CHEM F111 : General Chemistry
Semester I: AY 2020-21

Lecture-01, 04-11-2020

General Chemistry (Overview of handout)

Course Number : CHEM F111

Course Title : General Chemistry

Instructor-in-charge : INAMUR RAHAMAN LASKAR

Instructors : Ram Kinkar Roy, Indresh Kumar

Tutorial/Practical instructors : Saumi Ray, Ajay Kumar Sah, Bharti Khungar, Paritosh Shukla, Rajeev Sakhuja and Bibhas Ranjan Sarkar

Objectives: The course is composed of two parts. The first part provides a comprehensive survey of various topics in electronic structure of atoms, molecules, and spectroscopy, bonding, Coordination Chemistry and second part focuses on understanding of the structure and properties of organic compounds.

Books

Text Books

T1: P.W. Atkins and Julio de Paula, Elements of Physical Chemistry: 6th Edition, Oxford University Press, Oxford, reprinted in 2015.

T2: T. W. Graham Solomons, Craig B. Fryhle and Scott A. Snyder, Organic Chemistry, 12th Edition, John Wiley & Sons, Inc. New York, 2017

Reference Books:

R1: J. D. Lee, Concise Inorganic Chemistry, 5th Edition, Blackwell Science, Oxford, 1999.

R2: Physical Chemistry, David Ball

R3: Inorganic Chemistry: Principles of Structure and Reactivity, 4th Edition, Huheey, Keiter

R4: R. T. Morrison and R. Boyd, ‘Organic Chemistry’, 6th Edition, PHI, New Delhi, 1992.

General Chemistry (Overview of handout)

(12 Lectures)

- Quantum theory
- Application of Quantum Theory: Hydrogen atom
- Chemical Bonding

(14 Lectures)

- Molecular Spectroscopy:
  - Rotational & Raman
  - Vibrational
  - Electronic
- Coordination chemistry
- Bonding
- Distortion of complexes

(15 Lectures)

- NMR
- Conformations
- Stereochemistry
- Reaction Mechanism: S_N1, S_N2, S_NAr, E1, E2.
- Aromaticity and pericyclic reactions

General Chemistry (Evaluation components)

Component	**Weightage (%)**
MIDSEM Examination	30
Continuous Evaluation	30
Comprehensive Examination	40

All the tests will be conducted by online platform.

- **A total four tutorial evaluations will be conducted under continuous evaluation.**
- **Best three** will be considered for final evaluation.

Continuous Evaluation: 30% [90 Marks]

Tutorial Hour: Clarification of doubts, further discussion and interactions , problem solving, periodical and continuous evaluation

Continuous evaluation:

Four quizzes (20 Marks each) will be conducted in a common hour.

Best **three** will be considered for final evaluation.

How will you get the slides of the class?

Assignment/Lecture slides/Notices will be uploaded on the Nalanda *(upon activation)*.

Please register yourself on Nalanda

Until Nalanda is activated, **lecture slides will be uploaded at the 'Department of Chemistry' website:**

