More d-electrons

Fill in d-electrons:

e — — $d_{z^2}, d_{x^2-y^2}$

t_2 — — — d_{xy}, d_{yz}, d_{zx}

Aufbau principle (add the next electron to the lowest energy level available)

Hunds rules (arrange electrons in multiple orbitals of the same energy and with parallel spins)

1-3-2017 IC 6 CFSE 1

High-spin and low-spin

Octahedral d^4 – d^7 (aufbau & Hund)

high spin low spin

Δ

1-3-2017 IC 6 CFSE 2

One electron in an octahedral field

e — — $d_{z^2}, d_{x^2-y^2}$

t_2 — — — d_{xy}, d_{yz}, d_{zx}

Crystal Field Stabilisation Energy

$$CFSE = n_{t2} \cdot 0.4\Delta - n_e \cdot 0.6\Delta$$

1-3-2017 IC 6 CFSE 3

One electron in an octahedral field

Assumption : d-electrons do not interact so much as to ruin the one-electron splitting

d^n	1	2	3	4	5	6	7	8	9
high spin – –				↑	↑ ↑	↑ ↑	↑ ↑	↑ ↑	⇅ ↑
high spin – – –	↑	↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	⇅ ↑ ↑	⇅⇅ ↑	⇅⇅⇅	⇅⇅⇅
low spin – –							↑		
low spin – – –				⇅ ↑ ↑	⇅⇅ ↑	⇅⇅⇅	⇅⇅⇅		

CFSE									
high spin	.4 Δ	.8 Δ	1.2 Δ	.6 Δ	0 Δ	.4 Δ	.8 Δ	1.2 Δ	.6 Δ
low spin				1.6 Δ	2 Δ	2.4 Δ	1.8 Δ		

1-3-2017 IC 6 CFSE 4

21.39

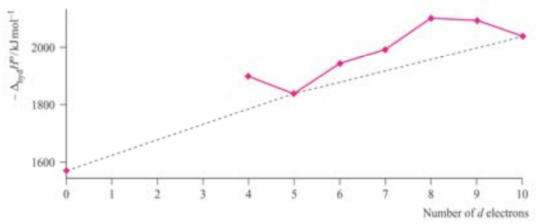


Fig. 21.34 Absolute enthalpies of hydration of the M^{2+} ions of the first row metals; the point for d^0 corresponds to Ca^{2+}. Data are not available for Sc^{2+}, Ti^{2+} and V^{2+}.

21.38

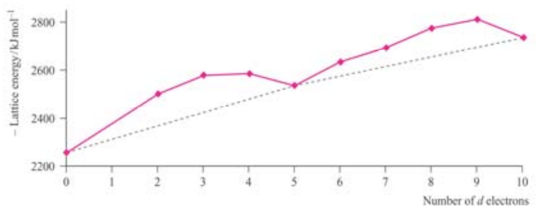


Fig. 21.33 Lattice energies (derived from Born–Haber cycle data) for MCl_2 where M is a first row d-block metal; the point for d^0 corresponds to $CaCl_2$. Data are not available for scandium where the stable oxidation state is +3.

Stability variations

M^{z+} size is important for stability of ML_x

Case study 1 question 4,5,6

see next slides

M^{2+} - 1,2-ethanediamine

$\log K_1$ and $\log K_2$ (Mn through Zn)

M^{2+}	$\log K_1$	$\log K_2$	$\log K_3$
Cr	5.15	4.04	-
Mn	2.77	2.10	0.92
Fe	4.34	3.31	2.05
Co	5.89	4.83	3.10
Ni	7.51	6.35	4.42
Cu	10.72	9.31	1.0
Zn	5.92	5.15	1.86
Cd	-	4.59	2.09

Case study 1; Q 6

Give other estimates of $\log K_1$ (Cd^{2+} case)

(using variations among metal ions)

M^{2+}	$\log K_1$	$\log K_2$	$\log K_3$
Cr	5.15	4.04	-
Mn	2.77	2.10	0.92
Fe	4.34	3.31	2.05
Co	5.89	4.83	3.10
Ni	7.51	6.35	4.42
Cu	10.72	9.31	1.0
Zn	5.92	5.15	1.86
Cd	-	4.59	2.09

CFSE significance?

