

THERMAL PHYSICS

- > Energy flowing from hot body to cold body is heat energy.
- > The sum of KE of vibration of molecular and molecular potential energy due to intermolecular force is the internal energy of the body / system.
- > Temperature of a body is the degree of hotness of the body and measures the avg. KE of vibration of molecules present in the body.

Measurement of temperature

- > Thermometer is used to measure temperature.
 - > Three scales are used, Celsius, Fahrenheit and Kelvin. degree Celsius ($^{\circ}\text{C}$), degree Fahrenheit ($^{\circ}\text{F}$), Kelvin (K).
 - > To construct a thermometer two standard points of hotness are chosen, called fixed points.
 - > These points are ice point 0°C and steam point (100°C) generally, at standard atmospheric pressure.
 - > Ice point is point ${}^{\text{temp}}$ at which pure ice is in equilibrium with water at standard atm. pressure. This is lower fixed point. 0°C , 31°F , 273.15 K .
 - > Steam point is temp at which steam and pure water are in eqm. at standard atm. pressure. This is upper fixed point. 100°C , 212°F , 373.15 K .
 - > The scale is divided uniformly between the lower fixed point and upper fixed point.
 - > $E - 32 = C - 0 = K - 273.15$
- 212 - 32 100 - 0 $373.15 - 273.15$

→ Important relation: $T/K = \theta/^\circ C + 273.15$.

- A physical quantity that varies uniformly and continuously with temperature over a wide range is used for measurement of temperature. This is the basic principle to construct a thermometer.
- Eg of such properties: density of liquid, volume of gas at constant temp pressure, resistance of a metal, emf of a thermocouple etc.

If

x_{100} - value of temp. measuring property at steam point

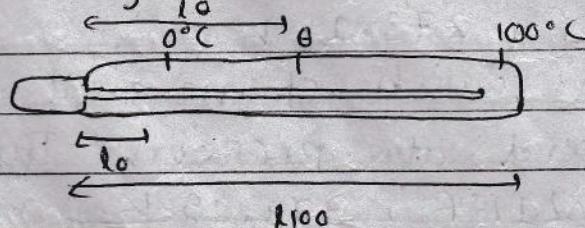
x_0 - at ice point

x_θ - at some temp. θ . Then,

$$\frac{\theta}{100} = \frac{x_\theta - x_0}{x_{100} - x_0}$$

Liquid in glass thermometer

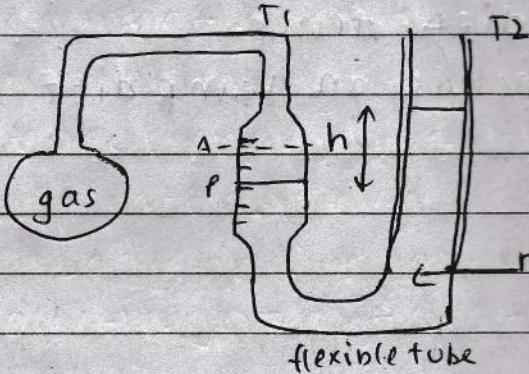
- Change in the volume of liquid due to change of temp causing change in length of liquid column in the capillary tube.



$$\frac{\theta}{100} = \frac{l_\theta - l_0}{l_{100} - l_0}$$

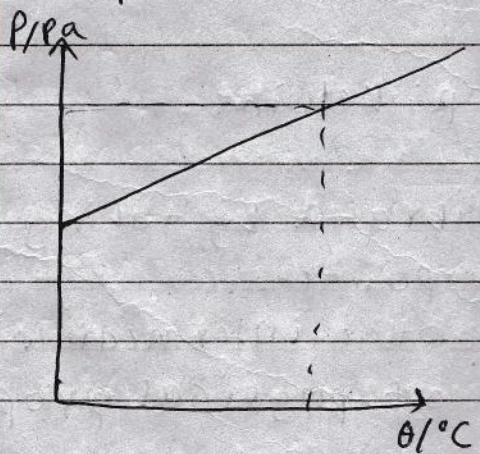
Constant volume gas thermometer

- Change in the pressure of gas at constant volume due to change in temperature.



When temp. increases, pressure increases and mercury moves up in second tube, under constant volume. $T \propto P$

We move T_2 up and down, so the liquid in T_2 returns to its initial point, B A , to create constant volume. During this process there is change in height h .



Then we measure temperature with the help of this calibration graph.

