HYDRODYNAMIC ELECTROCHEMICAL METHODS

Modern research methods in electrochemistry

7M05301 Chemistry

Al-Farabi Kazakh National University

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

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Purpose and Learning Outcomes

Purpose: connect controlled electrolyte flow with quantitative electrode kinetics.

- Explain forced convection and steady-state diffusion layers.
- Interpret RDE limiting-current plateaus and Levich plots.
- Describe RRDE collection and intermediate detection.
- Estimate diffusion coefficients and distinguish kinetic from transport control.

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Lecture Trajectory: From Flow to Mechanism

01

Flow field

RDE hydrodynamics

02

Transport

Levich equation

03

Kinetics

Koutecký–Levich

04

Detection

RRDE collection

05

Research

Indium electrodeposition

Applications: oxygen reduction • CO_2 electroreduction • corrosion • electrocatalysis • electrodeposition

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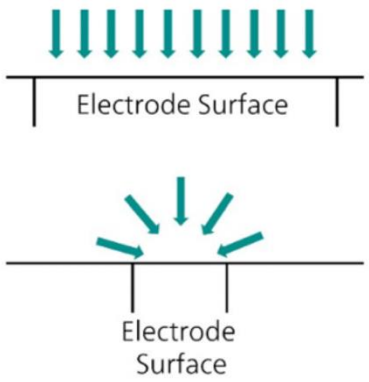
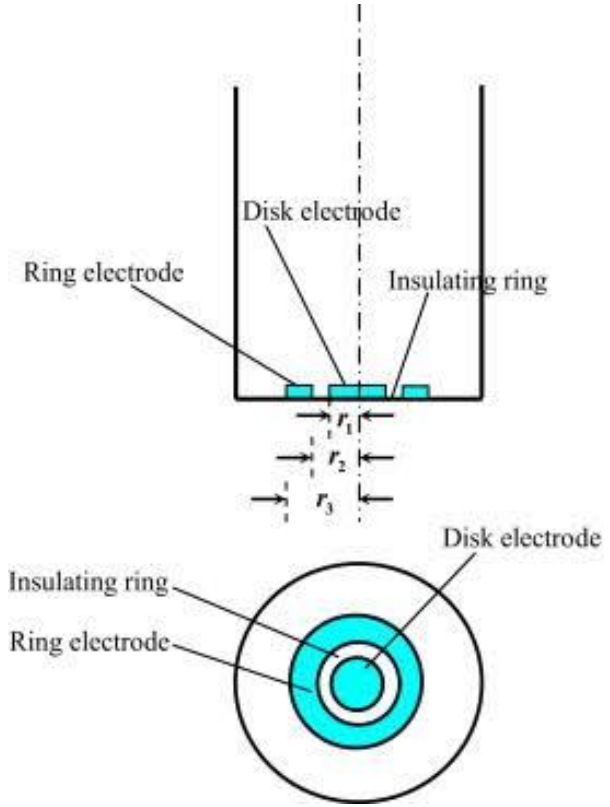
Why Force Convection?

- Unstirred: diffusion layer grows with time.
- RDE: rotation continuously renews solution near the disk.
- At a fixed rotation rate, a stable limiting-current plateau can form.
- Controlled flow makes kinetic comparisons reproducible.





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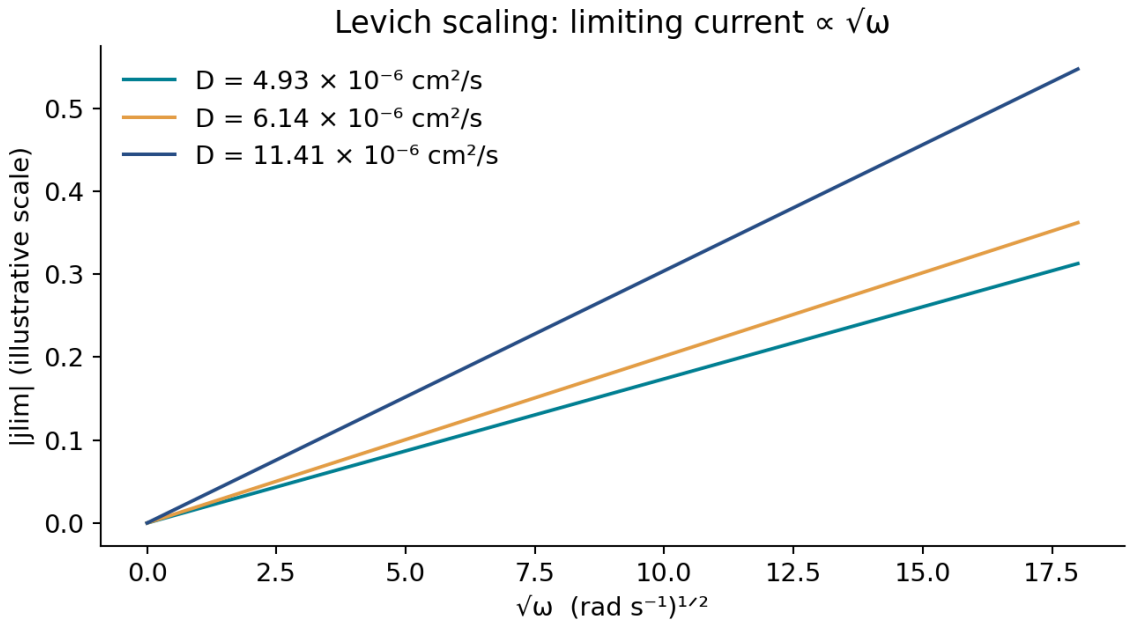
Rotating Disk Electrode: Levich Equation

