

Investigation of the Behavior of the Aqueous $I_3^- - I_2 - I^-$ System
Following Intense Irradiation

Thesis

by

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Notation

- M - moles/liter
- () - concentration of the bracketed molecule or ion, units M.
- K_I - $(I_3^-)/(I^-)(I_2) = 710 \text{ M}^{-1}$, the concentration equilibrium constant for the dissociation of the triiodide ion
- K_A - $(I_2^-)/(I)(I^-)$
- K_B - $(I^-)(HOI)(H^+)/(I_2) = 2.58 \times 10^{-13} \text{ M}^2$
- K_C - $(I^-)^5(IO_3^-)(H^+)^6/(I_2)^3 = 2.7 \times 10^{-48} \text{ M}^9$
- L_c - intensity of the constant monitor light incident on the reaction cell.
- L_o - intensity of the monitor light transmitted by the reaction cell just before the flash.
- L_t - intensity of monitor light transmitted at time t.
- ΔL_t - a small change in the intensity of the transmitted monitor light due to a small change in the optical density of the solution in the reaction cell at time t.
- $\epsilon'_{I_3^-}$ - ϵ_3' - the molar extinction coefficient for I_3^- for a particular wave length, units $\text{M}^{-1}\text{cm}^{-1}$
- ϵ'_{I_2} - ϵ_2' - the molar extinction coefficient for I_2 at a particular wave length, units $\text{M}^{-1}\text{cm}^{-1}$
- $\epsilon'_{I_2^-}$ - ϵ_1' - the molar extinction coefficient for the postulated I_2^- at a particular wave length, units $\text{M}^{-1}\text{cm}^{-1}$
- ϵ - $2.303 \epsilon'$
- l - the length of the reaction cell and the light path through the solution, 10 cm. in all cases.
- Optical density - $\log_{10}(L_c/L_t) = \epsilon'()l$
- I - photocurrent, units ampere.

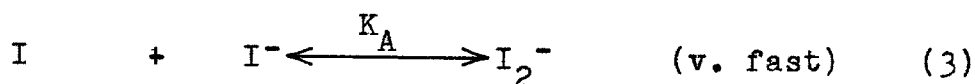
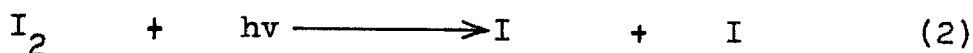
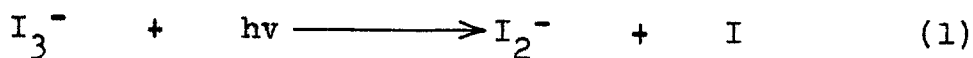
- ΔI_t - small change in photocurrent due to ΔL_t .
- e - $l \left[\epsilon_1 - \epsilon_3 K_I(I^-) / 2(1 + K_I(I^-)) - \epsilon_2 / 2(1 + K_I(I^-)) \right]$
- mmu. - millimicrons = 10^{-7} cm.
- $t_{\frac{1}{2}}$ - time required for the concentration of the reactive species to reach $\frac{1}{2}$ the original concentration.
- k_1 - rate constant for the reaction: $2I_2^- \longrightarrow I_3^- + I^-$
units $M^{-1}sec^{-1}$
- k_2 - rate constant for the reaction: $2I \longrightarrow I_2$
units $M^{-1}sec^{-1}$
- k_3 - rate constant for the reaction: $I_2^- + I \longrightarrow I_3^-$
units $M^{-1}sec^{-1}$
- a - low output amplification factor, nominally 1.
- b - high output amplification factor, nominally 100.
- c - oscillograph amplification factor for setting C.
- d - oscillograph amplification factor for setting D.
- w - height of square-wave on low output and setting C.
- p - height of square-wave on high output and setting D.
- g - displacement of trace with battery and setting D.
- h - displacement of trace with battery attenuator setting M and oscillograph setting C.
- m - amplification factor of attenuator setting M (less than one).
- G - gain of amplifier.
- R - enlargement of oscillograph screen due to camera and microfilm projector, approximately 3.1

- Σ - $(I_2^-) + (I)$, the total dissociation produced by the flash.
- A_2 - fraction of total (I_2) dissociated by flash.
- A_3 - fraction of total (I_3^-) dissociated by flash.
- ΔS_t - vertical displacement between oscillograph traces, one produced by monitor lamp and flash, the other by flash alone. Measured in inches on projected negatives.
- V - vertical sensitivity of a specific oscillograph setting, units volts/screen inch.

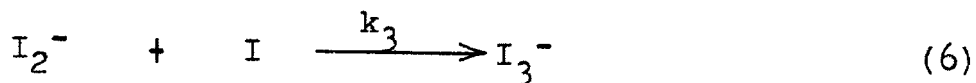
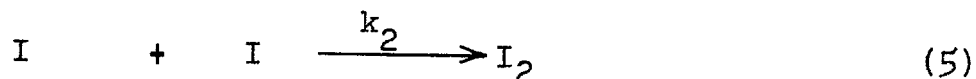
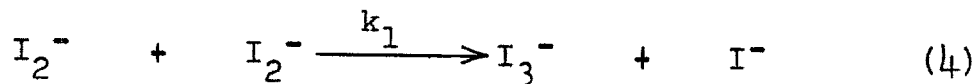
Abstract

Acidified aqueous solutions containing I_2 , I^- , and I_3^- have been irradiated by a high intensity flash lamp and the resulting change in the optical density of the solution has been observed spectrophotometrically as a function of time after the flash.

Immediately following the flash, there is an increase in the optical density of the solution. This is attributed to the photochemical production of the diiodide ion, I_2^- , by reaction (1) and/or reaction (2) and (3).



The disappearance of the colored species, in about 1.5--8 milliseconds after the flash, has been found to be kinetically of the second order with respect to that species and has been explained in terms of the recombination of I_2^- , principally by equation (4).



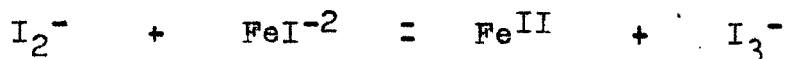
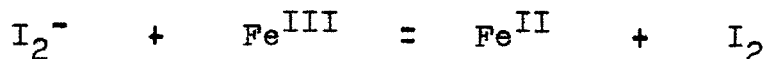
On the basis of these assumptions, the value of k_1/e has been determined at wave lengths 365 m μ . and 435 m μ . for (I^-) ranging from 10^{-6} to 10^{-3} M. The experimental dependence of the rate of disappearance of I_2^- on (I^-) has been found to agree qualitatively with the theoretical equation:

$$\begin{aligned} (-1/(I_2^-)^2)d(I_2^-)/dt = 1/(1 + K_A(I^-)) & \left[k_1 K_A(I^-) \right. \\ & \left. + k_2/K_A(I^-) + k_3 \right]. \end{aligned}$$

The calculated value of k_1/e has been found to vary with the wave length of the light used to observe the reaction as predicted by the equation:

$$(k_1/e_{\lambda_1})/(k_1/e_{\lambda_2}) = (\Delta I_t/I_0)_{\lambda_2}/(\Delta I_t/I_0)_{\lambda_1}.$$

The presence of Fe^{III} in concentrations about 1.8×10^{-4} M caused a slight increase in the value of k_1/e , which was attributed to one or both of the reactions:



Fe^{II} in concentrations less than 4×10^{-5} M appeared to decrease the rate of disappearance of I_2^- ; for this anomalous effect no explanation is given.

Experiments performed in which a large percentage

of the light absorbed by I_3^- was cut off by filters produced correspondingly smaller phenomena but gave no conclusive evidence as to the relative proportion of I_3^- and I_2 dissociated by the irradiation.

An extensive summary of data is presented.

Introduction

A short, intense pulse of light from a flash lamp can be used to produce an appreciable non-equilibrium concentration of atoms, free radicals, ions, or other photolysis products. If the flash time is comparable to or shorter than the lifetime of these reactive species, it may be possible to detect them and to measure their rates of reaction by flash spectroscopy or photoelectric spectrophotometry. This flash lamp technique has been independently introduced for the study of photochemical problems by Norrish and Porter,¹ Ramsey and Herzberg,² and Davidson et al.³

In the process of investigating the reversible change in the optical density of solutions of I_2 in various solvents under the influence of strong illumination, Rabinowitch and Wood⁴ noted that in CCl_4 and hexane a decrease in the optical density resulted, but that in CS_2 , CH_3OH , and H_2O an increase in the optical density during illumination took place. In the experiments described herein, in which acidified aqueous solutions of I_2 and I^- were intensely and briefly irradiated and any changes in the optical density observed, a reversible increase in the optical density was found. It is proposed that this increase in the optical density upon illumination is due to the production of a new ionic species, the diiodide ion, I_2^- , having an extinction coefficient comparable to that of I_3^- in the spectral region 350--440 m μ . It is further proposed that the diiodide ion

may be produced, detected, and the value of the product of its recombination rate constant and the reciprocal of an extinction coefficient (to be defined later), k_1/e , determined by the use of a flash lamp and photoelectric spectrophotometry. It will be seen that the experiments performed so far do not prove conclusively that the colored intermediate found is I_2^- ; however, in the interests of simplicity, this qualification will not be repeated throughout the text as the results are presented.

A schematic diagram of the apparatus used in the experiments to be described appears in Fig. 1. The actual laboratory setup is shown in Fig. 2.

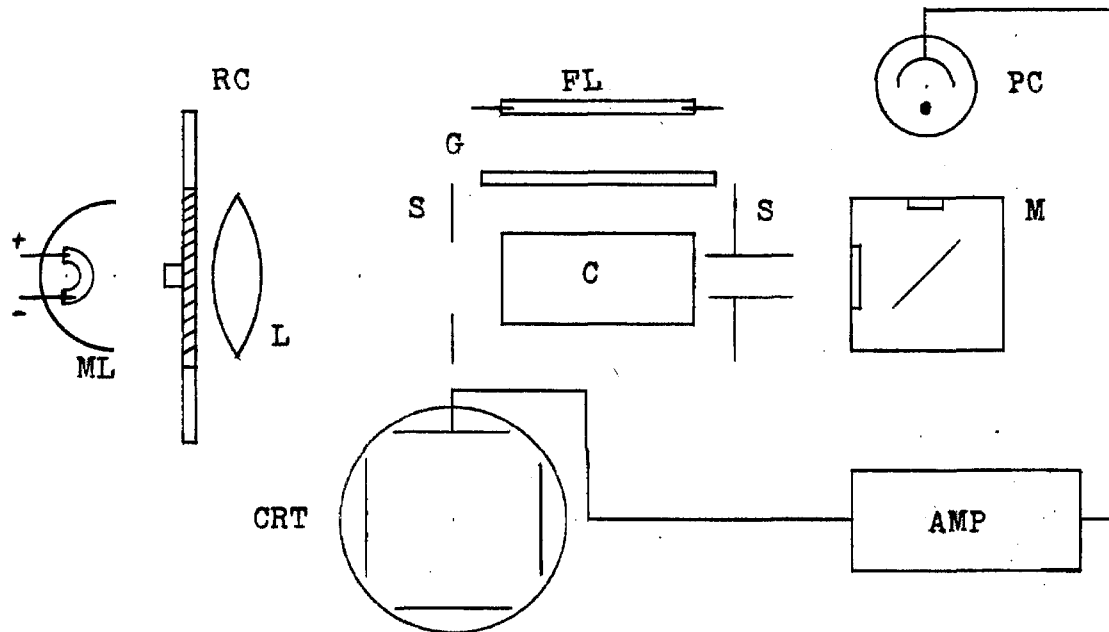


Fig. 1. Schematic diagram of apparatus. ML, constant monitor lamp; RC, rotary light chopper; L, focusing lens; C, reaction cell; M, monochromator; PC, photocell; AMP, amplifier; CRT, cathode-ray tube; G, filter; FL, flash lamp; S, shields.

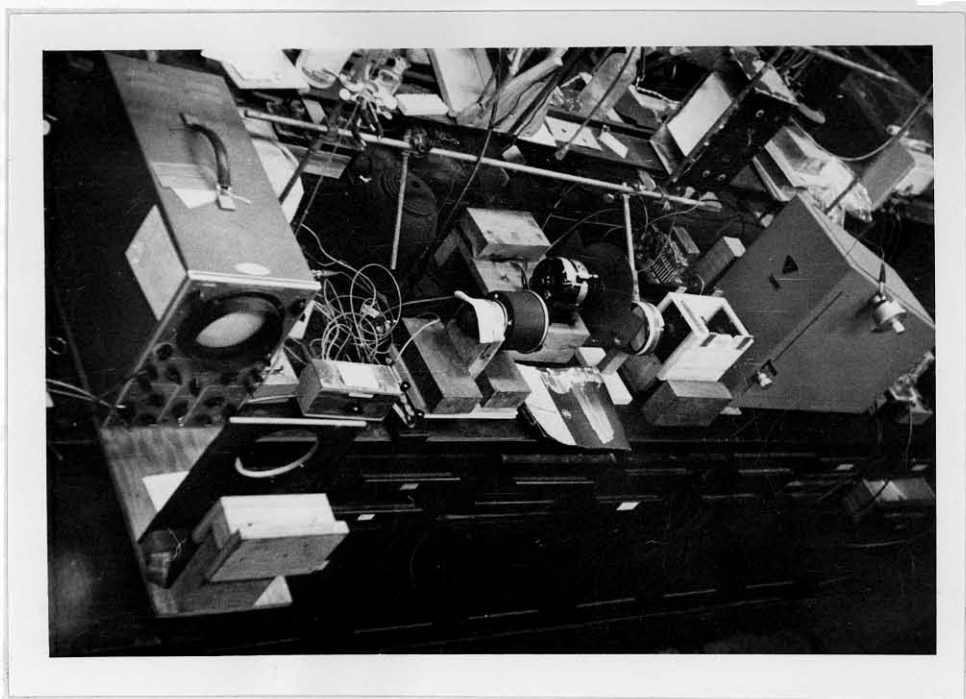


Fig. 2. A portion of the apparatus as assembled on the laboratory bench.

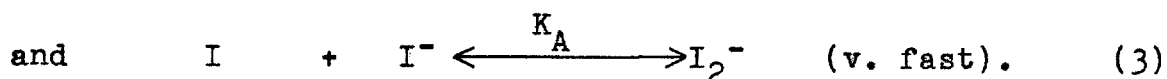
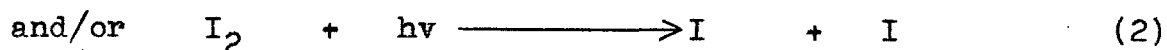
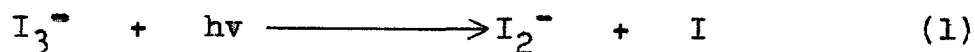
Introductory Discussion

The existence of the I_2^- ion has been postulated by numerous investigators⁵⁻¹⁰ as an intermediate in various oxidation-reduction reactions involving the $I_3^- - I^-$ system. There is substantial published evidence that the absorption of light of wave length less than about 5000 \AA . produces dissociation of the iodine molecule into one normal and one activated iodine atom.^{3,4,18} Griffith, McKeown and Winn¹⁰ have published evidence supporting the production of I_2^- by irradiation and have estimated the equilibrium constant of the reaction, $I^- + I \leftrightarrow I_2^-$, to be greater than 10^4 by several powers of ten. Recently Boyer and Ramsey,¹⁴ after studying

the kinetics of the simultaneous reduction of oxygen and pervanadyl ion by iodide ion in acid solution, presented evidence that I_2^- is the intermediate of the pervanadyl-iodide reaction which acts as the catalyst of the oxygen iodide reaction.

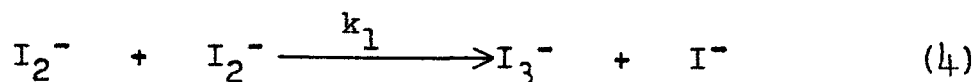
Dissociation

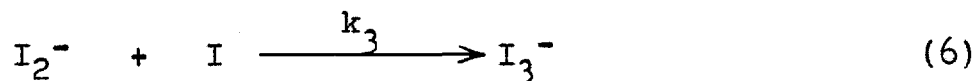
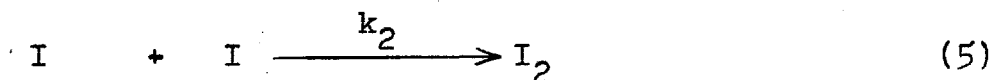
In solutions of I^- and I_2 the concentration of the triiodide ion, I_3^- , is determined by the equilibrium constant, K_I . The reactions postulated to explain the reversible increase in the optical density of a solution containing I^- , I_2 , and I_3^- following its intense irradiation are the following:



Recombination

The I_2^- and I produced by the flash may recombine by several paths:





At I^- concentrations greater than about 4×10^{-5} M, the experimental results indicate that reactions (5) and (6) may be neglected. The disappearance of the I_2^- is then due only to reaction (4). The second order rate expression is:

$$d(I_2^-)/dt = -k_1(I_2^-)^2 \quad (7)$$

which when integrated yields:

$$1/(I_2^-)_t - 1/(I_2^-)_0 = k_1 \cdot t. \quad (8)$$

It will be shown subsequently that the experimental results are in best agreement with a second order rate expression for the disappearance of the colored species.

I_2^- and Beer's Law

When the non-equilibrium concentration of I_2^- is produced by irradiation of the reaction cell containing the acidified $I_3^- - I_2^- - I^-$ solution, it is an experimental fact that less light in the region 353-460 mmu. can pass through the reaction cell. The absorption spectrum of I_3^- has a maximum at 353 mmu., at which ϵ'_3 is equal to $26,400 \text{ M}^{-1}\text{cm}^{-1}$.

For I_2 at this wave length ϵ_2^1 is $18 \text{ M}^{-1}\text{cm}^{-1}$. The molar extinction coefficient for I_3^- falls rapidly with increasing wave length until at $460 \text{ m}\mu$. its value is $975 \text{ M}^{-1}\text{cm}^{-1}$ while ϵ_2^1 is $746 \text{ M}^{-1}\text{cm}^{-1}$, which is the maximum for I_2 in this region¹⁵. Therefore, though for every two I_2^- ions produced in reactions (1) and/or (2) and (3), one I_3^- or one I_2 is destroyed, the fact that the solution becomes more highly colored is indicative that ϵ_1^1 must be quite large in this region, so large that the increased transmission due to the dissociation of I_3^- and/or I_2 is not detected.

Let L_c be the constant monitor light incident on the reaction cell. Then Beer's law may be written:

$$L_o = L_c \cdot e^{-l(\epsilon_1(I_2^-)_o + \epsilon_3(I_3^-)_o + \epsilon_2(I_2)_o)} \quad (9)$$

At any time after the flash

$$L_t = L_c \cdot e^{-l(\epsilon_1(I_2^-)_t + \epsilon_3(I_3^-)_t + \epsilon_2(I_2)_t)}. \quad (10)$$

Therefore,

$$-\ln(L_t/L_o) = l(\epsilon_1\Delta(I_2^-) + \epsilon_3\Delta(I_3^-) + \epsilon_2\Delta(I_2)) \quad (11)$$

The $(I_2^-)_o$ is essentially zero, for, although it is highly colored, it does not contribute to the normal absorption spectrum of an I_3^- solution.

