Unit 1: Atomic Structure

A HISTORY OF THE ATOM: THEORIES AND MODELS

How have our ideas about atoms changed over the years? This graphic looks at atomic models and how they developed.

SOLID SPHERE MODEL

JOHN DALTON

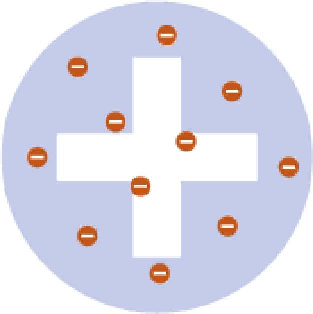
1803

Dalton drew upon the Ancient Greek idea of atoms (the word 'atom' comes from the Greek '*atomos*' meaning indivisible). His theory stated that atoms are indivisible, those of a given element are identical, and compounds are combinations of different types of atoms.

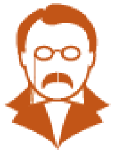
+ RECOGNISED ATOMS OF A PARTICULAR ELEMENT DIFFER FROM OTHER ELEMENTS

− ATOMS AREN'T INDIVISIBLE - THEY'RE COMPOSED FROM SUBATOMIC PARTICLES

PLUM PUDDING MODEL



J.J. THOMSON



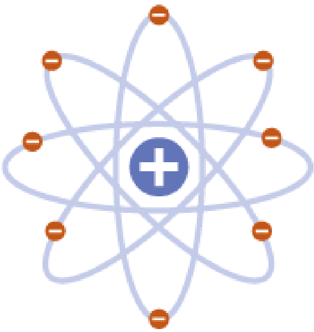
1904

Thomson discovered electrons (which he called 'corpuscles') in atoms in 1897, for which he won a Nobel Prize. He subsequently produced the 'plum pudding' model of the atom. It shows the atom as composed of electrons scattered throughout a spherical cloud of positive charge.

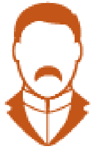
+ RECOGNISED ELECTRONS AS COMPONENTS OF ATOMS

− NO NUCLEUS; DIDN'T EXPLAIN LATER EXPERIMENTAL OBSERVATIONS

NUCLEAR MODEL



ERNEST RUTHERFORD



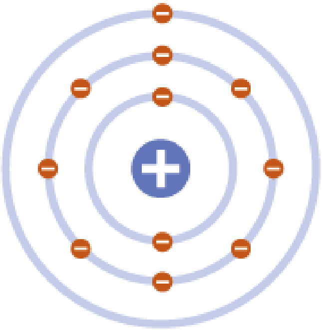
1911

Rutherford fired positively charged alpha particles at a thin sheet of gold foil. Most passed through with little deflection, but some deflected at large angles. This was only possible if the atom was mostly empty space, with the positive charge concentrated in the centre: the nucleus.

+ REALISED POSITIVE CHARGE WAS LOCALISED IN THE NUCLEUS OF AN ATOM

− DID NOT EXPLAIN WHY ELECTRONS REMAIN IN ORBIT AROUND THE NUCLEUS

PLANETARY MODEL



NIELS BOHR

1913

Bohr modified Rutherford's model of the atom by stating that electrons moved around the nucleus in orbits of fixed sizes and energies. Electron energy in this model was quantised; electrons could not occupy values of energy between the fixed energy levels.

+ PROPOSED STABLE ELECTRON ORBITS; EXPLAINED THE EMISSION SPECTRA OF SOME ELEMENTS

− MOVING ELECTRONS SHOULD EMIT ENERGY AND COLLAPSE INTO THE NUCLEUS; MODEL DID NOT WORK WELL FOR HEAVIER ATOMS

QUANTUM MODEL

ERWIN SCHRÖDINGER

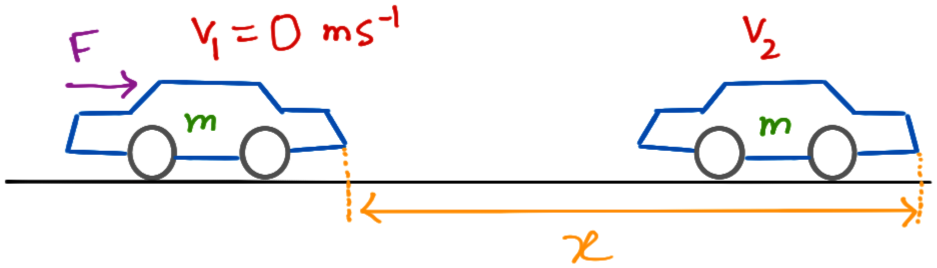
1926

Schrödinger stated that electrons do not move in set paths around the nucleus, but in waves. It is impossible to know the exact location of the electrons; instead, we have 'clouds of probability' called orbitals, in which we are more likely to find an electron.

