Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

First row d-block metals

Some properties

M		M^{2+} r(6) Å	$E^{o}_{2+/0}$ V	pK M_{aq}^{2+}	logK EDTA	logβ_3 en	M^{3+} r(6) Å	$E^{o}_{3+/0}$ V	pK M_{aq}^{3+}	logK EDTA	$E^{o}_{3+/2+}$ V
Sc	$[Ar]4s^23d^1$	-	-				0.73	-2.08	5.1		
Ti	$[Ar]4s^23d^2$	0.86	-1.6				0.67	-1.19	2.2		-0.37
V	$[Ar]4s^23d^3$	0.79	-1.18		12.7		0.64	-0.87	2.8	25.9	-0.25
Cr	$[Ar]4s^13d^5$	0.80	-0.91		13.6		0.62	-0.74	3.8	23.4	-0.41
Mn	$[Ar]4s^23d^5$	0.83	-1.18	10.6	13.6	5.7	0.65	-0.12			1.54
Fe	$[Ar]4s^23d^6$	0.78	-0.44	9.5	14.3	9.5	0.65	-0.4	2.2	25.5	0.77
Co	$[Ar]4s^23d^7$	0.75	-0.28	8.9	16.1	13.8	0.61	0.43	0.8		1.84
Ni	$[Ar]4s^23d^8$	0.69	-0.25	10.6	18.6	18.6	0.6				large
Cu	$[Ar]4s^13d^{10}$	0.72	0.34	6.8	18.8	18.7					2.4
Zn	$[Ar]4s^23d^{10}$	0.74	-0.76	8.8	16.5	12.1					

Some MF_n and $MF_m^{(m-n)-}$

+1	+2	+3	+4	+5	+6	Ox state	+1	+2	+3	+4	+5
		ScF_3							ScF_6^{3-}		
		TiF_3	TiF_4						TiF_6^{3-}	TiF_6^{2-}	
	VF_2	VF_3	VF_4	VF_5					VF_6^{3-}	VF_6^{2-}	VF_6^{-}
	CrF_2	CrF_3	CrF_4	CrF_5	CrF_6				CrF_6^{3-}	CrF_6^{2-}	
	MnF_2	MnF_3	MnF_4						MnF_6^{3-}	MnF_6^{2-}	
	FeF_2	FeF_3							FeF_6^{3-}		
	CoF_2	CoF_3							CoF_6^{3-}	CoF_6^{2-}	
	NiF_2							NiF_6^{4-}	NiF_6^{3-}	NiF_6^{2-}	
	CuF_2							CuF_4^{2-}	CuF_6^{3-}		

Some MCl_n and $MCl_m^{(m-n)-}$

+1	+2	+3	+4	+5	+6	OX state	+1	+2	+3	+4	+5
		$ScCl_3$							$ScCl_6^{3-}$		
	$TiCl_2$		$TiCl_4$						$TiCl_6^{3-}$	$TiCl_6^{2-}$	
	VCl_2	VCl_3	VCl_4	VCl_5					VCl_6^{3-}; VCl_4^-		
	$CrCl_2$	$CrCl_3$	$CrCl_4$						$CrCl_6^{3-}$, $CrCl_4^-$		
	$MnCl_2$							$MnCl_4^{2-}$	$MnCl_5^{2-}$		
	$FeCl_2$	$FeCl_3$						$FeCl_4^{2-}$	$FeCl_4^-$		
	$CoCl_2$							$CoCl_4^{2-}$			
	$NiCl_2$							$NiCl_4^{2-}$			
CuCl	$CuCl_2$						$CuCl_2^-$	$CuCl_4^{2-}$			

$M + O_2$

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+1									Cu_2O	
+2							CoO	**NiO**	**CuO**	**ZnO**
					Mn_3O_4	**Fe_3O_4**	**Co_3O_4**			
+3	**Sc_2O_3**	Ti_2O_3	V_2O_3	**Cr_2O_3**	Mn_2O_3	Fe_2O_3	Co_2O_3			
+4		**TiO_2**	VO_2	CrO_2	MnO_2					
+5			**V_2O_5**							
+6				CrO_3						
+7					Mn_2O_7					

