

PHY 205

Thermal Physics

$PV = nRT \rightarrow$ macroscopic properties

Microscopic cavation \rightarrow microscopic properties

Macroscopic cavation \rightarrow macroscopic properties

We can rewrite cavation q in terms of the boltzmann constant k_B ,

$$n = \frac{N}{N_A} \rightarrow \textcircled{c}$$

Recall cavation G_c

Putting G_c into cavation q

$$PV = \underbrace{\left(\frac{N}{N_A} \right)}_{\textcircled{a}} RT \quad \dots \textcircled{b}$$

$$\Rightarrow PV = N \underbrace{\left(\frac{R}{N_A} \right) T}_{\textcircled{c}} \quad \dots \textcircled{d}$$

$$PV = NC_B T \quad \text{where } C_B = \frac{R}{N_A} \quad \text{(Boltzmann constant)}$$

$$R = 8.314 \text{ J/mol/K}$$

$$N_A = 6.02 \times 10^{23} \text{ /mol}$$

$$C_B = \frac{R}{N_A} = \frac{8.314}{6.02 \times 10^{23}}$$

$$C_B = 1.38 \times 10^{-23} \text{ J/K}$$

Therefore the two versions of ideal gas

equations are

$$PV = nRT \quad (\text{macroscopic})$$

$$PV = Nk_B T \quad (\text{microscopic})$$

$$\text{Equating } ⑨ \text{ & } ⑩ \Rightarrow nR = Nk_B$$

where Nk_B = microscopic entities that define the system

nR = macroscopic properties that define the system

$$⑨ \quad PV = T \langle u \rangle_{\text{av}}$$

$$⑩ \quad T \langle u \rangle_{\text{av}} = Nk_B$$

$$nR = Nk_B$$

KINETIC THEORY OF GASES

The behaviour of gas in a system can be described using two approaches:

(a) Using macroscopic properties

In this approach, the system of gas can be described using parameters like temperature, Volume and pressure.

This parameters will enable us to describe the state of the gas at equilibrium condition.

(b) Using microscopic properties

In this case, we can define the property of the system by considering the interaction of the individual gas molecules, such as their average velocity and kinetic energy.

Lorentz theory of gases connects these two approaches to derive the equations of an ideal gas.

According to kinetic theory of gases, gas consists of an assembly of identical molecules. In order to ~~derive~~ the equation of an ideal gas using kinetic theory, the following assumptions were made:

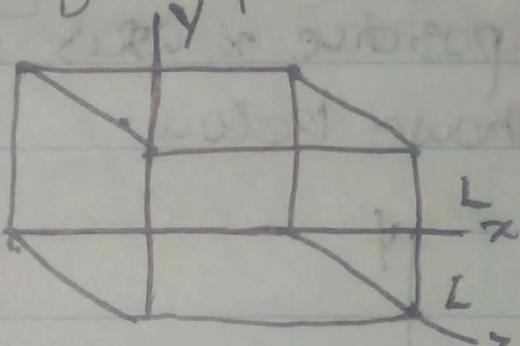
- 1) Any volume of gas contains identical numbers of gas molecules
- 2) The number of molecules in a given volume is very large and the molecules have small diameter (10^{-10} m) - 1 Å (Angstrom)
- 3) The volume of the individual gas molecules is small, compared to the volume of the entire gas.
- 4) The gas molecules obey Newton's Law, therefore they are free to move in any direction with speed.
- 5) The gas molecules move in a straight line. Collision with other molecules is random in nature.
- 6) The gas molecules can be modelled as hard spheres, so that their total kinetic energy, total momentum is conserved.
- 7) Molecules only interact when they collide. Collision between molecules (or with the walls of the container) is elastic (i.e. No energy is lost during collision).
- 8) The time of collision between molecule

negligible

EXP

We can obtain an expression for the pressure (p) exerted on the walls of the container due to the collision of the gas molecules with the wall as follows:

Consider a collection of N molecules of ideal gas in cube of volume (V). Let's assume the edge length of the cube is L as shown below.



$$\text{Volume of the cube} = L^3$$

Since the molecules can move in a straight line in any direction, let's assume that each molecule moves with a velocity \vec{v} .

We can resolve the total velocity in these three co-ordinates

$$(v_x, v_y, v_z)$$

$$v = v_x, v_y, v_z \dots \textcircled{1}$$

The resultant velocity v defined as

$$v^2 = v_x^2 + v_y^2 + v_z^2 \dots \textcircled{2}$$

Since the motion is random, we will be
looking for the average velocity of the mole
cules. Average Velocity

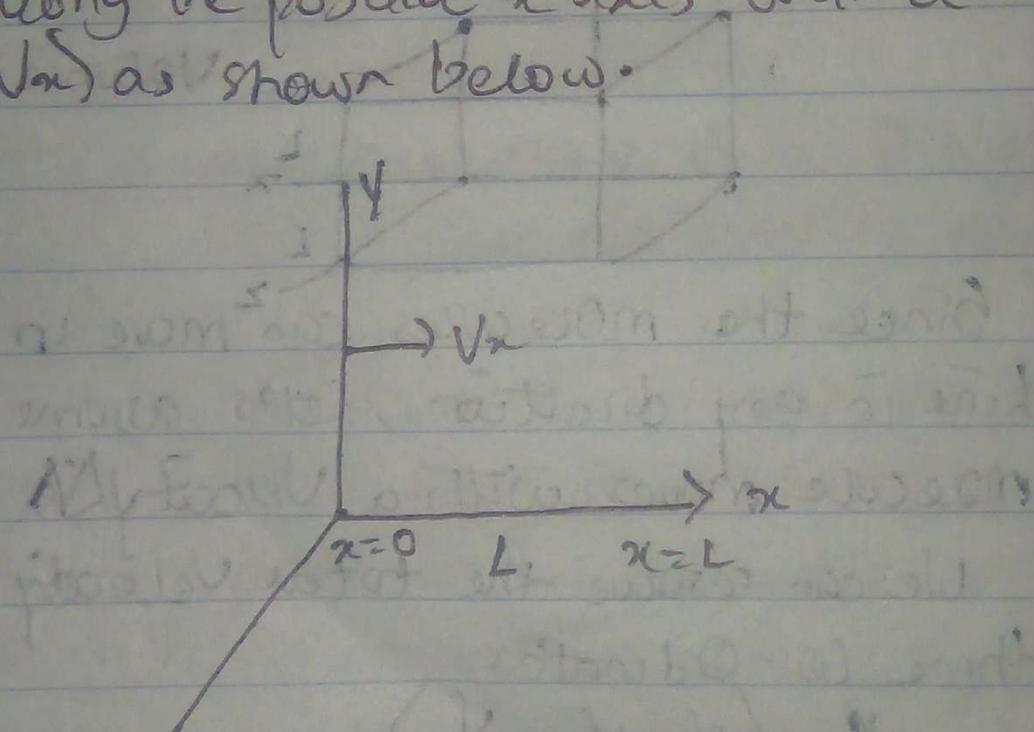
$$\bar{V} = \sqrt{V_x^2 + V_y^2 + V_z^2}$$

Average resultant Velocity

$$\bar{V}^2 = \bar{V_x^2} + \bar{V_y^2} + \bar{V_z^2} \quad \text{--- (3)}$$

~~→~~ \bar{V} = resultant ^{Average Velocity} of each
molecule

Let's assume that a gas molecule moves
along the positive x-axis with a velocity
(V_x) as shown below:



Since the collision is elastic (bounces back)
The distance covered when the gas molecule moves
from $x=0$ to $x=L$ and back to $x=0$ is $2L$

Therefore the time taken to cover this distance is $\rightarrow V = \frac{d}{t}$

$$t = \frac{d}{V} = \frac{2L}{V_x} = ④$$

Where t is the time between collision when the particle collides with the wall at $x=L$, the velocity is V_x , when it rebounds and collides at $x=0$ the velocity is $-V_x$.
The momentum is defined as follows

Momentum = mass \times Velocity

$$\left. m \right|_{x=L} = m V_x + \left. m \right|_{x=0} = -m V_x$$

Change in momentum $\geq m V_x - (-m V_x)$

$$\Delta p \geq 2m V_x \dots \textcircled{5}$$

Change in momentum $= \Delta p$

The force (F) exerted by one molecule on the wall of container is

$$F = \frac{\Delta p}{\Delta t} = \frac{\text{Change in momentum}}{\text{Change in time}} \rightarrow 6.$$

$$F = ma$$

$$F = m \frac{du}{dt} \Rightarrow \frac{d(mu)}{dt}$$

$$F = \frac{2mu}{\frac{2L}{V_n}} \Rightarrow \frac{mV_n^2}{L} \quad \text{--- (6)}$$

Note this is the force exerted by one molecule moving in the x direction.

Therefore the total force exerted by n molecules is defined as

$$F = \frac{mV_{n1}^2}{L} + \frac{mV_{n2}^2}{L} + \frac{mV_{n3}^2}{L} + \dots + \frac{mV_{nn}^2}{L}$$

$$F = \frac{m}{L} \langle V_{n1}^2 + V_{n2}^2 + V_{n3}^2 + \dots + V_{nn}^2 \rangle \quad \text{--- (7)}$$

Since we are concerned with the average value of all the molecules, therefore the average velocity in the x direction is given as:

$$\bar{V}_n^2 = \frac{1}{N} \langle V_{n1}^2 + V_{n2}^2 + V_{n3}^2 + \dots + V_{nn}^2 \rangle$$

$$NV_n^2 = V_{n1}^2 + V_{n2}^2 + V_{n3}^2 + \dots + V_{nn}^2 \quad \text{--- (8)}$$

Putting equation 8 into 7

$$F = \frac{\rho h}{L} \langle NV_n^2 \rangle \quad \text{--- (9)}$$

Course Outline

Module 1:

Behaviour of gases

i) Review of gas law

ii) Applications of gas law

iii) Concept of real gases

iv) Elementary and kinetic theory

Module 2:

Basic Statistical physics

i) Micro and macroscopic of thermodynamics

ii) Boltzmann counting and the derivation of maxwell boltzmann distribution function

iii) Application of boltzmann function to derive velocity, distribution of gases.

Module 3:

Foundation of thermodynamics

i) Foundation of classical thermodynamics

ii) Explanation of thermodynamics terminology, heat, work,

iii) Zero-law of thermodynamics

Module 4:

First law of thermodynamics and its applications

i) First law of thermodynamics

ii) Application of the first-law of thermodynamics (heat engine, heat pump, refrigerator, Auto, cycle, comot cycle).

Behaviour of Gases

Gas Laws

Are laws that governs the behaviour of gases (ideal gas). Ideal gas mostly exists at high temperature and low pressure. Here, the molecules are in constant random motion, this means that the potential energy of an ideal gas is assumed to be zero. Hence, only kinetic energy exist due to the physical collision between the atoms & molecules and the walls of the container.

Gas Laws describe the relationship between the Pressure, temperature ~~and~~ volume and the amount of gas.

Boyle's Law

This states that at constant temperature the pressure of a given mass of gas is inversely proportional to its volume. Mathematically

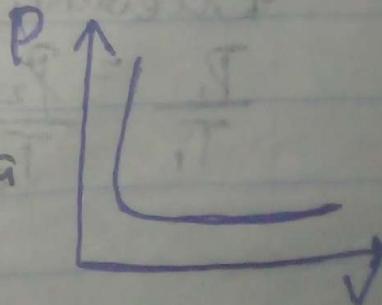
$$P \propto \frac{1}{V} \text{ or } V \propto \frac{1}{P} \Rightarrow P = \frac{k}{V} \text{ where } k \text{ is a constant.}$$

$$PV = k \quad (a)$$

Extending equation (a)

$$P_1 V_1 = P_2 V_2 \quad (b)$$

Charles Law



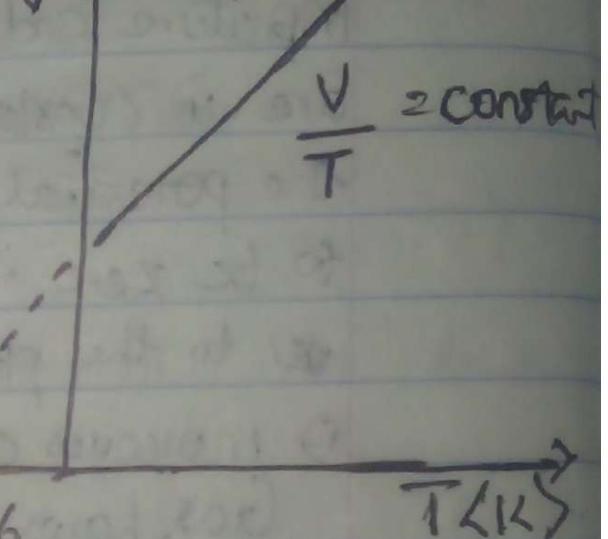
It states that at constant pressure the volume of a gas is proportional to its temperature mathematically.

$$V \propto T$$

$$V = kT$$

$$\frac{V}{T} = k \quad \text{--- (2a)}$$

graphically



Extending equation 2a

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{--- (2b)}$$

Pressure Law (Gay-Lussac's Law)

This states that at constant volume, pressure is proportional to temperature - mathematically

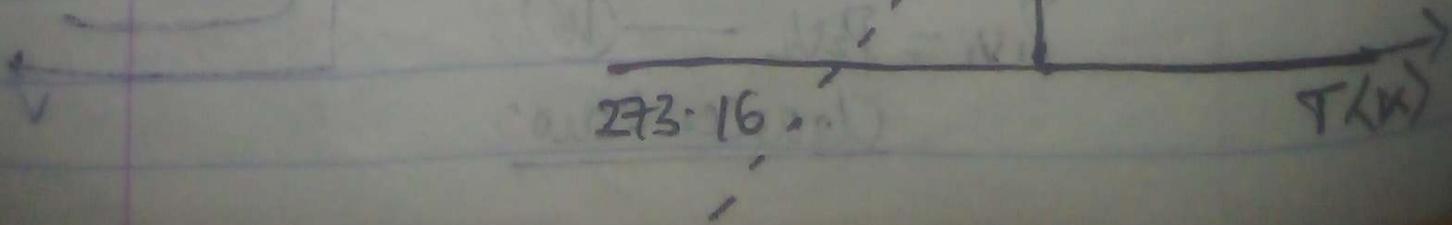
$P \propto T$ (proportional to temp) Graphically

$$P = kT$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{--- (3a)}$$

Extending equation 3a

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{--- (3b)}$$



Combining equation 1a, 2a and 3a

$$\frac{PV}{T} = \textcircled{4a}$$

Equation 4a is the general gas equation.

