

A LEVEL REVISION NOTES · PHYSICAL CHEMISTRY

Electrochemistry

AQA A Level Chemistry 7405 — Paper 1, Section 3.1.11: Electrode potentials & electrochemical cells.

Complete topic notes — typed, colour-coded and worked through, with the original handwritten class pages reproduced alongside every section.

Redox & Oxidation States

Balancing Half-Equations

Disproportionation

Standard Electrode Potential

The S.H.E.

Electrochemical Cells

E°_{cell} & Feasibility

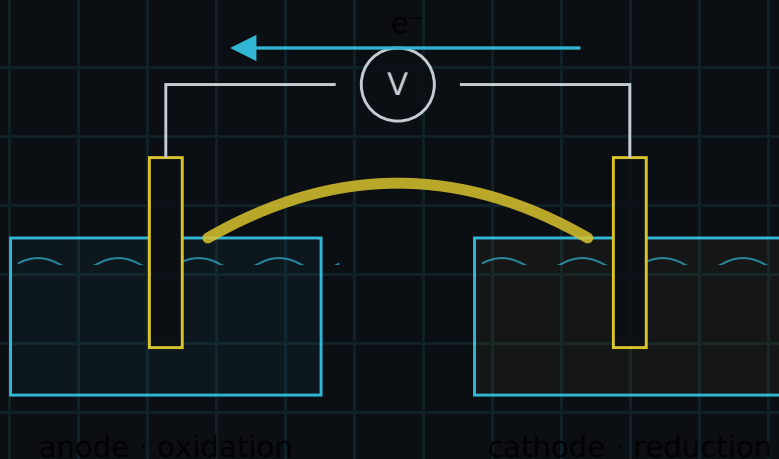
Chain Reactions

Nernst Equation

Homogeneous Catalysis

Electrolysis

Faraday Constant



PREPARED & TAUGHT BY

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TOPIC · PHYSICAL CHEMISTRY

Electrochemistry

Redox & oxidation states · standard electrode potentials · electrochemical cells · the Nernst equation · homogeneous catalysis · electrolysis · the Faraday constant. Typed notes with the original handwritten class pages alongside.



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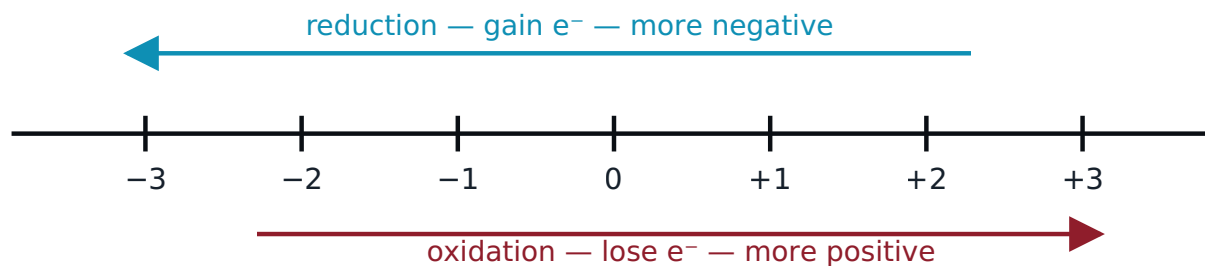
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|---------------------------------|--|
| 1. Redox Fundamentals | 8. Building Redox Equations from E° |
| 2. Oxidation States | 9. Chain Reactions (Excess Reagent) |
| 3. Balancing Redox Equations | 10. Non-Standard Conditions & Nernst |
| 4. Disproportionation | 11. Homogeneous Catalysis |
| 5. Standard Electrode Potential | 12. Electrolysis |
| 6. Electrode Types & the S.H.E. | 13. The Faraday Constant |
| 7. The Complete Cell | 14. Exam Checklist |

01 Redox Fundamentals

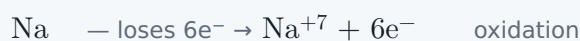
DEFINITIONS

Reduction — gain of electrons; oxidation state *decreases* (becomes more negative).

Oxidation — loss of electrons; oxidation state *increases* (becomes more positive).



Direction of change on the oxidation-state number line.

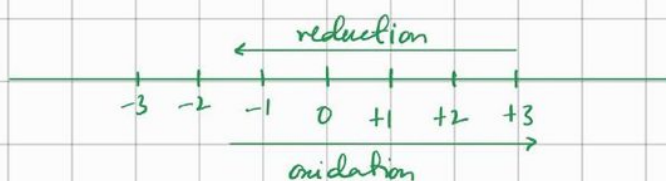


Electrochem

Revise Redox Reactions



reduction : gain of e^{-} (oxidation state decreases) more -ve
 oxidation : loss of e^{-} (oxidation state increases) more +ve



02 Oxidation States

DEFINITION

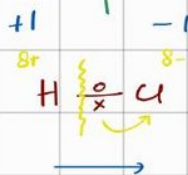
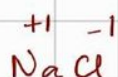
The **hypothetical or actual charge** on an element if the compound is considered to be ionic.

In ionic compounds the charge is real: in NaCl, Na is $+1$ and Cl is -1 . In covalent molecules the oxidation state is assigned by **electronegativity** — the more electronegative atom in each bond is given both electrons.

H—Cl H = +1, Cl = -1 Cl is more electronegative, so it takes the shared pair

Oxidation States

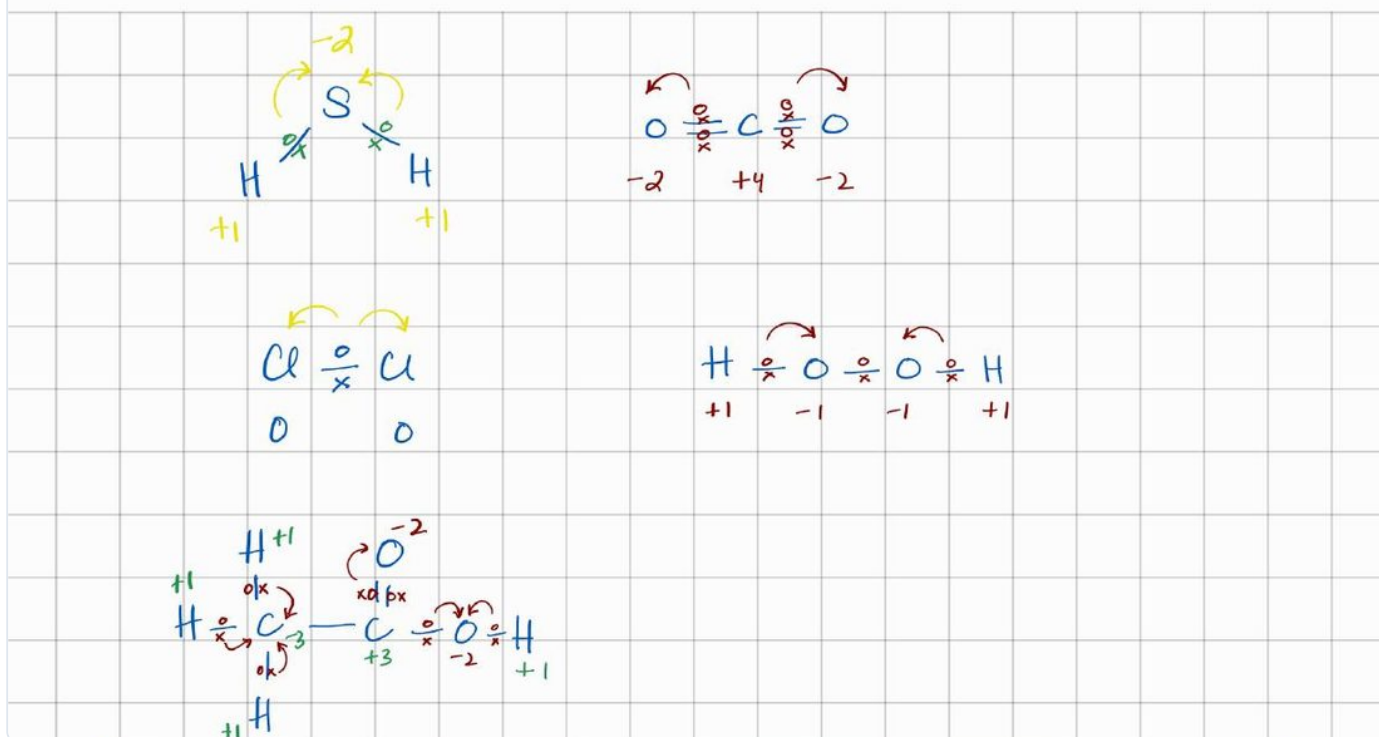
hypothetical or actual charge on an element if the compound is considered to be an ionic compound.



for covalent molecules
O.S is determined by
electronegativity.

Worked assignments from bonding

SPECIES	ASSIGNMENT	REASONING
H ₂ S	H = +1, S = -2	S more electronegative than H in both bonds
O=C=O	C = +4, O = -2 each	All four bonding pairs pulled to O
Cl—Cl	both 0	Identical atoms — pair shared equally
H ₂ O ₂	H = +1, O = -1 each	O—O bond splits evenly, so O is only -1
CH ₃ COOH	CH ₃ carbon = -3, COOH carbon = +3	Assign bond by bond; overall sum = 0

**THE RULES — LEARN THESE**

- **Oxygen** = -2, except with fluorine, or in peroxides (H₂O₂) where it bonds to another O.
- **Hydrogen** = +1 with non-metals; -1 with metals (e.g. Na⁺¹H⁻¹, since Na 0.9 < H 2.1 on electronegativity).
- **Group 1** = +1, **Group 2** = +2, **Group 3** = +3.
- **Fluorine** is always -1.
- **A neutral element** = 0.
- **Transition metals** show variable oxidation states — always calculate.

