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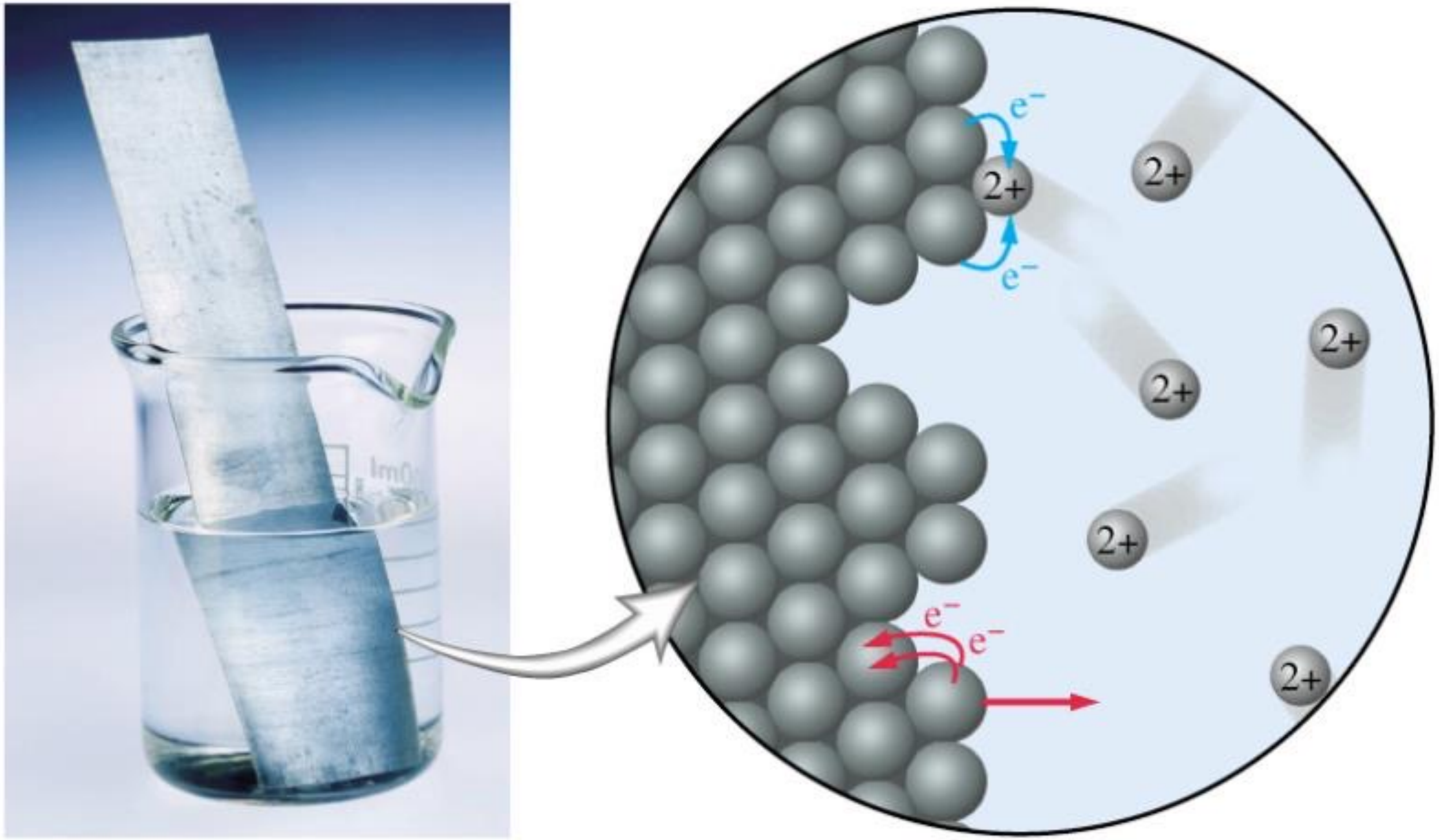
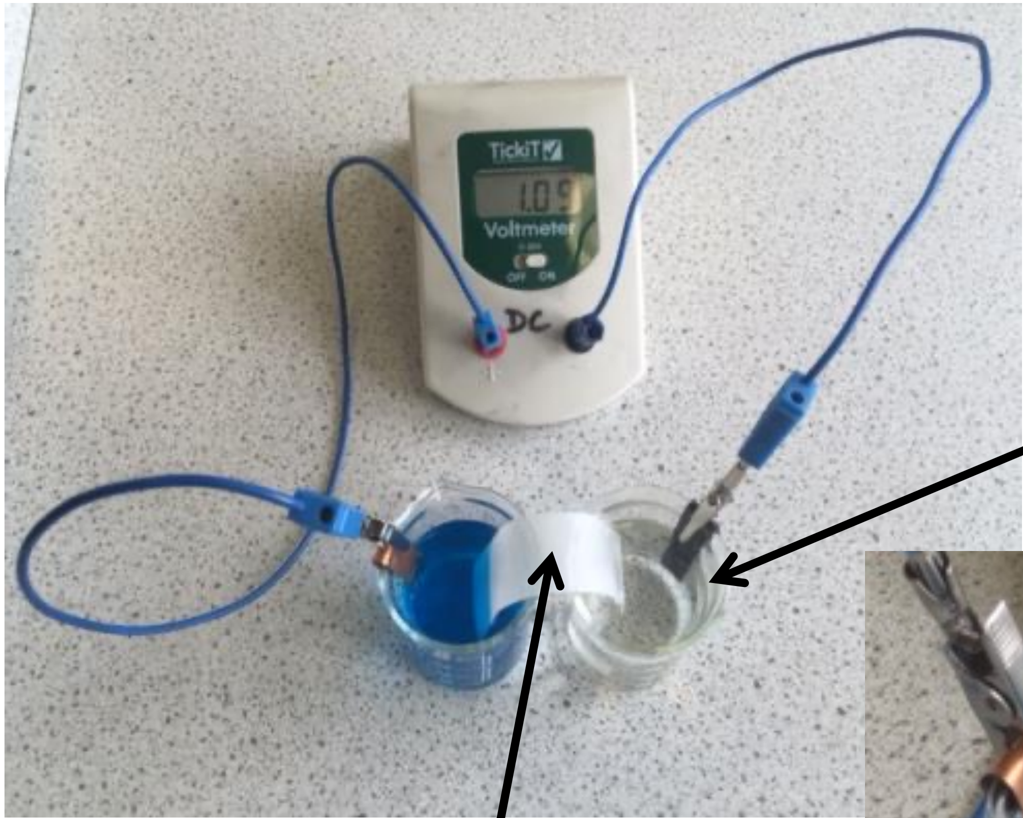
ELECTROCHEMISTRY

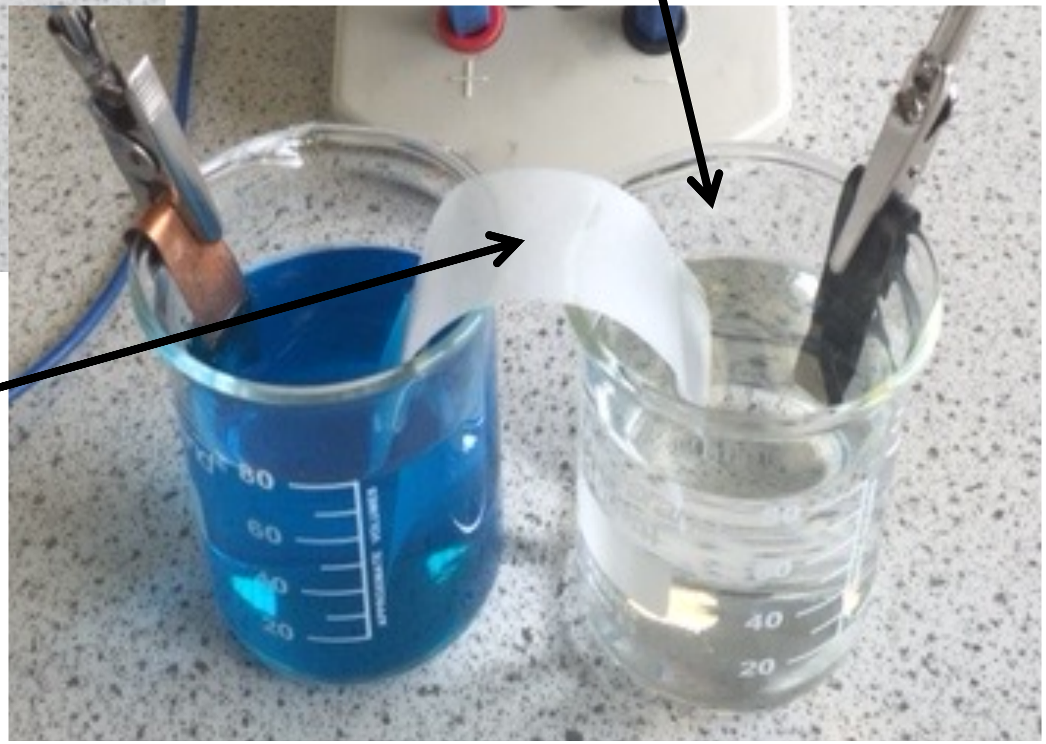


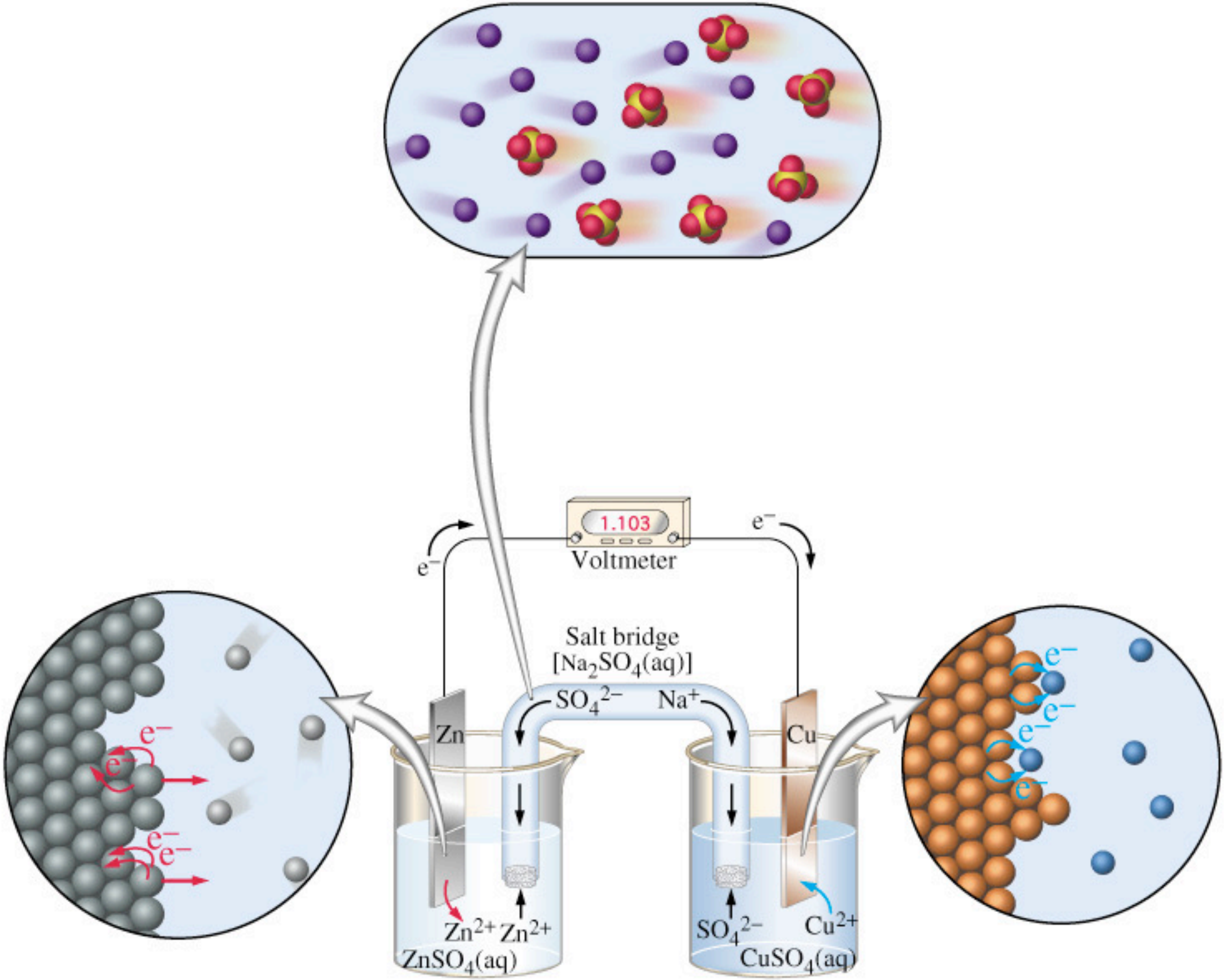
$$Zn^{2+}(aq) + 2\,e^{-} \rightleftharpoons Zn(s)$$



