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ARL 63-37

RADIATION CHARACTERISTICS OF METAL VAPORS

A. E. WECHSLER
P. E. GLASER

409 582

ARTHUR D. LITTLE, INC.
CAMBRIDGE, MASSACHUSETTS

FEBRUARY 1963

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Unclassified Report

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(over)

The results are reported in terms of the decrease in intensity of light passing through alkali metal vapors as functions of vapor pressure, temperature and path length. Calculated absorption cross sections are in the order of 10^{-18} to 10^{-19} cm² for sodium and potassium vapor over the wavelength region studied.

The absorption of radiation by alkali metal vapors has been shown to have an observable effect on the heat transfer in arc and plasma systems and warrants a more detailed study over a larger spectral range.

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CAMBRIDGE, MASSACHUSETTS**

FEBRUARY 1963

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PROJECT 7063

TASK 7063-01

**AERONAUTICAL RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

FOREWORD

This interim technical report was prepared by Division 500 of Arthur R. Little, Inc., Cambridge, Massachusetts, on Contract AF 33(657)-7974 for the Aeronautical Research Laboratories, Office of Aerospace Research, United States Air Force. The research reported herein was accomplished on Task 7063-01, "Research in Heat Transfer Phenomena," of Project 7063, "Mechanics of Flight covering the research program during the period 15 January 1962 to 30 November 1962. The work was done under the cognizance of Mr. Paul W. Schreiber of the Thermomechanics Research Laboratory of ARL.

The interest and guidance of Mr. Erich Soehngen of the Thermomechanics Research Laboratory of ARL throughout the course of this work was gratefully acknowledged. The support and assistance of Drs. Howard McMahon, Alfred Emslie, and Ivan Simon of Arthur D. Little, Inc., materially aided the conduct of this investigation. The thorough and careful experimental technique of Mr. E. Boudreau was greatly appreciated.

ABSTRACT

An experimental program is described in which semi-quantitative data on absorption of radiant energy by alkali metal vapors was obtained. The range of variables covered were: temperature, 250 to 600°C; sodium and potassium vapor pressure, 0 to 18 mm Hg; vapor path length, 4-1/2 and 8-1/2 inches; wavelength region 4000-8300 Å.

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1. SUMMARY

In high-temperature arc and plasma systems using alkali metal additives to modify electrical conductivity, absorption of radiant energy by alkali metal vapors and subsequent modification of heat transfer conditions can occur. The principal mechanisms of absorption are molecular band absorption in the visible and near infrared regions and absorption due to photoionization in the ultraviolet region.

An experimental program was conducted to obtain semi-quantitative data on absorption by sodium and potassium vapor in the visible region. Preliminary experiments showed that an absorption cell with a vapor path length of four to 10 inches could be used. We designed and constructed an absorption cell in which vapor path and temperature could be controlled, and vapor was prevented from diffusing to and attacking the optical components. Interference filters with band pass widths from 800 to 1500 Å were used to study absorption in various parts of the visible region. The range of variables covered in the experimental program were: temperature - 250 to 600°C; alkali metal vapor pressure - 0 to 18 mm Hg; vapor path length - 4-1/2 and 8-1/2 inches; light source temperature - 1000 to 2170°C; wavelength range - 4000 to 8300 Å.

The results of the investigation are reported in terms of decrease of intensity of light passing through alkali metal vapors as functions of vapor pressure, temperature, and path length. Absorption cross sections calculated from the experimental data range in the order of 10^{-18} to 10^{-19} cm² for sodium and potassium vapor; sodium is the stronger absorber for the region investigated. The absorption cross sections in the visible region are substantially higher than those in the photoionization effect in the ultraviolet (available in the literature). The results are applied to arc systems showing possible changes in radiation heat transfer for several pressure-path length conditions. From 10 to 70 percent of the energy in the visible region can be absorbed in systems radiating as black bodies with path length-pressure products from 10 to 100 cm mm Hg. Systems which radiate strongly in specific wavelengths rather than in a continuous spectrum can also undergo significant modifications in heat transfer due to alkali metal vapor absorption. Absorption of radiant energy by the photoionization effect requires higher alkali metal pressures and path lengths than those mentioned above.

Recommendations for future work and a proposed design for an improved absorption cell are given.

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II. INTRODUCTION

The optical properties of gases and vapors have been studied extensively by physicists, spectroscopists, and engineers for many years. Some of the objectives of these studies have been to obtain information on the physical and thermodynamic properties of the elements and compounds, to develop techniques for identification and analysis of materials, and to provide a better understanding of the chemical and physical behavior of materials under prescribed environmental conditions.

In heat transfer, the optical properties of several common gases are of great importance. Combustion products (such as water, carbon dioxide, carbon monoxide and sulfur dioxide), ammonia, the hydrocarbons, hydrogen chloride, and the alcohols absorb and emit radiant energy in wavelength regions which are important in radiant heat transfer operations encountered in industrial practice. Industrial furnaces, heat exchangers, and rocket nozzles are examples of systems in which absorption and emission by gases must be taken into account. The optical properties of the gases mentioned above have been studied both experimentally⁽¹⁾ and theoretically.⁽²⁾ Data on gas emissivity and absorptivity for a wide range of temperatures and pressures is available for carbon dioxide, carbon monoxide, water vapor, sulfur dioxide, ammonia, and several other gases.

