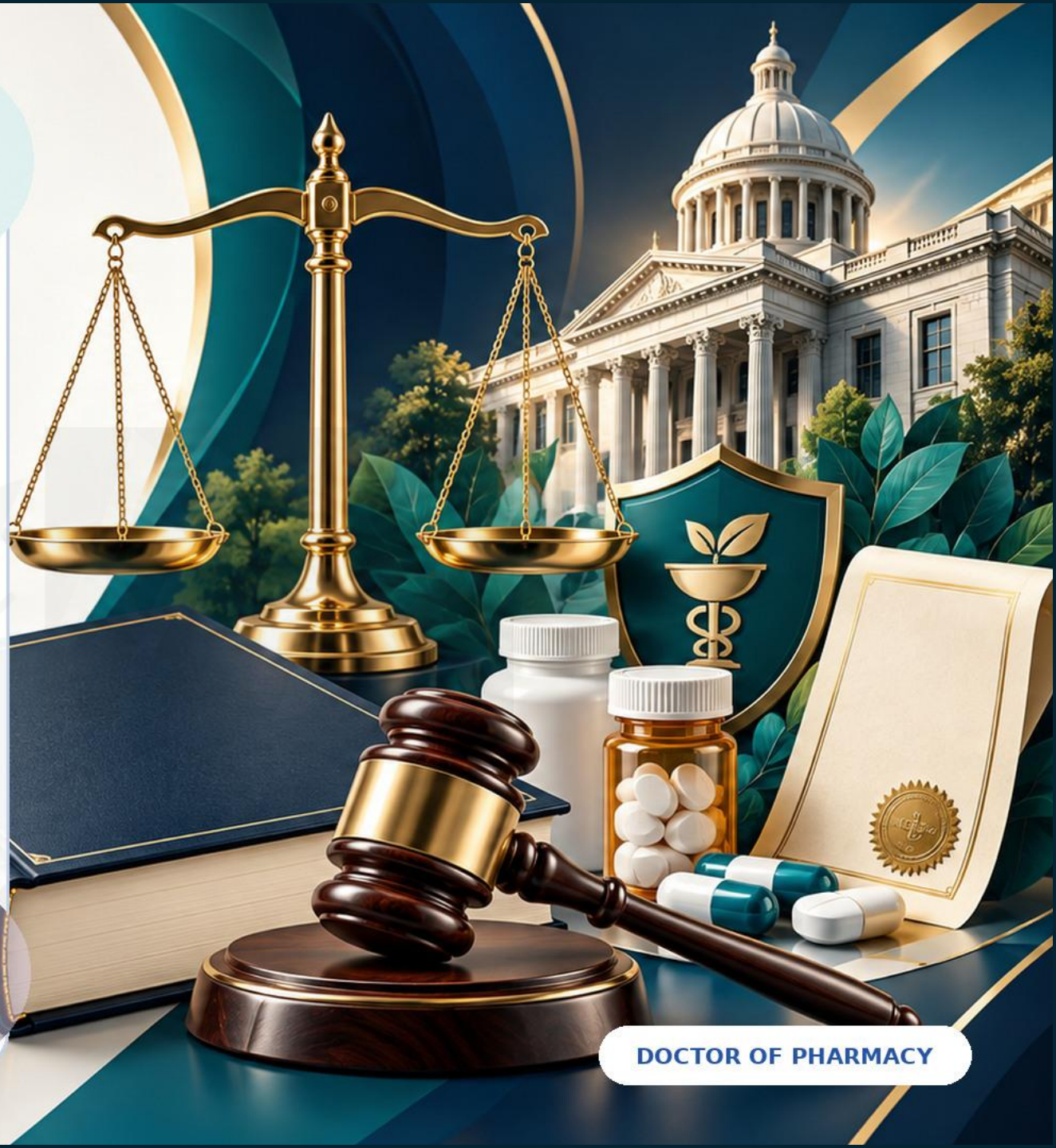
PHARM.D • YEAR 3

Pharmaceutical Analysis

CHAPTER 3.1

Potentiometry

PPT CHAPTER COVER



DOCTOR OF PHARMACY

ELECTROMETRIC METHODS: WHAT IS MEASURED?

Electrometric analysis measures an electrical property related to sample composition.

Potentiometry

- Measures potential at negligible current.