+ SHOWS ELECTRONS DON'T MOVE AROUND THE NUCLEUS IN ORBITS, BUT IN CLOUDS WHERE THEIR POSITION IS UNCERTAIN

+ STILL WIDELY ACCEPTED AS THE MOST ACCURATE MODEL OF THE ATOM

Classical mechanics: Newton's laws of motion

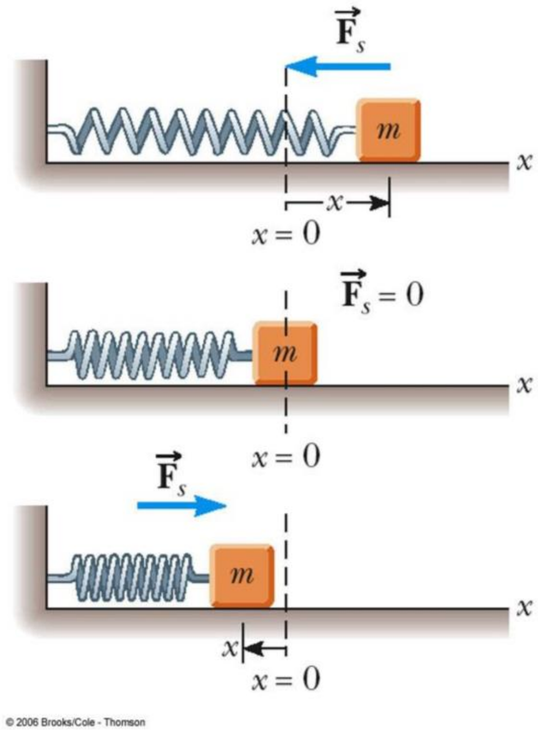


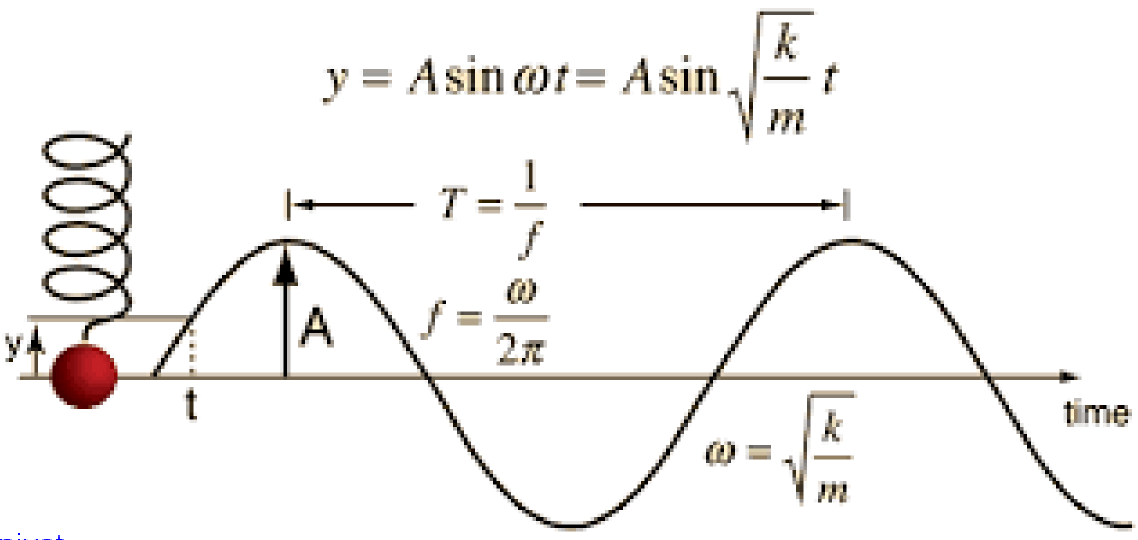
For Macroscopic Particle

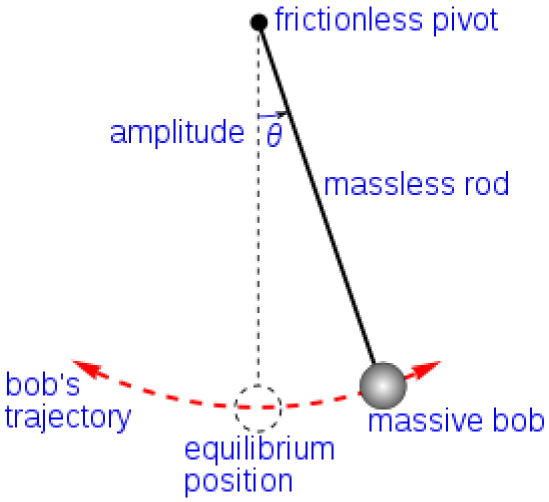
$$\text{Force, } F_x = m\frac{dv}{dt} = m\frac{dx^2}{dt^2}$$