Recent advances in materials development, energy conversion, and chemical physics have led to the use of high temperature systems both on an industrial and research basis. Investigations of arc and plasma systems, for example, have produced very high temperatures, and under these conditions, radiant energy may be exchanged in wavelength regions where the symmetric diatomic gases (N_2 , O_2 , halogens, and alkali-metal vapors) become optically active. The data on the optical properties of these materials is limited, but investigations are in progress to obtain more reliable information.⁽³⁾

The use of alkali metals in arcs and plasmas to modify the electrical properties of the system has been suggested and studied, since the ionization potentials of the alkali metals are low. In addition to changing the electrical properties, the alkali metals may have a significant effect on the radiant energy exchange within the system. The absorption and emission of radiant energy in the spectral lines by the alkali metals is well known and has been used in temperature measuring techniques. These metals also form diatomic molecules, and a substantial concentration of these molecular species can exist in cool portions of high temperature devices. Since the temperature in plasma and arc systems is high enough so that the visible and ultraviolet portions of the spectrum are important, it can be expected that the diatomic species may absorb and re-radiate energy in these regions and change the over-all heat transfer characteristics of the system. Experience in operation of equipment using alkali metal seeding has indicated some "peculiar" heat transfer characteristics; these effects have been attributed in part to the influence of the alkali metal.

The present study was undertaken to show whether or not alkali metal vapors could have a significant effect on the radiant energy transfer in gaseous systems. Although more general information could be gained from a complete study of the spectral absorption of alkali metal

vapors, the present program was designed to use a minimum of instrumentation to determine qualitative information on the optical properties of the alkali metal vapors. The preliminary data obtained here was to be used to determine if a more detailed study is required. This report contains: (1) a discussion of the principles by which alkali metal vapors may effect radiant energy transmission, (2) a description of the experimental method used to evaluate the transmission of energy through alkali metal vapors, (3) a discussion of the experimental results, and (4) a discussion of the application of the experimental results and data available in the literature to heat transfer in high temperature systems.

III. BACKGROUND INFORMATION AND LITERATURE REVIEW

A. ABSORPTION OF RADIATION BY GASES

Radiation passing through a vapor containing only unassociated atoms may be attenuated by two principal mechanisms: absorption in the spectral lines of the element, and absorption due to the photoionization or photoelectric effect. If the atoms are associated to form molecules, radiation may be attenuated by molecular band absorption. A molecular photoionization or dissociation effect may also exist. These radiation attenuation mechanisms may be important over different portions of the energy spectrum, depending upon the material considered. In general, photoionization effects may be expected in the ultraviolet region, spectral line absorption occurs primarily in the ultraviolet and visible regions (for the system temperature under consideration) and molecular band absorption may occur in the ultraviolet, visible, and infrared regions. Energy is re-radiated by the atoms or molecules when they return to their normal energy states after the absorption processes mentioned above. In the steady state operation, as much energy is re-radiated as is absorbed; the intensity of a beam of radiation traversing a vapor path is reduced, however, since the absorbing atoms generally re-radiate their energy in all directions. Following is a brief discussion of these absorption mechanisms, with particular attention paid to their importance in a system containing alkali-metal vapor.

1. Spectral Line Absorption

The study of atomic spectra has contributed much to our knowledge of the physical behavior and nature of matter; many volumes and articles have been written in the field. It is beyond the scope of this investigation to give a general treatment of atomic spectroscopy; instead, we will briefly discuss the importance of absorption spectra from a "heat transfer" viewpoint.

In cool gases, absorption of radiant energy takes place at specific wavelengths, due to energy transition of the atoms. The principal absorption occurs in the transition from the ground state of the atom to the first excited state (resonance lines), but absorption also takes place between the ground state and the higher excited states. This mechanism causes the series of dark absorption lines at specific wavelengths when black-body radiation passing through a vapor is viewed in a spectroscope. The lifetimes of the excited atoms are short, and the energy is re-radiated to the system. The natural breadth of the spectral lines is a function of the properties of the atom.

The atomic absorption coefficient within a spectral line can be given in the form:⁽⁴⁾

$$a_{\nu} = \frac{\pi e^2}{mc} f \frac{\Gamma}{4\pi^2} \frac{1}{(\nu - \nu_0)^2 + (\Gamma/4\pi)^2} \quad (1)$$

where e , m , and c represent the electronic charge, mass, and velocity of light; Γ is a quantum mechanical damping coefficient, ν_0 is the oscillation frequency, ν the frequency of the beam passing through the system, and f is the oscillator strength. The absorption coefficient (within a spectral line) falls off rapidly at short distances from the value of ν_0 ; therefore, the absorption lines are quite narrow. Typical half breadths of the natural lines are in the order of $1 \times 10^{-4} \text{ \AA}$.

