Electrochemistry

CHEM 5390

Hydrodynamic Methods

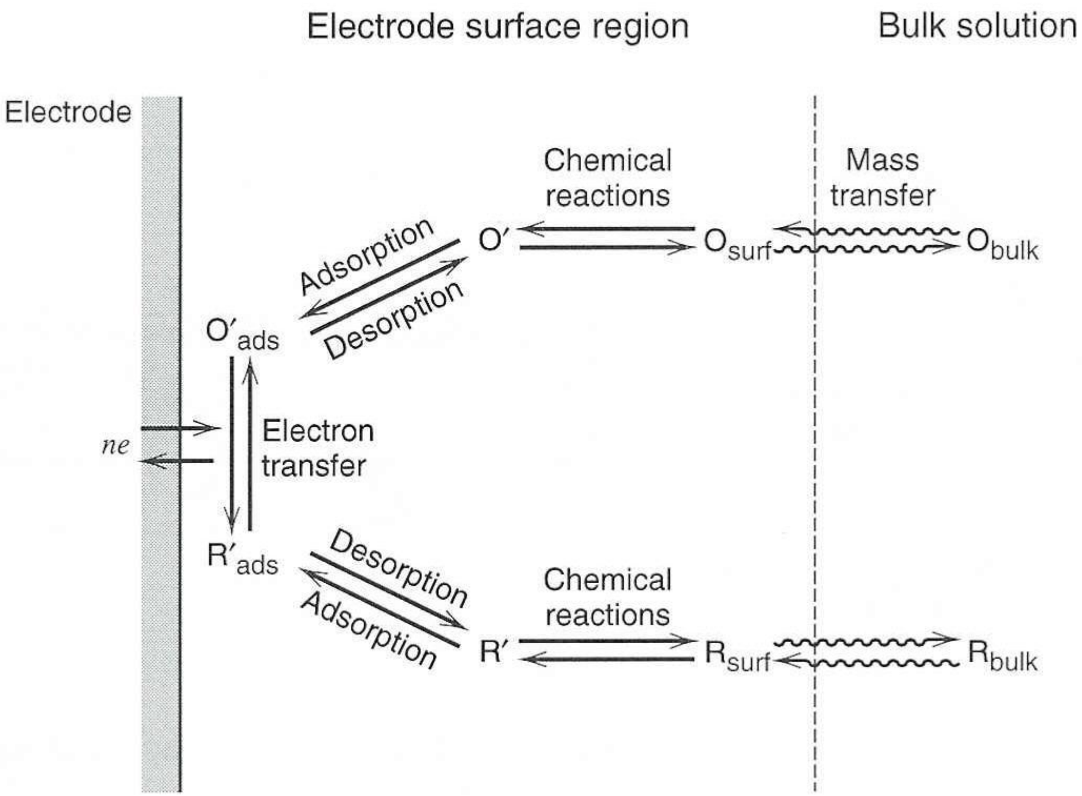


Figure 1.3.6 Pathway of a general electrode reaction.

Hydrodynamic Methods

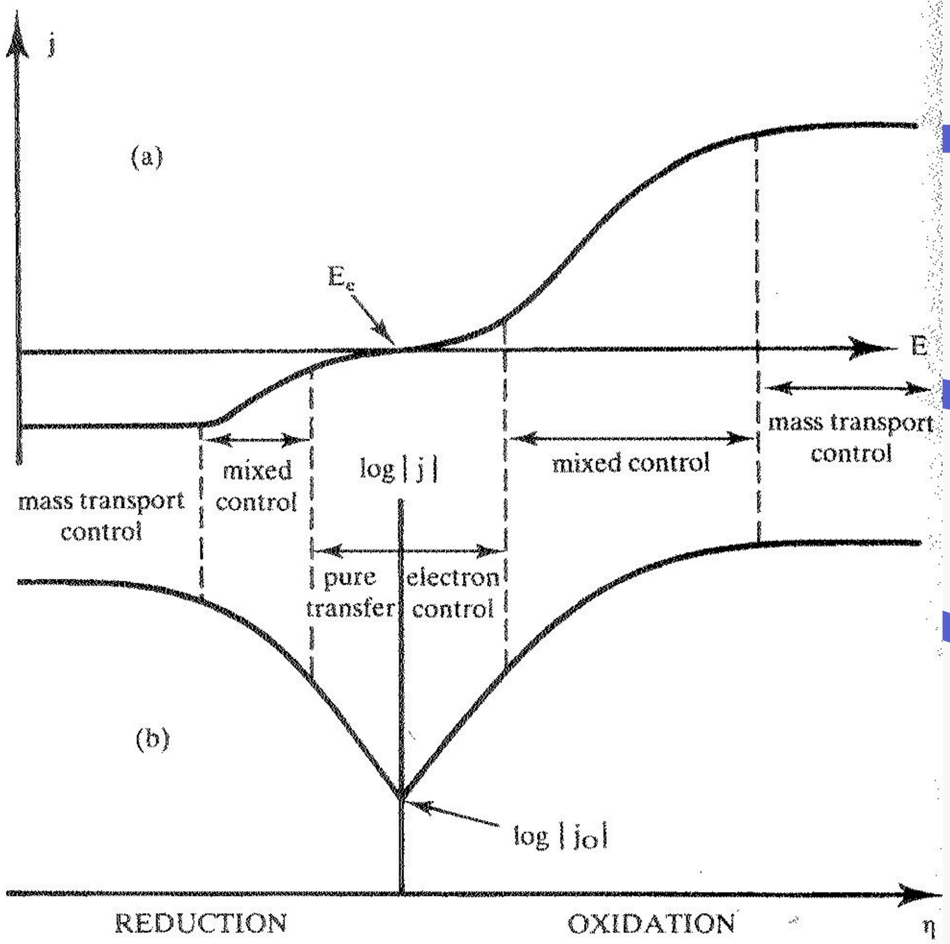


Figure 1.14 *$j - E$ response and the corresponding $\log j - \eta$ curve for an irreversible electrode reaction $O + e^- \rightleftharpoons R$. $c_R = 10c_O$.*

Hydrodynamic Methods

Movement of the solution or electrode during the electrochemical experiment.

