

STUDIES ON THE THERMAL AND OPTICAL
COAGULATION OF F-CENTERS IN KCl

by

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STUDIES ON THE THERMAL AND OPTICAL COAGULATION OF F-CENTERS IN KCl

I. INTRODUCTION

The first observations on colored alkali halide crystals appear to be the work of Goldstein (4); later work was then done by Pohl (11,12,13), Molnar (7,8), Kleinschrod (5), and Glaser (2) as notable examples, and the theory of color centers in alkali halides has been reviewed comprehensively by Mott and Gurney (9, pp.109-151) and by Seitz (15).

Coloring can be induced in alkali halide crystals by x-ray irradiation or by exposure to an atmosphere of the alkali metal vapor at various temperatures (additive coloring); the resulting color depends on the alkali halide crystal, and the color intensity depends on treatment history factors such as duration of x-ray exposure or temperature employed. KCl, which was used exclusively throughout the experiments undertaken in this work, is colored magenta. The absorption spectrum of additively colored KCl crystals shows a strong absorption peak around 560 m μ wave length which is theoretically considered to be due to an absorbing center consisting of an electron that migrated into the crystal from a surface-adsorbed alkali metal atom and became trapped in a halide ion vacancy (9, pp.111-113)

(15, pp.400-401). This absorbing center is called an F-center (from the German term for color centers "Farbzentren"), and the equilibrium concentration of F-centers in a crystal is related to the concentration of alkali metal atoms in the vapor surrounding the crystal at any given temperature by the formula:

$$n = Cn_v$$

n = number of F-centers per c.c.

n_v = number of alkali metal atoms per c.c. in vapor.

C = a constant which is temperature dependent.

It must be emphasized that the color induced in a crystal depends on the alkali halide employed and not on the alkali metal: KCl colored with Na gives the same absorption spectrum as KCl colored with K.

The concentration of F-centers in a given crystal is determined by applying Smakula's equation to the F-band (wave lengths of light absorbed by the F-centers) (19):

$$nf = \frac{18m}{\pi e^2 h} \frac{n'}{(n'+2)^2} a_m W$$

e, h, m, c = usual atomic constants

f = oscillator strength of absorbing centers

n' = refractive index of crystal

n = number of F-centers per c.c.

a_m = absorption coefficient at center of band

w = width at half maximum of the band

or, for samples too densely colored for determining a_m , F-center concentration might possibly be measured by determining the pH change due to the stoichiometric excess of alkali metal in the crystal (5) (18, pp. 983-984).

When a KCl crystal is quenched rapidly from the temperature of coloring to room temperature, the F-band is quite prominent; but if the crystal is cooled slowly, additional absorption bands appear on the long wave length side of the F-band, and the F-band itself is not so prominent as in a rapidly quenched sample (15, p. 386). If an attempt is made to obtain a large F-center concentration in a KCl crystal by additive coloring, the formation of the absorbing bands at longer wave lengths cannot be avoided even with the most rapid quenching experimentally possible (16, p. 341). Glaser and Lehfeldt (3) observed that irradiation of additively colored KCl crystals for twenty minutes at room temperature was sufficient to cause the

formation of the longer wave length bands and the destruction of all the F-centers. The foregoing processes and longer wave length bands will now be considered in more detail.

Molnar first observed the development of a band (M-band) around 820 mμ in addition to the F-band and an absorption band in the ultraviolet region when KCl was colored by x-rays (7, p.55). This M-band and the F-band were interconvertible by irradiation with light absorbed by the respective bands, but some of the prominence of the F- and M- bands was lost during interconversion and appeared as two new bands at about 675 and 730 mμ; these were called R-bands because of absorption in the red region of the spectrum. Scott and Bupp (16, pp.343-344) found that 85 minutes of white arc irradiation combined with air jet cooling of an additively colored KCl crystal resulted in a noticeable conversion of F- and M- centers to R-centers in accordance with Molnar's work, and that two minutes further treatment without the air jet caused the formation of a broad band, the R'-band, similar to that found by Glaser. The absorption spectrum of additively colored KCl crystals handled in total darkness or under red light and stored in light-tight containers was observed by Scott and Smith to show the M-band, which previously had been thought to occur only in optically treated or illuminated crystals, and in

some cases a quite narrow symmetrical band in the neighborhood of 760 mμ which was termed the "colloidal band" (18, p.982).

Heating an additively colored KCl crystal with a sufficient concentration of F-centers causes conversion of F-centers to the colloidal band. For each temperature of heating there is a concentration of F-centers in equilibrium with the colloidal band which is independent of the original F-center concentration (provided the original F-center concentration exceeds the equilibrium value) (18, pp.985-986). The colloidal band maximum shifts toward longer wave lengths at higher treatment temperatures, and R-bands have not been observed either accompanying the colloidal band nor following its reconversion to the F-band. Scott and Smith found that the attainment of equilibrium in heat treating varied from 90 minutes at 300° to 45 seconds at 500°. They were able to calculate the latent heat for the dissociation of the coagulated F-centers by plotting the logarithm of the equilibrium concentration against $1/T$, and found a value of 8.0 ± 0.3 kcal/mole of F-centers formed at 350°.

Scott and Bupp found the absorption curves of crystals treated by heating alone and by heating combined with irradiation to show considerable difference in the resulting band formation. The irradiation could possibly give

rise to the R-bands which would overlap the colloidal band considerably, but in both cases a pronounced shift in the maximum of the bands in the red region toward longer wave lengths for higher crystal treatment temperatures was observed.

Possible mechanisms for the formation of absorbing centers other than the F-centers are the aggregation of F-centers into larger clumps; the ionization of F-centers and the recapture of the released electron by a different type of trapping center, such as by a pair or a quartet of vacancies; the aggregation of alkali metal atoms dispersed throughout the crystal into colloidal clumps; or a combination of any of the above.

In the aggregation of F-centers into larger clumps, Seitz suggests that the M-center of Molnar is among the first products and may be a F-center attached to a pair of lattice vacancies; he also suggests that the R-centers may be first aggregates of F-centers such as pairs or singly ionized pairs. The shifting of the maximum of the R'-band and the red absorption peak toward longer wave lengths for higher treatment temperatures indicates a change in the nature or relative abundance of absorbing centers composing the band (16, p.344). This shifting is undoubtedly related to the increasing mobility of negative-ion vacancies with temperatures which should lead to the rapid formation of

aggregates containing several F-centers by direct diffusion and combination. Magnetic susceptibility studies on colored KCl crystals are in general consistent with this theoretical picture of F-center aggregation.

The independence of the equilibrium F-center concentration on the initial F-center concentration in crystals which have undergone thermal treatment indicates the presence of two phases (heterogeneous equilibrium); therefore, the absorption band formed during conversion was termed "colloidal". Light scattering experiments have not as yet demonstrated the presence of colloidal particles as was found in the case of a similar band frequently observed in NaCl (6) (14), but the temperature insensitivity of the band shape indicates their presence (18, p.986). The observed shifting of the absorption maximum of the colloidal band can be due to a change in the size distribution of the colloidal centers or to a thermal equilibrium between F- and M- centers.

Consideration of the above phenomena concerning additively colored KCl crystals indicates strongly that much more experimental data is necessary in order to understand better the nature of the various absorbing centers. The variation with temperature of the concentration of F-centers in equilibrium with colloidal centers has been determined by Scott and Smith (18, p.985); but the thermal

rate of conversion of F-centers, the affect of illumination combined with heating on the rate of conversion, and comparison of the results of the two processes were not considered in detail. In view of this, the following experimental procedures were undertaken:

1. A supply of crystals of approximately the same concentration were prepared by coloring additively, and cleaved as thin as possible. These cleaved crystal sections were mounted individually in a temperature controlled furnace in such a manner that monochromatic light of 560 mμ wave length could be directed alternately through a small aperture in the furnace, and through the aperture and crystal both so that percentage transmission of the light beam by the crystal could be measured at intervals with the aid of a photomultiplier tube and a shunted microammeter; this gave indirectly the rate of change of F-center concentration with time. From this experimental data the reaction order for the conversion of F-centers to colloidal centers, the velocity constant at several temperatures, and the activation energy were calculated.

2. The above heating was combined with strong illumination of the crystal with 560 mμ light from a filtered arc source in order to determine what affect this illumination would have on the rate of conversion of F- to colloidal centers. The order of the reaction and velocity

constant at several temperatures were determined and compared with those found for heating alone.

3. The absorption spectra for crystals which had undergone treatment in 1 and 2 were compared for any noticeable differences.

4. Cleaved crystals, A and B, adjacent to a sensitive thermocouple were illuminated at room temperature with:

A = 560 mμ wave length light

B = white light

from a carbon arc. The results were compared to determine whether conversion was due to an ionization process caused by absorption of the 560 mμ wave length light, or was mainly due to some process induced by the heating of the crystal with infra red radiations from the arc.

II. EXPERIMENTAL

CRYSTAL PREPARATION. All crystals were prepared by placing KCl stock wrapped in copper foil in the end of a sealed copper tube with a piece of metallic sodium at the other end. Sodium was used in preference to potassium metal because its lower vapor pressure resulted in a more uniformly colored crystal batch in shorter treatment time. This copper bomb was placed in a muffle furnace for 23 hours at 550° and then rapidly quenched by plunging into ice water. The resulting additively colored crystals averaged 1.5×10^{17} F-centers/c.c., and were handled or exposed only under a ruby safelight. The colored crystals, with dimensions about 0.25 by 0.25 by 1.25 cm., were cleaved with a razor blade into sections as thin as possible; only those sections with parallel and unmarred faces were used for the experiments. Any crystal which showed evidence of excessive bleaching around the edges during or at the completion of a run was not used in tabulating results.

APPARATUS. The apparatus used in the experiments is shown in Plate 1, and consists mainly of the following:

1. Thermostated furnace
2. Crystal holder
3. Monochromator
4. Photomultiplier circuit
5. Filtered carbon arc

1. Thermostated furnace: The furnace consisted of an iron pipe 4 inches long and $1\frac{1}{4}$ inches in diameter; this was wrapped with asbestos paper and ten feet of No. 24 Nichrome wire. A brass tube $1/2$ inch in diameter and fitted with a brass plug was inserted into one end of the iron pipe. A small hole, which acted as an exit aperture for light from the monochromator to pass through the furnace to the phototube, was drilled through the center of the brass plug. The furnace was mounted horizontally in a rigid plasterboard support, and a thermocouple, consisting of ten inches of Copnic wire, was inserted into the furnace through a small hole in the side. The tip of the thermocouple protruded beyond the furnace wall only $1/8$ inch, so that it did not obstruct light from the monochromator. Melting ice was used for the thermocouple cold junction, and temperature was measured by placing the bulb of a Centigrade thermometer at the position in the furnace where the crystal would be and noting the scale reading on a millivoltmeter for a given temperature. Temperature was controlled manually with a Variac transformer, and was maintained constant within ten degrees for the highest temperatures employed. Experiment indicated that heating the furnace twenty degrees above the desired temperature before inserting the cool metal crystal holder would compensate for the resulting temperature drop. The thermocouple was removable

from the furnace for measuring the heating effect of filtered and unfiltered arc light on the crystals; for this purpose it was calibrated against the freezing point and boiling point of water, and gave a scale reading of 0.788 divisions per degree on a millivoltmeter.

2. Crystal holder: The crystal holder consisted of an iron pipe, 1 inch in outer diameter and $2\frac{1}{2}$ inches long, with one end machined to fit snugly into the open end of the furnace. A metal rod $5\frac{1}{2}$ inches in length was fastened on the inside of the pipe parallel to the axis in such a manner that the rod could be turned by means of a perpendicular brass screw attached to the end projecting outside the furnace. The end of the metal rod extending into the furnace held a piece of U-shaped iron which acted as a clamp in holding the crystal by its edges. The crystal holder was anchored into the furnace by means of a notched brass strip attached to the furnace base and hinged in such a manner that it could be swung over the outer lip of the crystal holder pipe and screwed tight. With this holder (shown in Plate 2), the crystal could be swung back and forth in front of the small light aperture leading to the photomultiplier tube. A heat resistant cement consisting of litharge and water glass was used to keep the crystal rigid in the metal clamp, and an adjustable metal stop was set up outside the furnace so that the

metal rod could be turned only until the crystal was centered in front of the light aperture.

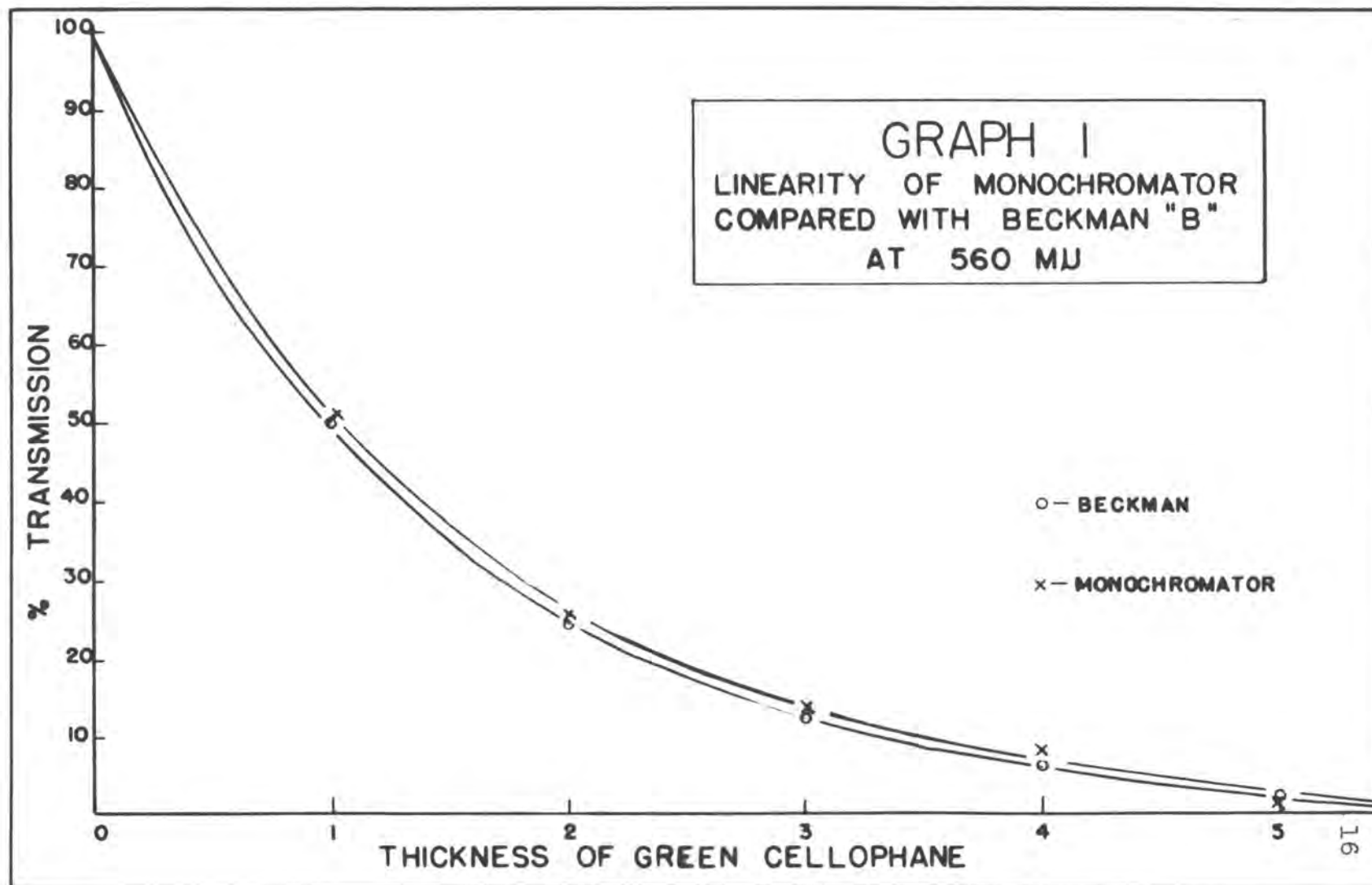
3. Monochromator: The monochromator was of glass prism design in order that it could be modified to transmit some other wave length besides 560 mμ at a later date. As shown in Plate 1, it was a conventional prism arrangement consisting of a light source, entrance slit, condensing lens, prism, focusing lens, and exit slit. A 100 watt projector lamp operated at 80 percent maximum power in order to cut down fluctuation effects was used as a light source. The entrance slit consisted of two razor blades; enough light passed through this slit to cover, after being condensed, about eighty percent of one face of the glass prism. The glass prism was mounted on a small brass turntable which could be rotated in either direction by means of a geared condenser knob as illustrated in Plate 3. A scale around the side of the condenser knob was convenient for assigning knob positions to various wave lengths. The refracted light leaving the prism passed through the focusing lens, and an exit slit consisting of two razor blade edges mounted at an inward angle of about sixty degrees on a metal plate was rigidly fixed at the focal point of the lens. The above mechanism, except for the exit slit, was enclosed in a box painted black on the inside to cut down reflection. The completed monochromator was permanently

placed in a position which allowed light of about 560 mμ to pass through the exit slit at minimum deviation by the glass prism. The spectrum was 1.36 cm. wide, and the exit slit was 0.004 cm. wide. Since the visible spectrum covered about 400 mμ from the violet to the red, a wave length band of about 2 mμ was isolated if dispersion of light by the prism were perfect. The 560 mμ wave length was picked out on the condenser knob by comparing the absorption curves found with the model B Beckman spectrophotometer for a two percent solution of CuCl_2 in ethyl alcohol and an actual additively colored KCl crystal with absorption curves found for the same materials with the monochromator.

