

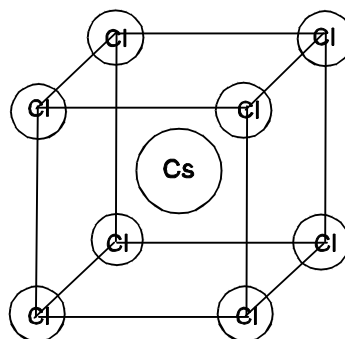
# X. Solid and Liquid States

## A) Types of Solids

### 1) Crystalline Solid

Crystals result from an orderly arrangement of atoms, ions, or molecules. Crystals have planar surfaces that intersect at specific angles.

**Example:** A crystal of CsCl is cubic. The *unit cell* (smallest repeating unit in the crystal) of CsCl is illustrated below.

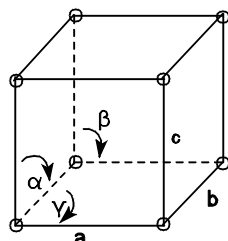


**Unit Cell: Cubic**

The physical properties of crystals are anisotropic (not the same in all directions). Crystalline solids have sharp melting points. For example the melting point of CsCl is  $1290^{\circ}\text{C}$ .

### Several Types of Unit Cells

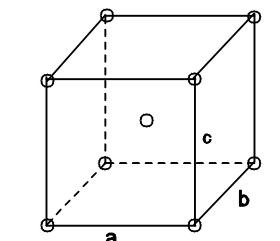
The lengths of the edges of the unit cell are **a**, **b**, and **c**. The angle between the **b** and **c** edges is called  $\alpha$ , the angle between the **a** and **c** edges is called  $\beta$ , and the angle between the **a** and **b** edges is called  $\gamma$ .



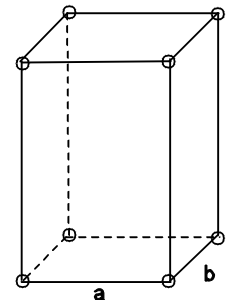
**Cubic**

$$a = b = c$$

$$\text{Angle } \alpha = \beta = \gamma = 90^{\circ}$$



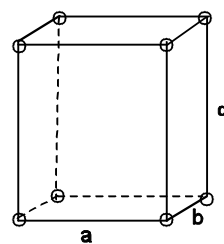
**Body - Centered Cubic**



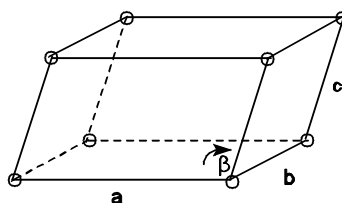
**Tetragonal**

$$a = b \neq c$$

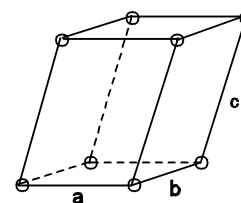
$$\text{Angle } \alpha = \beta = \gamma = 90^{\circ}$$



**Orthorhombic**  
 $a \neq b \neq c$   
 Angle  $\alpha = \beta = \gamma = 90^\circ$



**Monoclinic**  
 $a \neq b \neq c$   
 Angle  $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$



**Triclinic**  
 $a \neq b \neq c$   
 Angle  $\alpha \neq \beta \neq \gamma \neq 90^\circ$

## 2) Amorphous Solids

Amorphous solids result from the unorderly arrangement of atoms, ions, or molecules. Amorphous solids do not have characteristic shapes.

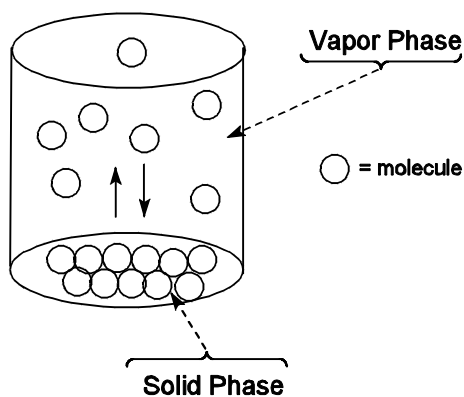
**Example:** Window glass

The physical properties of amorphous solids are isotropic (same in all directions). Amorphous solids melt over a broad temperature range. For example Pyrex glass softens at  $800^\circ\text{C}$  but does not completely liquefy until  $1250^\circ\text{C}$ .

