CHEM 1101B- Chemistry for Engineers

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HS (Health Sciences) 1301
Mondays & Wednesdays 8:35am - 9:55am

Lecture 12: Solids

Please feel free to introduce yourself to your neighbors– name, pronouns, a hobby, etc.

and/or

Answer first wooclap question

Learning outcome for Topic 12: Phases of Matter – Solids

Learning Outcomes:

- Describe intermolecular forces in solids
- Relate the intermolecular forces in crystalline solids to the crystal lattice energy
- Draw and use a Born-Haber cycle

Over 90% of naturally occurring and man-made solids are crystalline

Most solids form a **regular, repeating** arrangement of their particles since **overall attractive interactions between particles are maximized** and **total intermolecular energy is minimized**.

Crystals of vanadinite, quartz and stibnite

Development of new solids is an active area of STEM research

Solids play an ever-larger role in society:

- high-temperature superconductors
- heat-resistant tiles for the outer "skin" of the space shuttle
- new tissue-compatible solids for surgical implants.

Example:

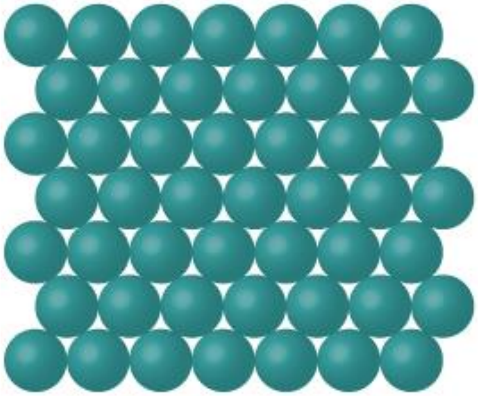
- NASA's recent breakthrough in 3D printable high-temperature materials (new metal alloy) can lead to stronger, and more durable parts for airplanes and spacecraft

https://www.nasa.gov/aeronautics/nasas-new-material-built-to-withstand-extreme-conditions/

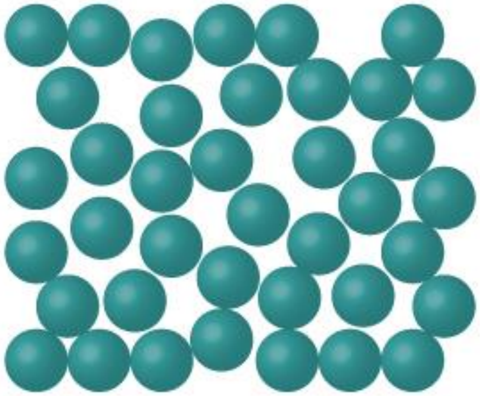
Solids are classified as crystalline or amorphous based on arrangement of their particles

Crystalline solids: atoms, ions, and molecules that have highly ordered structures

Amorphous solids: particles that are randomly arranged with no discernible pattern



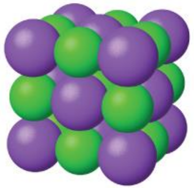
Crystalline



Amorphous

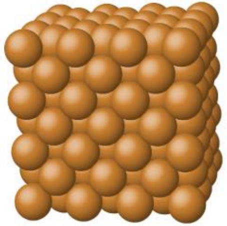
Major types of crystalline solids

Ionic solids: positive and negative ions held together by electrostatic attractions



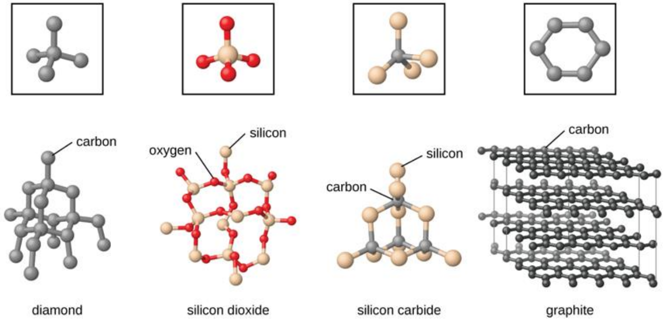
e.g., NaCl

Metallic solids: uniform distribution of atomic nuclei within a "sea" of delocalized electrons

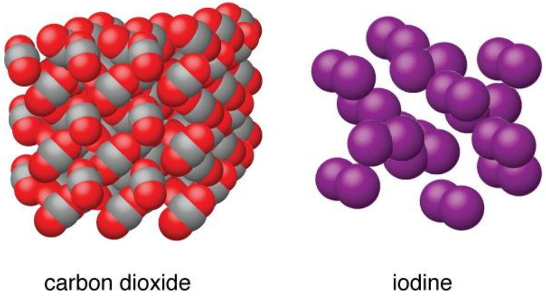


e.g., Copper metal

Covalent network solids: atoms held together by a network of covalent bonds



Molecular solids: discrete molecules held together by attractive forces



Types of crystalline solids and their properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al_2O_3
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO_2, SiC
molecular	molecules (or atoms)	IMFs – induced dipole & dipole-dipole forces	variable hardness, variable brittleness, not conductive, low melting points	H_2O, CO_2, I_2, $C_{12}H_{22}O_{11}$

Practice: Example 1 identifying types of solids

1) At very low temperatures oxygen, O_2, freezes and forms a crystalline solid. Which best describes these crystals?

