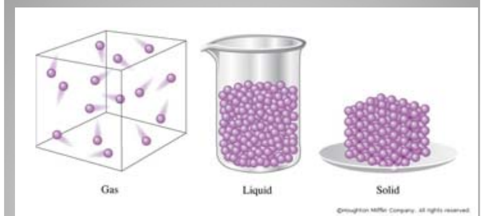
States of Matter

Liquids and Solids

Comparison of states of matter

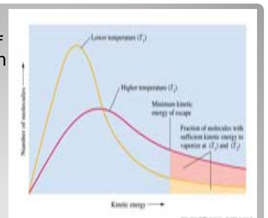


Phase Transitions

- Melting/Freezing
  - $H_2O_{(s)} \rightarrow H_2O_{(l)}$ / $H_2O_{(l)} \rightarrow H_2O_{(s)}$
- Vaporization/Condensation
  - $H_2O_{(l)} \rightarrow H_2O_{(g)}$ / $H_2O_{(g)} \rightarrow H_2O_{(l)}$
- Sublimation/Deposition
  - $H_2O_{(s)} \rightarrow H_2O_{(g)}$ / $H_2O_{(g)} \rightarrow H_2O_{(s)}$

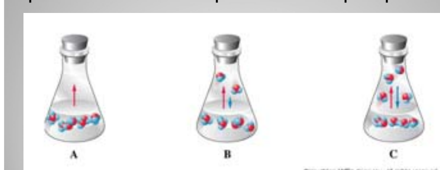
Vapor Pressure

- ***vapor pressure*** – is the partial pressure of the vapor of a liquid in equilibrium with the liquid at a given temperature
- At a given temperature a certain fraction of the molecules in a liquid have enough energy to go into the vapor phase.



Vapor pressure

- When the rate of condensation and evaporation are equal the system is in a dynamic equilibrium and the partial pressure of the vapor is the vapor pressure



Boiling point

- related to vapor pressure
- ***boiling point*** – the temperature at which the v.p. is equal to the external pressure
- ***normal boiling point*** – the temperature ate which the v.p. is equal to 1 atm.

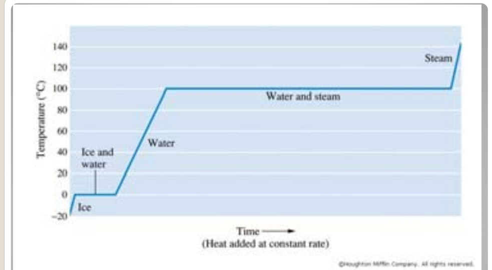
Freezing point

- Temperature at which the pure liquid changes to a solid.
- same as the melting point (solid changes into liquid).

Heat of phase transition

- To change from one state to another
  - requires the addition or removal of energy (heat)
  - the change occurs at one temperature (melting/boiling point)
- Melting/Freezing – ΔH_{fus} – heat of fusion
- Boiling/Condensing – ΔH_{vap} – heat of vaporization

Heat of phase transition



Heat and Phase transition review

- heat lost = - heat gained
- specific heat
- heat of phase transition
- sum of heats

Vapor pressure – Temperature dependence

- The vapor pressure changes with temperature
- related through the ΔH_{vap}

$$\ln p = -\frac{\Delta H_{vap}}{RT} + B$$

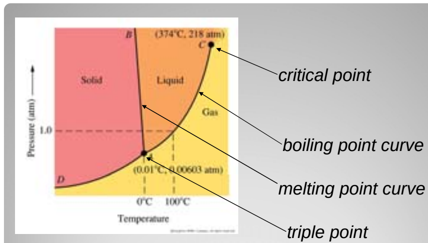
- B is a constant that depends on the substance

The Clausius-Clapeyron Equation

- Usually will use the two-point form

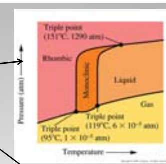
$$\ln \frac{p_2}{p_1} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

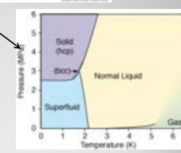
- allows us to calculate the v.p. at one temperature if we know it at another
- Also need the heat of vaporization
- R is 8.314 J mol^{-1} K^{-1}



Phase diagrams

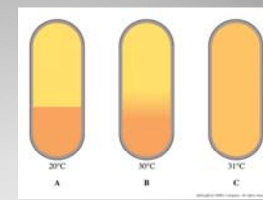
- Can have more than one solid (S) or liquid phase (He)
- Can have more than one triple point





Phase diagrams

- Critical temperature – the temperature above which the liquid phase no longer exists
- Critical pressure – the vapor pressure at the critical temperature



Phase diagrams

- Surface tension – the resistance of a liquid to an increase in surface area.
- Viscosity – resistance to flow in a fluid

Liquid State Properties

- All molecules and atoms have attractive forces between them. Otherwise we wouldn't be able to liquefy or solidify anything.
- The attractive forces present depend on the kind of molecule and the molecule's shape.
- Called ***van der Waals*** forces

Attractive forces

- London Forces
  - Exist between all molecules and atoms
  - Increase with increasing mass

Kinds of attractive forces

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- London Forces
  - Exist between all molecules and atoms
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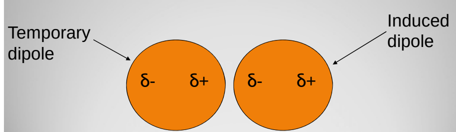
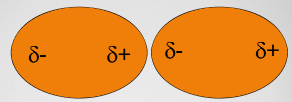
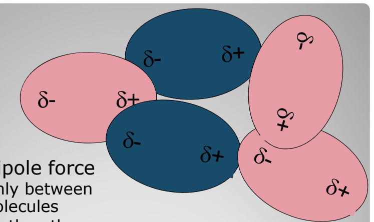


When the molecules get close, they distort each other's electron clouds, causing a temporary dipole.



