What Makes a Reaction Happen?

This must be one of the most basic and fundamental questions that we need to ask ourselves, at any level in chemistry. It is only at A level that we can begin to offer any kind of answer to that most fundamental question.

The answer requires a certain level of maturity to understand. At this level, the explanation does require a degree of numeracy; only those basic mathematical skills learned at GCSE. So, don't be put off just because of a few new symbols.
Taking this topic beyond A level will require more sophisticated maths (and some tighter definitions - I'm just getting that in before those thermodynamicists get too annoyed with me!).
When you've read through this, why don't you have a go at the quiz Entropy and Gibbs Energy in M5 Physical Chemistry on *CramNow*

An Introduction to Thermodynamics

In this context the word '*happen*' should be followed by the word '*spontaneously*'. So, what do we mean by **spontaneous**?

Because of its common usage, the word spontaneous is often confused with something that happens quickly. But there are many spontaneous processes that are desperately slow.

Take, for example, the following process:

$$C_{(s,\text{diamond})} \rightarrow C_{(s,\text{graphite})}$$

These are two of the allotropic forms of carbon, one being significantly more valuable than the other.

This process is spontaneous under normal atmospheric conditions. Graphite is the more stable of these two allotropic forms of carbon. As a result, diamonds are spontaneously converted into graphite. This does not mean that a diamond engagement ring will have developed the properties of a pencil, even if the engagement is very lengthy. Thankfully, the process is indeed very, very slow. We would describe diamond as **kinetically stable** but it is **thermodynamically unstable.** Maybe, Shirley Bassey would have been more accurate by including the word '*nearly*' in her famous James Bond movie theme, '***Diamonds Are Forever***'

A definition of ***spontaneous*** could be written:

> *A spontaneous process is a naturally occurring process that, once started, will continue to happen without outside intervention.* (A nonspontaneous process can be made to happen but only when outside action introduces energy to drive the process.)

One obvious way to find out whether a process is spontaneous is to try it. There are several possible problems with this approach. We are all aware that mixing hydrogen and oxygen in a balloon is generally pretty safe. In the absence of a spark or a pinch of platinum, the two gases seem to co-exist quite happily. One could wrongly form the conclusion that the reaction between hydrogen and oxygen, to form water, is nonspontaneous. In fact, it is spontaneous but takes place very slowly due to a very high activation energy for the reaction. Introduction of a spark or catalyst causes an enormous and rapid explosion. Quite obviously, it is **highly exothermic** ($\Delta_f H$ ($H_2O_{(l)}$)=-286 kJ mol^{-1}). We'll return to this later!

The Rule for Spontaneity

In many simple situations, the criterion (a rule) for spontaneity is self-evident. We don't need to be a physicist to know that the spontaneous change for a ball on a slope is for the ball to roll down the hill. The criterion for this **single particle** system is quite obvious. The spontaneous change involves the ball rolling to a position that **minimises its potential energy**, *i.e.* down the hill.

If we apply this rule to a typical chemical system (a system comprising an almost unimaginably high number of particles), then it would suggest that the process would be spontaneous only if it led to a reduction in chemical energy, *i.e.* an exothermic reaction. Indeed, for a long period, this was thought to be the case.

Today, we may not even give a second thought to the fact that mixing sodium hydrogencarbonate with hydrochloric acid gives a marked temperature decrease (accompanied by vigorous effervescence, which is far more than just an interesting observation!). Even the simple endothermic process of dissolving sodium chloride should cause the same amazement that a ball rolling spontaneously up a hill would cause. Clearly, there must be something that isn't immediately obvious which functions as the 'judge', deciding whether these processes can or cannot happen. The fact that so many processes are actually exothermic should give us the gut feeling that the **enthalpy change for that process** probably **has an influence** on this 'judge'. We will soon see how these are linked.

Entropy and Disorder

The concept of **entropy**, given the symbol **S**, is often reduced to the simple word '**disorder**'. Even the great Josiah Willard Gibbs, not otherwise known for his looseness with terms, referred to entropy as "mixed-up-ness." So, if you are asked the question at A level "What do you understand by the term, entropy?" you may be forgiven for your answer, "Disorder!".

So, what is this quantity called entropy?

Well, the answer does of course include the notion of disorder, but by **disordering a system**, a **greater number of ways in which energy quanta can be distributed amongst that system**. It's important to see it as **disordering of the energy within the system** rather than just concentrating on the 'mixed-up-ness' of its particles. That said, if you can instantly recognise that the **melting of a solid**, the **dissolving of a solid lattice**, the simple **warming of liquid** and the **evolution of a gas** all involve an **increase in entropy**, then you will surely be on the right track.
It should also be pointed out that the entropy of a perfect crystal at absolute zero has a value of 0 J $mol^{-1}K^{-1}$.
The crystal would be considered to have perfect order. This is brought out in the **third law of thermodynamics.**
Entropies have absolute values that can be looked up in tables. You will a collection of entropies at the end of this document. If you have a look, you'll see the differences in the molar entropies of diamond and graphite.
So, is a beautifully simple rule for spontaneity;

All spontaneous processes are accompanied by an increase in entropy

This is a common way of expressing the ***2nd Law of Thermodynamics*** (one of the 4 Laws of Thermodynamics)

I have been deliberately loose with the definition. Written like this, it can get some people to offer examples that seem to contradict this rule; for example, a hand warmer purchased from a local camping shop. The modern 'safe' type of hand warmer consists of a plastic sachet full of liquid (higher entropy). The liquid is typically a supersaturated solution of sodium acetate. Upon the 'snapping' of the small concave metal disc within the bag, the solution crystallises very rapidly to form a translucent solid (lower entropy). I've heard it claimed that this is a simple example of an obvious exception to the rule.