Advantages

-steady state is attained quickly

-measurements made with high precision

-rates of mass transfer larger than rates of diffusion

-dual electrode techniques can be used

Disadvantages

-electrode must be reproducible

-theoretical treatment more complicated

Hydrodynamic Methods

Theoretical Treatment

Convective-Diffusion Equation

$$J_j = -D\nabla C_j - Z_jF/RT\ D_jC_j\nabla\phi + C_jv$$

diffusion migration convection

With excess supporting electrolyte the migration term drops out. The velocity vector, v, represents motion of the solution.

$$v(x,y,z) = i\upsilon_x + j\upsilon_y + k\upsilon_z$$

i,j,k – are unit vectors, υ_x, υ_y,υ_z – are magnitudes of the solution velocities in x, y, z directions.

Hydrodynamic Methods

Theoretical Treatment

Assume

-concentration of all species is uniform and equal to the bulk values beyond distance δ.

-within layer, $0 < x < \delta$, no solution movement occurs, mass transfer occurs by diffusion.

This converts the concentration problem to a diffusional one.

Hydrodynamic Methods

Theoretical Treatment

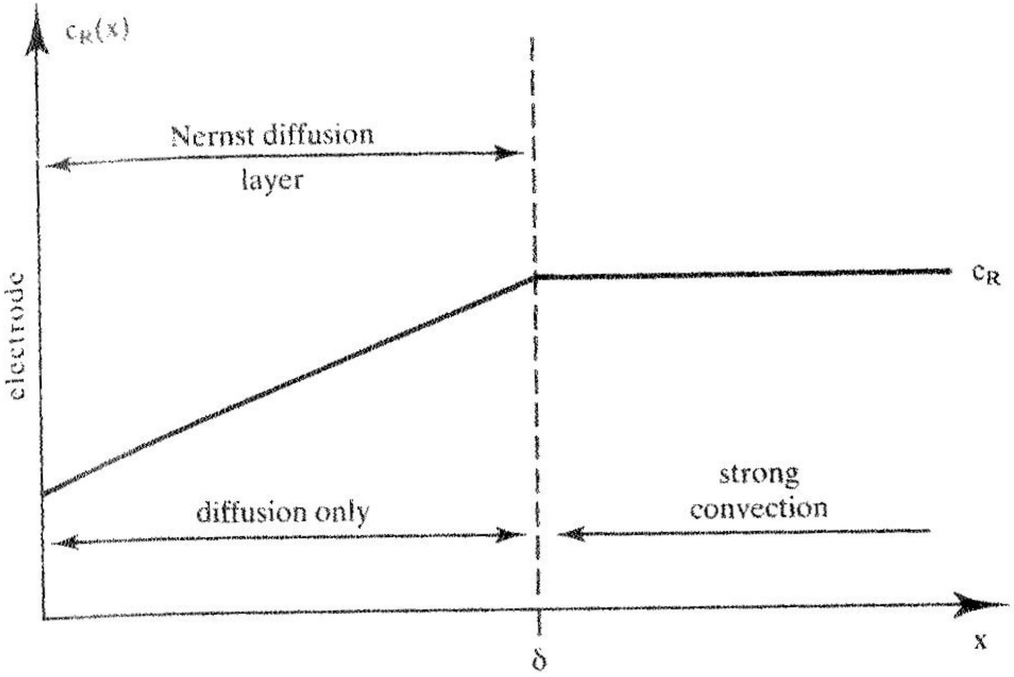


Figure 1.11 *The Nernst diffusion layer model for an oxidation of R → O at a rotating disc electrode. The solution initially contains only R.*

Hydrodynamic Methods

Theoretical Treatment

The experimental results are predicted by the Nernst diffusion layer.

$$\delta = 1.61\,\nu^{0.166}\,D^{0.33}\,\omega^{-0.5}$$

ν – kinematic viscosity (viscosity/density)

ω – rotation rate of the electrode

Hydrodynamic Methods

Theoretical Treatment

For RDE under this type of mass transport (controlled convection),

$$j_L = 0.62\, n\, F\, D^{0.66}\, \nu^{-0.166}\, C_R\, \omega^{0.5}$$

Must assume:

- system is symmetrical about the center of the disk
- there is a uniform supply of electroactive species over the surface of the disk
- only steady state current is measured
- there is laminar flow only

Hydrodynamic Methods

Flow Profiles

Fluid flow in hydrodynamic problems is either laminar (smooth and steady) with a parabolic flow profile or turbulent (unsteady and chaotic) with the net flow in one direction.

Upper and lower limit to the rotation rate of the electrode (upper ~500 radians/sec)

Hydrodynamic Methods

Flow Profiles

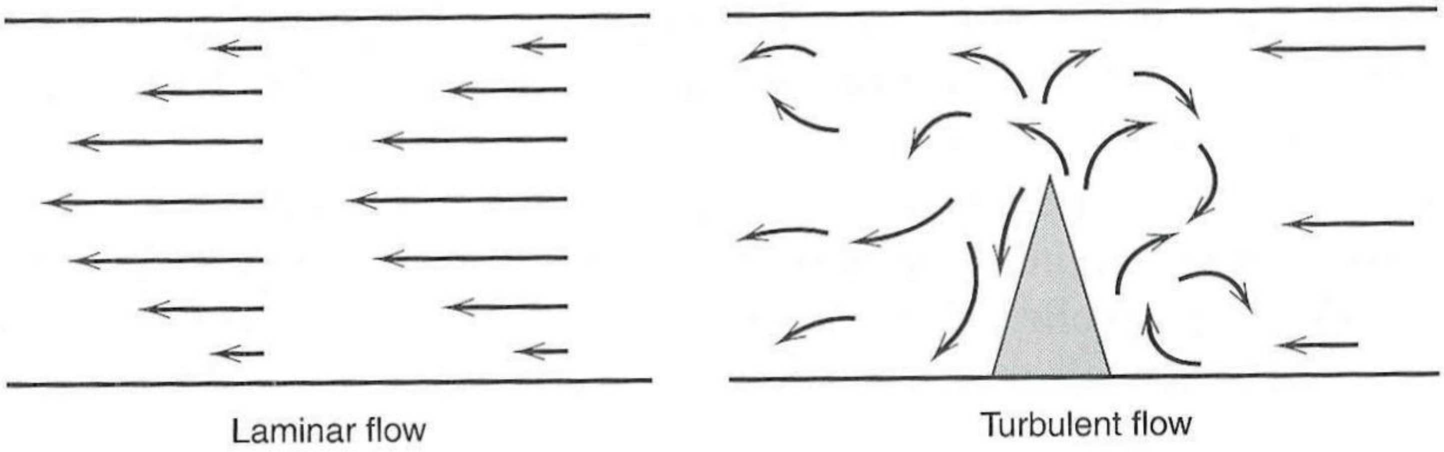


Figure 9.2.1 Types of fluid flow. Arrows represent instantaneous local fluid velocities.

