Supplemental Activities

Module: Thermodynamics

Section: Third Law of Thermodynamics – Key

Absolute Entropy

ACTIVITY 1

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

1. At absolute zero Kelvin we can consider a perfectly ordered system. In this perfectly ordered system, there is no positional disorder, temperature or kinetic energy meaning no thermal disorder. In this perfect state we can define an absolute scale for entropy. This theoretical system gives us an understanding of the third law of thermodynamics.

2. Which compound would you expect to have the lowest absolute entropy of the given pairs? Explain your choice.
   a. Br_2 (l) or Br_2 (g)?

      Bromine liquid has a lower absolute entropy because gases have greater positional disorder than their liquid phases.

   b. C (s) graphite or C (s) diamond?

      Diamond has a lower absolute entropy. A simpler structure than graphite and can form a more perfect crystal than graphite. Diamond is comprised of tetrahedral carbon atoms covalently bonded to other tetrahedral carbon atoms. Graphite is comprised of sheets of trigonal planar carbons bonded together in rings and the sheets are held together by IMFs.

   c. Fe_2O_3 (s) or Fe_3O_4 (s)?

      Iron (III) oxide (Fe_2O_3) has a lower absolute entropy because it has fewer atoms to arrange. This gives Fe_2O_3 lower positional disorder than Fe_3O_4.

   d. NH_3 (g) or NH_3 (aq)?

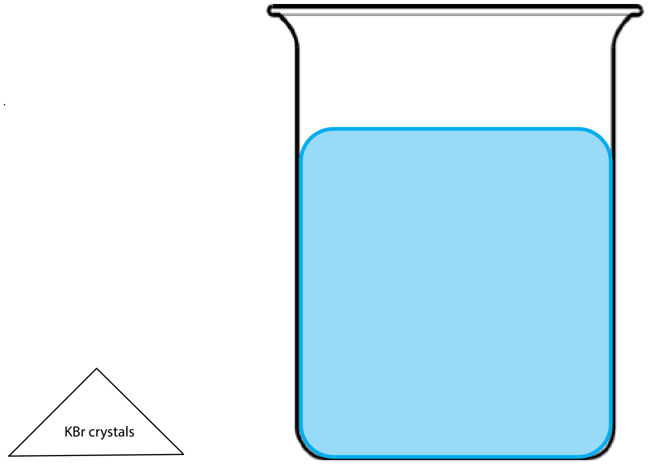
      Aqueous ammonia has a lower absolute entropy than gaseous ammonia. When dissolved in water, the interactions between ammonia and water give the ammonia lower positional disorder than gaseous ammonia.

ACTIVITY 2

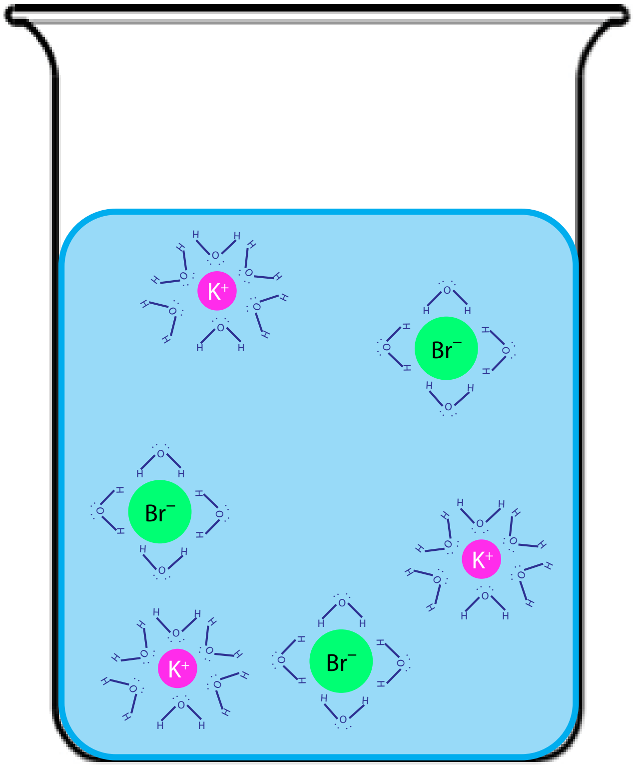
The purpose of this activity is to further develop your understanding of the concept of positional entropy from a molecular point of view.

1. A system with high positional entropy has many/a lot microstates, which are all the possible configurations/arrangements of energy in a system

2. Consider a small amount of potassium bromide (white crystalline solid) and a beaker of water. Draw these images.



3. Now dissolve the KBr into the beaker of water. Describe what happened to your salt.



The ionic crystals dissolved into ions K^+ and Br^- throughout the water. Water molecules arranged themselves around the ions.

4. Are there more or less microstates available when the salt is dissolved? Please explain.

When the salt is dissolved there are more microstates. There are more possible configurations available to the ions within the water than within their crystal lattice.

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

Yes. Many small amounts of ionic substances dissolve in room temperature water. Potassium salts are always soluble.Therefore, ΔS_{univ} must be positive. The change in entropy of the system is also positive because there are more available microstates when the salt has dissolved. The change in entropy of the surroundings could be positive or negative but is likely close to zero. The process of dissolution doesn't carry a significant associated change in enthalpy of the system in this case – the water surrounds the ions so while the water-water IMFs are interrupted water-ion interactions from. The ΔH for this process is likely negligible, so the change in entropy for the surroundings is also negligible.

