CHEM110 – Chapter 7
Condensed Phases:
Liquids and Solid

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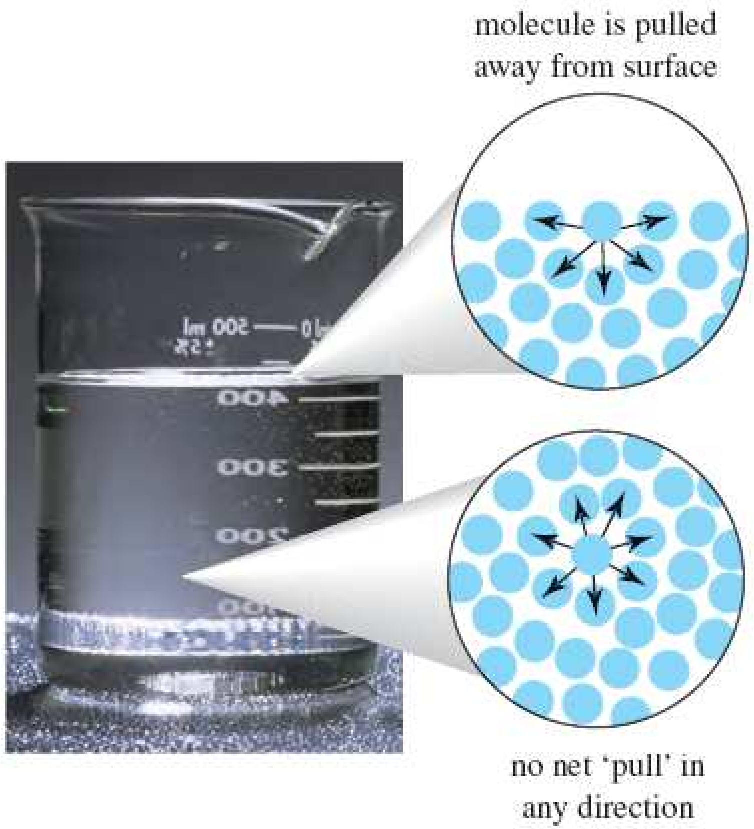
University of New England

7.1 Liquids

- In a liquid, intermolecular forces are strong enough to confine the molecules to a specific volume
- Molecules are able to move freely within a liquid
- Liquids are fluid
- Liquids cannot expand or contract significantly

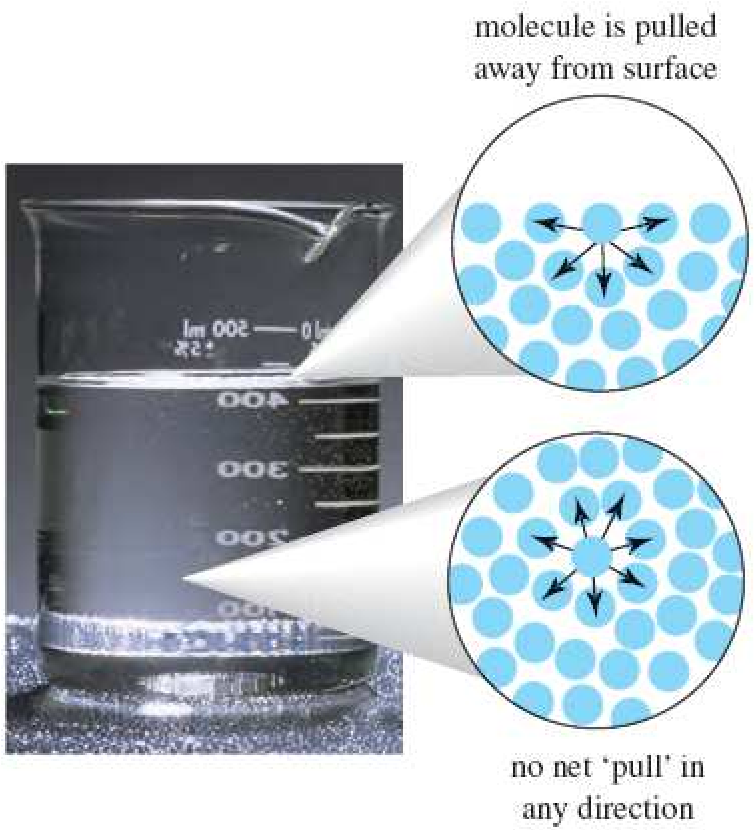
7.1 Liquids

- Properties of liquids
  - Surface tension
    - Measure of the resistance of a liquid to an increase in its surface area
    - There is a net attractive force on molecules at the surface that pulls them towards the interior of the liquid