It is obvious that this process generates a **local ordering of particles** within the ***system***, thus appearing to contradict the second law (entropy decreased). However, the whole point of owning such a device is that **it releases a lot of heat energy** during this process. This heat leaks out of the system, through the plastic, and warms one's cold hands. The cold hands are part of the ***surroundings***. Indeed, everything else in the universe is part of the surroundings. It always seems strange to people that one can connect an argument involving a reaction in a beaker to changes in deep space. Remember that photons of infra-red radiation, emitted from your warm beaker, hot coffee or warm bath in this part of the universe, head out into deep space just waiting for a chance to fall upon some distant planet and warm it a little. Sounds extreme but it is critical to understand this.

It should be clear that the ***universe*** can be summed up as a simple combination of a ***system*** (the hand warmer, for example) and the ***surroundings*** (the rest of the universe including the warmed hands and the distant planet).

So, the *2nd Law of Thermodynamics* should have been more tightly defined ;

> *All spontaneous processes are accompanied by an increase in entropy* ***of the universe***

We can write a simple equation to connect entropy changes in the *universe* ($\Delta S_{universe}$) with those in the *system* (ΔS_{system}) and the *surroundings* ($\Delta S_{surroundings}$). This is simply:

$$\boxed{\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}} \qquad (1)$$

Looking at our example of the hand warmer again, we would be correct in guessing that the entropy of the hand warmer (the *system*), ΔS_{sys}, will have a **-ve** value because it has become more ordered (liquid to solid). However, the heat energy that was released to the hands, as part of the *surroundings*, has clearly warmed them up. In fact, there must have been sufficient warming to create an increase in the surroundings' entropy, ΔS_{sur}, that is bigger (and positive!) than ΔS_{sys}. According to equation (1) this would give an answer to ΔS_{uni} which has a **+ve** value. So, there was no anomaly, after all. There will be no breaking of the 2nd Law!

The *2nd Law of Thermodynamics* fundamentally prohibits the possibility of many supernatural phenomena including theperpetual motion machine.

Even Homer Simpson knows this!

Lisa's Perpetual Motion Machine

Indeed, **no exceptions to the second law of thermodynamics have ever been observed.**

Despite this, there are still regular attempts to patent perpetual motion machines or parts of them. The UK Patent Office notes that you cannot get a patent on '*articles or processes alleged to operate in a manner clearly contrary to well-established physical laws*' as they are '*regarded as not having industrial application*'. Any machine that generates more energy than it consumes is either a nuclear reactor or breaches the second law of thermodynamics.

So now that you know a little bit about what **entropy** is, we need to look at how to go beyond a qualitative view of entropy, which we can have a stab at by looking at a chemical equation, to being able to calculate it.

The Calculation of Entropy Changes

The entropy change ΔS for a system can be calculated easily. As entropy is a **function of state**, like enthalpy, we can calculate the entropy change ΔS_{sys} using the following equation

$$\boxed{\Delta S^{\ominus}_{system} = \Sigma\, S^{\ominus}\,(\text{products}) - \Sigma\, S^{\ominus}\,(\text{reactants})} \tag{2}$$

Values of **standard entropies**, $S^{\ominus}$, **have an absolute value** and can be found in tables (see last page).

The other component of equation (1) is $\Delta S^{\ominus}_{surroundings}$.
It can be shown that this is related to the heat exchanged with the surroundings q_{surr} by the following relationship:

$$\boxed{\Delta S^{\ominus}_{surr} = \frac{q_{surr}}{T} = \frac{-\Delta H_{sys}}{T}} \tag{3}$$

Caveat (note of caution):
This relationship is only true when the process exchanges heat *'reversibly'* with the surroundings. Don't worry about this at A Level.

-where q_{surr} is the heat **absorbed by the surroundings** which must be the same as $-\Delta H_{sys}$
T represents the **absolute temperature** at which the process takes place.

It is reassuring that we can now see that the enthalpy for a process has appeared in the equations. We intuitively knew that it must, at some point!

Putting equations (2) and (3) together, we obtain:

$$\boxed{\Delta S^{\ominus}_{universe} = \Delta S_{sys}{}^{\ominus} - \frac{\Delta H_{sys}{}^{\ominus}}{T}} \tag{4}$$

It is important to note that we can say something about the effect upon the whole universe's entropy by simply knowing about the system. Isn't that amazing?

Let's look again at the example of the exploding hydrogen/oxygen balloon.

The reaction taking place can be written:

$$2\,H_{2(g)} + O_{2(g)} \rightarrow 2\,H_2O_{(l)} \qquad \Delta H^{\ominus}_{\text{reaction}} = -572\text{ kJ}$$

Note that the equation, as written, involves two moles of hydrogen and a mole of oxygen. This would involve a particularly large balloon!

Firstly, we need to calculate the entropy change for the system, ΔS_{system}

To do this we apply equation (2). So:

$$\Delta S^{\ominus}_{sys} = 2\,S^{\ominus}\,(H_2O) - [\,2\,S^{\ominus}\,(H_2) + S^{\ominus}\,(O_2)\,]$$

$$\Delta S^{\ominus}_{sys} = 2 \times (69.9\text{ Jmol}^{-1}\text{ K}^{-1}) - [2 \times (131\text{ Jmol}^{-1}\text{ K}^{-1}) + 1 \times (205\text{ Jmol}^{-1}\text{ K}^{-1})]$$

$$\Delta S^{\ominus}_{sys} = \underline{-327\text{ J mol}^{-1}\text{K}^{-1}}$$

Reassuringly, we obtain a **-ve** value for the entropy change for the system which is what we would expect given that for every **3** molecules of **gas** consumed, **2** molecules of **liquid** are formed. The ***system*** became more ordered.

