MEGA LECTURE

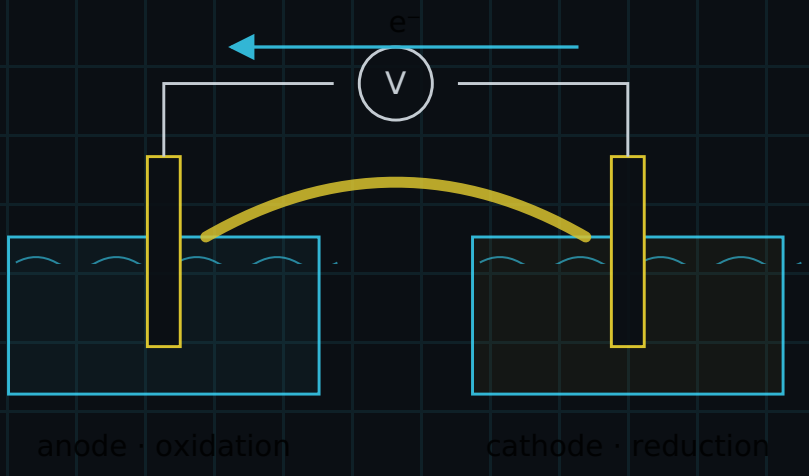
CAMBRIDGE INTERNATIONAL · CAIE
A Level Chemistry 9701 · Paper 4

A2 REVISION NOTES · PHYSICAL CHEMISTRY

Electrochemistry

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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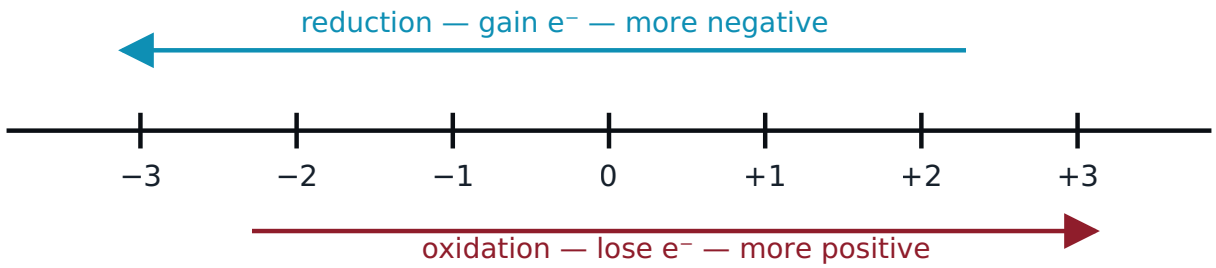
CONTENTS

01 Redox Fundamentals

DEFINITIONS

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

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

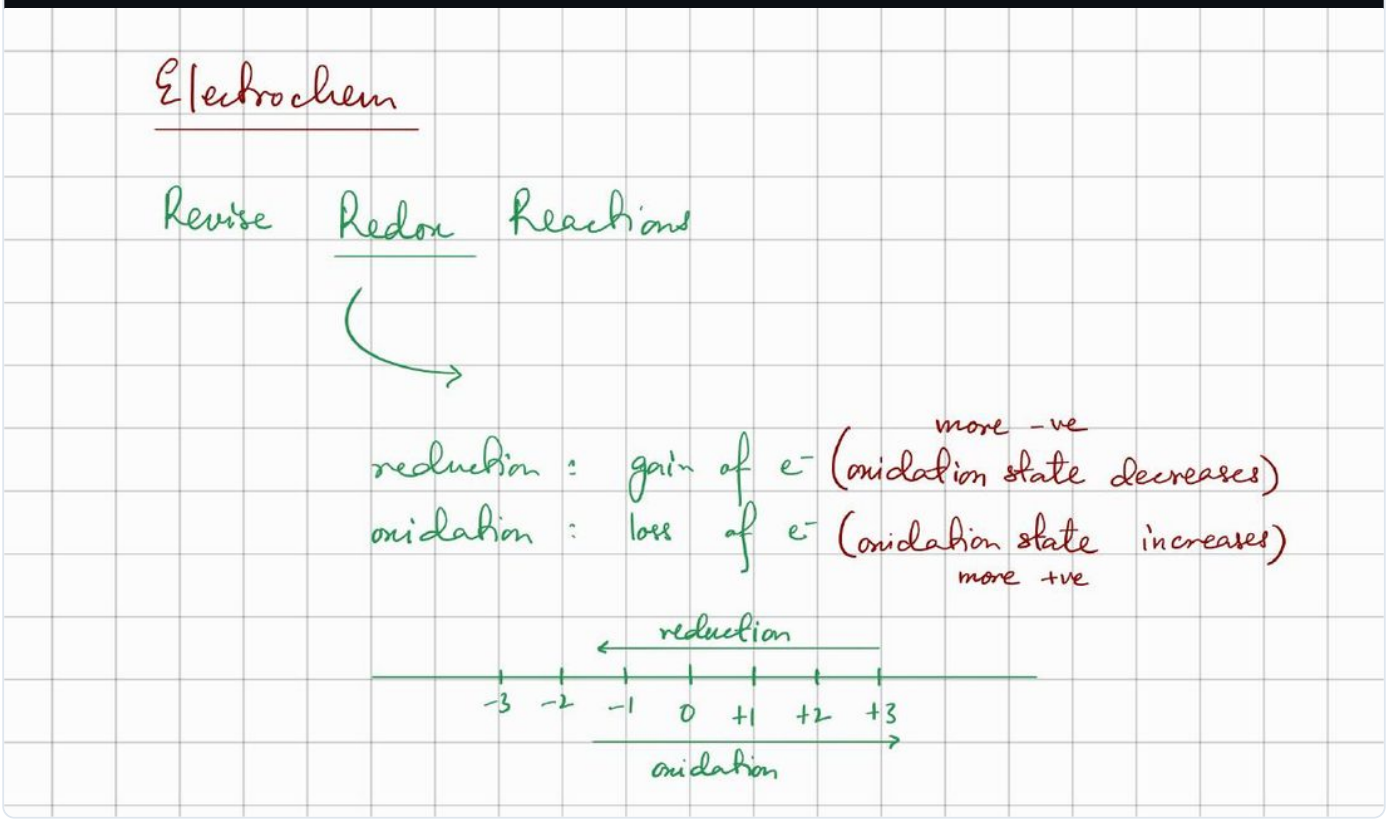


Direction of change on the oxidation-state number line.

Na — loses $6e^-$ → $\mathrm{Na}^{+7} + 6e^-$ oxidation

$2e^- + \mathrm{Al}^{3+}$ — gains $2e^-$ → Al^{+1} reduction

ORIGINAL CLASS NOTES — REDOX DEFINITIONS & NUMBER LINE PAGE 1



02 Oxidation States

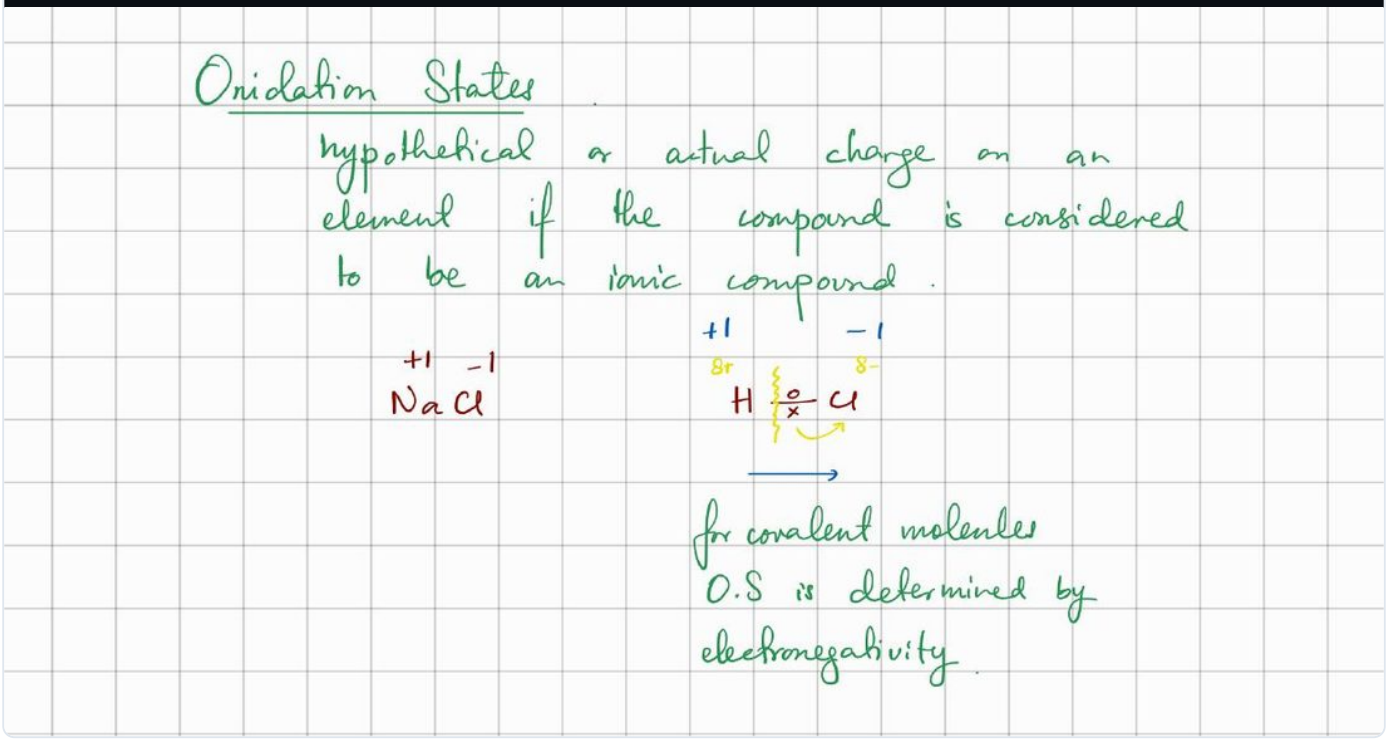
DEFINITION

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.

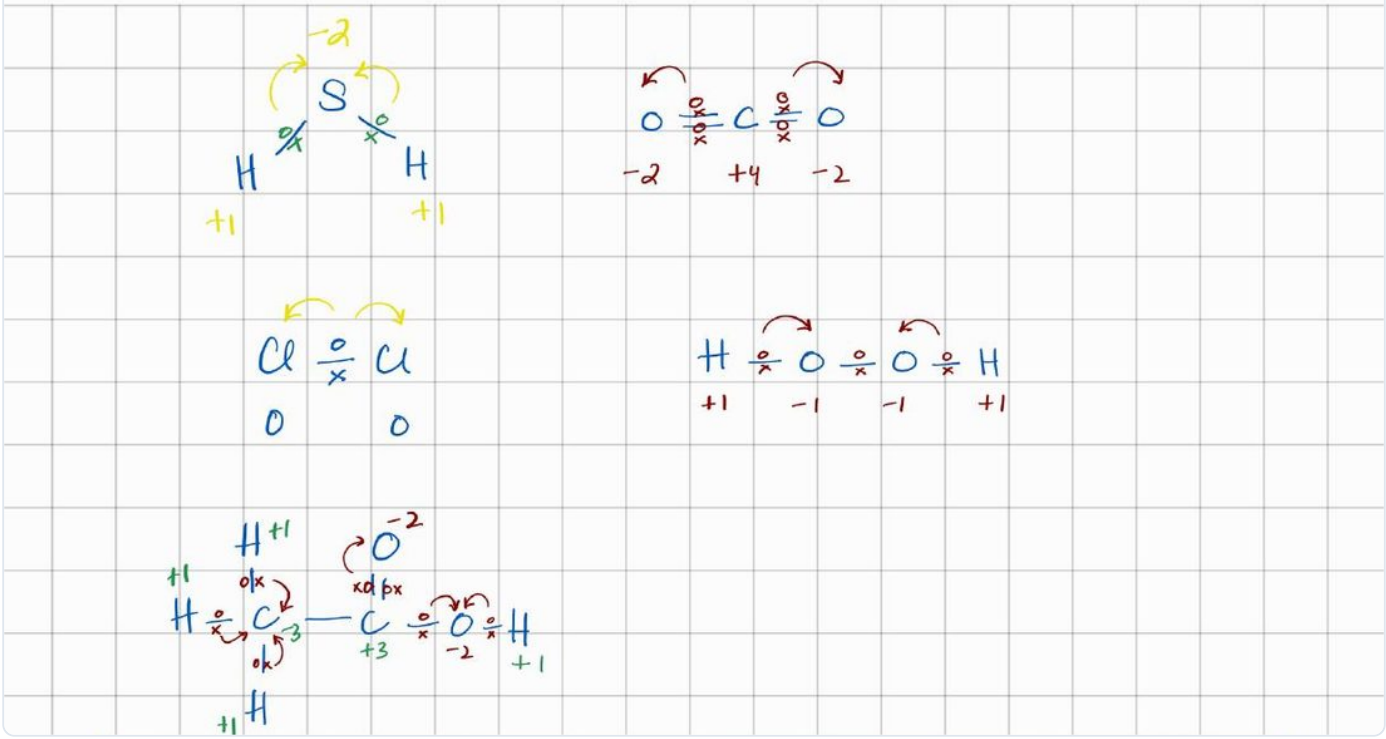
H—Cl	$H = +1,\ Cl = -1$	Cl is more electronegative, so it takes the shared pair

OXIDATION STATE DEFINED · IONIC VS COVALENT ASSIGNMENT PAGE 1



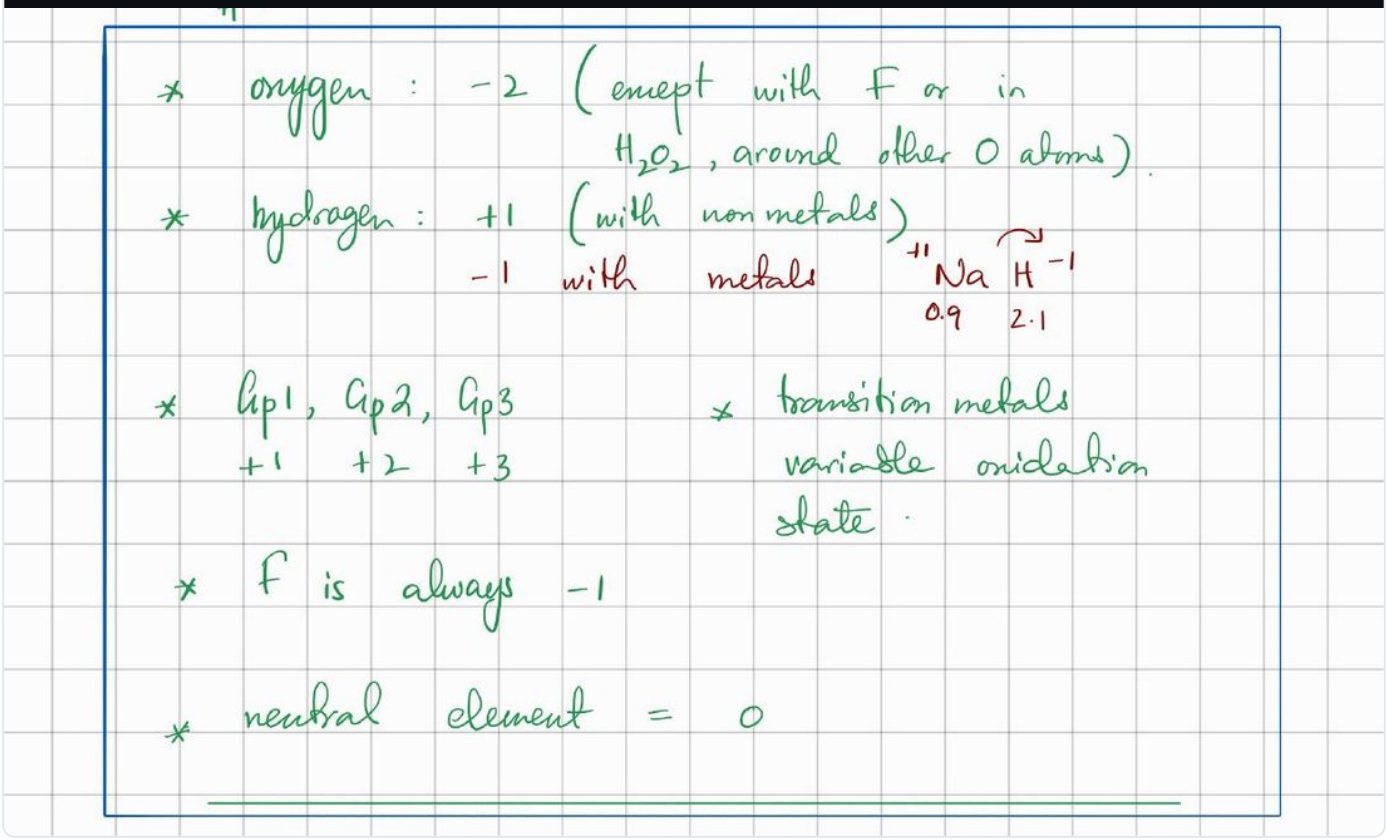
Worked assignments from bonding

SPECIES	ASSIGNMENT	REASONING
H_2S	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_2O_2	H = +1, O = −1 each	O—O bond splits evenly, so O is only −1
CH_3COOH	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 (H_2O_2) where it bonds to another O.
- **Hydrogen = +1** with non-metals; **−1** with metals (e.g. $Na^{+1}H^{-1}$, 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.