- CFSE contribution to stability ?
- $Nien^{2+}$ as an example

$Nien_3^{2+}$

CFSE contribution to stability

M^{2+} - 1,2-ethanediamine

Case study 1

M^{2+}	$logK_1$	$logK_2$	$logK_3$
Cr	5.15	4.04	-
Mn	2.77	2.10	0.92
Fe	4.34	3.31	2.05
Co	5.89	4.83	3.10
Ni	7.51	6.35	4.42
Cu	10.72	9.31	1.0
Zn	5.92	5.15	1.86
Cd	-	4.59	2.09

Ni^{2+} : $log\beta_3$ = 18.28

$Nien_3^{2+}$

Stability logβ$_3$ =18.28

Equilibrium?

$Ni(H_2O)_6^{2+}$ +3 en ⇆ $Nien_3^{2+}$

-ΔH° = -ΔG° - TΔS°

RTln10logβ$_3$ - T(-40 JK^{-1} mol^{-1})

104.3 + 12

116 kJ mol^{-1}

$Nien_3^{2+}$

CFSE contribution for ? $Nien_3^{2+}$

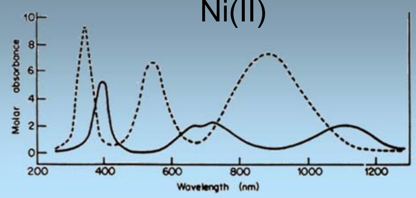
$Ni(H_2O)_6^{2+}$

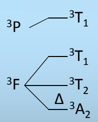
σ = 3·0.4Δ = 1.2 Δ =

Data ?

Ni(II)

- d^8





transition	$Niaq_6^{2+}$ λ/nm	σ/10^{-3}cm^{-1}	$Nien_3^{2+}$ λ/nm	σ/10^{-3}cm^{-1}
$^3A_2 \rightarrow {}^3T_2$	1180	8.5	890	11.25
$^3A_2 \rightarrow {}^3T_1$	702	14.0	545	18.4
$^3A_2 \rightarrow {}^3T_1$	400	25.3	345	29.0

Δ-values

Energy $10^3 cm^{-1}$	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$M(H_2O)_6^{2+}$		12.2	13.9	7.7	10.4	9.7	8.5	12.5
$M(H_2O)_6^{3+}$	20.4	19.0	17.4	21.0	14.0	20		
MF_6^{3-}	17.0		15.0			13.1		
MF_6^{2-}				21.8				
$M(NH_3)_6^{3+}$			21.6			22.9		
$M(NH_3)_6^{2+}$						10.2	10.8	
$M(CN)_6^{3-}$			26.6		35.0			
Men_3^{3+}						24.0		
Men_3^{2+}							11.5	

$Nien_3^{2+}$

CFSE contribution for $Nien_3^{2+}$

$Ni(H_2O)_6^{2+}$

$\sigma = 3 \cdot 0.4\Delta = 1.2\,\Delta =$ $1.2(11.5\text{-}8.5) \cdot 10^3\ cm^{-1}$

$E = h \cdot \nu$ $\nu\ (s^{-1}) = \sigma\ (cm^{-1}) \cdot c\ (cm \cdot s^{-1})$

$6.626 \cdot 10^{-34}\ (Js) \cdot 3.6 \cdot 10^3 \cdot 2.998 \cdot 10^{10} (s^{-1})$

$-\Delta H_{CFSE} =$ $E \cdot N_A\ (mol^{-1})$

$6.022 \cdot 10^{23}$

43 $kJ\ mol^{-1}$

$Nien_3^{2+}$

- Stability $-\Delta H^o = -\Delta G^o - T\Delta S^o$ $\log\beta_3 = 18.28$

  $= RT\ln 10 \log\beta_3 - T(-40\ JK^{-1}\ mol^{-1})$

  104.3 + 12 = 116 $kJmol^{-1}$
- CFSE contribution to stability:

  $\sigma \bullet c = \nu\ ;\ E = h \bullet \nu = \sigma \bullet c \bullet h \bullet N_A$

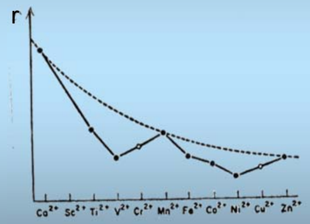
  $c = 2.998 \bullet 10^{10}\ cm\ s^{-1}$; $h = 6.626 \bullet 10^{-34}\ Js$; $N_A = 6.022 \bullet 10^{23}$ parts $\bullet mol^{-1}$;

  $\sigma = 3 \bullet 0.4 \bullet (\Delta_{en} - \Delta_{aq}) = 1.2(11.5\text{-}8.5)\ 10^3\ cm^{-1}$

  CFSE = 43 $kJmol^{-1}$

Sizes (cf. lattice energies)

- CFSE's reflected in bond lengths



1-3-2017 19 IC 6 CFSE