- * oxygen : -2 (except with F or in H_2O_2 , around other O atoms)
- * hydrogen : +1 (with non metals)
-1 with metals $\begin{array}{c} \text{Na} \quad \text{H}^{-1} \\ 0.9 \quad 2.1 \end{array}$
- * Grp1, Grp2, Grp3
+1 +2 +3
- * transition metals
variable oxidation state
- * F is always -1
- * neutral element = 0

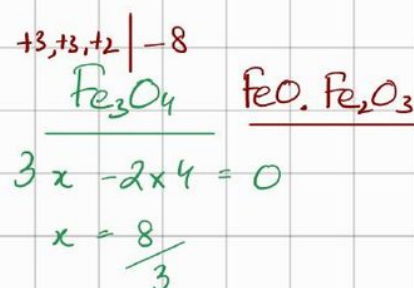
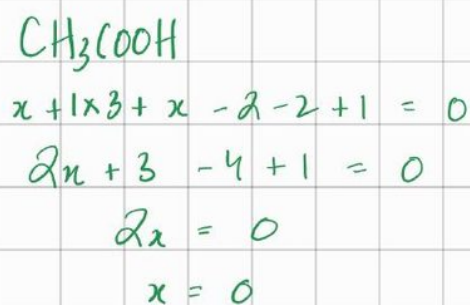
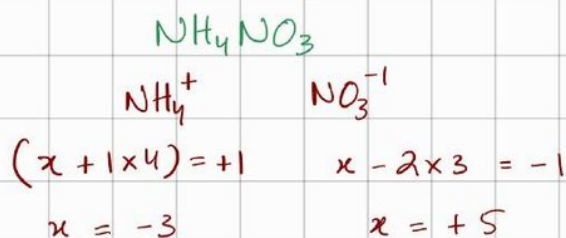
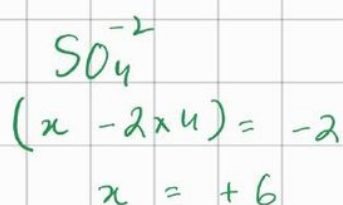
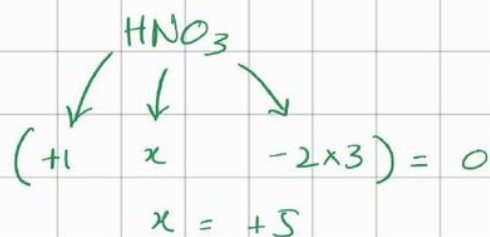
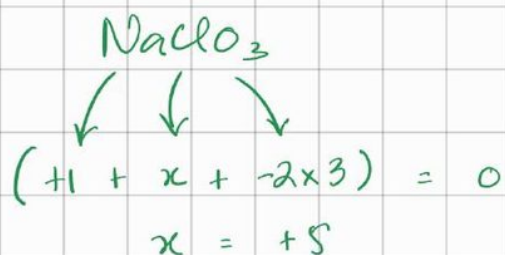
Calculating an unknown state

Set the sum of oxidation states equal to the overall charge and solve for x .

SPECIES	EQUATION	RESULT
$NaClO_3$	$(+1) + x + (-2 \times 3) = 0$	$Cl = +5$
HNO_3	$(+1) + x + (-2 \times 3) = 0$	$N = +5$
SO_4^{2-}	$x + (-2 \times 4) = -2$	$S = +6$
NH_4^+	$x + (+1 \times 4) = +1$	$N = -3$
NO_3^-	$x + (-2 \times 3) = -1$	$N = +5$
CH_3COOH	$2x + 3 - 4 + 1 = 0$	$C_{avg} = 0$
Fe_3O_4	$3x - (2 \times 4) = 0$	$Fe = +8/3$

WHY A FRACTIONAL ANSWER?

Fe_3O_4 gives $Fe = +8/3$ because it is really a mixed oxide — $FeO \cdot Fe_2O_3$, containing $Fe(+2)$ and two $Fe(+3)$. The $+8/3$ is only an average. For polyatomic salts such as NH_4NO_3 , split into ions first (NH_4^+ and NO_3^-) and treat each separately.



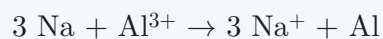
03 Balancing Redox Equations

GOVERNING PRINCIPLE

electrons gained = electrons lost

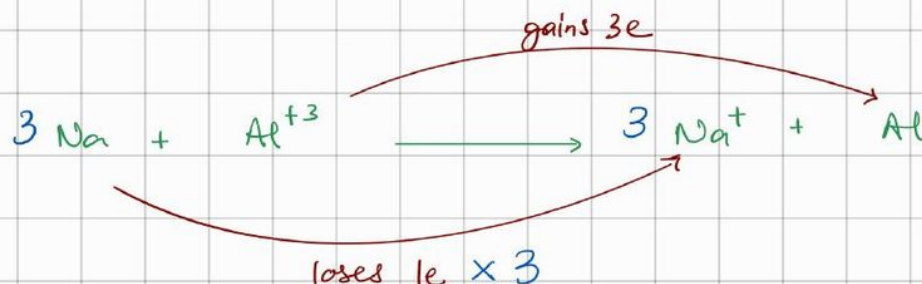
Example — $\text{Na} + \text{Al}^{3+}$

Al^{3+} gains 3e^- ; each Na loses 1e^- , so three Na are needed.



Balancing Redox Reactions

e^- gained = e^- lost

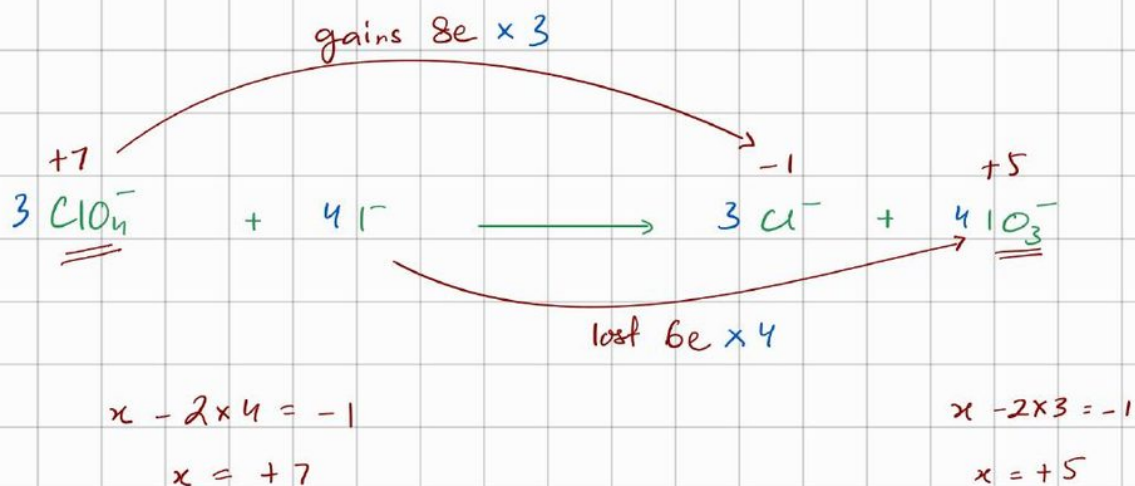


Example — $\text{ClO}_4^- + \text{I}^-$

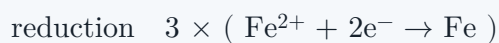
Cl goes $+7 \rightarrow -1$ (gains $8e^-$); I goes $-1 \rightarrow +5$ (loses $6e^-$). LCM of 8 and 6 is 24, so $\times 3$ and $\times 4$.

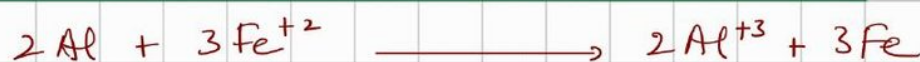
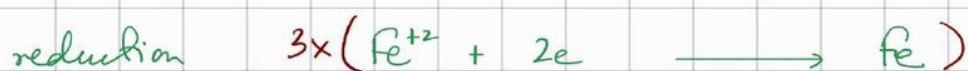
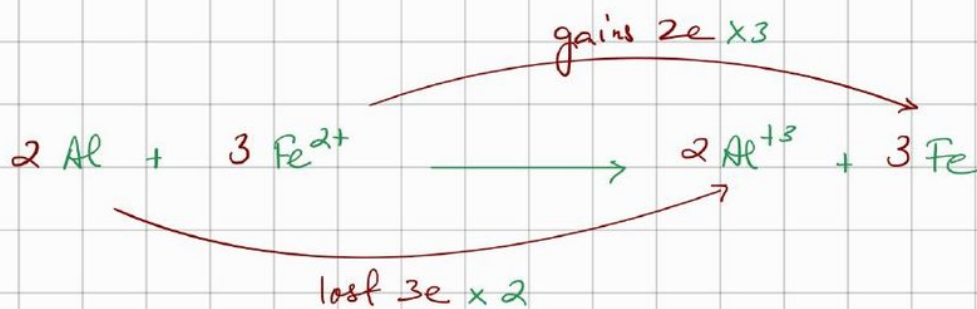


FINDING THE MULTIPLIERS FROM ELECTRONS GAINED AND LOST



Example — $\text{Al} + \text{Fe}^{2+}$, via half-equations



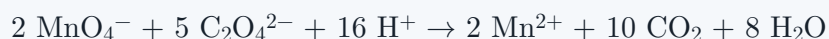
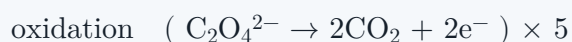
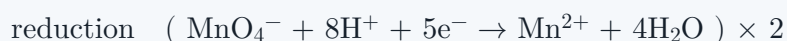
**ALGEBRA OF HALF-EQUATIONS**

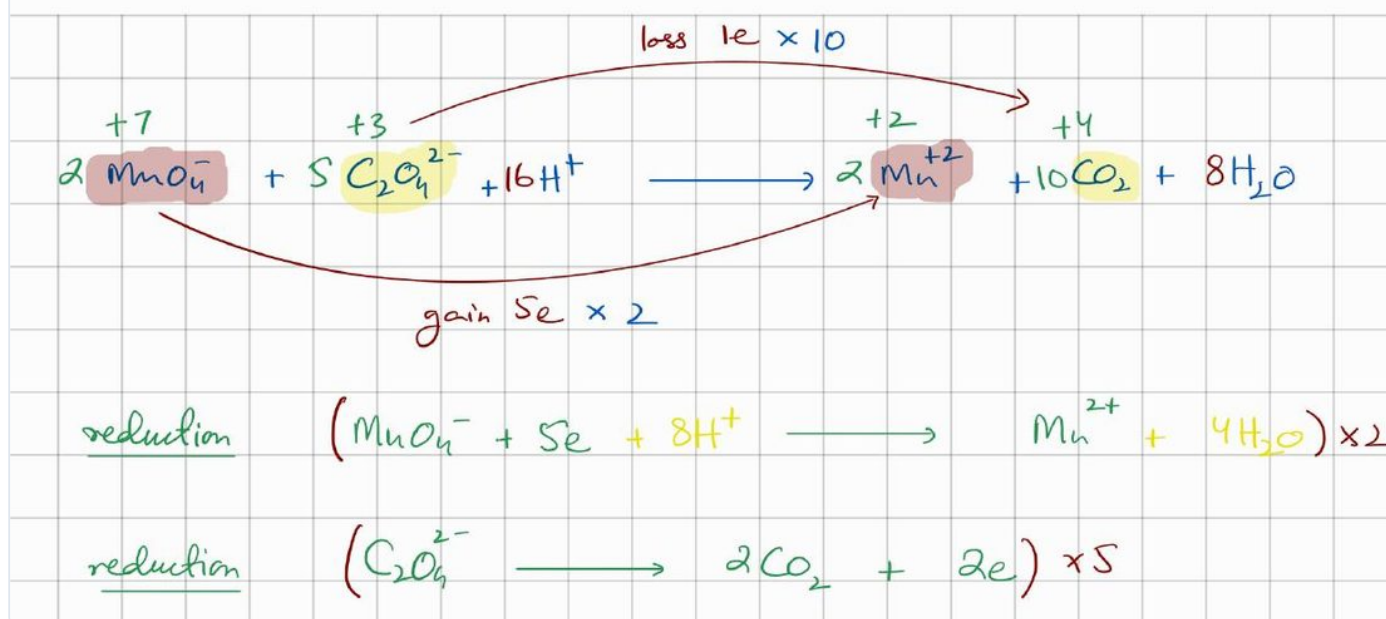
$a \times \text{oxidation} + b \times \text{reduction} = \text{overall redox equation}$

Rearranged: $\text{overall} - (a \times \text{oxidation}) = b \times \text{reduction}$ — useful when a question gives you the overall equation and one half-equation, and asks for the other.

