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Junior College 2

The Ultimate Exam Revision Notes

Syllabus 9729

H2 Chemistry

Electrochemistry

This set of revision notes is designed to help you evaluate your understanding of Electrochemistry and pinpoint areas that need improvement.

Use these notes to decide whether to strengthen your fundamentals or challenge yourself with more advanced questions.

Remember to attempt all questions before reviewing the answers — consistent practice leads to progress.

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Chapter 15. Galvanic Cells

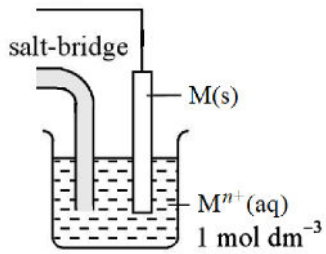
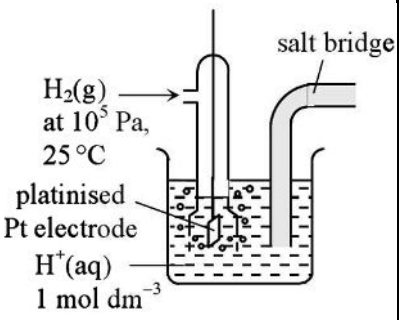
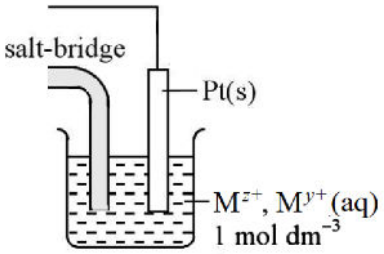
Electrode Potential of Cells

The **standard electrode** (or **reduction**) **potential** ($E^\ominus$) of a half-cell is defined as the potential difference between a standard hydrogen electrode (S.H.E.) and a half-cell measured at standard conditions of 298 K, 1 bar and 1 mol dm^{-3} of reacting aqueous species.

more positive E ⇒ higher tendency for reduction

- Standard conditions: 298 K, 1 bar, 1 mol dm^{-3} reacting aqueous species
- When drawing half-cells, ensure that all species present in the half-equation must appear in the setup of the half-cell:

To measure $E^\ominus$ value

Metal-Ion Half Cell	S.H.E. or Gas-Ion Half Cell	Ion-Ion Half-Cell
		
e.g. $Mg^{2+}(aq) + 2\,e^- \rightleftharpoons Mg(s)$	e.g. $2\,H^+(aq) + 2\,e^- \rightleftharpoons H_2(g)$	e.g. $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$

- The standard hydrogen electrode is *typically* drawn on the left of the galvanic cell.
- If the half-cell undergoes reduction when connected to the S.H.E., its $E^\ominus$ value will be positive (and vice versa). Electrons flow from oxidation half-cell to reduction half-cell.
- The salt bridge is usually soaked with an inert electrolyte (do not participate in the redox reactions) such as KNO_3(aq).

Worked Example

What is the purpose of the salt bridge?

Solution

- The salt bridge completes the circuit by allowing passage of ions between two half-cells,
- thereby maintaining electrical neutrality (prevent build-up of charges) in each half-cell.
- It also serves to separate the two electrolytes so that they do not mix.

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Full Electrochemical Cell

The **standard cell potential**, $E^{\ominus}_{cell}$, is a measure of tendency of electrons to flow through an external circuit due to a potential difference between two half-cells under standard conditions of 298 K, 1 bar and 1 mol dm^{-3} of reacting aqueous species.

$$E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation}$$

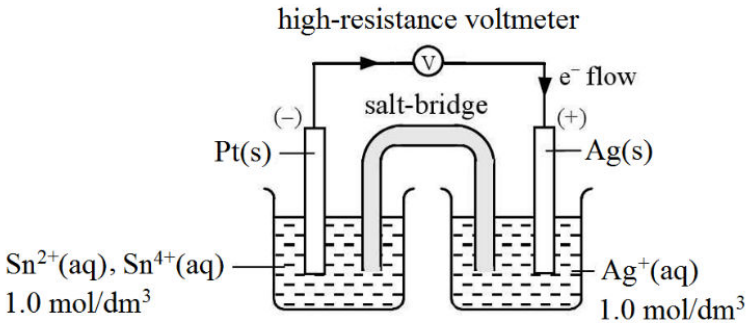
- The main principles include:
  - The half-cell with a more positive $E^{\ominus}$ undergoes reduction (and vice versa).