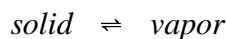
## B) Phase Change

### 1) Sublimation: Solid $\rightarrow$ Vapor

Molecules with  $KE_T$  (kinetic energy of translation) greater than the energy of the van der Waals forces in the solid will escape from the surface of the solid and enter the vapor phase. When molecules that are in the vapor phase and have a  $KE_T$  less than the energy of the van der Waals forces in the solid collide with the surface of the solid, the molecules will stick to the surface.



When the number of molecules leaving the solid and entering the vapor phase equals the number of molecules leaving the vapor and entering the solid phase, then the system is in *equilibrium*.



and

$$G_{\text{vapor}} = G_{\text{solid}}$$

and

$$\Delta G_{\text{sub}} = G_{\text{vapor}} - G_{\text{solid}} = 0$$

The pressure exerted by the vapor that is in equilibrium with the solid is called the *vapor pressure* of the solid. The magnitude of the vapor pressure depends on the magnitude of the van der Waals forces in the solid and the temperature. Over a narrow temperature range the vapor pressure is related to temperature by the equation

$$\ln(P_{\text{vapor}})_2 = \left[ \frac{\Delta H_{\text{sub}}}{R} \right] \left[ \frac{T_2 - T_1}{T_2 T_1} \right] + \ln(P_{\text{vapor}})_1$$

where  $\Delta H_{\text{sub}}$ , the enthalpy of *sublimation*, is the amount of heat required to convert one mole of a solid into a vapor;  $(P_{\text{vapor}})_2$  is the vapor pressure of the solid at temperature  $T_2$ ; and  $(P_{\text{vapor}})_1$  is the vapor pressure of the solid at temperature  $T_1$ .

At equilibrium

$$\Delta G_{\text{sub}} = \Delta H_{\text{sub}} - T \Delta S_{\text{sub}} = 0$$

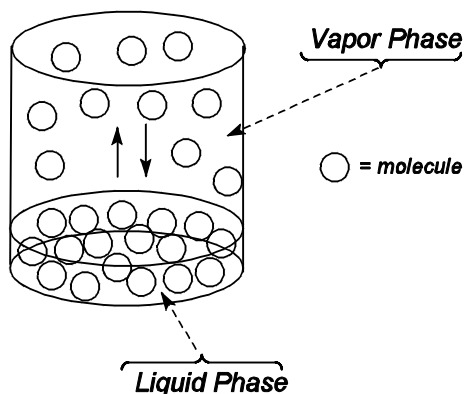
$$\Delta H_{\text{sub}} = T \Delta S_{\text{sub}}$$

Dividing by T

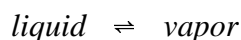
$$\Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T}$$

## 2) Evaporation: Liquid → Vapor

Molecules with  $KE_T$  greater than the energy of the van der Waals forces in the liquid will escape from the surface of the liquid and enter the vapor phase. When molecules that are in the vapor phase and have a  $KE_T$  less than the energy of the van der Waals forces in the liquid collide with the surface of the liquid, the molecules will stick to the surface.



