FIRST LAW OF THERMODYNAMICS

Thermodynamics is the study of the relationship between heat and other forms of energy. When the principle of conservation of energy is stated in relation to heat and work it is known as the first law of thermodynamics.

The heat energy supplied to a system ***(***Δ***Q)*** is equal to the increase in internal energy ***(***Δ***U)*** of the system plus the work done ***(***Δ***W)*** by the system on its surroundings.

$$\Delta Q = \Delta U + \Delta W$$

The internal energy of a system depends only on the initial and the final states of the system and not how the change was brought about.

An isolated system is one which is cut off from external influences ($\therefore\ \Delta W = 0$). Hence no heat can enter or leave it ($ie. \Delta Q = 0$). Therefore $\Delta U = 0$ and the internal energy is constant.

A system that undergoes adiabatic process ($\Delta Q = 0$) is reduced to $\Delta U = -\Delta W$. Thus this system undergoes an increase in internal energy which is equal to the work done on it.

N.B. the internal energy of an ideal gas is due entirely to the kinetic energy of the molecules. Hence the internal energy of one mole of an ideal monatomic gas in Kelvin temperature is given by

$$U = \frac{3}{2}RT$$

Hence and increase in internal energy ($\Delta \boldsymbol{U}$) due to an increase in temperature ***(***Δ***T)*** is given by

$$\Delta U = \frac{3}{2}R\Delta T$$

Molar Heat Capacities of Gases

Molar heat capacity of a substance is the heat required to produce a unit temperature rise in a mole of the substance.

Recall that a change in temperature involves a change in pressure and / or volume. Large changes occur with gases and in order to define heat capacity of a gas, we must first specify when the pressure constant.

Molar Heat Capacity of a Gas at a Constant Pressure (C_p)

This the heat energy required to produce a unit temperature rise in 1 mole of a gas when the pressure is constant.

$$E_H = n\,C_p\Delta\theta$$

Molar Heat Capacity of a Gas at a Constant Volume (C_v)

This the heat energy required to produce a unit temperature rise in 1 mole of a gas when the volume is constant.

$$E_H = n\,C_v\Delta\theta$$

(N.B. that when a gas is heated at a constant pressure it expands, hence some of the heat is used to increase the potential energy of molecules and to do external work.)

However, when a gas is heated at a constant volume ALL of the heat supplied is used to increase the temperature.

Hence the amount of the heat required to raise the temperature of a gas at a constant pressure is greater than the required to raise the temperature of the same amount at a constant volume. (i.e. $\boldsymbol{C_p > C_v}$)

Thus

$$C_p = R + C_v$$

$$\therefore\ C_p - C_v = R$$

To show that $\boldsymbol{C_p - C_v = R}$ (for an Ideal Gas)

Suppose 1 mole of an ideal gas is heated so that it increase in 1 unit temperature (ΔT) at a constant volume, the heat supplied (ΔQ) is given by

$$\Delta Q = C_v\Delta T$$

Since there is no change in volume, the external work done is zero (i.e. $\Delta W = 0$). From the first law of thermodynamics

$$\Delta Q = \Delta U + \Delta W$$

$$\therefore\ C_v\Delta T = \Delta U \qquad \ldots 1$$

where ΔU is the increase in the internal energy.

Suppose 1 mole of the same gas is heated so that its temperature increases at the same amount (ΔT) at a constant pressure, we can say that

$$\Delta Q = C_p \Delta T \quad \dots ②$$

The external work done is

$$\Delta W = p\Delta V \quad \dots ③$$

where p is the constant pressure

ΔV is the change in volume

Since $\Delta Q = \Delta U + \Delta W$, we can use ①, ② & ③ and say that

$$C_p \Delta T = C_v \Delta T + p\Delta V \quad \dots ④$$

The equation concerned with initial volume (V) and temperature (T) of 1 mole of an ideal gas is

