CHEM1201 Lecture Notes

Chemistry 2 (Australian National University)


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Intermolecular Forces:

- When a molecule changes from **solid to liquid to gas**, input of energy is needed
- Intermolecular attractions are much weaker than covalent bonds holding the atoms together, they do not involve the sharing of electrons and are often called **non-covalent bonds**
- Types of intermolecular forces: **London Dispersion Forces**, **Dipole-Dipole Forces, Hydrogen Bonding, Ion-Dipole Attractions,**
- **Intra**molecular forces (within a species) are stronger than **inter**molecular forces (between species)
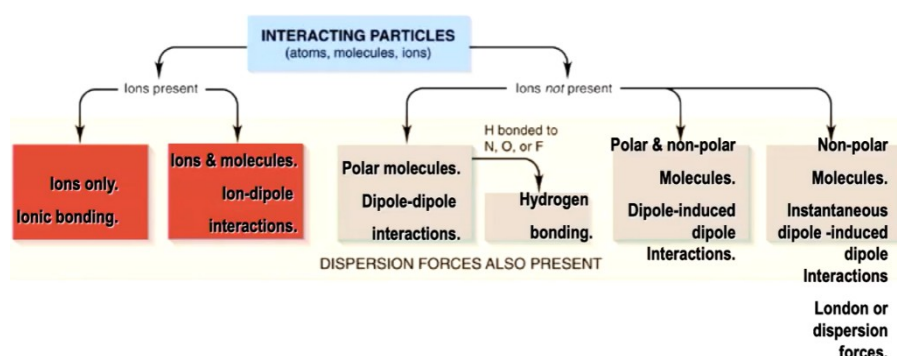
- **Molecule size** must be kept similar as this keeps the strength of the **dispersion forces constant**

London Dispersion Forces:

- Attraction between species is always the result of electrostatic attraction between opposite charges
- Also called instantaneous dipole-induced dipole interaction
- They arise because at a particular instant, the electrons in a species are unevenly distributed. We say that the **electron density** has been **polarised**. The species has an **instantaneous dipole** which induces a dipole in an adjacent species
- Size dependent, bigger/**larger surface area**/more **linear** molecules will have greater London
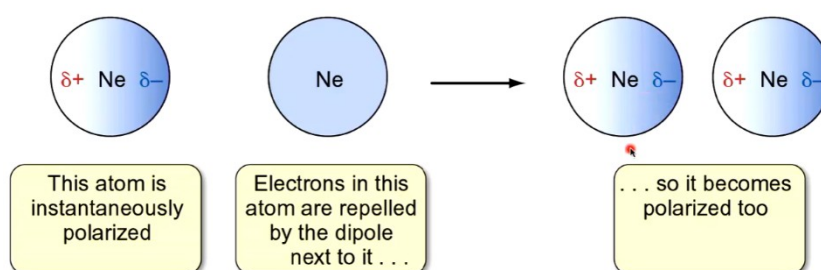
- The strength of a dispersion force depends on the ease with which the charge distribution in a molecule or atom can be distorted to induce a instantaneous dipole.
- The ease with which the charge distribution is distorted is called the atom's or molecule's **polarizability**

- Polarizability of an atom/molecule is a measure of the 'squishiness' of its electron cloud; the greater the polarizability, the more easily electron cloud can be distorted to give an instantaneous dipole
- Periodic Table Trend: **polarizability increases down a group** (valence electrons are further from the nucleus), **polarizability decreases across a period** (valence electrons are held more tightly)

Dipole-Dipole Interactions:

- Remember most **electronegative** atom in molecule will be delta negative
- When a species has a permanent dipole adjacent species align themselves to maximise attractions between +ve and -ve charges
- Such interactions are **stronger in the solid state** but are also present in liquids and gases
- There will also be dispersion interactions present between the species
- **Total attraction** between two species is sum of different attractions possible
- **Polarity dependent**

Hydrogen Bonding:

- H-bonding is an extreme form of **dipole-dipole interactions**
- An **H** atom attached to **O**, **F**, or **N**, is attracted to the lone pair of an electronegative adjacent form
- Without H bonds, H2O would be a gas at room temperature with a boiling point of -75 degrees Celsius.
- No life without H-bonds
- A H-bond is an interaction between a H-bond **donor** and a H-bond **acceptor**
- **Polarity dependent**
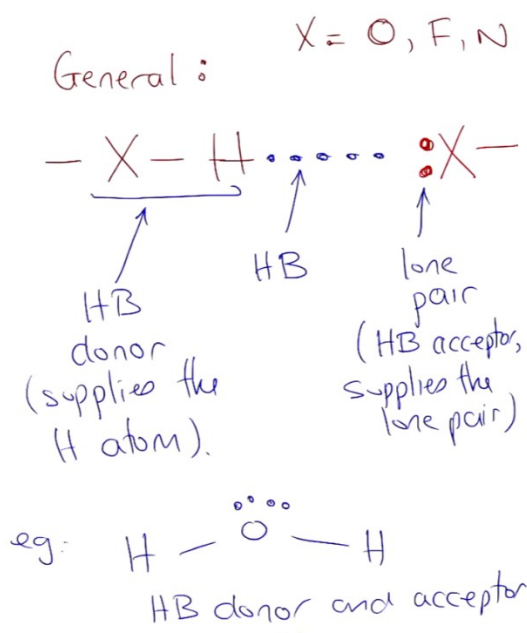
- **H-bonding in ice**; empty channels in the structure of ice make water less dense as a solid than as a liquid

Ion-Dipole Attractions:

- Ion-dipole attractions are responsible for the hydration of ions in water
- The attachment of water molecules to a central ion is known as **hydration**
- The interactions are particularly strong for **small ions with large charges** (large charge intensity) e.g. Al^{3+} ions
- **Charge density**: ratio of the charge on an ion to its volume i.e. a small ion with a +1 charge has a higher charge density than a larger ion with a +1 charge
- The larger the charge density, the stronger the ion-dipole interaction

Protic Solvent:

- H-bond **acceptor** and H-bond **donor**
- e.g. H_2O
- A protic solvent will **solvate** both **+ve** and **-ve** ions

Aprotic Solvent:

- H-bond **acceptor only**
- Aprotic solvent will only **solvate +ve** ions

CHEM1201 Lecture 2: Solutes and Solvents

- **Strongest dispersion forces =** largest molecule
- **Smallest polarizability** = smallest atom (electron cloud held more tightly to nucleus)
- 2 conditions for X and Y which are necessary for H-bonding to occur are;
  - X and Y should both be electronegative atoms (N, O, F)
  - Y needs to have a lone pair of electrons to be a H-bond acceptor

$$X-H\cdots Y$$
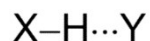
Substance Dissolving:

- **Step 1: Solute particles separate**
  - solute (aggregated) + heat = solute (separated)
  - endothermic
- **Step 2: Solvent particles separate**
  - solvent (aggregated) + heat = solvent (separated)
  - endothermic
- **Step 3: Solute and solvent particles mix**
  - solute (separated) + solvent (separated) = solution + heat
  - exothermic

The total ΔH that occurs when a solution forms is ΔH_{soln}.
$$\Delta H_{soln} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{mix}$$

If the sum of the **endothermic** terms ($\Delta H_{solute} + \Delta H_{solvent}$) is smaller than the **exothermic** term (ΔH_{mix}), ΔH_{soln} is negative; that is, the process is exothermic (mixing will occur to an appreciable extent).

If the sum of the **endothermic** terms ($\Delta H_{solute} + \Delta H_{solvent}$) is larger than the **exothermic** term (ΔH_{mix}), ΔH_{soln} is positive; that is, the process is endothermic (mixing may not occur to an appreciable extent).

Lattice Energy:

- Lattice energy of an ionic solid is a measure of the strength of the electrostatic interactions between oppositely charged ions
- Lattice energy works to keep **ions in the solid state**
- e.g. $\Delta H_{lattice}(KF) = -821 \text{ kJ/mol}$

    - $KF_{(s)}$ dissolves in H_2O; KF lattice is broken. This is endothermic (opposite of lattice energy).
    $$KF_{(s)} \rightarrow K^+_{(g)} + F^-_{(g)} \quad -(\Delta H_{lattice})(KF) = -(-821) \text{ kJ/mol}$$
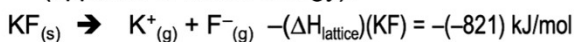
    - H_2O molecules are separated and K^+ and F^- ions are hydrated (surrounding the ions with H_2O)
    $$K^+_{(g)} + F^-_{(g)} \rightarrow K^+_{(aq)} + F^-_{(aq)} \quad \Delta H_{hydration} = -819 \text{ kJ/mol}$$
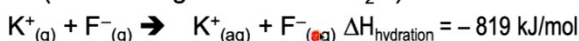
    [$\Delta H_{hydration}$ combines $\Delta H_{solvent}$ and ΔH_{mix}]

    Therefore, $\Delta H_{solution} = -(\Delta H)_{lattice} + \Delta H_{hydration} = -(-821)+(-819) = +2 \text{ kJ/mol}$

- Enthalpy of hydration depends on the charge density
- The higher the charge density, the more -ve is the enthalpy of hydration
- Thermodynamically favourable (exothermic)

Solutions and Entropy:

- ΔH_{soln} is one of two factors that determine whether a solute dissolves in a solvent
- When $\Delta S_{soln} > 0$ mixing is favourable
- The solution process involves the 'competition' between ΔH_{soln} and ΔS_{soln}
- Systems tend towards a state of **lower enthalpy and higher entropy**
- In many cases the magnitudes of ΔH_{soln} and ΔS_{soln} determine whether a solution will form

Vapour Pressure:

- Liquid molecules move at various speeds
- At any instance some liquid molecules possess enough KE to overcome the IMFs and escape into the gas (vapour) phase
- The **weaker the IMFs** the larger is the number of molecules that can escape and therefore the **higher is the vapour pressure**
- At a fixed temperature, the vapour pressure of a liquid is a measure of the tendency of its molecules to escape from the liquid and enter the gas phase
- Vapour pressure increases with **increasing temperature**
- To overcome the IMFs in a liquid, a species must have a **minimum KE**. As the temperature of the liquid is increased the fraction of molecules having sufficient KE to overcome these forces can escape into the vapour phases increases dramatically with temperature
- **Volatile** substances are those with a high vapour pressure
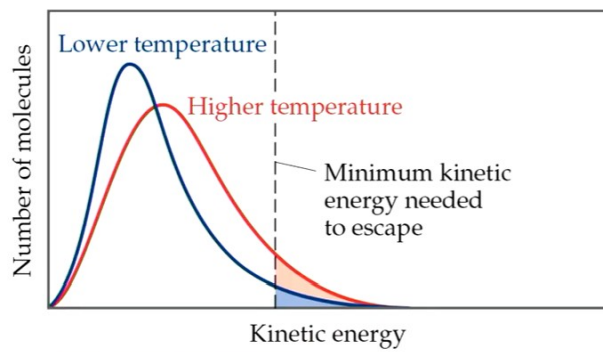
Blue area = number of molecules having enough energy to evaporate at lower temperature

Red + blue areas = number of molecules having enough energy to evaporate at higher temperature

- What would you expect to have a more negative enthalpy of hydration (exothermic)? Is asking for the stronger ion-dipole interaction = **largest charge density** = smallest ion to largest charge ratio
- **Enthalpy of vaporisation** = energy required to vaporise 1 mol of a liquid to the vapour
- Low vapour pressure = Hard to vaporise = Stronger IMFs
- Higher vapour pressure = Easy to vaporise = Weaker IMFs
- How is the vapour pressure of a liquid in a closed container affected when the quantity of liquid is doubled at constant temperature? Vapour pressure stays the same at constant temperature

Quantitative Expressions of Concentration:

- **Molarity (M)** = n(solute)/litre of **solution** (volume changes with temperature)
- **Molality (m)** = n(solute)/kg of **solvent** (mass does not change with temperature)
- In dilute solutions, 1kg = 1L therefore molarity and molality are almost the same in dilute water solutions
- **Volume % (%v/v)** = volume of solute/volume of solution x 100
- **Weight % (%w/w)** = mass of solute/mass of solution x 100
- Mole fraction, $\chi(A) = \frac{n(A)}{n(A)+n(B)}$

