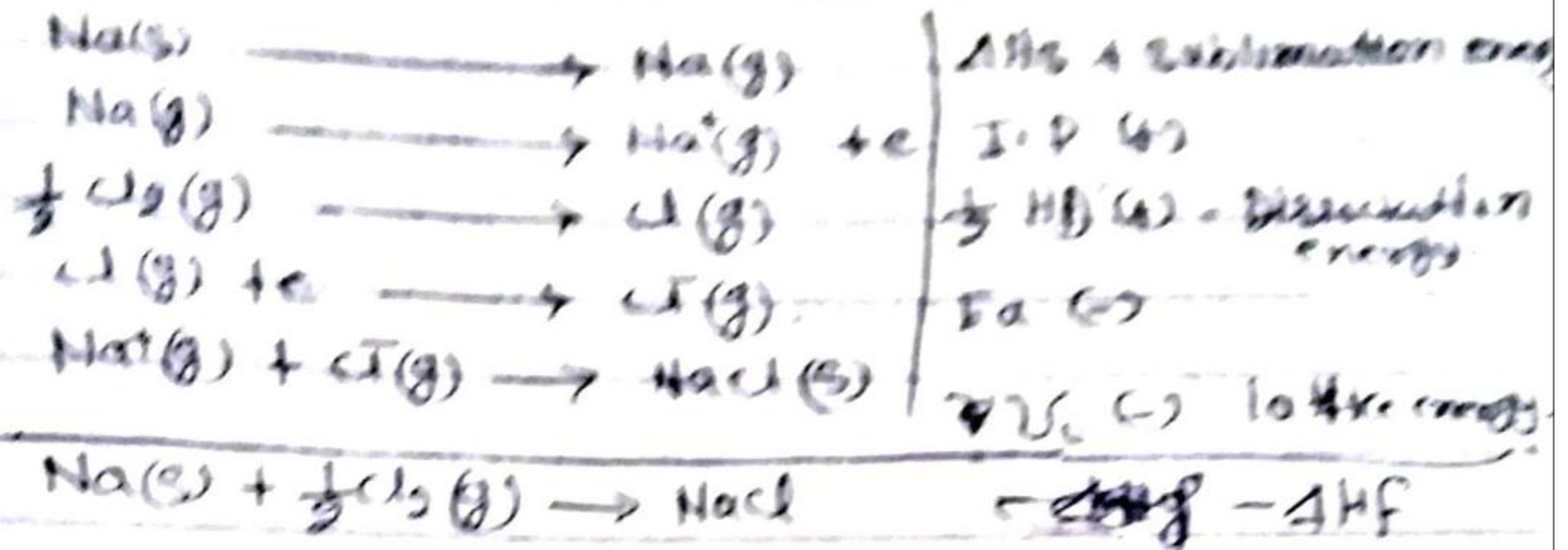


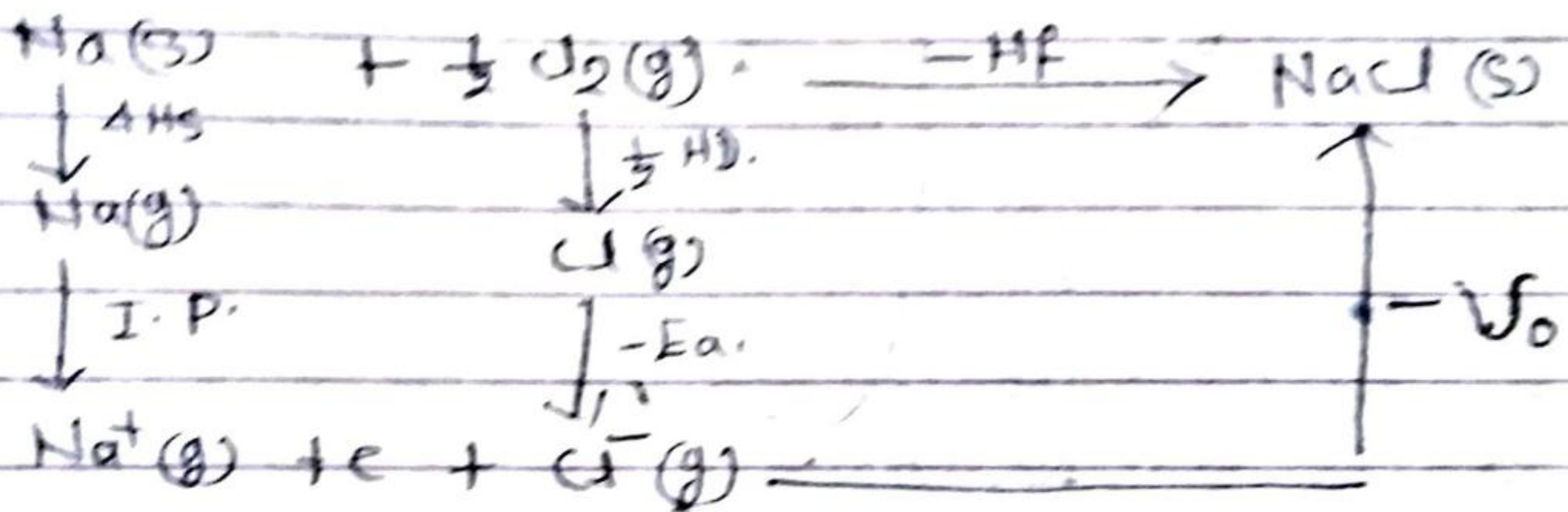
T. D. C. Part I ; Chem (Hons)  
 Paper I ; (Inorg. Chem) ; Chemical Bonding.