The spectral lines are broadened by temperature, pressure, and other effects. Increased motion of the atoms with increasing temperature results in a velocity or Doppler broadening of the lines. For a line broadened only by the Doppler effect, the absorption coefficient can be given as:

$$a_{\lambda} = \frac{\sqrt{\pi} e^2}{mc} f \frac{\lambda}{v} \exp \left[-\frac{c^2}{v^2} \left(\frac{\lambda - \lambda_0}{\lambda_0} \right)^2 \right] \quad (2)$$

where v is the most probable velocity of the atoms ($v = \sqrt{2kT/M}$), and the equation is now in terms of wavelength instead of frequency. By rearranging the equation, it can be seen that the line breadth is directly proportional to the square root of the gas temperature and the frequency of the radiated or absorbed energy, and is inversely proportional to the square root of the molecular weight. The magnitude of Doppler broadening is illustrated by the estimated half-intensity breadth (interval between two points where the intensity drops to half its maximum value) for the sodium D line in a gas at 500°K . The value, about $0.02 \text{ \AA}$, is a small number but many times greater than the natural half breadth. The Doppler and the natural line breadths have been estimated satisfactorily for the alkali metals.

Absorption and emission lines can also be broadened by collisions, i.e., collisions with other atoms during absorption or emission of radiation. The collision half-intensity breadth has been estimated as:(3)

$$\delta_{\nu}^c = \frac{4n\rho^2 P}{\sqrt{RT\mu\pi}} \quad (3)$$

where P is the pressure, ρ is the optical cross section or collision diameter, n is Avogadro's number, and μ is the molecular weight of the gas. Where foreign gases are present, μ is replaced by $mM/m + M$, where m and M are the molecular weights of the emitting and foreign gases, respectively. The optical cross section is found to be several times the value given by the kinetic theory, and in the case of foreign gases, optical cross sections of 10 times the kinetic cross section are not uncommon. From Equation 3, it can be seen that the collision broadening increases with the pressure of the system. For room temperature and pressure conditions, Doppler and collision broadening effects are of the same magnitude for radiation in the visible range.

Since the breadth of the atomic lines is small, even after the broadening effects are taken into account, it is difficult to envision a significant amount of absorption (from a heat transfer viewpoint) over such a narrow portion of the spectrum. Near the series limit, the lines come close together and may cover a sizable area. The absorption strength, however, becomes less; hence not much absorption can occur.

2. Photoionization Effect

In addition to discrete line absorption, atoms can absorb in continuous spectra, due to ionization of the electron from a bound level. The continuous absorption occurs on the short-wave length side of the principal series limit. Although continuous absorption coefficients have been theoretically evaluated for hydrogen, attempts by several authorities to evaluate the coefficients for the alkali metals⁽⁶⁾ have had only limited success.

Considerable experimental work has been carried out on the alkali metal vapors; however, there is disagreement in the actual values of the absorption coefficients and the interpretation of the data. Two experimental techniques have been used: measurement of ionization currents, and direct transmission measurements. Ionization current measurements were reported some 30 years ago, and their reliability is in doubt, because of experimental difficulties. The direct absorption method consists of measuring the decrease in intensity of radiation of known wavelengths when the radiation passes through a tube filled with vapor at a known temperature and pressure. This method is subject to considerable experimental difficulties, but the results have been self-consistent. One of the principal problems is that the method requires a cell with windows which will not be attacked by the alkali metal vapor, but which will transmit radiation of the required wavelength. The usual technique is to have a long cell and to prevent diffusion of the alkali vapor to the ends and to the windows.

The principal investigator in the alkali metal field is R. W. Ditchburn, who has studied all of the alkali metals and reported data on the absorption coefficients due to photoionization effects.⁽⁷⁻¹²⁾ A review article⁽¹²⁾ gives atomic absorption coefficients (for all the alkali metals) as a function of wavelength. The experimental results presented can be explained in part by theory, but some features cannot be predicted. These results are used in a later section in calculations of radiation attenuation in the ultraviolet region. To avoid duplication of existing data, we did not conduct additional experiments in this region.

In addition to a continuous absorption due to the photoionization effect on vapors in the atomic state, the molecular absorption coefficient has been evaluated by Ditchburn in some regions. Data on the molecular absorption coefficient is difficult to obtain and not as reliable as data on atomic absorption coefficients. In general, the molecular absorption coefficient is an order of magnitude greater than the atomic absorption coefficient. However, for most alkali metals under normally encountered conditions, the fraction of molecules is much smaller than that of unassociated atoms. Therefore, radiation attenuation by atomic absorption is the more important phenomenon.

