Entropy & Gibbs Free Energy

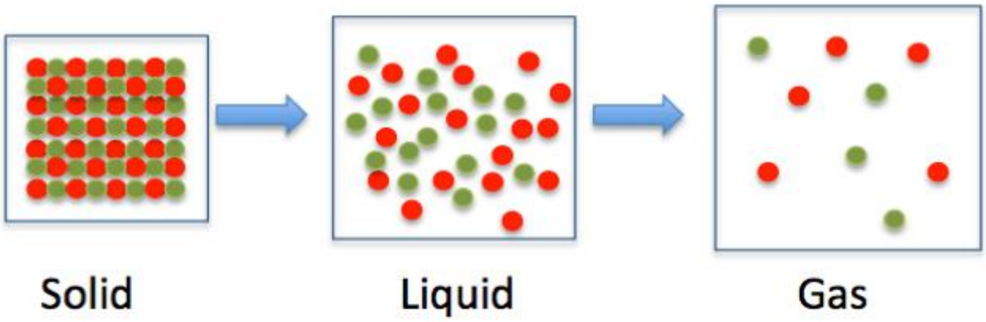
What is entropy?

Entropy comes under the thermodynamics category of chemistry, which is used to predict whether or not a reaction is likely to occur or not.

Entropy is said to be a measure of **chaos** or **disorder**. Or the number of ways particles can arrange themselves.

This means how the particles in a molecule are arranged and behaving. If the particles are **free** to move they will have **high entropy**.

The easiest way to imagine it is by looking at the structure of solids, liquids and gases.



In a solid, all the particles are rigid and fixed in position. This is said to be **ordered** and as a result will have **low entropy**.

In a liquid the particles can move more freely which means there is more disorder and higher entropy than a solid.

Gases have the most disorder, and therefore, **highest entropy**. The particles are free to whizz around all over the place.

✓ The electrode potentials (EMF) and equilibrium topics are also thermodynamics i.e. they are predicting whether a reaction will occur or not and possibly *how much* is made. Rates is the one topic that is on its own and just refers to how fast a reaction goes; it's very simple. It has nothing to do with how much or feasibility.

Entropy can be calculated using the following:

ΔS = (sum of the entropy of the products) – (sum of the entropy of the reactants)

The question will give you the values for each reactant and product. Just add them up and subtract!

You can do the same kind of thing for enthalpy.

ΔH = (sum of the enthalpy of the products) – (sum of the enthalpy of the reactants)

What do entropy values tell you?

A **positive** entropy value indicates a **feasible reaction** i.e. one that *should* occur. The more positive value obtained, then the more likely that the reaction will occur.

Ideally we'd be looking at the total entropy change but sometimes you only have information on the system or the surroundings.

- ✓ although this topic is all about entropy, you also have to remember enthalpy. If the enthalpy change (ΔH) is **negative**, this can also point towards a feasible reaction, as in the enthalpy of solution topic.

- ✓ when talking about whether a reaction is feasible, they sometimes talk about thermodynamically feasible or thermodynamically unstable. They all mean the same thing. If something is "unstable", it means it is reactive.

Chemical Equations

You can predict whether a reaction will occur or not by looking at chemical equations. This gives information on the entropy of the system. Two things to look out for:

Change in state: this is the big one. As was mentioned above, going from a solid to liquid or gas results in an increase in entropy. Always look for change of state first.

Change in number of moles: if the products have more moles than the reactants, this would be an increase in entropy.

- ✓ change in state is the first one to look for and is more important than the change in moles, particularly when a gas is involved as the entropy change is huge.

Examples

$H_2O(l) \rightarrow H_2O(s)$: this should be easy, liquid → solid means more order, therefore a **decrease in entropy**.

$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$: as CO_2 is produced, this will mean an **increase in entropy**. Also the products side has more moles.

$2O_3(g) \rightarrow 3O_2(g)$: as they are both gases, we need to look at the change in the number of moles. The products side has more moles, therefore an **increase in entropy**.

✓ It is often necessary to write out equations. For example, in the O_3 example above, if you don't write out the equation you might not get the correct change in moles.

Gibbs Free Energy

The Gibbs Free Energy (ΔG) equation is really useful as it takes both entropy an enthalpy into account. If there is one equation to remember it is definitely this one:

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

a **negative ΔG value** indicates a **feasible** reaction

✓ units of entropy are in **J mol^{-1} K^{-1}** but enthalpy is usually in **kJ mol^{-1}**. Therefore when using ΔG, you need to either convert enthalpy to joules or entropy to kJ.

