



additional BOD notes:  
 ↑ °C ↓ solubility of O<sub>2</sub> ∴ ↑ BOD  
 bacteria respire aerobically  
 O<sub>2</sub> can dissolve from air

C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> = organic matter

the Winkler method (redox titrations)

can be used to measure **biochemical oxygen demand (BOD)**

↗ anaerobic bacteria

↳ which is amt of O<sub>2</sub> required to decompose organic matter over time!

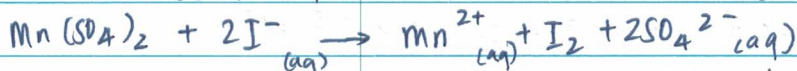
↳ HIGH BOD = low O<sub>2</sub> content. ∴ high pollution

↖ important

STEP 1. manganese hydroxide + oxygen (Mn(OH)<sub>2</sub> is made from MnSO<sub>4</sub> + alkali)



STEP 2. Add H<sub>2</sub>SO<sub>4</sub> to form Mn(SO<sub>4</sub>)<sub>2</sub> and then react this with KI



STEP 3. determine I<sub>2</sub> concentration using sodium tetrathionate (titration)



half equations



1/2 x

x



x/2

x/2



x

! S<sub>2</sub>O<sub>3</sub> : O<sub>2</sub> is 2 : 1

! I<sub>2</sub> : S<sub>2</sub>O<sub>3</sub> 2 : 4

other titrations



③ moles 1.3 × 10<sup>-2</sup> ← ----- 6.6 × 10<sup>-3</sup> ②



① moles 6.6 × 10<sup>-3</sup> 0.013

[be sure to ADD volumes!]

working back!

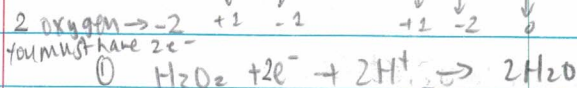
! titration conc old/new x moles

harder half equations

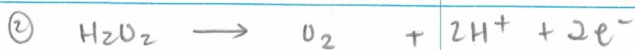


HOW TO FORM 1/2 EQUATION?

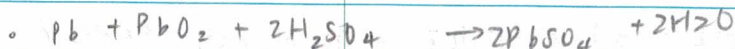
↳ must both have H<sub>2</sub>O<sub>2</sub> on RHS so they add up to 2H<sub>2</sub>O<sub>2</sub>



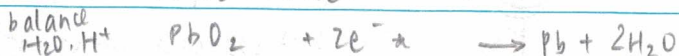
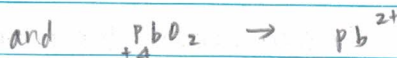
must have H<sup>+</sup> to balance out H<sub>2</sub>s



SO<sub>4</sub><sup>2-</sup> : spectator ∴ ignore



individually:



## 9.2 Electrochemical cells

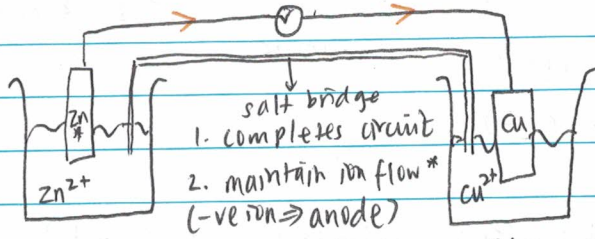
### voltaic cells

chemical energy  $\Rightarrow$  electrical energy (spontaneous)

$$\Delta G = -ve$$

gets oxidized = loss

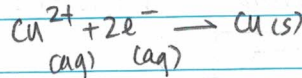
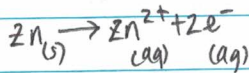
e.g. zinc has  $E^\ominus = -0.76$   $CuE^\ominus = +0.15$



voltage is the difference of 2 metals

zinc transfers electrons to copper  $\rightarrow \rightarrow \rightarrow$

$$E^\ominus = E^\ominus_{RED} - E^\ominus_{OXT}$$



oxidation @ Anode (ANOX)

reduction @ cathode (RED CAT)

- anode is -ve

cathode is +ve

\* maintain ion flow as  $Zn^{2+}$  is charged, needs  $NO_3^-$  to balance charges  
 \* if reaction contains solid metal = must have electrode made out of solid.  
 ↳ if not = platinum! (inert) (conducts)  
 because electrons are "produced"

charge from n-ve to p+ve

not theoretical value ...