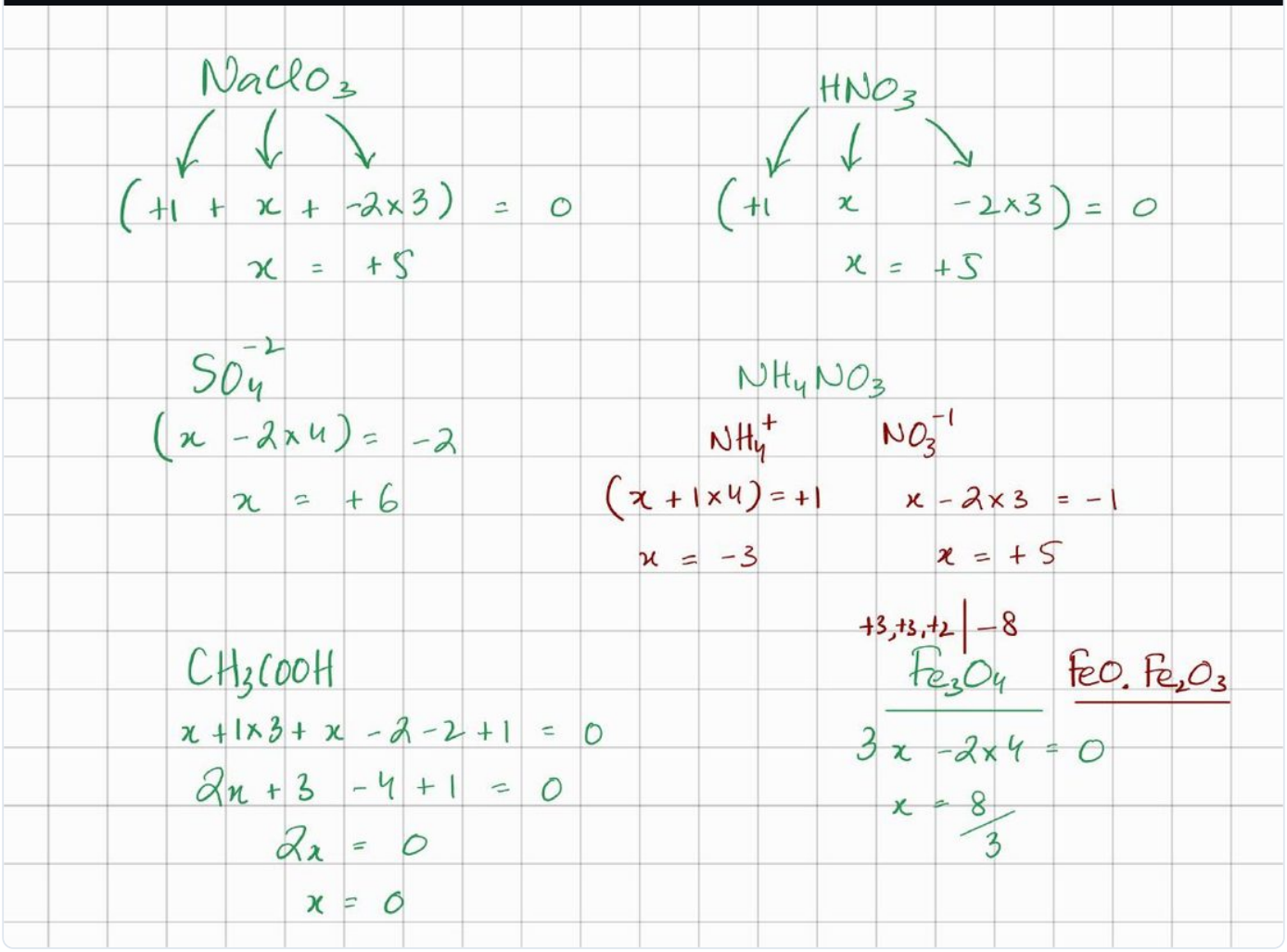
Calculating an unknown state

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

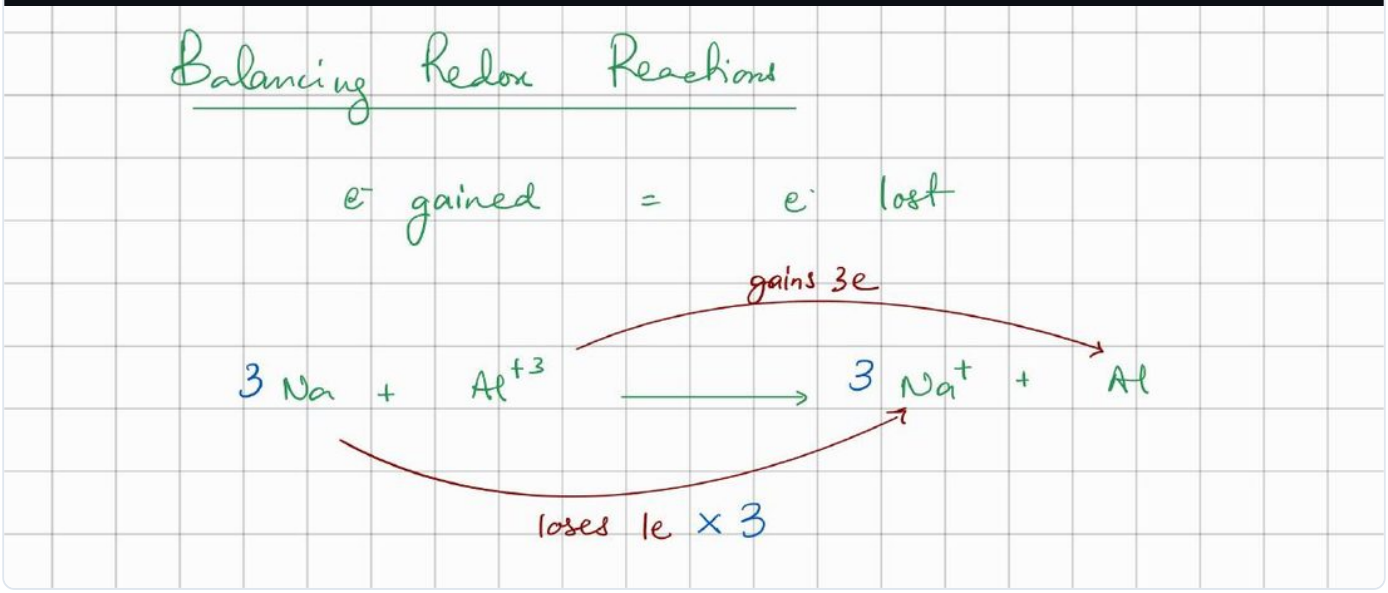
electrons gained = electrons lost

Example — Na + Al^{3+}

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

$$3\ Na + Al^{3+} \rightarrow 3\ Na^+ + Al$$

THE ELECTRON-BOOKKEEPING ARROWS PAGE 3

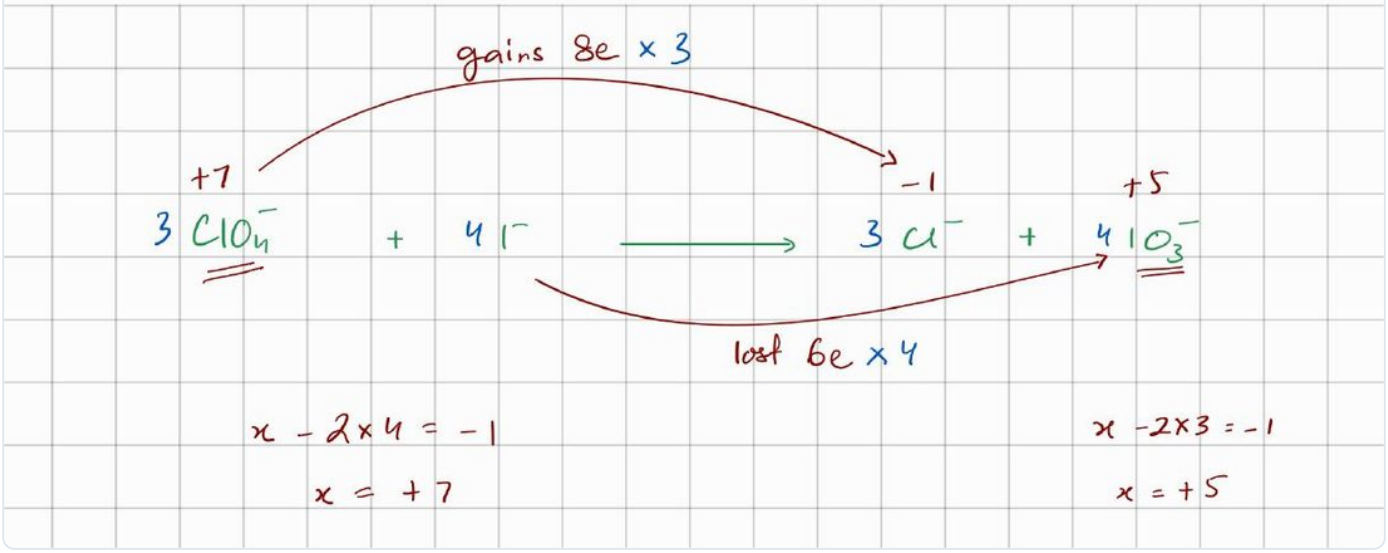


Example — $ClO_4^- + I^-$

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

$$3\ ClO_4^- + 4\ I^- \to 3\ Cl^- + 4\ IO_3^-$$

FINDING THE MULTIPLIERS FROM ELECTRONS GAINED AND LOST PAGE 4



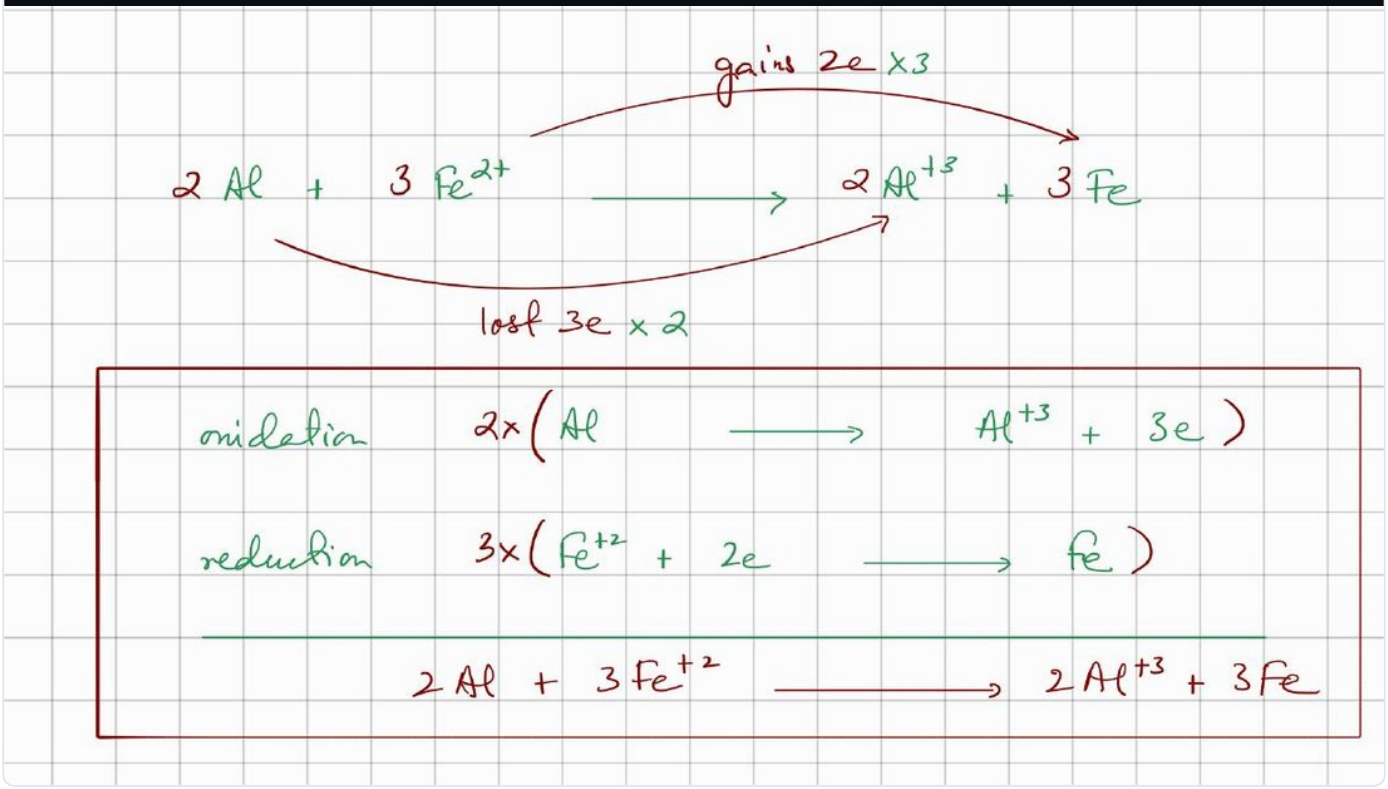
Example — Al + Fe^{2+}, via half-equations

oxidation $\quad 2 \times (\ Al \to Al^{3+} + 3e^- \ )$

reduction $\quad 3 \times (\ Fe^{2+} + 2e^- \to Fe \ )$

$$2\ Al + 3\ Fe^{2+} \to 2\ Al^{3+} + 3\ Fe$$

HALF-EQUATIONS SCALED AND ADDED PAGE 4

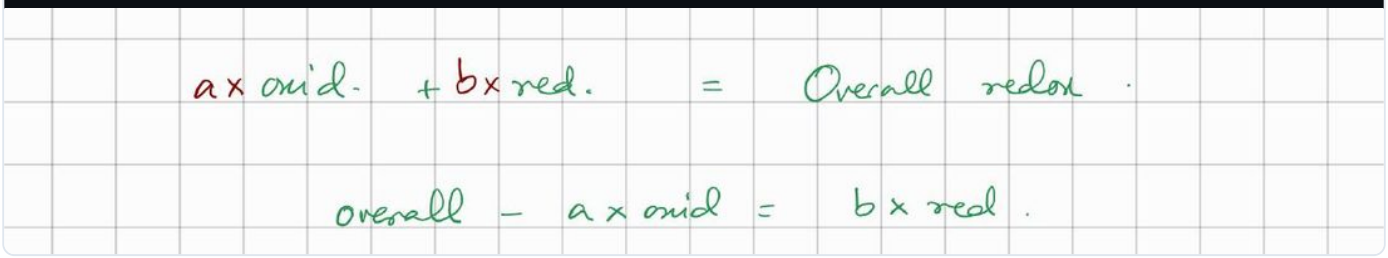


ALGEBRA OF HALF-EQUATIONS

a × oxidation + b × reduction = overall redox equation

Rearranged: overall − (a × oxidation) = b × 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 PAGE 4



