Width of spectral line:-

The instruments used in spectroscopic measurements influence the sharpness of spectrum lines due to their limited resolving power. No spectral lines are strictly sharp, but has a finite width, no matter how great the R.P. of the instrument is. A line appears densest at the centre & fades out on the edges.

$\Delta\lambda$ of a line is the distance between two points are on each side of the centre of the line. This is called half intensity width.

The causes of the line broadening are :-

(i) The Natural width
(ii) Doppler width
(iii) Width of line due to external effects.

(1) The natural width :- According to e.m. theory of vibrating el. charge radiates energy and so it is continually damped. Its energy (E) and amplitude (A) are given by

$$E = E_0 e^{-bt} \quad \text{——— (1)}$$

$$A = A_0 e^{-\frac{1}{2}bt} \quad \text{——— (2)}$$

E_0 and A_0 are the values of energy and amplitude at $t=0$. b is a constant given by.

$$b = \frac{8\pi^2 e^2 V_0^2}{3m_0 c^3} \quad \text{——— (3)}$$

The intensity of radiant energy on the basis of Fourier analysis of damped wave trains is given by

$$I(\nu) = \frac{b}{2\pi} \cdot \frac{1}{4\pi^2(\nu_0-\nu)^2 + (b/2)^2} \quad \text{——} (4)$$

This eqn suggests that $I(\nu)$ drops to half its max^{m} value when,

$$4\pi^2(\nu_0-\nu)^2 = (b/2)^2$$

or, $2\pi(\nu_0-\nu) = b/2$

or, $\nu_0 - \nu = \frac{b}{4\pi}$ —— (5)

Hence natural half intensity width is

$$2(\nu_0-\nu) = \frac{b}{2\pi} = \frac{4\pi^2 e^2 \nu_0^2}{2 m_0 c^3} \quad \text{——} (6)$$

And in terms of wave-length,

$$\Delta\lambda = \frac{4\pi e^2}{3 m_0 c^2} = 1.16 \times 10^{-12} \text{ cm.} \quad \text{——} (7)$$

$$\simeq 0.116 \times 10^{-3} A^0$$

$$\simeq \frac{\lambda^2}{c}\Delta\nu \simeq 0.0001 \overset{0}{A} \text{ for } \lambda = 6000 A$$

Where, $\Delta\nu \simeq \frac{1}{2\pi\Delta t} \simeq 10^{-7}$ sec.

= broadening of spectral line due to the finite width of an excited energy state

(II) Doppler width :- It arises from Doppler effect which modifies the apparent frequency of radiation from atoms moving with random thermal velocities. The change in frequency is given by

$$\frac{\Delta\nu}{\nu_0} = \frac{\nu-\nu_0}{\nu_0} = \frac{V\cos\theta}{c} = \frac{u}{c} \quad \text{——} (8)$$

where, v = velocity of atom.
θ = angle between v & direction of observation.
ν_0 = frequency of the line

According to maxwell's laws of distribution of velocities half intensity width is given by

$$(\Delta\nu) = \sqrt{\log e^2/\beta} \quad \text{—— (9)}$$

And intensity width is

$$\beta = \frac{mc^2}{2\pi RT\nu^2}$$

$$2\Delta\nu = 2\sqrt{\frac{\log e^2}{\beta}}$$

m = mol. wt
R = gas constant
T = abs. temp.

$$2\Delta\nu = 1.67\frac{\nu}{c}\sqrt{\left(\frac{2RT}{m}\right)} \quad \text{—— (10)}$$

and

$$\Delta\lambda = 1.67\frac{\lambda_0}{c}\sqrt{\left(\frac{2RT}{m}\right)} \quad \text{—— (11)}$$

Thus the Doppler broadening is proportional to

(i) $\sqrt{T}$ (ii) ν (iii) $\frac{1}{\sqrt{m}}$.

for $\lambda = 5893\ A^\circ$ at $T = 500^\circ K$

$$\boxed{2\Delta\lambda = 0.04\ A^\circ}$$

$\Delta\lambda$ is least for high atomic number and Hg^{198} is the ideal source for sharp sp. lines.

(iii) Width of a line due to external effect:

Collision damping is one of the important external causes in the broadening of sp. lines. The line breath due to collision process is given by

$$\Delta\lambda = \frac{1}{\pi\tau_0}\sqrt{\frac{8RT}{\pi m}} \quad \text{—— (12)}$$

When pressure as the emitting substance is large, the rate of collision increases and hence the broadening is enhanced.

The strong atomic fields in turn cause the <u>red shift</u> in spectrum to exist. The el. field also causes the broadening of sp. line. The effect of fields is to produce Stark effect broadening of observed spectrum lines.