In a typical experiment the (I^-) is greater than

the (I_2^-) or (I_3^-) to such an extent that the (I^-) is essentially constant throughout an experiment. The experimental evidence is that not all the I_3^- and/or I_2^- is dissociated by the flash. (I_2^-) is therefore less than (I^-) and also generally less than (I_2) . It follows that

$$(I_3^-)/(I_2^-) = K_I \times (I^-) \cong \text{constant for an experiment.} \quad (12)$$

From equations (1) -- (6)

$$\Delta(I_2^-) = -2\Delta(I_3^-) - 2\Delta(I_2) \quad (13)$$

From equation (12) is obtained:

$$\Delta(I_2^-) = \Delta(I_3^-)/K_I(I^-) \quad (14)$$

Substitution into (13) gives, upon rearrangement

$$\Delta(I_3^-) = -\Delta(I_2^-)K_I(I^-)/2(1 + K_I(I^-)) \quad (15)$$

and

$$\Delta(I_2^-) = -\Delta(I_2^-)/2(1 + K_I(I^-)) \quad (16)$$

Therefore, (11) becomes

$$-\ln(L_t)/(L_o) = \Delta(I_2^-) \left[\epsilon_1 - \epsilon_3 K_I(I^-)/2(1 + K_I(I^-)) - \epsilon_2/2(1 + K_I(I^-)) \right] \quad (17)$$

$$\text{or} \quad -\ln(L_t)/(L_o) = (I_2^-)e \quad (17A)$$

The product of this effective molar extinction coefficient and the cell length, e , is used in all subsequent calculations. Upon substitution in equation (8) there is obtained:

$$\frac{-e}{\ln(L_t)/(L_o)} + \frac{e}{\ln(L_{t=0})/(L_o)} = k_1 \cdot t \quad (18)$$

Obviously

$$\Delta L = L_t - L_o, \quad \Delta L < 0. \quad (19)$$

Therefore:

$$\frac{e}{\ln(1 + \Delta L_t/L_o)} - \frac{e}{\ln(1 + \Delta L_{t=0}/L_o)} = -k_1 t \quad (20)$$

By plotting $-1/\ln(1 + \Delta L_t/L_o)$ vs. time, a straight line of positive slope, k_1/e , and of positive intercept, $-1/\ln(1 + \Delta L_{t=0}/L_o)$, should be obtained. (It should be remembered that the quantity, $\ln(1 + \Delta L_t/L_o)$, is itself negative.)

Corrections and Approximations Due to Electronic Apparatus

In order to evaluate most accurately k_1/e from measurements of oscillographic traces, two small corrections should be applied to the equations derived above. The one correction is necessary because the photoelectric current produced by the photoelectric cell is not directly propor-

tional to the light intensity for all values of the light intensity, but rather is equal to the light intensity times a function of the voltage--slightly variable--across the photoelectric cell.

A second correction is necessary because of the fact that the signal decay observed on the oscillograph screen, from which the value of k_1/e is obtained, is due to the combination of the signal produced in the reaction cell by the change in its light transmission and by the resistance-capacitance decay of the alternating current amplifier and oscillograph combination.

However, since both the above corrections are small and since at best the absolute value of k_1 cannot be determined in these experiments, these corrections have been omitted. Photoelectric current, I_0 and ΔI_t , have been substituted directly for L_0 and ΔL_t , respectively, in equation (20). The rise of the light signal has been taken as caused solely by the recombination of the I_2^- ions.

Experimental Discussion

Chemistry

The solutions were prepared using Merck reagent grade KI, C. P. resublimed I_2 , and conductivity water. In order to reduce the concentration of HOI and IO_3^- in the solutions, for which the equilibrium constants are K_B and K_C respectively,¹⁵ the solutions were acidified to pH ca. 4 with J. P. Baker's reagent H_2SO_4 .

The optical density of each cell with only H_2O and H_2SO_4 was measured to obtain an accurate blank. The desired amounts of KI and I_2 were then pipetted into the cell and the concentration of I_3^- and I_2 determined spectrophotometrically. The concentration of I^- in very dilute solutions (10^{-6} M) was determined from the equilibrium constant, K_I . In more concentrated solutions, the amount of I^- added compared reasonably well, 80% or better, with that calculated from the equilibrium constant.

In several experiments either J. P. Baker's reagent grade $Fe(NH_4)(SO_4)_2$ or Merck reagent $Fe(NH_4)_2(SO_4)_2$ was added to produce (Fe^{III}) and (Fe^{II}) of about 4×10^{-5} M and 2×10^{-3} M respectively.

Persistent difficulty was encountered in obtaining cells with a reasonable concentration of either I^- or I_2 but with a small initial concentration of I_3^- that would remain nearly constant throughout an experiment. Introduction of boiling water, saturated with argon, into the cell

containing solid KI in an atmosphere of argon, was only moderately successful in eliminating the initial high (I_3^-). Reduction of the I_3^- with $NaHSO_3$ was successful only when (HSO_3^-) was several times the stoichiometric amount. This method of eliminating the initial high (I_3^-) was not adopted because of the obvious complications.

Apparatus and Its Function

The constant monitor light is produced by a Hanovia direct current mercury arc, 100 watts, operated at 120 volts from high capacity lead storage batteries. The lamp base is heavily weighted with lead bricks and floated on sponge rubber supports in order to reduce "noise" in the oscillograph sweep. The monitor light shines through a plano-convex soft glass lens, which produces an image on the source on the entrance slit of a Bausch and Lomb monochromator of dispersion, 33 \AA . per mm. The monochromator directs the light squarely onto the plate of a 929 phototube which is connected to an alternating current amplifier to be described later.

The reaction vessel is a pyrex cylinder 10 cm. long and 5 cm. in diameter, of volume ca. 175 ml., with corex windows and two filling arms 3 to 4 cm. long perpendicular to the axis of the cylinder. This cell is supported in an 8" x 5" x 6" box-like wooden holder placed between the focusing lens and the monochromator slit. The entrance and exit apertures in the holder are two tubes, 1" in diameter and $1\frac{1}{2}$ " long, coated internally with flat black paint and

placed so that the monitor light shines along the axis of the reaction cell in a cylindrical beam about 1" in diameter. Further to reduce scattered light and thereby reduce somewhat the recovery time of the amplifier, both front and back inner surfaces of the holder are also coated with flat black paint; the sides and bottom of the holder are coated with MgO. The upper edges of the holder serve as a framework on which may be placed a $4 \frac{3}{4}$ " x $6 \frac{1}{2}$ " glass filter to vary the wave length and the intensity of the flash light reaching the cell.

Directly above the longitudinal axis of the cell and fitting snugly onto the cell holder are the flash lamp reflector and quartz flash tube. The flash tube, similar to the General Electric FT-127, is 4 mm. i.d., 15 cm. long, and is filled with xenon at about 12 cm. pressure. It lies along the focal line of the MgO coated parabolic reflector. The flash lamp is connected by a coaxial cable to a high voltage firing device, pictured at the right in Fig. 3. A wiring diagram of the high voltage power supply and associated delay circuit is given in Fig. 4.

In other laboratories¹⁷ it was found that the intensity of light from a xenon filled General Electric FT-110 flash tube, when dissipating 100 watt seconds stored at 1000 volts, has maxima at 8000 Å. and 3800 Å. Since the distribution is a function of the voltage across the tube and the flash tube in these experiments was operated at

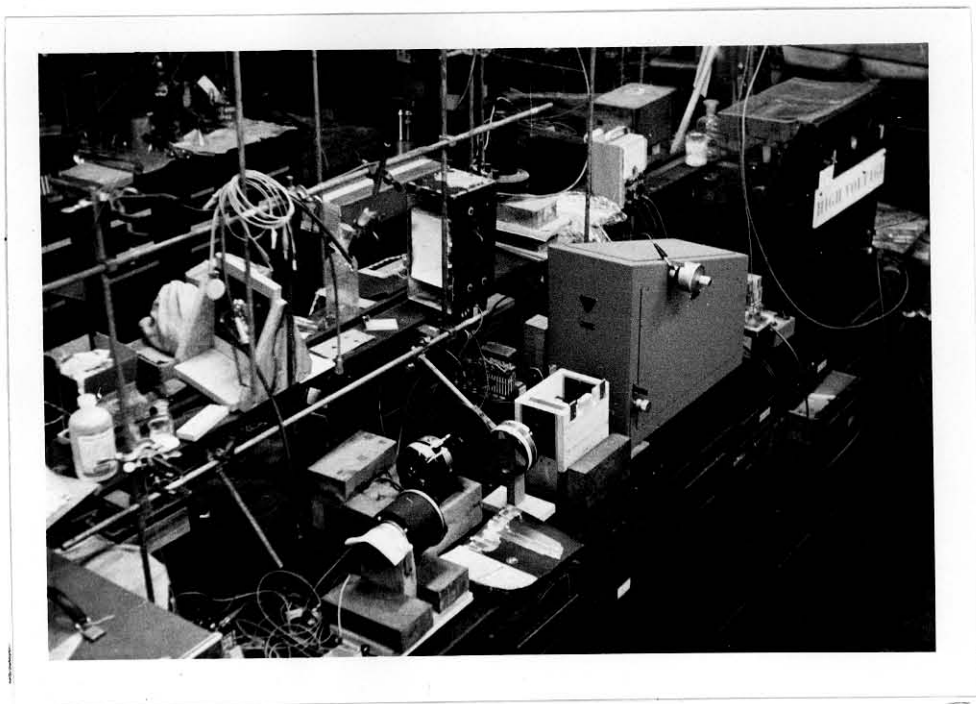


Fig. 3. The high voltage power supply is shown on the extreme right. Adjacent to it is the delay circuit and monochromator.

12,000 volts, the data above can be taken only as a general indication of the intensity distribution of the light from the flash tube used in these experiments.

When the switch is closed in the triggering circuit (Fig. 4), a positive pulse is applied through a small capacitor to the synchronization terminal of the oscillograph (set on external synchronization) to start the sweep. At the same time the pulse travels down a coaxial cable to a variable resistance-capacitance delay in the delay circuit. After the delay, the grid of the 2D21 thyatron is sufficiently positive to allow the tube to conduct until the

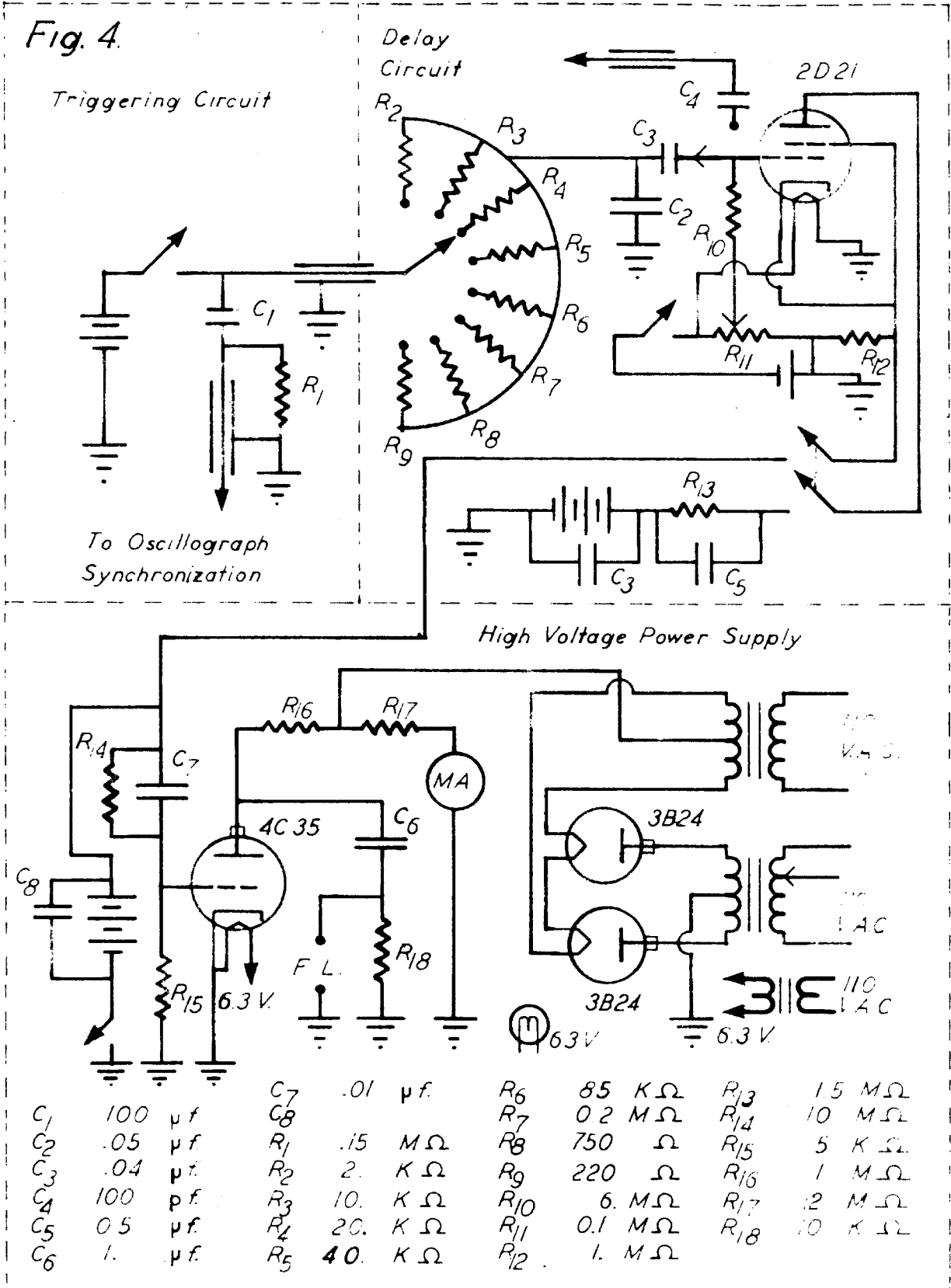


plate voltage drops to a certain value, and a positive signal is applied from the cathode resistor of the 2D21 grid of a 4C35 thyratron. This tube in turn conducts and rapidly discharges the highly positive side of a 1 microfarad capacitor. The side of the capacitor connected to ground through a resistor and the flash lamp in parallel is suddenly at a high negative potential, 12,000 volts, with respect to ground. Current arcs through the flash lamp, dissipating 72 joules of energy in parallel with the resistor.

When the flash lamp fires, a more colored species which is believed to be the diiodide ion is formed in the reaction cell. This ion absorbs strongly in the near ultraviolet; therefore, there is less monitor light passing through the reaction cell and entering the monochromator, which is usually set to transmit the Hg line at 365 m μ . and a band of 3.3 m μ . on either side of this wave length.

For a decrease in the light striking the photoelectric cell, a positive signal develops across the 1 megohm resistor in the alternating current amplifier (Fig. 5) and is applied to the grid on the triode-connected 6AK5. This positive signal causes a fall in the plate voltage and this negative signal, about 100 times larger than the input, is applied through a coaxial cable and multi-gang switch to the vertical input of a type 304-H DuMont Cathode-Ray Oscillograph. The filaments of the two 6AK5 tubes are connected through a switch to a 6 volt battery. There is common

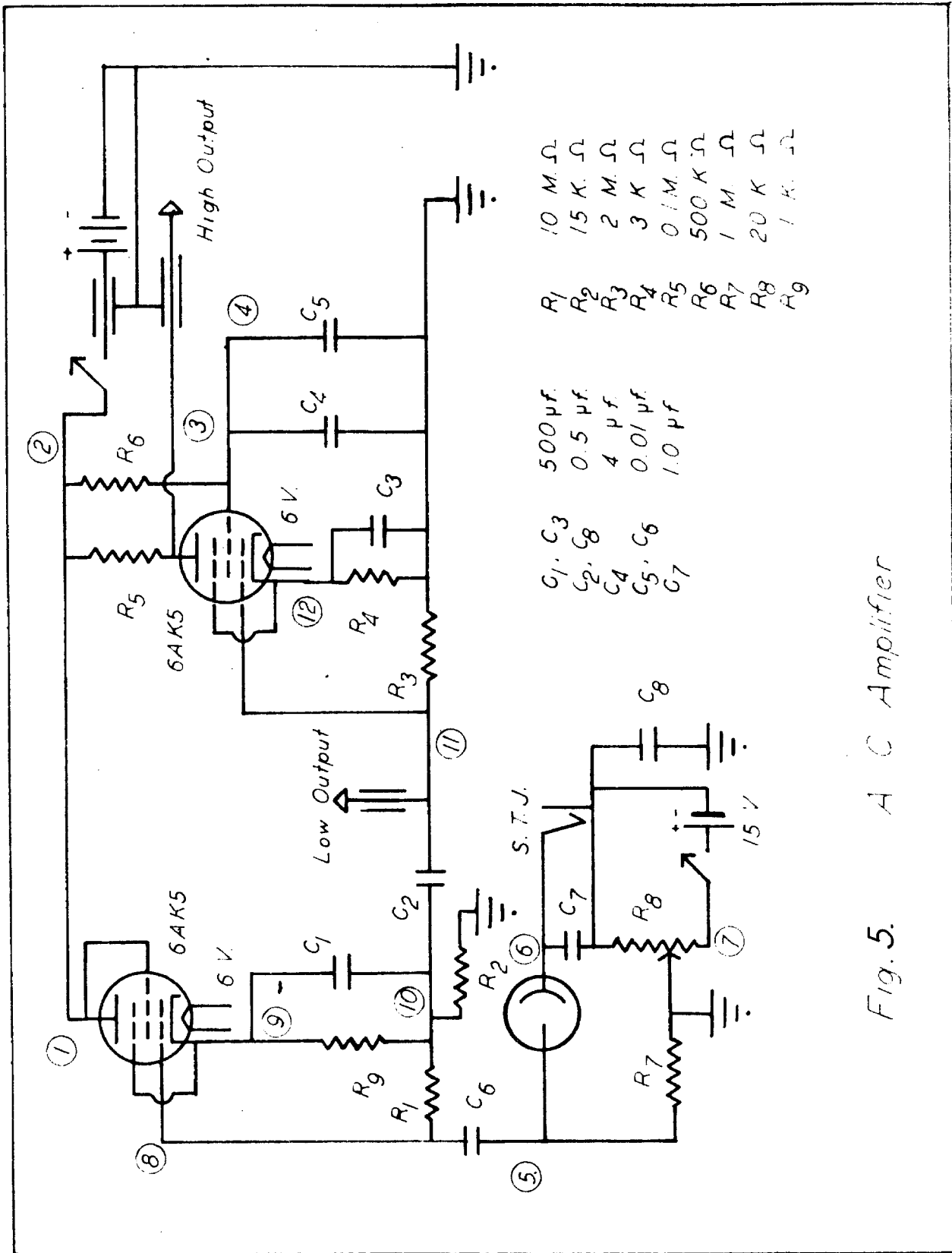


Fig. 5. A C Amplifier

ground for all the electronic circuits. Operating voltages of the amplifier as measured with a 20,000 ohms per volt voltmeter are given in Table 1.

Table 1

Operating Voltages of Amplifier

Point of measurement (Cf. circled nos. in Fig. 5)	Volts
1 - - - - -	180
2 - - - - -	180
3 - - - - -	112
4 - - - - -	71
5 - - - - -	0
6 - - - - -	-(-15)
7 - - - - -	0
8 - - - - -	(-1)
9 - - - - -	57
10 - - - - -	51
11 - - - - -	0
12 - - - - -	2.3

In order to determine the photoelectric current produced by the monitor light, a light chopper driven by an 1800 r.p.m. Bodine synchronous motor is placed between the d.c. arc and the focusing lens and so positioned that the two rotating blades of the chopper will completely cut off the light 3600 times a minute. The fair approximation of a square-wave produced on the oscillograph screen is measured as will be described later thus giving a value of I_0 .

A second interchangeable chopper disc with 20 blades is used with a small 6 volt d.c. tungsten lamp as a means of determining the oscillograph writing rate. The

vertical amplifier of the oscillograph may be calibrated by applying known voltages, obtained from three B batteries connected in parallel and a step attenuator, to the vertical input. A multi-gang switch enables rapid switching from the a.c. amplifier's two outputs to the battery and to the attenuator.

Photographic record of all oscillographic phenomena is made on Kodak Linagraph Pan film using a Kodak Retina I 35 mm. camera, set at 1/2 second and $f/3.5$, mounted firmly 10 inches from the oscillograph screen. Use of an auxiliary -3 Portra lens allows the screen to be brought into sharp focus. There is enough light from the laboratory and from the cathode-ray tube to make visible on the negative the grid pattern -- two mutually perpendicular sets of black lines 1/10 inch apart -- and both the accelerating potential of the oscillograph, 3,000 volts, and the film sensitivity are great enough that writing rates in excess of 2,000 screen inches per second are easily recorded. The negatives obtained are projected in a microfilm reader and measurements of the traces made to within 0.02 inch.

Experimental Procedure

While the various electrical instruments, except the monitor lamp, are reaching a constant operating temperature, the optical density of the cell and solution is measured at five wave lengths, 353, 365, 435, 460, and 560 m μ . using

a Beckman Model DU Spectrophotometer, in order to determine the composition of the solution. The values of the extinction coefficients¹³ for I_3^- and I_2 at these wave lengths are given in Table 2. The cell may be rechecked in the course of the experiment and is always remeasured at its conclusion.

