Introduction to d and f-Block Chemistry

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

s-block

d-block

p-block

*Lanthanides	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**Actinides	**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

f-block

Three Different Periodic Tables

1	1 H																	2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

s-block d-block p-block

*Lanthanides	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**Actinides	**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

f-block

1	1 H																	2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
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5	37 Rb	38 Sr	39 Y		40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

s-block d-block p-block

*Lanthanides	*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**Actinides	**	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

f-block

Three Different Periodic Tables

1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
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7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

s-block d-block p-block

*Lanthanides + 1	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**Actinides + 1	**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

f-block

Introduction to d and f-Block Chemistry

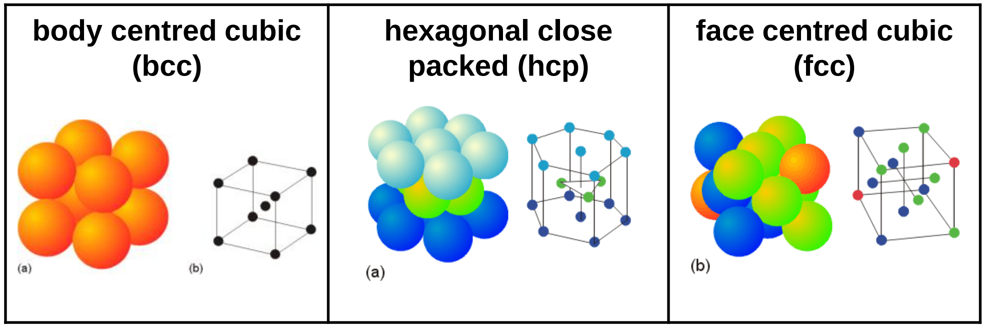
Melting Points (°C)

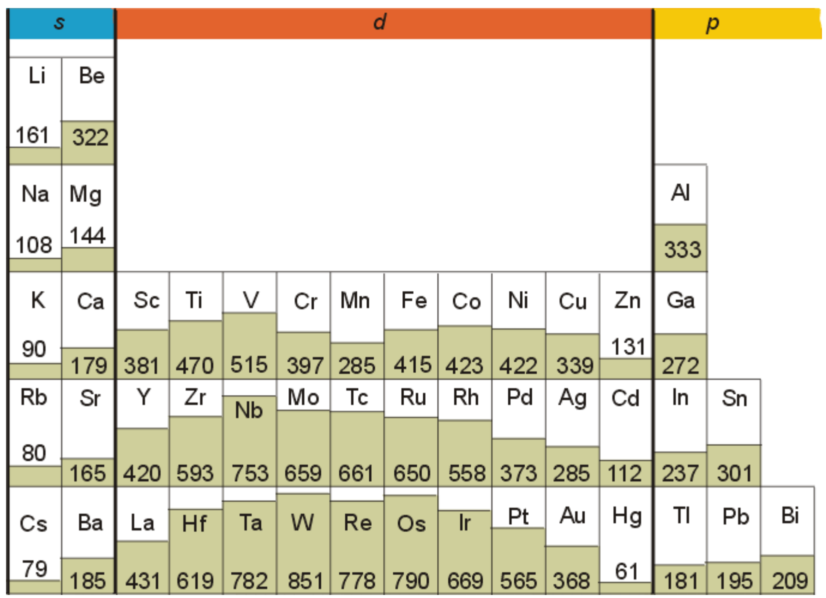
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
	-259.14																	-272
2	Li	Be											B	C	N	O	F	Ne
	180.54	1278											2300	3500	-209.9	-218.4	-219.62	-248.6
3	Na	Mg											Al	Si	P	S	Cl	Ar
	97.8	650											660.37	1410	44.1	112.8	-100.98	-189.3
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	63.65	839	1539	1660	1890	1857	1245	1535	1495	1453	1083	419.58	29.78	937.4	817	217	-7.2	-157.2
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	38.89	764	1523	1852	2468	2617	2200	2250	1966	1552	961.93	320.9	156.61	231.9	630	449.5	113.5	-111.9
6	Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	28.5	725		2150	2996	3410	3180	3045	2410	1772	1064.43	-38.87	303.5	327.5	271.3	254	302	-71
7	Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub						
	27	700		?	?	?	?	?	?	?	?	?						
			*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				920	795	935	1010	?	1072	822	1311	1360	1412	1470	1522	1545	824	1656
			**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
				1050	1750	1600	1132	640	639.5	994	1340	?	?	?	?	?	?	?

Boiling Points (°C)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
	-252.87																	-268.6
2	Li	Be											B	C	N	O	F	Ne
	1347	2970											2550	4827	-195.8	-183	-188.14	-246.1
3	Na	Mg											Al	Si	P	S	Cl	Ar
	552.9	1107											2467	2355	280	444.6	-34.6	-186
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	774	1484	2832	3287	3380	2672	1962	2750	2870	2732	2567	907	2403	2830	613	684.9	58.78	-153.4
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	688	1384	3337	4377	4927	4612	4877	3900	3727	2927	2212	765	2000	2270	1750	989.8	184	-108.1
6	Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	678.4	1140		5400	5425	5660	5627	5027	4527	3827	2807	356.58	1457	1740	1560	962	337	-61.8
7	Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub						
	677	1737		?	?	?	?	?	?	?	?	?						
			*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				3469	3257	3127	3127	?	1900	1597	3233	3041	2562	2720	2510	1727	1466	3315
			**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
				3200	4790	?	3818	3902	3235	2607	?	?	?	?	?	?	?	?