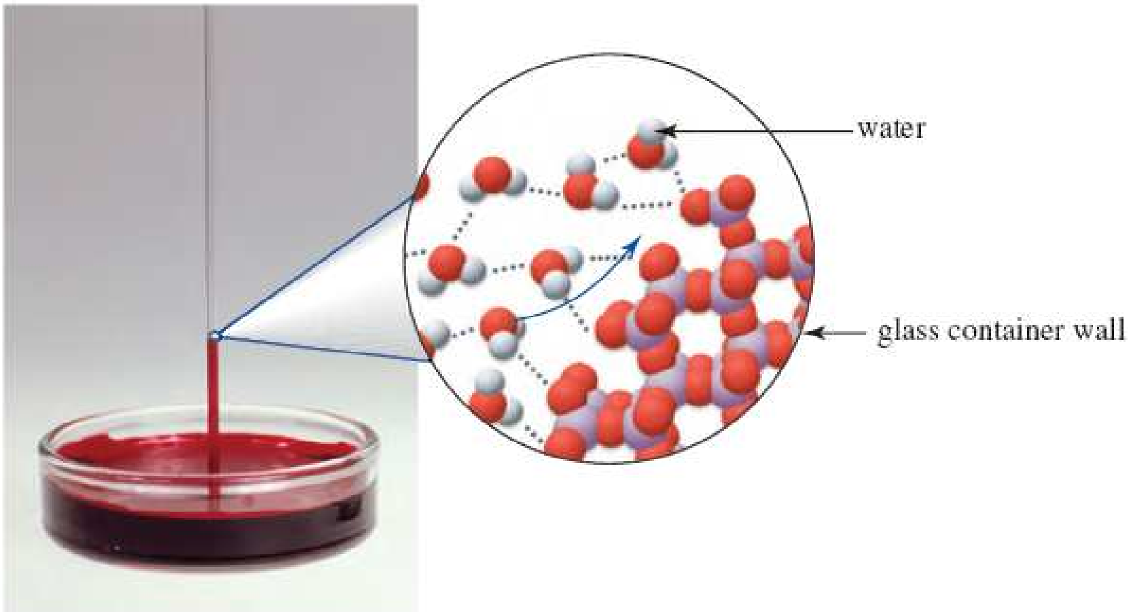
7.1 Liquids

– Surface tension
  - Cohesive forces attract molecules in the liquid to one another
  - Adhesive forces attract molecules in the liquid to the walls of the container



7.1 Liquids

- Properties of liquids
  - Capillary action
    - The upward movement of water against the downward force of gravity



7.1 Liquids

Properties of liquids

- Viscosity
  - A liquid’s resistance to flow
  - The greater the viscosity, the more slowly the liquid pours
  - A measure of how easily molecules slide by one another

7.1 Liquids

– This is affected by a combination of molecular shape and the strength of the intermolecular forces
– Viscosity is affected by temperature


Compare water to honey

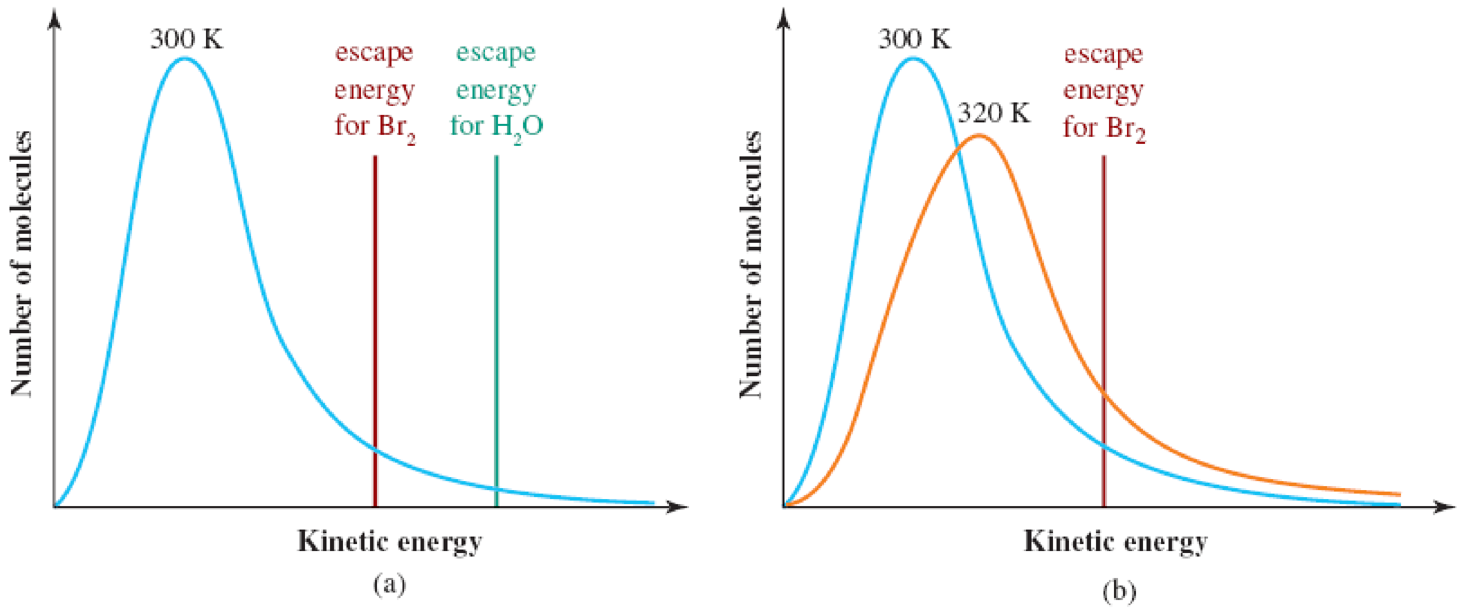
7.1 Liquids

- Vapour pressure
  - Due to the distribution of molecular energies some molecules in any liquid have enough kinetic energy to overcome the intermolecular forces that confine the liquid
  - Whenever a liquid has an exposed surface, some of its molecules will escape into the vapour phase

