CHEM 548: MATERIALS CHEMISTRY

LECTURE 5: ELECTRON COUNTING AND STOICHIOMETRY

Wed 09/09/2026

Electron counting from the octet rule to the generalized 8−N rule and Zintl phases, and the crystal chemical formula

Worked examples: SiO_2, $NaTl$, $SnCl_2$, $CaSb$, Al_2O_3, Na_3N

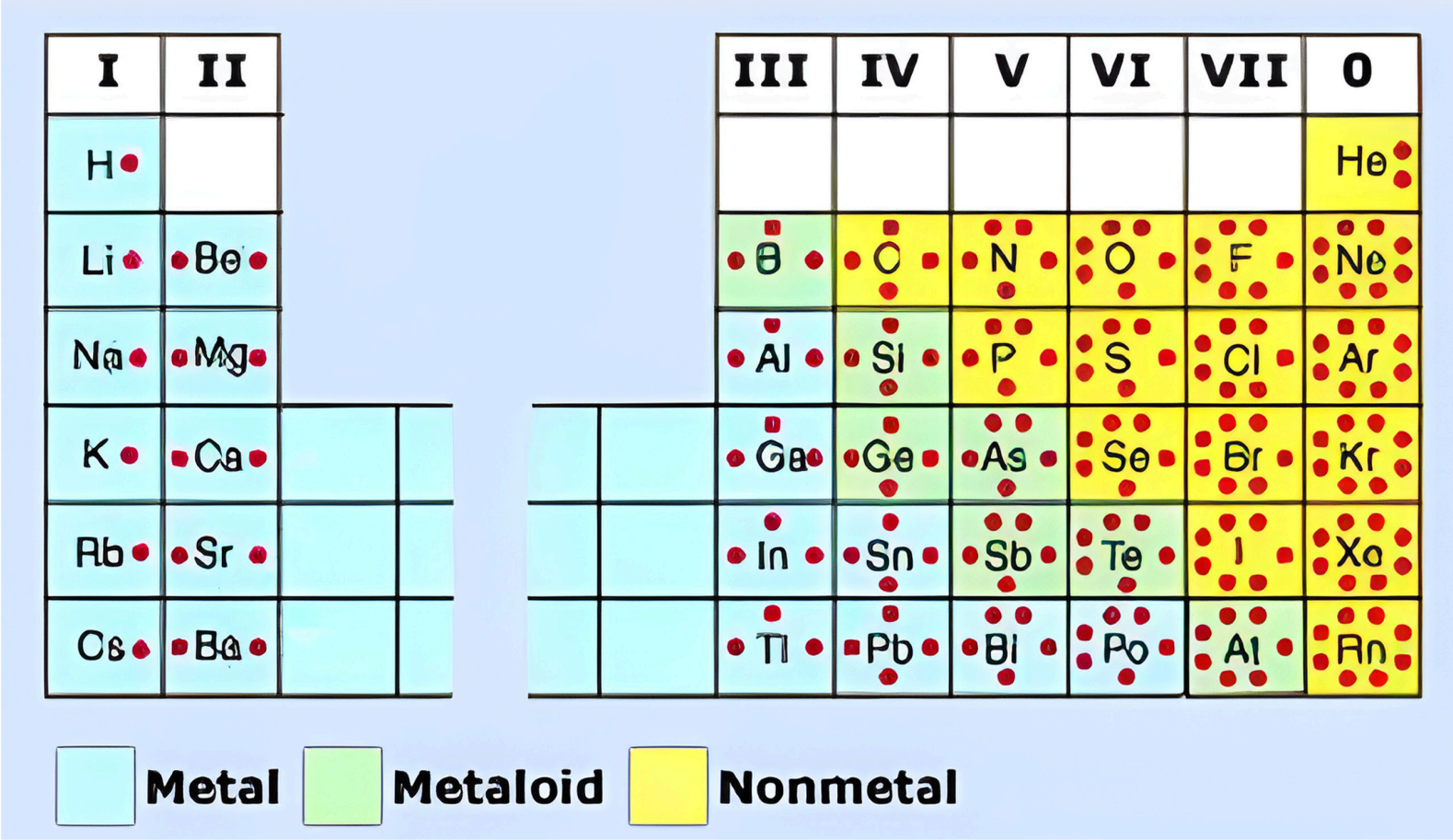
Reading: Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry* Ch. 1 §1.3, §1.5.6

