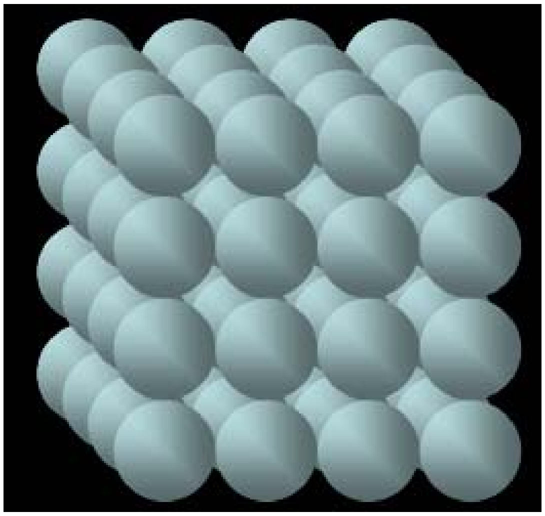
Sections 18.3 - 18.4: Entropy and the Boltzmann Formula

The entropy is a property that measures the disorder in a system. To better understand the concept of entropy, we first discuss the very famous equation proposed in 1877 by Ludwig Boltzmann.

The **Boltzmann equation** states that: $S = k \times \ln(W)$

where S is the entropy of the system, k, the Boltzmann constant, is the ratio of the gas constant, R, to Avagadro's number, N_a. ln is the natural logarithm, and W is the number of ways in which the atoms, ions or molecules of a system can be arranged without changing the system's energy.

For example: Consider a crystal of CCl_4 at 0 K:

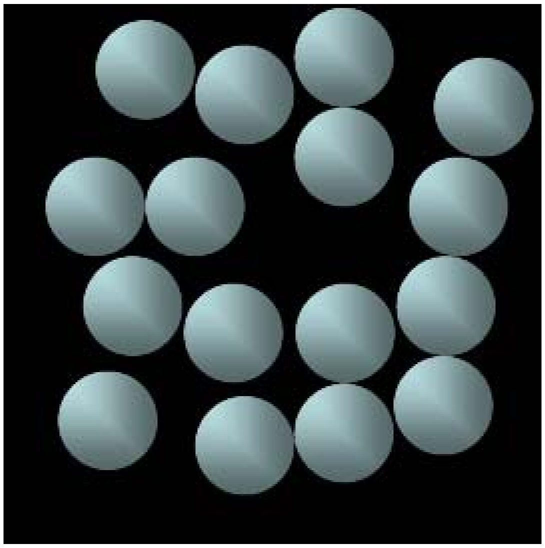


CCl_4 molecules are represented as spheres.

The crystal is represented as a three dimensional periodic array of CCl_4 molecules. At 0 K, a crystal is so perfectly ordered that there is only one way to arrange its components. When any two CCl_4 molecules switch positions, the crystal is still the same, because CCl_4 molecules are indistinguishable.

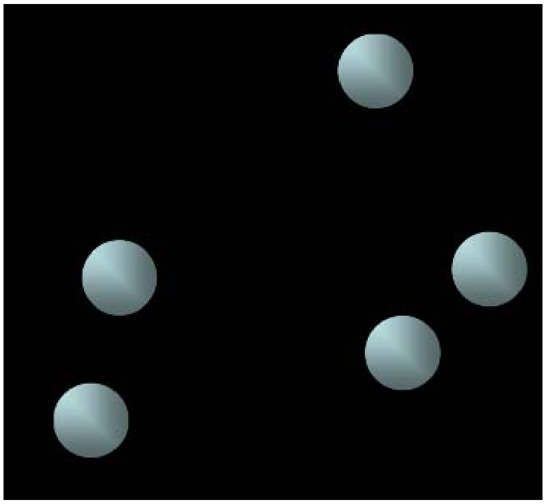
Hence, $W = 1$ and $S = k \times \ln(1) = 0$. The statement that the entropy of a perfectly ordered crystalline solid is equal to 0 at 0 K is known as the **Third Law of Thermodynamics**.

Now, consider CCl_4 in the liquid state:



In the liquid state, CCl_4 molecules do not pack orderly. The liquid state is usually less dense than the solid state. There is more empty space between molecules. Hence, molecules can occupy different sites. Since there are more ways to arrange these molecules in the liquid state than in the crystal state, $W > 1$ and $S > 0$.

Now, consider CCl_4 in the gas state:



The gas state is less dense than the liquid state. Hence, there is even more empty space between molecules in the gas state than in the liquid state. Since there are many many more ways to arrange these molecules in the gas state than in the liquid state, $W_{(gas)} >> W_{(liquid)}$ and $S_{(gas)} >> S_{(liquid)}$.

In summary:

<u>Crystal State</u>		<u>Liquid State</u>		<u>Gas State</u>
Order in crystal	>	Order in liquid	>>	Order in gas
Entropy of a solid	<	Entropy of a liquid	<<	Entropy of a gas

Hence, the entropy depends on the physical state of matter.

The entropy of matter also varies with:

1. Amount of Matter

The entropy of matter increases proportionally with the amount of matter. Hence, we define the **molar entropy** of a substance as the entropy of one mole of that substance. Molar entropy is expressed by the symbol, S_m. If a substance contains "n" moles, its entropy, S, is calculated as: $S = n \times S_m$.

2. Temperature

As a substance is heated, its particles (atoms, molecules or ions) exhibit a larger range of energies, motions and positions. Hence, the particles of a substance can be arranged in a more diverse fashion when the temperature is increased (larger W). As a result, the entropy of a pure substance always increases with increasing temperature.

