Chapter 11 Spectra of Alkali Elements :-

The experimental study of Spectra was taken up by Liveing, Dewar, Rydberg and Bergmann.

These investigators observed that the spectral lines in the emission spectrum of an alkali atom formed four series :- a principal series of bright and most persistent lines, a sharp series of fine lines, a diffuse series of comparatively broader lines and a fundamental or Bergmann series in the infra red region.

According to Balmer's formula for Hydrogen $\nu = \nu_\infty - \frac{R}{n^2}$, Rydberg pointed out that the alkaline series could be represented by similar formulae such as

Principal $\nu^p_m = \nu^p_\infty - \frac{R}{(m+P)^2}$, $m = 2, 3, 4 \sim \infty$

Sharp - $\nu^s_m = \nu^s_\infty - \frac{R}{(m+S)^2}$, $m = 2, 3, 4 \sim \infty$

Diffuse. $\nu^d_m = \nu^d_\infty - \frac{R}{(m+d)^2}$, $m = 3, 4, 5 \sim \infty$

Fundamental $\nu^f_m = \nu^f_\infty - \frac{R}{(m+f)^2}$, $m = 4, 5, 6 \sim \infty$

where ν_∞'s are the wave no. of the convergence limits of the corresponding series and are called fixed terms. In the so-called running terms.

∴ These above formulae may be written as following form :→

Principal $\nu^p_m = \frac{R}{(1+S)^2} - \frac{R}{(m+P)^2}$, $m = 2, 3, 4 \sim \infty$

Sharp $\nu^s_m = \frac{R}{(2+P)^2} - \frac{R}{(m+S)^2}$, $m = 2, 3, 4 \sim \infty$

Diffuse :- $\nu^d_m = \frac{R}{(2+P)^2} - \frac{R}{(m+d)^2}$, $m = 3, 4, 5, \sim \infty$

Fundamental $\nu^f_m = \frac{R}{(3+d)^2} - \frac{R}{(m+f)^2}$, $m = 4, 5, 6 \sim \infty$

Rydberg - Schuster law:—

The wave No. difference b/w the principal series limit and the sharp (or diffuse) series limit is equal to the wave No. of the first line of the principal series

$$\boxed{\nu^{p}_{\infty} - \nu^{(s\ or\ d)}_{\infty} = \frac{R}{(1+s)^2} - \frac{R}{(2+p)^2} = \nu^{p}_{2}}$$

Runge's law:— The wave no. difference b/w the diffuse series limit and the fundamental series limit is equal to the wave No. of the first line of the diffuse series.

$$\boxed{\nu^{d}_{\infty} - \nu^{f}_{\infty} = \frac{R}{(2+p)^2} - \frac{R}{(3+d)^2} = \nu^{d}_{3}}$$

Ritz Combination principle :→

Ritz pointed out the possibility of occurance of other series obtained by changing the Fixed term in the Formula for the cheif series.

example :- The (cheif) principal and sharp series of alkalies are represented in the relation

$\nu^{p}_{m} = 1s - mp$, $m = 2, 3, 4 - \infty$

$\nu^{s}_{m} = 2p - ms$, $m = 2, 3, 4 - \infty$

According to Ritz, changing the fixed terms 1s and 2p to 2s, 3s, — and 3p, 4p, — .

Thus we obtain combination principal series,

$2s - mp$, $m = 3, 4, 5, -- \infty$ — (1)

$3s - mp$, $m = 4, 5, 6 - \infty$ — (2)

and combination sharp series is represented

$3p - ms$, $m = 4, 5, 6 - \infty$ — (3)

$4p - ms$, $m = 5, 6, 7 - \infty$ — (4)