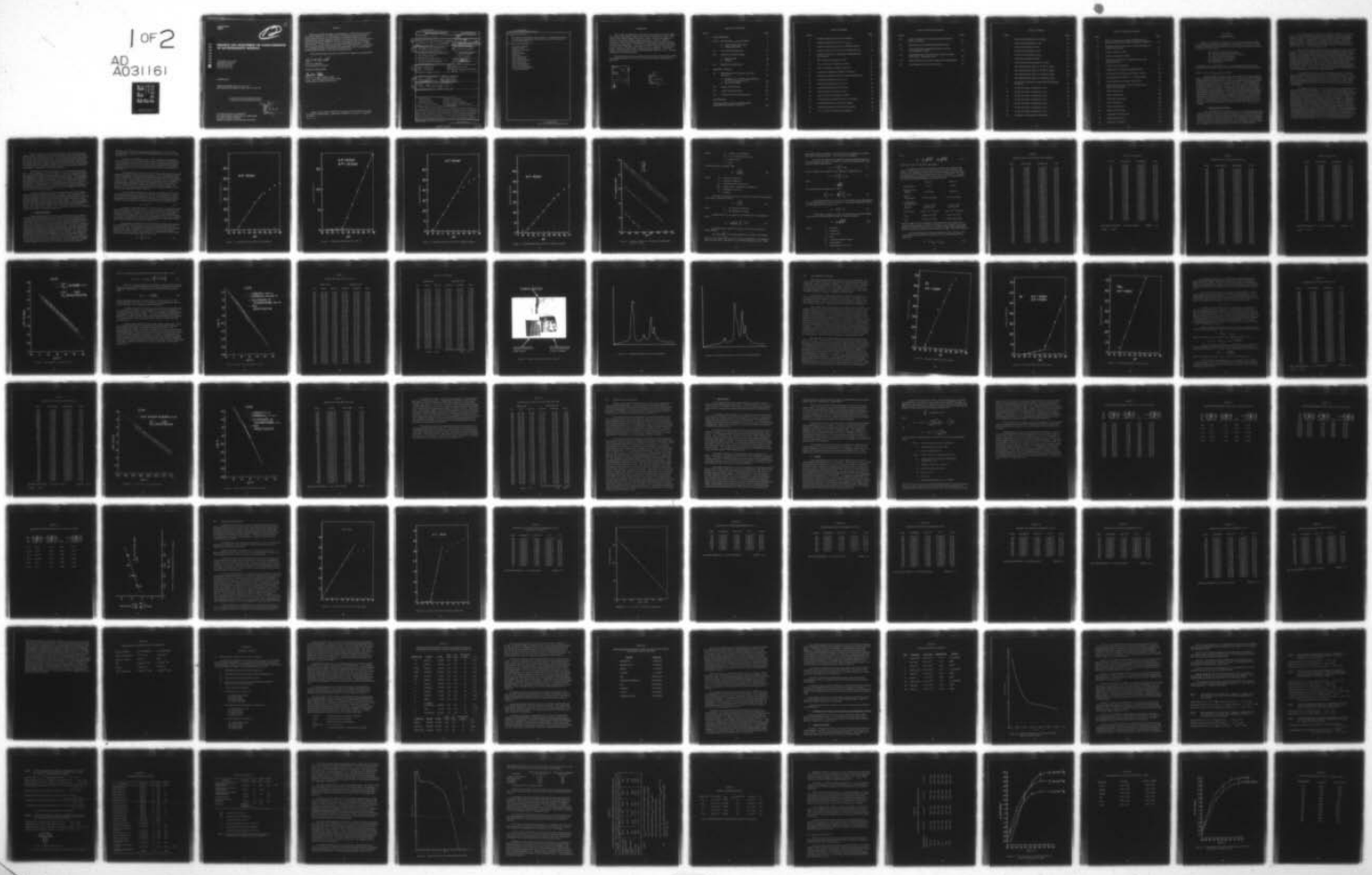
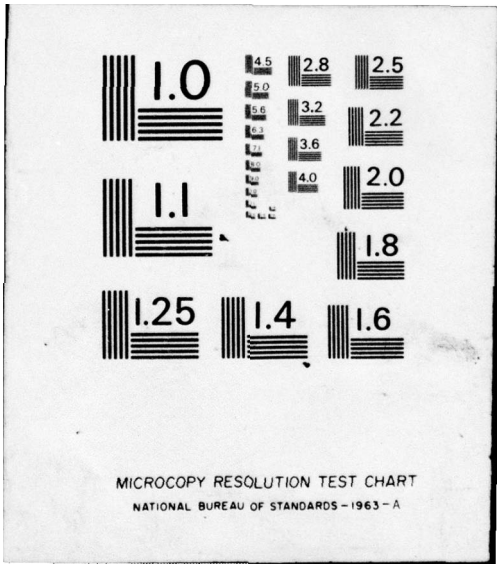
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RESEARCH AND DEVELOPMENT ON CHARACTERIZATION OF ELECTROMAGNETIC MATERIALS

UNIVERSITY OF DAYTON
RESEARCH INSTITUTE
300 COLLEGE PARK
DAYTON, OHIO 45469

DECEMBER 1975

TECHNICAL REPORT AFML-TR-74-37, Part II
FINAL REPORT FOR PERIOD 12 APRIL 1972 - 30 JUNE 1974

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This technical report has been reviewed and is approved for publication.

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FOR THE COMMANDER

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This report is in two sections. The first section covers research on thermodynamic property measurements and calculations of (Hg, Cd, Te) system, CdTe, ZnSe, samarium, cobalt and titanium-iron alloy systems. A bibliography on high temperature mass spectrometry from Chemical Abstracts from 1970-1973 includes 343 references. The second section includes chemical physical studies on dye laser materials. Dye laser materials were characterized as to: (1) absorption spectrum, (2) fluorescence emission spectrum,

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20. Abstract (Continued)

(3) radiative decay lifetime of fluorescence, (4) intersystem crossing rate and triplet-triplet absorption spectrum, and (5) various laser emission parameters.

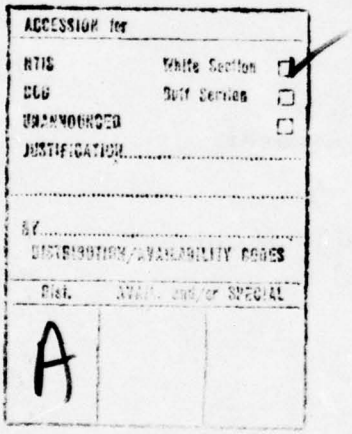
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Ester Azobenzenes
Carbonate Azobenzenes
Alkyl Azobenzenes
Ether Azoxylbenzenes
Ester Azoxylbenzenes
Carbonate Azoxylbenezenes
Alkyl Azoxybenzenes

FOREWORD

This report was prepared by the University of Dayton Research Institute, Dayton, Ohio 45469, under USAF Contract F33615-72-C-1666. This contract was initiated under Project No. 7360, "Thermal and Chemical Behavior of Advanced Weapon System Materials", Task No. 736001, "Chemical, Physical and Thermodynamic Properties of Aircraft, Missile, and Spacecraft Materials". The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command with Paul W. Dimiduk, AFML/LPH, acting as project engineer. One of the authors, Duane Earley, wishes to acknowledge the aid of Dr. E. J. Rolinski, AFML/LPJ, during this project.

This report covers work conducted from 17 April 1972 to 30 June 1974, in exploratory studies of the thermo- and chemical-physical properties of materials.



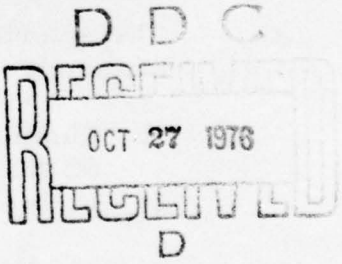


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SECTION I

THERMOPHYSICS

This work consisted of a program to make measurements and deduce thermodynamic properties of materials of interest to the Air Force. This program consisted of measurements in five (5) materials systems and others as required. These were:

(A) Cadmium Telluride Compounds
(B) Mercury Cadmium Tellurium System
(C) Zinc Selenide Compounds
(D) Titanium-Iron Alloy System
(E) Samarium-Cobalt System
(F) Bibliography

In addition to this experimental work, a bibliographical search was also performed from the time period of 1970 to 1973, using Chemical Abstracts.

(A&B) CdTe and $Hg_{(1-x)}Cd_xTe$ Systems

Electronically useful group IIB chalcogenides have been studied to provide thermodynamic properties. However, in the case of CdTe, thermal analysis studies of deNobel[1] and Lorenz[2] were primarily aimed to determine equilibrium compositions for crystal growth studies. The development of the phase diagram for CdTe was further studied by Brebrick and Strauss[3] by optical absorption methods. Knudsen cell experiments were performed by Korneeva et al.[4] assuming a composition of the vapor species. Mass spectrometric measurements were first obtained by Drowart and Goldfinger[5] and Goldfinger and Jeunehomme.[6] Their measurements indicated that the vapor above the subliming solid was primarily Cd and Te_2. Further mass spectrometric studies were made by DeMaria et al.[7] and Ivanov and Vanyukov[8] to determine relative values for electron impact ionization cross-sections. The purpose of this study was to systematically analyze the vaporization of CdTe with the intent to extend this work to the $Hg_{(1-x)}Cd_xTe$ system.

1. Experimental Description

This investigation of the vaporization of CdTe and $Hg_{(1-x)}Cd_xTe$ was conducted using the mass spectrometric technique. The details of such techniques as applied to the area of high temperature phenomena have been previously discussed.[9] The instrument used in this study is a Nuclide Analysis Associates 12-90-HT mass spectrometer. This instrument is a 90°-sector, 30-5 cm radius of curvature, first-order direction focusing mass spectrometer equipped with a high temperature Knudsen cell sample system.

The sample system consists of a cylindrical Knudsen cell centered on the axis of a bifilarly wound tungsten helix which serves as a heating element. Both the cell and heater are surrounded by radiation shielding, and cell heating is accomplished by radiative heat transfer. The entire furnace complex is mounted on an assembly which in turn is driven by a bellows drive arrangement, allowing the investigator to adjust the position of the furnace assembly when under vacuum.

The vacuum housing around the furnace assembly is water jacketed, and water cooling is also provided to some of the support members of the furnace. The housing contains viewports enabling the experimenter to sight the top, side and bottom of the Knudsen cell in order to make optical temperature measurements, and it has provision for thermocouple feedthroughs. A mechanically operated "shutter" is located above the cell and is driven by a micrometer-bellows assembly. This movable collimator between the sample system and the ion source serves to differentiate between species in the molecular beam from the cell and those present as background gases in the vacuum system. The "shutter" assembly also provides information concerning the intensity profile of the molecular beam.

The Knudsen cell used in this investigation consists of a tantalum jacket surrounding a POCO graphite cell. The graphite cell has a 0.1 cm diameter orifice. The channel length of the orifice in this design is 0.15 cm and the ratio of internal cell area to orifice area is 810 to 1. The tantalum jacket encapsulating the graphite cell serves as a holder, provides a convenient place for thermocouple attachment and helps to ensure isothermal cell conditions.

The sample temperatures in this investigation were determined using Chromel-Alumel thermocouples which were peened into blind holes in the bottoms of the cells or cell holders. The legs of the thermocouples were led out of the vacuum envelope through Conax fittings. The thermocouples were fabricated from calibrated 24 gauge Chromel and Alumel wire. The hot junctions were formed by arc-welding in an inert atmosphere. A typical hot junction had a 1.25 mm bead when made in this way. Prior to installation, the calibration of selected thermocouples was checked against a standard thermocouple. After installation, the calibration was again checked against the fusion point of zinc. A separate calibration run was made to check the sample temperature and the bottom-holder temperature. Where appropriate, corrections to actual sample temperatures were made. We take the error in our temperature measurements to be ±1.0°C based on our observations. The thermal emf's generated by these thermocouples were referenced to the ice point and were measured using a Leeds and Northrup Type K-5 potentiometer in conjunction with a L & N d.c. null detector, Model 9834-1.

The ion source on the Nuclide instrument is a Nier-type electron-impact source. During the course of these studies, data were taken using 18 eV electrons except where noted. The emission current was always held at 0.5 mA. The ions resulting from electron impact ionization processes occurring in the source were accelerated through 5000 volts and focused on the entrance slit to the magnetic analyzer which was set at 0.153 mm width. The exit slit from the analyzer field was set at the same width. With such a geometry, a resolution of 1/1500 was obtained.

The detector in use for this study was a 16-stage electron multiplier. This multiplier has Cu-Be dynodes. A series of experiments using ionic species of a range of atomic weights was carried out using an insertable Faraday cup collector to measure the multiplier gain. The dependence of multiplier gain on the inverse square root of the ionic mass, which has previously been reported,[10-12] was not observed. Within the scope of our experiments, the gain appears to be quite insensitive to the mass of the impinging ion. Such behavior is consistent with the findings of Gingerich.[13] In view of this observation, we took the gain of the multiplier to be 10^6 for all species under these conditions.

The CdTe samples used in this investigation were polycrystalline materials made by Gould Laboratories, Cleveland, Ohio, starting from Ventron "ultrapure" CdTe, Lot 4F-248 which had a listed purity of 99.9999%. Mass spectrographic analysis was performed on this material and listed element impurities were 65 ppm C, and 7 ppm Oxygen. The CdTe sample material was used as received following several hours of degassing at about 150°C. The $Hg_{(1-x)}Cd_xTe$ samples were obtained from Honeywell[14] as type N, 90V, Nos. 121-131 with x = 0.27. The $Hg_{0.73}Cd_{0.27}Te$ was degassed at about 60°C prior to elevated heating runs.

2. Experimental Data

Initial experiments were carried out to identify the ionic species resulting from the vaporization of the CdTe system. Mass spectra were recorded under isothermal conditions of 550°C and mass numbers assigned to the peaks by peak counting and by magnetic field measurements. The peaks of the ionic species originating from the Knudsen cell were differentiated from background peaks by their shutterability. The ionic species were identified by comparing the experimentally determined relative intensities within each peak group with calculated isotopic abundances for each ion and by appearance potential determinations for each species. The appearance potentials were determined by applying the linear extrapolation method to plots of the ionization efficiency curves for each species. The energy of the ionizing electrons was fixed by measurement of the appearance potential of Hg, which is present as a background gas. The ionic species identified and their appearance potentials were in good agreement with those of

Franklin et al.[15] for the first appearance potentials of Cd^+, Te^+, Te_2^+. The appearance potential for Te_3^+ was determined to be 8.5 ± 0.5 eV (see Figures 1-4)

The ionization efficiency curve for Te^+ displayed a sharp break. The first AP was taken to represent the simple ionization of the neutral Te. The second AP of 12.0 ± 0.5 eV marked by the discontinuity of the slopes of the ionization efficiency curve, was taken to represent the dissociative ionization of the Te_2 molecule substantiating the results of Drowart and Goldfinger.[5]

Calculations of the degree of dissociation at different pressures and temperatures indicate that at the temperatures of this investigation, dissociation is negligible. Measurements obtained indicate actual concentrations of Te^+ and Te_3^+ in the gas phase to be less than 2.0% and 0.2%, respectively, of that of Te_2^+. These findings justify the assumption, used in all of the thermodynamic calculations in this investigation, that the vaporization of CdTe is congruent and gives mainly the species $Cd_{(g)}$ and $Te_{2(g)}$. The presence of $Te_{(g)}$ and $Te_{3(g)}$ are minor and have no significant effect on the thermodynamic properties (see Figure 5).

The ion current intensity of each of the ions identified in the mass spectrum was recorded as a function of Knudsen cell temperature. It has been shown[16] that the partial pressure, P_i, of a neutral species is directly proportional to the product of the cell temperature and the intensity measured for an ion resulting from ionization of the neutral in question, thus

$$P_i = kI_i^+T \qquad (1)$$

In order to relate the intensity of a given species as measured by the mass spectrometer to the pressure of the neutral precursor of that species inside the equilibrium enclosure, it is necessary to carry out some type of calibration procedure. In the case of the present work such calibration was carried out by a quantitative vaporization of a quantity of CdTe. The rationale involved in the treatment of the data resulting from these quantitative vaporizations has been discussed in part previously.[9, 17]

The sample is introduced into the effusion cell and the cell is heated to a temperature at which the pressure of the equilibrium vapor is in the region of 10^{-5} atm. The intensity of the species resulting from the ionization of the effusing beam is followed as a function of time until the sample is exhausted. The total number of molecules of the standard which effuse from the cell during the vaporization may be written as

$$Z_t = \int_0^t \nu\, s\, dt \qquad (2)$$

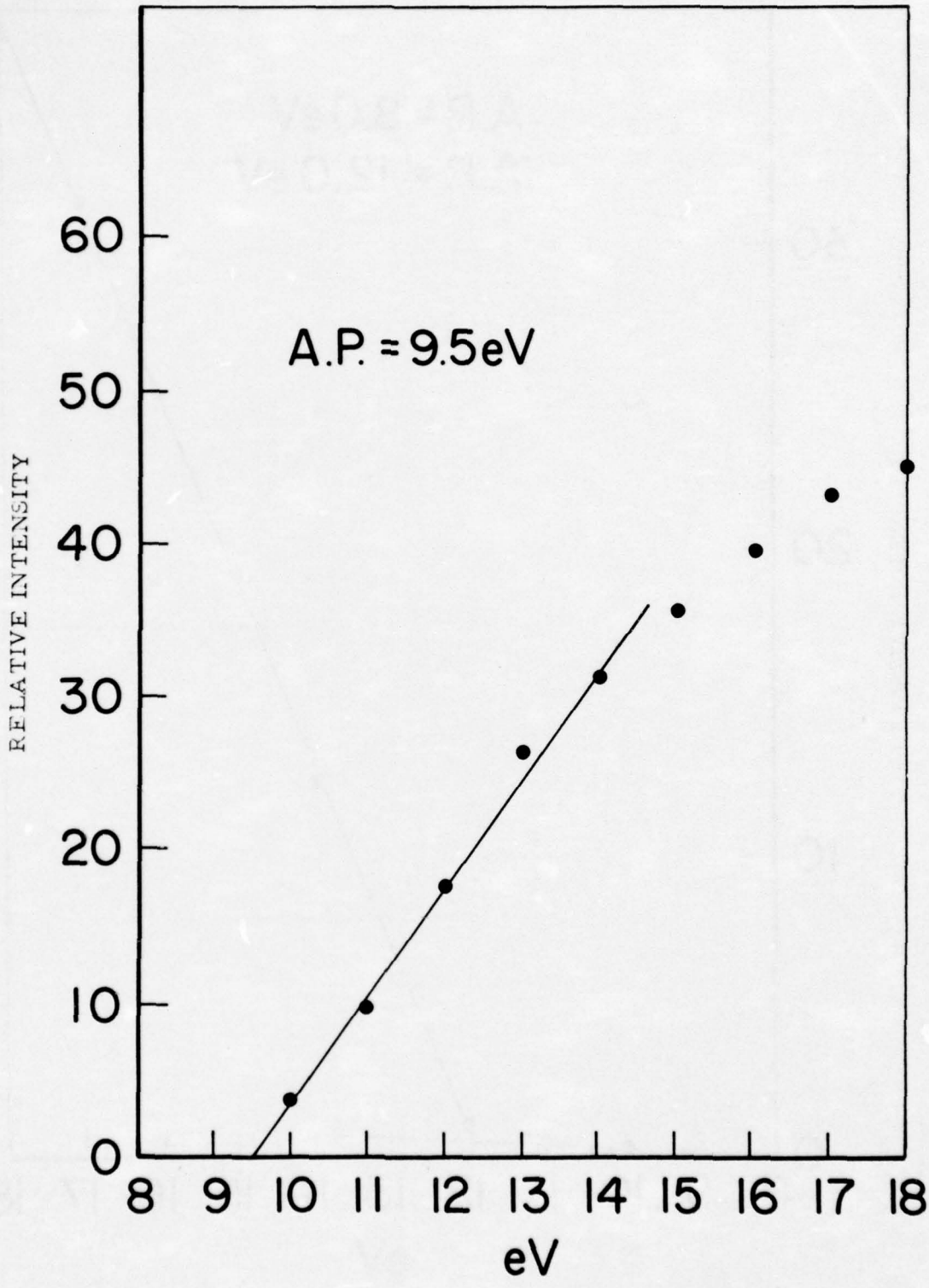


Figure 1. Ionization Efficiency Curve for Cadmium

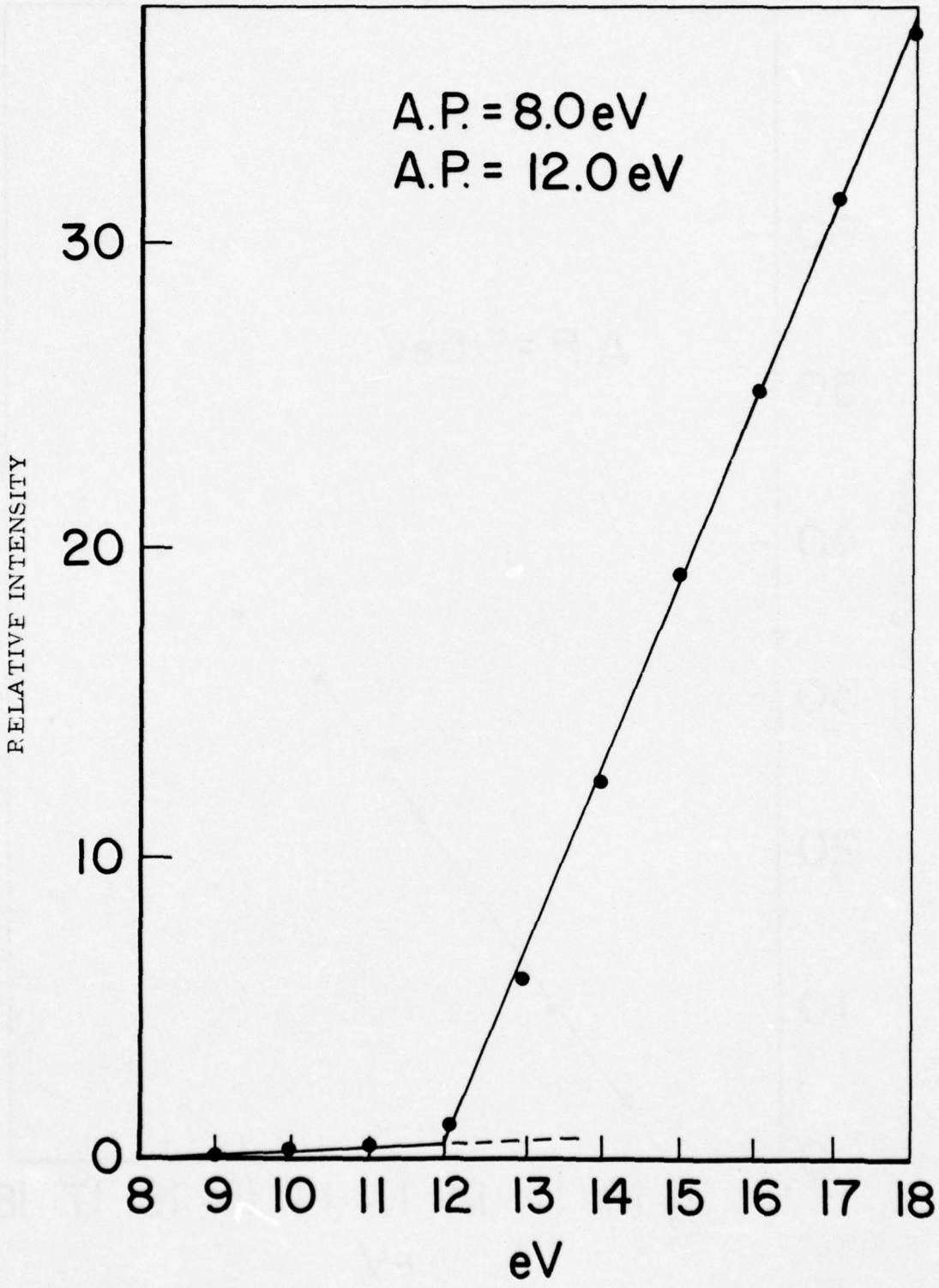


Figure 2 . Ionization Efficiency Curve for Te

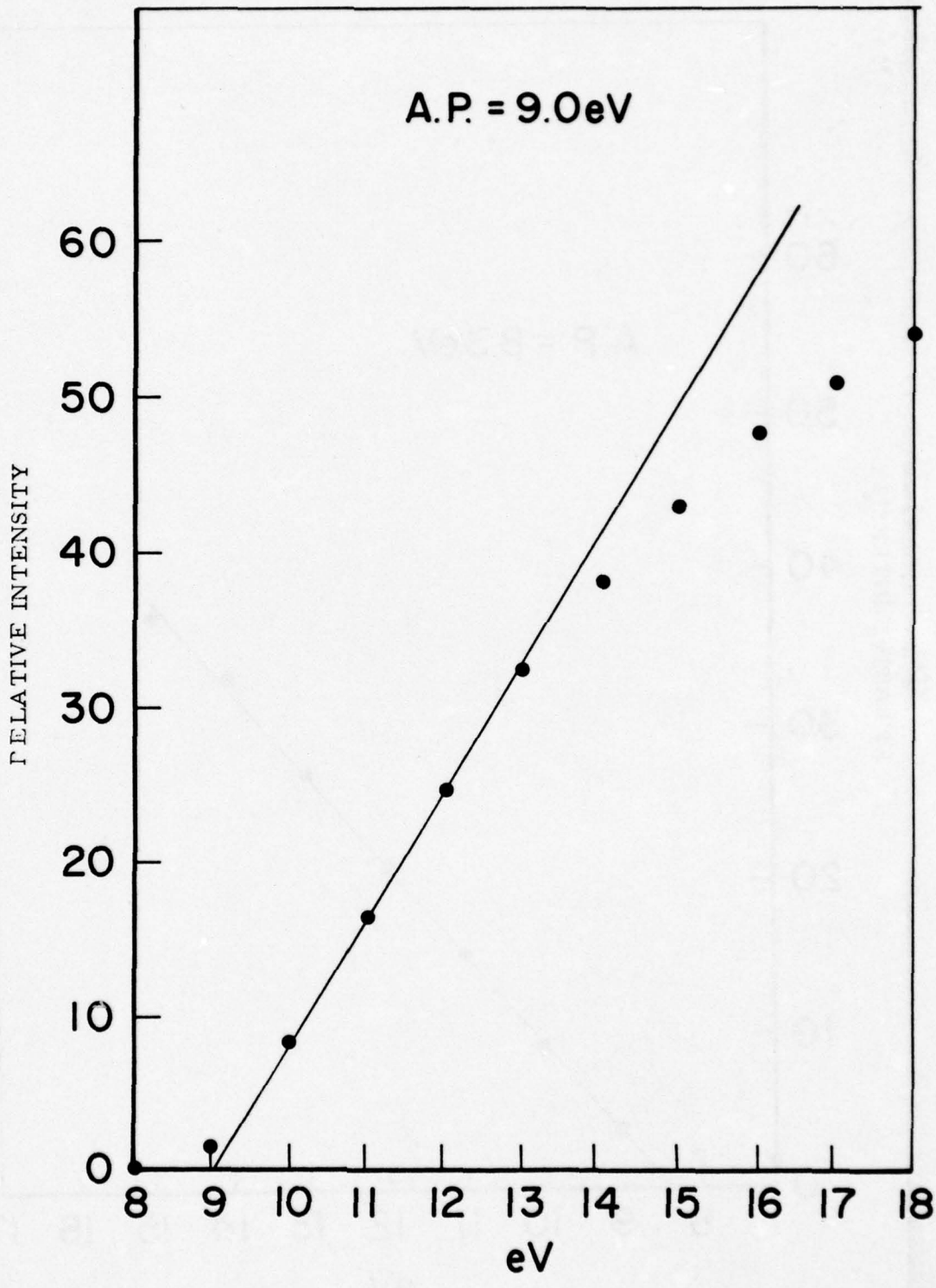


Figure 3. Ionization Efficiency Curve for Tellurium Dimer

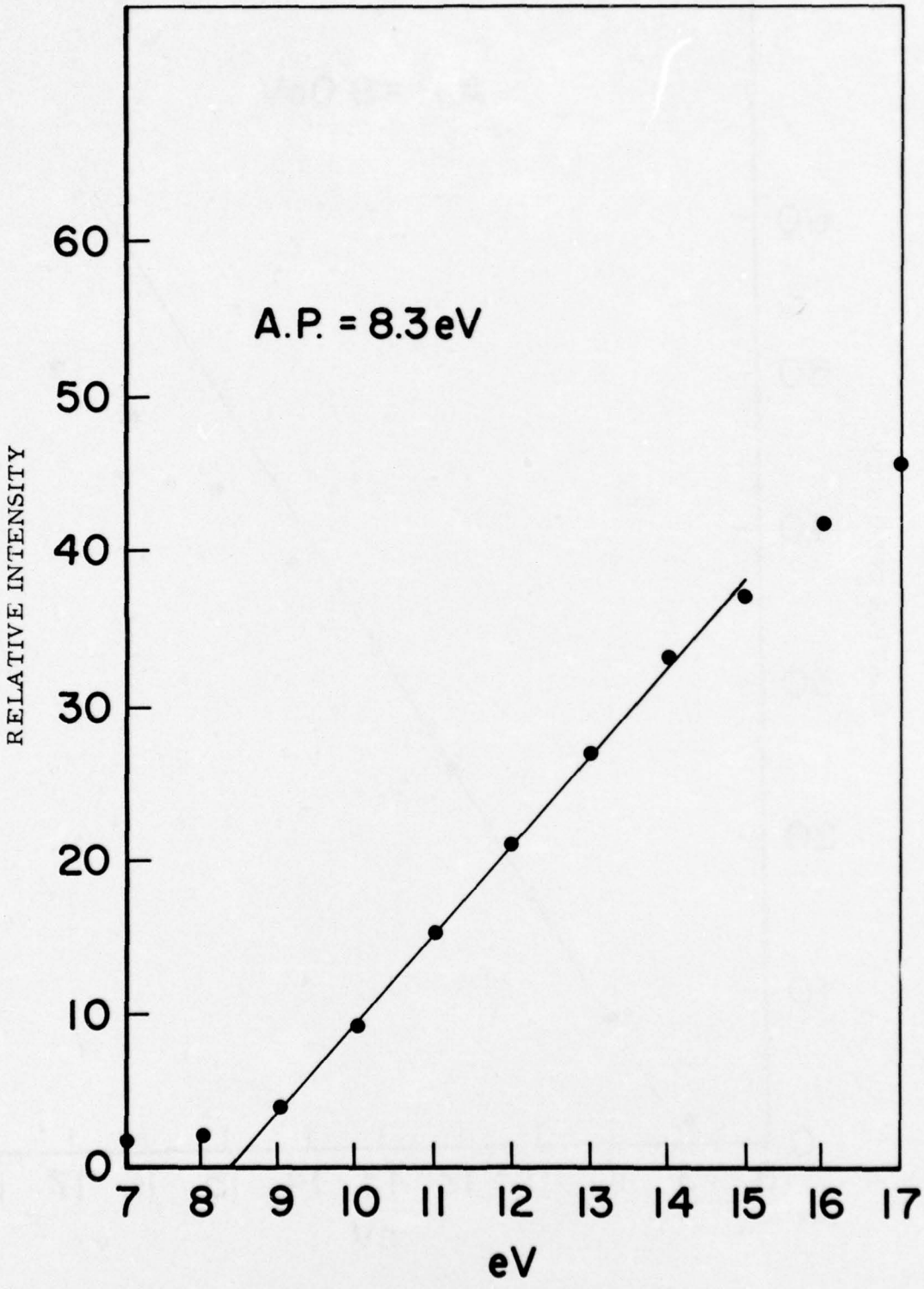


Figure 4. Ionization Efficiency Curve for Tellurium Trimer

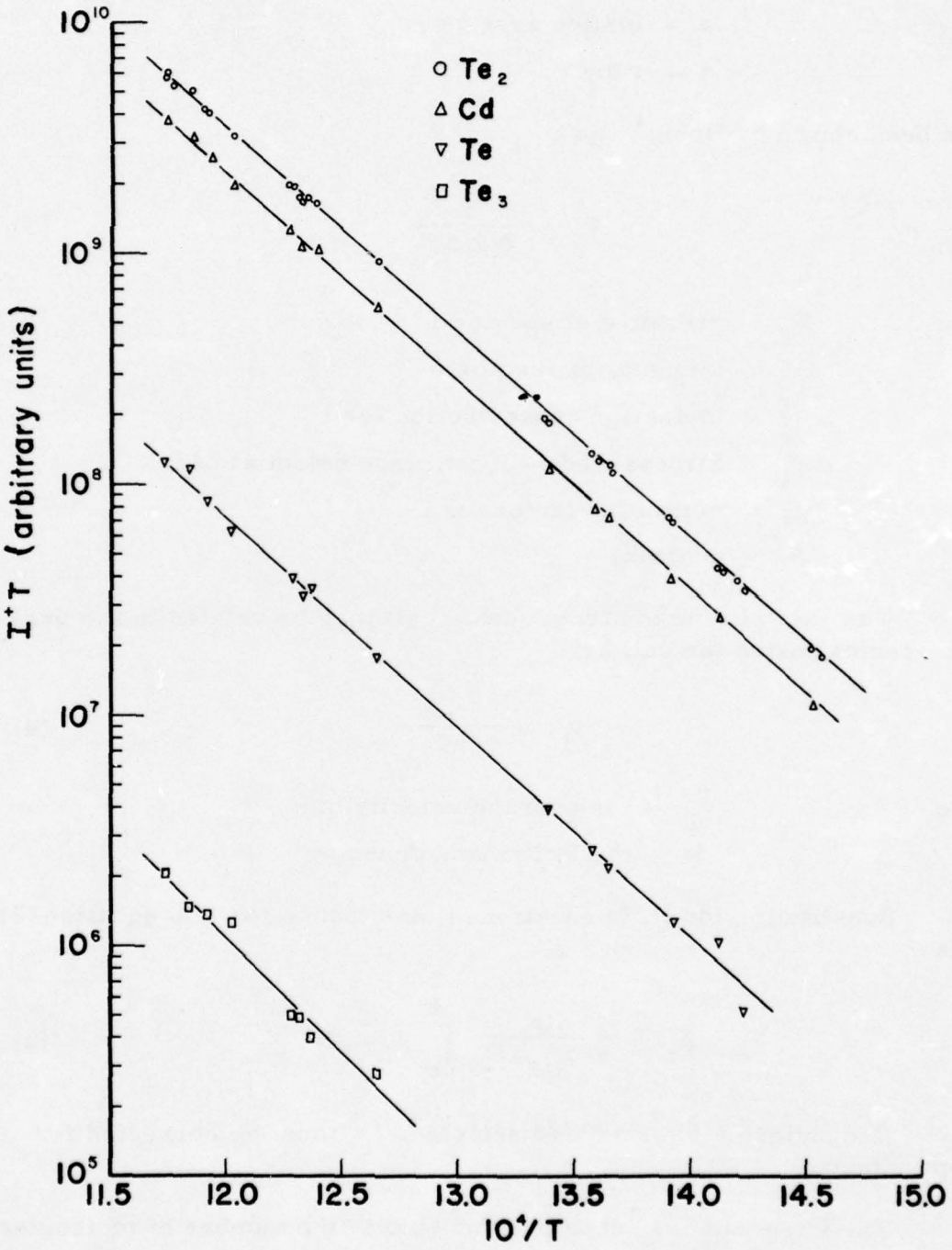


Figure 5. Relative Intensity vs. Reciprocal Temperature for CdTe System

where Z_t = total no. of molecules

ν = no. of molecules/cm^2 -sec

s = orifice area

t = time

It has been shown by Honig[16] that

$$P_i = \frac{KI_i^+ T}{\sigma_i \gamma_i \Delta E_i} \tag{3}$$

where P_i = pressure of species i

I_i^+ = intensity of species i

σ_i = ionization cross section for i

ΔE_i = E(measured) - appearance potential of i

γ_i = multiplier factor for i

K = constant

The rate of effusion from such a cell may be related to the pressure of the species inside the cell by

$$\nu_i = \frac{1}{4} \frac{P_i \bar{c}_i}{kT} \tag{4}$$

where $\bar{c}_i$ = the average velocity of i

k = the Boltzmann constant

Substituting for P_i in equation (4) and thence for ν in equation (2) yields

$$Z_t = \frac{Ks}{4k\sigma_i \gamma_i \Delta E_i} \int_o^t I_i^+ \bar{c}_i dt \tag{5}$$

Depending on the standard selected, I_i^+ must be corrected for isotope effects.

