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ABSTRACT

Interferograms of the transient condition of concentration gradient build-up have been recorded with a motion picture camera for horizontal electrodes in the cathode-over-anode position. The appropriate solution of Fick's Second Law for the unsteady state has been shown to predict the concentration gradient at times of the order of 150 seconds or greater. The interference fringes can be integrated as time dependent concentration contours and, hence, a measure of the diffusion current obtained. Logically, at $t=0$ seconds, $i_{diff} = 0$. Experimental data show that i_{diff} reaches a maximum at times greater than 150 seconds in the diffusion layer, and t goes from 0 to some value close to one during the same time. It has been impossible to decide on a definite value for the transference number and diffusion coefficient that would be appropriate.

CONCENTRATION GRADIENTS AT HORIZONTAL ELECTRODES

by

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Concentration gradients at working electrodes have been difficult to obtain until the advent of the modern optical methods of Schlieren patterns¹ and interferometry.² The recording system has always been a still camera until very recently when a motion picture camera was used.³ This recording technique should provide sufficient data of good quality to establish quantitatively the dependence of concentration changes in the electroactive species with time.

A series of interferograms of an experiment with the electrodes in the cathode-over-anode position were recorded on motion picture film and the results analyzed and compared to the theory of ionic transport. To the best of the author's knowledge this is the first recording of such transient concentration changes.

EXPERIMENTAL

A 0.5 M CuSO_4 solution, pH 4.5, made up in the usual way was electrolyzed in an interferometer (Fig. I) which has been described in detail elsewhere.⁴ Briefly, the cell had two copper electrodes 0.2 cm thick and 4 cm long sandwiched 0.313 cm apart between two coated glass flats. The flats were held in a specially shaped teflon cylinder which was placed in a clamp with which an appropriate wedge angle between the flats could be produced. Collimated sodium vapor light produced wedge fringes which were recorded by a Bolex Paillard 16 mm motion picture camera on Ansco

Hypan film at 24 frames per second. The film was underexposed, and therefore required overdeveloping by a factor of 2 to 4. The developed film was then projected at a magnification factor of 80, and from frames at selected times representative fringes were sketched on graph paper (Fig. II). Details of the type of fringes obtained and adjustments made to them appear in Appendix I.

Carefully prepared pure polycrystalline copper electrodes were used in the cell which was thermostated at 25°C. When a suitably oriented fringe system had been produced, the motion picture camera was started, then a preset constant current passed through the cell, in this case 0.9022 ma/cm².

THEORY

The theory of ionic mass transport in electrolysis has been reviewed by Tobias, Eisenberg, and Wilke.⁵ They give for the rate of transfer ions in the x direction (x perpendicular to the plane of the electrode)

$$N_t = CU \frac{\partial \psi}{\partial x} - D \frac{\partial C}{\partial x} + VC$$

where N_t = total rate of transfer, gram ions/cm²-sec; C = concentration in gram ions/cm³; U = mobility, cm²/sec-volt; ψ = potential, volts; x = distance in direction of transfer, cm; D = diffusion coefficient, cm²/sec; and V = velocity for steady state conditions. In the experimental set-up here used, horizontal electrodes, cathode-over-anode; $V=0$ since convection is absent leaving only electromigration and diffusion, represented by the first and second terms on the right side.

Tobias et al then give an expression for the rate of ionic transport by diffusion $N_d = N_t - N_m = I \frac{(1-t_+)}{nF}$ where N_m = rate of migration,

gram ions/cm²-sec; t_+ = cation transference number, and the other symbols have their usual meanings. Again this expression is for steady state conditions.

Considering the unsteady state, the solution of the equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

for the boundary conditions $\Delta C = 0$ at $t = 0$, $x = 0$ and $\Delta C = 0$ at $t \neq 0$, $x = l$ is

$$\Delta C(x,t) = \frac{2\sqrt{\frac{Dt}{l^2}} I l t^-}{nF D} \operatorname{ierfc} \frac{1-x/l}{2\sqrt{\frac{Dt}{l^2}}}$$

as given by Carslaw and Jaeger⁶, using only the first term of the complete series solution since $\operatorname{ierfc} z \rightarrow 0$ as $z \rightarrow \infty$. It is worth noting that the expression is independent of l , only requiring that $\Delta C \rightarrow 0$ as $x \rightarrow l$ ($2l$ = electrode separation). Inclusion of the anion transference number in the pre-error function coefficient (t^-), is to be expected and as in the steady state is intended to make allowance for the migration current. ierfc is the complement of the integrated error function⁶.

