Basic Chemistry Tutorial: Properties of Solutions

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- Solids
  - Structure of solids
- Liquids
  - Vapour pressure
- Solutions
  - Solubility of gases in liquids
  - Henrys law, Le Chatelier's principle
  - Solubility of liquids in liquids
  - Vapour pressure of solutions
  - Colligative properties

Solids

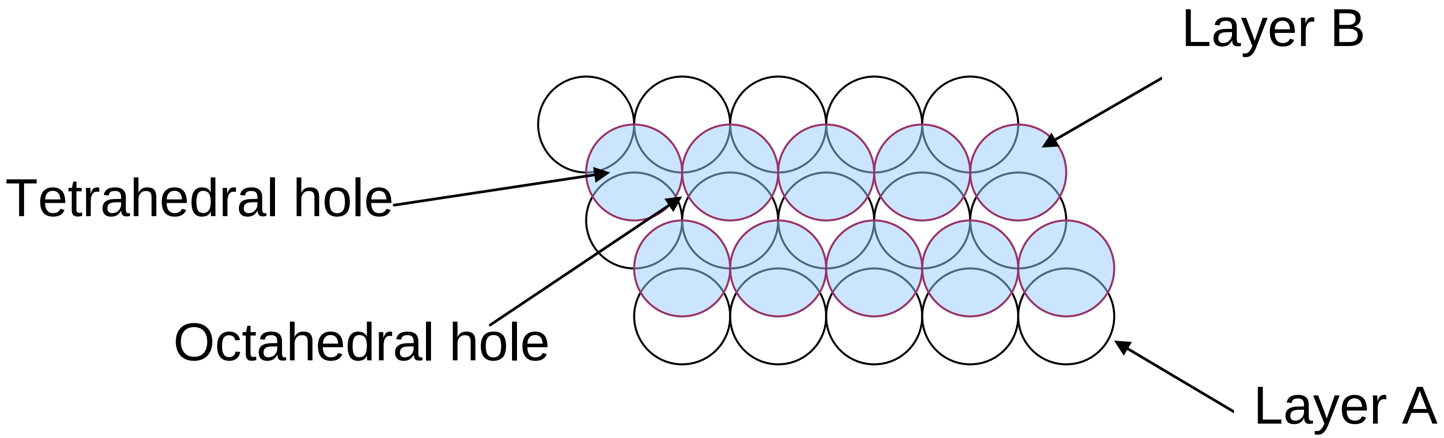
Structure of crystalline solids

- Very long-range ordering. Repeating pattern throughout the crystal called lattice
- Unit cell: smallest part of crystal that, if repeated, makes up the crystal itself
- Coordination number: number of nearest neighbours surrounding an atom in a crystal lattice
- Close packing: efficient way of arranging atoms.

  These can be

  1. Cubic close packed/Face centred cubic
     - ABCABC… pattern
     - Packing density = 74%
     - Each atom in a layer is surrounded by 6 in the plane; 3 above the plane, and 3 below $\Rightarrow$ coordination no is 12
  2. Hexagonal close packed
     - ABAB… pattern
     - Packing density = 74%
     - Coordination number = 12

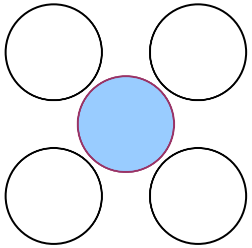
- tetrahedral and octahedral holes

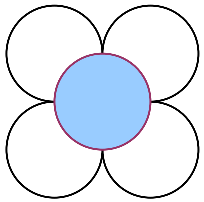


- when layer B is placed so that the atoms fit into the depressions in A, get tetrahedral holes (4 nearest neighbours) and octahedral holes (6 nearest neighbours

Body centred cubic

- less effective use of space
- packing fraction = 68%
- coordination number = 8





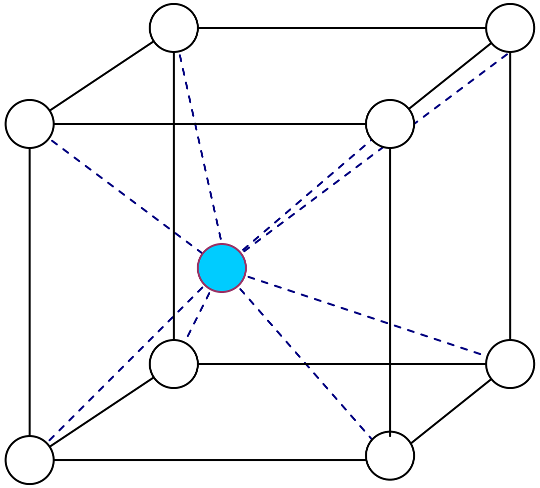
Calculating the number of atoms in a unit cell