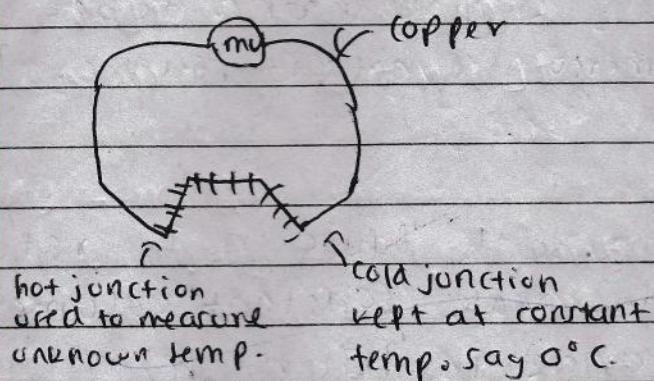
Resistance thermometer

- Change in resistance of a metal due to the change in temp. (platinum has uniform rate of change in temp.)

$$\frac{\Delta R}{R} = \frac{R_\theta - R_0}{R_0}$$

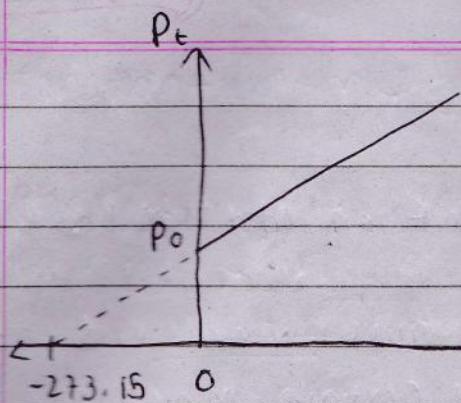
Thermocouple thermometer

- Pair of different metals connected to form two junctions is called a thermocouple that produces an emf when the junctions are kept at diff. temp.
- electron flows, emf depends on temp diff between the junctions.



i) Thermodynamic scale of temp; Kelvin;

- Temp scale in thermometer is calibrated by taking icept. and steam point as two fixed points.
- Inaccuracy may be there for other intermediate temps. due to non-linear variation of physical properties chosen.
- Kelvin scale is thermodynamic scale of temp. that don't depend on the property of a particular substance; also known as absolute scale.
- A constant volume gas thermometer is used to measure temp that is based on the variation of temp. as vol. of gas changes.



→ Extrapolated straight line meets the axis of kmp at -273.15°C at which gas pressure is zero.
+ zero pressure isn't obtained in practise.

$T(^{\circ}\text{C})$ → This is the lowest possible temp absolute zero (0K), hypothetical

Thermal Equilibrium

- Heat flows from ^{hot} to ^{not b} cold body.
- Two objects / systems / regions are said to be in thermal eqm when there is no net transfer of energy between them in bringing them in thermal contact.
- This happens when both have equal temp.
- Thus, a thermometer measures its own temperature.
- So for small masses thermometer is not accurate because small masses have less heat & thermometer needs some heat, so the heat lost from the small mass is more significant. \therefore
There is a large percentage error.
- If a sys. C is in thermal eqm with two systems A and B separately then A and B are also in thermal equilibrium with each other. (zeroeth law of thermodynamics.)

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Specific heat capacity

- One of the most imp. effects of heat on matter (a body) is the change in temperature.
- the quantity of energy (heat / thermal) required to increase the temp. of a mass of a certain material is found to be proportional to the temp. change & the mass.
- $Q \propto \Delta T$ $Q \propto m\Delta T$
- $Q \propto m$ $\therefore Q = mc\Delta T$.

$$dQ = mc dT$$

Here c is used as a constant called specific heat capacity.
 c can be used as a constant

$$c = \frac{dQ}{m dT}$$

- The quantity of energy required to increase the temp. of a unit mass of a material by $1^\circ C$ or $1K$ is called specific heat capacity of the material.
- In above eqn's, dQ and/or dT can be +ve or -ve.
- When they are positive, heat enters body & temp. increases.
- When they are negative, heat leaves the body & temp. decreases.
- Unit is $J kg^{-1} K^{-1}$ or $J kg^{-1} C^{-1}$.
- Specific heat capacity changes slightly with temp. but this is negligible.

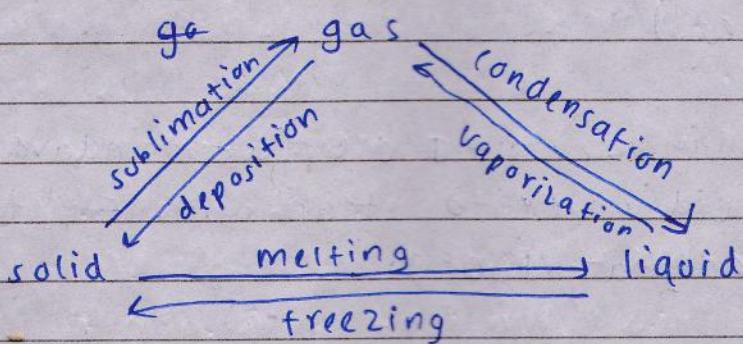
Thermal capacity of a substance is defined as the amount of heat required to raise the temp. of that substance by $1^\circ C / 1K$

$$Q = mc\Delta T \quad \therefore Q = mc_1$$

State of water.

