CHEM F111 : General Chemistry
Semester II: AY 2017-18

Lecture-01, 08-01-2018

General Chemistry (Overview of handout)

Course Number : **CHEM F111**

Course Title : **General Chemistry**

Instructor-in-charge : **Shamik Chakraborty**

Instructors : **Ajay K. Sah, Anil Kumar, Bibhas R Sarkar, Inamur R Laskar, Indresh Kumar, Madhushree Sarkar, Paritosh Shukla, Rajeev Sakhuja, Saumi Ray, Shamik Chakraborty, Subit Kumar Saha, and Surojit Pande.**

Objectives: The course is composed of two parts. The first part provides a comprehensive survey of various topics in electronic structure of atoms, molecules, bonding, spectroscopy, 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: 6^{th} 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, 5^{th} 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', 6^{th} Edition, PHI, New Delhi, 1992.

General Chemistry (Overview of handout)

innovate achieve lead

(20 Lectures)

- **Quantum theory**
- **Hydrogen atom**
- **Bonding**
- **Molecular Spectroscopy:**
  - **Rotational & Raman**
  - **Vibrational**
  - **Electronic**
  - **NMR**

(9 Lectures)

- **Coordination chemistry**
- **Distortion of complexes**

(12 Lectures)

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

General Chemistry (Evaluation components)

Component	Duration	Weightage % [Marks]	Date and Time	Remarks
Mid- Sem. Exam.	90 min.	30 [90 M]	TBA	Closed book
Continuous Evaluation‡	15 min. (each)	25 [75 M]	Continuous	(i) Assignment (Closed book) (ii) Quiz (Closed book)
Compre. Exam.	3 hours	45 [135 M]	14/05 AN	(i) 20% Closed Book :MCQ (ii) 25% Open Book: Descriptive

Continuous Evaluation: 25% [75 Marks]

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

(i) Assignments (Closed Book):

- A set of problems will be assigned (on Nalanda).

- Based on the concepts of the assigned problems, different questions will be given for solving in the Assignment test.

- **Three** Assignment test (15 Marks each) will be conducted at a common hour for all sections. Date, time, room number will be informed in advance

****Tentative dates: 08-02-2018, 22-03-2018, & 19-04-2018****

(ii) Quiz (Closed Book):

-Short questions/numerical/short notes

- Three quizzes (15 Marks each) will be conducted in respective tut.

**** Tentative time: Jan 23rd-29th, Feb 15th-20th, April 7th-12th ****

Best **FIVE** (out of **SIX** continuous evaluation components) will be considered for final evaluation.

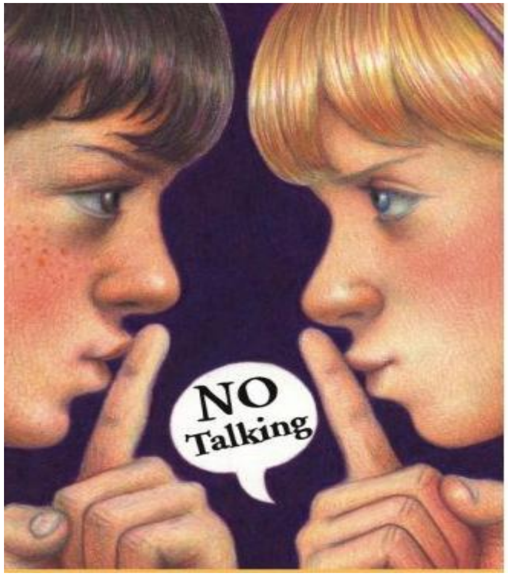
Assignment/Lecture slides/Notices will be uploaded on the Nalanda *(upon activation)*.