7.1 Liquids

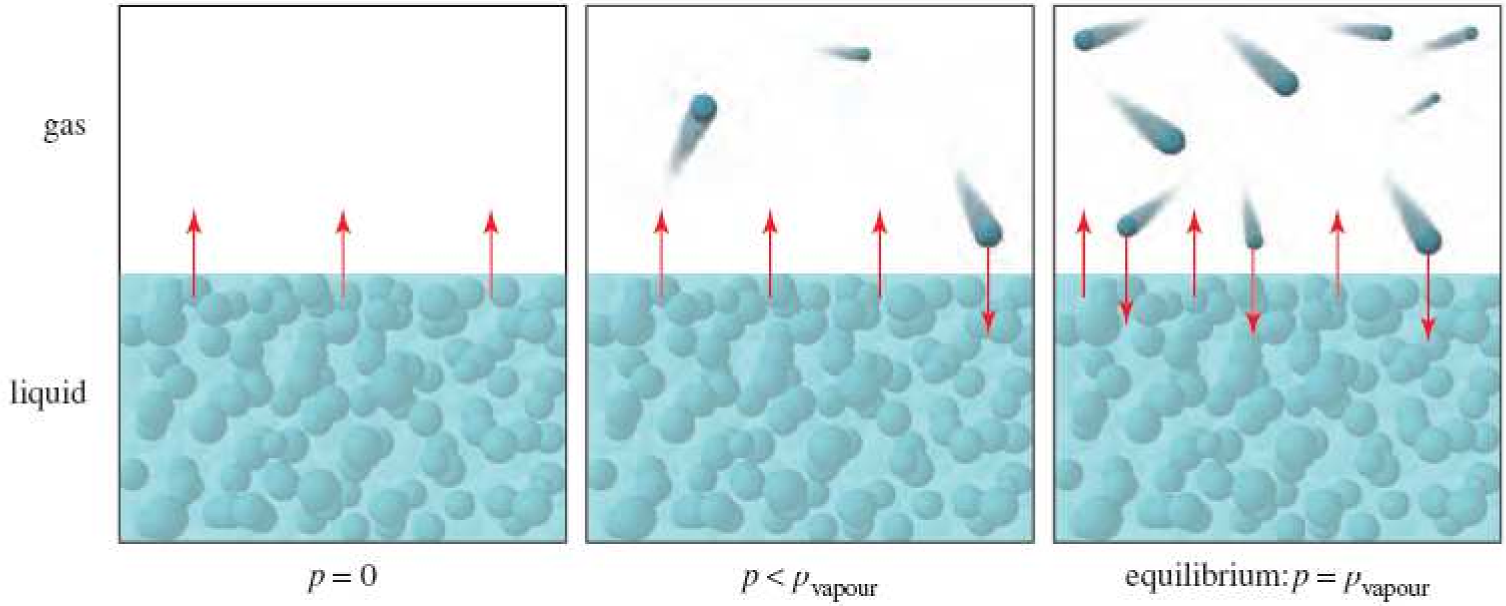
The number of molecules of a liquid that have enough energy to escape into the vapour phase depends on:

- The strength of intermolecular forces
- The temperature



7.1 Liquids

- Vapour pressure
  - Vapour pressure is the pressure at which dynamic equilibrium is achieved in a closed container



7.2 Solids

- Magnitudes of forces
  - Forces in solids range from very small to extremely large

  - Ions, atoms or molecules in solids can be bound together by various attractive forces:
    - Intermolecular forces: Molecular solids
    - Covalent bonds: Network solids
    - Delocalised bonding: Metallic solids
    - Electrostatic interactions: Ionic solids

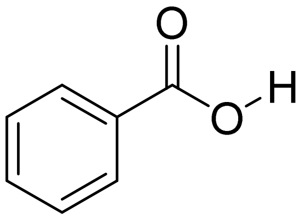
7.2 Solids

- Molecular solids
  - Aggregates of molecules bound together by intermolecular forces (i.e. dispersion, dipolar, hydrogen bonding or a combination)
  - Many larger molecules have sufficient dispersion forces to exist as solids at room temperature; e.g. naphthalene:

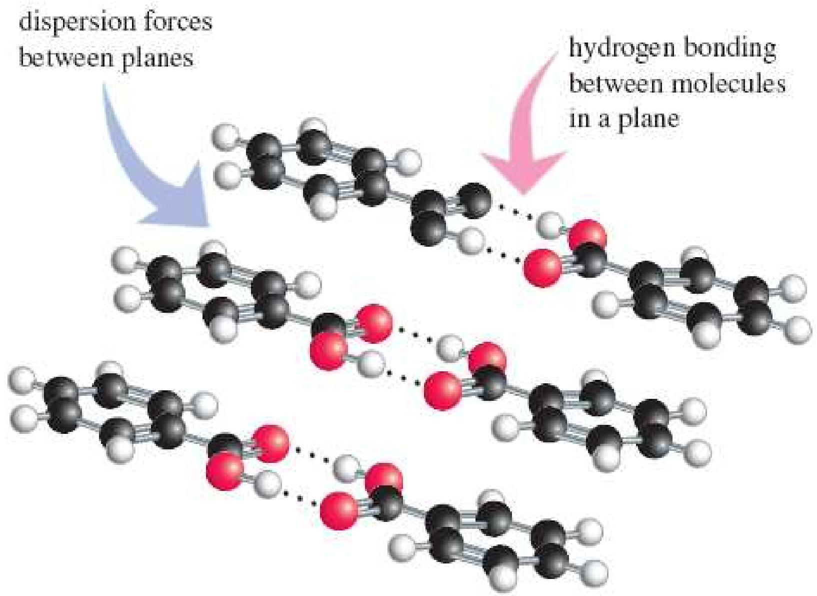
(a) (b) (c)

