

SPECTROSCOPIC STUDIES OF HEATED SALTS
BEHIND SHOCK FRONTS

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ABSTRACT

Part I: Qualitative Spectroscopic Studies of Heated Salts Behind Shock Fronts

Experimental studies have been conducted on the type of radiation produced from various materials by means of shock waves. As is to be expected, the observed spectra, which are similar to spark and arc spectra, are strongly dependent upon the shock conditions.

Part II: Quantitative Spectroscopic Studies

Experimental studies were made to determine whether an estimate of population temperature could be obtained from spectrographic records. These tests suggest that excessive cooling occurs in the shock tube. The data relating to temperature measurement are incomplete.

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LIST OF SYMBOLS

I	-	Radiation intensity
S	-	Spectral radiancy
β	-	Cooling rate constant
T	-	Temperature
T_R	-	Reflected shock temperature
h	-	Planck's constant
c	-	Speed of light
k	-	Boltzmann's constant

PART I

Qualitative Spectroscopic Studies of
Heated Salts Behind Shock Fronts

I. INTRODUCTION

The shock tube has found many diverse applications as a research tool because it can be used to produce exceedingly high temperatures for short periods of time. For this reason, it is an ideal instrument for providing excitation of materials at known temperatures. The first part of the experimental program has been devoted to a qualitative study of the emission spectra that result when solids are excited in a shock tube. Our studies constitute an extension of earlier work described by Nicholls et al (reference 1).

II. THE SHOCK TUBE AND ASSOCIATED MEASURING EQUIPMENT

In preliminary tests, a low pressure shock tube made from pyrex glass was employed. This tube was constructed of one inch pyrex tubing. In operation, the low-pressure section was sealed by means of a Saran Wrap diaphragm and the ambient atmosphere was used as the driver gas. Temperatures of the incident and reflected shocks could be varied by changing the pressure of the driven gas. Early studies on NaCl, which has an easily excited spectrum, showed that no spectral radiation could be found with the available instrumentation. For this reason, the glass tube was abandoned in favor of a metal tube which could be used to obtain higher temperatures.

The shock tube was constructed of one inch stainless steel seamless tubing. The low-pressure section was 51 inches long and the high-pressure section was 24 inches in length. The two sections were separated by means of a mylar diaphragm 0.005 inches thick. The low-pressure section was connected, by means of copper tubing, to a vacuum pump, manometer and a gas loading system. The high-pressure section was connected to a pressure gage and a bottle of high-pressure helium. Figure 1 shows a schematic diagram of the shock tube and gas-handling equipment. In all of the tests made in the first part of the program, argon was used as the driven gas in the low-pressure section. To provide for optical observation of the materials tested in the shock tube, a flange with a glass window was used at the end of the tube. With this window it was possible to obtain spectra by looking along the longitudinal

axis of the tube. Since the optical cutoff for the glass window was about 3600 \AA , a similar flange was constructed with a quartz window having a cutoff of about 1800 \AA . In connection with some of the later work, where it was desirable to have a short optical path, a lucite block was connected to the end of the tube and the instruments focused in a direction perpendicular to the tube axis. This arrangement is shown in Figure 2a. The lucite block was used for pressures up to 400 psi in the driver section. For pressures above 400 psi, the lucite block was replaced by one of the flanges.

The temperature and density of the shocked gases could be varied by adjusting the argon pressure in the low-pressure section together with the helium pressure of the high-pressure section. In operation, the solid materials under study were placed at the back end of the shock tube so that they were heated by the reflected shock waves. The low-pressure section was evacuated, flushed with argon and re-evacuated. It was then reloaded with argon to pressures of 5 to 60 mm depending upon the desired temperature. Subsequently, the high-pressure section was loaded with helium by means of a throttling valve until the mylar diaphragm burst. A single diaphragm, 0.005 inches thick, gave bursting pressures that varied from 275 to 330 psi. Pressures up to 580 psi could be obtained using two diaphragms.

The window of the shock tube flange or the lucite block was imaged on the slit of a Hilger f/9 spectrograph. The arrangement used is indicated in the schematic diagrams of

Figures 2a and 2b. The spectrum provided by the shock excitation was recorded on Royal X Panchromatic film, ASA 1600. After each shot, a mercury lamp was focused on the slit to provide a comparison spectrum.

III. OUTLINE OF THE EXPERIMENTAL PROGRAM

The first part of the experimental program was devoted to obtaining qualitative information about the emission spectra of various materials. Usually about 0.2 grams of solid material were placed in the shock tube at the point of observation. The arrangement used in these tests is that indicated in Figure 2a. When the shock passed over the salt, a very intense flash of light resulted and was recorded by the spectrograph. Several sodium and calcium salts were studied.

IV. DISCUSSION OF THE EXPERIMENTS AND ANALYSIS OF DATA

With a driver pressure of 300 to 330 psi and a driven pressure varying from 50 to 5 mm, it is possible to obtain calculated reflected shock temperatures between 5,500°K and 11,000°K. These temperatures have been calculated according to the methods outlined in references 2 and 3 and neglect the ionization of argon. As indicated in reference 4, a correction for argon ionization should be made at temperatures above 9,000°K. For this reason, the 11,000°K estimate represents an upper limit. A typical spectrum obtained with sodium chloride is shown in Figure 3. Several other sodium salts were examined (e.g., NaI, NaBr, etc) and all of them gave spectra similar to those shown in Figure 3. The shot indicated by Figure 3 was made with a driver pressure of 235 psi and a driven gas pressure of 35 mm. Under these conditions, a calculated reflected shock temperature of about 7,000°K was obtained. The most striking fact about the spectra is the very intense darkening of the plate in the region of 5,000 Å, i.e., in the vicinity of the sodium D lines which have an estimated effective width of 80 Å. Arc and spark spectra of this material give similar spectra but the darkening is considerably more diffuse and less sharp.

In addition to the sodium compounds, a series of shots was made using calcium chloride. Figure 4 represents the spectral record of CaCl_2 obtained with a reflected shock temperature of about 8,000°K. Some of the lines have been identified

and marked. It is to be noted that ionic as well as atomic lines were identified. A series of shots was also made with driven gas pressure of 50 mm, 30 mm, 15 mm, and 5 mm, under essentially constant driver pressure conditions (i.e., about 300 psi). The results of these shots are shown in Figure 5 and calculated reflected shock temperatures are indicated for each shot. At the lower temperatures, the atomic and molecular spectral lines are somewhat faint and the ionic lines fainter still. As the temperature is raised by lowering the pressure of the driven gas, the atomic and ionic lines become more intense. However, at the highest temperature (corresponding to 5 mm in the low-pressure section) the entire spectrum becomes very faint although the relative intensity of the ionic lines to the atomic lines has continued to increase. In Figure 5a we have shown the effective line widths as a function of temperature. Qualitatively we can explain Figures 5 and 5a on the basis that, even though the temperature has increased to rather high values, the number of exciting atoms available is considerably reduced so that a decrease in intensity is actually produced. On the other hand, when a collision does occur, the high temperatures involved cause the ionic excitation to predominate.

It has become apparent as a result of the tests described above that very small amounts of any of the salts give rise to rather intense spectra. Thus when the tube is cleaned at the conclusion of a test with sodium salt and then a shot is made

with nothing but argon in the low-pressure section, sodium spectral lines still appear faintly on the spectrograph; particularly the strong sodium D lines tend to persist.

8a

Part II

Quantitative Spectroscopic Studies

V. INTRODUCTION

It would be extremely useful to develop a relatively simple method for temperature measurements based upon spectroscopic observations. This procedure would provide an excellent tool in aerodynamic studies where the shock tube is used as a short duration wind tunnel. For example, an aerodynamic model could be coated with a salt (such as calcium chloride) and then a spectrographic record obtained of the radiation that results when it is subjected to the gas flow of a shock tube. From this record gas temperatures in the vicinity of the model could presumably be obtained.

Methods for measuring temperatures spectroscopically are described in reference 5. One of the procedures involves the peak spectral radiancy I for two different spectral lines belonging to the same emitter at the temperature T ; the relative values of the integrated intensity S must also be known. The basic relation for equilibrium radiation is

$$I_{\omega_{0,1}}/I_{\omega_{0,2}} = (\omega_{0,1}/\omega_{0,2})^3 (S_1/S_2) \frac{\exp(hc\omega_{0,2}/kT-1)}{\exp(hc\omega_{0,1}/kT-1)} \quad (1)$$

Equation (1) applies provided (a) the slit function is essentially constant over the wave number range covered by the emitting species and (b) no self absorption occurs. From the spectrographic record it should be possible to determine the ratio $I_{\omega_{0,1}}/I_{\omega_{0,2}}$ while the ratio S_1/S_2 can usually be obtained theoretically. Hence T should be calculable from the spectrographic record as long as the specified assumptions are met in practice.