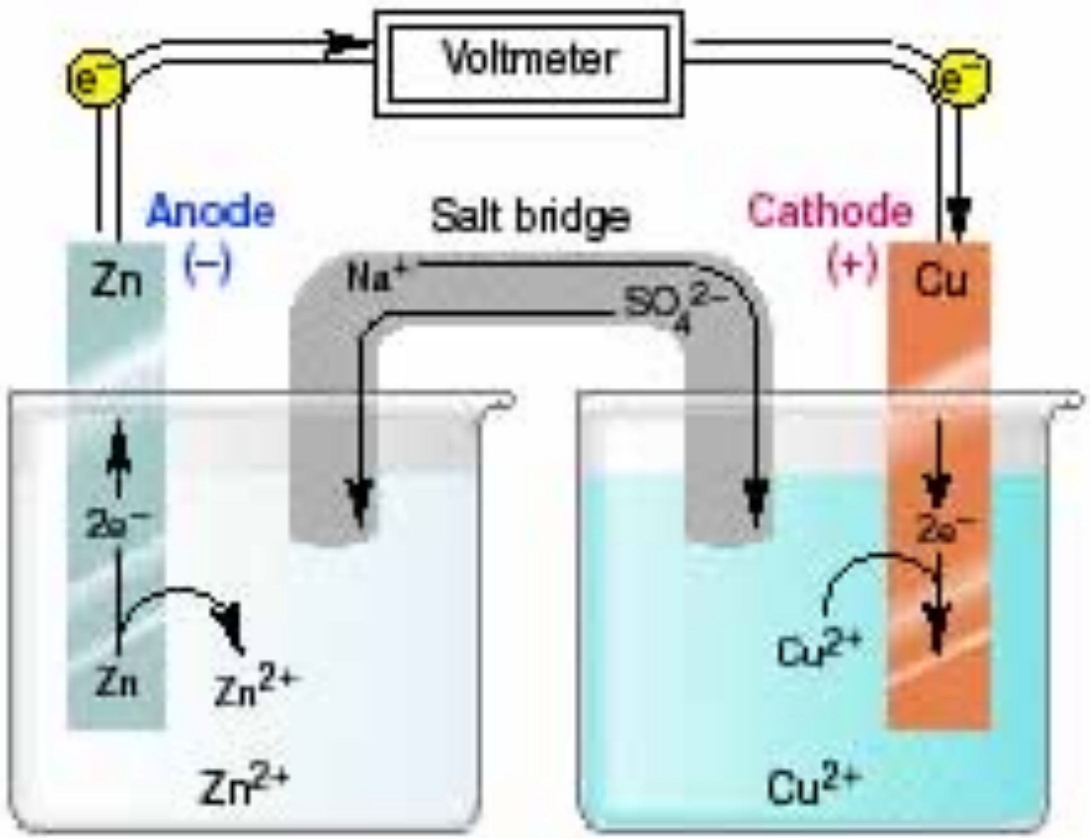
One of the two half cells [a piece of zinc in a solution of zinc nitrate(aq)]

Salt bridge [strip of filter paper soaked in saturated KNO_3(aq)]





1.103
Voltmeter
e⁻
e⁻
Salt bridge
[$Na_2SO_4(aq)$]
SO_4^{2-}
Na^+
Zn
Cu
e⁻
e⁻
e⁻
e⁻
e⁻
e⁻
e⁻
e⁻
Zn^{2+} Zn^{2+}
$ZnSO_4(aq)$
SO_4^{2-}
Cu^{2+}
$CuSO_4(aq)$



Oxidation half-reaction

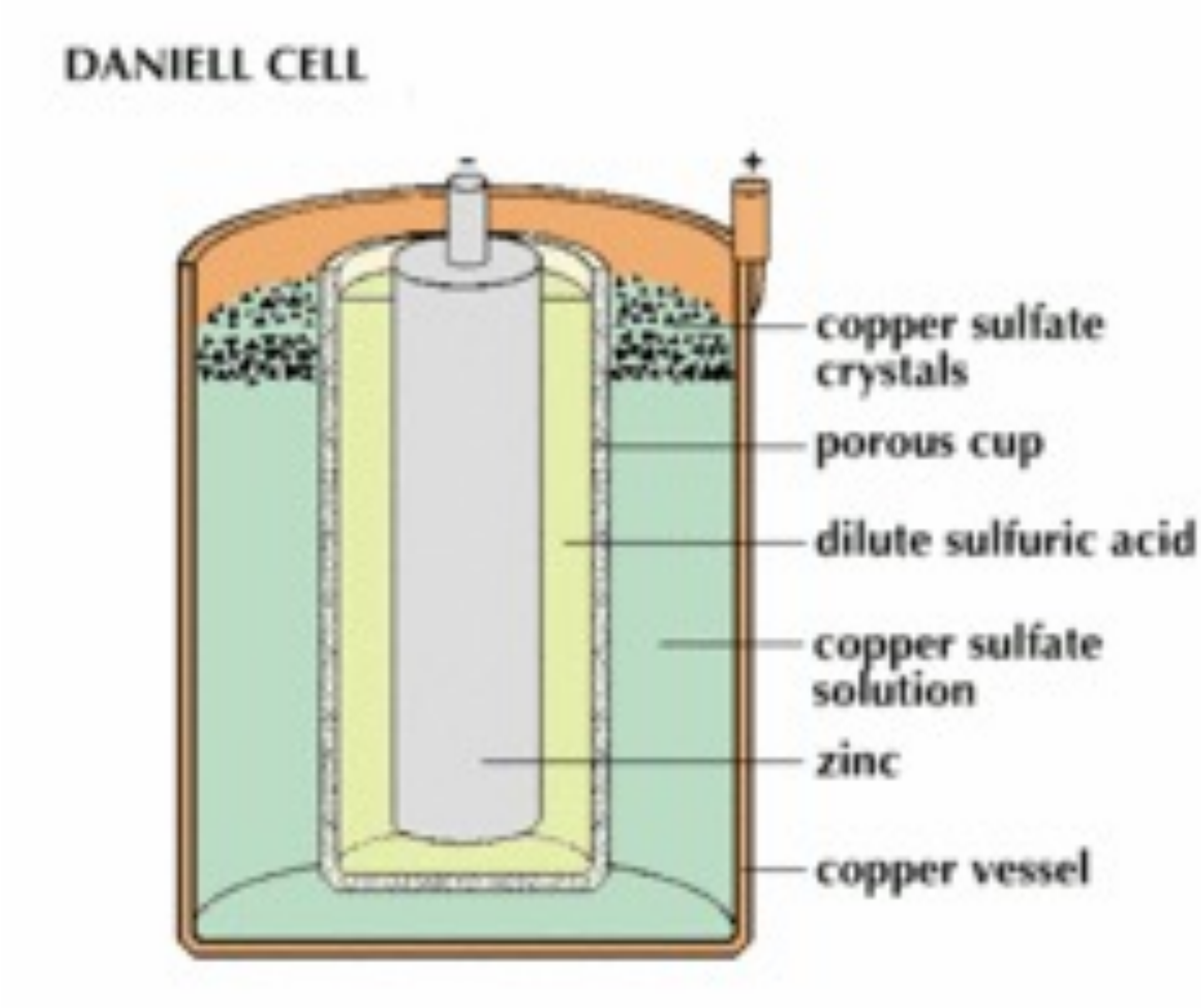
$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Reduction half-reaction

$2e^- + Cu^{2+}(aq) \longrightarrow Cu(s)$

Overall (cell) reaction

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$


DANIELL CELL
-
+
copper sulfate crystals
porous cup
dilute sulfuric acid
copper sulfate solution
zinc
copper vessel

Standard Conditions

Concentration

1.0 mol dm^{-3} (ions involved in ½ equation)

Temperature

298 K

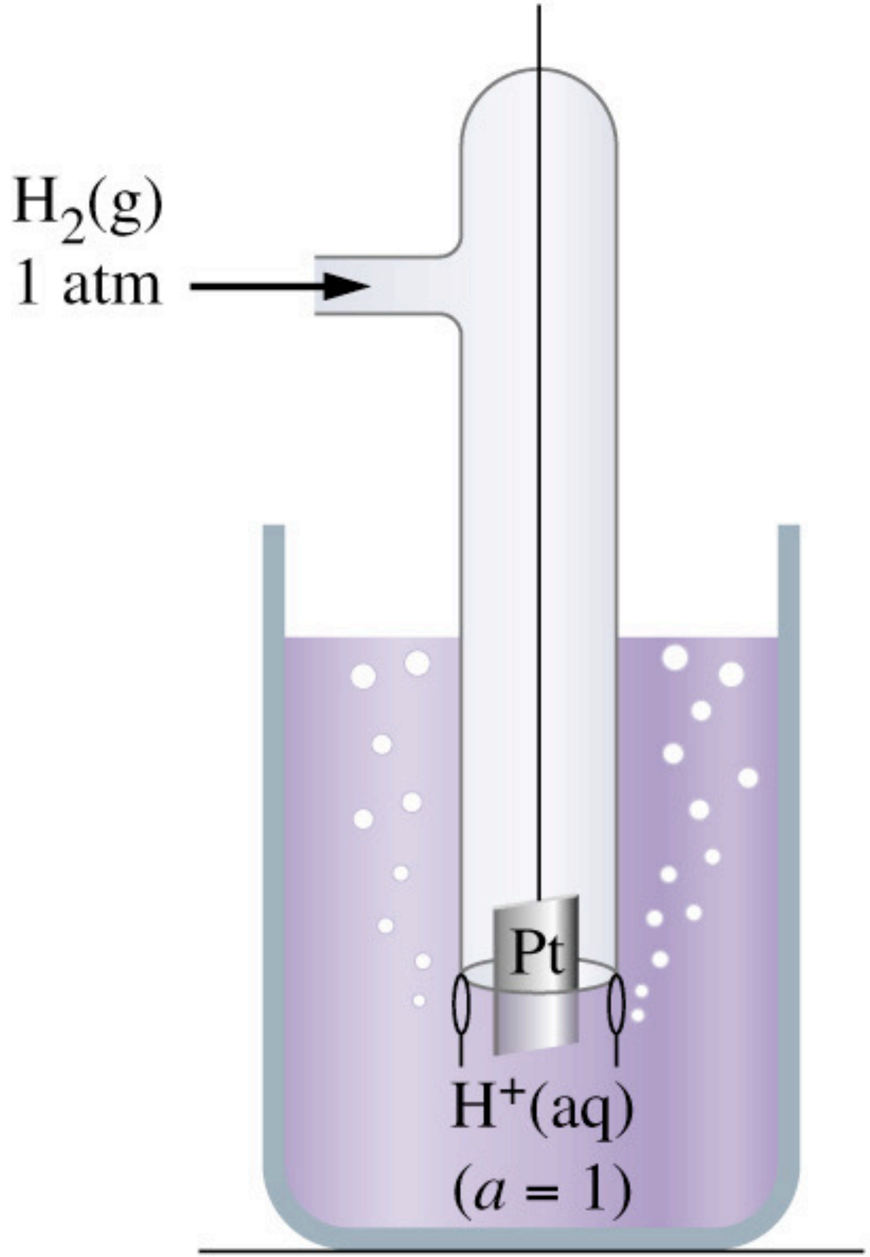
Pressure

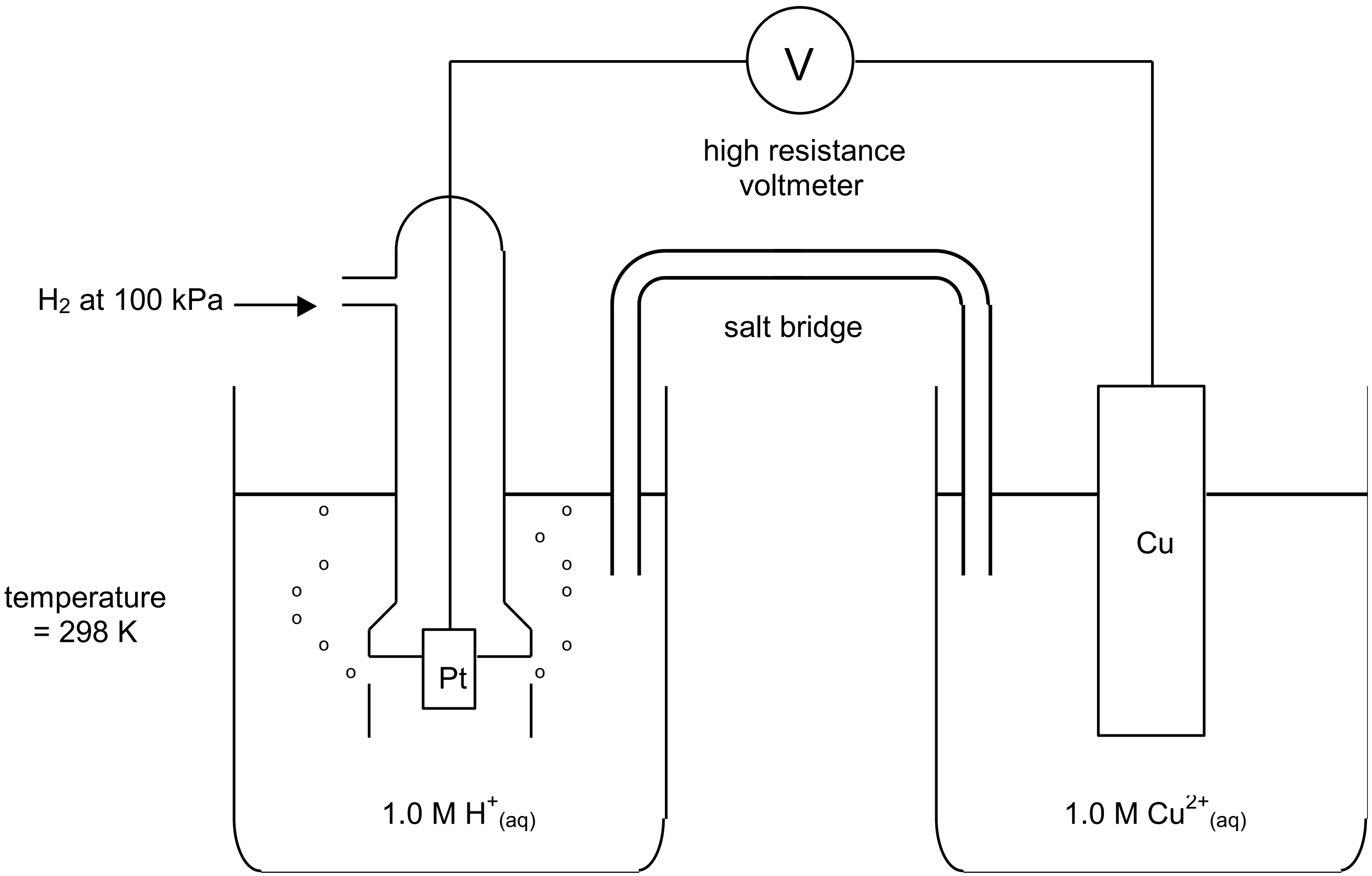
100 kPa (if gases involved in ½ equation)

