Development of Quantum Chemistry

Matter			Energy	
ancient civilizations	discrete matter			
Dalton	atoms	1803		
Avogadro	molecules	1811		
		1900	Planck	discrete energy
		1905-6	Einstein	heat capacities photoelectric
effect				
Rutherford	nuclear model of the atom	1909-11		
		1913	Bohr	discrete energy levels in atoms

de Broglie	1924	wave nature of matter
Heisenberg	1926-7	matrix mechanics
Schrödinger	1926-7	wave mechanics
Dirac	1928	relativistic quantum mechanics

Everything seemed fine at the time...

> *Our future discoveries must be*
> *looked for in the sixth decimal place.*
>
> Michelson, 1894
> Nobel Laureate

… until a Catastrophe

Problems:

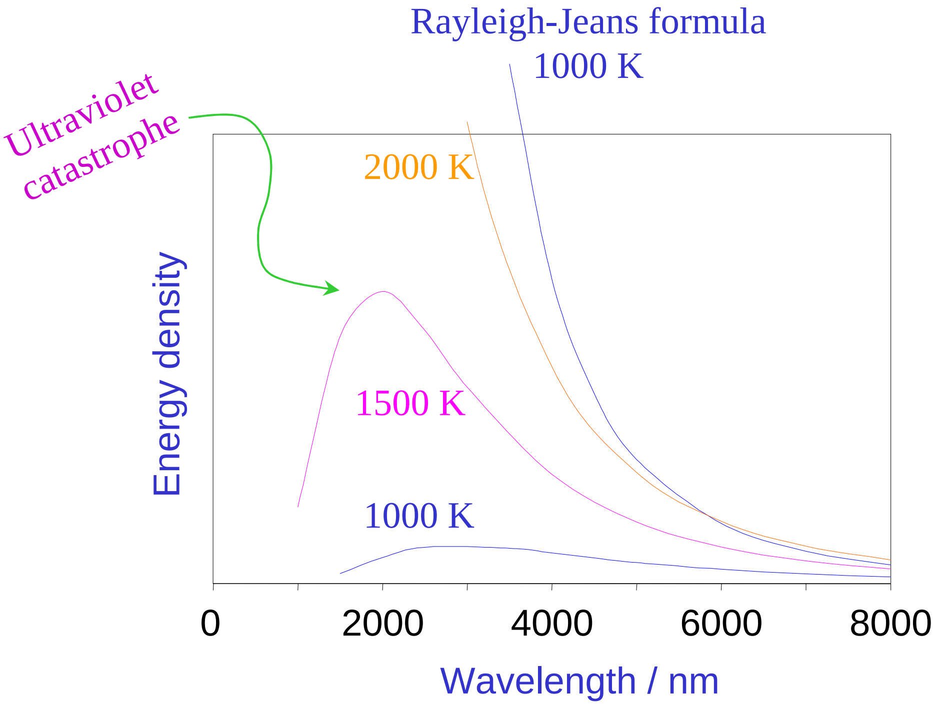
- Black-body radiation
- Heat capacities
- The photoelectric effect
- Atomic line spectra

Black-body Radiation

A black body absorbs all radiation which falls on it (no reflection).

It emits radiation according to its temperature.

Classical theory: $\rho = \dfrac{8\pi kT}{\lambda^4}$



Planck was able to predict the experimental finding of a maximum in the energy emitted at different wavelengths:

$$\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right) \rightarrow \frac{8\pi kT}{\lambda^4} \text{ at long } \lambda$$

Planck's Quantum Hypothesis

- Light comes in "packets" of $\varepsilon = h\nu$

$E\ (= U) = q\varepsilon \qquad q = 0,1,2,\ldots$

- These packets of energy are subject to statistics.

The observable is an average:

$$\overline{U} = \sum_q (q\varepsilon)\,\mathrm{Prob}(q\varepsilon) = \frac{\sum_q (q\varepsilon)\,\mathrm{e}^{-q\varepsilon/kT}}{\sum_q \mathrm{e}^{-q\varepsilon/kT}}$$

$$\Rightarrow \quad \overline{U} = \frac{\varepsilon}{\mathrm{e}^{\varepsilon/kT} - 1} \quad \to kT \quad \text{when } \varepsilon \ll kT$$

the classical limit

Heat Capacities

Planck's ideas were extended to the heat capacity of solids by Einstein.