7.2 Solids

- Molecular solids
  - Crystals of benzoic acid contain pairs of molecules held together head to head by hydrogen bonds. These pairs then stack in planes which are held together by dispersion forces:

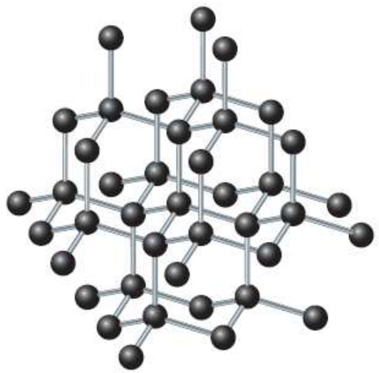


Benzoic acid

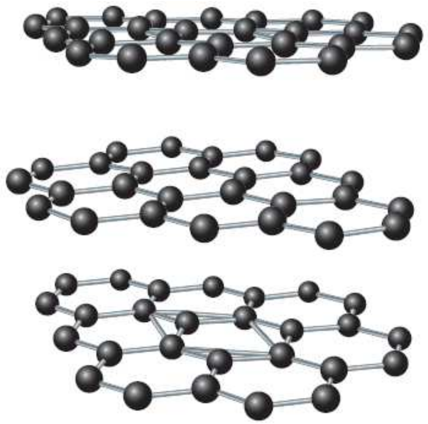


7.2 Solids

- Network solids
  - Have very high melting points
  - Held together by covalent bonds which are much stronger than intermolecular forces
  - Bonding patterns determine the properties of network solids; e.g. diamond vs. graphite:



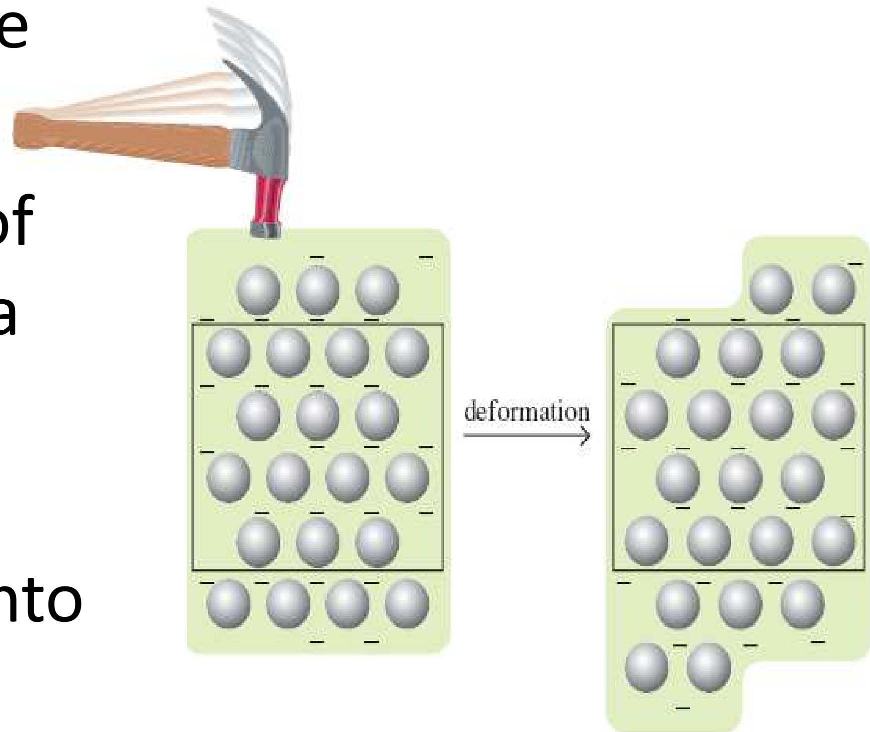
diamond



graphite

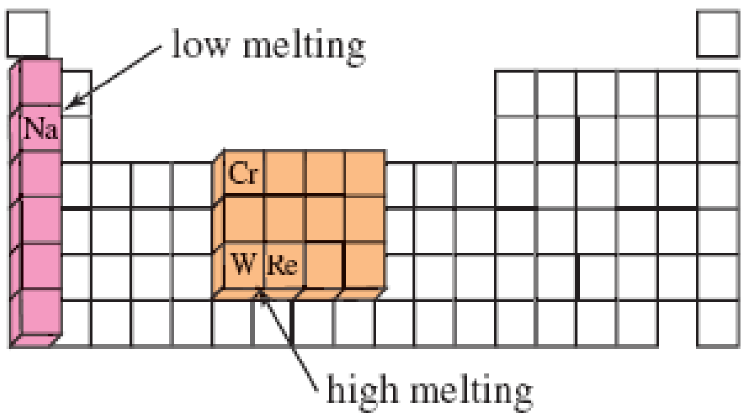
7.2 Solids

- Metallic solids
  - Derives primarily from electrons in highly delocalised valence orbitals
  - Consists of a regular array of metal atoms embedded in a 'sea' of mobile valence electrons
  - Metals are ductile (drawn into wires) and malleable (hammered into thin sheets)



