

CHAPTER 2 • ELECTROCHEMISTRY

2.2.1 Measurement of Electrode Potential

Understanding cell potential, the measurement problem, and the Standard Hydrogen Electrode (SHE).



Topic 2.2.1

Exam-Smart Review

Core Concepts

Defining Cell Potential and emf

Cell Potential:

The electrical potential difference between the two electrodes of a galvanic cell. It is measured in volts (V).

Electromotive Force (emf):

The specific cell potential measured when **no current** is drawn through the cell.

IUPAC Cell Convention



$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

i Takeaway: The anode is always placed on the left, and the cathode is always placed on the right.

The Limits of the Voltmeter



The Physical Limit

A voltmeter measures the **difference** in electrical potential between two distinct points. It is physically impossible to measure the absolute potential of a single, isolated half-cell because there is no closed circuit.

The Relative Solution

To find the potential of one electrode, we must pair it with a reference electrode. By arbitrarily assigning a potential of 0.00 V to one specific half-cell, the voltmeter's reading will equal the exact potential of the unknown half-cell.

Key Concept: Absolute potential is unmeasurable; we can only measure *relative* potential differences.



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$$E=mc^2$$



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The Standard Hydrogen Electrode (SHE)

Name:

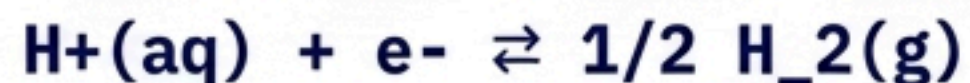
Standard Hydrogen Electrode

Assigned Potential:

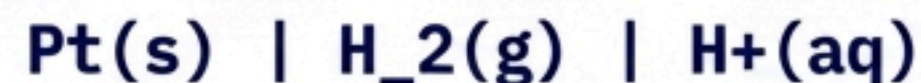
0.00 V

(At all temperatures)