Born-Haber Cycle

Born-Haber cycle is a cyclic process which traces the energy steps involved in the formation of an ionic solid from its constituent (gaseous ion) for NaCl. Born-Haber cycle would be :-



The above process represents a cycle.



Combination of above process is called Born-Haber cycle. The heat of formation  $\Delta H_f$  is given by the expression.

$$-\Delta H_f = \Delta H_s + \frac{1}{2} \Delta H_D + \text{I.P.} - E_a - U_0$$

Utility :-  $\rightarrow$  If  $\Delta H$  for all process is known but one is unknown, then that can be calculated from Born-Haber cycle.

$\therefore U_0$  is calculated from B.H.C. if  $E_a$  is known or vice-versa.

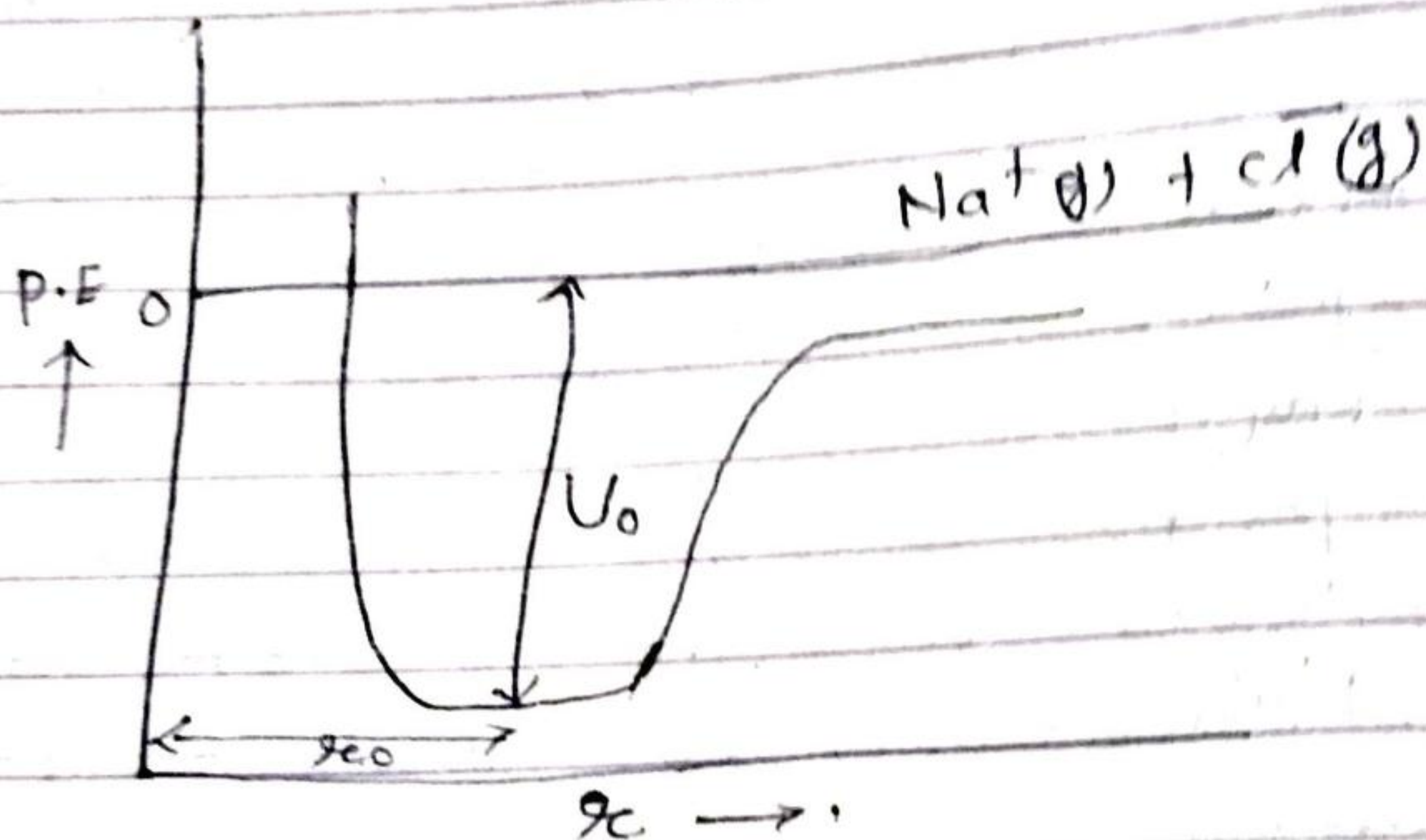
## Lattice Energy

Lattice energy is defined as the heat released in the formation of one mole of ionic solids from its gaseous ions. It is denoted by  $U_0$ .



$$U_0 = \Delta H = -Q$$

It is the decrease in the potential energy resulting from the combination of the ions. It may also be defined as the energy required to dissociate one molecule of a crystal completely into its gaseous state ions.



