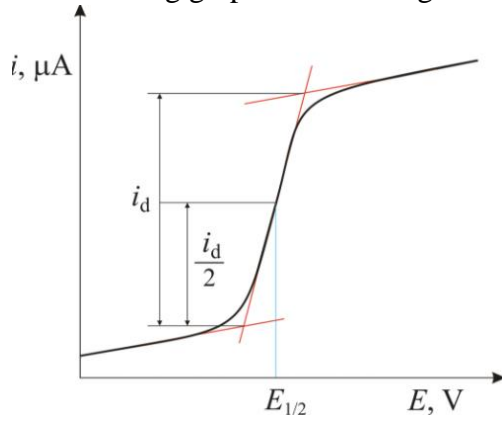**Lesson 1**

1) **Electrochemical Cells**

- There are two types of electrochemical cell:
  - **Galvanic cells** convert chemical energy into electrical energy; a spontaneous (ΔG = -ve) reaction is allowed to take place, with the reacting solutions connected electrically but not chemically; the solutions form a positive electrode (cathode) at which reduction takes place and a negative electrode (anode) at which oxidation takes place; as a result an electromotive force is set up and current can flow; the difference between the electrode potentials (E) at each electrode is the emf of the cell
  - **Electrolytic cells** convert electrical energy into chemical energy; a non-spontaneous (ΔG = +ve) reaction is forced to take place by driving electrons around a circuit, which includes an aqueous solution, in the opposite direction to that in which they would move if a spontaneous reaction was taking place; this process is known as electrolysis

- A Galvanic cell can be converted into an electrolytic cell if an external voltage is applied which is greater than the emf which the cell would generate if the cell were operating Galvanically (known as the back emf); this forces the non-spontaneous reaction to take place and this is how cells are re-charged

2) **General principles of electrolysis at low voltages**

- A minimum external voltage, known as the decomposition potential or back emf, is required to electrolyse a solution; below this voltage, very little current can flow; the minimum voltage required depends on the E_{CELL} of the reaction taking place

- Once the minimum voltage required for electrolysis is reached, the current will start to increase rapidly, due to the reduction of cations at the cathode (negative) or the oxidation of anions at the electrode (positive) which allows current to flow

- Once the electrolysis has started, the concentration of electroactive ions at the electrode starts to decrease; this creates a concentration gradient which causes the electroactive ions to migrate faster to the electrode, which in turn increases the current

- Once the concentration of cations around the electrode has fallen to zero, the concentration gradient has reached a maximum (which is the concentration of the solution); the ability of ions to move to the electrode then becomes a limiting factor and the current stops increasing rapidly, the maximum increase in current due is called the diffusion current (i_D); it is proportional to the concentration of the solution and can therefore be used as the basis for quantitative analysis

- The potential at which the current rises sharply is characteristic of the ion being reduced; it is taken to be the voltage at which the current has risen to half of the diffusion current ($\frac{i_D}{2}$) and is known as the half-wave potential ($E_{1/2}$); it is an intrinsic property of an ion at a particular temperature and can be used to identify the ion

- The resulting graph of current against applied voltage looks as follows:


- If there is more than one cation in solution, other sharp increases in current will be observed at slightly different voltages

Lesson 2

3) **Principles of polarography**

- **Polarography** is an analytical technique which in which voltage-current graphs obtained during electrolysis at low voltage are used for the quantitative and qualitative analysis of ions in solution, using an instrument known as a **polarograph**.

- A **polarograph** consists of an electrolytic cell; the cathode is a dropping mercury electrode, which is a fine capillary through which mercury drops slowly onto the anode; the anode is usually a calomel electrode, which provides a stable potential: $Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$ (electrode potential of saturated solution of KCl at $25\,^0C = 0.251$ V); the electrolytic cell is connected to a potentiometer which allows the voltage to be changed gradually; the circuit also includes a galvanometer which can record small changes in current:
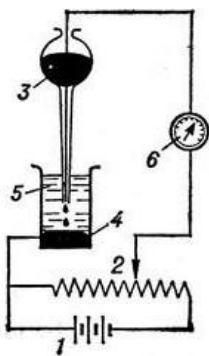
1 – battery, 2 potentiometer, 3 – dropping mercury electrode; 4 – calomel electrode; 5 solution to be analysed; 6 - galvanometer

- The resulting graph of current against voltage is a **polarogram**.
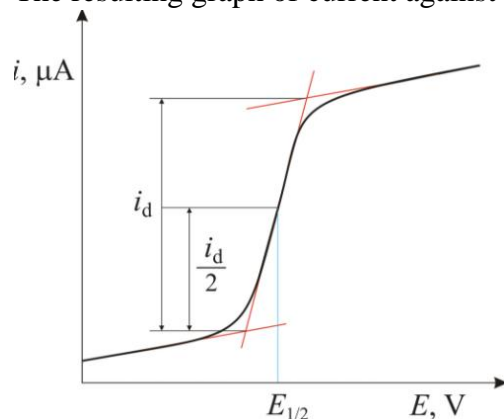
- Important features of a polarograph:
  - The anode is non-polarisable, which means that behaves as a good conductor and its potential remains constant; the large surface area of the anode decreases its polarizability further
  - The cathode is polarisable, which means it is difficult for current to actually flow between solution and electrode and the electrode behaves as a capacitor; the small surface area of the cathode increases its polarizability
  - The dropping of the mercury continually exposes fresh electrode to the electrolyte and prevents the products of electrolysis from accumulating

