1mol\ N_2}{28g\ N_2} = 1.607mol\ N_2$$

$$q_1 = (1.607mol)(5.92\,\tfrac{kJ}{mol})$$

$$q_1 = 9.514kJ$$

$$Heating:$$

$$q_2 = mC_{s,N_2gas}\Delta T$$

$$q_2 = (45g)(1.04\,\tfrac{J}{gK})(298.15K - 77K)$$

$$q_2 = 10349.82J = 10.34982kJ$$

$$Total:$$

$$q_{sys} = q_1 + q_2 = 9.514kJ + 10.34982kJ = 19.86kJ$$

$$q_{sys} \approx 20kJ$$

e. What is the change in entropy for the boiling of the liquid nitrogen? What is the change in entropy for the warming of the nitrogen gas? What is the change in entropy for the system?

$$\boxed{\begin{aligned}
&Boiling:\\
&\Delta S_1 = \frac{q_1}{T_{Boiling}}\\
&\Delta S_1 = \frac{9.514kJ}{77K}\\
&\Delta S_1 = 0.12356\,\tfrac{kJ}{K} = 123.56\,\tfrac{J}{K}\\
&\\
&Heating:\\
&\Delta S_2 = mC_{s,water}\ln\left(\frac{T_{final}}{T_{initial}}\right)\\
&\Delta S_2 = (45g)(1.04\,\tfrac{J}{gK})\ln\left(\frac{298.15K}{77K}\right)\\
&\Delta S_2 = 63.36\,\tfrac{J}{K}\\
&\\
&Total:\\
&\Delta S_{sys} = \Delta S_1 + \Delta S_2 = 123.56\,\tfrac{J}{K} + 63.36\,\tfrac{J}{K} = 186.92\,\tfrac{J}{K}\\
&\Delta S_{sys} \approx 187\,\tfrac{J}{K}
\end{aligned}}$$

2. Now let’s consider the surroundings for this particular system.
    a. Did heat flow into or out of the surroundings during this change?

       Heat flowed out of the surroundings during this change.

    b. What is the entropy change for the surroundings?

$$\boxed{\begin{aligned}
&\Delta S_{surr} = \frac{-q_{sys}}{T_{surr}}\\
&q_{sys} = 19.86kJ\\
&\Delta S_{surr} = \frac{-19.86kJ}{298.15K} = -0.0666\,\tfrac{kJ}{K} = -66.6\,\tfrac{J}{K}\\
&\Delta S_{surr} \approx -67\,\tfrac{J}{K}
\end{aligned}}$$

3. Now let’s consider the entropy change for the universe for this process.
    a. What is the entropy change for the universe?

$$\boxed{\begin{aligned}
&\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}\\
&\Delta S_{univ} = 187\,\tfrac{J}{K} + (-67\,\tfrac{J}{K})\\
&\Delta S_{univ} = 120\,\tfrac{J}{K}
\end{aligned}}$$

b. Did you expect this process to have a + or – ΔS_{univ}? Why?

Because this process happened spontaneously, we expected ΔS_{univ} to be positive.

c. Is there a condition in which you would expect this process to not be spontaneous? If so what effect would such a condition have on the ΔS_{surr}?

Yes, if this process were occurring in colder surroundings (below the boiling temperature for nitrogen) it would not be spontaneous. In this case, the magnitude of ΔS_{surr} would be greater than the magnitude of ΔS_{sys} thereby making ΔS_{unvi} negative (non-spontaneous).