4. Photomultiplier circuit: A RCA No. 931-A multiplier phototube with an S4 response was placed in the path of the light passing through the furnace aperture, and was operated by means of a 900 volt battery supply in the circuit shown in Plate 4. Resistances 1 to 9 were each 70,000 ohms, and 10 was 50,000 ohms. They were all wire wound, precision type resistors of high ohm value in order to cut down battery drain and help insure good linearity of the phototube output. The phototube was placed approximately ten inches from the furnace in order to cut down heating effects, and stray light was eliminated by enclosing the tube in a wooden box and operating the apparatus in a

darkened room. The phototube output was measured with a microammeter in parallel with a 50,000 ohm potentiometer, and one hundred percent transmission was measured by adjusting the potentiometer shunt to read full scale on the ammeter. The linearity of the phototube output was checked by comparing the curves obtained at 560 mμ with the Beckman model B spectrophotometer and with the monochromator for a varying number of thicknesses of a green cellophane and a Kodak Wratten filter No. 82 (Graph 1 shows the curves for the green cellophane). The results indicated that the monochromator and phototube output gave approximately the same linearity as the Beckman model B.

5. Filtered carbon arc: For illumination experiments with light of 560 mμ wave length, a carbon arc fitted with a condensing lens was arranged to one side of the furnace in such a manner that the condensed arc light beam could be reflected by a mirror arrangement into the furnace opening and onto the crystal. By proper shielding, the arc was operated continuously during the progress of a run, and the arc beam could be cut off from the furnace when it was necessary to take an absorption reading. A circular filter holder, with an extra aperture for allowing passage of the monochromator beam, was set up in front of the furnace opening and could be rotated for selection of the proper filter. The 560 mμ wave length was isolated by



using a Kodak Wratten filter No. 74 in conjunction with a cell about 2 cm. thick, composed of a metal ring and two glass plates, containing a $2\frac{1}{2}$ percent aqueous solution of CuCl_2 and utilizing a high vacuum silicone grease as a cementing agent. The CuCl_2 solution filtered out infra-red light, and the No. 74 Wratten filter transmitted light around the 560 m μ wave length. The two filters together transmitted approximately ten percent of the 560 m μ wave length present in the unfiltered beam. The approximate radiation flux density of the condensed arc light beam at a distance of two meters from the mirror reflecting the light into the furnace opening was found by comparison with a lamp of known flux density (calibrated by the Bureau of Standards) to be 18×10^{-2} watts per cm 2 .

EXPERIMENTAL PROCEDURE. The preparation and selection of crystals has already been explained. After the furnace reached the desired temperature, the crystal holder with the mounted crystal was inserted, and transmission readings were taken at appropriate time intervals. For thermal experiments without illumination, runs were made at 250, 275, 300, and 350 deg. C. Enough runs were made at each temperature so that the three which approximated the same curve with little or no apparent bleaching could be selected. The temperatures chosen for heating

combined with illumination were room temperature (25°), 100, 250, 275, and 300 deg. C.: The increase in conversion rate found in preliminary experiments involving combined heating and illumination, and the desire to determine the heating effect of the arc light on the crystals at room temperature were the determining factors in selecting these particular temperatures.

The experiments at room temperature were made with the crystal mounted on a $1/2$ by $1/2$ by 2 inch holder which would fit into the cell holder of the Beckman model B spectrophotometer. With this arrangement a thermocouple could be held next to the crystal for measuring small temperature changes during illumination, and conversion of the F-band could be determined by transferring the crystal holder to the Beckman model B.

The exact procedure followed in measuring percentage transmission with a crystal in the furnace was as follows:

1. The monochromator lamp and phototube circuit were allowed to warm up previous to taking a reading.
2. With the crystal swung out of the path of the light passing through the furnace aperture, and with the arc shielded (if operating) and arc filters rotated out of the light path, one hundred percent transmission was measured by adjusting the potentiometer shunt until the micro-

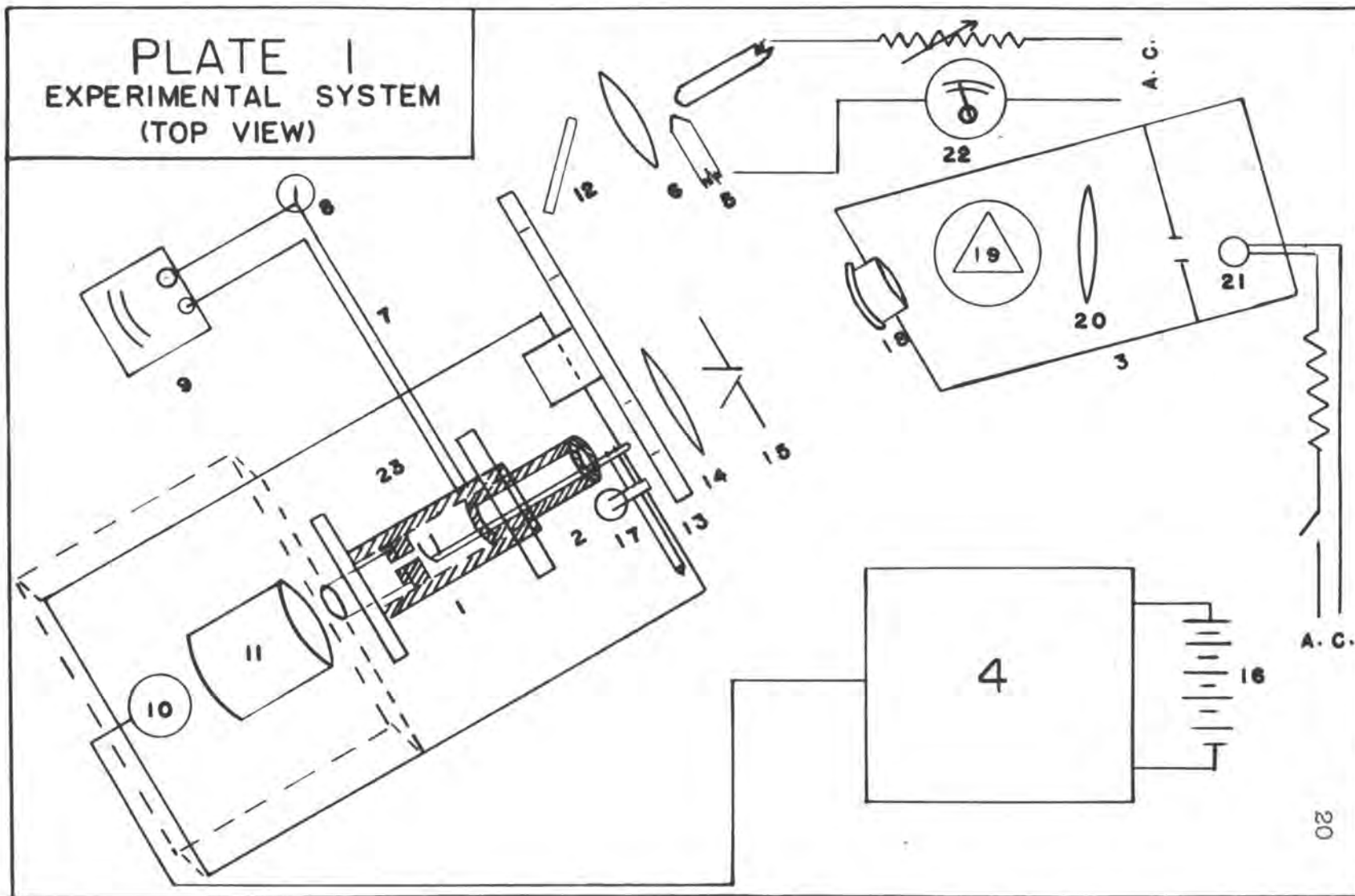
ammeter scale read 50 microamperes. Dark current was compensated for by:

- A - Measuring 100 percent transmission,
- B - turning off monochromator lamp,
- C - adjusting the ammeter needle to read zero transmission,
- D - repeating the above procedure until, when the monochromator lamp was turned off, the ammeter reading would fall from 100 percent transmission to zero transmission without requiring needle adjustment.

3. The crystal was swung into the path of the light and sample transmission was read.

4. In order to cut down errors due to current fluctuations in the various circuits, a reading required after a certain time interval (say, for example, five minutes) would be obtained by starting to take readings $1/2$ minute before the desired time ($4\frac{1}{2}$ minutes), and continuing to take readings until $1/2$ minute past the desired time ($5\frac{1}{2}$ minutes). The values obtained should give a smooth curve through the one minute interval if there were no serious current fluctuations, and the midpoint of the curve would give the desired value.

PLATE I
EXPERIMENTAL SYSTEM
(TOP VIEW)



III. LEGEND (PLATE 1)

1. Thermostated furnace
2. Crystal holder
3. Monochromator
4. Photomultiplier circuit
5. Carbon arc
6. Condensing lens
7. Thermocouple
8. Ice junction of thermocouple
9. Millivoltmeter
10. Photomultiplier tube
11. Extraneous light shield
12. Mirror
13. Circular filter holder
14. Focusing lens
15. Exit slit
16. 900 volt battery supply
17. Crystal rotator stop
18. Focusing lens
19. Glass prism
20. Condensing lens
21. Monochromator light
22. A.C. ammeter for arc

PLATE 2
CRYSTAL HOLDER

22

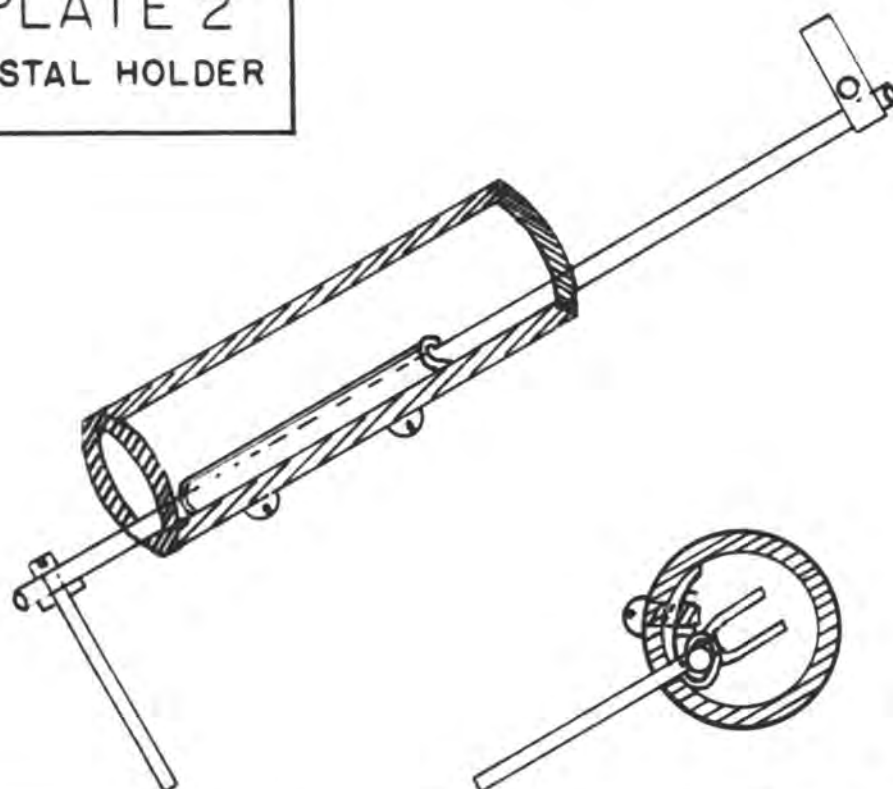


PLATE 3
PRISM MECHANISM

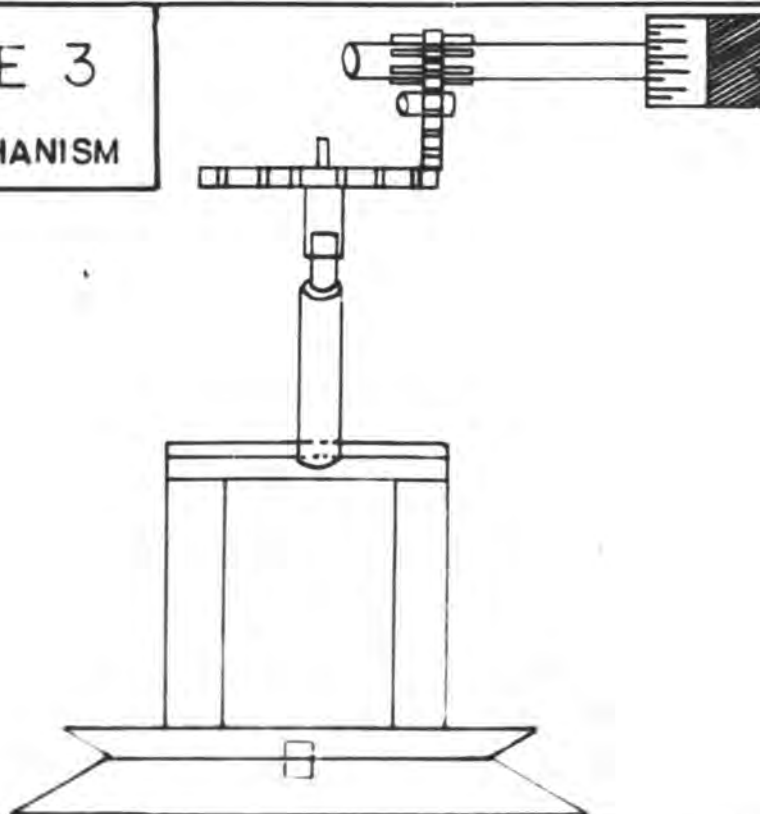
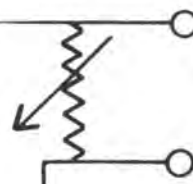
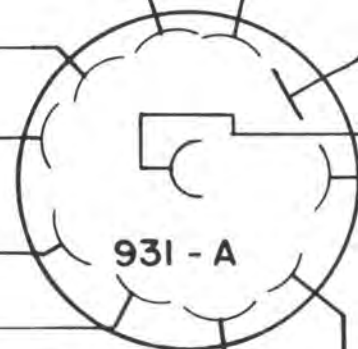


PLATE 4

PHOTOMULTIPLIER CIRCUIT

900 VOLTS



23

IV. CALCULATION OF RESULTS

The F-center concentration was determined by applying Smakula's equation to transmission data. This equation, using modern values for the physical constants involved reduced to:

$$n = (1.095 \times 10^{16}) (0.39) a_m$$

where the oscillator strength has been assumed to be unity because of lack of evidence supporting Kleinschrod's value of 0.81 (18, p.984). Since no systematic study of the dependence of W on temperature at temperatures much above 25° has been made, it was assumed to be 0.39 for all calculations, inasmuch as this represents the best estimated value in the neighborhood of 300°. This estimation was based on previous measurements of W at room temperature and at -195° (16, p.342) (18, p.984).

The absorption coefficient at the F-band maximum was determined by inserting the transmission data into the optical density formula:

$$2.303 \log \frac{I}{I_0} = a_m d$$

d = crystal thickness in cm.

The crystal thickness was measured microscopically with a calibrated eyepiece micrometer.

The energy of activation was found graphically by applying a form of Arrhenius's equation:

$$\text{Log } k = \frac{-H_a}{2.303R} \times \frac{1}{T} + C$$

k = velocity constant

H_a = activation energy

T = absolute temperature

V. ANALYSIS OF ERROR

SPECTROPHOTOMETER. The fluctuations of current through the light source were great enough to cause transmission readings to vary by plus or minus five percent. This error was largely eliminated by taking readings in the manner explained previously. Since a number of points were used in plotting the necessary curves, the remaining error probably cancelled itself and was certainly not greater than about 2 percent. The narrow band of wavelengths passed by the exit slit, and an examination of Graph 1, indicate that negligible error was introduced by incomplete resolution of the spectrum.

READING PERCENT TRANSMISSION AND CALCULATING a_m .

The relative error in I/I_0 was greater for the initial absorption readings when the F-center concentration was of maximum value, and for crystals with the greatest thickness. The average crystal thickness was around 0.065 cm., and the error in determining the crystal thickness was negligible compared to other error sources. The average error in measuring absorbancy, based on twenty-five percent transmission as the average mid-value for a run, was about one percent. The plotting of a large number of points would tend to cancel errors in reading I/I_0 .

TEMPERATURE CONTROL. Temperature variation was discussed previously. The ten degree temperature variation and the one percent error in reading percent transmission carried approximately equal weight in contributing to the error in determining the energy of activation.

REPRODUCIBILITY OF CRYSTAL PLACEMENT. The F-center concentration for any given crystal could vary as much as fifty percent throughout the crystal section; this made it necessary to be able to return the crystal to exactly the same position in front of the furnace aperture throughout the course of a run. The reproducibility of crystal positioning was checked by flipping a crystal back and forth in front of the aperture at room temperature a number of times, and observing whether it gave the same light transmission reading on the microammeter (resetting 100 percent transmission each time). Transmission on repositioning the crystal was found reproducible within one percent.

CRYSTAL BLEACHING. Although the crystals were examined carefully before and after a run for cracks and bleaching, and only those which showed little or no bleaching were used in calculations, it is not known definitely whether any significant bleaching occurred at the faces of the crystals, though microscopic examination of the faces indicated none.