Boiling point is actually the temp. when vapour pressure equals atm. pressure.

So at higher altitudes (lower pressures), water boils at temperatures lower than 100°C .



Boiling point only takes place at specific temperature, while evaporation can take place in any temperature.

All molecules have KE, so by chance if air is moving (having lower pressure than stationary air) and by chance the molecules at surface have higher KE, they can escape out. This evaporation is law by chance.

Boiling can take place from any point in a liquid, while evaporation can only happen from surface.

In boiling almost all molecules have KE to escape atm. pressure, while in evaporation, only some superficial molecules have this required KE.

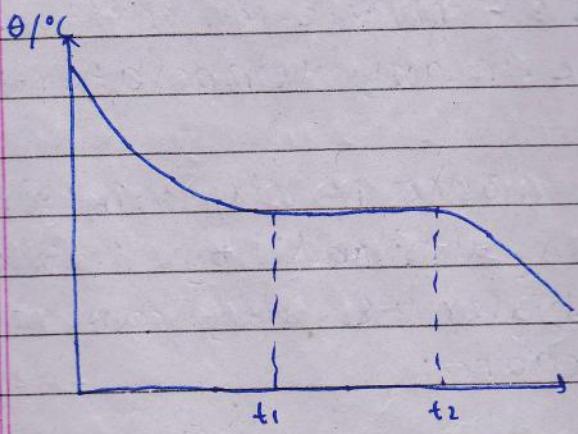
Specific Latent Heat

→ The heat energy given to ice at 0°C (at standard atm. pressure) is used to melt the ice without the change in temp. until all ice is melted.

(Melting pt. doesn't change with pressure drastically but boiling pt. does.)

→ The ^{heat} given to boiling water at 100°C (at standard atm) is used to change liquid water to steam with ~~st~~ temp. remaining steady at 100°C .

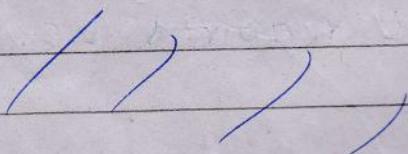
keeping liquid wax in test tube and allowing it to cool.



Between t_1 and t_2 , there is constant temp. This is when the wax is slowly changing to solid. Temp remains constant because energy is required to bring molecules closer. i.e. change molecular potential energy,

but not molecular or kinetic energy. (temp)

So temp remains constant, but internal energy changes.



ice at 0°C $\xrightarrow{\text{energy}}$ water at 0°C [At constant temp.]

water at 100°C $\xrightarrow{\text{energy}}$ steam at 100°C [At constant temp.]

One important effect of heat is that it increases temp. but here temp. doesn't increase even when energy is given.
So, some heat is hidden.

The amount of heat/thermal energy required by a unit mass of a substance to change its state from solid to liquid ^{at a constant temp.} is called specific latent heat of fusion.

Similarly, the change of state from liquid to gas is specific latent heat of vaporisation.

$$L_f = Q_f/m \Rightarrow Q_f = m \cdot L_f$$

$$L_v = Q_v/m \Rightarrow Q_v = m \cdot L_v$$

In general, $Q = mL$.

The amount of energy required or given out by a unit mass of a substance to change its state at a constant temperature is specific latent heat.

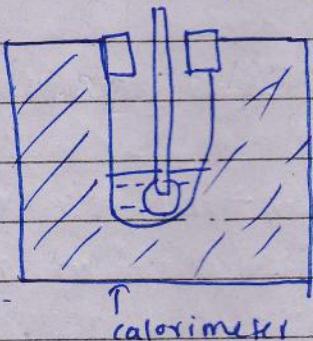
The hidden energy is used to do work against intermolecular forces to change states.

Latent heat of vaporization for a substance is greater than latent heat of fusion for the same substance because liquid and solid have smaller difference of distances while that in liquid and gas is far higher.

During vaporization some latent heat is used to do work against intermolecular forces, while some other external energy is required to make the gas particles overcome atm. pressure and fly. However this energy is so much smaller than latent heat so is generally neglected.

Latent heat increases molecular potential energy, but not molecular kinetic energy, as there's no change in temperature.

Determining specific latent heat of fusion of ice.



m_c = mass of calorimeter

m_w = mass of water added

θ_1 = initial temp at when H_2O is added

m_i = mass of ice

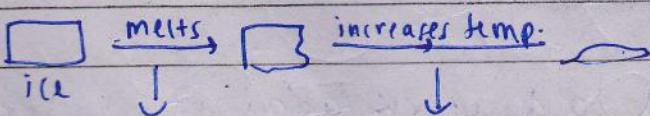
θ_2 = final temp.