Conductometry

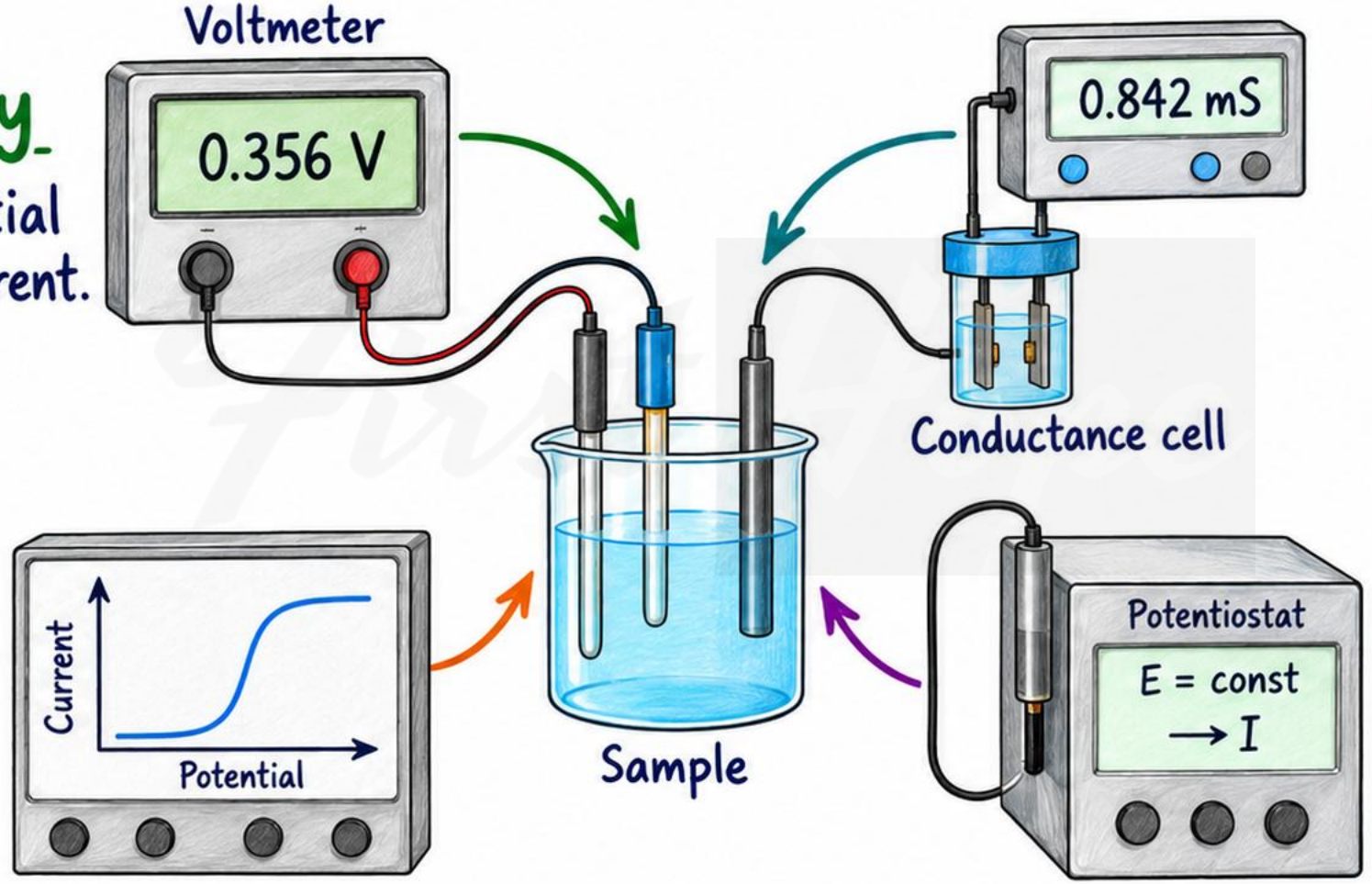
- Measures conductance.

Polarography

- Records current as potential changes.