Current

Zero (use high resistance voltmeter)

S tandard
H ydrogen
E lectrode

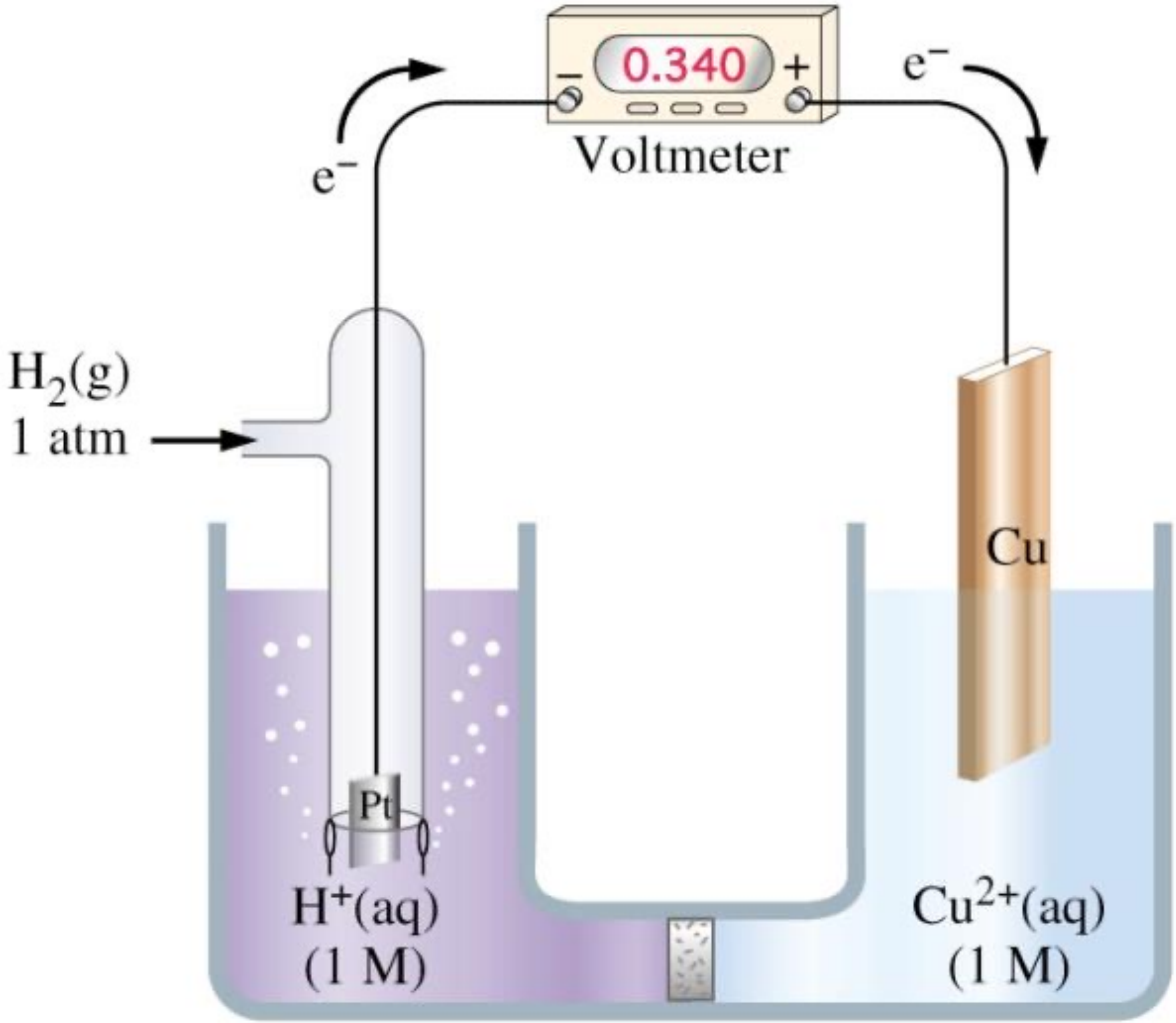




$Pt(s)\ |\ H_2(g)\ |\ H^+(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s)$

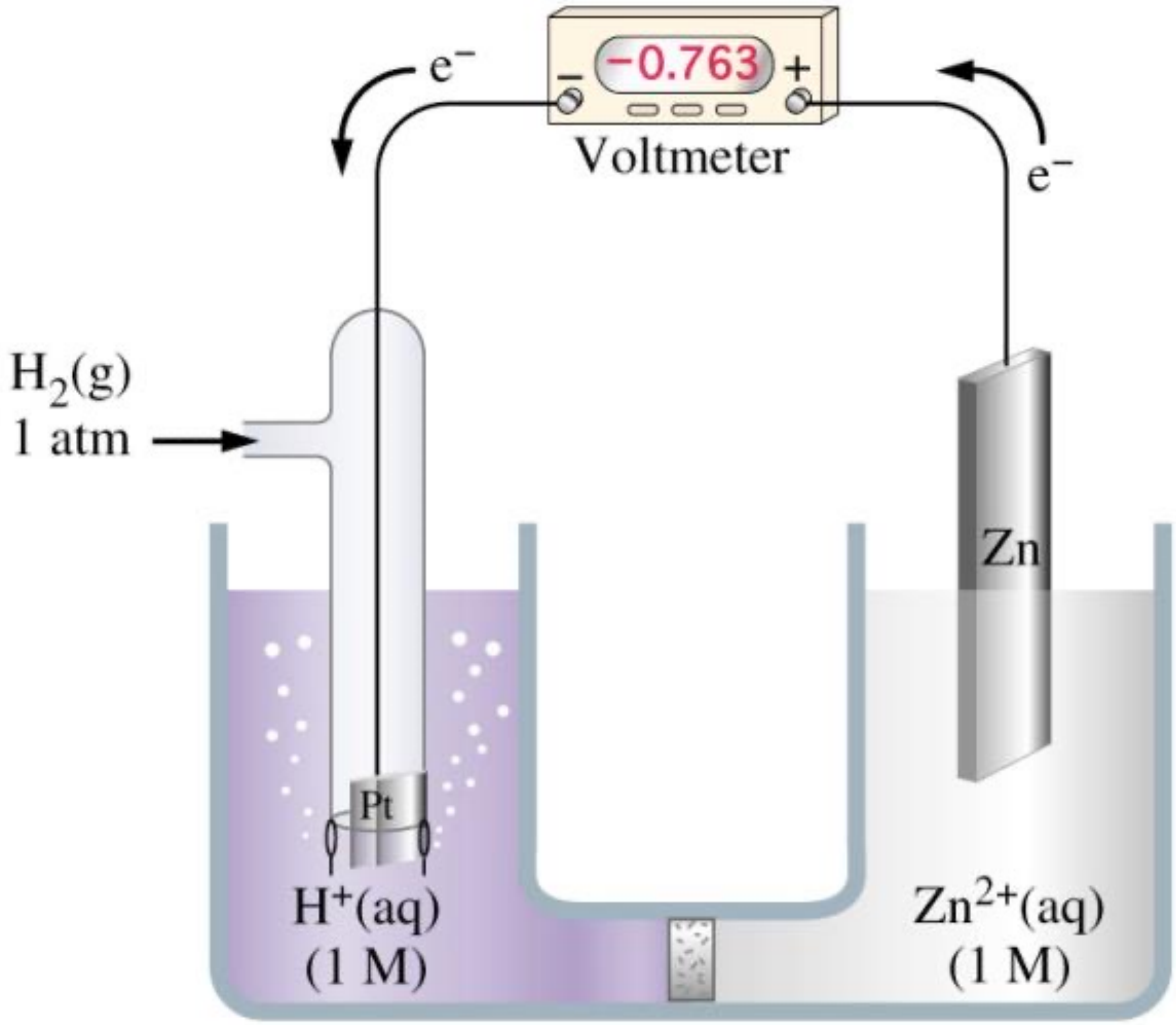
R O || O R

$Pt(s)\ |\ H_2(g)\ |\ H^+(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s)$



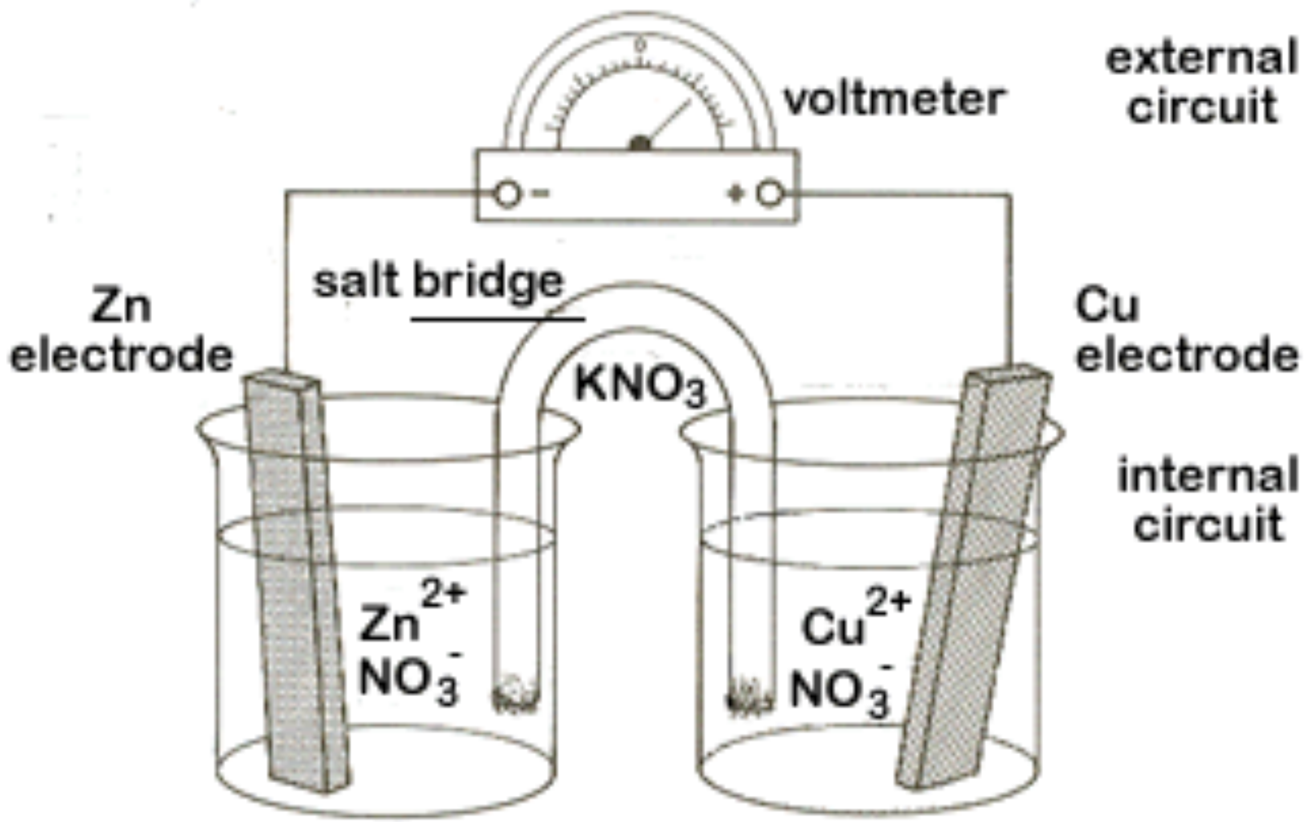
$Pt(s)$ | $H_2(g)$ | $H^+(aq)$ || $Cu^{2+}(aq)$ | $Cu(s)$