By principle of calorimetry.

Heat lost by water + calorimeter = Heat gained by ice.

$$m_w(c_w(\theta_1 - \theta_2) + m_c.c_c(\theta_1 - \theta_2)) = m_i L_f + m_i.c_w(\theta_2 - \theta_1)$$

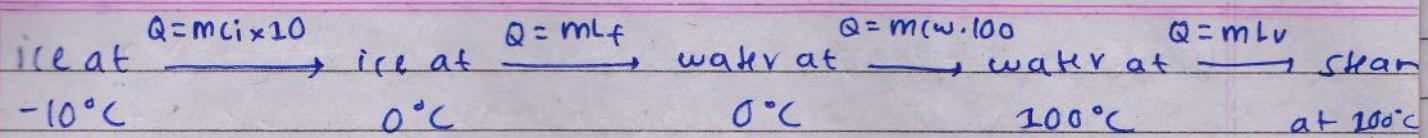
$$\therefore L_f = \dots \dots$$



$$m_i.L_f + m_i.c_w(\theta_2 - \theta_1) \rightarrow \text{Heat gained by ice.}$$

First the hidden energy is used, then only does temp.

start to rise, so, Heat gained by ice = $m_i.L_f + m_i.c_w\theta$



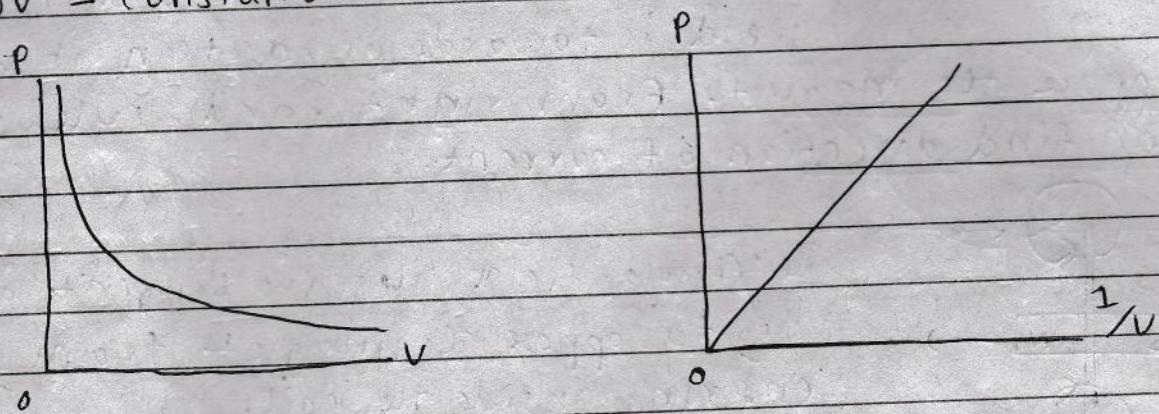
Heat required to change ice at -10°C to steam at 100°C =
 $mci \times 10 + mlf + m(w \cdot 100) + mlv$.

IDEAL GASES

→ Boyle's law states that the pressure exerted on a gas is inversely proportional to the volume of the gas at constant temperature, for a fixed mass.

$$P \propto 1/V$$

$$\therefore PV = \text{constant}$$

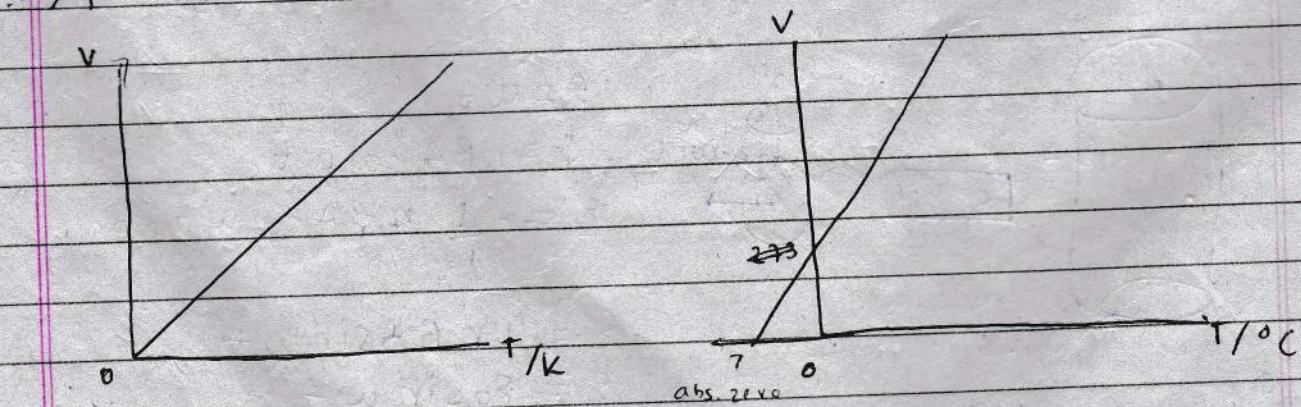


$$\therefore P_1V_1 = P_2V_2$$

→ Charles' law states that the volume of a fixed mass of a gas is directly proportional to the absolute / thermodynamic temperature, provided the pressure of the gas is constant.