The present experimental results should permit a testing of the efficacy of this treatment since the number of coulombs discharged at any time can be calculated by considering the number of ions required to be removed (discharged) to produce the observed concentration gradient. This can be done by a form of graphical integration which makes only the assumptions that the fringe selected is a typically average fringe for the whole electrode surface, that the diffusion coefficient is known and constant over the concentration range considered, and that all refractive index changes are due to CuSO_4 concentration changes.

RESULTS

The initial attempts to fit the interference fringe selected as typical at 150 seconds were made using the diffusion coefficient of CuSO_4

as reported by Eversole⁷ and co-workers and the transference number for SO_4^{2-} according to Fritz and Fuget.⁸ The diffusion coefficient and transference number for the concentration at the selected x were used for each point calculated. The results are shown in Fig. III. The agreement with the anode side of the interferogram is quite good, but for the cathode the prediction is everywhere short of that found. The predicted values for 15 seconds are almost 50% too high and so are not plotted.

Realizing that the results of other studies⁹ of the $\text{Cu}/\text{CuSO}_4/\text{Cu}$ system have shown values for the diffusion constant of about $4.4 \times 10^{-6} \text{ cm}^2/\text{sec}$, the requisite current densities to give agreement at ΔC_{max} using $D = 4.4 \times 10^{-6}$ were calculated, and are shown in Fig. IV to suggest that eventually a potential gradient will be produced such that $N_d = N_t$. If instead the diffusion constant is calculated for each time and using the appropriate transference number such that $\Delta C_{\text{calc}} = \Delta C_{\text{exp}}$ at the electrode ($x=0$), D obviously approaches $4.4 \times 10^{-6} \text{ cm}^2/\text{sec}$ at some time greater than 150 seconds (Fig. V).

Using the calculated required current density for $D = 4.4 \times 10^{-6} \text{ cm}^2/\text{sec}$ and average literature transference numbers, values at selected distances from the electrodes were plotted on Fig. III. The agreement is worse than the first attempt, but not much worse. Fig. VI shows the results of graphical integration to obtain the number of coulombs of charge required to discharge the necessary number of ions to form the concentration gradient found at various times. The successive current densities plotted in Fig. IV are again plotted here in a different way. Beginning at $3 \frac{1}{3}$ seconds the value found is plotted from zero time to $1/2$ the distance to the next calculated value, in this case

4 1/16 seconds since the next time is 5 seconds. The 5 second value is now plotted to join at this point and is drawn half-way across the next time interval. Plots for both the anode and cathode were made. The line drawn for the anode appears to be generally too high, but the cathode plot is reasonably representative of the charge-carried points. The current density plots appear to be approaching the same slope as the externally measured current density.

Assuming the diffusion constant to be fixed at $4.4 \times 10^{-6} \text{ cm}^2/\text{sec}$ the transference number necessary to give agreement at $x=0$ and $t=150$ seconds is $t^- = 0.58$ for 15 seconds $t^- = 0.298$. This suggests that t^- goes to zero at $t=0$, when of course $N_t = N_m$ since there is no diffusion gradient to support a diffusion current.

CONCLUSIONS

The quality of the fit of calculated points using

$$\Delta C(x,t) = \frac{2 \sqrt{\frac{Dt}{l^2}} I l t^-}{nF D} \text{ierfc} \frac{1-x/l}{2 \sqrt{\frac{Dt}{l^2}}}$$

is sufficiently good that apart from the theoretical reason for selecting it, it obviously is the correct form to represent the physical process considered, that is the sudden imposition of a constant current density between parallel, plane, horizontal electrodes in the absence of convection.

However, the problem of deciding on the values of the basic constants to use has not been solved. The assumption that a concentration contour, calculated from a refractive index contour with no allowance for pH change or extraneous reactions is probably as good as the data. If this

is so, then the problem becomes one of deciding what D and t to use, again assuming that the externally measured current density must be used unmodified. These problems can probably be resolved by electrolysis for longer times so that plots like Figs. IV and V could indicate the steady state diffusion constant and diffusion current. Electrolysis at the limiting current density should also give helpful information regarding these two quantities.

The author wishes to acknowledge the suggestion of E. J. Casey that the data be subjected to this type of analysis, the efforts of K. Kinoshita who did most of the experimental work and to John Newman for interesting and advisory conversations on the theoretical aspects.

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APPENDIX I

Fringes of Equal Inclination: Brewster's Fringes.

