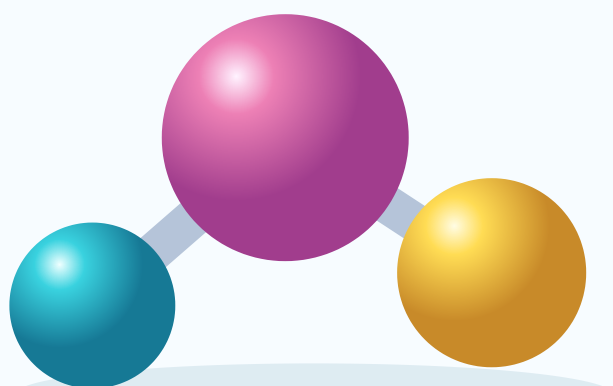


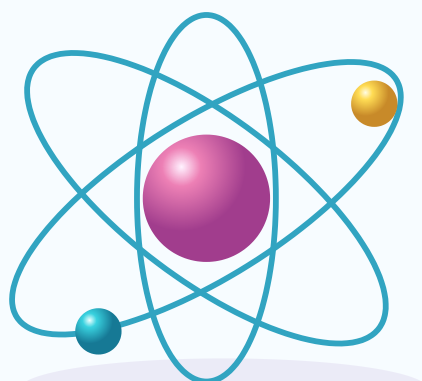
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- | | | |
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| 01 | Chemical Periodicity | 3 |
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Space to pause. Space to revise.

One completely blank buffer page follows every chapter, including the final chapter. Use it for quick recall, your own examples or extra notes.

Chapter opening numbers and the page numbers below match this separate volume.

CHAPTER 01

- | Group | 1 | 2 | 15 | 16 | 17 | 18 |
|--------|---------------|-----------------------|------------|------------|----------|-------------|
| Family | Alkali metals | Alkaline-earth metals | Pnictogens | Chalcogens | Halogens | Noble gases |

Groups 1-2 $\rightarrow$ s; 3-12 $\rightarrow$ d; 13-18 $\rightarrow$ p. He: $1s^2$, group 18. • f rows: Ce(58)–Lu(71); Th(90)–Lr(103). • d-row ends: Sc(21)–Zn(30); Y(39)–Cd(48); La(57)–Hg(80); Ac(89)–Cn(112). • This layout links 28 f-elements + 4 group-3 positions = 32 positions. All 32 are not formal group-3 members. Another layout uses Lu/Lr in group 3.

Period n	1	2	3	4	5	6	7
Subshells filled	1s	2s, 2p	3s, 3p	4s, 3d, 4p	5s, 4d, 5p	6s, 4f, 5d, 6p	7s, 5f, 6d, 7p
No. of elements	2	8	8	18	18	32	32
Last noble gas	He (2)	Ne (10)	Ar (18)	Kr (36)	Xe (54)	Rn (86)	Og (118)

Use $n = \text{period number}$. • Example: $n = 6 \rightarrow (6+2)^2/2 = 32 \text{ elements}$.

Chemical Periodicity

Names above atomic number 100 • Blockwise configurations

03 Names above atomic number 100

Digit	0	1	2	3	4	5	6	7	8	9
Root	nil	un	bi	tri	quad	pent	hex	sept	oct	enn

105
digits

un + nil + pent + ium
unnilpentium

Unp

temporary

Db
dubnium

official

• Join the digit roots + 'ium'. • 105 → un + nil + pent + ium → unnilpentium (Unp). • This was its temporary name. Official name → dubnium (Db).

Z	Official name	Symbol	Memory cue
101	Mendelevium	Md	Modi ka
102	Nobelium	No	Number
103	Lawrencium	Lr	Lahore ke
104	Rutherfordium	Rf	Refugee ne
105	Dubnium	Db	Dubai aur
106	Seaborgium	Sg	Singapore ke
107	Bohrium	Bh	Bahar diya
108	Hassium	Hs	Hans
109	Meitnerium	Mt	Mat
110	Darmstadtium	Ds	Dus
111	Roentgenium	Rg	Rang ka
112	Copernicium	Cn	Kansa
113	Nihonium	Nh	Nahi
114	Flerovium	Fl	Flower
115	Moscovium	Mc	Mac
116	Livermorium	Lv	Lover se
117	Tennessine	Ts	Tussi
118	Oganesson	Og	O god

04 Blockwise configurations

$$s : ns^{1-2} \quad p : ns^2 np^{1-6}$$

Exception → He = 1s². It belongs to group 18.

$$d : (n-1)d^{1-10} ns^{0-2}$$

ns² → usual • ns¹ → some exceptions • Pd → 4d¹⁰5s⁰

Chemical Periodicity

f-series + important exceptions • Case I: atomic number Z is given

05 f-series + important exceptions

$$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$$

Usual f-series form. • Special case: Th = [Rn]6d²7s². • Check the actual configuration for exceptions.

Element	Cr (24)	Cu (29)	Pd (46)	La (57)	Ac (89)	Gd (64)
Ground-state configuration	[Ar] 3d ⁵ 4s ¹	[Ar] 3d ¹⁰ 4s ¹	[Kr] 4d ¹⁰ 5s ⁰	[Xe] 5d ¹ 6s ²	[Rn] 6d ¹ 7s ²	[Xe] 4f ⁷ 5d ¹ 6s ²

06 Case I: atomic number Z is given



Check exceptions • f-series and shortcut limits are listed below

- 1 **Period** → Find the first noble gas with $Z \geq$ the given Z ; use its period.
- 2 **Groups 1–2** → s; 3–12 → d; 13–18 → p.
- 3 **Exception:** He has 1s².

- $Z = 58–71 \rightarrow$ Ce–Lu, period 6, f-series.
- $Z = 90–103 \rightarrow$ Th–Lr, period 7, f-series.
- These rows are linked to group 3 in this layout.
- $Z = 104–118 \rightarrow$ period 7; group = last two digits.
- III → group 11; 112 → group 12.

$$G = Z + 18 - Z_{\text{next noble gas}}$$

Shortcut for suitable main/d-block elements. • Skip f-series and $Z \leq 12$. • For period 6/7: if the result is negative, replace 18 by 32.

- 1 $Z = 21 \rightarrow$ period 4.
- 2 $\text{Group} = 21 + 18 - 36 = 3 \rightarrow$ d-block.
- 3 $Z = 55 \rightarrow$ period 6.
- 4 $55 + 18 - 86 = -13 \times$
- 5 $55 + 32 - 86 = 1 \checkmark \rightarrow$ s-block.

Chemical Periodicity

Case II: configuration is given • Find the block

07 Case II: configuration is given

- Usually, period = highest occupied n .
- $1s^2 2s^2 2p^6 3s^2 3p^3 \rightarrow n = 3 \rightarrow$ period 3.
- Exception to this shortcut: **Pd belongs to period 5.**

Block	Configuration	Group shortcut
s	ns^{1-2}	ns electrons; He $\rightarrow$ group 18
p	$ns^2 np^{1-6}$	$12 + np$ electrons
d	$(n-1)d^{1-10} ns^{0-2}$	$(n-1)d$ electrons + ns electrons
f	f-series configuration	Linked to group 3 in this layout; no single group number for all f-elements

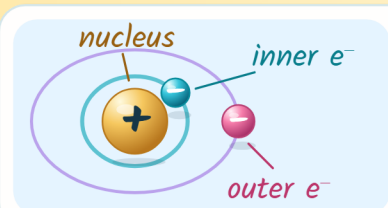
08 Find the block

- Block** $\rightarrow$ Check the subshell being filled.
- $[\text{Xe}]6s^1 \rightarrow$ Cs: period 6, group 1, s-block.
- $[\text{Ar}]3d^5 4s^2 \rightarrow$ Mn: period 4, d-block.
- Outermost $ns^2 np^{1-6} \rightarrow$ p-block.** A filled inner p-shell does not decide the block.

09 More configuration examples

- $[\text{Ar}]3d^{10} 4s^2 4p^3 \rightarrow$ period 4, p-block; group = $12+3 = 15$.
- $[\text{Kr}]4d^{10} 5s^1 \rightarrow$ period 5, d-block; group = $10+1 = 11$.
- f-series:** $(n-2)f^{1-14}(n-1)d^{0-1} ns^2$; linked to group 3 in this layout.

10 Shielding + effective nuclear charge



Inner electrons shield the nucleus

Less nuclear pull reaches an outer electron.

$$\text{Effective pull: } Z_{\text{eff}} = Z - \sigma$$

- Shielding** $\rightarrow$ Other electrons reduce the nucleus's pull on an outer electron.
- Same-shell shielding/penetration order:** $s > p > d > f$.
- d and f electrons shield poorly.

$$Z_{\text{eff}} = Z - \sigma$$

Z_{eff} = effective nuclear charge • Z = nuclear charge • σ = shielding constant

- > **Contraction trend in these notes:** transition < lanthanoid < actinoid.
- > **4f and 5f electrons shield poorly** $\rightarrow$ greater inward pull.
- > **Across a period:** n same; $Z_{\text{eff}} \uparrow \rightarrow$ size $\downarrow$.
- > **Down a group:** new shell added $\rightarrow$ size $\uparrow$.

Chemical Periodicity

Ionic size • s- and p-block size

11 Ionic size

$$r(M) > r(M^+) > r(M^{2+}) > r(M^{3+})$$

Same element: more electrons removed → stronger pull on remaining electrons → smaller cation.

$$r(X) < r(X^-) < r(X^{2-}) < r(X^{3-})$$

Same element: electrons added → repulsion ↑ → anion size ↑. • Compare only ions that can exist in the stated conditions.

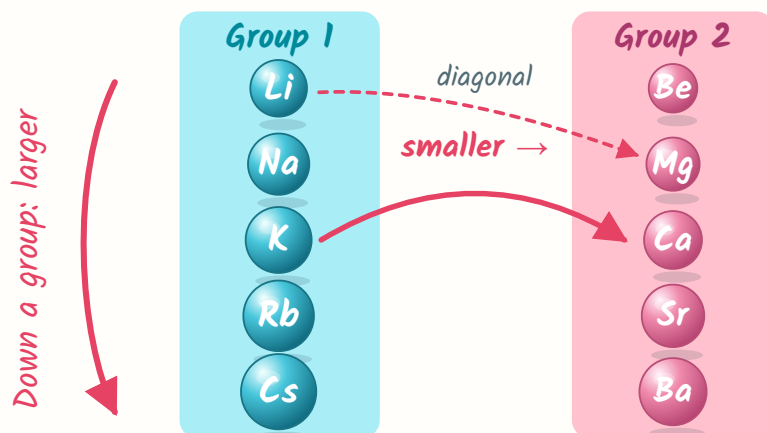
10 electrons each • nuclear charge ↑ → size ↓



• Isoelectronic = same number of electrons. • **Nuclear charge** ↑ → size ↓. • $Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$. • **Same-element trend**: positive charge ↑ → smaller; negative charge ↑ → larger.

12 s- and p-block size

Atomic size: spot the trend



Down a group:
larger

Across a period:
smaller →

$Li^+ \approx Mg^{2+}$
in comparable
coordination.

Sphere sizes are schematic, not numerical radii.

Down a group → size ↑. • Group 1 → group 2 → size ↓. • Diagonal ionic comparison: $Li^+ \approx Mg^{2+}$, using comparable radius data.

- **Group 13**: $B < Ga < Al < In < Tl$.
- $Ga = [Ar]3d^{10}4s^24p^1$.
- **Poor 3d shielding** → Z_{eff} ↑ → Ga smaller than Al (transition contraction).
- **Groups 14–18**: size generally ↑ downward.
- **Compare the same type of radius.**

Chemical Periodicity

3d-series size • Important size orders

13 3d-series size



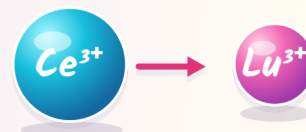
Metallic-radius pattern: falls at first → nearly constant in the middle → rises near the end. • Exact values depend on the radius data used.

- **Mn:** $3d^5$; weaker metallic bonding and looser packing give a larger radius in this sketch.
- **Early series:** nuclear pull dominates.
- **Near Cu/Zn:** d-shell filling and bonding changes reduce contraction.

14 Important size orders

- Nearby metals are generally larger than nonmetals.
- **Given size orders:** $\text{F} < \text{Cl} < \text{Br} < \text{I} < \text{Li}$; $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^- < \text{Li}^+$.
- **Period 2:** $\text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F}$.
- Ne appears larger because its van der Waals radius is used.
- **Always check radius type and coordination.**

15 d- and f-series size

4f electrons
poor shieldingInward pull ↑
 $Z_{\text{eff}} \uparrow$ Lanthanoid
contraction

Schematic sizes

- **Group 3:** $3d < 4d < 5d$ in this layout.
- **Groups 4–12:** $3d < 4d \approx 5d$.
- **Reason** → lanthanoid contraction.
- **Ce** → **Lu:** poor 4f shielding → $Z_{\text{eff}} \uparrow$ → size ↓; this offsets the extra shell in 5d.

- **Neutral-metal sketch:** $\text{Eu} > \text{Ce} > \dots > \text{Lu}$.
- **Eu** ($4f^7$) is unusually large because of its bonding/packing.
- **Common lanthanoid state:** +3.
- **Ln^{3+} size:** $\text{Ce}^{3+} > \dots > \text{Lu}^{3+}$.
- **Actinoids:** poor 5f shielding → larger, less regular contraction.

16 Ionization energy (IE)

Ionization: electron removal



+

energy in

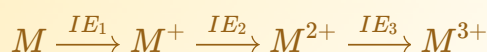


+

 e^- leaves $\Delta H > 0$

Energy is always supplied.

- **IE** → Minimum energy to remove the most loosely held electron from an isolated gaseous atom.
- **Always endothermic:** $\Delta H > 0$.
- **Successive removal becomes harder:** $\text{IE}_1 < \text{IE}_2 < \text{IE}_3$.

Same element: $\text{IE}_1 < \text{IE}_2 < \text{IE}_3$.

Chemical Periodicity

Ionization energy (IE) • IE orders + IE₂ tricks

continued

16 Ionization energy (IE)

Factor	IE trend
Size ↑	IE usually ↓
Z_{eff} ↑	IE ↑
Shielding ↑	IE usually ↓
Full shell: ns^2np^6	High IE; noble gas is the period maximum
Half-filled np^3	$N > O$; $P > S$
Penetration: $ns > np > nd > nf$	s electron held more strongly → $Be > B$; $Mg > Al$

17 IE orders + IE₂ tricks

$$ns^1 < ns^2np^1 < ns^2 < ns^2np^2 < ns^2np^4 < ns^2np^3 < ns^2np^5 < ns^2np^6$$

IE₁ order for periods 2 and 3. • Remember the s^2/p^1 and p^3/p^4 reversals.

• **IE₂ trick** → Remove one electron first; compare the cations. • C^+ : $2p^1$; N^+ : $2p^2$; O^+ : $2p^3$; F^+ : $2p^4$. • **IE₂**: $C < N < F < O$. • Na^+ : $2p^6$; Mg^+ : $3s^1$; Al^+ : $3s^2$; Si^+ : $3s^23p^1$. • **IE₂**: $Mg < Si < Al < Na$.

- **s-block IE₁**: left → right ↑; top → bottom ↓.
- Same period:
- **IE₁**: alkali metal < alkaline-earth metal.
- **IE₂**: alkali metal > alkaline-earth metal.
- **Reason** → alkali-metal cation already has a noble-gas shell.

18 p-block IE₁

- **Groups 15–18**: IE generally ↓ downward.
- **Group 13**: $B > Tl > Ga > Al > In$. Cue: 'Beet Gal'.
- **Group 14**: $C > Si > Ge > Pb > Sn$.
- **Poor d shielding** → $Ga > Al$.
- Lanthanoid contraction helps explain $Tl > In$ and $Pb > Sn$.

19 d- and f-block IE₁

Group	IE ₁ order down the group
3	$3d > 4d > 5d$; $Sc > Y > La$ in this layout
4	$Zr < Hf \approx Ti$ (Hf slightly below Ti); $4d < 5d < 3d$
5, 6, 10	$3d < 4d < 5d$
7, 8, 9, 11, 12	$4d < 3d < 5d$

- $5d$ usually has the highest IE in these vertical sets → lanthanoid contraction. • **Exceptions**: group 3; group 4 (Ti just above Hf). • Series ends: • $Sc(\text{min}) \dots Zn(\text{max})$ • $Y(\text{min}) \dots Cd(\text{max})$ • $La(\text{min}) \dots Hg(\text{max})$

Chemical Periodicity

d- and f-block IE_1 • What IE tells us

19 d- and f-block IE_1

continued



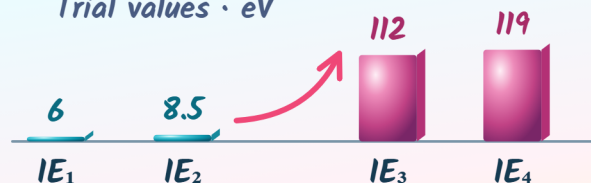
3d-series IE_1 order. • Memory cue: 'Suno Vinita tum kamal nahi kyon giro jaoge'.

- **f-block IE** → irregular.
- Lanthanoid IE_1 and IE_2 are broadly like Ca; IE_3 broadly like Al.
- This is a valence-pattern comparison, not equal numerical values.

