Chapter 9: Redox Reactions

Date _____ No. _____

Oxidation	Reduction
1) loss of e^-	1) gain of e^-
2) gain of O	2) loss of O
3) loss of H	3) gain of H

An oxidising agent induces oxidation in another compound, while the agent is reduced → [electron acceptor]

A reducing agent induces reduction in another compound, but in itself is ~~reduced~~ oxidised [electron donor]

Rules
1) In its elemental state (e.g S_8), the element's oxidation state is zero.
2) A monoatomic ion's oxidation state = the charge on it
3) Overall charge on a polyatomic ion = the total sum of all oxidation numbers
4) Oxygen is always -2, unless in peroxides (CH_2O_2) or superoxides (Na_2O_2). [-1]
5) Hydrogen is always $+1$, unless in metal hydrides [e.g LiH], [-1]
6) F is always -1

(Finding Oxidation States)

E.g 1) CH_2F_2 ← H always $+1$, F always -1, and total o. no. is 0
$[x][+1][-1]$
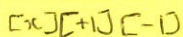
let x → $x + 2 - 2 = 0$
be o.no.
of new atom $x = 0$

E.g 2) $Cr_2O_7^{2-}$ ← O always -2, and total $= -2$ ∴ let Cr's oxidation number $= x$

$$2x + (-2)(7) = -2$$
$$2x - 14 = -2$$
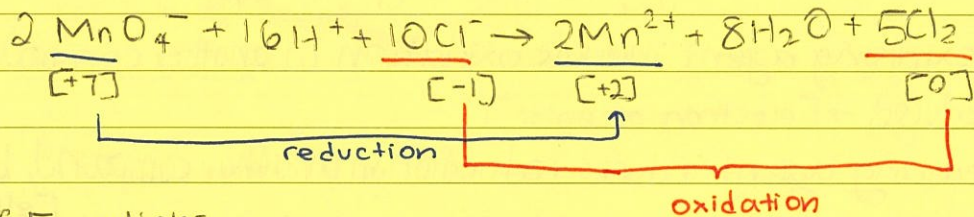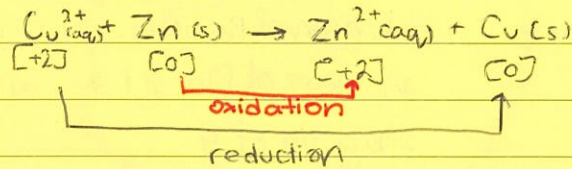$$2x = \cancel{18} \, 12$$
$$x = +6$$

(Naming compounds)

E.g 1 = $CuCl_2$ ← we can see that Cu's oxidation state $= \boxed{+2}$
$[+2][-1]$ So, we write this compound as Copper (II) sulfate

E.g = $CoSO_4$ ← Co's oxidation state is $\boxed{+2}$ so we write it as Cobalt (II) sulfate.

FALCON

A species oxidised in redox ~~loses dec~~ increases in oxidation number, a species reduced decreases in oxidation number.
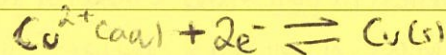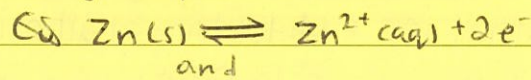
$$Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

[+2]   [0]   [+2]   [0]

oxidation

reduction

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$$

[+7]   [-1]   [+2]   [0]

reduction

oxidation

Redox Half Equations

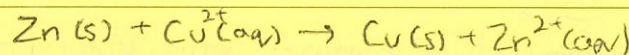Most of the redox equations we encounter can be split into half equations

Take: $Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
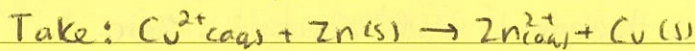
Can't we just split it into

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

and

$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$

↓ if combined,

we cancel out the e^- or any other similar quantities

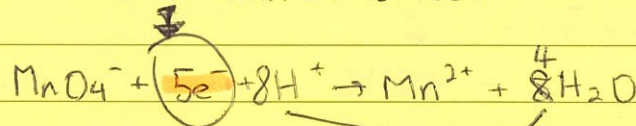$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$

Example 2: A reaction between MnO_4^- and Cr^{3+} to form $Cr_2O_7^{2-}$ and Mn^{2+}

MnO_4^- must go to Mn^{2+}, which differs by 4 Os $Cr_2O_7^{2-}$

Therefore, we add H^+ ions to RHS so the 4 Os form water

$MnO_4^- + H^+ \rightarrow Mn^{2+} + H_2O$

[+7]   [+2]
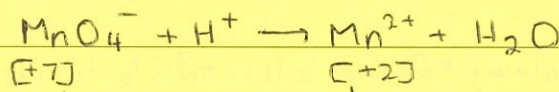
Note that this is a reduction, so we must add the difference in oxi numbers to LHS

$MnO_4^- + \boxed{5e^-} + 8H^+ \rightarrow Mn^{2+} + 8H_2O$

we now balance the H⁺s and H₂Os with respect to fixed number of oxygen

Date   No.

