Guided Practice Activities

**Module**: Thermodynamics

**Section**: Third Law of Thermodynamics – *Key*
Absolute Entropy

**Activity 1**

The purpose of this activity is to check your understanding of the concept of absolute entropy.

1. Because at absolute 0 K, one can imagine a perfectly ordered system which means no positional disorder and, because there is no temperature there is no KE, which implies no thermal disorder, one can define an absolute scale for entropy. This reality leads to the third law of thermodynamics. Please state the third law of thermodynamics using words and an equation.

The third law of thermodynamics states that at absolute zero temperature, a perfect crystal will have an entropy of zero.

\[
\Delta S = S_{final} - S_{abs \ zero}
\]
\[
S_{abs \ zero} = 0 \frac{J}{K}
\]
\[
\Delta S = S_{final}
\]

2. Study the values of absolute entropy below. Explain why you think the different compounds, all at the same temperature, 298K, have different values of \( S^\circ \).

\[ \begin{align*}
C(\text{graphite}) & = 5.740 \text{ J/K mol} \\
C(\text{diamond}) & = 2 \text{ J/K mol} \\
C(\text{g}) & = 158 \text{ J/K mol} \\
\text{CH}_4 (\text{g}) & = 186 \text{ J/K mol} \\
\text{C}_2\text{H}_5\text{OH} (\text{l}) & = 161 \text{ J/K mol}
\end{align*} \]

At 298K, these different materials have very different structures. First of all, two of these substances are gases. These substances have large positional disorder values. The liquid has a larger positional disorder than either of the solids but a lower positional disorder than either of the gases. The two solids are very similar, but diamond has a more rigid structure than graphite, which is why diamond has a smaller absolute entropy value.

**Activity 2**

The purpose of this activity is to further develop your understanding of the concept of positional entropy from a molecular point of view.

1. Define microstates in the context of positional entropy.

Microstates are possible configurations of the energy in a system. A system with high positional entropy has a high number of microstates.
2. Consider a gas in a divided container. On one side is the gas and on the other side is no gas (a vacuum). Draw the image.

![Image of divided container with gas on one side and no gas on the other side.]

3. Remove the divider and redraw the image. Describe what happened to your gas.

![Image of the same divided container without the divider, showing the gas spread across the volume.]

The gas particles spread out across the volume.

4. If each place that each gas particle could be on one side of the container was considered a microstate, then are there more or less microstates available when the divider is removed? Please explain.

When the divider is removed there are more microstates. There are more possible configurations available to the molecules across the larger volume.

5. Would you consider the above process to be spontaneous? If so, what must be true about the $\Delta S_{\text{univ}}$? What about the $\Delta S_{\text{sys}}$? What about the $\Delta S_{\text{surr}}$?

Yes. Gases spontaneously diffuse throughout a space. Therefore, $\Delta S_{\text{univ}}$ must be positive. The change in entropy of the system is also positive because there are more available microstates when the gas has diffused. The change in entropy of the surroundings could be positive or negative but is likely close to zero. The process of diffusion doesn’t carry a significant associated change in enthalpy of the system – the molecules are already in the gas phase with essentially no intermolecular forces between them. When they spread out there are still no intermolecular forces between them. The $\Delta H$ for this process is negligible, so the change in entropy for the surroundings is also negligible.
**ACTIVITY 3**

The purpose of this activity is to explore the equation associated with calculating absolute entropy.

1. In 1877 Ludwig Boltzmann proposed a molecular definition of entropy that enables one to calculate the absolute entropy of a given system at any temperature. Please write that equation here.

   \[ S = k \ln(\Omega) \]

2. Please explain each term in the equation.

   - \( S \) is the entropy of an atom or molecule with units of joules per Kelvin (J/K).
   - Boltzmann's constant, \( k \), is a constant with units of joules per Kelvin (J/K).
   - \( \Omega \) is the number of microstates associated with molecule in its current state and this variable carries no units.

3. Write the equation replacing "\( k \)" with "\( R \)" and explain the significance of this form of the equation.

   \[ S = R \ln(\Omega) \]

   By replacing \( k \) with \( R \), this equation now calculates absolute entropy per mole of a substance!

4. Calculate the entropy of a sample of a solid in which the molecules can take any one of three orientations with the same energy. Suppose there are 30 molecules in the sample.

