

Applications of First Law

Specific Heat : Thermal capacity is defined as the heat required to raise the temperature of a substance by unity. If the mass of the substance is unity, the required heat is called the **specific heat**. If the amount of the substance taken is one mole, it is called the **molar sp. Heat**.

If a rise in by temp. by an amount 'dT' requires 'dQ' amount of heat, then, for a unit rise in temp., heat required will be dQ/dT.

If we consider a gaseous substance, the state of which depends on more than one variable, there will be different paths along which the heating process may take place and consequently, dQ will be different, even if the initial and the final temperatures are given. For example, if the gas expands on heating, it will perform external work (and hence require extra energy), but if the volume remains constant, there no work performed. Hence a gaseous substance will have many sp. Heats. Two of them are of most importance : sp. Heat at const. volume (C_v) and that at constant pressure (C_p).

Let us take one mole of an ideal gas and heat it, while its volume remains constant. The heat absorbed will be : $dQ = dU$, since $dV = 0 \Rightarrow PdV = 0$.

$$\Rightarrow C_v = (\partial Q/\partial T)_v = (\partial U/\partial T)_v \text{ ---- (i)}$$

If we heat it instead, keeping it under a constant pressure, $dQ = dU + P dV$

$$\Rightarrow C_p = (\partial Q/\partial T)_p = (\partial U/\partial T)_p + P (\partial V/\partial T)_p \text{ ---- (ii)}$$

Clearly, there is an extra term, appearing due to the work done in the process.

The internal energy of an ideal gas depends only on the temperature and not on its pressure or volume. [The reason is that, there is no inter-molecular force, hence no potential energy of the molecules. So internal energy is solely due to the kinetic energy of the molecules, which depends on temp. only]

Thus, $(\partial U/\partial T)_v$ and $(\partial U/\partial T)_p$ are the same.*

Now, for an ideal gas, $PV = RT$. Differentiating under const. pressure, $P (\partial V/\partial T)_p = R$

$$\Rightarrow C_p - C_v = R \text{ ---- (iii)}$$

* More precisely, If we choose V and T as independent variables, $U = U(V, T)$

$$\Rightarrow dU = (\partial U/\partial T)_v dT + (\partial U/\partial V)_T dV$$

$$\Rightarrow (\partial U/\partial T)_p = (\partial U/\partial T)_v + (\partial U/\partial V)_T (\partial V/\partial T)_p$$

Now, Joule's experiment (**not** the law $W = JH$), the internal energy of an ideal gas doesn't depends on its volume. $\Rightarrow (\partial U/\partial V)_T = 0$ ---- (iv)

$$\Rightarrow (\partial U/\partial T)_p = (\partial U/\partial T)_v$$

Adiabatic Process : Adiabatic process is one, in which no heat transfer takes place, i.e., $dQ = 0$. Now, $dU = (\partial U/\partial T)_v dT + (\partial U/\partial V)_T dV$

For one mole of an ideal gas, $(\partial U/\partial T)_v = C_v$ [by (i)] and $(\partial U/\partial V)_T = 0$ [by Joule's law (iv)]

$$\Rightarrow dU = C_v dT \text{ ---- (v)}$$

$$\text{Thus, } dQ = 0 = C_v dT + PdV$$

Expressing P in terms of V and T as : $P = RT/V$,

$$0 = C_v dT + (RT/V) dV$$

$$\Rightarrow C_v dT/T + R dV/V = 0$$

By (iii) : $R = (C_p - C_v) \Rightarrow C_v dT/T + (C_p - C_v) dV/V = 0$

Dividing by C_v and introducing the notation : $(C_p / C_v) = \gamma$,

$$dT/T + (\gamma - 1) dV/V = 0$$

Integrating both sides, we get : $\ln T + (\gamma - 1) \ln V = \text{constant}$ (say C1)

$$\Rightarrow \ln (TV^{\gamma-1}) = C1$$

$$\Rightarrow TV^{\gamma-1} = e^{C1} = \text{another constant (say C2)}$$

Thus, the relation between the temperature and the volume of an ideal gas in an adiabatic process is : **$TV^{\gamma-1} = \text{constant}$** .

We can obtain the relation between P and V, or, P and T by simply replacing one variable by another, using the equation of state. For example,

$$PV = RT \Rightarrow V = RT/P$$

Substituting in the above relation : $T (RT/P)^{\gamma-1} = C2$

$$\Rightarrow T^{\gamma} R^{\gamma-1} P^{1-\gamma} = C2$$

$$\Rightarrow T^{\gamma} P^{1-\gamma} = C2/R^{\gamma-1} = \text{another constant (say C3)}$$

Thus, the relation between the temperature and the pressure is : **$T^{\gamma} P^{1-\gamma} = \text{constant}$** .

We can also obtain the relation between any pair of variables directly.

If, for example, we want the relation between P and V, start from :

$$dQ = 0 \Rightarrow C_v dT + PdV = 0$$

Now, you have to eliminate the variable T. So write : $PV = RT$

$$\Rightarrow P dV + V dP = R dT$$

Substituting for dT, we have : $C_v (P dV + V dP)/R + P dV = 0$

$$\Rightarrow P dV (C_v/R + 1) + V dP (C_v/R) = 0$$

$$\Rightarrow P dV (C_p/R) + V dP (C_v/R) = 0$$

Multiplying by (R/C_v) : $P dV (\gamma) + V dP = 0$

$$\Rightarrow \gamma dV/V + dP/P = 0$$

Integrating : $\ln V^{\gamma} + \ln P = \text{constant}$ (say C1)

$$\Rightarrow \ln (PV^{\gamma}) = C1$$

$$\Rightarrow PV^{\gamma} = e^{C1} = \text{another constant (say C2)}$$

Thus, the relation between the pressure and the volume is : **$PV^{\gamma} = \text{constant}$** .

Work done in an adiabatic process : We know that $W = \int P dV$

In order to perform the integration, we shall have to express 'P' as a function of 'V',

which can be done by using the P-V relation : $PV^{\gamma} = C \Rightarrow P = C/V^{\gamma}$

$$\text{Therefore, } W = \int P dV = C \int V^{-\gamma} dV = C[V^{-\gamma+1}/(-\gamma+1)]$$

between the limits V_1 and V_2 [the initial and the final volumes]

$$= (CV_2^{-\gamma+1} - CV_1^{-\gamma+1}) / (-\gamma + 1).$$

Now, we can write $C = P_2V_2^{\gamma}$ as well as $P_1V_1^{\gamma}$, since PV^{γ} is constant.

$$\Rightarrow W = (P_2V_2^{\gamma} V_2^{-\gamma+1} - P_1V_1^{\gamma} V_1^{-\gamma+1}) / (-\gamma + 1)$$

$$= (P_1V_1 - P_2V_2) / (\gamma - 1)$$

$$= (RT_1 - RT_2) / (\gamma - 1)$$

$$= (C_p - C_v) (T_1 - T_2) / (C_p/C_v - 1)$$

$$= C_v (T_1 - T_2)$$

$$= C_v (-\Delta T) = -\Delta U.$$

This result was expected, as $dQ = 0 \Rightarrow \text{work done} = -\Delta U$

Physically this means, that since no heat can enter the system from outside, the gas has to perform external work at the cost of its own internal energy. If $W > 0$, $T_2 < T_1$, showing that **the gas cools down on expansion**. This is known as the **adiabatic cooling**.