- Mercury is a suitable choice of cathode because
  - the small droplets can be reproduced exactly
  - hydrogen has a high over-voltage on mercury so the technique can be used in acid solutions
  - mercury forms stable alloys (amalgams) with many metals which can be analysed if the amalgam is used as the material at the electrode and it is made the anode

- The electrolysis should take place adding an excess of salt with an inert cation; this salt carries most of the current and thus means that the cation under investigation makes little contribution to the electrical gradient; the concentration of base electrolyte should be at least 50 times larger than reducible ion

- Oxygen must be removed from the solution as its reduction half-reactions significantly affect the current-voltage relationship

- The limits of operation of the dropping mercury electrode are -2.4 V (at potentials more negative than this even the most inert cation - tetramethylammonium - can be reduced) and +0.6 V (at potentials more positive than this the mercury can be oxidised)

- Polarography can be used to identify and estimate trace metallic impurities in commercial chemicals, particularly foods and fuels; it can also be used for the estimation of gases, especially oxygen

- Polarography works best as concentrations between 0.01 moldm^{-3} and 1 x 10^{-6} moldm^{-3}

Lesson 3

4) Diffusion current

- The rate of flow of a cation A through a solution is given by $v_A = k_A\frac{d\mu_A}{dx}$, where $\frac{d\mu_A}{dx}$ is the electrochemical gradient, and k_A is a constant linked to the diffusion coefficient D_A; $\frac{d\mu_A}{dx}$ in turn depends on the concentration gradient $\frac{dC}{dx}$ and the potential gradient $\frac{d\psi}{dx}$ as follows:
$$\frac{d\mu_A}{dx} = z_A F\frac{d\psi}{dx} + RT\frac{d(\ln C_A)}{dx}$$

- The flux f_A of cation through a solution is the product of the velocity of each ion and the concentration of A (C_A) $f_A = v_A C_A =$ Therefore $f_A = C_A k_A z_A F\frac{d\psi}{dx} + C_A k_A RT\frac{d(\ln C_A)}{dx}$
but $C_A\frac{d(\ln C_A)}{dx} = \frac{dC_A}{dx}$ so $f_A = C_A k_A z_A F\frac{d\psi}{dx} + k_A RT\frac{dC_A}{dx}$ (Equation 1)

- The total current flowing $I = AF\Sigma(fz)$, so $\frac{I}{AF} = \Sigma(fz) = F\frac{d\psi}{dx}\Sigma(Ckz^2) + RT\Sigma(kz\frac{dC}{dx})$
This expression can be rearranged to get an expression for $\frac{d\psi}{dx}$:
$F\frac{d\psi}{dx}\Sigma(Ckz^2) = \frac{I}{AF} - RT\Sigma(kz\frac{dC}{dx})$ so $\frac{d\psi}{dx} = \frac{1}{F\Sigma(ckz^2)}(\frac{I}{AF} - RT\Sigma(kz\frac{dC}{dx}))$
This can be substituted into equation 1 to give: $\mathbf{f_A = \frac{C_A k_A z_A}{\Sigma(ckz^2)}(\frac{I}{AF} - RT\Sigma(kz\frac{dC}{dx})) + k_A RT\frac{dC_A}{dx}}$ **(Equation 2)**

- The contribution made by A to the current based on the electrical gradient $i_A = C_A k_A z_A F\frac{d\psi}{dx}$
  - but the total current due to the electrical gradient $= F\frac{d\psi}{dx}\Sigma(Ckz^2)$
  - therefore the transport number t_A of A in the solution be expressed as: $t_A = \frac{C_A k_A z_A^2}{\Sigma(Ckz^2)}$ (Equation 3)

- Equation 3 can be rearranged to give $\frac{t_A}{z_A} = \frac{C_A k_A z_A}{\Sigma(ckz^2)}$ and this can be substituted into Equation 2 to give:
$$\mathbf{f_A = \frac{t_A}{z_A}(\frac{I}{AF} - RT\Sigma(kz\frac{dC}{dx})) + k_A RT\frac{dC_A}{dx}}\text{ (Equation 4)}$$
The first part of this expression $\frac{t_A}{z_A}(\frac{I}{AF} - RT\Sigma(kz\frac{dC}{dx}))$ gives the flux of A due to the potential gradient.
The second part of this expression $\mathbf{k_A RT\frac{dC_A}{dx}}$ gives the flux of A due to the concentration gradient.

If C_A is very small compared to the total concentration of ions, then the value of t_A is very small. Under these conditions, the equation can be simplified to:
$$\mathbf{f_A = k_A RT\frac{dC_A}{dx} = D_A\frac{dC_A}{dx}}\text{ where } D_A \text{ is the diffusion coefficient of ion A}$$
$$\text{The current I is therefore } \mathbf{I = AFz_A D_A\frac{dC_A}{dx}}$$
In other words, in the presence of a supporting electrolyte in much larger concentration than the electroactive anion, the current is directly proportional to the concentration gradient.