Extending equation 4a

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Where P is pressure in Pascal and 1 pascal is 1 N/m^2

V is Volume in m^3

T is temperature in Kelvin

Avgadro's Law

This law expresses ~~the~~ relationship between the volume of a gas and the amount of gas (in moles) at constant pressure and temperature.

This law states that equal volumes of all gases are the same pressure and temperature containing the same number of molecules.

This implies that for a given mass of an ideal gas, the volume (V) of the gas is directly proportional to the amount or the number of moles (n) at constant temperature and pressure.

Mathematically V \propto n, $V = kn$

$$\frac{V}{n} = k \quad (6a)$$

Extending 5a

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad (6b)$$

NOTE

One mole of a substance contains N_A (Avogadro's number) of atoms or molecules. $N_A = 6.02 \times 10^{23}/\text{mol}$ ----- (6a)

Molar Mass (m) is the mass of one mole of any substance.

∴ Molar mass of any substance contains N_A elementary entities (atoms/molecules)

$$\therefore n = \frac{\text{mass of the substance}}{\text{molar mass}} = \frac{m}{M} \quad (6b)$$

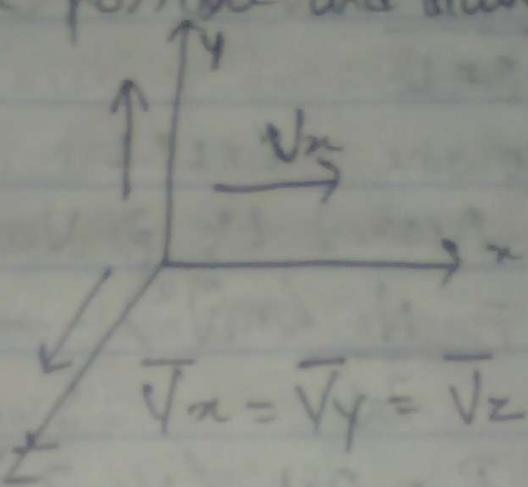
Number of moles (n) can also be expressed as a ratio of the number of molecules N to the number of molecules N_A .

$$n = \frac{N}{N_A} \quad \text{number of molecules in one mole of substance}$$

Combining these three laws: Boyle's law, Charles's law and Avogadro's law

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Since the motion of the ~~particle~~ molecule is random and can take place in any direction, this means that the average velocity in all directions is assumed to be possible and have the same value.



Recall equation 2

$$\bar{V}^2 = \bar{V}_x^2 + \bar{V}_y^2 + \bar{V}_z^2$$

$$\bar{V}^2 = \bar{V}_x^2 + \bar{V}_y^2 + \bar{V}_z^2$$

$$\left\{ \begin{array}{l} \bar{V}^2 = 3\bar{V}_x^2 \\ \bar{V}^2 = 3\bar{V}_y^2 \end{array} \right. \quad (1)$$

$$\left\{ \begin{array}{l} \bar{V}^2 = 3\bar{V}_z^2 \end{array} \right.$$

$$f = \frac{m}{L} \langle N \bar{V}^2 \rangle$$

$$f = \frac{mN}{L} \left\langle \frac{\bar{V}^2}{3} \right\rangle \quad \text{--- } (1a)$$

$$f = \frac{N}{L} \langle m \bar{V}^2 \rangle \quad \text{--- } (1b)$$

The pressure exerted at the walls of the container is written as: $P = \frac{F}{A}$

$$P = \frac{N}{3AL} \langle m\bar{v}^2 \rangle \quad \text{--- (4)}$$

$$\text{Volume} = L \times L \times L$$

$$\text{Area} = L^2 \Rightarrow \text{Volume} = AL$$

$$P = \frac{N}{3V} \langle m\bar{v}^2 \rangle \quad \text{--- (5)}$$

$$P = \frac{2N}{3V} \left\langle \frac{1}{2} m\bar{v}^2 \right\rangle \quad \text{--- (6)}$$

$$P = \frac{2N}{3V} \left\langle \frac{1}{2} m\bar{v}^2 \right\rangle$$

$$PV = \frac{2N}{3} \left\langle \frac{1}{2} m\bar{v}^2 \right\rangle$$

$$PV = \frac{2N}{3} \left\langle \frac{K \cdot E_{avg}}{2} \right\rangle \quad \text{--- (7)}$$

$$PV = Nk_B T$$

$$Nk_B T = \frac{2N}{3} \left\langle K \cdot E_{avg} \right\rangle$$

$$T = \frac{2 \langle K \cdot E_{avg} \rangle}{3k_B} \quad \text{--- (8)}$$

Equation (1) shows that the absolute temperature of a system of gases is directly proportional to the average kinetic energy of all the gas molecules.

The kinetic energy depicted in all these derivations, is the kinetic energy ~~resulting~~ from motion in a straight line, this is called the translational kinetic energy.

$$\text{from } Nk_B T = \frac{2N}{3} \langle K \cdot E_{\text{avg}} \rangle$$

$$\left\langle \frac{1}{2} m \bar{v}^2 \right\rangle = K \cdot E_{\text{avg}}$$

$$K \cdot E_{\text{avg}} = \frac{3}{2} k_B T \quad \text{--- (1)}$$

NOTE We can say that the average translational kinetic energy for one molecule is $\frac{3}{2} k_B T$. This means that for N -molecules,

$$K \cdot E_{\text{avg}} = \frac{3}{2} N k_B T$$

$$\Rightarrow \frac{3}{2} N k_B T = \frac{3}{2} N R T \quad \text{--- (2)}$$

Please note that for an ideal gas, there is no intermolecular force ∴ the kinetic energy is the total energy in the system.

$$E = \text{U} - E_{\text{avg}} = 3/2 N k_B T = 3/2 N R T$$

Deduction from the kinetic theory of gases

1) Definition for absolute temperature

$$T = 2/3 K_r$$

2) Law of equipartition of energy

Recall

$$\frac{1}{2} m \bar{V}^2 = U - E_{\text{avg}} = 3/2 k_B T$$

$$\bar{V}^2 = 3 \bar{V}_x^2$$

$$\cancel{\frac{1}{2} m \bar{V}^2} \quad \frac{1}{2} m \langle 3 \bar{V}_x^2 \rangle = \frac{3}{2} k_B T$$

$$\frac{1}{2} m \bar{V}_x^2 = \frac{3}{2} k_B T$$

$$\frac{1}{2} m \bar{V}_y^2 = \frac{3}{2} k_B T$$

$$\frac{1}{2} m \bar{V}_z^2 = \frac{3}{2} k_B T$$

$$\frac{1}{2} m \bar{V}_x^2 + \frac{1}{2} m \bar{V}_y^2 + \frac{1}{2} m \bar{V}_z^2 = \frac{3}{2} [k_B T + k_B T + k_B T]$$

$$\langle \frac{1}{2} m \bar{V}_x^2 + \bar{V}_y^2 + \bar{V}_z^2 \rangle = \frac{3}{2} k_B T$$

This law states that molecules in a system have the same average energy associated with

each independent degree of freedom of their motion and the energy is $\frac{1}{2} kT$ (per molecule)

$$\frac{1}{2} kT = \frac{1}{2} \times \frac{1}{2} RT$$

Degree of Freedom \rightarrow ways they move

Translational / Vibrational / rotational
(Three ways a molecule moves under high temperature / high pressure)

molccle	Degree of freedom	$U = F \cdot T$
1) Monoatomic, effe, Ar, Ne	Translational $\rightarrow dx, dy, dz \text{ (3)}$	$\frac{1}{2} kT$ $3 \times \frac{1}{2} kT$ $= \frac{3}{2} kT$
2) Diatomic $\rightarrow O_2, H_2, HCl$	6 \rightarrow 3 translational 1 \rightarrow vibrational 2 \rightarrow rotational	$\frac{1}{2} kT$ $6 \times \frac{1}{2} kT$ $\frac{6}{2} kT$ $= 3 kT$
3) Triatomic Linear molecules $\rightarrow CO_2$	3 translational 2 \rightarrow rotational 3 \rightarrow vibrational 9 total	$\frac{1}{2} kT$ $9 \times \frac{1}{2} kT$ $\frac{9}{2} kT$
4) Triatomic non-linear molecules	3 translational 3 \rightarrow rotational 3 \rightarrow vibrational 9 total	$\frac{1}{2} kT$ $9 \times \frac{1}{2} kT$ $\frac{9}{2} kT$

Root mean square speed of the gas molecule
recall ②

$$P = \frac{N}{3V} \langle m\bar{v}^2 \rangle$$

$$PV = Nk_B T$$

$$P = \frac{Nk_B T}{V} \quad \textcircled{3}$$

$$\frac{Nk_B T}{V} = \frac{N}{3V} \langle m\bar{v}^2 \rangle$$

$$k_B T = \frac{1}{3} \langle m\bar{v}^2 \rangle$$

$$\langle \bar{v}^2 \rangle = \frac{3k_B T}{m}$$

Taking Square roots of both sides

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3k_B T}{m}} \quad \textcircled{25}$$

In terms of molar mass

recall $n = \frac{m}{M}$ $n = \frac{N}{N_A}$

$$\frac{m}{M} = \frac{N}{N_A} \quad N = 1$$

$$m = \frac{M}{N_A}$$

~~$$m = \frac{M}{N_A}$$~~
$$\textcircled{26}$$

$$V_{r.m.s} = \sqrt{\frac{3k_B T}{M/N_A}} = \sqrt{\frac{3k_B T \cdot N_A}{m}}$$

$$k_B = \frac{R}{N_A} \quad \therefore R = k_B \cdot N_A$$

$$V_{r.m.s} = \sqrt{\frac{3RT}{m}}$$

In terms of density

$$\text{from } P = \frac{N}{3V} \langle m\bar{v}^2 \rangle$$

$$\rho = \frac{m}{V}$$

$$P = \frac{N}{3} \left\langle \frac{m}{V} \right\rangle \bar{v}^2 \Rightarrow P = \frac{N}{3} \langle \rho \bar{v}^2 \rangle$$

$$3P = N \rho \bar{v}^2, \quad N=1$$

for One molecule

$$\begin{aligned} 3P &= \rho \bar{v}^2 \\ \bar{v}^2 &= \frac{3P}{\rho} \end{aligned}$$

$$V_{r.m.s} = \sqrt{\frac{3P}{\rho}}$$

Three molecules of gas has Velocity $V_1 = 200 \text{ m/s}$

$$V_2 = 200 \text{ m/s}, \quad V_3 = 300 \text{ m/s}$$

Calculate the average velocity / Density of the gas
The $V_{r.m.s}$ at S-T-P.

$$a) \bar{V} = \frac{1}{N} (V_1 + V_2 + V_3)$$

$$= \frac{100 + 200 + 300}{3} = \underline{\underline{200 \text{ m/s}}}$$

$$b) V_{\text{rms}} = \sqrt{\bar{V}^2}$$

$$= \sqrt{\frac{1}{N} (V_1^2 + V_2^2 + V_3^2)}$$

$$V_{\text{rms}} \rightarrow \sqrt{\frac{1}{3} (100^2 + 200^2 + 300^2)}$$

$$\rightarrow \sqrt{\frac{10,000 + 40,000 + 90,000}{3}}$$

$$\rightarrow \sqrt{46,666.67}$$

$$\rightarrow 216.02 \text{ m/s}$$

$$c) V_{\text{rms}} = \sqrt{\frac{3P}{\rho}} \rightarrow \sqrt{\frac{3}{1}}$$

$$(216.02)^2 = \sqrt{\frac{3 \times 0.3 \times 10^3}{\rho}}$$

~~$$\frac{3}{\rho} = \frac{309000}{8} = 46,666.67$$~~

$$46,666.67 = 6.5 \text{ kg/m}^3$$

~~$$\frac{46,666.67}{6.5} = \frac{309000}{46,666.67} \rightarrow 6.62 \text{ kg/m}^3$$~~

2) An ~~air~~ compressor used for spraying paint has a tank capacity of 0.4 m^3 that contains air at 27°C and 6 atm, how many moles of ~~air~~ gas does the tank holds?

$$\text{Volume} = 0.4\text{ m}^3, T = 27^\circ\text{C}, P = 6\text{ atm}$$

$$PV = nRT$$

~~$R = 8.314 \text{ J/mol K}$~~

$$T = 27 + 273 = 300^\circ\text{K}$$

$$P = 101325 \times 6 = 607950$$

Pressure must be in Pascal (N/m^2):

$$\frac{PV}{RT} = \frac{nRT}{RT} \Rightarrow n = \frac{PV}{R} \Rightarrow n = \frac{607950 \times 0.4}{8.314 \times 300}$$

$$n = \frac{24380}{2494.2}$$

$$n = 97.5 \text{ moles}$$

CONT'D

$$V \propto \frac{1}{P}, V \propto T, V \propto n$$

We have

$$V \propto \frac{nT}{P} \quad \text{--- (7a)}$$

$$V = R \left\langle \frac{nT}{P} \right\rangle \quad \text{--- (7b)}$$

R is the constant of proportionality

$$R = 8.315 \text{ J/mol/K}$$

writing equation $PV = nRT$ — (ideal gas equation).

REAL GASES

An ideal gas obeys the ideal gas equation $PV = nRT$, when the behavior of a gas deviates from the above equation, we say that gas is a real gas, all gases are real but the specification of thermodynamic properties such as pressure, volume and temperature determines whether we will treat such a gas as a real gas or an ideal gas.

