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A View from the Conservation of Energy to Chemical Thermodynamics

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Additional information is available at the end of the chapter

1. Introduction

According to the **conservation of energy law**, **energy**, which is the capacity to do work or to supply heat, can be neither created nor destroyed; it can only be converted from one form into another. For example, the water in a reservoir of dam has potential energy because of its height above the outlet stream but has no kinetic energy because it is not moving. As the water starts to fall over the dam, its height and **potential energy**, *(Ep)* is energy due to position or any other form of stored energy, decrease while its velocity and **kinetic energy**, *(Eₖ)* is the energy related to the motion of an object with mass m and velocity v, increase. The total of potential energy plus kinetic energy always remains constant. When the water reaches the bottom and dashes against the rocks or drives the turbine of a generator, its kinetic energy is converted to other forms of energy-perhaps into heat that raises the temperature of the water or into electrical energy [6]. If any fuel is burned in an open medium, its energy is lost almost entirely as heat, whereas if it is burned in a car engine; a portion of the energy is lost as work to move the car, and less is lost as heat. These are also typical examples of the existence of the law.

Figure 1. Some examples showing the existence of the conservation of energy law

It is thought that the summation of the introduction as a detailed concept map related with the conservation of energy would be better. This map in Fig.2 presents a concise view for many concepts of thermodynamics and their relations.
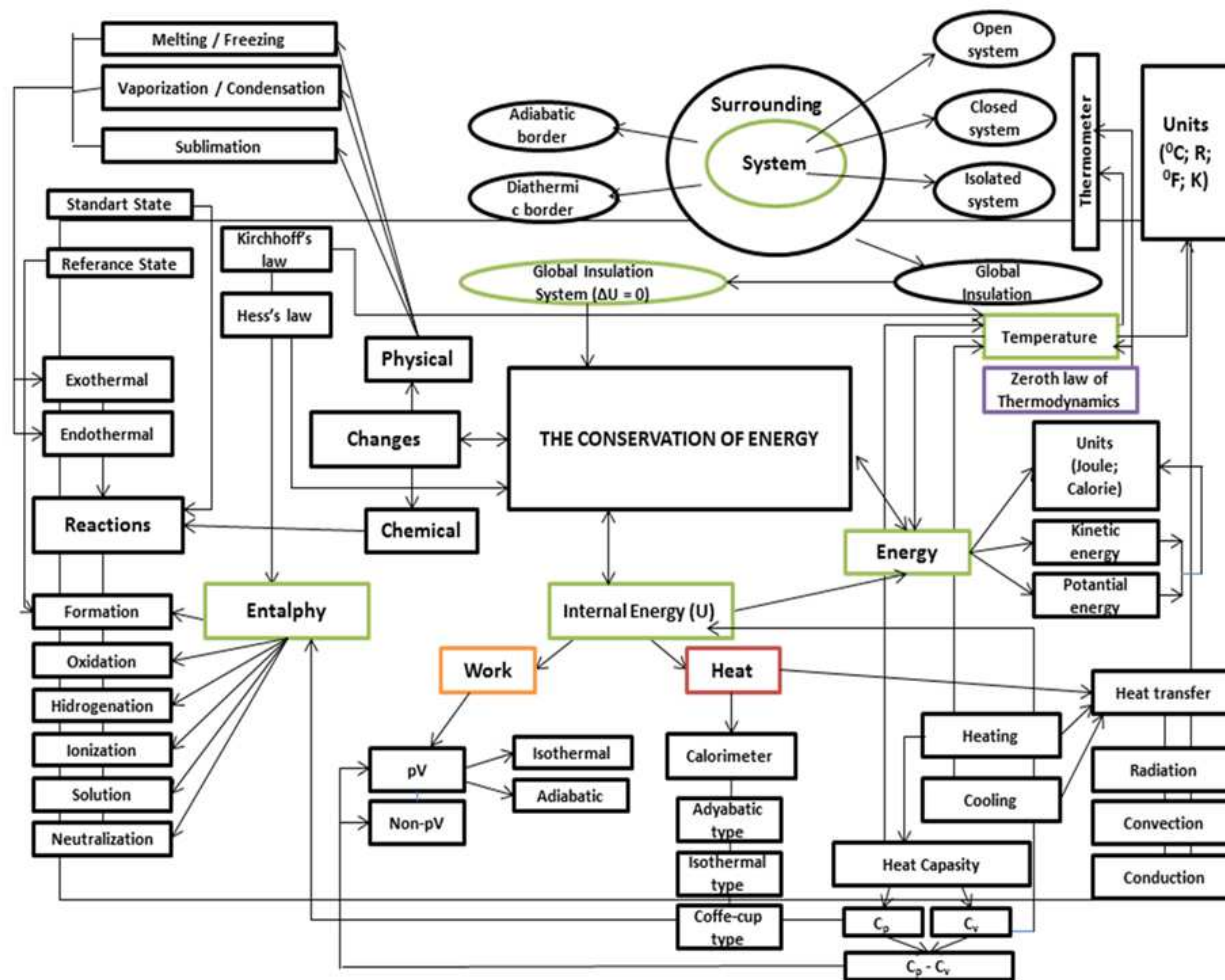

Figure 2. A concept map for the conservation of energy law

The macroscopic part of universe under study in thermodynamics is called the system. The parts of the universe that can interact with the system are called the surroundings [5]. In order to describe the thermodynamic behavior of a physical system, the interaction between the system and its surroundings must be understood. Thermodynamic systems are thus classified into three main types according to the way they interact with the surroundings (Fig.3); **open system:** matter and energy can be exchanged with the surroundings; **closed system:** can exchange energy but not matter with the surroundings and **isolated system:** cannot exchange matter or energy with the surroundings [4, 5]. Addition, a boundary that does permit energy transfer as heat (such as steel and glass) is called **diathermic** and a boundary that does not permit energy transfer as heat is called **adiabatic** [1;4].

The system may be homogeneous or heterogeneous. An exact definition is difficult, but it is convenient to define a **homogeneous system** as one whose properties are the same in all parts, or at least their spatial variation is continuous. A **heterogeneous system** consists of

two or more distinct homogeneous regions or **phases**, which are separated from one another by surfaces of discontinuity [4].
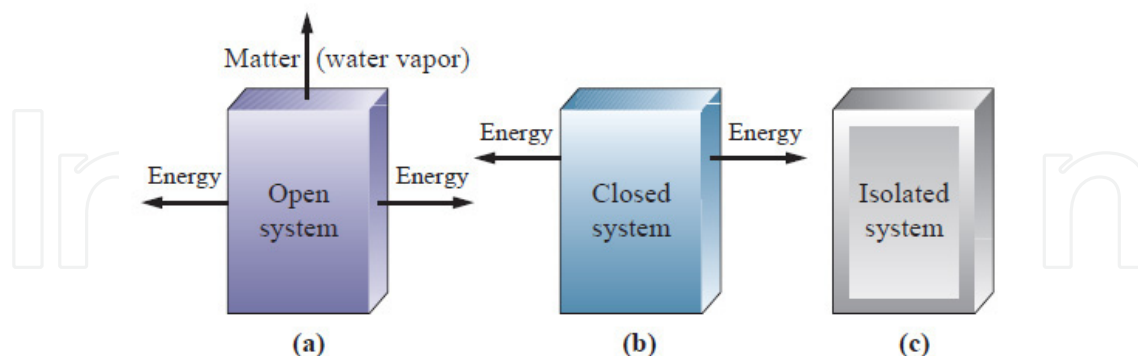

Figure 3. Systems and their surroundings; (a) open system (b) closed system and (c) isolated system.

Heating is a process in which the temperature of system, separated with diathermic border from its surrounding, is increased. This process leads to passing system from a state of lower energy to higher one. Heating process based on the energy difference between system and its surrounding provides identify of an important property which indicates the flow direction of energy. This property is called **temperature.** Temperature is a physical property of matter that quantitatively expresses the common notions of hot and cold. Objects of low temperature are cold, while various degrees of higher temperatures are referred to as warm or hot. Heat spontaneously flows from bodies of a higher temperature to bodies of lower temperature, at a rate that increases with the temperature difference and the thermal conductivity. No heat will be exchanged between bodies at same temperature; such bodies are said to be in "**equilibrium**". On the other hand, kinetic energy associated with the random motion of particles is called thermal energy, and the thermal energy of a given material is proportional to temperature. However, the magnitude of thermal energy in a sample also depends on the number of particles in the sample and so it is an **extensive property**. The water in a swimming pool and a cup of water taken from the pool has the same temperature, so their particles have the same average kinetic energy. The water in the pool has much more thermal energy than the water in the cup, simply because there are a larger number of molecules in the pool. A large number of particles at a given temperature have a higher total energy than a small number of particles at the same temperature [7]. Quantitatively, temperature which is an **intensive property** is measured with thermometers, which may be calibrated to a variety of temperature scales [9].