- As the concentration at the electrode falls, the value of $\frac{dC_A}{dx}$, and hence the current, gradually increases. In order to find the value of the $\frac{dC_A}{dx}$ at a particular time, it is necessary to solve Fick's 2nd law of diffusion ($\frac{dC}{dt} = D\frac{d^2C}{dx^2}$); it can be shown that $\frac{dC_A}{dx} = \frac{(C_A - C_{AE})}{\sqrt{\pi Dt}}$

- When the concentration of A at the electrode has reduced to zero, the current becomes the diffusion current.

$$\text{Therefore the diffusion current } I = \frac{C_A z_A FD}{\sqrt{\pi Dt}} = C_A z_A F\sqrt{\frac{D}{\pi t}}$$

- The main factor preventing a steady diffusion current is convection. For I_D to be steady, it is necessary to avoid the formation of convection currents; in the dropping mercury electrode, this is achieved by replacing the electrode before the diffusion layer is thick enough for convection currents to form

- The expression for the diffusion current at a dropping mercury electrode can be derived as follows:
  If the rate of flow of mercury (m) is constant, $m = \frac{V\rho}{t} = \frac{4\pi r^3 \rho}{3t}$ so $r^3 = \frac{V\rho}{t} = \frac{3mt}{4\pi\rho} = kt$ where $k = \frac{3m}{4\pi\rho}$

$$\text{surface area } A = 4\pi r^2 = 4\pi(kt)^{\frac{2}{3}}$$

$$I = z_A FAD_A\frac{dC_A}{dx} = 4\pi z_A FD_A(kt)^{\frac{2}{3}}\frac{dC_A}{dx}$$

If the diffusion is considered linear, the limiting value of $\frac{dC_A}{dx} = \frac{C_A}{\sqrt{\pi Dt}}$

So $I_{Dt} = 4\pi z_A FD_A(\gamma t)^{\frac{2}{3}}\frac{C_A}{\sqrt{\pi Dt}} = 4Fz_A\pi^{\frac{1}{2}}D_A^{\frac{1}{2}}k^{\frac{2}{3}}t^{\frac{1}{6}}C_A$

- A correction needs to be applied to this equation because the expanding size of the drop slows down the increase in thickness of the diffusion layer, causing a larger concentration gradient. Ilkovic showed that this factor was equal to $\sqrt{\frac{7}{3}}$, which gives $I_{Dt} = 4\sqrt{\frac{7\pi}{3}}Fz_A D_A^{\frac{1}{2}}k^{\frac{2}{3}}t^{\frac{1}{6}}C_A$

$k = \frac{3m}{4\pi\rho}$ so $k^{\frac{2}{3}} = m^{\frac{2}{3}}(\frac{3}{4\pi\rho})^{\frac{2}{3}}$ so $I_{Dt} = 4\sqrt{\frac{7\pi}{3}}F(\frac{3}{4\pi\rho})^{\frac{2}{3}}z_A D_A^{\frac{1}{2}}m^{\frac{2}{3}}t^{\frac{1}{6}}C_A$

It the lifetime of one drop is τ, then $I_D = \frac{A}{\tau}\int_0^\tau t^{\frac{1}{6}}dt = \frac{6A}{7}\tau^{\frac{1}{6}} = \frac{24}{7}\sqrt{\frac{7\pi}{3}}F(\frac{3}{4\pi\rho})^{\frac{2}{3}}z_A D_A^{\frac{1}{2}}m^{\frac{2}{3}}\tau^{\frac{1}{6}}C_A$

So $I_D = Xz_A D_A^{\frac{1}{2}}m^{\frac{2}{3}}\tau^{\frac{1}{6}}C_A$ in which X is a complex constant based on F and ρ

$$\mathbf{I_D = Xz_A D_A^{\frac{1}{2}}m^{\frac{2}{3}}\tau^{\frac{1}{6}}C_A \text{ is known as the Ilkovic equation}}$$

The Ilkovic equation makes I_D directly proportional to C_A for any given ion, provided that temperature, concentration of base electrolyte, m and τ are also constant

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- The limitations of the Ilkovic equation are that:

  - It is based on linear diffusion; the equation is only valid using spherically symmetrical diffusion if the thickness of the diffusion layer is small compared to the size of the drop; as a result it does not accurately express the dependence of I_D on τ and m; $\dfrac{I_D}{z_A D_A^{\frac{1}{2}}}$ should be a constant for any given electrolyte but experiments show that this is not the case; as a result calibration is often necessary if the values of m and τ change, which is often the case with a change of capillary

  - adjustments can be made by using more complex models of spherically symmetrical diffusion which improve the agreement but make the equation even more complex

  - The accuracy of the Ilkovic equation relies on accurate values of D_A being available; in practice these can only be easily calculated at infinite dilution $(D_A^0 = \dfrac{RT\Lambda_A^0}{z_A F^2})$

Lesson 4

5) Half-wave potential

- Consider the electrode reaction O + ne → R
  [O] = molarity of O in the solution; $[O]_e$ = molarity of O at the electrode
  [R] = molarity of R in the solution; $[R]_e$ = molarity of R at the electrode

- The electrode potential will depend on the relative concentration of $[O]_e$ and $[R]_e$ according to the
  Nernst equation: $\mathbf{E = E^o + \dfrac{RT}{nF}ln(\dfrac{[O]_e}{[R]_e})}$

- When the external applied voltage is equal to this potential, the oxidation and reduction processes will
  be at equilibrium; the current due to oxidation will be equal to the current due to reduction; the equation
  for the current at an electrode is given by: $I = \dfrac{(C-C_e)zF\sqrt{D}}{\sqrt{\pi t}}$; $\dfrac{zF}{\sqrt{\pi t}}$ is a constant at a particular moment so can
  be simplified to k, so $I = k(C - C_e)\sqrt{D}$

  For reduction, $I = k\sqrt{D_o}([O] - [O]_e)$ and $I_D = k\sqrt{D_o}[O]$
  $I = k\sqrt{D_o}[O] - k\sqrt{D_o}[O]_e = I_D - k\sqrt{D_o}[O]_e$
  Therefore $\mathbf{[O]_e = \dfrac{I_D - I}{k\sqrt{D_o}}}$
  For oxidation, $[R] = 0$ so $I = k\sqrt{D_r}[R]_e$
  Therefore $\mathbf{[R]_e = \dfrac{I}{k\sqrt{D_r}}}$
  Therefore $\dfrac{[O]_e}{[R]_e} = \dfrac{(I_D - I)k\sqrt{D_r}}{Ik\sqrt{D_o}} = \dfrac{(I_D - I)\sqrt{D_r}}{I\sqrt{D_o}} = \dfrac{(I_D - I)}{I}\sqrt{\dfrac{D_r}{D_o}}$