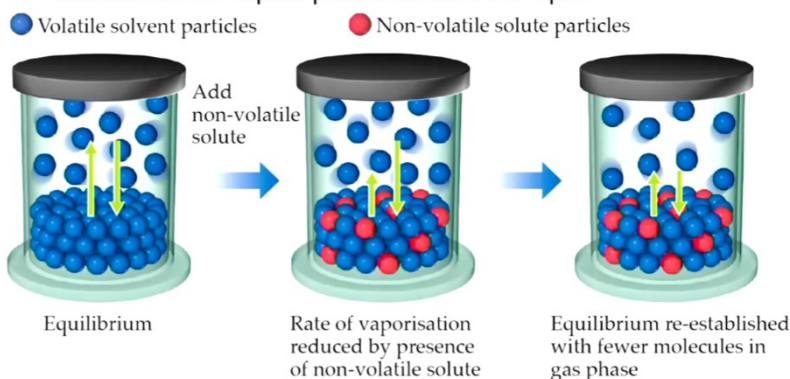Colligative Properties of Non-Volatile Non-Electrolytes:

- The lowering of the freezing point and the raising of the boiling point are physical properties that depend on the quantity (concentration) but not the **type** of solute particles
- Such properties are called **colligative properties**
- Why is salt put-on ice-covered roads? Salt **lowers freezing point** of ice, so easier to remove ice of roads
- Why is ethylene glycol added to car radiators? Ethylene glycol **increases boiling point** of radiator
- Colligative means depending on the collection
- Colligative properties depend on the collective effect of the number of solute particles
- Other colligative properties are **vapour pressure lowering** and **osmotic pressure**

Vapour Pressure Depression:

- A substance that no measurable vapour pressure is **non-volatile**
- Adding a non-volatile solute (negligible vapour pressure) to a solvent always lowers the vapour pressure depression of the solvent
- The extent of vapour pressure depression is proportional to the solute concentration
- **Vapour pressure depression is proportional to the number of particles (Vapour pressure is a colligative property)**
- Consider a closed system containing a pure solvent at a fixed temperature. The rates of condensation and vaporisation are equal
- Add a non-volatile solute to the solvent. What happens? The number of solvent particles on the surface is lower so fewer vaporise per unit time. To maintain equilibrium fewer solvent molecules need to condense and equilibrium is therefore established at a lower vapour pressure

- The presence of the NVS alters the behaviour of the solvent. The **NVS disrupts the evaporation process** by attracting solvent particles via IMFs
- The presence of the NVS does not affect condensation as the **NVS is not present in the vapour**

The presence of a non-volatile solute in a liquid solvent results in the reduction of the vapour pressure above the liquid.

● Volatile solvent particles   ● Non-volatile solute particles

Equilibrium

Add non-volatile solute

Rate of vaporisation reduced by presence of non-volatile solute

Equilibrium re-established with fewer molecules in gas phase

- **Thermodynamic argument to support vapour pressure depression**: A solution consisting of a NVS and a liquid solvent (H_2O), forms spontaneously because of the increase in entropy that accompanies mixing. In effect the solvent molecules are stabilised in their liquid state by this process, and thus have a lower tendency to escape into the vapour phase. Therefore when a **NVS is present, the VP of a solvent is lower than the VP of the pure solvent at a fixed temperature.**
- A pure solvent vaporises because the **vapour has a greater entropy than the liquid**
- However, as the solvent in a solution already has a greater entropy than the pure solvent, and so the solvent has less tendency to vaporise in order to gain entropy
- Thus by either argument, equilibrium is reached at a lower vapour pressure for the solution

Raoults Law:

Raoult's Law: $\Delta p = \chi_{solute} \times P°_{solvent}$

- Raoults Law predicts that the vapour pressure of a solvent in a solution is proportional to the amount of the solvent present

Δp is the vapour pressure lowering

χ_{solute} is the mole fraction of the solute [χ is the particle counter]

$P°_{solvent}$ is the vapour pressure of the pure solvent at a fixed temperature

- In an ideal solution, particles experience the same IMFs in solution as they do in the pure liquid
- This means that it takes the same amount of energy for solvent molecules to break away from the surface in either case – not very likely event

Raoult's Law (Non-Ideal Solutions)
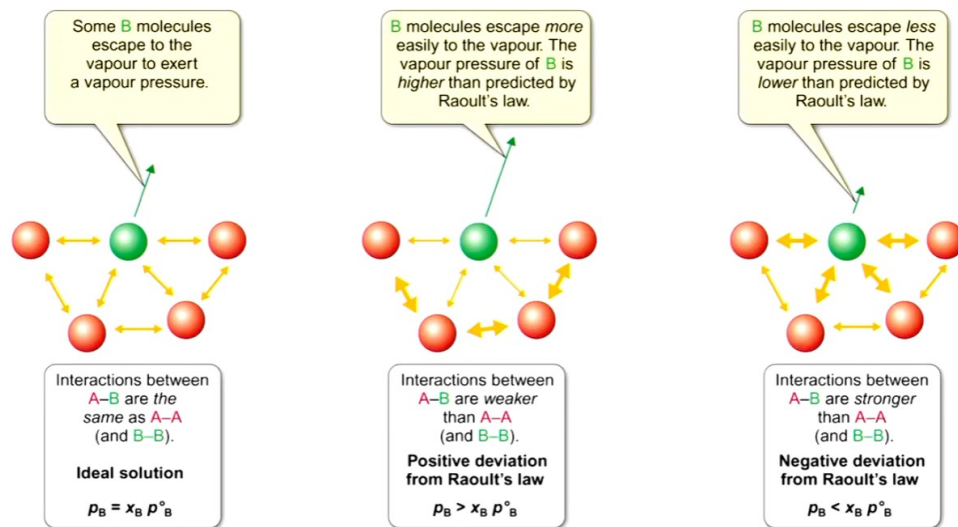
- **Raoults law** only works for **ideal solutions**. IMFs between particles in the mixture (solution) are exactly the same as those in the pure liquids. The tendency for particles to escape in the liquids is the same as in the solution – not likely!!
- **Raoults law** only works for **dilute solutions**
- **Positive deviation** from Raoults law: Here the VP of the mixture is higher than you would expect from an ideal mixture. IMFs between **A and B are weaker** than the IMFs between A and A, and B and B. Hence the enthalpy of mixing tends to be positive (**endothermic**)
- **Negative deviation** from Raoults law: Here the VP of mixture is lower than you would predict from an ideal mixture. IMFs between **A and B are stronger** than the IMFs between A and A, and B and B. Hence the enthalpy of mixing tends to be negative (**exothermic**)
- **Density of solution = Mass of solution/Volume of solution**
- If you are going from mass to volume, or volume to mass, you need to know density of the solution (for the conversions between %w/v to mole fraction, and molality to molarity, you need to know the density of the solution)
- **Mole fraction of component A + Mole fraction of component B = 1**
- **%w/v** means **g solute/100ml solution**