Lattice energy is given by the expression

$$U_0 = \frac{z^+ z^- A N e^2}{r_{eo}} \left(1 - \frac{1}{n}\right)$$

where,

$U_0$  = Lattice energy

$z^+$  = Effective charge of cation

$z^-$  = Effective charge of anion

$A$  = Madelung constant

$N$  = Avogadro's No.

$n$  = constant called Born exponent

$r_{eo} = r_{e^+} + r_{e^-}$  (internuclear distance)

The value of  $n$  depends upon the inner gas configuration of ions  $\rightarrow$ .

Ion configuration	value of $n$
He	5
Ne	7
Ar.	9
Kr.	10
Xe	12

For NaCl : —



Now the value of  $n = \frac{9+7}{2} = 8$ .

Lattice energy depends upon  $\rightarrow$ .

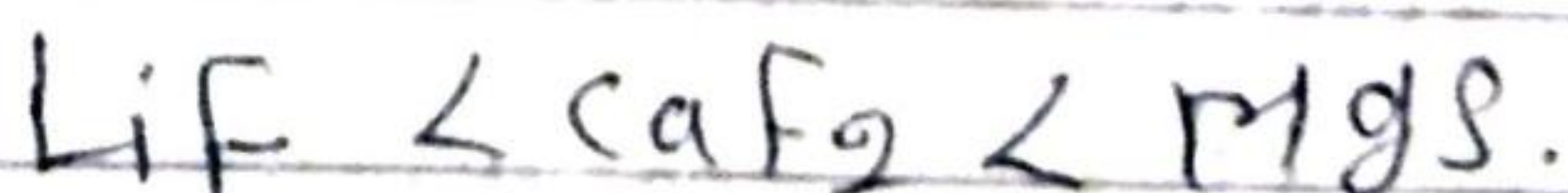
(i)  $U_0$  varies inversely as ( $r_0$ ) internuclear distance between the oppositely charged ions in an ionic crystal. Thus.

$U_0$  of NaCl  $>$   $U_0$  of KCl  
since  $r_0$  for  $\text{Na}^+$   $<$   $r_0$  for  $\text{K}^+$

$$U_0 \propto \frac{1}{r_0}$$

(ii) Charge of the ion  $\rightarrow$ .

