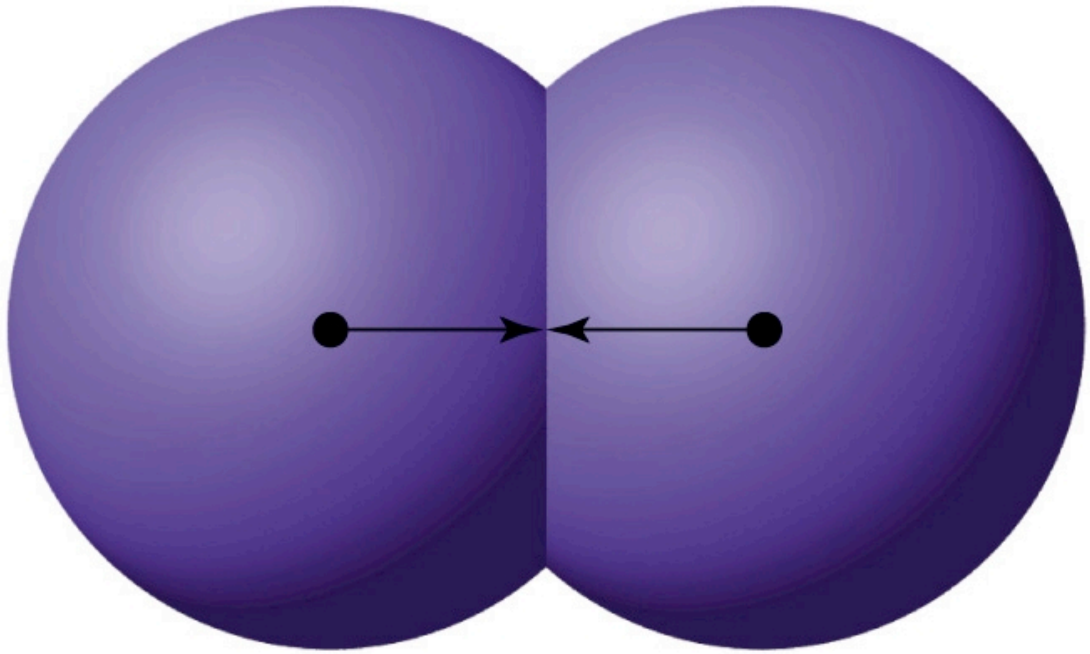
"My name is Bond."



N_2 (Double 07)

"Metallic Bond."

Element 3: Lithium

[He]$2s^1$

"My name is Bond."

In the last lecture we identified three types of molecular bonding:

van der Waals Interactions (Ar)

Covalent Bonding (I_2)

Metallic Bonding (Li)

Element 3: Lithium

electron configuration: [He]$2s^1$

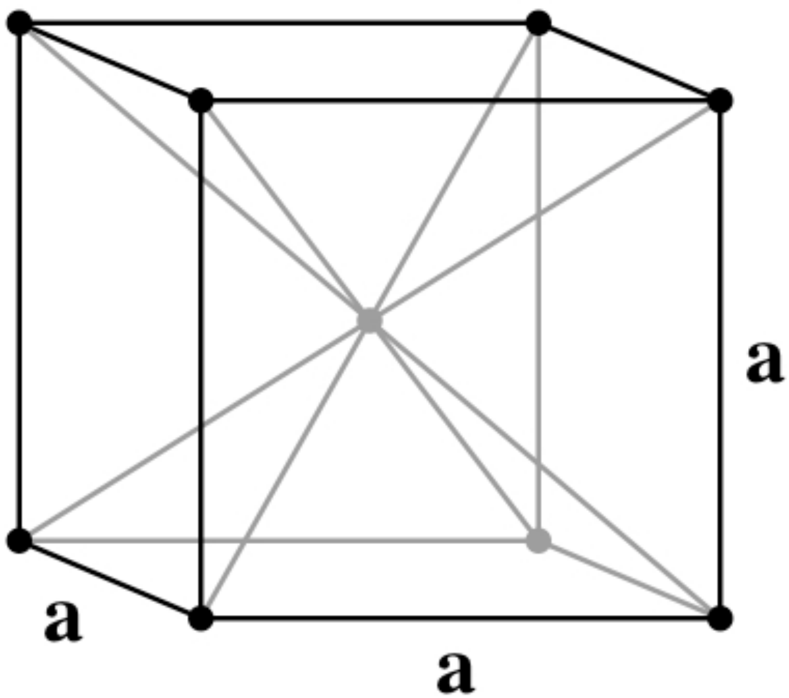
Lithium's valence shell is NOT full -- it needs seven more electrons to become Ne.

Solid Lithium

Melting Point:
453.7 K (180.5 C)

Boiling Point:
1615 K (1342 C)

Solid Lithium crystallizes in an "body-centered cubic" (bcc) crystal lattice.

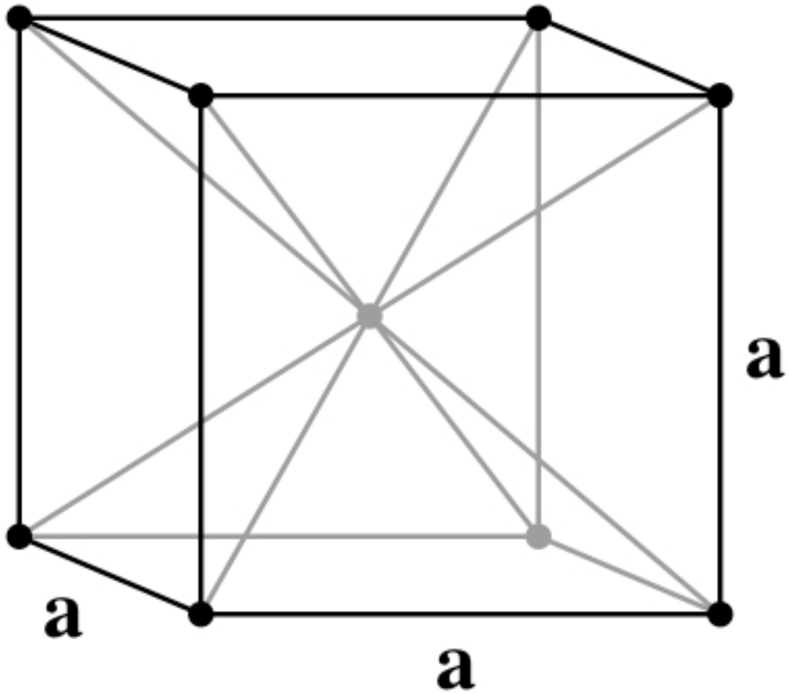


bcc Lithium
a = 349.0 pm

r = ?

Can you calculate r?

Solid Lithium crystallizes in an "body-centered cubic" (bcc) crystal lattice.



bcc Lithium
a = 349.0 pm

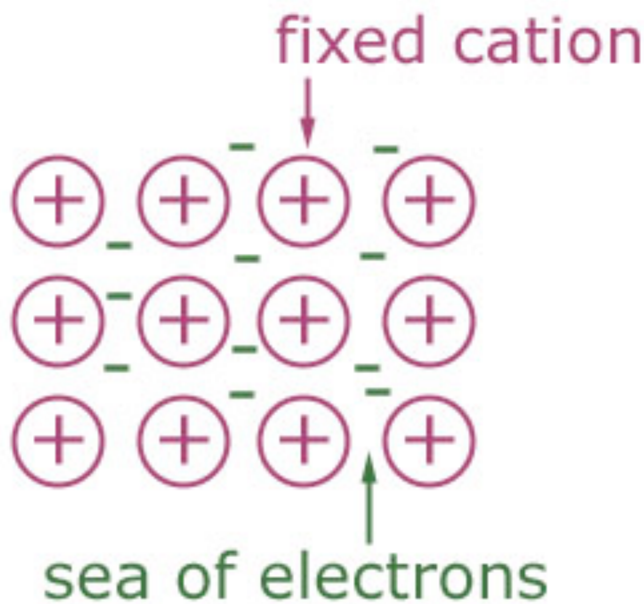
r = 151.1 pm

($4r = a\sqrt{3}$)

Element 3: Lithium

electron configuration: $[He]2s^1$

Metallic Bonding: fixed cations and a sea of electrons.

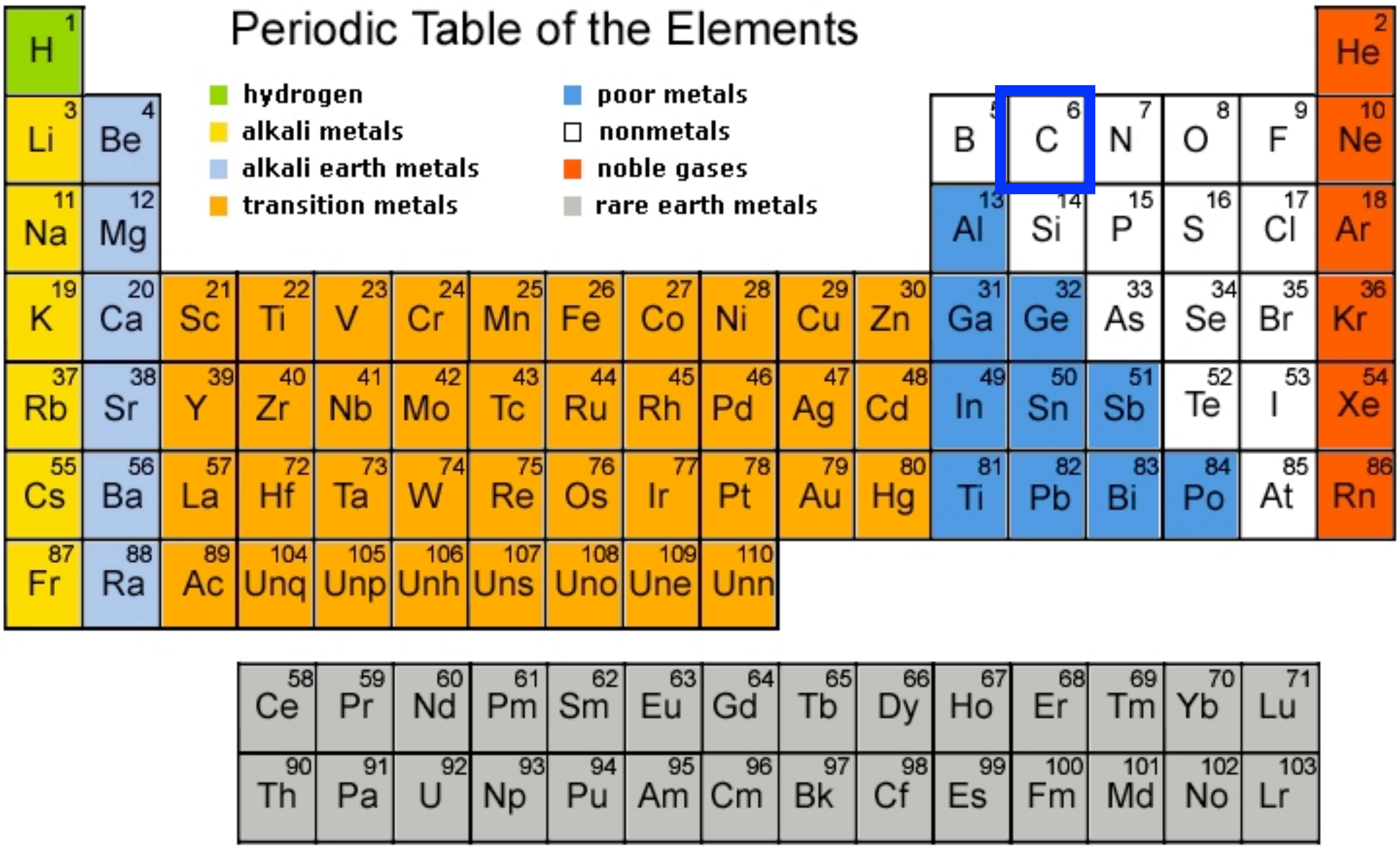


Lithium shares its valence electrons with ALL of its neighbors. It is a metal.

Lithium IP is 5.39 eV.

We will need very fancy QM for this.

