CH-110 Advanced General Chemistry I

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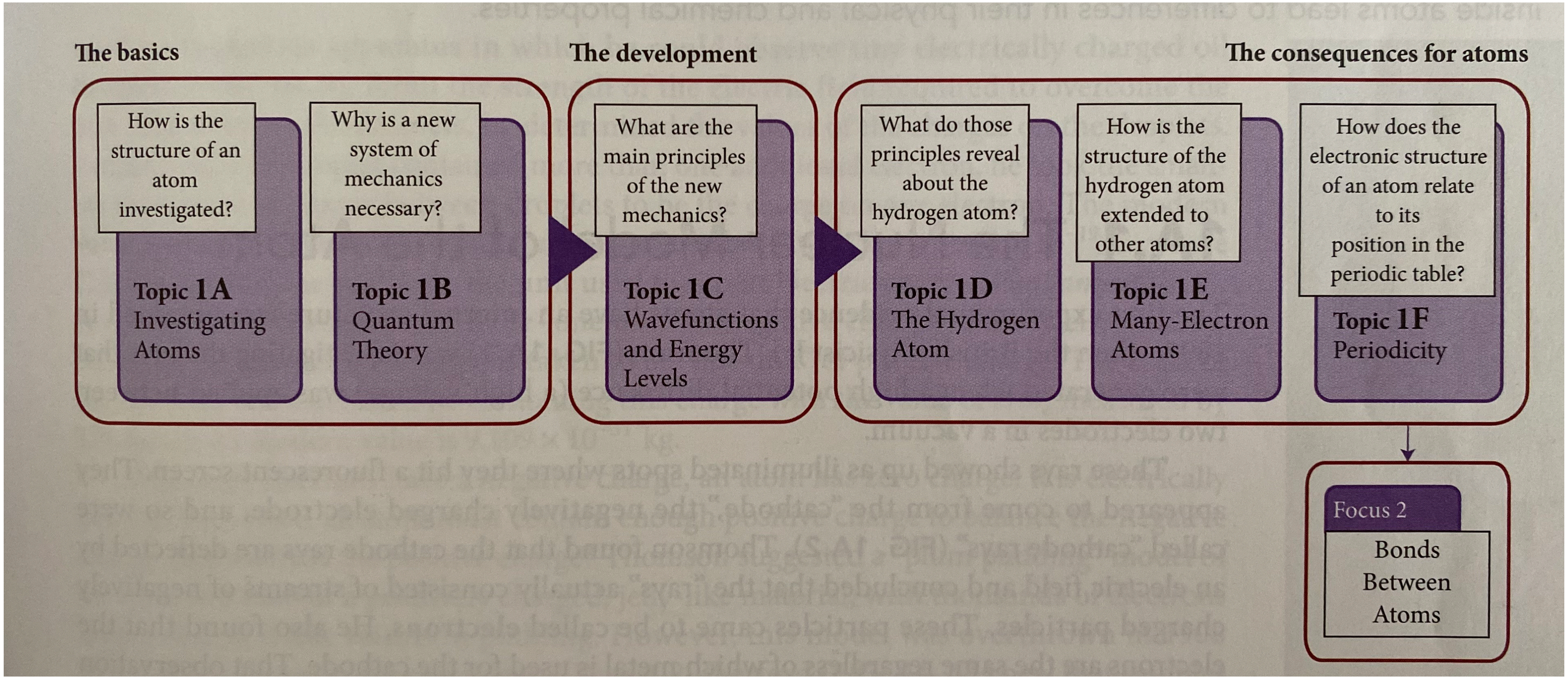
Investigating Atoms

Topic 1A

Overview Chapter 1 (Focus 1: Atoms)



Topic 1A.1: The nuclear model of the atom
Topic 1A.2: Electromagnetic radiation
Topic 1A.3: Atomic Spectra

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- **Understanding of the structures of atoms is essential for understanding the differences in physical and chemical properties of substances**.
- Therefore: important to understand what is going on inside atoms and how their structure is studied.

WHAT DO YOU NEED TO KNOW ALREADY?

- Familiarity with the **nuclear model of the atom**: a small, positively charged nucleus surrounded by negatively charged electrons (Fundamentals B)

1A.1 The nuclear model of the atom

Setting the Stage: What Was Known Before J.J. Thomson's Discovery

In the late 19th century, the atomic theory of matter had been widely accepted for several decades, but atoms were still thought of as indivisible, solid particles — essentially featureless spheres. Key historical context includes:

1. **The Atom as Indivisible:** According to **John Dalton's atomic theory** (early 1800s), atoms were the smallest indivisible particles of matter. Each element was made of identical atoms, and chemical reactions were thought to involve rearrangements of these atoms, but there was no knowledge of any internal structure.
2. **Laws of Electricity and Magnetism:** The work of scientists such as **Michael Faraday** and **James Clerk Maxwell** had led to an understanding of electric and magnetic fields, along with the behavior of electric currents. However, the relationship between electricity and atoms was not well understood, and no subatomic particles were known.
3. **Cathode Rays:** By the mid-1800s, scientists had discovered **cathode rays** — streams of particles emitted from the cathode (negative electrode) in vacuum tubes. These rays could cast shadows and were deflected by magnetic fields, but their nature was a mystery. Were they a new form of radiation, or particles? The concept of electrons was unknown.

1A.1 The nuclear model of the atom

J.J. Thomson cathode ray experiment

First experimental evidence for internal structure obtained in 1897 by British physicist **J. J. Thomson**.

- Cathode rays generated when a high potential difference (high voltage) was applied between two electrodes **in vacuum**:

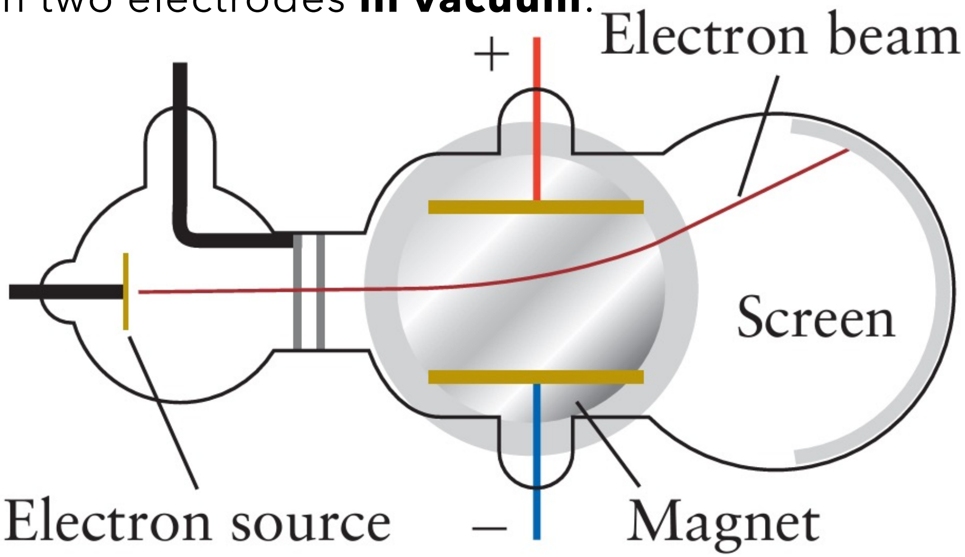


Figure 1A.2

1A.1 The nuclear model of the atom

J.J. Thomson cathode ray experiment

J.J. Thomson experiment

- Deflected by electric field → must be negatively charged (“corpuscules”) → later known as **electrons**
- Measured $e/m_{e:}$ electron charge and mass of electron
- Same regardless which metal was used → must be part of all atoms: UNIVERSAL
- Challenged the long-held view of atoms as indivisible

Why important?