Step 1: Any atoms whose nucleus is inside the unit cell counts as 1

Step 2: Any atoms with a nucleus lying on a face counts as ½

Step 3: Atoms with nuclei on edges count as 1/n, where n cells share

Example, CsCl



1 Cs atom in centre
8 surrounding Cl atoms

Each Cl at each cell corner is shared between 8 unit cells

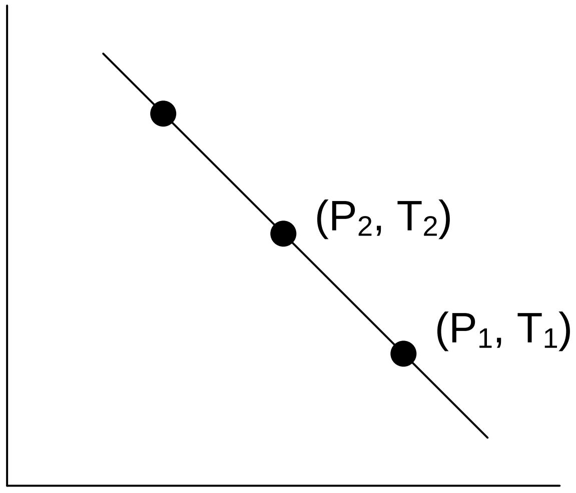
$\Rightarrow$ total no of atoms per cell = $1 + 0 + 8 \times 1/8$

$= 1 + 1$

$= 2$ (one Cs atom and one Cl atom)

Phase Changes

- Transformed from one phase to another (e.g. from solid to liquid to gas)
- Liquid molecules not in fixed lattice, like crystalline solids. They can be vaporised to a gas, usually by an increase in temperature
- When equilibrium between vaporisation of liquid molecules and condensation of gas molecules exists, it is called the equilibrium vapour pressure of the liquid.
- If *ln*(vapour pressure) is plotted against 1/T (K^{-1}), get straight line:



$$ln\ P_2 - ln\ P_1 = -\Delta H_{vap}/R\ (1/T_1 - 1/T_2)$$

$$ln\ \frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R}(1/T_1 - 1/T_2)$$

Clausius-Clayperon equation

- Can measure how vapour pressure varies with temperature
- At lower pressure, liquid will boil more readily

If the process is a closed system at constant pressure:

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

Solutions

- Solvent is the material present in largest amount
- Solute is dissolved in solvent. Can be solid, liquid, or gas.
- "Like dissolves like" rule: polar substances dissolve polar substances, non-polar substances dissolve non-polar substances

Gases in liquids

- Solubility decreases with temperature increase because liquid molecules have higher average kinetic energy and can enter gas phase

- Solubility increases with increasing pressure - Henry's Law: "$\text{solubility}_{(gas)}$ proportional to partial pressure of gas over liquid"

- As pressure is increase, greater number of collisions of gas molecules with liquid surface. Leads to increase in solubility

- these changes follow Le Chateliers Principle : "If a system at equilibrium is disturbed, the system will undergo a change to reduce the effect of the disturbance"

Solids in liquids

- saturated solution: maximum amount of dissolved solute at a given temperature in the presence of undissolved solute

- when solid solute is placed in solvent:
  - solute molecules separate $\Delta H_{solute} > 0$
  - solvent molecules separate $\Delta H_{solvent} > 0$
  - solute and solvent molecules mix $\Delta H_{mix} < 0$
  - therefore, $\Delta H_{solution}$ generally positive

- solubility depends on temperature. Most solids more soluble at higher temperature

Colligative Properties

- collective properties that depend on the concentration of solute particles present in a solution

- Molality: number of moles of solute dissolved in 1 kg of solvent (units: mol kg^{-1})

1. Vapour Pressure Depression

- if a nonvolatile solute is added to a pure solvent, the vapour pressure is decreased, i.e. get a vapour pressure depression