20 What IE tells us

- Metals lose electrons easily.
- $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$
- $\text{Be} \rightarrow \text{Mg} \rightarrow \text{Ca} \rightarrow \text{Sr} \rightarrow \text{Ba}$
- **Downward**: size ↑, IE ↓, metallic/electropositive character ↑; reactivity generally ↑.

Trial values • eV



Big jump after IE_2

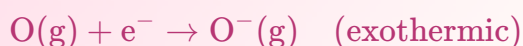
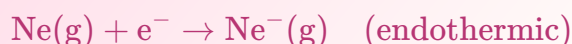
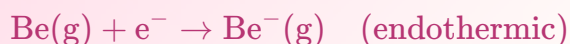
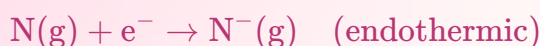
2 valence electrons → common state +2
These values do not uniquely identify Mg.

IE_1	IE_2	IE_3	IE_4
6 eV	8.5 eV	112 eV	119 eV

- **Big jump after IE_2** → 2 valence electrons → common state +2.
- **Oxide**: XO . **Nitride**: X_3N_2 .
- Mg is the example written in the notes; these trial values do not uniquely identify Mg.
- Small IE gap may help reach a higher oxidation state; a large gap resists it.
- The 11 eV / 16 eV cut-offs are unreliable.
- Also check bonding, lattice/hydration energy and reaction conditions.

21 Electron affinity + electron-gain enthalpy

- EA = energy released when an electron is accepted.
- ΔH_{eg} = enthalpy change for adding an electron to a gaseous species.
- **Favourable gain**: EA positive; ΔH_{eg} negative.
- Usually exothermic for neutral atoms.
- **Exceptions**: N, Be, Mg, noble gases → endothermic.



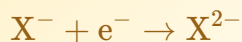
Chemical Periodicity

Electron gain: signs • EA and IE are linked

22 Electron gain: signs



Electron + positive ion → energy released. • This is the reverse of ionization.



Electron + gaseous anion → energy needed. • $\text{O} + 2\text{e}^- \rightarrow \text{O}^{2-}$ and $\text{S} + 2\text{e}^- \rightarrow \text{S}^{2-}$ are endothermic overall in the gas phase.

EA: energy released

ΔH_{eg} : enthalpy change

Positive EA

Negative $\Delta H_{\text{eg}} \rightarrow$ exothermic

Negative EA

Positive $\Delta H_{\text{eg}} \rightarrow$ endothermic

EA ≈ 0

Very little energy change; specify the species and state

23 EA and IE are linked

$$\text{EA}(\text{X}) = \text{IE}(\text{X}^-) \quad \text{EA}(\text{X}^+) = \text{IE}(\text{X})$$

EA is taken as energy released. • Forward electron gain and reverse electron removal have equal energy magnitudes.

• For chlorine: • $\text{IE}(\text{Cl}) > \text{IE}(\text{Cl}^-)$ • $\text{IE}(\text{Cl}^-) = \text{EA}(\text{Cl})$ • So $\text{IE}(\text{Cl}) > \text{EA}(\text{Cl})$. • Always check the ion/atom and the sign convention.

24 EA factors + orders

- > Size $\uparrow \rightarrow$ EA generally $\downarrow$.
- > $Z_{\text{eff}} \uparrow \rightarrow$ EA generally $\uparrow$.
- > Full shell resists electron gain.
- > Half-filled np^3 : $\text{O} > \text{N}$; $\text{S} > \text{P}$ in EA.
- > Penetration: $s > p > d > f$.
- > EA reminder for these pairs: $ns^1 > np^1 \rightarrow \text{Li} > \text{B}$; $\text{Na} > \text{Al}$.

Period-2 EA order: $\text{Ne} < \text{Be} < \text{N} < \text{B} < \text{Li} < \text{C} < \text{O} < \text{F}$

Approximate revision order. • Outer-subshell shorthand: • $2p^6 < 2s^2 < 2p^3 < 2p^1 < 2s^1 < 2p^2 < 2p^4 < 2p^5$. • Ne/Be anions are not normally bound; their EA values need care.

Period-3 EA order: $\text{Ar} < \text{Mg} < \text{Al} < \text{Na} < \text{P} < \text{Si} < \text{S} < \text{Cl}$

- > EA: $\text{Al} > \text{B}$; $\text{Si} > \text{C}$; $\text{P} > \text{N}$; $\text{S} > \text{O}$; $\text{Cl} > \text{F}$.
- > Reason $\rightarrow$ 2p is compact: electron repulsion $\uparrow$.
- > 3p is larger: repulsion $\downarrow \rightarrow$ electron gain easier.
- > Use these listed pairs.

$\text{S} > \text{Se} > \text{Te} > \text{Po} > \text{O} \quad \text{Cl} > \text{F} > \text{Br} > \text{I}$

Oxygen-family and halogen EA orders. • Cl has the highest EA.

Chemical Periodicity

Electronegativity (EN) • Mulliken scale

25 Electronegativity (EN)

$$EN(A) > EN(B)$$



More electronegative $\rightarrow \delta^-$

A pulls the shared electrons.

Electron cloud shifts toward A.

- **EN** $\rightarrow$ Pull of an atom on electrons.
- Pauling EN describes bonded atoms; it has no unit and depends on bonding, oxidation state and hybridization.
- Mulliken EN uses energy units.
- $EN(A) > EN(B) \rightarrow A\delta^- - B\delta^+$.
- $\Delta EN \uparrow \rightarrow$ bond polarity and ionic character generally $\uparrow$.

Change	EN trend
Size $\uparrow$	EN generally $\downarrow$
$Z_{eff} \uparrow$	EN generally $\uparrow$
Oxidation state $\uparrow$	EN usually $\uparrow$; compare P(+3) in PCl_3 and P(+5) in PCl_5
s character $\uparrow$	EN: $sp > sp^2 > sp^3$

• **Pauling scale** $\rightarrow$ based on bond energies. • Rounded values: • H 2.1 • C 2.5 • N 3.0 • O 3.5 • F 4.0 • S 2.5 • P 2.1 • Cl 3.0

26 Mulliken scale

$$\chi_{\text{Mulliken}} = \frac{IE + EA}{2}$$

Use the same units for IE and EA, usually eV.

$$\chi_{\text{Pauling}} \approx \frac{\chi_{\text{Mulliken}}}{2.8}$$

Rough conversion only. • Use numerical IE and EA values in eV, so Mulliken EN is also in eV.

- **EN** $\uparrow \rightarrow$ nonmetallic character generally $\uparrow$.

Chemical Periodicity

Bond length + ionic character • Acidic, basic or amphoteric?

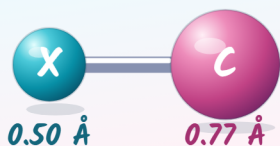
27 Bond length + ionic character

$$d_{A-B} \approx r_A + r_B - 0.09|\Delta\chi| \quad (\text{lengths in } \text{\AA})$$

Empirical estimate for covalent single bonds. • Use Pauling electronegativity difference $\Delta\chi$; all lengths in $\text{\AA}$.

$$r_A = \frac{d_{A-A}}{2} \quad r_B = \frac{d_{B-B}}{2}$$

Not to scale



Given example • hypothetical values

$$0.50 + 0.77 - 0.09 \approx 1.18 \text{ \AA}$$

$r_X + r_C - \text{correction} \rightarrow \text{bond length}$

- 1 Given: $X-X = 1.00 \text{ \AA}$; $C-C = 1.54 \text{ \AA}$.
- 2 Hypothetical question values: $EN(X) = 3.0$; $EN(C) = 2.0$.
- 3 $r_X = 0.50 \text{ \AA}$; $r_C = 0.77 \text{ \AA}$; $\Delta EN = 1$.
- 4 $C-X \text{ length} \approx 0.50 + 0.77 - 0.09 = 1.18 \text{ \AA}$.

$$\%IC \approx 16|\Delta\chi| + 3.5(\Delta\chi)^2$$

Approximate % ionic character; use within the range where this empirical formula works.

- 1 $EN(X) = 3.8$; $EN(Y) = 1.8$.
- 2 $\Delta EN = 3.8 - 1.8 = 2$.
- 3 $\%IC \approx 16(2) + 3.5(2^2) = 46\%$.

28 Acidic, basic or amphoteric?

Oxide rules

- **EN/nonmetallic character** $\uparrow \rightarrow$ acidity $\uparrow$, basicity $\downarrow$.
- **Metal oxides** $\rightarrow$ generally basic.
- **Nonmetal oxides** $\rightarrow$ generally acidic.
- **Neutral oxides**: CO , NO , N_2O , H_2O .
- **Amphoteric oxide/hydroxide** $\rightarrow$ reacts with both acids and bases.

- **Amphoteric list**: Zn , Al , Sb , As , Pb , Be , Sn , Ga ; also $Cr(III)$.
- **Partly unclear mnemonic**: 'Janab-e Ali ... Punjab ... gaya'.
- **Missing words remain unreadable**.

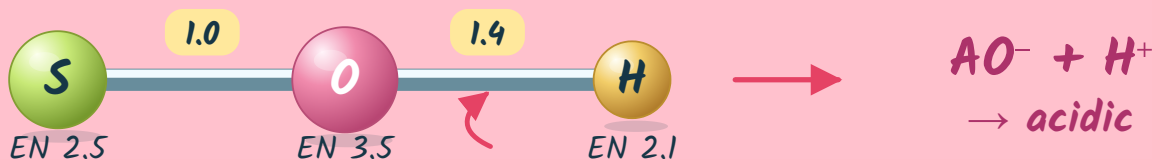
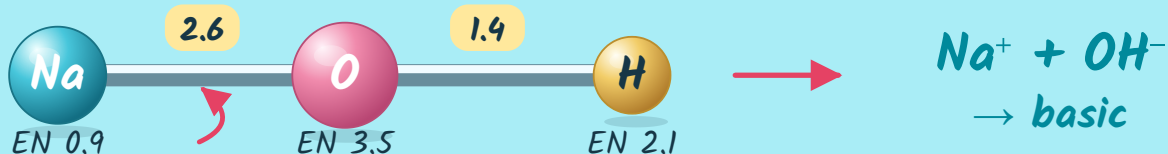
Chemical Periodicity

Acidic, basic or amphoteric? • Early periodic classification

28 Acidic, basic or amphoteric?

Bond picture + oxidation state

A—O—H: which bond gives way?



ΔEN values compare adjacent bonds; S—O—H is an acid fragment.

A—O breaks $\rightarrow \text{A}^+ + \text{OH}^- \rightarrow \text{base}$. • O—H breaks $\rightarrow \text{AO}^- + \text{H}^+ \rightarrow \text{acid}$. • Na—O—H: EN = 0.9, 3.5, 2.1; differences = 2.6, 1.4 $\rightarrow \text{base}$. • S—O—H: EN = 2.5, 3.5, 2.1; differences = 1.0, 1.4 $\rightarrow \text{acid}$.

d-block oxidation state	Usual oxide character
+1, +2, +3	Usually basic; Zn(II), Cr(III) $\rightarrow$ amphoteric exceptions
+4	Often amphoteric
+5, +6, +7, +8	Usually acidic

- These are general trends.
- The metal and the oxide formula also decide the behaviour.

29 Early periodic classification

- **Döbereiner triad** $\rightarrow$ 3 chemically similar elements.
- Middle atomic mass $\approx$ average of the other two.
- Li, Na, K: $\text{mass}(\text{Na}) \approx [\text{mass}(\text{Li}) + \text{mass}(\text{K})]/2$.
- Memory cue 'same group, same ΔZ ' is only a shortcut; check masses.
- **De Chancourtois** $\rightarrow$ Elements arranged by atomic weight on a cylinder.
- **Shape**: 3D helix (telluric screw), like a DNA helix.

30 Newlands' law of octaves

Sa	re	ga	ma	pa	dha	ni	Sa
Li	Be	B	C	N	O	F	Na

Every 8th: similar properties • works broadly only up to Ca

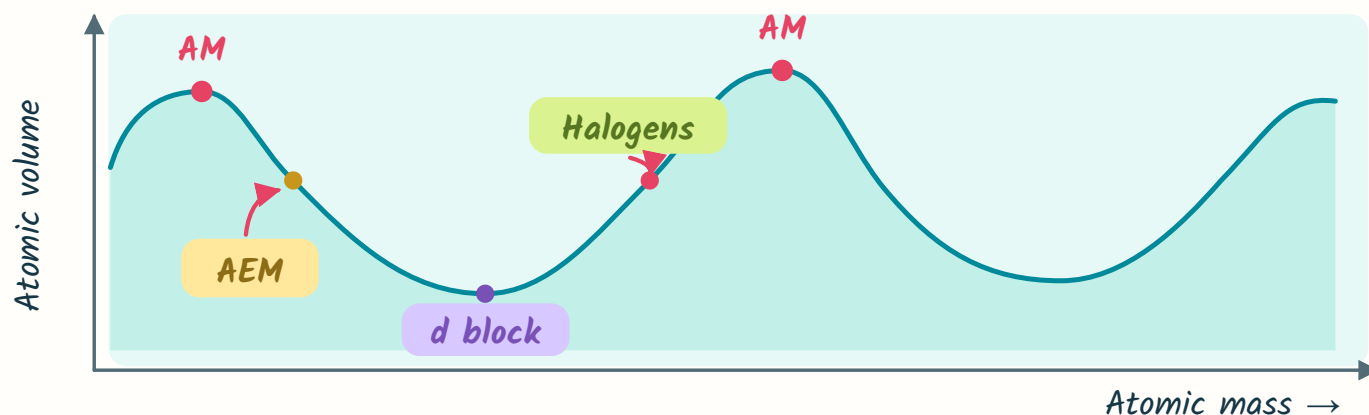
- **Increasing atomic weight** $\rightarrow$ similar properties at every 8th element.
- Sa re ga ma pa dha ni • Li Be B C N O F • Next 'sa' $\rightarrow$ Na. • **Early-sequence shortcut**: same family, $\Delta Z = 8$. • Works broadly only up to Ca.

Chemical Periodicity

Lothar Meyer's curve • Mendeleev's law + successes

31 Lothar Meyer's curve

Atomic volume repeats!



AM = alkali metals • AEM = alkaline earth metals • Schematic pattern, not measured data.

Graph: atomic volume vs atomic mass. • Peaks → alkali metals. • Falling side → alkaline-earth metals. • Lowest part → d-block. • Rising side → halogens.

32 Mendeleev's law + successes

- **Mendeleev's law** → Element properties repeat with atomic weight.
- He left gaps and predicted missing elements.

Element above gap	Predicted name	Discovered element
Al	Eka-aluminium	Ga
B	Eka-boron	Sc
Si	Eka-silicon	Ge
Mn	Eka-manganese	Tc

- **Ga, Sc, Ge, Tc cue** → 'gaya se jawana tak'.
- **Atomic weights corrected:** Au, In, Pt, Be, U.
- **Cue** → 'gold in platinum became ultimate'.

33 Problems with atomic-weight order

Pair kept in chemical order	Memory cue
Ar before K; Ar is heavier	Amir Khan
Te before I; Te is heavier	Tum Itcha
Th before Pa; Th is heavier	Thanda Pani
Co before Ni; Co is heavier	Kyo Nahi

- These pairs break the atomic-weight order.
- Modern atomic-number order solves this problem.

Chemical Bonding

Lewis structures • shapes • bonding

02

01 Why bonds form and bonding theories

Making a bond releases energy; breaking it needs energy



Formation → energy released ↓



Breaking → energy supplied ↑

- Chemical bond → attraction that holds atoms/ions together.
- Bond formation → energy released.
- Bond breaking → energy needed.
- Usually strong: ionic, covalent, coordinate, metallic.
- Usually weaker: H-bonds, van der Waals forces. Actual strength depends on the species.

- Stable bonding lowers the total energy; more bonds alone do not guarantee stability.
- Octet rule → many atoms acquire 8 valence electrons.
- H and He → 2-electron shell (duet).

- Bonding theories: Kossel–Lewis/octets; VSEPR = valence-shell electron-pair repulsion; VBT = valence-bond theory; MOT = molecular-orbital theory.
- Kossel–Lewis: transfer/share valence electrons → noble-gas-like shell.

02 Lewis bond-count shortcut

$$N_{\text{bond pairs}} = \frac{N_{\text{required shell electrons}} - N_{\text{available valence electrons}}}{2}$$

Octet/duet shortcut only.

Do not use directly for radicals, electron-deficient or hypervalent species.

$$\text{CO : } \frac{2(8) - (4 + 6)}{2} = 3$$

 $\text{C}\equiv\text{O}$; one lone pair on each atom.Formal charges: C^- , O^+ .

$$\text{O}_3 : \frac{3(8) - 3(6)}{2} = 3$$

Each resonance form: one single + one double bond.

Central O: +1; single-bonded terminal O: -1.

Chemical Bonding

Lewis bond-count shortcut • Limitations of the octet rule

02 Lewis bond-count shortcut

continued

$$\text{N}_3^- : \frac{3(8) - [3(5) + 1]}{2} = 4$$

Linear azide forms: $^-N=N^+=N^-$; $N\equiv N^+-N^{2-}$; and its mirror form.

