DEPARTMENT OF CHEMISTRY
FOURAH BAY COLLEGE
UNIVERSITY OF SIERRA LEONE

CHEM 211

THE PHYSICAL PROPERTIES OF GASES, LIQUIDS AND SOLUTIONS

CREDIT HOURS	2.0
MINIMUM REQUIREMENTS	Pass in CHEM 111
REQUIRED FOR	Honours

CHEM 211 – THE PHYSICAL PROPERTIES OF GASES, LIQUIDS AND SOLUTIONS

UNIT 1 – THE PHYSICAL PROPERTIES OF GASES

Course Outline:	What are the postulates of the kinetic model of matter and how do they apply to gases? What is the difference between a real and an ideal gas and what are the requirements for a gas to be "ideal"? What is the ideal gas equation and how is it derived? How can the ideal gas equation be used to derive Boyle's, Charles', Gay-Lussac's, Avogadro's and Dalton's Laws? How can the ideal gas equation be used to derive expressions for molecular energies, molecular velocities, molar masses, densities and heat capacities of ideal gases? How can the ideal gas equation be used to molar masses of gases? What is the Maxwell-Boltzmann distribution of molecular energies and velocities? How can this distribution be used to deduce the probability of a molecule having a certain energy or speed? What are the different ways to measure average molecular speed? How can the collision frequency in a gas be calculated? What is the mean free path of a gas and how can it be calculated? What are transport properties of gases and how can the different transport properties of ideal gases be predicted? What causes a gas not to behave like an ideal gas and how does its behaviour change as a result? What are PV isotherms and what is the compressibility factor? What is the Joule-Thompson effect and under what conditions do gases liquefy? How can the real behaviour of gases be used to calculate molecular mass accurately? How can the behaviour of real gases be predicted using equations of state? How do molecules behave in electric fields and how can this behaviour be used to determine the dipole moment of a molecule? How do molecules behave in magnetic fields and how can this behaviour be used to determine the number of unpaired electrons in a molecule?
Lesson 1:	*Kinetic Theory of Matter and the Ideal Gas Equation*
Lesson 2:	Derivation of the Gas Laws from first principles
Lesson 3:	Partial Pressures and Molar Heat Capacities
Lesson 4:	Maxwell-Boltzmann distribution of molecular energies and velocities
Lesson 5:	Collision Frequency and Mean Free Path
Lesson 6:	Transport Properties of Gases
Lesson 7:	The Behaviour of Real Gases
Lesson 8:	Equations of State for Real Gases
Lesson 9:	The effect of electric fields on molecules
Lesson 10:	The effect of magnetic fields on molecules

items in italics are covered at senior secondary level

CHEM 211 – THE PHYSICAL PROPERTIES OF GASES, LIQUIDS AND SOLUTIONS

UNIT 1 – THE PHYSICAL PROPERTIES OF LIQUIDS AND SOLUTIONS

Course Outline:	How does the vapour pressure of a liquid vary with temperature? What is the link between vapour pressure and boiling point? What is Raoult's Law? What is an ideal mixture? How can Raoult's Law be used to generate vapour pressure-composition and boiling point-composition curves for ideal mixtures? Why are some solutions not ideal? What are azeotropes? What is the theory of fractional distillation? What are colligative properties of liquids? How does the presence of non-volatile solutes affect the properties of liquids?
	What are electrolytes? What are strong and weak electrolytes? What are the colligative properties of electrolytes? What are Faraday's Laws of electrolysis? What is meant by the resistance and conductance of solutions and how are they measured? What is meant by the specific conductivity and molar conductivity of solutions and what is a cell constant?
	What is the relationship between molar conductivity and concentration for strong and weak electrolytes and why? What is meant by the molar conductivity of an ion? What is limiting molar conductivity and how is it determined for strong and weak electrolytes? What is Kohlrausch's Law? What are transport numbers and ionic velocities and how are they measured? Why do different ions have different mobilities? How can conductance measurements be used to determine acid dissociation constants and degree of dissociation for weak acids, and solubilities and solubility products of sparingly soluble salts? What are conductometric titrations?
Lesson 1:	*Vapour Pressure, Ideal Solutions and Raoult's Law*
Lesson 2:	Non-Ideal solutions and Azeotropes
Lesson 3:	Colligative Properties of Liquids
Lesson 4:	Strong and Weak Electrolytes
Lesson 5:	Resistance and Conductance of Solutions and *Faraday's Laws of Electrolysis*
Lesson 6:	Conductivity, molar conductivity and its dependence on concentration
Lesson 7:	Limiting molar conductivity and Kohlrausch's Law
Lesson 8:	Transport numbers, ionic velocities and ionic mobilities
Lesson 9:	Applications of Conductance Measurements

UNIT 1 – THE PHYSICAL PROPERTIES OF GASES

Lesson 1

1) OVERVIEW OF THE KINETIC MODEL OF MATTER

- The kinetic theory of matter proposes that gases behave as follows:
    - gas molecules are in constant motion in random directions
    - they frequently collide with one another and these collisions are elastic, but energy can be transferred from one molecule to another as a result of these collisions
    - the total energy of the particles in a closed system remains constant at a given temperature
    - the average kinetic energy of the particles is directly proportional to the temperature

2) REAL AND IDEAL GASES

- An ideal gas is a gas in which:
    - Gas particles are hard spheres which experience no attractive forces on each other
    - The volume occupied by the gases is negligible compared with the volume of the container
    The behaviour of ideal gases can be predicted using simple principles of Physics

- A real gas is a gas which does not model the expected behaviour of an ideal gas, because either the intermolecular forces are significant (large molecules at high pressures and low temperatures) or because the volume of the molecules is a significant fraction of the total space available (very high pressures) or because a significant amount of energy can be absorbed by the molecule without increasing its speed (complex molecules).

- Gases are therefore most likely to demonstrate ideal behaviour if the molecules are small and simple, the pressures are low and the temperatures are relatively high.

- The behaviour of real gases is much more difficult to model than the behaviour of ideal gases.

3) THE IDEAL GAS EQUATION

- An equation of state is an equation which describes how the physical state of a material depends on a particular physical condition or range of physical conditions. Equations of state are used to describe the physical properties of solids, liquids and gases.

- Gases differ from solids and liquids in that many cases their behaviour does not depend on the identity of the gas – in other words, all gases behave in very similar ways and so the same equations of state can be used to describe many gases

- The ideal gas equation is an equation of state which relates the pressure, volume, temperature and amount of substance for an ideal gas. It is made by combining three of the ideal gas laws:

  Boyle's Law: $PV = k_1$ Charles' Law: $\frac{V}{T} = k_2$ Avogadro's Law: $\frac{V}{n} = k_3$

  Combining all three laws you get: $\frac{PV}{nT} = R$ or $\mathbf{PV = nRT}$ This is the ideal gas equation

  P = pressure in Pa, V = volume in m^3, n = number of moles, T = temperature in K

  R = molar gas constant ($8.31 \text{ Jmol}^{-1}\text{K}^{-1}$) and represents the value of $\frac{PV}{T}$ for one mole of a gas

- The ideal gas equation can also be expressed in terms of individual molecules, by replacing the molar gas constant R with the Boltzmann constant k ($1.38 \times 10^{-23} \text{ JK}^{-1}$) to give $\mathbf{PV = nkT}$

  $K = \frac{R}{L}$ where L is Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$)

- The ideal gas equation can be used to calculate P, V, n or T of a gas if the other three quantities are known.

- If the mass can be measured, the ideal gas equation can also be used to calculate the molar mass (m_r) of a gas: $n = \frac{m}{m_r}$ and $n = \frac{PV}{RT}$ so $\mathbf{m_r = \dfrac{mRT}{PV}}$

  The **Victor-Meyer** apparatus is designed to measure the molar mass of a gas as follows:
  - A small glass bottle containing a known mass of the volatile substance under investigation is dropped into the inner part of a Victor Meyer tube, which has a bulb at the lower end and a side-arm at the upper end which leads to a trough filled with water; a liquid is placed in the outer part of the Victor Meyer tube which must have a boiling point at least 30 K higher than the substance under investigation; the outer liquid is heated until the liquid under investigation boils; when it does so it will displace a fixed volume of air, the volume of which can be measured; the ideal gas equation can be used to deduce the moles of air displaced, which will be equal to the number of moles of vapour produced by the substance

  The **Dumas** method involves the use of a retort shaped bulb of known volume, with a very thin side arm
  - The bulb is weighed, the mass of air inside is deduced from the volume of the bulb and the known density of air at that temperature; the mass of the bulb alone can therefore be calculated; a small quantity of the desired liquid is added to the bulb, which is then immersed in another liquid (with a higher boiling point) and heated until the liquid in the bulb has completely boiled; the tip of the bulb is then sealed and the bulb is allowed to cool to room temperature; the bulb is then weighed and the mass of the substance in the bulb can therefore be calculated; the pressure at the time of the experiment was atmospheric pressure and the temperature at the time of the experiment was the temperature of the liquid being heated

- Also, given that density $(\rho) = \frac{m}{V}$, the molar mass of a gas an also be expressed as a function of its density: $\mathbf{m_r = \dfrac{\rho RT}{P}}$

Note that mass, molar mass and density must all be in SI units (kg, kgmol^{-1} and kgm^{-3} respectively)

Lesson 2

4) DERIVING THE IDEAL GAS EQUATION FROM FIRST PRINICPLES

- Consider a cube of length l; each inner face of the cube will have an area l^2 so the total area (A) of the inner faces/walls of the cube will be $6l^2$ and the volume (V) of the cube will be l^3; this cube contains N molecules, each of mass m, moving with velocity u_x in the x direction
  The momentum of each molecule before a collision with a wall is mu_x. The momentum of each molecule after the collision is $-mu_x$, so the change in momentum during the collision is $2mu_x$.
  The distance between the walls is l, so the time between collisions is $\frac{l}{u_x}$, so there are $\frac{u_x}{l}$ collisions per second
  So the total change in momentum per second (ie the force exerted F) per molecule with the x walls is:
  change in momentum per collision x number of collisions per second $= 2mu_x \times \frac{u_x}{l} = F = 2\frac{mu_x^2}{l}$
  This is also happening in the y and z directions, so the total force exerted on the walls of the container by each molecule is:
  $2\frac{mu_x^2}{l} + 2\frac{mu_y^2}{l} + 2\frac{mu_z^2}{l} = \frac{2m}{l}(u_x{}^2 + u_y{}^2 + u_z{}^2) = 2\frac{mu^2}{l}$
  So the total force exerted by all the molecules in the container $= 2\frac{mNu^2}{l}$
  So the pressure in the container $P = \frac{F}{A} = = \frac{F}{6l^2} = \frac{2mNu^2}{6l^3} = \frac{mNu^2}{3V}$, so $PV = \frac{mNu^2}{3}$
  Molar mass $m_r = mL$ and n = N/L, then $mN = m_r n$ so $\mathbf{PV = \frac{m_r nu^2}{3}}$ **(equation 1)**

- The kinetic theory of matter states that the kinetic energy E of a gas is directly proportional to the temperature, so $E = k_1 T$
  The kinetic energy of one molecule can be given as $\frac{mv^2}{2}$, so $\frac{\mathbf{mv^2}}{\mathbf{2}} = k_4 T$
  The total kinetic energy of all the molecules is therefore $\frac{mNv^2}{2} = \frac{m_r nv^2}{2} = Nk_4 T = nLk_4 T$ (equation 2)

- Combining equations 1 and 2 gives the ideal gas equation:
  $PV = \frac{m_r nu^2}{3}$ so $\frac{3PV}{2} = \frac{m_r nu^2}{2} = nLk_4 T$ so $PV = \frac{2nLk_4 T}{3}$
  If $\frac{2Lk_4}{3}$ is expressed as a single constant R, then $\mathbf{PV = nRT}$

- If $k_4 = \frac{3R}{2L}$ then the kinetic energy for one molecule of a gas can be written $\mathbf{E = \frac{3RT}{2L}}$ or $\mathbf{\frac{3kT}{2}}$ and the kinetic energy for one mole of a gas can be written $\mathbf{E = \frac{3RT}{2}}$; E per molecule can also be expressed as $\frac{mv^2}{2}$, so E per mole is $\frac{m_r v^2}{2}$, so $3RT = m_r v^2$ and $\mathbf{v = \sqrt{\frac{3RT}{m_r}}}$

- The equations $PV = \frac{mNu^2}{3}$ and $\frac{mNu^2}{2} = k_4 T$ can be used to derive the three gas laws individually:
  - PV = nRT so PV is constant for a given number of moles of gas at constant temperature (Boyle's Law)
  - $\frac{V}{T} = \frac{nR}{P}$ so $\frac{V}{T}$ is constant for a given number of moles of gas at constant pressure (Charles' Law)
  - $\frac{V}{n} = \frac{RT}{P}$ so $\frac{V}{n}$ is constant at constant temperature and pressure (Avogadro's Law)

Lesson 3

5) HEAT CAPACITY OF IDEAL GASES

- The molar heat capacity of a gas is the energy required to heat one mole of the gas by 1 K. It can be measured either at constant volume (C_v) or at constant pressure (C_p).

- More energy is needed to heat a gas by 1 K at constant pressure (when the volume increases) than at constant volume (when the pressure increases). This is because extra energy is needed to increase the volume against an external pressure.