$2 < \omega/2\pi < 100$ (in rotations per second)

$100 < 60\omega/2\pi < 6000$ (in rpm)

f can be used for the rotation rate in revolutions per second, $\omega = 2\pi f$

Hydrodynamic Methods

Flow Profiles

The solution of hydrodynamic equations require laminar flow.

The equations can be written in terms of dimensionless groups of variables, Reynolds number, Re.

$$Re = \upsilon_{ch} l / v$$

υ_{ch} – characteristic velocity (cm/s)

l – characteristic length (cm)

v – kinematic viscosity (cm^2/s)

Hydrodynamic Methods

Flow Profiles

$$Re = \upsilon_{ch} l / v$$

υ_{ch} – characteristic velocity (cm/s)

l – characteristic length (cm)

v – kinematic viscosity (cm^2/s)

v – kinematic viscosity = η_s/d_s

η_s – viscosity of solution

d_s – density of solution

Hydrodynamic Methods

Flow Profiles

For most aqueous solutions v is close to 0.01cm^2/s

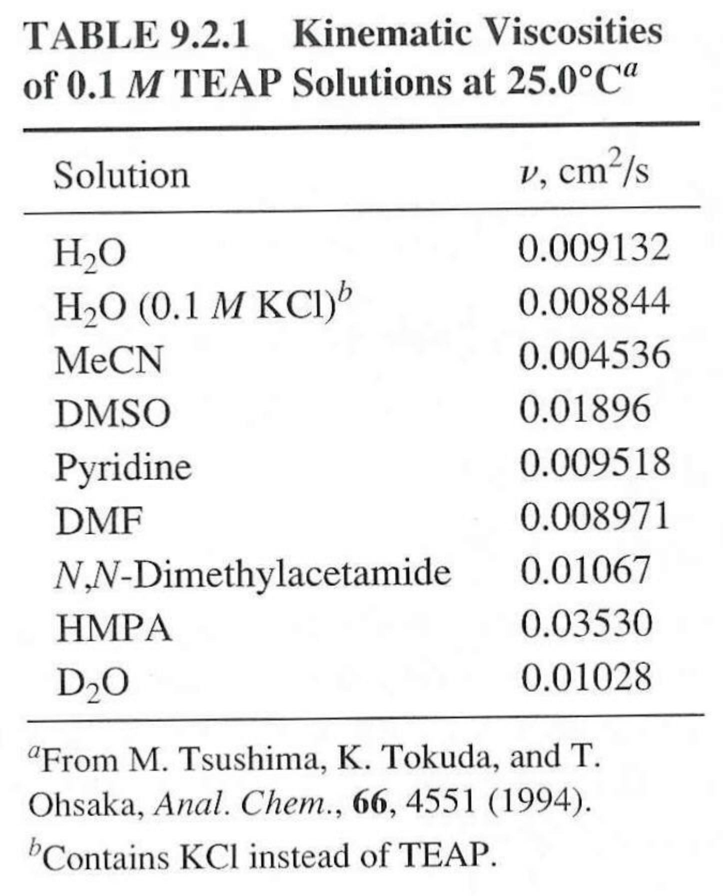


TABLE 9.2.1 Kinematic Viscosities of 0.1 *M* TEAP Solutions at 25.0°C[a]

Solution	ν, cm^2/s
H_2O	0.009132
H_2O (0.1 *M* KCl)[b]	0.008844
MeCN	0.004536
DMSO	0.01896
Pyridine	0.009518
DMF	0.008971
N,*N*-Dimethylacetamide	0.01067
HMPA	0.03530
D_2O	0.01028

[a] From M. Tsushima, K. Tokuda, and T. Ohsaka, *Anal. Chem.*, **66**, 4551 (1994).

[b] Contains KCl instead of TEAP.

Hydrodynamic Methods

Flow Profiles

Reynolds number is proportional to fluid velocity, so high values imply high flow or electrode reaction rates.

At flow rates below the critical Reynolds number, Re_{cr} – flow is laminar.

Hydrodynamic Methods

Current Distributions

Current distributions depend on solution resistance and mass and charge-transfer parameters of the electrode reaction.

Current density is larger at the edge ($r = r_1$) than at the center ($r = 0$), when electrode kinetics and mass-transfer effects are neglected. (Primary curve distribution)

