

## Thermodynamics-PEA

### Zeroth law of thermodynamics

When two bodies A and B are in thermal equilibrium with third body C then the body A and B also must be in thermal equilibrium with each other.

### First law of thermodynamics

When heat energy is given to a system then some part of heat energy supplied is used to change the internal energy of system and rest of energy is used to do external work.

$$\Delta Q = \Delta u + \Delta w$$

### Internal energy (U).

The sum of energy due to molecular motion (KE) and due to molecular configuration (PE) is called internal energy of gas.

$$\therefore \text{Internal energy (U)} = \text{PE} + \text{KE}$$

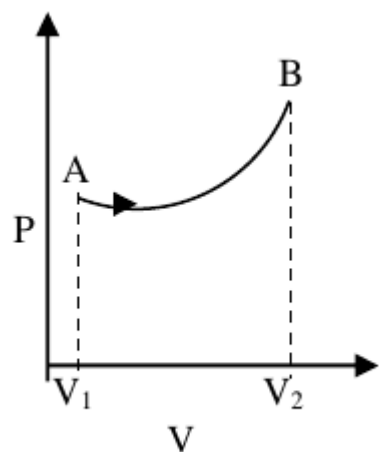
For ideal gas intermolecular force of attraction is neglected so PE = 0 so internal energy of ideal gas is KE which is only the function of temperature

### Work (W).

Work is said done only when volume of gas changes Work done by gas is taken positive (Expansion) and work done on gas is taken negative (compression).

At constant pressure,

$$\text{Work done (dw)} = Pdv$$



Area under PV curve between volume axis is equal to work done.

For closed cycle, area of closed loop gives the work done.

### Heat capacities of gas

Heat required to rise the temperature of certain amount of gas at constant pressure is always greater than heat required to rise same temperature at constant volume so gas has two types of heat capacities.

#### 1. Molar heat capacities

##### A. Molar heat capacity at constant pressure ( $C_p$ )

Heat required to rise the temperature of one mole of gas through  $1^\circ \text{C}$  at constant pressure. Its unit is  $\text{Jmol}^{-1}\text{K}^{-1}$ .

$$\therefore \text{Heat required (dQ)} = nC_p dT$$

##### B. Molar heat capacity at constant volume ( $C_v$ )

Heat required to rise the temperature of one mole of gas through  $1^\circ \text{C}$  at constant volume. Its unit is  $\text{Jmol}^{-1}\text{K}^{-1}$ .

$$\therefore \text{Heat required (dU)} = nC_v dT$$

##### C. Mayer's Formula

$$C_p - C_v = R$$

#### 2. Specific heat capacities

A. *Specific heat capacity at constant pressure ( $c_p$ )*

Heat required to rise the temperature of unit mass of gas through  $1^\circ \text{C}$  at constant pressure. It's unit is  $\text{Jkg}^{-1}\text{K}^{-1}$ .

$$\therefore \text{Heat required } (dQ) = nc_p dT$$

$$\implies C_p = M \cdot c_p$$

B. *Specific heat capacity at constant volume ( $c_v$ )*

Heat required to rise the temperature of unit mass of gas through  $1^\circ \text{C}$  at constant volume. It's unit is  $\text{Jkg}^{-1}\text{K}^{-1}$ .

$$\therefore \text{Heat required } (du) = nc_v dT$$

$$\implies C_v = M \cdot c_v$$

$$\text{Now, } c_p - c_v = R/M = r$$

Degree of freedom and value of  $\gamma$

The total number of independent coordinates required to specify the state of system is called degree of freedom

The degree of freedom =  $3N - R$

$N$  = No. of atoms (Particles) in molecule

$R$  = Relation

The KE of one mole of gas for 3 degree of freedom is  $3/2 RT$  so KE, of one mole of gas for one degree of freedom is  $1/2 RT$ . Similarly KE of each molecule of gas for each degree of freedom is  $1/2 KT$ .

