Dynamics of Chemical Systems-1: Part I

CY-1020 (total credit = 1)

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Course Details

Introduction of Quantum Mechanical Description of Atomic and Molecular Structure

- Experiments where classical mechanics fail!!
- The dawn of quantum mechanics
- Postulates of quantum mechanics
- Properties and definition of wave function
- Schrodinger equation
- Some exactly solvable problems and solutions
- Understanding the origin of experimental observables

Textbooks:

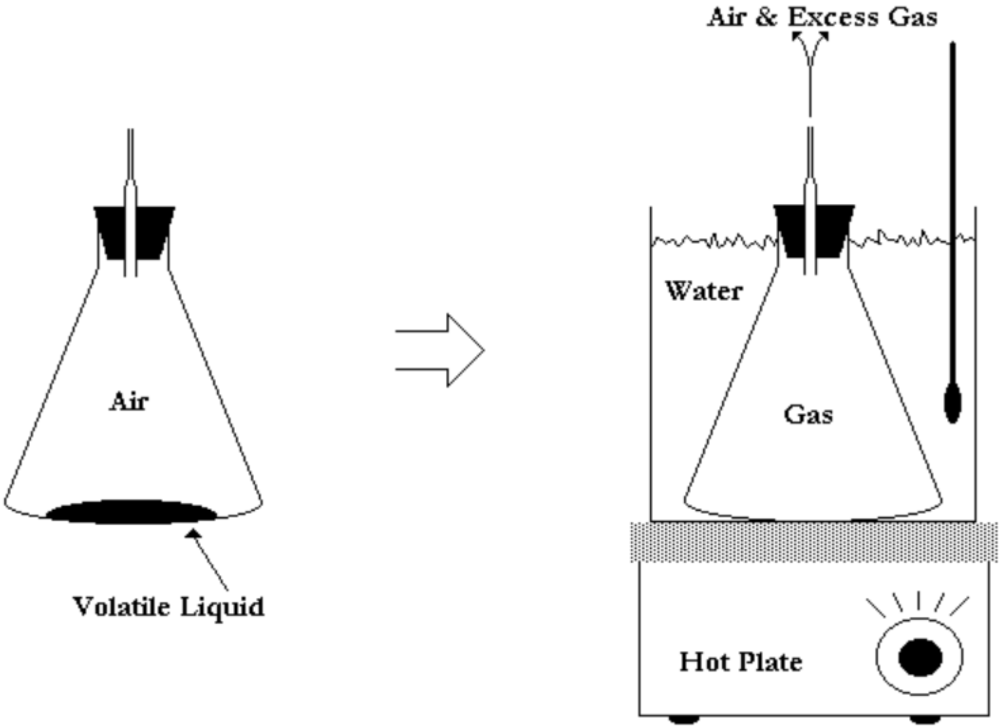
1. Physical Chemistry by Peter Atkins and Julio de Paula
2. Quantum Chemistry by Ira N. Levine
3. Physical Chemistry by McQuarrie and Simon

The Classical Theory: A Few Milestones

By 19th Century

- **Methods for determining atomic masses**

Jean-Baptiste Dumas



PV=nRT, Molecular Weight = mass of the substance/n

The Classical Theory: A Few Milestones

By 19th Century

- Methods for determining atomic masses
- **The periodic table based on physical and chemical**

	Gruppe I. R^1O	Gruppe II. RO	Gruppe III. R^1O^3	Gruppe IV. RH^4 RO^7	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^3 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H = 1							
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	N = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56 Co = 59 Ni = 60, Cu = 63.
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 56	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 104.
7	(Ag = 104)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	— — — —
9	)—)	—	—	—	—	—	—	
10	—	—	?Er = 178	?La = 180	Ta = 182	W - 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199.
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	— — — —

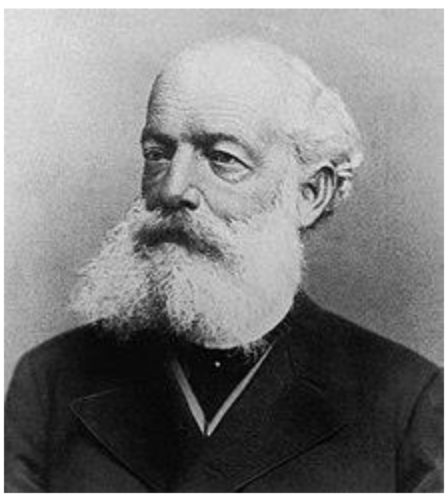
Mendeleev's Periodic Table of 1871, redrawn by J. O. Moran, 2013

Dmitri Mendeleev

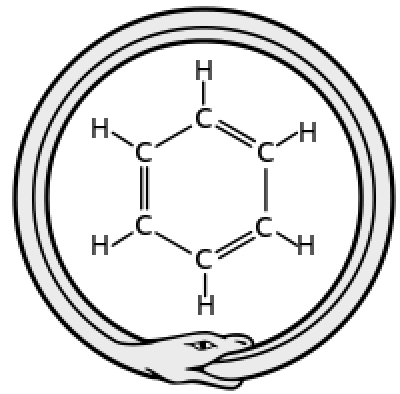
The Classical Theory: A Few Milestones

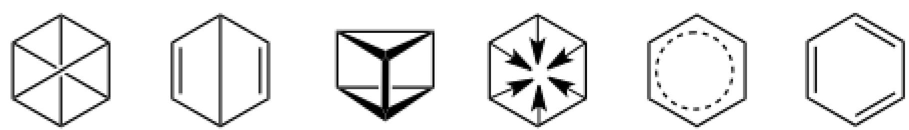
By 19th Century

- Methods for determining atomic masses
- The periodic table based on physical and chemical properties of atoms
- **Molecular structure of benzene**



August Kekulé





Historic benzene structures (from left to right)by Claus (1867),Dewar (1867),Ladenburg (1869), Armstrong (1887), Thiele (1899) and Kekulé (1865).

The Classical Theory: A Few Milestones

By 19th Century

- Laws of thermodynamics
- Newtonian mechanics
- Maxwell's equation for electromagnetic waves

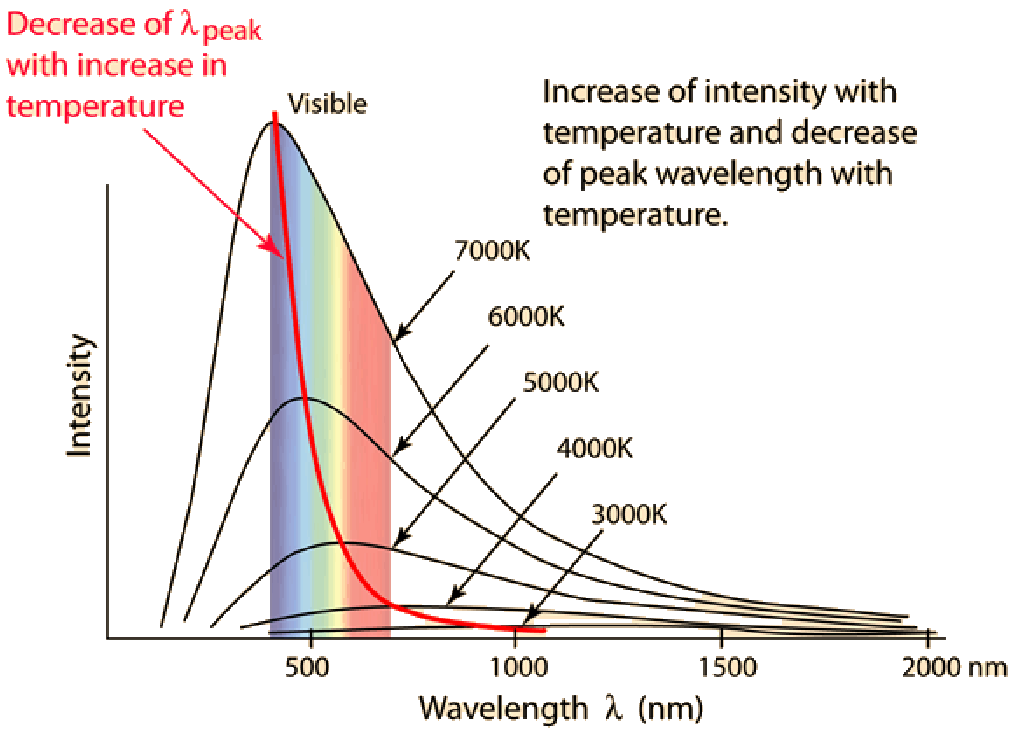
Sadi Carnot

James Clerk Maxwell

Sir Isaac Newton

Limitations of Classical Theory

- Blackbody radiation: Why radiation intensity decreases in the higher energy (low wavelength) region

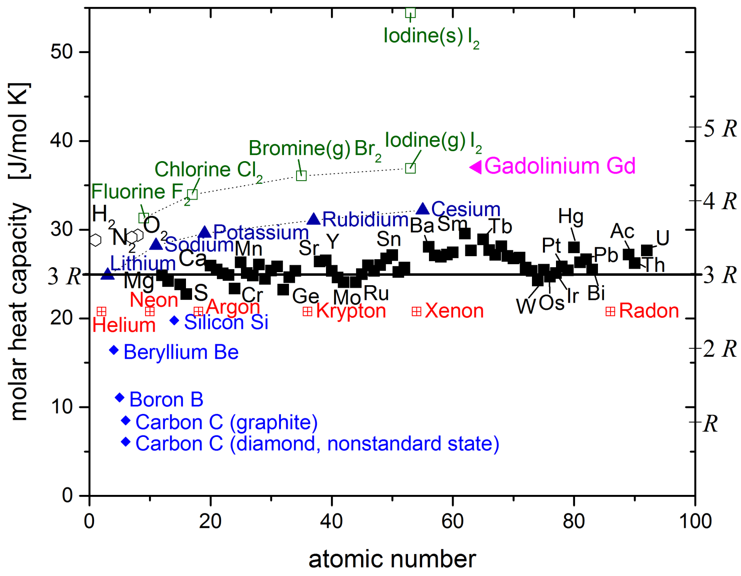


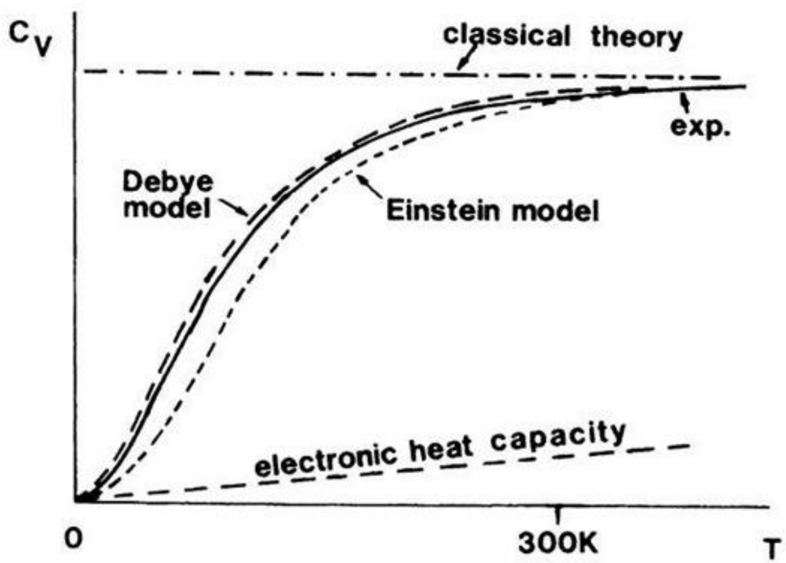
Limitations of Classical Theory

- Heat capacities of solids at low temperature T→0

$$Um = 3N_A kT = 3RT$$

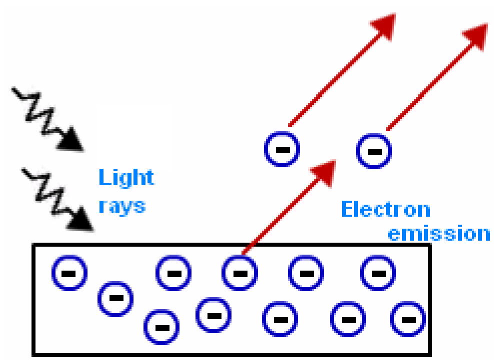
$$C_{V,m} = \left(\frac{\partial U_m}{\partial T}\right)_V = 3R \approx 25kJmol^{-1}$$

