

## Heat Capacity

The heat capacity of a system is the quantity capacity to absorb heat and store it. When system absorbs heat, the kinetic energy of the atoms or molecules increases and increased kinetic energy rises the temperature of the system. Thus, the heat capacity of the system is the heat absorbed by the system in raising the temperature by  $1^{\circ}\text{C}$ . If one gram substance is taken, it is called specific heat capacity. If one mole of substance is taken then it is called molar heat capacity.

The amount of heat required to raise the temperature of one gram substance by  $1^{\circ}\text{C}$  is called specific heat capacity. The amount of heat required to raise the temperature of one mole substance by one degree C is called molar heat capacity. The molar heat capacity is denoted by  $C$ . Mathematically, it is expressed as

$$C = \frac{dq}{dT}$$

where  $dq$  is the small amount of heat absorbed by one mole of substance to raise the small temperature,  $dT$ .

Heat capacity is not a state function. Its value depends upon the path by which change takes place. When molar heat capacity is measured at constant pressure then it is called molar heat capacity at constant pressure. It is denoted by  $C_p$ . When molar heat capacity is measured at constant volume then it is called molar heat capacity at constant volume. It is denoted by  $C_v$ .

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## ① Molar heat capacity at constant volume ( $C_v$ )

The amount of heat absorbed by one mole of substance to raise the temperature by  $1^\circ\text{C}$  at constant volume is <sup>called</sup> molar heat capacity at constant volume. It is denoted by  $C_v$ .

Mathematically

$$C_v = \left( \frac{dq}{dT} \right)_v$$

$$\text{or } dq = C_v dT \quad \text{--- (1)}$$

From first law of thermodynamics

$$dq = dE + p dv$$

At constant volume,  $dv = 0$ . and

$$dq = dE. \quad \text{--- (2)}$$

From equation (1) and (2)

$$C_v dT = dE$$

$$\text{or } C_v = \left( \frac{\partial E}{\partial T} \right)_v \quad \text{--- (3)}$$

The molar heat capacity at constant volume is the rate of change of internal energy with ~~respect~~ temperature at constant volume.

## ② Molar heat capacity at constant pressure.

The amount of heat absorbed by one mole of substance to raise the temperature by  $1^\circ\text{C}$  at constant pressure is called molar heat capacity at constant pressure.



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It is denoted by  $C_p$ . By the definition,

$$C_p = \left( \frac{dq}{dT} \right)_p$$

$$\text{or } dq = C_p dT \quad \text{--- (4)}$$

From the first law of thermodynamics

$$dq = dE + PdV \quad \text{--- (5)}$$

From equation (4) and (5)

$$C_p dT = dE + PdV$$

Dividing both sides by  $dT$  on both sides.

$$C_p = \left( \frac{\partial E}{\partial T} \right)_p + P \left( \frac{\partial V}{\partial T} \right)_p \quad \text{--- (6)}$$

By the definition of enthalpy

$$H = E + PV$$

Now differentiating the equation with respect to temp. at constant pressure we get,

$$\left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial E}{\partial T} \right)_p + P \left( \frac{\partial V}{\partial T} \right)_p \quad \text{--- (7)}$$

Comparing equation (6) and (7)

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad \text{--- (8)}$$

Heat capacity at constant pressure is the rate of heat content with temperature at constant pressure.

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## Relation between $C_p$ and $C_v$

Two heat capacities are not equal.  $C_p$  is always greater than  $C_v$ . At constant pressure, a part of heat absorbed is utilized in performing external work and another part is used in increasing the internal energy of the system. While at constant volume all the heat is utilized in increasing the internal energy of the system only. It follows that the temperature rise at constant pressure will be less for a given quantity of heat transferred. More heat would be required at constant pressure to cause the same temperature rise, so,  $C_p$  is greater than  $C_v$ .

The difference between two heat capacities can be deduced from thermodynamic considerations. We have

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad \text{and} \quad C_v = \left( \frac{\partial E}{\partial T} \right)_v$$

$$C_p - C_v = \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial E}{\partial T} \right)_v \quad \text{--- (1)}$$

But  $\left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial E}{\partial T} \right)_p + P \left( \frac{\partial V}{\partial T} \right)_p$ . Substituting this value

in equation (1) we get,

$$C_p - C_v = \left( \frac{\partial E}{\partial T} \right)_p + P \left( \frac{\partial V}{\partial T} \right)_p - \left( \frac{\partial E}{\partial T} \right)_v \quad \text{--- (2)}$$

The internal energy  $E$  is a function of two of the three variables - pressure, volume and temperature. If temperature and volume are taken as the independent variables, then

$$E = f(T, V)$$

Since  $E$  is a state function, the differential  $dE$  is given by.



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

on dividing both sides by  $dT$  at constant pressure, we get

$$\left( \frac{\partial E}{\partial T} \right)_P = \left( \frac{\partial E}{\partial T} \right)_V + \left( \frac{\partial E}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P$$

Substituting the value of  $\left( \frac{\partial E}{\partial T} \right)_P$  in equation (1) (2)

$$C_P - C_V = \left( \frac{\partial E}{\partial T} \right)_V + \left( \frac{\partial E}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P - \left( \frac{\partial E}{\partial T} \right)_V + P \left( \frac{\partial V}{\partial T} \right)_P$$

$$\therefore C_P - C_V = P \left( \frac{\partial V}{\partial T} \right)_P + \left( \frac{\partial E}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P$$

For an ideal gas, the variation of internal energy with ~~temperature~~ volume at constant temperature is zero.

i.e.  $\left( \frac{\partial E}{\partial V} \right)_T = 0$ . So, above equation can be reduced to

$$C_P - C_V = P \left( \frac{\partial V}{\partial T} \right)_P$$

For one mole of gas the ideal gas is,  $PV = RT$   
Differentiating with respect to temperature at constant pressure, we get,

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

or

$$\text{So, } \underline{C_P - C_V = R}$$