States of Matter; Liquids and Solids

**Phase transitions** - a change in substance from one state to another

- Melting - change from a solid to a liquid state
- Freezing - change of a liquid to the solid state
- Vaporization - change of a solid or a liquid to the vapor state
- Sublimation - change of a solid directly to the vapor state.

- Condensation - change of a gas to either the solid or liquid state
**Vapor Pressure** of a liquid - the partial pressure of the vapor over the liquid measured at equilibrium at a given temperature.

**Boiling point** - the pressure at which the vapor pressure of a liquid equals the pressure exerted on the liquid (atm pressure).

**Freezing point** - the temperature at which a pure liquid changes to a crystalline solid, or freezes.

**Melting point** - the temperature at which a crystalline solid changes to a liquid, or melts.

**Heat of Fusion** - the heat needed for the melting of a solid. Also known as the enthalpy of fusion, $\Delta H_{\text{fus}}$. 
**Heat of Vaporization** - the heat needed for the vaporization of a liquid. Also known as the enthalpy of vaporization, $\Delta H_{\text{vap}}$.

Calculating the Heat required for a Phase Change of a given mass of a substance

Example:

A particular refrigerator cools by evaporating liquefied CCl$_2$F$_2$. How many kilograms of this liquid must be evaporated to freeze a tray of water at 0ºC to ice at 0ºC. The mass of the water is 525g, the heat of fusion of ice is 6.01kJ/mol, and the heat of vaporization of CCl$_2$F$_2$ is 17.4 kJ/mol.

The heat of vaporization of ammonia is 23.4 kJ/mol. How much heat is required to vaporize 1.00kg of ammonia? How many grams of water at 0ºC could be frozen to ice at 0ºC by the evaporation of this amount of ammonia?
**Clausius-Clapeyron Equation**: vapor pressure of a substance depends on temperature.

\[ \ln P = -(A/T) + B \]

\( P = \) the natural log of the vapor pressure \( A \) and \( B \) are positive constants

assuming the vapor pressure behaves like an ideal gas, shows that the constant \( A \) is proportional to the heat of vaporization of the liquid. If you make your \( y = \ln P \) and \( x = 1/T \)

Example:

Estimate the vapor pressure of water at 85°C. Note that the normal boiling point of water is 100°C and that the heat of vaporization is 40.7 kJ/mol.

Calculate the heat of vaporization of diethyl ether from the following vapor pressures: 400 mmHg at 18°C, and 760 mmHg at 35°C.
**Phase Diagrams**

Solid liquid and gaseous states of $\text{H}_2\text{O}$ exist under different temperatures and pressure conditions.

A phase diagram is a graphical way to summarize the conditions under which the different states of a substance are stable.

![Phase diagram for water](image)

**Phase diagram for water**

Triple point - the point in a phase diagram representing the temperature and pressure at which three phases of a substance coexist in equilibrium.
Critical Temperature - the temperature above which the liquid state of a substance no longer exists regardless of the pressure.

Critical Pressure - the vapor pressure at the critical temperature.

Example:

Properties of Liquids; Surface Tension and Viscosity

Surface tension - the energy required to increase the surface area of a liquid by a unit amount.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molecular Weight (amu)</th>
<th>Vapor Pressure (mmHg)</th>
<th>Surface Tension (J/m²)</th>
<th>Viscosity (kg/m-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water, H₂O</td>
<td>18</td>
<td>1.8 × 10¹</td>
<td>7.3 × 10⁻²</td>
<td>1.0 × 10⁻³</td>
</tr>
<tr>
<td>Carbon dioxide, CO₂</td>
<td>44</td>
<td>4.3 × 10⁴</td>
<td>1.2 × 10⁻³</td>
<td>7.1 × 10⁻⁵</td>
</tr>
<tr>
<td>Pentane, C₅H₁₂</td>
<td>72</td>
<td>4.4 × 10²</td>
<td>1.6 × 10⁻²</td>
<td>2.4 × 10⁻⁴</td>
</tr>
<tr>
<td>Glycerol, C₃H₈O₃</td>
<td>92</td>
<td>1.6 × 10⁻⁴</td>
<td>6.3 × 10⁻²</td>
<td>1.5 × 10⁰</td>
</tr>
<tr>
<td>Chloroform, CHCl₃</td>
<td>119</td>
<td>1.7 × 10²</td>
<td>2.7 × 10⁻²</td>
<td>5.8 × 10⁻⁴</td>
</tr>
<tr>
<td>Carbon tetrachloride, CCl₄</td>
<td>154</td>
<td>8.7 × 10¹</td>
<td>2.7 × 10⁻²</td>
<td>9.7 × 10⁻⁴</td>
</tr>
<tr>
<td>Bromoform, CHBr₃</td>
<td>253</td>
<td>3.9 × 10⁰</td>
<td>4.2 × 10⁻²</td>
<td>2.0 × 10⁻³</td>
</tr>
</tbody>
</table>

Capillary rise is a phenomenon related to surface tension.

