Comparison of Hydrogen (H) and Helium (He) Spectra

We know that for hydrogen atom the expression of wavelength is given as.

$$\frac{1}{\lambda} = R_m Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right),$$ where R_m is Rydberg Constant

for Hydrogen atom $Z = 1$,

$$\frac{1}{\lambda} = \bar{\nu} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad \text{——— (1)}$$

for Helium (He^+) $Z = 2$.

$$\frac{1}{\lambda} = \bar{\nu} = R_{He}\, 4 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\boxed{\frac{1}{\lambda} = \bar{\nu} = 4 R_{He^+} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)} \quad \text{——— (2)}$$

$n_f = 4$, $n_i = 5, 6, 7$ ---- Pickering series (near ultraviolet and visible)

$n_f = 3$, $n_i = 4, 5, 6$ ---- Fowler series (ultraviolet and visible)

$n_f = 2$, $n_i = 3, 4, 5$ ---- Lyman series

A comparison of the Balmer series for R_H with the Pickering series formula for R_{He^+}

$$\frac{1}{\lambda} = \nu = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \quad n_i = 3, 4, 5 \ldots$$

and $$\frac{1}{\lambda} = \nu = 4R_{He^+}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \quad n_i = 5, 6, 7 \ldots$$

For H- atom

$$\frac{1}{\lambda} = R_H\left(\frac{1}{4} - \frac{1}{9}\right), \quad n_i = 3$$

$$\frac{1}{\lambda} = R_H\left(\frac{5}{36}\right)$$

$$\boxed{\frac{1}{\lambda} = \frac{5}{36}R_H}$$

For He^+

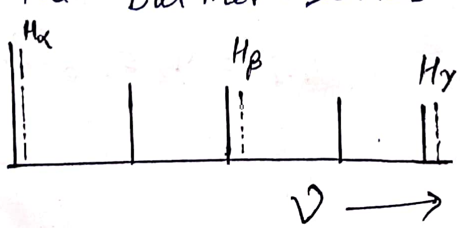
$$\frac{1}{\lambda} = 4R_{He^+}\left(\frac{1}{16} - \frac{1}{36}\right), \quad n_i = 6$$

$$\frac{1}{\lambda} = 4R_{He^+}\left(\frac{36-16}{16 \times 36}\right)$$

$$\frac{1}{\lambda} = \cancel{4}R_{He^+}\frac{\cancel{20}\,5}{\cancel{16}_4 \times 36}$$

$$\boxed{\frac{1}{\lambda} = \frac{5}{36}R_{He^+}}$$

Comparison shows that alternate member of the Pickering series $n_i = 6, 8, 10, \ldots$ must coincide with members $n_i = 3, 4, 5$ of the Balmer series Provided $R_H = R_{He^+}$



A careful examination shows that Balmer lines of H-atom are not exactly coincident with alternate lines of the Pickering series of He^+.

The small displacement between these lines is due to the difference in R_H and R_{He^+} which arises due to finite mass of the nucleus.

It is found that the series limits λ_{min} of Balmer and pickering series differ by 11 cm^{-1}

Now for H.

$$(\nu_{max})_H = \frac{R_H}{2^2} \quad (n_i = \infty) \text{ Balmer series}$$

For He^+

$$(\nu_{max})_{He^+} = \frac{4 R_{He^+}}{4^2} \quad (n_i = \infty) \text{ Pickering series}$$

$$R_H = 4 \nu_{max}$$

$$R_{He^+} = 4 \nu_{max}$$

$$R_{He^+} - R_H = 4 [(\nu_{max})_{He^+} - (\nu_{max})_H]$$

$$(\nu_{max})_{He^+} - (\nu_{max})_H = 11 \ cm^{-1}.$$

$$R_{He^+} - R_H = 4 \times 11. \ cm^{-1}$$

$$\boxed{R_{He^+} - R_H = 44 \ cm^{-1}}$$