At high temperature, gas particles have a lot of kinetic energy hence they move quickly and there are no intermolecular forces hence no attraction/bonding thereby behaving like an ideal gas, at low pressure, the gas molecules are far apart so that the volume occupied is small compared to the total volume of the container.

and the effects of intermolecular force is negligible. When gases deviate from the ideal gas behavior (high temperature, low pressure), thereby making intermolecular force and the volume of the gas particles significant. We say that gas is real. This happens at (low temperature, high pressure) ~~molecules~~

COMPRESSIBILITY FACTOR

When we apply kinetic theory of gases to explain and analyze the behaviour of an ideal gas we assume that -

- ① Intermolecular forces (attraction, repulsion) between the gas molecules are negligible.
- ② The volume occupied by the gas molecules was small and negligible compared to the volume of the container.
- Several experiments has shown that in certain ranges of pressure and temperature, the ideal gas equation deviates. This means that for real gases at certain pressure and temperature, the intermolecular force between molecules becomes

Significant also the volume of the gas molecule becomes significant. ∴ The ideal gas equation needs to be corrected or modified to account for this deviation. The correction term that is introduced into the ideal gas equation to describe the extent of deviation is called the \rightarrow COMPRESSIBILITY FACTOR (Z)

The compressibility factor is an indication of deviation of a gas from ideal gas behaviour.

Inserting Z into the ideal gas equation

$$PV = ZnRT \quad \text{---} \quad \textcircled{23a}$$

$$Z = \frac{PV}{nRT} \quad \text{---} \quad \textcircled{23b}$$

for one mole of gas

$$Z = \frac{PV}{RT} \quad \text{---} \quad \textcircled{23c}$$

The compressibility factor (Z) is a function of both Temperature (T) and Pressure (P)

$$Z = f(P, T) \quad \text{---} \quad \textcircled{24}$$

The values of Z determine whether the gas exhibit ideal or real behaviour.

$$\text{for ideal gas } Z = 1$$

For real gas $Z \neq 1$ ($Z < 1$ or $Z > 1$)

The Values of Z

- a) When $Z < 1$ (low temperature, moderate pressure)
- b) When $Z > 1$ (at high pressure)
- c) When $Z = 1$ (at low pressure) Ideal gas

Vander waal's Equation

This is an effort by Vander waal to develop an equation for real gas by modifying the equation of an ideal gas, to modify the ideal gas equation, Vander waal added correction terms to account for volume of the molecules and presence of intermolecular attractions.

Mathematically Vander waal's equation is

$$(p + \frac{a}{V^2})(V - b) = RT \quad \text{--- (25a)}$$

→ One mole of a gas

where a = correction term for pressure as a result of intermolecular force. This is also called Cohesive force

b = correction term for Volume as a result of the volume of the gas moreover. This is also called Co-volume

Note a & b are Vander waal's constants

Other forms of Vanderwaal's equations are:

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad \text{for } n \text{ moles of a gas}$$
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MODULE 3

INTRODUCTION

The behaviour of a system can be investigated using two approaches:

- (a) Microscopic approach
- (b) Macroscopic approach

Microscopic approach

This first approach is to find a way to take the system from the surroundings and leave the system undisturbed for a period of time such that the properties of the system become independent with time. The system is then said to be in thermal equilibrium.

Once the system is in thermal equilibrium,

wn, the average properties of the whole system are now independent with time, these average properties described the statistical properties of a system.

Macroscopic approach (physics, statistical)

Macroscopic approach

This approach is to ignore the internal structure of the system, here a system can be completely specified in terms of a small number of macroscopic quantities such as:

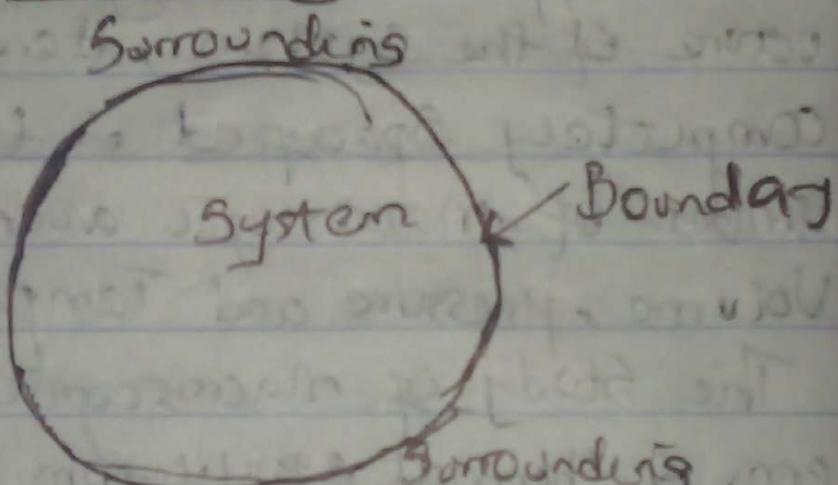
Volume, Pressure and Temperature.

The study of macroscopic properties of a system in thermal equilibrium is Thermodynamics (classical). ~~Based~~ thermodynamics is ~~the~~ macroscopic approach to study the relationships between ~~float~~, work, temperature & energy in systems at equilibrium. focussing on measurable properties like temperature, pressure & volume without diving into the microscopic details of the system (such as the individual behaviour of the constituent atoms / molecules).

Thermodynamics Termalogies

1) System, Surrounding & Universe

A thermodynamic System is defined as quantity of matter or a region in space that is under study or analysis, the region under study is clearly defined using a boundary, anything outside a boundary of a system is called the Surroundings.



System + Surroundings = Universe

2) Open, Closed and Isolated System

Based on energy and matter (or mass) the interaction of a system with the surroundings and other systems can be classified as

a) Open System

This is a system that can exchange energy and matter with its surroundings, they are also flow systems e.g. Human Body.

In this case,

$$\Delta E \neq 0$$

$$\Delta m \neq 0$$

② Closed System →

This is a system that can only exchange energy with its surroundings, they are called non-flow systems e.g. Pressure pot

In this case,

$$\Delta E \neq 0$$

$$\Delta m = 0$$

③ Isolated System →

In this system, neither energy nor matter can be exchanged e.g. flask (thermos)

In this case,

$$\Delta E = 0$$

$$\Delta m = 0$$

3) Intensive and Extensive Properties

Thermodynamic properties are observable characteristics that can be used to define the system. Some of these properties are: Pressure, Volume and temperature.

These observable properties can be divided into

Intensive and Extensive properties.

a) Intensive properties

These are properties that has the same value for any part of the system :- means that they are independent of the mass of the system e.g. Pressure, Temperature, etc.

b) Extensive properties

These are properties that depends on the mass of the system and do not have the same value for any part of the system e.g. Volume, energy, mass, enthalpy, etc.

NOTE All specific properties such as specific heat, volume and enthalpy are intensive properties.

4) Thermodynamic Path, Process and Cycle

A thermodynamic system undergoes change due to energy and mass interactions or exchanges. The mode in which ~~the~~ change of a system takes place is called The process. There are four types of thermodynamic processes,

they are :
a) adiabatic process → $\Delta Q = 0$

place
This is the process that takes at constant pressure

(i) Isochoric process → A process that takes place at constant volume.

(ii) Isothermal process → This is the process that takes place at constant temperature

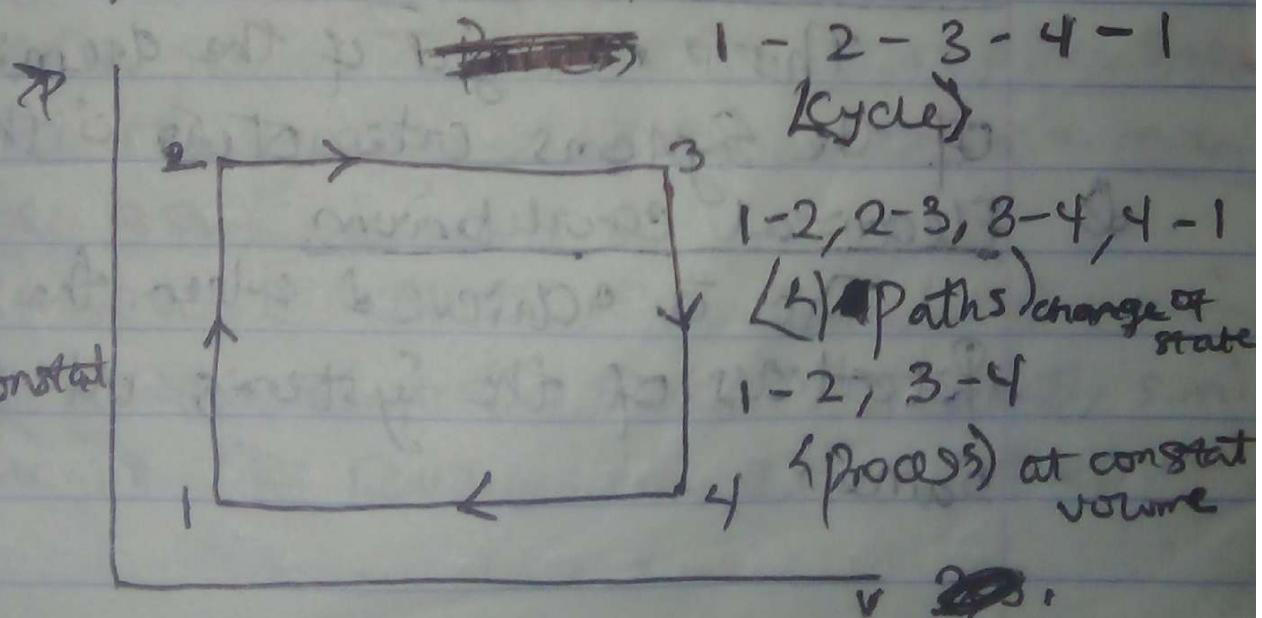
(iii) Adiabatic process → ^{a process that} takes place at no heat exchange

Phase

A path refers to the series of state

changes through which the system passes during a process.

A cycle refers to a typical sequence of a process in such a way that the initial and final states are identical.



B) Thermodynamic equilibrium

When a system is in equilibrium it means the state of the system does not change over time without the aid of any external agent.

Thermodynamic equilibrium can be maintained by ensuring mechanical, thermal, chemical and electrical equilibrium in a system.

a) Mechanical equilibrium →

This is attained when there is no tendency to change the mechanical state i.e. applied forces and developed stresses are fully balanced.

b) Thermal equilibrium →

This is achieved when there are no heat interactions.

c) Chemical equilibrium →

This is realized if the chemical potentials of the systems interacting are the same.

d) Electrical equilibrium

This is achieved when the electrical potentials of the systems interacting are the same.

Q

Reversibility & Irreversibility

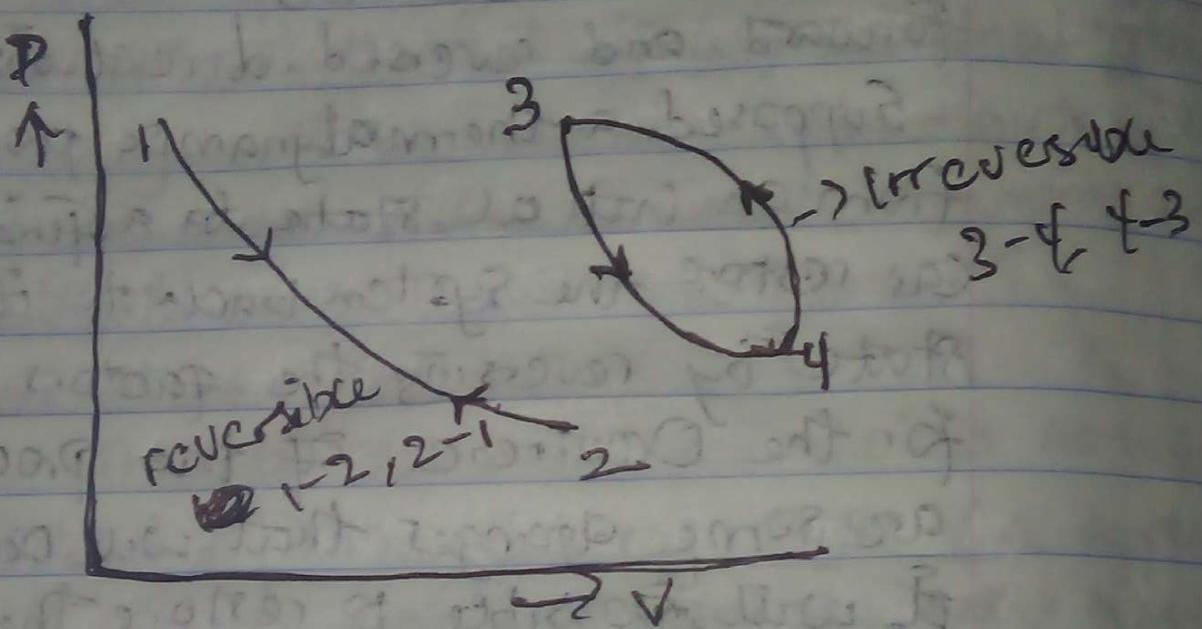
Thermodynamic processes may have a change of state occurring in two directions (forward and reversed directions)

Suppose a thermodynamic process changes from an initial state to a final state we can restore the system back to its original state by reversing the factors responsible for the occurrence of the process. There are some changes that will occur where it will ^{be} impossible to restore the system to its original state.

A thermodynamic system that is capable of ~~not~~ restoring its original state by reversing the factors responsible for the occurrence of the process is called a reversible system and the process involved is called a reversible process.

In reversible process, the forward direction of occurrence of the process is exactly similar to the reversed direction of the process.

for an irreversible process, the process takes a different path



→ Quasi Static process

Most times equilibrium state is difficult to attain in real life under such consideration Quasi static (almost static) Considered as ~~more~~ equilibrium state

A quasi static process is considered to remain in thermodynamic equilibrium just because of its infinitesimal (small) changes taking place during the occurrence of a process. Quasi static results from infinite slowing of occurrence of a process.

Phy 205.

Thermal Physics

Temperature

Temperature & Kinetic energy

Temperature is a thermodynamic quantity that expresses the degree of hotness or coldness of a body. Temperature is measured using a thermometer. Recent technology has created new ways to help measure temperature with electronics using a device called a thermistor.

Thermistor is a sensor that changes its resistance with ^{change in} temperature.

From our study of kinetic theory, we have seen that the temperature of a body or a system is proportional to the average kinetic energy of the internal atoms that make up the system.

Since temperature is a thermodynamic property to quantify the energy interactions of a body or a system, the definition of temperature as hotness or coldness of a body is conclusive.

