CH1201: Elements of Chemistry-II

General Physical Chemistry

- **Syllabus:**

- States of Matter:

  - The Gaseous State: Gas laws, Equation of state, Concept of temperature, pressure, partial pressure, density, Mole concept.

  - Kinetic Theory of Gases: The kinetic theory, Maxwells distribution of molecular velocities, Calculation of average, root mean square and most probable speed, Collisions in a gas, Collision number and diameter, mean free path, frequency of binary collision. Viscosity of gases. Energy distribution function, Average and most probable energy, Principle of equipartition of energy, Maxwell Boltzmann distribution.

  - Real Gases: Deviations from ideal behaviour, Intermolecular forces, Compressibility factors, Virial coefficients, Equations of state for real gases, principle of corresponding states.

  - The Liquid State: Liquid structure, Vapour pressure, Surface tension, Viscosity.

- Chemical Kinetics: Rate of a reaction, Order and molecularity, Integrated rate laws, Temperature dependence of reaction rate -Arrhenius equation and Activation energy, Elementary and Consecutive reactions, Steady state approximation, Rate determining step approximation, Enzyme kinetics, Introduction to collision theory, potential energy surfaces and transition state theory.

- To be taught by Prof. Prasun Mandal (Office # 330, TRC)

- Thermodynamics:
  - Introducing System, Surroundings, Boundaries, Intensive and Extensive properties, reversible and irreversible processes, zeroeth law.
  - The First Law: Interchangeability of Energy, Heat and work, Internal energy, State and path functions, exact and inexact differentials, First law, Enthalpy, specific heats Adiabatic and isothermal processes, Joule's and Joule-Thomson experiment, Thermochemistry.
  - The Second Law: Spontaneity and Irreversibility, Entropy, Heat engines and pump, Kelvin-Planck and Clausius statement, Carnot principle and Carnot cycle, Clausius inequality, Free energy and significance.

- To be taught by Prof. Susmita Roy

Examination Schedule:

Sl. #	Examinations	Marks	Syllabus	Instructor
1.	Class Test – I	15 Marks	The Gaseous State Kinetic Theory of Gases	PM
2.	Class Test – II	15 Marks	Real Gases Liquid State	PM
3.	Mid-Semester examination	20 marks	Chemical Kinetics	PM
4.	Class Test III	15 Marks	Thermodynamics	SR
5.	End-Semester examination	35 Marks	Thermodynamics	SR

Books to be followed:

1. ATKINS' PHYSICAL CHEMISTRY by Peter Atkins and Julio de Paula

2. Physical Chemistry by IRA N. LEVINE

3. PHYSICAL CHEMISTRY by GILBERT W. CASTELLAN

Lecture 1

Physical chemistry:

Subject that helps us understand the physical principles (property & behaviour) of chemical (or biological) systems and thus helps us develop modern techniques to probe complex chemical & biological systems.

Observation $\Rightarrow$ Hypothesis $\Rightarrow$ Model $\Rightarrow$ Theory $\Rightarrow$ Law

Matter: (a) Concept of mole & mole fraction

No. of atoms in 12 g of Carbon-12.

Avogadro Number: 6.023×10^{23} (pure number, no unit)

Avogadro Constant: 6.023×10^{23} mol^{-1} (not a pure number, with unit)

IUPAC definition of Mole: A mole of a substance is defined as that amount of the substance which contains as many numbers of stable elementary entities as there are atoms in 0.012 kg of C-12 isotope.
It is not just a number but a quantity of a substance. Recently "mole" has been included as one of the fundamental units. It is the unit for measurement of the amount of the substance.

Question: How many number of molecules are there in 2 mol O_2?

Ans: $2 \times 6.023 \times 10^{23}$ no. of molecules.

Question: How big is one mole?

Question: Does the IISER lake contain 1 mole drops of water?
Question: Does the Bay of Bengal contain 1 mole drops of water?

Volume of Bay of Bengal = 2173000 (sq. km) × 5 km (average depth)
$\simeq$ 11,000,000 km^3
$\simeq 1.1 \times 10^{22}$ cc
Volume of 1 mole drops of water = $6 \times 10^{23} \times 0.05$ cc
$\simeq 3 \times 10^{22}$ cc
Volume of Bay of Bengal is less than 1 mole of water drops !!!

