25. When a photon of frequency $1.0 \times 10^{15} s^{-1}$ was allowed to hit a metal surface, an electron having 1.988×10^{-19} J of kinetic energy was emitted. Calculate the threshold frequency of the metal. Show that an electron will not be emitted if a photon of wavelength 600 nm hits the metal surface.
(NCERT Exemplar Problem)

26. Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800Å. Calculate threshold frequency (v_0) and work function (w_0) of the metal.

27. The longest wavelength doublet absorption transition is observed at 589 and 589.6 nm. Calculate the frequency of each transition and energy difference between two excited states.
N.C.E.R.T.

Answers to Practice Problems

- 18. (i) 3.98×10^{-15} J (ii) 1.98×10^{-18} J
- 19. 7.96×10^{-21} J
- 20. 1.89×10^{-12} J
- 21. 2.01×10^{18} photons
- 22. 1.04×10^{14} sec^{-1}
- 23. 121 photons.
- 24. 1.99×10^{-19} J
- 25. $v_0 = 6.988 \times 10^{14} s^{-1}$. No, because the frequency of the photon of striking radiation is less than v_0
- 26. $4.41 \times 10^{14} s^{-1}$, 2.92×10^{-19} J
- 27. 3.44×10^{-22} J

Hints & Solutions on page 216

ATOMIC SPECTRA

When a beam of light from sun is passed through a prism, it splits into a series of colour bands known as *rainbow of colours* : violet, indigo, blue, green, yellow, orange and red (remembered as VIBGYOR). A similar spectrum is produced when a rainbow forms in the sky. This means that sunlight is composed of collection of electromagnetic waves having different wavelengths. The prism bends the light of different wavelengths to different extents. The red colour with the longest wavelength is deviated the least while the violet colour with the shortest wavelength is deviated the most. The splitting of light into series of colour bands is known as *dispersion* and *the series of colour bands* is called a **spectrum.** In this spectrum, there is continuity of colours *i.e.*, one colour merges into the other without any gap or discontinuity and such a spectrum is known as **continuous spectrum.** For example, violet merges into indigo, indigo merges into blue, blue merges into green and so on. The continuous spectrum can also be obtained from the light emitted from some incandescent substances.

Atomic Spectra

Unlike the spectrum obtained by analysing the sunlight, the spectra of atoms are not continuous. The spectra of atoms consist of sharp well-defined lines or bands corresponding to definite frequencies. There are two types of atomic spectra :

(i) *Emission spectra*

(ii) *Absorption spectra.*

(i) Emission spectra.

Emission spectra are obtained when the radiations emitted from substances that have absorbed energy (either by passing electric discharge through a gas at low pressure or by heating the substance to high temperature) are analysed with the help of spectroscope. Atoms, molecules or ions that have absorbed radiations are said to be excited. For example, when the gases or vapour of chemical substances are heated by electric spark, light is emitted. The colour of the light depends upon the substance under investigation. For example, sodium or salt of sodium gives off yellow light while potassium or salt of potassium produces a violet colour. When the radiations emitted by different substances are analysed, the spectrum obtained consists of sharp well-defined lines each corresponding to a definite frequency (or wavelength).

The emission spectrum obtained by analysing the radiation emitted by passing electric discharge through hydrogen gas at low pressure is shown in Fig. 22.

Such a spectrum consisting of lines of definite frequencies is called **line spectrum** or **discontinuous spectrum.**