Please register yourself on Nalanda

Until Nalanda is activated: **Lecture slides can be downloaded from Department of chemistry website:**

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

Password: BITSPILANI



- MOBILES ARE STRICKTLY NOT ALLOWED IN THE CLASS ROOM

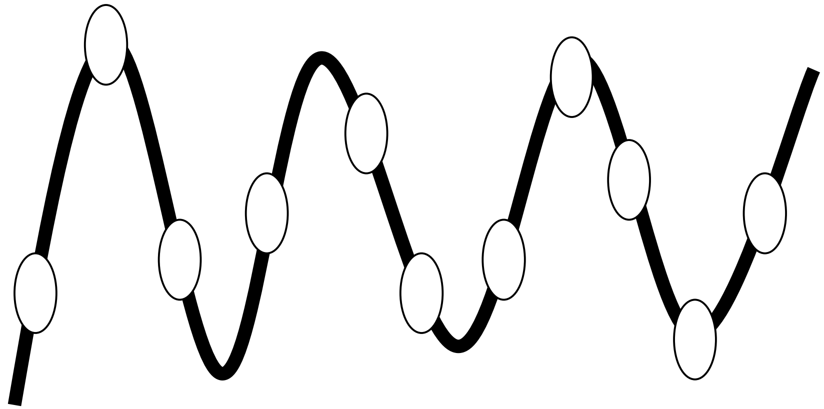
- SLIDES GIVE SELECTIVE DESCRIPTION ON A TOPIC RATHER THAN COMPREHENSIVE COVERAGE

Module -1

Introduction to Quantum Chemistry and Molecular Spectroscopy:

- Need for a new mechanics.
- Schröndinger 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



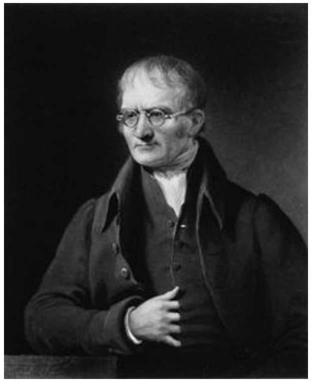
Newtonian Mechanics – Consider motion of a particle:

i) Initial position is known at t=0,

ii) Initial momentum is know 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.

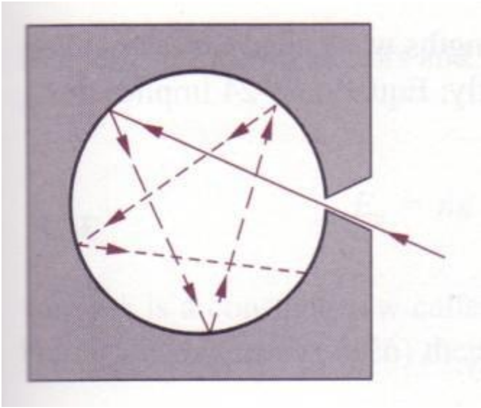
Experimental results can not be explained with the existing knowledge – was explained using a new concept, quantum concept – lead to the development of a new theory, quantum theory.

Radiation

- Simplest form of light familiar to early man?
  - Starlight
  - Light associated with heat
- Red embers of a camp fire
- Yellow color of candle flame

Blackbody radiation

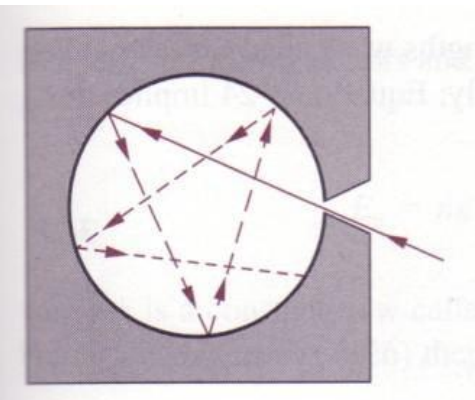
- Simplest model of starlight
- Any object radiates energy. The amount of energy emitted, and its frequency distribution depends on the temperature and on the material.
- Black body: It is *truly a theoretical object* that absorbs all radiation (100%!) that falls on it.
- Some materials, eg., graphite approximate such behaviour or a pinhole in a container

