

In Chemistry 1A, we have been concerned with the quantitative description of reaction systems. We have expressed the tendency of reactants to be converted to products in terms of the equilibrium constant K for the reaction. Now we question why some reactions have large equilibrium constants while other reactions have small equilibrium constants. The goal of chemical thermodynamics is to predict what types of chemical and physical processes are possible and under what conditions. Thermodynamics can also suggest ways in which conditions can be changed to make a process possible. It can tell us if a process can occur, but it cannot tell us how fast it will occur.

Thermodynamic reasoning is based on few apparently simple laws. These laws are not derived. Instead, they are generalizations that have been drawn from a vast number of observations of the way matter behaves. Note that thermodynamics is concerned only with the macroscopic properties of matter that, in principle, can be measured (such as temperature, pressure, volume, etc.). It does not depend on any particular model of the structure of matter such as atomic theory of matter.

Chapter 9 covers the fundamental concepts of energy; the chemistry of energy production and exchange.

First Law of Thermodynamics (the law of conservation of energy): The energy of the universe is constant.

The First Law stated mathematically: $\Delta E = q + w$ where ΔE = change in the system's internal energy,
 q = heat and w = work

Our convention will be to take the system's point of view:

By definition:	$q > 0 \Rightarrow$ heat is added <u>to</u> the system	$q < 0 \Rightarrow$ heat is lost <u>by</u> the system
	$w > 0 \Rightarrow$ work is done <u>on</u> the system	$w < 0 \Rightarrow$ work is done <u>by</u> the system
	$\Delta E > 0 \Rightarrow$ the system <u>gains</u> energy	$\Delta E < 0 \Rightarrow$ the system <u>loses</u> energy

The system's internal energy, E , can be changed by a flow of work, or heat or both work and heat.

Energy = Capacity to do work or to produce heat.

Heat involves the transfer of energy between two objects.

Work = force acting over a distance (work = force \times distance).

The **System** is that part of the universe on which attention is to be focused and the **Surroundings** is everything else in the universe. For example, in considering the reaction for the combustion of methane, we define the system as the reactants and products of the reaction. The surroundings consist of the reaction container, the room, and everything else other than the reactants and products.

The First Law states that energy is conserved. Thus, energy can be converted from one form to another but can be neither created nor destroyed, i.e. the energy of the universe is constant.

Energy is classified as potential energy or kinetic energy:

Potential Energy (PE) is due to position or composition. PE can be converted to useful work. For example:

- 1) Water behind a dam has potential energy that can be converted to work (water flows through turbines producing mechanical power).
- 2) Attractive or repulsive forces between particles lead to potential energy. Chemical reactions can either release or absorb heat depending on whether the potential energy stored in the bonds of the reactant molecules is greater or less than the energy stored in the bonds of the product molecules. The energy released when gasoline is burned results from the greater potential energy of reactants relative to the potential energy of the products.

Kinetic Energy (KE) is due to motion of an object.

Kinetic Energy depends on the mass of the object (m) and its velocity (v). $KE = (1/2) mv^2$

Exothermic reaction: A reaction which gives off heat. Energy (as heat) flows out of the system. At constant pressure, heat = q_p and $q_p = \Delta H$. When heat flows out of the system, $q_p < 0$ and $\Delta H < 0$

Endothermic reaction: A reaction that takes up heat. Heat flows into the system. At constant pressure, heat = q_p , $q_p = \Delta H$ When heat flows into the system, $q_p > 0$ and $\Delta H > 0$

Intensive property: A property of the system that is the same as the corresponding properties of the subsystems. Temperature and pressure are typical intensive properties; if a system at 298 K is divided in half, the temperature of each half will still be 298 K.

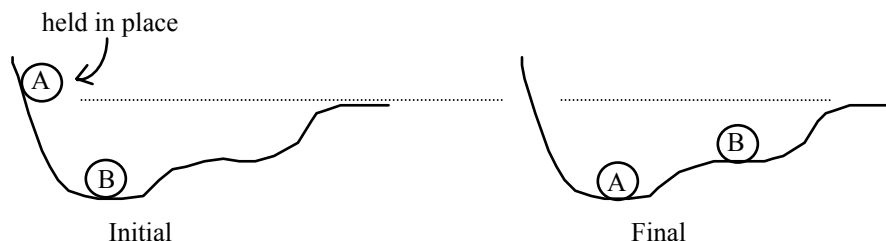
Extensive property: A property of the system that can be written as the sum of the corresponding properties of the subsystems. Volume, mass, and energy are typical extensive properties; the volume of a system, for example, is the sum of the volumes of the subsystems.

Heat capacity of any object is defined as the amount of energy necessary to raise its temperature by one degree.

