CH101 - Chemistry

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Physical Chemistry

Structure and Bonding

Origin of Quantum Theory

Class 1; July 28, 2011

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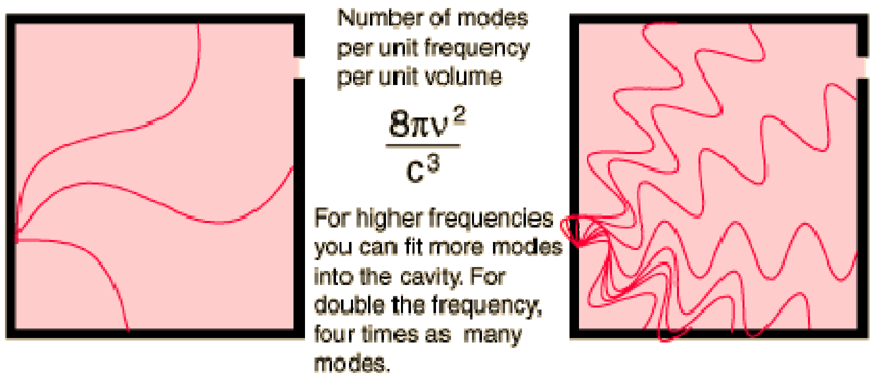
1. Blackbody Radiation

"Blackbody radiation" or "cavity radiation" refers to an object or system which absorbs all radiation incident upon it and re-radiates energy which is characteristic of this radiating system only, not dependent upon the type of radiation which is incident upon it. The radiated energy can be considered to be produced by standing wave or resonant modes of the cavity which is radiating

http://hyperphysics.phy-astr.gsu.edu/hbase/mod6.html

	No. of modes per unit frequency per unit volume	Probability of occupying modes	Average energy per mode
CLASSICAL	$\frac{8\pi v^2}{c^3}$	Equal for all modes	**kT**
QUANTUM	$\frac{8\pi v^2}{c^3}$	Quantized modes: require h**ν** energy to excite upper modes: less probable	$\frac{h\upsilon}{e^{\frac{h\upsilon}{kT}}-1}$



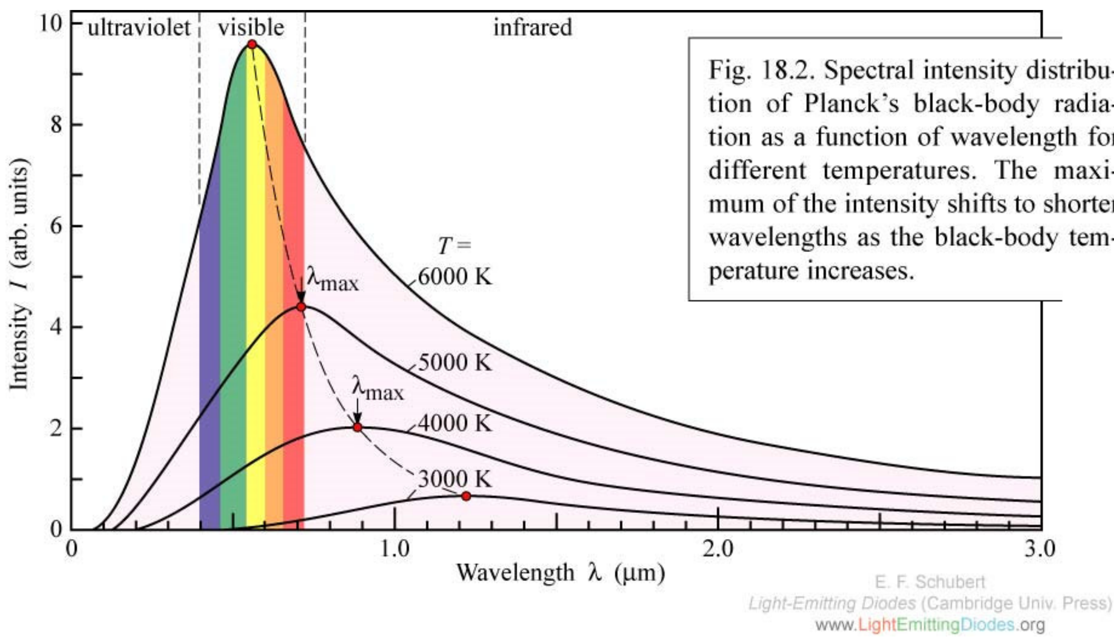
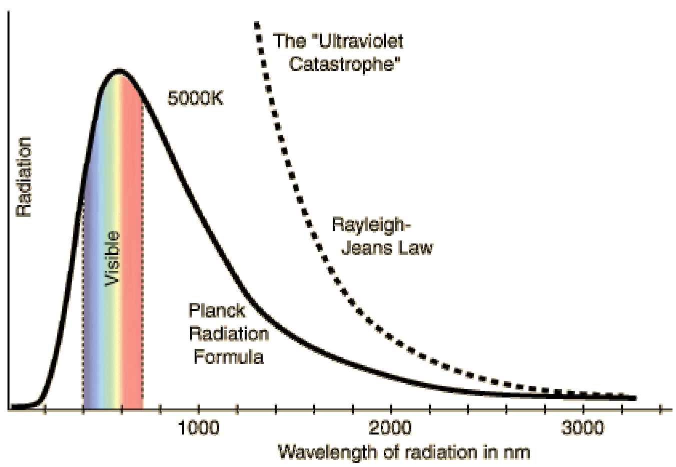


Fig. 18.2. Spectral intensity distribution of Planck's black-body radiation as a function of wavelength for different temperatures. The maximum of the intensity shifts to shorter wavelengths as the black-body temperature increases.



