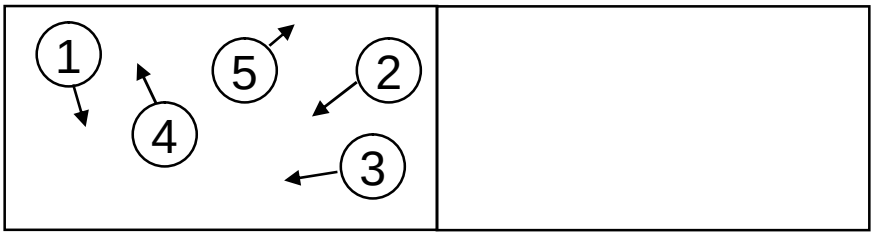
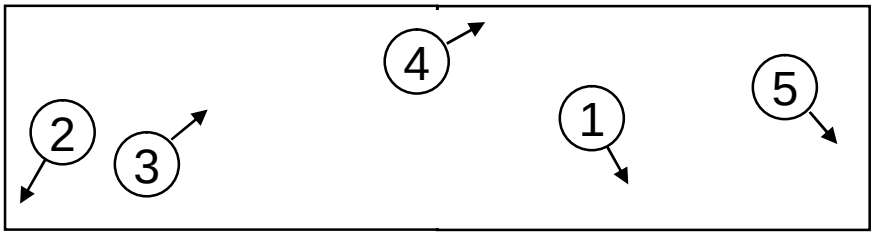
Entropy – Spontaneous processes happen by chance!



Above: A container has five molecules of a certain gas inside it. All of them are in the left-hand side of the container as a partition is preventing them from passing into the right-hand side. The molecules move along in straight lines until they bounce off the walls, partition or each other – their motion soon becomes hard to predict!



Above: the partition is removed and some of the gas molecules drift into the right-hand side of the chamber. The molecules continue to collide with the walls and each other, changing direction (and speed) as they do so and so they continue to pass at random between the left and right-hand parts of the chamber.

Q. Why does the gas expand to fill the whole chamber?

Since the process is random, chance determines in which half of the chamber each molecule will be found at any given instant in time. The probability that all five molecules will be found ***either*** in the left-hand half ***or*** in the right-hand half of the chamber is 1 in 2^5 = 1 in 32. This is unlikely and so the gas expands to fill both halves of the chamber as this is more likely!

Consider if we had one mole of gas in our chamber, what then would be the likelihood of finding the whole of the gas in only one half of the chamber? Gases fill all available space since probability dictates that they probably will!

The most probable events are those in which the number of ways in which they can occur is greatest.

Why do liquids mix?

•Take half a jar of roasted peanuts and pour half a jar of roasted cashew nuts on top. Now you have two different layers of nuts. Shake the jar and the nuts will mix!

•How long must you shake the jar until the nuts un-mix by chance to give you two separate layers again?!

•There are more ways of being mixed than unmixed and so mixing is highly likely!

•This is why some liquids mix!

Q. Oil and water or petrol and water do not mix, why?

A. In real liquids there are intermolecular forces. If the forces between the molecule of one liquid are much stronger than those in the other liquid, then molecules will not easily pass between the two liquids as the molecules in the first liquid cannot easily separate. ***It's as if your roasted peanuts were glued together by honey***!

Substances always tend to mix unless there is something stopping them.

So what is entropy?

Entropy (S) is a tricky concept (!) but it can be understood as a measurement of the number of ways – the greater the number of ways the higher the entropy.

Thus entropy is a measure of the disorder of the system – the more spread-out, mixed or disordered a system is, the higher is its entropy. This is the statistical definition of entropy.

Later on you will come across a more meaningful definition of entropy as a measure of the number of ways of distributing packets or quanta of energy among molecules.

Entropy and the spontaneity of change

•Entropy is a measure of how likely a given state of a system is.

•A system may change spontaneously from a low probability state (all the gas in one-half of the chamber) to a highly probably state (the gas evenly spread-out).

•Entropy thus indicates which changes, including chemical reactions, can occur spontaneously.

But: enthalpy also indicates this – exothermic reactions can occur spontaneously (with sufficient activation energy) whereas endothermic reactions require an input of energy.

The following reaction is endothermic but occurs spontaneously at room temperature, why?

$$HCl(aq) + NaHCO_3(s) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g), \qquad \Delta H > 0$$

Because the increase in entropy outweighs the positive ΔH! The Gibbs free energy change incorporates both enthalpy and entropy changes and indicates the spontaneity of a reaction.

A process can only occur if the total entropy of the Universe increases or remains unchanged!