Table 2

Molar Extinction Coefficients¹³ for I_3^- and I_2

<u>Wave L.</u>	<u>Coefficient</u>		<u>Wave L.</u>	<u>Coefficient</u>		<u>Wave L.</u>	<u>Coefficient</u>	
	I_3^-	I_2		I_3^-	I_2		I_3^-	I_2
5700 Å.	80		4300	2,400	559	3510	26,400	
5600	97	106	3800	14,200	65.2	3490	26,400	
5500	112	143	3750	17,000		3500		17.9
5460	120	164	3700	20,000	35.2	3480	26,350	
5400	130	195	3650	22,500	26.7	3460	26,800	
4800	468	690	3600	24,900	21.9	3450		18.4
4700	678	735	3560	26,000		3440	25,100	
4600	975	746	3550	26,200	19.0	3400	23,400	19.1
4570	1,100	742	3540	26,400		3280	16,700	
4400	1,880	655	3530	26,400		3200		29.5
4350	2,140		3520	26,400		3100		45

The horizontal amplifier of the oscillograph is then set to produce a 4 inch repetitive sweep at the desired frequency. The synchronization control is then set on external synchronization. With the 20 blade light chopper attached to the synchronous motor, using a 6 volt tungsten lamp as a light source, and having the monochromator slits open wide and the wave length scale set for the visible region, pictures

are taken of the 600 cps. square wave produced on the oscillograph. The writing rate at several different frequencies is thus recorded. If the experiment continues over several hours, the calibration is repeated at its conclusion and the results averaged. Unfortunately, this calibration technique was available only during the latter half of the investigation. Previously, reliance was placed on a calibration graph made in 1950 of the oscillograph frequency rate at various settings. A comparison of the writing rates is given in Table 3.

The vertical sensitivity of the oscillograph is determined on several settings by applying known voltages to the d.c. vertical amplifier and recording the trace displacements.

The monitor light is then turned on and allowed to reach a constant temperature; the cell is placed in the holder; the monochromator is set to the desired wave length and the entrance and exit slits each set to 1 mm. The light chopper blades are then switched and the photoelectric current determined by measuring on four gain settings the amplitude of the square wave produced. The average value obtained, knowing the gain of the amplifier and considering the original signal to have been developed across a precision 1 megohm resistor, is used as I_0 in the calculations. However, it is unnecessary to know the absolute value of I_0 for only the ratio, $\Delta I/I_0$, is used in the calculations.

In order to determine the gain, G , of the amplifier, let x represent the voltage developed by the photoelectric current flowing through the 10^6 ohm resistor. Then

$$w = x.a.c \quad \text{and} \quad p = x.b.d .$$

It follows that

$$G = b/a = p.c/d.w .$$

If y represents the voltage of the B battery, then

$$g = d.y \quad \text{and} \quad h = c.y.m .$$

Therefore,

$$G = p.h/w.g.m . \quad (21)$$

Four measurements thus suffice to determine the amplifier gain. Typical data and calculations of G and I_0 for an experiment are given below.

O-graph	Gain	S.W. Ampl.	Battery	Atten. Ampl.	Bat. Signal
G-1000,	V-100	.48"	21.25 V.	1.00	.85"
G-10	V-100	.46	21.25	.0291	2.40
G-1	V-30	1.01	21.25	.0099	1.85
G-1	V-50	2.09	21.25	.0099	3.69

$$G = (.48)(2.40)/(.46)(.85)(.0291) = 101.2$$

O-graph	Gain	Vert. Sensitivity in Volts/Inch	$I_0 \times 10^6$ Amp.
G-1000,	V-100	$(21.25)/(.85) = 25.0$.1185
G-10	V-100	$(21.25)(.0291)/(2.40) = 0.258$.1172
G-1	V-30	$(21.25)(.0099)/(1.85) = 0.114$.1138
G-1	V-50	$(21.25)(.0099)/(3.69) = 0.057$.1176

$$I_0 = (.48)(25.0)(10^{-6})/(101.2) = .1185$$

$$\text{Mean} = .1168 \pm .002$$

The high output of the a.c. amplifier is switched to the vertical input of the oscillograph and, with the oscillograph on repetitive sweep, the writing rate is set at a convenient figure and the vernier of the horizontal amplifier is adjusted to yield a 4 inch sweep. The oscillograph a.c. vertical amplifier is then adjusted to allow the maximum sensitivity consistent with the noise level of the signal. After the Variac of the flash tube power supply is set at operating voltage, 12,000 volts, and the proper delay in the flash tube firing circuit determined, several pictures are taken of the phenomena as recorded on the oscillograph screen. These pictures incorporate the delay and the change in the monitor light reaching the photoelectric cell as the diiodide ions recombine. Figures 7-9 show some typical experimental results.

After several good pictures are obtained -- some of the pictures are poor because the flash lamp may not break down as soon as the 4C35 thyatron discharges one side of the capacitor, thereby causing the resistor to dissipate a portion of the stored energy and making the desired trace late or throwing it off the screen entirely -- the monitor light is covered and with the same oscillograph settings a few pictures are taken of the scattered light the photoelectric cell receives from the flash alone. Fig. 6 shows a typical trace. The sweep starts and after a short time the delay circuit allows the flash lamp to fire. The high pulse from the flash

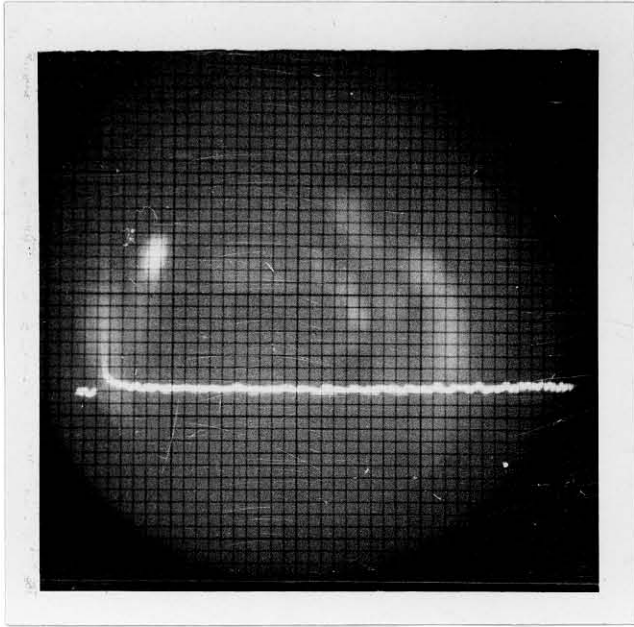


Fig. 6. A typical flash recorded at a rather slow writing rate, 3×10^{-3} Sec./Screen Inch. #6-84

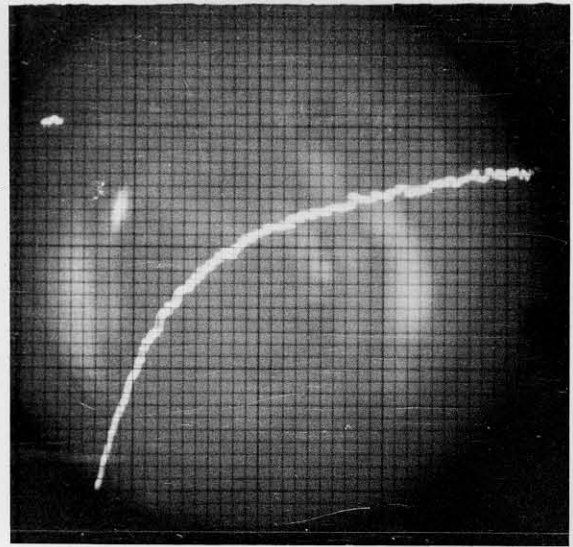


Fig. 7. Typical phenomenon. Corresponds to flash at left. 3×10^{-3} Sec./Screen Inch. #4-84

Fig. 8. Phenomenon showing the return to zero of the trace. 3×10^{-3} Sec./Screen Inch. #5-82

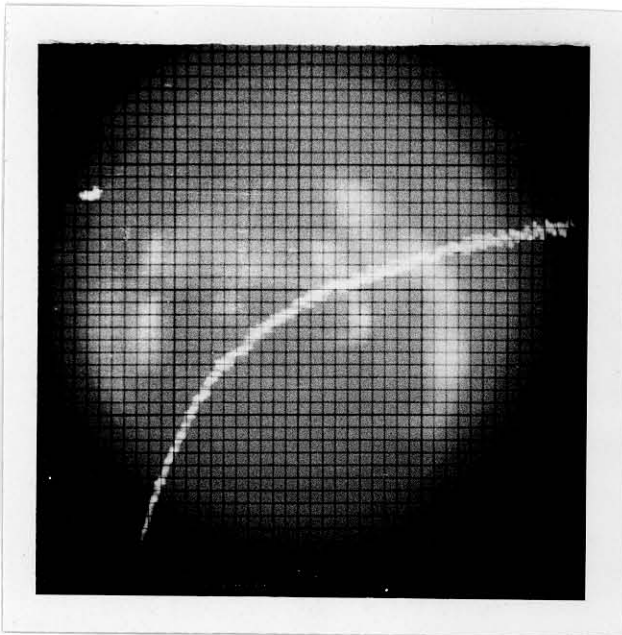
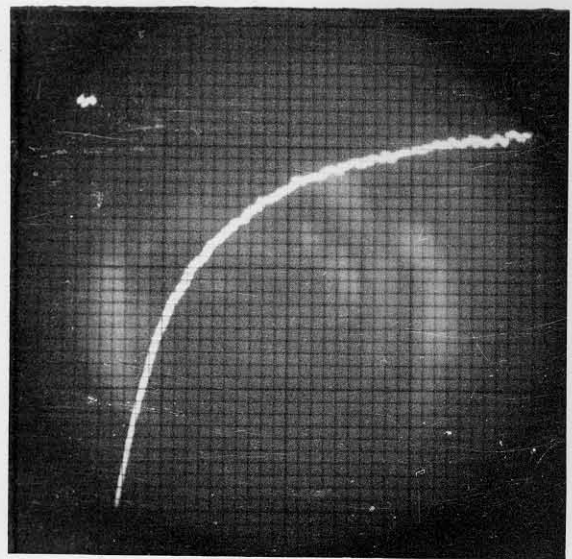


Fig. 9. Phenomenon showing the return to zero of the trace. 3×10^{-3} Sec./Screen Inch. #2-84



either returns to zero in about half a millisecond, drops beneath the base line -- a projection of the horizontal delay trace across the picture -- and then slowly returns to the base line (negative overshoot characteristic of a.c. amplification), or it decays exponentially in about 1.5 milliseconds. The differing phenomena depend upon the composition of the solution and the filter used over the flash lamp.

Results and Discussion

Calculation of the Quantity, k_1/e

From the measurements taken of the trace displacement produced by known voltages at definite vertical gain settings of the d.c. amplifier, the sensitivity in volts/inch at these settings is determined. The amplifier gain is calculated as shown on page 26.

The photographic negatives obtained are projected in a microfilm reader, the oscillograph screen thus being enlarged about 3.1 times life size. The number of grid units (10/screen inch) separating a convenient number of cycles of the 600 cps. calibration square-wave is measured across the calibration picture and the average found. The writing rate in 10^{-3} sec. per inch is then easily calculated. Table 3 gives a typical writing rate for various settings, based on a 4 inch sweep.

Table 3

		Oscillograph Writing Rate Milliseconds per Screen Inch					
Frequency Setting	Sector 7/7/50	Crystal	Sector 7/23/53	Sector 8/7/53 Old tube	Sector 8/8/53 New tube	Sector 8/14/53	
250	V-50	5.38	5.55		4.35	5.26	
	V-60	4.17	4.46		3.40	4.13	3.91
	V-70	3.13	3.33	2.22	2.51		
	V-80	2.08	2.40	1.46	1.73		2.14
	V-90	1.37	1.61		1.10	1.29	1.31
1250	V-10		1.47	1.07	1.16	1.23	1.21
	V-20		1.43	1.04	1.09	1.18	
	V-30	1.16	1.27		1.08	1.08	1.06
	V-40	.98	1.05		.78	.91	
	V-50	.79	.84	.61	.62	.73	.72
	V-60	.61	.65	.	.50	.57	

(New tube -- refers to the replacement of the 6Q5G thyratron in the sweep circuit of the DuMont Oscillograph.)

The oscillograph sweep as recorded by the camera against a plane grid is not exactly linear; the first and last portions are slightly compressed horizontally and their amplitudes slightly reduced. However, the accuracy of other measurements in the experiment and the fact that most of the measurements are made in the central portion make a correction for the convexity of the face of the cathode ray tube unimportant.

The projection of the picture of the delay and only scattered light from the flash lamp (Fig. 6) is traced. The delay is projected across the paper parallel to the horizontal grid lines, which are parallel to straight oscillograph sweeps. The projection of a picture showing the delay and the

recombination of the diiodide ions (Fig. 7) is superimposed upon the tracing so that the ends of the delays coincide and lie along the same line. From the beginning of the flash -- the end of the delay, usually -- points are selected along the horizontal line and the distance corresponding to each point is expressed in terms of the time from the beginning of the flash. At each point the distance between the flash curve and the recombination curve is measured. This distance, ΔS_t , is converted into ΔI_t according to the equation:

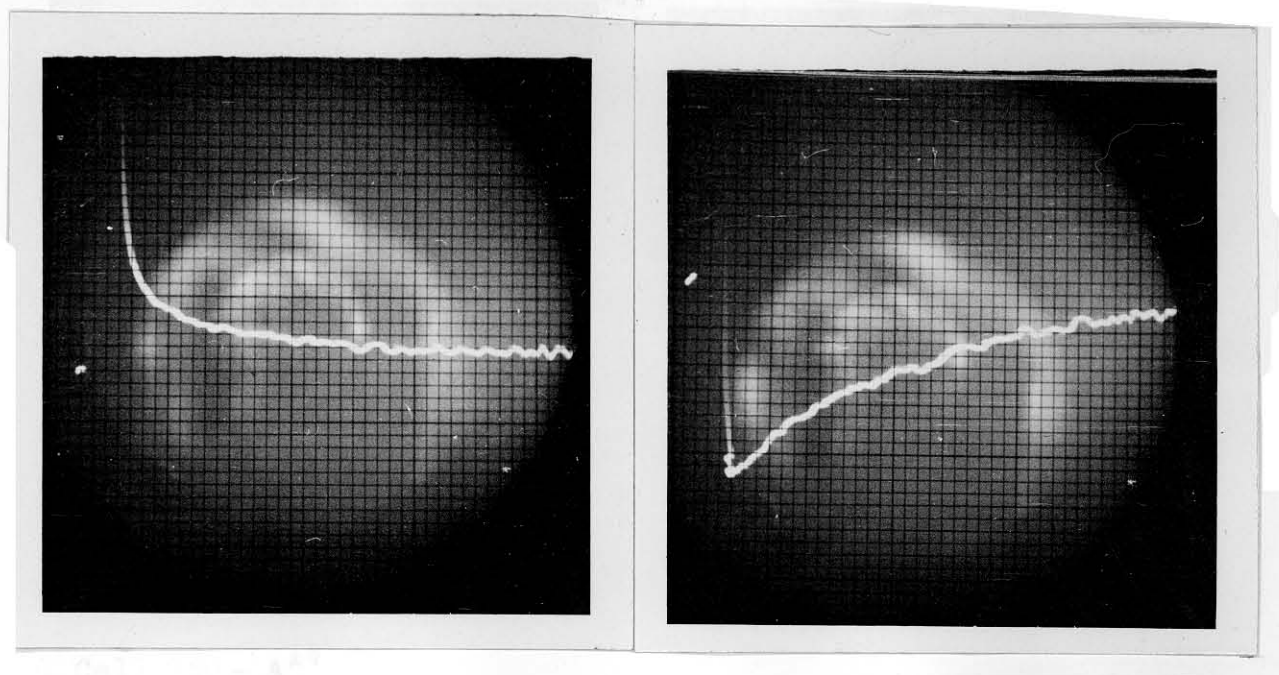
$$\Delta I_t = \Delta S_t \cdot V \cdot 10^{-6} / G \cdot R \quad (21A)$$

The numerical value of $-10^{-2} / \ln(1 + \Delta I_t / I_0)$ is then determined and plotted against time. The best straight line is drawn through the points and the slope and intercept determined. The slope is equal to $10^{-2} k_1 / e$; the intercept is equal to $-10^{-2} / \ln(1 + \Delta I_{t=0} / I_0)$. It is at present impossible to obtain a value for k_1 itself, for the value of the molar extinction coefficient of I_2^- is not known.

The half-life, $t_{\frac{1}{2}}$, of the reaction is found from the graph mentioned above by doubling the "y" intercept and drawing a line parallel to the time axis until it intersects the plotted curve. The value of t corresponding to this intersection is $t_{\frac{1}{2}}$.

Complete data, calculations, and graphs for several typical experiments* are given on pages 32 through page 45.

* Additional material of this nature is deposited with Dr. Norman Davidson.



Cell 16 - A^{IV}

Picture: #22 - P. 114. 435 mmu.

O-graph Vert. Sens., G-1, V-50 - .0564 volts/screen inch

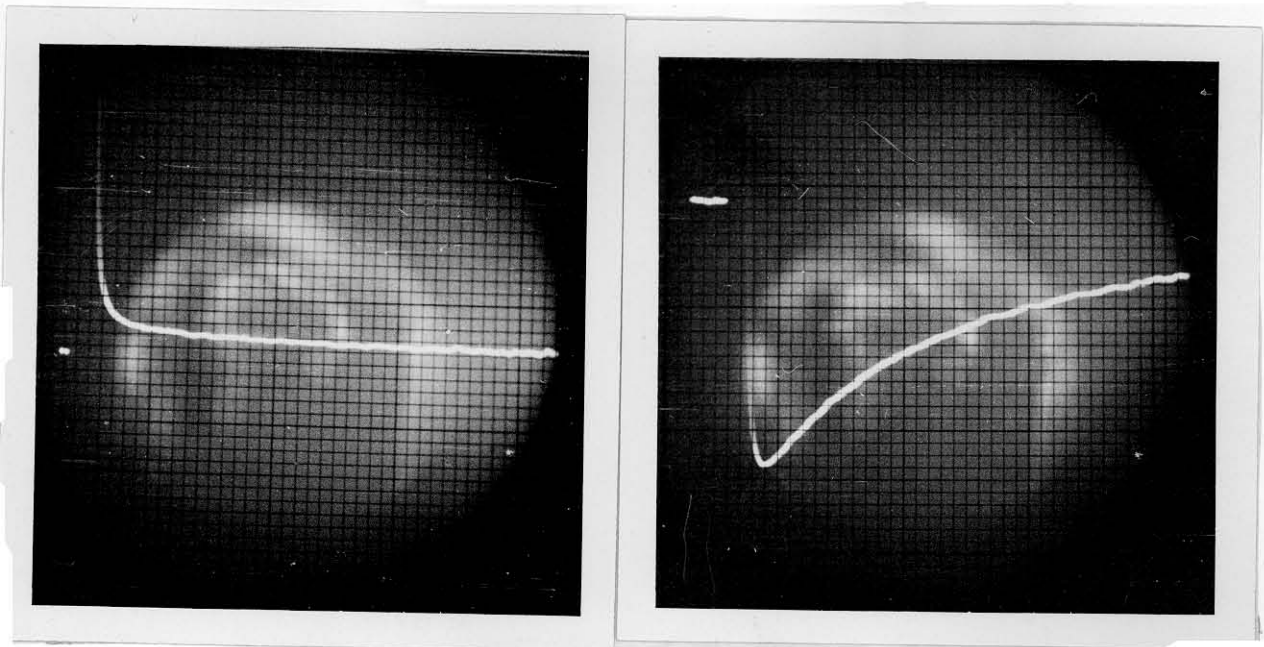
Writing Rate - 1250 V 50 - 0.60×10^{-3} sec./screen inch

$I_0 = .088 \times 10^{-6}$ A.