2) As it cools, olive oil slowly solidifies and forms a solid over a range of temperatures. Which best describes the solid?

a) Ionic
b) Covalent network
c) Metallic
d) Amorphous
e) Molecular Crystals

Practice: Example 2 identifying types of solids

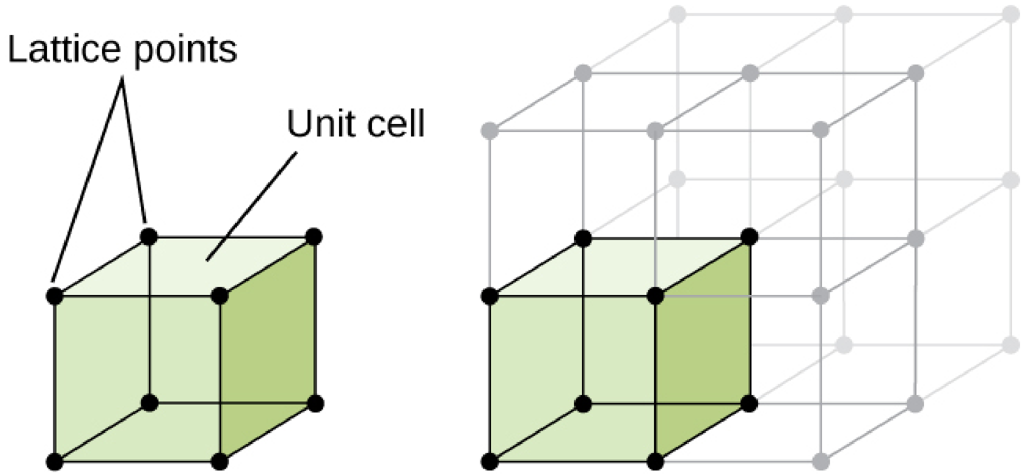
Explain why ice, which is a crystalline solid, has a melting temperature of 0°C, whereas butter, which is an amorphous solid, softens over a range of temperatures.

Structure of crystalline solids: unit cells

The structure of a crystalline solid, whether a metal or not, is best described by considering its **simplest repeating unit**, which is referred to as its **unit cell**.

The unit cell consists of **lattice points** that represent the locations of atoms or ions.

The **entire structure** then consists of this **unit cell repeating in three dimensions**.

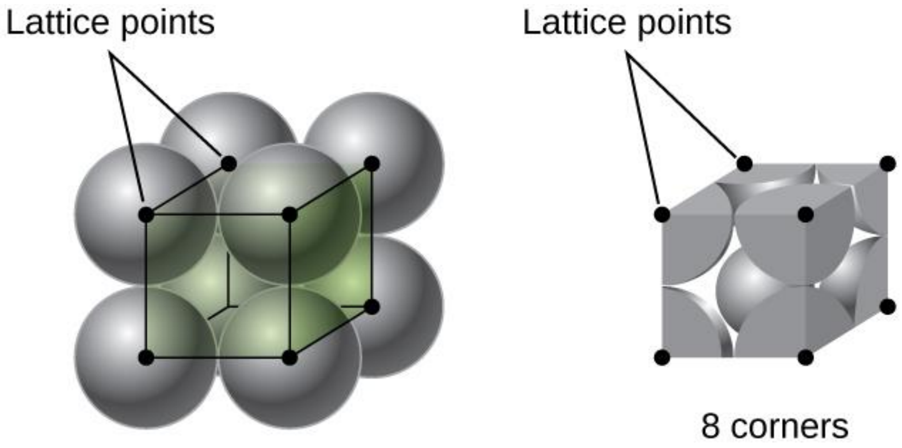


https://chem.libretexts.org/Courses/Oregon_Institute_of_Technology/OIT%3A_CHE_201_-_General_Chemistry_I_%28Anthony_and_Clark%29/Unit_4%3A_Quantifying_Chemicals/4.1%3A_Unit_Cells

Structure of crystalline solids: simple cubic

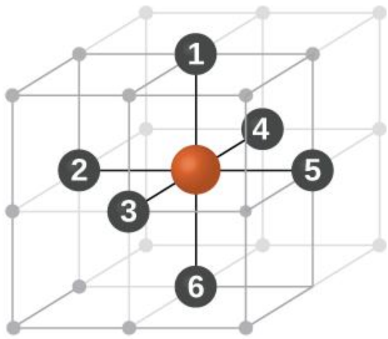
When metal atoms are arranged with spheres in one layer directly above or below spheres in another layer, the lattice structure is called **simple cubic**.

- Atoms occupy about 52% of the volume– relatively **inefficient arrangement**



Simple cubic unit cell

8 x 1/8 = 1 atom/unit cell



Simple cubic structure

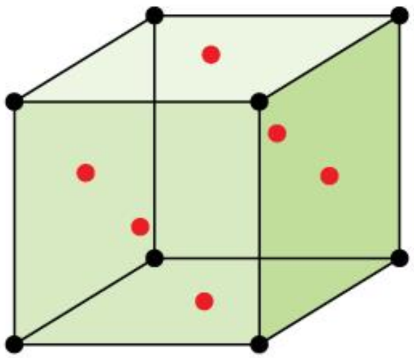
Coordination # = 6

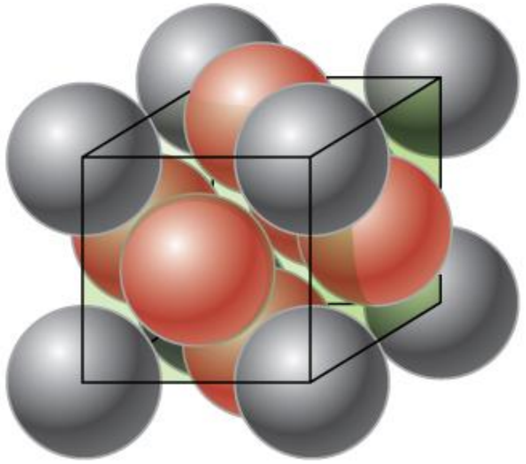
https://boisestate.pressbooks.pub/chemistry/chapter/10-6-lattice-structures-in-crystalline-solids/

