electrochemistry

sub-subject	physical chemistry
revised?	⚠️ not revised
Status	Not started

electrochemical cell

- anode: the electrode where oxidation occurs
- cathode: the electrode where reduction occurs

Salt Bridge

- it is an upturned U-shaped glass rod that contains a saturated solution of an inert electrolyte mixed with agar-agar powder.
    - we use agar-agar as it retains the ions' ability to move with the same freedom as if they were in water but ensures that there is no mixing of the solutions or change in the concentrations which would lead to change in the emf of the cell.
- salts are chosen based on
    - inert-ness: it should form a highly soluble salt such that the ions do not interfere by forming precipitates.
    - it should also be a strong electrolyte (complete dissociation)- maximum electrical efficiency.
    - its ions should have the same ionic mobility
        - if their mobility is not the same it causes a liquid junction potential- where the salt bridge acts as its own little battery against the main battery and hence decreases voltage and makes the battery weak and inefficient.
- KCl is preffered over $NaCl$ because it has the 1:1 mobility ratio while Na^+ is smaller it has a larger water cloud surrounding it and hence floats a little bit slower

than Cl^-

Liquid-Liquid Junction Potential

- **Set up:** lets say we have a cell set up with Zn as the anode (in $ZnSO_4$ soln)and Cu as the cathode (in $CuSO_4$ soln). the junction between the ions will be a porous ceramic layer
- in the anode solution there is a build up of Zn^{2+} ions (positive charge) and in the cathode solution there is a build up of SO_4^{2-} ions (negative charge). Therefore the ions trying to reach equilibrium will make an attempt to pass through the barrier and restore neutrality.
- BUT Zn^{2+}ions are faster than SO_4^{2-} ions and hence they move from the anode side to the cathode side pretty quickly.
    - this leads to a local positive charge at the cathode side and local negative at the anode (at the barrier only not the entire solution)
    - due to this- there will be an E field produced from the cathode side to the anode. this means that the field will push on the zinc ions newly formed making it more energetically harder for zinc to express its oxidation tendencies and hence EMF drops.
- this causes an inefficiency as it opposes the natural flow leading to lower EMF being produced than its ideal value.
- a salt bridge bypasses this whole problem by making sure that the buildup of charges is kept in check by restoring neutrality.

Electrode potential

- it is the tendency of a metal to either lose or gain electrons in a solution of its own salt.
- in such a half-cell set up- there are two reactions going on:
    - oxidation: losing electrons

    - reduction: gaining electrons; whichever reaction is faster **initially** shows the tendency of the metal.
- it eventually reaches equilibrium- this is because the ions cluster at the rod making either of the processes harder.
    - RHC- the positive rod repels the incoming ions trying to take the electrons
    - OHC- the positive ions in the sole repel the incoming ions trying to lose their electrons

oxidation potential

- **it is the tendency of a metal to lose electrons and become an ion.**
- in a half-cell the metal rod spontaneously loses its electrons and turns into ions making the rod more negatively charged compared to the solution and hence it acts as an **anode** when connected in a circuit

reduction potential

- **it is the tendency of a metal to gain electrons and transform from an ion to its solid state.**
- in a half-cell the ions from the solution grab the electrons from the sea and establish themselves in the rod making the rod more positively charged than the solution and hence it acts as a **cathode** when connected in a circuit

▼ incase its a lil dubious

Imagine the metal rod initially has exactly **100 Copper atoms** and a shared pool of **200 valence electrons**. The positive cores and negative electrons perfectly balance out. Net charge = 0.

1. **The Ion Arrives:** A Cu^{2+} ion approaches. It brings **1 positive copper core**, but **0 valence electrons**.

2. **The Theft:** It plucks 2 electrons out of the rod's shared pool so it can neutralize and glue itself onto the lattice.
3. **The New Balance:** * The rod now has **101 Copper cores** (the 100 originals + the 1 new guy).
    - But how many valence electrons are left in the shared pool? The pool started with 200, the ion took 2 to bond, so there are still only **200 valence electrons** total inside the rod.

Cell notation (IUPAC)

- anode on the left side and cathode on the right
- salt bridge (//)
- phase change (/)
- same phase electron transfer- (,)
- the inert electrodes always to be written in the extreme ends.
- the ions to be facing each other besides the salt bridge.
- conc of ions and pressure of gases to be mentioned in front or below.
- gas-electrode notation
    - anode: Pt, gas | gas-ion
    - cathode: gas-ion | gas, Pt

gas-gas ion electrode

- where the state from which an ion comes from is gaseous.
- cationic gas- hydrogen ; anionic gas-chlorine
- in these set ups we use an inert electrode on which the gas is adsorped

Standard electrode potential

- it is the potential between a metal ion its salt solution at 298K, 1 atm, and 1M solution.
- $E^o_{ion/solid}$- this means that the movement of electrons leads to a ion turning to its solid state (ions gain electrons and hence this is reduction) : aka **Standard Reduction Potential**
- $E^o_{solid/ion}$- this means that the movement of electrons leads to the solid state of a metal turning to its ion (metal loses electrons to turn into its ions and hence this is oxidation) : aka **Standard Oxidation Potential**
- $E^o_{OP} = -E^o_{RP}$
- $E^o_{cell} = E^o_{OP} + E^o_{RP}$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

- here both the electrodes' reduction potential is considered.

Standard Hydrogen Potential

- $E^o_{OP} = E^o_{RP} = 0.00$ V
- it acts as an anode or cathode depending on the tendency of the other metal that it is connnected to.

