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## Phase equilibrium and solutions

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### 18.1 Phase behaviour of single components

- Matter exists in three phases: solid; liquid; and gas (vapour).
- A phase can be defined as a part of a system that is homogeneous in chemical and physical state throughout and is separated from other phases by a definite boundary.
- The vapour pressure (sometimes called the saturated vapour pressure) is the equilibrium partial pressure exerted by a liquid in a closed container at a fixed temperature.
- A phase diagram is a plot of the pressures and temperatures where phase transitions take place.
- Phase diagrams show the conditions of temperature and pressure under which the various phases are stable (the areas on the diagram) and the conditions where phase transitions take place (the lines on the diagram).
- The triple point of a compound is the temperature and pressure at which solid, liquid, and vapour phases are in equilibrium.
- The critical point is the temperature and pressure where the distinction between liquid and vapour properties disappears.
- Supercritical fluids exist above the critical temperature and critical pressure of a compound. Above the critical temperature, a gas cannot be condensed by the application of pressure alone.

### 18.2 Quantitative treatment of phase transitions

- The phase with the lowest Gibbs energy at a particular temperature and pressure is the most stable.

- At a phase transition temperature,  $\Delta S = \frac{\Delta H}{T}$ .
- The gradients of the lines on the phase diagrams are given by the Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H}{T \Delta V_m}$$

- The Clapeyron equation applies to *any* phase transition. When applied to the melting/freezing transition to describe the effect of pressure on melting temperature, it is written as

$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}} H}{T \Delta_{\text{fus}} V}$$

where  $T$  is the melting temperature.

- The Clapeyron equation can be simplified for transitions involving gases and vapours. The variation of vapour pressure with temperature is then described by the Clausius–Clapeyron equation

$$\ln p = \text{constant} - \frac{\Delta H}{R} \left( \frac{1}{T} \right)$$

where  $\Delta H$  is  $\Delta_{\text{vap}} H$  or  $\Delta_{\text{sub}} H$

- A useful form of the Clausius–Clapeyron equation is

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

- The normal boiling point,  $T_b$ , is defined as the temperature at which the vapour pressure of a substance is 1 atm ( $1.013 \times 10^5$  Pa).
- The standard boiling point,  $T_{b(s)}$ , is defined as the temperature at which the vapour pressure of a substance is 1 bar ( $1.0 \times 10^5$  Pa).
- Trouton's rule. Many substances have an entropy change of vaporization  $\Delta_{\text{vap}} S^\ominus \approx +85 \text{ J K}^{-1} \text{ mol}^{-1}$ . Exceptions to this rule occur when molecular interactions are strong in the liquid or the vapour.

### 18.3 Intermolecular interactions

- Ionic interactions are strong and relatively long range and depend on  $1/r$ .

- The strength of ionic interactions depends on the relative permittivity of a medium.
- Non-covalent interactions (dipole–dipole, dipole–induced dipole, and dispersion interactions) are relatively weak and depend on  $1/r^6$ .
- Non-covalent interactions are influenced by the dipole moments, polarizabilities, and ionization energies of the molecules.
- At the equilibrium separation,  $r_0$ , between molecules, there is no net intermolecular force and the potential energy is at a minimum.
- Intermolecular interactions can be represented by the Lennard-Jones potential

$$E_{\text{PE}}(\text{total}) = +\frac{B}{r^{12}} - \frac{A}{r^6}$$

## 18.4 Phase behaviour in two component systems

- Two component mixtures can have one gas phase, but may have several liquid or solid phases.
- The enthalpy change of mixing,  $\Delta_{\text{mix}}H$ , usually determines whether two liquids are miscible or immiscible.
- Ideal solutions obey Raoult's law:  $p_A(\text{ideal}) = x_A p_A^\circ$

where  $p_A$  is the vapour pressure component A,  $x_A$  is its mole fraction, and  $p_A^\circ$  is the vapour pressure of the pure component (that is,  $x = 1$ ) at the temperature of the solution.

- Deviations from Raoult's law can be described in terms of an **activity coefficient**,  $\gamma$

$$p_A = \gamma_A x_A p_A^\circ$$

- When  $\gamma_A > 1$ , the system displays a positive deviation from Raoult's law.
- When  $\gamma_A < 1$ , the system displays a negative deviation from Raoult's law.
- The solute in dilute solutions obeys Henry's law for ideal dilute solutions

$$p_B = x_B K_B$$

where  $K_B$  is Henry's law constant.

- Colligative properties depend only on the number of molecules (or ions) of the dissolved species, not on their nature.
- Osmosis occurs when a solution and pure solvent are separated by a semi-permeable membrane. Solvent passes out of the solution through the membrane.
- Distillation can be used to separate the components of liquid mixtures. Non-ideal solutions often form azeotropes.

## Learning outcomes

By the end of this chapter you should be able to do the following.

- Draw and interpret single component phase diagrams and account for their main features.
- Use phase diagrams to interpret the phase behaviour of pure elements and compounds.
- Account for the effect of pressure on melting temperatures using the Clapeyron equation.
- Apply the Clausius–Clapeyron equation to describe the effect of pressure on vaporization and sublimation temperatures.
- Define normal and standard boiling temperatures.
- Describe the molecular properties that influence intermolecular interactions.
- Describe the origin and uses of the Lennard-Jones potential.
- Account for miscibility behaviour of mixtures in terms of the enthalpy change,  $\Delta_{\text{mix}}H$ , and entropy change,  $\Delta_{\text{mix}}S$ , of mixing.
- State and use Raoult's law to explain the properties of ideal solutions.
- Calculate activity coefficients and relate their values to the intermolecular interactions in solution.
- State and use Henry's law to explain the properties of ideal dilute solutions.
- Account for colligative properties such as osmotic pressure.
- Describe the separation of liquids by distillation and account for the formation of azeotropes.