LEARNING OBJECTIVES

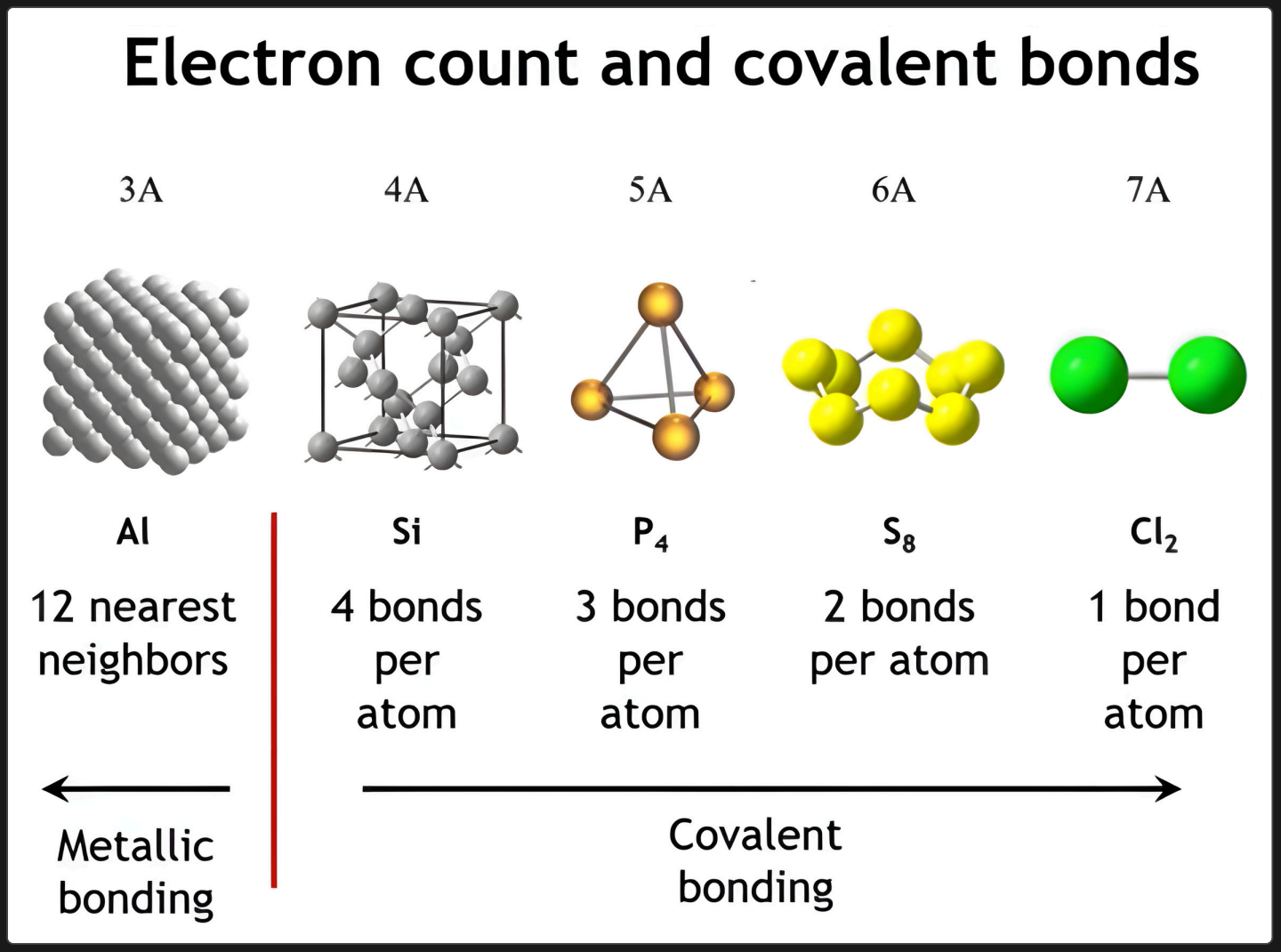
Octet rule	explain how directional covalent bonding satisfies it
Bond counts	predict them from Lewis structures and the trend from group 7A to 4A
Bonding classes	distinguish covalent, metallic, and ionic bonding by electron availability
VEC per anion	count the valence electrons an anion receives
Generalized 8−N rule	predict anion–anion bonds, cation–cation bonds, and cation lone pairs
Zintl phases	recognize an electropositive metal donating electrons into a covalent network or dimer