Cr^{3+} to $Cr_2O_7^{2-}$
$[+3]$ → $[+6]$

$Cr_2O_7^{2-}$ to Cr^{3+}
$[+6]$

Cr^{3+} to $Cr_2O_7^{2-}$
$[+3]$ $[+6]$
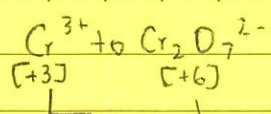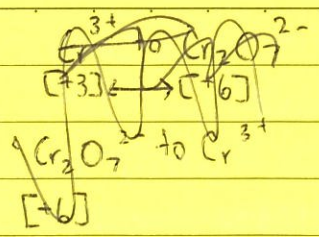
↑oxi number, therefore oxidation. So we add the diff in oxi to LHS but ×2 because 2 Cr atoms in final

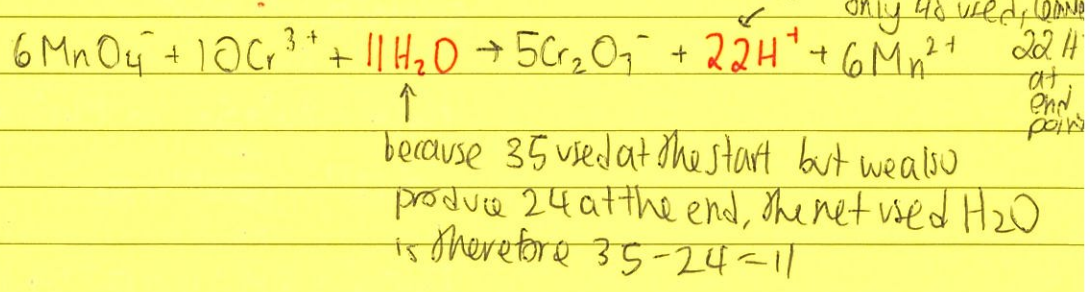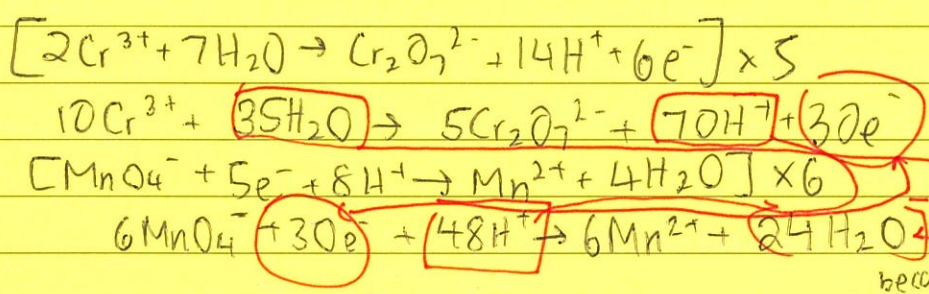$$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + \boxed{6e^-}$$
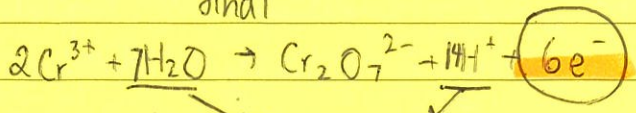
H_2O and H^+ added to give O that is needed for $Cr_2O_7^{2-}$. It is balanced with respect to final no of Oxygen atoms

HOLD-UP!

We have $6e^-$ being produced in the oxidation and only 5 being used in the reduction. We need to this equal. So, we take the lowest common multiple, which is in this case 30.
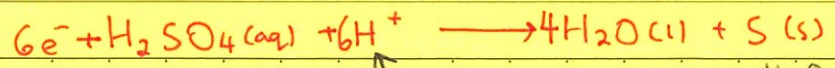
$$[2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-] \times 5$$
$$10Cr^{3+} + 35H_2O \rightarrow 5Cr_2O_7^{2-} + 70H^+ + 30e^-$$
$$[MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O] \times 6$$
$$6MnO_4^- + 30e^- + 48H^+ \rightarrow 6Mn^{2+} + 24H_2O$$

because 70 prod at start, only 48 used, leaves 22 H at end pairs

$$6MnO_4^- + 10Cr^{3+} + 11H_2O \rightarrow 5Cr_2O_7^- + 22H^+ + 6Mn^{2+}$$

because 35 used at the start but we also produce 24 at the end, the net used H_2O is therefore $35 - 24 = 11$

Doing the equations

1) Give a full equation for H_2SO_4 to S $[+6]$ $[0]$

1) Identify change in oxi state. It is +6 to 0, hence a reduction occurs

2) We need a source for the electrons, so let's take a strong reducing agent, i.e low FIE.

because $6e^-$ needed → $6[Na(s) \rightleftharpoons Na^+(aq) + e^-]$
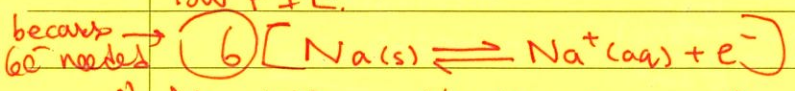
3) Now, let's consider the change from H_2SO_4 to S. The H_2O_4 needs to go out, but as water.

$$6e^- + H_2SO_4(aq) + 6H^+ \rightarrow 4H_2O(l) + S(s)$$

↑because more H^+ needed for H:O = 2:1

4) Combine using sorcery

$$6Na(s) + H_2SO_4(aq) + 6H^+(aq) \rightarrow 4H_2O(l) + 6Na^+(aq) + S(s)$$

FALCON
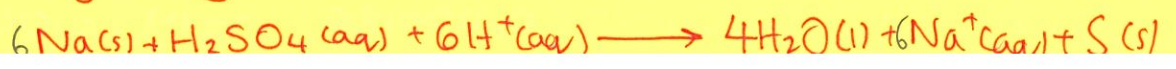
Feasability of certain reactions

Why doesn't this reaction happen? $Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$
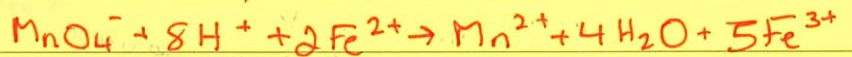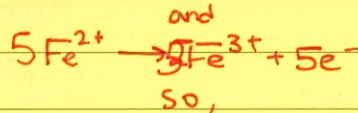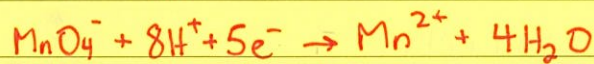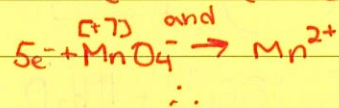would have to be oxidised