3. Molecular Band Absorption

Radiant energy absorption by molecules can be divided into several types according to the portions of the spectrum in which they occur. Absorption in the microwave and far infrared is due to changes in the rotational energy of the molecule; absorption in the near infrared corresponds to changes in vibrational energy of the molecule. Energy absorption in the ultraviolet and visible regions (electronic band absorption) is due to changes in electronic energies of the molecule. The molecular absorption bands are made up of groups or branches of lines which occupy specific positions, depending on the vapor under consideration. Individual lines may, in some cases, overlap, and these cannot be resolved with practical laboratory instruments. There are selection rules to specify what type of energy changes can occur and what the band structure will resemble in view of these changes. From a detailed knowledge of the band systems of gases, calculations can be made to predict the absorption coefficients, absorptivity, and emissivity of the gas. The calculations are, in general, long and complex, and require fairly detailed knowledge of the absorption spectra. Radiative properties of carbon dioxide and water vapor calculated in this way agree reasonably well with experimental data. A description of the calculation method and procedure is given by Penner.⁽²⁾

Since the alkali metals form only symmetric diatomic molecules (other weakly associated molecular forms are possible but have not been identified positively), the region of electronic band absorption will be of interest. Observed transitions and band frequencies are reported by Herzberg⁽¹³⁾ for the diatomic alkali metal molecules and for some combinations of the metals. The data is extensive in some cases, but fragmentary in others. Table I shows the location and source of several observed band heads for the alkali metals. In addition to these bands, diffuse bands near the principal series lines have been observed. These are due to weakly bonded van der Waals molecules and are probably of little significance in absorption of large amounts of energy.

From this background information, we have concluded that absorption of radiation by alkali metal vapors over broad portions of the spectrum encountered in radiant heat transfer operations is due to two principal mechanisms: photoionization and molecular band absorption. A direct transmission technique was used in this work to obtain semi-quantitative data on the molecular absorption. This data, when combined with available literature information on absorption due to photoionization, should supply information on absorption of radiation by and heat transfer through gases containing alkali metal vapors.

B. VAPOR PRESSURE OF ALKALI METALS

In the experimental study of absorption of radiation by alkali metal vapors and for the practical application of the results, it is necessary to know the vapor pressure of the alkali metal as a function of: (1) temperature, and (2) the fractions of the vapor which are in monatomic and diatomic form. Accurate vapor pressure data for the alkali metals is difficult, because of dimerization of the vapor. A review of experimental methods for obtaining vapor pressure data is given by Ditchburn and Gilmour⁽¹⁴⁾ along with vapor pressure data on the alkali metals. More information is available on sodium vapor than on the other alkali metals;

TABLE I

OBSERVED ABSORPTION BANDS OF ALKALI METAL VAPORS

<u>Vapor</u>	<u>Observed Transitions ($1/\nu_{\infty}$) ($\text{\AA}$)</u>					
Sodium	6281	4925	3410	3132	3013	
Potassium	8568	6507	4357	4063	3776	3629
Cesium	7669	6227	6185			
Rubidium	6822	4802	4392			
Lithium	7132	4902	3279			

Data from Herzberg⁽¹³⁾

an extensive review of the vapor pressure of sodium is given by Sittig.⁽¹⁵⁾ The following description of the principles for and problems of obtaining information on the vapor pressure of sodium is characteristic of all alkali metals.

As sodium vapor is heated, it dimerizes by the reaction:



The equilibrium for the reaction can be expressed as:

$$\frac{(P_{\text{Na}_2})^{1/2}}{P_{\text{Na}}} = K \quad (4)$$

where P_{Na_2} and P_{Na} are the partial pressures of diatomic and monatomic sodium vapor, and K is the equilibrium constant given by the relation:

$$\Delta F_D^0 = -RT \ln K \quad (5)$$

where ΔF_D^0 is the free energy of dimerization, T is the absolute temperature, and R is the gas constant. Equation (3-4) indicates that the partial pressure of sodium molecules (at equilibrium) is proportional to the square of the pressure of sodium atoms. The free energy of dimerization can be obtained from the relation:

$$\Delta F_D^0 = (\Delta F^0 - \Delta H_0^0)_D + \Delta D_0^0 \quad (6)$$

where ΔF^0 is the free energy change in the ideal gas state and ΔH_0^0 and ΔD_0^0 are the heat of dimerization in the ideal gas state at absolute zero. The sum $(\Delta F^0 - \Delta H_0^0)$ is available from molecular and spectroscopic data alone. Published values of the free energy functions given by several authors^(16, 17) differ only slightly. Accurate values of ΔD_0^0 are more difficult to obtain, and there is considerable discrepancy between reported values. Emission spectrum measurements⁽¹⁸⁾ gave a value of 9300 ± 500 cal/gm atom Na for $-\Delta D_0^0$. Other spectral techniques⁽¹⁹⁾ have resulted in values of $-\Delta D_0^0$ of from 8760 ± 230 to 8400 ± 100 cal/gm atom Na. An example of the effects of error in the evaluation of $-\Delta D_0^0$ has been given by Sittig.⁽¹⁵⁾ These effects are shown in the following table:

Dimerization Energy - ΔD_0^0 (cal/gm-atom _{Na})	Mole % Na ₂ in Equilibrium Vapor at Listed Temperatures	
	600° K	1000° K
8000	0.4	5.2
8500	1.0	8.1
9000	2.3	12.2
9500	4.9	17.7

Thus, a small error in dimerization energy greatly influences the fraction of molecules calculated from Equation (4).

