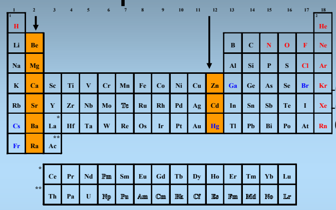
Group 2 and 12



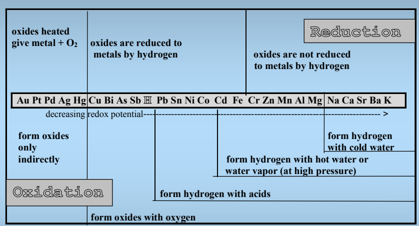
-1.85V
-2.37
-2.87
-2.89
-2.90
-2.92

-0.76V
-0.40
0.85

[Ng](ns)[2] | [Ng](n-1 d)[10](ns)[2]
Hg: [Xe](4f)[14](5d)[10](6s)[2]

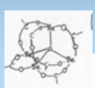
reactive metals - $M_s \leftrightarrows M_{aq}^{2+} + 2e^-$ - less or poorly reactive
hard lewis acids | soft lewis acids
electrostatic | forces | covalent
O^{2-},OH^-,CO_3^{2-},COO^- | NH_3 | phenolate, RS^-, ArN

Reactivity of metals

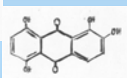


Group 2

- Identification in aqueous solution



textbook fig 12.6



Be^{2+}: OH^- blue solution
Mg^{2+}: CO_3^{2-} OH^- blue precipitate
Ca^{2+}: CO_3^{2-} to $C_2O_4^{2-}$ white ppt
Sr^{2+}: SO_4^{2-} to CO_3^{2-} to SO_4^{2-} white ppt
Ba^{2+}: SO_4^{2-} to CO_3^{2-} to CrO_4^{2-} yellow ppt

Some properties

	Be	Mg	Ca	Sr	Ba
Occurence %	$6x10^{-4}$	2.1	3.6	0.02	0.03
Ionisation energy	895	734	587	541	500
/ $kJxmol^{-1}$ 2	1746	1443	1059	959	~900
3	14000	9700	4930	4170	3580
Hydration enthalpy	-2994	-1924	-1580	-1485	-1276
Eo/V	-1.85	-2.37	-2.87	-2.87	-2.9
Ionic radius (r/Å)	0.31	0.65	0.99	1.13	1.35
Ionic potential (q/r)	6.45	3.08	2.02	1.77	1.48
Ionic mobility	4.8	5.5	6.2	6.2	6.6
Melting point/^{0}C	1278	651	850	770	704
Atomic radius /Å	1.11	1.6	1.97	2.15	2.17
pLM$(OH)_2$	-	11	4.2	3.3	1.5
pL MCO_3		5	8.3	9	8.3
pL MC_2O_4		4.1	8.7	7.2	7
pL MSO_4		~0	5	6.5	10
logK MF^+	4.95	1.82	0.63	0.15	-0.2
logK MEDTA		8.7	10.7	8.8	7.9
logK $Mgly^+$		3.4	1.4	0.9	0.8
logK $MP_2O_7^{2-}$		5.8	5	4.7	
logK MATP		4.2	4	3.5	3.3

Systematics?

Why "opposite"

- ionic mobilities

and ionic radii?

- Solubilities

of sulfates and hydroxides?

	Be	Mg	Ca	Sr	Ba
Ionic mobility	4.8	5.5	6.2	6.2	6.6
Ionic radius /Å	0.31	0.65	0.99	1.13	1.35
pLM$(OH)_2$	**-**	**11**	**4.2**	**3.3**	**1.5**
pL MSO_4		**~0**	**5**	**6.5**	**10**