1. *For monatomic gas*

Degree for freedom = 3

KE of 1 mole of gas (U) =  $3/2 RT$

$$\therefore C_v = \frac{du}{dT} = \frac{3}{2} R$$

$$C_p = C_v + R = \frac{5}{2} R$$

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.67$$

2. *For diatomic gas*

Degree of freedom =  $3 \times 2 - 1 = 5$

KE of 1 mole of gas (v) =  $\frac{5}{2} RT$

$$\therefore C_v = \frac{du}{dT} = \frac{5}{2} R$$

$$C_p = C_v + R = \frac{7}{2} R$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{7}{5} = 1.4$$

3. a. *For diatomic (non linear)*

Degree of freedom =  $3 \times 3 - 3 = 6$

KE of 1 mole of gas (U) =  $\frac{6}{2} RT = 3RT$

$$\therefore C_v = \frac{du}{dT} = 3R$$

$$C_p = C_v + R = 4R$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{4}{3} = 1.33$$

b. *For triatomic (linear)*

Degree of freedom =  $3 \times 3 - 2 = 7$

KE of 1 mole of gas (U) =  $\frac{7}{2} RT$

$$\therefore C_v = \frac{du}{dT} = \frac{7}{2} R$$

$$C_p = C_v + R = 9/2 R$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{9}{7} = 1.28$$

For n degree of freedom

$$\text{KE of 1 mole of gas}(U) = \frac{n}{2}RT$$

$$\therefore C_v = \frac{du}{dT} = \frac{n}{2}R$$

$$C_p = C_v + R = \left(\frac{n+2}{2}\right)R$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{n+2}{n} = 1 + \frac{n}{2}$$

#### Thermo dynamical process

##### 1. Isobaric process

The thermodynamical process in which pressure remain constant is called isobaric process

$$\implies \text{work done (dw)} = p dv$$

##### 2. Isochoric process

The process in which volume remain constant is called isochoric process.

$$\implies \text{work done (dw)} = 0$$

$$\implies \text{Heat supplied} = \text{change in internal energy}$$

##### 3. Isothermal process

The process in which temperature remain constant ie  $dT = 0$

- Change in internal energy  $du = 0$

- Gas equation,  $P_1 V_1 = P_2 V_2$

- Slope of curve  $\left(\frac{dP}{dV}\right) = -\frac{P}{V}$

- Heat capacity of gas is infinite

- Work done ( $w$ ) =  $nRT \ln \frac{V_2}{V_1}$   

$$= P_1 V_1 \ln \frac{V_2}{V_1} = P_1 V_1 \ln \frac{P_2}{P_1}$$

##### 4. Adiabatic Process

The process in which exchange of heat energy is zero ie.  $dQ = 0$  so,  $dw = -du$  ie work is done by gas on the expense of internal energy so cooling is observed after adiabatic expansion.

- Fast process in which wall of cylinder is perfectly insulator

- Heat capacity of gas is 0

- Slope of curve  $\left(\frac{dP}{dV}\right) = -\frac{\gamma P}{V}$

- Gas equation is

- $P_1 V_1^\gamma = P_2 V_2^\gamma$

- $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

- $\frac{T_1^\gamma}{P_1^{\gamma-1}} = \frac{T_2^\gamma}{P_2^{\gamma-1}}$  or  $\left(\frac{T_1}{T_2}\right)^\gamma = \left(\frac{P_1}{P_2}\right)^{\gamma-1}$

- work done ( $w$ ) =  $\frac{nR [T_1 - T_2]}{\gamma - 1} = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$