THE OCTET RULE

Octet Rule: Main-group atoms form bonds until they have **8 valence electrons**, like a noble gas.



ELECTRON COUNT AND COVALENT BONDS



VALENCE ELECTRON COUNT PER ANION

Cation C	the more electropositive element, m per formula unit
Anion A	the more electronegative element, n per formula unit

Valence electrons per anion, against the octet

valence electrons per cation — valence electrons per anion

$$\mathrm{VEC}_A = \frac{e_C \cdot m + e_A \cdot n}{n}$$

Octet obeyed

$$\mathrm{VEC}_A = 8$$

THE GENERALIZED OCTET RULE

SiO_2

$$\mathrm{VEC}_A = \frac{e_C \cdot m + e_A \cdot n}{n}$$

$$\mathrm{VEC}_A = \frac{4 \cdot 1 + 6 \cdot 2}{2} = \frac{16}{2} = 8$$

The octet rule is obeyed

NaTl

$$\mathrm{VEC}_A = \frac{e_C \cdot m + e_A \cdot n}{n}$$

$$\mathrm{VEC}_A = \frac{1 \cdot 1 + 3 \cdot 1}{1} = 4$$

GENERALIZED 8−N RULE

NaTl

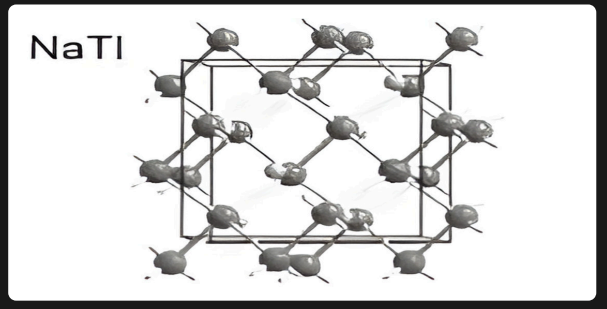
$$\mathrm{VEC}_A = \frac{e_C \cdot m + e_A \cdot n}{n}$$

$$\mathrm{VEC}_A = \frac{1 \cdot 1 + 3 \cdot 1}{1} = 4$$

$$\mathrm{VEC}_A = 8 + CC(m/n) - AA$$

$$4 = 8 + CC(m/n) - AA$$

$$AA = 4$$

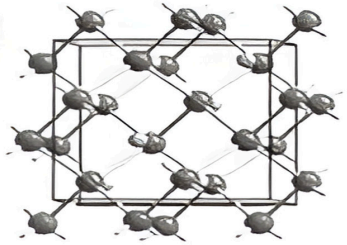


ZINTL PHASES

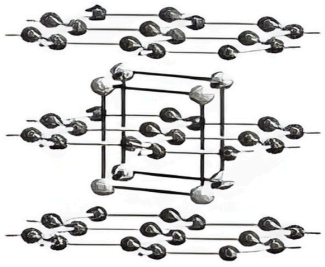
Zintl Phases

Follow the Zintl-Klemm concept: the electropositive metal donates its electrons to the electronegative metal(s)