Hydrodynamic Methods

Current Distributions

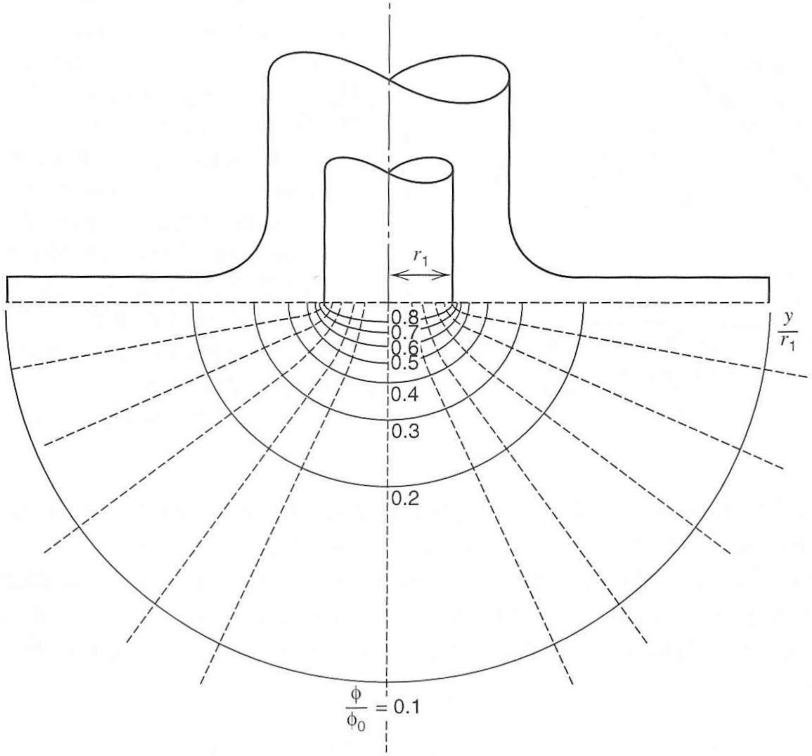


Figure 9.3.9 Primary current distribution at an RDE. Solid lines show lines of equal potential at values of ϕ/ϕ_0, where ϕ_0 is the potential at the electrode surface; that is, ϕ represents the potential of the disk measured against an infinitesimal reference electrode (whose presence does not perturb the current distribution) located at different indicated points in solution. Dotted lines are lines of current flow. The number of lines per unit length represents the current density j. Note that j is higher toward the edge of the disk than at the center. [From J. Newman, *J. Electrochem. Soc.*, **113**, 501 (1966). Reprinted with permission of the publisher, The Electrochemical Society, Inc.]

Hydrodynamic Methods

Current Distributions

When electrode kinetics and mass-transfer effects are taken into account the current distribution (secondary) is more uniform.

$$p = R_\Omega/R_E$$

p – dimensionless parameter for current distribution

R_Ω – overall resistance of solution

R_E – electrode resistance due to charge transfer and concentration polarization

Hydrodynamic Methods

Current Distributions

At high solution resistance and small R_E current distribution looks like the primary.

At low solution resistance and large R_E – distribution is uniform.

Hydrodynamic Methods

Current Distributions

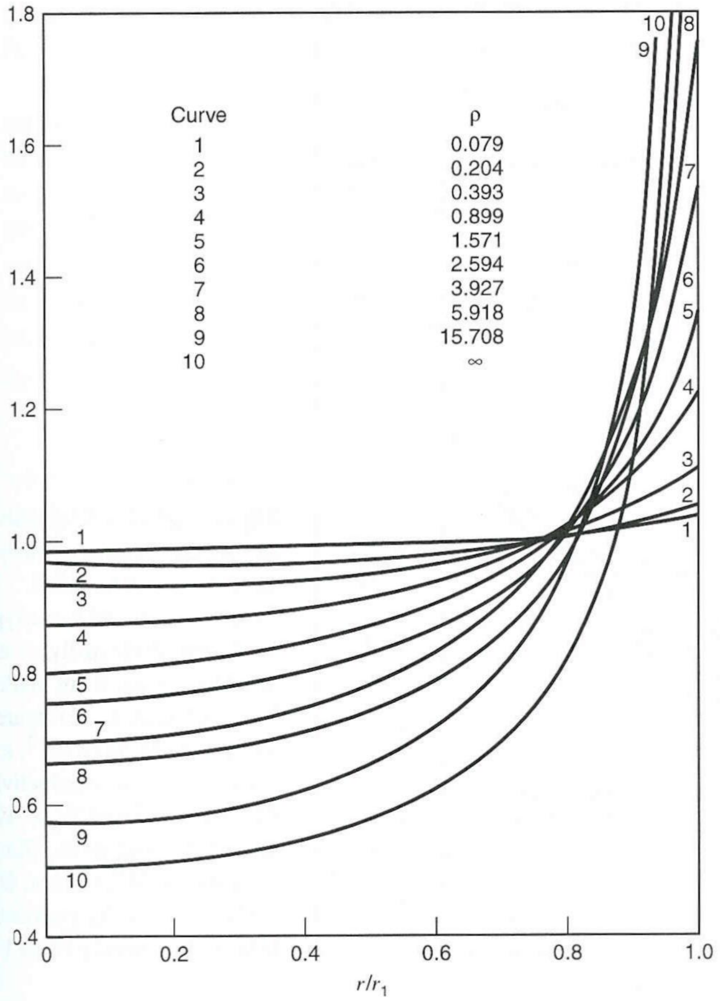


Figure 9.3.10 Secondary current distribution at an RDE. [From J. Newman, *J. Electrochem. Soc.*, **113**, 1235 (1966) as modified by W. J. Albery and M. L. Hitchman, "Ring-Disc Electrodes," Clarendon, Oxford, 1971, Chap. 4, with permission of the publishers, The Electrochemical Society, Inc., and Oxford University Press.]

Hydrodynamic Methods

Experimental Considerations

Theory for RDE breaks down at very small or very large values of ω.

At small values of ω, the hydrodynamic boundary layer becomes large.

The i-E curves are not S-shaped but show a peak similar to a stationary electrode.

Hydrodynamic Methods

Experimental Considerations

At high ω – turbulent flow occurs at a critical Reynolds number, Re_{cr}, larger than 2×10^5.