If two thermodynamic systems, A and B, each of which is in **thermal equilibrium** independently, are brought into thermal contact, one of two things will take place: either a flow of heat from one system to the other or no thermodynamic process will result. In the latter case the two systems are said to be in thermal equilibrium with respect to each other [11]. When same treatment has been repeated other system, C, if there is thermal equilibrium between B and C; the condition of thermodynamic equilibrium between them may be symbolically represented as follows,

$$\text{If} \ \ A = B \ \ \text{and} \ \ B = C \tag{1}$$

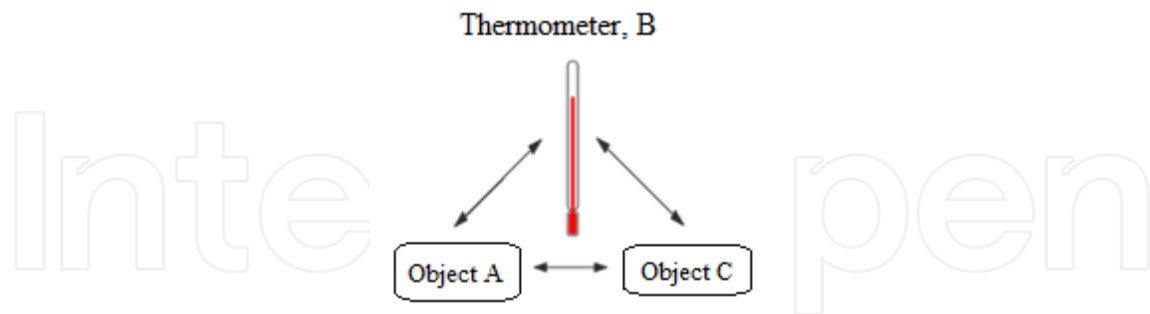This observation has also been schematically shown in Fig.4

Figure 4. A schematic presentation of the zeroth law of thermodynamics.

Based on preceding observations, some of the physical properties of the system B (Thermometer) can be used as a measure of the temperature, such as the volume of a fixed amount of a liquid merqury or any alcohol under standard atmospheric pressure. The **zeroth law of thermodynamics** is the assurance of the existence of a property called the temperatur*e* [11].

The zeroth law allows us to assert the existence of temperature as a state function. Having defined temperature, how do we measure it? Of course, you are familiar with the process of putting a liquid-mercury thermometer in contact with a system, waiting until the volume change of the mercury has ceased, indicating that thermal equilibrium between the thermometer and the system has been reached [5].

It is necessary to know four common different temperature scales, namely Fahrenheit (^{0}F), Celsius (^{0}C), Kelvin (K) and Rankine (^{0}R). To convert these scales one another can be used the following equations [9,10].

$$T \, / \, K \ = \ \theta \, / ^0 C \ + \ 273.15 \tag{2}$$

$$\left[oR \right] = \left[oF \right] + 459.67 \left[oF \right] = 1.8 \left[oC \right] + 32 \left[oR \right] = 1.8 \left[K \right] \tag{3}$$

2. The first law of thermodynamic (the conservation of energy)

In thermodynamics, the total energy of a system is called its **internal energy**, U. The internal energy is the total kinetic and potential energies of the particles in the system. It is denoted by ΔU the change in internal energy when a system changes from an initial state i with internal energy U_i to a final state of internal energy U_f :

$$\Delta U = U_f - U_i \tag{4}$$

The internal energy is a state function in the sense that its value depends only on the current state of the system and is independent of how that state has been prepared. In other words, internal energy is a function of the properties as variables that determine the current state of

the system. Changing any one of the state variables, such as the pressure and temperature, results in a change in internal energy. The internal energy is a state function that has consequences of the greatest importance. The internal energy is an extensive property of a system and is measured in joules (1 J = 1 kg m^2 s^{-2}). The molar internal energy, U_m, is the internal energy divided by the amount of substance in a system, $U_m = U/n$; it is an intensive property and commonly reported in kilojoules per mole (kJ mol^{-1}) [12].

A particle has a certain number of motional degrees of freedom, such as the ability to translate (the motion of its centre of mass through space), rotate around its centre of mass, or vibrate (as its bond lengths and angles change, leaving its centre of mass unmoved). Many physical and chemical properties depend on the energy associated with each of these modes of motion. For example, a chemical bond might break if a lot of energy becomes concentrated in it, for instance as vigorous vibration. According to it, the average energy of each quadratic contribution to the energy is 1/2 kT. The mean energy of the atoms free to move in three dimensions is kT and the total energy of a monatomic perfect gas is NkT, or nRT (because $N = nN_A$ and $R = N_A k$, N_A: Avogadro's number and k: Boltzman's constant). I t can therefore be written;

$$U_m(T) = U_m(0) + RT (monatomic\ gas;\ translation\ only)$$ (5)

where $U_m(0)$ is the molar internal energy at $T = 0$, when all translational motions have ceased and the sole contribution to the internal energy arises from the internal structure of the atoms. This equation shows that the internal energy of a perfect gas increases linearly with temperature. At 25°C, 3/2 RT = 3.7 kJ mol^{-1}, so translational motion contributes about 4 kJ mol^{-1} to the molar internal energy of a gaseous sample of atoms or molecules.

When the gas consists of molecules, we need to take into account the effect of rotation and vibration. A linear molecule, such as N_2 and CO_2, can rotate around two axes perpendicular to the line of the atoms, so it has two rotational modes of motion, each contributing a term 1/2 kT to the internal energy. Therefore, the mean rotational energy is kT and the rotational contribution to the molar internal energy is RT.

$$U_m(T) = U_m(0) + 5/2 RT (linear\ molecule;\ translation\ and\ rotation\ only)$$ (6)

A nonlinear molecule, such as CH_4 or H_2O, can rotate around three axes and, again, each mode of motion contributes a term 1/2 kT to the internal energy. Therefore, the mean rotational energy is 3/2 kT and there is a rotational contribution of 3/2 RT to the molar internal energy. That is,

$$U_m(T) = U_m(0) + 3RT (nonlinear\ molecule;\ translation\ and\ rotation\ only)$$ (7)

The internal energy now increases twice as rapidly with temperature compared with the monatomic gas. Another way: for a gas consisting of 1 mol of nonlinear molecules to undergo the same rise in temperature as 1 mol of monatomic gas, twice as more energy must be supplied. Molecules do not vibrate significantly at room temperature and, as a first

approximation; the contribution of molecular vibrations to the internal energy is negligible except for very large molecules such as polymers and biological macromolecules. None of the expressions we have been derived depends on the volume occupied by the molecules: there are no intermolecular interactions in a perfect gas, so the distance between the molecules has no effect on the energy. That is, the internal energy of a perfect gas is independent of the volume it occupies. The internal energy of interacting molecules in condensed phases also has a contribution from the potential energy of their interaction. However, no simple expressions can be written down in general. Nevertheless, the crucial molecular point is that, as the temperature of a system is raised, the internal energy increases as the various modes of motion become more highly excited [12].