Weight of earth? $\Rightarrow 6 \times 10^{24}$ kg = weight of ten mole apple (one apple $\simeq$ 100 g)

Mole fraction:

$$x_1 + x_2 + \ldots.. = \frac{n_1}{n_{total}} + \frac{n_2}{n_{total}} + \ldots.. = 1$$

Extensive property: Property that depends on amount of substance, e.g. mass & volume

Intensive property: Property that is independent of the amount of substance, e.g. temperature, mass density (mass/volume)

Any molar property is intensive property. Molar volume or molar mass is an intensive property.
Molar concentration $\rightarrow$ no. of moles of solute/litre of solvent

Question: What is the molar concentration of water?

NaCl solution in water: What is the distance between oppositely charged ions?

For 1M NaCl solution, distance between oppositely charged ion is 1 nm which is enough to accommodate 3 water molecules.

Width of hair? $\Rightarrow$ 10-200 μm

Weight of earth? $\Rightarrow 6 \times 10^{24}$ kg

Question: What is meant by kilo? Is kilo a number or weight? kilo $\neq$ kilogram
(Question: One kilo potato or one kilogram of potato: which one is heavier?

Homogeneous: When an intensive macroscopic property (say density, pressure) is constant throughout the system, then the system will be known as homogeneous. (e.g. NaCl in water)

If not, then the system may consist of a number of homogeneous parts; each such homogeneous part will be known as phase.

Heterogeneous: A system consisting of two or more phases is known as heterogeneous phase. (e.g. Benzene in water)

Unsaturated, saturated, supersaturated solution

When a system consists of solid AgCl & saturated solution of AgCl in water, then the system is heterogeneous.

Is pure water homogeneous ?

$$\left.\begin{array}{l}\text{length-scale?}\\ \text{time-scale?}\end{array}\right\}\text{Molecular picture is important}$$

Molecular Behaviour: To understand molecular behaviour $\Rightarrow$ need to have imagination !

Pressure:

Pressure (p) is defined as force (F) per unit area (A)

$$p = \frac{F}{A} \quad \text{(i.e. } p \propto F \text{ when A is constant}$$

$$\& \;\; p \propto \frac{1}{A} \text{ when F is constant)}$$

Force exerted by a solid of mass 'm'

$$F = mg$$

Assume Prof. Newton weighs 60 kg

Force (downward) exerted by Prof. Newton

$$= 60 \times 9.8 \text{ kg m/s}^2$$

$$= 588 \text{ kg m/s}^2$$

$$= 588 \text{ Newton } (1 \text{ N} = 1 \text{ kg m/s}^2)$$

Prof. Newton exerts force much more than 1 Newton !

Question: Which one weighs more? The Eiffel tower or a cylindrical column of air same as the dimension of the Eiffel tower?

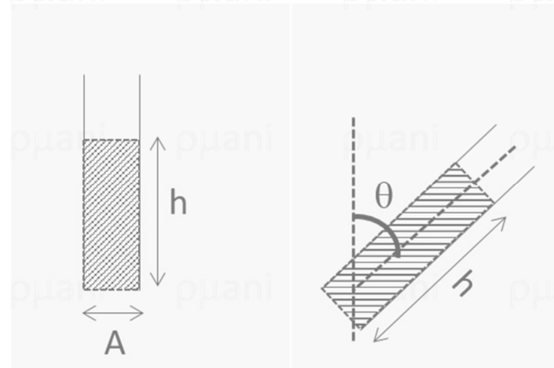
Question: How much pressure will be generated by Prof. Newton when he is wearing shoe with total area of 200 cm^2 or wearing ice-skates with total area of 2 cm^2?

Ans: $p = \frac{F}{A} = \frac{588\ N}{2 \times 10^{-2}\ m^2} = 2.94 \times 10^4$ Pascal (1 Pa = 1 N/m^2)

$= 29.4$ kilo Pascal $= 29.4$ kPa

$= \frac{588\ N}{2 \times 10^{-4}\ m^2} = 2.94 \times 10^6$ Pascal

$= 2.94$ MPa



Pressure exerted by a column of liquid (at the base):

$F = mg$

$= A \times h \times \rho \times g$ (A = cross-sectional area, h = height, ρ = density)

