General Chemistry I

NAC 1101

Lecture 3

Electronic structure of Atoms

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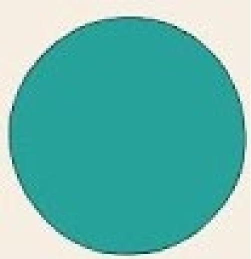
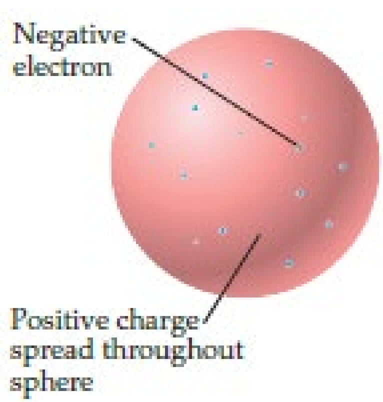
Outline

- Quantum Theory & Electronic Structure
- Electromagnetic radiation
- Polychromatic & Monochromatic light
- Hot Objects & Quantization of Energy
- Max Planck & quantization
- Photoelectric Effect (Albert Einstein)
- Work Function
- Dual wave-particle nature of light
- Bohr's Model



1803: John Dalton

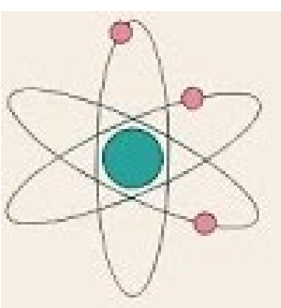
Each element is composed of extremely small "indivisible ×" particles (solid sphere) called atoms.



J. J Thompson

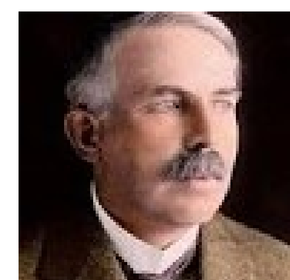
1856-1940

Plum Pudding



1911: Ernest Rutherford

Nuclear Model



20th century Quantum Theory & Electronic Structure

- Much of our present understanding of the electronic structure of atoms has come from analysis of the light either emitted or absorbed by substances.

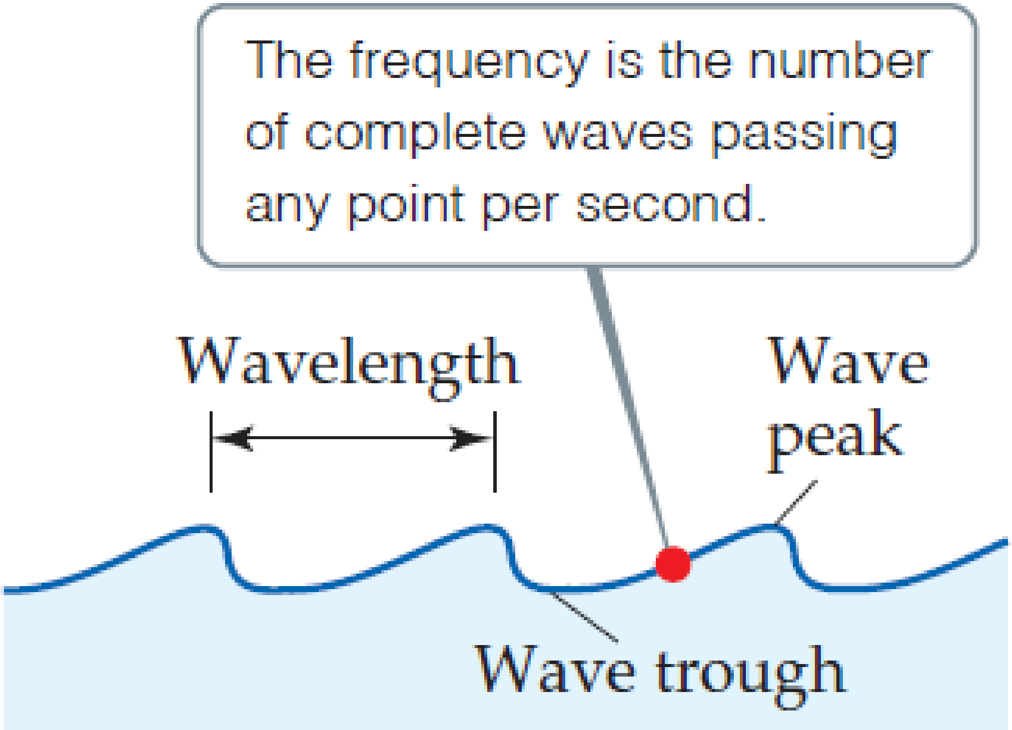
Light → **Electromagnetic radiation**

Radiant energy

- wave-like characteristics (like water waves)
- Periodic (pattern of peaks and troughs repeats itself at regular intervals)

Water Wave

Mechanical,
needs a medium (water)