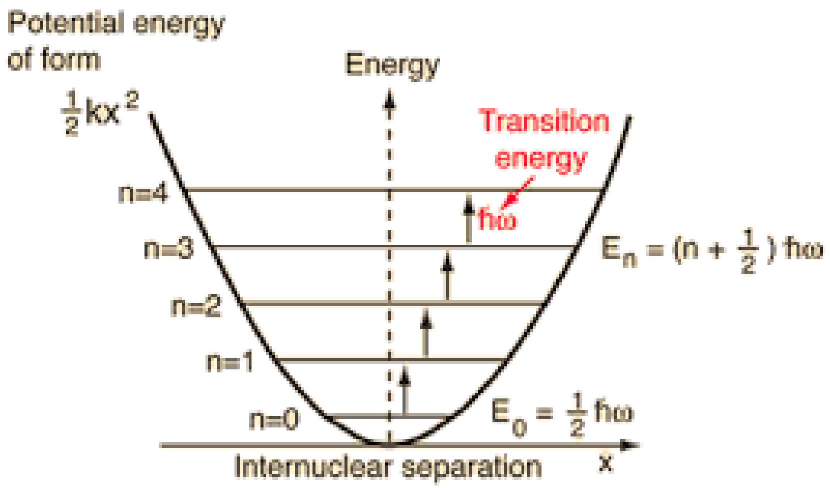
- The **state of an object** at any time can be determined by its **coordinate** and **velocity** which is are **continuous function of time**.
- If the **state of an object** as well as **force** applied is known at **any instance** then we can **predict** sate of the object **any other time**.