SMAKULA EQUATION. The errors involved in using Smakula's equation are systematic, affect all concentrations about the same way, and depend on the choice of method for arriving at a_m and W . Scott and Smith found by inspection of the curves showing both F- and colloidal bands that the uncertainty in the choice of the 560 mμ absorption, rather than some other neighboring value, as the proper basis for a_m calculation could introduce an error as high as ten percent in crystals showing greatest overlapping. Since overlapping was not serious for most of the runs made, the overall probably systematic error was 5-7 percent. The value for W , being determined on the basis of an average of a large number of measurements, introduced negligible error.

The largest probable error is therefore introduced into the results by the Smakula equation itself, with most of the other errors being negligible for graphing purposes or indeterminate.

VI. DISCUSSION OF RESULTS

The main purpose of the experiments undertaken was to determine if there are any apparent differences in the conversion of F-centers thermally, and the conversion of F-centers by thermal and optical treatment combined. The experimental results will be classified as room-temperature experiments, thermal experiments, and thermal experiments combined with illumination for discussion purposes.

ROOM-TEMPERATURE EXPERIMENTS. Graph No. 7 shows the change in percentage transmission of the F-band with time during white arc light and 560 mμ illumination at 25°. It is quite apparent that the white arc light illumination gave much more rapid conversion of F-centers in comparison with the rate of conversion induced by 560 mμ illumination. This increase in rate with white arc light could be due to absorption processes occurring at wave lengths of light other than 560 mμ or infra red wave lengths, heating of the crystal by absorption of infra red radiations, or to an increase in the intensity of the 560 mμ light striking the crystal because of the absence of filters. Thermocouple measurements of crystal temperature indicated that heating of crystals illuminated with white light was around nine degrees above room temperature, and the heating of crystals illuminated with light of 560 mμ wave length was negligible;

also, it was stated in the discussion of the apparatus that the filters used to isolate the 560 mμ wave length in the arc beam transmitted approximately ten percent of the desired light. The increase in the rate of conversion of F-centers could not possibly be due to the small temperature rise during illumination, but the combination of a temperature change and an increase in illumination intensity could explain it unless the presence of other wave lengths in the white arc light were influencing the conversion rate. This possibility was checked by comparing the absorption curves of crystals treated with white arc light and light of 560 mμ wave length at 100°. (This temperature was chosen in order to obtain conversion with 560 mμ light within a reasonable length of time.) The differences are shown in Graph No. 3, and outside of a loss of prominence of the M-band at 820 mμ (in accordance with the work of Glaser and of Scott and Bupp) and a greater loss of F-centers with white light illumination, there are no salient differences in the two absorption curves. It could therefore be reasoned that the conversion of F-centers by arc illumination is a function of the 560 mμ wave length intensity, and of heating of the crystal by infra red absorption.

THERMAL EXPERIMENTS. Graphs 8, 9, 11, 13, and 15 show the changes in F-center concentrations with time for

crystals held at various temperatures in the furnace; it is apparent from the curves that the thermal conversion rate increases with an increase in temperature. The noticeable leveling of the curves within several minutes for conversion at 350° is due to the higher equilibrium concentration of F-centers at this temperature, and the rapidity with which equilibrium is reached. Graphs 16-A and 16-B show the first order plots for these conversion curves, and Graphs 17-A, 17-B, 17-C, and 17-D are second order plots. By comparing the two sets of reaction order plots, one may conclude that the reaction is more nearly second order than first, though the distinction is not clear-cut.

Values for the velocity constant k , calculated from the slopes of the second order curves, are given in the following table:

TABLE 1.

$$k \times 10^{19} (\text{c.c.}) (\text{F-centers})^{-1} (\text{min})^{-1}$$

Temp.	250°	275°	300°	350°
1	.938	1.08	1.55	3.24
2	.89	1.14	2.1	4.0
3	.82	0.8	2.09	2.5
Ave.	.882	1.01	1.91	3.58

The log of these average values for k are plotted against the reciprocal of the absolute temperature in Graph No. 19, and the energy of activation for the thermal conversion of F-centers was found from the slope to be 8.7 ± 1.2 kcal/mole of F-centers.

THERMAL EXPERIMENTS COMBINED WITH ILLUMINATION.

Graphs 8, 10, 12, and 14 show the rates of change of F-center concentration with time for thermal plus 560 m μ illumination treatment of colored KCl crystals. Graph No. 8 indicates that at 100° the rate is quite measurable, but the others show that a considerable portion of the reaction has taken place within the first three minutes. The graphs were plotted with the same abscissas as were used for graphs at corresponding temperatures without illumination in order to compare the rates more easily. It is quite evident that illumination accelerates the reaction considerably, or makes possible another mechanism (or mechanisms) for the conversion processes.

The determination of the order of the reaction with illumination leaves much to be desired. Since the reaction was quite rapid at the temperatures involved, a revision of the present apparatus with the intention of measuring transmission at a much faster rate while continuously illuminating the crystal would be necessary in order to obtain any reasonably precise data. Graphs 18-A,

18-B, 18-C, and 18-D show that, after the first three minutes of illumination, the reaction approximates second order fairly well. Numerical calculation of the reaction order from the curves for the conversion of F-centers during illumination at 100° gave values of from fifth to sixth order, but these are to be considered lightly in view of the experimental error. The slopes of the dotted lines through the points for the first three minutes of F-center conversion on the second order plots are given in Table 2.

TABLE 2.

$$k \times 10^{19} (\text{c.c.}) (\text{F-centers})^{-1} (\text{min})^{-1}$$

Temp.	100°	250°	275°	300°
1	6.9	26	12	10.4
2	5.9	12	8.8	6.2
3	<u>4.9</u>	<u>12</u>	<u>8.7</u>	<u>4.9</u>
Ave.	5.9	16	9.8	7.0

It is apparent that this data is of little significance aside from its showing a greater value for k than similar runs without illumination.

It might be possible that the conversion of F-centers by illumination with light of 560 mμ wave length is governed by a mechanism different from that causing conversion by thermal treatment alone, and it might be possible that

the reaction caused by illumination is completed within the three minute period not conforming to the second order plot of the reaction curves; if this were the case, the solid line plots in the second order reaction graphs should yield the same values of k as were obtained from the corresponding plots without illumination. Examination of Table 3 shows that this does not seem to be the case.

TABLE 3.

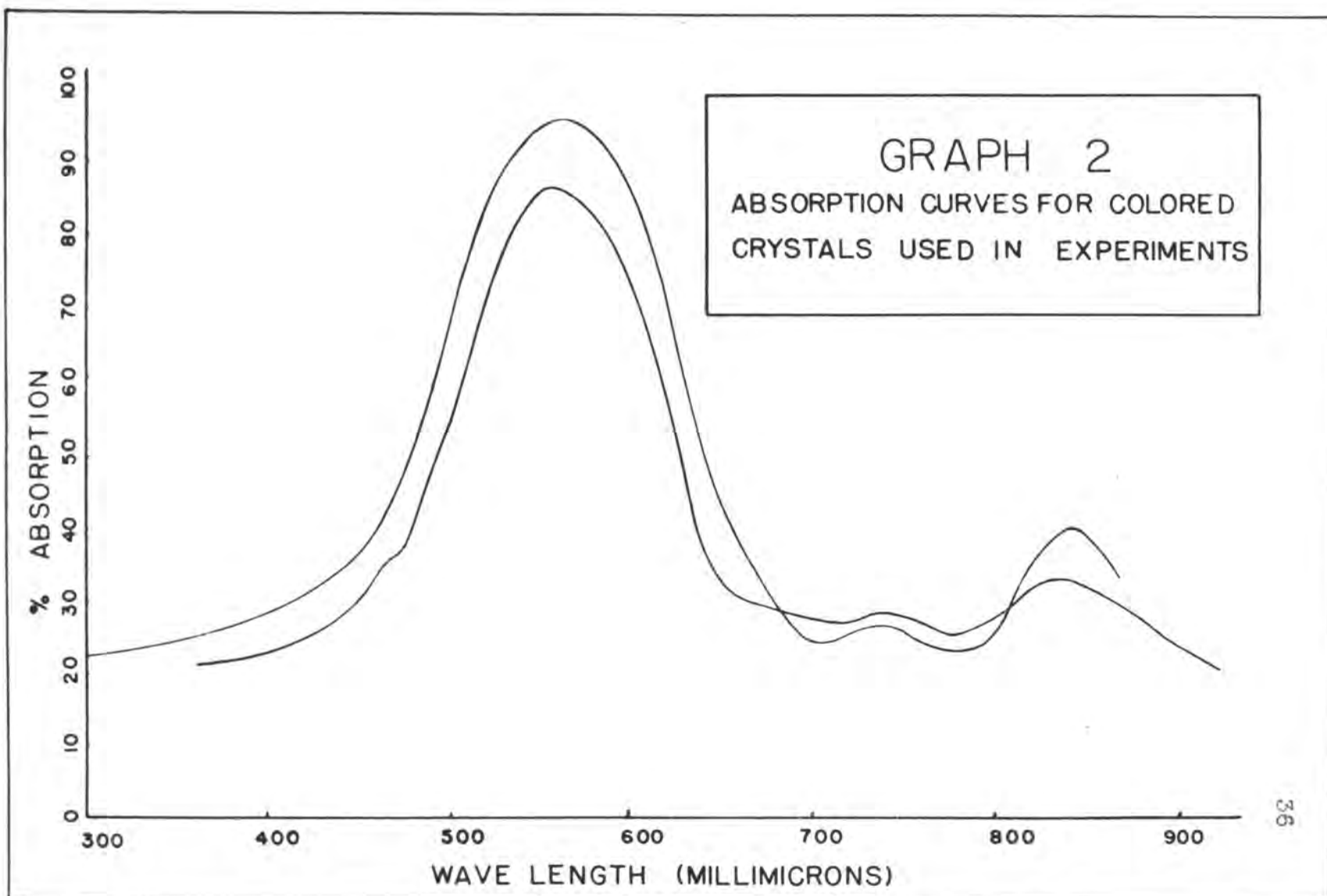
$$k \times 10^{19} (\text{c.c.}) (\text{F-centers})^{-1} (\text{min})^{-1}$$

Temp.	250°	275°	300°
1	5	2.2	.77
2	11	2.2	.73
3	5	1.8	.80
Ave.	7	2.1	.74

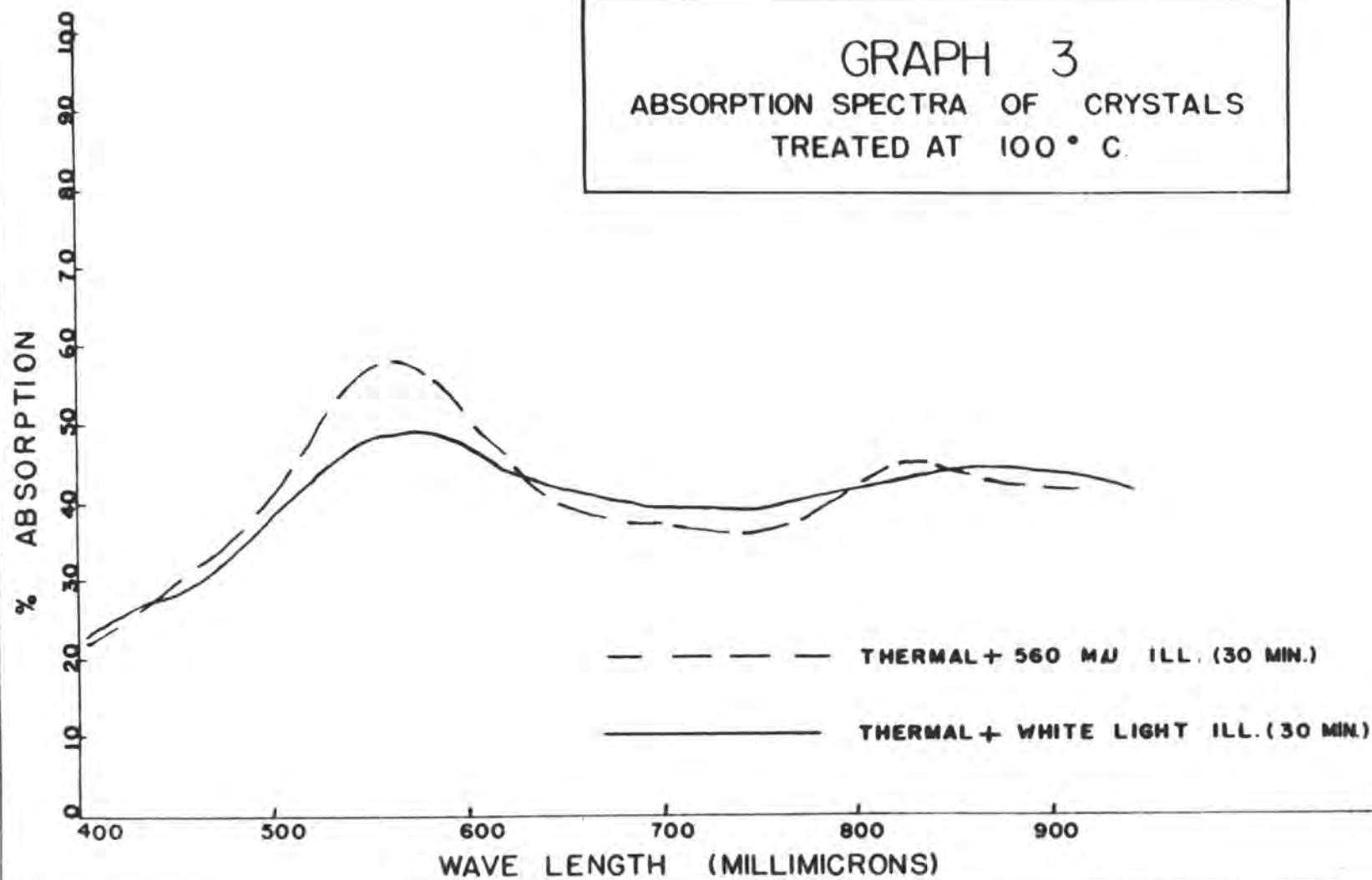
The negative temperature coefficient for the rate constant during the later stages of the conversion is a strong indication that the formation of colloid has been completed during the rapid initial stages, and that the later stages consist of a solely optical conversion of F-centers to R-centers. If R centers decrease in stability with increasing temperature, the negative temperature coefficient is readily explained.

COMPARISON OF THERMAL AND THERMAL-PLUS-ILLUMINATION EXPERIMENTS. Graphs 4, 5, and 6 show representative absorption curves of crystals after thermal, and thermal plus optical treatment. The treatment times for thermal conversion were in all cases longer than for combined treatment, and no attempt was made to compare crystals that had undergone approximately the same amount of conversion. The treatment times given represent the intervals after which the conversion of F-centers was practically complete. The only pronounced differences appear to be the shifting of the absorption peak between 600 and 800 μ toward shorter wave lengths (which is probably due to the formation of R-bands along with the colloidal band) and diminished prominence of the M-band (possibly due to transmission of light of 820 μ wave length by the filters, or masking of the M-band by other band formation). Also, the height of the absorption peak between 600 and 800 μ is greater in each case for the crystals which had undergone combined treatment; considering the differences in treatment times, this is probably due to the increase in F-center conversion rate with illumination.