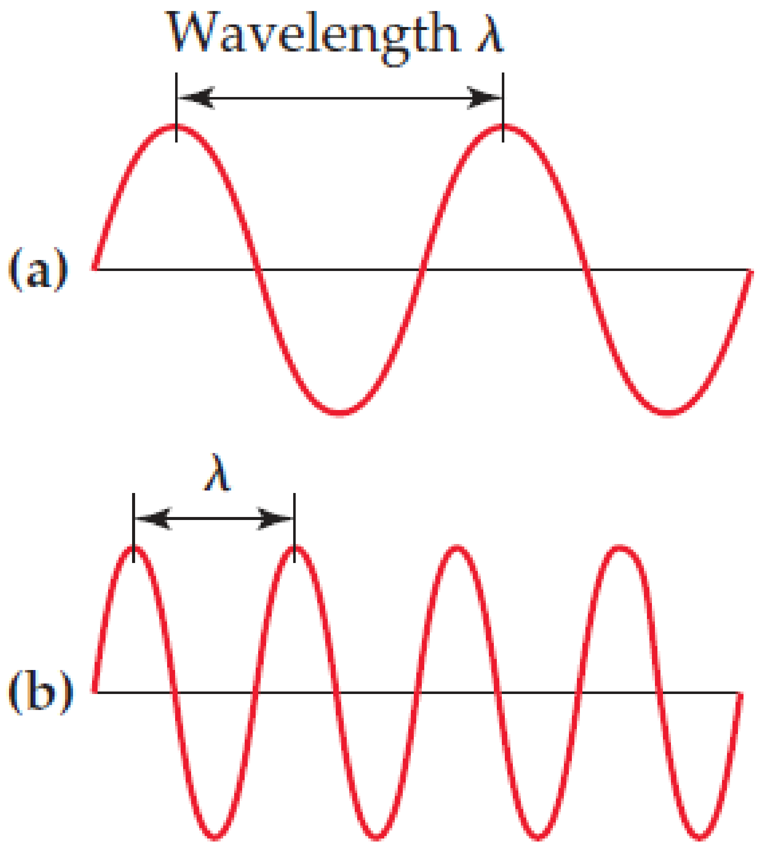
up-and-down movements of the water

- The wavelength is the distance between two adjacent peaks or two adjacent troughs.

λ: m

ν: s^{-1} = *hertz* = Hz

Electromagnetic Wave



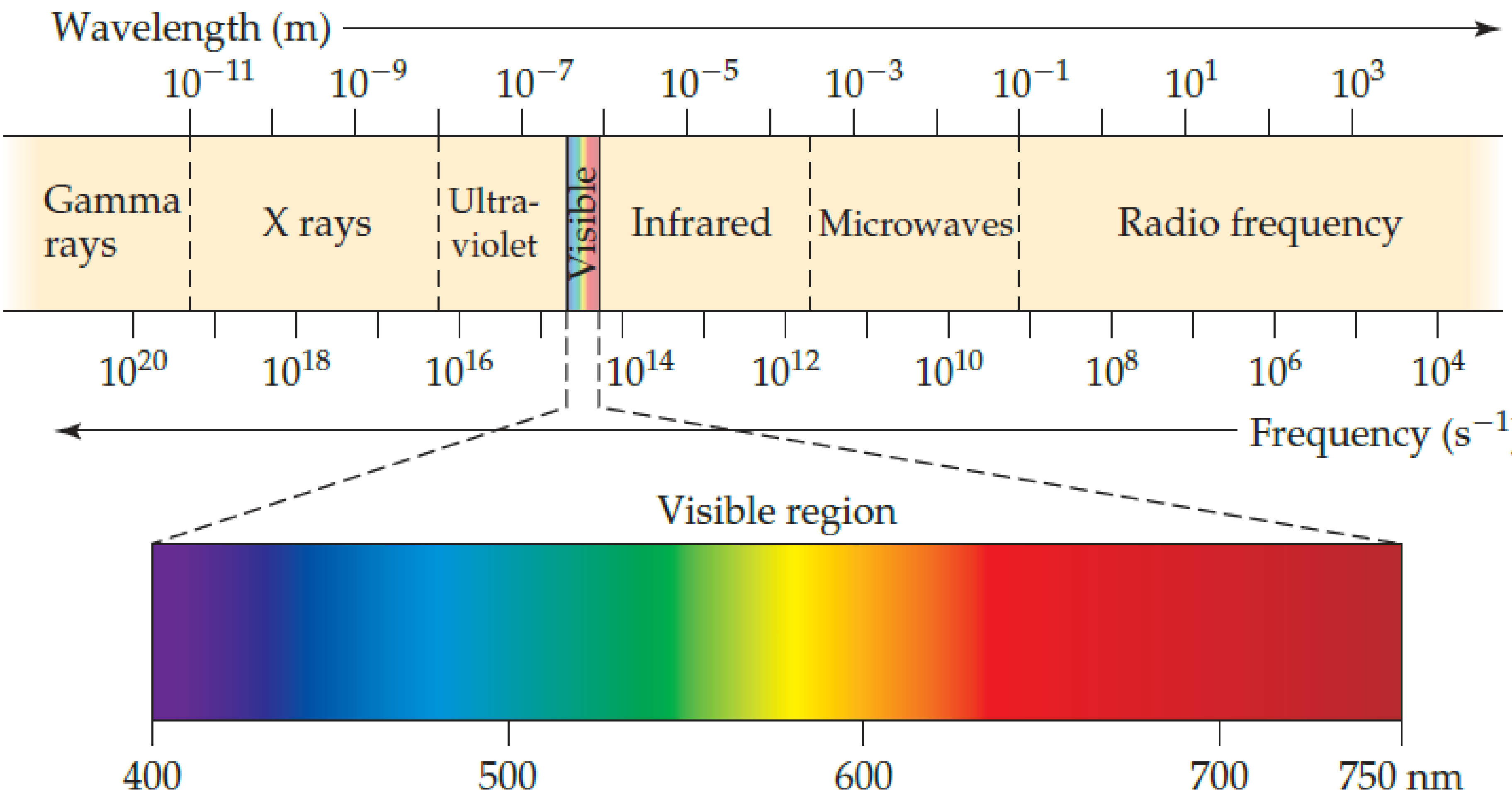
Periodic oscillations in the intensities of the electric and magnetic fields associated with the radiation.

- The shorter λ, the greater the frequency, ν.