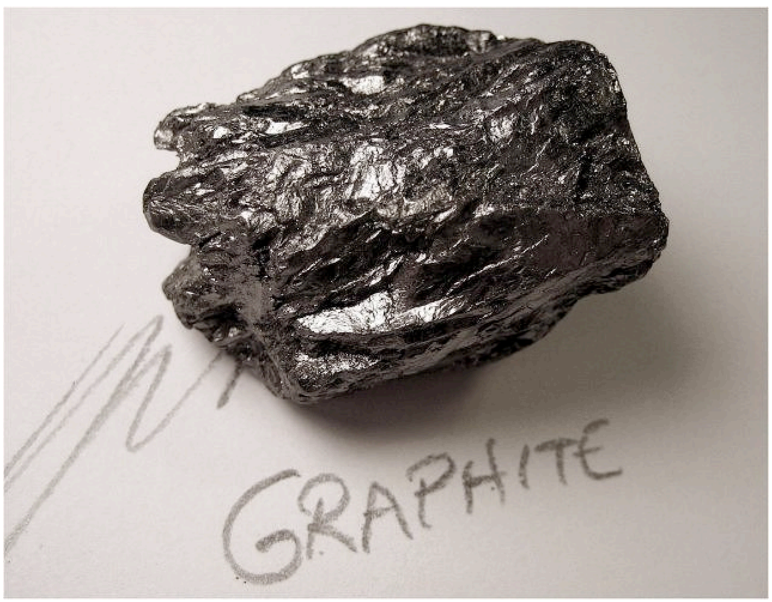
Element 6: Carbon



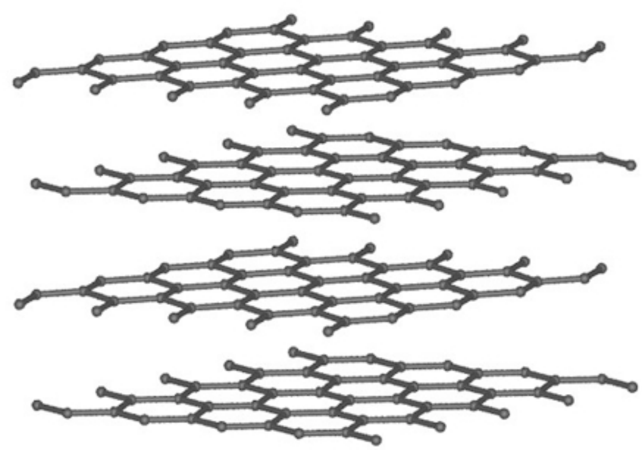
Element 6: Carbon

electron configuration: [He]$2s^2 2p^2$

Carbon's valence shell is NOT full -- it needs four more electrons to become Ne.



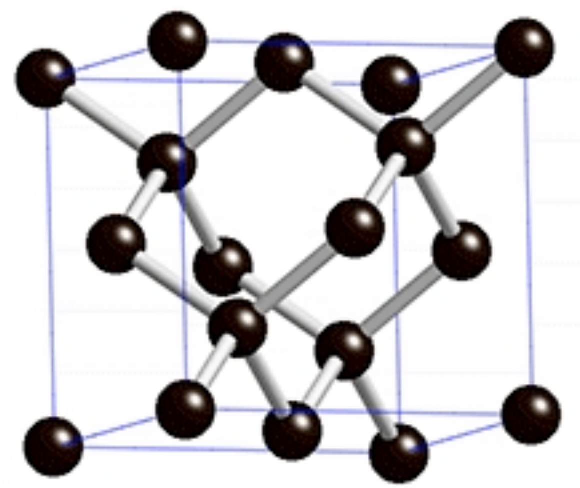
"Elemental Network Solid?"



Element 6: Carbon

electron configuration: [He]$2s^2 2p^2$

Allotropes are the various structural forms of an element in which the element's atoms are bonded together in a different manner.



Another Carbon allotrope.
(There are several.)

Element 6: Carbon

electron configuration: [He]$2s^2 2p^2$

Allotropes are the various structural forms of an element in which the element's atoms are bonded together in a different manner.

N_2 says: "Diamonds are Forever"

Element 6: Carbon

electron configuration: [He]$2s^2 2p^2$

We will come back to Carbon later.

"Elemental Network Solid?"
Covalent? Metallic?
Semimetallic?

We need more information.

N_2 says: "Diamonds are Forever"

"My name is Bond."

In the last lecture we identified three types of molecular bonding:

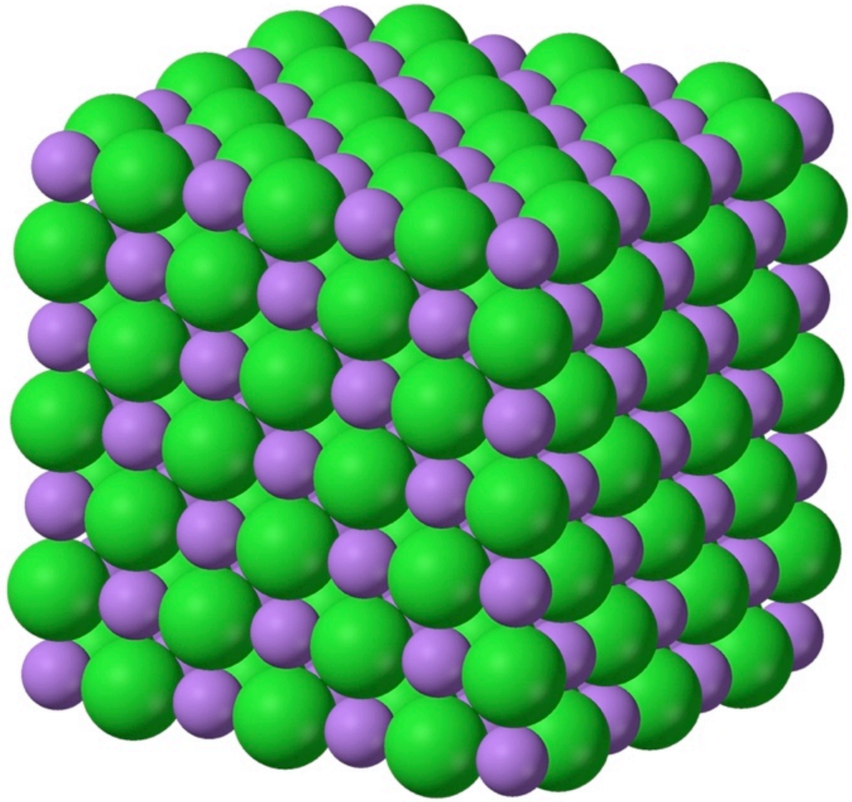
van der Waals Interactions (Ar)

Covalent Bonding (I_2)

Metallic Bonding (Li)

Another key type of bonding:

"My name is Bond."



"Ionic Bond."

Ion Formation: Lithium ion

electron configuration: [He]

Lithium readily ionizes to Li^+

Lithium ion charge can be stabilized/screened by placing it in a polarizable dielectric medium. The dielectric constant ε indicates how good a material is at screening charge.

liquid	ϵ
hexane	2
benzene	2.3
dimethyl ketone	15
acetone	21
ethanol	33
water	80

Lithium IP is 5.39 eV.

Many elements on the LHS of the Periodic Table will lose up to 3 or even 4 electrons in order to get to a noble gas electronic configuration:

Be^{2+} - Berylium cation.

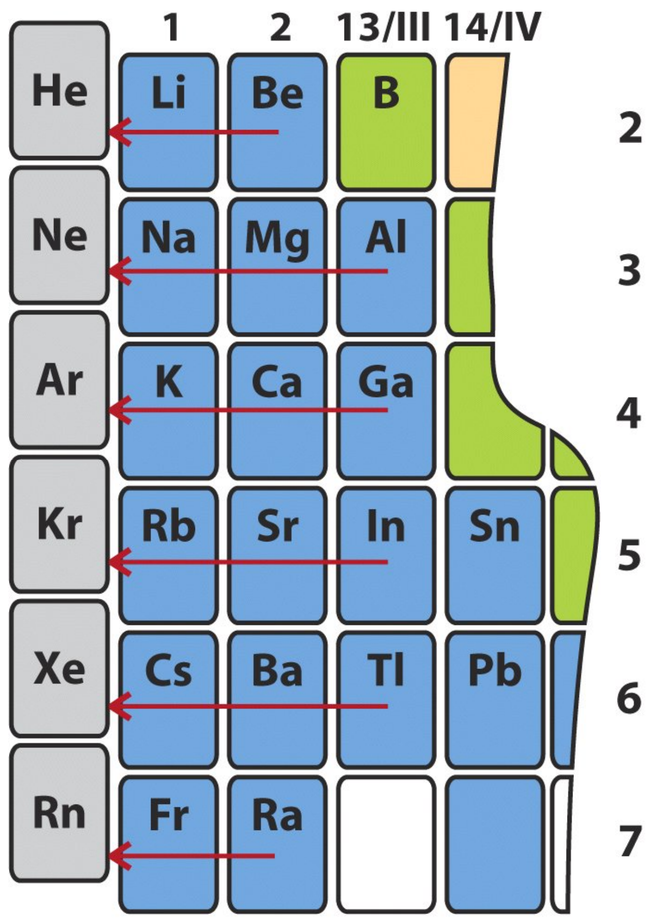
Al^{3+} - Aluminum

Ga^{3+} - Gallium

In^{3+} - Indium

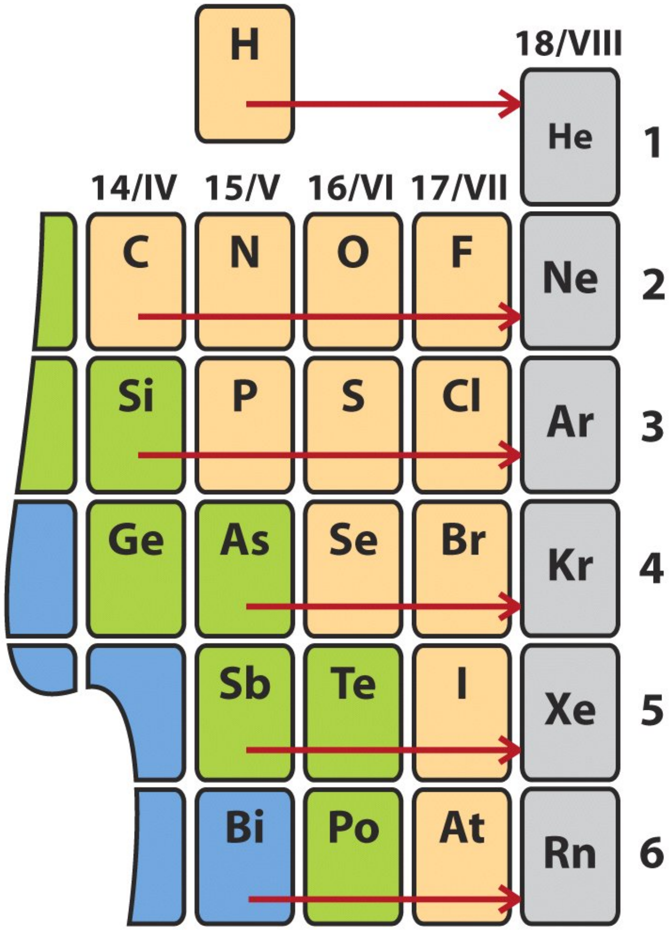
Tl^{3+} - Thallium

Rn^{2+} - Radium



Usually we employ the name of the element for the cation.

Similarly, many elements on the RHS of the Periodic Table will accept up to 3 or even 4 electrons in order to get to a noble gas electronic configuration:



H^- - hydride.

C^{4-} - carbide

Si^{4-} - silicide

As^{3-} - arsenide

Sb^{3-} - antimonide

Bi^{3-} - bismuthide?

Usually we end the name of the anion of an element with "ide".

A note on notation:

In Chemistry, ***Oxidation*** generally means the removal of electrons from an element or compound leading to a deficit of electrons.

