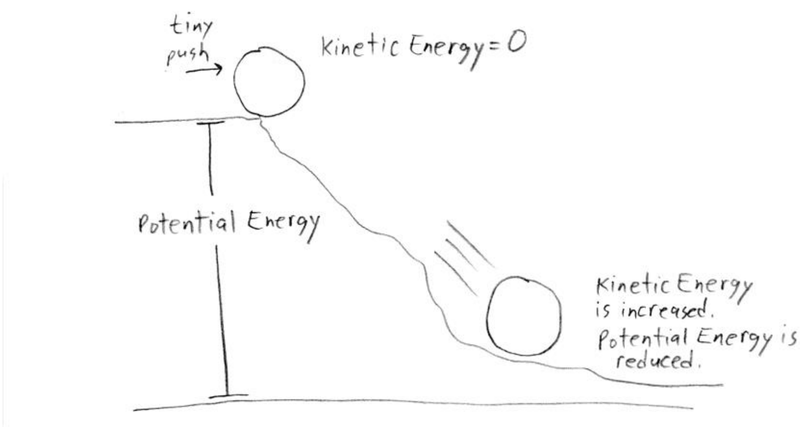
Chemistry Lecture #102: Factors Affecting the Spontaneity of a Reaction

Enthalpy and the Spontaneity of Reactions

Events that release stored energy have a greater tendency to occur spontaneously. For example, suppose there was a large rock perched precariously at the top of a short cliff above a hill. Since the rock is at rest, it has a kinetic energy of zero. But it took energy to bring the rock to the top of the cliff, so there is potential energy stored in the rock.

If the rock were given a tiny push, it would spontaneously roll down the hill and move faster and faster. As it moves faster, its kinetic energy increases and its potential energy decreases. Potential energy has been converted to kinetic energy.

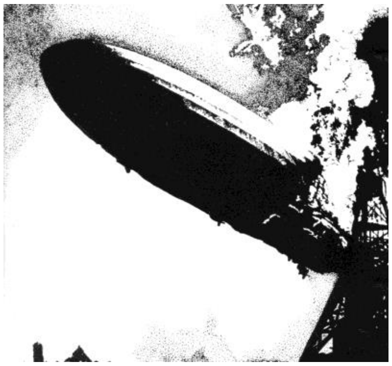


The tendency is for the rock to fall and release its potential energy. Likewise, a chemical reaction will tend to occur if it releases the potential energy stored in the bonds between atoms. Or, a reaction will occur spontaneously if the change in enthalpy, ΔH, is negative. Thus, exothermic reactions tend to be spontaneous.

For example, $H_{2(g)}$ and $O_{2(g)}$ can react to form $H_2O_{(l)}$. The reaction produces a great deal of energy.

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ $\Delta H = -572$ kJ spontaneous reaction

In fact, this is why the Hindenburg blimp exploded. It was filled with hydrogen gas. Static electricity may have initiated the reaction, and the blimp exploded into flames as the hydrogen gas combined with oxygen in the air.



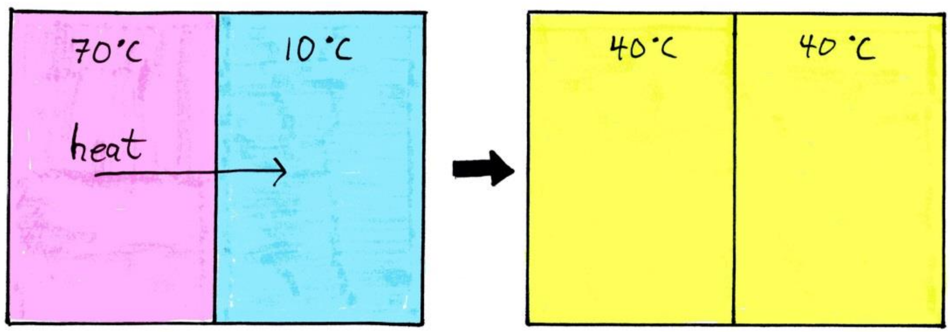
Can $H_2O_{(l)}$ spontaneously decompose into $H_{2(g)}$ and $O_{2(g)}$? It is not likely to occur. In the same way that a rock is unlikely to spontaneously roll *uphill* and store potential energy, it is unlikely that $H_2O_{(l)}$ will spontaneously form hydrogen and oxygen gas.

