Coordination Complex (Theory)

THEORITICAL DETERMINATION OF SPINEL STRUCTURE

1. With the help of lattice energy
2. OSSE : Octahedral site stabilization energy

	Tetrahedral	Octahedral
CFSE A^{+2}	|z|	|x|
CFSE B^{+3}	|w|	|y|

* If $(OSSE)_{B^{+3}} > (OSSE)_{A^{+2}}$ Normal spinel structure is favoured.

* If $(OSSE)_{B^{+3}} > (OSSE)_{A^{+2}}$ Inverse spinel structure is favoured.

Case 1:

A^{+2} $|x| = 0$ i.e. $(OSSE)_{A^{+2}}$ is zero

B^{+3} $|y| \neq 0$

$A^{+2} \rightarrow Zn^{+2}, Mn^{+2}, AE.M$ $\begin{bmatrix} d^{10} \\ d^5 \\ d^0 \end{bmatrix}$

$\Rightarrow$ Normal spinel structure will be favoured. E.g. $ZnCO_2O_4$

Case 2:

$|x| \neq 0$ $|y| = 0$

(A^{+2}) (B^{+3})

Generally (B^{+3}) is (a) Fe^{+3}

(b) Al^{+3}

Spinels of Fe^{+3} are inverse.

But spinels of Al^{+3} will be normal, because very high Lattice energy of Al^{+3} in octahedral void even more than CFSE of transition metal except for

$NiAl_2O_4 \rightarrow$ "Inverse"

$Ni^{+2} \rightarrow d^8$

Very high CFSE & verh high Z_{eff} of Ni^{+2} $\therefore$ occupies octahedral void $\Rightarrow$ Inverse spinel structure

Case 3:

$\lvert x \rvert = 0$	$\lvert y \rvert = 0$
A^{+2}	B^{+3}

$A^{+2} \Rightarrow Zn^{+2} / Mn^{+2} /$

Alkaline metals

Always normal, because high charge, high C.No. Except $MnFe_2O_4$ $(\lambda = 0.1)$

Questions: Predict the type of structure of spinel?

(a) Mn_3O_4 (Normal)

(b) CO_3O_4 (Normal)

(c) $ZnCO_2O_4$ (Normal)

(d) $NiAl_2O_4$ (Inverse)

(e) $FeAl_2O_4$ (Normal)

(f) $CoAl_2O_4$ (Normal)

(g) $NiFe_2O_4$ (Inverse)

Answer (d) Normal