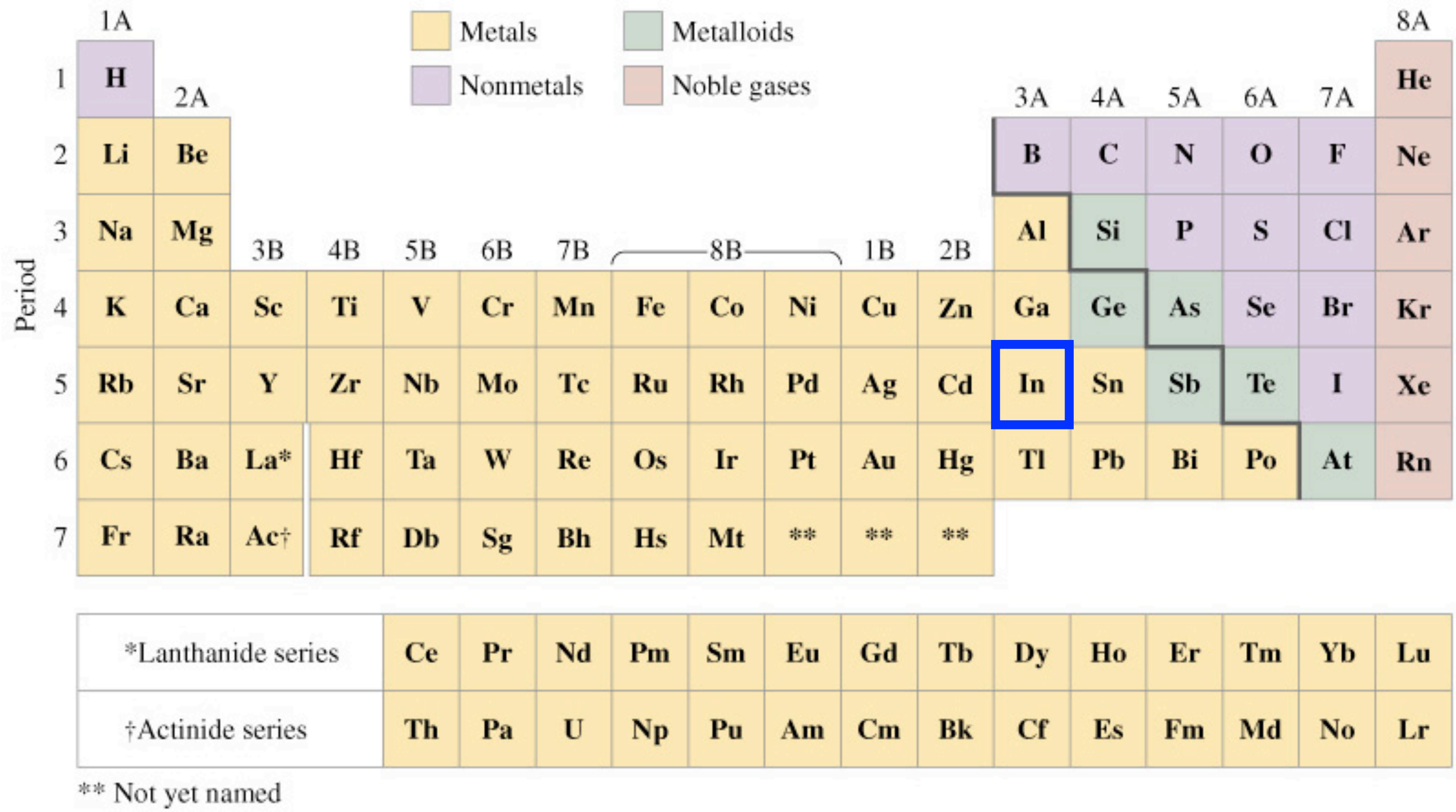
Reduction is the complementary term referring to the addition of electrons and the formation of a product having additional negative charge (relative to the initial state).

Oxidation: $Li \rightarrow Li^{+} + e^{-}$

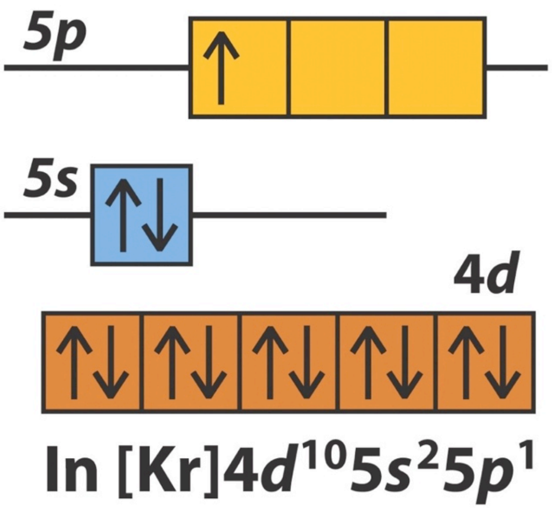
Reduction: $Cl + e^{-} \rightarrow Cl^{-}$

Many elements exhibit multiple, stable "oxidation states".
Example: **Indium**.

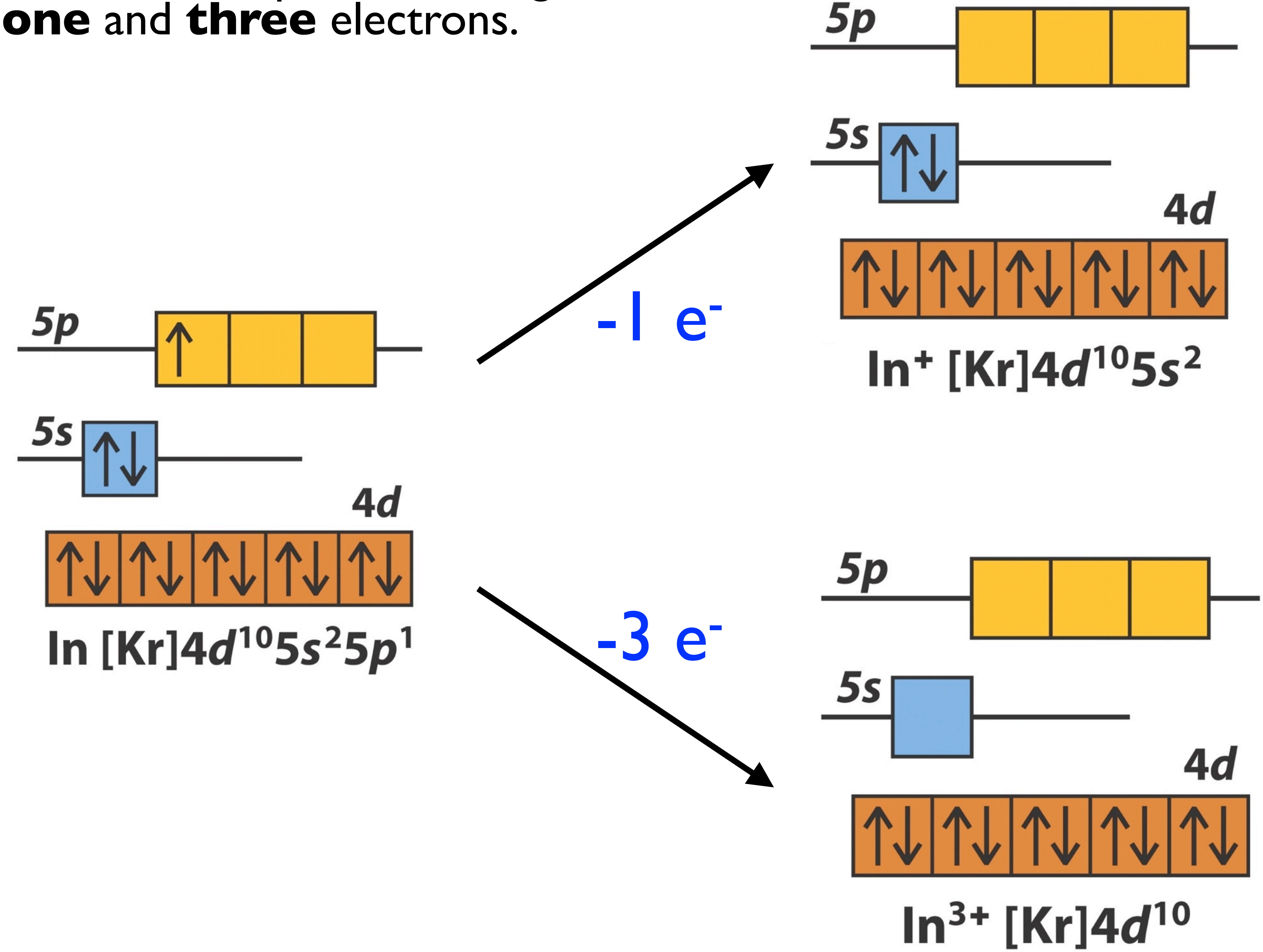
In: $[Kr]4d^{10}5s^{2}5p^{1}$



Indium has two stable ***oxidation states*** because it is $5s^2 5p^1$.

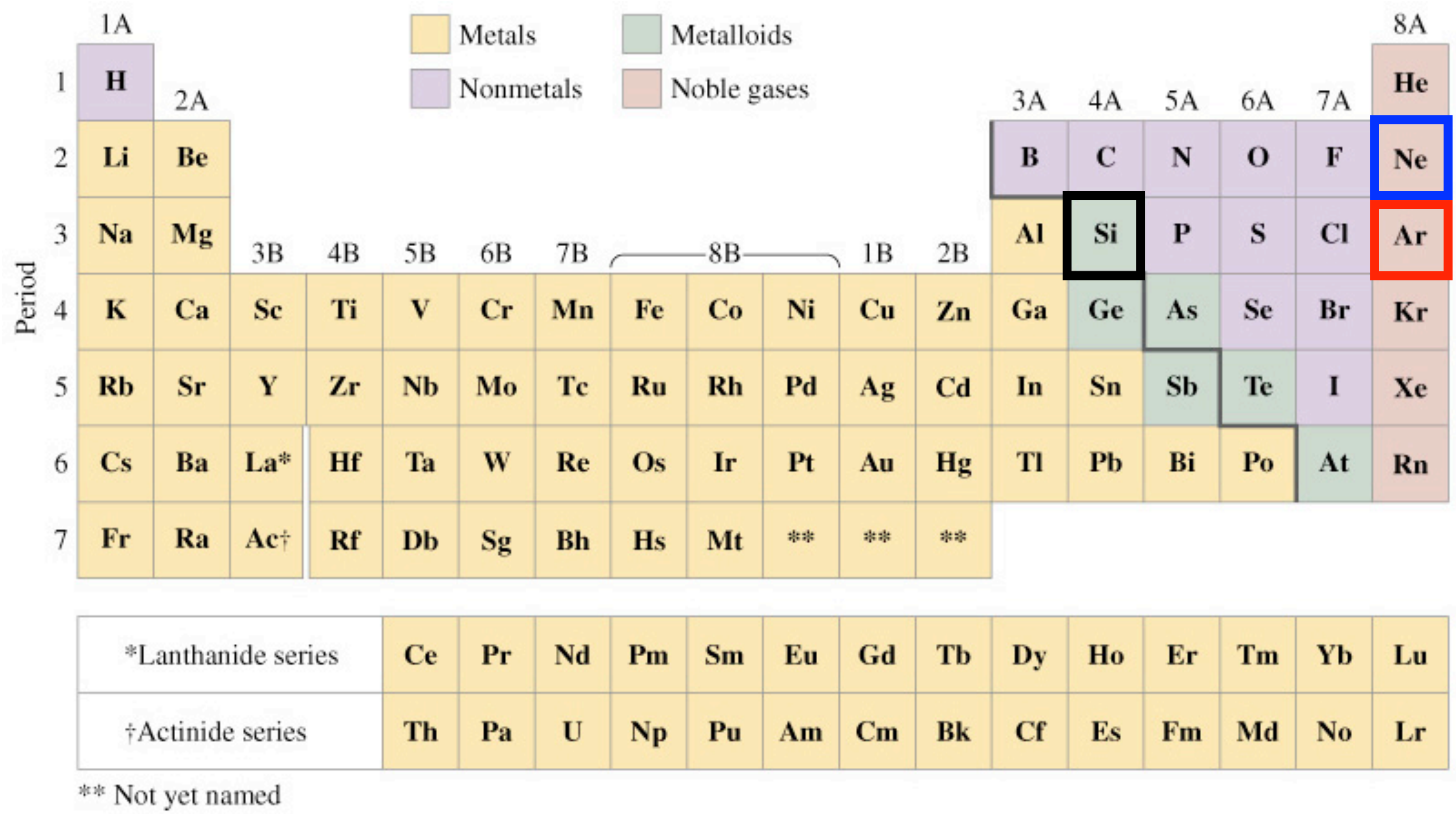


...these correspond to losing **one** and **three** electrons.



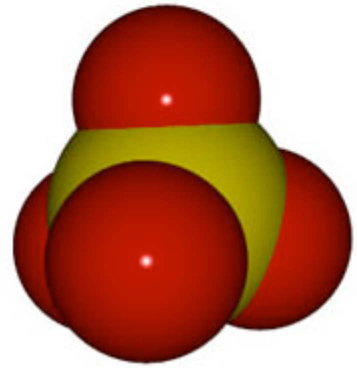
Some elements have both stable negative and positive oxidation states (Yes, an oxidation state be either positive or negative!).