Boiling Point Elevation:

- The bp of a liquid is the temperature at which its **vapour equals the external pressure**
- The vapour pressure of a solution is **lower** than the external pressure at the solvent's bp because the **vapour pressure of a solution is lower than that of the pure solvent at any temperature**
- Therefore the solution does not yet boil
- A higher temperature is needed to raise the solution's vapour pressure to equal the external pressure
- **When does a liquid boil?**
  - What does the addition of a non-volatile solute to a solvent do to the vapour pressure of the pure solvent? Lowers it
  - What does the addition of a non-volatile solute to a solvent do to the bp of the solution (solvent + solute)? Elevates it
- E.g. Consider pure water at 100 degrees Celsius
  - There is a much higher entropy in gaseous water than liquid water
  - Gaseous water and liquid water coexist
  - If sugar (NVS - colligative) were added, this would make the liquid water molecules more **disordered** in the solution (relative to pure liquid water)
  - Gaseous water is **not affected** as the sugar does not evaporate at 100 degrees Celsius – sugar does not enter the vapour phase
  - So, the **gain in entropy on evaporation of liquid water is now less because liquid water in solution (liquid water + sugar) is already more disordered**
  - To get evaporation to go after this, you need to increase the temperature further – thus **boiling point elevation**
  - Another way to view this is as soon as you dump sugar into water, the **intermolecular forces** occurring between sugar (NVS) and liquid water are **stopping liquid water molecules from reaching the surface and escaping into the vapour phase = slowing down rate of evaporation**
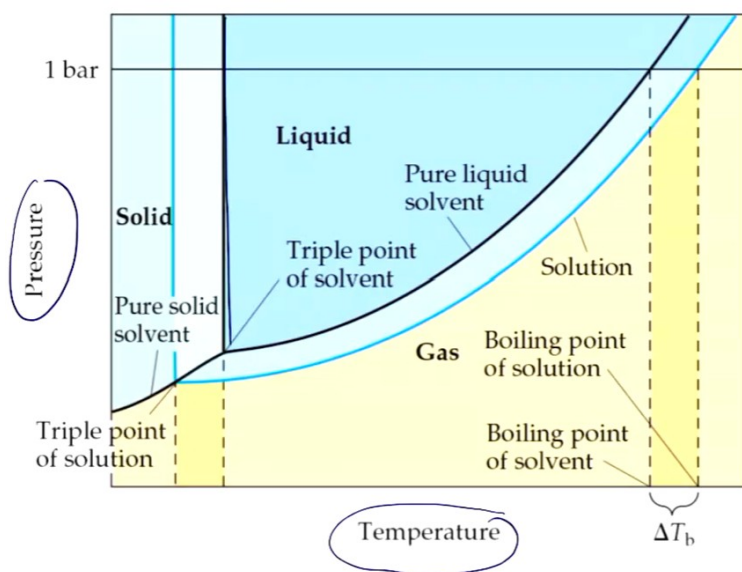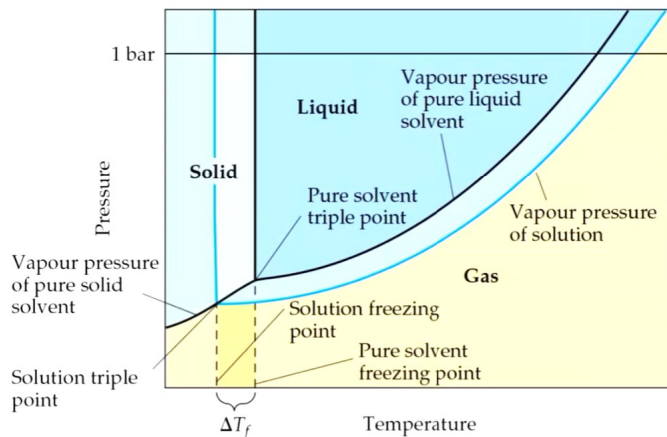
Phase diagram illustrating boiling point elevation.

Triple point: the temperature and pressure where solid, liquid and gas co-exist for a particular substance.

Freezing Point Depression:

- Pure water freezes at 0 degrees Celsius at 1atm pressure (recall vapour pressure of liquid water and ice are same at 0 degrees Celsius)
- Add a **NVS** to the water, and the water in the solution **does not freeze at 0 degrees Celsius** because the water in the solution has a lower vapour pressure (due to IMFs between new NVS and water molecules) than that of the pure ice. No ice forms in these conditions
- By putting NVS into water, you are disrupting (slowed) rate of conversion between liquid water to solid water (**rate of fusion** = liquid to solid)
- Cool the solution down, what happens? As the solution cools the **vapour pressure of ice and that of liquid water in the solution become equal**. The temperature at which this occurs is the new freezing point of the solution. The freezing point has been **depressed**
- To achieve **equilibrium**, a slower rate of melting must occur. This occurs at a lower temperature, hence the temperature of freezing for solution is lower than the temperature of freezing for pure liquid water
- The presence of a NVS alters the behaviour of the solvent. NVS disrupts the freezing process by attracting solvent particles. NVS does not affect melting as it is not in the solid
- Another way to say this;
  - Some water (solvent) molecules freeze leaving behind a slightly more **concentrated** solution. A dynamic equilibrium is set up between solution and solid pure solvent.
  - In the case of a freezing solution, the species in the solution in contact with the frozen pure solvent are not all solvent molecules, causing a slower rate at which particles move from solution to solid than in the pure liquid
  - To achieve dynamic equilibrium, a correspondingly slower rate of escape of molecules from the solid crystal lattice must occur. This slower rate occurs at a lower temperature and so the freezing point of the solution is lower than that of the pure solvent

Freezing Point Depression

Phase diagram illustrating freezing point depression.