VI. INSTRUMENTATION

The system used for the quantitative measurements included all of the equipment used in Part I (see Figure 2a) together with photoelectric measuring equipment which provided time-resolved spectra at a given wave length. A Jarrell-Ash scanning monochromator was imaged on one side of the lucite block (see Figure 6a). A IP28 photomultiplier tube was used together with the network indicated in Figure 7. The signal was amplified on a Tektronix 535 oscilloscope and recorded photographically with a Polaroid Land Camera.

The monochromator was set at a given wave length (e.g., 5042 \AA) and the emitted radiation in the region of this wave length was recorded. Preliminary experiments with the monochromator, arranged as shown in Figure 6b, were made and strong intensity readings were obtained at the dominant wave lengths. Tests were then conducted with the instrumentation arranged as shown in Figure 6a. This arrangement provided a short optical path and sufficient radiation still existed to give good records. All further tests were therefore made with the instrument as shown in Figure 6a. The instruments were imaged on the back end of the shock tube so that reflected shock conditions prevailed.

VII. OUTLINE OF EXPERIMENTAL PROGRAM

The same experimental procedure was used as in Part I except that measured amounts of calcium chloride were placed in the tube. A series of tests was made under essentially constant shock conditions (15 mm of argon in the low-pressure section and about 300 psi in the high-pressure section) with varying amounts of CaCl_2 .

Next a series of tests was made using a fixed amount of salt (0.005 gms.) and varying shock conditions. Records were taken with both the Hilger and Jarrell-Ash instruments.

It was planned to use the Hilger records to obtain temperatures. The time-resolved spectra added additional information (and, as it turned out, the more important information). On the basis of the results of Part I, it was decided to use the wavelengths 5042 Å, 4878 Å and 4527 Å for temperature measurements. Tests were made on the 5042 Å and 4527 Å lines with the Jarrell-Ash monochromator.

VIII. DISCUSSION OF EXPERIMENTS AND ANALYSIS OF DATA

Relevant data for all of the tests are given in Table I.

To determine what, if any, effect is produced by varying the amount of CaCl_2 , tests 40 to 47 were made. These tests were conducted under essentially constant shock conditions (i.e., 15 mm in the low-pressure section and about 300 psi in the high-pressure section). The monochromator was set at 5042 Å. Each test provided a time resolved intensity curve similar to that shown in Figure 8. By measuring the peak intensity and plotting it against the amount of CaCl_2 used, the curve shown in Figure 9 was obtained. This curve indicates that the peak intensity goes through a maximum at about 0.030 gms. The observed maximum value is probably associated with self-reversal. All later tests were made with carefully weighed amounts of CaCl_2 (0.005 gms was used in each case).

The records obtained from the monochromator (Figure 8) showed that the intensity decayed with time at a fairly rapid rate. This decay could be produced by either a relaxation phenomenon associated with chemiluminescent excitation or a cooling effect. The instrumentation was arranged in such a way that a certain minimum radiation intensity was required before the oscilloscope beam would trigger. The radiation was produced by an excited state and corresponded to a $4P$ to $3D$ transition for the 5042 Å line. A relaxation effect would be characterized by either a rise in intensity to some equilibrium value or else by a decay from an apparent initial maximum value. Similarly

a cooling effect would be characterized by a decay from an initial maximum value.

Since the tests run at 5 mm in the low-pressure section provide temperatures of the order of $10,000^{\circ}\text{K}$ behind the reflected shock wave, it is to be expected that a considerable amount of radiation cooling occurs. Shot 59 was made to obtain the time-resolved intensity curve with an initial pressure of 5 mm in the driven gas. Then the lucite block was covered with aluminum foil except for a narrow slit upon which the monochromator was imaged; test 60 was then performed under conditions which were otherwise similar to those employed in test 59. The results of these two tests are shown in Figures 10 and 11. Reference to the results shows that the decay rate has been considerably decreased by simply encasing the lucite block with aluminum foil. Since this foil could have no effect if the decay curve were produced by a relaxation phenomenon, we conclude that the data correspond to a cooling process. If we assume that the intensity (I) varies with the time (t) according to the expression

$$I(t) = I_0 \exp (- \beta t) \quad (2)$$

then the data from the oscillograph traces can be plotted on semi-log paper and the "cooling rate constant" β determined from the slope. This programme has been carried out for representative shots at different temperatures (see Figure 12). The value of β is indicated with each curve. The data in

Figure 13 correspond to all the tests made with 5 mm in the driven gas section both with and without aluminum foil covering the lucite block. It is apparent from Figure 13 that considerable variation in the cooling rate constant (β) occurs from shot to shot. However if an average is taken for all the tests made under the same shock conditions and $\ln I/I_0$ plotted as a function of time based on this average, the effect of the foil is quite pronounced as shown by the data of Figure 13a. The rate of decay is larger at the high temperatures as is to be expected. At temperatures of about 7000°K no difference in rate was noticed with or without the aluminum foil.

Since it was established that a strong cooling effect existed in the tube, it was felt that using the Hilger records for temperature measurement would at best provide only an average value. If we re-examine the significance of a typical monochromator record, such as shown in Figure 8, and assume that the intensity corresponds to thermodynamic equilibrium at all times, with the intensity decrease produced by a cooling effect, then it should be possible, knowing the peak intensities at two different wavelengths, to estimate temperature.

In order to obtain reliable information concerning the possibility of making temperature measurements from peak intensity data, it was decided to repeat at 4527 Å a series of tests similar to those made at 5042 Å (shots 68 to 76 in Table I). From the test results made at both wavelengths,

the peak intensities were measured and plotted against temperature using the data given in references 2 and 3. The results are shown in Figure 14. A straight line has been drawn through the data in such a way that each line represents a mean peak intensity. Equation (1) may be used to derive the expression

$$\frac{(I_{5042})}{(I_{4527})_{\text{Peak}}} = \left(\frac{4527}{5042}\right)^3 (S_1/S_2) \frac{\exp (hc/kT (4527) - 1)}{\exp (hc/kT (5042) - 1)}$$

This result may then be put in the form

$$d \left(\ln \frac{I_{5042}}{I_{4527}} \right) / d \left(\frac{1}{T} \right) = \frac{hc}{k} (1/4527 - 1/5042) \quad (3)$$

or

$$d \left(\ln \frac{I_{5042}}{I_{4527}} \right) / d \left(\frac{1}{T} \right) = 3270 \quad (4)$$

From Figure 14 we may obtain $\ln I_{5042}/I_{4527}$ which can be plotted against $1/T$ and then graphically differentiated. The results of this operation are shown in Figure 15 where $d(\ln I_{5042}/I_{4527})/d(1/T)$ is plotted against $1/T$ for the experimental data. The theoretical result is indicated by the dotted line. The experimental curve shows that the derivative is strongly temperature dependent. This surprising temperature dependence of the intensity ratio probably cannot be accounted for on the basis of a number of secondary factors which invalidate the use of equation (2), viz, self absorption, lack of reproducibility of successive shots, etc; but rather stems from a nonequilibrium shock phenomenon which requires further detailed study.

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- 4) Resler, E. L., Lin, S. C., and Kantrowitz, A.: J. Appl. Phys. Vol. 23, No. 12, pp 1390-1399 (1952)
- 5) Penner, S. S. "Quantitative Molecular Spectroscopy and Gas Emissivities", Addison-Wesley Co. (in press)

TABLE I

Shot No.	Atmospheric Pressure mm Hg	Amount of CaCl_2 grams	Argon Pressure in the Low-Pressure Section, mm Hg	Helium Pressure in the Driver Section psia	Wavelength setting of monochromator A	Remarks
40	740.0	.0717	15	320	5042	
41	739.5	.0889	15	305	5042	
42	739.5	.0296	15	300	5042	
43	740.0	.0127	15	290	5042	
44	739.5	.1701	15	320	5042	
46	739.5	.0028	15	305	5042	
47	739.5	.0300	15	300	5042	
48	739.0	.0051	30	310	5042	
49	739.0	.0058	5	310	5042	
51	739.0	.0058	155	335	5042	
52	739.0	.0050	30	315	5042	
53	739.0	.0050	51	295	5042	
58	740.0	.0050	8	290	5042	
59	739.0	.0050	5	295	5042	
60	738.5	.0050	5	285	5042	Lucite block covered with aluminum foil

TABLE I (Cont)