  Therefore $E = E^o + \dfrac{RT}{nF}ln(\dfrac{(I_D - I)}{I}) + \dfrac{RT}{nF}ln\sqrt{\dfrac{D_r}{D_o}}$
  At $E_{1/2}$, $\dfrac{(I_D - I)}{I} = 1$
  So $\mathbf{E_{1/2} = E^o + \dfrac{RT}{nF}ln\sqrt{\dfrac{D_r}{D_o}}}$
  $ln\sqrt{\dfrac{D_r}{D_o}}$ is usually very small, so $E_{1/2}$ is usually very close to E^0. It is, however, necessary to use the E^0
  values for the mercury amalgam rather than for an inert electrode.

- A more general expression for the variation of current with applied voltage is given by
  $$E = E_{1/2} + \dfrac{RT}{nF}ln(\dfrac{(I_D - I)}{I})$$
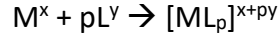 A plot of $ln(\dfrac{(I_D - I)}{I})$ against E^o will give a straight line of gradient $\dfrac{RT}{nF}$ and y-intercept $E_{1/2}$; this can be used
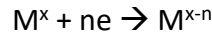 to determine $E_{1/2}$ and n

Lesson 5

6) Use of polarography to study complex ions

- Consider the following equation for the formation of a complex ion:
$$M^x + pL^y \rightarrow [ML_p]^{x+py}$$

The stability constant K_{stab} for this complex can be written as: $K_{stab} = \dfrac{\left[[ML_p]^{x+py}\right]}{[M^x][L^y]^p}$

At the cathode, the complex will dissociate into its free ions and be reduced:
$$M^x + ne \rightarrow M^{x-n}$$

- The electrode potential will depend on the relative concentration of $[M^x]_e$ and $[M^{x-n}]_e$ according to the Nernst equation: $E = E^o + \dfrac{RT}{nF}\ln\left(\dfrac{[M^x]_e}{[M^{x-n}]_e}\right)$

- $[M^x]_e$ depends on $[[ML_p]^{x+py}]_e$; assuming that $[L^y]_e$ is not significantly different from $[L^y]$, the relationship can be represented as: $[M^x]_e = \dfrac{[[ML_p]^{x+py}]_e}{K_{stab}[L^y]^p}$

- At equilibrium the current due to reduction is due to the current due to oxidation

   For reduction, given that almost all of M^x is complexed:
   $$I = k\sqrt{D_C}([ML_p]^{x+py} - [[ML_p]^{x+py}]_e) \text{ and } I_D = k\sqrt{D_o}[[ML_p]^{x+py}]$$
   $$\text{Therefore } [[ML_p]^{x+py}]_e = \frac{I_D-I}{k\sqrt{D_C}} \text{ and } [M^x]_e = \frac{I_D-I}{K_{stab}[L^y]^p k\sqrt{D_C}}$$
   For oxidation, $[M^{x-n}] = 0$ so $I = k\sqrt{D_r}[R]_e$ and $[M^{x-n}]_e = \dfrac{I}{k\sqrt{D_r}}$

   So $\dfrac{[M^x]_e}{[M^{x-n}]_e} = [M^x]_e = \dfrac{I_D-I}{K_{stab}[L^y]^p}\sqrt{\dfrac{D_r}{D_c}}$

   Therefore $E = E^o + \dfrac{RT}{nF}\ln\left(\dfrac{(I_D-I)}{I}\right) + \dfrac{RT}{nF}\ln\sqrt{\dfrac{D_r}{D_c}} - \dfrac{RT}{nF}\ln K_{stab} - \dfrac{pRT}{nF}\ln[L^y]$

   At $E_{1/2}$, $\dfrac{(I_D-I)}{I} = 1$

   So $E_{1/2} = E^o + \dfrac{RT}{nF}\ln\sqrt{\dfrac{D_r}{D_c}} - \dfrac{RT}{nF}\ln K_{stab} - \dfrac{pRT}{nF}\ln[L^y]$

   Given that $\dfrac{RT}{nF}\ln\sqrt{\dfrac{D_r}{D_c}}$ is generally very small, $E_{1/2} = E^o - \dfrac{RT}{nF}\ln K_{stab} - \dfrac{pRT}{nF}\ln[L^y]$

- A graph of $E_{1/2}$ against $\ln[L^y]$ should therefore give a straight line with:
   gradient **-** $\dfrac{pRT}{nF}$
   y-intercept $E^o - \dfrac{RT}{nF}\ln K_{stab}$

This allows p and K_{stab} for the complex ion to be deduced.