$Zn > Cu$ in terms of its ability to lose its electron, so it is more energetically favourable for it to lose the e^-, not Cu. Metals higher in terms of their ability to oxidise can therefore displace less capable metals in their ions.

The order (in descending) of decreasing reducting agents is the reactivity series
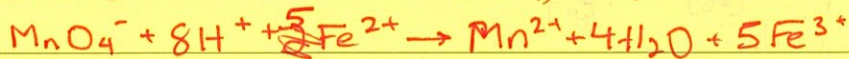
Redox titrations

○ We can use redox titrations to find the concentration of certain chemicals and

E.g 1) A solution contains both Fe^{2+} and Fe^{3+} ions. A $50cm^3$ sample of the solution is titrated with $35.0ml$ of 0.00280 mol/dm³ $KMnO_4$, which oxidises Fe^{2+} to Fe^{3+}. The permanganate ion is reduced to Mn^{2+}. Another $50cm^3$ sample is treated with zinc that reduces all Fe^{3+} to Fe^{2+}. The resulting solution is then titrated with 0.00280 mol dm⁻³ $KMnO_4$, but $48ml$ is needed. Find $[Fe^{2+}]$ and $[Fe^{3+}]$

1) Let's consider the first reaction. $Fe^{2+} \rightarrow Fe^{3+} + e^-$
   and
$5e^- + MnO_4^- \xrightarrow{(+7)} Mn^{2+}$ $\quad (0)$

∴

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

and

$$5Fe^{2+} \rightarrow 2Fe^{3+} + 5e^-$$

so,

$$MnO_4^- + 8H^+ + 2Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

2) Now we can do a ICE (ICE BABY) table.

$$MnO_4^- + 8H^+ + \tfrac{5}{2}Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

I $[0.00280 \times \frac{35}{1000}]$ $\downarrow$

$0.000098\,mol$ ∴ 0.000490

$Fe^{2+}\,mol = 0.000196mol$ $\quad$ $\frac{490}{}$

$[Fe^{2+}] = \dfrac{0.000196mol}{0.05dm^3}$ $= 0.00392moldm^{-3}$

$\quad 0.00980$

3) Let's find total moles of Fe^{2+} and Fe^{3+} by using the titration of MnO_4^- and Fe^{2+} again.   ∴ $[Fe^{3+}]$

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$
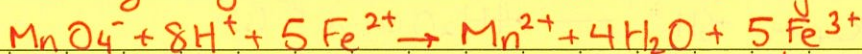
I 0.0001344 $0.000672\,moles$

$0.000672 - 0.000490$

$= 0.000182$ $[Fe^{3+}] = 0.00364moldm^3$

Winkler Method

- Used to measure Biological Oxygen Demand
- This measures dissolved oxygen in ppm required to decompose organic matter over a set period of time
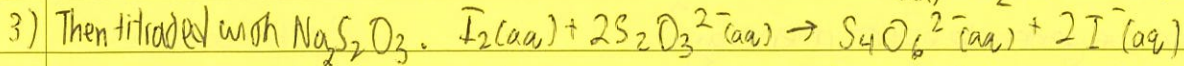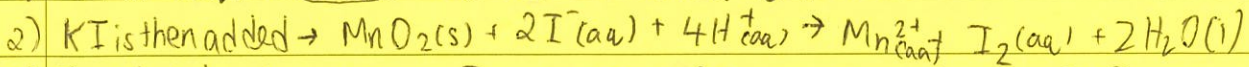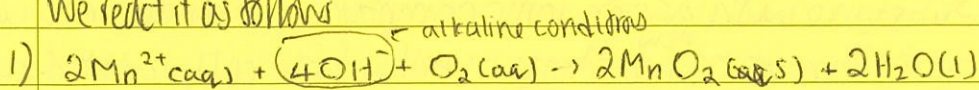- Initially saturated with oxygen, so we know first conc
- Later, we take a sample
- We react it as follows

alkaline conditions

1) $2Mn^{2+}_{(aq)} + (4OH^-) + O_2(aq) \rightarrow 2MnO_2(aq\,s) + 2H_2O(l)$

2) KI is then added $\rightarrow MnO_2(s) + 2I^-(aq) + 4H^+_{(aq)} \rightarrow Mn^{2+}_{(aq)} + I_2(aq) + 2H_2O(l)$

3) Then titrated with $Na_2S_2O_3$. $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

Example: all solutions used were 1mol 1×10^{-2} moldm^{-3}, $6cm^3$ $Na_2S_2O_3$ reacted with all the iodine, using starch as an indicator. When clear, all I reacted. Find $[O_2]$ in ppm. The sample was 100 cm^3