7.2 Solids

- Metallic solids
  - Metals display a range of properties
  - Differences arise in part due to variations in the number of valence electrons
  - Melting points relates to position in the periodic table:



7.2 Solids

- Ionic solids
  - Contain cations and anions strongly attracted to each other by electrostatic forces
  - Their stoichiometries are determined by the charges carried by each of the ions
  - Many ionic solids contain metal cations and polyatomic anions

7.3 Phase Changes

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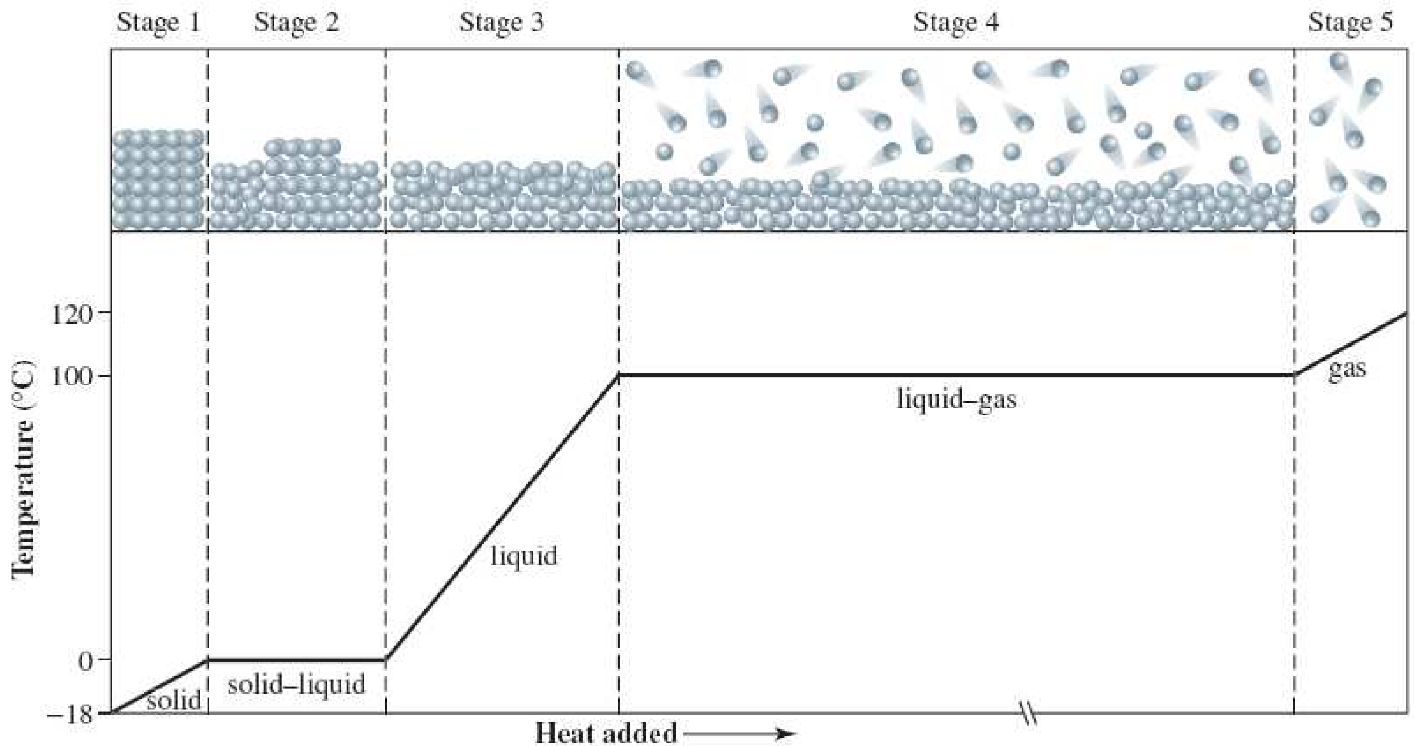
- The three main phases of matter are gas, liquid and solid
- A phase change is the transition of a substance from one phase to another
- Phase changes depend on temperature, pressure, and the magnitudes of bonding and intermolecular forces

7.3 Phase Changes

- Heating water at constant atmospheric pressure:



Adapted from: *Chemistry: The molecular nature of matter and change*, 3rd edition, Martin S Silberberg, p. 424,

7.3 Phase Changes

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- During a phase change the temperature of the system remains constant
- A substance must completely change phase before the temperature of the system can increase (or decrease)
- Phase changes require that energy (usually in the form of heat) be either supplied to or removed from the substance undergoing the phase change

7.3 Phase Changes

- Molar enthalpy of fusion, $\Delta_{fus}H$:
  - The heat needed to melt 1 mole of a substance at its normal melting point
  - Solid to liquid transition
- Molar enthalpy of vaporisation, $\Delta_{vap}H$:
  - The heat needed to vaporise 1 mole of a substance at its normal boiling point
  - Liquid to gas transition
- Molar enthalpy of sublimation, $\Delta_{sub}H$:
  - The heat needed to vaporise 1 mole of a substance from the solid phase
  - Solid to gas transition

7.3 Phase Changes

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Worked Example 7.1 (page 262)

Enthalpy of Phase Change

A swimmer emerging from a pool is covered with a film containing about 75 g of water. How much heat must be supplied to evaporate this water?