This was the first **experimental evidence of the internal structure of atoms** – they were not indivisible as previously thought, but contained smaller, negatively charged particles.

1A.1 The nuclear model of the atom

Summary of J.J. Thomson cathode ray experiment

At the time of Thomson's discovery, atoms were considered indivisible particles with no internal structure. Through his experiments with cathode rays, Thomson showed that atoms contained smaller, negatively charged particles (electrons), which was the first experimental evidence of the atom's internal structure. His discovery of the electron fundamentally altered the understanding of atomic theory and set the stage for the development of modern atomic physics.

1A.1 The nuclear model of the atom

The Millikan oil droplet experiment

- Used to determine value of e itself (only e/m_e known)
- Apparatus observed tiny electrically charged oil particles suspended in mid-air (oil sprayed as a fine mist)
- Strength of the electric field required to overcome the pull of gravity on the droplets → value of charge
- Millikan performed this experiment many times with different droplets and found that the charges on all the droplets were always **multiples of a fundamental value** (the smallest possible charge). The smallest increment of charge between droplets: **charge of one electron!**

  $E = 1.602 \times 10^{-19}\ C$
- C: Coulomb, unit of electric charge

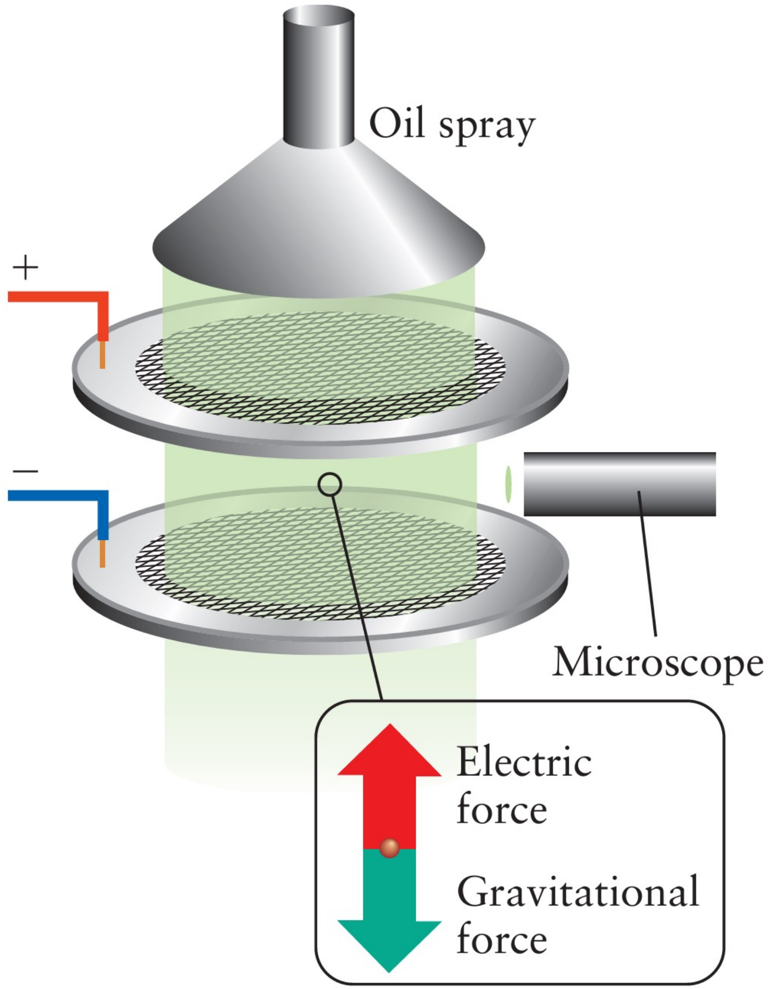


Figure 1A.3

1A.1 The nuclear model of the atom

The appartus included:

- A chamber with a fine mist of **oil droplets** (created by atomizing oil using an atomizer)
- A pair of **parallel metal plates**, creating a uniform electric field when a voltage was applied
- A **light source** and a **microscope** to observe the behavior of the droplets
- A source of **X-rays** to ionize air molecules, causing some oil droplets to pick up extra electrons and become negatively charged

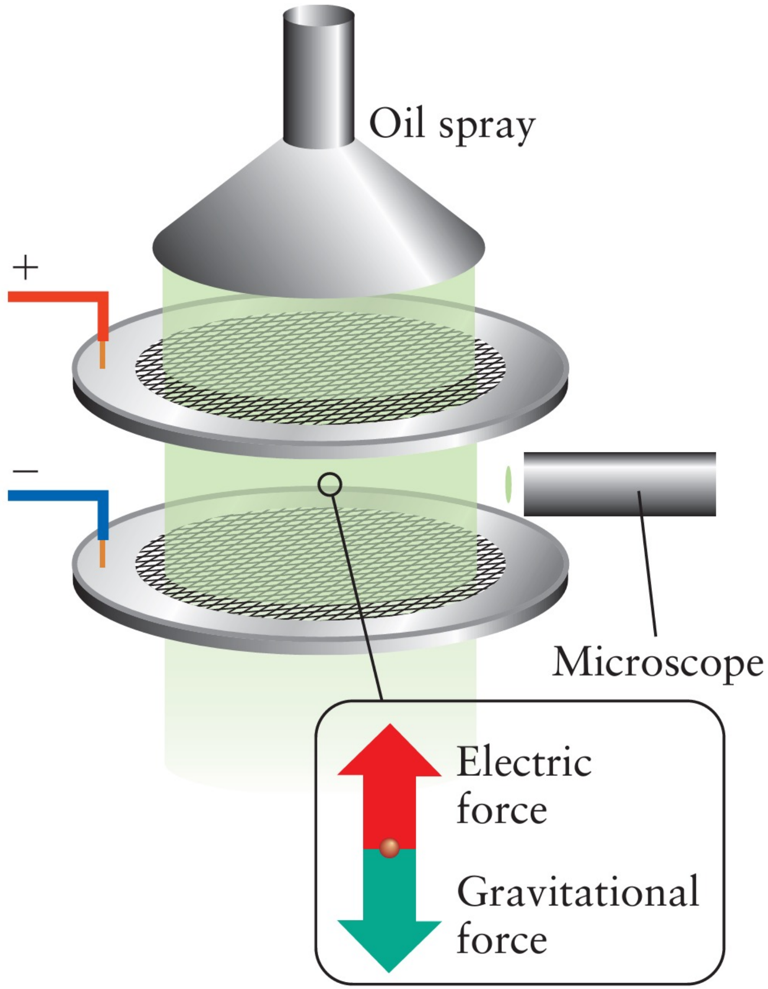


Figure 1A.3

1A.1 The nuclear model of the atom

Why Millikan was at the frontier

Millikan’s experiment was revolutionary for several reasons:

1. **Precision and Control:** His setup was extremely precise for its time, allowing him to manipulate individual microscopic oil droplets and balance the forces on them with remarkable accuracy.
2. **Direct Measurement of the Electron’s Charge:** This was the first direct and accurate measurement of the **elementary charge**. With this, Millikan confirmed the quantization of electric charge, meaning that charge always comes in integer multiples of a fundamental unit (the charge of an electron).
3. **Foundations for Modern Physics:** By measuring the electron’s charge and combining it with **J.J. Thomson’s charge-to-mass ratio** (e/m_e), Millikan could also calculate the **mass of the electron**, an essential step in furthering the understanding of atomic structure and quantum theory.