H^+ - Hydroxides - OH^-

	+	0	-	
Sc_2O_3	$Sc(H_2O)_6^{3+}$	$Sc(OH)_3$		$Sc(OH)_6^{3-}$
Ti_2O_3	$Ti(H_2O)_6^{3+}$	$Ti(OH)_3$		
TiO_2	TiO^{2+}	TiO_2		
V(II)	$V(H_2O)_6^{2+}$			
V_2O_3	$V(H_2O)_6^{3+}$	V_2O_{3aq}		
VO_2	VO^{2+}	VO_2	$[V_{18}O_{42}]^{12-}$	
V_2O_5	VO_2^+ V_2O_{5aq}	$[V_4O_{12}]^{4-}$	$VO_3(OH)^{2-}$	VO_4^{3-}
Cr_2O_3	$Cr(H_2O)_6^{3+}$	$Cr(OH)_3$	$Cr(OH)_4^-$	
CrO_3		H_2CrO_4	$Cr_2O_7^{2-}$	CrO_4^{2-}
Mn(II)	$Mn(H_2O)_2^{2+}$	$Mn(OH)_2$		
MnO_2				
Mn_2O_7		$HMnO_4$	MnO_4^-	
Fe(II)	$Fe(H_2O)_6^{2+}$	$Fe(OH)_2$		
Fe_2O_3	$Fe(H_2O)_6^{3+}$	Fe_2O_{3aq}		
CoO	$Co(H_2O)_6^{2+}$	$Co(OH)_2$		$Co(OH)_4^{2-}$
NiO	$Ni(H_2O)_6^{2+}$	$Ni(OH)_2$		
CuO	$Cu(H_2O)_4^{2+}$	$Cu(OH)_2$	$Cu(OH)_4^{2-}$	
ZnO	$Zn(H_2O)_6^{2+}$	$Zn(OH)_2$	$Zn(OH)_4^{2-}$	

Sulphides

• MnS	faintly red	acetic acid
• FeS	black	hydrochloric acid
• CoS	black	nitric acid
• NiS	black	nitric acid
• CuS	black	nitric acid
• ZnS	white	acetic acid
• FeS_2	fools gold	

M – L interactions: consider some general atomic properties

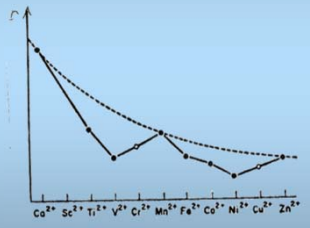
- Size
- Electron configuration
- Electronegativity
- Typical binding mode with metals
- Typical binding mode with non metals
- Typical oxidation state(s)
- Typical binding geometry (VSEPR p-block molecules)

M – L interactions: consider properties of M^{n+}

- Stability of oxidation states : E^o
- Hard or softer M^{n+}
- Acidity of M_{aq}^{n+}
- The d^n-system for M^{n+} - structure
  - Typical coordination number (+geometry)
  - Distortion of octahedral coordination (d^4, d^9)
- The d^n-system for M^{n+} - kinetics
  - d^3, d^6 ls, ….
  - redox, substitution reactions

Sizes (cf. lattice energies)

- CFSE's reflected in bond lengths



M – L interactions: consider properties of L

- Acid-base properties of L (σ-bonding)
- Hard or softer ligating atom(s) in L
- Ligating atom to give linkage isomers
- Chelation
- L in the spectrochemical series
- Stability towards oxidation or reduction (E^o)

M – L interactions: stability

- Match between hard/soft properties
- Influence of X in X-M - L
- Predictions: value of $\log K_n$
  - Series of stability of M^{2+} - L
  - Statistical ratio between consecutive K's
  - Variation down a group
- Competition between M^{2+} and H^+ for L
- Competition between L and OH^- for M^{2+}
- Match between redox properties

M – L interactions: structure

- Typical and max. coordination number
- Size of M^{n+} and chelate rings
- Isomerism
- Steric hindrance
- Spectra
  - position (λ_{max}) – average environment
  - intensity (ε_{max}) – spin forbidden, parity forbidden...
- d^n: High or low spin
  - magnetism
  - Structure

M – L interactions: Kinetics

- acid-base (very fast in water)
- redox (consider electron or atom transfer route - mechanism)
- substitution (bond breaking, d^n-electron configuration, crowding – mechanism, trans-effect…)