Tolansky has given an excellent treatment of fringes of equal inclination.¹⁰ However the difference between wedge or fizeau type fringes and Brewster's fringes will briefly be considered.

Fig. VII shows schematically the light path and how Brewster's fringes are produced. If the incident light is at an angle to the wedge whose angle is small (about 2 minutes of arc), instead of getting wedge fringes, that is, a continuous set of equally spaced parallel fringes, rings of fringes are produced. In this experiment it was intended to use wedge fringes, but since the radius of curvature of the fringes is relatively large and the two types can exist simultaneously, it is easy to confuse the two. The error was not discovered until a large number of tedious hand measurements had been made.

For wedge fringes, the fringes appear on a uniform wedge at positions where the thickness of the wedge is an integral multiple of the wavelength of the monochromatic light, that is since $n\lambda = 2\mu t \cos \phi$, whenever the thickness has increased by $\frac{\lambda}{2}$ from the last fringe, bright or dark, a new fringe appears. n is the order of interference, μ the refractive index, t the thickness and ϕ the angle of incidence of the light. If ϕ becomes a very little less than 90° for thick wedges, Brewster's fringes result.

Brewster's fringes are located at infinity and appear on the wedge as rings as shown in Fig. X, End View. The fringes will appear at positions governed by $n\lambda = \mu t (\text{Cosine of the angle of refraction in the first glass flat minus Cosine of the angle of refraction in the second$

glass flat) assuming $\text{Cos } \phi$ is about equal to 1, since the light passes only once through the cell.

Variations in the refractive index of the wedge of electrolyte cause displacement of the fringes up and down the wedge (toward the apex if the change is an increase in concentration) which takes the form of a perturbation to the arc of the circle seen between the electrodes. The fringes measured for the S/V position were a $2^\circ 35'$ arc of a circle of 3.43 cms radius and those for the C/A position had a similar radius of curvature. A detailed account of how to relate wedge fringe perturbation to concentration has been given by O'Brien and Rosenfield⁷ and complete review of the theory by O'Brien⁹.

To allow plots of concentration changes to be made on cartesian coordinates, these arcs had to be converted to straight lines. Frequently the increments at successive positions at which measurements were made were smaller than the expected precision of measurement. However, to ensure that some systematic method of correction for fringe curvature was used, a transparent plastic template whose plotting edge was cut in the mirror image of the curve was used in replotting the uncorrected values read from the display of the original fringes. In this way the curvature was plotted out and also any rotation of axis needed to correct the angle of the fringes to the electrode to 90° . Of course since both the plastic template and the pencil point had thickness, a further, but it is thought, random scatter of points resulted. A smooth curve was then drawn through the points. A scale in which fringe perturbations are shown as concentration change in moles/liter has been added to the figures where necessary. The limit of accuracy of the measurements is that with which the center of any fringe can be located relative to the

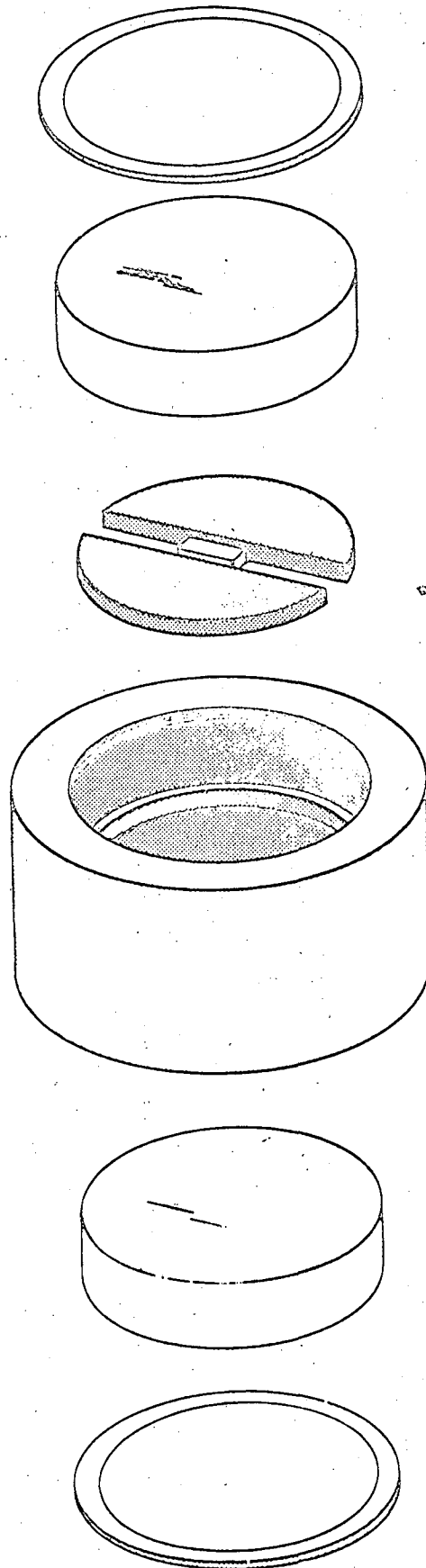
center of another fringe. In this case it is thought from the results of repeated measurements to be about $\pm 1/20$ th of a fringe width or about $\pm 7 \times 10^{-4}$ M. Details of this type of calculation have been given previously.⁴