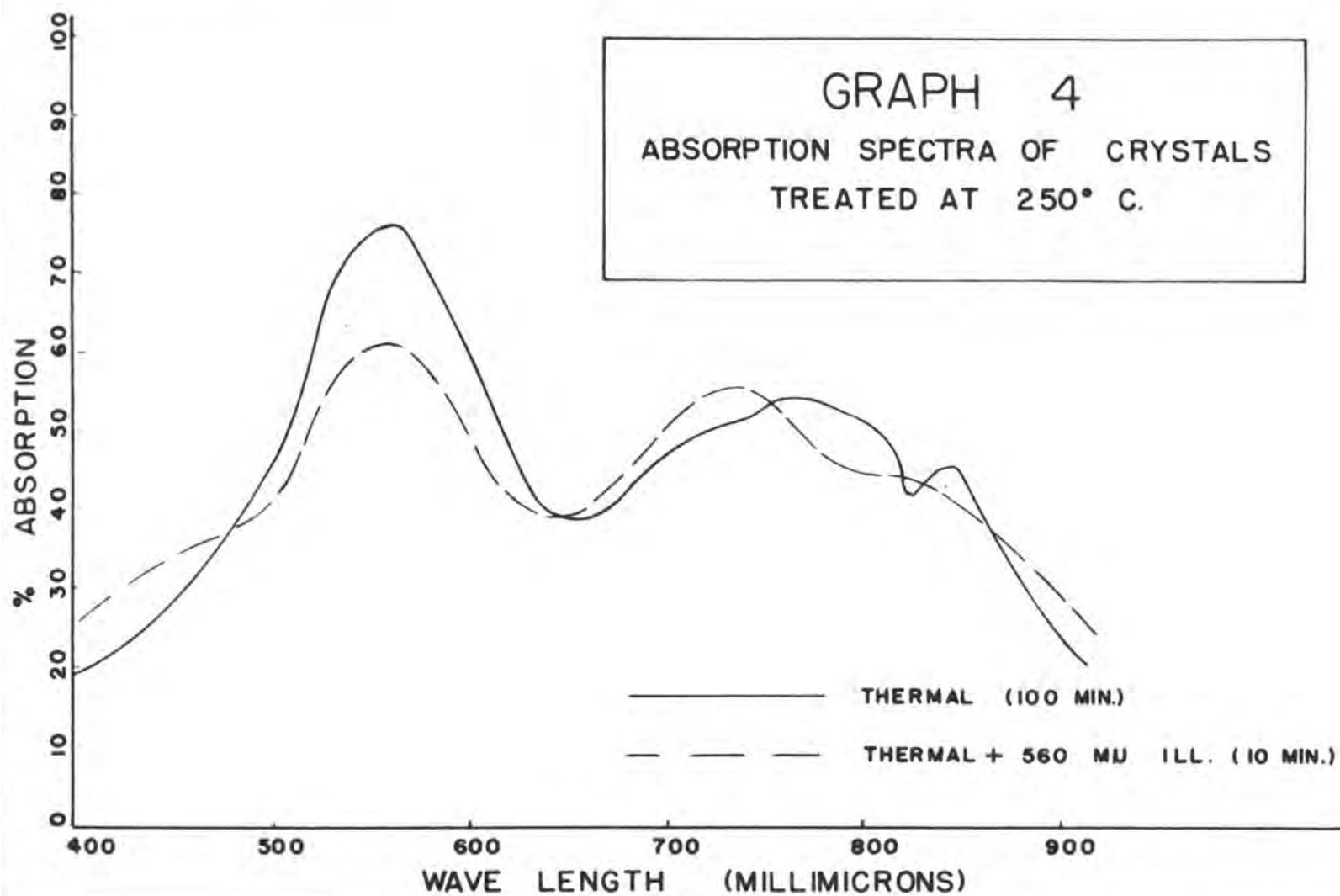
A possible explanation for the increased conversion rate of F-centers with illumination is that the absorption of the 560 μ wave length light ejects electrons into the conduction level bands; the released electrons can migrate



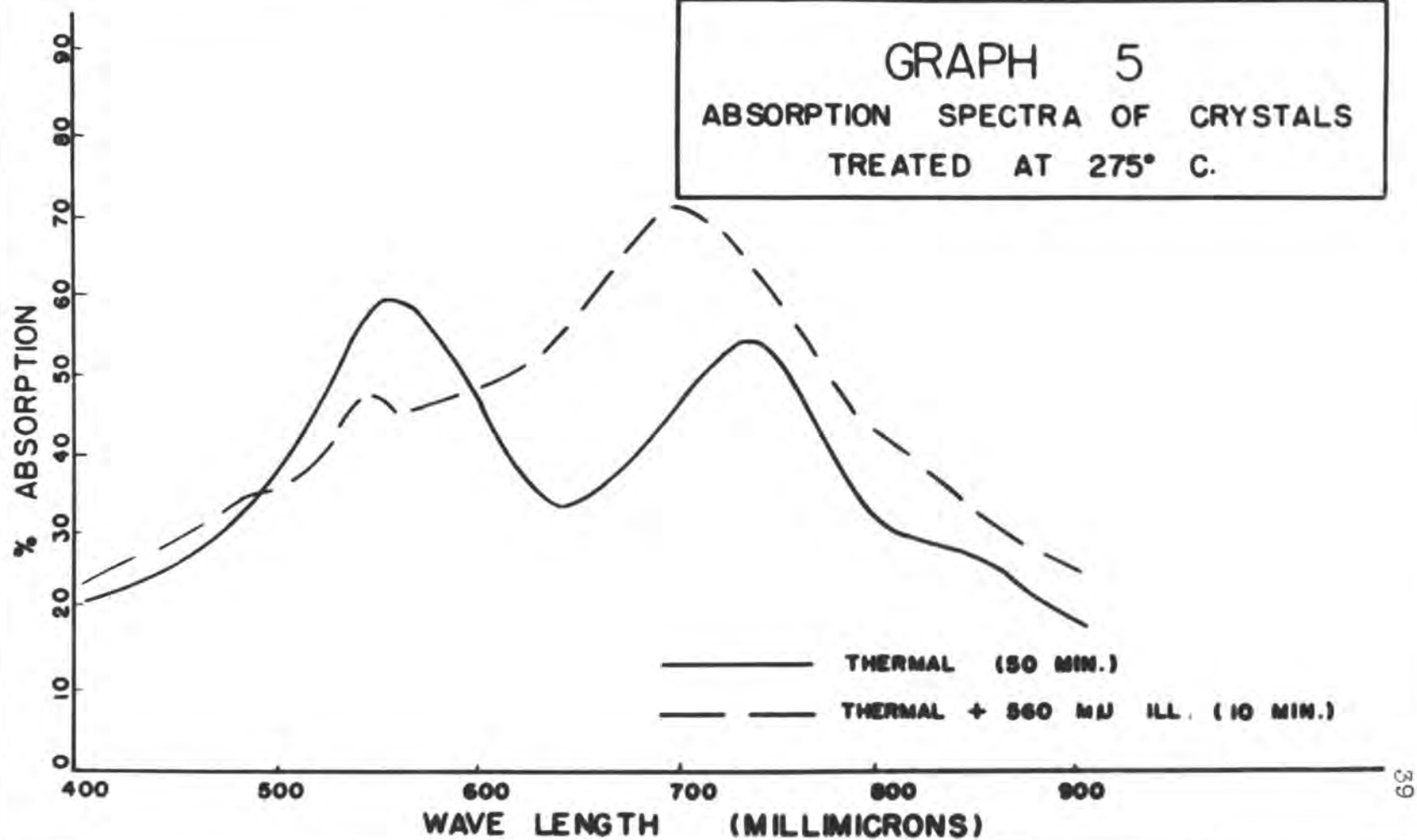
GRAPH 3
ABSORPTION SPECTRA OF CRYSTALS
TREATED AT 100° C.



GRAPH 4
ABSORPTION SPECTRA OF CRYSTALS
TREATED AT 250° C.

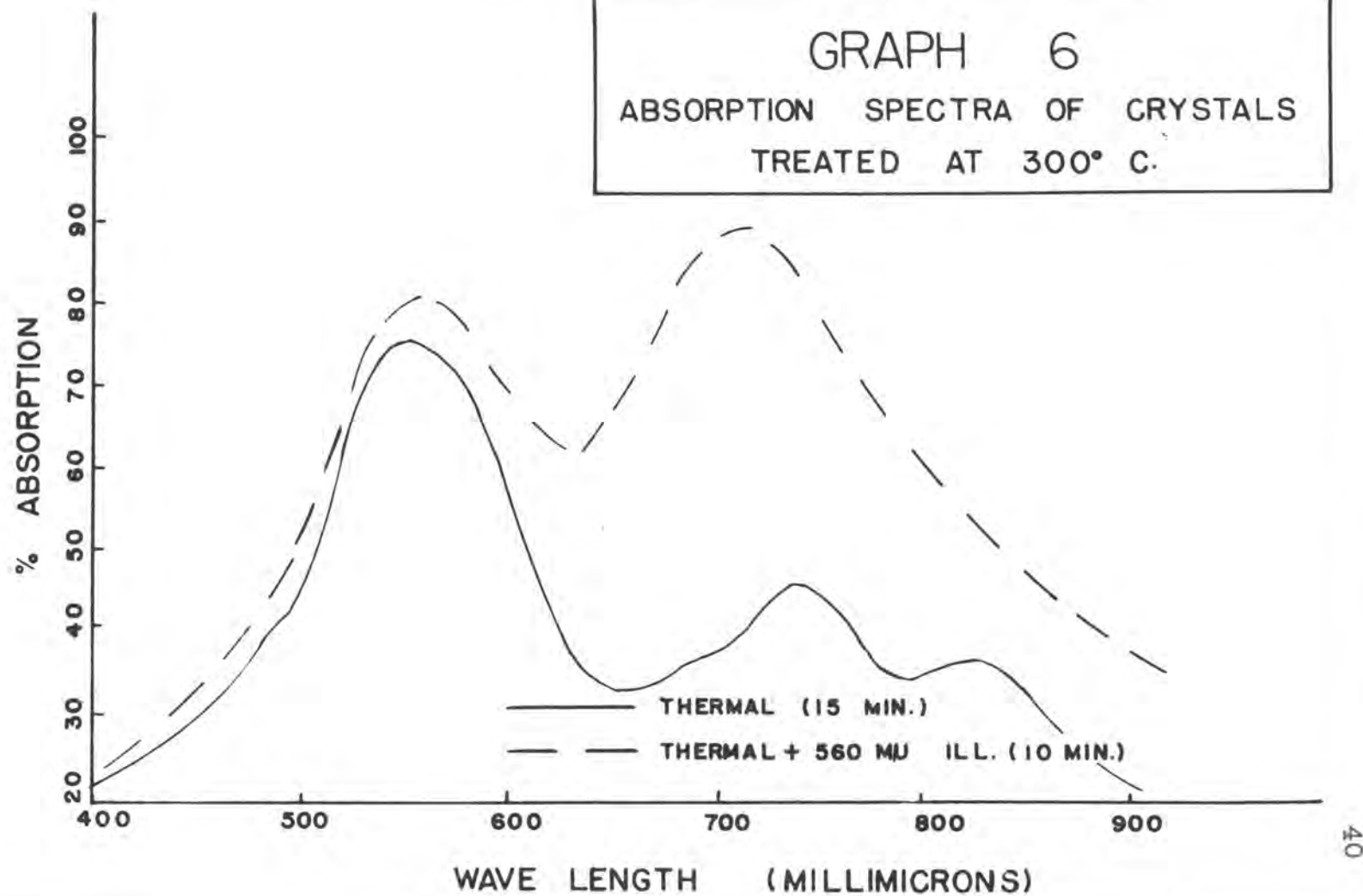


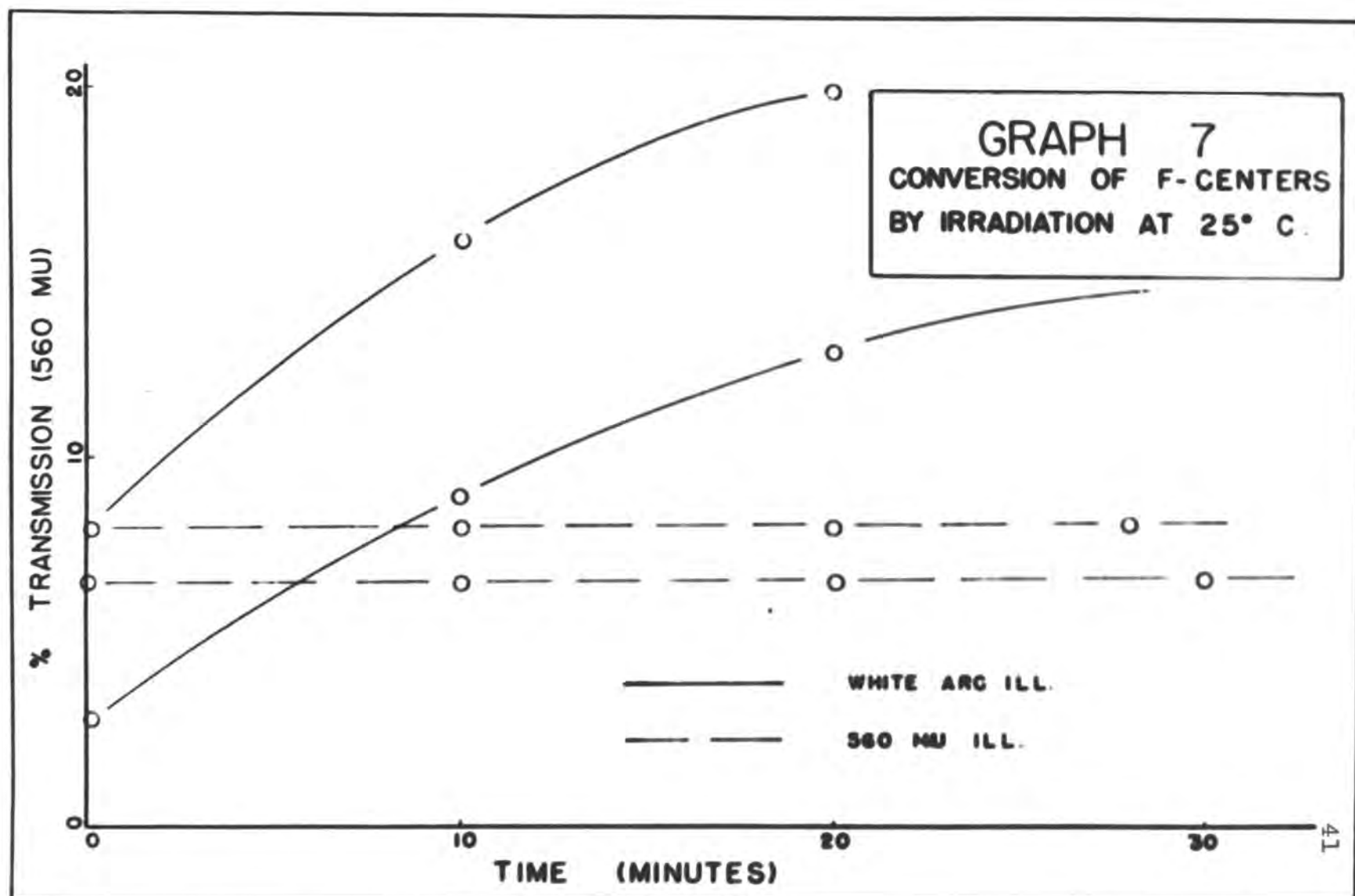
GRAPH 5
ABSORPTION SPECTRA OF CRYSTALS
TREATED AT 275° C.



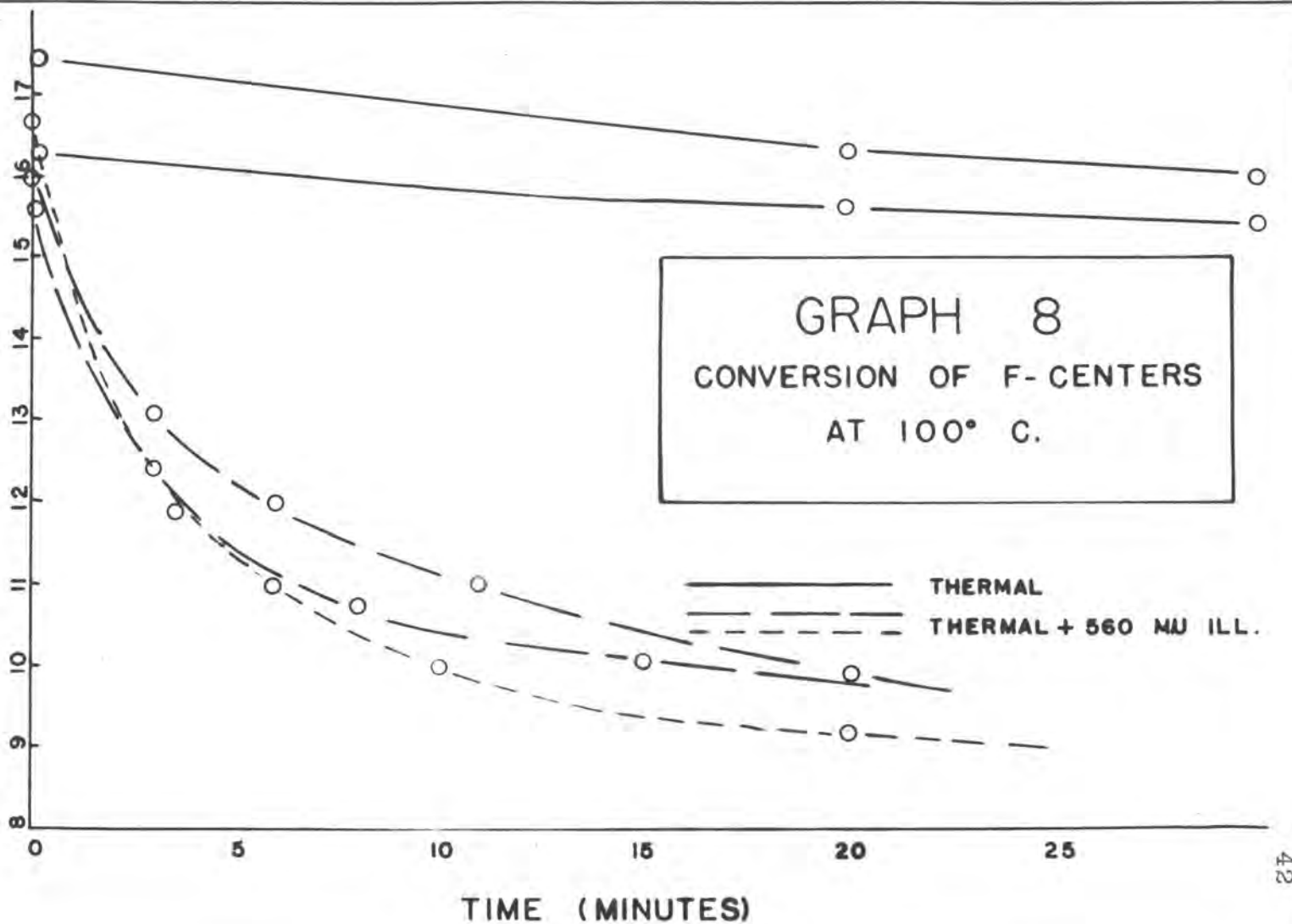
GRAPH 6

ABSORPTION SPECTRA OF CRYSTALS
TREATED AT 300° C.