- At constant volume, $E = \frac{3RT}{2}$ so $C_v = \frac{E}{T} = \frac{3R}{2}$

- At constant pressure, the same energy $\frac{3R}{2}$ is needed to heat the gas by 1 K, but energy is also needed to expand the gas; this energy $\Delta E = P\Delta V$; according to the ideal gas equation, $V = \frac{nRT}{P}$ so $\Delta V = \frac{nR\Delta T}{P}$, so
$\Delta E = nR\Delta T$
So $\frac{\Delta E}{\Delta T} = nR$ and so the energy required per mole for the expansion $= R$
So $C_p = \frac{3R}{2} + R = \frac{5R}{2}$

- So $C_v = \frac{3R}{2}$ and $C_p = \frac{5R}{2}$

- The heat capacity at constant volume and pressure for individual molecules can be written as $\frac{3k}{2}$ and $C_p = \frac{5k}{2}$ respectively

6) DALTON'S LAW OF PARTIAL PRESSURES

The ideal gas Law can be used to derive Dalton's Law of Partial Pressures:
The pressure exerted by gas A in a container can be given as: $p_A = \frac{n_a RT}{V}$
The pressure exerted by gas A in a container can be given as: $p_B = \frac{n_b RT}{V}$
The total pressure exerted by both gases is therefore $p_A + p_B = \frac{n_a RT}{V} + \frac{n_b RT}{V} = \frac{(n_a + n_b)RT}{V} = \frac{nRT}{V} = P$
So the total pressure in a mixture of gases is the sum of the partial pressures of individual gases.
$\frac{p_a}{P} = \frac{n_a RT}{V} / \frac{nRT}{V} = \frac{n_a}{n}$ so $p_A = \frac{n_a}{n}P$ where $\frac{n_a}{n}$ is the mole fraction of A in the mixture

Lesson 4

7) MAXWELL-BOLTZMANN DISTRIBUTION OF MOLECULAR ENERGIES AND VELOCITIES

- During collisions, energy is transferred from one molecule to another and as a result the speed of both molecules will change. As a result, not all of the molecules will have the same kinetic energy at a given time, but there will be a distribution of molecular energies and velocities.

- Maxwell and Boltzmann derived the probability distribution function for molecular velocities (v) in a single direction:

$$p = \left(\frac{m_r}{2\pi RT}\right)^{\frac{1}{2}} e^{\left(\frac{-m_r v^2}{2RT}\right)}$$

- This can be converted into a distribution function in three dimensions for molecular speeds (c):

$$p = 4\pi v^2 \left(\frac{m_r}{2\pi RT}\right)^{\frac{3}{2}} e^{\left(\frac{-m_r v^2}{2RT}\right)}$$

- Using $E = \frac{1}{2}mc^2$, this can also be converted into a distribution function for molecular energies:

$$p = \frac{2\pi E^{\frac{1}{2}}}{(\pi RT)^{\frac{3}{2}}} e^{\left(\frac{-E}{RT}\right)}$$

- The first part of this distribution $\frac{2\pi E^{\frac{1}{2}}}{(\pi RT)^{\frac{3}{2}}}$ is the Maxwell part and it shows p increasing with $\sqrt{E}$; this happens because the more energy there is, the greater the number of ways to distribute the energy amongst the molecules and so the more probable the energy (the entropy factor); the second part of this distribution $e^{\left(\frac{-E}{RT}\right)}$ is the Boltzmann part and shows p decreasing rapidly with increasing E; the number of molecules with energy much higher than the mean will be small and will decrease with increasing energy

- To calculate the probability of a molecule having a speed or energy within a particular range, it is necessary to integrate the distribution function within those two limits; however this is difficult because the function takes the form $y = \frac{e^{-x}}{\sqrt{x}}$ which is not easily integrated; an approximation can be made at high energies by assuming that the Maxwell part of the equation is approximately constant at high energies; the resulting integral then simplifies to $\int_{E_1}^{E_2} p\, dE = \frac{2}{\sqrt{\pi}}(e^{-\frac{E_1}{RT}} - e^{-\frac{E_2}{RT}})$; note that this approximately is only valid when the range of energies under consideration is significantly greater than the average energy

- Increasing the temperature and decreasing the value of m_r increases the proportion of molecules with higher speeds; the Maxwell-Boltzmann distribution of molecular energies is best demonstrated graphically (the plots of probability against speed and probability against energy are very similar)
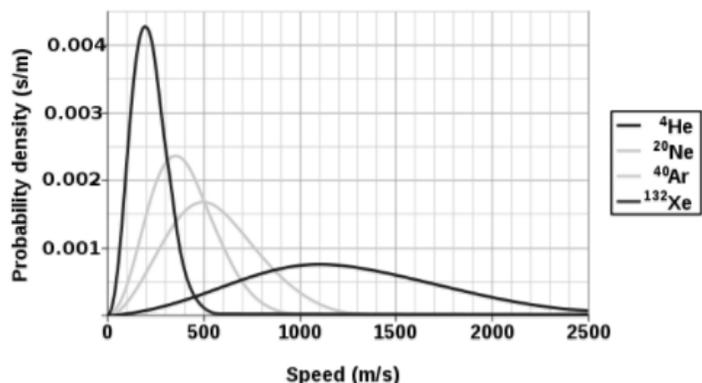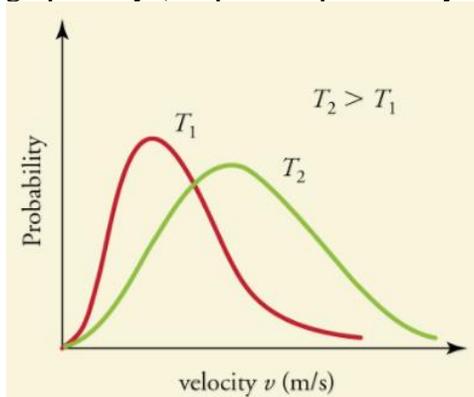
www.chem.libretexts.org

8) DIFFERENT MEASURES OF MOLECULAR SPEED

- We know that the total kinetic energy of one mole of molecules $= \tfrac{1}{2}m_r v^2 = \dfrac{3RT}{2}$

  Therefore $v^2 = \dfrac{3RT}{m_r}$

  Therefore **v (or the root mean square speed)** $= \sqrt{\dfrac{3RT}{m_r}}$

- Analysis of the Maxwell-Boltzmann distribution gives the **most probable speed** of the molecules as $\sqrt{\dfrac{2RT}{m_r}}$

- Further analysis of the Maxwell-Boltzmann distribution gives the **average speed** of the molecules as $\sqrt{\dfrac{8RT}{\pi m_r}}$

- The values of root mean square speed, average speed and most probable speed are therefore not the same value. Root mean square speed is important for kinetic energy considerations, but average speed is generally more useful in predicting individual particle behaviour

  $v_{rms} > v_{av} > v_{mp}$ in the ratio $\sqrt{3} : \sqrt{\dfrac{8}{\pi}} : \sqrt{2}$
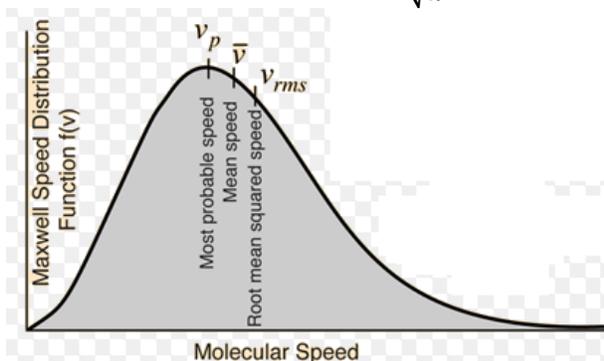
www.hyperphysics.phy-astr.gsu.edu

Lesson 5

9) MEAN FREE PATH AND COLLISION FREQUENCY

- The kinetic model of matter can also be used to predict two important quantities in gas kinetics – the collision frequency and the mean free path

- The effective collision area of a molecule with another of the same type can be given by $A = \pi d^2$

The effective collision area is

$$A = \pi d^2$$
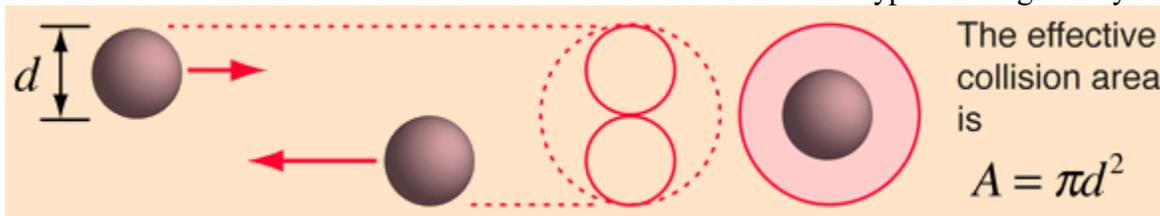
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- If the velocity of the particles is v, the relative velocity of the two particles is $v\sqrt{2}$ (this is the relative velocity when two particles collide at right angles)

- In one second, the volume swept by this collision area will be πd^2 x relative velocity $= \pi d^2 v\sqrt{2}$

- The number of collisions in this time depends on the number of other molecules in this volume of space N so the number of times a molecule will collide with other molecules in this volume of space per second $= N\pi d^2 v\sqrt{2}$

There are two useful consequences of this:

- The total number of colliding molecules in this space per second $= N \times N\pi d^2 v\sqrt{2} = N^2\pi d^2 v\sqrt{2}$
  so number of collisions per second, **or collision frequency** $Z = \dfrac{\pi v d^2 N^2 \sqrt{2}}{2} = \dfrac{\pi v d^2 N^2}{\sqrt{2}}$
  By substituting in the expression for $v = \sqrt{\dfrac{8RT}{\pi m_r}}$ you get $Z = \dfrac{\pi d^2 N^2}{\sqrt{2}}\sqrt{\dfrac{8RT}{\pi m_r}} = 2d^2 N^2 \sqrt{\dfrac{\pi RT}{m_r}}$

- If there are two different colliding particles A and B, the total number of times a particle A will collide with particle B will be $N_B\pi(r_A + r_B)^2 v\sqrt{2}$ so the total number of collisions between A and B will be $\pi(r_A + r_B)^2 N_A N_B v\sqrt{2}$
  The m_r in the velocity equation needs to be changed to 2μ, where μ is the reduced mass $\dfrac{\mu_A\mu_B}{\mu_A + \mu_B}$
  so $v = \sqrt{\dfrac{4RT}{\pi\mu_r}}$ so $Z_{AB} = (r_A + r_B)^2 N_A N_B \sqrt{\dfrac{8\pi RT}{\mu_r}}$

- The time interval between individual molecules colliding $= \dfrac{1}{\pi v d^2 N\sqrt{2}}$
  so the distance travelled in between collisions, or the **mean free path** λ, $(v \times t) = \dfrac{1}{\pi v d^2 N\sqrt{2}}, = \dfrac{1}{\pi d^2 N\sqrt{2}} = \dfrac{1}{\pi d^2 LC\sqrt{2}}$ so $\lambda = \dfrac{1}{\pi d^2 LC\sqrt{2}}$ **or** $\dfrac{RT}{\pi d^2 LP\sqrt{2}}$

Lesson 6

10) TRANSPORT PROPERTIES OF GASES

Transport properties are the properties of a compound or material associated with the transport of a particular quantity through it. Three common examples of transport properties are:
- diffusion or effusion: the transport of mass
- viscosity: the transfer of momentum
- thermal conductivity: the transfer of energy

The kinetic model of matter can be used to predict a number of transport properties of gases, including diffusion, thermal conductivity and viscosity.

(a) Diffusion and Effusion

- Diffusion is the mixing of gases until they reach a uniform composition. Effusion is the escape of gases through a small hole into a vacuum. The rates of diffusion and effusion both follow Graham's Law.

- The simple idea that all gases at the same temperature have the same average kinetic energy can be used to prove Graham's Law of diffusion (or effusion):

  At a given temperature, $m_1 v_1^2 = m_2 v_2^2$, so $\frac{v_2^2}{v_1^2} = \frac{m_1}{m_2}$ and $\frac{v_2}{v_1} = \sqrt{\frac{m_1}{m_2}}$

  Since masses are directly proportional to density, this relationship can also be expressed as: $\sqrt{\frac{\rho_1}{\rho_2}}$

  So the relative rates of diffusion of two gases v_1 and v_2 is inversely proportional to the square roots of their molar masses or densities – this is **Graham's Law**.

- The absolute rate of diffusion of a gas (f_n) in $molm^{-2}s^{-1}$ is proportional to the concentration gradient $\frac{d[C]}{dx}$:

  $f_n = D\frac{d[C]}{dx}$ (this is known as Fick's first Law)

  D is the **coefficient of diffusion** (m^2s^{-1})

- D is related to the velocity of the particles and their mean free path: $D = \frac{lv}{3}$

  It can therefore be shown that D is proportional to $T^{\frac{3}{2}}$, P^{-1}, d^{-2} and $m_r^{-\frac{1}{2}}$

(b) Viscosity

- Viscosity is the resistance offered by one part of a gas to the movement of another part of the gas. It results from the transfer of momentum from one part of the gas to another and is not a result of intermolecular attraction. It is therefore a feature of all gases.

- The rate of transfer of momentum in a gas (f_p) in $kgm^{-}s^{-2}$ is proportional to the velocity gradient $\frac{dv}{dx}$:

$$f_p = \eta \frac{dv}{dx}$$

η is the **viscosity** ($kgm^{-1}s^{-1}$)

- η is related to the velocity of the particles and their mean free path: $\eta = \frac{lvm_r[A]}{3}$

It can therefore be shown that η is proportional to $T^{\frac{1}{2}}$, d^{-2} and $m_r^{\frac{1}{2}}$

(c) Thermal Conductivity

- Energy flows from hot bodies to cold bodies until the temperature (or kinetic energy) of the molecules is equalised.

- The rate of heat flow f_E in a gas (Jm^2s^{-1}) is proportional to the temperature gradient $\frac{dT}{dx}$

$$f_E = \kappa \frac{dT}{dx}$$

κ is the **thermal conductivity** ($JK^{-1}m^{-1}s^{-1}$)

- κ is related to the velocity of the particles and their mean free path: $\kappa = \frac{lvC_V[A]}{3}$

It can therefore be shown that κ is proportional to $T^{\frac{3}{2}}$, d^{-2} and $m_r^{-\frac{1}{2}}$

(d) Summary of transport properties of gases

Transport Property	Rate of Transfer	Constant of Proportionality
Diffusion	$f_n = D \frac{d[C]}{dx}$	$D = \frac{\lambda v}{3}$
Viscosity	$f_p = \eta \frac{dv}{dx}$	$\eta = \frac{\lambda v m_r[A]}{3}$
Thermal Conductivity	$f_E = \kappa \frac{dT}{dx}$	$\kappa = \frac{\lambda v C_V[A]}{3}$

Lesson 7

10. THE BEHAVIOUR OF REAL GASES

(a) Observing deviations from ideal gas behaviour

(i) Compressibility factor

Most gases only obey the ideal gas laws at a limited range of pressures and temperatures – generally low pressure and high temperature.

