

# Chem 1B Topics

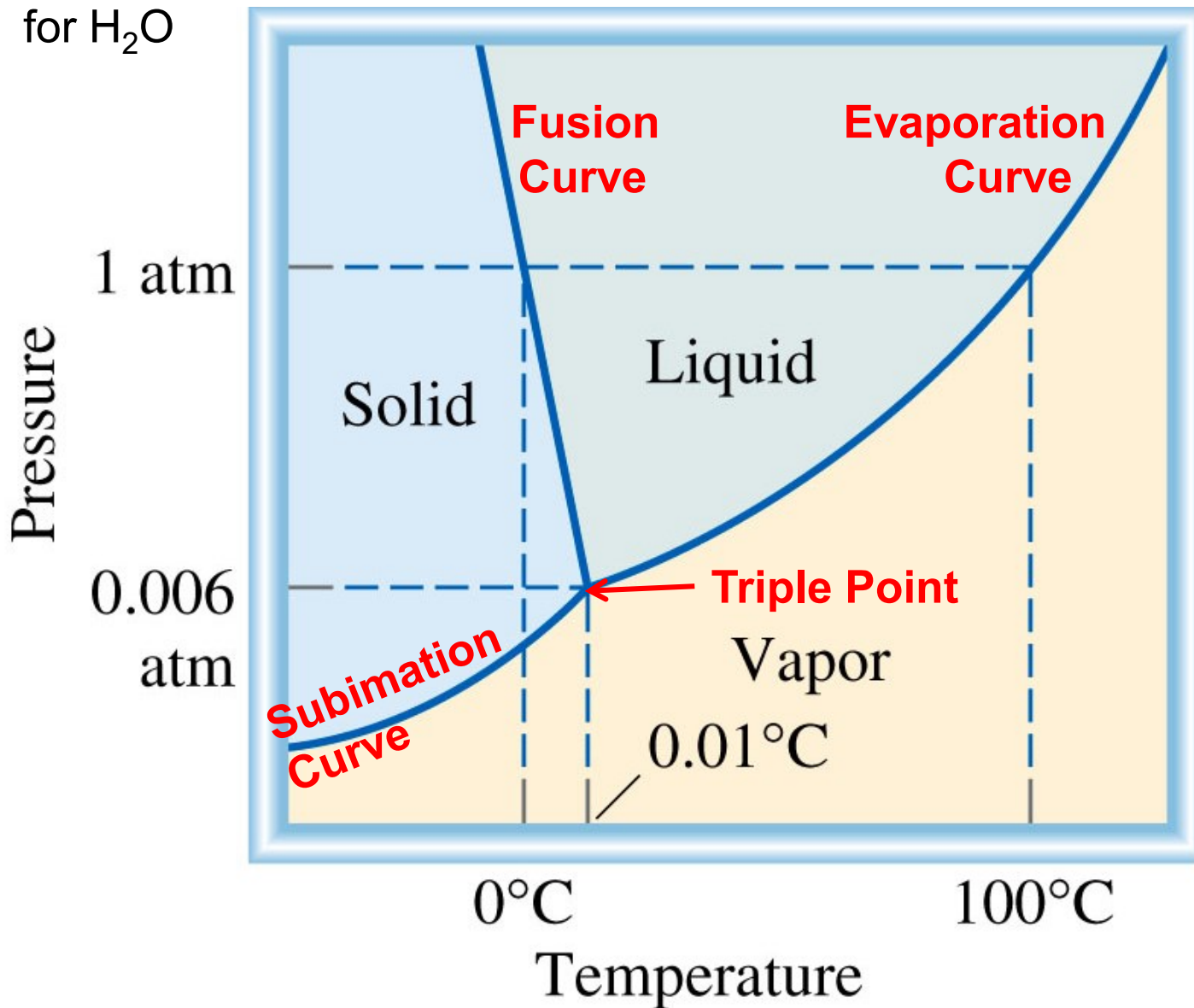
**Chemistry: Structure and Properties**, Nivaldo J. Tro;  
Pearson Education Inc. 2015, 2017.

Week*	Chapter	Topic
1-2	10 (11)	Gases
3-4	11 (12)	Liquids, Solids, Intermolecular Forces
5	12 (13)	Phase Diagrams & Crystalline Solids
6-7	13 (14)	Properties of Solutions
8-9	9 (10)	Thermochemistry
10	18 (19)	Free Energy & Thermodynamics

\* We will be adjusting the exact schedule as we go along...

# Phase Diagrams

Phase diagram  
for H<sub>2</sub>O



A **phase diagram** graphically represents the regions and boundaries between conditions at which a substance is stable as a solid, liquid, or gas.