Experimental measurements of sodium vapor pressure have been reviewed by Sittig,⁽¹⁵⁾ Ditchburn,⁽¹⁴⁾ and Kelley.⁽²⁰⁾ There is considerable variation of the experimental data; the data of Thiele⁽²¹⁾ is close to calculated values using 9100 cal/gm atom Na for $-\Delta D_0^0$ (the "best" value according to Sittig). Work is still necessary to obtain better values of $-\Delta D_0^0$ and more accurate values of the fraction of molecules and atoms in equilibrium vapors.

Figure 1 shows the vapor pressure and temperature data for monatomic and diatomic sodium vapor from several sources. The values calculated by Sittig⁽¹⁵⁾ have been accepted for use in this study. Figure 2 shows vapor pressure data for other alkali metals reported by several authors.

C. CHEMICAL REACTIVITY OF ALKALI METALS

The alkali metals and their vapors are very reactive with other materials, and consideration must be given to these reactions when an absorption cell is designed. The reactions of sodium or sodium-potassium alloys with metals and non-metals have been extensively studied, since the liquid metals have many applications in heat transfer operations. Safe handling techniques, and chemical properties of the liquid sodium and alloys are described by Sittig⁽¹⁵⁾ and by the Atomic Energy Commission.⁽²²⁾ The reactions of sodium vapor are expected to be similar to the liquid phase reactions. Information on reactivity of the other alkali metals is available in the Liquid Metals Handbook⁽²³⁾ and other reference texts.⁽²⁴⁾

In general, the alkali metals and their vapors react with water to form the hydroxides and hydrogen. The reaction may be slow or vigorous depending on the metal and the concentrations present. The reactivity of the alkali metals increases with increasing atomic weight. A brief summary of the properties of the alkali metals and of their reaction with other compounds, relative to this study, is presented here as a guide for laboratory precautions and to indicate which materials can be used in the presence of alkalis.