http://www.bits-pilani.ac.in/pilani/pilaniChemistry/courserelated

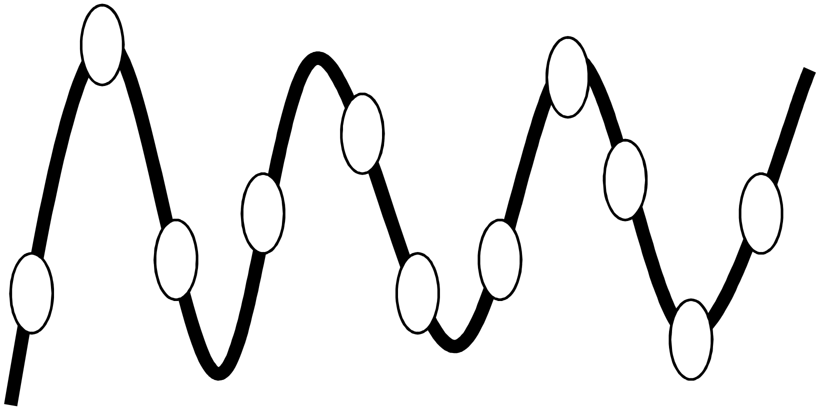
Password: BITSPILANI

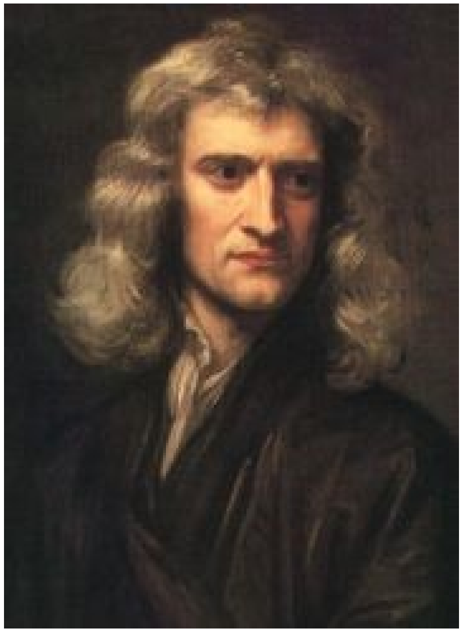
Module -1-6

Introduction to Quantum Chemistry and Molecular Spectroscopy:

- Need for a new mechanics.
- Schrödinger equation (time-independent)
- Application in simple model systems – validate the theory.
- Solve H-atom problem.
- Molecular energy states.
- Interaction with electromagnetic radiation.
- Molecular spectroscopy.

Trajectory of classical particles





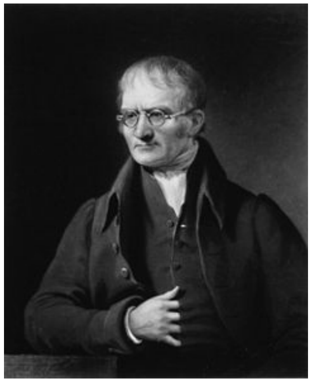
Newtonian Mechanics – Consider motion of a particle:

i) Initial position is known at t=0,

ii) Initial momentum is known at t=0,

iii) Force acting on the particle is taken into account.

Structure of atoms and molecules



John Dalton: Concept of atoms in 1803

Amedeo Avogadro: Concept of molecules in 1811

Sir J. J. Thomson: Concept of electron in 1897

Experimental observations > 1850

- Origin of radiation emitted by bodies of matter – idealized blackbody.
- Photoelectric effect.
- Line spectra of atoms.

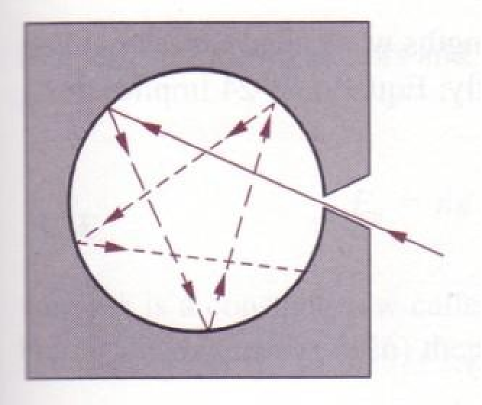
Experimental results can not be explained with the existing knowledge – was explained using a new concept, quantum concept – lead to the development of a new theory, quantum theory.

Blackbody radiation

- Any object radiates energy. The amount of energy emitted, and its frequency distribution depends on the temperature and on the material.

- Black body: It is *truly a theoretical object* that absorbs all radiation (100%!) that falls on it.

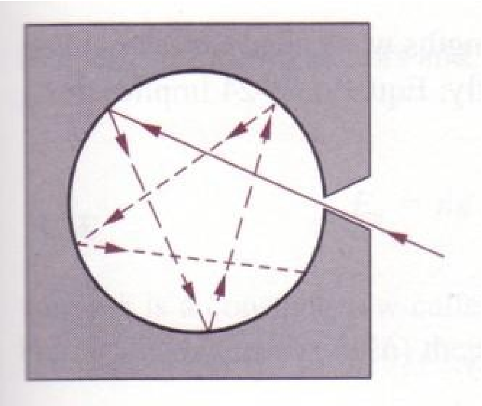
- Some materials, eg., graphite approximate such behaviour or a pinhole in a container