NaTl



$SrGa_2$

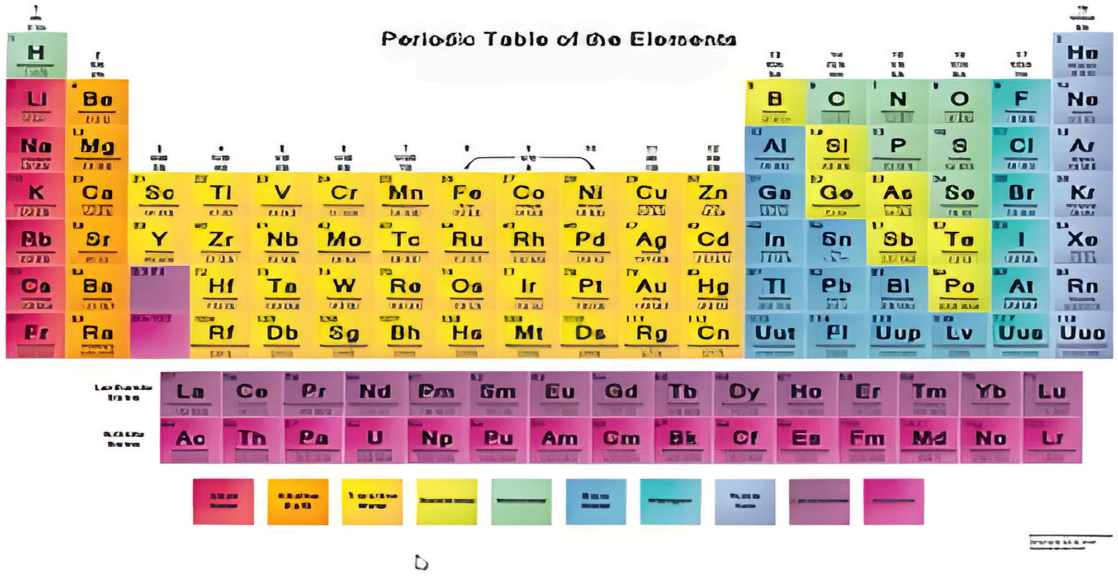


- Fixed stoichiometry
- Diamagnetic, brittle, and exhibit low electrical conductivity

APPLY THE GENERALIZED 8–N RULE

Apply the generalized 8–N rule

- $SnCl_2$
- CaSb



$SNCL_2$ AND CASB

CaSb

$$\mathrm{VEC}_A = \frac{2 \cdot 1 + 5 \cdot 1}{1} = 7$$

$$\mathrm{VEC}_A = 8 + CC(m/n) - AA$$

$$7 = 8 + \cancel{CC}(1/1) - AA$$

$$AA = 1$$

There is an Sb–Sb bond that leads to formation of Sb_2^{4-} dimers

SUMMARY

Valence electrons per anion (VEC/A) counts what the cations donate and the anions accept. The octet then fixes the bond count across the p block: 7A ($7e^-$) → 1 bond, 6A → 2, 5A → 3, 4A → 4 (diamond, Si, Ge); further left, bonding goes metallic through delocalized electrons.

VEC/A	What the generalized 8−N rule says	Example
= 8	The octet closes on the anion as drawn, even in a largely covalent solid	SiO_2
< 8	Too few electrons: anion–anion bonds form	Tl–Tl in NaTl Sb_2^{4-} in CaSb
> 8	Too many: the excess stays on the cation as lone pairs or cation–cation bonds	Sn^{2+} in $SnCl_2$

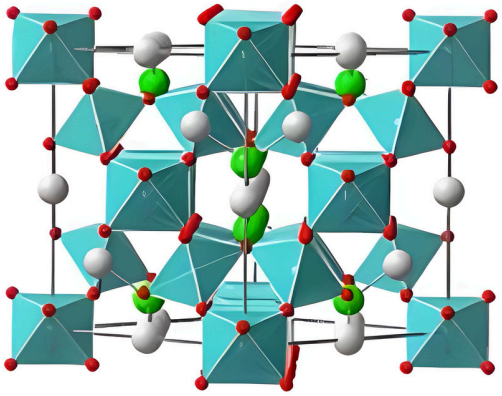
Zintl phases: an electropositive metal donates its electrons and the electronegative element builds the covalent structure — NaTl diamond-like, $SrGa_2$ graphite-like sheets.

