

KINETICS OF BLEACHING  
IN COLORED KCl

by

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# KINETICS OF BLEACHING IN COLORED KCl

## INTRODUCTION

Color centers in alkali halide crystals have been known for many years and have been studied extensively. However, much of the information is only of a qualitative nature. This is particularly true for the kinetics of bleaching of color centers. Although some work has been done for crystals colored by X-rays, relatively little quantitative work on the kinetic processes involved in the bleaching of additively colored crystals seems to have been carried out. Bleaching rates, however, were used by Ueta and Känzig to estimate the number of traps generated by plastic flow (13, p. 1591-1595). Kinetic studies on bleaching should yield information leading to a more realistic model for color centers and the electronic processes occurring. It should also increase knowledge of photochemical reaction rates in general occurring in the solid state. While this thesis will be concerned primarily with optical effects, the results might be applied to other types of radiation as well.

Although color centers are possible in any of the alkali halides, the present work deals only with potassium chloride due to factors of cost and convenience. To begin

a discussion of the kinetics of optical bleaching in additively colored KCl crystals, it will be necessary to assume a model and possible mechanism for the processes involved. Thermodynamic considerations show that a crystal is not "perfect" but must contain imperfections in its lattice structure, some of which may be anion and cation vacancies. That is, there are places in the ionic lattice of a crystal where there would normally be an anion or cation, but where one is missing. These vacancies in a crystal, being surrounded by ions of opposite sign, would be expected to carry a net electric charge of the same magnitude, but of opposite sign as the missing ion. For example, a chloride ion vacancy would have a net positive charge of one electronic unit. If by some process an electron wandering through a crystal lattice were to approach a chloride ion vacancy, it would be attracted by the net positive charge of the vacancy and might thus become energetically "trapped" at the chloride ion vacancy site. To remove the electron from the trap again would require energy at least as great as was given off when the electron first became trapped. If an energy source such as a beam of white light were passed through a crystal containing trapped electrons in the manner mentioned, it is possible that photons from one of the

many frequencies comprising white light might just have the right energy to release the trapped electron. If such were the case, photons of that energy would be absorbed in the crystal and the emergent beam would no longer be white, but colored. Hence the crystal would appear colored, the color arising because of interaction of certain photons with electrons trapped in chloride ion vacancies. Electrons trapped in negative ion vacancies will be referred to as "color centers" or "F-centers" from the German word "Farbzentren". The foregoing model of the F center applies both to the additively and X-ray colored crystals and was first proposed by de Boer (2).

Two methods commonly used for supplying electrons to form F-centers and thus coloring a crystal are X rays and adding a stoichiometric excess of alkali metal. In the former process an X-ray beam releases electrons, presumably from chloride ions, which then migrate to a chloride ion vacancy forming F-centers. Electron "holes" are left in the lattice by this method of coloration. For additive coloration, a crystal is heated in the presence of alkali metal vapor for a period of about twenty four hours or until equilibrium is reached. The commonly accepted mechanism for additive coloring is for a metal atom of the vapor surrounding the crystal to

deposit itself on the surface of the crystal and become ionized, the ionized electron wandering into the crystal. X-ray coloration produces "holes" in the crystal and results in non-uniform production of color centers, due to attenuation of the X-ray beam. Additive coloration produces no "holes" in the crystal and results in a uniform distribution of color centers.

Consider now a possible mechanism for optical bleaching of color centers in KCl. Such a mechanism should be capable of at least qualitatively describing effects associated with the bleaching process such as photoconductivity, appearance of other absorption bands, and temperature coefficients of bleaching. The model-mechanism herein described will be the one assumed throughout this present work. Photons of proper frequency are presumed to pass through a crystal containing color centers. Some photons strike F-centers and are absorbed, giving their energy to excite electrons in color centers. Thermal energy then raises the excited electrons into the conduction band increasing the conductivity of the crystal. Once in the conduction band the electron does not remain there indefinitely, but sooner or later becomes trapped again either in a chloride ion vacancy or some other stable trap. If retrapped in a

chloride ion vacancy, the net result is that no bleaching occurs and the photon is essentially wasted. However, if the electron is trapped out of the conduction band into some type of stable trap other than a chloride ion vacancy, the net result is one less F-center. If this process were to continue, a crystal would lose F-centers and become bleached.

Assuming an average light absorption throughout the crystal, the kinetics of bleaching for such a model might be expected to follow a first-order rate law. That is  $dC_F/dt = -kIC_F$ , where  $k$  is a rate constant,  $I$  is the average light intensity and  $C_F$  is the F-center concentration. Mador, Wallis, Williams, and Herman cite references to unpublished thesis work by Grant and Hesketh who worked on the rate of optical bleaching of F-centers in X-rayed KCl (7, p. 617-628). Grant found that the first order law was consistent with experimental data only at the beginning of optical bleach. Hesketh attempted to improve agreement between theory and experiment by taking into account a correction for the rate of capture of conduction electrons by negative ion vacancies. It was found that theory and experiment did not agree.

Mador, Wallis, Williams, and Herman investigated the possibility that the discrepancies found by Hesketh

were not due to a poor model, but to nonuniform light absorption and F-center concentration gradients in the crystal (loc. cit.). Using an equation for the rate of bleaching with a constant concentration gradient and uniform light intensity, they were able to show qualitatively by comparing theory and experiment that Hesketh's discrepancy could be attributed to F-center concentration gradients and nonuniform light absorption. Only a qualitative comparison was given because a quantitative treatment would have required the solution of non linear partial differential equations which had not then been attempted. In a later publication, Herman and Wallis (6, p. 435-442) solved the differential equations for nonuniform light absorption and consequent F-center concentration gradients. When theory and experiment were compared it was found that results were consistent with the model for X-ray colored sodium chloride crystals in the range  $10^{16}$  to  $10^{17}$  F-centers per  $\text{cm}^3$ . Thus it is necessary to take into account F-center concentration gradients whenever there is considerable light absorption by a crystal. Since the amount of light absorbed by a crystal is proportional to the concentration of F-centers and the thickness, two cases will result in considerable absorption, (1) a thin crystal with high F-center

concentration, or (2) a thick crystal with low F-center concentration. It happens that the most convenient and physically useful range of thickness vs concentration results in considerable light absorption so that it is desirable to be able to treat such situations theoretically.

Although rate equations in good agreement with experiment have been found for X-ray colored crystals, there is a basic difference between X-ray colored crystals and additively colored ones. The absence of "holes" in additively colored crystals will affect the bleaching kinetics and this thesis is an attempt to predict theoretical bleaching rates and compare with experimental rates by taking into account the absence of holes in additively colored crystals, the nonuniform light absorption and the development of F-center concentration gradients within a crystal during bleach.

The mathematical treatment presented here has not been previously developed. While applied specifically to the F-center case, it is generally applicable to any photochemical reaction where absorption of light on passage through a sample is significant, particularly those experiments where the intensity of transmitted light itself is used to determine the progress of a reaction. Figure 22 shows why such a treatment is needed.

## EXPERIMENTAL PROCEDURES

In order to prepare colored samples for bleaching experiments, single crystals of pure KCl about 8 x 8 x 10 mm were cleaved from large stock crystals obtained from the Harshaw Chemical Co. The cleaved crystals were then placed in one of two types of coloring containers along with a small amount of alkali metal. In the more simple case (illustrated in Figure 1), the coloring container was constructed from a five inch length of seamless half-inch copper tubing. One end of the copper tube was pounded flat and crimped over twice to make a seal after which the alkali metal and the crystal loosely wrapped in copper foil were introduced. Immediately after putting the crystal in the tube, the open end was pounded flat and crimped twice to seal it and to prevent moisture from attacking the alkali metal. At this point, the "bomb" was placed in a muffle furnace and heated for about 24 hours at a temperature between five and six hundred degrees Centigrade. Different temperatures were used in order to produce samples with a variety of color center concentrations. At the end of 24 hours in the furnace, the container was removed from the furnace and quickly plunged into a bucket of cold water. This produced a rapid quench. After quenching, the

## COLORING CONTAINERS

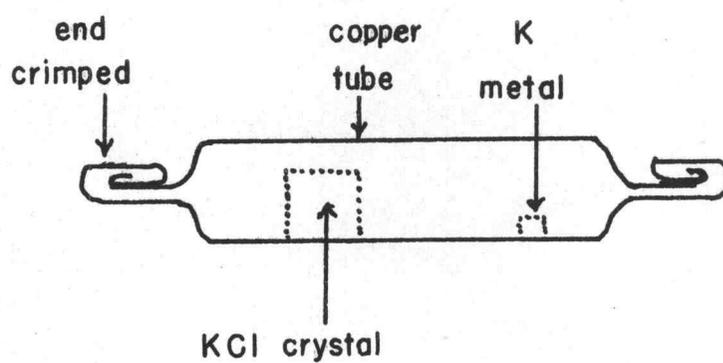


FIGURE 1

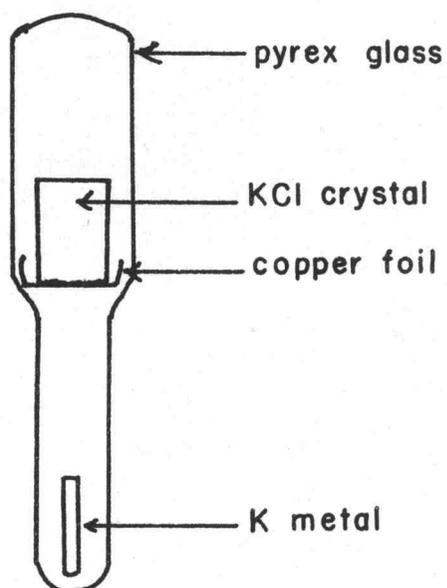


FIGURE 2

"bomb" was opened in a darkroom and the crystal removed and placed in a light-tight box in a desiccator.

A second type of coloring container (illustrated in Figure 2) consisted on two three-inch lengths of pyrex tubing a different diameters joined together in a smooth seal. The smaller one (10 mm o.d.) was sealed at one end and a small amount of potassium metal was introduced. A wad of copper foil was then placed at the joint of the two tubes, and a crystal sample to be colored was introduced next. Copper foil was used to prevent crystals from coming into direct contact with potassium metal. Next the larger end of the container was sealed off. Thus completed, a "bomb" was they ready to be placed in a two compartment furnace for coloring. The lower compartment received the end containing the metal and the upper compartment surrounded the crystal. Coloring was achieved in about 24 hours by keeping the upper furnace at about 600°C. Temperature regulation of the lower furnace compartment controlled the concentration of color centers. At the end of about 24 hours the "bomb" was removed from the furnace and quickly slipped into an aluminum envelope and quenches in cold carbon tetrachloride. After quenching, the container was broken open in a darkroom and the crystal was stored in a desiccator.

In preparing a sample for a bleaching experiment, a colored crystal was removed from the desiccator and slices about  $8 \times 8 \times \frac{1}{2}$  mm were cleaved off, under red safelight, using a razor blade taped lightly with forceps. A cleaved slice was mounted on a mask and placed in a small furnace, the temperature of which was controlled electrically. Construction of the furnace is shown in Figure 3. Microscope slide cover glasses were used as windows on the furnace to allow light passage but reduce convection currents within the furnace. Black non-glossy paint was used to reduce light reflections from furnace parts. Furnace temperatures were controlled manually to within one degree between room temperature and  $150^{\circ}\text{C}$  by means of a Variac transformer. The furnace was mounted in front of the objective lens of the optical system on a rapid scanning photoelectric spectrophotometer used to scan the bleaching spectrum. A rapid scanning spectrophotometer was particularly well suited to the experiment since it scanned the entire spectral region from 400 to 700 m $\mu$  sixty times per second and hence it was able to follow very rapidly any changes occurring in this region. It was necessary to use an external light source for bleaching and scanning as the source in the instrument itself was unsuitable. It was not a parallel beam, but

## BLEACHING FURNACE

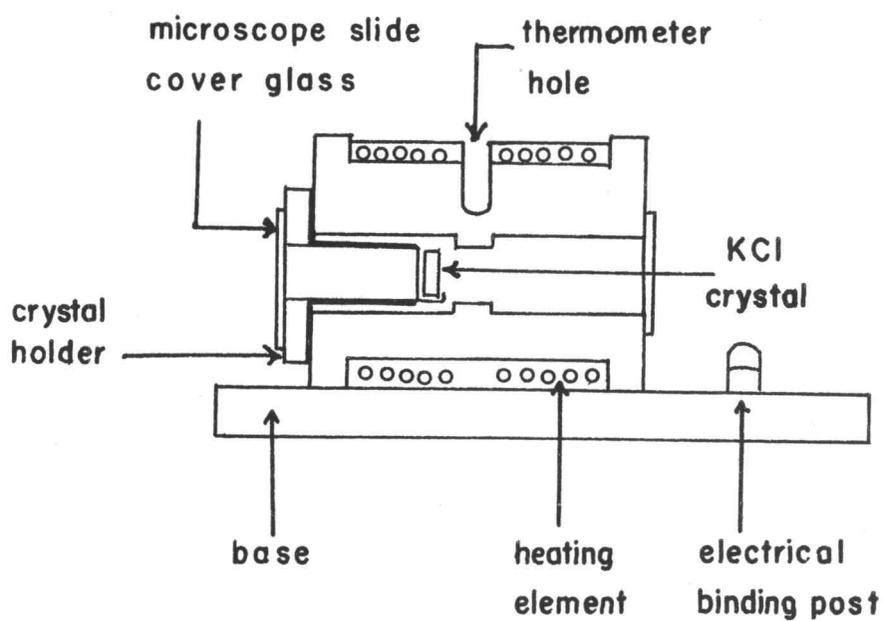


FIGURE 3

# OPTICAL AND MECHANICAL ARRANGEMENT

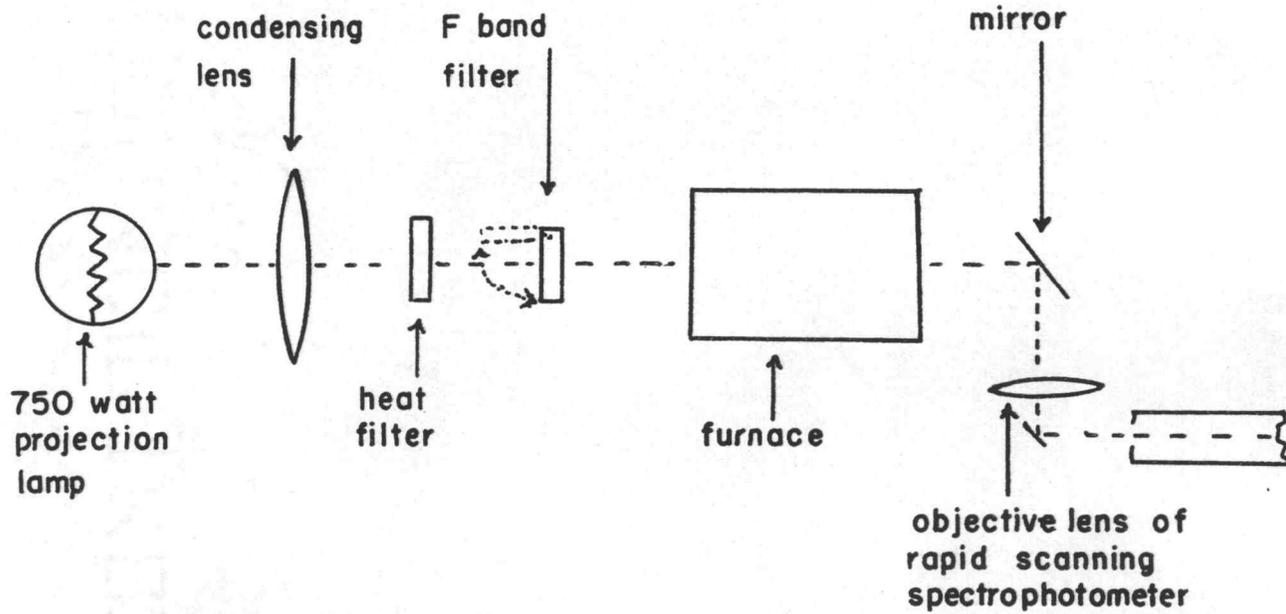


FIGURE 4

rapidly converging and a large part of it was blocked by the furnace. In order to secure a more parallel beam of light for the furnace and for bleaching crystals, a separate light source was constructed with proper optics. (Figure 4 shows the light source, optical and mechanical arrangements.)