The integral $\int_{t_1}^{t_2} I_i^+ dt$ is proportional to the number of molecules vaporized in the time interval $t_2 - t_1$ at a given temperature. An attempt is made to carry out the vaporization at a reference temperature T_r. If the

temperature of the cell differs from the reference temperature T_r during the course of the experiment, a correction must be applied.

If we were to vaporize the standard at an average temperature T_i over a given time interval i, the number of molecules effusing in that time interval could be expressed as

$$Z_i = K' \bar{c}_i \int_{t_1}^{t_2} I_i^+ \, dt_i \tag{6}$$

If a like number were vaporized at the reference temperature T_r,

$$Z_i = K' \bar{c}_r \int_{t_1}^{t_2} I_r^+ \, dt_r \tag{7}$$

where

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$$

For each interval of temperature T_i then,

$$\int_{t_1}^{t_2} I_r^+ \, dt_r = \sqrt{\frac{T_i}{T_r}} \int_{t_1}^{t_2} I_i^+ \, dt_i \tag{8}$$

An intensity-time plot is made over the duration of the vaporization. The intervals which have been corrected for isotope and temperature effects are then summed over the entire run:

$$A_t = \sum_i \int_i I_r^+ \, dt_r \tag{9}$$

The weight of standard, g, lost over the entire run may be related to the pressure of the standard through the Knudsen equation

$$P = \frac{g}{st} \sqrt{\frac{2\pi RT}{M}} \tag{10}$$

where

P = pressure

g = weight lost

s = orifice area

t = time

M = molecular weight of vapor

R = gas constant

T = temperature of the cell

then,

$$\frac{P}{I^+} = \frac{g}{sI^+t}\sqrt{\frac{2\pi RT}{M}} = \frac{g}{s A_t}\sqrt{\frac{2\pi RT}{M}} \qquad (11)$$

which is the relationship used in this study.

A further correction must also be made for non-ideality of the orifice of the Knudsen cell used, in this case, the correction factor was 0.4205. Two quantitative vaporization runs were made, one at 571°C and the other at 572°C, using the same orifice area of 0.0081 cm^2. The data and calculated vapor pressures of the Cd and Te_2 species are given below for both experimental quantitative vaporization runs:

	Run 4-16	Run 4-17
Temperature	571°C	572°C
Sample Charge (CdTe)	23.750 mg	13.449 mg
Time of Evaporation	11 hrs 57 seconds	6 hrs 46 seconds
A_t (intensity-time integral) for Te_2	1.1826×10^{12}	6.3195×10^{11}
for Cd	6.0805×10^{11}	3.1595×10^{11}
P/I^+ for Te_2	1.285×10^{-13} atm/div.	1.363×10^{-13} atm/div.
P_{Te_2}	3.853×10^{-6} atm.	5.243×10^{-6} atm.
P_{Cd}	7.7055×10^{-6} atm.	1.0486×10^{-5} atm.

Using the data from the quantitative vaporization runs as a point for an average vapor pressure of 4.548×10^{-6} atm for Te_2 at 844.5°K, the vapor pressures of all the other data were calculated for each experimental data point for cadmium and tellurium molecules (see Tables 1 and 2 and Figure 6).

Having established the partial pressures for P_{Cd} and P_{Te_2}, the calculations for the equilibrium constant can be carried out using the expression:

$$K = P^2_{Cd(g)} \cdot P_{Te_2(g)} \qquad (12)$$

TABLE 1

SECOND LAW CALCULATION FOR CADMIUM

T KEL	LOG PRESS	PRESSURE	T INV
841	-5.0788	8.34×10^{-6}	11.89
814	-5.4881	3.25×10^{-6}	12.28
801	-5.7011	1.99×10^{-6}	12.49
758	-6.4089	3.90×10^{-7}	13.20
734	-6.8125	1.54×10^{-7}	13.63
706	-7.3215	4.77×10^{-8}	14.16
678	-7.9626	1.09×10^{-8}	14.76
800	-5.6882	2.05×10^{-6}	12.50
818	-5.4225	3.78×10^{-6}	12.23
837	-5.1512	7.06×10^{-6}	11.95
826	-5.3116	4.88×10^{-6}	12.11
803	-5.6308	2.34×10^{-6}	12.45
781	-5.9666	1.08×10^{-6}	12.81
740	-6.6498	2.24×10^{-7}	13.51
727	-6.8601	1.38×10^{-7}	13.75
714	-7.1221	7.55×10^{-8}	14.00
701	-7.3686	4.28×10^{-8}	14.27
686	-7.6498	2.24×10^{-8}	14.58
704	-7.2907	5.12×10^{-8}	14.20
730	-6.8327	1.47×10^{-7}	13.69
796	-5.7011	1.99×10^{-6}	12.56
830	-5.2190	6.04×10^{-6}	12.05
741	-6.6556	2.21×10^{-7}	13.49
769	-6.1811	6.59×10^{-7}	13.01
806	-5.5901	2.57×10^{-6}	12.41
825	-5.3188	4.80×10^{-6}	12.12
847	-5.0168	9.62×10^{-6}	11.80
879	-4.6326	2.33×10^{-5}	11.38
853	-4.9431	1.14×10^{-5}	11.72
831	-5.2204	6.02×10^{-6}	12.04
810	-5.5200	3.02×10^{-6}	12.34
787	-5.8962	1.27×10^{-6}	12.71
762	-6.2749	5.31×10^{-7}	13.12
732	-6.8041	1.57×10^{-7}	13.67
721	-6.9914	1.02×10^{-7}	13.87
708	-7.2541	5.57×10^{-8}	14.13
696	-7.4498	3.55×10^{-8}	14.36
687	-7.6737	2.12×10^{-8}	14.56
677	-7.8794	1.32×10^{-8}	14.78

TABLE 1 (Concluded)

T KEL	LOG PRESS	PRESSURE	T INV
669	-8.0214	9.52×10^{-9}	14.94
661	-8.4157	3.84×10^{-9}	15.12
649	-8.5045	3.13×10^{-9}	15.40
732	-6.7825	1.65×10^{-7}	13.66
842	-5.0904	8.12×10^{-6}	11.88
867	-4.7620	1.73×10^{-5}	11.54
855	-4.9031	1.25×10^{-5}	11.69
846	-5.0429	9.06×10^{-6}	11.82
833	-5.2027	6.27×10^{-6}	12.00
822	-5.3675	4.29×10^{-6}	12.17
809	-5.5406	2.88×10^{-6}	12.36
798	-5.7055	1.97×10^{-6}	12.53
779	-6.0092	9.79×10^{-7}	12.83
764	-6.2510	5.61×10^{-7}	13.09
749	-6.5229	3.00×10^{-7}	13.36
782	-5.9508	1.12×10^{-6}	12.78
798	-5.7100	1.95×10^{-6}	12.53
786	-5.9066	1.24×10^{-6}	12.73
770	-6.1451	7.16×10^{-7}	12.98
754	-6.4283	3.73×10^{-7}	13.27
742	-6.6421	2.28×10^{-7}	13.48
730	-6.8386	1.45×10^{-7}	13.69
719	-7.0381	9.16×10^{-8}	13.91
706	-7.3010	5.00×10^{-8}	14.16
691	-7.6003	2.51×10^{-8}	14.48
676	-7.9393	1.15×10^{-8}	14.79
663	-8.3125	4.87×10^{-9}	15.08
649	-8.5003	3.16×10^{-9}	15.41
781	-5.9914	1.02×10^{-6}	12.81

2ND LAW ENTHALPY = 44.6 KCAL/MOLE ERROR = 0.2

T AVE. = 763°K

TABLE 2

SECOND LAW CALCULATION FOR Te_2

T KEL	LOG PRESS	PRESSURE	T INV
840	-5.3872	4.10×10^{-6}	11.90
814	-5.7721	1.69×10^{-6}	12.28
800	-5.9872	1.03×10^{-6}	12.50
757	-6.6737	2.12×10^{-7}	13.21
734	-7.0857	8.21×10^{-8}	13.63
706	-7.6003	2.51×10^{-8}	14.16
677	-8.1785	6.63×10^{-9}	14.77
800	-5.9830	1.04×10^{-6}	12.50
818	-5.7122	1.94×10^{-6}	12.23
837	-5.4437	3.60×10^{-6}	11.95
825	-5.6055	2.48×10^{-6}	12.12
803	-5.9245	1.19×10^{-6}	12.46
781	-6.2604	5.49×10^{-7}	12.81
741	-6.9318	1.17×10^{-7}	13.50
727	-7.1512	7.06×10^{-8}	13.75
714	-7.3635	4.33×10^{-8}	14.00
700	-7.6478	2.25×10^{-8}	14.28
686	-7.9393	1.15×10^{-8}	14.58
704	-7.5850	2.60×10^{-8}	14.20
730	-7.0985	7.97×10^{-8}	13.69
797	-5.9830	1.04×10^{-6}	12.54
833	-5.5045	3.13×10^{-6}	12.01
741	-6.9318	1.17×10^{-7}	13.50
768	-6.4584	3.48×10^{-7}	13.02
805	-5.8794	1.32×10^{-6}	12.42
825	-5.6055	2.48×10^{-6}	12.12
847	-5.3101	4.83×10^{-6}	11.81
879	-4.9355	1.16×10^{-5}	11.38
853	-5.2487	5.64×10^{-6}	11.73
831	-5.5058	3.12×10^{-6}	12.03
810	-5.8097	1.55×10^{-6}	12.34
786	-6.1675	6.80×10^{-7}	12.72
762	-6.5575	2.77×10^{-7}	13.13
732	-7.0851	8.22×10^{-8}	13.67
721	-7.2660	5.42×10^{-8}	13.87
708	-7.5229	3.00×10^{-8}	14.13
696	-7.7423	1.81×10^{-8}	14.36
686	-7.9469	1.13×10^{-8}	14.57
677	-8.1487	7.10×10^{-9}	14.78

TABLE 2 (Concluded)

T KEL	LOG PRESS	PRESSURE	T INV
669	-8.3316	4.66×10^{-9}	14.94
661	-8.4828	3.29×10^{-9}	15.12
649	-8.7670	1.71×10^{-9}	15.40
732	-7.0555	8.80×10^{-8}	13.66
842	-5.3686	4.28×10^{-6}	11.87
867	-5.0040	8.63×10^{-6}	11.54
855	-5.2076	6.20×10^{-6}	11.69
845	-5.3363	4.61×10^{-6}	11.84
833	-5.4902	3.19×10^{-6}	12.00
821	-5.6655	2.16×10^{-6}	12.18
809	-5.8447	1.43×10^{-6}	12.36
797	-6.0114	9.74×10^{-7}	12.54
778	-6.3054	4.95×10^{-7}	12.85
763	-6.5544	2.79×10^{-7}	13.11
749	-6.7959	1.60×10^{-7}	13.36
783	-6.2306	5.88×10^{-7}	12.77
796	-6.0173	9.61×10^{-7}	12.56
786	-6.1878	6.49×10^{-7}	12.73
770	-6.4318	3.70×10^{-7}	12.98
753	-6.7100	1.95×10^{-7}	13.28
741	-6.9101	1.23×10^{-7}	13.49
730	-7.1051	7.85×10^{-8}	13.69
718	-7.3261	4.72×10^{-8}	13.92
706	-7.5702	2.69×10^{-8}	14.17
690	-7.8794	1.32×10^{-8}	14.49
676	-8.1965	6.36×10^{-9}	14.79
663	-8.4647	3.43×10^{-9}	15.08
649	-8.7471	1.79×10^{-9}	15.41
781	-6.2708	5.36×10^{-7}	12.81

2ND LAW ENTHALPY = 43.8 KCAL/MOLE ERROR = 0.1

T AVE. = 763°K

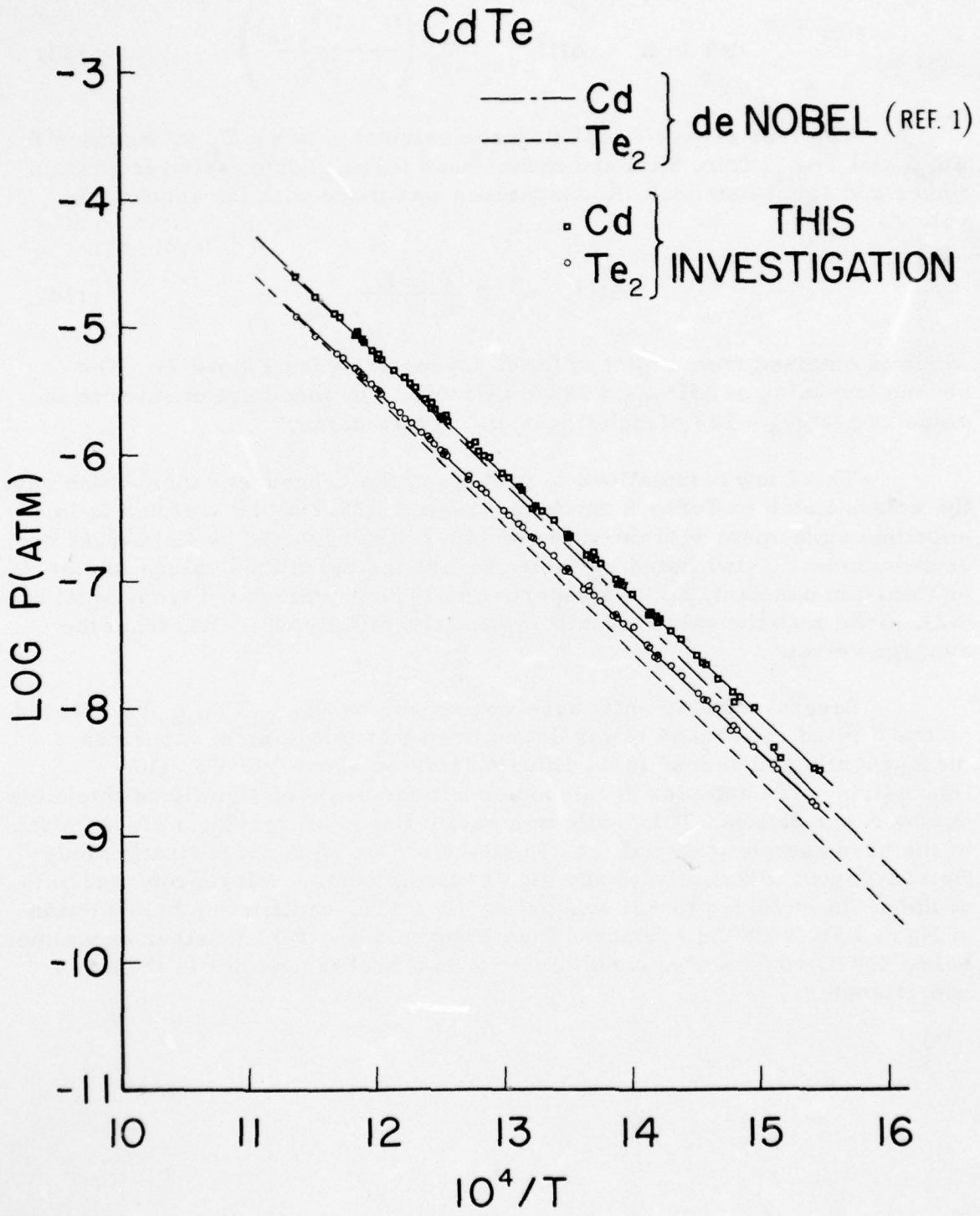


Figure 6. Plot of Second Law Data for CdTe

Heats of reaction were calculated using the third law method, since:

$$-RT \ln K = \Delta H^\circ_{298} + T\Delta \left(\frac{(G^\circ - H^\circ_{298})}{T} \right) \qquad (13)$$

The free energy functions were calculated using C_p information for $Cd_{(g)}$ and $Te_{2(g)}$ from Stull and Sinke[18] and $CdTe_{(s)}$ expression from Goldfinger and Jeunehomme.[6] A comparison was made with the second law value

$$\Delta H^\circ_T = -R \frac{d \ln K}{d (1/T)} \qquad (14)$$

which is obtained from a plot of log K versus 1/T (see Figure 7). The second law value of $\Delta H^\circ_{763} = 133$ kcal/mole is in good agreement with the value of $\Delta H^\circ_{874} = 134$ of Goldfinger and Jeunehomme.[6]

Third law calculations of ΔH°_{298} of the congruent vaporization gave the values listed in Table 3 whose average is 139.2 ± 0.5 kcal and is in excellent agreement with the value of 140.7 kcal reported by Goldfinger and Jeunehomme.[6] Also listed in Table 3 are the calculated values for the equilibrium constant, and the experimental values calculated from equation (12), along with the value for ΔH°_{298} and the difference (delta) from the average value.

Several experimental runs were made on $Hg_{0.73}Cd_{0.27}Te$. Based on the limited runs made it was determined that this system vaporizes incongruently and seems to be diffusion limited above 300°C. The $Hg_{0.73}Cd_{0.27}Te$ samples developed an outside scale of significant thickness during vaporization. This scale was easily flaked off leaving a clean surface of the base sample material (see Figure 8). During the vaporization only Hg and Te_2 were detected to any significant amounts. Microprobe analysis of the scale indicated that it was primarily CdTe, confirming the depletion of Hg and Te from the compound (see Figures 9 and 10). Further experiments below 300°C could not be made since Hg is a background gas in the mass spectrometer.

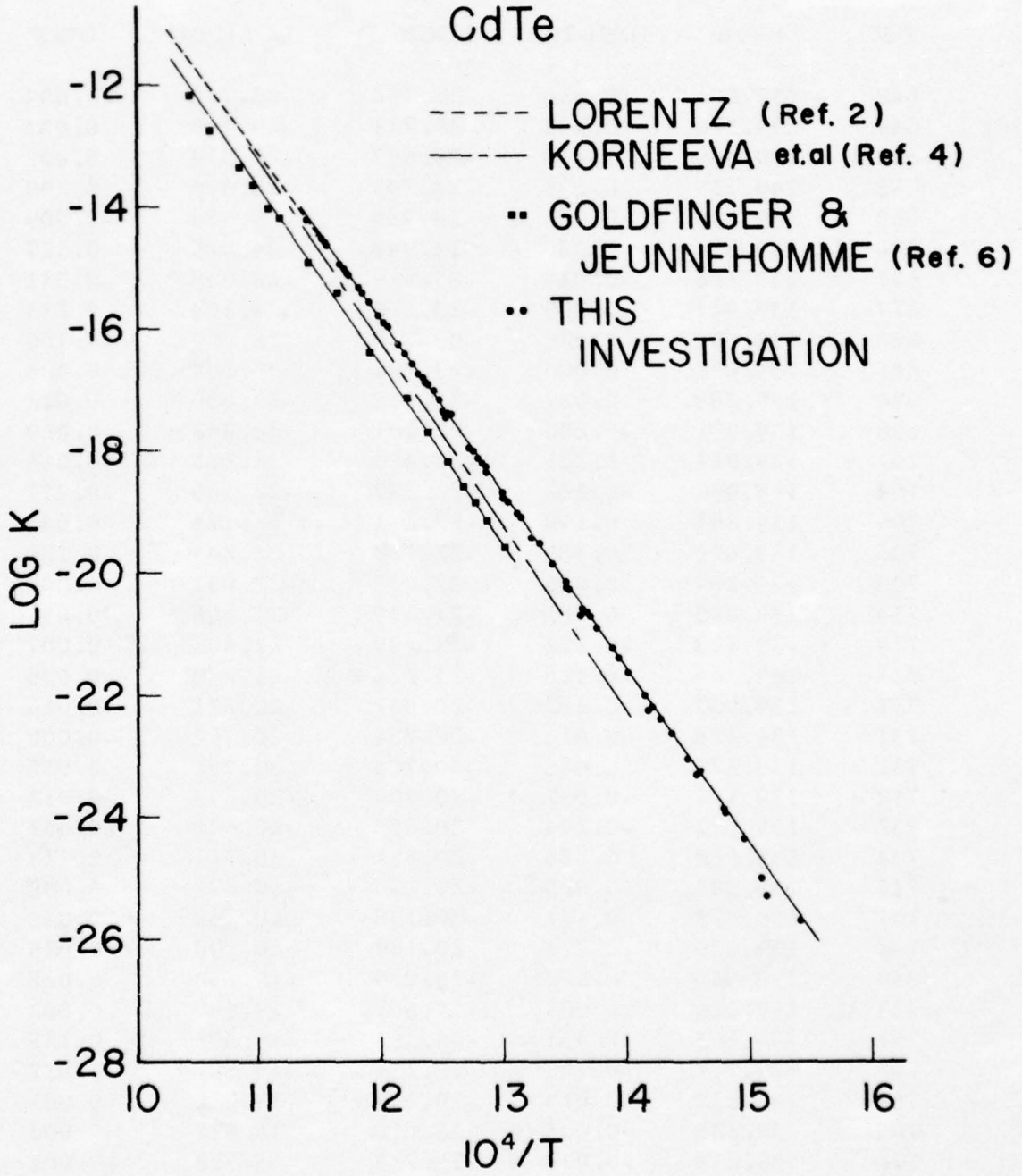


Figure 7. Plot of Third Law Analysis for CdTe

TABLE 3

THIRD LAW ANALYSIS FOR CdTe

	THIRD LAW		SECOND LAW		
T K	H298	DELTA	LOGK(C)	LOGK(0)	DIFF
649	139.206	-0.026	-25.752	-25.748	-0.004
649	139.376	0.144	-25.723	-25.776	0.053
661	140.449	1.218	-24.907	-25.314	0.407
663	140.125	0.893	-24.791	-25.090	0.299
669	139.190	-0.042	-24.384	-24.374	-0.009
676	139.612	0.380	-23.948	-24.075	0.127
677	139.184	-0.048	-23.919	-23.908	-0.011
677	139.941	0.709	-23.370	-24.104	0.233
686	138.906	-0.326	-23.338	-23.239	-0.100
687	139.232	0.000	-23.290	-23.294	0.004
690	139.288	0.057	-23.058	-23.080	0.022
696	139.031	-0.200	-22.701	-22.642	-0.059
701	139.011	-0.221	-22.450	-22.385	-0.065
704	138.990	-0.242	-22.237	-22.166	-0.071
706	139.351	0.119	-22.131	-22.172	0.041
706	139.612	0.380	-22.122	-22.243	0.122
708	139.207	0.025	-22.035	-22.031	-0.004
714	139.050	-0.181	-21.659	-21.608	-0.052
719	139.198	-0.034	-21.409	-21.402	-0.007
721	139.104	-0.128	-21.284	-21.249	-0.035
727	139.000	-0.232	-20.937	-20.871	-0.066
731	139.218	-0.014	-20.764	-20.764	-0.000
731	139.279	0.048	-20.764	-20.782	0.018
732	139.174	-0.057	-20.707	-20.693	-0.013
732	139.027	-0.204	-20.678	-20.621	-0.057
734	139.619	0.388	-20.591	-20.711	0.119
740	139.203	-0.028	-20.236	-20.231	-0.005
741	139.373	0.141	-20.198	-20.243	0.045
742	139.305	0.074	-20.169	-20.194	0.025
749	139.314	0.082	-19.814	-19.842	0.028
753	139.226	-0.006	-19.565	-19.567	0.002
757	139.663	0.431	-19.364	-19.492	0.128
762	139.127	-0.105	-19.134	-19.107	-0.027
764	139.217	-0.015	-19.057	-19.056	-0.001
768	139.228	-0.003	-18.818	-18.821	0.002
770	139.218	-0.014	-18.723	-18.722	-0.001
779	139.263	0.031	-18.312	-18.324	0.012

TABLE 3 (Concluded)

	THIRD LAW		SECOND LAW		
T K	H298	DELTA	LOGK(C)	LOGK(0)	DIFF
781	139.071	-0.161	-18.235	-18.194	-0.042
781	139.285	0.053	-18.235	-18.254	0.018
783	139.192	-0.039	-18.140	-18.132	-0.008
786	139.200	-0.031	-18.006	-18.001	-0.005
787	139.224	-0.007	-17.959	-17.960	0.001
797	138.798	-0.434	-17.501	-17.385	-0.116
797	139.126	-0.105	-17.463	-17.437	-0.026
798	139.142	-0.090	-17.444	-17.423	-0.021
800	139.259	0.028	-17.349	-17.359	0.011
800	139.439	0.207	-17.330	-17.389	0.060
803	139.112	-0.120	-17.215	-17.186	-0.029
806	139.067	-0.165	-17.161	-17.060	-0.042
809	139.134	-0.097	-16.949	-16.926	-0.023
810	139.063	-0.168	-16.892	-16.850	-0.042
814	139.323	0.091	-16.721	-16.743	0.027
818	139.141	-0.091	-16.578	-16.557	-0.021
822	139.159	-0.073	-16.417	-16.401	-0.016
825	139.137	-0.094	-16.265	-16.243	-0.022
826	139.155	-0.077	-16.246	-16.229	-0.017
831	138.911	-0.320	-16.023	-15.947	-0.081
831	138.896	-0.336	-16.028	-15.942	-0.086
833	139.137	-0.095	-15.924	-15.902	-0.022
837	139.085	-0.147	-15.782	-15.746	-0.035
841	138.930	-0.302	-15.621	-15.545	-0.076
842	139.129	-0.102	-15.573	-15.549	-0.024
846	139.185	-0.046	-15.431	-15.422	-0.009
847	139.161	-0.070	-15.365	-15.350	-0.015
853	139.209	-0.023	-15.138	-15.135	-0.003
855	139.104	-0.127	-15.044	-15.014	-0.030
867	139.099	-0.132	-14.619	-14.588	-0.031
879	139.361	0.129	-14.166	-14.201	0.035
			STANDARD DEVIATION =		0.084
	H298 = 139.2			H298 = 136.3	

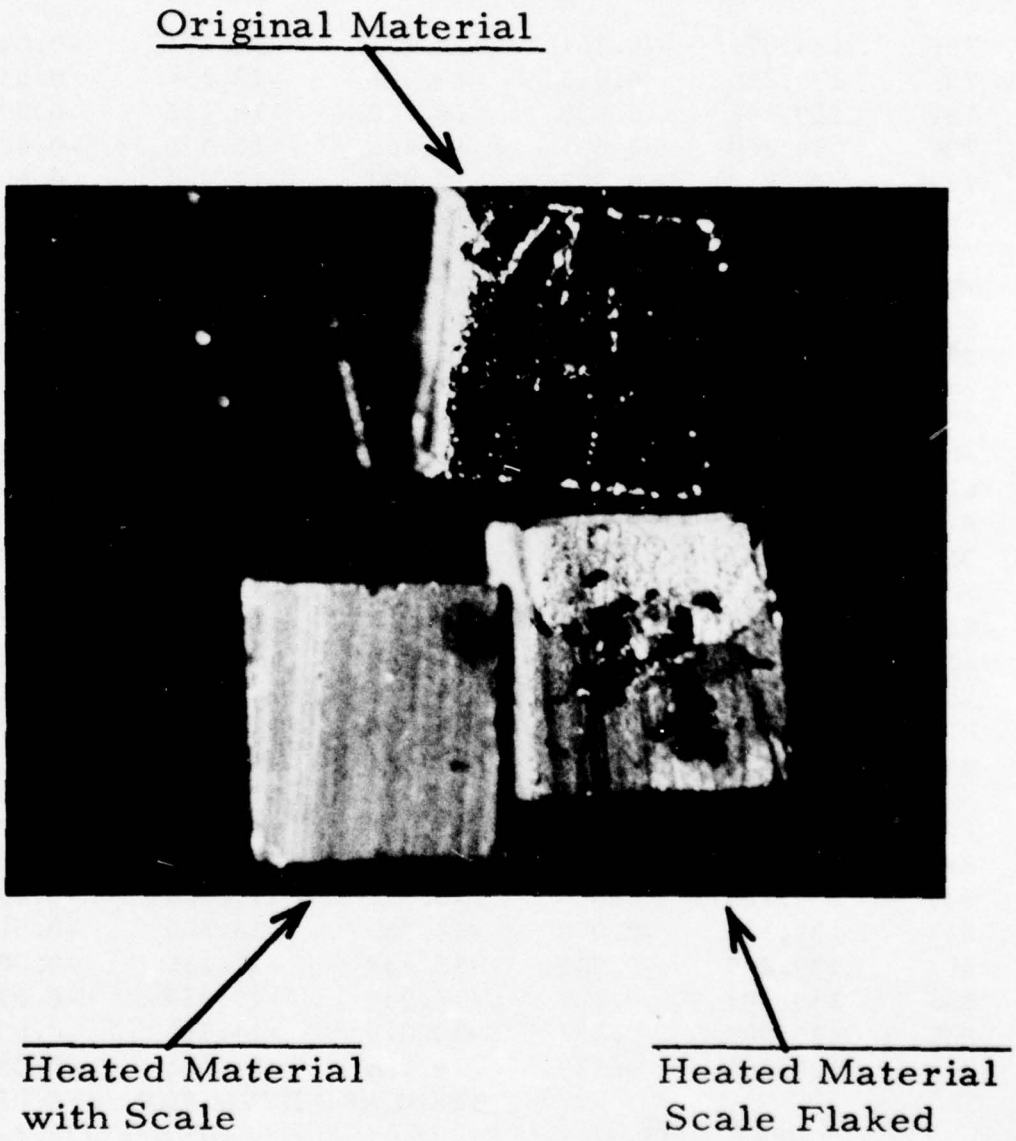


Figure 8. Effect of Heating on HgCdTe Material

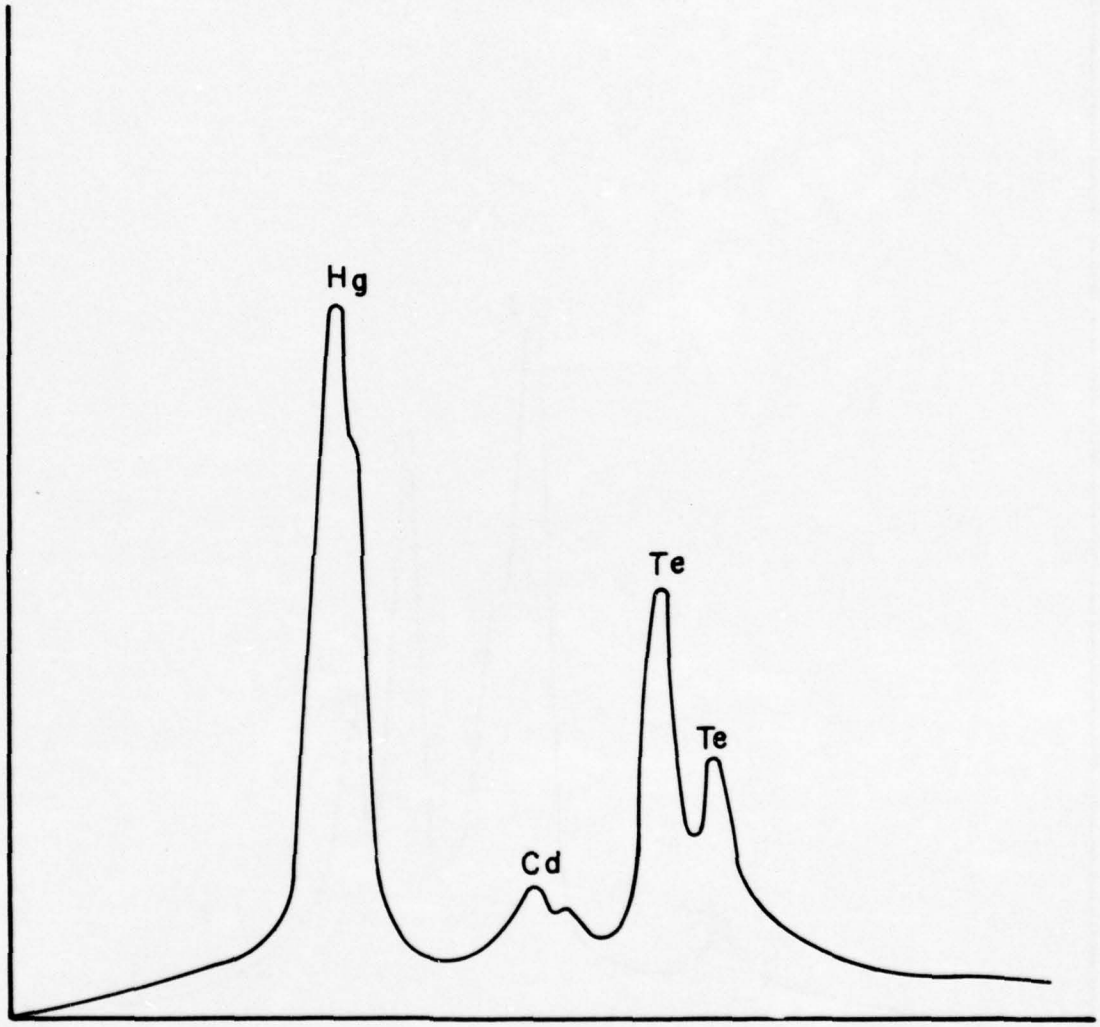


Figure 9. Microprobe Analysis of HgCdTe (unheated)