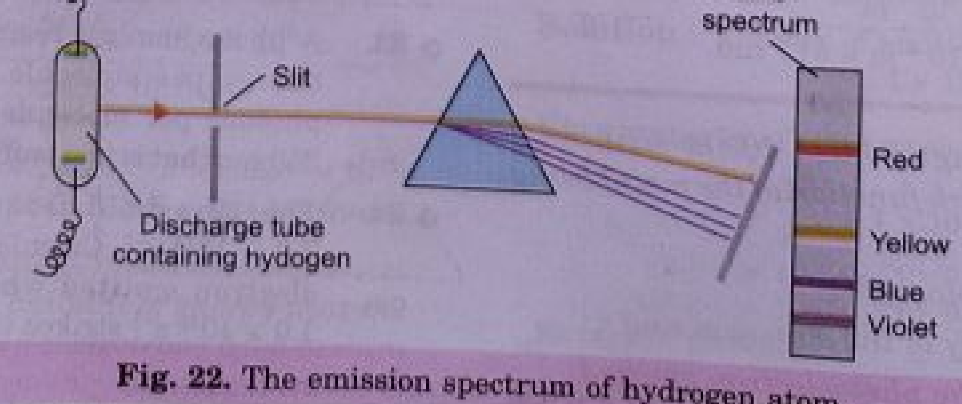

Fig. 22. The emission spectrum of hydrogen atom.

The line spectrum is also known as **atomic spectrum** because it is obtained by analysing the emitted radiations from atoms by the application of heat or any other form of energy. The pattern of lines in the spectrum of an element is characteristic of that element, and is different from those of all other elements. In other words, *each element gives a unique spectrum irrespective of even the form in which it is present.* For example, we always get two important lines at 589 nm and 589.6 nm in the spectrum of sodium whatever may be its source. It is for this reason that *the line spectra are also regarded as the* **finger prints of atoms.**

Since atoms of different elements give characteristic set of lines of definite frequencies, emission spectra can be used in chemical analysis to identify and estimate the elements present in a sample. The elements rubidium and cesium were discovered by spectral studies.

(*ii*) Absorption spectra

When a continuous electromagnetic radiation (say white light) is allowed to pass through a gas or a solution of some salt and the transmitted light is analysed, we obtain a spectrum in which dark lines are observed in an otherwise continuous spectrum. These dark lines indicate that the radiations of corresponding wavelengths have been absorbed by the substance from the white light (Fig. 23). *Such a spectrum containing a few dark lines due to absorption of light* is known as **absorption spectrum.**

The dark lines of definite wavelengths are also characteristic of the substance. It may be noted that these dark lines appear exactly at the same place where the lines in the emission spectrum appear. For example, the emission spectrum of sodium consists of two important yellow lines at 589 and 589.6 nm. On the other hand, when white light is passed through vapour of sodium, we get dark lines in the absorption spectrum at 589 and 589.6 nm.

The study of emission or absorption spectra is called **spectroscopy**. This has become very important and essential field for all chemists. It helps to study the electronic structure. The characteristic lines in atomic spectrum can be used in chemical analysis to identify elements.

Differences between Emission and Absorption Spectra

The essential differences between emission and absorption spectra are given below :

Emission spectrum	Absorption spectrum
1. Emission spectrum is obtained when radiations emitted by the excited substance are analysed with a spectroscope.	1. Absorption spectrum is obtained when the white light is first passed through the substance (in gaseous state or in solution) and the transmitted light is analysed with a spectroscope.
2. Emission spectrum consists of bright coloured lines separated by dark spaces.	2. Absorption spectrum consists of dark lines in an otherwise continuous spectrum.

Emission Spectrum of Hydrogen Atom

The spectrum of hydrogen atom has played a very important role in the development of atomic structure. The spectrum of hydrogen atom can be obtained by passing an electric discharge through the gas taken in the discharge tube under low pressure. The emitted light is analysed with the help of **spectroscope.** The spectrum consists of a large number of lines appearing in different regions of wavelengths. Some of the lines are present in the visible region while others in ultra-violet and infra-red regions.