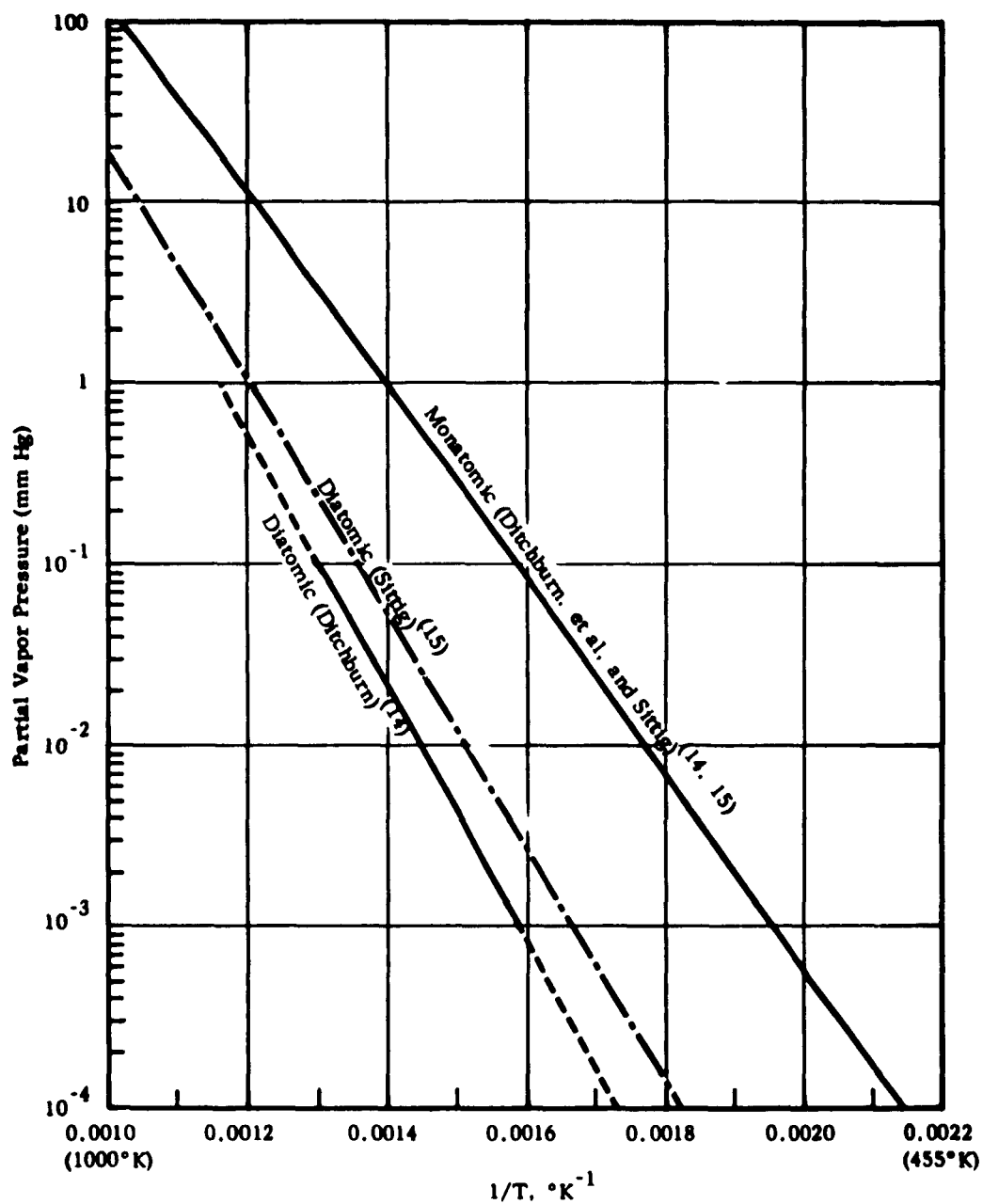


FIGURE 1
VAPOR PRESSURE OF MONATOMIC AND DIATOMIC SODIUM

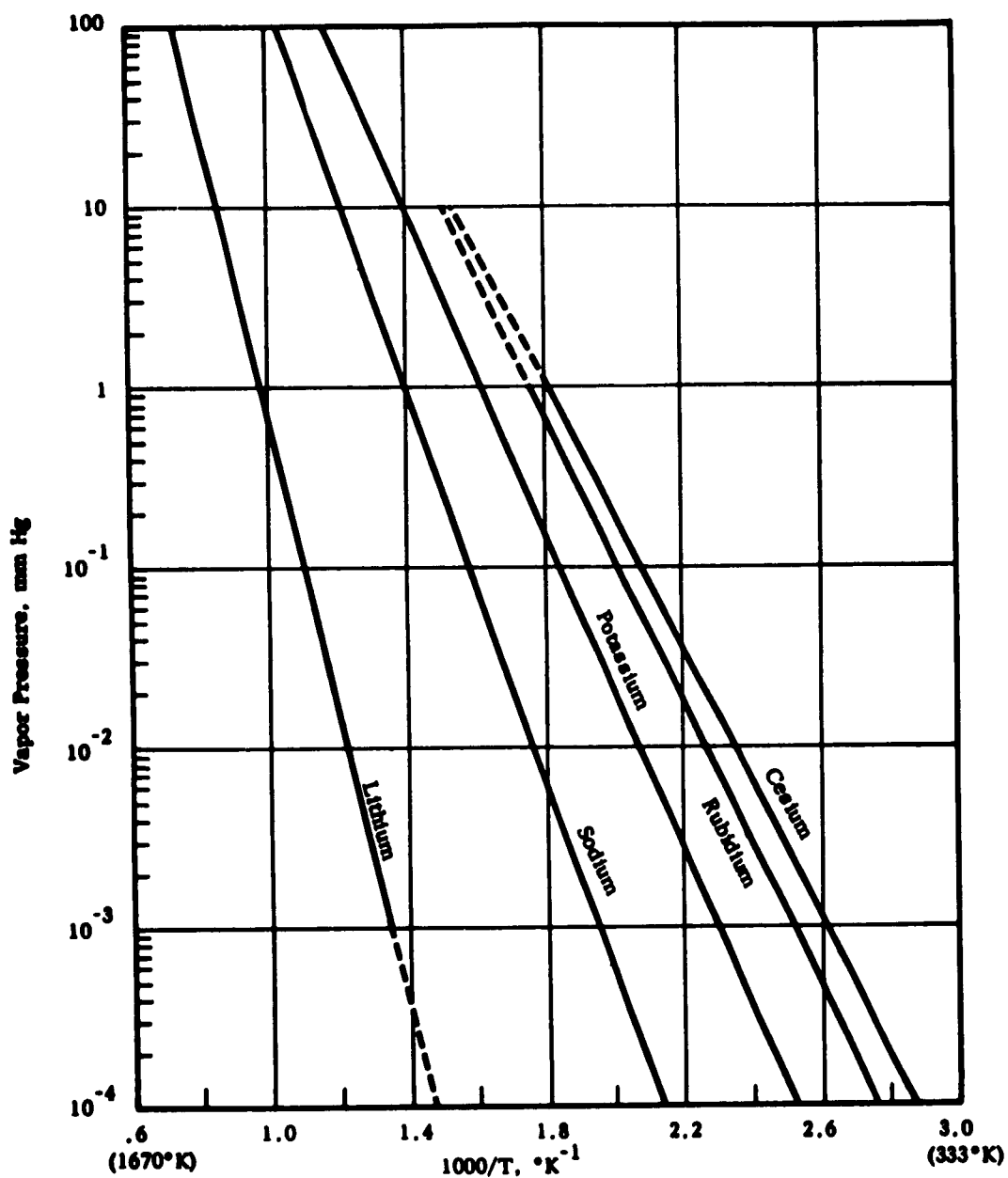


FIGURE 2
VAPOR PRESSURE OF MONATOMIC ALKALI VAPORS

1. Sodium

Sodium is a silvery white metal melting at 97.8°C and boiling at 883°C. It reacts with air to form the oxide. Sodium will burn with a yellow flame in oxygen, forming the oxide and peroxide. Its reaction with water is energetic and may result in explosions, due to the hydrogen formed in the reaction. Liquid sodium reacts with hydrogen gas to form the hydride, but does not react with nitrogen or the noble gases. Sodium may be easily handled in liquid or vapor form by eliminating moisture and oxygen from the system. Most stainless steels, nickel alloys, and refractory metals are usable as container materials and will not corrode at temperatures below 800 to 900°C. Copper and its alloys may be used at temperatures up to 300 to 400°C; aluminum alloys are not recommended for general use. Most glasses (Pyrex, Vycor, Lead) are rapidly attacked by sodium and its vapor at temperatures above 300°C; sapphire may be used for moderate times at 400°C. In an optical system, however, slight attack of windows can give very unreproducible results. In our work, Inconel Type 304 stainless steel, and graphite (ATJ or Reactor Grade E21) were used in contact with sodium; dry argon was used as the inert material for gas shielding. The sodium used in the experiments was analytical reagent grade.

