

Teacher's Tools[®] Chemistry

Thermodynamics: First, Second and Third Laws of Thermodynamics: Student Review Notes

Energy is the capacity to cause change through a work effect or heat effect. Work and heat are both forms of energy. The unit of energy in the SI system is the joule. $1 \text{ J} = 1 \text{ kgm}^2\text{s}^{-1}$

The First Law of Thermodynamics is the Law of Conservation of Energy. In any non-nuclear process, energy can neither be created nor destroyed, only transformed from one form to another.

Some familiar forms of energy:

Kinetic Energy (K.E.) is the energy of motion, an object in motion possesses kinetic energy.

$$\text{K.E.} = \frac{1}{2}mv^2 \quad \text{where, } m \text{ is the mass of the object and } v \text{ is the velocity}$$

Potential Energy (P.E.) is the energy of position, the “stored” energy. A good example of potential energy is a mass held at a height in a gravitational field.

$$\text{P.E.} = mgh \quad \text{where, } m \text{ is the mass of the object, } g \text{ is the acceleration constant of gravity and } h \text{ is the height.}$$

Applying the Law of Conservation of Energy. It is important that you understand how to analyze a process in terms of the Law of Energy Conservation. The following steps will help you do this:

Step 1: Imagine a global boundary around the process, this boundary defines the “system” This system can be open and therefore both energy and mass can pass across its boundary, closed in which case energy but not mass can pass across its boundary or isolated in which neither mass or energy can be transferred across the boundary. A sealed insulated container is a good example of a isolated system. A steaming cup of coffee is a good example of an open system. An unopened can of soda would be a closed system.

Step 2: Within this system, ask yourself the following questions: “Is anything gaining energy, and if so, from where is the energy coming?”; If one component within the system is gaining energy, then some other part must be losing energy. “Is anything losing energy, and if so, where is the energy going?”; If one component within the system is losing energy, then some other part must be gaining energy.

Here is an example:

A block of iron metal with a mass of 50.0 g was heated to 100.00 °C and then immersed in 100.0 mL of water initially at 25.00 °C and contained in a well insulated thermos. The final temperature of the overall system was 28.86 °C. Based on this data, what is the specific heat of iron given that the specific heat of water is 4.184 J/g°C?

In this example, the well insulated thermos is an isolated system and therefore both mass and energy must be conserved. Now ask yourself the questions. Is one component gaining energy? Yes, the water will increase in temperature and therefore gains energy in the form of heat. Where is this energy coming from or what component is losing energy? The iron sample will cool down when placed in the water and therefore it is losing energy in the form of heat. Mathematically, we can do the bookkeeping to track this transfer of energy:

$$\Delta E_{\text{system}} = 0 = \Delta E_{\text{water}} + \Delta E_{\text{iron}}$$

Both iron and water are changing temperature, so we can use the equation $\Delta E = mS\Delta T$ to calculate the change in energy for each component.

$$\Delta E_{\text{system}} = 0 = mS\Delta T_{\text{water}} + mS\Delta T_{\text{iron}}$$

$$0 = (100.0 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(28.68 \text{ }^\circ\text{C} - 25.00 \text{ }^\circ\text{C}) + (50.0 \text{ g})(S_{\text{Fe}})(28.68 \text{ }^\circ\text{C} - 100.00 \text{ }^\circ\text{C})$$

$$(S_{\text{Fe}}) = 0.45 \text{ J/g}^\circ\text{C}$$

Thermodynamics: First, Second and Third Laws of Thermodynamics: Student Review Notes**The First Law of Thermodynamics continued...**

The previous example demonstrated the conservation of energy within a closed system. What about the case in which energy is conserved but some energy in the form of heat is converted to energy in the form of work? This is big engineering topic and at this level of chemistry, you only need to perform the simplest types of calculations. These involve work associated with a change in volume, like the work done by a piston. In such a system, the pressure is typically assumed constant and the work done by the system is $P\Delta V$ or work is equal to the pressure times the change in volume. Watch the units for this type of calculation, you get atm-liters. Use the ideal gas constant to convert from these units to joules.

$$R = 8.314 \frac{\text{J}}{\text{mol K}} = 0.08206 \frac{\text{atm L}}{\text{mol K}} \text{ and therefore } 1 \text{ atm L} = 101.3 \text{ J}$$

Here is an example:

A system consisting of 18.02 g of water vapor at 100.0 °C and 1 atm has a volume of 30.12 L. It condenses at constant pressure to liquid at 100.0 °C. The density of the liquid is 0.9584 g/mL. There are 40,608 J of heat released to the surroundings during this process. Calculate the change in energy associated with the process. So this is like a steam piston that cools off. It is a closed system, energy in the form of heat is transferred across the boundary but mass is not. In order to calculate the energy change, we need to take into account both energy in the form of heat and energy in the form of work.

There are two conventions for writing out the First Law of Thermodynamics in terms of heat and work.

- 1) $\Delta E = q - w$ q is heat and w is work. In this case the work of expansion is considered positive.
- 2) $\Delta E = q + w$ q is heat and w is work. In this case the work of expansion is considered negative.

It does not matter which one you use as long as you are consistent with the sign convention.