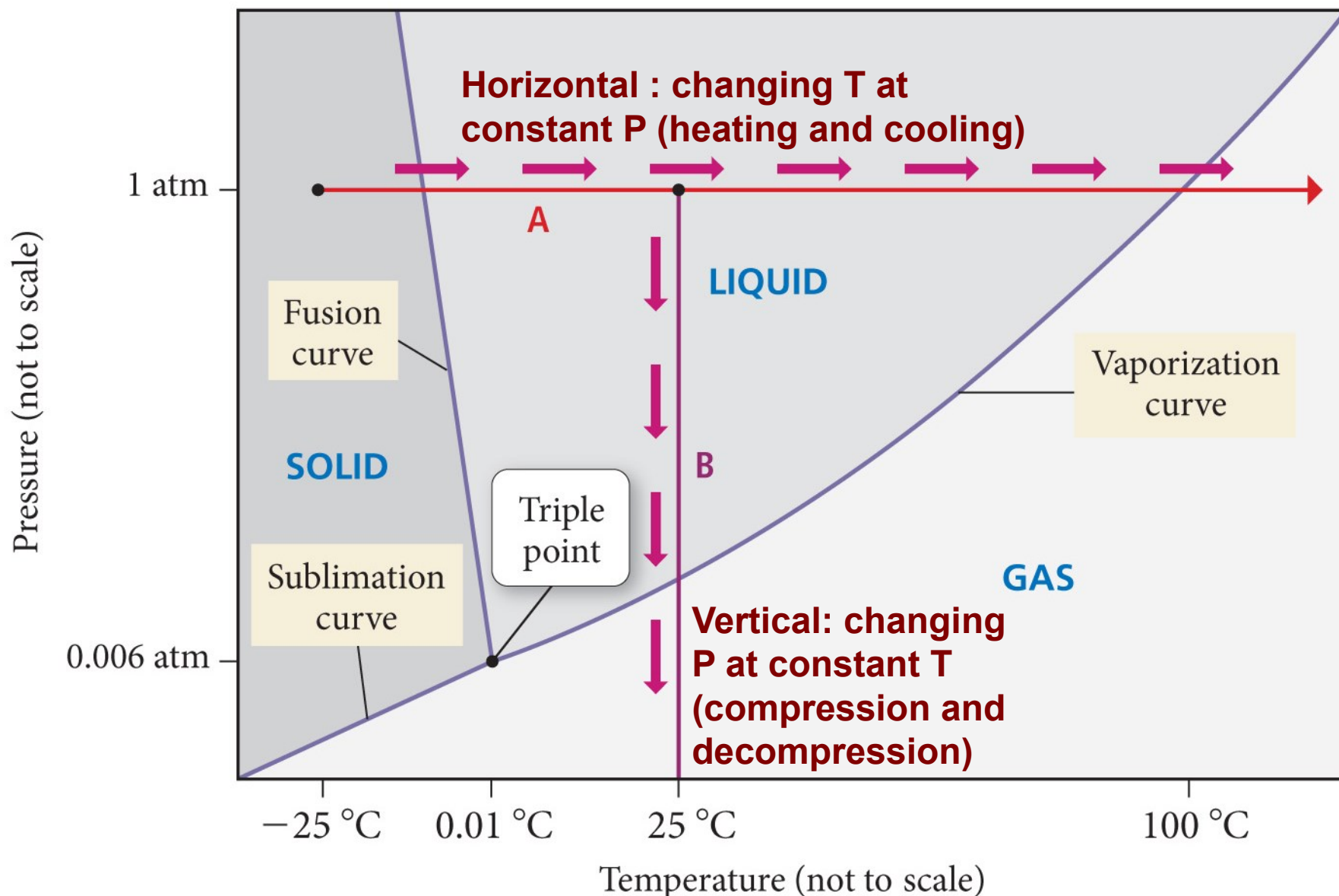
**Evaporation:**

At 1 atm, 100°C:  
 $\text{H}_2\text{O} (l) \rightarrow \text{H}_2\text{O} (g)$

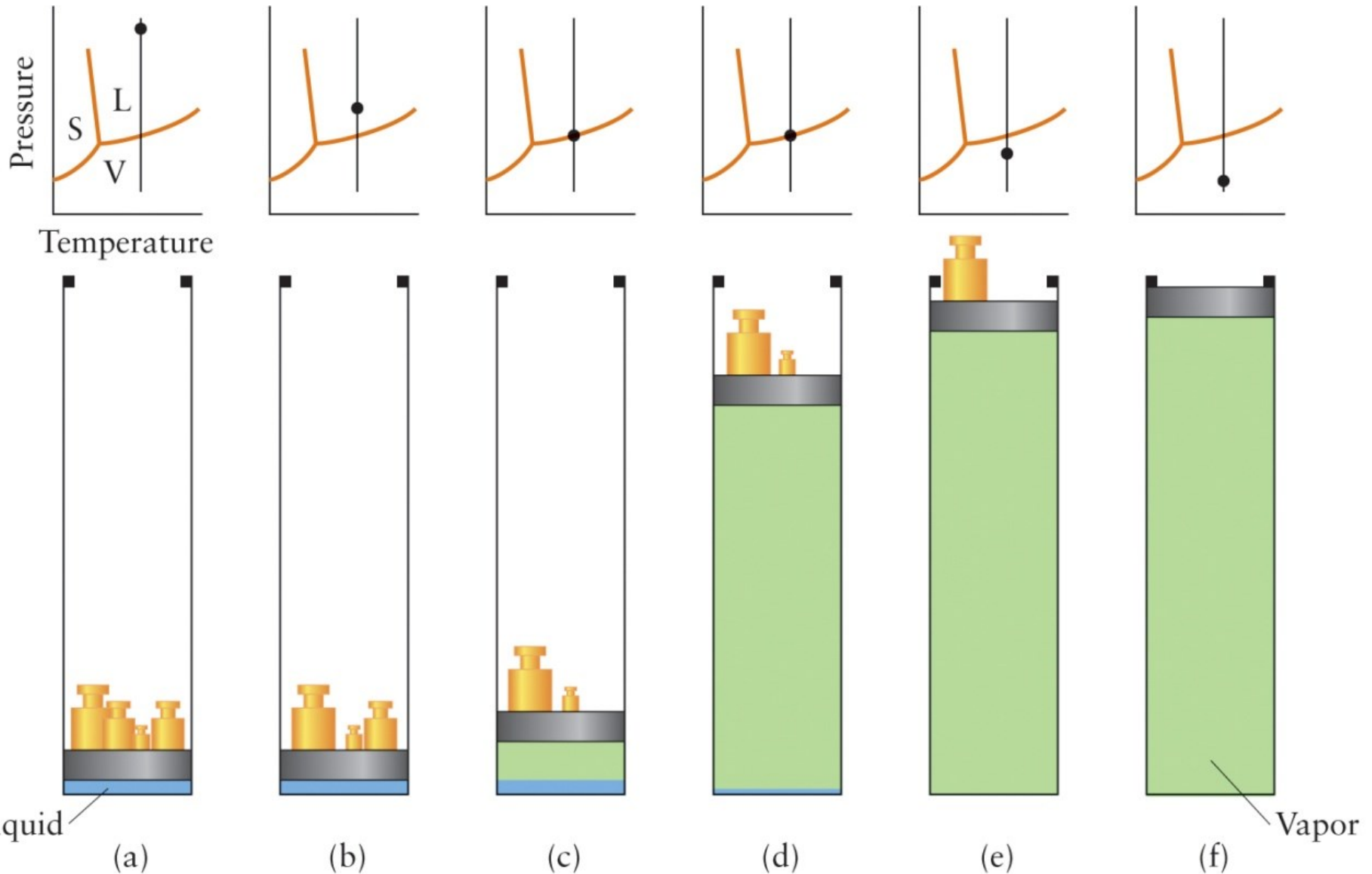
**Fusion:**

At 1 atm, 0°C:  
 $\text{H}_2\text{O} (s) \rightarrow \text{H}_2\text{O} (l)$

# Navigating Phase Diagrams

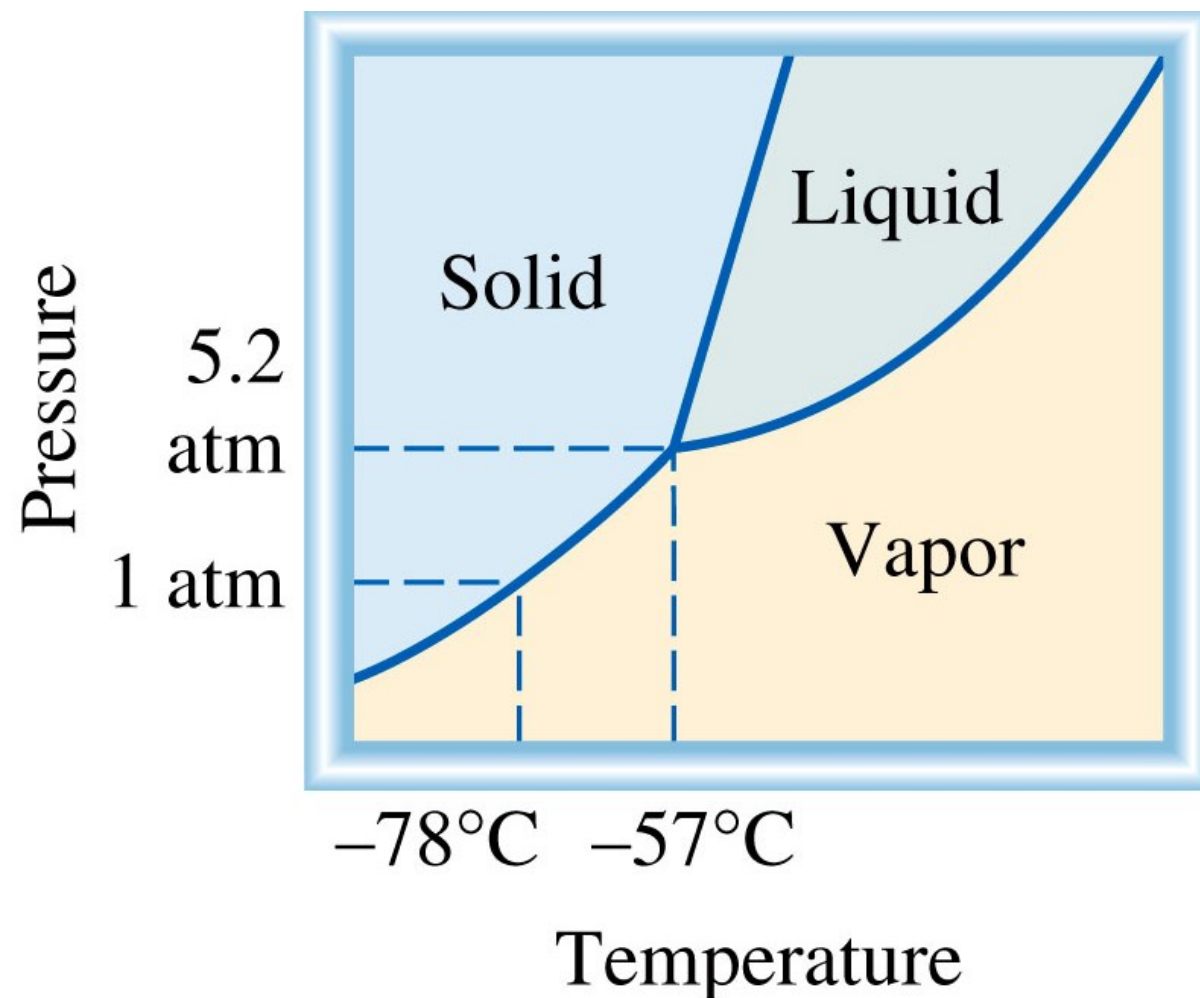


# Example of Decompression

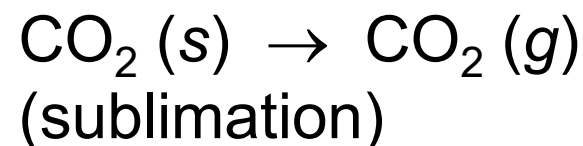


# Phase Diagram of CO<sub>2</sub>

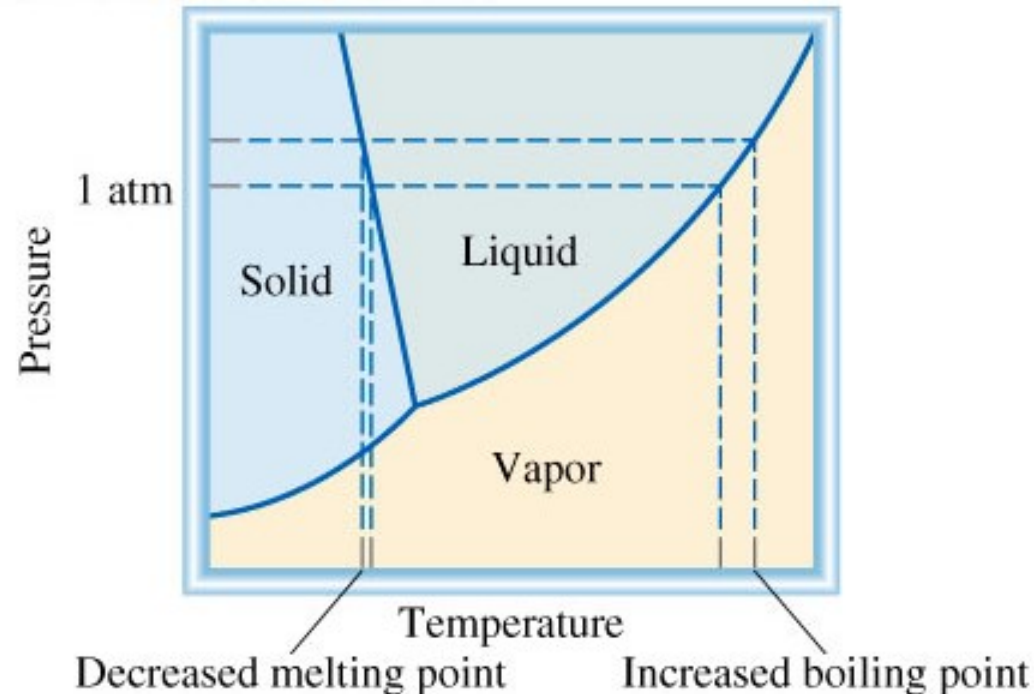
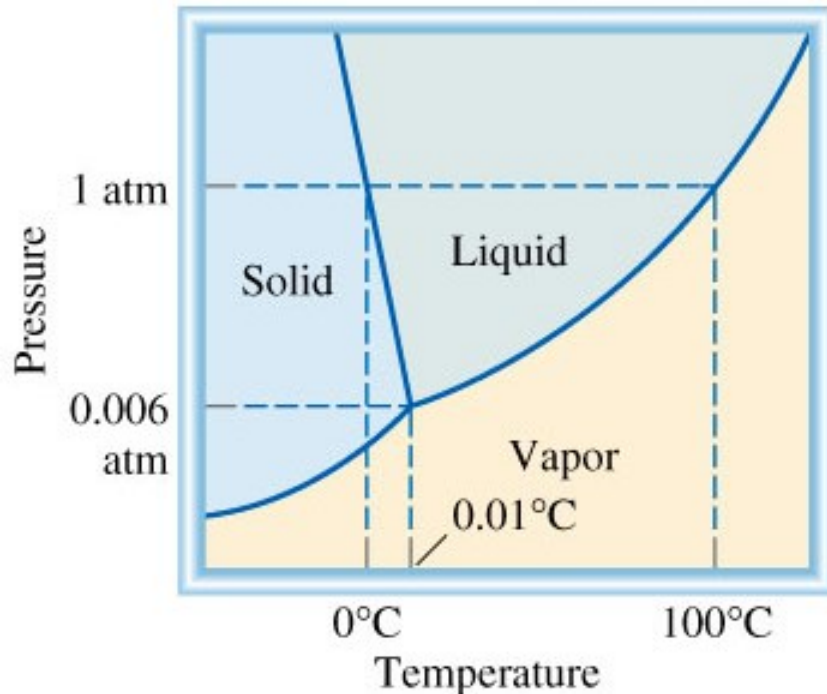
Phase diagram of CO<sub>2</sub> is representative of many compounds that form molecular solids



Unique for CO<sub>2</sub> – it cannot be liquid at 1 atm at any T!



# Effect of Increase in Pressure on the Melting Point of Ice and Boiling Point of Water

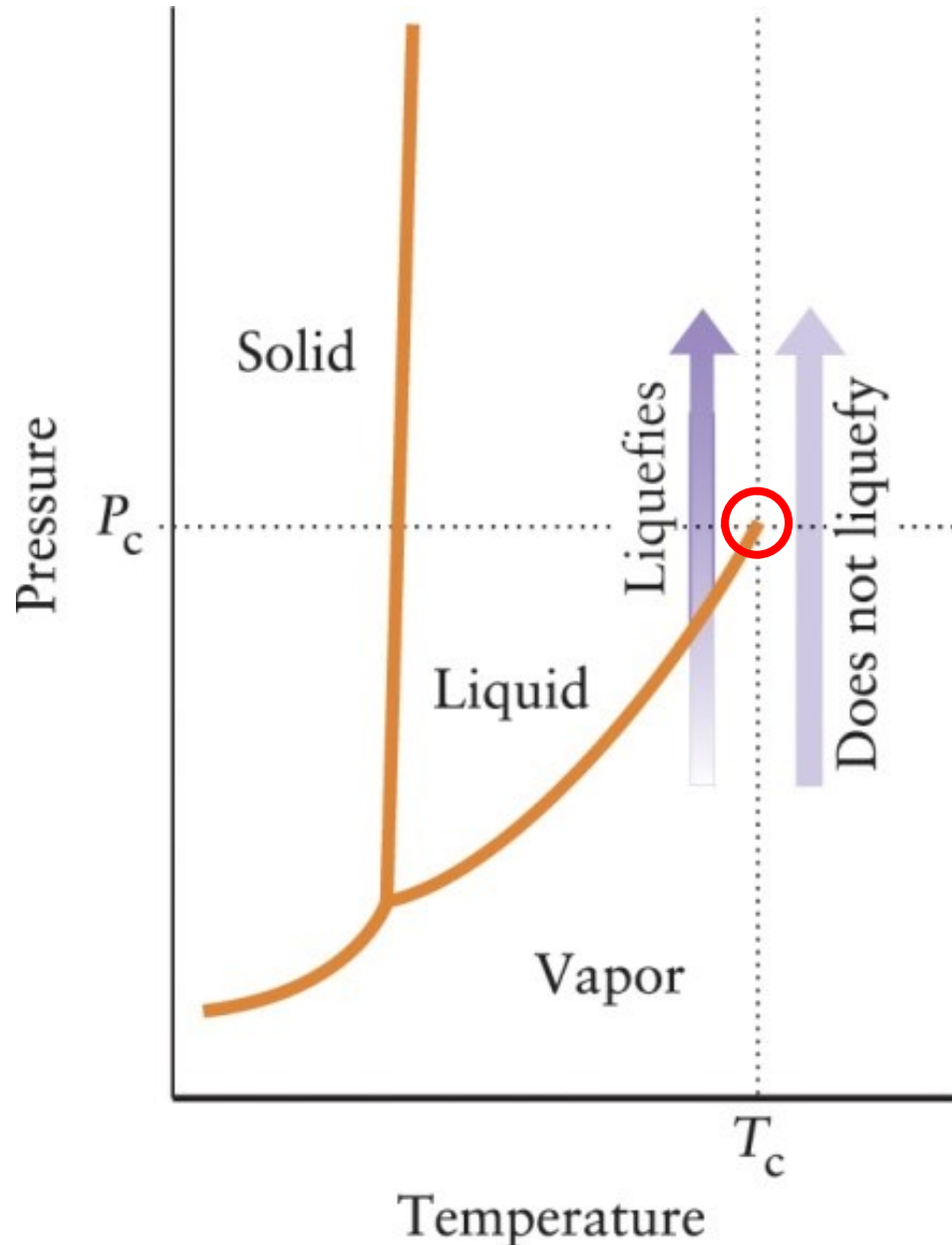


- Higher pressure: ice melts at a lower temperature
- Higher pressure: water boils at a higher temperature (recall the Clausius-Clapeyron equation)
- Discussion: does  $\text{CO}_2$  behave the same way as  $\text{H}_2\text{O}$ ?

# Critical Conditions

The **critical temperature** ( $T_c$ ) is the temperature above which the gas cannot liquefy, no matter how great the applied pressure is.

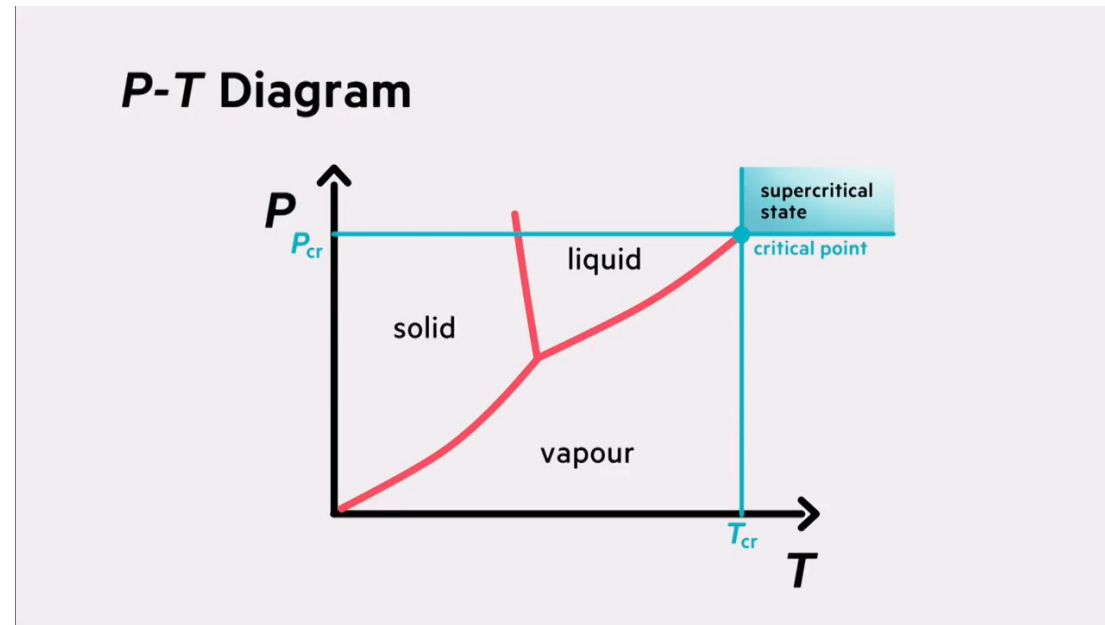
The **critical pressure** ( $P_c$ ) is the minimum pressure that must be applied to bring about liquefaction at the critical temperature.





# Critical Conditions

Critical  
behavior  
of CO<sub>2</sub>



Critical point is an important coordinate on the phase diagram, and it has been measured for many compounds

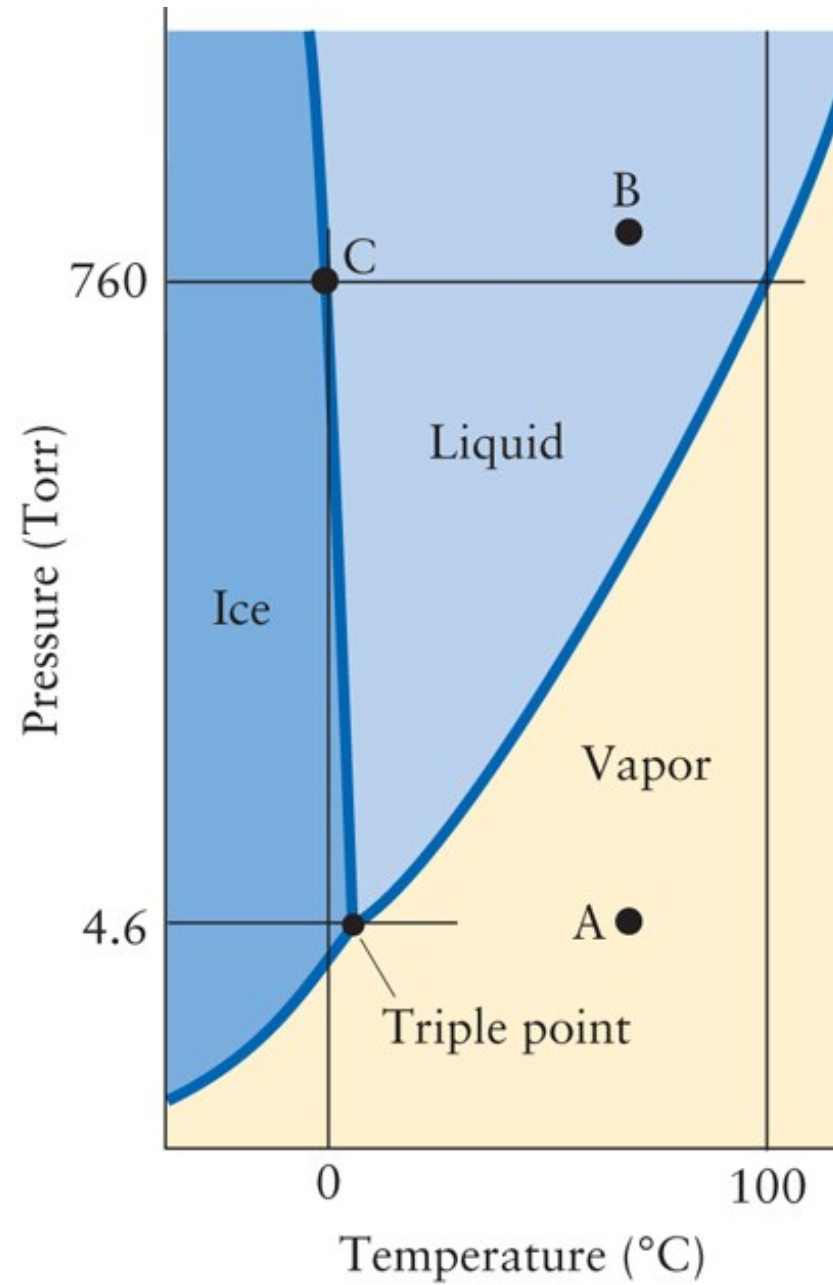
Substance	$T_c$ (°C)	$P_c$ (atm)
Ammonia (NH <sub>3</sub> )	132.4	111.5
Argon (Ar)	−186	6.3
Benzene (C <sub>6</sub> H <sub>6</sub> )	288.9	47.9
Carbon dioxide (CO <sub>2</sub> )	31.0	73.0
Ethanol (C <sub>2</sub> H <sub>5</sub> OH)	243	63.0
Diethyl ether (C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub> )	192.6	35.6
Mercury (Hg)	1462	1036
Methane (CH <sub>4</sub> )	−83.0	45.6