Summary:

- Both freezing point depression (ΔT_f) and boiling point elevation (ΔT_b) are proportional to the concentration of the solute particles
- ΔT_f and ΔT_b are colligative properties
- ΔT_f and ΔT_b are proportional to molality (molality is the particle counter – because molarity is not **temperature independent**, molality is)
- **$\Delta T_b = K_b$ x molality** and **$\Delta T_f = K_f$ x molality**
- **K_b** is a constant called the molal boiling point elevation constant (unit degrees Celsius kg/mol)
- **K_f** is a constant called the molal freezing point depression constant (unit degrees Celsius kg/mol)
- **K_b and K_f are properties of the solvent. Each solvent has a unique K_b and K_f**
- In term of water, much easier to use **ΔT_f (1.86)** rather than **ΔT_b (0.512)** because freezing point depression is much larger and thus easier to detect with less chance of errors.

- **Vapour Pressure Trend**: Why might VP go up, and then start to go down? As mixing occurs, VP increases, indicating positive deviation from Raoults Law (so the IMFs between A and B are **weaker** than the IMFs between A and A, & B and B, hence most likely the reaction is **endothermic** = **positive enthalpy of solution**
- Lowest boiling point = highest vapour pressure

Osmosis:

- Osmosis is an example of **passive transport**-species driven by thermal motion move **down a concentration gradient** set up between solutions separated by a semipermeable membrane (SMP) or biological membrane in living systems
- Osmosis is important because it determines where H2O goes and how it is controlled. H2O is never actively transported. No enzyme actively transports H2O. Organisms manage H2O by managing osmosis
- Certain materials including many membranes in biological systems are semi-permeable
- Semi-permeable membranes generally allow small molecules such as water to pass through, but block larger solute molecules
- If a SPM is placed between two solutions of different concentration, solvent molecules move in both directions through the SPM
- The concentration of the **solvent is higher** in the solution containing **less solute.** The rate with which the solvent passes from the less concentrated to the more concentrated is greater than the rate in the opposite direction
- There is a net movement of solvent molecules from the less concentrated solution into the more concentrated solution
- Or you can say water will move from an area of high-water concentration to an area of low water concentration
- **Osmosis: net movement of solvent from a source of high solvent concentration to low solvent concentration**
- In other words, you can't push the solvent uphill!
- The pressure required to prevent osmosis by the solvent is called **osmotic pressure** (Π)

Osmotic Pressure (Π):

- The osmotic pressure (Π) is proportional to the number of solute particles in a given volume of solution (molarity)
- Π is proportional to molarity (molarity is the particle counter)
- **Π = molarity x R x T**
- R is the gas constant = 0.08206 L atm mol^{-1} K^{-1}
- T is the temperature in Kelvin

Crenation and Lysis:

- If 2 solutions of identical osmotic pressure are separated by an SPM, no osmosis will occur. These 2 solutions are isotonic (relative term)
- If cells are bathed in a **hypertonic** solution (a solution having a higher Π than the cells) the cells will shrivel as a result of a **net flow of water out of the cells** – **crenation**
- The opposite effect, called **lysis**, occurs when cells are bathed in a **hypotonic** solution (a solution having a lower Π than the cells). The cells will rupture because of a **net flow of water into the cells**

- An example is osmosis through red blood cell wall
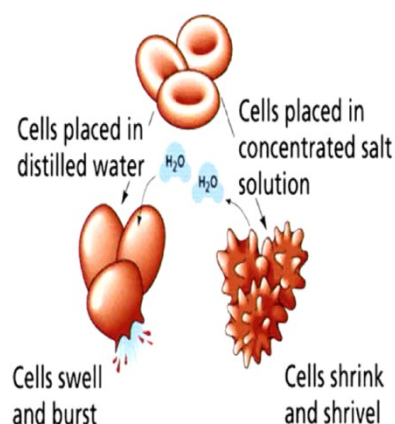
- **Contact lenses** consist of **isotonic** (0.15M) **NaCl** to prevent any changes to the volume of the corneal cell

Colligative Properties of Electrolyte Solutions:

- Colligative properties depend on what feature? **Number of solute particles**
- In a sugar (**non-electrolyte**) solution: 1 mol sugar gives how many moles of particles? **1 mol** particles, because the sugar does not dissociate into ions
- In a NaCl (**electrolyte**) solution: 1 mol NaCl gives how many moles of particles? **2 mol** particles, because NaCl dissociates into Na^+ and Cl^- ions
- The **Van't Hoff factor (i)** relates the number of moles of solute dissolved to the number of moles of particles in solution
- $i_{expected}$ can be obtained from a salts formula unit
- For NaCl, $i_{expected}$ = 2 (Na^+ and Cl^-)
- For $CaCl_3$, $i_{expected}$ = 3 (Ca^{2+} and 2 Cl^-)
- What does $i_{expected}$ assume?
  - It **assumes complete dissociation** of the solute. No ion interaction. Ions move independently of each other
  - However in reality this is **not true**, because the ions clump together (they **ion-pair**)
  - Consider NaCl, some Na^+ and Cl^- ions bump into each other, ion pair and are counted as an ion-pair (that is **one unit**)
  - Ion pairing is most important in concentrated solutions
  - In very dilute solutions, $i_{expected}$ = i_{actual} approximately
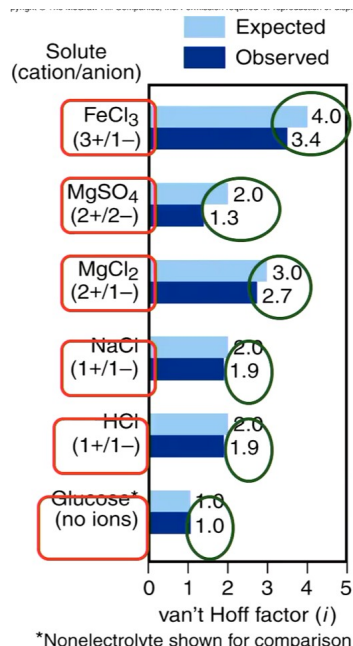
Non-ideal behavior of electrolyte solutions (0.05 molal). $i_{observed} <$ $i_{expected}$.