To measure temperature accurately,

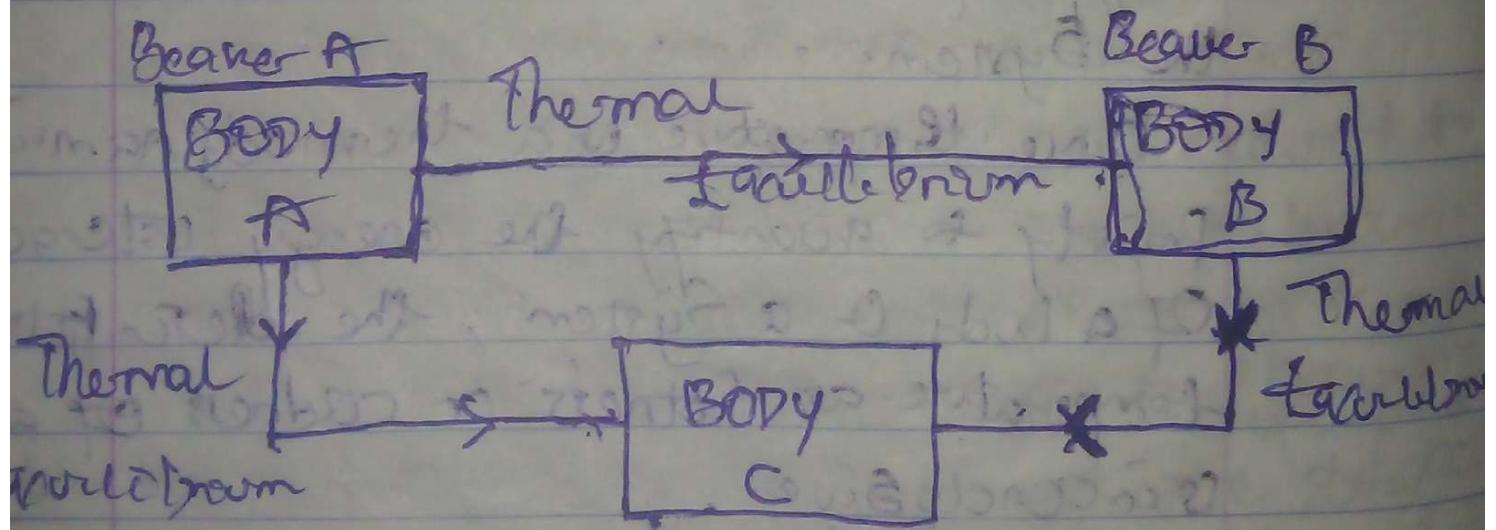
We need to measure some physical quantity or property that varies with temperature.

The underlying principle of temperature measurement is to bring a thermometer in thermal equilibrium with the body whose temperature is to be measured.

Thermometers work based on zero's law of thermodynamics.

ZEROTTI'S LAW OF THERMODYNAMICS

This law states that if bodies A & B are in thermal equilibrium with body C separately, then the two bodies A & B are also in thermal equilibrium with each other. And this is illustrated below:



Example If the temperature in Beaker-A is 60°C and Beaker-B is in thermal equilibrium with beaker A then the thermometer will also be 60°C .

Heat, Work & Internal Energy

In thermodynamics heat is a form of energy that flows between a thermodynamic system and its surroundings due to the temperature difference between them.

Heat is transferred from a system with higher temperature to a system at lower temperature. i.e. Heat can be added (absorbed) or taken from (removed) from a system.

Mathematically heat is represented as:

$$Q = m c \Delta T \quad \text{--- (1)}$$

Q = heat, m = mass, c = specific heat capacity

Capacity ΔT = Change in temperature

$$Q = m c (T_{final} - T_{initial})$$

Work = Force \times distance \rightarrow (2)

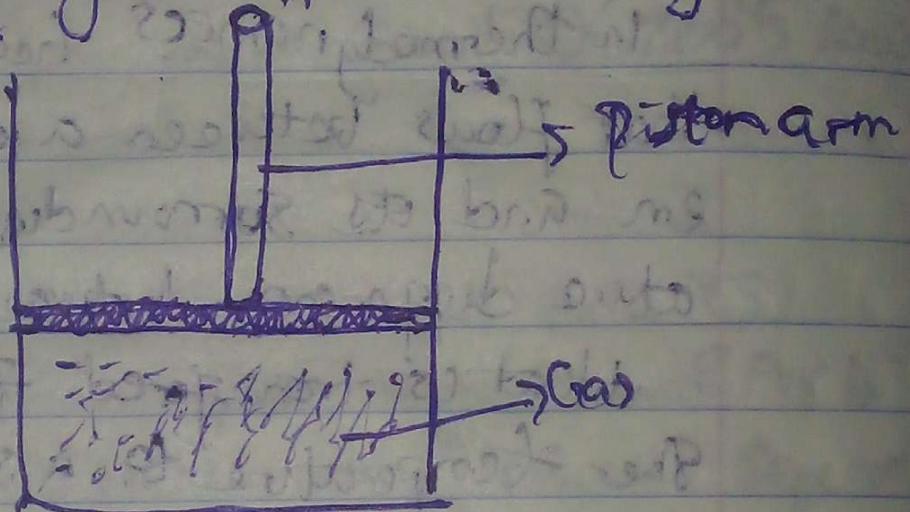
$$dW = F d\vec{x}$$

$$dW = \begin{cases} \text{Free} \\ \text{Pseudo} \\ \text{Actual} \end{cases} \rightarrow \text{--- (3)}$$

• Heat \rightarrow Thermal energy in Transit.
• done \rightarrow Mechanical energy in Transit

Work Done By EXPANDING A GAS DUE TO CHANGE IN VOLUME

Consider a gas confined in a Cylinder as shown below:



Suppose the cylinder is a cross-sectional area (A) when the piston arm is pressed down, work is done on the gas by compressing it. In similar case, when the gas expands, work is done on the piston by moving it upwards.

Let's assume the gas expands & exerts a force (F) on the piston and moves it upwards by a distance (dv)

$$\therefore \text{Change in Volume } (dv) = F \cdot dv$$

And work done in expanding the gas =

Or work done on the piston =

$$dW = F \times dx \rightarrow \textcircled{B}$$

But force = Pressure \times area $\rightarrow \textcircled{C}$

$$dW = P A dx$$

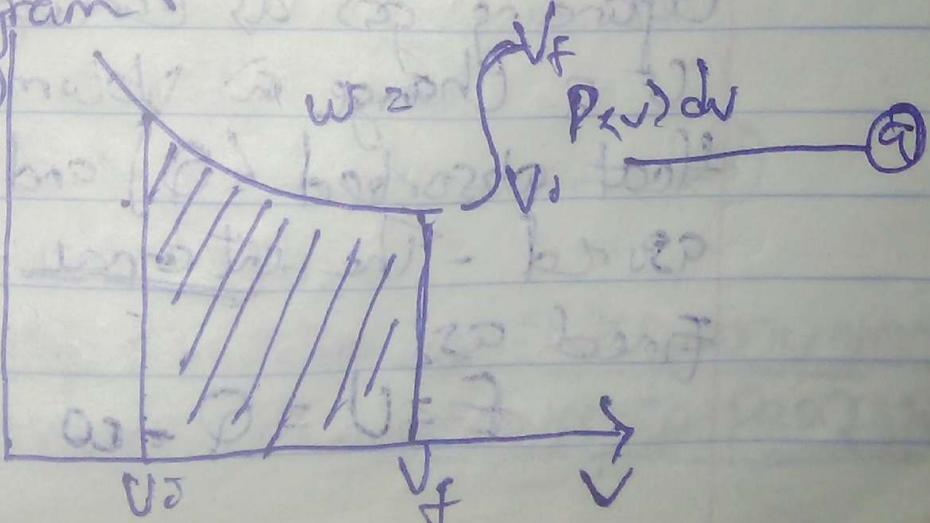
$$= P dv$$

$$W = \int_{V_i}^{V_f} P dv \rightarrow \textcircled{D}$$

It is important to note that work done during expansion is positive, while work done during compression is negative.

Equation \textcircled{D} can be represented by a PV diagram.

Such that when a gas expands from V_i to V_f , the work done is the total area under the curve of PV diagram.



INTERNAL ENERGY OF A THERMODYNAMIC SYSTEM

The total energy (E_{TOTAL}) of a system can be divided into two parts:

a) macroscopic energy → This represents energy due to the motion of a system ($\propto E$) and the potential energy (p, t)

b) internal energy (internal energy)

This represents energy of a system due to interactions of particles. When dealing with systems in equilibrium, we consider the macroscopic energy to be constant. No motion, no change, turbine, etc.

Hence the total energy of the thermal system is equal to the internal energy (U)

$$E_{\text{TOTAL}} = U \quad \text{---} \quad \textcircled{10}$$

Applying ~~this~~ this concept of internal energy to expanding gas as earlier discussed, where there is a change in volume from V_i to V_f and heat absorbed (Q) and work done ($-W$) are measured. The internal energy can then be defined as

$$U = Q - W \quad \text{---} \quad \textcircled{11}$$

FIRST LAW OF THERMODYNAMICS

This law is a statement of conservation of energy, it relates heat as Q and work as W as two different forms of energy.

This law states that the energy transferred to a closed system is equal to the sum of the increase in the internal energy of the system and the energy transferred to the surroundings by the system.

Mathematically it is $Q = \Delta E + W$

$$dQ = dE + pdV \quad \text{--- (2)}$$

$$dE = \dot{E} dt$$

E = Internal energy of the system

dE = Work done

Q = Heat transferred

Recall: $dE = \dot{E} dt$ expansion

$$(dE - dW) = \dot{E} dt - pdV$$

re-writing equation (2)

$$Q = E + pdV \quad \text{--- (3)}$$

$$dQ = dE + pdV$$

APPLICATION OF FIRST LAW OF THERMODYNAMICS TO DIFFERENT THERMODYNAMIC PROCESSES

(a) adiabatic process,

- a) Adiabatic process \rightarrow No heat is allowed to enter or leave the system.

We can achieve this by surrounding the system with thick layer of heat insulating material or by quickly performing the expansion before heat losses sets in.

Recall:

$$Q = \Delta E + \omega$$

$$\Delta Q = \Delta E + \omega$$

$Q = 0$, applying this to first law

$$0 = \Delta E + \omega$$

$$\Delta E = -\omega$$

$$E_f - E_i = -\omega$$

This means that a change in internal energy is equal to the absolute value of the work done for compression (work done on the gas).

Work is negative $\therefore W = -ve$

\therefore Expansion will return

$$\Delta E = E_f - E_i = -(-\omega)$$

$$\Delta E = +\omega$$

Expansion will indicate an increase in internal energy (This also implies an increase in

temperature)

for expansion, ΔU is positive i.e. energy becomes

$$\Delta E = -w \longrightarrow \textcircled{14}$$

This indicates a decrease in internal energy
(This implies a decrease in temperature)

Isodonic process → in this process volume

is constant

Recall 1st Law

$$dQ = dE + dw$$

$$= dE + PdV$$

$$\text{but } dV = 0$$

$$dQ = dE \rightarrow 0$$

$$Q = f_f - f_i \longrightarrow \textcircled{15}$$

This means that all the heat supplied is used to increase the internal energy of the system, no ~~work~~ is done.

Recall

$$KE = \frac{1}{2} m v^2 = \frac{3}{2} n k_B T$$

$$= \frac{3}{2} n k_B T$$

a) Isothermal Process: In that process $\Delta T = 0$
Temperature is constant

Recall 1st Law (Internal Energy)

$$dQ = dE + dU \quad \text{Since } dE \propto \Delta T \text{ and } \Delta T = 0$$

$$dQ = dU \quad \text{Therefore } dE = 0$$

Applying the first law

b) Isobaric process: In the process, pressure is constant, this process is predominant in chemistry and mechanical engineering.

In a typical change of phase problem we can apply the first law of thermodynamics as follows:

$$Q = E_{\text{final}} - E_{\text{initial}}$$

$$= E + pdV - E_0$$

If we consider a change of phase of a mass (m) of a liquid to vapour at constant pressure and temperature applying the first law of thermodynamics, we have:

$$Q = \Delta E + pdV$$

$$mL = (E_v - E_l) + p(V_v - V_l)$$

m = mass, L = latent heat, E_v = internal energy vapour state

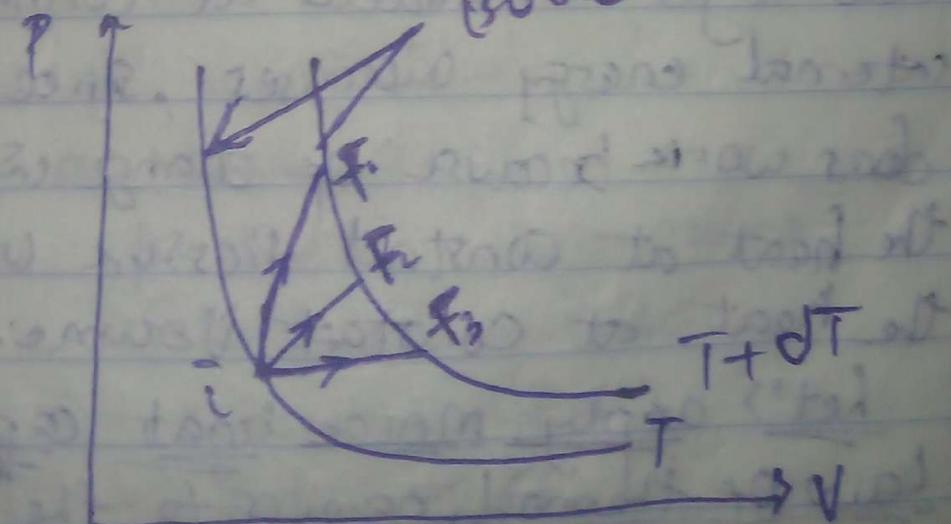
E_i = Internal energy in Liquid State

V_v = Volume in Vapour State

V_l = Volume in Liquid State

Molar Heat Capacity in Thermodynamics

CS → The energy required to raise the temperature of (n) moles of gas from an initial temperature, to a final temperature, depends on the path taken between the initial and the final state. Let's consider an ideal gas that undergoes several processes such that the change in temperature defined as dT or $\Delta T = \frac{T_f - T_i}{T}$ can be achieved by taking different paths between isotherms A & B as shown below!



for all paths taken during the process
 $(i \rightarrow T_1, T_1 \rightarrow T_2, T_2 \rightarrow T_3)$ The change
 in Temperature (ΔT) is the same, since it
 is the same. The external energy (ΔE)
 also the same & from first law of thermodynamics, the heat required for each path
 is different, this is because the work done
 (Area Under each of the curves).