$$V \propto T$$

$$\therefore V/T = \text{constant}$$



$$\therefore V_1/T_1 = V_2/T_2$$

$$V \propto \frac{1}{P} \quad \text{---(i) Boyle's law}$$

$$V \propto T \quad \text{---(ii) Charles' law}$$

$$V \propto \frac{T}{P} \leftarrow \text{combined gas law.}$$

$$\frac{PV}{T} = \text{constant} \quad (\text{for mixed mass of gas})$$

$$P_1 V_1 / T_1 = P_2 V_2 / T_2 \quad \leftarrow \text{combined gas equation.}$$

For n moles of gas, eqⁿ can be written as:

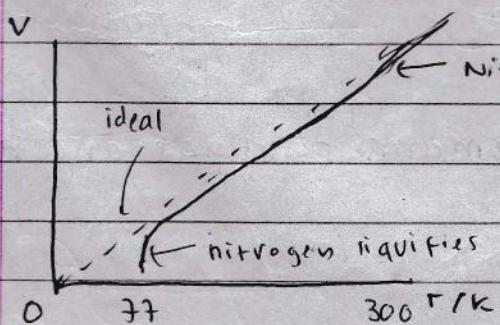
$$V \propto n \rightarrow P, T \text{ are constants}$$

$$\frac{PV}{nT} = \text{constant, now let the constant be } R.$$

$$\therefore PV = nRT \leftarrow \text{ideal gas equation. / Eq^n for state of an ideal gas}$$

An ideal gas is one for which the eqⁿ $PV = nRT$ holds precisely for all pressures and temperatures. At extremely high temp even real gases slightly behave like ideal, and at extremely low pressure. T must always be thermodynamic.

The eqⁿ is best applicable for high temp and low pressure, as molecules are far apart due to low pressure such that their intermolecular forces is negligible and high temp ensures molecules are in constant random motion.



Nitrogen gas

Thus, at high temp. N gas is collinear with ideal graph but at low temp. it is less ideal

The proportional constant R is found to be same for all gases at high temp. and low pressure (ideal case) as is called gas constant or ideal gas constant or universal molar gas constant.

$$pV = F_A \times V = F_S = W = J$$

$$\therefore R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$pV = \frac{m}{M} RT$$

$$\therefore pV = m r T$$

where $r = \frac{R}{M}$, and is gas constant per unit mass expressed

in the unit $\text{J kg}^{-1} \text{ K}^{-1}$. and this is diff. for all gases as M value for all gases is different.

The ideal gas equation, Boltzmann constant

Ideal gas eqⁿ is $pV = nRT$

If N is number of molecules in n moles of a gas, and N_A is Avogadro's number,

$$n = N$$

$$N_A$$

Ideal gas eqⁿ becomes $pV = \frac{N}{N_A} RT$

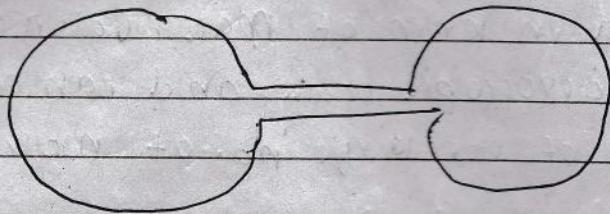
$$\therefore pV = N k T$$

$K = \frac{R}{N_A}$, which is called Boltzmann constant and has unit J K^{-1} (Joule per Kelvin.)

$$K = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

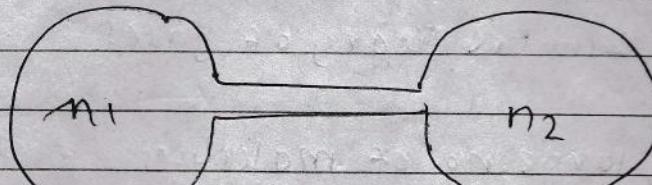
One mole of a substance is the amount of a substance containing a number of particles equal to that in 12g of C-12 element. (Avogadro's constant, N_A)

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glass bulbs with gas at s.t.p

0°C , 760 mm of Hg



melting ice
(273K)

water bath
(T K)

new pressure = ~~877.6~~ mm
of Hg

$$PV = nRT$$

$$n = n_1 + n_2$$

$$\frac{760 \times 2V}{R \times 273} = \frac{877.6 \times V}{R \times 273} + \frac{877.6 \times V}{RT}$$

$$\therefore T = 373\text{ K} = 100^\circ\text{C}.$$

As volume increases, pressure decreases as collisions are less frequent in larger volume.