- 1 mol dm<sup>-3</sup>?

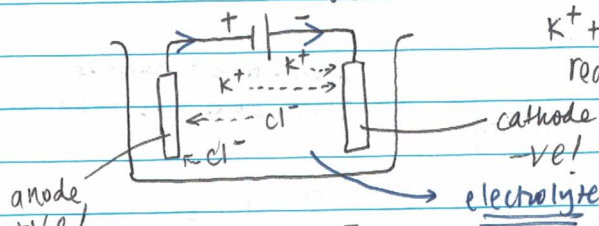
- stp? 1 atm, 293K

- not completion  $\rightleftharpoons$

anode will go wrong

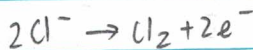
### electrolytic cells (MOLTEN SALT)

electrical energy  $\Rightarrow$  chemical energy (non-spont,  $\Delta G = +ve$ )



reduction @ CATHODE [RED CAT]

anode +ve!



oxidation @ ANODE [ANOX]

electrolyte

\* PANIC positive anode, negative cathode

\* charge from +ve to -ve

### application

- purify substances (reactive metals)
- plating (forms a layer of K on cathode)

factors affecting electrolysis: TIME, CURRENT,  $e^{-}$  (oxidation state)

$$Q = I \times t \rightarrow (\text{seconds})$$

charge  $\hookrightarrow$  current (amps)

importance = produce Na, Cl<sub>2</sub>, NaOH!

$$n(e^{-}) = \frac{Q(\text{charge})}{96500}$$

moles of  $e^{-}$

## 1.1 Standard electrode potential

A voltaic cell has an EMF (electromotive force)  $\therefore$  electrons move  $-ve \Rightarrow$  positive.

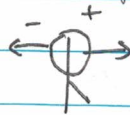
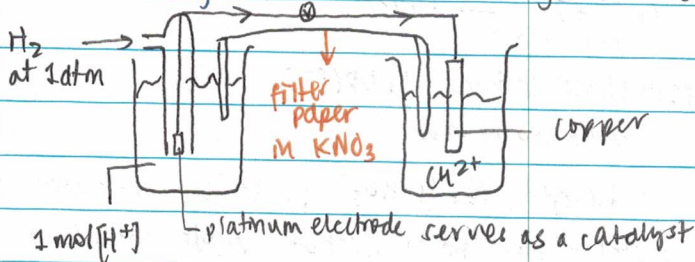
$\hookrightarrow$  this is called the cell potential ( $E^\ominus$ ) } reactivity  
 dependant on } concentration  
 } temperature

WILLING TO LOSE =  $-ve$  value ( $E^\ominus$ )

WILLING TO GAIN =  $+ve$  value ( $E^\ominus$ )

at 298K and  $1\text{mol dm}^{-3}$   
 it is a STANDARD.

Standard hydrogen potential (hydrogen = standard reference electrode)

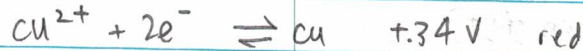
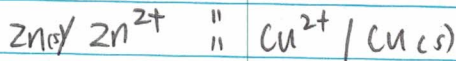


if it is more reactive than hydrogen  $\Rightarrow -ve$  value

less reactive  $\Rightarrow +ve$  value

## calculating cell potential

Zn and Cu. since Zn is more  $-ve \Rightarrow$  oxidized  $\Rightarrow$  LOSS



$$E_{\text{cell}} = E^\ominus_{\text{red}} - E^\ominus_{\text{ox}} \quad (0.34 - (-0.76) = 1.10 \text{ V})$$

$+ve$   $E_{\text{cell}}$  = spontaneous

amps  $\times$  time = coulombs

96500 coulombs = 1 faraday

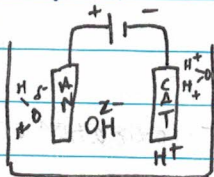
cell potential & spontaneity

$$\Delta G = -nFE^\ominus$$

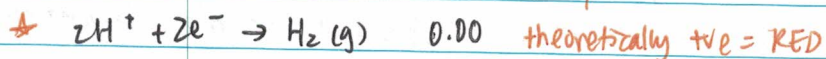
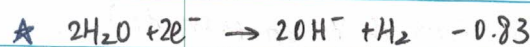
moles of  $e^-$   $\swarrow$   $\searrow$  cell potential  
 faraday