R O || O R



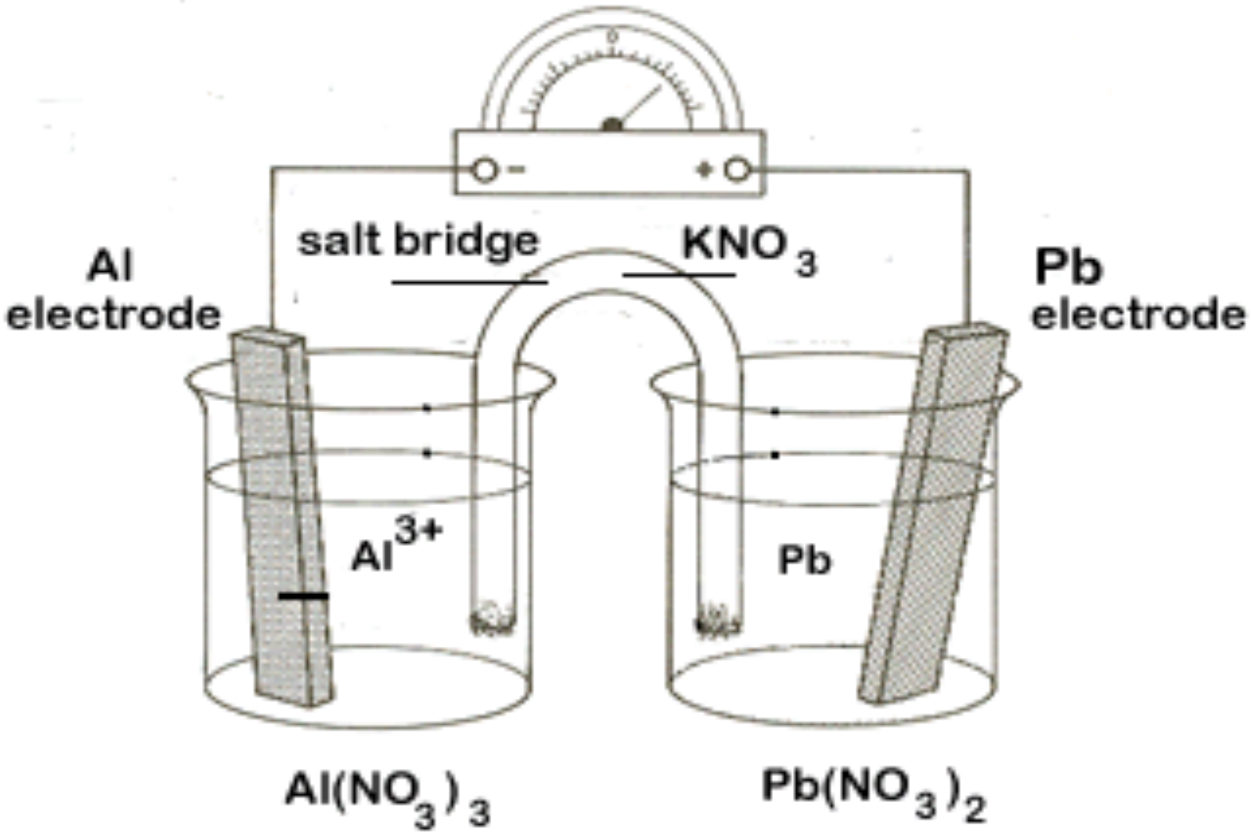
$Pt(s)$ | $H_2(g)$ | $H^+(aq)$ || $Zn^{2+}(aq)$ | $Zn(s)$

R O || O R



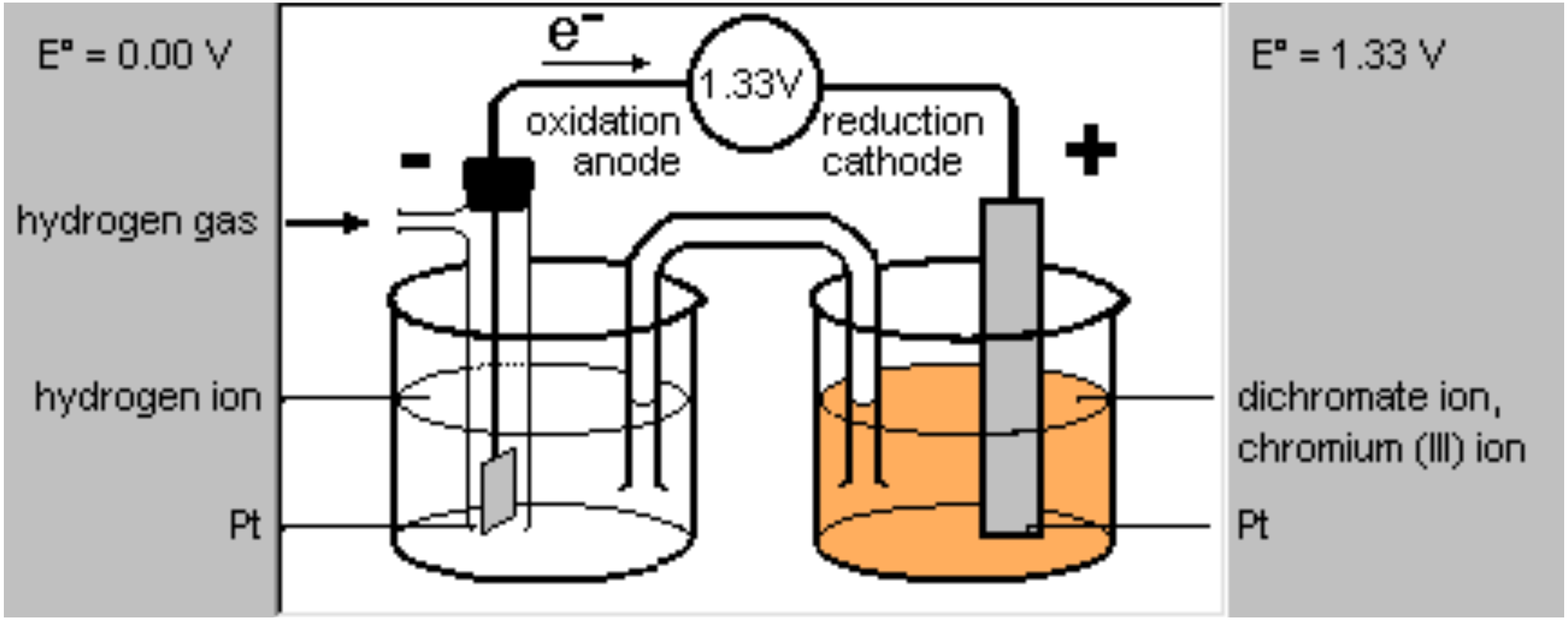
$$Zn(s)\ |\ Zn^{2+}(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s)$$

R　　O　||　O　　R



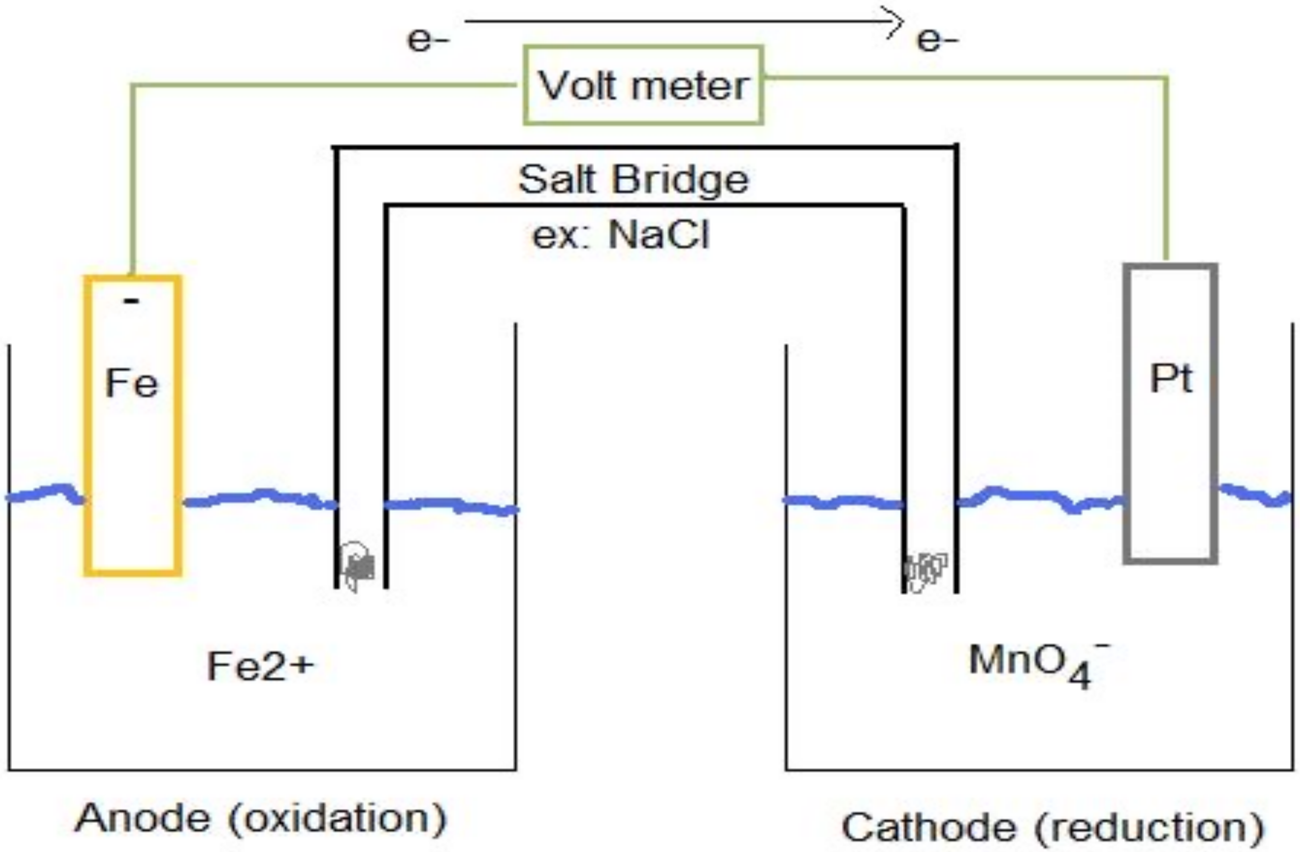
$$Al(s)\ |\ Al^{3+}(aq)\ ||\ Pb^{2+}(aq)\ |\ Pb(s)$$

R **O** || **O** **R**



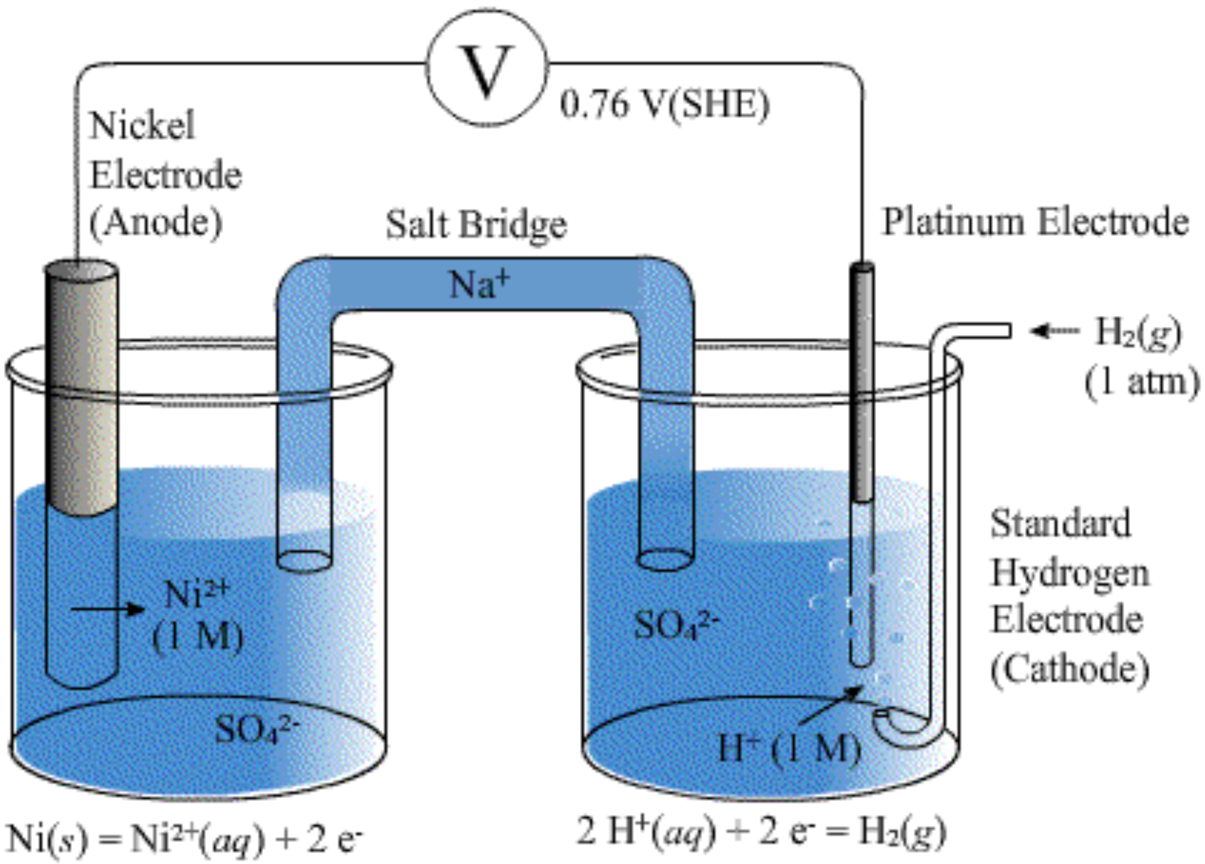
$Pt(s)\ |\ H_2(g)\ |\ H^+(aq)\ ||\ Cr_2O_7^{2-}(aq),\ H^+(aq),\ Cr^{3+}(aq)\ |\ Pt(s)$