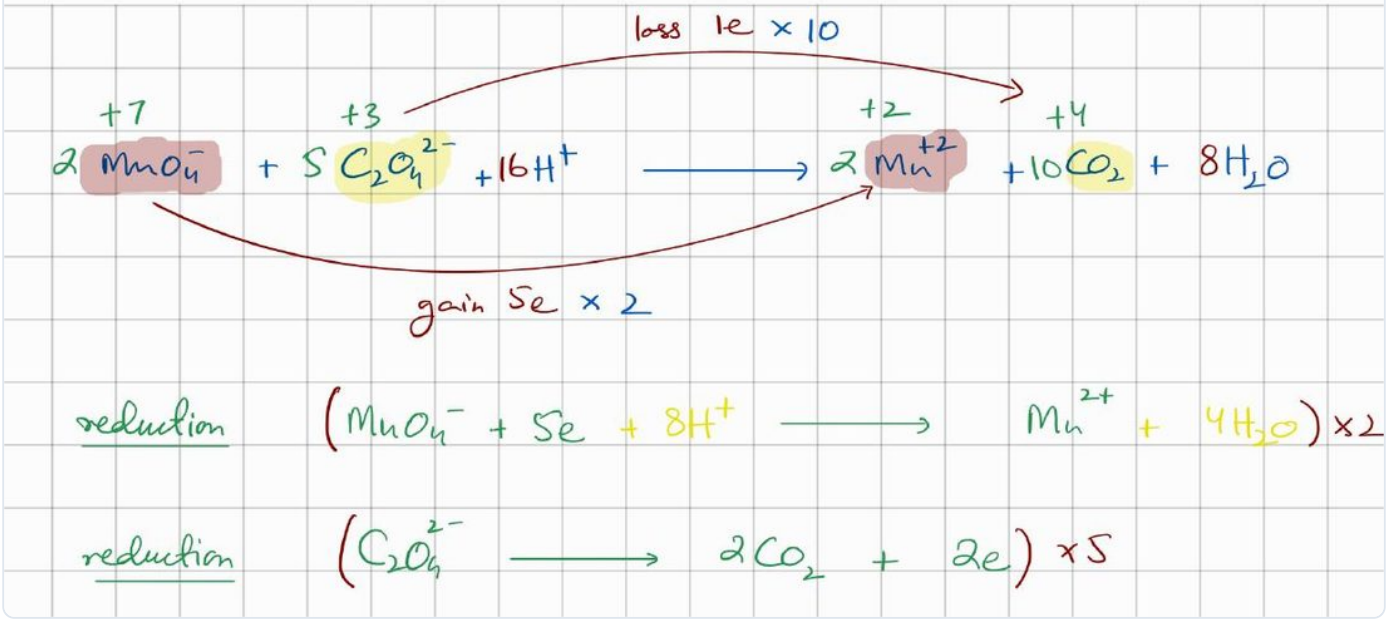
Acidic-medium example — MnO_4^- + $C_2O_4^{2-}$

Mn: +7 → +2 (gains 5e⁻). C: +3 → +4 (loses 1e⁻ per C, so 2e⁻ per $C_2O_4^{2-}$).

reduction $(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 2$

oxidation $(C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-) \times 5$

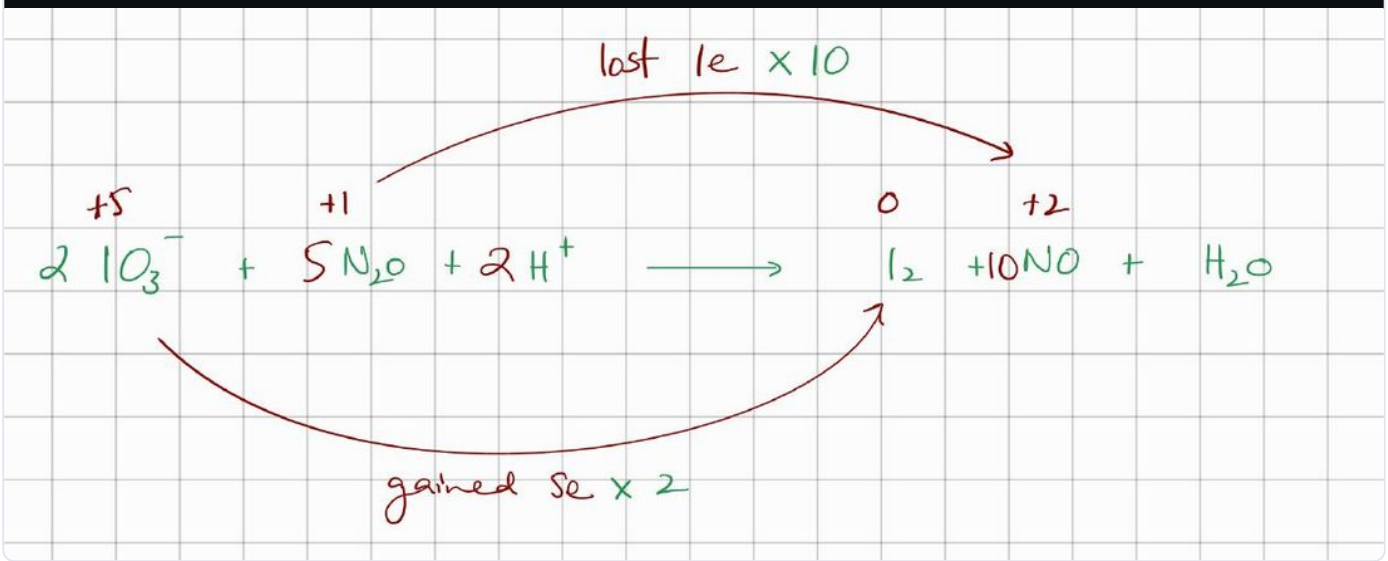
$$2\ MnO_4^- + 5\ C_2O_4^{2-} + 16\ H^+ \rightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$$



Example — IO_3^- + N_2O

$$2\ IO_3^- + 5\ N_2O + 2\ H^+ \rightarrow I_2 + 10\ NO + H_2O$$

I: +5 → 0 (gains 5e⁻, ×2). N: +1 → +2 (loses 1e⁻, ×10).



04 Disproportionation

DEFINITION

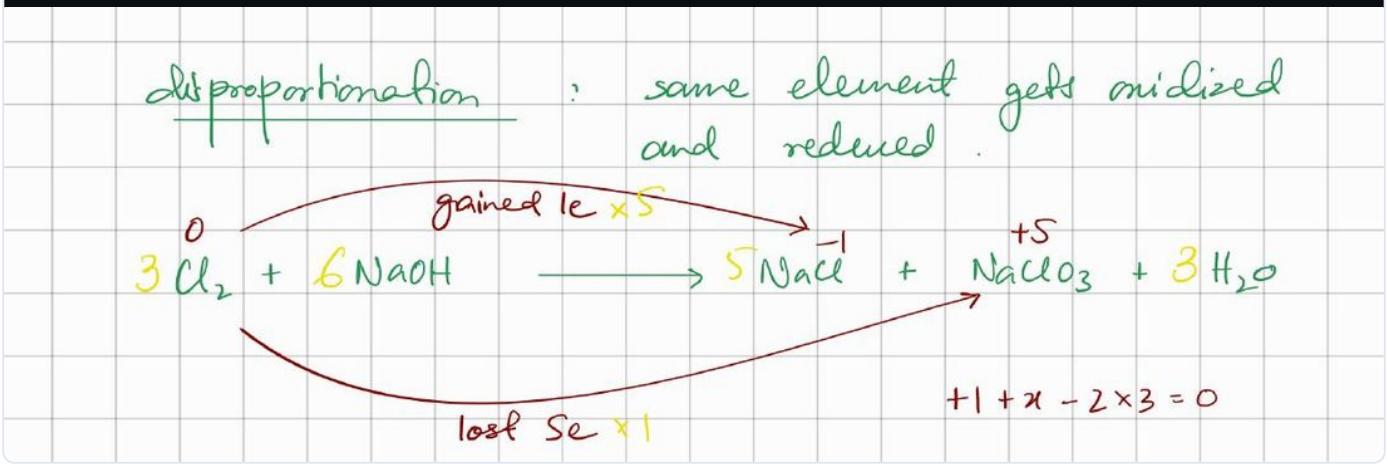
The **same element** is simultaneously oxidised and reduced in one reaction.

$$3\ Cl_2 + 6\ NaOH \rightarrow 5\ NaCl + NaClO_3 + 3\ H_2O$$

- Cl $^{0} \rightarrow {}^{-1}$ in NaCl — gains 1e⁻, ×5
- Cl $^{0} \rightarrow {}^{+5}$ in $NaClO_3$ — loses 5e⁻, ×1

Check on $NaClO_3$: (+1) + x + (−2 × 3) = 0 → x = +5. ✓

CHLORINE DISPROPORTIONATING IN HOT ALKALI — PAGE 5



05 Standard Electrode Potential, E°

DEFINITION

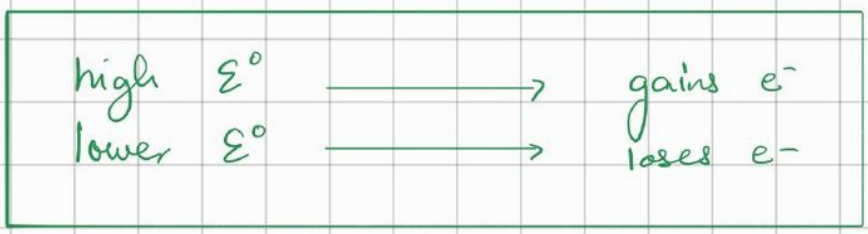
The **potential difference measured between a standard electrode and a standard hydrogen electrode**.

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 — PAGE 8



$Na^+ + e^- \rightleftharpoons Na \quad E° = -2.71\ V$ very negative → Na strongly wants to lose e^-

$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \quad E° = +1.36\ V$ very positive → Cl_2 strongly wants to gain e^-

Who gains e^- or loses e^- ?

