CH101 - Chemistry

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Physical Chemistry: Structure and Bonding

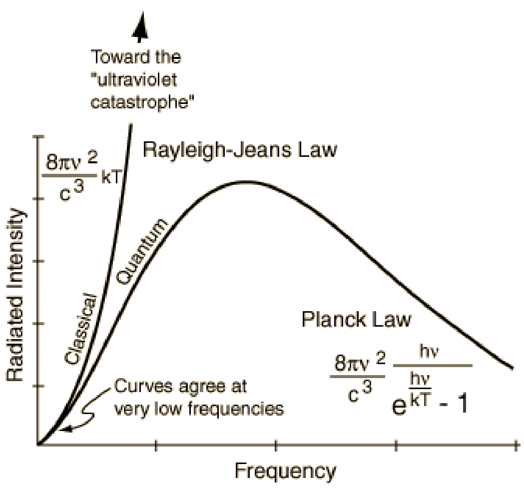
Origin of Quantum Theory

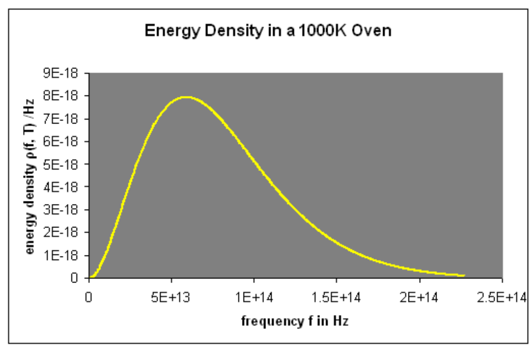
Class 1; 24 – 25 July 2019

1. Blackbody Radiation

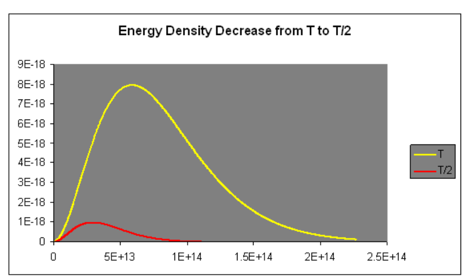
"Blackbody radiation" or "cavity radiation" refers to an object or system which absorbs all radiation incident upon it and re-radiates energy which is characteristic of this radiating system only, not dependent upon the type of radiation which is incident upon it. The radiated energy can be considered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

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





http://galileo.phys.virginia.edu/classes/252/black_body_radiation_files/image075.gif



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.

http://galileo.phys.virginia.edu/classes/252/black_body_radiation_files/image076.gif

Bose-Einstein function provides the average energy i.e. 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 ≈ 3R = 25 $JK^{-1}mol^{-1}$ = constant at all temperatures

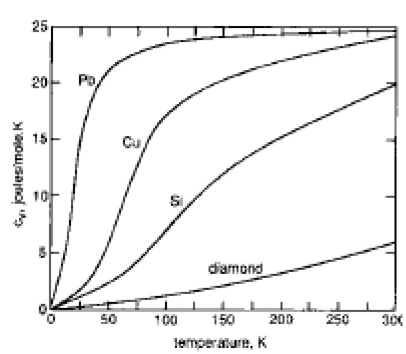
Classical equipartition of Energy:

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→0 K; Cv →0



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

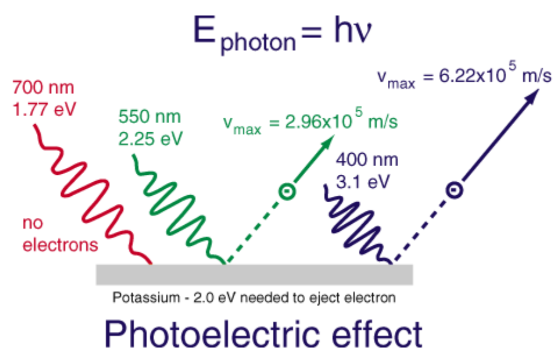
Energy of the ith state is $E_i = (i + ½)h\nu$; where i = 1, 2, 3, …

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

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 –Φ_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

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

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

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