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OPTICAL METHODS FOR THE STUDY OF CONVECTIVE
MASS TRANSFER BOUNDARY LAYERS ON EXTENDED ELECTRODES

Kirk Watson Beach
(Ph. D. Thesis)

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OPTICAL METHODS FOR THE STUDY OF CONVECTIVE
MASS TRANSFER BOUNDARY LAYERS ON EXTENDED ELECTRODES *

Kirk Watson Beach

Inorganic Materials Research Division, Lawrence Radiation Laboratory
and Department of Chemical Engineering, University of California,
Berkeley, California

ABSTRACT

Several optical techniques have been combined for the study of mass transfer boundary layers along extended horizontal electrodes in rectangular ducts. A Mach-Zehnder interferometer, supplemented by a focussing critical angle refractometer is used to determine the concentration boundary layer profiles as a function of the distance from the leading edge of the electrode with a consideration of the variation in the cross channel direction. A laser velocimeter is included in the system for the measurement of the electrolyte velocity near the electrode as a function of time and position.

A numerical analysis of light propagation in the nonuniform refractive index fields found in mass transfer boundary layers has shown that the previously used expressions for computing concentration profiles from interferometer fringe patterns often result in large errors in boundary layer dimensions and concentrations. A method for deriving concentration profiles from interferometer fringe patterns with a consideration of light deflection distortions is presented.

* Ph. D. thesis, research conducted under the direction of C. W. Tobias and R. H. Muller.

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I. INTRODUCTION

Most electrochemical reactors are parallel plate systems with one plate acting as the anode and the other as the cathode. Two separate reactions occur in the reactor, an electrochemical reduction at the cathode and an electrochemical oxidation at the anode. Since these are heterogeneous reactions they are rate limited by mass transfer more often than by charge transfer at the phase boundaries. In order to increase the mass transfer rate, forced or free convection is frequently employed. This study is concerned with a rectangular duct electrochemical reactor, and the investigation of mass transfer in regimes of combined forced and free convection in it.

Diverse technical processes such as the mercury amalgam cell process for the electrolytic production of chlorine, water desalinization by electro-dialysis, and the zinc air battery use the rectangular duct reactor. Several theoretical attempts have been made to describe the mass transfer processes in a rectangular duct^{10,31,36,39}, however none has been able to deal adequately with the variations in viscosity, density, conductivity and geometry which are important to the process.

Limiting current measurements have been used by Hickman¹⁵ in this laboratory to investigate mass transfer in copper deposition in the rectangular duct. It was found that the buoyant fluid formed over an upward facing cathode in forced convection could cause superimposed natural convection, which results in much higher limiting current values than those found when the cathode faced down, as shown in Fig. 1.¹⁵ The onset of the natural convection occurred when the boundary layer was so thick that buoyant forces exceeded viscous forces.

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Fig. 1.1 Current density on a horizontal cathode in a rectangular duct.¹⁵ The current at the leading edge of the electrode is unaffected by orientation but at low Reynolds numbers on an upward facing cathode a downstream current increase due to natural convection occurs.

The limiting current technique has several disadvantages. The current measurements must be made over relatively large electrode surface areas and therefore the resolution of the measurement is low. The measurement must be made in a quasi-steady-state condition; the applied current ramp must approach the limiting value slowly enough to prevent overshoot, but fast enough to prevent the electrode surface properties from changing before the limiting value is reached.* In addition limiting current measurements provide no direct information about the size or structure of the boundary layer.

The purpose of this work was to develop an alternate method of examining the mass transfer boundary layer over extended electrodes in rectangular ducts. The techniques should provide high spatial resolution measurements in both transient and steady state boundary layers at currents below and at the limiting value. Several optical instruments which had been used for the study of electrochemical mass transfer boundary layers were considered^{5,17,29,30,33,44}. Of the available methods, the Mach-Zehnder interferometric technique used by Lin, Moulton and Putman²⁵ for boundary layer studies in a rectangular channel was best suited to our needs.

An experimental arrangement consisting of a 3 meter long glass walled flow channel has been constructed with a 1 meter long electrode in the downstream end. A carriage mounted laser interferometer³ has been located so that it can be used to observe the boundary layer at any point along the electrode length. To complement the interferometer, a focussing refractometer and a Doppler velocimeter have been added to the system and an absorption densitometer has been designed for future use with the system.

*See J. Robert Selman, Ph.D. thesis, Chem. Eng., UC Berkeley, to be issued.

During early experiments with the interferometer, it was found that an adjustment of the focus of the instrument resulted in a change of the apparent boundary layer thickness and interfacial concentration. The thickness and concentration difference changes ranged as high as 300% with no degradation of fringe quality or image sharpness. This dependence on focus was due to light curvature in the interferometric cell. A numerical computation of light deflection effects shows that often the interferogram of a mass transfer boundary layer does not display the concentration profile directly but that the concentration profile can be found through a trial and error computation.

II. HYDRODYNAMIC CONSIDERATIONS IN A RECTANGULAR CHANNEL

The glass walled flow channel used for the initial optical tests was 1 cm wide (electrode width) and 2.54 cm high (electrode separation). These dimensions were chosen so that the electrode surface could be observed from both low and high, angles. The 1 meter long electrode was located at the downstream end of the channel, leaving an entry length of about 125 hydraulic diameters. Han¹² calculated that this entry length is sufficient to reach a center stream velocity which is 99% of the center velocity in fully developed laminar flow.

Happel and Brenner¹³ give an exact solution to flow in rectangular channels of width a and height b in directions x and y respectively for the coordinate system shown in Fig. 2.1.

$$v_z = -\frac{dp}{dz} \frac{x(x-a)}{2\mu} + \sum_{m=1}^{\infty} \sin\left(\frac{m\pi x}{a}\right) \left[A_m \cosh\left(\frac{m\pi y}{a}\right) + B_m \sinh\left(\frac{m\pi y}{a}\right) \right] \quad (2.1)$$

where

$$A_m = 2 \frac{dp}{dz} \frac{a^2}{\mu m^3 \pi^3} (\cos(m\pi) - 1)$$

and

$$B_m = -\frac{A_m (\cosh(m\pi b/a) - 1)}{\sinh(m\pi b/a)}$$

Since the Schmidt number is near 1000 and the mass transfer boundary layer begins after the flow is fully developed, the mass transfer boundary layer will be thin compared to the hydrodynamic boundary layer. The velocity is therefore considered to be a linear function of y , the distance away from the electrode. Solving Eq. 2.1 for the velocity

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Fig. 2.1. Coordinate system
in flow channel.

gradient at the electrode we find

$$V(x) = \left. \frac{dv_z}{dy} \right|_{y=0} = -2 \frac{dp}{dz} \frac{a}{\mu \pi^2} \sum_{m=1}^{\infty} \frac{(\cos(m\pi) - 1)(\cosh(m\pi b/a) - 1)}{m^2 \sinh(m\pi b/a)} \sin\left(\frac{m\pi x}{a}\right) \quad (2.2)$$

A plot of this gradient vs channel width is shown in Fig. 2.2. Curve C is the gradient profile for the 2.54 aspect ratio in this channel. The infinite height channel curve is indistinguishable from the $b/a = 2.54$ curve. In order to approximate a uniform velocity gradient at the electrode across 80% of a 1 cm electrode (curve A) the interelectrode spacing must be reduced to 1mm. Because of the light curvature an aspect ratio of 0.1 cannot be used at current densities high enough to create the natural convection patterns that we wish to observe.

In the initial experiments it was assumed that the boundary layer was uniform in the direction perpendicular to the glass walls, this is clearly not true.

Figure 2.3 shows how the boundary layer thickness varies in the cross channel direction. An estimate of the cross channel variation of the boundary layer thickness may be made from a consideration of the Levêque solution⁴ for the boundary layer at the leading edge of a semi-infinite plate in Couette flow. If, in the cross channel direction, the concentration at the electrode is constant and the boundary layer has the same shape but varies in thickness, the concentration profile at a particular distance z from the leading edge and time t may be written

$$c(x,y) \Big|_z = f\left(\frac{y}{\alpha(x)}\right) \quad (2.3)$$

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Fig. 2.2. Velocity gradient across the electrode in a rectangular channel at various aspect ratios

$$\bar{V} = \left. \frac{dv_z}{dy} \right|_{y=0} \frac{\mu \pi^2}{2 \frac{dp}{dz} a} \quad X = x/a$$

Curve

A, $\frac{b}{a} = 0.1$; B, $\frac{b}{a} = 1$; C, $\frac{b}{a} = 2.54$ and $\frac{b}{a} = \text{infinity}$

a, channel width

b, channel height

Fig. 2.3. Velocity and concentration profiles in the boundary layer over an upward facing cathode. The approximately linear velocity profile in the mass transfer boundary layer is shown with a zero velocity gradient at the glass wall which increases away from the wall as shown in Fig. 2.1. The concentration boundary layer is diffusion controlled at the wall and decreases in thickness with the increase in velocity.

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where $\alpha(x)$ is proportional to δ .

The ionic flux g , which is inversely proportional to δ and therefore α , is the sum of the diffusion flux j_d plus the convective flux j_c . The Levêque solution shows that

$$j_c \propto Nu (Re)^{1/3} \quad (2.4)$$

where Nu is the Nusselt number and Re is the Reynolds number. Since in the laminar flow the Reynolds number is proportional to the velocity gradient

$$j_c = K_1 V(x)^{1/3} \quad (2.5)$$

The diffusion flux j_d is assumed to be constant so setting $j_d = K_2$ results in

$$\alpha(x) = \frac{K_0}{j} = \frac{K_0}{j_c + j_d} = \frac{K_0}{K_1 V(x)^{1/3} + K_2} \quad (2.6)$$

At $x=0$ (where $V=0$) α can be normalized to 1 by setting $K_2 = K_0$

$$\alpha(x) = \frac{1}{K V(x)^{1/3} + 1} \quad (2.7)$$

so that, if the concentration profile at the glass wall is known, the concentration across the channel is in the form

$$C(x,y)|_z = C(0, \frac{y}{\alpha(x)})|_z \quad (2.8)$$

Substituting for $\alpha(x)$ from Eq. 2.7

$$C(x,y)|_z = C(0, y(K V(x)^{1/3} + 1))|_z \quad (2.9)$$

where y is the distance from the electrode, $V(x)$ is the velocity gradient function and K is an adjustable parameter relating the contributions of diffusion and convection to the flux. This expression will be used for the data analysis in Section V-C.

III. EXPERIMENTAL METHODS

The experimental system used to measure refractive index profiles and velocity in a rectangular electrochemical flow reactor is shown in Fig. 3.1. The system has been designed so that the operator can control the experiment while seated at the interferometer or the focussing refractometer. The interferometer, the focussing refractometer, (right foreground) and the Doppler velocimeter (left foreground) are mounted on carriages so that they can be moved to any location along the electrode. Experiment identification and timing marks allow the separately recorded interferograms on 16 mm movie film, the refractograms on 35 mm slide film, the velocimeter record on magnetic tape and the current, voltage, electrode overpotential and time information to be correlated for analysis.

A. The Flow System

The three meter long glass walled electrochemical reactor shown in Fig. 3.2 forms the heart of the system. The flow channel has been designed so that it can be easily converted to any rectangular cross section up to 10 cm square and can accomodate membranes and porous separators as well as the solid copper electrodes currently installed.

Figure 3.3 shows the cell construction. The main body consists of two three meter long lucite blocks 2" x 6", separated at the ends by 4" end pieces which contain the electrolyte inlet and outlet. The main body is given rigidity by 6" aluminum channels bolted to the top and bottom. The glass walls are sealed to the body by pneumatic O-rings shown in Fig. 3.4 which are expanded to 40 psig after the cell walls are in place, and evacuated for wall removal.

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Fig. 3.1. Flow channel with optical system; ready to operate -- The operator seated at the interferometer, can control the experiment with the control box above his left hand. The Doppler velocimeter (left foreground) and the focussing refractometer (right foreground) are mounted on a common carriage.

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Fig. 3.2. Glass walled flow reactor -- The flow direction is from right to left in the channel, the entry length is on the right and the reacting electrodes are on the left. The cell is mounted on screw jacks for adjustment of the angle of the incoming light. The laser interferometer which can be seen on the far right is mounted on a lathe bed carriage so that it may be moved to any desired location along the electrode.

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Fig. 3.3. Flow channel with the left glass wall removed. The lucite spacers in the entry region and the copper electrodes in the reaction region determine the channel dimensions.

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Fig. 3.4. Glass wall and backing plate -- The pneumatic O-ring around the edge of the glass frame allows the cell to be sealed with any channel width between the glass walls up to 10 cm. If the channel width is increased, shorter connecting bolts and screws are used between the backing plate and the glass frame so that the backing plate will fit flush against the cell body.

The channel dimensions are determined by lucite spacer blocks located between the glass walls in the entry and exit regions and by the electrodes in the reaction region. The spacer blocks can be seen in place in Fig. 3.3 forming a channel 1 cm wide and 2.54 cm high. The spacers are fastened in place by 3" long stainless steel retaining screws coming through the access holes in the cell body and sealed with o-rings under the screw heads. The 1 meter long electrodes shown in Fig. 3.5 receive electrical power through 3" brass retaining screws which also hold them in place.

The cross section of the assembled cell, shown in Fig. 3.6 was taken through the electrode region. From this view, it can be seen that the pneumatic O-ring H can be expanded to seal the cell with any desired separation between the glass walls up to 10 cm. The spacer sleeves between the backing plate and the frame of the glass can be replaced so that the backing plate will sit flush, against the cell body. When the O-rings are pressurized, they push the cell body apart causing leaks. To prevent this twelve clamp assemblies with contact screws K transfer the load from the cell body to the rigid steel backing plates.

A Luggin capillary shown in Fig. 3.7 was drilled in the spacer preceeding the cathode so that overpotential measurements could be made. The large slanted hole was sealed with a nylon screw. Connection is made to the capillary with a threaded tube through an access hole in the cell body. Originally a copper tube was used which acted as the reference electrode but more recently a brass tube has been used to connect to an external copper reference electrode.

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Fig. 3.5. Copper electrodes in the channel -- The 1 meter long copper electrodes were manufactured in three sections due to limited machining facilities. The electrical connection to the electrodes through the brass screws which also hold the electrodes in place can be seen.

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Fig. 3.6. Cross section of the flow channel through the electrodes

- A 6 inch aluminum channel to provide rigidity
- B 2 inch $\times$ 6 inch lucite cell body block
- C 3/8 inch steel backing plate to support glass walls
- D 1/2 inch thick glass cell wall
- E 1 cm wide replaceable copper anode (held in place by 2 1/2 inch brass screws which come through access holes in the cell body blocks. Electrical connection is also made through these screws)
- F 1 cm wide 2.54 cm high flow channel (dimensions adjustable)
- G 1 cm wide replaceable copper cathode (see note on E)
- H lucite frame for glass walls
- J replaceable connecting bolts which connect the backing plate to the glass frame
- K clamp bolt to stiffen cell (transfers force to the steel backing plate)

Note: Blunt labeling lines through the indicated objects; arrows point to the objects.

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Fig. 3.7. Drilled capillary in lucite channel spacer -- The connected holes shown drilled in the lucite spacer provide an electrolyte conduction path between the reference electrode connection hole (vertical, top) and the capillary hole (70° to horizontal, bottom) via an interconnecting hole (20° to horizontal) which is sealed in back with a nylon screw used as a plug. The reference electrode connection is made through an access hole in the cell body.

A diagram of the flow system is shown in Fig. 3.8. The flow cell A is supplied with electrolyte through an articulated 1-1/2" PVC pipe B using PVC pipe unions as joints. Electrolyte from the 130 liter fiber-glass supply tank F can flow to the cell through either the high rate flow meter C for flows up to $375 \text{ cm}^3/\text{sec}$ ($\text{Re} = 22,000$) or the low rate flow meter L for rates up to $37.5 \text{ cm}^3/\text{sec}$ ($\text{Re} = 2200$). The rest of the flow system is constructed mainly of plastic including the magnetically coupled recirculating pump N, the electrolyte preparation tank P and the cell outlet tank H. The outlet of the cell is kept slightly above atmospheric pressure by vent G. The rest of the system may be pressurized. A deionized water connection at Q allows the cell and tanks to be rinsed. The valve R allows the reference electrode capillary S and reference electrode T to be easily filled with electrolyte. In addition this valve allows deionized water to be forced through the capillary when the electrode is being polished to prevent blocking the capillary. Either line to the outlet tank H may be connected to the drain for rinsing or solution disposal.

Nitrogen is supplied to a manifold Z for deoxygenating solutions. The supply tank manifold allows the supply tank to be pressurized with nitrogen, vented to air or evacuated with a water jet vacuum connected to V. The O-ring manifold U allows the O-rings to be pressurized by the house air supply W or evacuated, through the O-ring connection tubes X.

B. The Interferometer

The Laser Mach-Zehnder Interferometer^{9,11,18,41,42} used in this study has been described elsewhere.^{2,3} Figure 3.9 shows the interferometer as originally constructed and Fig. 3.10 shows the interferometer

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Fig. 3.8. The Flow System.

- A. flow cell with vents and drains
- B. articulated cell connection arm
- C. high flowrate rotameter (0-375 cm³/sec)
- D. high flowrate control valve (1-1/2 inch PVC)
- E. supply tank valve (1-1/2 inch PVC)
- F. supply tank (fiberglass, 130 liter)
- G. atmospheric outflow vent (2 inch PVC)
- H. output collection tank (nalgene)
- J. electrolyte control manifold (1/2 inch PVC)
- K. low flow rate control valve (1/2 inch PVC)
- L. rotameter (0-37.5 cm³/sec)
- M. electrolyte return line (1/2 inch PVC)
- N. recycle pump (Serfilco, magnetically coupled)
- P. mixing and storage tank (nalgene)
- Q. house deionized water supply)
- R. reference electrode electrolyte supply
- S. reference electrode capillary connection
- T. reference electrode (copper)
- U. pneumatic O-ring control manifold
- V. water jet vacuum connection
- W. house air supply
- X. connections to pneumatic O-rings
- Y. supply tank pressurization control manifold
- Z. nitrogen distribution manifold

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Fig. 3.9. The original interferometer (Side view)

- A. modified laser (EOA LAS 101, emits from both ends)
- B. mirror
- C. space for experimental cell
- D. objective lens
- E. beam uniter (Optical Coating Laboratories)
- F. spatial filter (vertical slit)
- G. camera (motor drive Nikon F)
- H. reference lens
- I. aluminum mounting block
- J. lathe bed with interferometer on carriage

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Fig. 3.10. The present interferometer (side view).