$R = 3.10$, $G = 102$

Second Order

Time Inches on Tracing	Time \times 10^3 Sec.	ΔS Inches on Tracing	$-\Delta I/I_0$ \times 10^3	$\frac{-10^{-2}}{\ln(1 + \Delta I/I_0)}$
1.25	.242	7.28	14.74	.674
1.50	.290	6.44	13.03	.773
1.75	.339	5.97	12.10	.821
2.00	.388	5.60	11.34	.877
2.25	.435	5.20	10.52	.946
2.50	.484	4.90	9.93	1.008
3.00	.580	4.41	8.94	1.12
3.50	.677	4.05	8.20	1.22
4.00	.774	3.70	7.50	1.335
4.50	.870	3.36	6.80	1.47
5.00	.968	3.15	6.38	1.568
5.50	1.065	2.86	5.80	1.726
6.00	1.162	2.64	5.35	1.87



Cell 16 - A^{IV}

Picture: #15, 17 - P. 114. 365 mmu.

O-graph Vert. Sens., G-1, V-20 - .1915 volts/screen inch

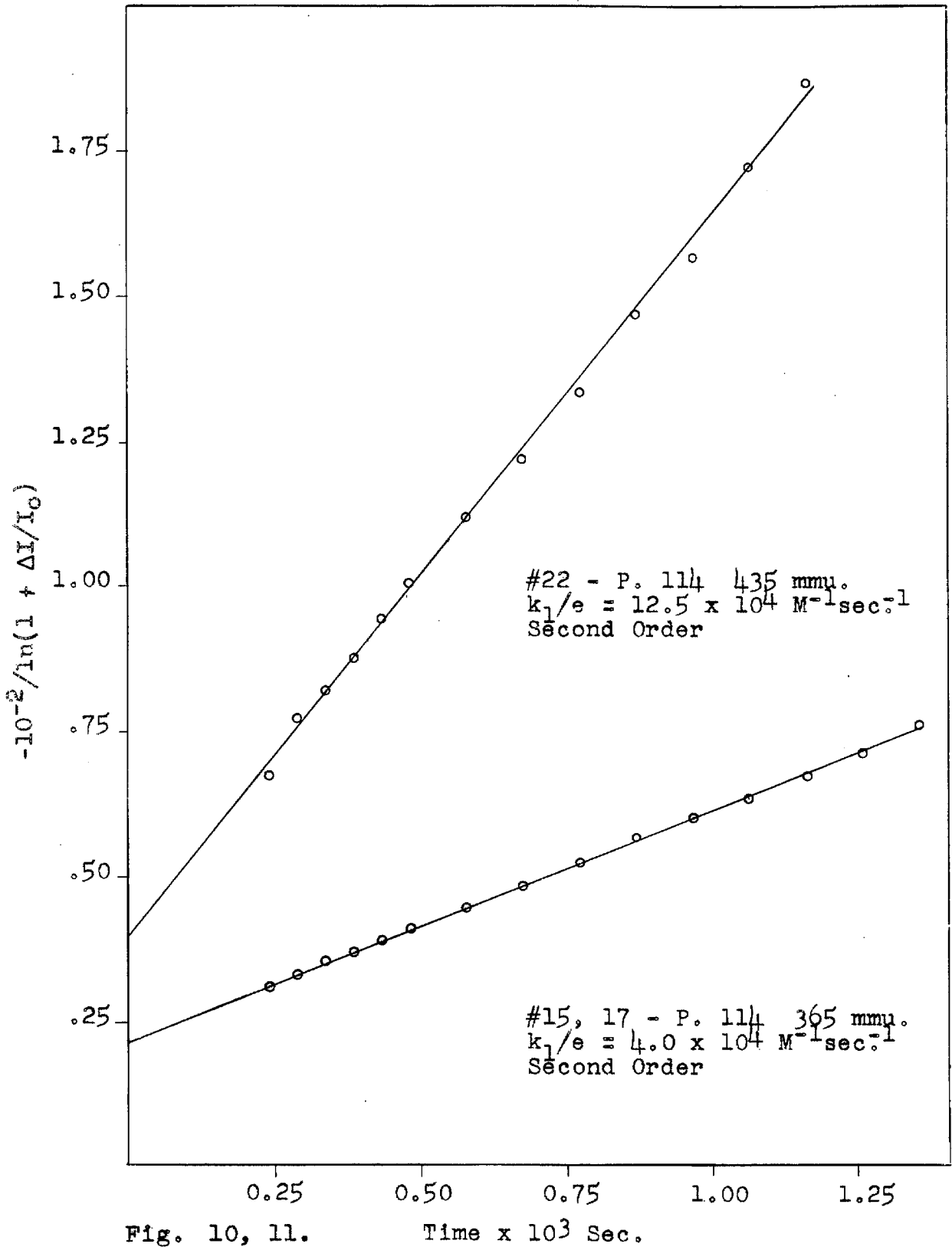
Writing Rate - 1250 V 50 - .60 x 10⁻³ sec./screen inch

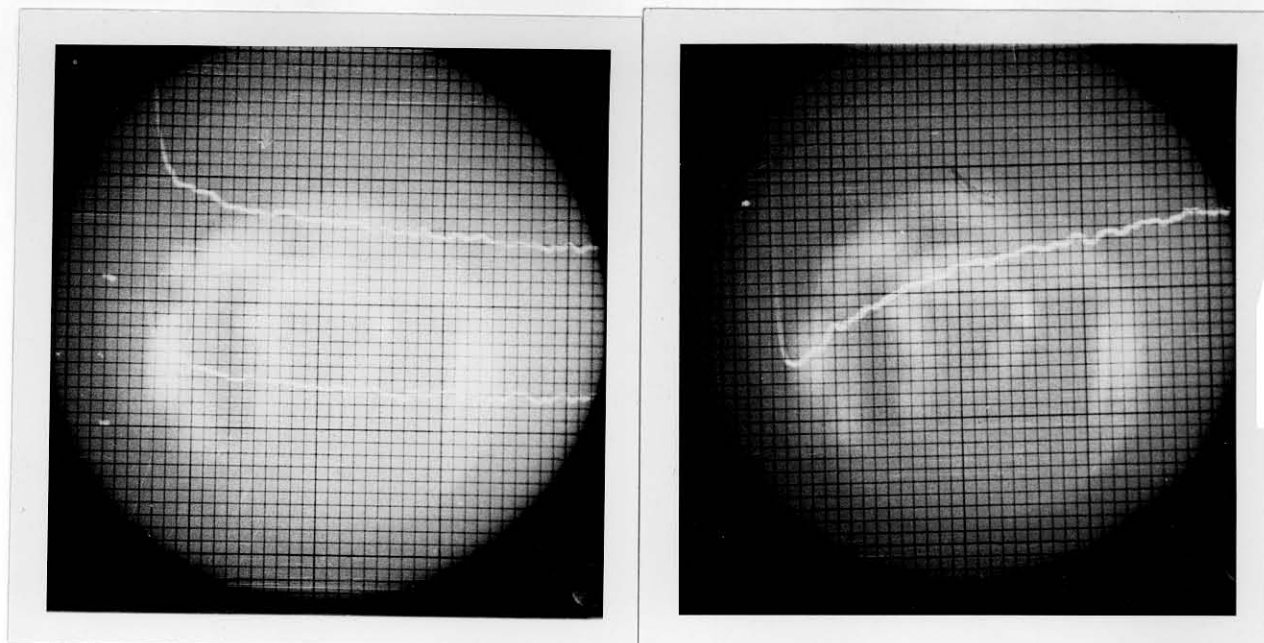
I₀ = .138 x 10⁻⁶ A.

R = 3.10, G = 102

Second Order

Time Inches on Tracing	Time x 10 ³ Sec.	ΔS Inches on Tracing	-ΔI/I ₀ x 10 ³	$\frac{-10^{-2}}{\ln(1 + \Delta I/I_0)}$
1.25	.242	7.25	31.8	.309
1.50	.290	6.80	29.81	.330
1.75	.339	6.38	28.0	.352
2.00	.388	6.07	26.65	.370
2.25	.435	5.76	25.27	.390
2.50	.484	5.49	24.07	.410
3.00	.580	5.03	22.08	.448
3.50	.677	4.66	20.46	.484
4.00	.774	4.29	18.81	.526
4.50	.87	3.97	17.42	.569
5.00	.968	3.76	16.5	.601
5.50	1.065	3.55	15.58	.636
6.00	1.162	3.35	14.70	.675
6.50	1.259	3.17	13.91	.714
7.00	1.355	2.96	12.99	.765





Cell 17 - AII

Picture: #16 - P. 119-120. 435 mmu.

O-graph Vert. Sens., G-1, V-50 - .0586 volts/screen inch

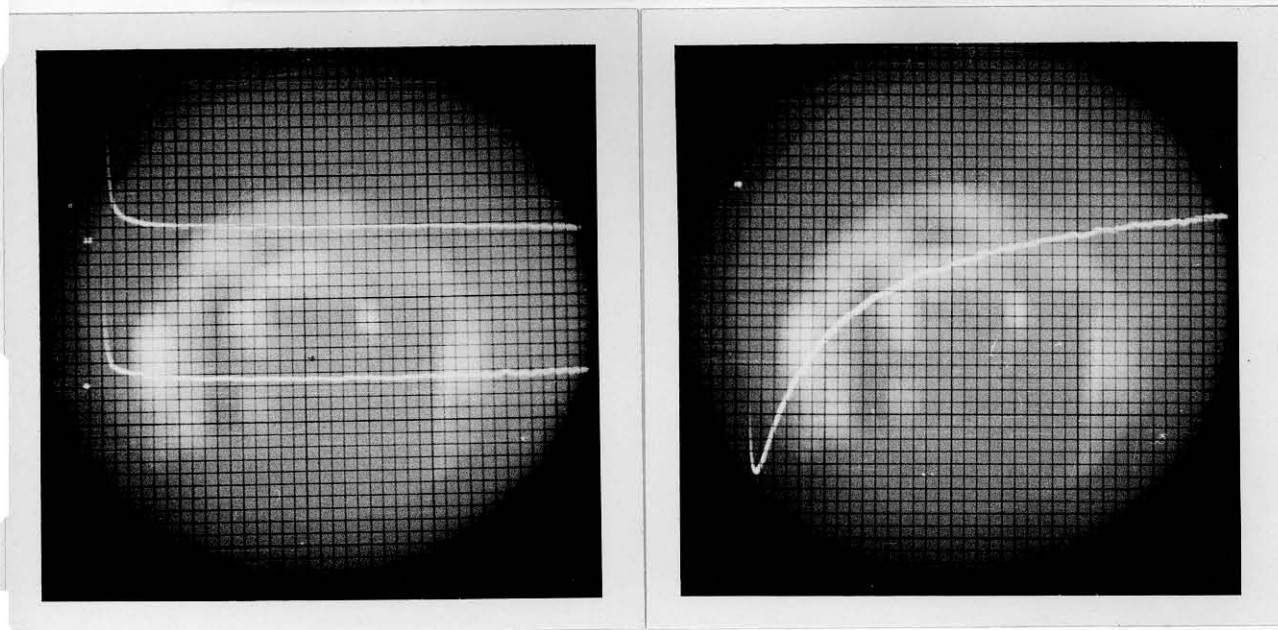
Writing Rate - 1250 V 50 - 0.60×10^{-3} sec./screen inch

$I_0 = 0.084 \times 10^{-6}$ A.

$R = 3.10$, $G = 107$

Second Order

Time Inches on Tracing	Time \times 10^3 Sec.	ΔS Inches on Tracing	$-\Delta I/I_0$ \times 10^3	-10^{-2} $\ln(1 + \Delta I/I_0)$
1.25	.242	5.98	12.58	.790
1.50	.290	5.5L	11.58	.860
1.75	.339	5.12	10.78	.925
2.00	.388	4.80	10.10	.986
2.25	.435	4.52	9.51	1.050
2.50	.484	4.26	8.97	1.114
3.00	.580	3.87	8.14	1.228
3.50	.677	3.53	7.43	1.347
4.00	.774	3.28	6.90	1.45
4.50	.87	3.05	6.41	1.559
5.00	.968	2.80	5.89	1.699
5.50	1.065	2.64	5.55	1.800
6.00	1.162	2.50	5.26	1.901
6.50	1.259	2.36	4.96	2.018
7.00	1.355	2.24	4.71	2.120



Cell 17 - AII

Picture: #13, 14 - P. 119. 365 mmu.

O-graph Vert. Sens., G-1, V-20 - .217 volts/screen inch

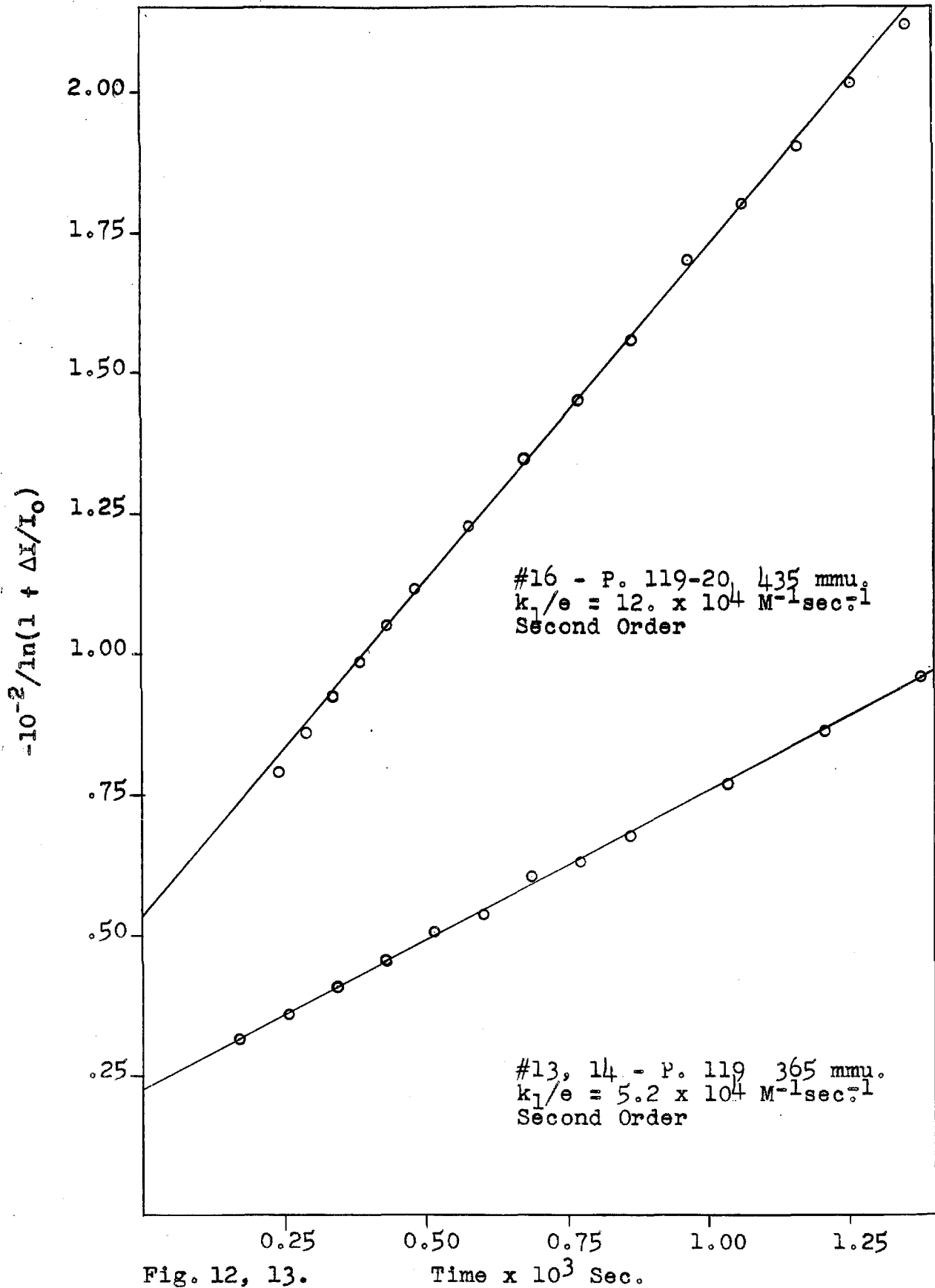
Writing Rate - 1250 V 10 - 1.07×10^{-3} sec./screen inch

$I_0 = .162 \times 10^{-6}$ A.

$R_0 = 3.10$, $G = 107$

Second Order

Time Inches on Tracing	Time 10^3 Sec.	ΔS Inches on Tracing	$-\Delta I/I_0$ $\times 10^3$	-10^{-2} $\ln(1 + \Delta I/I_0)$
.50	.1725	7.75	31.3	.3142
.75	.259	6.80	27.44	.359
1.00	.345	6.02	24.33	.406
1.25	.431	5.42	21.88	.452
1.50	.518	4.87	19.68	.5035
1.75	.604	4.56	18.42	.5375
2.00	.69	4.18	16.88	.603
2.25	.776	3.90	15.76	.630
2.50	.864	3.63	14.67	.677
3.00	1.035	3.20	12.92	.769
3.50	1.208	2.86	11.56	.861
4.00	1.38	2.57	10.38	.960
4.50	1.552	2.36	9.54	1.049
5.00	1.727	2.18	8.80	1.137
5.50	1.898	2.05	8.28	1.208
6.00	2.07	1.87	7.55	1.323



Cell 17 - A^{II}

Picture: #16 - P. 119-120. 435 mmu.

O-graph Vert. Sens., G-1, V-50 - .0586 volts/screen inch

Writing Rate - 1250 V 50 - 0.60 x 10⁻³ sec./screen inchI₀ = 0.084 x 10⁻⁶ A.

R = 3.10, G = 107

First Order

Time 10 ³ x 10 ³ Sec.	-ΔI/I ₀ x 10 ³	-ln(1 + ΔI/I ₀)	-log(-ln (1 + ΔI/I ₀))	-ln(-ln (1 + ΔI/I ₀))
.242	12.58	.01265	2.1021	4.36
.290	11.58	.01163	2.0656	4.45
.339	10.78	.01083	2.0346	4.52
.388	10.10	.01014	2.0060	4.59
.435	9.51	.00951	3.9782	4.65
.484	8.97	.00897	3.9528	4.71
.580	8.14	.00814	3.9106	4.81
.677	7.43	.00743	3.8704	4.90
.774	6.90	.00690	3.8388	4.975
.87	6.41	.00641	3.8069	5.05
.968	5.89	.00589	3.7701	5.13
1.065	5.55	.00555	3.7443	5.19
1.162	5.26	.00526	3.7210	5.24
1.259	4.96	.00496	3.6955	5.30
1.355	4.71	.00471	3.6730	5.36

Cell 17 - A^{II}

Picture: #13, 14 - P. 119 365 mmu.

O-graph Vert. Sens., G-1, V-20 - .217 volts/screen inch

Writing Rate - 1250 V 10 - 1.07 x 10⁻³ sec./screen inchI₀ = .162 x 10⁻⁶ A.