$= Ah\rho g$

$p = \frac{F}{A} = h\rho g$

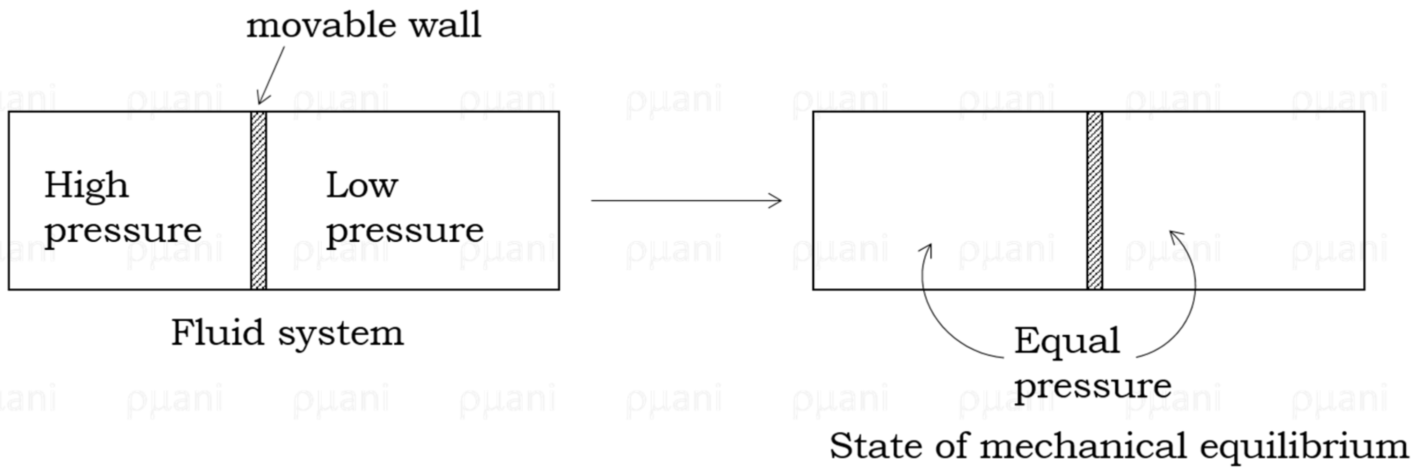
Thus, p is independent of shape and cross-sectional area of the column. But, force depends !

[mass (m) = density (d) × volume (v) or. $d = \frac{m}{v}$]

How much pressure will be exerted by a column of liquid that is tilted at an angle θ to the vertical?

$p = \rho g h \cos\theta$

Pressure exerted by a gas (will be discussed in detail later)



Units of Pressure:

Pascal $\Rightarrow$ Pa $\Rightarrow$ 1 N/m^2 or 1 kg m^{-1} s^{-2}

Hide & seek story
$N/m^2 \Rightarrow$ Pascal

Bar $\Rightarrow$ bar $\Rightarrow$ 10^5 Pa

Atmosphere $\Rightarrow$ atm $\Rightarrow$ 1.01325×10^5 Pa = 1.01325 bar

Torr $\Rightarrow$ Torr $\Rightarrow$ $(\frac{1.01325 \times 10^5}{760})$ Pa = 1 mm of Hg

- A few random thoughts:

- When heated, it creates "Jiggling and Wiggling" of atoms in a molecule and the system gets heated. Mostly the length increases, however, rubber shrinks when heated

- Glass breaks when hot water is poured into it but railway wheels don't breaks in a bending.
- Why in mirrors left and right hand gets interchanged and not head and leg?
- Why no lbw when ball falls outside the leg stamp, but it is not the case when ball falls outside the off stamp?
- When you are sharpening your pencil, how does the valency of last carbon get satisfied?

- Size ratio of earth to an apple is same as apple to an atom → Imagination is necessary !
  Extrapolation is useful sometimes.

- Concept of molecule ⇒ Covalently bonded (as H_2O)
  ⇒ Ionic (NaCl) (well it is difficult to say as NaCl remains as Na^+ and Cl^-

- It is necessary to write unit after a number
  If absolute say temperature in absolute scale, we write 0 A, in Celsius scale, we write 0 °C.
  or mass m = 0 (kg or g) ; length l = 0 (km or m)

Lecture 2

Energy: Energy is the capacity to do work (Bald definition)

Universal law of nature: The energy is conserved, i.e. it can neither be created or destroyed. However, it can be transferred from one location to another.

A body of mass 'm' can have two basic energies:

(a) Kinetic energy: arises because of motion

For a body of mass 'm' travelling at a speed 'v' has K.E. = $\frac{1}{2}$ mv^2

'm' is fixed, so for higher 'v', K.E. is higher

A standing body has zero K.E.

(b) Potential energy: arises because of position

A value of zero potential energy is arbitrary (unlike K.E.)

Gravitation P.E. (mgh) is set to zero at the surface of earth

Electrical P.E. of two charged particle is set to zero when the distance between them is infinite

Coulomb P.E.

$V = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$ [two point object of charge q_1, q_2, when they are separated by a distance 'r' in vacuum]

When $r = \infty$, $V = 0$ [ε_0 = vacuum permittivity (fundamental constant) = 8.85×10^{-12} C^2 J^{-1} m^{-1}]

[Important in chemistry to understand interaction between electron, nuclei, ions etc.]