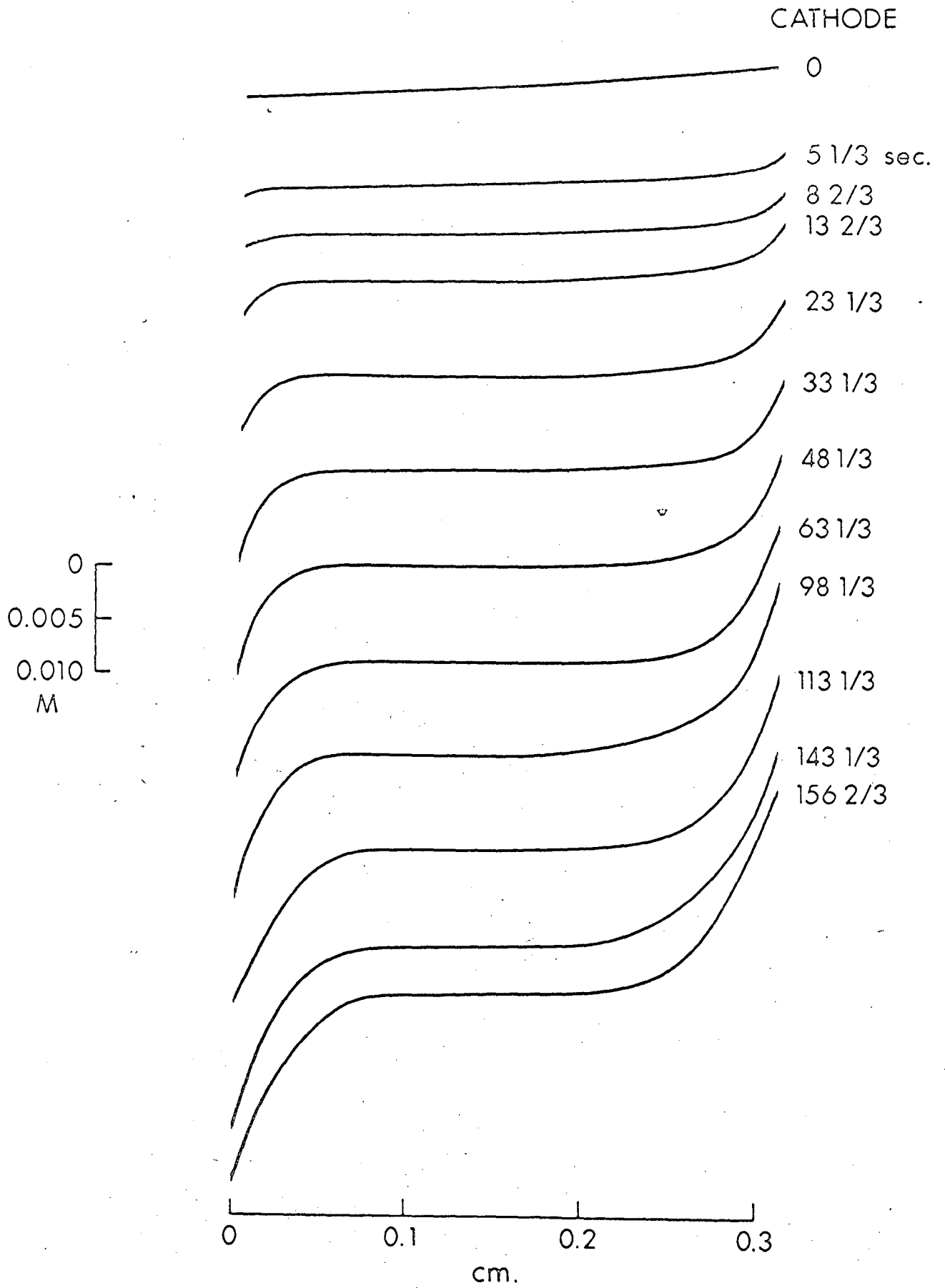
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