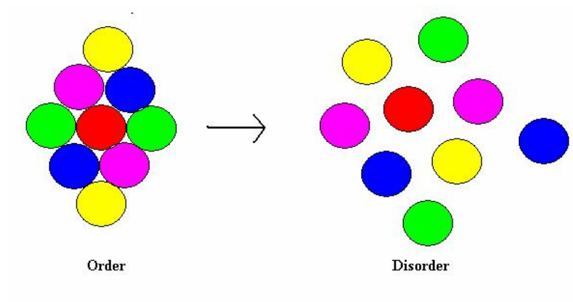
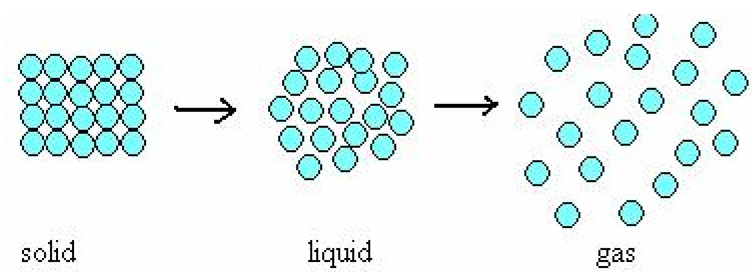
**Entropy**

It is clear from the previous section that the change in enthalpy is not enough to predict the spontaneity of a chemical process. We need another quantity known as entropy. **Entropy** (symbol S is used to indicate it) *is a measure of disorder or randomness of the system.* The greater the disorder of the system, the greater is the entropy; smaller the disorder of the system, smaller is the entropy. Therefore, the entropy increases going from order system to disorder system. Let us illustrate the order and disorder concept using a stack of books; when the books are stacked on top of each other in a proper way, it is an order, and when these stacked books are scattered around, it is a disorder. Similarly, when balls are arranged in a particular order, it is an ordered system and when they are scattered around, it is a disorder system:




Less entropy More entropy

As you know, there are three states of matter, solid, liquid, and gaseous- that exist in different entropic states. In general, the solids are more order and hence have less entropy, liquids are more disorder compared to solids, and hence have more entropy, and gases are much more disorder compared to liquids, and hence have much more entropy.

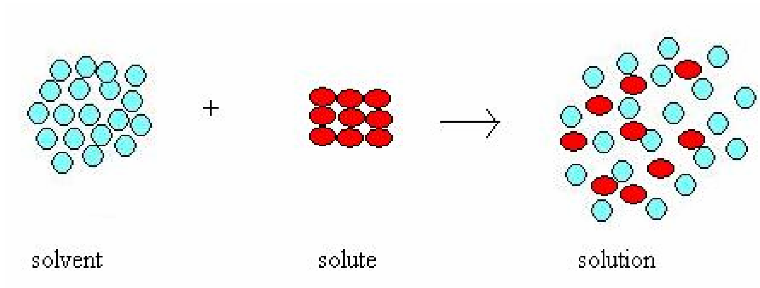



Example: ice → water → vapor

Thus, the entropy increases from solid state to gaseous state due to an increase in randomness due to an increase in kinetic energy of the molecules. Therefore, we can say that

$$S_{solid} < S_{liquid} < S_{gas}$$

Another example of increase in entropy would be the dissolution of a solute in a solvent;

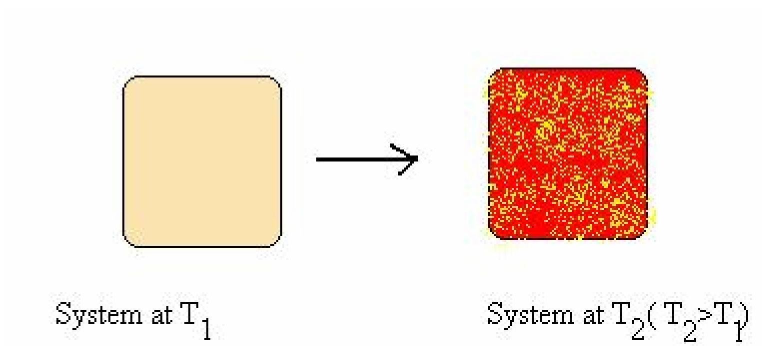



Example: Water + table salt → salt solution

Both solvent and solute have ordered state and due to that they have less entropy. When the solute is dissolved in the solvent, the disorder of the system (solution) increases due to an increase in number of collisions between solute and solvent molecules that increases in entropy.

$$S_{solvent} < S_{solution} \text{ and } S_{solute} < S_{solution}$$

If the same system exists at different temperatures, it has different entropies; lower the temperature, lower the entropy and higher the temperature, higher the entropy.