$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$ $\Delta H = 572$ kJ, non-spontaneous

Notice that the ΔH for this reaction is *positive* 572 kJ. To make this reaction occur, you need to continuously *add* energy (in the form of electricity) to water to drive the reaction. The moment you stop adding energy, the reaction stops. Thus, reactions where ΔH is positive, or endothermic reactions, tend to be non-spontaneous.

Entropy and the Spontaneity of Reactions

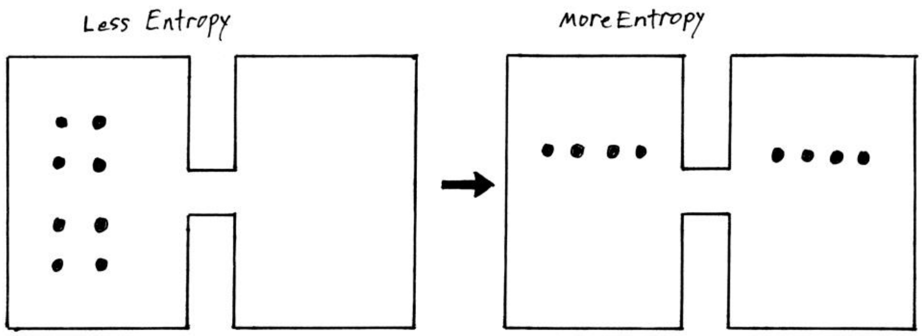
Entropy is a measure of how energy is spread out. The tendency in nature is for energy to spread out from a concentrated area to a less concentrated area. For example, if a hot piece of metal is pressed against a colder piece of metal, the heat will spread from the hot metal to the cold metal until both reach the same temperature.



Heat moves from a hot object to a colder object until both objects reach the same temperature.

When energy spreads out, there is often an increase in randomness or disorder. Thus, entropy is often defined as an increase in disorder.

For example, suppose that there are 8 gas atoms in the left side of a chamber. The atoms are allowed to move through a passage to the right side.



Gas atoms are more likely to spread out and occupy both chambers.

Since the atoms are moving and have kinetic energy, entropy increases since the atoms or energy is spread out over two chambers instead of one. In addition, there is a greater degree of randomness because there are two possible locations for each atom instead of one.

How likely is it for all 8 atoms to remain in the left chamber? Since there are 8 atoms and two choices for each atom (left or right chamber), the odds that all atoms would stay on the left are one in 2^8 chances, or 1 out of 256. This comes to a 0.39 percent chance. This is like flipping a coin 8 times and getting heads with each flip - an unlikely series of events. Thus, it is highly unlikely that all the atoms would stay on one side - they are more likely to spread to both chambers.

Likewise, it is also unlikely that heat energy would travel from a colder object to a hotter object. It could happen, but it probably won't.

Thus, the tendency in nature is for entropy or randomness to increase.

Entropy increases as a substance is converted from solid, to liquid to gas. Solids have the lowest entropy since the particles of a solid simply vibrate. Particles in a liquid, on the other hand, move and slide past each other, so liquids have more entropy than solids. Particles in a gas are far apart and moving rapidly, so gases have the highest degree of entropy.

Entropy also increases when the number of particles in a chemical reaction increases. If the number of particles increases, energy is spread out among more objects. For example, take the reaction

$$2C_2H_{6(g)} + 7O_{2(g)} \rightarrow 4CO_{2(g)} + 6H_2O_{(g)} \quad \Delta S = 92.7 \text{ J/mol K}$$

nine molecules → ten molecules

The reaction starts with nine molecules. After the reaction, there are ten molecules. Since the number of particles has increased, there has been an increase in entropy. The change in entropy, ΔS, has increased by 92.7 J/mol K.

When ΔS is a positive number, it indicates an increase in entropy. A negative number indicates a decrease in entropy. Reactions where ΔS is positive are more likely to be spontaneous. If ΔS is negative, the reaction is less likely to occur spontaneously.

We can summarize the effect of enthalpy and entropy on the spontaneity of a reaction as follows:

ΔH = -,spontaneous
ΔH = +, non-spontaneous

ΔS = +, spontaneous
ΔS = -, non-spontaneous.