In ideal gases, $\dfrac{PV}{nRT} = 1$

If ideal gas behaviour is not observed, however, then $\dfrac{PV}{nRT}$ is not equal to 1 and is given a value known as the compressibility factor (z).

At low temperatures and reasonably high pressures, the attractive forces between the particles need to be considered – these forces cause the V to be lower than expected for a particular P and cause P to be lower than expected for a particular V. These factors cause PV to be lower than expected (ie PV < nRT and z < 1); at low temperatures and relatively high pressures, z < 1.

At very high pressures, the size of the particles themselves becomes a consideration; the larger the particles, the less space there is in which for them to move. When this factor is significant, P is larger than expected for a particular V and V is larger than expected for a particular P. These factors cause PV to be higher than expected (ie PV > nRT and z > 1). At high temperatures and very high pressures, z > 1.

At low pressures, z = 1 and gases display ideal behaviour.

The stronger the intermolecular forces between gas molecules, and the larger the molecular size, the less likely a gas is to show ideal behaviour.

Non-ideal behaviour in gases can be illustrated in plots of compressibility factors against pressure (these plots are also called isotherms).
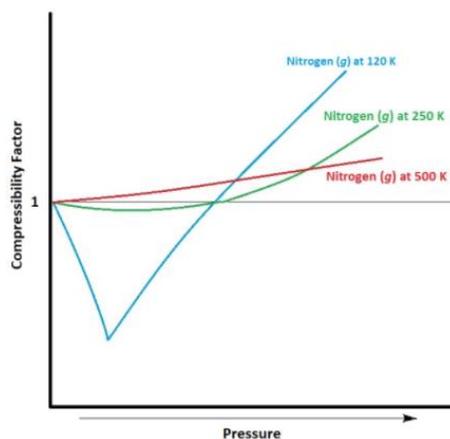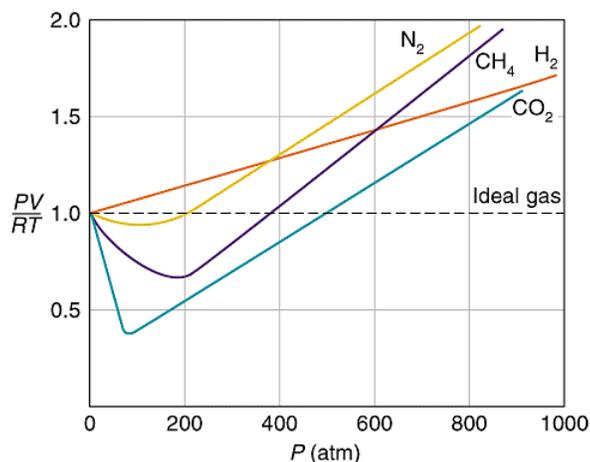
(ii)   The Joule-Thomson effect

- The Joule-Thomson effect describes how the temperature of a gas changes if a gas is expanded under conditions in which its total energy cannot change (ie an adiabatic process). It can be described in the form of a coefficient μ, in which $\mu = \frac{dT}{dP}$. M is positive if a decrease in pressure causes a decrease in temperature, and negative if a decrease in pressure causes an increase in temperature.

- The Joule-Thomson effect results from attractive and repulsive forces between molecules. Ideal gases do not display the Joule-Thomson effect and $\mu = 0$.

- If the attractive forces between molecules are more significant than the repulsive forces, then work is required to expand the gas, so kinetic energy will be converted into potential energy and the gas will cool down. This is the case for most typical gases at room temperature (μ is positive).

- If the repulsive forces between molecules are more significant than the attractive ones, then the expansion of the gas will reduce these repulsions, potential energy will be converted into kinetic energy and the gas will heat up. This is typical at very high pressures and temperatures (μ is negative).

(iii)   Liquefaction

- Below a certain temperature, the intermolecular forces will be strong enough to cause the molecules to stick together, meaning that the gas will begin to condense into a liquid. This will happen if the temperature is low enough for the kinetic energy of the molecules is insufficient to overcome the potential energy of attraction.

- The temperature above which a gas cannot be turned into a liquid, however high the pressure, is called the **critical temperature T_c**. The minimum pressure required to liquify a gas at the critical temperature is called the critical pressure **P_c**. The volume occupied by one mole of a gas at the critical temperature and pressure is called the critical volume **V_c**.

- Above the critical temperature, a decrease in volume will always result in an increase in pressure. Below the critical temperature, a decrease in volume will result in an increase in pressure until the pressure is sufficient to cause the gas to liquefy, at which point a decrease in volume may not cause an increase in pressure. At the critical temperature and the critical pressure, a small change in pressure will not affect the volume.
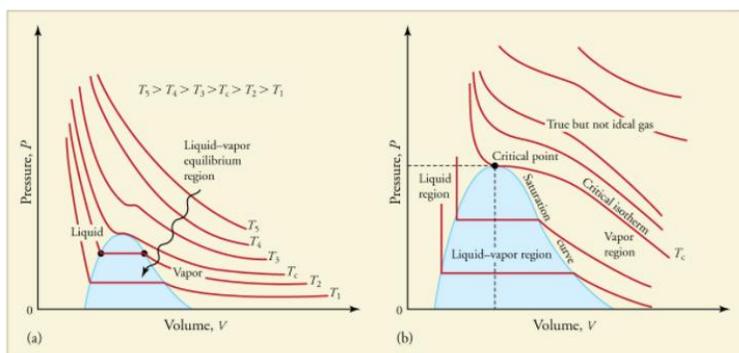
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Lesson 8

(b) Accurate determination of molecular mass

Given that $m_r = \frac{\rho RT}{P}$, it follows that $\frac{\rho}{P} = \frac{m_r}{RT}$ and that the value of $\frac{\rho}{P}$ should be a constant at a particular temperature. However this is only true at $P = 0$, when all gases behave ideally. At pressures close to atmospheric pressure, $z < 1$ and the value of $\frac{\rho}{P}$ is higher than expected.

However the value of $\frac{\rho}{P}$ increases linearly with increasing P at relatively low pressures, which means that a plot of $\frac{\rho}{P}$ against P is a straight line. This line can be extrapolated back to $P = 0$; where the intersect with the $\frac{\rho}{P}$ axis will be equal to $\frac{m_r}{RT}$ and the molecular mass can be determined very accurately.

(c) Modelling the behaviour of real gases:

There have been various attempts to make adjustments to the ideal gas equation to make it more applicable to real gases:

(i)   The Van der Waal's Equation

- Van der Waal proposed that the observed pressure of a real gas would be lowered by intermolecular attractions. These would be observable when particles approached each other and the likelihood of this happening depends on the collision frequency $\left(\frac{n}{V}\right)^2$, so the reduction in pressure would be equal to $\frac{an^2}{V^2}$, where a is a constant
  So **P(ideal) = P(real) $+ \frac{an^2}{V^2}$**

- Van der Waal also proposed that the actual volume of space in a container should be reduced by the volume occupied by the particles themselves, so actual the volume of space $= V - nb$, where n is a constant

- Therefore Van der Waal proposed that $\mathbf{(P + \frac{an^2}{V^2})(V - nb) = nRT}$; this is the Van der Waal's equation

- The stronger the intermolecular forces, the larger the value of a; and in general, the larger the molecular size, the larger the value of b

Gas	a (Pam^{6}mol^{-2})	b (m^{3}mol^{-1})
Hydrogen	0.0247	26.7 x 10^{-6}
Carbon Dioxide	0.364	42.7 x 10^{-6}
Helium	0.0034	23.7 x 10^{-6}
Ammonia	4.17	37.1 x 10^{-6}
Water Vapour	5.46	30.5 x 10^{-6}

- Van Der Waal also showed that when the volume, temperature and pressure of a gas a measured relative to their critical values, they all show very similar deviations from ideal behaviour.
  If reduced pressure $= \frac{P}{P_c}$, reduced temperature $= \frac{T}{T_c}$ and reduced volume $= \frac{V}{V_c}$, then all gases measured at the same reduced temperature, volume and pressure will have the same compressibility factor. This is known as the Law of Corresponding States.

- As a result Van der Waal was able to predict the critical temperature and pressure of different gases by measuring a and b. As a result, if the critical pressure and temperature are known, the Van Der Waal's constants a and b can be calculated.
  It can be shown that $a = \frac{27R^2T_c^2}{64P_c}$ and $b = \frac{RT_c}{8P_c}$

(ii) The Dieterici Equation

The Dieterici equation is very similar to the Van der Waal's equation, but instead of using an arithmetic pressure adjustment $(\frac{an^2}{V^2})$ to estimate the effect of intermolecular attraction, it uses an exponential function as follows: $\frac{P(V-b)}{RT} = e^{\frac{-a}{RTV}}$

- at high temperatures and volumes, $e^{\frac{-a}{RTV}} = 1$ and ideal gas behaviour is observed once the molecular size adjustment (V – b) is accounted for
- The value $e^{\frac{-a}{RTV}}$ is significantly less than one at low temperatures, showing a significant intermolecular attraction

(iii) The Kamerlingh-Onnes (or Virial) Equation

The virial equation expressed PV as a power series of the pressure at a given temperature:

$$\frac{PV}{n} = A + BP + CP^2 + DP^3 + \ldots.$$

In an ideal gas, A = RT and B, C and D are all zero. The coefficients A, B, C and D are known as virial coefficients, which are constant at a particular temperature.

A is always positive and is equal to RT
At low temperatures, B is negative (z < 1) but at high temperatures, B is positive (z > 1)
The remaining coefficients are only significant at very high pressures.

The virial equation can be conveniently written in terms of the compressibility factor of the gas:
$$\frac{PV}{nRT} = 1 + B\frac{P}{RT} + C(\frac{P}{RT})^2 + D(\frac{P}{RT})^3 + \ldots.$$

Lesson 9

1) Electric Fields and Dielectric constants

- The force of attraction between two charges in a vacuum is given by:
  $$F = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2}$$
  q_1 and q_2 = charges, r = separation, ε_o permittivity of free space (resistance to creating an electric field)

- In a different medium, the resistance of the medium to creating an electric field must be considered:
  $$F = \frac{q_1 q_2}{4\pi\varepsilon_0 \varepsilon_r r^2} \quad (\varepsilon_r = \text{dielectric constant of the medium})$$
  This can be converted into potential energy as follows: $E = \frac{q_1 q_2}{4\pi\varepsilon_0 \varepsilon_r r}$
  The greater the dielectric constant, the smaller the electric field strength per unit of charge

- Water has a very high dielectric constant (80) and so the attraction between oppositely charged ions in water is much lower than in a vacuum, which is why water is able to break up many lattices

- The capacitance of capacitors is directly linked to the dielectric constant of the medium between the plates and this is the most convenient way to measure dielectric constants: $\varepsilon_r = \frac{C}{C_o}$

- Dielectric constants are useful for deducing a number of useful properties of the substance:
  - Permanent dipole moments
  - Magnetic moments

2) Dipole Moments of Molecules

- A dipole moment is a separation of electrical charge resulting from the centre of positive charge (z) and the centre of negative charge (z) not being the same place, but separated by a distance l
  The dipole moment (Cm) on a molecule $\mu = zl$ (Cm); a typical dipole moment is in the order of 5 x 10^{-30} Cm, although they are more commonly expressed in Debye units (1D = 3 x 10^{29} Cm)

- All molecules can have a dipole moment induced (μ_i) by an electric field (induced polarization), as the molecules are distorted by the electric field, with the electrons moving closer to the positive plate and the nuclei moving closer to the negative plate. The degree of polarization depends on the electric field strength X (Vm^{-1}) and the polarizability of the molecule α_i: $\mu_i = \alpha_i X$; has units of m^3 and a typical value would be 2 x 10^{-30} m^3; its value is related to the ability of molecules to form Van der Waal's forces

- The induced molar polarization of the molecule $P_i = \frac{4\pi L\alpha_i}{3}$ is the distortion produced in one mole of a substance when the field strength is 1 Vm^{-1} (L = Avogadro's number); the induced molar polarization of the molecule is independent of temperature and has units of m^{3}mol^{-1}; a typical value would be 2 x 10^{-5} m^{3}mol^{-1}

- Some molecules have a permanent dipole moment (μ_o). In the presence of an electric field, these molecules will align themselves to the electric field (orientation polarization); the orientation polarization of the molecule α_o depends on the permanent dipole moment μ_o: $\alpha_o = \frac{3 \times 10^9 \mu_o^2}{kT}$; this leads to an expression for the molar orientation polarization called the Debye equation:
$$P_o = \frac{4\pi L\alpha_o}{3} = \frac{4\pi L \times 10^9 \mu_o^2}{kT}$$
Note that orientation polarization decreases with increasing temperature

- The total molar polarization will be equal to the sum of the induced molar molarization and the molar orientation polarization: $P_t = P_i + P_o$; it can thus be written $P_t = \frac{4\pi L\alpha_i}{3} + \frac{4\pi L \times 10^9 \mu_o^2}{kT}$, and this in turn can be written in the for $P_t = A + \frac{B}{T}$ where $A = \frac{4\pi L\alpha_i}{3}$ and $B = \frac{4\pi L \times 10^9 \mu_o^2}{k}$; a graph of P_t against $\frac{1}{T}$ should therefore give a straight line of gradient B, and from the gradient: $\mu_o = \sqrt{\frac{kB}{4\pi L \times 10^9}}$