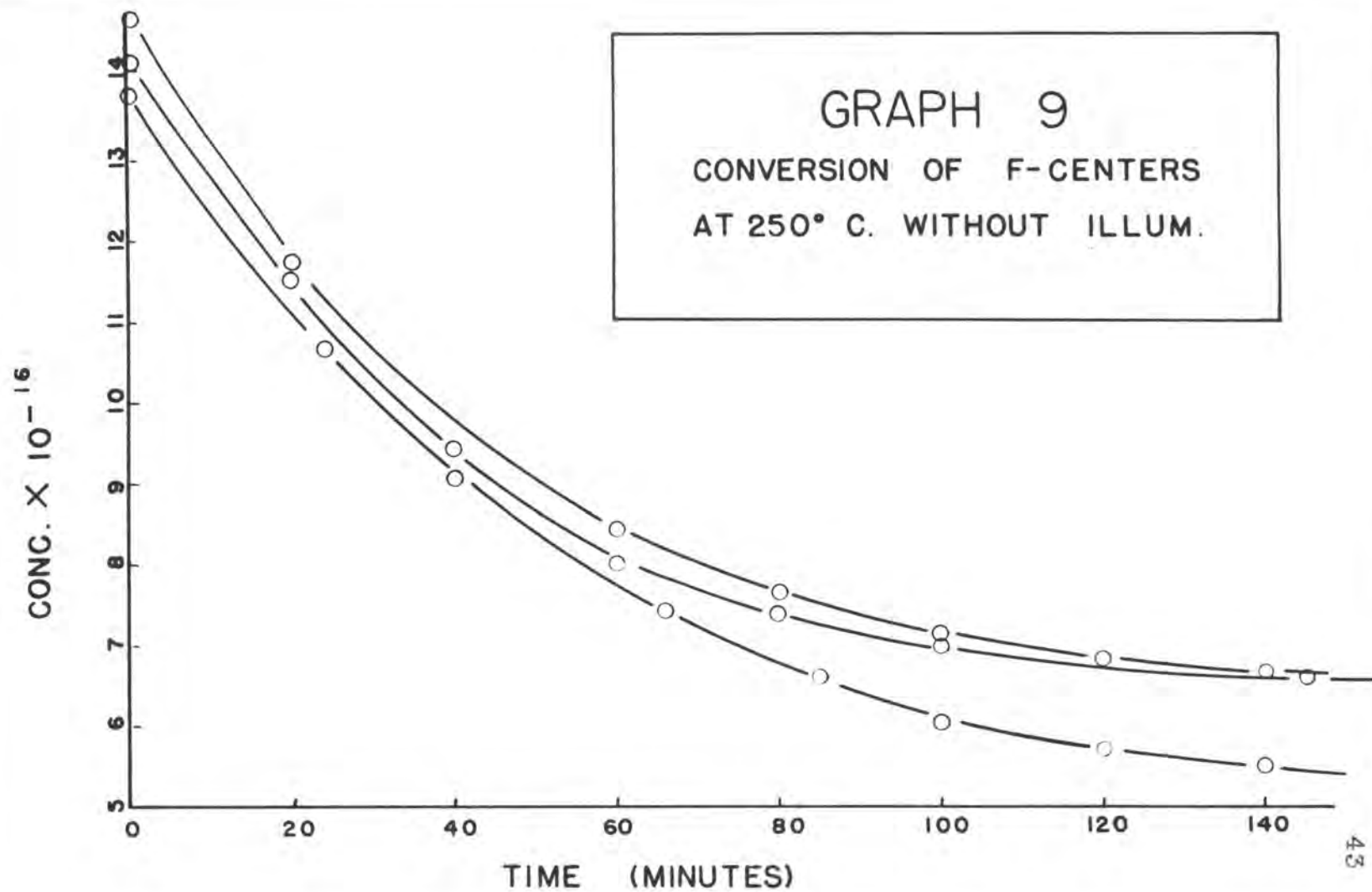


CONC. $\times 10^{-16}$



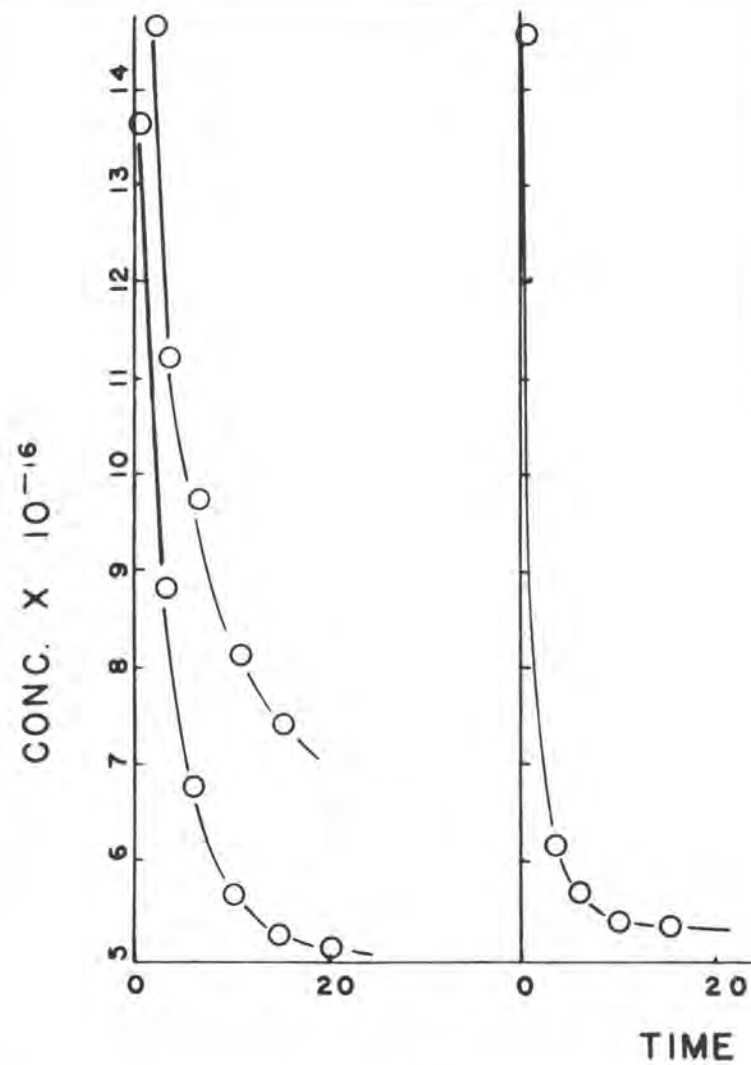
GRAPH 9

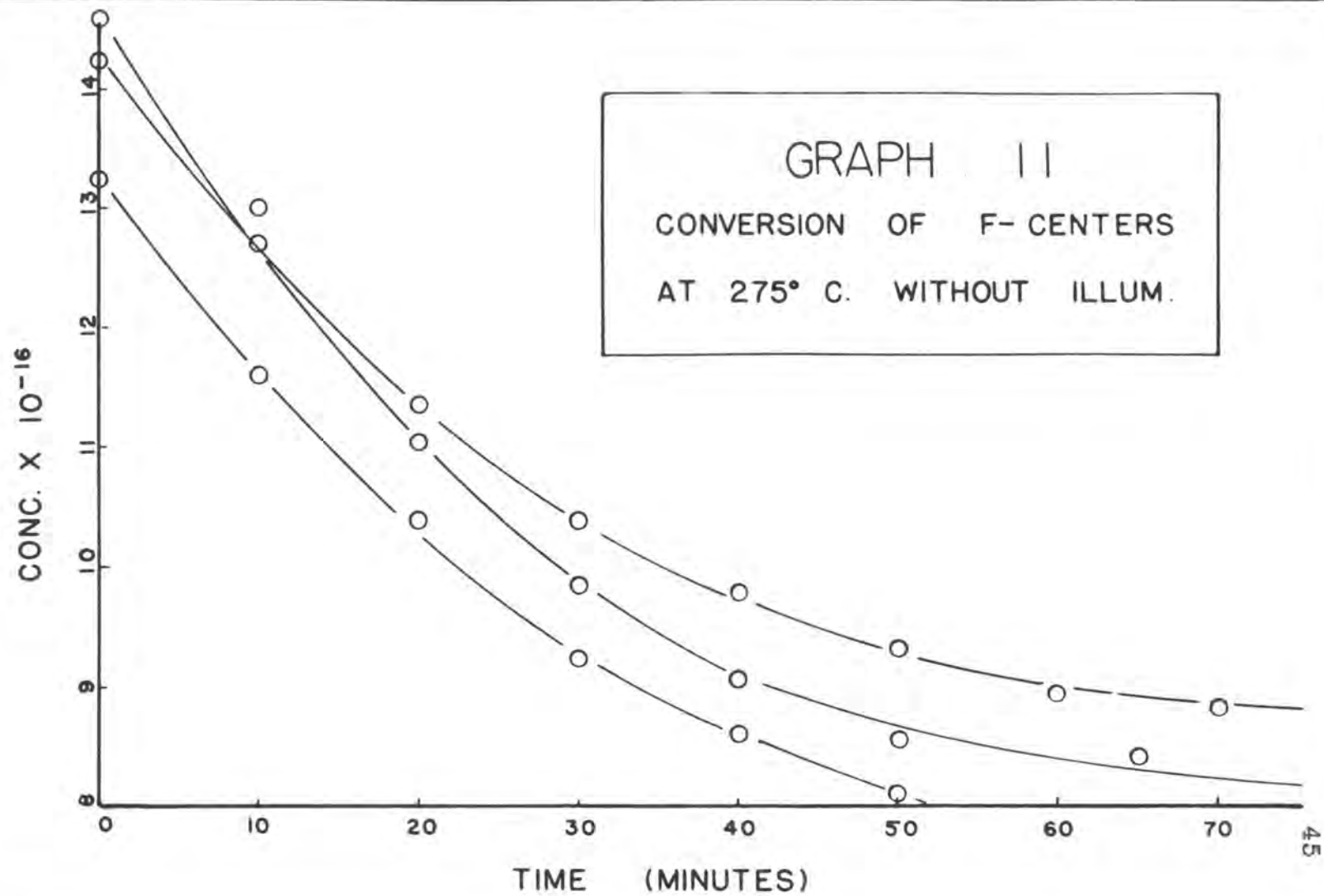
CONVERSION OF F-CENTERS
AT 250° C. WITHOUT ILLUM.



GRAPH 10

CONVERSION OF F-CENTERS
AT 250° C. WITH 560 MU ILLUM.





F-CENTER CONC. $\times 10^{-16}$

17
16
15
14
13
12
11
10
9
8
7

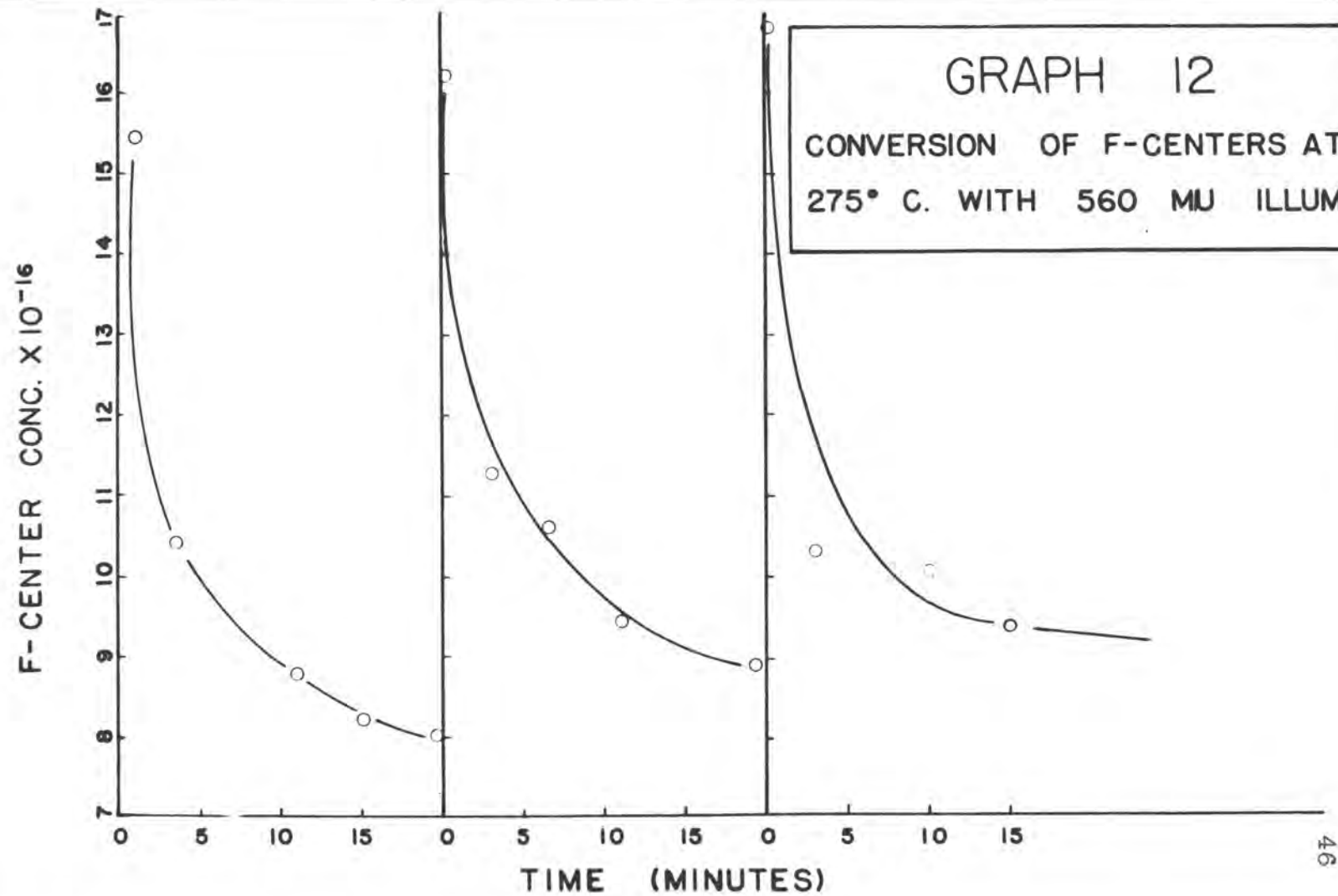
0 5 10 15 0 5 10 15 0 5 10 15

TIME (MINUTES)

GRAPH 12

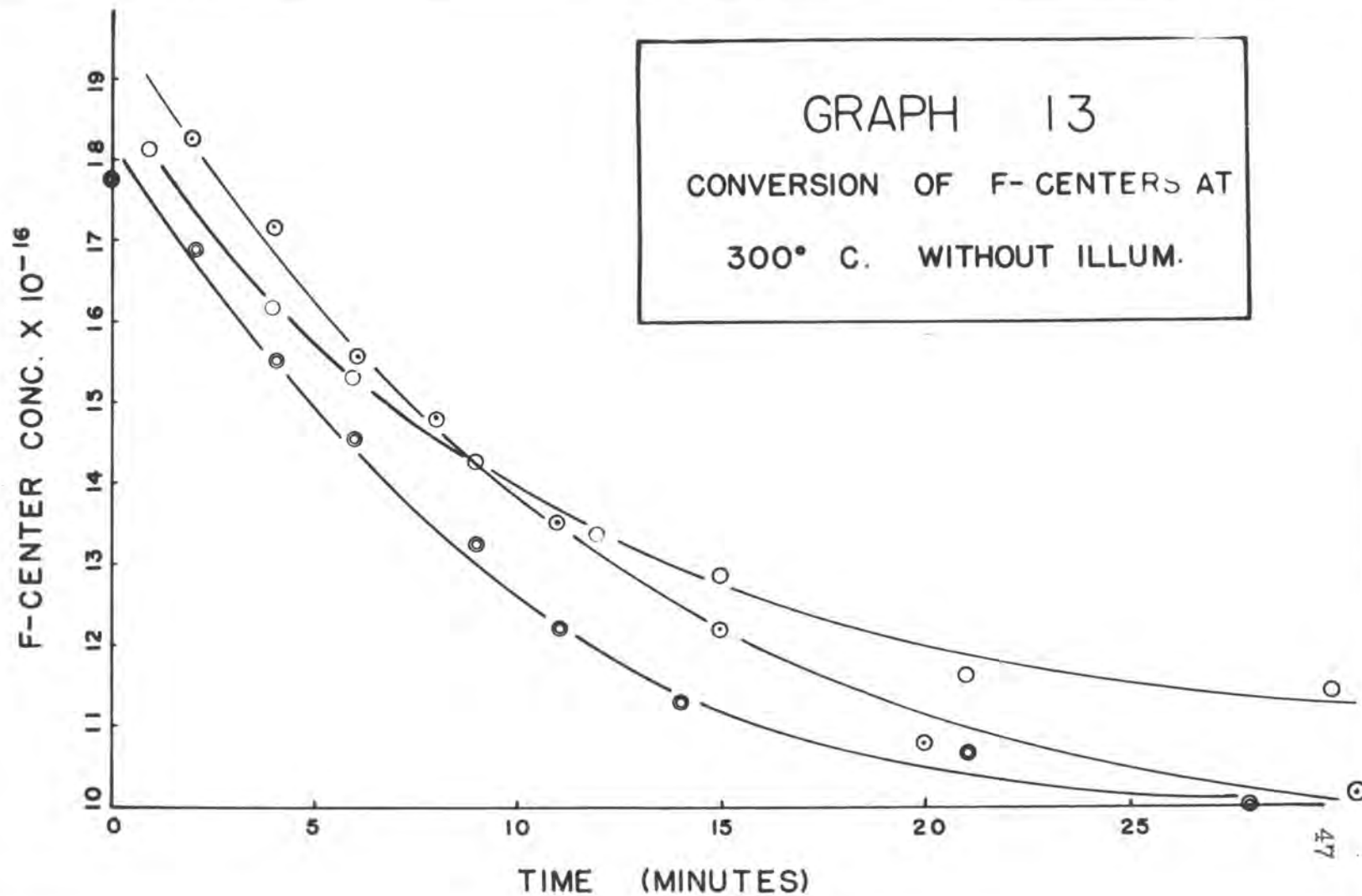
CONVERSION OF F-CENTERS AT
275° C. WITH 560 MU ILLUM.

