

Chemistry 12
Tutorial 2 - Enthalpy and Entropy

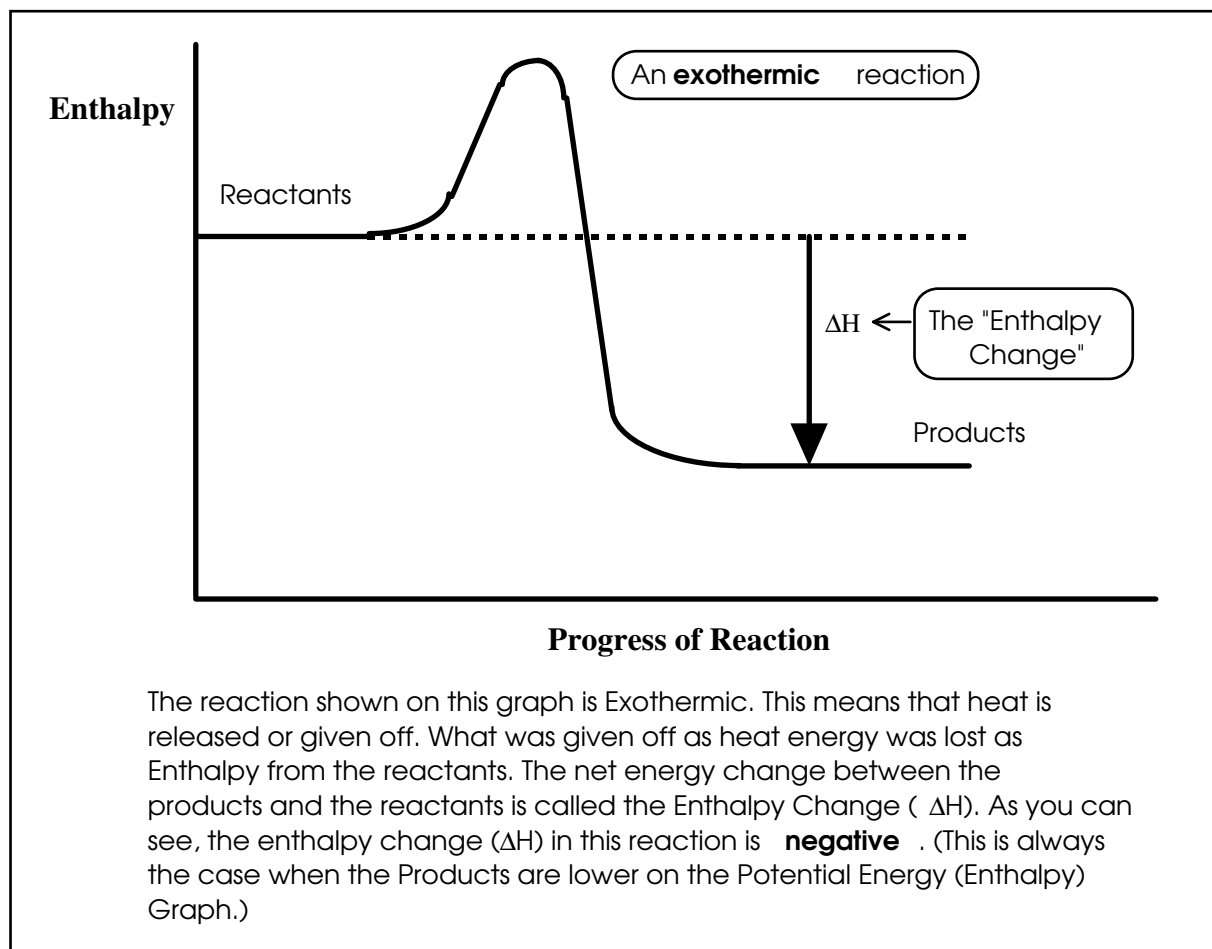
Tutorial 2 will help you to:

1. Define *enthalpy* and *entropy*.
2. Determine whether *enthalpy* and *entropy* is *increasing* or *decreasing* in a reaction.
3. Predict what will happen when two substances are mixed, based on *enthalpy* and *entropy* considerations.

Enthalpy

You have probably met with the concept of *enthalpy* in Unit 1 and in Chemistry 11. Looking it up in the glossary of the textbook defines it as: "The heat content of a system." Another way to think of *enthalpy* is as "Chemical Potential Energy".

Any change in the Potential Energy of a system means the same thing as the "Enthalpy Change". The symbol for Enthalpy is "H". Therefore the "change in Enthalpy" of a chemical reaction is called " ΔH ". As far as we're concerned in Chemistry 12, a Potential Energy Diagram (like we looked at in the last unit) is the same thing as an "Enthalpy Diagram". Let's look at an example:



So, we can make a statement here:

In an Exothermic Reaction (ΔH is negative), the Enthalpy is decreasing.

In an Endothermic Reaction (ΔH is positive), the Enthalpy is increasing.

Of course, you might remember another way to show an endothermic or exothermic reaction. In this case, the "Heat Term" is written *right in the equation*. (This is called a "thermochemical equation".)

If the heat term is on the *left* side, it means heat is being *used up* and it's *endothermic*.

If the heat term is on the *right* side, heat is being *released* and it's *exothermic*.

