Chapter 23

Transition Metals and Coordination Chemistry

The Transition Metals: Exact Definition

Transition metal: *An element whose atom has an* ***incomplete d*** *subshell or which can give rise to cations with an* ***incomplete d*** *subshell.* (official IUPAC definition)

1 1A																	18 8A
1 H	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
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
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
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
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112	(113)	114	(115)	116	(117)	(118)

The Transition Metals: Exact Definition

- What about Zn, Cd, and Hg?
  - Officially, they are **NOT** transition metals (often called "noble" metals)
  - Unofficially, they usually grouped with transition metals because of similarities in chemistry and because they are completing the ***d***-orbital filling.

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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
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
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
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Electronic Configuration of *d*-block metals

d-block

3	4	5	6	7	8	9	10	11	12
Sc 21 $-4s^2$ $3d^1$	Ti 22 $-4s^2$ $3d^2$	V 23 $-4s^2$ $3d^3$	Cr 24 $-4s^1$ $3d^5$	Mn 25 $-4s^2$ $3d^5$	Fe 26 $-4s^2$ $3d^6$	Co 27 $-4s^2$ $3d^7$	Ni 28 $-4s^2$ $3d^8$	Cu 29 $-4s^1$ $3d^{10}$	Zn 30 $-4s^2$ $3d^{10}$
Y 39 $-5s^2$ $4d^1$	Zr 40 $-5s^2$ $4d^2$	Nb 41 $-5s^1$ $4d^4$	Mo 42 $-5s^1$ $4d^5$	Tc 43 $-5s^2$ $4d^5$	Ru 44 $-5s^1$ $4d^7$	Rh 45 $-5s^1$ $4d^8$	Pd 46 $-5s^0$ $4d^{10}$	Ag 47 $-5s^1$ $4d^{10}$	Cd 48 $-5s^2$ $4d^{10}$
Lu 71 $-6s^2$ $5d^1$	Hf 72 $-6s^2$ $5d^2$	Ta 73 $-6s^2$ $5d^3$	W 74 $-6s^2$ $5d^4$	Re 75 $-6s^2$ $5d^5$	Os 76 $-6s^2$ $5d^6$	Ir 77 $-6s^2$ $5d^7$	Pt 78 $-6s^1$ $5d^9$	Au 79 $-6s^1$ $5d^{10}$	Hg 80 $-6s^2$ $5d^{10}$

Where Found? - Minerals

- Most metals, including transition metals, are found in solid inorganic compounds known as **minerals**.
- Minerals are named by common, not chemical, names.

TABLE 23.1 • Principal Mineral Sources of Some Transition Metals

Metal	Mineral	Mineral Composition
Chromium	Chromite	$FeCr_2O_4$
Copper	Chalcocite	Cu_2S
	Chalcopyrite	$CuFeS_2$
	Malachite	$Cu_2CO_3(OH)_2$
Iron	Hematite	Fe_2O_3
	Magnetite	Fe_3O_4
Manganese	Pyrolusite	MnO_2
Mercury	Cinnabar	HgS
Molybdenum	Molybdenite	MoS_2
Titanium	Rutile	TiO_2
	Ilmenite	$FeTiO_3$
Zinc	Sphalerite	ZnS

Properties of Transition Metals

- What's so special about transition metals
  - atoms and ions have partially filled ***d*** subshells
  - low energy, unoccupied ***d*** orbitals
- Results
  - ions of variable oxidation state (i.e. Fe^{2+} and Fe^{3+})
  - magnetic properties
  - Form complex ions (act as Lewis acids)
  - many make good catalysts (i.e. Pt, Pd, Rh in catalytic converter)
  - ion orbital energy differences = visible photon energy (colored)