LEARNING OBJECTIVES

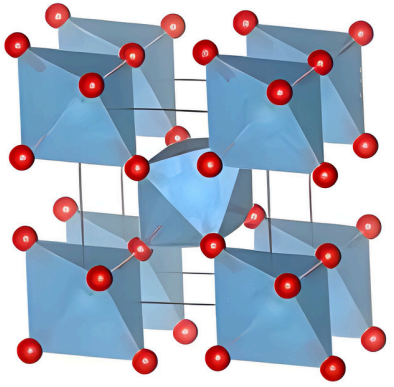
Stoichiometry constraint	explain how a formula constrains the crystal structure
Crystal chemical formula	define it and write it for a compound
Three balances	balance electroneutrality, connectivity, and bond valence
Bond graphs	construct one and read coordination numbers and bond valences back for SiO_2, TiO_2, CaF_2, Al_2O_3, and Na_3N
Parsimony and symmetry	apply Pauling's and Brown's rules to a candidate structure

STRUCTURES FOLLOW STOICHIOMETRY

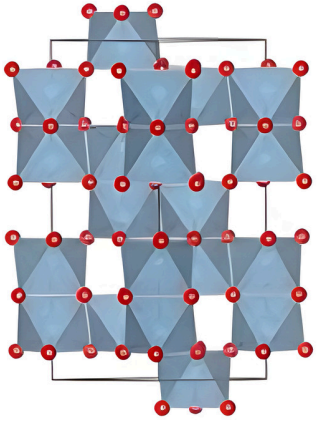
$La_2Zr_2O_7$



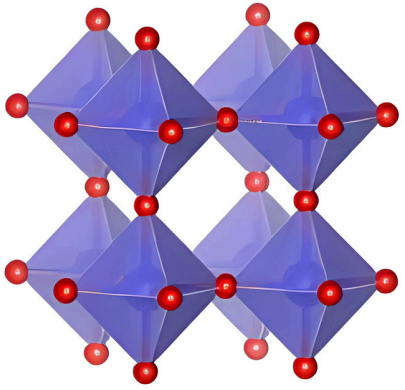
TiO_2



Al_2O_3



ReO_3



STOICHIOMETRY CONSTRAINTS

Given	silicon and oxygen, Si tetrahedral (CN 4), Si 4+, O 2−
Find	empirical formula, coordination number of oxygen, Si–O bond valence