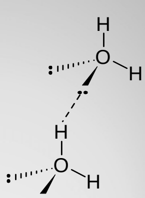
Kinds of attractive forces continued

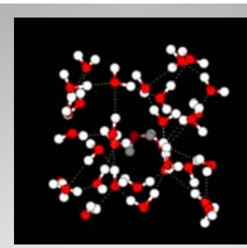


- Dipole-dipole force
  - Exists only between polar molecules
  - Stronger than the London forces

Kinds of attractive forces continued

- Hydrogen bonding
  - Requires a hydrogen attached to a very electronegative element (N, O or F)
  - Much stronger than London forces or Dipole-Dipole forces.
  - It is a weak covalent bond.





Hydrogen Bonding in Liquid water

- The stronger the intermolecular (van der Waals forces) the more tightly the molecules are held together
  - higher surface tension
  - higher viscosity
  - higher boiling point
  - lower vapor pressure at a given temperature

van der Waals forces and liquid properties

Solids – general types

- Molecular
  - Held together by the intermolecular forces just discussed
  - Examples: H_2O, Ne, CO_2
- Ionic
  - Held together by ionic bonds
  - Examples: NaCl, ZnS
- Metallic
  - Held together by metallic bonding
  - Examples: Fe, Cu, Li
- Covalent network
  - Held together by covalent bonds
  - Examples: Diamond, Graphite, Quartz, asbestos

Relative properties

- Molecular solids
  - Low melting points
  - Brittle
  - Non-conductive
- Ionic solids
  - Moderate to high melting points
  - Brittle
  - Non-conductive (except for liquid)
- Metallic solids
  - Low to very high melting points
  - Malleable and Ductile
  - Conductive
- Covalent solids
  - Very high melting points
  - Brittle
  - Usually non-conductive.

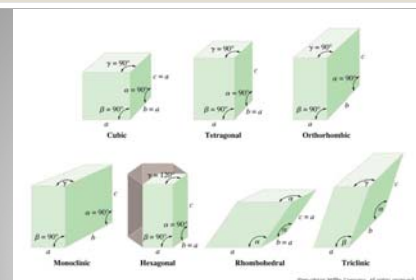
Crystalline Solids

- ***Crystalline solids*** have a regular structure
- ***Amorphous solids*** have a random structure
- We'll look at only crystalline solids in this class

Crystal lattice and unit cell

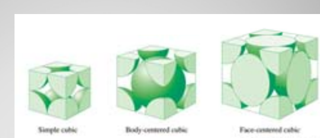
- The ***crystal lattice*** is the regular pattern that is present in a crystalline solid.
- The atoms are at the ***lattice points***
- The ***unit cell*** is the smallest parallelepiped that can be used to recreate the entire structure by stacking in three dimensions

Types of unit cells



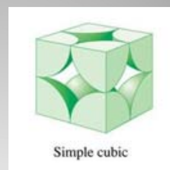
Cubic unit cells

- Simple cubic
  - there is an atom at each corner and nowhere else
- Body-centered cubic (bcc)
  - there is an atom at each corner and in the center of the cube
- Face-centered cubic (fcc or ccp)
  - There is an atom at each corner and in the center of each face of the cube.



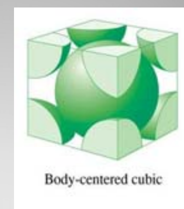
Cubic cells

- Simple cubic
  - 1 atom per unit cell (1/8th at each corner with 8 corners)
  - $e = 2r$
  - Coordination number = 6



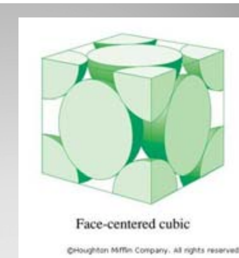
Cubic cells

- body-centered cubic
  - 2 atom per unit cell (1/8th at each corner with 8 corners + 1 in the center)
  - $e = \frac{4r}{\sqrt{3}}$
  - Coordination number = 8



Cubic cells

- Face-centered cubic
  - 4 atom per unit cell (1/8th at each corner with 8 corners + ½ in each of 6 faces)
  - $e = \frac{4r}{\sqrt{2}}$
  - Coordination number = 12



Packing Fraction

- The fraction of the space in a unit cell that is occupied by atoms

$$f = \frac{V_{atoms}}{V_{cell}}$$

Packing fraction in a simple cubic unit cell

$$f = \frac{V_{atoms}}{V_{cell}} = \frac{1\left(\frac{4}{3}\pi r^3\right)}{e^3} = \frac{4\pi r^3}{3(2r)^3} = \frac{4\pi r^3}{24r^3} = \frac{\pi}{6}$$

$$= 0.5236$$

Unit Cell calculations

- Unit cell type from cell length and density
- Atomic radius from cell type and density
- density from cell length and type
- atomic mass from density, cell length and type

Example

- Copper has a density of 8.96 g cm^{-3} and the unit cell has an edge length of 362.0 pm. What kind of unit cell does copper have?

$$? \frac{atom}{cell} = \frac{8.96\text{ g}}{\text{cm}^3} \times \frac{1\text{ mol}}{63.54\text{ g}} \times \frac{6.022 \times 10^{23}\text{ atom}}{1\text{ mol}} \times \left(\frac{1\text{ cm}}{10^{-2}\text{ m}}\right)^3$$

$$\times \left(\frac{10^{-12}\text{ m}}{1\text{ pm}}\right)^3 \times \frac{(362.0\text{ pm})^3}{1\text{ cell}} = 4\,\frac{atoms}{cell}$$

The unit cell is face-centered cubic (fcc).

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