Look at the following examples:

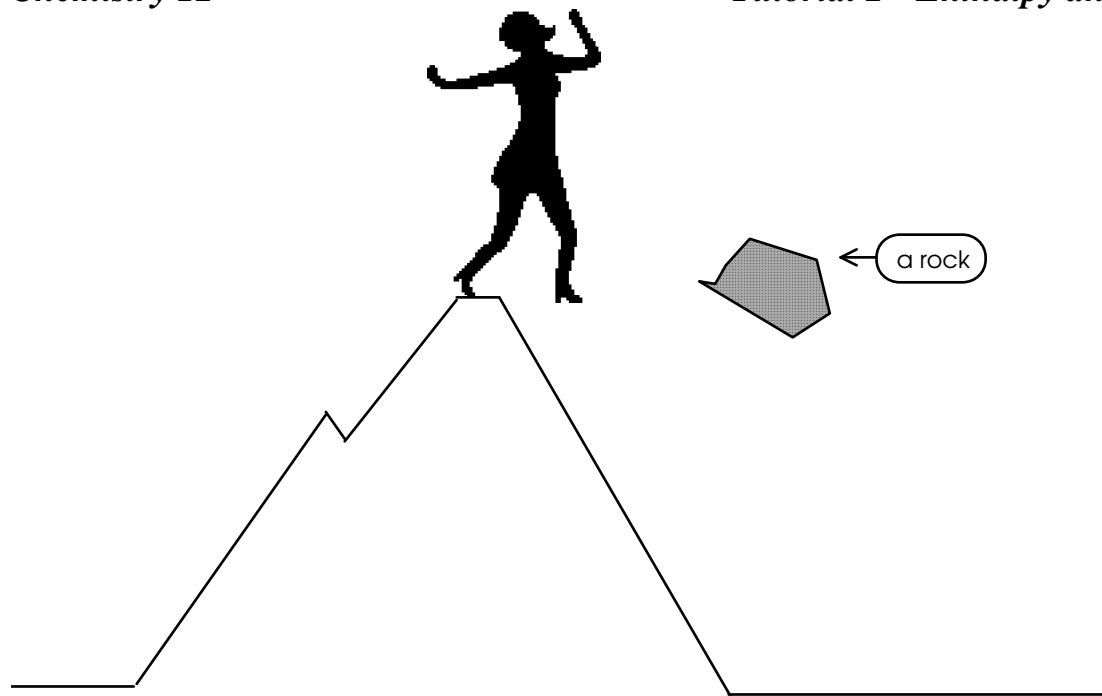
1. $A + B \rightleftharpoons C + D \quad \Delta H = -24 \text{ kJ}$ is *exothermic* so enthalpy is *decreasing*.
2. $X + Y \rightleftharpoons Z \quad \Delta H = 87 \text{ kJ}$ is *endothermic* so enthalpy is *increasing*.
3. $E + D \rightleftharpoons F + 45 \text{ kJ}$ is *exothermic* so enthalpy is *decreasing*.
4. $G + J + 36 \text{ kJ} \rightleftharpoons L + M$ is *endothermic* so enthalpy is *increasing*.

Make sure you are very familiar with the facts given above before you go on the the next section! Ask if you have any problems with it. Given an equation with the ΔH shown or a *thermochemical* equation with the *heat term* on left or right, you will be expected to identify it as *endothermic* or *exothermic* and to determine whether the *enthalpy is increasing or decreasing* as the reaction is proceeding in the forward direction.

Now, here's a little question. If a rock is pushed off the top of a mountain, will it

- a) stay where it is?
- b) fall up?
- c) fall down ?

Answer here, then turn to the next page to check your answer.... _____



Well, you probably guessed correctly. ***The rock will fall down!*** This of course is only true without a doubt if no forces other than gravity are acting on the rock. Let's assume that for now.

Let's say someone asks you ***why*** the rock falls down. Even though you might not say this right "off the bat" a good reason would be:

" The rock falls down because of a natural tendency to achieve a position of lower gravitational potential energy! "

It's true, systems will tend toward a state of lower potential energy if nothing else is acting upon them.

Now, in Chemistry, we are not particularly interested in *gravitational potential energy* (unless we are underneath the rock or skiing.) What we ***are*** interested in is *chemical potential energy*, otherwise known as (you guessed it) - ***enthalpy!***