Conclusion

Millikan’s oil drop experiment provided the first accurate measurement of the **fundamental unit of electric charge** – the charge of a single electron. By balancing the gravitational and electric forces on tiny charged oil droplets, Millikan demonstrated that electric charge is quantized and determined the charge of the electron to be approximately 1.6×10−19 C1.6 \times 10^{-19} \, \text{C}1.6×10−19C. His work was a landmark in the development of atomic theory and provided critical experimental evidence for the quantization of charge, which was a key step in the foundation of quantum mechanics.

1A.1 The nuclear model of the atom

What about the positive charge?

- Negative charge detectable, what about positive charge?
- **Plum pudding model** (Thomson):
- The atom was thought to be a relatively large, positively charged sphere with electrons scattered within it, balancing the charge.
- **Rutherford** discovered that some materials (e.g. Rn) emit positively charged particles, α (alpha) particles.

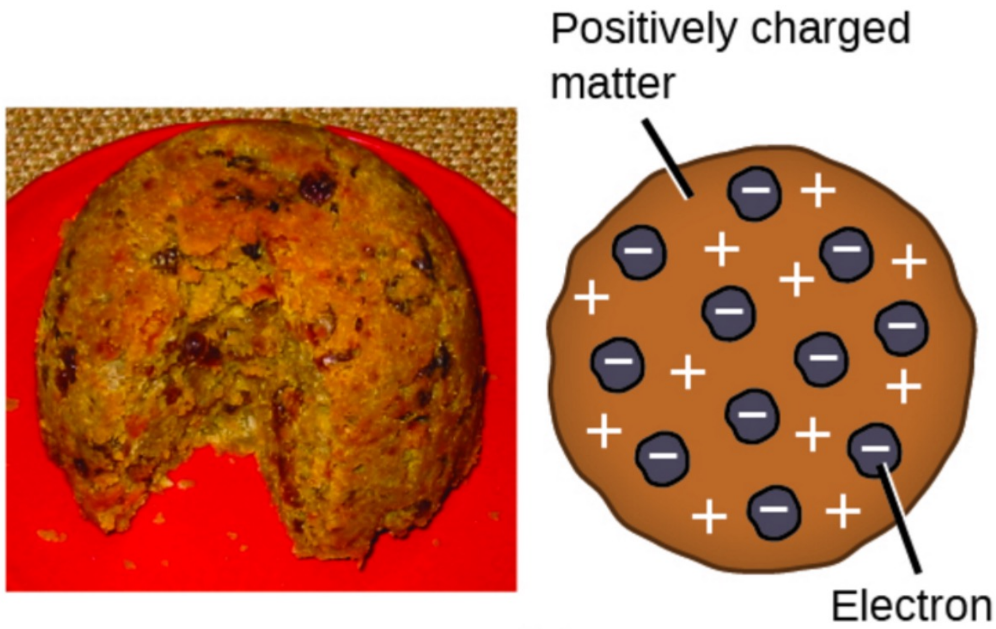


Image: https://www.khanacademy.org/science/chemistry/atomic-structure-and-properties/history-of-atomic-structure/a/discovery-of-the-electron-and-nucleus

1A.1 The nuclear model of the atom

The Rutherford gold foil experiment (Geiger-Marsden)

Expectation: if an atom is like a blob of positively charged material with electrons suspened in it, alpha particles should pass through clouds of positive charge of the foil, only slight deflection in path.

What they found: Almost all alpha particles went through with very little deflection. Every once in a while, large deflections were observed.

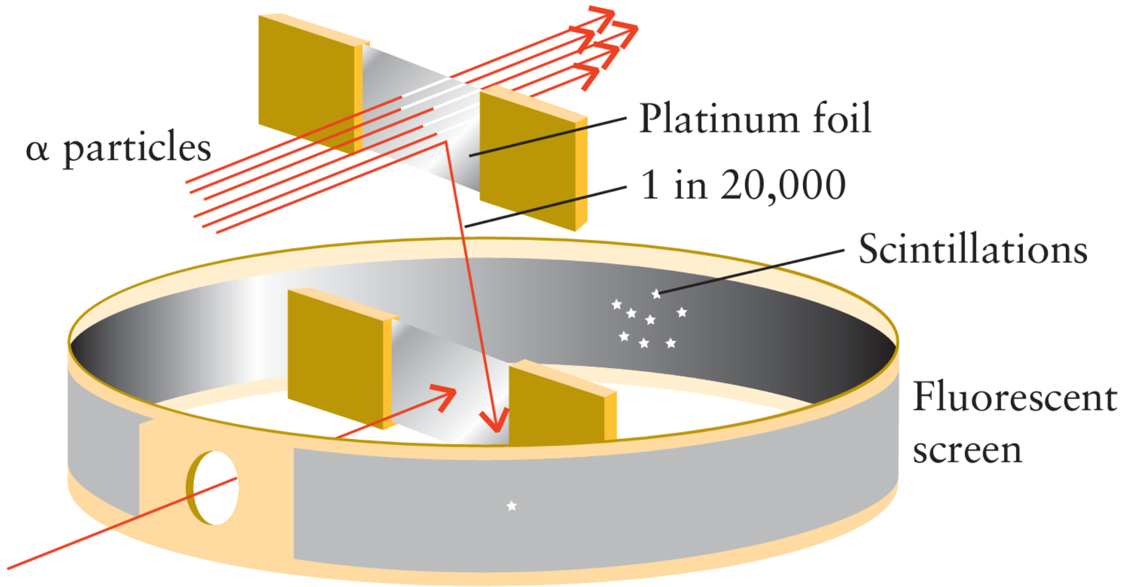


Figure 1A.5

1A.1 The nuclear model of the atom

The Rutherford gold foil experiment (Geiger-Marsden)

- Rutherford proposed a **new model of the atom:** most of the mass and all of the positive charge of the atom concentrated in a **tiny, dense core** at the center: **nucleus**.
- The **electrons** were assumed to **orbit this nucleus** at relatively large distances, much like planets orbiting the sun.
- The **small deflections** were due to the interactions of the **alpha particles with the electrons**, while the **large deflections** occurred when an **alpha particle came close to the nucleus**, experiencing a strong repulsive force from the highly concentrated positive charge.

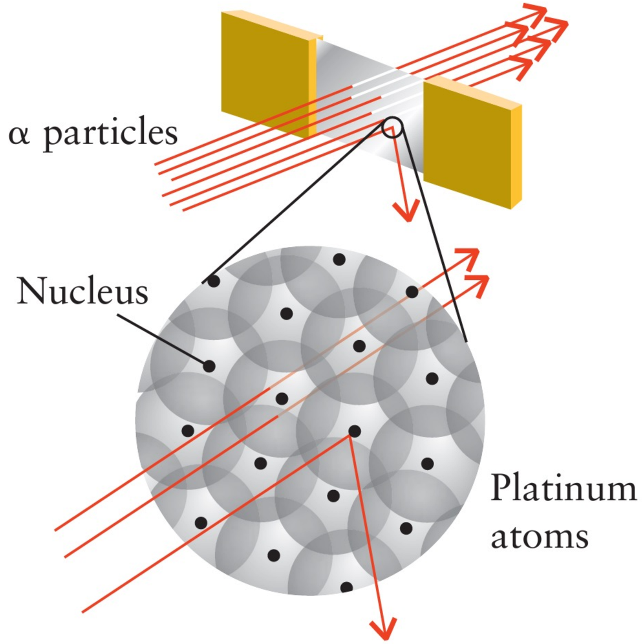


Figure 1A.6

Rutherford famously described the results as being as surprising as if you had **"fired a 15-inch shell at a piece of tissue paper and it came back and hit you."** The strong deflections indicated the presence of something very massive and compact within the atom.

