

## DEGREES OF FREEDOM

- For monoatomic gas,  $f = 3$
- For diatomic gas,
  - (a) at room temperature,  $f = 5$
  - (b) at high temperature,  $f = 7$
- For triatomic gas,
  - (a) Linear  $f = 5$
  - (b) Non-linear  $f = 6$
- For each vibrational mode,  $f = 2$

Q1

Ideal gas is composed of polyatomic molecule that has 4 vibrational modes. Total degrees of freedom is  
a) 12 b) 14 c) 8 d) 6

## SPECIFIC HEAT CAPACITY

- a)  $C_p - C_v = R$
- b)  $C_p - C_v = \frac{R}{M}$  (specific heat per unit mass) Mono- $\gamma = \frac{5}{3}$
- c)  $C_v = \frac{R}{\gamma - 1} = \frac{f}{2} R$  Dia- $\gamma = \frac{7}{5}$
- d)  $C_p = \frac{\gamma R}{\gamma - 1} = (1 + \frac{f}{2}) R$  Tri- $\gamma = \frac{4}{3}$
- e)  $\gamma = \frac{C_p}{C_v} = 1 + \frac{2}{f}$

Q2

If  $C_p$  and  $C_v$  denote the specific heats of unit mass of nitrogen at constant pressure and volume respectively, then

- a)  $C_p - C_v = \frac{R}{28}$  b)  $C_p - C_v = \frac{R}{14}$  c)  $C_p - C_v = \frac{R}{7}$  d)  $C_p - C_v = R$

## MIXING OF GASES

$$C_{vmix} = \frac{n_1 C_{v1} + n_2 C_{v2} + \dots}{n_1 + n_2 + \dots}$$

$$C_{pmix} = \frac{n_1 C_{p1} + n_2 C_{p2} + \dots}{n_1 + n_2 + \dots}$$

$$\gamma_{mix} = \frac{C_{pmix}}{C_{vmix}}$$

Q3

Consider a mixture of  $n$  moles of helium gas and  $2n$  moles of oxygen gas (molecules taken to be rigid) as an ideal gas. It's  $C_p/C_v$  value will be:

- a) 19/13 b) 67/45 c) 40/27 d) 23/15

## LAW OF EQUIPARTITION OF ENERGY

Energy for each molecule per  $f = \frac{1}{2} K_B T$   
 Total energy for molecule =  $\frac{f}{2} K_B T$   
 Monoatomic Molecule =  $\frac{3}{2} K_B T$   
 Total energy for a mole =  $\frac{f}{2} R T$   
 Total energy for  $n$  moles =  $nfRT$   
 Monoatomic =  $\frac{3}{2} R T$  (1 mole)  
 Diatomic =  $\frac{5}{2} R T$  (1 mole)  
 Translatory Kinetic energy =  $\frac{3}{2} R T$  (1 mole,  $f = 3$ )

Q4

A gas mixture consists of 2 moles of  $O_2$  and 4 moles of  $Ar$  at temperature  $T$ . Neglecting all vibrational modes, the total internal energy of the system is

- a)  $4RT$  b)  $15RT$  c)  $9RT$  d)  $11RT$

### Root Mean square speed:

Square root of mean of square of speeds of different molecules,

$$V_{rms} = \sqrt{\frac{V_1^2 + V_2^2 + \dots + V_n^2}{n}}$$

$$V_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3k_B T}{m}}$$

### Average Speed:

Arithmetic mean of speed of molecules of gas at given temperature.

$$V_{avg} = \frac{|\vec{V}_1| + |\vec{V}_2| + \dots + |\vec{V}_n|}{n}$$

$$V_{avg} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8P}{\pi \rho}}$$

### Most probable speed:

Speed possessed by maximum number of molecules of gas.

$$V_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2P}{\rho}} = \sqrt{\frac{2k_B T}{m}}$$

## VELOCITY OF GAS

$$V_{mp} : V_{avg} : V_{rms} = 1 : 1.13 : 1.225$$

## MEAN FREE PATH

Average distance travelled by molecules between two successive collisions

$$\lambda_{mean} = \frac{1}{\sqrt{2} \pi d^2 n}$$

$$\lambda \propto \frac{1}{d^2}$$

$$\lambda \propto \frac{1}{n^2}$$

$$\lambda \propto \frac{1}{P}$$

$d$  = diameter of molecules.  
 $n$  = no. of molecules per unit volume

## FIRST LAW OF THERMODYNAMICS

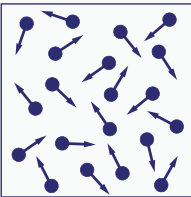
$$Q_p = \Delta U + W$$

$$\Delta U = nC_v \Delta T$$

$$W = \int P dv$$

$$\frac{\Delta U}{Q_p} = \frac{1}{\gamma}$$

$$\frac{W}{Q_p} = 1 - \frac{1}{\gamma}$$



Q5

Consider a gas of triatomic molecules. The molecules are assumed to be triangular, made up of massless rigid rods whose vertices are occupied by atoms. The internal energy of a mole of the gas at temperature  $T$  is:

- a)  $\frac{9}{2} RT$  b)  $\frac{3}{2} RT$  c)  $\frac{9}{2} RT$  d)  $3RT$

Q6

The rms speeds of the molecules of Hydrogen, Oxygen & Carbon dioxide at the same temperature are  $V_H$ ,  $V_O$  and  $V_C$  respectively, then:

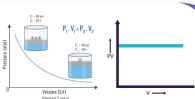
- a)  $V_H > V_O > V_C$  b)  $V_C > V_O > V_H$
- c)  $V_H = V_O > V_C$  d)  $V_H = V_O = V_C$

Q7

The mean free path of molecules of gas, (radius  $r$ ) is inversely proportional to

- a)  $r^3$  b)  $r^2$
- c)  $r$  d)  $\sqrt{r}$

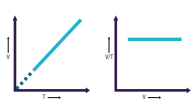
## BOYLE'S LAW



$PV = \text{constant}$ , if  $T = \text{Constant}$

$P_1 V_1 = P_2 V_2$ , when gas changes its state under constant temperature.

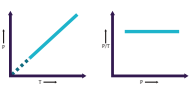
## CHARLE'S LAW



$V \propto T$ ;  $\frac{V}{T} = \text{constant}$ ;  $P = \text{constant}$ .

$\frac{V_1}{T_1} = \frac{V_2}{T_2}$ , when gas change its state under constant pressure.

## GAY LUSSAC'S LAW



$P \propto T$ ;  $\frac{P}{T} = \text{constant}$ ;  $V = \text{constant}$ .

$\frac{P_1}{T_1} = \frac{P_2}{T_2}$ , when gas changes its state under constant Volume.

## PRESSURE OF GAS

$$PV = \frac{1}{3} mn V_{rms}^2 = \frac{1}{3} mn \overline{V^2}$$

Relation between pressure and Kinetic Energy.

$$E = \frac{3}{2} PV$$

## IDEAL GAS LAW

$$PV = nRT$$

$$R = 8.314 \text{ JK}^{-1} \text{mol}^{-1}$$

$$\rho = \frac{PM}{RT}$$

Specific heat of Solids =  $3R$   
 WATER =  $9R$

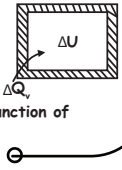
## Internal Energy(U)

$$(1) \Delta U = \Delta Q = nC_v \Delta T = n \frac{f}{2} R \Delta T$$

$$= \frac{nR \Delta T}{\gamma - 1} = \frac{\Delta(PV)}{\gamma - 1}$$

$$= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

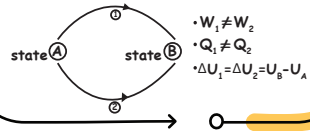
(Internal Energy is only the function of temperature of the gas)



First law of T.D  $\Rightarrow Q = \Delta U + W$

Q, W  $\Rightarrow$  path functions

$\Delta U \Rightarrow$  state function



$$\cdot W_1 \neq W_2$$

$$\cdot Q_1 \neq Q_2$$

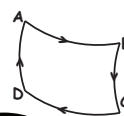
$$\cdot \Delta U_1 = \Delta U_2 = U_B - U_A$$

Isothermal process  $\Rightarrow \Delta T = 0 \Rightarrow \Delta U = 0$

Cyclic process

A  $\rightarrow$  B  $\rightarrow$  C  $\rightarrow$  D  $\rightarrow$  A

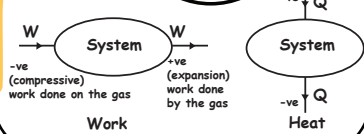
$$\Delta U = U_A - U_A = 0$$



## WORK

Work done:  
path function  
 $W = \int F \cdot dx = \int P \cdot dV$   
Unit: Joule(J)

Sign Convention



## HEAT

Heat: path function  
 $\Rightarrow$  unit: calorie/Joule

For any process,  
 $Q = nC \Delta T$

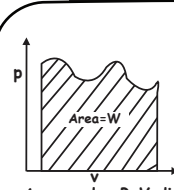
where, C = Specific heat capacity for the process

Adiabatic process  $\Rightarrow \Delta Q = 0$  [No heat transfer]

At constant volume  $\Rightarrow Q_v = \Delta U = nC_v \Delta T$

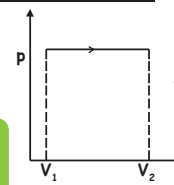
At constant pressure  $\Rightarrow Q_p = \Delta U + W = nC_p \Delta T$

## Work done from P-V Graph



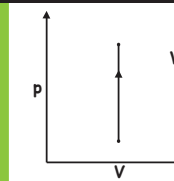
Area under P-V diagram gives work done by the gas