Energy units:

Cal: Energy to raise temperature of 1 g of water by 1 °C

Joule (SI unit): Energy necessary for one human heart-beat

1 Cal = 4.184 J   [$J = 1\ kg\ m^2\ s^{-2}$]

e.V. = K.E. acquired or lost by an electron when it is accelerated through potential difference of 1 Volt.

1 e.V. = 1.6×10^{-19} J

meV $\Rightarrow$ milli eV,
MeV $\Rightarrow$ Mega eV

To remove one electron for sodium atom, 5 eV of energy is required.

Quantization of energy:

Classical mechanics of Newton: For macroscopic bodies; treats waves and particles separately

Quantum mechanics: necessary for subatomic particles like electrons. Particles have some properties of waves and waves have some properties of particles.

A particle of mass 'm', velocity 'v' has a linear momentum of 'p' (p= mv), and according to quantum mechanics it has (in some sense) a wavelength 'λ'

$\lambda = \frac{h}{p}$ where h is the Planck constant (6.626×10^{-34} kg m^2 s^{-1})

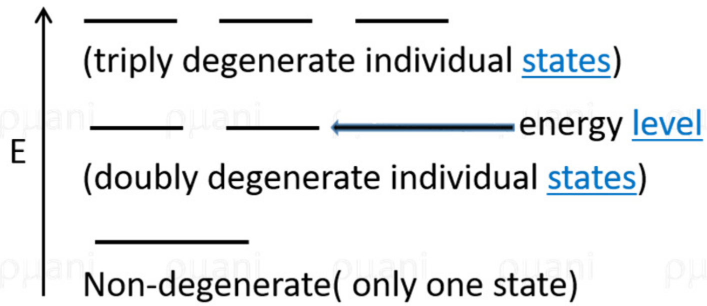
⇒ de Broglie relation

According to classical mechanics, for macroscopic bodies energy levels form a continuum

According to quantum mechanics, a particle cannot have a continuum energy, rather only discrete energy values/levels are allowed.

⇒ Energy quantization, discrete permitted energies are called energy levels

Although energy levels are discrete but several distinct states can have same energy



Note the difference between “level” & “state”

Quantization of energy for different types of Motion:

Translational: permitted energy levels for free translational motion in an infinite region is not quantized, rather it forms a continuum.

Rotational: Rotational energy states/levels are quantized. Separation between levels depends on moment of inertia of molecule. Typical values $\simeq 1\ cm^{-1}$ (spectroscopic unit)

Vibrational: Vibrational energy states/levels are quantized. Separation between levels depends on the mass of atoms in the molecule. Typical values $\simeq 10^2$-$10^3\ cm^{-1}$

Electronic: Quantized. Separation are larger. Typical values $\simeq 10^4\ cm^{-1}$

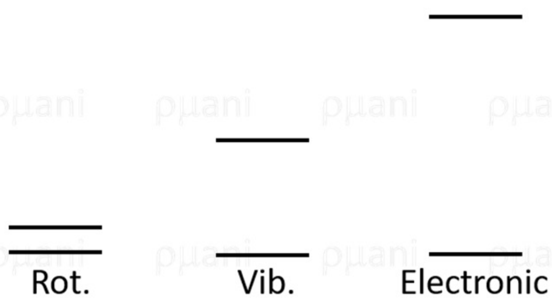
Separation between levels: Electronic > Vibrational > Rotational

Question. Arrange in order of increasing magnitude, Cal, J, e.V., cm^{-1}

1 e.V. = 8066 cm^{-1}

Population of states:

Because of energetic (thermal, photonic etc.) agitation, different energy states will be populated differently. The distribution of atom/molecules at a particular state can be calculated by the following equation:



$$\frac{N_i}{N_j} = e^{-\frac{(E_i - E_j)}{kT}}$$ ⇒ Boltzmann equation

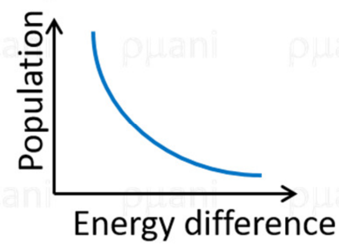
[Considering, no degeneracy]

[Exponential function of Energy difference & T]

k = Boltzmann const. (fundamental const.) = 1.38×10^{-23} J/K

At a particular temperature more rotational states will be populated than vibrational than electronic states.

Question: How will the plot of (i) Population vs. Temperature and (ii) Population vs. Energy difference look like?