$\Delta G = -ve$   
 = spontaneous

## electrolysis of water

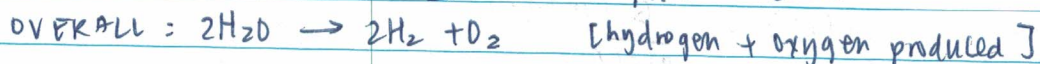
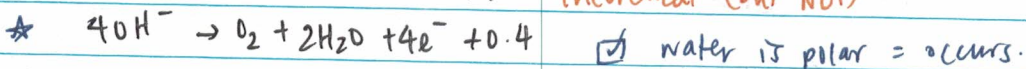
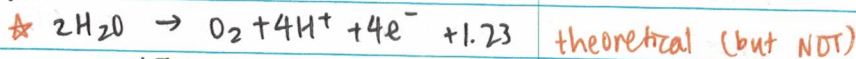


at cathode: reduction (RIG)



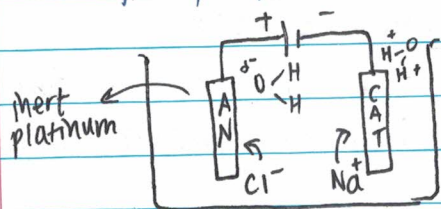
but!  $[\text{H}^+] = 1 \times 10^{-7}$   $\therefore$  v small  
 $\therefore$  doesn't usually happen

at anode:

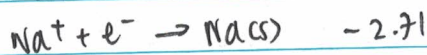
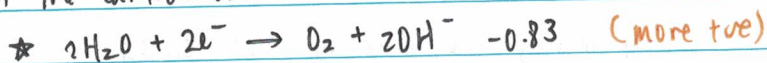


not molten! (molten = will def produce the solid/gas)

### electrolysis of aqueous solutions



at the cathode ...

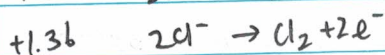
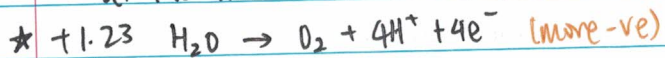


$O_2$  produced in both cases UNLESS  $[Cl^-] \uparrow 25\%$

then... solution will have  $Cl_2(g)$

and  $Na^+$  ions and  $OH^- \therefore NaOH!$

at the anode



$\uparrow [Cl_2/Br_2/I_2] \uparrow \rightarrow O_2$

factors that determine products @ anode + cathode

trans metals  
hydrogen

① position in electrochemical series compared to hydrogen

MORE +ve = REDUCED MORE -ve = OXIDIZED

② concentration (e.g.  $[Cl^-]$  in example above)

③ nature of electrode e.g. copper in  $Cu^{2+} SO_4^{2-}$ , anode itself will be OXIDIZED

$\therefore Cu$  forms in cathode,  $Cu$  lost in anode,  $CONC = \underline{SAME}$  (in solution)

### factors affecting quantity discharged (products)

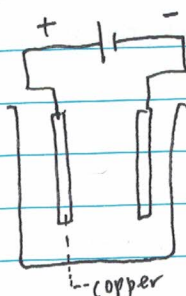
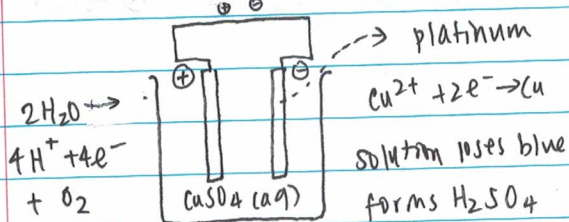
① no. of electrons: current doubles, product doubles ;

② charge (Ox. No): e.g. need  $1e^-$  or  $2e^-$ ? if you have  $Na^+$  and  $Pb^{2+}$

.  $Na^+$  produced 2x rate of Pb

. cells are connected in series and SAME current = SAME moles of  $e^-$

additional example -  $CuSO_4$



at the cathode:  
 $Cu^{2+} + 2e^- \rightarrow Cu$

at the anode  
 $Cu \rightarrow Cu^{2+} + 2e^-$   
solution stays blue!