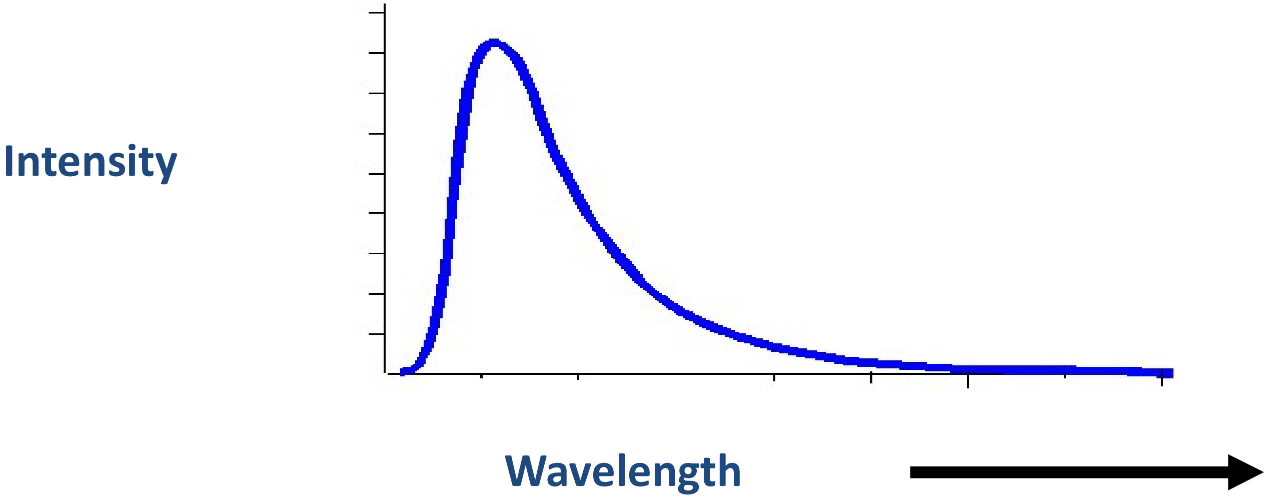


Point of introducing the idealized blackbody: We can now disregard the precise nature of whatever is radiating – all blackbody behaves identically.

Blackbody radiation

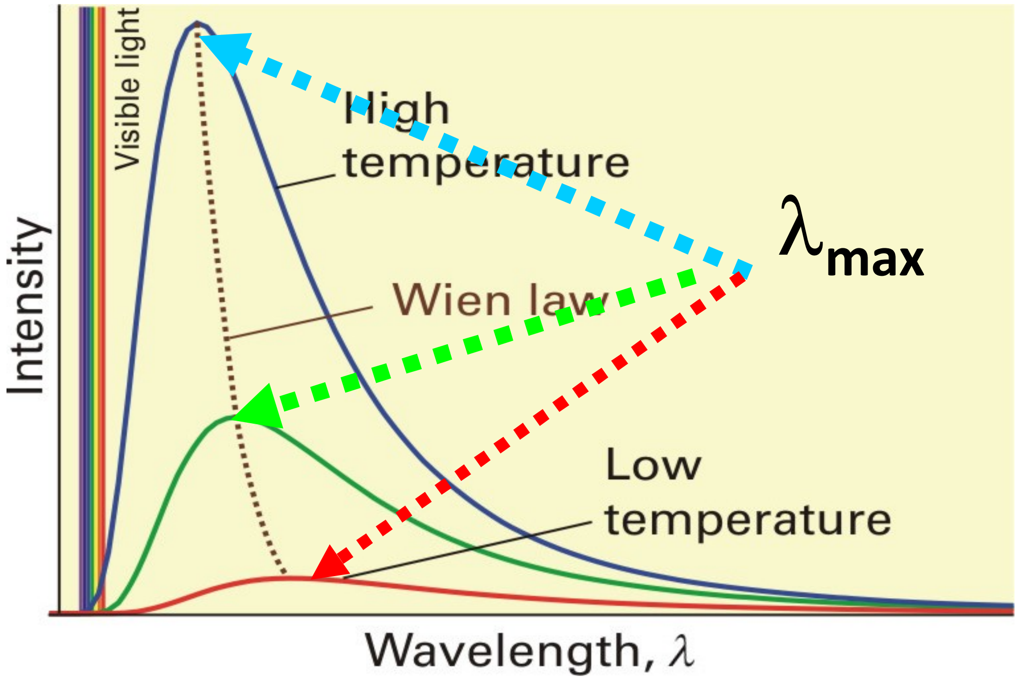
The spectral distribution of the power emitted by a black body:

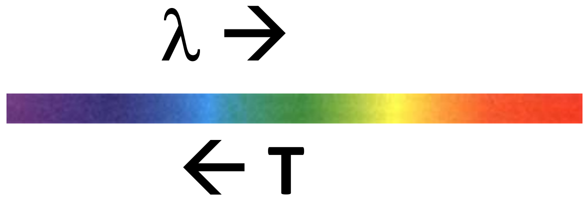




- An ideal emitter – emits at all wavelengths.
- Thermal motion of atoms (oscillators) in the walls of blackbody excites corresponding oscillations of electromagnetic field.
- Experimental observations were obtained by measuring the energy density of a cavity at desired T.

Blackbody radiation



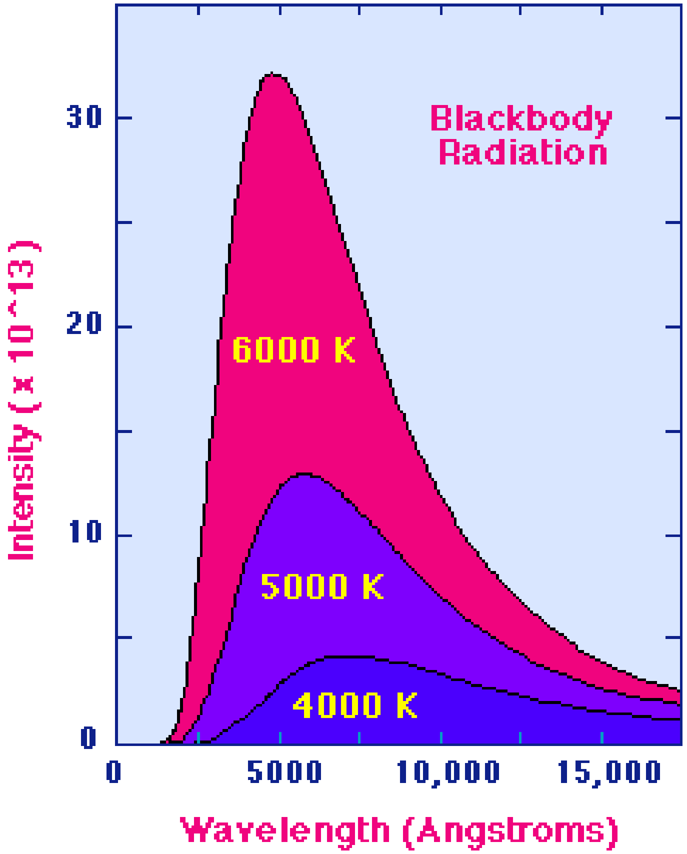


Common observation with heated bodies; Red → blue

Major observations:

- Wien's law: **$\lambda_{max}T$ = 2.99 mm K (Constant)**

Blackbody radiation



Rapid increase in area under curve with increasing temperature

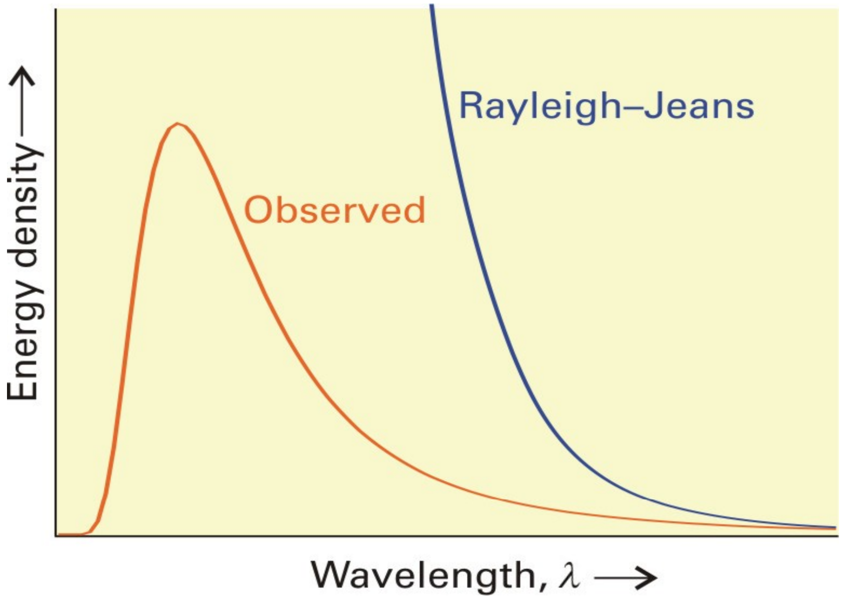
Stefan-Boltzmann Law:

Emittance M = aT^4

(Power emitted per unit surface area is proportional to the 4th power of temperature)

'a' $= 56.7 \times 10^{-9}\ Wm^{-2}K^{-4}$

Blackbody radiation



Radiation viewed as a collection of **harmonic oscillators** of all possible frequencies.

Energy density $\rho(\lambda)d\lambda$ is the energy per unit volume associated with radiation of wavelength from λ to $\lambda+d\lambda$, and is proportional to the emittance

$$\rho(\lambda)d\lambda = (8\pi\, k_B T/\ \lambda^4)\ d\lambda$$

Blackbody radiation

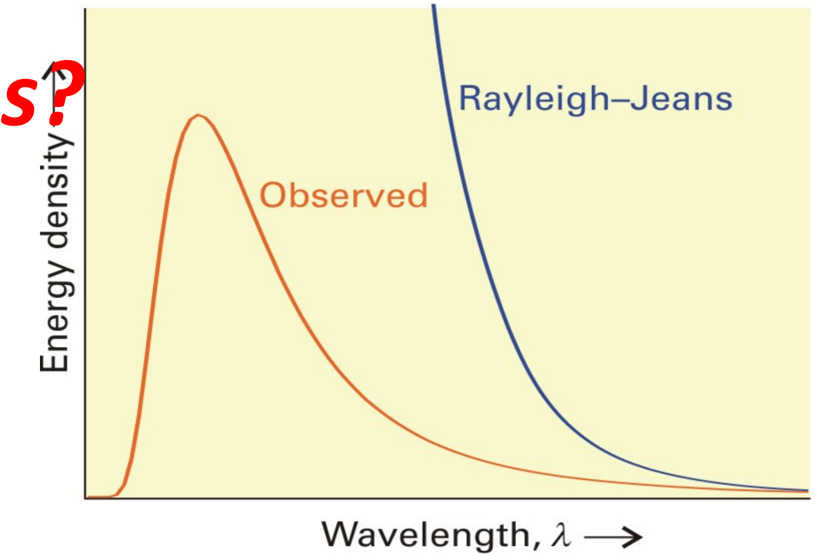
Rayleigh-Jeans:

$\rho(\lambda)d\lambda = (8\pi kT/\lambda^4)d\lambda$ with k the Boltzmann constant.

- **The function rises without bound as λ decreases**
- **Oscillators of short wavelength (UV) is excited (ρ is very high) even at room temperature**

How do we expect darkness?