Step 1: Calculate q , the heat energy transferred.

$$q = -40,608 \text{ J}, \text{ the problem statement says that much heat energy leaves the system.}$$

Step 2: Calculate the work done by the system

$$w = P\Delta V = P(V_{\text{final}} - V_{\text{initial}})$$

The pressure is 1 atm and remains constant

The initial volume is 30.12 L

The final volume is the mass of the water divided by its density

$$\text{Final volume} = (18.02 \text{ g}) / (0.9584 \text{ g/mL}) = 18.80 \text{ mL} = .0188 \text{ L}$$

$$w = P\Delta V = 1 \text{ atm}(0.0188 \text{ L} - 30.12 \text{ L}) = -30.10 \text{ atm L} = -3,049 \text{ J}$$

Step 3: $\Delta E = q - w$

$$\Delta E = q - w = -40,608 \text{ J} - (-3,049 \text{ J}) = -37,559 \text{ J}$$

Thermodynamics: First, Second and Third Laws of Thermodynamics: Student Review Notes**The Second Law of Thermodynamics, Entropy, S, the measure of randomness of a system**

Configurational Entropy

What is entropy? In the most general sense, entropy is disorder, or randomness. So-called configurational entropy is easy to visualize. You can think of it as the state of disorder of objects in space. A yard full of fallen leaves illustrates configurational entropy. When you rake the leaves into piles, you decrease the randomness of the system and therefore decrease the entropy.

In terms of physical processes and chemical reactions, you can also predict the change in entropy in a general way. Think of a phase change from solid to liquid to gas. In each of these phase changes, the volume available to the molecules or atoms becomes greater, allowing for more disorder of the particles in space. Consider 1 mole-- 6.022×10^{23} particles of carbon monoxide at 1 atm. of pressure. In the solid phase, the molecules occupy a volume of about 2×10^{-5} L and are fixed in position by intermolecular forces. In the liquid phase, the molecules occupy a volume of about 4×10^{-5} L (not a big increase in volume) but they are not longer fixed in position by intermolecular forces. They can now tumble over each other and therefore access more configurations, thus creating more disorder and resulting in an increase in configurational entropy. In the gas phase, the 6.022×10^{23} molecules occupy about 22.4 L and are virtually unconstrained by intermolecular forces. The number of additional configurations compared to the solid or liquid phases is enormous. Understand that,

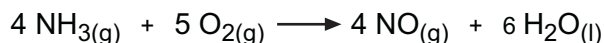
$$S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$$

With configurational entropy in mind, we can often predict whether entropy changes in chemical reactions will be positive or negative. If the reaction produces a net number of products that are in phases of higher entropy than the reactants, then ΔS for the reaction will most likely be positive, **especially if the moles of gas increase.**

Here are some examples:



Predicts $\Delta S_{\text{rxn}} > 0$, since the moles of gas increases. The increase in moles of liquid also contributes to a positive ΔS_{rxn} .



Predicts $\Delta S_{\text{rxn}} < 0$, since the moles of gas decrease.



Even though the reaction destroys two moles of liquid and makes only 1 mole of gas, the entropy of a gas is so big compared to that of a liquid the we would predict $\Delta S_{\text{rxn}} > 0$.

Thermal Entropy

Entropy is much more than just configurational disorder that we can see. Most importantly, perhaps, entropy is a measure of the energy quality (usefulness) and an index of spontaneity. To understand this, we need to consider thermal entropy.

Thermal Entropy and the Second Law of Thermodynamics

The First Law of Thermodynamics places no restriction on the spontaneity (direction) of a process, as long as energy is neither created nor destroyed. According to the First Law, for example, a ball that falls onto a tabletop, possibly heating the tabletop up a bit, may just as readily bounce back up to its original height at the expense of the energy in the tabletop. We know from experience that this never happens, just as we know that heat energy flows from regions of higher temperature to those at lower temperature.

The Second Law of Thermodynamics --the Entropy Principle-- governs the direction of natural processes.

Formally, it states that the entropy of the universe is increasing and it states that the change in entropy of a system and its surroundings is always greater than or equal to zero.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

When $\Delta S_{\text{universe}} > 0$ for a process, the process is said to be natural or spontaneous. It is very important to notice that this is the change in entropy of the universe, not the system. The change in entropy of a system can be positive but that does not indicate spontaneity. You'll see this in the form of Gibbs Free Energy.

The condition that $\Delta S_{\text{universe}} = 0$ corresponds to a state of equilibrium, in which there is no tendency for the process to proceed in one direction or the other.

Standard Entropy Values

Entropy can also be calculated using standard entropies of the reactants and products:

$$\Delta S^{\circ}_{\text{rxn}} = \left(\sum v_i S^{\circ}_i \right)_{\text{products}} - \left(\sum v_i S^{\circ}_i \right)_{\text{reactants}}$$

Note that the entropy of a molecule is not written ΔS , but rather just S° . This is because unlike enthalpy, entropy can be measured relative to a specific quantity, namely, the entropy of a substance at absolute zero, which is zero.

You can qualitatively compare the entropies of a bunch of substances by looking at their phases (solids have the lowest entropies, followed by liquids and then gases) or by looking at their intermolecular forces. Molecules with weak intermolecular forces can move around more, and therefore have a higher entropy.

The "°" in S° refers to standard conditions, which are 1.0 M for aqueous substances and 1.0 atm for gaseous substances. Standard conditions does not imply 25°C, although the entropies of most substances are fairly temperature independent.

The Third Law of Thermodynamics

Standard entropy values are tabulated as absolute values, not change values. The reason is that there is an absolute referende for the zero value of entropy for all substances. **According to the Third Law of Thermodynamics, a perfect crystal at 0 K and 1 atm has zero entropy.** Furthermore, all molecular motion ceases at 0 K so there is no thermal entropy.