Molar enthalpy of vaporisation of water, $\Delta_{vap}H$ = 40.79 kJ mol^{-1}

7.3 Phase Changes

- The reverse process of melting:
  - Liquid to solid: solidification

- The effect of pressure is mainly seen for phase transitions involving gases

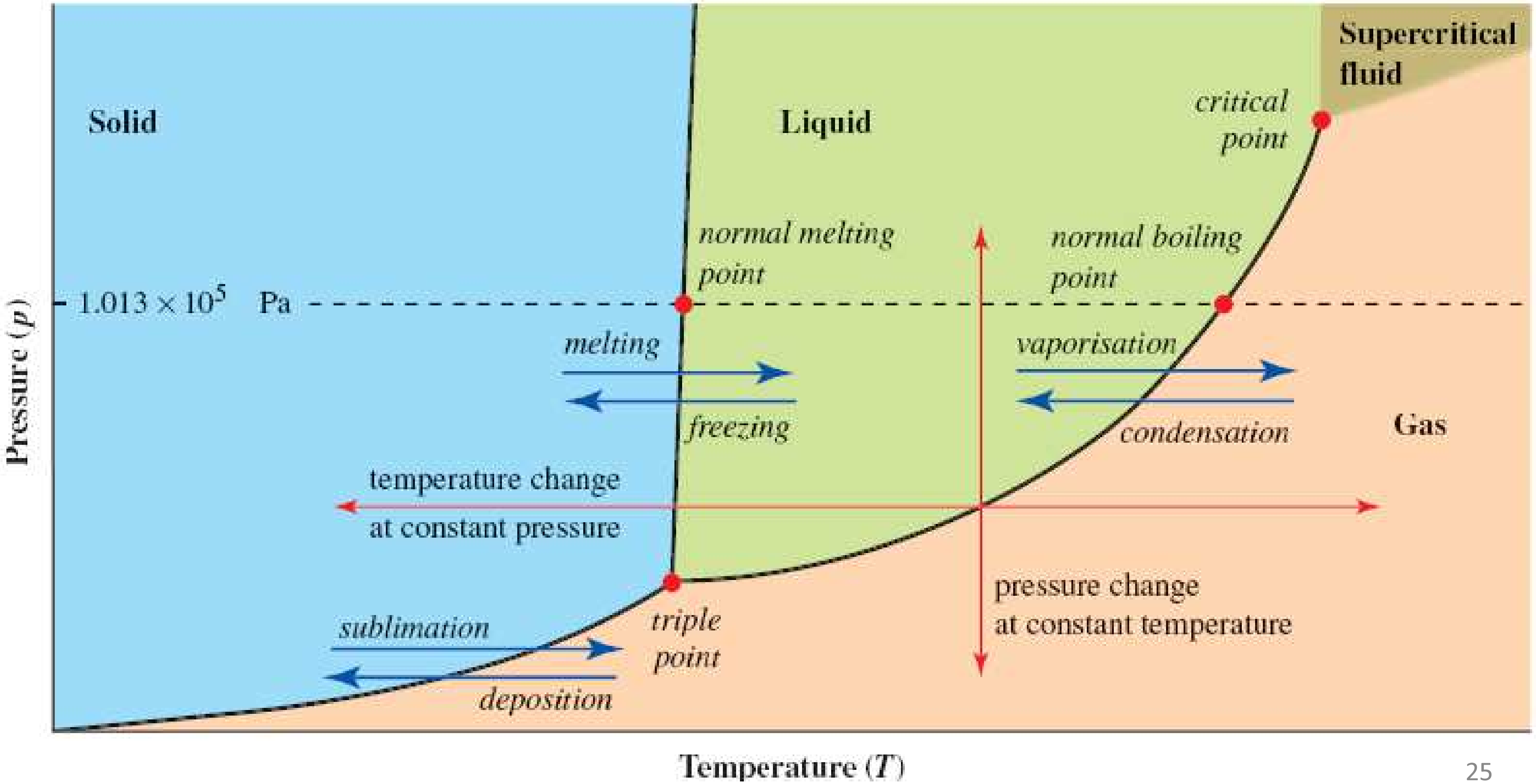
- A gas at constant temperature can be liquefied or deposited (depending on temperature) by increasing the pressure
  - Gas to liquid: condensation
  - Gas to solid: deposition

7.3 Phase Changes

- Supercritical fluids
  - Form upon compression of gases at high temperature or heating a liquid to very high temperature at high pressure
  - A supercritical fluid has certain properties of both liquids and gases
  - At the critical temperature or critical pressure the densities in the gas phase and liquid phase become equal and no phase boundary can be observed
  - The combination of these is the critical point