Ultraviolet catastrophe

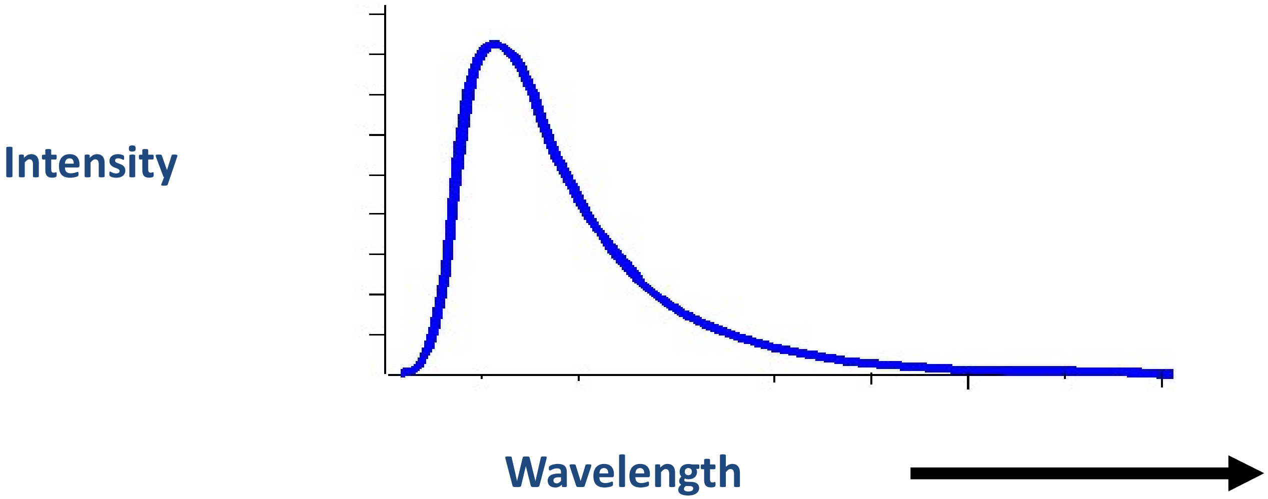


Classical to quantum description

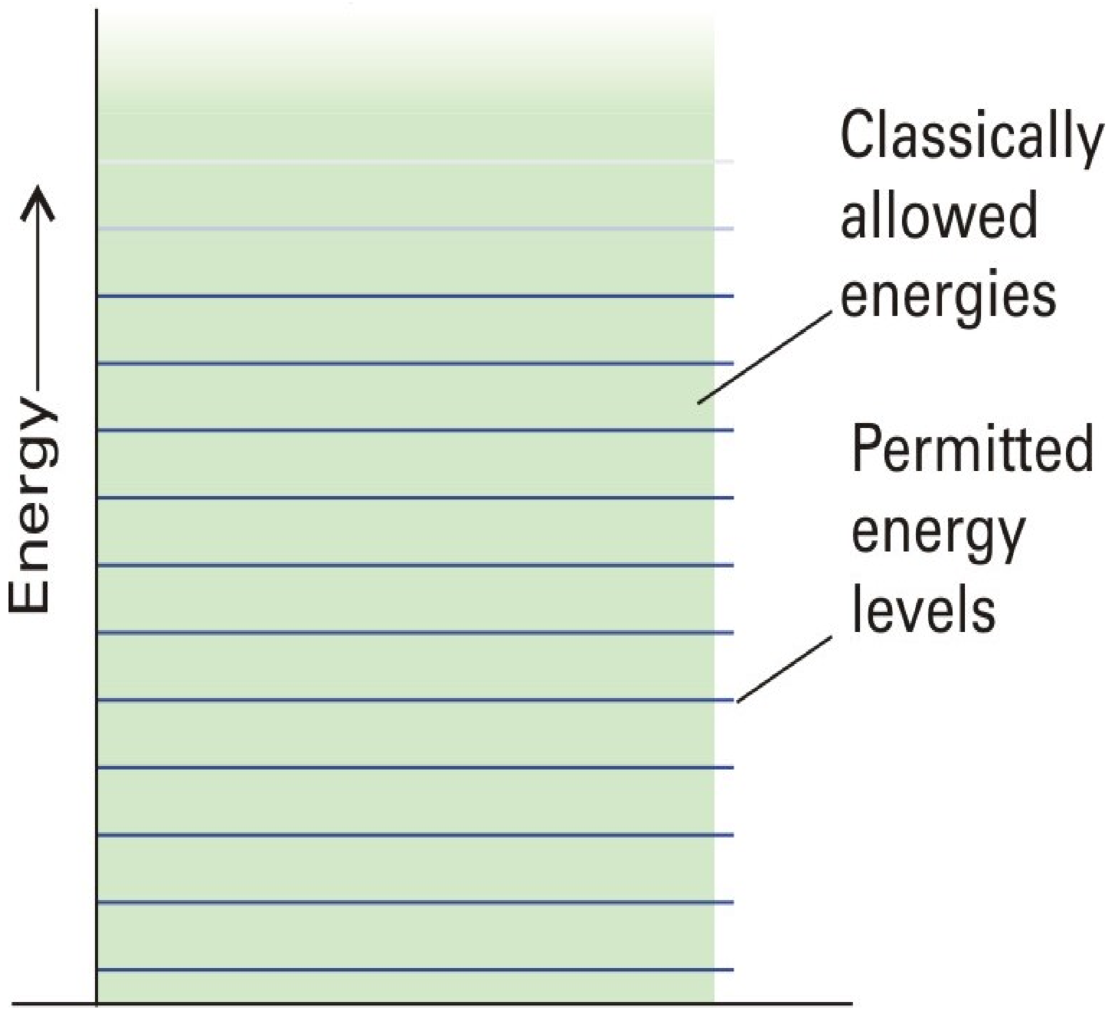
Max Karl Ernst Ludwig Planck

" If a revolution occurred in physics in December 1900, nobody seemed to notice it. Planck was no exception.. Energy quantization - was scarcely noticed.. during the first few years of the 20th century no one considered his (Planck's) results to conflict with the foundations of classical physics."-