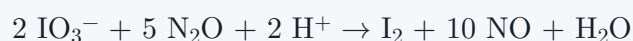
THE REARRANGEMENT, IN THE ORIGINAL HAND**Acidic-medium example — $\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-}$**

Mn: $+7 \rightarrow +2$ (gains 5e^-). C: $+3 \rightarrow +4$ (loses 1e^- per C, so 2e^- per $\text{C}_2\text{O}_4^{2-}$).

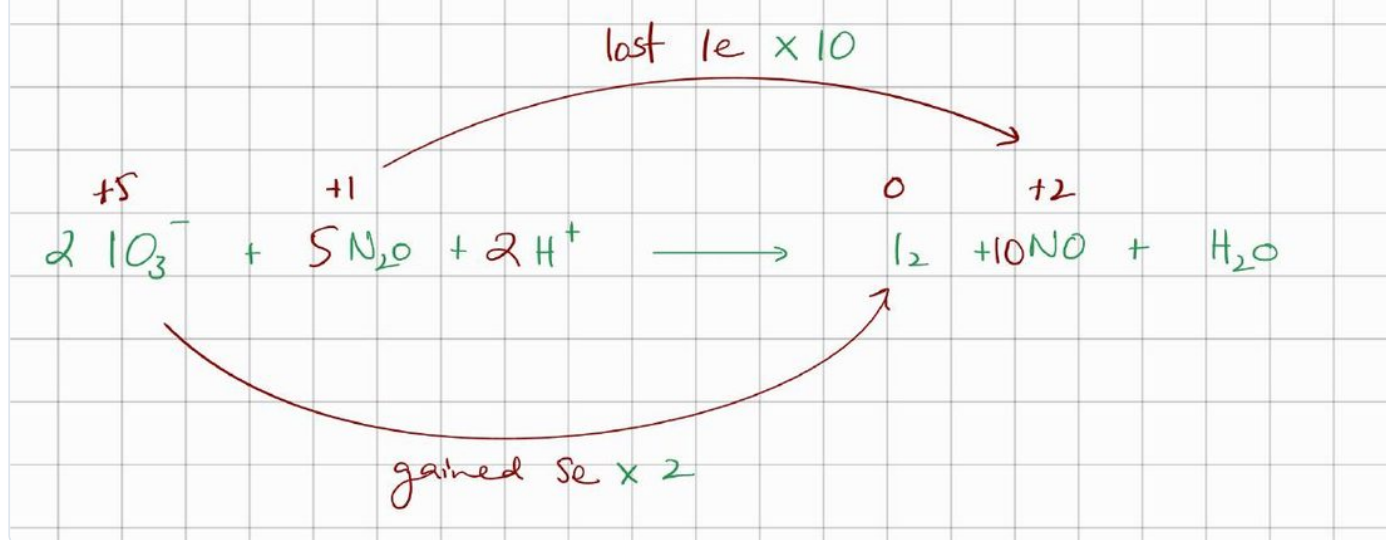




Example — $\text{IO}_3^- + \text{N}_2\text{O}$



I: $+5 \rightarrow 0$ (gains $5e^-$, $\times 2$). N: $+1 \rightarrow +2$ (loses $1e^-$, $\times 10$).



04 Disproportionation

DEFINITION

The **same element** is simultaneously oxidised and reduced in one reaction.

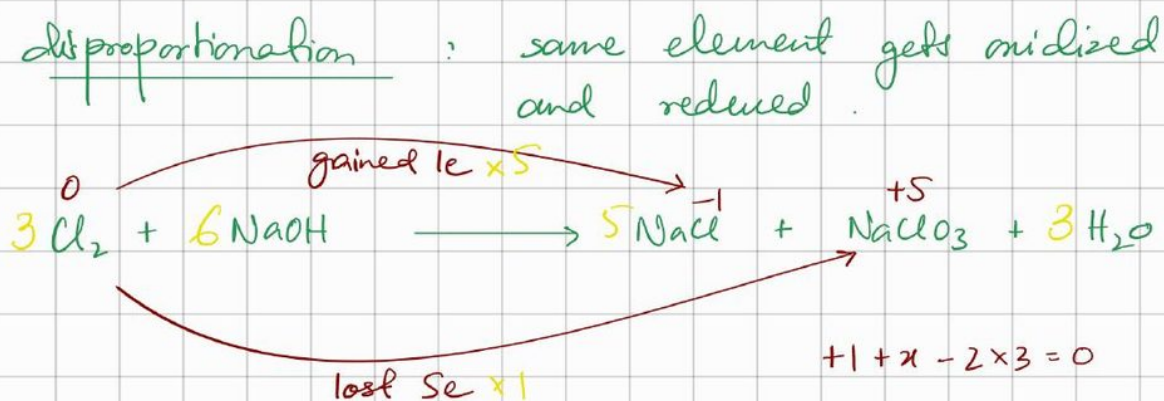


- Cl $^0 \rightarrow -1$ in NaCl — gains 1e^- , $\times 5$
- Cl $^0 \rightarrow +5$ in NaClO₃ — loses 5e^- , $\times 1$

Check on NaClO₃: $(+1) + x + (-2 \times 3) = 0 \rightarrow x = +5$. ✓

CHLORINE DISPROPORTIONATING IN HOT ALKALI

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05 Standard Electrode Potential, E°

DEFINITION

The potential difference measured between a standard electrode and a standard hydrogen electrode.

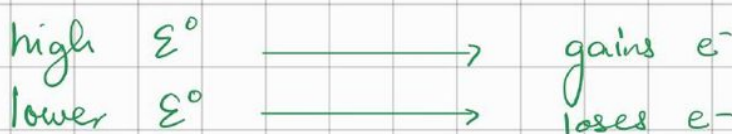
Standard conditions: 298 K, 1 atm, all solutions 1 mol dm^{-3} .

The core interpretation

ELECTRODE POTENTIAL	TENDENCY	ROLE IN A CELL
Higher / more positive E°	Wants to gain electrons	Is reduced — forward direction
Lower / more negative E°	Wants to lose electrons	Is oxidised — backward direction

THE RULE IN ONE LINE — WORTH MEMORISING

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DEFINITION OF E° AND THE $\text{Na} \mid \text{Na}^+$ METAL / METAL-ION ELECTRODE

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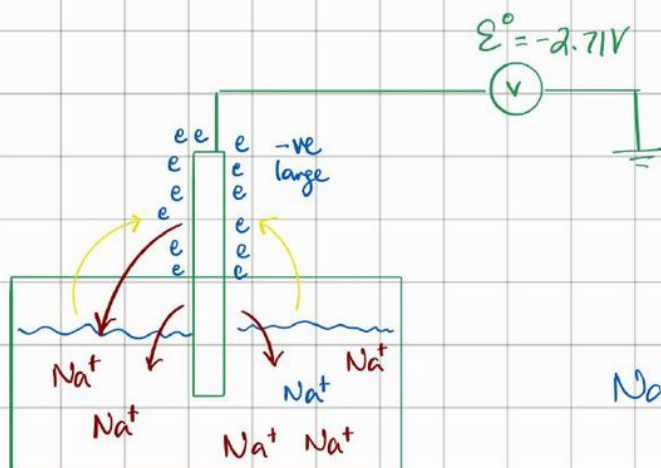
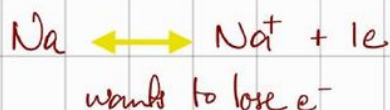
Who gains e^- or loses e^- ?



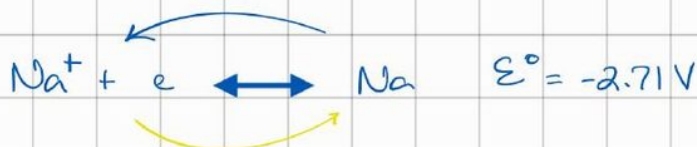
Standard Electrode Potential E°

it is the potential difference calculated b/w a standard electrode and a standard hydrogen electrode

standard
298 K, 1 atm



lower E° indicates that Na wants to lose electrons



metal / the ion

WATCH THE SIGN CONVENTION

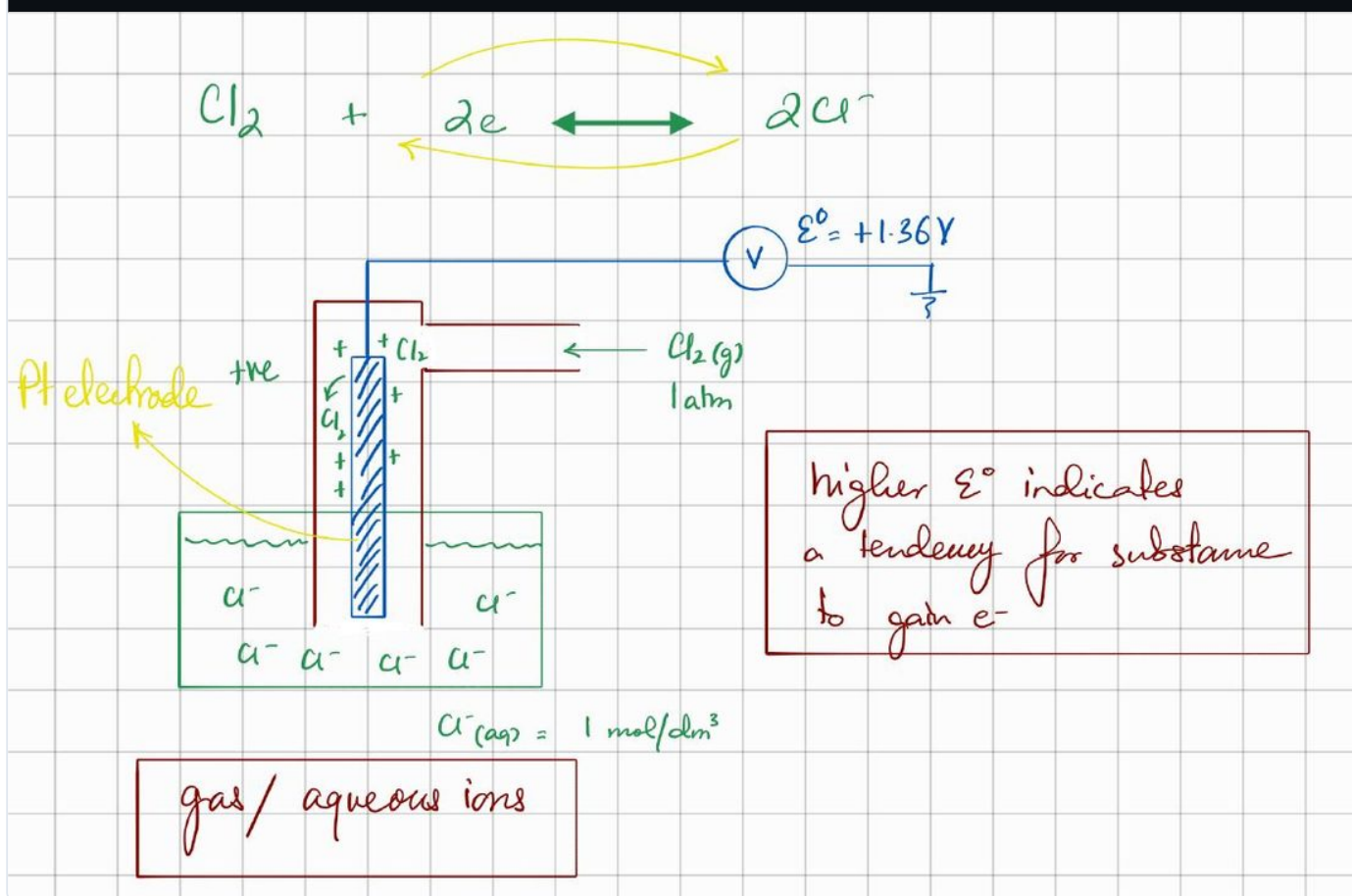
All electrode potentials are quoted as **reduction** potentials — always written left-to-right as gaining electrons. A negative E° simply means the reverse (oxidation) is favoured.

