## **19. Electrochemistry**

## Definitions

Disproportionation reaction: A redox reaction whereby the same species is simultaneously oxidised and reduced.

Electrolyte: A compound which will conduct an electric current when it is in aqueous solution or in the molten state. An electrolyte conducts electricity due to the flow of charge carried by its ions.

Standard electrode potential: The emf, measured at 298 K, between the half-cell and the standard hydrogen electrode, in which the concentration of any reacting species is 1 moldm<sup>-3</sup> and any gaseous species is 1 atm.

Standard cell potential: The maximum potential difference between 2 half cells under standard conditions.

- Note that when stating observations of an electrolytic cell, besides, effervescence, depositing of solid on an electrode or corrosion of an electrode also note for colour changes in the electrolyte, for e.g. if Cu2+ in the electrolyte is used up then the blue colour of the solution will fade.
- If asked why in practice, a certain reaction does not occur or a certain gas or wtv is not used to reduce blah, it could be because gas is explosive, expensive to store, etc. OR the reaction has **high activation energy/kinetically unfavourable**.

# Limitations of spontaneity based on E cell values

- 1. Non standard conditions
- 2. Kinetic factor (high activation energy)
  - Energetically feasible but not kinetically feasible
- 3. Occurrence of side reactions
  - If a certain species is readily reduced, it could be reduced by carbon, however, if not, it can only be reduced through electrolysis.

## **Questions**

1. Describe how the redox potential may be measured in the laboratory. Ans:

- Draw the diagram of the SHE and the other half cell
- Indicate that the experiment has to be carried out in standard conditions of 298K, 1 atm for gases involved and 1 moldm<sup>^-3</sup> concentration of solutions in both half-cells.
- The SHE is used as the reference electrode and the 2 half cells are connected by a salt bridge.
- Potential difference measured by a voltmeter, value shown will be the standard electrode potential.

2. Why is the colour change slow? (for e.g. when CrO4<sup>2</sup>- is reduced to Cr<sup>3+</sup> by SO2 in the atmosphere)

Ans: The concentration of SO2 in the atmosphere is low and hence the reaction is slow, thus causing colour change to be slow too.

3. Explain why although standard conditions are unlikely, the reaction is still highly probable to proceed.

Ans: Although the concentration of \_\_\_\_ may not be 1moldm^-3, however it would not be too low to make the E cell negative since the E cell is relatively far from zero. Hence the reaction still proceeds with a positive E cell.

4. Explain why a solution of H2O2 gives off bubbles of oxygen on standing. Ans: H2O2 spontaneously decomposes to H2O and O2.

5. Advantage of ethanol fuel cell over hydrogen fuel cell Ans:

- Easier to transport (less cost)
- Less explosive (less danger)

6. Why does the graphite electrode need to be replaced from time to time? Ans: The carbon in graphite will react with oxygen produced at higher temperatures, forming CO2. Hence the graphite electrode becomes smaller and would need to be replaced when they become too small.

7. Explain why the E cell value would increase drastically when excess acidified KMnO4 is added to the Fe3+/Fe2+ half cell.

Ans: When excess is added, all the Fe2+ is used up and a new half-cell MnO4-/Mn2+ is generated due to excess MnO4-. The electrode potential of this half cell is much larger than that of Fe3+/Fe2+ and hence causes E cell to increase drastically.

8. Suggest a reason why the battery is rechargeable.

Ans: Both products are coated on the electrodes, and hence there is conservation of material and if an external source of direct current is applied, it will recharge the battery by driving the cell in the opposite direction.

Ans: Both electrodes are coated with \_\_\_\_ (s) after they react.

13 The diagram represents an experiment to confirm the value of E<sup>9</sup>(Cu<sup>2+</sup>(aq)/Cu(s)), the standard electrode potential of copper.



Which of the following possible explanations could be correct?

- **1** [Cu<sup>2+</sup>(aq)] was less than 1.00 mol dm<sup>-3</sup>.
- 2 The pressure of  $H_2(g)$  was less than 101 kPa (1 atm).
- 3 The pH of the solution at the hydrogen electrode was 1.0.

In this question, 2H+ + 2e-  $\rightarrow$  H2. For

option 3, calculate [H+] using the pH, since it is less than 1 mol dm^03, eqm position shifts to the left and therefore e half cell of anode decreases and thus is not correct.

#### GENERAL

- NH3 is a better nucleophile than H2O as N is less electronegative, therefore donates electron pair more readily.
- If a substance only contains a COOH group and has pKa of e.g. 2, and it is in an environment where pH is 1, then the uncharged form of the link is predominant, and will be able to dissolve in non-polar environment.
- If question asks how will \_\_\_\_ react with \_\_\_\_, answer through nucleophilic/electron rich/electron deficient/etc.
- HCI (g) does NOT substitute -OH of COOH!!!
- NOTE THAT delocalisation into a double bond (e.g. C=O) can only occur if it is directly bonded to the carbonyl carbon, if it is further away, then it is due to the electron withdrawing effect of C=O, not because of delocalisation.
- In hydrolysis of ester, if extracted with organic solvent, and there is an aqueous and an organic layer, the carboxylate salt (if present) will be the aqueous layer while the alcohol will be in the organic layer.
- If question mentions organic distillate collected from heating in a flask, it is usually NOT the ionic salt formed but the neutral organic compound, because the ionic salt would have very high boiling point and thus wouldn't be able to be collected as distillate and will remain in the reaction flask as residue.
- ESTERS and AMIDES CANNOT undergo nucleophilic addition!