- A. laser (EOA LAS 101)
- B. mirrors
- C. 3x beam expanding telescopes
- D. experimental cell
- E. objective lens
- F. reference lens
- G. beam uniter (Oriel Optics)
- H. spatial filter (vertical slit)
- J. camera (16 mm motor driven Bolex)
- K. beam interrupter for timing marks
- L. photodiode to create timing marks on the other recordings

with beam expanding telescopes and timing marker added.

A 0.5 mm diameter collimated light ray from the left end of the laser A reflects from a mirror B and passes through an expanding telescope C. The expanded 4 mm diameter beam is directed by another mirror B to the experimental cell D. The light emerging from the cell is focused on the film plane J by the objective lens E. For cathodic deposition studies the objective lens is adjusted so that a 1/2 mm reticle placed on the inside of the glass wall farthest from the objective lens is focused on the film plane.

The diverging reference beam emitted from the right end of the laser²⁰ is reflected from a mirror B and passes through the timing interrupter K and an expanding telescope C. The expanded reference beam passes through the compensating lens F and combines with the experimental beam in the beam uniter G. The beam uniter is a 50% transmitting 50% reflecting dielectric coating mirror which splits each beam into two separate beams, one going up and one going to the right.

The alignment of an interferometer with a laser light source is much easier than with a conventional light source.³⁵ To form an interference pattern on the film plane the two horizontal beams are simply adjusted so that they are coincident on the film plane and so that their points of convergence between the beam uniter and the film plane are nearly coincident. If one convergence point is farther from the film than the other, the fringes will be circular. If the convergence points are vertically displaced the fringe pattern is horizontal and if they are horizontally displaced in the cross beam direction the fringe pattern is vertical. The fringe pattern is adjusted so that the fringes are perpendicular to the electrode.

A spatial filter H is located at the point of convergence of the light rays to filter out the spurious diffraction patterns characteristic of laser light. The spatial filter, a slit oriented perpendicular to the electrode, decreases the intensity of the spurious diffraction patterns without reducing spatial resolution in the direction parallel to the slit.

A photodiode L is located at the point of convergence of the vertical portion of the reference beam. When the interrupter K blocks the reference beam each second the photodiode sends a timing signal to the other recorders on the system so that the experimental times in the records may be correlated for analysis.

A 16 mm Bolex movie camera³⁴ with an electric motor drive serves as film transport. The operation of this camera, the electrolysis power supply and all of the other recording devices are automatically controlled by a preset electrolysis timer and the timing signals from the photodiode.

In order to assure proper alignment of the experimental cell before each experiment, a mirror is placed against the glass wall of the cell nearest the objective lens in the path of the experimental beam. If the cell is correctly oriented and the glass is perpendicular to the beam, the light will be reflected exactly back down its incoming path. Multiple reflections will occur since the end of the laser is also a mirror. By placing a viewing screen with a small hole for the beam in the beam path deviations from normal incidence as small as 10^{-4} radians can be easily detected by observing a higher order reflection which is not collinear with the rest and strikes the screen outside the hole.

C. The Focusing Refractometer

In order to determine the boundary layer concentration profile in the cross channel direction, the direction which is averaged by the

interferometer, a focusing refractometer was constructed to determine the concentration profile on the inside of the glass wall.

A diagram of the refractometer is shown in Fig. 3.11. Light from a high intensity mercury vapor light source A is filtered by a dichroic filter B to remove the ultraviolet and focused by a lens C on the pinhole D. The light passing through the pinhole is collimated by another lens C and filtered by a 5460A⁰ monochromatic interference filter B. The collimated monochromatic light is directed by a mirror E to the contact prism assembly F.

The contact prism assembly is in optical contact with the glass wall of the flow channel G, and the two operate together as the prism of a critical angle refractometer.²² A cylindrical lens has been cemented on the right end of the prism with its axis vertical. The lens has been located so that the collimated light passing through it will converge in the shape of a wedge to a vertical line on the glass-liquid interface.

The light which is reflected from the interface passes through a focusing cylindrical lens with its axis horizontal and into the camera lens H which is focussed at infinity. The resultant effect of the focusing cylindrical lens and the camera lens together is that the illuminated vertical line at the glass-liquid interface is focused on the film in the vertical direction by both lenses while the angle of the reflected light is focused on the film in the horizontal direction by the camera lens alone. The angle of the light at which the transition from partial to total reflection occurs depends upon the refractive index of the liquid in the cell.

The refraction at the glass liquid interface obeys Snell's law¹⁹

$$\eta_1 \sin \theta_1 = \eta_2 \sin \theta_2 \quad (3.1)$$

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Fig. 3.11 Focussing refractometer (Top view)

- A. mercury vapor light
- B. dichroic interference filters passing $5460\text{\AA}$ (Optics Technology)
- C. collimating lenses
- D. pinhole spatial filter
- E. mirror
- F. contact prism assembly with converging cylinder on right and focussing cylinder lens (horizontal axis on left)
- G. glass wall of cell
- H. 500 mm camera lens focussed at infinity
- J. electrolyte with refractive index profile in the vertical direction

where η_1 is the refractive index in the glass, θ_1 is the angle of light incidence or reflection in the glass, η_2 is the refractive index in the liquid and θ_2 is the angle of light refraction in the liquid. Since $\eta_1 > \eta_2$ an angle of incidence θ_1 can be found which requires $\sin \theta_2$ to be greater than one. The condition is

$$\theta_1 > \arcsin (\eta_2/\eta_1)$$

In this region of angles no light can be transmitted and total reflection occurs at the interface. The limit of this region is θ_c the critical angle

$$\theta_c = \arcsin (\eta_2/\eta_1) \quad (3.2)$$

Below this angle, some of the light is transmitted through the interface and some is internally reflected. Since the refractive index of the glass is constant, the critical angle is a function of the refractive index of the liquid located adjacent to the illuminated vertical line and is a function of distance y along the line

$$\theta_c(y) = \arcsin (\eta_2(y)/\eta_1) \quad (3.3)$$

If, in the refractometer, the illuminating wedge of light includes the critical angle, the reflected wedge will show a sharp change in intensity at the critical angle value. Since the angle of the light appears as displacement on the film horizontally, the picture will show the critical angle as a change in film density. A refractive index variation in the vertical direction which is focused on the film plane will result in a picture like Fig. 3.12. Distance is focused vertically while critical angle, which is a measure of refractive index and therefore concentration, appears horizontally.

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Fig. 3.12 Refractograms from the focussing refractometer of the boundary between water and 1.0 molar copper sulfate at two different times after the boundary was formed. -- The concentration is indicated on the horizontal axis. The separation between the marks on the vertical axis is 1 mm.

If in Fig. 3.11 the cell wall G is separated from the contact prism F total reflection will occur within the prism as shown by the dotted lines, because the glass/air critical angle is too low to be included in the light wedge. The camera then sees an image of a set of 1/2 mm spaced lines scribed on the back center of the prism, as shown in Fig. 3.13. This provides a convenient dimensional scale for the system.

The apparatus, set up for calibration is shown in Fig. 3.14. A calibration cell J with a 1/2 inch glass wall, G, is pressed against nylon set screws protruding from the prism mounting plate, F so that its orientation is carefully controlled. A contact fluid of high refractive index (methylene iodide, $n = 1.74$) is introduced into the small space between the prism and the glass so that the critical angle will not be exceeded there. A set of calibration liquids are then introduced into the cell and photographs taken to provide a set of calibration lines as shown in Fig. 3.15. Now, as long as all optical components remain fixed, absolute concentration vs. relative distance can be read directly from the refractograms.

Once the calibration is complete, the calibration cell is removed, the refractometer is rolled into experimental position, the prism mounting plate is pressed against the experimental cell wall and contact fluid is reintroduced. On the electrochemical experimental cell, the prism is located so that the upward facing cathode is located near the bottom of the field of view of the camera. Even though in the cell the electrode side is pressed against the inside of the continuous glass wall, a small space between the glass and the electrode prevents the

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Fig. 3.13. 1/2 mm scale lines etched on the back of the contact prism in the focussing refractometer. -- When the refractometer is not in optical contact with the cell wall, internal prism reflections make the scale marks visible. Optical distortion can be seen in the curvature of the lines. Only the slanted edges of the lines scatter light away and appear dark.

XBB 7011-5249A

Fig. 3.14. Focussing refractometer (Top view)

- A. water cooled mercury light source and collimating optics
- B. mirror
- C. cylindrical converging lenses with vertical axis on the input end of the prism assembly
- D. calibration cell in place attached to the alligning plate
- E. cylindrical focussing lens with horizontal axis on the output end of the prism assembly
- F. motor drive camera with 500 mm lens focussed at infinity (Nikon F)

XBB 7011-5053

Fig. 3.15. Calibration of the focussing refractometer. -- The refractometer is calibrated by putting solutions of known concentration in the test cell and observing the location of the critical angle line on the film plane. Solution concentrations are marked in the right column.

electrode surface from appearing in the camera image. In order to locate the electrode surface a line was etched on the inside of the cell wall about 1.7 mm above the electrode. This line appears in the refractogram and the electrode location is determined from this line. The refractograms of the mass transfer boundary layers which have been obtained in the flow channel show such slight variation in concentration that they must be carefully evaluated on a measuring machine with a 1 micron resolution.

D. Determination of Concentration Profiles in the Presence of a Supporting Electrolyte

In order to avoid high ohmic resistance in electrochemical systems, non-reacting "supporting electrolytes" are frequently added to increase solution conductivity. The added ions transport a major portion of the current in the bulk electrolyte and thereby decrease the amount of reacting ion transported by ionic migration. The fraction of current carried by the migration of each ion in the bulk solution is called the transference number t and can be represented by

$$t_i = \frac{c_i u_i n_i}{\sum_j c_j u_j n_j} \quad (3.4)$$

where c_i is the concentration, u_i is the velocity at which an ion of type i would travel under the influence of a unit electric field, and n_i is the valence of the ion. In the limit when the transference number of the reacting ion approaches zero, the ion is transported only by convection and diffusion. This affords a great simplification in the theoretical model of the mass transport.

Both the reacting electrolyte and the supporting electrolyte form boundary layers; the reacting electrolyte because it must diffuse to

the electrode and the supporting electrolyte because it migrates toward the electrode and must diffuse away resulting in a zero net flux in steady state. The two boundary layers are usually not of the same thickness, varying with the diffusivities of the respective solutes. These concentration gradients may be in the same direction or in opposite directions. In the case of the cathodic deposition of copper from a mixture of copper sulfate and sulfuric acid, the copper sulfate concentration decreases in the boundary layer and the sulfuric acid concentration increases. The sulfuric acid boundary layer is usually thicker than the copper sulfate boundary layer because the acid diffusivity is approximately four times as high as that of the salt.

The acid does not affect the electrical measurement at the limiting current because the acid does not react at the electrode and therefore does not contribute to the current. Optical methods however, which measure the solution refractive index at one wavelength cannot, without other independent measurements, separate salt and acid concentrations since both solutes contribute to the total solution refractive index.

The deposition rate cannot be determined from the refractive index gradient at the wall since both the acid and the salt exhibit concentration gradients at the wall. The salt concentration gradient results from copper being deposited at the electrode and it is proportional to the deposition rate. The acid gradient is present at the electrode even though there is no acid flux there because the complete transport term includes migration and diffusion. For the total acid flux to be zero a sufficient acid concentration gradient must exist at the wall so that diffusion is equal and opposite to migration at the electrode.

It was first hoped that since cupric ion absorbs red light strongly the change of refractive index with cupric concentration in red light would not equal the change in blue light. If this were true, measuring refractive index profiles at two wavelengths would allow separation of the copper sulfate concentration profile from the sulfuric acid profile.³⁸ To test this, a set of measurements of the refractive index of mixtures of $\text{CuSO}_4 \cdot \text{H}_2\text{SO}_4$ was made using light of three different wavelengths. Sodium yellow (5890Å), mercury green (5460Å) and mercury blue (4360Å) were chosen simply because they were the light sources supplied with the refractometer. The refractive index values at these three wavelengths are given in Table A. The resultant isofracs, (lines of constant refractive index) are plotted in Fig. 3.16. Since the isofracs of different wavelengths do not cross, the separation of salt and acid concentrations is not possible at these wavelengths.

Figure 3.17 shows an absorption curve for copper sulfate. An examination of this curve shows that the three colors which we had used for the measurements were poor choices. Even though the colors appear quite different, the range of absorption covered in copper sulfate is relatively narrow. Further, measurements should be made at the He-Ne laser wavelength (6328Å) and at the argon ion laser wavelength (4880Å). For this purpose we have modified our refractometer to include a He-Ne laser source and a white light source with ten interchangeable monochromatic filters in addition to the standard sodium and mercury sources. The modified refractometer is shown in Fig. 3.18.

Another approach to the problem of optically separating the copper sulfate concentration from the sulfuric acid concentration is to measure the amount of red light absorbed by the solution. The amount of red

Table A. Refractive index of CuSO_4 , H_2SO_4 , and $\text{CuSO}_4\text{-H}_2\text{SO}_4$ mixtures.

Wavelength $\text{\AA}$	Molar Conc.	CuSO_4	H_2SO_4	$\text{CuSO}_4\text{-H}_2\text{SO}_4$
5890	1.0	1.35878	1.343066	1.366358
5460		1.360425	1.344654	
4360		1.36659	1.3504	
5890	0.8	1.353788	1.341082	1.360166
5460		1.35546	1.342532	1.361811
4360		1.361434	1.3486	1.367966
5890	0.64	1.34968	1.339482	1.354959
5460		1.351246	1.34098	1.357171
4360		1.357108	1.3469	1.362558
5890	0.511	1.346362	1.338096	1.350416
5460		1.347854	1.339568	1.351982
4360		1.353888	1.3456	1.357945
5890	0.4095	1.34361	1.33752	1.346874
5460		1.345166	1.33902	1.348270
4360		1.3511	1.3448	1.354336
5890	0.246	1.339194	1.335255	1.341018
5460		1.34072	1.33670	1.34266
4360		1.3466	1.3425	1.350
5890	0.1475	1.336577	1.334095	1.337712
5460		1.33815	1.33556	1.339148
4360		1.3441	1.3415	1.345
5890	0.0885	1.334995	1.333448	
5460		1.336405	1.335625	
4360		1.3423	1.3405

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Fig. 3.16. Refractive index of copper sulfate/sulfuric acid solutions at three wavelengths of light. -- The lines of constant refractive index (isofracs) all have slopes of about -2.5 irrespective of wavelength. If the lines at one wavelength had a strikingly different slope than at another wavelength, the separate concentrations of copper sulfate and sulfuric acid could be found from a measurement of refractive index at the two wavelengths.

XBL 7011-7090

Fig. 3.17. Absorption of copper sulfate vs. wavelength⁽⁴⁶⁾

The horizontal axis is linear in $1/\lambda$, wavelength is indicated in mm.

Ne Helium-Neon laser wavelength
 Na Sodium lamp wavelength
 Hg Mercury lamp wavelengths
 Ar Argon laser wavelengths
 Cd Helium-Cadmium laser wavelengths

XBB 7011-5250A

Fig. 3.18 Precision refractometer set up for multiple wavelength refractive index measurements.

- A. precision Abbe refractometer (B & L)
- B. laser light source (EOA LAS 101)
- C. mercury light source
- D. sodium light source
- E. white light source with interchangeable monochromatic filter carousels providing 10 equally spaced optical wavelengths (filters from Optics Technology)
- F. power supply rack
- G. constant temperature bath

light absorbed will be logarithmically proportional to the cupric ion concentration and to the optical path length in the cell. In order to examine the concentration profile, it would be convenient to photograph the absorption profile and analyze it later. Unfortunately, variations in light source intensity and in film age, quality and developing processes preclude determination of the amount of light absorbed in the cell by a simple film density measurement.

An alternative method using the absorption apparatus shown in Fig. 3.19 allows the analysis to be made in a cell with a copper sulfate concentration variation in the direction normal to the page. Light from a collimated light source A-C passes through a red monochromatic filter D and a neutral density wedge E with its density gradient oriented perpendicular to the optical density gradient due to cupric ion concentration gradient in the cell F. The camera G focuses in the cell and photographs the resultant superimposed density pattern. An isodensity line in the image is a line of points where the sum of the wedge density and the cupric ion density are constant. The processing of the film, as long as it is uniform across a single frame, is unimportant because the wedge provides the reference density. An isodensitometer²⁷ plot of the image provides a picture which looks like an interferogram, where the displacement of an isodensity line is a direct measurement of cupric ion concentration change. The wedge could be marked in units of cupric ion concentration differences.

Figure 3.20 shows a negative image from the absorption apparatus. The circular pattern is divided in the center by a meniscus shadow separating air from 0.1 M CuSO_4 . The optical density on the left side of the

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Fig. 3.19. Monochromatic wedge Densitometer (top view).

- A. light source
- B. diaphragm
- C. collimating lens
- D. monochromatic interference filter
(Optics Technology)
- E. optical density reference wedge
- F. experimental cell oriented so that the
optical density gradient in the cell is
perpendicular to the gradient in the
reference wedge
- G. camera focussed in the cell

XBB 7011-5341

Fig. 3.20. Densigram from the absorption densitometer -- The region above the meniscus line (crossing the center of the image) shows the reference wedge alone. The region below the meniscus shows the addition of 1 cm of 0.1 molar copper sulfate into the light path. The shift of an isodensity line as it crosses the meniscus, in this case it is nearly the full image width, is proportional to concentration.

air region is approximately equal to the density on the right of the solution section. The total width of the picture is 35 mm.