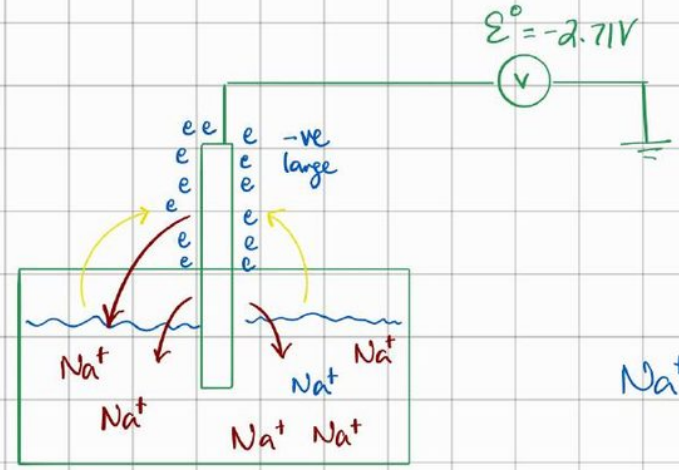
$Pb^{+2} + Sn^{+2}$

Standard Electrode Potential $\mathcal{E}^\circ$ → standard 298 K, 1 atm

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

$Na \longleftrightarrow Na^+ + 1e$

wants to lose e^-



lower $\mathcal{E}^\circ$ indicates that Na wants to lose electrons

$Na^+ + e \longleftrightarrow Na \quad \mathcal{E}^\circ = -2.71V$

metal / +ve ion

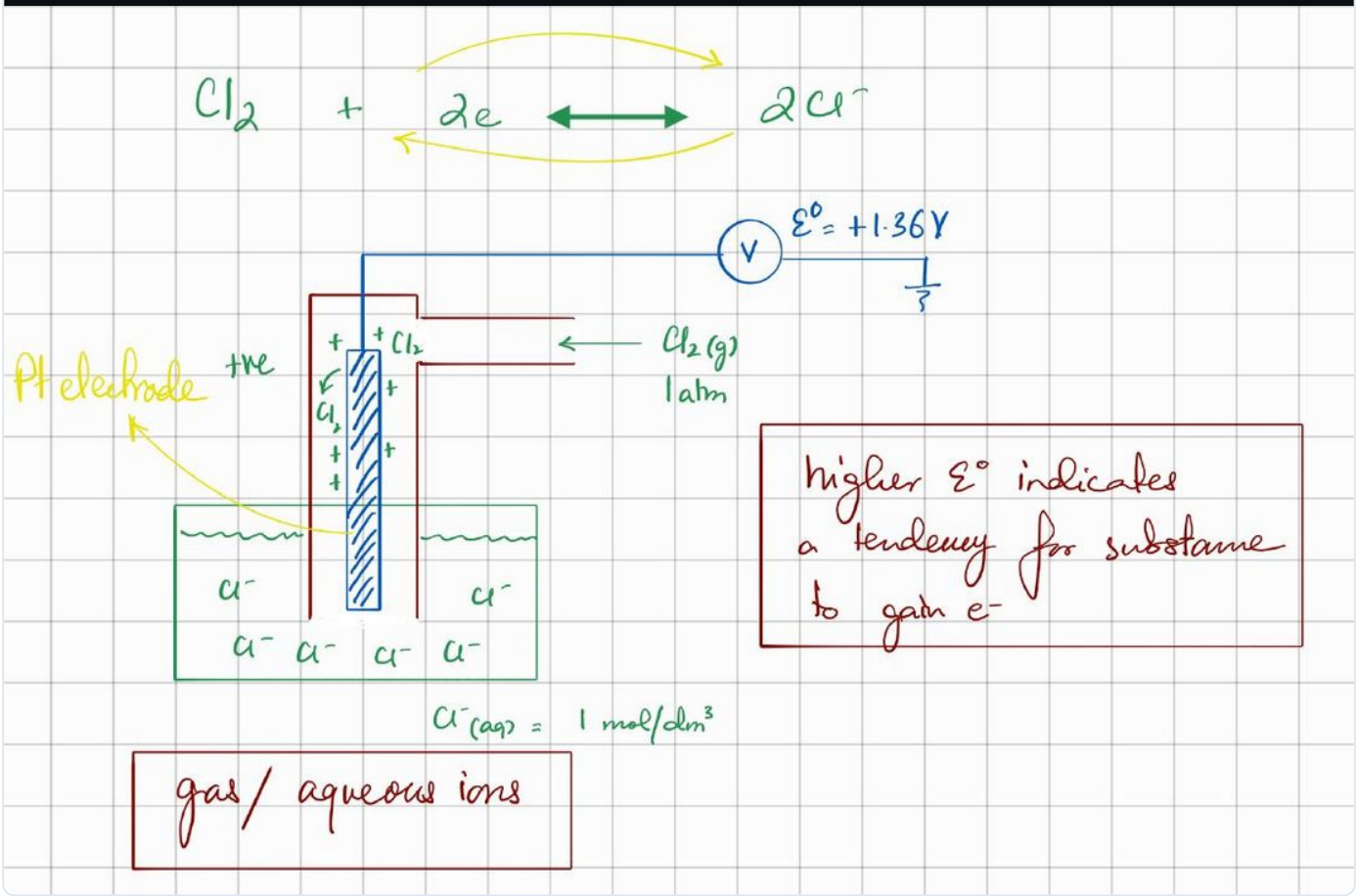
WATCH THE SIGN CONVENTION

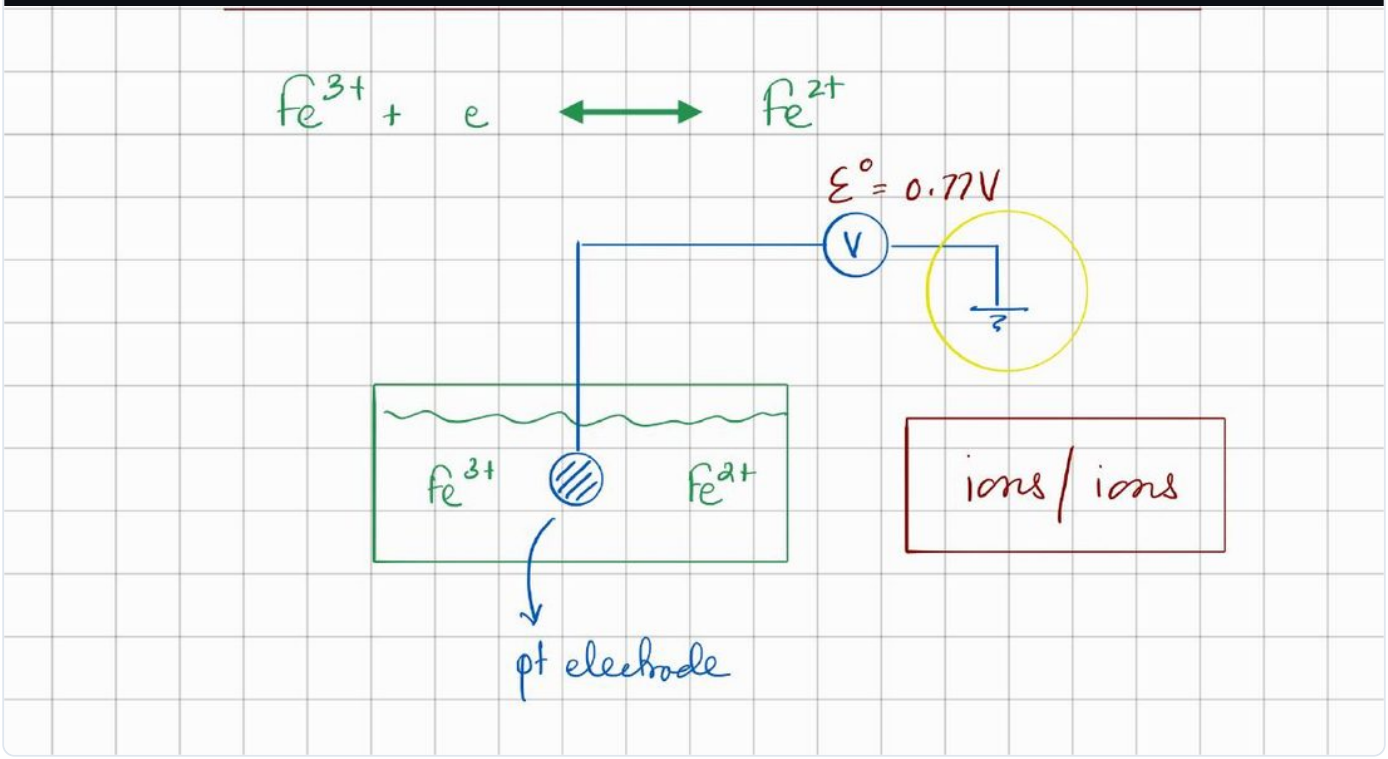
All electrode potentials are quoted as **reduction** potentials — always written left-to-right as gaining electrons. A negative E° simply means the reverse (oxidation) is favoured.

06 Electrode Types & the S.H.E.

TYPE	CONSTRUCTION	EXAMPLE
Metal / metal ion	Metal rod dipped into a solution of its own ion	Na | Na^+ $E° = -2.71$ V
Gas / aqueous ion	Inert Pt electrode, gas bubbled at 1 atm over it, in 1 mol dm^{-3} ion solution	Pt | Cl_2 | Cl^- $E° = +1.36$ V
Ion / ion	Inert Pt electrode in a solution containing both oxidation states	Pt | Fe^{3+}, Fe^{2+} $E° = +0.77$ V

GAS / AQUEOUS-ION ELECTRODE — CL_2 OVER A PT ELECTRODE PAGE 7



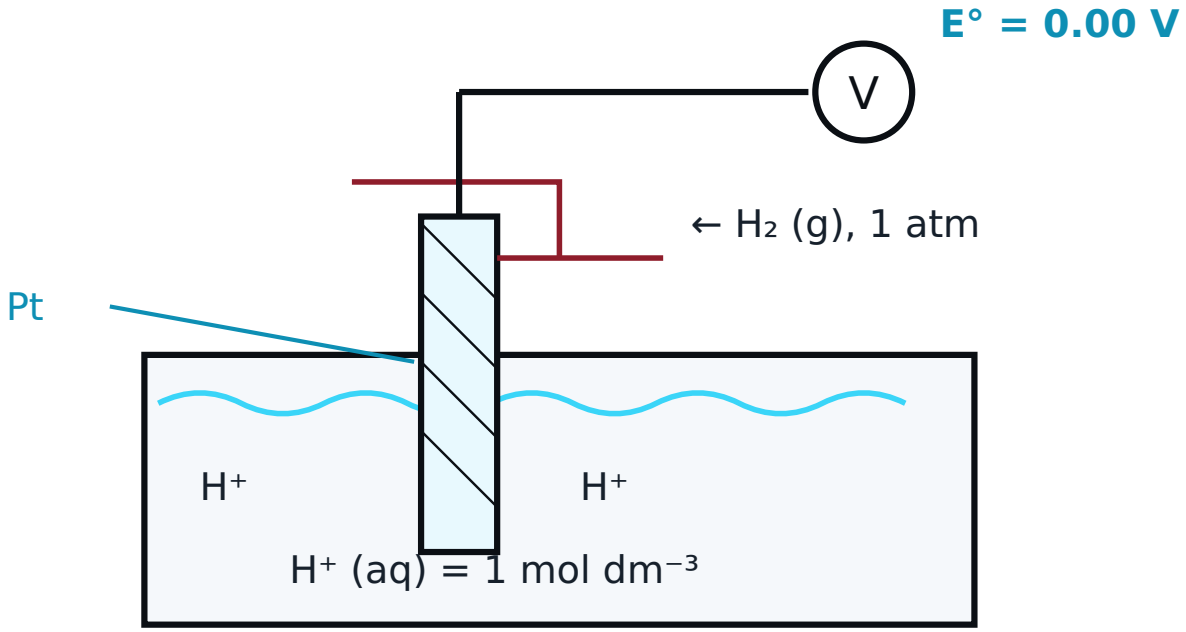


REFERENCE ELECTRODE — S.H.E.

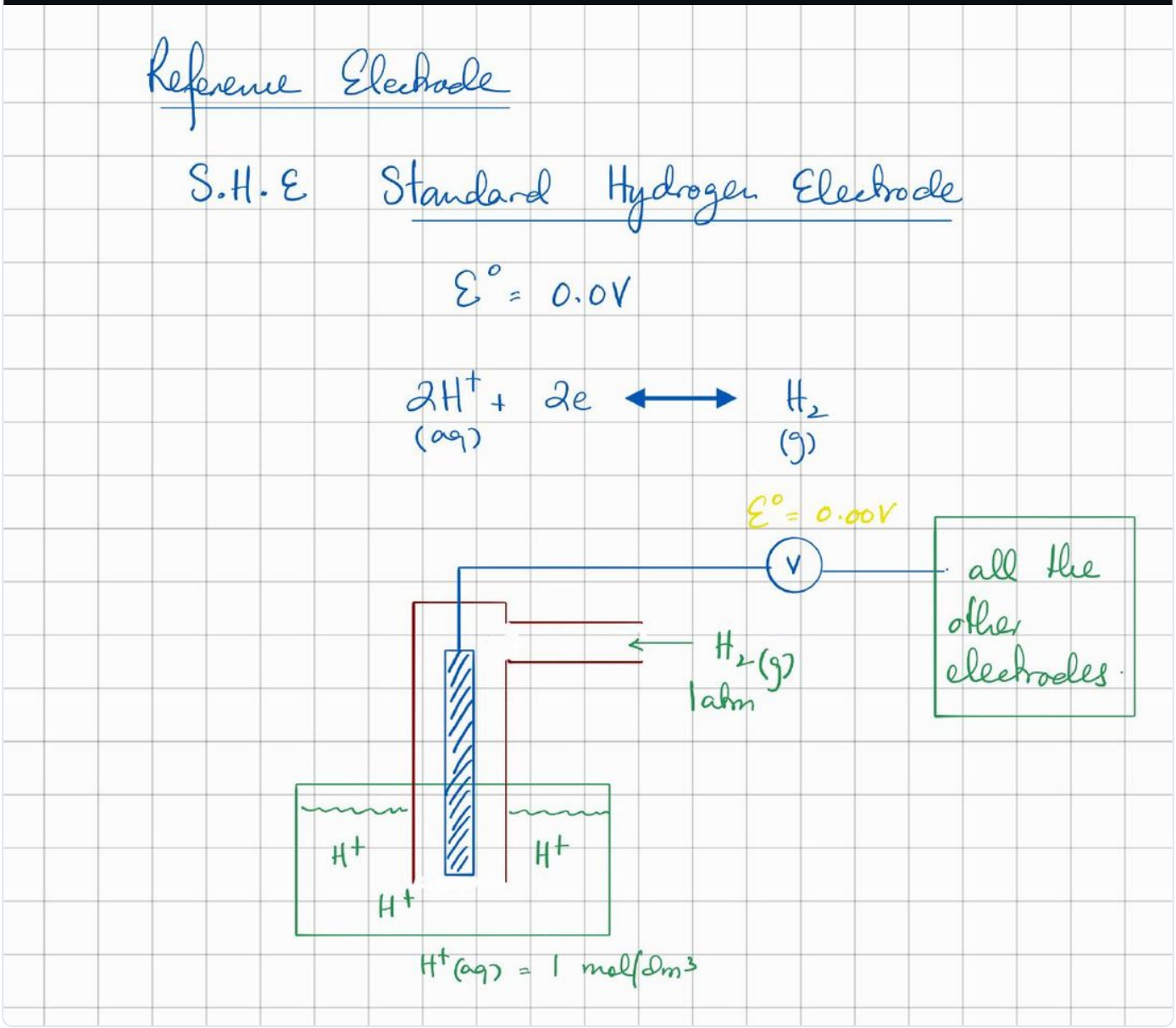
The **Standard Hydrogen Electrode** is assigned **E° = 0.00 V** by definition. Every other electrode potential is measured against it.

$$2\ H^{+}_{(aq)} + 2e^{-} \rightleftharpoons H_{2(g)} \qquad E^{\circ} = 0.00\ V$$

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



The Standard Hydrogen Electrode — the universal reference, E° = 0.00 V.

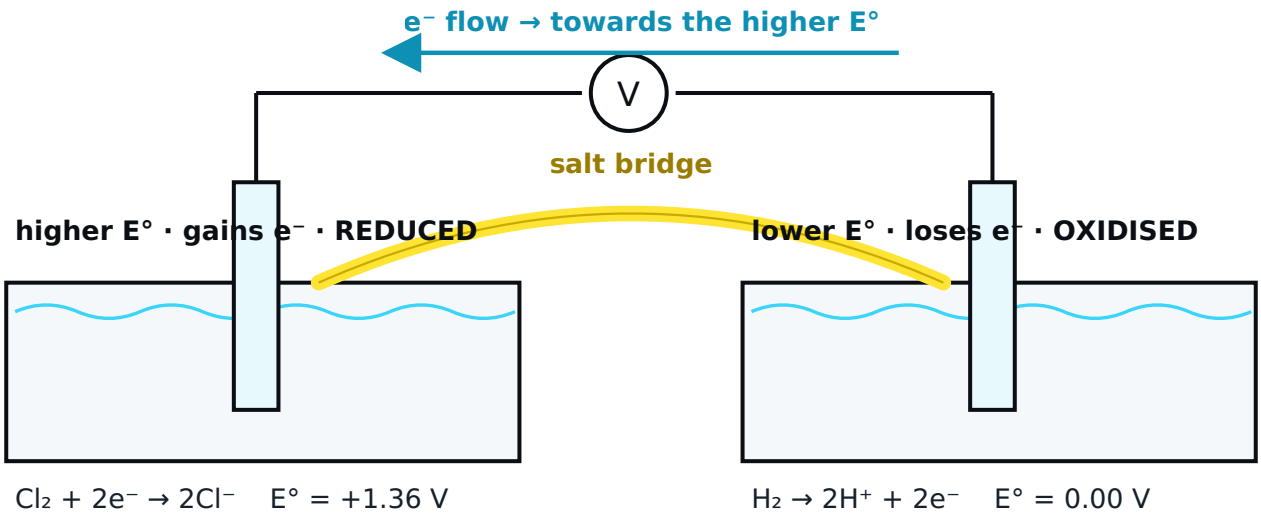


07 The Complete Cell

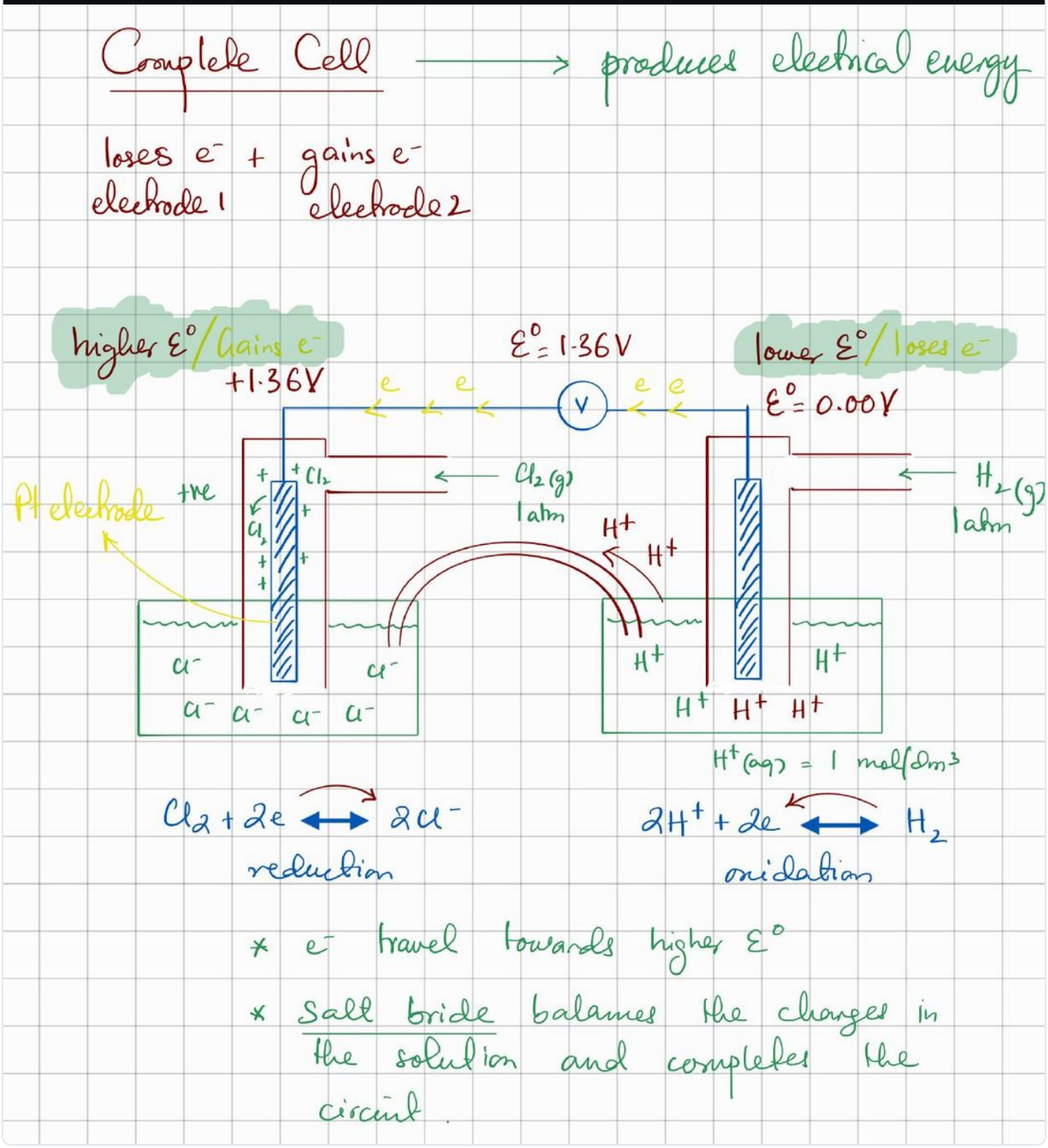
Connecting two half-cells — one that **loses** electrons and one that **gains** them — produces **electrical energy**.

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.