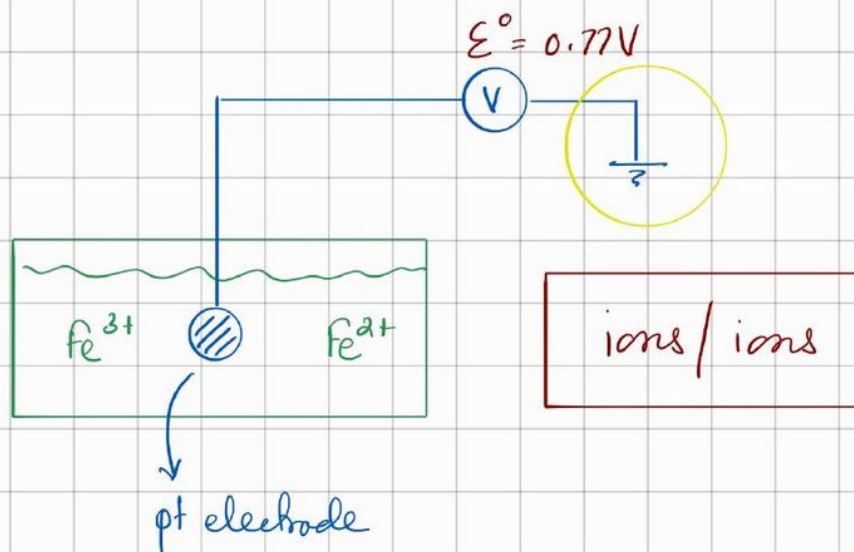
06 Electrode Types & the S.H.E.

TYPE	CONSTRUCTION	EXAMPLE
Metal / metal ion	Metal rod dipped into a solution of its own ion	$\text{Na} \mid \text{Na}^+ \quad E^\circ = -2.71 \text{ V}$
Gas / aqueous ion	Inert Pt electrode, gas bubbled at 1 atm over it, in 1 mol dm ⁻³ ion solution	$\text{Pt} \mid \text{Cl}_2 \mid \text{Cl}^- \quad E^\circ = +1.36 \text{ V}$
Ion / ion	Inert Pt electrode in a solution containing both oxidation states	$\text{Pt} \mid \text{Fe}^{3+}, \text{Fe}^{2+} \quad E^\circ = +0.77 \text{ V}$

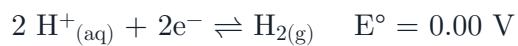
GAS / AQUEOUS-ION ELECTRODE — Cl_2 OVER A PT ELECTRODE

PAGE 7

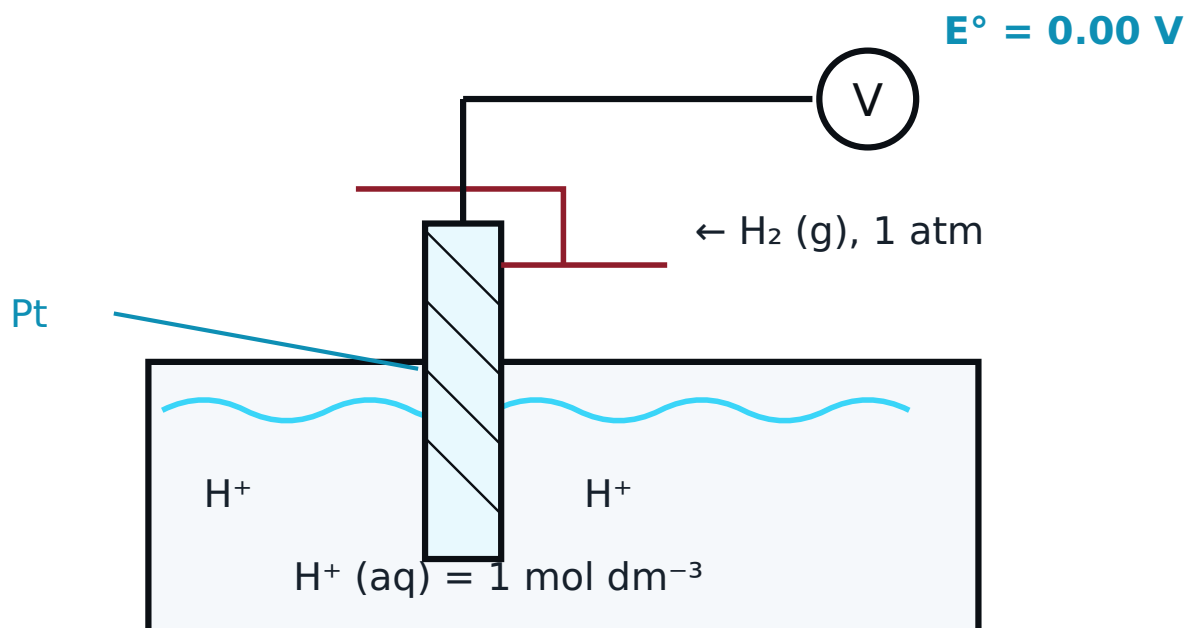


**REFERENCE ELECTRODE — S.H.E.**

The **Standard Hydrogen Electrode** is assigned $E^\circ = 0.00\text{ V}$ by definition. Every other electrode potential is measured against it.



Set-up: Pt electrode, H_2 gas at 1 atm, $\text{H}^+_{(\text{aq})} = 1\text{ mol dm}^{-3}$, 298 K.

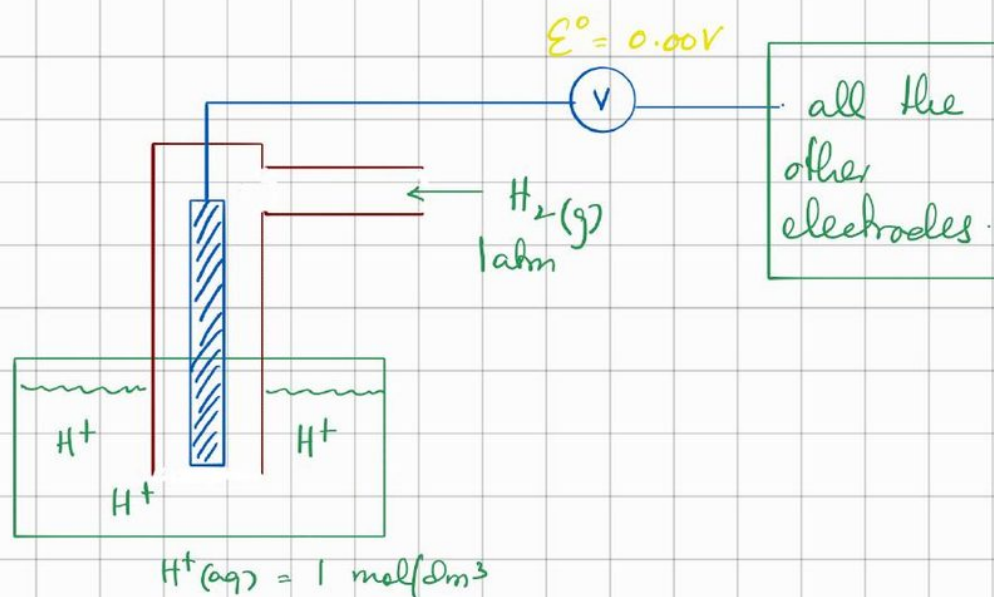
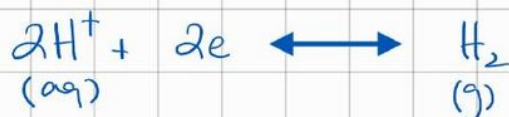


The Standard Hydrogen Electrode — the universal reference, $E^\circ = 0.00 \text{ V}$.

Reference Electrode

S.H.E. Standard Hydrogen Electrode

$$E^{\circ} = 0.0V$$

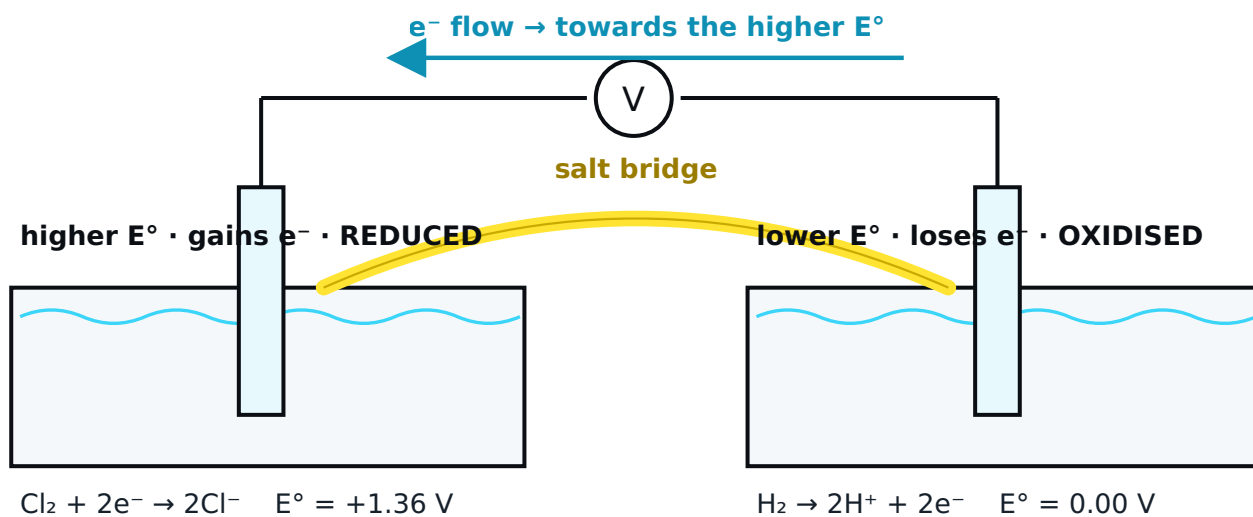


07 The Complete Cell

Connecting two half-cells — one that **loses** electrons and one that **gains** them — produces **electrical energy**.