Example: Silicon ([Ne]$3s^2 3p^2$) can be both Si^{4-} and Si^{4+}.

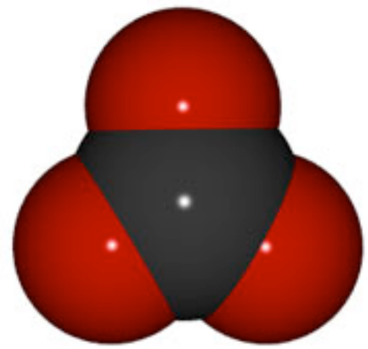


Also, please be aware that many ions contain several covalently bound atoms:

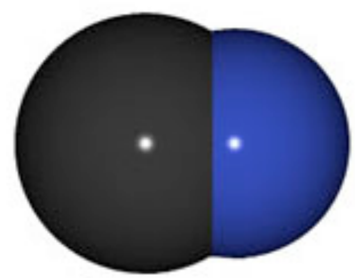
SO_4^{2-} sulf**ate**



CO_3^{2-} carbon**ate**



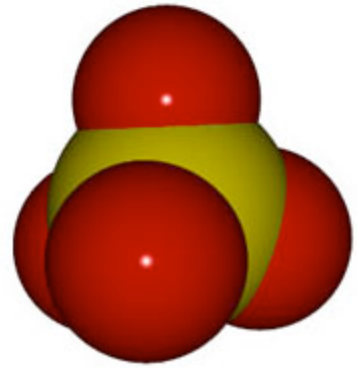
CN^- cyanide



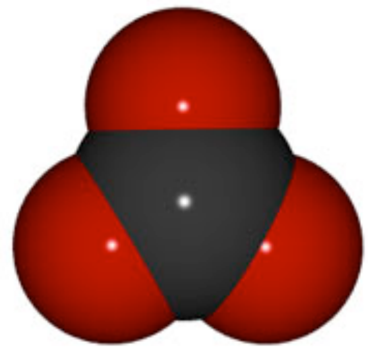
and many others...

Also, please be aware that many ions contain several covalently bound atoms:

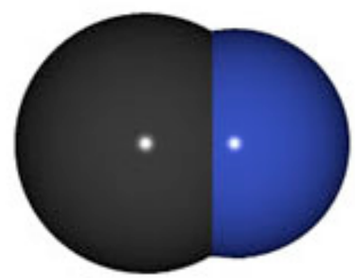
SO_4^{2-} sulf**ate**



CO_3^{2-} carbon**ate**

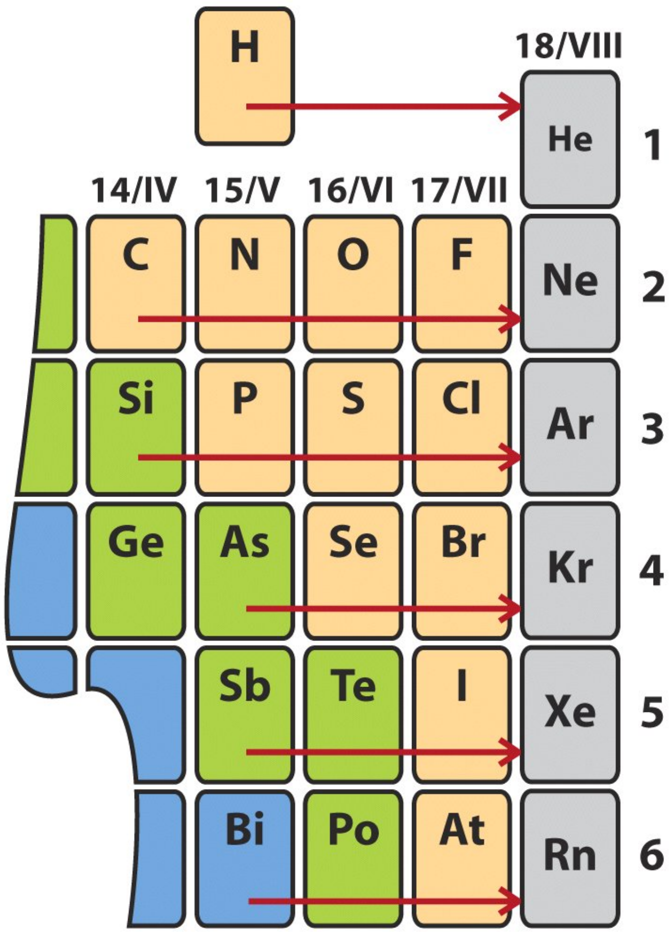


CN^- cyanide



Note: the "***...ate***" suffix also denotes a anionic species.

How much energy does ion formation cost?



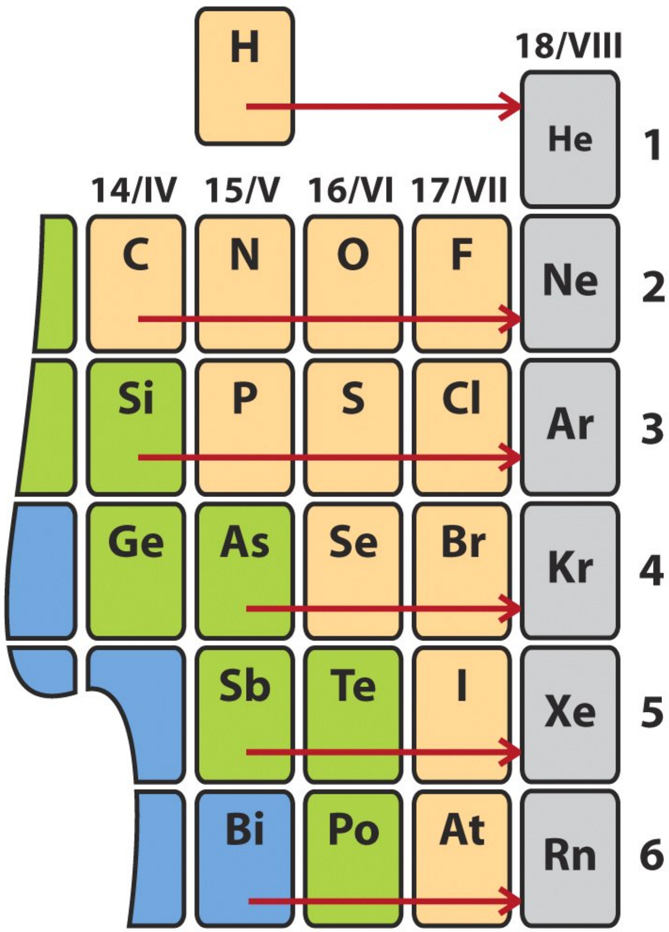
Take Oxygen:

$O + 1e^- \rightarrow O^-$ 1st EA = -142 kJ/mol

$O^- + 1e^- \rightarrow O^{2-}$ 2nd EA = +844 kJ/mol

So WHY DOES THIS HAPPEN?

How much energy does ion formation cost?



Take Oxygen:

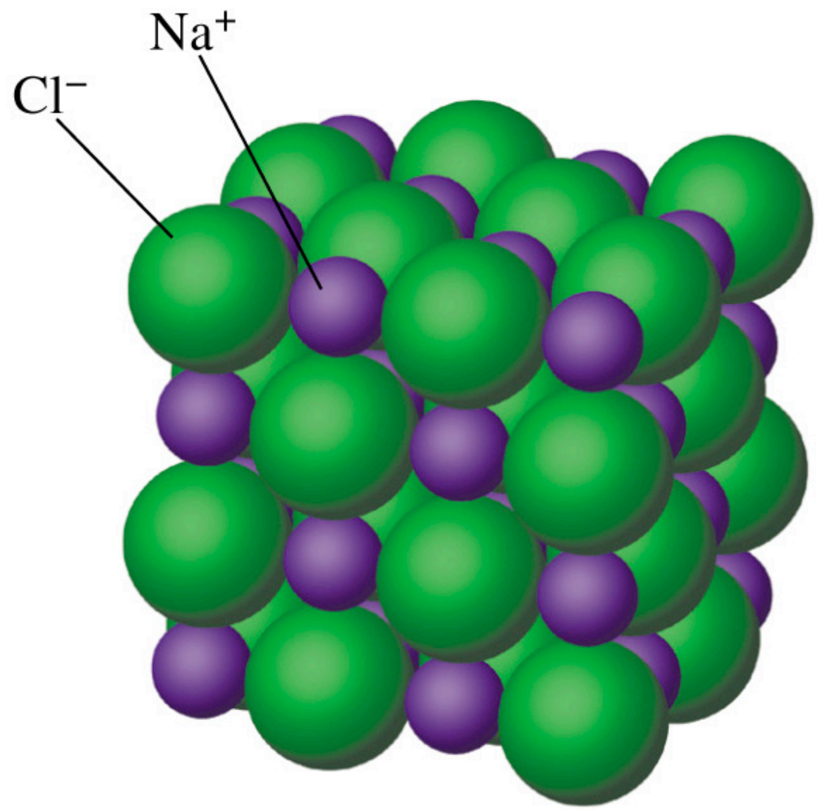
$O + 1e^- \rightarrow O^-$ 1st EA = -142 kJ/mol

$O^- + 1e^- \rightarrow O^{2-}$ 2nd EA = +844 kJ/mol

The short answer:

The energy is gained back by forming an Ionic Bond!

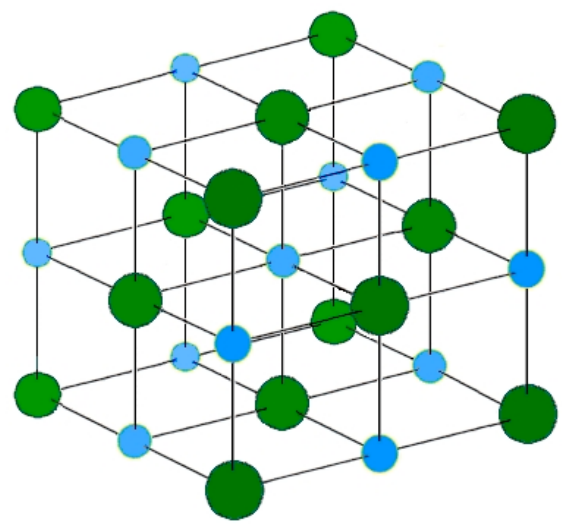
Ionic Bonding leads to the formation of compounds of two different atoms -- one that's lost electrons and one that's gained electrons.



A well known ionic compound: Sodium Chloride (table salt).

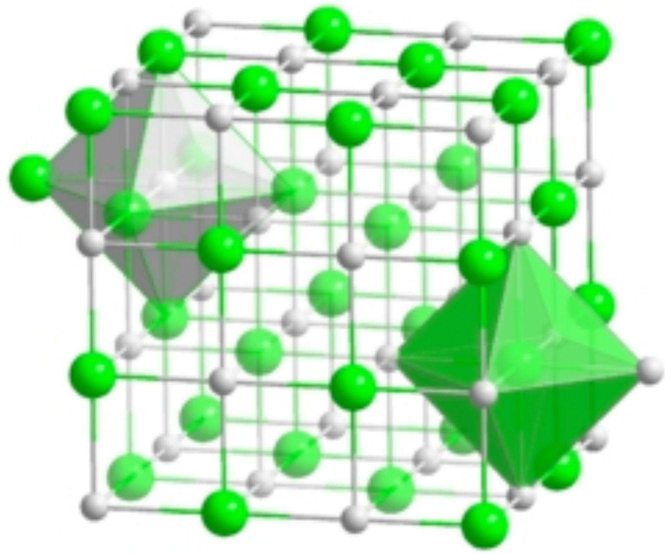
Sodium Chloride

Melting Point: 801 C
Boiling Point: 1465 C
Lattice: fcc
Lattice Parameter a = 564 pm