- can measure mole fraction and hence molecular weight of solute from Raoults law

$$P_{solvent} = x_{solvent}\, P^{\circ}_{solvent}$$

where $P_{solvent}$ is the vapour pressure of the solvent

$x_{solvent}$ is the mole fraction of the solvent

$P^{\circ}_{solvent}$ is the vapour pressure of the pure solvent

$$x_{solvent} + x_{solute} = 1 \qquad \Rightarrow x_{solvent} = 1 - x_{solute}$$

$$\Rightarrow P_{solvent} = (1 - x_{solute})P^{\circ}_{solvent}$$

$$\Rightarrow P_{solvent} = P^{\circ}_{solvent} - x_{solute}P^{\circ}_{solvent}$$

$$\Rightarrow \underbrace{P^{\circ}_{solvent} - P_{solvent}}_{\Delta P,\ \text{Vapour pressure depression}} = x_{solute}\, P_{solvent}$$

Question

If the vapour pressure of water at 25°C is 23.76 torr, calculate the vapour pressure of a solution of 50.0g of glucose, $C_6H_{12}O_6$, in 600g of water at 25°C.

Step 1: Calculate the number of moles of solute and solvent

$$1 \text{ mol } C_6H_{12}O_6 = 180.16\text{g} \qquad \Rightarrow 50\text{g} = 0.278 \text{ mol glucose}$$

$$1 \text{ mol } H_2O = 18.016 \text{ g} \qquad \Rightarrow 600\text{g} = 33.3 \text{ mol } H_2O$$

Step 2: Calculate the mole fraction of solute

$$x_{glucose} = \frac{0.278 \text{ mol}}{(0.278 + 33.3)\text{mol}} = 0.008$$

$$\Delta P = x_{solute}P_{solvent}$$

$$= (0.008)(23.76 \text{ torr})$$

$$= 0.197 \text{ torr}$$

Vapour pressure of solution = (23.76 – 0.197 torr) = 23.56 torr

Question

Calculate the vapour pressure depression of a solution of 40.0g of sucrose ($C_{12}H_{22}O_{11}$) in 450g of water at 25°C. The vapour pressure of water at 25°C is 23.76 torr.

Answer: 0.1 torr

Calculate the vapour pressure depression of 56g of glycerol ($C_3H_8O_3$) in 450g of water at 25°C.

Answer: 0.56 torr

2. Boiling Point Elevation

- A solution typically boils at higher temperature than the pure solvent
- Proportional to concentration of solute molecules

$$\Delta T_b = k_b M_b$$

where k_b is the ebullioscopic constant (°C/m)

M_b is the molality

$\Delta T_b = T_{b\ solution} - T_{b\ solvent}$ $\quad\quad$ $T_{b\ solution} = \Delta T_b + T_{b\ solvent}$

Example

What is the boiling point of 0.5 *m* lactose in water? K_b for water is 0.512 °C/*m*.

$$\Delta T_b = k_b M_b$$

$$= (0.512\ °C/m)(0.5m)$$

$$= 0.26°C$$

$$T_{b\ solution} = \Delta T_b + T_{b\ solvent}$$

$$T_{b\ solution} = 0.26\ °C + 100°C$$

$$T_{b\ solution} = 100.26\ °C$$

Question

What is the boiling point of 150g glycerol ($C_3H_8O_3$) in 1 kg of water? K_b for water is 0.512°C/*m*.

Answer: 100.83 °C

What is the boiling point of 35g of $C_2H_6O_2$ in 250g ethanol? The boiling point of ethanol is 78.5 °C and k_b is 1.22 °C/*m*.

Answer: 81.25 °C

3. Freezing Point Depression

- Solution has lower freezing point that solvent
- Given by

$$\Delta T_f = k_f M_f$$

where k_f is the cryoscopic constant

M_f is the molality

$$\Delta T_f = T_{f\,solvent} - T_{f\,solution}$$

Example

What is the freezing point of 500g of antifreeze ($C_2H_6O_2$) in 2.5 kg of water? (K_f for water is 1.86 °C/*m*)

No of moles of $C_2H_6O_2$ = 8.05 mol

$$\text{Molality} = \frac{8.05\ \text{mol}}{2.5\ \text{kg}} = 3.2\ \text{mol kg}^{-1} = 3.2m$$