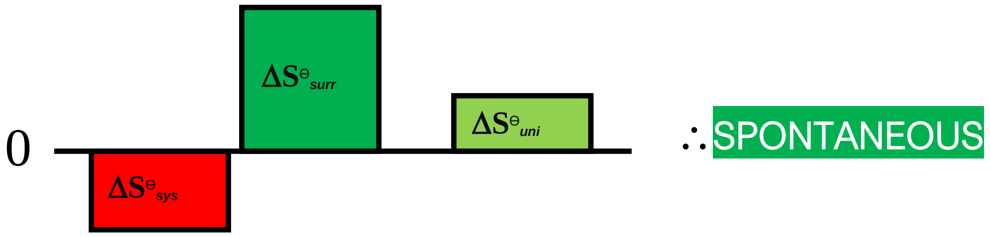
We now need to turn our attention to the effect that all of this has on the *surroundings*.
According to the data books, the energy, ***q***, blasted out during the explosion would be about **-572 kJ**.
Using equation (3) and assuming that the temperature in the lab is 18.0°C, we have:

$$\Delta S^{\ominus}_{surr} \quad = -\,(-572\text{kJ}) / 291\text{ K} \quad = \mathbf{+1966\text{ J K}^{-1}}$$

Plugging both results into (1) we have:

$$\Delta S^{\ominus}_{universe} \quad = -327\text{ JK}^{-1} + -1920\text{ JK}^{-1} = \mathbf{+1639\text{ J K}^{-1}}$$

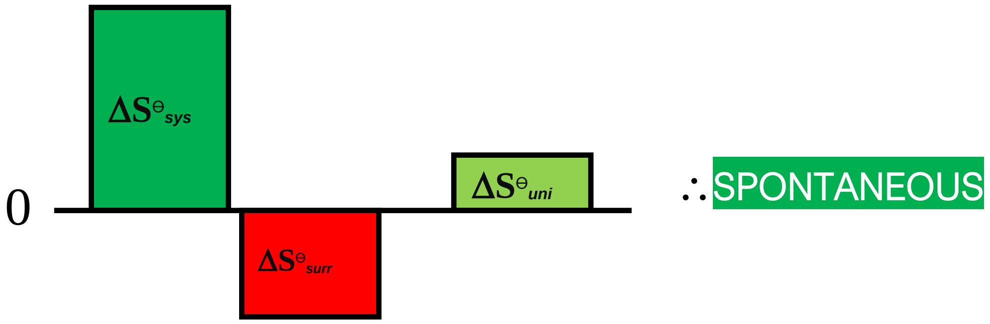
It should be clear to see that the **highly unfavourable -ve $\Delta S^{\ominus}_{sys}$** is outweighed by the **highly favourable +ve $\Delta S^{\ominus}_{surr}$**
The conclusion is that the **reaction should be spontaneous**.



Contrasting with this example of a hydrogen explosion, is the case of the **spontaneous endothermic reaction** of sodium hydrogencarbonate and hydrochloric acid that I mentioned earlier.

$$NaHCO_{3(s)} + HCl_{(aq)} \rightarrow H_2O_{(aq)} + NaCl_{(aq)} + CO_{2(aq)} \qquad \Delta H^{\ominus}_{\text{ reaction}} = +28\text{kJ}$$

It should be clear to see that the **highly unfavourable -ve $\Delta S^{\ominus}_{surr}$** is outweighed by the **highly favourable +ve $\Delta S^{\ominus}_{sys}$**.
The conclusion is that the **reaction should be spontaneous**. This is principally driven by the **highly favourable evolution of a gas**. Also, no solid remains.



Gibbs Energy, G

Although we have arrived at a criterion (rule) for spontaneous change, it has some limitations. Although a numerical answer is produced which will indicate spontaneity or otherwise, there is little else that can be done with the answer.
However, there is a simple way in which we can convert an equation focussed on entropy changes into something more useful.

Multiplying equation (4) through by –T, we arrive at:

$$\boxed{-T\Delta S_{universe} = \Delta H_{sys} - T\Delta S_{sys}} \qquad (5)$$

The term $-T\Delta S_{universe}$ is given a new name and a new symbol. It is the change in *Gibbs Energy* (*Gibbs Free Energy*[5] *or Gibbs Function* are also used) and its symbol is ΔG:

$$\Delta G = -T\Delta S_{universe} \qquad (6)$$

-where ΔG represents the difference in the Gibbs energy between reactants and products.

Combining (5) and (6) we arrive at the famous Gibbs equation:

$$\boxed{\Delta G = \underset{\substack{\uparrow \\ \textbf{Energy}\text{ term}}}{\Delta H_{system}} - \underset{\substack{\uparrow \\ \textbf{Entropy}\text{ term}}}{T\Delta S_{system}}} \qquad (7)$$

For a process to be spontaneous, the value of ΔG for this process must be -ve
The units of ΔG are kJ mol^{-1} which are, quite clearly, more familiar units.
Although very simplistic, we may consider three possible situations to exist for a process under a given set of conditions:

1) $\Delta G < 0$ spontaneous process, i.e. ‘it goes’
2) $\Delta G = 0$ a system at equilibrium
3) $\Delta G > 0$ non-spontaneous process, i.e. ‘it doesn’t go’

The equality shown in the second example is useful as it allows us to calculate the temperature at which a process will just become spontaneous, for example, the melting of ice.

If $\Delta G = 0$ then $\Delta H_{fusion} = T\Delta S_{fusion}$

$\therefore$ $T_{fusion} = \Delta H_{fusion} / \Delta S_{fusion}$

$T_{fusion} = 6.01 kJmol^{-1} / 22.0 Jmol^{-1} = 273\ K$

Both ΔH_{system} and ΔS_{fusion} can be looked up or calculated.

n.b. there are processes where the value of ΔG is in the interesting region relatively close to 0 kJ mol^{-1} (between about +60 kJ mol^{-1} and -60 kJ mol^{-1}). Many industrial processes have a value of ΔG in this range. For these processes, equilibrium considerations are significant. Application of Le Chatelier’s principle is essential to shift equilibrium position to generate a commercially viable yield. See later.