Blue: Na^+

Sodium Chloride



Melting Point: 801 C
Boiling Point: 1465 C
Lattice: fcc
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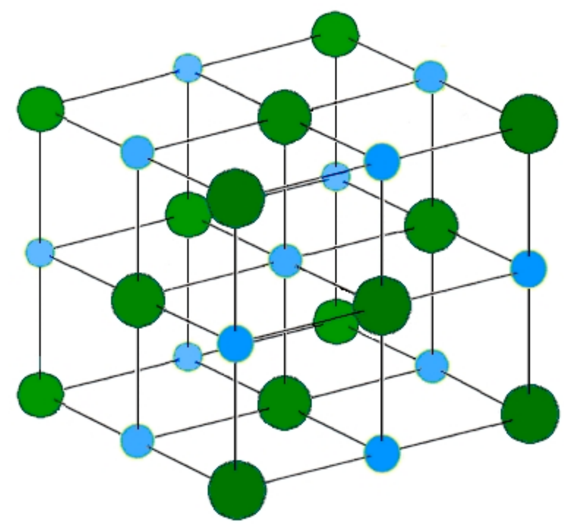
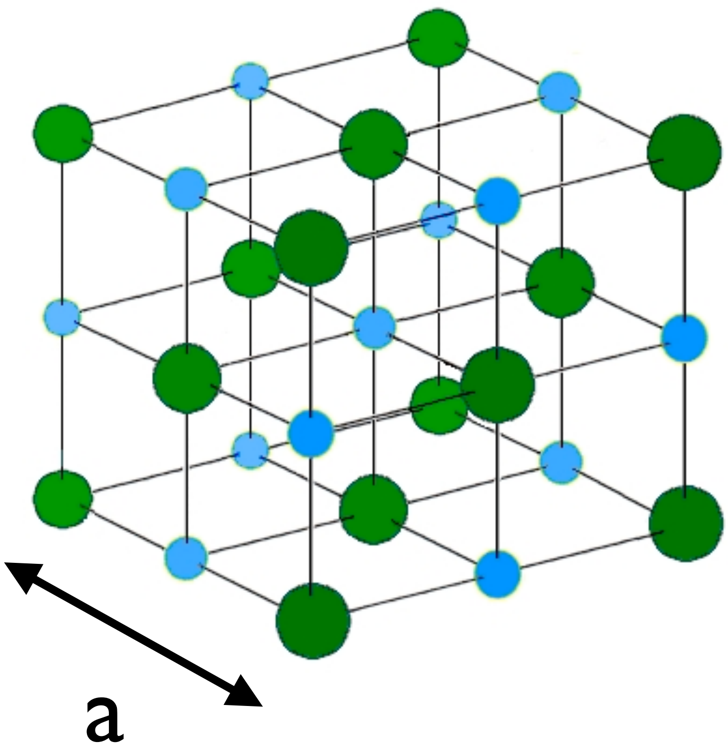


NaCl lattice
Two interpenetrating fcc lattices.
Each ion is surrounded by six oppositely charged ions in an octahedron.

Blue: Na^+

Sodium Chloride



Ionic Radius Calculation:
a= 564 pm

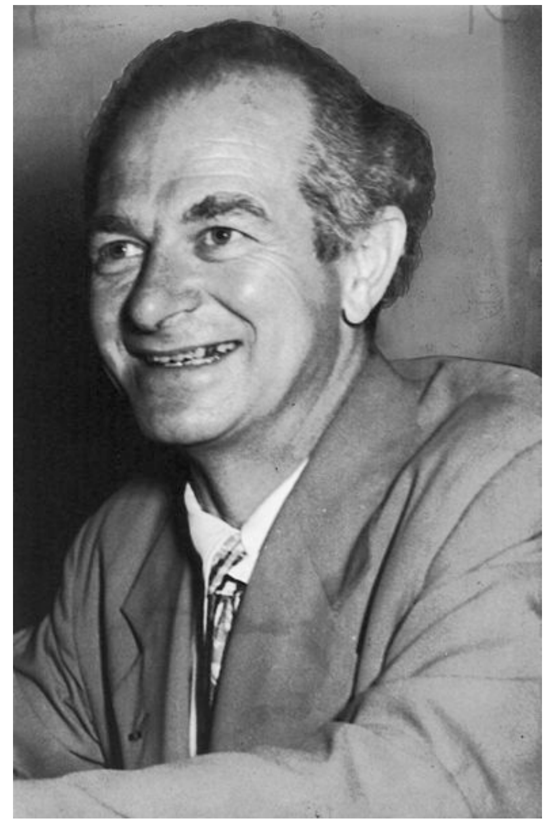
$$564 = 2[r_{ion}(Na^+) + r_{ion}(Cl^-)]$$

How do we distinguish between the two radii?

Sodium Chloride

$$564 = 2[r_{ion}(Na^{+}) + r_{ion}(Cl^{-})]$$

The concept of ionic radius was developed independently by Goldschmidt and Pauling in the 1920s to summarize the data being generated by the (at the time) new technique of X-ray crystallography: it is Pauling's approach which proved to be the more influential.

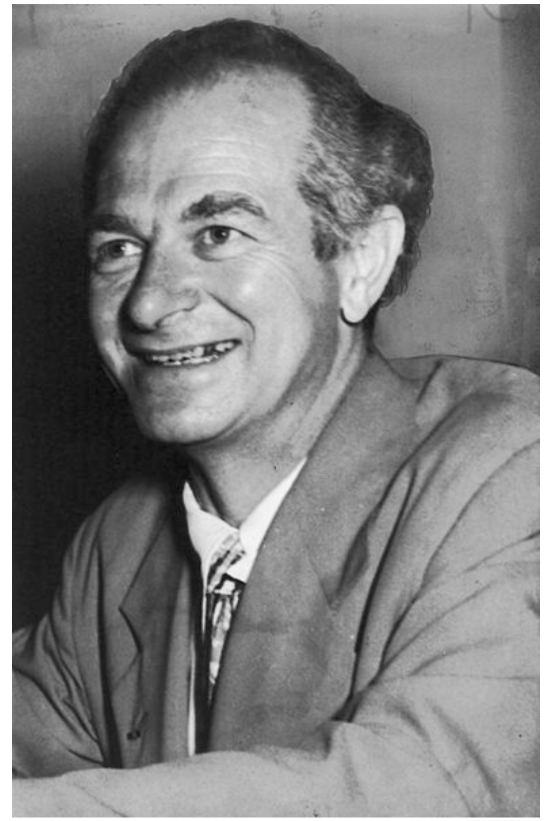


Linus Pauling
1901-1994

Sodium Chloride

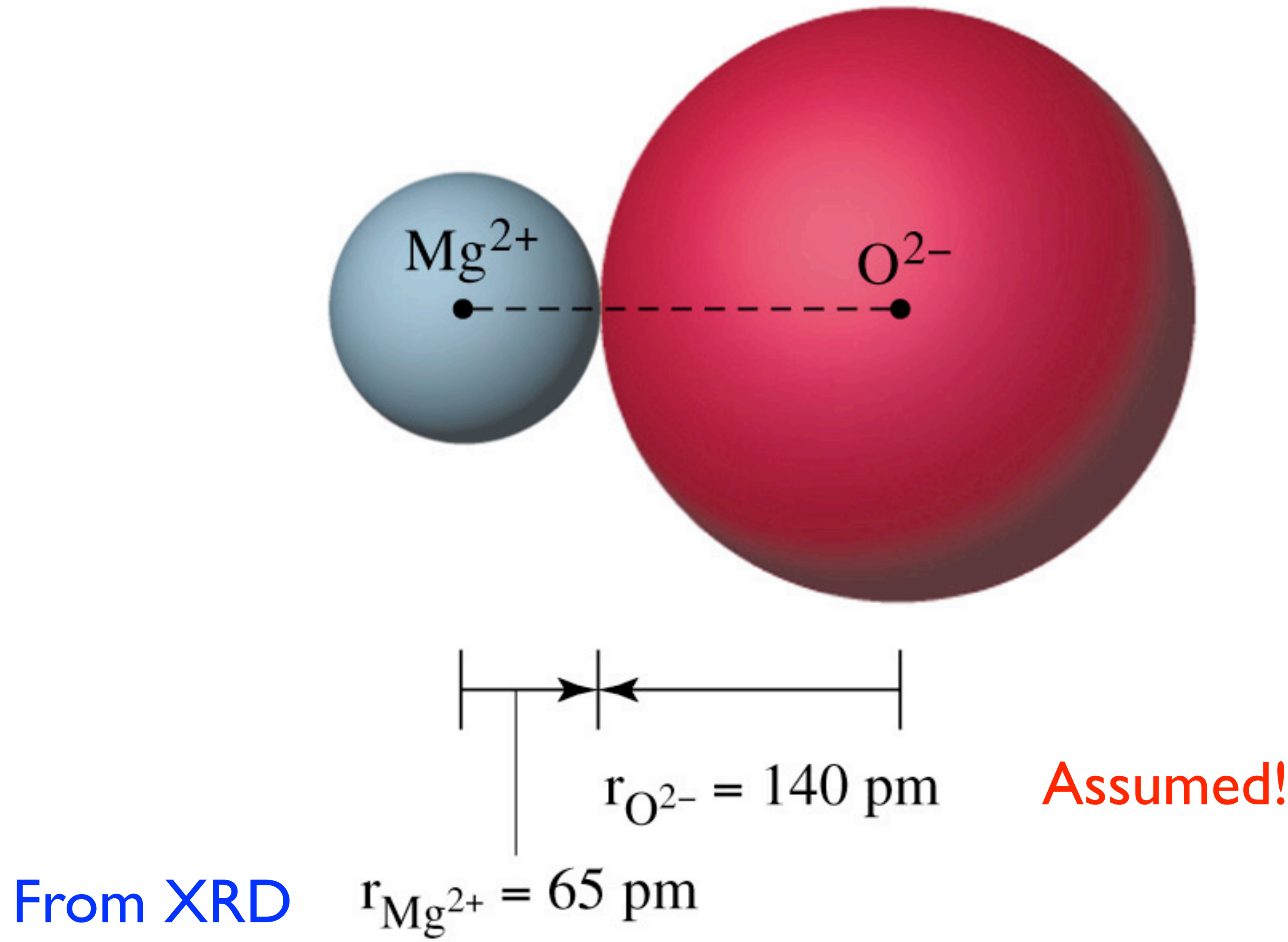
$$564 = 2[r_{ion}(Na^{+}) + r_{ion}(Cl^{-})]$$

It is not apparent what proportion of this distance is due to the size of the sodium ion and what proportion is due to the size of the chloride ion. By comparing many different compounds, and with a certain amount of chemical intuition, Pauling decided to assign a radius of 140 pm to the oxide ion O^{2-}, at which point he was able to calculate the radii of the other ions by subtraction.



Linus Pauling
1901-1994

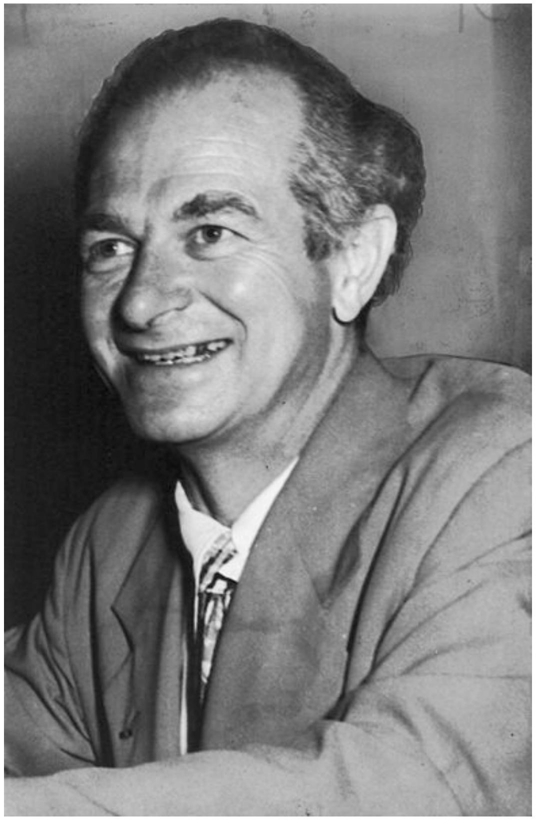
If we fix the ionic radius of O^{2-} to 140 pm, we can calculate all others from the XRD of compounds (like MgO), and build up a table.



Sodium Chloride

O^{2-}: 140 or 126 pm?

