

Ans-1

Suppose two atoms, exert attractive & repulsive force on each other such that the bonding force is.

$$F(x) = \underbrace{\frac{A}{x^M}}_{\text{attractive}} - \underbrace{\frac{B}{x^N}}_{\text{repulsive}} \quad \text{with } \underbrace{N > M}_{\text{due to repulsive}}$$

; x = centre to centre spacing b/w atoms.
 A, B, M & N are constants characteristic of the molecule.

At equilibrium, when $x = x_0$

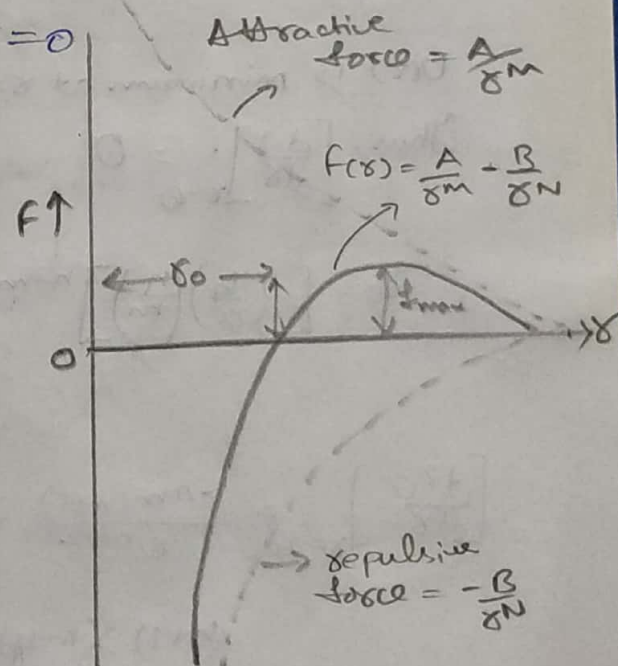
$$F(x) = 0 \Rightarrow \frac{A}{x^M} - \frac{B}{x^N} = 0$$

$$\frac{A}{x^M} = \frac{B}{x^N}$$

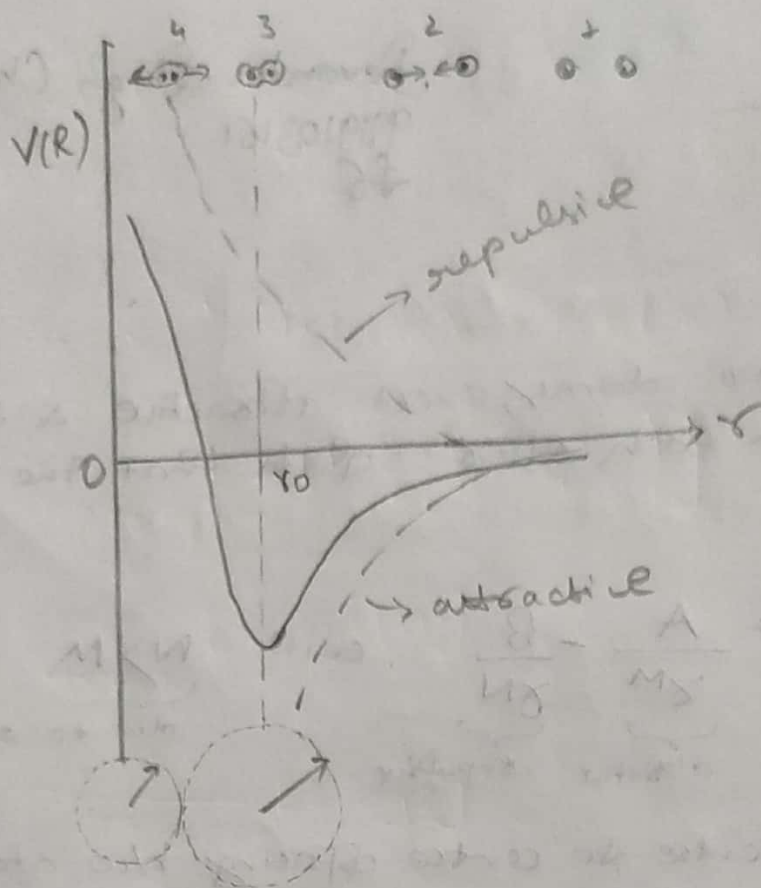
$$x_0^{N-M} = \frac{B}{A}$$

$$F(x) =$$

$$x_0 = \left(\frac{B}{A} \right)^{\frac{1}{N-M}}$$



Ans 2.