Structure of crystalline solids: face-centered cubic (FCC)

Many other metals, such as aluminum, copper, and lead, crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and at the centers of each face – **face-centered cubic.**

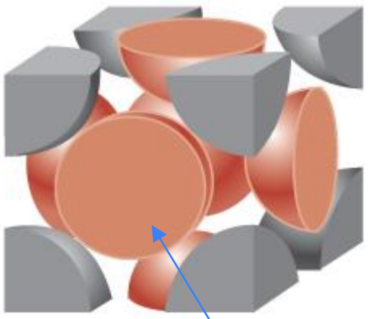
- Atoms occupy 74% of the volume– relatively **efficient arrangement**





Face-centered cubic structure

Coordination # = 12



8 x 1/8 + 6 x 1/2

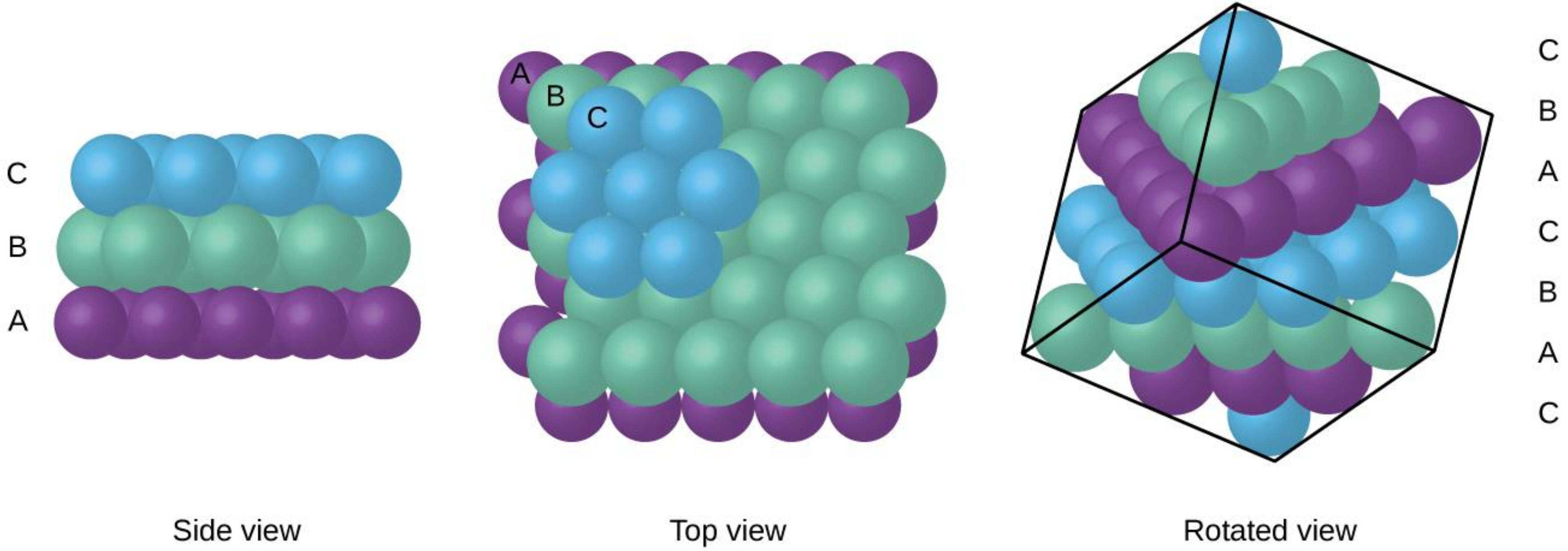
= 4 atoms/unit cell

https://boisestate.pressbooks.pub/chemistry/chapter/10-6-lattice-structures-in-crystalline-solids/

Structure of crystalline solids: cubic closest packing (CCP)

Cubic Closest Packing (CCP): three repeating layers of hexagonally arranged atoms in an **abc pattern**

- Each atom contacts 6 atoms in its own layer, 3 layer above, and 3 layer below



Cubic closest packed structure

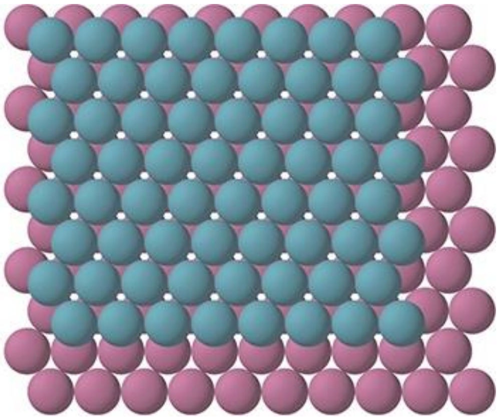
Coordination # = 12

https://bc
structures

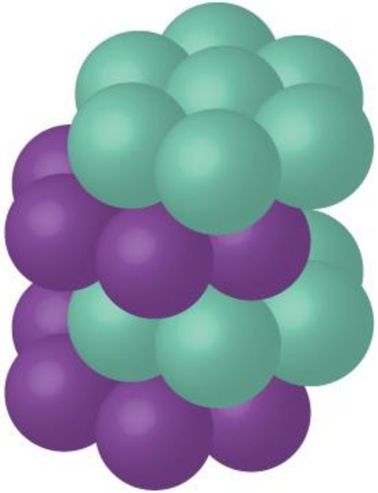
Structure of crystalline solids: hexagonal closest packing (HCP)