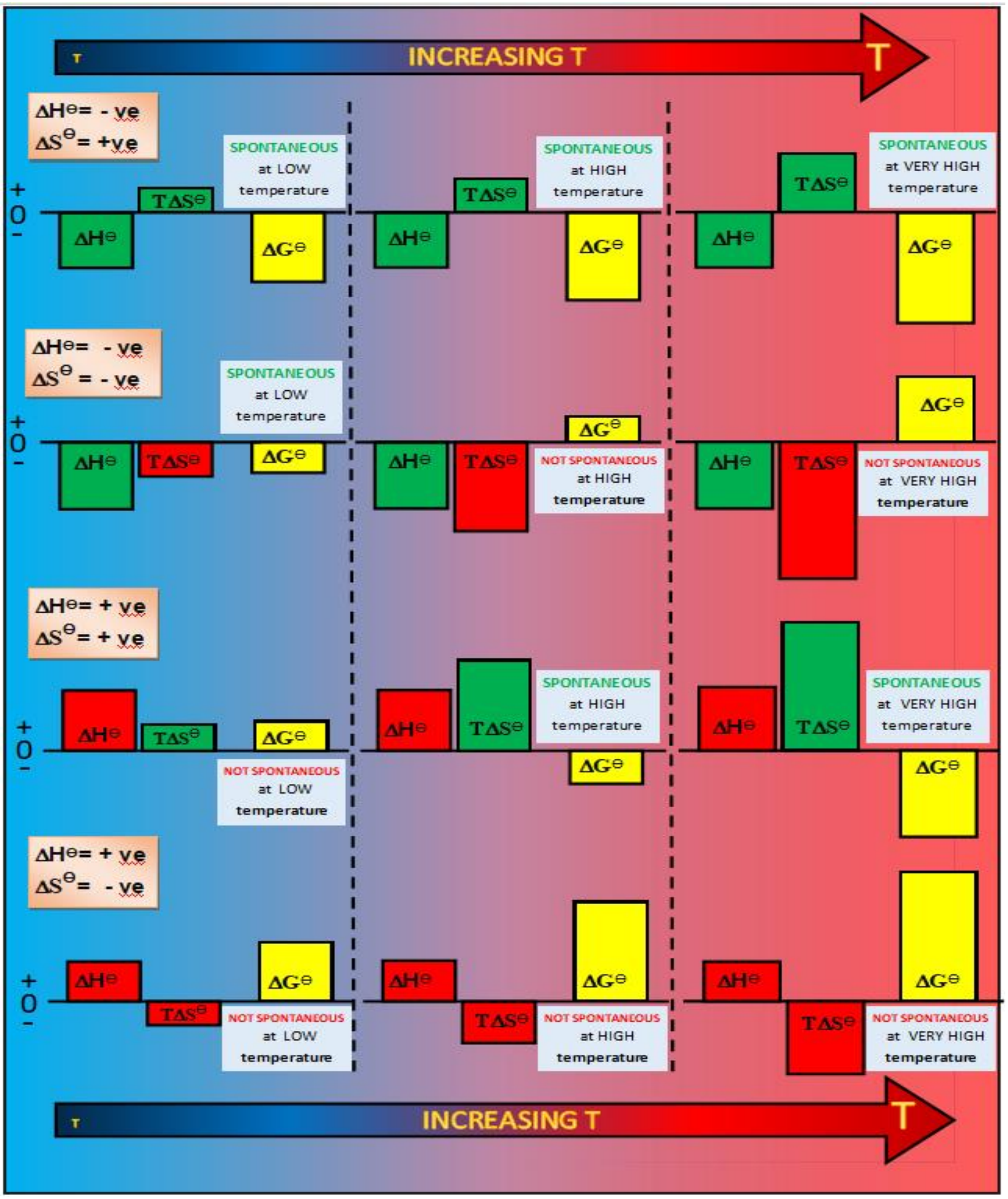
How does changing the Temperature Affect ΔG?

The Gibbs Equation clearly shows that changing the absolute temperature, T, must influence the value of ΔG. Values of Δ*H* are approximately constant over a large temperature range.

Although values of S for substances vary with temperature, values of ΔS*system* are approximately constant over a large temperature range.

So, changing T will affect ΔG. The effect depends upon whether ΔS*system* has a positive or a negative value. The diagram below helps to illustrate the effect of temperature in **4 scenarios**. These are shown in the boxes.

e.g. **ΔH⊖= - ve**
ΔS⊖= +ve



Why was it originally called the Gibbs Free Energy?

Well, the Gibbs part comes from Josiah Willard Gibbs, American physicist, chemist and engineer. The 'Free' part has a literal origin.
Let us again consider the simple reaction which is the combustion of hydrogen to produce water.

The reaction $2 H_{2(g)} + O_{2(g)} \rightarrow 2 H_2O_{(l)}$ ΔH reaction $= -572$ kJ

So this tells us that this reaction, as written, will **release 572** kJ of **heat** to the surroundings. This **more than compensates** for the negative value for $\Delta S_{system.}$

It is true that **some** of the $\Delta H_{reaction}$ **must be handed out to the surroundings** so that the reaction can go ahead sontaneoulsy. But the surroundings don't require all of it. The 'extra' Joules can be used to do **work**.
The amount that must be handed over is rather like a tax. Sure, you can give all of your hard earned cash to the the goverment as tax. I'm sure that it would be welcomed by any govenement. However, if you want to do something with your monthly pay packet, like eat for instance, then you can have whatever is left over after you've paid your tax. Legal jobs are only permitted if the minimum tax is paid. Similarly, all of the $\Delta H^{\ominus}{}_{reaction}$ could be handed over as heat. You could enjoy **all** of the joules handed out by the reaction as **heat**. But there will be a limit to what you can do if you decide to convert these joules into **work**.
Not all of the heat produced in a steam engine can be converted into useful work that could power a mill or drain water from a flooded coal mine. Not all of the heat generated in a power station's furnace can be truned into electrical energy in the turbines. It's not about a lack of engineering efficiency, it's the **2nd Law** and that you're up against!
I have attempted to illustrate this below.