Typical bleaching experimental procedure was as follows. Concentration of F-centers in a colored stock crystal of KCl was determined optically with the aid of Smakula's equation (12, p. 603-614) using the method of Scott and Smith (10, p. 341-346). Both Beckman Models DU and DK1 spectrophotometers were used for determining optical absorption at F-center peaks for Smakula's equation. Crystal thicknesses were measured with the aid of a microscope having a calibrated eyepiece. A crystal slice cleaved from a colored stock piece was mounted on a mask and when proper furnace temperature was reached, the mask with a crystal slice in place was inserted into position in the furnace. Three minutes were allowed for temperature equilibrium to be established between furnace and crystal. When ready to begin bleaching, the light source was turned on and the oscilloscope trace of the rapid scanning spectrophotometer was recorded on a Polaroid-Land oscilloscope camera mounted in front of the screen.

Immediately thereafter, a filter (described below) which was transparent to F-band light was inserted between the bleaching light source and the crystal. At successive short intervals the filter was removed momentarily and a new trace recorded of the 400 to 700  $\mu$  region. This produced a multiple exposure showing progress of bleaching of the F-band as well as changes in any other absorption bands. When bleaching was complete as determined by observing when the rate of further bleaching became essentially zero, the crystal was removed from the mask and wavelength and percent transmission scales were calibrated by inserting an interference filter and recording the trace. This superimposed a calibration curve directly on each photograph. Calibration each time was necessary because the instrument was supplied with controls for amplifying either percent transmission or wavelength scales or both. After calibration the film was removed from the camera and the developed negative and print were pulled apart. Crystal thickness was measured on each sample bleached.

A filter used to transmit primarily F-band light was constructed from two three-inch-square pieces of clear glass held in place by a wooden frame which had been thoroughly soaked in hot paraffin wax. A portion

# F BAND FILTER AND HINGE

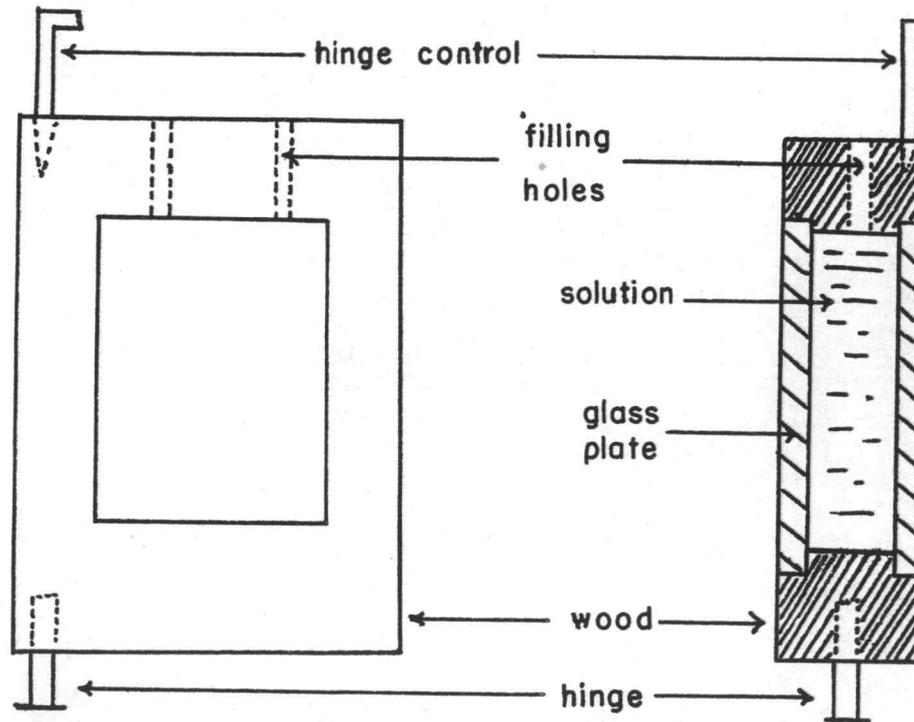


FIGURE 5

of a solution made by dissolving 7.0 gm of nickel sulfate and 100 mg of potassium dichromate in 100 ml of water was then used to fill the filter producing about 13 mm light path through the solution. In order to facilitate rapid injection and removal of the filter into the light beam during a bleaching run, a hinge arrangement was used to mount the filter. (See Figure 5.)

Bleaching measurements were conducted on samples ranging in concentration from  $2 \times 10^{16}$  to  $20 \times 10^{16}$  color centers per cubic centimeter as determined by Smakula's equation. Concentrations were calculated on the assumption that the oscillator strength for F centers in KCl at room temperature was unity. Samples with F-center concentrations less than  $2 \times 10^{16}$  were so dilute that inconveniently thick slices were needed in order to detect concentration changes with sufficient accuracy. On the other hand, samples more concentrated than about  $20 \times 10^{16}$  color centers per cubic centimeter had to be sliced so thin to allow enough light transmission for measurements, that extreme cleaving difficulties were encountered. It was extremely difficult to cleave optically good slices 8 x 8 mm square which were less than about 0.3 to 0.5 mm thick. Practical considerations thus limited the range of concentrations investigated.

Bleaching rate curves were obtained at a series of temperatures from room temperature to 150°C. At room temperature optical bleaching occurred quite slowly but increased with temperature until at 150°C bleaching reactions were essentially complete in less than one minute. At temperatures much above 150°C, thermal bleaching of the F-band began to be significant. Actual rate studies were conducted for the most part at temperatures of 50°, 75°, 100°, 125°, 150°C, as these were most convenient experimentally.

## THEORETICAL

The first step in a kinetic study is to set up suitable rate equations for the process being studied. In setting up rate equations describing bleaching in colored KCl it was found necessary to work in terms of a model which was quite mechanical and probably greatly oversimplified. If all of the possible variables and parameters of a more complete model were considered, the mathematics would soon become hopelessly complex. Thus the model considered here is simply a transparent three dimensional rectangular prism with F centers uniformly distributed throughout. Also in the prism or crystal there is a uniform distribution of electron traps which may or may not all be of the same type but have only the requirement that they be thermally stable. That is, once an electron is trapped there, it remains trapped. Bleaching is accomplished when photons from the incident bleaching light, which is considered as a uniform shower of small particles, pass into the crystal and strike an F center. When this happens, the photon is completely used up in exciting the electron which passes into the conduction band and wanders through the crystal.

Letting  $f_0$  = initial F center concentration

$f$  = F center concentration at time (t)

A = total concentration of anion vacancies  
filled and unfilled

B = total concentration of filled and un-  
filled trap sites other than anion  
vacancies

V = concentration of anion vacancies = A - f

$n_e$  = conduction band electron concentration

$I_{x,t}$  = local light intensity (photons/cm<sup>2</sup> sec)

T = concentration of traps other than anion  
vacancies

Bleaching reactions are:

F center +  $h\nu$  → ionized F center + e

e + ionized F center → F center

e + trap → trapped electron (thermally  
stable)

The net rate of disappearance of F centers is the rate at which they are destroyed by photons plus the rate at which they are re-formed in a back reaction. Expressed kinetically:

$$(1) \quad \frac{\partial f}{\partial t} = -k_0 I f - K_1 V n_e$$

Assuming a steady state approximation for conduction band electron concentration we have

$$(2) \quad \frac{\partial n_e}{\partial t} = 0$$

This means that each time an electron is promoted into the conduction band, one must also leave, presumably going either to an anion vacancy or some other trap. Bleaching, however, results only when non-anion vacancy traps capture an electron. The probability that an electron is captured by a given kind of traps is proportional to the concentration of the traps times their capture cross section. If it is assumed that capture cross sections for different kinds of traps do not vary too greatly, then the total number of electrons leaving the conduction band in unit time which enter traps other than anion vacancies is roughly proportional to the ratio between the number of non-anion vacancy traps and the total number of traps. The quantum efficiency for F center bleaching then, once the conduction band is filled, is equal to the ratio of electrons leaving the conduction band which enter traps other than anion vacancies. Hence

$$q = \frac{T}{T + V} = \frac{B - f_0 + f}{A + B - f_0}$$

where  $q$  represents the quantum efficiency and the other quantities are defined as above. The kinetic equation (1) then might equally well be expressed in terms of  $q$  thus:

$$(3) \quad \frac{\partial f}{\partial t} = -\delta f I q$$

where  $\delta$  is the capture cross section for photons by F centers. Substituting into (3) the expression for  $q$ , one obtains

$$(4) \quad \frac{\partial f}{\partial t} = -\delta f I \frac{B - f_0 + f}{A + B - f_0} \quad \text{or}$$

$$(5) \quad \frac{\partial f}{\partial t} = -k f I (C + f)$$

where  $C = B - f_0 \quad (5-A)$

and  $k = \frac{\delta}{A + B - f_0} \quad (5-B)$

Intensity of light passing through a crystal is not constant but is attenuated due to absorption. If the Beer-Lambert law is assumed, then the expression for the light intensity is:

$$(6) \quad \frac{\partial I}{\partial x} = -a I f$$

Equations (5) and (6) are simultaneous, non linear partial differential equations whose solution has been worked out apparently only for the special case where  $C$  is equal to zero. For the special case of  $C = 0$ , Herman and Wallis (6, p. 435-442) found the solution in terms of the exponential integral function for which tables are

available. When  $C \neq 0$ , a method of solution worked out here is as follows. Let

$$(7) \quad n = \ln \frac{C + f}{k f},$$

then

$$(8) \quad C + f = k f e^n, \quad f = \frac{C}{k e^n - 1}$$

$$(9) \quad \frac{\partial n}{\partial t} = \frac{k f}{C + f} \left[ \frac{k f - (C + f)k}{k^2 f^2} \right] \frac{\partial f}{\partial t}$$

$$= - \frac{C}{f(C + f)} \frac{\partial f}{\partial t}$$

Substituting (5) into (9):

$$(10) \quad \frac{\partial n}{\partial t} = k C I$$

$$(11) \quad \frac{\partial^2 n}{\partial t \partial x} = k C \frac{\partial I}{\partial x} = k C a I f \quad \text{by (6)}$$

Using the expression for  $f$  from (8), equation (11) becomes:

$$\frac{\partial^2 n}{\partial t \partial x} = -k C a I \frac{C}{(k e^n - 1)}$$

$$(12) \quad \frac{\partial^2 n}{\partial t \partial x} = \frac{a C}{(k e^n - 1)} \frac{\partial n}{\partial t} \quad \text{by (10)}$$

Integrating (12) with respect to time between limits:

$$\left. \frac{\partial n}{\partial x} \right|_{t=0}^{t=t} = -aC \int_{t=0}^{t=t} \frac{dn}{ke^n - 1} = aC \int_{t=0}^{t=t} \frac{dn}{1 - ke^n}$$

$$(13) \quad \left. \frac{\partial n}{\partial x} \right|_{t=0}^{t=t} = aC \left[ n - \ln(1 - ke^n) \right]_{t=0}^{t=t}$$

Applying the boundary condition that when  $t = 0$ ,  $\partial n / \partial x = 0$ , (13) becomes:

$$(14) \quad \left. \frac{\partial n}{\partial x} \right|_{t=0}^{t=t} = aC \ln \frac{e^n}{1 - ke^n} \Big|_{t=0}^{t=t}$$

Remembering that  $\partial n / \partial x = (\partial n / \partial f)(\partial f / \partial x)$  and since  $\frac{\partial n}{\partial f} = -\frac{C}{f(C+f)}$ , (14) becomes

$$(15) \quad -\frac{C}{f(C+f)} \frac{\partial f}{\partial x} = aC \ln \frac{e^n}{(1 - ke^n)} \Big|_{t=0}^{t=t}, \text{ but } e^n = \frac{C+f}{kf}$$

$$-\frac{C}{f(C+f)} \frac{\partial f}{\partial x} = aC \ln \frac{(C-f)/kf}{1 - ((C-f)/f)} \Big|_{t=0}^{t=t}$$

$$= aC \ln \frac{C+f}{-kC} \Big|_{t=0}^{t=t}$$

at  $t = 0$ ,  $f = f_0$

$$-\frac{C}{f(C+f)} \frac{\partial f}{\partial x} = aC \ln \frac{(C+f)/(-kC)}{(C+f)/(-kC)} = -aC \ln \frac{C+f}{C+f_0} \text{ or}$$

$$(16) \quad -\frac{\partial f}{f(C+f) \ln (C+f)/(C+f_0)} = a \partial x$$

Integrating (16)

$$(17) \quad \int_{x=0}^{x=x} \frac{df}{f(C+f) \ln (C+f)/(C+f_0)} = -ax$$

We need now to evaluate the variation of F center concentration with time at the front surface, i.e., at  $x = 0$ .

At  $x = 0$ ,  $I = I_0 = \text{constant}$ , so that at  $x = 0$  which is the side toward the light, equation (5) becomes

$$\frac{df}{dt} = -kI_0(C+f) \quad \text{or} \quad \frac{df}{f(C+f)} = -kI_0 dt$$

$$-kI_0 t = \int_{t=0}^{t=t} \frac{df}{f(C+f)} = -\frac{1}{C} \ln \left[ \frac{C+f}{f} \right] \Bigg|_{t=0}^{t=t}$$

but at  $t = 0$ ,  $f = f_0$  so that

$$kI_0 t = \frac{1}{C} \ln \frac{(C+f)/f}{(C+f_0)/f_0} = \frac{1}{C} \ln \frac{f_0 (C+f)}{f (C+f_0)}$$

$$e^{kCl_0 t} = \frac{f_0 (C+f)}{f (C+f_0)} \quad \text{and solving for } f,$$

$$(18) \quad f = \frac{f_0 C}{e^{kCl_0 t} (C+f_0) - f_0} \quad \text{at } x = 0 \text{ for all values}$$

of  $t$ .

Using (18) equation (17) is:

$$(19) \quad \int_{\frac{f_0 C}{e^{kCl_0 t} (C+f_0) - f_0}}^f \frac{df}{f(C+f) \ln \frac{C+f}{C+f_0}} = -ax$$

To our knowledge the left-hand-side of equation (19) has not been integrated in analytical form so a combination of graphical and numerical methods was used. Before integrating, however, equation (19) is more conveniently expressed in slightly different form. If  $f = \varepsilon f_0$  (19 A) and  $C = \alpha f_0$  (19 B), equation (19) takes the form

$$(20) \quad \int_G^\varepsilon \frac{d\varepsilon}{(\alpha + \varepsilon) \ln [\alpha + \varepsilon / \alpha + 1]} = -a'x$$

where  $G$  is the value of  $\varepsilon$  at  $x = 0$ , and is found to be

$$(20 A) \quad G = \frac{\alpha}{e^{kf_0\alpha I_0 t} (\alpha+1)^{-1}}, \text{ and } a' = af_0$$

Experimentally, the variable observed is  $I$ , that is the light intensity after passage through a distance  $d$  which is the crystal thickness. The case of interest is that in which the RHS of (20) is  $-a'd$ , i.e., a constant. However, since the lower limit is a function of time and is constantly changing, the upper limit must change in such a way as to maintain a constant value for the integral. The problem then is to determine the upper limit for any given value of the lower limit while keeping the value of the integral constant. Graphical methods must be employed since the integrated form of (20) has not been found.

$$\text{Let } F(\varepsilon) = \frac{1}{\varepsilon(\alpha + \varepsilon) \ln(\alpha + \varepsilon/\alpha + 1)}$$

Graphically an integral may be represented by an area under a curve of the function. In the present instance the integral of  $F(\varepsilon) d\varepsilon$  between the limits of  $G$  and  $\varepsilon$  could be approximated by finding the area under the curve made by plotting  $F(\varepsilon)$  vs  $\varepsilon$  for various values of  $\alpha$ . Some limitation on the number of plots needed is made by noting that  $0 < \varepsilon \leq 1$  and for a real or non-imaginary solution  $\alpha > -1$ ,  $\alpha + > 0$ . However, since

finding the area beneath a curve with accuracy is extremely tedious, a better method was sought. A plot of  $F(\varepsilon)$  vs  $\varepsilon$  somewhat resembles an unsymmetrical parabola and Simpson's Rule for approximate integration was found to be adaptable and to give a very good approximation. Simpson's Rule is given by the formula:

$$\int_a^b y dx = \frac{\Delta x}{3} (y_0 + 4y_1 + 2y_2 + 4y_3 + 2y_4 + \dots + 4y_{n-1} + y_n)$$

This rule holds providing  $n$  is even. Adapted to the variables at hand, Simpson's Rule takes the form:

$$\int_G^\varepsilon F(\varepsilon) d\varepsilon = \frac{\Delta \varepsilon}{3} F(\varepsilon)_0 + 4F(\varepsilon)_1 + 2F(\varepsilon)_2 + 4F(\varepsilon)_3 + \dots + 4F(\varepsilon)_{n-1} + F(\varepsilon)_n$$

The actual mechanics or methods of calculation will now be described.