By considering how the internal energy varies with temperature when the pressure of the system is kept constant; many useful results and also some unfamiliar quantities can be obtained. If it is divided both sides of eqn $((dU = (\partial U/\partial V)_T\, dV + (\partial U/\partial T)_v\, dT\,)$ $((\partial U/\partial V)_T = \pi_T$ and π_T called as **the internal pressure ;** $(\partial U/\partial T)_v = C_v$ and it is called as **heat capacity at constant volume**)) by dT and impose the condition of constant pressure on the resulting differentials, so that dU/dT on the left becomes $(\partial U/\partial T)_p$, So;

$$\left(\partial U\,/\,\partial T\right)_p = \pi_T\left(\partial V\,/\,\partial T\right)_p + C_v \tag{8}$$

It is usually sensible in thermodynamics to inspect the output of a manipulation like this to see if it contains any recognizable physical quantity. The differential coefficient on the right in this expression is the slope of the plot of volume against temperature (at constant pressure). This property is normally identified as thermal expansion coefficient, α, of a substance, which is defined as

$$\alpha = 1\,/\,V\left(\partial V\,/\,\partial T\right)_p \tag{9}$$

When it is introduced the definition of α into the equation for $(\partial U/\partial T)_p = \alpha\pi_T V + C_v$,this equation is entirely general (provided the system is closed and its composition is constant). It expresses the dependence of the internal energy on the temperature at constant pressure in terms of C_v, which can be measured in one experiment, in terms of α, which can be measured in another, and in terms of the quantity π_T, for a perfect gas, $\pi_T = 0$, so

$$\left(\partial U\,/\,\partial T\right)_p = C_v \tag{10}$$

That is, the constant-volume heat capacity of a perfect gas is equal to the slope of a plot of internal energy against temperature at constant pressure as well as (by definition) to the slope at constant volume. It can also be predicted that the change of internal energy with temperature at constant pressure means a total energy change raised from increase in both energy of kinetics and potential energy of particles in higher temperature. The translational motion of particles against constant external pressure will lead to expansion, but thermal expansion characteristics of substance control its magnitude. Thus, we can see that heating in constant volume only changes internal energy as q_v ($\Delta U = q_v$), whereas its change in

constant pressure additionally includes changing of potential energy of particles due to translation motion. That is, changes in constant pressure require a different definition of the transferred energy [12].

3. From conservation of energy to heat and work

It has been found experimentally that the internal energy of a system may be changed either by doing work on the system or by heating it. Whereas we may know how the energy transfer has occurred (because we can see if a weight has been raised or lowered in the surroundings, indicating transfer of energy by doing work, or if ice has melted in the surroundings, indicating transfer of energy as heat), the system is blind to the mode employed. Heat and work are equivalent ways of changing a system's internal energy. It is also found experimentally that, if a system is isolated from its surroundings, then no change in internal energy takes place. This summary of observations is now known as the **First Law of thermodynamics** or the **Conservation of Energy** and is expressed as follows [1;12].

The internal energy of an isolated system is constant.

$$\Delta U = 0 \tag{11}$$

A system cannot be used to do work, leave it isolated, and then come back expecting to find it restored to its original state with the same capacity for doing work. The experimental evidence for this observation is that no 'perpetual motion machine', a machine that does work without consuming fuel or using some other source of energy, has ever been built. These remarks may be summarized as follows. If we write w for the work done on a system, q for the energy transferred as heat to a system, and ΔU for the resulting change in internal energy, and then it follows that

$$\Delta U = q + w \tag{12}$$

Equation summarizes the equivalence of heat and work and the fact that the internal energy is constant in an isolated system (for which $q = 0$ and $w = 0$). The equation states that the change in internal energy of a closed system is equal to the energy that passes through its boundary as heat or work. It employs the 'acquisitive convention', in which w and q are positive if energy is transferred to the system as work or heat and are negative if energy is lost from the system. In other words, we view the flow of energy as work or heat from the system's perspective [1;12].

Heat (q)

Heat flows by virtue of a temperature difference. Heat will flow until temperature gradients disappear [8]. When a heater is immersed in a beaker of water (the system), the capacity of the system to do work increases because hot water can be used to do more work than cold water [1].

An **exothermic process** is a process that releases energy as heat. All combustion reactions are exothermic. An **endothermic process** is a process that absorbs energy as heat. An example of an endothermic process is the vaporization of water. An endothermic process in a diathermic container results in energy flowing into the system as heat. An exothermic

process in a similar diathermic container results in a release of energy as heat into the surroundings. If an endothermic process in nature was taken place by a system divided an adiabatic boundary from its surroundings, a lowering of temperature of the system results; conversely if the process is exothermic, temperature rises [1]. These are the expected results of conversation of energy.

Work (*w*)

Energy is the essence of our existence as individuals and as a society. Just as energy is important to our society on a macroscopic scale, it is critically important to each living organism on a microscopic scale. The living cell is a miniature chemical factory powered by energy from chemical reactions. The process of cellular respiration extracts the energy stored in sugars and other nutrients to drive the various tasks of the cell. Although the extraction process is more complex and more subtle, the energy obtained from "fuel" molecules by the cell is the same as would be obtained from burning the fuel to power an internal combustion engine [3].

The fundamental physical property in thermodynamics is work is done when an object is moved against an opposing force. Doing work is equivalent into raising a weight somewhere in the surrounding. An example of doing work is the expansion of a gas that pushes out a piston and raises a weight. A chemical reaction that derives an electric current through a resistance also does work, because the same current could be driven through a motor and used to raise a weight [1].

Work is the transferred energy by virtue of a difference in mechanical properties from a boundary between the system and the surroundings. There are many types of work; such as mechanical work, electrical work, magnetic work, and surface tension [8].

The SI unit of both heat and work (kg m^2/s^2) is given the name joule (J), after the English physicist James Prescott Joule (1818-1889) [6].

$$1 \text{ J} = 1 \text{ kg } m^2/s^2$$

In addition to the SI unit joule, some chemist's still use the unit calorie (cal). Originally defined as the amount of energy necessary to raise the temperature of 1 g of water by 1°C (specially, from 14.5 °C to 15.5 °C), one calorie is now defined as exactly 4,184 J [6].

The work–energy theorem

In mechanics, the work–energy theorem demonstrates that the total work done on a system is transformed into kinetic energy. This is represented in a very simple and meaningful equation as follows:

$$W_{total} = \Delta E_k \tag{13}$$

in which, W_{total} is the total work done on the system, including the work carried out by all the external forces (W_{ex}), as well as the work developed by the internal forces within the system (W_{in}). Thus;

$$W_{total} = W_{ex} + W_{in} \tag{14}$$

Now, if the external work is separated into two terms, namely the work done by the external conservative forces ($W_{ex,c}$), which are associated with an external potential energy ($E_{p,ex}$), and the non-conservative external work ($W_{non-cex}$), the whole external work can be written as:

$$W_{ex} = W_{ex,c} + W_{non-cex} = -\Delta E_{p,ex} + W_{non-cex} \tag{15}$$

Similarly, the work developed by the internal forces within the system can be also expressed as the sum of a conservative work term plus the non-conservative internal work. Thus;

$$W_{in} = W_{in,c} + W_{non-c'in} = -\Delta E_{p,in} + W_{non-cin} \tag{16}$$

Where, $\Delta E_{p,in}$ is the internal potential energy of the system.

As for the kinetic energy of a system, mechanics shows that it can be considered as consisting of two terms, as follows:

$$E_k = 1/2Mv^2_{CM} + E_{k,CM} \tag{17}$$

M being the total mass of the system, v_{CM} the velocity of its center of mass, and $E_{k,CM}$ the kinetic energy of the system with respect to its center of mass. The first term on the right-hand side of equation above represents the kinetic energy of the center of mass of the system, as if it had the mass of the whole system. Thus, as the velocity v_{CM} is taken with respect to an external reference frame, this first term can be called the external kinetic energy of the system ($E_{k,ex}$), whereas the second term would be its internal kinetic energy ($E_{k,in}$). Accordingly, the increase of the kinetic energy of a system can be written in the following way:

$$\Delta E_k = \Delta E_{k,ex} + \Delta E_{k,in} \tag{18}$$

Then, the substitution of equations 14, 15, 16 and 18 into equation 13 allows us to order terms as follows:

$$W_{ex} = \Delta E_{p,ex} + \Delta E_{k,ex} + \Delta E_{p,in} + \Delta E_{k,in} - W_{in} \tag{19}$$

Equation 19 is a general developed expression of the work–energy theorem derived from mechanics. It should be noticed that, though it does not describe the details of the energetic terms, each of them is explicitly stated, which will be of great help both to define and to understand the contribution of thermodynamics when establishing the first law [17].

