

Unit 5, Lesson 01: Driving Forces in Chemical Reactions: Enthalpy and Entropy

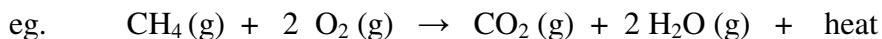
We have been looking at different aspects of chemical reactions- how they occur, whether or not they will occur, how fast they will occur. So far:

1. **Collision Theory** tells us that a chemical reaction occurs when particles collide with sufficient energy and in the correct orientation to allow bonds in reactants to break, so new bonds can form.
2. **Activation Energy** is the amount of energy that must be supplied to break the bonds in the reactants so that the reaction can begin.
3. The **Reaction Rate** tells us how quickly a reaction will occur, once it gets started. The reaction rate of a reaction is equal to the rate of the slowest step in a reaction mechanism (the rate-determining step). Reactions with low activation energies have fast rates.
4. The **Enthalpy change** (ΔH) of a reaction tells us whether a reaction will be favourable. Reactions tend to favour lower energy products.

As always, it is not quite so simple. There is one more (really, just one) factor that affects whether or not a reaction will be favourable. Going back to reactions and enthalpy changes:

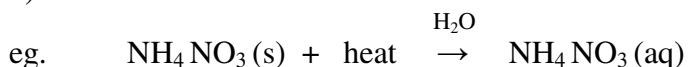
In an **exothermic** reaction,

- a) the enthalpy (total potential energy) of the reactants is **less** than the enthalpy of the products
- b) the reaction tends to proceed to the right (toward the products) to achieve a lower energy arrangement
- c) the energy released by the reaction is given off as heat to the surroundings
- d) heat can be written as a product of the reaction



In an **endothermic** reaction,

- a) the enthalpy (total potential energy) of the reactants is **greater** than the enthalpy of the products
- b) the reaction tends not to proceed spontaneously to the left. Rather, the reaction will favour the reactants and the reaction will proceed to the right to achieve a lower energy arrangement
- c) if the reaction does proceed to left, the required energy is absorbed as heat from the surroundings
- d) heat can be written as a reactant of the reaction



Now, let's think about the above example of an endothermic reaction- this is the reaction that is used in cold packs. As the ammonium nitrate dissolves in water, it absorbs energy from the surroundings. This reaction is endothermic- it is absorbing energy and proceeding to a **higher** energy state, but we all know that it happens anyway. Obviously, the tendency to lower enthalpy can not be the only factor that drives reactions.

There is another driving force in chemical reactions:

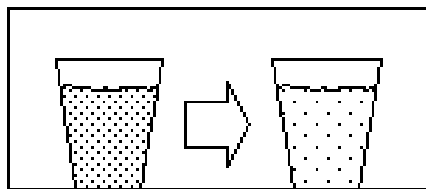
Entropy

Enthalpy describes the **TOTAL AMOUNT** of chemical potential energy in a system. All systems tend to move to lower enthalpy.

But, the energy in a system is distributed between all of the parts of that system- all of the reactants and products.

Entropy (symbol "S") describes how the energy is **SPREAD OUT** within a system. All systems tend to move toward maximum entropy- the energy spreads out as much as possible.

Let's look at an example. Say that we place two cups of water (one hot and one cold) in an insulated container. Because the system is insulated, no energy can be lost or gained from outside the box so the **TOTAL AMOUNT** of thermal energy in the system will be constant. However, the thermal energy will spread from the hot cup of water to the cold cup of water, until all of the particles in the system have the same amount of thermal energy. After sufficient time, the temperature in both cups of water will be the same. So, the **TOTAL AMOUNT** of energy has not changed, but the energy is more **SPREAD OUT** and entropy has increased.

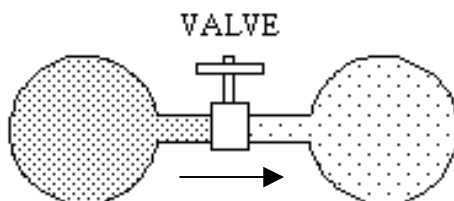


Insulated
box

HEAT MOVES FROM HOT TO COLD (FROM HIGH THERMAL ENERGY TO LOW THERMAL ENERGY)

Now, if we took the lid off of the insulating container, some of the thermal energy from the water will be passed to the surroundings and the energy will be spread out even further. Again, the total energy of the system and the surroundings has not changed, but the entropy has increased. The energy is more spread out.

Let's look at a second example, we all know that particles move from areas of high concentration to areas of lower concentration- but why? If the temperature of the system stays the same, then there is no change in the total amount of energy, so we can not use the tendency of a system to move to lower enthalpy to explain why particles spread out. Instead, when particles spread out, they carry their energy with them- so by spreading out the particles, the energy of the system is also spreading out, and entropy is increased. It is the drive toward maximum entropy that causes particles to spread out.