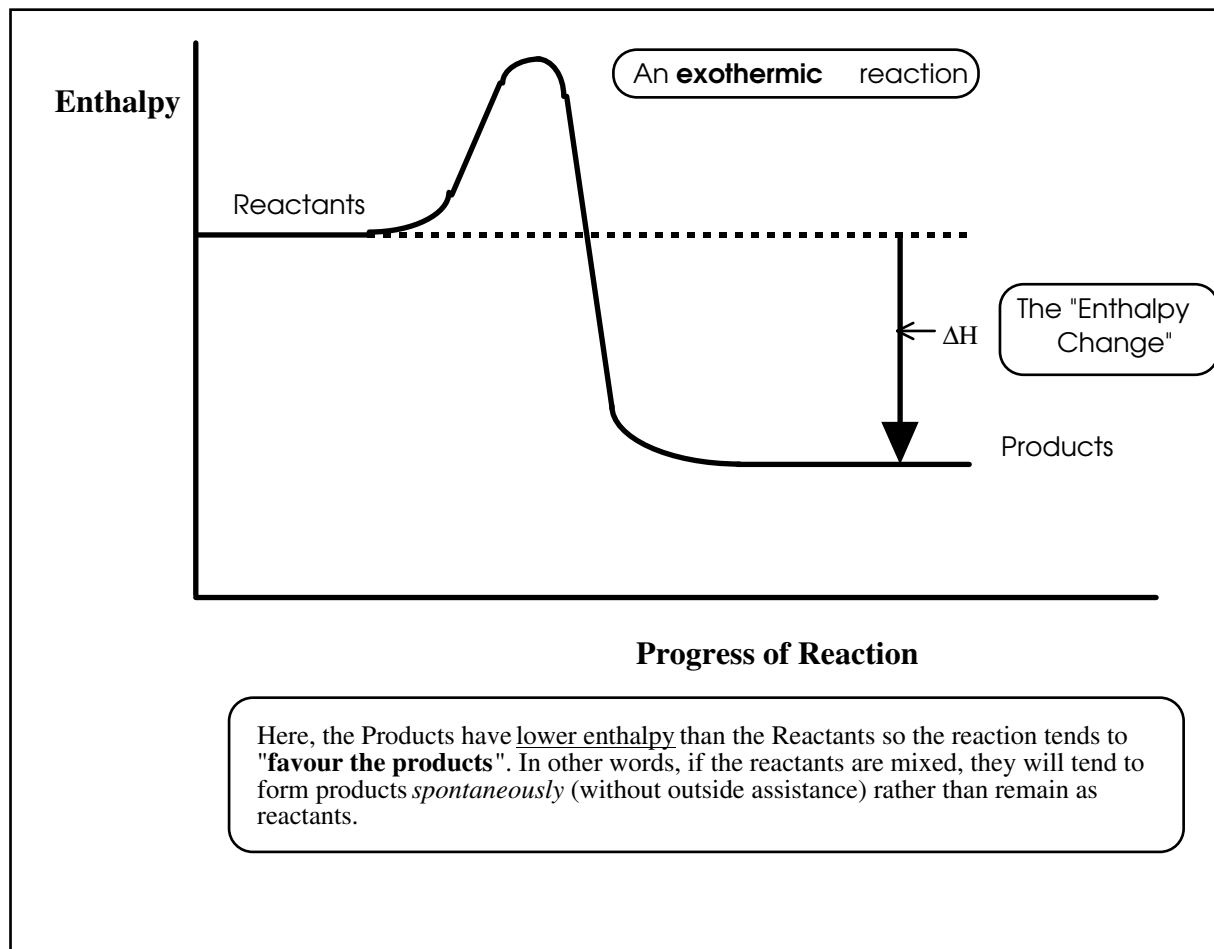
Like the example of gravitational potential energy,

Chemical systems will tend toward a state of minimum enthalpy if sufficient activation energy is available and no other factors are considered.

Another way of stating this might be:

A chemical reaction will favour the side (reactants or products) with minimum enthalpy if no other factors are considered.

Thus for an *exothermic reaction*, if no other factors are considered:



The *products will be favoured* because the products have *minimum enthalpy*. In other words, there is a natural tendency here for reactants to spontaneously form products.

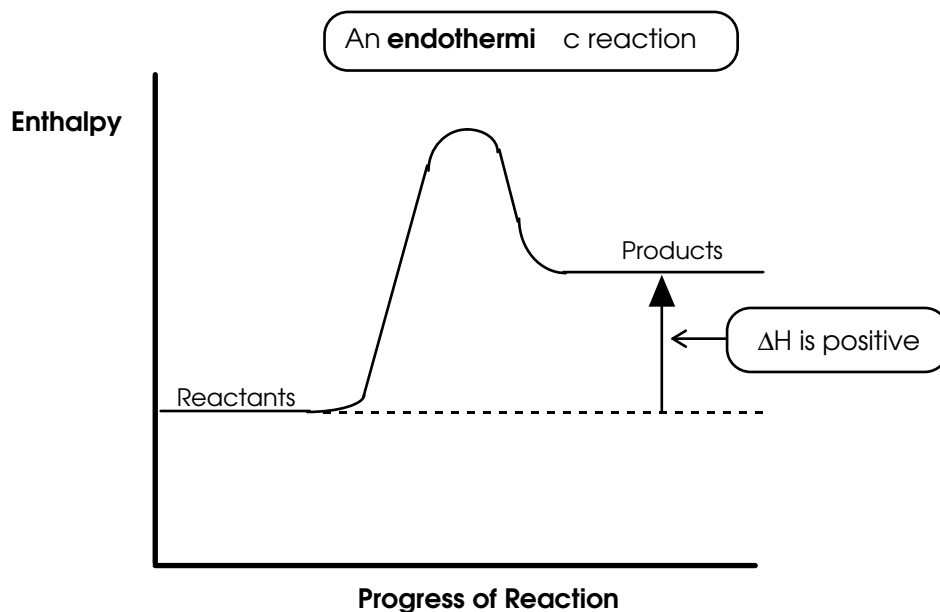
Before you turn to the next page, see if you can predict what would happen in an *endothermic reaction*.

