Entropy and free energy

DISORDER

In nature systems naturally tend towards disorder. An increase in disorder can result from:

- mixing different types of particles, e.g. the dissolving of sugar in water
- a change in state where the distance between the particles increases, e.g. liquid water → steam
- the increased movement of particles, e.g. heating a liquid or gas
- increasing the number of particles, e.g. $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$.

The greatest increase in disorder is usually found where the number of particles in the gaseous state increases.

The change in the disorder of a system is known as the entropy change, ΔS. The more disordered the system becomes the more positive the value of ΔS becomes. Systems which become more ordered will have negative ΔS values.

$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ $\quad \Delta S = -284\ J\ K^{-1}\ mol^{-1}$

(two moles of gas) → (one mole of solid)

SPONTANEITY

A reaction is said to be spontaneous if it causes a system to move from a less stable to a more stable state. This will depend both upon the enthalpy change and the entropy change. These two factors can be combined and expressed as the Gibbs energy change ΔG, often known as the 'free energy change'.

The standard free energy change $\Delta G^{\ominus}$ is defined as:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

Where all the values are measured under standard conditions. For a reaction to be spontaneous it must be able to do work, that is $\Delta G^{\ominus}$ must have a negative value.

POSSIBLE COMBINATIONS FOR FREE ENERGY CHANGES

Some reactions will always be spontaneous. If $\Delta H^{\ominus}$ is negative or zero and $\Delta S^{\ominus}$ is positive then $\Delta G^{\ominus}$ must always have a negative value. Conversely if $\Delta H^{\ominus}$ is positive or zero and $\Delta S^{\ominus}$ is negative then $\Delta G^{\ominus}$ must always be positive and the reaction will never be spontaneous.

For some reactions whether or not they will be spontaneous depends upon the temperature. If $\Delta H^{\ominus}$ is positive or zero and $\Delta S^{\ominus}$ is positive, then $\Delta G^{\ominus}$ will only become negative at high temperatures when the value of $T\Delta S^{\ominus}$ exceeds the value of $\Delta H^{\ominus}$.

Type	$\Delta H^{\ominus}$	$\Delta S^{\ominus}$	$T\Delta S^{\ominus}$	$\Delta H^{\ominus} - T\Delta S^{\ominus}$	$\Delta G^{\ominus}$
1	0	+	+	(0) – (+)	–
2	0	–	–	(0) – (–)	+
3	–	+	+	(–) – (+)	–
4	+	–	–	(+) – (–)	+
5	+	+	+	(+) – (+)	– or +
6	–	–	–	(–) – (–)	+ or –

Type 1. Mixing two gases. $\Delta G^{\ominus}$ is negative so gases will mix of their own accord. Gases do not unmix of their own accord (Type 2) as $\Delta G^{\ominus}$ is positive.

Type 3. $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + Cr_2O_3(s) + 4H_2O(g)$

The decomposition of ammonium dichromate is spontaneous at all temperatures.

Type 4. $N_2(g) + 2H_2(g) \rightarrow N_2H_4(g)$

The formation of hydrazine from its elements will never be spontaneous.

Type 5. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

The decomposition of calcium carbonate is only spontaneous at high temperatures.

Type 6. $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

Above a certain temperature this reaction will cease to be spontaneous.

Note: the fact that a reaction is spontaneous does not necessarily mean that it will proceed without any input of energy. For example, the combustion of coal is a spontaneous reaction and yet coal is stable in air. It will only burn on its own accord after it has received some initial energy so that some of the molecules have the necessary activation energy for the reaction to occur.