-H. Kragh, *Phys. World*, Dec. 2000



Energy quantization



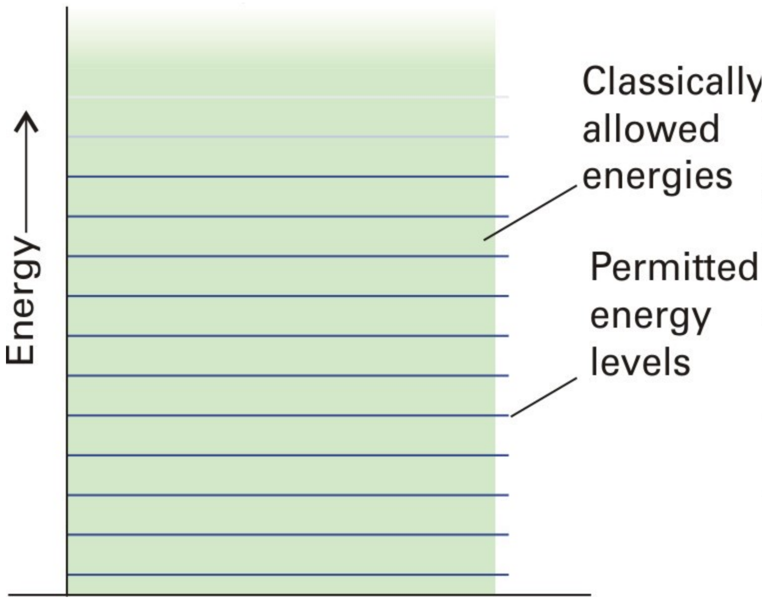
Planck Formula (1900)

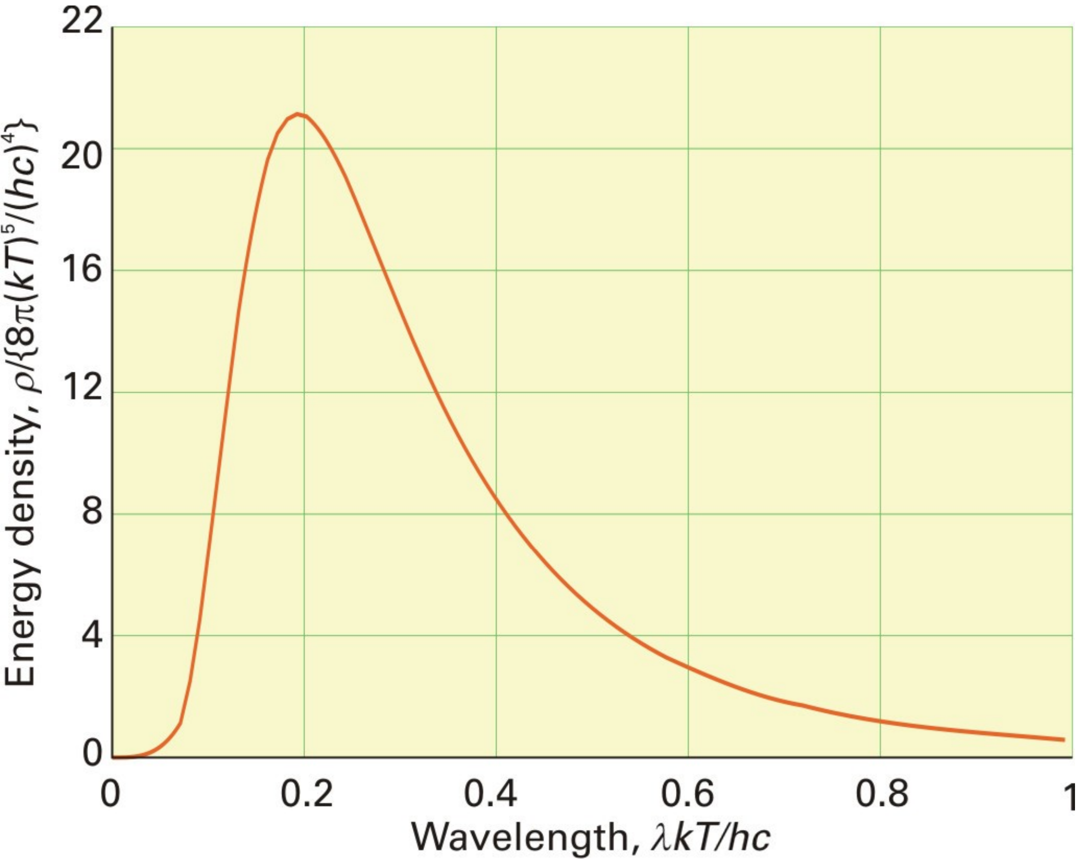
$\rho(\lambda)d\lambda = (hc/\lambda)(e^{hc/\lambda kT} - 1)^{-1}(8\pi/\lambda^4)d\lambda$