1. The value of LHS (20) between definite increments of  $\varepsilon$  was calculated going as near as practical to the limits for  $\varepsilon$  of zero and one. To do this it was first necessary to select an appropriate value of  $\alpha$ . Then a table listing  $F(\varepsilon)$  values corresponding to

## ISO-G CURVES

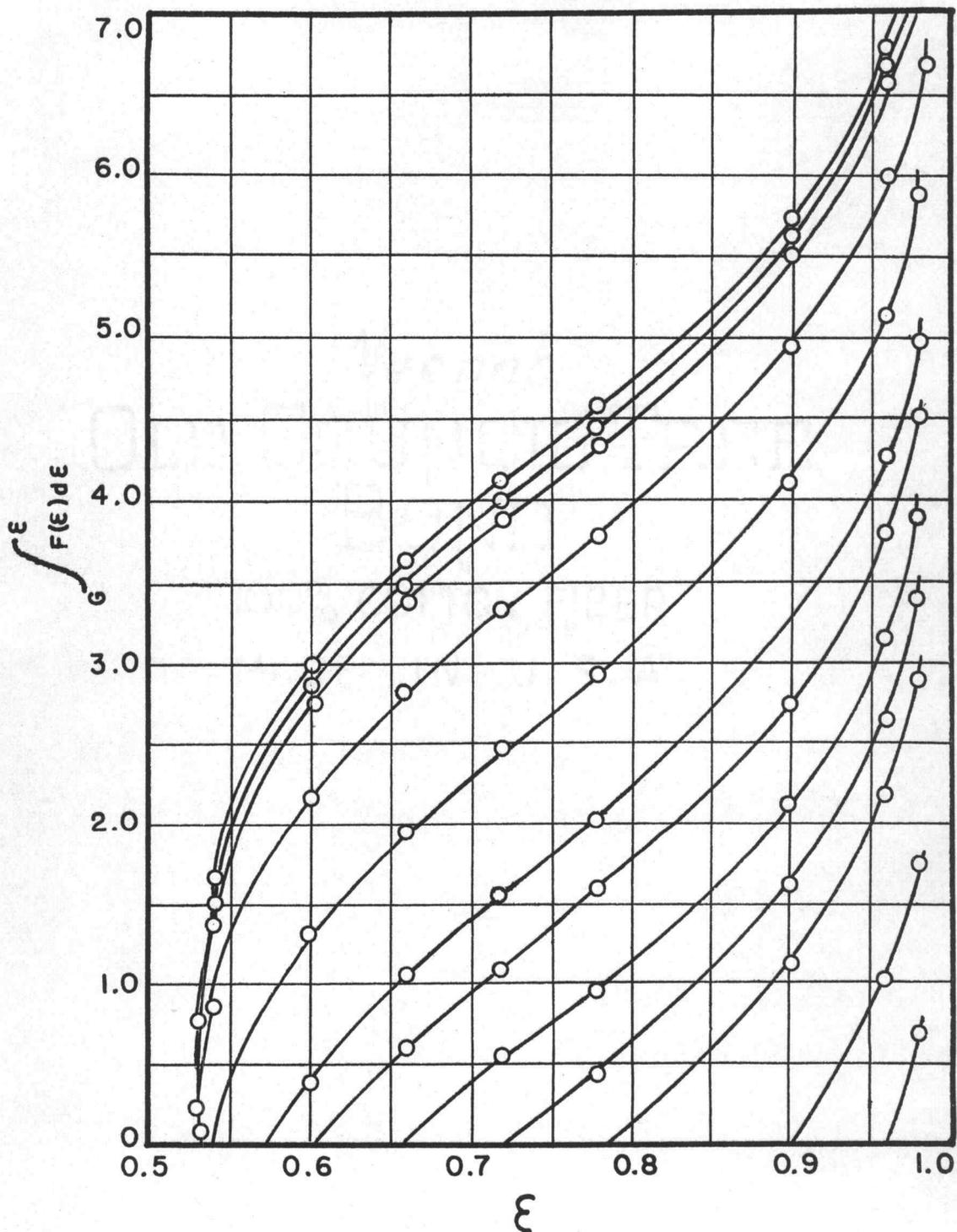


FIGURE 6

various values of  $\varepsilon$  was computed. Table I is an example. A log-log duplex slide rule was found to be very convenient for computing. Values of  $\varepsilon$  were chosen in definite increments keeping in mind the requirement that  $n$  in Simpson's Rule be even.  $\varepsilon$  covered the portion of the range between zero and one permitted by the requirement that  $\alpha + \varepsilon > 0$ .

2. Values of  $G$  were selected which gave a convenient range of values for  $t$  as determined from the equation

$$(21) \quad t = \frac{1}{\alpha \lambda} \ln \frac{\alpha + G}{G(\alpha + 1)} \quad \text{where } \lambda = k f_o I_o \quad (21 B)$$

Then Simpson's Rule was applied to calculate the value of

$$\int_G^{\varepsilon} F(\varepsilon) d\varepsilon \quad \text{in the intervals of } \varepsilon_n = G_n \text{ to } \varepsilon_{n+\Delta n} =$$

$G_n + \Delta n$  and the results were recorded in a table.

Table II is an example.

3. The value of LHS (20) was then plotted vs for each value of  $G$ . See Figure 6.

From a plot as in Step 3 it is possible to determine  $\varepsilon$  at any value of  $x$  and at any time  $t$

TABLE I

F( $\varepsilon$ ) vs  $\varepsilon$  for  $\alpha = -0.53$ 

$\varepsilon$	F( $\varepsilon$ )	$\varepsilon$	F( $\varepsilon$ )
0.53003	6510	0.57	17.8
0.53004	5040	0.60	12.5
0.53005	4120	0.63	10.25
0.530075	2885	0.66	9.05
0.53010	2230	0.69	8.40
0.53015	1560	0.72	8.10
0.53020	1215	0.75	7.99
0.5304	666	0.78	8.10
0.5306	470	0.81	8.50
0.5308	369	0.84	9.25
0.5310	306	0.87	10.48
0.5315	218	0.90	12.55
0.5320	172	0.93	16.53
0.533	124	0.96	27.2
0.534	98.5	0.97	34.9
0.537	63.4	0.98	50.4
0.540	48.1	1.00	$\alpha$

TABLE II

$$\int_G^{\varepsilon} F(\varepsilon) d\varepsilon \text{ vs } G (F \times 1000)$$

$\varepsilon \times 100 \backslash G$	.53003	.53005	.5301	.531	.54	.57	.60	.66	.72	.78	.90	.96	.98
53.003	0												
53.005	103	0											
53.01	219	116	0										
53.1	775	672	556	0									
54	1656	1553	1437	881	0								
57						0							
60	2974	2871	2755	2199	1318	442	0						
66	3600	3497	3381	2825	1944	1067	626	0					
72	4107	4004	3888	3332	2451	1574	1133	507	0				
78	4589	4486	4370	3814	2933	2056	1615	989	482	0			
90	5740	5637	5521	4965	4084	3207	2765	2140	1633	1151	0		
96	6799	6696	6580	6024	5143	4266	3824	3199	2692	2210	1059	0	
98	7523	7420	7304	6748	5867	4990	4548	3923	3416	2934	1783	724	0