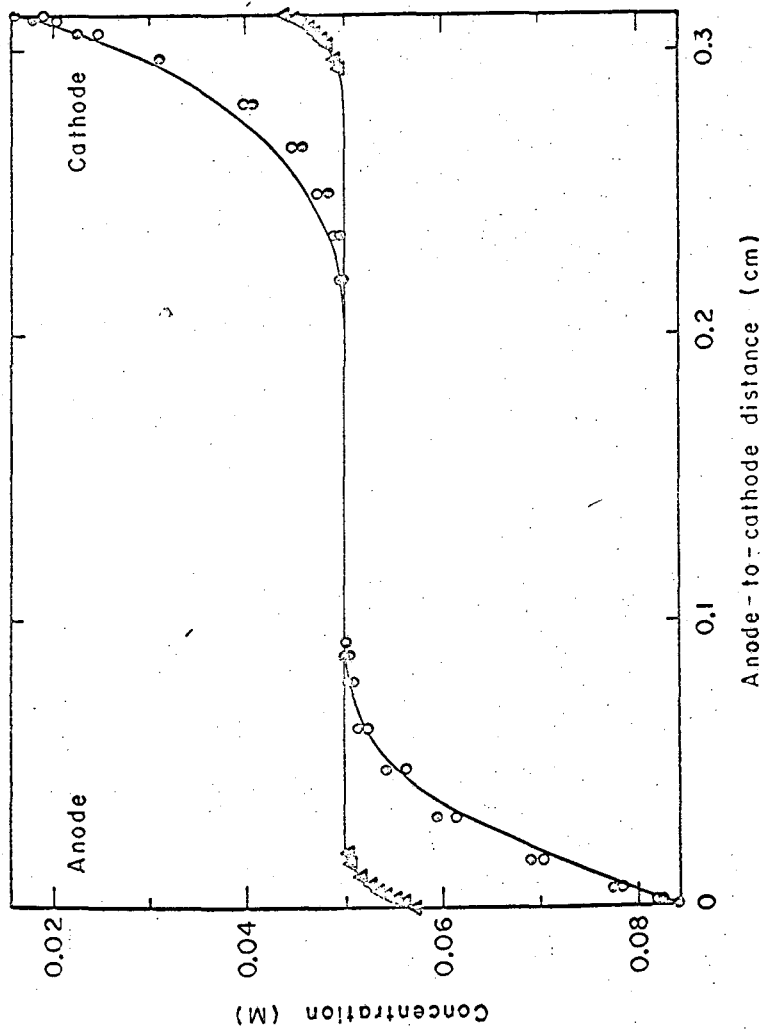
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Captions for Figures