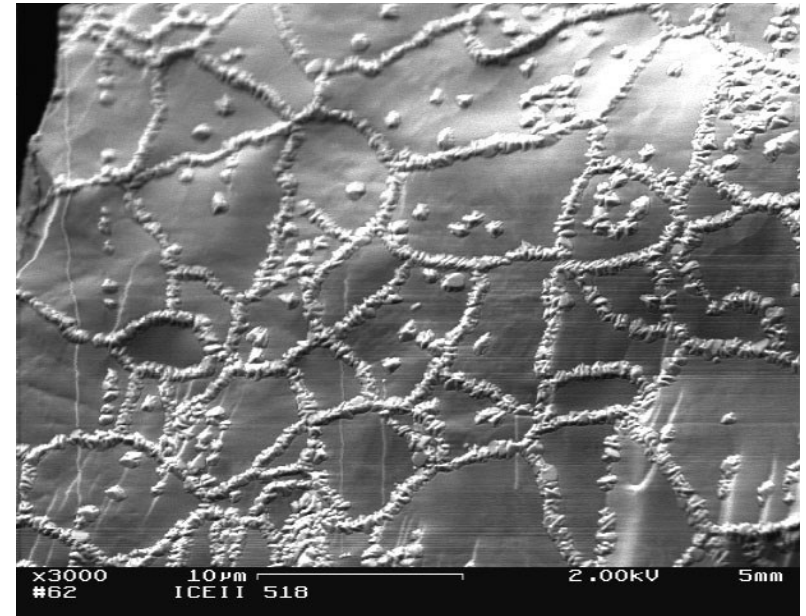
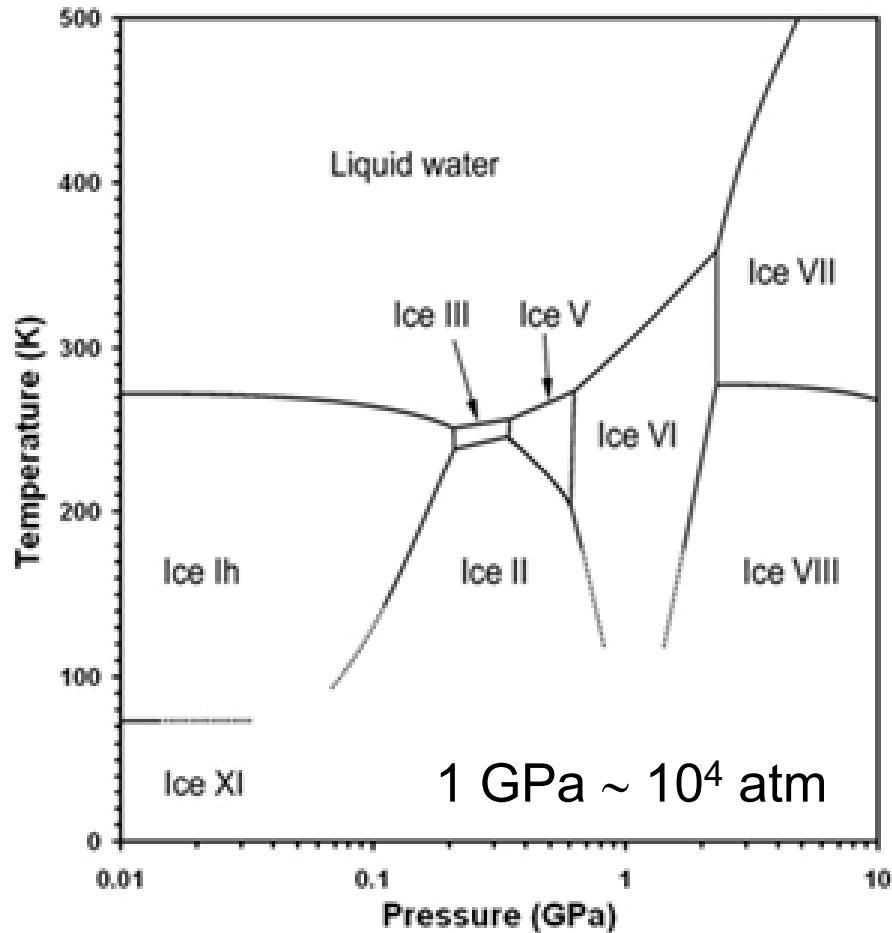
# Sample Problem

Use this phase diagram to describe the physical states and phase changes of water as the pressure is increased from 5 Torr (point A) to 800 Torr (point B) at  $70^{\circ}\text{C}$ .

Point A is at 5 Torr and  $70^{\circ}\text{C}$  which is a vapor. Increasing the pressure passes the liquid-vapor phase boundary, at which point liquid begins to form. At 800 Torr, point B, the phase is in the liquid phase region.



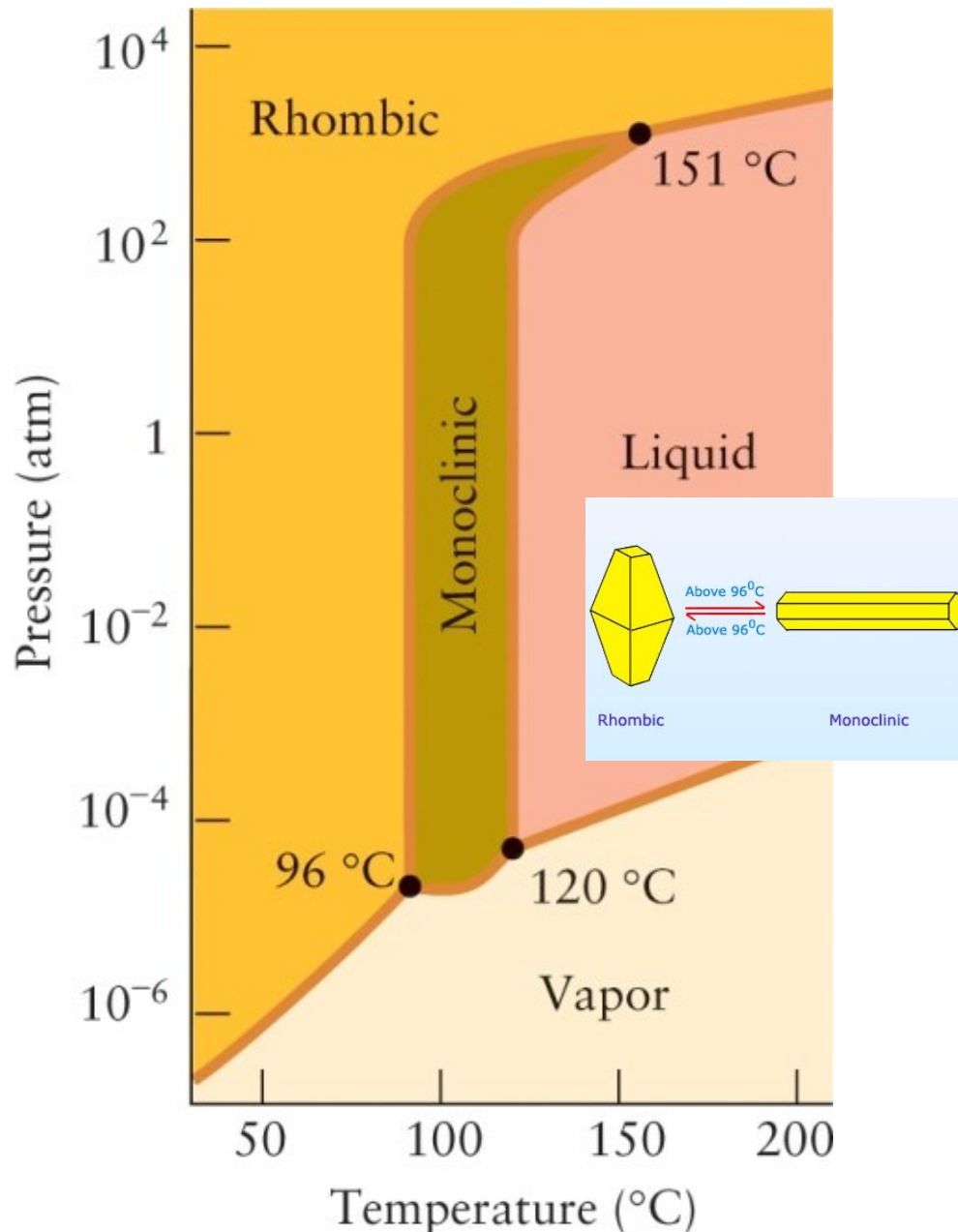
# More Complicated Phase Diagrams



Ice II imaged by a cryogenic electron microscope ([link to the source](#)); believed to be important inside ice planets

There are different types of [ice](#) in addition to the "normal" hexagonal ice. In fact, water remains the most studied substance to this day: there are scientific conferences devoted exclusively to different phase states of water!

# Sample Problem



How many triple points exist in the phase diagram of sulfur shown?

What are the co-existing phases at the triple points?

What is the most stable state of sulfur under normal conditions?

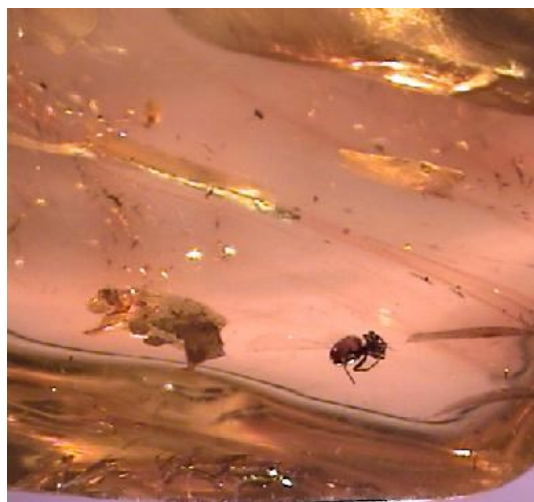
What phase transitions do you expect if you heat sulfur at 1 atm from room T to 200  $^{\circ}\text{C}$ ?

# Classification of Solids

**Amorphous solids** have no well-defined long-range arrangement of the atoms, but are approximately ordered over short distances.



Sucrose and many other sugars  $(\text{CH}_2\text{O})_n$



Amber, a blend of organic resins, with the average molecular formula of  $\text{C}_{10}\text{H}_{16}\text{O}$ .

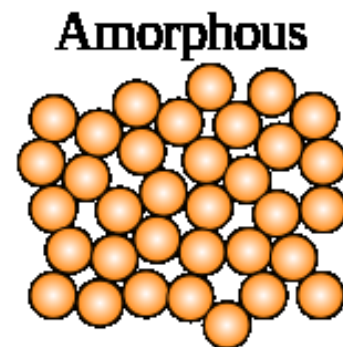
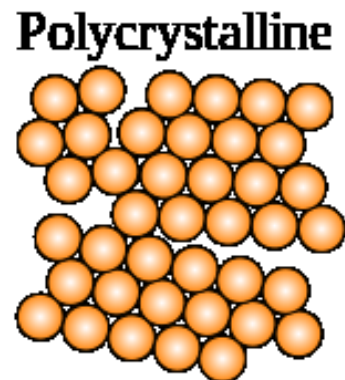
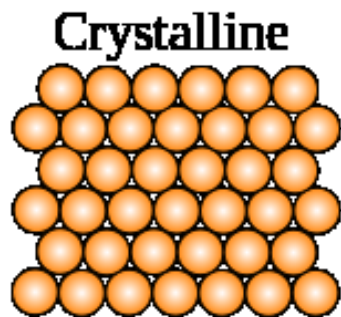


Chocolate ( $\text{C}_7\text{H}_8\text{N}_4\text{O}_2$ , sugar, etc.)