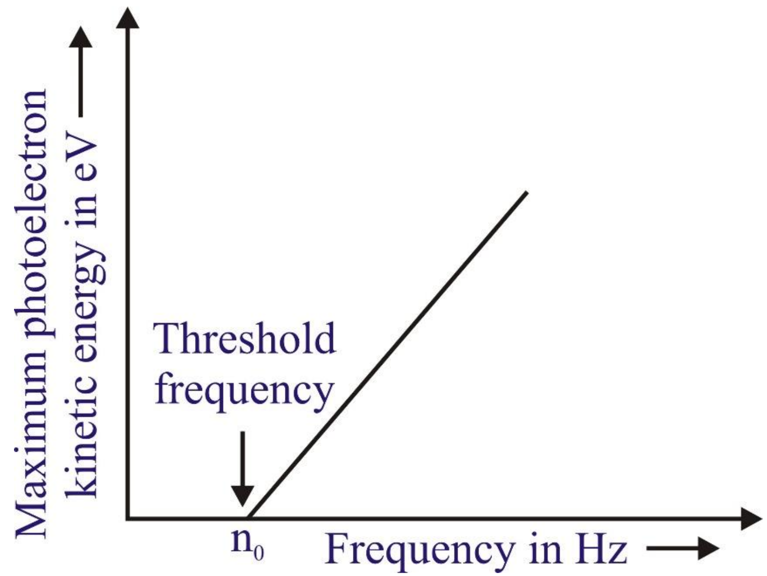




Limitations of Classical Theory

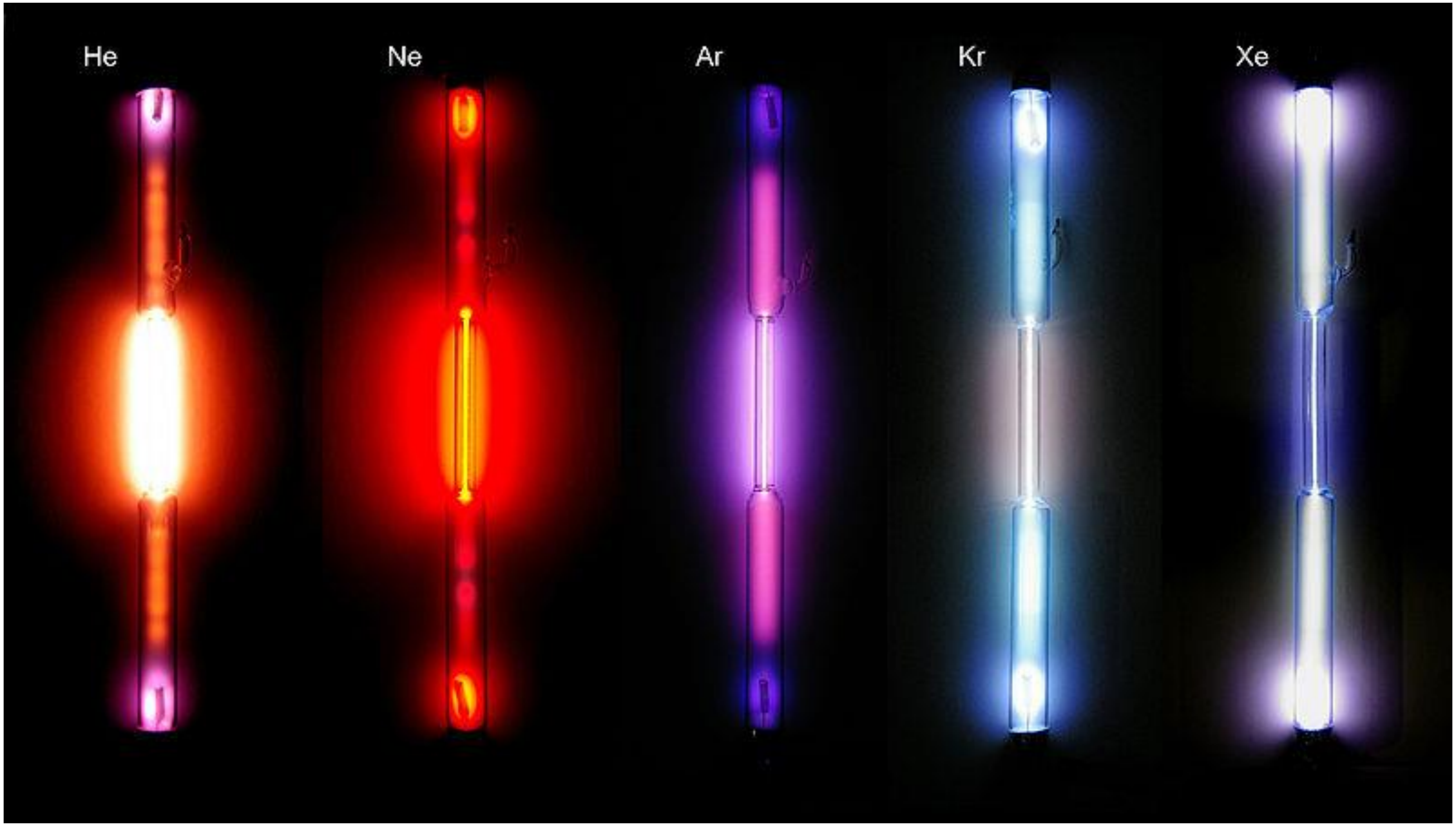
- Photoelectric effect





Limitations of Classical Theory

➢ Atomic Spectra

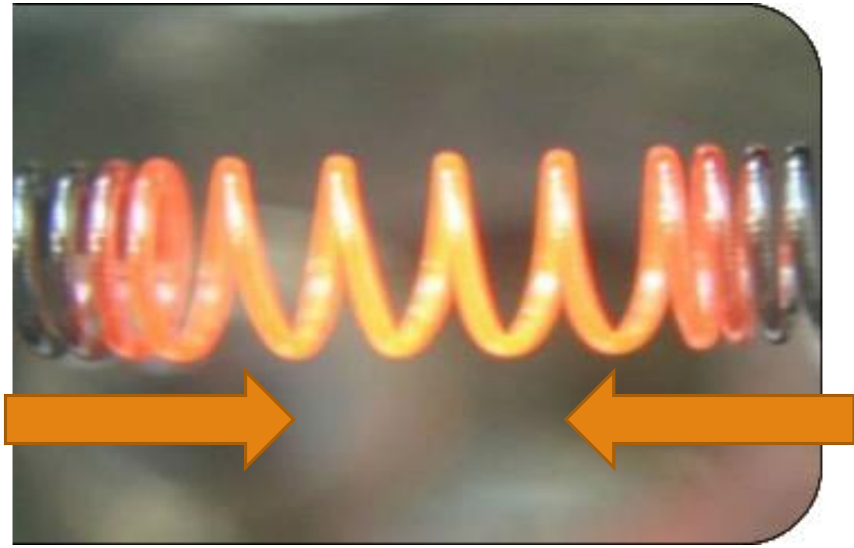


Radiation from Hot Objects

Any object radiates photons above 0 K

Radiation wavelength depends on the temperature of the object and independent of the material

Heated Metal Blocks



Filament

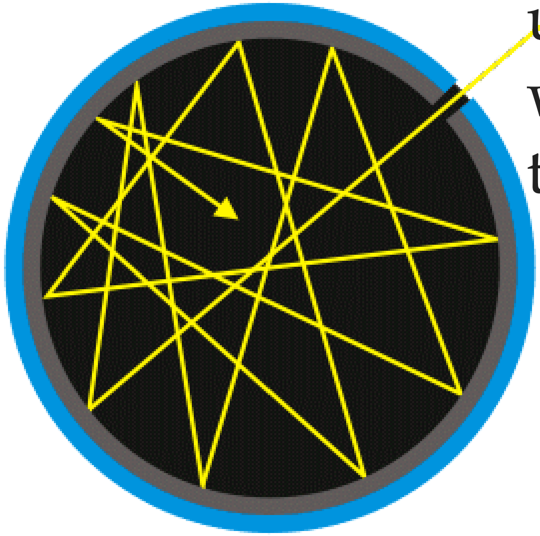
Blackbody Radiation

Ideal Blackbody?

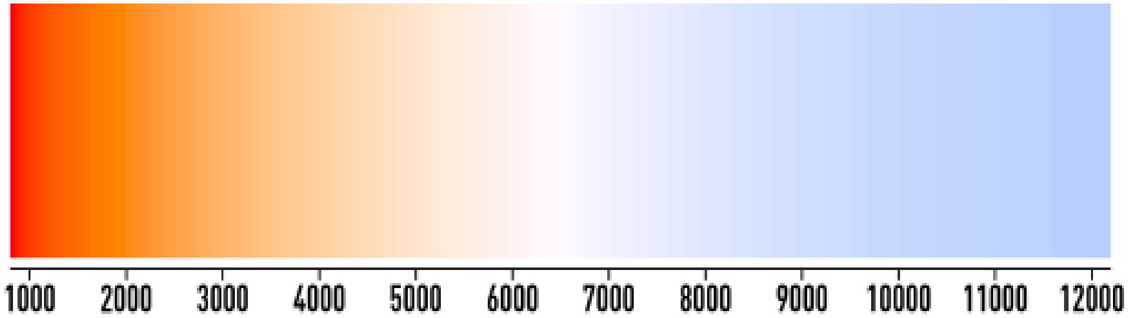
Completely absorbs incoming radiations of all frequency and none is reflected

Blackbody Radiation

The radiative emission of a blackbody at a uniform temperature has a characteristic wavelength distribution that depends on the temperature of the blackbody



Conceptual Blackbody



Blackbody Radiation

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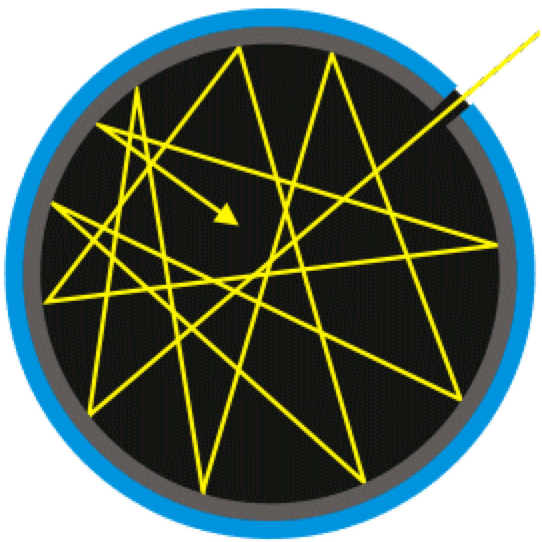

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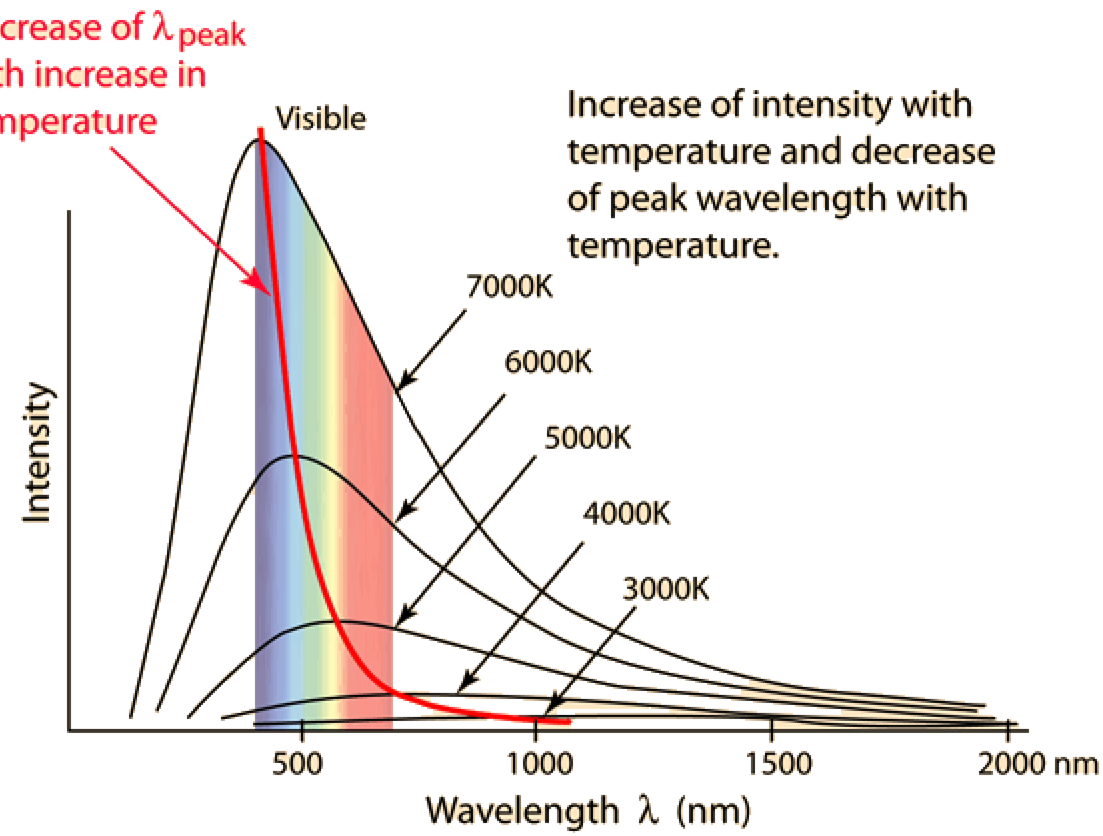


Blackbody Radiation: Energy Flux

Stefan-Boltzmann Law (1879)

Total radiation energy (M) at temperature T(K)

$M = \sigma T^4$

σ = Stefan-Boltzmann Constant = 56.7×10^{-9} W m^{-2} K^{-4}

Example 1-1: if an object is at 1000 K,

$M = 56.7 * 10^{-9} \times 10^{12}$ Wm^{-2} = 5.67 W cm^{-2} ($1m^2 = 10000\ cm^2$)