- Light Speed in vacuum = 2.998×10^{8} m s^{-1}

$$C = \lambda\nu = 2.998 \times 10^{8} \text{ m s}^{-1}$$

Different types of electromagnetic radiation have different properties due to their different wavelengths



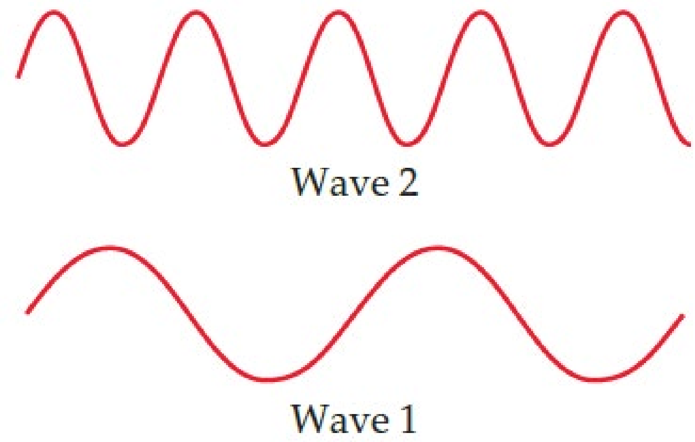
Is the wavelength of a microwave longer or shorter than the wavelength of visible light? By how many orders of magnitude?

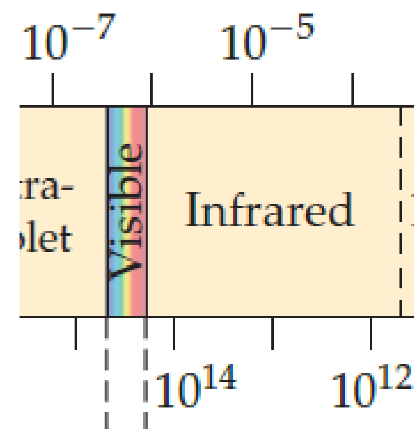
Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Length (m)	Type of Radiation
Angstrom	Å	10^{-10}	X ray
Nanometer	nm	10^{-9}	Ultraviolet, visible
Micrometer	μm	10^{-6}	Infrared
Millimeter	mm	10^{-3}	Microwave
Centimeter	cm	10^{-2}	Microwave
Meter	m	1	Television, radio
Kilometer	km	1000	Radio

Exercise

- Which of these electromagnetic waves has a higher frequency? If one of them is for visible light and the other for infrared radiation, which wave is which?





Answer

- Wave 1 has a **longer** λ but Wave 2 has a **higher** ν
- Infrared radiation has a **longer** λ than visible light. Thus, Wave 1 is infrared radiation.

Exercise

- The yellow light given off by a sodium vapor lamp used for public lighting has a wavelength of 589 nm. What is the frequency of this radiation?

Answer

$$\nu = \frac{C}{\lambda} = \left(\frac{3.00 \times 10^{8}\ m\ s^{-1}}{589\ nm}\right)\left(\frac{1\ nm}{10^{-9}\ m}\right)$$

$$\nu = 5.09 \times 10^{14}\ s^{-1}$$

Polychromatic & Monochromatic light

White light

- a combination of the colors of the visible spectrum, surrounds us and consists of all the wavelengths in the range 400–750 nm.

Laser radiation

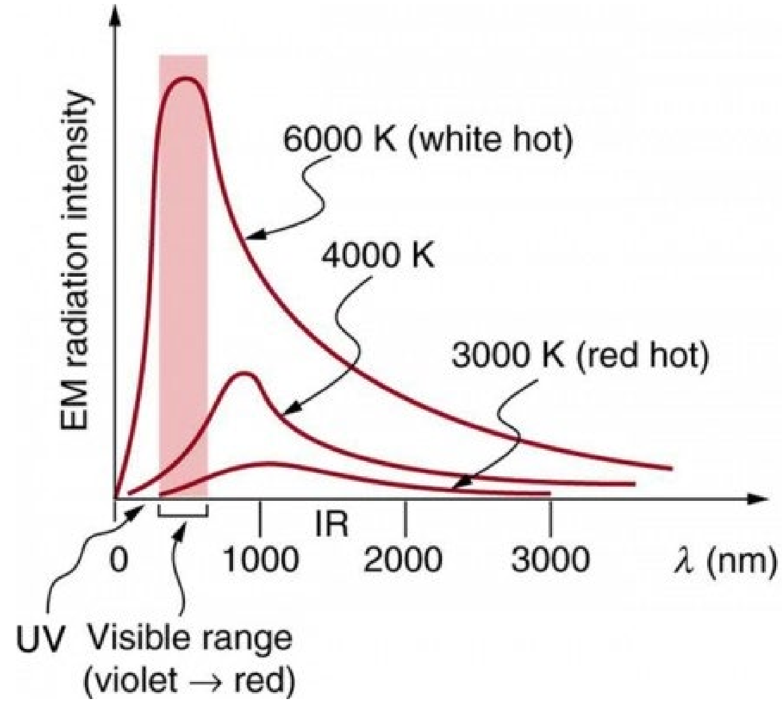
- consists of just a single wavelength, a result of a quantized process.