Shot No.	Atmospheric Pressure mm Hg	Amount of CaCl ₂ grams	Argon Pressure in the Low-Pressure Section, mm Hg	Helium Pressure in the Driver Section psia	Wavelength setting of monochromator A	Remarks
61	738.5	.0050	15	285	5042	Lucite block covered with aluminum foil
62	739.0	.0050	5	295	5042	Lucite block covered with aluminum foil
63	738.5	.0050	5	300	5042	Lucite block covered with aluminum foil
64	739.0	.0050	5	280	5042	
65	739.0	.0050	15	280	5042	
66	739.0	.0050	5	275	5042	Lucite block covered with aluminum foil
67	739.0	.0050	15	280	5042	Lucite block covered with aluminum foil
68	741.0	.0050	5	275	4527	
69	741.0	.0050	5	285	4527	
70	740.5	.0050	15	275	4527	
71	740.5	.0050	15	270	4527	

TABLE I (Cont)

Shot No.	Atmospheric Pressure mm Hg	Amount of CaCl_2 grams	Argon Pressure in the Low-Pressure Section, mm Hg	Helium Pressure in the Driver Section psia	Wavelength setting of monochromator A	Remarks
72	740.5	.0050	30	275	4527	
73	740.5	.0050	30	275	4527	
74	740.5	.0050	5	280	4527	Lucite block covered with aluminum foil
75	740.5	.0050	5	280	4527	Lucite block covered with aluminum foil
76	740.5	.0050	15	280	4527	Lucite block covered with aluminum foil

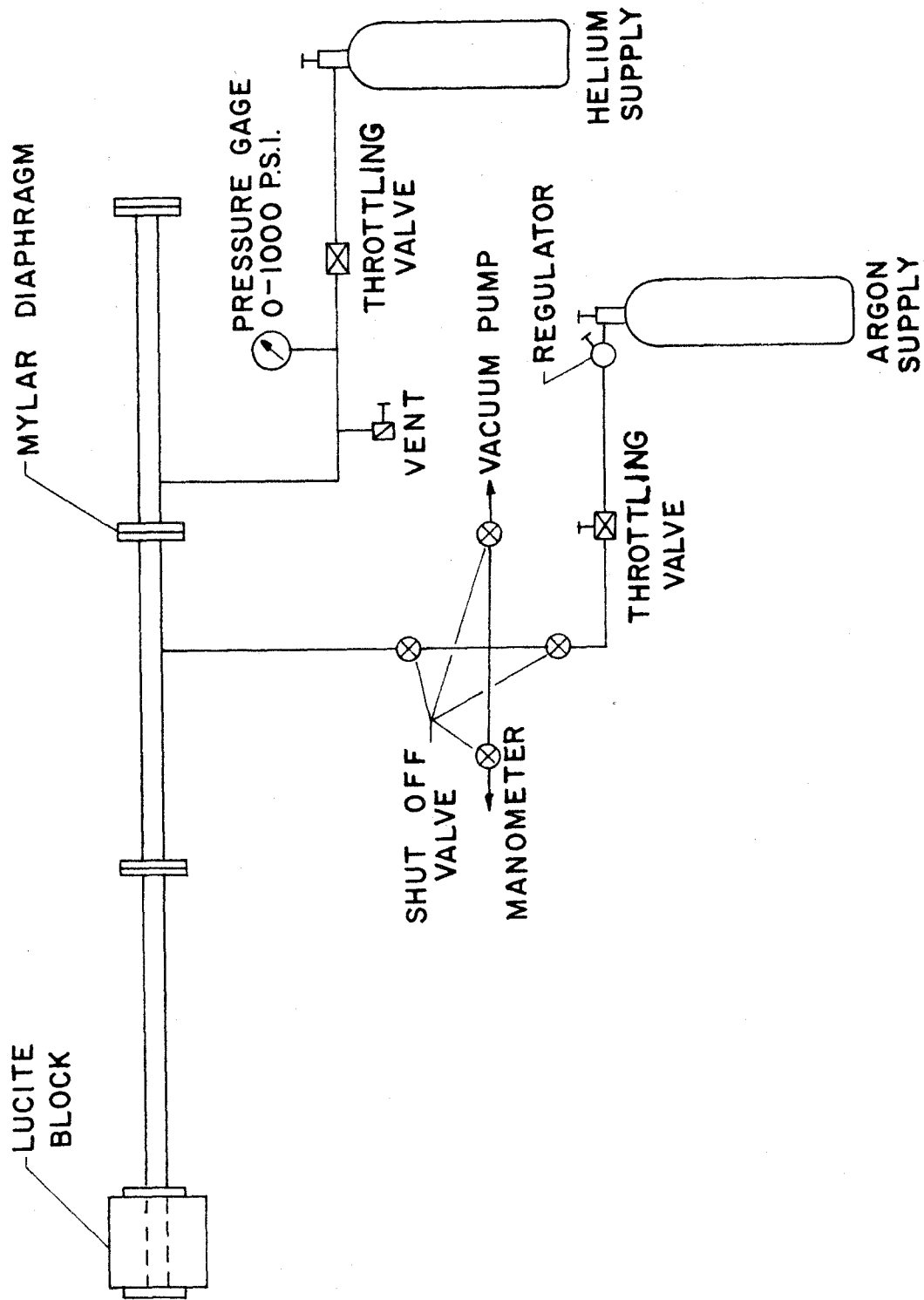


FIGURE 1. - SCHEMATIC DIAGRAM OF SHOCK TUBE AND GAS HANDLING EQUIPMENT.