- The total molar polarization P_t is related to the dielectric constant of the molecule by the Clausius-Mosotti equation and so can be determined by measuring the dielectric constant and the density:
$$P_T = \frac{(\varepsilon_r - 1)m_r}{(\varepsilon_r + 2)\rho}$$
For gases, $\frac{m_r}{\rho} = \frac{RT}{P}$ so $P_T = \frac{(\varepsilon_r - 1)RT}{(\varepsilon_r + 2)P}$

- The molar polarization P_t of a substance in solution can be measured if the mole fraction of solute and the P_t of the solvent are known: $P_t = n_A P^0_A + n_B P^0_B$; if the mole fraction and P^0_A is known, P^0_B can be calculated

- The dipole moment of a molecule can be determined by measuring the dielectric constant and the density at different temperatures

Lesson 10

3) Magnetic Properties of Molecules

- In a vacuum the attraction between two magnetic point poles is given by $F = \frac{\mu_0 p_1 p_2}{4\pi r^2}$; p_1 and p_2 are the magnitudes of the magnetic poles, r is the distance between them, and μ_0 is the permeability of a vacuum; in any other medium, this is adapted to $F = \frac{\mu_0 \mu_r p_1 p_2}{4\pi r^2}$; μ_r is the relative permeability of the medium

- Diamagnetic substances have no unpaired electrons and so the individual electrons cannot align themselves to the magnetic field; a magnetic field is induced in the electrons which opposes the magnetic field and $\mu_r < 1$ for diamagnetic substances

- Paramagnetic substances have unpaired electrons; these can align themselves to the magnetic field which enhances the magnetic field strength, so $\mu_r > 1$ for paramagmetic substances and μ_r is large for ferromagnetic substances

- The permeability of a particular medium is more conveniently expressed as molar magnetic susceptibility (in $JT^{-2}mol^{-1}$) $\chi_m = \frac{m_r(\mu_r - 1)}{4\pi\rho}$ (for pure substances) or $\chi_m = \frac{(\mu_r - 1)}{4\pi C}$ (for solutions); χ is therefore positive for paramagnetic and ferromagnetic materials and negative for diamagnetic materials

- The total molar magnetic susceptibility of a substance is the sum of its diamagnetic susceptibility and its paramagnetic susceptibility $\chi_m = \alpha_m + \frac{\mu_m^2 L}{3kT}$; α_m is the molar diamagnetic susceptibility and is always negative; $\frac{\mu_m^2 L}{3kT}$ is the molar paramagnetic susceptibility and is related to the value of the inherent magnetic moment μ_m; in practice, if the substance is paramagnetic, the value of α_m is small and can be ignored

- The value of μ_m is related to the number of unpaired electrons in a molecule: $\mu_m = \frac{eh}{4\pi m_e}\sqrt{n(n+2)}$; it can be expressed in SI units of JT^{-1} but is more commonly stated in Bohr-Magnetons (1 BM $= \frac{eh}{4\pi m_e} =$ 9.28 x 10^{-24} JT^{-1})
  For example, a species with one paired electron has an inherent magnetic moment of $\sqrt{3}$ BM and a species with two unpaired electrons has an inherent magnetic moment of $\sqrt{8}$ BM; this can be used to predict the molar paramagnetic susceptibility of a substance

- Specific magnetic susceptibility can be measured by Gouy's method:
  - A cylinder containing the sample is suspended by a wire from one arm of a balance until its lower part is centred between the poles of an electromagnet
  - The mass of the cylinder is counterbalanced by weights in the other
  - The mass needed to restore balance after the electromagnet is switched on is measured
  - $\Delta mg = \frac{\rho \chi_m AH^2}{2m_r}$ or $\frac{C \chi_m AH^2}{2}$

- the diamagnetic component (α_m) is not temperature-dependent but the paramagnetic component decreases with increasing temperature ($\frac{\mu_m^2 L}{3kT}$, where μ_m = inherent magnetic moment); $\chi_m = \alpha_m + \frac{\mu_m^2 L}{3kT}$; A graph of χ_m againt $\frac{1}{T}$ gives you a gradient of $\frac{\mu_m^2 L}{3k}$ and a y-axis intersect of α_m

UNIT 2 – THE PHYSICAL PROPERTIES OF LIQUIDS AND SOLUTIONS

1. PURE LIQUIDS

- In liquids, all particles are **close together** but able to move past each other because some of the bonds between the particles have been broken. The particles are therefore vibrating as well as moving around. Most of the bonds holding the particles together, however, are still intact.
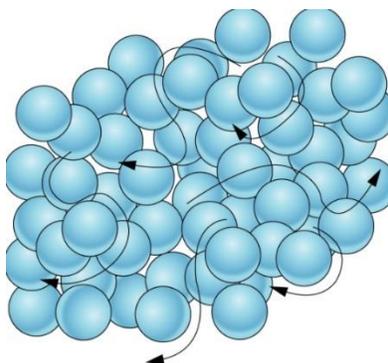
- Liquids do not have a fixed shape and can flow, because the particles can move past each other. Liquids cannot be compressed or squashed because the particles are already close together and have no space to move in to.

- A liquid is a state with lower order (more disorder) and more randomness than a solid.

- As liquids are heated, the particles gain more energy and move around faster. Eventually, the particles have sufficient energy to break the remaining bonds holding the particles together, so the particles are no longer attracted to each other and move apart. When the particles are no longer close together, a change of state from liquid to gas has taken place. This change of state is known as **boiling** (the reverse is known as **condensing**).

- Not all particles in a liquid are moving at the same speed at the same time – the speed changes every time two particles collide. Sometimes, particles at the surface of a liquid have enough energy to escape from the liquid and temporarily become gas particles. This process is known as **evaporation**. As a result, all liquids contain a small amount of vapour immediately above it. The pressure exerted by this vapour is known as the **vapour pressure** of the liquid. In a closed system, this vapour pressure will reach an equilibrium with the liquid. This pressure is known as the **saturated vapour pressure**, and it depends on the liquid and the temperature only (ie it is an intrinsic property of the liquid).

- The saturated vapour pressure is the equilibrium constant K_p for the following equation:

$$H_2O(l) \rightleftharpoons H_2O(g)$$

$K_p = \dfrac{p_{H2O(g)}}{p_{H2O(l)}}$ but because $p_{H2O(l)}$ is fixed, $K_p = p_{H2O(g)}$
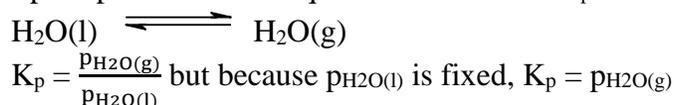
$\Delta G^o = -RT\ln K_p = \Delta H - T\Delta S$ so $\ln K_p = \dfrac{T\Delta S - \Delta H}{RT} = \dfrac{\Delta S}{R} - \dfrac{\Delta H}{RT}$

The ratio of the vapour pressures at two different temperatures, T_1 and T_2, will be $\dfrac{K_{pT1}}{K_{pT2}}$

So $\ln(\dfrac{K_{pT1}}{K_{pT2}}) = \ln K_{pT1} - \ln K_{PT2} = \dfrac{\Delta H}{RT_2} - \dfrac{\Delta H}{RT_1} = \dfrac{\Delta H}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$; this relationship is known as the **Van't Hoff equation**

- As the temperature increases, the vapour pressure of the liquid increases. When the vapour pressure of a liquid equals the atmospheric pressure, the liquid turns into a gas.
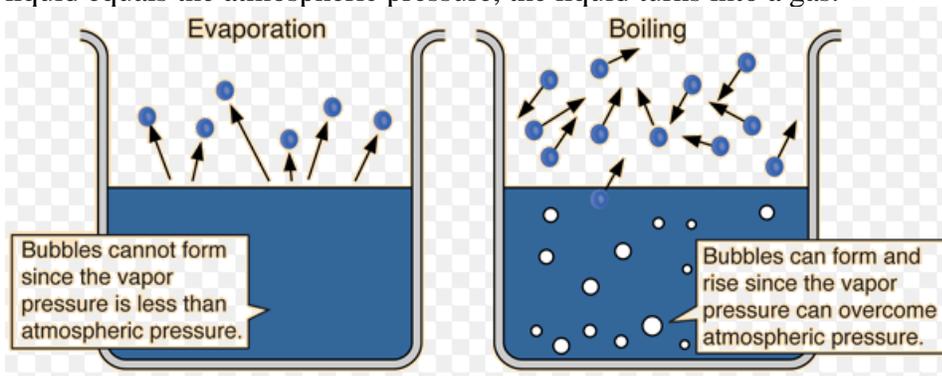
- The temperature at which a liquid turns into a gas is known as the **boiling point** of the liquid. The **standard boiling point** of a liquid is therefore the temperature at which the vapour pressure of the liquid is equal to 1 atm pressure (100,000 Pa – this is normal atmospheric pressure).

2. SOLUTIONS OF LIQUIDS IN LIQUIDS

(a) Ideal Solutions

- If two volatile liquids are mixed together to form a solution, then the vapour pressure of each liquid will depend on the mole fraction of each liquid in the solution: $p_A = \frac{n_A}{n_T}P^0_A$, where p_A is the partial vapour pressure of liquid A, $\frac{n_A}{n_T}$ is the mole fraction of A in the mixture and P^0_A is the vapour pressure of pure A. This is known as Raoult's Law. The total vapour pressure, according to Dalton's Law, is the sum of the vapour pressures of the components:
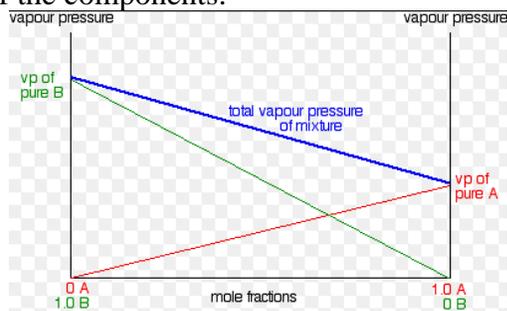
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- The composition of the vapour above a mixture is generally not the same as the composition of the liquid; the more volatile component will make a larger contribution to the vapour pressure and the vapour will therefore be richer in that component. This means that if a mixture of two components A and B is boiled, and then condensed again, its composition will change.
This change can be shown in boiling point-composition graphs for a mixture of two liquids:
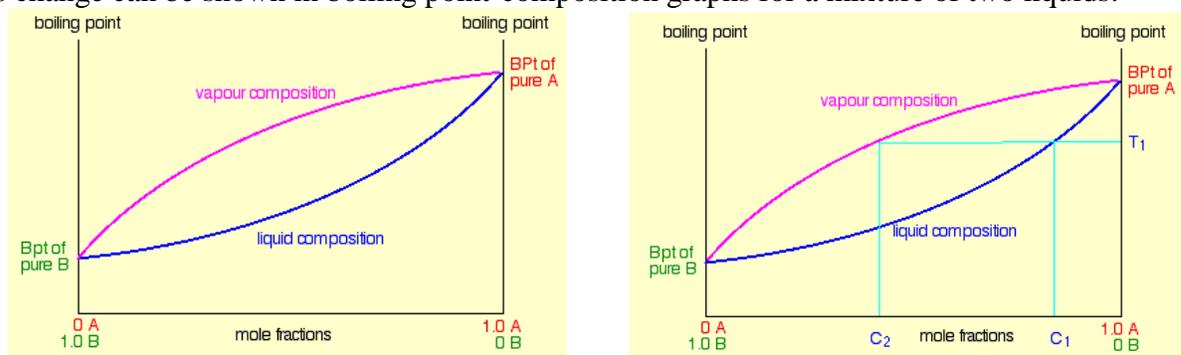
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- A mixture of composition C_1 will boil at temperature T_1 to give a vapour of composition T_2, which when cooled will give a liquid of composition T_2. This is the basis of fractional distillation.

- A solution which obeys Raoult's Law is called an ideal solution. It assumes that the ΔH of the mixing process is 0.

(b) Non-ideal solutions

- Many solutions do not obey Raoult's Law. If $\Delta H_{mixing} = +ve$, the vapour pressure is higher than predicted by Raoult's Law. This is known as a positive deviation from Raoult's Law:
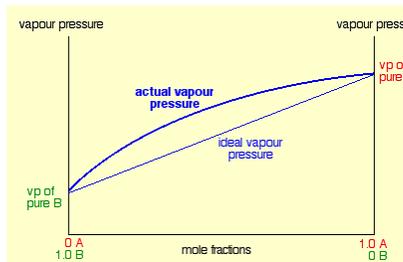
Small positive deviation   large positive deviation

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- If $\Delta H_{mixing} = -ve$, the vapour pressure is lower than predicted by Raoult's Law. This is known as a negative deviation from Raoult's Law:

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Large negative deviation

If there is a large positive or negative deviation from Raoult's Law, the vapour pressure at some compositions may be greater (with positive deviations) or lower (with negative deviations) than either pure substance. This means that the boiling points also reach maxima or minima:

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Large positive deviation   large negative deviation

- At the compositions at which the boiling point reaches a maximum or minimum, the vapour will have the same composition as the liquid. Such a mixture is called an **azeotrope**.
- Azeotropic mixtures cannot be separated by fractional distillation, which means that other physical methods are required to separate them
- Mixtures containing a lower composition of A than the azeotrope can be fractionally distilled to give pure A and the azeotrope. Mixtures containing a higher composition of A than the azeotrope can be fractionally distilled to give pure B and the azeotrope.

3. SOLUTIONS OF SOLIDS IN LIQUIDS

- Solutions of solids in liquids can be considered as solutions of liquids in liquids, except that the solute is non-volatile and hence has zero vapour pressure.

- Assuming the solution is ideal, the effect of the solute on the behaviour of the solvent depends on the concentration of the solution but not on the identity of the solute. These properties are known as colligative properties.

- Solutions show four important colligative properties which depend on the concentration of the solute
    - Reduction in vapour pressure
    - Increase in boiling point
    - Depression of freezing point
    - Osmotic Pressure

(a) Reduction in Vapour Pressure

- The vapour pressure of a solution containing a non-volatile solvent is always lower than the vapour pressure of the pure solvent.