7.3 Phase Changes

- General phase diagram

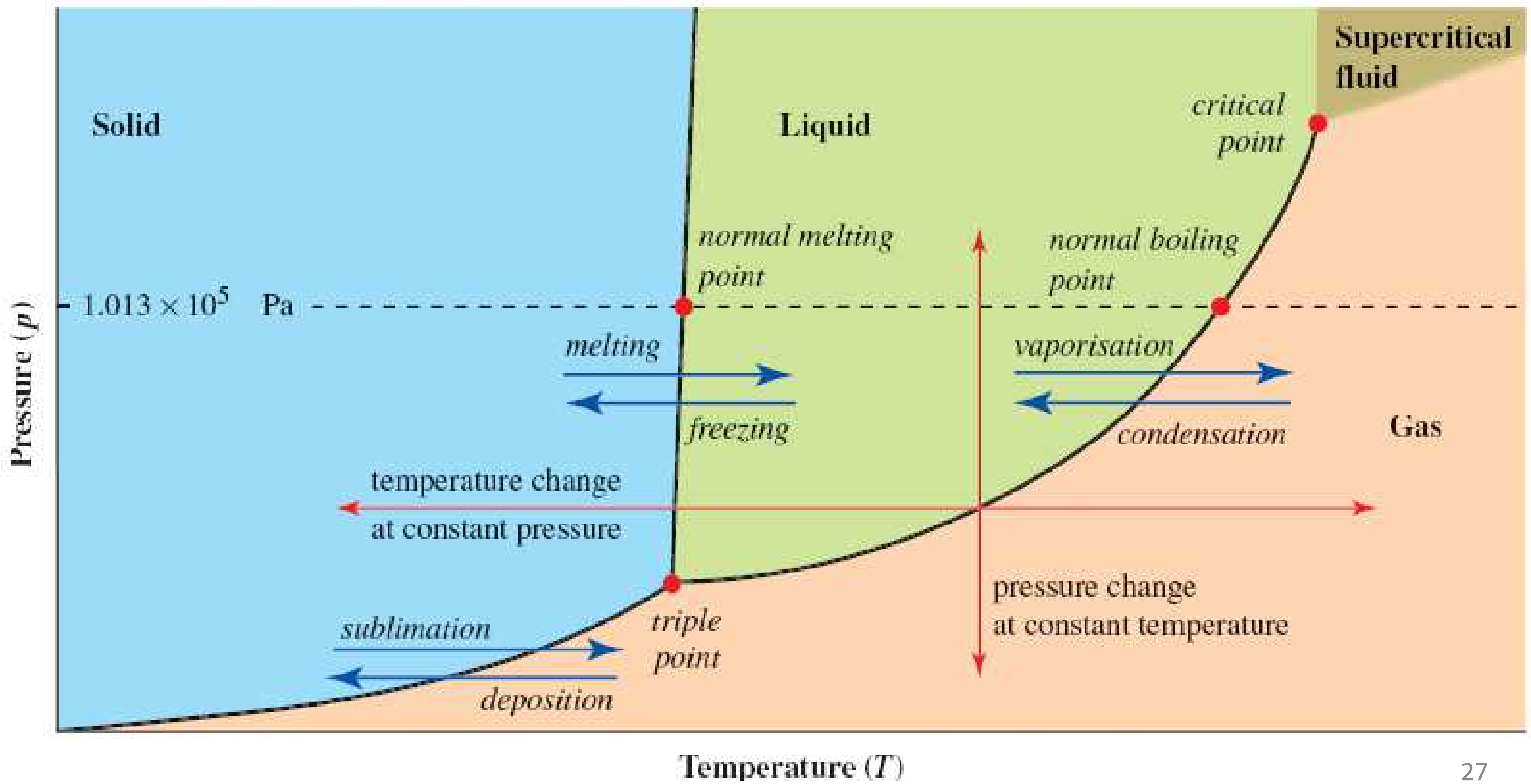


7.3 Phase Changes

- Phase diagrams – characteristic features:
  - Boundary lines between phases separate the regions where each phase is thermodynamically stable
  - Movement across a boundary line corresponds to a phase change
  - At any point along a boundary line, the two neighbouring phases coexist in a dynamic equilibrium
  - Three boundary lines meet at a single point called a triple point