Fill in the blanks below, then turn to the next page and check:

In an *endothermic reaction*, the _____ have minimum enthalpy, so the _____ will be favoured. In other words, if the reactants are mixed they will (tend to remain as reactants / spontaneously form products) _____

(This, of course, is assuming that **no other factors** are affecting the system!)

Let's look at a diagram for an *endothermic reaction*:

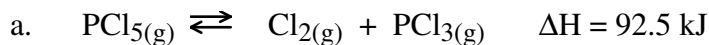


In the case of an **endothermic** reaction, the *enthalpy of the Reactants* is **lower** than the *enthalpy of the Products*. Since chemical systems favour a state of minimum enthalpy, the **Reactants are favoured** in this case. In other words if the reactants are mixed, they will tend to remain as reactants rather than forming products.

Now you can check (and modify if necessary) the questions on page 5.

Do the following exercises and **check the answers on page 1 of Tutorial 2 - Solutions**:

1. Tell whether each of the following is *endothermic* or *exothermic* and state which has **minimum enthalpy**, the *reactants* or the *products*:



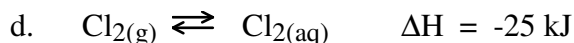
_____ thermic and the _____ have *minimum enthalpy*.



_____ thermic and the _____ have *minimum enthalpy*.



_____ thermic and the _____ have *minimum enthalpy*.



_____ thermic and the _____ have *minimum enthalpy*.

2. When no other factors are considered, a reaction will move in such a way (left or right) in order to achieve a state of _____ enthalpy.
3. Given the equation: $2\text{NH}_3(\text{g}) + 92.4 \text{ kJ} \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
If only the *enthalpy* is considered, the (reactant / products) _____ will be favoured at equilibrium.
4. Given the equation: $\text{Cl}_2(\text{g}) \rightleftharpoons \text{Cl}_2(\text{aq}) \quad \Delta\text{H} = -25 \text{ kJ}$
If only the *enthalpy* is considered, the (reactant / products) _____ will be favoured at equilibrium.
5. If the reaction: $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) + 49.3 \text{ kJ}$
was proceeding to the *right*, the enthalpy would be _____ing. Is this a *favourable* change? _____.
6. If the reaction: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{Cl}_2(\text{g}) + \text{PCl}_3(\text{g}) \quad \Delta\text{H} = 92.5 \text{ kJ}$
was proceeding to the *right*, the enthalpy would be _____ing. Is this a *favourable* change? _____.
7. If the reaction: $\text{Cl}_2(\text{g}) \rightleftharpoons \text{Cl}_2(\text{aq}) \quad \Delta\text{H} = -25 \text{ kJ}$
was proceeding to the *right*, the enthalpy would be _____ing. Is this a *favourable* change? _____.
8. If the reaction: $2\text{NH}_3(\text{g}) + 92.4 \text{ kJ} \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
was proceeding to the *right*, the enthalpy would be _____ing. Is this a *favourable* change? _____.

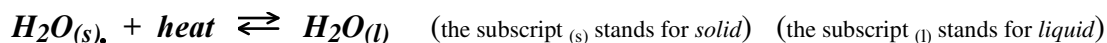
Check the answers on page 1 of Tutorial 2 - Solutions

As you can see by looking at the exercises above, there are two ways of looking at what happens to the *enthalpy*:

*If the reaction is **exothermic**, the **products** have minimum enthalpy and the formation of products (move toward the **right**) is **favourable**.*

*If the reaction is **endothermic**, the **reactants** have minimum enthalpy and the formation of products (move toward the **right**) is **unfavourable**. In this case the formation of **reactants** (move toward the **left**) is **favourable**.*

Now, consider the simple *melting* of water:



If we were to look at only the enthalpy in this process, you can see that the reactant ($\text{H}_2\text{O}_{(s)}$) would have minimum enthalpy and would be favoured. Can you see what this statement would mean? It would mean that *all of the water in the universe should exist only as a **solid**!* (It would not be favourable for water to exist as a liquid!) We would all be frozen solid!!!!

Obviously there is something wrong with this reasoning! We know that there *is* liquid water in the universe, so what gives?

The answer to this problem lies in looking at *another factor* that governs equilibrium. That factor is called **entropy** (or *randomness* or *disorder*)