$$|j_L| = 0.620\, n\, F\, D^{2/3}\, \nu^{-1/6}\, C^{*}\, \omega^{1/2}$$

- n electrons transferred
- D diffusion coefficient ($cm^2\ s^{-1}$)
- ν kinematic viscosity ($cm^2\ s^{-1}$)
- C^* bulk concentration ($mol\ cm^{-3}$)
- ω angular velocity ($rad\ s^{-1}$)



Experimental test: plot $|j_L|$ versus $\sqrt{\omega}$; slope yields D if n, ν and C^* are known.

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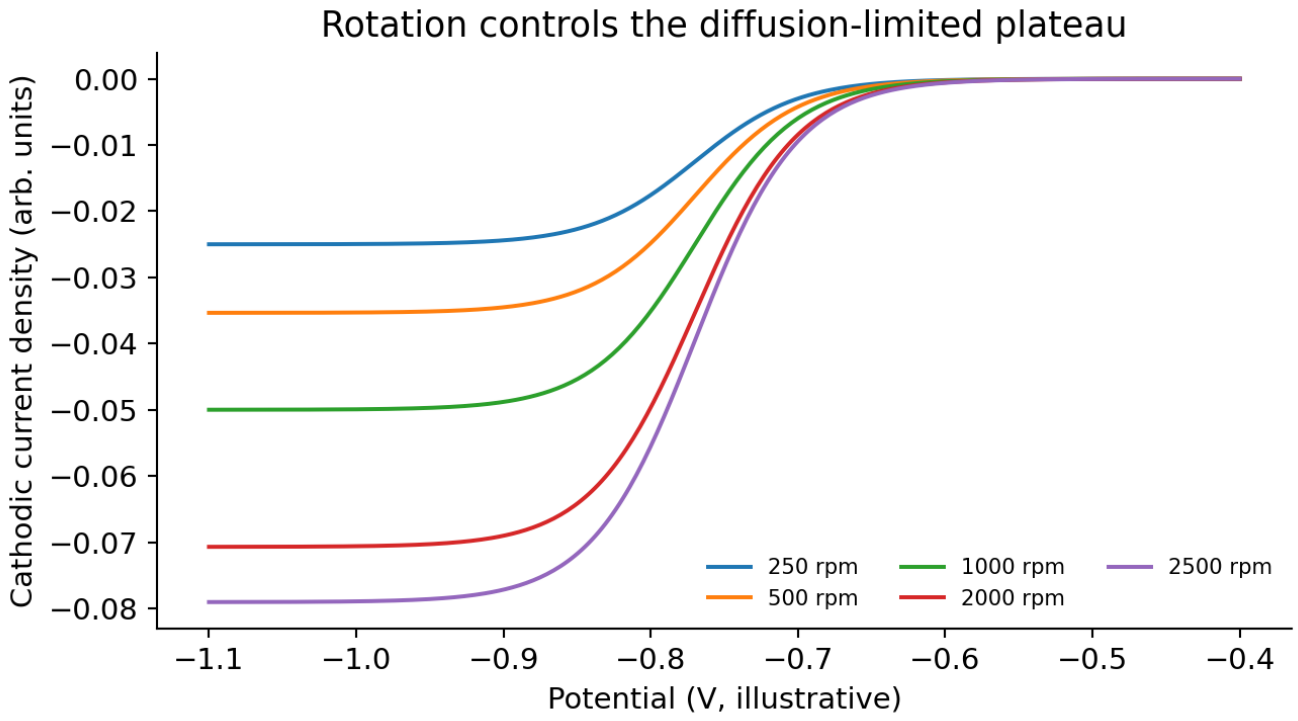
How Rotation Changes a Polarization Curve



- Higher rpm → thinner diffusion layer.
- Plateau magnitude increases with $\sqrt{\omega}$.
- A plateau is transport-limited, not a kinetic ceiling.
- Deposition and surface changes can complicate ideal RDE behavior.