$$PV = RT \quad \dots ⑤$$

Then an increase in temperature and volume can be shown as

$$P(V + \Delta V) = R(T + \Delta T) \quad \dots ⑥$$

Subtracting ⑤ from ⑥ we get that

$$P\Delta V = R\Delta T \quad \dots ⑦$$

If we substitute ⑦ into ④ we will have that

$$C_p \Delta T = C_v \Delta T + R\Delta T$$

And since we are dealing with a temperature increase of only one unit ($\Delta T = 1$), we can say that

$$C_p = C_v + R$$

$$\therefore\ C_p - C_v = R \quad (as\ required)$$

Work done by a Gas

Consider a gas in a container, as shown in the diagram below, occupying a volume, V. If the volume is increased, ΔV, then work done by the gas on the surroundings.

Since $work\ done = force \times distance\ (W = Fx)$ and $force = pressure \times area\ (F = PA)$ we can say that

$$W = PAx$$

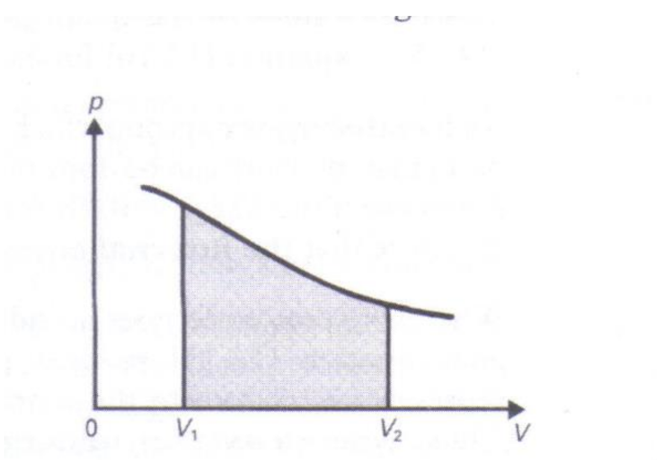
But $volume = area \times distance\ (V = Ax)$. Hence

$$W = p\Delta V \qquad (as\ reqired)$$

(i.e. the work done by a gas equals to the pressure exerted by the gas multiplied by the volume change)

Work done from a P – V Graph

A graph of pressure vs. volume (*P* vs. *V*) for a gas gives the work done when the area under the curve is calculated.



The work done by the gas is represented by the shaded area under the curve, as the gas increases from V_1 to V_2.

Examples

1. A vessel of volume 10 litres contains 1.3×10^{-2} g of a gas at 10 atmospheric pressure at 20^oC. Thermal energy of value 8.0×10^3 J is released in the gas and raises the pressure to 14 atmospheres. Assuming no loss of heat to the vessel and ideal gas behaviour, calculate the specific heat capacity of the gas and the molar heat capacity at a constant volume.
   [$R = 8.31\ J\ mol^{-1} K^{-1}$ $\quad$ $1\ atm = 1.0 \times 10^5\ Pa$]

2. A sample of gas is enclosed in cylinder with a frictionless piston of area 100 cm^2. The cylinder is heated so that 250J of heat is transferred to the gas which pushes the piston back 15 cm. Calculate the work done by the gas if atmospheric pressure was 1.0×10^5 Pa and determine the change in the internal energy of the gas.

3. The work done by the gas is represented by the shaded area under the curve, as the gas increases from V_1 to V_2.
   A fixed mass of gas at volume $1.0 \times 10^{-3}\ m^3$ and a pressure of 1.0×10^5 Pa is heated so that its pressure increased to 6.0×10^5 Pa while its volume remain constant. It is then allowed to expand to a volume of $5.0 \times 10^{-3}\ m^3$ under a constant pressure of 6.0×10^5 Pa. From here, it is allowed to cool to reach a pressure of 1.0×10^5 Pa at a volume of $5.0 \times 10^{-3}\ m^3$. Finally the gas is compressed at a constant pressure till it reaches its original volume of $1.0 \times 10^{-3}\ m^3$. Draw a P –V graph for the cycle through which the gas goes and calculate:
   a) the work done on the gas
   b) the work done by the gas
   c) the net work done by the gas