2. Potassium

Potassium has a melting point of 63.7°C, a boiling point of 760°C, and is slightly more reactive than sodium. It reacts with air and oxygen to form the monoxide at low temperatures and the peroxide at higher temperatures. It reacts violently with water and may form an explosive carbonyl when reacted with carbon monoxide. The vapor appears to have a greenish color at low temperatures and a violet color at high temperatures. Container materials suitable for sodium are generally useful for potassium. Potassium also attacks most glass surfaces. In our work we found it impossible to use potassium in contact with graphite; stainless steel, however, showed no reaction. Potassium is generally stored under saturated aromatic and aliphatic hydrocarbons to prevent oxidation. Nitrogen and the noble gases do not react with potassium significantly. Potassium used in our experiments was technical grade with sodium as the major impurity.

3. Lithium, Cesium, and Rubidium

These materials were not used in the experimental portion of this work. Lithium is similar to sodium and potassium, but less reactive. It reacts with oxygen and water to form the oxide or peroxide. It reacts with nitrogen to form Li_3N , in contrast with other alkali metals. Although it is generally less reactive, it forms many alloys with metals and thus may be difficult to contain.

Cesium is the most volatile of the alkali metals and is very reactive. It burns in air and must be kept shielded with oil or inert gas. Cesium reacts violently with water and water vapor, but is inert to argon, helium, and nitrogen. At low temperatures, cesium does not attack other metals and glasses as rapidly as the other alkalis.

Rubidium lies between potassium and cesium in reactivity and other properties. It ignites in air and oxygen and burns with a bluish flame. It is also stored under an inert fluid such as oil or benzene. Rubidium reacts violently with water and forms alloys with many metals. It is inert to nitrogen, argon, and helium.

IV. PRELIMINARY EXPERIMENTS

In order to confirm the type and size of the apparatus required to measure the absorption of radiant energy by alkali metal vapors, we constructed an experimental absorption cell and conducted several introductory experiments. The initial study indicated that the significant absorption of light by sodium vapor could be measured by fairly simple techniques. The work also pointed out some of the difficulties which we might encounter in later experiments.

A. PRELIMINARY APPARATUS

Figure 3 shows a photograph of the preliminary absorption cell and accessory apparatus. The cell was constructed from a stainless steel tube one inch in diameter and 36 inches long. Pyrex windows were mounted in flanges attached to the ends of the tube. Vacuum and inert gas connections were placed at each end of the tube. Water cooling coils were fixed to the ends of the cell. A chromel-alumel thermocouple (contained in a stainless steel sheath) was placed within the cell. The absorption cell was placed in a standard tube furnace; the temperature of the furnace and cell was regulated by using a variac transformer. We did not attempt to control temperature along the length of the cell. A tungsten strip lamp placed at one end of the cell was used as a radiation source. A Weston light meter or type 931-A photomultiplier tube was placed at the other end of the cell. Visual observation of the vapor was made with a Beck reversion spectroscope.

The sodium to be vaporized was placed in a small tantalum-foil boat and located at the center of the absorption tube. From thermocouples located on the outside of the absorption cell, we determined the location of the highest furnace temperature; and the alkali metal boat was placed at this corresponding location within the cell. The sheathed thermocouple was positioned close to the boat so that its temperature and the corresponding vapor pressure of the alkali metal vapor could be determined.

In the attempt to establish a fixed vapor path, two vapor barriers were placed within the cell. Each of these consisted of a tube $\frac{1}{2}$ inch in diameter, 8 to 10 inches long, and held concentric with the cell by spacers. (See Figure 8.) The spacers filled the one-inch tube and prevented diffusion of vapor through the annulus formed by the two tubes. The vapor barriers were placed in the cell leaving free spaces of two or four inches. These vapor barriers did not perform satisfactorily, for reasons discussed later.

In the operation of this apparatus, the tungsten bulb was set at a fixed temperature, the furnace temperature was raised in small increments, and the reading of the light meter or photomultiplier tube (connected to a micro-ammeter) was recorded. After the maximum temperature for any experiment was reached, the furnace was cooled slowly and cleaned before the next test.