When the number of molecules leaving the liquid and entering the vapor phase equals the number of molecules leaving the vapor and entering the liquid phase, then the system is in *equilibrium*.



and

$$G_{\text{vapor}} = G_{\text{liquid}}$$

and

$$\Delta G_{\text{vap}} = G_{\text{vapor}} - G_{\text{liquid}} = 0$$

The pressure exerted by the vapor that is in equilibrium with the liquid is called the *vapor pressure* of the liquid. The magnitude of the vapor pressure depends on the magnitude of the van der Waals forces in the liquid and the temperature. Over a narrow temperature range the vapor pressure is related to temperature by the equation

$$\ln(P_{\text{vapor}})_2 = \left[ \frac{\Delta H_{\text{vap}}}{R} \right] \left[ \frac{T_2 - T_1}{T_2 T_1} \right] + \ln(P_{\text{vapor}})_1$$

where  $\Delta H_{\text{vap}}$ , the enthalpy of *vaporization*, is the amount of heat required to convert one mole of a liquid into a vapor.

At equilibrium

$$\Delta G_{\text{vap}} = \Delta H_{\text{vap}} - T \Delta S_{\text{vap}} = 0$$

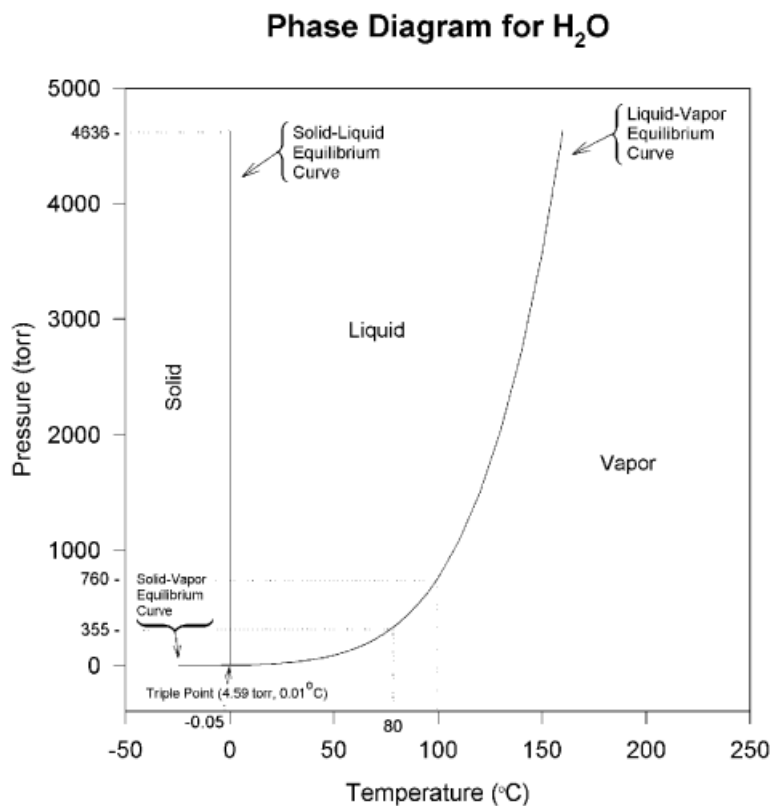
$$\Delta H_{\text{vap}} = T \Delta S_{\text{vap}}$$

Dividing by T

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$$

### 3) Phase Diagram

A plot of the temperatures and pressures at which two or more phases are in equilibrium.



#### Salient Features of a Phase Diagram

- Points on the curves indicate the temperatures and pressures at which two phases are in equilibrium. The *triple point* is the temperature and pressure at which all three phases are in equilibrium.
- Vapor pressures at specific temperatures can be read from the phase diagram.

**Example:** The vapor pressure of water at 80 °C is 355 torr (see above phase diagram for H<sub>2</sub>O).

- Boiling points at specific external pressures can be read from the phase diagram. The *boiling point* is the temperature at which the vapor pressure of a liquid equals the external pressure.

**Example:** The boiling point of water at an external atmospheric pressure of 1.00 atm is 100°C. If the external pressure is reduced to 355 torr, then water will boil at 80°C ( see above phase diagram for H<sub>2</sub>O).

- Melting points at specific external pressures can be read from the phase diagram. The *melting point* is the temperature at which liquid and solid coexist, i.e. the temperature at which the vapor pressure of the solid equals the vapor pressure of the liquid.