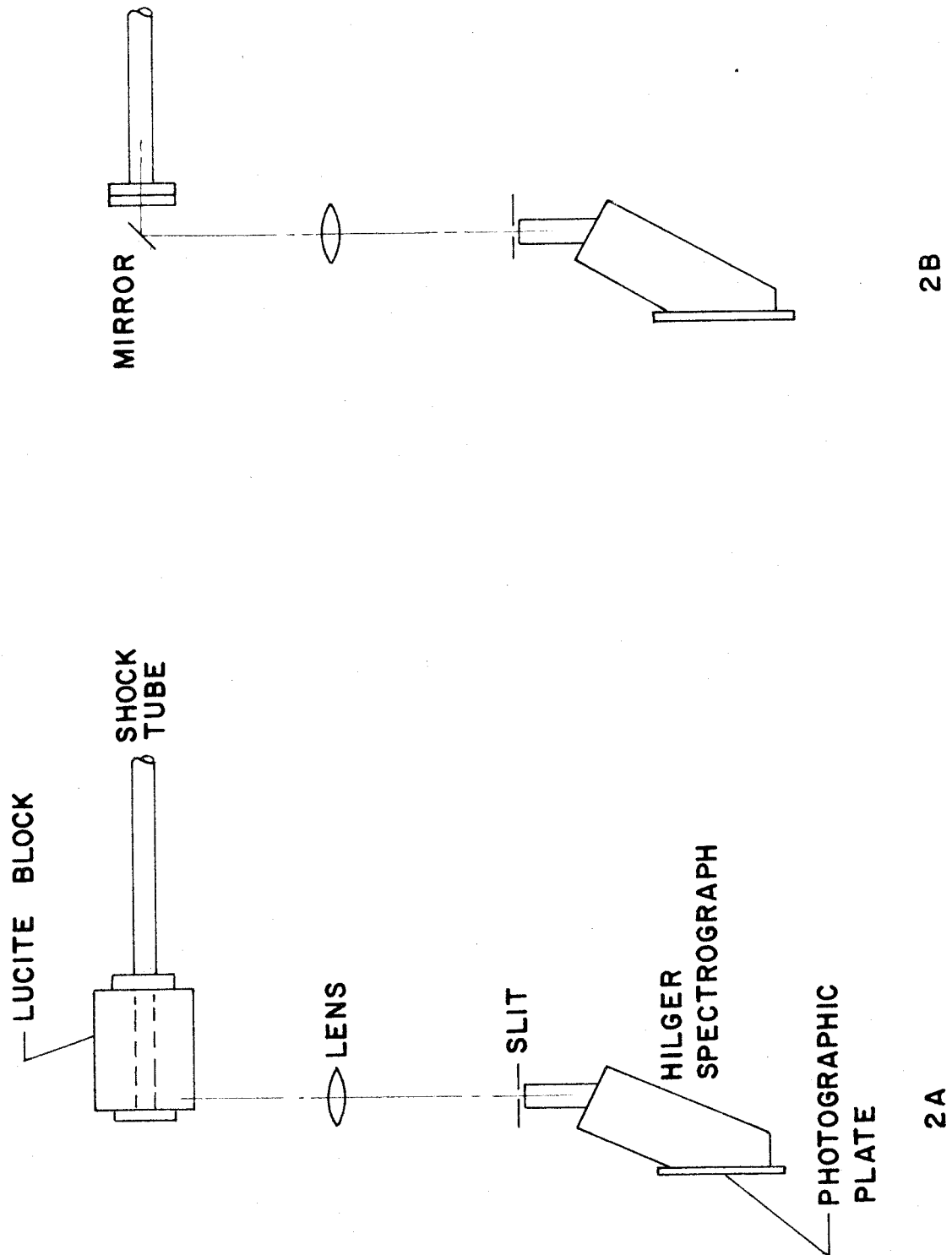


FIGURE 2. OPTICAL INSTRUMENTATION - PART 1

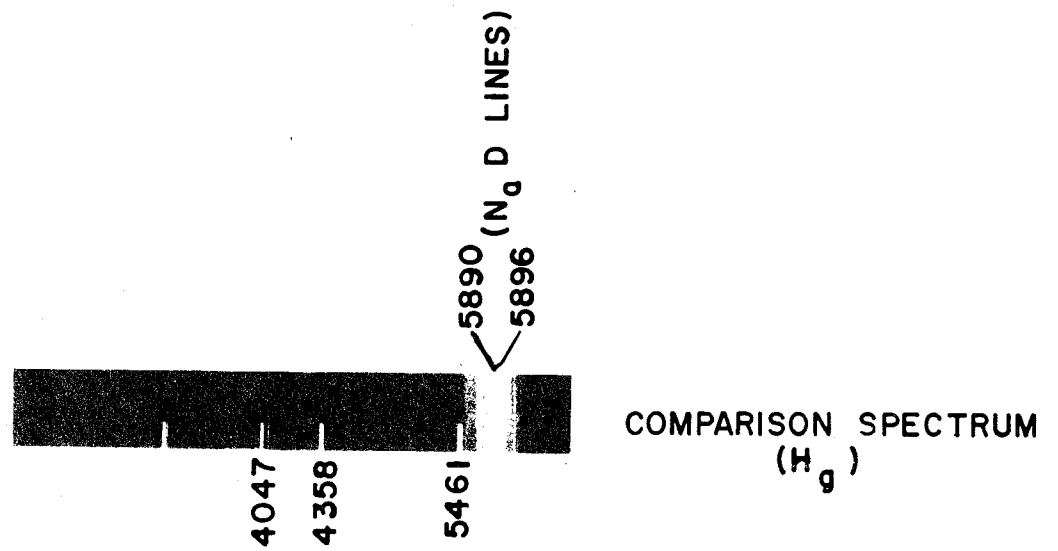


FIGURE 3. SPECTRUM OF SODIUM CHLORIDE,
REFLECTED SHOCK TEMPERATURE $\approx 7000^\circ K$.

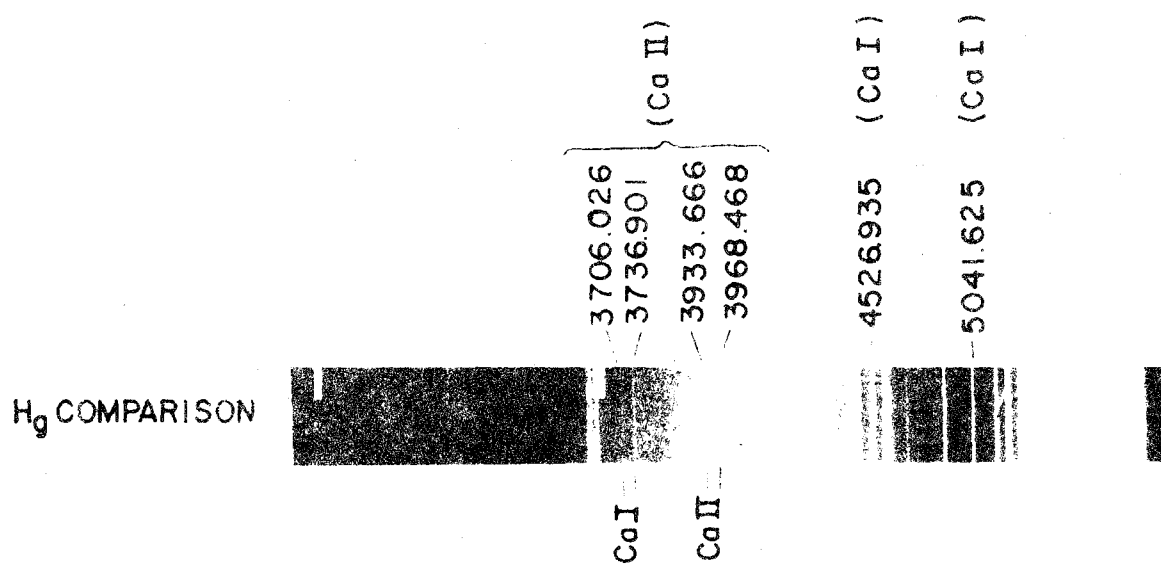


FIGURE 4. SPECTRUM OF CALCIUM CHLORIDE;
REFLECTED SHOCK TEMPERATURE $\approx 8000^{\circ}\text{K}$.

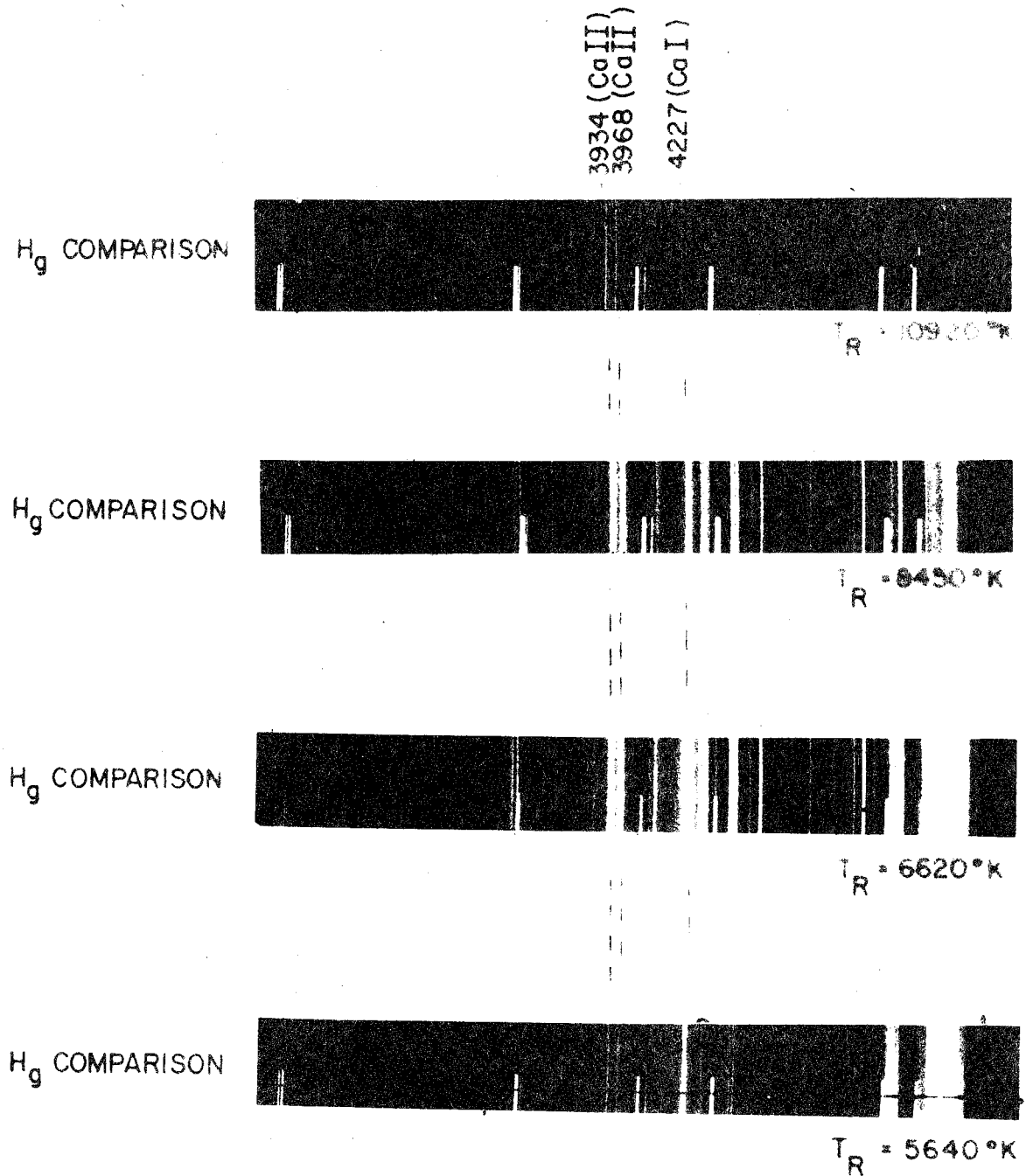


FIGURE 5. SPECTRUM OF CALCIUM CHLORIDE
AT DIFFERENT TEMPERATURES.