Example 1-2: Temperature of the Sun's Photosphere

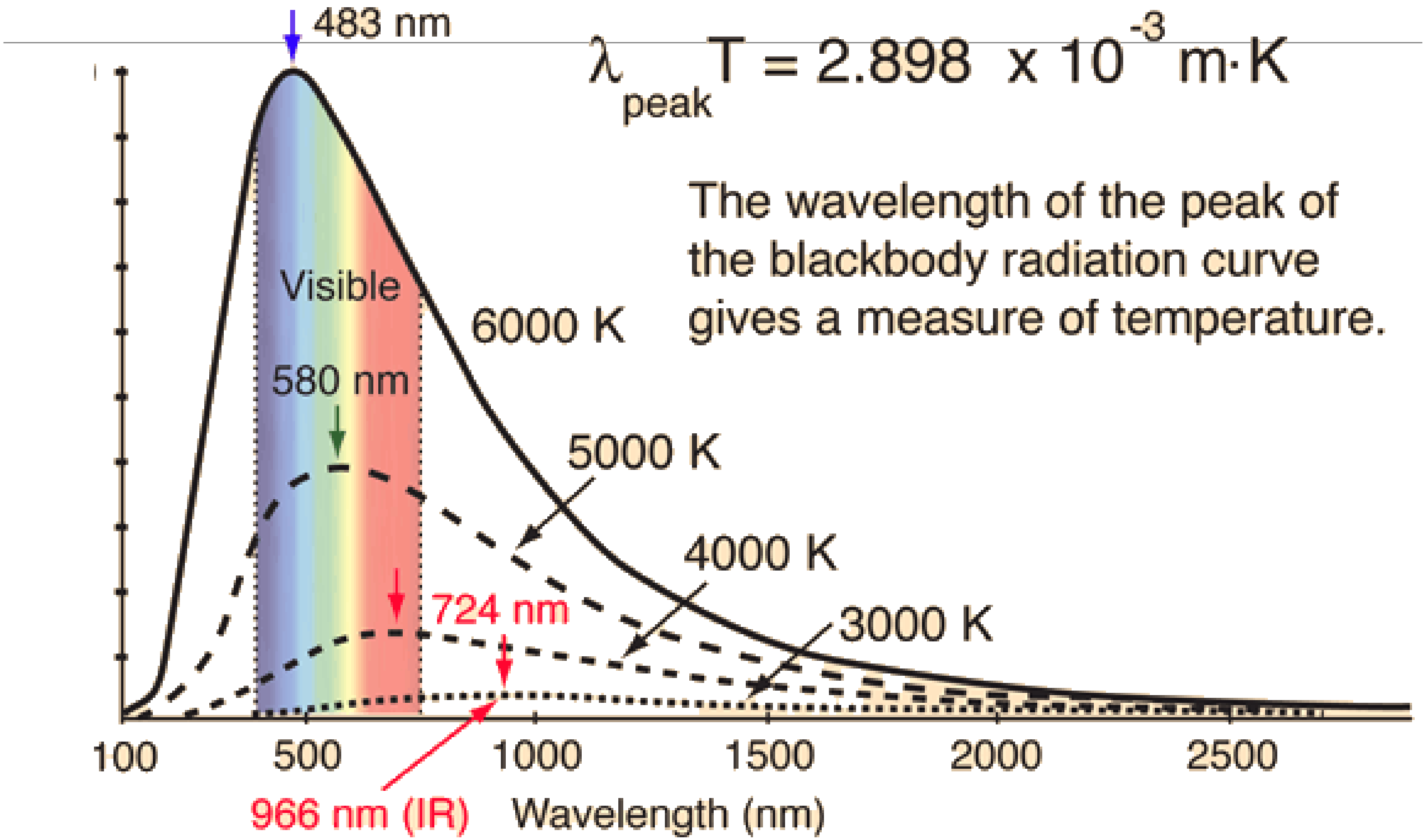
Energy flux M (average) = 6285 W cm^{-2} = 6285 0000 W M^{-2}

$T^4 = 62850000/\ 56.7/10^{-9}$; T = 5770K

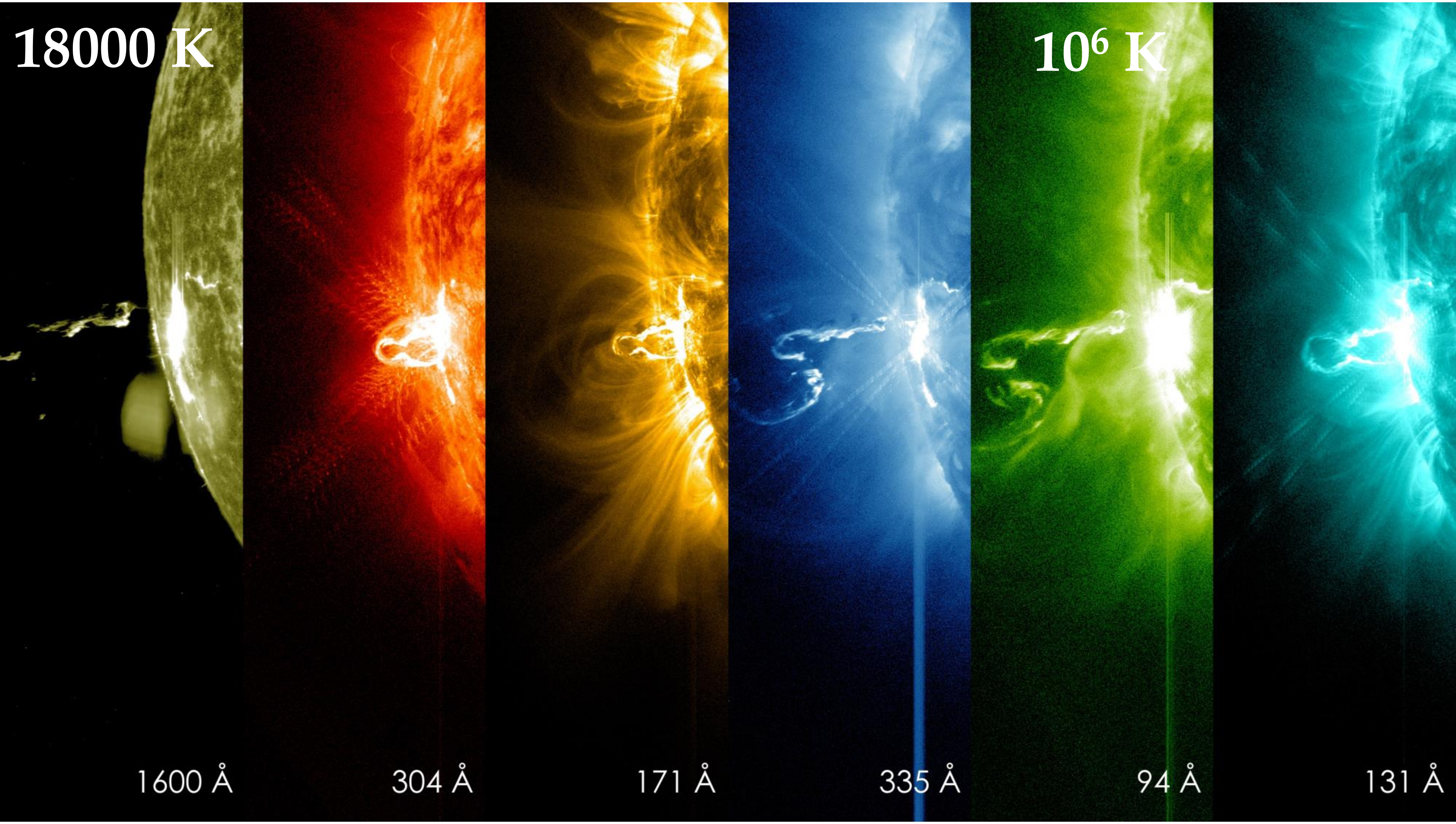
Actual temperature of the sun at the surface is ~5777 K

Blackbody Radiation: Distribution

Wien's Displacement Law (1893)



Radiation from the Sun



Taken from NASA.org

Blackbody Radiation: Distribution

Classical physics assumed this emission of light was a result of oscillating electrons and can oscillate equally well at any frequency

Rayleigh-Jeans Law

spectral density, ρ(ν, T), and ν

$$d\rho(\nu,T) = \rho_\nu(T)d\nu = \frac{8\pi k_B T}{c^3}\nu^2 d\nu \rightarrow \boxed{\rho_\nu(T) \propto \nu^2}$$

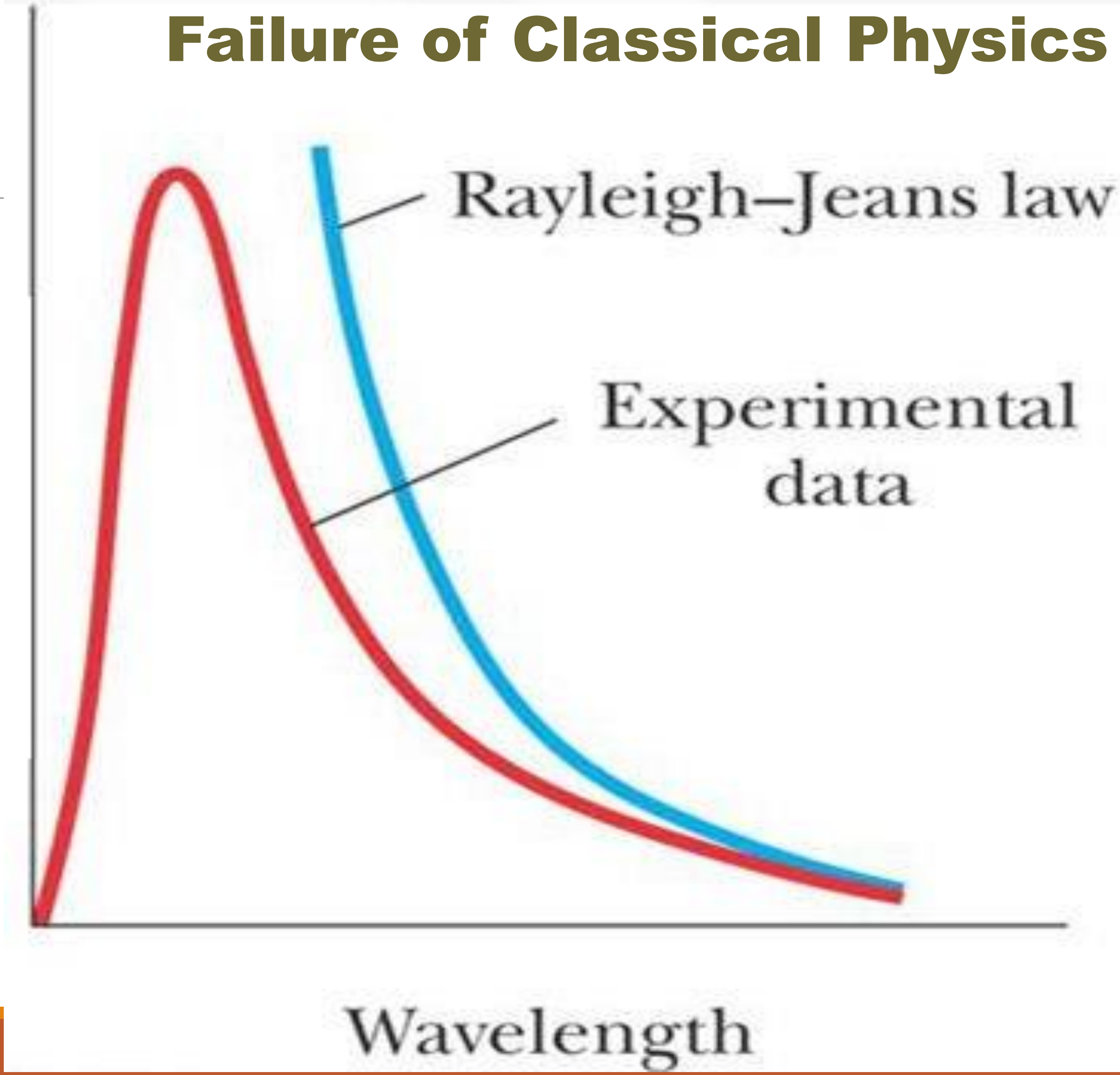
where $\rho_\nu(T)d\nu$ is the radiant energy density btwn ν and $\nu + d\nu$

A modified **Rayleigh-Jeans Law**

Radiation energy density at T K

$\rho(\lambda) = 8\pi\kappa T/\lambda^4$; k=Boltzmann's Constant =1.3815E-23 JK^{-1}

Blackbody Radiation: Failure of Classical Physics



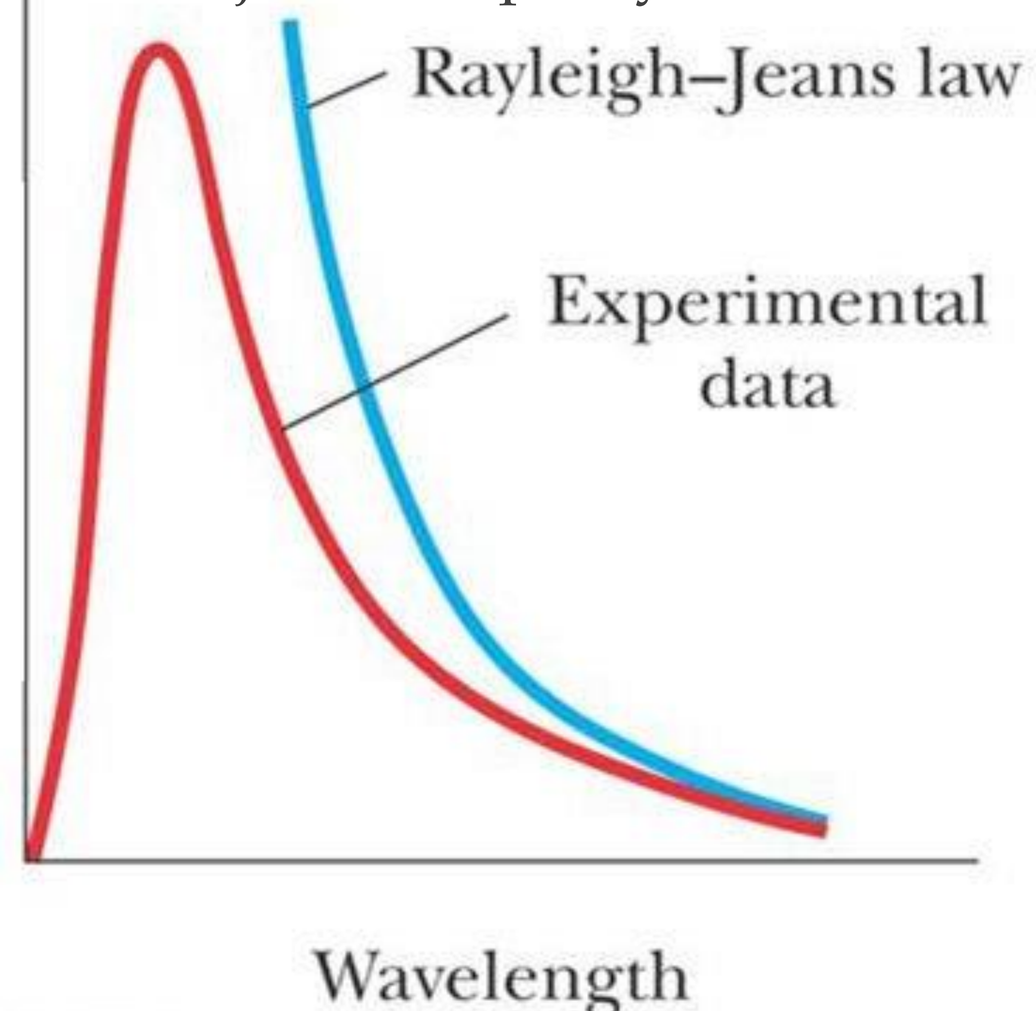
Blackbody Radiation: Distribution

Rayleigh-Jeans Law: Ultraviolet Catastrophe

- At shorter wavelengths, there is a major discrepancy between the theory and the experiment

- This divergence is termed as

Ultraviolet Catastrophe



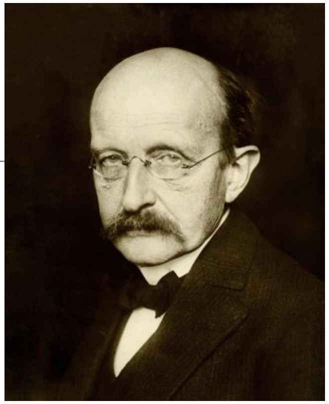
Blackbody Radiation: Planck's Law

Planck's Law (1900):

Planck's hypothesis: The permitted values of energies are integral multiples of frequencies; i.e.