Lesson 6

6) Pulse polarography

Traditional polarography has largely been replaced with various forms of pulse polarography, which allows I_D and $E_{1/2}$ to be determined with greater sensitivity. There are three main types of pulse polarography:
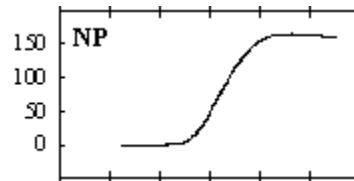
(a) Normal Pulse Polarography

In normal pulse polarography, the potential is kept constant for most of the drop cycle at a value which means that only residual current can flow. The potential of interest is applied only at the last stage of the drop-life for a few milliseconds. This process is repeated for each drop, with a higher potential of interest being applied each time but the same base potential being used.
This technique limits the thickness of the diffusion layer which means in better agreement with the Ilkovic equation. It also means that a significantly larger current is obtained (150 µA for a 0.001 moldm^{-3} solution compared with 10 µA for normal polarography), which in turn means that much smaller concentrations can be detected.
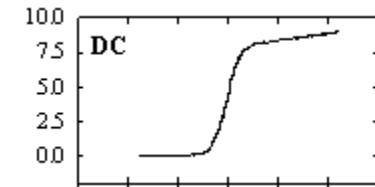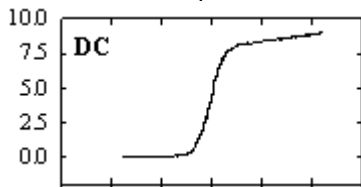
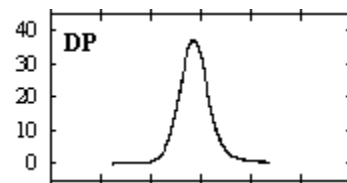DC (regular) polarogram   NP (normal pulse) polarogram

(b) Differential Pulse Polarography

In differential pulse polarography, the potential is kept constant for most of the drop cycle at a value which means that only residual current can flow, but the base potential is increased after each drop; the current is measured twice; firstly just before the potential is increased and then just before the end of the cycle; the difference between the two currents is measured and plotted as a function of base potential. The curve reaches a peak:
- the height of the peak is proportional to the concentration
- the $E_{peak} = E_{1/2} - 0.5\Delta E$, where ΔE is the change in base potential in between each drop
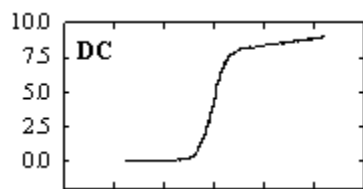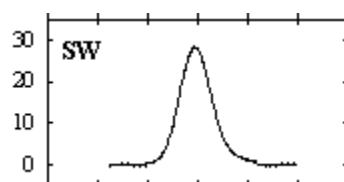
DC (regular) polarogram   DP (differential pulse) polarogram

(c) Square Wave Polarography

In square wave polarography, the same technique is used as in DPP but the entire range of potentials is applied within the lifetime of a single drop.

DC (regular) polarogram   SW (square wave) polarogram

Lesson 7

7) Chronopotentiometry

- In chronopotentiometry, a constant current is applied between the electrodes and the potential of one electrode is measured relative to a reference electrode. A graph of potential against time is plotted.

- The solutions are not generally stirred and contain an excess of a supporting electrolyte; under these conditions, diffusion is the principle mechanism of mass transport of the electroactive species.

- Once a current is applied, a redox reaction will take place at the electrode under investigation (usually the cathode); $O + ne == R$; the potential at the electrode will depend on the relative values of [R] and [O] at the electrode: $E = E^o - \frac{RT}{nF} \ln \frac{[R]_e}{[O]_e}$

- As the reaction starts the potential increases quickly to the decomposition potential; initially $[R]_e = 0$ so $E = E^o + \frac{RT}{nF} \ln [O]_e$; over time, $[R]_e$ increases and $[O]_e$ decreases, so E increases slightly until there is insufficient O remaining to sustain the current; when this happens a different reduction reaction is required and the potential increases sharply until it reaches the decomposition potential of the next reaction

- Transition time is the time between cell turn on and the rapid change in potential is known as the **transition time (τ)**

- A typical chronopotentiogram looks like this:
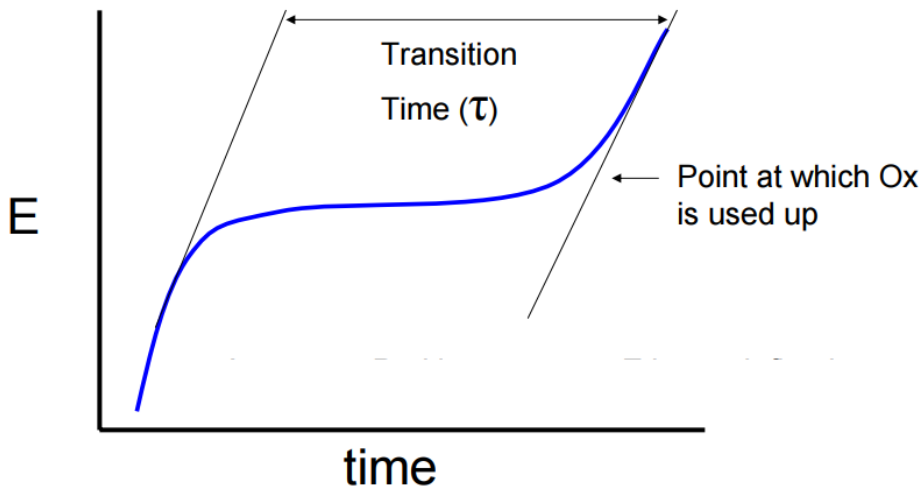
- It can be shown that $\tau^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} nFAD_o^{\frac{1}{2}} [O]}{2I}$; this is known as the Sand Equation; the main limitation of the Sand equation is the difficulty involved in measuring transition time accurately, because it is difficult to account for the current due to the capacitance of the cell; obtaining accurate values for D_o can also be problematic

- The V at $\frac{\tau}{4}$ is equal to the half-wave potential, so chronopotentiometry can also be used in qualitative analysis

8) **Chronopotentiometry vs Polarography**

- It is easier to account for the change in potential due to the resistance of the solution if the current is constant; in polarography, the current varies so it is more difficult to account for
- The Sand equation does not require a correction for spherical diffusion, so there is better theoretical agreement between τ and [O] than there is between I_D and [O]; this also means that chronopotentiometry is better at measuring diffusion coefficients
- Chronopotentiometry can measure a wider range of concentrations than polarography

- Transition times cannot be measured as accurately as diffusion currents
- Transition times are affect by capacitance current and it is very difficult to control this in chronopotentiometry

For these reasons, chronopotentiometry is mainly used in electrode kinetic studies.