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

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

oxidation $4\ OH^- \rightarrow O_2 + 2H_2O + 4e^-$ $\quad E^\circ = +0.40\ V$

$$4\ Fe^{3+} + 4\ OH^- \rightarrow 4\ Fe^{2+} + O_2 + 2\ H_2O$$

CELL POTENTIAL

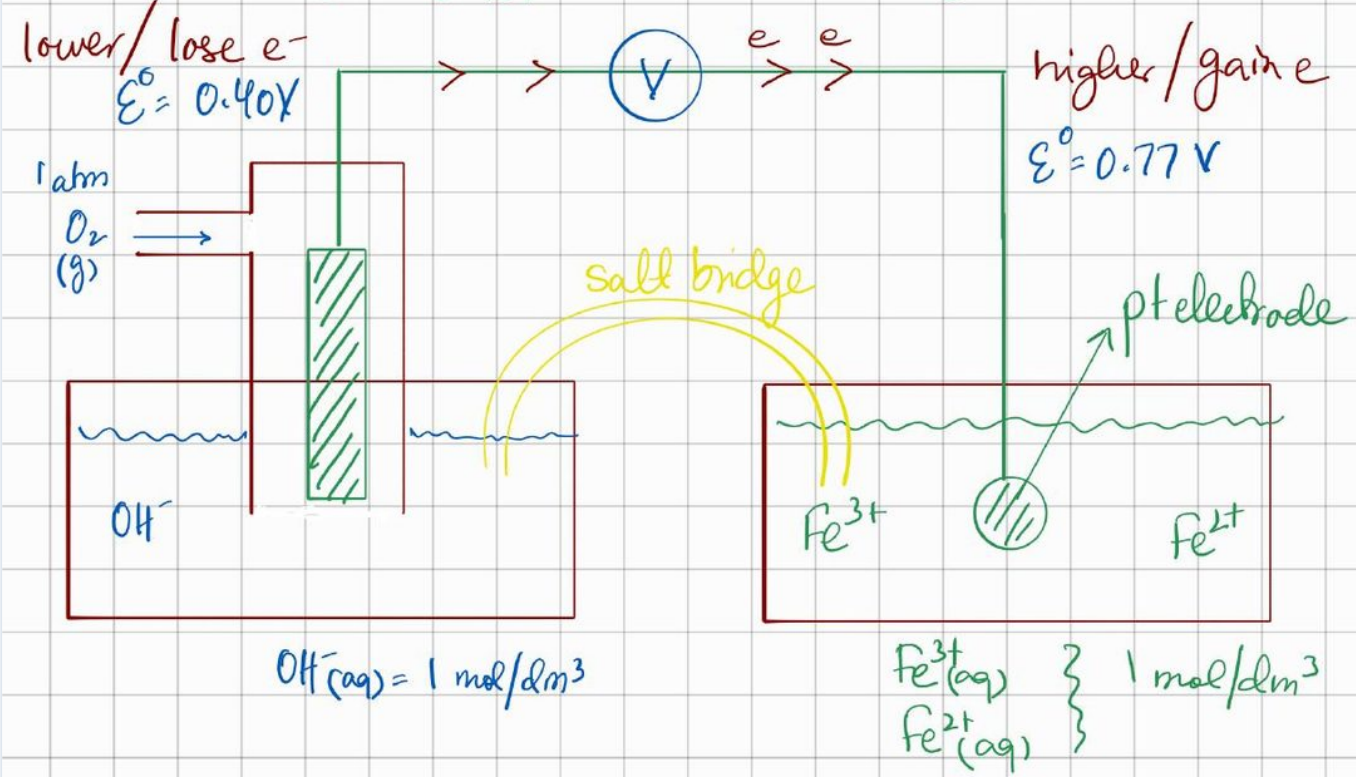
$$\mathbf{E^\circ_{cell} = E^\circ(reduction,\ higher) - E^\circ(oxidation,\ lower)}$$

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

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

$O_2 + 2H_2O + 4e \leftrightarrow 4OH^-$ $\quad E^\circ = 0.40V$

$Fe^{3+} + e \leftrightarrow Fe^{2+}$ $\quad E^\circ = 0.77V$



$OH^-_{(aq)} = 1\ mol/dm^3$

$Fe^{3+}_{(aq)}$, $Fe^{2+}_{(aq)}$ } $1\ mol/dm^3$

reduction $\quad 4Fe^{3+} + 4e \longrightarrow 4Fe^{2+}$

oxidation $\quad 4OH^- \longrightarrow O_2 + 2H_2O + 4e$

$$4Fe^{3+} + 4OH^- \longrightarrow 4Fe^{2+} + O_2 + 2H_2O$$

E°_{cell} = Reduction E° (higher) − Oxidation E° (lower)

$0.77 - 0.40 = 0.37V$

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

08 Building Redox Equations from E° Data

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

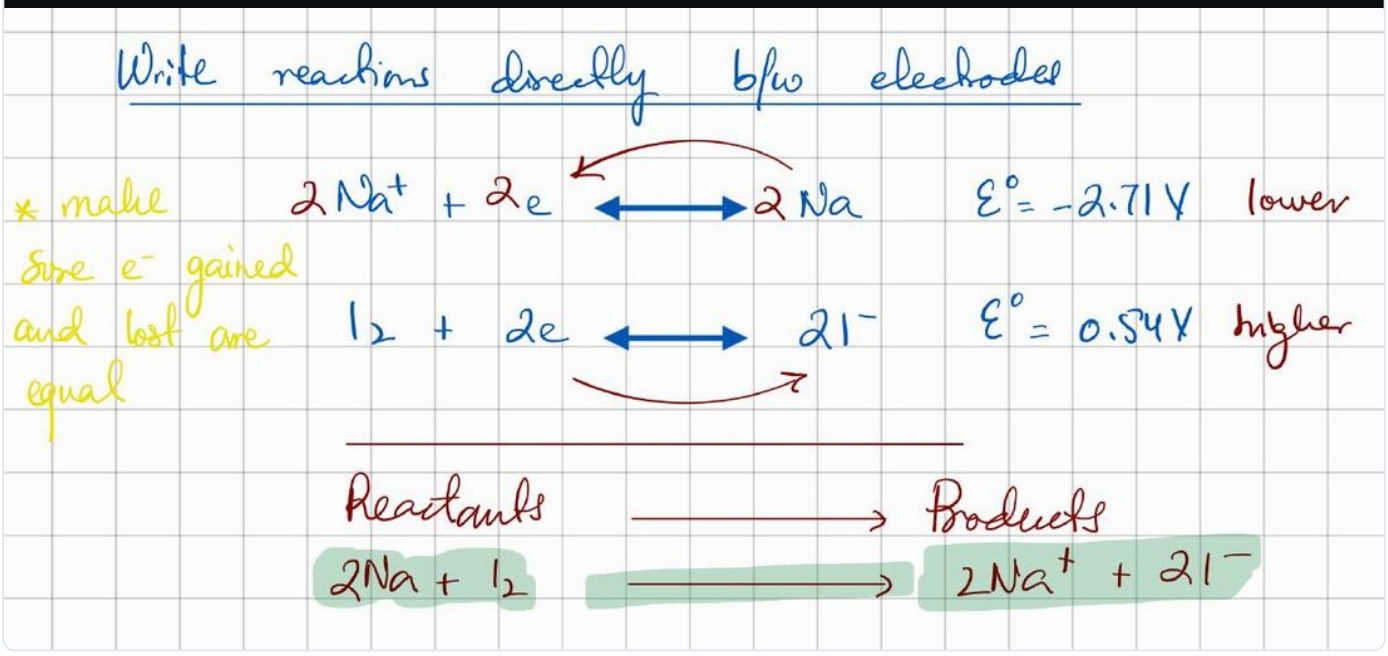
1. **Identify every species actually present**, including spectator ions from the salts.
2. **List all electrode reactions** from the data booklet that involve those species.
3. **Highest E° gains electrons** (forward direction); **lowest E° loses electrons** (reverse direction).
4. **Check the species 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 → products**.

e.g. $2Na^+ + 2e^- \rightleftharpoons 2Na$ (−2.71 V) and $I_2 + 2e^- \rightleftharpoons 2I^-$ (+0.54 V) give **$2Na + I_2 \rightarrow 2Na^+ + 2I^-$**

READING REACTANTS AND PRODUCTS STRAIGHT OFF THE TWO HALF-EQUATIONS PAGE 11



WORKED EXAMPLE 1 — $FECL_{3(AQ)}$ + CU

Species present: $Fe^{3+}_{(aq)}$, $Cl^{-}_{(aq)}$, $Cu_{(s)}$

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

$$2\ Fe^{3+} + Cu \rightarrow Cu^{2+} + 2\ Fe^{2+}$$

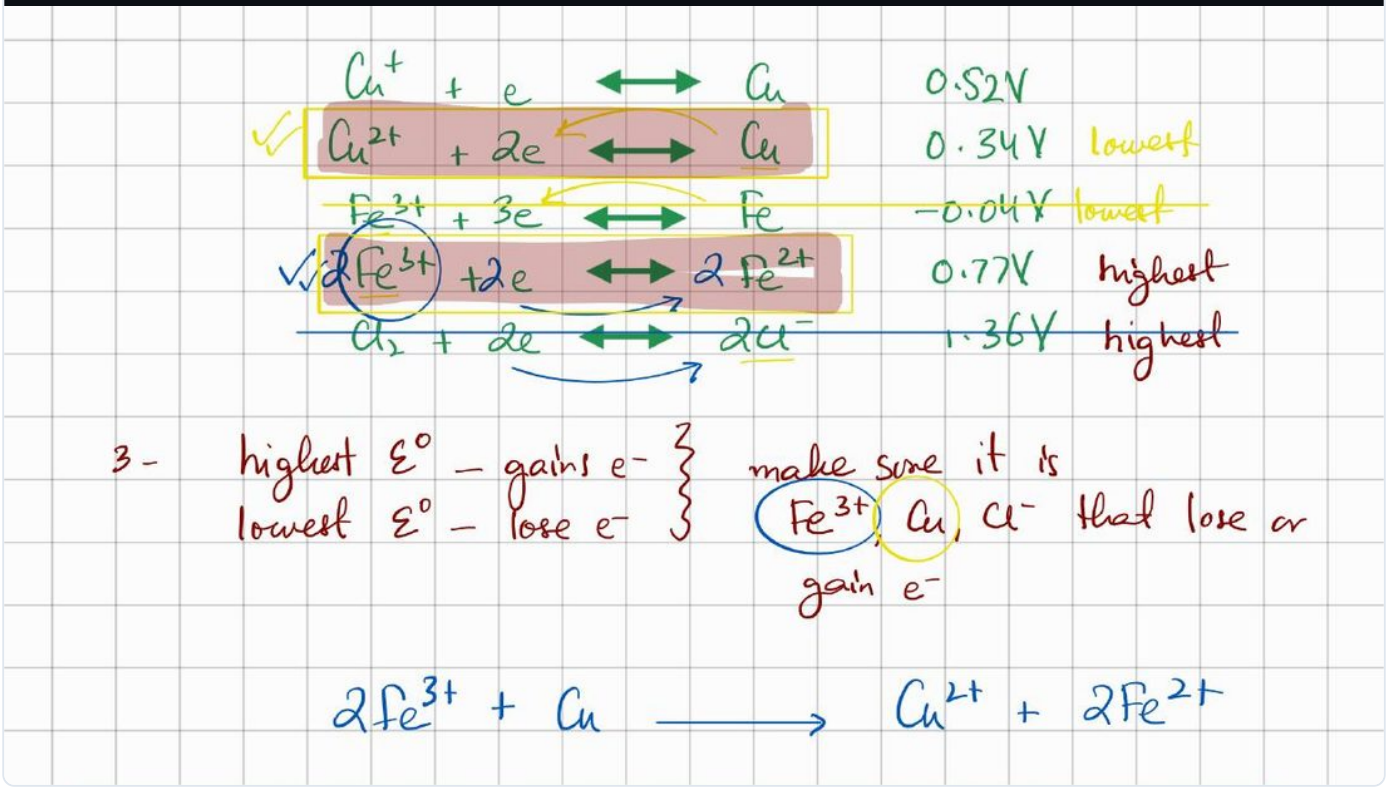
STEPS 1–2: IDENTIFY SPECIES, THEN LIST EVERY RELEVANT ELECTRODE REACTION PAGE 11

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

$FeCl_3$ (aq) + Cu

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

2- list all electrode reactions involving reactants



WORKED EXAMPLE 2 — $FECL_2 + H_2O_2$ / H^+

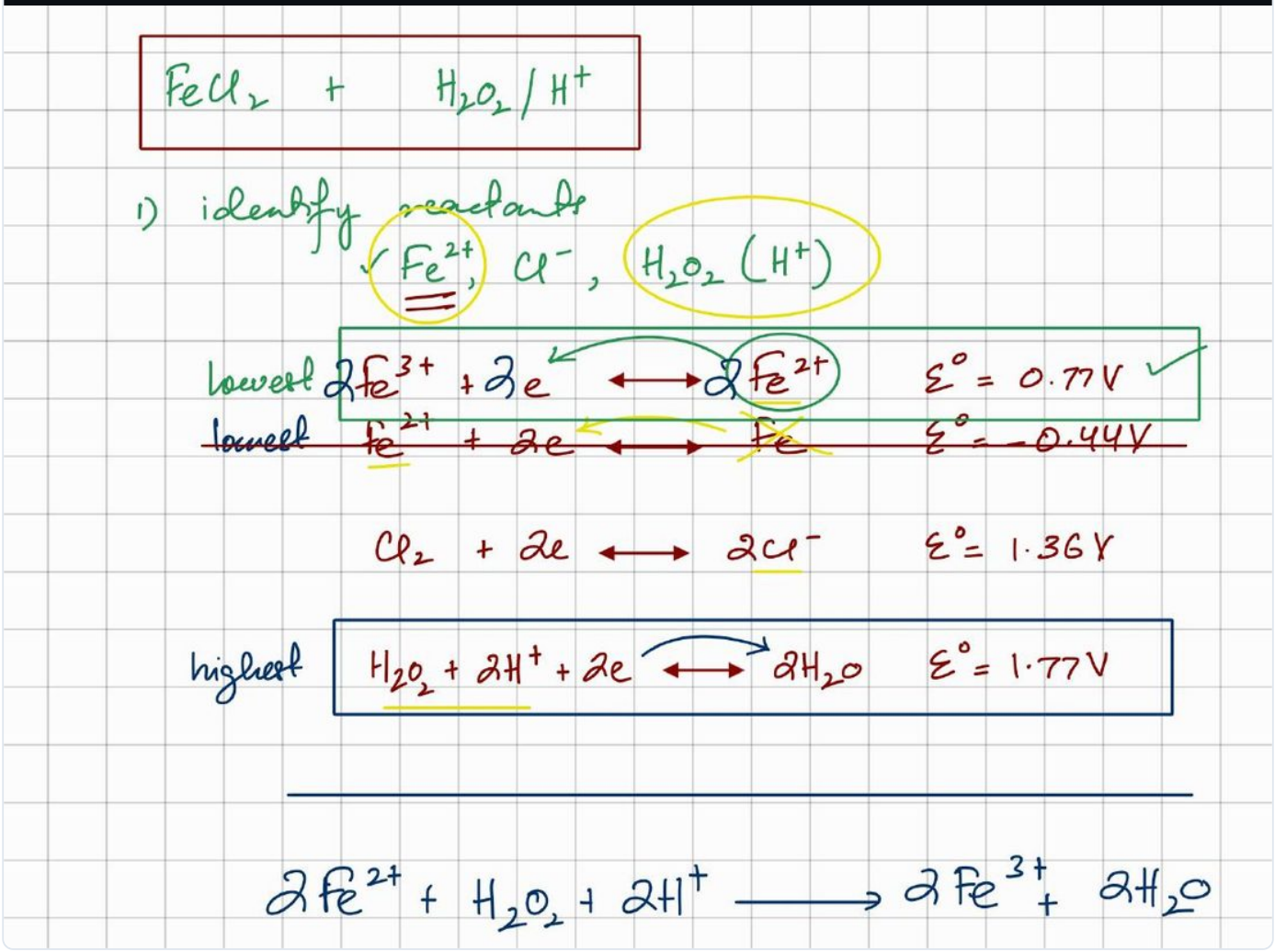
Species present: Fe^{2+}, Cl^-, H_2O_2, H^+

reduction (highest) $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E° = +1.77$ V

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

$$2\ Fe^{2+} + H_2O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + 2\ H_2O$$