$E = nh\nu = nhc/\lambda$; n = 0,1,2,…

Energy is Quantized



Max Planck

Value of 'h' (6.626×10^{-34} J s) was determined by fitting the experimental curve to the Planck's radiation law

Higher energy oscillators (at lower wavelengths) are less populated.

Blackbody Radiation: Planck's Law

$$d\rho(\nu,T) = \rho_\nu(T)d\nu = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_BT}-1}d\nu \rightarrow \boxed{\rho_\nu(T) \propto \nu^3}$$

Rayleigh-Jeans law from Planck's formula

or for $h\nu << k_BT$

Recall the Taylor Series for $e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \ldots$ for $-\infty < x < \infty$

$$\therefore\ e^{h\nu/k_BT} - 1 = 1 + \frac{h\nu}{k_BT} + \left(\frac{h\nu}{k_BT}\right)^2 \frac{1}{2!} + \ldots - 1$$

as $h\nu \rightarrow 0$ $\quad e^{h\nu/k_BT} - 1 = 1 + \frac{h\nu}{k_BT} + \left(\frac{h\nu}{k_BT}\right)^2 \frac{1}{2!} + \ldots - 1 \sim \frac{h\nu}{k_BT}$

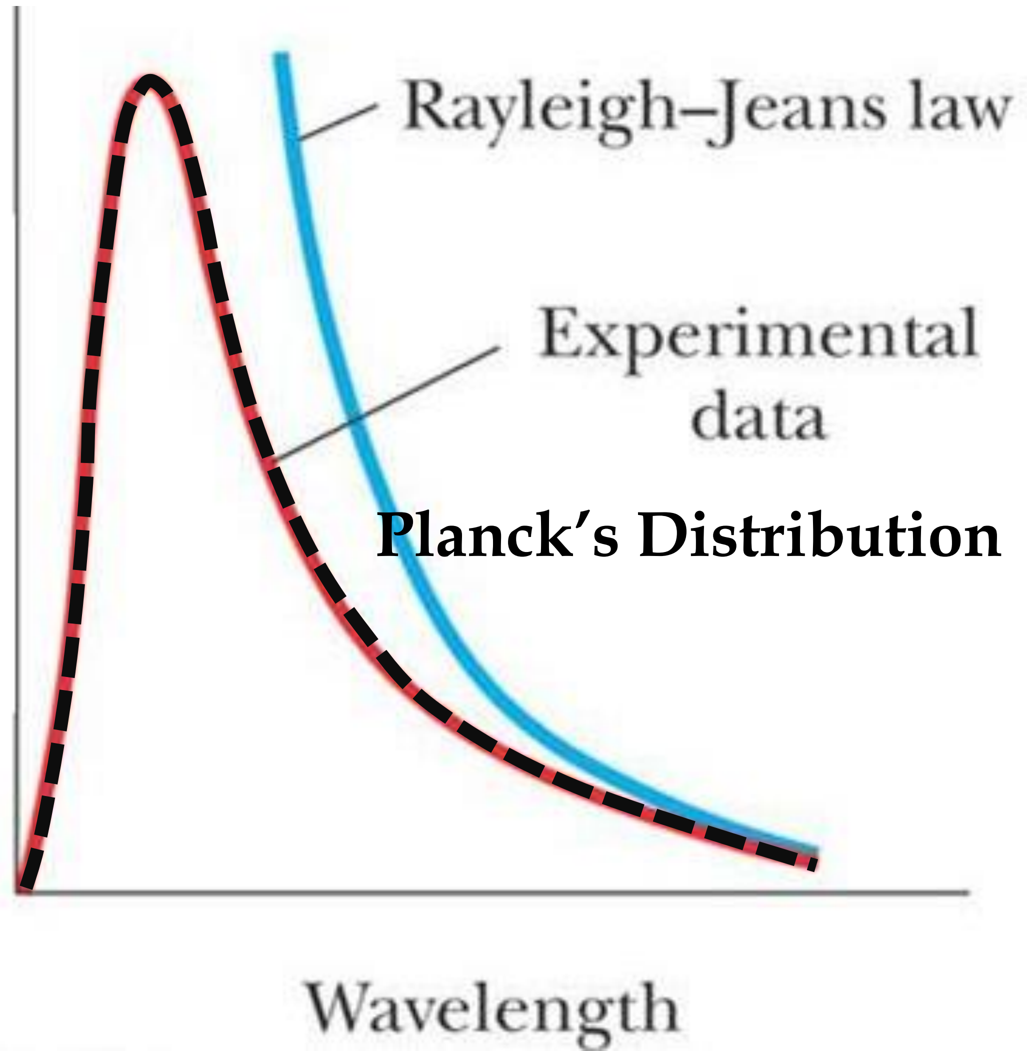
$$\rho_\nu(T)d\nu = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_BT}-1}d\nu = \frac{8\pi \cancel{h}}{c^3}\frac{\nu^{\cancel{3}\,2}k_BT}{\cancel{h}\,\cancel{\nu}}d\nu = \boxed{\frac{8\pi k_BT}{c^3}\nu^2 d\nu}$$

Blackbody Radiation: Distribution

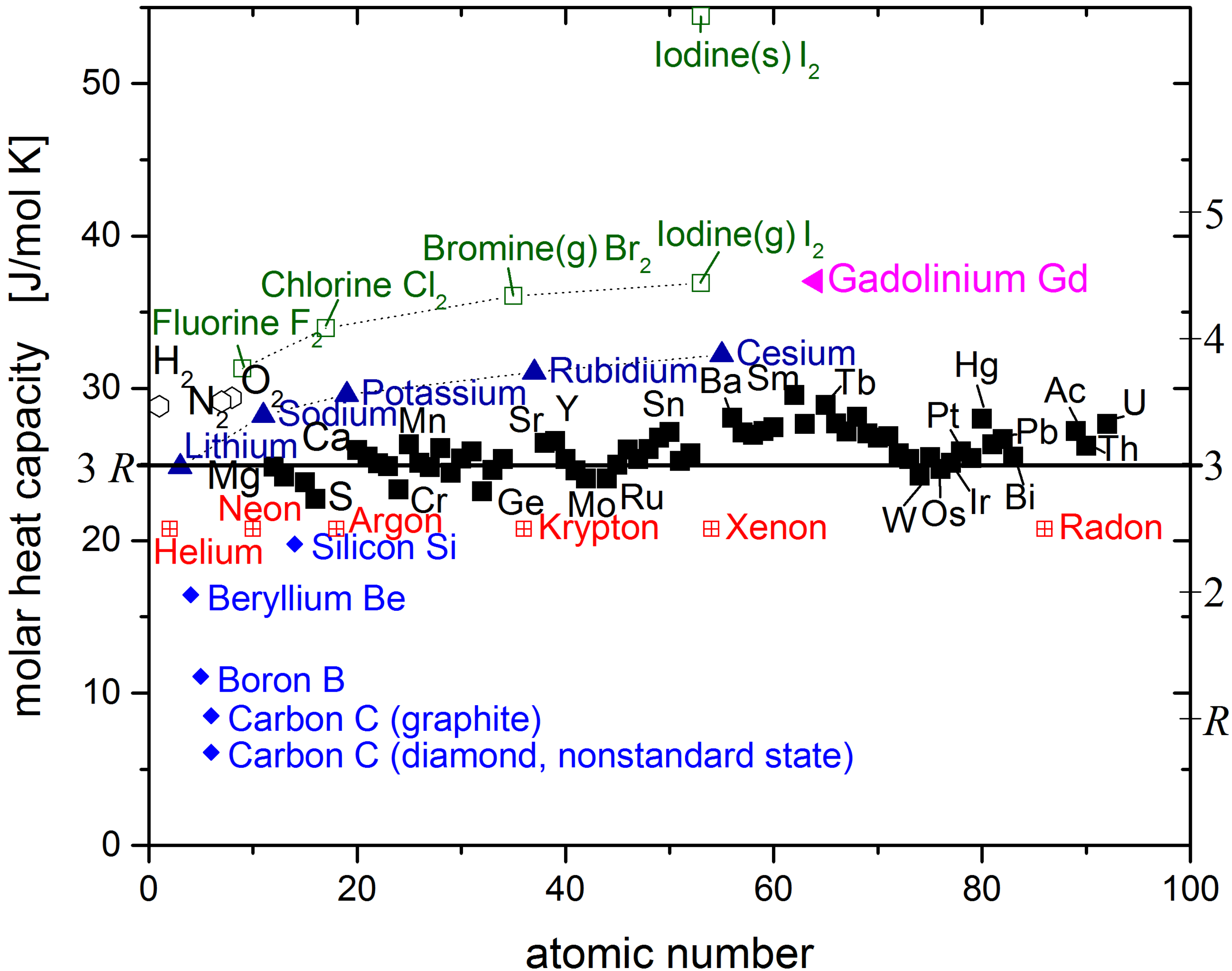
Modified Planck's Distribution:

The radiated energy density at T

$\rho(\lambda) = 8\pi hc/(\lambda^5 (e^{hc/\lambda kT} - 1))$



Heat Capacities of Solid



Heat Capacities of Solid

$$Um = 3N_A kT = 3RT$$

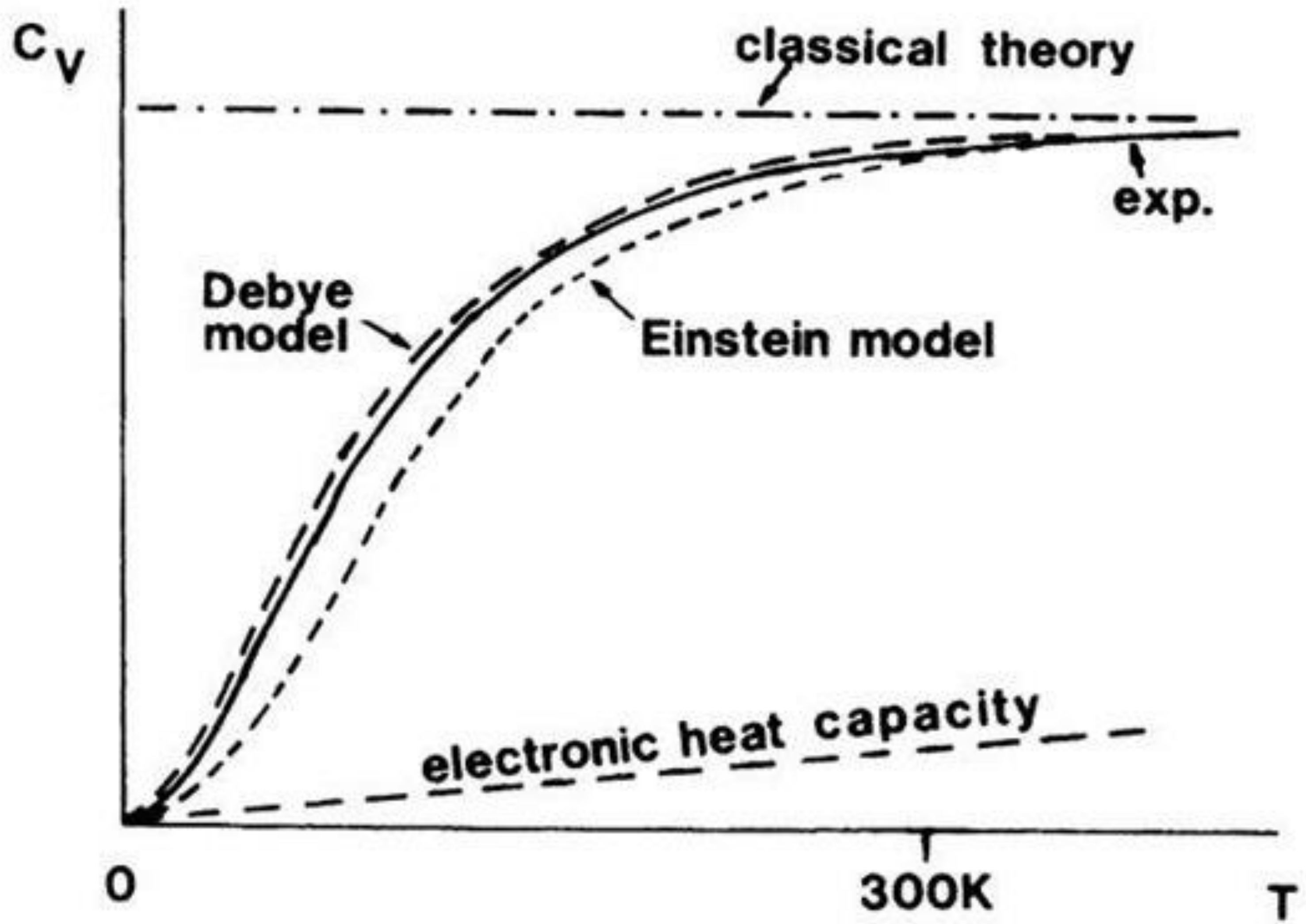
$$C_{V,m} = \left(\frac{\partial U_m}{\partial T} \right)_V = 3R \approx 25kJmol^{-1}$$