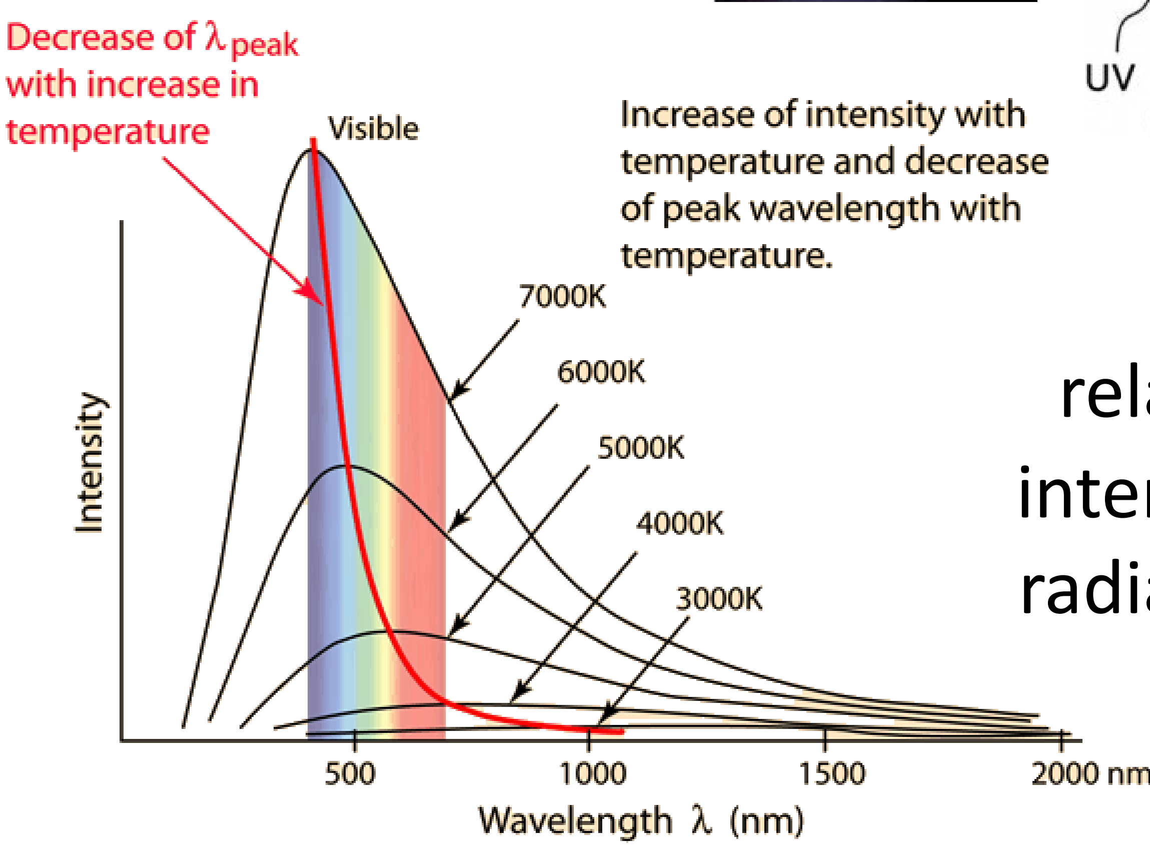
Hot Objects & Quantization of Energy

- When solids are heated, they emit radiation.
  - red glow of an electric stove burner.
  - bright white light of a tungsten light bulb.

The color and intensity of emitted light by a hot nail depend on its T.

- The wavelength distribution of the radiation depends on T.
  - a red-hot object is cooler than a yellowish or white-hot one.





relationship between T, intensity and λ of emitted radiation is not clear !!!!!!

Max Planck (1900)

- proposed that energy can be either released or absorbed by atoms only in discrete "chunks" of some minimum size.

Planck

- gave the name quantum (meaning "fixed amount") to the smallest quantity of energy that can be emitted or absorbed as electromagnetic radiation.

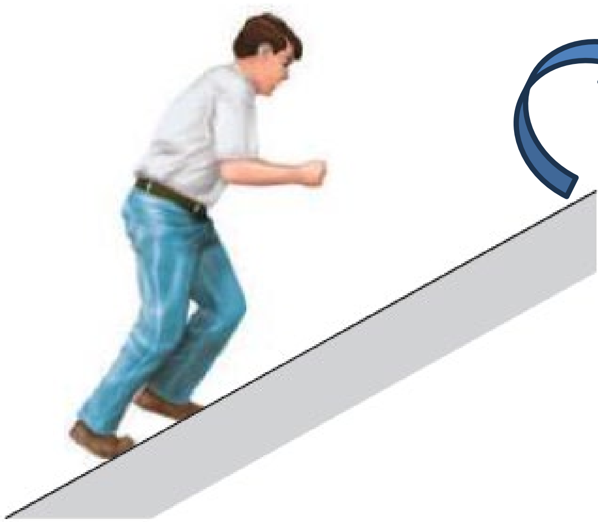
- Energy, E, of a single quantum is given by

$$E = h\nu = \frac{hC}{\lambda}$$

h: Planck constant
= 6.626×10^{-34} J.s

Matter can emit and absorb energy only in whole number multiples of $h\nu$, such as $h\nu$, 2 $h\nu$, 3 $h\nu$ (3 quanta), etc.