$\Delta T_f = k_f M_f$ $\quad \Delta T_f = (1.86\ °C/m)(3.2m)$ $\quad \Delta T_f = 5.99\ °C$

$T_{f\,solution} = T_{f\,solvent} - \Delta T_f = 0°C - 5.99°C$ $\quad T_{f\,solution} = -5.99°C$

Question

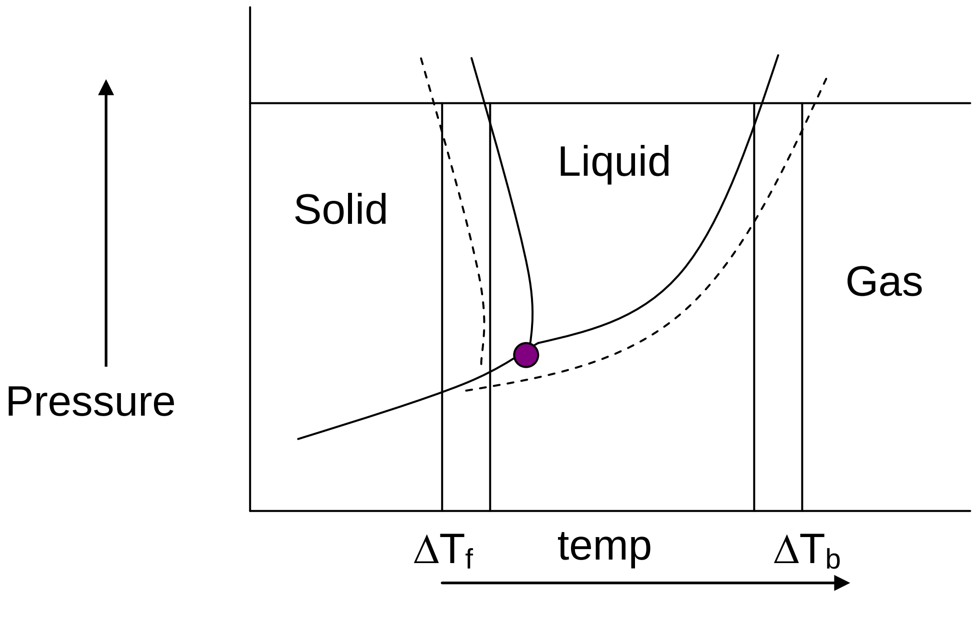
What is the freezing point of 0.11*m* glucose in water? K_f for water is 1.86 °C/*m*.

Answer: -0.2 °C

What is the freezing point of 0.52*m* of $C_3H_8O_3$ in water?

Answer: -0.97 °C

The boiling point elevation and freezing point depression may be explained by studying a phase diagram of solvent and solution



Dashed line: solution
Solid line: pure solvent
Filled circle: Triple point

4. Osmotic Pressure, Π

- an applied pressure to prevent the movement of water from solvent to solution

- only considered for aqueous solutions

- Given by

$$\Pi V = n_B RT$$

where Π is the osmotic pressure

V is the volume of solution

n_b is the moles of solute

R is the gas constant

T is the temperature

- can be used to determine the molecular mass of solute

Example

7.5g of PVA is dissolved in 150mL water. At 25°C, the osmotic pressure of the solution is 0.272 atm. What is the molar mass of the polymer sample?

$$\Pi V = n_B RT$$

$$n_b = \frac{\text{mass in g}}{\text{molar mass}} = \frac{7.5\text{ g}}{M_r}$$

$\Pi = 0.272$ atm $\quad V = 0.15\text{L} \quad T = 298\text{K} \quad R = 8.206 \times 10^{-2}$ L atm K^{-1} mol^{-1}

$$n_b = \frac{\Pi V}{RT} \Rightarrow \frac{7.5\text{g}}{M_r} = \frac{(0.272\text{ atm})(0.15\text{ L})}{(8.206\times 10^{-2}\text{ LatmK}^{-1}\text{mol}^{-1})(298\text{K})}$$

$$\frac{7.5\text{g}}{M_r} = \frac{0.0408}{24.45\text{ mol}^{-1}} \quad M_r = \frac{(7.5\text{ g})(24.45\text{ mol}^{-1})}{0.0408} = 4495.2\text{ g mol}^{-1}$$

Question

If a 0.30 M solution of sucrose at 37°C has the same osmotic pressure as blood, what is the value for Π of blood?

Answer: 7.6 atm