ENTROPY

In everyday language *spontaneous* is defined as 'performed or occurring as a result of a sudden impulse or inclination and without premeditation or external stimulus'. An example: "the audience broke into spontaneous applause".

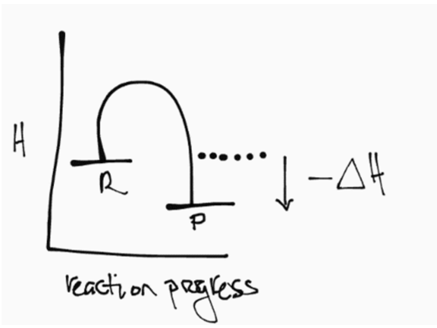
In Chemistry, a spontaneous reaction is one that favours the formation of products, under the conditions at which the reaction is occurring. The reaction *may* need an input of energy to get the reaction started but then it proceeds without the need to be driven by a continual input of energy e.g. the burning (combustion) of a piece of wood is spontaneous once the wood is heated to a high enough temperature. Spontaneity has nothing to do with the rate of a reaction, and both fast and slow reactions can be spontaneous.

- An explosion is a very fast spontaneous reaction.
- The corrosion (rusting) of iron is a slow spontaneous reaction.

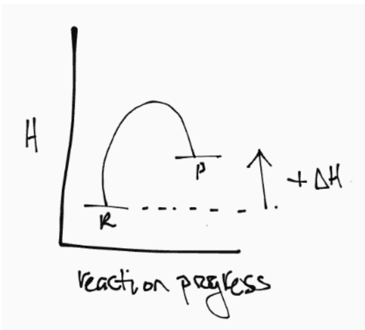
To understand whether reactions are spontaneous or not, we need to consider both enthalpy and entropy changes.

Enthalpy is represented by H, and a change in enthalpy by ΔH.

Most spontaneous reactions are exothermic. The decrease in enthalpy drives the reaction as the products are in a lower energy state, a state that is more energetically stable.



Since endothermic reactions result in a gain of enthalpy and products are in a less energetically stable state, spontaneous endothermic reactions are much less likely.



But the fact that some endothermic reactions are spontaneous is due to the fact that there is another factor 'driving' the reaction. This factor is entropy.

Entropy is hard to define and explain at this level of Chemistry but it can be considered as a measure of the random motion of particles or the dispersal of matter and energy or as a measure of the disorder. Whether a chemical reaction (or process such as a phase change like melting or a chemical dissolving in water) is spontaneous depends on the **total entropy change** accompanying a reaction or process and has to take into account both the entropy of **system** (the reaction or process) and the entropy of the **surroundings**.

For a reaction or process to be spontaneous the total entropy change for the system and surroundings must be positive.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

The surroundings

If a reaction or process is exothermic, heat energy is released into the surroundings, the particles that make up the surroundings increase in temperature and so there is an increase in the dispersal of energy and matter, so the entropy of the surroundings increases.

If the process is endothermic, the opposite occurs. Heat energy is absorbed from the surroundings which cool down, and there is a decrease in the dispersal of energy and matter, so the entropy of the surroundings decreases.

The system

The entropy of a system can increase in a number of ways, for example

- as a solid melts or a liquid vaporises. Here there is a change from high order of particles (low disorder) to low order of particles (high disorder).
- When a solid dissolves in a solvent e.g. sodium chloride in water.

  $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

- When a reaction produced an increase in the number of particles e.g. If a reaction has less moles of gaseous reactants and more moles of gaseous products, this increase in the numbers of gaseous particles increases the dispersal of energy and matter.
  $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$
  2 mol gas 4 mol gas

Sample Question:

Ammonium nitrate dissolves readily in water despite the process being endothermic process.

$$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$$

Justify why this occurs, in terms of the entropy change of the system and the surroundings.

Sample Answer:

When ammonium nitrate dissolves in water, the entropy of the system increases. This is because there are more moles of particles formed and (*any one of the following bullet points*)

- the ions (particles) in the solution are more disordered than the solid.
- there is greater random movement of products particles.
- there is a greater dispersal of matter and energy.

Since the process is endothermic, the entropy of the surroundings decreases because heat energy has been absorbed from the surroundings so there is decreased random motion of the surroundings / a decrease in the dispersal of matter and energy.

However, since the NH_4NO_3 readily dissolves in water, that is the process occurs spontaneously, the total entropy change must be positive (or the total entropy increases).

The increase in entropy of system must therefore outweigh the decrease in the entropy occurring in the surroundings.

Extra Info:

The solid ammonium nitrate has a close packed crystal lattice arrangement made up of ammonium and nitrate ions held together by ionic bonds. When it comes into contact with polar water molecules, the polar water molecules will interact with these ions and attract individual ions out from the lattice structure which breaks down and dissolves. To overcome the ionic attraction requires energy which is absorbed from the surrounding environment, which explains why the overall solution becomes cold. While some energy is released when the ammonium ions and nitrate ions become hydrated (interact with the water molecules) it is less than was required for the water molecules to be able to break the ionic bonds in the solid ammonium nitrate. So, overall, the dissolving (dissolution) of the ammonium nitrate in water is endothermic. However, this is more than made up for by the large increase in the entropy of the system as the solid dissolves and separates into its ions, meaning a large increase in disorder / increase in the random movement of the ions and water molecules / greater dispersal of matter and energy.

So, the total entropy change is positive, and the change is spontaneous in this instance.

Summary

Any process that occurs spontaneously, at a particular temperature is, has to be thermodynamically favoured.

To be spontaneous there must be an overall increase in the total entropy of the system and the surroundings ($\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$).

Changes to the entropy of the system occurs as a result of the increase or decrease of random motion of the particles within the system / increase or decrease the dispersal of energy / matter.

Exothermic or endothermic changes due to the system result in changes to the entropy of the surroundings; this occurs with the gain or loss of heat (kinetic energy) in the surrounding particles.

Extra for experts

Questions on Entropy would be a lot easier if NZQA had included something called Gibbs free energy change, how to calculate it, and how to interpret the answers BUT they didn't.

Calculating $\Delta G°$

Standard Gibbs free energy change is calculated using this formula. For a reaction to be spontaneous, $\Delta G°$ has to be negative.

$$\Delta G° = \Delta H° - T\Delta S°$$

If you are told the enthalpy change for the reaction ($\Delta H°$) , and the entropy change ($\Delta S°$), and you know the temperature, T (in Kelvin), then it would be possible to work out $\Delta G°$.

You do NOT need to know this equation or about Gibbs free energy, but you may come across it in workbooks or on the internet. It 'explains' why the spontaneity of some reactions depends on the temperature.

	$-\Delta H°$	$+\Delta H°$
$+\Delta S°$	Spontaneous at all temperature (as $\Delta G° < 0$)	Spontaneous at high temperatures (when $T\Delta S°$ is large then $\Delta G° < 0$)
$-\Delta S°$	Spontaneous at low temperatures (when $T\Delta S°$ is small then $\Delta G° < 0$)	Non-spontaneous at all temperatures (as $\Delta G° > 0$)

At the end of the day just remember that

- a reaction / process that is exothermic (products in a lower energy state) and that has an increase in entropy will <u>always</u> be spontaneous (because ΔS_{total} will always be +)
- a reaction / process that is endothermic (products in a higher energy state) and has a decrease in entropy will <u>never</u> be spontaneous (because ΔS_{total} will always be -).
- The other two combinations of enthalpy and entropy may be spontaneous, depending on the temperature.