$m\ NaS_2O_3^{2-} \rightarrow 1\times10^{-2} \times \dfrac{6}{1000} = 6\times10^{-5}$ mol

moles of I_2 ∴ $= 3\times10^{-5}$ mol (according to eqn it is $\frac{1}{2}$ of $m\ NaS_2O_3^{2-}$)

moles of I_2 & $Mn^{2+}O_2 \rightarrow 3\times10^{-5}$ mol

∴ moles of $O_2(aq) = 1.5\times10^{-5}$ mol

Note: ppm $= \dfrac{g}{dm^3}$

$[O_2(aq)] = \dfrac{1.5\times10^{-5} mol \times 32}{0.100 dm^3}$ ← finding O_2 mass here

$= 4.8$ ppm

Voltaic (galvanic cells)

- convert energy from spontaneous, exothermic chemical processes to electrical energy
- Basically, it looks like this

← Voltmeter
less reactive metal
solution of ions of less reactive metal
the more reactive metal
solution with the reactive metal's ions
salt bridge
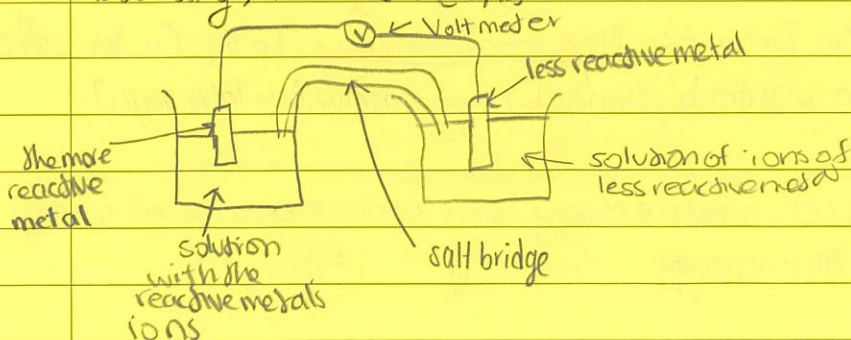
- Anode is on the left, cathode on right
- The anode electrode is the metal that oxidises more readily i.e if $Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn(s)$, equilibrium lies to LHS.
- The cathode is where reduction occurs, where the metal is more likely to be reduced than oxidised so ie, $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu(s)$, equil lies to reduced form, so RHS.

FALCON

<u>Terms</u>
Half cell : a metal in contact with an aqueous solution of its own ions
Voltaic Cell : 2 half cells connected together

Why is a salt bridge needed? →

<u>1) complete circuit</u>
<u>2) allow movement of ions between electrolytes</u>
<u>3) keep electrical neutrality</u>

Date   No.

- to complete the circuit + maintain P.D.
- keeps half cells electrically neutral. The anode develops a positive charge because of the loss of e^-, so the negative ions in a salt bridge flow to it to maintain neutrality
- Cathode develops a negative charge because of a build up of e^-, hence cations in salt bridge move into the cathode half cell
- Usually a porous substance with an ionic compound [so can diss in solution] that has inert ions so there are <u>no</u> ^{new} reactions in either half cell, no interference

How do we generate electrical energy?
- Let us consider the following example.
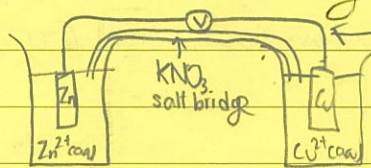
we need the metal wire to facilitate the flow of e^-

<u>Observations</u>
1) paler colour in electrolyte being reduced
2) increase in size of cathode
3) decrease anode size

1) In the Zn half cell, Zinc atoms form ions by <u>being oxidised</u>, releasing electrons, that make the electrode <u>negatively charged</u> with respect to the solution

2) This creates a charge seperation, known as a th electrode potential between the $Zn^{2+}_{(aq)}$ and Zn atoms. This creates the following equil. $Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$
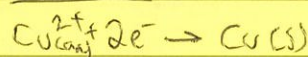
NOTE: We write all half cell equations as reduction because it's standard.

3) Looking at a data booklet, we can see that the ^{standard} electrode potential of $Zn_{(s)}$ [E°] is - 0.76V. This indicates that the oxidation reaction is favoured.

4) The th electrode potential of the copper is +ve on the other hand, so the reduction reaction is favoured. $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$. This is because there are fewer e^- in the $Cu_{(s)}$ so we have a lower charge seperation.

5) Therefore, the electrons from the Zinc anode <u>flow spontaneously</u> to the Cu the cathode because of the <u>difference in electrode potentials</u> being positive. (see later pages)

Syllabus Key Phrase: Voltaic cells convert energy from spontaneous exothermic chemical reactions to electrical energy
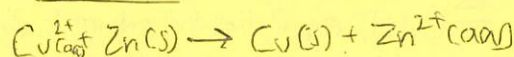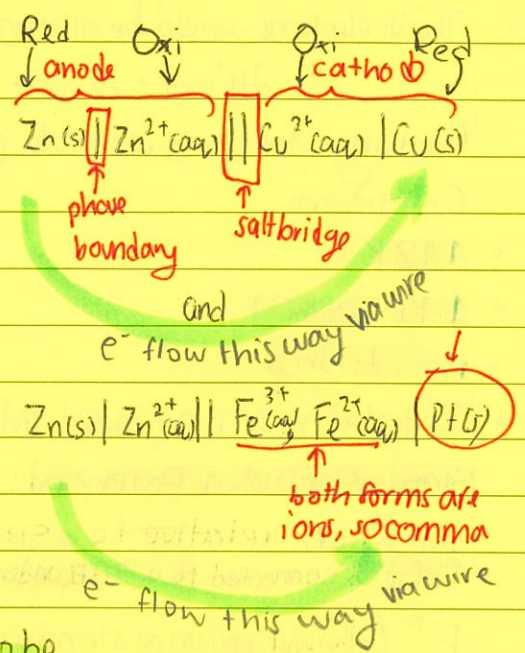
6) We then write the reactions

