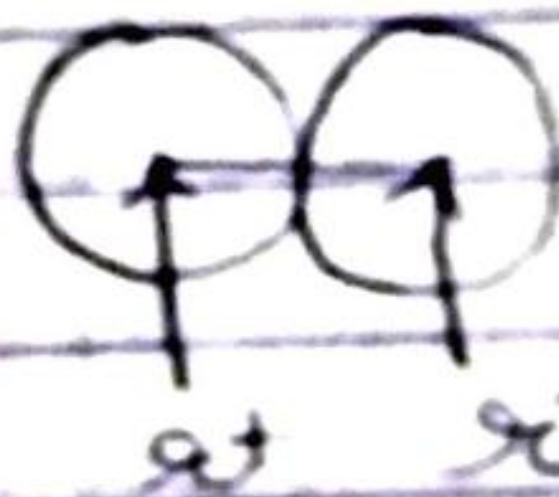


Unit III Limiting Radius Ratio

or  
Radius Ratio

It is the minimum value of ratio radius of +ve ion to radius of -ve ion ( $\frac{r^+}{r^-} = \text{minimum}$ ) and it has this value when +ve and -ve ions are touching each other. The ions are separated, this value increases. It has important bearing on structure of crystal and is related to coordination no.

For trigonal str.



$\frac{r^+}{r^-} = \text{max}$

$$\cos 30^\circ = \frac{BC}{AB}$$

$$= \frac{r^-}{r^+ + r^-}$$

$$\frac{\sqrt{3}}{2} = \frac{r^-}{r^+ + r^-}$$

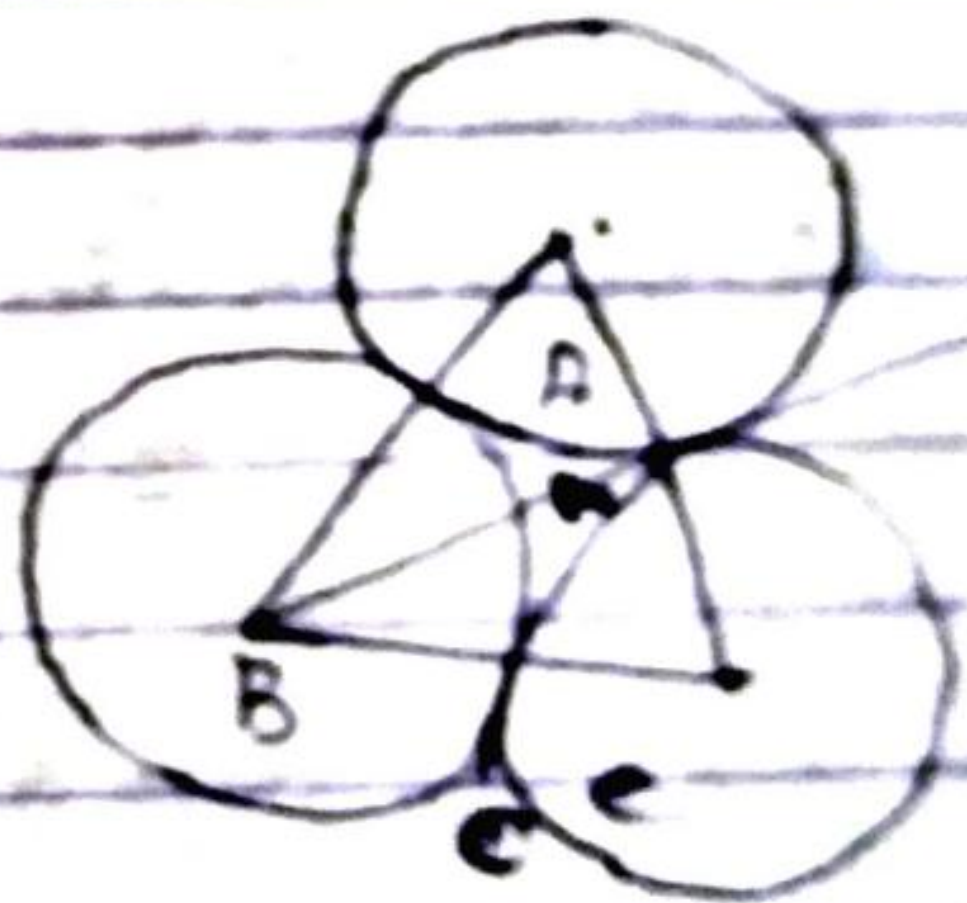
$$\frac{r^+ + r^-}{r^-} = \frac{2}{\sqrt{3}} = \frac{2}{1.732}$$

