كيمياء عام (٤١٩ ك كيمياء غير عضوية)

شعبة : ك/ حيوي ، ميكروبيولوجي/ك ، نبات/ك ، حيوان/ك ، جيولوجيا/ك

الفرقة الرابعة – كلية العلوم

جامعة دمياط

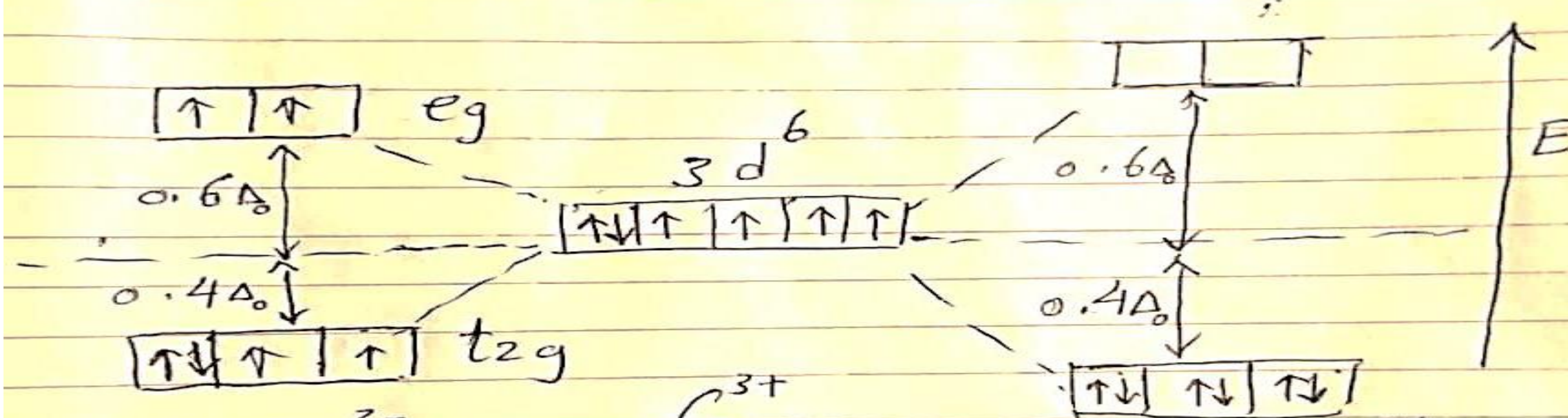
إعداد/ أ.د. أحمد الهنداوي

Crystal Field Stabilization Energy (CFSE)
OR Ligand Field " " (LFSE)

Calculation of CFSE :

P.19

In O_h :



$[Co^{III}F_6]^{3-}$ (weak ligand) High-spin

Co^{3+}

$[Co^{III}(NH_3)_6]^{3+}$ (strong-ligand) Low spin

$CFSE = 4 \times 0.4\Delta_o - 2 \times .6\Delta_o$
$= 0.4\Delta_o$

$CFSE = 6 \times 0.4\Delta_o$
$= 2.4\Delta_o$

Calculation of CFSE for d^{1-10} Configuration

For High spin Complexes

$[M(H_2O)_6]^{2+}$, M = 3d-element (1st Series)

CFSE

$d^1 : (t_{2g})^1(e_g)^0 = 1 \times 0.4\Delta_o = 0.4\Delta_o$

$d^2 : (t_{2g})^2(e_g)^0 = 2 \times 0.4\Delta_o = 0.8\Delta_o$

$d^3 : (t_{2g})^3(e_g)^0 = 3 \times 0.4\Delta_o = 1.2\Delta_o$

$d^4 : (t_{2g})^3(e_g)^1 = 3 \times 0.4\Delta_o - 1 \times 0.6\Delta_o = 0.6\Delta_o$

$d^5 : (t_{2g})^3(e_g)^2 = 3 \times 0.4\Delta_o - 2 \times 0.6\Delta_o = 0$

$d^6 : (t_{2g})^4(e_g)^2 = 4 \times 0.4\Delta_o - 2 \times 0.6\Delta_o = 0.4\Delta_o$

