

## Applications of first law of thermodynamics:

# General relation between  $C_p$  and  $C_v$ :

Specific heat  $\equiv$  specific heat capacity.

It is defined as the amount of heat required to raise the temperature of a substance of unit mass by  $1^\circ\text{C}$  or  $1\text{K}$ .

Depending on the conditions of measurement, there are two types of specific heat for a hydrostatic system, namely  $C_p$  and  $C_v$ .

$C_p \rightarrow$  specific heat at constant pressure and

$C_v \rightarrow$  specific heat at constant volume.

Total heat capacity is an extensive quantity because

it depends on the mass of the system but specific heat is intensive physical quantity. (36)

~~Molar specific heat: -~~

Molar heat capacity: Let  $m$  be the mass of an atom. One mole of a substance contains  $N_A$  (Avogadro number) number of atoms.

$\therefore$  molar mass =  $m N_A$ , it is also called molecular weight. =  $M$

$\therefore$  molar heat capacity =  $M C_p$  at constant pressure and  $M C_v$  at constant volume

Definitions of  $C_p$  and  $C_v$ :

$$C_v = \left. \frac{dQ}{dT} \right|_v \text{ --- (1) and } C_p = \left. \frac{dQ}{dT} \right|_p \text{ --- (2)}$$

Relation between  $C_v$  and  $C_p$ :

From first law of thermodynamics,

$$dQ = dU + dW \text{ --- (3)}$$

For a hydrostatic system,  $dW = p dV$ .

$$\therefore dQ = dU + p dV \text{ --- (4)}$$

$U$  is internal energy function. It is a function of any two of the thermodynamic variable  $p$ ,  $V$  and  $T$ . Considering  $U$  as a function of  $V$  and  $T$ , we have

$$U = U(V, T)$$

$$\therefore dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \quad \text{--- (5)}$$

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

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

$$\text{or, } \frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] \frac{dV}{dT} \quad \text{--- (6)}$$

This equation is true for any process involving any temperature change  $dT$  and any volume change  $dV$ .

case I: If volume is constant, then  $dV=0$  and

$$\left.\frac{dQ}{dT}\right|_V = \left(\frac{\partial U}{\partial T}\right)_V$$

The term in the left hand side is the specific heat at constant volume ( $c_v$ ).

$$\therefore \boxed{c_v = \left(\frac{\partial U}{\partial T}\right)_V} \quad \text{--- (7)}$$

case II: If pressure  $p$  is constant, then

$$\left.\frac{dQ}{dT}\right|_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_p$$

$$\text{or, } \boxed{c_p = c_v + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_p} \quad \text{--- (7)}$$

Equation (7) is the most general relationship between the two specific heat  $c_p$  and  $c_v$ . (38)

Now, the volume expansion coefficient or volume expansivity  $\beta$  is defined as change in volume per unit volume per unit change of temperature at constant pressure, i.e.

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P.$$

$$\text{or } \left( \frac{\partial V}{\partial T} \right)_P = \beta V.$$

Putting the value of  $\left( \frac{\partial V}{\partial T} \right)_P$  in equation (7), we get

$$c_p = c_v + \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right] \beta V \quad \text{--- (8)}$$

$$\text{or } c_p - c_v = \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right] \beta V \quad \text{--- (9)}$$

For ideal gas, internal energy is a function of temperature only. So,

$$U = U(T) \text{ only.}$$

$$\therefore \left( \frac{\partial U}{\partial V} \right)_T = 0.$$

$$\therefore \text{for an ideal gas, } c_p - c_v = [p + 0] \left( \frac{\partial V}{\partial T} \right)_P \quad \text{[from eqn (8)]}$$

The equation of state of an ideal gas is  $PV = RT$  (for one mole of ideal gas)

or  $V = \frac{RT}{P}$

or  $(\frac{\partial V}{\partial T})_P = \frac{R}{P}$

$\therefore C_p - C_v = p \cdot \frac{R}{P}$   
 $= R$

$\therefore$  for an ideal gas,

$C_p - C_v = R$

(10)

For n mole ideal gas  
 $pV = nRT$   
and  
 $C_p - C_v = nR$

$C_p$  is greater than  $C_v$ : why?

$C_v$   $\rightarrow$  heat required to raise the temperature by one degree while keeping the volume constant. This means that the system does not do any external work during this process. The heat is used to raise the temperature only.

$C_p$   $\rightarrow$  heat required to raise the temperature by one degree while keeping the pressure of the system constant. In this case the volume may change i.e.,  $dV \neq 0$  which means that the system does some external work with the supplied heat apart from raising the temperature by one degree. This indicates that some more heat is needed while ~~measuring~~ measuring specific heat at constant pressure compared to the heat while measuring specific heat at constant volume. Therefore,  $C_p$  is greater than  $C_v$ .

The ratio of two specific heat i.e.  $C_p/C_v$  is denoted by ' $\gamma$ '. It is always greater than 1.