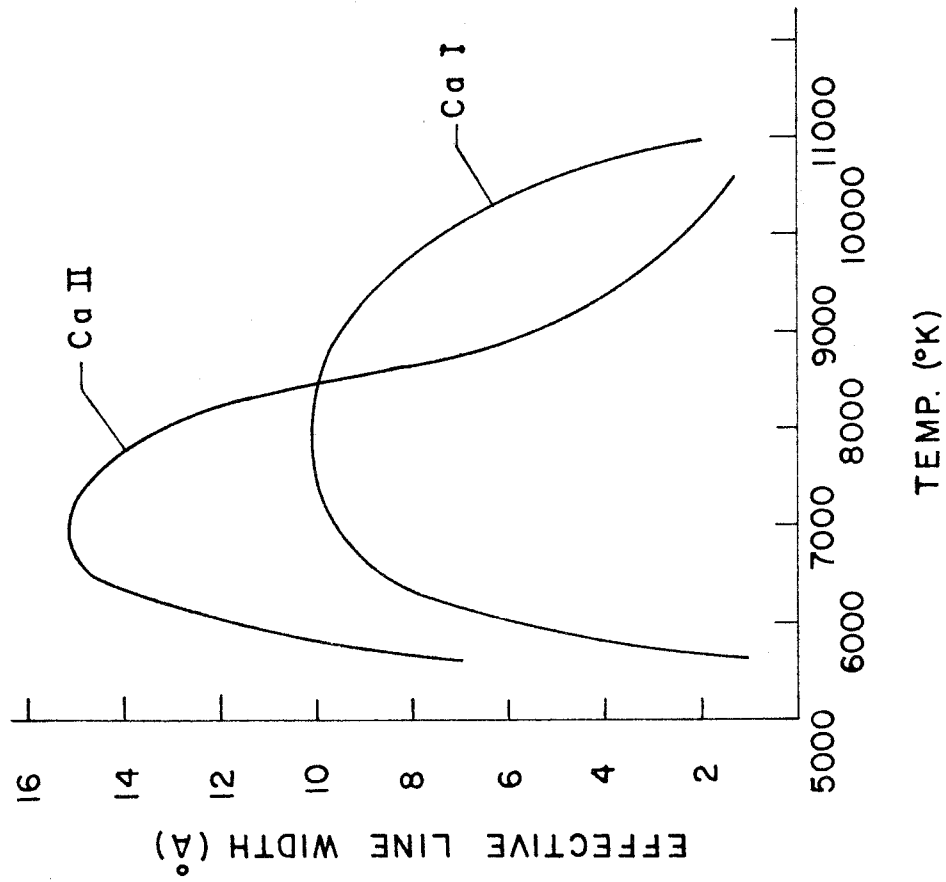


FIGURE 5A EFFECTIVE LINE WIDTH OF Ca I AND Ca II AS A FUNCTION OF TEMPERATURE.

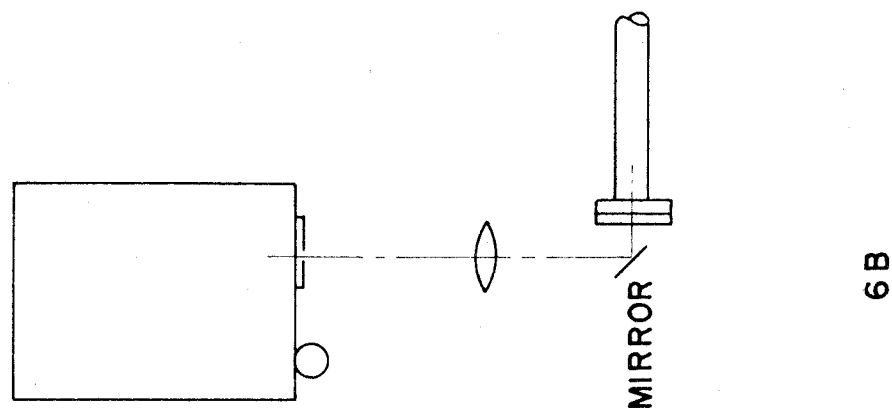
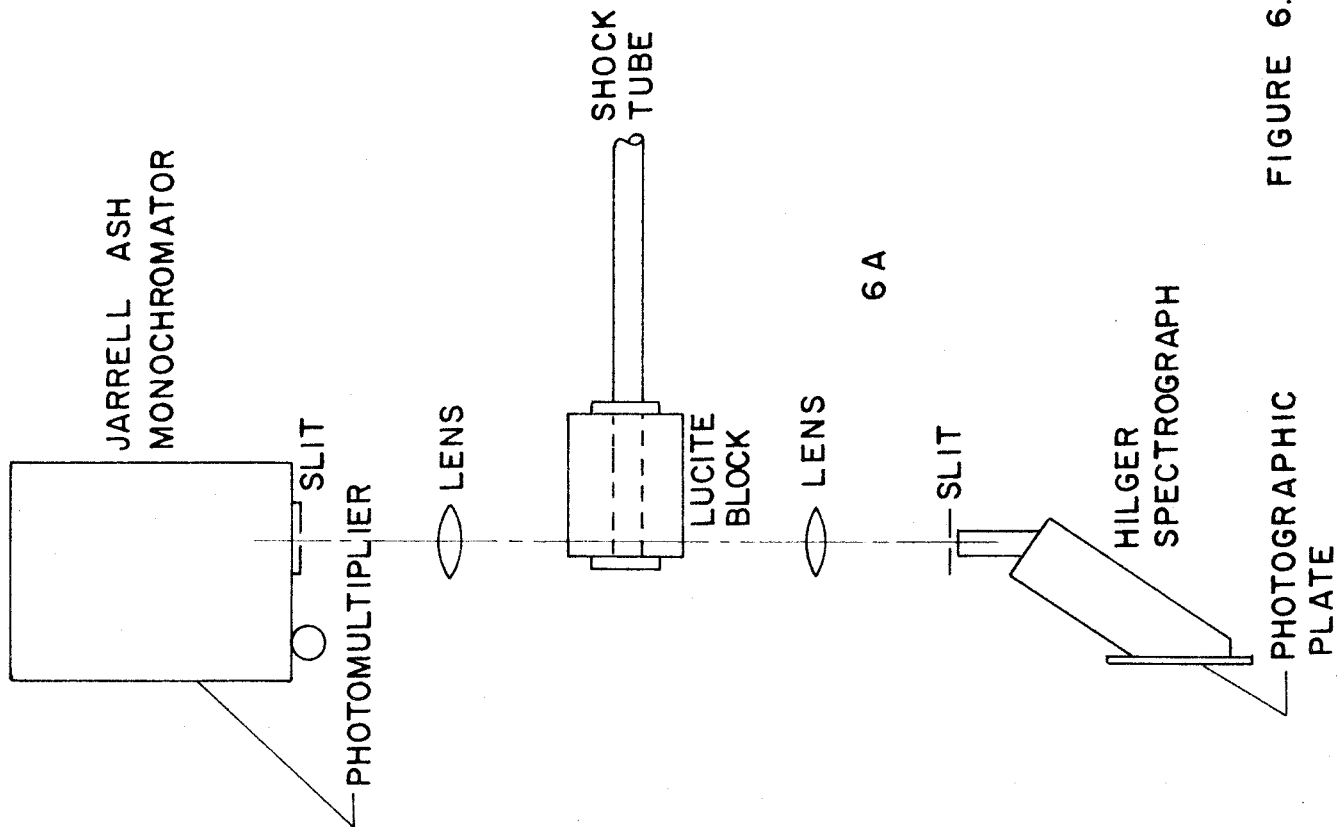


FIGURE 6. OPTICAL INSTRUMENTATION PART II

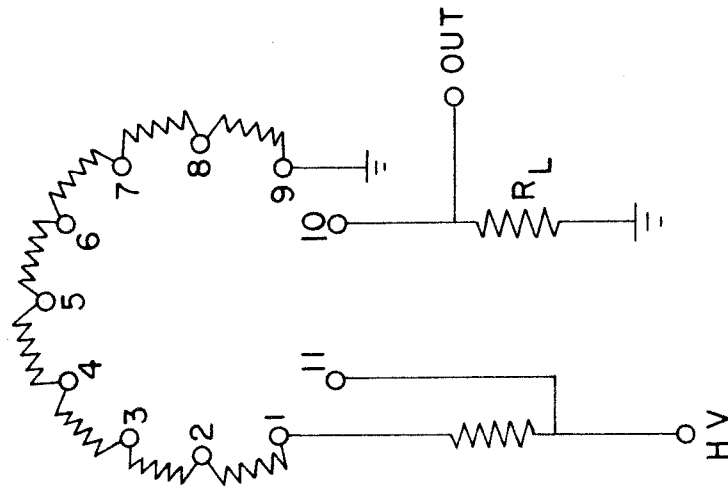


FIGURE 7. CIRCUIT FOR THE STAGE TO STAGE VOLTAGE
DIVIDER OF PHOTOMULTIPLIER TUBE - $R_L = 1K$
ALL OTHER RESISTANCES = $100K$

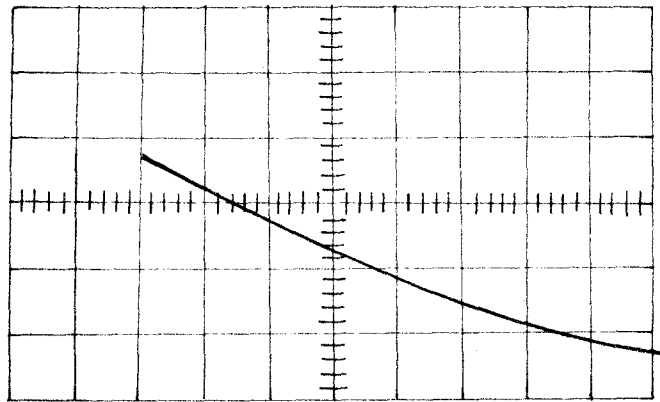


FIGURE 8. REPRODUCTION OF OSCILLOSCOPE
TRACE-INTENSITY AS A FUNCTION
OF TIME - 10 MICROSEC/CM SWEEP
SPEED.