Entropy

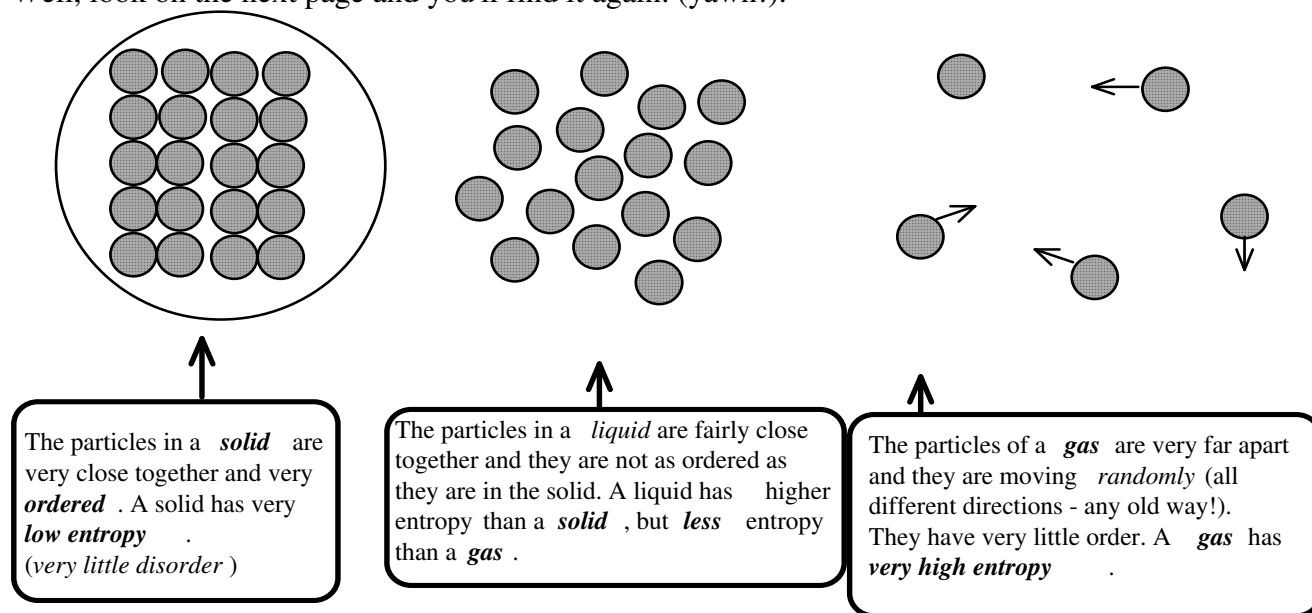
*Entropy simply means **disorder**, or lack of order.*

Student's Chemistry binders are a good example. At the beginning of the semester, papers are neat and ordered. By the end of the semester, pages are torn and falling out. The thing has been overloaded and the rings are usually bent or broken. Pages are loose and often the plastic coating is in shreds. The *entropy* of the binder has *increased* over time! This situation is not unusual, even in chemical reactions!

Chemistry 12

Tutorial 2 - Enthalpy and Entropy

In Grade 8, you probably learned about the arrangement of molecules in solids, liquids and gases. Well, look on the next page and you'll find it again. (yawn!):



So we can summarize by saying that:

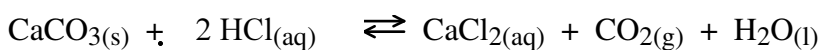
Entropy of a Solid < Entropy of a Liquid < Entropy of a Gas

Chemists and successful Chemistry Students (THAT'S YOU!) can look at a chemical equation with subscripts showing the phases and tell which has **maximum entropy**, the **reactants** or the **products**.

In other words, they can look at an equation and tell whether **entropy** is **increasing** or **decreasing** as the reaction **proceeds to the right**.

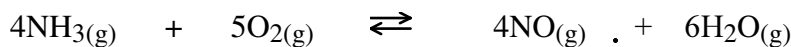
In the following examples, the **entropy is increasing** (or the **products** have **greater entropy**):

1. There is a **gas** (or gases) on the **right**, when there are **no gases** on the **left** of the equation:



a gas is formed on the right.

2. When there are **gases on both sides**, the **products** have **greater entropy** when there are **more moles of gas on the right** (add up coefficients of gases on left and right.):



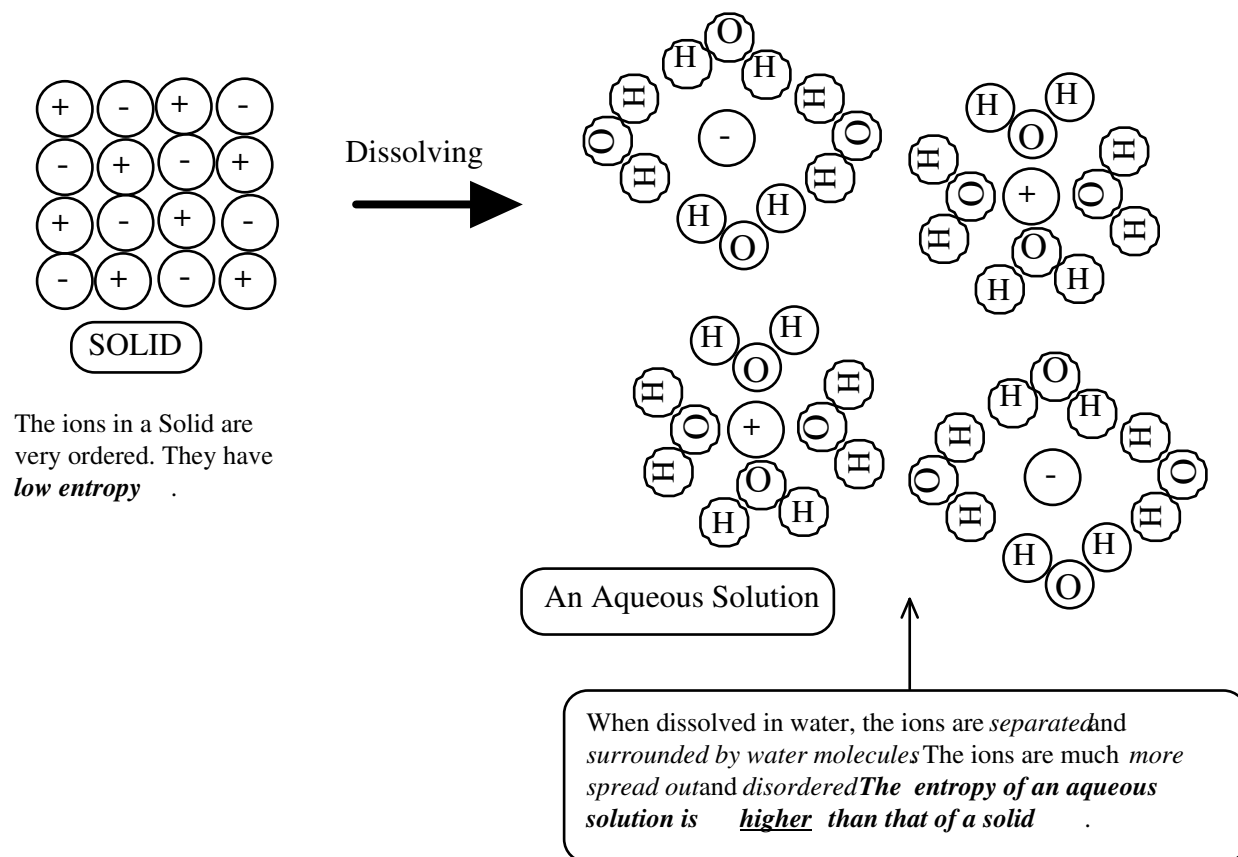
There are $(4 + 5) = \underline{9}$ moles of gas on the left