The deviation is due to ionic interactions that reduce the number of "free" ions in solution.

*Nonelectrolyte shown for comparison

- To calculate the colligative properties of electrolyte solutions, incorporate the van't Hoff factor into the 4 equations
- $\Delta T_b = K_b \times$ molality $\times i$
- $\Delta T_f = K_f \times$ molality $\times i$
- $\Pi =$ molarity $\times R \times T \times i$
- $\Delta p = \chi_{solute} \times P^{\circ}_{solvent}$ where $\chi_{solute} = \dfrac{n(solute) \times i}{n(solute) \times i + n(solvent)}$

CHEM1201 Lecture 6: Review of Colligative Properties and Introduction to Kinetics

- During **osmosis**, solvent diffuses through a membrane, but solutes do not
- **Isotonic** = two solutions with the same osmotic pressure
- For electrolytes, the actual **van't hoff factor** will be slightly lower than the expected van't hoff factor due to **ion-paring**
- If a patient were given an intravenous drip of pure water, then **red blood cells** would swell and possibly burst = water goes from area of high-water concentration to area of low concentration = **osmosis**
- e.g. if you have 50**% w/v**, that means 50g per 100ml of solution
- Higher boiling point = larger $i_{expected}$ = larger ΔT_b
- **Osmolality** = molality measured by a colligative property and so it takes into account the number of particles in solution
- In **dilute solutions**, **osmolarity = osmolality (approximately)**
- **True Molality** = what you make up in the lab and does not take into account solute dissociation
- i_{actual} **= osmolality/true molality**

Underlying Theme of Colligative Properties:

- 4 colligative properties of non-volatile solutes (NVS)
- Each property rests on the inability of solute particles to cross between 2 phases
- They cannot enter the gas phase, which leads to **vapour pressure lowering** and **boiling point elevation**
- They cannot enter the solid phase, which leads to **freezing point depression**
- They cannot cross a semipermeable membrane which leads to the development of **osmotic pressure**
- The presence of a solute decreases the mole fraction of the solvent, which lowers the number of solvent particles leaving the solution per unit time. This lowering requires an adjustment to reach equilibrium again. This adjustment to reach the new balance in numbers of particles crossing between two phases per unit time results in the measure colligative property

Collision Theory:

- **Collision theory** is used to explain why chemical reactions occur at different **rates**
- Collision theory states that for a reaction to proceed, the reactant particles must collide. The **more collisions** per unit time, the **faster the reaction**
- For a reaction to proceed, reactant particles must;
    a) Collide with sufficient energy to break reactant bonds = overcome activation energy (E_A)
    b) Be in an orientation favourable for breaking these bonds

Factors Affecting Reaction Rate:

- **Concentration Effects**:

- Rate of reaction generally increases with increasing reactant concentration. Here, more reactant particles are available to collide per unit time and so the more often a reaction can occur between them
- **Temperature Effects:**
  - Reaction rate of most chemical processes increases with increasing temperature. As the average KE increases, the particles move faster so they collide more frequently per unit time and possess greater energy when they collide
- **Phase and Surface Area Effects:**
  - If the reactants are uniformly dispersed in a single **homogeneous** solution, the number of collisions per unit time depends on concentration and temperature
  - If the reaction is **heterogeneous** the reactants are in 2 different phases and the reactant collisions can occur only at the **interface**
  - The number of collisions per unit time is reduced relative to the homogeneous case and so is the reaction rate
  - e.g. car engines use surface area effects to increase reaction rates – microscopic droplets of fuel burn more rapidly than a liquid stream
- **Solvent Effects:**
  - The nature of the solvent (**protic** vs **aprotic**) can affect reaction rate
  - An increase in solvent polarity accelerates the rates of reactions where a charge is developed in the activated complex from neutral or slightly charged reactant.
- **Catalyst Effect:**
  - Most catalysts are highly selective and so determine the product of a reaction by accelerating only one of several possible reactions that could occur

CHEM1201 Lecture 7: Reactions and Reaction Rates

- Ions that are least likely to **ion-pair** = ions with the smallest charge density

- The larger the **charge density**, the higher the magnitude of **heat of hydration**
- **Electrolyte** solutions generally behave less ideally (that is, they don't obey **Raoults Law**) as the solute concentration increases

Reaction Rates:

- Reaction rates are usually expressed as the **concentration of reactant consumed** or the **concentration of product produced** per unit time
- Unit: **mole per litre per unit time (mol $L^{-1}s^1$)**
- Consider a reaction A → B:

$$\text{Rate} = \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$$

- Convention: all reaction rates are expressed as positive numbers
- A negative sign is inserted in front of $\Delta[A]/\Delta t$ to make it a positive number
- For the reaction;

  $C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow$ ④ $CH_3CH_2OH(aq) + 4\ CO_2(g)$
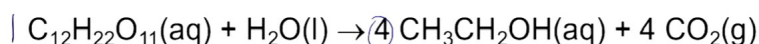
- It can be said that ethanol is formed 4 times faster than sucrose is consumer, or that is;

$$\text{Rate} = \left(\frac{\Delta[C_2H_5OH]}{\Delta t}\right) = \ominus\ \frac{4\Delta[\text{sucrose}]}{\Delta t}$$

- Convention: Rate of reaction is expressed in terms of the reactant or product that has the smallest coefficient in the balanced equation, or that is;

$$\text{Rate} = -\frac{\Delta[\text{Sucrose}]}{\Delta t} = \frac{1}{4}\frac{\Delta[C_2H_5OH]}{\Delta t}$$

Example $Rate = \frac{-\Delta[SO_2]}{\Delta t} = -2\frac{\Delta[O_2]}{\Delta t} = \frac{+\Delta[SO_3]}{\Delta t}$

The key step in the industrial production of sulfuric acid is the reaction of SO_2 with O_2 to produce SO_3.

$$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$$
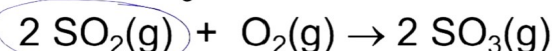
Write the expressions for the reaction rate in terms of the rate of change of concentration of each species.