$U_0$  varies directly as the product of the charges on the ions of the ionic crystals. Thus  $U_0$  of ionic crystals containing uni-univalent (e.g.  $\text{Li}^+ \text{F}^-$ ), univalent ( $\text{Ca}^{+2} \text{F}_2^-$ ) and bivalent ( $\text{Mg}^{+2}$ ) are in order:

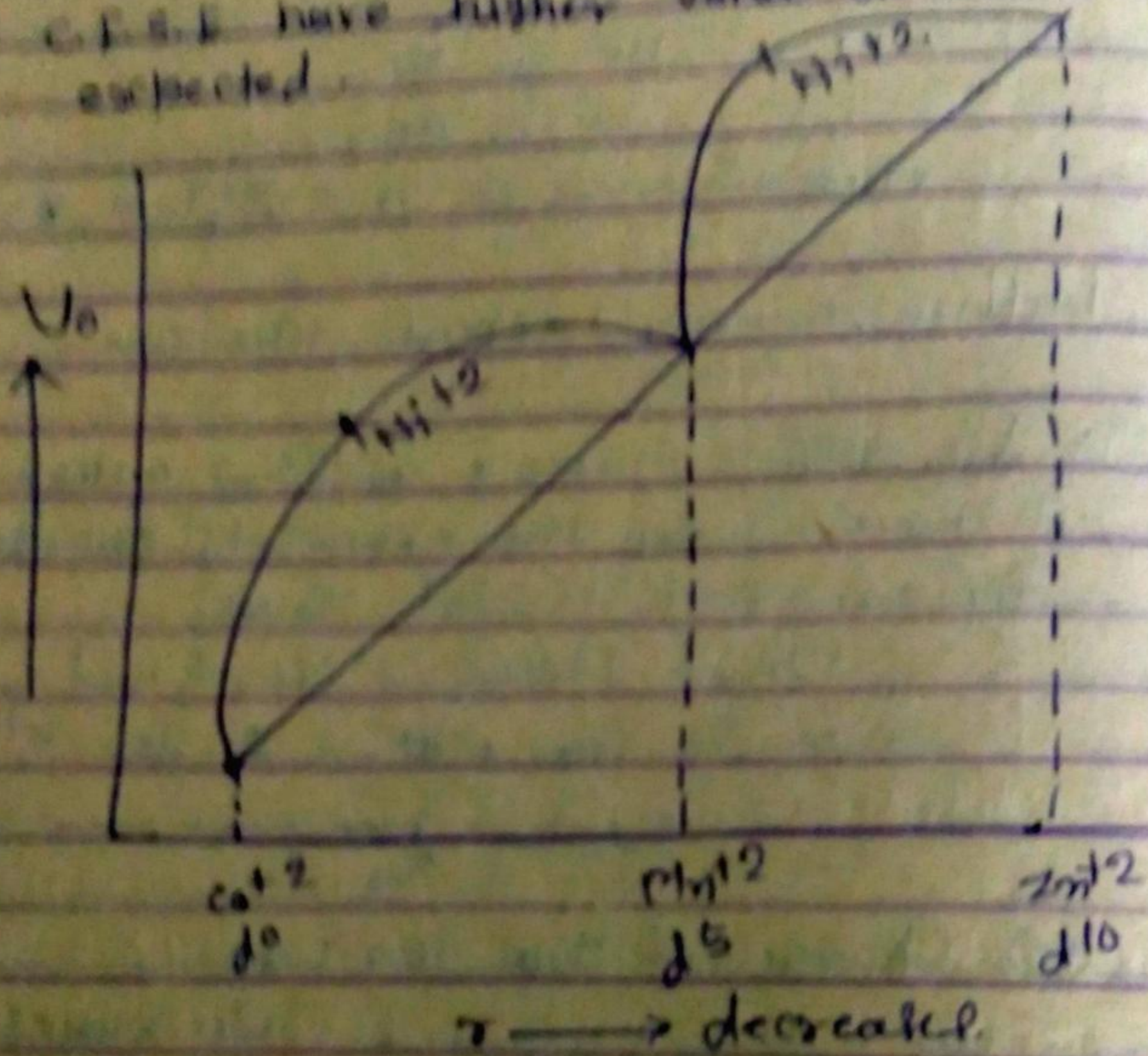


(iii) Effective Nuclear Charge

Greater the effective nuclear charge greater is the  $U_0$   
 $U_0$  for  $Ag > Cu > Ni$   
 since  $Z^*$  for  $Ag > Z^*$  for  $Ni$   
 $U_0 \propto Z^*$

(iv) C.F.S.E

Transition metal cations having C.F.S.E have higher value of  $U_0$  than expected.