Example: water at $25^0$ C → water at $90^0$ C

The system at lower temperature ($T_1$) is more order because of less kinetic energy and hence it has less entropy. If the system is heated to a higher temperature $T_2$, its kinetic energy increases that increases the disorder and hence its entropy increases.

Entropy of system at $T_1$ < Entropy of system at $T_2$

**Example**

How does the entropy of the system change (decreases or increases) in the followings? (a) melting an ice, (b) freezing a water, (c) subliming the dry ice (solid $CO_2$), (d) boiling water to make a cup of tea, (e) cooling a gas from $80^0$ C to $25^0$ C.

**Answer**

(a) entropy increases ( system becomes more disorder) , (b) entropy decreases (system becomes more order), (c) entropy increases(system becomes more disorder), (d) entropy increases (system becomes more disorder), (e) entropy decreases(system becomes less disorder)

The above examples illustrate the qualitative way of understanding what happens to the entropy when the system goes from one state to another state. Very often, we are interested to know the change in entropy of the system going from one state to another in a qualitative manner. In that case, we use terminology of change entropy ($\Delta S$) that is given by

$$\Delta S = S_{\text{final state}} - S \text{ initial state} = S_f - S_i$$

There are three possibilities for this equation:

| | | | | |
|---|---|---|---|---|
| If | $\Delta S = 0$, | means $S_f = S_i$ | → | no change in entropy |
| | $\Delta S > 0$, | means $S_f > S_i$ | → | final state has more entropy than initial state ( system becomes more disorder) |
| | $\Delta S < 0$, | means $S_f < S_i$ | → | final state has less entropy than initial state(system becomes less disorder) |

**Example**

Predict whether the entropy change is greater or less than zero for each of the following processes; (a) dissolving a sugar in water, (b) freezing oxygen gas, (c) letting the gas out of the gas cylinder, (d) chopping vegetables, (e) lowering hot water temperature from $100^0$ C to $60^0$ C.

**Answer**

(a) $\Delta S > 0$, (b)$\Delta S < 0$, (c) $\Delta S > 0$, (d) $\Delta S > 0$, (e) $\Delta S < 0$

**Standard Entropy**

**Standard entropy** is *the absolute entropy of a substance at 1 atm and $25^0$ C,* the unit of which is J/K. mol. It is interesting to note that it is possible to determine the absolute entropy of a substance, which we couldn't do for enthalpy. Just to give an idea, few standard enthalpies are given in the following table. For more extensive data, you may refer to any standard general chemistry textbook.

| **Substance** | **$S^0$ (J/K.mol)** | **Substance** | **$S^0$ (J/K.mol)** |
|---|---|---|---|
| C (graphite) | 5.69 | Acetic acid(l) | 159.8 |
| C(diamond) | 2.4 | Acetone(l) | 198.7 |
| $H_2O$(g) | 188.7 | Benzene(l) | 172.8 |
| $H_2O$(l) | 69.9 | Ethanol(l) | 161.04 |
| $O_2$(g) | 205.0 | Glucose(s) | 212.1 |
| $O_3$ g) | 237.6 | Methane (g) | 186.19 |
| S(rhombic) | 31.88 | Methanol (l) | 126.78 |
| S(monoclinic) | 32.55 | Sucrose (s) | 460.24 |

In the first column, I have listed only allotropic forms. It is interesting to note their differences; diamond is more order than graphite, water is more order than water vapor, oxygen gas is more order than ozone, and sulfur in rhombic form is a little more order than its monoclinic form.

In the third column, I have given some organic substances, whose entropies depend on their molecular structure as well as their physical states.

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