Let's define the heat associated with two fundamental processes -

$$Q = nC_p dT \text{ (Isobaric process)} \quad (1)$$

$$Q = nC_v dT \text{ (Isochoric process)} \quad (2)$$

C_p = molar heat capacity at constant pressure
 C_v = molar heat capacity at constant volume

Q When a gas is heated at constant pressure, external energy increases, since the gas also does work because of change in volume then the heat at constant pressure is greater than the heat at constant volume - $C_p > C_v$

Let's apply Molar heat capacity and Law of thermodynamics to the processes

Q

Isochoric process

Recall 1st Law

$$dQ = dE + dw$$

$$dQ = dE + pdv \quad \text{--- (2)}$$

$$dQ = nC_v dT \Rightarrow dv = 0$$

$$nC_v dT = dE + 0$$

$$nC_v dT = dE$$

If molar ^{specific} heat capacity is constant
 $dE = nC_v T$

Q

Isobaric process \Rightarrow

Recall 1st Law

$$dQ = dE + dw$$

$$dQ = dE + pdv$$

$$dQ = nC_p dT$$

Since dE is the same for all paths \therefore

$$dE = nC_v dT$$

For an ideal gas

$$PV = nRT \quad (\text{differentiating})$$

$$Pdv \neq Vdp = nRdT$$

But for isobaric $\therefore dp = 0$

$$Pdv = nRdT$$

$$nC_p dT = nC_v dT + nRT$$

$$C_p = C_v + R$$

$$C_v + R = C_p \Rightarrow$$

$$R = C_p - C_v \quad \rightarrow \text{Eq 1}$$

$$- \nu b + \nu b = 0$$

$$\nu = \frac{1}{V} \cdot V = T b u \Delta v = Q L$$

$$\frac{1}{V} P$$

3) Adiabatic process →

Recall 1st Law

$$dQ = dE + dw$$

$$TdQ = dE + pdv \quad \text{--- Eq 2}$$

$$dQ = 0$$

$$dE = nC_v dT \quad \text{--- Eq 3}$$

from ideal gas $\therefore PV = nRT$

$$P = \frac{nRT}{V} \quad \text{--- Eq 4}$$

$$0 = nC_v dT + nRT \frac{dy}{dx}$$

dividing both sides by nC_v

$$dT + \frac{RT}{C_v} \frac{dy}{dx} = 0$$

Recall

$$R = C_p - C_v$$

$$dT + \left[\frac{C_p - C_v}{C_v} \right] T dy = 0$$

$$dT + \left[\frac{C_p}{C_v} - \frac{C_v}{C_v} \right] T \frac{dv}{v} = 0$$

$$dT + \left[\frac{C_p}{C_v} - 1 \right] T \frac{dv}{v} = 0$$

$$\frac{C_p}{C_v} = \gamma$$

$$dT + (\gamma - 1) T \frac{dv}{v} = 0$$

Multiply all through by $v^{\gamma-1}$

$$V^{\gamma-1} dT + T(\gamma - 1) V^{\gamma-2} dv = 0$$

$$d(LTV^{\gamma-1}) = 0$$

$$TV^{\gamma-1} = \text{constant} \quad \text{--- (23)}$$

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

We can also express the equation in terms of pressure and volume

$$PV = nRT \Rightarrow T = \frac{PV}{nR}$$

$$\left[\frac{P_1 V_1^{\gamma-1}}{nR} \right] V_1^{\gamma-1} = \left[\frac{P_2 V_2^{\gamma-1}}{nR} \right] V_2^{\gamma-1}$$

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$P V^{\gamma} = \text{constant} \quad \text{--- (24)}$$

Summary: Equations 21 $\Rightarrow R = C_p - C_v$, ~~22~~
 23 $\Rightarrow TV^{\gamma-1} = \text{constant}$

$$24 - PV^{\gamma} = \text{constant}$$

$$\textcircled{*} - \frac{C_p}{C_v} = \gamma$$

$$\textcircled{*} - T_p \frac{\gamma-1}{\gamma} = \text{constant}$$

These are all Mayer's equations

Questions

- Q) The density of a gas is 1.775 kg/m^3 at 300K and 10^5 Pa pressure. If its specific heat capacity at constant pressure is 846.5 J/kg/K , what is the ratio of its specific heat capacity at constant pressure to that at constant volume.

Solution:

$$\rho = 1.775 \text{ kg/m}^3, C_p : C_v$$

$$T = 300\text{K}, \frac{C_p}{C_v} = ?$$

$$P = 10^5 \text{ Pa}, C_p = 846.5 \text{ J/kg/K}$$

$$PV = nRT \text{ for 1 mole } \approx 1\text{kg}$$

$$1 - PV = RT$$

$$P = \frac{m}{V} \Rightarrow V = \frac{m}{P}$$

$$V = \frac{1}{1.775} \Rightarrow V = 0.5634$$

$$R = \frac{PV}{T} \Rightarrow$$

$$R = \frac{10^3 \times 0.5634}{300}$$

$$R = \frac{56340}{300} \Rightarrow R = 187.8 \approx$$

$$R = 188 \text{ J/Kmol}$$

$$\text{Recall : } R = C_p - C_v$$

$$188 = 846 - C_v$$

$$846 - C_v = 188$$

$$-C_v = 188 - 846$$

$$fC_v = f658$$

$$C_v = 658 \text{ J/Kmol}$$

$$\frac{C_p}{C_v} = \frac{846}{658} \Rightarrow 1.29$$

- 2) In a container, 2 moles of an ideal gas initially at a pressure of 1 atm and 300 K expands until its volume doubles - if the expansion is isobaric, calculate the work done ($fA_{\text{Take}} = 1.67$ and $R = 8.31 \text{ J/Kmol}$)

$$\text{SOLN (cont)}$$

$$W = PdV$$

for an ideal gas

$$PV = nRT$$

$$1 \text{ atm} =$$

$$\Delta w = P\Delta V$$

$$dw = pdV$$

$$2 PV_f - V_i \Rightarrow V_f = 2V_i$$

$$\Rightarrow PV = nRT$$

$$\frac{V}{1.013 \times 10^5} = \frac{2 \times 8.314 \times 300}{1.013 \times 10^5}$$

$$V_i = 4.92 \times 10^{-2}$$

$$V_f = 2 \times 4.92 \times 10^{-2}$$

$$V_f = 9.84 \times 10^{-2}$$

$$\omega = P(V_f - V_i)$$

$$\omega = 1.013 \times 10^5 \times (9.84 \times 10^{-2} - 4.92 \times 10^{-2})$$

$$\omega = 4.983 \times 10^3$$

$$\omega = 4.98 \times 10^3$$

- 13) 2 moles of an ideal gas expands slowly and adiabatically from a pressure of 5 atm and volume of 12m³ to a final volume of 30m³. Calculate the final pressure of the gas given that

$$\gamma = (-40)$$

SOLUTION

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

$$P_i V_i^\gamma = P_f V_f^\gamma$$

$$P_i = 5 \text{ atm}, V_i = 12 \text{ L}$$

$$P_f = ? \quad V_f = 30 \text{ L}$$

$$P_f = \frac{P_i V_i^\gamma}{V_f^\gamma} \rightarrow P_f = P_i \left(\frac{V_i}{V_f} \right)^\gamma$$

~~$$P_f = 5 \left(\frac{12}{30} \right)^{-40}$$~~

$$P_f = 1.4 \text{ atm}$$

ASSIGNMENT

- 1) When 0.005 kg of water is boiled at a constant pressure of 2 atm it becomes 3600 cm^3 of steam. Calculate the work done.
- 2) Calculate the internal energy of the water given that $L_v = 2.26 \times 10^6 \text{ J/kg}$ & $1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$

$$Q = mL$$

Important concepts of the First Law of thermodynamics

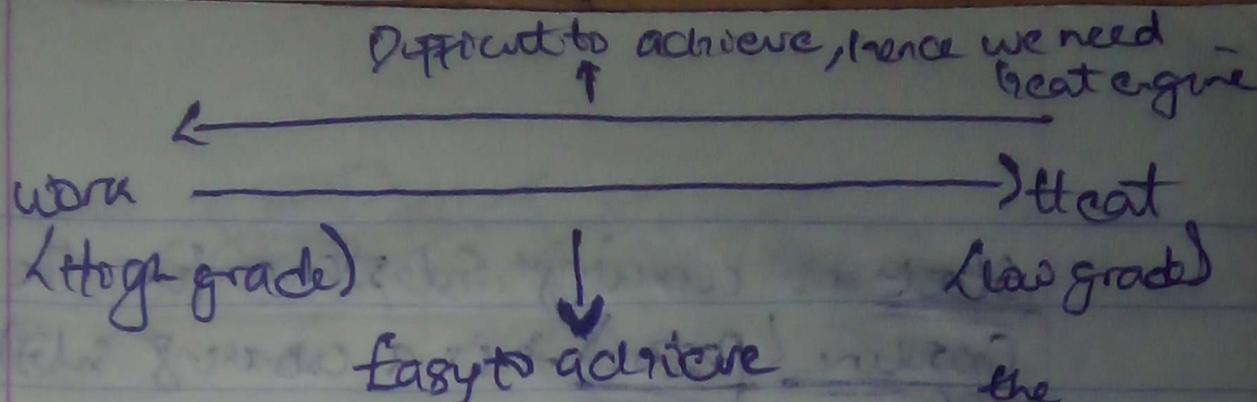
heat Reservoir

This is a system having very large heat capacity. A heat reservoir is capable of absorbing or releasing finite amount of heat energy without any appreciable change in the temperature. e.g. The atmosphere, the large river, sea, etc.

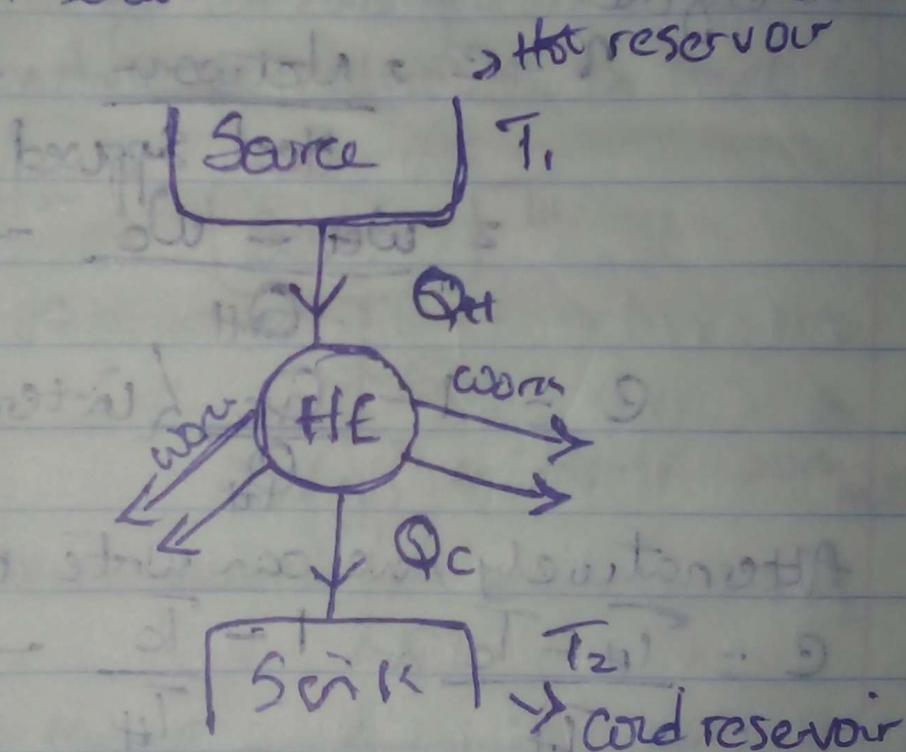
A heat reservoir that releases heat energy is called a source. While a heat reservoir that absorbs heat energy or heat is called a sink.

Other applications of the First law of thermodynamics

- 1) heat engine: This is a device used to convert heat to work, naturally conversion of work to heat is easy to realise. But vice-versa is simple to realise. Heat and work are classified into two forms of energy:
 - 1) Heat \rightarrow low grade energy
 - 2) Work \rightarrow High grade energyTo convert



A heat engine receives heat from a source, transforms some portion of that heat into work, and rejects the balanced heat to a sink as shown below:



Block diagram of a heat engine
Heat engine does work

All the processes occurring in a heat engine constitutes a cycle. Example of a heat engine a gas turbine in a gas plant.