$$\frac{r^+}{r^-} + 1 = \frac{2}{1.732}$$

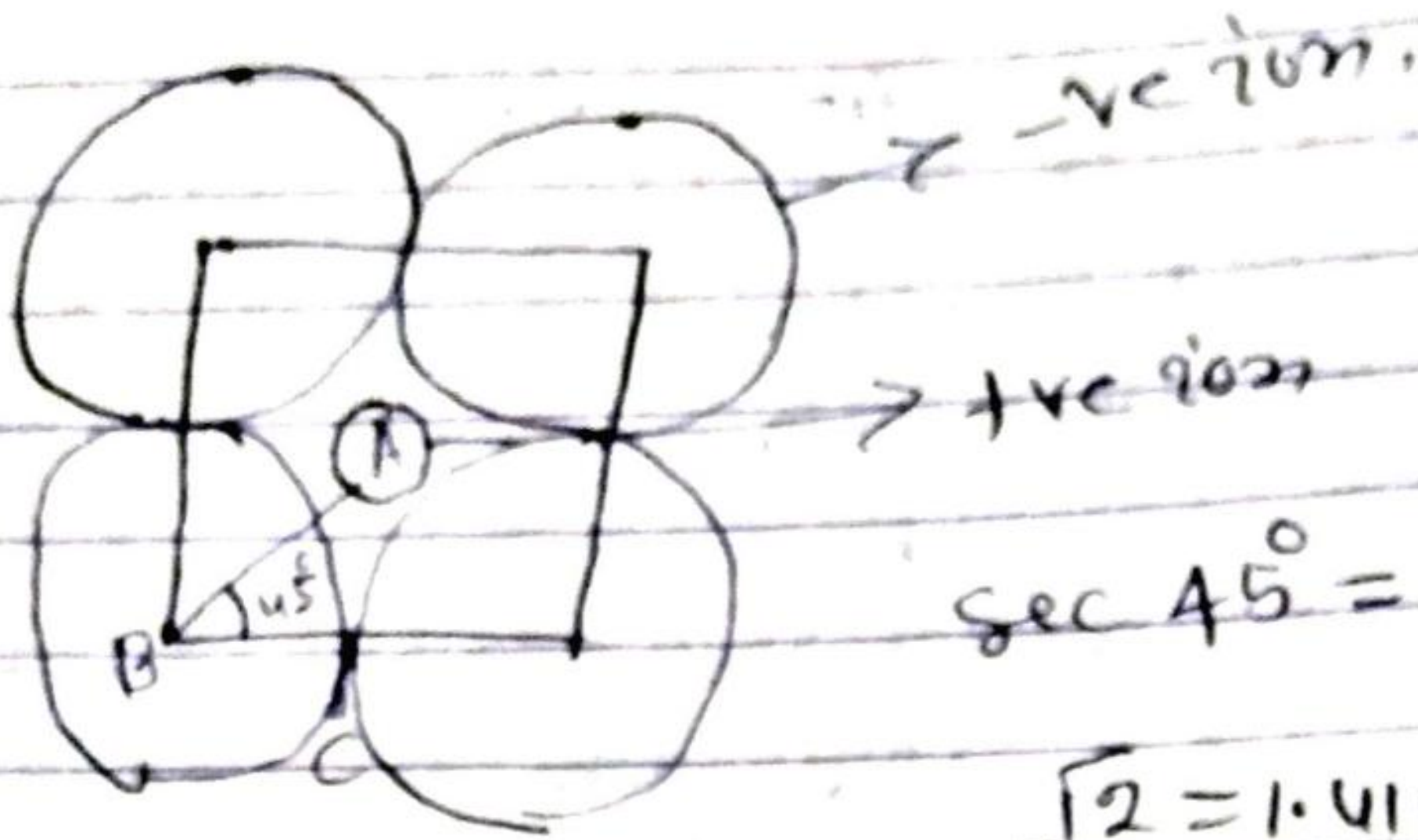
$$\frac{r^+}{r^-} = \frac{2}{1.732} - 1 = \frac{2 - 1.732}{1.732} = \frac{0.268}{1.732} = 0.155$$