In order to properly analyze the image, the focal plane must be chosen by applying the same criteria as in the case of the interferometer to be discussed in Section IV. Since the light is transmitted through the cell it will follow the same path as the interferometer light. Therefore the analysis of this image must use the refractive index profile and light path obtained from refractive index measurements. The cupric ion concentration is determined by a trial and error integration of optical density along the previously determined light path.

An attempt was made to produce a color image using red and green light in the hope that a narrow yellow band would form between the red and green which would be equivalent to an isodensity line. The displacement of the yellow would then represent a change in copper ion concentration. Figure 3.21 shows the two color apparatus. The interference filter D passed red light while reflecting the rest, filter G passed green while reflecting the rest. The density wedges F were oriented so that the red light intensity increased in one direction while the green increased in the other. The resultant yellow band in between was too diffuse to be usable.

When used in conjunction with an interferometer, the wedge type monochromatic isodensitometer will be able to separate the cupric ion concentration from the acid concentration.

XBL 7011-7149

Fig. 3.21. Two color wedge densitometer (top view).

- A. light source
- B. diaphragm
- C. collimating lens
- D. interference filter, transmits a narrow red band, reflects the rest
- E. mirror
- F. neutral density wedge
- G. interference filter, transmits green, reflects other colors
- H. experimental cell oriented so that the optical density gradient in the cell is perpendicular to the gradients in the reference wedges
- J. camera, focussed in the cell

E. The Laser Doppler Velocimeter

The velocity profile in the mass transfer boundary layer varies with the viscosity and density of the solution. Since there is no convenient method for deriving the velocity variations theoretically, they must be obtained experimentally if the equations of convective transport are to be compared with the concentration profiles found experimentally.

A laser Doppler velocimeter has been constructed for the point by point measurement of electrolyte velocity in the mass transfer boundary layer. The velocimeter is shown in Figs. 3.22 and 3.23. Unlike previous velocimeters of this type,^{1,24,37,47} all optical components in this unit are mounted on one side on the channel so that the unit can easily be moved from location to location.

The Laser A emits a collimated beam which passes through a beam splitter B to a small deflecting mirror D. The adjustable lens E causes the beam to converge to a point at the measurement location V. The light scattered from a moving object at V has experienced a Doppler frequency shift which is a function of the velocity and the angle of reflection. The reflected light is collimated by the adjustable lens R and passes around the deflecting mirror to another lens F. The location of lens F is chosen so that its focal point coincides with a pinhole, acting as a spatial filter located on the rotational axis of the angle selection mirror G. The angle of this mirror is adjusted so that the desired light ray reflected from the moving object passes through the center of the collimating lens H. A reference beam from the beam splitter B is

XBL 7011-7052

Fig. 3.22. Laser Doppler velocimeter (top view).

- A. laser (University Laboratories model 261)
- B. beam splitter (uncoated microscope slide)
- C. neutral density filter to equalize beams
- D. mirror
- E. adjustable objective lens
- F. converging lens
- H. recollimating lens
- J. beam uniter (uncoated microscope slide)
- K. monochromatic filters and polarizer
- L. diaphragm
- M. photo multiplier (RCA 6342A)
- V. point where velocity is measured

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Fig. 3.23. Laser Doppler velocimeter (Top view)

- A. laser (University Laboratories Model 261)
- B. beam splitter (uncoated microscope slide)
- C. neutral density filter to equalize beams
- D. mirror
- E. adjustable objective lens
- F. converging lens
- H. recollimating lens
- J. beam uniter (uncoated microscope slide)
- K. photomultiplier assembly

attenuated by a neutral density filter C and combined with the measurement beam at the beam unit J. The two equal intensity, collinear collimated beams then pass through a monochromatic filter, diverging lens and a polarizing filter at K to improve the signal to noise ratio. The resultant interference pattern due to the interaction of the two coherent beams reaches the photomultiplier M through a small circular aperture L.

If the frequency of the laser light is f_1 , and the measured velocity V is separated into components V_x away from the incident beam and V_z perpendicular to the incident beam as shown in Fig. 3.24, the frequency of the light scattered at the angle θ can be calculated. The frequency of light received by the moving particle has been shifted to f_2 due to the particle velocity in the direction of the incident beam.

$$f_2 = f_1 - \frac{f_1 v_x}{c} \quad (3.5)$$

The frequency f_3 of the reflected beam shows an additional Doppler shift due to the velocity of the moving particle in the direction of the reflected beam.

$$f_3 = f_2 - \frac{f_3 v_z \sin \theta}{c} - \frac{f_3 v_x \cos \theta}{c} \quad (3.6)$$

By substituting for f_2 and simplifying, f_3 is calculated in terms of f_1 .

$$f_3 = \frac{f_1 (1 - v_x/c)}{1 + 1/c (v_z \sin \theta + v_x \cos \theta)}$$

By dividing through by the denominator and discarding the remainder because $v \ll c$ the expression can be simplified to

$$f_3 = f_1 [1 - 1/c (v_z \sin \theta + v_x (1 + \cos \theta))] \quad (3.7)$$

XBL 7012-7375

Fig. 3.24. Velocity-Doppler shift relationship

- v velocity of particles to be measured
- v_z downstream velocity
- v_x velocity across the stream
- I incident light
- R reflected light
- θ angle between the incident and the reflected light
- f_1 frequency of incident light
- f_2 frequency of reflected light

The two beams of light, the reference beam with frequency f_1 and the scattered beam with frequency f_3 are mixed forming a temporal interference pattern on the face of the photomultiplier. The intensity of the pattern is equal to the sum of the incident wave functions squared.

$$I = (A_1 \sin 2\pi f_1 t + A_2 \sin 2\pi f_3 t)^2 \quad (3.8a)$$

or

$$I = A_1^2 \sin^2 2\pi f_1 t + A_2^2 \sin^2 2\pi f_3 t + 2A_1 A_2 \sin 2\pi f_1 t \sin 2\pi f_3 t \quad (3.8b)$$

and simplifying results in

$$I = A_1^2/2 (1 - \cos 4\pi f_1 t) + A_2^2/2 (1 - \cos 4\pi f_3 t) + A_1 A_2 (\cos 2\pi(f_1 - f_3)t \cos 2\pi(f_1 + f_3)t). \quad (3.8c)$$

The double of the original frequency appears in the first, second and fourth terms while in the third term a low frequency $\Delta f = f_1 - f_3$ appears where $f_1 \approx f_3$. The value of Δf is calculated using Eq. 3.7

$$\Delta f = f_1 - f_3 = f_1/c (v_z \sin \theta + v_x (1 + \cos \theta)) \quad (3.9)$$

substituting $\lambda_1 = c/f_1$

$$\Delta f = \frac{1}{\lambda_1} (v_z \sin \theta + v_x (1 + \cos \theta)) \quad (3.10)$$

v_x and v_z can be obtained separately by measuring the frequency at two reflected angles and solving the resultant pair of simultaneous equations.

The frequency spectrum of the photomultiplier output shown in Fig. 3.25 was taken while scanning the surface of a revolving paper disk with the velocimeter. The wave analyser^{*(48)} used to plot the spectrum has a

*Quan. Tech. Laboratories Model 2213 wave analyzer.

XBL 711-20

Fig. 3.25. Frequency spectrum from the laser velocimeter for two test velocities on the surface of a revolving disk. -- $\theta \approx 10^\circ$. The angle between the incident light and the disk surface was not well controlled in the test so the frequency at .3 cm/s is not .75 times the frequency at .4 cm/s.

frequency range of 0 to 5 kc and a variable scan rate of 18 sec to 30 min. Since spectrum analysis is a slow process with respect to the expected velocity transients, and only a limited frequency range is available, the use of a 60 ips 120 kc tape recorder is contemplated to record the photo-multiplier output during experiments. The spectrum will be scanned later at 1-3/4 ips playback. Since the frequencies at 7-1/2 ips playback would span the range of audio frequencies, an alternate analysis could be carried out by audio frequency analysis.²¹

IV. LIGHT CURVATURE IN A REFRACTIVE INDEX FIELD AND ITS EFFECTS ON INTERFEROGRAMS

Interferograms obtained in this laboratory with a wedge type multiple beam interferometer⁽⁴³⁾ have shown a disturbing irreproducibility in the characteristics of the observed boundary layer. Frequently the shadow of a dissolving electrode would be seen advancing into the cell or the shadow of a depositing electrode receding. During one experimental run it was observed that, backing the camera a few millimeters away from the 2 mm thick cell resulted in a doubling of the apparent boundary layer thickness and the apparent concentration change in the boundary layer, while the apparent interfacial gradient and the sharpness of the image remained unchanged. Since the camera location and focus were experimentally determined by image sharpness, it was not possible to know where the camera had been focused in previous experiments.

Previous examinations of such phenomena^{40,49} have been unsuccessful because analytical techniques required oversimplification of the problem and computerized numerical techniques were not available at the time. An experimental and theoretical analysis has shown the source of these discrepancies and how the interferograms are related to the actual boundary layer. The analysis is applicable to all forms of interferometer which have been used for boundary layer studies.^{14,23}

A. The Cathodic Deposition Boundary Layer

Figure 4.1 shows four Mach-Zehnder interferograms of the same cathodic deposition mass transfer boundary layer. This boundary layer

Fig. 4.1 The effect of the change of the focal plane on the appearance of interference fringes for a cathodic deposition boundary layer

- a. interferogram with the focal plane inside the glass wall farthest from the objective lens
- b. interferogram with the focal plane on the inside of the glass wall farthest from the objective lens
- c. interferogram with the focal plane approximately half way across the cell.
- d. interferogram with the focal plane near the inside of the glass wall nearest to the objective lens
- E. incoming collimated light
- F. glass wall farthest from the objective lens
- G. electrolyte and electrode
- H. glass wall nearest to the objective lens
- J. objective lens

current density = 5.0 ma/cm^2 ; cell width 1.0 cm; glass width = 1.27 cm

The zero of the vertical scale was located at the electrode shadow before the boundary layer was formed.

has a lower refractive index near the electrode than in the bulk. The interferogram at right was taken with the plane of focus in the electrolyte close to the glass wall nearest the observer, as indicated by the drawing below the figure. The interferogram at left was taken with the focal plane in the middle of the glass wall farthest from the observer. In all four experiments the electrode shadow had been aligned with the zero mark on the scales before the boundary layer was formed. The upper edge of the boundary layer appears at 2.5 mm in all of the images.

The displacement of the electrode shadow is due to light deflection in the refractive index gradient. This deflection is the effect exploited in the Schlieren Optical System, which is a sister technique to interferometry. In both techniques a collimated beam of light is passed through the refractive index field. A light ray passing through a region of high refractive index is retarded with respect to a ray passing through a region of low refractive index. A wavefront which travels more slowly in the higher refractive index region becomes increasingly tilted toward the higher refractive index as shown in Fig. 4.2. Thus the light, which propagates in a direction perpendicular to the wavefront, bends toward the region of higher refractive index. In passing through the experimental region each ray experiences a total phase change corresponding to the refractive index field traversed and a total angle change corresponding to the refractive index gradient perpendicular to the path of the ray. If the refractive index and its gradient are continuous functions of the spatial coordinates, both the phase change and the angular change will be continuous (if overlapping rays are not superimposed). In addition the derivative of the phase change gives the change in angle.

XBL 7011-7091

Fig. 4.2. Light bending in a refractive index gradient

- V_i initial light direction
- V_f final light direction
- $n(y)$ refractive index (increasing upward)
- $V(y)$ velocity of light (decreasing upward)

The path of light rays ^{26,28} propagating in the x direction with gradients in the x and y directions shown in Fig. 4.3 can be found by solving Eq. 4.1. (The derivation of Eq. 4.1 is reproduced in Appendix I-A)

$$\frac{d^2y}{dx^2} = \frac{1}{\eta(x,y)} \left(1 + (dy/dx)^2 \right) \left[\left(\frac{\partial \eta}{\partial y} \right)_{x,z} + \left(\frac{\partial \eta}{\partial x} \right)_{y,z} \left(\frac{dy}{dx} \right) \right] \quad (4.1)$$

where η is the refractive index. The phase of the light is found by integrating along the path of the ray

$$P = \frac{2\pi}{\lambda} \int_0^x \eta(x,y) \left(1 + (dy/dx)^2 \right)^{1/2} dx \quad (4.2)$$

A numerical computation of the shape of the interference fringes resulting from a given boundary layer has been developed based on Eq. 4.1. Such a computation resulted in Fig. 4.4 (which can be compared to Fig. 4.1). The difference between the hypothetical boundary layer on the left and the resulting fringes is most apparent. The fringe curve E on the right shows the fringe doubling back on itself. The electrode shadow, at the tip of this fringe curve is above the lowest part of the fringe. The result is the horizontal hatching on the fringes apparent in part d of Fig. 4.1.

The cause of the displacement of the electrode shadow can be seen in Fig. 4.5. If the side of the cell nearest the objective lens is chosen as the focal plane as shown in (a), the ray which enters the cell nearest the electrode appears to originate from a point D far from the electrode. Thus the electrode shadow appears advanced into the electrolyte on the film plane J. If the focal plane is chosen near the center of the cell as shown in (b) the electrode shadow may appear in its correct location on the film plane. If the focal plane is located

XBL 7011-7092

Fig. 4.3. Curving light rays as they pass through a nonuniform cathodic deposition boundary layer

- A. electrode
- B. electrolyte with a thin boundary layer near center and a thick boundary layer near walls
- C. collimated light entering
- D. deflected light leaving

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Fig. 4.4. Computed fringe shapes for four choices of focal plane for an error function cathodic deposition boundary layer (compared with Fig. 4.1).

- A. given refractive index profile
- B. fringe shape if focal plane is 3.4 mm inside the glass wall farthest from the objective lens
- C. fringe shape if focal plane is on the inside of the glass wall farthest from the objective lens
- D. fringe shape if the focal plane is 3.75 mm from the inside of the glass wall farthest from the objective lens
- E. fringe shape if the focal plane is 7.5 mm from the inside of the glass wall farthest from the objective lens

Current density = 4.0 ma/cm^2 , cell width = 1.0 cm, glass width = 1.27 cm;
Concentration scale : 0.04 molar CuSO_4 per division increasing to the right.

NBL697-3200

Fig. 4.5. Displacement of the electrode shadow

- A. electrolyte
- B. electrode
- C. curved light ray entering the cell nearest to the electrode
- D. virtual origin of the light ray for focus on the inside of the glass wall nearest to the objective lens
- E. auxiliary ray through the focal point of the lens
- F. focal point of the lens nearest to the cell
- F'. focal point of the lens nearest to the film
- G. objective lens
- H. image of the edge of the electrode shadow
- I. film plane
- J. image on the film (inverted)
- K. virtual origin of the light ray for focus near the center of the cell
- L. virtual origin of the light ray for focus on the inside of the glass wall farthest from the objective lens

Note: The distance from the lens to the film is the same in all three examples, therefore the image magnification is the same.

at the cell wall farthest from the objective lens as in (c), the ray nearest the electrode will appear receded.

The cause of the apparent concentration change from one focal point choice to another can be seen in Fig. 4.6. Light originating from a point on the focal plane will arrive at the film plane with a fixed phase change, independent of its path. The phase of this light is compared to the reference beam from the other arm of the interferometer which has a horizontal, virtual path through the cell. This comparison is done by constructing an arc of constant phase centered on the focal plane at the apparent point of origin. For the focal plane 3 nearest the objective lens, the apparent phase of the experimental ray with respect to the reference beam is indicated by the intersection of the equiphase line 3" with the virtual reference ray 3' ray passes through the virtual origin of the ray at its intersection with the focal plane. For the focal plane 2 near the middle of the cell, the equiphase line 2" crosses the virtual reference ray 2' at a point to the right of case 3 making the phase appear more advanced, and therefore the concentration that the ray traverses appears lower. Similarly for case 1 the concentration appears lower or, for the cathodic deposition case, the concentration difference appears larger than in the other focal plane choices.

The concentration in the boundary layer usually appears larger than it is because the curving of light results in a longer path through regions of higher refractive index than if the ray passes through the cell along a straight path. Moreover, the interfacial fringe slope is lower than it should be and it is independent of choice of focal plane. The gradient appears low because the apparent distances in the boundary

XBL 7011-7088

Fig. 4.6. The effect of a change of the focal plane on the apparent concentration in the boundary layer

- A. electrode
- B. electrolyte with a cathodic deposition boundary layer
- C. light ray entering the cell nearest the electrode at normal incidence
- D. deflected light ray leaving the cell
- 1 focal plane at the inside of the glass wall farthest from the objective lens
- 1' virtual reference light ray for the deflected light ray and the focal
- 1'' equiphase of the deflected light ray for focal plane 1
- 2 focal plane inside the cell
- 2' virtual reference light ray for the deflected light ray and the focal plane at location 2
- 2'' equiphase of the deflected light ray for focal plane 2
- 3 focal plane at the inside of the glass wall nearest to the objective lens
- 3' virtual reference light ray for the deflected light ray and the focal plane at location 3
- 3'' equiphase line of the deflected light ray for focal plane 3

layer are generally increased while the concentration difference is generally decreased. The fringe slope is constant, independent of the choice of focal plane, because it depends only on the angle at which the light ray leaves the cell.

Figures 4.7 through 4.13 show examples of distortions in cathodic deposition boundary layers for theoretical concentration profiles in a 1 cm wide channel with a 1.27 cm thick glass wall. Figure 4.7 shows a .5 mm thick error function boundary layer with a concentration depletion difference of .1 molar CuSO_4 representing a current of 5 ma/cm^2 . The fringe (the lower curve) was calculated assuming focus at the left cell wall, farthest from the objective lens. Even though the light leaves the boundary layer before leaving the cell the concentration difference in this case appears about right. The apparent boundary layer thickness however is in error.