<u>Cathode</u>
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

<u>Anode</u>
$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

<u>Net</u>

$Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$

Writing notations

- single vertical line seperating different states of matter
- double vertical line for salt bridge
- aqeous ions adjacent to salt bridge
- Anode on left, cathode on right
- No spectator ions
- If same phase, speperated by comma
- Pt electrodes used if the ~~cathode/anode~~ metal used has reduced + oxidised form in aq.
- We label the Pt as the anode or cathode in such a case

Red   Oxi   Oxi   Red
↓anode ↓   ↓cathode↓

$Zn_{(s)} | Zn^{2+}_{(aq)} || Cu^{2+}_{(aq)} | Cu_{(s)}$

↑ phase boundary   ↑ saltbridge

and
e^- flow this way via wire

$Zn_{(s)} | Zn^{2+}_{(aq)} || Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)} | Pt_{(s)}$

↑ both forms are ions, so comma

e^- flow this way via wire

Recall: the metal higher on reactivity series with more negative $E^\ominus$ is the anode as it is more likely to be ~~reduced~~ oxidised and the other has a higher reducing power, hence it has a
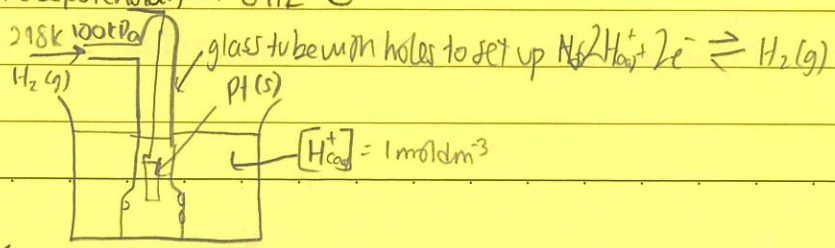
VIP
- electrons move from anode to cathode via the external circuit
- anions migrate from the salt bridge to the ~~cat~~ cathode to the anode via salt bridge
- cations migrate from the anode to the cathode via salt bridge

Electromotive force
- A voltaic cell generates a potential difference dubbed electromotive force
- One to half cell with negative electrode potential, another with a positive electrode potential. This generate EMF, which causes the movement of e^- from anode to cathode
- EMF = E_{cell}

Standard Hydrogen Electrode (SHE)
- consists of an inert electrode, usually $Pt_{(s)}$ in contact with $1 mol dm^{-3}$ H^+ [e.g in 1 M HCl]
- 100 kPA and 298 K
- $E^\ominus$ (standard electrode potential) of SHE = 0

298k 100kPa →
$H_2(g)$

glass tube with holes to set up $H_2 \rightleftharpoons 2H^+_{(aq)} + 2e^- \rightleftharpoons H_2(g)$

Pt (s)

$[H^+_{(aq)}] = 1 mol dm^{-3}$

- always placed to the right of diagram

FALCON

- Pt(s) used because it is inert and catalyses the proton reduction to $H_2(g)$
- The in electrode would be alternatively bathed in $H_2(g)$ and $H_{(aq)}^+$ setting up an equilibrium

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_2(g)$$
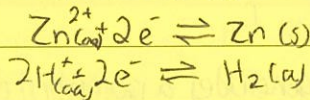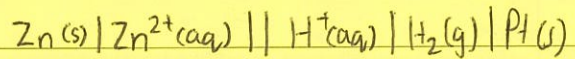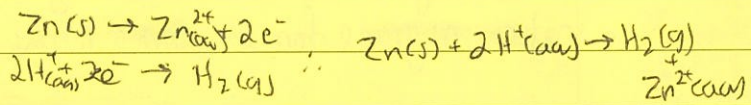
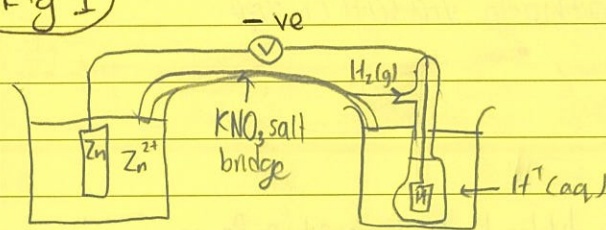Measuring standard electrode potentials

Conditions

- 298 K
- 1 M (moldm^{-3})
- Pure substances
- If tested metal is aq, in red and oxi form, Pt(s) electrode used

Standard Electrode Potential : Voltage of the reduction half equation under standard conditions, relative to a SHE. Better: the potential difference obtained when a half cell is connected to a SHE under standard conditions

$E^\ominus$ (otherwise known as standard reduction potentials)