Quantized vs. continuous change in energy

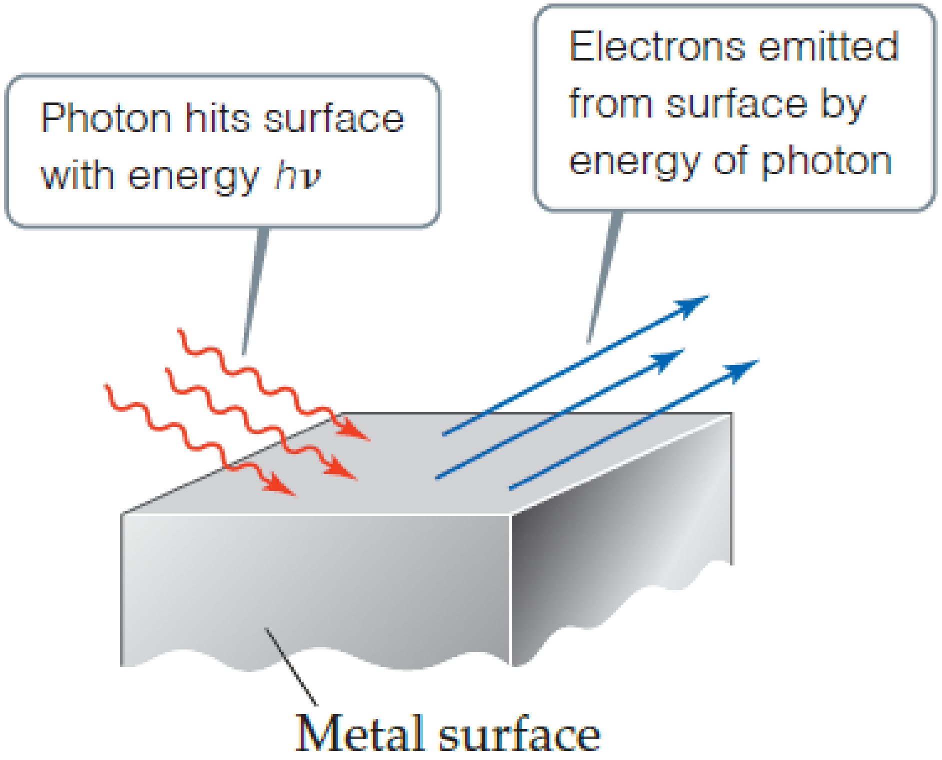


- Potential energy of person walking up ramp increases in uniform, continuous manner

- Potential energy of person walking up steps increases in stepwise, quantized manner.

Analogy to electromagn
etic radiation

Photoelectric Effect (Albert Einstein) 1905



- Light shining on a clean metal surface causes e's to be emitted from the surface.
- A minimum frequency of light, different for different metals, is required for the emission of e's.

- Radiant energy striking the metal surface behaves like a stream of tiny energy packets, each like "particle" of energy, called a **photon** of energy, E= $h\nu$. **<u>Quantized</u>**

Work Function

- A certain amount of energy required for the e's to overcome the attractive forces holding them in the metal.
- If the photons striking the metal have less energy than the the **work function**, the e's do not escape from the metal and increasing the intensity of the light source **doesn't** lead to emission of e's from the metal.
- The intensity (brightness) of the light is related to the number of photons striking the surface per unit time but not to the energy of each photon.
- Only changing the **frequency** of the incoming light can emit e's.

- When the frequency is such that photons have energy greater than the **work function** of the metal, e's are emitted; any excess energy of the photon is converted into kinetic energy of emitted electron.

Exercise

- Calculate the energy of one & moles of photon(s) of yellow light that has a wavelength of 589 nm.

Answer

$$E = h\nu = \frac{hC}{\lambda}$$

$$E = \frac{(6.626 \times 10^{-34}\ J.s)(3.00 \times 10^{8}\ m\ s^{-1})}{589\ nm}\left(\frac{1\ nm}{10^{-9}\ m}\right)$$

$$E = 3.37 \times 10^{-19}\ J$$ Per Photon

$$E = (3.37 \times 10^{-19}\ J/photon) \times (6.023 \times 10^{23} photons\ /mol)$$

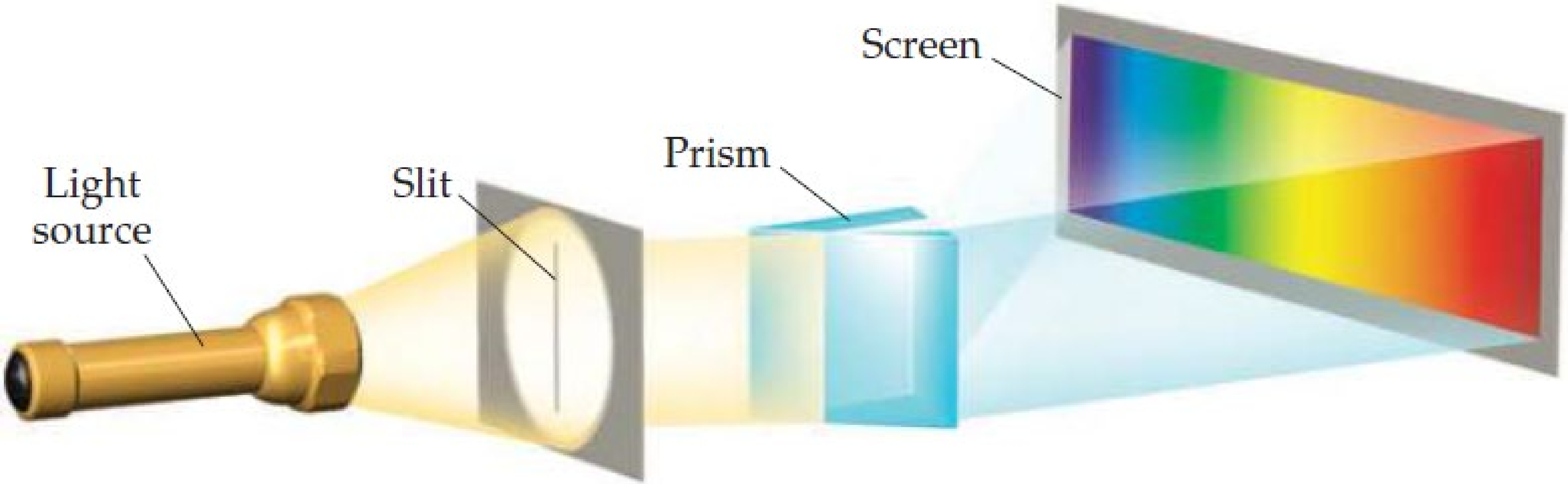
$$E = 2.03 \times 10^{5}\ J/mol$$

Dual wave-particle nature of light

- Although Einstein's theory of light as a stream of photons rather than a wave explains the photoelectric effect and a great many other observations, it also poses a dilemma.
  - Is light a wave, or does it consist of particles?
- Later we will consider that light possesses both wave-like and particle-like characteristics and, depending on the situation, will behave more like waves or more like particles.