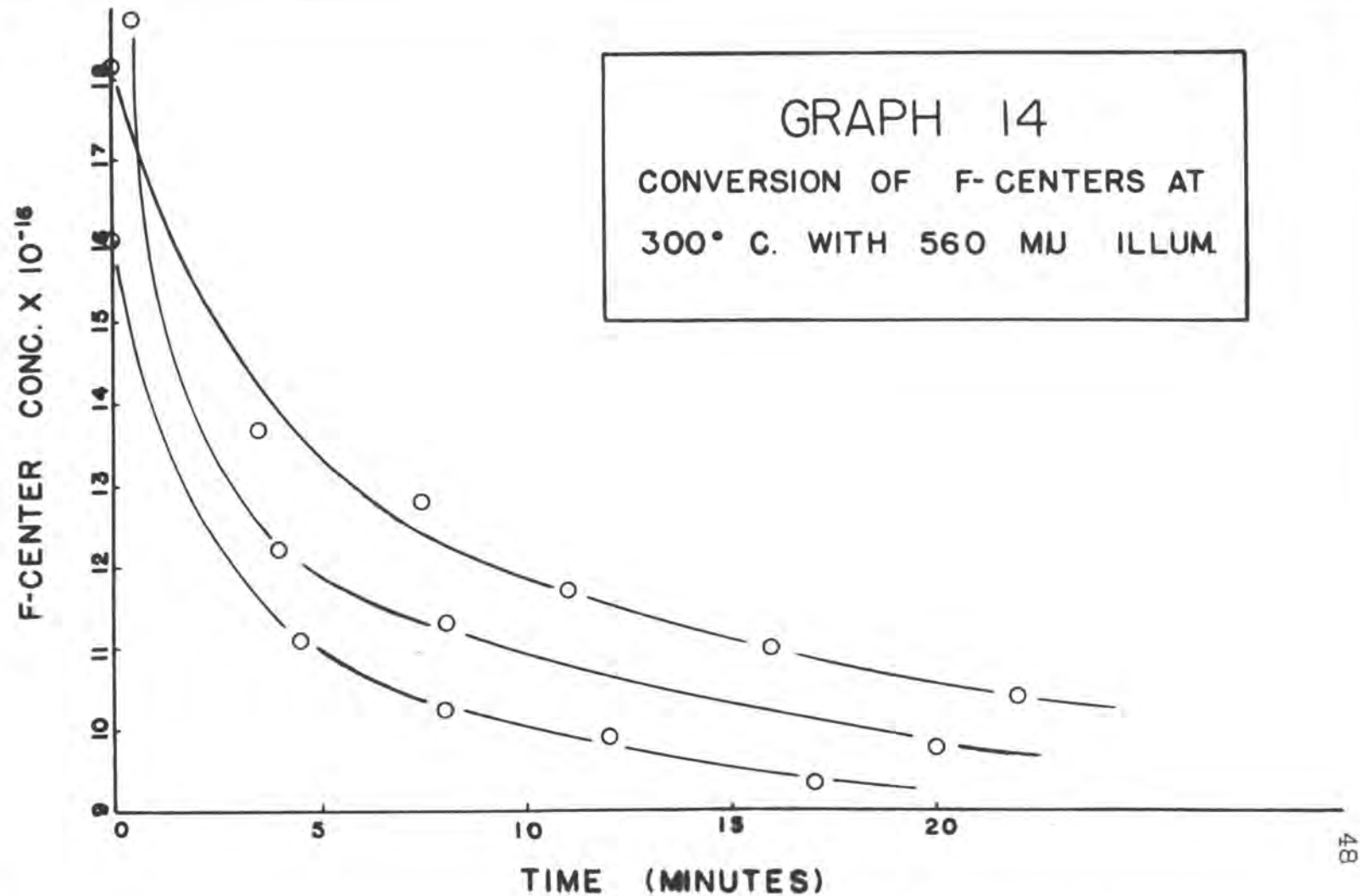
46



GRAPH 13

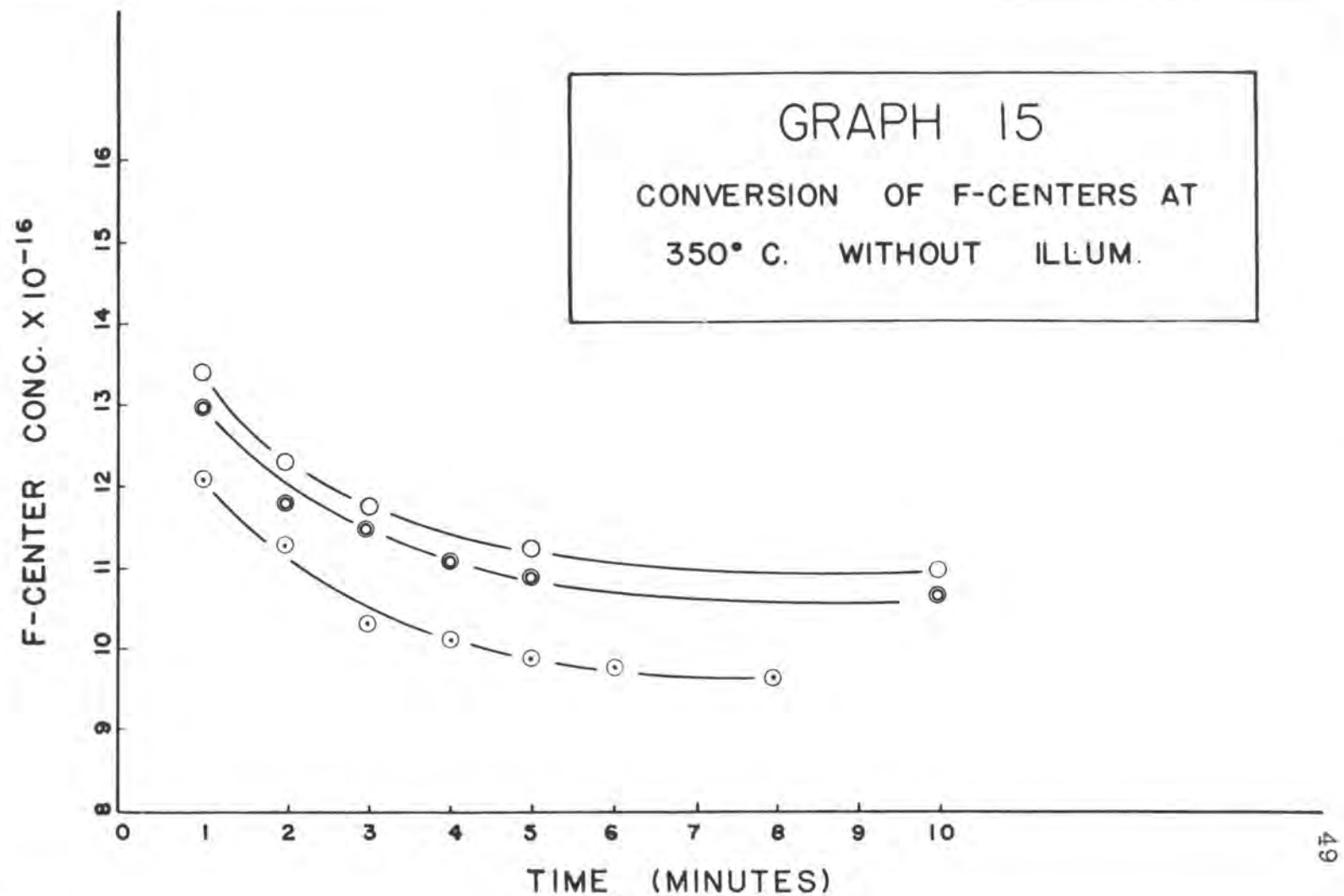
CONVERSION OF F-CENTERS AT
300° C. WITHOUT ILLUM.





GRAPH 15

CONVERSION OF F-CENTERS AT
350° C. WITHOUT ILLUM.



GRAPH 16-A

FIRST ORDER PLOTS FOR THE THERMAL
CONVERSION OF F-CENTERS

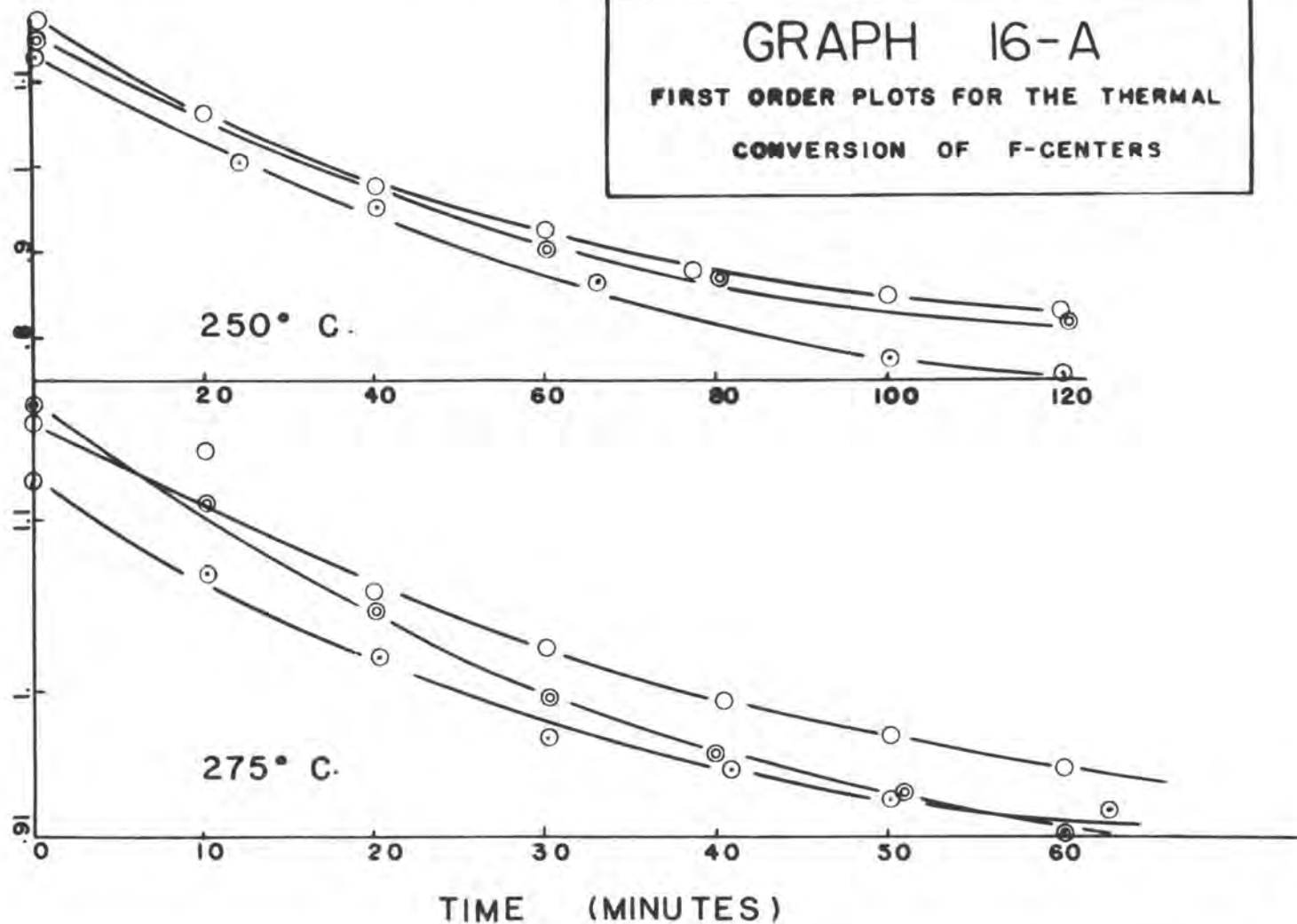
LOG(F-CENTER CONC.) - 16

250° C.

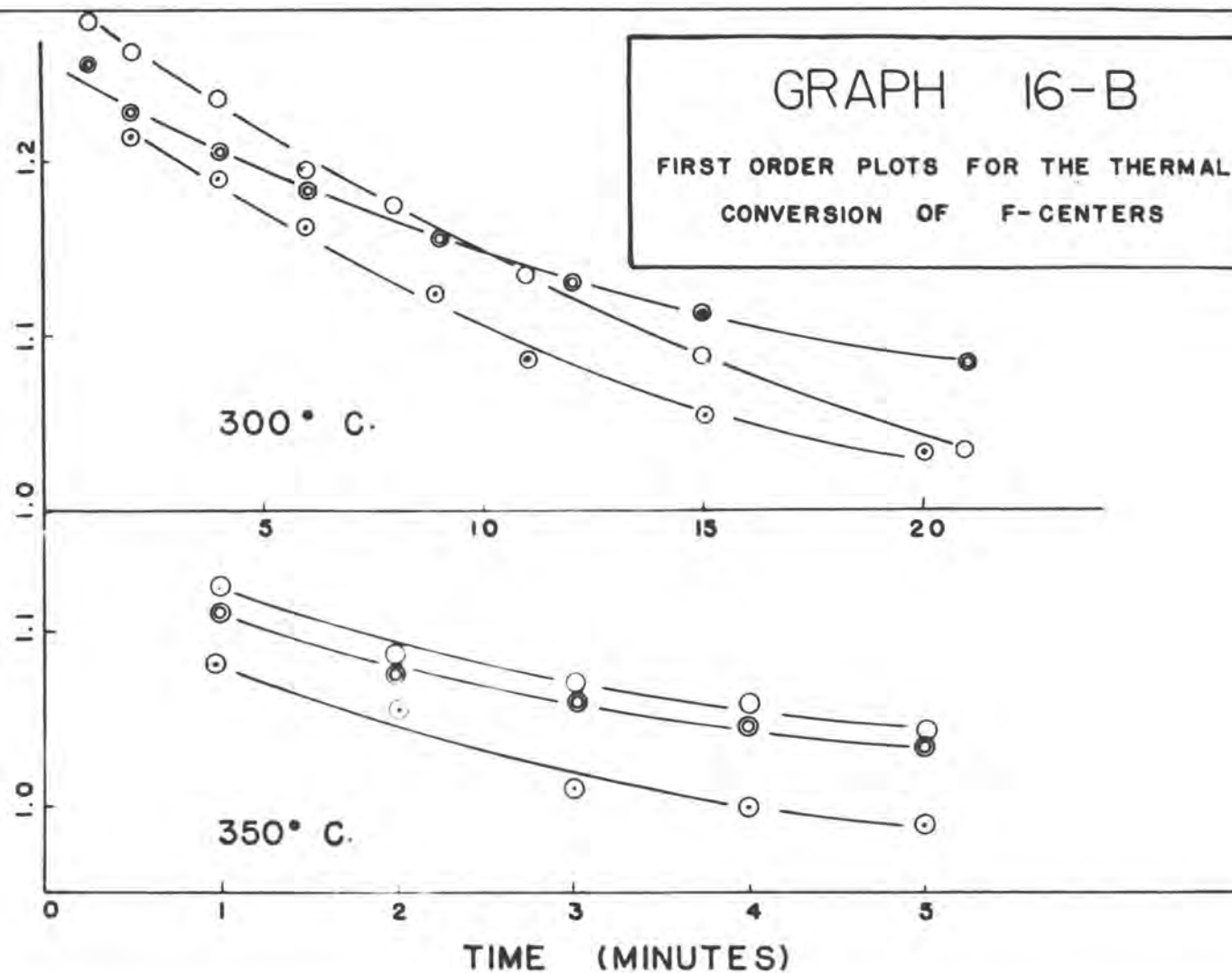
275° C.