# Classification of Solids

**Ordered solids** have atoms arranged in a highly ordered fashion



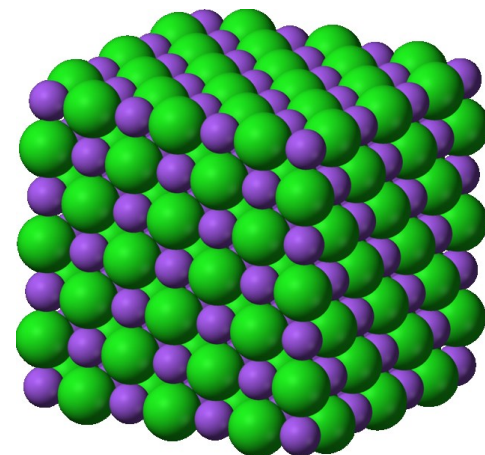
**Crystalline solids** have the highest degree of order



Iron pyrite,  $\text{FeS}_2$   
(Fool's gold)

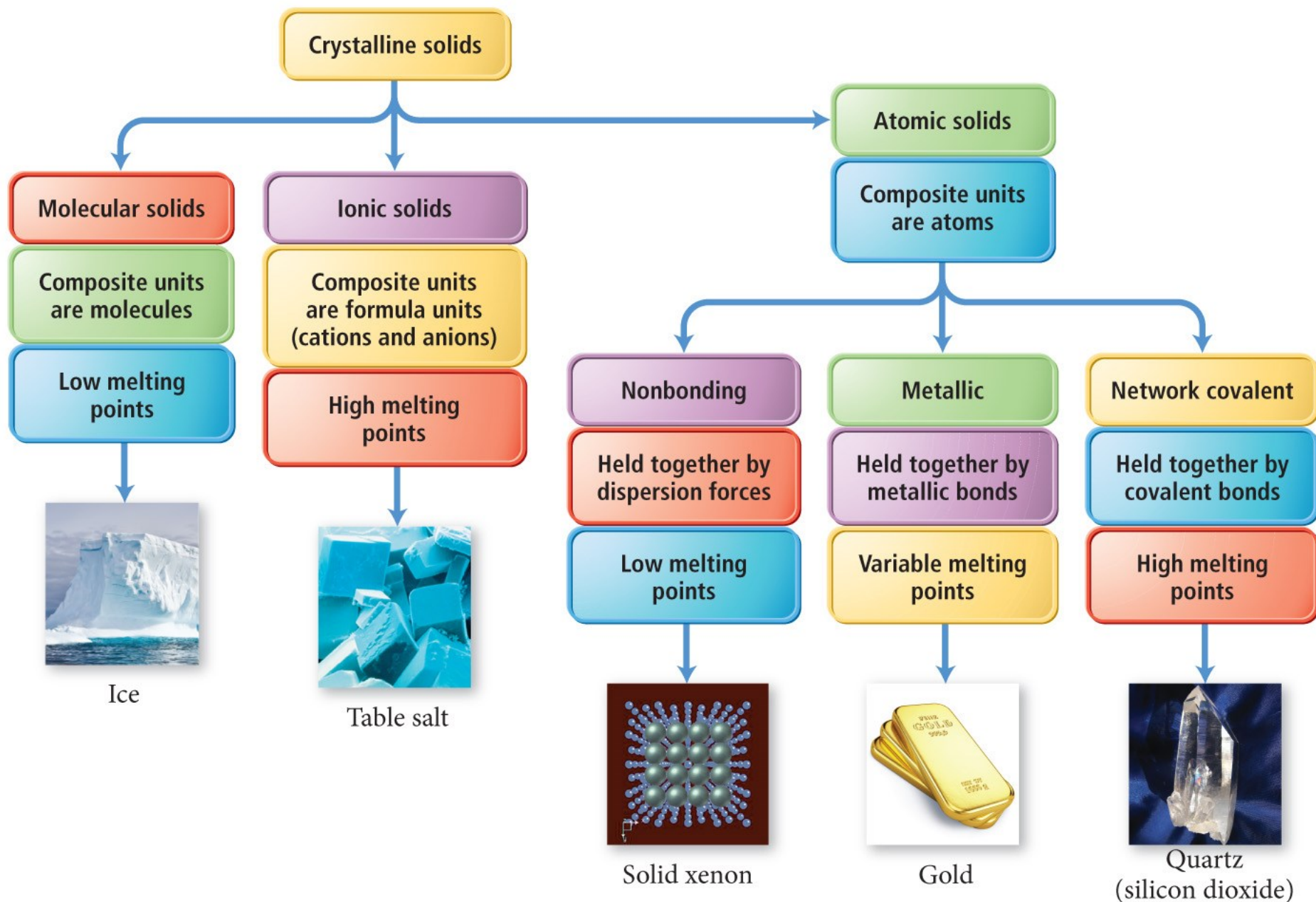


Rock Salt  
 $\text{NaCl}$



Model of a  $\text{NaCl}$   
nanocrystal

# Types of Ordered Solids



# Molecular & Atomic Non-bonding Solids

- Composite units are molecules or atoms
- Held together by weak *intermolecular forces*
- Soft, low melting points
- Poor conductors of heat and electricity

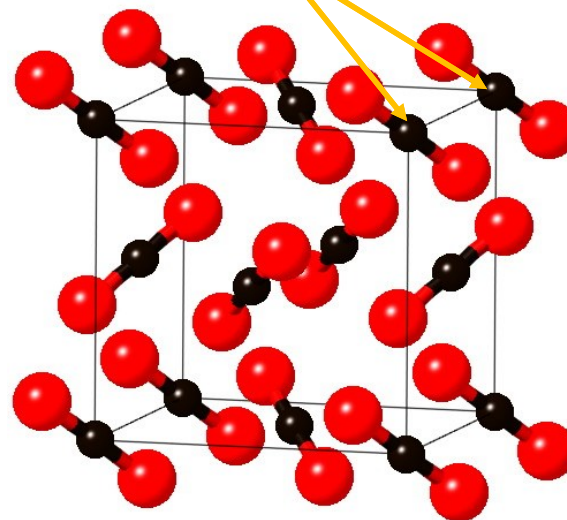
Examples:

- solid Xe
- water ice
- dry ice (frozen  $\text{CO}_2$ )



Crystal structure of dry ice

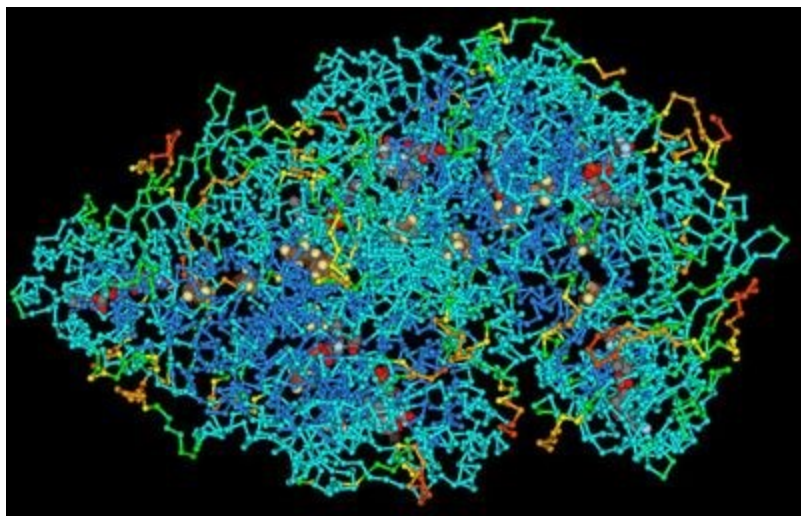
“lattice points”





# Molecular Solids

Crystallizing molecules becomes increasingly more difficult if the molecules become larger. Nonetheless, crystals can be made from molecules as big as large proteins!



# Covalent Network Solids

- Lattice points occupied by atoms
- Held together by covalent bonds
- Hard, high melting point, poor conductors of heat & electricity (exception: graphite).
- Usually formed by nonmetallic elements with valence  $>2$  such as C, Si, As or by oxides of nonmetallic elements



Quartz,  $\text{SiO}_2$



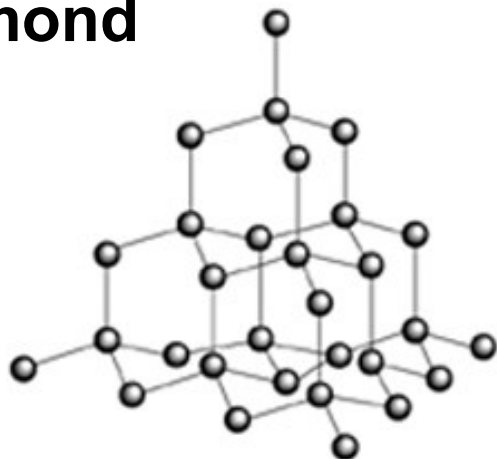
Diamond, C



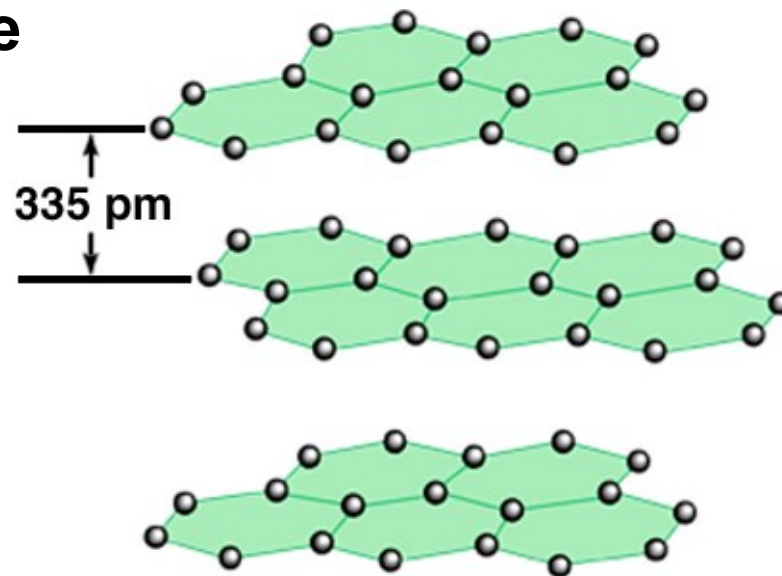
Silicon, Si

# Diamond and Graphite

## Diamond



## Graphite

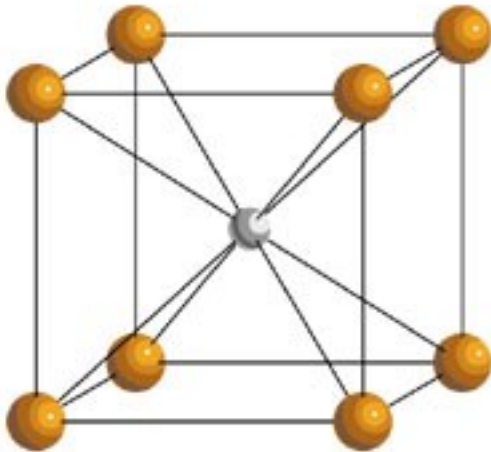


- Each C shares electrons with 4 other C's.
- Does not conduct electricity
- High melting point  $\sim 4000^{\circ}\text{C}$
- Very hard

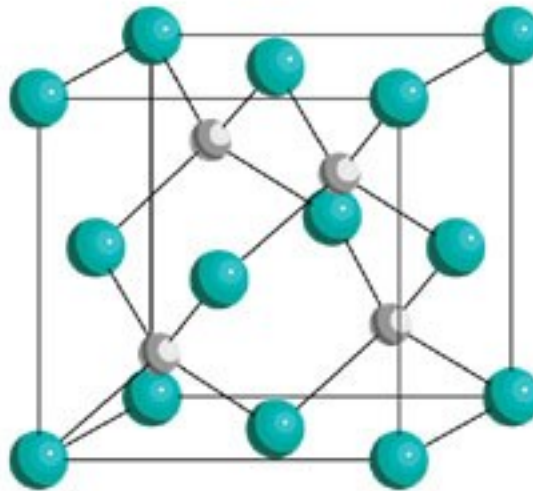
- Each C shares 3 electrons with 3 other C's ... the 4<sup>th</sup> valence electron is free to float over the whole sheet.
- Excellent electrical conductor
- High melting point (like diamond)
- Very soft (makes good pencils!)

# Ionic Crystals

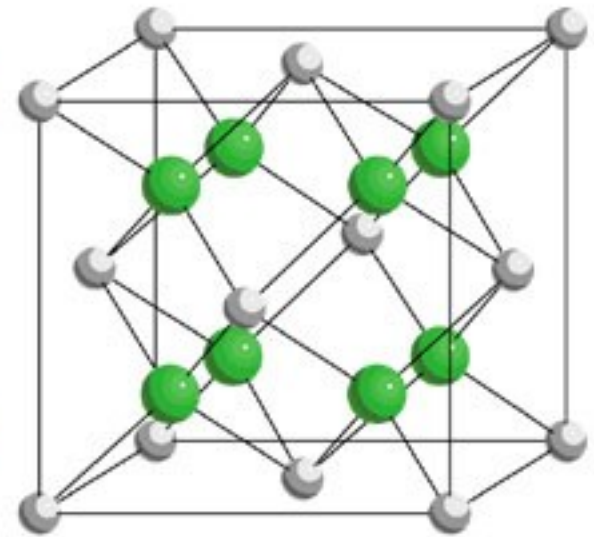
- Lattice points occupied by cations and anions
- Held together by electrostatic attraction
- Hard, brittle, high melting point
- Poor conductors of heat and electricity
- Can have rather complex structures



CsCl



ZnS



CaF<sub>2</sub>



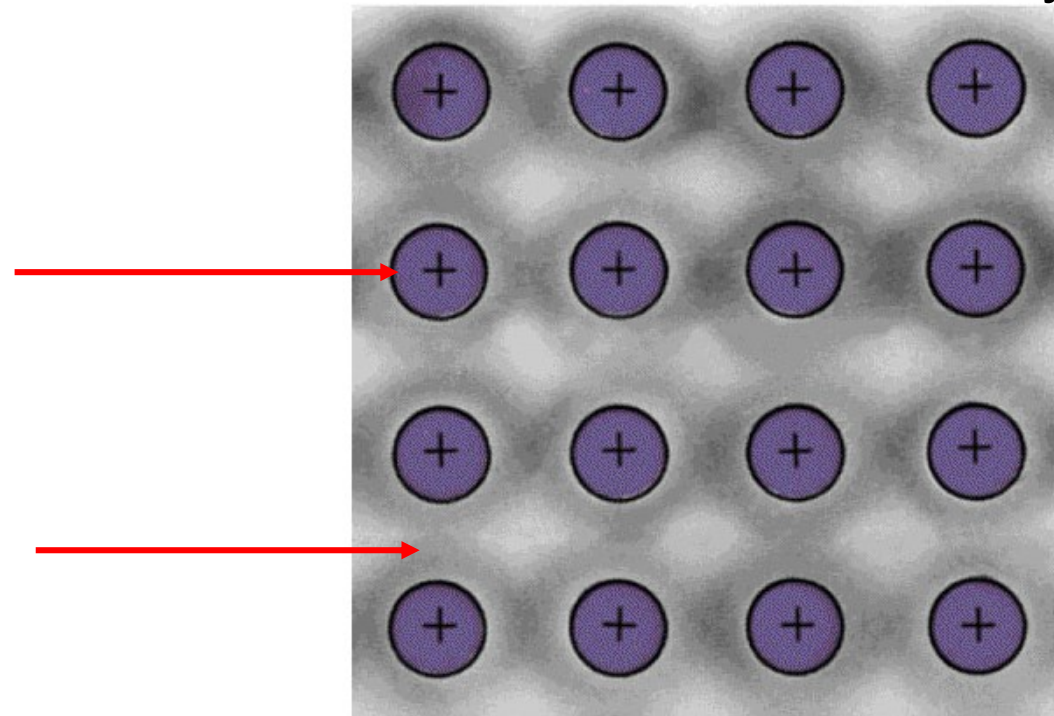
# Metallic Solids

- Lattice points occupied by metal atoms
- Metal ions "swimming" in a "sea" of mobile electrons
- Soft to hard, low to high melting point
- Good conductors of heat and electricity
- Usually adopt a close-packed structure (see below)

Cross Section of a Metallic Crystal

nucleus &  
inner shell  
electrons

"sea" of  
mobile  
electrons



# Metallic Solids

... are formed by the majority of group 1, group 2, group 3, and transition elements in the periodic table.

