

Chapter 2

Thermochemistry

Material and Heat Balance in Combustion Process

1. Introduction

Thermo chemistry is the branch of physical chemistry which deals with the heat changes that accompany chemical reactions. There are two types of chemical reactions; an exothermic reaction, proceeds accompanied with the evolution of heat, e.g. combination of hydrogen gas with nitrogen gas to produce ammonia. An endothermic reaction, on other hand, is one which should be supplied with heat so as to proceed, e.g. production of nitric acid from combination of oxygen gas with nitrogen gas, dissociation of calcium carbonate into calcium oxide and carbon dioxide gas, etc. Most spontaneous chemical reactions which proceed virtually to completion at ordinary temperature are exothermic reactions. Endothermic reactions are often incomplete except at high temperatures.

2. Energy and its units

Energy can be defined as the capacity to supply heat or to do work.

$$\text{Energy} = \text{Work} + \text{Heat}$$

There are two classifications of energy:

Kinetic Energy; energy of motion of an object (abbreviated E_k), it is calculated from an object's mass and its velocity according to the formula: $E_k = 1/2 m V^2$

Potential Energy (abbreviated E_p), stored energy, and may result from an object's position relative to other objects, or the energy that is contained in chemical bonds. Beside E_k and E_p , other forms of energy exist, such as Electrical Energy, Nuclear Energy & Chemical Energy which is the energy stored in chemical bonds of the molecules.

The Mechanical Energy is the amount of energy required to move an object a certain distance, d , when it is subjected to a force F .

$$w = F \times d.$$

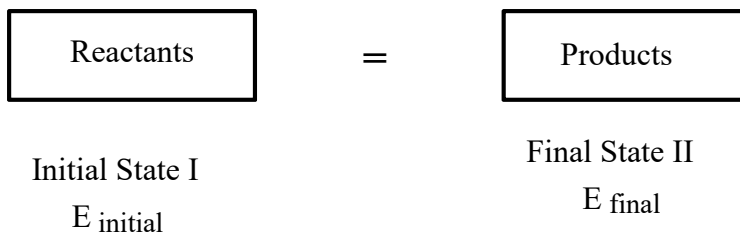
The unit of measuring energy follows from the kinetic energy expression and is called **joule**, abbreviated J. It can be defined as the kinetic energy of mass of 2 kg moving at velocity of 1m/sec

($1\text{J} = (\text{kg}\cdot\text{m}^2)/\text{s}^2$, A large unit kilo joule, kJ, is used frequently. Another unit of measuring energy is calorie (cal), originally defined as the amount of energy required to raise the temperature of 1 g of water by 1°C . ($1\text{ cal} = 4.184\text{ J}$).

3. Internal Energy and State Functions

The total energy of a system is the sum of all kinetic and potential energies of its component parts. This total energy is called the internal energy of the system (abbreviated **E**). As we study energy changes in chemical reactions, the reactants and products are collectively called the system. Everything else - the reaction flask, the laboratory, the building, etc. are called the surroundings. If the system is isolated from the surroundings so that no energy transfer could occur, then the total internal energy of the system would be conserved and would remain constant throughout the reaction. The *internal energy* E of the system is classified as a state function. The value of state function depends on the present state of the system and not by the way this state is approached.

consider the chemical change



When the reaction proceeds to completion from left to right i.e. the system is converted from state I to state II we define the change an internal energy, which we represent as ΔE as the difference in internal energy between the final and initial states of the system.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

Thermodynamic quantities such as ΔE consist of two parts: a *number*, giving the magnitude of the change, and a *sign*, indicating the direction of the flow.

As shown in Figure (1), energy changes are measured from the point of view of the system:

- Energy that flows from the system to the surrounding has a negative sign, ($E_{\text{final}} < E_{\text{initial}}$), i.e. exothermic reaction.
- Energy that flows to the system from the surrounding has a positive sign ($E_{\text{final}} > E_{\text{initial}}$), i.e. endothermic reaction.

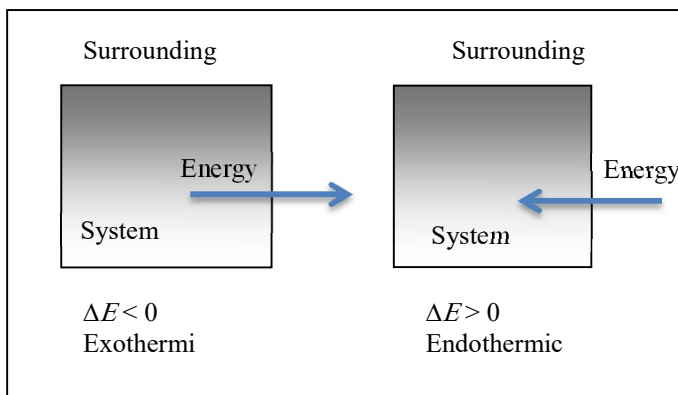


Fig. (1): If the system gains energy (right) ΔE will be positive,
If the system loss energy (left) ΔE will be negative.