The Reaction



Cell Notation

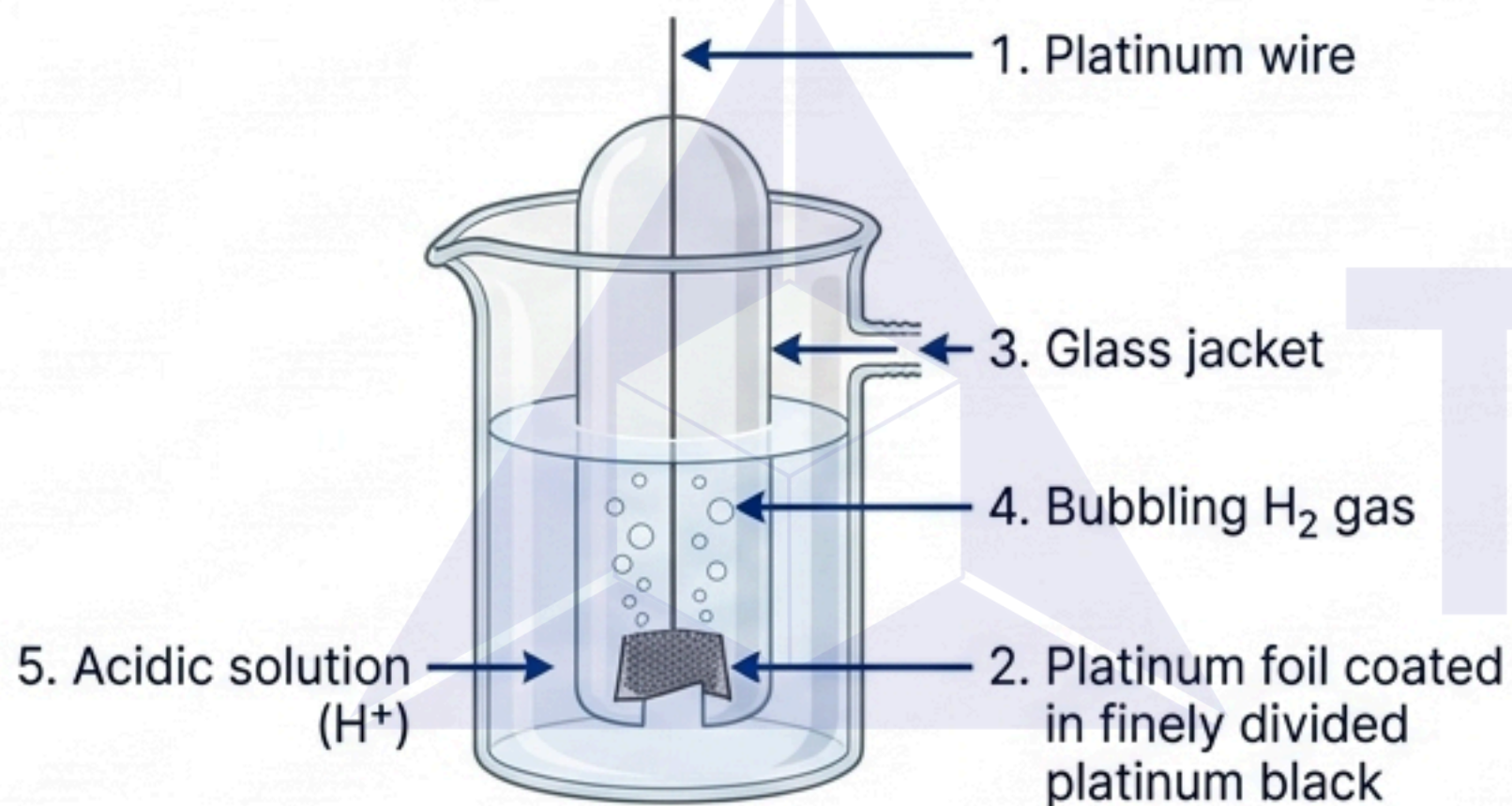


The Function

SHE acts as the **universal zero mark** on the electrochemical ruler.

When paired with another half-cell, the resulting emf directly gives the **standard electrode potential (E°)** of that specific half-cell.

Construction & Standard Conditions



Condition 1: Pressure of H₂ gas = 1 bar

Condition 2: Concentration of H⁺ ions = 1 M

Condition 3: Temperature = 298 K

Why Platinum?

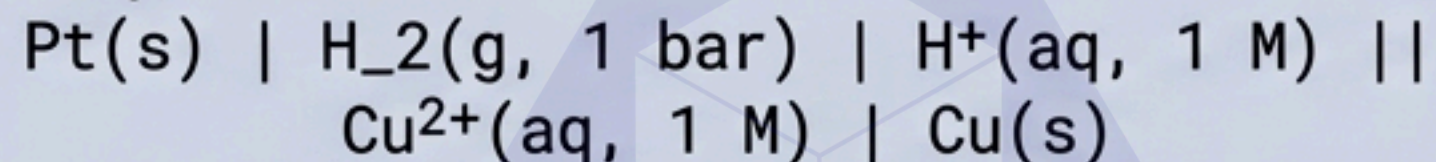
Platinum is an inert metal. It conducts electrons and provides a surface for the oxidation/reduction reaction to occur, but it does not participate in the chemical reaction itself.

Measuring Unknown Potentials

By pairing unknown half-cells with SHE, we determine their Standard Reduction Potentials (E°).

Copper vs. SHE (Right-side Cathode)

Setup Notation:



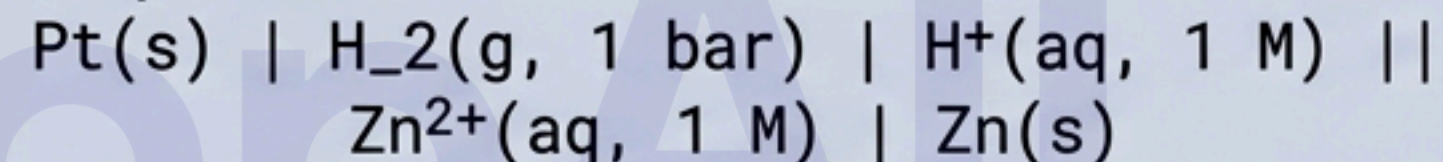
Voltmeter Reading:

+0.34 V

Meaning: A positive value means Cu^{2+} ions get reduced more easily than H^+ ions. Copper acts as the cathode.

Zinc vs. SHE (Right-side Anode)

Setup Notation:



Voltmeter Reading:

-0.76 V

Meaning: A negative value means H^+ ions reduce more easily than Zn^{2+} . Hydrogen oxidizes the zinc. Zinc acts as the anode.

Rule: Positive E° = Weaker reducing agent than H_2 . Negative E° = Stronger reducing agent than H_2 .

Calculating Standard Cell Potential

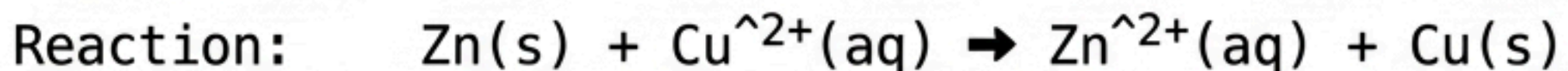
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{right}} - E^{\circ}_{\text{left}}$$

Step 1: Establish Standard Reduction Potentials (E°) using the SHE.

Step 2: Identify the Anode (oxidation, left) and Cathode (reduction, right).

Step 3: Subtract the left electrode's potential from the right electrode's potential.

Example: The Daniell Cell



Calculation: $E^{\circ}_{\text{cell}} = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$



Exam Checklist: Remember: standard potentials are inherently reduction potentials. Do not flip the signs before subtracting. The negative sign in the formula already accounts for the oxidation happening at the anode!



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