✓ ΔG units are usually KJ mol^{-1}.

Examples

Calculate the value of ΔS_{system} for the reaction below at 298K.

$$\mathbf{CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2} \qquad \Delta H = +206.1 \text{ kJ mol}^{-1}$$

	S (J mol^{-1} K^{-1})
CO	197.6
CH_4	186.2
H_2	130.6
H_2O	186.2

ΔS = (3 x 130.6 + 197.6) - (186.2 + 188.7) = **214 J mol^{-1} K^{-1}**

It's an easy calculation, just be careful with the number of moles in the equation. In this example, make sure to multiply the H_2 value by **3**.

Calculate the value of ΔG for the above reaction at 298K.

Just put in the numbers and make sure to convert entropy to kJ or enthalpy to J:

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

$$\Delta G = 206 - 298 \times 214.5/1000$$

$$\Delta G = +142.71 \text{ KJ mol}^{-1}$$

We have a positive value so we can assume that the reaction is **not** feasible.

Theoretical Questions

There are often hypothetical questions in exams where they change something (usually temperature) and ask if it will make a reaction more or less feasible.

With these questions you just have to refer back to $\Delta G = \Delta H - T\Delta S$

There are various combinations of ΔH and ΔS values that give different ΔG values i.e. look to see if ΔH and ΔS positive or negative? They might both be the same sign or they could be opposite signs, and this has a great effect on whether a reaction is feasible or not.

1.When ΔH and ΔS have opposite signs ΔG is **independent** of temperature:

A **negative ΔH** and **positive ΔS** value → reaction is **always** feasible as **ΔG is always negative**.

A **positive ΔH** and **negative ΔS** value → reaction is **never** feasible as **ΔG is always positive**.

2.When ΔH and ΔS have the same signs ΔG is **dependent** on temperature:

A **negative ΔH** and **negative ΔS** value → **temperature dependent** i.e. lower temperature means more likely to be feasible.

A **positive ΔH** and **positive ΔS** value → **temperature dependent** i.e. higher temperature means more likely to be feasible.

✓ students often assume that increasing the temperature will make a reaction more feasible as they are confusing it with rates.

Minimum temperature

A common question is to work out the temperature at which a reaction will become feasible.

What is the minimum temperature at which the reaction will occur, where $\Delta H = 206.1\ kJ\ mol^{-1}$ and $\Delta S = 225\ J\ mol^{-1}\ K^{-1}$?

To do this you need to use **ΔG = ΔH – TΔS** and set **ΔG = 0** to give:

$$0 = \Delta H - T\Delta S \text{ then rearrange} \rightarrow T\Delta S = \Delta H$$

or

$$\boxed{T = \Delta H/\Delta S}$$

To do this question, convert the ΔS units → $kJ\ mol^{-1}$ then put the numbers into the equation:

$$T = 206.1 \times 1000/225$$

T = **916 K**

Kinetics

You can look at kinetics (rates) to explain something unusual. We are talking about thermodynamics in this topic and ignoring kinetics (poor old rates ☹) but in a real reaction both are there! You can't remove one of them.

So…if you get a positive value for ΔS or a negative value for ΔG, this indicates that the reaction is feasible by the laws of thermodynamics. Occasionally, a situation could arise where this happened but nothing appears to happen in the reaction. In this situation, talk about kinetics…or more accurately → activation energy.

The reaction is actually occurring but it is just so slow it *appears* like nothing is happening. In this case, you have to say that the reaction has a **very high activation energy**.

✓ Diamond is the classic example. It technically is decomposing in front of us (positive entropy value) but it happens so slow you can't notice it. It takes thousands of years!

ΔG Graph

This is something that is probably unnecessary but I have seen it once before (in the June 2017 AQA Paper 3) so you might as well be aware of it.

Using the ΔG equation, we could plot a straight-line graph of **ΔG versus T**.

Using y = mx + c: **$\Delta G = \Delta H - T\Delta S$**

$y \;=\; c \;+\; mx$

ΔH = where it cuts the y-axis

gradient = $-\Delta S$

The graph also shows when a reaction becomes feasible. $\Delta G = 0$ where the line cuts the x-axis, so any temperature below ~ 675 K gives a negative ΔG and therefore a feasible reaction.