$Rate = \frac{-\Delta[O_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[SO_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[SO_3]}{\Delta t}$
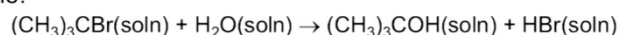
Rate Laws:

- A **rate law** describes the relationship between **reactant rates** and **reactant concentrations** (often called a differential rate law)
- Rate laws are mathematical descriptions of experimentally verifiable data

Reaction Orders:

- For a reaction with the general equation:

aA + bB → cC + dD

- The experimentally determined rate law has the form:

Rate = k [A]^x [B]^y

- k is the rate constant (dependent on type of reaction and reaction conditions)
- x and y are the **experimentally** determined reaction **orders** with respect to [A] and [B]. That is the degree to which the reaction rate depends on the [A] and [B]
- overall order is x + y

Example: Consider the following reaction done in the solvent acetone.

$$(CH_3)_3CBr(soln) + H_2O(soln) \rightarrow (CH_3)_3COH(soln) + HBr(soln)$$

$$Rate = -\frac{\Delta[(CH_3)_3CBr]}{\Delta t} = k[(CH_3)_3CBr]^x[H_2O]^y$$

The experimentally determined rate law is:

$$Rate = k[(CH_3)_3CBr]^1[H_2O]^0$$

Reaction is first-order wrt [$(CH_3)_3CBr$] and zero-order wrt [H_2O].
Overall order = 1+0 = 1 (first)

What do the reaction orders tell us in practical terms?
Doubling the [$(CH_3)_3CBr$] will double the reaction rate.
In a first-order process the rate is directly proportional to the change in that reactant concentration.
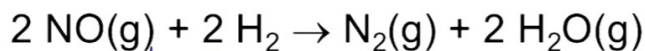Changing the [H_2O] will have no effect on the reaction rate.
In a zero-order process the rate is not affected by the change in that reactant concentration.

Rate Constant:

- The **rate constant (k)** is related to how fast a reaction proceeds at a fixed temperature
- Rate constants are the key to deciding on the relative importance of reactions in a system of interconnected reactions, such as in the atmosphere
- Rate constant, k, **changes with temperature** and determines the way the reaction rate varies with temperature – shown by **Arrhenius equation**

Example

The following data were measured for the reaction of nitric oxide with hydrogen.

$$2 NO(g) + 2 H_2 \rightarrow N_2(g) + 2 H_2O(g)$$

initial concentration

Exp	$[NO]_0$(M)	$[H_2]_0$(M)	Initial rate (mol L^{-1} s^{-1})
1	0.10	0.10	1.23 x 10^{-3}
2.	0.10	0.20	2.46 x 10^{-3}
3.	0.20	0.10	4.92 x 10^{-3}

Determine the rate law for this reaction and calculate the rate constant, k.

$$Rate = k [NO]^X [H_2]^Y$$

X : order WRT [NO] ; Y : order WRT [H$_2$]

Exp 1, 3 : [H$_2$] is constant
Double [NO]
Rate ↑ 4 times
$\left(\dfrac{4.92 \times 10^{-3}}{1.23 \times 10^{-3}} \approx 4 \right)$

∴ **2ND order WRT [NO]**

$\underset{\uparrow}{2} \overset{X \leftarrow \text{order WRT [NO]}}{=} \underset{\uparrow}{4}$

Double [NO]   rate ↑ 4 times

∴ X = 2

Exp 1, 2 : [NO] is constant
Double [H$_2$]
Rate doubles

∴ 1st order WRT [H$_2$]

Y ← order WRT [H$_2$]

$\underset{\uparrow}{2} \overset{Y}{=} \underset{\uparrow}{2}$

double [H$_2$]   Rate doubles

∴ Y = 1

$$Rate = k [NO]^2 [H_2]^1$$

⇑ rate law

$$k = \frac{Rate}{[NO]^2 [H_2]^1}$$

$$= \frac{1.23 \times 10^{-2}}{(0.10)^2 (0.10)} = \boxed{1.2}$$

unit: $\frac{mol\,L^{-1}\,s^{-1}}{mol\,L^{-1}\,mol\,L^{-1}\,mol\,L^{-1}}$

$$\Rightarrow \frac{s^{-1}}{mol^2 L^{-2}}$$

$$\Rightarrow \boxed{L^2\,mol^{-2}\,s^{-1}}$$

$\underset{3^{RD}\,order\,rate\,constant\,unit.}{\uparrow}$

zero: $mol\,L^{-1}\,s^{-1}$

1st order: s^{-1}

2ND order: $L\,mol^{-1}\,s^{-1}$

3RD order: $L^2\,mol^{-2}\,s^{-1}$

Integrated Rate Laws:

- **Zero Order elementary reactions.**

  For a reaction of the type: $A \rightarrow$ products
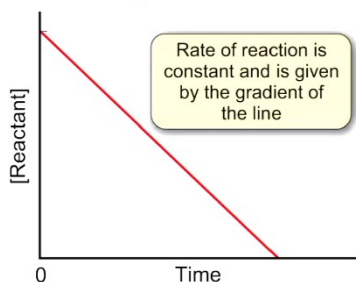
  $$\text{Rate} \ = \ -\frac{\Delta[A]}{\Delta t} = k[A]^0 = k \text{ since } [A]^0 = 1$$

  That is, rate is independent of [A].

  The integrated rate law is: $[A]_t = -kt + [A]_0$

  A plot of $[A]_t$ vs t gives a straight line with slope –k.

  ### Shapes of zero-order curves

  Rate of reaction is constant and is given by the gradient of the line

  For the zero-order reaction A→ products, a plot of [A] vs time is a straight line. k can be found from the gradient.

- **First Order elementary reactions.**

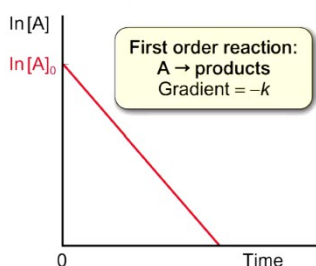 For a reaction of the type: $A \rightarrow$ products

  $$\text{Rate} \ = \ -\frac{\Delta[A]}{\Delta t} = k[A]^1$$

  That is, rate is directly proportional to [A].