Ti^{3+} Cr^{3+} Mn^{2+} Fe^{3+} Co^{2+} Ni^{2+} Cu^{2+}

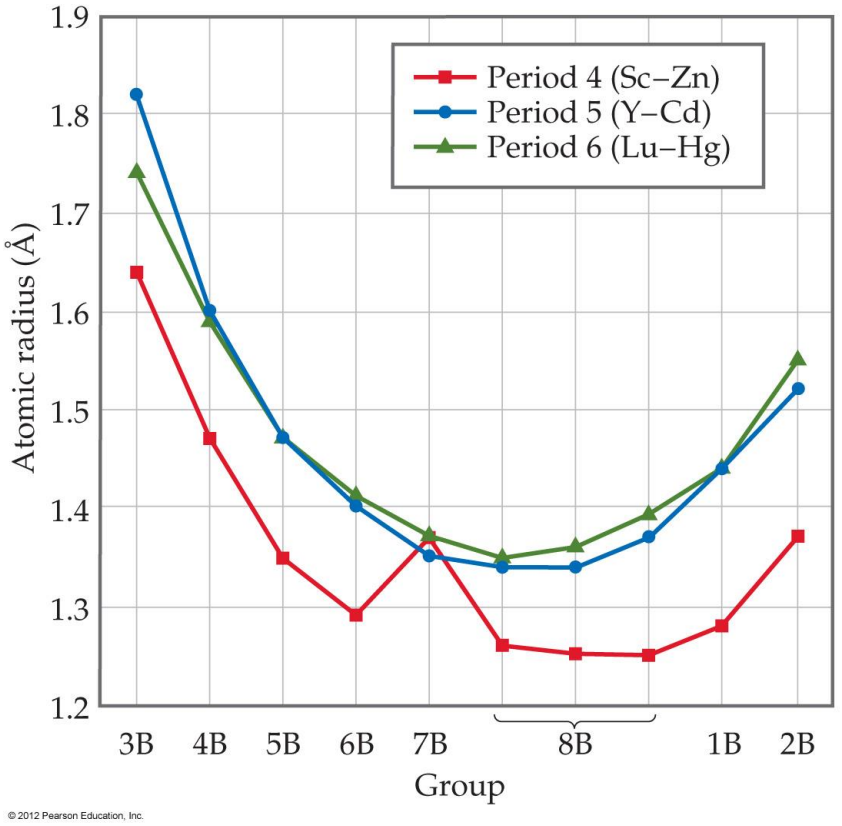
Properties of "First-Row" TM

TABLE 23.2 • Properties of the Period 4 Transition Metals

Group	3B	4B	5B	6B	7B	8B			1B	2B
Element:	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Ground state electron configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
First ionization energy (kJ/mol)	631	658	650	653	717	759	758	737	745	906
Radius in metallic substances (Å)	1.64	1.47	1.35	1.29	1.37	1.26	1.25	1.25	1.28	1.37
Density (g/cm^3)	3.0	4.5	6.1	7.9	7.2	7.9	8.7	8.9	8.9	7.1
Melting point (°C)	1541	1660	1917	1857	1244	1537	1494	1455	1084	420

Atomic Radii

- Left to right across a row, the radius of TM decrease then increase.
- Increasing effective nuclear charge tends to make atoms smaller.
- However, the strongest (and shortest) metallic bonds are found in the center of TM. Move further to right filling anti-bonding orbitals so bonds weaken.



Atomic Radii

- Mn: radius inc. – likely due to electron going into ½-filled 4*s* subshell and Mn still fairly small
  – more repulsion

- Periods 5 and 6 – size about same.

  period 6 – lanthanide contraction

  adding protons to nucleus & filling *4f* orbitals which don't shield well
  - inc. effective nuclear chg.
  - offsets expected inc. in size due to adding electrons as go down group
  - similar chemical prop.

Electron Config. & Oxidation States

For a given TM the (n-1)*d* orbitals smaller than n*s* and n*p* orbitals (wave fncs drop off more rapidly than n*s* and n*p*)

- *d*-electrons can behave like valence electrons or like core electrons

- depends on location in PT and atom's environment

TM charges and oxidation states

TM lose outer *s*-electrons before *d*-electrons

Fe : [Ar]3$d^6$4s^2

Fe^{2+} : [Ar]3d^6

Fe^{3+} : [Ar]3d^5

Cu : [Ar]3d^{10}4s^1

Cu^{+} : [Ar]3d^{10}

Cu^{2+} : [Ar]3d^9

Ex: What are the electron config. for Co^{2+} and Co^{3+}?

Ex: What is the electron config. for Cr^{3+}?