Situation 1

All the joules taken as **HEAT**

Situation 2

WORK is done but some **heat** MUST still be 'spilled' into the surroundings

OR (less artistically)

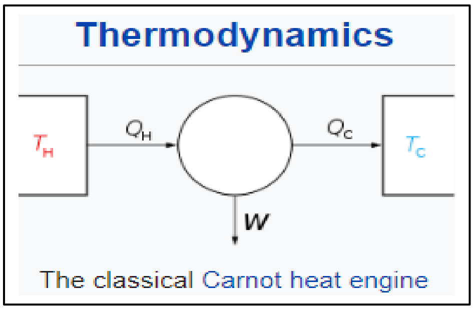
Situation 1

All the joules taken as **HEAT**

Situation

WORK is done but some **heat** MUST still be 'spilled' into the surroundings

So, **Gibbs (Free) Energy** represents the amount of energy that is '**free to do work**' once the surroundings have had their entropy requirements catered for.
The conversion of **heat** into **work** is the reason why this subject is called **Thermodynamics.**
Just think of what a steam engine (a heat engine) does!



An Application of the Gibbs Equation - a worked example

Consider the mineral calcium carbonate, $CaCO_{3(s)}$. This compound is stable at room temperature. One glance at the White Cliffs of Dover is a big clue.

Let’s see if we can show that calcium carbonate should be stable in typical atmospheric conditions.

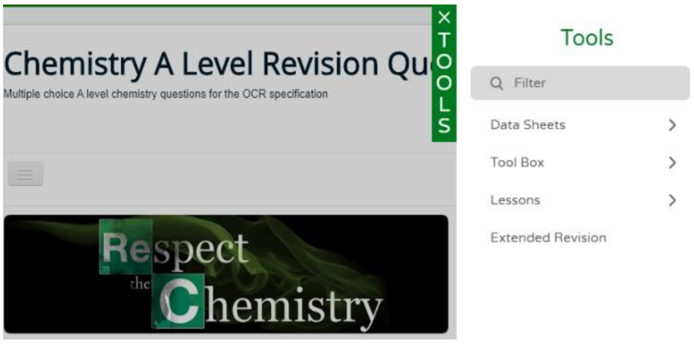
The decomposition of calcium carbonate is represented by the following equation:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

We can calculate the value of ΔG at this temperature. This will give as the evidence we require to show that $CaCO_{s(s)}$ is stable at, let’s say 20°C.

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

All of this data can be found tabulated at the end of this document or separately in the **TOOLS>Data Sheets** on *CramNow*



Chemistry A Level Revision Qu

Multiple choice A level chemistry questions for the OCR specification

ΔS is calculated using:

$$\Delta S^{\ominus} = \Sigma S^{\ominus}\text{ (products)} - \Sigma S^{\ominus}\text{ (reactants)}$$

$$\Delta S = [\ S^{\ominus}(CaO) + S^{\ominus}(CO_2)\ ] - [\ S^{\ominus}\ CaCO_3\ ]$$

$$\Delta S = [\ (39.7\ Jmol^{-1}K^{-1}) + (214\ Jmol^{-1}K^{-1})\ ] - [\ 97.2Jmol^{-1}K^{-1}\ ]$$

$$\Delta S = +157\ J\ mol^{-1}K^{-1}\ \text{(you should predict it to be a positive value)}$$

Get these values from data tables (often presented in a question)

ΔH is typically calculated using a Hess Cycle involving **Enthalpies of Formation, $\Delta_f H$**.

You should recall this very useful equation (learn it!) that comes out of the Hess Cycle

$$\boxed{\Delta H_{reaction} = \Sigma\ \Delta_f H\text{ (products)} - \Sigma\ \Delta_f H\text{ (reactants)}}$$

$$\Delta H_{reation} = [\ \Delta_f H(CaO_{(s)}) + \Delta_f H(CO_{2(g)})\ ] - [\ \Delta_f H(CaCO_{3(s)})\ ]$$

$$\Delta H_{reation} = [\ -635.1\ kJmol^{-1} + -393.5\ kJmol^{-1}\ ] - [\ -1206.5\ kJmol^{-1}\ ]$$

$$\Delta H_{reation} = +178\ kJmol^{-1}$$

Get these values from data tables (often presented in a question)

T must be ‘**absolute temperature**’. We chose to calculate ΔG at 20°C so T = 20 + 273= 293K

$$\text{So, } \Delta G = 178\ kJmol^{-1} - \left(293K \times \frac{+157\ J\ mol^{-1}K^{-1}}{1000\ J/kJ}\right) = +132\ kJmol^{-1}$$

NOT SPONTANEOUS at 20°C!

WARNING! Don’t forget that the **units of entropy** are usually quoted in $Jmol^{-1}K^{-1}$ whereas ΔH are typically $kJmol^{-1}K^{-1}$. So we usually **divide ΔS by 1000** (J/kJ) to convert $Jmol^{-1}K^{-1}$ to $kJmol^{-1}K^{-1}$

Now let's repeat that calculation at a much higher temperature, say 1000°C

Now remember what I said earlier about the effect of temperature on $\Delta H_{reation}$ and $\Delta S_{reaction.}$ I said that these values are **reasonably constant over a wide temperature range**. So, the data calculated earlier can be reused.

We simply need to alter T to 1273K.

So, at 1273K:

$$\Delta G = 178\ \text{kJmol}^{-1} - \left(1273\text{K} \times \frac{+157\ \text{J mol}^{-1}\text{K}^{-1}}{1000\ \text{J/kJ}}\right) = -21.9\ \text{kJmol}^{-1}$$

SPONTANEOUS at 1000°C!

This should leave you asking yourself, "Well, when does it switch from **not spontaneous** (e.g. at 20°C) to **spontaneous** (e.g.at 1273)?"

To do this we should assume that this switch occurs when ΔG goes from having a positive value **(not spontaneous)** to a negative one **spontaneous**. This surely happens as ΔG becomes negative by an infinitesimal amount. Let's say this happens when $\Delta G = 0\ \text{kJmol}^{-1}$

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

And, $\quad \Delta G = 0\ \text{kJmol}^{-1}$

So, $\quad \Delta H = T\Delta S$

So, $\quad T = \dfrac{\Delta H}{\Delta S} = \dfrac{+178\ \text{kJmol}^{-1}}{+157\ \text{J mol}^{-1}\text{K}^{-1}} = 1130\ \text{K}$

We can decompose a sample of calcium carbonate (a marble chip for instance) in a school laboratory. This temperature can be easily reached by a school Bunsen burner with the air hole open. The tip of the inner blue cone of a Bunsen with airhole open can reach in excess of 1500°C!