In 1885, J.J. Balmer developed a simple relationship among the different wavelengths of the series of visible lines in the hydrogen spectrum. The relationship is :

$$\frac{1}{\lambda} = \bar{\nu}\ (\text{cm}^{-1}) = 109677\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

n is an integer equal to or greater than 3 (*i.e.*, $n = 3, 4, 5$ ...). It is known as **Balmer formula.**

The Balmer formula gives only the spectral lines in the visible region. These series of lines which appear in visible region were named *Balmer series.*

Soon afterwards, a series of spectral lines of hydrogen atom in different regions were discovered. These lines in different regions were grouped into five different series of lines, each being named after the name of its discoverer. These are *Lyman series, Balmer*

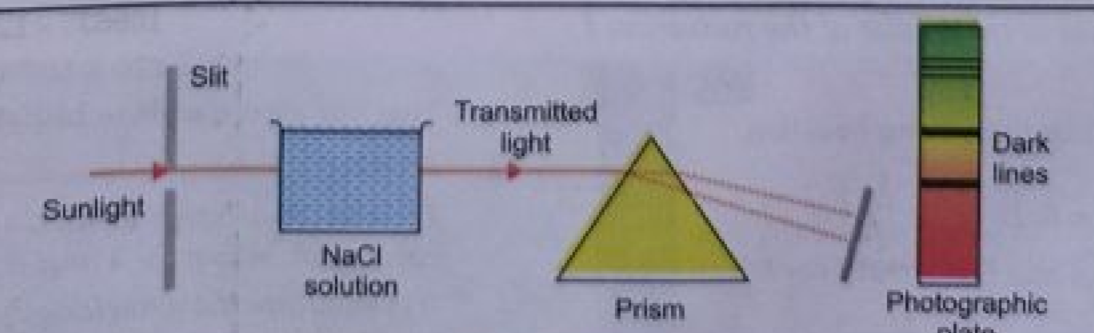

Fig. 23. Absorption spectrum of sodium chloride.

series, *Paschen series*, *Brackett series* and *Pfund series*. Lyman series appears in the ultra-violet region. Balmer series appears in visible region while the other three series lie in the infra-red region.

Rydberg Equation

As the other series of hydrogen spectral lines were discovered, a more general expression was found as :

$$\frac{1}{\lambda} = \bar{\nu} \text{ (in cm}^{-1}) = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where n_1 and n_2 are integers, such that $n_2 > n_1$. R is a constant, now called the **Rydberg constant.** The value of R is **109677 cm^{-1}.** The expression is found to be valid for all the lines in the hydrogen spectrum and is also known as **Rydberg equation.**

Limiting line. The limiting line of any spectral series in the hydrogen spectrum is the line when n_2 in the Rydberg equation is infinity *i.e.*, $n_2 = \infty$. This line will have the *shortest wavelength and largest wave number.*

The complete spectrum of hydrogen atom is shown in Fig. 24.

For a given spectral series, n_1 remains constant while n_2 varies as $n_1 + 1, n_1 + 2, n_1 + 3$ .... from line to line in the same series. For example, for Lyman series $n_1 = 1$ and $n_2 = 2, 3, 4, 5$ ... and for Balmer series $n_1 = 2$ and $n_2 = 3, 4, 5$ ... All the five series, the regions in which lines appear and the values of n_1 and n_2 are given in Table 2.

Table 2. Different spectral lines in the spectrum of hydrogen atom.

Series	Region	n_1	n_2
Lyman	Ultra-violet	1	2, 3, 4, 5...
Balmer	Visible	2	3, 4, 5, 6 ...
Paschen	Infra-red	3	4, 5, 6, 7 ...
Brackett	Infra-red	4	5, 6, 7, 8 ...
Pfund	Infra-red	5	6, 7, 8, 9 ...

It may be noted that the above equation is true only for the spectral lines of hydrogen atom or hydrogen like ions. Hydrogen like ions are those which contain only one electron. For example, He^+, Li^{2+}, etc. The **Rydberg equation** for hydrogen like ions may be expressed as :

$$\frac{1}{\lambda} = \bar{\nu} \text{ (cm}^{-1}) = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)Z^2$$

where Z is the nuclear charge, which is equal to atomic number and R is Rydberg constant. For example, for He^+, Z = 2, for Li^{2+}, Z = 3 and so on.