EXPERIMENTAL BLEACHING CURVES FOR K KCl AT 50° C

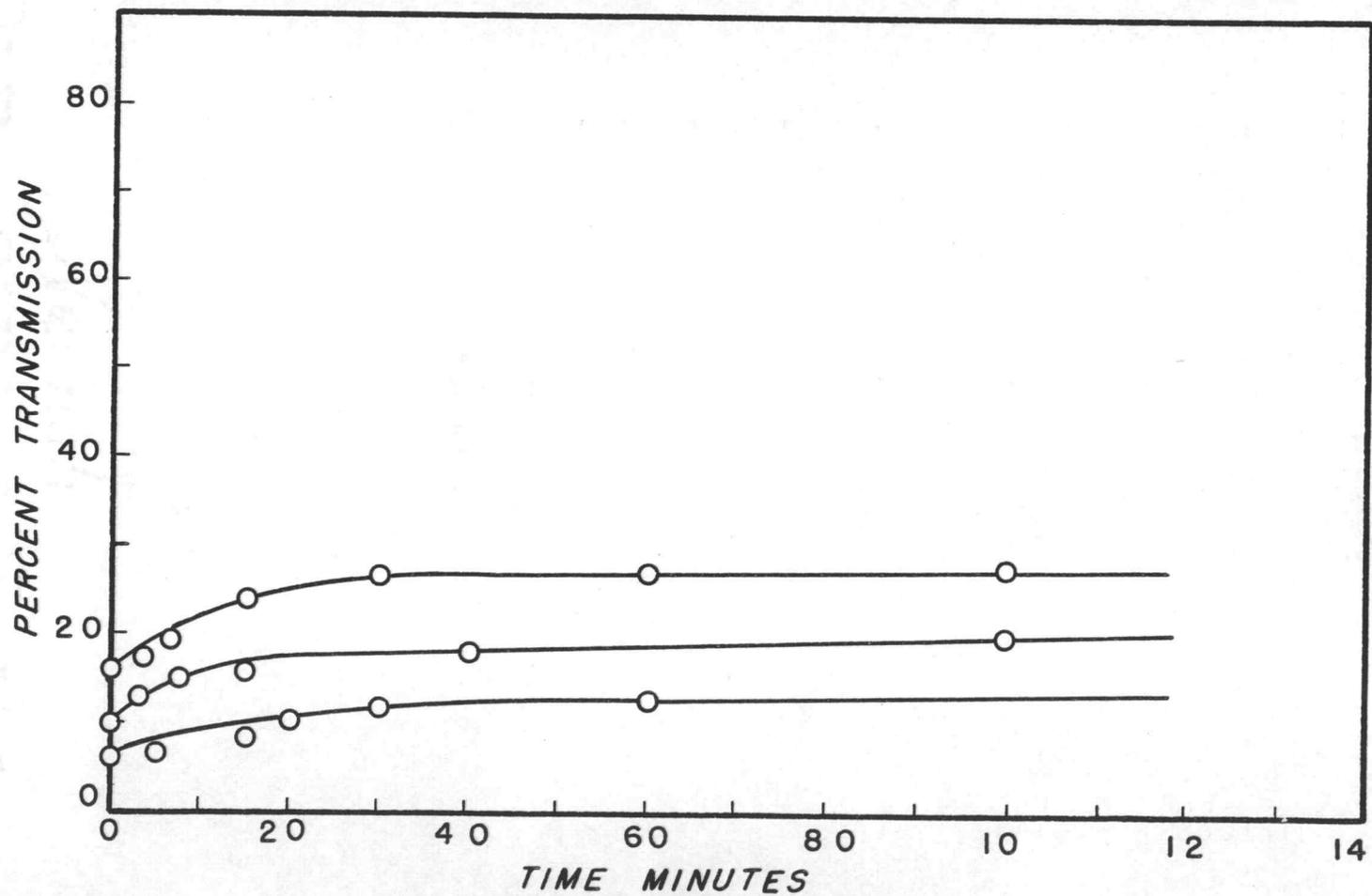


FIGURE 7

EXPERIMENTAL BLEACHING CURVES FOR K KGI AT 75° C

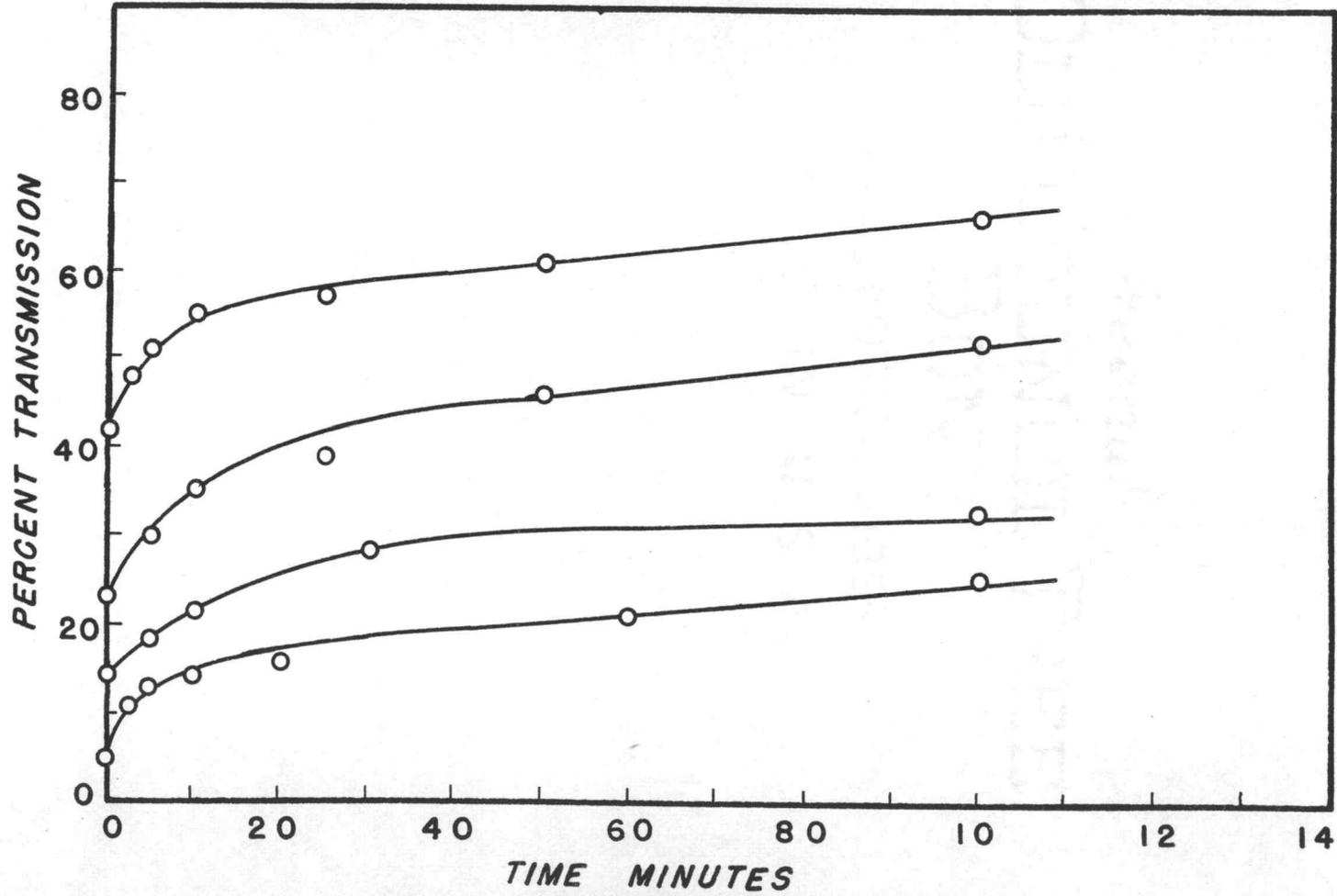


FIGURE 8

EXPERIMENTAL BLEACHING CURVES FOR K KCl AT 100° C

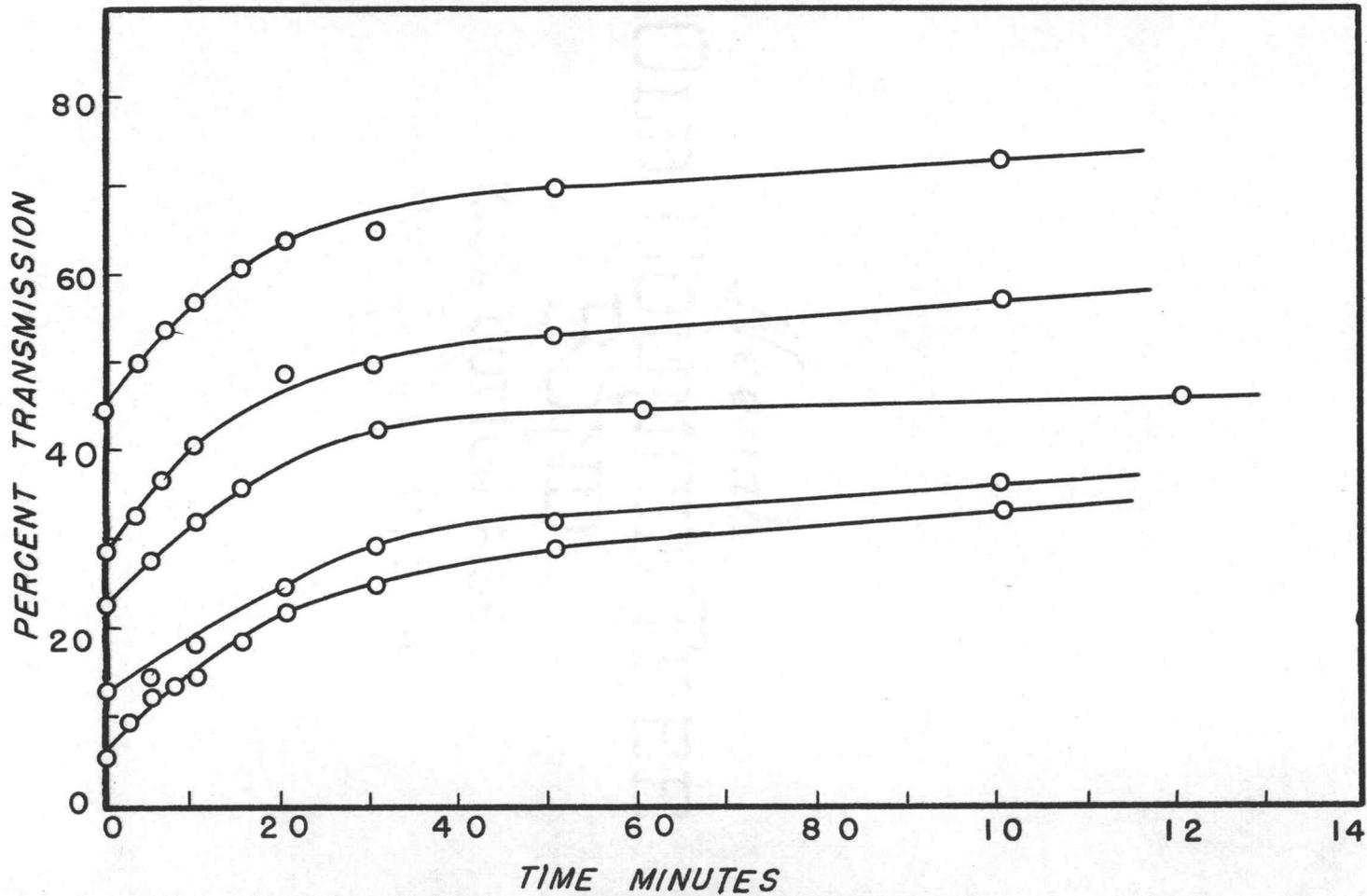


FIGURE 9

EXPERIMENTAL BLEACHING CURVES FOR K KCl AT 125° C

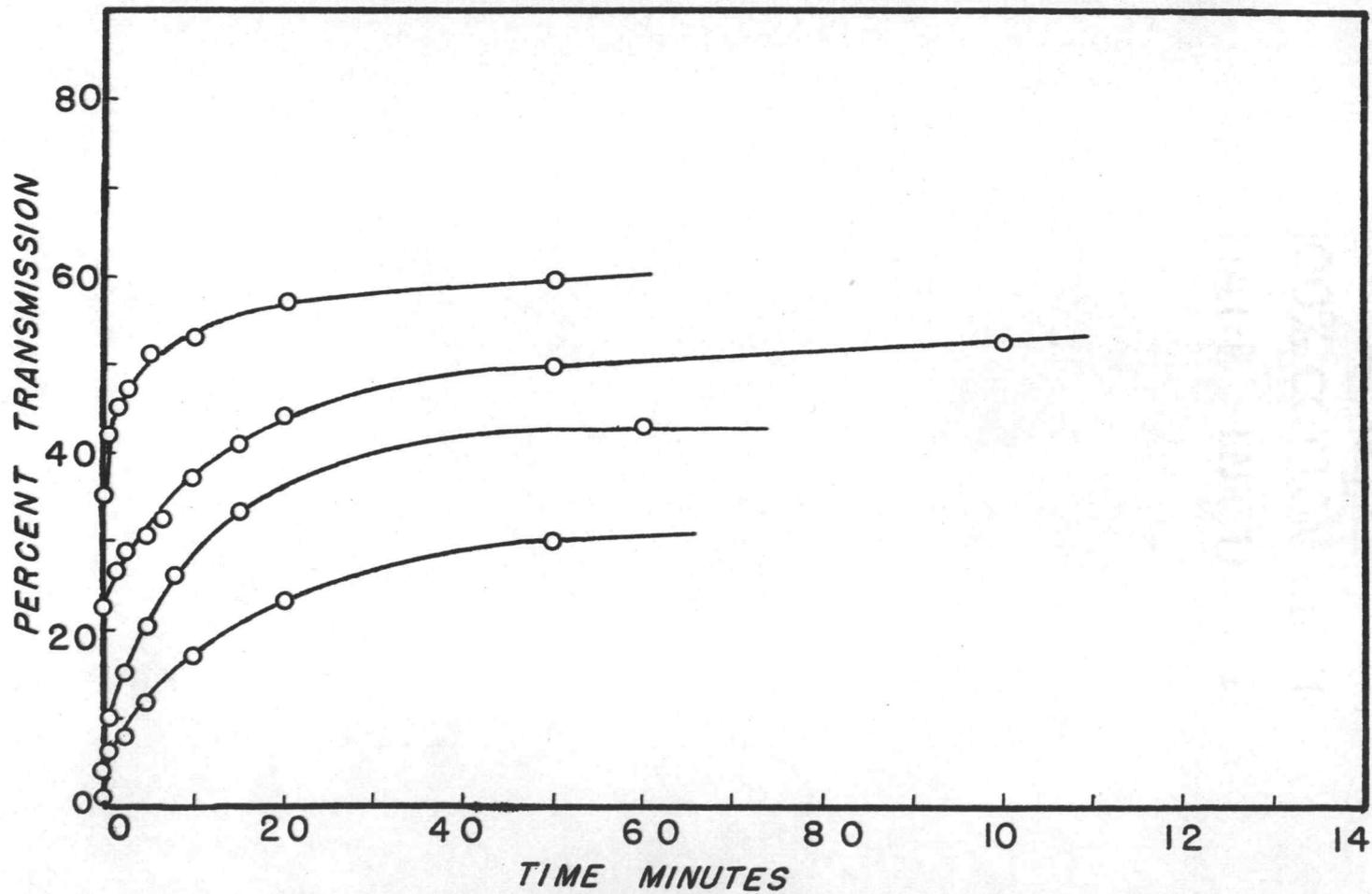


FIGURE 10

EXPERIMENTAL BLEACHING CURVES FOR K KCl AT 150° C

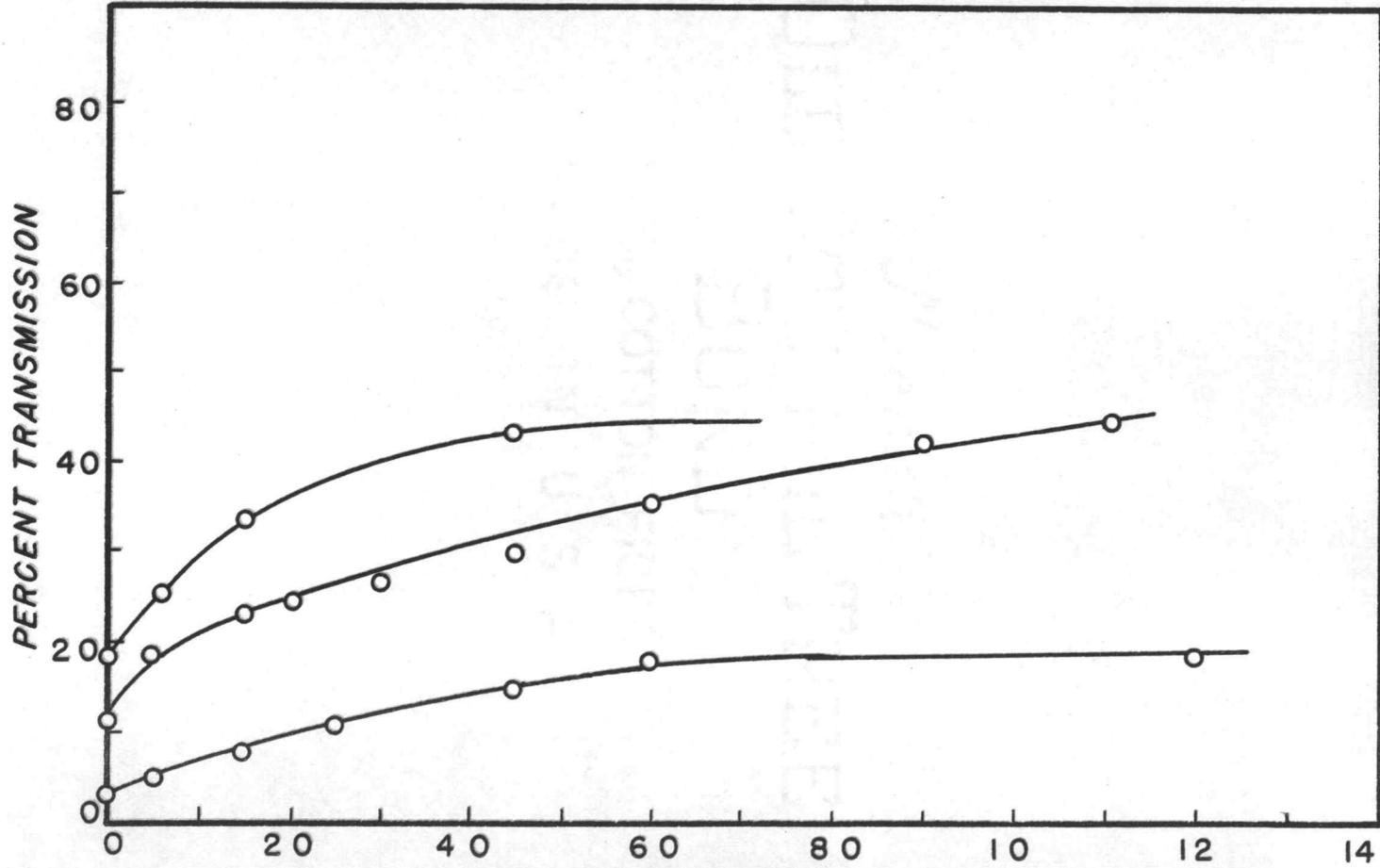


FIGURE II

corresponding to one of the G values. Selecting a value for x determines the value of LHS (20) which has been plotted in step 3 as ordinate.  $\varepsilon_{x,t}$  is found by following along the proper G curve to the point where the ordinate is determined by x. The abscissa of this point is  $\varepsilon_{x,t}$ .

4. I at depth x and time t ( $I_{x,t}$ ) can also be found from Figure 6. For this the differential equation (6)  $\partial I / \partial x = -a'I$  must be solved.

Equation (6) expressed in terms of  $\varepsilon$  becomes  $\partial I / \partial x = -a'I\varepsilon$  where a' is given by (20 A).

$$(22) \quad \frac{\partial I}{I} = -a'\varepsilon \partial x$$

Integrating (22) gives

$$\ln I \Bigg|_{x=0}^{x=x} = -a' \int_{x=0}^{x=x} \varepsilon \, dx \quad \text{or}$$

$$(23) \quad \ln \frac{I_x}{I_0} = -a' \int_{x=0}^{x=x} \varepsilon \, dx$$

But  $\varepsilon$  is a function of x for any given t. This integral can be evaluated graphically by determining the area between  $x = 0$  and  $x = x$  under the curve made by

plotting  $\varepsilon$  vs  $x$ . The plots made in step 3 can be used for this purpose since they are essentially a plot of  $\varepsilon$  vs  $x$  for values of  $\varepsilon = G$  to  $\varepsilon = \varepsilon$ . For a given  $G$  (and hence a given  $t$ ), the value of RHS (23) is the area between the curve for the appropriate  $G$  and the

$\int_G^\varepsilon F(\varepsilon) d\varepsilon$  axis. If  $D$  equals this area, then

$$\ln I_x/I_0 = -a'D \quad \text{or}$$

$$(24) \quad I_x = I_0 e^{-a'D}$$

$I_d$  where  $d$  is the crystal thickness can be followed as a function of time from a plot made of  $I_{x=d}$  vs values of  $t$  corresponding to selected values of  $G$ . By plotting  $I_{x=d}$  vs  $t$  for various values of the parameters  $\alpha$  and  $\lambda$  and comparing these theoretical curves with experimental ones, experimental values for these parameters are determined.

Boundary conditions can now be considered.