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



WORKED EXAMPLE 3 — $CrCl_2 + K_2Cr_2O_7 / H^+$

Species present: Cr^{2+}, Cl^-, K^+, $Cr_2O_7^{2-}$, H^+

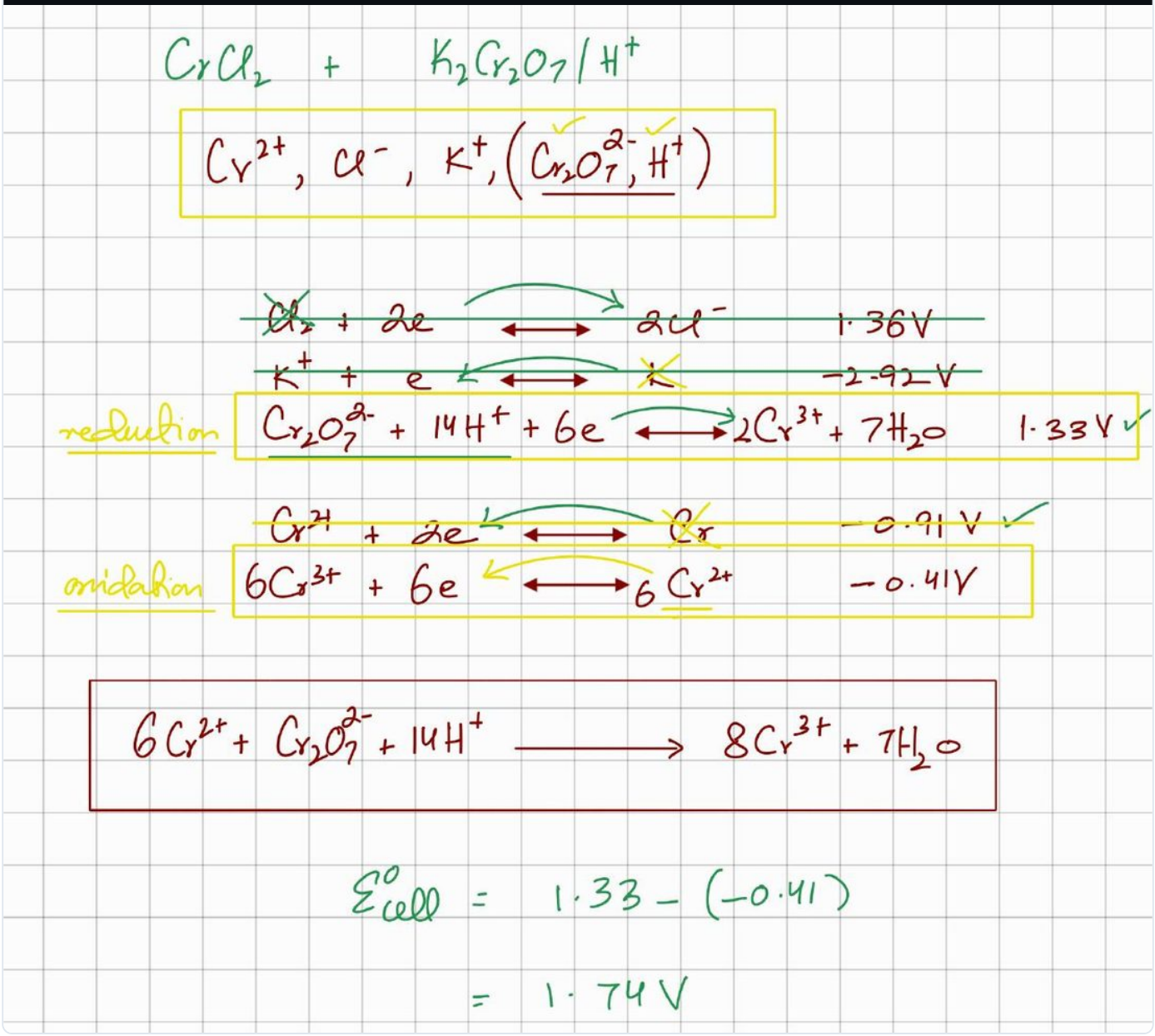
reduction $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $\quad E^\circ = +1.33$ V

oxidation $6\ Cr^{2+} \rightarrow 6\ Cr^{3+} + 6e^-$ $\quad E^\circ = -0.41$ V

$$6\ Cr^{2+} + Cr_2O_7^{2-} + 14\ H^+ \rightarrow 8\ Cr^{3+} + 7\ H_2O$$

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

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



WORKED EXAMPLE 4 — $FECL_{3(AQ)} + KI_{(AQ)}$

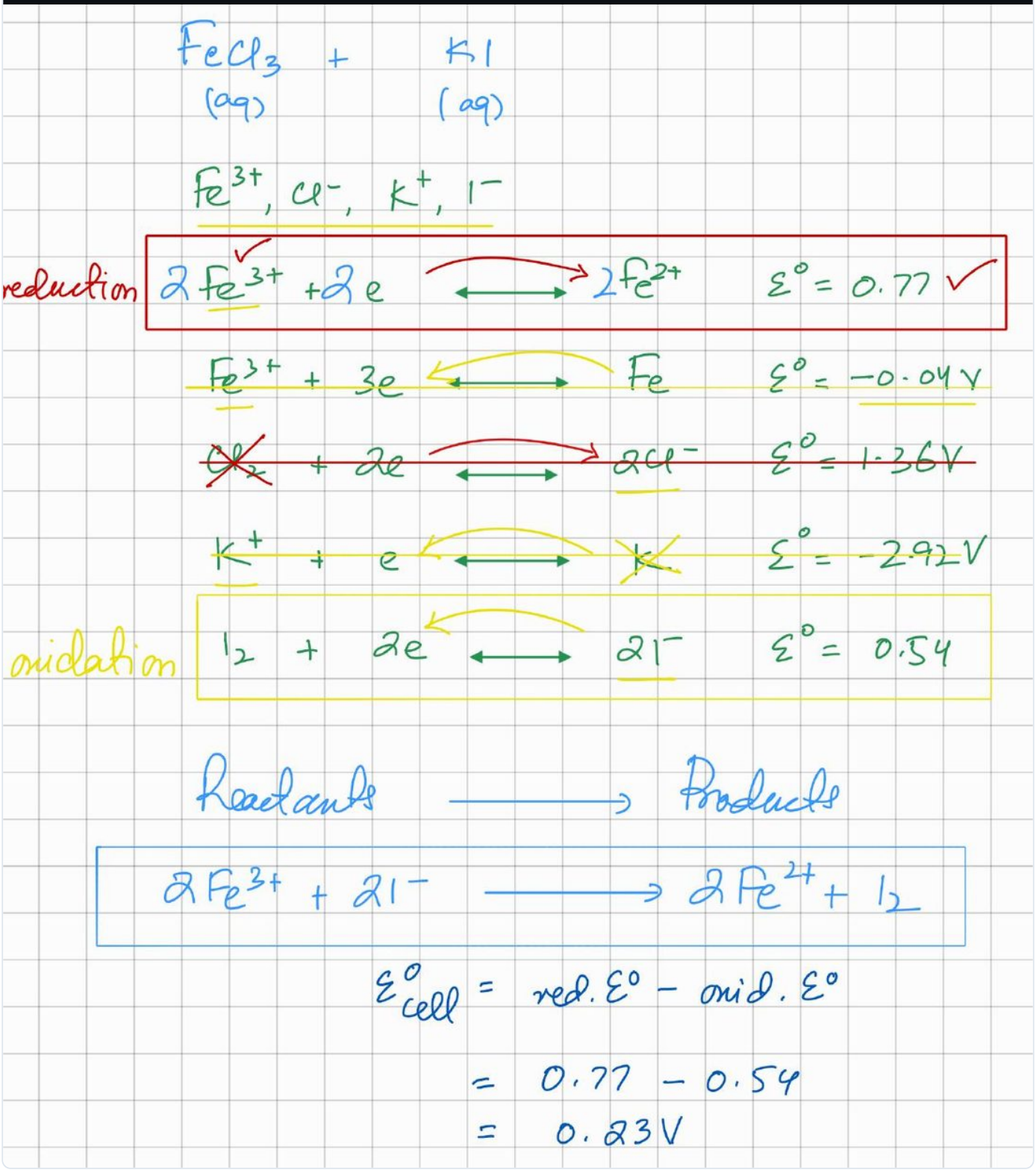
Species present: Fe^{3+}, Cl^-, K^+, I^-

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

oxidation $2\ I^- \rightarrow I_2 + 2e^-$ $E° = +0.54$ V

$$2\ Fe^{3+} + 2\ I^- \rightarrow 2\ Fe^{2+} + I_2$$

$E°_{cell} = 0.77 - 0.54 =$ **+0.23 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 I_2

Step 1 — from I_2/I^- (+0.54 V) and Sn^{2+}/Sn (−0.14 V):

$$I_2 + Sn \rightarrow Sn^{2+} + 2\ I^- \qquad E^\circ_{cell} = 0.54 - (-0.14) = +0.68\ V$$

Step 2 — Sn^{2+} now meets the remaining excess I_2; from I_2/I^- (+0.54 V) and Sn^{4+}/Sn^{2+} (+0.15 V):

$$Sn^{2+} + I_2 \rightarrow 2\ I^- + Sn^{4+}$$

Step 1 + Step 2, cancelling Sn^{2+}:

$$Sn + 2\ I_2 \rightarrow 4\ I^- + Sn^{4+}$$

Difficult Example Chain Reactions

(a) $Sn + {}^{(excess)}I_2$

$I_2 + 2e \rightleftharpoons 2I^-$ 0.54V

$Sn^{2+} + 2e \rightleftharpoons Sn$ −0.14V

step 1 $I_2 + Sn \longrightarrow Sn^{2+} + 2I^-$

$E^\circ_{cell} = 0.54 - (-0.14)$

$= 0.68\ V$

$Sn^{2+} + \text{excess } I_2$

+

$I_2 + 2e \rightleftharpoons 2I^-$ 0.54V

$Sn^{4+} + 2e \rightleftharpoons Sn^{2+}$ 0.15

step 2 $Sn^{2+} + I_2 \longrightarrow 2I^- + Sn^{4+}$

$2I_2 + Sn + Sn^{2+} \longrightarrow Sn^{2+} + 2I^- + 2I^- + Sn^{4+}$

step 1 + step 2 $Sn + 2I_2 \longrightarrow 4I^- + Sn^{4+}$

EXCESS Fe^{3+} + V

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

$$2\ Fe^{3+} + V \rightarrow 2\ Fe^{2+} + V^{2+}$$

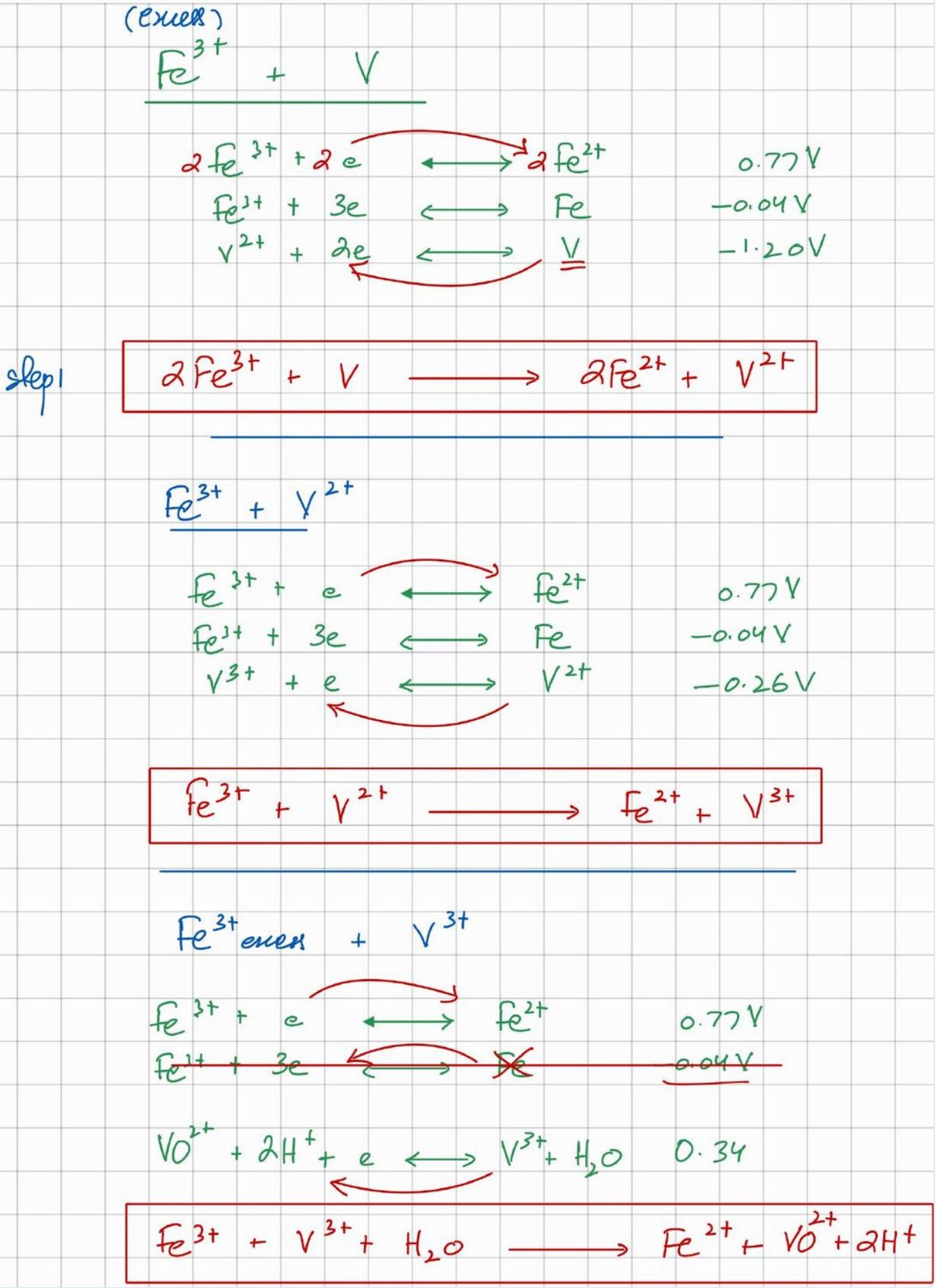
Step 2 — Fe^{3+}/Fe^{2+} (+0.77 V) vs V^{3+}/V^{2+} (−0.26 V):

$$Fe^{3+} + V^{2+} \rightarrow Fe^{2+} + V^{3+}$$

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

$$Fe^{3+} + V^{3+} + H_2O \rightarrow Fe^{2+} + VO^{2+} + 2\ H^{+}$$

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


(excess)
Fe^{3+} + V
$2Fe^{3+} + 2e \rightleftharpoons 2Fe^{2+}$ 0.77 V
$Fe^{3+} + 3e \rightleftharpoons Fe$ −0.04 V
$V^{2+} + 2e \rightleftharpoons V$ −1.20 V
step 1
$2Fe^{3+} + V \longrightarrow 2Fe^{2+} + V^{2+}$
$Fe^{3+} + V^{2+}$
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ 0.77 V
$Fe^{3+} + 3e \rightleftharpoons Fe$ −0.04 V
$V^{3+} + e \rightleftharpoons V^{2+}$ −0.26 V
$Fe^{3+} + V^{2+} \longrightarrow Fe^{2+} + V^{3+}$
Fe^{3+} excess + V^{3+}
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ 0.77 V
$Fe^{3+} + 3e \rightleftharpoons Fe$ 0.04 V
$VO^{2+} + 2H^+ + e \rightleftharpoons V^{3+} + H_2O$ 0.34
$Fe^{3+} + V^{3+} + H_2O \longrightarrow Fe^{2+} + VO^{2+} + 2H^+$