THREE RULES THAT DECIDE EVERYTHING

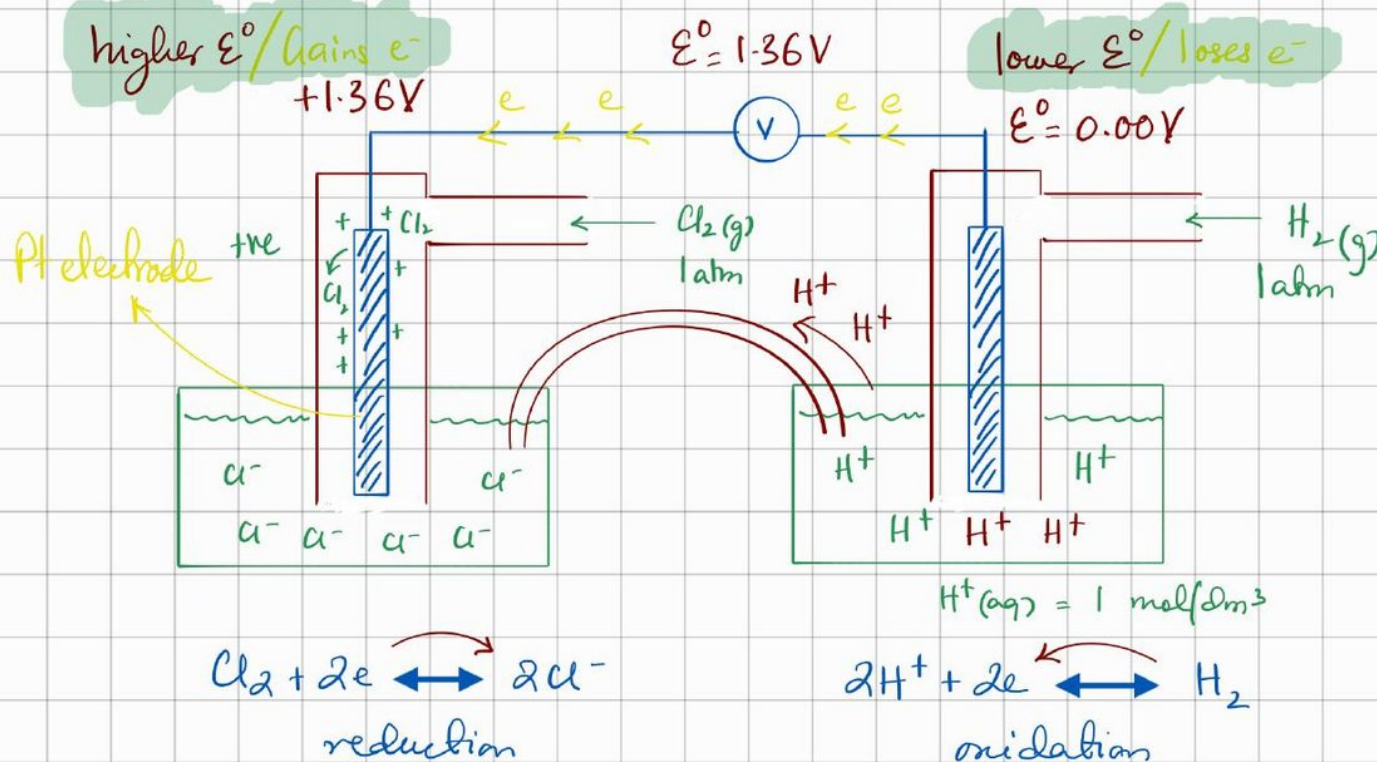
- Electrons travel through the wire **towards the higher E°** .
- The higher- E° half-cell is **reduced**; the lower- E° half-cell is **oxidised**.
- The **salt bridge** balances the charges in the solutions and completes the circuit.



A complete cell: electrons flow externally to the higher- E° electrode; the salt bridge carries ions to balance charge.

Complete Cell $\longrightarrow$ produces electrical energy

loses e^- + gains e^-
electrode 1 electrode 2



* e^- travel towards higher E°

* Salt bridge balances the charges in the solution and completes the circuit.

Example — $\text{Fe}^{3+}/\text{Fe}^{2+}$ against O_2/OH^-

reduction $4 \text{Fe}^{3+} + 4e^- \rightarrow 4 \text{Fe}^{2+}$ $E^\circ = +0.77 \text{V}$

oxidation $4 \text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^-$ $E^\circ = +0.40 \text{V}$

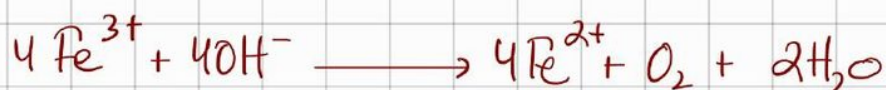
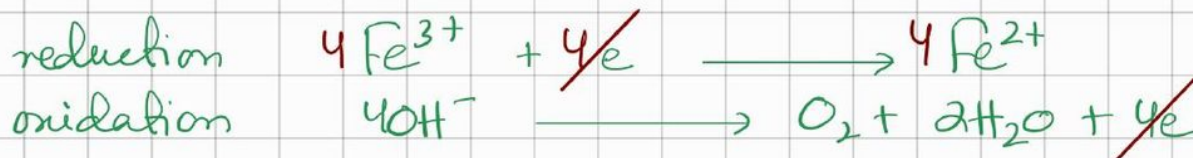
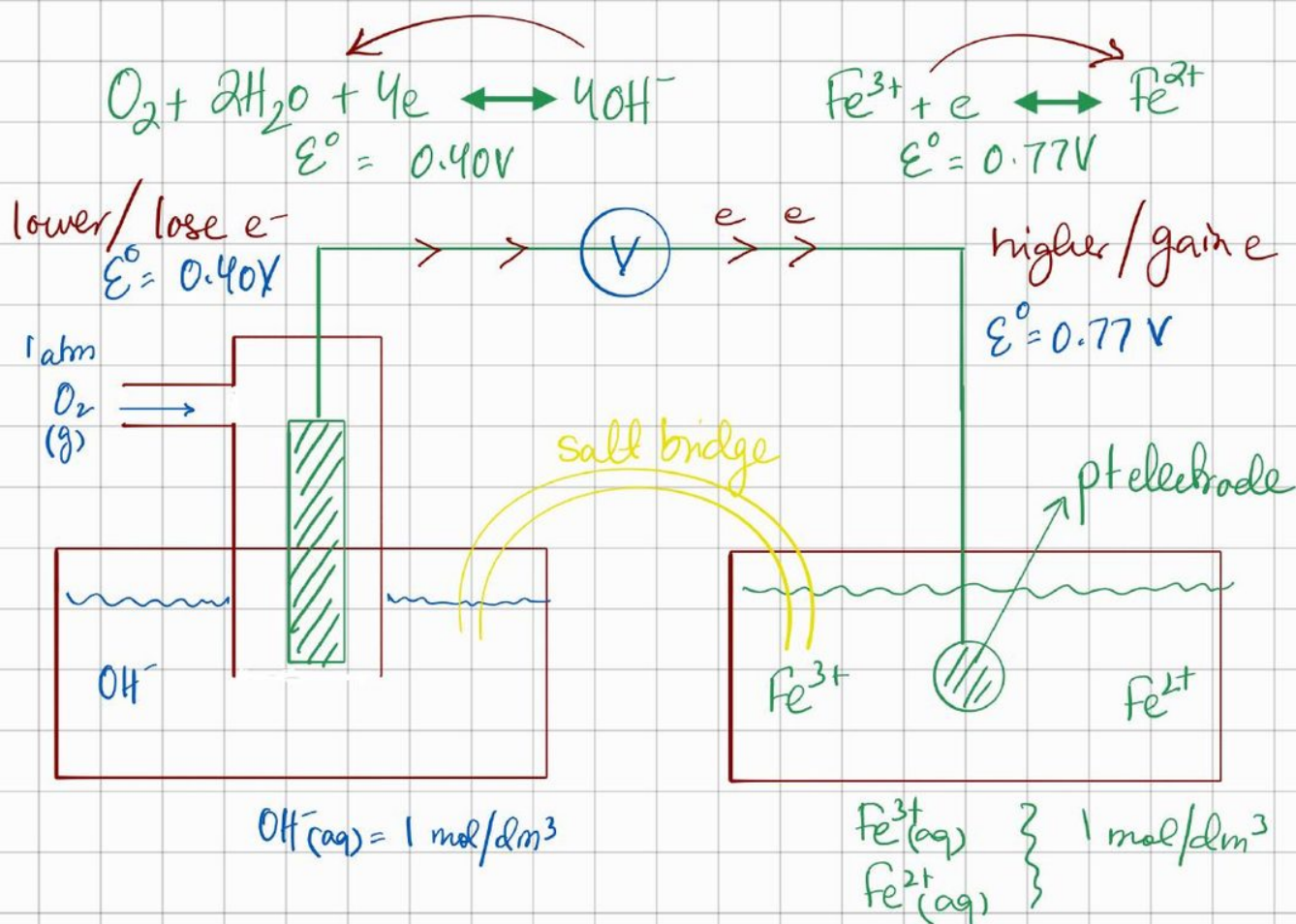


CELL POTENTIAL

$$E^{\circ}_{\text{cell}} = E^{\circ}(\text{reduction, higher}) - E^{\circ}(\text{oxidation, lower})$$

$$0.77 - 0.40 = +0.37 \text{ V}$$

$E^{\circ}_{\text{cell}} > 0 \rightarrow$ the reaction is **feasible**.



$$E^\circ_{\text{cell}} = \text{Reduction } E^\circ - \text{Oxidation } E^\circ$$

(higher) (lower)

$$0.77 - 0.40 = 0.37\text{V}$$

$$E^\circ_{\text{cell}} > 0 \text{ feasible}$$

When a question gives you only the *substances* — no electrode reactions — follow this routine.

- 1 Identify every species actually present, including spectator ions from the salts.
- 2 List all electrode reactions from the data booklet that involve those species.
- 3 Highest E° gains electrons (forward direction); lowest E° loses electrons (reverse direction).
- 4 Check the species you selected are ones you actually have. You cannot oxidise something that is already fully oxidised, or reduce something absent from the mixture.
- 5 Balance electrons, then combine into the overall equation and compute E°_{cell} .