ω has to be lower than $2 \times 10^5\ s^{-1}$

In practice, maximum rotation rates are at 10,000 rpm or at $\omega = 1000\ s^{-1}$

So RDE studies are done at:

$100\ \text{rpm} < f < 10{,}000\ \text{rpm}$

$10 s^{-1} < \omega < 1000\ s^{-1}$

Hydrodynamic Methods

Levich equation

To test if the mass transport control is correct, can plot j_L versus $\omega^{1/2}$ (should be linear and pass through the origin) and

$j_L \propto C$

Hydrodynamic Methods

Levich equation

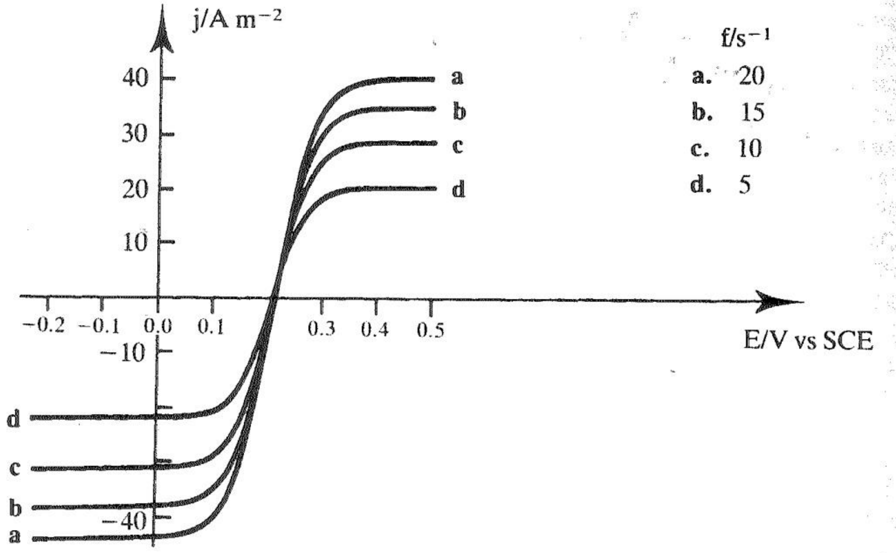


Figure 6.8 *Current density vs potential curves as a function of rotation rate for a solution of ferrocyanide (10 mmol dm^{-3}) and ferricyanide (10 mmol dm^{-3}) in KCl (0.5 mol dm^{-3}) at a gold RDE.*

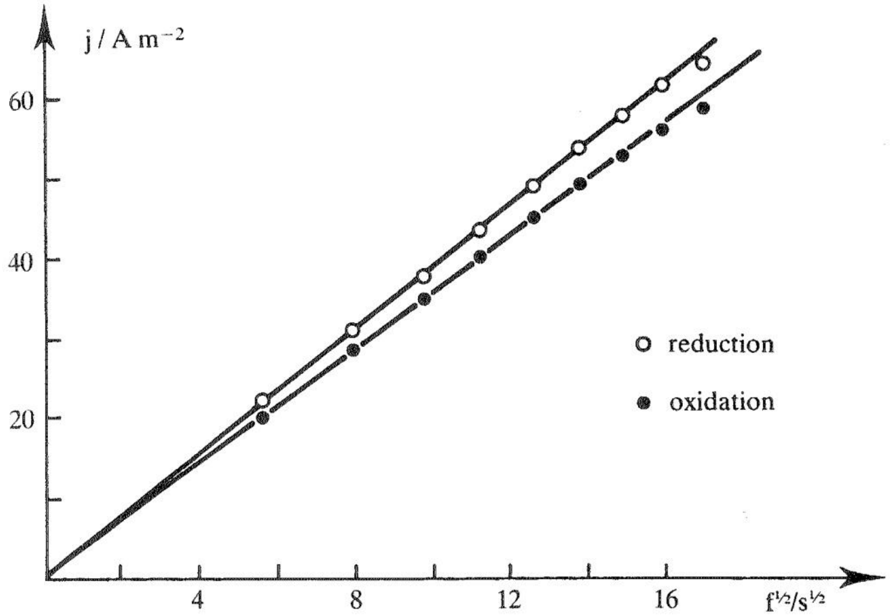
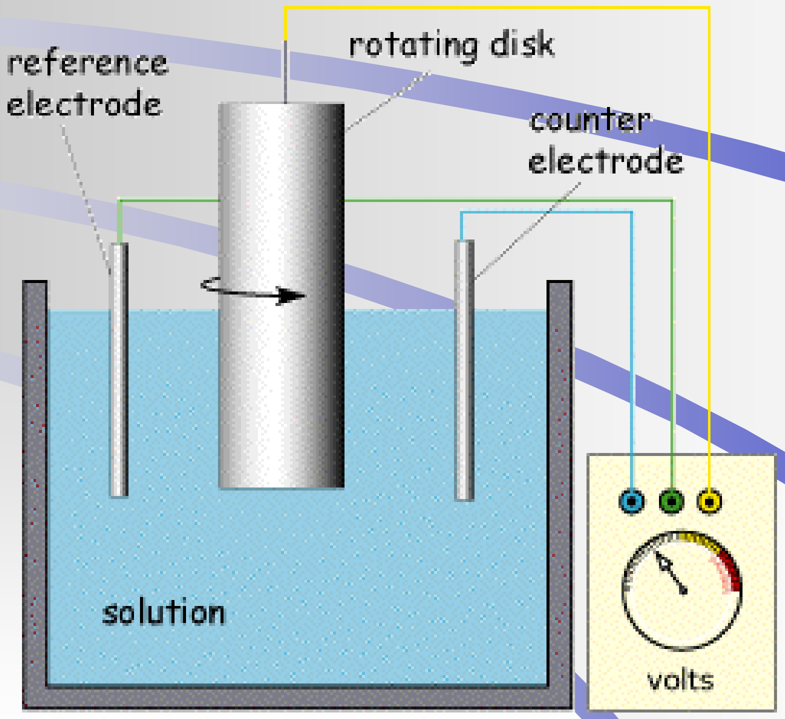


Figure 6.9 *Plots of j_L versus $f^{1/2}$ from the curves in figure 6.8.*

Hydrodynamic Methods

Rotating Disk Electrode (RDE)

Consist of a disk of electrode material imbedded in a rod of insulting material (usually teflon, epoxy resin or plastic).