10 Non-Standard Conditions & the Nernst Equation

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

REASONING

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

NERNST EQUATION

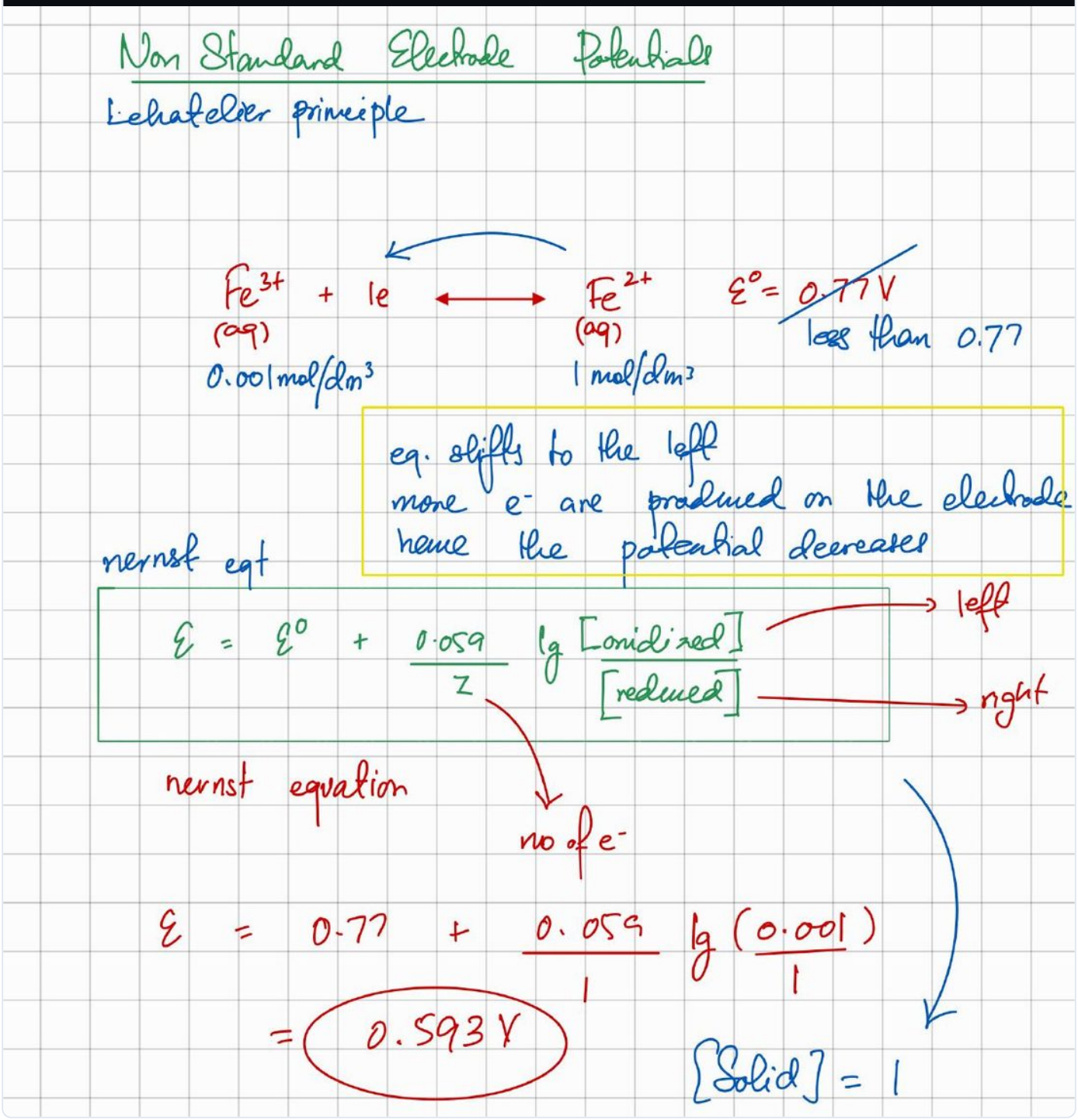
$$E = E^\circ + \frac{0.059}{z} \lg \frac{[\text{oxidised}]}{[\text{reduced}]}$$

- **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 MOL DM^{-3}, Fe^{2+} AT 1 MOL DM^{-3}

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

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



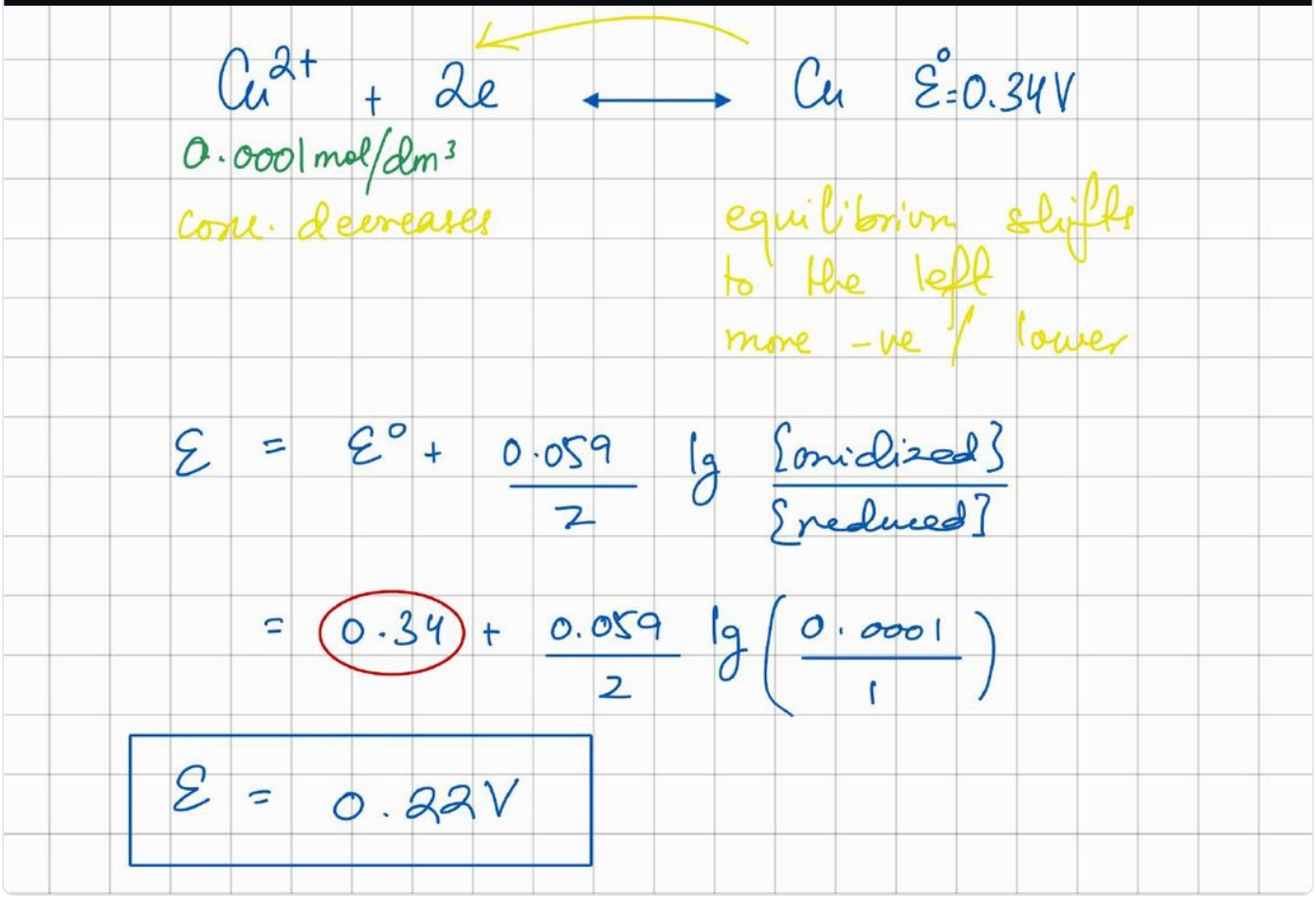
EXAMPLE — Cu^{2+} AT 0.0001 MOL DM^{-3}

$Cu^{2+} + 2e^- \rightleftharpoons Cu$, $E^\circ = +0.34$ V, $z = 2$, [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.



11 Homogeneous Catalysis

DEFINITION

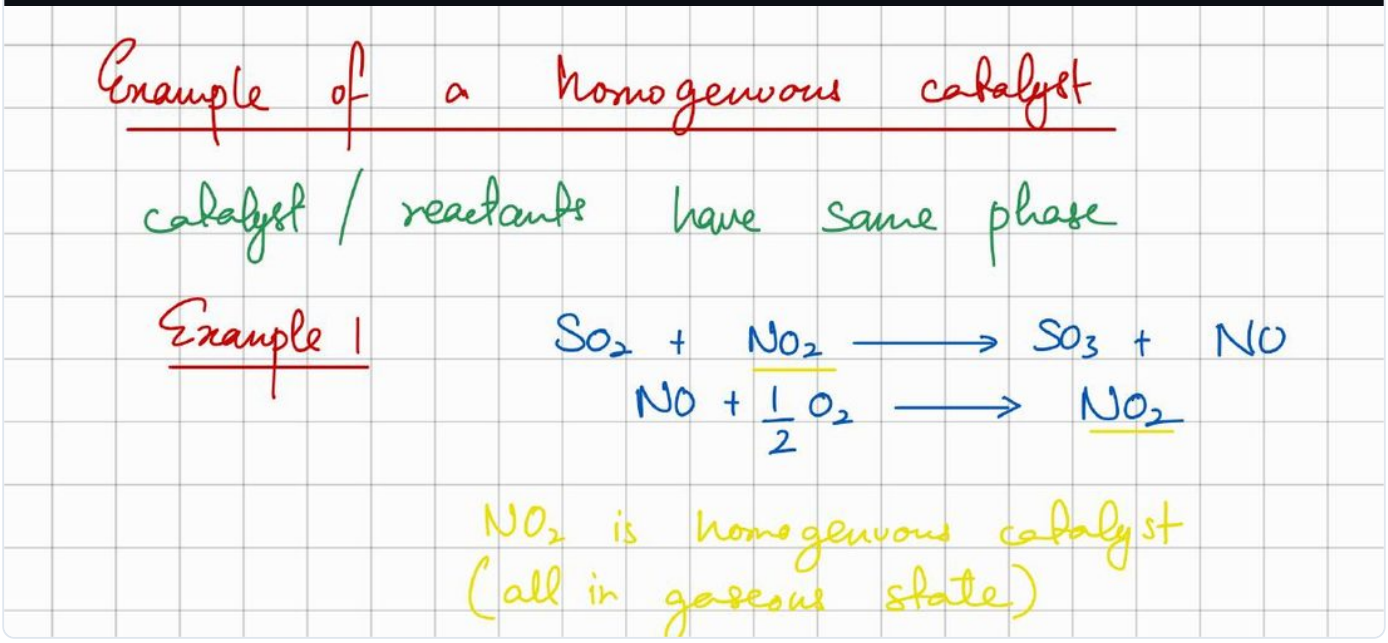
A **homogeneous catalyst** is in the **same phase** as the reactants.

Example 1 — NO_2 in the Chamber process

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

$$NO + ½\ O_2 \rightarrow NO_2$$

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



Example 2 — Fe^{2+}/Fe^{3+} catalysing $S_2O_8^{2-} + I^-$

MEMORISE THIS ONE

Uncatalysed: $2\ I^- + S_2O_8^{2-} \rightarrow I_2 + 2\ SO_4^{2-}$, with $E^\circ_{cell} = 2.01 - 0.54 =$ **+1.47 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 Fe^{2+}/Fe^{3+} provides a two-step route in which each step involves **oppositely charged** ions:

$$2\ I^- + 2\ Fe^{3+} \rightarrow I_2 + 2\ Fe^{2+}$$

$$S_2O_8^{2-} + 2\ Fe^{2+} \rightarrow 2\ SO_4^{2-} + 2\ Fe^{3+}$$

- Fe^{2+}/Fe^{3+} are **regenerated — unchanged overall**.
- Ions are oppositely charged in both steps → attraction → much **lower E_a** → much faster.

Relevant potentials: I_2/I^- +0.54 V · Fe^{3+}/Fe^{2+} +0.77 V · $S_2O_8^{2-}/SO_4^{2-}$ +2.01 V. The Fe couple sits between the other two — that is why it works.