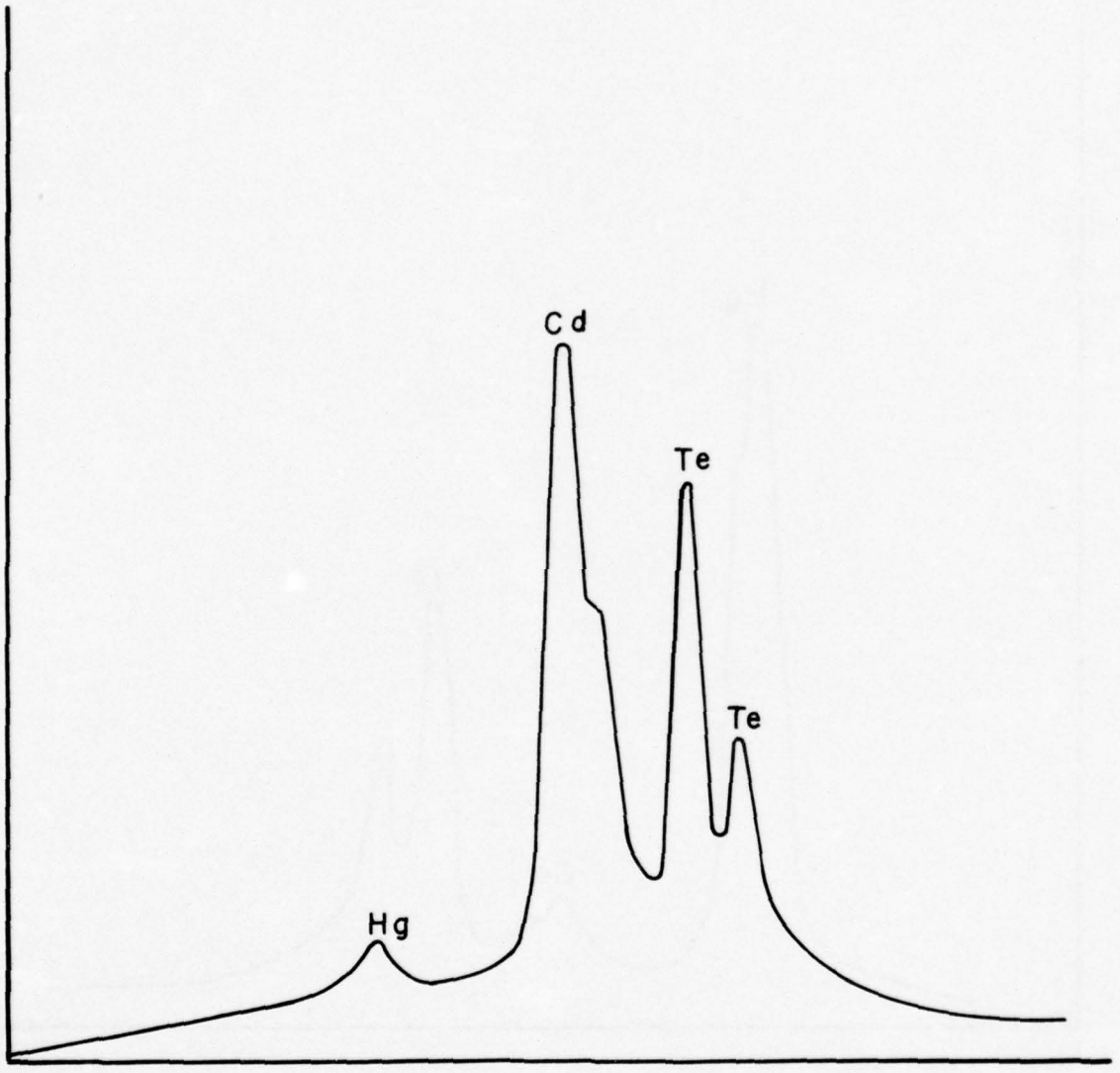


Figure 10. Microprobe Analysis of Scale from Heated HgCdTe

(C) Zinc Selenide Compounds

The same experimental arrangement was used in the study of the zinc selenide system as described previously for the experiments on CdTe compounds, with a few notable exceptions. The ZnSe used was crystalline form, and the experiments were performed on a single crystal, with the exception of the calibration run. The sample surface area to orifice area was approximately 500 to 1. The samples supplied were CVD ZnSe manufactured by Raytheon Company, Waltham, Massachusetts.

Previous work on the ZnSe system has been done by Korneeva, et. al[4] and by Lorentz[19] using the Knudsen cell technique. Goldfinger and Jeunehomme,[6] also utilized the Knudsen cell technique and coupled it with mass spectrometry. More recently, Hassan and Munir[20] investigated the free surface sublimation of ZnSe along with the equilibrium sublimation.

The results of this investigation, using ZnSe crystal, indicates very similar results as those reported by Hassan and Munir.[20] Using the same method as described previously for CdTe system, but starting with a temperature range between 875 and 1100°K, experiments with ZnSe were performed in a POCO graphite cell. The Knudsen cell used consisted of a tantalum jacket surrounding the graphite cell. The graphite cell has a 0.1 cm diameter orifice and the channel length of the orifice in this design is 0.15 cm, and the ratio of internal cell area to orifice area is 810 to 1. The tantalum jacket encapsulating the graphite cell serves as a holder, provides a convenient place for thermocouple attachment and helps to ensure isothermal cell conditions. Temperature calibration experiments were performed in this cell arrangement, using the melting point of zinc and antimony, and by attaching a thermocouple to a copper block inside the Knudsen cell. With this calibration scheme, it is not expected that an error $> \pm 1$°C was obtained, based on our observations. All other data was obtained as indicated previously.

The vaporization of crystal ZnSe showed that the dominant species were Zn, Se, Se_2. The usual tests of shutterability and ionic species comparison for each peak group with calculated isotopic abundance were obtained. The appearance potentials were determined by applying the linear extrapolation method to plots of the ionization efficiency curves for each species, corrected using mercury. The ionic species identified and their appearance potentials were in good agreement with those of Franklin, et. al[15] for the first appearance potentials of Zn^+, Se^+ and Se_2^+. The ionization efficiency curves are shown as Figures 11, 12 and 13. The ionization efficiency curve for Se^+ displayed a sharp break. The first appearance potential was taken to represent the simple ionization of the neutral Te. The second appearance potential of 13.8 eV ± 0.5 eV marked by the discontinuity of the slopes of the ionization efficiency curve, was taken to represent the dissociative ionization of the Se_2 molecule substantiating the results of Drowart and Goldfinger.[5]

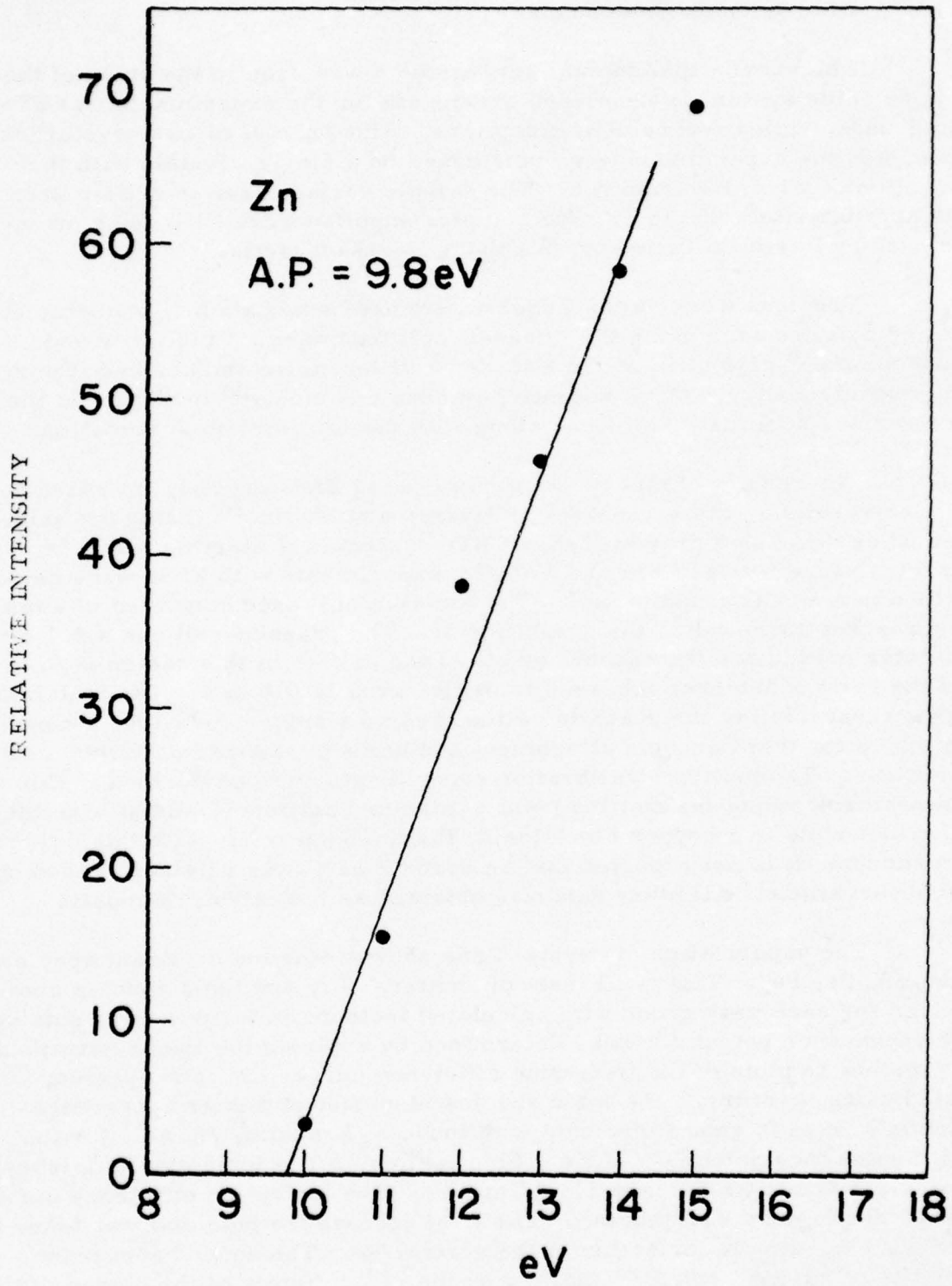


Figure 11. Ionization Efficiency Curve for Zn

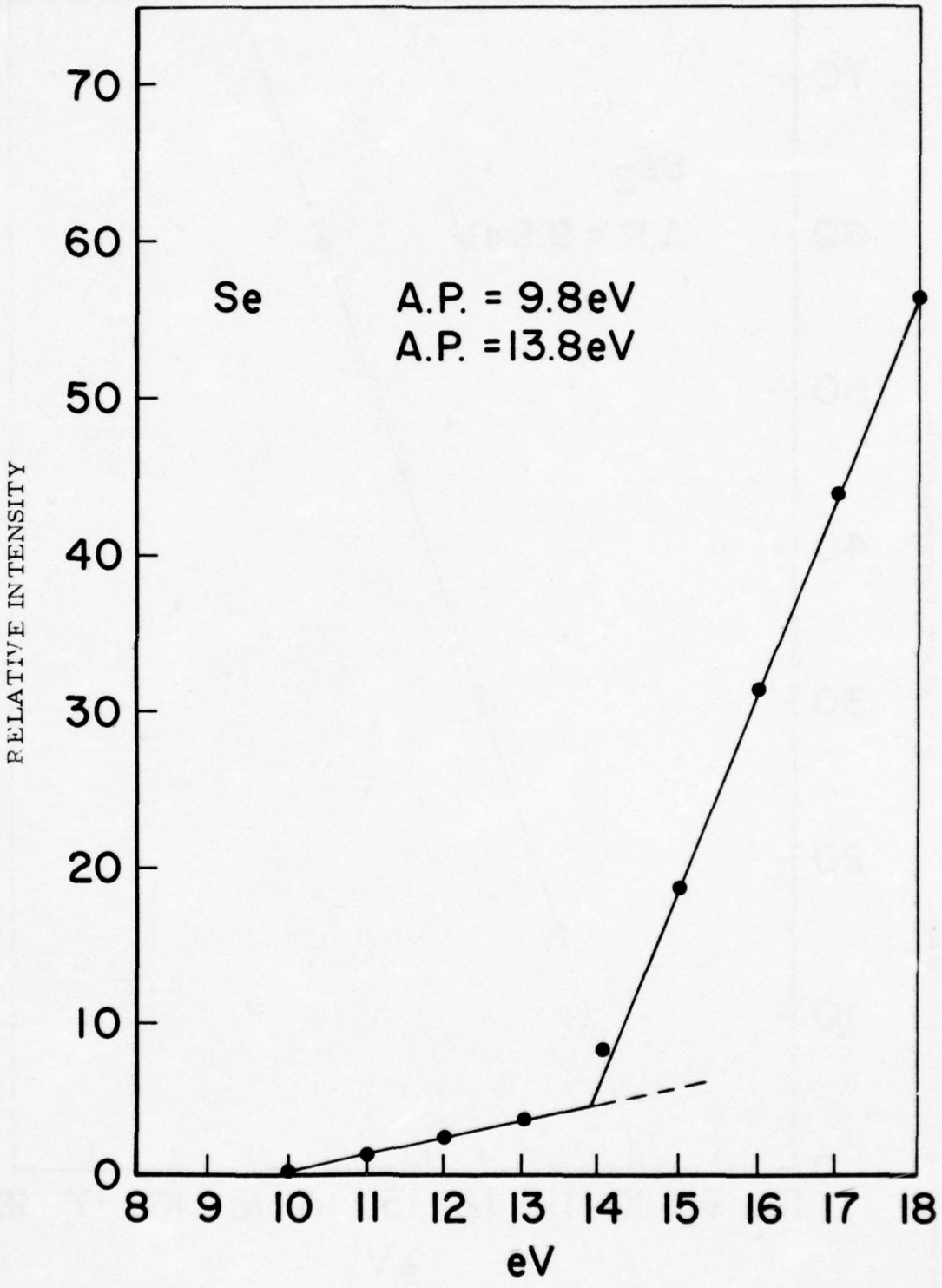


Figure 12. Ionization Efficiency Curve for Se

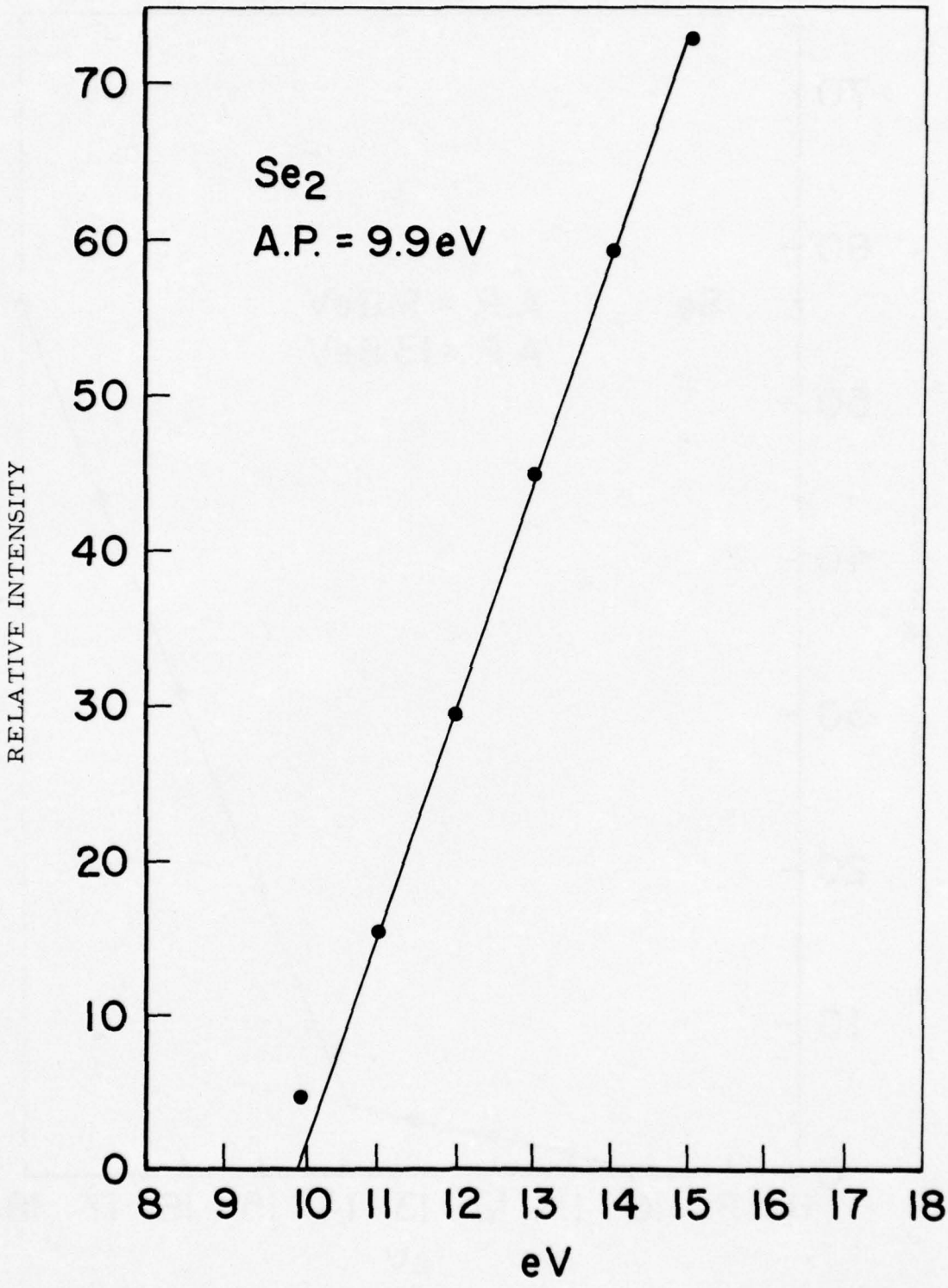


Figure 13. Ionization Efficiency Curve for Se_2

Calculations of the degree of dissociation at different pressures and temperatures indicate that at the temperatures of this investigation, dissociation is negligible. Based on our measurements, the vaporization of ZnSe is congruent and gives mainly species Zn(g) and Se_2(g). The presence of Se(g) is minor and has no significant effect on the thermodynamic properties.

The ion current intensity of each of the ions identified in the mass spectrum was recorded as a function of Knudsen cell temperature. It has been shown[16] that the partial pressure, P_i, of a neutral species is directly proportional to the product of the cell temperature and the intensity measured for an ion resulting from ionization of the neutral in question, thus

$$P_i = kI_i^+T$$

In order to relate the intensity of a given species as measured by the mass spectrometer to the pressure of the neutral precursor of that species inside the equilibrium enclosure, it is necessary to carry out some type of calibration procedure. In the case of the present work such calibration was carried out by a quantitative vaporization of a quantity of ZnSe. The rationale involved in the treatment of the data resulting from these quantitative vaporizations has been discussed in part previously.[9,17] This will establish the partial pressures of the individual species as shown in Tables 4 and 5 and plotted in Figure 14.

Having established the partial pressures for P_{Zn} and P_{Se_2}, the calculations for the equilibrium constant can be carried out using the expression:

$$K = P^2_{Zn(g)} \cdot P_{Se_2(g)}$$

Heats of reaction were calculated using the third law method, since:

$$-RT \ln K = \Delta H^\circ_{298} + T\Delta \frac{(G^\circ - H^\circ_{298})}{T}$$

The free energy functions were calculated using C_p information for Zn(g) and Se_2(g) from Stull and Sinke[18] and ZnSe(s) expression from Goldfinger and Jeunehomme.[6] A comparison was made with the second law value

$$\Delta H^\circ_T = -R \frac{d \ln K}{d (1/T)}$$

which is obtained from a plot of log K versus 1/T (see Figure 15).

The second law value of ΔH°_{982} = 195 K cal/mole and a third law calculated value of 199 K cal/mole for ΔH°_{298}. However, the second law value calculated using the third law data indicates a value of 178 K cal/mole for ΔH°_{298} (see Table 6).

TABLE 4

SECOND LAW CALCULATION FOR Zn

T KEL	LOG PRESS	PRESSURE	T INV
1062	-5.2255	5.95×10^{-6}	9.42
1070	-5.1129	7.71×10^{-6}	9.35
1096	-4.8447	1.43×10^{-5}	9.12
1089	-4.9281	1.18×10^{-5}	9.18
1080	-5.0343	9.24×10^{-6}	9.26
1066	-5.1811	6.59×10^{-6}	9.38
1044	-5.4634	3.44×10^{-6}	9.58
1032	-5.6180	2.41×10^{-6}	9.69
1022	-5.7352	1.84×10^{-6}	9.78
1004	-5.9872	1.03×10^{-6}	9.96
986	-6.2306	5.88×10^{-7}	10.14
957	-6.6326	2.33×10^{-7}	10.45
1037	-5.5436	2.86×10^{-6}	9.64
1029	-5.6073	2.47×10^{-6}	9.72
1018	-5.7905	1.62×10^{-6}	9.82
1006	-5.9547	1.11×10^{-6}	9.94
997	-6.0942	8.05×10^{-7}	10.03
986	-6.2328	5.85×10^{-7}	10.14
973	-6.4535	3.52×10^{-7}	10.28
962	-6.6021	2.50×10^{-7}	10.40
953	-6.7447	1.80×10^{-7}	10.49
944	-6.8794	1.32×10^{-7}	10.59
932	-7.0696	8.52×10^{-8}	10.73
921	-7.2403	5.75×10^{-8}	10.86
971	-6.4584	3.48×10^{-7}	10.30
965	-6.5406	2.88×10^{-7}	10.36
953	-6.7077	1.96×10^{-7}	10.49
943	-6.8761	1.33×10^{-7}	10.61
935	-7.0083	9.81×10^{-8}	10.69
919	-7.2907	5.12×10^{-8}	10.88
911	-7.4248	3.76×10^{-8}	10.98
903	-7.5560	2.78×10^{-8}	11.07
896	-7.7352	1.84×10^{-8}	11.16
890	-7.8633	1.37×10^{-8}	11.24
883	-7.9914	1.02×10^{-8}	11.32
876	-8.1543	7.01×10^{-9}	11.42
1027	-5.7055	1.97×10^{-6}	9.74

2ND LAW ENTHALPY = 65.1 KCAL/MOLE ERROR = 0.4

T AVE. = 982 °K

TABLE 5

SECOND LAW CALCULATION FOR Se_2

T KEL	LOG PRESS	PRESSURE	T INV
1060	-5.5058	3.12×10^{-6}	9.43
1070	-5.4078	3.91×10^{-6}	9.35
1096	-5.1487	7.10×10^{-6}	9.12
1089	-5.2358	5.81×10^{-6}	9.18
1080	-5.3288	4.69×10^{-6}	9.26
1060	-5.4841	3.28×10^{-6}	9.38
1043	-5.7520	1.77×10^{-6}	9.59
1031	-5.9101	1.23×10^{-6}	9.70
1022	-6.0343	9.24×10^{-7}	9.78
1004	-6.2807	5.24×10^{-7}	9.96
985	-6.5287	2.96×10^{-7}	10.15
957	-6.9208	1.20×10^{-7}	10.45
1037	-5.8416	1.44×10^{-6}	9.64
1030	-5.9431	1.14×10^{-6}	9.71
1017	-6.0953	8.03×10^{-7}	9.83
1006	-6.2588	5.51×10^{-7}	9.94
997	-6.3936	4.04×10^{-7}	10.03
986	-6.5452	2.85×10^{-7}	10.14
973	-6.7496	1.78×10^{-7}	10.28
962	-6.9136	1.22×10^{-7}	10.40
953	-7.0472	8.97×10^{-8}	10.49
944	-7.1791	6.62×10^{-8}	10.59
932	-7.3595	4.37×10^{-8}	10.73
921	-7.5452	2.85×10^{-8}	10.86
971	-6.7423	1.81×10^{-7}	10.30
965	-6.8356	1.46×10^{-7}	10.36
953	-7.0173	9.61×10^{-8}	10.49
943	-7.1798	6.61×10^{-8}	10.61
935	-7.3002	5.01×10^{-8}	10.69
918	-7.5834	2.61×10^{-8}	10.89
910	-7.7235	1.89×10^{-8}	10.99
903	-7.8601	1.38×10^{-8}	11.07
896	-8.0039	9.91×10^{-9}	11.16
890	-8.1643	6.85×10^{-9}	11.24
883	-8.2832	5.21×10^{-9}	11.32
875	-8.4522	3.53×10^{-9}	11.43
1027	-6.0013	9.97×10^{-7}	9.74

2ND LAW ENTHALPY = 64.9 KCAL/MOLE ERROR = 0.4

T AVE. = 982°K

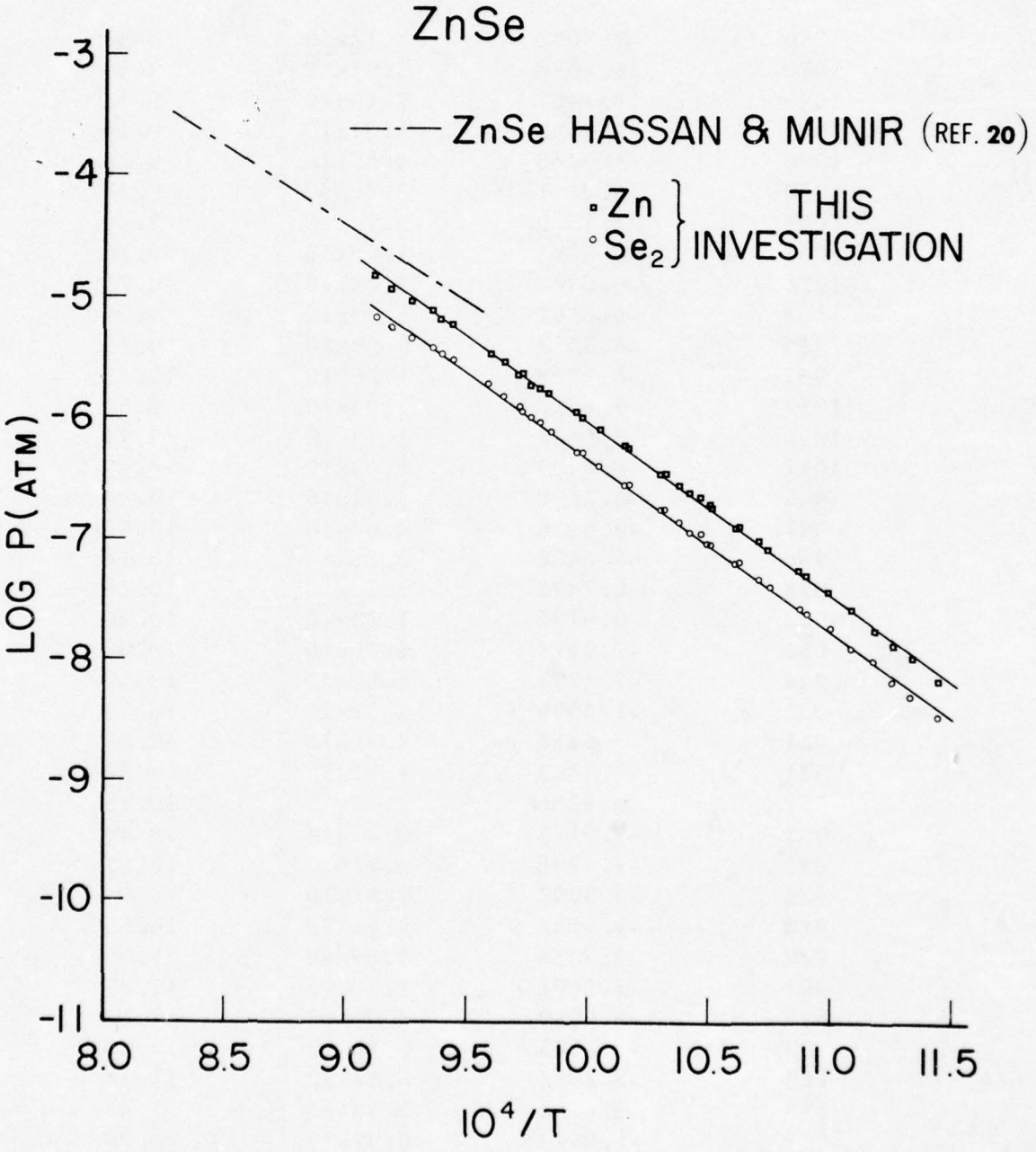


Figure 14. Plot of Second Law Data for ZnSe

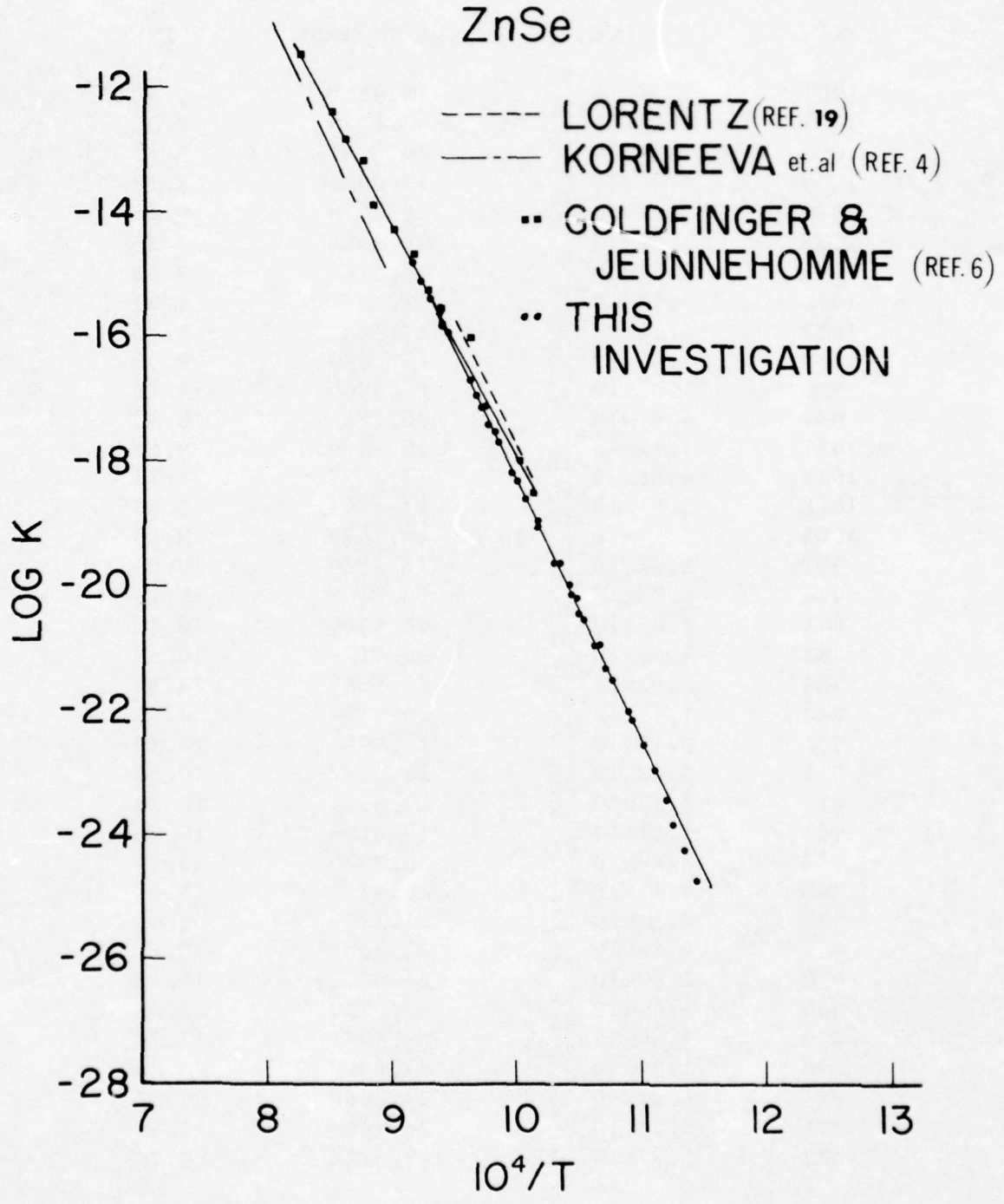


Figure 15. Plot of Third Law Analysis for ZnSe

TABLE 6

THIRD LAW ANALYSIS FOR ZnSe

T KEL	K (EQ)	LOGK (EQ)	T INV
1061	1.10×10^{-16}	15.9568	9.42
1070	2.32×10^{-16}	15.6337	9.35
1096	1.45×10^{-15}	14.8381	9.12
1059	8.09×10^{-16}	15.0921	9.18
1080	4.00×10^{-16}	15.3975	9.26
1066	1.42×10^{-16}	15.8464	9.38
1043	2.09×10^{-17}	16.6789	9.58
1032	7.14×10^{-18}	17.1461	9.69
1022	3.13×10^{-18}	17.5047	9.78
1004	5.56×10^{-19}	18.2550	9.96
986	1.02×10^{-19}	18.9900	10.14
957	6.51×10^{-21}	20.1861	10.45
1037	1.18×10^{-17}	16.9289	9.64
1029	6.96×10^{-18}	17.1577	9.72
1018	2.11×10^{-18}	17.6763	9.82
1006	6.79×10^{-19}	18.1682	9.94
997	2.62×10^{-19}	18.5820	10.03
986	9.75×10^{-20}	19.0108	10.14
973	2.21×10^{-20}	19.6565	10.28
962	7.62×10^{-21}	20.1178	10.40
953	2.91×10^{-21}	20.5367	10.49
944	1.15×10^{-21}	20.9380	10.59
932	3.17×10^{-22}	21.4986	10.73
921	9.42×10^{-23}	22.0258	10.86
971	2.19×10^{-20}	19.6592	10.30
965	1.21×10^{-20}	19.9169	10.36
953	3.69×10^{-21}	20.4328	10.49
943	1.17×10^{-21}	20.9321	10.61
935	4.82×10^{-22}	21.3168	10.69
919	6.84×10^{-23}	22.1648	10.88
910	2.67×10^{-23}	22.5732	10.98
903	1.07×10^{-23}	22.9720	11.07
896	3.36×10^{-24}	23.4743	11.16
890	1.29×10^{-24}	23.8909	11.24
883	5.42×10^{-25}	24.2660	11.32
875	1.73×10^{-25}	24.7608	11.42
1027	3.87×10^{-18}	17.4124	9.74

HEAT OF REACTION = 195.1 KCAL/MOLE ERROR = 1.1

This difference may be reconciled by the fact that crystal samples were used in this investigation. Hassan and Munir[20] have reported that $\Delta H^+/\Delta H°$ for ZnSe is 1.26 which would yield an apparent accommodation coefficient, α, of $0.07 < \alpha < 0.22$. The data used in this calculation yields a value of $\Delta H^+/\Delta H°$ of 1.12 which is within the range of Hassan and Munir[20] and would represent an apparent α of about 0.13 from our data. Upon examination of the data in Table 7, as the higher temperature data were obtained, the third law determinations show more randomness, than at the lower temperatures. This is a further indication of a systematic perturbance of the lower temperature data indicative of an accommodation coefficient dependency. This is depicted in Figure 15, where the higher temperature data are in agreement with Goldfinger and Jeunehomme[6] but the data begin to deviate from theirs around 1050°K and below.