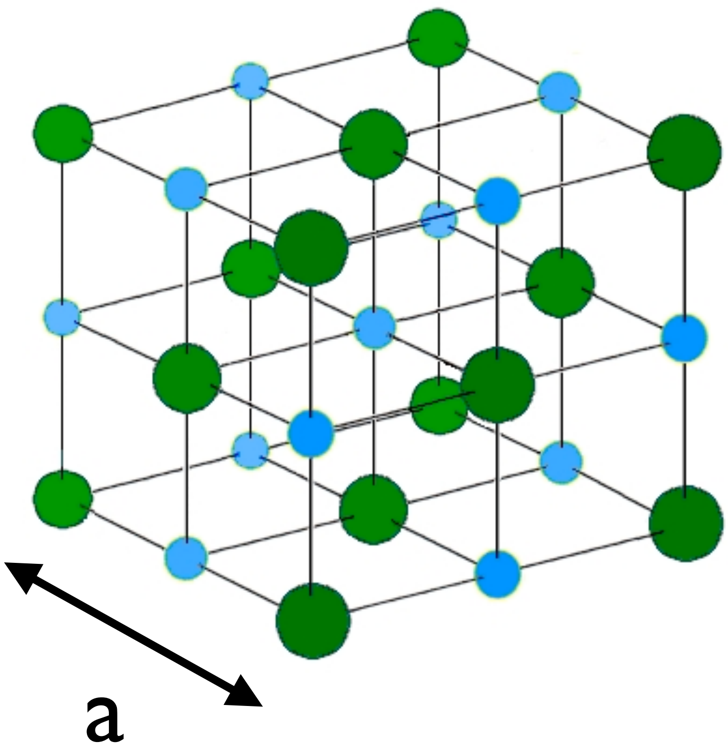
A major review of crystallographic data led to the publication of a revised set of ionic radii in 1976, and some prefer these to Pauling's original values. Some sources have retained Pauling's reference of $r_{ion}(O^{2-})$ = 140 pm, while other sources prefer to list "effective" ionic radii based on $r_{ion}(O^{2-})$ = 126 pm.



Linus Pauling
1901-1994

So finally...

Sodium Chloride



Ionic Radius Calculation:
a= 564 pm

$$564 = 2[r_{ion}(Na^{+}) + r_{ion}(Cl^{-})]$$

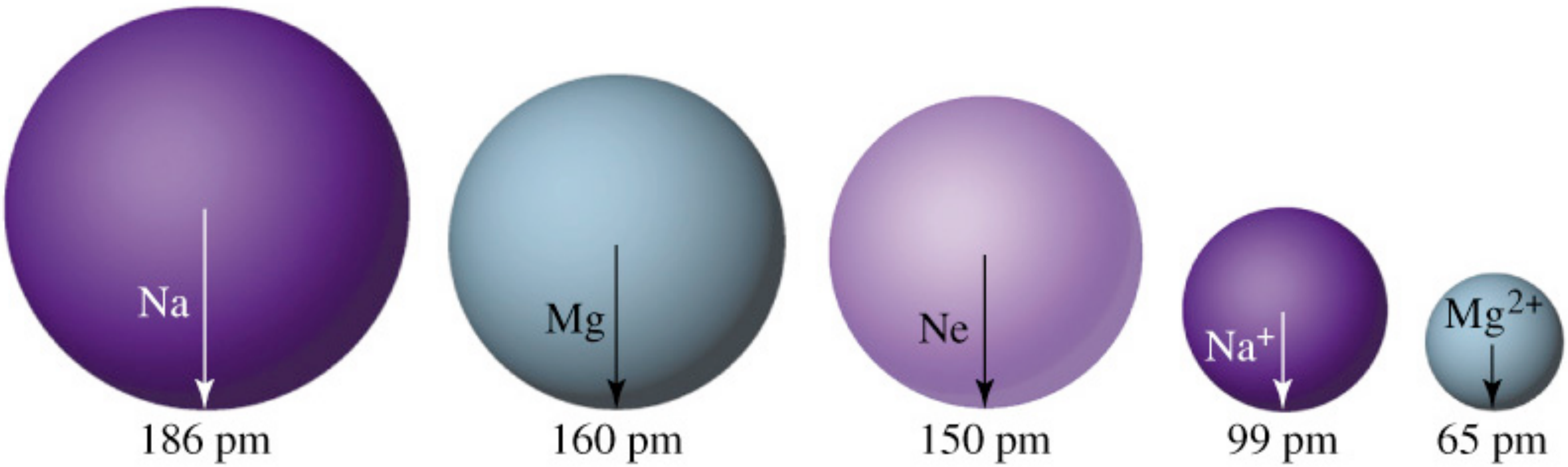
$r_{ion}(Na+) = 102$ pm

$r_{ion}(Cl^{-}) = 181$ pm

$2 \times 102 + 2 \times 181 = 566$

close enough!

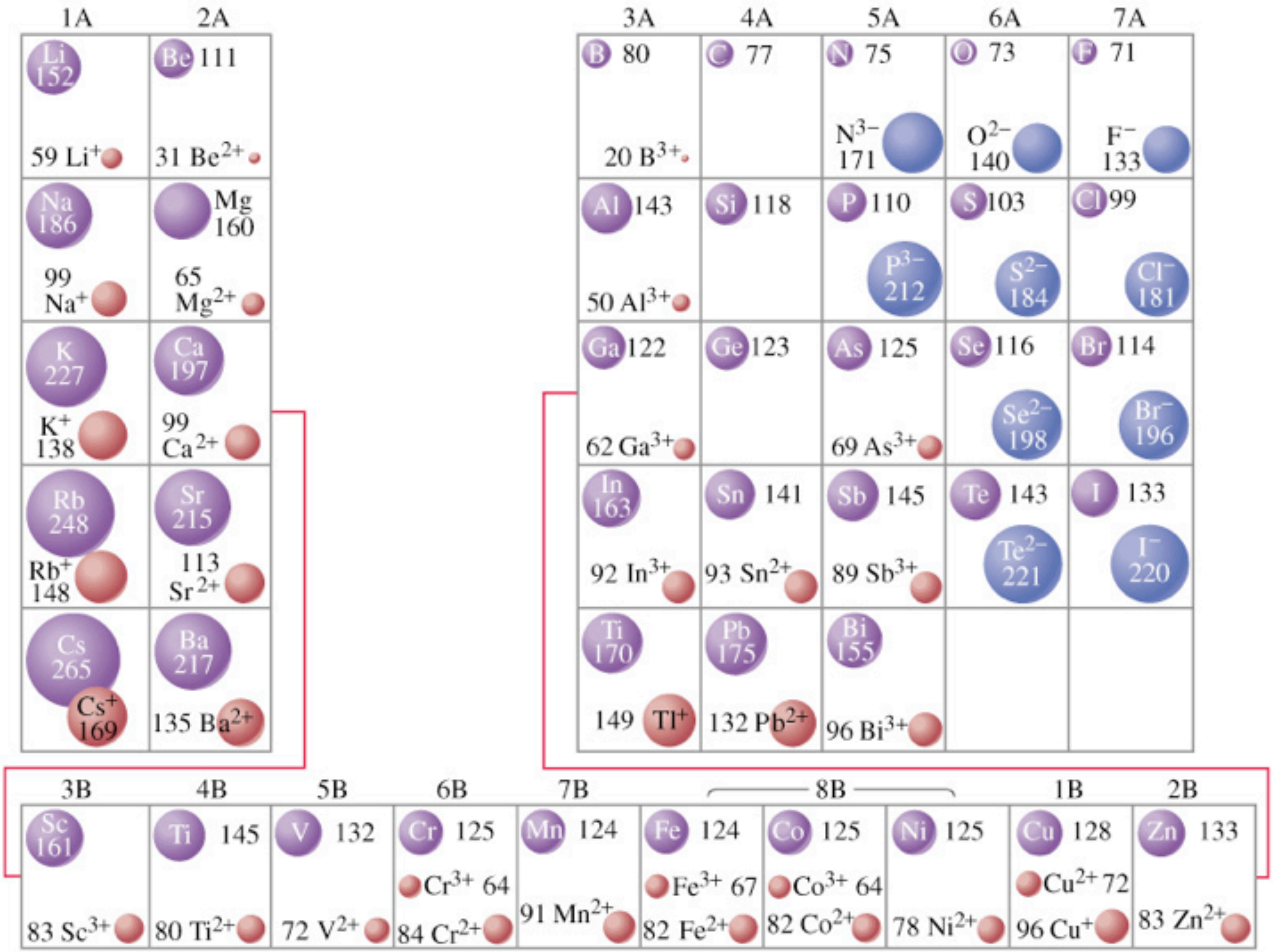
Cations are smaller than their parent atoms; anions considerably larger.



Na vs. Na^+: 186 pm vs 99 pm

Li vs. Li^+: 151 pm vs 59 pm

Cations are smaller than their parent atoms. Anions considerably larger.



Ionic compounds must be electrically neutral.

Question: What ionic compound contains fluorine and calcium?

<u>Step 1</u>: What are the stable ions for each element?

$F \rightarrow F^{-}$

$Ca \rightarrow Ca^{2+}$

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
Li^{+}														N^{3-}	O^{2-}	F^{-}	
Na^{+}	Mg^{2+}											Al^{3+}		P^{3-}	S^{2-}	Cl^{-}	
K^{+}	Ca^{2+}				Cr^{2+} Cr^{3+}	Mn^{2+}	Fe^{2+} Fe^{3+}	Co^{2+} Co^{3+}	Ni^{2+}	Cu^{+} Cu^{2+}	Zn^{2+}					Br^{-}	
Rb^{+}	Sr^{2+}									Ag^{+}			Sn^{2+}			I^{-}	
Cs^{+}	Ba^{2+}												Pb^{2+}				

Question: What ionic compound contains fluorine and calcium?

Step 1: What are the stable ions for each element?

$F \rightarrow F^-$

$Ca \rightarrow Ca^{2+}$

Step 2: How can these two ions be combined to form an *electrically neutral* compound?

CaF? No, this has a charge of +1 (2-1).

Ca_2F? No, this has a charge of +3 (4-1).

CaF_3? No, this has a charge of -1 (2-3).

The answer is: CaF_2.

We call this: **Calcium fluoride.**

Ionic compounds must be electrically neutral.

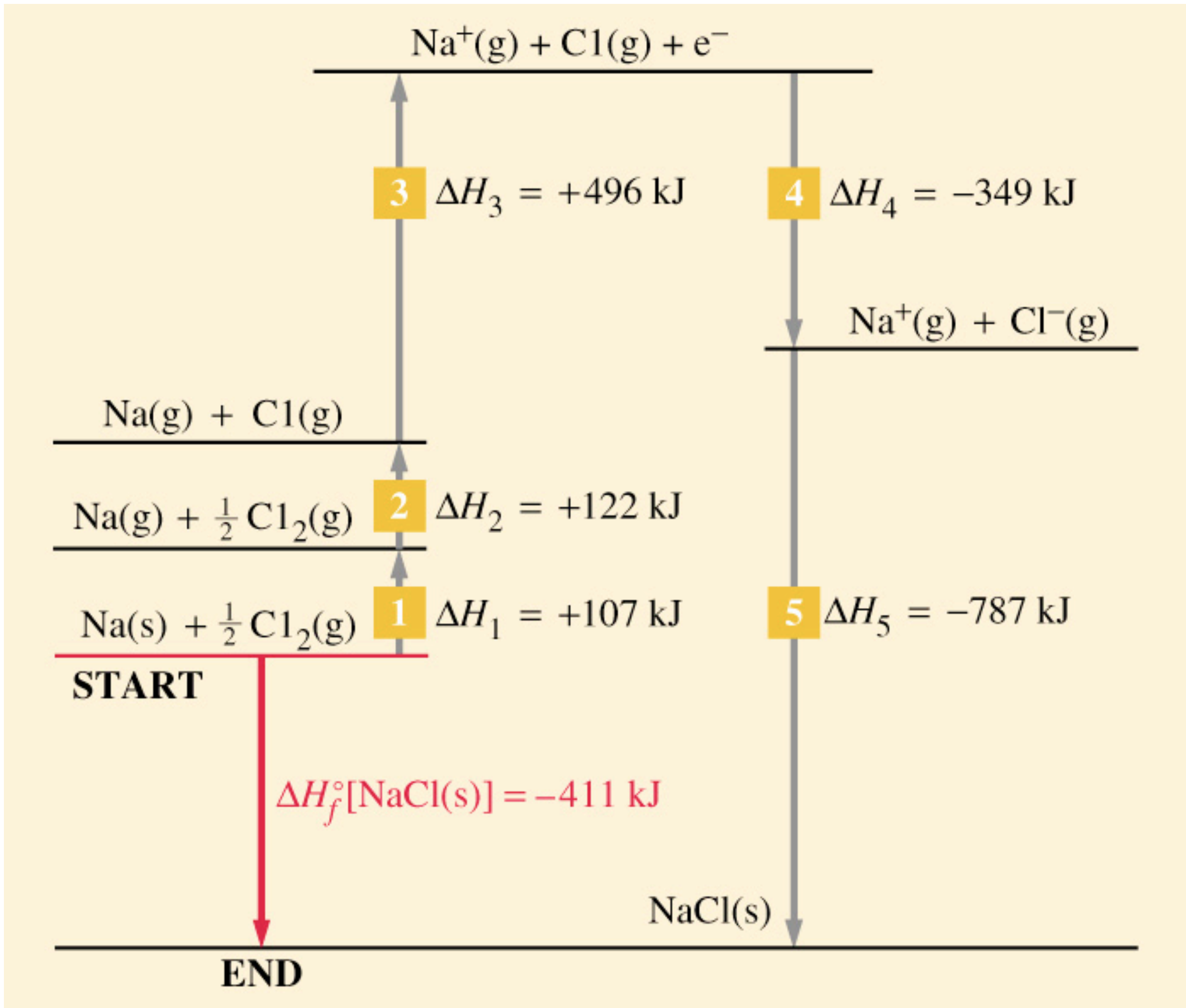
Sodium Chloride: Thermodynamic Stability