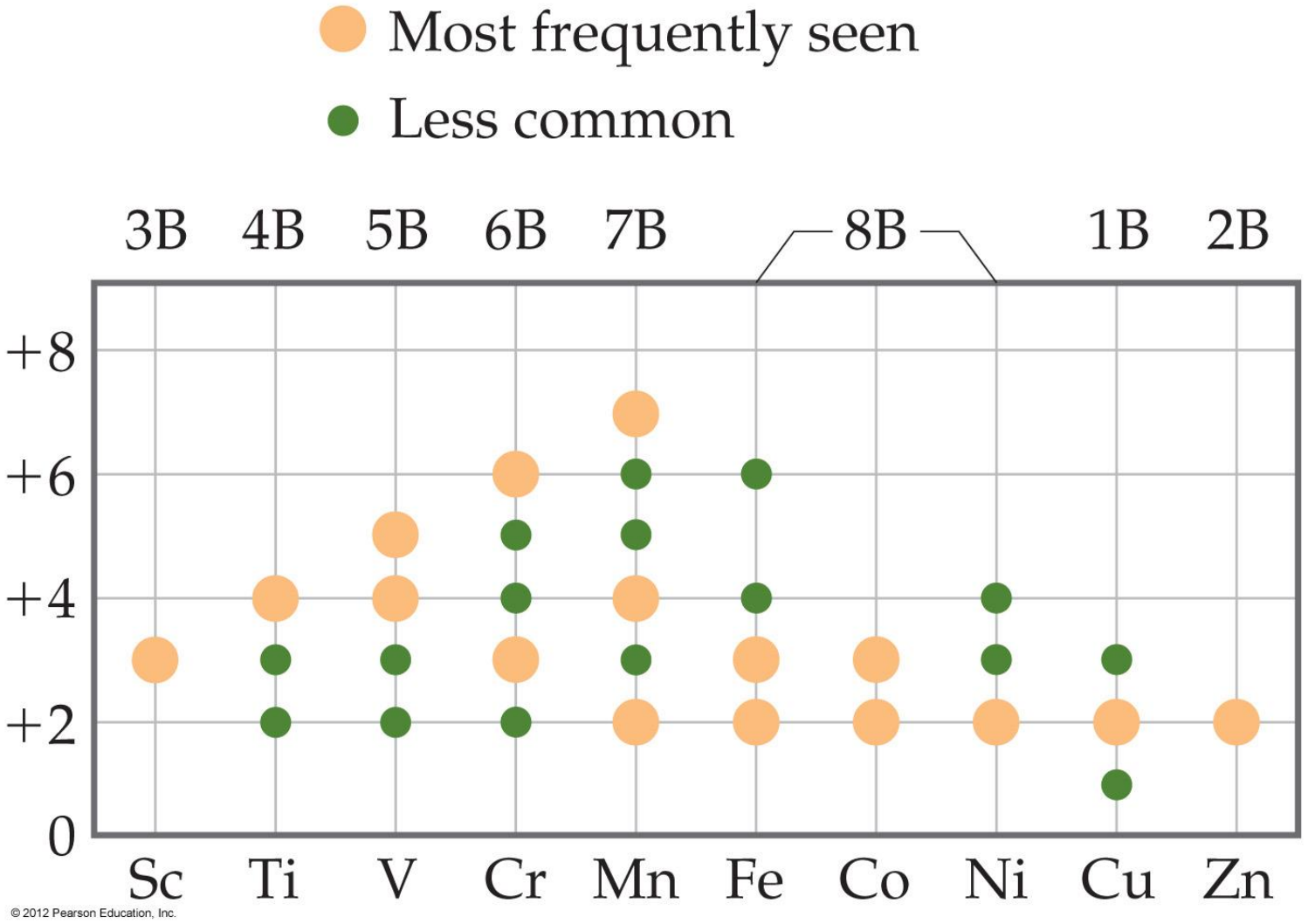
Because most TM have partially occupied *d* subshells, the metals and/or their cmpds often:

- Have more than one oxidation state

- colored

- exhibit magnetic properties

Oxidation States



Most common: +2

- due to loss of 4*s* e^-

Next most common: +3

- Sc (grp 3B) always +3
  - noble gas config. (Sc^{3+} is [Ar])

Max. ox. st. inc from +3 to +7 from Sc to Mn then dec. beyond Mn

- *d* electrons become more core like
- Zn always +2 (can't remove *d* e^-)

Higher ox. st.

- No isolated ions > +4 (e.g. in soln.)

- inc. covalent character

most common oxidation state for Ti is +4, but the Ti^{4+} ion not found as an isolated ion

- bonding is highly covalent

$Ti \Rightarrow [Ar]4s^2 3d^2$

TiO_2 Ti ox. # = +4

Mn highest oxidation state is +7,

- only found in MnO_4^-

Periods 5 & 6 : ox. st. as high as +8

- larger 4*d* & 5*d* orb

Max. ox. st. – only when metal combined w. most electroneg. elements

O, F, sometimes Cl

	VO^{3+}	VO^{2+}	V^{3+}	V^{2+}
Ox. St.	+5	+4	+3	+2
Color	yellow	blue	blue-grn	violet

Magnetism

Electron possesses spin

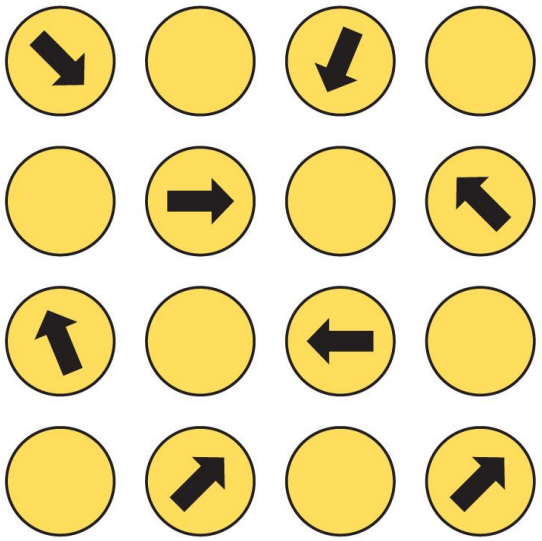
- has magnetic moment
  (behaves like a tiny magnet)