Electrochemical series

- increasing order of reduction potential down the series

Li : -3.07 V

K

Ca

Na

Mg

Al

Zn : -0.76V

Cr

Fe : -0.45 V

Cd

Ni : -0.25 V

Sn : -0.14 V

[H]: 0.00 V

Cu : 0.339 V

I : 0.537 V

Ag

Hg

Br

Cl

Au

F : 2.87 V

- greater the value of SRP- **more tendency to reduce (**tendency to be a cathode**)** and hence better oxidising agent
- lesser the value of SRP- **more tendency to oxidise (**tendency to be a anode**)** and hence better reducing agent
- reactivity of metals decreases down the series while the reactivity of non-metals **increases** down the series.
- the thermal stability of oxides decreases down the series.
    - this is because- thermal decomp means that the metal is reducing which is more spontaneous with metals located lower in the series- and hence are more unstable and form their metals easily.

Gibb's Free Energy

- it is the maximum energy produced in a chemical reaction which is usable.

$$\Delta G = -nFE^o_{cell}$$

- the total energy produced by a cell will be the total energy produced by it.
- $voltage = energy/charge$
- here charge is taken as: $no.\ of\ electrons\ per\ mole\ of\ metal \times avagadros\ number \times charge\ on\ each\ electron$
- Faraday's constant= $avagadros\ number \times charge\ on\ each\ electron$

- EMF is an intensive property and hence we cannot add two reactions and add their EMFs (this is because it is a ratio and depends more on the electrical intensity: amount of charge done PER electron rather than absolute values of properties which can change with the number)

▼ why u cant add two EMFs tgr

2. Why Can't We Just Add Two EMFs Together? 🛑

Let's look at what happens mathematically when you try to add two half-reactions together to form a third, new half-reaction.

Imagine you want to combine these two steps:

- **Step 1:** $Fe^{3+} + e^- \rightarrow Fe^{2+} (E1^\circ = +0.77\ V)$
- **Step 2:** $Fe^{2+} + 2e^- \rightarrow Fe(s) (E2^\circ = -0.44\ V)$

If you just add the chemical equations together, the Fe^{2+} cancels out, leaving you with a target reaction:

- **Target:** $Fe^{3+} + 3e^- \rightarrow Fe(s) (E3^\circ = ?)$

If you blindly add the voltages $(0.77 + (-0.44))$, you get **+0.33 V. This is completely wrong.** #### Why the simple addition fails: Look at the electron "packet sizes" (n) for each step:

- Step 1 transfers **1 mole** of electrons.

- Step 2 transfers **2 moles** of electrons.
- The Target reaction transfers **3 moles** of electrons.

Because each step is dividing its energy by a *different* number of electrons, their voltages are on entirely different scales! You are trying to add fractions that have different denominators.

- gibb's free energy is an extensive property and we can add two reactions and add their EMFs

Nernst Equation

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} log_{10} Q$$

Nernst Equation: The Deep Summary

1. The Variable Connections

- **Your Question:** Why do we connect these variables this way, and how do we derive it?
- **The Clarification:** The Nernst equation is secretly just the fundamental Gibbs Free Energy equation (ΔG=ΔG∘+RTlnQ) dressed up in electrical units. By using your own derived substitution (ΔG=−nFE), we divided the whole thermodynamic equation by −nF to isolate the real-time voltage (Ecell).

2. The Thermal Energy Term (RT)

- **Your Question:** Why is RT equal to the thermal kinetic energy?
- **The Clarification:** Temperature (T in Kelvin) is literally the measurement of the average microscopic jiggling of particles. The Universal Gas Constant (R) is the translator—its entire job is to convert that temperature into Joules per mole.

Therefore, RT represents the raw baseline currency of **thermal chaos** in the system.

3. The Energy-to-Voltage Converter (nF)

- **Your Question:** Why do we divide by nF in that specific term?
- **The Clarification:** We cannot subtract raw energy (Joules from RT) from electrical pressure (Volts from E∘). Dividing the thermal energy (RT) by the total charge per mole (nF) converts the units into Joules/Coulomb. This makes nFRT the **voltage equivalent of thermal chaos**.

4. The Mystery of the Logarithm (ln vs. log10)

- **Your Question:** Why a log? How does it count concentration? And why ln instead of base 10?
- **The Clarification:** * **Why a log:** When you add particles to a solution, the physical space combinations (crowding/entropy) explode **exponentially**. A logarithm is a mathematical "un-multiplier" that scales that giant exponential explosion back down into a neat, linear step-by-step impact on voltage.
    - **Why ln:** Nature operates continuously, not in neat blocks of 10. The calculus of continuous chemical diffusion naturally spits out the natural log (base e).
    - **The Shortcut:** We only use log10 in school because humans have 10 fingers. Multiplying the base-conversion factor (2.303) by the thermal constants (FRT) at room temperature is exactly how the textbook shortcut number **0.0591** is born.

pH and Hydrogen electrodes

- in the Q term we also include P_{H_2} because it tells us how much and with how much agitation the gas above is hovering which gives us an insight as to how much of that gas turns into ions changing the concentation and hence, the potential of the cell.

Types of electrodes

1. metal/ metal-ion electrode (less reactive metals are more preferred for this)
2. gas/ gas-ion electrode
3. metal/ insoluble salt/anion electrode
4. redox electrode

Metal/ insoluble salt/anion electrode

cathodic representation
anion/ salt/ metal

anodic representation
metal/salt/anion

<u>questions</u>