Reversibility and Reversible changes

A reversible change in thermodynamics is a change that can be reversed by an infinitesimal modification of a variable. One example of reversibility that we have encountered already is the thermal equilibrium of two systems with the same temperature. The transfer of energy as heat between the two is reversible because, if the temperature of either system is lowered infinitesimally, then energy flows into the system with the lower temperature. If the

temperature of either system at thermal equilibrium is raised infinitesimally, then energy flows out of the hotter system. There is obviously a very close relationship between reversibility and equilibrium: systems at equilibrium are poised to undergo reversible change. Suppose a gas is confined by a piston and that the external pressure, p_{ex}, is set equal to the pressure, p, of the confined gas. Such a system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions. If the external pressure is reduced infinitesimally, the gas expands slightly. If the external pressure is increased infinitesimally, the gas contracts slightly. In either case the change is reversible in the thermodynamic sense. If, on the other hand, the external pressure differs measurably from the internal pressure, then changing p_{ex} infinitesimally will not decrease it below the pressure of the gas, so will not change the direction of the process. Such a system is not in mechanical equilibrium with its surroundings and the expansion is thermodynamically irreversible [12].

To achieve reversible expansion we set p_{ex} equal to p at each stage of the expansion. In practice, this equalization could be achieved by gradually removing weights from the piston so that the downward force due to the weights always matches the changing upward force due to the pressure of the gas. When we set $p_{ex} = p$, eqn ($dw = -p_{ex}dV$) becomes

$$dw = -p_{ex}dV = -pdV \qquad \textit{reversible expansion work} \qquad (20)$$

(Equations valid only for reversible processes are labeled with a subscript rev.) Although the pressure inside the system appears in this expression for the work, it does so only because p_{ex} has been set equal to p to ensure reversibility. The total work of reversible expansion from an initial volume V_i to a final volume V_f is therefore

$$w = -\int_{Vi}^{Vf} pdV \qquad (21)$$

The integral can be evaluated once it is known how the pressure of the confined gas depends on its volume [12].

At the isothermal, reversible expansion of a perfect gas, the work made by keeping the system in thermal contact with its surroundings can be stated as follows;

$$w = -nRT\int_{Vi}^{Vf} dV / V = -nRT\ln V_f / V_i \qquad (22)$$

When the final volume is greater than the initial volume, as in an expansion, the logarithm in Eqn. 22 is positive and hence $w < 0$. In this case, the system has done work on the surroundings and there is a corresponding reduction in its internal energy, but due to there is a compensating influx of energy as heat, overall the internal energy is constant for the isothermal expansion of a perfect gas, which clearly indicates **the Conservation of Energy Law.** The equations also show that more work is done for a given change of volume when the temperature is increased: at a higher temperature the greater pressure of the confined

gas needs a higher opposing pressure to ensure reversibility and the work done is correspondingly greater (Fig. 5) [12].
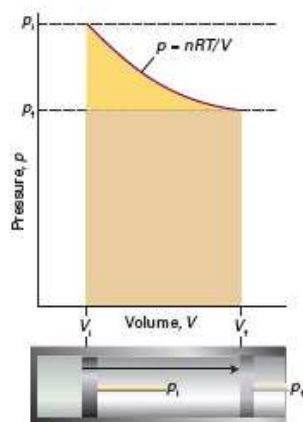

Figure 5. The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm $p = nRT/V$. The work done during the irreversible expansion against the same final pressure is equal to the rectangular area shown slightly darker. It can be seen that the reversible work is greater than the irreversible work [12].

Adiabatic changes

We are now equipped to deal with the changes that occur when a perfect gas expands adiabatically. A decrease in temperature should be expected: because work is done but no heat enters the system, the internal energy decrease, and therefore the temperature of the working gas also decrease. In molecular terms, the kinetic energy of the particles decrease as work is done, so their average speed decreases, and hence the temperature decrease. This means that in the case of perfect gas, change in the distance between particles cannot be responsible for the changing of internal energy but **the Conservation of Energy Law** requires a measurable reduction in kinetic energy of particles, i.e. a reduction in their velocities. The change in internal energy of a perfect gas when the temperature is changed from T_i to T_f and the volume is changed from V_i to V_f can be expressed as the sum of two steps (Fig. 6).

In the first step, only the volume changes and the temperature is held constant at its initial value. However, because the internal energy of a perfect gas is independent of the volume the molecules occupy, the overall change in internal energy arises solely from the second step, the change in temperature at constant volume. Provided the heat capacity is independent of temperature, this change is

$$\Delta U = C_V \left(T_f - T_i \right) = C_V \Delta T \tag{23}$$

Because the expansion is adiabatic, we know that $q = 0$; because $\Delta U = q + w$, it then follows that $\Delta U = $ ad. The subscript 'ad' denotes an adiabatic process. Therefore, by equating the two expressions we have obtained for ΔU, we obtain
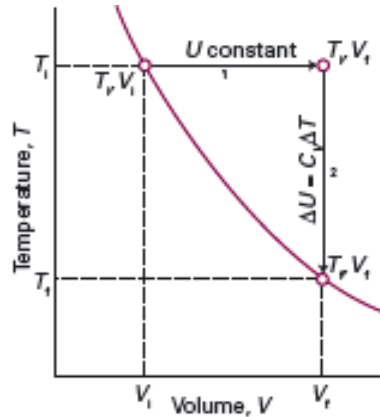
$$W_{ad} = C_V \Delta T \tag{24}$$

Figure 6. To achieve a change of state from one temperature and volume to another temperature and volume, we may consider the overall change as composed of two steps. In the first step, the system expands at constant temperature; there is no change in internal energy if the system consists of a perfect gas. In the second step, the temperature of the system is reduced at constant volume. The overall change in internal energy is the sum of the changes for the two steps [12].

That is, the work done during an adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final states. That is exactly what it can be expected on molecular grounds and according to **Conversation of Energy**, because the mean kinetic energy is proportional to T, so a change in internal energy arising from temperature alone is also expected to be proportional to ΔT [12].

$$T_f = Ti \left(V_i / V_f \right)^{1/c} \tag{25}$$

where $c = C_V /R$ (*C_V :molar heat capacity in constant volume and R: universal gas constant*). By raising each side of this expression to the power c, an equivalent expression is

$$V_i T_i^{c} = V_f T_f^{c} \tag{26}$$

This result is often summarized in the form VT^c = constant

4. From the conservation of energy to heat transfer, heat capacity and the enthalpy

The process of heat moving from one object into another is called heat transfer. The difference in temperature defines the direction in which the heat flows when two objects come into contact; heat always flows from a hotter object at a higher temperature into a colder object at a lower temperature. Heat transfer which can mainly occur in three ways, namely conduction, convection and radiation changes the temperature of matter; it can also cause changes in phase or state [7].

When energy is added to a substance and no work is done, the temperature of the substance usually rises i.e. substance is heated; exception to the case in which a substance undergoes a change of state-also called a phase transition, such as vaporization/condensation,

melting/freezing, and sublimation. The quantity of energy required to raise the temperature of given mass of a substance by some amount varies from one substance to another. The amount of increase also depends on the conditions in which heating takes place. Heat capacity (C) of a substance is the quantity of energy required to raise its temperature by 1°C or 1 K. The heat capacity differs from substance to substance. In the case of a monatomic gas such as helium under constant volume, if it is assumed that no electronic or nuclear quantum excitations occur, each atom in the gas has only 3 degrees of freedom, all of a translational type. No energy dependence is associated with the degrees of freedom which define the position of the atoms. While, in fact, the degrees of freedom corresponding to the momenta of the atoms are quadratic, and thus contribute to the heat capacity. In the somewhat more complex case of a perfect gas of diatomic molecules, the presence of internal degrees of freedom is apparent. Table1 shows C_v values for some mono and diatomic gases at 1 atm and 25°C.

Monoatomic Gases	C_v (J/Kmol)	Diatomic Gases	C_v (J/Kmol)
He	12.5	H_2	20.18
Ne	12.5	CO	20.2
Ar	12.5	N_2	19.9
Kr	12.5	Cl_2	24.1
Xe	12.5	Br_2 (vapor)	28.2

Table 1. C_v values for some mono and diatomic gases at 1 atm and 25°C.

From Table 1, it can be seen clearly that the heat capacities of all monoatomic gasses have exactly same values, but they are lower than those of diatomic gasses which include the contributions of translation vibration, and rotation.