1A.2 Electromagnetic radiation

How are the electrons arranged around the nucleus?

- Scientists used **light** to study this:
- They monitored the properties of light the atoms emit when stimulated by heat or an electric discharge.
- The analysis of emitted or absorbed light is called **spectroscopy**.
- In contrast to **spectrometry**: The measurement and quantification of the results from spectroscopy
- It often involves the use of instruments, like **spectrophotometers** or **mass spectrometers**, to determine the **intensity** of light as a function of wavelength or mass-to-charge ratio.
- Spectrometry focuses more on obtaining numerical results (such as concentrations, masses, or energies) and is often used for practical applications in chemical analysis.

1A.2 Electromagnetic radiation

Spectroscopy vs. spectrometry

Spectroscopy: Comes from **"spectrum"** (Latin for "appearance" or "image") and **"-scopy"** (Greek for "to observe"). It refers to the observation and study of the spectrum of light.

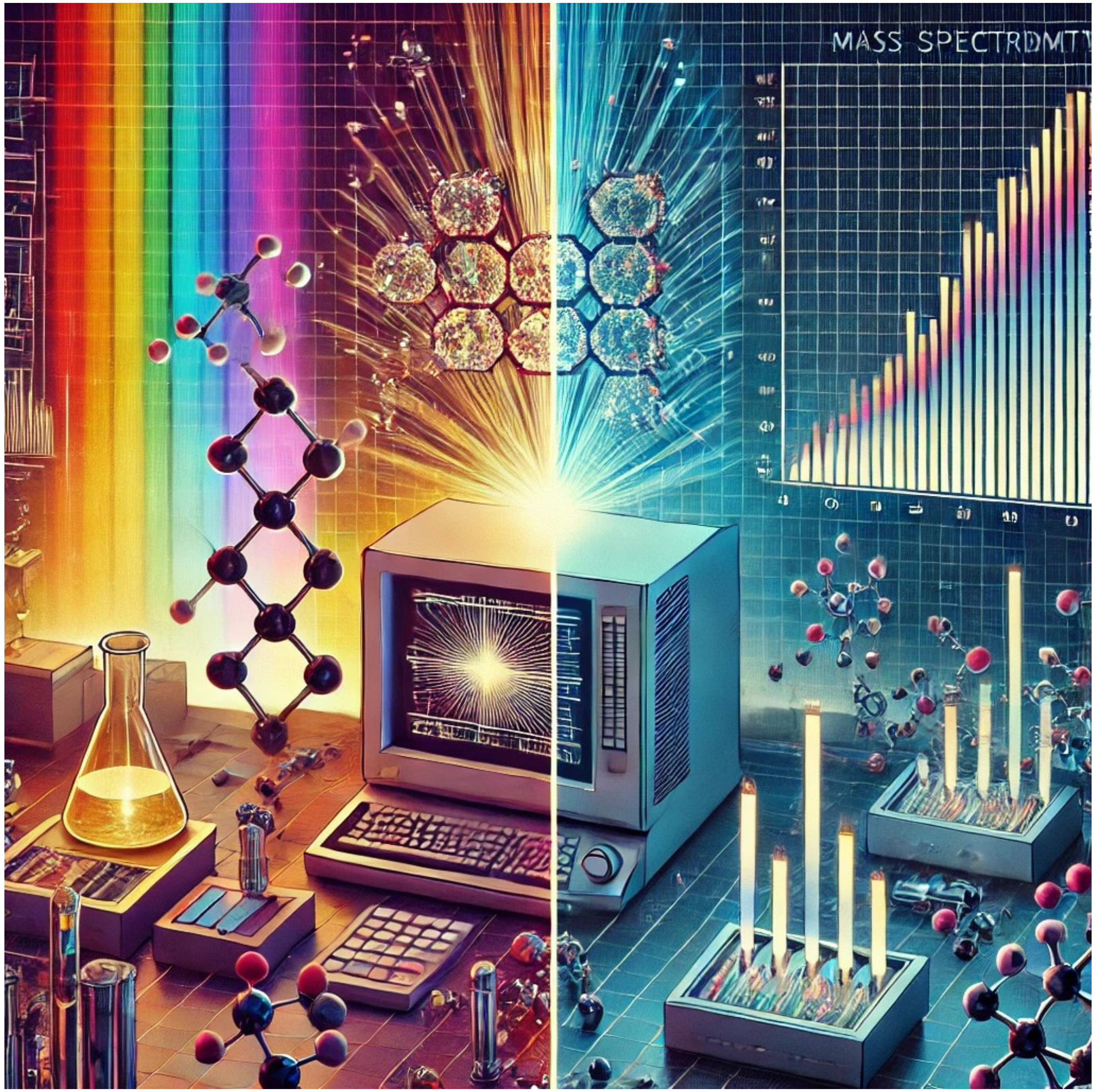
To remember:

Spectroscopy: **S** for "**S**tudying" the light spectrum.

Spectrometry: Comes from **"spectrum"** and **"-metry"** (Greek for "to measure"). It refers to the measurement of properties of light or particles.

To remember:

Spectrometry: **M** for "**M**easuring" the light spectrum.


MASS SPECTRDMT

1A.2 Electromagnetic radiation

Light is a form of electromagnetic radiation

- Light: form of electromagnetic radiation
- Consists of **oscillating** (time-varying) **electric** and **magnetic** fields
- Travel through empty space at about 3×10^8 m s^{-1} (speed of light)
- Visible light, radio waves, microwaves, X-rays
- All forms of radiation **transfer energy** from one region of space to another.