Spontaneous Heat Transfer

" Why does a hot drink spontaneously cool down?"

Firstly, it only spontaneously cools down when;
(a) it is placed in a colder place or
(b) it is not in an 'isolated system', such as a perfectly efficient flask (which, of course doesn't exist).

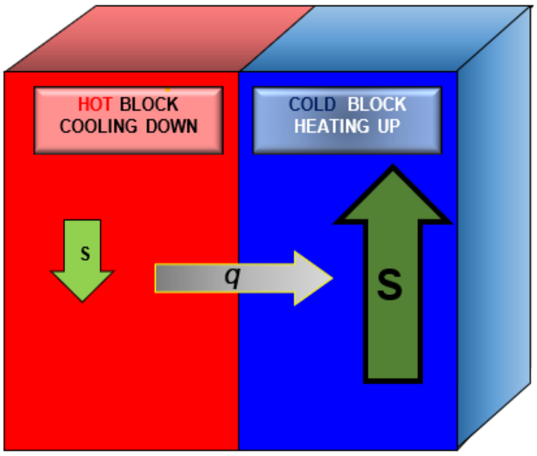
Put simply, when a hot body absorbs or emits an amount of heat, ***q***, its entropy is affected less than when an equivalent amount of heat, ***q***, is absorbed or emitted by a colder body.

If a hot block of iron (energy rich) was bolted to a cold block of iron (energy poor), heat would be transferred from the hot body to the cold body (see fig. 1). The hot block would cool down and the cold block would heat up. No news there! A rewording of the second law is

'*Heat cannot spontaneously flow from a material at lower temperature to a material at higher temperature*.'

Let us assume that there is no exchange of heat with any other surroundings. The entropy of the hot body would decrease and the entropy of the cold body would increase. However, the magnitude of the hot body's negative entropy change is less than the positive entropy change of the cold body. This is because the size of ΔS caused by warming is dependent on temperature, T (not a contradiction on what I said earlier). When both entropy changes are added together, a positive total value is obtained, *i.e.* the process takes place spontaneously. With students, I use a financial analogy which is, to all intents and purposes, a variant of the widow's mite parable.
The handing over of a crisp £10 note to the Porsche driving investment banker (the hotter and richer body) is likely to have less of an effect on their general levels of happiness than it would have had if the same £10 note had been given to a school teacher (the colder and poorer body). So, if £10 was transferred from the banker to the teacher, the decreased happiness of the trader (£10 poorer) would be more than compensated by the increased happiness levels of the teacher (£10 richer). Overall, the universe would get happier through this process. One would like to feel that the spontaneous process would lead to a spontaneous readjustment of wealth until equilibrium was met. Sadly, this is only an analogy.
So, there we have it, a criterion that we can apply to any process from the spontaneous cooling of a cup of coffee to the thermal decomposition of calcium carbonate.

Figure 1.



ΔS_{hot} is small and –ve	ΔS_{cold} is large and + ve
$\Delta S_{total} = \Delta S_{hot} + \Delta S_{cold} = +ve$ The transfer of heat, ***q***, from the hot block to the cold block is spontaneous.	

Most A level Chemistry specifications choose to leave thermodynamics at this point. However, the Cambridge Pre-U has extended the topic to the point where there is a connection made between the value of ΔG and the position of equilibrium. I have always found it uncomfortable to leave students with the idea that there are just three discrete outcomes for the value of ΔG; ‘it does go’, ‘it does not go’ or ‘it’s at equilibrium’.

Personally, I would prefer all students to appreciate the very interesting region where ΔG has a value in the range -60 kJ mol^{-1} and +60 kJ mol^{-1}. In this region, the equilibrium position for a process lies somewhere between the two extremes. There are many industrial processes that have ΔG values that are positive at their operating temperature. Yet, they can still be engineered to produce significant products at equilibrium. The Haber-Bosch Process is an example.

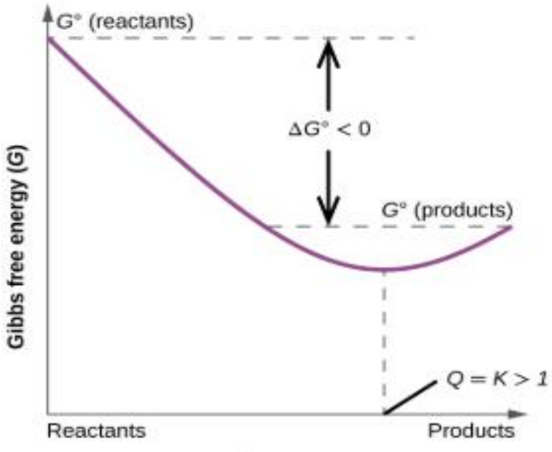
The equation given below equates the Gibbs energy change for a process with the equilibrium constant, K, for the process:

$$\boxed{\Delta G^{\ominus} = -RT\,ln\,K} \qquad (7)$$

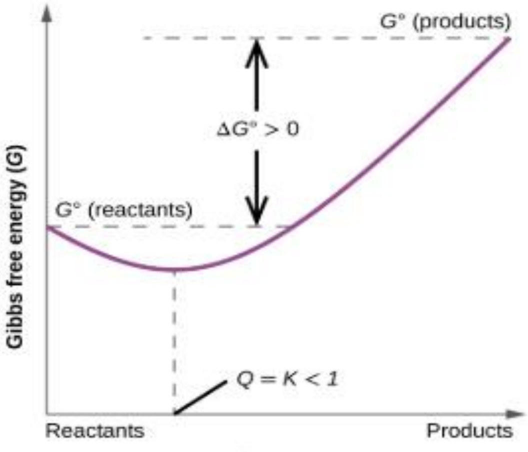
- where **R** is the universal gas constant and **K** is an equilibrium constant.