R **O** || **O** **R**



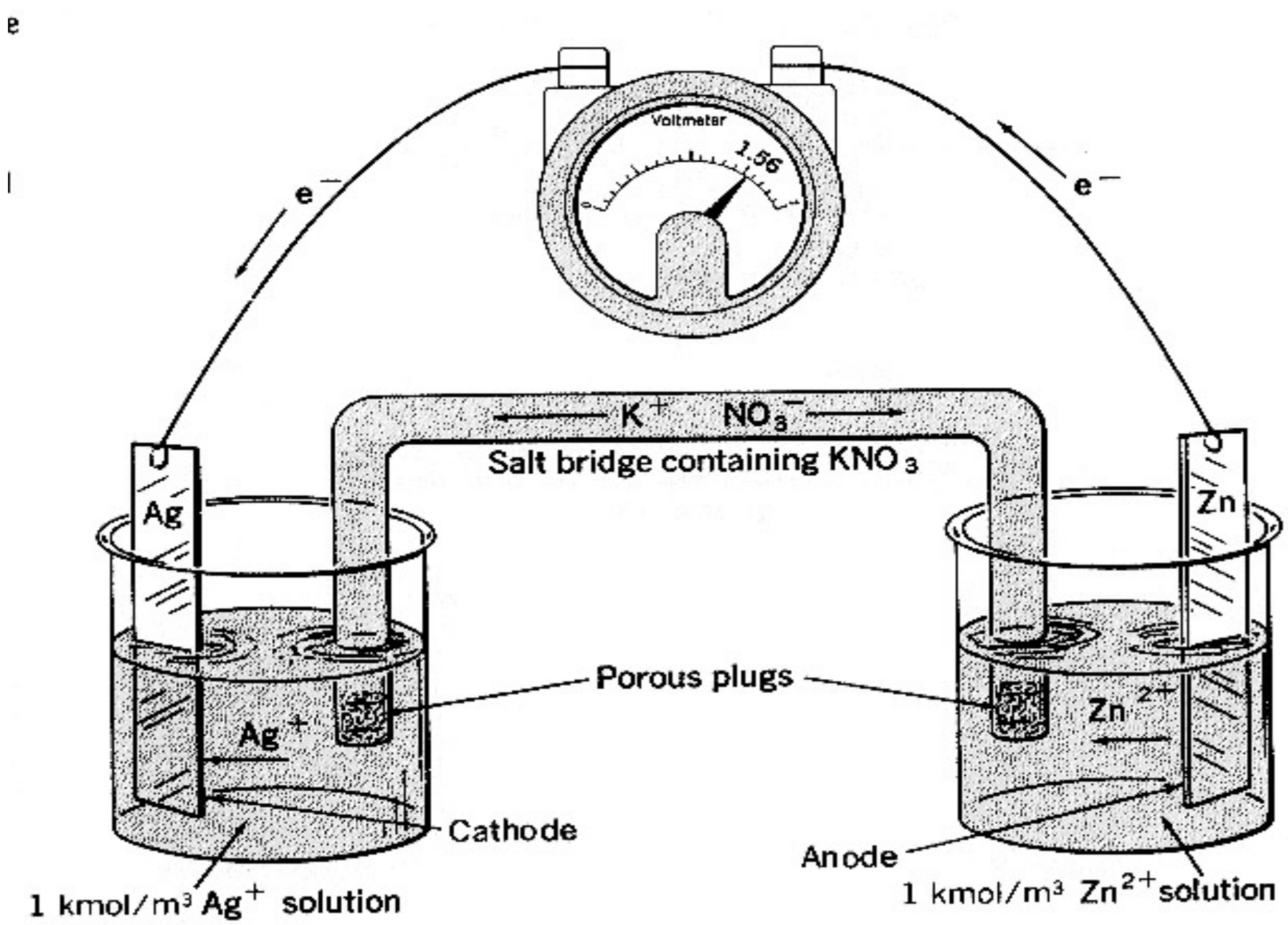
$Fe(s)\ |\ Fe^{2+}(aq)\ ||\ MnO_4^{-}(aq), H^{+}(aq), Mn^{2+}(aq)\ |\ Pt(s)$

R O || O R



$Ni(s) \mid Ni^{2+}(aq) \parallel H^{+}(aq) \mid H_2(g) \mid Pt(s)$

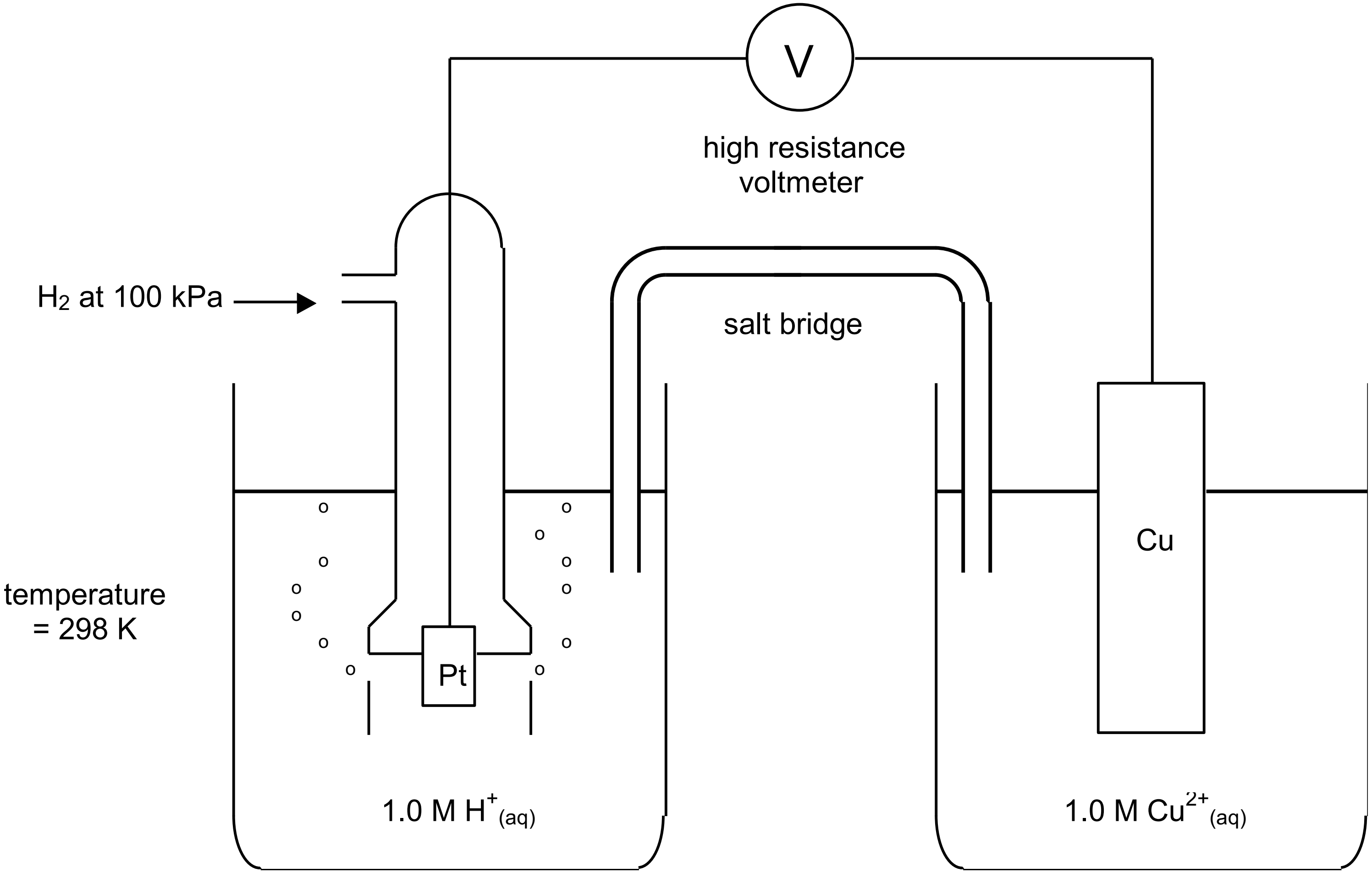
R O || O R



$Ag(s) \mid Ag^{+}(aq) \parallel Zn^{2+}(aq) \mid Zn(s)$

R O || O R

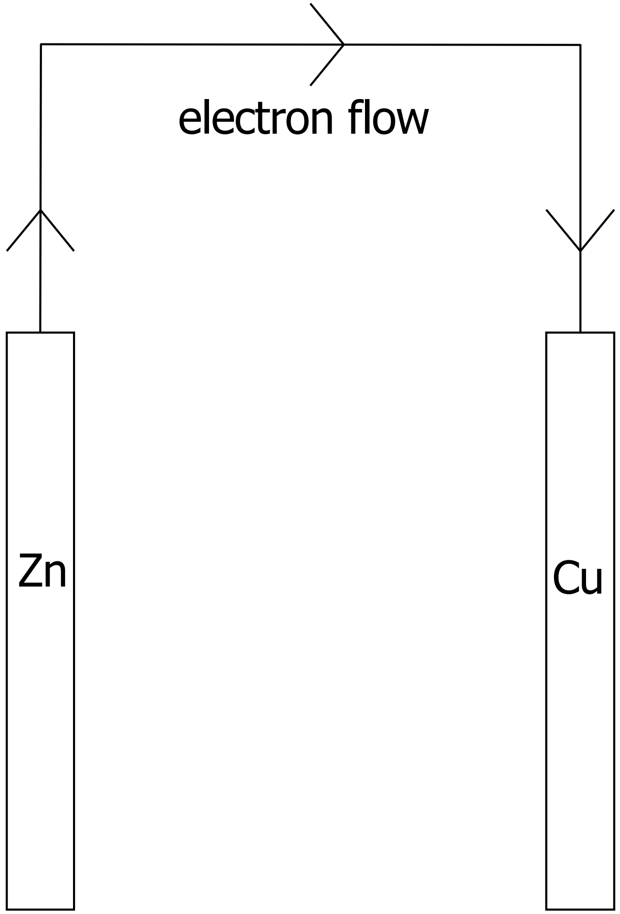
$$\mathbf{emf} = E^\circ_{right} - E^\circ_{left}$$



$$\mathbf{emf} = E^\circ_{right}$$

- electrode
anode
oxidation

+ electrode
cathode
reduction



At this electrode the metal loses electrons and so is oxidised to metal ions.

These electrons make the electrode negative.

At this electrode the metal ions gain electrons and so is reduced to metal atoms.

As electrons are used up, this makes the electrode positive.

$$Zn \rightarrow Zn^{2+} + 2\,e^-$$

oxidation

$$Cu^{2+} + 2\,e^- \rightarrow Cu$$

reduction

The electrochemical series

Increasing oxidising power

best oxidising agents

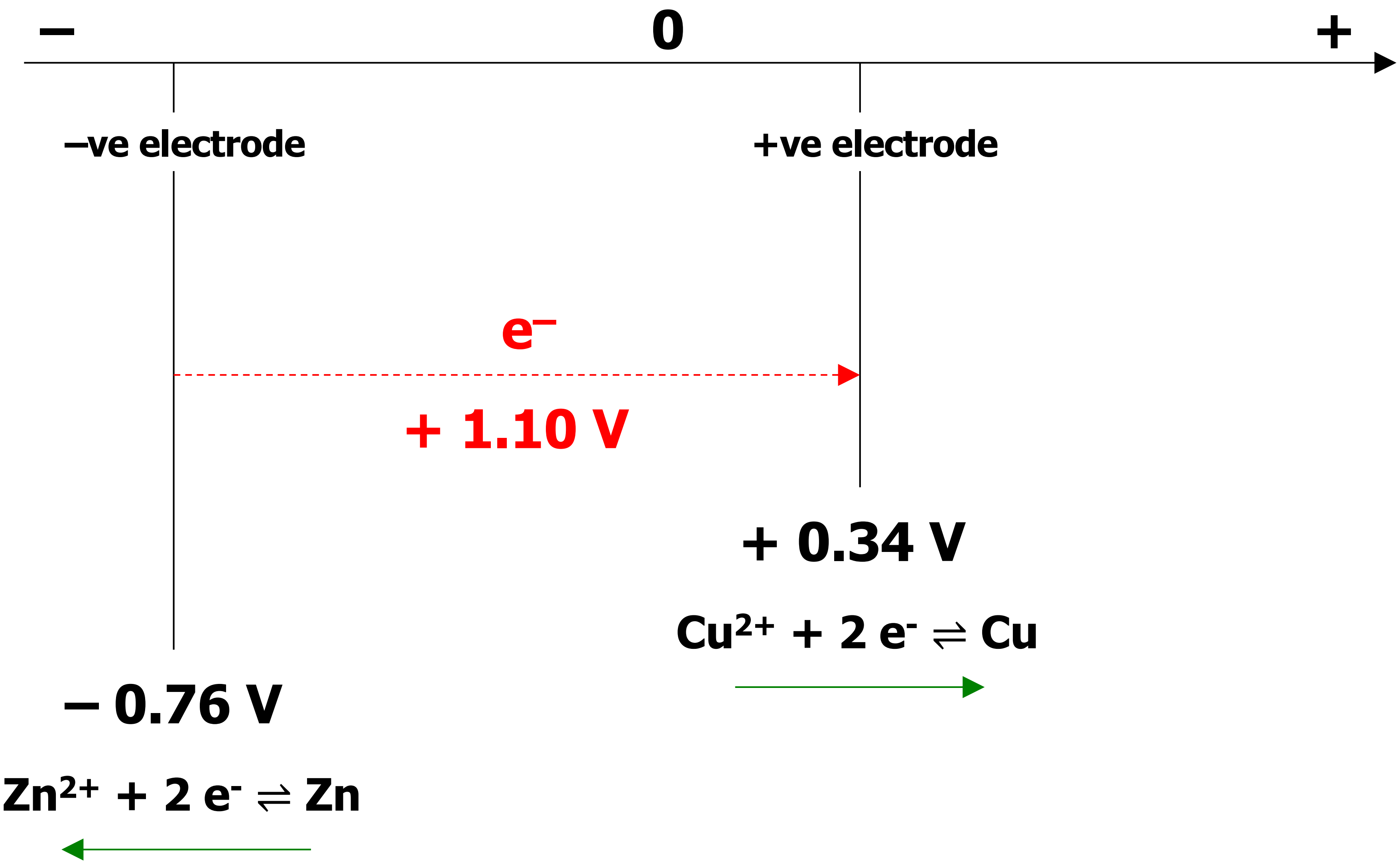
Standard electrode potentials			E°/V
$F_2(g) + 2e^-$	⇌	$2F^-(aq)$	+ 2.87
$MnO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	⇌	$MnO_2(s) + 2H_2O(l)$	+ 1.55
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	⇌	$Mn^{2+}(aq) + 4H_2O(l)$	+ 1.51
$Cl_2(g) + 2e^-$	⇌	$2Cl^-(aq)$	+ 1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	⇌	$2Cr^{3+}(aq) + 7H_2O(l)$	+ 1.33
$Br_2(g) + 2e^-$	⇌	$2Br^-(aq)$	+ 1.09
$Ag^+(aq) + e^-$	⇌	$Ag(s)$	+ 0.80
$Fe^{3+}(aq) + e^-$	⇌	$Fe^{2+}(aq)$	+ 0.77
$MnO_4^-(aq) + e^-$	⇌	$MnO_4^{2-}(aq)$	+ 0.56
$I_2(g) + 2e^-$	⇌	$2I^-(aq)$	+ 0.54
$Cu^{2+}(aq) + 2e^-$	⇌	$Cu(s)$	+ 0.34
$Hg_2Cl_2(aq) + 2e^-$	⇌	$2Hg(l) + 2Cl^-(aq)$	+ 0.27
$AgCl(s) + e^-$	⇌	$Ag(s) + Cl^-(aq)$	+ 0.22
$2H^+(aq) + 2e^-$	⇌	$H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^-$	⇌	$Pb(s)$	- 0.13
$Sn^{2+}(aq) + 2e^-$	⇌	$Sn(s)$	- 0.14
$V^{3+}(aq) + e^-$	⇌	$V^{2+}(aq)$	- 0.26
$Ni^{2+}(aq) + 2e^-$	⇌	$Ni(s)$	- 0.25
$Fe^{2+}(aq) + 2e^-$	⇌	$Fe(s)$	- 0.44
$Zn^{2+}(aq) + 2e^-$	⇌	$Zn(s)$	- 0.76
$Al^{3+}(aq) + 3e^-$	⇌	$Al(s)$	- 1.66
$Mg^{2+}(aq) + 2e^-$	⇌	$Mg(s)$	- 2.36
$Na^+(aq) + e^-$	⇌	$Na(s)$	- 2.71
$Ca^{2+}(aq) + 2e^-$	⇌	$Ca(s)$	- 2.87
$K^+(aq) + e^-$	⇌	$K(s)$	- 2.93