Hydrodynamic Methods

Rotating Disk Electrode (RDE)

-most widely used hydrodynamic electrode

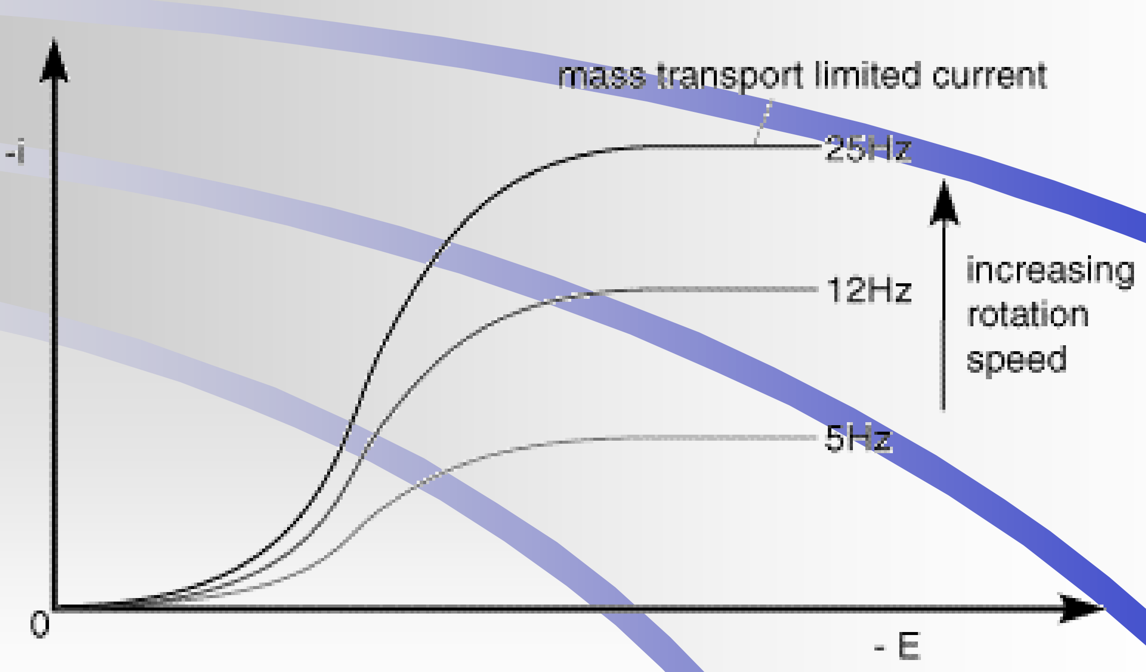
-efficient mass transport

- highly reproducible

Hydrodynamic Methods

Rotating Disk Electrode (RDE)

For this electrode system the hydrodynamic equations and convective-diffusion equation have been rigorously solved for the steady state.

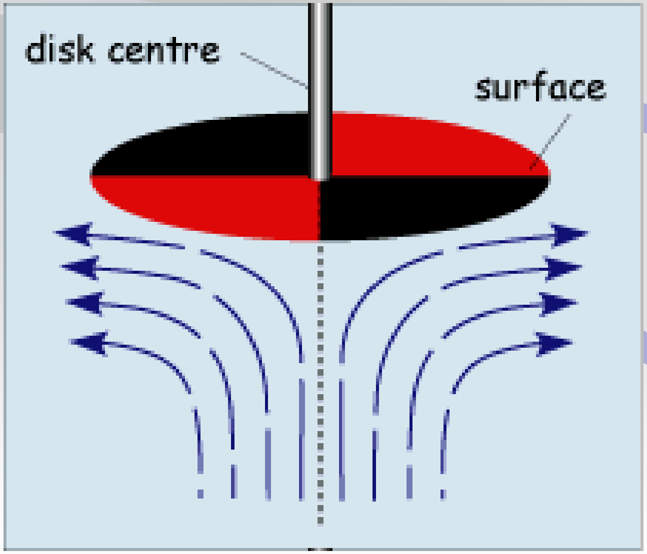


Hydrodynamic Methods

Rotating Disk Electrode (RDE)

The rod is attached to a motor through a flexible rotating shaft and can rotate at a certain frequency, f (revolutions per second).

The rotation rate can be described as the angular velocity, ω (s^{-1}), where $\omega = 2\pi f$.



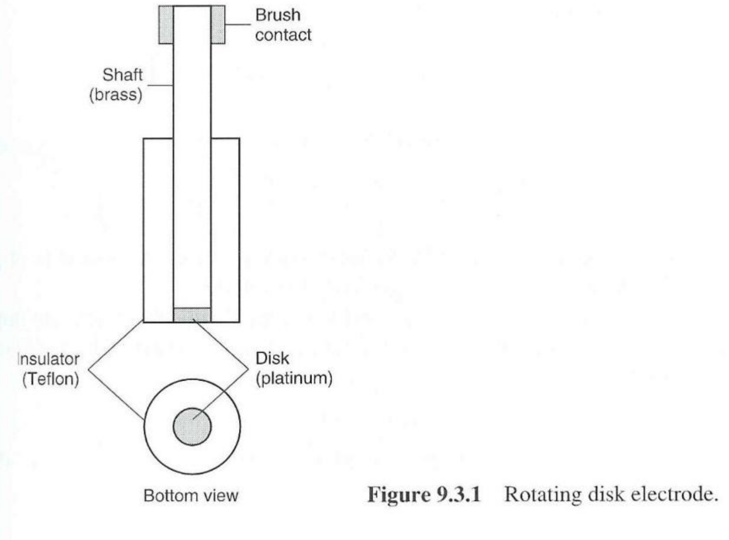


Figure 9.3.1 Rotating disk electrode.

Hydrodynamic Methods

Velocity Profile

The spinning disk drags the fluid at its surface across it and flings the solution outward from the center in a radial direction.

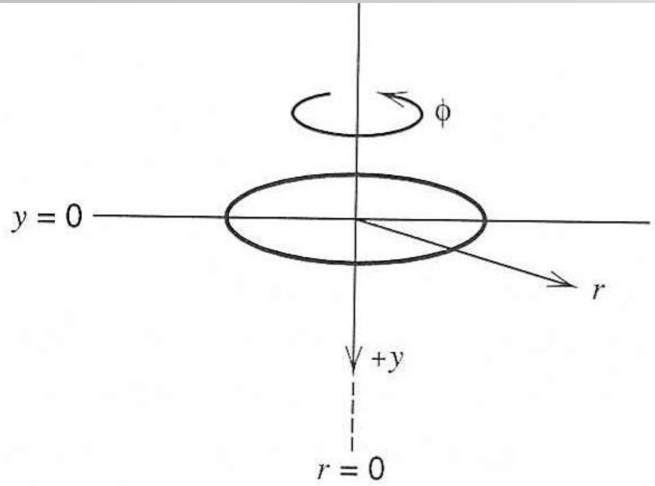


Figure 9.3.2 Cylindrical polar coordinates for the rotating disk.