- Raoult's Law can be used to predict the effect of a non-volatile solute on the vapour pressure of a liquid. Assuming that the partial vapour pressure of the non-volatile solute B is always zero, the vapour pressure of the solution will be $\frac{n_A}{n_T}P^0{}_A$.

- The change in vapour pressure $\Delta P = P^0{}_A - P = P^0{}_A - \frac{n_A}{n_T}P^0{}_A = P^0{}_A(1 - \frac{n_A}{n_T}) = P^0{}_A\frac{n_B}{n_T}$

  So $\frac{\Delta P}{P_A^0} = \frac{n_B}{n_T}$

- The ratio of the change in vapour pressure to the vapour pressure of the pure solvent is equal to the mole fraction of the solute.

(b) Increase in boiling point

- Because solid solutes always lower the vapour pressure of a solution, it follows that they will also increase the boiling point of a solution

- If the change in boiling point is small relative to the original boiling point, and the solution is fairly dilute, it is possible to derive an expression for the change in boiling point as follows:
  $\Delta T_b = \frac{RT_0^2}{\Delta H_v n}m$
  T_o = boiling point of the solvent, ΔH_v = enthalpy of vaporisation of the solvent, n = $1000/m_r$ of the solvent and m = molality of the solution

- $\frac{RT_0^2}{\Delta H_v n}$ can be converted into the single constant K_b, so that $\Delta T_b = K_b m$

- K_b is known as the ebullioscopic constant of the liquid

(c) Depression of freezing point

- The presence of solutes in a solution also lowers the freezing point of the solution

- If the change in freezing point is small relative to the original freezing point, and the solution is fairly dilute, it is possible to derive an expression for the change in freezing point as follows:
  $\Delta T_f = \frac{RT_0^2}{\Delta H_m n}m$
  T_o = boiling point of the solvent, ΔH_m = enthalpy of fusion (melting) of the solvent, n = $1000/m_r$ of the solvent and m = molality of the solution

- $\frac{RT_0^2}{\Delta H_m n}$ can be converted into the single constant K_f, so that $\Delta T_f = K_f m$

- K_b is known as the cryoscopic constant of the liquid

(d) Osmotic Pressure

- Osmosis is the movement of solvent through a semi-permeable membrane from an area of low solute concentration to an area of high solute concentration

- The mechanical pressure which must be applied to the solution to prevent osmosis from taking place is called the osmotic pressure (Π) of the solution.

- For dilute solutions, the osmotic pressure can be shown to obey the equation $\Pi V = nRT$ (n = number of moles of solute); this is known as Van't Hoff's Law for ideal solutions. It can also be expressed as $\Pi = \dfrac{nRT}{V} = CRT$

4. SOLUTIONS OF ELECTROLYTES IN LIQUIDS

(a) Electrochemistry and Electrolytes

- Electrochemistry is the general study of the behaviour of ions in solution.

- In other words, electrochemistry is the study of electrolytes. An electrolyte is a species which can conduct electricity due to the movement of ions. Most electrolytes are liquids (eg aqueous solutions of ionic compounds), but there are some examples of solid electrolytes (eg superionic conductors) and gaseous electrolytes (eg HCl at high temperature or low pressure).

- A narrower interpretation of electrochemistry would be to define it as the relationship between electricity and chemical change – or the study of electrochemical cells. There are two types of electrochemical cell:
- a device which can use electricity to create a chemical change is called an electrolytic cell
- a device which can create electricity as a result of a spontaneous chemical reaction is called a voltaic cell

  All electrochemical cells consist of two electrodes and an electrolyte.

- Electrolytes are formed when an ionic compound dissolves in a solvent resulting in the complete separation of the ions, or when a covalent substance dissolves in a solvent and then dissociates into ions. Electrolytes can be classified as strong electrolytes or weak electrolytes, depending on the extent of dissociation:

- Strong electrolytes are those which are fully dissociated in solution:
  $$A_xB_y \quad \rightarrow \quad xA^{z+} + yB^{z-}$$
  If the molarity of a strong electrolyte is C, the molarity in solution of A^{z+} will be xC, the molarity of B^{z-} will be yC and the molarity of undissociated A_xB_y will be zero.
  A strong electrolyte should be almost fully dissociated at all moderate concentrations.

- Weak electrolytes are only partially dissociated in solution
  $$A_xB_y \quad \rightleftharpoons \quad xA^{z+} + yB^{z-}$$
  If the molarity of a weak electrolyte is C, the molarity in solution of A^{z+} will be αxC, the molarity of B^{z-} will be αyC and the molarity of undissociated A_xB_y will be $C(1-\alpha)$; where α is the degree of dissociation of the weak electrolyte.

- The study of electrolytic cells requires an understanding of the basic physical relationships involving electrical charge (Q), current (I), time (t), voltage (V), power (P) and energy (E or W)

  $Q = It$ $\qquad\qquad$ $P = VI$ $\qquad\qquad\qquad$ $W = VIt = QV$

(b) Colligative properties of electrolytes

- Colligative properties can be given by the general expression $C = kn_t$

  $\qquad$ C = colligative property, k = constant, n_t = total molarity

- For non-electrolytes = n_t = molarity (n), but for electrolytes, $n_t > n$ due to the dissociation of the electrolyte; hence solutions of electrolytes show greater colligative effects than solutions of non-electrolytes of the same concentration

- The Van't Hoff ratio i = ratio of colligative effect of an electrolyte to the colligative effect of a non-electrolyte of the same concentration so $i = \frac{n_t}{n}$

  $\qquad$ $C = kn_t$ or $C = ikn$

  The ratio can be used to describe any of the four colligative properties:

  $\qquad$ $i = \frac{\Delta T_f}{(\Delta T_f)_0} = \frac{\Delta T_b}{(\Delta T_b)_0} = \frac{\Delta P}{(\Delta P)_0} = \frac{\Pi}{(\Pi)_0} = \frac{C}{C_0}$

  If the electrolyte is fully dissociated, i should be equal to the total number of ions per molecule v (so for NaCl, i = 2 and for $BaCl_2$, i = 3)

- If the electrolyte is not fully dissociated, i will also depend on the degree of dissociation.

  $\qquad$ A_xB_y $\qquad\qquad$ = $\qquad\qquad$ $xA^{z+} + yB^{z-}$
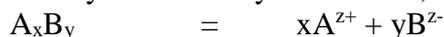
  $\qquad$ $n(1-\alpha)$ = $\qquad\qquad$ $xn\alpha + yn\alpha$

  total moles of electrolyte n_t $\quad$ = $n - n\alpha + xn\alpha + yn\alpha$

  $\qquad\qquad$ = $n(1 - \alpha + x\alpha + y\alpha)$

  $\qquad\qquad$ = $n(1 + \alpha(x + y - 1))$

  Total number of ions per molecule v = x + y, so n_t $\quad$ = $n(1 + \alpha(v - 1))$

  $\qquad\qquad\qquad\qquad\qquad$ so $\frac{n_t}{n} = i = 1 + \alpha(v - 1)$

So $\alpha = \frac{i-1}{v-1}$

In weak electrolytes, α is small; in strong electrolytes, α = 1

(c) Electrolysis

- During electrolysis, cations move to the cathode, where there is a reduction half-reaction. Anions move to the anode, where there is an oxidation half-reaction

- Faraday's 1st Law: mass of a substance produced at electrodes is directly proportional to the quantity of charged passed through the solution

  Faraday's 2nd Law: mass of substances produced at each electrode are directly proportional to their equivalent weights

- Consider the cathode reaction $Cu^{2+} + 2e \rightarrow Cu$

  It is clear that if two moles of electrons are passed through the solution, one mole of Cu will be deposited at the cathode. Each electron carries a charge (e) of 1.6×10^{-19} C, so one mole of electrons carries a charge of eL = 96500 C. This is known as the Faraday constant.

  One Faraday of charge will deposit 0.5 moles of Cu (or one equivalent of Cu) at the cathode.

- Consider the anode reaction $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

  One Faraday of charge will deposit 0.25 moles of O_2 (or one equivalent of O_2) at the anode.

- Note that one mole of electrons (1 F) only produces 0.5 moles of copper and 0.25 moles of oxygen. The mass of an element produced at an electrode as a result of the passage of 1 F of charge is called the electrochemical equivalent (z) of that element. For Cu, z = 31.8 g, for O, z = 8 g, for Na, z = 23.0 g
  (d) Electrical Conductance of solutions containing electrolytes

  (i) Important terms concerning the electrical conductance of solutions

- In solution, it is usual to measure **conductance** L rather than resistance R: $L = \frac{1}{R}$

- The resistance of a material, like its conductance, depends on the length of the material (l) and its cross-sectional area (A); in the case of solutions, this means the distance between the electrodes and their cross-sectional area

  Resistance can be expressed as $R = \frac{\rho l}{A}$; ρ is an intrinsic property of a material at a given temperature and is called the resistivity (units Ωm)

  Conductance can be expressed as $L = L_S \frac{A}{l}$; L_S is an intrinsic property at a given temperature and is called the **conductivity** (units $\Omega^{-1}m^{-1}$); $L_S = \frac{1}{\rho}$; L_S can be considered the conductance per metre, or the conductance of the solution when the two electrodes are 1 m apart

- The ratio $\frac{l}{A}$ is known as the **cell constant** K, so $L_S = KL$ or $L_S = \frac{K}{R}$. K is fixed for a particular cell, and can be found by measuring the conductance or resistance of a solution of known conductivity in that cell. Once K is known, L_S can be determined easily from conductance or resistance measurements.

- The **molar conductivity** Λ of a solution it its conductivity per unit concentration $\Lambda = \frac{L_S}{C}$ (units $\Omega^{-1}m^2mol^{-1}$); (sometimes equivalent conductivity is used instead, which is the conductivity per concentration equivalent)

- The conductance of a solution is in part due to the movement of the cation, and in part due to the movement of the anion: $\Lambda = l_+ + l_-$; l_+ and l_- are the **molar ionic conductivities** of the individual cation and anion respectively. The conductance of a solution is the sum of the conductances of the ions involved; this is known as Kohlrausch's Law of independent mobilities $\Lambda = l_+ + l_-$

(ii) Measuring the Resistance of a Solution

- Conductance is measured via resistance, which is measured via a Wheatstone bridge.
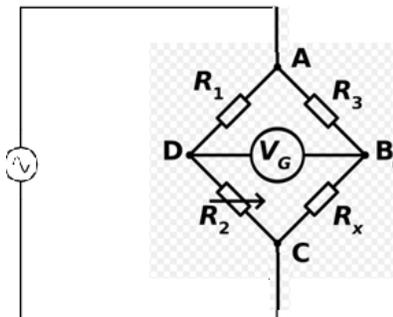
- The cell is placed in the R_X position. R_1 and R_3 are known and fixed. R_2 is known and variable. When $\frac{R_X}{R_3} = \frac{R_2}{R_1}$, the potential at points B and D are equal and no current will flow through the ammeter (V_g). R_2 is adjusted until this is the case. $R_x = \frac{R_2 R_3}{R_1}$, and so the resistance of the cell can be calculated.

- In the special case of measuring the resistance of cells, alternating current must be used, as direct current would cause electrolysis and therefore a change in concentration.

- Because the conductance of electrolytes varies so much, it may be necessary to adjust the cell in order to ensure that its resistance allows R_2 to operate within its range. For solutions with very high conductivities, cells with electrodes far apart should be used to reduce the conductance, and for solutions with very low conductivities, cells with electrodes close together should be used to increase the conductance.

- Because the cell behaves as a capacitor, it will store and discharge current which creates an error in the reading. To compensate for this, another variable capacitor should be placed across one of the other resistors whose capacitance should be adjusted so that it compensates for the capacitance of the cell

- It is not possible to measure the conductances of individual ions by this method; it is only possible to measure the conductance of a solution.

(iii) Molar conductivities of solutions

- Weak electrolytes have a much lower molar conductivity than strong electrolytes, as the degree of dissociation is much lower. According to the laws of chemical equilibrium, the degree of dissociation of a weak electrolyte will decrease as the concentration of electrolyte increases; in other words, the dissociation is highest at very low concentrations. It can be shown that for very weak electrolytes at relatively high concentrations, $\alpha \propto \frac{1}{\sqrt{C}}$. The electrolyte is only fully dissociated in infinitely dilute solutions.
- The molar conductivities of weak electrolytes therefore decrease significantly with increasing concentration due to the smaller degree of dissociation of the electrolyte.

- Strong electrolytes are fully dissociated at almost all concentrations and so according to Arrhenius theory, the molar conductivity of strong electrolytes should be independent of concentration. It is observed, however, that molar conductivity decreases with increasing concentration even for strong electrolytes. The decrease in molar conductivity of strong electrolytes with increasing concentration can be explained by the Debye-Huckel theory of interionic attraction:
    - Ions in solution do not behave independently of each other but are attracted to each other; as a result each ion is surrounded by more ions of opposite charge than of the same charge. This is called the ionic atmosphere of an ion.
    - When a potential difference is applied, the ionic atmosphere becomes distorted as the ion starts moving in the opposite direction to its atmosphere; the force exerted by the atmosphere behind the ion than in front of it, which slows the ion down and reduces the molar conductivity
    - In addition, many of the solvent molecules are attached to the oppositely charged ion and therefore moving in the opposite direction, making it more difficult for the ion to move
    - Both of these effects are more pronounced at increasing concentration, and hence the molar conductivity decreases with increasing concentration
- The molar conductivity of strong electrolytes decreases with increasing concentration because interionic attractions are more significant at higher concentrations.