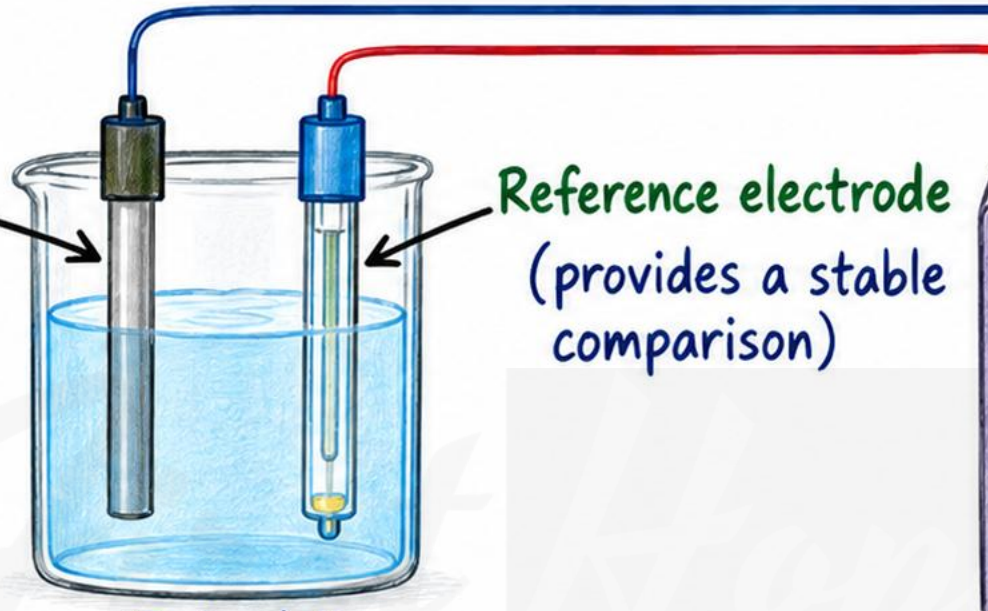
Amperometry

- Measures current at a controlled potential.



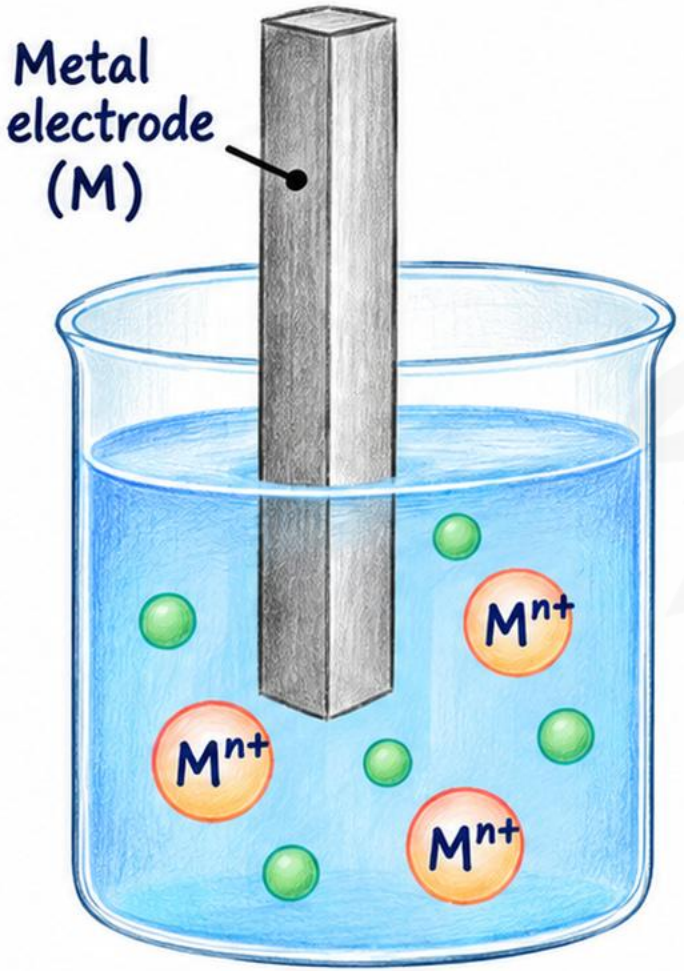
Each method needs suitable electrodes, controlled solution conditions and calibration.
The measured signal and underlying chemical reaction determine which analytical question can be answered.