Hydrodynamic Methods

Velocity Profile

The limiting velocity in the y direction, U_o is given by:

$$U_o = \lim_{y \to \infty} \upsilon_y = -0.88447(\omega v)^{1/2}$$

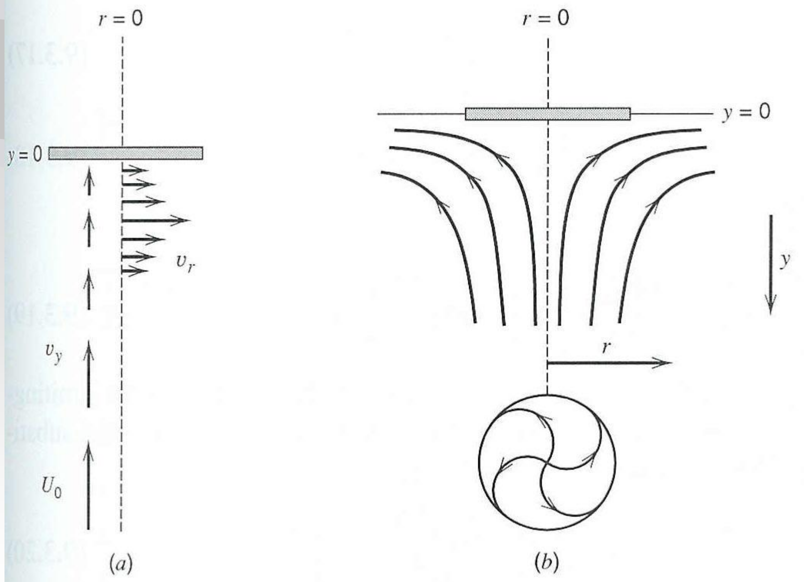


Figure 9.3.4 (*a*) Vector representation of fluid velocities near a rotating disk. (*b*) Schematic resultant streamlines (or flows).

Hydrodynamic Methods

Velocity Profile

The corresponding distance,

$y_h = 3.6(v/\omega)^{1/2}$

is called the hydrodynamic boundary layer thickness and approximates the thickness of the layer of liquid dragged by the rotating disk.

Hydrodynamic Methods

Levich Equation

$$i_{l,c} = 0.62nFA\, D_O^{2/3}\, \omega^{1/2}\, v^{-1/6}\, C_O^*$$

C_O^* - solution concentration, mol/cm^3

i_l – limiting current, A

v – kinematic viscosity, cm^2/s

ω – angular velocity (ω = 2πf, f- rps)

This equation applies to the mass-transfer limited condition at the RDE and predicts $i_{l,c}$ is $\propto C_O^*$ and $\omega^{1/2}$.

Hydrodynamic Methods

Levich Equation

$m_o = D_O/\delta_O = 0.62\ D_O^{2/3}\ \omega^{1/2}\ v^{-1/6}$

Under Nernstian conditions

$E = E^{1/2} + RT/nF \ln (i_{l,c} - i)/(i - i_{l,a})$

$E^{1/2} = E^{o'} + RT/nF \ln (D_R/D_O)^{2/3}$

For a reversible reaction, the shape of the voltammetric wave is independent of ω.

Hydrodynamic Methods

Irreversible Reactions

For irreversible reactions:

$$i_K = FAk_f(E)C_O^*$$

can rearrange to the Koutecky-Levich equation:

$$1/i = 1/i_K + 1/i_{l,c} =$$

$$1/i_K + 1/\left(0.62nFA\,D_O^{2/3}\,\omega^{1/2}\,v^{-1/6}\,C_O^*\right)$$

i_K – current under efficient mass transfer under kinetic control.

When k_f is large, i versus $\omega^{1/2}$ gives a straight line, otherwise i versus $\omega^{1/2}$ will curve as $\omega^{1/2} \rightarrow \infty$

Hydrodynamic Methods

Irreversible Reactions

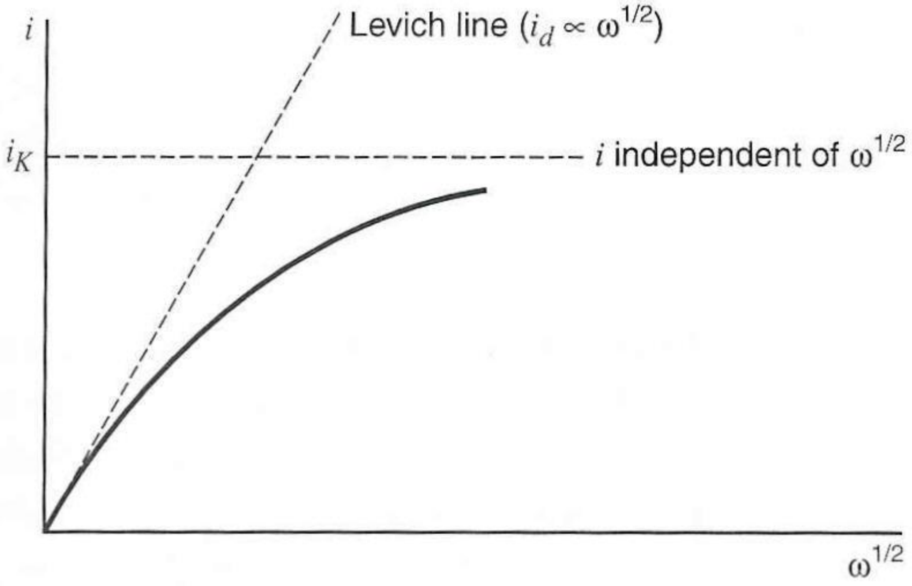


Figure 9.3.6 Variation of i with $\omega^{1/2}$ at an RDE (at constant E_D) for an electrode reaction with slow kinetics.