Every engine utilises a working substance to operate - for example

Steel is a working substance for the gas turbine
Petrol → is a working substance for
an ~~car~~ engine

Water is a working substance for steam power

We can calculate the efficiency of the heat engine

$$\eta = \frac{e}{c} = \frac{\text{Net work}}{\text{Heat supplied}} \quad \text{--- (25)}$$

$$= \frac{W_{et} - W_c}{Q_{Ht}} = \frac{Q_{Ht} - Q_c}{Q_{Ht}}$$

$$e = 1 - \frac{Q_c}{Q_{Ht}} \quad \{ \text{in terms of heat} \} \quad \text{--- (26)}$$

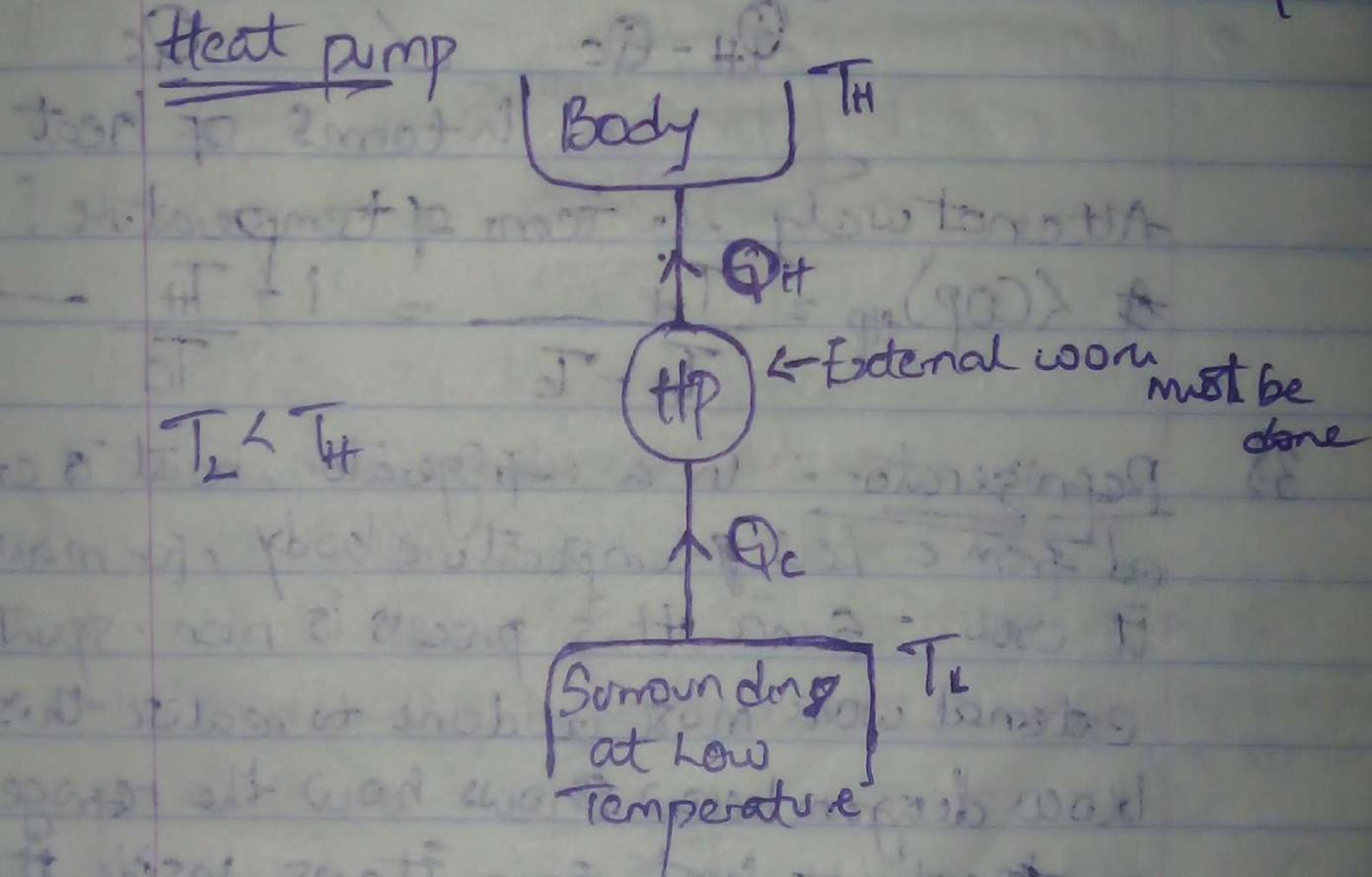
Alternatively, we can write it in terms of Temperature

$$e = \frac{T_{Ht} - T_c}{T_{Ht}} = 1 - \frac{T_c}{T_{Ht}} \quad \text{--- (27) \quad Pressure}$$

2) heat pump → This refers to a device used for extracting heat from a low temperature surroundings and sending it to high temperature body while operating in a cycle. A heat pump maintains a body or a system at a temperature higher than the temperature of the surroundings.

~~PHY 201~~
~~General Physics I (Elementary Modern Physics)~~

Since a heat pump transfers heat from a low-temperature to a high temperature, which is a non-spontaneous process, external work must be done to realise such heat transfer.



NOTE The purpose of a heat pump is to maintain a body at a higher temperature. Since it is not a work producing machine unlike the heat engine, we quantify the performance using

A parameter called the Co-efficient of Performance (C.O.P) \rightarrow It is the ratio of the desired effect and the Net work done to produce desired effects.

$$(COP)_{HP} = \frac{\text{Desired effect}}{\text{Net work done}}$$

$$\Rightarrow \frac{Q_H}{Q_H - Q_C} = 1 + \frac{Q_H}{Q_C} \quad - (2)$$

in terms of heat

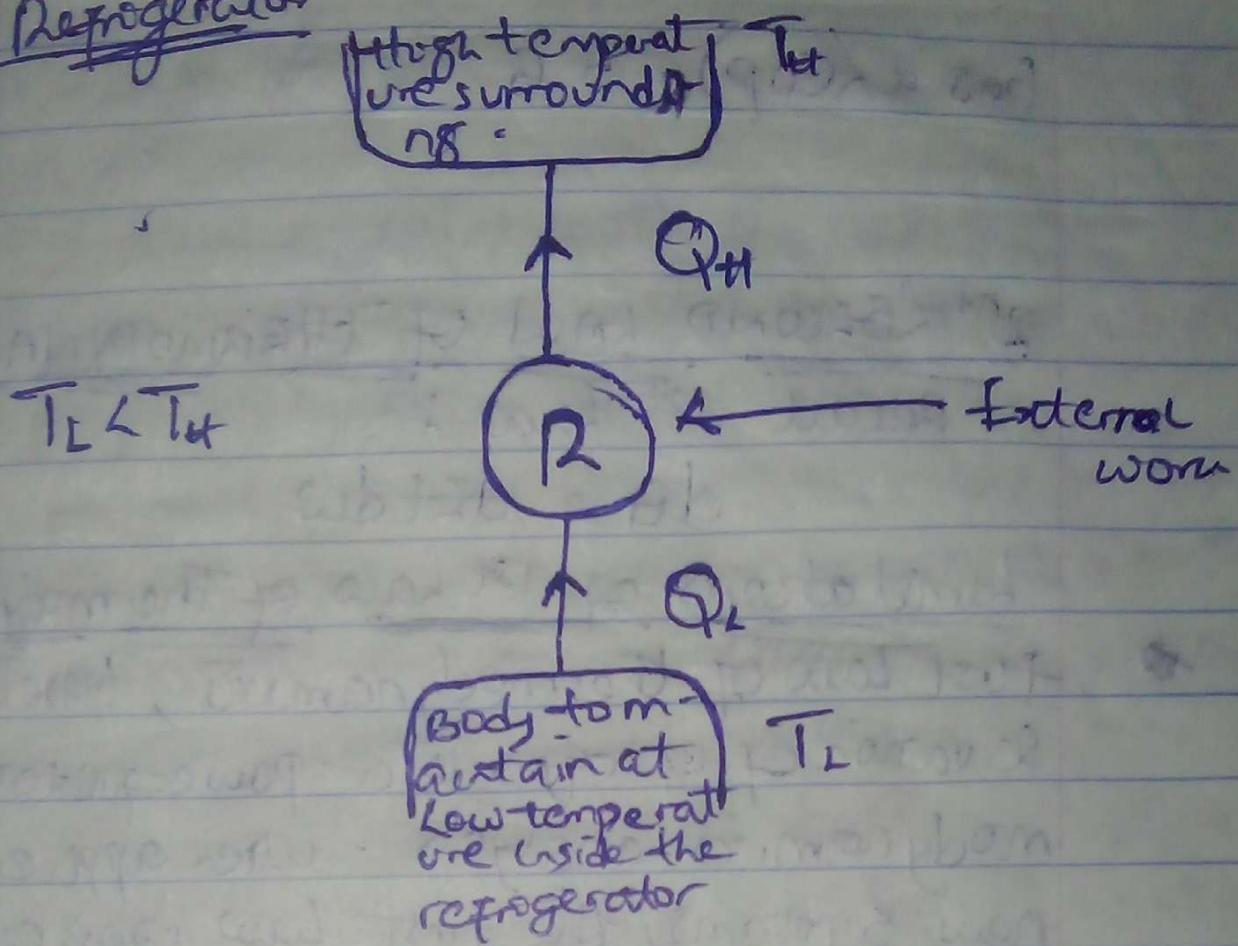
Alternatively, in terms of temperature

$$(COP)_{HP} = \frac{T_H}{T_H - T_C} = 1 + \frac{T_H}{T_C} \quad - (2)$$

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Refrigerator \rightarrow In a refrigerator, heat is extracted from a low temperature body, for maintaining it cool. Since this process is non-spontaneous external work must be done to realise this. The block diagram below shows how the refrigerator extracts heat from items inside it, in order to maintain the items at low-temperature through the action of the workdone by the motor and rejects the heat to the high temperature surroundings.

Refrigerator



$$(\text{COP})_R = \frac{\text{Desired Effect}}{\text{Net work done}}$$

$$\Rightarrow \frac{Q_L}{Q_H - Q_L} \quad \text{(in terms of heat)} \quad (30)$$

Alternatively, we can write in terms of temperature

$$(\text{COP})_R = \frac{T_L}{T_H - T_L} \quad (31)$$

The relationship between $(\text{COP})_{HP}$ and $(\text{COP})_R$ is given as:

$$(\text{COP})_{HP} = (\text{COP})_R + 1 \quad (32)$$

A good commercial refrigerator for home use

has a Cop) = 6

2nd SECOND LAW OF THERMODYNAMICS

Recall 1st Law:

$$dQ = dE + dw$$

LIMITATIONS OF 1ST LAW OF THERMODYNAMICS

First Law of thermodynamics, based on conservation of energy, is a powerful tool for thermodynamics analysis - when applied to some new systems, the first law was observed to stand valid theoretically even though the processes could not be realised practically. Some of the limitations of the first law are:

- (1) It does not differentiate between heat and work and assumes a 100% convertibility of one into the other form.
- (2) Heat \rightarrow Work (100% conversion possible)
Work \rightarrow Heat (not 100% conversion possible)
- It does not explain the direction of a process according to First (or) "Law". Theoretically permits heat transfer from a low temperature body,

to a high temperature body which is not visibly practical

~~Note~~ 2nd Law explains both the nature and the direction of a process. It even outlines conditions for a process to occur practically.

The violation of practically visible process by the 1st Law of thermodynamics led to the conception of the device called \rightarrow Perpetual motion machine of the 1st kind $Lpmn^{-1}$

When heat ~~engine~~ and heat pump were analysed as applications of the 1st Law it was based on the fact that heat and work are the thermodynamic parameters by which they operate. However, their designs and practical workings based on both the 1st Law and the 2nd Law of thermodynamics.

~~This~~ This means that the 2nd Law of thermodynamics came as an embodiment of real life happenings while retaining the basic nature of the first law.

There are two statements of the second law of thermodynamics:

④ ^{Clausius} The ~~State~~ Statement → He said that it is impossible to have a device that while working in a cycle produces no effect other than heat from a body at a low-temperature to a body at a high-temperatue.

Alternatively, we can ^{rephrase} Clausius statement to say; No process is possible whose sole result is to transfer heat from a colder body to a hotter body.

2) The Kelvin Planck Statement → He stated that it is impossible for a device operating in a cycle to produce a net work while exchanging heat with bodies at a fixed temperature.

Alternatively, we can rephrase the Kelvin Planck's statement as; No process is possible whose sole result is the complete conversion of heat ~~to~~ → work.

b) For any device operating in a cycle the efficiency is always less than 100% to fully understand the application of the second law.

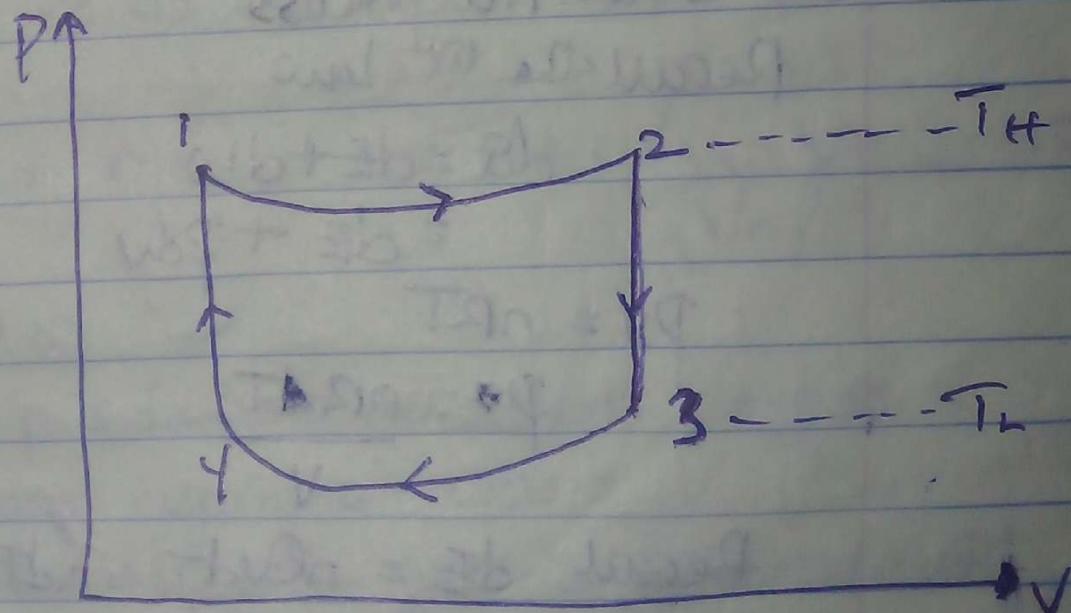
we would look at the Carnot engine as an example

CARNOT ENGINE & CARNOT CYCLE

An engine is any device that operates in a cycle converting energy into mechanical work.

A Carnot engine is a heat engine that operates based on the process called a Carnot cycle.

A Carnot cycle is a reversible thermodynamic cycle comprising of 4 (four) reversible processes as shown in the Pv diagram below:



Carnot cycle

Analysis of the Carnot cycle

- i) path 1 → 2: This is a reversible isothermal

process. ~~increasing temperature~~

- 2) Path 2 \rightarrow 3: This is a reversible adiabatic process. The gas expands.
- 3) Path 3 \rightarrow 4: This is a reversible isothermal process - The gas compresses and heat Q is released at low temperature.
- 4) Path 4 \rightarrow 1: This is a reversible adiabatic process where work is done \bullet on the gas.