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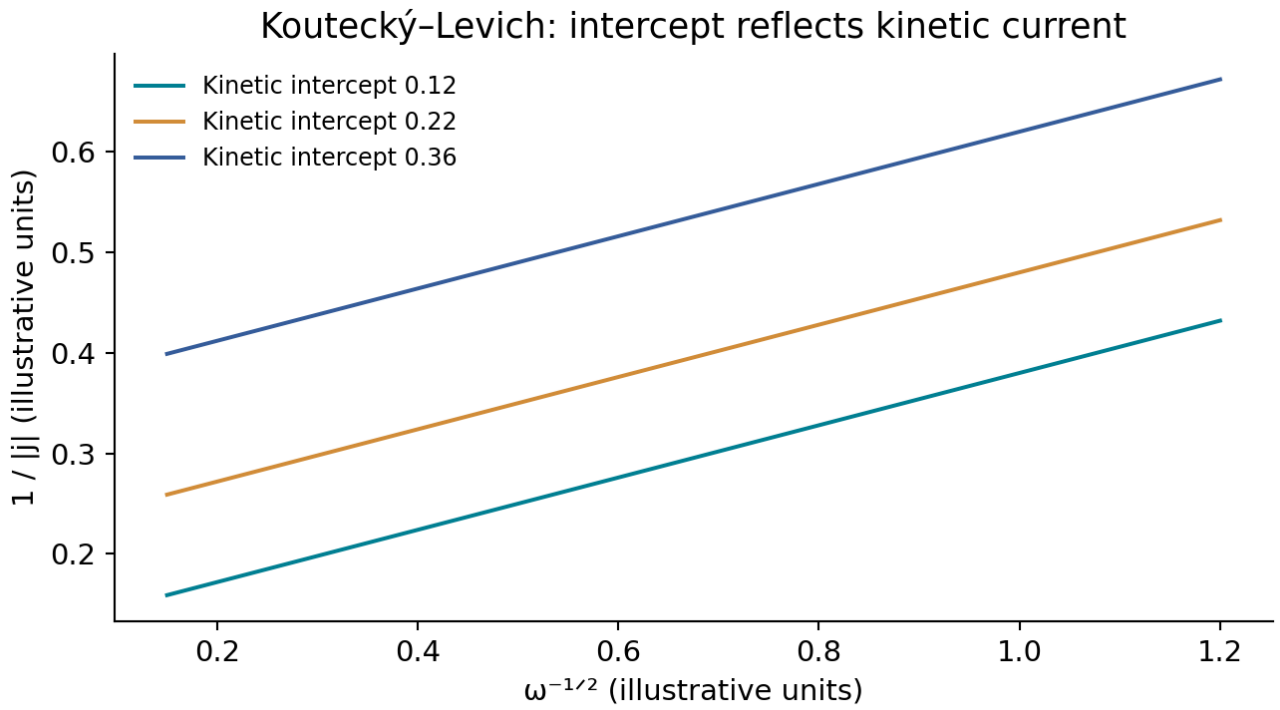
Separating Charge Transfer and Mass Transport

1 / |j| = 1 / |jk| + 1 / |jL|



- At a fixed potential, measure current at several rotation rates.
- Plot $1/|j|$ against $\omega^{-1/2}$.
- Intercept estimates $1/|jk|$ under model assumptions.
- Check linearity, electrode stability and reaction order.

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RRDE: Detecting Species Leaving the Disk



Top view: disk / insulating gap / ring

- Disk generates a soluble intermediate.
- Rotation carries a fraction toward the ring.
- Ring potential is selected to oxidize or reduce the product.
- Collection efficiency N = |iR| / |iD| for an ideal one-product collection case.
- Ring signals depend on selectivity, collection efficiency and side reactions.