03 Limitations of the octet rule

- Octet-rule exceptions:
- Expanded Lewis octet $\rightarrow \text{PCl}_5, \text{SF}_6, \text{H}_2\text{SO}_4$.
- Incomplete octet $\rightarrow$ gaseous $\text{LiCl}, \text{BF}_3, \text{BeCl}_2$ (check state/bonding).
- Odd electrons $\rightarrow \text{NO}, \text{NO}_2$.
- Noble-gas compounds $\rightarrow \text{XeF}_2, \text{KrF}_2, \text{XeOF}_2$.
- Octet rule does not give molecular shape, energy or relative stability.

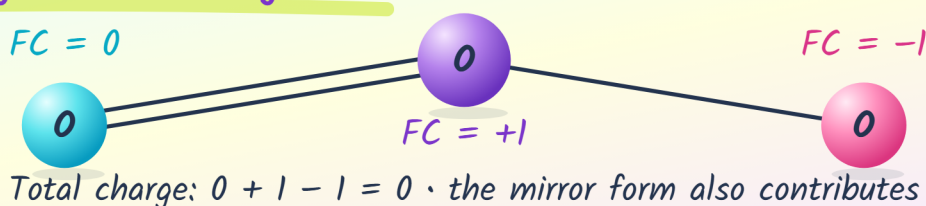
04 Formal charge

$$FC = V - N_{\text{nonbonding}} - \frac{N_{\text{bonding}}}{2} = V - 2L - B$$

V = neutral atom's valence electrons; L = lone pairs; B = sum of bond orders.
Memory: expected electrons – electrons assigned in the Lewis structure.

05 Formal charge and resonance

Ozone: assign formal charges to one Lewis form



- O_3 formal charges:
- Central O: $6 - 5 = +1$.
- Double-bonded O: $6 - 6 = 0$.
- Single-bonded O: $6 - 7 = -1$.
- Better contributors usually have less charge separation, smaller charges and negative charge on the more electronegative atom.
- Symmetry-related forms contribute equally.

Chemical Bonding

Formal charge and resonance • Covalent bonding and valency

05 Formal charge and resonance

continued

$$\overline{FC}_O = \frac{\begin{array}{l} \text{negative charge distributed} \\ \text{among equivalent O sites} \end{array}}{\text{number of those O sites}}$$

Average over equivalent resonance forms; different from one atom's formal charge in a single structure.

$$\overline{BO}_{X-O} = \frac{\begin{array}{l} \text{sum of X-O bond orders in} \\ \text{a representative contributor} \end{array}}{\text{number of equivalent X-O bonds}}$$

Ion	Average O charge in source scheme	Average X-O bond order
CO_3^{2-}	-2/3	4/3
SO_4^{2-}	-2/4	6/4 (expanded-octet Lewis representation)

- 0 shortcut (usual closed-shell structures):
- 1 bond $\rightarrow -1$; 2 bonds $\rightarrow 0$; 3 bonds $\rightarrow +1$.
- Use the matching lone-pair count.
- Sulfate's 6/4 average is Lewis-model bookkeeping, not a directly measured bond count.

06 Covalent bonding and valency

- Covalent bond $\rightarrow$ shared electron pair; sharing may be equal or polar.
- Covalency here = $\sigma + \pi$ bonds made by the atom.
- Valency = combining capacity.
- Electrovalency = ionic combining capacity/charge magnitude.
- NaCl: Na^+ and Cl^- .

- Second-period main-group atoms: octet; classical covalency usually ≤ 4 .
- Heavier atoms can be hypervalent. Vacant 3d promotion is not required to explain this.
- F normally makes one covalent bond.

07 Coordinate bond

- Coordinate/dative bond $\rightarrow$ both electrons initially come from one atom.
- Donor = Lewis base; acceptor = Lewis acid.
- Arrow: donor A $\rightarrow$ acceptor B.
- Once formed, it is a covalent bond; electron origin and bond polarity are different ideas.

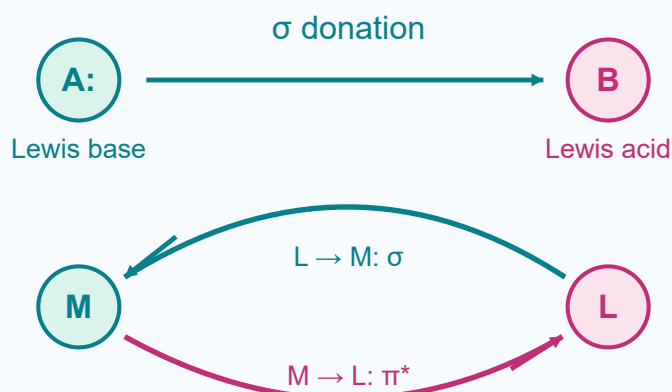
Chemical Bonding

Coordinate bond • Species represented with dative formation

07 Coordinate bond

continued

Donation and back-donation



Coordinate bonding tracks the source of the donated electron pair; back-donation can reinforce the metal–ligand interaction.

08 Species represented with dative formation

Species	Source donor–acceptor construction
O_3	One resonance form can be drawn with terminal O donating to O; equivalent bonds require resonance
NH_4^+	NH_3 donates a lone pair to H^+
H_3O^+	H_2O donates a lone pair to H^+
NO_3^-	Resonance forms: central N^+ ; average O charge $-2/3$; average N–O bond order $4/3$
PCl_6^-	Cl^- donates to PCl_5
BF_4^-	F^- donates to BF_3
$NH_3 \cdot BF_3$	$H_3N: \rightarrow BF_3$
PH_4^+	PH_3 donates to H^+
$B(OH)_4^-$	OH^- donates to $B(OH)_3$

09 VSEPR principles

- Electron pairs repel $\rightarrow$ spread apart around the central atom.
- Count σ -bond domains + lone pairs.
- A multiple bond counts as one domain but may repel more strongly.
- B–A–B can be linear; central lone pairs can give a bent shape.

Chemical Bonding

VSEPR principles • Shape table

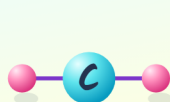
09 VSEPR principles

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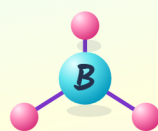
$$LP - LP > LP - BP > BP - BP$$

Repulsion: lone pair–lone pair > lone pair–bond pair > bond pair–bond pair.

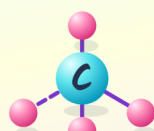
Count bond domains + lone pairs → predict the shape



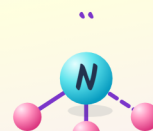
CO_2 : 2 + 0



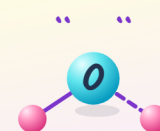
BF_3 : 3 + 0



CH_4 : 4 + 0



NH_3 : 3 + 1



H_2O : 2 + 2

- AB_nL_m : A = central atom; n = surrounding atoms/ σ bonds; m = lone pairs.
- Steric number = n + m.

10 Shape table

Formula	Molecular shape
AB_2L_0	Linear
AB_3L_0	Trigonal planar
AB_2L_1	Bent / V-shaped
AB_4L_0	Tetrahedral
AB_3L_1	Trigonal pyramidal
AB_2L_2	Bent / angular
AB_5L_0	Trigonal bipyramidal
AB_4L_1	Seesaw
AB_3L_2	T-shaped
AB_2L_3	Linear
AB_6L_0	Octahedral (square bipyramidal)
AB_5L_1	Square pyramidal
AB_4L_2	Square planar
AB_7L_0	Pentagonal bipyramidal
AB_6L_1	Distorted octahedral (source seven-domain model)
AB_5L_2	Pentagonal planar

Chemical Bonding

hybridization labels • Octet quotient/remainder shortcut

11 hybridization labels

Domains $n+m$	Conventional label	Orbitals in elementary model
2	sp	$s+p$
3	sp^2	$s+p+p$
4	sp^3	$s+p+p+p$
5	sp^3d	$s+p+p+p+d$

- Use these traditional labels to remember geometry. Main-group hypervalence does not require strong d-orbital participation.

12 Octet quotient/remainder shortcut

$$N_{\text{valence}} = 8Q + R$$

$$\Rightarrow$$

$$n = Q$$

$$m = R/2$$

Use only for the listed single-centre, closed-shell octet examples.

Skip odd-electron species and H-surrounded cases. Check a Lewis structure.

Species	Total valence electrons	Q,R	Result
BF_3	$3+7+7+7=24$	3,0	AB_3L_0 ; sp^2 ; trigonal planar
NO_2^+	$5+6+6-1=16$	2,0	AB_2L_0 ; sp ; linear
NO_3^-	$5+3\times6+1=24$	3,0	AB_3L_0 ; sp^2 ; trigonal planar
SO_2	$6+6+6=18$	2,2	AB_2L_1 ; sp^2 ; bent

13 H/halogen surroundings examples

- H/halogen shortcut: adjust central valence electrons for charge, subtract one per single bond; pair the electrons left.
- CH_4 : $4-4 = 0$ LP $\rightarrow \text{AB}_4\text{L}_0$, sp^3 , tetrahedral.
- NH_4^+ : $(5-1)-4 = 0$ LP $\rightarrow \text{AB}_4\text{L}_0$.
- NH_2^- : $(5+1)-2 = 4$ electrons = 2 LP $\rightarrow \text{AB}_2\text{L}_2$.

14 Oxo Lewis structures and hybrid orbitals

- XeO_3 Lewis picture: three $\text{Xe}=\text{O}$ bonds + one Xe lone pair.
- A neutral oxo species does not always have only double bonds. Check electron count, octet limits and formal charges.

Chemical Bonding

Oxo Lewis structures and hybrid orbitals • Bond-angle guidance

14 Oxo Lewis structures and hybrid orbitals

continued

- Hybridization = mixing atomic orbitals.
- Orbitals mixed = hybrids formed.
- Ideal hybrids in one set have equal energy/shape; hold σ bonds or lone pairs.
- Hybrids = σ domains + LP.
- More p character $\rightarrow$ larger hybrid: $sp < sp^2 < sp^3$.
- Memory: s is the 'angle shop', p the 'direction shop'; mixing changes directionality/angles.

15 Bond-angle guidance

Hybrid label	s character	Ideal angle
sp	50%	180°
sp^2	$33\frac{1}{3}\%$	120°
sp^3	25%	109.5°

- LP usually compresses bond angles.
- The 2.5° – 2.8° drop per LP is only a rough memory aid.
- Same domain geometry; more LP $\rightarrow$ smaller angle.
- Size guide at equal hybridization/LP: larger outer atoms may enlarge the angle; larger central atom may reduce it. Check the molecule.
- No central LP: BF_3 and $BCl_3 \rightarrow$ trigonal planar, 120° .

16 Traditional d-orbital hybridization notation

Label	d orbitals conventionally listed
sp^3d	dz^2
sp^3d^2	dz^2, dx^2-y^2
sp^3d^3	dz^2, dx^2-y^2, dxy

- SF_6 : AB_6L_0 ; traditional $sp^3d^2 = s+px+py+pz+dz^2+dx^2-y^2$.
- XeF_2 : AB_2L_3 ; traditional $sp^3d = s+px+py+pz+dz^2$.
- Unused orbitals remain pure, e.g. dyz, dxz .
- These are geometry labels, not proof of large d participation.

17 Odd-electron examples

- Radical examples:
- $CH_3\cdot \rightarrow$ planar, roughly sp^2 ; odd electron in a p orbital.
- $CF_3\cdot$ and $ClO_3\cdot \rightarrow$ pyramidal/ sp^3 -type descriptions in these notes.
- Source memory cue: outer atoms less electronegative than the centre $\rightarrow CH_3\cdot$ pattern; more electronegative $\rightarrow CF_3\cdot/ClO_3\cdot$ pattern.
- This cue is not universal. Check each radical's actual geometry.

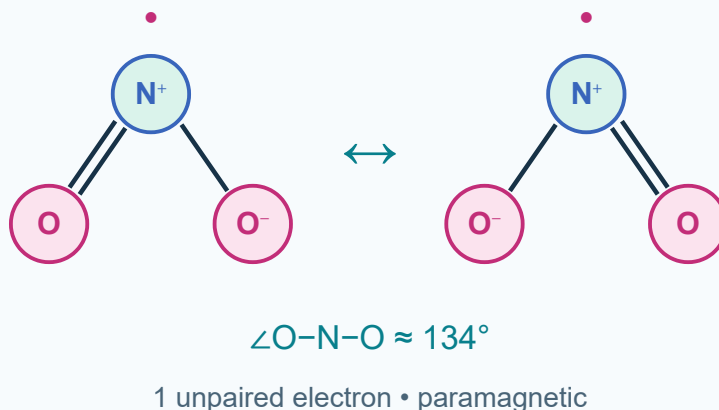
Chemical Bonding

Odd-electron examples • Solid-state halides and existence comparisons

17 Odd-electron examples

continued

NO₂: bent radical



NO₂ is a bent radical with resonance-equivalent N–O bonds and one unpaired electron.

- NO₂: brown, paramagnetic, acidic oxide; contributes to acid rain.
- $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$.
- High pressure + low temperature favour N₂O₄.

18 Solid-state halides and existence comparisons

- Solid PCl₅ → [PCl₄]⁺[PCl₆][−].
- PCl₄⁺: AB₄L₀, tetrahedral, sp³.
- PCl₆[−]: AB₆L₀, octahedral; traditional sp³d².
- Solid PBr₅ → [PBr₄]⁺Br[−].
- Large Br ligands make PBr₆[−] much less favourable than PBr₄⁺.

Source category	Exists / conventional example	Source non-existing/disfavoured comparison
Hypervalent fluorides versus hydrides	XeF ₆ , XeF ₂ , SF ₆	XeH ₆ , XeH ₂ , SH ₆
Covalency limit	NCl ₃ ; BF ₄ [−] ; ClF ₃	NCl ₅ ; BF ₆ ^{3−} ; FCl ₃
Steric crowding	PCl ₆ [−] ; SiF ₆ ^{2−} ; IF ₇	PBr ₆ [−] ; SiCl ₆ ^{2−} ; ICl ₇ / IBr ₇

- Why the listed contrasts?
- Second-period centres obey octet limits; F is usually monovalent; large ligands cause crowding.
- ‘d-orbital contraction’ is an old explanation of hypervalence.
- The table compares ordinary examples; unusual phases/conditions can change what exists.

Chemical Bonding

σ and π overlap • Overlap signs

19 σ and π overlap

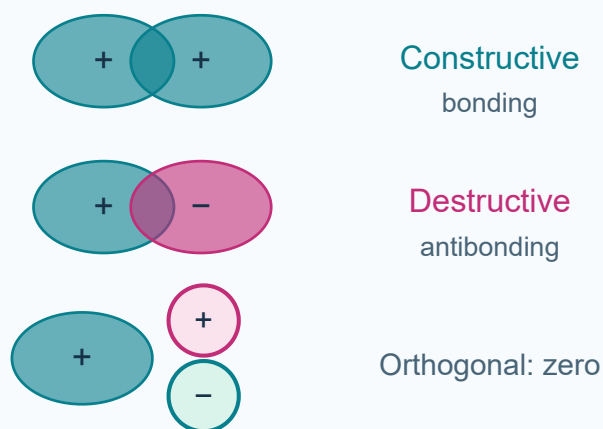
- Head-on/coaxial overlap along the internuclear axis (INA) $\rightarrow \sigma$.
- Sideways overlap $\rightarrow \pi$.
- Comparable orbitals: σ usually stronger than π .
- Hybrid-hybrid or hybrid-pure directed overlap $\rightarrow \sigma$.
- Pure orbitals may give σ , π or δ , depending on direction.
- Pure-orbital pairs: $s-s$, $s-p$, $p-p$, $p-d$, $d-d$.
- Spherical s orbitals cannot make π overlap.

Orbital pair	INA x	INA y	INA z
$s + s$	σ	σ	σ
$s + px$	σ	0	0
$px + px$	σ	π	π
$px + py$	0	0	0
$dxy + px$	0	π	0
$px + dyz$	0	0	0
$dxy + dxy$	π	π	δ
$dxz + dyz$	0	0	0

- Table assumes matching Cartesian axes on both atoms and the stated bond axis.
- Rotating orbitals changes overlap.
- $dxy-dxy$ along z gives δ symmetry.

20 Overlap signs

Wavefunction phase and overlap



Orbital signs show wavefunction phase. Matching phases reinforce; opposite phases cancel.

Chemical Bonding

Orbital identities and π -bond cautions • bond-strength comparisons

21 Orbital identities and π -bond cautions

Bond	σ -overlap identity
H-H	1s-1s
H-Cl	1s-3p
Cl-Cl	3p-3p
C-C in ethane	sp^3-sp^3
C-H in ethane	sp^3-1s

- Second-period valence bonding uses 2s/2p, not d π orbitals.
- Older memory scheme: $sp \rightarrow p\pi-p\pi$; $sp^2 \rightarrow$ first π called $p\pi-p\pi$, remaining π called $d\pi-d\pi$; sp^3 /others $\rightarrow d\pi-d\pi$.
- This scheme is unreliable. Identify actual orbitals/delocalization; hybridization alone cannot do it.

22 bond-strength comparisons

- Better overlap usually strengthens comparable bonds.
- Illustrations: 1s-1s > 2s-2s > 3s-3s.
- Head-on, same shell: 2s-2s < 2s-2p < 2p-2p.
- Greater directionality/overlap can help; these are not fixed bond-energy rankings for every molecule.

- Overlap memory chains:
- $3p\pi-3p\pi < 3p\pi-3d\pi < 3d\pi-3d\pi$.
- $2p\pi-2p\pi > 3d\pi-3d\pi > 3p\pi-3d\pi > 3p\pi-3p\pi$.
- σ sketch: 1s-1s > 2p-2p > 2s-2p > 2s-2s > 3s-3s.
- Also: 1s-2s < 1s-2p; $p-p(\sigma) > p-p(\pi)$.
- Treat as qualitative sketches; actual species/orbital energies matter.