Introduction to d and f-Block Chemistry





ΔH_{vap} ($kJmol^{-1}$) for the metallic elements in the s-, p- and d-blocks

Introduction to d and f-Block Chemistry

Abundances of the elements in the earth's crust:

(Note: significant differences between the core and mantle)

% abundance	elements
>10	O, Si
10^{-1}	Al, Fe, Ca, Na, K, Mg
$1\text{-}10^{-1}$	H, Ti, Cl, P
$10^{-1}\text{-}10^{-2}$	Mn, F, Ba, Sr, S, C, N, Zr, V, Cr
$10^{-2}\text{-}10^{-3}$	Rb, Ni, Zn, Ce, Cu, Y, La, Nd, Co, Sc, Li, Nb, Ga, Pb, Th, B
$10^{-3}\text{-}10^{-4}$	Pr, Br, Sm, Gd, Ar, Yb, Cs, Dy, Hf, Er, Be, Xe, Ta, Sn, U, As, W, Mo, Ge, Ho, Eu
$10^{-4}\text{-}10^{-5}$	Tb, I, Tl, Tm, Lu, Sb, Cd, Bi, In
$10^{-5}\text{-}10^{-6}$	Hg, Ag, Se, Ru, Te, Pd, Pt
$10^{-6}\text{-}10^{-7}$	Rh, Os, Ne, He, Au, Re, Ir
$10^{-7}\text{-}10^{-9}$	Kr
$10^{-9}\text{-}10^{-20}$	Ra, Pa, Ac, Po, Rn, Np, Pu, Pm
$< 10^{-20}$	Fr, At, transplutonium elements

Blue = 1st row TM, Red = 2nd row TM, Green = 3rd row TM

- In general, 1st row TMs are more abundant than 2nd or 3rd row TMs.

Introduction to d and f-Block Chemistry

Mineral sources and methods of recovery for some commercially important d-block metals:

Metal	Principal minerals	Method of recovery
Titanium	Ilmenite, $FeTiO_3$ Rutile, TiO_2	$TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO$ followed by reduction of $TiCl_4$ with Na or Mg
Vanadium	Vanadinite, $Pb_5(VO_4)_3Cl$	
Chromium	Chromite, $FeCr_2O_4$	$FeCr_2O_4 + 4C \rightarrow Fe + 2Cr + 4CO$
Molybdenum	Molybdenite, MoS_2	$2MoS_2 + 7\ O_2 \rightarrow 2MoO_3 + 4SO_2$ followed by either: $MoO_3 + 2Fe \rightarrow Mo + Fe_2O_3$ or $MoO_3 + 3H_2 \rightarrow Mo + 3H_2O$
Tungsten	Scheelite, $CaWO_4$ Wolfamite, $FeMn(WO_4)_2$	$CaWO_4 + 2HCl \rightarrow WO_3 + CaCl_2 + H_2O$ followed by $2WO_3 + 6H_2 \rightarrow 2W + 6H_2O$
Manganese	Pyrolusite, MnO_2	$MnO_2 + C \rightarrow Mn + CO_2$
Iron	Hematite, Fe_2O_3 Magnetite, Fe_3O_4 Limonite, FeO(OH)	$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
Cobalt	Cobaltite, CoAsS Smaltite, $CoAs_2$ Linnaeite, Co_3S_4	byproduct of copper and nickel production
Nickel	Pentlandite, $(Fe,Ni)_6S_8$	$2NiS + 2O_2 \rightarrow 2Ni + 2SO_2$
Copper	Chalcopyrite, $CuFeS_2$ Chalcocite, Cu_2S	$2CuFeS_2 + 2SiO_2 + 5O_2 \rightarrow 2Cu + 2FeSiO_3 + 4SO_2$

- **Oxides** preferred for 1st row and early TMs
- **Sulfides** preferred for 2nd/3rd row and late TMs

Oxidation States

Common oxidation states for transition metal coordination complexes:

- the most important/common oxidation states are highlighted in bold

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	0	0	0	0	0	0	0	0	
		1	1	1	1	1	1	**1**	
	2	2	**2**	**2**	**2**	**2**	**2**	**2**	**2**
3	3	**3**	**3**	3	**3**	**3**	3	3	
	4	**4**	4	4	4	4	4	4	
		5	5	5					
			6	6	6				
				7					

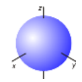
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
			0	0	0	0	0		
				1		**1**		**1**	
	2	2	2	2	**2**	2	**2**	2	**2**
3	3	3	3	3	**3**	**3**		3	
	4	4	4	**4**	**4**	4	**4**		
		5	5	**5**	5	5			
			6	6	6	6			
				7	7				
					8				

Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
			0	0	0	0	0	0	
				1		**1**		**1**	**1**
	2	2	2	2	**2**	2	**2**	2	**2**
3	3	3	3	**3**	3	**3**		**3**	
	4	4	**4**	**4**	**4**	4	**4**		
		5	**5**	**5**	5	**5**	5		
			6	**6**	6	6	6		
				7	7				
					8				

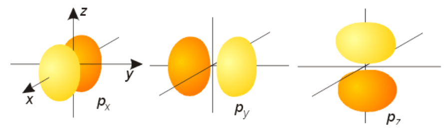
- Many transition metals exhibit a wide range of oxidation states (remember that oxidation states imply an exaggeration of ionic character)

Boundary Surface Diagrams

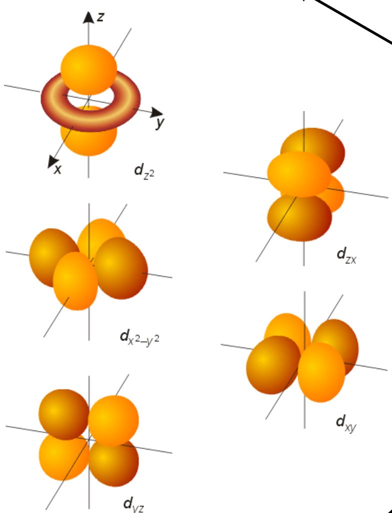
1s-orbital (g)



2p-orbitals (u)



3d-orbitals (g)



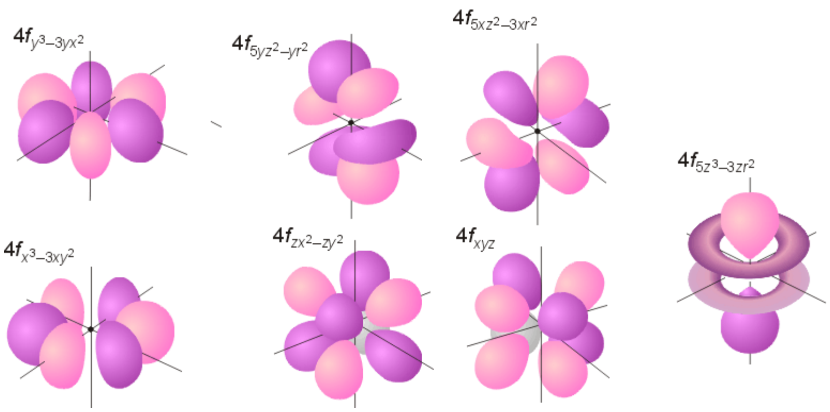
- The d_{z2} and $d_{x2\text{-}y2}$ orbitals are called AXIAL orbitals because they lie along the x/y/z-axes.
- The d_{xy}, d_{xz} and d_{yz} orbitals are named INTER-AXIAL orbitals because they lie between the x/y/z-axes

g = gerade (German)
u = ungerade (German)

g and u indicate *parity*, which is the symmetry of an object with respect to inversion.

g = inversion centre
u = no inversion centre

4f-orbitals (u)



Electron Configuration

For *transition metal cations* or *transition metal complexes*, electron configuration is more simple than for the bulk metal:

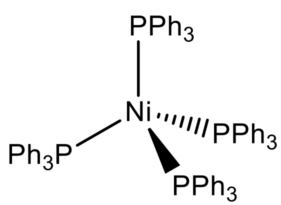
- All valence electrons are in (n-1)d orbitals
- There are no electrons in ns orbitals

THIS IS VERY IMPORTANT

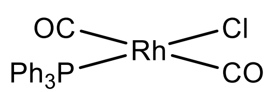
- The result is that TM cations always have the electronic configuration: **$ns^0(n-1)d^x$**.

- The ability to work out the number of d-electrons is crucial to understanding the behaviour of transition metal complexes, so is crucial for Chemistry 3840 and 4000! Therefore, you should take the time to practice working out the electronic configuration of transition metal ions such as Ti^{II}, Fe^{III}, Zn^{II}, Ru^{VII}, Pt^{II}, Mo^{III}, Ti^{IV}, V^{IV}, Rh^{I}, Pt^{IV} *etc*.

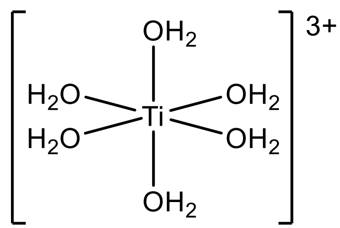
Examples:



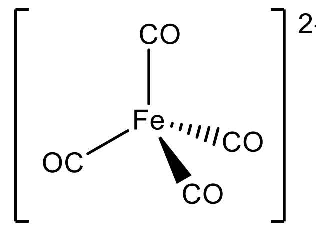
$Ni^0 = d^{10}$



$Rh^I = d^8$



$Ti^{III} = d^1$



$Fe^{2-} = d^{10}$

Note that this is a highly unusual oxidation state, and is only possible with ligands such as CO. However, it is included to illustrate, that you only need to worry about d-electrons, regardless of whether the metal carries a formal positive charge, is neutral or carries a negative charge.