Hydrodynamic Methods

Irreversible Reactions

- A plot of $1/i$ versus $1/\omega^{1/2}$ should be linear and extrapolation to $\omega^{-1/2} = 0$ gives $1/i_K$.
- Determination of i_K at different E allows determination of the kinetic parameter k^o and α.

Hydrodynamic Methods

Irreversible Reactions

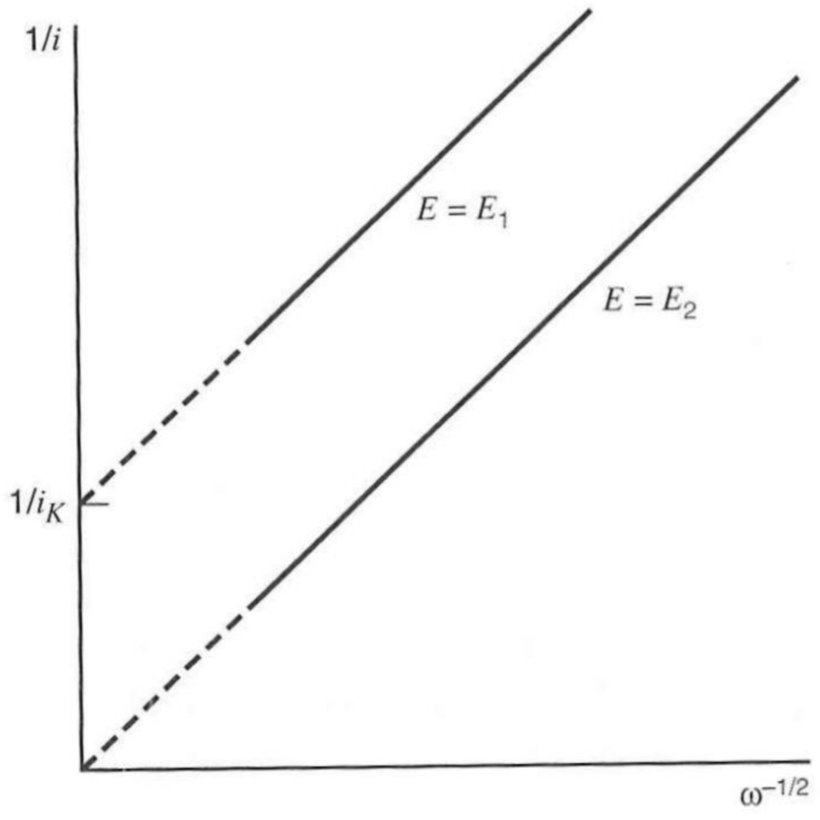


Figure 9.3.7 Koutecký–Levich plots at potential E_1, where the rate of electron transfer is sufficiently slow to act as a limiting factor, and at E_2, where electron transfer is rapid, for example, in the limiting-current region. The slope of both lines is $(0.62nFAC_O^*D_O^{2/3}\nu^{-1/6})^{-1}$.

Hydrodynamic Methods

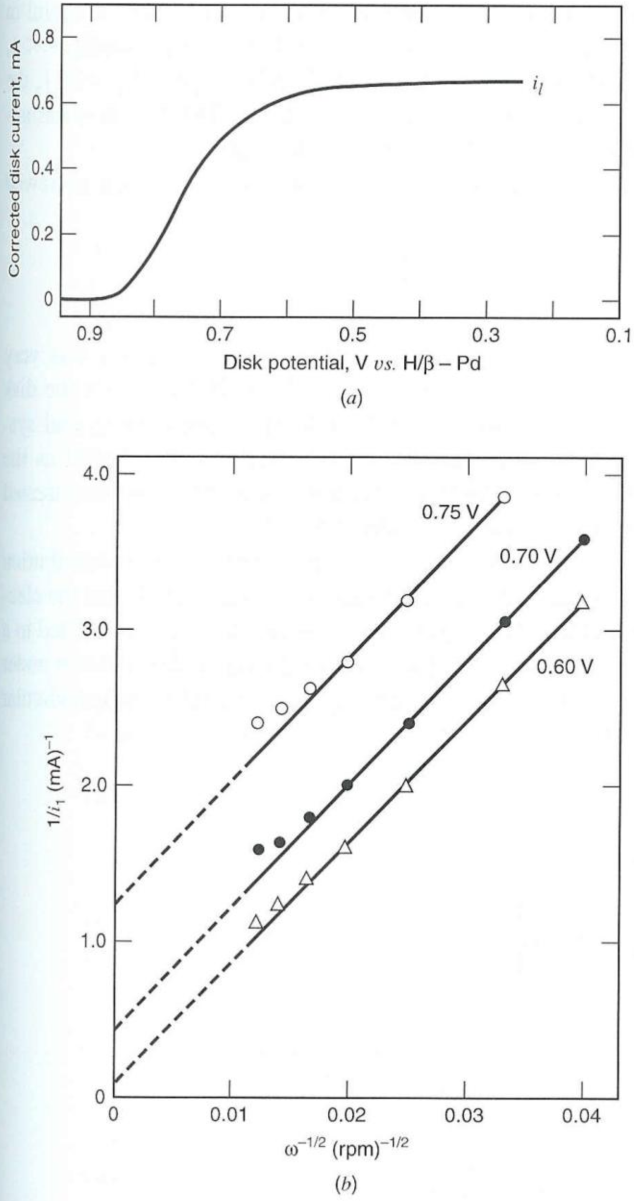


Figure 9.3.8 (*a*) i_D *vs.* *E* at 2500 rpm and (*b*) Koutecký–Levich plots for the reduction of O_2 to HO_2^- at a gold electrode in O_2-saturated (~1.0 m*M*) 0.1 *M* NaOH at an RDE ($A = 0.196$ cm^2). The potential was swept at 1 V/min. $T = 26$°C. (i_1 represents the corrected current attributable to O_2 reduction.) [From R. W. Zurilla, R. K. Sen, and E. Yeager, *J. Electrochem. Soc.*, **125**, 1103 (1978). Reprinted by permission of the publisher, The Electrochemical Society, Inc.]

Class Assignment

- Read Chapter 9 – Bard and Faulkner