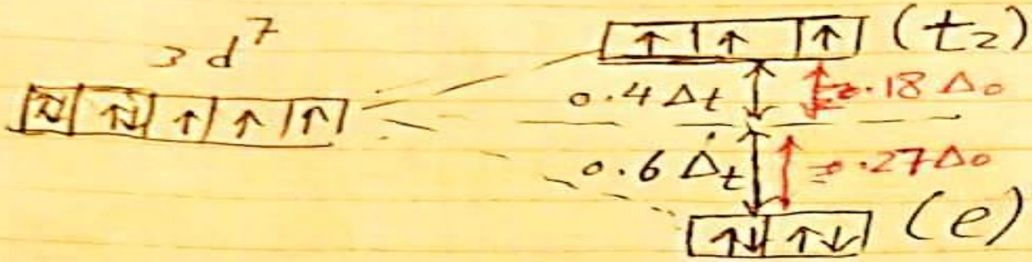
$d^7 : (t_{2g})^5(e_g)^2 = 5 \times 0.4\Delta_o - 2 \times 0.6\Delta_o = 0.8\Delta_o$

$d^8 : (t_{2g})^6(e_g)^2 = 6 \times 0.4\Delta_o - 2 \times 0.6\Delta_o = 1.2\Delta_o$

$d^9 : (t_{2g})^6(e_g)^3 = 6 \times 0.4\Delta_o - 3 \times 0.6\Delta_o = 0.6\Delta_o$

$d^{10} : (t_{2g})^6(e_g)^4 = 6 \times 0.4\Delta_o - 4 \times 0.6\Delta_o = 0$

* Calculation of CFSE in Tetrahedral Complexes (T_h)



$0.4\Delta_t = 0.4 \times \frac{4}{9}\Delta_o = 0.18\Delta_o$

$0.6\Delta_t = 0.6 \times \frac{4}{9}\Delta_o = 0.27\Delta_o$

Co^{2+}

$Hg[Co^{II}(CNS)_4]$

CFSE $= 4 \times .27\Delta_o - 3 \times 0.18\Delta_o$
$= 0.54\Delta_o$

* Calculation of CFSE for d^{1-10} in T_h complexes.

		CFSE	
d^1 :	$(e)^1(t_2)^0$:	$1 \times 0.27\Delta_o$	$= 0.27\Delta_o$
d^2 :	$(e)^2(t_2)^0$:	$2 \times 0.27\Delta_o$	$= 0.54\Delta_o$
d^3 :	$(e)^2(t_2)^1$:	$2 \times .27\Delta_o - 1 \times 0.18\Delta_o$	$= 0.36\Delta_o$
d^4 :	$(e)^2(t_2)^2$:	$2 \times 0.27\Delta_o - 2 \times 0.18\Delta_o$	$= 0.18\Delta_o$
d^5 :	$(e)^2(t_2)^3$:	$2 \times 0.27\Delta_o - 3 \times 0.18\Delta_o$	$= 0$
d^6 :	$(e)^3(t_2)^3$:	$3 \times 0.27\Delta_o - 3 \times 0.18\Delta_o$	$= 0.27\Delta_o$
d^7 :	$(e)^4(t_2)^3$:	$4 \times 0.27\Delta_o - 3 \times 0.18\Delta_o$	$= 0.54\Delta_o$
d^8 :	$(e)^4(t_2)^4$:	$4 \times 0.27\Delta_o - 4 \times 0.18\Delta_o$	$= 0.36\Delta_o$
d^9 :	$(e)^4(t_2)^5$:	$4 \times 0.27\Delta_o - 5 \times 0.18\Delta_o$	$= 0.18\Delta_o$
d^{10} :	$(e)^4(t_2)^6$:	$4 \times 0.27\Delta_o - 6 \times 0.18\Delta_o$	$= 0$

We can summarize CFSE for O_h + T_h (high-spin) in the Figure below:

* Max. CFSE for d^2 & d^8 at $1.2\Delta_o$
  i.e., d^2 & d^8 complexes prefere O_h

* Max. CFSE for d^3 & d^7 at $0.54\Delta_o$
  i.e; d^3 & d^7 complexes prefere T_h