### Isoobaric process

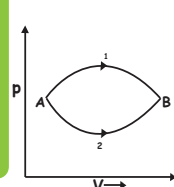


$$W = P(V_2 - V_1)$$

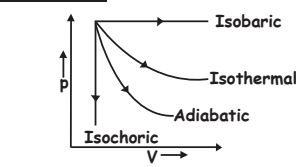
### Isochoric process



$$W = P \Delta V = 0$$

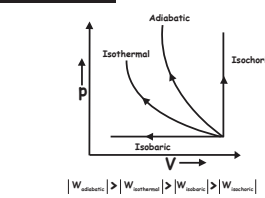


### Expansion



$$W_{\text{isobaric}} > W_{\text{isothermal}} > W_{\text{adiabatic}} > W_{\text{isochoric}}$$

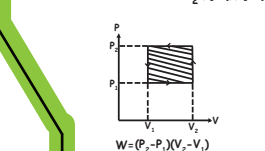
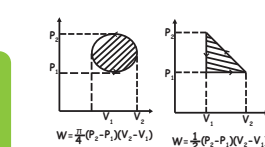
### Compression



$$|W_{\text{adiabatic}}| > |W_{\text{isothermal}}| > |W_{\text{isochoric}}|$$

### Cyclic process

- W = area inside the graph
- For clockwise process, W = +ve
- For anti-clockwise process, W = -ve



## Thermodynamic processes

### 01 Adiabatic process

- Q = 0 [no exchange of heat]

Rapid or spontaneous process/insulated vessel

$$Q = \Delta U + W$$

$$Q = 0 \Rightarrow \Delta U = -W$$

Compression

$$W = -ve \quad \Delta U = +ve$$

$\Delta U \uparrow \Rightarrow$  Temperature  $\uparrow$

$\Rightarrow$  Pressure  $\uparrow$

Expansion

$$W = +ve \quad \Delta U = -ve$$

$\Delta U \downarrow \Rightarrow$  Temperature  $\downarrow$

$\Rightarrow$  Pressure  $\downarrow$

Equation of state

$$PV^\gamma = \text{constant}$$

$$TV^{\gamma-1} = \text{constant}$$

$$PT^{\frac{\gamma}{\gamma-1}} = \text{constant}$$

Work done by the gas

$$W = -\Delta U = nC_v(T_1 - T_2)$$

$$= n \frac{f}{2} R(T_1 - T_2)$$

$$W = \frac{nR}{\gamma-1}(T_1 - T_2)$$

$$W = \frac{P_1 V_1 - P_2 V_2}{\gamma-1}$$

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## 04 Isochoric process

Isochoric process

$\Delta V = 0$  or  $V = \text{constant}$

$$\text{equation of state} \Rightarrow P \propto T \Rightarrow \frac{P_1}{P_2} = \frac{T_1}{T_2}$$

Work done by the gas

$$\Delta V = 0 \Rightarrow W = 0$$

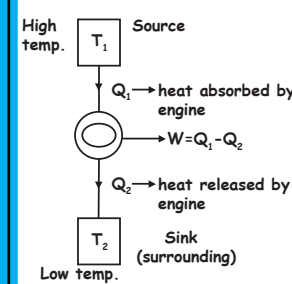
$$\text{specific heat}$$

$$\Rightarrow C_v = \frac{f}{2} R$$

$$= \frac{R}{\gamma-1}$$

## Heat Engine

'Device that converts heat into work'



High temp.

Low temp.

efficiency( $\eta$ )

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

$$\eta_{\text{max}} \Rightarrow \text{When } Q_2 = 0 \text{ or } T_2 = 0K$$

(not possible)

## Carnot Engine

$\rightarrow$  Ideal engine

$$\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

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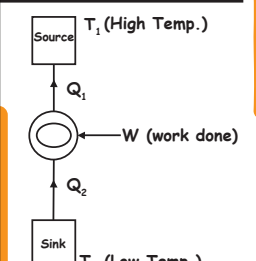
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## Refrigerator and heat pump



Coefficient of performance of refrigeration(B)

$$\beta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} \quad \beta = \frac{T_2}{T_1 - T_2}$$

Coefficient of performance of heat pump

$$\beta = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}$$

## Relationship between

$$\beta = \frac{1}{1 - \eta}$$

$$(COP)_{\text{heat pump}} = 1 + (COP)_{\text{refrigerator}}$$

Cascaded engine

Same work output

$$W_1 = W_2$$

$$T_1 - T = T - T_3$$

$$2T = T_1 + T_3$$

$$T = \frac{T_1 + T_3}{2}$$

Same efficiency

$$1 - \frac{T}{T_1} = 1 - \frac{T_3}{T}$$

$$T^2 = T_1 T_3$$

$$T = \sqrt{T_1 T_3}$$

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# THERMODYNAMICS