At constant pressure and constant volume, more molecules need to move faster to maintain constant temp and thus KE is more & temp. is more, thus $T \propto \ln v$

Kinetic Theory of Gases

- A gas contains a very large number of small particles (molecules or atoms).
- A gas can be described in terms of mass, volume, temp., pressure etc., on the macroscopic scale and can be described in terms of the motion of its large no. of molecules on the microscopic scale.
- Kinetic Theory of gas explains behaviour of gases by considering the motion of their particles.

Basic Assumptions of Kinetic Theory of gases

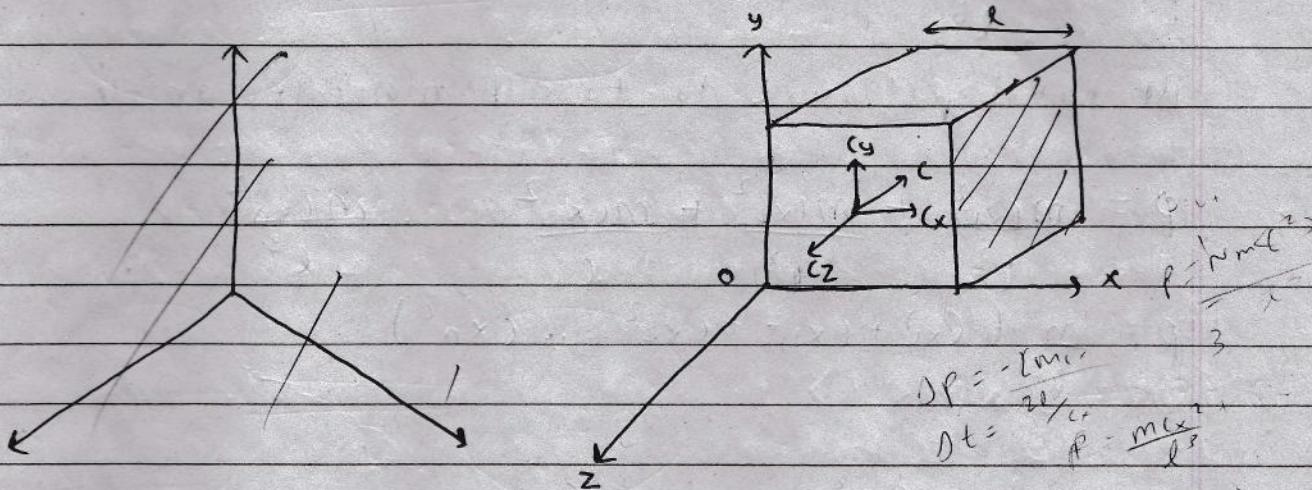
- A gas contains a very large no. of molecules.
- Total volume of molecules is negligible compared to volume occupied by gas.
- Intermolecular force (force between molecules) is negligible except during collision.
- Molecules are in random ^{motion} but they move with uniform velocity between collisions.
- The collisions of molecules with each other and with the wall of the container are perfectly elastic. (Gas molecules behave as if they are hard, elastic identical spheres.)
- The time of collision is negligible compared with the time between collision.

/ / h

Calculation of pressure exerted by gas

A gas exerts pressure on the walls of container due to collision of molecules as they are in random motion.

Suppose there are N molecules each of mass m of a gas in a cube container of side l .



Let's consider one molecule inside the cube with speed c and its components divided.

$$c^2 = c_x^2 + c_y^2 + c_z^2$$

As the collision is elastic, the change in momentum of the molecule in ox direction striking on the wall is

$$u = c_x, v = -c_x$$

$$\Delta p = -2mc_x$$

The time taken for the molecule to move across the cube to the opp. face and back to shaded face is

$$\Delta t = \frac{2l}{c_x} \quad \leftarrow \text{This is time taken for one collision with the wall.}$$

The force on the wall in ox direction due to collision of that molecule is $F_x = \frac{\Delta p}{\Delta t} = \frac{2mc_x}{\frac{2l}{c_x}} = \frac{mc_x^2}{l}$

In this time, momentum changes ^{two} four times as it first hits shaded part and also hits non-shaded wall.