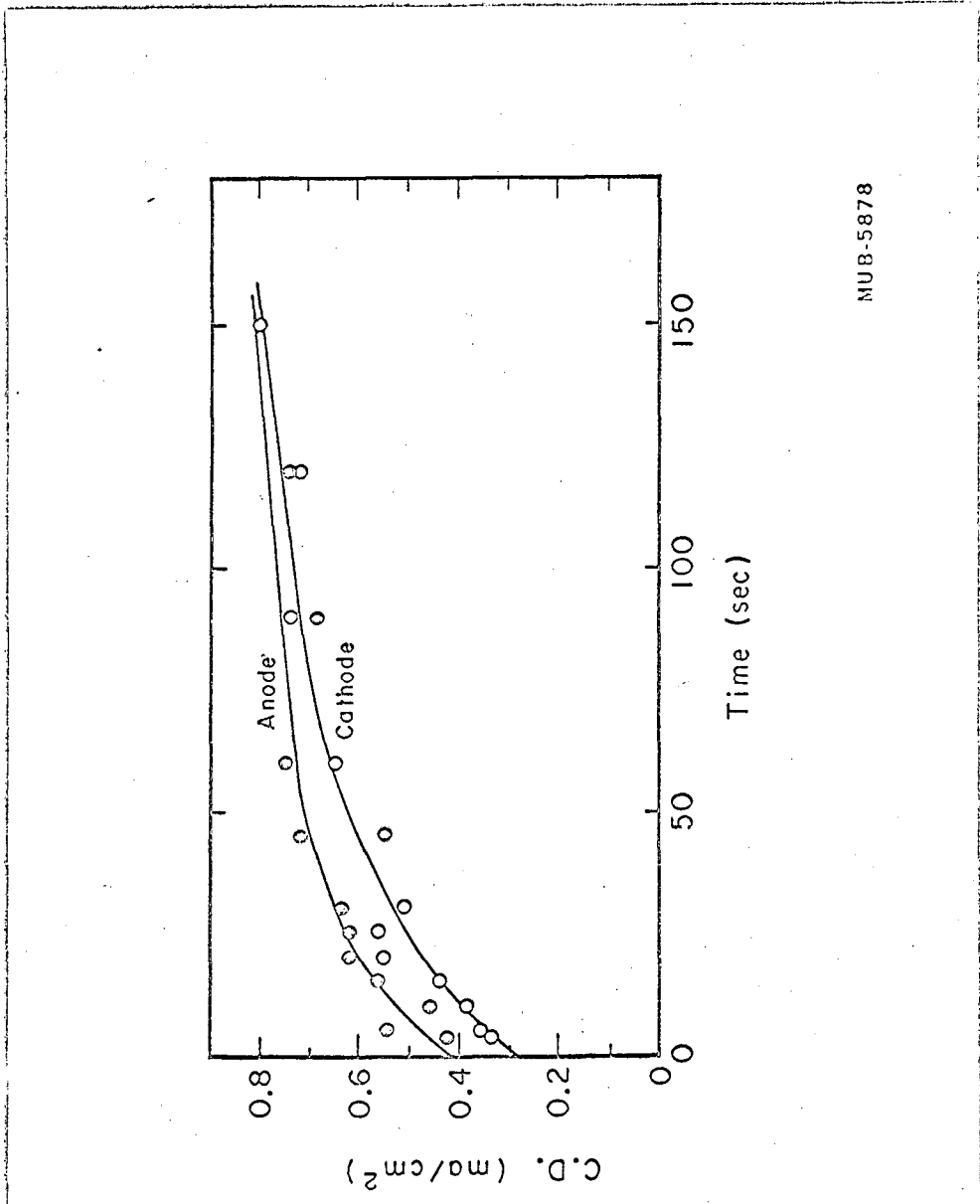
- Fig. I An exploded view of the cell without the thermostating clamp.
- Fig. II Interference fringes (as sketched from 16 mm film) at various times after the beginning of electrolysis in the system Cu/CuSO₄/Cu. Electrolyte concentration 0.1N, pH 4.5.
- Fig. III Comparison of calculated and experimental values at 15 and 150 seconds. O calculated using best literature values of D and t- for each concentration, ⊙ calculated using $D = 4.4 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$, appropriate literature t- and current densities from Fig. IV. ▲ calculated using $D = 4.4 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ appropriate literature t- and current densities from Fig. IV.
- Fig. IV Current densities calculated at various times, using $D = 4.4 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ and appropriate literature t- such that the concentration change found experimentally at $x = 0$ is equal to the calculated concentration change. ⊙ anode, O cathode.
- Fig. V Diffusion constants calculated to give agreement with concentration change found at the electrode using appropriate literature t- values. ⊙ anode, O cathode.
- Fig. VI Charge transferred vs time. Line 1 is the externally measured current density, Line 2 is the calculated required value of the current density at the anode from Fig. IV. Line 3 is the same value for the cathode. ⊙ number of charges transferred at the anode at a given time found by integrating under the concentration contour. O cathode values obtained in the same way.
- Fig. VII The Production of Brewster's Fringes.