Solutions to the simultaneous bleaching equations are

$$\int_G^\varepsilon F(\varepsilon) d\varepsilon = -a'x \quad \text{and} \quad I_x/I_0 = e^{-a'D}$$

where  $D$  is the area under the curve of  $\int_{x=0}^{x=d} \varepsilon dx$

when  $t = 0$ ,  $\varepsilon = 1$  for all values of  $x$ . Therefore,

$$(25) \quad \frac{I_{x=d}}{I_0} = e^{-a'd}$$

which allows  $a'$  to be calculated from a knowledge of the crystal thickness and initial percent transmission. As bleaching continues,  $\varepsilon$  continually decreases. But  $\alpha + \varepsilon > 0$  for a real solution and for  $\alpha < 0$ , which is apparently the case for additively colored crystals,  $-\varepsilon \rightarrow \alpha$  and  $G \rightarrow -\alpha$  as  $t \rightarrow \infty$ . Therefore,

$$(26) \quad \frac{I_{x=d}}{I_0} \rightarrow e^{+a'\alpha d} \quad \text{as } t \rightarrow \infty \quad \text{since}$$

$$\frac{I_{x=d}}{I_0} = -a' \frac{1}{a'} \int_G^\varepsilon F(\varepsilon) d\varepsilon$$

Thus it is possible to determine  $\alpha$  from an experiment simply by knowing initial and final values of  $I_d/I_0$ .  $\lambda$ , the only remaining parameter, determines the slope of a theoretical bleaching curve. A method of finding  $\lambda$  is explained later. The solution of the bleaching equations is now complete inasmuch as  $\varepsilon$  for every  $x$  and  $t$ ,  $I$  for every  $x$  and  $t$  and all parameters have been determined. Experimental and theoretical

EXPERIMENTAL BLEACHING AT 50°C vs THEORY FOR  $\alpha = -0.7, \lambda = 1.8$

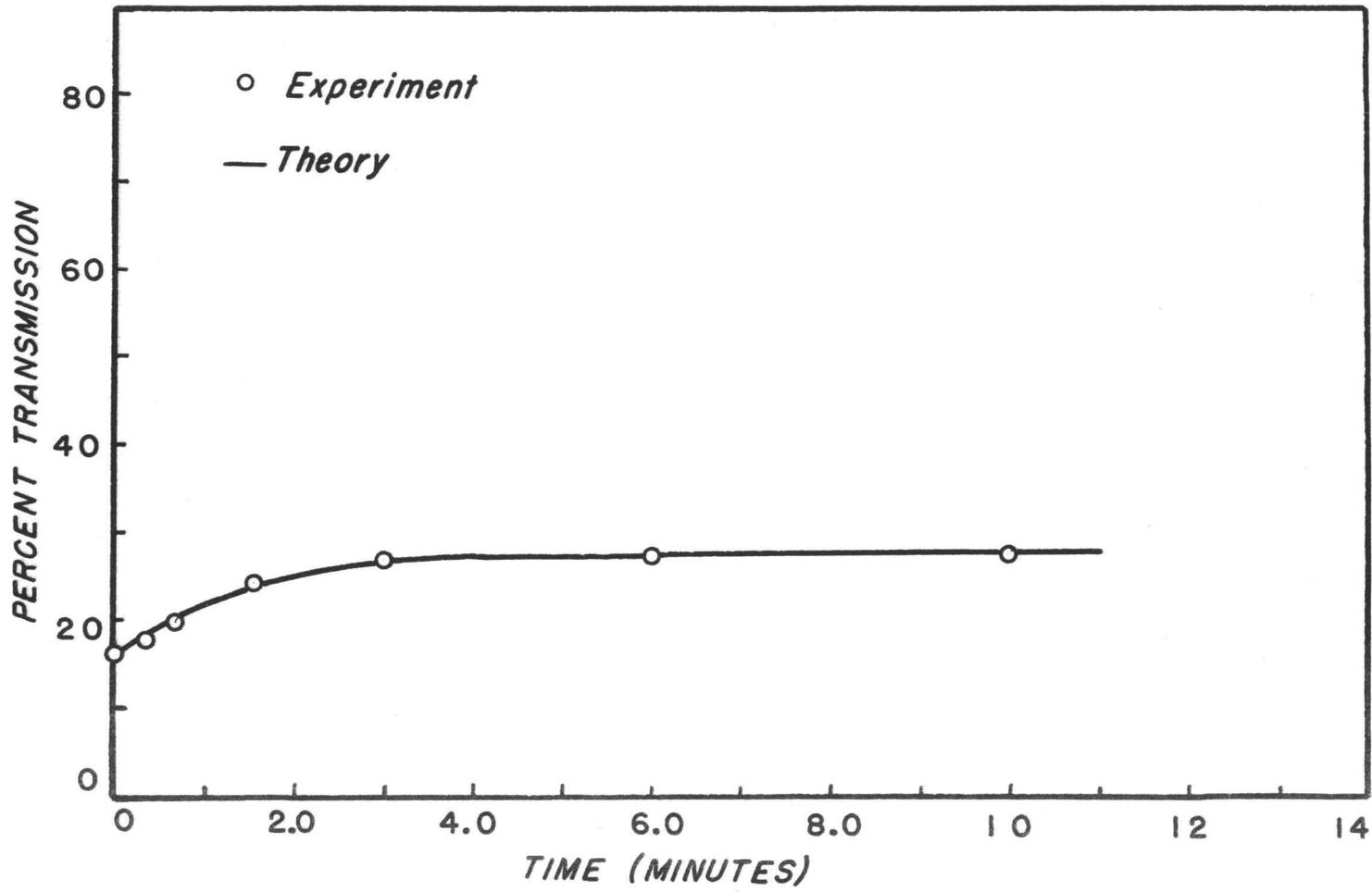


FIGURE 12

EXPERIMENTAL BLEACHING AT 75°C vs THEORY FOR  $\alpha=-0.54, \lambda=1.6$

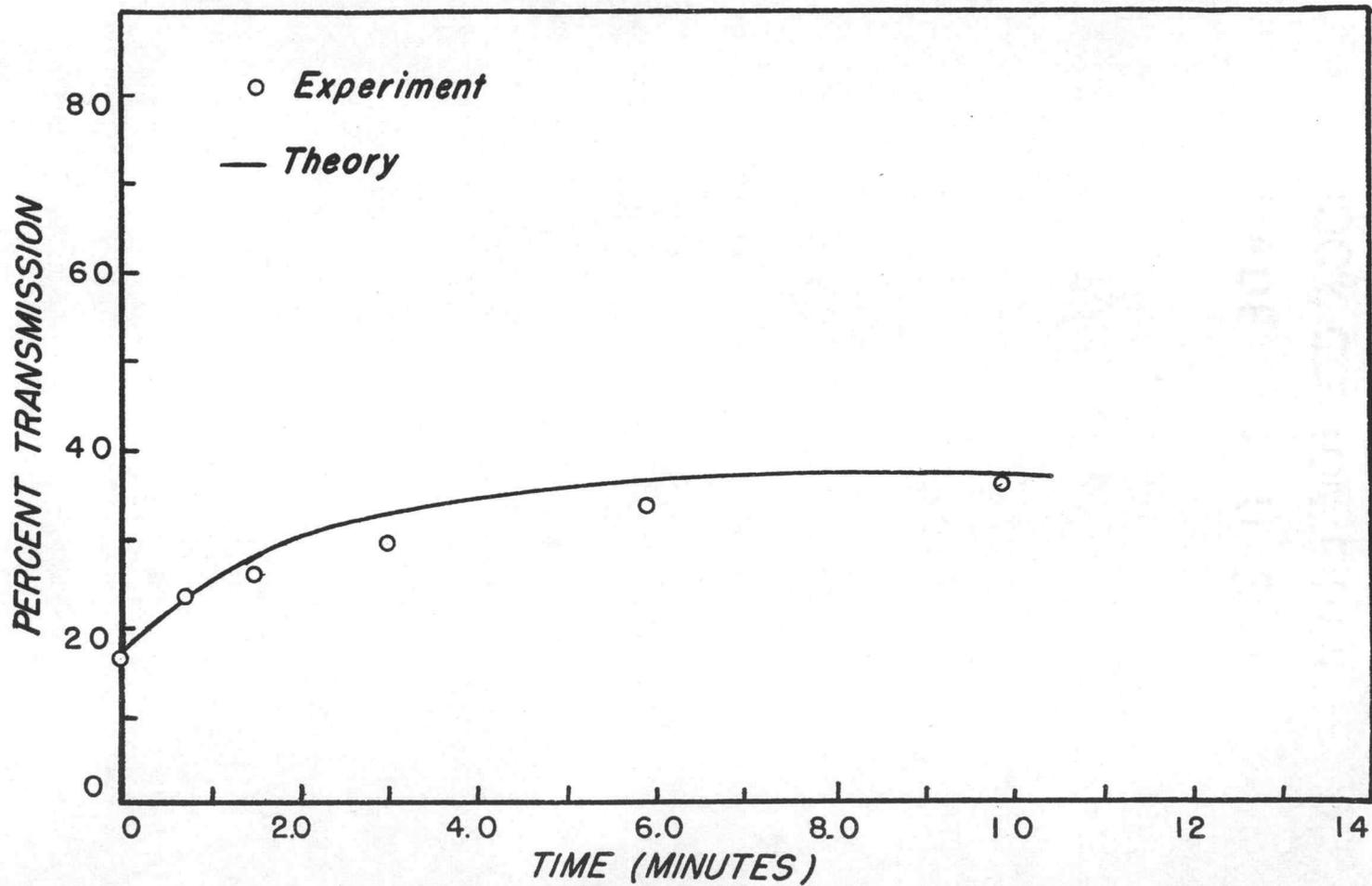


FIGURE 13

EXPERIMENTAL BLEACHING AT 100°C vs THEORY FOR  $\alpha = -0.53, \lambda = 1.52$

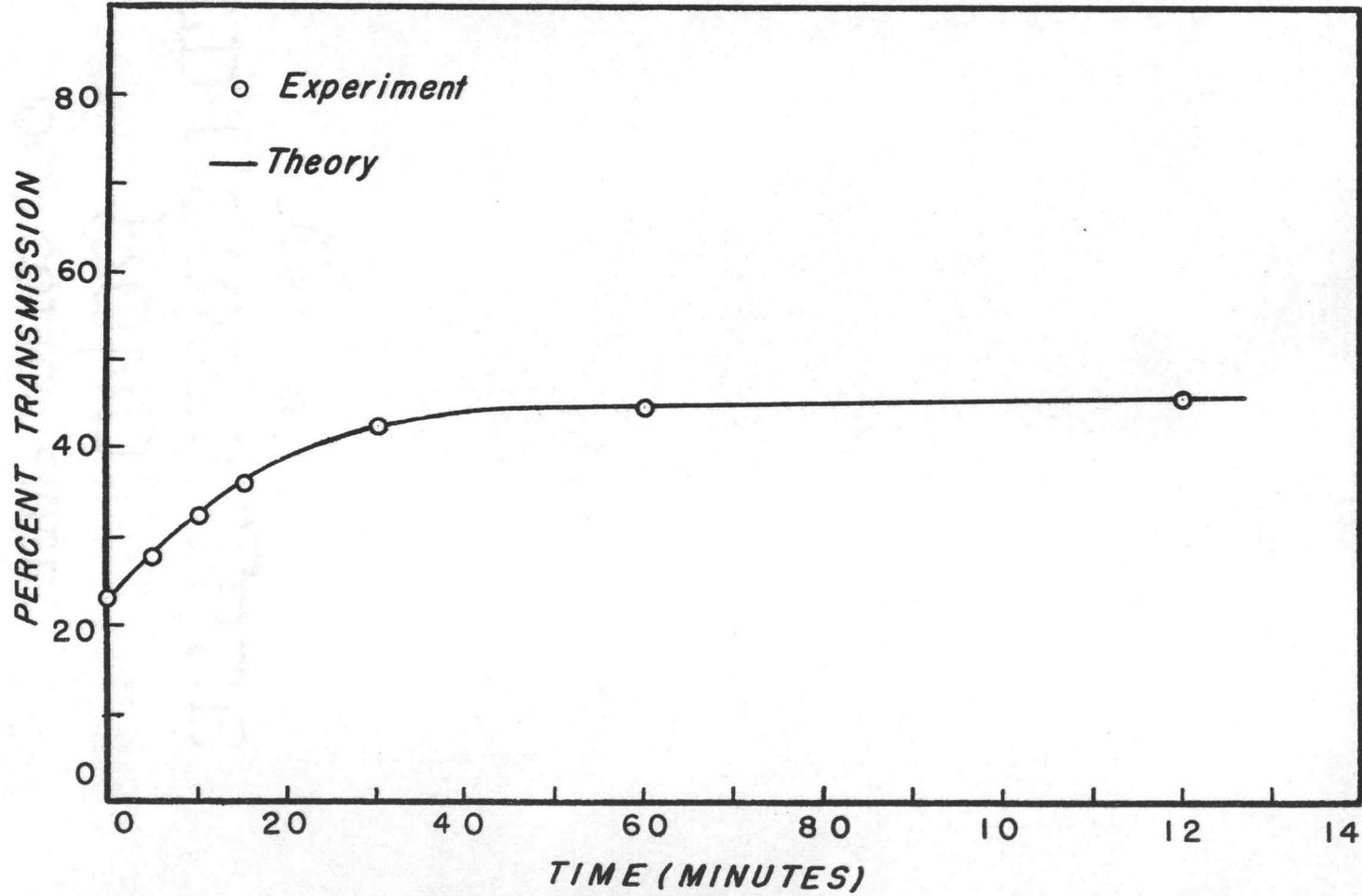
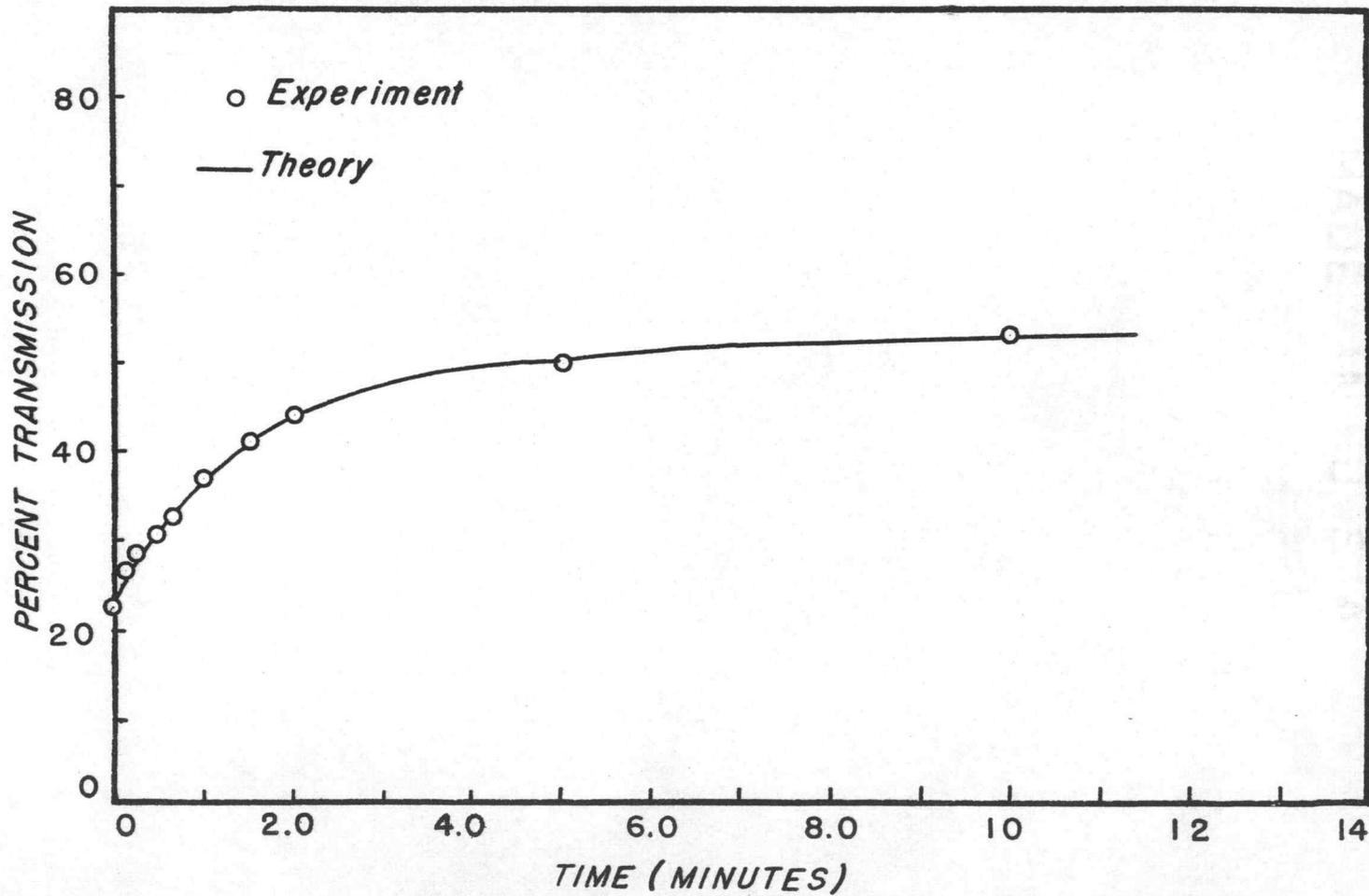


FIGURE 14

EXPERIMENTAL BLEACHING AT 125°C vs THEORY FOR  $\alpha=-0,42, \lambda=1.70$



TIME (MINUTES)