Continuous Spectra

- Spectra produced when radiation from a polychromatic (as incandescent light bulbs and stars, contains many different wavelengths) source is separated into its component wavelengths.

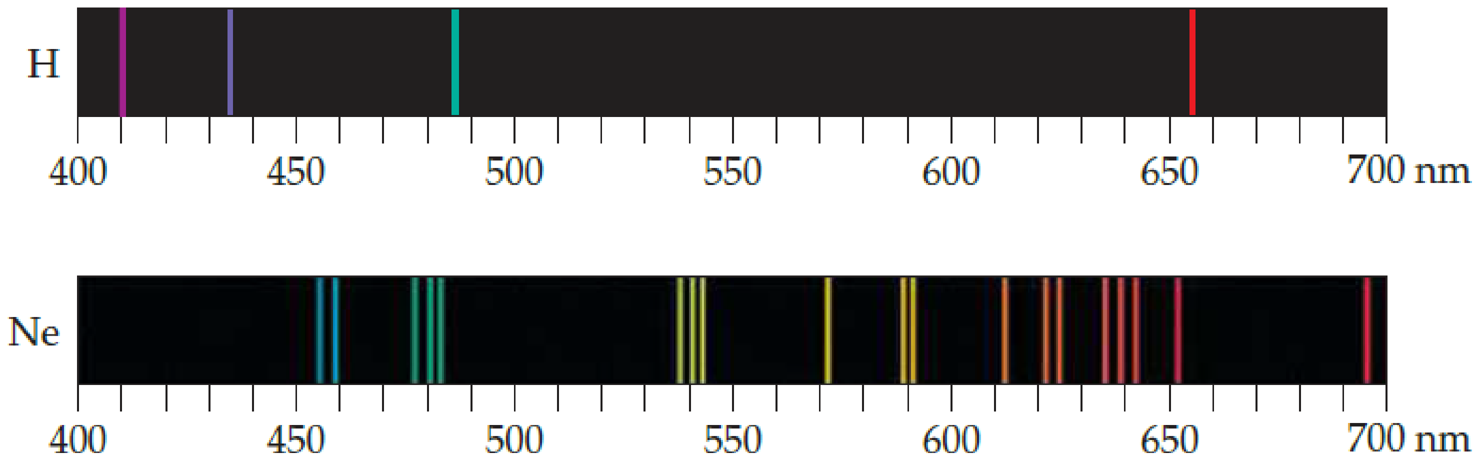


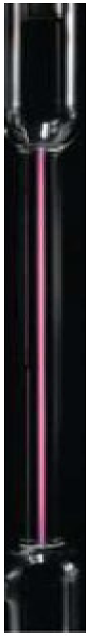
Similar to when raindrops or mist acts as a prism for sunlight

Continuous range of colors

Line Spectra

- Spectra containing radiation of only few (specific) wavelengths.
- When a high voltage is applied to tubes that contain different gases under reduced pressure, the gases emit different colors of light.





Neon (Ne)

Hydrogen (H)

Rydberg equation

- calculated the wavelengths of all the spectral lines of hydrogen.

$$\frac{1}{\lambda} = (R_H)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

- $R_H = 1.096776 \times 10^7\ m^{-1}$ is the Rydberg constant.
- n_1 and n_2 are positive integers, with n_2 being larger than n_2.

Bohr's Model

- In 1913, the Danish physicist Niels Bohr offered a theoretical explanation of line spectra.
- He assumed that e's in hydrogen atoms move in circular orbits around the nucleus. Problem?
- According to classical physics, a charged particle (such as an electron) moving in a circular path should continuously lose energy.
- As an electron loses energy, therefore, it should spiral into the positively charged nucleus.
- This behavior, however, does not happen—hydrogen atoms are stable.
- Bohr assumed that the prevailing laws of physics were inadequate to describe all aspects of atoms.

Bohr's Postulates:

1) Only orbits of certain radii, corresponding to certain specific energies, are permitted for the electron in a hydrogen atom.

2) An electron in a permitted orbit is in an "allowed" energy state. An electron in an allowed energy state does not radiate energy and, therefore, does not spiral into the nucleus.

3) Energy is emitted or absorbed by the electron only as the electron changes from one allowed energy state to another. This energy is emitted or absorbed as a photon that has energy $E = h\nu$.

Energy of allowed orbits for electron in H atom

$$E = (-hcR_H)\left(\frac{1}{n^2}\right) = (-2.18 \times 10^{-18})\left(\frac{1}{n^2}\right)$$

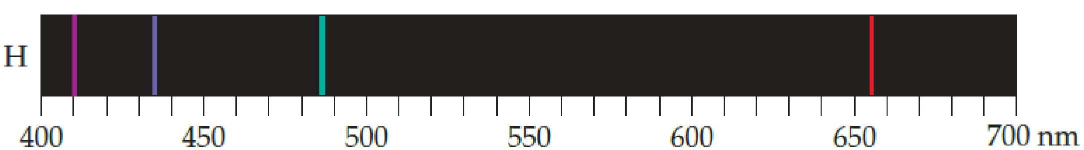
- h, c, and R_H are the Planck constant, the speed of light, and the Rydberg constant, respectively.
- The integer n is whole-number values of 1, 2, 3, …∞, is called the **principal quantum number**.