Figure 4.8 shows a concentration profile A about equal to that in Fig. 4.7. Calculated fringes B, C, D, E are for focal planes at different locations in the cell, B at the side of the cell furthest from the lens, E at the side closest to the lens and C and D $1/3$ and $2/3$ of the way between. The tip of fringe B extends farther than the supposedly identical fringe in Fig. 4.7 because the traced rays were more closely spaced in Fig. 4.8.

Figure 4.9 is identical to Fig. 4.8 except the glass walls were assumed infinitely thin in this computation. The difference between them is small.

Figure 4.10 shows the same boundary layer as Fig. 4.8 except that in this case the incoming light had an initial upward slope of 0.04 (2.3 degrees). The resultant fringes are drastically different.

Figure 4.11 shows the path of the light rays and a fringe for the same boundary layer if the light is tilted downwards at an angle of 1.1 degrees. The fringe, focused at the wall farthest from the lens, shows a greater concentration difference than actually exists.

Figure 4.12 and 4.13 show a boundary of the same thickness but lower concentration difference. In Fig. 4.12, the light enters angled down at 1.1 degrees and the concentration difference appears greater than before. In Fig. 4.13 the light is angled down at 2.3 degrees and some of the light strikes the electrode making the concentration difference appear low. In addition, an apparent maximum forms in the fringe because part of the beam leaves the cell at a low angle compared to the rest and the phase is not advanced by the optics like the phase of the rest of the beam is (see Fig. 4.6).

Figure 4.14 shows a computed fringe B for a Nernst boundary layer A. The assumed cell width was 2.5 mm. The fringe slope at the electrode shadow is equal to the concentration gradient in the boundary layer. The slope of the fringes will always be accurate for linear refractive index profiles as long as the light rays traverse the cell without leaving the boundary layer region. The fringes will be simply shifted in location and in phase, the amount of shift depending on the choice of focal plane. The fringes will be discontinuous near the discontinuous change of slope where the three phases overlap.

Three recommendations result from a study of the computed fringes of cathodic deposition boundary layers.

1. When high refractive index gradients are present in the boundary layer the experimental cell should be as narrow as possible to minimize light deflection effects.

EXPLANATORY NOTES FOR FIGURES 4.7 TO 4.48

The figures in this group are computer plots generated with program NEWAB or Program NEWAF listed in the appendix. The figure formats are explained below and all parameters are as stated here except as noted in the individual figure captions.

The ordinate indicates the distance in mm from the interface or electrode surface. The cell width was 10 mm and the width of the glass wall was 12.7 mm. The incoming light was normally incident to the glass cell walls.

NOTE [A]. Fringe Shape and Light Path in the Cell for an Assumed Refractive Index Profile

The left hand graph shows the assumed concentration profile and the resultant fringe for the focal plane indicated below. The short connecting lines connect the incident light ray location on the assumed concentration profile with the point formed by the same ray on the fringe profile. The abscissa indicates copper sulfate molarity.

The right hand graph shows the path of the light as it traverses the cell through the concentration profile given. The left glass wall is not shown because all of the rays pass through it at the same angle.

NOTE[B]. Fringe Shape for Four Choices of Focal Plane within the Cell for an Assumed Refractive Index Profile

Curve A shows the assumed refractive index profile. The abscissa indicates concentration; 0.1 molar copper sulfate per division increasing to the right. Curves B to E represent fringe profiles for different focal planes as indicated below.

Focus B The focal plane is on the inside of the glass wall farthest from the objective lens.

Focus C The focal plane is 1/3 of the way across the cell from B.

Focus D The focal plane is 2/3 of the way across the cell from B.

Focus E The focal plane is on the inside of the glass wall nearest to the objective lens

i is current density

CuSO₄ concentration may be converted to refractive index as shown below

$$\eta = 1.3313 + .027952 C$$

where C is CuSO₄ concentration in moles/liter. This equation is based on a polynomial fit* to refractive index data for CuSO₄ and H₂SO₄ solutions. Its applicability to solutions without H₂SO₄ may be restricted.

* J. Robert Selman, Ph.D. Thesis Chem. Eng., U. C. Berkeley, to be issued.

XBL 7012-7193

Fig. 4.7. Cathodic deposition boundary layer. See note [A]

$$i = 10 \text{ ma/cm}^2$$

focus B

XBL 7012-7215

Fig. 4.8. Cathodic deposition boundary layer. See Note [B]

$$i = 10 \text{ ma/cm}^2$$

XBL 7012-7211

Fig. 4.9. Cathodic deposition boundary layer. See Note [B]

$$i = 10 \text{ ma/cm}^2$$

width of glass wall = 0. mm

A

B

C

D

E

XBL 7012-7210

Fig. 4.10. Cathodic deposition boundary layer. See Note [B]

$$i = 10 \text{ ma/cm}^2$$

$$\text{angle of incidence} = +2.3^\circ$$

XBL 7012-7201

Fig. 4.11. Cathodic deposition boundary layer. See Note [A]
 $i = 10 \text{ ma/cm}^2$
 angle of incidence = -1.5°
 Focus B

KDL 7012-7180

Fig. 4.12. Cathodic deposition boundary layer. See Note [A]

$$i = 7.5 \text{ ma/cm}^2$$

angle of incidence = -1.15°

Focus B

XBL 7012-7191

Fig. 4.13. Cathodic deposition boundary layer. See Note [A]

$$i = 7.5 \text{ ma/cm}^2$$

angle of incidence = -2.3°

Focus B

XBL 7011-7055

Fig. 4.14 Fringe shape for Nernst boundary layer .

- A. Nernst boundary layer concentration profile
- B. fringe shape if the focal plane is on the inside of the glass wall nearest to the objective lens

current density - 7.5 ma/cm^2
 cell width = 2.5 mm
 glass thickness = 7 mm

2. To prevent fringe crossover, the interferometer should be focussed in the cell on the inside of the glass wall farthest from the objective lens and the incident light should be parallel to the electrode.

3. The electrode boundary layer thickness must be found by a comparison of the electrode shadow location found before the boundary layer is formed and the upper edge of the boundary layer found during the experiment.

B. The Anodic Dissolution Boundary Layer

Optical studies of the anodic boundary layer are also subject to the effects of light deflection. In this case however the refractive index near the electrode is higher than in the bulk. The light bends toward the electrode and the nearer portion of the beam strikes it. If the electrode is optically absorbing, the light terminates there, as shown in Fig. 4.15. If the electrode is diffusely reflecting, fringes form but have a reduced contrast due to the additional diffuse light. If the electrode is specularly reflecting (mirror like), the ray reenters the solution. The reflected ray may return to the electrode and be reflected again; in any case such reflected light traverses a long and complicated optical path and appears on the film plane with a greatly retarded phase at a location which is difficult to predict. Shiny electrodes should not be used.

If the interferometer is focussed on the glass wall nearest the objective lens, the boundary layer will appear to have the correct thickness because the electrode edge nearest the objective lens is illuminated and no distorting gradients are present between it and the objective lens. The phase of the ray which leaves the cell, nearest

XBL 7012-7200

Fig. 4.15. Anodic dissolution boundary layer. See Note [A] p. 65.
 $i = -7.5 \text{ mA/cm}^2$
 Focus E

the electrode has not been retarded as much as the phase of a hypothetical ray which runs just above and parallel to the electrode. The fringe shift indicates a concentration difference lower than the actual concentration difference in the boundary layer (Fig. 4.15).

If the incident light enters the cell at an upward angle as shown in Fig. 4.16, light which enters the cell near the electrode is able to leave the cell without striking the electrode but the resultant fringes are not significantly improved.

In Fig. 4.17 the rays enter the cell at such a high angle that those just inside the outer edge of the boundary layer have a more advanced phase than the rays beyond because of their shorter curved path.

Figures 4.18 and 4.19 show the effect of changing the focal plane with the anodic boundary layer. Figure 4.18 shows the ray paths and Fig. 4.19, the fringes for various focal plane choices. A change similar to that of the cathodic case takes place. Figure 4.20 shows the resultant fringes when the incident light has a large upward slope. (It is interesting to note that the electrode shadow appears at a nearly constant y value in this case, this is because the ray nearest to the electrode happens to leave the cell horizontally for these conditions).

Figure 4.21 shows the ray path through a 10 cm wide cell with a small concentration gradient. In this case of normal incidence and the case of slight upward incidence in Fig. 4.22 the optical distortions are small when the focus is on the cell wall nearest the objective lens. However, as shown in Fig. 4.23 other choices of focal plane reduce the apparent boundary layer thickness. Even downward incident light produces little error as long as the focus is on the glass wall nearest the objective lens

XBL 7012-7192

Fig. 4.16. Anodic dissolution boundary layer. See Note [A]

$$i = -7.5 \text{ ma/cm}^2$$

$$\text{angle of incidence} = +1.15^\circ$$

Focus E

XBL 7012-7184

Fig. 4.17. Anodic dissolution boundary layer. See Note [A]

$$i = -7.5 \text{ ma/cm}^2$$

angle of incidence = $+2.3^\circ$

Focus E

XBL 7012-7181

Fig. 4.18. Anodic dissolution boundary layer. See Note [A]

$$i = -10 \text{ ma/cm}^2$$

Focus E

XBL 7012-7217

Fig. 4.19. Anodic dissolution boundary layer. See Note [B].
 $i = -10 \text{ ma/cm}^2$

XBL 7011-7046

Fig. 4.20. Anodic dissolution boundary layer. See Note [B]

$i = -10 \text{ ma/cm}^2$

angle of incidence = $+3.4^\circ$

XBL 7011-7155

Fig. 4.21. Anodic dissolution boundary layer. See Note [A]

$i = -0.019 \text{ ma/cm}^2$
cell width = 99 mm

Focus E
glass width = 9.54 mm

XBL 7011-7156

Fig. 4.22 Anodic dissolution boundary layer. See Note [A]

$i = -0.019 \text{ ma/cm}^2$
cell width = 99 mm
angle of incidence = $+0.115^\circ$

Focus E
glass width = 9.54 mm

XBL 7011-7043

Fig. 4.23. Anodic dissolution boundary layer. See Note [B]

$i = -0.019 \text{ ma/cm}^2$

glass width = 9.54 mm

cell width = 99 mm

concentration scale : 0.003 molar CuSO_4 per division

XBL 7011-7030

Fig. 4.24. Anodic dissolution boundary layer. See Note [A]

$i = 0.019 \text{ ma/cm}^2$
 cell width - 99 mm
 angle of incidence = -0.580

Focus E
 glass width = 9.54 mm

XBL 7011-7048

Fig. 4.25. Anodic dissolution boundary layer. See Note [B]

$i = 0.019 \text{ ma/cm}^2$ glass width = 9.54 mm
 angle of incidence = -0.58°
 concentration scale : 0.003 molar CuSO_4 per division

XBL 7011-7154

Fig. 4.26. Anodic dissolution boundary layer. See Note [A]

$i = 0.019 \text{ ma/cm}^2$

cell width = 99 mm

angle of incidence = $+0.58^\circ$

concentration scale : 0.003 molar CuSO_4 per division

Focus E

glass width = 9.54 mm

XBL 7011-7047

Fig. 4.27 Anodic dissolution boundary layer. See Note [B]

$i = 0.019 \text{ ma/cm}^2$ glass width = 9.54 mm
 angle of incidence = $+0.58^\circ$
 concentration scale: 0.003 molar CuSO_4 per division

as shown in Figs. 4.24 and 4.25. However, high upward angles of incidence give incorrect boundary layer thicknesses. At large upward angles of incidence, as in Figs. 4.26 and 4.27, the boundary layer appears thin when the focus is at the glass wall nearest the objective lens and approximately correct when the focus is at the far glass wall. In boundary layers with low refractive index gradients the errors in boundary layer measurements can be low if the optical orientation and focal plane are properly chosen.

From a consideration of the computed fringe patterns, it is clear that the best choice of focal plane when observing an anodic deposition boundary layer is the location inside the cell glass wall nearest to the objective lens. In that case, if the incident light is parallel to the electrode, the boundary layer appears in its true thickness and the concentration at the electrode appears low.

C. The Boundary Between Two Bulk Solutions

When two solutions of different refractive indexes are brought into contact, with the solution of lower density on top, a boundary layer forms which increases in thickness with time. In a cell of finite depth, the shape of the boundary layer at long times approximates a cosine curve with the argument ranging from 0 to π .⁷ Even at short times, the boundary layer has the appearance of a cosine curve.

Figure 4.28 shows a cosine curve approximating the boundary layer in a 1 cm wide cell and the fringe derived from it. While the fringe is displaced slightly from the concentration profile, and the half concentration difference value is slightly displaced; the boundary thickness and the concentration differences appear correct. Figure 4.29 shows the fringe

XBL 7012-7183

Fig. 4.28. Diffusion interface between two solutions. See note [A] p. 65.

XBL 7012-7213

Fig. 4.29. Diffusion interface between two solutions.
See Note [B]

patterns of the same boundary layer for four different choices of focal planes within the cell. Fringe D, taken .33 cm from the glass wall nearest the objective lens appears to be the most accurate representation of the boundary layer, although all are very close.

An angle of incidence inclined downward as in Fig. 4.30 can cause a false concentration extremum to appear in the fringe pattern. As the angle increases, the extremum becomes more pronounced (Fig. 4.31). A change in focal plane to the other side of the cell moves the extremum to the other side of the boundary layer (Fig. 4.32). An upward angle of incidence produces smaller, wider extrema which are located on the side of the boundary opposite to those in the downward incidence case as shown in Fig. 4.33. As the boundary increases in thickness, the fringe error disappears in normal incidence as shown in Fig. 4.34 and the extrema disappear in nonnormal incidence as shown by comparing Fig. 4.35 with Fig. 4.30.

Concentration difference between two regions with zero gradient can always be measured accurately. Boundary profiles observed with normal incidence appear nearly accurate even though, as can be seen from the ray tracing figures, the distance and phase values are both shifted. As in the boundary layer case, any shadow producing marks on the cell would immediately reveal these distortions.

D. The Concentration Minimum

It has been shown that false extrema can appear in interferograms when the light enters the cell at non-normal incidence. Real maxima and minima can appear in interferometric cells under several conditions;

XBL 7012-7198

Fig. 4.30. Diffusion interface between two solutions.
angle of incidence = -1.15°

XBL 7012-7208

Fig. 4.31. Diffusion interface between two solutions. See
 Note [A] p. 65
 Focus E
 Angle of incidence = -3.4°

XBL 7012-7214

Fig. 4.32. Diffusion interface between two solutions.
See Note [B]

Angle of incidence = 2.3°

XBL 7012-7212

Fig. 4.33. Diffusion interface between two solutions.
See Note [B]

Angle of incidence = $+2.3^\circ$

XBL 7012-7182

Fig. 4.34. Diffusion interface between two solutions.
See Note [A]

Focus E

The gradient is lower than in Figs. 4.28 to 4.33

XBL 7012-7189

Fig. 4:35 Diffusion interface between two solutions. See Note [A]

Focus E

Angle of incidence = -1.15°

in electrodialysis extrema appear in the middle of the electrolyte chambers; in electrophoresis maxima appear at the locations of separated finite bands; and in electrochemical systems, extrema can be formed by current reversal.

As in the previous refractive index profiles discussed, if the refractive index gradients around a minimum are small, the fringe accurately represents the refractive index profile irrespective of focal plane (Fig. 4.36) because the light deflection is small (Fig. 4.37). However, when the concentration gradients become large (Fig. 4.38), the choice of focal plane becomes critical. Focussing in the half of the cell nearest the objective lens results in an accurately observed concentration difference and some distortion of the width of the minimum. Focussing far from the objective lens results in the fringe crossover which obscures the correct concentration difference even though it is present as one of the three superimposed phases. The spreading of the rays responsible for this is shown in Fig. 4.39.

Distortion in the profile becomes more serious as the width of the minimum decreases (Fig. 4.40) and additional complications become significant with these sharp minima. As can be seen by the wide ray separation at the focal plane in Fig. 4.41 the light intensity of the experimental beam is greatly reduced near the minimum (the light intensity is proportional to the density of rays). It is possible in this case for the light intensity to become so low that the fringe contrast approaches zero causing the fringes to disappear. This effect is the same as the Schlieren shadowgraph effect.

While the concentration difference in the minimum appears correct with normal light incidence, if the light incidence is non-normal the

XBL 7011-7035

Fig. 4.36. Concentration minimum. See Note [B] p. 65.

XBL 7012-7187

Fig. 4.37. Concentration minimum. See Note [A]
Focus E

XBL 7011-7041

Fig. 4.38. Concentration minimum. See Note [B]

XBL 7012-7190

Fig. 4.39. Concentration minimum. See Note [A]
Focus E

XBL 7011-7037

Fig. 4.40. Concentration minimum. See Note [B]

XBL 7012-7196

Fig. 4.41. Concentration minimum. See Note [A]
Focus E

concentration difference appears larger than it is (Fig. 4.42). This is because the rays approaching the minimum refractive index region at an angle tend to curve to be normal to the glass walls; they therefore traverse a shorter path in the cell, suffering less phase retardation. A more extreme case in Fig. 4.43 shows a maximum appearing also for the reasons discussed in the previous section. A similar severe case for several focal planes is shown in Fig. 4.44 but in this case the incident rays were angled upwards rather than downwards.

Concentration minima can be accurately observed if the focal plane is chosen nearest to the objective lens and the incident light is normal to the cell walls.

E. The Concentration Maximum

In the case of a refractive index maximum, the light rays converge on the maximum (Fig. 4.45). If only small gradients are present the resultant fringe represents the profile with little error. However, when the refractive index gradients become large as in Fig. 4.46, fringe cross-over is present in the image regardless of the choice of focal plane, at the one extreme, B, occurring at the boundary layer edges and at the other, E, in the center.