FIGURE 15

EXPERIMENTAL BLEACHING AT 150°C vs THEORY FOR  $\alpha = -0.50$ ,  $\lambda = 0.175$

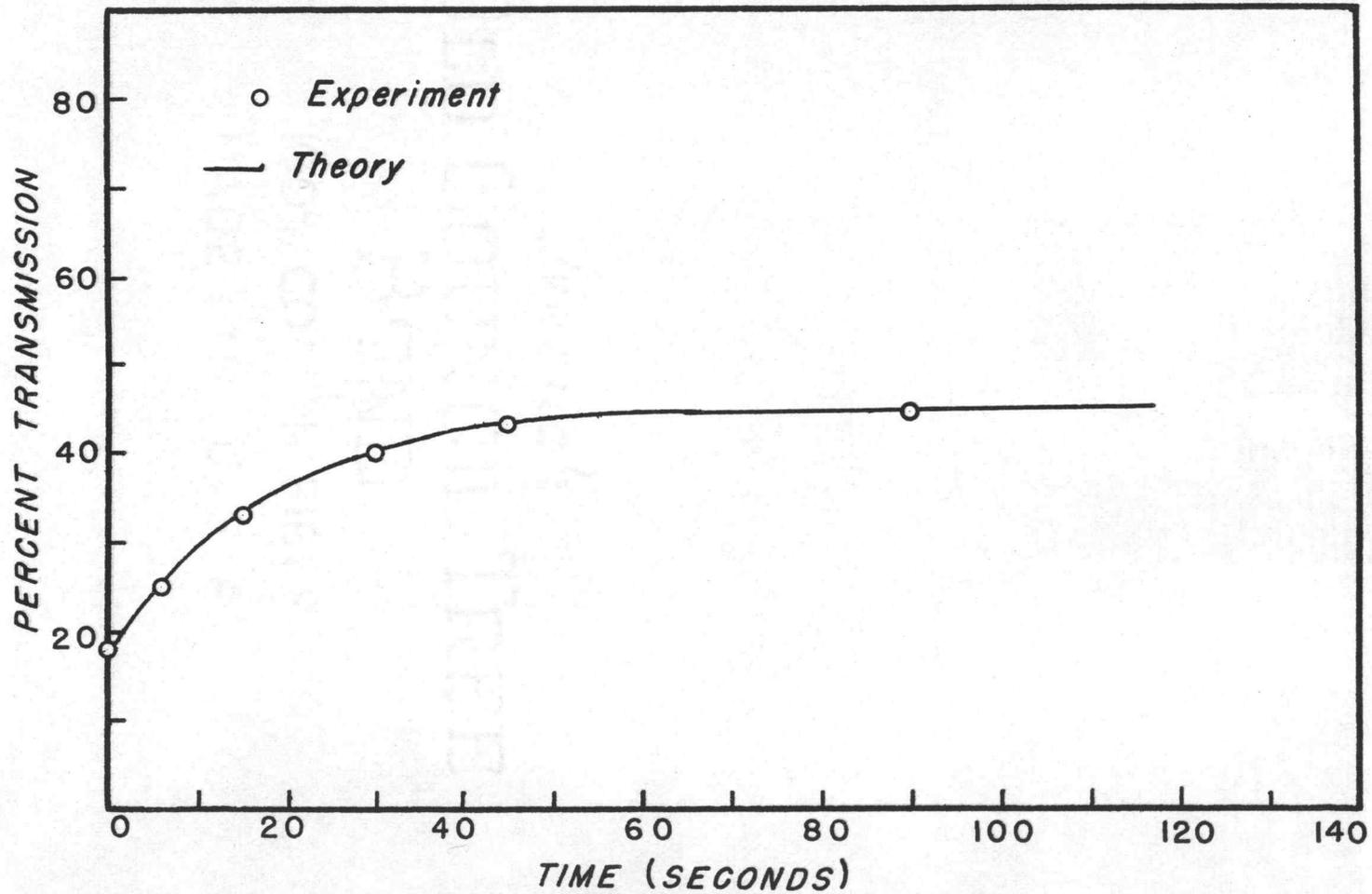


FIGURE 16

results will now be compared after which physical significance of the various variables and parameters in the bleaching equations will be discussed.

## EXPERIMENT AND THEORY

A series of bleaching experiments was conducted at each of five different temperatures (50, 75, 100, 125, and 150°C) since this was found to be a convenient range experimentally. Below a temperature of about 50°C bleaching rates were so slow that times for complete bleach became inconveniently long. An upper limit in temperature of 150°C was selected for two reasons, (1) bleaching rates became too rapid for accurate measurement with equipment at hand and (2) thermal bleaching began to be significant much above 150°C.

All samples colored and bleached were obtained from the Harshaw Chemical Company but were not all from the same stock piece. Samples colored under a variety of conditions were studied at each temperature. Some difficulty was encountered in cleaving very thin samples and a tendency to slight curling was noted. Percent transmission magnified to a convenient value electronically changed with time during bleach and was plotted against time. A series of such plots for various colored samples was obtained at each temperature and are illustrated in Figures 7 to 11. Although the general shape for such plots was of the same form for all five temperatures studied, deviations of certain individual samples

from the general type for a given temperature of bleach were noted. Since other samples of about the same thickness and from the same colored stock piece bleached as expected, it is thought that these individual deviations were due to indeterminate experimental errors. Such errors might have been due to a temperature drift during bleach, optical and mechanical defects introduced during cleavage or to timing errors during bleach. Also Ueta and Känzig have demonstrated the differences in bleaching rates caused by mechanical deformation such as might have been encountered here during cleaving of very thin slices (13, p. 1591-1595). Such plots, while included in plates 7 to 11, were not used in comparing with theoretical plots.

To check theory with experiment, experimental curves which appeared to be representative of their group at each temperature were chosen. For each of these curves an experimental value for  $\alpha$  was obtained as explained above. Using these values of  $\alpha$ , solutions to the bleaching equations were worked out. Next, time-values from (21)  $t = 1/\alpha\lambda \ln((\alpha+G)/G(\alpha+1))$  for  $\lambda = 1$  corresponding to each solution versus percent transmission were entered in a table, as in Table III. However, the theoretical time for a given percent

TABLE III

 $F(\varepsilon)dx$  vs time when  $\alpha = -0.53$ 

G	$t_{\lambda=1}$	$\int_G^{a'x=1.47} F(\varepsilon)dx$	$I_{x=d} (\%I_0)$	$t_{\lambda=1.52}$
1.00	0.00	1.47	23.0	0.00
0.96	0.0921	1.43	24.1	0.06
0.90	0.250	1.38	25.2	0.16
0.78	0.724	1.26	28.5	0.47
0.72	1.088	1.19	30.4	0.72
0.66	1.645	1.099	33.4	1.09
0.60	2.63	0.995	37.0	1.74
0.54	6.10	0.834	43.4	4.00
0.531	10.4	0.796	45.1	6.75
0.53003	17.0	0.783	45.7	11.2

transmission did not necessarily coincide with the experimental time for the same percent transmission. By adjusting  $\lambda$  in equation (21), the theoretical time could be made to coincide with the experimental one. The required value of  $\lambda$  was found in each case by substituting the experimental time into (21) and solving for  $\lambda$ . If experiment and theory are in agreement, values of  $\lambda$  calculated in this manner should be constant. Values of  $\lambda$  were then calculated for each theoretical curve at different times during bleach and if  $\lambda$  was found to be fairly constant, an average  $\lambda$  was calculated. Such an average value of  $\lambda$  was then used to calculate time values for theoretical curves by means of equation (21) and the results were entered as in Table III as  $t_{\lambda \text{ ave}}$ . Plots were then made of percent transmission vs  $t_{\lambda \text{ ave}}$  and superimposed on experimental curves. These results are shown in Figures 12 to 16. It can be seen that quite good agreement between theory and experiment was obtained in most cases. However, at 75°  $\lambda$  was not constant, but varied continuously. Using a value for  $\lambda$  intermediate between 50° and 100°C it is seen that bleaching is somewhat less rapid than would be predicted by theory. The cause of this is unknown. Also in some cases bleaching was found to be slightly more rapid toward the end of

the bleaching process for temperatures of 150°C although good agreement was observed for most of the earlier bleach. This might be explained by a slight thermal bleaching being superimposed on optical bleach. Although individual samples sometimes gave poor agreement with theory, agreement between experimental bleaching curves and theory was generally quite good. It is seen then that by assuming only the simple model of an F center as proposed by de Boer and by taking into account concentration gradients and nonuniform light absorption, theory and experiment agree. These facts explain the initial rapid bleaching rate and the slower later rate which some have used as evidence for two types of F centers. One wonders whether there are really two types of F centers, "hard" and "soft" as has been claimed since bleaching is adequately explained for only one type of F center in a treatment as here. We tend to agree with Seitz (11, p. 68) that there is only one type of F center.

When theoretical bleaching curves were matched with experimental ones at a given bleaching temperature, it was found that  $\alpha$  was not entirely constant but varied slightly from sample to sample. In general, however,  $\alpha$  becomes more negative at lower bleaching temperatures.

Because of the many possible variables introduced in using several different samples, it would be difficult to determine very precisely how  $\alpha$  depends on temperature. An experiment was designed to eliminate as many variables as possible while studying the temperature dependence of  $\alpha$ . A large single crystal was colored homogeneously and used for all bleaching experiments in the hope that by using only one colored stock crystal, the number of variables other than temperature would be reduced to a minimum. Results of this experiment showed that for samples bleached at successively lower temperatures  $\alpha$  became consistently more negative in value. In the limiting case where  $\alpha = -1$ , it can be predicted from the bleaching equations that no bleaching should occur at all.

It is seen from equation (19B)  $C = \alpha f_0$ , that when  $\alpha = -1$ ,  $C = -f_0$ . By substituting this value of  $C$  into (5)  $\partial f / \partial t = -kfI(f-f_0)$ . Since  $f = f_0$  at the start of the bleaching,  $\partial f / \partial t = 0$  and no bleaching occurs. On the other hand as  $\alpha \rightarrow 0$  or even becomes slightly positive, bleaching rates should become very rapid.

Consider now possible physical significance for  $\alpha$ . Equation (19B) defines  $\alpha$  as  $\alpha = C/f_0$  and by (5A) we get  $\alpha = (B-f_0)/f_0$ . This interpretation is quite interesting

when it is remembered that a limiting case of no bleaching is encountered when  $\alpha = -1$  as was shown above. For  $\alpha$  to equal  $-1$ , B would have to assume a value of zero.

B represents the total concentration of traps other than anion vacancies. If no traps of type B are available, that is if  $B = 0$ , no bleaching is possible on the basis of the assumed model. Since it is very improbable that a crystal with  $B = 0$  could ever be prepared, it can be concluded that it is possible to bleach any crystal optically at least to some extent. Such a conclusion seems to be in agreement with observation.

Still another possibility is to consider the other extreme, i.e., when  $\alpha \rightarrow 0$  or even  $\alpha > 0$  and bleaching becomes very very rapid.  $\alpha$  could approach or exceed zero if B approached or exceeded  $f_0$ . Physically this could be interpreted by saying that there was available one or more bleaching type traps for each electron trapped in an anion vacancy. This would minimize any back reactions and would have an overall effect of raising the quantum efficiency for bleaching.

Also, as was shown previously,  $\alpha + \varepsilon > 0$  for the bleaching equations to have a nonimaginary solution (see equation 20).  $\varepsilon$  was defined by (19A) as  $\varepsilon = f/f_0$ . In all experimental cases studied,  $\alpha$  was found to have a

negative value between zero and one. Therefore, for  $\alpha + \epsilon$  to be positive,  $\epsilon$  must at least be equal to or slightly greater than  $-\alpha$ . This means that complete bleaching could not occur for negative values of  $\alpha$  but that there would still be some F centers present even when bleaching equilibrium was reached. Thus  $\alpha$  relates not only the rate of optical bleaching but also the extent. The fact that complete bleaching does not occur when  $\alpha$  is negative could also be explained in terms of the concentration of traps other than anion vacancies, that is, not enough traps were available.

Experimentally it is observed that temperature very markedly affects bleaching rates and also the extent of bleaching. For example, bleaching equilibrium was reached in about 30-40 minutes at 50°C with only a relatively small fraction of the initial F centers being bleached, while with the same apparatus at 150°C it required only about 45 seconds to reach equilibrium and almost complete bleach. A higher temperature, therefore, seems to be associated with a more positive value for  $\alpha$  and an increase in  $\alpha$  seems to indicate an increase in the concentration of available traps other than anion vacancies, as was explained above.

In their study of electron trap generation by

plastic flow, Ueta and Känzig (13, p. 1591-1595) observed effects on bleaching rates similar to those caused by an increase in temperature. They showed that vacancy aggregates generated by cold work act as effective electron traps and result in enhanced initial bleaching rates and a greater extent of bleaching. In addition these authors used bleaching rates to estimate the number of traps generated by plastic strain. To accomplish the latter, it was necessary to evaluate a proportionality factor between the absolute number of traps per  $\text{cm}^3$  and the initial slope of the bleaching curve. The proportionality factor was assumed valid for given experimental conditions such as initial concentration of F centers, intensity of bleaching light, and thickness of crystal.

In the present work trap concentrations can also be calculated from bleaching rates and, we feel, more easily due to the lack of the necessity for constancy of as many experimental conditions. Trap concentration can be calculated from  $\alpha$  and a knowledge of the initial F center concentration. Solving equation (27) for B, the trap concentration, one obtains  $B = f_0(\alpha+1)$  (28). At  $50^\circ\text{C}$  for example, it was found that  $\alpha$  had a value in the neighborhood of  $-0.7$  for crystals containing initially about  $1 \times 10^{17}$  F centers per  $\text{cm}^3$ . Substitution of this