There are $(4 + 6) = \underline{10}$ moles of gas on the right.

Another way to look at the last example is to say that:

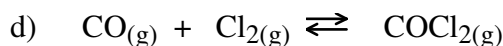
" The side with the greater number of moles of gas has the greatest entropy. "

3. When a *solid* dissolves in water, the *products* (the aqueous solution of ions) have *greater entropy*. This makes sense because:

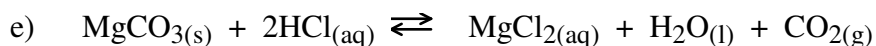


Here are few exercises for you:

9. For each of the following, decide whether the *reactants* or the *products* have *greater entropy*:
- a) $I_{2(s)} \rightleftharpoons I_{2(aq)}$ The _____ have greater entropy.
- b) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$
The _____ have greater entropy.
- c) $NH_{3(g)} \rightleftharpoons NH_{3(aq)}$
The _____ have greater entropy.



The _____ have greater entropy.



The _____ have greater entropy.

Check page 2 of Tutorial 2 - Solutions for the answers to these questions.

If you have any questions about these, check with your teacher!

Now, way back on page 8, we looked at the process: $\text{H}_2\text{O}_{(s)} + \text{heat} \rightleftharpoons \text{H}_2\text{O}_{(l)}$

Remember we decided that all the H_2O in the universe should remain as a *solid* because $\text{H}_2\text{O}_{(s)}$ has **lower enthalpy** than $\text{H}_2\text{O}_{(l)}$ and nature *favours a state of minimum enthalpy*.

Well, now we can explain why there is some liquid water in the universe (lots of it):

$\text{H}_2\text{O}_{(l)}$ has **higher entropy** than $\text{H}_2\text{O}_{(s)}$

If left alone for a long time, systems tend to get more disordered. (Like this classroom, your bedroom or your binders!)

There is a natural tendency in nature toward *maximum disorder* or ***maximum entropy***!

*Chemical systems will tend toward a state of **maximum entropy** if no other factors are considered.*

Another way of stating this might be:

*A chemical reaction will favour the side (reactants or products) with **maximum entropy** if no other factors are considered.*

Remember, the other factor which controlled reactions was **enthalpy**. (chemical potential energy). Also remember that:

*Chemical systems will tend toward a state of **minimum enthalpy** if sufficient activation energy is available and no other factors are considered.*

or (see next page).....

A chemical reaction will favour the side (reactants or products) with minimum enthalpy if no other factors are considered.

Be careful that you don't get the terms **enthalpy** (chemical potential energy) and **entropy** (disorder) confused. They do look and sound somewhat the same! Sorry!

Remember you figure out which has the most **enthalpy** (reactants or products) by looking at the ΔH or the *heat term*. (Review pages 2-6 of this tutorial if you can't remember)

Also, remember that you can figure out which has the more **entropy** (reactants or products) by looking at the subscripts which represent the phases. (Review pages 9-11 or this tutorial).

Also, we can combine the rules about "natural tendencies" to come up with this:

In nature, there is a tendency toward minimum enthalpy and maximum entropy.

Now, let's consider this process again:



The two tendencies are said to "**oppose each other**" in this case:

The tendency toward **minimum enthalpy** would **favour the reactant** ! (since you have to add heat energy to $H_2O_{(s)}$ to get $H_2O_{(l)}$, $H_2O_{(s)}$ has **minimum enthalpy**)

In this case the tendency toward **maximum entropy** would tend to **favour the product**. (A liquid has more **entropy** (disorder) than a *solid*)

We say that:

When the two tendencies **oppose each other** (one favours reactants, the other favours products), the reaction will **reach a state of equilibrium**.

That is, there will be some reactants and some products present. The relative amounts of each depends on conditions like temperature, pressure, concentration etc.