R = 3.10, G = 107

First Order

.1725	31.3	.0318	2.502	3.440
.259	27.44	.0278	2.444	3.603
.345	24.33	.0247	2.3924	3.70
.431	21.88	.0221	2.345	3.81
.518	19.68	.01986	2.298	3.92
.604	18.42	.0186	2.2695	3.982
.69	16.88	.0170	2.2305	4.075
.776	15.75	.01588	2.2005	4.146
.864	14.67	.01478	2.1694	4.215
1.035	12.92	.0130	2.114	4.344
1.208	11.56	.01162	2.0654	4.453
1.38	10.38	.01042	2.018	4.56
1.552	9.54	.00954	3.9794	4.653
1.727	8.80	.0088	3.9442	4.723
1.898	8.28	.00828	3.918	4.796
2.07	7.55	.00755	3.878	4.88

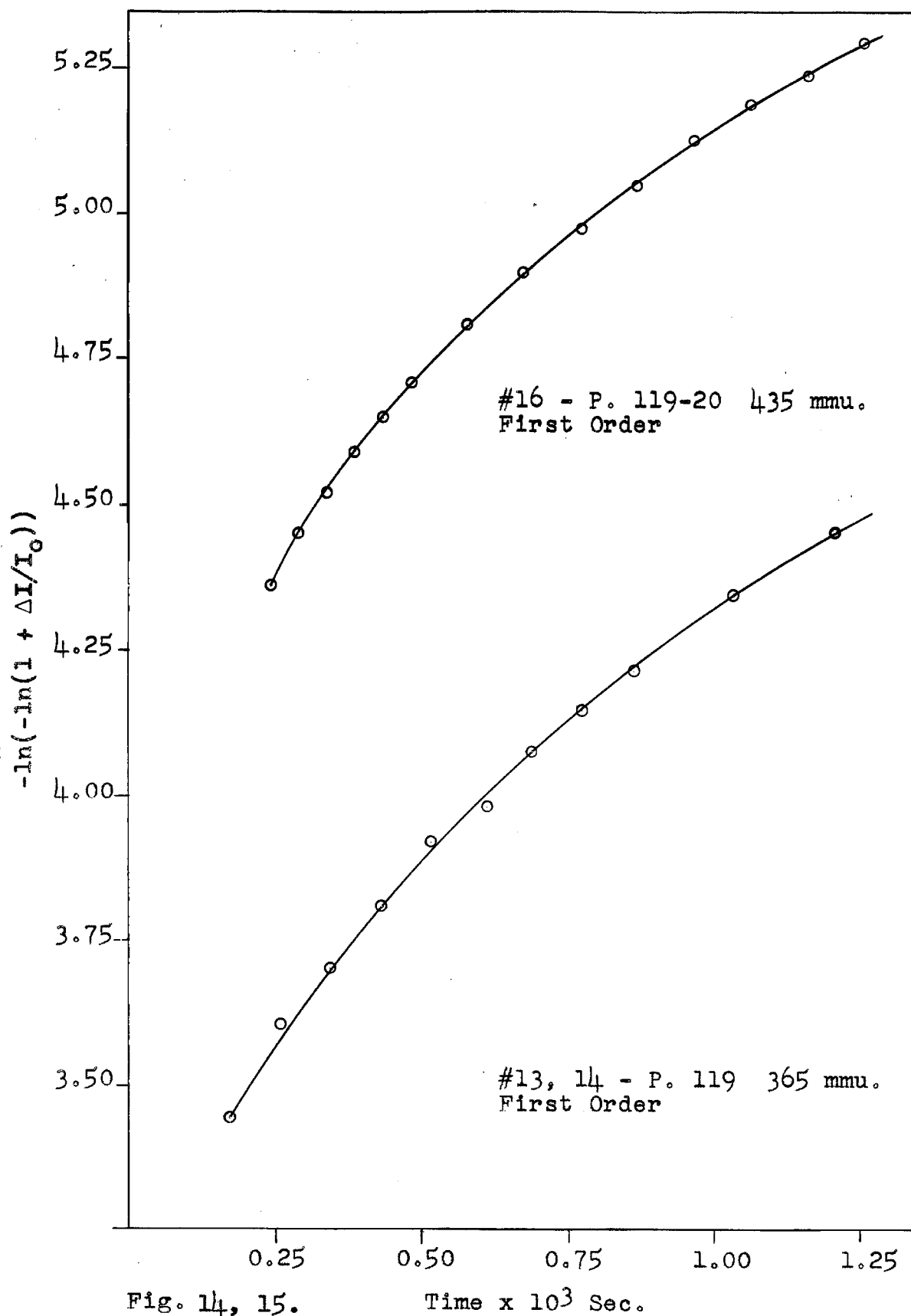
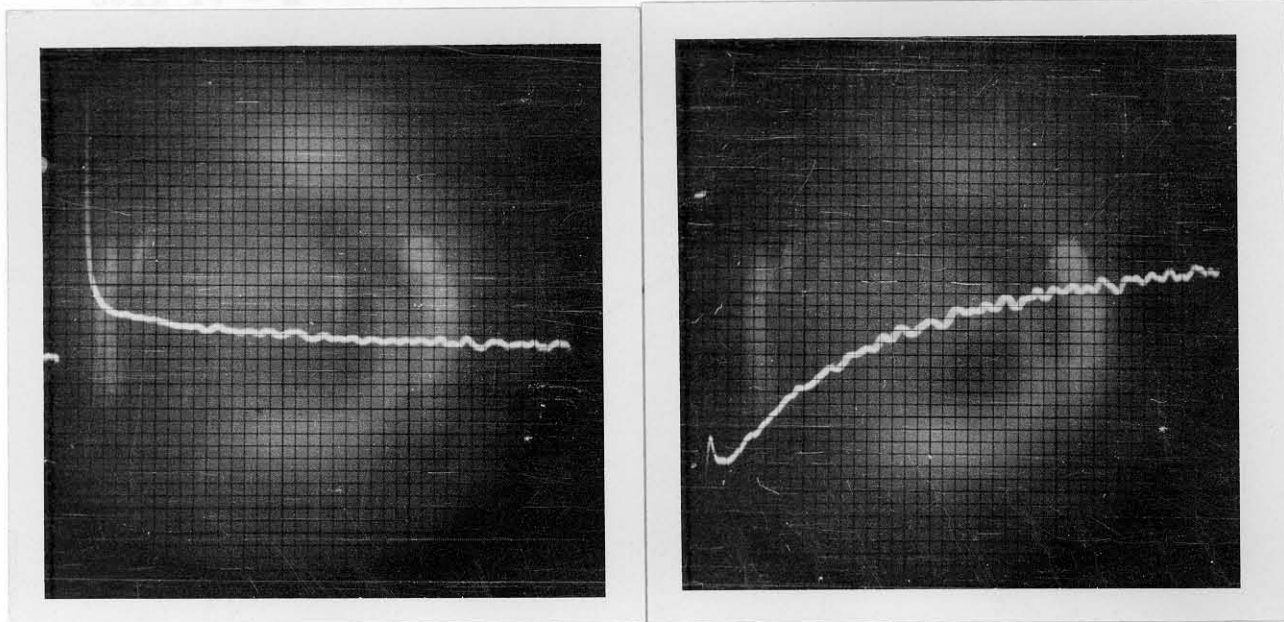


Fig. 14, 15.

Time x 10³ Sec.



Cell 19 - A

Picture: #6 - P. 124. 365 mmu.

O-graph Vert. Sens., G-1, V-30 - .114 volts/screen inch

Writing Rate - 1250 V 50 - .71 x 10⁻³ sec./screen inch

I₀ = .1177 x 10⁻⁶ A.

R⁰ = 3.15, G = 101.2

Second Order

Time Inches on Tracing	Time x 10 ³ Sec.	ΔS Inches on Tracing	-ΔI/I ₀ x 10 ³	$\frac{-10^{-2}}{\ln(1 + \Delta I/I_0)}$
1.00	.226	7.76	25.53	.386
1.25	.283	7.23	23.8	.415
1.50	.3396	6.86	22.58	.4375
1.75	.396	6.54	21.5	.460
2.00	.4525	6.27	20.63	.480
2.25	.509	5.98	19.68	.504
2.50	.566	5.74	18.88	.525
2.75	.622	5.49	18.05	.550
3.00	.679	5.28	17.38	.5705
3.50	.791	4.93	15.22	.611
4.00	.905	4.58	15.07	.659
4.50	1.019	4.28	14.09	.705
5.00	1.131	4.07	13.40	.741
5.50	1.244	3.84	12.62	.786
6.00	1.358	3.63	11.94	.832

Cell 19 - A

Picture: #6 - P. 124. 365 mmu.

O-graph Vert. Sens., G-1, V-30 - .114 volts/screen inch

Writing Rate - 1250 V 50 - .71 x 10⁻³ sec./screen inchI₀ = .1177 x 10⁻⁶ A.

R = 3.15, G = 101.2

First Order

Time x 10 ³ Sec.	-ΔI/I ₀ x 10 ³	-ln(1 + ΔI/I ₀)	-log(-ln (1 + ΔI/I ₀))	-ln(-ln (1 + ΔI/I ₀))
.2262	25.53	.02583	2.413	3.655
.283	23.8	.0241	2.3815	3.723
.3396	22.58	.02286	2.359	3.780
.396	21.5	.0217	2.337	3.830
.4525	20.63	.02082	2.3186	3.875
.509	19.68	.01986	2.298	3.920
.566	18.88	.01904	2.280	3.960
.622	18.05	.01820	2.260	4.008
.679	17.38	.01752	2.244	4.046
.791	15.22	.01635	2.2135	4.110
.905	15.07	.01518	2.1814	4.190
1.019	14.09	.01419	2.152	4.255
1.131	13.40	.01349	2.130	4.308
1.244	12.62	.01270	2.104	4.365
1.358	11.94	.01201	2.080	4.420

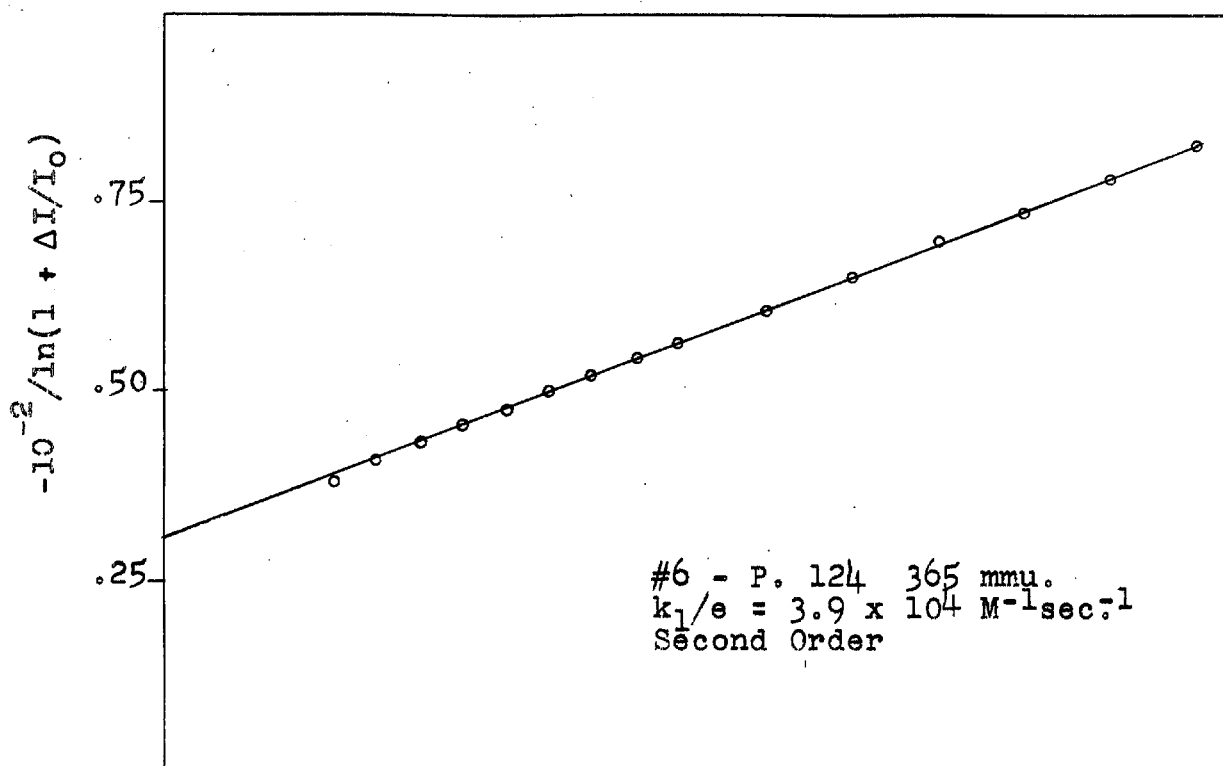


Fig. 16

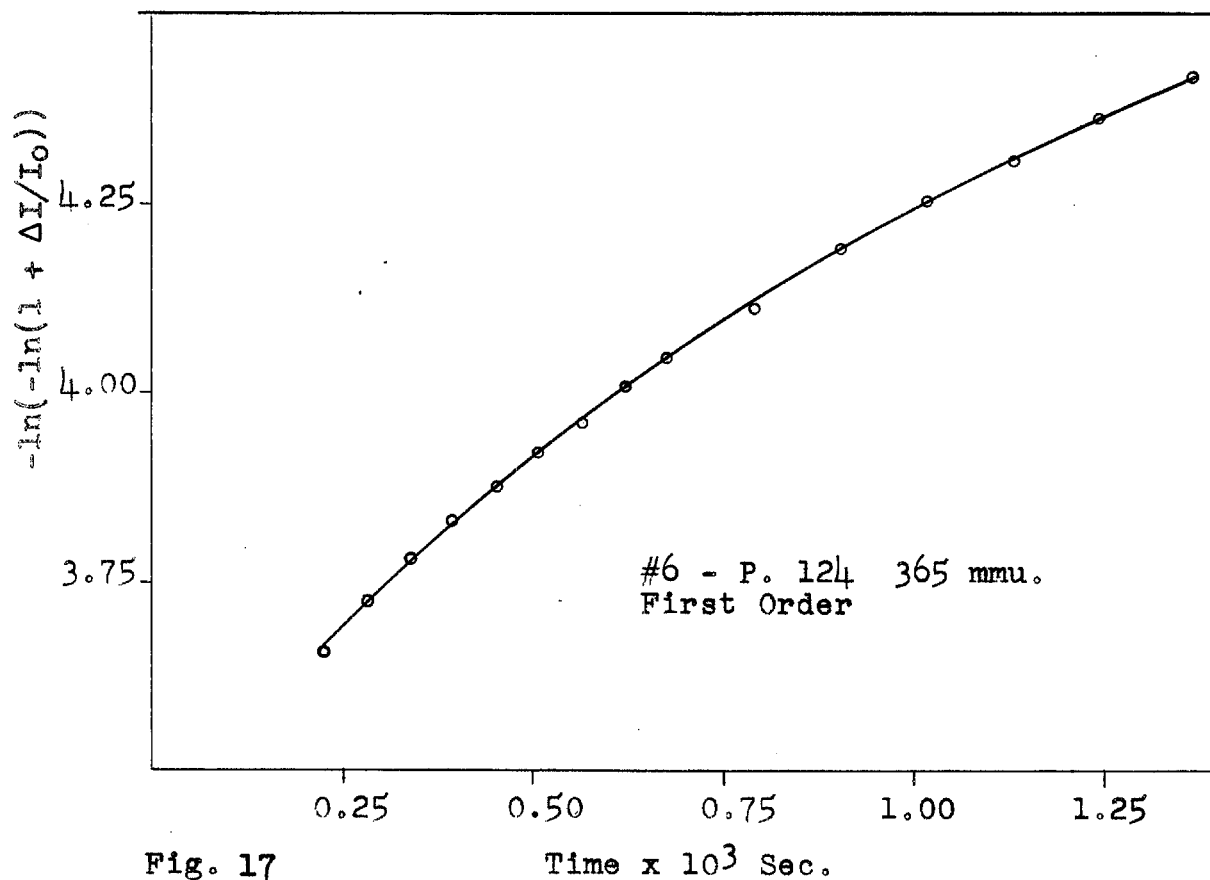
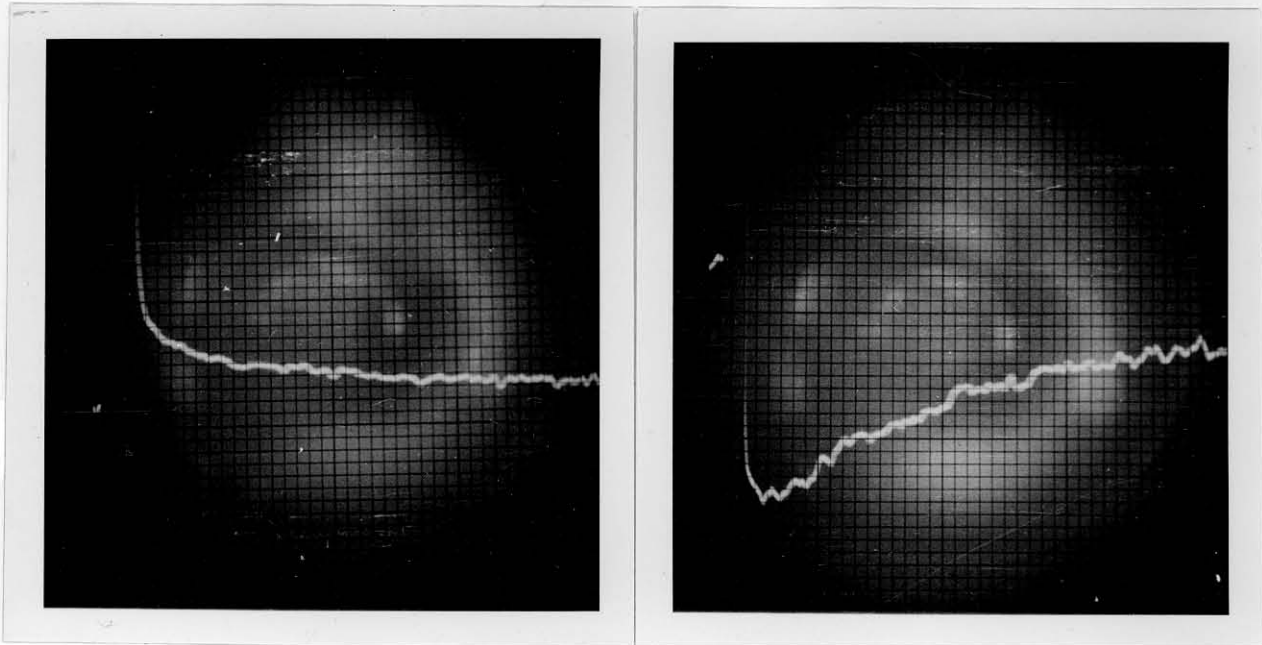


Fig. 17



Cell 18 - AII

Picture: #14 - P. 123. 365 mmu.

O-graph Vert. Sens., G-1, V-50 - .057 volts/screen inch

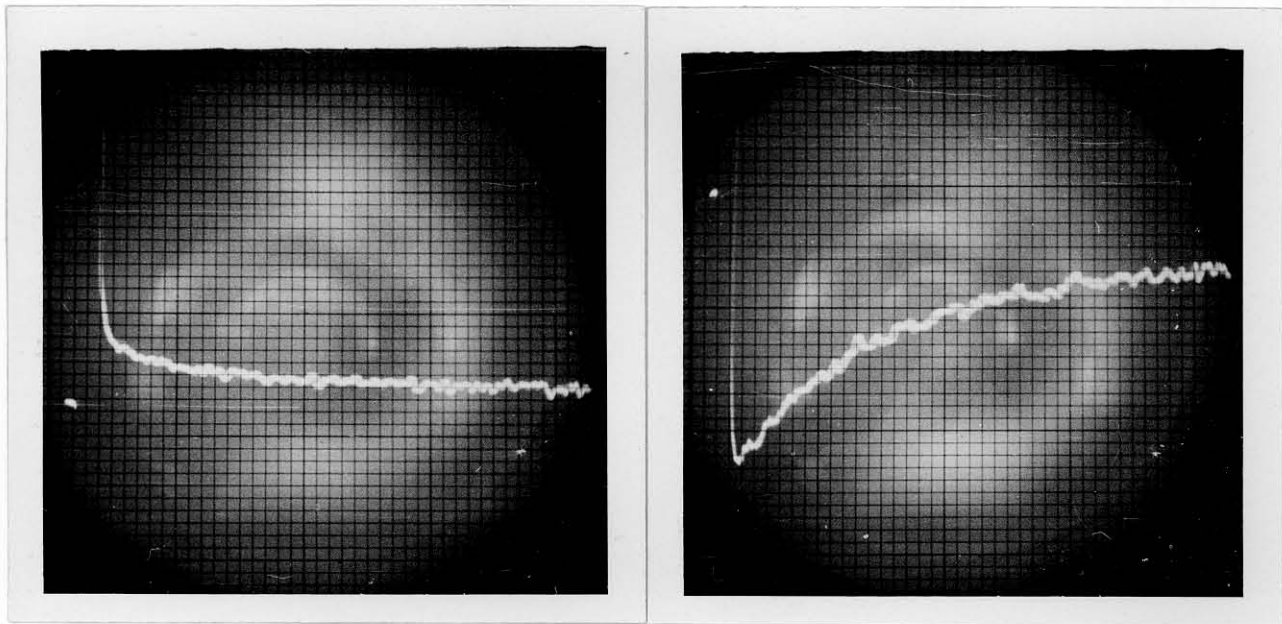
Writing Rate - 1250 V 50 - $.715 \times 10^{-3}$ sec./screen inch

$I_0 = .2177 \times 10^{-6}$ A.