This equation helps you to connect the sign <u>and magnitude</u> of $\Delta G^{\ominus}$ and the values of *K and T* and therefore links $\Delta G^{\ominus}$ with the **position of equilibrium**!

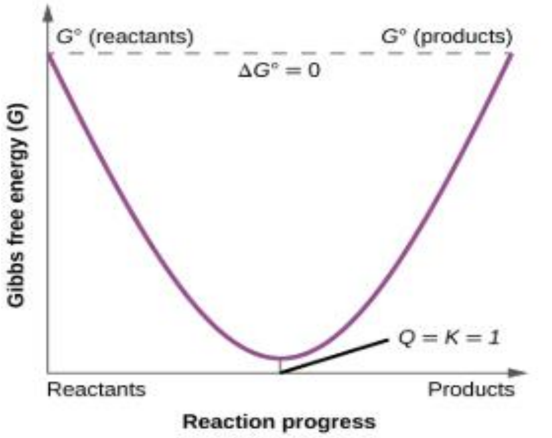
Diagrams below help illustrate this. These diagrams need explaining in the classroom. But, in essence, the bigger the +ve value of $\Delta G^{\ominus}$ the further to the left the equilibrium lies and the bigger the -ve value of $\Delta G^{\ominus}$ the further to the right the equilibrium lies. Imagine the solid purple line on the graph to be loose and droopy elastic, the equilibrium position being represented by the point on the x axis corresponding to the lowest part of the elastic (the minimum value of Gibbs Energy).



(a)



(b)



(c)

Going a Bit Further

The creators of the Pre-U have also included the relationship between ΔG and the standard cell potential for a cell reaction, $E^{\ominus}_{\text{cell}}$

$$\boxed{\Delta G^{\ominus} = -nFE^{\ominus}_{\text{cell}}} \qquad (8)$$

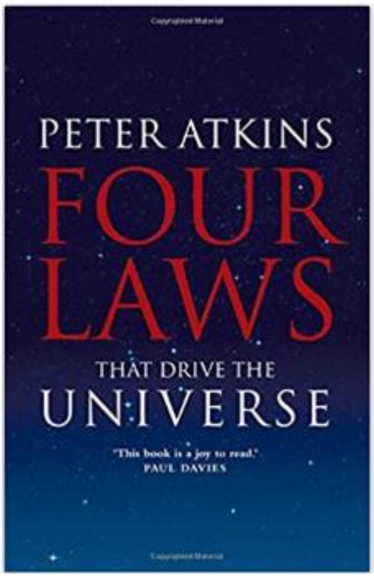
-where n is the number of electrons exchanged, **F** is the Faraday constant and $E^{\ominus}_{\text{cell}}$ is the standard cell potential. Again, I consider the inclusion of this to be important from an historical viewpoint as it was through electrochemistry that much of the thermochemical data was originally obtained.

Thermodynamics can be used to answer so many interesting questions. It can be applied to the processes of life itself. There is a community, typically web-based, for whom thermodynamic arguments form the backbone to the theory of evolution. Interestingly, there are creationists who attempt to use the second law to advance their theory of creation. Their heated exchanges make for interesting reading.

Students (and teachers) can actually enjoy thermodynamics. It is an area of chemistry that enjoys such a rich and interesting history. It developed hand in hand with the steam engine, each feeding off the other. Together, they drove our industrial revolution; the wealth and benefits of which we continue to enjoy. Today, the theories are used to improve jet engines and develop fuel cells. Thermodynamics can help us to understand how living organisms (local 'far from equilibrium' regions of low entropy) have emerged from the increasing chaos around us.

On a final sobering note, it will be the second law and its application to mass food production that sets a limit for human expansion.

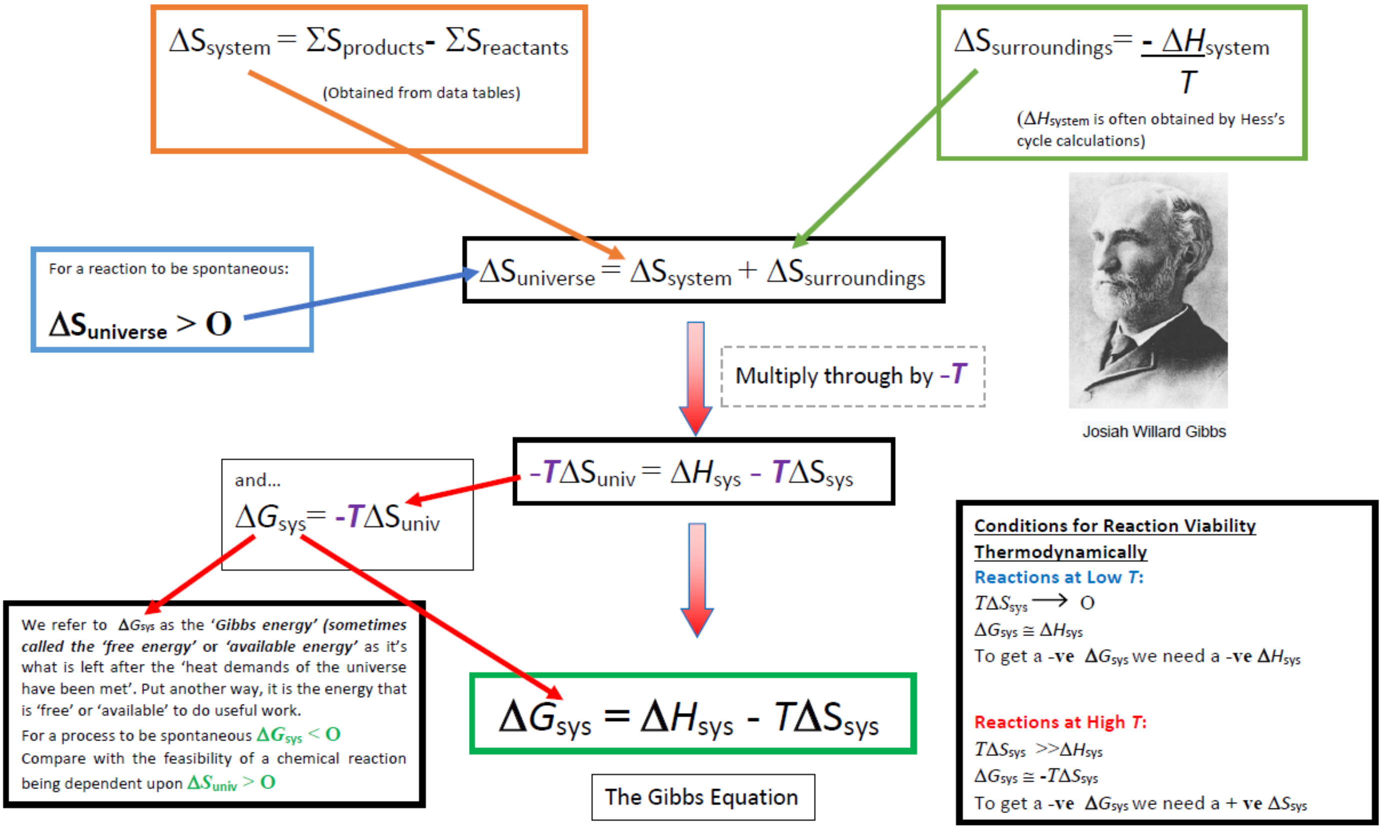
If you want to learn more about the four laws of thermodynamics, then I would suggest that you read Peter Atkins' fabulous book, ***'The Four Laws That Drive the Universe'***. (Oxford University Press).