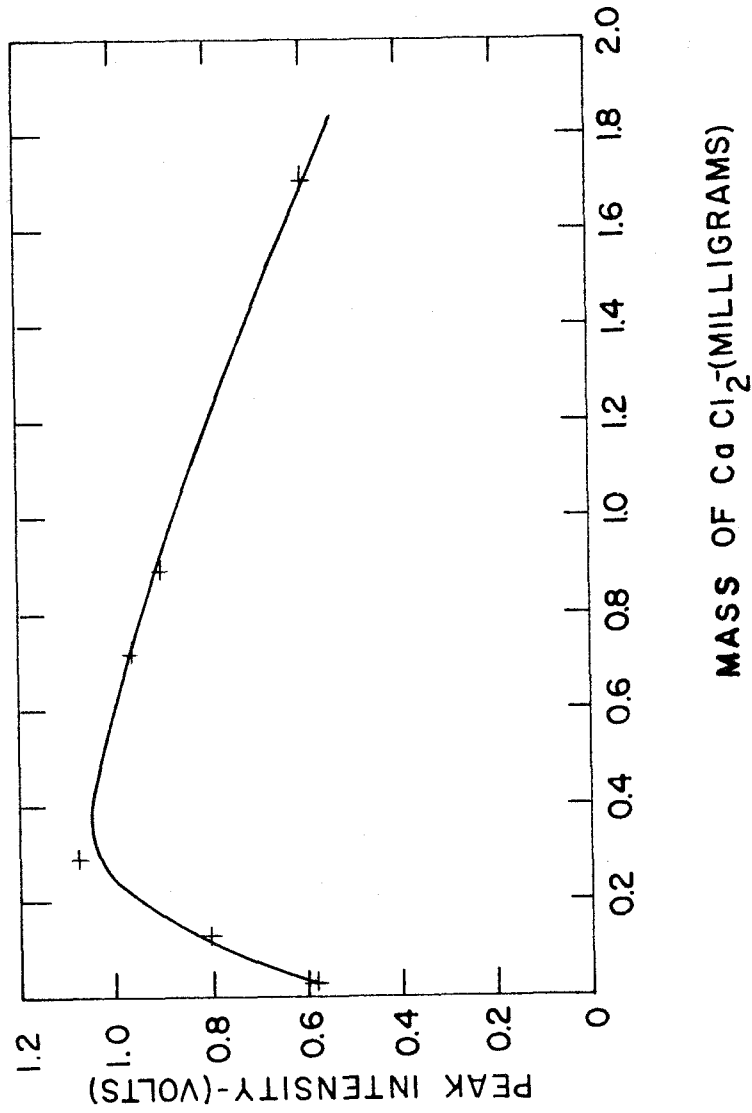


FIGURE 9. PEAK INTENSITY AS A FUNCTION OF MASS OF CaCl_2 AT 5042 Å - ALL TESTS CONDUCTED AT CONSTANT SHOCK CONDITIONS.

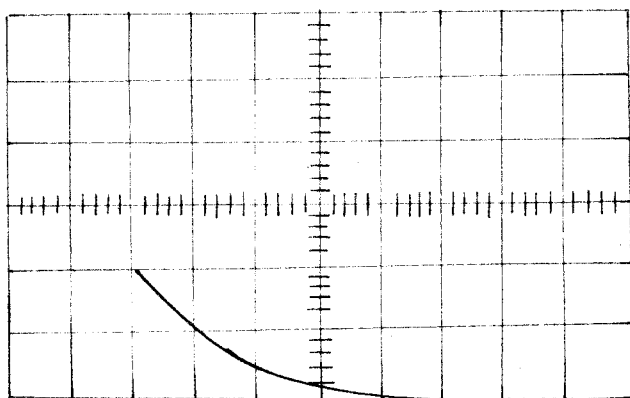


FIGURE 10. REPRODUCTION OF OSCILLOSCOPE
TRACE-INTENSITY AS A FUNCTION
OF TIME-10 MICROSEC/CM SWEEP
SPEED.

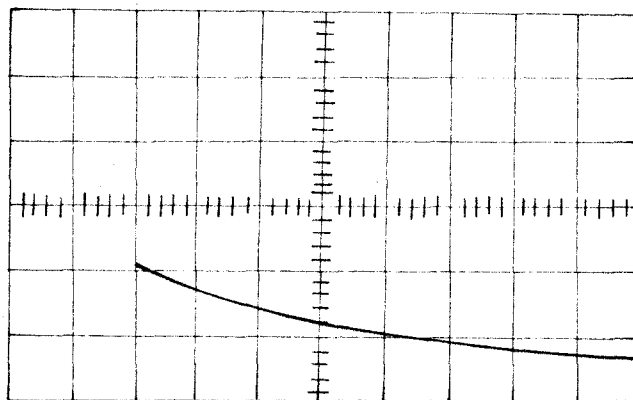


FIGURE II. REPRODUCTION OF OSCILLOSCOPE
TRACE-INTENSITY AS A FUNCTION
OF TIME-10 MICROSEC/CM SWEEP-
LUCITE BLOCK COVERED WITH
ALUMINUM FOIL.

