Introduction to Thermodynamics

Thermodynamics is the branch of physical chemistry that deals with the interconversion of heat, which is based on few laws known as *laws of thermodynamics*. The word "thermodynamic" is derived from two Greek words *thermes,* meaning heat, and *dynamikos*, *meaning* powerful/efficacious. When we say the word dynamic we think of motion or movement and energy. Thus the term thermodynamics means heat movement or heat flow.

In the concept of thermodynamics, we study the changes in the **state of a system**, usually from initial to final state and not concerned with the way the change has been taken place. This concept applies to macroscopic properties like temperature, volume, pressure, and energy, which are known as **state functions** because any change in property can be defined by only initial and final states, regardless of how the final state is being achieved. We denote this change by a Greek symbol *delta* (Δ) and write the change as the difference between final and initial states. For example, change in volume and change in energy are written as

$$\Delta V = V_{final} - V_{initial} = V_f - V_i$$

$$\Delta E = E_f - E_i$$

where V_i and V_f are the initial and final volume respectively. Similarly, E_i and E_f respectively are the initial and final energy.

It is important to keep in mind that how the change in property is written; it is always a difference between final state and initial state.

The First Law of Thermodynamics

The **first law of thermodynamics** is based on the law of conservation of energy and stated as *energy can neither be created or destroyed, but it can be converted from one form to another*. How do we prove this? It is impossible to prove the validity of this law if we try to determine the total energy content of the universe. However, the validity of this law can be tested by measuring the change in internal energy (ΔE) of the system going from initial state (E_i) to final state (E_f) that is expressed as

$$\Delta E = E_f - E_i$$

The internal energy of a chemical system consists of two parts; potential energy and kinetic energy. Potential energy arises due to various interactions, such as, attractive interactions between electrons and nuclei, repulsive interactions between electrons and between nuclei, and interactions between molecules. Kinetic energy, on the other hand, arises due to various types of motions that include electron motions within molecules and molecular motions. It is impossible to measure accurately all these various contributions

to the total energy of the system. However, changes in energy can be determined experimentally with great certainty.

Consider the flowing reaction between one mole of carbon and one mole of oxygen gas to form one mole of carbon dioxide gas:

$$C(s) + O_2\,(g) \rightarrow CO_2\,(g)$$

In this example, the system consists of reactants (C(s), O2 (g)) and product (CO_2 (g)). We do not know the internal energy content of either the reactants (E_r) or the product (E_p), but we can measure the change in the energy content, ΔE, given by

$$\begin{aligned}\Delta E &= E_p - E_r \\ &= [\text{energy content of 1 mol of } CO_2\,(g)] - [\text{energy content of 1 mol of C(s)} \\ &\quad + \text{energy content of 1 mol of } O_2\,(g)]\end{aligned}$$

This reaction is an exothermic reaction because it releases the heat to the surrounding. Where the heat is coming from? During the chemical reaction, some of the chemical energy is transformed into the thermal energy (heat), which eventually ends up in the surrounding.

According to the *law of conservation of energy*, the total energy of the universe is constant, that is, the sum of energy changes must be zero:

$$\Delta E_{system} + \Delta E_{surrounding} = 0$$

or $$\Delta E_{system} = -\Delta E_{surrounding}$$

In the world of chemistry, we are more interested in energy changes of the system but not of the surrounding. However, the change in the internal energy is manipulated by two factors; heat exchange (q) between the system and the surrounding and the work done on or by the system (w). Based on this, the first law of thermodynamics takes the following form:

$$\Delta E = q + w$$

This equation is interpreted as the change in internal energy equal to the sum of heat and work functions. The sign on ΔE depends upon the either the heat flown in the system or flown out of the system and work done by the system or done on the system. To make it easier to understand, the following conventions are adopted:

Process	**Sign**
Work (w)	
Work done on the system by the surround	+
Work done by the system on the surrounding	-
Heat (q)	
Heat gained by the system from the surrounding (endothermic process)	+
Heat lost by the system to the surrounding (exothermic process)	-

Example

The work done when a gas is compressed in a cylinder is 820 J. At the same time, the system lost the heat of 320 J to the surrounding. What is the energy change of this system?

Answer

Here the gas is the system. First you must decide the sign on w and q using the convention provided above. Work is done on the system, so w = + 820 J and heat is lost by the system, so q = -320 J. Therefore

$$\begin{aligned}\Delta E &= q + w \\ &= -320\ J + 820\ J \\ &= 500\ J\end{aligned}$$

This result indicates that the energy of the gas is increased by 500 J. That means, at the end of the process the gas has more energy than in the beginning.

Questions

1. At constant pressure, in which of the following processes is (a) work on the system by the surrounding , (b) work done by the surrounding on the system, (c) no work is done. Indicate the sign (+ or -) on w for each process.

   a. You chop vegetable to pieces (system is the vegetable)
   b. You exhale (you are the system)
   c. You are driving the car (your car is the system)
   d. Cook a turkey in an oven (turkey is the system)
   e. $CO_2(s) \rightarrow CO_2(g)$
   f. $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

g. $H_2(g) + I_2(g) \rightarrow 2HI(g)$

2. In which of the following processes, (a) heat is gained by the system and (b) heat is lost by the system. Indicate the sign (+ or -) on q for each process.

   a. You take cold shower when you are hot (you know when!) (Your body is the system)
   b. You lay on the beech on a hot summer day (your body is the system).
   c. You eat ice-cream (ice-cream is the system)
   d. You light a candle (candle is the system)
   e. You blow-dry your hairs (your hair is the system)
   f. In a cold winter day, you rub your hands (your hands are system)
