Lecture 2 | Electrode-Reaction Stages and Modeling of the Diffuse Double Layer

Al-Farabi Kazakh National University

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Discipline: Modeling in Electrochemistry

Educational program: 7M07103 Chemical Engineering

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Purpose and Expected Learning Outcomes

PURPOSE

Build a quantitative understanding of electrode-reaction stages and modeling of the diffuse double layer.

01 Explain the physical assumptions and governing electrochemical equations.

02 Calculate relevant kinetic, transport, and interfacial parameters.

03 Interpret simulated responses and compare them with measurements.

04 Evaluate model limitations and propose a reproducible validation plan.

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Lecture Trajectory and Practical Relevance



Scientific value: link measurable current, potential, concentration, or impedance to mechanistic parameters.

Applications: electroanalysis • energy conversion • electrodeposition • corrosion • process engineering

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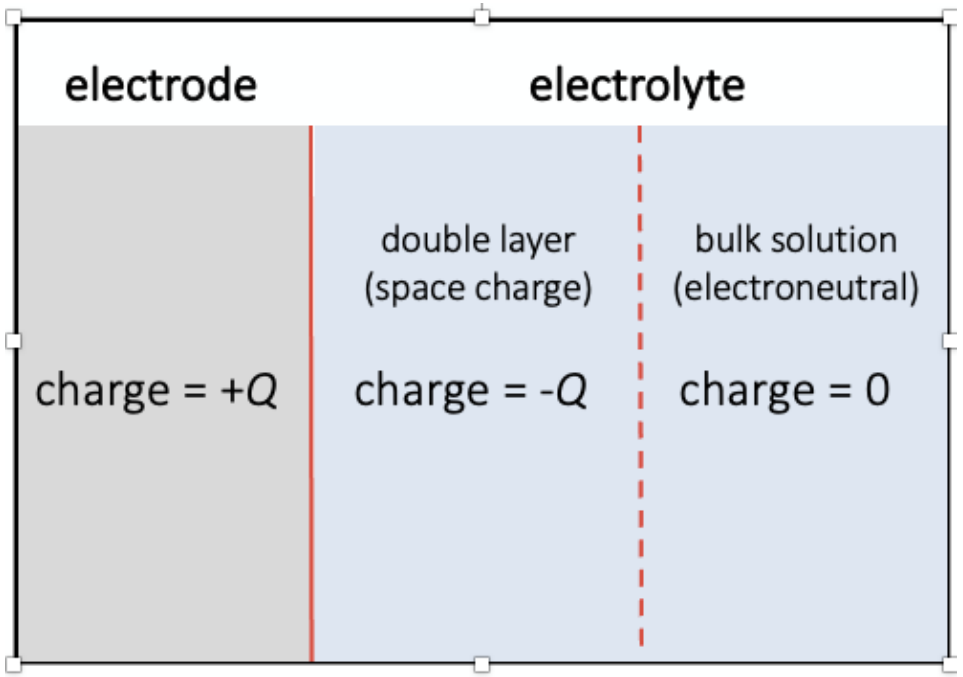
Electrostatic foundations

$$\nabla\cdot(\varepsilon\nabla\phi) = -\rho \; ; \;\; \rho = F\Sigma z_i c_i$$

Charge separation occurs near a polarized interface.

Poisson equation couples electrolyte potential to local ionic concentrations.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

Reference: Bard, Faulkner & White, Electrochemical Methods (3rd ed.)