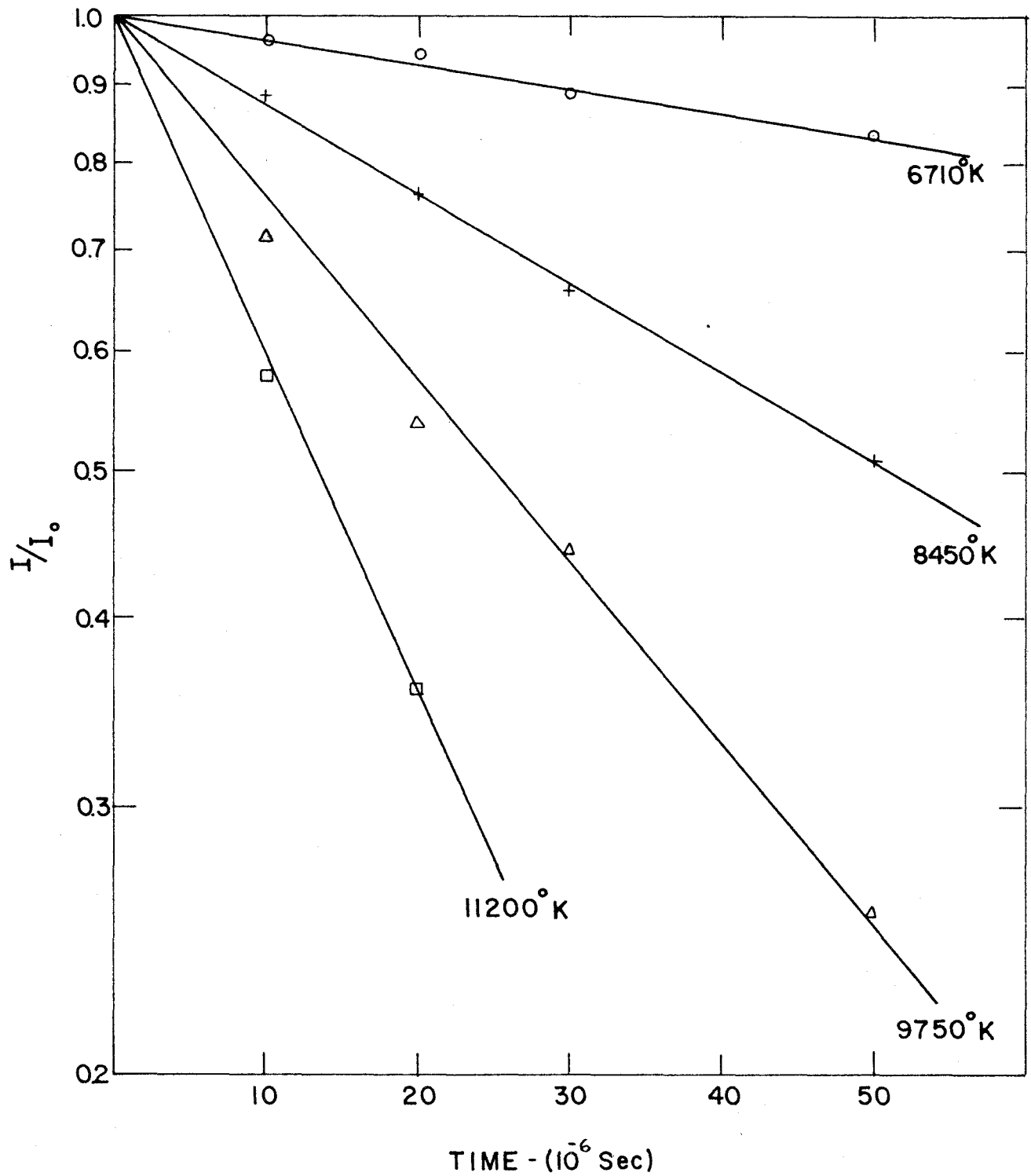


FIGURE 12. $\ln I/I_0$ AS A FUNCTION OF TIME
FOR REPRESENTATIVE SHOTS.

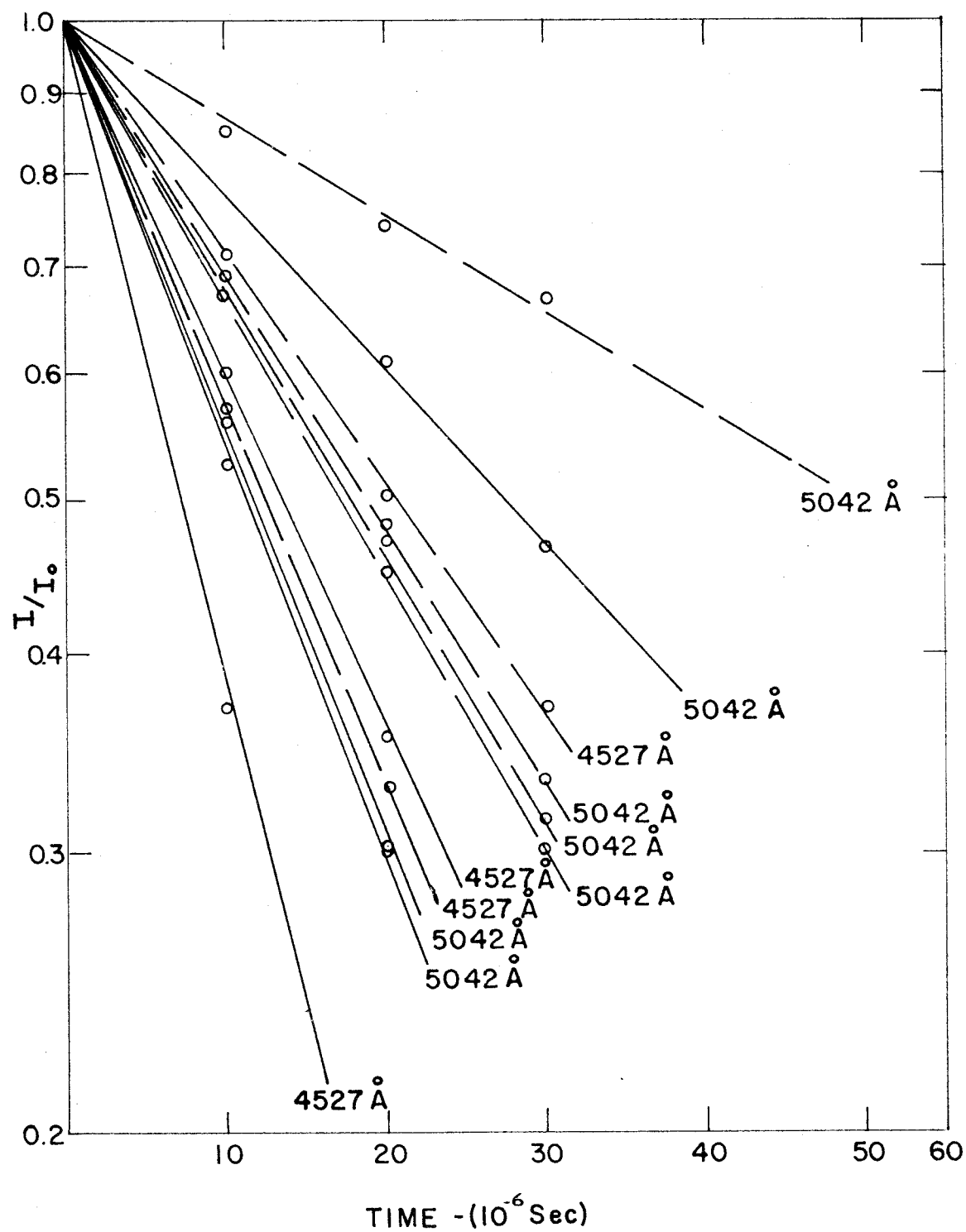


FIGURE 13. $\ln I/I_0$ AS A FUNCTION OF TIME FOR ALL TESTS MADE AT 5MM. DOTTED LINES REPRESENT TESTS MADE WITH LUCITE BLOCK COVERED WITH ALUMINUM.

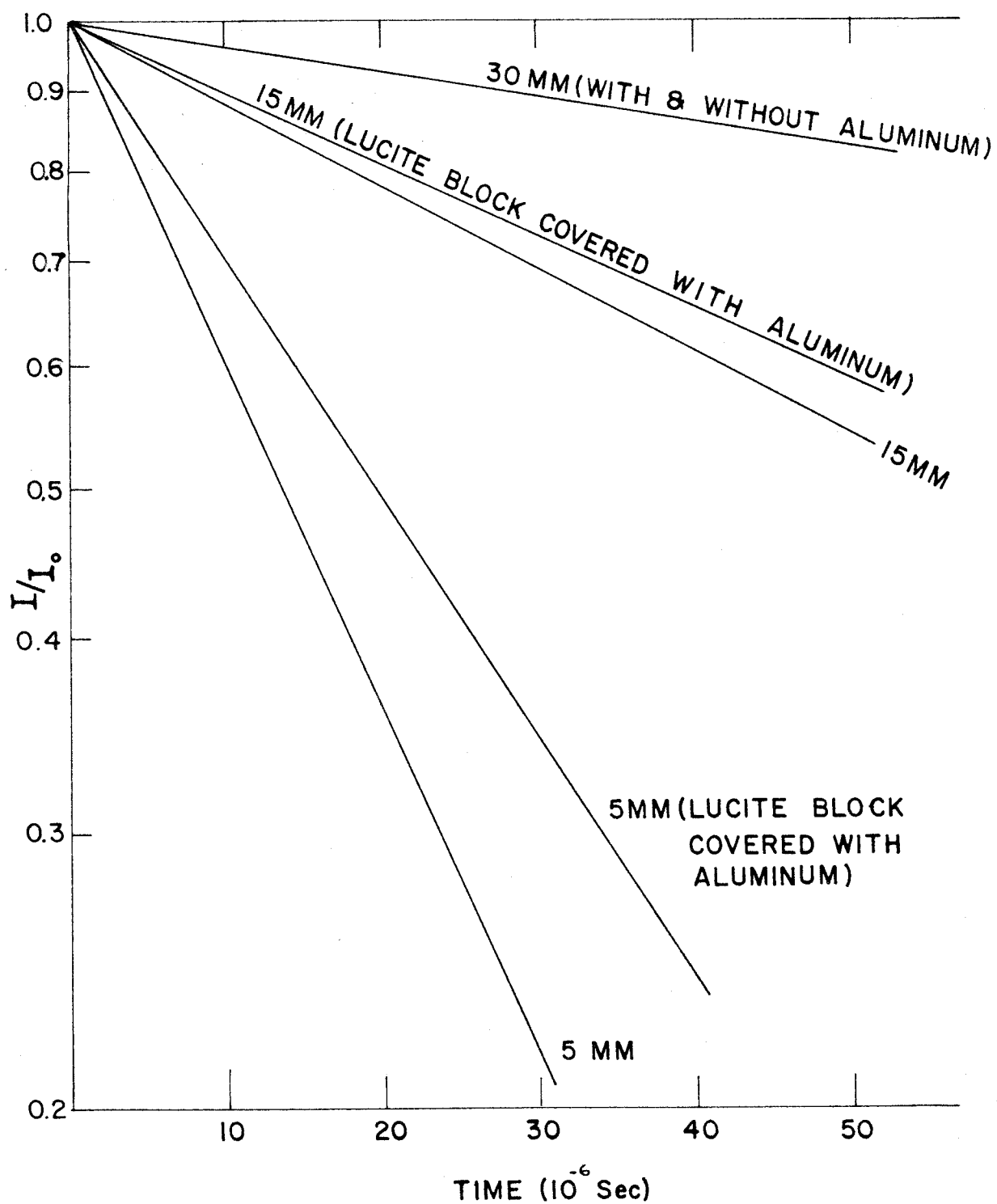


FIGURE 13A AVERAGE VALUE OF $\ln I/I_0$ FOR ALL TESTS MADE UNDER SIMILAR CONDITIONS AS A FUNCTION OF TIME.

