

# Thermodynamics I

## Chapter 2

### Lecture no.1

The First Law of Thermodynamics

Conservation of Energy

Non – Flow Equation

Flow Energy Equation

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# Introduction

To understand and perform any sort of thermodynamic calculation, we must first understand the fundamental laws and concepts of thermodynamics. For example, work and heat are interrelated concepts. Heat is the transfer of thermal energy between two bodies that are at different temperatures, and is not equal to thermal energy. Work is the force used to transfer energy between a system and its surroundings. Both work and heat together allows systems to exchange energy. The relationship between the two concepts can be analysed through the topic of Thermodynamics, which is the scientific study of the interaction of heat and other types of energy.

To understand the relationship between work and heat, we need to understand a third, linking factor: the change in internal energy. The principle of conservation of energy state that **“Energy cannot be created nor destroyed, but it can be converted or transferred”**. With the interactions of heat, work and internal energy, there are energy transfers and conversions every time a change is made upon a system. However, no net energy is created or lost during these transfers. The relation being given by the famous equation,

$$E = m C^2$$

Where : Energy is a scalar quantity, not a vector quantity,  $m$  : mass ,  $C$ : velocity of light



# Types of Energy

Now that the conservation of energy has been defined, one can now study the different energies of a system. Within a system, there are three main types of energy. These three types are kinetic (the energy of motion), potential (energy stored within a system as a result of placement or configuration), and internal (energy associated with electronic and intramolecular forces). Thus, the following equation can be given

$$E_{\text{total}} = KE + PE + U$$

Where KE is the kinetic energy, PE is the potential energy, U is the internal energy, and  $E_{\text{total}}$  is the total energy of the system. While all forms of energy are very important, the internal energy, U, is what will receive the remainder of the focus.

The law of Conservation of Energy refers to an isolated system in which there is no net change in internal energy and where energy is neither created nor destroyed. Although there is no change in internal energy, energy can change forms, for example from potential to kinetic energy. In other words, potential energy ( PE ) and kinetic energy ( KE ) sum to a constant total energy ( $E_{\text{total}}$ ) for a specific isolated system.

$$E_{\text{total}} = KE + PE$$



# First Law of Thermodynamics

The First Law of Thermodynamics states that heat is a form of energy, and thermodynamic processes are therefore subject to the principle of conservation of energy. This means that heat energy cannot be created or destroyed. It can, however, be transferred from one location to another and converted to and from other forms of energy. To obtain the general form of the first law of the thermodynamics the following equation can be given :

$$\Delta U = Q + W$$

If the change of  $\Delta U$  is infinitesimal, then Equation can be altered to

$$du = dq + dw$$

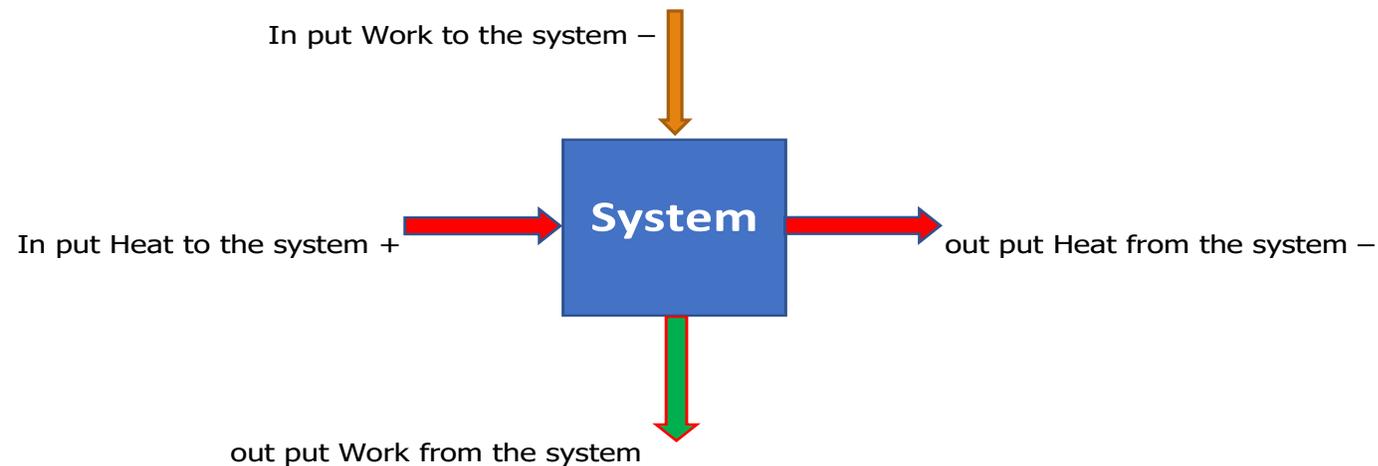
Within this equation it should be noted that U is a state function and therefore independent of pathways while q and w are not.



Having defined heat and work, it becomes necessary to define whether a process is exhibiting positive or negative values of  $Q$  and  $W$ . Table describes the sign conventions of both work and heat.