Viscosity - the resistance to flow that is exhibited by all liquids and gases.

Intermolecular forces - the forces of interaction between molecules, normally weakly attractive.
Three types of intermolecular forces are known to exist between neutral molecules.

1. London Dispersion forces

   A weak attractive force between molecules resulting from the small, instantaneous dipoles that occur because of the varying positions of the electrons during their motion at the nuclei.

2. Dipole - dipole

   An attractive intermolecular force resulting from the tendency of polar molecules to align themselves such that the positive end of one molecule is near the negative end of another.

3. Hydrogen Bonding

   A weak to moderate attractive force that exists between a hydrogen atom covalently bonded to a very electronegative atom, X, and a lone pair of electrons on another small electronegative atom, Y.

Example:

1. List the different intermolecular forces you would expect for each of the following compounds:

   A) propanol

   B) methane

   C) fluoromethane

2. Arrange the following hydrocarbons in order of increasing vapor pressure: ethane, propane, butane, hexane.
Classification of Solids

Types of solids:

1. Molecular solid - a solid that consists of atoms or molecules held together by intermolecular forces.

2. Metallic solid - consists of a positive core of atoms held together by a surrounding sea of electrons.

3. Ionic solid - consists of cations and anions held together by the electrical attraction of opposite charges.

4. Covalent network solid - consists of atoms held together in large networks or chains by covalent bonds

<table>
<thead>
<tr>
<th>Type of Solid</th>
<th>Structural Units</th>
<th>Attractive Forces Between Structural Units</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular</td>
<td>Atoms or molecules</td>
<td>Intermolecular forces</td>
<td>Ne, H₂O, CO₂</td>
</tr>
<tr>
<td>Metallic</td>
<td>Atoms (positive cores surrounded by electron “sea”)</td>
<td>Metallic bonding (extreme delocalized bond)</td>
<td>Fe, Cu, Ag</td>
</tr>
<tr>
<td>Ionic</td>
<td>Ions</td>
<td>Ionic bonding</td>
<td>CsCl, NaCl, ZnS</td>
</tr>
<tr>
<td>Covalent network</td>
<td>Atoms</td>
<td>Covalent bonding</td>
<td>Diamond, graphite, asbestos</td>
</tr>
</tbody>
</table>

Physical Properties:

Structural effects on:

Melting point - an increase in intermolecular forces gives an increase in melting points.

Hardness - depends on how easily the structural units of a solid can be moved relative to one another.

Electrical Conductivity - dependent on the availability of delocalized valence electrons.
**Crystalline Solids:**

Crystalline solid is composed of one or more crystals; each crystal has a well defined ordered structure in 3 dimensions.

Example: table salt

Amorphous solid has a disordered structure; it lacks the well defined arrangement of basic units found in a crystal.

Example: window glass

**Crystal Lattices**

A crystal is a three-dimensional ordered arrangement of basic units, where the basic unit can be an atom, a molecule, or ion.

Crystal Lattice is a geometric arrangement of lattice points of a crystal, in which we choose one lattice point at the same location within each of the basic units of the crystal.

Example:

![Crystal Lattice Diagram]

The **unit cell of a crystal** is the smallest boxlike unit from which you can imagine constructing a crystal by stacking the units in three dimensions.

There are seven basic shapes that give rise to seven crystal systems used to clarify crystals. Most of the crystal systems have more than one possible crystal lattice.
The cubic unit system has three possible cubic unit cells:

**Simple cubic unit cell** - in which lattice points are situated only at the corners.

**Body centered cubic unit cell** - in which there is a lattice point at the center of the cubic cell in addition to those at the corners.

**Face centered cubic unit cell** - in which there are lattice points at the centers of each face of the unit cell in addition to those at the corners.
We have discussed the structure of crystals in a general way. Now we can look, in
detail, at the structures of crystalline solids that represent:

Molecular, metallic, ionic and covalent network

Coordination number - the number of nearest neighbor atoms of an atom.

Types of closed pack structures:

Hexagonal closed packed structure    Cubic closed pack structure

Molecular solids - closest packing, the forces are non directional and the maximum
attraction is obtained when each atom is surrounded by the largest possible number
of other atoms.

Example:

Metallic solids, with few exceptions, have either a closed packed or a body
centered structure.

Example:

Ionic solids - are complicated by the fact that you must give the position in the
crystal structure of both the cations and anions.

Example: CsCl
Covalent Network Solids - are determined primarily by the directions of the covalent bonds

Example: diamond