The heat capacity is directly proportional to the amount of substance. Heat capacity is an extensive property, meaning it is a physical property that scales with the size of a physical system .That means by doubling the mass of substance, heat capacity can be doubled. The heat required to increase the temperature from T_1 to T_2 of a substance can be calculated using the following equation.

$$Q = C \ x \ \Delta T \qquad (27)$$

The unit of heat capacity is $J°C^{-1}$ or JK^{-1}. For many experimental and theoretical purposes it is more convenient to report heat capacity as an **intensive property**, as an intrinsically characteristic property of a particular substance. This is most often accomplished by the specification of the property per a unit of mass. In science and engineering, such properties are often prefixed with the term *specific*. International standards now recommend that specific heat capacity always refer to division by mass. The units for the specific heat capacity are [C] = J/kg K in chemistry, the heat capacity is also often specified relative one mole, the unit for amount of substance, and is called the molar heat capacity, having the unit, J/mol K. For some considerations it is useful to specify the volume-specific heat capacity, commonly called volumetric heat capacity, which is the heat capacity per unit

volume and has SI units $[S] = J/m^3\ K$. This is used almost exclusively for liquids and solids, since for gasses it may be confused with specific heat capacity at constant volume.

In thermodynamics, two types of heat capacities are defined; C_P, the heat capacity at constant pressure and C_v, heat capacity at constant volume. The total energy of a system in thermodynamics is called internal energy which specifies the total kinetic and potential energy of particles in the system. Internal energy of a system can be changed either by doing work on the system or heating it as a result of the conversation of energy law. The internal energy of a substance increases when its temperature is increased. By considering the total change in internal energy of a substance which is heated at constant pressure, the difference between heat capacities at two different conditions can be meaningfully interpreted. Heat capacity in terms of derivative at constant volume is expressed as follows:

$$C_v = \left(\partial U / \partial T \right)_v \tag{28}$$

The first law of thermodynamics argues that the internal energy of a system which is heated at constant-pressure differs from that at the constant-volume by the work needed to change the volume of the system to maintain constant pressure. This work arises in two ways: One is the work of driving back the atmosphere (external work); the other is the work of stretching the bonds in the material, including any weak intermolecular interactions (internal work). In the case of a perfect gas, the second makes no contribution.

In order to find out how the internal energy varies with temperature when the pressure rather than the volume of the system is kept constant; it can be divided both sides of ($dU = (\partial U / \partial V)_T\ dV + (\partial U / \partial T)_v\ dT$) by dT and thus;

$$\left(\partial U / \partial T \right)p = \left(\partial U / \partial V \right)_T \left(\partial V / \partial T \right)p + \left(\partial U / \partial T \right)_v \tag{29}$$

It is usually sensible in thermodynamics to inspect the output of a manipulation like this to see if it contains any recognizable physical quantity. The partial derivatives on the right in this expression are the slope of the plot of volume against temperature at constant pressure, the slope of the plot of internal energy against volume at constant temperature and the slope of the plot of internal energy against temperature at constant volume, respectively. These properties are normally tabulated as the expansion coefficient, α, of a substance, which is defined as $\alpha =1/V\ (\partial U/\partial T)_p$, internal pressure, π_T, and constant volume heat capacity, C_v, respectively. Thus;

$$\left(\partial U / \partial T \right)_p = \alpha \pi_T V + C_v \tag{30}$$

Equation (30) is entirely general for a closed system, which may be in solid, liquid, or gas states, with constant composition. It expresses the changing of internal energy with the temperature at constant pressure depends on two terms on the right in this expression The first term is related to the potential energy of particles and it comprises internal work made against internal pressure due to thermal expansion which can be considered for all substances in solid, liquid, or gas states, but weakness of inter-particles interactions in gas

state requires to take account of an additional contribution to identify the real change in internal energy of any system in gas state heated at constant pressure. The fact that for a perfect gas, $\pi_T = 0$ and so $(\partial U/\partial T)p = C_v$,supports to this remark. The second term also is interested in the kinetic energies of particles. That is, the energy at the constant-pressure of any substance must defined by an another thermodynamic property or function and this function must include external work made to external pressure due to volumetric expansion of any system in gas state. This thermodynamic function which takes account of external work is the enthalpy.

The enthalpy

The change in internal energy is not equal to the heat supplied when the system is free to change its volume. Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work, so ΔU is less than q [1].

To determine ΔE, it must be measured both heat and work which done by expanding of a gas. It can be found the quantity of pV work done by multiplying the external pressure (P) by the change in volume of the gas (ΔV, or $V_{final} - V_{initial}$). In an open flask (or a cylinder with a weightless, frictionless piston), a gas does work by pushing back the atmosphere (Figure 7) [18].
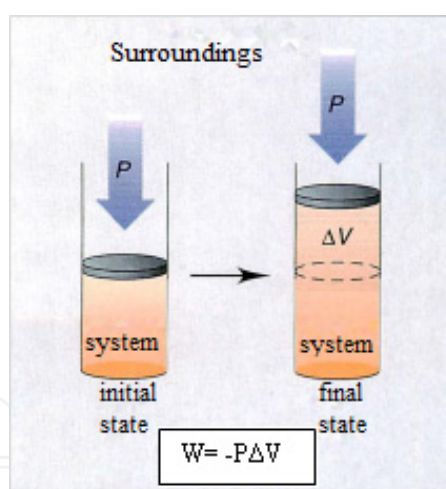
$$w = -p\Delta V \tag{31}$$

Figure 7. Pressure-volume work. When the volume (V) of a system increases by an amount of ΔV against an external pressure (p), the system pushes back, and thus does pV work on the surroundings (w = -p ΔV) [18].

For changes at constant pressure, a thermodynamic variable called the enthalpy, H, is mathematically defined as follows [1],

$$H = U + pV \tag{32}$$

where U is the internal energy of the system, p is the pressure of the system, and V is the volume of the system [3].

Since internal energy, pressure, and volume are all state functions, enthalpy is also a state function. But what exactly is enthalpy? To help answer this question, consider a process carried out at constant pressure and where the only work allowed is pressure-volume work ($w = -p\Delta V$). Under this conditions, the expression

$$\Delta U = q_P + w \tag{33}$$

becomes

$$\Delta U = q_p - p\Delta V \tag{34}$$

or

$$q_p = \Delta U + p\Delta V \tag{35}$$

where q_P, ΔU and $p\Delta V$ are the transferred energy as heat to the system heated at constant pressure, change in internal energy and change in pV, respectively. Since p is constant; the change in pV is due only to a change in volume. Thus

$$\left(pV\right) = p\,\Delta V \tag{36}$$

$$\Delta H = q_p \tag{37}$$

Heat capacity in terms of derivative at constant pressure, i.e. changes in the energy of a system heated at constant pressure is also expressed as follows:

$$C_p = \left(\partial H / \partial T\right)_p \tag{38}$$

The slope of a plot of internal energy against temperature at constant volume, for a perfect gas C_v is also the slope at constant pressure. In order to obtain an easy way to derive the relation between C_p and C_v for a perfect gas, both heat capacities can be used in terms of derivatives at constant pressure:

$$Cp - Cv = \left(\partial H / \partial T\right)p - \left(\partial U / \partial T\right)v = \left(\partial H / \partial T\right)p - \left(\partial U / \partial T\right)p \tag{39}$$

Then, if $(H = U + pV = U + nRT)$ is introduced into the first term, which results in

$$Cp - Cv = \left(\partial U / \partial T\right)p + nR - \left(\partial U / \partial T\right)p \quad \text{and}\left(C_p - C_v = nR\right) \tag{40}$$

This means that in the case of a perfect gas, R, universal gas constant may be considered as the work done to push back the atmosphere per unit increase in temperature. However, the general relation between the two heat capacities for any pure substance is demonstrated as follows;

$$C_p - C_v = \alpha^2 TV / \kappa_T \tag{41}$$

This formula is a thermodynamic expression, which means that it applies to any substance (that is, it is universally true). It reduces to previous equation for a perfect gas when it was set as $\alpha = 1/T$ and $\kappa_T = 1/p$

Because thermal expansion coefficients, α, of liquids and solids are small, it is tempting to deduce from last equation that for them $Cp \approx Cv$. But this is not always so, because the compressibility κ_T might also be small, so α^2/κ_T might be large. That is, although only a little work need be done to push back the atmosphere, a great deal of work may have to be done to pull atoms apart from one another as the solid expands. As an illustration, for water at 25 ^{0}C, Eqn (41) gives $C_P = 75.3$ J/Kmol compared with $C_v = 74.8$ J/Kmol. In some cases, the two heat capacities differ by as much as 30 per cent [21]. The constant-pressure heat capacity C_P differs from the constant-volume heat capacity C_v by the work needed to change the volume of the system to maintain constant pressure. This work arises in two ways. One is the work of driving back the atmosphere (external work); the other is the work of stretching the bonds in the material, including any weak intermolecular interactions (internal work). In the case of a perfect gas, the second makes no contribution. This suggests that the difference between two heat capacities is related to both internal work and external work done by the particles of a substance as an expended result of the conservation of energy.