$R = 3.10$, $G = 104$

Second Order

Time Inches on Tracing	Time x 10^3 Sec.	ΔS Inches on Tracing	$-\Delta I/I_0$ x 10^3	$\frac{-10^{-2}}{\ln(1 + \Delta I/I_0)}$
1.00	.231	7.68	6.23	1.605
1.25	.289	7.30	5.925	1.69
1.50	.347	6.94	5.63	1.776
1.75	.405	6.74	5.465	1.83
2.00	.463	6.49	5.265	1.900
2.25	.521	6.27	5.09	1.965
2.50	.579	6.01	5.875	2.05
2.75	.636	5.73	4.65	2.15
3.00	.695	5.48	4.45	2.25
3.50	.81	5.15	4.18	2.39
4.00	.925	4.87	3.95	2.53
4.50	1.04	4.59	3.72	2.69
5.00	1.157	4.30	3.49	2.865
5.50	1.27	4.04	3.28	3.05



Cell 18 - A^{II}

Picture: #17, 22 - P. 123. 365 mmu.

O-graph Vert. Sens., G-1, V-50 - .057 volts/screen inch

Writing Rate - 1250 V-30 - 1.058×10^{-3} sec./screen inch

$I_0 = 0.2177 \times 10^{-6}$ A.

$R_0 = 3.10$, $G = 104$

Second Order

Time Inches on Tracing	Time x 10 ³ Sec.	ΔS Inches on Tracing	$-\Delta I/I_0$ x 10 ³	$\frac{-10^{-2}}{\ln(1 + \Delta I/I_0)}$
.75	.256	8.46	6.87	1.455
1.00	.341	7.73	6.27	1.593
1.25	.426	7.28	5.91	1.692
1.50	.511	6.84	5.55	1.800
1.75	.596	6.48	5.26	1.90
2.00	.682	6.14	4.98	2.01
2.25	.767	5.87	4.76	2.10
2.50	.8525	5.63	4.57	2.19
2.75	.938	5.39	4.375	2.287
3.00	1.023	5.16	4.19	2.385
3.50	1.193	4.79	3.89	2.57
4.00	1.364	4.47	3.63	2.76
4.50	1.535	4.15	3.37	2.97
5.00	1.705	3.88	3.15	3.18
5.50	1.876	3.64	2.955	3.385
6.00	2.047	3.45	2.80	3.57

Fig. 18, 19.

Time x 10³ Sec.

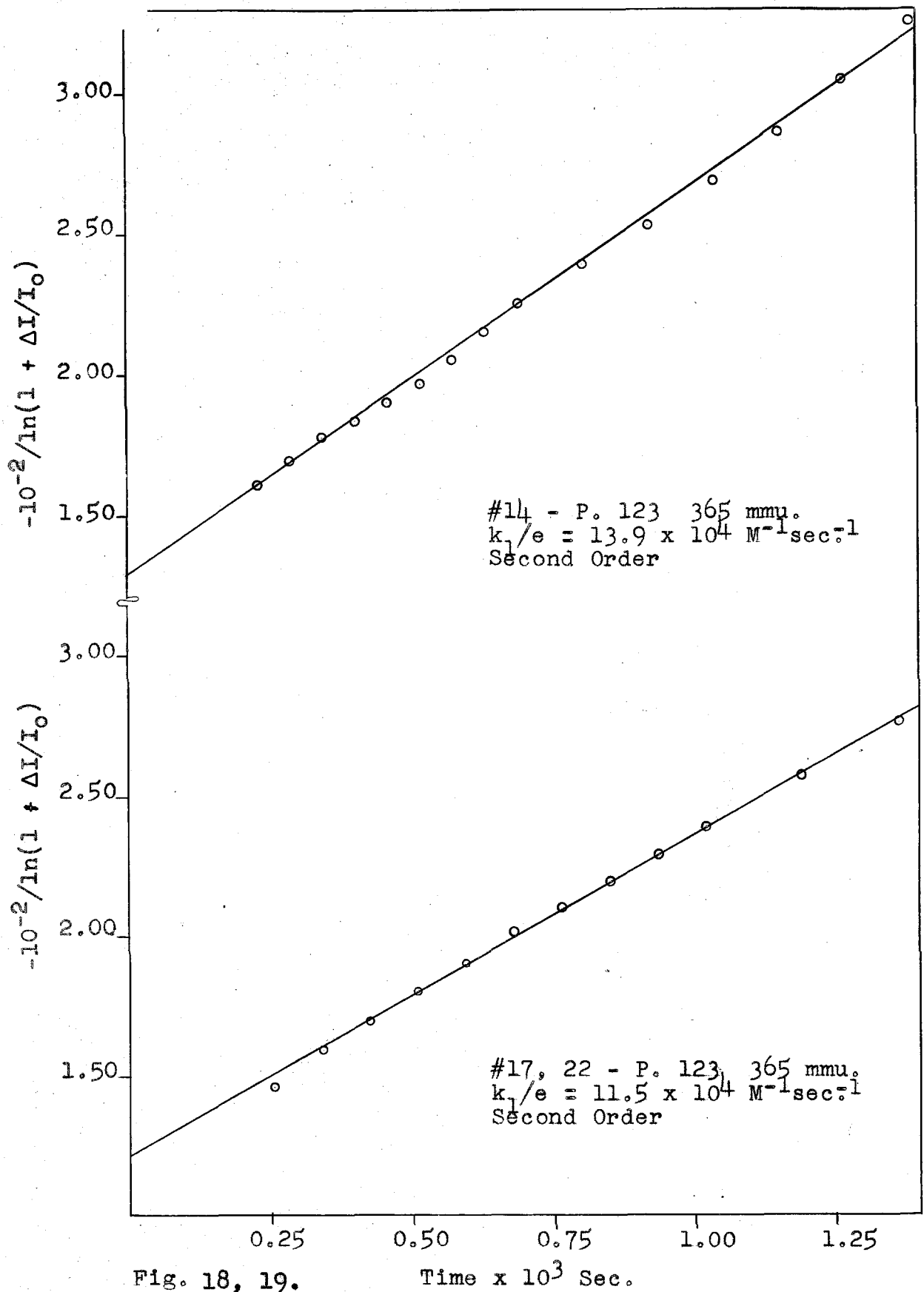


Fig. 18, 19.

Time x 10³ Sec.

Reaction Order

Thus far it has been tacitly assumed that the disappearance of the I_2^- ion is kinetically of the second order. Technical difficulties are such that only under the most favorable experimental conditions may data be obtained that prove, in an accepted manner, the order of the reaction.

If the disappearance of the colored species were first order in that species, the rate law

$$\begin{aligned} -\ln(-\ln(1 + \Delta I_t/I_0)) + \ln(-\ln(1 + \Delta I_{t=0}/I_0)) \\ = k_3' \cdot t \end{aligned} \quad (22)$$

would apply. Plotting $-\ln(-\ln(1 + \Delta I_t/I_0))$ vs. time should give a straight line with slope equal to k_3' if the reaction were first order.

For the purpose of comparison three sets of good data have been plotted both by equation (22) and by equation (20). Figures 14, 15, and 17 for the first order reaction show a gradual decrease in the value of k_3' as time increases. The same data plotted as a second order reaction give Figs. 12, 13, and 16 which show a nearly constant slope. This is as conclusive evidence of the reaction order as the present technique is capable of producing.

Irreversible Production of I_3^-

During the course of irradiation and flashing of the cells the optical density at 353 m μ . generally increased slightly (.003) for the cells with low I^- concentration

(5×10^{-5} M). In cells with higher (I^-) the increase was generally larger (.010 - .030). This is not unreasonable in light of the investigations by Rigg and Weiss.¹⁶ They found that in the absence of atmospheric oxygen irradiation of I^- solutions with light in the region 2000 - 2400 Å. caused the production of H_2 and I_2 , therefore, I_3^- , in the solutions. The quantum yield depended markedly on pH and on (I^-), decreasing with increase in the former and increasing linearly with increase in the latter at low concentrations. Therefore, it is not unlikely that the irreversible increase in I_3^- encountered in the present investigation is at least partly due to the photochemical oxidation of I^- in the cell, although the short wave length limit of transmission of pyrex glass, from which the reaction cell is made, is about 2900 Å. The balance may be due to oxidation by atmospheric oxygen dissolved in the acidified solution. This increase in I_3^- amounted at most to about a 7% change during any series of pictures. Experimental evidence indicates, but does not prove, that this irreversible increase in I_3^- is small if compared to the summation of the I_3^- which is dissociated photochemically and which is subsequently reformed by the recombination of I_2^- in a complete experiment.

Variation of k_1/e with Wave Length

The combination of the Bausch and Lomb monochro-

mator and the line spectrum of the mercury arc facilitated observation of the reaction cell at wave lengths, 365 mmu. and 435 mmu. In one experiment a General Electric spotlight (No. 4515, 30 watts, 6-8 volts) was used as a monitor lamp and observations were made at 460 mmu. and at 500 mmu.

Experimentally it was found that k_1/e showed a marked variation with the wave length used for observation.

If the ratio $e_{\lambda_1}/e_{\lambda_2}$ is considered, it will be seen that this quantity may be determined in two ways.

(1) Measurement of the slope of the graph of $-1/\ln(1 + \Delta I_t/I_o)$ vs. time for experiments observed at different wave lengths gives k_1/e_{λ_1} and k_1/e_{λ_2} independent of the initial (I_2^-) or the intensity of the flash. Therefore, the ratio of the slopes is $e_{\lambda_1}/e_{\lambda_2}$.

(2) If it is assumed that the light output of the flash lamp and the degree of dissociation are the same for different experiments at different wave lengths, λ_1 and λ_2 , then it can be shown that

$$e_{\lambda_1}/e_{\lambda_2} = (\Delta I_t/I_o)_{\lambda_1} / (\Delta I_t/I_o)_{\lambda_2} .$$

In Table 4 are given the values of $e_{\lambda_1}/e_{\lambda_2}$ obtained by each of these methods from the same data. It will be noted that $e_{\lambda_1}/e_{\lambda_2}$ calculated by method (2) at times other than $t = 0$ agree better with the value of the ratio obtained by method (1). This is indicative that the flash lamp light

Table 4

Cell	$k_1/e \times 10^{-4}$ at 365 mmu.	Time of Obs.	Ratio = $\frac{(\Delta I_t/I_o)_{365}}{(\Delta I_t/I_o)_{435}}$	$k_1/e \times 10^{-4}$ at 435 mmu.	Ratio = $\frac{(k_1/e)_{435}}{(k_1/e)_{365}}$	
13-A	3.72	0	1.71	9.1	2.44	
		3.0	2.09			
13-C	4.7	0	1.59	8.4	1.79	
		3.0	1.73			
	3.9	0	1.47	8.4	2.15	
		3.0	1.95			
	3.7	0	.79	4.96	1.34	
3.0		1.15				
15-B	6.2	0	4.4	21.8	3.52	
		2.0	2.2			
	6.2	0	3.3	12.6	2.03	
		2.0	1.77			
16-A ^{II}	6.15	0	2.33	15.2	2.47	
		.5	2.46			
	6.2	0	2.84			2.45
		.5	2.72			
	4.9	0	2.44			3.10
.5		2.76				
15-C ^{IV}	4.6	0	1.05	10.5	2.28	
		.5	1.41			
	4.9	0	1.27			2.14
		.5	1.50			
	4.6	0	1.15			2.28
		.5	1.41			
6.7	0	1.12	1.57			
	.5	1.22				
17-A ^{III}	5.5	0	2.47	9.6	1.75	
		.5	2.04			
	5.3	0	2.70			11.8
.5		2.40				
17-A ^I	4.9	0	3.18	15.9	3.24	
		.5	3.29			
	4.8	0	3.18			3.31
.5		3.32				

Time of Observation is given in units of 10^{-3} seconds.

output is not perfectly reproducible from flash to flash, as may be seen from the following argument.

Repeating equation (8) for convenience:

$$1/(I_2^-)_t - 1/(I_2^-)_{t=0} = k_1 \cdot t \quad (8)$$

$$\text{At } t_{\frac{1}{2}}, \quad (I_2^-)_{t_{\frac{1}{2}}} = (I_2^-)_{t=0} / 2. \quad (23)$$

Substituting into (8) and solving for $t_{\frac{1}{2}}$ gives

$$t_{\frac{1}{2}} = 1/k_1 (I_2^-)_{t=0}. \quad (24)$$

Therefore, (8) may be written in the alternate form

$$(I_2^-)_t = 1/k_1 (t_{\frac{1}{2}} + t) \quad (25)$$

If the flash lamp's light output were not reproducible, $(I_2^-)_{t=0}$ would not be constant from flash to flash and, therefore, $t_{\frac{1}{2}}$ would vary inversely as $(I_2^-)_{t=0}$. Let $t_{\frac{1}{2}}$ for flash A equal 1.0×10^{-3} sec. and $t_{\frac{1}{2}}$ for flash B equal 0.8×10^{-3} sec., both observations being made at the same wave length. Then, at $t = 0$,

$$(I_2^-)_A / (I_2^-)_B = k_{1B}(0.8) / k_{1A}(1.0) = 0.8$$

since $k_{1A} = k_{1B}$. But at $t = 1.5 \times 10^{-3}$ sec.

$$(I_2^-)_A / (I_2^-)_B = (0.8 + 1.5) / (1.0 + 1.5) = 0.92.$$

Thus the further from $t = 0$ that observations are made, the

less the effect of small variations in the flash lamp output and the nearer the value of the observation to the "true" or average value.

Dependence of Rate of Recombination of I_2^- on (I^-)

If equation (3) is true at all times and if we assume that (I^-) is essentially constant, the theoretical dependence of k_1/e on (I^-) may be derived in the following manner.

From the definition of K_A is obtained

$$(I_2^-)/((I_2^-) + (I)) = K_A(I^-)/(1 + K_A(I^-)) = (I_2^-)/\Sigma \quad (26)$$

and $(I)/\Sigma = 1/(1 + K_A(I^-))$. (27)

From equations (4), (5) and (6) is obtained

$$-d\Sigma/dt = k_1(I_2^-)^2 + k_2(I)^2 + k_3(I_2^-)(I). \quad (28)$$

Differentiating (26) and rearranging gives

$$d(I_2^-)/dt = \left[K_A(I^-)/(1 + K_A(I^-)) \right] d\Sigma/dt. \quad (29)$$

Combining equations (27), (28) and (29) and rearranging gives

$$\begin{aligned} (-1/(I_2^-)^2)d(I_2^-)/dt = 1/(1 + K_A(I^-)) \left[k_1 K_A(I^-) \right. \\ \left. + k_2/K_A(I^-) + k_3 \right]. \quad (30) \end{aligned}$$

If $k_2 = k_3 = 0$, then when $K_A(I^-) \gg 1$, the right side of equation (30) reduces to k_1 . When $K_A(I^-) \ll 1$, the right side of equation (30) becomes $k_1 K_A(I^-)$, a small quantity. Under these conditions the variation of $(-1/(I_2^-)^2)d(I_2^-)/dt$ with (I^-) is as indicated in Fig. 20.

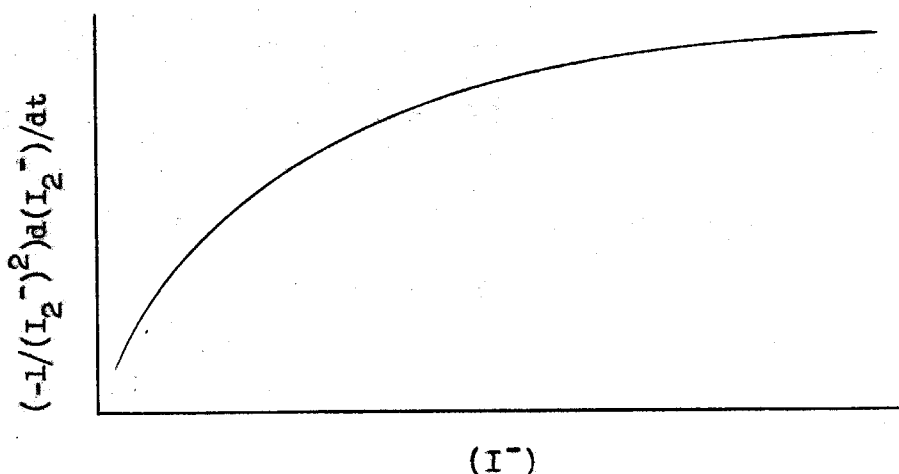


Fig. 20. Variation of the recombination rate of I_2^- with (I^-) as in Eq. (30), when $k_2 = k_3 = 0$.

If, however, k_2 and k_3 do not equal zero, then, when $K_A(I^-) \gg 1$, the right side of (30) equals $k_1 + k_2/K_A(I^-)^2 + k_3/K_A(I^-)$, where the second and third terms are probably small compared to k_1 . When $K_A(I^-) \ll 1$, the right side of (30) becomes $k_1 K_A(I^-) + k_2/K_A(I^-) + k_3$, where the second term is quite large. Figure 21 indicates this behavior.

From these considerations and from the graph of

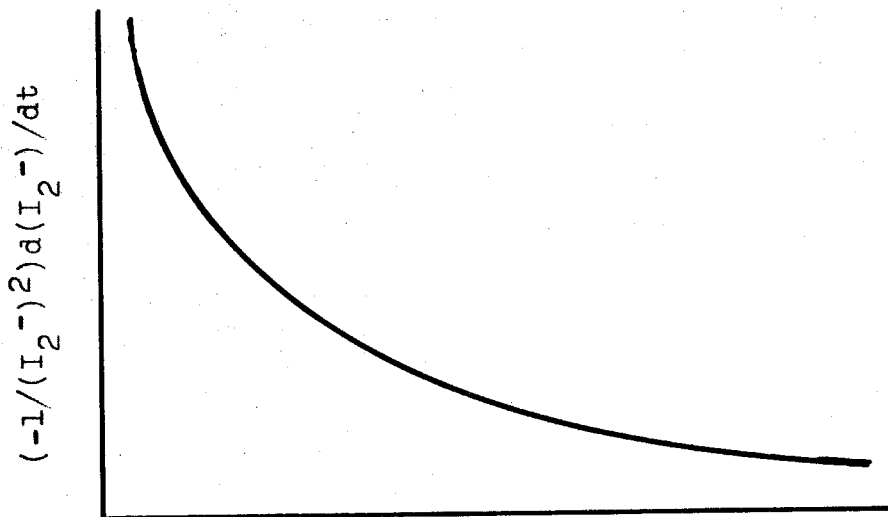


Fig. 21. Variation of the recombination rate of (I_2^-) with (I^-) as in Eq. (30), when k_2 and $k_3 \neq 0$.

the actual dependence of the recombination rate on (I^-) , Fig. 22, it is evident that k_2 and $k_3 \neq 0$, but that reactions (5) and/or (6) proceed to an appreciable extent at very low (I^-) . At (I^-) greater than about 4×10^{-5} M and up to 10^{-3} M, k_1/e is constant within the accuracy of these experiments, indicating that (I^-) is so large that reactions (5) and (6) proceed to a negligible extent.