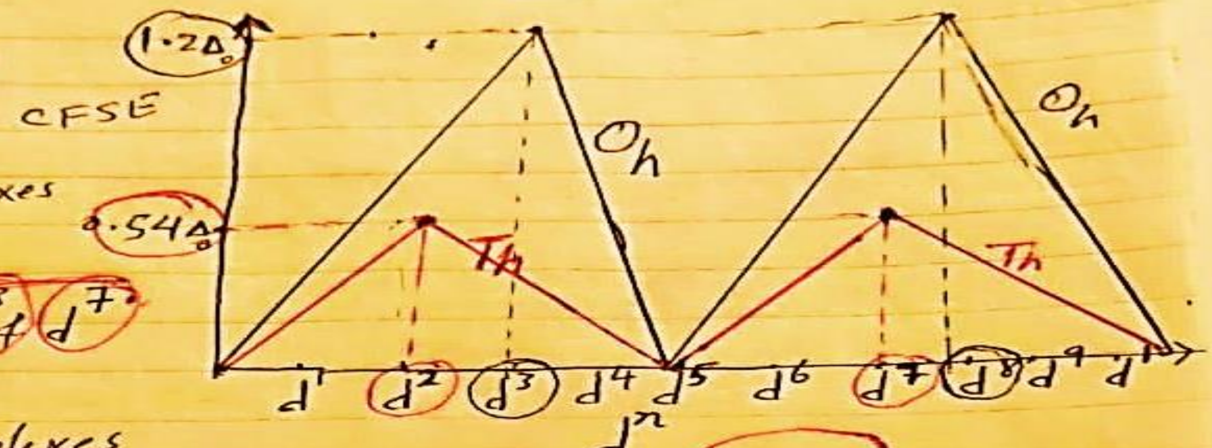


Fig. 1.

Stability of Hexaquo Ions

P. 20

$[M(H_2O)_6]^{2+}$; M^{2+}: 3d-metal ion

$$M^{2+}_{(g)} + H_2O_{(excess)} \longrightarrow [M(H_2O)_6]^{2+}_{(aq)} + \Delta H_{hydration}$$

Key Factor: $\frac{\text{Charge}}{\text{Radius}}$ ratio — Charge: Constant (+2)

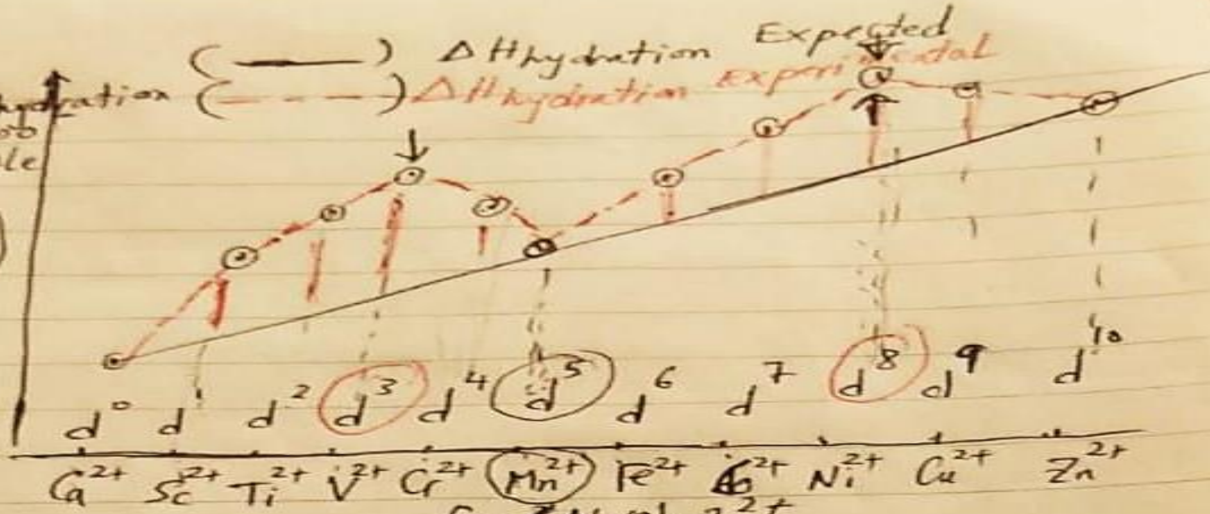
$\Delta H_{hydration}$ expected to increase steadily from $Sc^{2+} \rightarrow Zn^{2+}$ aquo complexes (solid Line, Fig. 2)

d^1 d^2 d^3 --- d^9 d^{10}

Sc^{2+} Ti^{2+} V^{2+} --- Cu^{2+} Zn^{2+}

- Nuclear charge increases (Z)
- Radius Decreases
- $\Delta H_{hydration}$ increases

P.21



— Max. ΔH hydration for d^3 & d^8
* for their Max. CFSE.

$[M(H_2O)_6]^{2+}$

Fig. 2

* If the value of the CFSE for each hydrated ion (All high spin) is deducted from the observed (Experimental) value of the hydration energy, We get the expected the smooth Curve (solid Line).

* What you expect for ΔH hydration f in $[M(H_2O)_6]^{3+}$ (M^{3+}: 3d element ion)

Note:

- ① ΔH hydration for $[M(H_2O)_6]^{3+}$ is expected to increase doubly amounts for increase of Oxidation state of M^{2+}.

② d^0 Sc^{3+}, d^1 Ti^{3+}, d^2 V^{3+} ------ d^8 Cu^{3+}, d^9 Zn^{3+}, d^{10} Ga^{3+}