### electroplating

- electrolytic coating of a metal e.g. copper

THE CATHODE (-ve) is made from the METAL TO-BE PLATED

THE ANODE (+ve) is made from the IMPURE ONE

$\hookrightarrow$  as oxidation happens, producing metal ION ( $Cu \rightarrow Cu^{2+} + 2e^-$ )

$\hookrightarrow$  which then deposits itself into the cathode ( $Cu^{2+} + 2e^- \rightarrow Cu$ )

- prevent from using: more easily/readily oxidized in comparison to another metal!

$\rightarrow$  RHS: spoon!

# be careful w/ agents!

## past paper questions

- "what happens to  $\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}$ "? or oxidation number  $\downarrow +6 \rightarrow +3$
- "describe standard conditions"  $\cdot 1 \text{ mol dm}^{-3}$  of SOLUTION & 298K
- explain why the electrolysis of  $\text{ZnSO}_4$  is not used for the electroplating of zinc
  - more free ions in solution ( $\text{Zn}^{2+}$  and  $\text{H}^+$ ):  $[\text{H}_2]$  will be produced, reduced readily.
- define "standard electrode potential".
  - potential of a reduced half-equation under standard conditions
  - measured compared to a S. Hydrogen Electrode.

displacement reactions  $\cdot$  bromine when displaced = ORANGE & iodine = BROWN

- how is electricity conducted in an electrolytic cell?
  - ① electron movement in metal wires
  - ② ion movement in electrolyte (molten/ionic liquid)

explain the mechanism of reactivity/displacement.

a strong reducing agent has the greatest ability to donate electrons and displace a weaker reducing agent.

oxidation number of N in  $\text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+$  and  $\text{Cl}^-$   $\therefore \text{H}_4 = 4+$ ,  $\text{N} = -3$

if  $\text{Mg} >$  reactive  $\text{Cu}$ , what is strongest ox. agent?  $\text{O}_2$  oxid agent = gets reduced

$\therefore$  gets reduced = GAIN electrons + won't be  $\text{Mg}$ .  $\text{Cu}^{2+}$  (NOT  $\text{Cu}$ ,  $\text{Cu} \rightarrow \text{gain } e^-$ )

3 things that impact electrolysis

- ① magnitude of current
- ② time of electrolysis
- ③ oxidation / charge on ion

define "biochemical oxygen demand"

amt of dissolved oxygen needed by AEROBIC organisms to BREAK DOWN organic material in water over time.

factors affecting aqueous electrolysis ① electrode potential ② electrode ③ concentration  $\rightarrow \text{Cu! RMB}$   $\rightarrow \text{Cl}_2!$

voltage cells

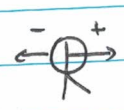
$E^\ominus = E_{\text{cath}} - E_{\text{anode}}$

$E^\ominus = E_{\text{red}} - E_{\text{ox}}$   
(+ve - -ve)

e.g.  $\text{Cu}^{2+} + 0.34 \text{ Mg} - 2.37$

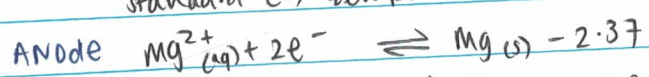
Cu gets reduced / Mg is oxidized

$\therefore 0.34 - (-2.37) = +2.71$  is voltage



experimental voltages vs literature values

- reaction does not go to completion
- standard (0) temperature



when you ADD water to anode...

the conc of  $\text{Mg}^{2+}(\text{aq})$  decreases

$\therefore$  equilibrium moves to left,  $E^\ominus$  becomes more -ve e.g. 2.40

THEREFORE e-cell value =  $0.34 - (-2.40)$

= 2.74 (o.g. no water +2.71)

when you ADD water to cathode

$\downarrow [\text{Cu}^{2+}] \therefore \uparrow [e^-]$  (equilibrium moves to left)



$\therefore 0.30 - (-2.37)$

$\therefore 2.67 = E^\ominus$   $E^\ominus$  has  $\downarrow$

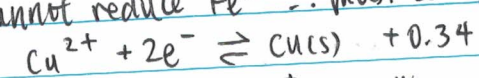
ANODE	CATHODE	EFFECT $E^\ominus$
increase [ion]	-	more -ve
-	increase [ion]	more +ve

ANODE  $\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}(s) - 2.37$   
CATHODE  $\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}(s) + 0.34$