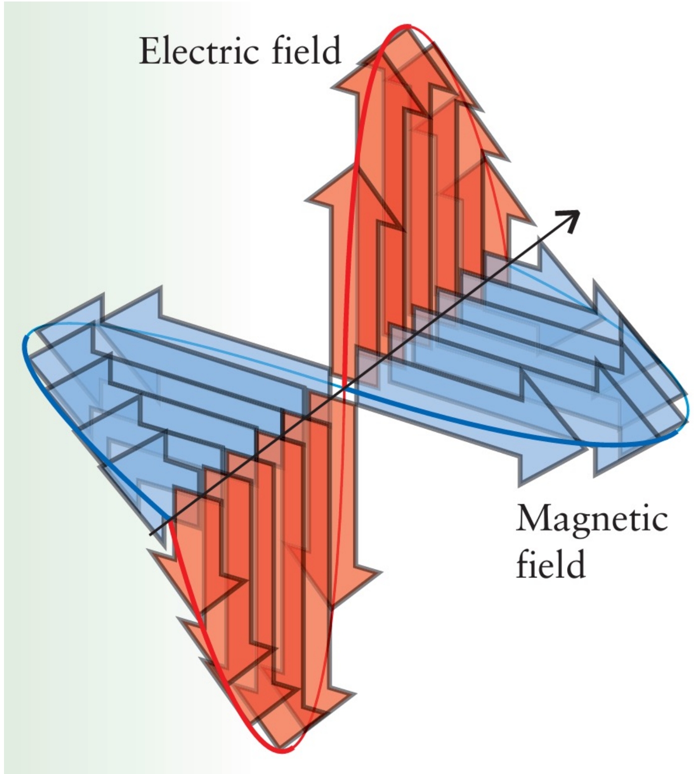
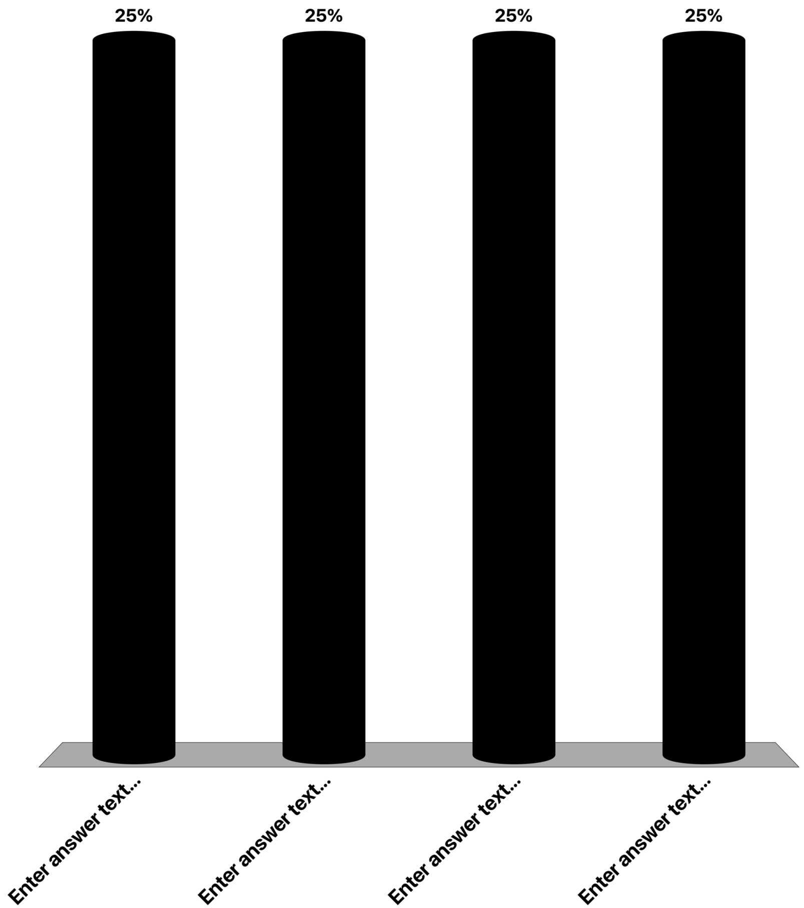


Figure A.8
(Fundamentals A)

Which of these everyday scenarios does NOT PRIMARILY involve electromagnetic radiation?

A. Heating food in a microwave oven.
B. Seeing your reflection in a mirror.
C. Using a Wi-Fi signal to stream a video.
D. Feeling warmth from a campfire.



1A.2 Electromagnetic radiation

Frequency of light

- Ray of light
- Electric field oscillates:

  (1) in direction

  (2) in strength
- Number of cycles per second:

  Frequency, ν (Greek letter nu)
- Unit:

  Hertz (Hz), 1 Hz = 1 s^{-1}

  Frequency of visible light radiation: 10^{15} Hz

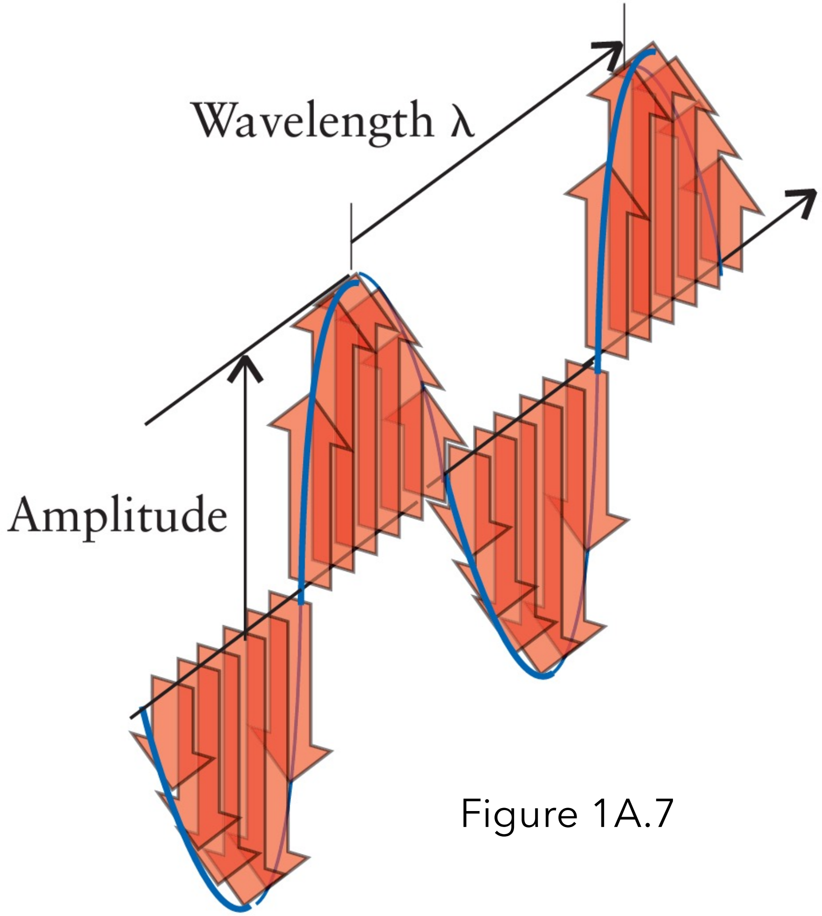


Figure 1A.7

1A.2 Electromagnetic radiation

Amplitude, intensity, and wavelength

- The amplitude is the height of the wave above the center line.
- The square of the amplitude determines the intensity, or brightness, of the radiation.
- The wavelength, λ (the Greek letter lambda), is the peak-to-peak distance.