If the maximum is sharp enough, the light rays can cross over the maximum and bend back (Fig. 4.47) and if the cell is wide enough they may cross over the maximum again; such zigzagging rays would suffer a maximum phase retardation having an exceptionally long path in the highest refractive index region. Because in a given refractive index profile, the exit angle of these rays can assume a range of positive and

XBL 7012-7179

Fig. 4.42. Concentration minimum. See Note [A] p. 65.

Focus E

Angle of incidence = -1.15°

XBL 7012-7197

Fig. 4.43. Concentration minimum. See Note [A]

Focus E

Angle of incidence = -2.3°

XBL 7012-7218

Fig. 4.44. Concentration minimum. See Note [B]
Angle of incidence = $+3.4^\circ$

XBL 7012-7185

Fig. 4.45. Concentration maximum. See Note [A]
Focus B

XBL 7011-7042

Fig. 4.46. Concentration maximum. See Note [B]

XBL 7012-7202

Fig. 4.47. Concentration maximum. See Note [A]
Focus B

XBL 7012-7204

Fig. 4.48. Concentration maximum. See Note [A].

Focus B

Angle of incidence = -2.3°

negative values depending on the exact location of the exit window, the virtual origin of these rays varies greatly with cell width and focal plane location. It is therefore not possible to choose an optimum focal plane for fringe evaluation for thick cells, however for thin cells the optimum is chosen far from the objective lens.

If the incident light is not normal to the cell walls, the maximum will appear larger than it actually is (Fig. 4.48).

F. The Multiple Beam Interferometer

In earlier electrochemical mass transfer studies in this laboratory the multiple beam interferometer designed by O'Brien³³ was used. In this arrangement the cell and the interferometer form an integral unit (Fig. 4.49). Incident light C enters the cell through a partially transmitting mirror B. Following the path of the ray nearest the electrode A, it passes through the electrolyte E curving upwards due to an assumed cathode deposition boundary layer. A part of it, D, leaves the cell through a second partially transmitting mirror. The reflected portion of this beam crosses a second time back through the electrolyte and a part is reflected by the first partially transmitting mirror to cross the electrolyte a third time. A portion of this "third pass" beam leaves the cell as ray F. With 90% reflecting 10% transmitting mirrors, a part of the ray would continue to reflect back and forth in the cell giving higher order output rays. All odd order rays would leave the cell through the second mirror to the right while even orders leave the cell through the first mirror to the left.

An interference pattern forms on the film plane of a camera focussed in this cell between all rays which have their virtual origin coincident on the plane of focus in the cell. If the light enters perpendicular to

XBL 7011-7157

Fig. 4.49 Light path in a multiple beam interferometer cell with a cathodic deposition boundary layer (side view).

- A. reacting electrode
- B. glass cell walls with partially transmitting interferometer mirrors on the inside surfaces
- C. incoming collimated light
- D. outgoing first order light ray nearest to the electrode
- E. electrolyte with a concentration gradient in the vertical direction. The second order ray nearest to the electrode is passing just above E.
- F. outgoing third order ray nearest to the electrode
- G. outgoing first order ray which interferes with F if the focal plane is at the inside of the cell wall farthest from the objective lens. In this case rays F and G interfere to form the lowest end of the interference pattern, only first order rays alone strike the film between the image of the virtual origin of D and the image of F and G.

Note: The wedge angle between the mirrors has a vertical apex parallel to plane of the page, the fringes formed are parallel to the apex.

the mirrors and passes through a region of zero refractive index gradient all multiple reflections of a ray will be collinear and F and D will be collinear. The interference pattern will be independent of choice of focal plane. But if a cathodic boundary layer exists over the electrode, the light will curve upward in the cell as depicted in Fig. 4.49. In this case no other ray has a virtual origin coincident with D, therefore ray D does not interfere and produces a medium intensity region on the film.

Ray G is the lowest "first order" exit ray with another ray F coincident at the focal plane. Therefore the virtual intersection of the rays F and G locates the lowest edge of the interference pattern. Farther from the electrode higher odd orders of interference contribute to the pattern.

Figure 4.50 shows the way in which a fringe shape is calculated in the multiple beam cell. The refractive index profile A (the solid line) represents a concentration profile above the electrode at limiting current having zero concentration at the electrode. The phase of the first order transmitted light in the 2 mm cell with focus at the mirror farthest from the camera is indicated by the dashed curve B. The phase of the third order transmitted light is shown by curve C. Curve C is generated by assuming the cell is three times as thick as it is since the light makes three passes, and that the focal plane is in the cell $1/3$ of the triple thickness from the exit mirror. The phase to concentration conversion is also calculated from $1/3$ the triple cell width. Since the light traverses the cell twice between the first order transmitted light and the third order transmitted light, the resultant fringe is found by taking half the difference between the two phases at each distance from

the electrode. In this example the electrode shadow formed by the third order light C, is lower than the electrode shadow formed by the first order light, B, so a region of light with no interference occurs at E between the apparent electrode shadow and the lower edge of the interference pattern.

In the cathodic case, the interfacial concentration appears to be higher than it is because the region of measurement in the cell for the apparent interfacial concentration is not next to the electrode but between the exit of the lowest first order ray and the lowest third order ray.

The apparent boundary layer thickness of an anodic dissolution boundary layer is correct if the camera is focussed on the mirror surface nearest the lens. In that case the fringes always contact the electrode shadow.

An example of a multiple beam interference pattern of desalinization membrane (Fig. 4.51) shows both the concentration (anodic dissolution) and dilution (cathodic deposition) boundary layer effects. On the dilution side, the fringes do not extend to the electrode shadow (see Region E, Fig. 4.50) as they do on the concentration side.

XBL 7011-7158

Fig. 4.50. Cathodic deposition concentration profile and the resulting multiple beam interference fringe shape

- A. (solid line from coordinates 0,0 upward) concentration profile
- B. (dotted line extending below and to the left of coordinates 0,0) phase (horizontally) and location (vertically) of the first order light as it is focussed on the film plane.
- C. phase of the third order light as it is focussed on the film (the phase is normalized to single pass concentration).
- D. resultant multiple beam fringe profile formed by dividing the the phase difference between the first order light and the third order light in half
- E. region where only the third order light strikes the film, no interference forms.

current density = 1.1 ma/cm^2 , cell width = 2 mm, focus at the inside of the glass wall farthest from the objective lens

t=0 sec.

t=4 sec.

A

B

XBB 711-1

Fig. 4.51. Dialysis through a potassium permeable membrane

0.03 N KCl [10 ma/cm² [stagnant solution cell thickness 2 mm

- A. Dilution (cathodic deposition) side of the membrane. The surface of the membrane appears advanced into the solution and the fringe pattern does not extend to the membrane shadow. The region between the fringe end and the membrane shadow is the region where only the first order rays are focussed. The fringes begin where the third order light rays are focussed superimposed on the first order rays.
- B. Concentration (anodic dissolution) side of the membrane. The fringe pattern extends up to the membrane shadow and the shadow appears slightly receded. The plane of focus was probably located on the camera side of the glass liquid interface nearest the camera.

Scale: The field width was 2.7 mm.

V. ANALYSIS OF DATA

A. Simple Analysis of Interferograms

Interferograms of the cathodic deposition boundary layer at constant current were photographed with a Bolex 16 mm movie camera. By comparing an interferogram taken before the electrolysis began with interferograms taken at fixed times after the electrolysis began it was possible to determine the growth of boundary layer thickness with time. As explained in Section IV, the boundary layer thickness at time t , after the current is on is found by measuring the distance between the electrode shadow located before the current is on and the bulk solution edge at time t . (The electrode shadow has moved to a false location due to light deflection). This boundary layer thickness is not the Nernst equivalent boundary layer thickness but the complete boundary layer thickness to the position in the solution where the concentration gradient equals zero.

Figure 5.1 is an example of the development of the boundary layer downstream from the leading edge for a Reynolds Number of 750. The curve on the left is the Levêque solution for a boundary layer in a rectangular channel in steady-state. The points are the measured boundary layer thicknesses in steady state. The points were measured using a Bell and Howell stop motion movie projector and a projection table with graph paper as the screen. Every interferogram movie starts with a photograph of a 1/2 mm grid etched on the inside of the cell wall farthest from the objective lens which is used for focusing the objective system as well as scaling the pictures.

XBL 7011-7053

Fig. 5.1. Boundary layer thickness in a rectangular channel over an upward facing cathode in laminar flow--the solid curve from 0 to 5 cm is the Leveque solution for a laminar boundary layer in fully developed flow. The circles are the corresponding boundary layer thicknesses found interferometrically with a 0.1 molar copper sulfate solution in a 1 cm wide, 2.54 cm high channel above the cathode in steady state. A groove across the cathode at 69.5 cm caused a time dependent step in the boundary layer thickness as shown.

Since the solution was 0.1 molar CuSO_4 , a solution of relatively low conductivity, ohmic overpotential caused a current density that was higher than predicted by the Levêque solution at the leading edge of the electrode. The boundary thickness as measured by interferometry should be greater than the predicted Nernst layer, and the Nernst thickness should be independent of the presence of supporting electrolyte depending only on the diffusivity of the reaction ion.

At 69.5 mm from the leading edge the curves show a transient boundary layer development measured at a groove across the electrode, which is drawn to scale. The change in boundary layer thickness across this groove is about twice its depth. In intentionally sectioned electrode systems, such as used by Hickman, and after long times in deposition or dissolution when the surface becomes rough, similar effects should occur.

If the concentration gradients are sufficiently low so that light deflection effects in the cell are negligible, the concentration profile in the boundary layer can be determined by using Eq. 5.1. The concentration difference ΔC at any distance from the electrode y is

$$\Delta C(y) = \frac{1}{dn/dc} \Delta f(y) \lambda/a \quad (5.1)$$

where, Δf is the fringe shift (amount of displacement of the fringe from a projection of the straight portion in the uniform concentration region divided by the fringe spacing), λ is the wavelength of light, and a is the width of the cell.

In the boundary layers of concern in this study, the effect of light deflection is much too great for this simple analysis. A test can be performed to verify this based on the calculation of light deflection in

Schlieren optics. From an estimate of the highest refractive index gradient expected $(dn/dy)_{\max}$ Eq. 5.2 can be used to calculate the approximate slope of the light ray which leaves the cell after traversing this highest refractive index region (a is the cell width).

$$\left(\frac{dy}{dx}\right)_{\text{light exit}} \cong a \left(\frac{dn}{dy}\right)_{\max} \quad (5.2)$$

The slope of the leaving ray may also be found from an interferogram by measuring the maximum fringe slope $(df/dy)_{\max}$ and using Eq. 5.3

$$\left(\frac{dy}{dx}\right)_{\text{light exit}} \cong \lambda \left(\frac{df}{dy}\right)_{\max} \quad (5.3)$$

Using Fig. 5.2 where B is the solution, A is the electrode, and D is the ray of slope $(dy/dx)_{\text{light exit}}$, for small angles the light makes a nearly circular curve F through the electrolyte which can be approximated by a cord E of that circle with slope $1/2 (dy/dx)_{\text{light exit}}$. The ray leaves the cell at a distance d from the electrode. The fractional error in using the simple analysis will be of the order of d/δ where δ is the Nernst boundary layer thickness. The approximate percent error E then is defined in Eq. 5.4.

$$E \cong 100 \frac{a}{2\delta} \left(\frac{df}{dy}\right)_{\max} \cong 100 \left(\frac{a^2}{2\delta}\right) \left(\frac{dn}{dy}\right)_{\max} \quad (5.4)$$

The error estimated is the error in boundary layer concentration difference and in the boundary layer thickness.

XBL 7011-7089

Fig. 5.2. Estimation of error due to light deflection in interferometry

- A. electrode
- B. electrolyte with refractive index increasing upward
- C. incoming light
- D. outgoing light
- E. approximate straight ray path
- F. actual ray path

Even when the error is small, careful choice of focal plane is important for proper results as indicated in Section IV-B. If the exit slope is larger, limited apertures in the optics may block the higher angle light resulting in a loss of part of the fringe pattern.

An idea of the usefulness of the error expression (Eq. 5.4) can be obtained by computing the expected errors on boundary layers in Section IV. In the table below the boundary layer error is based on the Nernst equivalent boundary layer thickness. The error depends on the choice of focal planes, the error using the recommended focal plane is listed first.

Figure	Error Estimate		Error Measured		
	From dn/dy	From df/dy Eq. 5.4	B.L. Thickness	ΔC	dc/dy
4.8	300	170	130 to -200	9 to -140	-37
4.18	300	160	0 to -200	-44 to -120	-46
4.23	7	7	0 to -12	-3 to -8	0
All errors in percent					

B. Analysis of Fringes Including Light Deflection In the Cell

As described in Section IV, when refractive index gradients in the experimental cell become large, the light passing through the cell follows a curved path causing systematic discrepancies between the simplified fringe analysis excluding light curvature and the actual fringe pattern observed. In order to calculate a resultant fringe from an assumed arbitrary refractive index profile a numerical technique is required. It is not possible to calculate the refractive index profile from a given fringe. Since the

refractive index to fringe conversion is tedious, it is most easily done on a computer: the reverse conversion uses a trial and error method based on the forward conversion.

The original fringe data was prepared for computation by measuring the interferograms on a measuring microscope. The measuring microscope consists of a binocular microscope head mounted over a two directional translating stage. The two in plane translations are controlled by screws connected to counters with electrical output. The counters were connected directly to a keypunch where each coordinate could be automatically punched on a card in a given digit format. The resolution of the translational measurement is one micron.

The movie film to be measured was placed on the translating stage. The stage was moved to a location such that the desired point appeared at the cross hair in the microscope, and a pedal pressed to record the desired coordinates on a punched card. The first frame measured was a photograph of the 1/2 mm lines etched on the wall of the experimental cell. Four or five points on each of the lines were recorded to provide an accurate dimensional reference for the later analysis. The next frame measured was the fringe pattern before the electrolysis began; it gives the true electrode location. The following frames measured were fringe patterns taken at predetermined times after the electrolysis began.

Each frame was measured in the same way. First the sprocket hole locations were measured to orient and position the frame in the computational coordinate system. Then a set of points on the edge of the electrode shadow were taken. Following that six curves were measured; two edges of each of three fringes. Last the number of fringe shifts in the boundary

layer were recorded by taking a point in the middle of each fringe as the crosshair was moved in the direction perpendicular to the electrode shadow across the boundary layer. The seven fringe measurements were then moved together and fitted to an expression of the form used to compute the error function.

$$f(y) = \exp(A_4 y)^2 \left(\frac{A_1}{1 + p A_4 y} + \frac{A_2}{(1 + p A_4 y)^2} + \frac{A_3}{(1 + p A_4 y)^3} \right) \quad (5.5)$$

where f is fringe shift, $p = .47047$, y is the distance from the electrode and the A 's are adjustable parameters. A plot of the result shown in Fig. 5.3 is displayed on a cathode ray tube. The slashes are measured points and the diamonds are the fitted curve. A systematic error sometimes appears as in Fig. 5.4. In that case additional functions are added to the fitting function by the operator at the CRT display to improve the curve fit.

Once an acceptable fit is obtained, the fitted fringe (diamonds) and an automatically guessed fringe (slashes) are plotted together as in Fig. 5.5. The operator then guesses parameters A_1 to A_4 for the actual refractive index profile until a satisfactory fit is obtained as in Fig. 5.6. The guessed refractive index profile is then used to compute and print current density, interfacial concentration at the electrode, boundary layer thickness and other pertinent boundary layer information.

C. A Method for Including The Variation of The Boundary Layer Across a Flow Channel

As pointed out in Section II, the velocity gradient at the electrode is not uniform across the channel and the mass transfer boundary layer varies in thickness. Since that is the direction of light propagation,

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Fig. 5.3 Cathode ray tube console display of a satisfactory fringe fit for a cathodic deposition boundary layer

points measured with the measuring microscope showing actual fringe shape

analytical function with parameters set to best fit the points. This function is used in the later analysis rather than the data points.

Experimental Conditions: $i = 10 \text{ mA/cm}^2$; $C = 0.10 \text{ M CuSO}_4$; z (distance from leading edge of electrode) = 7.7 cm.

XBL 7011-7033

Fig. 5.4 Cathode ray tube console display of an unsatisfactory fringe fit for a cathodic deposition boundary layer

\points measured with the measuring microscope showing actual fringe shape

\analytical function with parameters set to best fit the points
This function must be modified to obtain a better fit.

XBL 7011-7032

Fig. 5.5 Cathode ray tube console display at the start of the refractive index profile guessing procedure for a cathodic deposition boundary layer

- \ fringe shape computed from the guessed refractive index-profile
- ◇ analytical function representing fringe shape

The parameters for the guessed refractive index profile are labeled guess in the graph. Note: The zero line represents the actual location of the electrode.

XBL 7011-7029

Fig. 5.6. Cathode ray tube console display after a satisfactory refractive index profile has been found, the computed fringe fits the measured fringe for a cathodic deposition boundary layer

- fringe shape computed from the guessed refractive index profile
- ◇ analytical function representing fringe shape

The parameters for the guessed refractive index profile are labeled guess in the plot. Note: the zero line represents the actual location of the electrode.

the interferogram is a result of an integral effect across a nonuniform boundary layer. In the preceding analysis we have assumed that this variation across the channel does not exist.

In order to evaluate the dependence of the boundary layer thickness on the cross channel dimension, the use of a focusing refractometer (Section IIIC) is proposed for the measurement of the boundary layer adjacent to the glass wall. The resultant refractogram and corresponding interferogram are measured on a large screen projection type measuring machine similar to the measuring microscope used previously for fringe measurement. The large screen is required because the critical angle boundary in the refractogram cannot be seen with the measuring microscope due to the low contrast in the image.

From the refractogram measurement a concentration profile at the two glass walls may be deduced; $C(0,y)|_z = C(a,y)|_z$ recalling that the glass walls are at $x=0$ and $x=a$. The fringe is then fitted by manually inserting adjustable parameters while watching the resultant computed fringe on a CRT display as done in the previous section.