The pressure on the wall is,

$$p_x = \frac{m(x^2)}{l^3}$$

The total pressure due to all molecules on the wall is,

$$p = \frac{m(x_1^2)}{l^3} + \frac{m(x_2^2)}{l^3} + \frac{m(x_3^2)}{l^3} + \dots + \frac{m(x_n^2)}{l^3}$$

$$\therefore p = \frac{m}{l^3} (x_1^2 + x_2^2 + x_3^2 + \dots + x_n^2)$$

$$\text{Avg. } (x^2) = \langle x^2 \rangle = \frac{(x_1^2 + x_2^2 + x_3^2 + \dots + x_n^2)}{n}$$

$$\therefore n \langle x^2 \rangle = x_1^2 + x_2^2 + x_3^2 + \dots + x_n^2$$

~~$$p = \frac{n \langle x^2 \rangle}{l^3}$$~~

$$\therefore p_x = \frac{Nm \langle x^2 \rangle}{l^3} \quad \text{--- (i)}$$

With large no. of molecules of varying speed in random motion, $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$

$$p_y = \frac{Nm \langle y^2 \rangle}{l^3}, \quad p_z = \frac{Nm \langle z^2 \rangle}{l^3}, \quad p_x = \frac{Nm \langle x^2 \rangle}{l^3}$$

$$\langle c^2 \rangle = \langle c_x^2 \rangle + \langle c_y^2 \rangle + \langle c_z^2 \rangle$$

$$\therefore \langle c^2 \rangle = \frac{(c_1^2 + c_2^2 + \dots + c_N^2)}{N}$$

$$\therefore \langle c^2 \rangle = 3 \langle c_x^2 \rangle$$

$$\therefore \langle c_x^2 \rangle = \frac{1}{3} \langle c^2 \rangle$$

$$P = \frac{Nm \langle c_x^2 \rangle}{\ell^3} = \frac{Nm \langle c^2 \rangle}{3\ell^3}$$

$$\therefore P = \frac{1}{3} \frac{Nm \langle c^2 \rangle}{V}$$

$$\therefore PV = \frac{1}{3} Nm \langle c^2 \rangle$$

As Nm is total mass of gas, let ρ be density of gas,

$$\therefore P = \frac{1}{3} \rho \langle c^2 \rangle$$

Comparing this with $PV = NkT$, we can deduce that avg. KE translational kinetic energy of a molecule is $\frac{3}{2} kT$.

The root-mean-square speed (v_{rms}) is given by

$$(v_{rms})^2 = \sqrt{\langle c^2 \rangle}$$

The mean square speed of gas molecules is the average of the square of the speed of all molecules of the gas.

The rms speed of gas molecules is the square root of the avg. of the square of the speed of all molecules in the gas.

Why is $p \propto \langle c^2 \rangle$

- Because pressure is force per unit area, and force is rate of change of linear momentum. As $\dot{p} \propto v$ and $\dot{t} \propto v^2/t$
 $\therefore p \propto v^2$ and thus pressure $\propto v^2$.
- The rms speed of gas molecules is in same order of magnitude as the avg. speed, but not quite equal.
- Mean square speed is not equal to square of avg. speed.

Temperature and Kinetic Energy of Gas molecules

$$PV = \frac{1}{3} Nm \langle c^2 \rangle \quad \text{--- (i)}$$

$$PV = NkT \quad \text{--- (ii)}$$

$$\frac{1}{3} Nm \langle c^2 \rangle = NkT$$

$$\frac{1}{2} m \langle c^2 \rangle = \frac{3}{2} kT$$

∴ Avg. translational kinetic energy of a molecule is:

$$E_{k(\text{av})} = \frac{3}{2} kT$$

2

Variation of rms speed

$$PV = nRT$$

$$PV = \frac{1}{3} Nm \langle c^2 \rangle$$

$$nRT = \frac{1}{3} Nm \langle c^2 \rangle$$

$$\therefore \langle c^2 \rangle = \frac{3nRT}{Nm} = \frac{3nRT}{M'} \quad \text{where } M' = \text{total mass of gas.}$$

Using Molar mass $M = \frac{M'}{n}$

$$\therefore \langle c^2 \rangle = \frac{3RT}{M}$$

As M and R are constants, rms speed can only vary with temperature of gas.

$$\therefore C_{rms} = \sqrt{\frac{3RT}{M}} \quad \therefore (C_{rms}) \propto \sqrt{T}$$

where T is in Kelvin scale

For the same gas)

For diff. gases at same temp

$$\frac{C_1}{C_2} = \sqrt{\frac{T_1}{T_2}} \quad \therefore C_{rms} \propto \frac{1}{\sqrt{M}}$$

where M is molar mass of gas.

Variation of rms speed with pressure

$$P = \frac{1}{3} \rho \langle c^2 \rangle$$

$$\therefore C_{rms} = \sqrt{\frac{3P}{\rho}}$$

So long as temp is same, there is no variation of rms speed with pressure as changing pressure also changes density ρ .