4. The First Law of Thermodynamic

Thermo chemistry is a branch of thermodynamics, which deals with all kinds of energy effects in all kinds of processes. Thermodynamics distinguishes between two types of energy. One of these is heat (q); the other is work, (w). The thermodynamic definition of work is quite different from its colloquial meaning, since work includes all forms of energy except heat.

The law of conservation of energy states that energy (E) can be neither created nor destroyed; it can only be transferred between system and surroundings. That is,

$$\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}}$$

The first law of thermodynamics goes a step further. Taking account of the fact that there are two kinds of energy, heat and work,

The first law of thermodynamics states:

In any process, the total change in energy of a system, ΔE , is equal to the sum of the heat, q , and the work, w , transferred between the system and the surroundings.

$$\Delta E = q + w$$

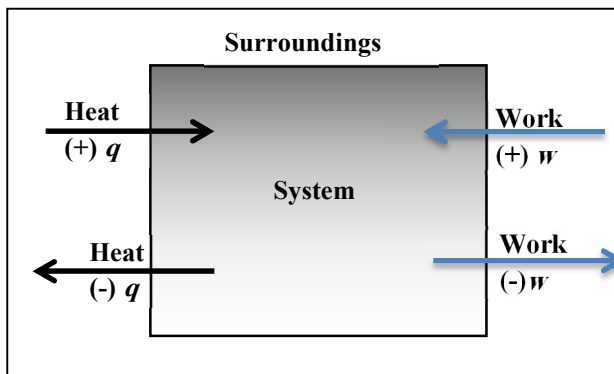


Fig. (2): Heat and work are positive when they enter a system and negative when they

Applying the first law. The internal energy of the system changes in magnitude as heat is added or removed from the system or as work is done in it or by it. q and w are positive when heat or work enters the system from the surroundings. If the transfer is in the opposite direction, from system to surroundings, q and w are negative.(Fig.2)

Sample Exercise.

Calculate ΔE of a gas for a process in which the gas

- (a) Absorbs 20 J of heat and does 12 J of work by expanding.
- (b) Evolves 30 J of heat and has 52 J of work done on it as it contracts.

Solution:

$$\Delta E = q + w$$

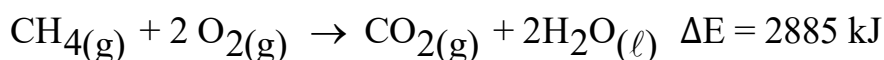
(a) $q = +20 \text{ J}$; $w = -12 \text{ J}$, then, $\Delta E = +20 \text{ J} - 12 \text{ J} = +8 \text{ J}$

(b) $q = -30 \text{ J}$; $w = 52 \text{ J}$, then $\Delta E = -30 \text{ J} + 52 \text{ J} = +22 \text{ J}$

Practice Exercise:

The hydrogen and oxygen gas in a cylinder are ignited. As the reaction occur, the system losses 1150 J of heat to its surrounding. The reaction also causes the piston to move upward as the gases expand. The expanded gas does 480 J work on the surroundings. What is the change in the internal energy of the system? (Answer -1630 J).

Ordinarily, when a chemical reaction is carried out in the laboratory, any energy evolved is in the form of heat. Consider, for Exercise, the reaction of oxygen with methane, the principal constituent of natural gas.



When you ignite methane in a Bunsen burner, the amount of heat evolved is very close to 885 kJ/mol. There is a small work effect, due to the decrease in volume that occurs when the reaction takes place Figure (3), but this amounts to less than 1% of the energy change.

The situation changes if methane is used as a substitute for gasoline in an internal combustion engine. Here a significant fraction of the energy evolved in combustion is converted to useful work, propelling your car uphill, overcoming friction, charging the battery, or whatever. Depending on the efficiency of the engine, as much as 25% of the available energy might be converted to work; the amount of heat evolved through the tail pipe or radiator drops accordingly.

Finally, the energy available from the above reaction might be used to operate a fuel cell such as those involved in the space program. In that case, as much as 818 kJ/mol of useful electrical work could be obtained; relatively little heat is evolved. Summarizing this discussion in terms of an energy balance (per mole of methane reacting):

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	ΔE	q	w
Bunsen burner	- 885 kJ	- 890 kJ	+5 kJ
Automobile engine	- 885 kJ	- 665 kJ	-220 kJ
Fuel cell	- 885 kJ	- 67 kJ	-818 kJ

Notice that ΔE , like ΔH , is a *state property*; it has the same value regardless of how or where or why the reaction is carried out. In contrast, q and w are path-dependent; their values vary depending on whether the reaction is carried out in the atmosphere, an engine, or an electrical cell.