The spectra of other atoms are complex, consisting of very large number of lines whose wavelengths cannot be related by a simple relation as the Rydberg equation.

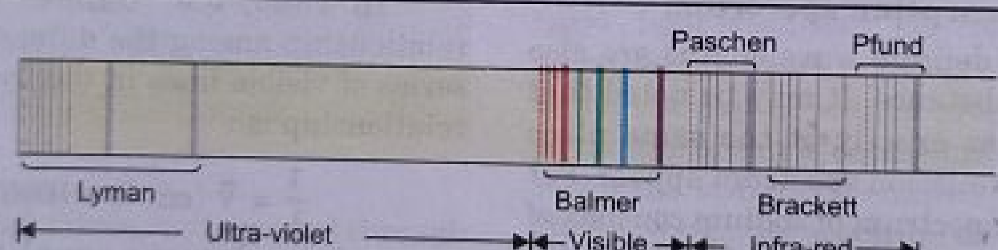

Fig. 24. Spectrum of hydrogen atom.

SOLVED EXAMPLES

Example 27.

What is the wavelength of light emitted when the electron in hydrogen atom undergoes transition from an energy level with n = 4 to an energy level with n = 2 ? What is the colour of the radiation ?

N.C.E.R.T.

Solution: According to Rydberg equation,

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

Here $n_1 = 2$, $n_2 = 4$ and R = 109677 cm^{-1}

$$\frac{1}{\lambda} = 109677\left(\frac{1}{2^2} - \frac{1}{4^2}\right) \text{ cm}^{-1}$$

$$= 109677\left(\frac{1}{4} - \frac{1}{16}\right) \text{ cm}^{-1}$$

$$= 109677 \times \frac{12}{64} \text{ cm}^{-1}$$

or $$\lambda = \frac{64}{109677 \times 12} \text{ cm} = 4.86 \times 10^{-5} \text{ cm}$$

or $$\lambda = 486 \times 10^{-9} \text{ m} = \mathbf{486\ nm}$$

This line corresponds to **bluish green colour.**

Example 28.

In the Rydberg equation, a spectral line corresponds to $n_1 = 3$ and $n_2 = 5$.

(i) Calculate the wavelength and frequency of this spectral line.

(ii) To which spectral series does this line belong?

(iii) In which region of the electromagnetic spectrum, will this line fall ?

Solution: (*i*) According to Rydberg equation,

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

where $R = 109677 \text{ cm}^{-1}$, $n_1 = 3$ and $n_2 = 5$

Substituting the values,

$$\frac{1}{\lambda} = 109677\left(\frac{1}{3^2} - \frac{1}{5^2}\right) \text{cm}^{-1}$$

$$= 109677\left(\frac{1}{9} - \frac{1}{25}\right) \text{cm}^{-1}$$

or $$= 109677 \times \frac{16}{225} \text{ cm}^{-1}$$

$\therefore$ $$\lambda = \frac{225}{109677 \times 16} \text{ cm}$$

$$= 12.82 \times 10^{-5} \text{ cm} = 1282 \times 10^{-9} \text{ m}$$

or $$\lambda = \mathbf{1282 \text{ nm}}$$

Now $\lambda \times \nu = c$ or $\nu = \frac{c}{\lambda}$

where $c = 3.0 \times 10^8 \text{ m s}^{-1}$, $\lambda = 1282 \text{ nm} = 1282 \times 10^{-9} \text{ m}$

$$\nu = \frac{3.0 \times 10^8 \text{m s}^{-1}}{1282 \times 10^{-9} \text{m}} = \frac{3}{1282} \times 10^{17} \text{ s}^{-1}$$

$$= \mathbf{2.34 \times 10^{14} \text{ s}^{-1}}$$

(*ii*) Since this line corresponds to $n_2 = 3$, it belongs to **Paschen series.**

(*iii*) The spectral line will fall in **infra-red region.**

Example 29.