The first adjustable parameter is K from Eq. 2.9

$$C(x,y)|_z = C(0,y(K[V(x)]^{1/3} + 1))|_z \quad (2.9)$$

used to introduce the velocity dependence into the boundary layer thickness. If adjusting K does not lead to a satisfactory fringe fit an additional set of general scaling factors can be multiplied times y of the form $K_{m,n}y^m(x^2-ax)^n + 1$. The local current density and boundary layer thickness can then be found from $C(x,y)|_z$. The interfacial concentration is found near the glass wall from the refractogram and is assumed constant

across the channel. The z and t dependence of the concentration profile is found by curve fitting each of the adjustable parameters to functions of $z^{1/3}$ and t .

The analysis breaks down in the presence of natural convection, because periodic concentration variations occur in that case. The period of these variations can perhaps be found with the Doppler velocimeter or with an interferometric technique which reflects the light off of the electrode. However even if the period is known a quantitative analysis of the interferograms may not lead to a unique correct result.

D. Uniqueness of Results

In Sections B and C iterative guessing techniques were described for fringe analysis. It is conceivable that an incorrect boundary layer shape may be found which results in a satisfactory fringe fit. While no method exists for assuring that a correct solution of the boundary layer has been obtained, some assurance of the reasonableness of the results may come from substituting the results into the applicable mass transfer equations for verification.

The total current I , measured externally must equal the integral of the local current density over the total electrode surface. I contains both a diffusion component and a migration component and can be computed from the concentration profile. The migration component is most easily included by using the transference number t_j , where it is defined as follows

$$t_j = \frac{u_j n_j C_j}{\sum u_k n_k C_k} \quad (5.6)$$

u is ionic mobility, n is valence, and C is local concentration. The local current density can be written¹⁶

$$i(x,z) = - \frac{D n_+ F \frac{\partial C}{\partial y}(x,y,z)}{1 - t_+} \quad (5.7)$$

where D is the salt diffusivity, n_+ is the valence of the reacting ion, F is the Faraday constant (96,500 coul/equiv), C is the concentration of the reacting ion and t_+ is the transference number of the reacting ion. The total current is then calculated by integrating over the electrode area.

$$I = \int_0^L \int_0^a i(x,z) dx dz \quad (5.8)$$

The total current should equal the externally measured electrode current.

A second check of the validity of the results may be made by writing a mass balance over a portion of the electrode in steady state. For the electrode region between the leading edge and a location at distance z down the electrode the mass balance is Eq. 5.9.

$$\int_0^z \int_0^a i(x,z) dx dz = \int_0^{b/2} \int_0^a (C_{\text{bulk}} - C(x,y,z)|_z) dx dy \quad (5.9)$$

For the unsteady state a local balance may be written

$$\int_0^a i(x,z) dx = - \int_0^{b/2} \int_0^a \left[\frac{\partial C(x,y,z,t)}{\partial z} + \frac{\partial C(x,y,z,t)}{\partial t} \right] dx dy \quad (5.10)$$

VI. CONCLUSIONS

Interferometry, previously thought to be a simple accurate method of examining concentration, temperature and density profiles in transport systems suffers from serious distortions when high refractive index gradients are observed. Interferometry is not alone with this problem, all optical observations involving refractive index gradients including Schlieren optics, densitometry, refractometry, photography, and holography can suffer from these distortions. The distortions can only be detected by performing theoretical, interferometric, or Schlieren optical tests on the optical systems. Error estimation based on equations such as Eq. 5.4 which only include the first derivative of the refractive index profile can only give an approximate idea of the error because the error depends strongly on the second derivative of the profile. A computed trace of light rays as they pass through the refractive index field is the most reliable way to test for error in an interferometric system.

A series of such computations presented in Section IV has shown that no distortions appear in regions with no refractive index gradient nearby. With proper focus, maxima and minima also appear with no distortion at the point of zero gradient.

False maxima, minima and interfacial boundaries may appear in the interferograms due to fringe overlap and to introducing the light into the experimental cell at non normal incidence. Such anomalies can be detected by changing the plane of focus and by checking the cell orientation.

Unfortunately none of the interferometric studies of mass transfer boundary layers discussed in the literature properly considered the problem of light deflection nor included information about the exact focal

* A recent work by Tvarusko and Watkins⁵⁰ excepted.

plane used in the experiments. It is therefore impossible to extract quantitative information about the boundary layers observed in these studies.

Several other optical systems may be advantageously used in conjunction with an interferometer to provide additional information about the boundary layer. The instruments developed for use in this study include a focussing refractometer, an absorption densitometer, and a Doppler velocimeter. Independently, the auxilliary instruments cannot provide sufficient information to describe the concentration profile in the boundary layer.

SYMBOLS

a	channel width and electrode width	cm
A	channel cross sectional area	cm ²
A	coefficient	
A	angstroms	10 ⁻⁸ cm
b	channel height and electrode spacing	cm
B	coefficient	
c	speed of light	3×10 ¹⁰ cm/sec
C	concentration	moles/liter
d	distance between a ray leaving the cell and the electrode	cm
D	hydraulic diameter	4A/P
D	diffusivity	cm ² /sec
E	percent error in fringe shift and boundary layer thickness	
f	function	
f	frequency	cy/sec
Δf	fringe shift	
F	Faraday's constant	96,500 coul/equiv
g	gravitational constant	980 cm/sec ²
Gr	Grashof Number	ΔρL ³ g/v ² ρ
i	integer	
i	local current density	amp/cm ²
I	total current	amp
j	integer	
j	ionic flux and molecular flux	moles/cm ² sec
K	coefficient	
L	electrode length	cm

m	integer	
n	valence	
Nu	Nusselt Number for mass transfer	$JD/C\mathcal{D}$
p	pressure	dyne/cm^2
P	Channel perimeter	cm
P	phase of light	radians
Re	Reynolds Number	Dvp/μ
Sc	Schmidt Number	$\mu/D\rho$
t	(subscript) transmitted	
t	time	sec
t	transference number	$nuc/\Sigma nuc$
u	ionic mobility	$\text{cm}^2/\text{volt sec}$
v	velocity	cm/sec
V	velocity of light and particles in figures	
V	velocity gradient at electrode	$(\partial v/\partial y) _{y=0}$
x	cross channel direction and light propagation	
y	direction perpendicular to electrodes	
z	direction parallel to channel axis	

α	scaling factor for y	
γ	absorption coefficient for light	
δ	boundary layer thickness	mm
λ	wavelength of light	A
n	refractive index	
μ	viscosity	gpa/cm sec
ρ	density	gpa/cm ³
θ	angle of incidence measured to a line normal to the intersected plane	
θ	(velocimeter) angle between incident and reflected light	

REFERENCES

1. Angus, John C. D. L. Morrow, J. W. Dunning and M. J. French, "Motion Measurement by Laser Doppler Techniques," *Ind. Eng. Chem.*, 61, 8, (1969).
2. Beach, Kirk W., "A Laser Interferometer for Mass Transfer Studies," MS Thesis, Chemical Engineering, UC Berkeley, UCRL-18037, * (1968).
3. Beach, K. W., R. H. Muller, and C. W. Tobias, "Laser Interferometer for Mass Transfer Studies," *Rev. Sci. Instr.*, 40, 1248 (1969).
4. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, John Wiley, (1960).
5. Colello, Ralph G., and George S. Springer, "Mass Transfer Measurements with the Technique of Electrochemiluminescence," *Int. J. Heat Mass. Transfer* 9, 1391 (1966).
6. Chapman, Thomas W., and John Newman, "A Compilation of Selected Thermodynamic and Transport Properties of Binary Electrolytes in Aqueous Solution," UCRL-17767, * (1968).
7. Chapman, Thomas W., "The Transport Properties of Concentrated Electrolytic Solutions," Ph.D. Thesis, Chem. Eng. UC Berkeley, UCRL -17768, * (1968).
8. Davis, Donald T., "Analysis of a Laser Doppler Velocimeter," *Instr. Soc. Am. Trans.* 7, 43 (1968).
9. Francon, M., Optical Interferometry, Academic Press, New York, (1966).
10. Gill, William N., Eduardo Del Casal, "A Theoretical Investigation of Natural Convection Effects in Forced Horizontal Flows," *AIChE Journ.* 8, 513 (1962).

11. Goldstein, R. J., "Interferometer for Aerodynamic and Heat Transfer Measurements," Rev. Sci. Instr., 36, 1408, (1965).
12. Han, L. S., "Hydrodynamic Entrance Lengths for Incompressible Flow in Rectangular Ducts," J. Applied Mechanics, 82, 403 (1960).
13. Happel, John and Howard Brenner, Low Reynolds Number Hydrodynamics, Prentice Hall, Englewood Cliffs N. J., (1965).
14. Hariharan, P., and D. Sen, "3 Beam Interferometer for Diffusion Measurements," J. Sci. Instr. 39, 165 (1962).
15. Hickman, R. G., "The Effect of Buoyancy Forces on Forced Convection Ionic Mass Transfer at Horizontal Planar Electrodes," Ph.D. Thesis, Chem. Eng. UC Berkeley (1958).
16. Hsueh, Limin, "Diffusion and Migration in Electrochemical Systems," Ph.D. Thesis, Chem. Eng. UC Berkeley, UCRL-18597, * (1968).
17. Ibl, N., "Methods for the Study of the Diffusion Layer," Proc. of the Seventh Meeting of the International Committee of Electrochemical Thermodynamics and Kinetics, (CITCE) 112, (1955).
18. Jackson, R. A., "The Laser as a Light Source For the Mach Zehnder Interferometer," J. Sci. Instr. 42, 282 (1965).
19. Jenkins, Francis A., Harvey E. White, Fundamentals of Optics, McGraw Hill, New York, (1957).
20. Kaneko, M., and M. Takashima, "Laser Interferometer and Interference Experiments with Beams From Opposing Ends of a Gas Laser," Oyo Butsuri, (Japanese J. of Appl. Physics - in Japanese) 34, 181 (1965).
21. Kapuskar, Wisu T., and Christopher J. Balmforth, "Real Time Measurement and On-Line Processing of Acoustical and Other Audio-Frequency Spectra," Hewlett-Packard Journal, July 1969.

22. Karaser, F. W., "Analytic Instruments in Process Control," Sci. Amer. 220, 6, 112 (1969).
23. Knox, C., R. R. Sayano, E. T. Seo, and H. P. Silverman, "Holographic Interferometry in Electrochemical Studies," J. Phys. Chem., 71, 3102 (1967).
24. Lennert, A. E., D. B. Brayton, W. H. Goethert, and F. H. Smith, "Laser Applications for Flow Field Diagnostics", Electro-Technology, Feb. (1970).
25. Lin, C. S., R. W. Moulton and G. L. Putman, "Interferometric Measurements of Concentration Profiles in Turbulent and Streamline Flow," Ind. Eng. Chem. 45, 636 (1953).
26. Marchand, Eric W., "Ray Tracing in Gradient-Index Media," J. Opt. Soc. Am., 60, 1 (1970).
27. Miller, Carlton S., Fredrick G. Parsons, and Irving L. Kofsky, "Simplified Two-Dimensional Microdensitometry," Nature, 202, 1196 (1964).
28. Montagnino, L., "Ray Tracing in Inhomogeneous Media", J. Opt. Soc. Am., 58, 1667 (1968).
29. Muller, R. H., "Optical Techniques for the Study of Diffusional Mass Transfer," UCRL-11542, * (1964).
30. Muller, Rolf H., "Optical Techniques for the Study of Phase Boundaries," UCRL-11997, * (1965).
31. Newman, John, "Current Distribution and Mass Transfer in Electrochemical Systems," UCRL-17294, * (1967).
32. Newman, John, "Engineering Design of Electrochemical Systems," Ind. Eng. Chem., 60, 12 (1968).
33. O'Brien, R. N., "Interferometer for Electrochemical Investigations," Rev. Sci. Instr., 35, 803 (1964).

34. O'Brien, Robert N., "The Use of the Motion Picture Camera in Interferometric Electrochemical Investigations," J. Electrochem. Soc., 111, 1300, (1964).
35. Paranjpe, M. K., "The Convection and Variation of Temperature Near a Hot Surface, Part II Applications of Interferometry," Proc. Indian Acad. Sci., Sec. A4, 639.
36. Parrish, W. R., and J. Newman, "Current Distribution on a Plane Electrode Below Limiting Current," J. Electrochemical Soc., 116, 169 (1969).
37. Pike, E. R., D. A. Jackson, P. J. Bourke, and D. I. Page, "Measurement of Turbulent Velocities From the Doppler Shift in Scattered Laser Light," AERE-R-5648, Harwell Berkshire, England, (1967).
38. Sadovnikov, G. V., B. M. Smol'skiy, and V. K. Shchitnikov, "Investigation of Simultaneous Heat and Mass Transfer Using an Interferometer," Heat Transfer Soviet Research, 1, 1 (1969).
39. Sparrow, E. M., and W. J. Minkowycz, "Buoyancy Effects on Horizontal Boundary-Layer Flow and Heat Transfer," Int. J. Heat Mass Trans, 5, p. 505 (1965).
40. Svensson, Harry, "The Second Order Aberrations in the Interferometric Measurement of Concentration Gradients," Opt. Acta, 1, 25 (1954).
41. Tanner, L. H., "Some Laser Interferometers for Use in Fluid Mechanics," J. Sci. Instr., 42, 834 (1965).
42. Tanner, L. H. "The Design of Laser Interferometers for Use in Fluid Mechanics," J. Sci. Instr. 43, 878 (1966).
43. Tolansky, S., Multiple-Beam Interferometry, Clarendon Press, Oxford, England, (1948).

44. Tvarusko, A, and L. S. Watkins, "Laser Interferometric Study of the Diffusion Layer at a Vertical Cathode During Non-Steady State Conditions," *Electrochimica Acta*, 14, 1109, (1969).
45. Wagner, Carl, "Theoretical Analysis of the Current Density Distribution in Electrolytic Cells," *J. Electrochem. Soc.*, 98, 116 (1951).
46. Washburn, Edward W., Ed., International Critical Tables, National Research Council, McGraw Hill, New York, 5, 330, (1933).
47. Watson, R. C., R. D. Lewis, and H. J. Watson, "Instruments for Motion Measurement Using Laser Doppler Heterodyning Techniques," *Instr. Soc. Am. Trans.* 8, (1969).
48. Whatley, Larry A., "Rapid Analysis of Low Frequency Spectra," *Hewlett-Packard Journal*, Dec. 1968.
49. Winckler, John, "The Mach Interferometer Applied to Studying an Axially Symmetric Supersonic Air Jet," *Rev. Sci. Instr.*, 19, 307, (1948).
50. Tvarusko, A. and Watkins, L. S., "Determination of the Diffusion Layer Thickness at a Cathode in CuSO_4 Solutions," *J. Electrochem. Soc.*, 118, 248 (1971).

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Laser

APPENDIX I

A. Derivation of Equation of Light Deflection

Consider light passing through a refracting medium $\eta = \eta(x,y)$ in the x,y plane with a slope $\frac{dy}{dx}$ at any point. Consider a coordinate system s,q in the xy plane with s parallel to the light propagation direction, as shown below.

The optical path, W , of the light can be expressed as a product of refractive index and distance.

$$W = \eta s$$

From an examination of a short section of the optical path with two rays of equal ΔW

it is found that where $(dq/ds)_m = 0$

$$\Delta\left(\frac{dq}{ds}\right) = \left(\frac{dq}{ds}\right)_n - \left(\frac{dq}{ds}\right)_m = \frac{\Delta s_1 - \Delta s_2}{\Delta q}$$

since equal optical path differences give equal phase shifts

$$\Delta W = \eta_1 \Delta s_1 = \eta_2 \Delta s_2$$

so

$$\Delta \left(\frac{dq}{ds} \right) = \frac{\Delta W \left(\frac{1}{\eta_1} - \frac{1}{\eta_2} \right)}{\Delta q} = \frac{\Delta W \Delta \eta}{\eta_1 \eta_2 \Delta q} \quad \text{where } \Delta \eta = \eta_2 - \eta_1$$

substituting

$$\Delta \left(\frac{dq}{ds} \right) = \frac{\eta \Delta s \Delta \eta}{\eta_1 \eta_2 \Delta q}$$

and simplifying

$$\frac{\Delta}{\Delta s} \left(\frac{dq}{ds} \right) = \frac{\eta}{\eta_1 \eta_2} \frac{\Delta \eta}{\Delta q}$$

is obtained.

Taking the limit as $\Delta s \rightarrow 0$ and $\Delta q \rightarrow 0$

$$\frac{d^2 q}{ds^2} = \frac{1}{\eta} \frac{d\eta}{dq} .$$

The conversion to x,y coordinates may be made by the following identities. For $\frac{dy}{dx} = \tan \alpha = \text{slope of light path}$

$$\frac{d}{dq} = \left(\frac{\partial}{\partial y} + \frac{\partial}{\partial x} \left(\frac{dy}{dx} \right) \right) \frac{1}{\sqrt{1 + \left(\frac{dy}{dx} \right)^2}}$$

$$\frac{d^2 y}{dx^2} = \frac{d^2 q}{ds^2} \left(1 + \left(\frac{dy}{dx} \right)^2 \right)^{3/2}$$

Making the substitutions for $\frac{d}{dq}$ and $\frac{d^2 q}{ds^2}$

$$\frac{d^2 y}{dx^2} = \frac{1}{\eta} \left(1 + \left(\frac{dy}{dx} \right)^2 \right) \left(\frac{\partial \eta}{\partial y} + \frac{\partial \eta}{\partial x} \left(\frac{dy}{dx} \right) \right) \quad (4.1)$$

is obtained.

B. Interpretation of Fringes

Interferometry and Schlieren optics are the two principal ways of observing refractive index gradients. The phenomenon which they observe is a phase change across the beam which results in a light deflection. Interferometry observes the phase change directly, effectively plotting phase vs distance on the film plane. It is the easiest to interpret of the two methods and is often used to measure small phase changes. The Schlieren technique requires simpler optics, but observes only the light deflection and is difficult to interpret. It therefore is used for large objects where interferometers are not easily used.