By considering the variation of H with temperature at constant volume, the validity of the enthalpy function can be differently verified. Firstly; for a closed system of constant composition, H is expressed in the total differential of T and p;

$$dH = ((\partial H / \partial p)_T \, dp + (\partial H / \partial T)_p \, dT \tag{42}$$

and then, divided this equation though by dT;

$$(\partial H / \partial T)_v = (\partial H / \partial p)_T (\partial p / \partial T)_v + C_p \tag{43}$$

The manipulation of this expression provides more involved equation which can be applied to any substance. Because all the quantities that appear in it can be measured in suitable experiments.

$$(\partial H / \partial T)_v = (1 - \alpha \mu / \kappa_T) \, C_p \tag{44}$$

where the isothermal compressibility, κ_T, is defined as

$$\kappa_T = -1/V \, (\partial V / \partial p)_T \tag{45}$$

and the Joule – Thomson coefficient, μ, is defined as

$$\mu = (\partial T / \partial p)_H \tag{46}$$

This expression derived for the changing of the enthalpy with temperature at constant volume suggests that change in H with increased temperature at constant V is lower than that at constant p and the difference between them depend on some characteristic

properties of particles, such as κ_T, μ and α,, indicating its relation with the absence of external work.

The measurement of an enthalpy change

An enthalpy change can be measured calorimetrically by monitoring the temperature change that accompanies a physical or chemical change occurring at constant pressure. A calorimeter for studying processes at constant pressure is called an isobaric calorimeter. A simple example is a thermally insulated vessel open to the atmosphere: the heat released in the reaction is monitored by measuring the change in temperature of the contents. For a combustion reaction an adiabatic flame calorimeter may be used to measure ΔT when a given amount of substance burns in a supply of oxygen. Another route to ΔH is to measure the internal energy change using a bomb calorimeter, and then to convert ΔU to ΔH. Because solids and liquids have small molar volumes, for them both pV_m , external work and internal work is so small that the molar enthalpy and molar internal energy are almost identical ($H_m = U_m + pV_m \approx U_m$). Consequently, if a process involves only solids or liquids, the values of ΔH and ΔU are almost identical. Physically, such processes are accompanied by a very small change in volume; the system does negligible work on the surroundings when the process occurs, so the energy supplied as heat stays entirely within the system, as a expended result of the conversation of energy.

Calorimeters

The heat that is given out or taken in, when a chemical reaction occurs can be measured using a calorimeter. A simple, constant-pressure calorimeter (Coffee-cup calorimeter) for measuring heat for reactions in solution is shown in Fig. 8. This figure also shows a bomb calorimeter. The container is an expanded polystyrene cup with a lid. This material provides insulation which ensures that heat loss to, or gains from the surroundings is minimized; the outer cup in Fig. 8 provides additional insulation. As the reaction takes place, the thermometer records any change in temperature.
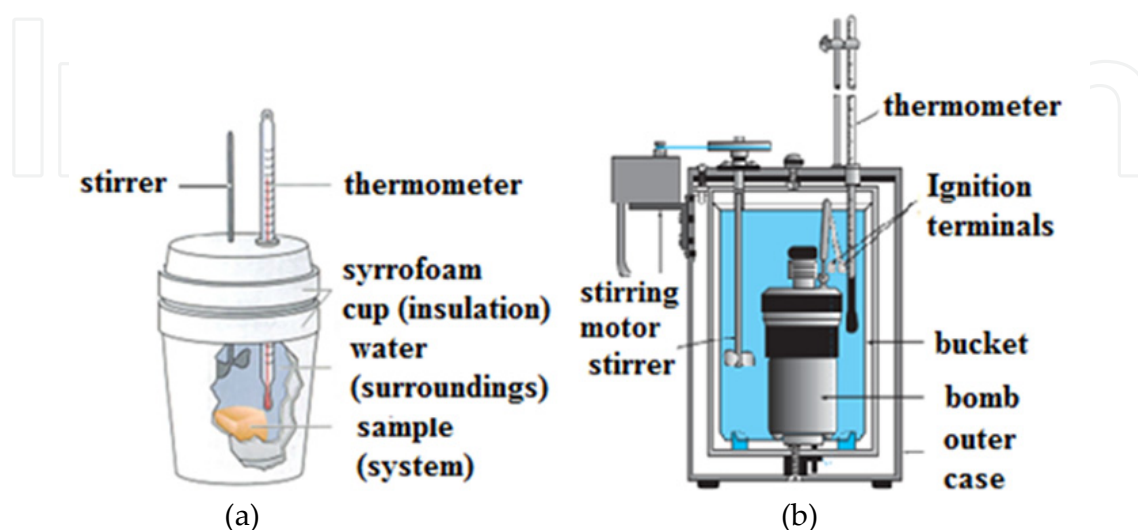

Figure 8. Calorimeter types; (a) Coffee-cup calorimeter [18] and (b) Bomb calorimeter [22].

The relationship between the temperature change and the energy is given as follows;

$$Energy\ change\ in\ J\ =\ m\ (g).C\ (J\ /\ gK).\ \Delta T\ (K) \tag{47}$$

where C is the specific heat capacity of the solution. Since the reaction is carried out at constant pressure, the energy is equal to the enthalpy change. For dilute aqueous solutions, it is usually sufficient to assume that the specific heat capacity of the solution is the same as for water: C_{water} 4.18 J/gK. It is assumed that no heat is used to change the temperature of the calorimeter itself. Where a calorimeter is made from expanded polystyrene cups, this is a reasonable assumption because the specific heat capacity of the calorimeter material is so small. However, the approximation is not valid for many types of calorimeter and such pieces of apparatus must be calibrated before use. Measurements made in the crude apparatus shown together with in Figure 8 are not accurate, and more specialized calorimeters, such as **bomb calorimeter** must be used if accurate results are required [18;19]. A bomb calorimeter is ideally suited for measuring the heat evolved in a combustion reaction. The system is everything within the double-walled outer jacket of the calorimeter. This includes the bomb and its contents, the water in which the bomb is immersed, the thermometer, the stirrer, and so on. Before using above equation, it must be emphasized that a rise in temperature of a system insulated with its surrounding does not occur by any heat transferred from the surroundings to the system because of the temperature difference between them. The difference in temperature observed during the measuring may be arisen from the change in the composition of system and considered as if the involved reaction occurs as exothermic or endothermic in diathermic condition. At constant pressure (where only pV work is allowed), the change in enthalpy ΔH of the system is equal to the energy flow as heat. This means that for a reaction studied at constant pressure, the flow of heat is a measure of the change in enthalpy for the system. For this reason, the terms heat of reaction and change in enthalpy are used interchangeably for reactions studied at constant pressure. For a chemical reaction, the enthalpy change is given by the equation

$$\Delta H\ =\ H_{products}\ -\ H_{reactants} \tag{48}$$

In a case in which the products of a reaction have a greater enthalpy than the reactants, ΔH will be positive. Thus heat will be absorbed by the system, and the reaction is **endothermic**. On the other hand, if the enthalpy of the products is less than that of the reactants, ΔH will be negative. In this case the overall decrease in enthalpy is achieved by the generation of heat, and the reaction is **exothermic** [3]. Energy diagrams for exothermic and endothermic reactions are shown in Figure 9.