$C_{v,m}$=molar heat capacity
R=Ideal gas constant=8.314 $kJmol^{-1}$

N_a=Avogadro number

Dulong – Petit Law
The molar heat capacity of all solids have nearly same value of ~25 kJ

Heat Capacities of Solid at T→0



Heat Capacities of Solid at T→0

Einstein formula (1905) :

$$C_{V,m} = 3R\left(\frac{\theta_E}{T}\right)^2\left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T}-1}\right)^2 ;\theta_E = \frac{h\nu}{k}$$

The atoms in the crystal oscillate with a single frequency **v** and invoked the Planck's hypothesis that these vibrations have quantized energies **nh*ν***

θ_E is Einstein temperature, related to the frequency of atomic oscillators

Debye formula (1912)

(Oscillating freq. ranges from 0 to v_D)

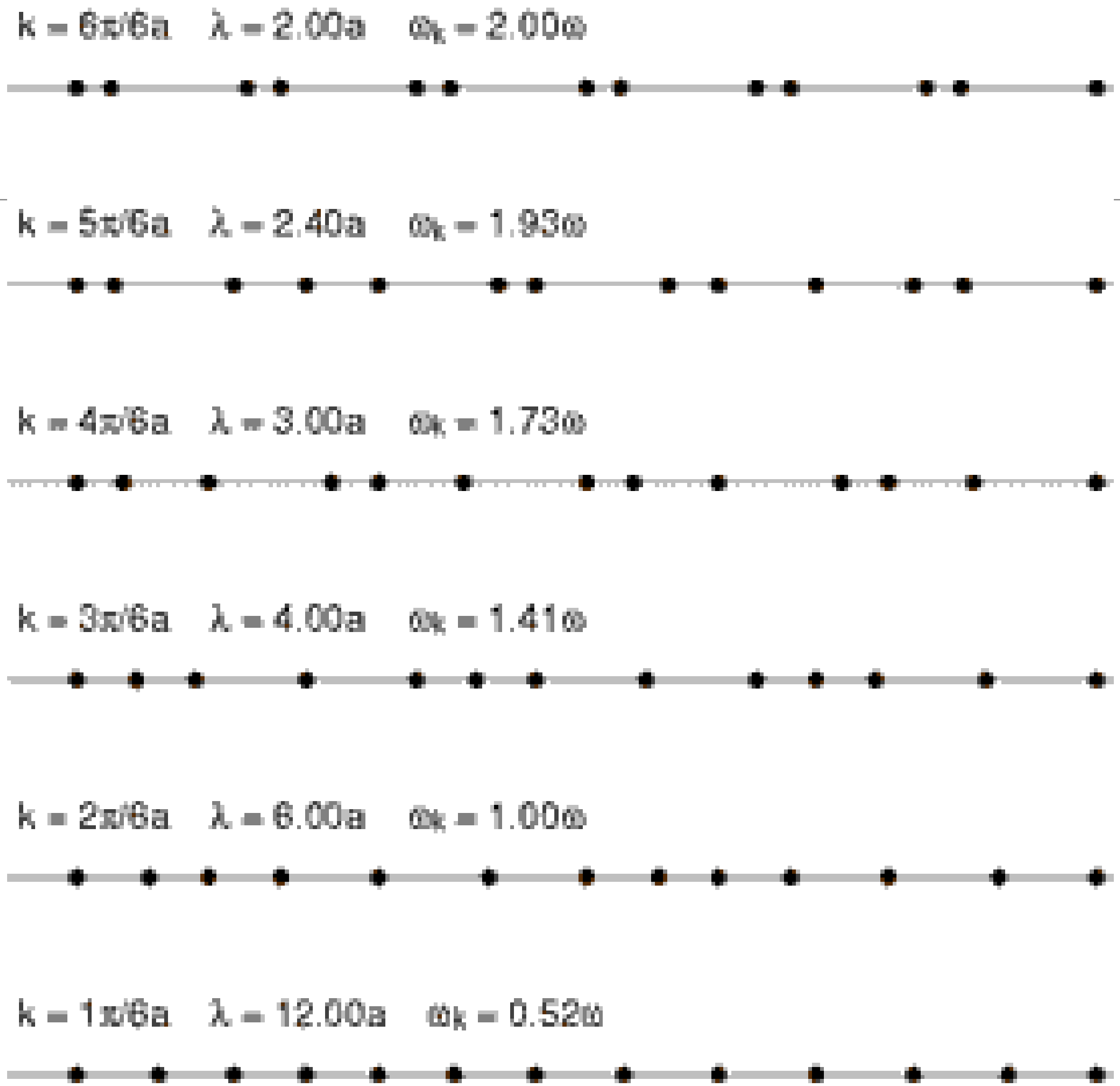
$$C_{V,m} = 3R\left(\frac{\theta_D}{T}\right)^3\int_o^{\theta_D/T}\frac{x^4e^x}{(e^x-1)^2}dx;\theta_D = \frac{h\nu_D}{k}$$

$$x = \frac{hc_s n}{2LkT}$$

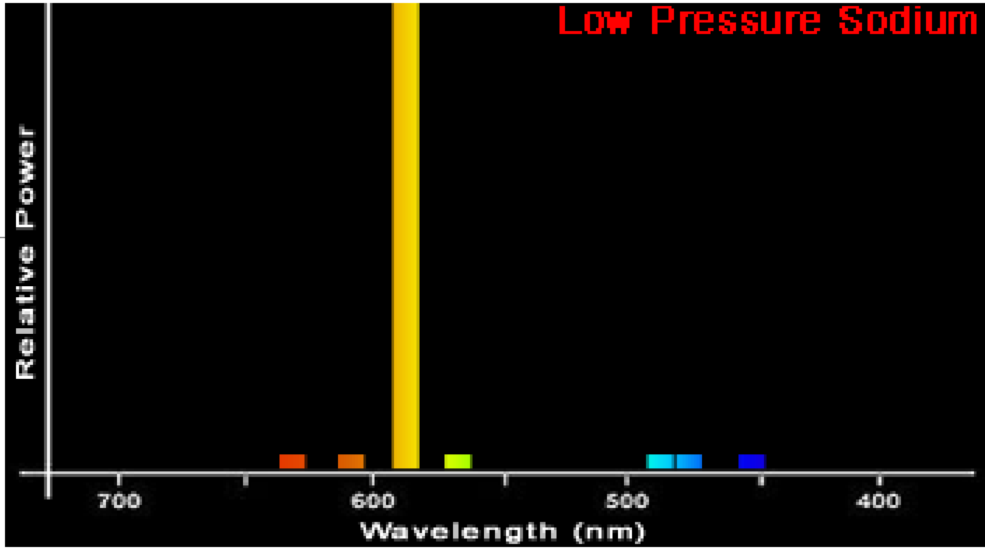
θ_D is Debye temperature, related to the frequency of phonon vibrations

At high temperature
Cv=3R

Lattice Vibrations



Atomic Spectra



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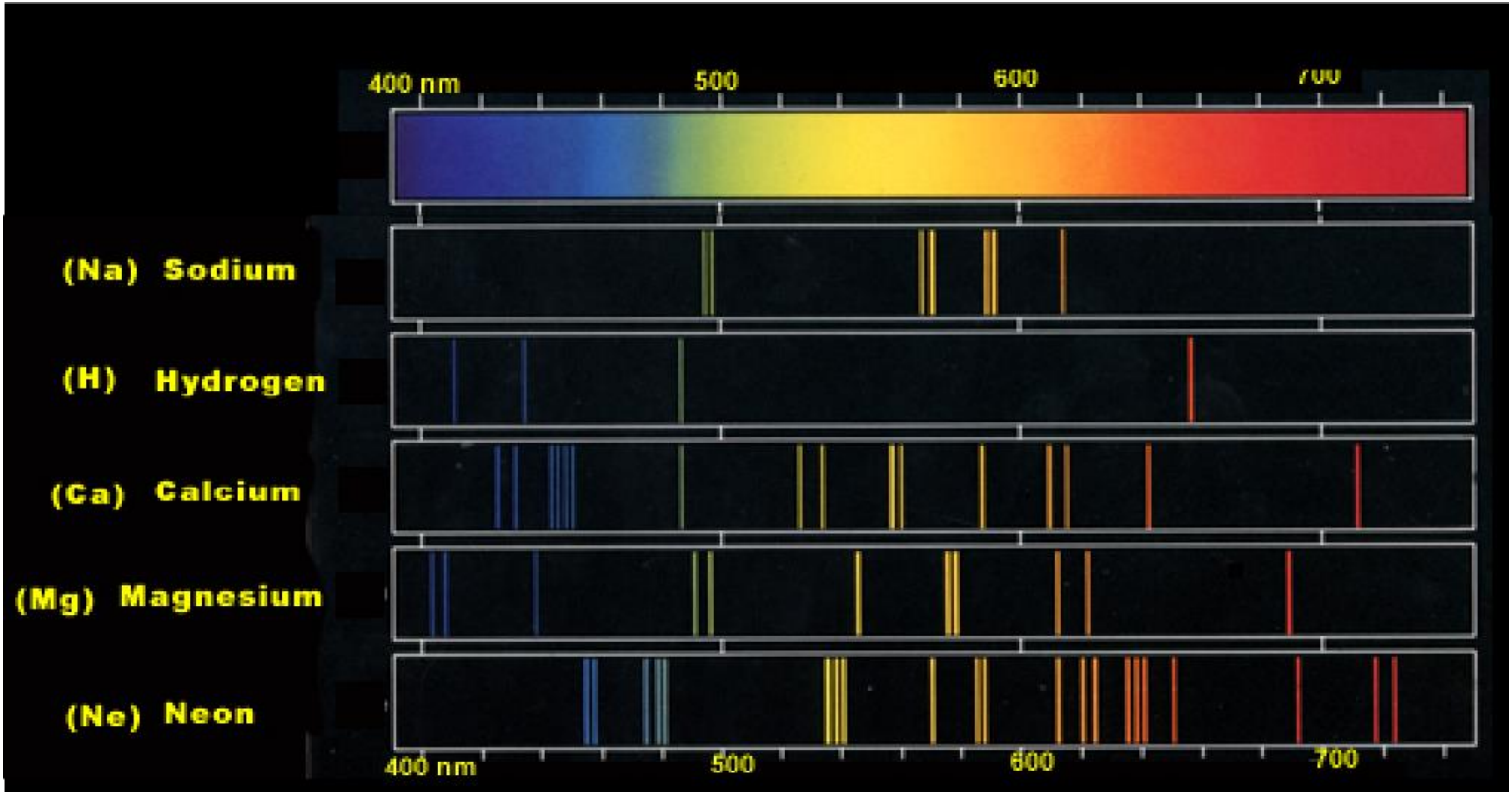

Atomic Spectra

Hydrogen atom
Balmer (1885)

	3→2	4→2	5→2	6→2
nm	656.5	486.3	434.2	410.2
Color	Red	Aqua	Blue	Violet

Balmer's Formula

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

Atomic Spectra

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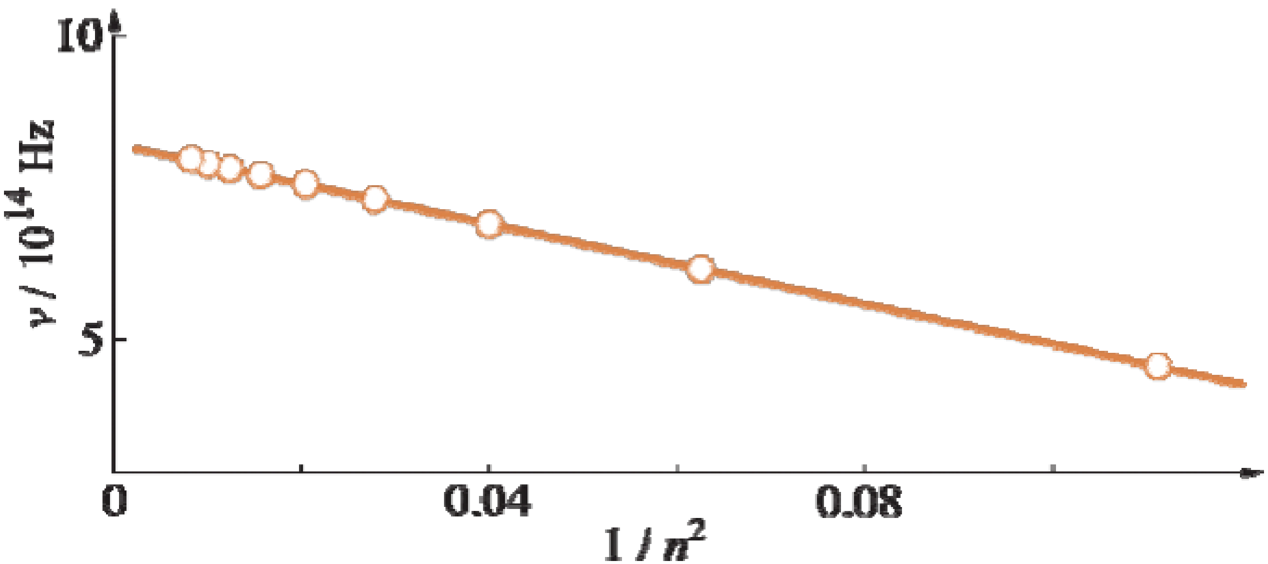