As the effects observed are closely related, it is expected that in either observation technique, artifacts resulting from the other effect could be observed. If a Schlieren system has a coherent light source, interference lines will appear in addition to the desired pattern. Similarly in interferometry, the interference pattern will be displaced due to the light deflection. In addition, the deflection results in a longer optical path which passes through regions of different refractive index. In early studies in this work, displacements were seen to be responsible for errors of up to 50% in boundary layer dimensions.

Svensson⁴⁰ examined the problem of the longer optical path and found that by choosing his focal plane carefully, he could eliminate the path length error. In his system he had no interface so he did not consider the change in apparent location of an interface in a gradient. Müller* considered both the electrode shadow displacement and the optical path length error for the case of a linear gradient in the boundary region.

* Unpublished data

The following analysis is more general in derivation than the previous two analyses but the resulting equations are so complex that a numerical solution is required for all but the simplest cases.

Light Deflection in the Electrolyte

As a first approximation, consider the case of light passing through a cell in the x direction, as shown below, from $x = 0$ to $x = x_1$.

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Without deflection, the optical path p_s is

$$p_s(y,z) = \int_0^{x_1} \eta(x,y,z) dx$$

where $\eta(x,y,z)$ is the refractive index. The x dependence of refractive index is inaccessible. For measurement convenience, fringes are created parallel to the y axis and the y dependence of refractive index is obtained most easily and accurately.

To consider the deflection of a light ray crossing a cell from $x = 0$ to $x = x_1$ we must consider the following differential equation for light deflection (derived in Appendix I-A).

$$\frac{d^2 y}{dx^2} = \frac{1}{\eta(x,y,z)} \left(1 + \left(\frac{dy}{dx} \right)^2 \right) \left[\left(\frac{\partial \eta}{\partial y} \right)_{x,z} + \left(\frac{\partial \eta}{\partial x} \right)_{y,z} \left(\frac{dy}{dx} \right) \right] \quad (4.1)$$

$$\frac{d^2 z}{dx^2} = \frac{1}{\eta(x,y,z)} \left(1 + \left(\frac{dz}{dx} \right)^2 \right) \left[\left(\frac{\partial \eta}{\partial z} \right)_{x,y} + \left(\frac{\partial \eta}{\partial x} \right)_{y,z} \left(\frac{dz}{dx} \right) \right] \quad (4-2a)$$

Equation (4.1) is not easily solved when $(\partial \eta / \partial y)_{x,z}$ is nonzero, but it may be handled by numerical techniques.

For the case $\eta = \eta(y)$ an analytical solution is found as follows

$$\frac{d^2 y}{dx^2} = \frac{1}{\eta(y)} \left(1 + \left(\frac{dy}{dx} \right)^2 \right) \frac{d\eta}{dy}$$

Introducing

$$P = \frac{dy}{dx}$$

$$\frac{d^2 y}{dx^2} = \frac{dP}{dx} = \frac{dP}{dy} \frac{dy}{dx} = P \frac{dP}{dy}$$

Substituting

$$P \frac{dP}{dy} = \frac{1}{\eta(y)} (1 + P^2) \frac{d\eta}{dy}$$

$$\int_{P_0}^P \frac{PdP}{(1+P^2)} = \int_{y_0}^y \frac{1}{\eta(y)} \frac{d\eta}{dy} dy = \int_{\eta_0}^{\eta} \frac{d\eta}{\eta}$$

$$P = \sqrt{\left(\frac{\eta(y)}{\eta_0}\right)^2 (P_0^2 + 1) - 1}$$

Substituting

$$P_0 = \gamma = \left. \frac{dy}{dx} \right|_{x=0}$$

$$\eta_0 = \eta(y) \Big|_{y=0}$$

$$\frac{dy}{dx} = \sqrt{(\eta(y)/\eta_0)^2 (\gamma^2 + 1) - 1}$$

For light passing from $(0, y_1)$ to (x, y) we can write

$$x = \int_0^x dx = \int_{y_0}^y \frac{dy}{\sqrt{(\eta(y)/\eta_0)^2 (\gamma^2 + 1) - 1}} \quad (I-B.1)$$

where y is dependent on x .

The optical path can now be obtained by the integration

$$P = \int_{x=0}^{x=x_1} \eta(x, y, z) ds$$

where

$$ds = \sqrt{dx^2 + dy^2 + dz^2} = \sqrt{1 + (dy/dx)^2 + (dz/dx)^2} dx$$

$$p = \int_{x=0}^{x=x_1} \eta(x,y,z) \sqrt{1 + (dy/dx)^2 + (dz/dx)^2} dx$$

For the case

$$\eta(x,y,z) = \eta(y)$$

$$p = \int_{y_1}^y \frac{\eta(y)}{\eta_0} \sqrt{\frac{\eta^2(y) (\gamma^2 + 1)}{\eta^2(y) (\gamma^2 + 1) - 1}} dy$$

Light Deflection in the Glass Wall

The above discussion is sufficient to find the location, direction and phase of a light ray leaving the electrolyte if the ray is characterized upon entry and if the refractive index function is known. Since it is only the light ray in air that can be measured, the effect of the glass and the interface must be included. The discussion will be limited to the case of negligible deflection in the z direction and perpendicular^{*} incidence.

As shown in Fig. I-B.1, the effect of the first glass wall need not be considered, as it affects the idealized undeflected ray in the same way as it affects the actual ray. The deflected ray enters the cell at (x_0, y_0) and leaves the electrolyte at (x_1, y_1) and an angle of α_1 , passes through the glass at angle α_2 and enters the air at (x_2, y_2) and α_3 .

^{*} Normal to the first initial wall.

XBL 682-159

Fig. I-B.1. Deflected light path through interferometric cell.

Snell's Law

$$\eta(x_1, y_1) \sin \alpha_1 = \eta_g \sin \alpha_2 = \sin \alpha_3$$

with the substitution

$$\sin \alpha = \frac{1}{\sqrt{1 + 1/(\frac{dy}{dx})^2}}$$

results in

$$\left(\frac{dy}{dx}\right)_3 = \frac{\eta(x_1, y_1) (\frac{dy}{dx})_1}{\sqrt{1 + (\frac{dy}{dx})_1^2 - \eta^2(x_1, y_1) (\frac{dy}{dx})_1^2}} \quad (\text{I-B.2})$$

and

$$\left(\frac{dy}{dx}\right)_2 = \frac{\eta(x_1, y_1) (\frac{dy}{dx})_1}{\sqrt{\eta_g^2 + \eta_g^2 (\frac{dy}{dx})_1^2 - \eta^2(x_1, y_1) (\frac{dy}{dx})_1^2}}$$

The expression

$$y_2 - y_1 = \left(\frac{dy}{dx}\right)_2 (x_2 - x_1)$$

results in

$$y_2 = y_1 + \frac{(x_2 - x_1) \eta(x_1, y_1) (\frac{dy}{dx})_1}{\sqrt{\eta_g^2 + \eta_g^2 (\frac{dy}{dx})_1^2 - \eta^2(x_1, y_1) (\frac{dy}{dx})_1^2}} \quad (\text{I-B.3})$$

The optical path in the glass is

$$p_g = \eta_g \sqrt{1 + (\frac{dy}{dx})_2^2} (x_2 - x_1)$$

or

$$p_g = \eta_g \sqrt{\frac{1 + (dy/dx)_1^2}{1 + (dy/dx)_1^2 - (\eta(x_1, y_1)/\eta_g)^2 (dy/dx)_1^2}} (x_2 - x_1)$$

(I-B.4)

A focal plane is now chosen so that a ray passing nearest the electrode will arrive at the same point on the film plane after passing through the lens whether or not a gradient exists. The electrode will then appear at the same location on the film plane with and without light deflection. This choice allows direct observation of the boundary layer thickness.

As shown in Fig. I-B.2, focusing on point x_f would image both the undeflected and the deflected rays on point I_f . If the focal plane is chosen at the point x_f derived from the ray originating at $y_0 = 0$, the electrode shadow will appear at I_f , so

$$(y_2 - 0) = \left(\frac{dy}{dx}\right)_3 (x_2 - x_f) \quad (I-B.5)$$

and substituting Eq. (4-11) into (4-14)

$$x_f = x_2 - \frac{y_1 \sqrt{1 + \left(\frac{dy}{dx}\right)_1^2 - \eta^2(x_1, y_1) \left(\frac{dy}{dx}\right)_1^2}}{\eta(x_1, y_1) (dy/dx)_1}$$

$$= \frac{(x_2 - x_1) \sqrt{1 + \left(\frac{dy}{dx}\right)_1^2 - \eta^2(x_1, y_1) \left(\frac{dy}{dx}\right)_1^2}}{\eta_g \sqrt{1 + \left(\frac{dy}{dx}\right)_1^2 - \left(\frac{\eta(x_1, y_1)}{\eta_g}\right)^2 \left(\frac{dy}{dx}\right)_1^2}}$$

is obtained.

XBL 682-158

Fig. I-B.2. Focusing in interferometric cell.

The optical path length error must be found for this choice of focal plane. The actual path length from $x = 0$ to $x = x_2$ is

$$P_T(y) = \int_0^{x_1} \eta(x, f(x)) \sqrt{1 + (dy/dx)^2} dx + \eta_g(x_2 - x_1) \sqrt{\frac{1 + (dy/dx)_1^2}{1 + (dy/dx)_1^2 - (\eta(x_1, y_1)/\eta_g)^2 (dy/dx)_1^2}} \quad (I-B.6)$$

where $y = f(x)$ is the solution to Eq. (4.1). The straight path length from $x = 0$ to $x = x_2$ is

$$P_S = \int_0^{x_1} \eta(x, y_0) dx + \eta_g(x_2 - x_1) \quad (I-B.7)$$

Referring again to Fig. I-B.2 it can be seen that an equiphase line which appears to originate from x_1 is an arc centered on x_f . The straight path must include the distance from the wall to the arc which passes through point (x_2, y_2) . This distance is

$$P_C = \left(\sqrt{1 + (dy/dx)_3^2} - 1 \right) (x_2 - x_f)$$

Substituting in Eq. (I-B.1)

$$P_C = \left(\frac{\sqrt{1 + (dy/dx)_1^2}}{\sqrt{1 + (dy/dx)_1^2 - \eta^2(x_1, y_1)(dy/dx)_1^2}} - 1 \right) (x_2 - x_f) \quad (I-B.8)$$

is obtained.

The path error Δp obtained is

$$\Delta p = p_T - p_s - p_c \quad (\text{I-B.9})$$

or substituting Eqs. (I-B.6), (I-B.7) and (I-B.8) into (I-B.9)

$$\begin{aligned} \Delta p(y_0) = & \int_0^{x_1} \left(\eta(x, f(x)) \sqrt{1 + (dy/dx)^2} - \eta(x, y_0) \right) dx \\ & + \eta_g(x_2 - x_1) \left(\sqrt{\frac{1 + (dy/dx)_1^2}{1 + (dy/dx)_1^2 - \left[\frac{\eta(x_1, y_1)}{\eta_g} \right]^2 (dy/dx)_1^2}} - 1 \right) \\ & - (x_2 - x_f) \left(\sqrt{\frac{1 + (dy/dx)_1^2}{1 + (dy/dx)_1^2 - \eta^2(x_1, y_1) (dy/dx)_1^2}} - 1 \right) \end{aligned} \quad (\text{I-B.10})$$

For any ray other than the one closest to the electrode and those passing through uniform medium, the fringe image will be at a different location than expected. This displacement can also be calculated. The apparent location of a fringe, y_f , is expressed by

$$y_2 - y_f = (dy/dx)_3 (x_2 - x_f) \quad (\text{I-B.11})$$

and substituting Eq. (I-B.1) and (I-B.2) into (I-B.8)

$$y_f = y_1 + \frac{(x_2 - x_1) \eta(x_1, y_1) (dy/dx)_1}{\sqrt{\eta_g^2 + \eta_g^2 (dy/dx)_1^2 - \eta^2(x_1, y_1) (dy/dx)_1^2}} + \frac{(x_f - x_2) \eta(x_1, y_1) (dy/dx)_1}{\sqrt{1 + (dy/dx)^2 - \eta^2(x_1, y_1) (dy/dx)_1^2}} \quad (\text{I-B.12})$$

results.

C. Analytical Calculation of the Optical Error Due to a Linear Gradient

If a medium with a refractive index gradient exists which is linear in y , it can be expressed in the following way,

$$\eta(y) = ay + b$$

A ray which enters the medium in the x direction $x = 0$, $y = 0$ with $\left. \frac{dy}{dx} \right|_{x=0} = \gamma = 0$ may be easily studied analytically.

Substituting $\eta(y)$ into Eq. (I-B.1)

$$x = \int_0^y \frac{dy}{\sqrt{\frac{\eta(y)}{\eta_0}}} \quad (\text{I-B.1})$$

The result

$$y = \frac{2b}{a} \sinh^2 \left(\frac{ax}{2b} \right) = \frac{b}{a} \left(\cosh \left(\frac{ax}{b} \right) - 1 \right)$$

is obtained. This is identical to the result obtained by Müller.⁶

The slope is easily found to be

$$\frac{dy}{dx} = \sinh \left(\frac{ax}{b} \right)$$

The optical path can be found by integration

$$p = \int_{x=0}^{x=x_1} \eta(y) ds$$

where

$$ds = \sqrt{1 + \left(\frac{dy}{dx} \right)^2} dx$$

and

$$\eta(y) = b \cosh \left(\frac{ax}{b} \right)$$

Substituting

$$p(x) = \int_0^x b \cosh\left(\frac{ax}{b}\right) \cosh\left(\frac{ax}{b}\right) dx$$

and integrating

$$p(x) = \frac{b^2}{4a} \sinh\left(\frac{2ax}{b}\right) + \frac{xb}{2}$$

is obtained.

The ray must now pass through the glass wall into the air. The slope with which it enters the air can be found from Eq. (I-B.2)

$$\left(\frac{dy}{dx}\right)_3 = \frac{\eta(y_1) \left(\frac{dy}{dx}\right)_1}{\sqrt{1 + \left(\frac{dy}{dx}\right)_1^2 - \eta^2(y_1) \left(\frac{dy}{dx}\right)_1^2}} \quad (\text{I-B.2})$$

by substitution

$$\left(\frac{dy}{dx}\right)_3 = \frac{b \sinh\left(\frac{ax_1}{b}\right)}{\sqrt{1 - b^2 \sinh^2\left(\frac{ax_1}{b}\right)}} \quad (\text{I-C.1})$$

The point at which the ray enters the air (see Fig. I-B.1) can also be found from Eq. (I-B.3)

$$y_2 = y_1 + \frac{(x_2 - x_1) \eta(y_1) \left(\frac{dy}{dx}\right)_1}{\sqrt{\eta_g^2 + \eta_g^2 \left(\frac{dy}{dx}\right)_1^2 - \eta^2(y_1) \left(\frac{dy}{dx}\right)_1^2}} \quad (\text{I-B.3})$$

By substitution

$$y_2 = \frac{b}{a} \left(\cosh\left(\frac{ax}{b}\right) - 1 \right) + \frac{x_2 - x_1}{\sqrt{\left(\frac{\eta_g}{b}\right)^2 \operatorname{csch}^2\left(\frac{ax_1}{b}\right) - 1}} \quad (\text{I-C.2})$$

The optical path in the glass may be found from Eq. (I-B.4)

$$p_g = (x_2 - x_1) \eta_g \sqrt{\frac{1 + \left(\frac{dy}{dx}\right)_1^2}{1 + \left(\frac{dy}{dx}\right)_1^2 - \left(\frac{\eta(y_1)}{\eta_g}\right)^2 \left(\frac{dy}{dx}\right)_1^2}} \quad (\text{I-B.4})$$

by substituting

$$p_g = \frac{(x_2 - x_1) \eta_g \cosh\left(\frac{ax}{b}\right)}{\sqrt{\cosh^2 \frac{ax}{b} - \left[\frac{\eta(y_1)}{\eta_g}\right]^2 \sinh^2\left(\frac{ax}{b}\right)}}$$

The focal point x_f for the shadow of the electrode appearing at its location can be found by substituting (I-C.1) and (I-C.2) into Eq. (I-B.5)

$$(y_2 - 0) = \left(\frac{dy}{dx}\right)_{\text{air}} (x_2 - x_f) \quad (\text{I-B.5})$$

$$x_f = x_2 - \frac{1}{a} \sqrt{1 - b^2 \sinh^2 \frac{ax_1}{b}} \left(\text{ctnh} \left(\frac{ax_1}{b} \right) - \text{csch} \left(\frac{ax_1}{b} \right) + \frac{x_2 - x_1}{\sqrt{\eta_g^2 - b^2 \sinh^2 \left(\frac{ax_1}{b} \right)}} \right)$$

APPENDIX II

The computer programs listed here were used to generate some of the figures in Sections II and IV. The plotting routines should not be examined too carefully because they use some features peculiar to our plotting system. The complete program regularly used for fringe analysis has not been included here because it takes 55 pages to list and the heart of the program is used in both NEWAB and NEWAF.

A brief listing of the important variables and functions is included here for the convenience of the reader.

CRT plotting system

XMIN,XMAC,YMIN,YMAC define the plot limits

TVXMIN,TVXMAX, etc ignore

CALL TVPLOT(X,Y,K,⁴HJOIN
⁶HNOJOIN, L,M)

plots x_n, y_n for $n=1$ to K if X and Y are within plot limits. JOIN connects points plotted. L and M define the symbols which mark the points

CALL TVGRID(K,L,⁶H^{LABELS}
^{NOLBLS},M,N)

draws grid lines for the plot with lines and marks defined by K,L,M,N , and labels the lines as in Figs. 5.3 to 5.6.