best reducing agents

Increasing reducing power

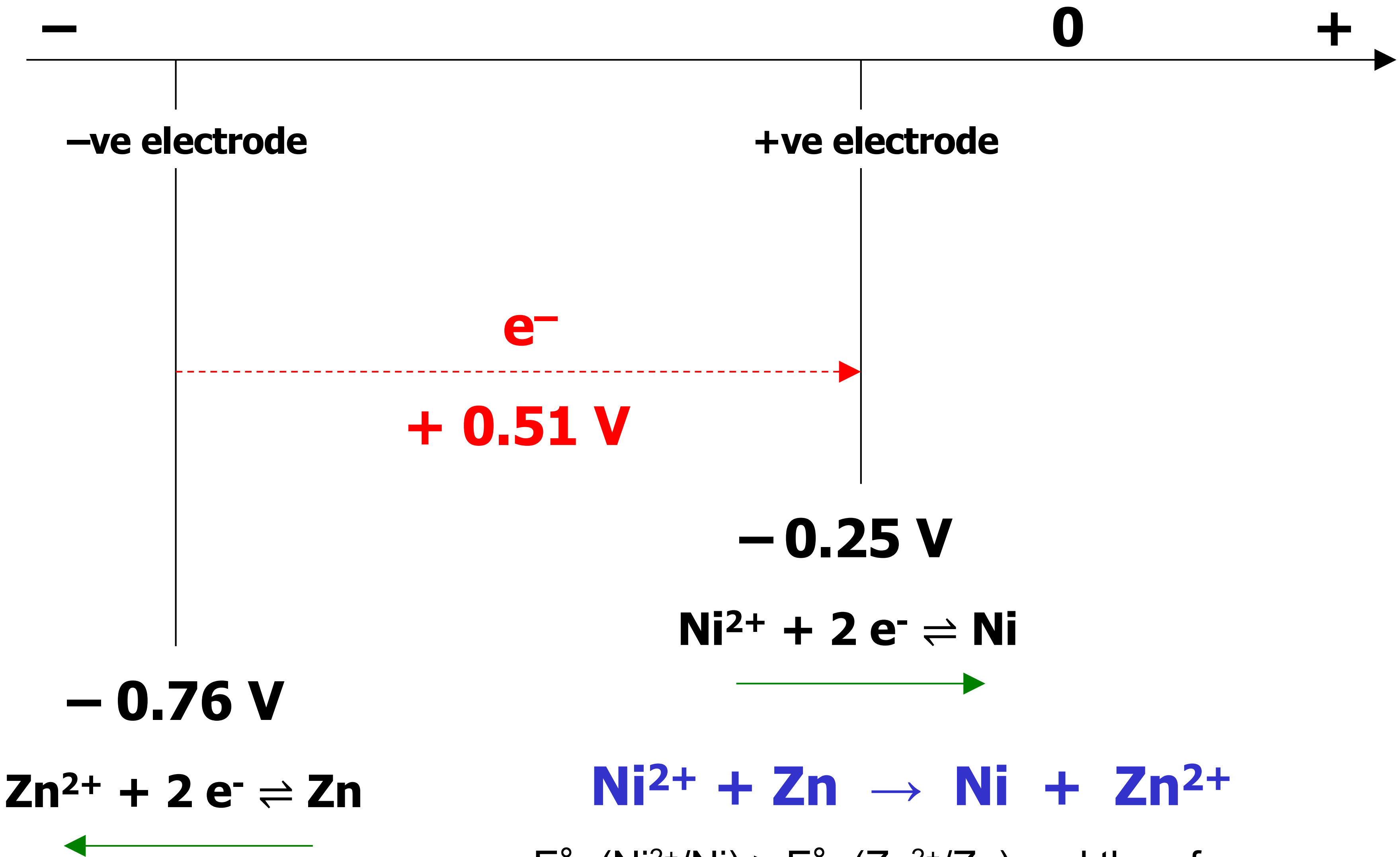
The more +ve electrode
gains electrons

(+ charge attracts electrons)



$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

TASK 9 – Q1



$$Ni^{2+} + Zn \rightarrow Ni + Zn^{2+}$$

$E^\circ\ (Ni^{2+}/Ni) > E^\circ\ (Zn^{2+}/Zn)$ and therefore Ni^{2+} gains electrons from Zn

TASK 9 – Q2

0

+

–ve electrode

+ve electrode

e^-

+ 0.46 V

+ 0.80 V

$Ag^+ + e^- \rightleftharpoons Ag$

+ 0.34 V

$Cu^{2+} + 2e^- \rightleftharpoons Cu$

$$2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$$

E° (Ag^+/Ag) > E° (Cu^{2+}/Cu) and therefore Ag^+ gains electrons from Cu

TASK 9 – Q3

0 +

+ 1.36 V

$Cl_2 + 2\,e^- \rightleftharpoons 2\,Cl^-$

+ 0.77 V

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

NO

+ 1.33 V

$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O$

NO

+ 1.51 V

$MnO_4^- + 8\,H^+ + 5\,e^- \rightleftharpoons Mn^{2+} + 4\,H_2O$

YES

MnO_4^- will oxidise Cl^- to form Cl_2 as $E°\ (MnO_4^-/Mn^{2+}) > E°\ (Cl_2/Cl^-)$ and therefore MnO_4^- gains electrons from Cl^-

TASK 9 – Q4a

$Pt(s)|H_2(g)|H^+(aq)||Br_2(aq),Br^-(aq)|Pt(s)$

0 **+**

–ve electrode
)anode

+ve electrode

e^-

+ 1.09 V

+ 1.09 V

$Br_2 + 2\,e^- \rightleftharpoons 2\,Br^-$

0.00 V

$2\,H^+ + 2\,e^- \rightleftharpoons H_2$

$H_2 + Br_2 \rightarrow 2\,H^+ + 2\,Br^-$

E° $(Br_2/Br^-) > E^\circ$ (H^+/H_2) and therefore Br_2 gains electrons from H_2

TASK 9 – Q4b

$Cu(s)|Cu^{2+}(aq)||Fe^{3+}(aq),Fe^{2+}(aq)|Pt(s)$

0 +

–ve electrode

+ve electrode

e^-

+ 0.43 V

+ 0.77 V

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

+ 0.34 V

$Cu^{2+} + 2e^- \rightleftharpoons Cu$

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

E° (Fe^{3+}/Fe^{2+}) > E° (Cu^{2+}/Cu) and therefore Fe^{3+} gains electrons from Cu

TASK 9 – Q6a

$Fe(s) | Fe^{2+}(aq) || H^{+}(aq) | H_2(g) | Pt(s)$

–

0

–ve electrode

+ve electrode

e^-

+ 0.44 V

0.00 V

$2\,H^+ + 2\,e^- \rightleftharpoons H_2$

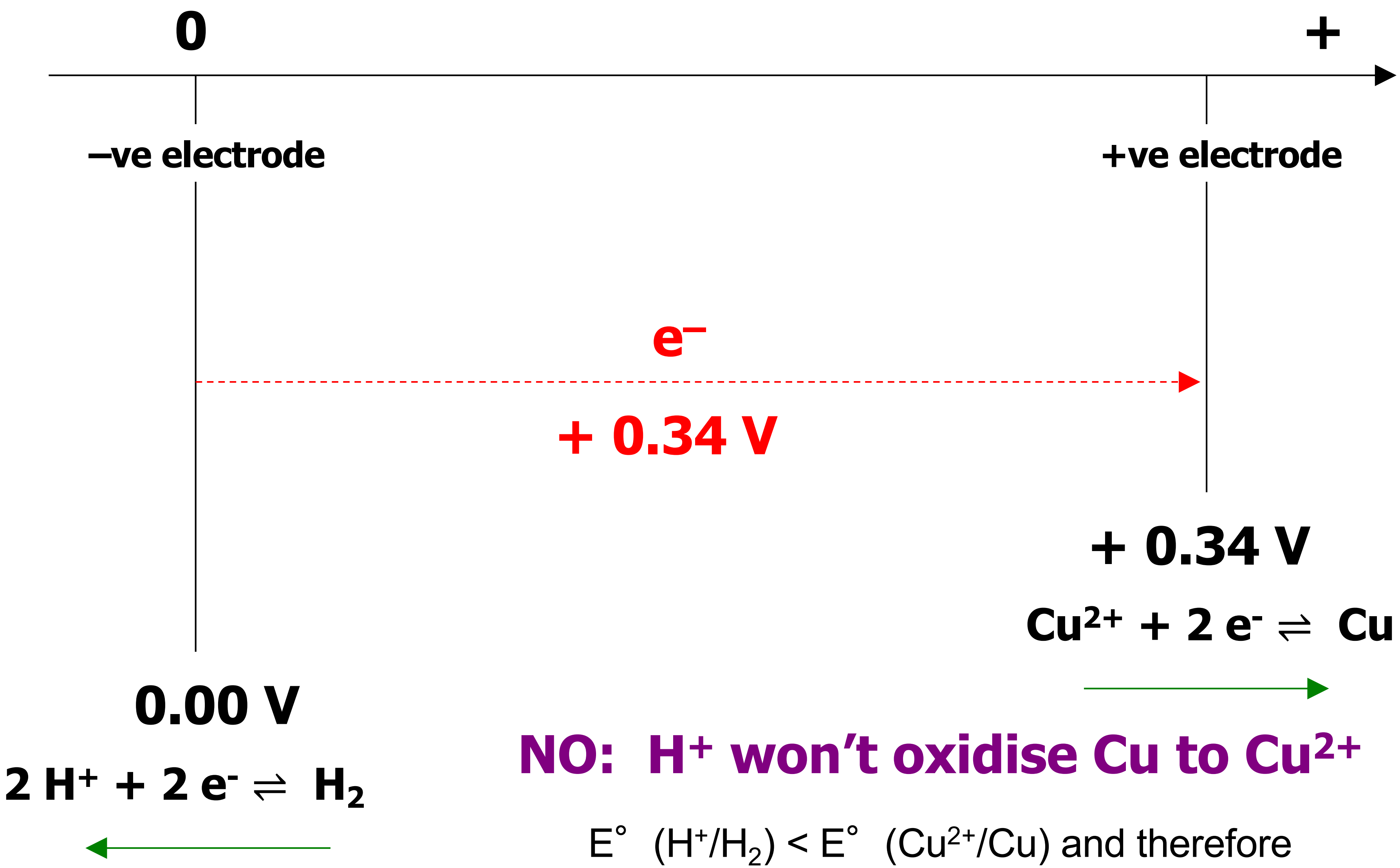
– 0.44 V

$Fe^{2+} + 2\,e^- \rightleftharpoons Fe$

YES: H^+ oxidises Fe to Fe^{2+}

$E^\circ\ (H^+/H_2) > E^\circ\ (Fe^{2+}/Fe)$ and therefore
H^+ gains electrons from Fe