$$\lambda \ x \ \nu = c$$

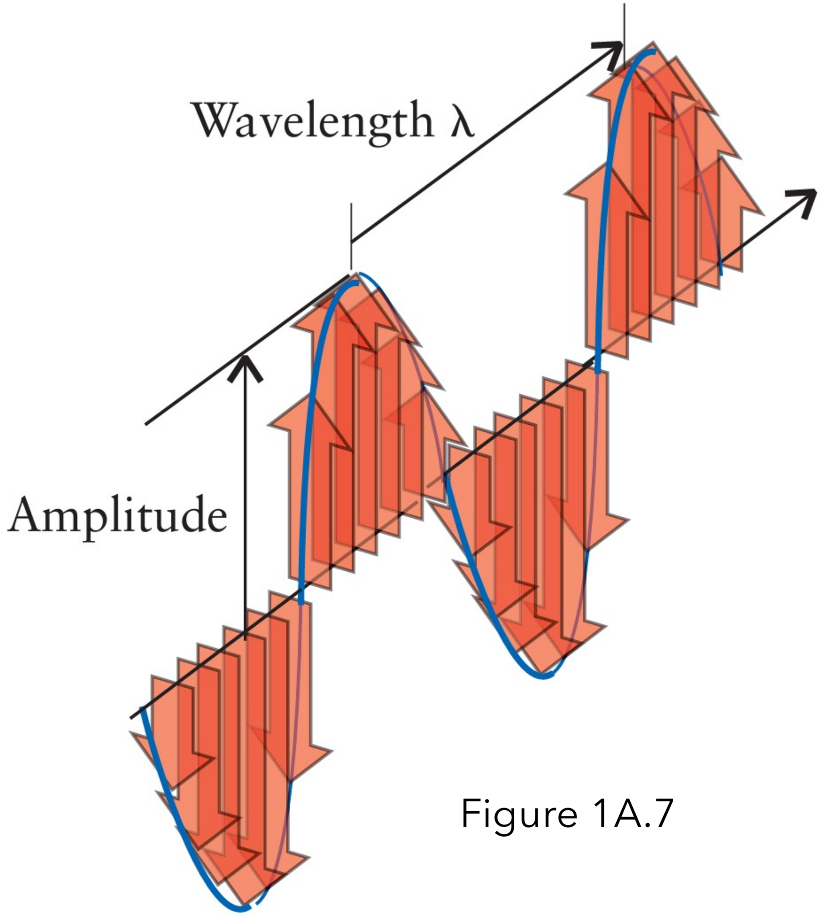


Figure 1A.7

1A.2 Electromagnetic radiation

The wave equation for electromagnetic waves

$$\lambda \times \nu = c$$

- Expresses the relationship between the wavelength (λ), frequency (ν), and the speed of light (c).
- If the wavelength of light is short, many complete oscillations pass a given point in a second, if the wavelength is long, fewer complete oscillations pass the point in a second.

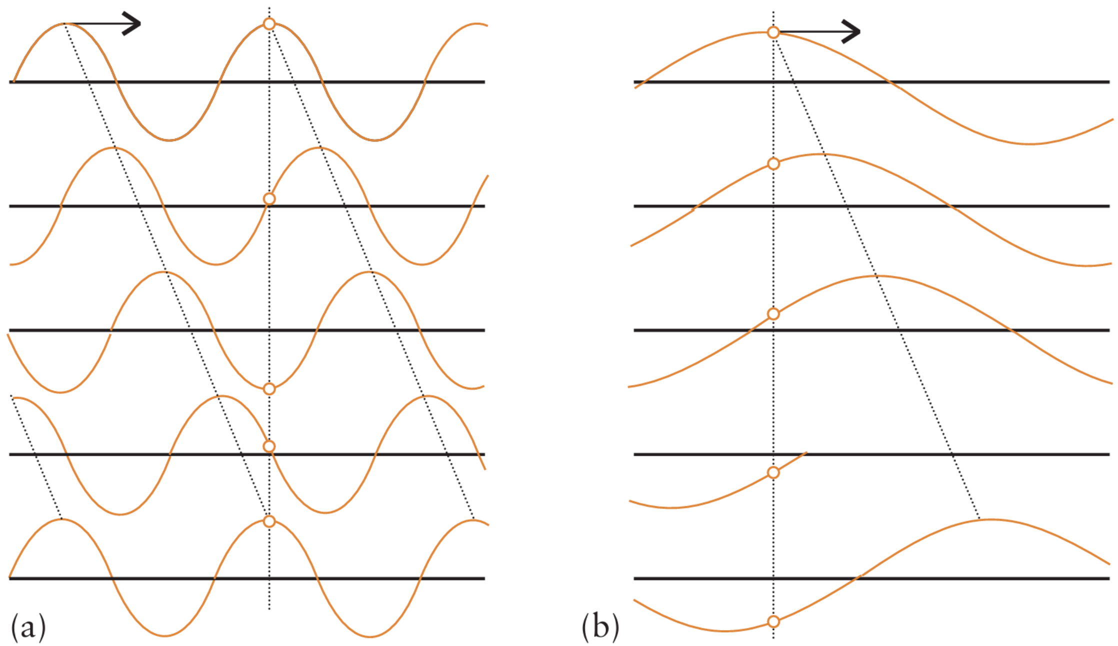


Figure 1A.8

1A.2 Electromagnetic radiation

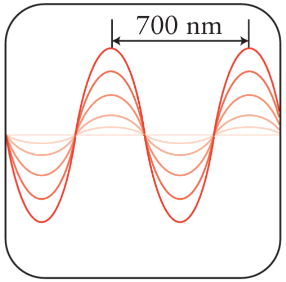
Example 1A.1: **Calculating the wavelength of light of a known frequency**

Identify which color of light has the shorter wavelength: red light of frequency 4.3 x 10^{14} Hz or blue light of frequency 6.4 x 10^{14} Hz.

SOLVE

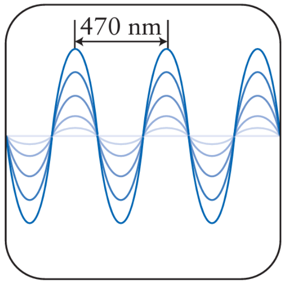
For red light: from $\lambda\nu = c$ written as $\lambda = c/\nu$,

$$\lambda = \frac{\overbrace{2.998 \times 10^{8}\ \mathrm{m \cdot s^{-1}}}^{c}}{4.3 \times 10^{14}\ \underbrace{\mathrm{s^{-1}}}_{\mathrm{Hz}}} = \frac{2.998 \times 10^{8}}{4.3 \times 10^{14}}\ \mathrm{m} = 7.0 \times 10^{-7}\ \mathrm{m}$$



For blue light: from $\lambda\nu = c$ written as $\lambda = c/\nu$,

$$\lambda = \frac{\overbrace{2.998 \times 10^{8}\ \mathrm{m \cdot s^{-1}}}^{c}}{6.4 \times 10^{14}\ \underbrace{\mathrm{s^{-1}}}_{\mathrm{Hz}}} = \frac{2.998 \times 10^{8}}{6.4 \times 10^{14}}\ \mathrm{m} = 4.7 \times 10^{-7}\ \mathrm{m}$$



1A.2 Electromagnetic radiation

The electromagnetic spectrum

TABLE 1.1 Color, Frequency, and Wavelength of Electromagnetic Radiation

Radiation type	Frequency (10^{14} Hz)	Wavelength (nm, 2 sf)*	Energy per photon (10^{-19} J)
x-rays and γ-rays	$\geq 10^3$	≤ 3	$\geq 10^3$
ultraviolet	8.6	350	5.7
visible light			
violet	7.1	420	4.7
blue	6.4	470	4.2
green	5.7	530	3.8
yellow	5.2	580	3.4
orange	4.8	620	3.2
red	4.3	700	2.8
infrared	3.0	1000	2.0
microwaves and radio waves	$\leq 10^{-3}$	$\geq 3 \times 10^6$	$\leq 10^{-3}$

*The abbreviation sf denotes the number of significant figures in the data. The frequencies, wavelengths, and energies are typical values; they should not be regarded as precise.