Cathode	Anode
reduction occurs	oxidation occurs
positive terminal	negative terminal

  - Electrons always flow from oxidation (loss of electrons) half-cell to reduction (gain of electrons) half-cell (i.e. from anode to cathode).
  - The overall equation is obtained by adding the two half-equations together.
    - The oxidation half-equation needs to be reversed.
    - Do not reverse the sign of $E^{\ominus}_{oxidation}$.

Worked Example

Study the following electrochemical cell.



Deduce the overall chemical equation, $E^{\ominus}_{cell}$ and direction of electron flow in the wire of the electrochemical cell. Also, state the name and polarity of the platinum and silver electrodes.

Solution

$Sn^{4+}(aq) + 2\,e^- \rightleftharpoons Sn^{2+}(aq)$ $\quad E^{\ominus} = +0.15$ V

$Ag^{+}(aq) + e^- \rightleftharpoons Ag(s)$ $\quad E^{\ominus} = +0.80$ V

Since $E^{\ominus}(Ag^+/Ag)$ is more positive, Ag^+ undergoes reduction.

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Reduction half-equation: $Ag^+(aq) + e^- \rightarrow Ag(s)$

Oxidation half-equation: $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\,e^-$

Half-equations are always written using full arrows (→).

Overall equation: $2\,Ag^+(aq) + Sn^{2+}(aq) \rightarrow 2\,Ag(s) + Sn^{4+}(aq)$

$$E^{\ominus}_{cell} = +0.80 - (+0.15) = +0.65\ V$$

Electrons flow from platinum electrode to silver electrode.

Electrode	Half-Reaction	Name	Polarity
platinum	oxidation	anode	–
silver	reduction	cathode	+

For galvanic cells, $E^{\ominus}_{cell}$ is always positive and $\Delta G^{\ominus}$ is always negative.

Spontaneity of Redox Reactions

- In redox reactions not involving electrochemical cells, the half-equations occurring depends on the reactants present in the reacting mixture.
- Species getting reduced appears on left side of half-equation from *Data Booklet* while species getting oxidised appears on right side of half-equation from *Data Booklet*.

Worked Example

Three standard electrode potentials are listed below.

$I_2(aq) + 2\,e^- \rightleftharpoons 2\,I^-(aq)$ $\quad E^{\ominus} = +0.54\ V$

$2\,H^+(aq) + O_2(g) + 2\,e^- \rightleftharpoons H_2O_2(aq)$ $\quad E^{\ominus} = +0.68\ V$

$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^- \rightleftharpoons 2\,H_2O(l)$ $\quad E^{\ominus} = +1.77\ V$

What will be observed when a few drops of acidified aqueous hydrogen peroxide are added to an excess of aqueous potassium iodide?

Decide which species is getting reduced or oxidised based on reactants present, not their $E^{\ominus}$ values.

Solution

Since iodide ions can only get oxidised, hydrogen peroxide must be the oxidising agent (gets reduced).

Reduction half-equation: $H_2O_2(aq) + 2\,H^+(aq) + 2\,e^- \rightarrow 2\,H_2O(l)$

Oxidation half-equation: $2\,I^-(aq) \rightarrow I_2(aq) + 2\,e^-$

Overall equation: $H_2O_2(aq) + 2\,H^+(aq) + 2\,I^-(aq) \rightarrow 2\,H_2O(l) + I_2(aq)$

The solution turns brown without any effervescence of gas.

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Relating ΔG and E_{cell}

$$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$$

where $\Delta G^{\ominus}$ is the Gibbs' free energy change in J mol^{-1},

n is the number of electrons transferred in a given chemical equation,

F is the Faraday's constant (96500 C mol^{-1}),

$E^{\ominus}_{cell}$ is the cell potential in V.

$\Delta G^{\ominus}$	$E^{\ominus}_{cell}$	Implications
> 0	< 0	Forward reaction is not spontaneous.
< 0	> 0	Forward reaction is spontaneous.