1 1A	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
Li	Be											Al					
Na	Mg	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	Ga					
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	In	Sn				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Tl	Pb				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg						



Hexagonal close-packed

Face-centered cubic

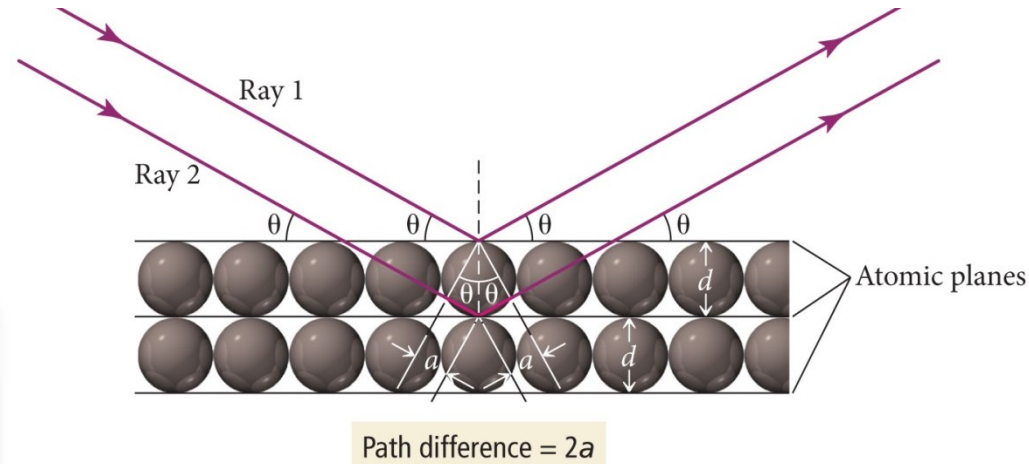
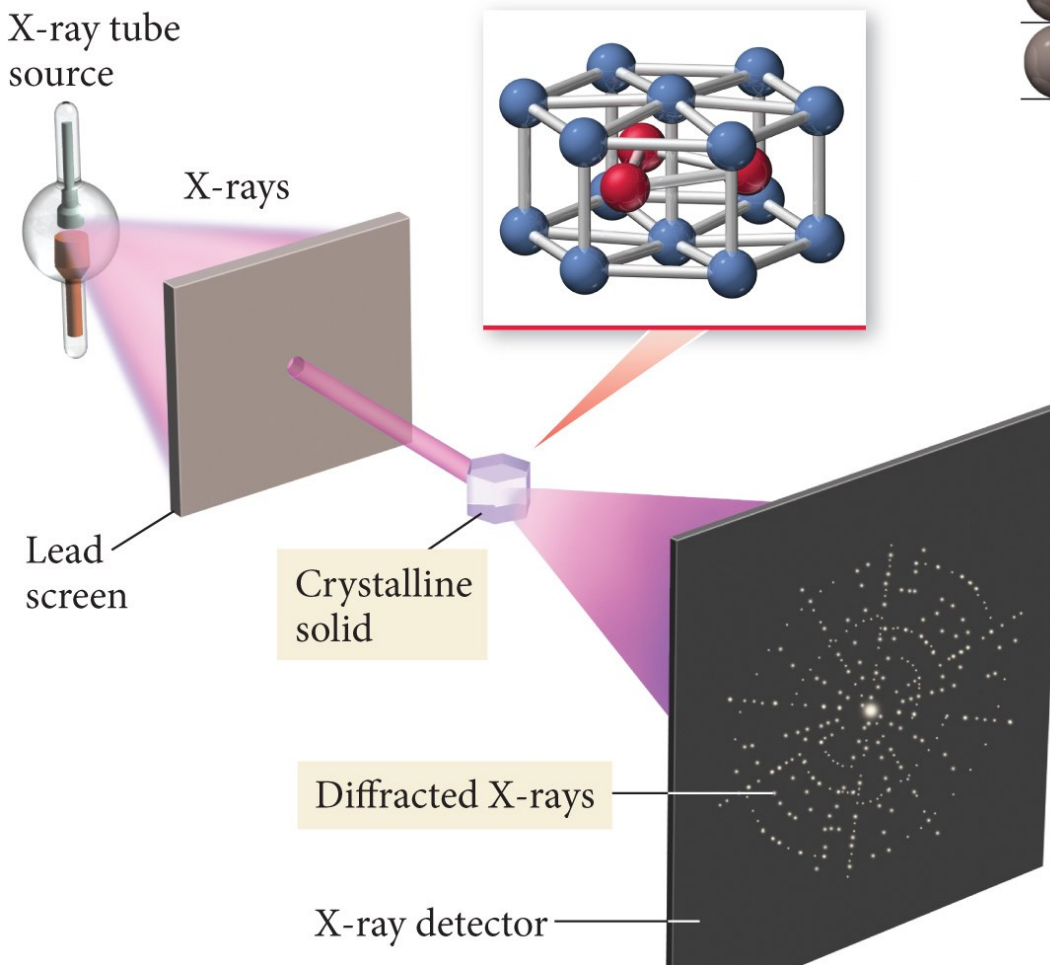


Body-centered

Other structures (see caption)

# X-Ray Crystallography

Ordered (e.g., crystalline) solids produce distinct X-ray diffraction patterns



X-rays interfere constructively at angles ( $\theta$ ) related to atomic plane separation ( $d$ ), X-ray wavelength ( $\lambda$ ), and diffraction order ( $n = 1, 2, \dots$ ) via **Bragg's law**

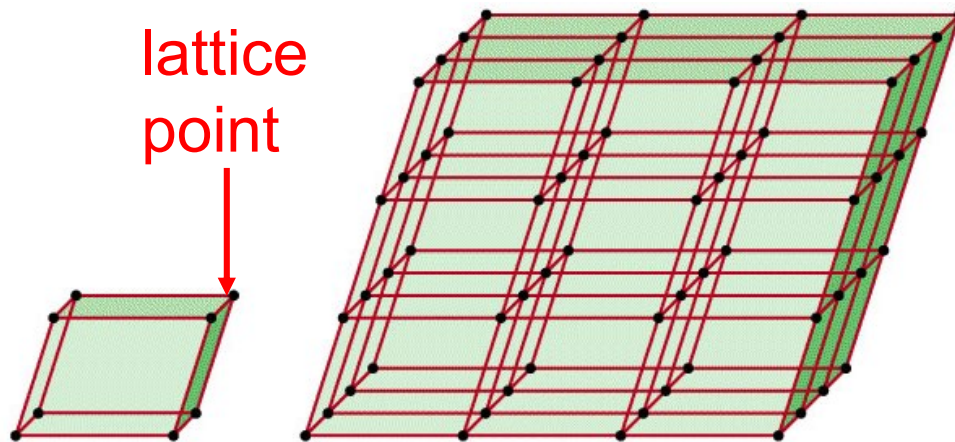
$$n\lambda = 2d \sin \theta$$



# Crystal Lattice and Unit Cell

A **crystalline solid** possesses a long-range order. In a crystalline solid, atoms, molecules or ions occupy specific (predictable) positions.

A **unit cell** is the basic repeating structural unit of a crystalline solid.



At lattice points:

- Atoms
- Molecules
- Ions

[Link to a good website on unit cells](#)

# New Phase of Water: Superionic Ice

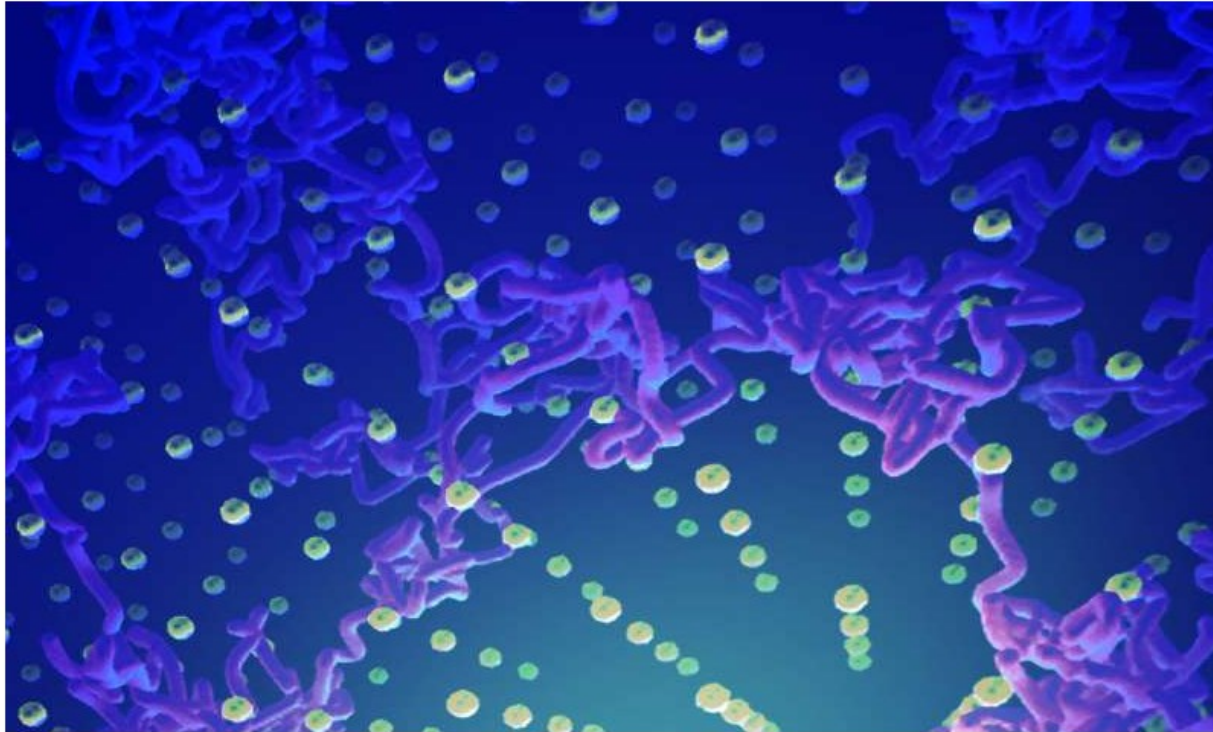
water is heated to several thousand degrees at high pressure

The New York Times

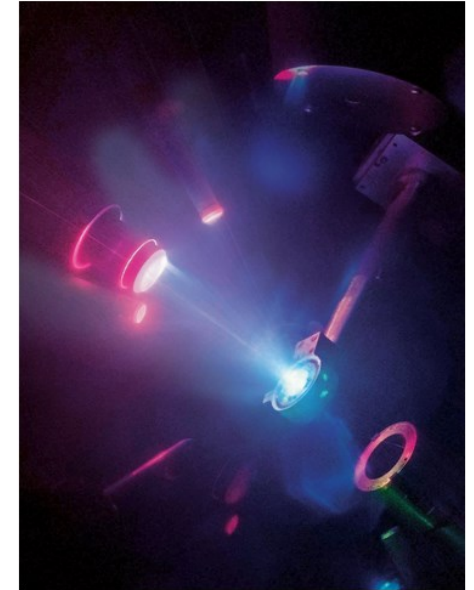
SCIENCE

SCIENCE

*New Form of Water, Both Liquid and Solid, Is 'Really Strange'*



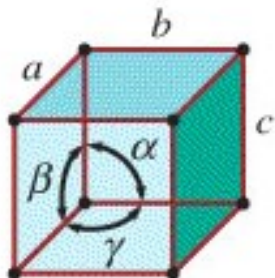
Visualization of molecular dynamics simulations showing the fast diffusion of hydrogen ions (pink trajectories) within the solid lattice of oxygen in superionic ice. Credit: S. Hamel/M. Millot/J.Wickboldt/LLNL/NIF



Researchers used a laser pulse to study superionic water, which is simultaneously solid and liquid.  
M. Millot/E. Kowaluk/J.Wickboldt/LLNL/LLE/NIF

liquid-like hydrogen ions moving within a solid lattice of oxygen

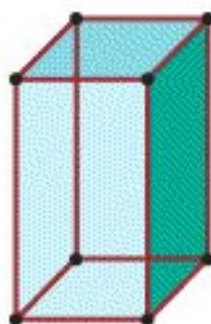
# Common types of Unit Cells



**Simple cubic**

$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$



**Tetragonal**

$$a = b \neq c$$

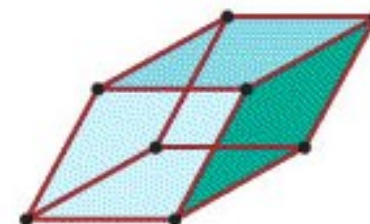
$$\alpha = \beta = \gamma = 90^\circ$$



**Orthorhombic**

$$a \neq b \neq c$$

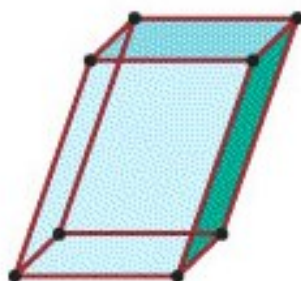
$$\alpha = \beta = \gamma = 90^\circ$$



**Rhombohedral**

$$a = b = c$$

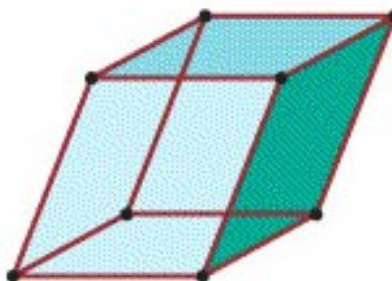
$$\alpha = \beta = \gamma \neq 90^\circ$$



**Monoclinic**

$$a \neq b \neq c$$

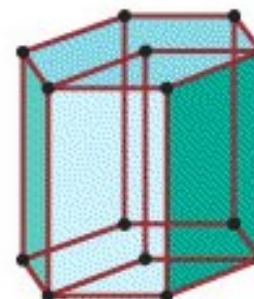
$$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$$