POTENTIOMETRY: THE BASIC PRINCIPLE



- Potentiometry measures the potential difference between an indicator electrode and a reference electrode using a high-input-impedance meter.
- Very little current flows during measurement.
- The indicator potential responds to the activity of a selected ion or redox system.
- The reference provides a stable comparison.
- Stable temperature, solution composition and junction behaviour are important for reproducible readings.

Potential and the Nernst Equation



Solution containing M^{n+} (activity in Q)

General Nernst equation

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

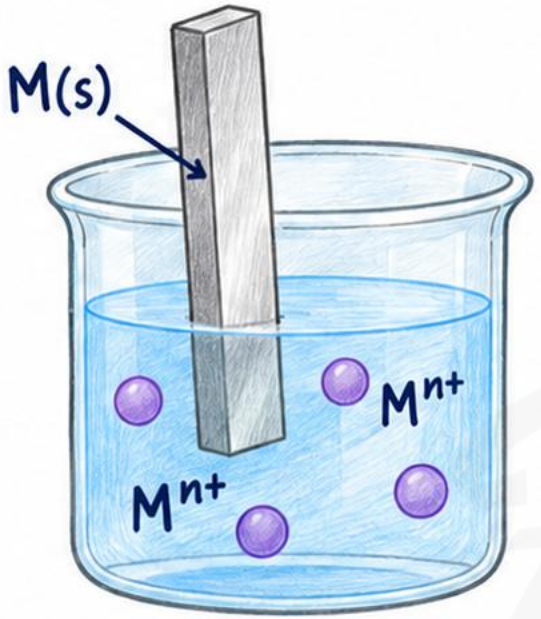
E = electrode potential
E° = standard potential
R = gas constant
T = absolute temperature
n = electron number
F = Faraday constant
Q = reaction quotient

Nernst equation at 25°C

$$E = E^\circ - \frac{0.05916}{n} \log_{10} Q$$

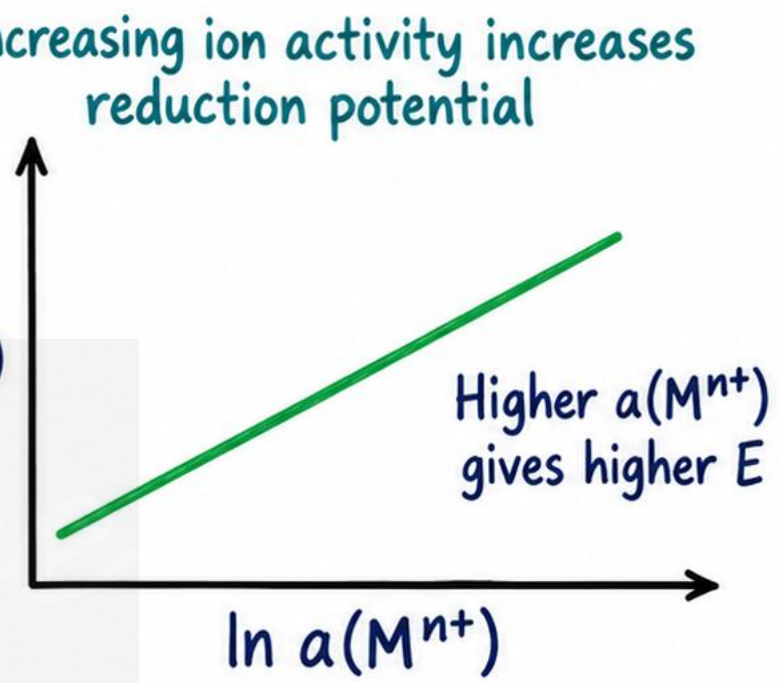
Activities, not simply analytical concentrations, belong in Q.

NERNST SIGN: A METAL-ION EXAMPLE



Metal M(s) dipping in a solution containing M^{n+} ions

$$M^{n+} + n\,e^- \rightleftharpoons M(s)$$



1. REACTION AND REACTION QUOTIENT

- For $M^{n+} + n\,e^- \rightleftharpoons M(s)$, the pure metal has unit activity and $Q = 1/a(M^{n+})$.

2. NERNST EQUATION (POSITIVE SIGN)

- Therefore $E = E^\circ + (RT/nF)\ln a(M^{n+})$.
- At 25°C the slope is +0.05916/n volts per tenfold activity change.

3. IMPORTANT POINT

- The sign follows the written reaction; do not apply one memorized sign indiscriminately to every electrode.

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