M^{2+}

Atom	Me^{2+}	r (Å)	E^0 (V)	$E^0(n^+/m^+)$	pK_{aq}	$logK_{EDTA}$	$log\beta en_3$	colour(Maq_n^{2+})
Be	[He]	.31	-1.85					
Mg	[Ne]	.65	-2.37		11.4	8.7		
Ca	[Ar]	.99	-2.37		12.6	10.6		
Sr	[Kr]	1.13	-2.87		13.2	8.6		
Ba	[Xe]	1.35	-2.89			7.8		
Zn	$[Ar]3d^{10}$	.74	-.76		8.8	16.5	12.1	
Cd	$[Kr]4d^{10}$	.97	-.40		9.0	16.5	12.4	
Hg	$[Xe]4f^{14}5d^{10}$	1.10	.85	2/1: .92	3.7	21.8		
Ge	$[Zn^{2+}]4s^2$	.73	.23					
Sn	$[Cd^{2+}]5s^2$	.93	-.14	4/2: .15				
Pb	$[Hg^{2+}]6s^2$	1.20	-.13	4/2: 1.8	7.8	18.0		
Ti	$[Ar]3d^2$	.70	-1.6	3/2: -.37				
V	$[Ar]3d^3$	.65	-1.18	3/2: -.25		12.7		violet
Cr	$[Ar]3d^4$	.73	-.91	3/2: -.41		13.6		blue
Mn	$[Ar]3d^5$	.80	-1.19	3/2: 1.54	10.6	13.6	5.7	light red
Fe	$[Ar]3d^6$	.76	-.44	3/2: .77	9.5	14.3	9.5	light green
Co	$[Ar]3d^7$	.74	-.28	3/2: 1.84	8.9	16.1	13.8	red
Ni	$[Ar]3d^8$	.69	-.25		10.6	18.6	18.6	green
Cu	$[Ar]3d^9$	.72	.34	2/1: .15	6.8	18.8	18.7	light blue
Pd	$[Kr]4d^8$	.90	.99			18.5		
Pt	$[Xe]4f^{14}5d^8$ 1.0	1.2		4 ?				
Eu	$[Xe]4f^7$	1.10	-3.43	3/2: -.36				
Yb	$[Xe]4f^{14}$	1.02	-2.80	3/2: -1.2				

Calcium carbonate

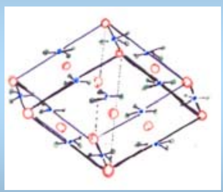
Calcite (low temperature)

Aragonite (high temperature)

Calcite

Same structure MCO_3

M	a/Å	α
Ca	6.41	101° 55’
Mg	6.04	102° 58’
Fe	6.02	103° 05’
Mn	6.01	102° 50’
Zn	5.93	103° 27’



Grignard reagent

Formation of C-C bonds using carbanions:

$$\text{R-Cl} + \text{Mg} \rightarrow \text{R-MgCl}$$

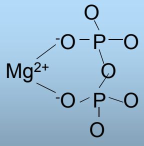
$$\text{R-MgCl} + \text{R'R''C=O} \rightarrow \text{R-C(R')(R'')-O}^{-}\text{MgCl}^{+}$$

Also R-Cl + Zn → R-ZnCl → R_2Zn

Mg^{2+} and Ca^{2+} in life

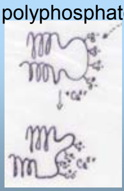
Hydrolytic enzymes

- Chlorophylls
- In bones
- Hydrolysis of poly-phosphates : Lewis acid polarisation of bonds



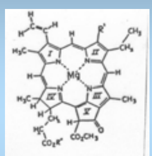
- Calcium pectate (cell wall)
- In bones, teeth, shells
- Triggers
- Striated muscle contraction

polyphosphates- carboxylates



calmodulin

Chlorophylls

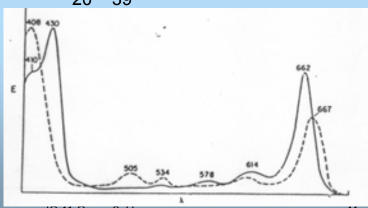


$R' = CH_3$ Chl. A

$R' = CHO$ Chl. B

$R'' = C_{20}H_{39}$

Green colour:



End of Chapter problems 22

- $M + NH_{3,\ell} \rightarrow A$

$A_s \rightarrow B + C_g$ (slow)

M flame: crimson (violet through blue glass)

$Sr(NH_3)_6 \rightarrow Sr(NH_2)_2 + H_2 + 4NH_3$ (12.9)

- XCO_3 ; $X + H_2O$ (0 °C) $\rightarrow$ D (strong base*)

D: $X^{2+} + 2OH^- + CO_2$ (qual. test)

$X + H_2 \rightarrow XH_2$ drying agent

(drying agents : MgH_2 CaH_2)

X = Ba-Ca; $X^{2+} + 2OH^- + CO_2 \rightarrow XCO_3$

End of Chapter problems 24

$CaCl_2$	A	Polymeric in the solid state	1
BeO	B	Soda lime	2
$Be(OH)_2$	C	Strong oxidising agent	3
CaO	D	Qualitative analysis: sulphate test	4
CaF_2	E	Hygroscopic – used for de-icing	5
$BaCl_2$	F	Amphoteric	6
$BeCl_2$	G	Quicklime	7
MgO_2	H	Crystallises with Würtzite structure	8
$Ca(OH)_2/NaOH$	I	A prototype crystal structure	9

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Kalk - Lime

Trivial navne (names)
Kalk (limestone)
Kridt (chalk) marmor, (marble) $CaCO_3 \rightarrow$
brændt kalk (lime, quick lime) $CaO + CO_2$

$CaO + H_2O \rightarrow Ca(OH)_2$ (0.025M 0 °C, 0.01M 100°C)
Læsket kalk (slaked lime)

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Group 12

	Zn	Cd	Hg
r_m/Å	1.34	1.51	1.51
25°C 1 atm	HCP	HCP	ℓ
mp/°C	480	320	-39
bp/°C	907	765	357
d/g·cm^{-1}	7.14	8.65	13.5
resistivity*	5.8	7.5	95.8
E°	-0.76	-0.40	0.85
ΔH^o_{ion2+}	2632	2492	2805
r(M^{2+})/Å	0.74	0.95	1.1

***Mg: 4.2**

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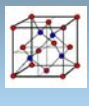
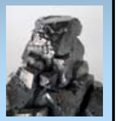
Group 12

Sphalerite (zinkblende) ZnS
Galena PbS
Cinnober HgS



(NaCl-structure)



$MS + 3/2O_2 \rightarrow MO + SO_2$

$ZnO + C \rightarrow Zn + CO$ (Cd)

$Zn + CO_2 \rightarrow ZnO + CO$

HgO (heat) $\rightarrow Hg + ½O_2$

Aqueous chemistry

	H_2O	Cl^-	OH^-	NH_3	S^{2-}	xS^{2-}
Zn^{2+}	$Zn(H_2O)_6^{2+}$	$ZnCl_4^{2-}$	$Zn(OH)_4^{2-}$	$Zn(NH_3)_4^{2+}$	ZnS	ZnS
Cd^{2+}	$Cd(H_2O)_6^{2+}$	$CdCl_4^{2-}$	$Cd(OH)_2$	$Cd(NH_3)_6^{2+}$	CdS	CdS
Hg^{2+}	$Hg(H_2O)_2^{2+}$	$HgCl_4^{2-}$	HgO	$Hg(NH_3)_2^{2+}$	HgS	HgS_2^{2-}

$M(NH_3)_4^{2+}(T_d) + 2NH_3 \leftrightarrows M(NH_3)_6^{2+}(O_h)$

L-Hg(II)-L

Group 12

Identification

$Zn(OH)_4^{2-} \rightarrow ZnS$ white

CdS Yellow

$HgS_2^{2-} \rightarrow HgS$ Black (cinnober)