crystal chemical formula

charge

coordination number

$$\mathrm{Si}_{m}^{4+}\,[4]\;\mathrm{O}_{n}^{2-}\,[M]$$

atoms in the formula

Electroneutrality

$m \times 4 = n \times (2)$

$\mathrm{SiO_2}$

Connectivity

$1 \times 4 = 2 \times M$

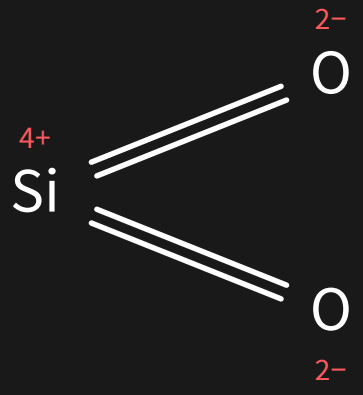
$M = 2$

Bond valence

$4/4 = 2/2$

$= 1$

BOND GRAPHS

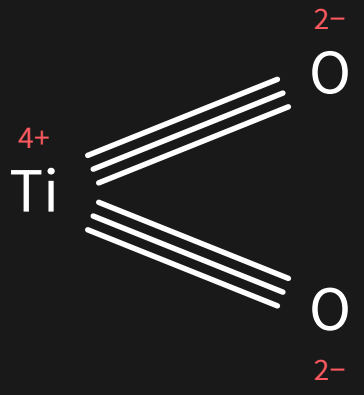


$$\mathrm{Si}^{4+\,[4]}\mathrm{O}_2^{2-\,[2]}$$

bond valence

charge / coordination number

$4/4 = 2/2 = 1$

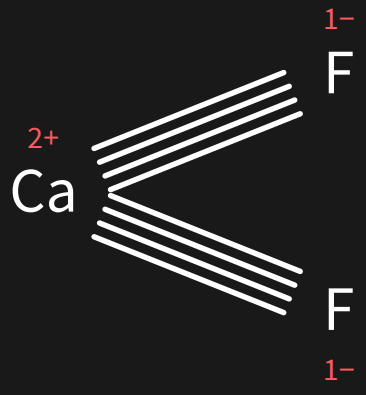


$$\mathrm{Ti}^{4+\,[6]}\mathrm{O}_2^{2-\,[3]}$$

bond valence

charge / coordination number

$4/6 = 2/3$



$$\mathrm{Ca}^{2+\,[8]}\mathrm{F}_2^{1-\,[4]}$$

bond valence

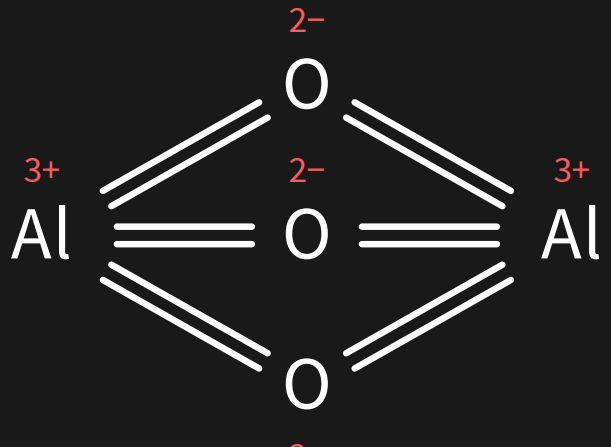
charge / coordination number

$2/8 = 1/4$

ALL THINGS EQUAL NATURE FAVORS SYMMETRIC STRUCTURES

Pauling, parsimony	few chemically distinct coordination environments per ion, ideally one
Brown, maximum symmetry	the most symmetric structure the constraints allow

BOND GRAPHS: AL_2O_3 AND NA_3N

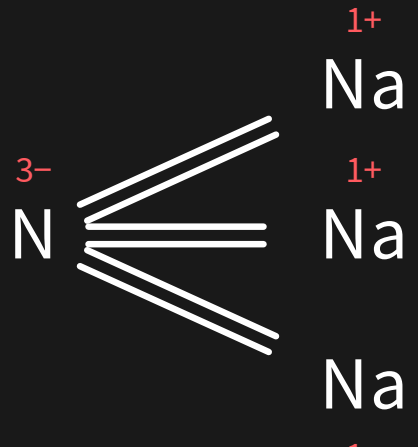


$$Al_2^{3+\,[6]}O_3^{2-\,[4]}$$

bond valence

charge / coordination number

$3/6 = 2/4 = \frac{1}{2}$



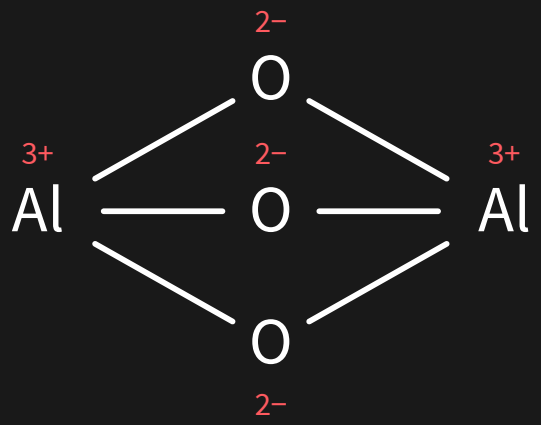
$$Na_3^{1+\,[2]}N^{3-\,[6]}$$

bond valence

charge / coordination number

$1/2 = 3/6 = \frac{1}{2}$

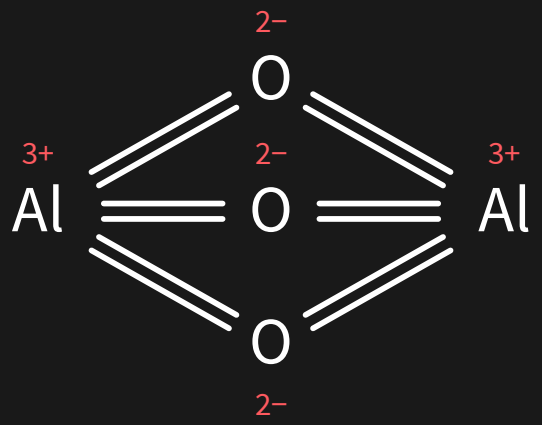
WHY NOT ANOTHER BOND GRAPH?