The partial vapor pressure data obtained in this investigation are in good agreement with other data.[6,20] The difficulties encountered in this investigation were that of establishing equilibria at the lower temperatures, caused by the attendant difficulty of an accommodation coefficient different from unity. Exact agreement for third law and second law values for ΔH^o_{298} therefore were not obtained, and the accommodation coefficient variation is in agreement with data obtained by Hassan and Munir.[20]

TABLE 7

SECOND AND THIRD LAW ANALYSIS FOR ZnSe

	THIRD LAW		SECOND LAW		
T K	H298	DELTA	LOGK (C)	LOGK (O)	DIFF
875	181.794	4.045	-23.746	-24.761	1.014
883	181.365	3.617	-23.367	-24.266	0.899
890	181.060	3.311	-23.073	-23.891	0.818
896	180.579	2.830	-22.780	-23.474	0.694
903	179.889	2.140	-22.450	-22.972	0.522
911	179.567	1.818	-22.133	-22.573	0.440
919	179.405	1.656	-21.767	-22.165	0.398
921	179.183	1.434	-21.682	-22.026	0.344
932	178.978	1.229	-21.207	-21.499	0.292
936	178.829	1.081	-21.061	-21.317	0.256
943	178.437	0.689	-20.769	-20.932	0.163
944	178.779	1.031	-20.696	-20.938	0.242
953	178.176	0.427	-20.331	-20.433	0.102
953	178.629	0.880	-20.331	-20.537	0.205
957	177.735	-0.013	-20.186	-20.186	0.001
962	178.236	0.487	-20.004	-20.118	0.114
965	177.993	0.244	-19.858	-19.917	0.059
971	177.819	0.071	-19.640	-19.659	0.019
973	178.131	0.383	-19.567	-19.656	0.089
986	177.370	-0.379	-19.071	-18.990	-0.081
986	177.518	-0.230	-19.058	-19.011	-0.048
997	177.380	-0.368	-18.659	-18.582	-0.077
1004	177.041	-0.708	-18.406	-18.255	-0.151
1006	176.974	-0.775	-18.333	-18.168	-0.165
1018	176.640	-1.109	-17.911	-17.676	-0.235
1023	176.566	-1.183	-17.754	-17.505	-0.250
1027	176.807	-0.942	-17.610	-17.412	-0.197
1029	176.002	-1.747	-17.525	-17.158	-0.368
1032	176.341	-1.408	-17.441	-17.146	-0.295
1037	176.217	-1.532	-17.249	-16.929	-0.320
1044	175.990	-1.759	-17.044	-16.679	-0.365
1061	175.254	-2.495	-16.468	-15.957	-0.511
1066	175.464	-2.284	-16.312	-15.846	-0.465
1070	174.945	-2.804	-16.204	-15.634	-0.570
1080	175.349	-2.400	-15.880	-15.397	-0.483
1089	175.237	-2.511	-15.593	-15.092	-0.501
1097	175.026	-2.722	-15.378	-14.838	-0.540
				STANDARD DEVIATION =	0.424
	H298 = 177.7			H298 =	199.8

(D) Titanium-Iron Alloy System

There is presently a substantial interest in the theory and properties of transition metal alloys. The investigation of the thermodynamic properties of transition metal binary systems can also yield useful information if the thermodynamic behavior can be related to the observed physical properties. In addition, mass spectrometer techniques have been shown to be quite useful in several binary alloys systems studies.[21-23]

The purpose of the present study was to investigate titanium-iron binary alloys since they have some practical implications and as part of a more systematic study of titanium alloy characteristics. Previous studies made on other titanium alloy combinations have been reported elsewhere.[24] The results reported here are of a preliminary nature since previous studies in this laboratory were made using the time-of-flight mass spectrometer.[25] However, this study is based on measurements carried on with a magnetic deflection mass spectrometer with better overall stability features.[26] The experimental arrangement is similar to that employed by Wagner, Sodeck and Neckel[27] which makes use of the Knudsen effusion technique.

The use of the effusion technique coupled with the mass spectrometer presents certain problems of calibration, sensitivity, and reproducibility which have in part been discussed by Belton and Fruehan,[21,22] Sodeck, Enter, and Neckel[28] and Wagner[29] for alloy activity determination. In order to circumvent these problems, Hackworth, Hoch and Gegel,[31] developed the triple Knudsen cell technique where isotopic ratios of an element in the alloy and in the pure state can be measured simultaneously. However, this technique decreases the ion current signal because of back diffusion, and calibration runs are frequently necessary and discussed by Bidwell.[32] The triple Knudsen cell has been used by Bergman-Desnuelle[33] in a very similar fashion. The intensity ratio method employed by Belton and Fruehan[21,22] and developed further by Wagner[29] was the method chosen in this study. This method depends on utilizing the ion current intensity ratio directly by application of the Gibbs-Duhem equation. This requires a graphical integration procedure which would lead to certain inaccuracies. Wagner, Sodeck and Neckel[27] have shown how an error in the heats of mixing can be detected by means of the use of the constant of integration. This error can be eliminated by using a channel type effusion orifice to avoid interaction of the molecular beam within the heat shields. A more direct measurement of ion currents was employed by Jones, Stafford and Whitemore[34], however geometrical factors were not exactly identical in their experiment. This method would be a preferred technique if the geometrical considerations could be overcome. Grimley and Joyce[35] have recently developed a dual Knudsen cell arrangement where identical geometry for both cells could be maintained. However, their technique has not been applied beyond 600°C. Bearing these factors in mind, the method we chose to follow has been the single Knudsen cell method using ion current intensity ratios.

1. Experimental

The instrument used in the present study is a Nuclide Analysis Associates 12-90-HT mass spectrometer. This instrument is a 90° sector, 30.5 cm radius of curvature, first order direction focusing mass spectrometer which is equipped with a high temperature Knudsen cell sample system.

The sample system consists of a cylindrical Knudsen cell centered on the axis of a bifilarly wound tungsten helix which serves as a heating element. Both the cell and heater are surrounded by radiation shielding and cell heating is accomplished by radiative heat transfer. The entire furnace complex is mounted on an assembly which in turn is driven by a bellows drive arrangement, allowing the investigator to adjust the position of the furnace assembly when under vacuum.

The vacuum housing around the furnace assembly is water jacketed and water cooling is also provided to some of the support members of the furnace. The housing contains viewports enabling the experimenter to sight the top, side, and bottom of the Knudsen cell in order to make optical temperature measurements and has provision for thermocouple feedthroughs. A mechanically operated "shutter" is located above the cell and is driven by a micrometer-bellows assembly. This movable collimator between the sample system and the ion source serves to differentiate between species in the molecular beam from the cell and those present as background gases in the vacuum system. The "shutter" assembly also provides information concerning the intensity profile of the molecular beam.

Two types of Knudsen cell configurations were employed in this study. One type was a tantalum cell which had a 0.05 cm diameter knife edge orifice. The ratio of internal cell area to orifice area in this investigation was about 2700 to 1. The second type was a cell with 0.1 cm diameter orifice and a channel length of the orifice in this design was a 0.15 cm and the ratio of internal cell area to orifice area was about 800 to 1.

The sample temperatures in this investigation were determined Pt-Pt 10% Rh thermocouples which were peened into blind holes in the bottom of the Knudsen cell. The legs of the thermocouples were led out of the vacuum envelope through CONAX fittings. The thermocouples were fabricated from 24 gauge Platinum and Platinum 10 at % Rhodium wire. The hot junctions were formed by arc welding in an inert atmosphere. A typical hot junction had a 1.25 mm bead made in this way. Prior to installation, the thermocouples were annealed and calibration was checked against a standard thermocouple. Optical pyrometer measurements were made by sighting into the orifice of the Knudsen cell during the experiment. The thermal emf's generated by these thermocouples were referenced to the ice point and were

measured using a Leeds and Northrup Type K-5 potentiometer in conjunction with a L&N D.C. null detector, Model 9834-1.

The Ion source on the Nuclide instrument is a Nier-type electron impact source. During the course of these studies, data were taken using 18 eV electrons except where noted. The emission current varied from 0.5 mA to 2.0 mA. The ions resulting from electron impact ionization processes occurring at the source were accelerated through 5000 volts and focused on the entrance slit to the magnetic analyzer which was set at 0.153 mm width. The exit slit from the analyzer field was set at the same width. With such a geometry, a resolution of 1/1500 was obtained.

The detector in use for this study was a 16-stage electron multiplier. This multiplier has a Cu-Be dynode. A series of experiments using ionic species of a range of atomic weights was carried out using an insertable Faraday cup collector to measure the multiplier gain. The dependence of multiplier gain on the inverse square root of the ionic mass, which has previously been reported,[10,11] was not observed. Within the scope of our experiments, the gain appears to be quite insensitive to the mass of the impinging ion. Such behavior is consistent with the findings of Gingerich.[13] In view of this observation, we took the gain of the multiplier to be 10^6 for all species under these conditions.

The samples used in this study were prepared from materials with nominal purity of 99.9% by repeated vacuum arc melting. They were then vacuum annealed for 24 hours at 1200°C. The chemical compositions of the alloys were determined by atomic absorption spectrophotometry. Other impurities in the mass spectrometer were not detected to any great extent.

2. Results

Initial experiments were carried out to identify the ionic species resulting from the vaporization of Ti-Fe alloys. Mass spectra were recorded, under isothermal conditions of above 1400°C and mass numbers assigned to the peaks by peak counting and magnetic field measurements. The peaks of the ionic species originating from the Knudsen cell were differentiated from background peaks by their shutterability. The ionic species were identified by comparing the experimentally determined relative intensities within each peak group with calculated isotopic abundances for each ion and by appearance potential determinations for each species. The appearance potentials were determined by applying the linear extrapolation method to plots of the ionization efficiency curves for each species. The energy of the ionizing electrons was fixed by measurement of the appearance potential for Hg, which is present as a background gas. The ionic species identified and their appearance potentials were in good agreement with those of Franklin et. al.[15] For this study Ti-48 and Fe56 were the primary isotopes measured.

During the course of this study, surface depletion was estimated by considering a mass balance of the surface of the vaporization area, by applying the rate equation for vaporization and by solving the unsteady state diffusion equation with proper boundary conditions as given by Bolsaitis and Skolnick.[36] The solution of the diffusion equation is[37]

$$\frac{X^S}{X_0} = \exp(\xi^2)\,\mathrm{erfc}(\xi)$$

where

$$\xi = 5.83 \times 10^{-2} \frac{kA_0\gamma t^{1/2} P_0}{A\rho (MT)^{1/2} D^{1/2}} = B \frac{t^{1/2} P_0}{D^{1/2}}$$

and

$$B = 5.83 \times 10^{-2} \frac{kA_0\gamma}{A\rho (MT)^{1/2}}$$

B varies slowly with temperature, whereas P_0 and D vary exponentially, where

X^S/X_0 = ratio of surface to bulk concentration

k = clausing factor of orifice ($\simeq \frac{1}{2}$)

γ = activity coefficient ($\simeq 1$)

A_0/A = ratio of orifice to sample surface area

P_0 = vapor pressure of effusing component at temperature, torr

D = diffusion coefficient, $cm^2\ sec^{-1}$

ρ = molar density, g per mole

M = at. wt, g ~ 50

t = time, sec

T = absolute temperature, °K (~ 1700°K)

For $D \simeq 10^{-8}$ sq cm per sec, and making approximations for the other quantities, the ratio of surface to bulk concentration was calculated to be a maximum of 5 pct with orifice-to-surface area ratios of less than 0.01 and

time of 3 min. Since the use is based on approximations, surface depletion effects are best tested by experimental results. Usually, the maximum errors for surface depletion effects are less than the overall accuracy of the data since no measurable change in ion current was detected for sample surface-to-orifice area ratios > 100. Values of $D \simeq 10^{-8}$ sq cm per sec have been reported by Murdock and McHargue[38] for vanadium in Ti-V binary alloys and for titanium in Ti-V binary alloys in the temperature range of 1600°C. If values of $D \simeq 10^{-11}$ sq cm per sec or three orders of magnitude less than those observed at the experimental temperature are used, then errors arising from surface depletion can become significant.

The weight loss of a sample during an experimental run was usually about 0.3 wt pct so that no noticeable composition change was taking place in the alloy during the experiment, since both species were monitored and detected.

Experimental runs were made on four alloys of interest, since it is of interest to determine the range of applicability of the regular solution model. Since ratios of ion current intensities are used in calculating the interaction parameter, Ω, the ion current intensities for I_{Ti}^{+} and I_{Fe}^{+}, 48 and 56 respectively were not corrected for isotopic abundances. This data are tabulated in Tables 8, 9, 10, and 11 for 10, 20, 30, and 40 atomic % Fe respectively. These data were plotted (see Figure 16) in a manner similar to that described by Rolinski, et. al.[25] The resultant data indicates that the pairwise interaction parameter, $\Omega_{Ti\text{-}Fe}$ is about 3.2 ± 1 Kcal/mole and is positive. This result in general agrees with the findings of other investigators and a discussion of attendant features of such an alloy system is discussed elsewhere. The positive interaction parameter indicates positive deviation from ideal behavior and for this system seems to hold for the range of $0 < X < 0.4$ atomic % iron.

TABLE 8

MASS SPECTROMETER DATA FOR Ti-10% Fe ALLOYS

$\frac{I^+_{56}}{I^+_{48}}$	$\left(\frac{I^+_{56}}{I^+_{48}}\right)\left(\frac{N_{Ti}}{N_{Fe}}\right)$	$\ln\left(\frac{I^+_{56}}{I^+_{48}}\right)\left(\frac{N_{Ti}}{N_{Fe}}\right)$	T°C	$-RT \ln\left(\frac{I^+_{56}}{I^+_{48}}\right)\left(\frac{N_{Ti}}{N_{Fe}}\right)$
3.95	35.61	3.57	1514	12.76
3.79	34.10	3.53	1511	12.59
4.42	39.78	3.68	1474	12.86
4.18	37.69	3.63	1450	12.51
4.65	41.88	3.73	1443	12.80
4.39	39.51	3.67	1415	12.39
4.58	41.23	3.72	1433	12.69
4.88	43.99	3.78	1392	12.59
4.98	44.79	3.80	1405	12.75
4.72	42.52	3.74	1426	12.71
4.85	43.72	3.77	1413	12.72
5.01	45.12	3.80	1427	12.92
4.81	43.34	3.77	1449	12.98
4.84	43.57	3.77	1438	12.90
4.71	42.36	3.75	1444	12.88
4.54	40.84	3.71	1457	12.84
4.17	37.55	3.62	1475	12.65
4.30	38.71	3.65	1485	12.83

TABLE 9

MASS SPECTROMETER DATA FOR Ti-20% Fe ALLOYS

$\frac{I^+_{56}}{I^+_{48}}$	$\left(\frac{I^+_{56}}{I^+_{48}}\right)\left(\frac{N_{Ti}}{N_{Fe}}\right)$	$\ln\left(\frac{I^+_{56}}{I^+_{48}}\right)\left(\frac{N_{Ti}}{N_{Fe}}\right)$	T°C	$-RT \ln\left(\frac{I^+_{56}}{I^+_{48}}\right)\left(\frac{N_{Ti}}{N_{Fe}}\right)$
9.05	36.2	3.59	1500	12.73
8.33	33.3	3.51	1517	12.56
9.26	37.0	3.61	1513	12.90
9.39	37.56	3.62	1527	13.05
9.48	37.92	3.63	1500	12.89

TABLE 10

MASS SPECTROMETER DATA FOR Ti-30% Fe ALLOYS

$\frac{I^+_{56}}{I^+_{48}}$	$\left(\frac{I^+_{56}}{I^+_{48}}\right)\left(\frac{N_{Ti}}{N_{Fe}}\right)$	$\ln\left(\frac{I^+_{56}}{I^+_{48}}\right)\left(\frac{N_{Ti}}{N_{Fe}}\right)$	T°C	$-RT \ln\left(\frac{I^+_{56}}{I^+_{48}}\right)\left(\frac{N_{Ti}}{N_{Fe}}\right)$
14.32	33.42	3.51	1406	11.78
14.22	33.18	3.50	1420	11.85
14.40	33.59	3.51	1370	11.53
14.43	33.68	3.52	1380	11.64
12.89	30.09	3.40	1391	11.31
13.91	32.47	3.48	1430	11.85
15.14	35.33	3.56	1448	12.25
14.83	34.60	3.54	1470	12.34

TABLE 11

MASS SPECTROMETER DATA FOR Ti-40% Fe ALLOYS

$\frac{I^+_{56}}{I^+_{48}}$	$\left(\frac{I^+_{56}}{I^+_{48}}\right)\left(\frac{N_{Ti}}{N_{Fe}}\right)$	$\ln\left(\frac{I^+_{56}}{I^+_{48}}\right)\left(\frac{N_{Ti}}{N_{Fe}}\right)$	T°C	$-RT \ln\left(\frac{I^+_{56}}{I^+_{48}}\right)\left(\frac{N_{Ti}}{N_{Fe}}\right)$
13.7	20.55	3.02	1438	10.33
12.02	18.03	2.89	1432	9.85
12.33	18.49	2.92	1482	10.25
12.11	18.165	2.90	1521	10.40
13.6	20.4	3.01	1503	11.01
15.0	22.5	3.11	1470	10.84

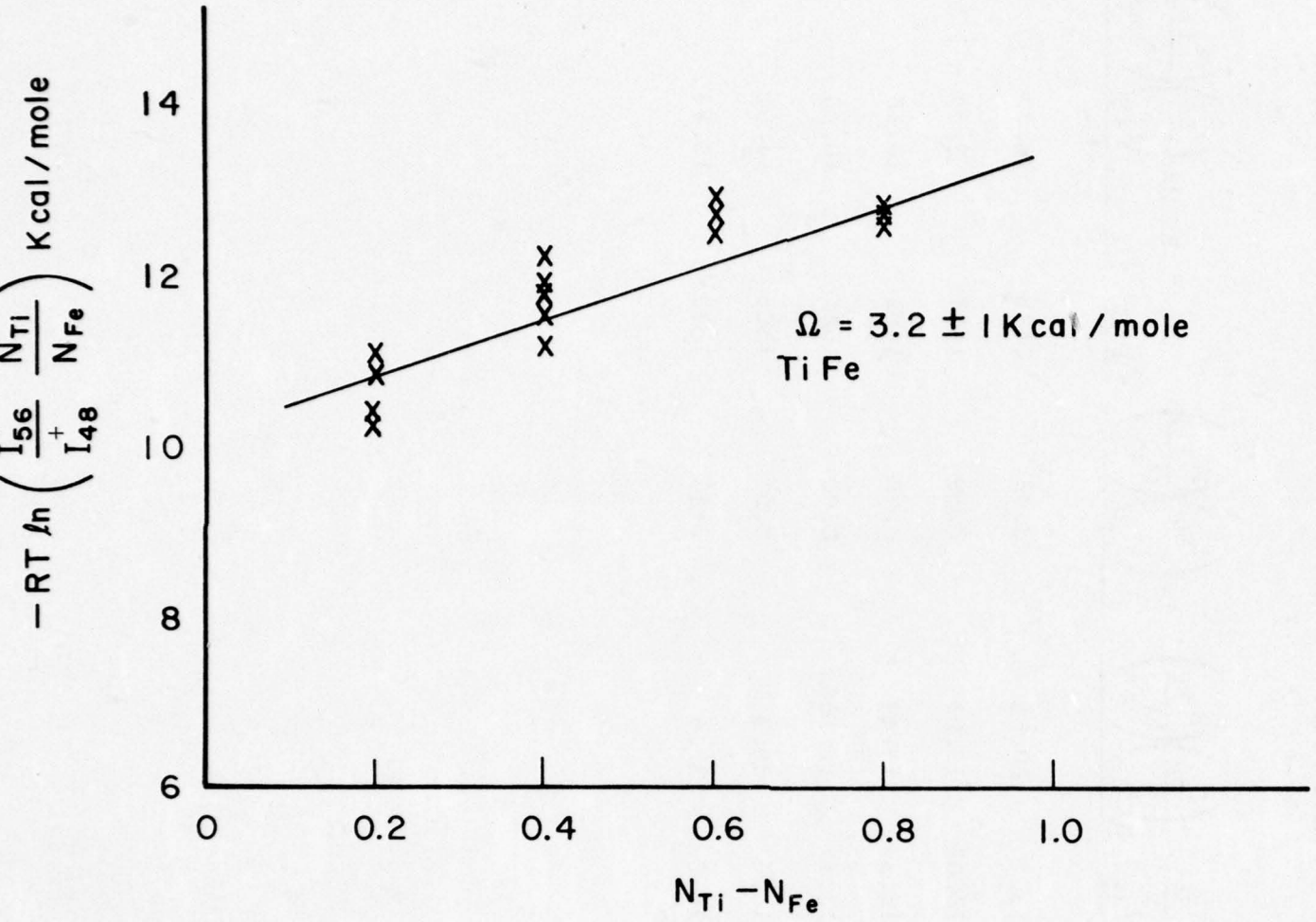


Figure 16. Regular Solution Model Plot for Ti-Fe Alloys

(E) Samarium-Cobalt System

Initial runs were performed on both cobalt and samarium in pure form as calibration tests to ascertain the correction factors and procedural problems involved in this system. The test runs with cobalt showed that the temperature region of interest in this study produces diffusion problems between the cobalt sample and the tantalum Knudsen cell and possibly even the formation of a tantalum-cobalt eutectic. Cell liners of boron nitride were fabricated to eliminate these problems. These problems were not evident with the samarium.

In sweeping the mass spectrum of samarium, a series of shutterable peaks were found which, when identified, showed the samarium to have impurities of europium and chlorine.

Isotopic abundance calculations were also made for Sm, Sm_2, Sm_2O, Sm_2O_2 and Sm_2O_3 also to be used in identifying other isotopes in the Sm spectrum, however, only the Sm species were identified.

Ionization efficiency data were obtained and plots of these data were used to determine the Appearance Potential (A.P.) by linear extrapolation method, for Co, Sm and corrected by Hg. The A.P. for Hg is used for calibration since mercury is present from the diffusion pumps and is well characterized. The A.P.'s on the other isotopes are used as additional evidence for positive identification. Figures 17 and 18 show the plots of the ionization efficiency data for these species.

Ion current intensity data were obtained using the mass spectrometer experiments outlined previously, as a function of temperature (See Table 12). The data were treated using the Second Law arguments, and are plotted in preliminary form as log I^+T versus $1/T$ for samarium (see Figure 19). A similar result for cobalt was not obtained because of the reaction occurring with tantalum crucible. Duplicate runs were made on samarium for the purpose of verifying the second law value for the temperature range between about 750 to 1000°K, but below the $\alpha \rightarrow \beta$ transition temperature of 1184°K. The second law plot for a typical run is shown in Figure 19. However, the ΔH seemed to be too low so that more duplicative experiments were performed. The data further obtained are given in Tables 13 through 19. The second law values for ΔH range from 41.1 to 48.0 K cal/mole so that a true estimate of this data would be 45 ± 3 K cal/mole, which is in fairly good agreement with a value of 48.7 ± 0.4 K cal/mole at a mean temperature of 811°K obtained by Sarage, Hudson and Spedding,[39] and with others.[40, 41, 42]

The next step was to establish the true vapor pressure of samarium. In order to relate the ion intensity of a given species as measured by the mass spectrometer to the vapor pressure of the neutral precursor of

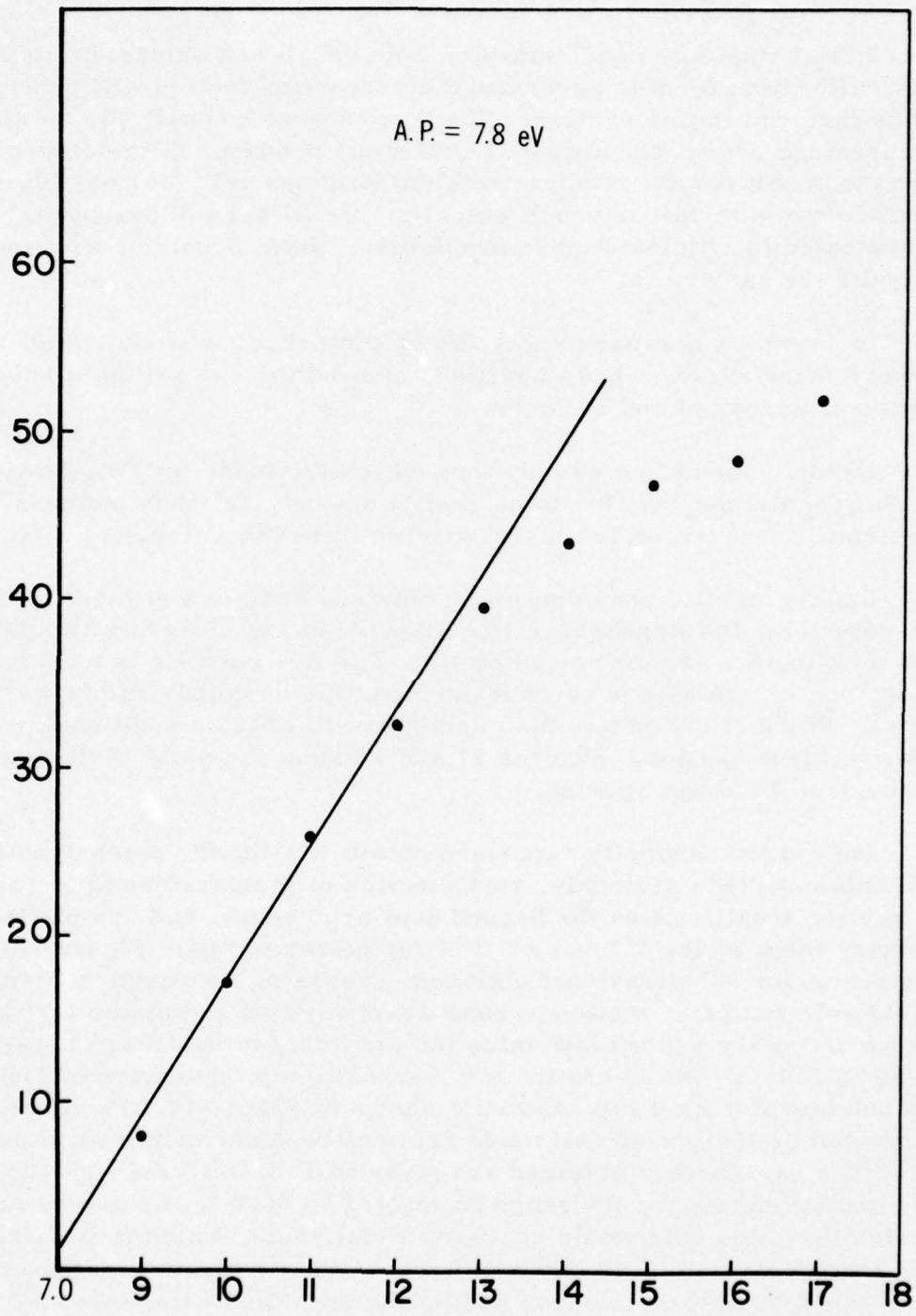


Figure 17. Ionisation Efficiency Curves for Cobalt

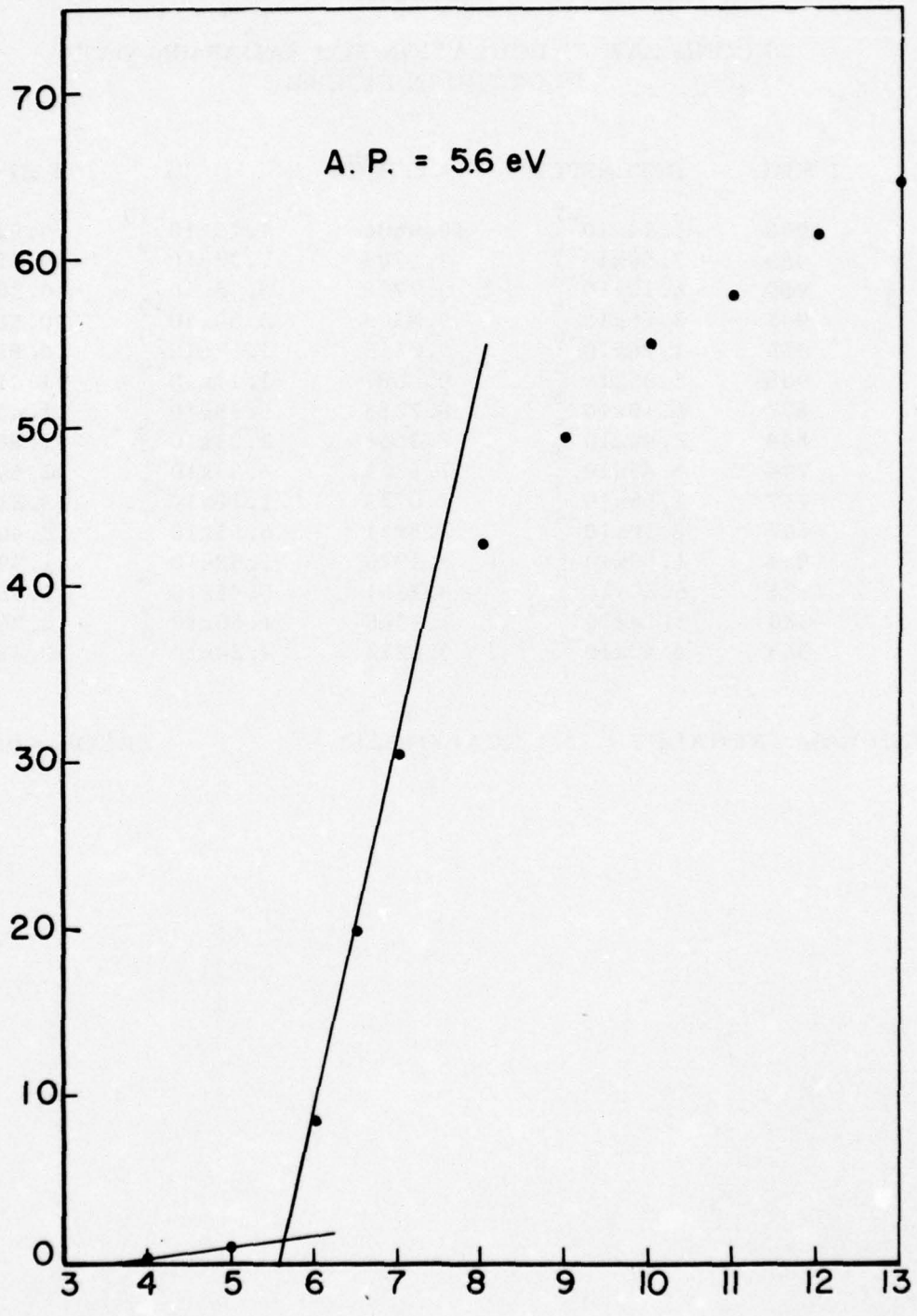


Figure 18. Ionization Efficiency Curves for Samarium

TABLE 12

SECOND LAW CALCULATION FOR SAMARIUM DATA
PLOTTED IN FIGURE 3

T KEL	INTENSITY	LOG (I^+T)	(I^+T)	T INV
1008	1.14×10^{-7}	10.0606	1.15×10^{-10}	9.92
989	7.50×10^{-6}	9.8704	7.42×10^{-9}	10.11
980	6.10×10^{-6}	9.7768	5.98×10^{-9}	10.20
945	2.85×10^{-6}	9.4305	2.69×10^{-9}	10.58
925	1.80×10^{-6}	9.2215	1.67×10^{-9}	10.81
908	1.29×10^{-6}	9.0687	1.17×10^{-9}	11.01
877	6.10×10^{-5}	8.7285	5.35×10^{-8}	11.40
844	2.40×10^{-5}	8.3066	2.03×10^{-8}	11.85
794	5.45×10^{-4}	7.6363	4.33×10^{-7}	12.59
757	1.56×10^{-4}	7.0723	1.18×10^{-7}	13.21
807	8.10×10^{-4}	7.8151	6.53×10^{-7}	12.40
834	1.89×10^{-5}	8.1976	1.58×10^{-8}	11.99
878	6.20×10^{-5}	8.7361	5.45×10^{-8}	11.38
920	1.74×10^{-6}	9.2045	1.60×10^{-9}	10.86
963	4.40×10^{-6}	9.6272	4.24×10^{-9}	10.38