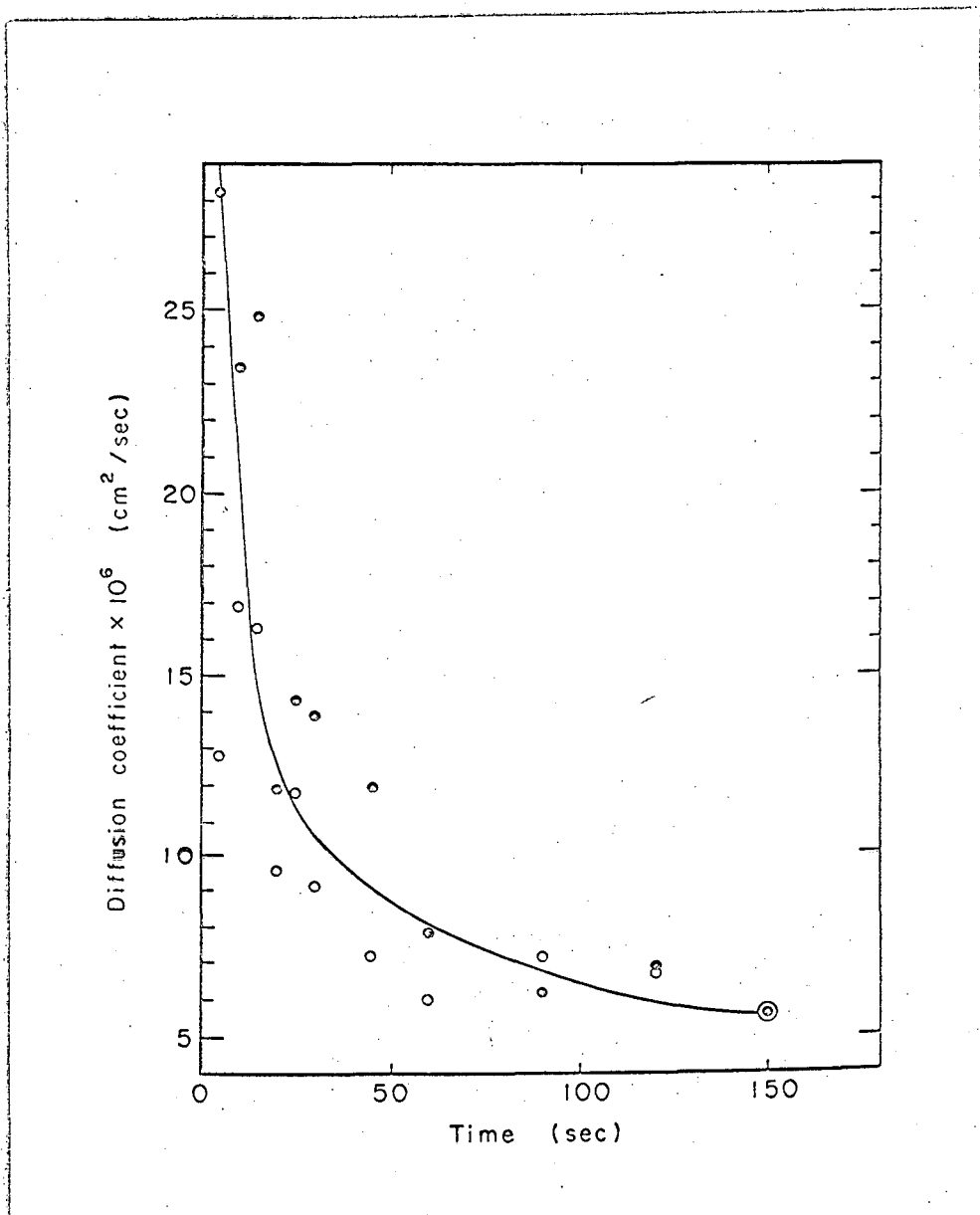


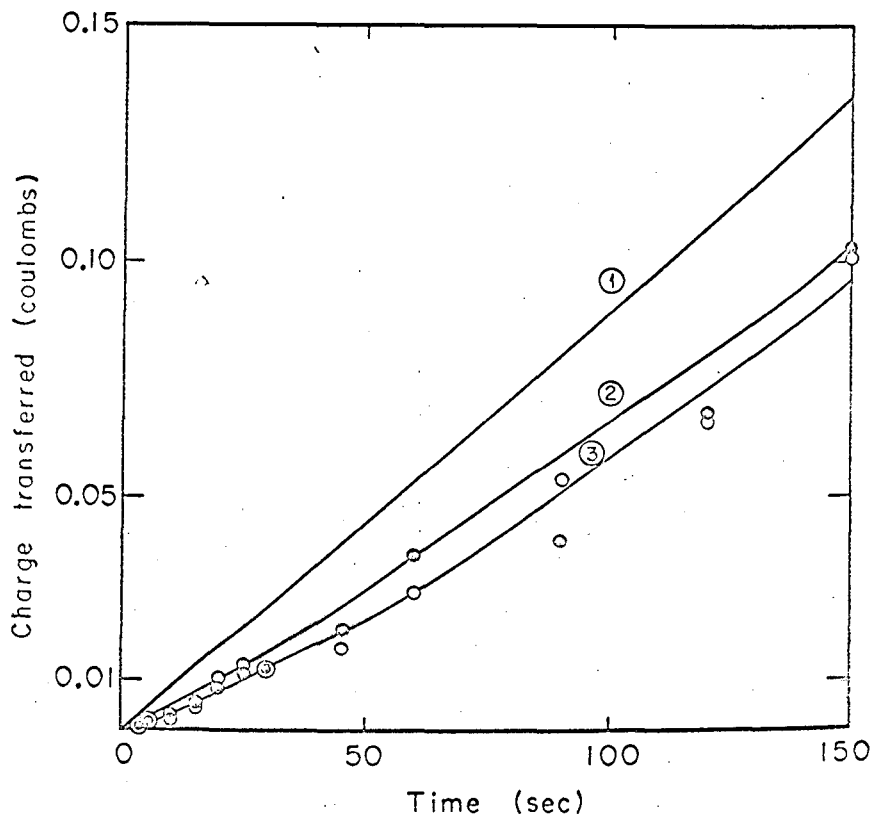


