Thermodynamics

Unit: Thermochemistry (Heat)

MA Curriculum Frameworks (2016): HS-PS3-4b

Mastery Objective(s): (Students will be able to…)

- Explain the laws of thermodynamics.
- Apply the laws of thermodynamics conceptually to hypothetical situations.

Success Criteria:

- Explanations account for enthalpy and entropy differences.
- Explanations account for the conservation of energy.

Tier 2 Vocabulary: system, free

Language Objectives:

- Explain the laws of thermodynamics.

Notes:

In the universe, energy is what "makes things happen". In chemistry, we use the following terms to distinguish between the molecules we are talking about vs. the ones we aren't:

system: the collection of molecules under consideration for a given situation.

surroundings: everything that is not part of the system

E.g., for a bunch of chemicals in a beaker, the chemicals would be the ***system***, and the beaker, the air in the room, and everything else would be the ***surroundings***.

Use this space for summary and/or additional notes:

Heat Flow

We generally use the variable Q to represent heat.

Heat flow is always represented in relation to the system.

Heat Flow	Sign of Q	System	Surroundings
from surroundings to system	+ (positive)	gains heat (gets warmer)	lose heat (get colder)
from system to surroundings	− (negative)	loses heat (gets colder)	gain heat (get hotter)

A positive value of Q means heat is flowing ***into*** the system. Because the heat is transferred from the molecules outside the system to the molecules in the system, the temperature of the system increases, and the temperature of the surroundings decreases.

A negative value of Q means heat is flowing ***out of*** the system. Because the heat is transferred from the molecules in the system to the molecules outside the system, the temperature of the system decreases, and the temperature of the surroundings increases.

endothermic reaction: a chemical reaction in which heat energy in the system is used to make the reaction proceed. This causes the system to get colder, which then causes heat to flow into the system from the surroundings. (Positive value of Q.)

exothermic reaction: a chemical reaction in which heat energy is released as the reaction proceeds. This causes the system to get hotter, which then causes heat to flow out of the system into the surroundings. (Negative value of Q.)

This is confusing for most people.

If you add sodium hydrogen carbonate (baking soda) to a strong acid, the solution will get colder, and the beaker will feel cold to the touch. The reaction took heat away from the solution. What makes this an endothermic reaction is that the system (the solution) is now colder than the surroundings, which means heat flows from the surroundings into the system to warm it back up.

If you add sodium hydroxide (lye) to a strong acid, the solution will get hotter, and the beaker will feel hot to the touch. The reaction released heat into the solution. What makes this an exothermic reaction is that the system (the solution) is now hotter than the surroundings, which means heat flows from the system into the surroundings to heat up the surroundings (and therefore cool off the system).

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A quick and simple way to think of this is by thinking of a glass of ice water. The ice water is the system and your hand is part of the surroundings. When you pick up the glass, your hand gets colder because heat is flowing from your hand (the surroundings) into the system (the ice water). This means the system is gaining heat, and the surroundings are losing heat. The value of Q would be positive in this example.

thermal equilibrium: when all of the particles in a system have the same average kinetic energy (temperature).

When a system is at thermal equilibrium, no net heat is transferred. (*I.e.,* collisions between particles still transfer energy back and forth, but the average temperature of the particles in the system—the macroscopic quantity that we can measure with a thermometer—is not changing.)

Use this space for summary and/or additional notes:

Usable *vs.* Non-Usable Energy

In any system, some of the energy

enthalpy: the total usable thermal (heat) energy of a system.

entropy: thermal energy that exists in a system, but cannot be transferred to other molecules or objects.

Energy can only be transferred in a reasonable amount of time if there is enough of an energy difference between the particles that are supplying the energy and the particles receiving it. For example, if your body temperature is 37 °C (98.6 °F) and you jump into water that is 10 °C (50 °F), you will lose heat very quickly. However, if you climb into a 36.9 °C spa ("hot tub"), you can stay in for an hour and your body temperature will be unaffected.

Entropy is therefore the energy that has been dispersed ("lost") into the surroundings, because there is so little difference between its heat content and the heat content of the surroundings that the energy cannot be transferred to other particles.

However, in many cases it is possible to reduce the entropy of a system by adding energy.

For example, if you open a bottle of ethyl acetate (the solvent in nail polish), the molecules will gradually diffuse into the room, and the entire room will smell like nail polish. The entropy of the gases in the room has increased, because the molecules of ethyl acetate (and the energy they contain) are more spread than they were before.

You could build a machine to pump all of the air in the room through a −40 °C condenser. This would condense 99 % of the ethyl acetate to a liquid, which you could then pour back into the bottle. This would indeed reduce entropy, but you would have to use much more energy to condense the ethyl acetate than the amount of energy you would recover in the form of reduced entropy.

Use this space for summary and/or additional notes:

Thermodynamics

In chemistry, we categorize energy in the following ways:

kinetic energy (K): the energy contained in the particles due to motion of the particles or sub-particles (atoms, molecules, atomic nuclei, electrons, *etc.*) The equation for kinetic energy is $K = \frac{1}{2}mv^2$, so kinetic energy depends on the masses and velocities (speeds) of the particles.

temperature (T): the average kinetic energy of the particles in a system. You can think of it as "heat per molecule". Increasing the temperature makes the molecules move faster; decreasing the temperature makes the molecules move more slowly.

internal energy (U): the total kinetic energy* of the molecules in a system.