THERMODYNAMICS

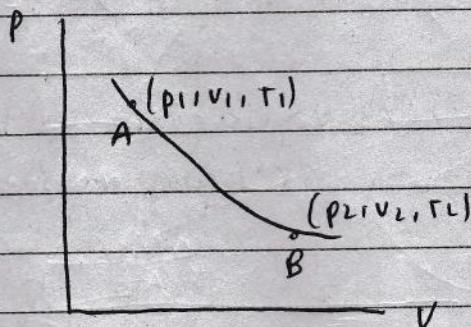
It's rather easy to convert mechanical energy to heat energy but vice versa is quite difficult.

Thermodynamics deals with the relation between heat energy & mechanical energy/work done.

Gases are very good tools to convert heat energy into work done.

Internal energy is the sum of molecular potential energy and kinetic energy (of vibration) of molecules due to their random motion. Molecular potential energy is due to intermolecular forces.

Internal energy of a system is the state function of a system. i.e. internal energy of a system depends on the state of a system. (i.e. solid, liquid, gas)



But state scopes out to more than solid, liquid and gas.

If the p-V graph is of a gas whose state function is $pV = nRT$.

A and B are two different states of the same gas.

So water at 10°C and at 20°C are different states even though both are water.

Similarly, water at 40 atm and at 10 atm are still at different states.

Internal energy is affected by internal changes of system and not external changes.

Internal energy of the system is the function of intermolecular space and temperature.

Internal energy of a system changes due to change in molecular kinetic energy when temp changes and change due to change in molecular potential energy when the state changes.

For ideal gases,

- Separation between molecules is large.
- Intermolecular force is negligible.
- Molecular potential energy is negligible.
- Sum of $k\epsilon$ of random motion of all the molecules is total internal energy.

$$U = N \times \frac{3}{2} kT$$

- Total internal energy is function of thermodynamic temp.
- Change in internal energy of a given mass of a gas is directly proportional to change in temp.

Work done by/on a gas.

$$W = p\Delta V$$

Where ΔV is change in volume.

- If gas expands, work is said to be done by gas.

THERMODYNAMICS...

First law of thermodynamics

The change of internal energy of a system (gas) depends on the quantity of heat energy transferred to/from the system and the amount of work done by/on the system.

If, q - heat added to system, w - work done on system
then, from principle of consu. of energy, the increase in internal energy of the sys. is given as:

$$\Delta U = q + w$$

This eqⁿ is the mathematical representation of the first law of thermodynamics.

The increase in internal energy of a system is equal to the quantity of heat supplied to the system and the amount of work done on the system.

$q = +ve$ (when heat is added to system)

$q = -ve$ (when heat is given out by system)

$w = +ve$ (decrease in volume / ^{conver.} work done in system internal energy increases)

$w = -ve$ (Increase in vol. (expansion), work done by system)
decrease in internal energy)

If $U = +ve$, internal energy increases. $U = -ve$, internal energy decreases

$$U = q + w \quad q = nC\Delta T \quad (mC\Delta T)$$

thermodynamic processes

(change in thermodynamic variables : $pV = nRT$, p, V, T)

- At constant pressure (Isobaric) $\Delta U = q + w$
- At constant volume (Isochoric) $\Delta U = q$ $w = p\Delta V = p \cdot 0$
- At constant temp. (Isothermal) $\Delta U = w$ $0 = q + w$ $q = -w$
- With no heat transfer (Adiabatic) $\Delta U = w$ $q = 0$

In isothermal process, if gas is heated, work is done by the gas to expand to maintain constant temp; and if gas gives heat, gas contracts, work is done on gas.

i) When we blow, it is cooler as expansion is very fast & gas doesn't have enough time to gain heat from surrounding to compensate for work it does and follows Adiabatic process, where $q = 0$ and $\Delta U = w$ ~~and $q = 0$~~

ii) But when we gently do a "hah", it is hotter as now gas expands slowly and gets time to gain heat from mouth → surroundings; thus air is hotter. It follows $\Delta U = q + w$, isothermal process.

Process i is almost ideal when blowing of air is done fast enough.

$J\text{mol}^{-1}\text{K}^{-1}$ is molar heat capacity, not specific heat capacity
 $q = m(c_s)AT$, $n(C_m)AT$

for a gas, c_s and/or C_m is different for a constant pressure and constant volume.

This means if a gas is heated at constant pressure its C_p could be x , but for same gas, if it is heated at constant volume, C_v could be y .

$$\Delta U = q + w \quad \therefore q = \Delta U - w \quad \therefore mc\Delta T = \Delta U - w \quad \leftarrow \text{const. press.}$$

$$\Delta U = q \quad \therefore q = \Delta U \quad \therefore mc\Delta T = \Delta U \quad \leftarrow \text{constant volume.}$$

So more heat is required to raise temp. at constant pressure as whilst heating W becomes negative as gas expands and work is done by system and $q = \Delta U + w$, so c is larger.