Hexagonal Closest Packing: three repeating layers of hexagonally arranged atoms in an **ab pattern**

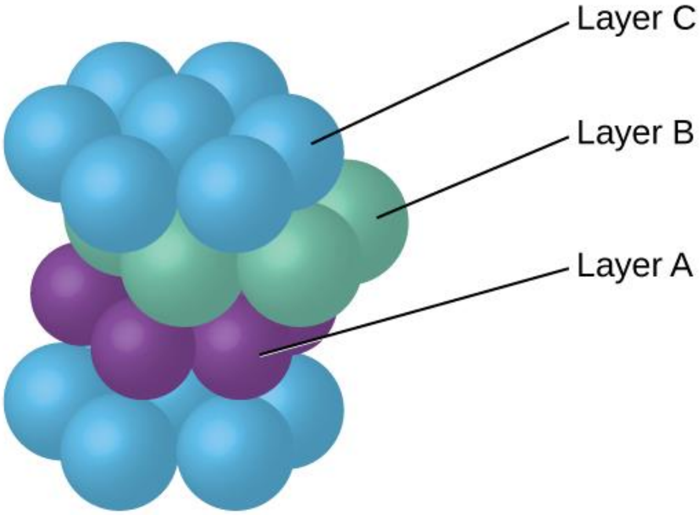
- Each atom contacts 6 atoms in its own layer, 3 layer above, and 3 layer below



Two ways to place third layer as two types of spaces from second layer



Hexagonal closest packed

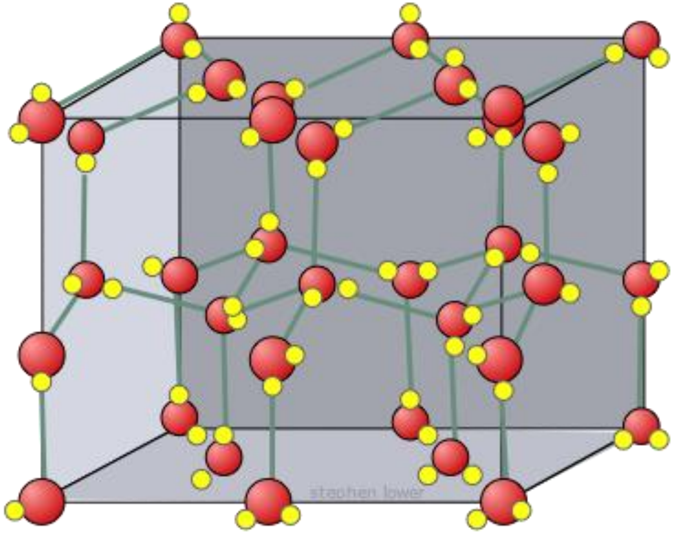


Cubic closest packed

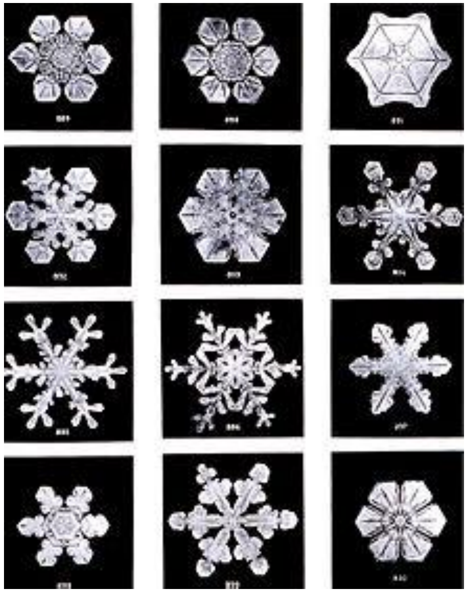
https://boisestate.pressbooks.pub/chemistry/chapter/10-6-lattice-structures-in-crystalline-solids/

Structure of molecular crystals are less symmetrical

The pattern is hexagonal, but NOT closest packing – the atoms are more separated, and there are extra ones inserted in between the pure hexagons.



http://johncarlosbaez.wordpress.com/2012/04/15/ice/



Snowflakes (ice crystals) by Wilson Bentley, 1902

Crystal Lattice Energies

The NET forces of attraction holding the ions together in the crystal.

Since it is an attraction, you have to *add energy* to separate the ions from each other.

The converse must be true (law of conservation of energy); you must have *energy released* when the ions come together.

Crystal Lattice Energies

Energy must be released when the ions come together.

M+

Too far apart to have any significant forces of attraction acting between them

what phase must they therefore be???

X–

$M^{+}_{(g)} + X^{-}_{(g)} \rightarrow MX_{(s)}$

The energy of this reaction is called the **crystal lattice energy (always negative value- energy is released)**.

M+ X–

in a 3-D crystal of the appropriate crystal structure – now solid

Crystal Lattice Energies

$$M^{+}_{(g)} + X^{-}_{(g)} \xrightarrow{\mathbf{U}} MX_{(s)}$$

This energy is very useful to know.
Why?

- Helps to predict the heat of the solution (solubilities)
- Gives some idea of heat of the reaction (reactivities)

This energy is very hard to measure directly in the lab.
Why?

- We need plasma which are really hard to make!

How can we calculate Crystal Lattice Energies?

We work around this.