Simple Harmonic Oscillator







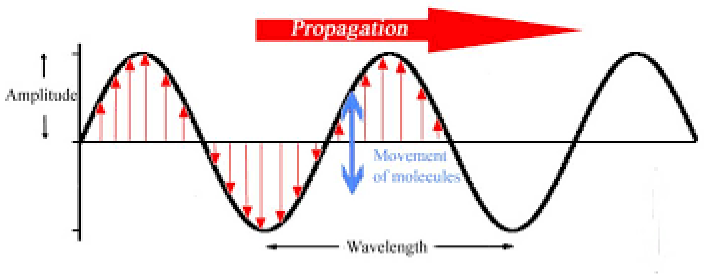


$$F = -kx$$

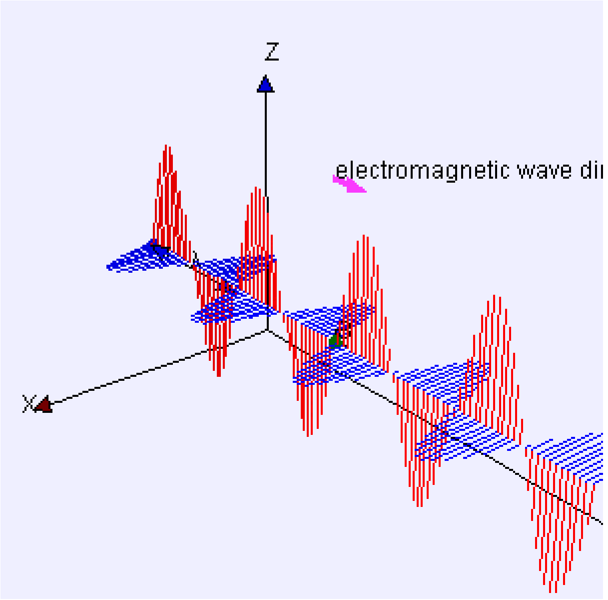
$$E = 1/2kx^2$$

$$E_n = (n + \frac{1}{2})\hbar\omega$$

Electromagnetic radiation



Transverse Wave



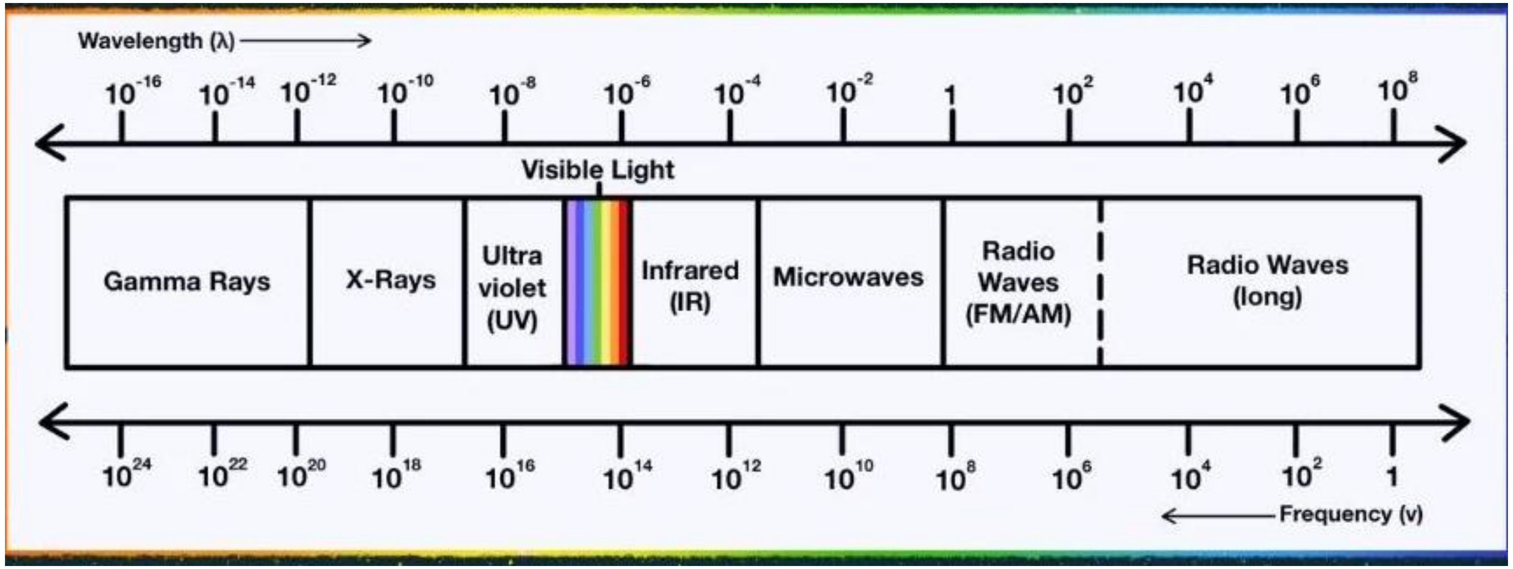
Electromagnetic Wave

Speed, $c = 2.998 \times 10^8$ m/s

$$\lambda \nu = c$$

$$\text{Energy, } E = h\nu = h\frac{c}{\lambda}$$

- The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.

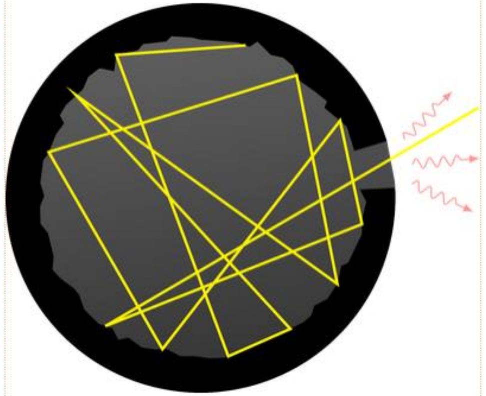


Black Body Radiation

Max Planck

An ideal body, which emits and absorbs radiations of all frequencies uniformly, is called a black body and the radiation emitted by such a body is called black body radiation.