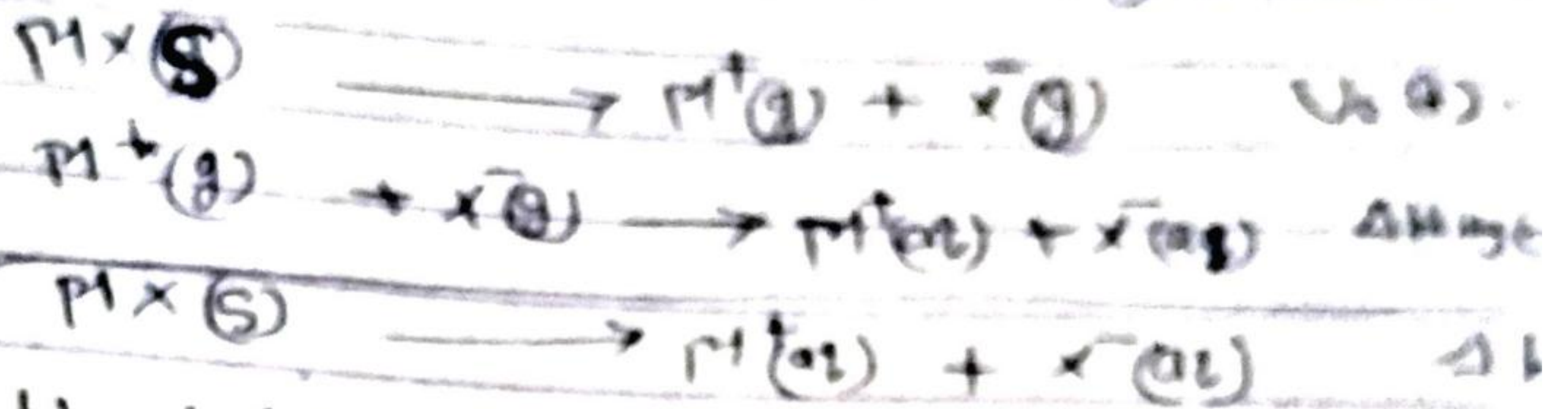


System	C.F.S.E	System	C.F.S.E
$Ca^{+2} d^0$	0 D <sub>2</sub>	$Fe^{+2} d^6$	-4 D <sub>2</sub>
$Sc^{+2} d^1$	-4 "	$Co^{+2} d^7$	-8 "
$Ti^{+2} d^2$	-8 "	$Ni^{+2} d^8$	-12 "
$V^{+2} d^3$	-12 "	$Cu^{+2} d^9$	-6 "
$Cr^{+2} d^4$	-6 "	$Zn^{+2} d^{10}$	0 "
$Mn^{+2} d^5$	0 "		

As  $Sc^{3+}$  to  $Cr^{3+}$   $Fe^{3+}$  to  $Co^{3+}$  ions have c.f.s.f. thus experimental value of  $U_0$  is greater than theoretical expected value.  $La^{3+}$ ,  $Mn^{2+}$  and  $Zn^{2+}$  ions have no c.f.s.f. so their experimental and theoretical values of lattice energy are same.

### Application: →

(i) Determination of solubility of salt:



(a) If  $U_0 < \Delta H_{\text{sol}}$  the salt is soluble

(b) If  $U_0 > \Delta H_{\text{sol}}$  the salt is insoluble.

(ii) Estimation of internuclear distance: →

$$U_0 = \frac{z^+ \cdot z^- \cdot A N e^2}{r_0} \left(1 - \frac{1}{n}\right)$$

Knowing  $U_0$ ,  $z^+$ ,  $z^-$ ,  $A$  and  $n$  internuclear distance  $r_0$  can be calculated.

(iii) Estimation of thermodynamical data such as I.P.,  $E_a$  etc. →

$$-HF = \Delta H_S + \frac{1}{2} \Delta H_D + I.P. - E_a - U_0$$

Thus knowing  $\Delta H_F$ ,  $\Delta H_S$ ,  $\frac{1}{2} \Delta H_D$ , I.P. and  $E_a$  can be calculated.