Formation reactions:

- Reactions that produce:
    - 1 mol of one compound as their product

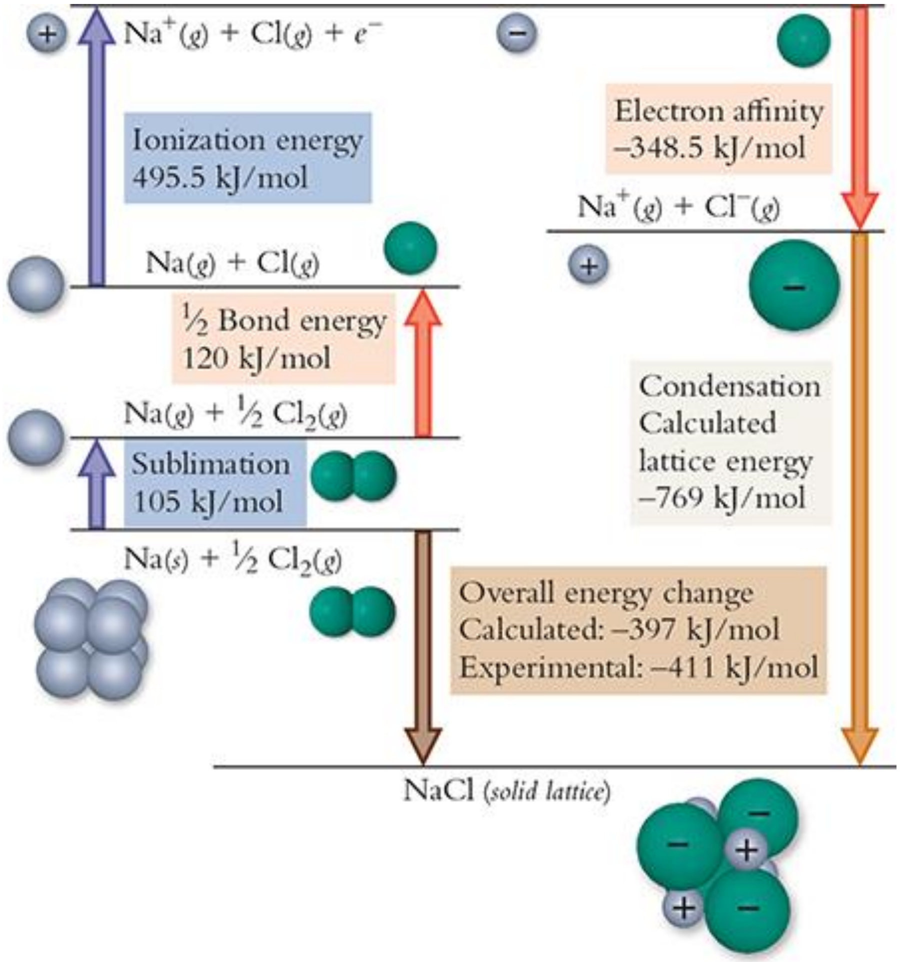
- from starting materials that MUST be:
    - neutral elements
    - in their standard states

These formation energies are relatively simple to measure symbol:

standard heat of formation: ΔH°_f

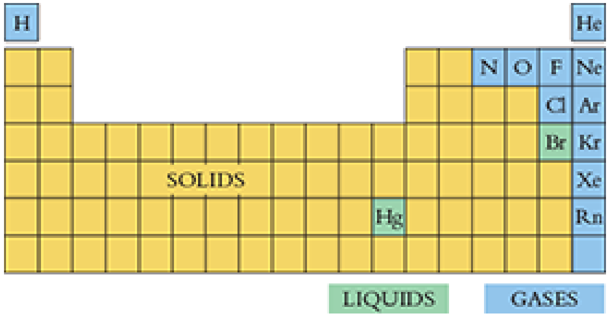
Born-Haber Cycle

Add up all the possible reactions to go from standard states to a solid lattice. This will equal your crystal lattice energy!



Crystal Lattice Energies: Writing formation reactions

Example 1: write a formation reaction for $NaCl_{(s)}$.



1. Write down 1 mole of the product:

2. write down each element in it

3. write their standard states

4. Balance!

Crystal Lattice Energies: Writing formation reactions

Example 2: Write a formation reaction for $Mn_2O_{3\,(s)}$ (Manganese(III) oxide)

1.

2.

3.

4.

Practice: Identifying formation reaction

Select the correct formation reaction for solid magnesium hydroxide, $Mg(OH)_{2(s)}$.

1) $Mg_{(s)} + 2\ O_{(g)} + 2\ H_{(g)} \rightarrow Mg(OH)_{2(s)}$

2) $Mg^{2+}{}_{(s)} + 2\ OH^{-}{}_{(g)} \rightarrow Mg(OH)_{2(s)}$

3) $Mg_{(s)} + H_2O_{(l)} + O_{(g)} \rightarrow Mg(OH)_{2(s)}$

4) $Mg^{2+}{}_{(aq)} + 2\ OH^{-}{}_{(aq)} \rightarrow Mg(OH)_{2(s)}$

5) $Mg_{(s)} + O_{2(g)} + H_{2(g)} \rightarrow Mg(OH)_{2(s)}$

wooclap

Using formation reactions to predict crystal lattice energies

We want some way to compare formation energies – which are relatively easy to measure – to crystal lattice energies – which are very difficult to measure directly, but useful to know.

STEPS:

1. Write down the compound you're interested in in the lower right hand corner of your working space
2. Show the formation reaction leading to it along the bottom of your working space
3. Show the crystal lattice reaction leading to it down the right hand side of your working space.