Visible light: 400-700 nm

White light: mixture of all wavelengths of visible light

Radiation of sun: white light plus shorter and longer wavelength radiation (UV and IR)

Figure 1A.9

1A.2 Electromagnetic radiation

The electromagnetic spectrum

- **Ultraviolet (UV) radiation**: shorter than violet, less than about 400 nm, causes sunburn and tanning, ozone layer protects us from it
- **Infrared (IR) radiation**: longer than red light, greater than about 800 nm, experienced as heat
- **Microwaves**: in the millimeter-to-centimeter range, used in radar and microwave ovens

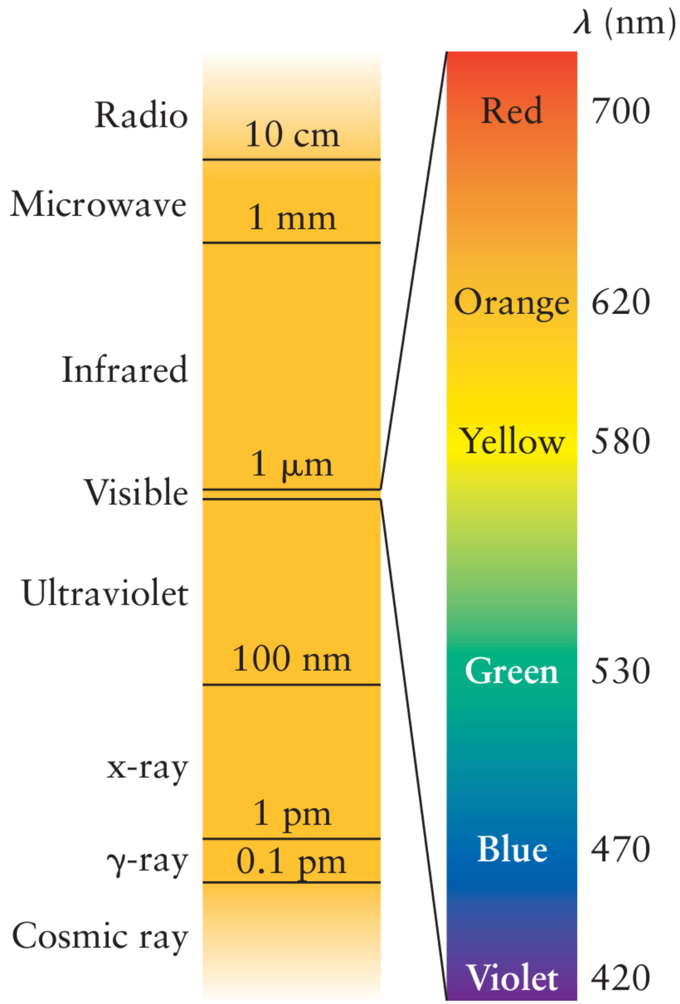
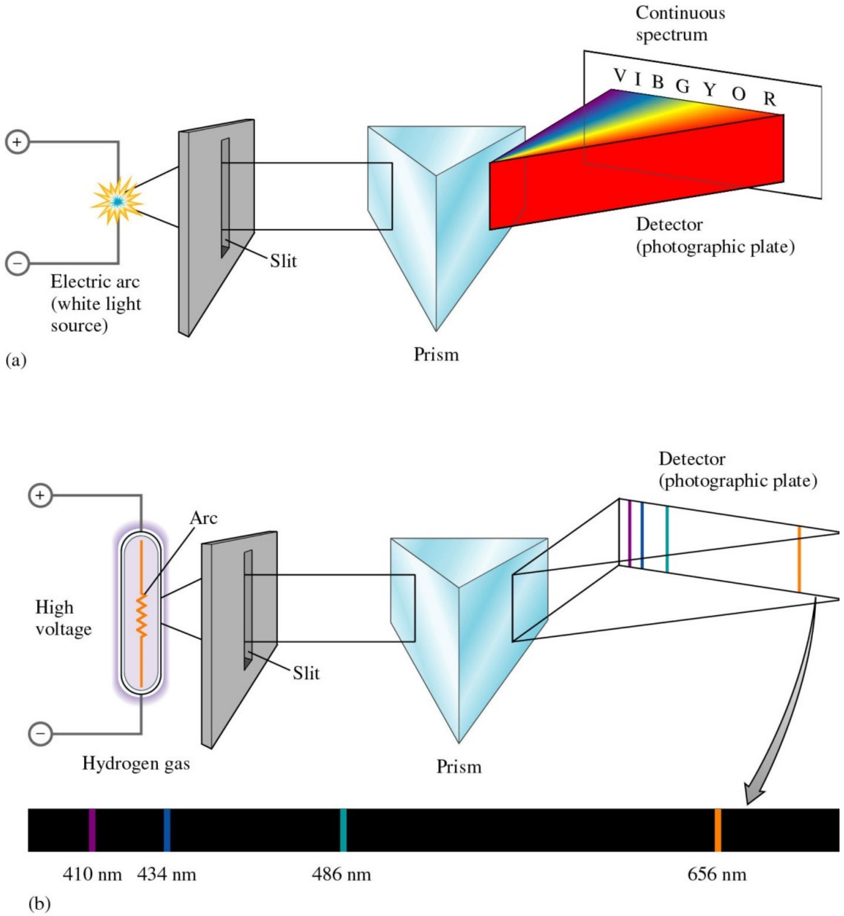


Figure 1A.9

1A.3 Atomic spectra

The atomic spectrum of hydrogen



- When white light is passed through a prism, a continuous spectrum of light results because white light consists of all wavelengths of visible radiation.

- **Hydrogen gas** + **electric current** → sample emits light
- Electric current, which is like a storm of electrons, breaks up the H_2 molecules and **excites the free hydrogen atoms to higher energies**.
- These excited atoms quickly discard their excess energy by giving off **electromagnetic radiation**
- Then they combine to form H2 molecules again.
- **Red glow**
- Red light through a prism results in **spectral lines**
- Most prominent at 656 nm (red).
- Excited hydrogen atoms also emit in IR and UV.