Lesson 8

9) **Amperometry and Amperometric Titrations**

- Amperometry is the analysis of a solution based on the current produced when the solution is electrolysed at constant voltage

- The most common type of amperometry is amperometric titration, in which the current is measured as function of volume of solution B (titrant) added to solution A (titrand) at constant voltage; if the applied voltage is below that required to decompose the base solution, a diffusion current is measured; the variation of diffusion current with volume of titrant added can be used to find the equivalence point of the titration
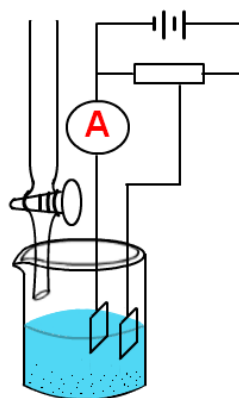
Examples of amperometric titration curves when current is diffusion-controlled:

type	Titrand	Titrant	Product
A	reducible	non-reducible	non-reducible
B	non-reducible	reducible	non-reducible
C	non-reducible	non-reducible	Reducible

A) Ttrand is reducible but titrant and product not.
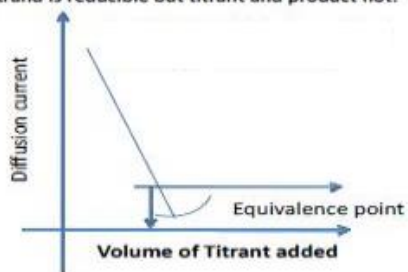
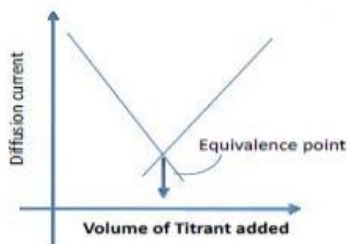eg precipitation titration of Pb^{2+} against SO_4^{2-}

B) Titrant is reducible but titrand and product not
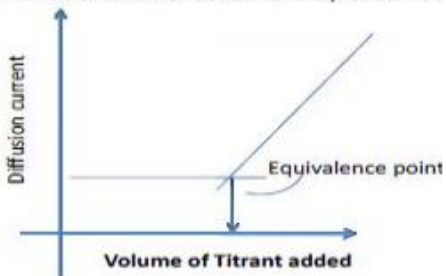
eg precipitation titration of SO_4^{2-} against Pb^{2+}

C) Ttrand and titrant both are reducible but product not

eg precipitation titration of Pb^{2+} against $Cr_2O_7^{2-}$

10) Potentiometric Titrations

- Potentiometric titrations involve the measurement of the change in potential at an electrode with the volume of titrant added; the current is kept constant; the potential will depend on the concentration of the electroactive species; when this is completely eliminated from the solution, the potential will change sharply

- The apparatus used is the same as with an amperometric titration

- The equivalence point is sometimes more accurately measured using dE/dV or even using d^2E/dV

Measurements, first and second derivative in a potentiometric titration.
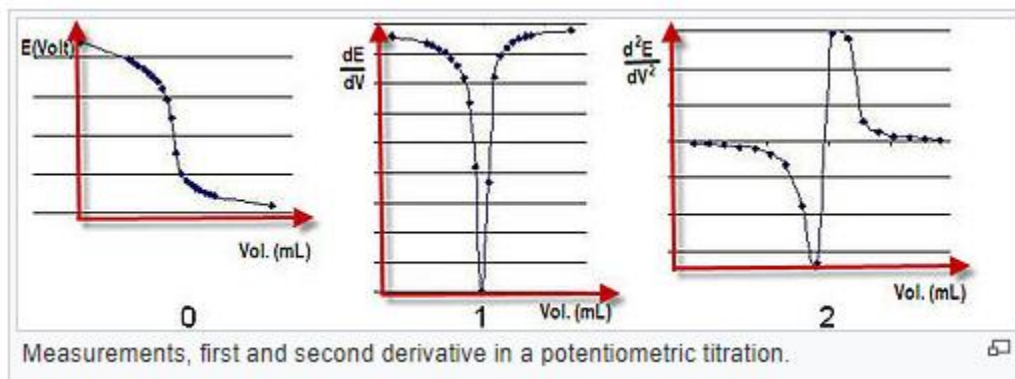
Lecture 9

11) Decomposition of water

Reduction: $H^+ + e \rightarrow \frac{1}{2}H_2$ $E_r^o = 0.00$ V $\qquad E_r = E_r^o + \frac{RT}{nF}\ln[H^+]$; $n = 1$ so $E_r = E_r^o + \frac{RT}{F}\ln[H^+]$

Oxidation: $OH^- \rightarrow \frac{1}{2}O_2 + \frac{1}{2}H_2O + e$ $E_o^o = +0.40$V $\quad E_o = E_o^o - \frac{RT}{nF}\ln[OH^-]$; $n = 1$ so $E_o = E_o^o + \frac{RT}{F}\ln[OH^-]$