- Compact lone pairs repel strongly $\rightarrow$ N-N and O-O single bonds weaker than P-P and S-S.
- Halogen bond strength: $Cl_2 > Br_2 > F_2 > I_2$.
- This effect is especially strong for second-period atoms.

23 Dipole moment

$$\mu = qd$$

$$1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$$

Molecular dipole = vector sum of charge-separation effects.

$\mu = 0 \rightarrow$ nonpolar; $\mu \neq 0 \rightarrow$ polar.

Chemical Bonding

Dipole moment • Dipole comparisons

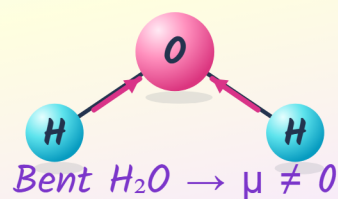
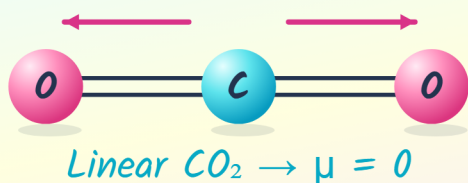
23 Dipole moment

continued

- Chemical bond-dipole arrow $\rightarrow$ more electronegative end.
- LP contribution is drawn outward.
- Identical outer atoms + symmetric geometry $\rightarrow$ cancellation: AB_2L_0 to AB_7L_0 , square-planar AB_4L_2 and linear AB_2L_3 have $\mu = 0$.

24 Dipole comparisons

Molecular dipoles add as vectors



Comparison	Reason/shape
$CO_2 < SO_2$	Linear $CO_2 \mu=0$; bent $SO_2 \mu \neq 0$
$SO_2 > SO_3$	Bent versus trigonal planar
$CCl_4 < CH_2F_2$	Equivalent tetrahedral ligands cancel in CCl_4 ; different ligands do not
$XeF_2 = XeF_4$	Linear and square planar, both $\mu=0$
$NH_3 > NF_3$	NH_3 bond and lone-pair contributions reinforce; NF_3 contributions oppose
$H_2O > OF_2$	Bent species; different bond-dipole vector contributions
$HF > HCl > HBr > HI$	Source hydrogen-halide data order
$HF > NH_3 > PH_3$	Source measured-magnitude comparison
$H_2O > NH_3 > PH_3$	Source measured-magnitude comparison
$H_2O > H_2S$	Source measured-magnitude comparison

- Dipole depends on q , bond length d and geometry.
- Electronegativity difference alone does not decide molecular μ .

25 Additional dipole data and ionic character

- Dipole orders:
- $CH_3Cl > CH_3F > CH_3Br > CH_3I$.
- $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$.
- $H_2O > HF$ (NCERT comparison).

Chemical Bonding

Additional dipole data and ionic character • Ionic/electrovalent bonding

25 Additional dipole data and ionic character

continued

$$\%IC = \frac{\mu_{\text{observed}}}{\mu_{100\% \text{ ionic}}} \times 100$$

$$\mu_{100\% \text{ ionic}} = ed$$

$$\%IC(\text{HCl}) = \frac{1.02 \times 3.3 \times 10^{-30}}{1.6 \times 10^{-19} \times 1.27 \times 10^{-10}} \times 100 \approx 16.6\%$$

Given: $\mu(\text{HCl}) = 1.02 \text{ D}$; bond length = $1.27 \text{ \AA}$.

Rounded constants give 16.6%; more precise constants give about 16.7%.

26 Ionic/electrovalent bonding

- Ionic bond → attraction between opposite charges, often after metal→nonmetal electron transfer.
- Ionic solids: usually hard, brittle, nonmolecular lattices.
- Attraction is nondirectional; simple lattices lack molecular directional isomerism.
- Many dissolve in polar solvents, but solubility varies.

$$|F| = k \frac{|q_1 q_2|}{r^2}$$

Coulomb attraction: larger charges and smaller separation give stronger force.

- NH_4Cl shows:
- Covalent N–H bonds.
- NH_3 donates to H^+ to form NH_4^+ .
- Ionic attraction: $\text{NH}_4^+ \cdots \text{Cl}^-$.
- After formation, all four N–H bonds in NH_4^+ are equivalent.

27 Hydration and ionic mobility

- Hydration = water molecules surround an ion.
- Dissolving a salt can separate its ions first.
- Higher ionic potential/charge density → usually stronger hydration and larger energy release.

$$\phi = \frac{|q|}{r}$$

Ionic potential = charge magnitude/radius.

Be^{2+} has greater ionic potential than Li^+ .

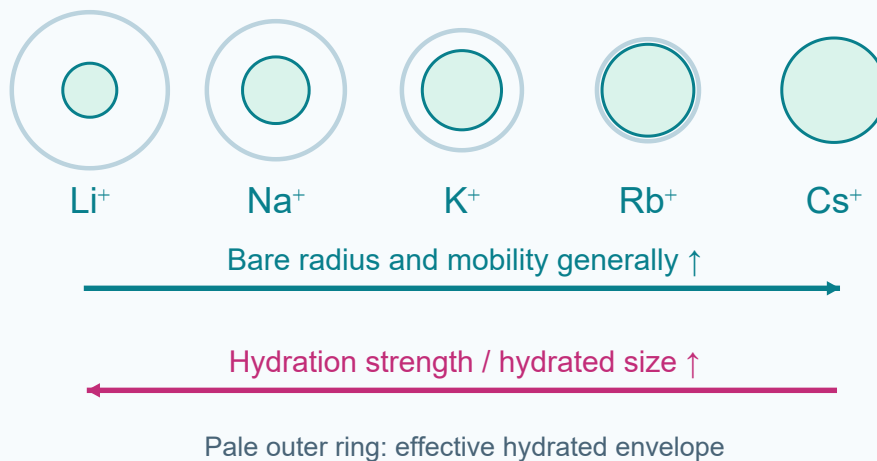
Chemical Bonding

Hydration and ionic mobility • Conductivity and lattice energy

27 Hydration and ionic mobility

continued

Bare ions and hydration



From Li⁺ to Cs⁺, bare radius increases while hydration generally weakens and aqueous mobility rises.

28 Conductivity and lattice energy

Ionic compounds conduct when their ions can move



Material/state	Ions present?	Mobile charge carriers?	Conducts?
Ionic solid	Yes	No (ions fixed)	No, in ordinary conditions
Molten ionic compound	Yes	Yes	Yes
Aqueous ionic solution	Hydrated ions	Yes	Yes
Typical molecular covalent solid	No free ions	No	No
Typical molecular covalent melt	No free ions	No	No
Typical nonelectrolyte aqueous solution	No ions produced	No ionic carriers	Poor/no conductivity

Chemical Bonding

Conductivity and lattice energy • Lattice energy comparisons

28 Conductivity and lattice energy

continued

- Ionic lattices usually melt/boil above small molecular substances.
- Molecular solids: molecules held by intermolecular forces.
- Metals conduct through mobile electrons.
- Covalent substances that form ions in water can conduct; the table's no-conduction rows are nonelectrolytes.
- Energy balance guide:
 - Released by electron gain + lattice formation must offset sublimation, ionization and bond breaking.
 - Full thermodynamics also includes entropy and conditions.
- Lattice dissociation energy $U \rightarrow$ energy to turn 1 mol ionic solid into separate gaseous ions.
- Lattice formation energy has the opposite sign.

29 Lattice energy comparisons

$$U \propto \frac{|q_1 q_2|}{r}$$

Similar lattices: charge $\uparrow$ or separation $\downarrow \rightarrow$ lattice-energy magnitude $\uparrow$.

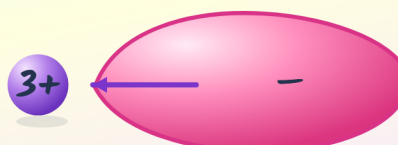
- Lattice-energy comparisons: $\text{NaCl} < \text{NaF}$; $\text{MgO} < \text{Al}_2\text{O}_3$; $\text{Li}_3\text{N} > \text{Na}_3\text{N}$ (small-cation guide).
- Among ordinary alkali metals, Li uniquely forms a stable nitride directly under ordinary conditions.
- Alkaline-earth nitrides include Be_3N_2 , Mg_3N_2 ; +2 charge gives strong lattice attraction.

30 Fajans' rules

Fajans: a stronger polarizer pulls the anion cloud



Less distortion $\rightarrow$ more ionic



More distortion $\rightarrow$ more covalent

- Fajans' rule $\rightarrow$ cation distorts the anion's electron cloud.
- More distortion $\rightarrow$ more covalent character.
- Cation: polarizing power.
- Anion: polarizability.

Chemical Bonding

Fajans' rules • Molecular orbital theory

30 Fajans' rules

continued

Condition	Illustration
Smaller cation → stronger polarization	$\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+}$
Larger anion → greater polarizability	$\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$
Higher cation charge	$\text{M}^+ < \text{M}^{2+} < \text{M}^{3+}$
More highly charged same-element anion (formal trend)	$\text{X}^- < \text{X}^{2-} < \text{X}^{3-}$

$$\phi_{\text{cation}} = \frac{|q|}{r}$$

Radius ↑ → ionic potential ↓.

 Na^+ , K^+ , Rb^+ , Cs^+ have relatively low polarizing power.

- Poor d shielding can make comparable d-block cations stronger polarizers than s-block cations.
- LiCl , BeCl_2 , MgCl_2 show covalent character and can interact with organic donor solvents.
- Listed solvents: benzene, pyridine, acetone. Pyridine/acetone are polar; solubility depends on the salt/solvent.

- Related salts: covalent character ↑ often means mp ↓.
- SnCl_4 is more covalent; $\text{mp}(\text{SnCl}_2) > \text{mp}(\text{SnCl}_4)$.
- Covalent-character orders:
- $\text{LiF} < \text{LiCl} < \text{LiBr} < \text{LiI}$.
- $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl}$.
- $\text{SnCl}_2 < \text{SnCl}_4$.
- $\text{NaCl} < \text{CuCl}$.

31 Molecular orbital theory

- MOT explains O_2 paramagnetism.
- Atomic orbitals combine → lower-energy bonding MO + higher-energy antibonding MO.
- Fill using Aufbau, Pauli and Hund rules.
- These notes focus on diatomics up to 20 electrons; MOT also applies more widely.

$$\text{BO} = \frac{N_b - N_a}{2}$$

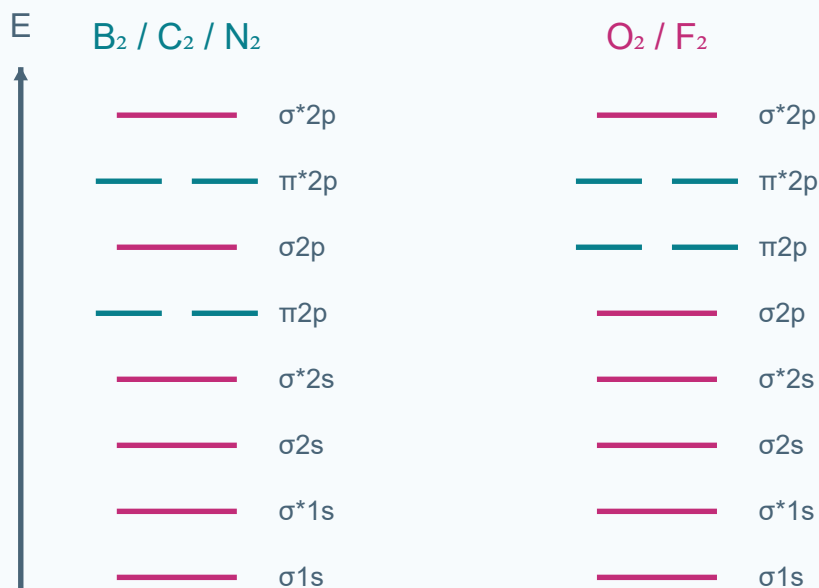
Chemical Bonding

Molecular orbital theory • Nitrogen MO example and bond-order shortcuts

31 Molecular orbital theory

continued

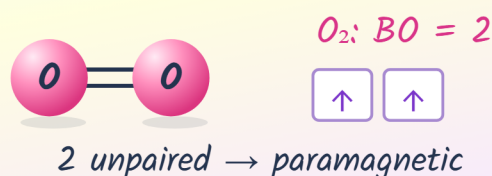
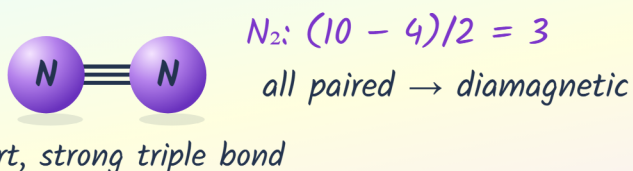
Second-period diatomic MO ordering

* = antibonding; each π pair is degenerateThe $\pi 2p/\sigma 2p$ ordering changes with s-p mixing; degenerate π orbitals fill according to Hund's rule.

- O_2 : 16 electrons.
- $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$.
- $N_b = 10$; $N_a = 6$.
- $BO = (10-6)/2 = 2$.
- 2 unpaired electrons $\rightarrow$ paramagnetic.

32 Nitrogen MO example and bond-order shortcuts

Bond order = (bonding electrons – antibonding electrons) / 2



- N_2 : 14 electrons.
- $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2$.
- $BO = (10-4)/2 = 3$; valence-only: $(6-0)/2 = 3$.
- Comparable series: $BO \uparrow \rightarrow$ bond stronger/shorter, usually more stable.
- At equal BO , fewer antibonding electrons may help; BO alone is insufficient.

Chemical Bonding

Nitrogen MO example and bond-order shortcuts • Magnetic behaviour and MO overlap

32 Nitrogen MO example and bond-order shortcuts

continued

Total electrons (source simple diatomic sequence)	Bond order
1	0.5
2	1
3	0.5
4	0
5	0.5
6	1
7	0.5
8	0
9	0.5
10	1
11	1.5
12	2
13	2.5
14	3
15	2.5
16	2
17	1.5
18	1
19	0.5
20	0

- Memory peak → 14 electrons gives BO 3 in this sequence.
- Remove a bonding electron or add an antibonding electron → BO falls by 0.5.
- Use the table only with its assumed first/second-period diatomic filling.

33 Magnetic behaviour and MO overlap

- Unpaired electron → paramagnetic.
- Odd electron total guarantees an unpaired electron.
- Even total can still be paramagnetic: B_2 , O_2 , S_2 .
- Check orbital filling, not just odd/even count.

$$\mu_{\text{spin-only}} = \sqrt{n(n+2)} \mu_B$$

n = unpaired electrons.

Quick estimate: μ is close to $n+1$.

$n = 5 \rightarrow \mu = \sqrt{35} \mu_B$.

Chemical Bonding

Magnetic behaviour and MO overlap • Hydrogen-bonding types

33 Magnetic behaviour and MO overlap

continued

Atomic-orbital overlap (INA=z)	MO types
s-s	$\sigma 1s/\sigma^* 1s$ and $\sigma 2s/\sigma^* 2s$
p _z -p _z	$\sigma 2p_z/\sigma^* 2p_z$
p _x -p _x , p _y -p _y sideways	$\pi 2p_x$, $\pi 2p_y$ and corresponding π^* levels

- σ MO: cylindrical symmetry around the bond axis.
- π MO: a nodal plane passes through the axis.

34 Hydrogen-bonding types

- Hydrogen bond → polar X-H interacts with a lone-pair acceptor; common X = F, O, N.
- Pattern: $X\delta^- \cdots H\delta^+ \cdots X\delta^- \cdots H\delta^+$.
- It is directional, with electrostatic and other bonding contributions.

Feature	Intermolecular hydrogen bonding	Intramolecular hydrogen bonding
Location	Between molecules	Within one molecule
Ring association	May occur in cyclic dimers	Commonly stabilizes an internal ring
Molecular association	Generally increased	May reduce association with other molecules
Boiling point/volatility	Often higher bp/lower volatility	Often lower bp/higher volatility versus a comparable intermolecular isomer
Viscosity	Often increased	Often lower in matched comparisons
Melting point	Depends strongly on crystal packing	No universal melting-point rule

- Cellulose and amino acids H-bond with water.
- Room temperature: H₂O liquid; H₂S gas.
- Comparable ethers are more volatile than alcohols.
- H-bond association can raise bp and viscosity.
- o-Nitrophenol: intramolecular H-bond → more volatile than p-isomer.
- o-Hydroxybenzaldehyde (salicylaldehyde) is liquid; p-hydroxybenzaldehyde is solid at room temperature.

- Petrol does not mix with water and floats; many alcohols mix with water.
- These facts alone do not tell us how to extinguish every fuel fire.

Chemical Bonding

Hydride melting/boiling trends • Hydrogen bonding in ice and other solids

35 Hydride melting/boiling trends

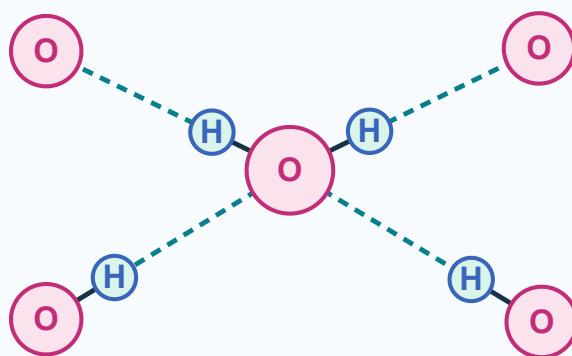
- Groups 15–17 hydrides: larger, more polarizable molecules → stronger dispersion.
- NH_3 , H_2O , HF have unexpectedly high bp because of H-bonding.