By the way, there were 3 Laws but the Zeroth Law needed to be added before the others. Thankfully, it's a good prequel, unlike some of the efforts that have emerged in the movie industry.

Below is a simplified derivation of the Gibb's Equation. It makes some assumptions (about reversibility) but we don't need to worry excessively about that at A level.
An downloadable A4 version is available in **TOOLS** on *CramNow*

Entropy and Gibbs Energy



$\Delta S_{system} = \Sigma S_{products} - \Sigma S_{reactants}$

(Obtained from data tables)

$\Delta S_{surroundings} = \dfrac{-\Delta H_{system}}{T}$

(ΔH_{system} is often obtained by Hess's cycle calculations)

For a reaction to be spontaneous:

$\Delta S_{universe} > 0$

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

Multiply through by $-T$

$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$

and...

$\Delta G_{sys} = -T\Delta S_{univ}$

We refer to ΔG_{sys} as the *'Gibbs energy' (sometimes called the 'free energy'* or *'available energy'* as it's what is left after the 'heat demands of the universe have been met'. Put another way, it is the energy that is 'free' or 'available' to do useful work.

For a process to be spontaneous $\Delta G_{sys} < 0$

Compare with the feasibility of a chemical reaction being dependent upon $\Delta S_{univ} > 0$

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

The Gibbs Equation

Josiah Willard Gibbs

Conditions for Reaction Viability Thermodynamically

Reactions at Low *T*:

$T\Delta S_{sys} \longrightarrow 0$

$\Delta G_{sys} \cong \Delta H_{sys}$

To get a **-ve** ΔG_{sys} we need a **-ve** ΔH_{sys}

Reactions at High *T*:

$T\Delta S_{sys} >> \Delta H_{sys}$

$\Delta G_{sys} \cong -T\Delta S_{sys}$

To get a **-ve** ΔG_{sys} we need a **+ ve** ΔS_{sys}

And, finally,

It is said that the novelist and physicist CP Snow devised three clever phrases to help one remember the three laws of thermodynamics. Can you see the connection? I personally find these strangely ominous.

1. First Law - You can't win.
2. Second Law - You can't even break even.
3. Third Law - You can't get out of the game.

Why don't you have a go at the quiz Entropy and Gibbs Energy in M5 Physical Chemistry on *CramNow*

A Selection of Useful Thermodynamic Data

substance	$\Delta H_f^{\ominus}$ /kJ mol^{-1}	$\Delta G_f^{\ominus}$ /kJ mol^{-1}	$S^{\ominus}$ /J mol^{-1} K^{-1}
$Na_2CO_{3\,(s)}$	-1130.7	-1044.5	135.0
$Na_2CO_3 \bullet 10H_2O_{(s)}$	-4081.3	-3428.2	564.0
$NaHCO_{3\,(s)}$	-950.8	-851.0	101.7
$Na_2S_2O_{3\,(s)}$	-1123.0	-1028.0	155.0
$Na_2S_2O_3 \bullet 5H_2O_{\,(s)}$	-2607.9	-2230	372.4
$CaCO_{3\,(s)}$	-1206.9	-1128.8	92.7
$CaO_{\,(s)}$	-635.1	-604.0	39.7
$MgCO_{3\,(s)}$	-1095.8	-1012.1	65.7
$MgO_{\,(s)}$	-601.7	-569.4	26.9
$Al_2O_{3\,(s)}$	-1676	-1582	50.9
$Fe_2O_{3\,(s)}$	-824.2	-742.2	87.4
$HgO_{(s)}$	-90.8	-58.6	70.3
$NH_{3(g)}$	-46.1	-16.4	192
$CH_{4\,(g)}$	-74.8	-50.8	186.2
$C_2H_{6\,(g)}$	-84.7	-32.9	229.5
$C_3H_{8\,(g)}$	-104.5	-23.4	269.9
$CO_{\,(g)}$	-110.5	-137.2	197.6
$CO_{2\,(g)}$	-393.5	-394.4	214
$H_2O_{(gas)}$	-241.8	-228.6	188.7
$H_2O_{(liquid)}$	-285.8	-237.2	69.9
$H_2O_{(solid)}$	-291.8		47.9
$H_{2\,(g)}$			131
$O_{2\,(g)}$			205
$C_{\,(graphite)}$			5.74
$C_{\,(diamond)}$			2.38
$N_{2(g)}$			192
$Fe_{(s)}$			27.3
$Al_{(s)}$			28.3
$Mg_{(s)}$			32.7
$Hg_{(l)}$			76.0