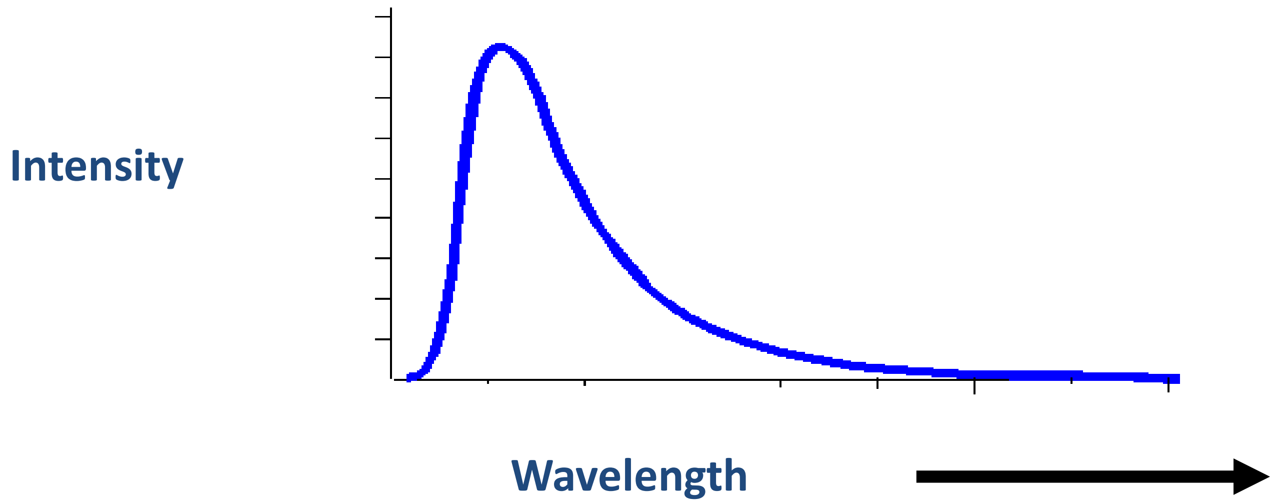


Point of introducing the idealized blackbody: We can now disregard the precise nature of whatever is radiating – all blackbody behaves identically.