i.e. if C.N = 3 and  $\frac{r^+}{r^-} \geq 0.155$

Structure is trigonal.



For square planar or octahedral structure as in simple cube  $\Rightarrow$



$$\sec 45^\circ = \frac{AB}{BC} = \frac{r^+ + r^-}{r^-}$$

$$\sqrt{2} = 1.414 = \frac{r^+}{r^-} + 1$$

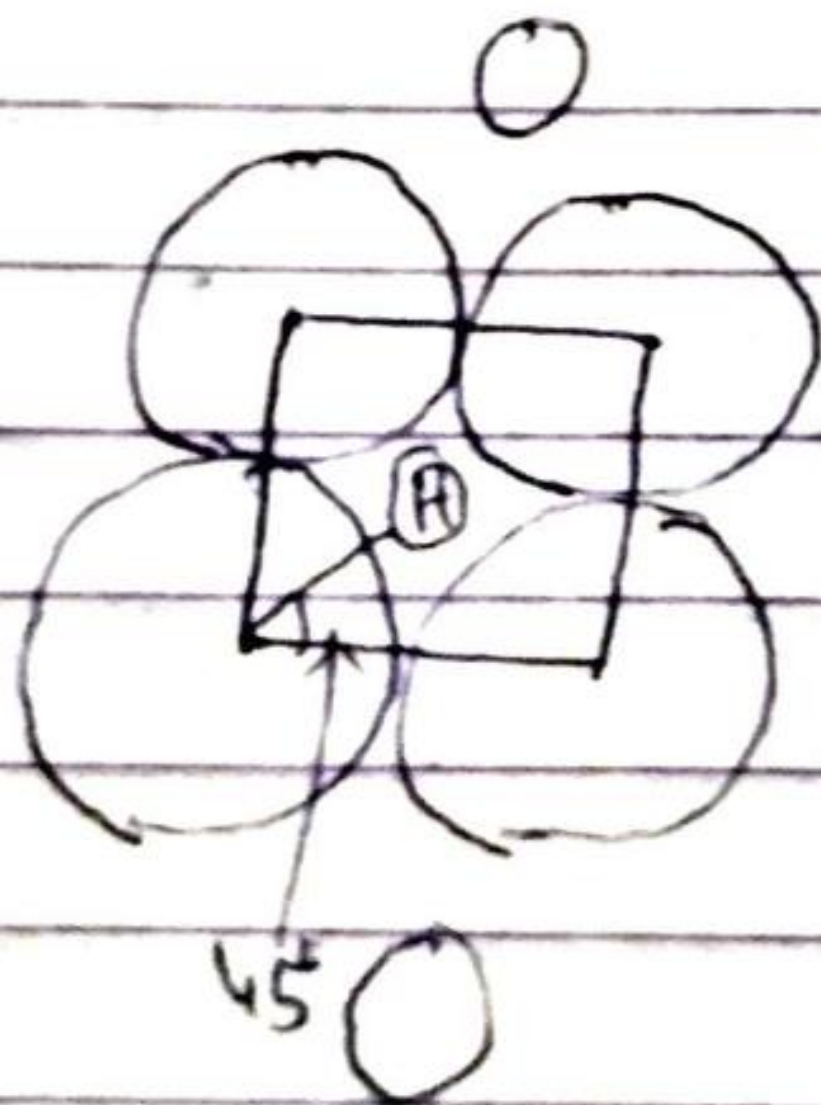
$$\frac{r^+}{r^-} = 1.414 - 1 = 0.414$$

$$z \cdot n = 4 \text{ and}$$