7.3 Phase Changes

- General phase diagram



7.3 Phase Changes

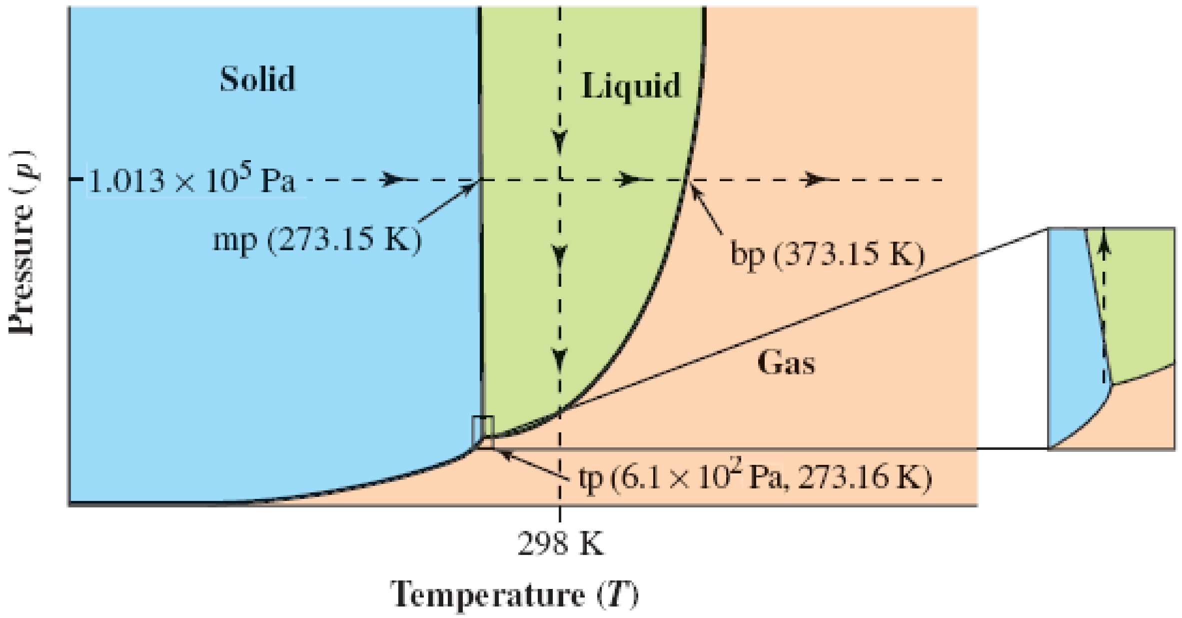
- Phase diagrams – characteristic features:
  - Above the temperature specified by the critical point, the gas cannot be liquefied under any pressure
  - What happens as temperature changes at constant pressure can be determined by drawing a horizontal line at the appropriate pressure on the phase diagram
  - The temperature for conversion between the gas phase and a condensed phase depends strongly on pressure

7.3 Phase Changes

- Phase diagrams – characteristic features:
  - What happens as pressure changes at constant temperature can be determined by drawing a vertical line at the appropriate temperature on the phase diagram
  - The melting temperature is almost independent on pressure; making the boundary line between solid and liquid nearly vertical
  - The solid-gas boundary line extrapolates to p = 0 Pa and T = 0 K

7.3 Phase Changes

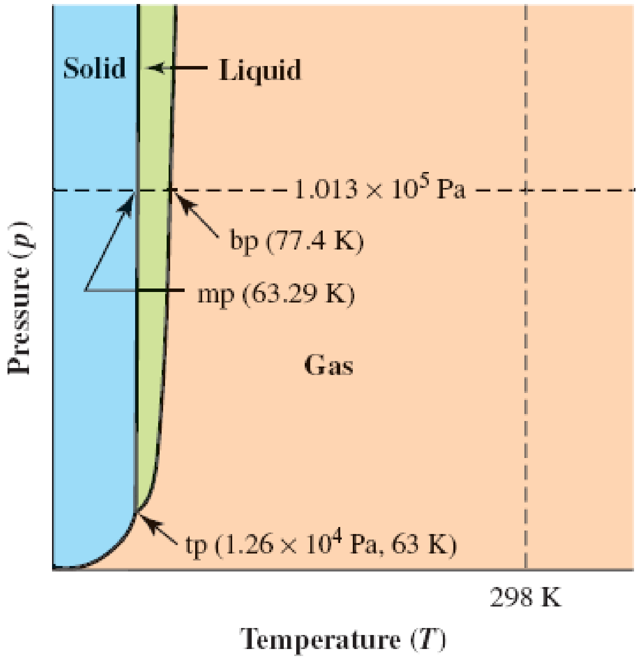
- Phase diagram of water



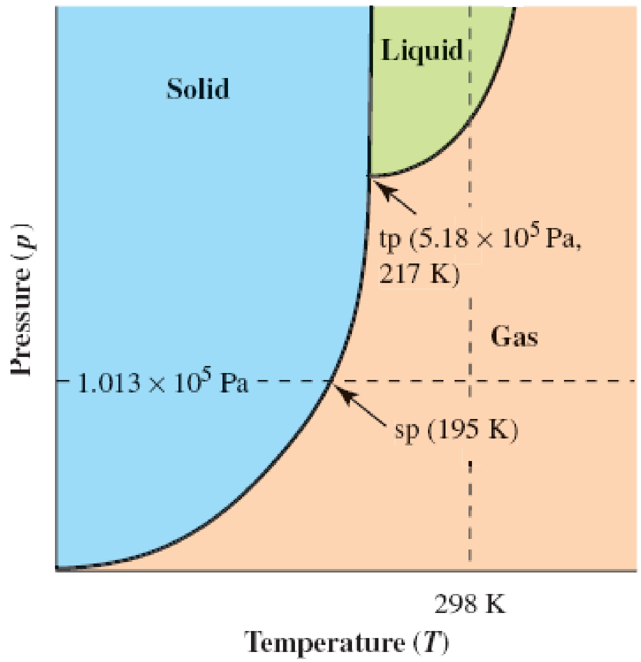
7.3 Phase Changes

- Phase diagrams of:

N_2



CO_2



7.3 Phase Changes

- Worked Example 7.2 (page 265)
- Constructing a phase diagram
- Ammonia is a gas under ambient conditions. Its normal boiling point is 239.8 K, and its normal melting point is 195.5 K. The triple point for NH_3 is $p = 0.0612 \times 10^5$ Pa and $T = 195.4$ K. Use this information to construct an approximate phase diagram for NH_3.