  The integrated rate law is: $\ln[A]_t = -kt + \ln[A]_0$.

  A plot of $\ln[A]_t$ vs t gives a straight line with slope –k.

  ### Shapes of first-order curves

  First order reaction:
  A → products
  Gradient = –k

  For the first order reaction A→ products, a plot of ln[A] vs time is a straight line. k can be found from the gradient.

- **Pattern**: if a plot of [reactant] vs time is not linear, but a plot of ln[reactant] vs time is linear, reaction is first-order in respect to [reactant]

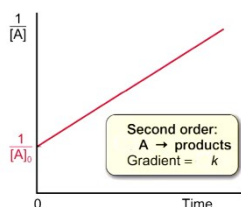- **Second Order elementary reactions.**

  For a reaction of the type: $A \rightarrow$ products

  $$\text{Rate} = \ -\frac{\Delta[A]}{\Delta t} \ = k[A]^2$$

  That is, rate is directly proportional to $[A]^2$
  The integrated rate law is: $1/[A]_t = kt + 1/[A]_0$.

For the second order reaction A➜ products, a plot of 1/[A] vs time is a straight line. k can be found from the gradient.

- **Pattern**: If a plot of ln[reactant] vs time is not linear, but a plot of 1/[reactant] vs time is linear, reaction is second-order in respect to [reactant]

Half Lives:

- Another approach to describing reaction rates is based on the time required for the concentration of a reactant to decrease to one-half its initial value for $[A_0]$ to $[A]_{0/2}$)
- This period of time is called the half-life ($t_{1/2}$)
- Independent of its initial concentration
- The half-life of a first-order reaction is independent of the reactant concentration

- Zero-order reactions

$$t_{1/2} = \frac{[A]_0}{2k}$$

- First-order reactions

$$t_{1/2} = \frac{0.693}{k}$$

- Second-order reactions

$$t_{1/2} = \frac{1}{k[A]_0}$$

Summary

	ZERO	FIRST	SECOND
Rate Equation	Rate = k[A]^0	Rate = k[A]^1	Rate = k[A]^2 for A → products
Integrated rate equation	[A]$_t$ = −kt + [A]$_0$	ln[A]$_t$ = −kt + ln[A]$_0$	1/[A]$_t$= 1/[A]$_0$ + kt
Plot [A]$_t$ vs time	**Straight line**	Curve	Curve
Plot ln[A]$_t$ vs time	Curve	**Straight line**	Curve
Plot 1/[A]$_t$ vs time	Curve	Curve	**Straight line**
Half life	Not constant	Constant	Not constant for A → products

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Molecularity and the Rate Determining Step

The molecularity of an elementary reaction is the number of molecules that collide during that step in the mechanism.
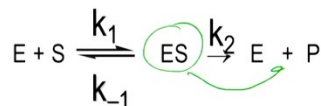
If there is a single reactant molecule in an elementary step the step is <u>unimolecular</u>.

Two reactant molecules: <u>bimolecular</u>.

Three reactant molecules: <u>termolecular</u>.

Enzyme Kinetics

Michaelis and Menten proposed a simple model to account for the kinetic behaviour of enzymes.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \overset{k_2}{\rightarrow} E + P$$

A reactant molecule known as the substrate (S) binds to a specific location on the enzyme (E) to form an ES complex.

The substrate binds to the active site through IMFs.

k_1 is the rate constant for the association of E and S.

k_{-1} is the rate constant for the dissociation of S from ES.

k_2 is the rate constant for the formation of product from ES.

The ES complex has two possible fates!

1. It can dissociate into E and S with rate constant k_{-1}.

2. It can proceed to form a product, P with rate constant k_2.

It is assumed that none of the product reverts to the initial substrate.

Enzyme Kinetics $E + S \underset{k_{-1}}{\overset{k_{-1}}{\rightleftharpoons}} ES \overset{k_2}{\rightarrow} E_1$

Two assumptions:
1. [S]>>[E] ← all E is as ES.
2. (System is in steady-state). ES complex is being formed and broken down at the same rate so that the overall [ES] is constant. That is, [ES] during the reaction, is constant.

Rate of formation of ES = $k_1 [E][S]$
Rate of breakdown of ES = $k_{-1}[ES] + k_2[ES]$

Assuming steady-state:

Enzyme Kinetics

$$[ES] = \frac{[E][S]k_1}{(k_{-1} + k_2)}$$

This is simplified by defining a new constant, K_M called the Michaelis constant.

$$K_M = \frac{k_{-1} + k_2}{k_1}$$

Therefore: $[ES] = \frac{[E][S]}{K_M}$

K_M is equal to the dissociation of the ES complex if k_2 is $<< k_{-1}$.

K_M is a measure of the strength of the ES complex.

High K_M: weak binding

Low K_M: strong binding.

K_M is specific for a particular enzyme.

Enzyme Kinetics

In addition to the Michaelis constant, there is also the Michaelis-Menten equation.

$$V = \frac{V_{max}[S]}{[S] + K_M}$$

V_{max}(maximum reaction rate) is attained when the enzyme sites are saturated with substrate.

[S] is the substrate concentration.

V is the reaction rate.

$V_{max} = k_2[E]_{total}$. That is, when [ES] is at a maximum. That is, $[ES]=[E]_{total}$. That is, 100%of the enzyme is subtrate-bound.

Formulas:

$\Delta T_b = K_b$ x molality x i

$\Delta T_f = K_f$ x molality x i

Π = molarity x R x T x i

$\Delta p = \chi_{solute}$ x $P^\circ_{solvent}$ where $\chi_{solute} = \dfrac{n(solute) \text{ x } i}{n(solute) \text{ x } i + n(solvent)}$

$\Delta H_{soln} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{mix}$

Raoult's Law: $\Delta p = \chi_{solute}$ x $P^\circ_{solvent}$

$$\text{Rate} = \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$$

Rate = k $[A]^x [B]^y$

zero: $mol\,L^{-1}s^{-1}$

1st order: s^{-1}

2nd order: $L\,mol^{-1}s^{-1}$

3rd order: $L^2\,mol^{-2}s^{-1}$