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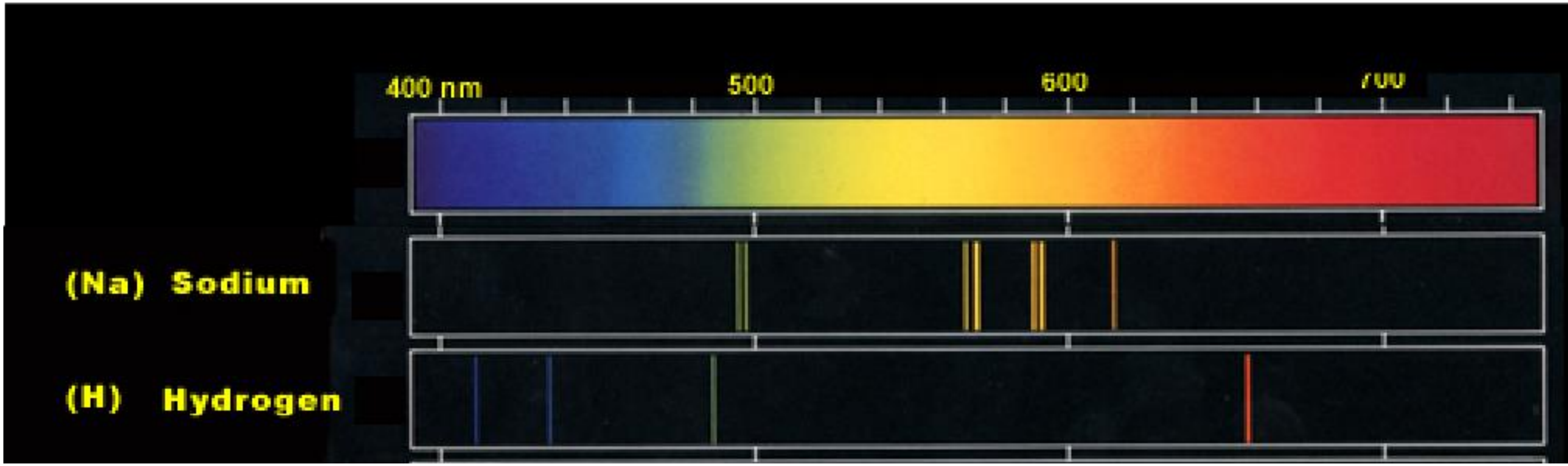


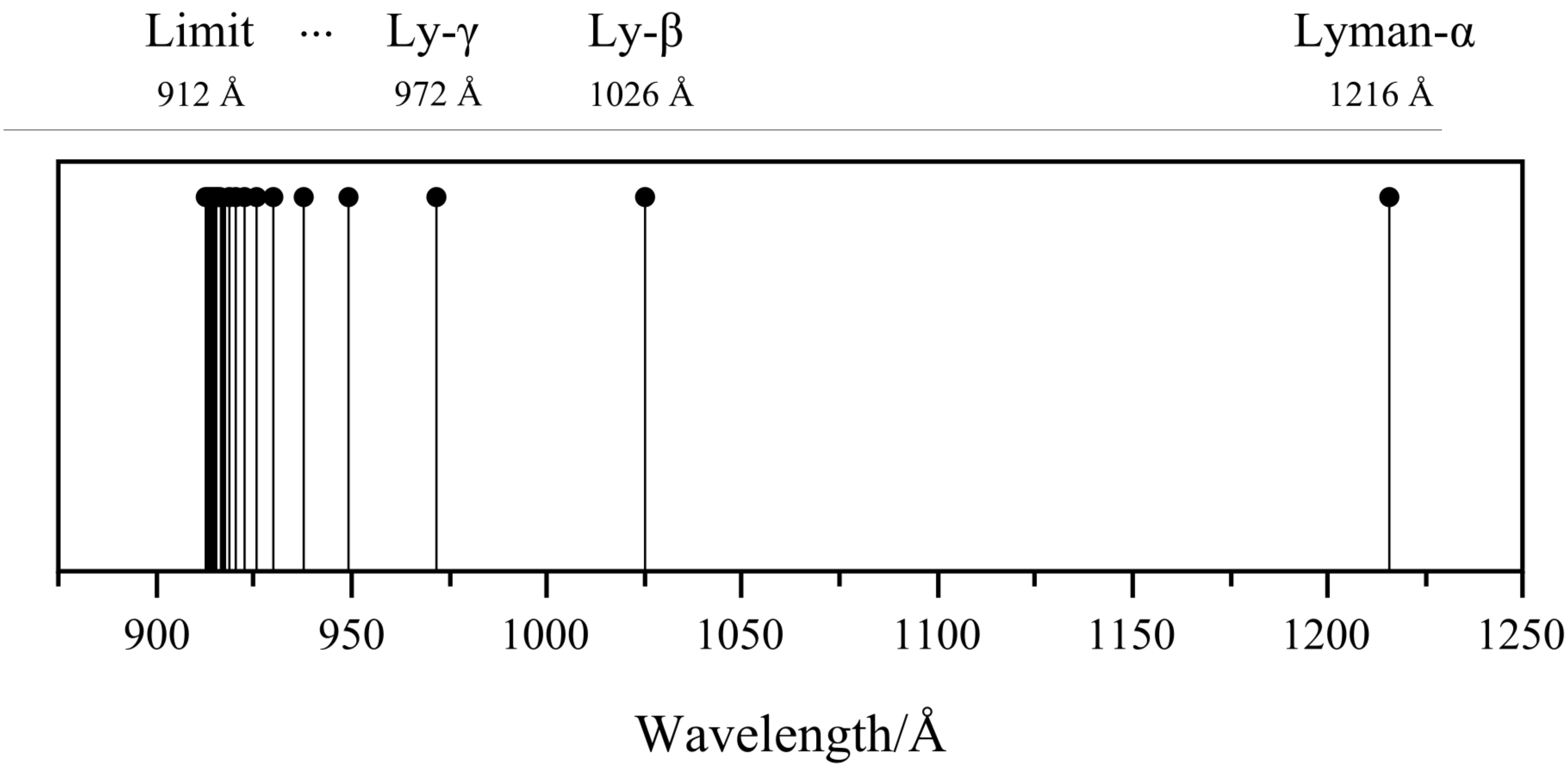
Rydberg Formula (1888): relation between the wavelengths in a series of lines

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right);\ n_2 > n_1$$

R_H = Rydberg Constant=109678 cm^{-1}

Atomic Spectra

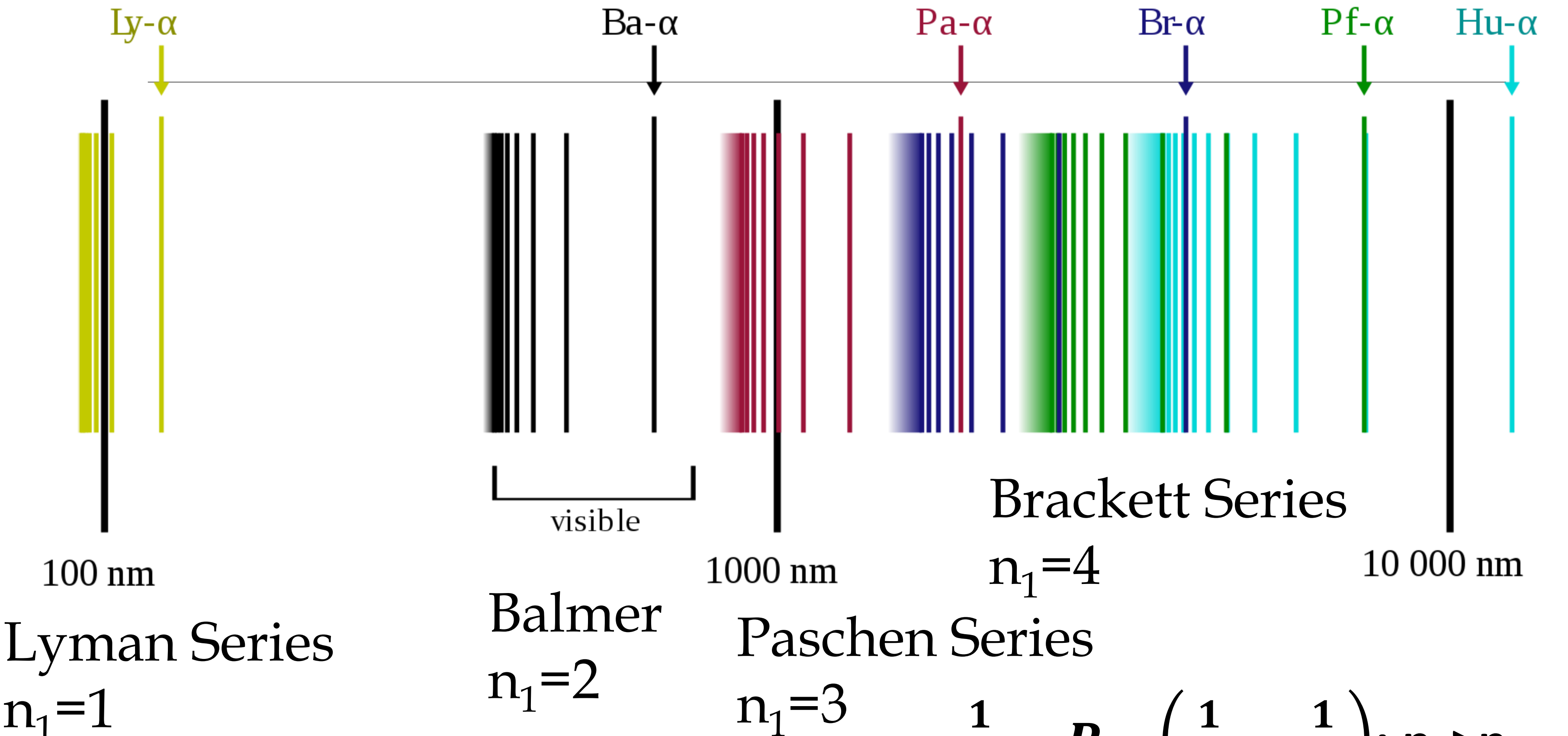
Lyman (1908-1914)