### Sign Conventions for Work and Heat

Process	Sign
Work done by the system on the surroundings ( out put Work from the system )	+
Work done on the system by the surroundings ( In put Work to the system )	-
Heat absorbed by the system from the surroundings ( In put Heat to the system )	+
Heat absorbed by the surroundings from the system (out put Heat from the system)	-



# Non – Flow Equation ( Closed System )

## A. Applied to a thermodynamic cycle

It states that when a system undergoes a cycle, then the net heat supplied to the system from its surroundings is equal to net work done by the system on its surroundings or net work done on the system is equal to the net heat rejected by the system. i.e.

$$Q_{1-2} = W_{1-2} + (U_2 - U_1)$$

For a cycle, initial state is same as final state and as internal energy is a point function depending on state only, so net change in internal energy in a complete cycle is zero. By putting  $\Delta U = 0$  in equation, it is reduced to equation which is applicable to a cycle.

or Cyclic Integral of Heat Exchange = Cyclic Integral of Work Exchange, or  $\oint \delta Q = \oint \delta W$

$$\Sigma dQ = \Sigma dW$$

Where  $\Sigma$  represents the sum for a complete cycle.

**That means :**

A device or machine is impossible, which can produce work continuously without absorbing energy from its surroundings.



## B. Applied to a thermodynamic process

If the first law is applied to a thermodynamic process in which initial and final state of the system are different, then it can be stated that the net heat exchange between system and surroundings is equal to the sum of net work exchange between system and surrounding and change in its internal energy (U).

$$Q_{1-2} = W_{1-2} + (U_2 - U_1)$$

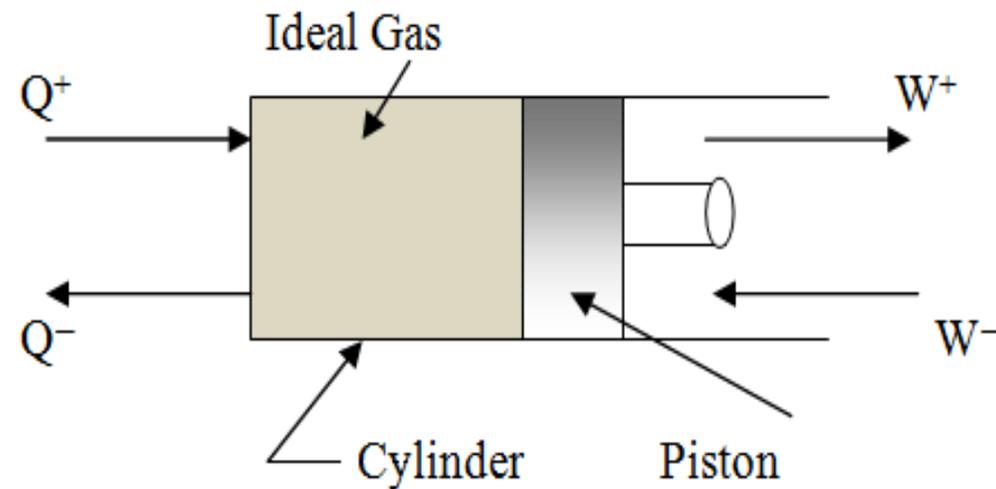
Or

$$Q = W + \Delta U$$

Heat Exchanged in a process = Work Exchange + Change in Internal Energy



As shown in below figure, the quantity  $Q$  is taken as positive if the systems absorbs or takes heat from its surroundings and negative if the system rejects heat to the surroundings. Unlike to that, the quantity  $W$  is taken as positive if the system is doing work on its surroundings and negative if the work is being done on the system by some external agency. The quantity  $\Delta U$ , change in internal energy of the system is taken as positive or negative depending on its increase or decrease.



## Internal Energy, U

Internal energy refers to the all the energy within a given system, including the kinetic energy of molecules and the energy stored in all of the chemical bonds between molecules. the internal energy is a property of the system and depends on temperature only. From the first law of thermodynamics as discussed previously :  $Q = W + dU$

If there is a case when heat is supplied to a fix volume of gas (thermodynamic system) confined in fix boundary of the system i.e. there is no change in volume of gas during supplying of heat, then there will not be any work. So

$$W = 0 \quad \text{and} \quad dU = Q$$

As Q is heat supplied to gas keeping it at constant volume, it can be calculated as  $m C_v$  . Thus change in internal energy is heat exchanged at constant volume and can be calculated as

$$dU = Q = m C_v dt$$

Where  $m$  = mass of the system



Change in internal energy per unit mass

$$\text{Specific Intrnal Energy} = \frac{dU}{m} = du = C_v dt$$

Thus internal energy is a property derived from first law of thermodynamics. It accounts for the difference between heat exchange and work exchange and shows that energy cannot be created nor be destroyed. Change in specific internal energy of a system is always calculated as  $C_v dt$  i.e. as a function of temperature change.

If we consider a fixed mass  $m$  of a gas confined in closed boundaries and remaining at constant pressure  $P$ , while absorbing heat  $Q$ . The temperature of gas will increase and simultaneously it will expand from initial volume  $V_1$  to final volume  $V_2$ . So, by first law of thermodynamics.

$$Q = W + \Delta U$$

Or

$$Q = m C_p (T_2 - T_1) = (U_2 - U_1) + P (V_2 - V_1)$$



Also enthalpy change during this constant pressure process 1- 2

$$H_2 - H_1 = mC_p(T_2 - T_1)$$

$$\text{or } \Delta H = mC_p \Delta T$$

$$\text{or } \Delta h = C_p \Delta T$$

$\therefore P_1 = P_2$  in constant pressure process

$$(H_1 - H_2) = (U_2 - U_1) + P(V_2 - V_1)$$

Thus change in enthalpy is also dependent on temperature only and is always calculated as