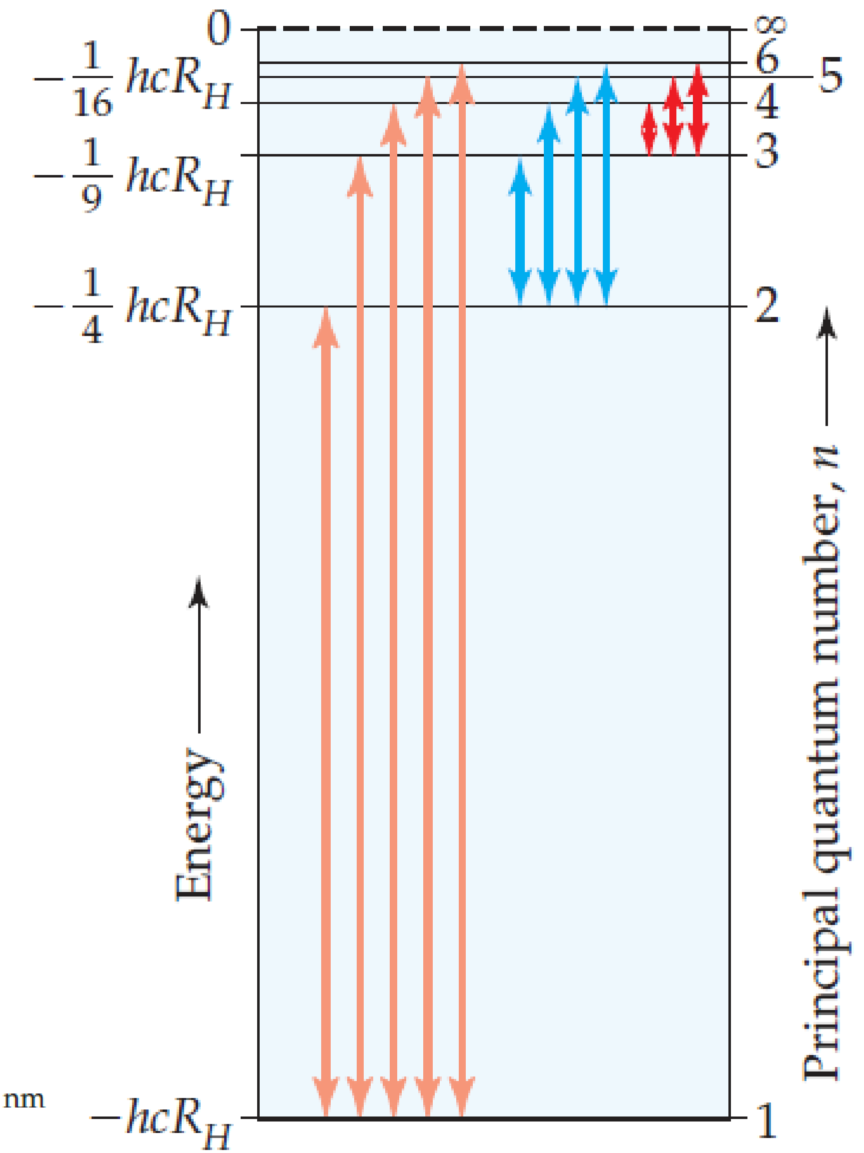
- The radius of the orbit gets larger as n increases.
- The electron in the hydrogen atom can be in any allowed orbit.
- Noting the negative sign in Eq., the lower (more negative) the energy is, the more stable the atom is.
- The energy is lowest (most negative) for n = 1.

Ground & Excited States

- The lowest-energy state (n = 1) is called the ground state of the atom.

- When the electron is in a higher-energy state (n = 2 or higher), the atom is said to be in an excited state.





Reference, or zero-energy State

When $n = \infty$

$$E = (-2.18 \times 10^{-18})\left(\frac{1}{\infty^2}\right) = 0$$

- The orbit radius increases.
- The energy of attraction between the electron and the nucleus approaches zero.
- The electron is completely separated from the nucleus.
- The energy of the electron is zero.

Excitation & Relaxation

- If an electron jumps from an initial state of n_i and energy E_1 to a final state with principal quantum number n_f and energy E_f.

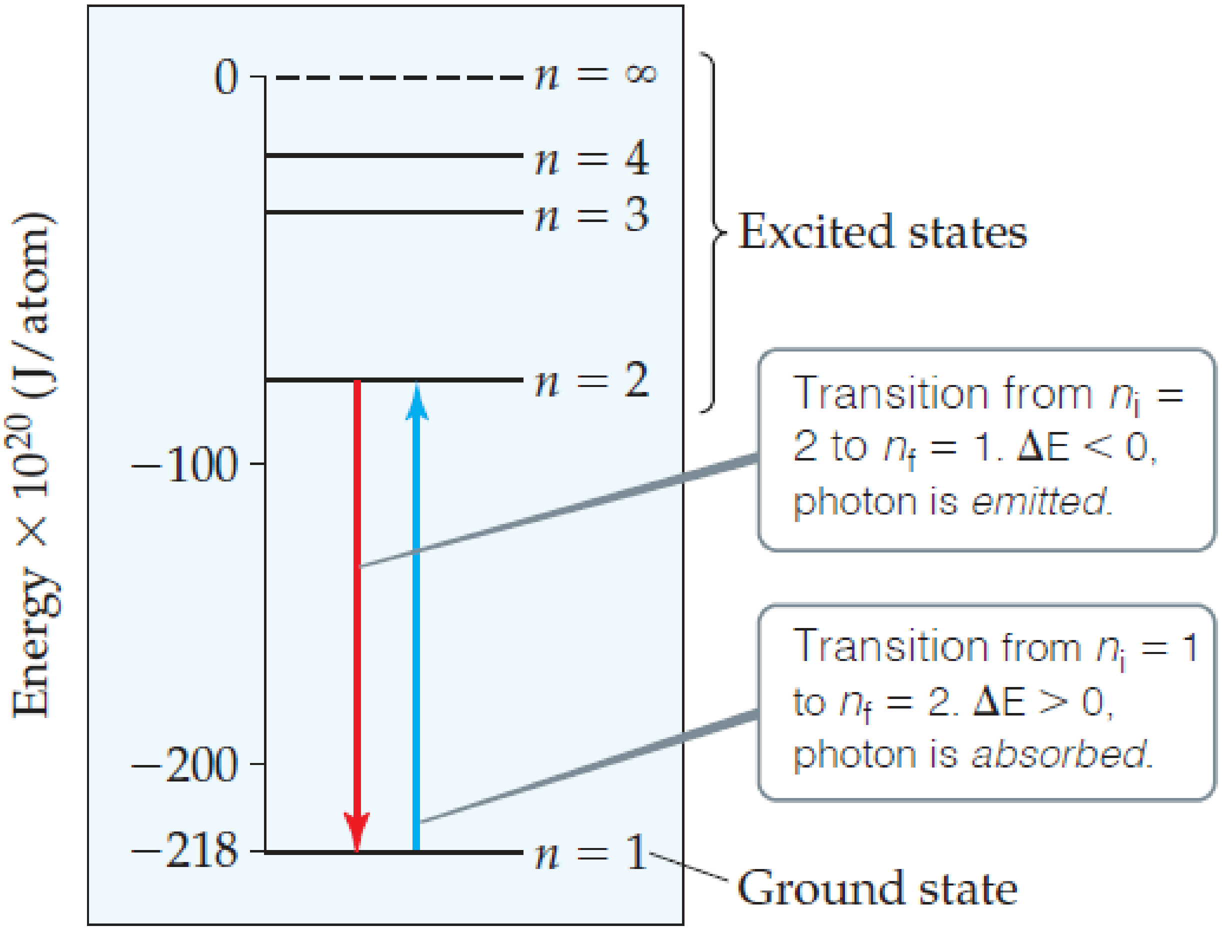
$$\Delta E = (-2.18 \times 10^{-18})\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$n_f > n_i$ ➡ ΔE is positive ➡ e jumps to a higher-energy orbit.