Density of oscillators as before, but with $\nu = c/\lambda$, average energy is $h\nu/(e^{h\nu/kT} - 1)$.

Crucial assumption that Planck had to make was that an oscillator of frequency ν cannot be excited to any arbitrary energy, but only to integral multiples of a fundamental unit or quantum of energy $h\nu$, with $h = 6.626 \times 10^{-34}$ J s, the Planck constant, i.e., $E = nh\nu$, $n = 0,1,2,\ldots$.

Planck Formula





Quantization

Planck expression reproduces the experimental distribution with h = 6.626 x 10 $^{-34}$ J s

Success of Planck's formula

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

Integrate $\rho(\lambda)$ over $d\lambda$ to get total power radiated

Take derivative of ρ w-r-t λ to get peak

aT^4

Stefan Boltzman Law is obtained

$\lambda_{max}T$

Wien's Law is obtained

Success of Planck's formula

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

- At small λ, $e^{hc/\lambda kT} \rightarrow \infty$ faster than λ^5

(Exponential is large)

- $\rho(\lambda) \rightarrow 0$ as $\lambda \rightarrow 0$
- Energy density →0 as $\lambda \rightarrow 0$
- UV Catastrophe avoided

Work out:

(i) Derive Stefan-Boltzman law from Plank's distribution law. Derive an expression for the Stefan-Boltzman constant.

(ii) Express Plank's distribution law in frequency domain.

Success of Planck’s formula

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

- **Planck's hypothesis: An oscillator cannot be excited unless it receives an energy of at least hν (as this is the minimum amount of energy an oscillator of frequency *ν* may possess above zero.**
- **For high frequency oscillators (large *ν*), the amount of energy hν is <u>too large to be supplied by the thermal motion of the atoms</u> in the walls, and so they are not excited.**
- **Catastrophe avoided**

Application of BB radiation

Simulation of BB spectrum

https://phet.colorado.edu/en/simulation/blackbody-spectrum

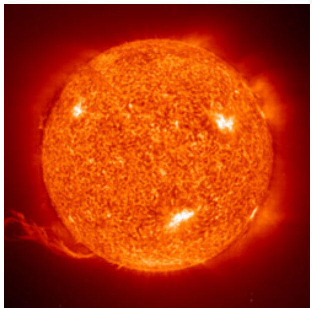
The **Stefan–Boltzmann law** describes the power radiated from a black body in terms of its temperature.

$M = \sigma T^4$ **[Stefan-Boltzmann Law]**

σ = 5.6697 x 10^{-8} $Wm^{-2}K^{-4}$

We can use Wien's law:

Determine the temperature of hot object: Sun



Summary

- Wien's Law: $\lambda_{\mathbf{max}}\mathbf{T = 2.99\ mm\ K\ (Constant)}$
- Stefan-Boltzman Law: $\mathbf{M = aT^4}$
- Rayleigh-Jeans: $\rho(\lambda)\mathbf{d}\lambda = (8\pi\mathbf{kT}/\lambda^4)\mathbf{d}\lambda$
- Planck's Formula:

$$\rho(\lambda)\mathbf{d}\lambda = (\mathbf{hc}/\lambda)(\mathbf{e}^{\mathbf{hc}/\lambda\mathbf{kT}} - 1)^{-1}(8\pi/\lambda^4)\mathbf{d}\lambda$$