Emission transitions in the Paschen series end at orbit n = 3 and start form an orbit n and can be represented as

$$\nu = 3.29 \times 10^{15} (Hz) \left(\frac{1}{3^2} - \frac{1}{n^2}\right)$$

Calculate the value of n if the transition is obtained at 1285 nm. Find the region of spectrum.

N.C.E.R.T.

Solution: $\nu = 3.29 \times 10^{15} \left(\frac{1}{3^2} - \frac{1}{n^2}\right) \text{ s}^{-1}$

$\lambda = 1285$ nm

$\therefore$ $$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ms}^{-1}}{1285 \times 10^{-9} \text{m}}$$

$$= 2.33 \times 10^{14} \text{ s}^{-1}$$

$$2.33 \times 10^{14} = 3.29 \times 10^{15}\left(\frac{1}{9} - \frac{1}{n^2}\right)$$

or $$\frac{1}{9} - \frac{1}{n^2} = \frac{2.33 \times 10^{14}}{3.29 \times 10^{15}} = 0.0708$$

$$-\frac{1}{n^2} = 0.0708 - \frac{1}{9} = -0.0403$$

$$\frac{1}{n^2} = 0.0403$$

or $$n^2 = 24.82$$

$\therefore$ $$n = 5$$

Transition is obtained in infrared region.

Example 30.

What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition, n = 4 to n = 2 of He^+ spectrum ?

N.C.E.R.T.

Solution: For He^+ spectrum,

$$\frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Now, $n_1 = 2$, $n_2 = 4$ and $Z = 2$

$$\frac{1}{\lambda} = R \times (2)^2\left[\frac{1}{2^2} - \frac{1}{4^2}\right] = \frac{3}{4}R \quad ...(i)$$

For H atom $$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad ...(ii)$$

Since λ is the same, equating equations (*i*) and (*ii*)

$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

Now, if $n_1 = 1$ and $n_2 = 2$.

Therefore, the transition from $n = 2$ to $n = 1$ in H atom will have the same wavelength as the transition from $n = 4$ to $n = 2$ in He^+.

Example 31.

Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen.

Solution: For Balmer series

$$\bar{\nu} = 109677\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

For shortest wavelength, energy should be largest, and therefore, $n_2 = \infty$ and $n_1 = 2$ for Balmer series

$$\therefore \quad \bar{\nu} = 109677\left(\frac{1}{2^2}-\frac{1}{\infty^2}\right)$$

$$= \frac{109677}{4}$$

$$= \mathbf{27419.25\ cm^{-1}}$$

Practice Problems

28. The first line in Balmer series corresponds to $n_1 = 2$ and $n_2 = 3$ and the limiting line corresponds to $n_1 = 2$ and $n_2 = \infty$. Calculate the wavelengths of the first and limiting lines in Balmer series.

29. Calculate the wavelength of spectral line in Lyman series corresponding to $n_2 = 3$.

30. Calculate the wavelength and energy of radiation emitted for the electronic transition from infinity (∞) to the stationary state of the hydrogen atom.

31. Calculate the wave number for the longest wavelength transition in the Balmer series of atomic hydrogen. **N.C.E.R.T.**

32. What is the maximum number of emission lines when the excited electron of a H atom in n = 6 drops to the ground state ? **N.C.E.R.T.**

33. What are the frequency and wavelength of a photon emitted during a transition from the $n = 5$ state to $n = 2$ state in the hydrogen atom ? **N.C.E.R.T.**

Answers to Practice Problems

28. First line = 656 nm, limiting line = 364.7 nm.
29. For Lyman series $n_1 = 1$; $\lambda = 102.6$ nm.
30. $\lambda = 9.11 \times 10^{-8}$ m, E = 2.18×10^{-18} J
31. $1.523 \times 10^{6} m^{-1}$
32. 15 lines
33. $6.91 \times 10^{14}\ s^{-1}$ and 434 nm.

Hints & Solutions on page 216

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