Specific heat capacity is the energy necessary to raise the temperature of one gram of a substance by one degree. Thus, the units are: $J K^{-1}g^{-1}$ or $J ^\circ C^{-1}g^{-1}$

Molar heat capacity is the energy necessary to raise the temperature of one mole of a substance by one degree. Thus, the units are: $J K^{-1}mol^{-1}$ or $J ^\circ C^{-1}mol^{-1}$

Conversion of Energy :



Initially: The PE of ball A is greater than the PE of ball B. When ball A is released it moves down the hill and hits ball B. PE of A has decreased and PE of B increased. Energy must be conserved. Initially, PE of A is converted to KE and some of this KE is transferred to B, raising B to a higher position thereby increasing the PE of B. Note, however, that the final position of B is lower than the initial position of A. What happened to the remaining energy? Some of the KE of A is transferred to the surface of the hill as heat due to friction. The temperature of the hill increased slightly.

Heat versus Temperature:

Recall kinetic theory of gases (Chapter 5): **temperature** is associated with the average KE of a large number of molecules. $KE_{av} = (3/2) RT$ Random motion is often called thermal motion. Temperature is a measure of how cold or hot an object is.

Heat involves the transfer of energy between two objects due to a temperature difference between the two objects. When a hot body is brought into contact with a colder body, the two temperatures change until they become equal to one another. This process is sometimes described as the "flow" of heat from the hotter to the colder body. This statement is somewhat misleading because it implies that heat is a substance that is contained in matter. Instead heat (like work) is a way in which energy is exchanged between a system and its surroundings.

Ball B gains PE because work was done by ball A on B. Because **work** is force acting over a distance, work is required to raise B from its original position to its final one. That is, some PE of A is transferred through work to B, increasing PE of B.

This implies that there are **two ways to transfer energy:** through work and through heat. As ball A rolls down the hill, the PE of A lost will always be the same amount. However, the way that this energy transfer is divided between work and heat depends on the specific conditions, i.e. the **pathway**. For example, if the hill has a very rough surface and all the PE of A is lost to frictional heating of the surface, then A moves so slowly that when it hits B it can not move B to the next level which implies no work is done. Regardless of the conditions of the hill, the total energy transferred will be constant. The amounts of heat and work will differ. Energy change is independent of the pathway, whereas work and heat are both dependent on the pathway. A property that is independent of the pathway is called a **state function**. Energy is a state function. Work and heat are not state functions. (Reference: Zumdahl, S. Chemical Principles, 5th Ed. Houghton Mifflin 2005).

Formulas: (You need to understand the following formulas; know where they came from and when they apply).

$\Delta E = q + w$	NOTE: Although q and w both depend on the path followed between a given pair of states, their sum, ΔE , does not depend on the path because E is a state function.
$q = mC\Delta T$	The heat absorbed by a substance depends on its mass (g), its heat capacity, C ($J g^{-1} K^{-1}$) or ($J g^{-1} ^\circ C^{-1}$) and the change in temperature, ΔT .
$w = -P_{ext}\Delta V$	Why is there a negative sign in this equation?
$w = -\Delta n_{gas}RT$	When a chemical reaction occurs at constant temperature and pressure, the work done by the system or on the system depends on the change in moles of gas in the reaction. $\Delta n_{gas} = \Delta n_{gas} \text{ products} - \Delta n_{gas} \text{ reactants}$
$q_v = n c_v \Delta T$	Holds for ideal gas processes. Volume must be constant to calculate q_v using this formula.
$q_p = n c_p \Delta T$	Holds for ideal gas processes. Pressure must be constant to calculate q_p using this formula.
$c_v = (3/2) R$	monatomic ideal gas (for polyatomic gases $c_v > (3/2) R$)
$c_p = c_v + R$	Holds for any ideal gas Why is c_p greater than c_v ?
$PV = nRT$	Ideal gas law
$\Delta E = n c_v \Delta T$	Holds for any ideal gas processes. This equation holds when either pressure or volume change or when both pressure and volume change. E is a state function, ΔE is independent of path.
$\Delta H = n c_p \Delta T$	Holds for any ideal gas processes. This equation holds when either pressure or volume change or when both pressure and volume change. H is a state function. ΔH is independent of path.
$\Delta H = \Delta E + \Delta (PV)$	Enthalpy, H, is defined as: $H = E + PV$

Hess's law: If two or more chemical equations are added to give another chemical equation, the corresponding enthalpies of reaction must be added. (Enthalpy is a **state function**. The calculated ΔH for a reaction is independent of how many steps were taken to get from reactants to products. It can be calculated in one step or a series of steps.)

Standard Enthalpy ΔH° is defined as the enthalpy change for a reaction when all reactants and products are in their standard states. The **standard state** is the stable form of an element or compound at 1 atm pressure and a specified temperature. The standard state for dissolved species in solution corresponds to 1 M concentration and 1 atm external pressure.

Standard enthalpy of formation, ΔH_f° is defined as the enthalpy change to produce one mole of a compound from its elements in their standard states (in their stable form at 1 atm and a specified temperature (generally $25^\circ C$)).

For the reaction: $a A + b B \longrightarrow c C + d D$ $\Delta H^\circ = [c \Delta H_f^\circ (C) + d \Delta H_f^\circ (D)] - [a \Delta H_f^\circ (A) + b \Delta H_f^\circ (B)]$