TIME (MINUTES)

50

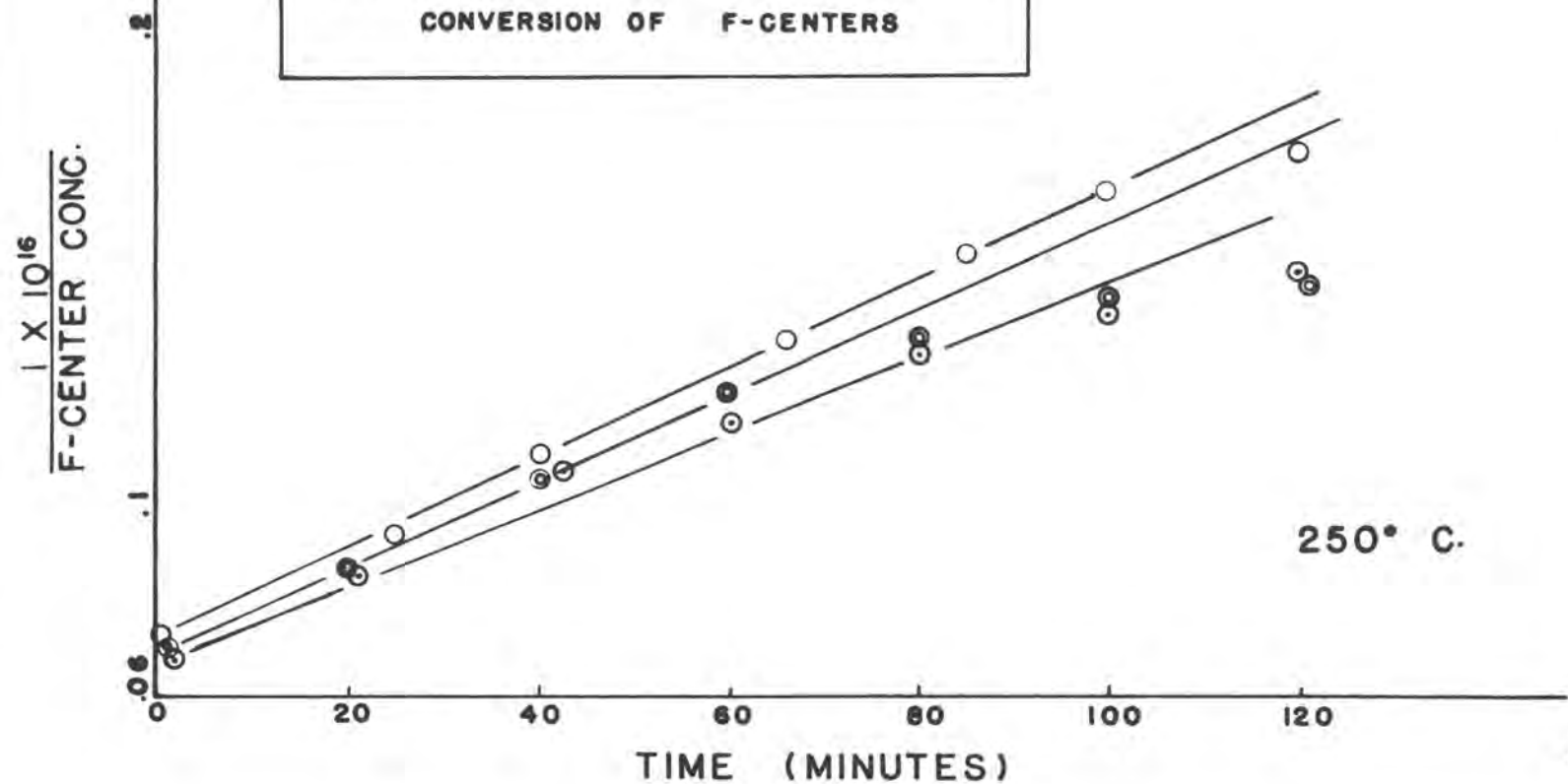


LOG (F-CENTER CONC.) - 16



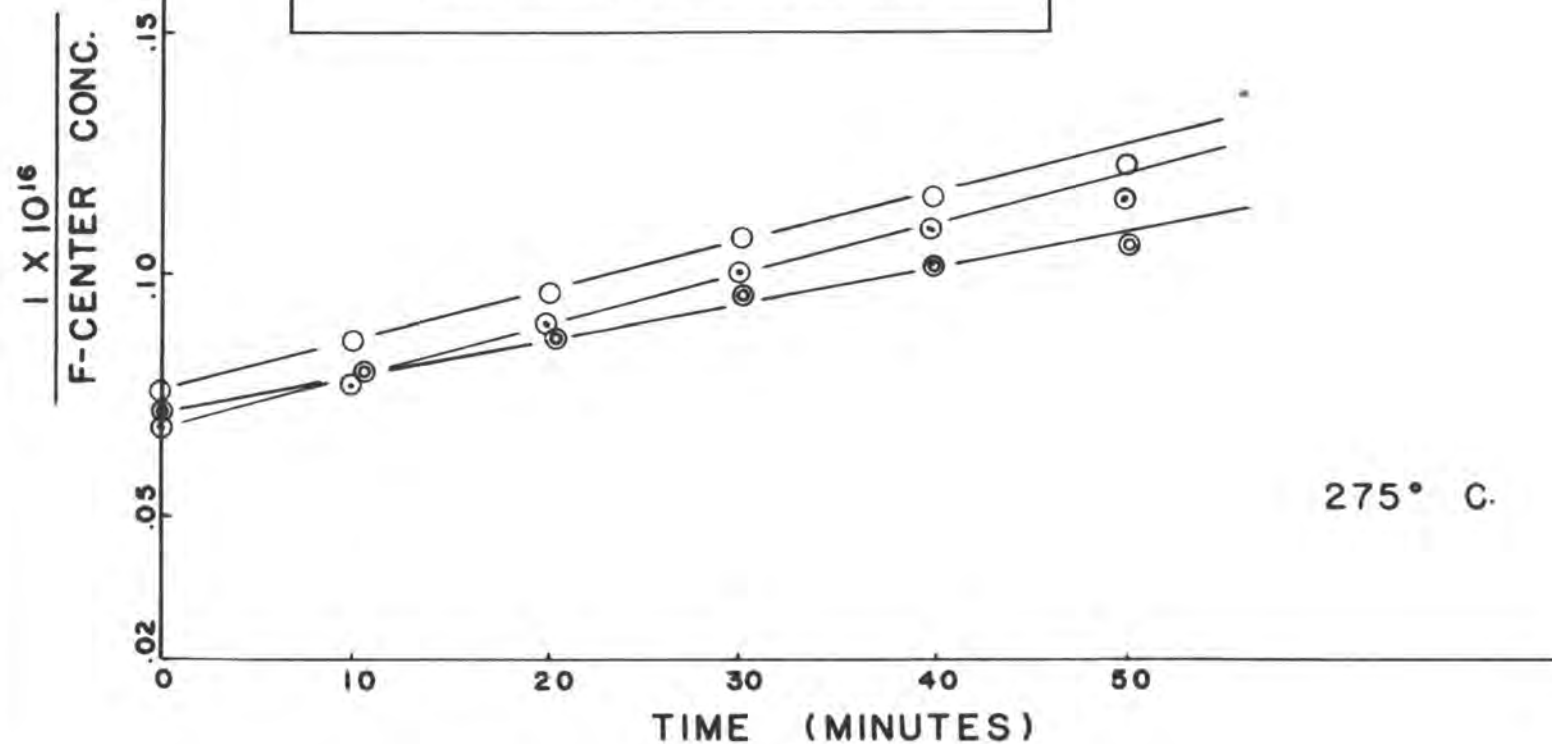
GRAPH 17-A

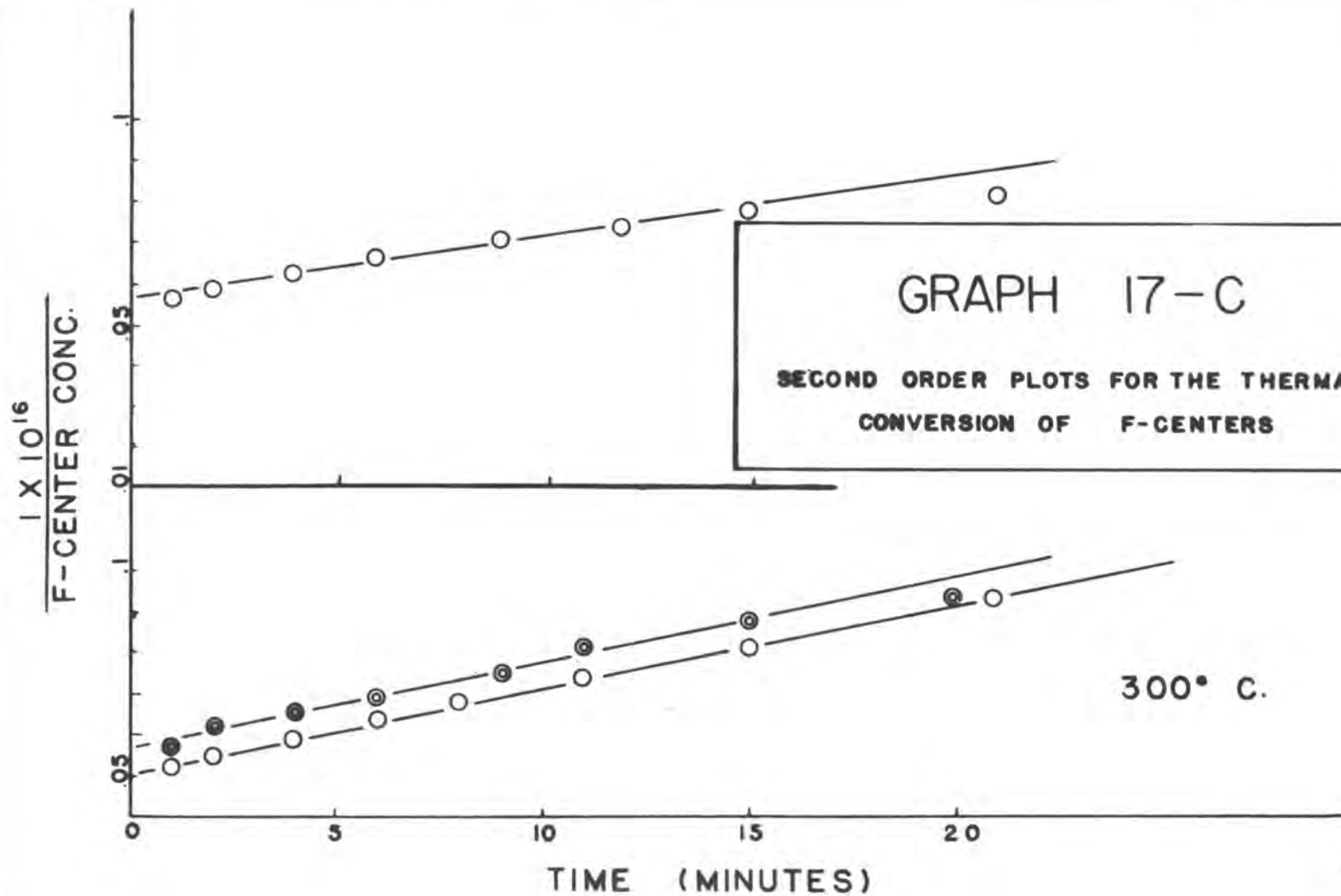
SECOND ORDER PLOTS FOR THE THERMAL
CONVERSION OF F-CENTERS

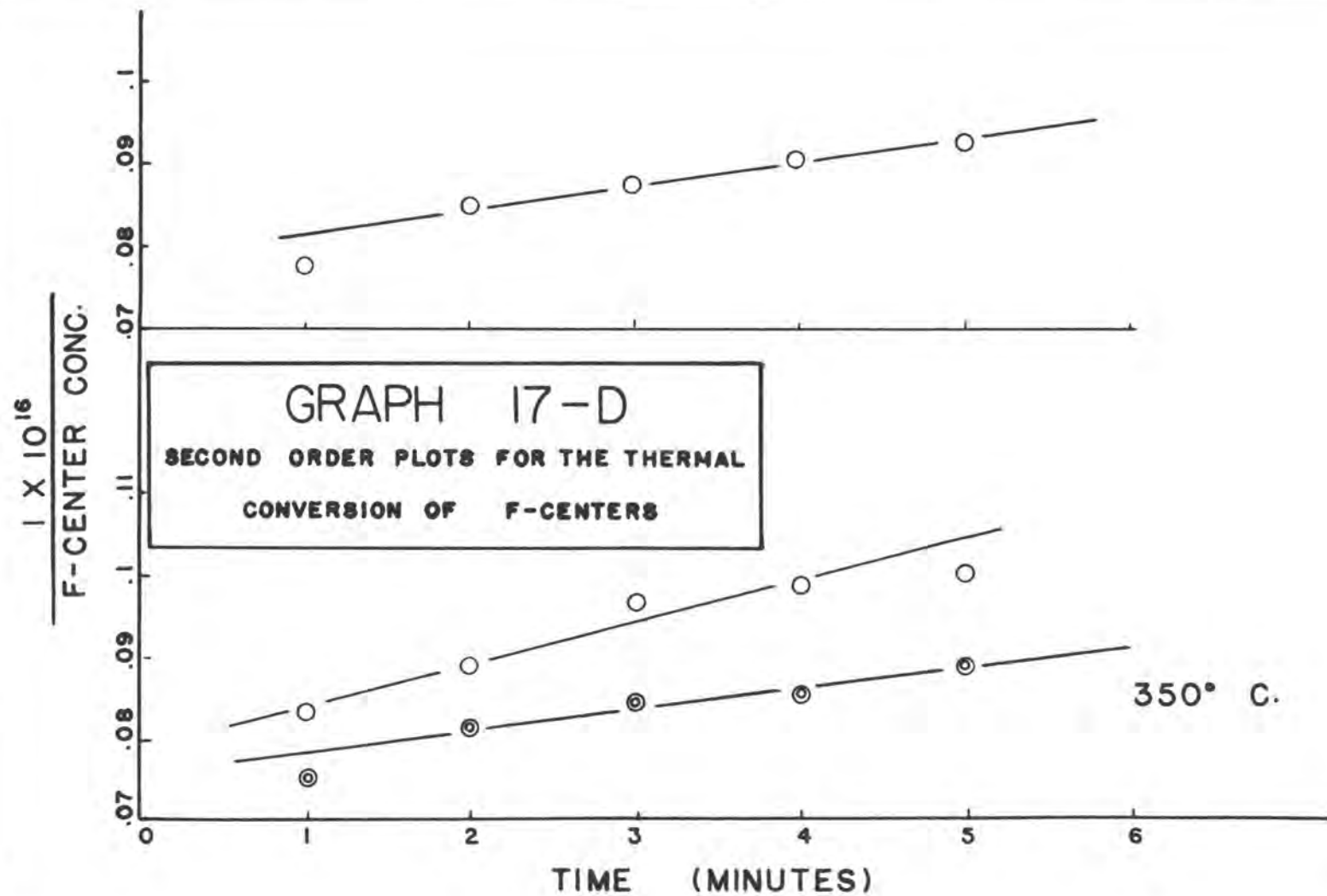


GRAPH 17-B

SECOND ORDER PLOTS FOR THE THERMAL
CONVERSION OF F-CENTERS







GRAPH 18-A

SECOND ORDER PLOTS FOR THERMAL +
560 MU ILL. CONVERSION OF F-CENTERS

$\frac{1 \times 10^{16}}{\text{F-CENTER CONG.}}$

.05

.1

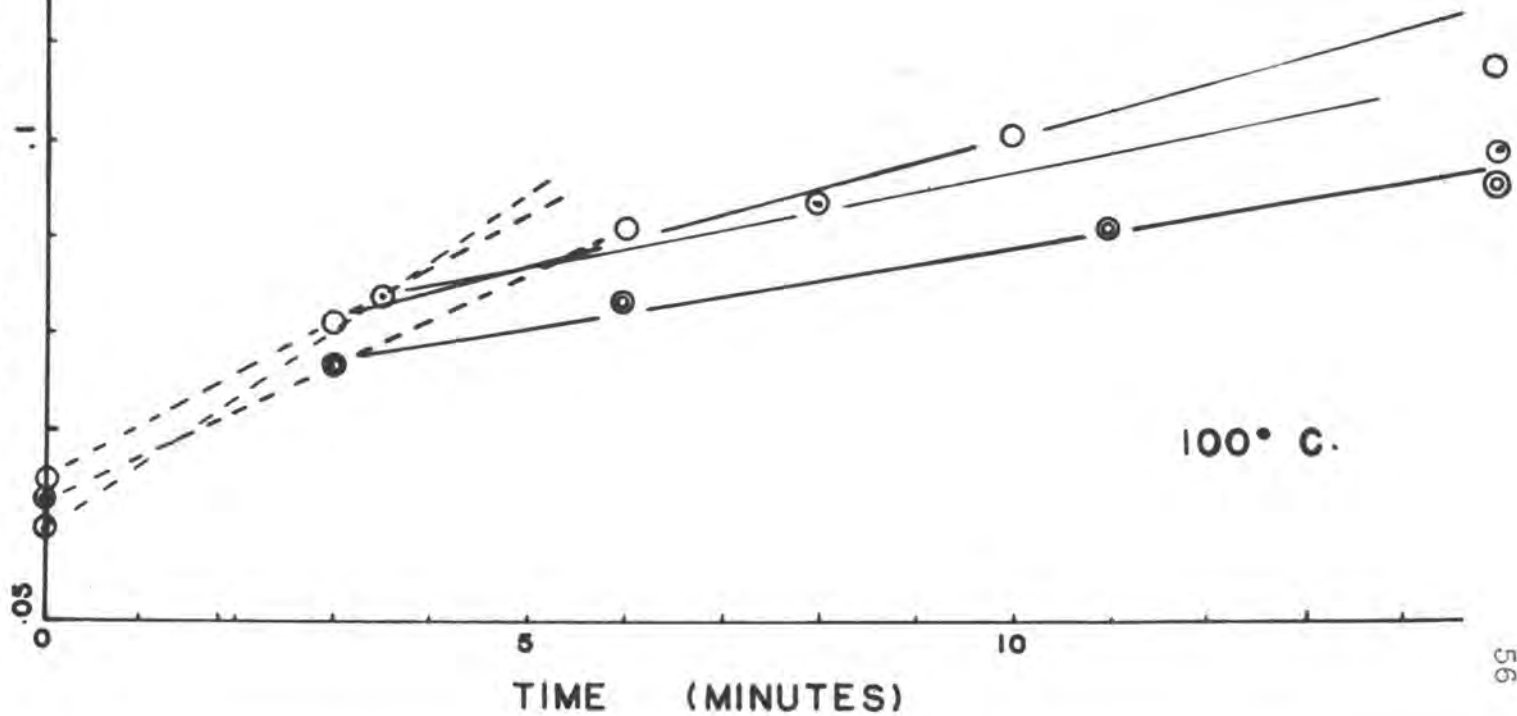
TIME (MINUTES)