$$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right)$$

Atomic Spectra

Hydrogen atom: All the lines in the atomic hydrogen spectrum

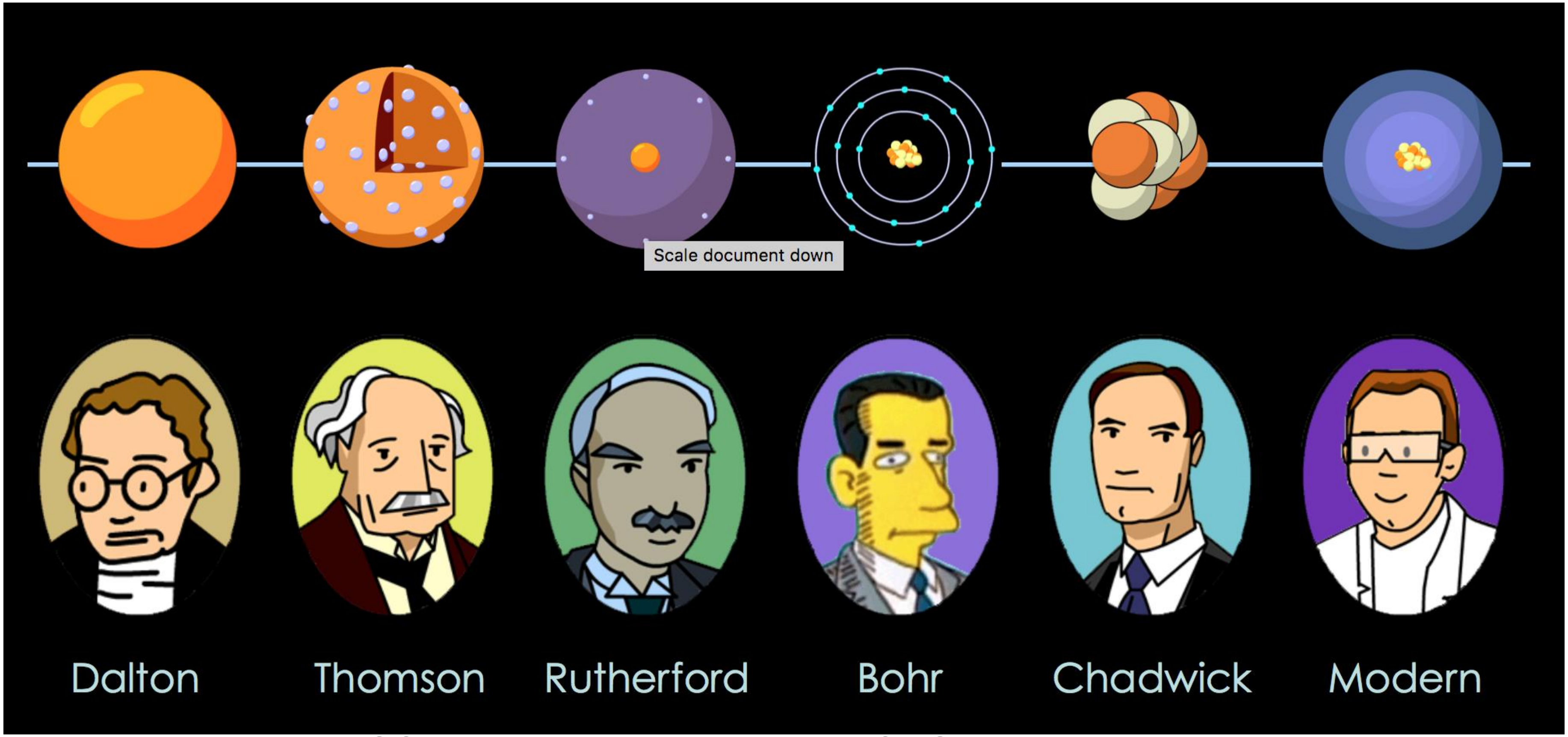


$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right);\ n_2>n_1$$

Rydberg Formula: For all combinations

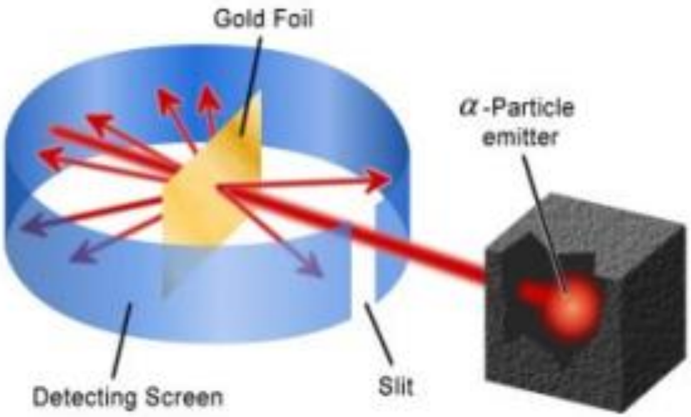
R_H = Rydberg Constant=109678 cm^{-1}

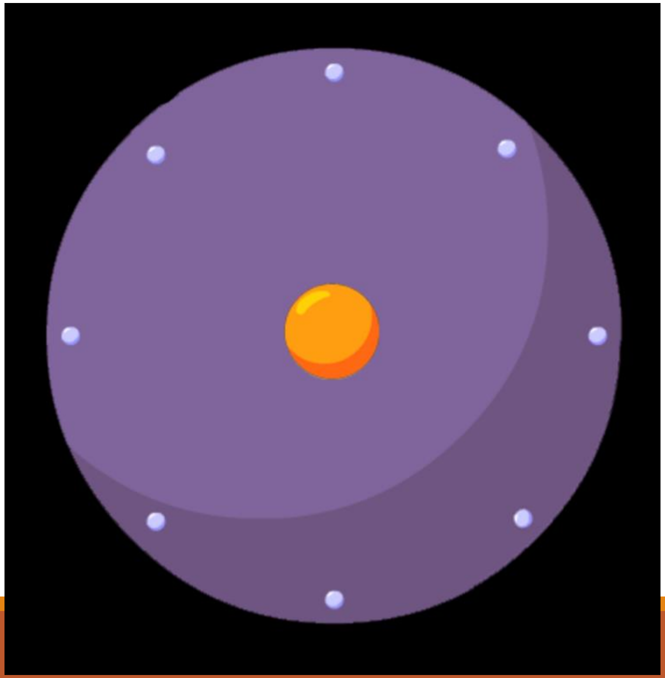
Atomic Structure Model

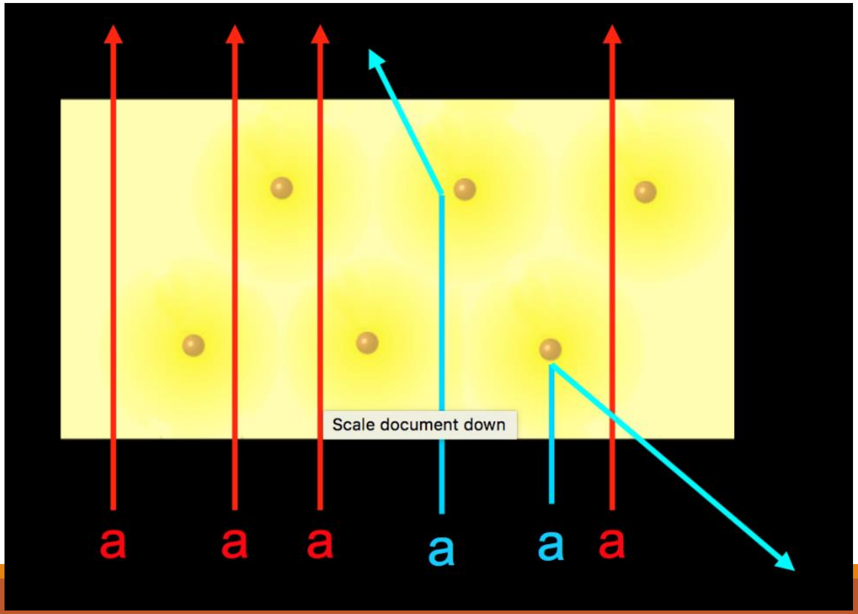


1803	1897	1911	1913	1932
Atom	Electron	Protons	Planetory model	Neutron

Rutherford Model (1911)







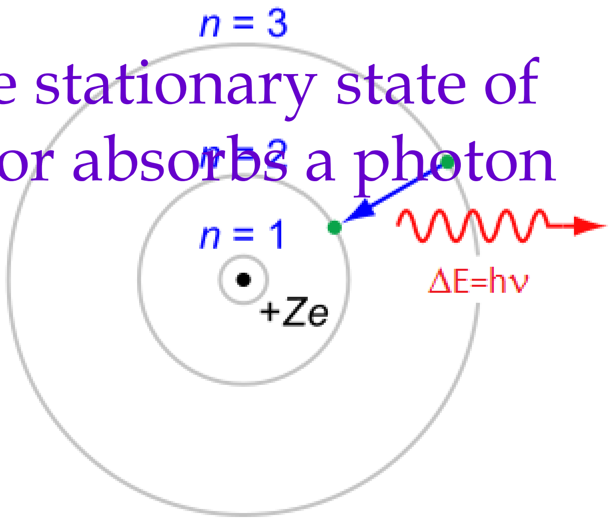
Bohr Model of Hydrogen Atom

- Electrons rotate in circular orbits around a central (massive) nucleus, and obeys the laws of classical mechanics.

- Allowed orbits are those for which the electron's angular momentum equals an integral multiple of **h/2π** i.e. $\mathbf{m_e vr = nh/2\pi}$

- Energy of H-atom can only take certain discrete values: "Stationary States"; The Atom in a stationary state does not emit electromagnetic radiation.

- When an atom makes a transition from one stationary state of energy $\mathbf{E_a}$ to another of energy $\mathbf{E_b}$, it emits or absorbs a photon of light: $\mathbf{E_a – E_b = hv}$



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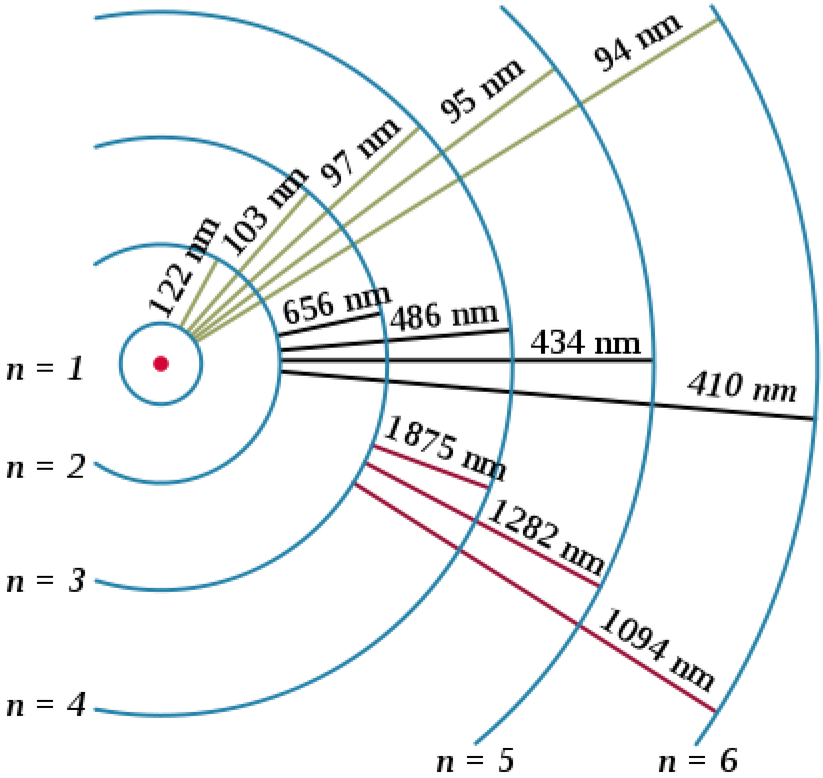


- Angular momentum quantized

  mvr=nh/2π, n=1, 2, 3…

- Energy $\mathbf{E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2} \frac{1}{n^2}}$

- $\mathbf{\Delta E_n = \frac{m_e e^4}{8\varepsilon_0^2 h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$

- $\mathbf{R_\infty = \frac{m_e e^4}{8\varepsilon_0^2 c h^3}}$ **equal to Rydberg constant**

Bohr Theory

For an hydrogen atom

- Combining $\lambda = \frac{h}{mv}$ and 2πr=nλ → $\boldsymbol{m_e v r = \frac{nh}{2\pi}}$

Angular momentum is quantized and integral multiples of $\frac{h}{2\pi}$ *or* ħ

- Centrifugal force $(\frac{m_e v^2}{r})$ is equal to coulombic force

$$\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m_e v^2}{r}$$

- Put $v = \frac{nh}{2\pi m_e r}$ in $\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m_e v^2}{r}$ to obtain $\boldsymbol{r = \frac{4\pi\varepsilon_0 \hbar^2 n^2}{m_e e^2}}$
- Calculate the smallest radius (when n=1) is r=a_0=52.92 pm

Bohr Theory

For an hydrogen atom

- Potential energy from Coulomb's law **V(r)=** $-\dfrac{\boldsymbol{e^2}}{\boldsymbol{4\pi\varepsilon_0 r}}$. The "–" sign indicate attractive interaction.
- Total energy **E=KE +PE=**$\dfrac{\mathbf{1}}{\mathbf{2}}\boldsymbol{m_e v^2} - \dfrac{\boldsymbol{e^2}}{\boldsymbol{4\pi\varepsilon_0 r}}$
- $(m_e v^2$ from $\dfrac{e^2}{4\pi\varepsilon_0 r^2}=\dfrac{m_e v^2}{r})$; **E=**$\dfrac{\mathbf{1}}{\mathbf{2}}\left(\dfrac{\boldsymbol{e^2}}{\boldsymbol{4\pi\varepsilon_0 r}}\right) - \dfrac{\boldsymbol{e^2}}{\boldsymbol{4\pi\varepsilon_0 r}} = -\dfrac{\boldsymbol{e^2}}{\boldsymbol{8\pi\varepsilon_0 r}}$
- Use $r=\dfrac{4\pi\varepsilon_0\hbar^2 n^2}{m_e e^2}$; $E_n=-\dfrac{\boldsymbol{e^2}}{\boldsymbol{8\pi\varepsilon_0 r}}$=- $\dfrac{m_e e^4}{8\varepsilon_0^2 h^2 n^2}$; n=1, 2, 3,…….

Derive Rydberg formula from Bohr Theory

- For the ground state n=1, for excited states n=2,3,4...
- Excited states of $n_2>1$ radiates photons during transition to lower electronic state n_1 which is $<n_2$ and

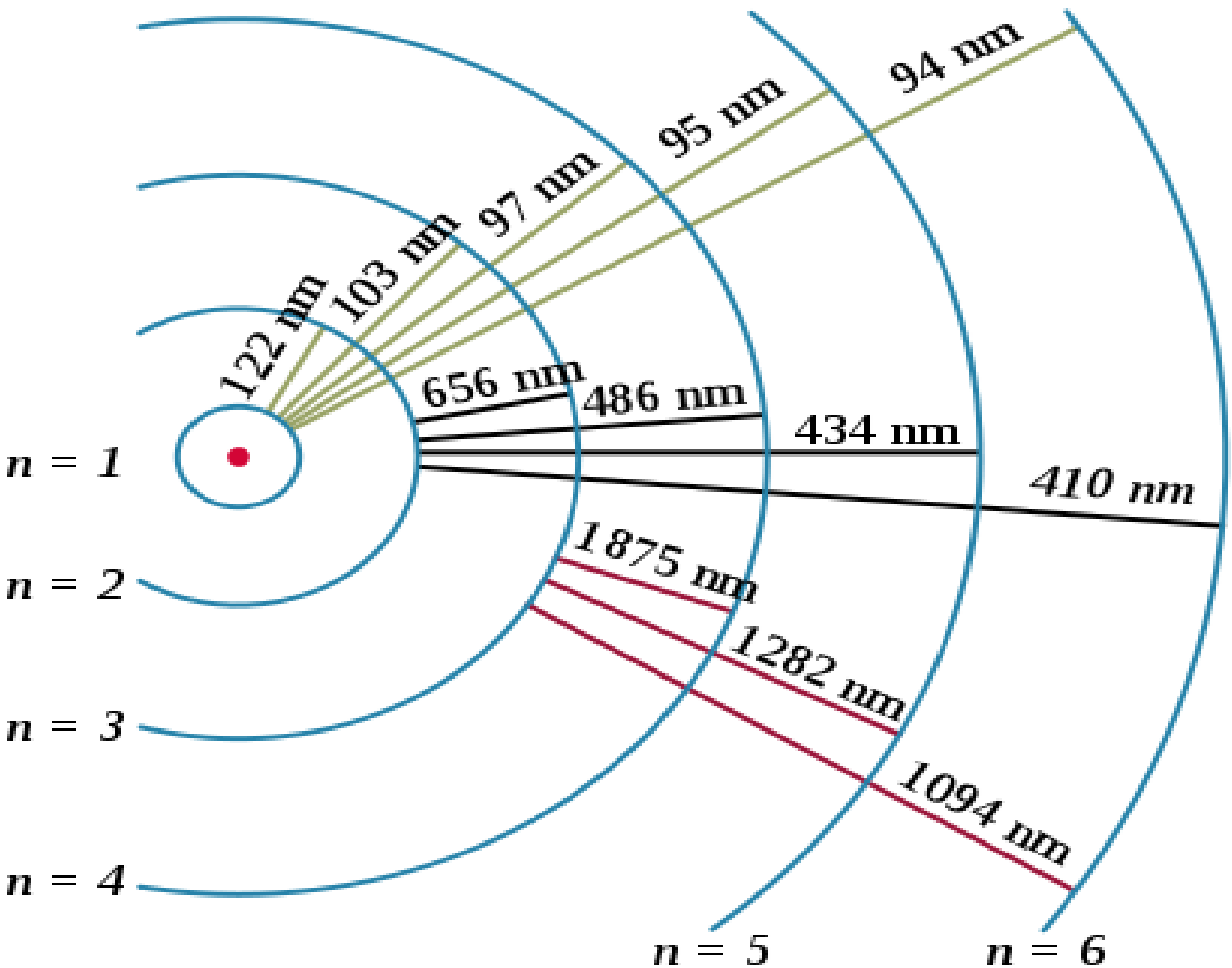
E_2-E_1=hv=$\frac{m_e e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$

- Replace v=$\frac{hc}{\lambda}$; $\quad \frac{1}{\lambda}=\frac{m_e e^4}{8\varepsilon_0^2 c h^3}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$= $R_\infty\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$ in cm^{-1}
- This equation is similar to the Rydberg formula and the derived value of R_∞ is very similar to the Rydberg constant.