**Triclinic**

$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



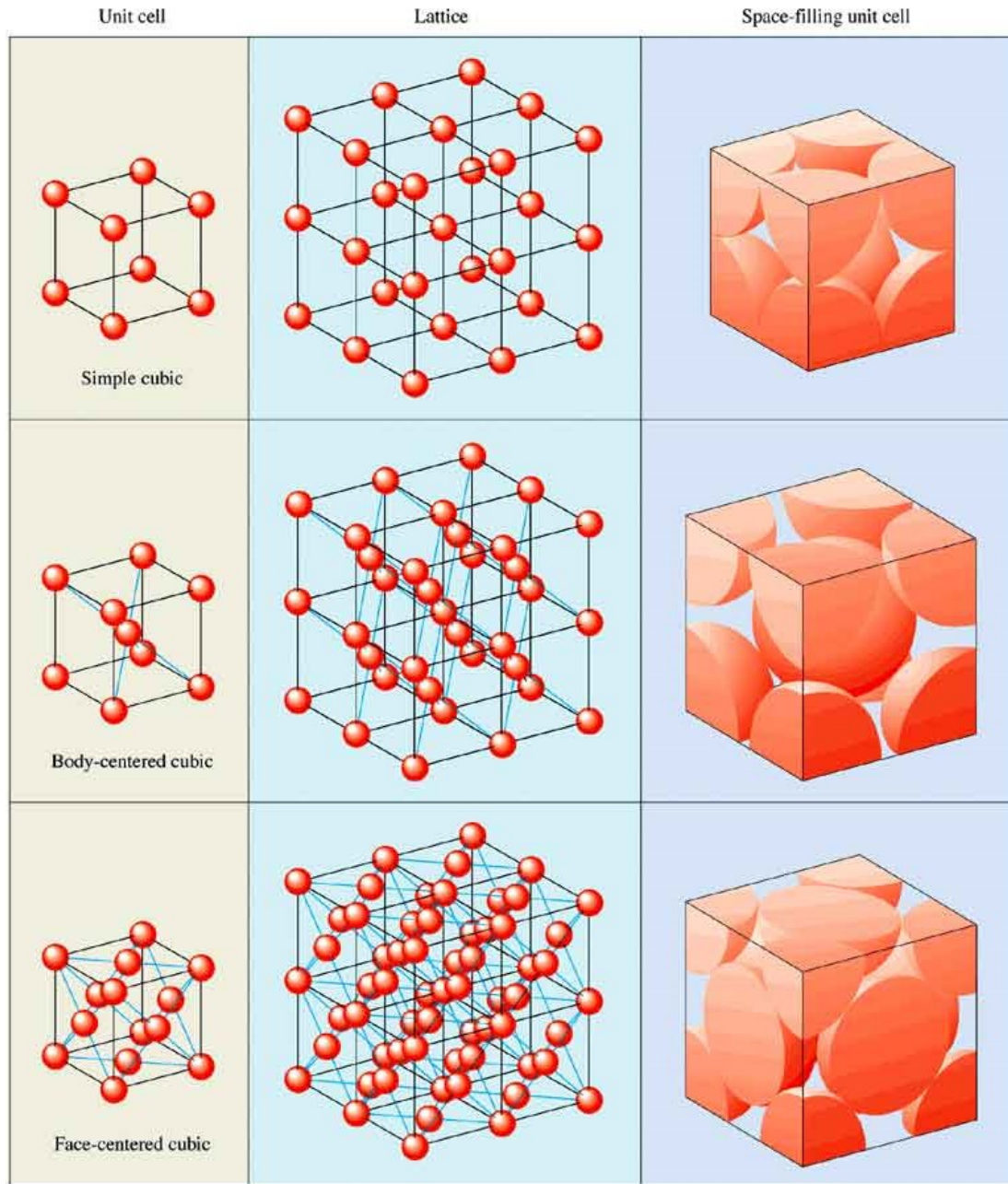
**Hexagonal**

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ, \gamma = 120^\circ$$



# Cubic Cells



Simple Cubic (SC)  
– example **Polonium** metal

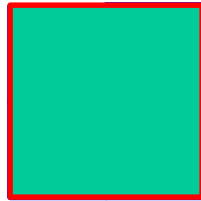
Body-Centered  
Cubic (BCC) –  
example **Uranium**  
metal

Face-Centered  
Cubic (FCC) –  
example **Gold**  
metal

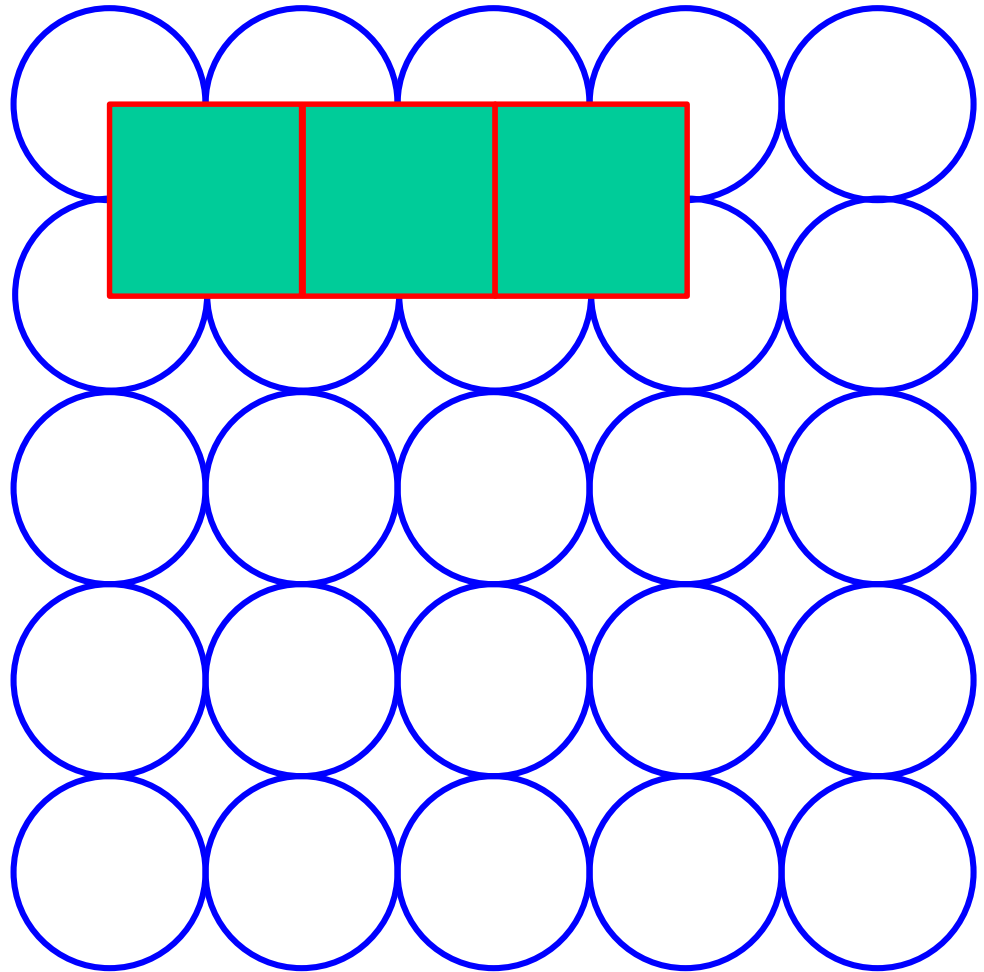
# Two-Dimensional Simple Cubic Cell

Imagine identical atoms arranged in ***one plane*** in a square fashion

- We can draw two-dimensional unit cells as shown. Each unit cell is identical and contains four atoms segments adding to a total of one atom



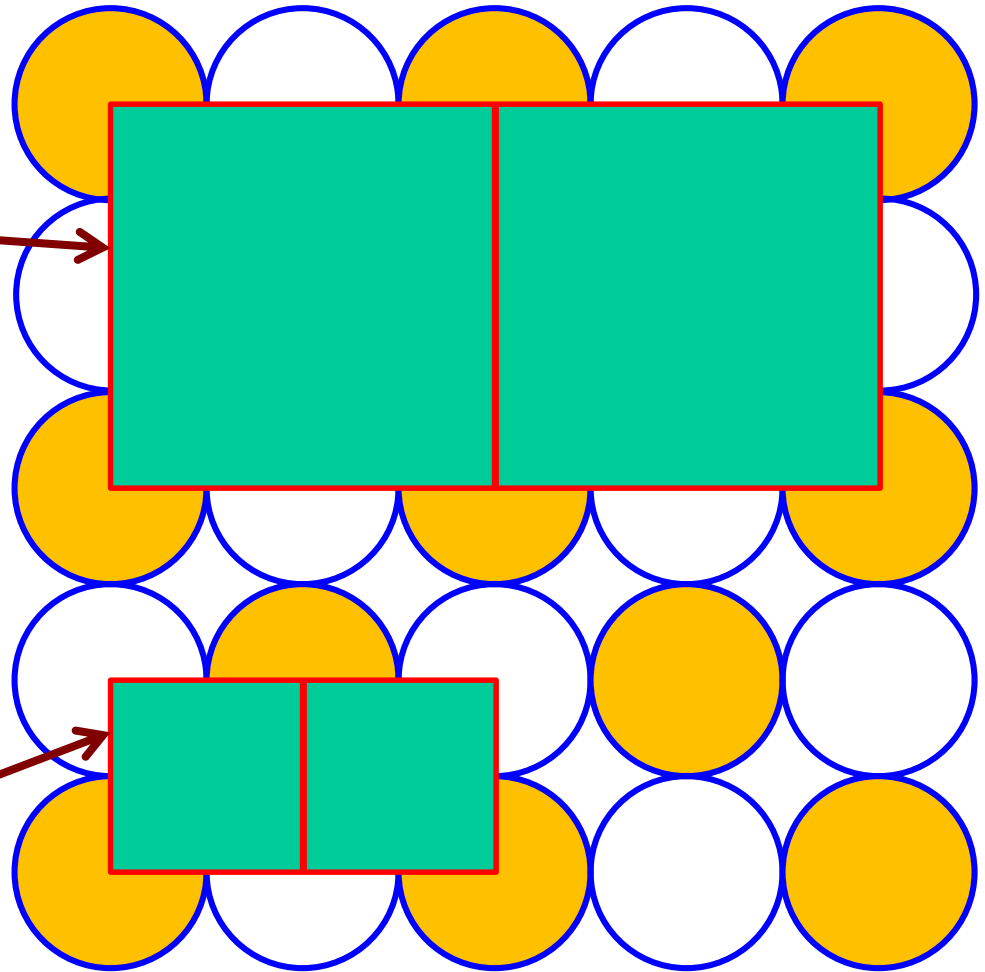
- Each atom touches 4 other atoms (coordination number = 4)



# Two-Dimensional Simple Cubic Cell

What if there are 2 different types of atoms?

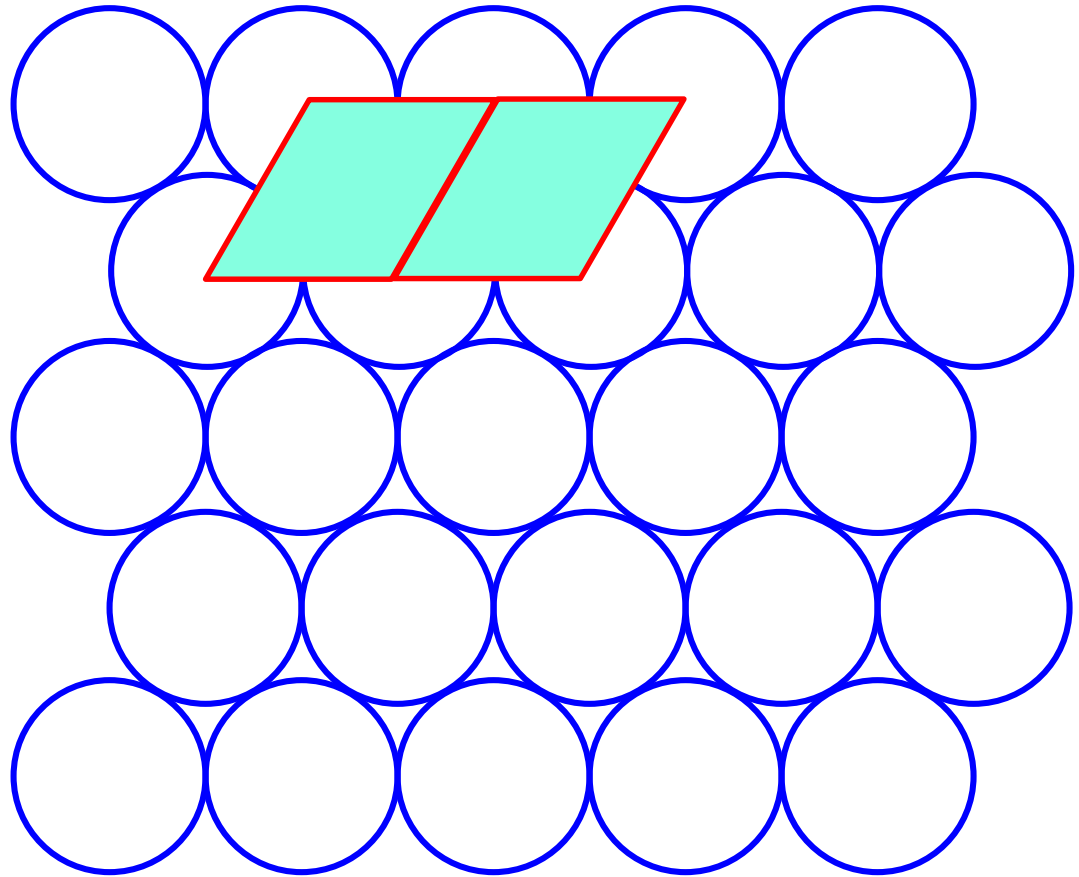
- In order for the unit cells to be identical they now have to be larger
- Inside each unit cell:
  - Two yellow atoms
  - Two white atoms
- The smaller squares cannot serve as unit cells because you cannot cover the entire plane by repeating one unit cell (there will be a color mismatch if you try)



# Two-Dimensional Close-Packed Cell

Atoms are in one plane but now they are close-packed

- Each unit cell is no longer square. It still contains four atoms segments adding to a total of one atom
- Each atom now touches 6 other atoms (coordination number = 6)

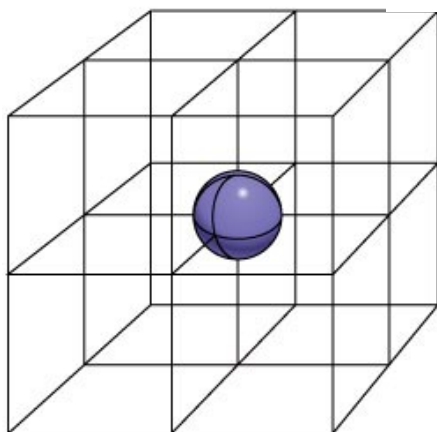




# 3-Dimensional Unit Cells

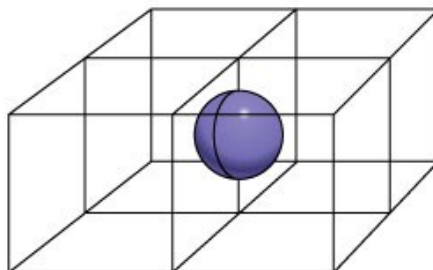
Depending on the location of the particle in the unit cell, it may be shared by multiple unit cells