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Research Example: Indium in Chloride Electrolyte

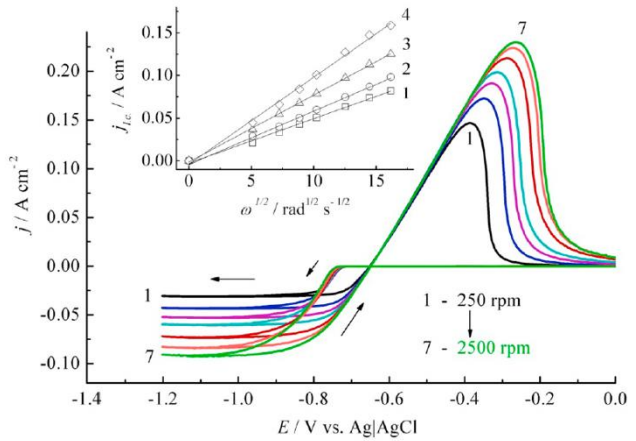

Fig. 2. Cyclic voltammograms obtained at 25 °C on GC electrode in 0.05 M $InCl_3$ + 2 M NaCl solution for various rotating rates (250, 500, 750, 1000, 1500, 2000 and 2500 rpm). Scan rate of 10 mV s^{-1}. Inset: Levich plot performed at various temperatures: 1–25 °C; 2–35 °C; 3–45 °C; 4–55 °C.

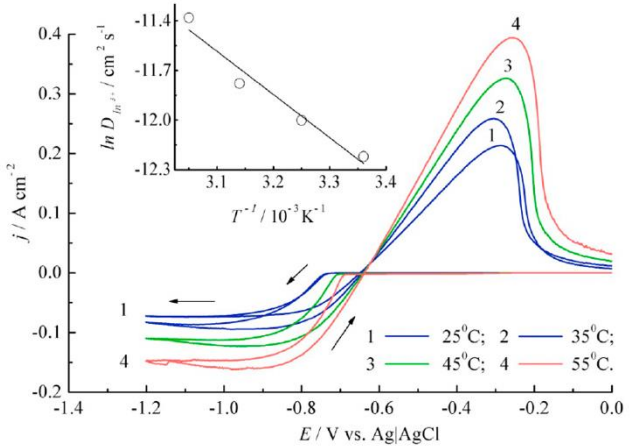

Fig. 3. Cyclic voltammograms obtained at the rotation rate 2000 rpm on GC electrode in 0.05 M $InCl_3$ + 2 M NaCl solution for various temperatures. Scan rate of 10 mV s^{-1}. Inset: evolution of $D_{In^{3+}}$ versus T^{-1} (R^2 = 0.97).

Table 1
The diffusion coefficients of In^{3+} ions and the activation energy of diffusion for a blank electrolyte (BE) and blank electrolyte containing 10^{-4} M tetrabutylammonium chloride solution (ME), respectively.

$D_{In^{3+}}$ (10^{-6} cm^2 s^{-1})			
T, °C	BE		ME
	RDE method	*Eq. (1)*	*RDE method*
25	4.93	8.99	2.13
35	6.14	11.39	4.69
45	7.67	14.07	6.68
55	11.41	17.02	9.54
		E_a (kJ mol^{-1})	
	22.2		39.6

Source: Avchukir et al., Journal of Electroanalytical Chemistry 842 (2019) 176–183.

Reported experimental data

- 0.05 M $InCl_3$ + 2 M NaCl; glassy carbon electrode.
- Increasing temperature increases measured $D(In^{3+})$.
- TBACl addition changes apparent diffusion behavior.
- Interpretation requires attention to viscosity, speciation and deposition.

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Conclusions: What Hydrodynamic Methods Reveal

- RDE provides reproducible convection and a controllable mass-transfer rate.
- Levich plots connect rotation-dependent limiting current with diffusion coefficients.
- Koutecký–Levich analysis can separate kinetic and diffusion contributions when assumptions hold.
- RRDE adds product/intermediate detection through collection at the ring.
- Real deposition systems require checking surface evolution and solution chemistry.

Further reading: Bard, Faulkner & White (2022); Chauhan et al., J. Phys. Chem. C (2023).

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Homework and Research Problems

- 1. Derive the predicted ratio of limiting currents at 1600 and 400 rpm (all else constant).
- 2. Convert 900 rpm to angular velocity in rad s^{-1}.
- 3. Given $|i_D|$ = 200 µA, |iR| = 48 µA and N = 0.30, calculate the product fraction collected relative to ideal single-product generation.
- 4. Explain how a Levich plot differs from a Koutecký–Levich plot.
- 5. Using the reported indium data, calculate D(55 °C)/D(25 °C) for both electrolytes; discuss possible causes of differences.
- 6. Propose an RRDE experiment to distinguish a soluble intermediate from direct product formation.

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