1A.3 Atomic spectra

The atomic spectrum of hydrogen

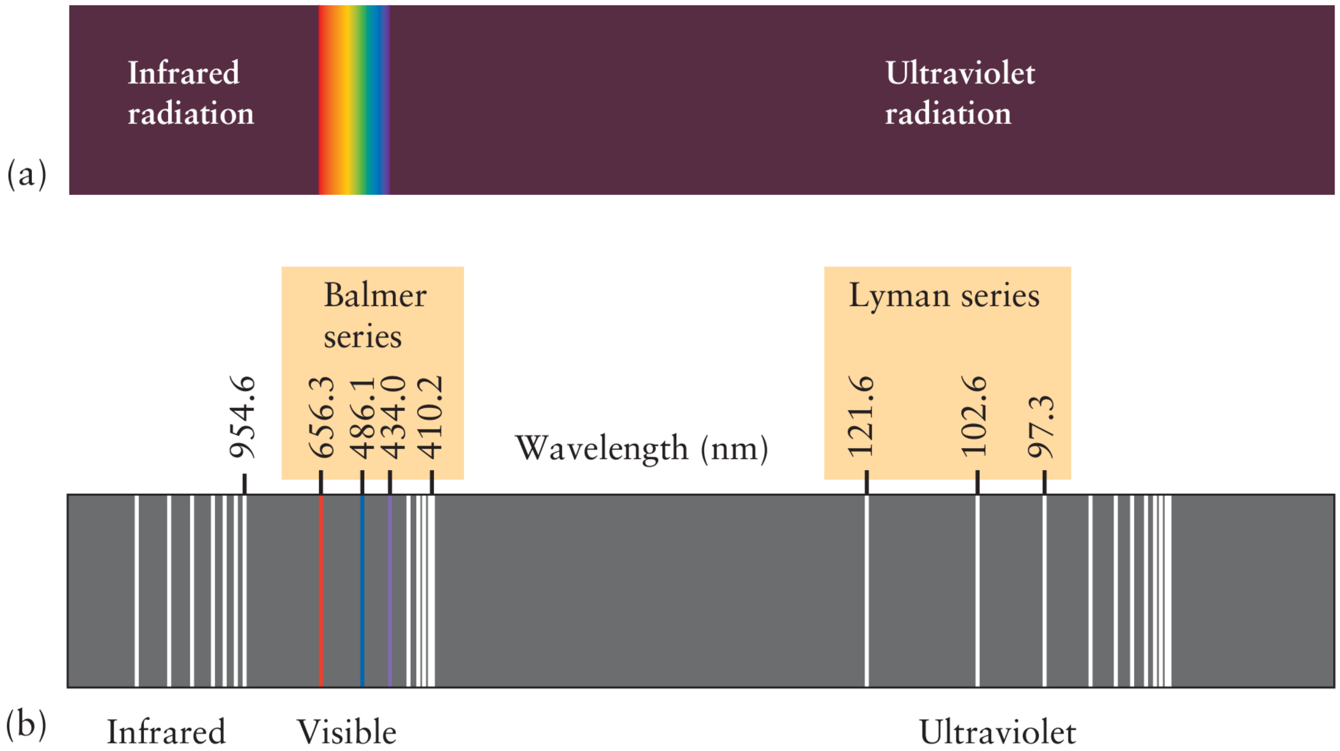


Figure 1A.10

(a) The infrared, visible, and ultraviolet spectrum.

(b) The complete **emission spectrum** of **atomic hydrogen**. The spectral lines have been assigned to various groups called series, two of which are shown with their names.

1A.3 Atomic spectra

The Rydberg formula

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \; n_1 = 1,2,\dots, n_2 = n_1 + 1, n_1 + 2, \dots$$

With *R* is e empirical (experimentally determined) Rydberg constant; its value is 3.29 1015 Hz.

The Rydberg formula describes the wavelengths of the spectral lines in the **Balmer**, **Paschen**, and **Lyman series** for hydrogen.

The **Paschen** series is a set of lines in the **infrared** region with n_1 = 3 (and n_2 = 4, 5, . . .)
The **Balmer** series is the set of lines in the **visible** region with n_1 = 2 (and n_2 = 3, 4, . . .)
The **Lyman** series, a set of lines in the **ultraviolet** region of the spectrum, has n_1 = 1 (and n_2 = 2, 3, . . .).

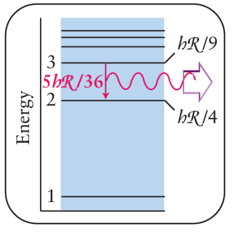
Example A1.2: **Identifying a line in the hydrogen spectrum**

Calculate the wavelength of the radiation emitted by a hydrogen atom for $n_1 = 2$ and $n_2 = 3$. Identify the spectral line in Fig. 1.10b.

SOLVE

From Eq. 2 with $n_1 = 2$ and $n_2 = 3$,

$$\nu = \mathcal{R}\left\{\frac{1}{2^2} - \frac{1}{3^2}\right\} = \frac{5}{36}\mathcal{R}$$

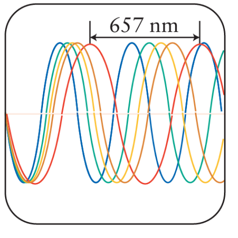


From $\lambda\nu = c$,

$$\lambda = \frac{c}{\nu} = \frac{c}{(5\mathcal{R}/36)} = \frac{36c}{5\mathcal{R}}$$

Now substitute the data:

$$\lambda = \frac{36 \times \overbrace{(2.998 \times 10^8\ \text{m}\cdot\text{s}^{-1})}^{c}}{5 \times \underbrace{(3.29 \times 10^{15}\ \text{s}^{-1})}_{\mathcal{R}}} = 6.57 \times 10^{-7}\ \text{m}$$

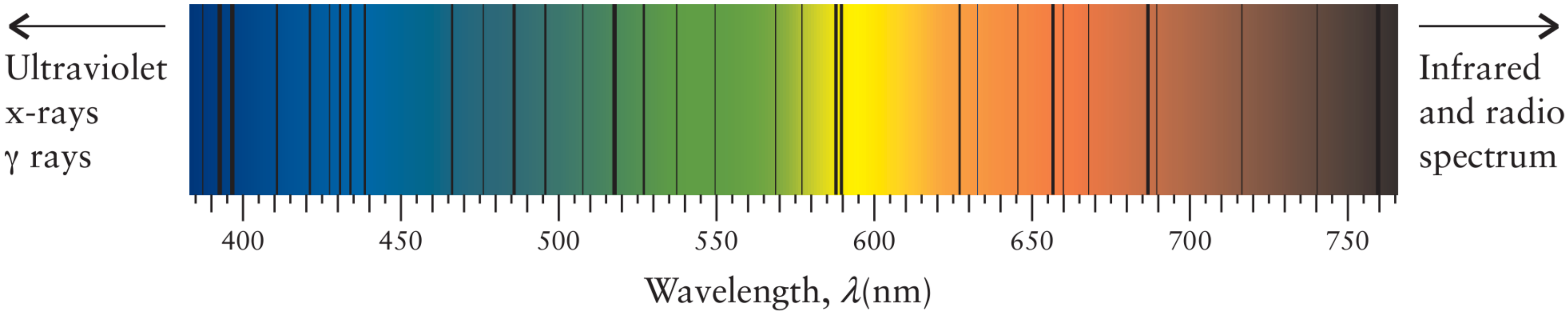


This wavelength, 657 nm, corresponds to the red line in the Balmer series of lines in the spectrum.

1A.3 Atomic spectra

Absorption spectrum

Figure 1A.10



White light passed through a **vapor** composed of the **atoms of an element**
→ absorption spectrum: a series of dark lines on an otherwise continuous spectrum (Fig. 1.11).

- The absorption and emission lines have the same frequencies
- Suggests an atom can absorb and emitt radiation at same frequencies
- Absorption spectra are used by astronomers to identify elements in the outer layers of stars

1A.3 Atomic spectra

So what are these lines??

- Electron in hydrogen atom can only exist with certain energies
- A line in the spectrum arises from a transition between two of the allowed energies
- Hydrogen atom's electron has discrete energy levels
- The difference in energy is emitted as electromagnetic radiation

The observation of discrete spectral lines suggests that an electron in an atom can have only certain energies.

The skills you have mastered are the ability to

- Describe the experiments that led to the formulation of the nuclear model of the atom
- Calculate the wavelength or frequency of light from the relation $\lambda\nu = c$ (example 1A.1)
- Calculate the wavelength of a transition in a hydrogen atom from the Rydberg formula (example 1A.2)

Summary: Scattering experiments show that an atom of element with atomic number Z consists of a tiny but massive nucleus surrounded by Z electrons. Electromagnetic radiation is a wave of characteristic frequency and wavelength that travels through space at speed c. Atomic spectroscopy is the analysis of the light emitted or absorbed by atoms. The observation of spectral lines strongly suggests that electrons in atoms can have only certain energies.