2ND LAW ENTHALPY = 41.1 KCAL/MOLE ERROR = 0.2

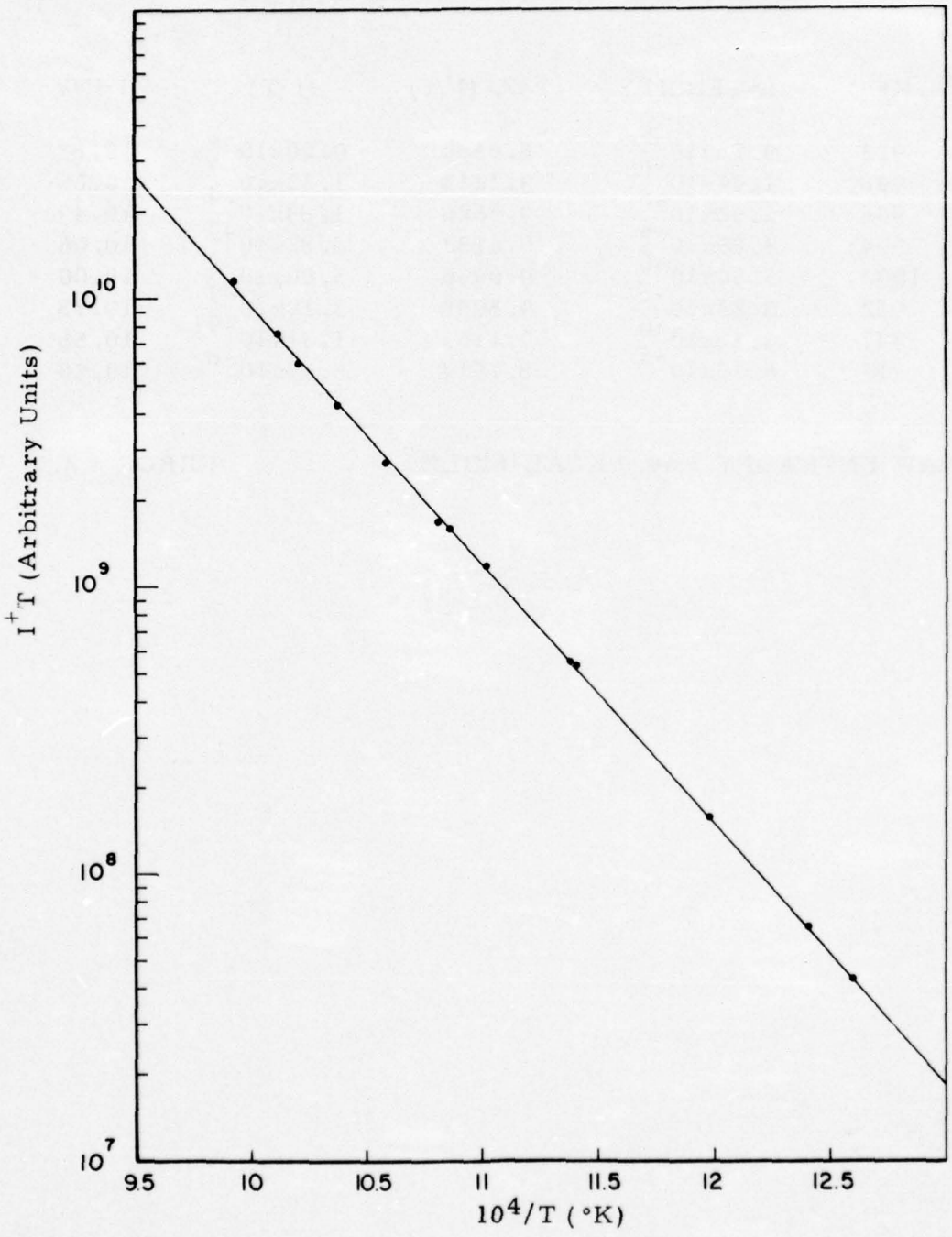


Figure 19. $I^+ T$ vs. $10^4/T$ (°K) Plot for Samarium

TABLE 13

SECOND LAW DATA ON SAMARIUM, RUN 1

T KEL	INTENSITY	LOG (I^+T)	(I^+T)	T INV
923	9.75×10^{-5}	8.9542	9.00×10^{-8}	10.83
938	1.41×10^{-6}	9.1213	1.32×10^{-9}	10.66
954	1.92×10^{-6}	9.2626	1.83×10^{-9}	10.49
994	4.85×10^{-6}	9.6832	4.82×10^{-9}	10.06
1000	5.00×10^{-6}	9.6990	5.00×10^{-9}	10.00
982	3.25×10^{-6}	9.5039	3.19×10^{-9}	10.18
947	1.38×10^{-6}	9.1163	1.31×10^{-9}	10.56
917	6.15×10^{-5}	8.7514	5.64×10^{-8}	10.90

2ND LAW ENTHALPY = 44.9 KCAL/MOLE ERROR = 2.7

TABLE 14

SECOND LAW DATA ON SAMARIUM, RUN 2

T KEL	INTENSITY	LOG (I^+T)	(I^+T)	T INV
964	2.00×10^{-6}	9.2840	1.92×10^{-9}	10.38
964	2.03×10^{-6}	9.2907	1.95×10^{-9}	10.37
955	1.50×10^{-6}	9.1559	1.43×10^{-9}	10.48
943	1.11×10^{-6}	9.0199	1.05×10^{-9}	10.60
928	7.35×10^{-5}	8.8338	6.82×10^{-8}	10.78
917	5.55×10^{-5}	8.7067	5.09×10^{-8}	10.90
896	3.05×10^{-5}	8.4364	2.73×10^{-8}	11.17
878	1.91×10^{-5}	8.2236	1.67×10^{-8}	11.38

2ND LAW ENTHALPY = 48.1 KCAL/MOLE ERROR = 0.6

TABLE 15

SECOND LAW DATA ON SAMARIUM, RUN 3

T KEL	INTENSITY	LOG (I^+T)	(I^+T)	T INV
970	2.76×10^{-6}	9.4275	2.68×10^{-9}	10.31
1005	5.70×10^{-6}	9.7582	5.73×10^{-9}	9.05
982	3.45×10^{-6}	9.5298	3.39×10^{-9}	10.19
951	1.82×10^{-6}	9.2372	1.73×10^{-9}	10.51
922	8.85×10^{-5}	8.9117	8.16×10^{-8}	10.85
892	4.00×10^{-5}	8.5523	3.57×10^{-8}	11.22
860	1.61×10^{-5}	8.1401	1.38×10^{-8}	11.62
827	5.70×10^{-4}	7.6733	4.71×10^{-7}	12.09
789	1.55×10^{-4}	7.0858	1.22×10^{-7}	12.68
821	4.85×10^{-4}	7.6002	3.98×10^{-7}	12.18
854	1.37×10^{-5}	8.0664	1.17×10^{-8}	11.72
888	3.50×10^{-5}	8.4926	3.11×10^{-8}	11.26
920	7.90×10^{-5}	8.8613	7.27×10^{-8}	10.87
953	1.68×10^{-6}	9.2042	1.60×10^{-9}	10.50
982	3.15×10^{-6}	9.4904	3.09×10^{-9}	10.18
1010	5.70×10^{-6}	9.7600	5.76×10^{-9}	9.90

2ND LAW ENTHALPY = 44.2 KCAL/MOLE ERROR = 0.3

TABLE 16

SECOND LAW DATA ON SAMARIUM, RUN 4

T KEL	INTENSITY	LOG (I^+T)	(I^+T)	T INV
964	2.01×10^{-6}	9.2873	1.94×10^{-9}	10.37
981	2.84×10^{-6}	9.4443	2.78×10^{-9}	10.19
996	3.95×10^{-6}	9.5947	3.93×10^{-9}	10.04
1006	4.95×10^{-6}	9.6973	4.98×10^{-9}	9.94
974	2.33×10^{-6}	9.3551	2.27×10^{-9}	10.26
963	1.80×10^{-6}	9.2390	1.73×10^{-9}	10.38
951	1.34×10^{-6}	9.1038	1.27×10^{-9}	10.51
942	1.04×10^{-6}	8.9890	9.75×10^{-8}	10.62
928	7.30×10^{-5}	8.8309	6.78×10^{-8}	10.77
915	5.05×10^{-5}	8.6648	4.62×10^{-8}	10.93

2ND LAW ENTHALPY = 48.0 KCAL/MOLE ERROR = 0.7

TABLE 17

SECOND LAW DATA ON SAMARIUM, RUN 5

T KEL	INTENSITY	LOG (I^+T)	(I^+T)	T INV
997	4.30×10^{-6}	9.6320	4.29×10^{-9}	10.03
987	3.30×10^{-6}	9.5129	3.26×10^{-9}	10.13
977	2.72×10^{-6}	9.4236	2.65×10^{-9}	10.24
965	2.06×10^{-6}	9.2975	1.98×10^{-9}	10.36
955	1.56×10^{-6}	9.1731	1.49×10^{-9}	10.47
946	1.25×10^{-6}	9.0709	1.18×10^{-9}	10.57
936	9.45×10^{-5}	8.9466	8.84×10^{-8}	10.69
922	6.60×10^{-5}	8.7844	6.09×10^{-8}	10.84
904	4.05×10^{-5}	8.5638	3.66×10^{-8}	11.06
893	2.80×10^{-5}	8.3978	2.50×10^{-8}	11.20
879	1.95×10^{-5}	8.2338	1.71×10^{-8}	11.38

2ND LAW ENTHALPY = 47.6 KCAL/MOLE ERROR = 0.3

TABLE 18

SECOND LAW DATA ON SAMARIUM, RUN 6

T KEL	INTENSITY	LOG (I^+T)	(I^+T)	T INV
964	2.01×10^{-6}	9.2873	1.94×10^{-9}	10.37
981	2.84×10^{-6}	9.4443	2.78×10^{-9}	10.19
996	3.95×10^{-6}	9.5947	3.93×10^{-9}	10.04
1006	4.95×10^{-6}	9.6973	4.98×10^{-9}	9.94
974	2.33×10^{-6}	9.3551	2.27×10^{-9}	10.26
963	1.80×10^{-6}	9.2390	1.73×10^{-9}	10.38
951	1.34×10^{-6}	9.1038	1.27×10^{-9}	10.51
942	1.04×10^{-6}	8.9890	9.75×10^{-8}	10.62
928	7.30×10^{-5}	8.8309	6.78×10^{-8}	10.77
915	5.05×10^{-5}	8.6648	4.62×10^{-8}	10.93
997	4.30×10^{-6}	9.6320	4.29×10^{-9}	10.03
987	3.30×10^{-6}	9.5129	3.26×10^{-9}	10.13
977	2.72×10^{-6}	9.4236	2.65×10^{-9}	10.24
965	2.06×10^{-6}	9.2975	1.98×10^{-9}	10.36
955	1.56×10^{-6}	9.1731	1.49×10^{-9}	10.47
955	1.25×10^{-6}	9.0709	1.18×10^{-9}	10.57
936	9.45×10^{-5}	8.9466	8.84×10^{-8}	10.69
922	6.60×10^{-5}	8.7844	6.09×10^{-8}	10.84
904	4.05×10^{-5}	8.5638	3.66×10^{-8}	11.06
893	2.80×10^{-5}	8.3978	2.50×10^{-8}	11.20
879	1.95×10^{-5}	8.2338	1.71×10^{-8}	11.38

2ND LAW ENTHALPY = 47.3 KCAL/MOLE ERROR = 0.4

TABLE 19

SECOND LAW DATA ON SAMARIUM, RUN 7

T KEL	INTENSITY	LOG (I^+T)	(I^+T)	T INV
982	3.00×10^{-6}	9.4691	2.94×10^{-9}	10.19
994	3.95×10^{-6}	9.5939	3.93×10^{-9}	10.06
984	3.20×10^{-6}	9.4980	3.15×10^{-9}	10.17
970	2.27×10^{-6}	9.3416	2.20×10^{-9}	10.31
955	1.58×10^{-6}	9.1774	1.50×10^{-9}	10.47
938	1.04×10^{-6}	8.9874	9.71×10^{-8}	10.66
924	7.25×10^{-5}	8.8262	6.70×10^{-8}	10.82
907	4.60×10^{-5}	8.6205	4.17×10^{-8}	11.02
889	2.85×10^{-5}	8.4040	2.53×10^{-8}	11.24
872	1.71×10^{-5}	8.1735	1.49×10^{-8}	11.47
856	1.05×10^{-5}	7.8537	8.99×10^{-7}	11.68
839	6.35×10^{-4}	7.7267	5.33×10^{-7}	11.91
819	3.15×10^{-4}	7.4114	2.58×10^{-7}	12.22
796	1.37×10^{-4}	7.0358	1.09×10^{-7}	12.57

2ND LAW ENTHALPY = 46.5 KCAL/MOLE ERROR = 0.1

that species inside the equilibrium enclosure, it is necessary to carry out some type of calibration procedures. In the Nuclide instrument the equilibrium enclosure is a Knudsen cell. The method used was quantitative vaporization and has been described previously by Grimely.[9] Two quantitative vaporizations were performed, the data are shown in Table 20 . Although the quantitative vaporization data yields an average value of P/I^+ for samarium which can be used to convert the intensity data to vapor pressure data, this was not deemed to be warranted in view of the large scatter in the second law data plots. Furthermore, the calibration runs were much longer than predicted from other vapor pressure data,[39-42] indicating that perhaps a unity accommodation coefficient assumption is not a good assumption for samarium, and that a correction factor would be required. However, the basic second law data would not be changed significantly and that higher precision data would be extremely difficult to obtain, using the same experimental arrangement. In view of the above difficulties, the approximate value of ΔH°_{875} would be 45 ± 3 K cal/mole, and further experiments on this system were not conducted.

TABLE 20

QUANTITATIVE VAPORIZATION OF SAMARIUM

Weight of Sample	12.1 milligrams	3.331 milligrams
Time of Experiment	16.33 hours	7.318 hours
Reference Temp.	729.5°C	729°C
A(t)	8.602×10^{11} div.	2.197×10^{11} div.
Orifice	0.020 inch	0.020 inch
(P/I^+) Calculated	2.405×10^{-13} atm.	2.592×10^{-13} atm.

SECTION II

CHEMICAL PHYSICS

(A) Characterization of Organic Dye Laser Materials

A program was initiated to characterize various organic dye materials for use as laser components. It was determined by literature search and basic knowledge of lasers that the following parameters should be determined to fully characterize organic dyes as possible laser materials:

I Absorption spectrum (200-1200 nanometers).

II Fluorescence emission spectrum (200-1200 nanometers).

III Radiative decay lifetime of fluorescence.

IV Intersystem crossing rate and triplet-triplet absorption spectrum (200-1200 nanometers).

V Laser emission parameters.

(a) Efficiency as a function of:

(1) concentration of dye
(2) cavity length
(3) output coupling
(4) tuned wavelength

(b) Central lasing wavelength as a function of:

(1) concentration of dye
(2) cavity length
(3) output coupling
(4) input energy

(c) Pulse shape as a function of:

(1) concentration of dye
(2) cavity length
(3) output coupling
(4) input energy

Existing equipment was available for the determination of absorption and emission spectra. These are a Cary Model 14 Spectrophotometer and an Aminco Bowman Spectrophotofluorometer. In order to determine the radiative decay lifetime, the purchase of a TRW model 75A Decay Time Fluorometer and a model 81A infrared attachment was recommended. The determination of intersystem crossing and triplet-triplet absorption spectra will require the purchase of a Xenon model 720 flash Photolysis System with modification for infrared application. The determination of the listed laser parameters requires the purchase of an EG&G model 580 radiometer and 580-00-11 narrow beam adapter.

Absorption, fluorescence, and excitation spectra have been recorded for Cresyl Violet chloride obtained from K&K Laboratories. These spectra were recorded for ethanol solutions of the compound and an acidity dependent impurity has been found. It has been hypothesized that this impurity is the free base associated with the Cresyl Violet molecule. To verify this, studies of the absorption spectra of water solutions of the compound at $10^{-5}\underline{M}$ concentration and at pH values ranging from 2 to 12 are being conducted. It is hoped that an isosbestic relationship will be found. Subsequent experiments verified the isosbestic relationship of Cresyl Violet. Calculation showed that the pKa for protonation of the free base to the dye form is approximately 4.5.

A similar impurity has been found in Nile Blue A from Matheson, Coleman, and Bell (MCB). This compound is a higher homolog of Cresyl Violet so similar behavior was expected. The behavior was observed as expected and an additional protonation occurred in glacial acetic acid.

Several counter-ion derivatives of Rhodamine 6G were characterized for optical properties. These compounds were made from Rhodamine 6GCl from Eastman Kodak (EKO) by ion exchange reactions in aqueous solution. Each compound was precipitated by adding an excess of the acid of the counter-ion desired and then was recrystallized from an ethanol-ether solution. Table 21 lists the properties of these derivatives. The same optical properties were determined for Rhodamine B chloride, Rhodamine B fluoborate, and Rhodamine 5GL fluoborate and are also listed in Table 21. In these tables of properties, the symbols have the following meanings:

E max	=	maximum molar extinction coefficient
λ max	=	peak absorption wavelength
λ fl	=	peak fluorescence wavelength
Stokes Shift	=	λ fl - λ max, and
α	=	a relative indicator of fluorescence strength.

TABLE 21

OPTICAL PROPERTIES OF COUNTER-ION DERIVATIVES OF RHODAMINE 6G AND SOME OTHER RHODAMINE COMPOUND

Counter-Ion	Solvent	E max	λ max (nm)	λ fl (nm)	Stokes Shift (nm)	a
Cl^-	Ethanol	96,000	531	548	17	0.19
Cl^-	Ethanol	94,000	531	547	16	0.17
ClO_4^-	Ethanol	97,000	531	546	15	0.18
ClO_4^-	Methanol	102,000	528	546	18	0.18
BF_4	Ethanol	91,000	530	547	17	0.16
$^4B^-$	Ethanol	150,000	531	548	17	0.16
F^1	Ethanol	88,000	518	538	20	0.26
F^-	Methanol	96,000	520	539	19	0.25
F^-	Ethanol	89,000	518	538	20	0.28
F^-	Dioxane	1,240	537	556	19	0.015
F^-	DMSO	4,500	539	560	21	0.11
F^-	N-Methyl Formamide	108,000	526	547	21	0.21
F^-	DMF	4,400	535	553	18	0.012
F^-	Formamide	124,000	527	545	18	0.14

Compound	Solvent	E max	λ max (nm)	λ fl (nm)	Stokes Shift (nm)	a
RhBCl	Ethanol	96,000	544	561	17	0.08
RhB BF_4	Ethanol	84,000	544	562	18	0.085
Rh5GL BF_4	Ethanol	97,000	531	548	17	0.15

The absorption spectrum of Cresyl Violet was taken in ethanol at 10^{-4}M, 10^{-5}M and 10^{-6}M concentration and the concentration of the dye and the free base were calculated from the known extinction coefficients of the two species at their absorption maxima. From these data and the known value of the pKα of ethanol, the pKα of the dye was calculated to be 4.5. Some inconsistency was observed in this value at 10^{-6}M concentration. This was thought to be caused by unknown acid impurities in the ethanol.

The Cresyl Violet was found to photodegrade under ultraviolet illumination. This was manifested by a decrease in laser energy output with successive shots and an increase in lasing wavelength. The absorption spectrum showed a decrease in magnitude at the peak absorption wavelength and a slight increase in magnitude in the long wavelength tail. The dye recovered partially after a few hours with no illumination but failed to return to the original state. This is strong indication that two processes are occurring simultaneously, the main reversible process and a weaker irreversible process. The dye was subjected to continuous long-term ultraviolet illumination and total photobleaching occurred. An investigation of the photolysis was undertaken. The dye was made up in 10^{-5}M solution in solvents including ethanol, methanol, water, isopropanol, A-butanol, hexafluoroisopropanol, and ethylene glycol and was being irradiated with UV to determine rates of photobleaching. Also, attempts were made to isolate and identify the photoproducts. These attempts did not work so the photoproducts were not identified.

A sample of Cresyl Violet chloride was made into the nitrate salt. This was then made up into solutions of 2×10^{-5}M concentration in various solvents and monitored during irradiation in a Rayonet reactor with light at 3000A wavelength. The half lives of the various solutions are shown in Table 22.

The photodegradation proceeded with an exponential relationship only for solutions having H_2O, D_2O and t-butanol as solvents. This exponential relationship indicates a one-step process involved in the degradation. The other solvent solutions showed non-exponential degradation indicating two or more processes contributing.

A solution of the dye in isopropanol with one drop of acetone added showed very fast degradation, indicating that the acetone was acting as a sensitizer in the process. This would explain the non-exponential degradation in the isopropanol since acetone is a photoproduct of the solvent; that is, as the dye degrades, a sensitizer for the degradation is being formed and thereby accelerating the degradation process. Similar processes are thought to occur in the other solvents which exhibit non-exponential degradation.

TABLE 22

PHOTODEGRADATION HALF-LIVES OF VARIOUS SOLUTIONS OF CRESYL VIOLET NITRATE

Solvent	Half-Life
isopropanol	13 minutes
ethylene glycol	18 minutes
ethanol	37 minutes
t-butanol	11 minutes
H_2O	500 minutes
hexafluoroisopropanol	505 minutes
D_2O	450 minutes
methanol	175 minutes
acetone	90 minutes
hexafluoroacetone	115 minutes

An anion effect was noted in the lasing efficiency of Cresyl Violet with the nitrate and the acetate being more efficient than in the chloride, perchlorate, and the fluoride, but the consistency of this effect is not good. For example, the data scatter among different samples of the acetate overlaps the data scatter among chlorides. This would indicate that the effect may be due to sample purity and not anion effects. Differences in purity between samples of different anions arise from the fact that variation in solubility and crystalline structure cause the purification of the dye with different anions to proceed with varying degrees of efficiency. Alternate methods of purification were tried to attempt to determine if the purity is the cause of the apparent anion effect. No conclusive results were obtained from these experiments since the absolute purity of the dye could not be determined to the required accuracy.

Rhodamine 6G was combined with nitrate, fluoride, chloride, sulfate, fluoborate, and perchlorate and again with this compound an apparent anion effect was noted. An investigation paralleling that for Cresyl Violet was done for this compound. The fluorescent lifetime for Rhodamine 6G, as determined with a TRW Nanosecond Decay Time Fluorometer, was found to be $6.4 \pm .2$ nanoseconds with no detectable variations due to different anions. However, in the end, results of this experiment were inconclusive, since the purity of the dyes was not known to sufficient accuracy to draw valid conclusions.

A concentration effect on the observed fluorescent lifetime was seen for Rhodamine 6G on the TRW Decay-Time fluorometer. This is attributed to self-absorption and subsequent re-emission of the fluorescent radiation. This effect was found to be exponentially related to the observed fluorescence maximum wavelength, as measured on the Aminco-Bowman Spectrophotofluorometer, in the concentration region where collisional deactivation can be neglected. At concentrations greater than about $10^{-3}\underline{M}$, the collisional deactivation quenches the fluorescence and gives rise to non-exponential behavior in the above mentioned process.

Calibration of the Aminco-Bowman Spectrophotofluorometer was accomplished. The excitation monochromator and xenon excitation lamp were calibrated using front face fluorescence at 630 nm from Rhodamine B Cl at high concentration ($\sim 10^{-1}\underline{M}$) in ethylene glycol and running in both ratio and manual modes. The calibration of the emission monochromator was done first by using a Ludox scatterer placed in the standard 90° fluorescence cell holder, stepping the excitation monochromator through the spectrum and scanning at each step with the emission monochromator. A 200 watt quartz iodide lamp was then used by setting it up to reflect at 45° from the freshly cleaned surface of a magnesium carbonate crystal into the emission monochromator. A spectral scan was then run with the photomultiplier voltage at 270V and a 0.1 mm slit in place. The second technique was judged to be the more accurate, so this was the calibration curve used.

The relative quantum yields of fluorescence for Fluorescein Disodium salt, Rhodamine 6G nitrate and Rhodamine B chloride were determined three times. The fluorescein was from Eastman, the Rhodamine B was from Matheson, Coleman and Bell and was recrystallized from ethanol-ether (~1:2) and the Rhodamine 6G nitrate was made from Rhodamine 6G chloride (also Matheson, Coleman and Bell) by ion exchange in aqueous solution and recrystallized from ethanol-ether (~1:1). In all three determinations, the fluorescein was assumed to have a fluorescence quantum efficiency of 0.90. In the third determination, all samples were again recrystallized from ethanol-ether (~1:2) and dried at 100°C under vacuum for three hours. The results of the three determinations are shown in Table 23.

The value for Rhodamine $6GNO_3$ is reasonably close to the literature values (0.75-0.85) while the value for Rhodamine BCl is low (0.69-0.72). This low value may be due to impurities or to possible inaccuracies caused by the low red response of the instrument.

The Aminco-Bowman Spectrophotofluorometer was refitted with a photomultiplier with S-1 response and set up for liquid nitrogen cooling of the detector.

A sample of Quinine sulfate (Matheson, Coleman and Bell) was purified by three recrystallizations from hot water and a sample of 7-hydroxy-coumarin was column chromatographed and recrystallized from hot methanol-water (~1:30) in preparation for use as blue fluorescing quantum yield standards.

The Aminco-Bowman Spectrophotofluorometer was calibrated with the S-1 photomultiplier tube using a quartz iodide standard lamp. Figure 20 shows the relative response curve obtained.

Several compounds were purified as follows for fluorescence quantum yield standards:

1. Rhodamine B Cl (MCB) and Rhodamine 6G NO_3 (prepared in house)

One gram of each was dissolved in 100 ml ethanol and ether added slowly to recrystallize the dye. The crystals were filtered off and dried under vacuum at 100°C. They were then packaged in light-tight containers (RH-49-1 and RH-49-2 respectively).

2. Fluorescein (EKO)

RH-49-3: One gram was taken up in 50 ml ethanol and 5-6 volumes of acetone added. A powdery precipitate was filtered off and dried under vacuum at 100°C. This was put into a light-tight container. The powder was extremely hygroscopic and quickly formed a green gummy mass.

TABLE 23

RELATIVE QUANTUM YIELDS

Case	Compound	Conc. (M)	Quantum Eff.	Solvent
I	Fluorescein	2.00×10^{-7}	0.90	0.1 N NaOH
I	R6G NO_3	0.99×10^{-7}	0.70	etOH
I	Rh B Cl	1.63×10^{-7}	0.44	etOH
II	Fluorescein	2.00×10^{-6}	0.90	0.1 N NaOH
II	R6G NO_3	1.60×10^{-6}	0.83	etOH
II	RhB Cl	1.31×10^{-6}	0.59	etOH
III	Fluorescein	2.30×10^{-6}	0.90	0.1 N NaOH
III	R6G NO_3	1.93×10^{-6}	0.72	etOH
III	Rh B Cl	1.36×10^{-6}	0.48	etOH

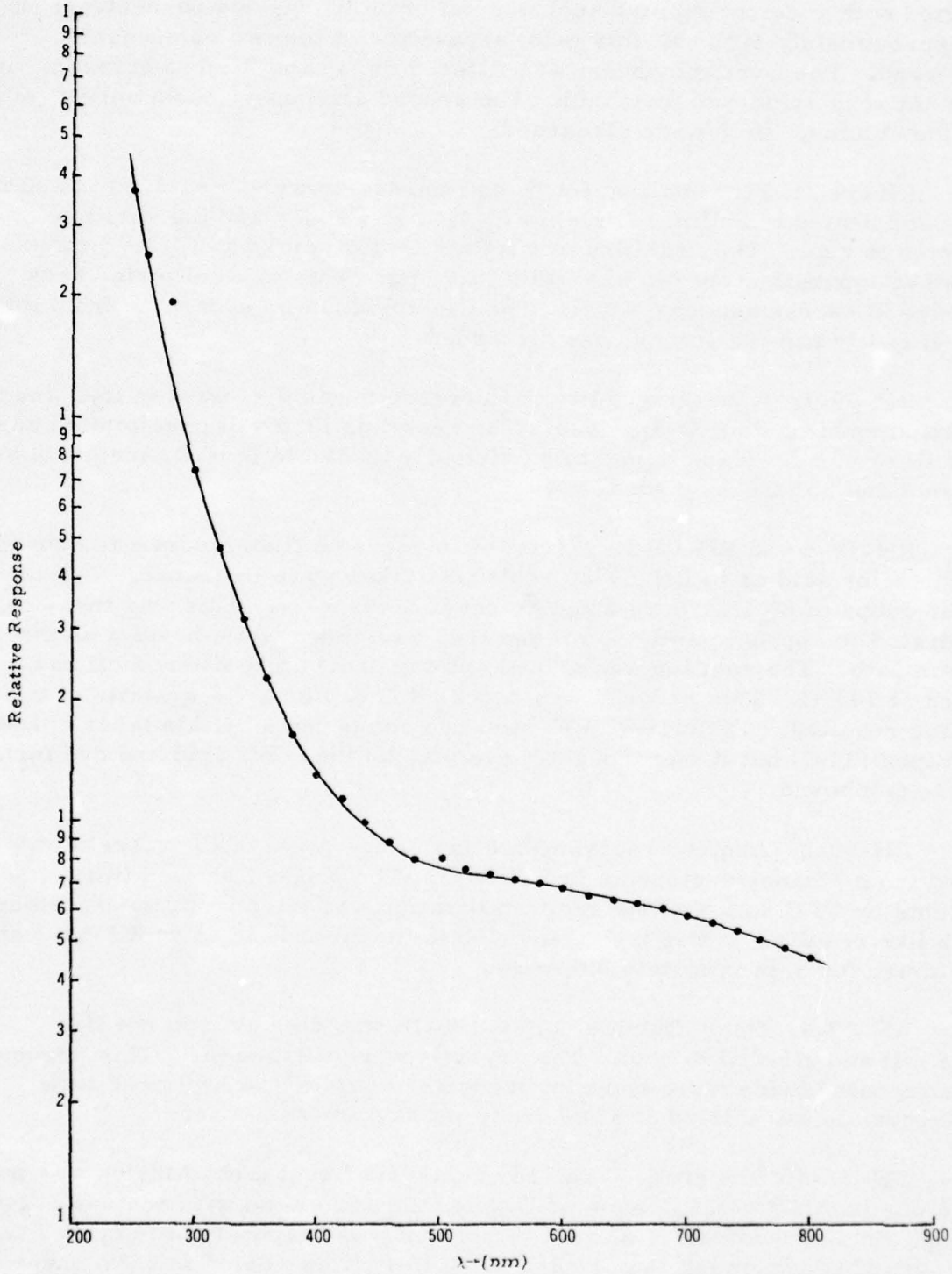


Figure 20. Relative Response Curve Aminco-Bowman Spectrophotofluorometer

RH-59-1: Two-hundred and fifty (250) mg were put on an activity 2 column of approximately 12 inches in solution with methanol. Elution was started with acetone and methanol was put on in increasing percentages up to approximately 50%. At this point separation of the two components occurred. The first component was filtered and evaporated to dryness. It was not very soluble in methanol. The second component could not be gotten off the column. Both were discarded.

RH-59-2: Five hundred (500) mg fluorescein were dissolved in 200 ml H_2O and heated to boiling. Five ml 6N HCl was added and the solution allowed to cool. The resulting precipitate (color acid) was filtered off and dried at approximately 140°C yielding 150 mg. This was converted back to the dye in excess aqueous NaOH. The dye could not be separated from the NaOH easily and the sample was discarded.

RH-59-3: A small quantity of fluorescein was dissolved in H_2O and a small amount of $Pb(NO_3)_2$ added. The resulting lead salt precipitated and was filtered off. It was found to be virtually insoluble in H_2O, methanol and ethanol and so was discarded.

RH-59-5 and RH-60-1: A total of four grams fluorescein was converted to the color acid as in RH-59-2. This was taken up in methanol. Two to three drops of 6N HCl were added to get it to dissolve. This was then concentrated to approximately 40 ml and H_2O was added while heating on the steam bath. The solution was cooled and the precipitate filtered off and dried at 140°C. This process was repeated once more. A quantity of two grams resulted. The material showed two components by thin layer chromatography (TLC) but it was thought these may be the color acid and dye forms of the compound.

RH-60-2: Another recrystallization of one gram of fluorescein was tried from ethanol/acetone as in RH-49-3. The product showed two components by TLC so a similar recrystallization was tried from H_2O/acetone with like results. It was then converted to the color acid as in RH-59-2 and air-dried for approximately one week.

RH-57-1: One g Quinine sulfate (MCB) was dissolved in hot H_2O (125 ml) and allowed to cool. The crystals were filtered off. This process was repeated twice more reducing the water volume by 25 ml each time. The crystals were dried at 55°C under vacuum for 24 hours.

RH-57-2: One gram 7-hydroxy coumarin (tech) from Aldrich was put on a one inch diameter column 12 inches long and eluted with acetone. Two components separated. The first component was evaporated to dryness and recrystallized from hot methanol/H_2O (1:30). It was dried at 55°C under vacuum for 24 hours. The second component would not come off the column.

RH-59-4; One-half gram 3-aminophthalimide (EKO) was recrystallized from 50 ml hot ethanol three times and dried at 55°C under vacuum for three hours yielding 285 mg.

RH-69-1: One gram of Rhodamine 6G Cl (EKO) was recrystallized from ethanol/ether (1:10) twice and (1:5) once. The crystals were dried at 55°C under vacuum yielding one-half gram.

RH-69-2: Twenty grams Pyrene (MCB) were recrystallized three times from 50 ml hot toluene; 5.5 grams resulted. The mother liquor was evaporated to dryness and the residue saved.

RH-69-3: One gram 4-dimethylamino-4'-nitrosostilbene was recrystallized from 100 ml hot benzene yielding 600 mg.

Approximately 800 ml toluene was shaken with cold concentrated H_2SO_4, H_2O, 5% NaOH, H_2O successively and dried over Na_2SO_4. It was then distilled and placed in a clean bottle over molecular sieves.

The following determinations of fluorescence quantum yield (ϕ_f) were made on the Aminco-Bowman Spectrophotofluorometer (A = area under corrected spectrum, n = index of refraction):

Run I — Ratio photometer in manual mode, chopper on, sample slit 1.0 mm, PM slit 0.2 mm, PM at 100V (pot 898), sensitivity 0.3, S-5 PM tube.