Insulating wall



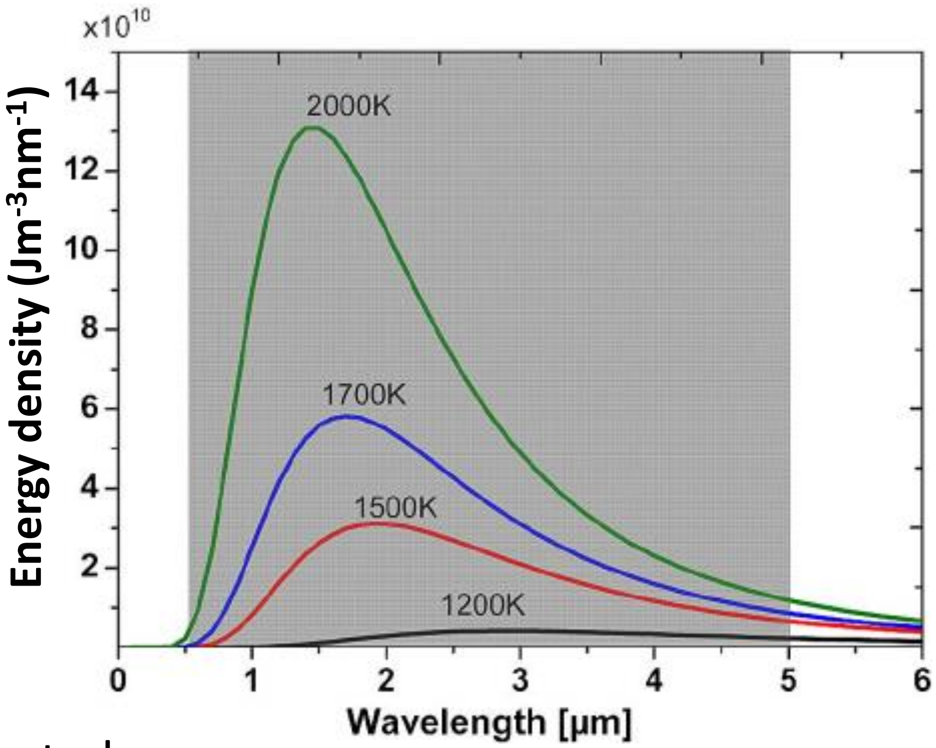
A perfect black body

Kirchoff's law

- A black body not only absorbs all the radiation falling upon it but also acts as a **perfect radiator** when heated.
- The radiation given out by a black body is **dependent on the temperature** of the cavity and is **independent on the nature of the interior material**.

Observations

- Wavelength corresponding to a peak, shifts from higher to lower values as temperature is raised.
- Energy density per unit wavelength is more at high temperature than at low temperature.



Two fundamental Laws

(a) Wein Displacement Law

Relation between wavelength corresponding to maximum of a spectral distribution (λ_m) and the temperature (T),

$$\lambda_m T = c;\ c = 2.88\ \text{mmK}$$

(b) Stefan-Boltzmann Law

Energy density per unit volume (ε) is related to temperature (T) as,

$$\varepsilon = aT^4;\ a = 7.565767 \times 10^{-16}\ \text{Jm}^{-3}\text{K}^{-4}$$

The same reaction can be written in terms of emmitance (R)

$$R = \sigma T^4\ ;\ \sigma = \frac{ac}{4} = 5.67 \times 10^{-8}\ \text{Wm}^{-2}\text{K}^{-4}\ \text{(Stefan Boltzmann constant)}$$

Theoretical interpretation

(a) Wein Distribution Law

Amount of energy ($E_\lambda d\lambda$) emitted by a black body at a temperature T within the wavelength wavelength range λ and $d\lambda$,

$$E_\lambda d\lambda = A_1 \lambda^{-5} e^{-A_2/\lambda T} d\lambda$$

A_1 and A_2 are constants.

When $\lambda = 0$ or ∞, $E_\lambda d\lambda = 0$; i.e. no energy is emitted by a wave of zero or infinite wavelength.

(b) Rayleigh-Jean Distribution Law

Black body radiation consists of a number of oscillator with one possible frequency per oscillator.

Energy of each oscillator in equilibrium with source at temperature T, is kT; k = Boltzmann constant

The number of oscillator per unit volume (dN) in the frequency range ν and $\nu + d\nu$ is given by,

$$dN = \frac{8\pi\nu^2}{c^3} d\nu$$

$$\text{Energy density, } E_\nu d\nu = \frac{8\pi\nu^2}{c^3} kT d\nu$$

Planck's Quantum hypothesis

- An oscillator emits or absorbs radiation discontinuously, in the form of energy packet called quanta. Energy of a quantum radiation given by,

$$E = h\nu = h\frac{c}{\lambda}$$

- Planck considered the black body radiations to consist of linear oscillators of molecular dimensions and that the energy of a linear oscillator can assume only the discrete values 0, hv, 2hv, 3hv.... nhv
- If N_0, N_1, N_2... are the number of oscillators per unit volume of the hologram possessing energies 0, hv, 2hv.... respectively, then the total number of oscillators N per unit volume will be

$$N = N_0 + N_1 + N_2 + ...$$

But the number of oscillators, N_r having energy E_r is given by (Maxwell's formula)