Diamagnetic – all e^- paired

- magnetic moments cancel
- "non"magnetic
  - actually very weakly repelled by magnet

Paramagnetic

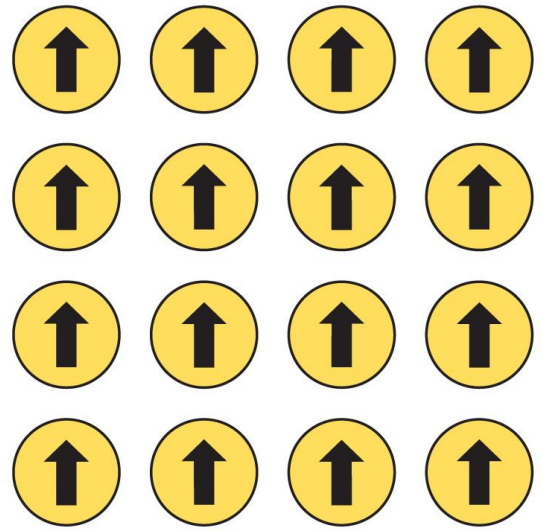
- Results from an atom having unpaired electrons.
- Not influenced by e^- on adjacent atoms or ions
- Magnetic moments randomly oriented
- In magnetic field mag. mom. align parallel to each other
- Net attraction to mag. field



(a) Paramagnetic; spins random; spins do align if in magnetic field

Ferromagnetic

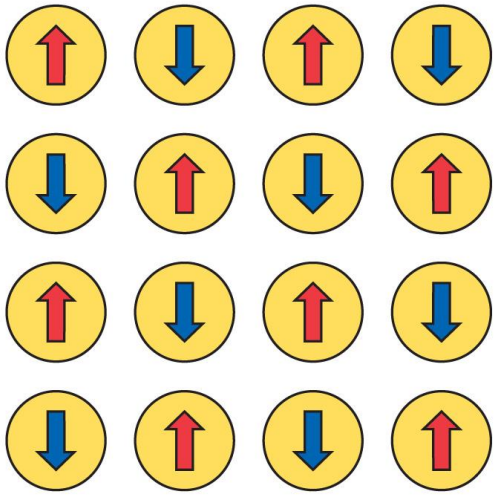
- Unpaired e^- influence each other to align in the same direction
- Exhibit strong attractions to an external mag. field
- Permanent magnets.
- Fe, Co, Ni,
  alloys (CrO_3, Fe_2O_4)



(b) Ferromagnetic; spins aligned; spins become random at high temperature

Antiferromagnetism

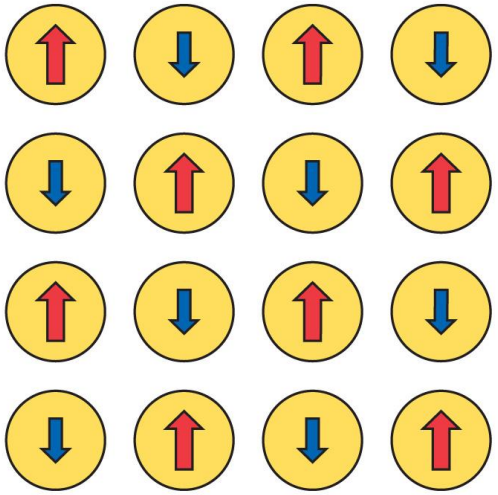
- Unpaired e^- on adjacent atoms align in opposing directions.
- These magnetic fields tend to cancel each other.
- Cr, FeMn alloys, Fe_2O_3, $LaFeO_3$, MnO



(c) Antiferromagnetic; spins opposed and cancel; spins become random at high temperature

Ferrimagnetic

- Spins align opposite each other, but the spins are not equal
- NET magnetic field
- Prop. similar to ferromag. materials
- Examples are $NiMnO_3$, $Y_3Fe_5O_{12}$, and Fe_3O_4.



(d) Ferrimagnetic; unequal spins opposed but do not cancel; spins become random at high temperature

Ferromag, Ferrimag & Antiferromag become paramag. at temp. above a critical temp.

- spins become random
- Curie Temp., T_C, ferromag & ferrimag
- Néel Temp., T_N, antiferromag