- The following graph shows the variation of molar conductivities of strong and weak electrolytes with concentration:

www.chem.libretexts.org
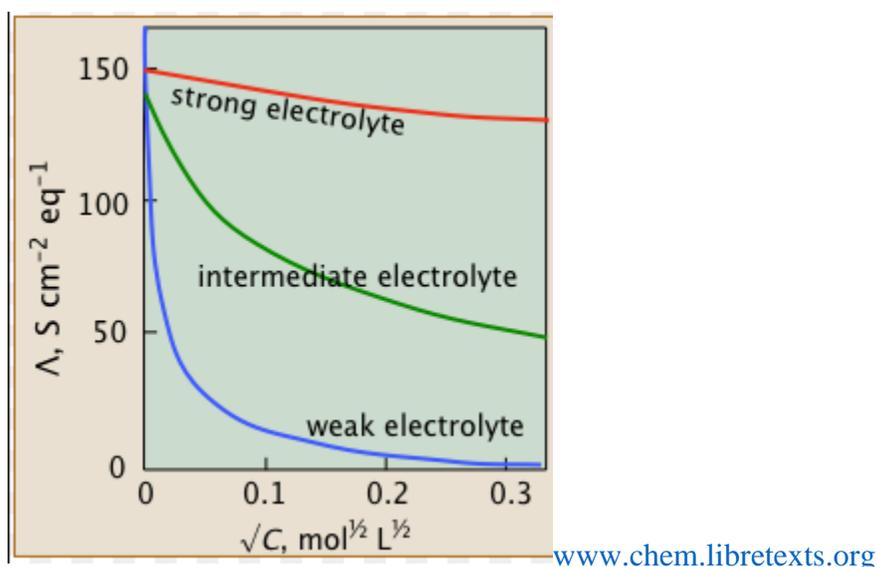
- Note that although molar conductivity decreases with increasing concentration for all electrolytes, the variation is much stronger for weak electrolytes because of the different reasons for the variation

(iv) Limiting Molar Conductivity

- Molar conductivities reach an upper limit, as the concentration becomes so low that dissociation is complete (for weak electrolytes) and the effect of interionic attractions is negligible (for strong electrolytes).

- This upper limit is called the limiting molar conductivity or the molar conductivity at infinite dilution (Λ_o). It is an intrinsic property of the solute, and a measure of its ability to move through a potential difference in the absence of any interionic effects.

- The ratio of molar conductivity to the limiting molar conductivity $\frac{\Lambda}{\Lambda_0}$ is called the conductivity ratio. In weak electrolytes the conductivity ratio is the degree of dissociation: $\alpha = \frac{\Lambda}{\Lambda_0}$ but in weak electrolytes the conductivity ratio depends on the strength of the interionic attractions.

- At infinite dilution, when dissociation is complete and there are no interionic effects, the limiting molar conductivities of each ion $l^0{}_+$ and $l^0{}_-$ should be independent of each other and so also have a fixed value at a particular temperature

- Kohlrausch's Law can be used to predict the Λ_0 value of a solution without measuring it directly – if the Λ_0 value of three solutions AC, AD and BC are known, the Λ_0 value of solution BD can be determined:
$$\Lambda^0{}_{BC} + \Lambda^0{}_{AD} - \Lambda^0{}_{AC} = \Lambda^0{}_{BD}$$
$$\Lambda^0{}_{BC} + \Lambda^0{}_{AD} - \Lambda^0{}_{AC} = l^0{}_B + l^0{}_C + l^0{}_A + l^0{}_D - l^0{}_A - l^0{}_C = l^0{}_B + l^0{}_D = \Lambda^0{}_{BD}$$

- The limiting molar conductivity of strong electrolytes can be measured using a relationship observed by Kohlrausch - that the variation of Λ with $\sqrt{C}$ is linear for strong electrolytes at low concentrations:
$$\Lambda = \Lambda_0 - b\sqrt{C}.$$
Λ_0 for strong electrolytes can therefore be deduced by measuring the molar conductivities at different concentrations, plotting a graph of Λ against $\sqrt{C}$ and extrapolating the line to $C = 0$.

  This method does not work for weak electrolytes as the concentrations required for the Λ vs $\sqrt{C}$ relationship to be linear are so low that the dissociation of water becomes a significant contributor to the total conductance. Λ_0 for weak electrolytes must be determined by Kohlrausch's Law – the Λ_0 of a weak electrolyte BD can be determined from the Λ_0 of three strong electrolytes AC, AD and BC.

(v) Transport numbers

- The **transport number** (t_+ or t_-) of an ion in an electrolyte is the fraction of the total current it carries. Ions with higher l_0 values move faster than ions with lower l_0 values and so carry a greater proportion of the total current.
$t_+ = \frac{I_+}{I}$ and $t_+ + t_- = 1$
The transport number must be related to the ionic molar conductivities as follows:
$$l_+ = t_+\Lambda \qquad l_- = t_-\Lambda$$

- The ratio of transport numbers (and hence ionic molar conductivities) is also the ratio of the velocities of the two ions:
  If an ion is moving at velocity v m/s between two plates d m apart, the total charge carried by the ion in one second will be the total number of ions n, multiplied by the charge on each ion ze, multiplied by the proportion able to reach the electrode in one second $\frac{v}{d}$

  So $I^+ = \frac{N_+ v_+ z_+ e}{d}$ $I^- = \frac{N_- v_- z_- e}{d}$ so $I = \frac{N_- v_- z_- e + N_+ v_+ z_+ e}{d}$

  Due to the electrical neutrality of solutions $n_- z_- = n_+ z_+ = nv$, where nz is the total charge (+ or -)

  So $I = \frac{Nze(v_+ + v_-)}{d}$ so $t_+ = \frac{I_+}{I} = \frac{v_+}{v_+ + v_-}$ and $t_- = \frac{I_-}{I} = \frac{v_-}{v_+ + v_-}$ and therefore $\frac{t_+}{t_-} = \frac{v_+}{v_-}$.

- It is possible to determine transport numbers experimentally by the Hirtoff method. This is because unequal velocities of two ions will result in a build up of ions at the electrode to which the faster ion is migrating and a shortage of ions at the electrode to which the slower ion is migrating. Faster ions will migrate into or out of an electrode compartment more rapidly than anion. This is the basis of Hirtoff's rule, which states that the increase of decrease in the number of ions in an electrode due to migration is directly proportional to the velocity of the ion, which is in turn proportional to the transport number:

  $$\frac{\Delta n_+ z_+}{\Delta n_- z_-} = \frac{v_+}{v_-} = \frac{t_+}{t_-}$$

  Hirtoff's rule can be used to determine transport numbers experimentally by the following method:
  - from original concentration, determine original moles of ion in electrode compartment
  - by analysis, determine final moles of ion in electrode compartment
  - hence calculate change in moles of ion in electrode compartment
  - from total Faradays used, calculate expected change in moles of ion due to electrolysis
  - hence determine change in moles of ion due to migration
  - hence determine change in charge passed due to migration of that ion
  - calculate the transport number by expressing this charge as a fraction of the total charge passed

- It is also possible to determine transport numbers experimentally by the **moving boundary method**.
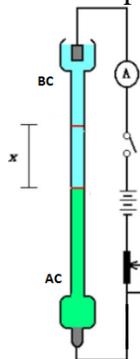
A cell is arranged vertically with cathode at the top and the anode at the bottom. In order to determine the transport number of a cation B in a solution of BC, two different solutions AC and BC – C being an anion common to both solutions - should be placed in the vessel, one (AC) at the bottom surrounding the anode and one (BC) at the top surrounding the cathode. Solution AC should have a higher density than solution BC the solution at the top so that a clearly visible boundary can form between the two solutions, and the electrode at the anode should be made of A (ie the same as the cation in AC) so that the electrode dissolves during electrolysis. Usually, the anode is made of cadmium and solution AC is cadmium chloride. During electrolysis, Cd dissolves in the anode and B migrates upwards to the cathode. The boundary will therefore move upwards.

- measure the distance x moved by the boundary
- record It and hence Q, the total charge passed
- measure x, the distance moved by the boundary, and hence calculate the volume of solution displaced (=Ax, where A is the cross-sectional area of the vessel)
- hence the number of moles of solution BC, and hence of cation B, which has been displaced
- hence calculate the total charge displaced due the migration of B
- calculate the transport number of B by expressing this number as a fraction of the total charge passed

If an ion is moving at velocity v m/s between two plates d m apart, the total charge carried by the ion in one second will be the total number of ions n, multiplied by the charge on each ion ze, multiplied by the proportion able to reach the electrode in one second $\frac{v}{d}$

So $I^+ = \frac{n_+ v_+ z_+ e}{d}$ $I^- = \frac{n_- v_- z_- e}{d}$ so $I = \frac{n_- v_- z_- e + n_+ v_+ z_+ e}{d}$

Due to the electrical neutrality of solutions $n_- z_- = n_+ z_+ = nv$, where nz is the total charge (+ or -)

So $I = \frac{nze(v_+ + v_-)}{d}$ so $t_+ = \frac{I_+}{I} = \frac{v_+}{v_+ + v_-}$ and $t_- = \frac{I_-}{I} = \frac{v_-}{v_+ + v_-}$ and therefore $\frac{t_+}{t_-} = \frac{v_+}{v_-}$.

- By measuring transport numbers, it is therefore possible to calculate molar conductivities of individual ions if the total conductivity of the solution is known. This is how individual ionic molar conductivities can be determined.

(vi) Ionic velocities

- Ionic velocities can be measured directly by the moving boundary method: $v = x/t$

- It is also possible to deduce ionic speeds from molar ionic conductivities as follows:
  We know that $I = \dfrac{nze(v_+ + v_-)}{d}$
  n and z are the number and charge of either ion, v_+ and v_- are the speeds of the individual ions and d is the distance between the electrodes
  If one mole of electrolyte A_xB_y dissociates fully into $xA^{z+} + yB^{z-}$, the solution will contain x moles of A^{z+} and y moles of B^{z-} and $xz^+ = yz^-$.
  So one mole of electrolyte contains Nxz^+ or Nyz^- ions (call this quantity Nxz)
  So for one mole of A_xB_y, $I = \dfrac{Nxze(v_+ + v_-)}{d} = \dfrac{zxF(v_+ + v_-)}{d}$
  $\Lambda = \dfrac{L_s}{C}$ so $L_s = \Lambda C$ $L = L_s\dfrac{A}{d}$ so $L = \dfrac{\Lambda CA}{d}$ so $I = VL = \dfrac{V\Lambda CA}{d}$
  The concentration of A ions is $xC = \dfrac{xn}{V} = \dfrac{xn}{Ad}$, so $I = \dfrac{V\Lambda CA}{d} = \dfrac{V\Lambda xn}{d^2}$
  So I for one mole of $A_xB_y = \dfrac{V\Lambda x}{d^2}$
  therefore $\dfrac{V\Lambda x}{d^2} = \dfrac{Fxz(v_+ + v_-)}{d}$, so $\dfrac{V}{d}\Lambda = Fz(v_+ + v_-)$, so $\Lambda = Fz(\dfrac{v_+}{\frac{V}{d}} + \dfrac{v_-}{\frac{V}{d}})$
  V/d is the voltage gradient (in Vm^{-1}). The velocity of an ion per unit voltage gradient is called the **ionic mobility** (μ_+ or μ_-) of an ion. The equation than therefore be written: $\Lambda = Fz(\mu_+ + \mu_-) = Fz\mu_+ + Fz\mu_-$

  But $\Lambda = l_+ + l_-$, which suggests that $l_+ = Fz\mu_+$ and $l_- = Fz\mu_-$, so $\mu_+ = \dfrac{l_+}{Fz}$ and $\mu_- = \dfrac{l_-}{Fz}$

- The ionic velocities can be calculated from the ionic mobilities using $\mu = \dfrac{vd}{V}$ so $v = \dfrac{\mu V}{d}$

- For weak electrolytes, Nxz becomes αNxz, so $\mu_+ = \dfrac{\alpha l_+}{Fz}$

(vii)   Explaining differences in molar conductivities of ions

- The molar conductivity of an ion depends on the mass of the ion (ions with lower mass move faster), the cross-sectional area of the ion (ions with a lower cross-sectional area move faster) and the charge of the ion (ions with a higher charge move faster).

- The effect of charge is clearly apparent in the conductivity data of different ions. Ions with a +2 charge have molar conductivities approximately twice as high as ions with a +1 charge. This effect can be eliminated by considering the equivalent conductivities.

- The effect of mass and area, however, is less clear – in fact some small ions with low m_r values such as Li^+ appear to have low conductivities. This is because ions in solution are hydrated – which means that they are surrounded by water. So the formula of aqueous Li^+ is actually $Li(H_2O)_n^+$, and the value of n is different for different ions. In fact, the smaller the ion, the greater its charge density, so the greater the number of water molecules it attracts and the larger the hydrated ion. As a result, there is no clear correlation between ionic size and mass and ionic conductivity – the lower conductivity of small ions can be explained by the higher degree of hydration.

- H^+ and OH^- have a much higher conductivity than all other ions in aqueous solution. This is because these ions are able to move through water in a different way from other ions, which have to migrate gradually through the water and other ions.
- When H^+ and OH^- are hydrated in water, they form complex ions with the formula $(H_{2n+1}O_n)^+$ and $(H_{2n-1}O_n)^-$. The hydrated H^+ ion is often simplified to H_3O^+. When these ions collide with water molecules, H^+ ions can be passed from one molecule to another simply by the movement of a lone pair of electrons on the oxygen atom:

$$\begin{array}{ccccc} H_3O^+ & H_2O & H_2O & H_2O & H_2O \\ H_2O & H_3O^+ & H_2O & H_2O & H_2O \\ H_2O & H_2O & H_3O^+ & H_2O & H_2O \\ H_2O & H_2O & H_2O & H_3O^+ & H_2O \\ H_2O & H_2O & H_2O & H_2O & H_3O^+ \end{array}$$

- The same thing can happen with OH^-

$$\begin{array}{ccccc} OH^- & H_2O & H_2O & H_2O & H_2O \\ H_2O & OH^- & H_2O & H_2O & H_2O \\ H_2O & H_2O & OH^- & H_2O & H_2O \\ H_2O & H_2O & H_2O & OH^- & H_2O \\ H_2O & H_2O & H_2O & H_2O & OH^- \end{array}$$

- So the higher mobility of H^+ and OH^- ions in solution is because they can be passed from hydrated ion to hydrated ion without having to migrate. All other ions have to migrate

(viii)   Applications of Conductance Measurements

(α) Determining degree of dissociation and acid dissociation constants

- For weak electrolytes, $\alpha = \dfrac{\Lambda}{\Lambda_0}$, and so α can be determined from conductance measurements

- This can be used to determine the acid dissociation constant K_a:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(\alpha C)(\alpha C)}{(1-\alpha)C} = \frac{\alpha^2 C}{(1-\alpha)}$$

(β) Determining the solubility and solubility products of sparingly soluble salts

- The solubility of a sparingly soluble salt can be determined by measuring the conductance of a saturated solution of the salt.