Blackbody radiation

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

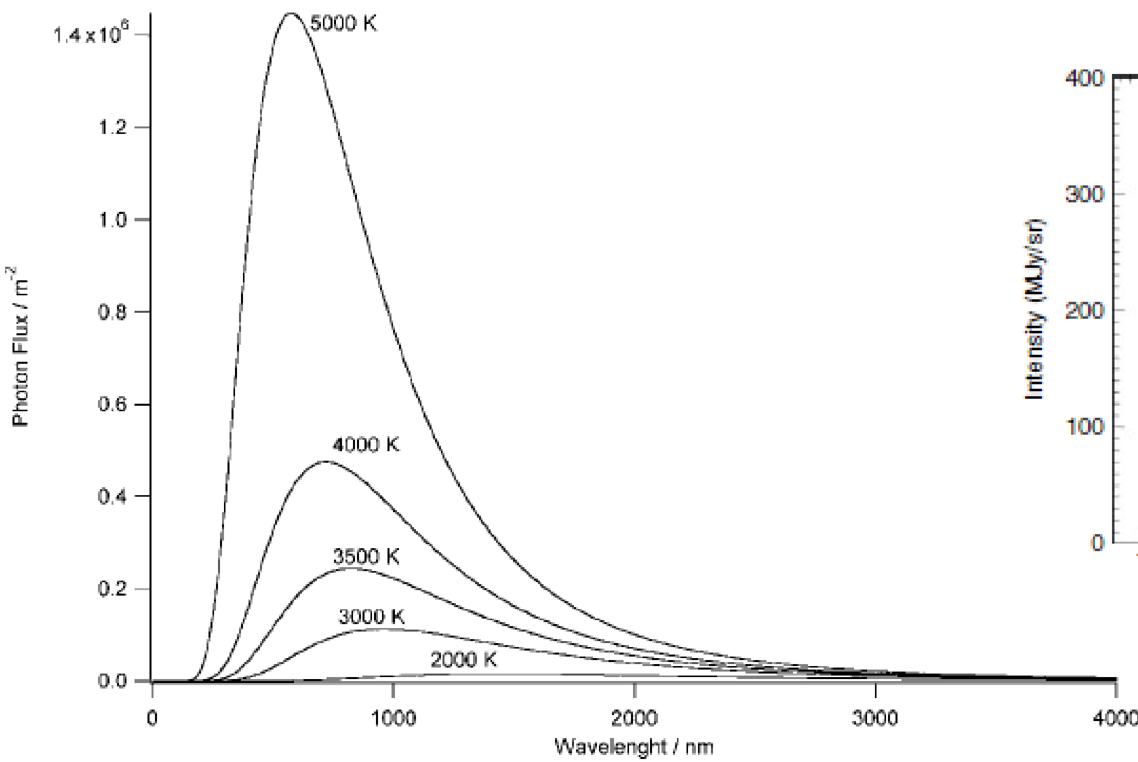


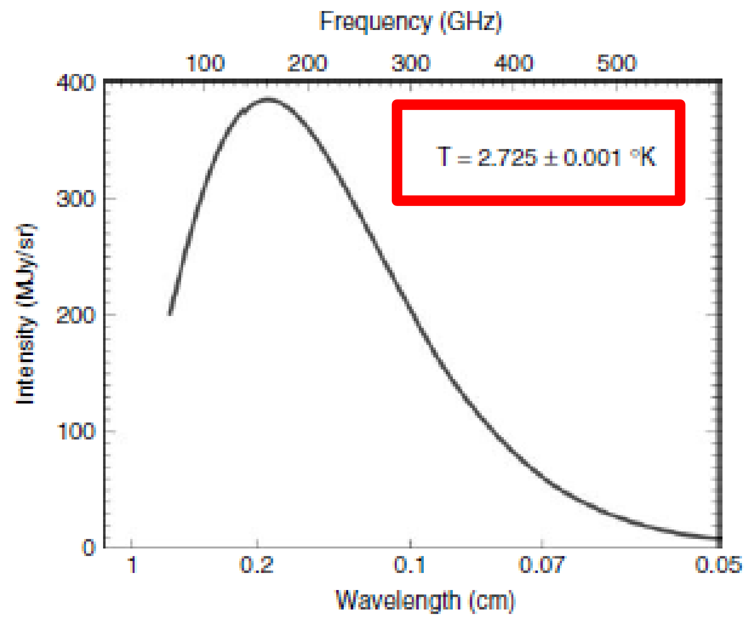


- An ideal emitter – emits at all wavelengths.
- Thermal motion of atoms (oscillators) in the walls of blackbody excites corresponding oscillations of electromagnetic field.
- Experimental observations were obtained by measuring the energy density of a cavity at desired T.

Properties that defines Blackbody

1. A black body with $T > 0$ K emits radiation at all wavelengths;
2. A hotter black body emits more light at all wavelengths than a colder body;
3. A hotter black body emits more of its radiation at shorter wavelengths;
4. Black bodies emit and reflect radiation at all wavelengths with equal efficiency.