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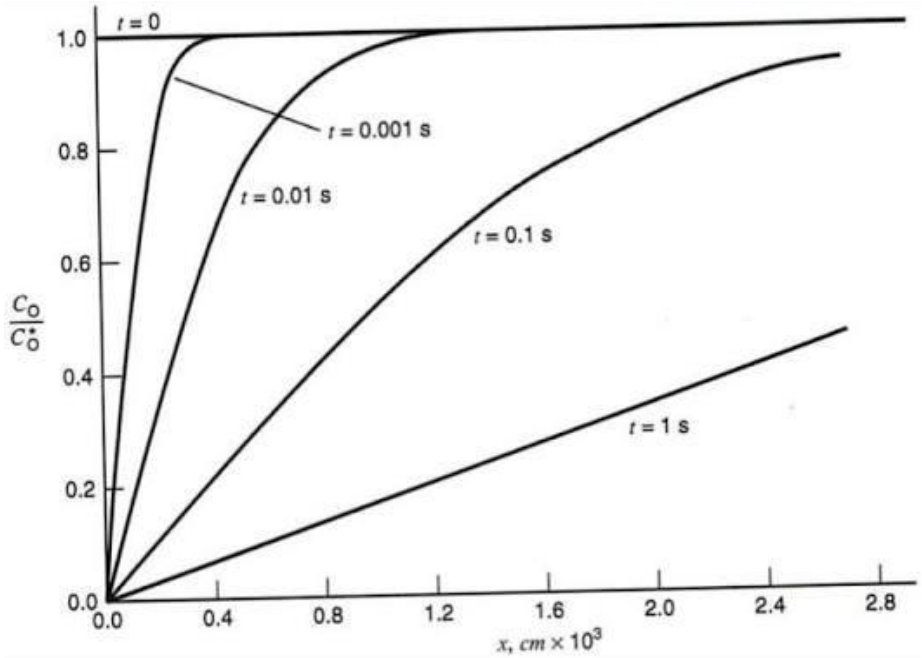
Nernst–Planck transport

$$N_i = -D_i \nabla c_i - (z_i F D_i / RT) c_i \nabla \phi + c_i v$$

Diffusion responds to concentration gradients; migration to electric fields.

Convection is absent in a quiescent electrolyte.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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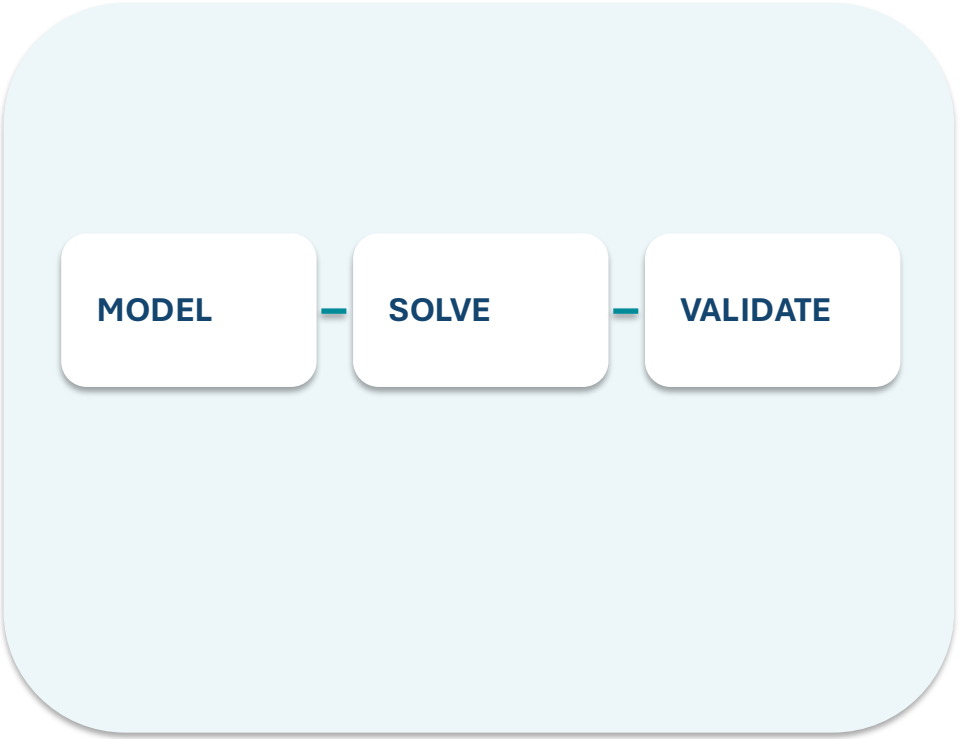
Poisson–Nernst–Planck system

$$\partial c_i/\partial t = -\nabla \cdot N_i$$

Solve ion conservation together with electrostatics.