- If +, the metal reduces to a greater extent than the hydrogen, so its equilibrium would lie to the RHS. e^- flow from H here
- If —, the metal oxidises to a greater extent and less for red than H so equil favours LHS. e^- flows to H here.
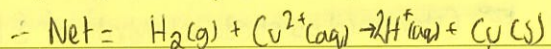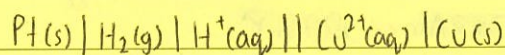
Fig 1

$$Zn(s) \rightarrow Zn^{2+}_{(aq)} + 2e^-$$
$$2H^+_{(aq)} + 2e^- \rightarrow H_2(g)$$

$$Zn(s) + 2H^+_{(aq)} \rightarrow H_2(g) + Zn^{2+}_{(aq)}$$

$$Zn(s)\,|\,Zn^{2+}(aq)\,||\,H^+(aq)\,|\,H_2(g)\,|\,Pt(s)$$
$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn(s)$$
$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_2(g)$$

— ve value demonstrates Zinc's greater ability to lose e^- relative to Hydrogen.
∴ Zn on LHS for the notation as e^- flow to H

Eg 2

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_2(g)$$
$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu^x(s)$$

$$Pt(s)\,|\,H_2(g)\,|\,H^+(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)$$
∴ Net = $H_2(g) + Cu^{2+}(aq) \rightarrow 2H^+_{(aq)} + Cu(s)$
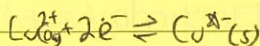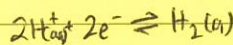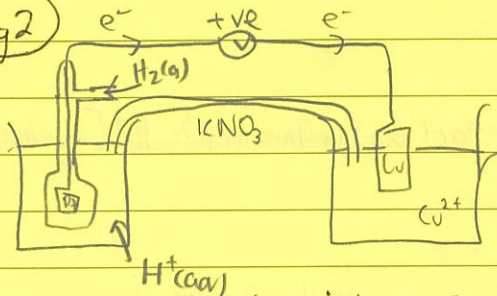
+ve because Cu reduced to a greater extent than H ∴ e^- go from H

Finding E^{θ}_{cell}

$E^{\theta}_{cell} = E^{\theta}_{cathode} - E^{\theta}_{anode}$

Think about it this way. We always know E^{θ} of a metal when it acts as a cathode, so $E^{\theta}_{anode} = -E^{\theta}_{cathode}$ because e^- flow in opposite direction of PD is reversed.

e.g Find E_{cell} of the Zn and Cu half cell

$$Zn_{(s)} | Zn^{2+}_{(aq)} || Cu^{2+}_{(aq)} | Cu_{(s)}$$

$E^{\theta}_{Zn} = -0.76$

E^{θ}

we flip this to find E^{θ} for oxi

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \quad E^{\theta} = -0.76 \, V$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \quad E^{\theta} = +0.34 \, V$$

$$Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^- \quad E^{\theta} = 0.76$$
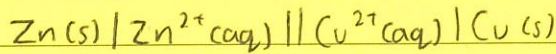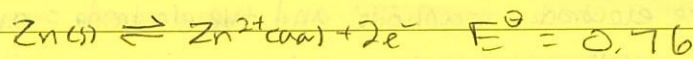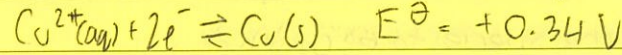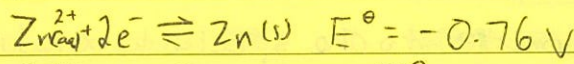
$$\therefore E_{cell} = 0.34 + 0.76$$

$$= 1.10 V$$

eg2. Find E^{θ} of Ag if $E_{cell} = 1.25$ with H

A E^{θ} that is $+$ and $\uparrow$ is a good oxidising agent, a E^{θ} that is $-ve$ and very low (e.g -1000) is a good reducing agent. e^- flow to cell with highest $+ve$ E^{θ}

A $-E^{\theta}$ cell simply means that electrons flow from that electrode / is a better reducing agent than the other electrode (if the other is $+ve$)

(Free Energy and Spontanuity)

○ We can relate ΔG to E^{θ} by $\Delta G = -nFE^{\theta}$, where F is the Faraday constant, which is 96,500 coloumbs per mole, and n is number of moles of e^- transfered [just use coefficient]

○ Therefore, if we have $+ E^{\theta}_{cell}$, the reaction is spontaneous, requires no additional energy other than E_a, so could occur in a test tube

○ If we have a negative E^{θ}_{cell}, ΔG is positive, so the reaction is not spontaneous.

○ Could only proceed with an external energy source to force the reaction to occur in the reverse [so e^- flow to cathode]

Electrolytic Cells

- convert electrical energy to chemical energy, by way of non-spontaneous processes
- Oxidation still occurs at the anode and reduction at the cathode
- However, given that a electrolytic cell looks like this
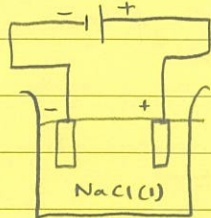

- the -ve electrode can donate e^- to the species to be reduced and the positive electrode attracts electrons from the species to be oxidised
- Hence, the -ve electrode = cathode and +ve electrode = anode
- electricity is passed through an electrolyte, a substance that does not conduct electricity in solid form, but can in aq or l
- It is decomposed in the process
- We can get reactive metals from common ores → e.g $Al(s)$ or $Fe(s)$
- Take Na for instance, v. high on reactivity series, to produce $Na(s)$, we need an even stronger reducing agent