How can Sodium Chloride:

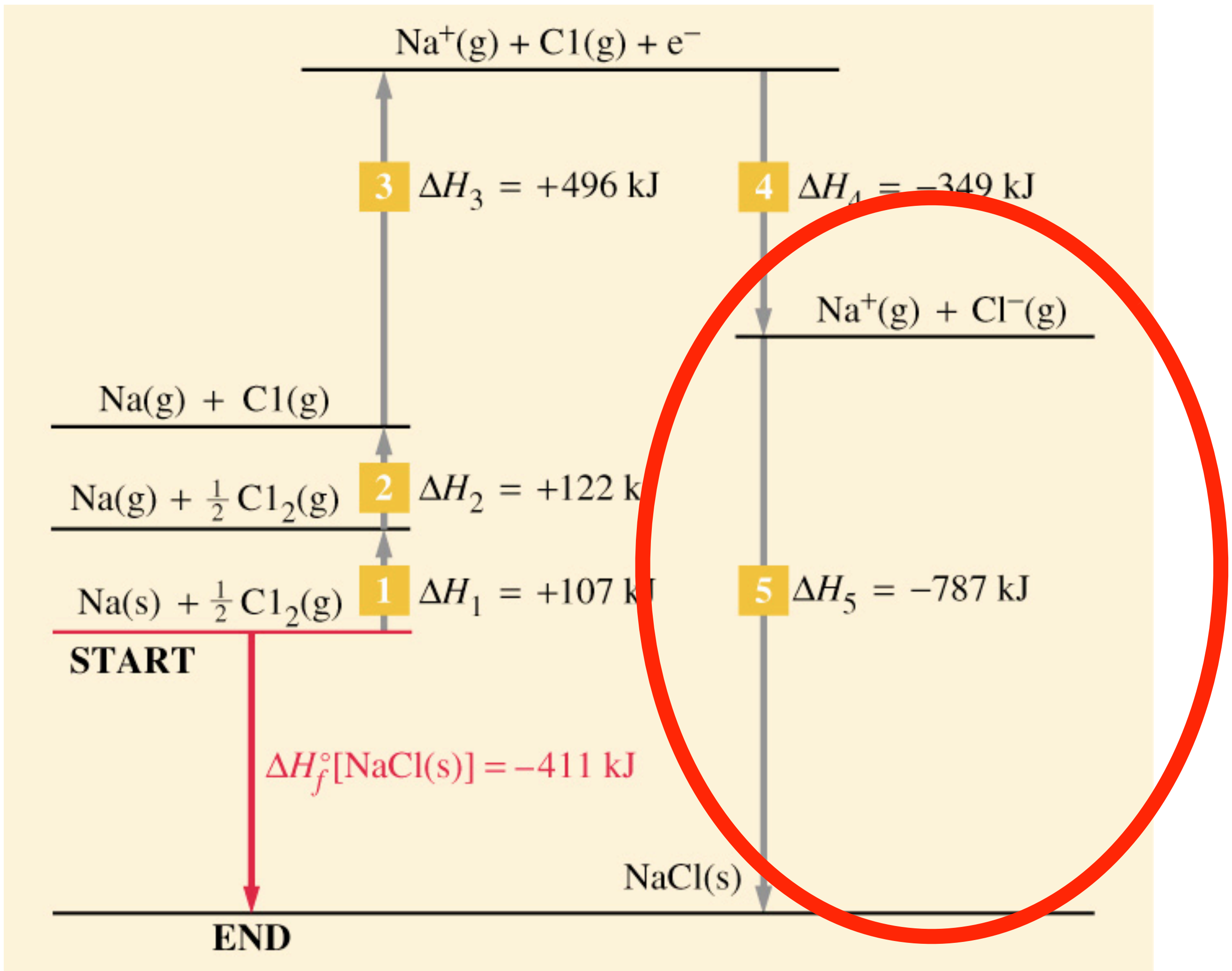
- have a melting point of 800.8 °C?
- dissociate, spontaneously, into separate ions in water?

Here is concept that you will see again in Chapter 6 when you study thermodynamics:

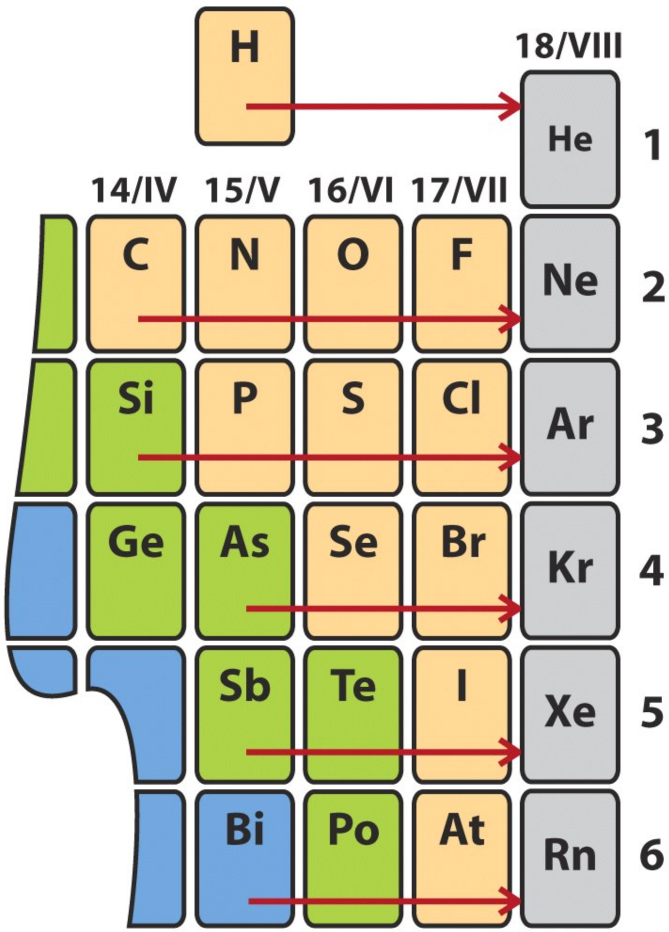
The infamous ***Born-Haber cycle:***



When oppositely charged ions are brought together to form an ionic compound, a HUGE amount of heat is liberated. This process is energy releasing, or *exothermic*.



So now we can quantitatively answer this question:



Take Oxygen:

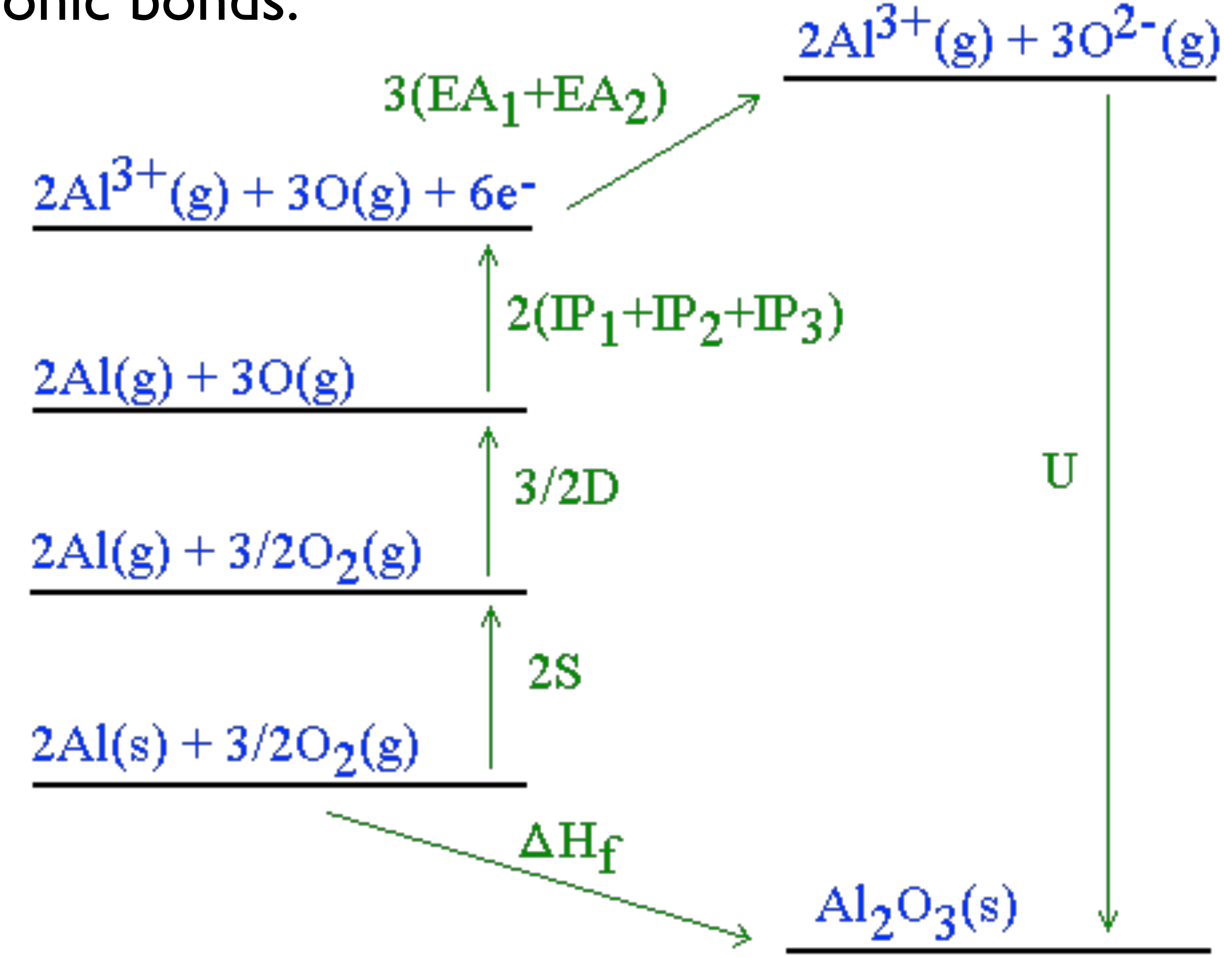
$O + 1e^- \rightarrow O^-$ 1st EA = -142 kJ/mol

$O^- + 1e^- \rightarrow O^{2-}$ 2nd EA = +844 kJ/mol

WHY DOES THIS HAPPEN?

What drives the energetically unfavorable *endothermic* formation of O^{2-} from O?

Answer: The lattice energy recovered from the formation of ionic bonds.

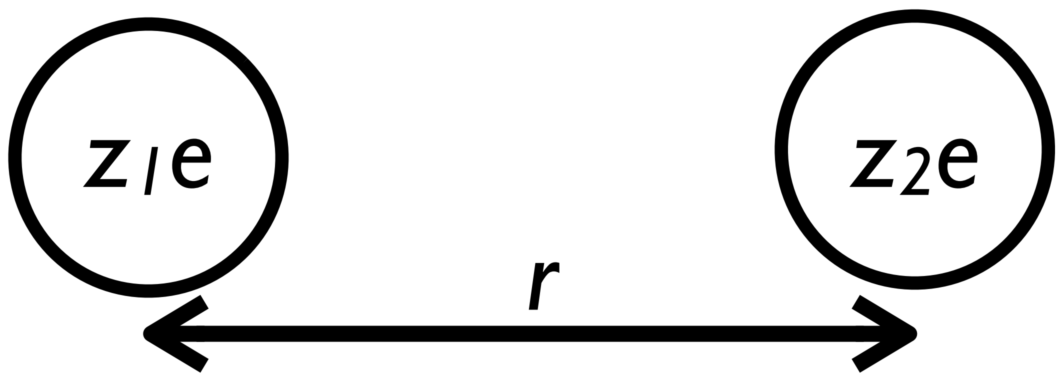


sapphire!