ACTIVITY 3

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

1. What is the equation to calculate absolute entropy of a particular sample (not per mole)? Define each of the variables and give units for each.

$$\boxed{S = k\ln(\Omega)}$$

S is the absolute entropy of a molecule and it usually has units of joules per Kelvin (J/K). k is Boltzmann's constant it has the same units as entropy – joules per Kelvin (J/K). Ω represents the number of microstates and has no units.

2. What is the equation to calculate absolute entropy of a mole of a substance? Define each of the variables and give units for each.

$$\boxed{S = R\ln(\Omega)}$$

S is the absolute entropy of a mole of a substance and it usually has units of joules per mole per Kelvin (J/molK). R is the universal gas constant it has the same units as entropy – joules per mole per Kelvin (J/molK). Ω represents the number of microstates and has no units.

3. Calculate the number of microstates **and** the number of molecules of a sample of a solid in which the molecules can take any one of three orientations with the same energy and the absolute entropy is 6.58051 x 10^{-22} J/K

   We need to determine the number of microstates these molecules can have. Each We are not given a per mole value so we will use *k* not *R*.

$$\boxed{\begin{aligned}
&S = k\ln(\Omega)\\
&k = 1.38\times10^{-23}\,\tfrac{J}{K}\\
&S = 6.58051\times10^{-22}\,\tfrac{J}{K}\\
&6.58051\times10^{-22}\,\tfrac{J}{K} = (1.38\times10^{-23}\,\tfrac{J}{K})\ln(\Omega)\\
&\ln(\Omega) = 47.685\\
&\Omega = e^{47.685} = 5.12\times10^{20}\,microstates\\
&molecules = \sqrt[3]{\Omega} = \sqrt[3]{5.12\times10^{20}} = 8.0\times10^{6}\,molecules
\end{aligned}}$$

Change in Entropy from Absolute Entropy

ACTIVITY 1

The purpose of this activity is to practice your ability to compute *ΔS* from *S*° tabulated data.

1. Use the equation to determine the ΔS_{rxn} for the combustion of 1 mole of diamond (C (s, diamond)) at room temperature.   You will need to look up the *S*° values from a thermodynamic table.

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

   $$\mathrm{C\ (s,\ diamond)} + \mathrm{O_2\ (g)} \rightarrow \mathrm{CO_2\ (g)}$$

   We need to look up the absolute entropies of diamond, O_2 gas and CO_2 gas at room temperature.

$$
\begin{aligned}
\Delta S_{rxn} &= \sum nS^{\circ}_{prod} - \sum nS^{\circ}_{react} \\
S^{\circ}_{C(s,diamond)} &= 2\,\tfrac{J}{molK} \\
S^{\circ}_{O_2(g)} &= 205\,\tfrac{J}{molK} \\
S^{\circ}_{CO_2(g)} &= 213.74\,\tfrac{J}{molK} \\
\Delta S_{rxn} &= \left[(1mol)(S^{\circ}_{CO_2(g)})\right] - \left[(1mol)(S^{\circ}_{C(s,diamond)}) + (1mol)(S^{\circ}_{O_2(g)})\right] \\
\Delta S_{rxn} &= \left[(1mol)(213.74\,\tfrac{J}{molK})\right] - \left[(1mol)(2\,\tfrac{J}{molK}) + (1mol)(205\,\tfrac{J}{molK})\right] \\
\Delta S_{rxn} &= (213.74\,\tfrac{J}{K}) - (207\,\tfrac{J}{K}) \\
\Delta S_{rxn} &= +6.74\,\tfrac{J}{molrxn \cdot K}
\end{aligned}
$$

ACTIVITY 2

The purpose of this activity is to practice your ability to compute ΔS_{rxn} from $S°$ tabulated data, compute the ΔS_{sur} and predict the spontaneity of a chemical change.

1. Consider the system in Activity 1, above. Given that $\Delta H_f°(CO_2(g))]$ = −393.51 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 diamond is actually the formation reaction of one mole of carbon dioxide gas! So the ΔH_f° value for the formation of carbon dioxide is the ΔH_{rxn}.

$$
\begin{aligned}
\Delta S_{surr} &= \frac{-q_{sys}}{T_{surr}} \\
\Delta S_{surr} &= \frac{-\Delta H_{sys}}{T_{surr}} = \frac{-\Delta H_{rxn}}{T_{surr}} \\
q_{sys} = \Delta H_{sys} = \Delta H_{rxn} &= -393.51\,\tfrac{kJ}{molrxn} = -393{,}510\,\tfrac{J}{molrxn} \\
\Delta S_{surr} &= \frac{-(-393{,}510\,\tfrac{J}{molrxn})}{298.15K} \\
\Delta S_{surr} &= 1319.84\,\tfrac{J}{molrxn \cdot K}
\end{aligned}
$$

2. What is the ΔS_{univ} for this particular change, the combustion of 1 mole of diamond at room temperature?

$$
\begin{aligned}
\Delta S_{univ} &= \Delta S_{sys} + \Delta S_{surr} \\
\Delta S_{univ} &= 6.74\,\tfrac{J}{molrxn \cdot K} + 1319.84\,\tfrac{J}{molrxn \cdot K} \\
\Delta S_{univ} &= 1326.58\,\tfrac{J}{molrxn \cdot K}
\end{aligned}
$$

3. Is this change spontaneous or nonspontaneous? 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.

So take note that the combustion of diamond is spontaneous at room temperature!!! Later on in chemistry, you'll learn why your diamonds are still safe to wear and use.