

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

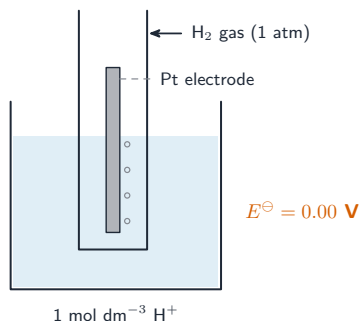
Build the skills to answer exam questions on **standard electrode potentials** 标准电极电势 — the **standard hydrogen electrode** 标准氢电极, **cell potentials** 电池电势, **feasibility** 可行性, and the **Nernst equation** 能斯特方程.

You must be able to:

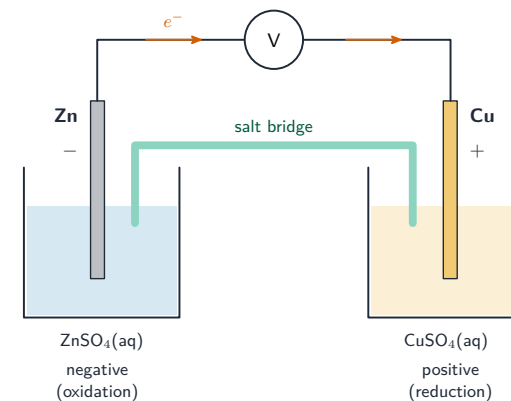
- describe the standard hydrogen electrode and how $E^\ominus$ is measured
- calculate a cell potential and deduce polarity, electron flow and feasibility
- use $E^\ominus$ values to compare oxidising/reducing agents and construct redox equations

1 Worked examples

■ Electrode and cell potentials



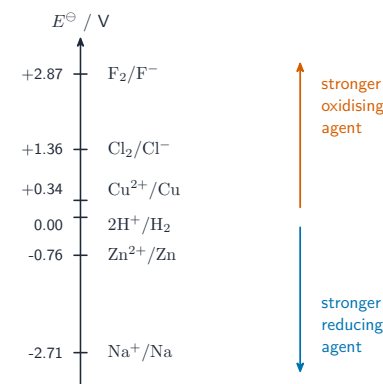
$E^\ominus$ is measured against the standard hydrogen electrode (defined as 0.00 V), under standard conditions, as a reduction



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

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

■ Feasibility and the series



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

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

■ Reading a table of $E^\ominus$ values

A **standard electrode potential** $E^\ominus$ is measured against the **standard hydrogen electrode** ($E^\ominus = 0.00\text{ V}$) 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:

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

A **positive** $E_{\text{cell}}^\ominus$ means the reaction is **feasible** — thermodynamically. Δ 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 $E^\ominus(\text{Zn}^{2+}/\text{Zn}) = -0.76\text{ V}$ and $E^\ominus(\text{Cu}^{2+}/\text{Cu}) = +0.34\text{ V}$, deduce the cell reaction and $E_{\text{cell}}^\ominus$.

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. $E_{\text{cell}}^\ominus = +0.34 - (-0.76) = +1.10\text{ V}$, positive, so the reaction is feasible.

2 Practice

2.1 Describe the standard hydrogen electrode. [2]

2.2 State the condition on $E_{\text{cell}}^\ominus$ 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 $E_{\text{cell}}^\ominus$ 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 | B |
| C | D |
- 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 | B |
| C | D |
- A more positive
B more negative
C unchanged
D zero

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

(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	$E^\ominus / \text{V}$
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.52
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}$	+0.15
$\text{V}^{3+} + \text{e}^- \rightleftharpoons \text{V}^{2+}$	-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 $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell is made with $[\text{Fe}^{3+}] = 2.0 \text{ mol dm}^{-3}$ and $[\text{Fe}^{2+}] = 1.0 \text{ mol dm}^{-3}$. State and explain the effect on its electrode potential. [2]