WRITING THE EQUATION DIRECTLY

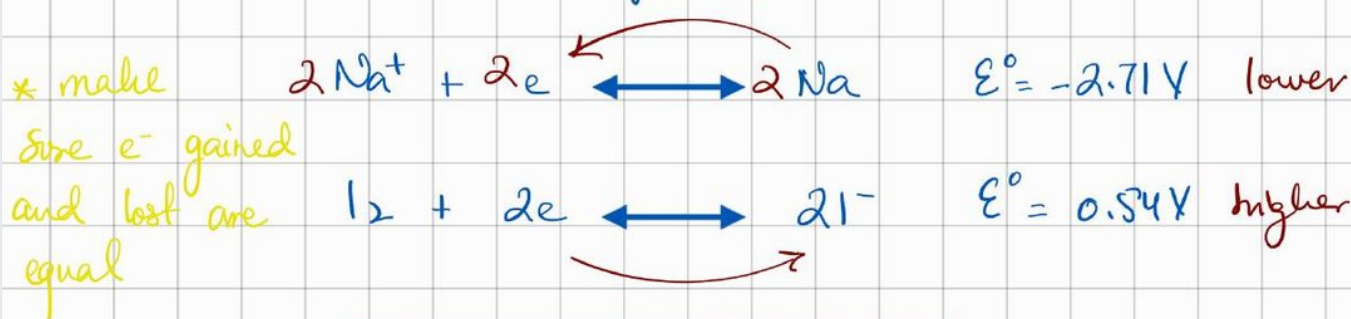
Take the two half-equations, run the higher- E° one **forwards** and the lower- E° one **backwards**, scale so electrons cancel, then read **reactants** $\rightarrow$ **products**.

e.g. $2\text{Na}^+ + 2\text{e}^- \rightleftharpoons 2\text{Na}$ (-2.71 V) and $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$ ($+0.54\text{ V}$) give $2\text{Na} + \text{I}_2 \rightarrow 2\text{Na}^+ + 2\text{I}^-$

READING REACTANTS AND PRODUCTS STRAIGHT OFF THE TWO HALF-EQUATIONS

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Write reactions directly b/w electrodes



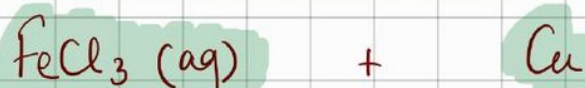
WORKED EXAMPLE 1 — $\text{FeCl}_3(\text{aq}) + \text{Cu}$

Species present: $\text{Fe}^{3+}(\text{aq})$, $\text{Cl}^{-}(\text{aq})$, $\text{Cu}(\text{s})$

HALF-EQUATION	E° / V	AVAILABLE?
$\text{Cu}^{+} + \text{e}^{-} \rightleftharpoons \text{Cu}$	+0.52	no Cu^{+} present
$\text{Cu}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Cu}$	+0.34	lowest available $\rightarrow$ Cu oxidised
$\text{Fe}^{3+} + 3\text{e}^{-} \rightleftharpoons \text{Fe}$	-0.04	would need Fe metal
$\text{Fe}^{3+} + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}$	+0.77	highest available $\rightarrow$ Fe^{3+} reduced
$\text{Cl}_2 + 2\text{e}^{-} \rightleftharpoons 2\text{Cl}^{-}$	+1.36	no Cl_2 present

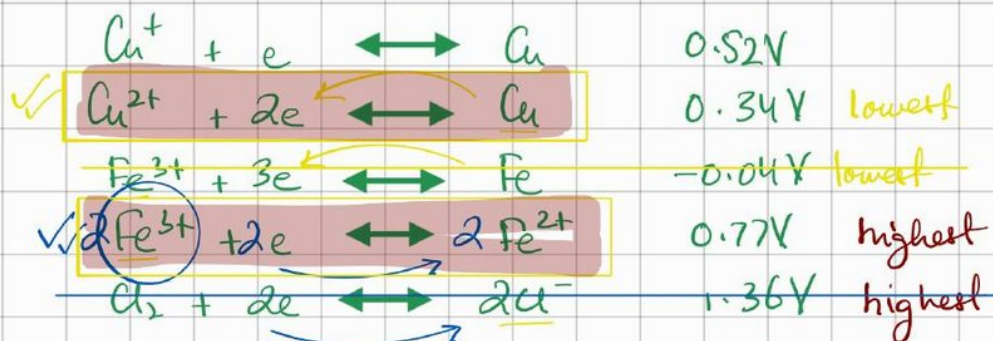
**STEPS 1-2: IDENTIFY SPECIES, THEN LIST EVERY RELEVANT ELECTRODE REACTION****PAGE 11**

How to write redox reaction if only substances are provided (no electrode reactions are given)

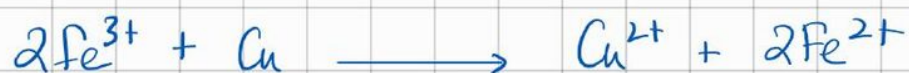


1- identify reactants $\text{Fe}^{3+}(\text{aq})$, $\text{Cl}^{-}(\text{aq})$, Cu

2- list all electrode reactions involving reactants



3 - highest E° — gains e^- } make sure it is
 lowest E° — lose e^- } Fe^{3+} , Cu , Cl^- that lose or gain e^-

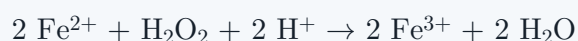


WORKED EXAMPLE 2 — $\text{FeCl}_2 + \text{H}_2\text{O}_2 / \text{H}^+$

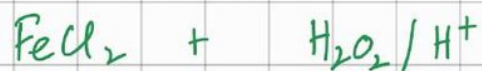
Species present: Fe^{2+} , Cl^- , H_2O_2 , H^+

reduction (highest) $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$ $E^\circ = +1.77\text{V}$

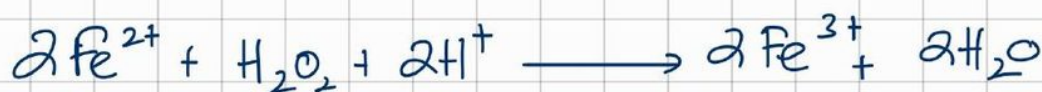
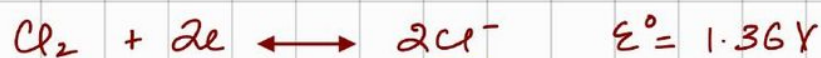
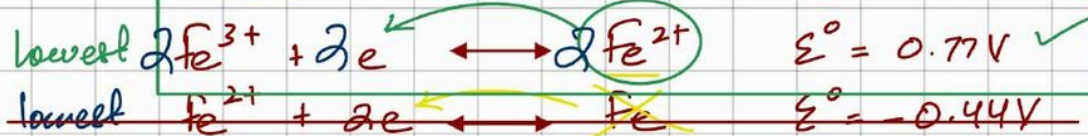
oxidation (lowest available) $2\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + 2e^-$ $E^\circ = +0.77\text{V}$



$\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$ (-0.44V) is rejected: it would require Fe^{2+} to be reduced, but the higher- E° H_2O_2 takes the reduction role.

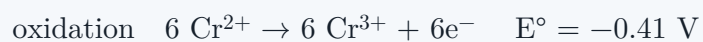
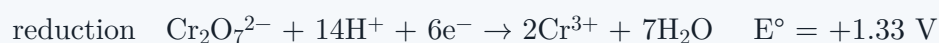


1) identify reactants



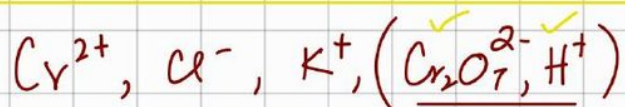
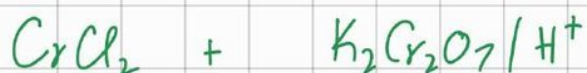
WORKED EXAMPLE 3 — $\text{CrCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+$

Species present: Cr^{2+} , Cl^- , K^+ , $\text{Cr}_2\text{O}_7^{2-}$, H^+



$$E^\circ_{\text{cell}} = 1.33 - (-0.41) = +1.74\text{V}$$

Cl_2/Cl^- (+1.36 V) is rejected — no Cl_2 present; K^+/K (-2.92 V) is rejected — no K metal present.



$$E^\circ_{\text{cell}} = 1.33 - (-0.41)$$

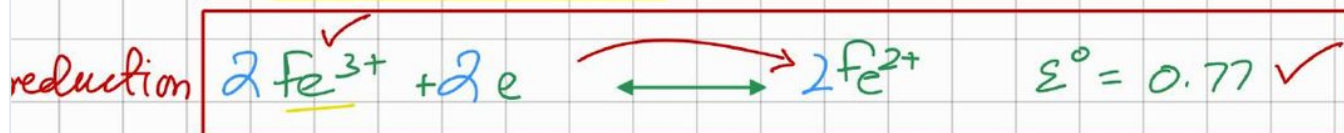
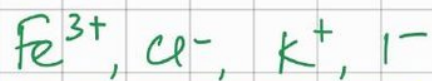
$$= 1.74\text{V}$$

WORKED EXAMPLE 4 — $\text{FeCl}_3(\text{aq}) + \text{KI}(\text{aq})$

Species present: Fe^{3+} , Cl^- , K^+ , I^-



$$E^\circ_{\text{cell}} = 0.77 - 0.54 = +0.23\text{V}$$



Reactants $\longrightarrow$ Products



$$\epsilon^\circ_{\text{cell}} = \text{red. } \epsilon^\circ - \text{oxid. } \epsilon^\circ$$

$$= 0.77 - 0.54$$

$$= 0.23 \text{ V}$$

09 Chain Reactions with Excess Reagent

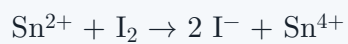
If one reagent is in **excess**, the product of step 1 can be attacked again. Work step by step, then add the steps and cancel.

SN + EXCESS I₂

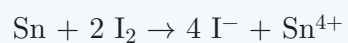
Step 1 — from I₂/I⁻ (+0.54 V) and Sn²⁺/Sn (-0.14 V):



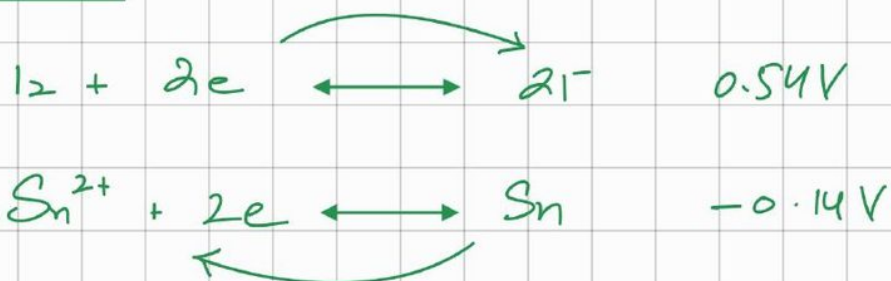
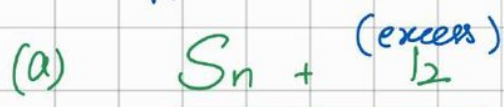
Step 2 — Sn²⁺ now meets the remaining excess I₂; from I₂/I⁻ (+0.54 V) and Sn⁴⁺/Sn²⁺ (+0.15 V):



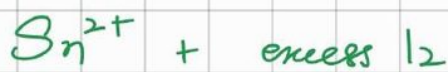
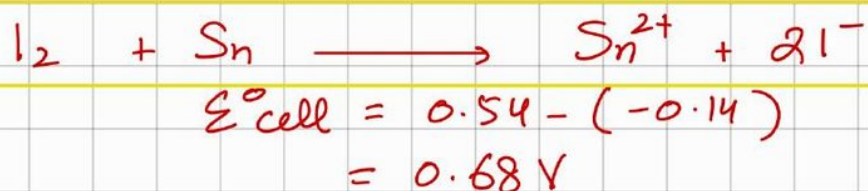
Step 1 + Step 2, cancelling Sn²⁺:



Difficult Example Chain Reactions



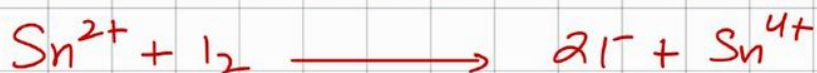
step 1



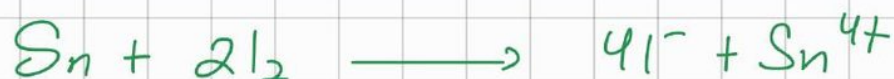
+



step 2

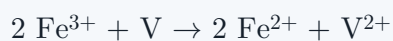


step 1 +
step 2



EXCESS Fe^{3+} + V

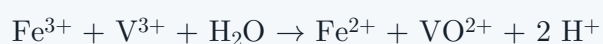
Step 1 — $\text{Fe}^{3+}/\text{Fe}^{2+}$ (+0.77 V) vs V^{2+}/V (−1.20 V):



Step 2 — $\text{Fe}^{3+}/\text{Fe}^{2+}$ (+0.77 V) vs $\text{V}^{3+}/\text{V}^{2+}$ (−0.26 V):

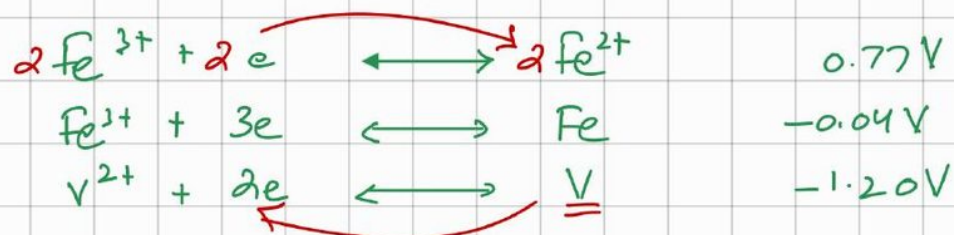
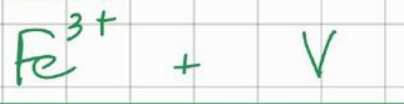


Step 3 — $\text{Fe}^{3+}/\text{Fe}^{2+}$ (+0.77 V) vs $\text{VO}^{2+}/\text{V}^{3+}$ (+0.34 V):

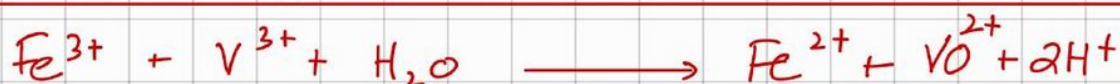
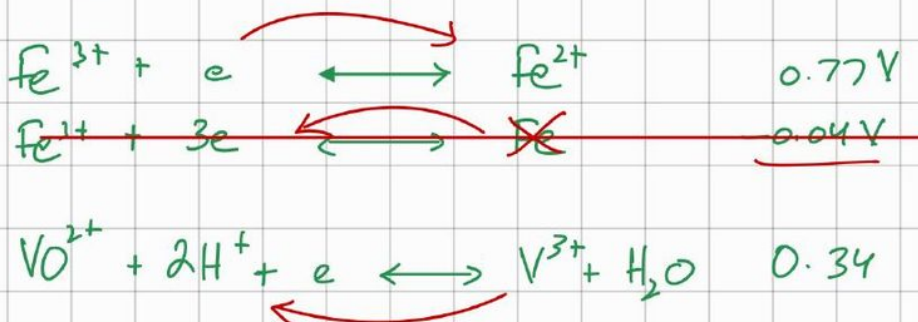
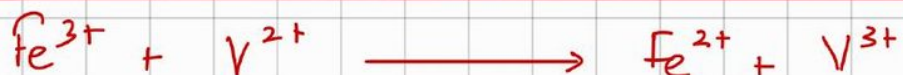
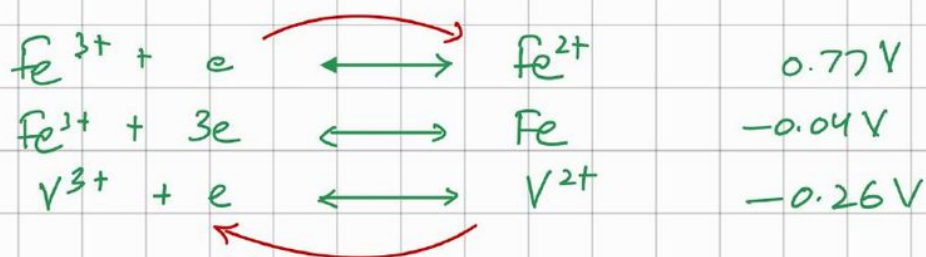
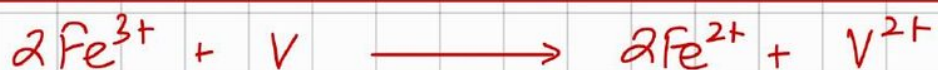


Vanadium is oxidised in stages: $\text{V} \rightarrow \text{V}^{2+} \rightarrow \text{V}^{3+} \rightarrow \text{VO}^{2+}$, as long as Fe^{3+} remains in excess.

(excess)



step 1



Away from 1 mol dm^{-3} , apply **Le Chatelier's principle** to the electrode equilibrium.

REASONING

For $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$, lowering $[\text{Fe}^{3+}]$ shifts the equilibrium **left**. More electrons are produced on the electrode, so the electrode potential **decreases** (becomes less than $+0.77 \text{ V}$).

NERNST EQUATION

$$E = E^\circ + \frac{0.059}{z} \lg \frac{[\text{oxidised}]}{[\text{reduced}]}$$

- z = number of electrons transferred in the half-equation
- **[oxidised]** = species on the *left* of the half-equation
- **[reduced]** = species on the *right*
- **[solid] = 1** — pure solids and the electrode metal do not appear

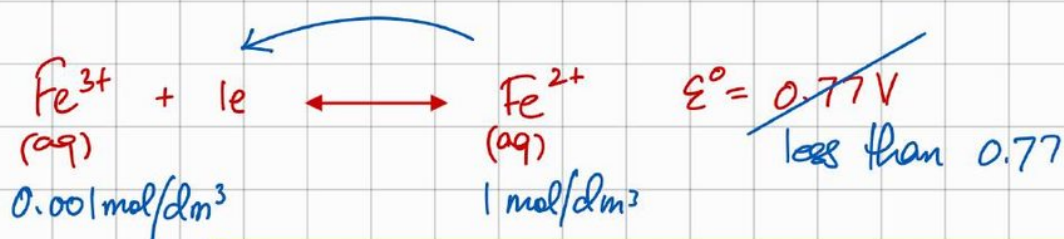
EXAMPLE — Fe^{3+} AT $0.001 \text{ MOL DM}^{-3}$, Fe^{2+} AT 1 MOL DM^{-3}

$$E = 0.77 + (0.059 / 1) \times \lg(0.001 / 1)$$

$$E = 0.593 \text{ V} \quad \text{lower than } E^\circ, \text{ as Le Chatelier predicts}$$

Non Standard Electrode Potentials

Le Chatelier principle



eq. shifts to the left
more e^- are produced on the electrode
hence the potential decreases

nernst eqn

$$E = E^\circ + \frac{0.059}{z} \lg \frac{[\text{oxidised}]}{[\text{reduced}]}$$

→ left (for oxidised)
 → right (for reduced)

nernst equation

no of e^-

$$E = 0.77 + \frac{0.059}{1} \lg \left(\frac{0.001}{1} \right)$$

$$= 0.593 \text{ V}$$

$$[\text{Solid}] = 1$$

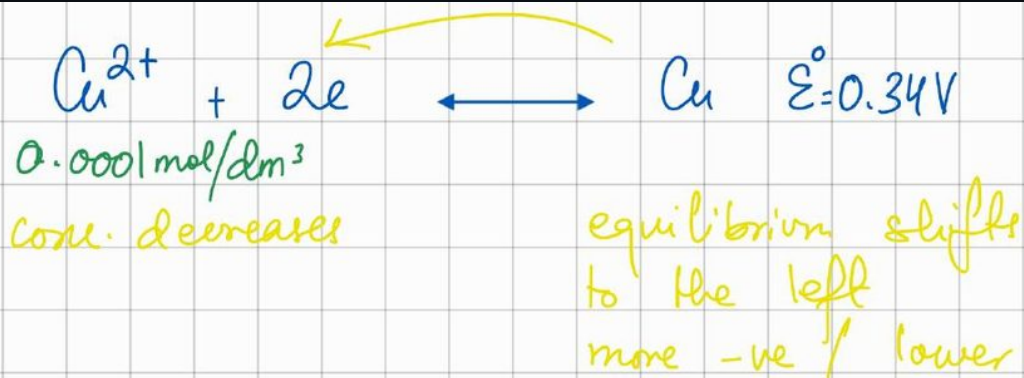
EXAMPLE — Cu^{2+} AT $0.0001 \text{ MOL DM}^{-3}$

$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$, $E^\circ = +0.34 \text{ V}$, $z = 2$, $[\text{Cu}] = 1$ (solid).

$$E = 0.34 + (0.059 / 2) \times \lg(0.0001 / 1)$$

$$E = 0.22 \text{ V}$$

Concentration decreased → equilibrium shifts left → potential becomes lower / more negative.



$$E = E^\circ + \frac{0.059}{Z} \lg \frac{\{\text{oxidized}\}}{\{\text{reduced}\}}$$

$$= 0.34 + \frac{0.059}{2} \lg \left(\frac{0.0001}{1} \right)$$

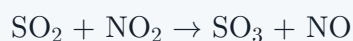
$$E = 0.22\text{V}$$

11 Homogeneous Catalysis

DEFINITION

A homogeneous catalyst is in the same phase as the reactants.

Example 1 — NO_2 in the Chamber process

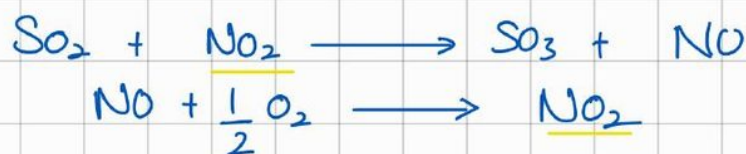


NO_2 is regenerated — a homogeneous catalyst, since everything is gaseous.

Example of a homogeneous catalyst

catalyst / reactants have same phase

Example 1



NO₂ is homogeneous catalyst
(all in gaseous state)

Example 2 — Fe²⁺/Fe³⁺ catalysing S₂O₈²⁻ + I⁻

MEMORISE THIS ONE

Uncatalysed: $2 \text{I}^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{I}_2 + 2 \text{SO}_4^{2-}$, with $E^\circ_{\text{cell}} = 2.01 - 0.54 = +1.47 \text{ V}$.

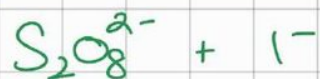
Yet no reaction occurs. Both ions are negatively charged and repel each other, so the activation energy is very high — despite the large, favourable E°_{cell} .

Adding Fe²⁺/Fe³⁺ provides a two-step route in which each step involves **oppositely charged** ions:

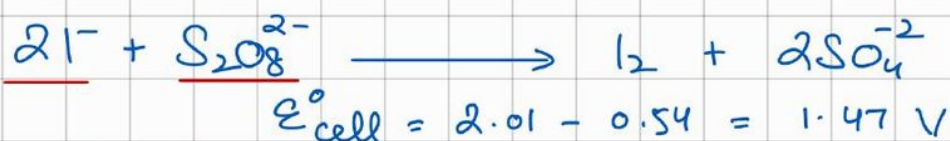


- Fe²⁺/Fe³⁺ are **regenerated** — **unchanged overall**.
- Ions are oppositely charged in both steps → attraction → much **lower** E_a → much faster.

