A-LEVEL CHEMISTRY • EXERCISE SHEET

24.2 Standard electrode potentials and the Nernst equation

Name: _____ Class: _____ Date: _____ **Total: 34 marks**

KEY WORDS electrode potential 电极电势 • standard electrode potential 标准电极电势 • nernst equation 能斯特方程 • standard cell potential 标准电池电势 • standard hydrogen electrode 标准氢电极

Objective

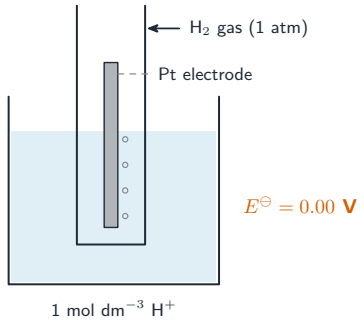
Build the skills to answer exam questions on **standard electrode potentials** 标准电极电势 — the **standard hydrogen electrode** 标准氢电极, **cell potentials** 电池电势, **feasibility** 可行性, and the **Nernst equation** 能斯特方程.

You must be able to:

- describe the standard hydrogen electrode and how $E^\ominus$ is measured
- calculate a cell potential and deduce polarity, electron flow and feasibility
- use $E^\ominus$ values to compare oxidising/reducing agents and construct redox equations

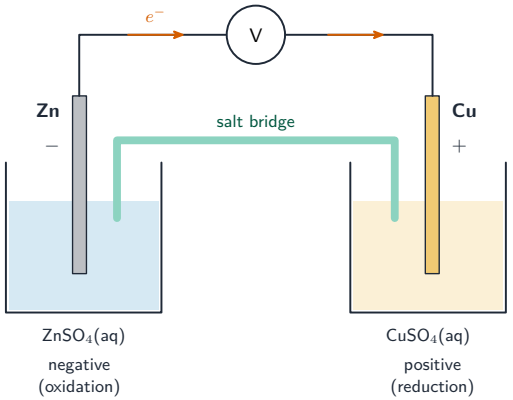
1 Worked examples

Electrode and cell potentials



$E^\ominus = 0.00$ **V**

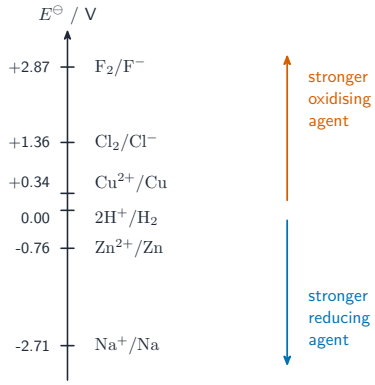
$E^\ominus$ is measured against the standard hydrogen electrode (defined as 0.00 V), under standard conditions, as a reduction



$E^\ominus_{cell} = E^\ominus$(more positive) $- E^\ominus$(less positive). Electrons flow from the more negative electrode

Example. Zn^{2+}/Zn (−0.76 V) + Cu^{2+}/Cu (+0.34 V): $E^\ominus_{cell} = (+0.34) - (-0.76) = +1.10$ V.

Feasibility and the series



A more positive $E^\ominus$ = better oxidising agent; more negative = better reducing agent

A reaction is feasible when $E^\ominus_{cell}$ is **positive**. ($\Delta G^\ominus = -nE^\ominus_{cell}F$.) The **Nernst equation** corrects for non-standard concentrations: $E = E^\ominus + \frac{0.059}{z} \log \frac{[ox]}{[red]}$.

■ **Reading a table of $E^{\ominus}$ values**

A **standard electrode potential** $E^{\ominus}$ is measured against the **standard hydrogen electrode** ($E^{\ominus} = 0.00$ V) under standard conditions: **298 K, 1 bar, and all solutions at 1 mol dm^{-3}**. Quoting those three conditions is routinely a mark.

What the sign tells you. A **more positive** $E^{\ominus}$ means the species on the LEFT of the half-equation is a **better oxidising agent** (more readily reduced). A **more negative** $E^{\ominus}$ means the species on the RIGHT is a **better reducing agent**.

Will a reaction happen? Combine the two half-cells:

$$E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{reduction, the more positive}) - E^{\ominus}(\text{oxidation, the more negative})$$

A **positive** $E^{\ominus}_{\text{cell}}$ means the reaction is **feasible** — thermodynamically. △ Feasible is not the same as fast: a positive value says nothing about rate, and a reaction with a large activation energy may not be observed at all. That caveat is a mark in almost every "suggest why no reaction was seen" question.

Non-standard conditions, by Le Chatelier. Write the half-equation and treat it as an equilibrium. Increasing the concentration of the **oxidised** species (the left-hand side) shifts it right, so the electrode potential becomes **more positive**; increasing the **reduced** species makes it more negative.

Worked example. Given $E^{\ominus}(\text{Zn}^{2+}/\text{Zn}) = -0.76$ V and $E^{\ominus}(\text{Cu}^{2+}/\text{Cu}) = +0.34$ V, deduce the cell reaction and $E^{\ominus}_{\text{cell}}$.