Variation of $(I_2^-)_{t=0}/(I_2)$ with (I^-)

The variation of $(I_2^-)_{t=0}/(I_2)$ with (I^-) may be obtained as follows. Repeating equation (26) for convenience:

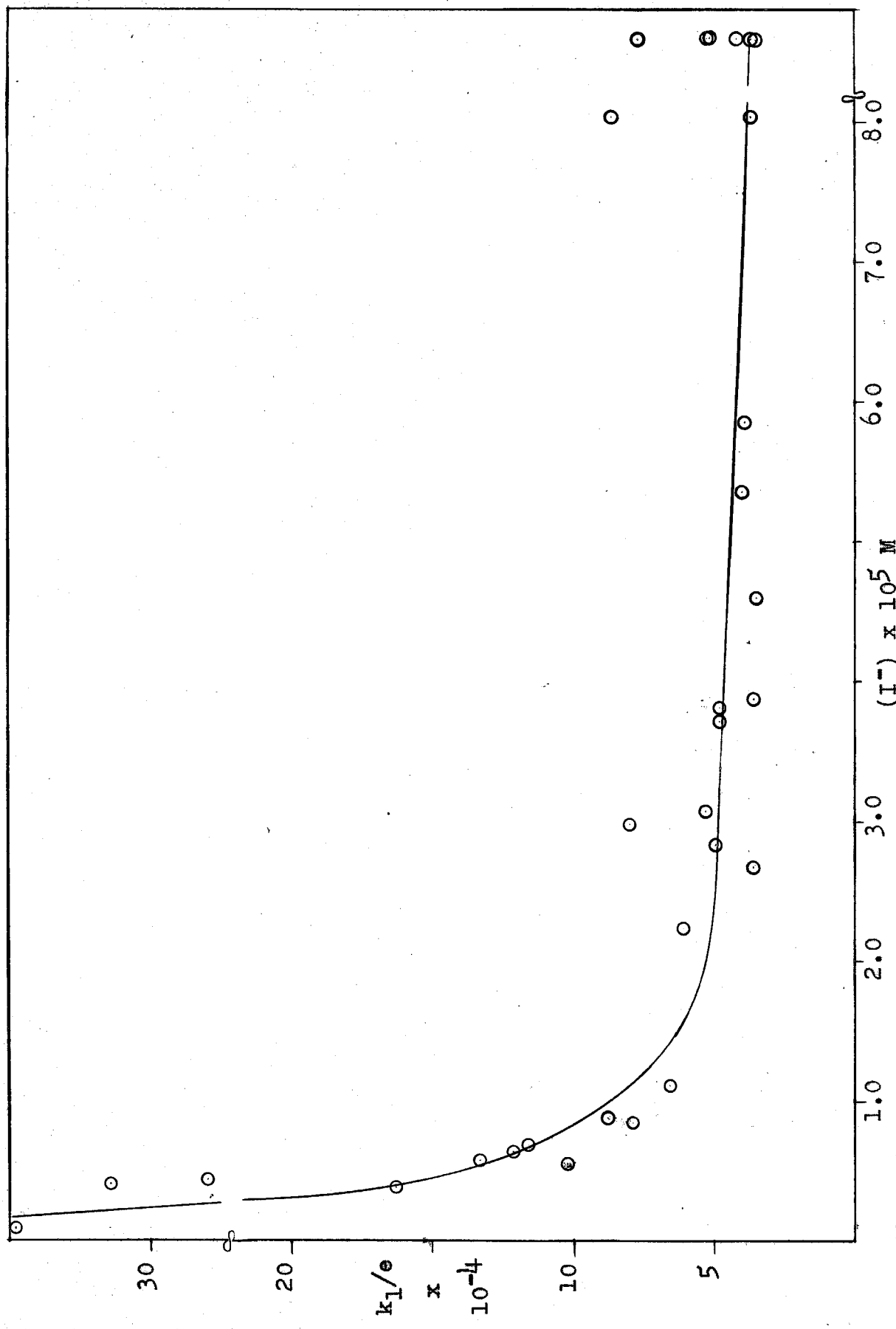


Fig. 22.

$$(I_2^-)/\Sigma = K_A(I^-)/(1 + K_A(I^-)) \quad (26)$$

If we assume reproducible flash lamp light intensity, then for any experiment:

$$\Sigma = 2A_2(I_2) + 2A_3(I_3^-) . \quad (31)$$

Therefore,

$$(I_2^-)_{t=0} = K_A(I^-)/(1 + K_A(I^-)) \left[2A_2(I_2) + 2A_3(I_3^-) \right]$$

$$(I_2^-)_{t=0}/(I_2) = K_A(I^-)/(1 + K_A(I^-)) \left[2A_2 + 2A_3K_I(I^-) \right]$$

For small values of x , $\ln(1 + x)$ equals $+x - x^2/2$ ----.

Therefore, equation (17A) gives

$$1/(I_2^-)_t = -e_{\lambda_1}/(\Delta I_t/I_0) \quad (32)$$

Substitution above using equation (32) yields

$$-(\Delta I_{t=0}/I_0)/e(I_2) = K_A(I^-)/(1 + K_A(I^-)) \left[2A_2 + 2A_3K_I(I^-) \right] . \quad (33)$$

The graph of $(\Delta I_{t=0}/I_0)/(I_2)$ vs. (I^-) , Fig. 23, agrees qualitatively with that predicted by equation (33) if $K_A \geq 5 \times 10^3$. More data should be obtained at intermediate concentrations of I^- before attempting to evaluate K_A .

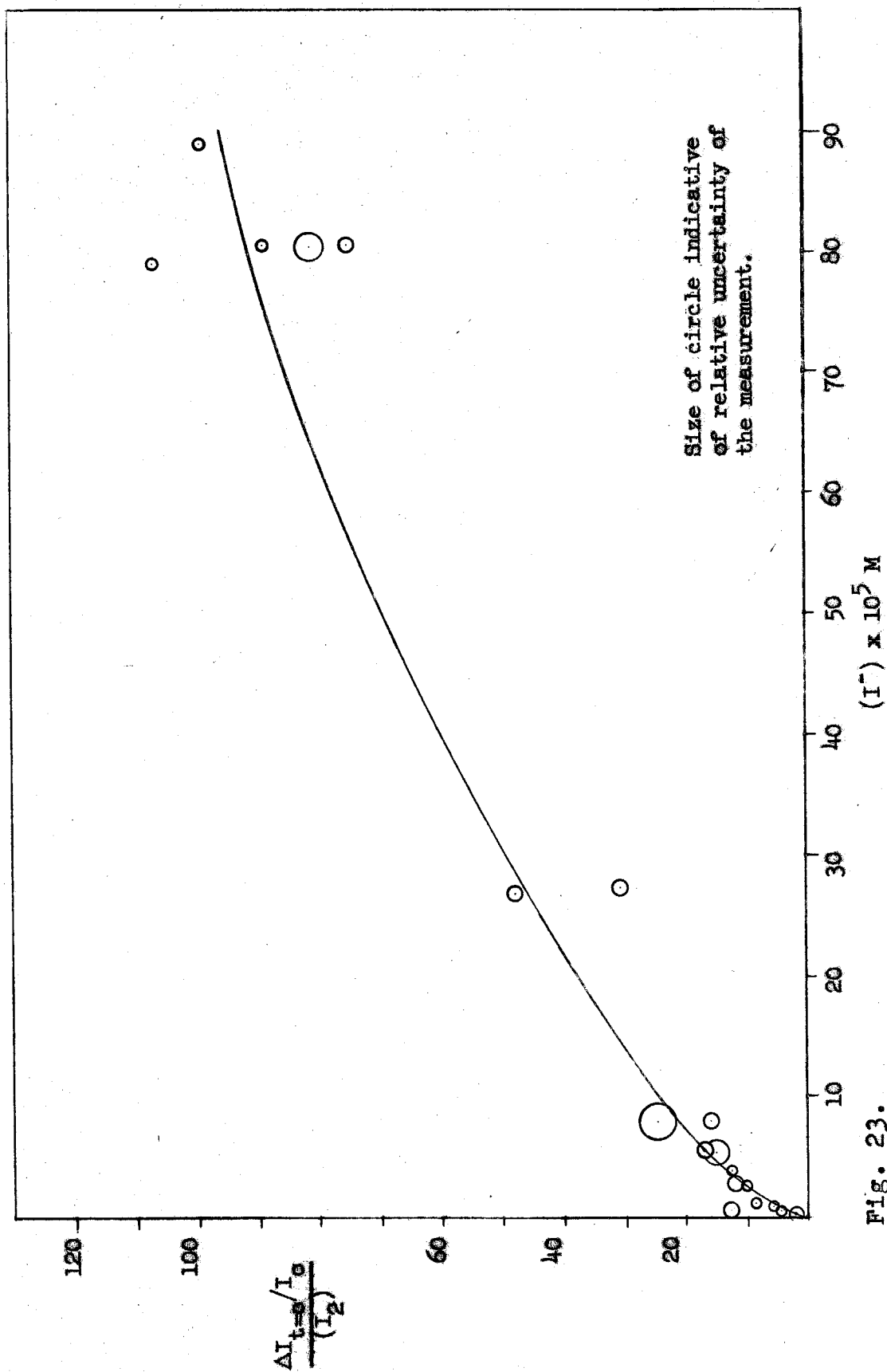
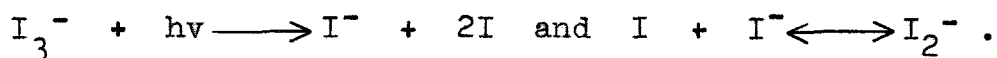


Fig. 23.

Filter Effects

Since Berthoud and Bellenot¹¹ investigated the photochemical reaction of oxalate with halogens in 1924, the question of whether light absorption by I_2 and/or by I_3^- in aqueous solution is effective in producing dissociation has received attention by several different investigators. The above authors stated that only light absorbed by I_2 is effective. However, Dickinson and Ravitz⁹ found that when a ferrocyanide-ferricyanide iodine-iodide solution is illuminated with light absorbable by I_3^- but not by the complex cyanides, reduction of ferricyanide and oxidation of iodide occurs.

Their proposed mechanism involved the reactions:



Further, they showed that the kinetic expression which Berthoud and Bellenot had derived for the rate of change of $(C_2O_4^{--})$ could be obtained without considering the light absorbed by I_3^- to be ineffective in causing dissociation.

In further studies of the oxalate-iodine photochemical reaction Allmand and Young¹² postulated that absorption by both I_2 and I_3^- was effective in producing atomic iodine, and that the quantum efficiencies are about the same for both I_2 and I_3^- at any given wave length. Griffith, McKeown and Winn,¹⁰ who also investigated the oxalate-iodine

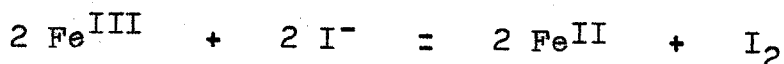
reaction, formulated two mechanisms, one with the primary process the photodissociation of I_3^- with I_2 acting as an internal filter; in the second mechanism I_2 dissociated while I_3^- acted as an internal filter. Though their results were consistent with either mechanism, they favored the former.

In an attempt to determine whether absorption and dissociation by I_3^- and/or I_2 gives the proposed production of I_2^- , i.e., to find the value of A_2 and A_3 , rate measurements as previously described were made with one of three Corning sharp cut glass filters placed between the flash lamp and the reaction cell. Transmission curves of these filters are shown in Fig. 24.

Results are tabulated in the general summary of data. The variation of k_1/e with change in the filters is believed to be due to the increased experimental inaccuracies attendant with the smaller phenomena produced by the filtered light. However, results are inconclusive.

Ferrous-Ferric Effects

In an investigation of the well-known reaction



Hershey and Bray⁷ proposed a mechanism involving I_2^-

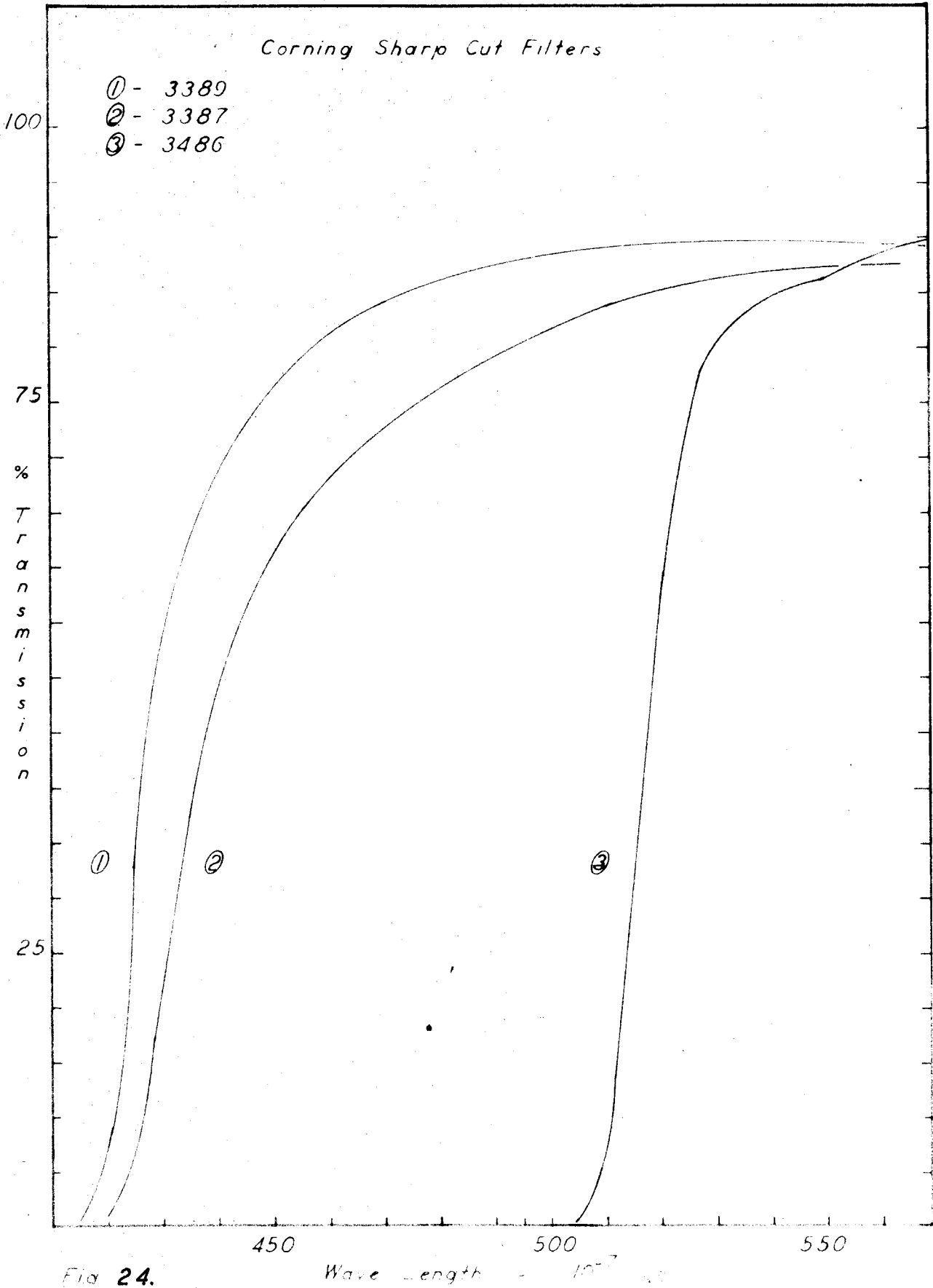
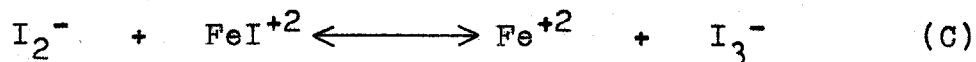
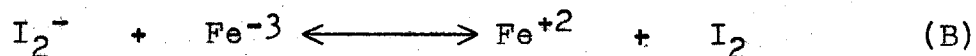
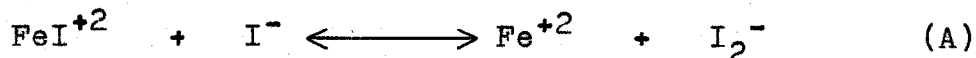


Fig 24.

Wave Length - 10^7 \AA

According to these authors the following are three of the steps occurring in the reduction of Fe^{III} by I^- :



In an effort to substantiate the production of I_2^- by irradiation as proposed in this thesis and to determine the effect of any possible Fe^{III} impurity in the reagents or water, several cells with varying concentrations of Fe^{III} and Fe^{II} were irradiated and the resulting optical density change observed.

Qualitatively, with $(\text{Fe}^{\text{III}}) = 3 \times 10^{-5} \text{ M}$, a slight increase was found in the value of k_1/e above that for the same solution with no Fe^{III} . At $(\text{Fe}^{\text{III}}) = 1.8 \times 10^{-4} \text{ M}$, the graph of $-10^{-2}/\ln(1 + \Delta I_t/I_0)$ vs. time was parabolic with slope increasing, indicating the operation of both a first and a second order reaction, possibly reactions (A) plus (B) and/or (C).

Cells with (Fe^{II}) about $4 \times 10^{-5} \text{ M}$ gave values of k_1/e which were, on the average, smaller than for the same cell with no Fe^{II} . Experimental results are tabulated in the complete summary of data. Further work should be done on solutions containing Fe^{II} and Fe^{III} .

Evaluation of Experimental Errors

The estimated maximum errors in percent in the quantities measured in these experiments are given in Table 5. These values should be taken only as indicative of the precision of the measurements and not necessarily their accuracy.

Table 5

Quantity	% Error (\pm)
I_0	3
ΔI_t	4
t	5
$t_{\frac{1}{2}}$	30
G	5
k_1/e	40
(I_3^-)	6
(I^-)	2
(I_2)	2

An indication of the reliability of any one measurement of $(I_2^-)_{t=0}$ may be found as follows. Upon differentiating equation (8) partially, there is obtained

$$1/(I_2^-)_0^2 \partial (I_2^-)_0 / \partial (k_1/e) = -t.$$

Substitution from equation (24) and rearrangement gives

$$\frac{\partial(I_2^-)_0}{(I_2^-)_0} = - (t/t_{\frac{1}{2}}) \frac{\partial(k_1/e)}{(k_1/e)} \quad (34)$$

where t is considered to be the value of the time for the first plotted point that falls on the curve extrapolated to $t = 0$. Therefore, the smaller is the value of $t/t_{\frac{1}{2}}$, the more reliable is the value of $(I_2^-)_{t=0}$.

References

1. R. G. W. Norrish and G. Porter, Nature, 164, 658 (1949)
G. Porter, Proc. Royal Soc., (London) A200, 284 (1950)
2. G. Herzberg and D. A. Ramsey, Disc. Faraday Soc.,
No. 9, 80 (1950)
3. Davidson, Marshall, Larsh, and Carrington, J. Chem. Phys.,
19, No. 10, 1811 (1951)
4. E. Rabinowitch and W. C. Wood, Trans. Faraday Soc.,
32, 547 (1936)
5. C. Wagner, Z. physik. Chem., 113, 261 (1924)
6. H. Taube, J. Am. Chem. Soc., 64, 161 (1942)
7. A. V. Hershey and W. C. Bray, J. Am. Chem. Soc., 58
1760 (1936)
8. R. O. Griffith and A. McKeown, Trans. Faraday Soc.,
28, 752 (1932)
9. R. G. Dickinson and S. F. Ravitz, J. Am. Chem. Soc.,
52, 4770 (1930)
10. R. O. Griffith, A. McKeown and A. Winn, Trans. Faraday
Soc., 29, 386 (1933)
11. A. Berthoud and H. Bellenot, J. Chim. Phys., 21, 308 (1924)
12. A. J. Allmand and K. W. Young, Trans. Faraday Soc., 27,
515 (1931)
13. Alice D. Awtrey, Dissertation, Univ. of Calif., (1950)
14. M. H. Boyer and J. B. Ramsey, J. Am. Chem. Soc., 75,
3802 (1953)
15. A. D. Awtrey and R. Connick, J. Am. Chem. Soc., 73,
1842 (1951)
16. T. Rigg and J. Weiss, J. Chem. Soc., IV, 4198 (1952)
17. Photo. Sci. and Tech., 1, 15 (1950)
18. R. Marshall and N. Davidson, J. Chem. Phys., 21, No. 4,
659 (1953)

Explanation of Data Headings

Cell Identity

Example: 12 - A, 1, 4-81. Twelfth usable preparation of solution in glass reaction vessel A. Pictures 1 and 4 recorded on workbook page 81 were so nearly identical as to warrant plotting only one.

12 - A^I. Prepared from Cell 12 - A by the addition of either I⁻ or I₂.

(I₃⁻)

The concentration of I₃⁻ in the cell, units 10⁻⁷ M, as determined from measurements of the optical density of the solution made in a Beckman DU Spectrophotometer at wave length 353 mmu. at the end of an experiment. Molar extinction coefficient used is given in Table 2. Corrections to the optical density for the cell blank and for I₂ absorption at 353 mmu. have been made.