corner particle



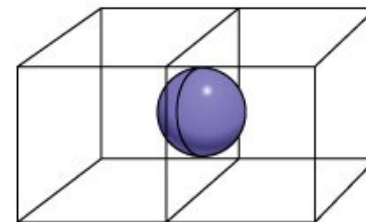
Shared by  
8 unit cells

edge particle



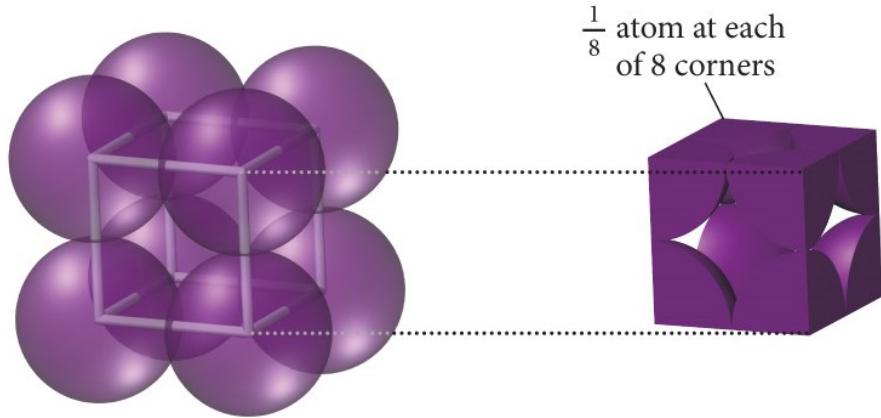
Shared by 4  
units cells

face particle



Shared by 2  
unit cells

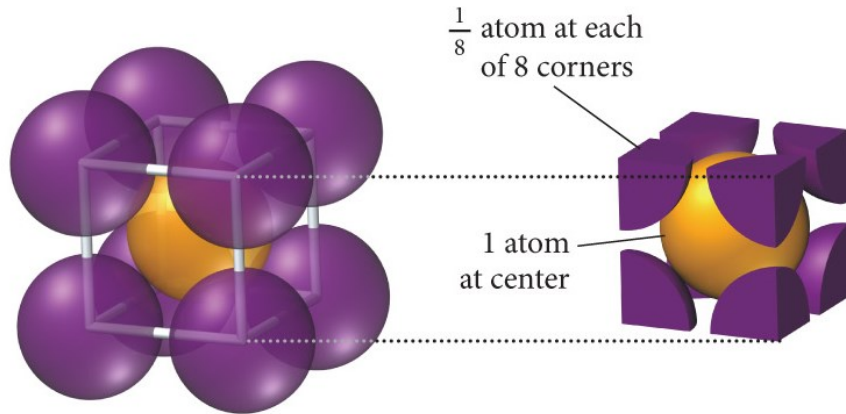
# 3-Dimensional Unit Cells



## ***Simple Cubic***

$$8 \times \frac{1}{8} = 1 \text{ atom/unit cell}$$

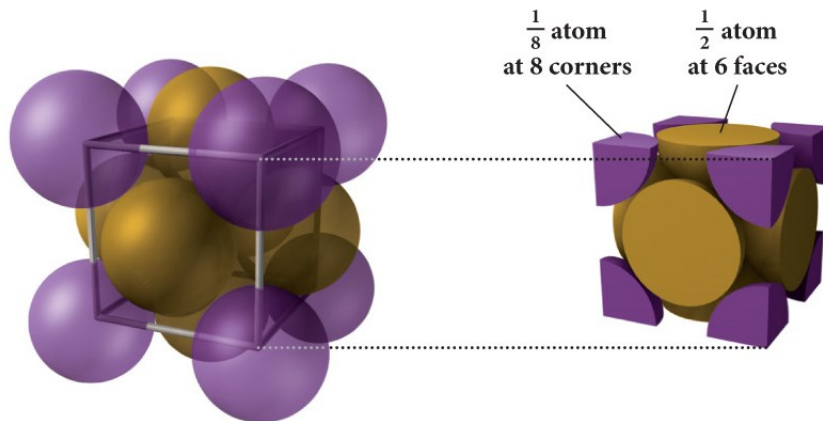
$$\text{Coordination number} = 6$$



## ***Body-Centered Cubic (BCC)***

$$8 \times \frac{1}{8} + 1 = 2 \text{ atoms/unit cell}$$

$$\text{Coordination number} = 8$$



## ***Face-Centered Cubic (FCC)***

$$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4 \text{ atoms/unit cell}$$

$$\text{Coordination number} = 12$$

# Sample Problem

When silver crystallizes, it forms FCC cells. The unit cell edge length is 409 pm. Atomic weight of silver is 107.9 g/mol. Calculate the density of silver.

# Close Packing of Spheres



Metals adopt **close-packed structures**, wasting as little space as possible.

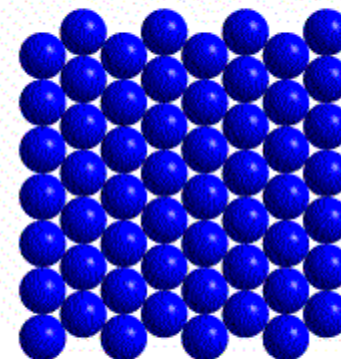
**Video on close packing**

Close packing



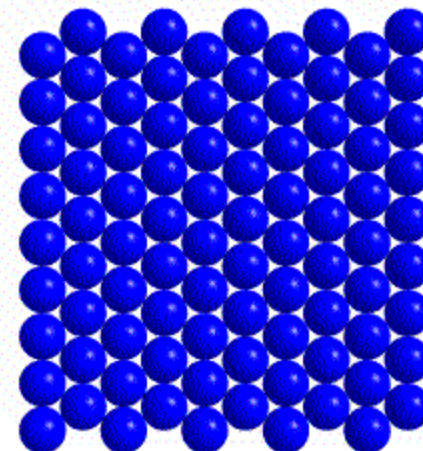
**Hexagonal closed packed (hcp)**; animation from [this website](#)

**ABABAB...**  
pattern



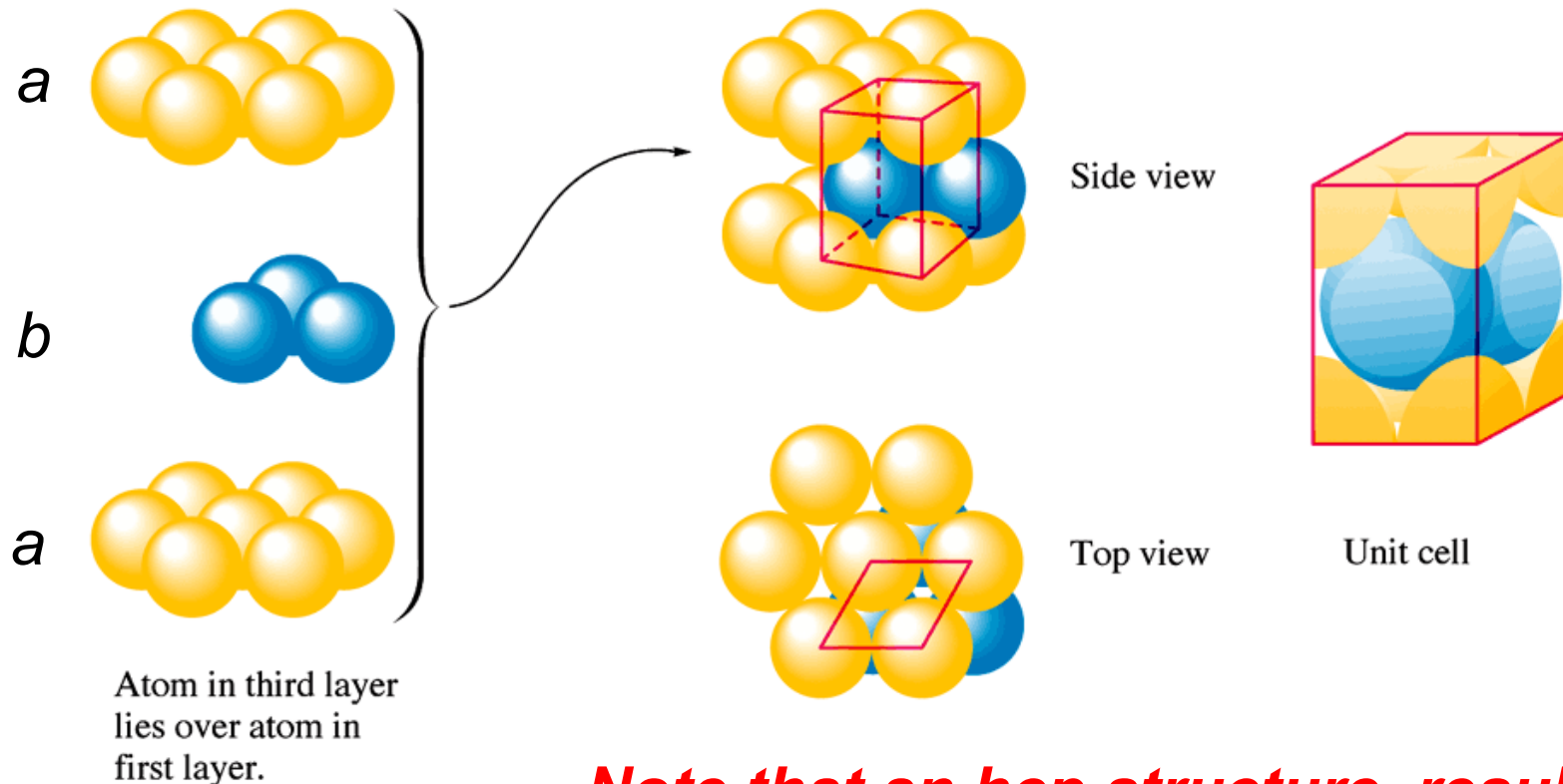
**Cubic closed packed (ccp)**; animation from [this website](#)

**ABCBABC....**  
pattern



# Hexagonal Close Packing (HCP)

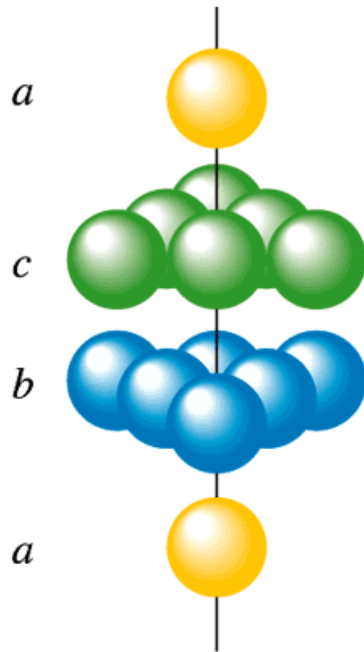
Hexagonal arrangement of atoms offers the closest packing, such as in the **Hexagonal Close Packed** (hcp) structure, forming **ABAB** pattern of atomic planes and hexagonal arrangements of atoms within each plane.



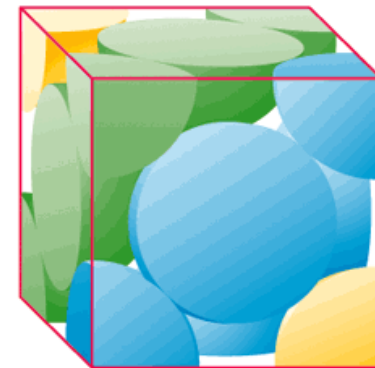
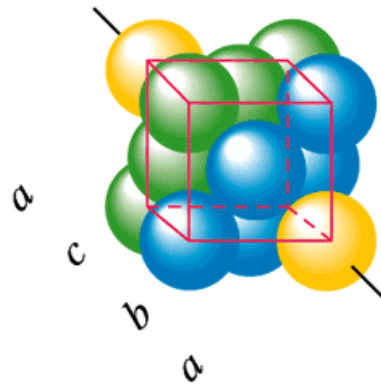
***Note that an hcp structure results in a body-centered unit cell, but that cell is not cubic in shape!***

# Cubic Close Packing (CCP)

**Cubic Close Packed** (ccp) structure is another way to achieve close packing of spheres; it can be thought of as having **ABCABC...** pattern



An atom in every fourth layer lies over an atom in the first layer.



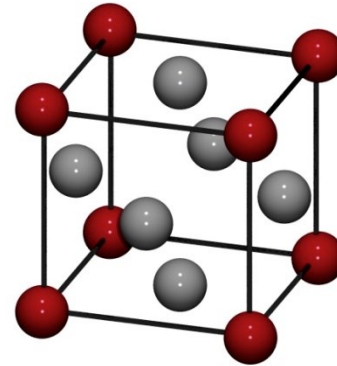
Unit cell

***Note that a ccp structure results in an fcc unit cell (face centered cubic)***

# Sample Problem

The element copper has ccp packing with a face-centered cubic unit cell. The density of Cu is  $8920 \text{ kg/m}^3$ . Calculate the volume ( $\text{m}^3$ ) of the unit cell of Cu. Calculate the effective radius of Cu atom. Atomic weight of Cu is  $63.55 \text{ g/mol}$ .

1. Determine the number of atoms per unit cell



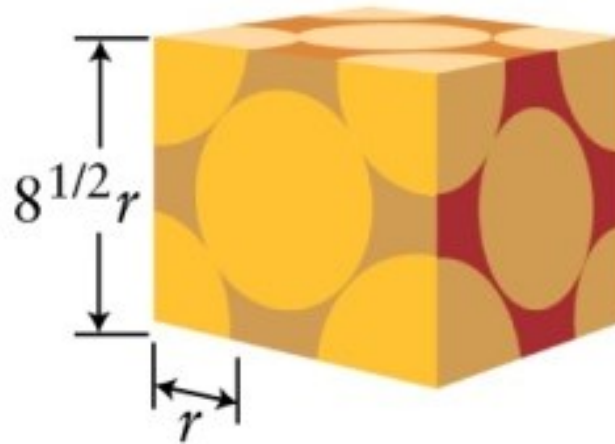
2. Determine the mass of a unit cell

3. Determine the volume by making use of the density of Cu



4. Determine the side length of the unit cell

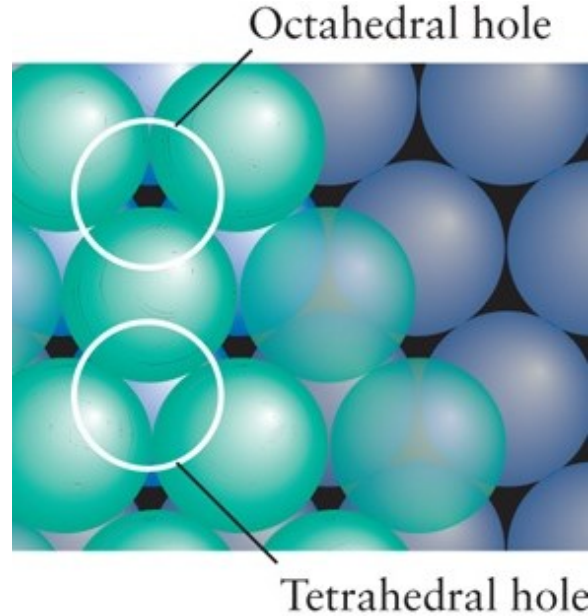
5. Figure out the relationship between the length of the unit cell and the atom radius in a CCP cell. We are going to need some geometry here (hint: use the Pythagorean theorem)



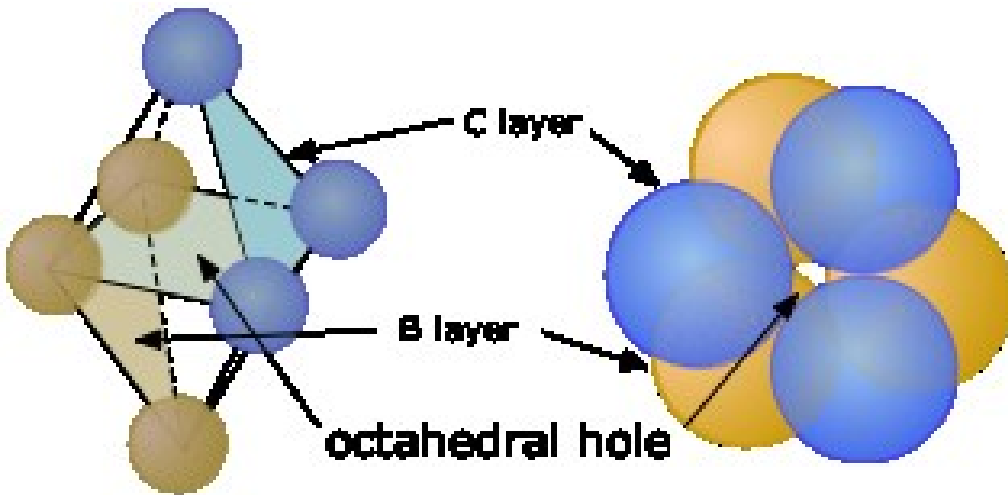
6. Calculate the radius

# Holes in Close-Packed Structures

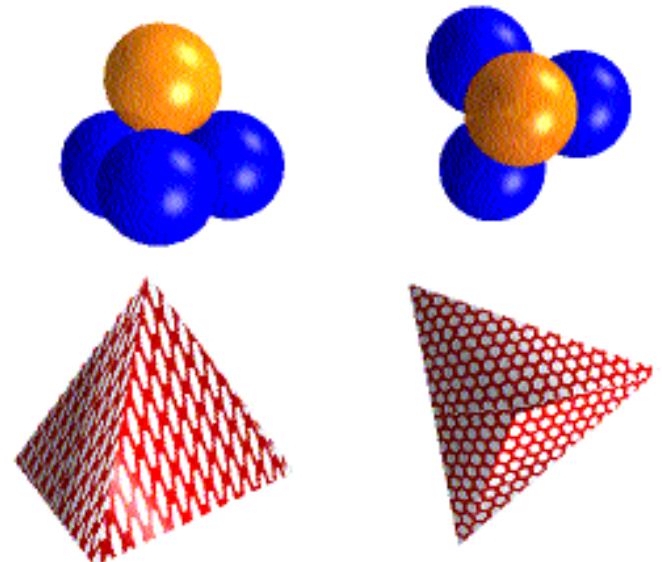
If a dip in a layer coincides with a dip in the **next layer**, we obtain an octahedral hole.