Example

- anions oxidised at anode (+)
- cations are reduced at cathode
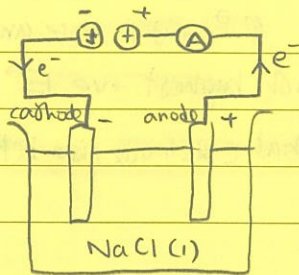
Summary (mark scheme)
- Na^+ move to cathode, Cl^- move to anode
- In the anode, electrons are released from Cl^- (oxidation)
- Accepted from the at cathode by the Na^+ ions [reduction]
- $Na^+_{(l)}$ reduced, $Cl^-_{(l)}$ oxidised
- $2Na^+_{(l)} + 2e^- → 2Na(s)$
- $2Cl^-_{(l)} → Cl_2(g) + 2e^-$

✳ - Current because of the movement of electrons through the external circuit and the movement of ions in electrolyte

① = if oxygen evolved, anode has a lower pH (acidic)

Observations to write
② = if $H_2(g)$ evolved, cathode region acidic alkaline ~ ↑(OH^-)

1) ①↑[OH^-]/↓ ②or ↑[H^+]/↓, then note pH ↑ or ↓ [effervescence]
2) Colour of gases or metals produced
3) Cl_2 identified by bleaching damp blue litmus paper
4) Possible app of molar ratios

Electrolysis of Aqeueous solutions

- we can have H_2O oxidised to O_2 at anode $[\;\;\;\; \rightleftharpoons \; \text{or} \; \frac{1}{2}O_2\text{(g)} + H_2O\text{(l)} + 2e^- \rightleftharpoons 2OH^-\text{(aq)}]$
- and we can have H_2O reduced to H_2 (g) at cathode $[H_2O\text{(l)} + 2e^- \rightleftharpoons H_2\text{(g)} + OH^-\text{(aq)}]$
- This only would happen if $E°$ cell of these oxidations and reductions are higher than the other ions. What I mean is this. Consider the reduction to H_2. It has $E°_{OH}$ of $-0.83V$
- If the other ion is Pb^{2+} [whose reduction is $E° = -0.13$], H_2 produced because $|E°|$ is higher for H_2O reduction. So H_2O is a better oxidising agent than Pb^{2+}
- Consider the anode, where O_2 produced $[\;\;\; \frac{1}{2}O_2\text{(g)} + H_2O\text{(l)} + 2e^- \rightleftharpoons 2OH^-\text{(aq)}]$ with $E° = 0.40$ for reduction, but oxidation is $-0.40V$.
- ~~This is why in electrolysis of $NiCl_2$, nickel not formed as $E° = -0.26$, ~~ for~~ H_2O oxidation, therefore H_2O stronger oxidising reducing agent~~
- ~~This $E°$ is greater than that for the K^+ reduction, so it is more likely for K to be reduced instead of~~
- If we have Sn for example, more likely to oxidise than

$$2H_2O + 2e^- \rightleftharpoons H_2\text{(g)} + 2OH^-\text{(aq)}$$
$$2H_2O\text{(l)} + O_2\text{(g)} + 4e^- \rightleftharpoons 4OH^-\text{(aq)}$$
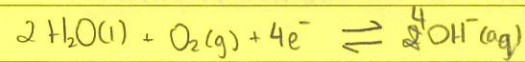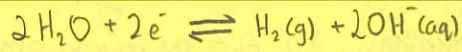
To Sum Up!

- If $E°$ is lower than $E°$ of the $H_2O\text{(l)} + e^- \rightleftharpoons \frac{1}{2}H_2\text{(g)} + OH^-\text{(aq)}$ [i.e more $-ve$], ~~the species will be reduced and no H_2O produced as the species is a stronger~~ H_2O is a stronger oxidising agent [as it has $\uparrow E°$] and will be reduced as opposed to the species
- If $E°$ is greater than $E°$ of $O_2\text{(g)} \; \frac{1}{2}O_2\text{(g)} + H_2O\text{(l)} + 2e^- \rightleftharpoons 2OH^-\text{(aq)}$, the H_2O OH^- is a stronger reducing agent than the species, so it is O_2 is produced, not the species

Example 1
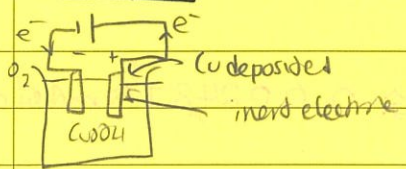
Why is Cu (s) deposited?
- Cu^{2+} is a stronger oxidising agent than H_2O and hence is deposited / displaced to form Cu (s)

Why is O_2 (g) formed?
- SO_4^{2-} weaker reducing agent than H_2O so OH^- decomposes into O_2 (g)
- Note that pH↓ because ↑ pOH.

Ion Concentration

- If one ion is more concentrated than another, it will be selectively discharged
- E.g conc of NaCl would produce Cl_2 gas rather than O_2 at an anode because ↑$[Cl^-]$ than $[OH^-]$, so ~~now it would be discharged~~. In dilute, O_2 evolved because ~~OH stronger reducing agent than Cl^- normally~~ shifts this equil $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ to RHS, ↑e^- that can flow so ↓E^θ and therefore becomes a stronger reducing agent than OH^- so selectively discharged

Electrodes

- if we have $Cu^{2+}(aq)$ in sol and use $Cu(s)$ electrodes, +ve electrode is oxidised to release e^- and form $Cu^{2+}(aq)$
- $Cu(s)$ simultaneously deposited at cathode, so no conc change → stays constant
- Same sit if we have a metal as electrode and it's ion in electrolyte

Factors affecting Quantities of Products

1) Current - ↑current, increased flow of charge and e^-. E.g if doubled, 2x amount of electrons flowing through system, 2x as ~~many~~ much products formed. If time is doubled, 2x as many e^- flow through, so 2x as much product

Recall!