$E_r - E_o = E_r^o - E_o^o + \frac{RT}{F}\ln[H^+] + \frac{RT}{F}\ln[OH^-] = E^o + \frac{RT}{F}\ln([H^+][OH^-]) = E^o + \frac{RT}{F}\ln K_w = -0.40 - 0.83 = -1.23$ V

This value depends on K_w and not on $[H^+]$ or $[OH^-]$, so the decomposition of water is independent of pH

12) Back emf

- The potential difference between two electrodes during electrochemical reactions is always lower than the applied potential difference in electrolytic cells; the difference is called the back emf
- In all cells, back emf is caused by the tendency of the products of the electrochemical process to reverse their reaction
- The back emf always reduces the potential difference between the electrodes, so during electrolysis it results in a lower potential difference across the electrodes than the applied emf, which means that no current flows until the back emf is exceeded
- All electrolytic cells demonstrate a back emf
- Some electrodes also show overpotential – this is not the same as back emf

Irreversible Electrode Phenomena

13) Overpotential

- In electrolytic cells, overpotential is the potential difference which must be applied over and above the theoretical decomposition potential in order to liberate a substance at an electrode; $E_{obs} = E_{calc} + \eta$, where η is the overpotential

- In Galvanic cells, overpotential is the decrease in in emf of a cell from its theoretical value based on the relative concentrations of oxidant and reductant in solution

- Overpotential is caused by the **polarisation** of electrodes during the operation of the cell; the polarisation of the electrodes is caused by a difference arising between the concentration of species at the electrodes and the concentration of species in the bulk solution

- There are two causes of polarisation:

    (i) **Concentration polarisation** occurs when the rate of the reaction at the electrode is limited by the ability of the species to diffuse to the electrode; as a result, the concentration of the electroactive species at that electrode is lower than predicted, changing the potential at the electrode; concentration polarisation can be minimised by effective agitation of the solution

    (ii) **Activation polarisation** occurs when the rate of the reaction at the electrode is limited by one of the steps in the electrode reaction being slow – in other words, the electroactive species diffuses to the electrode faster than it can be discharged; and the current cannot flow freely between the electroactive species and the electrode

- The overpotential due to concentration polarisation can be calculated from the Nernst equation:

    - The expected potential is based on the bulk concentration of O: $E_{exp} = E^o + \frac{RT}{nF}\ln[O]$, but the observed potential is $E_{obs} = E^o + \frac{RT}{nF}\ln[O]_e$; the overpotential η therefore is: $E_{exp} - E_{obs} = \frac{RT}{nF}\ln\left(\frac{[O]}{[O]_e}\right)$

    - The current I at the electrode is given by $I = nFD\frac{d[O]}{dx} = nFD\frac{[O]-[O]_e}{\delta}$

      so $[O] - [O]_e = \frac{I\delta}{nFD}$ and $[O]_e = [O] - \frac{i\delta}{nFD}$

    - the diffusion current I_D is reached when $[O]_e = 0$: at this point $I = I_D$

        therefore $[O] = \frac{I_D\delta}{nFD}$ and $I_D = \frac{[O]nFD}{\delta}$

        so $\frac{I}{I_D} = \frac{nFD([O]-[O]_e)\delta}{[O]\delta nFD} = \frac{([O]-[O]_e)}{[O]} = 1 - \frac{[O]_e}{[O]}$, so $\frac{[O]_e}{[O]} = 1 - \frac{I}{I_D} = \frac{(I_D-I)}{I_D}$

    - so the concentration overpotential $\eta = \frac{RT}{nF}\ln\frac{(I_D-I)}{I_D}$

- Activation potential is explained by considering the various stages involved in an electrode reaction; for example, the stages in the discharge of hydrogen at a cathode are as follows:
    - Migration of ions to the cathode
    - Transfer of an electron to from the cathode to the hydrogen ion ($H_3O + e^- \longrightarrow H_2O + H\cdot$)
    - Dehydration of the ion
    - Adsorption of hydrogen atoms onto the electrode
    - Combination of H atoms to form H_2
    - Desorption of H_2 from the cathode

- There are different theories of hydrogen overpotential depending on which of the above steps is the rate determining step:

(i)   Catalytic theory of hydrogen overpotential
This theory assumes that the combination of H atoms to form H_2 is the slow step, and that the metal surface becomes saturated with adsorbed H atoms, which prevents discharge, slows the reaction down and requires an additional potential to compensate for it; this explains why metals known to catalyse the production of hydrogen create a much lower overpotential than metals which do not catalyse the reaction

(ii)   Slow discharge theory of hydrogen overpotential
This theory assumes that the transfer of electrons from the electrode to the cation is the slow step, and that this step requires an activation energy which is supplied by the overpotential

- Most electrodes involving a metal and its ion in solution are reversible and cause negligible activation overpotentials, but activation overpotentials are most commonly found in gas electrodes, especially involving hydrogen

Introduction to Polarography

1.   What is meant by the terms:
     (a)   Decomposition potential
     (b)   Back emf

2.   (a)   What is polarography?
     (b)   What is the difference between a polarograph and a polarogram? Draw diagrams to show the main features of each.
     (c)   Use your polarogram to explain how polarography can be used in both quantitative and qualitative analysis.
     (d)   Give three common applications of polarography.