RhBCl (RH-22-1) 1.63×10^{-7} M in ethanol, 500 nm ex $\longrightarrow An^2 = 0.561$

Fluorescein (EKO) 2.00×10^{-7} M in 0.1 N NaOH, 450 nm ex $\longrightarrow An^2 = 1.185$

R6GCl (RH-12-2) 0.99×10^{-7} M in ethanol, 500 nm ex $\longrightarrow An^2 = 0.922$

Run II — Ratio photometer in manual mode, chopper on, sample slit 1.0 mm, PM slit 0.5 mm, PM at 960V (pot 889), sensitivity 1.0, S-5 PM tube, 390 nm excitation.

RhBCl (RH-22-1) 1.31×10^{-6} M in ethanol $\longrightarrow An^2 = 0.706$

$R6GNO_3$ (RH-12-2) 1.60×10^{-6} M in ethanol $\longrightarrow An^2 = 1.013$

Fluorescein (EKO) 2.0×10^{-6} M in 0.1 N NaOH $\longrightarrow An^2 = 1.081$

Run III — Ratio photometer in manual mode, chopper on, sample slit 1.0 mm, PM slit 0.5 mm, PM at 900V (pot 886), S-5 PM tube, sensitivity 1.0, 395 nm excitation.

$R6GNO_3$ (RH-49-2) 1.93×10^{-6} M in ethanol ——→ $An^2 = 0.830$

RhBCl (RH-49-1) 1.36×10^{-6} M in ethanol ——→ $An^2 = 0.554$

Fluorescein (RH-49-3) 2.30×10^{-6} M in 0.1 N NaOH ——→ $An^2 = 1.035$

Run IV — Ratio photometer in manual mode, chopper off, sample slits; ex. 0.5 mm - em 1.0 mm, PM slit 2.0 mm, PM at 1450V (pot 929), S-1 PM tube, sensitivity 0.1, vernier 100, 375 nm excitation (except 250 nm for 6-hydroxy coumarin).

Quinine SO_4 (RH-57-1) 2.12×10^{-6} M in 0.1 N H_2SO_4 ——→ $An^2 = 1.552$

RhBCl (RH-49-1) 1.50×10^{-6} M in ethanol ——→ $An^2 = 2.246$

$R6GNO_3$ (RH-49-2) 1.55×10^{-6} M in ethanol ——→ $An^2 = 2.359$

Fluorescein (RH-49-3) 1.57×10^{-6} M in 0.1 N NaOH ——→ $An^2 = 1.900$

3-aminophthalimide (RH-59-4) 0.87×10^{-6} M in 0.1 N H_2SO_4 ——→ $An^2 = 1.020$

7-hydroxy coumarin (RH-57-2) 8.9×10^{-6} M in ethanol ——→ An^2 = *

Fluorescein color acid (RH-60-1) 1.53×10^{-6} M in 0.1 N NaOH ——→ $An^2 = 2.063$

*not calculated due to fluorescent impurity

Run V — 10-280 microphotometer, chopper off, sample slits; ex. 0.5 mm - em 1.0 mm, PM slit 2.0 mm, PM at 1500V (pot 755), sensitivity 0.1, vernier 50, S-1 PM tube, 330 nm excitation.

RhBCl (RH-49-1) 2.00×10^{-6} M in ethanol ——→ $An^2 = 2.200$

R6GCl (RH-69-1) 1.66×10^{-6} M in ethanol ——→ $An^2 = 1.382$

Run VI — 10-280 microphotometer, chopper off, sample slits; ex. 0.5 mm - em 1.0 mm, PM slit 2.0 mm, PM at 1500V (pot 754), sensitivity 0.1, vernier 50, 285 nm excitation.

7-diethylamino-4-methylcoumarin (MCB) 4.75×10^{-6} M in p-dioxane ——→ $An^2 = 1.419$

7-diethylamino-4-trifluoromethylcoumarin (in house by R.N. Steppel) 4.50×10^{-6} M in p-dioxane ——→ $An^2 = 1.328$

Run VII 10-280 microphotometer, chopper off, sample slits; ex. 0.5 mm - em 1.0 mm, PM slit 2.0 mm, PM at 1500V (pot 754), sensitivity 0.1, vernier 50, 330 nm or 290 nm excitation.

RhBCl (RH-49-1) 1.64×10^{-6} M in ethanol 330 nm ex ——→ $An^2 = 1.376$

Quinine SO_4 (RH-57-1) 1.62×10^{-6} M in 0.1 N NaOH 330 nm ex ——→ $An^2 = 1.919$

Quinine SO_4 (RH-57-1) 4.36×10^{-6} M in 0.1 N NaOH 290 nm ex ——→ $An^2 = 0.889$

4-dimethylamino-4'-nitrosostilbene (RH-69-3) conc unknown in toluene 330 nm ex ——→ $An^2 = 1.813$

Pyrene (RH-69-2) 2.69×10^{-6} M in toluene 290 nm ex ——→ $An^2 = 0.300$

Fluorescent yellow 3G (Hoechst) conc unknown in toluene 330 nm ex ——→ $An^2 = 2.672$

7-diethylamino-4-methylcoumarin (MCB) 3.06×10^{-6} M in ethanol 290 nm ex ——→ $An^2 = 1.402$

7-diethylamino-4-trifluoromethylcoumarin 4.36×10^{-6} M in ethanol 330 nm ex ——→ $An^2 = 0.459$*

*a fluorescent impurity was observed in this sample

Run VIII 10-280 microphotometer, chopper off, sample slits; ex 0.5 mm - em 1.0 mm, PM slit 2.0 mm, PM at 1500V (pot 754), sensitivity 0.1, vernier 50, 375 nm and 327 nm excitation.

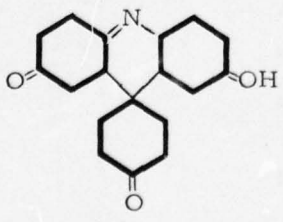
RhBCl (RH-49-1) 2.58×10^{-6} M in ethanol 375 nm ex ——→ $An^2 = 2.906$

RhBCl (RH-49-1) 2.58×10^{-6} M in ethanol 327 nm ex ——→ $An^2 = 1.826$

Quinine SO_4 (RH-57-1) 1.97×10^{-6} M in 0.1 N H_2SO_4 327 nm ex ——→ $An^2 = 2.261$

Carbozine* 2.59×10^{-6} M in methanol** 375 nm ex ——→ $An^2 = 0.970$

*



**2.29×10^{-4} M triethylamine added

The fluorescent quantum yields of these compounds are shown in Table 24.

TABLE 24

FLUORESCENT QUANTUM YIELDS

Compound	Solvent	Run	$\phi_f^{(1)}$	$\phi_f^{(2)}$	
RhBCl (RH-22-1)	Ethanol	I	70%	--	
RhBCl (RH-22-1)	Ethanol	II	70%	--	
RhBCl (RH-49-1)	Ethanol	III	70%	--	
RhBCl (RH-49-1)	Ethanol	IV	70%	75%	
RhBCl (RH-49-1)	Ethanol	V	70%	--	
RhBCl (RH-49-1)	Ethanol	VII	70%	37%	
RhBCl (RH-49-1)	Ethanol	VIII	70%	42%	
R6GNO$_3$ (RH-12-2)	Ethanol	I	115%	--	
R6GNO$_3$ (RH-12-2)	Ethanol	II	100%	--	
R6GNO$_3$ (RH-49-2)	Ethanol	III	105%	--	
R6GNO$_3$ (RH-49-2)	Ethanol	IV	74%	79%	
R6GCl (RH-69-1)	Ethanol	V	44%	--	
Fluorescein (EKO)	0.1N NaOH	I	148%	--	
Fluorescein (EKO)	0.1N NaOH	II	107%	--	
Fluorescein (RH-49-3)	0.1N NaOH	III	131%	--	
Fluorescein (RH-49-3)	0.1N NaOH	IV	59%	64%	
Fluorescein color acid (RH-20-1)	0.1N NaOH	IV	64%	69%	
Quinine SO$_4$ (RH-57-1)	0.1N H_2SO_4	IV	48%	52%	
Quinine SO$_4$ (RH-57-1)	0.1N H_2SO_4	VII	98%	52%	
Quinine SO$_4$ (RH-57-1)	0.1N H_2SO_4	VIII	87%	52%	
3-aminophthalimide (RH-59-4)	0.1N H_2SO_4	IV	32%	34%	
7-diethylamino-4-methyl-coumarin	p-dioxane	VI	155%*	90%**	83%$^+$
7-diethylamino-4-methyl-coumarin	Ethanol	VII	--	82%	

TABLE 24 (Concluded)

Compound	Solvent	Run	$\phi_f^{(1)}$	$\phi_f^{(2)}$	
7-diethylamino-4-trifluoro-methylcoumarin	p-dioxane	VI	145%*	84%**	78%+
7-diethylamino-4-trifluoro-methylcoumarin	Ethanol	VII	23%***	--	
4-dimethylamino-4'-nitroso-stilbene (RH-69-3)	Toluene	VII	92%	49%	
Pyrene (RH-69-2)	Toluene	VII	--	18%	
Fluorescent Yellow 3G (Hoechst)	Toluene	VII	136%	72%	
Carbozine	methanol / triethylamine	VIII	23%	--	

$\phi_f^{(1)}$ - assumes 70% for RhBCl

$\phi_f^{(2)}$ - assumes 52% for Quinine SO_4

* - based on RhBCl in Run VII

** - based on Quinine SO_4 290 Ex. in Run VII

*** - this sample had a fluorescent impurity

\+ - based on Quinine SO_4 330 Ex. in Run VII

NOTE: These excitation wavelength corrections taken from front face fluorescence data described in next experiment.

The Aminco-Bowman Spectrophotofluorometer was set up for front face fluorescence with the 10-280 microphotometer PM at 1500V (pot 754), sensitivity 0.1, vernier 50, sample slits; ex 0.5 mm - em 3.0 mm, PM slit 3.0 mm, emission monochromator at 800 nm, S-1 PM tube. The lamp was run for three hours to reach equilibrium. A 5×10^{-7}M solution of RhBCl (RH-07-1A) in ethylene glycol was placed in the cell holder and the excitation spectrum was scanned. At 400 nm the meter pegged due to second order light so that position was rescanned at sensitivity 1.0, vernier 20 into 700 nm emission. The resulting data is the output intensity of the lamp/monochromator combination in photons/λ.

The Aminco-Bowman was set up for phosphorescence and Cresyl Violet, Nile Blue and Oxazine were run at 10^{-4} and 10^{-5}M in EPA. No phosphorescence was observed even at maximum sensitivity and 5 mm slits. Benzophenone was added and delayed fluorescence and possibly some phosphorescence were observed in Nile Blue and Cresyl Violet. The results were marginal.

Solutions of R6GCl, Kiton Red S, and RhBCl at approximately 10^{-4}M in ethanol/methanol (4:1) were run. No phosphorescence was observed for Kiton Red S and only marginal signals (very slightly above noise level) were noted for R6GCl and RhBCl. Cresyl Violet was run in a brominated solvent and again no signal was detected. R6GCl (RH-69-1), RhBCl (RH-49-1), Kiton Red S (from R.N. Steppel) and Eosin Y (MCB) were run in 9:1 ethanol/methanol with 0.9M bromobenzene. Eosin Y gave a fairly strong signal compared with the other three compounds (about a factor of 50 or better) which were again marginal. All were run at 10^{-4}M except Kiton Red S which was run at 10^{-3}M. Cresyl Violet NO_3 (RH-13-1) was tried in this solvent system but again produced no detectable signal.

An Aminco photomultiplier tube holder was fitted to the Spex spectrometer and the S-1 end-on tube placed in it. The Aminco 10-280 microphotometer was connected and trial spectra of fluorescence from Nile Blue A and Carbozine were run. The quartz iodide standard lamp was then set up to illuminate the entrance slit of the Spex. The slits set at 500μ and the photomultiplier tube voltage at 600V. A scan was made from 200 nm to 1500 nm. To prevent second order diffraction effects from the grating showing on the curve obtained a 556 nm cut off filter was inserted in front of the entrance slit at 600 nm in the run. This was changed to a 745 nm cut off filter at 950 nm and to a 921 nm cut off filter at 1325 nm. The calibration curve obtained is shown in Figure 21.

The American Optical microscope light was collimated through a Bausch & Lomb quartz condenser lens system, passed through a 100 A band pass filter centered at 3830 A and focused on a sample cell in front of the entrance slit of the Spex. With this arrangement and using the 10-280

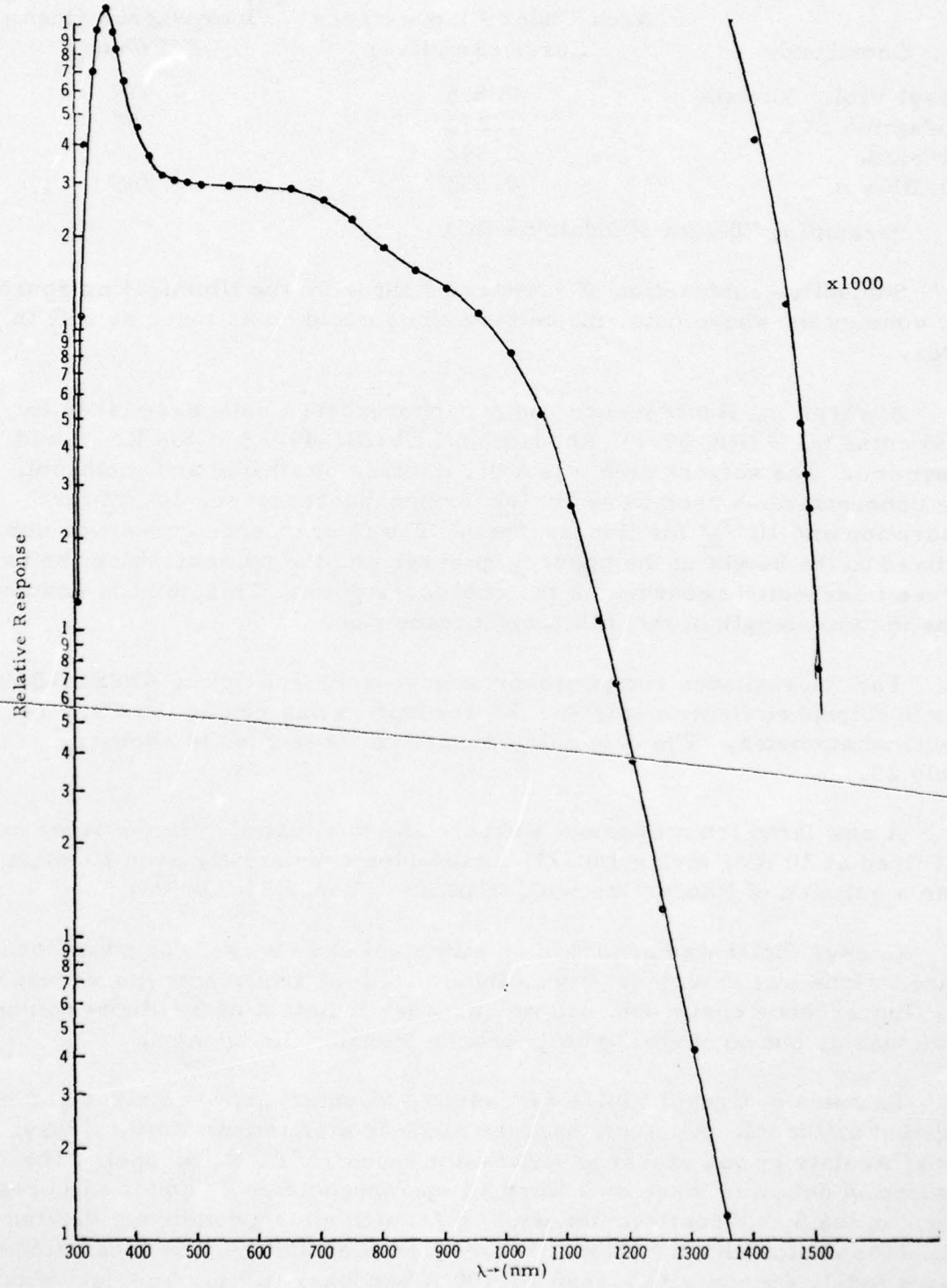


Figure 21. Calibration Curve Modified Spex Spectrometer

microphotometer with the S-1 PM tube at 1600V and the Spex slits at 3 mm, the following fluorescence data at 90° incidence was obtained:

Compound	Area Under Fluorescence Curve (Relative)	Fluorescence Quantum Efficiency*
Cresyl Violet Acetate	0.856	47%
Rhodamine BCl	1.273	70%
Carbazine	0.592	33%
Nile Blue A	0.552	30%

*assuming 70% for Rhodamine BCl

Subjective subtraction of scattered light from the illuminating source was done on the above data, hence the values could be as much as 25% in error.

Absorption, fluorescence and phosphorescence data were taken for Rhodamine 6GCl (RH-69-1), Rhodamine BCl (RH-49-1), Kiton Red S and Rosamine. The solvent used was a 9:1 mixture of ethanol and methanol. The concentrations used were $10^{-3}\underline{M}$ for phosphorescence, $10^{-5}\underline{M}$ for absorption and $10^{-7}\underline{M}$ for fluorescence. The fluorescence curve was normalized to the height of the absorption curve and the point at which the two curves intersected recorded as the crossover point. This point is assumed to be the wavelength of the 0→0 singlet transition.

The fluorescence and phosphorescence were run on the Aminco-Bowman Spectrophotofluorometer and the absorption was run on the Cary 14 Spectrophotometer. The data calculated from these runs is shown in Table 25.

A new lamp from Phase-R Corporation was installed in the laser and test fired at 20 KV, giving 160-175 millijoules consistently over 20 shots from a solution of Rhodamine 6GCl in ethanol (conc. $5 \times 10^{-5}\underline{M}$).

Cresyl Violet was adsorbed on silica gel and checked for phosphorescence. None was detected. It was then tested for front face fluorescence. The fluorescence curve obtained was broader than that of the fluorescence in methanol, but no obvious phosphoresce signal could be seen.

Samples of Cresyl Violet with various counter-ion were dissolved in distilled methanol. All samples were made from Eastman Kodak Cresyl Violet Acetate by ion exchange reaction in house by R. N. Steppel. The absorption data was taken on a Cary 14 spectrophotometer and the fluorescence on the Spex spectrometer with an Aminco microphotometer driving an RCA 7102 photomultiplier tube. Fluorescence excitation was done using a quartz iodide source with a 5650 A, 100 A bandpass filter. The data obtained is shown in Table 26.

TABLE 25

DATA FROM FLUORESCENCE, PHOSPHORESCENCE AND ABSORPTION RUNS

Compound	$\bar{\nu}_{max}$ (abs)	$\bar{\nu}_{max}$ (fl)	$\Delta\bar{\nu}_S$	E_S (cm^{-1})	E_T (cm^{-1})	ΔE_{ST} (cm^{-1})
Rhodamine 6GCl	18850	18051	799	18484	15208	3276
Rhodamine BCl (acid)	18051	17301	750	17683	14795	2888
Rhodamine BCl (base)	18365	17271	1094	17825	15228	2597
Kiton Red S	18002	17331	671	17699	14618	3081
Rosamine	18100	17331	769	17746	14755	2991

where $\bar{\nu}_{max}$ (abs) is the wave number of the absorption maximum

$\bar{\nu}_{max}$ (fl) is the wave number of the fluorescence maximum

$\Delta\bar{\nu}_S$ is the Stokes Shift (= $\bar{\nu}_{max}$ (abs) - $\bar{\nu}_{max}$ (fl))

E_S is the energy of the 0→0 singlet transition

E_T is the energy of the 0→0 triplet transition (= $\bar{\nu}_{max}$ (phos) + $\Delta\bar{\nu}_S$)

and ΔE_{ST} is the energy difference between the singlet and triplet levels (= E_S - E_T)

TABLE 26

CRESYL VIOLET IN METHANOL

Counter-Ion	Conc (absorb)	ε_{max}	λ_{max} (absorb) nm	Conc (fl)	ϕ_f *
OA_c	2.12×10^{-5}	57,500	595	4.24×10^{-7}	.96
NO_3	2.06×10^{-5}	69,500	595	3.52×10^{-7}	1.00
BF_4	2.30×10^{-5}	67,500	595	3.61×10^{-7}	.90
Cl	2.08×10^{-5}	61,500	595	3.97×10^{-7}	.98
ClO_4	2.04×10^{-5}	69,000	595	3.55×10^{-7}	.98

* ϕ_f is a relative fluorescence quantum yield assuming 1.00 for the NO_3

Rhodamine 6GCl was made up in various concentrations in ethanol and put in the laser. At each concentration, a series of 10 shots each was taken at 15 KV, 16.5 KV, 18 KV, 19.5 KV, 21 KV, and 22.5 KV input voltages. Table 27 shows the results in % efficiency out of the laser. $R_1R_2 = 0.35$ at 595 nm. Figure 22 shows the results graphically.

A solution of Cresyl Violet ClO_4 was made up to 5×10^{-5} in distilled methanol and compared to Cresyl Violet ClO_4 at 5×10^{-5} plus Rhodamine 6GCl at 3×10^{-5}. Table 28 shows the results and Figure 23 shows them graphically.

Cresyl Violet NO_3 was made up to 5×10^{-5}M in methanol. The grating was put in as a back reflector of the laser to tune the output wavelength. The energy out was determined with the EG&G 580 Radiometer and the wavelength was determined simultaneously by reflecting a small portion of the beam into the Spex spectrometer and recording it on Polaroid color film. The laser was fired at 18 KV at 30 second intervals. Table 29 and Figure 24 show the results. Each point is the average of five shots.

Cresyl Violet acetate, nitrate, chloride, perchlorate, and fluoborate (from R. N. Steppel) were dissolved in distilled methanol and run in the laser. Table 30 and Figure 25 show the results obtained. All solutions were made to have the same absorbance at 595 nm. All samples were purified in-house except $CVClO_4$ (EKO) which was used as received from Eastman Kodak.

A solution of Kiton Red S was checked for photo-degradation in the laser at the Avionics Lab. It was found to have a 1/2 life of 1750 shots at 18 KV in. Comparison of the absorption spectra of the initial solution and the final solution (4000 shots) showed the presence of an impurity which photodegrades at a slower rate than the Kiton Red S. This impurity has an absorption maximum at 522 nm.

(B) Organic Dye Synthesis

Some previously prepared dye materials with favorable lasing characteristics were again synthesized and purified to replenish the supply on hand for further laser experimentation.

Cresyl violet chloride (K&K) was purified by dissolving a 5.0g sample in water (150 ml) and adding 10% NaOH (5.0 ml) and filtering the resulting solids. These solids were suspended in water (150 ml) and 1N HCl (5.5 ml) was added with stirring. The solution was filtered, and the solvent was removed. The residue was recrystallized from methanol with the addition of small amounts of ether. A 1.5g sample of Cresyl Violet acetate (MCB) was treated in like manner.

TABLE 27

% EFFICIENCY OF LASING FOR RHODAMINE 6GCℓ

Concentration→ Energy in↓	3.3×10^{-5}	4.5×10^{-5}	5.5×10^{-5}	6.5×10^{-5}
33.75j	.056 ± .006	.022 ± .010	.074 ± .003	.071 ± .006
40.8j	.129 ± .002	.103 ± .007	.160 ± .010	.125 ± .002
48.6j	.191 ± .004	.206 ± .006	.224 ± .010	.183 ± .008
57j	.225 ± .007	.273 ± .009	.260 ± .005	.232 ± .007
66.2j	.233 ± .008	.310 ± .006	.284 ± .009	.278 ± .008
75.9j	.233 ± .004	.314 ± .008	.274 ± .007	.242 ± .007

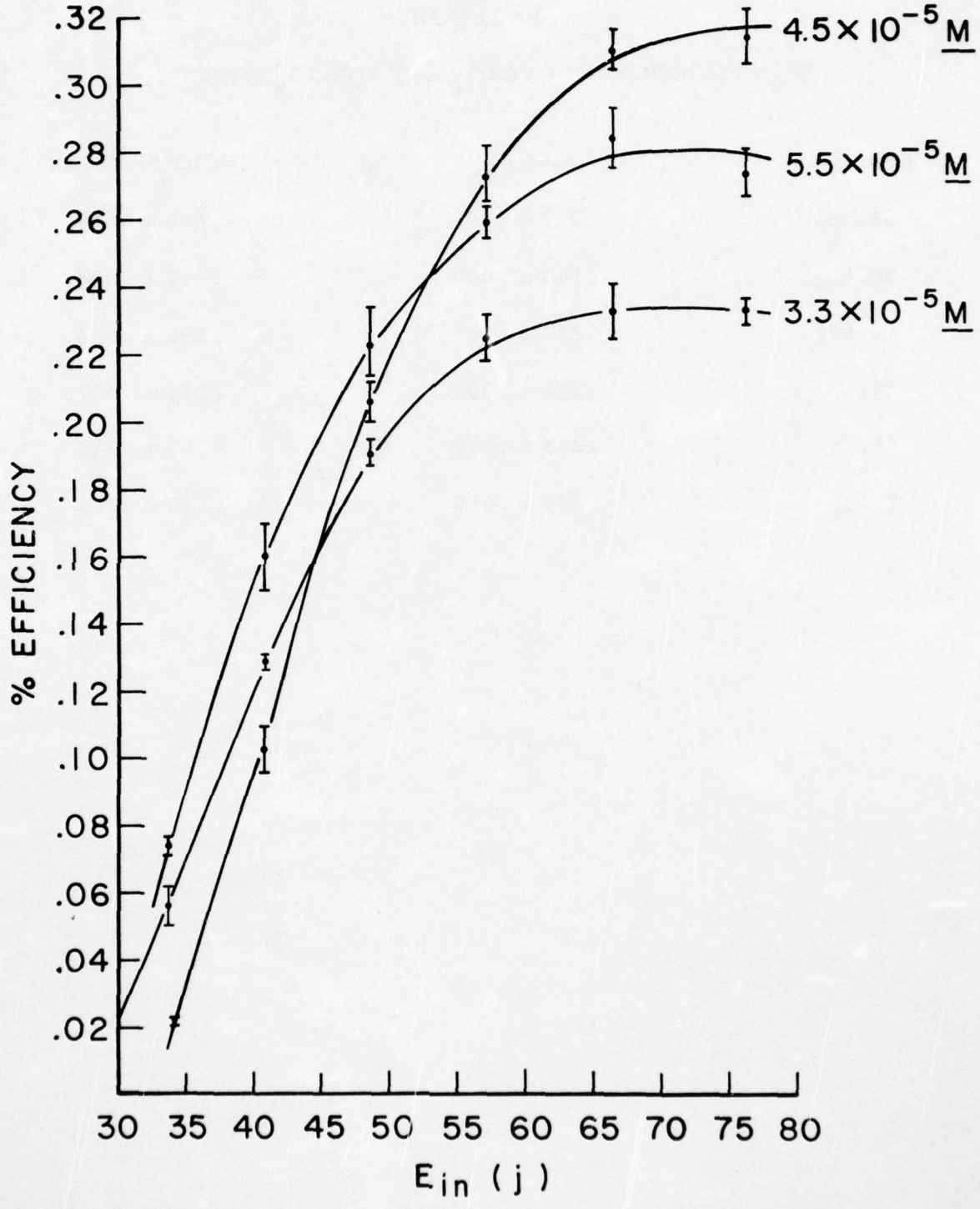


Figure 22. Lasing Efficiency of Rhodamine 6GCℓ at Various Concentrations in etOH

TABLE 28

% EFFICIENCY OF $CVC\ell O_4$ AND $CVC\ell O_4$ + R6GCℓ

Energy in	$CVClO_4$	$CVClO_4$ + R6GCl
33.75j	.079 ± .006	.059 ± .009
40.80j	.160 ± .009	.132 ± .004
48.60j	.227 ± .003	.193 ± .004
57j	.256 ± .003	.233 ± .007
66.2j	.293 ± .009	.257 ± .012
75.9j	.293 ± .011	.270 ± .013

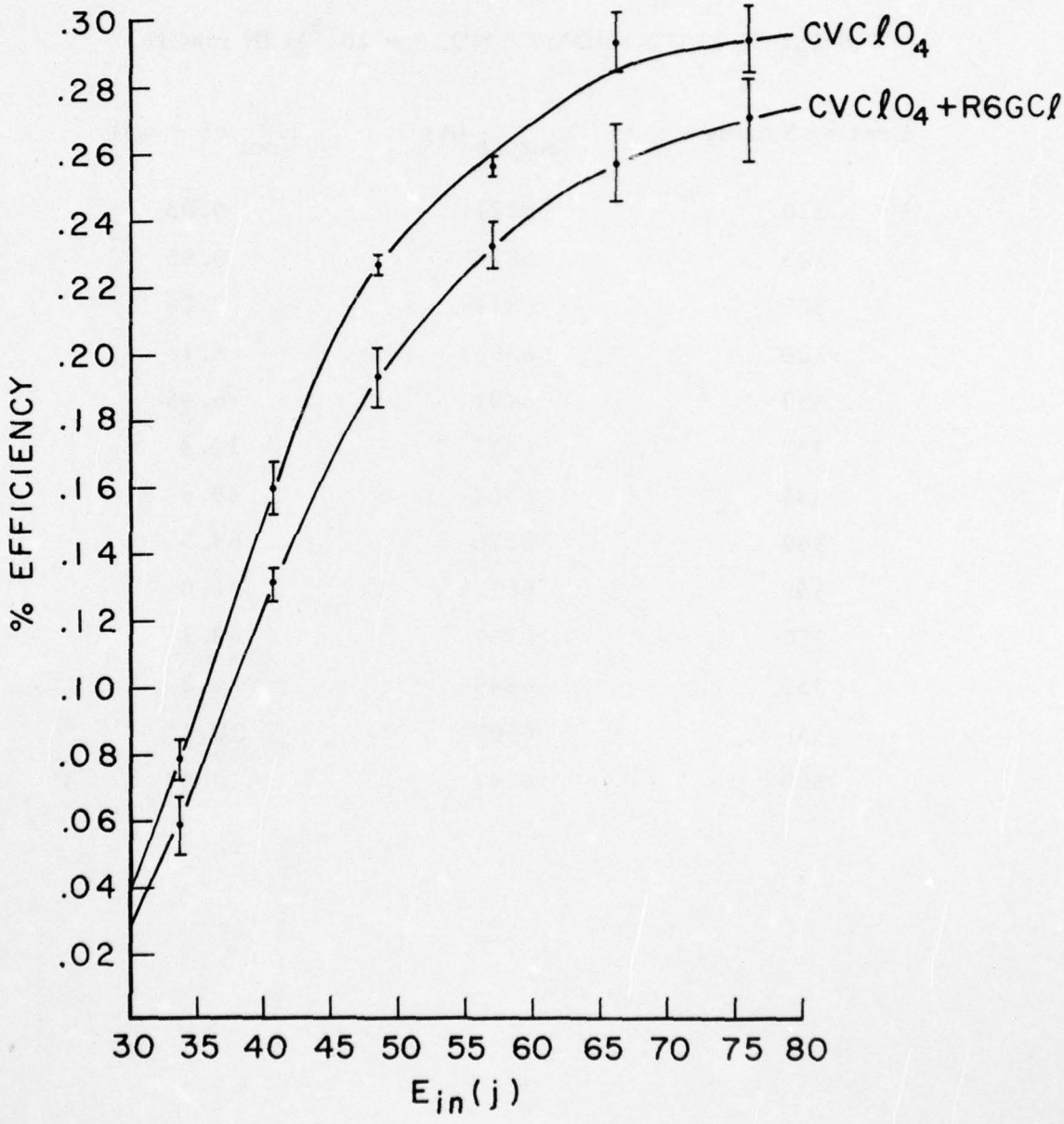


Figure 23. Lasing Efficiency of Cresyl Violet CℓO_4 and Cresyl Violet CℓO_4 + Rhodamine 6GCℓ

TABLE 29

TUNED OUTPUT FROM CVNO, 5×10^{-5} M IN meOH

Grating Setting	λ_{output} (A)	E_{out} ave (mj)
320	6221	0.03
323	6275	0.95
325	6311	2.26
328	6365	4.16
330	6401	6.45
332	6437	14.4
335	6484	45.6
340	6576	64.5
345	6671	58.0
350	6759	48.3
355	6845	29.2
358	6905	10.5
360	6941	0.57