The dilute-solution model neglects finite ion size and correlations.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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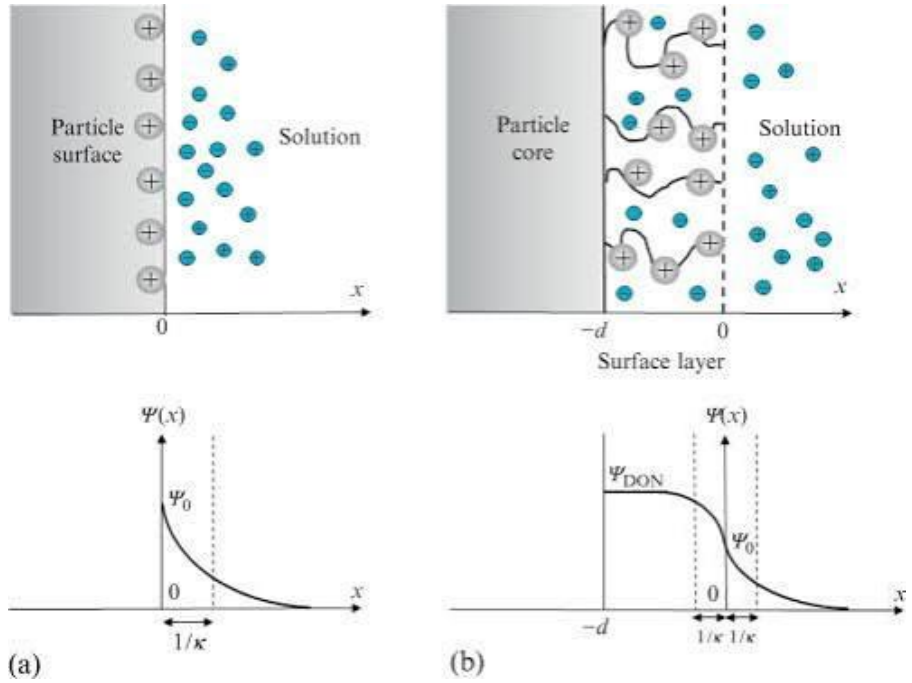
Debye screening and ionic strength

$$\lambda_D = \sqrt{(\varepsilon RT/(2F^2 I))}$$

$I = \frac{1}{2}\Sigma z_i^2 c_{i,bulk}$ with c_i in mol m^{-3}.

Screening length decreases as electrolyte ionic strength increases.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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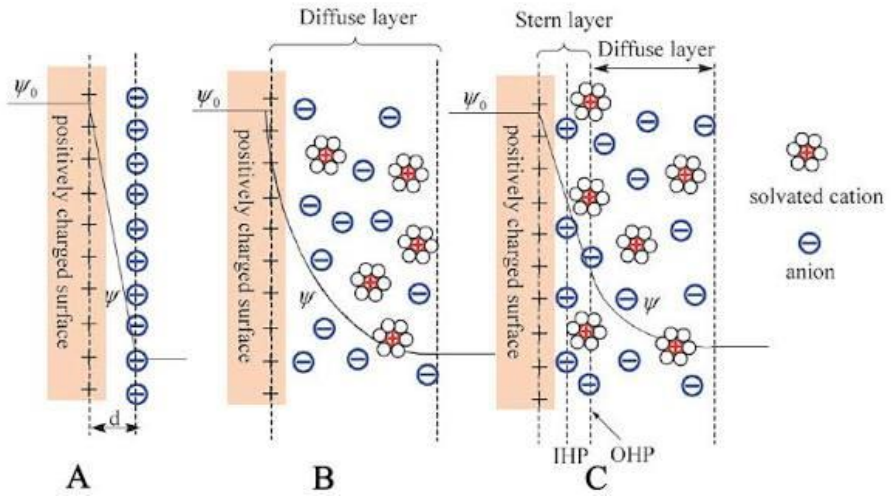
Gouy–Chapman–Stern description

$$1/C_{dl} \approx 1/C_S + 1/C_D$$

The compact Stern region and diffuse region act as series capacitances.