##### 5. Cyclic process

Complete a closed cycle

- Change in internal energy is zero

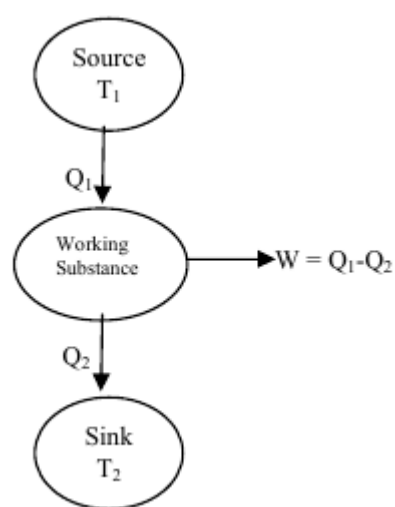
- work done( $w$ ) = Area of closed loop in PV diagram

#### Heat Engine

Device that convert heat energy into mechanical work is called heat engine.

It consist following parts

$Q_1$  heat energy is absorbed from source of temperature  $T_1$  and  $Q_2$  heat energy is rejected to sink of temperature  $T_2$  after doing work  $w$  so



$$\begin{aligned}
 \text{Efficiency } (\eta) &= \frac{\text{work done}}{\text{input}} \times 100\% \\
 &= \frac{w}{Q_1} \times 100\% \\
 &= \left(1 - \frac{Q_2}{Q_1}\right) \times 100\% \\
 &= \left(1 - \frac{T_2}{T_1}\right) \times 100\%
 \end{aligned}$$

- When heat engines are placed in series then sink of  $1^{st}$  engine act as source for  $2^{nd}$  engine and so on

$$\text{Efficiency } (\eta) = \left(1 - \frac{T_f}{T_i}\right) \times 100\%$$

$T_f$  = Temp. of sink of last engine

$T_i$  = Temp. of sink of first engine

## Second law of thermodynamics

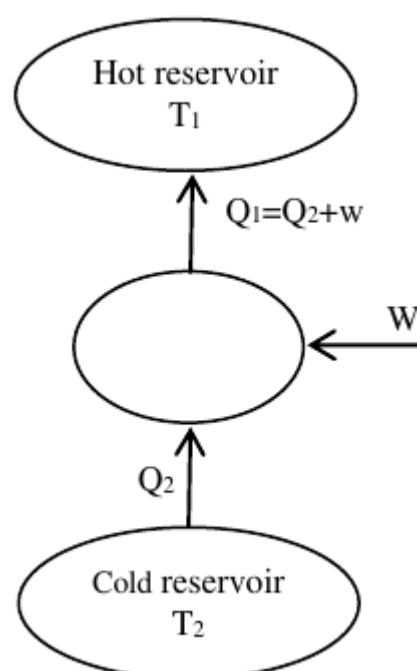
### a. Kelvin Planck statement

It is impossible for engine to convert all the heat energy into work without rejecting some energy to sink ie no engine will have 100% efficiency.

### b. Clausius statement

It is impossible to absorb heat energy from cold body and reject to hot body without doing work on it i.e. self acting refrigerator is impossible.

In refrigerator,  $Q_2$  heat is absorbed from cold reservoir on doing work ' $w$ ' on it then  $Q_1 = Q_2 + w$  heat is rejected to hot reservoir then



## Coefficient of performance

$$\begin{aligned}
 (\beta) &= \frac{\text{Heat extracted}}{\text{work done}} \\
 &= \frac{Q_2}{w} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2} \\
 \therefore \beta &= \frac{Q_2}{w} = \frac{1}{\frac{Q_1}{Q_2} - 1}
 \end{aligned}$$

## Entropy

The measure of disorder of molecule of system is called entropy. On increasing the disorder, the entropy of system increases

∴ Change in entropy

$$(\Delta S) = \frac{\text{Heat absorbed}}{\text{Absolute temperature}}$$

$$\therefore \Delta Q = T\Delta S$$

The change in entropy during change in state of matter  $\Delta S = \pm \frac{ML}{T}$

Where +ve sign indicates heat absorbed and -ve sign indicates heat evolved. When temperature of body changes from  $T_i$  to  $T_f$  then the change in entropy  $(\Delta S) = ms \ln \frac{T_f}{T_i}$