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

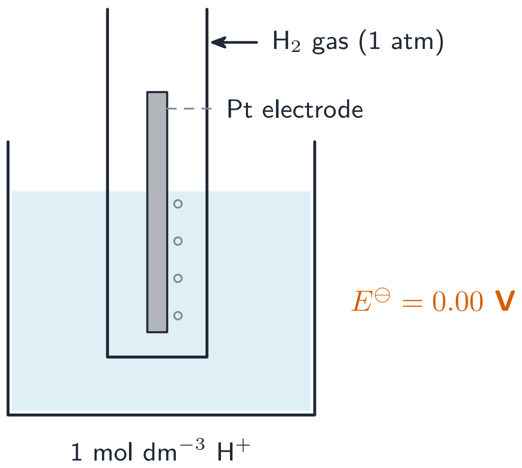
Build the skills to answer exam questions on **standard electrode potentials 标准电极电势** — the **standard hydrogen electrode 标准氢电极**, **cell potentials 电池电势**, **feasibility 可行性**, and the **Nernst equation 能斯特方程**.

You must be able to:

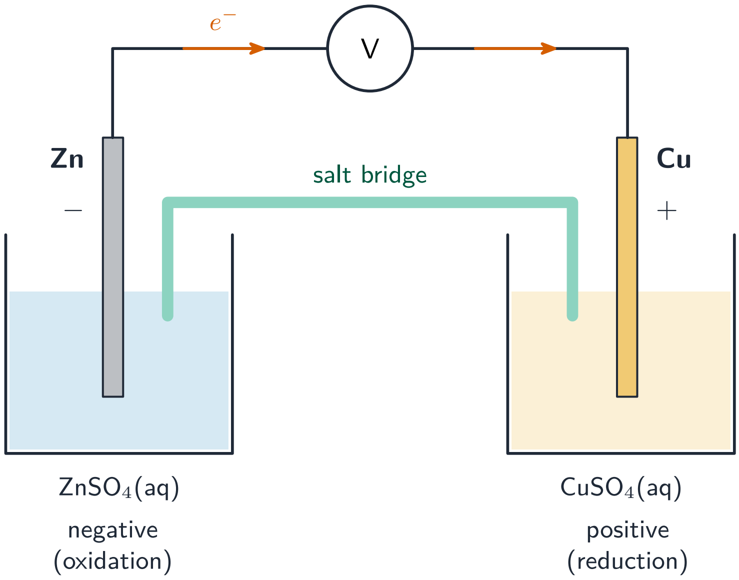
- describe the standard hydrogen electrode and how $E^\ominus$ is measured
- calculate a cell potential and deduce polarity, electron flow and feasibility
- use $E^\ominus$ values to compare oxidising/reducing agents and construct redox equations

1 Worked examples

■ Electrode and cell potentials



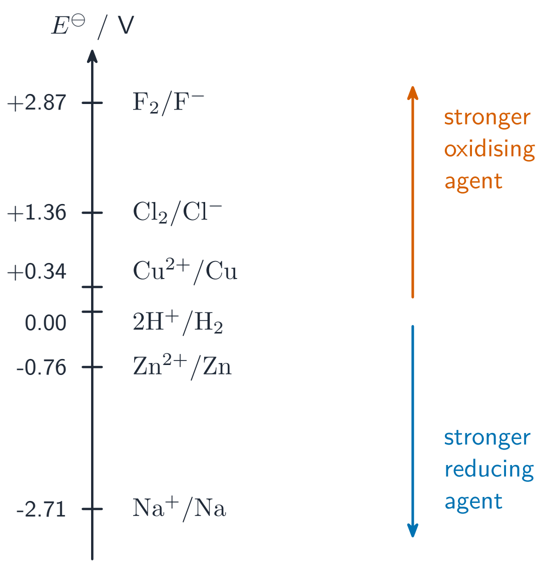
$E^\ominus$ is measured against the standard hydrogen electrode (defined as 0.00 V), under standard conditions, as a reduction



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

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

■ Feasibility and the series



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

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

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

A **standard electrode potential** $E^\ominus$ is measured against the **standard hydrogen electrode** ($E^\ominus = 0.00$ 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** $E^\ominus_{\textbf{cell}}$ 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 $E^\ominus(Zn^{2+}/Zn) = -0.76$ V and $E^\ominus(Cu^{2+}/Cu) = +0.34$ V, deduce the cell reaction and $E^\ominus_{\text{cell}}$.

1. The more positive electrode is reduced: $Cu^{2+} + 2e^- \rightarrow Cu$.
2. The more negative is oxidised, so its equation is reversed: $Zn \rightarrow Zn^{2+} + 2e^-$.
3. Overall: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$.
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 $E^\ominus_{cell}$ does not guarantee that a reaction is observed. [2]

2.5 State the effect on $E^\ominus(Fe^{3+}/Fe^{2+})$ of increasing $[Fe^{3+}]$, 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 $E^\ominus_{cell}$. [4]

(c) Write the overall ionic equation for the reaction of acidified MnO_4^- with Fe^{2+}, and calculate $E^\ominus_{cell}$. [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 $[Fe^{3+}] = 2.0\ \text{mol dm}^{-3}$ and $[Fe^{2+}] = 1.0\ \text{mol dm}^{-3}$. State and explain the effect on its electrode potential. [2]