(I₂)

Concentration of I₂ in the cell, units 10⁻⁵ M, determined as above but at wave length 460 mmu. Appropriate corrections to the optical density have been made.

(I⁻)

Concentration of I⁻ in the cell, units 10⁻⁵ M. Determined generally both from the value of K_I and the above concentrations and from the stoichiometric amount of I⁻ added to the cell (bracketed value).

(Acid)

The concentration of H₂SO₄, units 10⁻² F, in the solution. Determined from the stoichiometric quantity of 0.0178 N. H₂SO₄ added to the cell.

K_I

The equilibrium constant as defined previously, either the accepted value of 710 M⁻¹ or the value (bracketed) calculated using the concentrations determined as described above.

O. D. at 353 mmu.

The optical density of the solution measured at the end of a set of experiments. Corrected only for cell blank. Used to calculate (I₃⁻).

O. D. at 365 mmu.

Similar to the above. Determined because spectrophotometric observations are generally made at this wave length.

O. D. at 435 m μ .
Same as above.

O. D. at 460 m μ .
Same as above. Used to calculate (I_2).

ΔO . D. at 353 m μ .
The irreversible change in the optical density at 353 m μ . due to irradiation and/or air oxidation of the I^- in the cell during an experiment.

Ratio I
The ratio of the optical density at 353 m μ . or at 365 m μ . to the optical density at 435 m μ .

I_0 at 365 m μ .
The photocurrent, units 10^{-6} Amp., proportional to the intensity of the constant monitor light at wave length 365 m μ . impinging upon the photocell.

$\Delta I_t/I_0$ at 365 m μ .
The ratio $\times 10^3$ of the change in photocurrent to the constant photocurrent, recorded at time $t = 0$, and $t = 3, 2, 1$, or 0.5×10^{-3} seconds after the flash; time indicated by superscript.

k_1/e at 365 m μ .
The value $\times 10^{-4}$ obtained from graphing data obtained from oscillograph trace. See page 31.

Ratio II
The ratio of $\Delta I_t/I_0$ at 365 m μ . to $\Delta I_t/I_0$ at 435 m μ . evaluated at $t = 0$ and at $t = 3, 2, 1$, or 0.5×10^{-3} seconds after the flash. See page 48. Time indicated by superscript.

I_0 at 435 m μ .]	As above but for 435 m μ .
$\Delta I_t/I_0$ at 435 m μ .		
k_1/e at 435 m μ .		

$T_{\frac{1}{2}}$
Half-life for the reaction, units 10^{-3} sec. See page 31.

First Good T
Value of time in milliseconds at which first

reliable data was obtained from photograph of oscillograph trace.

$T/T_{\frac{1}{2}}$ An indication of the amount of change in $\Delta I_{t=0}/I_0$ produced by a small change in the value of k_1/e . See page 62.

G Gain of the a.c. amplifier. Calculated as on page 26.

Cell Identity	(I ₁)	(I ₂)	(I ₃)	(Acid)	K _I	O.D. at 353 mm.	O.D. at 365 mm.	O.D. at 435 mm.	O.D. at 460 mm.	ΔO.D. at 365 mm.	Ratio I	I ₀ at 365 mm.	ΔI ₁ /I ₀ at 365 mm.	K _{I/e} at 365 mm.	Ratio II	I ₀ at 435 mm.	ΔI ₁ /I ₀ at 435 mm.	K _{I/e} at 435 mm.	T _{1/2}	First Good T	T/T _{1/2}	Q		
12 - A 1, 4-81 9, 15-81	7.69	1.89	(5.36)	3.4	760	.203	---	---	.128	.000	---	2.15	14.433 4.533	5.0	1.813	.828	22.0 2.513	11.8	.40	3.0	1.01	2.1	2.5	119
12 - A 2-82 9, 10-82 4-82	7.77	1.89	(5.36)	3.4	766	.205	---	---	.128	-.005	---	.277	26. 6.843	4.37	1.403	.127	64.5 3.1773	7.8	1.12	1.50	1.2	6.0	2.1	105
12 - B ^I 23-82 26-82 23-82	4.31	1.92	(2.68)	3.4	840	.114	---	---	.127	.000	---	.127	22. 6.353 36. 7.553 80. 8.663	3.65 3.47 3.37	1.713	.176	17.4 3.063	9.1	1.26	2.0	1.6	1.2	5.9	119
13 - A 1, 2, 3, 4-84 7, 9-84	11.1	1.87	(8.04)	3.4	739	.293	.135	.150	-.001	2.17	.183	29.8 6.403	3.72	1.71	2.093	.176	17.4 3.063	9.1	.96	0.50	.52	.78	103	
13 - B 1, 2, 4-84 7, 8, 9-84 5-84	8.33	1.87	(5.36)	3.4	830	.220	.131	.128	-.003	1.68	.223	30.8 6.813	3.8	2.42	2.48	.178	12.75 2.1723	8.8	.92	1.5	1.63	.59	.89	102
13 - C 4, 5-86 7, 8, 9-86 2, 3, 14-86	14.0	.259	(80.7)	3.4	670	.371	.044	.033	+0.16	8.44	.124	19.4 5.963	3.9	1.47 1.953	1.733	.210	13.2 3.063	8.4	1.00	1.0	1.0	1.1	.37	107

Cell Identify	(S)	(Z)	(T)	(Asid)	KI	O.D. at 359	O.D. at 365	O.D. at 435	O.D. at 460	ΔO.D.	Ratio I	I ₀ at 365	ΔI ₀ /I ₀ at 365	KI/e at 365	Ratio II	I ₀ at 435	ΔI ₀ /I ₀ at 435	KI/e at 435	T ₂	First Good I	T/T ₂	Q	
14 - B 9, 10-93	4.62	1.25	(4.51)	3.4	802	.122	.0386	.0998	.000	1.42	.295	17.4 ₃	5.90 ₃	3.7	.79	.287	22.0	4.96	.92	1.0	1.1	106	
6-93												18.70	6.72 ₃	3.1	.85		5.11		1.68	1.0	.60		
13 - A 1, 2, 3, 7-96	11.0	1.82	(8.02)	3.4	750	.294	.132	.146	-.009	2.24	.197	44.4	10.39 ₂	8.65	2.47	.189	18.0	8.65	.60	1.0	1.66	97.6	
10-90												2.39 ₂	4.35 ₂	26.1 _x	6.48 _x		4.35 ₂		0.64	.50	.78	97.6	
16, 17-90 _x											.222 _x	9.5	1.60 _{2x}	26.1 _x	11.4 _x		4.35 ₂		.40 _x	.75	1.37	103.2	
23-97											.302 _#	3.9	.921 _{#2}	37.5 _#	11.4 _#		4.35 ₂		.72 _#	.75	1.04	103.2	
24-97											.302 _#	2.6	.921 _{#2}	61.0 _#	17.1 _#		4.35 ₂		.64 _#	.50	.78	103.2	
14 - A 2-98	.34	1.17	.41	3.4	710	.013	.073	.087	-.0005	.15	.261	3.3	1.09 ₂	31.6					.96	.75	.78	98	
14 - A _I 9-98	.356	1.145	(.43)	3.4	723	.0215	.071	.085	.000	.16	.258	3.8	1.18 ₂	27.9					.90	.75	.78	98	
14 - A _{II} 20, 21-98	.645	1.145	(.69)	3.4	816	.019	.072	.085	+.001	.264	.258	5.6	2.42 ₂	11.6					1.54	.50	.374	98	
15 - B 3, 5-100	.341	.82	.585	0	710	.010	.045	.061	-.003	.20	.286	3.7	2.37 ₂	13.3					2.06	.25	.122	103.6	
15 - B _I 20, 21, 33-100	.398	.83	(.833)	.0	563	.0125	.0505	.062	-.0005	.25	.265	5.2	2.30 ₂	7.9					—	.40	.40	105	
31-100											.304	4.8	2.52 ₂	8.01					2.57	.40	.156		

X - 460 mμ. monochromator setting.
- 500 mμ. monochromator setting.

Cell Identity	(I ₃ ⁻)	(I ₂)	(I ⁻)	(Acid)	K _I	O.D. at 353 mm.	O.D. at 365 mm.	O.D. at 435 mm.	O.D. at 460 mm.	ΔO.D. at 365 mm.	Ratio I	I ₀ at 365 mm.	ΔI ₀ /I ₀ at mm.	k _I /e at 365 mm.	Ratio II	I ₀ at 435 mm.	ΔI ₀ /I ₀ at mm.	k _I /e at 435 mm.	T ₂	First Good ?	T/T ₂	Q
15 - BII	.795	.87	(1.12)	0	815	.0225		.0535	.065	-.0015	.42				1.70	.195	4.4	21.8	1.04	.80	.77	108
15-101															1.892		2.202		2.08	.40	.193	108
24, 35-101																			1.62	.30	.186	
33, 34-102																			2.36	1.50	.64	
17-101															2.27	.195	3.3	12.6	2.52	.30	.119	
32-102															2.302		1.772		2.18	.24	.110	
3-101																			1.66	.24	.145	
2, 4-101																			2.10	.30	.143	
8, 10-101																						
16 - A ⁺																						
20, 21-112	2.89	1.43	2.85	4.95	710	.079	.0695	.092	.109	.000		.219	18.7	4.8					1.13	.33	.29	104
16-112																			1.25	.20	.16	104
16-112	4.55	2.18	2.94	4.95	710	.124	.1095	.141	.167	+.004	.65	.208	24.1	6.15	2.33				1.09	.40	.34	
16-112															2.46				.68	.30	.44	109
16-112															2.46				.55	.23	.42	
16-112			(2.85)		(731)										2.84				.66	.50	.74	
11-112															2.54				.81	.19	.24	
21, 22-113												.206	14.5	4.9	2.44				1.19	.40	.34	
21, 22-113															2.76				1.09	.35	.32	
28, 29-113															9.405				1.09	.35	.32	
26-113															7.385				.64	.29	.46	
19-113																						

* - used to compute Ratio II.

Cell Identity	(I ₁)	(I ₂)	(I ₃)	(Acid)	H ₂	O.D. at 353 mm.	O.D. at 365 mm.	O.B. at 435 mm.	O.D. at 460 mm.	ΔO.D. at 365 mm.	Ratio I	I ₀ at 365 mm.	ΔI ₀ /I ₀ at 365 mm.	K ₁ /ε	Ratio II	I ₀ at 435 mm.	ΔI ₀ /I ₀ at 435 mm.	K ₂ /ε	T ₂	First Coord T	π ₁ /π ₂	θ
16 - A ^{IV} 31, 32-113	6.2	2.86	3.08	4.95	7.10	.169	.142	.135	.219	.000	.80	.202	29. 16.4.5	5.5					.64	.24	.38	102
2, 3, 4-113			(2.94)		(7.38)								27.4. 15.9.5	5.9					.63	.24	.38	102
31, 32-113													23.8 15.7.5	4.4					.39	.39	.40	111
16 - A ^{IV} 31, 4-114	11.3	2.76	5.78	4.95	7.10	.303	.262	.190	.217	-.005	1.38	.134	7.9 6.80.5	4.0					.38	.30	.79	102
22-114	13.5	2.76	5.38		7.10	.308	.266	.190	.217	-.003	1.39	.138	44.4. 24.0.5	3.9	1.93	.088	#3387 filter 23. 9.9	11.7	.58	.24	.42	
15, 17-114			(5.64)		(7.20)								51.2.5 26.0.5	4.0	2.42			.50	.29	.58		
14-114													21.2 15.0.5	3.2	2.63			1.32	.58	.44		
25, 29-114			#3389 filter										18.4. 13.7.5	3.3				1.46	.29	.20		
26-114			#3389 filter										16.9.5 12.9.5	3.7				1.56	.29	.19		
27-114			#3389 filter																			
16 - A ^{IV} 30-107	3.39	2.30	(1.576)	4.95	(7.15)	.1045	.6235		.6235	.000		.282	21.0 0.231	11.0				.43	.47	1.09		113.4
31-107													27.4. 6.621	11.5				.32	.55	1.72		113.4
3-108													32.7. 7.921	9.4				.35	.40	1.14		113.4
4-108													21.9 7.561	8.8				.49	.40	.82		113.4
12-107			#3389 filter										14.6 5.911	10.1				.68	.41	.61		113.4
5, 6-107			#3389 filter										13.4 5.481	8.60				.88	.55	.63		113.4
7, 8-107			#3389 filter										8.9 4.351	11.8				.96	.55	.57		113.4
15 - A ^{IV} 2, 2-104	5.75	9.15	.885	2.5	7.10	.179 ^c	.679		.679	.011		.186	60.5 9.531	8.8				.22	.48	2.18		107
12, 13-104			#3389 filter										21.5 7.561	8.6				.55	.26	.47		107
9, 10-104			#3387 filter										16.5 7.131	8.2				.77	.20	.26		107
4, 5-104			#3486 filter										4.1 2.781	12.3					.27			107

Cell Identity	(I ₁)	(I ₂)	(I ₃) (Acid)	K _I	O.D. at 353 mm.	O.D. at 365 mm.	O.D. at 435 mm.	O.D. at 480 mm.	ΔO.D. at 365 mm.	Ratio I	I ₀ at 365 mm.	ΔI ₀ /I ₀ at 365 mm.	K _I /e at 365 mm.	Ratio II	I ₀ at 435 mm.	ΔI ₀ /I ₀ at 435 mm.	K _I /e at 435 mm.	T _g	First Good T	1/T _g	σ	
15 - C ^{IV}	13.0	.17	106.8	4.95	710	.343	.290	.038	.0255	.000	7.6	.125	12.3	4.6	1.05	1.06	19.1	1.64	.34	.21	107.4	
21-117												.125	10.2	4.9	1.41				1.38	.29	.21	107.4
22-117													10.8	4.6	1.50				1.62	.24	.15	107.4
24-117													13.5	1.41	1.15							
25-117													10.2	1.41	1.12				1.14	.68	.60	107.4
28-117													13.1	6.7	1.22							
28-117													8.8						.57	.33	.58	107.4
28-117																			.82	.29	.36	107.4
17 - A	3.60	1.30	3.89	4.95	710	.0975	.085	.0866	.101	-.002		.254	16.4	4.7	1.31				1.31	.30	.23	107
2, 3, 4-118													11.9	4.0	1.43					.20	.14	107
1-118													18.1	2.0								
9-118													13.5	14.8	1.50					.35	.35	107
10-118													12.7	1.7	1.15					.35		107
22-119			#3387 Filter									.257	14.8	3.2	1.41					.43		107
22-119			#3387 Filter										5.9	4.0						.43		107
22-119			#3387 Filter										7.6	6.2						.43		107
16, 17-119			#3389 Filter										6.1	6.2						.23		107
13-118			#3389 Filter										5.1	6.3						.26		107
19, 20-119			#3387 Filter										5.4	3.9						.43		107
17 - A	7.17	2.64	3.82	4.95	710	.194	.1685	.1730	.204	.000	.97	.211	32.7	4.9	3.18				.63	.19	.30	107
2, 3-119													18.4	4.8	3.29					.65	.19	107
29, 30, 1-119			(3.89)									(698)	32.7		3.18					.24	.41	107
6, 7-119													18.6		3.28					.24	.41	107

* - used to compute Ratio II.

Cell Identity	(I ₁)	(I ₂)	(I ₁)	(Acid)	K _I	O.D. at 353 mm.	O.D. at 365 mm.	C.D. at 435 mm.	O.D. at 460 mm.	ΔO.D. at 365 mm.	Ratio I	I ₀ at 365 mm.	ΔI ₁ /I ₀ at 365 mm.	k ₁ /e at 365 mm.	Ratio II	I ₀ at 435 mm.	ΔI ₁ /I ₀ at 435 mm.	k ₁ /e at 435 mm.	T _g	First Order T	T ² /T _g	C
17 - AII 9, 10-110	10.56	4.0	3.72	4.95	710	.2865	.250	.2621	.309	+.001	.95	.162	46.5 22.6	4.9					.45	.15	.34	107
8-119			(3.82)		(692)							.162	50. 21.4	5.5					.37	.15	.41	107
19, 20, 21-120												.277	48. 21.8	4.4					.56	.29	.52	107
16-120															2.47 2.04	.084	20.2 10.5	9.6	.52	.24	.46	107
13, 14-119												.162	43.4 19.7	5.3	2.70 2.40	.084	18.5 8.9	11.8	.46	.17	.37	107
16-120																			.29	.29	.62	107
18 - A 12, 15-122	.09	1.45	.0885	4.95	710	.005	.0055	.067	.108	.000	.06	.2286	2.8 1.905	34.8					1.03	.29	.30	107
18 - A ¹ 16-122	.39	1.45	.384	4.95	710	.013	.0125	.068	.108	.000		.2212	6.7 4.36	15.6					.96	.29	.30	107
17, 19-122			(.354)		(776)								6.7 4.17	17.5					.86	.46	.54	107
25-122													4.9 3.48	15.4					1.30	.29	.23	107
26-122													5.8 3.93	15.6					1.11	.29	.27	107
18 - AII 2, 6, 8-122	.674	1.45	.654	4.95	710	.0205	.0185	.088	.109	-.0015		.2177	9.1 5.59	13.5					.82	.29	.36	104
1-123			(.620)		(748)								8.7 5.83	10.7					1.07	.35	.33	104
3, 5, 7-123													8.4 5.67	10.7					.98	.29	.29	104
3 ¹ , 5 ¹ , 7 ¹ -123													8.9 5.79	11.3					1.12	.23	.21	104
14-123	.674	1.45	.654	4.95	710	.0205	.0185	.088	.109	-.0015		.2177	5.8 4.21	12.3					.93	.23	.25	104
32-123			(.620)		(748)								7.8 5.09 ⁵	13.7					1.42	.29	.20	104
17, 22-123													8.3 5.55	11.5					1.05	.34	.32	104
21-123													7.0 4.77	13.2					1.08	.34	.32	104

Cell Identity	(Fe:II) Oxi	(I ₂ ⁻)	(I ₂)	(I ⁻)	(acid)	K ₁	O.D. at 353 mm.	O.D. at 365 mm.	O.D. at 435 mm.	O.D. at 460 mm.	ΔO.D. at 365 mm.	Ratio I	I ₀ at 365 mm.	ΔI ₀ /I ₀ at 365 mm.	K ₁ /e at 365 mm.	Ratio II	I ₀ at 435 mm.	ΔI ₀ /I ₀ at 435 mm.	K ₁ /e at 435 mm.	T ₁	First Good T	T/T ₁	G
14 - B ^I 3, 4-94	.378 Fe:II	(4.65)	1.22	4.61	3.4	(826)	.123		.083	.095	-.002	1.48	.290	18.3 7.902 15.5 7.172	3.7	1.35	.282	16.5 5.862	5.1	1.50	1.50		106
5-94																				1.50			106
11-94																				.76			106
14 - B ^{II} 27-94	4.16 Fe:II	(5.41)	(1.22)	4.61	3.4	(960)	.143		.081	.095	+.002	1.78	.264	22.95 7.142 20.2 6.29	4.8					.92	.75		103
24-94																				.90	.50		
28-95													.283	28.1 11.12 25.3 12.4	1.36					1.32	1.25		
23-95															.76					1.94	1.50		
33-95																				2.632	.75		
34-95																				2.80	.50		
																				5.642			
16 - B ^{III} 18-108	3.3 Fe:II	(4.05)	(8.22)	(.69)	4.9		.209			.601	+.087		.268	15.0 5.801 13.8 5.941	9.3					.73	.34		
16, 17-108		(7.39)	(7.96)	(1.31)		#3389 filter								28.1 8.11	9.5					.75	.40		
6-108						#3387 filter									8.8					.41	.54		
16 - B ^{IV} 22-109	36. Fe:II	(8.6)	(7.86)	(1.54)	4.9								.195	24.6 11.2.5 24.1 12.5	8.0					.53	.27		113
1-109		(13.1)	(7.46)	(2.47)											8.5					.44	.27		
15 - A ₂ ^I 12, 13-110	2.9 Fe:II	(17.4)	8.54	2.97	4.9		.475	.375	.540	.644	-.033		.107	57.0 16.2.5 105. 20.7.5 284. 23.5	9.2					.19	.19	1.0	106
18-110															8.0					.10	.35		106
17-110															8.0					.04			