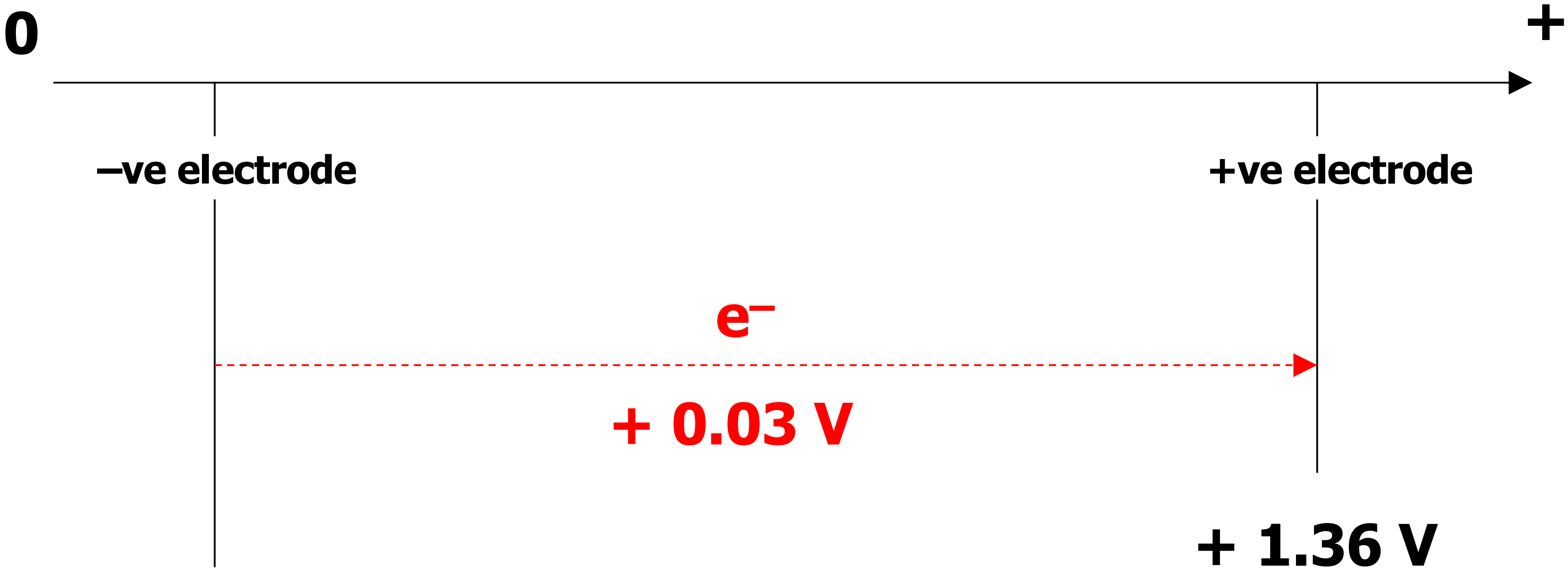
TASK 9 – Q6b



NO: H^+ won't oxidise Cu to Cu^{2+}

$E°$ $(H^+/H_2) < E°$ (Cu^{2+}/Cu) and therefore
H^+ cannot gain electrons from Cu

TASK 9 – Q6c



+ 1.36 V

$Cl_2 + 2\,e^- \rightleftharpoons 2\,Cl^-$

+ 1.33 V

$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O$

NO: $H^+/Cr_2O_7^{2-}$ won't oxidise Cl^- to Cl_2

$E^\circ\ (Cr_2O_7^{2-}/Cr^{3+}) < E^\circ\ (Cl_2/Cl^-)$ and therefore $Cr_2O_7^{2-}$ cannot gain electrons from Cl^-

TASK 9 – Q6d

$Pt(s)|Cl^-(aq)|Cl_2(g)||MnO_4^-(aq),H^+(aq),Mn^{2+}(aq)|Pt(s)$

0 **+**

–ve electrode **+ve electrode**

e^-

+ 0.03 V

+ 1.51 V

$MnO_4^- + 8\,H^+ + 5\,e^- \rightleftharpoons Mn^{2+} + 4\,H_2O$

+ 1.36 V

$Cl_2 + 2\,e^- \rightleftharpoons 2\,Cl^-$

YES: H^+/MnO_4^- oxidises Cl^- to Cl_2

E° (MnO_4^-/Mn^{2+}) > E° (Cl_2/Cl^-) and therefore MnO_4^- gains electrons from Cl^-

TASK 9 – Q6e

$Mg(s)\,|\,Mg^{2+}(aq)\,||\,V^{3+}(aq),V^{2+}(aq)\,|\,Pt(s)$

– 0

–ve electrode

+ve electrode

e^-

+ 2.10 V

– 0.26 V

$V^{3+} + e^- \rightleftharpoons V^{2+}$

– 2.36 V

$Mg^{2+} + 2\,e^- \rightleftharpoons Mg$

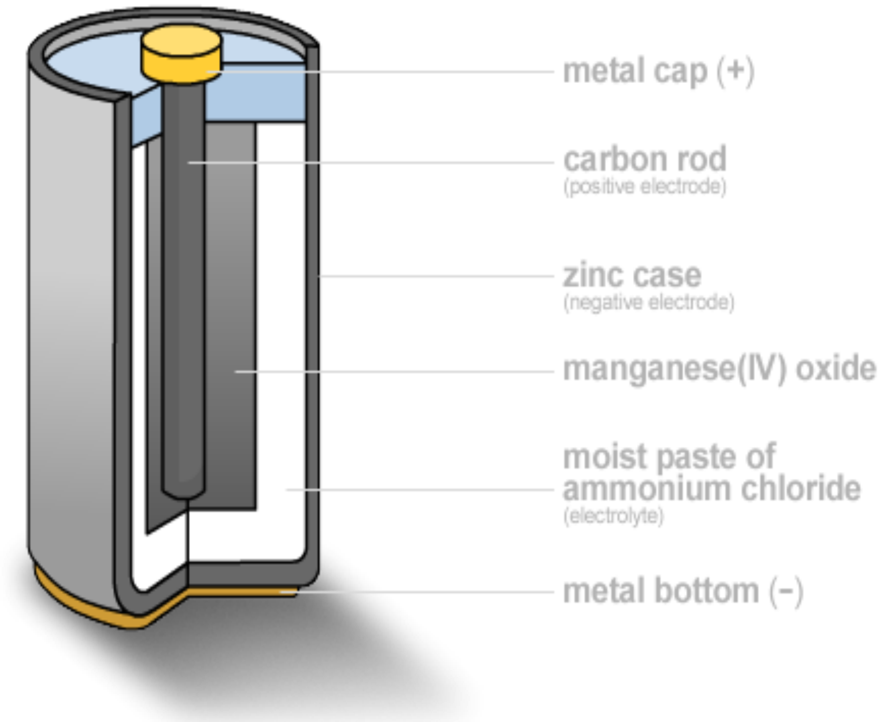
YES: Mg reduces V^{3+} to V^{2+}

$E^\circ\ (V^{3+}/V^{2+}) > E^\circ\ (Mg^{2+}/Mg)$ and therefore V^{3+} gains electrons from Mg

Commercial Cells Non rechargeable

Non-rechargeable cells – Zinc-carbon

- **Standard cell**
- **Short life**



$$-0.80\ \text{V} \quad Zn(NH_3)_2^{2+} + 2\,e^- \rightleftharpoons Zn + 2\,NH_3$$

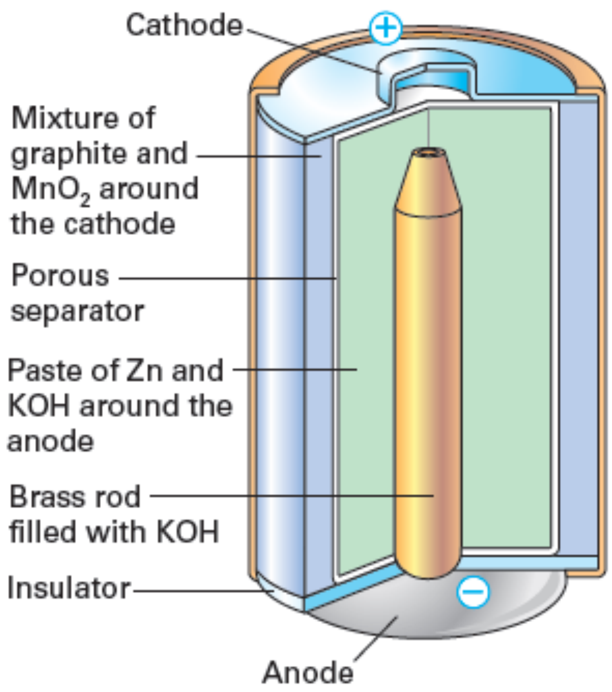
$$+0.70\ \text{V} \quad 2\,MnO_2 + 2\,H^+ + 2\,e^- \rightleftharpoons Mn_2O_3 + H_2O$$

$$\mathbf{2\,MnO_2 + 2\,H^+ + Zn + 2\,NH_3 \rightarrow Mn_2O_3 + H_2O + Zn(NH_3)_2^{2+}}$$

Emf = +1.50 V

Non-rechargeable cells – alkaline

- Longer life



The construction of a typical alkaline dry cell.

–0.76 V $Zn^{2+} + 2e^- \rightleftharpoons Zn$

+0.84 V $MnO_2 + H_2O + e^- \rightleftharpoons MnO(OH) + OH^-$

$2MnO_2 + 2H_2O + Zn \rightarrow 2MnO(OH) + 2OH^- + Zn^{2+}$

Emf = +1.60 V

Commercial Cells **Rechargeable**

Rechargeable cells – Li ion

- Rechargeable
- Most common rechargeable cell

+0.60 V $Li^+ + CoO_2 + e^- \rightleftharpoons LiCoO_2$

–3.00 V $Li^+ + e^- \rightleftharpoons Li$

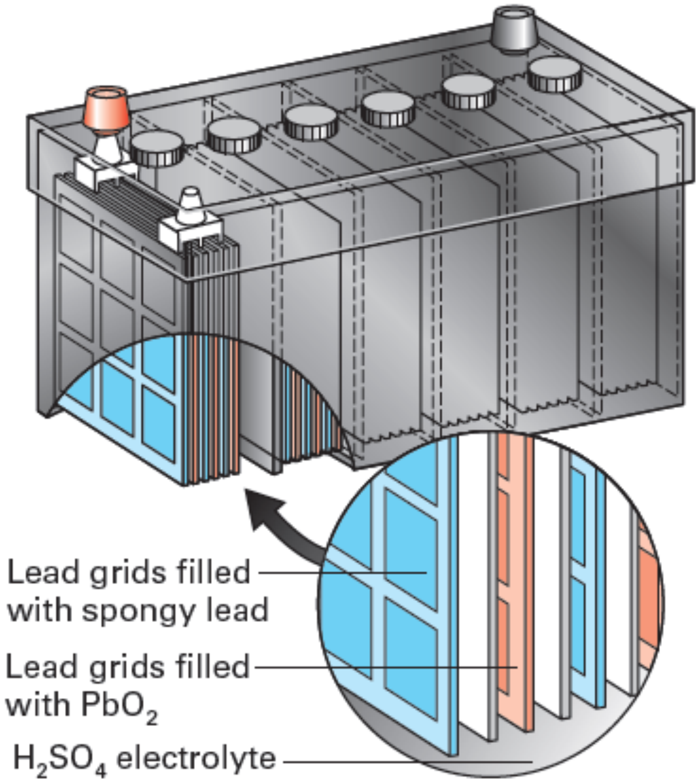
In use: $CoO_2 + Li \rightarrow LiCoO_2$

Charging: $LiCoO_2 \rightarrow CoO_2 + Li$

Emf = +3.60 V

Rechargeable cells – lead-acid

- Used in sealed car batteries (6 cells giving about 12 V overall)



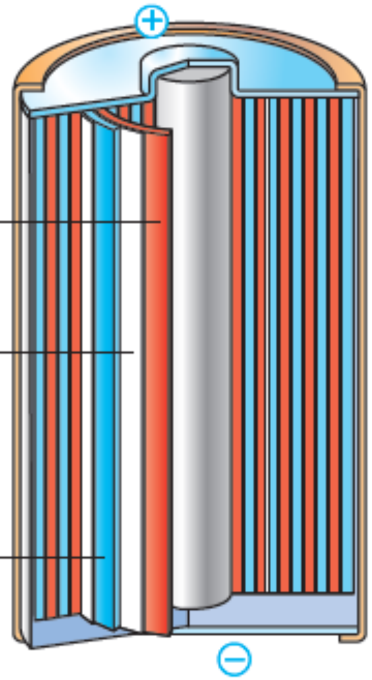
$$+1.68\text{ V} \quad PbO_2 + 3H^+ + HSO_4^- + 2e^- \rightleftharpoons PbSO_4 + 2H_2O$$

$$-0.36\text{ V} \quad PbSO_4 + H^+ + 2e^- \rightleftharpoons Pb + HSO_4^-$$

In use: $PbO_2 + Pb + 2H^+ + 2HSO_4^- \rightarrow 2PbSO_4 + 2H_2O$

Charging: $2PbSO_4 + 2H_2O \rightarrow PbO_2 + Pb + 2H^+ + 2HSO_4^-$ **Emf = +2.04 V**