**Example:** The melting point of water at an external atmospheric pressure of 1.00 atm is 0°C. If the external pressure is increased to 4636 torr, then water will melt at - 0.05°C (see above phase diagram for H<sub>2</sub>O).

- Points off the curves in the phase diagram indicate the temperatures and pressures at which only one phase exists.

## C) Types of Crystalline Solids

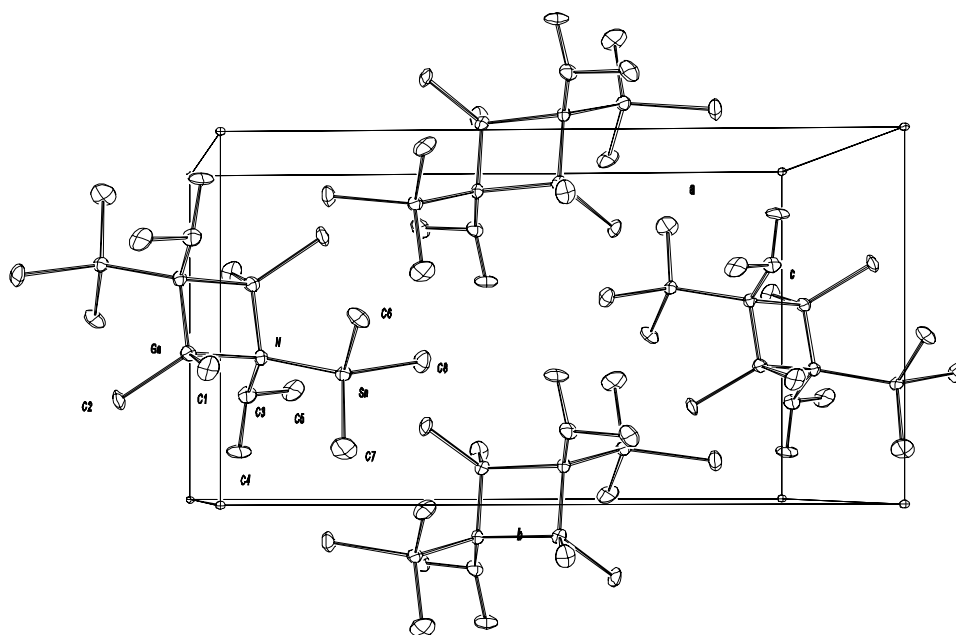
### 1) Molecular Crystals.

**Component unit:** molecules

**Cohesive forces of attraction:** van der Waals forces

**Properties:** soft, low melting points, volatile, nonconductors

**Example:** [(H<sub>3</sub>C)<sub>2</sub>GaN(CH(CH<sub>3</sub>)<sub>2</sub>)Sn(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, mp = 151°C