Since this is the case with : $H_2O_{(s)} + \text{heat} \rightleftharpoons H_2O_{(l)}$, there is some solid water and some liquid water in the universe. (In other words, there is a state of equilibrium) Which one is present in the greater amount is determined largely by the **temperature**.

Chemistry 12

Tutorial 2 - Enthalpy and Entropy

Now, let's consider another simple process: A glass bottle is knocked down from a high shelf onto a concrete floor and the glass shatters:

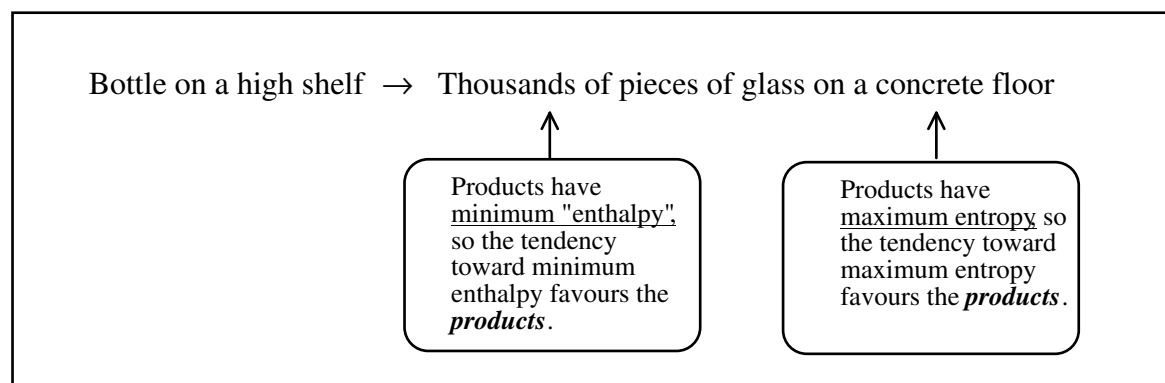
Bottle on a high shelf → Thousands of pieces of glass on a concrete floor

The bottle falls **down** and not up! This happens because there is a natural tendency toward **minimum gravitational potential energy** (like **minimum enthalpy** in chemistry)

In other words the tendency toward **minimum gravitational potential energy** favours the **products** (the low bottle rather than the high)

(To stretch this analogy further, we could consider that the person who knocked the bottle off of the shelf was simply supplying the "activation energy")

Remember that the bottle broke into thousands of pieces when it hit the concrete. The broken pieces of glass have **more disorder (entropy)** than the bottle, so in this process, the tendency toward **maximum entropy** also **favours the products!**



There is no "equilibrium" here when the process is finished. That bottle has completely fallen down and it is all broken. (This bottle is no longer on the shelf and it is no longer an "unbroken bottle")

We can summarize what happened here:

Processes in which **both** the tendency toward **minimum enthalpy** and toward **maximum entropy** favour the **products**, will **go to completion**.

(ie. All reactants will be converted into products. There will be no reactants left once the process is finished!)

Here's an example of a chemical reaction in which this happens:



This process is **exothermic** (the heat term is on the right) so the **products have lower enthalpy**.

The tendency toward **minimum enthalpy** favours the **products**.

There is a mole of gas on the right ($H_2(g)$) and no gases in the reactants. Therefore, the **products have greater entropy**.

The tendency toward *maximum entropy* favours the products.

Since both tendencies favour the products, this reaction will go to completion.

That is, all of the reactants (assuming you have the correct mole ratios eg. 2 moles of K to 2 moles of H₂O) will be converted to products.

If one reactant is *in excess*, the *limiting reactant* will be *completely consumed*.

So, if you put a little bit of potassium in a beaker of water, the reaction will keep going until all of the potassium is used up. There will be *no* potassium left once the reaction is complete.

In other words, the reverse reaction does not occur!

Let's consider one more process:



In this case, *the tendency toward minimum enthalpy* favours the reactants, and the *tendency toward maximum entropy* also favours the reactants.

Processes in which both the tendency toward *minimum enthalpy* and toward *maximum entropy* favour the reactants, will not occur at all!

(ie. None of the reactants will be converted into products. There will be no products formed!)

NOTE: This would be like thousands of pieces of glass spontaneously sticking together, forming a bottle and jumping up onto a high shelf! This does not occur at all. (At least I've never seen it happen!)

To summarize:

When the two tendencies oppose each other (one favours reactants, the other favours products), the reaction will reach a state of equilibrium.

Processes in which both the tendency toward *minimum enthalpy* and toward *maximum entropy* favour the products, will go to completion.

Processes in which both the tendency toward *minimum enthalpy* and toward *maximum entropy* favour the reactants, will not occur at all!

Here's something for you to do:

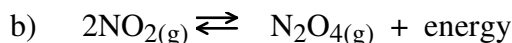
10. For each of the following reactions decide which has **minimum enthalpy** (reactants or products), which has **maximum entropy** (reactants or products), and if the reactants are mixed, what will happen? (go to completion/ reach a state of equilibrium/not occur at all).



The _____ has/have minimum enthalpy.

The _____ has/have maximum entropy.

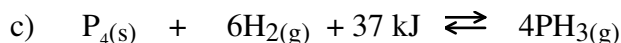
If PCl_3 and Cl_2 are put together, what should happen?(go to completion/ reach a state of equilibrium/not occur at all)



The _____ has/have minimum enthalpy.