Group	Boiling-point order shown	Melting-point order shown
15	$\text{PH}_3 < \text{AsH}_3 < \text{NH}_3 < \text{SbH}_3$; source extended: $\text{BiH}_3 > \text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$	$\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{NH}_3$
16	$\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} < \text{H}_2\text{O}$	$\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} < \text{H}_2\text{O}$
17	$\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$	$\text{HCl} < \text{HBr} < \text{HF} < \text{HI}$

- BiH_3 is very unstable; its extended bp order is a prediction, not a routine measured comparison.
- bp: $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$.
- mp: $\text{H}_2\text{O} > \text{NH}_3 > \text{HF}$.
- Individual H-bond strength guide: $\text{HF} > \text{H}_2\text{O} > \text{NH}_3$.
- Bulk properties also depend on network connectivity.

36 Hydrogen bonding in ice and other solids

Ice: four hydrogen-bond neighbours



2 donated + 2 accepted H bonds

Open network → ice less dense than water

Each water molecule can donate two and accept two hydrogen bonds in ice's open tetrahedral network.

Chemical Bonding

Hydrogen bonding in ice and other solids

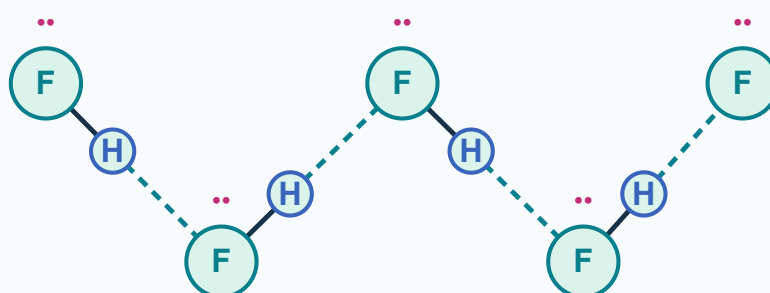
36 Hydrogen bonding in ice and other solids

continued

- Ice melts near 0°C $\rightarrow$ open network partly collapses $\rightarrow$ volume $\downarrow$, density $\uparrow$.
- So liquid water is denser than ice.
- This is a melting change, not contraction of solid ice at every temperature.

Substance	Source hydrogen-bonded structure
$\text{H}_2\text{O}(s)$	Open cage, 3D network
$\text{H}_3\text{BO}_3(s)$	2D sheets
$\text{HF}(s)$	Zigzag chains
$\text{KHCO}_3(s)$	Anionic dimers
$\text{NaHCO}_3(s)$	Anionic polymer chains

Hydrogen-bonded HF zigzag



Solid: covalent $\text{F}-\text{H}$ • Dotted: $\text{H}\cdots\text{F}$

Solid HF forms hydrogen-bonded zigzag chains.

Chemical Bonding

Hydrogen bonding in ice and other solids • Dipole-based intermolecular forces

36 Hydrogen bonding in ice and other solids

continued

Source row	N (undefined)	SN (undefined)	Total
O	2	2	4
H	2	4	6

- **Unclear original table: N and SN are not defined.**
- Counts are retained above for reference. The H total of 6 must not be read as 6 H-bonds per water molecule.

37 Dipole-based intermolecular forces

Interaction	Partners	Source examples	Distance dependence of energy / force
Ion-dipole	Ion + polar molecule	Na^+ , H_2O	Fixed orientation $U \propto r^{-2}$; $F \propto r^{-3}$
Dipole-dipole (Keesom)	Polar molecules	HCl , HCl	Fixed orientation $U \propto r^{-3}$; $F \propto r^{-4}$; thermal orientation averaging changes dependence
Ion-induced dipole	Ion + polarizable nonpolar molecule	Na^+ , Br_2	$U \propto r^{-4}$; $F \propto r^{-5}$
Dipole-induced dipole (Debye)	Polar + nonpolar molecule	$\text{H}_2\text{O}/\text{Xe}$; $\text{H}_2\text{O}/\text{Br}_2$	$U \propto r^{-6}$; $F \propto r^{-7}$
London dispersion / instantaneous induced-dipole-induced-dipole	All polarizable particles; emphasized for nonpolar molecules	H_2/H_2 ; F_2/F_2 ; Xe/Xe ; Cl_2/Cl_2	$U \propto r^{-6}$; $F \propto r^{-7}$

- Memory order: ion-dipole > dipole-dipole > ion-induced dipole > dipole-induced dipole > London.
- Actual strength depends on charge, dipole, polarizability, distance and shape.
- Down comparable series: size/polarizability $\uparrow \rightarrow$ London forces usually $\uparrow$. Mass alone is not the cause.

d- and f-Block Elements

Configurations • oxidation states • compounds

03

01 Definition and electronic configurations

- Transition element → atom or a cation has an incomplete d shell (d^1 – d^9).
- Zn, Cd, Hg: usual atoms/cations are d^0 → conventionally excluded.
- Ag qualifies through $Ag^{2+}(4d^9)$.
- Ag: $[Kr]4d^{10}5s^1$; Ag^+ : $4d^{10}$; Ag^{2+} : $4d^9$.

$$d \text{ block : } (n-1)d^{1-10}ns^{0-2}$$

ns^2 usual; ns^1 in several exceptions; Pd has ns^0 .

Element	Configuration
Cr	$[Ar]3d^54s^1$
Cu	$[Ar]3d^{10}4s^1$
Nb	$[Kr]4d^45s^1$
Mo	$[Kr]4d^55s^1$
Ru	$[Kr]4d^75s^1$
Rh	$[Kr]4d^85s^1$
Pd	$[Kr]4d^{10}5s^0$
Ag	$[Kr]4d^{10}5s^1$

$$f \text{ series : } (n-2)f^{1-14}(n-1)d^{0-1}ns^2$$

Usually d^0 ; d^1 in exceptions.

Th(90): $[Rn]6d^27s^2$.

The formula is a broad family pattern.

02 Atomic and metallic radii

- Group-3 layout here: $Sc < Y < La$ in size.
- Groups 4–12: $3d < 4d \approx 5d$.
- Poor 4f shielding → lanthanoid contraction.
- Example: $Ti < Zr \approx Hf$.

$$Sc > Ti > V > Cr < Mn > Fe \approx Co \approx Ni < Cu < Zn$$

Metallic-radius sketch: also $Sc > Zn$; $Mn \approx Zn$, near 137 pm in these data.

Exact values depend on radius definition.

d- and f-Block Elements

Ionization-energy orders • Spin-only moment

03 Ionization-energy orders

- Series ends: first metal has low IE; terminal d^{10} metal high IE.
- Sd IE is usually high, partly because of contraction. Exceptions: $Sc > Y > La$; group 4 has $Zr < Hf < Ti$ ($Hf \approx Ti$).
- 3d IE_1 : $Sc < V < Cr < Ti < Mn < Ni < Cu < Co < Fe < Zn$.
- Cue: 'Suno Vinita tum Kamal Nahi Man kyu uska giro Jaoge'.

Comparison	Reason from configurations
$IE_1(Cr) < IE_1(Mn)$	$Cr 3d^5 4s^1$ vs $Mn 3d^5 4s^2$
$IE_2(Cr) > IE_2(Mn)$	Cr^+ loses from stable $3d^5$; Mn^+ loses $4s^1$
$IE_3(Cr) < IE_3(Mn)$	$Cr^{2+} 3d^4$ vs $Mn^{2+} 3d^5$
$IE_1(Mn) < IE_1(Fe)$	$Mn 3d^5 4s^2$ vs $Fe 3d^6 4s^2$
$IE_2(Mn) < IE_2(Fe)$	$Mn^+ 3d^5 4s^1$ vs $Fe^+ 3d^6 4s^1$
$IE_3(Mn) > IE_3(Fe)$	$Mn^{2+} 3d^5$ especially stable; $Fe^{2+} 3d^6 \rightarrow Fe^{3+} 3d^5$

04 Spin-only moment

$$\mu = \sqrt{n(n+2)} \mu_B$$

n = unpaired electrons; quick estimate $\approx n+1$.

- High spin:
- $Cr^{2+} \rightarrow d^4$, $n = 4$.
- $Fe^{2+} \rightarrow d^6$, $n = 4$.
- Both: $\mu = \sqrt{24} \approx 4.90 \mu_B$.
- Strong ligand fields may change pairing.

05 Alloys and interstitial compounds

- Substitutional-alloy guide: metallic radii within about 15% helps mixing.
- Brass: Cu 60%, Zn 40%.
- German silver example: $Cu:Zn:Ni = 1:1:2$; commercial mixtures vary.
- Bronze: Cu + Sn.
- Interstitial compounds $\rightarrow$ small B/H/C/N atoms occupy metal-lattice gaps.
- Nonstoichiometric examples: $VH_{0.56}$, $TiH_{1.7}$.
- Often hard, high-melting, chemically resistant; retain metallic conductivity.
- NiB is a hard example; hardness varies.
- Bonding is not simply purely ionic or covalent.

d- and f-Block Elements

Melting-point trends • Catalysis through variable oxidation state

06 Melting-point trends

- Melting point depends on metallic bonding, electronic structure and packing; unpaired d electrons give a rough guide.
- W has the highest mp among d-block metals.
- Orders: $Zn > Cd > Hg$; $Sc > Y > La$; $Cu > Au > Ag$.

Group set	Source vertical melting-point sketch
3 and 12	$3d > 4d > 5d$
4–10	$3d < 4d < 5d$
11	$3d > 5d > 4d$

- Use these as trend patterns. Atomic mass alone does not predict melting point.

07 Catalysis through variable oxidation state



Overall reaction: iodine changes from -1 to 0 .



Fe^{3+}/Fe^{2+} cycle provides a catalytic pathway.

08 Named catalytic processes

Process	Reaction/use	Catalyst
Haber	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	Finely divided Fe
Contact	$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$	V_2O_5
Oil hydrogenation	Vegetable oil + $H_2 \rightarrow$ more saturated fat	Ni or Pd
Wacker	$CH_2=CH_2 \rightarrow CH_3CHO$ (with oxidant/water)	$PdCl_2$ -based system
Ziegler–Natta	Alkene polymerization	$TiCl_4 + Al(C_2H_5)_3$ in source
Wilkinson	Alkene hydrogenation	$RhCl(PPh_3)_3$



d- and f-Block Elements

Variable oxidation states • High versus low oxidation-state stability

09 Variable oxidation states

- Close ns and $(n-1)d$ energies $\rightarrow$ variable oxidation states.
- Sc is mainly $+3$; Sc^{2+} , Cr^+ and Fe^{5+} are not ordinary stable aqueous ions.
- Cu^{2+} is stable in water; Cu^+ can be stabilized in solids/complexes.

Element	Source highlighted oxidation states
Sc	+3
Ti	+4
V	+5
Cr	+3,+6
Mn	+2,+4,+7
Fe	+2,+3
Co	+2,+3
Ni	+2
Cu	+2
Zn	+2

Source heuristic oxidation-state range: y to $x + y$

$y = ns$ electrons; $x =$ unpaired d electrons.

Mn: $3d^5 4s^2 \rightarrow +2$ to $+7$ as a memory range.

Not every intermediate state is equally stable or universally accessible.

- Oxidation-state variety rises towards the middle, then falls.
- Early metals have few available electrons; late metals have fuller/paired d shells.
- $Sc(II)$ is uncommon; $Ti(IV)$ often more stable than $Ti(III)/(II)$.
- Zn is usually $+2$; d electrons remain filled.

10 High versus low oxidation-state stability

- Down d -block groups 4–10, high oxidation states often become more stable.
- p -block inert-pair trend often favours lower states instead.
- Group 6: $Mo(VI)$, $W(VI)$ more stable than $Cr(VI)$.
- Acidic dichromate is strongly oxidizing; MoO_3/WO_3 much less so.

d- and f-Block Elements

High versus low oxidation-state stability • High oxidation states in halides

10 High versus low oxidation-state stability

continued

Group 6: stability of the +6 state

Cr(VI)



Mo(VI)



W(VI)



High oxidation-state stability increases

Strong oxidant

Less oxidizing

The +6 state becomes more stable down Cr→Mo→W, reducing the oxidizing tendency of the corresponding high-state species.

- σ -donor + π -acceptor ligands can stabilize low oxidation states.
- $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$; metal oxidation state = 0.

11 High oxidation states in halides

- High-state examples: TiX_4 , VF_5 .
- CrF_6 is a disputed historical assignment; earlier spectra were reassigned to CrF_5 .
- $\text{Mn}(+7)$: no ordinary simple halide; MnO_3F exists.
- $\text{MnF}_5/\text{MnF}_6/\text{MnF}_7$ are not ordinary stable fluorides.
- Beyond Mn, notable trihalides include FeX_3 and CoF_3 .

- F stabilizes high states through strong lattice attraction (CoF_3) or M–F bonds (VF_5).
- V(V) example: VF_5 .
- Other high-state halides readily form VOX_3 on hydrolysis.
- VBr_5 and VX_5 ($\text{X} = \text{Cl}/\text{Br}/\text{I}$) are unstable ordinary examples.

- Low-state fluorides can exist: crystalline VF_2 is known.
- F often favours higher oxidation states, but this does not rule out every low-state fluoride.

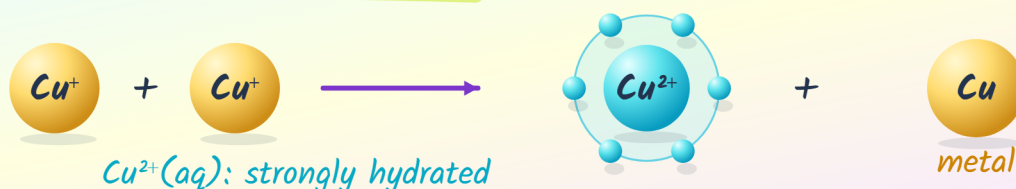
d- and f-Block Elements

Copper halides and disproportionation • Aqueous copper and iodide reduction

12 Copper halides and disproportionation

- Known Cu(II) halides: CuF_2 , CuCl_2 , CuBr_2 .
- CuI_2 is unstable: Cu^{2+} oxidizes $\text{I}^- \rightarrow \text{I}_2$, leaving CuI .
- Cu(I) may be stable in solids/complexes; simple aqueous Cu^+ tends to disproportionate.

Simple aqueous Cu^+ can disproportionate



- Cu^{2+} hydration releases much energy; it can offset the second-ionization cost.
- $\text{Cu}(\text{g}) \rightarrow \text{Cu}^+(\text{g}) \rightarrow \text{Cu}^{2+}(\text{g})$: energy needed.
- $\text{Cu}^{2+}(\text{g}) \rightarrow \text{hydrated Cu}^{2+}$: energy released.
- This helps favour $\text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s})$ over simple $\text{Cu}^+(\text{aq})$.

13 Aqueous copper and iodide reduction

- $2\text{Cu}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s})$; strong Cu^{2+} hydration helps.
- I^- reduces: $\text{Ti}^{3+} \rightarrow \text{Ti}^+$; $\text{Pb}^{4+} \rightarrow \text{Pb}^{2+}$; $\text{Bi}^{5+} \rightarrow \text{Bi}^{3+}$; $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$; $\text{Cu}^{2+} \rightarrow \text{Cu}^+$.
- I^- becomes I_2 .
- Ordinary PbI_4 and CuI_2 are unstable; CuI (compositionally Cu_2I_2) is stable.



14 High oxidation states in oxides

- First-row metals commonly form MO (+2) oxides.
- Sc mainly forms Sc_2O_3 with +3.
- Sc $\rightarrow$ Mn (groups 3–7): highest common oxide oxidation state = group number.
- O/F stabilize high states. Strong multiple/delocalized M–O bonding can favour even higher states with O.
- Examples: MnO_2 (+4), uncommon Mn_2O_5 (+5), uncommon MnO_3 (+6), Mn_2O_7 (+7), MnO_3F (+7).
- Ordinary Mn fluoride maximum: MnF_4 .
- Fe_2O_3 is a common high-state simple oxide; ferrate(VI), FeO_4^{2-} , exists in alkali and is strongly oxidizing.

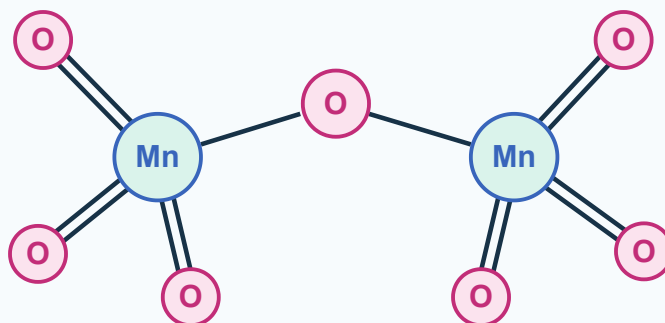
d- and f-Block Elements

High oxidation states in oxides • Oxide acidity and covalency

14 High oxidation states in oxides

continued

Mn_2O_7 : an oxygen bridge



Each Mn: +7 and four O neighbours

Mn_2O_7 contains two tetrahedral Mn centres joined by one bridging oxygen.