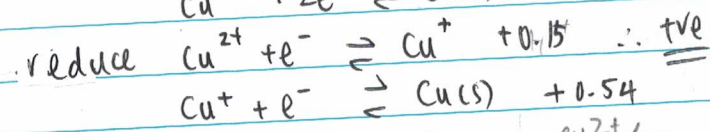
what will reduce  $\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+} + 0.77$  ? OILRIG

but NOT  $\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe} - 0.45$  Ni, Sn, Pb, H

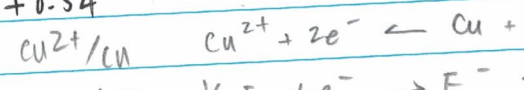
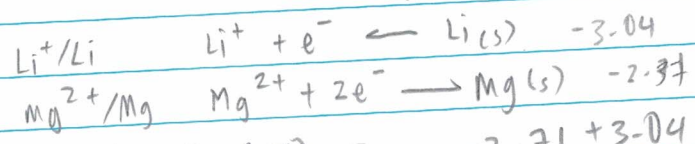
MUST be oxidized itself : must be more -ve than +0.77  
but cannot reduce  $\text{Fe}^{2+}$  : must be less -ve than -0.45



(if Ox anything other oxid.)

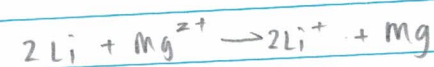


ion cell



$E_{\text{cell}} \text{ tve } - (-\text{ve}) = -2.71 + 3.04 = 0.67$

$E^\ominus = -2.53$  (can power itself since there is additional power)



spontaneity =  $\Delta G = \Delta H - T\Delta S$

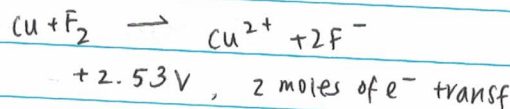
• entropy / disorder

• exo/endothemic = enthalpy change

CELL POTENTIAL & SPONTANEITY

$$\Delta G = -n F E_{cell}$$

moles  $\swarrow$   $\searrow$   $E^{\ominus}$   
 faraday's constant (96500) C/mol<sup>-1</sup>



$$\Delta G \text{ in Joules} = -2 \times 2.53 \times 96500$$

$$= -498290 \text{ J}$$

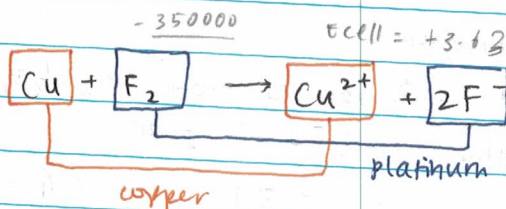
$$= -498.29 \text{ kJ}$$

$\therefore$  if  $E^{\ominus}$  is +ve =  $\Delta G = -ve$   $\therefore$  spontaneous.

if  $\Delta G = -350$ , reaction = 1e<sup>-</sup>

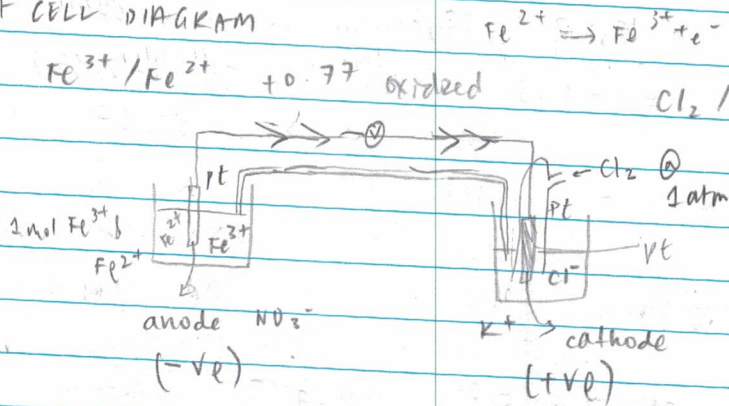
$\Delta G$  is always kJ

$$-350,000 = -F E_{cell}$$



oil ANox  
 Cu being oxidized, RIG, anode.