The _____ has/have maximum entropy.

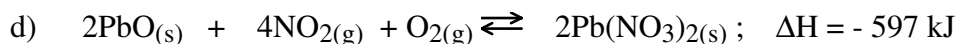
If NO_2 was put in a flask, what should happen?(go to completion/ reach a state of equilibrium/not occur at all)



The _____ has/have minimum enthalpy.

The _____ has/have maximum entropy.

If $\text{P}_4(\text{s})$ and $6\text{H}_2(\text{g})$ was put in a flask, what should happen?(go to completion/ reach a state of equilibrium/not occur at all)



The _____ has/have minimum enthalpy.

The _____ has/have maximum entropy.

If $\text{PbO}(\text{s})$ and $\text{NO}_2(\text{g})$ were put in a flask, what should happen?(go to completion/ reach a state of equilibrium/not occur at all)

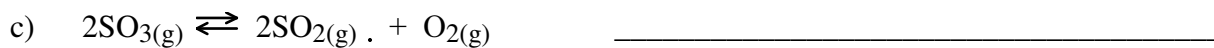
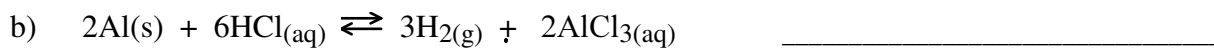
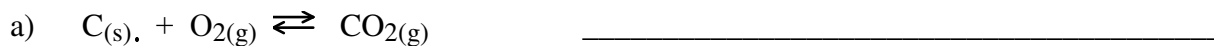
Check Answers on page 3 of Tutorial 2 - Solutions

Self Test on Tutorial 2 - Enthalpy and Entropy

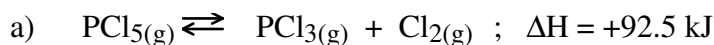
1. What is meant by *enthalpy*? _____

2. What is meant by *entropy*? _____
3. In an *endothermic reaction*, the _____ have *minimum enthalpy*.
4. In an *exothermic reaction*, the _____ have *minimum enthalpy*.
5. Arrange the following in order from *least entropy* to *greatest entropy*:
a) liquids b) gases c) aqueous solutions d) solids
_____ < _____ < _____ < _____
6. There is a natural tendency toward _____ *enthalpy*
and _____ *entropy*.
7. A process in which *entropy increases* and *enthalpy decreases* will
(go to completion/ reach a state of equilibrium/not occur at all) _____
8. A process in which *entropy increases* and *enthalpy increases* will
(go to completion/ reach a state of equilibrium/not occur at all) _____
9. A process in which *entropy decreases* and *enthalpy decreases* will
(go to completion/ reach a state of equilibrium/not occur at all) _____
10. A process in which *entropy decreases* and *enthalpy increases* will
(go to completion/ reach a state of equilibrium/not occur at all) _____
11. A process in which *both the enthalpy and entropy trends favour reactants* will
(go to completion/ reach a state of equilibrium/not occur at all) _____
12. A process in which *both the enthalpy and entropy trends favour products* will
(go to completion/ reach a state of equilibrium/not occur at all) _____
13. A process in which *the enthalpy and entropy trends oppose each other* will
(go to completion/ reach a state of equilibrium/not occur at all) _____

14. In each of the following, state which has the **maximum entropy**, (reactants or products)



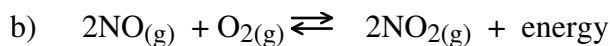
15. For each of the following reactions decide which has **minimum enthalpy** (reactants or products), which has **maximum entropy** (reactants or products), and if the reactants are mixed, what will happen? (go to completion/ reach a state of equilibrium/not occur at all). Assume there is sufficient activation energy to initiate any spontaneous reaction.



The _____ has/have minimum enthalpy.

The _____ has/have maximum entropy.

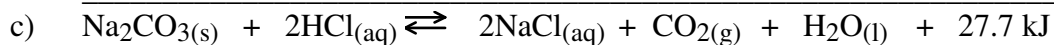
If PCl_5 is put in a flask what should happen? (go to completion/ reach a state of equilibrium/not occur at all)



The _____ has/have minimum enthalpy.

The _____ has/have maximum entropy.

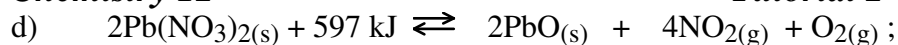
If NO and O_2 were put in a flask, what should happen? (go to completion/ reach a state of equilibrium/not occur at all)



The _____ has/have minimum enthalpy.

The _____ has/have maximum entropy.

If $Na_2CO_{3(s)} + 2HCl_{(aq)}$ were put in a flask, what should happen? (go to completion/ reach a state of equilibrium/not occur at all)



The _____ has/have minimum enthalpy.

The _____ has/have maximum entropy.

If $\text{Pb}(\text{NO}_3)_2$ was put in a flask, what should happen?(go to completion/ reach a state of equilibrium/not occur at all)

16. Reactions which result in a/an _____ in enthalpy and a/an _____ in entropy will *always* be **spontaneous**.

17. Reactions which result in a/an _____ in enthalpy and a/an _____ in entropy will *always* be **non-spontaneous**.

Check answers to Self-Test on page 4 of Tutorial 2 - Solutions