$$N_r = N_0 e^{-E_r/kT}$$

$$N = N_0 + N_0e^{-E_1/kT} + N_0e^{-E_2/kT} + \ldots..$$
$$= N_0 + N_0e^{-hv/kT} + N_0e^{-2hv/kT} + \ldots..$$
$$= N_0(1 + e^{-hv/kT} + e^{-2hv/kT} + \ldots..)$$
$$= N_0(1 + x + x^2 + \ldots..)$$
$$= N_0/(1-x)$$

$$E = E_0N_0 + E_1N_1 + E_2N_2 + \ldots.$$
$$= 0.N_0 + hv.N_0e^{-E_1/kT} + 2hv.N_0e^{-E_2/kT} + \ldots..$$
$$= = N_0.hv(0 + e^{-hv/kT} + 2e^{-2hv/kT} + \ldots..)$$
$$= N_0 .hv(x + 2x^2 + 3x^3 + \ldots..)$$
$$= N_0hvx/(1-x)^2$$

Average energy per oscillator, $\bar{E} = E/N = \frac{N_0hvx(1-x)}{N_0(1-x)2}$

$$= \frac{hvx}{(1-x)}$$
$$= \frac{hve^{-hv/kT}}{(1-e^{-hv/kT})}$$
$$= \frac{hv}{(e^{-hv/kT}-1)}$$

The number of oscillator per unit volume (dN) in the frequency range ν and ν + dν is given by,

$$dN = \frac{8\pi\nu^2}{c^3}\, d\nu$$

$$\text{Energy density, } E_\nu d\nu = \frac{8\pi\nu^2}{c^3}\, \frac{h\nu}{(e^{-h\nu/kT} - 1)}\, d\nu$$

$$= \frac{8\pi h\nu^3}{c^3(e^{-h\nu/kT} - 1)}\, d\nu$$

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5(e^{-hc/\lambda kT} - 1)}\, d\lambda$$

$$d\nu = (c/\lambda^2)d\lambda$$

(a) Wein Disstribution Law

When, hc>> λkT; $E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda kT} d\lambda = A_1 \lambda^{-5} e^{-A2/\lambda T} d\lambda$

(b) Rayleigh-Jean Distribution Law

When, hc<< λkT; $e^{-hc/\lambda kT} = 1 + hc/\lambda kT + \frac{1}{2!}(hc/\lambda kT)^2 + \ldots\ldots = 1 + hc/\lambda kT$ (neglecting higher terms)

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{1 + hc/\lambda kT - 1}$$

$$= \frac{8\pi}{\lambda^4} kT d\lambda$$

$$= \frac{8\pi \nu^2}{c^3} kT d\nu$$

(a) Wein Displacement Law

At short wavelength $\exp(hc/\lambda kT) >> 1$

$$E_\lambda = \frac{8\pi hc}{\lambda^5}\exp(-hc/\lambda kT)$$

Differentiating E_λ with respect to λ and equating to zero

$$dE_\lambda/d\lambda = 8\pi hc\frac{d}{d\lambda}[\lambda^{-5}\exp(-hc/\lambda kT)] = 0$$

$$\Rightarrow \left[(-5)\lambda^{-6} + \lambda^{-5}\left(\frac{hc}{\lambda^2 kT}\right)\right]\exp\left(-\frac{hc}{\lambda kT}\right) = 0$$

$$\Rightarrow \left[5\lambda^{-6} + \frac{\lambda^{-7}hc}{kT}\right] = 0$$

$$\Rightarrow \lambda T = \frac{hc}{kT} = 2.88mmK$$

(b) Stefan Boltzmann Law

If we integrate energy density over the interval $\lambda = 0$ to ∞

$$\int_0^\infty E_\lambda \, d\lambda = \int_0^\infty \frac{8\pi hc}{\lambda^5} \frac{1}{\exp\left(\frac{hc}{\lambda kT}\right) - 1} d\lambda$$

Substituting $\frac{hc}{\lambda kT} = x$ and $\mathbf{d}\lambda = -\frac{hc\,\mathbf{d}x}{x^2 kT}$

$$\int_0^\infty E_\lambda \, \mathbf{d}\lambda = \int_\infty^{\mathbf{0}} \frac{8\pi hc}{\left(\frac{hc}{xkT}\right)^5} \frac{1}{(\mathbf{e}^x - 1)} \left(-\frac{hc}{x^2 hT}\right) \mathbf{d}x$$

$$= -\frac{8\pi k^4 T^4}{(\boldsymbol{hc})^3} \int_\infty^0 \frac{x^3}{\mathbf{e}^x - 1} \mathbf{d}x$$

