Basic Chemistry Tutorial: Properties of Solutions
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  • Henry's law, Le Chatelier’s principle
  • Solubility of liquids in liquids
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**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 ⇒ coordination no is 12

2. **Hexagonal close packed**
   - ABAB… pattern
   - Packing density = 74%
   - Coordination number = 12
- tetrahedral and octahedral holes

Layer A

Layer B

Tetrahedral hole

Octahedral hole
- 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 $\frac{1}{2}$
Step 3: Atoms with nuclei on edges count as $\frac{1}{n}$, where $n$ cells share
Example, CsCl

Each Cl at each cell corner is shared between 8 unit cells
⇒ total no of atoms per cell = 1 + 0 + 8 × 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:

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

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

$P_1$

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: “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 \( \Delta H_{\text{solute}} > 0 \)
  - solvent molecules separate \( \Delta H_{\text{solvent}} > 0 \)
  - solute and solvent molecules mix \( \Delta H_{\text{mix}} < 0 \)
  - therefore, \( \Delta H_{\text{solution}} \) 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:

\[
P_{\text{solvent}} = x_{\text{solvent}} P^\circ_{\text{solvent}}
\]

where \( P_{\text{solvent}} \) is the vapour pressure of the solvent,
\( x_{\text{solvent}} \) is the mole fraction of the solvent,
\( P^\circ_{\text{solvent}} \) is the vapour pressure of the pure solvent.

\[
x_{\text{solvent}} + x_{\text{solute}} = 1 \quad \Rightarrow \quad x_{\text{solvent}} = 1 - x_{\text{solute}}
\]

\[
\Rightarrow P_{\text{solvent}} = (1 - x_{\text{solute}}) P^\circ_{\text{solvent}}
\]

\[
\Rightarrow P_{\text{solvent}} = P^\circ_{\text{solvent}} - x_{\text{solute}} P^\circ_{\text{solvent}}
\]

\[
\Rightarrow P^\circ_{\text{solvent}} - P_{\text{solvent}} = x_{\text{solute}} P_{\text{solvent}}
\]

\( \Delta P \), Vapour pressure depression
**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

\[
1 \text{ mol } C_6H_{12}O_6 = 180.16 \text{ g} \quad \Rightarrow \quad 50 \text{ g} = 0.278 \text{ mol glucose} \\
1 \text{ mol } H_2O = 18.016 \text{ g} \quad \Rightarrow \quad 600 \text{ g} = 33.3 \text{ mol } H_2O
\]

Step 2: Calculate the mole fraction of solute

\[
x_{\text{glucose}} = \frac{0.278 \text{ mol}}{0.278 + 33.3 \text{ mol}} = 0.008
\]

\[
\Delta P = x_{\text{solute}} P_{\text{solvent}} \\
= (0.008)(23.76 \text{ torr}) \\
= 0.197 \text{ torr}
\]

Vapour pressure of solution = \((23.76 - 0.197 \text{ torr}) = 23.56 \text{ torr}\)
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_{3}H_{8}O_{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

\[ \Delta T_b = T_{b \, solution} - T_{b \, solvent} \quad T_{b \, solution} = \Delta T_b + T_{b \, solvent} \]
Example
What is the boiling point of 0.5 m lactose in water? $K_b$ for water is 0.512 °C/m.

$$\Delta T_b = k_b M_b$$

$$= (0.512 \degree C/m)(0.5 m)$$

$$= 0.26 \degree C$$

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

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

$$T_{b \text{ solution}} = 100.26 \degree C$$

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 than solvent
- Given by
  \[ \Delta T_f = k_f M_f \]
  where \( k_f \) is the cryoscopic constant
  \( M_f \) is the molality
  \[ \Delta T_f = T_{f \text{ solvent}} - T_{f \text{ solution}} \]

Example

What is the freezing point of 500g of antifreeze (C\(_2\)H\(_6\)O\(_2\)) in 2.5 kg of water? (\( K_f \) for water is 1.86 °C/m)

No of moles of C\(_2\)H\(_6\)O\(_2\) = 8.05 mol

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

\[ \Delta T_f = k_f M_f \]
\[ \Delta T_f = (1.86 \text{ °C/m})(3.2m) \]
\[ \Delta T_f = 5.99 \text{ °C} \]

\[ T_{f \text{ solution}} = T_{f \text{ solvent}} - \Delta T_f \]
\[ T_{f \text{ solution}} = 0 \text{ °C} - 5.99 \text{ °C} \]
\[ T_{f \text{ solution}} = -5.99 \text{ °C} \]
Question
What is the freezing point of 0.11\textit{m} glucose in water? $K_f$ for water is 1.86 °C/m.

\textit{Answer: -0.2 °C}

What is the freezing point of 0.52\textit{m} of $\text{C}_3\text{H}_8\text{O}_3$ in water?

\textit{Answer: -0.97 °C}

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

\begin{center}
\begin{tikzpicture}
\fill[blue!20] (-2,-2) rectangle (2,2);
\draw[->] (-2.5,0) -- (2.5,0) node[right] {\textbf{\textit{Pressure}}};
\draw[->] (0,-2.5) -- (0,2.5) node[above] {\textbf{\textit{Solid}}};
\draw[->] (0,-2) -- (0,2) node[above] {\textbf{\textit{Liquid}}};
\draw[->] (0,-1) -- (0,1) node[above] {\textbf{\textit{Gas}}};
\draw (-1,0) -- (-1,-2) node[below] {$\Delta T_f$};
\draw (1,0) -- (1,-2) node[below] {$\Delta T_b$};
\draw[->] (0,-2) -- (0,-1) node[below] {\textbf{\textit{Solid line: pure solvent}}};
\draw[->] (0,-2) -- (0,-2.5) node[below] {\textbf{\textit{Dashed line: solution}}};
\draw[->] (0,-1) -- (0,-2) node[below] {\textbf{\textit{Filled circle: Triple point}}};
\end{tikzpicture}
\end{center}
4. Osmotic Pressure, $\Pi$
- 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 $\Pi$ 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?

\[ \Pi V = n_B R T \]

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

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

\[ n_b = \frac{\Pi V}{R T} \quad \Rightarrow \quad 7.5 \text{ g} = \frac{(0.272 \text{ atm})(0.15 \text{ L})}{M_r} \left(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}\right)(298 \text{ K}) \]

\[ 7.5 \text{ g} = \frac{0.0408}{M_r} \quad M_r = \frac{(7.5 \text{ g})(24.45 \text{ mol}^{-1})}{0.0408} = 4495.2 \text{ g mol}^{-1} \]
Question
If a 0.30 M solution of sucrose at 37°C has the same osmotic pressure as blood, what is the value for \( \Pi \) of blood?

Answer: 7.6 atm