For a crystal of N atoms:

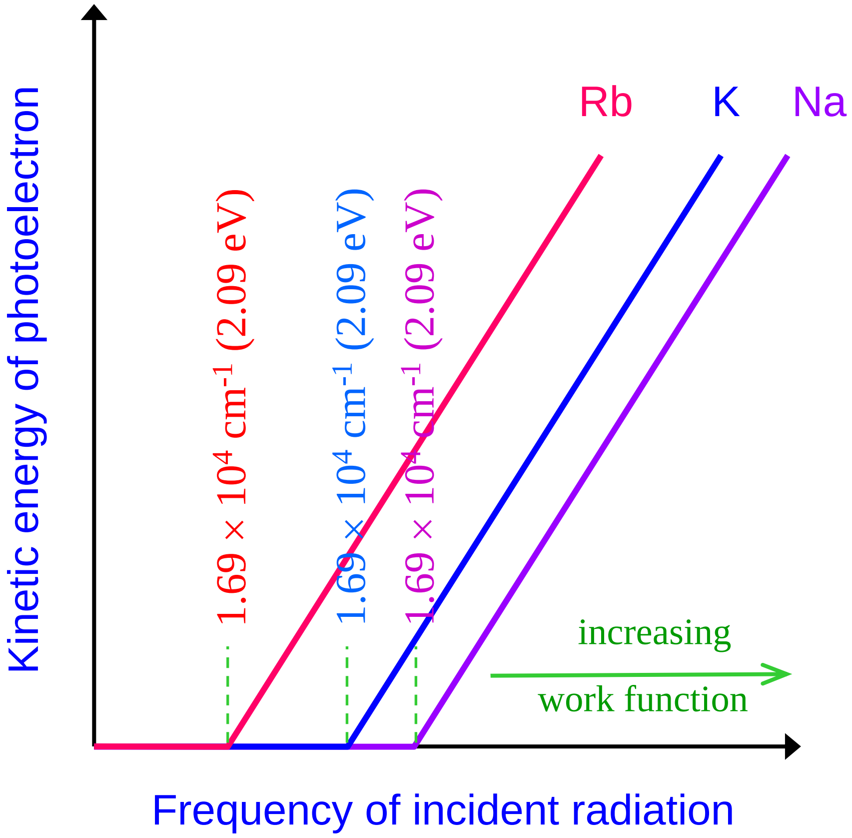
$$C_\mathrm{V} = 3N\frac{dU}{dT} = 3Nk\left(\frac{\varepsilon}{kT}\right)^2 \frac{\mathrm{e}^{\varepsilon/kT}}{\left(\mathrm{e}^{\varepsilon/kT} - 1\right)^2} \quad \to 3R \quad \text{when } \varepsilon \ll kT$$

Dulong and Petit

3-D vibrations

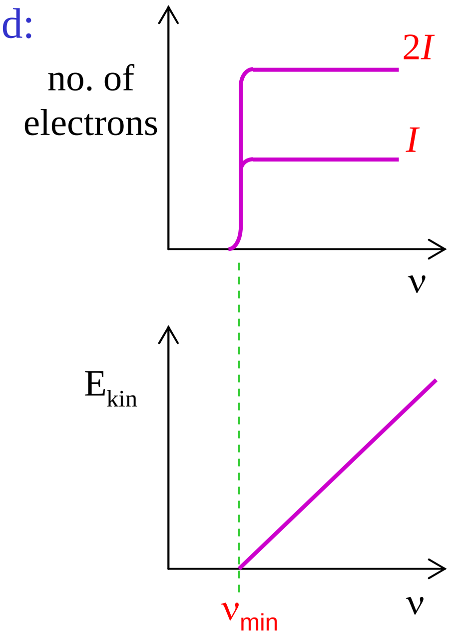
$Nk = R$, the gas constant

The Photoelectric Effect



The Photoelectric Effect - 2

When high frequency radiation (UV and up) falls on a metal surface, electrons are emitted.



Three observations must be explained:

- no emission below ν_{min}.
- Above ν_{min} the emission current depends on light intensity *I*, not ν.
- The kinetic energy of the emitted electrons depends linearly on $(\nu - \nu_{min})$.

Einstein showed that these are consistent
with Planck's hypothesis of the quantization of radiation.

Light of frequency ν is considered as a stream of photons, each with energy hν. A photon is annihilated on collision with an electron and gives up its energy. Part is used to overcome the binding energy to the metal, the remainder appears as kinetic energy.

$$h\upsilon = \phi(M) + \tfrac{1}{2}mv^2$$

$$h\upsilon_{min} = \phi(M)$$

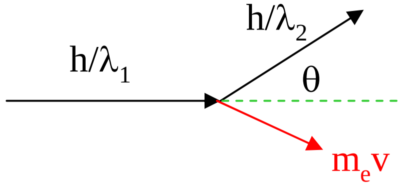
This phenomenon is the basis for photoelectron spectroscopy.

Wave - Particle Duality

Compton Effect

If a beam of light (X-rays) falls on a stream of electrons, it is scattered and the frequency is shifted. The shift depends on scattering angle only:

$$d\lambda = \frac{h}{m_e c}(1 - \cos\theta)$$



Which is exactly the result expected from conservation of momentum and energy for a photon of momentum h/λ .

=> Light behaves like particles.

Electron Diffraction

Electrons (and other particles) can be diffracted by crystals or thin foils.

=> Particles behave like light.

Laser Cooling

Recent atomic physics and particle physics experiments use lasers to “cool” particle beams.

De Broglie relation: $p = h / \lambda$