Worked Example

Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the following reaction:

$$Al(s) + \frac{3}{2}Cu^{2+}(aq) \rightarrow Al^{3+}(aq) + \frac{3}{2}Cu(s)$$

Solution

$$Al^{3+}(aq) + 3\,e^- \rightleftharpoons Al(s) \qquad E^{\ominus} = -1.66\ V$$

$$Cu^{2+}(aq) + 2\,e^- \rightleftharpoons Cu(s) \qquad E^{\ominus} = +0.34\ V$$

Since Al is getting oxidised while Cu^{2+} is getting reduced,

$$E^{\ominus}_{cell} = +0.34 - (-1.66) = +2.00\ V$$

There are 6 electrons transferred in that chemical equation.

For $2\,Al(s) + 3\,Cu^{2+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,Cu(s)$,

$$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$$

$$\Delta G^{\ominus} = -6(96500)(+2.00)$$

$$\Delta G^{\ominus} = -1158000\ J\ mol^{-1} = -1158\ kJ\ mol^{-1}$$

For $Al(s) + \frac{3}{2}Cu^{2+}(aq) \rightarrow Al^{3+}(aq) + \frac{3}{2}Cu(s)$,

$$\Delta G^{\ominus} = \frac{1}{2} \times (-1158) = \underline{-579\ kJ\ mol^{-1}}$$

ΔG is referenced against the balanced chemical equation.

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Limitations in using $E^{\ominus}_{cell}$ to predict spontaneity

1. Kinetic factor is not taken into consideration

- $E^{\ominus}_{cell}$ is used to predict if a reaction can occur spontaneously (thermodynamic feasibility) but cannot predict how fast the reaction occurs (kinetic feasibility).

  e.g. $H_2(g) + Cu^{2+}(aq) \rightarrow 2\ H^+(aq) + Cu(s)$ $\quad E^{\ominus}_{cell} = +0.34\ V > 0$

- When hydrogen gas is bubbled into a solution of copper(II) ions, no reaction occurs (despite a positive $E^{\ominus}_{cell}$) because of the high activation energy and occurs very slowly.
- Despite the reaction being thermodynamically feasible, it is kinetically unfeasible.

2. Non-standard conditions

- $E^{\ominus}_{cell}$ is the cell potential under standard conditions. Predictions using $E^{\ominus}_{cell}$ under non-standard conditions may not be valid.
- Changes in temperature, pressure and concentration of solutions will affect the respective electrode potentials and result in cell potentials deviating from $E^{\ominus}_{cell}$.

  For e.g., the reaction between Cu^{2+} and V^{3+}

  $\mathbf{Cu^{2+}}(aq) + 2\ e^- \rightleftharpoons Cu(s)$ $\quad E^{\ominus} = +0.34\ V$

  $VO^{2+}(aq) + 2\ H^+(aq) + e^- \rightleftharpoons \mathbf{V^{3+}}(aq) + H_2O(l)$ $\quad E^{\ominus} = +0.34\ V$

  $E^{\ominus}_{cell} = +0.34 - (+0.34) = 0\ V$ (this means reaction reaches equilibrium with no net reaction)

  The redox reaction could be made to occur by increasing $[Cu^{2+}]$ (this makes $E_{reduction}$ more positive) or decreasing $[V^{3+}]$ (this makes $E_{oxidation}$ less positive).

3. Side reactions may occur

- If a side reaction (especially precipitation) occurs, a non-spontaneous reaction may turn spontaneous.

  For e.g., the reaction between Cu^{2+} and I^-,

  $I_2(aq) + 2\ e^- \rightleftharpoons 2\ \mathbf{I^-}(aq)$ $\quad E^{\ominus} = +0.54\ V$

  $\mathbf{Cu^{2+}}(aq) + e^- \rightleftharpoons Cu^+(aq)$ $\quad E^{\ominus} = +0.15\ V$

$E^{\ominus}_{cell} = +0.15 - (+0.54) = -0.39\ V$ (forward reaction is non-spontaneous)

- In reality, a reaction does occur: $2\ Cu^{2+}(aq) + 4\ I^-(aq) \longrightarrow 2\ CuI\ (s) + I_2(aq)$

  Precipitation of CuI decreases the $[Cu^+]$ and the equilibrium position of Cu^{2+}/Cu^+ shifts to the right, causing $E_{reduction}$ to become more positive and E_{cell} increasing beyond 0V.