$$\frac{r^+}{r^-} \geq 0.414$$

Structure is square planar

For octahedral  $\Rightarrow$

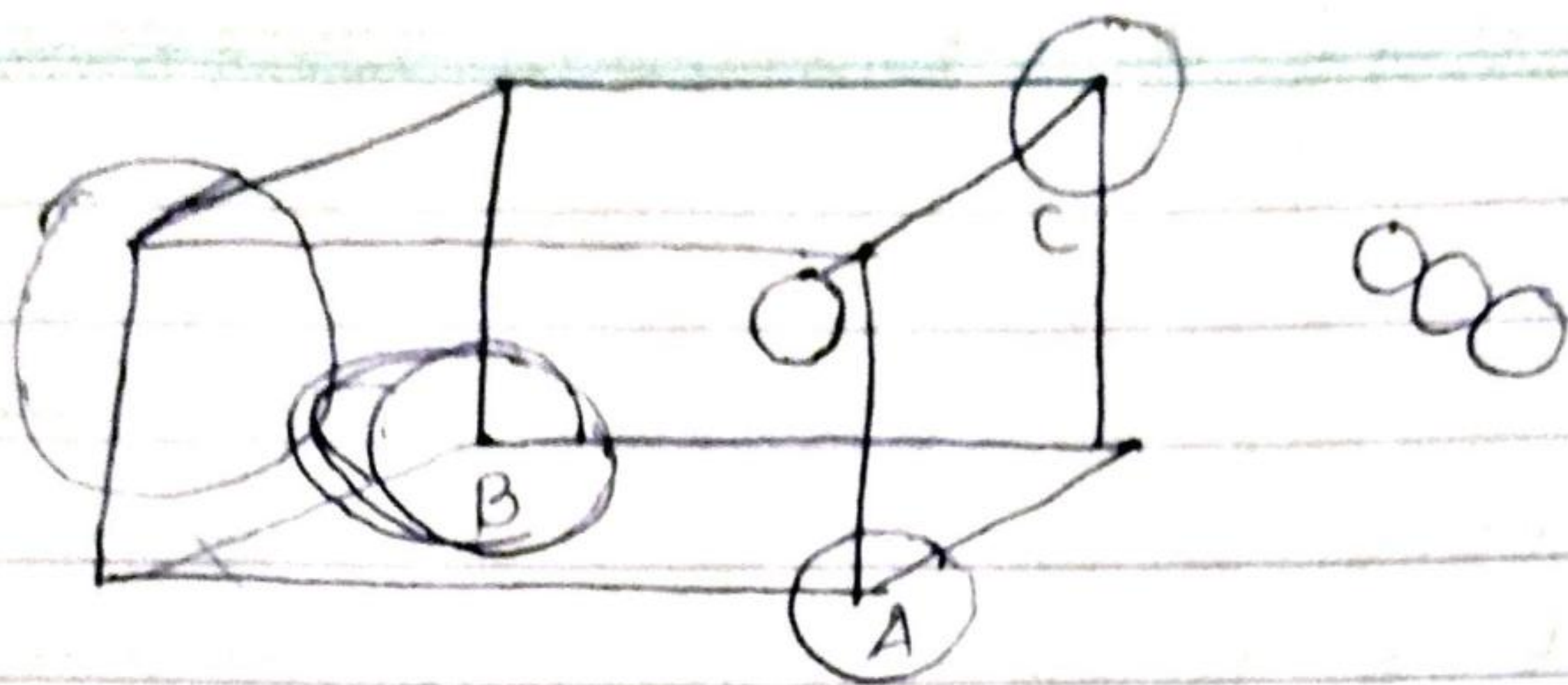


$$\frac{r^+}{r^-} = 0.414$$

$$z \cdot n = 6$$

For tetrahedral structure  $\Rightarrow$

-ve ion lying on alternate corner touch along face diagonal and +ve ion lying in the tetrahedral hole touches -ve ion along the body diagonal.