Tetrahedral oxoanion	Metal oxidation state
VO_4^{3-}	+5
CrO_4^{2-}	+6
MnO_4^{3-}	+5
MnO_4^{2-}	+6
MnO_4^-	+7

15 Oxide acidity and covalency

- Oxidation state $\uparrow \rightarrow$ oxide covalency/acidity usually $\uparrow$; ionic character $\downarrow$.
- High-state $\text{CrO}_3/\text{V}_2\text{O}_5$ have relatively low mp.
- V_2O_5 is mainly acidic but amphoteric:
- Base $\rightarrow$ vanadates, e.g. VO_4^{3-} .
- Acid $\rightarrow \text{VO}_2^+$, dioxovanadium(V).

16 Reduction potentials and acid reactions

- Common first-row M^{2+}/M : E° usually negative; Cu^{2+}/Cu is positive.
- Cu does not normally release H_2 from dilute nonoxidizing acids; Zn does.
- Cu dissolves in concentrated HNO_3 or hot concentrated H_2SO_4 .

d- and f-Block Elements

Reduction potentials and acid reactions • Redox comparisons

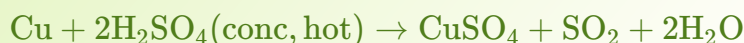
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16 Reduction potentials and acid reactions

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

Use full-cell E° . $E^\circ_{\text{cell}} > 0 \rightarrow \Delta G^\circ < 0$ for the written reaction.

17 Redox comparisons



Couple	Source approximate E° / V
$\text{Cr}^{3+}/\text{Cr}^{2+}$	-0.41
$\text{Fe}^{3+}/\text{Fe}^{2+}$	+0.77 (source rounds +0.79)
$\text{Co}^{3+}/\text{Co}^{2+}$	+1.97 in source
$\text{Mn}^{3+}/\text{Mn}^{2+}$	+1.59 in source (later line gives +1.57)
$\text{V}^{3+}/\text{V}^{2+}$	-0.26

- Reducing strength: $\text{Cr}^{2+} > \text{Fe}^{2+}$.
- Oxidizing strength: $\text{Co}^{3+} > \text{Mn}^{3+}$ under these conditions.
- Potential values require specified species and standard conditions; the approximate handwritten values are retained for comparison.

Source observation	Electronic explanation
$\text{Sc}^{3+}/\text{Sc}^{2+}$ strongly negative	Sc^{3+} has a noble-gas configuration
$\text{Zn}^{3+}/\text{Zn}^{2+}$ strongly positive/unfavourable +3	Zn^{2+} is d^{10}
$\text{Mn}^{3+}/\text{Mn}^{2+}$ strongly positive	Mn^{2+} is stable half-filled d^5
$\text{Fe}^{3+}/\text{Fe}^{2+}$ less positive than Mn/Co examples	Fe^{3+} is d^5
$\text{V}^{3+}/\text{V}^{2+}$ negative	V^{2+} is d^3 with t_{2g}^3 stability in an octahedral field

- Mn^{3+} and $\text{Co}^{3+} \rightarrow$ strong aqueous oxidants.
- Ti^{2+} , V^{2+} , $\text{Cr}^{2+} \rightarrow$ strong reductants; can reduce H^+ to H_2 under suitable conditions.

d- and f-Block Elements

Chromate–dichromate equilibrium and structures • Potassium versus sodium dichromate

18 Chromate–dichromate equilibrium and structures

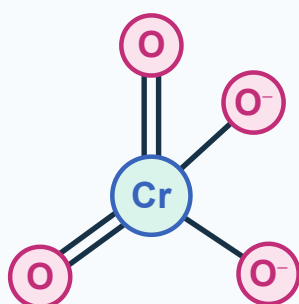


Base favours yellow CrO_4^{2-} .

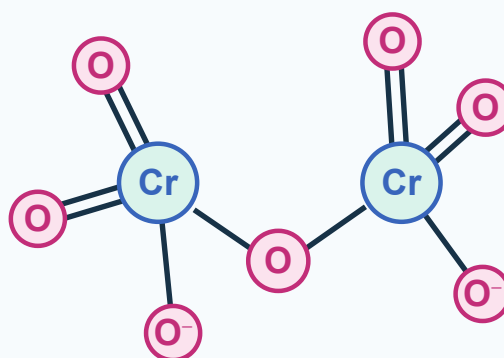
Acid favours orange $\text{Cr}_2\text{O}_7^{2-}$.

Cr stays +6 → no redox change.

Chromate $\rightleftharpoons$ dichromate



yellow • tetrahedral



Acid → dichromate; base → chromate

Chromate is tetrahedral; dichromate contains two tetrahedral units sharing one oxygen. Bridging Cr–O links are longer.

19 Potassium versus sodium dichromate

Property	$\text{K}_2\text{Cr}_2\text{O}_7$	$\text{Na}_2\text{Cr}_2\text{O}_7$
Solubility	Lower	Higher
Primary standard in redox analysis	Suitable when pure/dried	Generally not preferred
Moisture behaviour	More suitable stable crystalline standard	Hygroscopic
Crystallization	Crystallizes preferentially when KCl added	Remains more in solution

20 Preparation from chromite

- Chromite = $\text{FeCr}_2\text{O}_4 = \text{FeO} \cdot \text{Cr}_2\text{O}_3$.
- Roast with air + $\text{Na}_2\text{CO}_3 \rightarrow$ yellow sodium chromate.
- Acidify $\rightarrow$ orange sodium dichromate.
- Add KCl $\rightarrow$ less-soluble orange $\text{K}_2\text{Cr}_2\text{O}_7$ crystallizes.

d- and f-Block Elements

Preparation from chromite • Manganate versus permanganate

20 Preparation from chromite

continued



Crystallization step.

Memory pathway: Cr_2O_3 oxidized to acidic CrO_3 ; basic Na_2CO_3 traps it as chromate.

21 Manganate versus permanganate



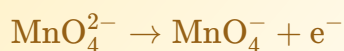
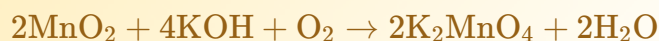
Acid promotes disproportionation of manganate(VI).

Feature	MnO_4^{2-} (manganate)	MnO_4^- (permanganate)
Colour	Dark green	Dark purple/violet
Oxidation state	+6	+7
d count / unpaired electrons	d^1 / 1	d^0 / 0
Ordinary spin classification	Paramagnetic	Diamagnetic
Shape	Tetrahedral	Tetrahedral
Source Lewis bond-order average	6/4	7/4
M–O bonds	Equivalent within free ion	Equivalent within free ion

- Permanganate has stronger/shorter Mn–O bonds than manganate.
- ‘Two/three $d\pi$ – $p\pi$ bonds’ is older localized Lewis bookkeeping.
- MnO_4^- is d^0 ; ordinary spin classification = diamagnetic. A temperature-independent magnetic contribution needs separate susceptibility evidence.

22 Preparation of KMnO_4

- Pyrolusite MnO_2 + fused KOH + oxidant (air/ O_2 , KNO_3 or KClO_3) $\rightarrow$ green K_2MnO_4 .
- Convert to KMnO_4 by electrolysis, ozone oxidation or controlled acid disproportionation.



Anode: manganate loses one electron.

Acid disproportionation also produces MnO_2 .

d- and f-Block Elements

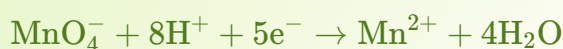
Oxidizing strength and medium-dependent products • oxidation-conversion checklist

23 Oxidizing strength and medium-dependent products

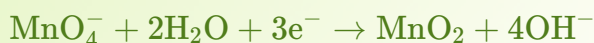
Permanganate: the medium decides the reduction product



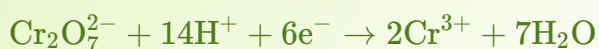
- KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow$ high metal states, strong oxidants.
- Acidic oxidizing order: $\text{MnO}_4^- > \text{Cl}_2 > \text{Cr}_2\text{O}_7^{2-} > \text{VO}_2^+$.
- $\text{MnO}_4^- \rightarrow$ stable d^5 Mn^{2+} .
- $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$.



Acid: purple $\rightarrow$ very pale pink Mn^{2+} ; dilute solution may look colourless.



Neutral/weak base: brown MnO_2 precipitate.



Acid: orange dichromate $\rightarrow$ green Cr(III) ; colour depends on ligands.

24 oxidation-conversion checklist

Oxidant/medium	Substrate $\rightarrow$ oxidation product
Acidic MnO_4^-	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$; $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$; $\text{H}_2\text{S} \rightarrow \text{S}$; $\text{Cl}^-/\text{Br}^-/\text{I}^- \rightarrow \text{Cl}_2/\text{Br}_2/\text{I}_2$; $\text{C}_2\text{O}_4^{2-} \rightarrow \text{CO}_2$; $\text{NO}_2^- \rightarrow \text{NO}_3^-$; $\text{SO}_2/\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$
Neutral/weakly basic MnO_4^-	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ (often hydroxide precipitate); $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$; $\text{C}_2\text{O}_4^{2-} \rightarrow \text{CO}_2/\text{carbonate}$ depending pH; $\text{H}_2\text{S} \rightarrow \text{S}$; $\text{I}^- \rightarrow \text{IO}_3^-$; $\text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-}$
Acidic $\text{Cr}_2\text{O}_7^{2-}$	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$; $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$; $\text{H}_2\text{S} \rightarrow \text{S}$; $\text{I}^- \rightarrow \text{I}_2$; $\text{SO}_2 \rightarrow \text{SO}_4^{2-}$
Source dichromate comparison	Does not readily oxidize Cl^- under standard aqueous conditions; concentrated HCl /other conditions require separate treatment
$\text{Cr}_2\text{O}_7^{2-} + \text{CO}_2$	No redox reaction
$\text{Cr}_2\text{O}_7^{2-} + \text{SO}_2$ in acid	Reduction to Cr^{3+} ; sulfate forms, e.g. $\text{Cr}_2(\text{SO}_4)_3$ in sulfate medium
$\text{Cr}_2\text{O}_7^{2-} + \text{KOH}$	Yellow CrO_4^{2-} ; acid-base conversion, no oxidation-state change

d- and f-Block Elements

oxidation-conversion checklist • f-series configurations and ionization

24 oxidation-conversion checklist

continued

- Use the listed conditions: acidity, reactant amounts and temperature can change the product.

25 f-series configurations and ionization

- This layout: lanthanoids Ce–Lu (58–71), period 6; actinoids Th–Lr (90–103), period 7, linked to group 3.
- Broader family names include La/Ac.
- Rough lanthanoid $IE_1 \approx 600$, $IE_2 \approx 1200 \text{ kJ mol}^{-1}$; broadly like Ca.
- La/Gd/Lu have relatively low IE_3 : removal gives stable $La^{3+}(4f^0)$, $Gd^{3+}(4f^7)$, $Lu^{3+}(4f^{14})$.
- Neutral atoms:
- La: $[Xe]5d^1 6s^2$.
- Gd: $[Xe]4f^7 5d^1 6s^2$.
- Lu: $[Xe]4f^{14} 5d^1 6s^2$.

26 Lanthanoid-actinoid comparison

Property	Source broad comparison
Size	Corresponding actinoids generally larger than lanthanoids; specify ions/state
Ionization energy	Source generally $L_n > A_n$
Reactivity	Actinoids often more reactive
Electronegativity	Source generally $A_n < L_n$
Hydroxide basicity	Source generally A_n hydroxides more basic
Common oxidation state	+3 in both
Other states	L_n : Eu^{2+} , Yb^{2+} , Ce^{4+} ; A_n : many states because 5f/6d/7s energies are close
High actinoid state in source	Np and Pu can reach +7

- Actinoid trends are less regular; check individual pairs.
- Many L_n^{3+} ions are coloured by f–f transitions.
- La^{3+} , Lu^{3+} and Gd^{3+} are essentially colourless in visible light.

27 Special configurations and redox

- $La^{3+}/Ce^{4+} \rightarrow f^0$; $Yb^{2+}/Lu^{3+} \rightarrow f^{14}$. All diamagnetic.
- $Eu^{2+}(f^7)$, $Yb^{2+}(f^{14})$ can reduce other species and become +3.
- $Ce^{4+}(f^0)$, $Tb^{4+}(f^7)$ can oxidize others and become Ce^{3+}/Tb^{3+} .

d- and f-Block Elements

Special configurations and redox • Lanthanoid metal reaction map

27 Special configurations and redox

continued



Ce(IV)/Ce(III): positive reduction potential.

Ce⁴⁺ is an analytical oxidant; its reaction with water may be slow.

28 Lanthanoid metal reaction map

Reagent	Products shown in source
HCl	$\text{LnCl}_3 + \text{H}_2$
H ₂ O	$\text{Ln}(\text{OH})_3 + \text{H}_2$
N ₂	LnN
S	Ln_2S_3
O ₂	Ln_2O_3 (usual +3 oxide; some elements give other oxides)
X ₂	LnX_3
C	Ln_3C , Ln_2C_3 , LnC_2 carbides

- Ln here means lanthanoid metal.
- The +3 label describes its usual product oxidation state, not the starting free ion.

29 Applications and memory facts

- Nd → useful in strong permanent magnets; not simply 'most paramagnetic'.
- Gd³⁺: 7 unpaired electrons → largest Ln³⁺ spin-only moment. Actual moments also include orbital effects.
- Sm → steel-like appearance.
- Pm → radioactive.
- Mischmetal ≈ 95% lanthanoids + 5% Fe; traces of C, S, Ca, Al.
- Ruby: red Cr³⁺ in Al₂O₃.
- Emerald: green Cr³⁺ in beryl.
- Copper-coloured steel utensil → copper coating.
- Silver-coloured Cu/Ni alloy → cupronickel.

Coordination Compounds

Ligands • nomenclature • isomerism

04

01 Double salts versus coordination compounds

- Two salts crystallized together may form an addition compound:
- Double salt or complex/coordination salt.

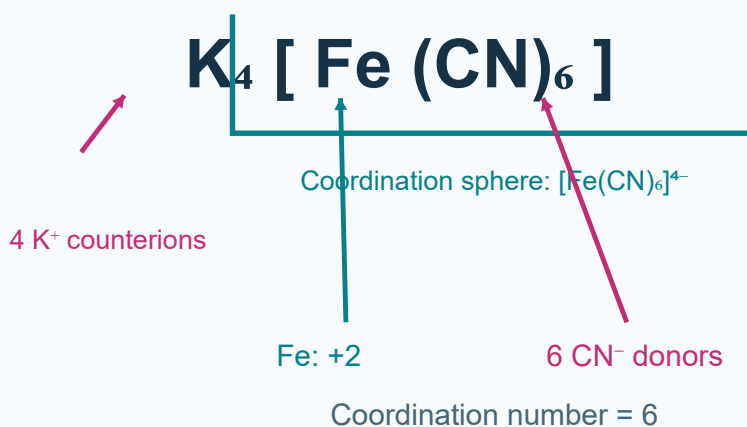
Feature	Double salt	Complex salt
In water	Dissociates into ordinary constituent ions	Complex coordination entity can remain intact; counterions dissociate
Identity	Crystal addition compound loses its identity on dissolution	Complex ion retains a distinct identity
Ion tests	Constituent simple ions give their usual tests	Coordinated groups do not necessarily give free-ion tests

Double salt	Composition
Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$
Mohr's salt	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
Potash alum	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

- Examples: $K_4[Fe(CN)_6]$, $[Pt(NH_3)_2Cl_2]$.
- Ligand donates an electron pair; metal accepts.
- Transition metals form complexes readily: favourable size/charge density + accessible orbitals. Metal-ligand bonds can have covalent character.

02 Coordination sphere and oxidation number

Read the coordination formula



Brackets separate the coordination entity from its counterions; Fe is +2 with six cyanido donors.

Coordination Compounds

Coordination sphere and oxidation number • Other definitions

02 Coordination sphere and oxidation number

continued

- Coordination number (CN) = donor atoms directly bonded to metal.
- In the simple model, count metal–donor σ links; do not add π links separately.
- Oxidation number $\rightarrow$ balance ligand, complex and counterion charges.

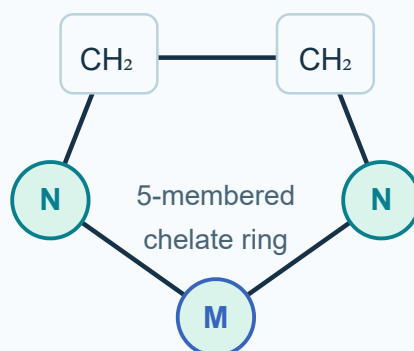
- $K_4[Fe(CN)_6]$: Fe = +2; CN = 6.
- $[Pt(en)_2]Cl_2$: en is neutral and bidentate; Pt = +2; CN = 4.

03 Other definitions

- Homoleptic $\rightarrow$ one ligand type: $[Fe(CN)_6]^{4-}$.
- Heteroleptic $\rightarrow$ different types: $[Pt(NH_3)_2Cl_2]$.
- Denticity $\rightarrow$ donor atoms of ONE ligand bound to a metal.
- NH_3 : 1 (monodentate).
- en = $H_2N-CH_2-CH_2-NH_2$: 2 N donors (bidentate).