HgS + aqua regia $\rightarrow HgCl_2$

$Hg^{2+} + Cu \rightarrow Hg,Cu + Cu^{2+}$

Hg_2^{2+}

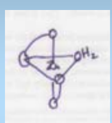
In solid $(HgCl)_n$ Hg-Hg shorter than in metal
Low vibrational frequency 172 cm^{-1}
$(HgCl)_n$ diamagnetic
E-measurements not consistent with Hg^+
$[Hg_2^{2+}]$ rather than $[Hg^+]^2$ in equilibria

"M^+"

$Zn + Zn^{2+} \leftrightarrows Zn_2^{2+}$ in fused salts
$Cd + Cd^{2+} \leftrightarrows Cd_2^{2+}$ in fused salts
$Hg + Hg^{2+} \leftrightarrows Hg_2^{2+}$ in aqueous solution
K~160
Calomel Hg_2Cl_2 insoluble
$Hg_2(NO_3)_2$ soluble

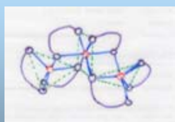
Zn - acac$^-$

CH_3
O=C
CH_2 – H^+
O=C
CH_3



$Zn(acac)_2H_2O$

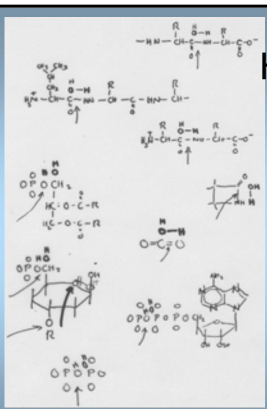
$[Zn(acac)_2]_3$



Some hydrolytic enzymes

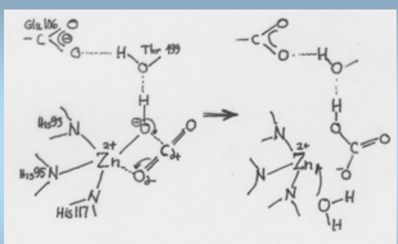
Enzyme	Hydrolysis catalysed	Metal ion
Carboxypeptidase	C-terminal peptide residues	Zn^{2+}
Leucine aminopeptidase	Leucine N-terminal peptide residue	Zn^{2+}
Dipeptidase	dipeptides	Zn^{2+}
Neutral protease	peptides	Zn^{2+}, Ca^{2+}
Collagenase	collagen	Zn^{2+}
Phospholipase C	phospholipids	Zn^{2+}
β-Lactamase II	β-Lactam ring	Zn^{2+}
Thermolysin	peptides	Zn^{2+}, Ca^{2+}
Alkaline phophatase	phosphate esters	Zn^{2+}
Carbonic anhydrase	carbondioxide	Zn^{2+}
A-amylase	glucosides	Zn^{2+}, Ca^{2+}
Phopholipase A_2	phospholipids	Ca^{2+}
Inorg. pyrophosphatase	pyrophosphate	Mg^{2+}
ATPase	ATP to ADP	Mg^{2+}

Hydrolytic enzymes



Carboxypeptidase
Leucine aminopeptidase
Dipeptidase
Neutral protease
Collagenase
Phospholipase C
β-Lactamase II
Thermolysin
Alkaline phophatase
Carbonic anhydrase
α-amylase
Phopholipase A_2
Inorg. Pyrophosphatase
ATPase

Carbonic anhydrase



$(H_2O)_5ZnOH_2^{2+} \leftrightarrows (H_2O)_5ZnOH^{+} + H^{+}$ pK~9.0

$CAZnOH_2^{2+} \leftrightarrows CAZnOH^{+} + H^{+}$ pK~7.1

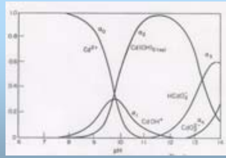
Apo- and M- CA

CAZn ⇆ apo CA + Zn^{2+}

apo CA + M^{2+} ⇆ CAM

CACd inactive in biological systems except in some Diatomers !,

but active at higher pH



$pK_1 \sim 9.7 \leftarrow$

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