1. The more positive electrode is reduced: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$.
2. The more negative is oxidised, so its equation is reversed: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$.
3. Overall: $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$.
4. $E^{\ominus}_{\text{cell}} = +0.34 - (-0.76) = +1.10$ V, positive, so the reaction is feasible.

2 Practice

2.1 Describe the standard hydrogen electrode. [2]

2.2 State the condition on $E^{\ominus}_{\text{cell}}$ for a reaction to be feasible. [1]

2.3 State the three standard conditions for measuring $E^{\ominus}$. [3]

2.4 Explain why a positive $E^{\ominus}_{\text{cell}}$ does not guarantee that a reaction is observed. [2]

2.5 State the effect on $E^{\ominus}(\text{Fe}^{3+}/\text{Fe}^{2+})$ of increasing $[\text{Fe}^{3+}]$, and give your reasoning. [2]

3 Exam-style questions

3.1 A more **positive** standard electrode potential indicates a: [1]

- **A** stronger reducing agent
- **B** stronger oxidising agent
- **C** more reactive metal
- **D** higher concentration

3.2 Increasing the concentration of the oxidised species in a half-cell makes its electrode potential: [1]

- **A** more positive
- **B** more negative
- **C** unchanged
- **D** zero

3.3 Use these $E^{\ominus}$ values: $Fe^{2+}/Fe = -0.44$ V; $Ag^{+}/Ag = +0.80$ V.

(a) Calculate the standard cell potential of a cell made from these half-cells. [2]

(b) Deduce which electrode is the negative terminal and the direction of electron flow. [2]

3.4 Using the values above, state whether silver can oxidise iron metal, and explain using $E^{\ominus}_{\text{cell}}$. [2]

3.5 Use the standard electrode potentials below.

half-equation	$E^{\ominus}$ **/ V**
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.15
$V^{3+} + e^- \rightleftharpoons V^{2+}$	−0.26

(a) Identify the strongest oxidising agent and the strongest reducing agent in the table, giving your reasoning. [3]

(b) Deduce whether Fe^{3+} will oxidise Sn^{2+}. Write the overall equation and calculate $E^{\ominus}_{\text{cell}}$. [4]

(c) Write the overall ionic equation for the reaction of acidified MnO_4^- with Fe^{2+}, and calculate $E^{\ominus}_{\text{cell}}$. [4]

(d) A student mixes V^{3+} and Sn^{2+} and observes no change. Use the data to explain whether a reaction is feasible, and give one reason a feasible reaction might still not be observed. [3]

(e) The Fe^{3+}/Fe^{2+} half-cell is made with $[Fe^{3+}] = 2.0$ mol dm^{-3} and $[Fe^{2+}] = 1.0$ mol dm^{-3}. State and explain the effect on its electrode potential. [2]

Solutions

2.1 hydrogen gas at 1 atm bubbled over a platinum electrode in 1 mol dm^{-3} H^+, defined as 0.00 V.

2.2 it must be positive.

2.3 298 K; a pressure of 1 bar for any gas; all solutions at a concentration of 1 mol dm^{-3}.

2.4 $E^{\ominus}_{cell}$ describes only the thermodynamic feasibility, not the rate; a large activation energy can make the reaction immeasurably slow, so nothing is seen.

2.5 It becomes more positive; Fe^{3+} is on the left of the half-equation, so raising its concentration shifts the equilibrium to the right by Le Chatelier's principle.

3.1 B. A more positive $E^{\ominus}$ is a stronger oxidising agent.

3.2 A. More oxidised species makes the potential more positive.

3.3 (a) $E^{\ominus}_{cell} = (+0.80) - (-0.44) = +1.24$ V.
(b) the Fe^{2+}/Fe electrode (more negative) is the negative terminal; electrons flow from the iron to the silver electrode in the external circuit.

3.4 yes; $E^{\ominus}_{cell}$ for Ag^+ oxidising Fe is positive (+1.24 V), so the reaction is feasible.

3.5 (a) The strongest oxidising agent is MnO_4^-, because it has the most positive $E^{\ominus}$ and is most readily reduced; the strongest reducing agent is V^{2+}, because its half-cell has the most negative $E^{\ominus}$.
(b) $E^{\ominus}_{cell} = +0.77 - 0.15 = +0.62$ V, which is positive, so the reaction is feasible; $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$.
(c) $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$; $E^{\ominus}_{cell} = +1.52 - 0.77 = +0.75$ V.
(d) For Sn^{2+} to reduce V^{3+}: $E^{\ominus}_{cell} = -0.26 - 0.15 = -0.41$ V, which is negative, so that reaction is not feasible. Even where a value is positive, a high activation energy can make the reaction too slow to observe.
(e) It becomes more positive; the oxidised species is in excess, so by Le Chatelier's principle the equilibrium shifts to the right, favouring reduction.