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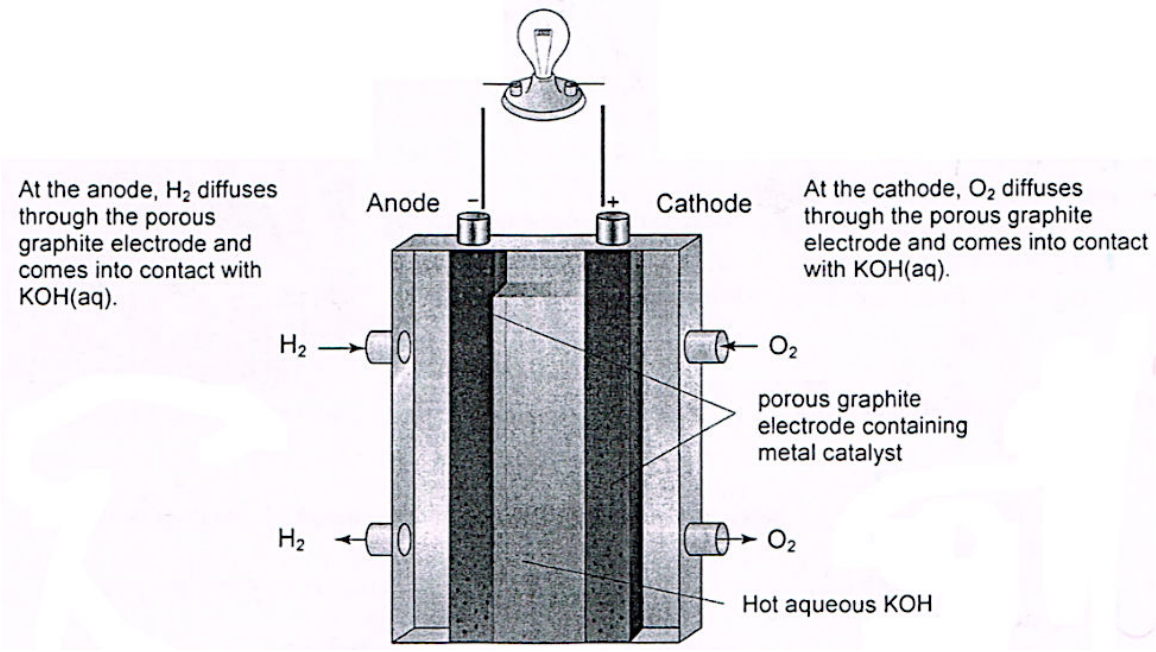
Case Study: Fuel Cell

- A **fuel cell** is a galvanic cell that converts chemical energy from fuels into electrical energy (power) *directly* using oxidation. A fuel (e.g. hydrogen and methane etc) is supplied to one electrode and an oxidant (usually oxygen) to the other.
- Consider the hydrogen-oxygen fuel cell, which uses hydrogen gas as main fuel, and is oxidised by oxygen gas to give harmless water.



- In the cell, H_2 and O_2 are bubbled through porous carbon electrodes which contains Pt catalyst in a concentrated solution of the alkali KOH(aq) electrolyte.

Anode	Cathode
Hydrogen diffuses through the porous graphite electrode and comes into contact with KOH(aq).	Oxygen diffuses through the porous graphite electrode and comes into contact with KOH(aq).
$H_2(g) + 2\ OH^-(aq) \rightarrow 2\ H_2O(l) + 2\ e^-$	$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$
$E^{\ominus}_{oxidation} = -0.83$ V	$E^{\ominus}_{reduction} = +0.40$ V

Overall equation: $O_2(g) + 2\ H_2(g) \rightarrow 2\ H_2O(l)$

$E^{\ominus}_{cell} = +0.40 - (-0.83) = +1.23$ V

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- Some advantages and disadvantages of the hydrogen-oxygen fuel cell include:

Advantages	Disadvantages
➢ Able to attain maximum power with minimum weight and volume, important e.g. for space flight. ➢ High efficiency of conversion of chemical energy to electrical energy (up to 70% vs about 30% for power stations). ➢ Fuel cells do not "go dead" as reactants are supplied continuously, and products are continually removed. An ordinary battery stops working as soon as the electrode materials are used up. ➢ The product of the reaction is non-polluting.	➢ Expensive due to large amounts of Ni (or Pt) used. ➢ Requires high temperature and pressure to operate. ➢ Not portable.