3. Pressure

As a substance is compressed at constant temperature, its volume decreases (Boyle's Law for gases). Hence, increasing the pressure leads to a decrease in the number of possible sites that the particles of that substance may occupy. Thus, increasing the pressure leads to a decrease in the number of possible arrangements for the particles of that substance (lower W). Hence, increasing pressure lowers the entropy at constant temperature.

4. Structure of Matter

The entropy of a substance increases with the size of its constituents. For example, consider the following group 2 metals at 25°C and 1 atm.

$$Be_{(s)}, Mg_{(s)}, Ca_{(s)}, Sr_{(s)}, Ba_{(s)}$$

Their molar entropies are, respectively:

$$9.5 < 32.7 < 41.6 < 54.4 < 62.5 \ (J.K^{-1}.mol^{-1})$$

Hence, in a group the molar entropy increases from top to bottom.

Now, consider the following gases at 25° C and 1 atm.

$CH_{4\ (g)}$, $C_2H_{6\ (g)}$, $C_3H_{8\ (g)}$, $C_4H_{10\ (g)}$, $C_5H_{12\ (g)}$

Their molar entropies are, respectively:

$$183.6 < 229.6 < 270.2 < 310.1 < 349.0\ (J.K^{-1}.mol^{-1})$$

The molar entropy of molecules increases with their size because larger molecules have more chemical bonds and can store energy in more ways than smaller molecules.

Hence, the entropy depends on temperature, pressure, physical state, amount and structure of matter. In examples discussed earlier, we compared the molar entropy of substances in the same physical state (either solids, liquids or gases).

Hence, remember that the entropy of a substance is primarily controlled by the physical state of that substance (solid, liquid or gas) and to a smaller extent by the size or complexity of the substance.

For example, consider benzene (C_6H_6) and methane (CH_4) at 25^oC. The standard molar entropies of C_6H_6 and CH_4 are 173.3 and 186.3 $J.K^{-1}.mol^{-1}$, respectively. While benzene is a larger molecule than methane, at 25^oC benzene is a liquid, hence, it has a lower molar entropy than methane, which is a gas at the same temperature.

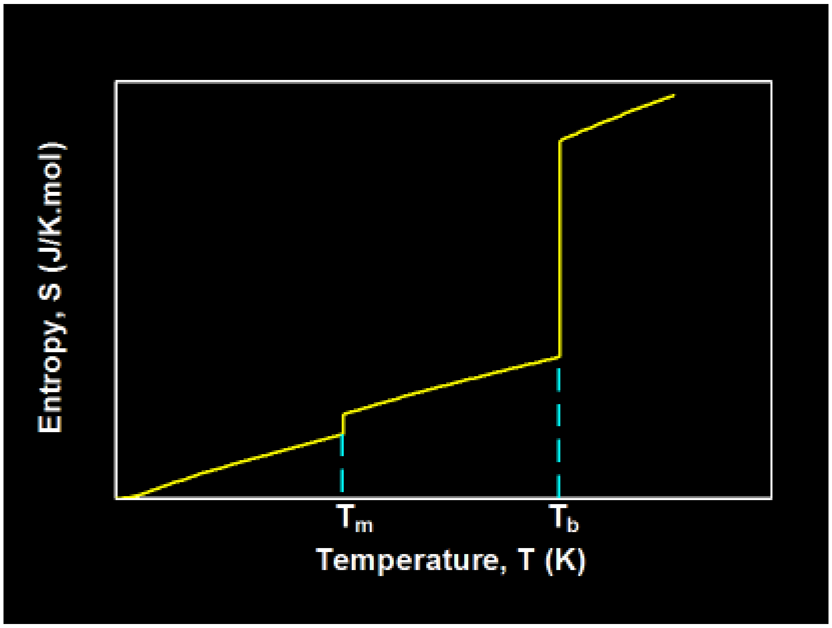
When comparing entropies of substances or calculating the change in entropy for a reaction, we always use **standard molar entropies**. Standard molar entropies are expressed with the symbol S^o_m.

Recall the definition of **standard states**:

For gases: pure gas at 1 atmosphere,
For solutions: solute at 1 M concentration,
For liquids: pure liquid,
For solids: pure solid in its most stable form.

The S.I. unit for entropy is joule per kelvin or J/K. The S.I. unit for molar entropy and standard molar entropy is joule per kelvin per mol, J/(K.mol) or $J.K^{-1}.mol^{-1}$.

In the figure below, we show the change in the standard molar entropy of a typical substance, as it is heated from low temperatures, where the substance is a solid, to high temperatures, where the substance is a gas.



Note the steady increase in the standard molar entropy with increasing temperature for:

1. the solid crystal phase between 0 K and the melting point, T_m.
2. the liquid phase between the melting point, T_m, and the boiling point, T_b.
3. the gas phase above the boiling point, T_b.

Note the large increase in the standard molar entropy at the melting point, T_m, where the crystalline solid transforms into a liquid. The change in entropy at T_m between the solid and the liquid is called the **entropy of melting** or **entropy of fusion**. The entropy of melting is denoted by $\Delta S^o_{melting}$ and is defined by:

$$\Delta S^o_{melting} = S^o_m \text{ (liquid)} - S^o_m \text{ (crystal)}$$

Note the dramatic increase in the standard molar entropy at the boiling point, T_b, where the substance transforms from a liquid into gas. The large change in entropy at T_b between one mole of liquid and one mole of gas is called the **entropy of vaporization**. The standard entropy of vaporization is denoted by ΔS^o_{vap} and defined by:

$$\Delta S^o_{vap} = S^o_m \text{ (gas)} - S^o_m \text{ (liquid)}$$