CALL TVLTR writes from TAPE 98 onto graph

PROGRAM CHNDR

AN

plots Fig. 2.1

channel aspect ratio height/width

N

subscript of AN

I

subscript of X and Y

X

location across channel

Y

normalized velocity derivative

```

PROGRAM CHNDR( INPUT, OUTPUT, TAPE98, FILM)
C THIS PROGRAM PLOTS SHEAR RATE AT THE ELECTRODE IN RECT CHANNELS
COMMON /TVPOOL/ XMIN,XMAX,YMIN,YMAX,TVXMIN,TVXMAX,TVYMIN,TVYMAX
DIMENSION X(101), Y(101), AN(4)
DATA AN / .1, 1., 2.54, 500./
XMIN = 0.
XMAX = 1.
YMIN = 0.
YMAX = 1.
DO 1 N=1,4
PRINT 5
FORMAT(1H1)
X(1) = 0.
Y(1) = 0.
DO 2 I = 1,100
X(I+1) = I / 100.
SUM = 0.
DO 3 M = 1,100
MO = M * 2 - 1
A = .031415926 * I
U = MO * AN(N) * 3.1415926
AO = MO * A
IF (U .GT. 25.) GO TO 6
COSH = (EXP(U) + EXP(-U))/2.
SINH = (EXP(U) - EXP(-U))/2.
SUM = SUM + (1./(MO**2))*((COSH-1.)/SINH)*SIN(AO)
GO TO 3
6 CONTINUE
SUM = SUM + (1./(M**2))*SIN(AO)
3 CONTINUE
Y(I+1) = SUM
PRINT 4,N,I,AN(N),X(I),Y(I)
4 FORMAT(5X,2I5,3F20.5)
2 CONTINUE
I = I + 1
PRINT 4,N,I,AN(N),X(I),Y(I)
CALL TVPLOT(X,Y,101,4HJOIN,1,1)
1 CONTINUE
CALL TVGRID(1,10,6HNOLBLS,1,10)
CALL TVEND
STOP
END

```

PROGRAM NEWAB

IR	number of rays traced
CB	bulk solution concentration of CuSO_4
XNO	refractive index of water
XNG	refractive index of glass
W	cell width
WG	glass wall thickness
FUNCT(X)	converts concentration into refractive index
SCALE(X)	converts phase into concentration
ASF	defines boundary layer thickness
CO	concentration at the interface
DYDXO	slope of the incident light
ACD	current density
YA(1) 3rd line after 950	location of the first ray computed
FUNCTION ZETA	defines the boundary layer shape
FUNCTION ZETAP	takes the derivative of ZETA
1st step above 78	defines the interval between rays computed
PS,YAF	shape of the given profile
F	focal distance from the outside of the glass wall nearest to the objective lens
SP,SYAF	computed fringe shape
YA,	path of light rays as they cross the cell


```

PROGRAM NEWAR( INPUT, OUTPUT, TAPE98, FILM)
C. BOUNDARY LAYER SYSTEMS.
C. ALL P IN ANGSTROMS      ALL OTHER DIMENSIONS IN MM EXCEPT CONC
COMMON YA(1010),DYDX(1010),PA(1010),ZA(1010),ZAP(1010),
1YAF(110),SYAF(110),SP(110),PS(110),P(110),Y(110),D(110)
COMMON /A/ CO, CB, XNO, ASF
COMMON /TVPOOL/ XMIN,XMAX,YMIN,YMAX,TVXMIN,TVXMAX,TVYMIN,TVYMAX
DATA IR / 51 /
DATA CB / .1 /
DATA XNO / 1.3313 /
DATA XNG / 1.5231 /
DATA W / 10. /
FUNCT(X) = XNO + .027952*X
SCALE(X) = X/(279520. * W)
SEC(X) = 1. / COS(X)
XNR = FUNCT(CB)
DO 81 LW = 1,2
WG = (LW - 1) * 12.7
DO 81 IASF = 1,2
ASF = IASF * 4.
DO 81 ICO = 1,5
IF(ICO .EQ. 3) GO TO 81
CO = (ICO - 1) * .05
DO 81 KD = 1,5
DYDX0 = (KD - 3)**2
IF(KD .LT. 3) DYDX0 = -DYDX0
AR = ATAN(DYDX0)
SRAR = XNR * SIN(AR)
AG = ASIN(SRAR/XNG)
CCNP = XNG*WG*1.E7*(1.-SEC(AG))+XNR*W*1.E7*(1.-SEC(A3))
ACD = ASF * 12.5 * (CB - CO)
PRINT A00, ACD,CB,CO
600 FORMAT(5H 1 =,F6.2,9H MA/CM**2,/,5H CB =,F6.2,6H MOLAR,/,5H CO =,
1F6.2,6H MOLAR,///)
XMAX = .5
XMIN = -.1
YMAX = 2.
YMIN = -2.
CALL TVGRID( 6, 6HNOLBLS, 2, 4, 5)
WRITE (98,710)
710 FORMAT(3H 4,////////,3H ),/,3H MM,////////,3H -4,/,2BH
A B
1 C D E)
CALL TVLTR(20.,992.,0.4)
YA(1) = 1.E-6
IEND = IFIX(10.*W)
IEND = IEND + 1
IRA = 1
IRB = 200
DO 781 I = 1,IR
P(I) = 0.
D(I) = 0.
Y(I) = 0.
SP(I) = 0.
DYDX(1) = DYDX0
YAF(I) = YA(1)
PA(1) = 0.0
DO 76 J=2,IEND
YA(J) = YA(J-1) + .1 * DYDX(J-1)
ARJ = YA(J-1) + .05 * DYDX(J-1)

```

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ZA(J) = ZETA(ARG)
PA(J) = PA(J-1) + (XNB-ZA(J)/COS(ATAN(DYDX(J-1)))) * 10.**6
ZAP(J) = ZETA(ARG)
DYDX(J) = DYDX(J-1) + .1*ZAP(J)*((1.+DYDX(J-1))**2 / ZA(J))
IF(YA(J) .LT. 0.) GO TO 75
IF(YA(J) .GT. YMAX) GO TO 75
76 CONTINUE
DYDX101 = TAN(ASIN(ZA(IEND)*SIN(ATAN(DYDX(IEND)))/XNG))
Y(I) = WG*DYDX101 + YA(IEND)
P(I) = PA(IEND) + XNG*WG*1.0E+7*(1.-SEC(ATAN(DYDX101)))
D(I) = TAN(ASIN(XNG*SIN(ATAN(DYDX101))))
IF(IRB .GT. 1) IRB = I
IF(IRA .LT. 1) IRA = I
75 CONTINUE
YA(1) = YA(1) + .04
781 CONTINUE
DO 78 I = 1,IR
PS(I) = (ZETA(YAF(I)) - XND)/.027952
PS(I) = PS(I) - .1
78 CONTINUE
CALL TVPLOT(PS, YAF, IR, 4HJOIN, 0, 1)
IF(IRA .LT. IRB) GO TO 782
IM = IM + 1
DO 782 L=1,4
F = -WG/XNG - W/XNB/3. * (4-L)
FCNP = F * 1.E7 * (1. - SEC(ASIN(SRAB)))
DO 780 I = IRB,IRA
SYAF(I) = Y(I) + D(I) * F
SP(I) = P(I) + F * 1.E+7 * (1. - SEC(ATAN(D(I))))
SP(I) = SP(I) - FCNP - CCNP
SP(I) = CR - SCALE(SP(I))
SP(I) = SP(I) - .1
SP(I) = SP(I) + .1*L
780 CONTINUE
IF(IRA .LT. IRB) GO TO 786
IRC = 0
DO 785 IRD = IRB,IRA
IRC = IRC + 1
SP(IRC) = SP(IRD)
SYAF(IRC) = SYAF(IRD)
IF(SYAF(IRC) .LT. YMAX) IRD = IRC
785 CONTINUE
CALL TVPLOT(SP, SYAF, IRP, 4HJOIN, 0, 1)
786 CONTINUE
782 CONTINUE
CALL TVNEXT
WRITE (98,700) ACD,CR,CD,DYDXD
700 FORMAT(5H I =,F6.2,9H MA/CM**2,/,5H CB =,F6.3,6H MOLAR,/,5H CD =,
1F6.3,6H MOLAR,/,11H (DY/DX)0 =,F6.2)
CALL TVLTR(150.,992.,0.4)
CALL TVNEXT
81 CONTINUE
CALL TVEND
STOP
END

```

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053

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088

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PROGRAM NEWAF

IR

CB

XNO

XNG

W

WG

FUNCT(X)

SCALE (X)

ASF

CO

DYDXO

ACD

YA(1) 3rd stop after 710

FUNCTION ZETA

FUNCTION ZEPTA

1st step after 75

PS, YAF

F

SP,SYAF

YA,EX

YG,XA,XG

SB,SY,BF

YQ,PQ

plots figures like Fig. 4.7.

number of rays traced

bulk solution concentration of CuSO_4

refractive index of water

refractive index of glass

cell width

glass wall thickness

converts concentration into refractive index

converts phase into concentration

defines boundary layer thickness

concentration at the interface

slope of the incident light

current density

location of the first ray computed

defines the boundary layer shape

takes the derivative of ZETA

defines the interval between rays computed

shape of the given profile

focal distance from the outside of the glass wall nearest to the objective lens

computed fringe shape

path of light rays as they cross the cell

surface of glass walls

computed fringe shape

joins incoming ray location on profile with outgoing ray on fringe

```

C      PROGRAM NEWAF( INPUT, OUTPUT, TAPE98, FILM)
C      THIS PROGRAM TRACES THE LIGHT THROUGH THE CELL
C      FOR THE CASE OF THE MACH ZEHNDER INTERFEROMETER
C      BOUNDARY LAYER SYSTEMS
C      ALL P IN ANGSTROMS      ALL OTHER DIMENSIONS IN MM EXCEPT CONC
COMMON YA(10025),DYDX(10025),ZA(10025),ZAP(10025),SX(10025),
1PS(200),XG(2),XA(2),YG(2),PA(1025),PQ(2),YQ(2),SYAF(200),SP(200),
2SYBF(200),SR(200),D(200),YAF(200)
COMMON /A/ CO, CB, XNO, ASF
COMMON /TVPOOL/ XMIN,XMAX,YMIN,YMAX,TVXMIN,TVXMAX,TVYMIN,TVYMAX
DATA IR / 96 /
DATA CR / .1 /
DATA W / 99. /
DATA XNO / 1.3313 /
DATA XNG / 1.5231 /
DATA WG / 9.54 /
TVXMAX = 32.
TVXMIN = 928.
SCALE(X) = X/(279520. * W)
FUNCT(X) = XNO + .027952*X
SEC(X) = 1. / COS(X)
XNB = FUNCT(CR)
CO = .103
L = 4
F = -WG/XNG - W/XNB/3. * (4-L)
ASF = .4
ACD = ASF * 12.5 * (CR - CO)
DO 80 IA = 1,17
DYDX0 = -.0045 + .0005 * IA
AR = ATAN(DYDX0)
SRAB = XNB * SIN(AR)
AG = ASIN(SRAB/XNG)
CCNP = XNG * WG * 1.E7 * (1. - SEC(AG)) + XNB * W * 1.E7 * (1. -
1SEC(AB))
FCNP = F * 1.E7 * (1. - SEC(ASIN(SRAB)))
YMIN = 0.
YMAX = 130.
XMIN = -2.
XMAX = 4.
CALL TVGRID( 3, 10, 6HNOLBLS, 1, 3)
WRITE (98,950)
950 FORMAT(3H 4,/////,3H MM,/////,3H 0,/////,3H -2,/,6X,4HCELL,8X,5HG
1LASS,5X,3HAIR)
CALL TVLIR(32.,18.,1,4)
YA(1) = 1.E-6
IRA = 1
IRB = 200
DO 78 I = 1,IR
D(I) = 0.
SYAF(I) = 0.
SP(I) = 0.
YAF(I) = YA(1)
PS(I) = ZETA(YAF(I)) - XNO
79 PS(I) = PS(I) / .027952
IEND = 5. * W
IEND = IEND + 1
DYDX(1) = DYDX0
PA(1) = 0.0
SP(1) = 0.
SX(1) = 0.

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DO 76 J=2,IFND
YA(J) = YA(J-1) + .2 * DYDX(J-1)
ARG = .5 * (YA(J-1) + YA(J))
ZA(J) = ZETA(-RG)
SY(J) = .2 * (J-1)
PA(J) = PA(J-1) + (XNB-ZA(J)/COS(ATAN(DYDX(J-1))))*2.F6
26 ZAP(J) = ZETAP(ARG)
DYDX(J) = DYDX(J-1) + .2*ZAP(J)*((1.+DYDX(J-1))**2)/ZA(J)
IF(YA(J) .LT. 0.) GO TO 75
IF(YA(J) .GT. XMAX) GO TO 75
76 CONTINUE
DYDX101 = TAN(ASIN(ZA(IFND)*SIN(ATAN(DYDX(IFND)))/XNG))
Y101 = WG*DYDX101 + YA(IFND)
P101 = PA(IFND) + XNG*WG*.05+7*(1.-SEC(ATAN(DYDX101)))
DYDX102 = TAN(ASIN(XNG*SIN(ATAN(DYDX101))))
P101 = P101 - COMP
SP(1) = P101
SVAF(1) = Y101
D(1) = DYDX102
IF(IPA .LT. 1) IPA = 1
IF(IPR .GT. 1) IPR = 1
ICMP = IFND
GX(IFND + 1) = W + WG
GY(IFND + 1) = YMAX - .01
YA(IFND + 1) = Y101
IF(YA(IFND + 1) .LT. XMIN) GO TO 77
IF(YA(IFND + 1) .GT. XMAX) GO TO 77
ICMP = IFND + 1
YA(IFND + 2) = YA(IFND + 1) + DYDX102 * (YMAX - W - WG)
IF(YA(IFND + 2) .LT. XMIN) GO TO 77
IF(YA(IFND + 2) .GT. XMAX) GO TO 77
ICMP = IFND + 2
GO TO 77
75 ICMP = J - 1
77 IF(MOD(1-1,5) .EQ. 0) CALL TVPLOT(YA, SX, ICMP, 4HJOIN, 0, 1)
YA(1) = YA(1) + .04
78 CONTINUE
XG(1) = W
XG(2) = W
YA(1) = W + WG
XA(2) = W + WG
YG(1) = XMIN
YG(2) = XMAX
CALL TVPLOT(YG, XA, 2, 4HJOIN, 0, 1)
CALL TVPLOT(YG, YG, 2, 4HJOIN, 0, 1)
CALL TVTEXT
YMAX = .105
YMIN = .005
CALL TVGRID(3, 10, 6HOLBLS, 4, 10)
WRITE (99, 960)
960 FORMAT(3H 4, //, 3H MM, //, 3H 0, //, 3H -2, //, 8X, 2H, 1, 15X, 4H, 1
104)
1X, 2H, 2)
CALL TVL2(32, 18, 1, 4)
PRINT 600, ACQ, CR, CO, F

600 FORMAT(6H I =, F4, 2, 9H MA/CM**2, //, 5H CB =, F6, 2, 6H MOLAR, //, 5H CO =,
1F, 2, 6H MOLAR, //, 5H F =, F6, 2, 3H MM)
CALL TVPLOT(YA, P, 1, 4HJOIN, 0, 1)
IF(IPA .LT. IPR) GO TO 10

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FUNCTION ZETAP(X)
DX = .000001*X
XP = X + DX
ZP = ZETA(XP)
XM = X - DX
ZM = ZETA(XM)
ZETAP = (ZP-ZM)/(2.*DX)
RETURN
END

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C FUNCTION ZETA(X)
ERROR FUNCTION BOUNDARY LAYER
COMMON /A/ C0, C3, XN0, ASF
DIMENSION A(3)
DATA A / .3480242, -.0958798, .7478556 /
DATA P / .47047 /
Y = ASF * X
IF( Y .GT. 10.0 ) GO TO 2
IF( Y .EQ.0. ) GO TO 3
IF( Y .LT.0. ) GO TO 3
T = 1. / (1.+P*Y)
TT = T
SUM = 0.0
DO1 I=1,3
SUM = SUM + A(I)*TT
TT = TT * T
1 CONTINUE
SUM = SUM * EXP(-Y**2)
ZETA = XN0 + .027952 * (C0+(C3-C0)*(1.-SUM))
RETURN
2 CONTINUE
ZETA = XN0 + .027952 * C3
RETURN
3 CONTINUE
ZETA = XN0 + .027952 * C0
RETURN
END

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FUNCTION ZETA(X)
CORRECT GRID, RANGE, AND TITLES
EXTREMA IN CELL
COMMON /A/ C0, C3, XN0, ASF
SUM = 1/(2*ASF*X**2 + 1)
ZETA = XN0 + .027952 * (C0+(C3-C0)*(1.-SUM))
RETURN
END

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FUNCTION ZETA(X)
COSINE IN CELL
COMMON / A / C0, C3, XN0, ASF
FI = 12.56636 * X/ASF
FIL = 3.14159/2
IF(FI .GT. FIL) FI = FIL
IF(FI .LT. -FIL) FI = -FIL
SUM = .5 * (1. + SIN(FI))
ZETA = XN0 + .027952 * (C0+(C3-C0)*(1.-SUM))
RETURN
END

```

```
IRC = 0
DO 85 IRD = IRR,IRA
SP(IRD) = SP(IRD) - FCNP
SP(IRD) = CB- SCALE(SP(IRD) + F * 1.E7 * (1. - SEC(ATAN(D(IRD))))))
SYAF(IRD) = SYAF(IRD) + F * D(IRD)
IRC = IRC + 1
SR(IRC) = SP(IRD)
SYAF(IRC) = SYAF(IRD)
85 CONTINUE
CALL TVPLOT(SYAF,SR,IRC,4HJOIN,0,1)
DO 10 I = IRR,IRA
IF MOD(I-1,5) .NE. 0) GO TO 10
PQ(1) = PS(I)
YQ(1) = YAF(I)
PQ(2) = SP(I)
YQ(2) = SYAF(I)
CALL TVPLOT(YQ,PQ,2,4HJOIN,0,1)
10 CONTINUE
CALL TVNEXT
80 CONTINUE
CALL TVEND
STOP
END
```

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