Specific adsorption and concentrated electrolytes require extended models.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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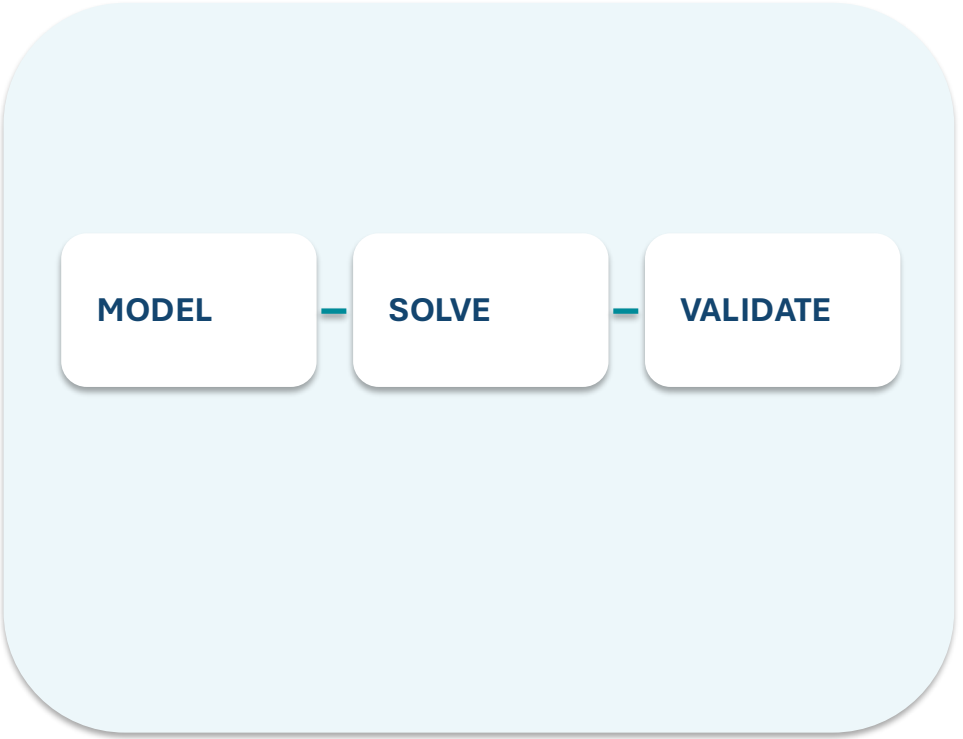
Numerical setup and validation

$$\phi_{(bulk)}=0 \; ; \; \Sigma z_i c_{i,bulk}=0$$

Choose bulk boundaries several Debye lengths away.

Use mesh refinement near the interface and verify global charge balance.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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Conclusions: From Physical Mechanisms to Predictive Models

1. Electrostatic foundations

$\nabla\cdot(\varepsilon\nabla\phi) = -\rho\ ;\ \rho = F\Sigma z_i c_i$

2. Nernst–Planck transport

$N_i = -D_i\nabla c_i - (z_i F D_i/RT)c_i\nabla\phi + c_i v$

3. Poisson–Nernst–Planck system

$\partial ci/\partial t = -\nabla\cdot N_i$

4. Debye screening and ionic strength

$\lambda D = \sqrt{(\varepsilon RT/(2F^2 I))}$

5. Gouy–Chapman–Stern description

$1/C_{dl} \approx 1/C_S + 1/C_D$

6. Numerical setup and validation

$\phi(bulk)=0\ ;\ \Sigma zici,bulk=0$

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Homework: Quantitative and Research-Oriented Problems

CONCEPTUAL Compare the assumptions underlying “Electrostatic foundations” and “Poisson–Nernst–Planck system”.

CALCULATION Given $T = 298.15$ K, $F = 96485$ C mol^{-1}, $R = 8.314$ J mol^{-1} K^{-1}, $D = 1.0 \times 10^{-9}$ m^2 s^{-1}, $c = 1.0$ mol m^{-3}, $A = 1.0$ cm^2, $n = 1$, compute a relevant transport or kinetic prediction and state assumptions.

DATA INTERPRETATION For simulated normalized signals (t/s, response): (0.2,0.82), (0.5,0.61), (1.0,0.44), (2.0,0.30), identify the trend and test a plausible physical model.

CRITICAL THINKING Predict how a tenfold change in the controlling kinetic or transport parameter changes the response; distinguish hypotheses.

RESEARCH TASK Design a COMSOL or Python model with geometry, boundary conditions, mesh-convergence test, and an experimental validation plan.

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