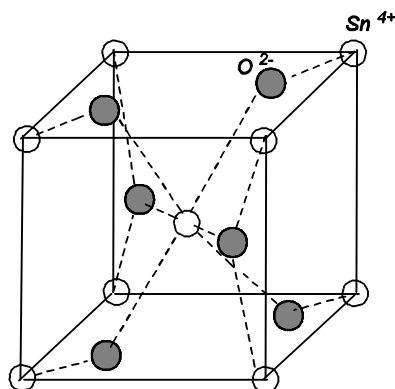
## 2) Ionic Crystals

**Component unit:** ions

**Cohesive forces of attraction:** electrostatic attractions between the ions (ionic bond)

**Properties:** hard and brittle, high melting points, nonvolatile, nonconductors in the solid state

**Example:**  $\text{SnO}_2$ , mp =  $1630^\circ\text{C}$



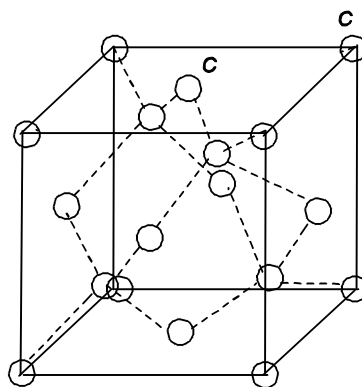
## 3) Covalent Crystals

**Component unit:** atoms

**Cohesive forces of attraction:** covalent bonds

**Properties:** very hard, very high melting points, nonvolatile, insulator

**Example:** Diamond, mp =  $3500^\circ\text{C}$



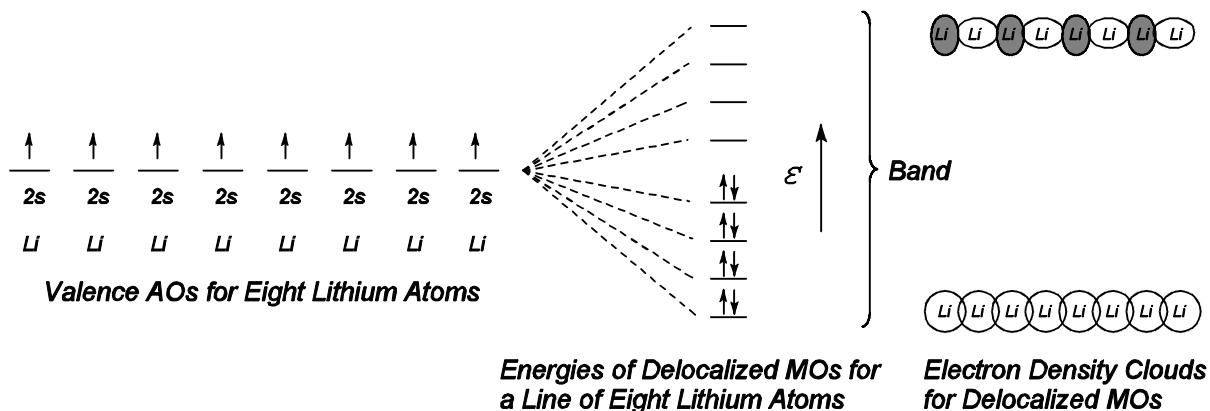
## 4) Metallic Crystals

**Component unit:** atoms

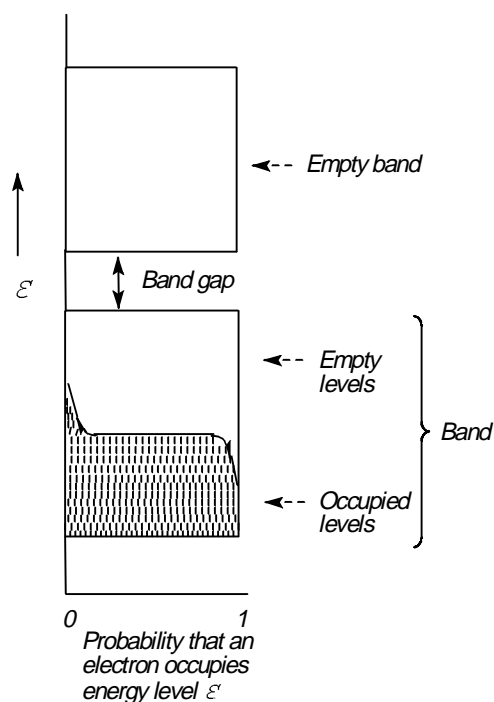
**Cohesive forces of attraction:** electrostatic attractions

**Properties:** malleable and ductile, high melting points, nonvolatile, good conductors

**Band Theory: An Explanation of Bonding in Metallic Crystals**



A *band* is a collection of closely associated molecular orbital energies. As the number of energy levels in the band increases, the difference in energy between the levels decreases.



Rectangles Represent Bands of  $6.022 \cdot 10^{23}$  Energy Levels

At room temperature a number of the energy levels in the partially filled band are half-filled (see diagram above). Electrons in the half-filled levels are mobile and free to move anywhere in the solid. When an electrostatic potential is applied to the solid, there will be a net flow of electrons toward the positive charge. A partially filled band is called a *conduction band*.