

- Moseley discovered experimentally in 1913 that the atomic number, Z , of an element is inversely proportional to the square root of the wavelength, λ , of fluorescent X-rays emitted when an electron drops from the $n = 2$ to the $n = 1$ shell.

$$i.e. \quad \frac{1}{\sqrt{\lambda}} = kZ$$

Derive an expression for the constant of proportionality, k , for a hydrogen-like atom which would allow the value of k to be theoretically calculated.

The energy of an X-ray with wavelength λ is given by $E = \frac{hc}{\lambda}$ where h is

Planck's constant and c is the speed of light. Using this and as $\frac{1}{\sqrt{\lambda}} = kZ$

$$\frac{1}{\lambda} = (kZ)^2$$

$$E = hc(kZ)^2 \quad (1)$$

For a hydrogen like atom, an electron in an orbital with quantum number n has energy $E = -Z^2 E_R \left(\frac{1}{n^2} \right)$ where E_R is the Rydberg constant. The energy emitted when an electron moves from an orbital with quantum number n_i to an orbital with quantum number n_f is:

$$E = E_{n_i} - E_{n_f} = [-Z^2 E_R \left(\frac{1}{n_i^2} \right)] - [-Z^2 E_R \left(\frac{1}{n_f^2} \right)] = Z^2 E_R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (2)$$

Equating (1) and (2) gives:

$$hc(kZ)^2 = Z^2 E_R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Rearranging for k gives:

$$k^2 = \frac{Z^2 E_R}{hcZ^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = \frac{E_R}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$k = \sqrt{\frac{E_R}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)}$$

For the case where $n_i = 2$ and $n_f = 1$, this becomes

$$k = \sqrt{\frac{E_R}{hc} \left(\frac{1}{1^2} - \frac{1}{2^2} \right)} = \sqrt{\frac{3E_R}{4hc}}$$