- At very low concentrations, the conductance of water becomes significant and so must be taken into account.

- $L_S = L_{S(salt)} + L_{S(water)}$, so $L_{S(salt)} = L_S - L_{S(water)}$
  $L_{S(salt)} = \Lambda C$ so $C = \dfrac{L_{S(salt)}}{\Lambda}$

- Assuming $\Lambda = \Lambda_0$ because the concentration is low, the concentration can be estimated from the following calculation: $C = \dfrac{L_S}{\Lambda_0}$

(γ) Determining the degree of dissociation and the ionic product of water

- The degree of dissociation of water can be determined by measuring the L_S of pure water
- The molarity C of water can be determined from its density: $C = \frac{n}{V} = \frac{m}{Vm_r} = \frac{\rho}{m_r}$

- Therefore Λ for pure water can be deduced from the equation $L_S = \Lambda C = \frac{\Lambda \rho}{m_r}$ so $\Lambda = \frac{L_S m_r}{\rho}$

- Λ_0 for pure water $= l^0{}_{H+} + l^0{}_{OH-}$ so $\alpha = \frac{\Lambda}{\Lambda_0} = \frac{L_S m_r}{\rho \Lambda_0}$

- $[H^+] = [OH^-] = \alpha C = \frac{\alpha \rho}{m_r} = \frac{L_S}{\Lambda_0}$ so $K_w = [H^+][OH^-] = (\frac{L_S}{\Lambda_0})^2$

(δ) Determining concentration by conductimetric titrations

- Because different ions have different mobilities, the conductance of a solution will change as the ions present in solution change.

- The determination of an equivalence point by monitoring changes in conductance is called a conductometric titration.

- Conductometric titrations are most commonly used to determine the equivalence point of precipitation reactions. Conductance decreases rapidly as the insoluble salt is formed, before increasing rapidly again after the equivalence point.

- Conductometric titrations are also useful in acid-base titrations, especially if the solution is coloured (which means that indicators cannot be used). The variation of conductance with the volume of base added depends on whether the acid and base are strong or weak.

  Strong acid-strong base titrations:
  - on addition of base, the highly mobile H^+ is replaced with the less mobile Na^+ so the conductance decreases rapidly
  - the conductance then increases rapidly after the equivalence point as $[OH^-]$ increases

  Weak acid-strong base titrations:
  - on addition of base, there is an initial decrease in conductance as H^+ is replaced by the less mobile Na^+, but the conductance then increases slowly as the weak electrolyte (with H^+) is replaced with a strong electrolyte (without H^+)
  - conductance then increases rapidly after the equivalence point as $[OH^-]$ increases

  Strong acid-weak base titrations:
  - on addition of base, the highly mobile H^+ is replaced with the less mobile Na^+ so the conductance decreases rapidly
  - after the equivalence point, there is little change in conductance as the additional weak base is unable to dissociate in the presence of its salt

  Weak acid-weak base titrations:
  - on addition of base, there is an initial decrease in conductance as H^+ is replaced by a less mobile cation, but the conductance then increases slowly as the weak electrolyte (with H^+) is replaced with a stronger electrolyte (without H^+)
  - after the equivalence point, there is little change in conductance as the additional weak base is unable to dissociate in the presence of its salt

- The graphs of conductance vs volume of base added for the different types of acid and base are shown below:
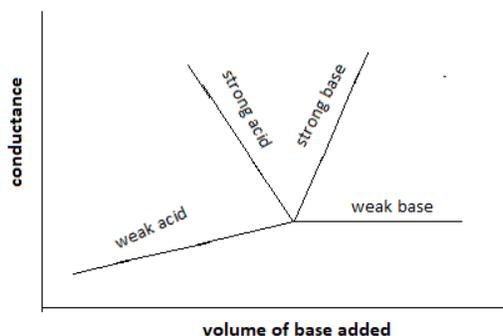
PRACTICE QUESTIONS FOR CHEM 211

Unit 1

Lesson 1

1.   (a)   Describe the main postulates of the kinetic model of matter
       (b)   What is an ideal gas?
       (c)   Under which conditions is a gas most likely to display ideal behaviour? Which gases will show ideal behaviour over the widest range of conditions?

2.   (a)   State the ideal gas equation and use it to explain the meaning of the term "equation of state"
       (b)   State three laws which can be combined to give the ideal gas equation
       (c)   Calculate the volume occupied by one mole of a gas at 25 ^{o}C and 100 kPa
       (d)   Calculate the temperature of a gas if 0.5 moles occupy 1.2 dm^3 at a pressure of 200 kPa
       (e)   Calculate the mass of a sample of carbon dioxide which occupies 20 dm^3 at 27 ^{o}C and 100 kPa
       (f)   Calculate the relative molecular mass of a gas if a 500 cm^3 sample at 20 ^{o}C and 1 atm has a mass of 0.66 g
       (g)   Calculate the density of nitrogen gas at 298 K and 100 kPa
       (h)   A volatile organic compound weighing 0.2 g, on heating in Victor Meyer's tube, displaced 30 cm^3 of air at 27°C; the pressure was found to be 98 kPa once the contribution of water vapour was removed; determine the molecular mass of the compound.
       (i)   A sample of an unknown compound is vaporised at a pressure of 103 kPa in a flask which, when empty and evacuated, has a mass of 25.3478 g; when vaporisation is complete and excess gas has escaped, the temperature is found to be 98 ^{o}C. The flask is sealed and found to have a mass of 25.6803 g. The flask and contents are then cooled to 25 ^{o}C, emptied, cleaned, filled with water and found to have a mass of 128.12 g when filled with water (the density of water is 0.997 gcm^{-3} at 25 ^{o}C). Determine the relative molecular mass of the compound.
       (j)   Calculate the total number of molecules remaining per cm^3 if a vessel is evacuated until its pressure is 7.7 Pa at 298 K

Lessons 2 and 3

3. (a) By considering N molecules each of relative molecular mass m_r moving with velocity v inside a cube of length l and volume V, derive the expression $PV = \frac{m_r n v^2}{3}$

(b) Given that $\frac{mv^2}{2} \propto T$ is one of the postulates of the kinetic model, use the expression $PV = \frac{m_r n u^2}{3}$ to derive the ideal gas equation

(c) Use the ideal gas equation to derive Dalton's law of partial pressures

4. (a) Use the ideal gas equation, the postulate $\frac{mv^2}{2} \propto T$ and the expression $PV = \frac{m_r n u^2}{3}$ to show that for one mole of a gas, $KE = \frac{3RT}{2}$

(b) Hence derive expressions for the heat capacity of a gas at constant volume (C_v) and at constant pressure (C_p)

(c) Deduce the root mean square velocity of a nitrogen molecule at 25 °C

(d) Calculate the average kinetic energy in kJmol^{-1} of a sample of gas at 25 °C

5. (a) Assuming that dry air contains 79% N_2 and 21% O_2 by volume, calculate the density of moist air at 298 K at an atmospheric pressure of 101 kPa given that the partial pressure of the water vapour in the air is 3.2 kPa

(b) Calculate the total pressure in a 5 dm^3 vessel containing 2 g of ethane and 3 g of carbon dioxide at 50 °C

Lessons 4 and 5

6.   (a)   Sketch the Maxwell-Boltzmann of molecular velocities in a sample of nitrogen gas at 25 ºC
     (b)   On the same axes, sketch the Maxwell-Boltzmann of molecular velocities in a sample of hydrogen gas at 25 ºC
     (c)   On the same axes, sketch the Maxwell-Boltzmann of molecular velocities in a sample of nitrogen gas at 0 ºC

7.   (a)   Estimate the fraction of molecules at 300 K with a kinetic energy in excess of 50 kJmol^{-1}
     (b)   Estimate the fraction of molecules at 310 K with a kinetic energy in excess of 50 kJmol^{-1}
     (c)   Hence deduce the relative rates of reaction at 300 K and 310 K for a reaction with an activation energy of 50 kJmol^{-1}

8.   Calculate the root mean square velocity, average velocity and most probable velocity of the molecules in a sample of argon gas at 298 K.

9.   (a)   Show that the collision frequency Z between identical molecules in a container is given by
$$2d^2 N^2 \sqrt{\frac{\pi RT}{m_r}}$$ and state the meaning of the terms d and N.
     (b)   An apparatus of volume 500 cm^3 is evacuated at 298 K until the total pressure is just 7.0 Pa. Assuming that the remaining gas is oxygen, which has a diameter of 3.0 x 10^{-10} m, calculate:
        (i)   The frequency with which the oxygen molecules collide in the apparatus
        (ii)   The mean free path of the oxygen molecules in the apparatus

10.   (a)   Use your answer to 9 (a) to derive an expression for the collision frequency between two reacting particles A and B.
     (b)   An apparatus of volume 500 cm^3 is evacuated at 298 K until the total pressure is just 7.0 Pa. Assuming that the remaining gas is 80% nitrogen (d = 3.1 x 10^{-10} m) and 20% oxygen (d = 3.0 x 10^{-10} m, calculate the frequency of the collisions between nitrogen and oxygen atoms in the apparatus.

Lesson 6

9.   Explain what is meant by the "transport properties" of gases and give three examples.

10.   (a)   State Graham's Law of diffusion
         (b)   How many times faster will hydrogen effuse compared to neon?
         (c)   A gas is found to effuse 6.0 times slower than hydrogen. Deduce the rmm of the gas and suggest its identity.

11.   Ammonia and hydrogen chloride react according to the following equation:
$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$
If both gases are allowed to diffuse towards each other from opposite ends of a cylinder, white fumes will be seen at the point at which the different gases come into contact.
         (a)   What is the ratio of the rate of diffusion of ammonia to that of hydrogen chloride?
         (b)   If the cylinder is 10 cm long, how far from the ammonia source should the white fumes be visible?

12.   (a)   Two identical porous containers are filled with neon and argon respectively. After 6 hours, two thirds of the neon has escaped from the first container. How long will it take for half of the argon to escape from the other container?
         (b) 2.278×10^{-4} mol of an unidentified gas effuses through a tiny hole in 95.70 s. Under identical conditions, 1.738×10^{-4} mol of argon gas takes 81.60 s to effuse. What is the molar mass of the unidentified gas?

13.   (a)   Given that the molecular diameter of propane is 4.3×10^{-10} m, calculate the coefficient of diffusion, the viscosity and the thermal conductivity of propane at 298 K and 100 kPa.
         (b)   The viscosity of carbon dioxide is 1.38×10^{-5} kgm^{-1}s^{-1} at 298 K. Estimate the molecular diameter of a carbon dioxide molecule.
         (c)   The mean free path of an ammonia molecule is 4.4×10^{-8} m at 298 K and 100 kPa; estimate the molecular diameter of ammonia and the diffusion coefficient of ammonia under these conditions.

Lesson 7

14.   (a)   Explain the meaning of the term "compressibility factor"
       (b)   Explain why the compressibility factor of all gases is close to 1 at low pressures
       (c)   At 200 atm and 298 K, the compressibility factor of methane is 0.7 and the compressibility factor of hydrogen is 1.1. Explain why.
       (d)   At 298 K, the compressibility factor of carbon dioxide is 0.6 at 200 atm and 1.4 at 800 atm. Explain why.
       (e)   At 150 atm, the compressibility factor of nitrogen is 0.6 at 120 K but 1.1 at 500 K. Explain why.

15.   (a)   What is the Joule-Thomson effect?
       (b)   Explain why hydrogen has a positive value of μ at all pressures
       (c)   Explain why most gases have a negative value of μ at low pressures and a positive value of μ at high pressures

16.   (a)   Explain why it is not possible to liquefy gases below a certain temperature (the critical temperature), however high the pressure.
       (b)   Explain the meaning of the terms "critical pressure" and "critical volume"

Lesson 8

17. The density of methane gas at 298 K is found to vary with pressure as follows:

Pressure/ kPa	Density/kgm^{-3}
25	0.118
50	0.358
75	0.537
100	0.717

Use this information to calculate the molar mass of methane to 2 decimal places.

18. (a) State the Van der Waal's equation.

(b) Given that T_c and P_c for NH_3 are 405 K and 11.2 MPa respectively, calculate the Van der Waal's constants a and b for NH_3 (a $= \frac{27R^2T_c^2}{64P_c}$ and b $= \frac{RT_c}{8P_c}$)

(c) Hence calculate the pressure exerted by 3.5 moles of NH_3 in a 1 dm^3 vessel at 300 K:
   (i) Using the ideal gas equation
   (ii) Using the Van der Waal's equation

(d) Calculate the compressibility factor of NH_3 under these conditions.

(e) Calculate the critical temperature and the critical pressure of carbon dioxide, given that the Van der Waal's constants are: a = 0.364 Pam^{6}mol^{-2}, b = 4.27 x 10^{-5} m^{3}mol^{-1}

19. (a) State the virial (Kamerlingh-Onnes) equation of state.

(b) The first two virial coefficients for N_2 at 298 K are: B = -4.5 x 10^{-6} m^{3}mol^{-1}, C = 1.1 x 10^{-9} m^{6}mol^{-2} Calculate the compressibility factor for N_2 at 100 kPa:
   (i) Using virial coefficient B
   (ii) Using virial coefficients B and C

(c) Repeat Q19b using 1 MPa and 10 MPa

Lesson 9

20. (a) Two point charges exert a force on each other in free space of 1.4×10^{-4} N. When a homogeneous dielectric medium is added, the same point charges at the same distance apart exert a force of 0.9×10^{-4} N. What is the dielectric constant of the medium?