5

10

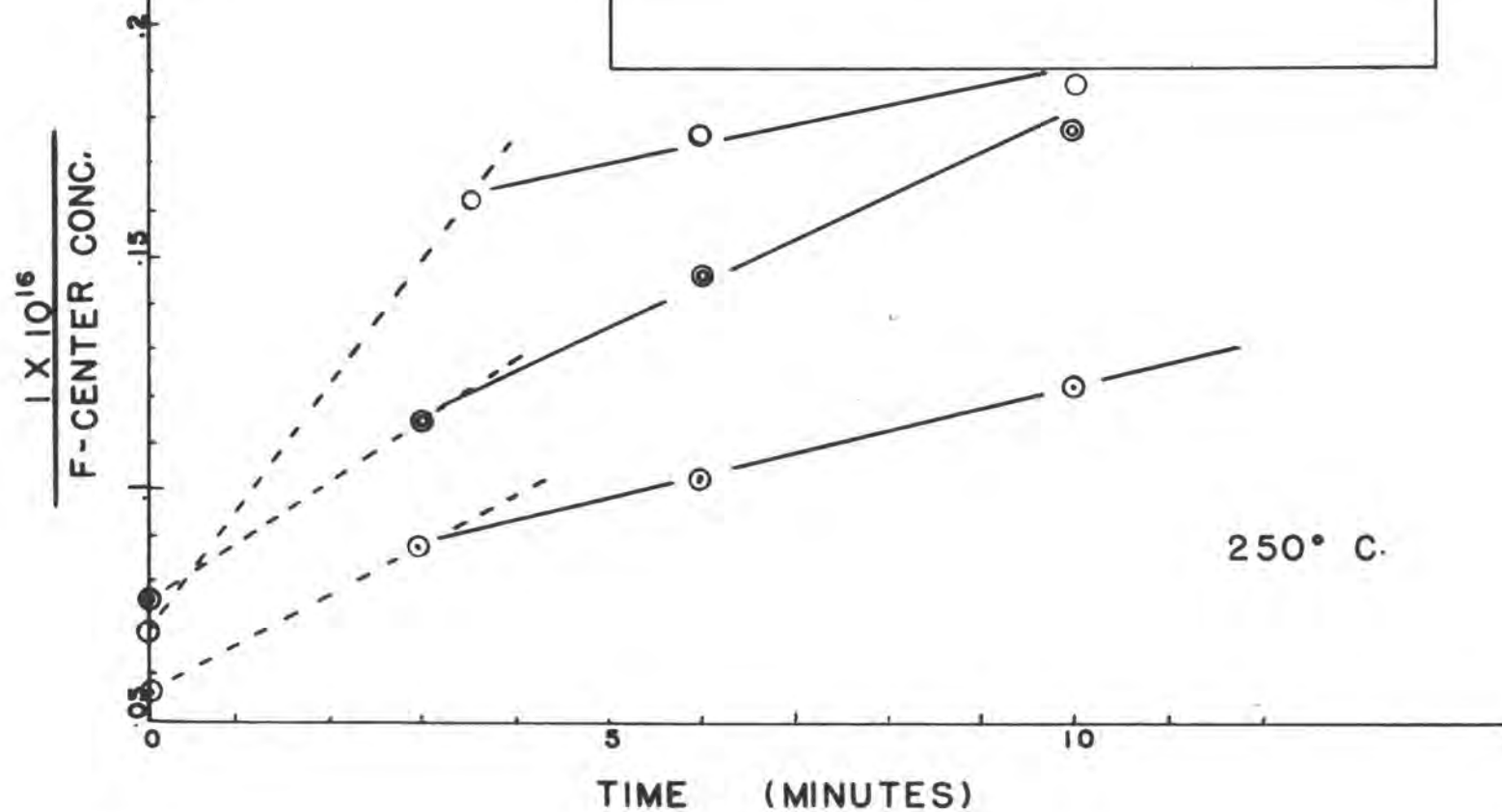
56

100° C.



GRAPH 18-B

SECOND ORDER PLOTS FOR THERMAL +
560 MJ ILL. CONVERSION OF F-CENTERS



GRAPH 18-C

SECOND ORDER PLOTS FOR THERMAL +
560 MU ILL. CONVERSION OF F-CENTERS

$\frac{1 \times 10^{16}}{\text{F-CENTER CONC.}}$

0.05

.1

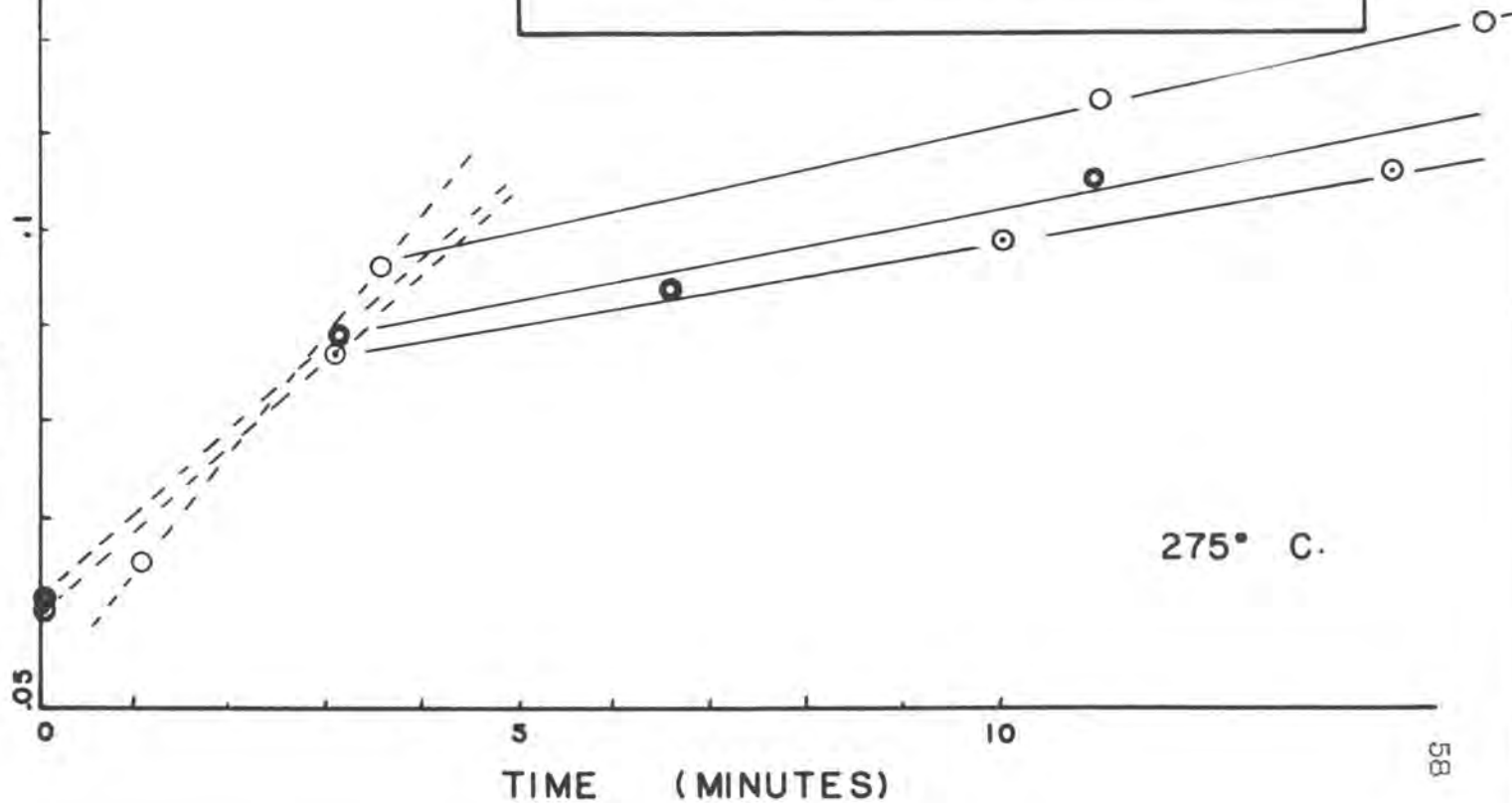
TIME (MINUTES)

5

10

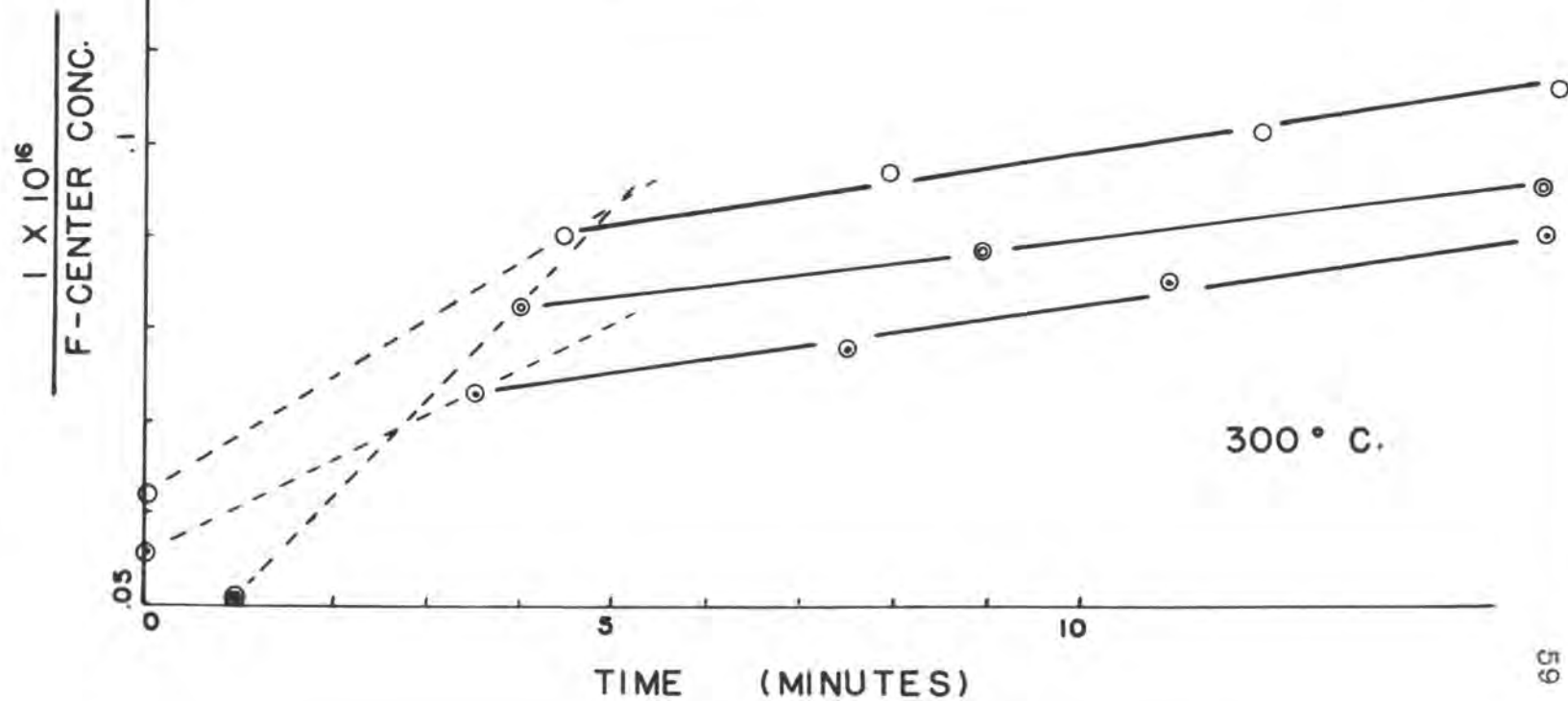
15

275° C.



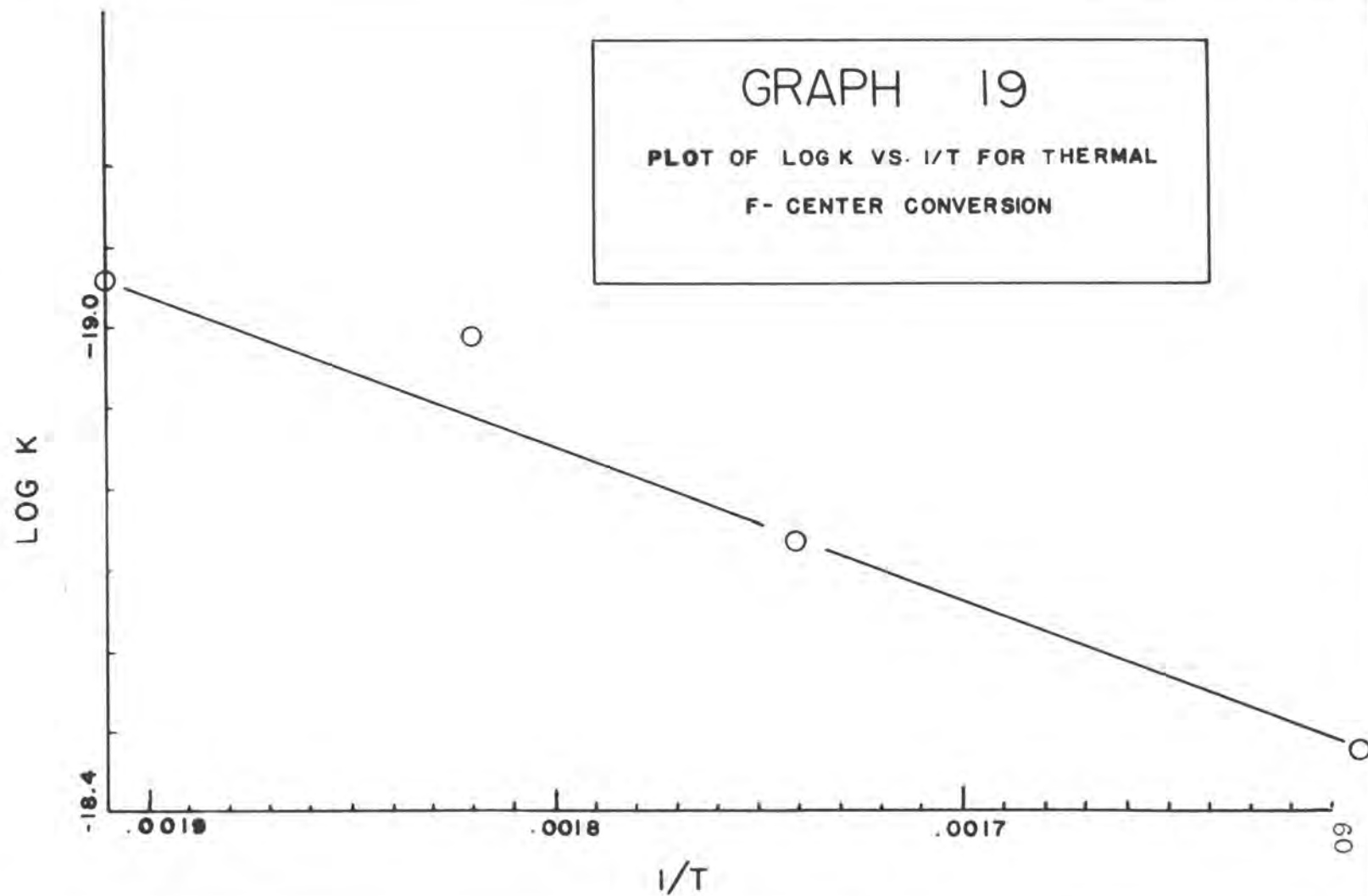
GRAPH 18-D

SECOND ORDER PLOTS FOR THERMAL +
560 MJ ILL. CONVERSION OF F-CENTERS



GRAPH 19

PLOT OF LOG K VS. $1/T$ FOR THERMAL
F-CENTER CONVERSION



through the crystal lattice until they are recaptured by an ionized F-center, an alkali metal ion, or some trapping center, such as colloidal alkali metal, which is of lower potential energy than the rest of the crystal structure. A colloidal particle, after capturing one or more electrons, would possess a negative charge and could then act as a force for the attraction of the negative ion vacancies which have previously lost an electron, and for alkali metal ions. The vacancies and ions attracted to the colloidal particle neutralize part of its charge, but neutralization of metal ions increases the size of the colloidal particle and makes it a center of still lower potential energy for the capture of electrons. In this manner the rate of coagulation of the F-centers during combined treatment would be considerably greater than during thermal treatment alone, where the attractive force for coagulation would presumably be absent. This mechanism is similar to the one suggested by Gurney and Mott for the formation of the photographic latent image in silver halide emulsions, in which electrons released by absorbed light are attracted to sulfide impurities, and silver granules are formed from silver ions attracted to the negatively charged centers (1).

VII. CONCLUSIONS

The experimental evidence indicates that the rate of conversion of F-centers by thermal means without illumination most closely approximates second order. There is a decided increase in reaction rate when crystals are illuminated with light of 560 mμ wave length while being treated thermally. The absorption spectra for crystals that have undergone combined treatment, compared with the absorption spectra for crystals treated thermally, show no marked differences outside of a greater degree of conversion in shorter time, and formation of R-bands. The affect of illumination on the conversion of F-centers is not as yet fully understood, but a solely optical conversion of F-centers is believed to occur; possibly, a more precise means of measuring conversion of F-centers while illumination is in progress will add to the present knowledge of optical conversion phenomena. Conversion of F-centers during illumination with light at 560 mμ wave length at room temperature is influenced by the intensity of the light and by heating due to infra-red absorption of the crystal. A more complete picture of the conversion of F-centers can be obtained by making thermal runs on crystals with different initial concentrations of F-centers, and measuring the rate of conversion of M-centers, and the rate of formation of R-centers and the colloidal band.

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