Caution:

Boltzmann distribution talks about the population of states (not levels). All degenerate states belonging to same energy level will be equally populated.

Question: Calculate the ratio of population of 2 electronic states (separated by an energy of 3 e.V. $\simeq$ 300 kJ/mol) at room temperature (25 °C). At which temperature 1% of upper electronic state will be populated?

Question: Find de Broglie wavelength of an electron moving at a speed of 5×10^6 m/s ($m_e = 9.1 \times 10^{-31}$ kg).

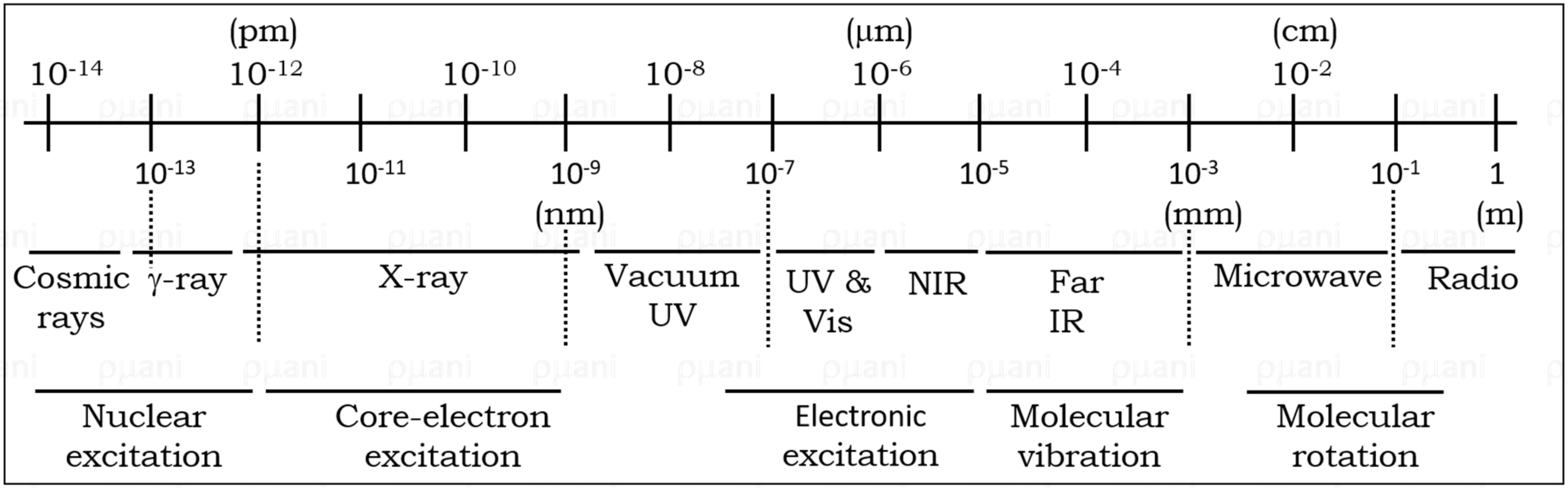
Ans: 1.46×10^{-10} m

Thermal energy can populate higher rotational energy levels, photonic energy is required to populate higher electronic energy levels.

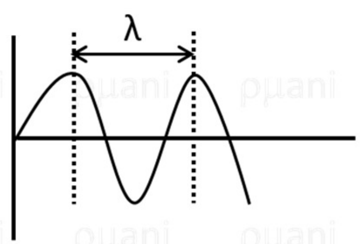
Temperature: will be discussed in detail later.

Electromagnetic spectrum:

An electromagnetic field is an oscillating electric and magnetic disturbance that spreads through vacuum. The wave travels at the speed of light (i.e. 3×10^8 m/s)



Each electromagnetic field is characterized by a wavelength λ and a frequency ν. (unit of frequency = Hz = 1/sec)



λ and ν are related as $\lambda\nu = c$

Shorter the λ, higher the ν

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$$

Einstein's theory of matter & energy

$$E = mc^2$$

Planck's theory of (quantum of) wave having a discrete energy

$$E = h\nu \quad [h = 6.6 \times 10^{-34} \text{ J s}]$$

de Broglie believed particles and wave have same traits

So, $mc^2 = h\nu$

As particles may not travel at a speed of light, so 'c' is replaced by 'v'

$$\text{or, } mv^2 = h\nu = \frac{hv}{\lambda}$$

$$\Rightarrow \boxed{\lambda = \frac{hv}{mv^2} = \frac{h}{mv} = \frac{h}{p}}$$