Using formation reactions to predict crystal lattice energies

STEPS

1. Write down the compound you're interested in in the lower right hand corner of your working space
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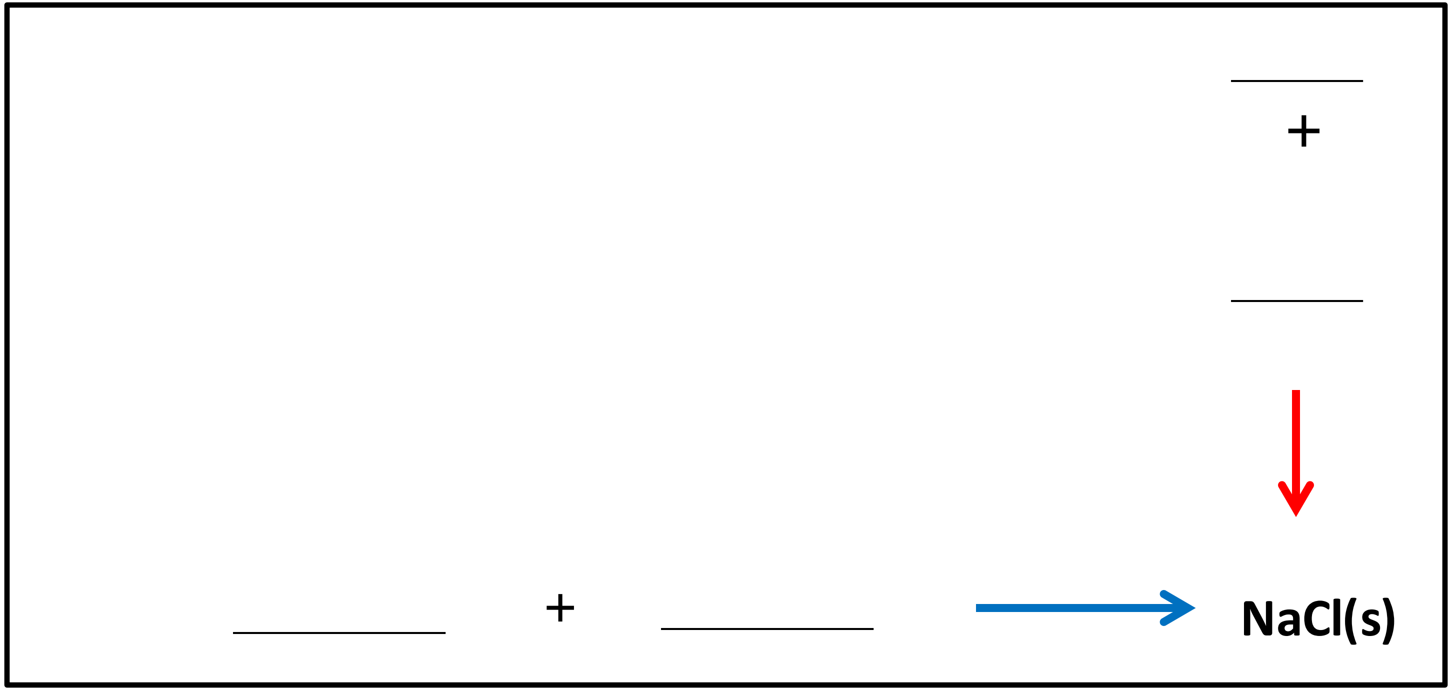


Linking formation and crystal lattice reactions

To link the reactions we work *one element at a time* from the formation reaction:

Figure out what has to change to relate it to the same element's ion in the crystal lattice reaction.

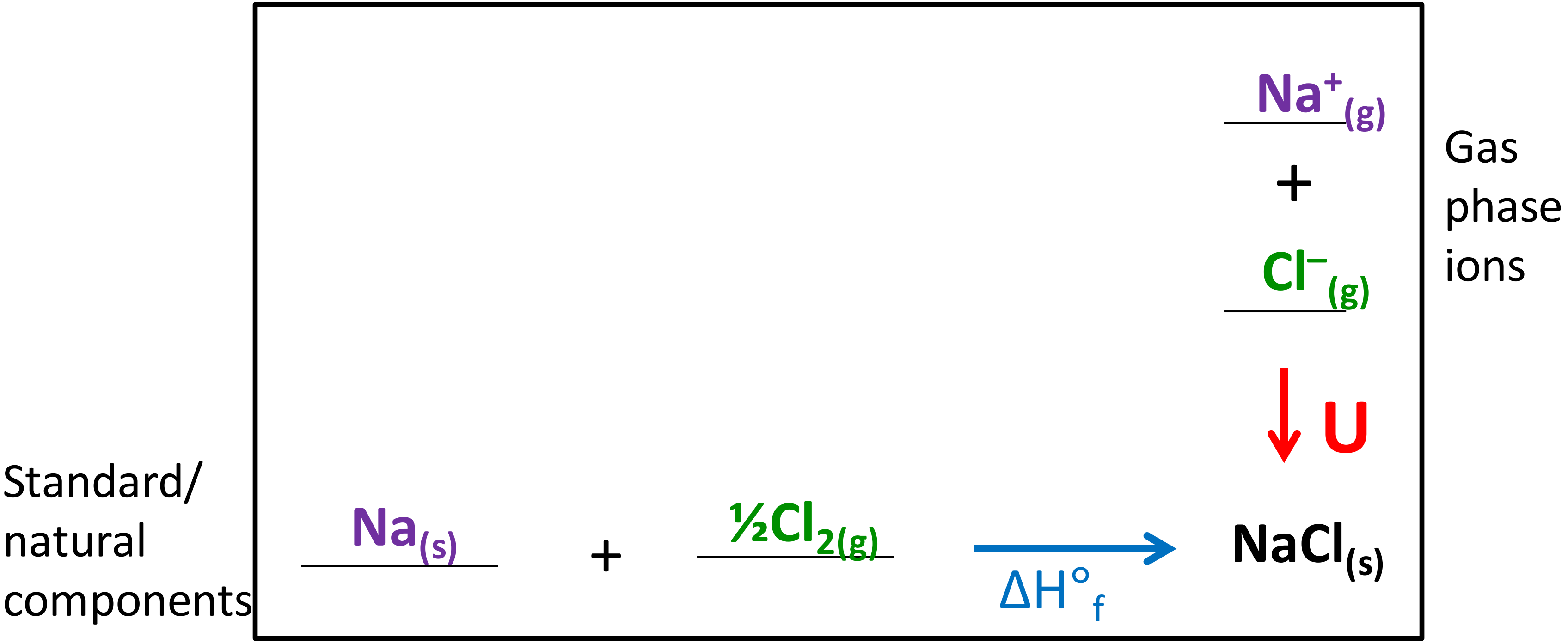
1. Show the reaction for changing the ***phase*** **(**solid, liquid, gas) and/or the ***form*** (monatomic/diatomic)
2. Show the reaction to change the ***charge*** (**always do the charge last**.)