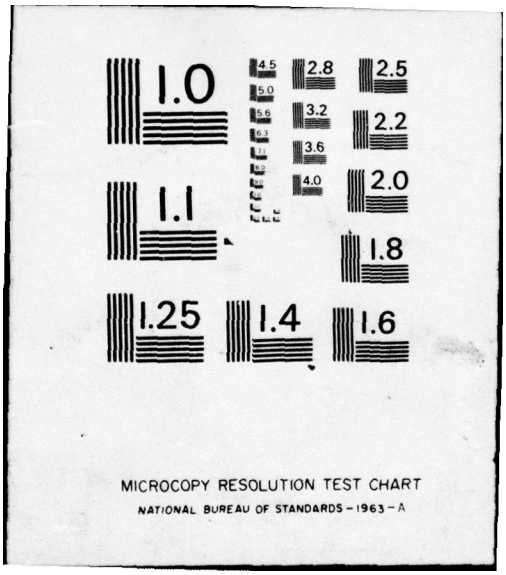
AD-A031 161 DAYTON UNIV OHIO RESEARCH INST F/G 20/12
RESEARCH AND DEVELOPMENT ON CHARACTERIZATION OF ELECTROMAGNETIC--ETC(U)
DEC 75 D EARLEY, P FRANKLIN, R HARRIS F33615-72-C-1666
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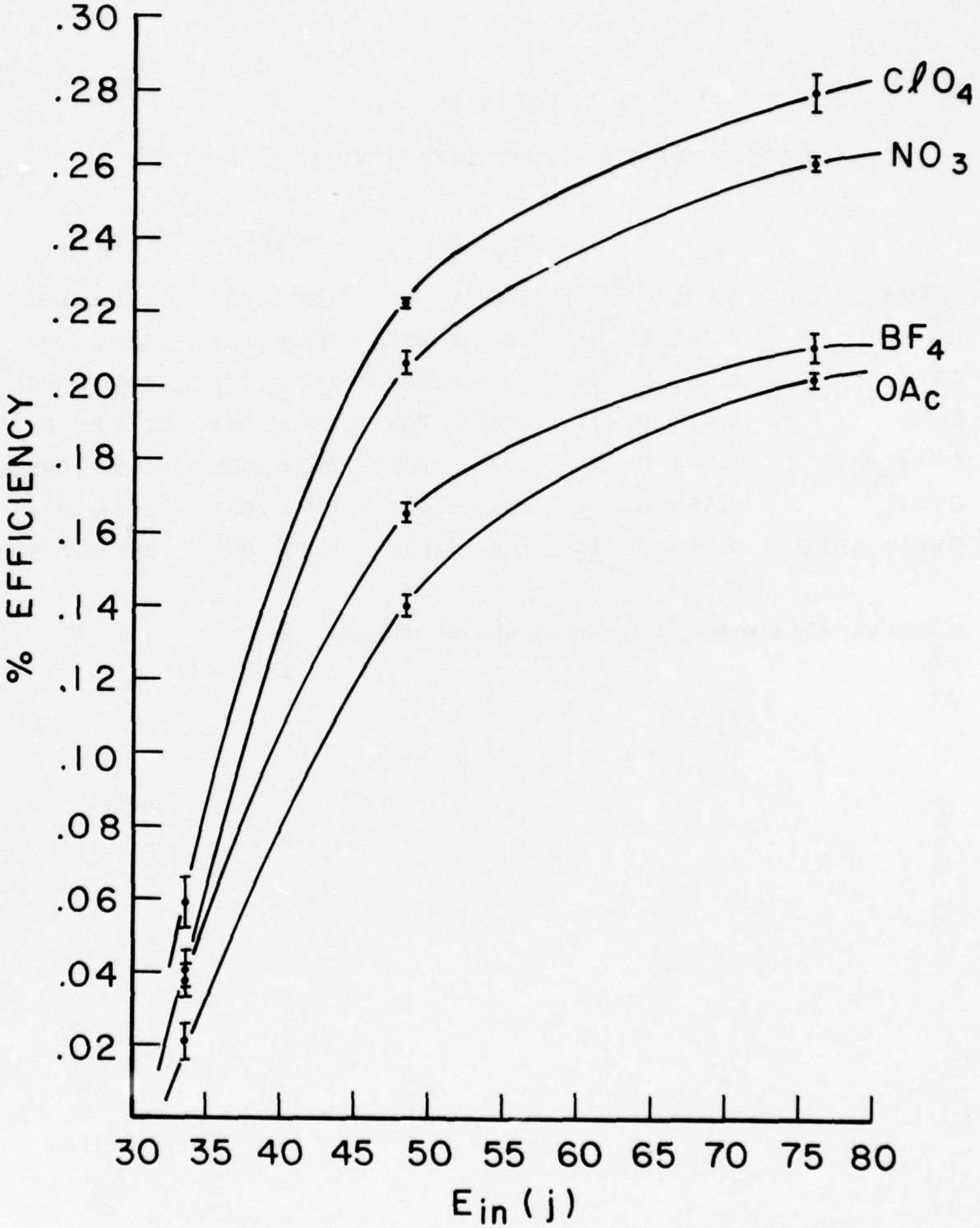


Figure 24. Lasing Efficiency of Cresyl Violet with Various Anions

TABLE 30

LASING EFFICIENCY OF CRESYL VIOLET (IN %)

		E_{in} = 33.75j	48.6j	66.2j
CV OA_c	5.0×10^{-5} M	.021 ± .005	.140 ± .003	.201 ± .002
CV NO_3	4.14×10^{-5} M	.041 ± .005	.206 ± .003	.260 ± .002
$CVClO_4$	4.16×10^{-5} M	.059 ± .007	.222 ± .001	.279 ± .005
CVCl	4.67×10^{-5} M	.057 ± .006	.200 ± .003	.278 ± .003
$CVBF_4$*	4.26×10^{-5} M	.039 ± .005	.200 ± .005	.254 ± .003
$CVBF_4$	4.35×10^{-5} M	.038 ± .004	.165 ± .003	.210 ± .004
$CVClO_4$ (EKO)	4.16×10^{-5} M	.054 ± .005	.198 ± .003	.258 ± .003

* This sample showed 3% ash by elemental analysis

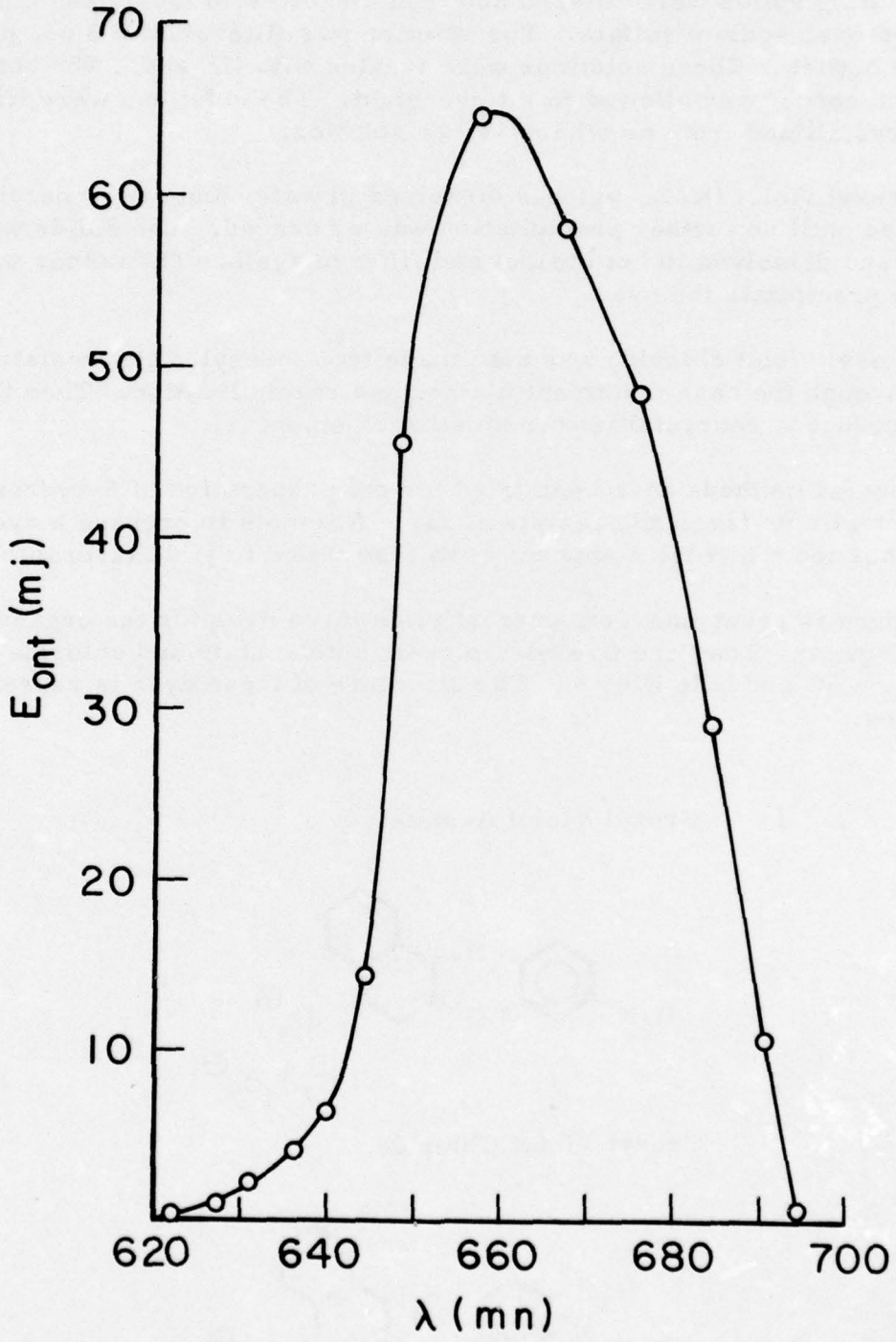


Figure 25. Tuned Output from Cresyl Violet NO_3

Rhodamine 6G (3g, Kodak) was dissolved in 300 ml of hot water, and then filtered and the filtrate was washed with additional hot water. To this 10% NaOH was added until there was no evidence of increased precipitation. The resulting solids were filtered and then dissolved in methylene chloride and dried over sodium sulfate. The solution was filtered into 8 oz. polyethylene bottles. These solutions were treated with HF gas. The bottles were then capped and allowed to sit overnight. The solutions were filtered and recrystallized from an ethanol-ether solution.

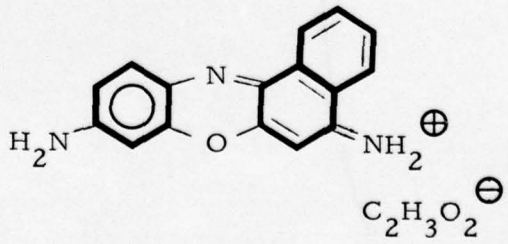
Cresyl violet (K&K, 6g) was dissolved in water and silver perchlorate was added until no further precipitation was evidenced. The solids were filtered and dissolved in hot ethanol and filtered again. Then ether was added to precipitate the dye.

Cresyl violet chloride was also made from cresyl violet acetate (MCB) (1.5g) through the base treatment method and reacidification. Then the crude product is recrystallized from ethanol-ether.

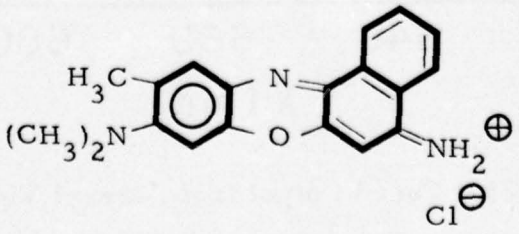
Several methods have been tried for the preparation of 8-hydroxyjulolidine but with no favorable results so far. Attempts to prepare a dye from B-naphthol and a nitroso compound have also failed to yield favorable results.

There is great interest, currently, in three dyes for the organic dye laser program. They are Cresyl Violet (in both acetate and chloride forms), Rhodamine 6G and Nile Blue A. The structure of these dyes is represented as follows:

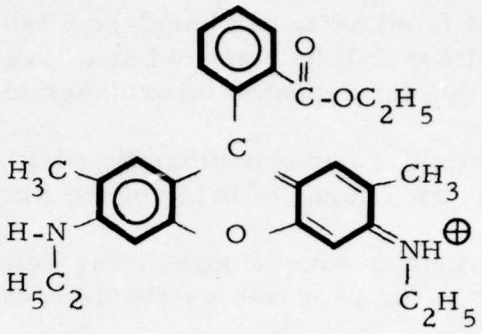
I Cresyl Violet Acetate



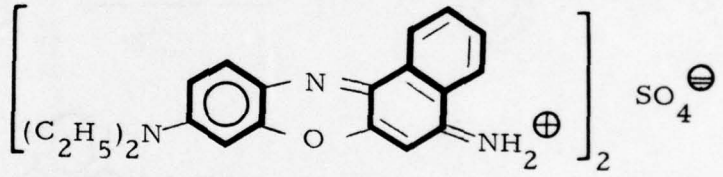
II Cresyl Violet Chloride



III Rhodamine 6G



IV Nile Blue A



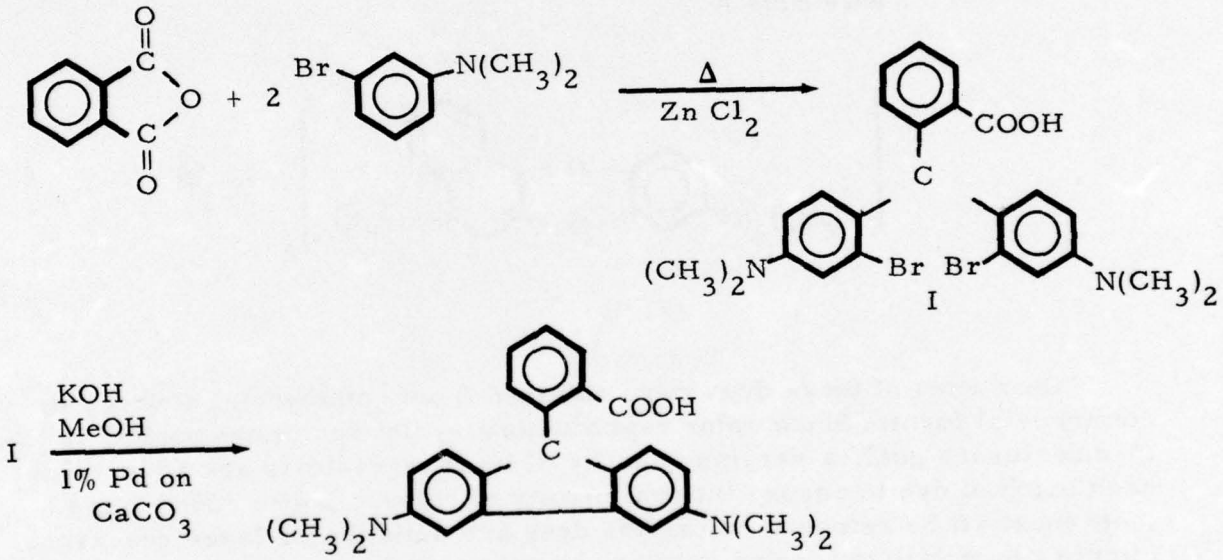
Quantities of these dyes were obtained from commercial sources in commercial form. Since color reproducibility, not analytical purity, is the manufacturers goal, a varying quantity of inert ingredients are added to each batch of dye to assure this uniformity of color. These added ingredients must all be removed before the dyes are suitable for laser research. Simple recrystallization and column chromatography techniques did not prove successful in removing the contaminates. Sublimation gave rather dubious results in the case of Cresyl Violet chloride. The Cresyl Violet chloride and the Rhodamine 6G were purified by a forced precipitation from ethanol solution with ether. The Cresyl Violet acetate was dissolved in distilled water and continuously extracted with toluene. The dye was then treated with the ethanol-ether procedure with fair success.

The purified dyes were then used in the preparation of new dyes by changing the counter-ion in order to determine the counter-ion's effect on solubility and laser output. In the case of the fluorides, perchlorates and fluoborates simple ion exchange reactions were run with the precipitation of silver chloride. In order to obtain the acetates, some fluorides and regenerated chlorides, the dyes were neutralized in an aqueous solution with sodium hydroxide to form the free base and then reacidified with the acid of the appropriate counter-ion.

The crude material thus obtained was purified until it reached a maximum molar extinction coefficient. Table 31 shows some of the compounds which have been prepared by these procedures along with maximum molar extinction coefficient e, peak absorption wavelength λmax (nm) and the solvent used. Now that familiarity has been established with the procedure, most of these reactions will be repeated on a larger scale to produce sufficient quantities of dye for repeated laser experiments.

Extensive work was performed on the NMR in determining the best solvents for and the structures of many of the Rhodamine G dyes.

3,6 - Bis (dimethylamino) fluorene was selected as good candidate material for lasing. The proposed synthesis route to this product is:



The N,N-dimethylamino-m-bromoaniline was prepared by refluxing m-bromoaniline and trimethyl phosphate according to the procedure of Billman J. Am. Chem. Soc., 64, 2977 (1942). This did not give a good yield so an alternate method using m-bromoaniline and dimethyl sulfate as proposed by Gilman J. Am. Chem. Soc., 62, 345 (1940).

When the phthalic anhydride condensation reaction was run using dimethylaniline, the corresponding product was obtained and yield was improved by extending the time of the reaction. However, the brominated aniline was so much less reactive that several attempts at varying the temperature and the duration of reaction yielded only a small quantity of the desired product which could not be isolated for complete identification product. If this yield cannot be improved, an alternate route will be attempted.

TABLE 31

SOME COUNTER-ION DERIVATIVES WHICH HAVE BEEN MADE IN THIS PROGRAM

Compound	λ max (nm)	e	Solvent
I $C_2H_3O^-$	602	44,800	Ethanol
I Cl^-	602	47,600	Ethanol
I ClO_4^-	602	60,100	Ethanol
II Cl^-	613	58,000	Ethanol
II F^-	613	--	--
II ClO_4^-	613	--	--
II $C_2H_3O_2^-$	613	--	--
III Cl	532	96,000	Ethanol
III F^-	518	89,000	Ethanol
III ClO_4^-	532	97,000	Ethanol
III BF_4	532	99,500	Ethanol
IV $SO_4^=$	627	64,000	Methanol
IV Cl^-	627	64,700	Methanol
IV ClO_4^-	627	68,000	Methanol

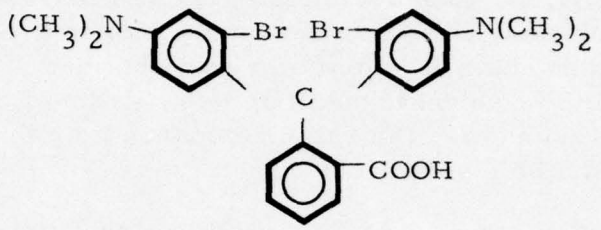
The rationale for this procedure is based on work done by Otto Fischer Annalen, 206, 83 (1880) with dimethylaniline and phthalic anhydride. Later work done by H. Limpricht Annalen, 300, 228 (1898) and A. Haller and A. Guyot Bull. Chem. Soc. de France, 25, 165 (1901) indicated a possibility of reacting equimolar quantities of phthalic anhydride and dimethylaniline to form the keto-acid which could subsequently be condensed with a second dimethylaniline molecule. This reaction was run on a 0.02 molar scale using unsubstituted dimethylaniline as an investigative procedure prior to following Fischer's method. However, due to the difficulty in obtaining pure N,N-dimethyl-m-bromoaniline, our supply was used at this time to investigate the direct condensation of two aniline molecules with the phthalic anhydride.

a. The synthesis of 4-methoxy-1-phenylbenzotriazole was successfully completed. A solution of 7 gms of anthranilic acid in 60 ml of acetone was added over a two hour period to a refluxing mixture of 0.05 moles of p-methoxyphenylazide and 0.058 moles of butyl nitrite in 200 ml of dichloromethane. The volatiles were stripped from the reaction mixture with an aspirator to leave a brown gum. The brown gum was dissolved in ethanol and recrystallized twice. Further purification was accomplished by dissolving the crystals in CCl_4 and chromatographing them through a silica gel column. A 70%-30% mixture of CCl_4 and chloroform was used on the column. After the initial solvent had eluted, the desired compound was next off the column. The solvent was evaporated and light orange-brown crystals were left. These crystals were recrystallized in benzene and petroleum ether. The compound was then oxidized with peracetic acid and allowed to reflux overnight. The one oxide benzotriazole was then changed to a two oxide by photochemical means. The photolyzed compound was verified by NMR spectroscopy.

b. The compound 2-nitrophenoxazine was successfully synthesized by starting with 10 gms of practical grade 2,4-dinitrochlorobenzene and 6 gms o-aminophenol. This mixture was heated to reflux with 50 ml of anhydrous ethanol. Next, 4 gms of anhydrous sodium acetate were added in small portions to the mixture. After cooling, the precipitate of the mixture of diphenylamine derivative and sodium chloride was filtered off and washed with dilute alcohol and water. The sodium salt of this compound was prepared by mixing 2,4-dinitro-2'-hydroxydiphenylamine with one equivalent of 1 N NaOH solution, grinding fine, and drying over NaOH in vacuum to constant weight. A 100 mg portion of the sodium salt was then heated to 100°C in 5 ml of DMSO in moisture-free atmosphere. After two hours, the solution was poured into 30 ml of ice water, which contained 60 mg of urea, and acidified with dilute H_2SO_4 to pH4. The red-brown precipitate which formed was filtered, washed with water, dried and chromatographed with benzene on silica gel. The nitrophenoxazine was isolated as the fast-running red-brown main zone and, after reduction in volume, was recrystallized

from benzene. The 2-nitrophenoxazine was acetylated by using 30 ml pyridine and 5 ml acetic anhydride. It was allowed to set overnight and then the mixture was poured on to one liter of ice and stirred until the ice melted. This was filtered and the filtrate allowed to dry.

Attempts to synthesize



by two methods were unsuccessful. The first method entailed preparing N,N-dimethyl-m-bromoaniline and condensing it with phthalic anhydride using $ZnCl_2$ as a catalyst. The second method used the same reactants with $AlCl_3$ as a catalyst. Both approaches gave very small yields of the desired product.

An alternate method for preparing the fluorine analogue of Rhodamine 6G was also tried by applying the procedure given in U.S. Patent #3,344,189 example 4 to crystal violet lactone and to malachite green lactone. Both reactions failed to yield the reported products.

So a new route attempted was to condense N,N-dimethylaniline and phthalic anhydride in CS_2 with an $AlCl_3$ catalyst to obtain the keto acid. This product was then heated with dimethylamino-m-acetanilide in acetic anhydride to form the intermediate which should yield the desired fluorene after it has been nitrosated and deazatized.

Attempts were made to isolate the colored products of the keto-acid and acetanilide condensation reactions. First, a small column (one inch dia.) was packed with silica gel to a height of six inches. Elution with $CHCl_3$ showed at least six colored components. The fastest moving fraction was isolated and verified by IR to be an unacetylated lactone. The next fraction contained four components (TLC) with the major one being the blue-green spot on the plate. The small column was repacked to a height of 12 inches and the same quantity of residue eluted with CH_2Cl_2 to see if better separation could be achieved. Again, the unacetylated lactone was isolated but the blue-colored band was not. The fraction contained three components (TLC) but it did solidify and an IR spectrum indicated two carbonyl absorptions at 1690 and 1780 cm^{-1}.

The remaining residue was placed in a two-inch diameter column, packed with silica gel, 24 inches high and eluted with CH_2Cl_2. Very poor separation was noted. It was supposed that this was due to the large sample size and uneven column packing. The colored components moved very slowly with CH_2Cl_2 so $CHCl_3$ was tried with no significant gain in separation or speed of the bands. Acetone was tried next with the result of a dark red band moving down with the supposed products. The first acetone fraction with the least amount of red component was taken up in CH_2Cl_2 and swirled in 100g silica gel and filtered. The resulting "short column" was washed first with 600 ml CH_2Cl_2, then 500 ml $CHCl_3$ and finally with 500 ml acetone. The three solutions were left to evaporate over a weekend. Instead of the desired solid product, a gummy tar was obtained. The aqueous reaction mixture, from the condensation step, was extracted with $CHCl_3$. TLC of the organic solution showed the same components as the residue except for the absence of the blue spot product.

It was decided to attempt to improve the yield of the condensation reaction by a micro-investigation of product formation. A properly proportioned mixture of reactants was prepared and thoroughly mixed. A series of melting point tubes were charged to about 3/8" with the reactant mixture and placed in an oil bath at 120°C. To each half of the tubes was added 1.5μl acetic anhydride and to each of the other half was added 10.0μl acetic anhydride to see the difference in the reaction between solvent quantities and catalytic quantities. It was found that more brown tar was produced when solvent quantities were used. After seven hours, the catalytic samples also showed evidence of tar formation, but there was still evidence of starting material as shown on the TLC plate.

A 0.02 molar scale reaction of phthalic anhydride and N,N-dimethylamino-m-acetanilide in CS_2 with $AlCl_3$ was run to see if this approach would give a neater reaction mixture. An evaluation of the rate study of this reaction showed that product was formed even in the first hour of reaction time. The difference between employing acetic anhydride in solvent or catalytic quantities was also apparent in the first hour and remained constant for the duration of the reaction. A brown tar was formed when a solvent quantity was used and showed extraneous spots under TLC investigation. The catalytic samples were neater but gave evidence that degradation began well before the starting materials could react completely. The formation of the lactone, which has been tentatively identified by mass spec as the deacetylated product, is a slow process which is first evidenced in the reaction mixture after the fourth hour. When allowed to stand, all reaction mixtures gave evidence of this component.

The original Friedel-Crafts reaction to form the keto-acid was attempted on a 0.02 molar scale using phthalic anhydride and N,N-dimethylamino-m-acetanilide in CS_2 with $AlCl_3$ as a catalyst. It appeared that the

$AlCl_3$ was not as active as it should be or that some water was present because the reaction was not vigorous. However, approximately 30 mg of solids were obtained with a melting point of 229-31°C, but showing only one low-frequency carbonyl absorption under IR. This product proved to be even more difficult to separate than the reaction product of the keto-acid and acetanilide, so the reaction was considered infeasible for our purposes.

The Friedel-Crafts reaction of N,N-dimethylaniline and phthalic anhydride was repeated on a 0.5 molar scale using CS_2 as the solvent and $AlCl_3$ as the catalyst. The acid solution of the CS_2 insoluble residue was allowed to stand over the weekend. Recrystallization produced 53.2 grams of product from the first batch of crystals and an additional 9.1 grams were obtained by a second recrystallization.

A 0.6 gram sample of the above keto-acid was ground in a mortar with 0.4 grams of acetanilide and placed in a flask with 0.2 ml acetic anhydride and heated to 120°C for five hours. Then, 15 ml absolute ethanol were added and the mixture refluxed for 15 minutes. The pot residue was mixed with approximately three grams of silica gel and the solvent evaporated. The remaining mixture was placed at the top of a 14-inch silica gel column (one inch dia.) and eluted with CH_2Cl_2. A trace component came off first and then a blue band. This material gave two carbonyl absorptions at 1700 and 1775 cm^{-1} under IR. On the basis of this, it was assumed that the pale yellow gel-like material was the product of interest, and 0.8 grams were obtained. This reaction was repeated on the same scale, and a 10-inch column was used because this gave sufficient separation, and 0.98 grams of product was obtained. This product was subsequently used for the attempted nitrosation. The reaction was repeated twice more and 4.2 grams of product were obtained.

The nitrosation of the 0.98 grams of product was carried out in a dried three-neck flask fitted with an additional funnel, a drying tube and a thermometer and a magnetic stirrer. The flask was charged with 3.2 ml acetic anhydride, 0.5 grams $KC_2H_3O_2$ and 0.2 grams P_2O_5. A mixture of 0.1 grams $NOCl_2$ in 5 ml acetic anhydride was added slowly to the reaction mixture which had been cooled to 8°C. This mixture was stirred for 30 minutes and then poured over ice. A gummy oil with some evidence of solids was produced. The water was decanted, and the residue dissolved in 25 ml cold $CHCl_3$. This solution was added to a flask containing $CHCl_3$ at 35°C and stirred for 30 minutes. TLC on silica gel using $CHCl_3$ gave two spots, neither of which corresponded to starting material. IR of the residue gave no evidence of acetyl of nitroso absorption. A preparative TLC plate was streaked with approximately half of the residue and eluted with $CHCl_3$. Several bands were evident. The orange band (second from the top) and the green band (supposedly the product) were scraped off and washed with $CHCl_3$ to obtain the components. Neither of these gave infrared absorption peaks, so it was concluded that the desired product did not form.

It was decided to obtain the fluorene derivatives by a route suggested by American Dyanamid so the following reactions were run. A mixture of 50.8 grams of 4,4'-bis(dimethylamino)diphenylmethane and 62.4 grams of Ag_2SO_4 was stirred in 600 ml conc. H_2SO_4 and 64.0 grams Br_2 were added slowly and the whole solution stirred for three hours, with the temperature maintained at 25°C with a water bath. The reaction mixture was then filtered through a bed of Celite in a C porosity sintered glass funnel. The resulting acid solution was neutralized with conc. NH_4OH. The solids produced were filtered out and dissolved in approximately 600 ml of boiling ethanol. The insoluble material, as well as the recrystallized solids, gave a melting point of 103-104°C and an IR spectrum corresponding to a pure sample of the desired product. A quantity of 61.0 grams of product was obtained. This reaction was repeated at half the scale and an additional 20.6 grams of product obtained.

The fluorene was prepared by mixing 51.5 grams of 4,4'-bis(dimethylamino)-2,2'-dibromodiphenylmethane into 500 ml of methanol and stirring, while adding 50 ml 10N KOH and 15 grams of 1% Pd on $CaCO_3$. The resulting mixture was stirred under reflux for six hours. The hot reaction mixture was filtered and the solids washed with approximately 50 ml hot methanol. The solution was cooled and filtered. The solids were dissolved in 300 ml boiling ethanol and allowed to stand over the weekend. The resulting white crystals (bluish tinge) had a melting point of 148-149°C and an IR spectrum almost exactly the same as a pure sample of the desired product. Yield was low, with only 3.0 grams being obtained.

Next, more of the 1% Pd on $CaCO_3$ was prepared by adding a hot aqueous solution of $CaCl_3$ (one mole) to a hot aqueous solution of $Na_2CO_3 \cdot H_2O$ (one mole). The resulting precipitate was filtered and washed with water. Then the solids were suspended in approximately one liter of H_2O. A solution of two grams $PdCl_2$ in 30 ml 1:5 HCl was heated until sample dissolution and almost neutralized with 5N NaOH and then added to the suspended solids with constant stirring. The mixture was then heated and stirred for two hours, until all the Pd was precipitated on the $CaCO_3$. The solids were filtered, washed with about 300 ml H_2O and then air dried.

The 3,6-bis(dimethylamino)fluorene was again prepared on a 0.08 mole scale. The reaction was treated as before, and again some white crystals were obtained from the ethanol solution. However, TLC on silica gel using $CHCl_3$ as an eluent gave evidence that the fluorene was present in the mother liquor, the methanol, and in the blue gum produced when the ethanol was evaporated. So the solutions were all evaporated and the solids filtered off and washed, first with H_2O then with acetic acid, and again with H_2O. This was an attempt to remove some of the impurities to facilitate recrystallization of the fluorene. However, only 5.1 grams were recovered.

The 3,6-bis(dimethylamino)fluorene was prepared by dissolving 2.0 grams of the fluorene in 100 ml of pyridine and adding 0.8 ml of Triton B. Air was bubbled through the solution for five hours. Then the solution was brought to boiling and H_2O added until precipitation began. The solution was cooled slowly and the resulting solids were filtered off with a yield of 1.3 grams. Upon the addition of more H_2O to the mother liquor, more solids were obtained. These were recrystallized from ethanol and an additional 1.0 grams were obtained.

This reaction was repeated with 5.0 grams of the fluorene, and TLC was used to follow the reaction. After five hours, there was no evidence of starting material remaining. The reaction mixture was treated as before with a yield of 3.4 grams with evidence of more product still in the liquids.

The synthesis of 4,4'-bis(dimethylamino)-2,2'-dibromophenylmethane was repeated twice on a 0.2 mole scale yielding 111.0 grams. Part (62.2 grams) of this product was used in a repeat of the synthesis of 3,6-bis (dimethylamino)fluorene. After filtering the methanol solution, the solids were washed with $CHCl_3$ and 45.3 grams of the starting dibromide were recovered. No fluorene has as yet been isolated from this reaction, although there is evidence of its presence on TLC. Some methane base and the bromo compound were recovered from the methanol and ethanol, but even water wash and acetic acid treatment did not facilitate recrystallization of the product. The starting materials were reacted again yielding 27.8 grams of solids but no product was isolated.

More methane base was prepared by stirring 121.0 grams of N,N-dimethylaniline at 30-35°C into a solution of 600 ml of 25% ethanol, 45 ml of 36% formaldehyde and 2.0 ml of concentrated HCl over a weekend. There was no evidence of reaction after three days, so the temperature was raised to reflux and the reaction continued overnight. The liquid had a pale purple cast and, upon cooling, produced grey solids which were filtered off. Since attempts to remove unreacted aniline by melting the solids under water failed, the crude product was recrystallized from approximately two liters of methanol in two steps with a total yield of 91.0 grams.

The remaining 47.8 grams of 4,4'-bis(dimethylamino)-2,2'-dibromophenylmethane was stirred at reflux in a mixture of 500 ml methanol, 50 ml 10N KOH and 15 grams of 1% Pd on $CaCO_3$ for 18 hours. Recrystallization of the solids yielded 2.9 grams of the pure fluorene in the first crop of crystals. Further attempts yielded a mixture of the product and reactants. The pure product was dissolved in 150 ml of pyridine and 1.0 ml of Triton B. Air was bubbled through the yellow solution which slowly turned to red-orange. After five hours the solution was heated to boiling and H_2O was added until crystal formation was evident. The solution was cooled slowly and filtered. The crude fluorenone was recrystallized from 95% ethanol yielding 1.4 grams.

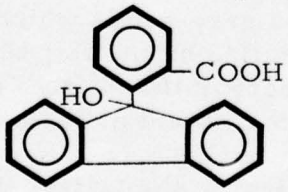
Water was added to the original pyridine solution to force out the remaining fluorenone. This crude material was combined with the ethanol and allowed to slowly recrystallize, giving an additional 1.0 grams of product.

The sulfone of methane base was prepared by slowly adding 0.1 mole (25.4 grams) of methane base to 250 ml of 20% fuming sulfuric acid. The solution was stirred and heated to 150°C for two hours. It was then cooled, poured over ice and neutralized with 25% NaOH yielding 27.4 grams of product (melting point 218-220°C). This product was then used to prepare the ketone by air oxidation in the same manner as the fluorenone, giving 14.35 grams of product with a melting point of 319.5-320°C. An additional 6.4 grams of crude product, melting point 305-306°C, was also obtained.

The bromination of methane base was repeated on a 0.2 mole scale. Only 42.1 grams of product were obtained, which was a poorer yield than usual.

Preparation of 3,6-bis(dimethylamino)-9 methyl fluorene-9-al was attempted. Under positive nitrogen pressure, 3,6-bis(dimethylamino) fluorenone (0.66g or 0.0025 moles) was stirred in 150 ml of dry ether. Only approximately one-third seemed to dissolve. Then, 5 ml of methyl lithium (0.64 molar in ether) was added from a syringe through a septum. Stirring continued for six hours. After four hours, a sample was removed and treated with water, then extracted with ether. The ether layer gave evidence on a silica gel TLC plate eluted with $CHCl_3$ that a very small quantity of product had been formed. After two additional hours, there was no change in the composition of the ether layer, so the reaction was quenched on ice and extracted with ether. No product was separated from the starting material.

Next, a trial experiment was done to prepare



A solution of o-bromo benzoic acid (1.0g or 0.005 moles) in 20 ml of ether was quickly added to a stirred solution of 8 ml BuLi (2.04 molar) in 20 ml of ether under positive nitrogen pressure at -78°C. The mixture was bright yellow. After ten minutes of stirring fluorenone (0.9g or 0.005 moles) in 20 ml of ether was added as quickly as possible. The reaction mixture turned brown-orange and was allowed to warm slowly to room temperature. TLC indicated a substantial amount of product formation.

Since the limited solubility of 3,6-bis(dimethylamino)fluorenone in ether was suspected as the deterrent to the addition reactions. The reaction of the substituted fluorenone and methyl lithium was repeated on the same scale, using 600 ml of dry ether as a solvent. The reaction mixture was allowed to stir overnight. The reaction was quenched on ice, and the ether layer was examined by TLC and indicated two additional components. The ether was evaporated and the residue was chromatographed on a one inch diameter column of silica gel eluting with $CHCl_3$. The fast moving yellow and orange components were isolated in small quantities.