$$AB^2 = AC^2 + BC^2 = a^2 + a^2 = 2a^2$$

face diagonal

$$AB = a\sqrt{2}$$

and  $BD^2 = AD^2 + AB^2$

$$= (a)^2 + (a\sqrt{2})^2$$

$$= a^2 + 2a^2 = 3a^2$$

Body diagonal,

$$BD = a\sqrt{3}$$

then  $ze^+ + ze^- = AB = a\sqrt{2}$

$$\therefore \frac{ze^+ + ze^-}{2ze^-} = \frac{a\sqrt{3}}{2a\sqrt{2}}$$

$$\frac{ze^+}{ze^-} + 1 = \frac{\sqrt{3}}{\sqrt{2}}$$

$$\frac{ze^+}{ze^-} = \frac{1.732}{1.414} - 1 = \frac{1.732 - 1.414}{1.414}$$

$$= \frac{0.318}{1.414} = 0.225$$

i.e.  $c:N = 4$

and  $\frac{ze^+}{ze^-} \geq 0.225$

Structure is tetrahedral

Thus,

C:N

$$\lim \frac{2e^+}{e^-} \geq$$

Sto

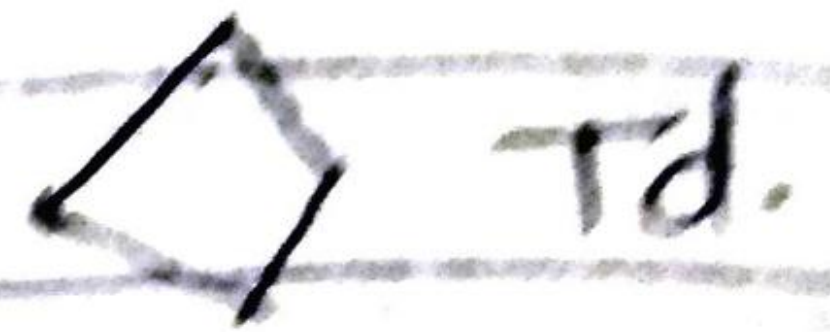
3

0.155

$\Delta$  triangular

4

0.225



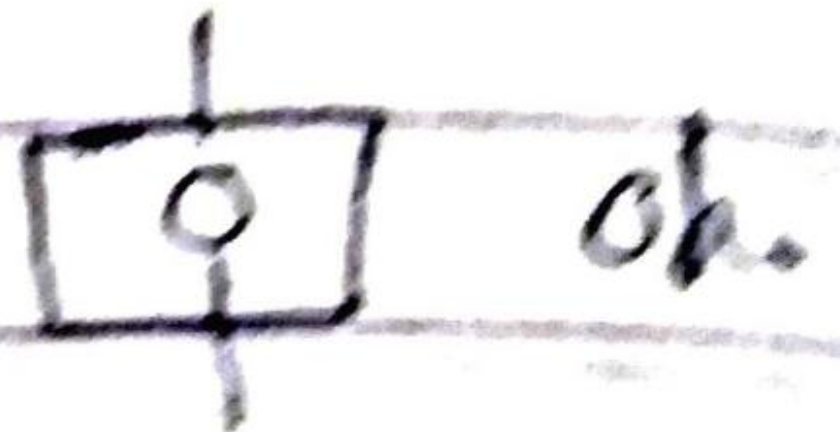
4

0.414



6

0.414



8

0.732

B.C.C.