Path 3 \rightarrow 4 Isothermal Process

Applying the 1st Law of Thermodynamics to the isothermal process

Recall the 1st Law

$$\begin{aligned} dQ &= dE + dW \\ &\approx dE + PdV \end{aligned}$$

$$PV = nRT$$

$$P = \frac{nRdT}{V}$$

Recall $dE = nC_V dT$ ($dT = 0$)

$$\therefore \int dQ = PdV \quad (dE = 0)$$

$$= \int \frac{nRT}{V} dV$$

$$Q = nRT \ln \left(\frac{V_2}{V_1} \right)$$

Adiabatic

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

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

$$\gamma = \frac{C_p}{C_v} = 1 + \frac{\beta}{\alpha}$$

① Path 1 → 2

- a) Process is a reversible isothermal process.
- b) Heat is added $\rightarrow Q_{th}$
- c) Path is maintained at constant temperature (T_{th})

② Equations $\Rightarrow Q_{th} = nRT \ln \left(\frac{V_2}{V_1} \right) \quad \text{--- } ②$

2) Path 2 → 3

- a) Process a adiabatic reversible process
- b) Adiabatic expansion occurs
- c) Work is done by the gas due to expansion

③ Relationship between T_2, V_2, T_3, V_3

$$\left(\frac{T_3}{T_2} \right) = \left(\frac{V_3}{V_2} \right)^{\gamma} \quad \text{--- } ③$$

3) Path 3 → 4

- a) process is isothermal
- b) it is maintained at constant temperature (T_L)
- c) Heat is released
- d) So we have a relationship between

$$Q_L = -nRT_L \ln \left(\frac{V_4}{V_3} \right) \rightarrow \textcircled{D}$$

4) Path 4 → 1

- a) process is adiabatic
- b) compression occurs
- c) work is done on the gas due to compression
- d) And the relationship between T & V is given as:

$$\left(\frac{T_L}{T_4} \right) = \left(\frac{V_1}{V_4} \right)^{\gamma-1} \rightarrow \textcircled{D}$$

Eliminating T_4 & T_L from ~~$\textcircled{B} \& \textcircled{D}$~~

$$\Rightarrow \frac{V_1}{V_2} = \frac{V_3}{V_4} \quad (\text{Volume})$$

Eliminating V_2 & V_1 from $\textcircled{A} \& \textcircled{C}$

$$\Rightarrow \frac{Q_{th}}{Q_L} = \frac{T_{th}}{T_L}$$

Recall,

$$\text{Efficiency} = \frac{\text{Net work}}{\text{Heat Supplied}}$$

∴ The efficiency of a Carnot engine =

$$E = \frac{Q_{H\ddagger} - Q_L}{Q_{H\ddagger}} = 1 - \frac{T_L}{T_{H\ddagger}}$$

Alternatively; it can be written as (in terms of temperature)

$$\frac{T_{H\ddagger} - T_L}{T_{H\ddagger}} = 1 - \frac{T_L}{T_{H\ddagger}}$$

NOTE: If we know the heat absorbed & heat rejected

Carnot Theorem

This states that any engine cannot have efficiency more than that of a reversible engine operating between the same temperatures.

Other ways of putting this are :-

- 1) All of these engines working between two given temperatures none is more efficient than a Carnot engine.
- 2) The efficiency of a reversible engine does not depend on the working fluid in the cycle.

Thermodynamic Temperature Scale

A standard thermometer has two components:

- ① A thermometric substance that is sensitive to changes e.g. alcohol, mercury, etc.
- ② It has a container that houses the thermometric substance and provides a scale to read the temperature changes.

However after Carnot's theorem was stated & verified there was a need to develop a temperature scale that would be independent of a thermometric substance.

The new temperature scale was developed by assigning numerical values to different temperatures using a reversible heat engine since the efficiency of the reversible heat engine depends on the temperatures of the reservoir we can say that

$$\eta = f(T_H, T_L) \quad \rightarrow ①$$

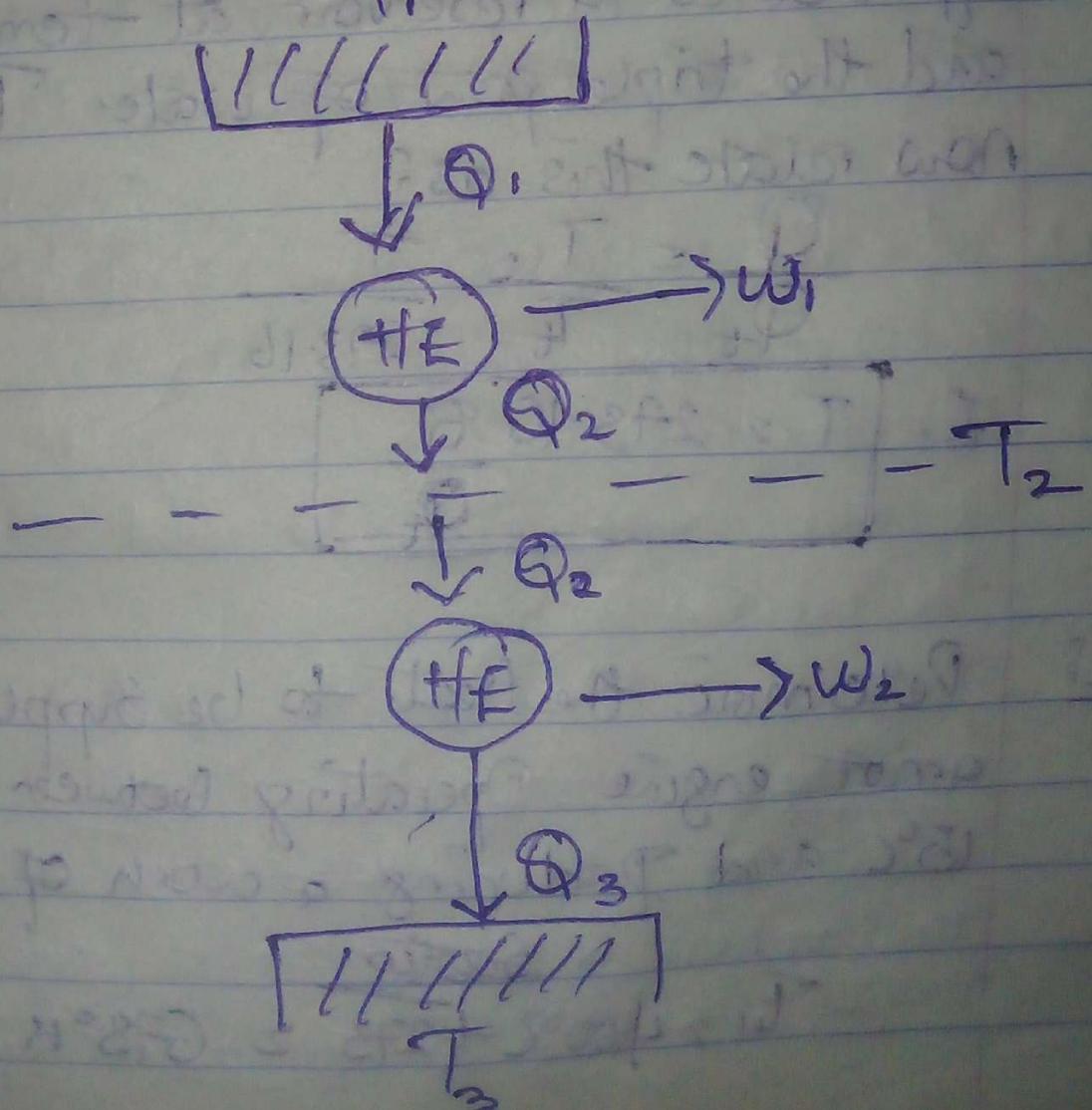
Efficiency is a function of $\frac{\text{Temperature of the source}}{\text{Temperature of the sink}}$

$$\text{Recall } \eta = 1 - \frac{Q_{out}}{Q_{in}} = f(T_H, T_L) \quad ②$$

Since $\frac{Q_{HT}}{Q_L} = \frac{T_H}{T_L}$, then we can rewrite
(2B)

equation 2 using an arbitrary function Φ
 $\therefore \frac{Q_{HT}}{Q_L} = \Phi(T_H, T_L) \quad \text{--- } (3)$

Assuming we have two heat engines, operating between a source (T_H) & sink (T_L) in between there is a hypothetical one at a temperature $\frac{1}{2}(T_1 + T_2)$



$$\frac{Q_1}{Q_2} = \phi(T_1, T_2)$$

$$\frac{Q_2}{Q_3} = \phi(T_2, T_3)$$

$$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \times \frac{Q_2}{Q_3}$$

$$\frac{Q_1}{Q_3} = \phi(Q_1, Q_2) \times \phi(Q_2, Q_3)$$

Applying this to the Carnot engine, operating between a reservoir at temperature T_1 and the triple point of water T_t we can now relate this as:

$$\frac{Q_1}{Q_t} = \frac{T_1}{T_t} = \frac{T}{273.16}$$

I. $T = 273.16 \frac{Q_1}{Q_t}$

Determine the heat to be supplied to a Carnot engine operating between 400°C and 15°C and producing a work of 200kJ

Solution

$$T_1 = 400^\circ\text{C} + 273 = 673^\circ\text{K}$$

$$T_L = 15^\circ\text{C} + 273 = 288^\circ\text{K}$$

$$\text{wärmeleistung} : 200 \text{ kJ} = Q_H - Q_L$$

Recall

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L}$$

$$\frac{Q_H}{Q_L} = \frac{693}{288}$$

$$\therefore \frac{Q_H}{Q_L} \times \frac{693}{288} \quad \text{---} \quad \text{②}$$

$$Q_H = ?$$

$$Q_H - Q_L = 200 \times 10^3 \text{ J} \quad \text{---} \quad \text{③}$$

$$Q_L = 149 \cdot 6 \text{ kJ}$$

$$Q_H = 349 \cdot 6 \text{ kJ}$$

III ^{Zerth's} The ~~second~~ Law of thermodynamics helped to establish the principle of Temperature measurement.

The First Law of thermodynamics helped to understand the relationship between heat & work and how it affects the internal energy of a system.

The second Law of thermodynamics has been declared in two statement forms, will still need a mathematical function which will serve as a parameter to determine:

- a) whether a process can be ~~possible~~ ^{feasible} spontaneous or non-spontaneous).
- b) whether a process is reversible, irreversible or not even ~~possible~~ ^{possible} and the nature of the process.

This mathematical function is called Entropy.

Entropy is the measure of disorderliness or randomness in a system.

It is a key concept used to describe the

direction of a thermodynamic process

Claussius Inequality

This inequality forms the basis of the definition of Entropy, it is a mathematical statement of the Second Law of Thermodynamics.

It states that the cyclic integral of $\frac{dQ}{T} \leq 0$

$$\oint \frac{dQ}{T} \leq 0 \rightarrow \textcircled{1}$$

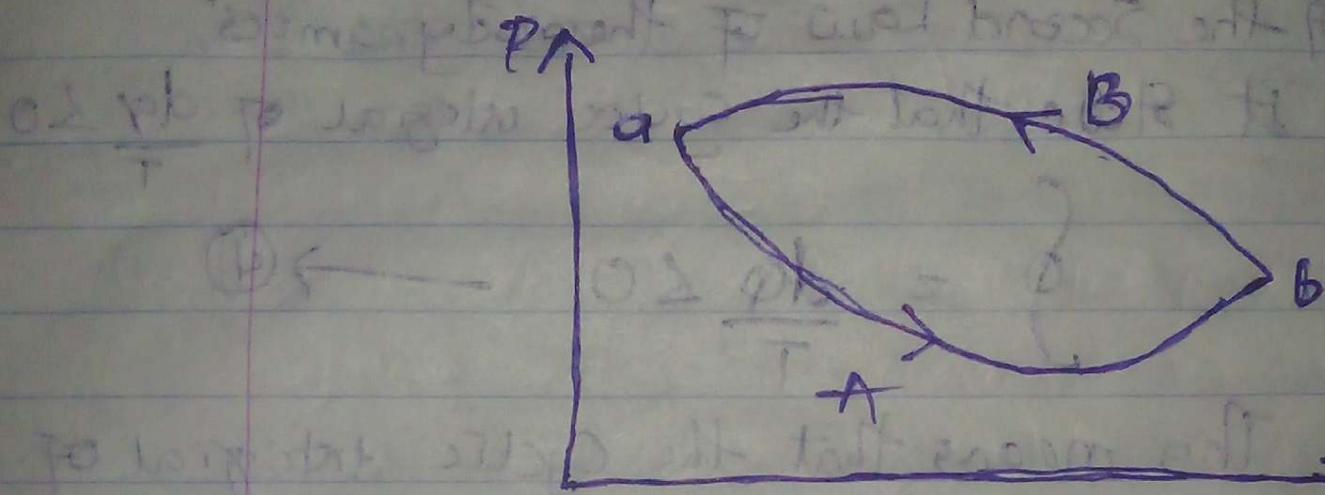
This means that the Cyclic integral of every process or cycle is always less than or equal to Zero (0). This is valid for a reversible or irreversible process:

$$\oint \frac{dQ}{T} \leq 0 \rightarrow \begin{array}{l} \text{Irreversible} \\ \text{Process} \end{array} \text{cycle}$$

$$\oint \frac{dQ}{T} = 0 \rightarrow \begin{array}{l} \text{reversible} \\ \text{process/cycle} \end{array}$$

$$\oint \frac{dQ}{T} > 0 \rightarrow \begin{array}{l} \text{impossible} \\ \text{cycle} \end{array}$$

Since equation ④, is a closed integral
 this means that the entropy (S) does not depend on the path followed rather it depends on the end point of the process / cycle.