GAS PARTICLES MOVE FROM AREAS OF HIGH CONCENTRATION TO AREAS OF LOW CONCENTRATION

You will see entropy (S) described or defined as the tendency toward randomness or disorder in a system (like your room becoming messy unless you work hard to keep it tidy). Please remember that the reason systems move toward randomness is because this allows the **energy** in the system to spread out, and entropy correctly refers to the distribution (spreading out) of energy in a system.

The **Second Law of Thermodynamics** states that all systems will move toward maximum entropy.

It is often a relatively simple matter to predict whether a particular change will become more or less random. One of the things to look for is the state of the reactants and products. Gases have more entropy than liquids, which have more than solids. Also, solutions have more entropy than liquids or solids.

So, referring back to the cold packs: $\text{NH}_4\text{NO}_3(\text{s}) + \text{heat} \xrightarrow{\text{H}_2\text{O}} \text{NH}_4\text{NO}_3(\text{aq})$

As the ammonium nitrate dissolves, it spreads out through the solution, carrying its energy with it. So, even though the forward reaction is endothermic, the reaction proceeds spontaneously to the right because the forward reaction greatly increases the entropy of the system.

Entropy may also be changed by changing the number and type of the particles in the system.

For example, the reaction: $2\text{NO}(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$

The forward reaction takes two molecules of NO gas and combines them to make one molecule of N₂O₄ gas. There are fewer gas particles as products, so the overall entropy of the system has decreased.

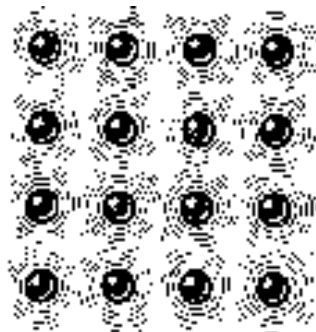
eg. For the reaction: $\text{CaCO}_3(\text{s}) + \text{heat} \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

The reactant is a single molecule of a solid, which has very low entropy. The products are a smaller molecule of a solid and a molecule of a gas. The products have much higher entropy than the reactants.

The entropy of a system depends on the temperature. As the temperature of a substance increases, the particles in the substance overcome some of the inter-molecular forces of attraction, and the particles have more freedom of movement. They also spread out slightly (thermal expansion). Both of these changes increase the entropy of the system. Using similar logic, as temperature decreases, particles slow down and become more organized, so entropy decreases.



low temperature, little molecular motion and low entropy



higher temperature, more molecular motion and higher entropy

In order to measure entropy, chemists need a reference point. **The Third Law of Thermodynamics** states that a pure crystal at 0 K (absolute zero) has zero entropy because the particles are not moving and the crystal has absolutely no disorder. The entropy of all other systems can be measured relative to this. There are charts available that report the entropy of different substances at a standard state (SATP).

It is the difference between the entropy, or the change in entropy (ΔS) between the products and reactants that is important.

So, there are two driving forces behind chemical reactions:

1. the tendency to minimum enthalpy ($-\Delta H$)
2. the tendency to maximum entropy ($+\Delta S$)

There are several possibilities when chemical reactions occur:

a) if the enthalpy decreases ($-\Delta H$) and the entropy increases ($+\Delta S$)



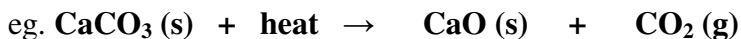
- this reaction is exothermic, so the products have lower enthalpy than the reactants
- this reaction has 9 moles of gas on the reactant side of the equation, and produces 11 moles of gas as products. The entropy of the system increases
- both of the driving forces favour the products, so the reaction is spontaneous and proceeds far to the right
- because both driving forces favour the products, this reaction is “irreversible”

b) if the enthalpy increases ($+\Delta H$) and the entropy decreases ($-\Delta S$)



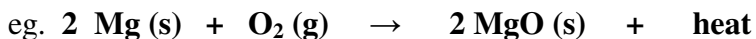
- this reaction is endothermic, so the products have higher enthalpy than the reactants
- this reaction has 3 moles of gas on the reactant side of the equation, and produces 2 moles of gas as products. The entropy of the system decreases
- both of the driving forces favour the reactants, so the reaction is non-spontaneous and does not proceed to the right
- this reaction is essentially impossible as written

c) if the enthalpy increases ($+\Delta H$) and the entropy increases ($+\Delta S$)



- the reaction is endothermic, so the products have higher enthalpy than the reactants
- this reaction has one mole of solid on the reactant side of the equation, and produces one mole of solid and one mole of gas as products. The entropy of the system increases
- the driving forces act in opposite directions
- this reaction is reversible

d) if the enthalpy decreases ($-\Delta H$) and the entropy decreases ($-\Delta S$)



- the reaction is exothermic, so the products have lower enthalpy than the reactants
- the reaction has two moles of solid and one mole of gas on the reactant side of the equation, and produces two moles of solid. The entropy of the system decreases
- the driving forces act in opposite directions
- this reaction is reversible

Remember: enthalpy and entropy do not tell us anything about the activation energy, reaction mechanism or rate of a chemical reaction.