$n_f < n_i$ ➡ ΔE is negative ➡ e jumps to a lower-energy orbit.

An electron's transition involve a photon of Energy (always positive) = $h\nu = \Delta E$

For +ve ΔE, photons are absorbed and for –ve ΔE, photons are emitted



- Which transition will lead to the emission of light with longer wavelength, n = 3 to n = 2, or n = 4 to n = 3?

Exercise

- Calculate the energy associating the transition of hydrogen electron from in which the electron moves from $n = 3$ to $n = 1$ and the photon wavelength involved in this transition.

Answer $\Delta E = (-2.18 \times 10^{-18})\left(\frac{1}{3^2} - \frac{1}{1^2}\right)$

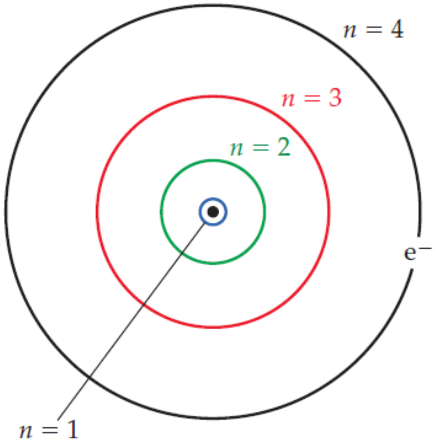
$= -1.94 \times 10^{-18}\ J$ ↓ **emission**

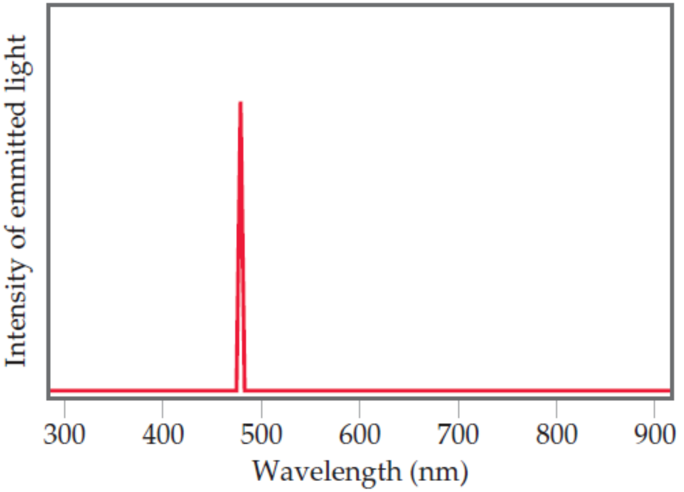
For emission $-\Delta E = h\nu = \frac{hC}{\lambda}$

$$\lambda = \frac{(6.626 \times 10^{-34}\ J.s)(3.00 \times 10^{8}\ m\ s^{-1})}{1.94 \times 10^{-18}\ J}\left(\frac{1\ nm}{10^{-9}\ m}\right)$$

$= 102\ nm$

Test Understanding





- In the Bohr model of the hydrogen atom, e's are confined to orbits with fixed radii that are calculated to be 0.53, 2.12, 4.76, and 8.46 Å, respectively, for the first four orbits.
  a) If an e makes a transition from the n_i = 4 level to a lower-energy level, n_f = 3, 2, or 1, which transition would produce a photon with the highest λ?
  b) What is the energy of this, and in which region of the electromagnetic spectrum does it lie?
  c) According to the detector's measurement, if a H atom begins with an electron in the n_i = 4 state, what will be the final state, n_f, of the transition (480 nm)?

Limitations of Bohr's Model

- It can not explain the spectra of other atoms, except in a crude way.
- Bohr also avoided the problem of why the negatively charged electron would not just fall into the positively charged nucleus, by simply assuming it would not happen.
- Bohr's model of an electron orbiting the nucleus at a fixed distance is not a realistic picture.
  - We will see later that the electron exhibits wave-like properties, a fact that any acceptable model of electronic structure must accommodate.

Most Significance points of Bohr's Model

- Electrons exist only in certain discrete energy levels, which are described by quantum numbers.

- Energy is involved in the transition of an electron from one level to another.