3.   Explain why mercury is a suitable choice of material for the cathode.

Diffusion Current

5.   The full expression for the rate of discharge at the metal ion M^{n+} at the cathode due to electrical migration and diffusion is given by:
$$f_A = \frac{t_M}{z_M}\left(\frac{I}{AF} - RT\Sigma\left(kz\frac{dC}{dx}\right)\right) + D_M\frac{d[M]}{dx}$$
(a)   Explain how the use of a supporting electrolyte allows this expression to be simplified to
$$f_M = D_M\frac{d[M]}{dx}$$
(b)   Hence derive an expression linking the current at an electrode to the concentration gradient, in the presence of a supporting electrolyte.
(c)   Fick's Law of diffusion relates the concentration gradient to the rate of change of concentration as follows: $\frac{dC}{dt} = D\frac{d^2C}{dx^2}$

This equation can be solved to show that $\frac{d[M]}{dx} = \frac{[M]}{\sqrt{\pi D t}}$ when [M] has reduced to zero at the electrode.

Hence derive an expression for the diffusion current I_D
(d)   Derive an expression for the surface area of mercury at the dropping electrode in terms of the flow rate m, the density of mercury and the time.
(e)   Hence show that I_D is proportional to $D_M^{\frac{1}{2}}m^{\frac{2}{3}}t^{\frac{1}{6}}[M]$
(f)   Show that the average current throughout the lifetime of a drop is directly proportional to the time interval between drops (τ).
(g)   Hence derive the Ilkovic equation.
(h)   Discuss some of the limitations of the Ilkovic equation.

Half-wave potential

6. (a) For the equation $O + ne \rightarrow R$, use the Nernst equation to write an expression for the potential E at the electrode in terms of E^o, n, $[O]_e$ and $[R]_e$

    (b) Show that $[O]_e = \frac{I_D - I}{k\sqrt{D_o}}$ and that $[R]_e = \frac{I}{k\sqrt{D_r}}$

    (c) Hence show that $V_{\frac{1}{2}} = E^0 + \frac{RT}{nF}\ln\sqrt{\frac{D_r}{D_o}}$

    (d) Discuss the validity of the approximation that $V_{\frac{1}{2}} = E^0$.

7. An electroactive species gives a cathodic reduction wave with a diffusion current of 10 μA. The following data were obtained from the polarographic wave:

V/V	I/μA
-0.200	1
-0.221	2
-0.245	4
-0.267	6
-0.291	8
-0.312	9

    Use the data to deduce graphically the value of the half-waye potential and the value of n in the reduction half-equation.

Polarographic analysis of complex ions

8. (a) Write an equation for the formation of the complex ion $[ML_p]^{x+py}$ and hence write an expression for the stability constant K_{stab} of the complex

    (b) The value of $E_{1/2}$ for a complex ion can be shown to be $E_{1/2} = E^o - \frac{RT}{nF}\ln K_{stab} - \frac{pRT}{nF}\ln[L^y]$

    (i) Explain the meaning of the terms in this expression

    (ii) Show how the expression can be used to deduce values for p and K_{stab}

Abnormal Polarographic Waves

9. State three types of pulse polarography. In each case, describe how the potential is varied and state how the polarogram differs from conventional direct current polarography.

Chronopotentiometry

10. (a) What is transition time (τ) in chronopotentiometry?
    (b) Draw a typical potential-time curve encountered in chronopotentiometry, and hence illustrate one graphical method of determining transition time (τ)
    (c) The transition time (τ) in chronopotentiometry is related to the concentration of electroactive species ([O]) by the Sand Equation:

$$\tau^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} n F A D_o^{\frac{1}{2}} [O]}{2I}$$

Explain the meaning of the remaining terms in the Sand equation and give two problems associated with determining [O] by this method.

11. (a) State three advantages of chronopotentiometry over polarography
    (b) State two advantages of polarography over chronopotentiometry

Amperometric Titrations

12. (a) What is amperometry?
    (b) Draw three different shapes of curves obtained in amperometric titrations; in each case, suggest a possible titrand and titrant which could give each type of curve and explain the shape of the curves obtained.

Potentiometric Titrations

13. (a) What is a potentiometric titration?
    (b) During a potentiometric titration, NaCl was added gradually to a solution of $AgNO_3$ and the potential at the cathode measured. The following data were obtained:

Volume of NaCl/cm³	Potential/V	Volume of NaCl/cm³	Potential/V
3.0	347	4.1	309
3.1	346	4.2	299
3.2	344	4.3	249
3.3	340	4.4	243
3.4	338	4.5	237
3.5	335	4.6	233
3.6	333	4.7	232
3.7	330	4.8	229
3.8	325	4.9	227
3.9	323	5.0	225
4.0	319		

Plot a graph of $\Delta E/\Delta V$ against V and hence determine the equivalence point of the titration to two significant figures.

General Principles of Electroanalytical Chemistry

14. (a) Name the electroanalytical method used to obtain the following graphs:
     (i) potential vs volume of titrant
     (ii) current vs volume of titrant
     (iii) current vs potential
     (iv) potential vs time
   (b) Sketch a typical graph for each method
   (c) Briefly explain the principles behind each method
   (d) Describe the instrumentation used for each method

Overpotential and other electrolytic phenomena

15. (a) Explain the meaning of back emf in electrolytic cells and explain what causes it.
   (b) What is meant by the polarisation of electrodes and what are the two causes of electrode polarisation?
   (c) Why are the decomposition potentials of acids and bases the same?

16. (a) What is overpotential? State the two causes of overpotential.
   (b) Show that concentration overpotential is given as $\Delta E = \frac{RT}{nF} \ln(\frac{I_D}{I_D - I})$. Explain fully the meaning of I_D and I.
   (c) Explain why the experimental decomposition potential of acids and bases (1.70 V) is different from the theoretical value of 1.23 V

17. (a) List the stages involved in the discharge and evolution of H_2 at the cathode during electrolysis.
   (b) Outline two theories of hydrogen overpotential.