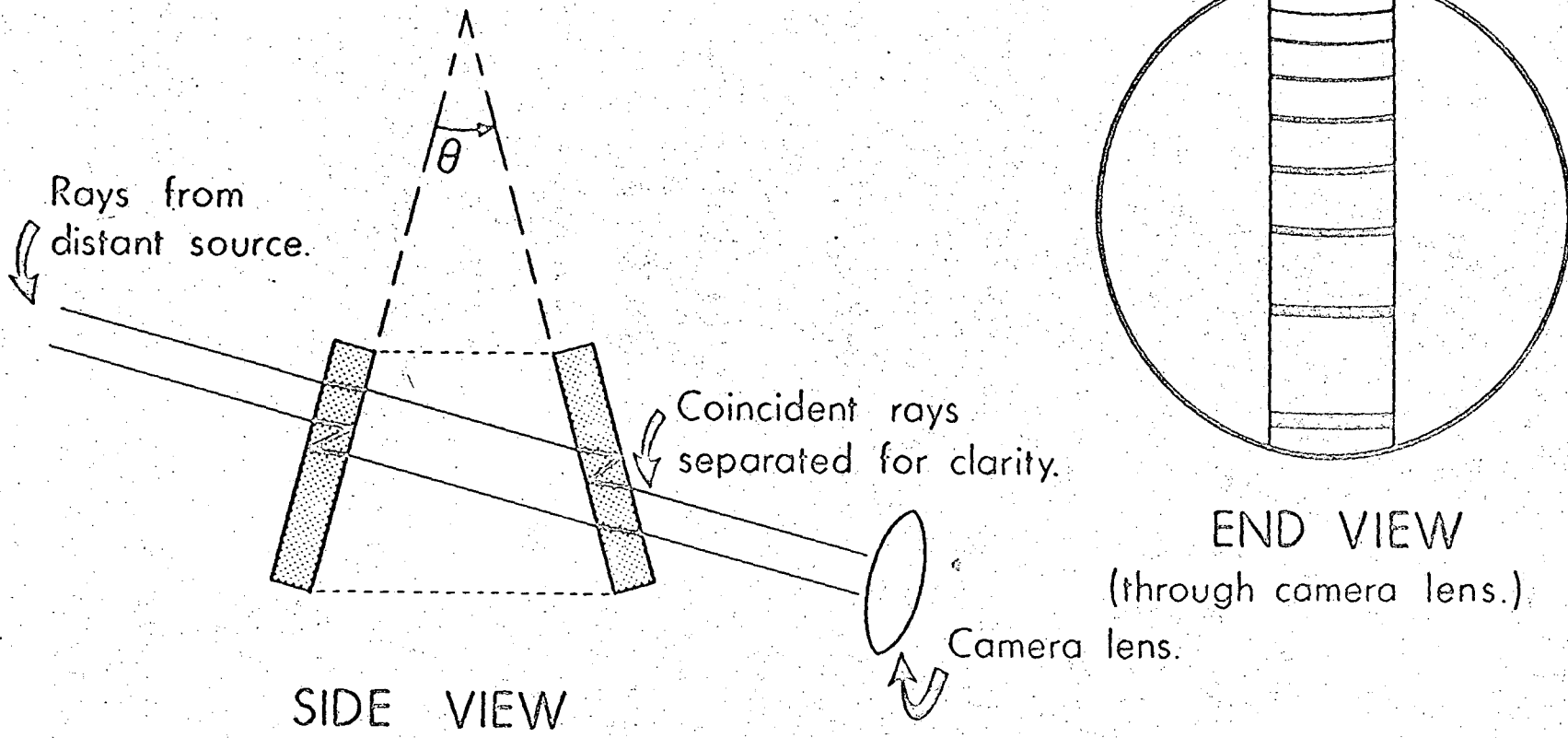
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