$$= \frac{8\pi k^4 T^4}{(\boldsymbol{hc})^3} \int_{\mathbf{0}}^\infty \frac{x^3}{\mathbf{e}^x - 1} \mathbf{d}x$$

$$= \frac{8\pi k^4 T^4}{(\boldsymbol{hc})^3} \frac{\pi^4}{15}$$

$$= aT^4$$

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$$

$$a = \frac{8\pi^5 k^4}{15(hc)^3} = \frac{4\sigma}{c}$$

and

$$\sigma = \frac{2\pi^5 k^4}{15 c^2 h^3}$$

Photoelectric Effect

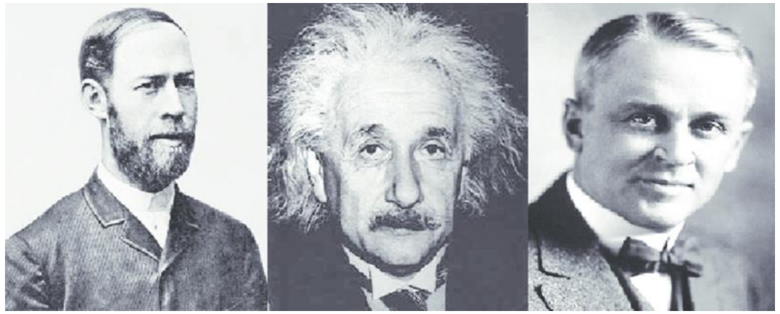
- When a beam of visible and ultraviolet light falls on the surface of an alkali metal, **electrons are emitted from surface**.
- This occurs to all solid, liquid and gases; if radiation of **appropriate frequency** is used.

- When a monochromatic radiation of **same frequency** and **varying intensities** are allowed to fall upon a metal surface:
- **When V is positive (accelerating);** the current increases to a until a saturation current is reached
- **When V is negative (retarding)**; current decreases until it reaches zero. Limiting retarding potential is called **stopping potential** of the surface at that frequency.
- Voltage V_0 is required to stop electrons of maximum speed v_m

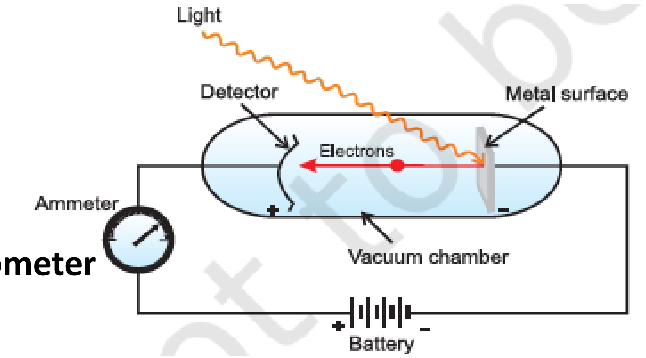
$$\frac{1}{2}mv_m^2 = eV_0$$

Conservation of energy

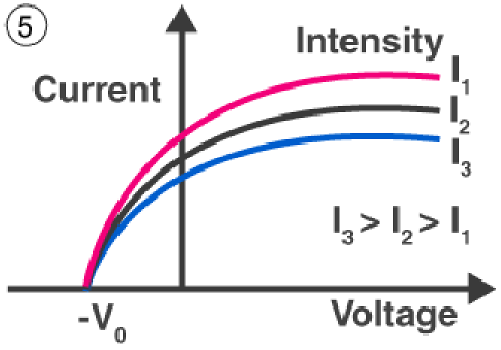
- **Stopping potential is independent of intensity, but dependent of frequency**