CN	Possible coordination polyhedron
2	Linear
3	Trigonal planar
4	Tetrahedral or square planar
5	Trigonal bipyramidal (square pyramidal is another possibility)
6	Octahedral / square bipyramidal

en: one ligand, two N donors



$H_2N-CH_2-CH_2-NH_2$ • denticity 2

One ethane-1,2-diamine ligand binds through two nitrogen atoms to make a five-membered chelate ring.

Coordination Compounds

Classification and anionic ligand names • Oxalato and glycinato

04 Classification and anionic ligand names

- Ligand → molecule/ion donating electron density to metal.
- Classify by charge, denticity or σ -donor/ π -acceptor behaviour.
- ' ≤ 3 atoms means monodentate' is not a safe shortcut: bridging/side-on bonding needs care.

Formula	Name / donor
SO_4^{2-}	Sulfato
CO_3^{2-}	Carbonato
Cl^-	Chlorido
Br^-	Bromido
OH^-	Hydroxido
F^-	Fluorido
NH_2^-	Amido
NH^{2-}	Imido
N_3^-	Azido
N^{3-}	Nitrido
O^{2-}	Oxido
O_2^-	Superoxido
O_2^{2-}	Peroxido
CN^- , C-bound	Cyanido- κC
NC^- , N-bound	Cyanido- κN (source: isocyanido)
NO_2^- , N-bound	Nitrito- κN / nitro
ONO^- , O-bound	Nitrito- κO
OCN^- , O-bound	Cyanato- κO
NCO^- , N-bound	Isocyanato- κN
SCN^- , S-bound	Thiocyanato- κS
NCS^- , N-bound	Thiocyanato- κN

05 Oxalato and glycinato

- Oxalato (ox), $\text{C}_2\text{O}_4^{2-}$: two O donors; symmetric bidentate; 5-membered ring.
- Glycinato (gly), $\text{NH}_2\text{CH}_2\text{COO}^-$: N + O donors; unsymmetric bidentate; 5-membered ring.

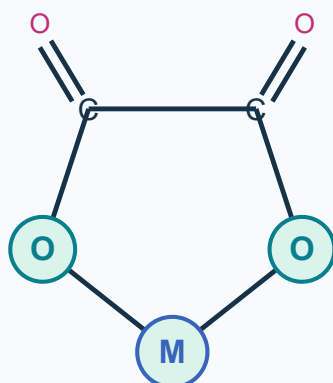
Coordination Compounds

Oxalato and glycinato • Dimethylglyoximato nickel test

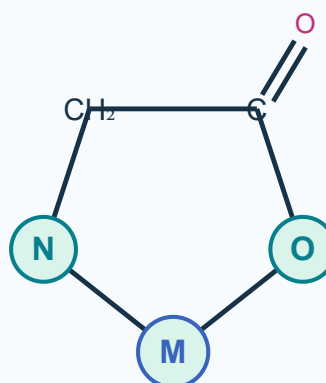
05 Oxalato and glycinato

continued

Two five-membered chelates



Oxalato²⁻
O,O donors



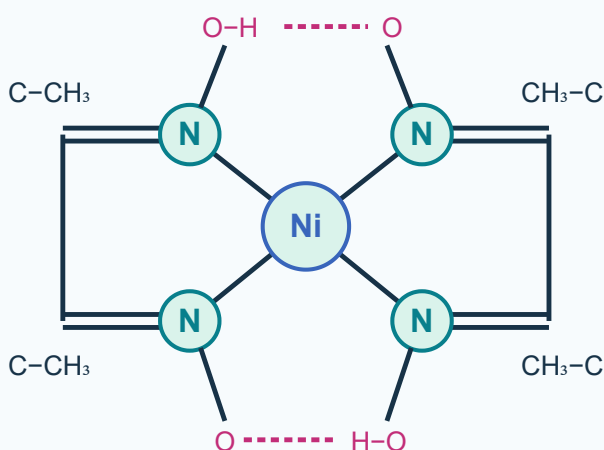
Glycinato⁻
N,O donors

Oxalato binds O,O; glycinato binds N,O. Both commonly form five-membered chelate rings.

06 Dimethylglyoximato nickel test

- Ni^{2+} + dimethylglyoxime in ammonia $\rightarrow$ rosy/cherry-red precipitate.
- Write $[\text{Ni}(\text{dmgH})_2]$, or simplified $\text{Ni}(\text{dmg})_2$.
- Each monoanionic ligand gives 2 N donors.
- CN 4; square planar; traditional dsp^2 ; optically inactive (symmetry plane).

Nickel dimethylglyoximato



Square-planar NiN_4 • cherry-red precipitate

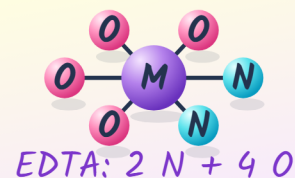
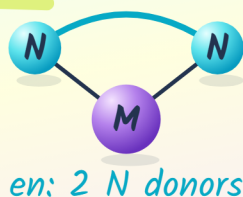
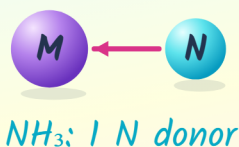
The cherry-red nickel dimethylglyoximate precipitate has a square-planar NiN_4 centre and hydrogen-bonded ligand pair.

Coordination Compounds

EDTA and neutral ligands

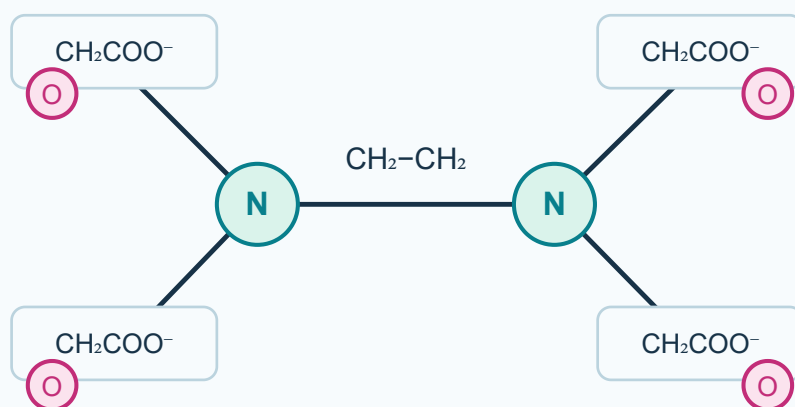
07 EDTA and neutral ligands

Denticity counts donor atoms from ONE ligand



- EDTA^{4-} = ethylenediaminetetraacetato.
- Usually hexadentate: 2 N + 4 O donors.
- Full coordination forms five 5-membered chelate rings.
- Nonplanar arrangements can be chiral; optical activity depends on the actual structure/sample.

EDTA⁴⁻: 2 N + 4 O donors



6 coordination sites → 5 chelate rings

Each carboxylate usually supplies one O

EDTA normally supplies six donors: two nitrogen and four oxygen atoms.

Coordination Compounds

EDTA and neutral ligands • Cationic, ambidentate and flexidentate ligands

07 EDTA and neutral ligands

continued

Neutral ligand	Name	Usual denticity
H_2O	Aqua	1
NH_3	Ammine	1
CO	Carbonyl	1
NO	Nitrosyl	Formal bonding/charge requires context
PH_3	Phosphine	1
PPh_3	Triphenylphosphine	1
py	Pyridine	1, N donor
en	Ethane-1,2-diamine	2, N donors
pn	Propane-1,2-diamine / propylenediamine	2
tn	Propane-1,3-diamine / trimethylenediamine	2
$dien$	Diethylenetriamine	3
$trien$	Triethylenetetramine	4

08 Cationic, ambidentate and flexidentate ligands

- Cationic ligands: NO^+ (nitrosonium); $NH_2-NH_3^+$ (hydrazinium).
- Ambidentate → different possible donor atoms, usually one mode at a time: CN^- , NO_2^- , OCN^- , SCN^- .
- Polydentate chelate → several donor atoms bind together.
- Flexidentate → denticity can change.
- SO_4^{2-}/CO_3^{2-} : 1 or 2 O donors.
- EDTA: usually 6; sometimes fewer, e.g. 4.
- Classical ligand → mainly σ donor.
- π -acid ligand → also accepts metal density: ethene, CO , CN^- , benzene.

09 Naming rules

- Naming steps:
- 1. Cation before anion.
- 2. Ligands alphabetically; count with di/tri/tetra/penta/hexa.
- 3. Metal + oxidation number in Roman numerals.
- 4. Anionic complex: metal ends in '-ate', e.g. ferrate/zincate.
- Use bis/tris/tetrakis + parentheses for complex ligand names or names already containing number prefixes.

Formula	Name
$[NiCl_2(PPh_3)_2]$	Dichloridobis(triphenylphosphine)nickel(II)
$[Co(en)_3]Cl_3$	Tris(ethane-1,2-diamine)cobalt(III) chloride

Coordination Compounds

IUPAC practice • Nitrosyl complexes + tests

10 IUPAC practice

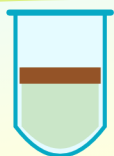
Formula	Name / oxidation state
$[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$	Triamminetriaquachromium(III) chloride
$[\text{Ni}(\text{CO})_4]$	Tetracarbonylnickel(0)
$[\text{CoCl}_2(\text{en})_2]^+$	Dichloridobis(ethane-1,2-diamine)cobalt(III) ion
$[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$	Diamminechlorido(nitrito- κN)platinum(II)
$[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$	Pentaamminecarbonatocobalt(III) chloride
$\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$	Potassium tris(oxalato)aluminate(III)

- $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$ is neutral with Pt(II).
- No extra chloride belongs outside the brackets or at the end of this name.

11 Nitrosyl complexes + tests

- Brown-ring nitrate test: $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]\text{SO}_4$.
- Formal NO^+ counting gives Fe(I): pentaqua(nitrosyl)iron(I) sulfate.
- Fe–NO shares electrons in a more complex way ('non-innocent' ligand); 'Fe + NO always means NO^+ ' is unsafe.

Two memorable coordination-compound colour tests



NO_3^- test $\rightarrow$ brown ring
iron-nitrosyl complex



S^{2-} + nitroprusside
 $\rightarrow$ purple / violet

- Sodium nitroprusside: $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$.
- Usual formal count: Fe(II), five CN^- , linear NO^+ .
- Name: sodium pentacyanonitrosylferrate(II).
- Sulfide S^{2-} + SNP $\rightarrow$ purple/violet colour.

12 Werner's primary and secondary valence

Primary valence	Secondary valence
Equals metal oxidation state	Equals coordination number
Satisfied by anions	Satisfied by neutral/anionic ligands
Associated with ionizable counterions, though anions can also coordinate	Coordinated links are not ordinarily released as free ions on dissolution
Nondirectional in the simple ionic picture	Directional; determines coordination geometry
Source dotted-line representation	Source solid-line representation

Coordination Compounds

Werner's primary and secondary valence • VBT geometry labels

12 Werner's primary and secondary valence

continued

- $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$:
- $\text{Pt} = +4$; $\text{CN} = 6$.
- 4 Cl^- balance primary valence; only 2 are outside the sphere.
- Excess $\text{AgNO}_3 \rightarrow 2 \text{ mol AgCl per mol complex}$.
- More/mobile dissolved ions $\rightarrow$ generally higher molar conductivity.
- At comparable conditions:
- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3 > [\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 > [\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$.

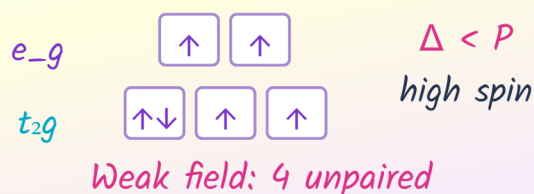
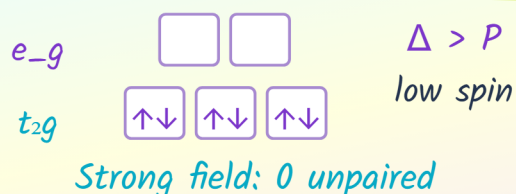
13 VBT geometry labels

- VBT: metal orbitals combine to accept ligand lone pairs.
- CN, electron configuration and ligands together decide geometry; CN alone is insufficient.

CN	Geometry	Conventional hybrid label
2	Linear	sp
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3
4	Square planar	dsp^2 (dx^2-y^2)
5	Trigonal bipyramidal	sp^3d or dsp^3 (dz^2)
6	Octahedral	d^2sp^3 (inner) or sp^3d^2 (outer), using dz^2 and dx^2-y^2

14 Strong- versus weak-field ligands

Same d^6 count, different splitting $\rightarrow$ different spin



- Strong field can favour pairing/low spin.
- Weak field favours high spin when a spin choice exists.
- Inner/outer-orbital labels come from VBT.
- Low spin can still be paramagnetic if unpaired electrons remain.

Coordination Compounds

Strong- versus weak-field ligands • VBT shortcuts

14 Strong- versus weak-field ligands

continued

Complex	Metal/d count	VBT/geometry	Unpaired <i>n</i> and magnetism
$K_4[Fe(CN)_6]$	Fe^{2+} , d^6 ; CN^- strong	CN_6 ; d^2sp^3 , octahedral, inner, low spin	0; diamagnetic
$K_3[FeF_6]$	Fe^{3+} , d^5 ; F^- weak	CN_6 ; sp^3d^2 , octahedral, outer, high spin	5; paramagnetic, $\mu = \sqrt{35} \approx 5.92 \mu_B$
$[Ni(CN)_4]^{2-}$	Ni^{2+} , d^8 ; CN^- strong	CN_4 ; dsp^2 , square planar	0; diamagnetic
$K_3[Mn(CN)_6]$	Mn^{3+} , d^4 ; CN^- strong	CN_6 ; d^2sp^3 , octahedral, low spin	2; paramagnetic, $\mu = \sqrt{8} \approx 2.83 \mu_B$
$Ni(CO)_4$	$Ni(0)$, formal d^{10}	CN_4 ; sp^3 , tetrahedral	0; diamagnetic

Electron occupancy and magnetism



Electron pairing depends on both d count and ligand-field splitting; low spin need not mean diamagnetic.

15 VBT shortcuts

- Octahedral CN_6 :
- $d^1/d^2/d^3 \rightarrow 1/2/3$ unpaired; traditional inner d^2sp^3 ; no spin choice.
- $d^8/d^9/d^{10} \rightarrow 2/1/0$ unpaired; traditional outer sp^3d^2 .
- $d^4-d^7 \rightarrow$ high/low-spin alternatives.

Coordination Compounds

VBT shortcuts · Crystal-field model

15 VBT shortcuts

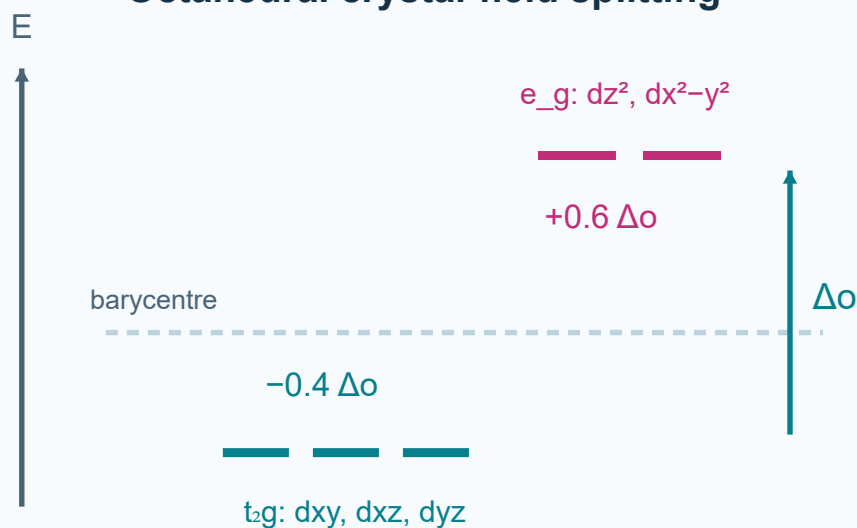
continued

- $[\text{Co}(\text{CN})_6]^{4-}$: Co^{2+} , d^7 , low spin; 1 unpaired electron.
- Old VBT 'transfer rule' promotes an electron to free 2 inner d orbitals.
- CFT simply uses $t_{2g}e_g$; no such promotion is needed.
- Higher metal charge (e.g. Ni^{4+}) and 4d/5d series often give larger splitting.
- Many Co^{3+} complexes are low spin.
- NH_3 can still give high-spin $\text{Cr}^{2+}/\text{Mn}^{2+}/\text{Fe}^{2+}/\text{Co}^{2+}$ complexes.
- Check the actual metal, ligand and geometry.
- Unclear handwritten fragment: ' Co^{3+} — 0 donor ligands — S.L.', with '0 donor' crossed/marked.
- Its exact exception is unreadable.
- Use actual splitting versus pairing energy.

16 Crystal-field model

- CFT: ligand electron density repels metal d electrons.
- Different d orbitals rise by different amounts $\rightarrow$ splitting; geometry sets the pattern.
- Along axes: d_{z^2} , $d_{x^2-y^2}$.
- Between axes: d_{xy} , d_{xz} , d_{yz} .

Octahedral crystal-field splitting

Low spin if $\Delta_o >$ pairing energy P Octahedral: $t_{2g} = -0.4\Delta_o$; $e_g = +0.6\Delta_o$ relative to the barycentre.