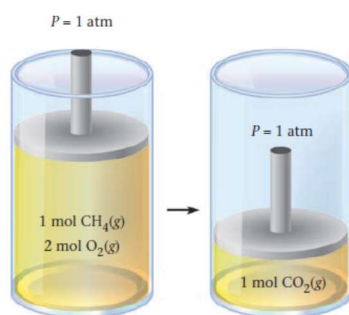
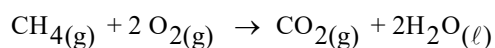


Fig. (3) Pressure-volume work.
When the reaction



is carried out in a cylinder fitted with a piston that exerts a pressure of 1 atm., a contraction occurs (3 mol gas : 1 mol gas). The piston falls, and a small amount of work is done on the reaction system

5. P-V work

A common type of work associated with chemical processes is work done by a gas (through *expansion*) or work done to a gas (through *compression*). For Example, in an automobile engine, the heat from the combustion of the gasoline expands the gases in the cylinder to push back the piston, and this motion is then translated into the motion of the car.

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Suppose we have a gas confined to a cylindrical container with a movable piston as shown in Figure 4, where F is the force acting on a piston of area A . Since pressure is defined as force per unit area, the pressure of the gas is $P = \frac{F}{A}$

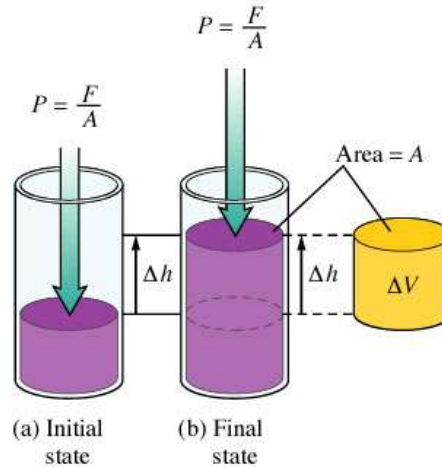


Fig. (4)

- (a) The piston, moving a distance Δh against a pressure P does work on the surroundings.
- (b) Since the volume of a cylinder is the area of the base times its height, the change in volume of the gas is given by $\Delta h \times A = \Delta V$.

Work is defined as force applied over a distance, so if the piston moves a distance Δh , as shown in Fig. 4, then the work done is

$$\text{Work} = \text{Force} \times \text{distance} = F \times \Delta h$$

Since $P = \frac{F}{A}$ or $F = P \times A$

Then

$$\text{work} = F \times \Delta h = P \times A \times \Delta h$$

Since the volume of a cylinder equals the area of the piston times the height of the cylinder (see Fig. 4), the change in volume ΔV resulting from the piston moving a distance Δh is

$$\Delta V = \text{final volume} - \text{initial volume} = A \times \Delta h$$

Substituting $\Delta V = A \times \Delta h$ into the expression for work gives:

$$\text{Work} = P \times A \times \Delta h = P\Delta V$$

$$W = P\Delta V$$

This gives us the *magnitude* (size) of the work required to expand a gas ΔV against a pressure P .

What about the sign of the work? The gas (the system) is expanding, moving the piston against the pressure. Thus the system is doing work on the surroundings, so from the system's point of view the sign of the work should be negative.

For an *expanding* gas, ΔV is a positive quantity because the volume is increasing. Thus ΔV and w must have opposite signs, which leads to the equation

$$w = -p \Delta V$$

Note that for a gas expanding against an external pressure p , w is a negative quantity as required, since work flows out of the system. When a gas is *compressed*, ΔV is a negative quantity (the volume decreases), which makes w a positive quantity (work flows into the system).

Sample Exercise:

Calculate the work associated with the expansion of a gas from 46 L to 64 L at a constant external pressure of 15 atm.

Solution:

$$w = -p \Delta V$$

In this case $p = 15$ atm. And $\Delta V = 64 - 46 = 18$ L.

Hence $w = -15 \text{ atm} \times 18 \text{ L} = -270 \text{ L} \cdot \text{atm}$

Note that: since the gas expands it does work on its surroundings. since the energy flows out of the gas, so w is a negative quantity.

Practice Exercise:

Consider a mixture of air and gasoline vapor in a cylinder with a piston. The original volume is 40. cm³. If the combustion of this mixture releases 950. J of energy, to what volume will the gases expand against a constant pressure of 650. torr if all the energy of combustion is converted into work to push back the piston?

(Answer 11.0 L)