(b) Calculate the energy needed to separate Na^+ from Cl^- from a distance of 0.2 nm apart.
(i) in a vacuum
(ii) in water (ε_r of water = 84)

21. (a) Explain the difference between induced polarisation and orientation polarisation. How does each type of polarisation vary with temperature?

(b) Calculate the dipole moment of NaCl given a bond length of 0.236 nm, assuming it is completely ionic.

(c) Find the magnitude of the partial charge on C-F in CH_3F, given that the dipole moment is 1.847 D and the bond length is 1.385×10^{-10} m ($1D = 3.34 \times 10^{-30}$ Cm)

(d) Calculate the Cl-F bond length if its dipole moment is 2.96×10^{-30} m and the bond is 11.3% ionic.

(e) For the HBr molecule, the dipole moment is 1.76 D and the bond length is 0.098 nm. Calculate its percentage ionic character.

22. (a) The dielectric constant of CH_4 at 297 K and 101 kPa is 1.00094. Assuming that CH_4 behaves as an ideal gas, calculate its induced molar polarisation and hence its polarizability.

(b) The dielectric constant of SO_2 at 273 K and 101 kPa is 1.00993. The gas has a permanent dipole moment of 1.63 D. Assuming that CH_4 behaves as an ideal gas, calculate its total molar polarisation, molar orientation polarisation and molar induced polarization.

(c) The dielectric constant of cyclohexane at 20 °C is 2.033 while its density is 0.7784 gcm^{-3}. For a solution of ethyl ether in cyclohexane, for which the mole fraction of solute is 0.04720 and density 0.7751gcm^{-3}, the dielectric constant is 2.109. Find the total molar polarisation of the ethyl ether.

23. The dielectric constant of gaseous HCl was measured at different temperatures and the following results were obtained:

T/K	ε
198	1.0076
273	1.0046
373	1.0026
473	1.0016

Estimate the dipole moment of HCl in Debye units.

Lesson 10

23. (a) Explain why the molar magnetic susceptibility is positive for paramagnetic materials but negative for diamagnetic materials

(b) Explain how total magnetic susceptibility can be measured

(c) Explain how paramagnetic susceptibility can be measured

(d) Calculate, in Bohr-Magnetons, the inherent magnetic moment of a species with two unpaired electrons.

24. A 0.10 moldm^{-3} solution of a complete ion was placed in a test tube of diameter 1 cm and suspended in Gouy's apparatus. When an electric field of 1 T was applied, the apparent mass increase of the test tube was 0.0415 g. Given that g = 9.81 kgms^{-2}, deduce the number of unpaired electrons in the complex ion.

Unit 2

Vapour Pressure, Boiling point, Raoult's Law and Azeotropes

1. The vapour pressure of ethoxyethane at 18 ^{o}C is 53 kPa and ΔH_{vap} for ethoxyethane is 26.0 kJmol$^{-1.}$ calculate the vapour pressure of ethoxyethane at 32 ^{o}C.
    (a)   Calculate the vapour pressure of ethoxyethane at 32 ^{o}C.
    (b)   Calculate the boiling point of ethoxyethane at 100 kPa

2. The vapour pressure of water at 25 ^{o}C is 3.1 kPa. Given that water boils at 100 ^{o}C at atmospheric pressure, calculate the molar heat of vaporisation of water.

3. (a)   State Raoult's Law and define an ideal solution.
    (b)   Pentane (C_5H_{12}) and heptane (C_7H_{16}) have vapour pressures of 55 kPa and 4.8 kPa respectively at 20 ^{o}C. A mixture is known to contain 252 g of pentane and 1400 g of heptane. Calculate:
        (i)   The mole fraction of each component in the liquid mixture
        (ii)   The total vapour pressure of the mixture
        (iii) The mole fraction of each component in the vapour above the mixture
    (d)   Sketch vapour pressure-composition and boiling point-composition diagrams for a mixture of pentane and heptane.
    (e)   Hence explain how fractional distillation can be used to separate an ideal solution into its two components.

4. Ethyl ethanoate (bpt 77 ^{o}C) and water (bpt 100 ^{o}C) form an azeotrope containing 9% water with a boiling point of 70 ^{o}C.
    (a)   Sketch vapour pressure-composition and boiling point-composition diagrams for a mixture of ethyl ethanoate and water.
    (b)   Explain why the mixture forms an azeotrope.
    (c)   Explain what is formed when a mixture of ethyl ethanoate and water containing 5% water is fractionally distilled.
    (d)   Explain what is formed when a mixture of ethyl ethanoate and water containing 50% water is fractionally distilled.

5. Nitric acid (bpt 83 ^{o}C) and water (bpt 100 ^{o}C) form an azeotrope containing 32% water with a boiling point of 121 ^{o}C.
    (a)   Sketch vapour pressure-composition and boiling point-composition diagrams for a mixture of nitric acid and water.
    (b)   Explain why the mixture forms an azeotrope.
    (c)   Explain what is formed when a mixture of nitric acid and water containing 5% water is fractionally distilled.
    (d)   Explain what is formed when a mixture of nitric acid and water containing 50% water is fractionally distilled.

Colligative Properties of Solutions

6. (a) The vapour pressure of pure water is 3.14 kPa at 25 °C. The vapour pressure of a solution of urea is 3.04 kPa at 25 °C. If the density of water is 1000 kgm^{-3} and assuming that the volume of water does not change when a small amount of urea is added, deduce the molarity of the urea solution.

  (b) The addition of 114 g of sucrose to 1000 g of water reduces the vapour pressure from 3.173 kPa to 3.154 kPa. Calculate the molar mass of sucrose.

7. What mass of glucose ($C_6H_{12}O_6$) should be added to 552 g of water to reduce the vapour pressure of pure water at 20 °C from 2.33 kPa to 2.07 kPa?

8. Calculate the boiling point and freezing point of a solution containing 478 g of ethan-1,2-diol ($C_2H_6O_2$) in 3202 g of water, given that K_f and K_b for water are 1.86 K/m and 0.52 K/m respectively.

9. 7.85 g of a compound is dissolved in 301 g of benzene (C_6H_6) and the freezing point depression is found to be 1.05 °C. Given that K_f for benzene is 5.12 K/m, calculate the molar mass of the compound.

10. (a) Calculate the molarity of a solution of sodium chloride which has an osmotic pressure of 3000 kPa at 25 °C.

  (b) Calculate the osmotic pressure of an 0.084 moldm^{-3} solution of sucrose at 16 °C.

  (c) Calculate the molar mass of a polymer if 2.47 of the polymer has an osmotic pressure of 1.15 kPa when dissolved in 202 cm^3 of benzene at 21 °C

11. (a) The freezing point depression of a 0.10 moldm^{-3} solution of MgSO$_4$ is 0.225 °C. Calculate the Van't Hoff factor of MgSO$_4$ at this molarity.

  (b) Calculate the freezing point and boiling point of a solution of 21.2 g NaCl in 135 cm^3 of water, given that K_f and K_b for water are 1.86 K/m and 0.52 K/m respectively.

Faraday's Laws of Electrolysis

12. (a) Calculate the mass of copper, and the volume of oxygen at 298 K and 100 kPa, which can be produced by passing a current of 0.5 A through a solution of copper sulphate for 10 minutes.

(b) Calculate the time required for 56 g of silver to be deposited from $AgNO_3$ solution using a current of 4.5 A.

(c) How long must a current of 3 A be applied for through a solution of silver nitrate to coat a metal surface of 80 cm^2 with 0.005 cm thick layer? Density of silver is 10.5 g/cm^3.

(d) Calculate the current used if 4.76 g of copper was deposited from copper sulphate solution in 5 hours.

(e) A current of 3.7 A is passed for 6 hours between platinum electrodes in 500 cm^3 of a 2 moldm^{-3} solution of $Ni(NO_3)_2$. What will be the molarity of the solution at the end of the electrolysis?

Conductance, specific conductivity and molar conductivity

13. (a) Describe the method commonly used to measure the resistance of a solution. Explain why alternating current should be used and describe how the cell can be adjusted to deal with very high or very low conductances.

(b) A solution of 0.1 moldm^{-3} H_2SO_4 in a cell containing electrodes with an area of 2 cm^2 and placed 1 cm apart is found to have a resistance of 50 Ω. Calculate:
  (i) The cell constant
  (ii) The specific conductivity of the solution
  (iii) The molar conductivity of 0.1 moldm^{-3} H_2SO_4.
  (iv) The resistance obtained if 0.05 moldm^{-3} KCl is placed in the same cell (Λ of 0.05 moldm^{-3} KCl = 0.0133 m^2 Ω^{-1}mol^{-1})

(c) The resistance of a cell containing 0.1 moldm^{-3} $ZnSO_4$ was found to be 72.2 Ω. The resistance of the same cell containing 0.02 moldm^{-3} KCl was 550 Ω. If the molar conductivity of 0.02 moldm^{-3} KCl is 0.0140 m^2 Ω^{-1}mol^{-1}, calculate the cell constant and hence the molar conductivity of 0.1 moldm^{-3} $ZnSO_4$.

Limiting Molar Conductivity

14. (a) Explain why the molar conductivity of strong electrolytes increases with dilution to a limiting value.
    (b) The specific conductivities of solutions of NaCl of different molarities are given below:

Molarity of NaCl (moldm^{-3})	Specific conductivity ($\Omega^{-1}m^{-1}$)
1.0×10^{-3}	1.237×10^{-2}
1.0×10^{-2}	1.185×10^{-1}
2.0×10^{-3}	2.315×10^{-1}
5.0×10^{-3}	5.553×10^{-1}
1.0×10^{-1}	1.067

   Use this data to determine the limiting molar conductivity of NaCl.
    (c) Explain why the molar conductivity of weak electrolytes increases with dilution to a limiting value.
    (d) Use the following limiting molar conductivities to calculate the limiting molar conductivity of NH$_4$OH:
    Λ^o for Ba(OH)$_2$ = 4.576 x 10^{-2} Ω^{-1}m^2 mol^{-1}
    Λ^o for BaCl$_2$ = 2.406 x 10^{-2} Ω^{-1}m^2 mol^{-1}
    Λ^o for NH$_4$Cl = 1.298 x 10^{-2} Ω^{-1}m^2 mol^{-1}

Transport numbers, ionic mobilities and velocities

15. 0.01 moldm^{-3} HCl was electrolysed in a Hittorf cell using a current of 0.1 A for 1 hour. The cathode and anode compartment each contained 500 cm^3 of solution. After the electrolysis, the molarity of the HCl in the cathode compartment was found to be 8.66 x 10^{-3} moldm^{-3}.
    (a) Calculate the transport numbers of H$^+$ and Cl$^-$ in 0.01 moldm^{-3} HCl
    (b) Calculate the molarity of HCl in the cathode compartment after the electrolysis.
    (c) Given that the molar conductivity of 0.01 moldm^{-3} HCl is 4.12 x 10^{-2} Ω^{-1}m^2 mol^{-1}, calculate the molar ionic conductivities of H$^+$ and Cl$^-$ in this solution.
    (d) Hence calculate the mobilities of the H$^+$ and Cl$^-$ ions.
    (e) Given that the electrolysis was carried out at 12 V and the electrodes were 20 cm apart, calculate the velocities of the H$^+$ and Cl$^-$ ions.
    (f) Explain why the ionic molar conductivity of H$^+$ is significantly greater than that of Cl$^-$.

16. A solution of AgNO$_3$ containing 7.39 g of AgNO$_3$ per kg of H$_2$O is electrolysed until 0.078 g of Ag has been deposited at the cathode. At the end of the experiment the anode compartment of the cell is found to contain 23.14 g of H$_2$O and 0.236 of AgNO$_3$. Calculate the transport numbers of Ag$^+$ and NO$_3^-$.

17. A moving boundary cell was set up using 1.0 moldm^{-3} KCl and using CdCl$_2$ as the following solution. Using a current of 0.0142 A, it took 1675 s for the boundary to sweep through a volume of 0.1205 cm^3. Calculate the transport numbers of K$^+$ and Cl$^-$.
18. Explain why the ionic molar conductivity of Li$^+$ is significantly lower than that of Na$^+$.

Applications of Conductance Measurements

19. (a) The molar conductivity of 0.0140 moldm^{-3} chloroethanoic acid (CH$_2$ClCOOH) is 1.090 x 10^{-2} Ω^{-1}m^2 mol^{-1}. The limiting molar conductivity of CH$_2$ClCOOH is 3.890 x 10^{-2} Ω^{-1}m^2 mol^{-1}. Calculate the acid dissociation constant of CH$_2$ClCOOH.

    (b) The specific conductance of a saturated solution of SrSO$_4$ at 25 ºC is 1.482 x 10^{-2} Ω^{-1}m^{-1}. The specific conductance of the water used is 1.5 x 10^{-4} Ω^{-1}m^{-1}. Deduce the solubility product of SrSO$_4$ at 25 ºC, given that the Λ^o for SrSO$_4$ is 2.788 x 10^{-2} Ω^{-1}m^2 mol^{-1}.

    (c) The specific conductance of pure water at 25 ºC is 5.8 x 10^{-6} Ω^{-1}m^{-1}. Determine the ionic product of water at 25 ºC.

20. During a conductometric titration of CH$_3$COONa against 0.0972 moldm^{-3} HCl the following data were obtained:

Volume of HCl added/cm^3	Conductance/Ω^{-1}
10.0	3.32 x 10^{-4}
15.0	3.38 x 10^{-4}
20.0	3.46 x 10^{-4}
45.0	4.64 x 10^{-4}
50.0	5.85 x 10^{-4}
55.0	7.10 x 10^{-4}

    (a) Explain the shape of the graph.
    (b) Deduce the molarity of the CH$_3$COONa solution.

21. Sketch, and explain, the shape of the following curves:
    (a) C$_6$H$_5$COOH against NaOH
    (b) CuSO$_4$ against NaOH
    (c) HCl against NaOH