One assumes that the electromagnetic modes in a cavity (of a black body) were quantized in energy.

Planck wrote that this energy E α ν and then E = hν;

h = Planck's constant = 6.62 x 10^{-34}Js

ν = frequency of the mode.

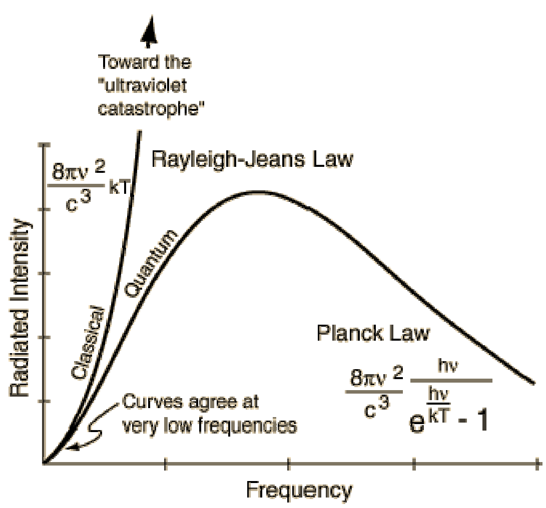
Bose-Einstein function provides the average energy, that is average energy per quantum (hν) times the probability that it will be occupied.

$$< E >= \frac{h\upsilon}{e^{\frac{h\upsilon}{kT}} - 1}$$

ρ(ν) = Energy per unit volume per unit frequency

Planck's radiation law

$$\rho(\upsilon)d\upsilon = \frac{8\pi\upsilon^2}{c^3}\frac{h\upsilon}{e^{\frac{h\upsilon}{kT}} - 1}d\upsilon = \frac{8\pi h\upsilon^3}{c^3}\frac{1}{e^{\frac{h\upsilon}{kT}} - 1}d\upsilon$$



2. **Heat Capacity of Solid:** Dulong and Petit Law;

$Cv \approx 3R = 25\ JK^{-1}mol^{-1}$ = constant at all temperatures

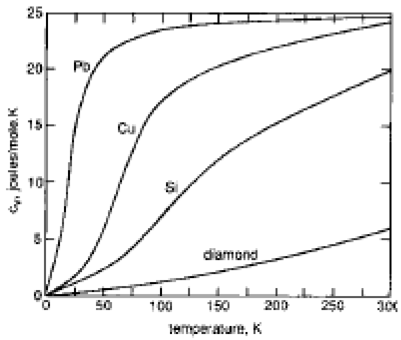
Classical Equipartition of Energy:

Total Energy (U) = Potential Energy (P) + Kinetic Energy (K)

$$\langle P(t)\rangle = \langle K(t)\rangle = \frac{3}{2}k_B T \qquad U = 3N_A kT = 3RT \qquad c_v = [dU/dT]_v = 3R$$

Heat Capacity of Solids at temperatures less than room temperature depends on temperature.

As T→0K; Cv →0



Using Harmonic Oscillator Approximation Einstein Applied Bose-Einstein Statistics to Derive the formula for Heat Capacity

Energy of the ith state is

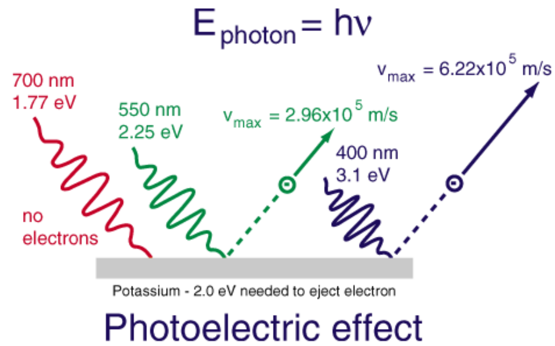
$E_i = (i + ½)h\nu$; where i = 1, 2, 3, …

The average energy per degree of freedom (mode) for an oscillator is $\langle U(t)\rangle = \dfrac{h\upsilon}{e^{\frac{h\upsilon}{k_B T}} - 1}$

Thus for N_A oscillators $3N_A$ degrees of freedom: So the total energy per mole is

$$U = 3N_A < U(t) >= 3N_A \frac{h\upsilon}{e^{\frac{h\upsilon}{kT}} - 1} \qquad c_v = \left[\frac{dU}{dT}\right]_v = \frac{3N_A k_B \left(\frac{h\upsilon}{k_B T}\right)^2 e^{h\upsilon/k_B T}}{\left(e^{h\upsilon/k_B T} - 1\right)^2}$$

3. **Photoelectric Effect**



Incoming electromagnetic radiation on the left ejects electrons, depicted as flying off to the right, from a substance.

Einstein

K. E. (Max) = hν $-\Phi_0$ = ½ mv^2; ν = frequency of light, Φ_0 = work function
v = Speed of electron

4. **Structure of atom (Spectral Emission by atoms)**

Emissions: Lymann; Balmer; Paschen; Bracket and Pfund

Bohr model

$$Energy = E_n = -\left(\frac{2\pi^2 me^4}{h^2}\right)\left(\frac{1}{n^2}\right) = -R_h\left(\frac{1}{n^2}\right)$$

$$\Delta E = h\upsilon = -R_h\left(\frac{1}{n_2{}^2} - \frac{1}{n_1{}^2}\right)$$

$$Radius(Bohr) = a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} 0.529\ \mathring{A}$$