Standard enthalpy change

The standard enthalpy change of a reaction refers to the enthalpy change when all the reactants and products are in their **standard states**. The notation for this thermochemical quantity is $\Delta_r H^0$ (T) where the subscript 'r' stands for 'reaction', the superscript 'o' means 'standard state conditions', and (T) means 'at temperature T'. This type of notation is found for other thermodynamic functions that we meet later on.
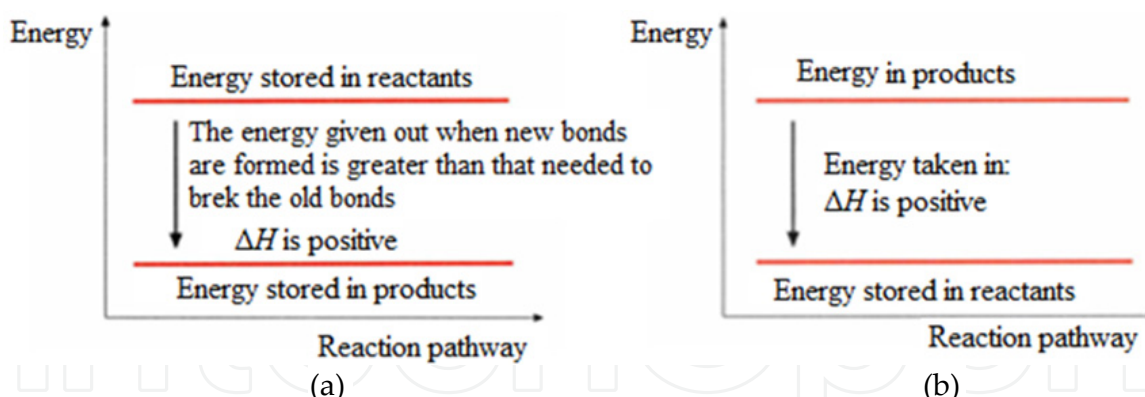
Figure 9. Energy diagrams for exothermic (a) and endothermic reactions (b) [20].

The standard state of a substance is its most thermodynamically stable state under a pressure of 1 bar (1.00 x 10^5 Pa) and at a specified temperature, T. Most commonly, T = 298.15 K, and the notation for the standard enthalpy change of a reaction at 298.15K is then $\Delta_r H^0$ (298.15 K). It is usually sufficient to write $\Delta_r H^0$ (298 K) [19].

Standard enthalpies of formation

The standard enthalpy of formation (ΔH_f^0) of a compound is defined as the change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their reference states. The reference state of a element is its most thermodynamically stable state under a pressure of 1 bar (1.00 x 10^5 Pa) and at a specified temperature, T.

A degree symbol on a thermodynamic function, for example, ΔH, indicates that the corresponding process has been carried out under standard conditions. The standard state for a substance is a precisely defined reference state. Because thermodynamic functions often depend on the concentrations (or pressures) of the substances involved, it must be used a common reference state to properly compare the thermodynamic properties of two substances. This is especially important because, for most thermodynamic properties, it can be measured only *changes* in the property

Enthalpy is a state function, so it can be chosen *any* convenient pathway from reactants to products and then sums the enthalpy changes along the chosen pathway. A convenient pathway, shown in Fig. 10, involves taking the reactants apart to the respective elements in their reference states in reactions (a) and (b) and then forming the products from these elements in reactions (c) and (d). This general pathway will work for any reaction, since atoms are conserved in a chemical reaction [3].

From Fig. 10, it can be seen that reaction (a), where methane is taken apart into its elements,

$$CH_4(g) \rightarrow C(s) + 2H_2(g) \tag{49}$$

is just the reverse of the formation reaction for methane:

$$C(s) + 2H_2(g) \rightarrow CH_4(g) \quad \Delta H^0{}_f = -75 \; kJ / mol \tag{50}$$
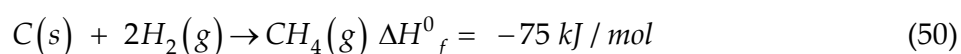
Since reversing a reaction means changing the sign of ΔH, but keeping the magnitude the same, ΔH for reaction (a) is $-\Delta H^0_f$, or 75 kJ. Thus ΔH^0 (a) = 75 kJ.

It can be secondarily considered reaction (b). Here oxygen is already an element in its reference state, so no change is needed. Thus ΔH^0 (b) = 0.
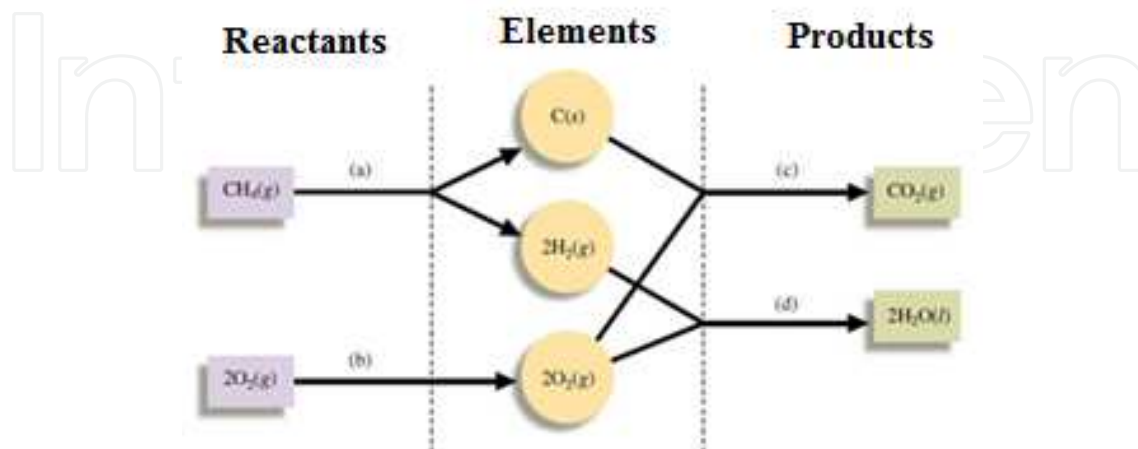

Figure 10. In this pathway for the combustion of methane, the reactants are first taken apart in reactions (a) and (b) to form the constituent elements in their reference states, which are then used to assemble the products in reactions (c) and (d) [3].
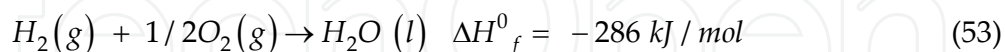
The next steps, reactions (c) and (d), use the elements formed in reactions (a) and (b) to form the products. That is, reaction (c) is simply the formation reaction for carbon dioxide:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^0_f = -394 \ kJ \ / \ mol \tag{51}$$

and
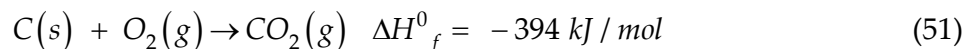
$$\Delta H^0_{(c)} = \Delta H^0_f \ for \ CO_2(g) = -394 \ kJ \ / \ mol \tag{52}$$

Reaction (d) is the formation reaction for water:

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O \ (l) \quad \Delta H^0_f = -286 \ kJ \ / \ mol \tag{53}$$

However, since 2 moles of water are required in the balanced equation, it must be formed 2 moles of water from the elements:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O \tag{54}$$

Thus

$$\Delta H^0_{(d)} = 2 \ x \ \Delta H^0_f \ for \ H_2O \ (l) = 2(-286 \ kJ \ /) = -572 \ kJ \ / \ mol \tag{55}$$

It has now been completed the pathway from the reactants to the products. The change in enthalpy for the reaction is the sum of the ΔH values (including their signs) for the steps:

$$\Delta H^0_{reaction} = \Delta H^0_{(a)} + \Delta H^0_{(b)} + \Delta H^0_{(c)} + \Delta H^0_{(d)} \tag{56}$$

$$= \left[-\Delta H^0_f \text{ for } CH_4(g) + 0 + \left[\Delta H^0_f \text{ for } CO_2(g) \right] + \left[2 \text{ x } \Delta H^0_f \text{ for } H_2O(l) \right] \right.$$
$$= -(-75 \text{ kJ}) + 0 + (-394 kJ) + (-572 \text{ kJ}) = -891 \text{ kJ} \tag{57}$$