$$\mathrm{Al}_2^{3+}[3]\mathrm{O}_3^{2-}[2]$$

connectivity $2 \times 3 = 3 \times 2$

bond valence $3/3 = 2/2 = 1$



$$\mathrm{Al}_2^{3+}[6]\mathrm{O}_3^{2-}[4]$$

connectivity $2 \times 6 = 3 \times 4$

bond valence $3/6 = 2/4 = \frac{1}{2}$

$\mathrm{Al}_2[12]\mathrm{O}_3[8]$ balances too: $2 \times 12 = 3 \times 8$ and $3/12 = 2/8 = \frac{1}{4}$

Both graphs balance. Lecture 4 decides between them.

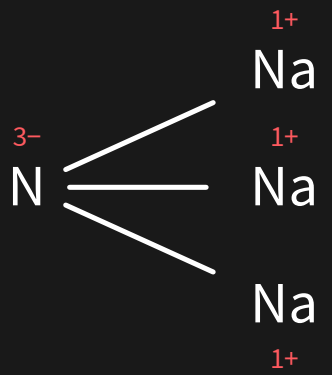
Lecture 4: an ionic solid maximizes cation–anion contact. Each touching oxide is one more attraction.

Three neighbors leave room. A fourth oxide touches Al and nothing stops it until six.

Twelve neighbors collide. Oxides touch each other before reaching Al, so every bond is long.

Observed: Al^{3+}/O^{2-} is 0.38, just under the 0.414 octahedral limit. Al is 4 or 6 coordinate in oxides; corundum has six.

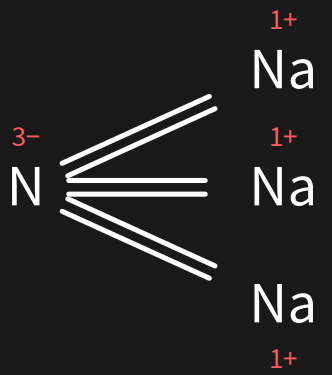
WHY NOT ANOTHER BOND GRAPH? NA_3N



$$\mathrm{Na}_3^{1+}[1]\mathrm{N}^{3-}[3]$$

connectivity $3 \times 1 = 1 \times 3$

bond valence $1/1 = 3/3 = 1$



$$\mathrm{Na}_3^{1+}[2]\mathrm{N}^{3-}[6]$$

connectivity $3 \times 2 = 1 \times 6$

bond valence $1/2 = 3/6 = \frac{1}{2}$

$\mathrm{Na}_3[6]\mathrm{N}[18]$ balances too: $3 \times 6 = 1 \times 18$ and $1/6 = 3/18 = \frac{1}{6}$ — sodium at its usual six

Both graphs balance, so lecture 4 decides again, this time from the anion's side.

- Six neighbors per Na would require eighteen Na around each N: too much Na–Na repulsion.
- In Na_3N, N has six neighbors and Na has two: octahedral N, linear Na.
- One-coordinate Na cannot bridge nitrogen atoms.

SUMMARY

Crystal structures are not random. The crystal chemical formula records the oxidation states, coordination numbers, and bonding, and three balances have to close on it.

Balance	What balances	Rule
Electroneutrality	Charges	Cation and anion charges sum to zero across the formula
Connectivity	Bond counts	Bonds leaving the cations equal the bonds arriving at the anions
Bond valence	Bond strength	Oxidation state ÷ coordination number; fractional values are allowed

A bond graph draws that bookkeeping out; Pauling's parsimony minimizes distinct environments and Brown's maximum symmetry takes the most symmetric structure the stoichiometry allows.

SiO_2, TiO_2, CaF_2, Al_2O_3, and Na_3N all fall out of those rules, the rare ones included: Na_3N was first synthesized in 2002 and is unstable at 360 K.

PRACTICE QUESTIONS

Work the Lecture 5 practice questions before the next class. They cover the valence electron count per anion, the generalized 8−N rule and Zintl phases, and the crystal chemical formula with its three balances.

Open the Lecture 5 practice questions

Every question carries a worked explanation, so you can check your reasoning as you go.