$$C = A \times t = (Coulomb = current \times time \; (s))$$

and $F = 96,500 \; C \, mol^{-1}$ so $\dfrac{C}{F}$ = moles of e^- flowing

Example

(a) How many grams of Cu are formed on cathode of an electrolytic cell holding $CuCl_2(aq)$ with 2.00 A current for 2min

(b) What if $CuCl(aq)$ used.
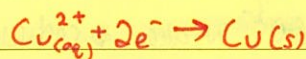
① Find C → $C = A \cdot t$
$$C = 2 \cdot 120$$
$$= 240 \, C$$

① This time it is $Cu^+ + e^- \rightarrow Cu(s)$
So you need less moles of e^- to produce $Cu(s)$, ergo more $Cu(s)$ would be produced

② Find moles → $\dfrac{C}{F} = moles = \dfrac{240C}{96,500 \, C\,mol^{-1}} \approx 0.0024870$ moles of e^-

③ Look at Eqn for Cu
$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu(s)$$
↯ If 0.0024870 moles of $e^- \rightarrow$ moles of $Cu(s) = \frac{1}{2}$ mol of e^-
↯ 0.00124 mol

④ Find mass
$$0.00124 \cdot 63.55 = 0.0790g$$

FALCON

② Ion Charge

- If ↑ + charge, more moles of electrons needed to reduce so make one mole of metal
- ∴ as ↑ charge, mass of prod formed ↓, (assuming relative to a lower cation at same current + time)

Note: Cells in series like the one below, ensure same amount of e⁻ flow to each electrode

$$2OH^-_{(aq)} \rightarrow H_2O_{(l)} + \tfrac{1}{2}O_{2(g)} + 2e^-$$

if conc
$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} 2e^-$$

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$$

$PbCl_{2(aq)}$ $H_2SO_{4(aq)}$
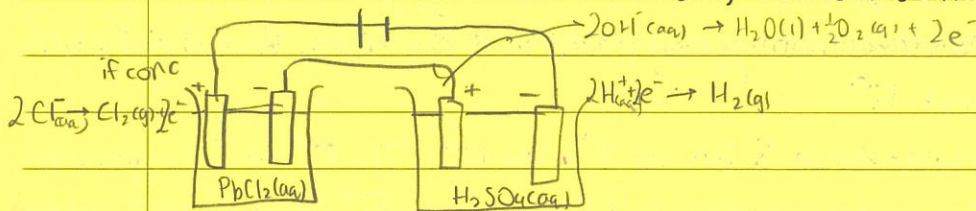
Relative amount of products

$Cl_2 : Pb : O_2 : H_2$ → if you think about, for $4e^-$, 2 moles of $H_2(g)$, $Pb(s)$ and $Cl_2(g)$ produced but only 1 mole of
$\;\;2 \; : \; 2 \; : \; \boxed{1} : 2$ → $O_2(g)$.

$\tfrac{1}{2}O_2(g)$ for $2e^-$, the rest all 1 for $2e^-$

Electroplating

Def: Process of using electrolysis to deposit a layer of metal onto a conductive object

Requires 1) An electrolyte with the ions of the metal to plate with

2) or the thing to be plated is the cathode

3) Anode can be of same metal to continuously replenish supply of ions

Purpose: Decorative : silver plated utensils

Corrosion: Fe with zinc layer is galvanised Iron and is ∴ protected from corrosion

Concentration and ~~Electrolysis~~ Voltaic Cells

- To assess the impact of a concentration or T change, we need to look at the reduction or oxidation reaction. E.g if $[Hg^{2+}]\uparrow$, we look at $Hg_{(s)} \rightleftharpoons Hg^{2+}_{(s)} + e^-$.
- Then observe equil. If for oxi, shift to side with fewer e^-, $\uparrow E^\ominus_{reduction}$, so looking at E_{cell}, $E_{cell} \downarrow$ provided no change in other factor. Recall the Hg example, equil shifts to favour reduction so $\downarrow E^\ominus_{cell}$
- If for reduction, a shift to the reduction reaction increases E_{red} and a shift to favour red $\uparrow E_{red}$, so $\downarrow E_{cell}$ and $\uparrow E_{cell}$ respectively

Question Feedback   Date   No.

- If asked for **best reducing/oxidising agent**, use these phrases [if asked in terms of e^-]
  - best reducing agent = greatest tendency to lose electrons
  - best oxidising agent = greatest tendency to gain electrons
- "State and explain the symbol of $\Delta G^{\ominus}$ → -ve or +ve and then spontaneous or not
- In **sacrificial protection**, the layer that is a **better reducing agent than Fe is optimal.** This is because it will be **oxidised preferentially** compared to the Fe (s). Recall that the best reducing agent has the lowest $E^{\ominus}$
- "Identify a substance that will oxidise X but not Y" → use $E^{\ominus}$. The $E^{\ominus}$ of Z is greater than X, so it will oxidise X while it is reduced but Y has a higher $E^{\ominus}$ than Z, so Z cannot oxidise it. The $E^{\ominus}$ value of the oxidation of X by Z is positive, whereas for oxidation of Y by Z, it is negative because $\frac{Y}{Z}$ is a stronger oxidising agent than $\frac{X}{Z}$
- 5 things for a SHE → **1** atm H_2 (g), 298 K, Pt electrodes, 1 mol dm^{-3} $[H^+$ (aq)]

If electrical conductivity is discussed on a redox question, do standard answer but then say cations move to cathode + anions to anode