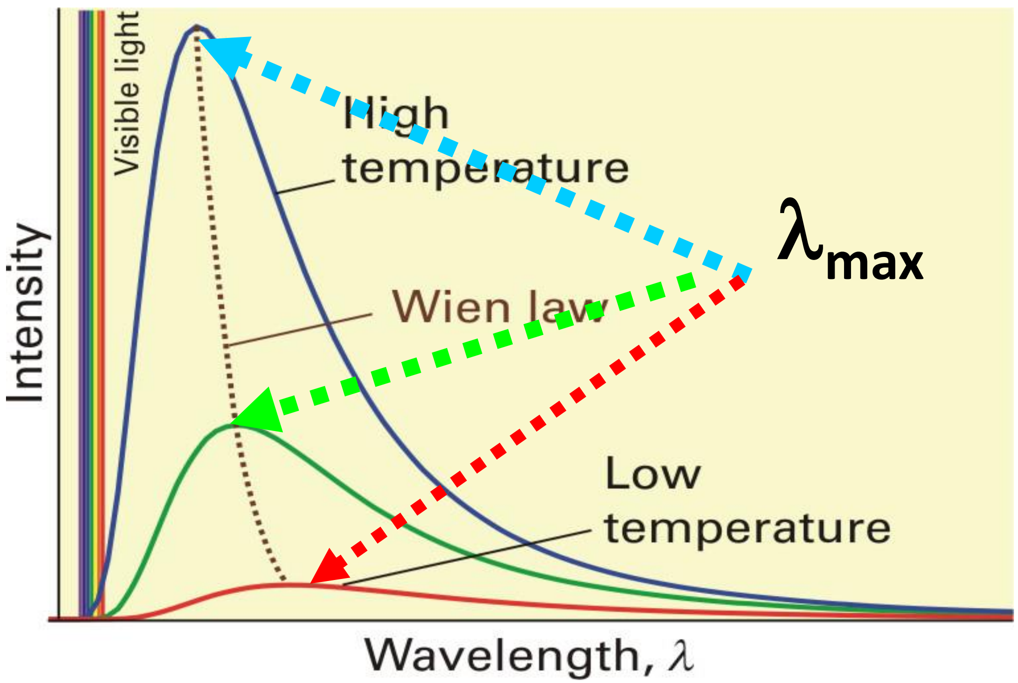




NASA/COBE Science Mission

COBE: Cosmic Background Explorer

Blackbody radiation



$\lambda \rightarrow$

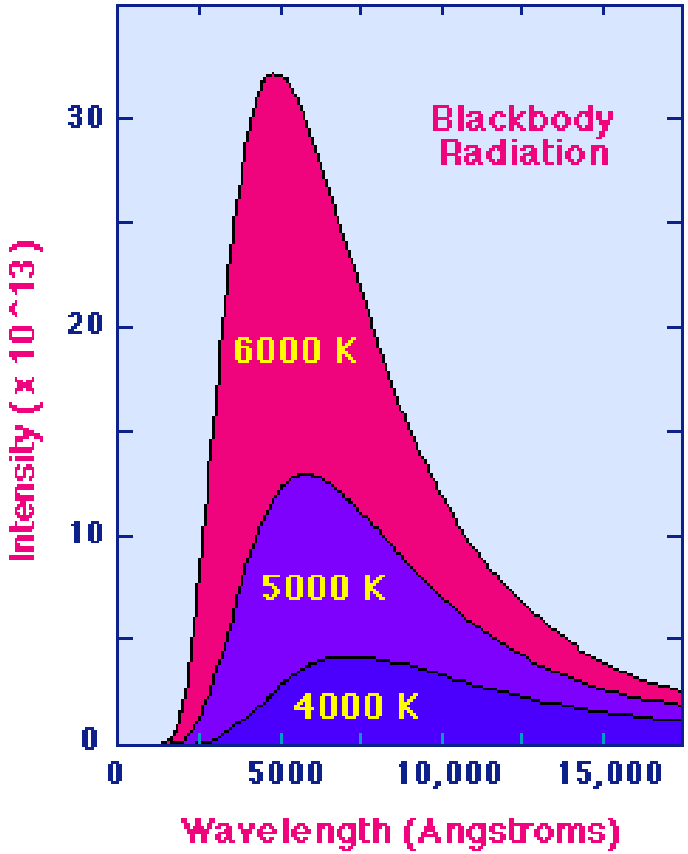
$\leftarrow T$

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

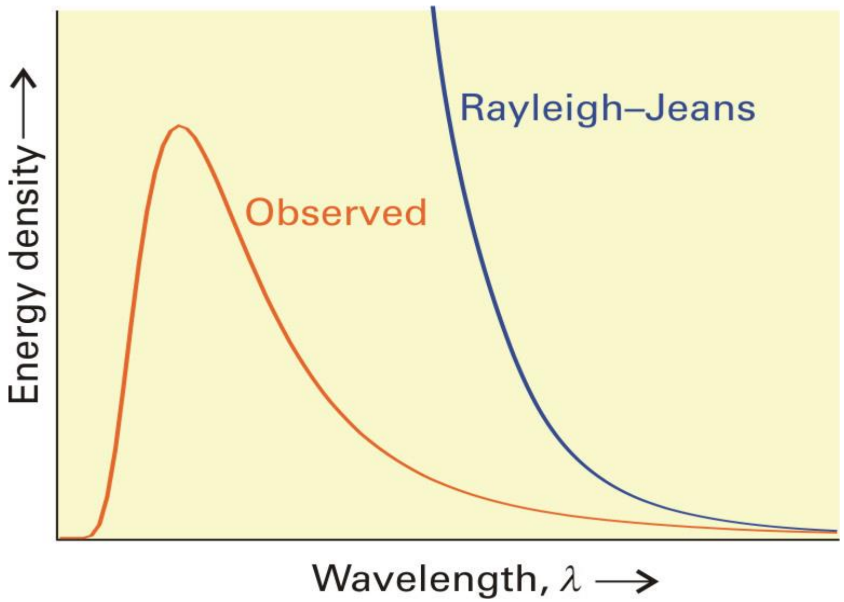
Stefan-Boltzmann Law:

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

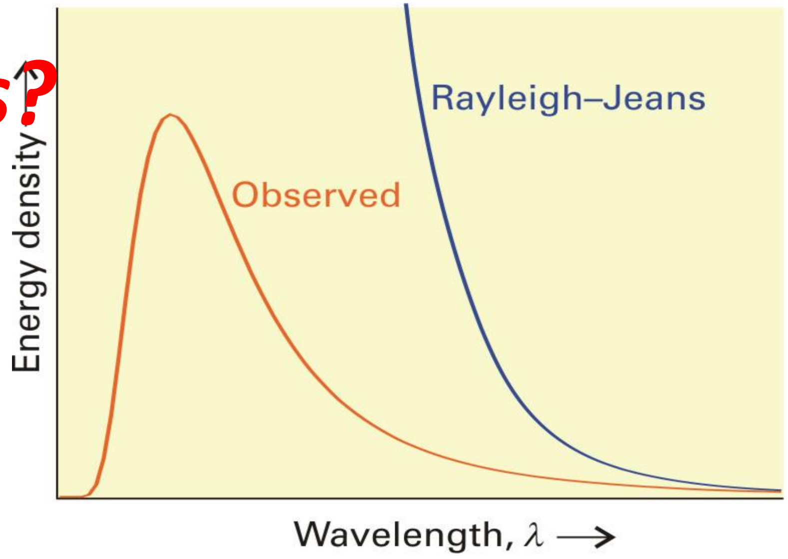
Rayleigh-Jeans:

$\rho(\lambda)d\lambda = (8\pi kT/\lambda^4)d\lambda$ 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