Relevant potentials: I₂/I⁻ +0.54 V · Fe³⁺/Fe²⁺ +0.77 V · S₂O₈²⁻/SO₄²⁻ +2.01 V. The Fe couple sits between the other two — that is why it works.

Example 2

memorize this



No Reaction: both ions are $-ve$ and repel each other.
reaction has high E_a even though it has
a high E°_{cell} .

* $\text{Fe}^{2+}/\text{Fe}^{3+}$ are added as catalyst



DEFINITION

The **opposite of an electrochemical cell**: electrical energy is converted into chemical energy — the **decomposition of an electrolyte using electrical energy**.

ELECTRODE	WHAT HAPPENS	WHICH SPECIES	DIRECTION OF EQUATION
Anode (+)	Oxidation — loses e^-	The one with the lower E°	Written backwards
Cathode (-)	Reduction — gains e^-	The one with the higher E°	Written forwards

ELECTROLYSIS DEFINED AS THE REVERSE OF A CELL

PAGE 20

* Fe^{2+}/Fe^{3+} remain unchanged

* ions are oppositely charged, so much faster reaction

Electrolysis

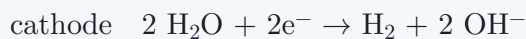
Opposite of an electrochem
Cell :

Electrical energy to chemical energy
decomposition of an electrolyte
by using electrical energy.

Dilute $NaCl_{(aq)}$

Species present: Na^+ , Cl^- , H_2O . Note that **water ionises very little**, so H_2O itself is the species discharged.





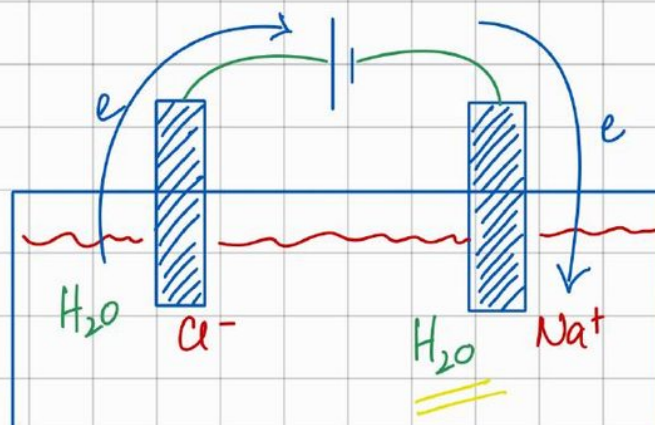
ANODE AND CATHODE LABELLED BY E° — DILUTE NaCl

PAGE 20

water ionizes
very little

anode

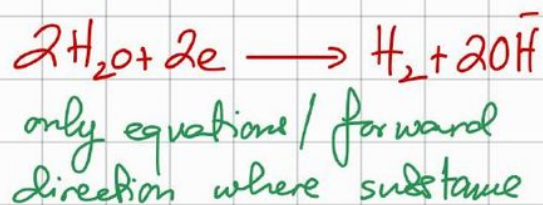
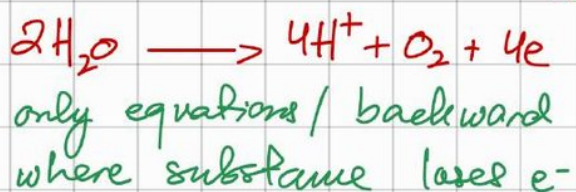
who loses e^-
lower E°



cathode

who gains e^-
higher E°

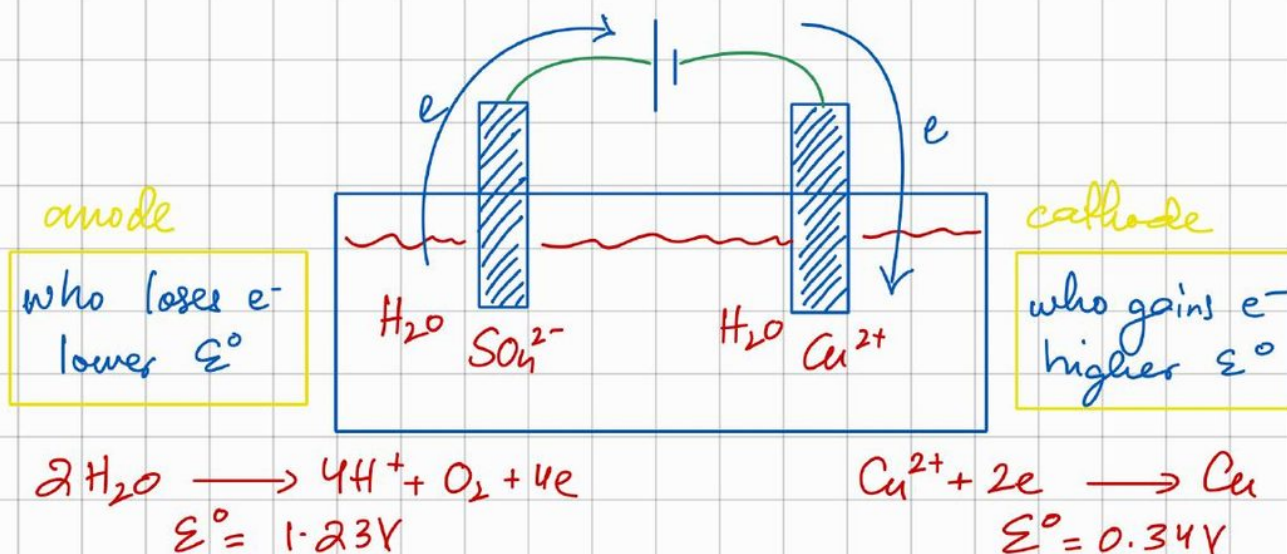
NaCl(aq)



$\text{CuSO}_4(\text{aq})$

Species present: Cu^{2+} , SO_4^{2-} , H_2O .



**CLASSIC EXAM QUESTION — WHY IS Cl^- DISCHARGED FROM CONCENTRATED NaCl ?**

At the anode the candidates are Cl^- and H_2O :



Under standard conditions $\text{O}_2/\text{H}_2\text{O}$ has the lower E° , so water should be oxidised. **But** when Cl^- is concentrated, the Cl_2/Cl^- equilibrium shifts to the **left**, so its electrode potential **decreases** (to roughly +1.20 V) and becomes the **lowest**. Hence **Cl^- is discharged** and chlorine gas is produced.

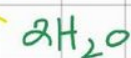
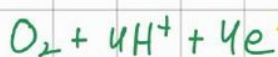
Why does Cl^- get discharged at anode if NaCl is concentrated?

+ve anode

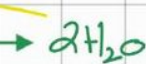
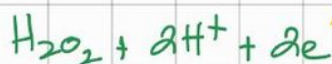
Cl^- , H_2O



$$E^\circ = \cancel{+36\text{V}} \quad \text{lowest} \quad \checkmark$$



$$E^\circ = 1.23\text{V} \quad \text{lowest}$$



$$E^\circ = 1.77\text{V}$$

if Cl^- are concentrated, equilibrium Cl_2/Cl^- shifts to the left, so electrode potential decreases and becomes the lowest and hence Cl^- are discharged.

13 The Faraday Constant

QUANTITY	VALUE
Charge on one electron	$1.6 \times 10^{-19} \text{ C}$
Avogadro constant, L	$6.02 \times 10^{23} \text{ mol}^{-1}$
Faraday constant, $F = L \times e$	$96\,500 \text{ C mol}^{-1}$

THE TWO EQUATIONS

$$1 \text{ mol e}^- \equiv 96\,500 \text{ C}$$

$$Q = I \times t \quad (\text{coulombs} = \text{amperes} \times \text{seconds})$$

Faraday Constant

$$1e^- : 1.6 \times 10^{-19} \text{ C}$$

$$1 \text{ mol } e^- : 6.02 \times 10^{23} \times 1.6 \times 10^{-19} \text{ C}$$

↙
avogadro
constant

↘
charge on e^-

$$F = L e = 96500 \text{ C}$$

total charge on 1 mol of e^-

$$1 \text{ mol } e^- : 96500 \text{ C}$$

$$Q = I \times t$$

(Amperes) (seconds)

WORKED EXAMPLE — CuSO_4 ELECTROLYSED AT 2 A FOR 30 MINUTES. FIND THE MASS OF CU DEPOSITED.

- 1 $Q = I \times t = 2 \times (30 \times 60) = 3600 \text{ C}$
- 2 $\text{mol } e^- = 3600 / 96500 = 0.0373 \text{ mol}$
- 3 $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$, so $\text{mol Cu} = 0.0373 / 2 = 0.0187 \text{ mol}$
- 4 $m = n \times M_r = 0.0187 \times 63.5 = 1.184 \text{ g}$

Q CuSO_4 is electrolysed using a current of 2A for 30 min.

Calculate the mass of Cu deposited.

$$Q = I \times t = 2\text{A} \times 30 \times 60\text{sec} = 3600\text{C}$$

$$\begin{array}{ccc} 1 \text{ mol } e^- & \longrightarrow & 96500\text{C} \\ x \text{ mol} & \longrightarrow & 3600\text{C} \end{array}$$

$$x = \frac{3600}{96500} = 0.0373 \text{ mol of } e^-$$



$$\begin{aligned} m &= n \times M_r \\ &= 0.0187 \times 63.5 \\ &= 1.184\text{g} \end{aligned}$$

METHOD IN ONE LINE

$Q = I t \rightarrow \div 96\,500 \text{ for mol } e^- \rightarrow \div (\text{electrons in the half-equation}) \text{ for mol product} \rightarrow \times M_r \text{ for mass}$
(or $\div 24\,000 \text{ cm}^3 / 24 \text{ dm}^3 \text{ for gas volume at r.t.p.}$).

- Quote standard conditions in full: **298 K, 1 atm, 1 mol dm⁻³**.
- Define E° as a **potential difference against a standard hydrogen electrode** — not just "the voltage".
- Higher $E^\circ \rightarrow$ reduced (gains e^-); lower $E^\circ \rightarrow$ oxidised (loses e^-). Electrons flow towards higher E° .
- $E^\circ_{\text{cell}} = E^\circ(\text{reduction}) - E^\circ(\text{oxidation})$. Positive $\rightarrow$ feasible.
- **Feasible $\neq$ fast**. A high E°_{cell} can still give no reaction if E_a is large ($\text{S}_2\text{O}_8^{2-} + \text{I}^-$).
- Always check that the species you assign are **actually present** in the mixture.
- For non-standard concentrations, argue with **Le Chatelier** first, then use Nernst if numbers are required.
- In electrolysis, remember the anode reaction is written **backwards** (as oxidation).
- Concentration changes can **reorder** electrode potentials — that is the whole point of the concentrated-NaCl question.
- Faraday problems: never forget to divide by the number of electrons in the half-equation.

Fahad H. Ahmad

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