$$U(r) = -\frac{a}{r^m} + \frac{b}{r^n} \quad \text{--- (1)} \quad ; \quad r_0 = \text{distance b/w the centers for this minimum } U(r) \text{ to occur}$$

$$U(r=r_0)_{\min} \rightarrow -ive$$

$U(r)$ is minimum at $r=r_0$

Thus, $\left[\frac{dU}{dr} \right]_{r=r_0} = 0$

$$r_0 = \left[\left(\frac{b}{a} \right) \left(\frac{n}{m} \right) \right]^{\frac{1}{n-m}}$$

The minimum $U(r)$ occurs only if $n > m$.

\Rightarrow The attractive force should vary more slowly with r than repulsive force.

$$\left[\frac{d^2U}{dr^2} \right]_{r=r_0} = \frac{-am(n+1)}{r_0^{m+2}} + \frac{bn(n+1)}{r_0^{n+2}} > 0$$

$$\frac{(n+1) \times (m+1)}{n > m}$$

$$\left[\frac{dv}{dx} \right]_{x=x_0} = \frac{ma}{x_0^{m+1}} - \frac{nb}{x_0^{n+1}} = 0 \rightarrow$$

$$x_0^n = x_0^m \left[\left(\frac{b}{a} \right) \frac{n}{m} \right]$$

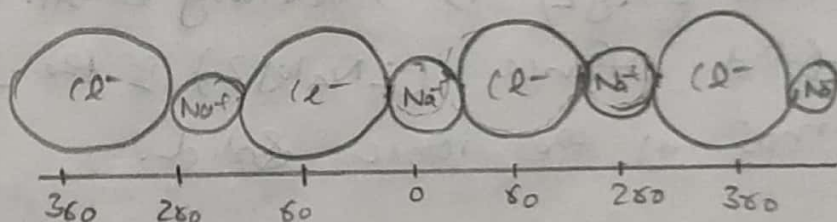
Putting x_0^n in (1)

$$U_{\min} = \frac{-a}{x_0^m} + b \left(\frac{a}{b} \right) \left(\frac{m}{n} \right) \frac{1}{x_0^m}$$

$$U_{\min} = \frac{a}{x_0^m} \left(\frac{m}{n} \right) - \left[\frac{a}{x_0^m} \right]$$

$$U_{\min} = \frac{-a}{x_0^m} \left(1 - \frac{m}{n} \right)$$

Ans. 3



Modeling constant (A) in a linear chain of ions of alternative sign.

The attractive Coulomb energy due to nearest neighbours is

$$\frac{-e^2}{4\pi\epsilon_0 x_0} + \left[\frac{-e^2}{4\pi\epsilon_0 x_0} \right] = \frac{-2e^2}{4\pi\epsilon_0 x_0}$$

The repulsive energy due to two next neighbours at a distance of $2x_0$ is $\frac{2e^2}{4\pi\epsilon_0 (2x_0)}$

... of $3x_0$ is $\frac{-2e^2}{4\pi\epsilon_0 (3x_0)}$ and so on

Thus, the total energy due to all the ions in the linear array is

$$\begin{aligned}
 & \frac{-2e^2}{4\pi\epsilon_0 r_0} + \frac{2e^2}{4\pi\epsilon_0(2r_0)} - \frac{2e^2}{4\pi\epsilon_0(3r_0)} + \dots \\
 &= \frac{-e^2}{4\pi\epsilon_0 r_0} \left[2 \left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right) \right] \\
 &= \frac{-e^2}{4\pi\epsilon_0 r_0} [2 \log(1+1)] \\
 &= \frac{-e^2}{4\pi\epsilon_0 r_0} [2 \log 2]
 \end{aligned}$$

Thus $(2 \log 2)$ is Madelung constt. per molecule of the ionic solid. Hence $(2N_A \log 2)$ is the Madelung constant per mol of the ionic solid.