In an attempt to improve the yield, the Grignard reaction of CH_3MgI and 3,6-bis(dimethylamino)fluorenone was run. However, when the organic material was isolated from unreacted starting material, there was evidence of about ten components in limited quantity. Then the methyl lithium reaction with the substituted fluorenone was repeated and stirred at reflux overnight. There was evidence of reaction, but the product was not stable in air and water. However, some traces of another component (evidenced before) were found. The residue was combined with that of the first attempt and dissolved in ethanol. It was hoped that the fluorenone could be crystallized, leaving a product-rich mother liquor, but both components crystallized.

The methyl Grignard reagent was made and reacted with fluorenone to give the desired fluorenol. So it was determined that the dimethylamino substituents sufficiently deactivated the carbonyl to prevent the desired reaction.

0-Bromobenzoic acid (1.0g) in 100 ml of dry ether was rapidly added to BuLi (2.5 ml 2 molar) in 30 ml of ether. This mixture was stirred at -75°C for 10 minutes. 3,6-bis(dimethylamino)fluorenone (0.66g) in 500 ml of dry ether was added slowly over a 10 minute period. The mixture was allowed to stir for three hours. Then it was poured over ice and separated. The fluorenone was recovered unchanged.

This facet of the project was then set aside in order to investigate other dyes with possible absorption in the infrared region.

The preparation of 4-nitro-4'-aminodiphenyl-amine-2-carboxylic acid. A mixture of 5.0g of 2-chloro-5-nitrobenzoic acid, 5.0g of p-phenylene-diamine, 5.0g of anhydrous K_2CO_3 and 0.1g copper powder was stirred at 150°C and diluted with 15 ml n-amyl alcohol for 45 minutes. Then water was added and the alcohol removed by steam distillation. The hot aqueous mixture was filtered through celite. Additional boiling water was added to dissolve the lumpy residue in the filter. The filtrate was then cooled in ice, and crystals formed. The cold aqueous mixture was filtered and 3.5g of solids were recovered. These solids were dissolved in 800 ml of water and made acid to litmus with glacial acetic acid. The aqueous was filtered

and the resulting pasty brown-black residue was washed with 50 ml boiling toluene four times. The attempts to crystallize the product from this toluene solution resulted in yellow-green powder. The reaction was repeated and the solids were combined (m.p. 236-9) and a sample was sent for mass spectral data. The desired parent peak appeared, but the compound was not sufficiently stable to get a reliable spectrum.

To a Grignard reagent, prepared by adding 262.4g of methyl iodide in 400 ml of dry ether to a dried flask containing 40.3g magnesium turning in 100 ml of ether, was added 85.7g of methyl-m-hydroxybenzoate over a two hour period. The mixture was refluxed an additional two hours and allowed to stir overnight. Then the reaction mixture was poured into a solution of 192g NH_4Cl in 500 ml of water. The yellow ether layer was easily separated. Then the residue of insoluble material was treated with additional NH_4Cl in 500 ml of water. The yellow ether layer was easily separated. The aqueous solution was washed twice with 100 ml ether and the organic phases were combined and the solvent was removed. The residue was boiled for 1.5 hours in a 10% NaOH solution. It was filtered hot and allowed to cool. It was stirred in an ice bath and neutralized with HCl. The resulting solids were filtered and suspended in a stirred dilute solution of $NaHCO_3$ overnight. The suspension was then filtered and yielded 35g of white solid (m.p. 100-102°C).

The reaction of p-phenylenediamine and 2-chloro-5-nitrobenzoic acid was repeated three times with freshly prepared copper powder and recrystallized amine. The residues from the toluene solutions were all similar but difficult to purify. The only product different from those previously isolated was ruled out by elemental analysis. Since the IR absorption of the NO_2 function is very strong, it was used to determine if the residue might possibly be desired product. The resulting spectra were not promising.

Next, attempts were made to produce dyes from the 3,6-bis(dimethylamino)fluorene. 0.5g of the fluorene was dissolved in glacial acetic acid and filtered. Then lead tetra-acetate in glacial acetic acid was filtered into the solution which immediately changed to deep green. An aqueous solution of NH_4ClO_4 was added and the solutuion was filtered. No suitable solvent for the perchlorate salt of the dye could be found, so the reaction was repeated and the acetate salt of the dye was used for absorption measurement. The dye weakly absorbed in the visible with a λ max 420 nm. There was no absorption in the IR region up to 1200 nm.

Methane base was again sulfonated in 20% fuming sulfuric acid at 150°C for 1.5 hours. It was poured over ice and neutralized with aqueous NaOH. The resulting solids were filtered (m.p. 216-220 and IR consistent with authentic sample). The sulfone (0.01 moles) was then dissolved in glacial acetic acid and 0.01 moles of lead tetra-acetate in glacial acetic

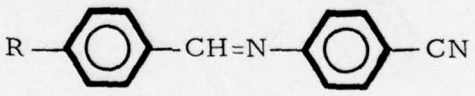
was added. The solution turned intense blue, then gradually changed to green. The absorption spectrum showed a small peak at 410 nm corresponding to the fulfone ketone and a very intense peak at 720 nm corresponding to the dye. The solution became more green due to continued formation of the ketone. So the reaction was repeated and quenched with sulfate ion as soon as the blue appeared to limit further oxidation.

(C) Liquid Crystal Research

Three anil compounds were synthesized for further research on their electro-optical properties. The preparation of the compounds proceeded as follows:

0.010 moles each of the parasubstituted benzaldehyde and p-cyanoaniline were refluxed for four hours in 150 ml of benzene containing 0.1 gm of benzenesulfonic acid. A Dean-Stark trap was used to collect the water from condensation. The solvent was removed under vacuum and the product recrystallized from n-hexane.

The difference in structure of the three anils appears only in the para-substituent of the starting benzaldehyde. The basic structure of the anil is:



with the R substituents being:

$$R_1 = C_4H_9O -$$

$$R_2 = C_6H_{13}O -$$

$$R_3 = C_7H_{15}COO -$$

for the three respective anils synthesized. The nematic ranges of the liquid crystals were:

anil	m.p., °C	n → i*
R_1	62.4 - 63.4 ⟶	108.0
R_2	54.7 - 55.6 ⟶	101.2
R_3	56.0 - 58.8 ⟶	96.4

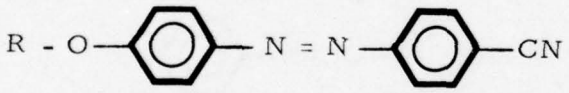
*nematic-to-isotropic transition, °C

The R groups had to be synthesized before the condensation reaction could be used to prepare the anils. R_1 and R_2 were each prepared by dissolving 25 gm of p-hydroxybenzaldehyde in 300 ml of methanol and adding 15 gm of KOH and butyliodide (for R_1) or hexyliodide (for R_2). This mixture was refluxed on the steam bath for six hours.

After completion of the refluxing, water was added to the mixture to precipitate the organic layer. The organic material was extracted with ether. The ether solution was washed several times with 10% NaOH solution, then several times with water. The ether solution was dried with anhydrous sodium sulfate. The ether was removed and the residue vacuum distilled. The product was collected at about 150°C and 6 mm Hg pressure.

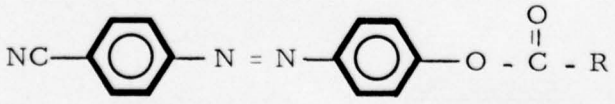
R_3 was prepared by dissolving 12.2 gm (0.1 mole) of p-hydroxybenzaldehyde in 100 ml pyridine. This mixture was cooled in an ice bath and 15.2 gm octanoylchloride were added slowly. The mixture was allowed to stand overnight. Next day the mixture was again put in an ice bath and a cold 50% solution of H_2SO_4 added dropwise. The organic material was extracted with ether. The ether layer was washed several times with water, the ether removed and the residue vacuum distilled to produce the product.

Several homologs of the basic compound



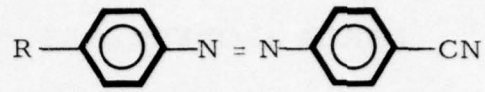
were synthesized. The procedure was to reflux a mixture of p-hydroxy-p'-cyanoazobenzene, an alkyl iodide or bromide and anhydrous K_2CO_3 in 2 ml of acetone for 48 hours on a steam bath. The acetone was then removed and 20 ml of H_2O added with some $CHCl_3$. This was washed with 10% NaOH and then with distilled H_2O. The $CHCl_3$ was removed and the product recrystallized from cyclohexane.

The homologs of the basic compound



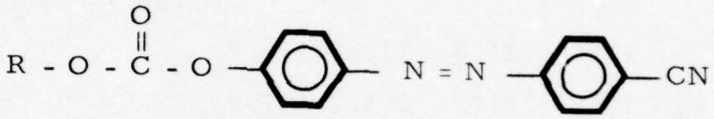
were synthesized by dissolving p-hydroxyazobenzene in 50 ml of toluene and adding 10 ml of dry pyridine. The next step was the slow addition of 10 ml of the acid chloride appropriate for the desired homolog. This mixture was heated in reflux for 30 minutes, cooled and 200 ml H_2O added. The water layer was separated and discarded. The toluene solution was further washed with H_2O and then dried. The product was removed from the toluene and recrystallized from methanol.

The homologs of the compound



were prepared by refluxing a mixture of p-nitrosobenzonitrile and the necessary p-substituted aniline in 10 ml acetic acid for one hour. The mixture was cooled, the solid filtered off and allowed to dry. The solid was purified by recrystallizing in petroleum ether or aqueous methanol.

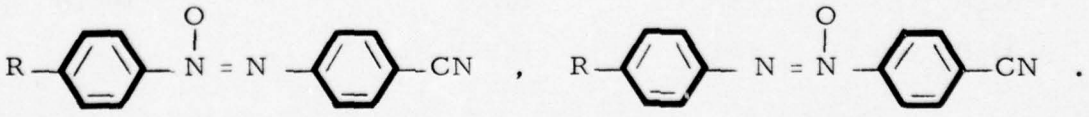
The homologs of the compound



were prepared by the dropwise addition of the necessary R-chloroformate to a solution of p-hydroxy-p'-cyanoazobenzene and dry pyridine in 20 ml of dry benzene. This solution was stirred overnight, followed by the addition of 100 ml of ether and then washed three times with 50 ml portions of H_2O. The solution was dried, the ether evaporated, and the product recrystallized from n-hexane.

The azoxybenzene of each of the above azobenzenes was synthesized by adding the azobenzene to 5 ml acetic acid and 2 ml of 30% hydrogen peroxide. This mixture was heated on a steam bath until the solution turned yellow, cooled and filtered to remove the yellow crystalline azoxybenzene.

The melting point and nematic transition properties of the axo and azoxy compounds are given in Tables 32-39. Since the starting azobenzenes are unsymmetrically parasubstituted, the oxidation to the azoxybenzene occurs at either azo nitrogen atom. One isomeric pair is shown here



The isomeric ratios for all R-substituted azoxybenzenes were determined by nuclear magnetic resonance and lanthanide shift reagents. Results of the NMR experiments showed that in the oxidation of all five alkyl compounds, the isomerization occurred with a 1:1 distribution.

The experience gained from working with azoxy benzenes, information gleaned from the literature, and the accurate melting points and nematic to isotropic transition temperatures obtained with the Differential Thermal

TABLE 32

ETHER AZOBENZENES

Set A

R-	c → n	n → i	c → i	i → n
CH_3O -	-	-	143.4-144.1	146.0
C_2H_5O -	-	-	147.0-148.6	152.0
C_3H_7O -	-	-	136.7-137.0	133.0
C_4H_9O -	118.0-118.6	118.6-126.7	-	132.0
$C_5H_{11}O$ -	101.5-101.7	101.7-117.0	-	125.0
$C_6H_{13}O$ -	100.3-101.0	101.0-116.5	-	123.0
$C_7H_{15}O$ -	93.2- 94.1	94.1-111.2	-	113.0
$C_8H_{17}O$ -	102.8-103.8	103.8-112.3	-	115.0

Set B

CH_3O -	144.8	-	-	-
C_2H_5O -	149.8	-	-	-
C_3H_7O -	135.1	-	-	121.4
C_4H_9O -	118.8	123.2	-	122.3
$C_5H_{11}O$ -	103.4	115.4	-	114.4
$C_6H_{13}O$ -	101.6	114.4	-	113.1
$C_7H_{15}O$ -	92.9	107.1	-	106.9
$C_8H_{17}O$ -	104.6	108.1	-	-

Set A = obtained optically

Set B = obtained from DTA

c = crystal

n = nematic

i = isotropic

(centigrade scale)

TABLE 33

ESTER AZOBENZENES

Set A

R-	c → n	n → i	c → i	i → n
CH_3CO_2 -	-	-	138.2-139.0	133.0
$C_2H_5CO_2$ -	128.0-129.4	-	-	135.0
$C_3H_7CO_2$ -	112.0-113.3	-	-	125.0
$C_4H_9CO_2$ -	101.0-101.8	-	-	114.0
$C_5H_{11}CO_2$ -	97.0- 97.4	-	-	115.0
$C_6H_{13}CO_2$ -	105.5-106.8	-	-	110.0
$C_7H_{15}CO_2$ -	-	-	106.7-107.7	103.0

Set B

CH_3CO_2	135.7	-	-	-
$C_2H_5CO_2$	126.9	131.0	-	129.1
$C_3H_7CO_2$	113.6	119.9	-	119.2
$C_4H_9CO_2$	100.9	107.5	-	106.3
$C_5H_{11}CO_2$	104.9	108.2	-	107.7
$C_6H_{13}CO_2$	96.4	102.5	-	101.1
$C_7H_{15}CO_2$	107.5	-	-	100.9

TABLE 34

CARBONATE AZOBENZENES

Set A

R-	c → n	n → i	c → i	i → n
CH_3CO_3 -	153.0-155.0	155.0-168.5	-	150.0
$C_2H_5CO_3$ -	125.5-127.0	127.0-147.1	-	147.0
$C_3H_7CO_3$ -	107.1-108.2	108.2-125.4	-	132.0
$C_4H_9CO_3$ -	87.1- 87.6	87.6-116.7	-	124.0
$C_5H_{11}CO_3$ -	79.1- 79.5	79.5-112.5	-	116.0
$C_6H_{13}CO_3$ -	81.2- 82.5	82.5-102.1	-	109.0

Set B

CH_3CO_3 -	150.5	161.5	-	148.5
$C_2H_5CO_3$ -	124.0	142.8	-	141.3
$C_3H_7CO_3$ -	107.1	121.4	-	121.1
$C_4H_9CO_3$ -	86.3	114.8	-	113.1
$C_5H_{11}CO_3$ -	78.8	108.5	-	110.2
$C_6H_{13}CO_3$ -	80.0	101.6	-	100.6

TABLE 35

ALKYL AZOBENZENES

Set A

R-	c → i	i → n
CH_3 -	169.1-171.4	153.0
C_2H_5 -	115.3-116.9	103.0
C_3H_7 -	79.5- 81.3	91.0
C_4H_9 -	98.2- 99.0	80.0
C_5H_{11} -	88.1- 89.0	85.0

Set B

CH_3 -	164.7	-
C_2H_5 -	114.2	-
C_3H_7 -	77.2	70.0
C_4H_9 -	100.2- 98.2	73.0
C_5H_{11} -	84.8	-

TABLE 36

ETHER AZOXYBENZENES

Set A

R-	c → n	n → i	c → i	i → n
CH_3O -	-	-	151.0-193.5	-
C_2H_5O -	140.2-143.2	171.2	-	-
C_3H_7O -	114.0-116.0	153.2	-	-
C_4H_9O -	87.0- 88.0	155.3	-	-
$C_5H_{11}O$ -	93.1- 94.1	144.4	-	-
$C_6H_{13}O$ -	85.1- 86.0	143.2	-	-
$C_7H_{15}O$ -	87.2- 89.0	137.8	-	-
$C_8H_{17}O$ -	72.7- 73.3	140.8	-	-

Set B

CH_3O -	-	-	153.1-185.1	-
C_2H_5O -	140.8	166.0	-	162.6
C_3H_7O -	117.3	147.2	-	146.3
C_4H_9O -	86.0	148.4	-	147.0
$C_5H_{11}O$ -	90.6	137.7	-	137.2
$C_6H_{13}O$ -	81.8	139.7	-	139.0
$C_7H_{15}O$ -	87.9	130.8	-	131.7
$C_8H_{17}O$ -	67.0	134.9	-	134.6

TABLE 37

ESTER AZOXYBENZENES

Set A

R-	c → n	n → i	c → i	i → n
CH_3CO_2	122.1-123.5	159.1	-	-
$C_2H_5CO_2$	130.3-131.6	164.1	-	-
$C_3H_7CO_2$	64.0- 65.2	148.4	-	-
$C_4H_9CO_2$	79.2- 82.3	141.2	-	-
$C_5H_{11}CO_2$	58.2- 60.0	137.6	-	-
$C_6H_{13}CO_2$	60.0- 62.3	135.5	-	-
$C_7H_{15}CO_2$	54.1- 55.6	132.8	-	-

Set B

CH_3CO_2	121.3	155.4	-	154.5
$C_2H_5CO_2$	129.3	159.8	-	157.7
$C_3H_7CO_2$	57.5~ 66.2	149.8	-	148.7
$C_4H_9CO_2$	85.7	136.8	-	136.3
$C_5H_{11}CO_2$	75.6	138.8	-	137.6
$C_6H_{13}CO_2$	67.0	131.7	-	131.3
$C_7H_{15}CO_2$	75.3	-	-	126.2

TABLE 38

CARBONATE AZOXYBENZENES

Set A

R-	c → n	n → i	c → i	i → n
CH_3CO_3	129.4-131.2	194.8	-	-
$C_2H_5CO_3$	107.2-108.1	172.2	-	-
$C_3H_7CO_3$	85.0- 86.0	152.8	-	-
$C_4H_9CO_3$	75.7- 77.0	146.7	-	-
$C_5H_{11}CO_3$	78.0- 80.2	140.6	-	-
$C_6H_{13}CO_3$	79.3- 71.0	133.9	-	-

Set B

CH_3CO_3	129.5	189.1	-	186.4
$C_2H_5CO_3$	106.6	167.2	-	166.0
$C_3H_7CO_3$	83.6	149.5	-	147.8
$C_4H_9CO_3$	75.7	141.0	-	140.6
$C_5H_{11}CO_3$	59.7	129.0	-	128.7
$C_6H_{13}CO_3$	68.4	129.5	-	129.0

TABLE 39

ALKYL AZOXYBENZENES

Set A

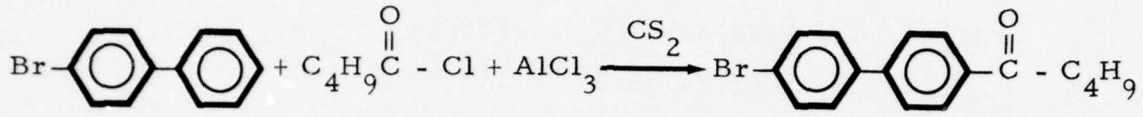
R-	c → n	n → i	c → i	i → n
CH_3 -	126.2-127.5	138.3	-	-
C_2H_5 -	92.2- 93.5	119.7	-	-
C_3H_7 -	71.0- 72.2	125.0	-	-
C_4H_9 -	60.3- 63.7	113.3	-	-
C_5H_{11} -	81.3- 83.6	125.1	-	-

Set B

CH_3 -	122.3	128.1	-	-
C_2H_5 -	87.1	112.1	-	112.7
C_3H_7 -	55.5~ 72.8	120.9	-	119.7
C_4H_9 -	61.9	113.1	-	111.9
C_5H_{11} -	75.3	120.7	-	122.3

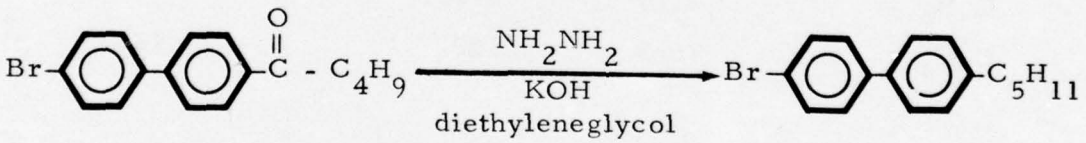
Analyzer were correlated and used as a basis to start a series of trial and error attempts to form room temperature nematic liquid crystal mixtures, having relatively high nematic to isotropic transition temperatures. The mixtures which had favorable results are given in Table 40.

A synthesis was carried out for p-pentyl-1-cyanobiphenyl, which is the only room temperature nematic liquid crystal that has a positive dielectric anisotropy. The first step of the synthesis:



was accomplished by suspending 15.8 gms $AlCl_3$ in 40 ml of dry CS_2. Next, a solution of 23.3 gms p-bromobiphenyl and 12.0 g of valeryl chloride dissolved in 80 ml CS_2 was added gradually to the rapidly stirring suspension of $AlCl_3$ over a 20 minute period. Stirring was continued for 30 minutes, followed by heating on the steam bath at reflux for four hours. The CS_2 was evaporated, and the residue added to 100 ml of ice water. An ether extraction was run, the ether layer washed with water and dried over anhydrous Na_2SO_4. The ether was evaporated and the resulting material recrystallized in hexane yielding white crystals melting at 96-97 °C.

The next step in the synthesis:



was carried out by heating a mixture of 15.9 gms p-bromo-p-valeryl biphenyl, 50 ml diethyleneglycol, 6 ml 85% hydrazine hydrate and 5.9 gms KOH on a steam bath until the mixture was homogeneous and one hour more. The mixture was then moved from the steam bath to a heating mantle and distilled until the temperature reached 200 °C, then heated under reflux for six hours. Extraction, washing, drying and recrystallizing yielded a product which melted at 94-95.5 °C.

The final step of the synthesis:

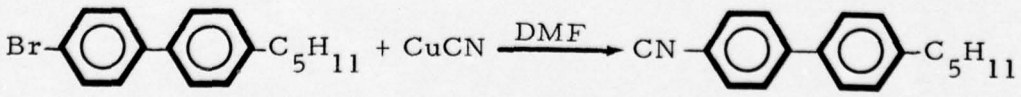
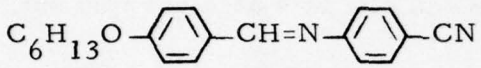
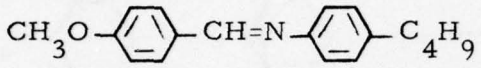
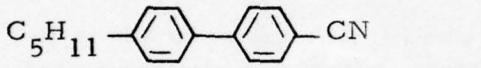
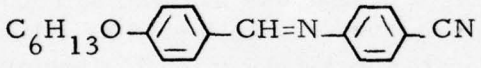
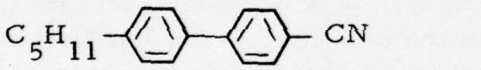
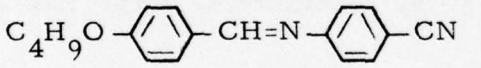
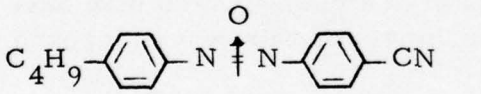
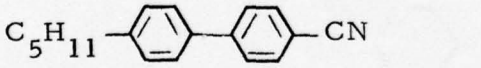
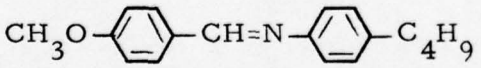
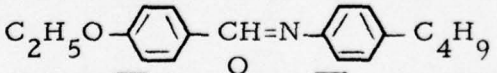
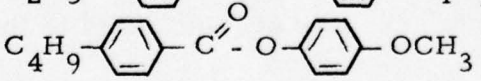


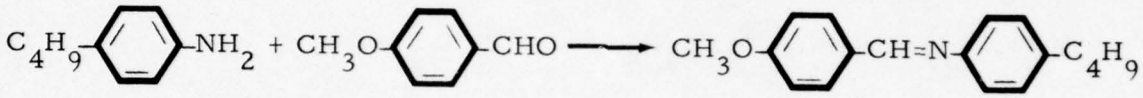
TABLE 40

MIXTURES OF NEMATICS

Components	mole %	n → i	c → n
	34.5	71.4°	below R.T.
	65.5		
	69.0	66.0°	below R.T.
	31.0		
	60.0	62.7°	below R.T.
	40.0		
	34.0	54.7°	below R.T.
	66.0		
	33.33	45.2°	below R.T.
	33.33		
	33.33		

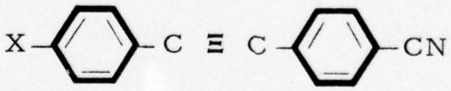
was conducted by heating a mixture of 6 gms p-bromo-p'-pentylbiphenyl, 6.5 gms CuCN, 80 ml dimethyl formamide and one drop pyridine under reflux for eight hours. The hot reaction mixture was then poured into a warm solution of 10 gms sodium cyanide and 30 ml water. The mixture was shaken vigorously and the lower aqueous layer separated. The organic layer was washed with 10 ml 10% aqueous sodium cyanide and then several times with water. The solution was dried and the solvent evaporated. The remaining material was vacuum distilled at 0.1 mm Hg, the product coming off at 170°C. The nematic to isotropic transition temperature was 34.8°C.

The synthesis of N-(4'-methoxybenzylidene)-4-n-butylaniline, which is a negative dielectric room temperature nematic was also carried out.



p-anisaldehyde (0.1 mole) and n-butyl aniline (0.1 mole) were added to 50 ml toluene in a round bottom flask. This solution was allowed to reflux six hours, and the water produced by this reaction was collected by a Dean-Stark trap. When the theoretical yield of water was collected, the toluene was removed by evaporation. The resulting anil was purified distillation. A short path distilling column proved to be the best method of distillation, b.p. 173° - 175° at 0.05 mm. The yield of the reaction was very good (83%).

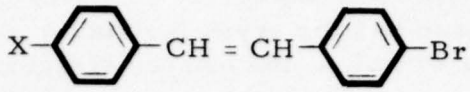
Work was conducted on the synthesis of acetylenes which may have liquid crystal properties. The general structure for this type compound is:



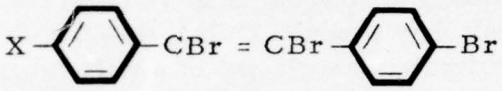
Two of these compounds were successfully synthesized in which X = C_3H_7 and C_4H_9, respectively.

Synthesis of the propyl and butyl acetylenes was accomplished in the following manner.

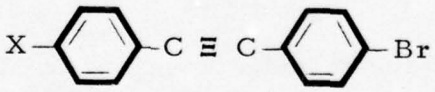
A mixture of 0.02 moles phosphonium bromide and 150 ml dry benzene was stirred at room temperature for two hours. To this suspension, 0.023 moles butyl lithium was added under nitrogen atmosphere. Then, 0.023 moles of p-butyl or propyl benzaldehyde was added, and the mixture allowed to stir for three hours. The benzene was diluted with petroleum ether and the solution filtered. The benzene-petroleum ether solution was washed several times with water and then dried over Na_2SO_4. The solvents were evaporated off and the product recrystallized from ethanol. Light yellow crystals were formed in approximately 60% yield having the structure



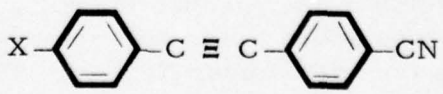
A solution of this trans-stilbene (0.01 mole) in 50 ml ether was placed in a flask equipped with a condenser and dropping funnel. To the well-stirred solution, 0.012 mole of Br_2 was added slowly. Precipitation started within five minutes, but stirring continued for one hour. The product was collected on a Buchner funnel and washed with a small amount of ether. The white stilbene dibromide was produced in 49% yield with the structure



A solution of two grams potassium hydroxide in 25 ml absolute ethanol was prepared and placed in a flask fitted with a condenser. It was necessary to heat the solution on an oil bath to dissolve the potassium hydroxide. The solution was then cooled somewhat and 0.006 mole of stilbene dibromide was added slowly in several small portions. The mixture was refluxed for 24 hours. The hot solution was then poured into ice water, filtered, washed with water and dried in a dessicator. The acetylene was produced in 55% yield with the structure

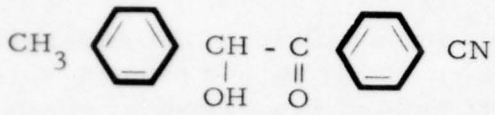


A mixture of the above acetylene, 0.005 mole of CuCN and 50 ml dimethylformamide with one drop of pyridene was heated under reflux for 20 hours. The hot solution was poured into a warm solution of two grams sodium cyanide in 10 ml water. The mixture was shaken vigorously and allowed to separate into an aqueous lower layer and an organic upper layer. The addition of some benzene aided the separation. The organic layer was washed once with 10% aqueous sodium cyanide solution, then twice with water, dried over Na_2SO_4 and the solvent evaporated off. Product was recrystallized from ethanol in 60% yield with the structure



Another method for synthesizing these acetylenes was attempted. This method started with the formation of the benzoins by mixing a solution of 0.02 mole tolualdehyde and 0.02 mole p-cyanobenzaldehyde in 10 ml of 95% ethanol, with a solution of one gram potassium cyanide in two ml water.

This mixture was allowed to reflux for 1-1/2 hours on a steam bath, chilled to form crystals, filtered and the crystals dried in a dessicator. The crystals were obtained in a 70% yield and had the structure



A mixture of the above product in methanol and 0.028 mole cupric acetate in 24 ml of 50% acetic acid was placed in a flask equipped with a stirrer and condenser, heated to reflux and refluxed for two hours. The color of the mixture changed from blue to red at 75°C. The solution was partially cooled and filtered through Celite on a glass funnel to rem the cuprous oxide. The filtrate was placed in a separatory funnel, saturated NaCl solution added, shaken and extracted with ether. The ether extract was washed three times with saturated NaCl solution, four times with 5% $NaHCO_3$ solution and again with NaCl solution. The extract was dried over Na_2SO_4 and the ether evaporated. The product was recrystallized from a benzene-hexane mixture. Analysis of the product showed that it was not the desired compound, so it was decided to use the original method of synthesis for future work.

Another acetylene was tried by the same method, where X is an isobutyl group. It was necessary that the ixobutylbenzaldehyde be synthesized as follows.

A solution of (0.05 mole) isobutylbenzene in 32 ml methylene chloride was placed in a 100 liter three neck flask equipped with a reflux condenser, stirrer and dropping funnel. The solution was cooled in an ice bath and 0.08 mole of titanium tetrachloride was added over a three minute period. While the solution was stirred and cooled, 0.04 mole of dichloromethyl methyl ether was added dropwise over a 25 minute period. The reaction began (as indicated by evolution of hydrogen chloride) when the first drop of the ether was added. After the addition was complete, the mixture was stirred five minutes in the ice bath, 30 minutes without cooling and 15 minutes at 35°C. The reaction mixture was poured into a separatory funnel containing about 50g of crushed ice and shaken thoroughly. The organic layer was separated and the aqueous solution extracted with two portions of methylene chloride. The combined organic solution was washed three times with water. A crystal of hydroquinone was added to the solution to prevent autoxidation of the aldehyde, which was then dried over Na_2SO_4. The solvent was removed by evaporation and the product distilled at 68°C and 0.45 mm Hg.

The dichloromethyl methyl ether, which was used in the above reaction, was synthesized by the following method. In a two liter, three necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel,

4.0 moles of phosphorus pentachloride was stirred with 250 ml of phosphorus oxychloride. To this was added 264g (272 ml; 4.4 moles) of methyl formate, while stirring. During the addition, the reaction vessel was cooled in an ice bath to maintain a reaction temperature of 10-20°. The addition required about 1.75 hours. When the addition was complete, the solution was stirred at a temperature under 30° until all the phosphorus pentachloride dissolved (about one hour). The stirrer was then removed, the condenser replaced by a distilling head, and the reaction mixture was distilled under a pressure of 80-120 mm with a bath temperature of 50-65°. The material was collected and redistilled through a Todd fractionation column using a 10:1 reflux ratio, b.p. 82-85.5°.

(D) Conclusions and Recommendations

The characterization study has shown the need for careful purification of the various laser dyes investigated. The ease with which any particular dye can be purified is strongly dependent on the associated counterion of the dye. For Cresyl Violet, Nile Blue, and Rhodamine 6G the optimum counterion appears to be nitrate or fluoborate. With these two counterions, the purification by recrystallization proceeded with much greater facility than with any other counterion.

The lasing efficiency is also affected by the counterion; however, this is probably due to the purity of the dye. The nitrate and fluoborate salts of the dyes consistently showed better lasing efficiency than the other salts investigated with the exception of Cresyl Violet acetate. The acetate salt of Cresyl Violet also turns out to be easy to purify. The perchlorate salt of Cresyl Violet as received from EKO showed the best lasing efficiency of any of the salts tested. The fluorescence quantum efficiency showed a counterion effect which roughly paralleled the lasing efficiency effect.

Solutions of Cresyl Violet and Nile Blue showed an acidity dependent behavior. This was shown to be caused by an equilibrium reaction between the dye and its free base. As the solutions became more basic, more of the dye assumed its free base form. The free base form is nonfluorescing and, thus, it hinders lasing action in the solution. As long as the solution is maintained slightly acidic, the equilibrium is held in the dye form and no great problem is encountered in lasing.

All the dyes investigated showed photodegradation when irradiated with ultraviolet light. This effect was studied in some detail for Cresyl Violet nitrate. A very strong solvent effect was seen, with hexafluoroisopropanol giving the longest lifetime of the dye and isopropanol giving the shortest lifetime.

The photodegradation of the dyes manifests itself in laser operation as a slow degradation in lasing efficiency over the course of repeated shots. An example of the process is seen in the test of Kiton Red S which was conducted at the Avionics Laboratory. This test showed a 10^{-5}M solution of the dye to have a 1/2 life of 1750 shots.

As stated earlier, the single most important process affecting the performance of laser dyes is the purity of the dye. Once a viable purification process is developed for a particular dye, further studies of the efficiency and photostability can be reasonably undertaken.

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(b) Knudsen

(c) vapor pressure

(d) constant (equilibrium)

(e) mass spectrometry

(f) sublimation

(g) thermodynamics

(h) high temperature

(i) vapor

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