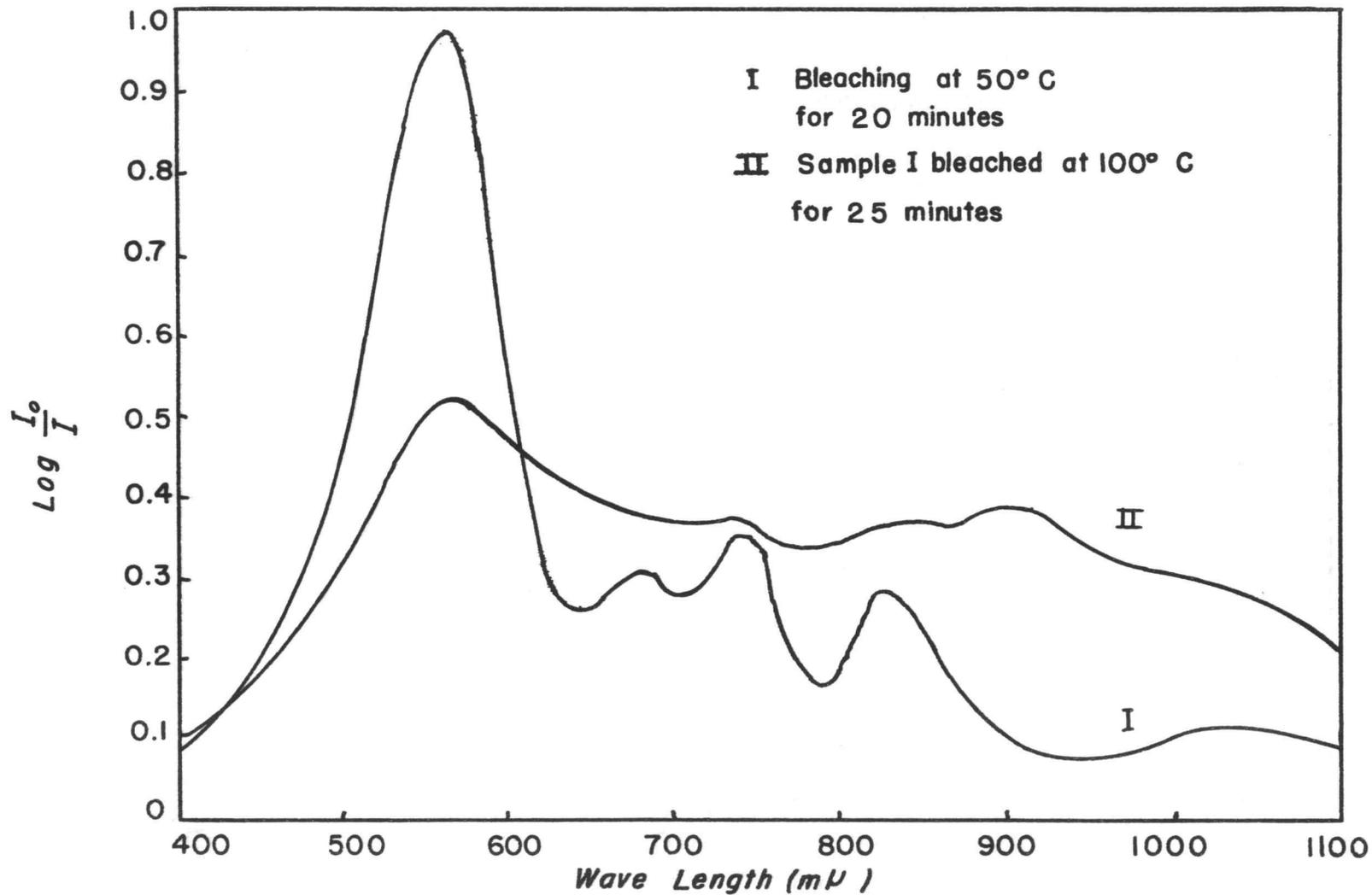


FIGURE 17

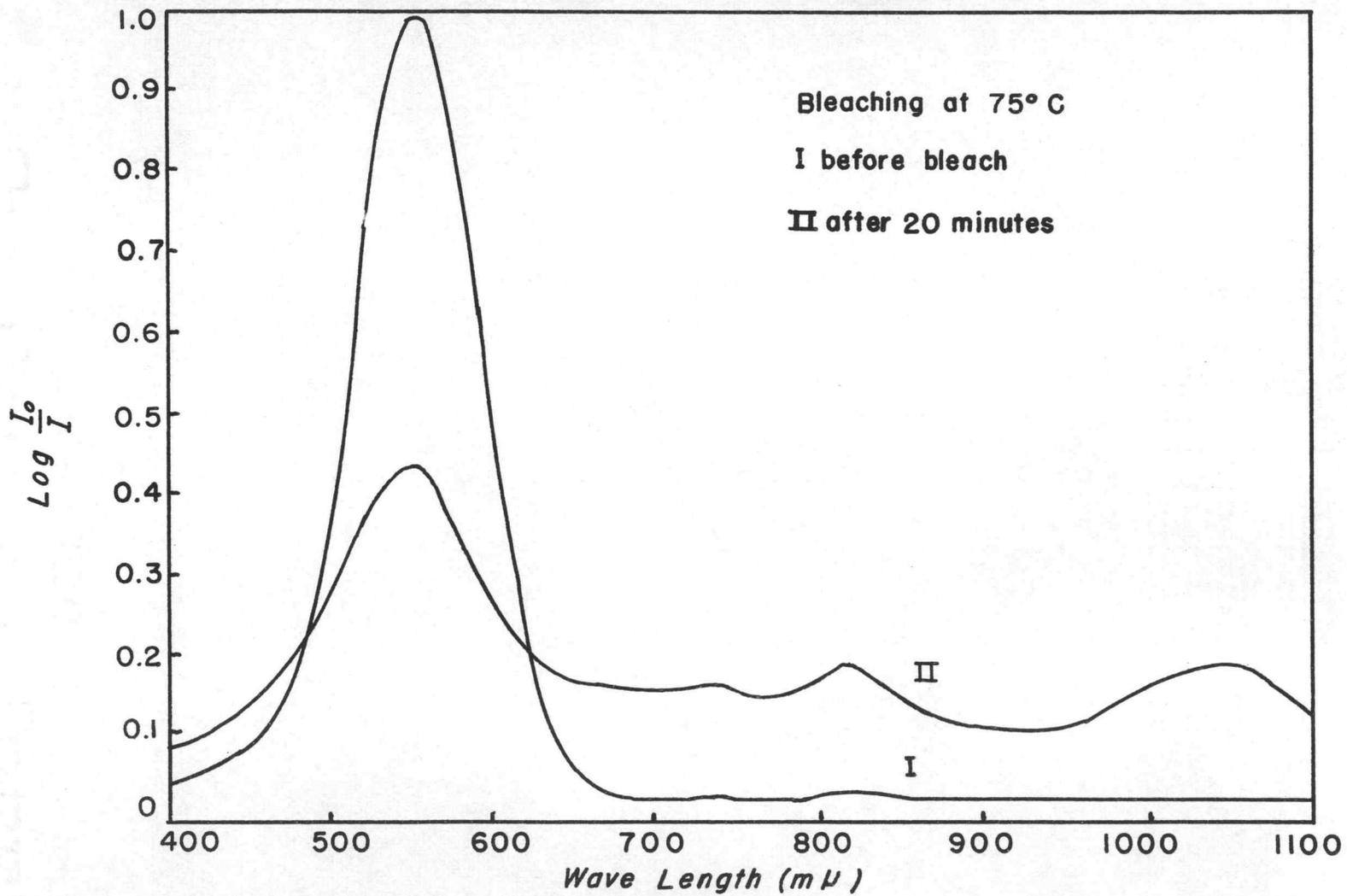


FIGURE 18

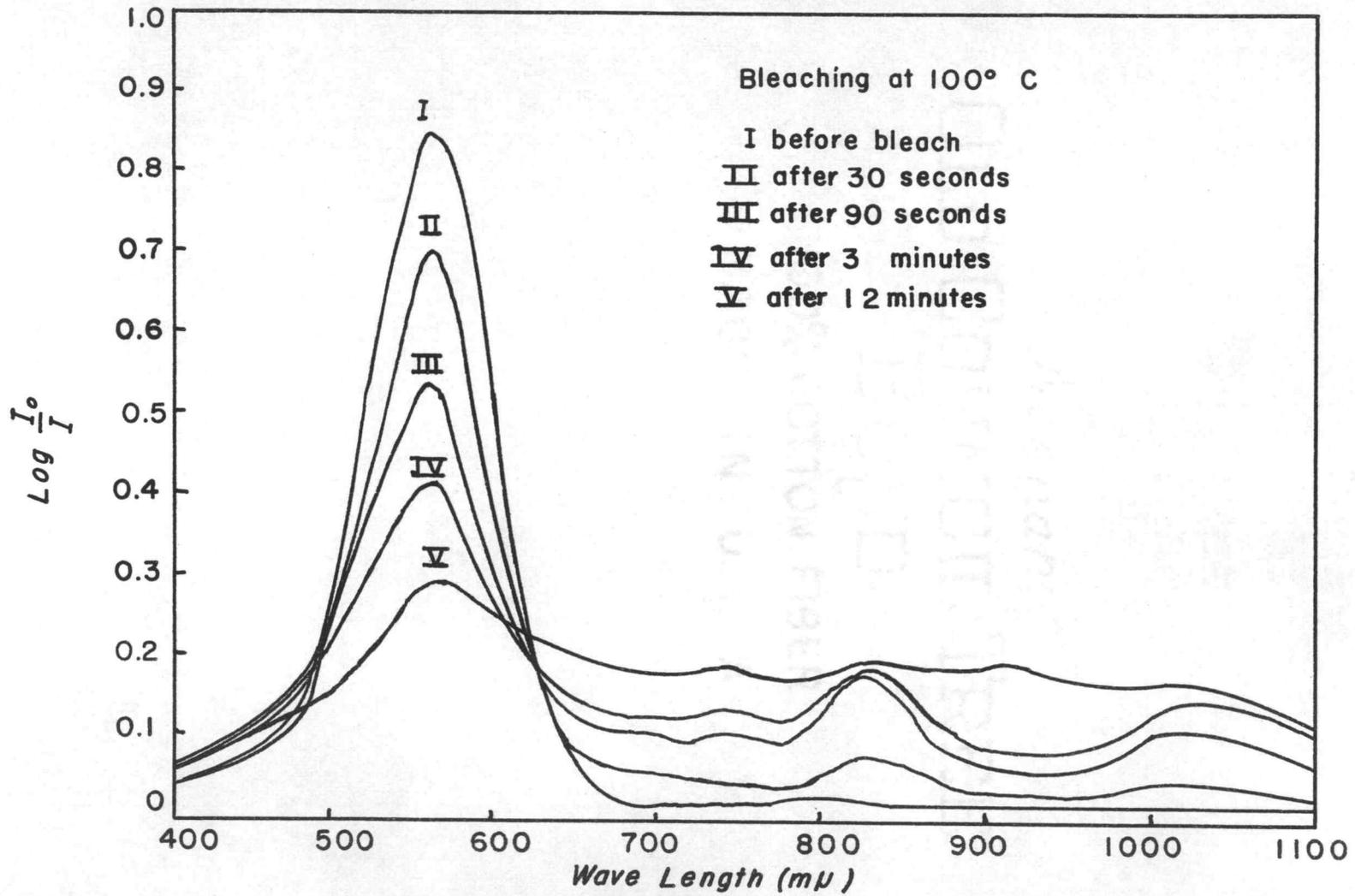


FIGURE 19

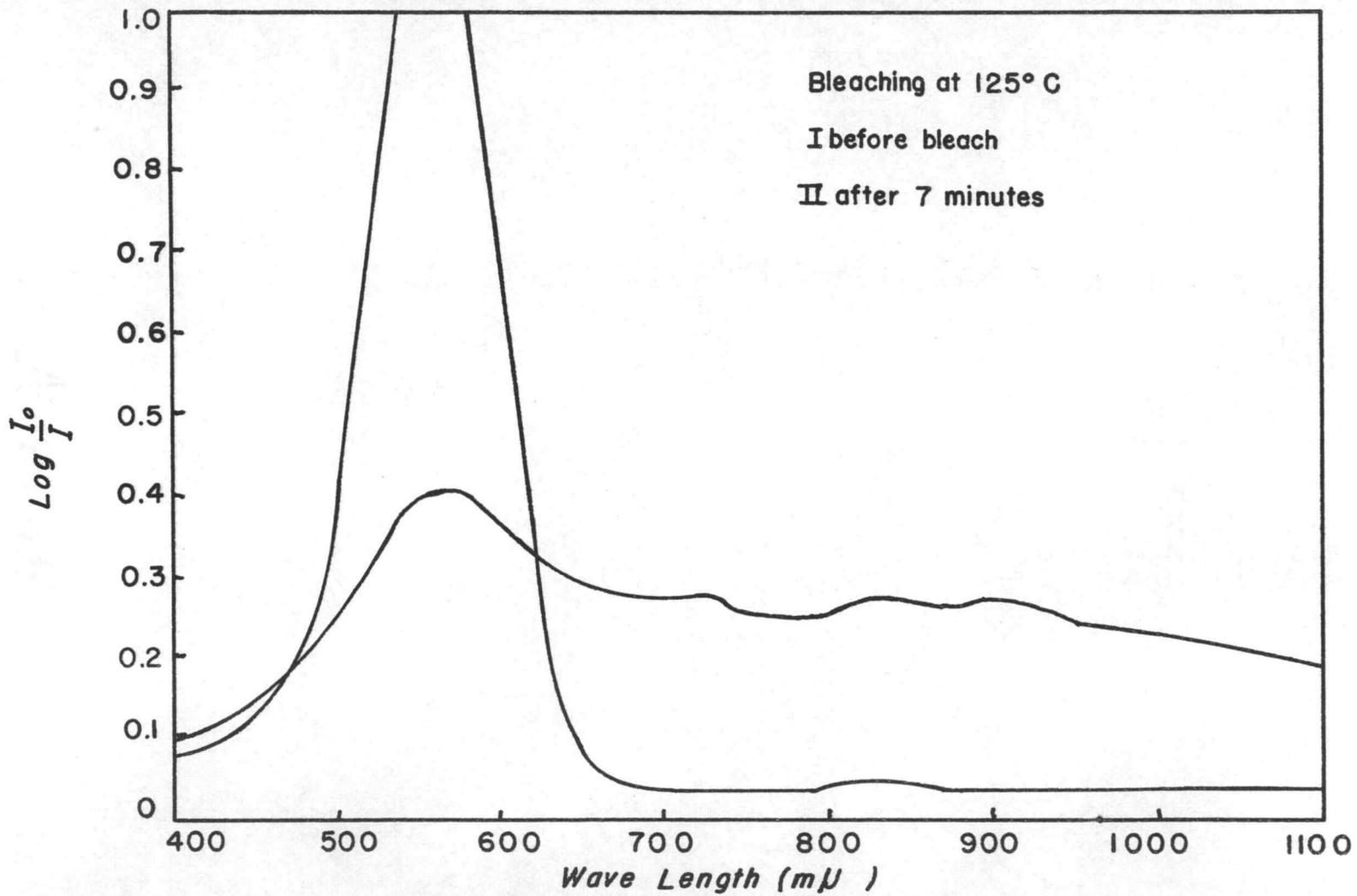


FIGURE 20

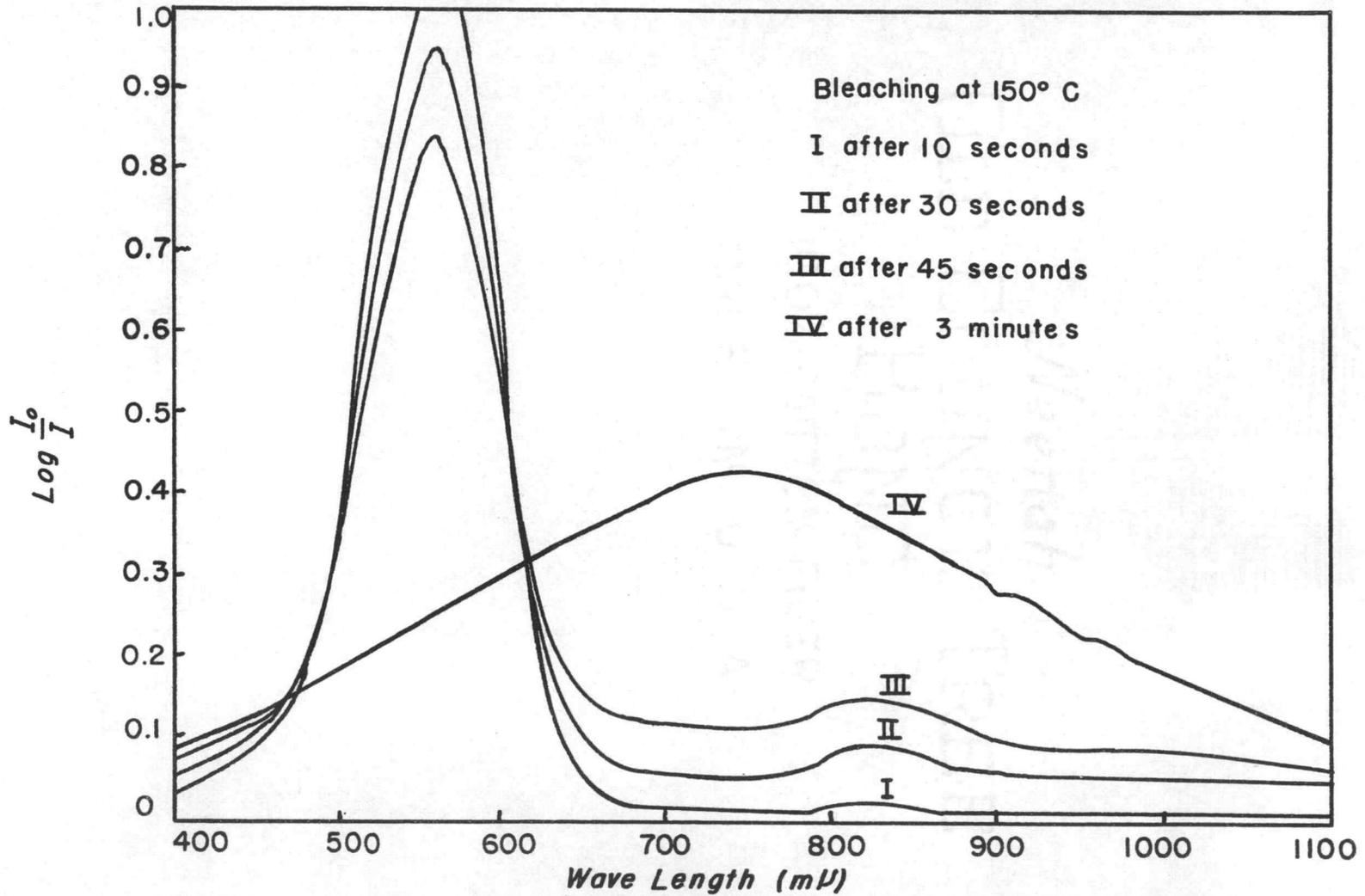


FIGURE 21

value for  $\alpha$  into (28) yields  $B = 0.3f$  or about  $3 \times 10^{16}$  traps per  $\text{cm}^3$ . This is in agreement with the value quoted by Ueta and Känzig for undeformed additively colored KCl crystals at room temperature. The same authors also found about  $1 \times 10^{17}$  traps per  $\text{cm}^3$  were formed by a plastic strain of ten percent which would roughly correspond in our case to the effect caused by raising the temperature to  $150^\circ\text{C}$ .

