The First Law of Thermodynamics

The first law of thermodynamics is actually a statement about the conservation of energy for thermodynamical systems and recognition of heat as a form of energy. It tells us that heat and other form of energies are equivalent. For a closed system (constant mass) the first law of thermodynamic is expressed by

$$\Delta E = Q - W \qquad\qquad (01)$$

where ΔE is the total energy change of the system, Q is heat added to the system and W is work done by the system. In words, *it says that the total energy change of a closed system is equal to the heat transferred to the system minus the work done by the system*.

The total energy change ΔE can be divided into several terms, each representing the change in energy of a particular form;

Total energy = Change in kinetic energy + Change in potential energy + Change in internal energy

$$\Delta E = \Delta E_k + \Delta E_p + \Delta U$$

where $\Delta E_k = \frac{1}{2} mv^2$ is the change in kinetic energy, $\Delta E_p = mgh$ is the change in gravitational potential energy and ΔU is the change in internal energy. If ΔE is expanded, we get the equation

$$\Delta E_k + \Delta E_p + \Delta U = Q - W$$

In the static cases, the sum of kinetic and potential energy of the system does not changes, thus the equation becomes

$$\Delta U = Q - W \qquad\qquad (02)$$

or in the differential form

$$dU = \delta Q - \delta W \qquad\qquad (03)$$

This equation states that, *the change in internal energy of a closed system is equal to the heat transferred to the system minus the work done by the system*.

Or, $\qquad\qquad \delta Q = dU - \delta W \qquad\qquad (04)$

This is **the first law of thermodynamics**, which states that *the amount of heat given to a system is equal to the sum of the increase in the internal energy of the system and the external work done*. It will be noted that a complete statement of the first law comprises two results: (1) Heat is a form of energy, (2) Energy is conserved in thermodynamic systems.

Applications of the First Law

1. Specific Heat of a Body

We have seen that the internal energy as defined above is a single-valued function of the variables of state. Now in the case of a simple homogeneous body any two of the variables p, V, T are sufficient to define its state uniquely. Choosing therefore V and T as the independent variables we have

$$U = U(V, T) \qquad\qquad (05)$$

where U and V refer to a gram-molecule of the substance. Differentiating we get

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{06}$$

If an amount of heat δQ be added to a thermodynamical system, which expand by a volume dV against the pressure p then $\delta W = pdV$, we have by the first law

$$\delta Q = dU + pdV \tag{07}$$

Substituting for dU from eq. (06) in (07) we get

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

Differentiating with respect to temperature at constant pressure

$$\left(\frac{\delta Q}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{08}$$

Now $\delta Q/dT = C$, the gram-molecular specific heat. This will have different values according to varying external conditions. If pressure be kept constant

$$C_p = \left(\frac{\delta Q}{dT}\right)_p \tag{09}$$

where C_p is the specific heat at constant pressure. Again if the heat δQ be supplied at constant volume

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{10}$$

where C_V is the specific heat at constant volume. Using this result in eq. (08) we have

$$C_p - C_V = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{11}$$

A perfect gas is defined by the following assumptions;

1. There are no inter-molecular attractions so that its internal energy is totally kinetic. As a result, it remains unchanged in any expansion at constant temperature. Hence $(\partial U / \partial V)_T = 0$.

2. Its molecules are point masses and its equation of state is perfect gas law; i.e., $pV = RT$. Hence $p(\partial V / \partial T)_p = R$.

   Therefore, for perfect gas

$$C_p - C_V = R \tag{12}$$

which is known as *Mayer's formula*.

For a real gas, the internal energy changes with volume because work has to be done against the intermolecular forces. We therefore use the Vander Walls equation as the equation of state;

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \tag{13}$$

As we know, for a real gas

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2} \tag{14}$$

Thus, on substituting eq. (14) and (13) into (11)

$$C_p - C_V = \left[p + \frac{a}{V^2} \right] \left(\frac{\partial V}{\partial T} \right)_p = \frac{RT}{(V-b)} \left(\frac{\partial V}{\partial T} \right)_p \qquad (15)$$

Differentiate Vander Walls equation with respect to temperature at constant pressure

$$\left[p + \frac{a}{V^2} - (V-b)\frac{2a}{V^3} \right] \left(\frac{\partial V}{\partial T} \right)_p = R$$

$$\left[\frac{RT}{(V-b)} - (V-b)\frac{2a}{V^3} \right] \left(\frac{\partial V}{\partial T} \right)_p = R$$