- *Calculate R_∞ and find out the difference between R_H and R_∞ in cm^{-1}*

Rydberg formula V/S Bohr Theory

$$r = \frac{4\pi\varepsilon_0\hbar^2 n^2}{m_e e^2};\ E_n = -\frac{\boldsymbol{e^2}}{\boldsymbol{8\pi\varepsilon_0 r}} = \frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2};\ n = 1, 2, 3, \ldots\ldots.$$



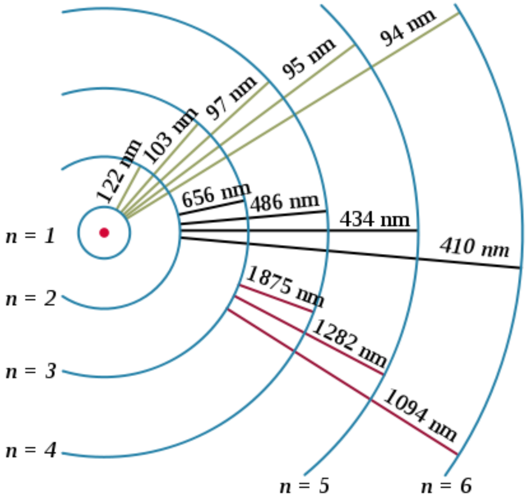
Rydberg formula V/S Bohr Theory

Johannes Rydberg

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right); n_2 > n_1$$

$$R_H = 109678\ \mathrm{cm}^{-1}$$

Niels Bohr



- Circular orbits around a central (massive) nucleus
- $m_e vr = nh/2\pi$
- The Atom in a stationary state does not emit electromagnetic radiation
- $E_a - E_b = h\nu$

Derive Ionization Energy from Bohr Theory

- Ionization energy= energy required for the ground state electron to reach an unbound state (energy required to create H+ from H)

  for this, $n_2 = \infty$ and $n_1=1$; I.E.= R_∞ in cm^{-1}

  I.E (in J)=hcR_∞; (in J mol^{-1})= hcN_aR_∞

Lecture 2:
Photoelectric effect: Wave-particle Duality

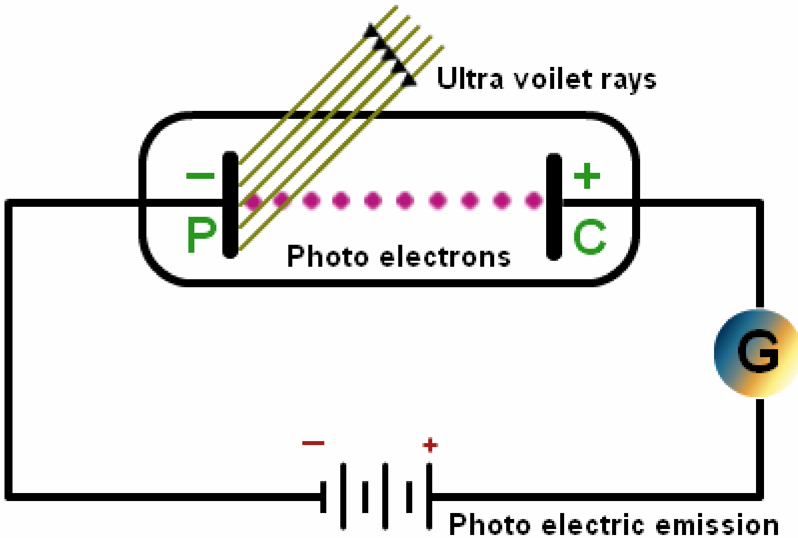
According to Classical Physics:

- Electromagnetic Radiation

$E=E_0 Sin(kx-t)$

- Wave energy is related to Intensity, $I \propto E_0^2$
- With an increase in intensity, electrons oscillate more violently, and eventually eject from the surface
- Kinetic energy of electrons depend on the intensity of the radiation but not frequency of incident radiation

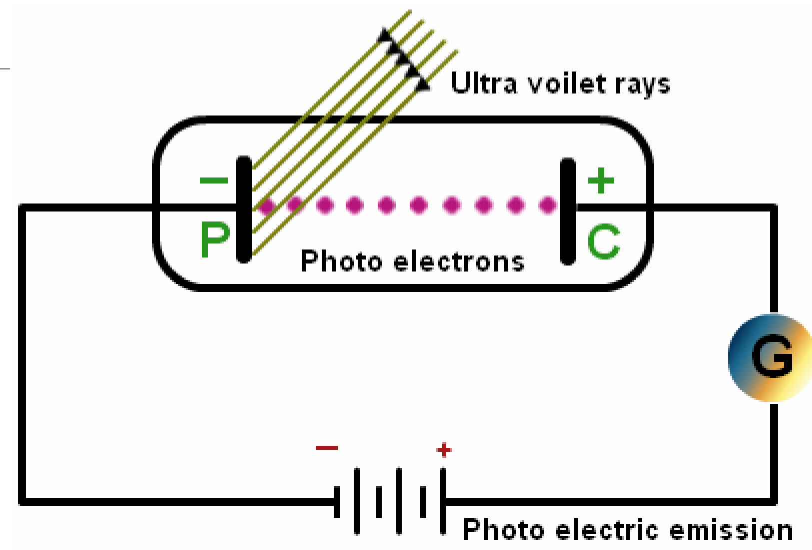
Experimental observation

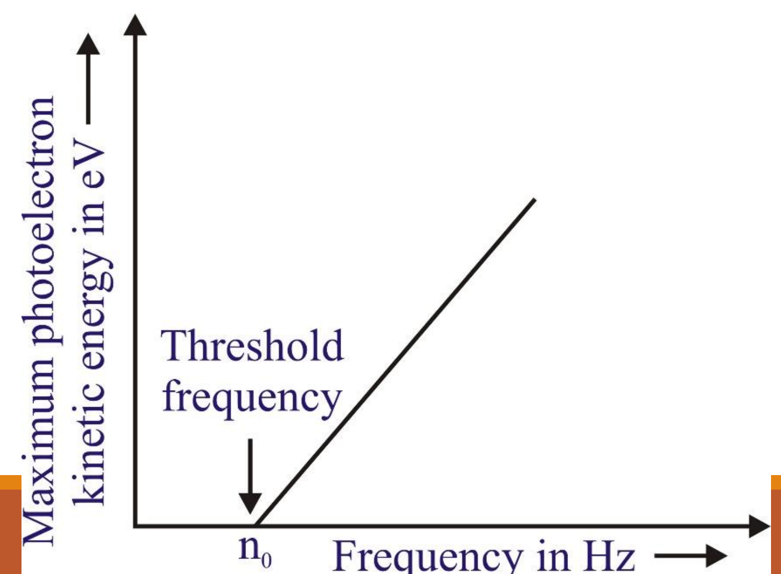


Photoelectric effect: Wave-particle Duality

- Radiation causes photoelectron above certain frequency
- Increase in light intensity increases the number of photoelectrons, but not their maximum kinetic energy!
- Weak violet light will eject only a few electrons! But their maximum kinetic energies are greater than those for very intense light of longer (red) wavelengths

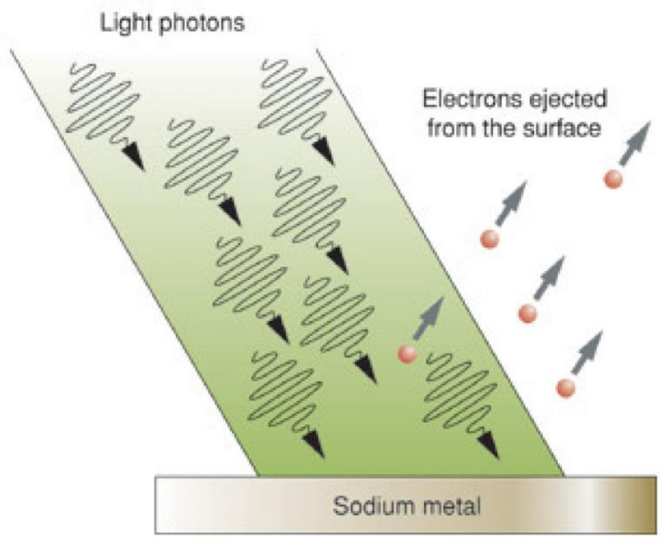
Experimental observation





Photoelectric effect: Wave-particle Duality

Einstein applied Planck's idea that $\Delta E=hv$ and proposed that radiation itself existed as small packets of energy (Quanta) and now known as PHOTONS



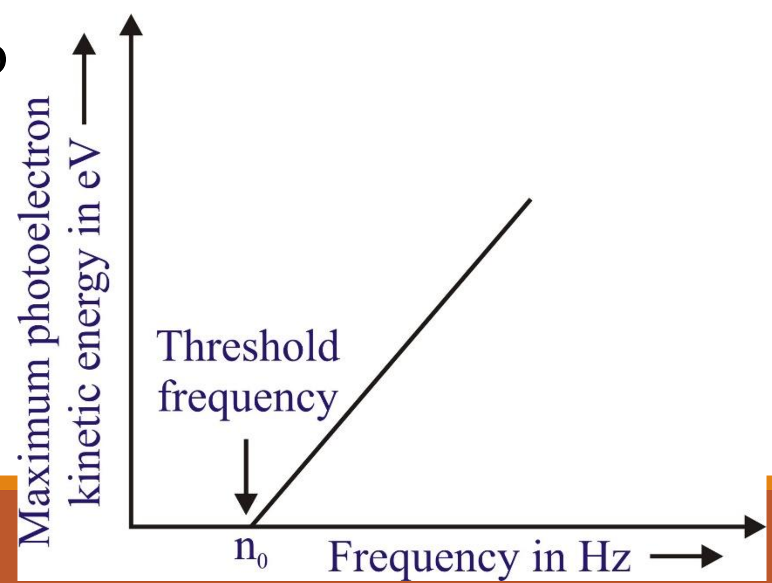
$E_p=hv$; Energy is frequency dependent

$E_p=hv=KE_e + \varphi$

φ = work function; Energy required to remove electron from surface=hv_0

$KE=h(v-v_0)$

Is photon a particle?



Photoelectric effect: Wave-particle Duality

- The photoelectric effect provides evidence for the particle nature of light.
- It also provides evidence for quantization.
- If light shines on the surface of a metal, there is a point at which electrons are ejected from the metal.
- The electrons will only be ejected once the threshold frequency is reached .
- Below the threshold frequency, no electrons are ejected.
- Above the threshold frequency, the number of electrons ejected depend on the intensity of the light.

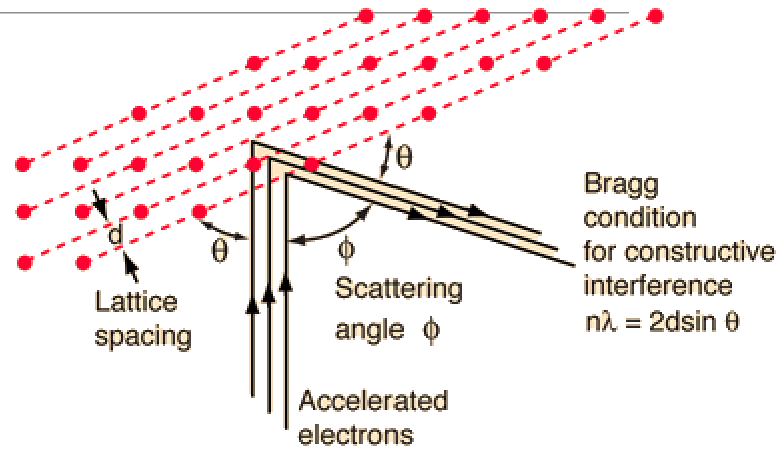
Wave-particle Duality

Diffraction of Electrons

Davisson-Germer Experiment

A beam of electrons is directed onto the surface of a nickel crystal. Electrons are scattered, and are detected by means of a detector that can be rotated through an angle θ. When the Bragg condition

$m\lambda = 2d\sin\theta$ was satisfied (d is the distance between the nickel atom, and m an integer) constructive interference produced peaks of high intensity



Is electron a wave?

Wave-particle Duality

Light can be Waves or Particles

Electron (matter) can be particles or waves

For photons (m=0), change in wavelength results a change in momentum

de Broglie Hypothesis: wave-particle duality of light (1924)

De Broglie wavelength **λ = h/p; p** is momentum