Internal energy depends on the average kinetic energy of the molecules (temperature, T) and the number of molecules (or number of moles of molecules, n). For the units to work out so the energy comes out in units of joules, we multiply by the gas constant, giving the equation:

$$U = \frac{3}{2}nRT$$

work (W): the energy that a gas can transfer by its pressure causing a change in volume. Work can be done on the surroundings (the gas decreases its energy), or work can be done by the surroundings on the gas (the gas increases its energy).

$$W = P\Delta V$$

enthalpy (H): the total usable energy of a system, which includes its internal energy plus energy in the form of work that could be transferred between the system and surroundings.

$$H = U + PV$$

* Actually, internal energy also includes microscopic potential energy, which the energy of chemical and nuclear particle bonds, and the other physical force fields within the system (internal induced electric or magnetic dipole moment, stress-strain energy due to deformation of solids, *etc.*). Microscopic potential energy is beyond the scope of this course.

Use this space for summary and/or additional notes:

<u>entropy</u> (S): energy that exists in a system, but cannot be transferred to other molecules or objects.

<u>free energy</u>: the energy of a system that is "free" (available) to do work. (Sometimes called the usable energy of the system.)

<u>Helmholtz free energy</u> (A): the usable energy of a system with a constant volume. Named after the German physicist Hermann von Helmholtz. (Useful in physics; rarely used in chemistry.)

$$A = U - TS$$

<u>Gibbs free energy</u> (G): the usable energy of a system with constant pressure. Named after the American physicist J. Willard Gibbs. (Useful in chemistry; rarely used in physics.)

$$G = H - TS$$

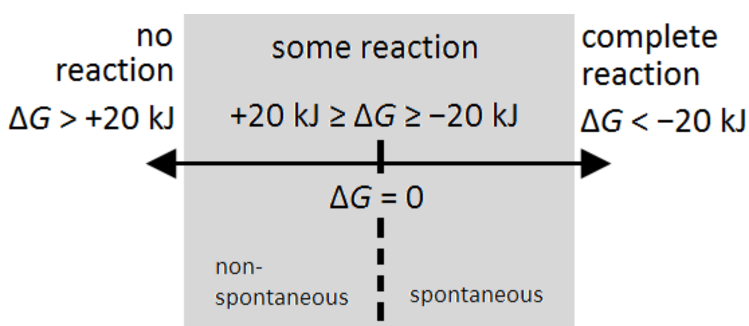
In chemistry, Gibbs free energy is the most useful in predicting whether (and to what extent) a chemical reaction will happen.

A chemical reaction is <u>*spontaneous*</u> if the change in Gibbs free energy is negative ($\Delta G < 0$), *i.e.,* if the reaction *releases* energy and the total energy of the products is less than the total energy of the reactants.

A chemical reaction is <u>*non-spontaneous*</u> if the change in Gibbs free energy is positive ($\Delta G > 0$), *i.e.,* if the reaction *consumes* energy and the total energy of the products is more than the total energy of the reactants.

A rule of thumb is that if a chemical reaction releases more than approximately 20 kJ of free energy (meaning $\Delta G < -20$ kJ), then the reaction "goes to completion," which means there will essentially be no detectable amount of the reactants left after the reaction takes place.

Similarly, if a chemical reaction would require more than 20 kJ of free energy (meaning $\Delta G \geq +20$ kJ), then "no reaction occurs," meaning there will essentially be no detectable amount of products made.



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Laws of Thermodynamics

Thermodynamics allows us to predict much of what happens in the universe based on energy changes. These predictions can be summed up in the four* laws of thermodynamics:

0. If you allow objects/systems in contact with each other to exchange heat for an infinite amount of time, they will have the same temperature.
   ("You have to play the game.")
1. Chemical reactions proceed in a way that releases energy, *i.e.,* usable heat energy (enthalpy) moves from particles with higher temperature to particles with lower temperature. Heat energy cannot flow from a lower temperature to a higher temperature.
   ("You can't win.")
2. Some heat energy is always lost to the surroundings (entropy) and cannot be recovered. Therefore, the entropy of the universe is always increasing.
   ("You can't break even.")
3. In a completely closed system, the total energy (enthalpy plus entropy) is constant. A change that would cause an increase in enthalpy (positive ΔH) would normally not happen spontaneously, but it can occur spontaneously if there is a sufficient increase in entropy (positive ΔS).
   ("You can't get out of the game.")

What You Need to Know

This is a lot of information, and yet only the tip of the iceberg; there are entire college courses on thermodynamics. Most of the information in this section is included to explain the bigger picture; in this course, you do not need to use any of these equations. The important points you need to understand in a first-year chemistry class are:

- Some energy, called enthalpy (H), exists in the form of usable heat that can be taken up or given off in chemical reactions, and/or used to do work.
- Some energy, called entropy (S), exists in the form of heat that is dispersed ("lost") to the surroundings and cannot be recovered.
- The combination of enthalpy and entropy, called Gibbs free energy (G), determines whether and to what extent a chemical reaction occurs.

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* Originally there were three laws numbered 1–3. The "zero" law was added later, and was numbered zero in order to preserve the numbering of the first, second, and third laws.

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