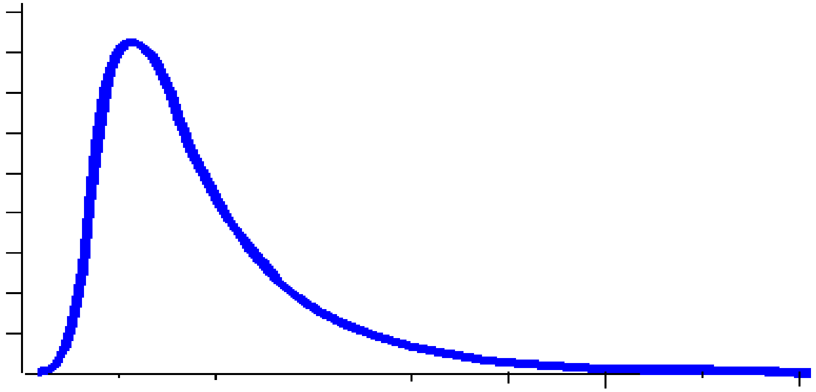
Classical to quantum description

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."-

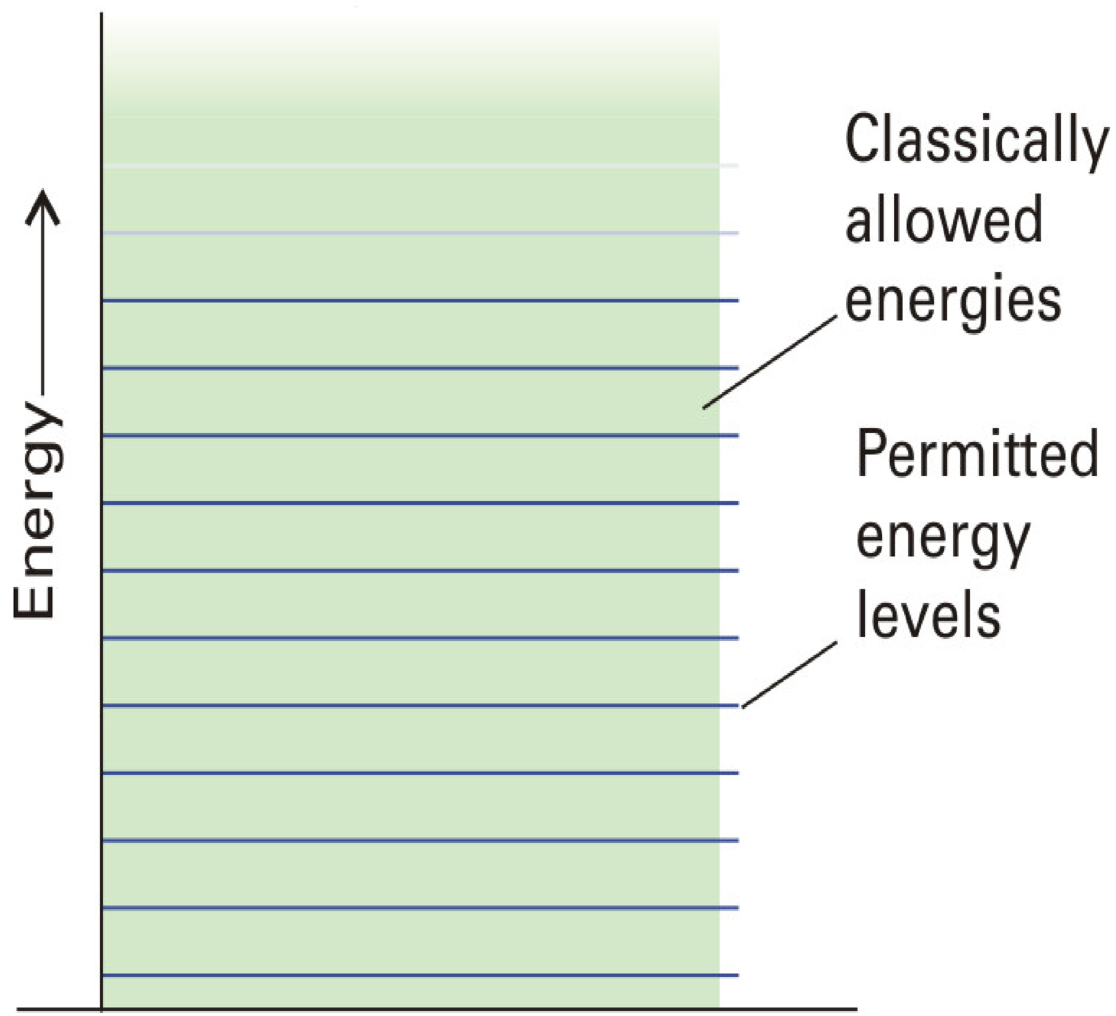
-H. Kragh, *Phys. World*, Dec. 2000

Intensity



Wavelength

Energy quantization



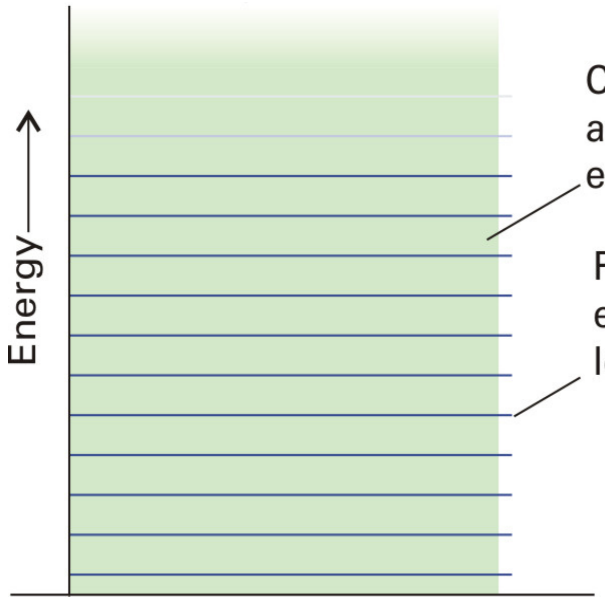
Planck Formula (1900)

