Enthalpy and Entropy

Entropy

Entropy is a measure of the 'disorder' of a system.
A system becomes energetically more stable when it becomes disordered.
The units for entropy are J mol^{-1} K^{-1}.

Comparison of entropy values

1. Solids have the lowest entropy. This is because they consist of very ordered, regular arrays of particles.
   Liquids have a higher entropy as they are more disordered - the particles not being in fixed positions, but free to move around.
   Gases have the highest entropy as they are most disordered. Their particles move randomly, and generally with great speed.

2. The dissolved ions are far more disordered than the solid, ionic crystal from which they came (twice as many particles and in a more disordered state):

   $NaCl_{(s)} + (aq) \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$

   So the entropy of a solution is greater than the entropy of the solid lattice.

3. $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

   During this reaction 4 moles of gas becomes 2 moles of gas. Therefore there is a decrease in the number of gas moles during the reaction. Therefore entropy decreases.

Calculating the entropy change for a reaction

During a reaction the chemicals in the reaction change, and may become more or less disordered. This is called the entropy change of the system, ΔS_{system}.

If ΔS_{system} is positive this indicates an increase in the disorder of the system.
If ΔS_{system} is negative this indicates a decrease in the disorder of the system.

We can work out a numerical value by adding up the entropies of the products, and taking away the entropies of the reactants. This is written as an equation:

$$\Delta S_{system} = \Sigma S(\text{products}) - \Sigma S(\text{reactants})$$

For example: $\mathbf{MgCO_3(s) \rightarrow MgO(s) + CO_2(g)}$

The standard entropy values of the substances involved:

Substance	Entropy (J mol^{-1} K^{-1})
$MgCO_3(s)$	65.7
$MgO(s)$	26.9
$CO_2(g)$	213.6

So $\Delta S_{system} = 26.9 + 213.6 - 65.7 =$ **+ 174 .8 J mol^{-1} K^{-1}**

This is a positive value as we expected because a gas is formed from a solid, and one particle becomes two. Don't forget to include the sign and correct units with your answer.

Balance between entropy and enthalpy changes

The tendency of a process to take place depends on temperature, T, the entropy of the system, ΔS, and the enthalpy change, ΔH, with the surroundings.

This balance between entropy and enthalpy changes is the **free energy change, ΔG,** which determines the feasibility of a reaction.

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

ΔH = enthalpy change of the reaction
T = temperature of reaction in Kelvin
ΔS = entropy change of the reaction

Note: as entropy is usually given in J mol^{-1} K^{-1} and enthalpy in kJ mol^{-1} they must be converted so they are both either in kJ or J.

All **spontaneous** physical and chemical changes involve a decrease in free energy – a negative value of ΔG.

In an endothermic reaction:

ΔH is positive, therefore ΔG is negative **only** if $T\Delta S$ has a large positive value

ΔG = (positive value) – (large positive value) = negative value

To give $T\Delta S$ a large positive value:

ΔS must be positive: entropy must increase. A large value of ΔS helps, and a high temperature helps to make $T\Delta S$ term outweigh a positive value of ΔH.

Note that ΔG only predicts whether a reaction is feasible not how fast the reaction is.