If a dip **between three atoms** is directly covered by another atom, we obtain a smaller tetrahedral hole.



octahedron



tetrahedron

# Alloys

Holes in a close-packed structure can be filled with smaller atoms to form **alloys**.

There is **one octahedral hole** and **two tetrahedral holes** per each atom in a close-packed lattice  $\rightarrow$  AB, AB<sub>2</sub>, A<sub>2</sub>B alloy stoichiometries are possible.

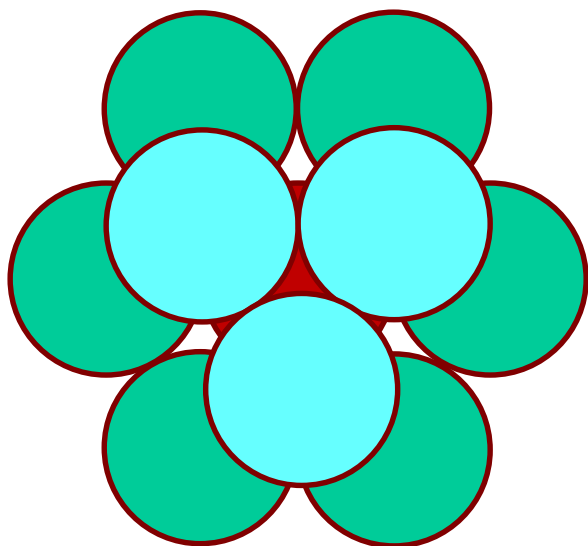
## Sample Problem

Find the formula of a compound in which element A occupies all the hcp lattice points and element B occupies half of the octahedral holes?

Answer: since there are as many octahedral holes as lattice points, the stoichiometry must be AB<sub>0.5</sub>, or equivalently A<sub>2</sub>B

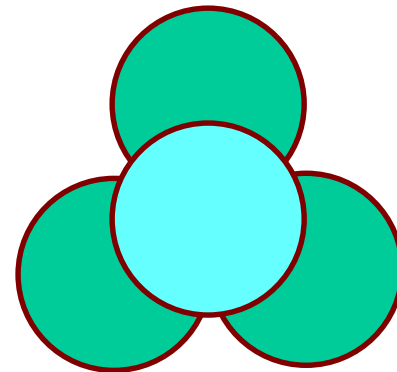
# Coordination Numbers

In close-packed structures built from the same atoms, each atom has a **coordination number** (the number atoms in direct contact with it) of **CN = 12**.

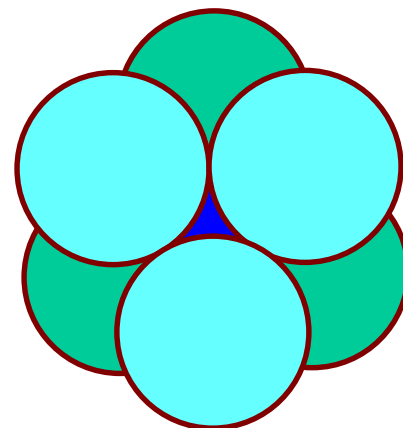


6 neighbors in this layer  
3 neighbors in the layer above  
3 neighbors in the layer below

Tetrahedral hole atom has **CN = 4**



Octahedral hole atom has **CN = 6** (not 8!)

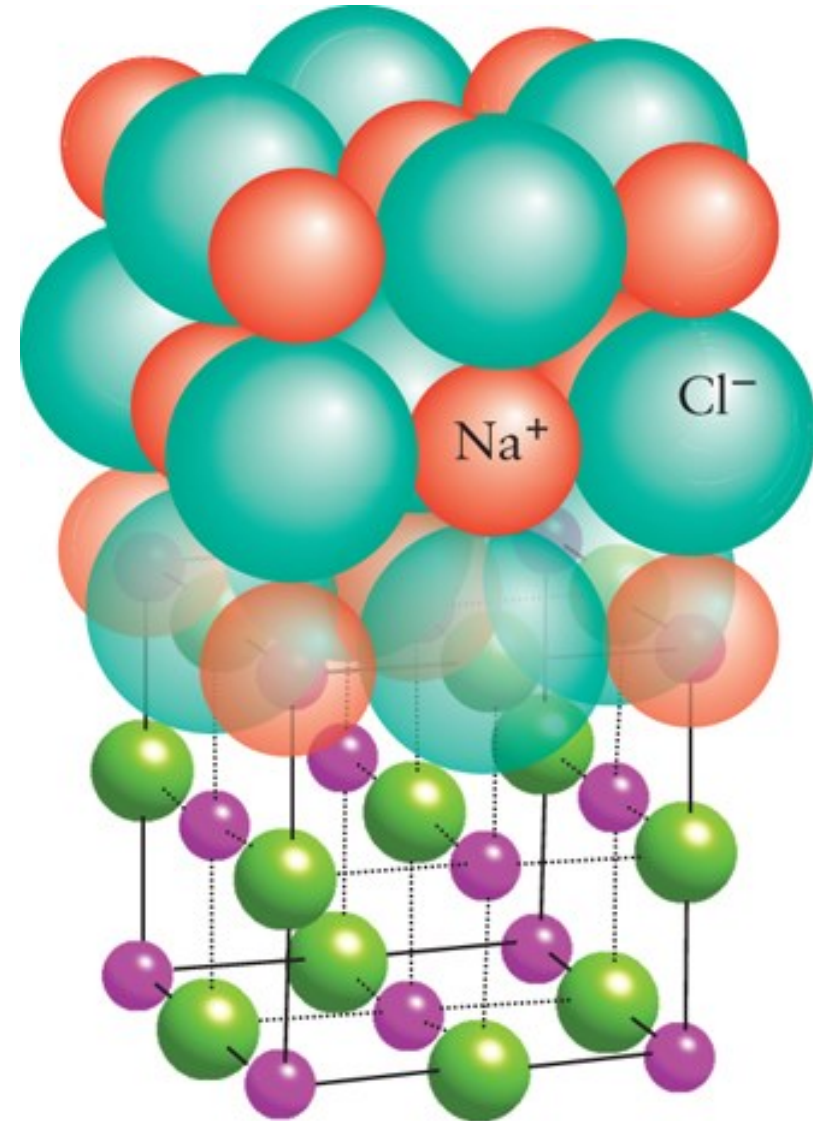


# Ionic Crystals

Rock-salt, a common name for the mineral NaCl, has a **Cl<sup>-</sup> ccp arrangement** of atoms.

**Na<sup>+</sup>** is small enough to fit into the **octahedral holes** resulting in a 1:1 stoichiometry, NaCl.

Both the cation and anion are each bound to 6 other ions. The overall coordination scheme is therefore *(6,6)-coordination* (each cation is in a direct contact with 6 anions).





# Life Under High Pressures

Under pressure, common salt can take on some exotic structures such as  $\text{NaCl}_3$  shown. Na (purple); Cl (green)

At pressures up to 250GPa (2.5 million atmospheres)  $\text{Na}_3\text{Cl}$ ,  $\text{Na}_2\text{Cl}$ ,  $\text{Na}_3\text{Cl}_2$ ,  $\text{NaCl}_3$  and  $\text{NaCl}_7$  are theoretically stable!

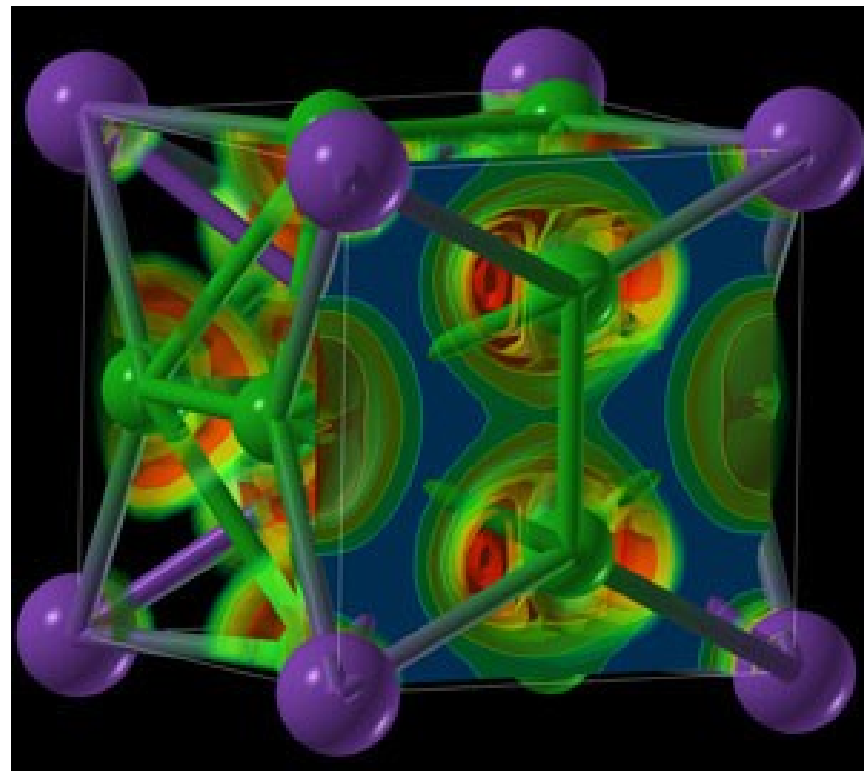


Image from an [RCS Chemistry World article](#)

# Ionic Crystals

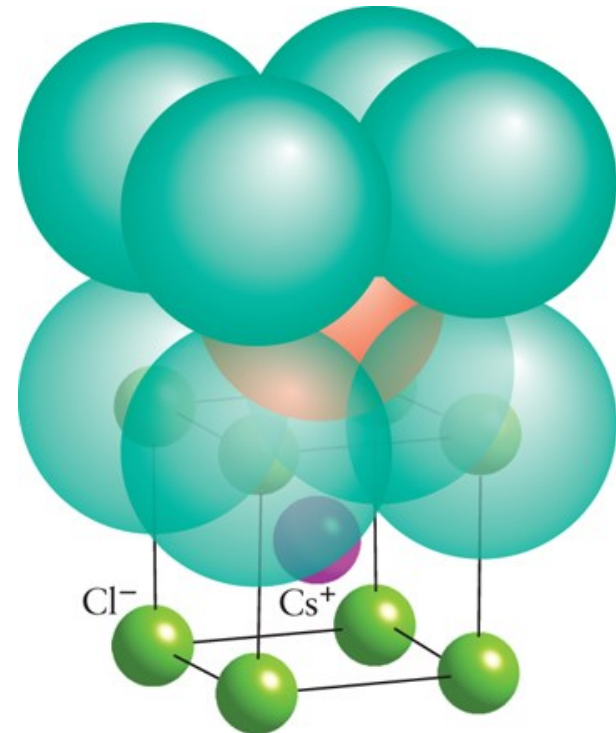
$$\text{Radius Ratio} = \rho = \frac{R_{\text{smaller ion}}}{R_{\text{larger ion}}}$$

For a typical fcc structure like rock-salt the range for the values of  $\rho$  is 0.4-0.7.

When  $\rho > 0.7$  the cation and anion are about the same size, so more anions can fit around each cation.

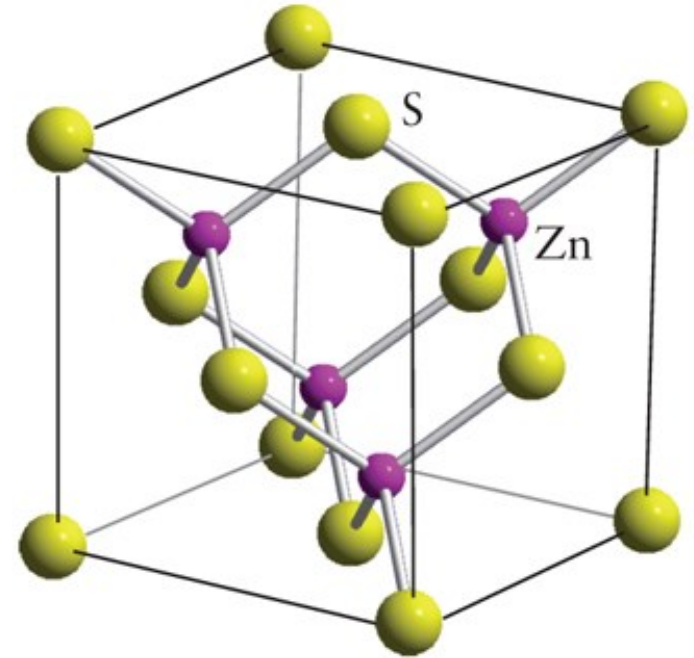
$\rho$  for CsCl is 0.92, resulting in a primitive cubic structure for  $\text{Cl}^-$  with body-centered  $\text{Cs}^+$  insertions (= cubic holes).

The structure corresponds to a (8,8)-*coordination* (each cation is in a direct contact with 8 anions).



# Ionic Crystals

When  $\rho < 0.4$  the smaller tetrahedral holes open up for the smaller ion (typically cation). Consider the examples of ZnS:



This structure is cubic close-packed lattice of the big S<sup>2-</sup> anions, with the small Zn<sup>2+</sup> cations occupying half the tetrahedral holes, hcp.

Each Zn<sup>2+</sup> ion is surrounded by four S<sup>2-</sup> ions, and each S<sup>2-</sup> ion is surrounded by four Zn<sup>2+</sup> ions. The zinc-blended structure has (4,4) coordination with a ccp structure.