Using Clausius's inequality;

$$\int_a^b \frac{dQ}{T} + \int_b^a \frac{dQ}{T} = 0 \quad \text{--- ⑤}$$

Path A

$$\int_a^b \frac{dQ}{T} = - \int_b^a \frac{dQ}{T} \rightarrow ⑥$$

$$\int_a^b \frac{dQ}{T} \geq \int_a^b \frac{dQ}{T} \rightarrow ⑦$$

$$S = \int \frac{dQ}{T}$$

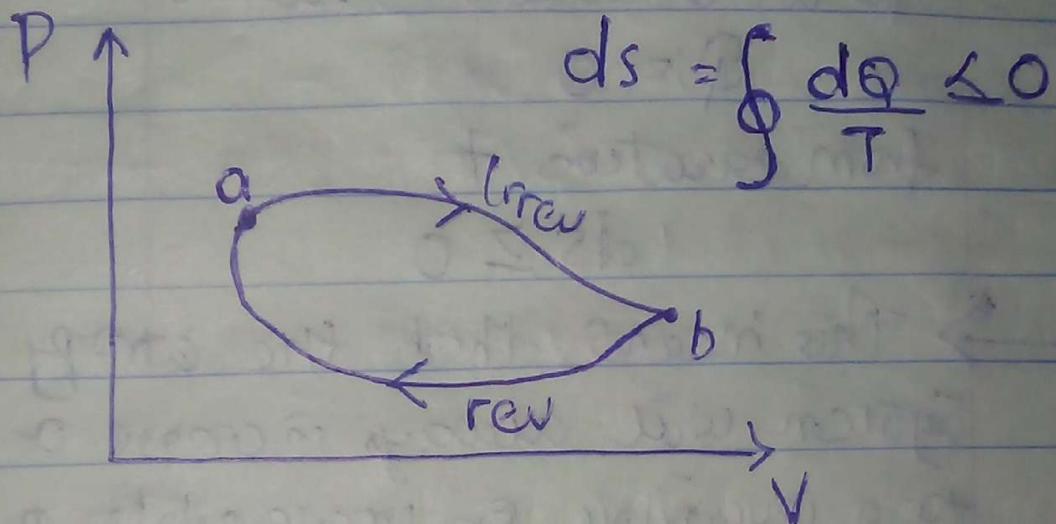
$$\int_a^b \frac{dQ}{T} = \int_a^b \frac{dQ}{T} = S_b - S_a$$

path A path B

②

unit of Entropy

$$\langle S \rangle = J/K$$



$$\int_a^b \frac{dQ}{T} + \left\langle \int_b^a \frac{dQ}{T} \right\rangle_{rev} \leq 0$$

$$\int_a^b \frac{dQ}{T} \leq - \left\langle \int_b^a \frac{dQ}{T} \right\rangle_{rev}$$

$$\int_a^b \frac{dQ}{T} \leq \left\langle \int_a^b \frac{dQ}{T} \right\rangle_{rev}$$

Claussius inequality

$$ds = \left\langle \frac{dQ}{T} \right\rangle_{rev}$$

$$\int \frac{dQ}{T} \leq dS \quad (1)$$

$$[dS \geq \frac{dQ}{T}] \quad (2)$$

for an isolated system:

$$Q = 0$$

from equation 7.

$$dS \geq 0$$

→ This means that the entropy of an isolated system will always increase or remain constant for a reversible or irreversible process. The statement is known as The Entropy Principle.

The Universe is an isolated system.

Applying this to the Universe:

Recall:

$$\text{Universe} = \text{Surroundings} + \text{System}$$

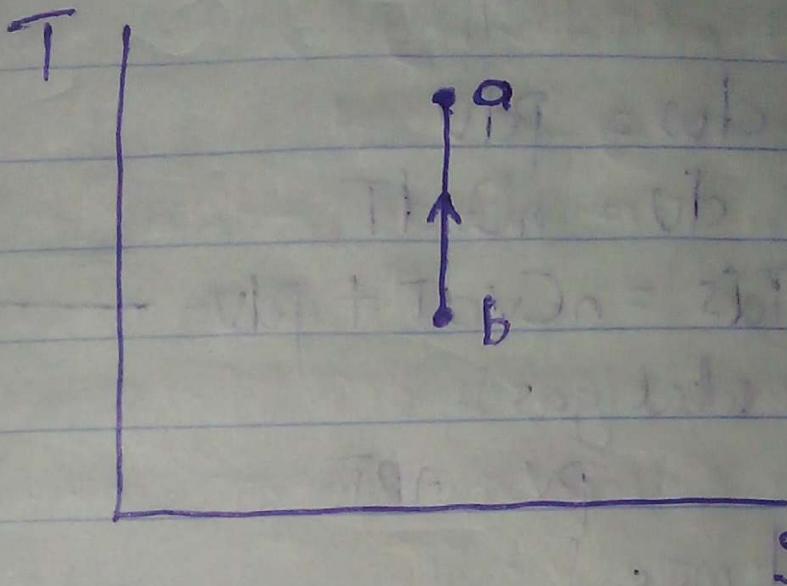
$$dS_{\text{universe}} \geq 0$$

~~Applying this to the Universe~~

Application of Entropy Changes

Isoentropic Process

This is a process that has entropy constant
i.e $dS = 0$



$$\Delta S_{a \rightarrow b} = 0$$

$$\Delta S_{b \rightarrow a} = 0$$

If $dS = 0$ then,

$$dQ = 0$$

Since there is no heat interaction during the process, you can say that the process is an adiabatic process.

Note: An adiabatic process may or may not be isentropic but every reversible adiabatic process is isentropic i.e.

From 1st Law

$$dQ = dU + dW$$

for an isentropic process \rightarrow

Recall

$$ds = \frac{dq}{T} \quad \therefore dQ = Tds$$

$$\& dw = Pdv$$

$$\text{Also, } dv = nCvdt$$

$$Tds = nCvdt + Pdv \quad \text{--- (8)}$$

for an ideal gas

$$PV = nRT$$

For 1 mole

$$PV = RT$$

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

From equation 8 we have;

$$Tds = nCvdt + RT \frac{dv}{V}$$

$$ds = nCv \frac{dT}{T} + R \frac{dv}{V}$$

$$\int_1^2 ds = nCv \int_1^2 \frac{dT}{T} + R \int_1^2 \frac{dv}{V}$$

$$\left[S_2 - S_1 = nCv \left[\ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \right] \right] \quad \text{--- (9)}$$

This is when C_V is constant
we can derive equation ④ in terms of Entropy

Mathematically:

$$\text{Entropy } (h) = Ut + Pv \quad \text{--- } ③$$

$$dh = du + d(pv)$$

$$dh = du + pdv + vdp$$

$$dh = dQ + Vdp$$

$$dh = Tds + Vdp$$

$$Tds = dh - Vdp$$

$$dS = \frac{dQ}{T}$$

$$dQ = Tds$$

Mathematically:

$$dE = nC_VdT$$

$$dh = nC_pdT$$

For one mole of an ideal gas:

$$PV = RT$$

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

$$ds = nC_p \frac{dT}{T} - \frac{Rdp}{P}$$

$$\int_1^2 ds = nC_p \int_1^2 \frac{dT}{T} - R \int_1^2 \frac{dp}{P}$$

$$\left[S_2 - S_1 = nC_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \right] \quad ④$$

Example Calculate the change in entropy of air if it is throttled from 5 bar at 27°C to 2 bar adiabatically - [take $C_p = 1.004 \text{ kJ/kgK}$, $R = 0.287 \text{ kJ/kgK}$]

$$S_2 - S_1 = n C_p \underbrace{\ln \frac{T_2}{T_1}}_{\text{SOLENT}} - R \ln \frac{P_2}{P_1} =$$

for a throttled process Entropy at point One is the same as point Two (2)

$$\therefore T_1 = T_2$$

$$S_2 - S_1 = 1 \times 1.004 \left\{ \ln \frac{300}{500} \right\} - 0.287 \left\{ \ln \frac{2}{5} \right\}$$

$$S_2 - S_1 = 0.264 \text{ J/K}$$

- 2) A heat engine operates ~~between~~ source at 600 K and sink at 300 K, heat supplied by source is 600 kcal/s. Evaluate the feasibility and the nature of the cycle for the following conditions.

When heat rejected is 200 kcal/s

When heat rejected is 400 kcal/s

When heat rejected is 250 kcal/s

Solution

$$\oint \frac{dQ}{T}$$

$$\left\langle \frac{Q}{T} \right\rangle_{\text{source}} - \left\langle \frac{Q}{T} \right\rangle_{\text{sink}}$$

a) $\oint \frac{dQ}{T} \rightarrow \left\langle \frac{500}{600} \right\rangle - \left\langle \frac{200}{300} \right\rangle$

$$\rightarrow 0.833 - 0.667$$

$\rightarrow 0.166$ < The process is (impossible)
(irreversible/not feasible)

b) $\oint \frac{dQ}{T} = \left\langle \frac{500}{600} \right\rangle - \left\langle \frac{400}{300} \right\rangle$

$$\rightarrow 0.833 - 1.333$$

$\rightarrow -0.5$ (irreversible/impossible)

c) $\oint \frac{dQ}{T} = \left\langle \frac{500}{600} \right\rangle - \left\langle \frac{250}{300} \right\rangle$

$$\rightarrow 0.833 - 0.833$$

$\rightarrow 0$ < reversible process/possible

MATHEW'S RELATIONS

The thermodynamic properties, can be grouped into two types

- measurable properties such as, pressure, volume and temperature, these properties can be measured directly.
- immeasurable / non-measurable properties these properties cannot be measured directly. e.g., Entropy (S), Enthalpy (H) ~~Heat~~, Gibbs free energy (G), Helmholtz free energy (F).

INTRODUCTION

Catalysis is what we use to solve Maxwell relations of a thermodynamic system because a thermodynamic system observes changes from time to time. Undergoes

EXAMPLE → work done by an expanding gas at constant pressure is given as

$$dw = PdV \quad \text{--- (1)}$$

workdone is a function of V

$$w = f(V) \quad \text{--- (2)}$$

(e.g.) Isobaric process : $w = P(V_2 - V_1)$

Isothermal process : $w = nRT \ln \left(\frac{V_2}{V_1} \right)$

When we have One Variable we use $\frac{dy}{dx}$
when we have more than One Variable we use
the Partial derivative $\frac{\partial y}{\partial x}$

→ Workdone is a function of Only Volume

GASE 2F

from 1st law of thermodynamics:

$$dQ = dU + dw \quad \textcircled{3}$$

2nd law

$$ds = \frac{dQ}{T} \therefore dQ = Tds$$

$$dU = Tds - dw$$

From equation ~~1~~ $dU = Tds - Pdv$

$$dU = Tds - Pdv \quad \textcircled{4}$$

$$U = f(S, V)$$

U is a function of Entropy & Volume

Exercise

Given that $f = x^2 + y^2$

$$\left(\frac{\partial f}{\partial x} \right)_y = 2x$$

$$\left(\frac{\partial f}{\partial y} \right)_x = 2y$$

when there is a constant you do not differentiate

Exercise

$$f = x^2y + 2xy^2$$

$$\left(\frac{\partial f}{\partial x} \right)_y$$

$$= 2xy + 2y^2$$

$$x^n = n x^{n-1} \quad \text{and such as}$$

$$\left(\frac{df}{dy} \right)_x = x^2 + 4xy$$

$$\left(\frac{\partial F}{\partial x^2} \right)_y = 2y$$

$$\left(\frac{\partial^2 F}{\partial y^2} \right)_x = 4x$$

$$\frac{\partial}{\partial y} \left(\frac{\partial F}{\partial x} \right) = 2x + 4y$$

$$\frac{\partial}{\partial x} \left(\frac{\partial F}{\partial y} \right) = 2x + 4y$$

$$\therefore \frac{\partial^2 F}{\partial y \partial x} = \frac{\partial^2 F}{\partial x \partial y}$$

This only works for continuous functions.

Frost differentials

This is the most important partial derivative concept in thermodynamics. Suppose we have a system given as

~~$$F = f(x, y)$$~~

When there is a small change in x , from x to $x + \Delta x$ and a small change in y , from y to $y + \Delta y$, the corresponding change in F using the concept of partial derivative, we can find

that is $df = \left\langle \frac{\partial f}{\partial x} \right\rangle dx + \left\langle \frac{\partial f}{\partial y} \right\rangle dy$

Suppose $\left\langle \frac{\partial f}{\partial x} \right\rangle_y = P$

$$\left\langle \frac{\partial f}{\partial y} \right\rangle_x = Q$$

We can write it as

$$df = Pdx + Qdy$$

Suppose P & Q are continuous we have that

$$\left\langle \frac{\partial P}{\partial y} \right\rangle_x = \frac{\partial}{\partial y} \left[\left\langle \frac{\partial f}{\partial x} \right\rangle_y \right]_x = \frac{\partial^2 f}{\partial y \partial x}$$

$$\left\langle \frac{\partial Q}{\partial x} \right\rangle_y = \frac{\partial}{\partial x} \left[\left\langle \frac{\partial f}{\partial y} \right\rangle_x \right]_y = \frac{\partial^2 f}{\partial x \partial y}$$

Thermodynamic Relations

Thermodynamic properties like pressure, volume and temperature can be directly measured experimentally. There are other thermodynamic properties such as internal energy (U), Enthalpy (H), Helmholtz free energy (F) and gibbs function (G) which cannot be measured directly.

There is need to develop thermodynamic relat

cons which would assist to estimate these properties. Maxwell relation provides a way to express these measurable and non-measurable properties using partial differential equations.

Derivation of Maxwell Relations

* Internal Energy (U) = This is the energy of a system due to its molecular constitution and motion. Since most thermodynamic systems are taken to be in equilibrium, external forces are neglected so that the thermal energy can be taken as the only energy due to motion and interaction of the particles that make up the system.

from 1st law:

$$dQ = dU + dw$$

$$\therefore dw = dQ - dU$$

Recall:

$$dQ = Tds \quad \& \quad dw = pdv$$

$$\therefore dU = Tds - pdv$$

Hence, $U = f(S, V)$

Exact differentials

$$ds = \left. \frac{\partial u}{\partial s} \right\rangle_v ds + \left. \frac{\partial u}{\partial v} \right\rangle_s dv \\ = \left. \frac{\partial u}{\partial s} \right\rangle_v = T$$

$$\left. \frac{\partial u}{\partial v} \right\rangle_s = -P$$

Differentiating further

$$\frac{\partial}{\partial s} \left(\left. \frac{\partial u}{\partial s} \right\rangle_v \right) = \frac{\partial^2 u}{\partial s^2} = \left. \frac{\partial T}{\partial v} \right\rangle_s$$

$$\frac{\partial}{\partial s} \left(\left. \frac{\partial u}{\partial v} \right\rangle_s \right) = \frac{\partial^2 u}{\partial s \partial v} = - \left. \frac{\partial P}{\partial s} \right\rangle_v$$

so that (for a continuous function)

Hence, $\left. \frac{\partial T}{\partial v} \right\rangle_s = - \left. \frac{\partial P}{\partial s} \right\rangle_v$