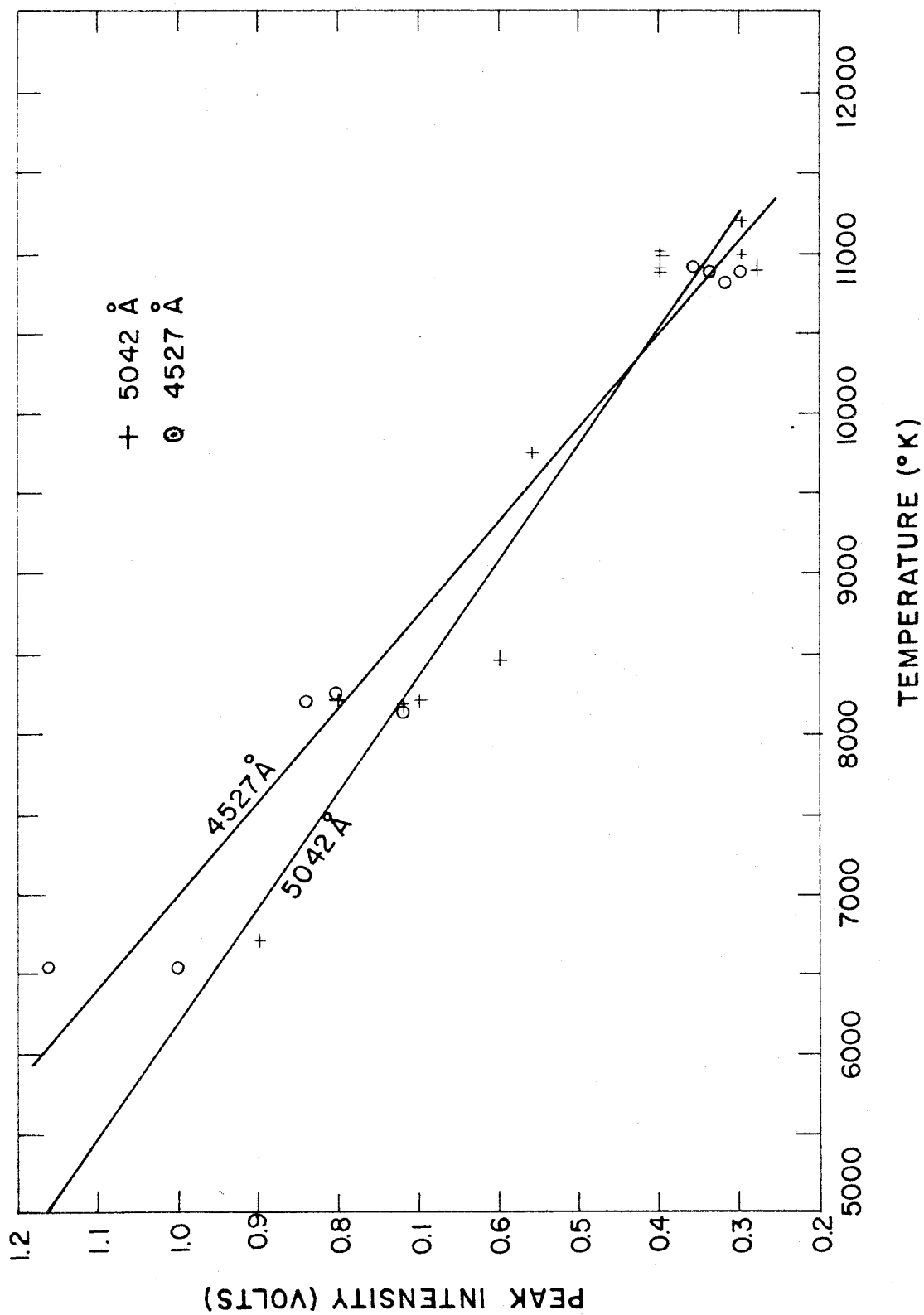
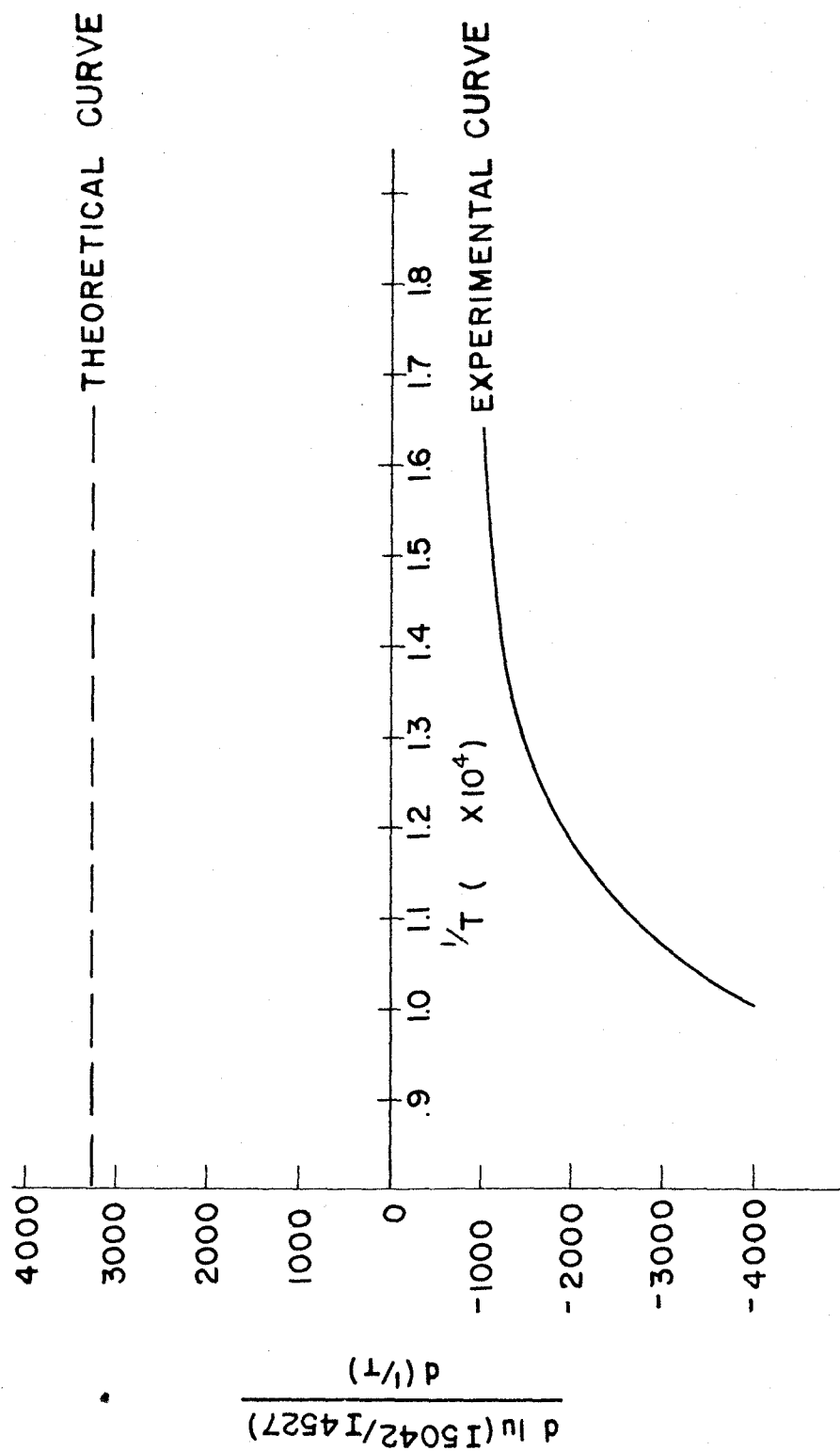


FIGURE 14. PEAK INTENSITY AS A FUNCTION OF THEORETICAL TEMPERATURE FOR SPECTRAL LINES 5042 Å & 4527 Å



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FIGURE 15 $\frac{d(\ln I_{5042}/I_{4527})}{d(1/T)}$ AS A FUNCTION OF RECIPROCAL TEMPERATURE.