Coordination Compounds

Crystal-field model • Tetrahedral field

16 Crystal-field model

continued

$$\Delta_o > P \Rightarrow \text{low spin;}$$

$$\Delta_o < P \Rightarrow \text{high spin}$$

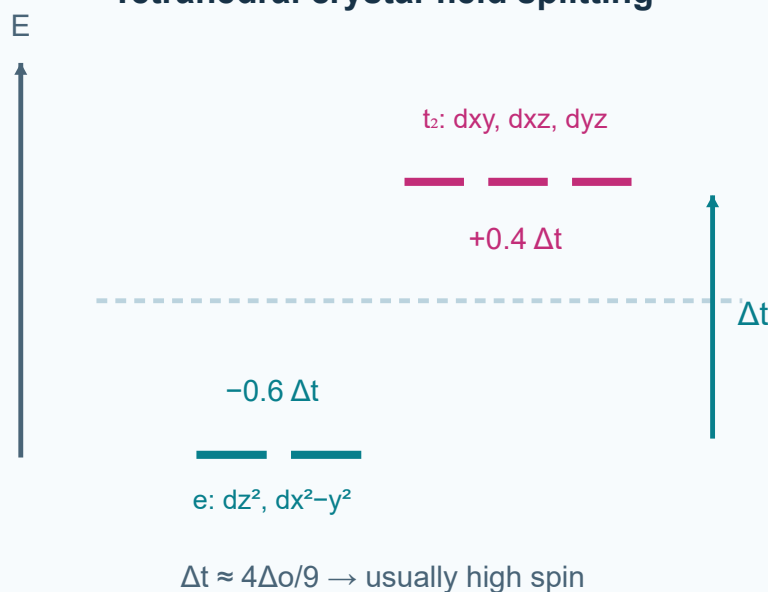
P = pairing energy. Apply when different spin occupations are possible.

d count	Octahedral occupation
d^1	$t_2g^1e_g^0$
d^2	$t_2g^2e_g^0$
d^3	$t_2g^3e_g^0$
d^4 high spin	$t_2g^3e_g^1$
d^4 low spin	$t_2g^4e_g^0$

- High spin $\rightarrow$ fill t_2g singly, then e_g singly, then pair.
- Low spin $\rightarrow$ fill/pair t_2g first, then e_g .
- Common square-planar order: $dx^2-y^2 > dxy > dz^2 > dxz = dyz$. Other geometries have different orders.

17 Tetrahedral field

Tetrahedral crystal-field splitting



Tetrahedral e levels lie below t_2 ; the smaller gap usually produces high-spin occupation.

$$\Delta_t \approx \frac{4}{9} \Delta_o < \Delta_o$$

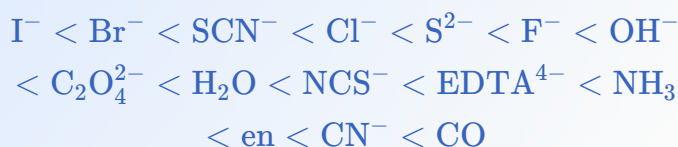
Compare the same metal, oxidation state and ligands.
Tetrahedral Δ_t is usually below $P \rightarrow$ high spin.

Coordination Compounds

Ligand dependence and spectrochemical series • Factors affecting splitting

18 Ligand dependence and spectrochemical series

- Stronger field $\rightarrow$ splitting $\uparrow$.
- Rough donor-atom cue: $C > N > O >$ halogen.
- Actual ligand and π interactions also matter.



Weak $\rightarrow$ strong field.

SCN^- : S donor, weaker; NCS^- : N donor, stronger.

Exact position can vary with metal/oxidation state.

19 Factors affecting splitting

- Same metal/ligand: higher oxidation state $\rightarrow$ usually larger Δ .
- $[Fe(CN)_6]^{3-} > [Fe(CN)_6]^{4-}$.
- Comparable ions: $3d < 4d < 5d$; $Fe^{2+} < Ru^{2+} < Os^{2+}$.
- $[NiCl_4]^{2-} \rightarrow$ tetrahedral, sp^3 .
- $[Ni(CN)_4]^{2-} \rightarrow$ square planar, dsp^2 . Both ligand and geometry change.
- Simple guide: $\Delta_{sp} > \Delta_o > \Delta_t$.
- $\Delta_o \approx 9\Delta_t/4$; $\Delta_t \approx 4\Delta_o/9$.
- $\Delta_{sp} \approx 1.33\Delta_o$ is a rough model value; square-planar fields have several gaps.

20 Octahedral CFSE and pairing

$$E_{\text{relative}} = n(-0.4\Delta_o) + m(+0.6\Delta_o) + xP$$

$n = t_{2g}$ electrons; $m = e_g$ electrons; x = extra pairs versus the chosen high-spin/free-ion reference.
First two terms = CFSE; $+xP$ adds the pairing cost.

$$d^4 \text{ high spin : } t_{2g}^3 e_g^1 \Rightarrow CFSE = 3(-0.4\Delta_o) + 0.6\Delta_o = -0.6\Delta_o$$

$$d^4 \text{ low spin : } t_{2g}^4 e_g^0 \Rightarrow E = -1.6\Delta_o + P$$

$$x = N_{\text{pairs, low spin}} - N_{\text{pairs, high spin}}$$

'New pairs' = low-spin pairs - high-spin pairs.

$x = 0$ for the high-spin reference does not mean it has no paired electrons.

Coordination Compounds

Complex stability and colour • Effective atomic number

21 Complex stability and colour

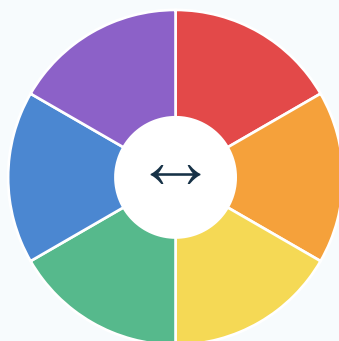
- Stability depends on metal charge, M–L interaction strength and chelation.
- Colour may come from d–d or charge-transfer transitions.
- Charge transfer can colour d^0/d^0 species too.
- CFT links transition energy with splitting.

$$E = \frac{hc}{\lambda}$$

Absorbed energy $\uparrow \rightarrow$ absorbed wavelength $\downarrow$.
Observed colour is complementary to absorbed colour.

- $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$: purple $\text{Ti}(\text{III})$, d^1 . Anhydrous TiCl_3 is also coloured.
- Heat blue $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow$ white CuSO_4 ; ligand environment changes.
- Hydrate: 4 waters coordinate closely to Cu^{2+} ; the fifth mainly H-bonds in the lattice; sulfate contacts also matter.

Absorbed and observed colours



Opposite sectors
are approximate
complementary colours

$$E = hc / \lambda$$

Shorter $\lambda \rightarrow$ higher E

Observed colour is not the absorbed colour

A complex shows the complementary colour of the light it absorbs; photon energy rises as wavelength falls.

22 Effective atomic number

$$EAN = Z - OS + \text{electrons donated by ligands}$$

Many complexes reach a noble-gas count; EAN/18-electron rules have exceptions.

$$[\text{Fe}(\text{CN})_6]^{4-} : \\ EAN = 26 - 2 + 6(2) = 36$$

Coordination Compounds

Effective atomic number · Organometallic classes

22 Effective atomic number

continued

$$\text{Ni(CO)}_4 :$$

$$EAN = 28 - 0 + 4(2) = 36$$

$$\text{Mn}_2(\text{CO})_{10} :$$

$$EAN \text{ per Mn} = 25 + 5(2) + 1 = 36$$

Mn–Mn bond contributes 1 electron per metal.
 Combined arithmetic: $(2 \times 25 + 10 \times 2 + 2)/2 = 36$.

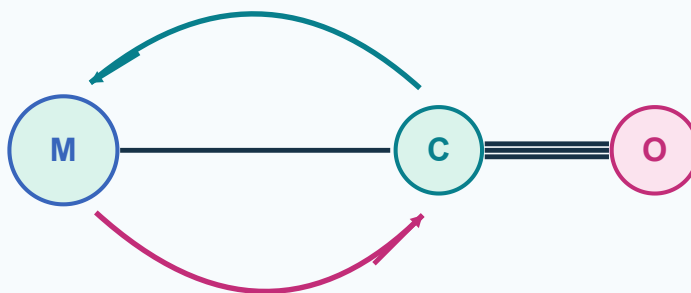
23 Organometallic classes

- Organometallic compound → direct metal–carbon interaction.
- Types here: σ , π or $\sigma + \pi$.

Class	Source examples
σ -bonded	RMgX (Grignard), R_2Zn (Frankland), R_2CuLi (Gilman), $\text{Pb}(\text{C}_2\text{H}_5)_4$ (tetraethyllead); Ziegler–Natta systems $\text{TiCl}_4 + \text{R}_3\text{Al}$ or $\text{TiCl}_3 + \text{R}_2\text{AlCl}$
π -bonded	Ferrocene, cobaltocene, ruthenocene, Zeise's salt
σ donation + π backbonding	Ni(CO)_4 , Fe(CO)_5 and other metal carbonyls

24 Synergic metal–carbonyl bonding

Synergic metal–carbonyl bonding

CO → M: σ donationM → CO π^* : back-donation

M–C stronger/shorter • C–O weaker/longer

CO → M σ donation and M → CO π back-donation strengthen M–C while weakening C–O.

Coordination Compounds

Synergic metal–carbonyl bonding • Structural versus stereoisomerism

24 Synergic metal–carbonyl bonding

continued

- Covalent counting: CO donates 2e; neutral NO is counted as 3e. Ionic NO⁺ counting is different.
- $M(CO)_6 \rightarrow M(NO)_4$ keeps 12 donated electrons: $6 \times 2 = 4 \times 3$.
- Thus $3CO \leftrightarrow 2NO$ electronically. This is counting, not a reaction guaranteed for every metal.

25 Structural versus stereoisomerism

- Isomers: same overall composition.
- Structural $\rightarrow$ different connections/distribution: ionization, linkage, hydrate/solvate, coordination.
- Stereo $\rightarrow$ different spatial arrangement: geometrical, optical.

Type	Definition	Source examples
Ionization	Exchange a coordinated ligand with a counterion; different ions released	$[Pt(NH_3)_3Cl]Br$ gives AgBr with $AgNO_3$; $[Pt(NH_3)_3Br]Cl$ gives AgCl. $[Co(NH_3)_5SO_4]Br$ / $[Co(NH_3)_5Br]SO_4$
Linkage	Alternative donor atoms of an ambidentate ligand	Nitro/nitrito binding in $[Pt(NH_3)_3(NO_2)]Cl_2$ and $[Pt(en)_2Cl(NO_2)]$
Hydrate/solvate	Exchange water/solvent inside and outside coordination sphere	$[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$ and $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$
Coordination	Exchange ligand distribution between cationic and anionic complex ions	$[ML_6][M'L'_6]$ compared with redistributed $[ML_5L']$ $[M'L'_5L]$

26 Isomer-counting examples and hydrate conductivity

- Linkage shortcut 2ⁿ works only for independent, distinguishable choices.
- Two equivalent ligands give NN, NO, OO donor-mode compositions; geometry may add spatial variants.
- Count symmetry.
- First nitrite example $\rightarrow$ 2 modes.
- Second written formula has ONE nitrite, although the notes say $n = 2 \rightarrow 4$; mismatch retained.

$CrCl_3 \cdot 6H_2O$ hydrate	Number of ordinary dissolved ions	Readily precipitable Cl ⁻ per formula
$[Cr(H_2O)_6]Cl_3$	4	3
$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$	3	2
$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$	2	1
$[Cr(H_2O)_3Cl_3] \cdot 3H_2O$ (source formal candidate)	1 neutral entity	0

Coordination Compounds

Isomer-counting examples and hydrate conductivity • Stereoisomerism definitions

26 Isomer-counting examples and hydrate conductivity

continued

- First 3 rows are the commonly taught $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ hydrates.
- Conductivity/ AgCl yield: $1 > 2 > 3$.
- Fourth row is a formal candidate in the notes.
- Neutral complexes can contain lattice water; check which hydrate is actually isolated.
- Restricted coordination-isomer shortcuts:
- $[\text{ML}_n][\text{ML}'_n]$ (same metal) $\rightarrow n/2$.
- $[\text{ML}_n][\text{M}'\text{L}'_n]$ $\rightarrow n$.
- Examples in this scheme: $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4] \rightarrow 2$; $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6] \rightarrow 6$.
- Check charge balance, allowed distribution, metal identity and geometry before using.

27 Stereoisomerism definitions

- Stereoisomers: same connections, different 3D arrangement.
- Geometrical isomerism commonly occurs in heteroleptic complexes.
- Geometrical: cis = adjacent (often 90°); trans = opposite (180°).
- Optical: nonsuperimposable mirror images = enantiomers. A single enantiomer can rotate plane-polarized light.

28 Square-planar and tetrahedral counts

Square-planar formula	Geometrical arrangements
MA_4	1 (no GI)
MA_3B	1 (no GI)
MA_2B_2	2: cis/trans
MA_2BC	2
MABCD	3
$\text{M}(\text{AA})_2, \text{M}(\text{AA})\text{B}_2, \text{M}(\text{AA})\text{BC}$; symmetric chelateAA	1 each in simple source treatment
$\text{M}(\text{AB})_2$; unsymmetric chelateAB	2
$\text{M}(\text{AB})\text{B}_2$	1
$\text{M}(\text{AB})\text{BC}$	2

Coordination Compounds

Square-planar and tetrahedral counts • Octahedral isomers

28 Square-planar and tetrahedral counts

continued

- Ordinary square-planar complexes have a symmetry plane → achiral.
- AA: equal donor ends, e.g. en/ox.
- AB: unlike donors, e.g. N/O glycinato.
- Tetrahedral: no usual cis/trans; MABCD and some $M(AB)_2$ arrangements can be chiral.
- CN 4 trends:
- Zn/Cd/Hg often tetrahedral.
- Pt(II)/Pd(II), d^8 , often square planar.
- These are common patterns, not rules for every complex.

29 Octahedral isomers

- Octahedral complexes can show GI and optical isomerism.
- A mirror plane makes a structure achiral.
- Identical trans ligands/coplanar rings are only clues; check full symmetry.
- Noncoplanar chelate helicity can give Δ/Λ mirror-image forms.

Octahedral formula	Geometrical arrangements	Total stereoisomers in source cases
MA_6	1 (noGI)	1
MA_5B	1 (noGI)	1
MA_4B_2	2	2
MA_4BC	2	2
MA_3B_3	2:fac/mer	2
$M(AA)_3$, e.g. $[Co(en)_3]^{3+}$	1 geometry	2 enantiomers (Δ/Λ)
$M(AA)_2B_2$	2:cis/trans	3:cis Δ , cis Λ , achiraltrans
$M(AA)_2BC$ (source symmetric chelate case)	2	3 in source treatment: chiral cis pair+achiraltrans

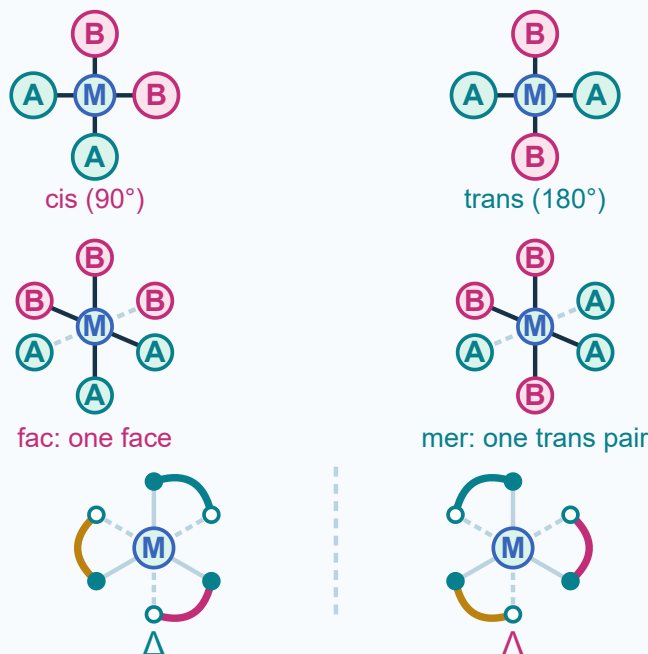
Coordination Compounds

Octahedral isomers • Applications of coordination compounds

29 Octahedral isomers

continued

Geometrical and optical isomers

Cis/trans and fac/mer change spatial arrangement; Δ/Λ chelate forms are mirror-image enantiomers.

30 Applications of coordination compounds

Application	Source example
Water hardness determination	Complexometric titration using disodium EDTA
Metal extraction/purification	Selective formation and decomposition of complexes
Alkene hydrogenation	Wilkinson's catalyst $\text{RhCl}(\text{PPh}_3)_3$
Photographic fixing	Thiosulfate ('hypo') dissolves unexposed AgBr as $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$
Lead-poisoning treatment	Appropriate calcium disodium EDTA chelation under medical supervision; source calls it EDTA
Anticancer medicine	Cisplatin
Photosynthesis pigment	Chlorophyll contains Mg
Oxygen transport	Haemoglobin contains Fe
Vitamin B_{12}	Cyanocobalamin contains Co
Uniform Ag/Au electroplating	Complex-ion baths using $[\text{Ag}(\text{CN})_2]^-/[\text{Au}(\text{CN})_2]^-$ control available metal-ion concentration



Thiosulfate dissolves unexposed AgBr during photographic fixing.