This process is diagramed in Fig. 11. It can be seen that the reactants are taken apart and converted to elements [not necessary for $O_2{}_{(g)}$] that are then used to form products. It can be seen that this is a very exothermic reaction because very little energy is required to convert the reactants to the respective elements but a great deal of energy is released when these elements form the products. This is why this reaction is so useful for producing heat to warm homes and offices. If it is examined carefully the pathway used in this example, it can be understood that first, the reactants were broken down into the elements in their reference states and then the products were then constructed from these elements. This involved formation reactions and thus enthalpies of formation. The entire process can be summarized as follows:

$$\Delta H^0_{reaction} = \sum \nu_p \Delta H^0_{f \text{ (products)}} - \sum \nu_p \Delta H^0_{f \text{ (reactants)}} \tag{58}$$

where, ν is stoichiometric coefficients for both reactants and products. The enthalpy change for a given reaction can be calculated by subtracting the enthalpies of formation of the reactants from the enthalpies of formation of the products.
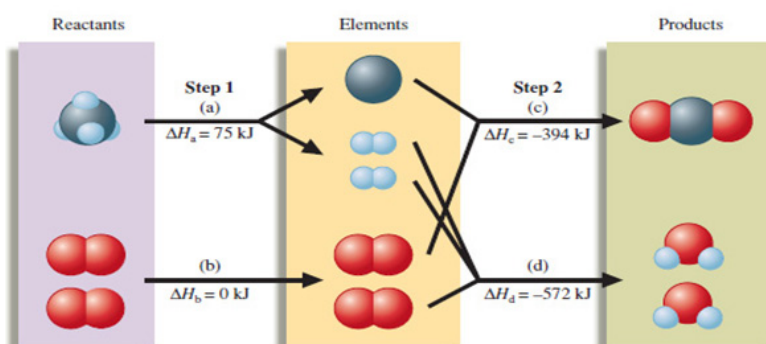

Figure 11. A schematic diagram of the energy changes for the reaction $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ [3].

Hess's law

Another way to calculate values of ΔH for reactions involves manipulating equations for other reactions with known ΔH values. When chemical equations are added to yield a different chemical equation, the corresponding ΔH values are added to get the ΔH for the desired equation. This principle is called **Hess's law** and it is an application of the **first law of thermodynamic** or the **conservation of energy**. For example, it can be calculated the ΔH for the reaction of carbon with oxygen gas to yield carbon dioxide from the values for the reaction of carbon with oxygen to yield carbon monoxide and that of carbon monoxide plus oxygen to yield carbon dioxide [9].

Desired

$$C(s) + O_2(g) \rightarrow CO_2(g) \tag{59}$$

Given

$$C(s) + 1/2\,O_2(g) \rightarrow CO(g) \qquad \Delta H = -110\,kJ \tag{60}$$

$$CO(g) + 1/2\,O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -283\,kJ \tag{61}$$

Adding the two chemical equations given:

$$C_{(s)} + CO_{(g)} + O_{2(g)} \rightarrow CO_{2(g)} + CO_{(g)} \tag{62}$$

Eliminating CO from both sides results in the desired equation:

$$C(s) + O_2(g) \rightarrow CO_2(g) \tag{63}$$

Therefore, adding these two ΔH values will give the ΔH desired:

$$\Delta H = \left(-110\,kJ\right) + \left(-283\,kJ\right) = -393\,kJ \tag{64}$$

It must be noticed that enthalpies of formation have not been used explicitly in this process [9]. The Hess's law is shown schematically in Fig 12 [3].
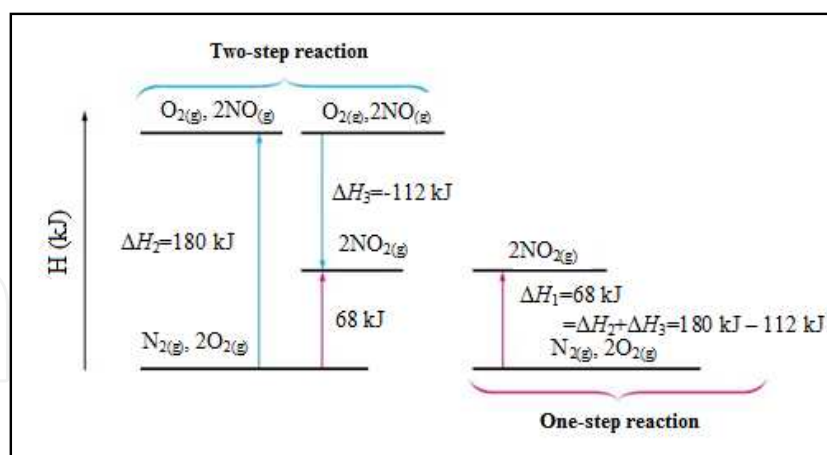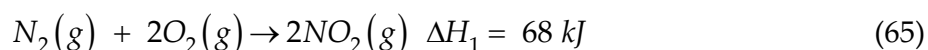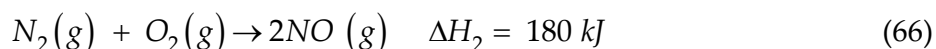

Figure 12. A schematic diagram of Hess's law. The same change in enthalpy occurs when nitrogen and oxygen react to form nitrogen dioxide, regardless of whether the reaction occurs in one (red) or two (blue) steps [3].
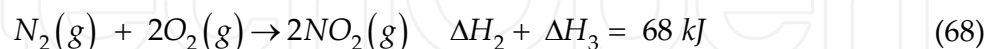
The overall reaction can be written in one step, where the enthalpy change is represented by ΔH_1 [3].

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \quad \Delta H_1 = 68\,kJ \tag{65}$$

This reaction also can be carried out in two distinct steps, with enthalpy changes designated by ΔH_2 and ΔH_3:

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \Delta H_2 = 180 \; kJ \tag{66}$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \quad \Delta H_3 = -112 \; kJ \tag{67}$$

Net reaction:

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \quad \Delta H_2 + \Delta H_3 = 68 \; kJ \tag{68}$$

The sum of the two steps gives the net, or overall, reaction and that

$$\Delta H_1 = \Delta H_2 + \Delta H_3 = 68 \; kJ \tag{69}$$

The temperature dependence of reaction enthalpies

The standard enthalpies of many important reactions have been measured at different temperatures. However, in the absence of this information, standard reaction enthalpies at different temperatures may be calculated from heat capacities and the reaction enthalpy at some other temperature (Fig. 13). In many cases heat capacity data are more accurate than reaction enthalpies. It follows from eqn $(dH = C_p dT$ at constant pressure) that, when a substance is heated from T_1 to T_2, its enthalpy changes from

$H(T_1)$ to

$$H(T_2) = H(T_1) + \int_{T1}^{T2} CpdT \tag{70}$$

(It has been assumed that no phase transition takes place in the temperature range of interest.) Because this equation applies to each substance in the reaction, the Standard reaction enthalpy changes from $\Delta H^0_r(T_1)$ to

$$\Delta H_r^0(T_2) = \Delta H_r^0(T_1) + \int_{T1}^{T2} \Delta CpdT \tag{71}$$

where ΔCp is the difference of the molar heat capacities of products and reactants under standard conditions weighted by the stoichiometric coefficients that appear in the chemical equation [12];

$$\Delta C_p = \sum \nu C_{p(Products)} - \sum \nu C_{p(Reactants)} \tag{72}$$

Equation 71 is known as **Kirchhoff's law**. It is normally a good approximation to assume that ΔCp_r is independent of the temperature, at least over reasonably limited ranges. Although the individual heat capacities may vary, their difference varies less significantly. In some cases the temperature dependence of heat capacities is taken into account by using equation below.

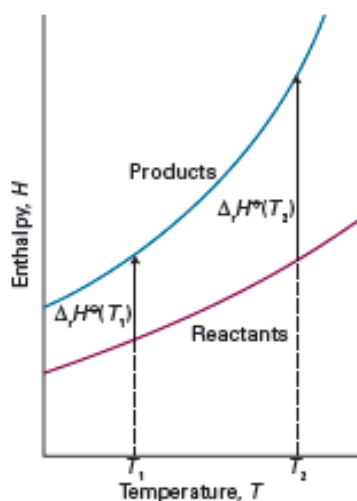$$C_p = a + bT + c/T^2$$

(73)

Figure 13. An illustration of the content of Kirchhoff's law. When the temperature is increased, the enthalpy of both the products and the reactants increases. In each case, the change in enthalpy depends on the heat capacities of the substances. The change in reaction enthalpy reflects the difference in the changes of the enthalpies [12].

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