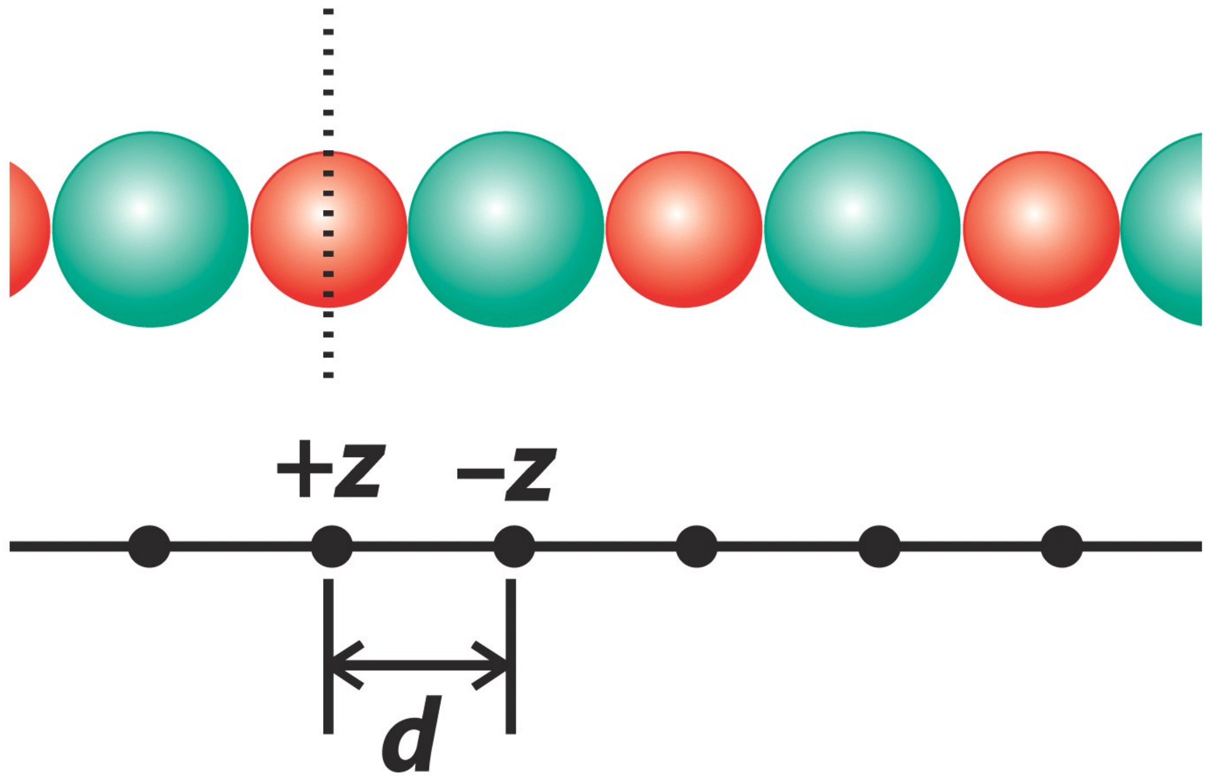
To understand ionic solids, you do not need to understand quantum mechanics. You just need:

Coulomb's Law

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{z_1 z_2 e^2}{r}$$



...let's see if we can apply Coulomb's Law to a simple, 1-dimensional, 1:1 ionic solid...



$$V(r) = \frac{1}{4\pi\varepsilon_0}\left[\frac{-z^2e^2}{d} + \frac{z^2e^2}{2d} - \frac{z^2e^2}{3d} + \frac{z^2e^2}{4d} \ldots\right]$$

...let's see if we can apply Coulomb's Law to a simple, 1-dimensional, 1:1 ionic solid...

$$V(r) = \frac{1}{4\pi\varepsilon_0}\left[\frac{-z^2e^2}{d} + \frac{z^2e^2}{2d} - \frac{z^2e^2}{3d} + \frac{z^2e^2}{4d} \ldots\right]$$

...factor out $(-z^2e^2)/d$:

$$V(r) = \frac{-z^2e^2}{4\pi\varepsilon_0 d}\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \ldots\right]$$

...let's see if we can apply Coulomb's Law to a simple, 1-dimensional, 1:1 ionic solid...

$$V(r) = \frac{1}{4\pi\varepsilon_0}\left[\frac{-z^2e^2}{d} + \frac{z^2e^2}{2d} - \frac{z^2e^2}{3d} + \frac{z^2e^2}{4d}\ldots\right]$$

$$V(r) = \frac{-z^2e^2}{4\pi\varepsilon_0 d}\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4}\ldots\right]$$

$$V(r) = \frac{-z^2e^2}{4\pi\varepsilon_0 d}(ln2)$$

this is for just one side of the "central ion"...

...let's see if we can apply Coulomb's Law to a simple, 1-dimensional, 1:1 ionic solid...

$$V(r) = \frac{-z^2e^2}{4\pi\varepsilon_0 d}(ln 2)$$

this is for just one side of the "central ion"...

$$V(r) = \frac{-2z^2e^2}{4\pi\varepsilon_0 d}(ln 2)$$

multiply by 2 to get both sides...

in 1-d:

$$V(r) = \frac{-2z^2e^2}{4\pi\varepsilon_0 d}(ln2)$$

in 3-d:

$$V(r) = -A \times \frac{|z_1z_2|N_Ae^2}{4\pi\varepsilon_0 d}$$

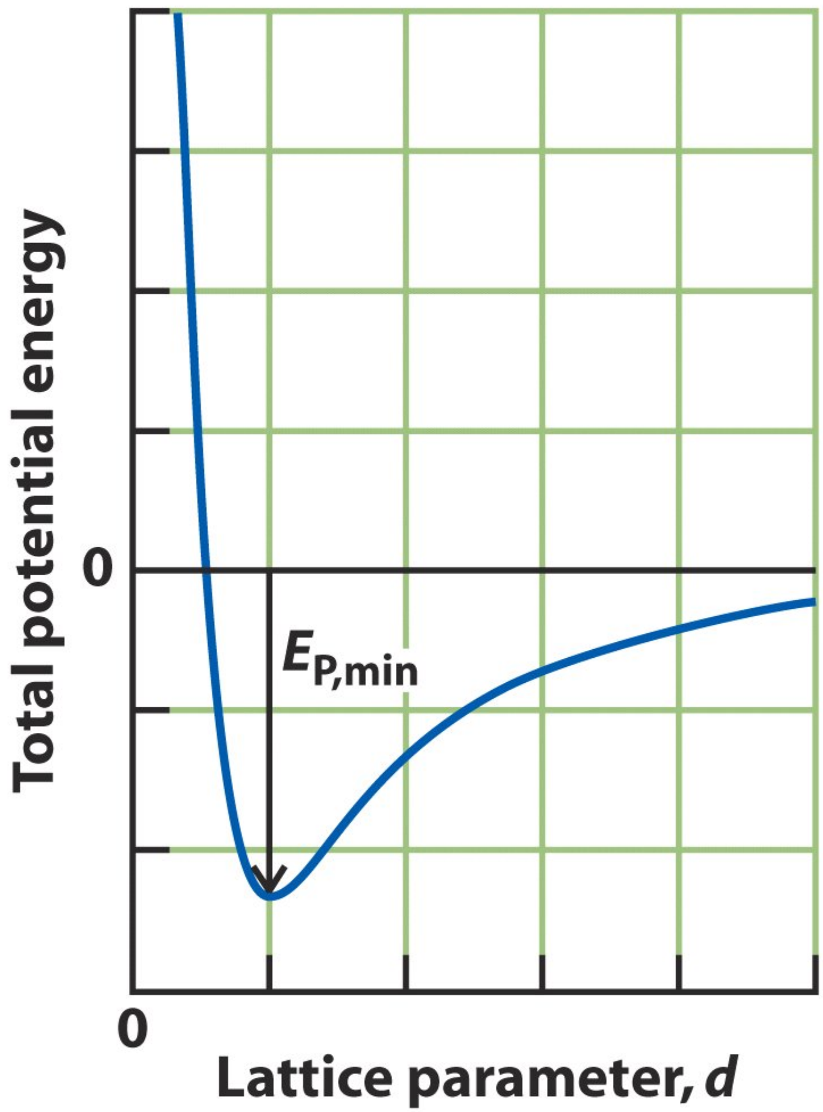
the *Madelung Constant*
it depends on the spatial
arrangement of ions in 3-d.

TABLE 2.1 Madelung Constants

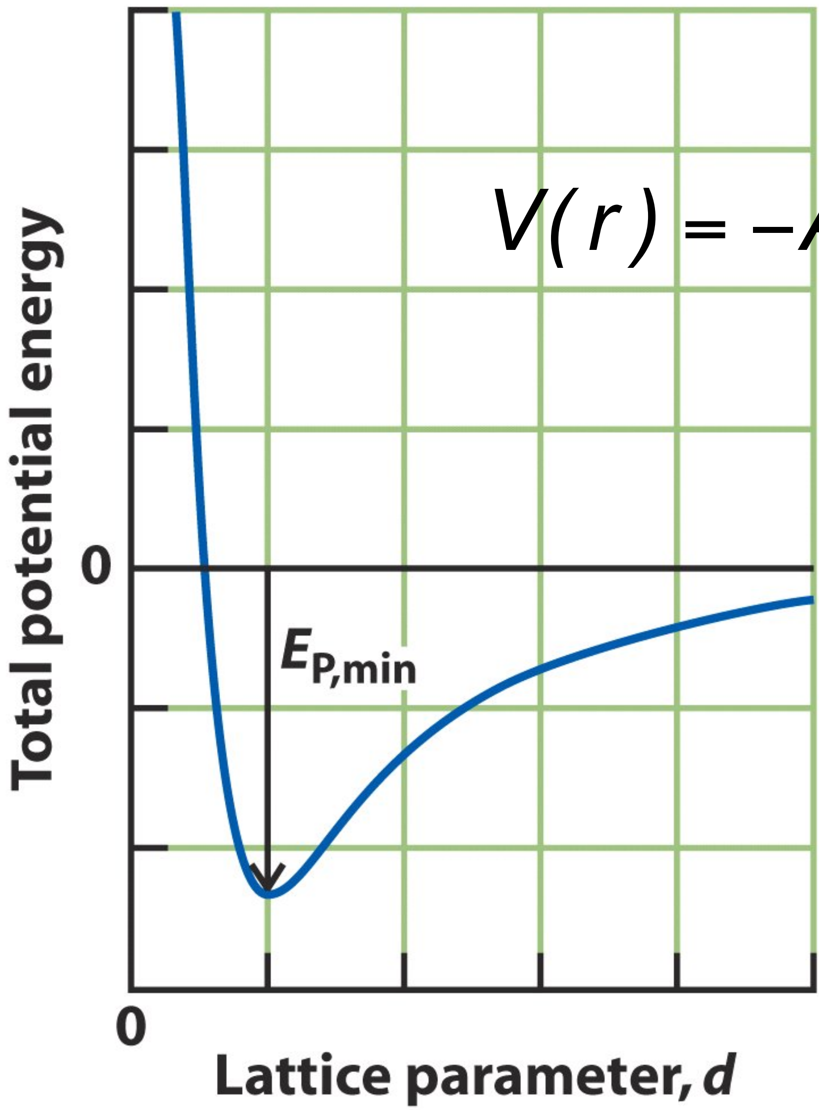
Structural type*	*A*
cesium chloride	1.763
fluorite	2.519
rock salt	1.748
rutile	2.408

*For information about these structures, see Chapter 5.

...of course, attraction can not provide the whole story, or the lattice would electrostatically collapse.



...of course, attraction can not provide the whole story, or the NaCl would collapse into itself behave like a black hole with terrible consequences for all mankind.



$$V(r) = -A \times \frac{|z_1 z_2| N_A e^2}{4\pi\varepsilon_0 d} \times \left(1 - \frac{d^*}{d}\right)$$

the ***Born-Meyer Equation***...

d* is a constant that is often taken to be 34.5 pm (0.345 Å).

if we know A, and the identities of the ions (and hence z_1 & z_2)...

then we can calculate d!