Example 2

$S_2O_8^{2-} + I^-$ memorize this

$I_2 + 2e \rightleftharpoons 2I^-$ $\quad E° = 0.54\,V$

$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{-2}$ $\quad E° = 2.01\,V$

$$2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{-2}$$

$$E°_{cell} = 2.01 - 0.54 = 1.47\,V$$

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

* Fe^{+} / Fe^{3+} are added as catalyst

$I_2 + 2e \rightleftharpoons 2I^-$ $\quad E° = 0.54\,V$

$2Fe^{3+} + 2e^- \rightleftharpoons 2Fe^{2+}$ $\quad E° = 0.77\,V$

$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{-2}$ $\quad E° = 2.01\,V$

$$2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+}$$

$$S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{-2} + 2Fe^{3+}$$

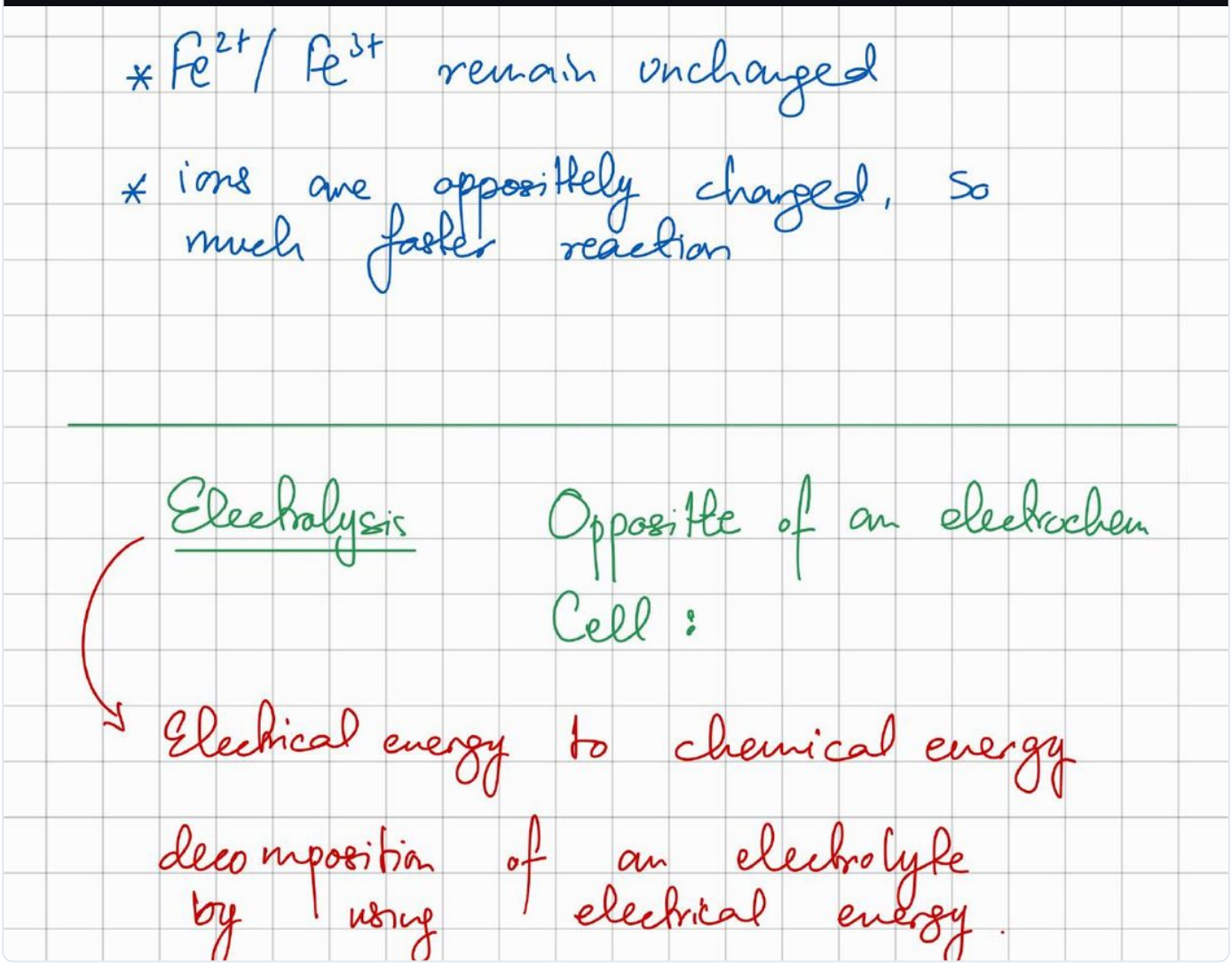
12 Electrolysis

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



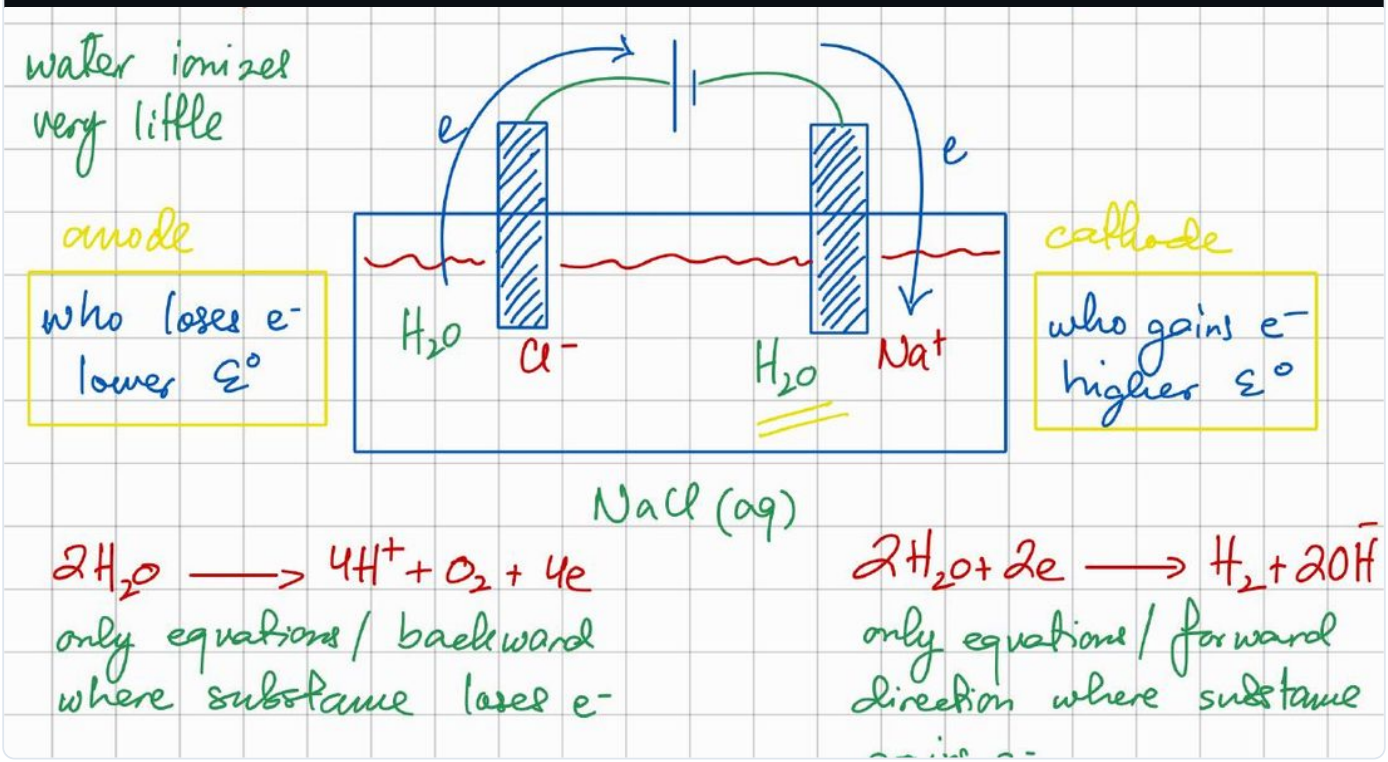
Dilute $NaCl_{(aq)}$

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

anode $2\ H_2O \rightarrow 4\ H^+ + O_2 + 4e^-$

cathode $2\ H_2O + 2e^- \rightarrow H_2 + 2\ OH^-$

ANODE AND CATHODE LABELLED BY E° — DILUTE NACL PAGE 20

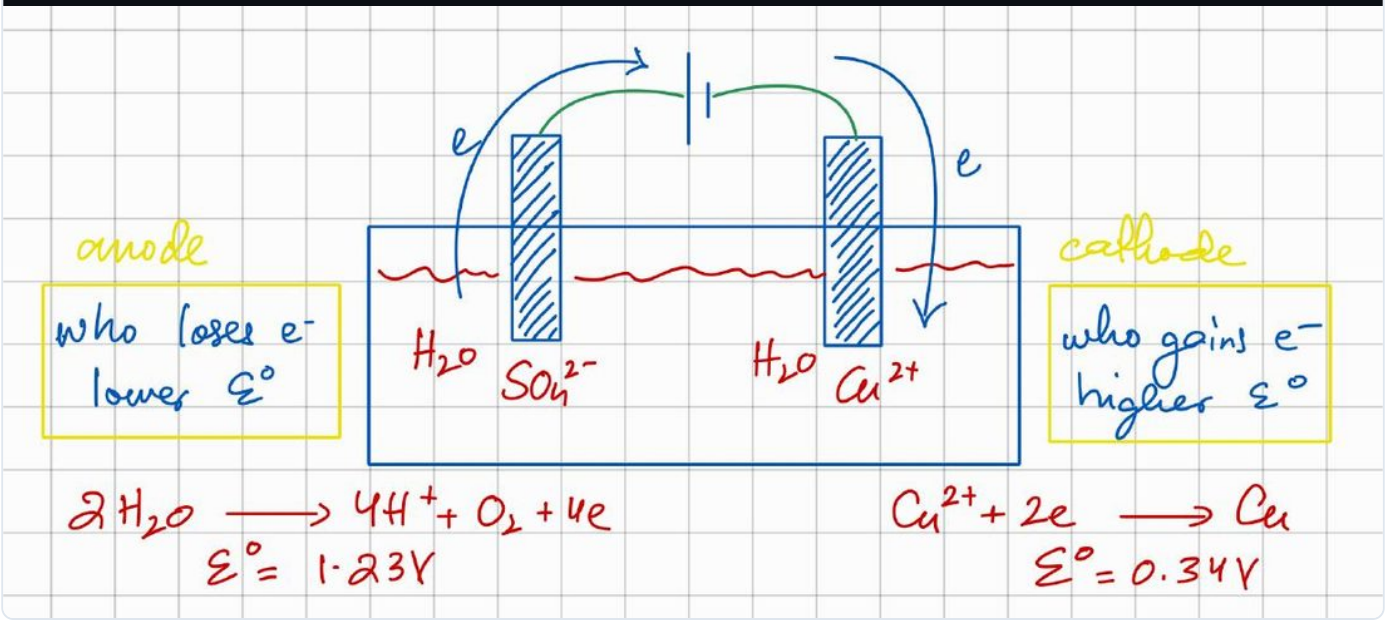


$CuSO_{4(aq)}$

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

anode $2\ H_2O \rightarrow 4\ H^+ + O_2 + 4e^-$ $E° = +1.23$ V

cathode $Cu^{2+} + 2e^- \rightarrow Cu$ $E° = +0.34$ V



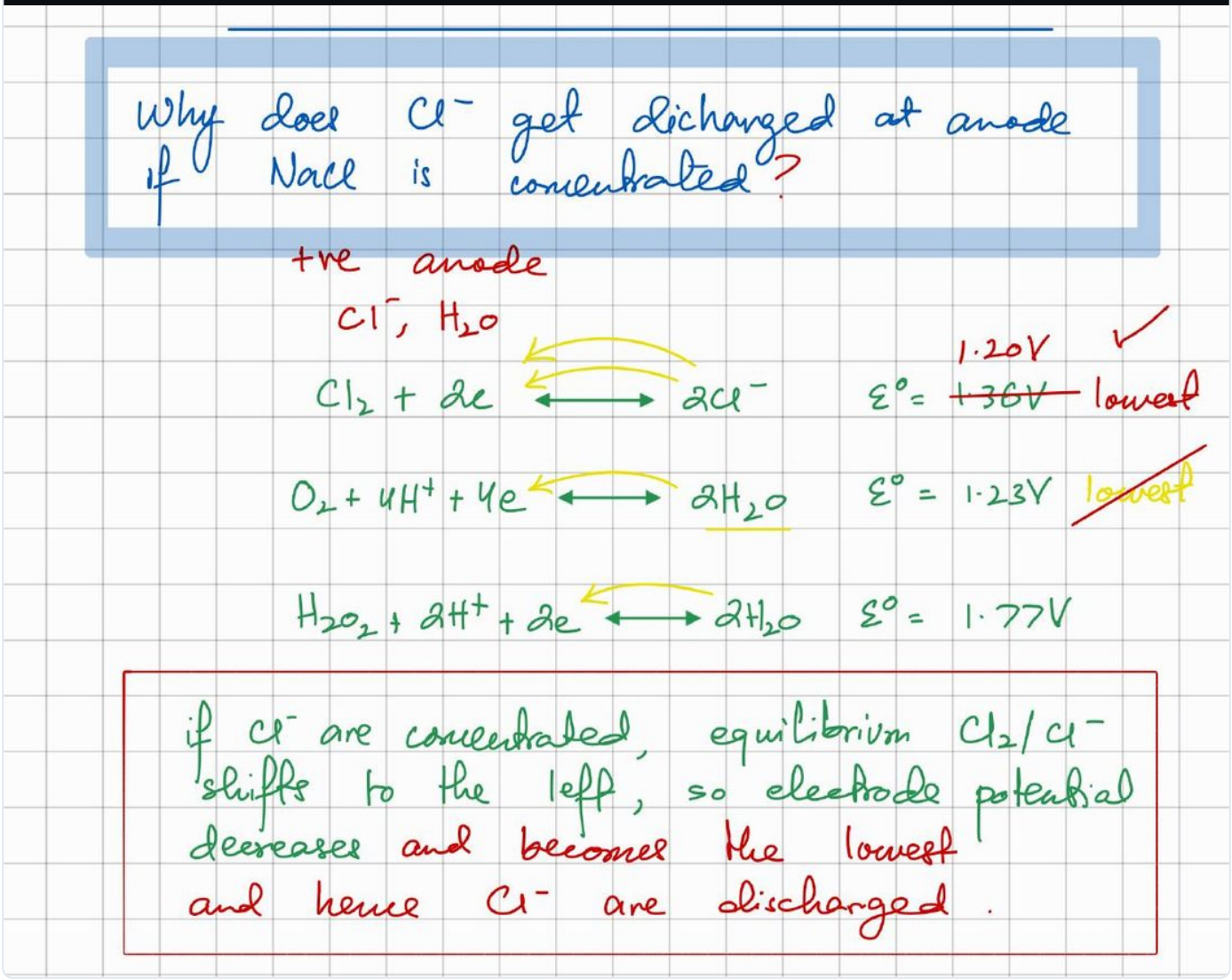
CLASSIC EXAM QUESTION — WHY IS CL⁻ DISCHARGED FROM CONCENTRATED NACL?

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

$Cl_2 + 2e^- \rightleftharpoons 2\ Cl^-$ $\quad E^\circ = +1.36$ V standard

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2\ H_2O$ $\quad E^\circ = +1.23$ V

Under standard conditions O_2/H_2O 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.



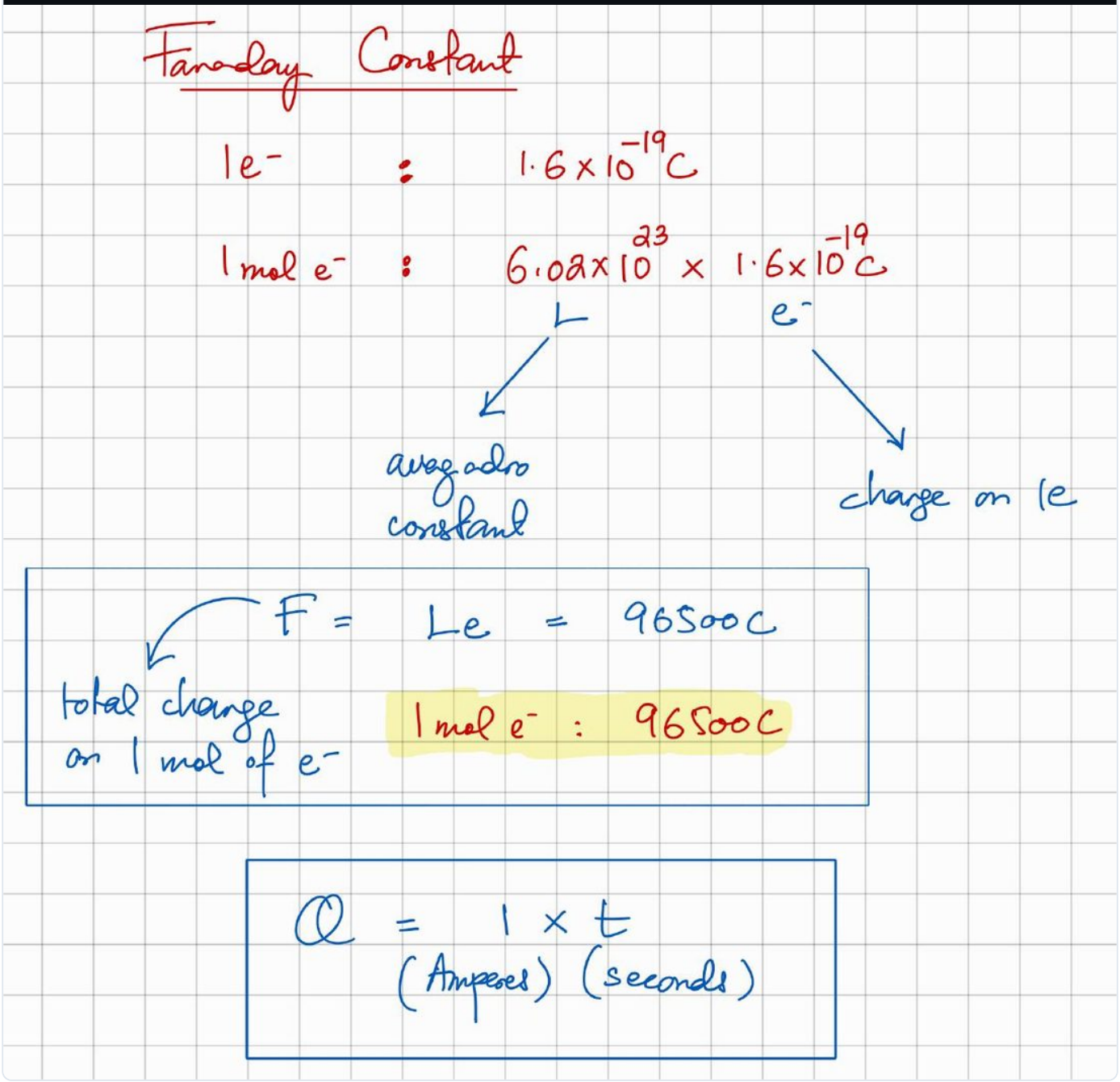
13 The Faraday Constant

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

THE TWO EQUATIONS

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

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



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 C**
2. mol e^- = 3600 / 96 500 = **0.0373 mol**
3. $Cu^{2+} + 2e^- \rightarrow Cu$, so mol Cu = 0.0373 / 2 = **0.0187 mol**
4. $m = n \times M_r = 0.0187 \times 63.5 =$ **1.184 g**

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

Calculate the mass of Cu deposited.

$Q = I \times t = 2A \times 30 \times 60 sec$

$= 3600C$

1 mol e^- ⟶ 96500C

x mol ⟶ 3600C

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

$Cu^{2+} + 2e \longrightarrow Cu$

0.373 mol — 0.0187 mol

$m = n \times M_r$

$= 0.0187 \times 63.5$

$= 1.184 g$.

METHOD IN ONE LINE

Q = I t → ÷ 96 500 for mol e^- → ÷ (electrons in the half-equation) for mol product → × M_r for mass (or ÷ 24 000 cm^3 / 24 dm^3 for gas volume at r.t.p.).

14 Exam Checklist

- 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° → reduced (gains e$^-$); lower E° → oxidised (loses e$^-$). Electrons flow towards higher E°.
- $E°_{cell}$ = E°(reduction) − E°(oxidation). Positive → feasible.
- **Feasible ≠ fast.** A high $E°_{cell}$ can still give no reaction if E_a is large ($S_2O_8^{2-}$ + 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.