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Effect of Concentration on E_{cell}

- Changes in concentration of aqueous species causes a shift in equilibrium position of half-reactions by Le Chatelier's principle, leading to a change in its E value. It may affect the energetic spontaneity of the reaction.

Worked Example

Consider a solution containing 1 mol dm^{-3} $Cr_2O_7^{2-}$(aq), 1 mol dm^{-3} H^+(aq) and 1 mol dm^{-3} Cl^-(aq) at 298 K.

(i) Using suitable calculations, deduce the energetic feasibility of the reaction.

Solution

$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightleftharpoons 2\ Cr^{3+}(aq) + 7\ H_2O(l)$ --- (1) $\quad E^{\ominus}_{reduction} = +1.33$ V

$Cl_2(g) + 2\ e^- \rightleftharpoons 2\ Cl^-(aq)$ --- (2) $\quad E^{\ominus}_{oxidation} = +1.36$ V

$$E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation}$$
$$= (+1.33\text{ V}) - (+1.36\text{ V}) = -0.03\text{ V}$$

Since $E^{\ominus}_{cell} < 0$, reaction is not energetically spontaneous under standard conditions.

(ii) State and explain how energetic spontaneity of the reaction changes if the concentration of Cl^-(aq) increases from 1 mol dm^{-3} to 2 mol dm^{-3}.

Solution

Do not put '$^{\ominus}$'.

By Le Chatelier's principle, an increase in [Cl^-] shifts position of equilibrium (2) to left, causing $E_{oxidation}$ to become less positive. As a result, E_{cell} becomes more positive, making the reaction more energetically spontaneous.

$E_{oxidation}$ and E_{cell} has positive relationship.
$E_{reduction}$ and E_{cell} has opposite relationship.

Do not use 'increase'.

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(iii) State and explain how E_{cell} changes if NaOH(aq) is added to the reaction mixture.

Solution

The addition of NaOH(aq) reacts with $Cr^{3+}(aq)$ to produce $Cr(OH)_3$ precipitate, causing $[Cr^{3+}]$ in mixture to decrease.

By Le Chatelier's principle, a decrease in $[Cr^{3+}]$ shifts position of equilibrium (1) to right, causing $E_{reduction}$ to become more positive. As a result, E_{cell} becomes more positive, making the reaction more energetically spontaneous.

Do not write '$[H_2O]$ increases' if water is a solvent!

(iv) State and explain how E_{cell} of reaction changes if water is added into the solution.

Solution

- Adding water <u>decreases</u> the concentration of all aqueous species (e.g. ions). By LCP, equilibrium position <u>shifts to the side with more aqueous species</u> to increase the concentration of aqueous species.
- By LCP, the decrease in [aqueous species] causes the equilibrium position of (1) to <u>shift left</u>, favouring the backward reaction and the equilibrium position of (2) to shift right, favouring the forward reaction.
- $E_{reduction}$ becomes less positive and $E_{oxidation}$ becomes more positive.
- Thus, E_{cell} becomes <u>less positive</u>, making the reaction <u>less spontaneous</u>.

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Question 1: Drawing an Electrochemical Cell

The zinc-air battery involves a porous zinc electrode that reacts to form zincate, $Zn(OH)_2$.

$$Zn(OH)_4^{2-}(aq) + 2e^- \rightleftharpoons Zn(s) + 4\ OH^-(aq) \qquad E^{\ominus} = -1.25\ V$$

The other electrode in the battery is the oxygen electrode in an alkaline medium.

(i) Draw a fully labelled diagram of the experimental set-up used to measure this $E^{\ominus}_{cell}$ and indicate the direction of electron flow. [3]

(ii) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the oxidation of one mole of zinc in the zinc-air battery. [2]

(iii) Predict how the E_{cell} will change when water is added into the $Zn(OH)_4^{2-}/Zn$ half-cell. [2]

[Total: 7]

Question 2: Constructing Half-Equations

Methanol can be used in direct-membrane alkaline fuel cells to generate electricity. At the anode, methanol is diluted in potassium hydroxide solution and undergoes oxidation to become carbonate, CO_3^{2-}, and water. At the cathode, oxygen gas is being supplied into water.