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{R(V-b)}{RT - \left(\frac{2a}{V^3} \right)(V-b)^2}$$

$$\frac{1}{(V-b)} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{T\left[1 - \left(\frac{2a}{RTV^3} \right)(V-b)^2 \right]}$$

Using binomial expansion we can write for very small a,

$$\frac{1}{(V-b)} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{T}\left[1 + \left(\frac{2a}{RTV^3} \right)(V-b)^2 \right] \qquad (16)$$

Substituting eq. (16) into eq. (15), we have

$$C_p - C_v = R\left[1 + \left(\frac{2a}{RTV^3} \right)(V-b)^2 \right] \qquad (17)$$

2. Adiabatic Expansion of Ideal Gas

It is clear above that, in general, the internal energy of a closed system may be considered a function of T and V; i.e., $U = U(T,V)$ and we can write

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

in view of specific heat,

$$dU = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

An ideal gas requires that at all temperatures and pressure; $pV = RT$. Hence $p(\partial V / \partial T)_p = R$. For an ideal gas

$$dU = C_V dT \qquad (18)$$

i.e., for an ideal gas both U and C_V are function of temperature only, independent of V and p of the system.

In an adiabatic change, there is no thermal contact between the system and its surroundings so that no heat exchange takes place, i.e., $\delta Q = 0$. For an adiabatic changes the first law of thermodynamics has the form

$$dU + \delta W = 0$$

This shows that if a gas is permitted to expand adiabatically, it does work at the cost of its internal energy. For an ideal gas this equation will become

$$C_V dT + p dV = 0$$

$$C_V dT + \frac{RT}{V} dV = 0$$

Dividing throughout by $C_V T$, we get

$$\frac{dT}{T} + \frac{R}{C_V}\frac{dV}{V} = 0$$

integrating

$$\ln T + \frac{R}{C_V}\ln V = K$$

where K is an integrating constant. Changing from logarithms to numbers, we have

$$TV^{R/C_V} = constant$$

$$TV^{\gamma-1} = constant \qquad\qquad (19a)$$

where $\gamma = C_p/C_V$ and $C_p - C_V = R$ for an ideal gas.

On substitution, $pV = RT$ this result can also be put in the following manner

$$pV^{\gamma} = constant \qquad\qquad (19b)$$

and

$$T^{\gamma} p^{\gamma-1} = constant \qquad\qquad (19c)$$

It is important to note here that on the *p-V* diagram, the adiabatic lines given by eq. (19b) form a family like the isotherms (which follow *pV = constant*). But, adiabatics are steeper than isotherms since γ >1.

Reversible and Irreversible Changes

All processes the effect of which can be completely nullified everywhere are called reversible. Thus, for the process to be ***reversible***, it must be performed in such a way that, at the end of the process, both the system and the surroundings may be fully restored to their initial states without producing any net change anywhere in the universe. If the whole system (including the surroundings) cannot be completely restored to its initial condition everywhere even with the use of all possible physical means, the process is said to be ***irreversible***.

A reference to *the second law of thermodynamics* is often necessary to determine whether a process is reversible or irreversible. In fact it will be seen that it is necessary consequence of the second law that *all natural processes are irreversible*.

(a) Conditions: It has been seen from various considerations that for process to be reversible two conditions are necessary, namely (1) process should be ***quasi-static***, i.e., it should be carried out extremely slowly so that every state through which the system passes departs only infinitesimally from equilibrium and (2) ***non-dissipative***, i.e., there should not be any loss of energy due to in-elasticity, viscosity, friction, electrical resistance, magnetic hysterisis, etc.

It will be observed that it is impossibile to satisfy perfectly the above conditions of reversibility. In fact a reversible process is purely an ideal abstraction, useful for theoretical calculations but we do not come across such process in nature.

(b) Example: The transfer of heat from one body to another by conduction or radiation can be reversibile only when the two bodies are at the same temperature or differ by an infinitesimal amount. If the two bodies have a finite difference of temperature the process of heat transfer is irreversible, since in order to nullify the process we should be able to transfer the heat from the colder to the hotter body without producing changes anywhere in the universe which is impossibile from the second law.