Hertz, Einstein and Millikan



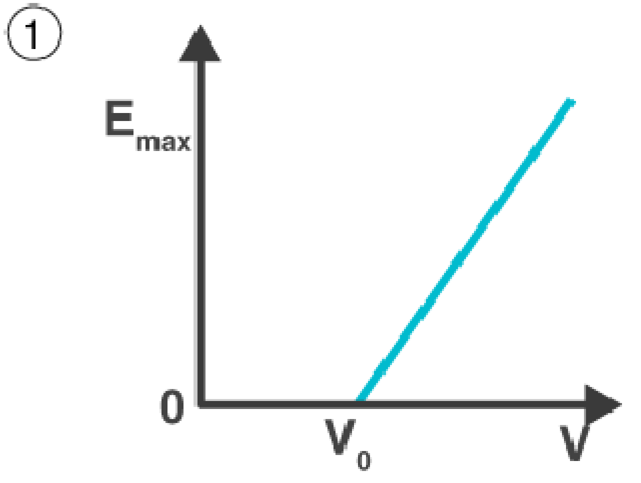
Or galvanometer



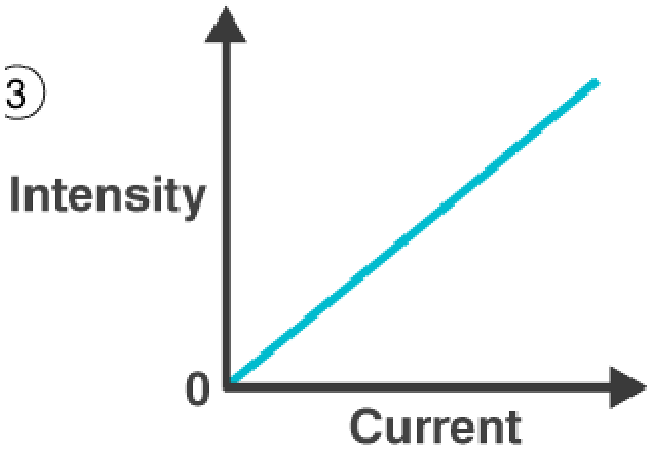
Potential V/s Current

- The relation between Potential, V and frequency, ν is **linear**.
- Stopping potential becomes zero at a certain frequency, called **threshold frequency**.
- A radiation with frequency above threshold frequency can eject electron from a metal surface.
- Threshold frequency is **different** for different metals.

- The maximum kinetic energy of a photoelectron is independent of the incident radiation, but varies directly with frequency.
- The total **photoelectric current** is directly proportional to the **number of electrons emitted per unit time** and this in turn is directly proportional to the **intensity of incident radiation**.



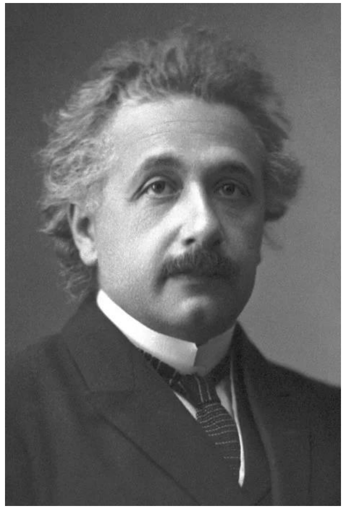
Kinetic energy V/s frequency



Saturated current V/s Intensity

Limit of classical theory:

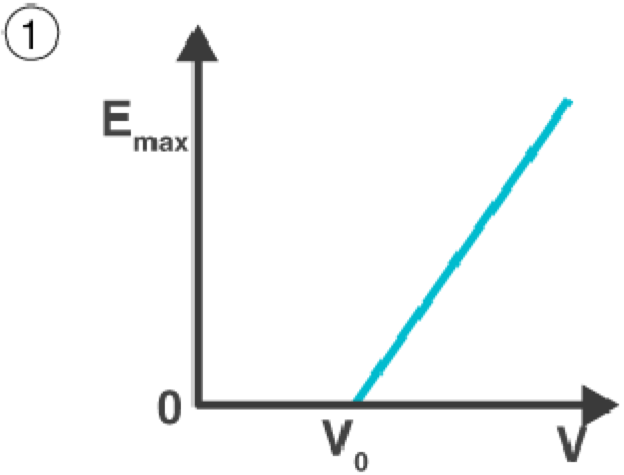
- Kinetic energy of an electron should increase with increasing intensity (number of photon per unit surface area).
- Regardless of the frequency; any radiation that falls for a sufficient time should emit electrons.



Albert Einstein
Nobel prize for physics, 1921

When a photon of frequency, v [Energy = hv] falls upon a metal surface:

- The entire energy of the photon is transferred to the metal surface.
- A part of the total energy is used to eject electrons from the surface. This is called work function (hv_0): the energy corresponding to the threshold frequency (v_0).
- The rest of the energy is given to the ejected electron as kinetic energy.
- $h\nu = h\nu_0 + \frac{1}{2}mv_m^2$ (Einstein's equation of photoelectric emission)
- m is the mass of electron, v_m is the maximum velocity.
- Slope of potential energy vs frequency: Planck's constant.



Kinetic energy V/s frequency

$$h\nu = h\nu_0 + eV_0$$

$$\Rightarrow \nu = \nu_0 + \left(\frac{e}{h}\right)V_0$$

Slope of the plot of incident frequency vs stopping potential is e/h

From here value of Planck's constant h is calculated as 6.55 x 10^{-34} Js