(i) Construct half equations for the cathode and anode reactions. [2]

(ii) Hence, write the overall equation. [1]

(iii) The cell can produce an e.m.f of +1.21 V under standard conditions. By using relevant data from the *Data Booklet*, suggest a value for the $E^{\ominus}$ of the anode reaction. [1]

(iv) Calculate $\Delta G^{\ominus}$ for the oxidation of 1 mol of methanol. [1]

[Total: 5]

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Question 3: Predicting the Spontaneity of Redox Reactions

The use of *Data Booklet* is relevant to this question.

When iron is heated with chlorine, $FeCl_3$ is produced. However, when heated with iodine, FeI_2 is produced instead.

(i) Explain why when iron is heated with iodine, FeI_2 is produced but not FeI_3. [2]

(ii) Draw a fully labelled diagram to show how the standard electrode potential of the $Fe^{3+}(aq)/Fe^{2+}(aq)$ system could be measured. Show the direction of electron flow in the circuit. [3]

(iii) A few drops of acidified potassium manganate(VII) is added to the $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell. Predict and explain how the cell potential would change. [2]

[Total: 7]

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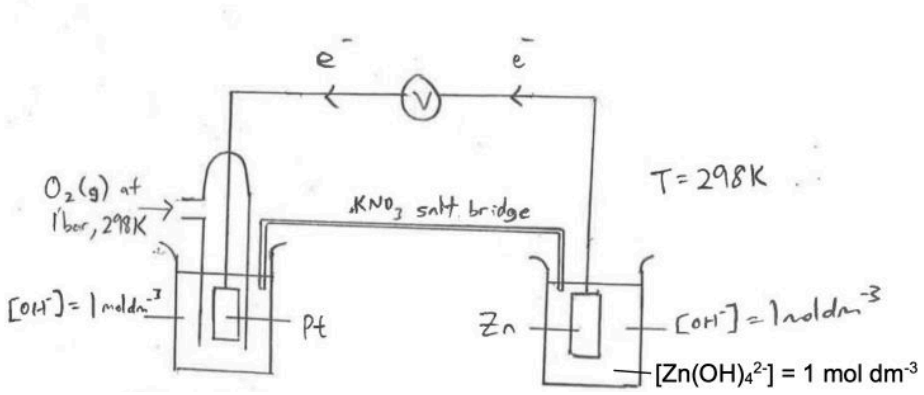
Question 1: Drawing an Electrochemical Cell

(i) Correct answers should include:

Correct electron flow (Zn to Pt)	O_2 at 1 bar, 298 K	$[OH^-] = 1$ mol dm^{-3} at cathode
Salt bridge and voltmeter	Both Pt and Zn electrodes	$[Zn(OH)_4]^{2-} = [OH^-] = 1$ mol dm^{-3} at anode



(ii) $E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation}$

$= +0.40 - (-1.25) = +1.65$ V

$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

$= -(2)(96\,500)(+1.65)$

$= -3.18 \times 10^5$ J mol^{-1}

$= -318$ kJ mol^{-1}

(iii) Addition of water/dilution decreases the concentration of aqueous particles.

Position of equilibrium shifts right for $Zn(OH)_4^{2-}(aq) + 2\,e^- \rightleftharpoons Zn(s) + 4\,OH^-(aq)$ as there are more aqueous ions in the products than aqueous ions in the reactants.

$E(Zn(OH)_4^{2-}/Zn)$ will become more positive (or less negative).

E_{cell} becomes less positive (or more negative).

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Question 2: Constructing Half-Equations

(i) Cathode: $O_2 + 2\ H_2O + 4\ e^- \longrightarrow 4\ OH^-$

Anode: $CH_3OH + 8\ OH^- \longrightarrow CO_3^{2-} + 6\ H_2O + 6\ e^-$

(ii) Overall: $CH_3OH + \frac{3}{2} O_2 + 2\ OH^- \longrightarrow CO_3^{2-} + 3\ H_2O$

(iii) $E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation}$

$+1.21 = +0.40 - E^{\ominus}_{oxidation}$

$E^{\ominus}_{oxidation} = -0.81$ V

(iv) $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

$= -(6)(96\,500)(+1.21) = -701$ kJ mol^{-1}

Question 3: Predicting the Spontaneity of Redox Reactions

(i) Firstly pick out the half–equations that contain I_2 and Fe:

$\mathbf{I_2} + 2\ e^- \rightleftharpoons 2\ I^-$ $\quad E^{\circ} = +0.54$ V

$Fe^{2+} + 2\ e^- \rightleftharpoons \mathbf{Fe}$ $\quad E^{\circ} = -0.44$ V

~~$Fe^{3+} + 3\ e^- \rightleftharpoons \mathbf{Fe}$ $\quad E^{\ominus} = -0.04$ V~~ (**reject** because Fe has a greater tendency to oxidise to Fe^{2+} than Fe^{3+} because –0.44 is more negative)

$E^{\ominus}_{cell}$ between Fe and $I_2 = +0.54-(-0.44) = +0.98$ V > 0, reaction is spontaneous:

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

Note that Fe^{2+} could potentially oxidise further to Fe^{3+} by I_2:

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

$E^{\ominus}_{cell}$ between Fe^{2+} and $I_2 = +0.54-(+0.77) = -0.23$ V < 0, reaction is non-spontaneous.

Iodine can only oxidise Fe to Fe^{2+} and not to Fe^{3+}.

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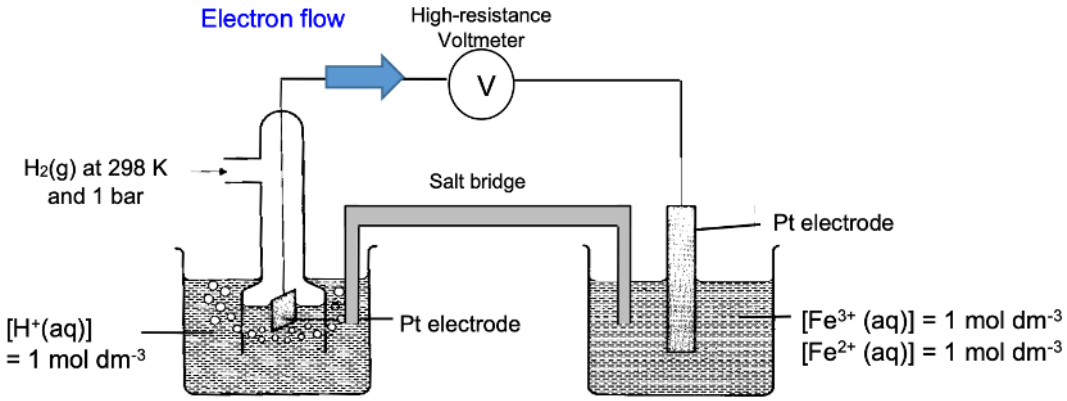
(ii) **[1]** Fully labelled SHE with respective standard conditions and inert electrode.

[1] Fully labelled Fe^{3+}/Fe^{2+} half-cell with respective standard conditions and inert electrode

[1] Direction of electron flow, voltmeter as V, salt bridge



(iii) **Working:**

We need to lookout for a potential reaction between acidified MnO_4^- with Fe^{2+} or Fe^{3+}.

Find the half-equation that represents acidified MnO_4^-:

$\mathbf{MnO_4^-} + 8\,\mathbf{H^+} + 5\,e^- \rightleftharpoons Mn^{2+} + 4\,H_2O$ $\quad E^\circ = +1.52$ V

Since MnO_4^- is on the LHS of the half-equation, this means that MnO_4^- can only be reduced, the species that reacts with MnO_4^- must be oxidised.

Find the half-equation that represents Fe^{3+} and Fe^{2+}:

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

MnO_4^- cannot react with Fe^{3+} because Fe^{3+} can only be reduced (LHS of the half-equation); MnO_4^- can react with Fe^{2+} because Fe^{2+} can be oxidised (RHS of the half-equation).

Answer:

- $E^\ominus_{cell}$ between Fe^{2+} and MnO_4^- = +1.52–(+0.77) = +0.75 V > 0, reaction is spontaneous.
- Therefore, $[Fe^{2+}]$ decreases.
- By LCP, the position of equilibrium of $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ shifts right to increase $[Fe^{2+}]$.
- $E(Fe^{3+}/Fe^{2+})$ becomes more positive, and since this is the reduction half-cell, E_{cell} becomes more positive.

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