Drawing Born-Haber Diagrams

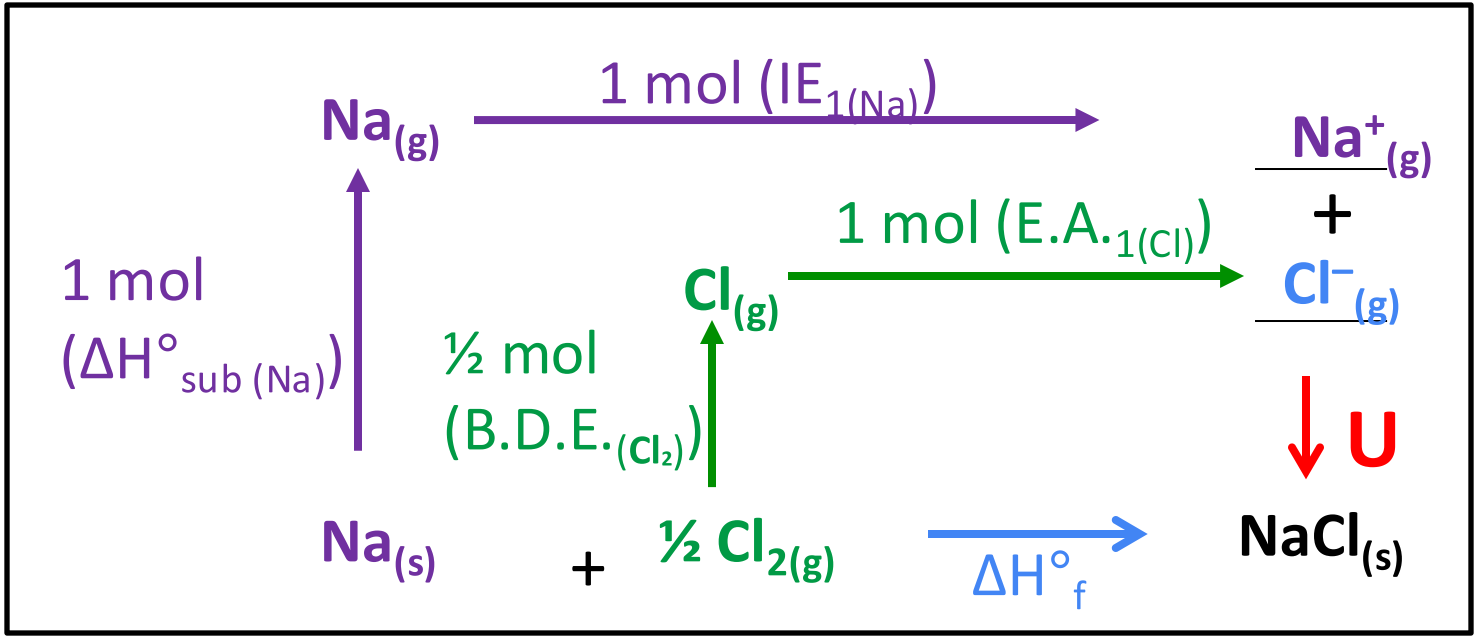
Working *one element at a time* from the formation reaction:

Figure out what has to change to relate it to the same element's ion in the crystal lattice reaction.

1. Show the reaction for changing the *phase* (solid, liquid, gas) and/or the *form* (monatomic/diatomic)
2. Show the reaction to change the *charge* (**always do the charge last.**)



Calculating Crystal Lattice Energy, U



Energy (path 1) = Energy (path 2)

Learning check: crystal lattice reactions

Select the correct crystal lattice reaction for aluminum chloride, $AlCl_{3(s)}$. (Be careful about phases - that's part of what you need to recognize.)

1) $Al^{3+}_{(s)} + 3\ Cl^{-}_{(g)} \rightarrow AlCl_{3(s)}$

2) $Al^{3+}_{(g)} + 3\ Cl^{-}_{(g)} \rightarrow AlCl_{3(s)}$

3) $Al_{(s)} + 3/2\ Cl_{2(g)} \rightarrow AlCl_{3(s)}$

4) $Al^{3+}_{(s)} + Cl_3{}^{3-}_{(g)} \rightarrow AlCl_{3(s)}$

Summary of steps: Born-Haber Diagrams

1. Write down the compound you're interested in in the lower right hand corner of your working space
2. Show the formation reaction leading to it along the bottom of your working space
3. Show the crystal lattice reaction leading to it down the right hand side of your working space.
4. For each material: show the reaction for changing the *phase* (solid, liquid, gas) and/or the *form* (monatomic/diatomic)
5. For each material: show the reaction to change the *charge* (**always do the charge last**.)