Rechargeable cells – nickel-cadmium



$+0.52$ V $\quad NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^-$

-0.88 V $\quad Cd(OH)_2 + 2e^- \rightleftharpoons Cd + 2OH^-$

In use: $2NiO(OH) + 2H_2O + Cd \rightarrow 2Ni(OH)_2 + Cd(OH)_2$

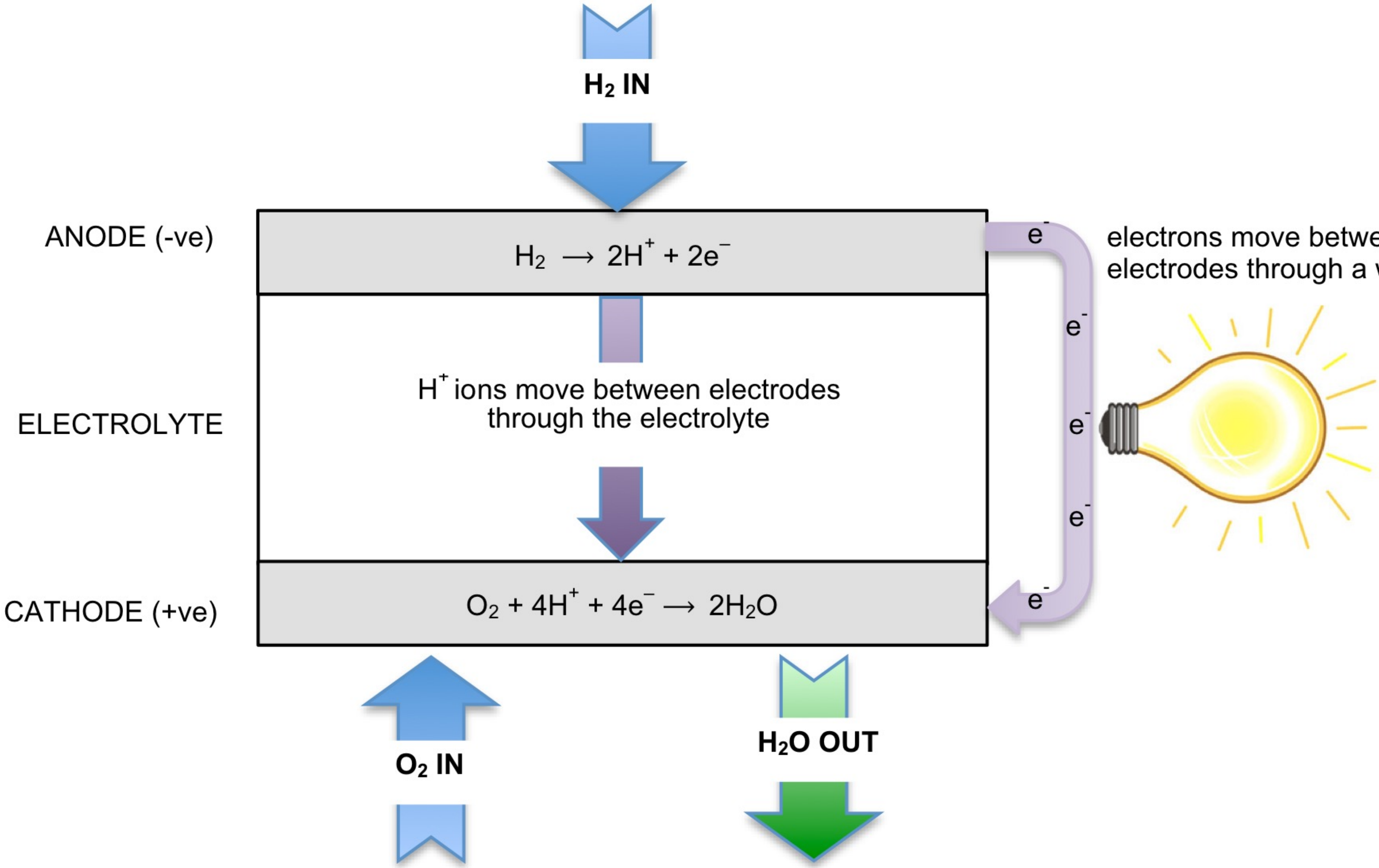
Charging: $2Ni(OH)_2 + Cd(OH)_2 \rightarrow 2NiO(OH) + 2H_2O + Cd$ **Emf = +1.40 V**

Commercial Cells Fuel Cells


Powered by Hydrogen

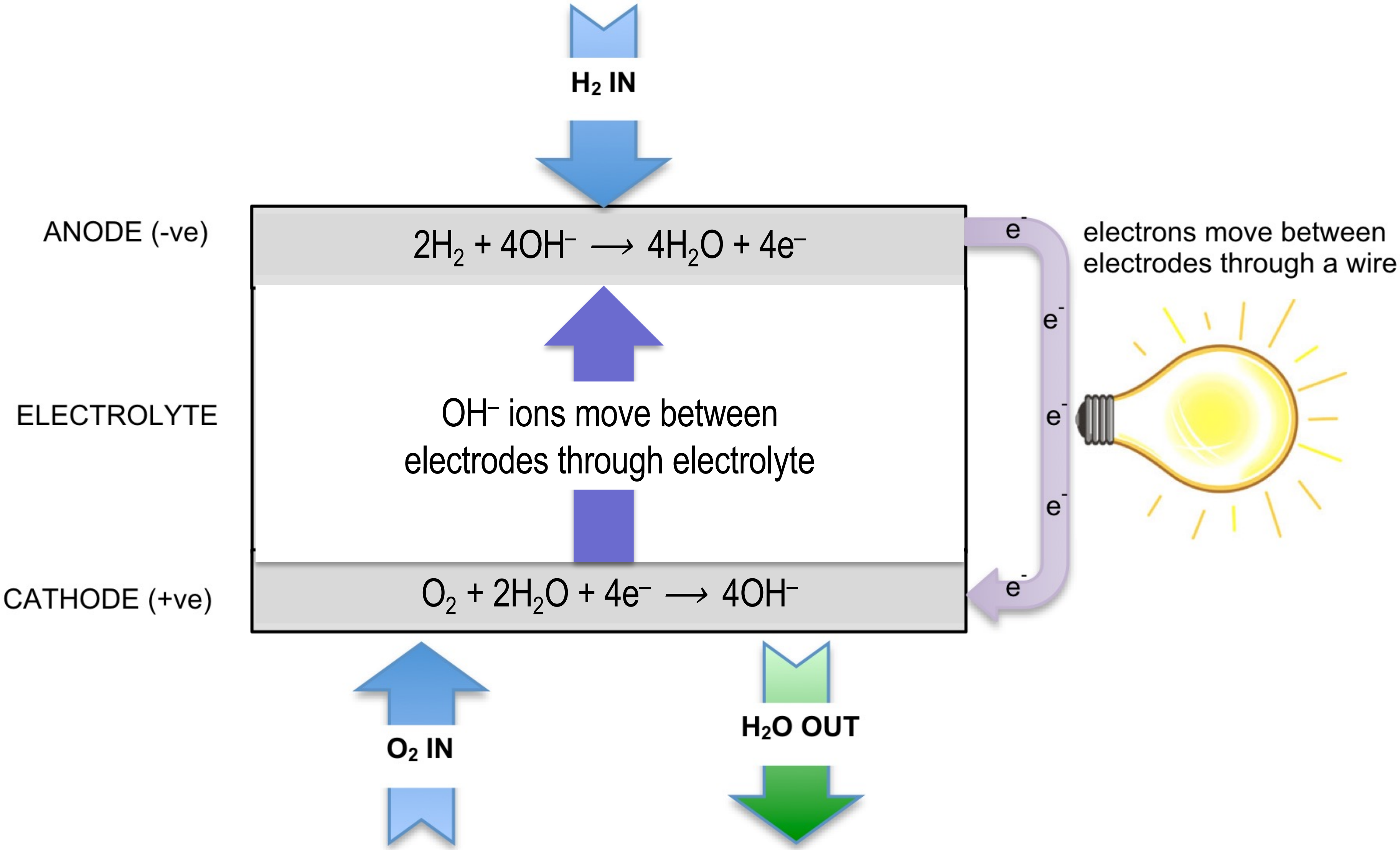
Hydrogen-Oxygen FUEL CELLS

(acidic conditions)

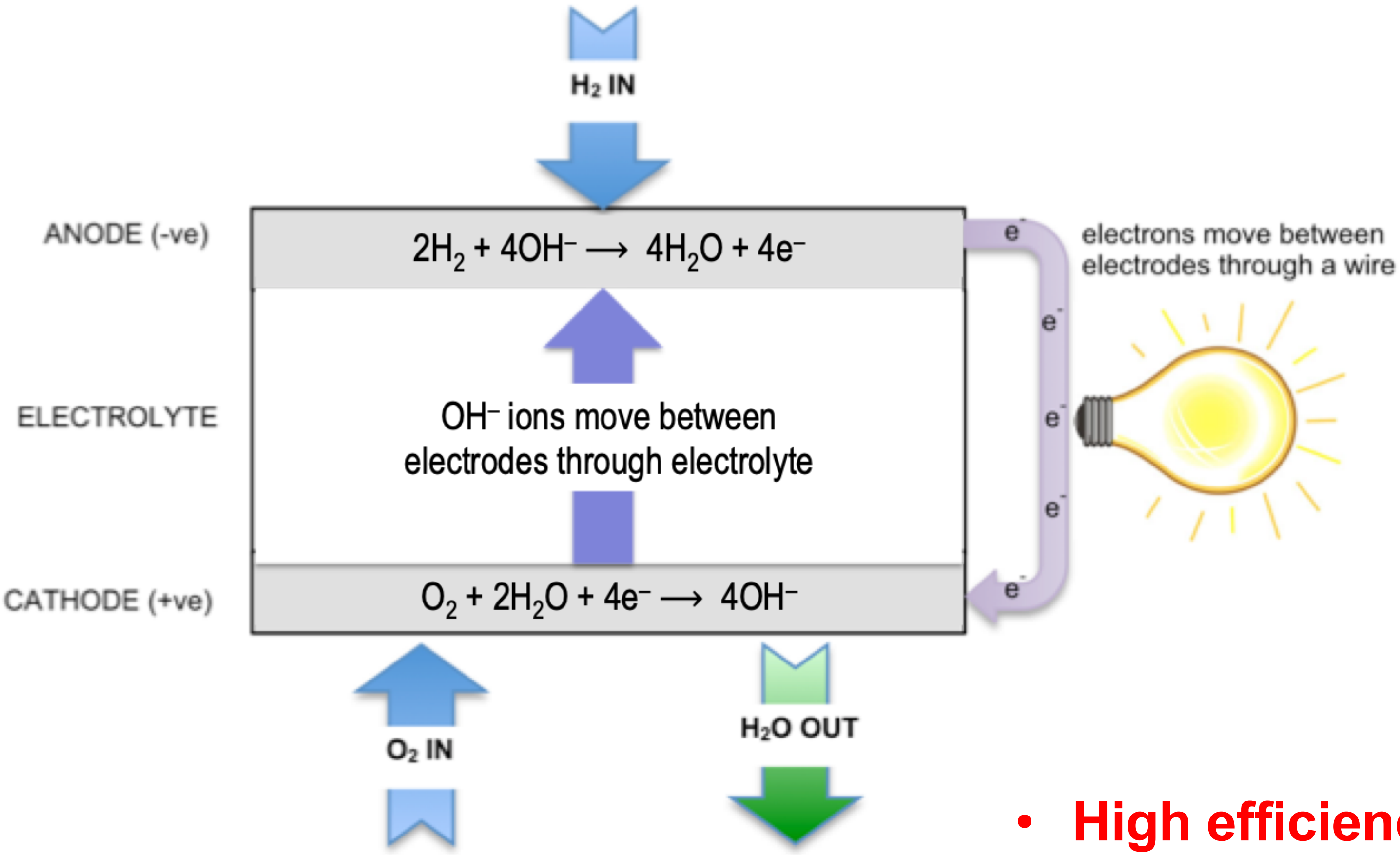


Hydrogen-Oxygen FUEL CELLS

(alkaline conditions)



Hydrogen-Oxygen FUEL CELLS



+0.40 V $O_2 + 2\,H_2O + 4\,e^- \rightleftharpoons 4\,OH^-$

-0.83 V $2\,H_2O + 2\,e^- \rightleftharpoons H_2 + 2\,OH^-$

- **High efficiency (more efficient than burning hydrogen)**
- **How is H_2 made?**
- **Input of H_2/O_2 to replenish so no need to recharge**

Determine: a) cell emf b) overall reaction

	hydrogen fuel cell (alkaline)	hydrogen fuel cell (acidic)
Negative electrode (anode)	$H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$ $E^\circ = -0.83$ V	$H_2 \longrightarrow 2H^+ + 2e^-$ $E^\circ = +0.00$ V
Positive electrode (cathode)	$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ $E^\circ = +0.40$ V	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ $E^\circ = +1.23$ V
Overall equation	$2H_2 + O_2 \longrightarrow 2H_2O$	$2H_2 + O_2 \longrightarrow 2H_2O$
Cell emf	+1.23 V	+1.23 V

Benefits & risks of using cells

	Benefits	Risks
Using cells	• portable source of electrical energy	• waste issues
Using non-rechargeable cells	• cheap	• waste issues
Using re-chargeable cells	• less waste • cheaper in the long run • lower environmental impact	• some waste issues (at end of useful life)
Using hydrogen fuel cells	• only waste product is water • do not need re-charging • very efficient	• need constant supply of fuels • hydrogen is flammable & explosive • hydrogen usually made using fossil fuels • high cost of fuel cells