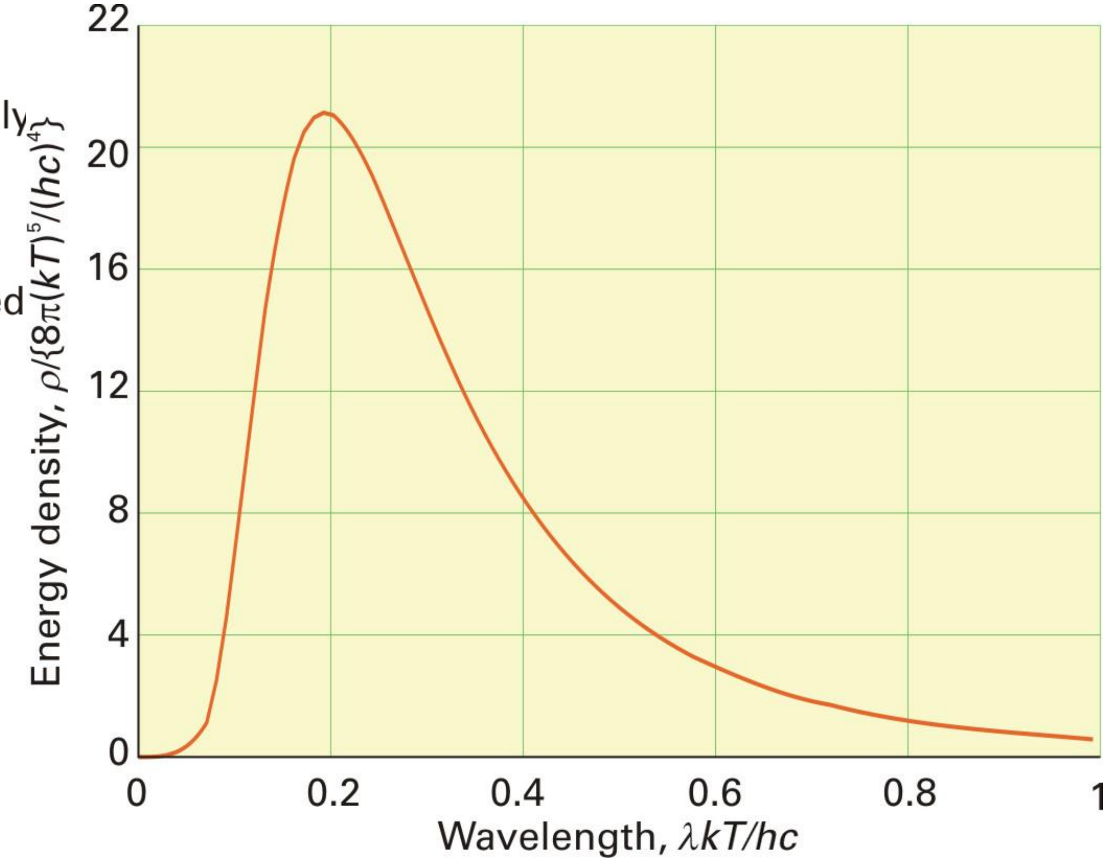
$\rho(\lambda)d\lambda = (hc/\lambda)(e^{hc/\lambda kT} - 1)^{-1}(8\pi/\lambda^4)d\lambda$

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 $\rightarrow 0$ as $\lambda \rightarrow 0$
- UV Catastrophe avoided

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

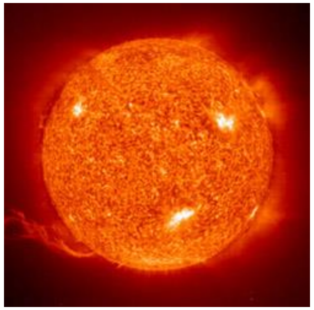
The **Stefan–Boltzmann law** describes the power radiated from a black body in terms of its temperature.

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

$\sigma = 5.6697 \times 10^{-8}\ Wm^{-2}K^{-4}$

We can use Wien's law:

Determine the temperature of hot object: Sun



Summary

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

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