It would be interesting to apply the present bleaching treatment to plastically deformed crystals and check results with Ueta and Känzig. Also it would be interesting to find out if  $\alpha$  is a function of the initial concentration of F centers since it can be seen from (28) that either B or  $\alpha$  must be. It seems more reasonable to assume that  $\alpha$  is.

An increase in trap concentration would result in a decrease for the mean lifetime of conduction band electrons. The number  $n_e$  of conduction band electrons is the rate of their liberation from F centers times their mean lifetime  $\tau$  or

$$(29) \quad n_e = k_0 I f \tau$$

By substituting  $n_e$  from (29) into equation (1) and rearranging, one obtains equation (5) where

$$(30) \quad k = k_0 k_1 \gamma \quad \text{and}$$

$$(31) \quad C = \frac{1}{k_1 \gamma} - A$$

Solving (31) for  $\gamma$  and substituting (19B)  $C = \alpha f_0$ , we have

$$\gamma = \frac{1}{k_1 (\alpha f_0 + A)}$$

If  $k_1$  does not vary appreciably with temperature, it can be concluded that the mean lifetime of conduction band electrons is decreased by raising the temperature since  $\alpha$  is found to increase at higher temperatures.

If an increase in temperature actually results in an increase in traps other than anion vacancies, some mechanism whereby this could be accomplished should be discussed. Traps originally present in an additively colored crystal result largely from the quenching process and are believed to be mostly in the form of vacancy clusters such as neutral quartets of positive and negative ion vacancies. During bleaching these traps capture electrons with the result that new absorption bands appear. One of the first to appear is the M band. An M center is believed to appear when a vacancy quartet captures an electron and ejects a positive ion vacancy (9, p. 341-346). Such positive ion vacancies may diffuse

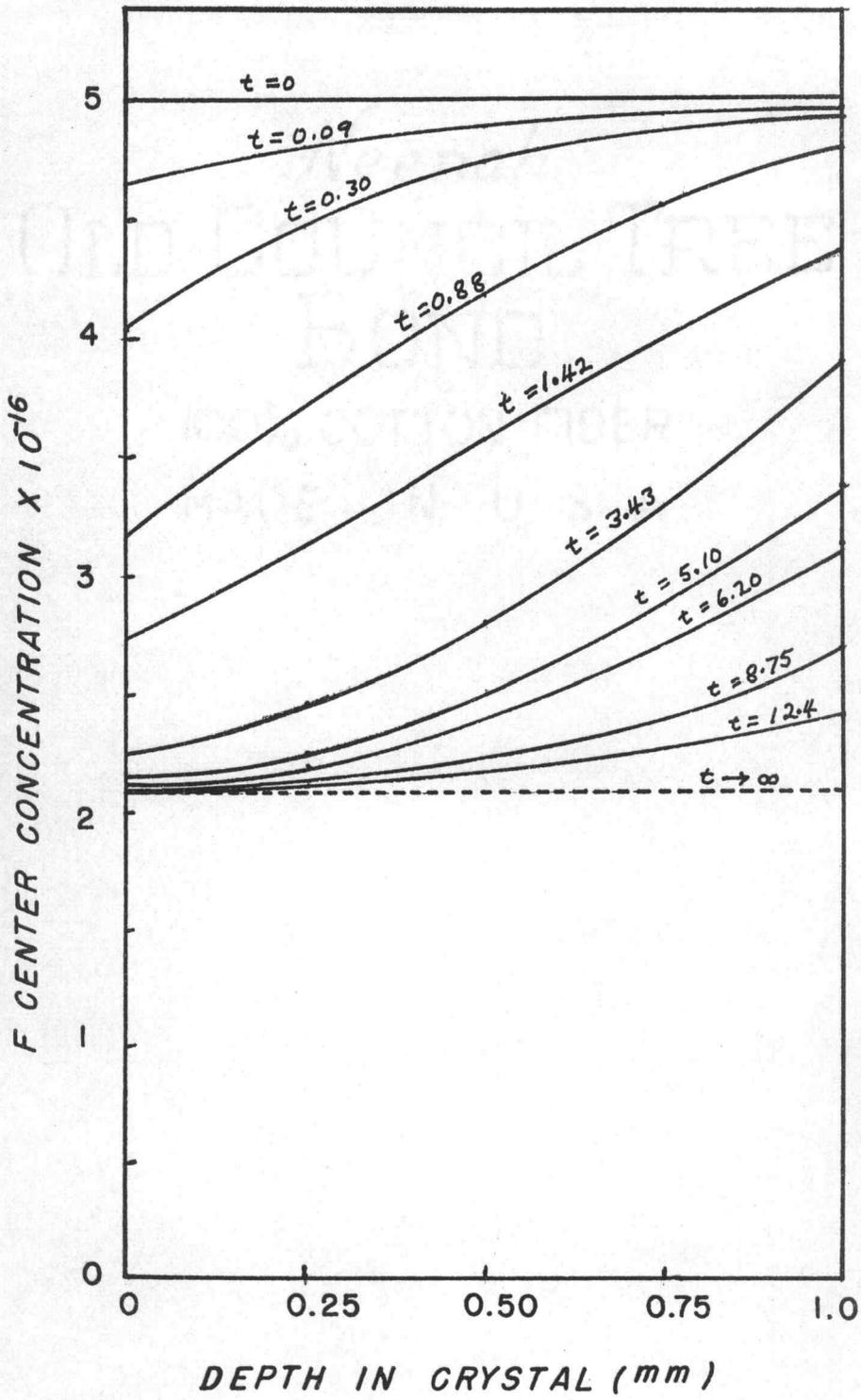


FIGURE 22

through the crystal and unite with an ionized F center or other anion vacancy forming a mobile vacancy pair. The mobile vacancy pair would be expected to unite with another like pair and product a new quartet. Bleaching rates would be somewhat enhanced by such a process because not only more bleaching type traps would be formed, but reformation of F centers or back reactions would be decreased since the anion vacancy concentration would be decreased. Also bleaching would be more extensive because of a higher concentration of bleaching type traps. An increase in temperature would increase diffusion rates and would increase the rate of the process just described.

One difficulty with this explanation, however, is that diffusion even at elevated temperatures is still a relatively slow process. It does not seem that diffusion alone could account for the experimental fact of immediate further bleach at some higher temperature as observed in this work. That is, experiments were conducted in which a crystal was bleached at some definite temperature, e.g. 75°C, until the rate of further bleaching was negligible. When such a crystal was heated in the dark to a slightly higher temperature, e.g. 100°C, and again illuminated with bleaching light, immediate

bleaching was observed to occur. Such a process was repeated again at 125°C on the same crystal and similar results were noted.

Still another source of further bleaching traps at higher temperatures may be from impurities present in a crystal. Pringsheim (8, p. 31) showed that natural rock salt bleached easier after annealing and attributed it to solution of precipitated impurities which would then result in a greater trap concentration. However, he used relatively high annealing temperatures ( $\sim 500^\circ\text{C}$ ) and it does not seem very likely that the relatively low temperatures used in this work would have much effect on impurities.

Another possibility is to assume that an increase in temperature may not actually generate traps, but that it may redistribute the equilibrium between traps already present in the crystal. For example, an equilibrium between anion vacancies and bleaching type traps may be shifted in favor of the latter by increased temperature. Such a situation would allow an increased rate of bleaching and also a greater degree of bleach. This explanation would overcome the intuitive objection one has to believing that small temperature changes in the neighborhood of  $100^\circ\text{C}$  could generate traps and it would still

satisfy the demand of theory for more bleaching traps. The major question in this explanation is the time required for the point of equilibrium to shift from one point to another. If the three minutes allowed in this work for going from one temperature to another allow sufficient time to reach the new point of equilibrium, then this explanation might be valid.

If anion vacancies are converted into bleaching traps, it should be possible to show this from the theoretical bleaching equations since they included terms for vacancies and traps. Equation (5B) defines  $k$ , the only other constant in the main bleaching equation (5) not yet discussed, as

$$k = \frac{\delta}{A + B - f_0}$$

Using (5A) and (19B) we get

$$(33) \quad k = \frac{\delta}{A + \alpha f_0}$$

Experimentally  $k$  is determined from (21B) as

$$k = \frac{\lambda}{f_0 I_0}$$

and is found to vary only slightly with temperature, i.e., it increases very slightly with an increase in

temperature.  $\alpha$ , however, increases markedly with temperature as was shown above. If  $\sigma$  which is the capture cross section for photons by F centers does not increase much with temperature then A must decrease with increased temperature. Otherwise k would decrease with temperature and this was not observed to be the case experimentally. Furthermore it was shown above that an increase in  $\alpha$  was associated with an increase in B. Therefore, it can be concluded that it is reasonable from the point of view of the bleaching equations at least, to assume that a raise in bleaching temperature converts anion vacancies A into bleaching type traps B.

Knowledge of trapping processes occurring during bleaching is gained by observing the absorption spectrum of a crystal at different stages of bleaching. In the present work a Beckman Model DK-1 recording spectrophotometer was employed to examine the optical spectrum of samples which had undergone varying degrees of bleaching. All measurements were made at room temperature and covered the 400 to 1100 m $\mu$  region of the spectrum. Different spectra were obtained for crystals bleached at different temperatures.

Curve I of Figure 17 illustrates a typical spectrum for a crystal bleached at 50°C until no apparent

further bleach occurred. The well known R, M and N bands were developed at this temperature. Curve II shows the spectrum obtained when the same sample was bleached further at 100°C. As before, the R, M and N bands are detectable although flattened considerably. In addition, however, a new band seems evident at about 900  $\mu$ . This band was not observed at 75°C but became even more prominent in crystals bleached at 125° and 150°C as is shown in Figures 18, 20 and 21. At 150°C there seemed to be another new absorption peak appearing at about 960  $\mu$ . Crystals bleached at 75°C showed very weak R bands but had fairly prominent M and N bands as shown in Figure 19 for sample.

Absorption spectra obtained on a crystal at different stages of optical bleach at 100°C are shown in Figure 19. Curves I through V were obtained at 0, 0.5, 1.5, 3, and 12 minutes of bleaching, respectively. It can be seen that the M band forms most rapidly and has nearly reached its maximum after 1.5 minutes. The N band develops rapidly up to about 3 minutes of bleaching after which a broad general absorption band develops between the F band and the N band. Also a slight peak is noted around 900  $\mu$ .

A similar experiment at 150°C again showed a rapid

initial rise in the M band with the eventual formation of the broad R' band noted by Scott and Bupp (9, p. 341-346). An attempt to explain these observations will not be given here, as this work is concerned mainly with the development of more suitable mathematics to describe bleaching processes. They are included only to substantiate the possibility that increased temperature may make a greater number of electron traps available as indicated by the broad absorption bands.

The necessity for a better mathematical description of bleaching than has been available can be illustrated by using results from the theory presented in this work to calculate F center concentrations at different depths within crystal during bleaching. For example, a typical case might be a one mm thick crystal having an initial F center concentration of  $5 \times 10^{16}$  color centers per cc. The initial percent transmission of such a crystal would be about 4.57%. Choosing typical experimental conditions such that  $\alpha = -0.42$ ,  $\lambda = 1.5$ , time measured in minutes and by solving the bleaching equations for these conditions one obtains values for  $I_d$  and  $\epsilon_x$  at various times during bleach such as are listed in Table IV.  $I_d$  is the percent transmission at the back side of the crystal, i.e., after the bleaching light has

TABLE IV

G	$t_{\lambda=1.5}$	$I_d\%$	$\frac{\epsilon_{a'd}}{4}$	$\frac{\epsilon_{a'd}}{2}$	$\frac{\epsilon_{3a'd}}{4}$	$\epsilon_{a'd}$
1.00	0.00	4.57	1.000	1.00	1.00	1.00
0.93	0.091	5.41	0.960	0.979	0.990	0.995
0.81	0.30	6.75	0.890	0.948	0.976	0.986
0.63	0.88	9.25	0.745	0.835	0.911	0.960
0.55	1.42	11.2	0.595	0.700	0.800	0.880
0.45	3.43	12.2	0.491	0.560	0.660	0.775
0.43	5.10	19.6	0.451	0.501	0.572	0.672
0.425	6.20	21.2	0.440	0.475	0.535	0.622
0.421	8.75	24.1	0.425	0.439	0.476	0.538
0.4201	12.4	26.1	0.424	0.425	0.441	0.480

traversed one mm of crystal.  $\epsilon_{a,d}$  is the ratio at depth  $d$  of the F center concentration at any time to the initial F center concentration. Figure 22 shows the F center concentration at various times of bleach as a function of depth in the crystal described here.

A few further simple calculations should serve to illustrate the importance of the concentration gradients which develop during bleaching from nonuniform light absorption. When Smakula's equation is used to calculate F center concentration in the example of Figure 22 at  $t = 3.43$  minutes one obtains a value of  $\epsilon = -.665$  as determined from the percent transmission at the thickness of the crystal, i.e., one mm. However, this is the value of  $\epsilon$  at only one point in the crystal and in this instance it corresponds to a point about 0.75 mm or  $3/4$  of the distance through the crystal. In other words  $3/4$  of the crystal has an F center concentration considerably less than that predicted by Smakula's equation and  $1/4$  has a concentration which is significantly greater. Also by examining curve  $t = 3.43$  in Figure 22 it can be seen that bleaching has nearly reached equilibrium at the crystal face toward the bleaching light source while the bleaching process is only about 50% toward equilibrium at the back side of the crystal. It is apparent that

concentration gradients must be considered whenever bleaching reactions are studied by means of the light transmitted.

Summarizing it is felt that the objectives of this kinetic study have been realized. Differential bleaching equations which include terms for such factors as nonuniformity of bleaching light intensity throughout a crystal, concentration gradients resulting from this, and the concentration of trapping sites other than anion vacancies have been set up in terms of a simple model and solved. Reasonably good agreement between theory and experiment has been achieved which seems to justify at least as a good first approximation the simple model assumed for bleaching. In addition certain predictions for further experiments are obtained from theory. For example, since  $\alpha$  is a function of nonanion vacancy traps, a crystal which had undergone plastic deformation should have smaller negative values of  $\alpha$  than an undeformed sample at any given temperature. Plastic deformation should produce additional traps and such a crystal might be expected to bleach faster. Also a treatment such as has been developed here of concentration gradients in the solid state resulting from irradiation of any type should be useful. Hence it is felt that effort spent on the

present work has been worthwhile in that it has contributed, even if in a minor way, to man's understanding of his surroundings.

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