HALF CELL DIAGRAM



$$E^{\ominus} = 1.36 - 0.77$$

$$= 0.6V$$

$E^{\ominus}$  flow = -ve to +ve

$$\Delta G = \frac{-2 \times 96500 \times 0.6}{1000} = -115.9 \text{ kJ}$$

- $\Delta G$  diff - reaction X completion
- conditions X standard
- not 1 mol dm<sup>-3</sup>

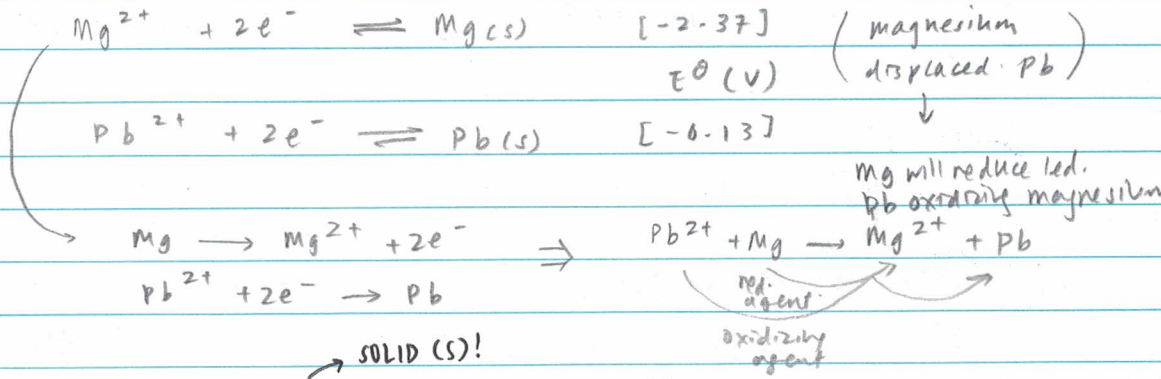


REACTIVITY SERIES

more reactive species displaces less reactive

↳ MORE REACTIVE METAL REDUCES less reactive metal

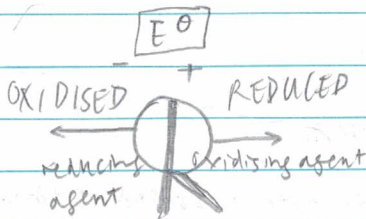
(other way is NOT spontaneous)



best reducing agents e.g. Caesium → low electronegativity (↑ shielding ↑ shells) ∴ ↓ attract

oxidising agents e.g. Fluorine → high electron-v. (↓ radius ↓ shielding) ↑ attract

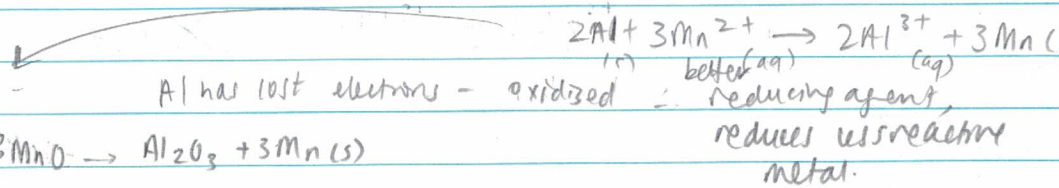
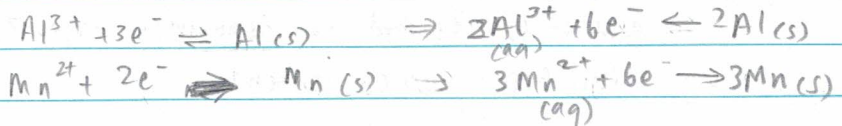
↳ F<sub>2</sub>(g)



e.g.

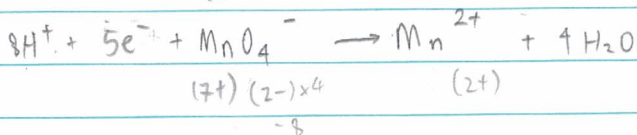
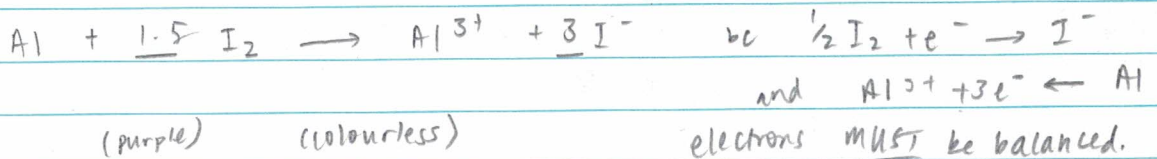