MAKE SURE EVERYTHING IS BALANCED!!!

Example 2: Born-Haber Cycle

a) Draw and label a Born-Haber diagram for $Mn_2O_{3\,(s)}$

b) Given the following data, calculate its crystal lattice energy

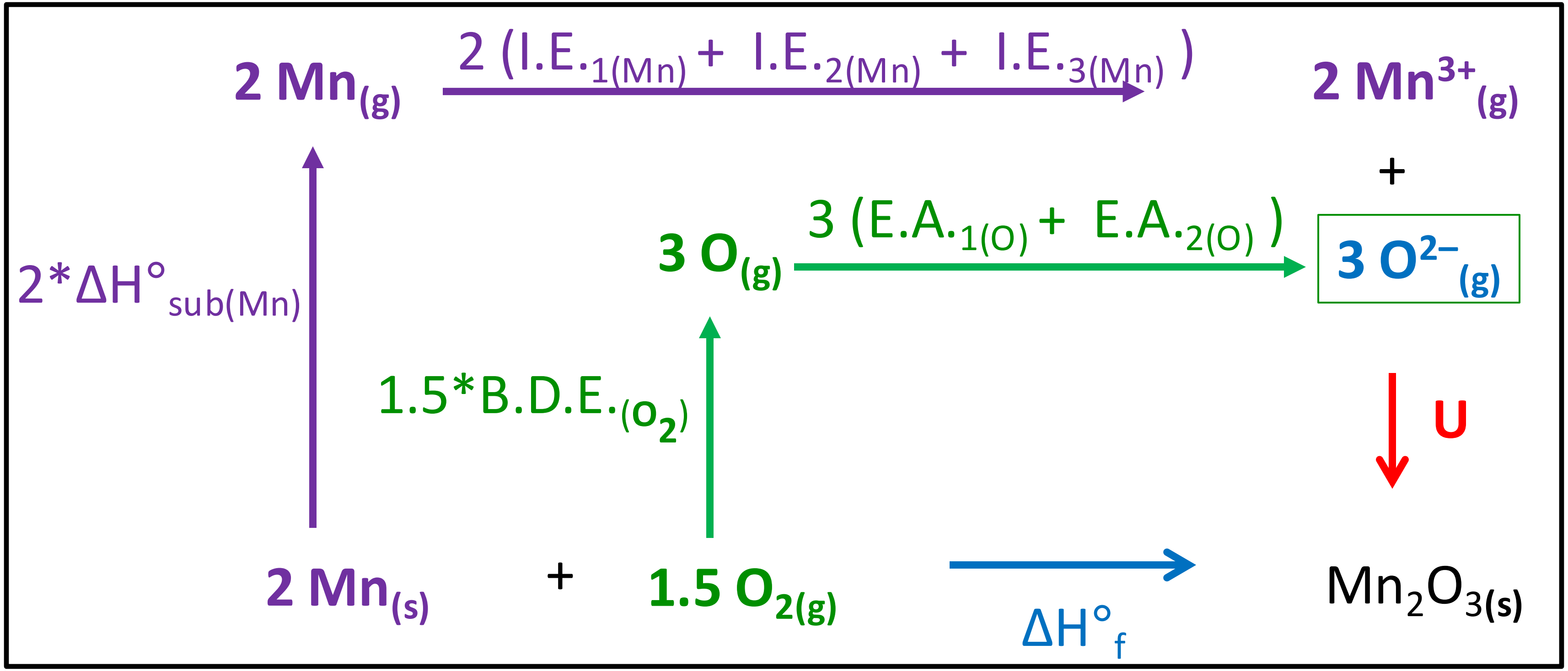
$\Delta H_f°\ (Mn_2O_3)$	=	–497 kJ/mol
$\Delta H_{sub}°\ (Mn)$	=	415.5 kJ/mol
$I.E._1(Mn)$	=	718 kJ/mol
$I.E._2(Mn)$	=	1509 kJ/mol
$I.E._3(Mn)$	=	3249 kJ/mol
$I.E._4(Mn)$	=	4940 kJ/mol *
$E.A._1\ (O)$	=	–133 kJ/mol
$E.A._2\ (O)$	=	247 kJ/mol
$B.D.E.(O_2)$	=	495 kJ/mol

* I may give you more data than you need!

Example 2: Born-Haber Diagram

a) Draw and label a Born-Haber diagram for $Mn_2O_{3\,(s)}$

b) Given the following data, calculate the crystal lattice energy for Mn_2O_3



$$\Delta H^\circ_f = 2^*\Delta H^\circ_{sub} + 2\,(I.E._1 + I.E._2 + I.E._3) + 1.5^*B.D.E. + 3\,(E.A._1 + E.A._2) + U$$

b) Given the following data, calculate the crystal lattice energy for Mn_2O_3

$\Delta H_f°$ (Mn_2O_3)	=	–497 kJ/mol
$\Delta H_{sub}°$ (Mn)	=	415.5 kJ/mol
I.E.$_1$(Mn)	=	718 kJ/mol
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E.A.$_2$ (O)	=	247 kJ/mol
B.D.E.(O_2)	=	495 kJ/mol

$$\Delta H°_f = 2*\Delta H°_{sub} + 2\,(I.E._1 + I.E._2 + I.E._3) + 1.5*B.D.E. + 3\,(E.A._1 + E.A._2) + \mathbf{U}$$