   We need to determine the number of microstates these molecules can have. Each molecule has the opportunity take one of three positions. Therefore, each molecule has three microstates. With 30 molecules overall, there are \( 3^{30} \) possible orientations overall (\( \Omega \)). We are not calculating a per mole value so we will use \( k \) not \( R \).

   \[ S = k \ln(\Omega) \]
   \[ k = 1.38 \times 10^{-23} \frac{J}{K} \]
   \[ \Omega = 3^{30} \]
   \[ S = (1.38 \times 10^{-23} \frac{J}{K}) \ln(3^{30}) \]
   \[ S = 4.55 \times 10^{-22} \frac{J}{K} \]
Change in Entropy from Absolute Entropy

**Activity 1**

The purpose of this activity is to test your ability to compute $\Delta S$ from $S^\circ$ tabulated data.

1. Write a working equation for computing $\Delta S_{\text{rxn}}$ from standard molar entropies.

   \[ \Delta S_{\text{rxn}} = \sum nS_{\text{prod}}^\circ - \sum nS_{\text{react}}^\circ \]

2. Use the equation to determine the $\Delta S_{\text{rxn}}$ for the combustion of 1 mole $H_2$ ($g$) at room temperature. You will need to look up the $S^\circ$ values from a thermodynamic table.

   First we need to write the balanced equation for the combustion of 1 mole of $H_2$ gas:

   \[ H_2 (g) + \frac{1}{2}O_2 (g) \rightarrow H_2O (l) \]

   We need to look up the absolute entropies of $H_2$ gas, $O_2$ gas and $H_2O$ liquid at room temperature.

   \[
   \begin{align*}
   \Delta S_{\text{rxn}} &= \sum nS_{\text{prod}}^\circ - \sum nS_{\text{react}}^\circ \\
   S_{H_2(g)}^\circ &= 131 \frac{J}{mol K} \\
   S_{O_2(g)}^\circ &= 205 \frac{J}{mol K} \\
   S_{H_2O(l)}^\circ &= 70 \frac{J}{mol K} \\
   \Delta S_{\text{rxn}} &= \left[ (1 mol)(S_{H_2O(l)}^\circ) \right] - \left[ (1 mol)(S_{H_2(g)}^\circ) + \left( \frac{1}{2} mol \right)(S_{O_2(g)}^\circ) \right] \\
   &= \left[ (1 mol)(70 \frac{J}{mol K}) \right] - \left[ (1 mol)(131 \frac{J}{mol K}) + \left( \frac{1}{2} mol \right)(205 \frac{J}{mol K}) \right] \\
   &= (70 \frac{J}{K}) - (233.5 \frac{J}{K}) \\
   \Delta S_{\text{rxn}} &= -163.5 \frac{J}{mol K} 
   \end{align*}
   \]

**Activity 2**

The purpose of this activity is to test your ability to compute $\Delta S_{\text{rxn}}$ from $S^\circ$ tabulated data, compute the $\Delta S_{\text{sur}}$ and predict the spontaneity of a chemical change.

1. Consider the system in Activity 1, above. Given that $\Delta H_f^\circ (H_2O)l = -286$ kJ/mol, determine the change in entropy for the surroundings for this change under standard conditions.
The equation for the combustion of exactly 1 mole of hydrogen is actually the formation reaction of one mole of water! So the $\Delta H^\circ$ value for the formation of water is the $\Delta H_{\text{rxn}}$.

$$\Delta S_{\text{sur}} = -\frac{q_{\text{sys}}}{T_{\text{sur}}}$$

$$\Delta S_{\text{sur}} = \frac{-\Delta H_{\text{sys}}}{T_{\text{sur}}} = \frac{-\Delta H_{\text{rxn}}}{T_{\text{sur}}}$$

$q_{\text{sys}} = \Delta H_{\text{sys}} = \Delta H_{\text{rxn}} = -286 \text{ kJ/mol}_\text{rxn} = -286,000 \text{ J/mol}_\text{rxn}$

$$\Delta S_{\text{sur}} = \frac{-286,000 \text{ J/mol}_\text{rxn}}{298.15 K}$$

$$\Delta S_{\text{sur}} = 959.2 \frac{\text{J}}{\text{mol}_\text{rxn} \cdot K}$$

2. What is the $\Delta S_{\text{univ}}$ for this particular change, the combustion of 1 mole of H$_2$(g) at room temperature?

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

$$\Delta S_{\text{univ}} = -163.5 \frac{\text{J}}{\text{mol}_\text{rxn} \cdot K} + 959.2 \frac{\text{J}}{\text{mol}_\text{rxn} \cdot K}$$

$$\Delta S_{\text{univ}} = 795.7 \frac{\text{J}}{\text{mol}_\text{rxn} \cdot K}$$

3. Is this change spontaneous or nons spontaneous? Why or why not?

Yes, this change is spontaneous because the change in entropy of the universe for this process is positive. The entropy of the universe increases during this combustion under standard conditions and therefore the reaction is spontaneous.