Al is a better reducing agent ←



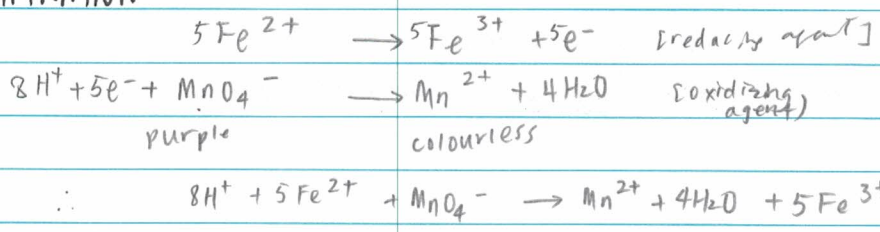
→ "negative goes to left" gets reduced

positive goes to right & get oxidising agent

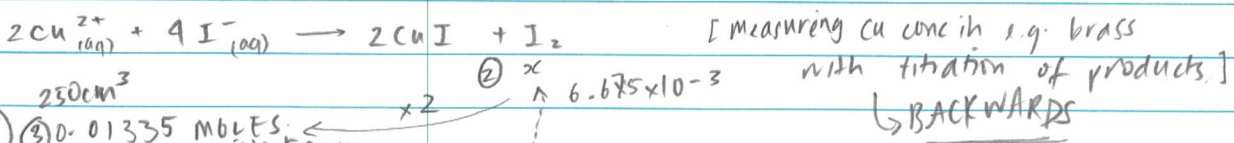


- x glass electrode  
 - x colourimetry  
 - activation energy  
 - titration if thiosulphate  
 -  $MnO_2$  (vid c conc?)

### REDOX TITRATION

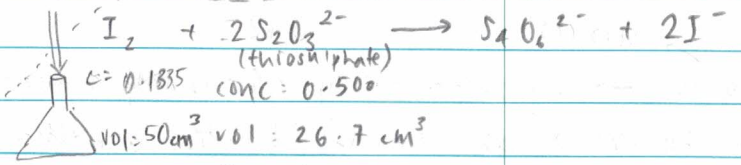


- iodometric (from HI)



250cm<sup>3</sup>  
 ② 0.01335 moles in 50cm<sup>3</sup>

② x 6.675 x 10<sup>-3</sup>



④  $\frac{50}{250} \times 0.01335 = 0.06675 \text{ moles}$

Vol: 50cm<sup>3</sup> vol: 26.7cm<sup>3</sup>  
 ① moles:  $6.675 \times 10^{-3}$  moles: 0.01335  
 $6.675 \times 10^{-3} = c \times v$

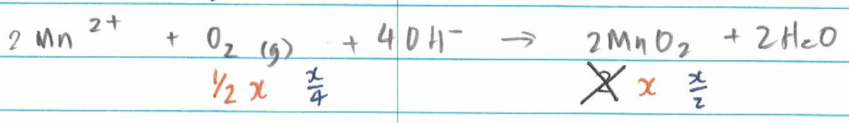
$g = 4.238125g$   
 $4.24 (3.s.f)$   
 14%

### BIOLOGICAL OXYGEN DEMAND

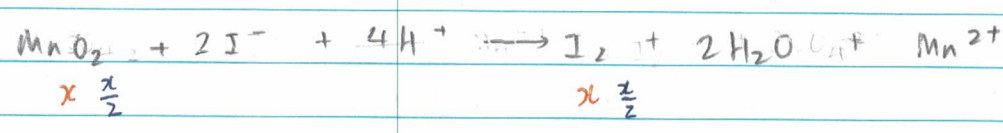
anaerobic bacteria

amt of O<sub>2</sub> required to decompose organic matter over a period of time

high BOD: low O<sub>2</sub> content



moles of  $2S_2O_3^{2-} = 4 = O_2 \text{ moles}$



① conc: 0.0125  
 vol: 7.71cm<sup>3</sup> 25cm<sup>3</sup>  
 work out mass of O<sub>2</sub>  
 moles:  $1.6375 \times 10^{-5} \div 4 = 2.409375 \times 10^{-5}$  moles of O<sub>2</sub>

of the mass.  $\frac{25cm^3}{250cm^3}$

$\times 32 \times 10 = 7.71 \times 10^{-4} = 7.71 \times 10^{-3}$