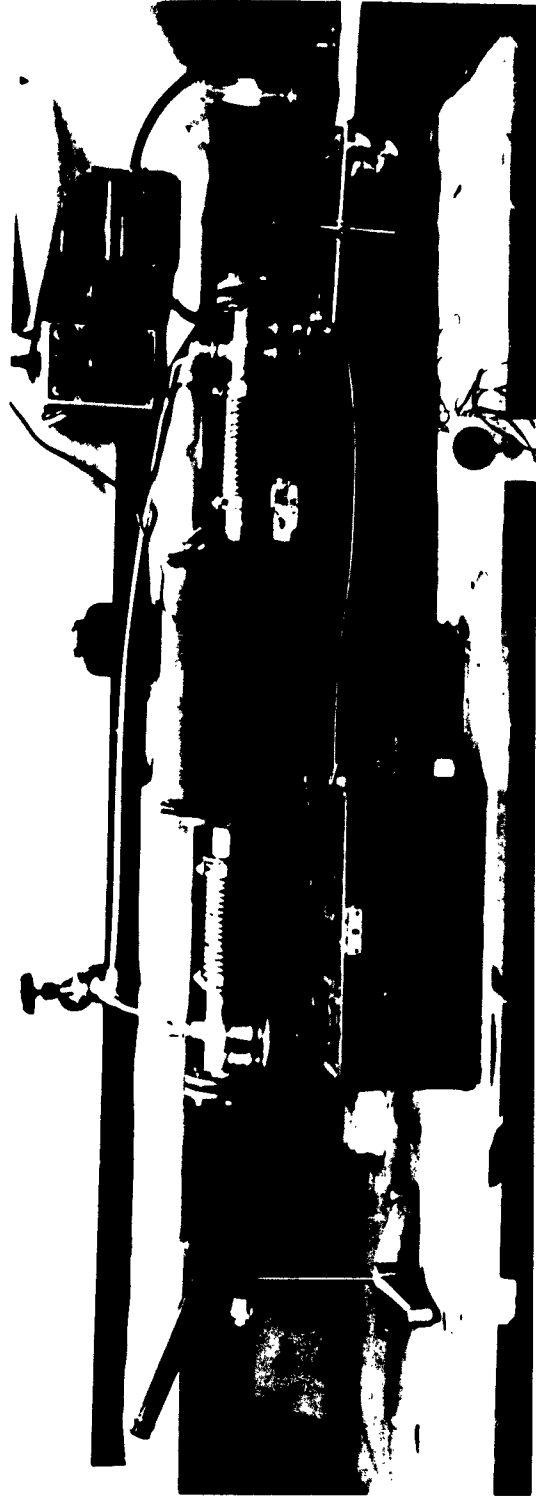


FIGURE 3
PHOTOGRAPH OF PRELIMINARY APPARATUS

B. RESULTS OF PRELIMINARY TESTS

Figure 4 shows the results of the preliminary tests. The relative transmission of radiant energy through sodium vapor is plotted as a function of the maximum vapor pressure in the tube. The maximum vapor pressure is assumed to be that in equilibrium with liquid sodium at the temperature of the tantalum boat. Three curves are shown, representing different detectors and different vapor path lengths. It is apparent that the relative transmission of light decreases rapidly with increasing vapor pressure. The results using the photomultiplier and light meter were quite similar. This would be expected if the absorption of energy is uniform throughout the entire spectrum measured by these detectors or if the detectors measure essentially the same spectral region with the same sensitivity. An example of the absorption in different regions of the spectrum is given in Figures 5, 6, and 7, which show spectrograms observed through the reversion spectrometer. At low temperatures and corresponding low partial pressures of the alkali vapor only the narrow "D" lines are observed (Figure 5). As the vapor pressure is raised, the "D" lines become broader. Further increase in the pressure produces bands in the red and blue regions, due to the formation of sodium molecules (Figure 6). At the point where Figure 7 was taken, only a small amount of light was transmitted through the vapor column, and the vapor appeared dark green.

Experiments conducted with two apparently different vapor path lengths gave unexpected results. This can be resolved by consideration of the actual vapor path and the dimensions indicated in the diagram in Figure 8. The vapor can be assumed to fill the large central section of the cell to almost a constant pressure, i.e., a constant partial pressure of the alkali metal vapor. The partial pressure of the vapor within the vapor barrier zones varies from P_0 at the end adjacent to the central section to a very small value near zero at the cold end. The product of path length times partial pressure, the quantity which is important in determining the intensity of the transmitted light, can be given approximately by the following expression:

$$\text{path length} \times \text{pressure} = P_0 L_0 + (2) (1/2) (P_0) L \quad (7)$$

since the average pressure in the barrier zone is approximately $1/2 P_0$. The dimensions are shown in Figure 8. Thus, changing the path L_0 from two to four inches--as was done in the experiments--actually only increases the "total" path length-pressure product by about 17 per cent. The energy transmission through the cell would not be expected to decrease greatly for the change in length of the central portion actually used in the experiments.

The preliminary experiments pointed out that with absorption cells with vapor path lengths of from four to ten inches, absorption of radiation in the visible region would be large enough to be easily measurable. The problem of accurately specifying the vapor pressure distribution and the path length was emphasized. Preliminary results also showed that use of interference filters to measure transmission in different spectral regions would be valuable in studying the absorption of alkali metal vapors.

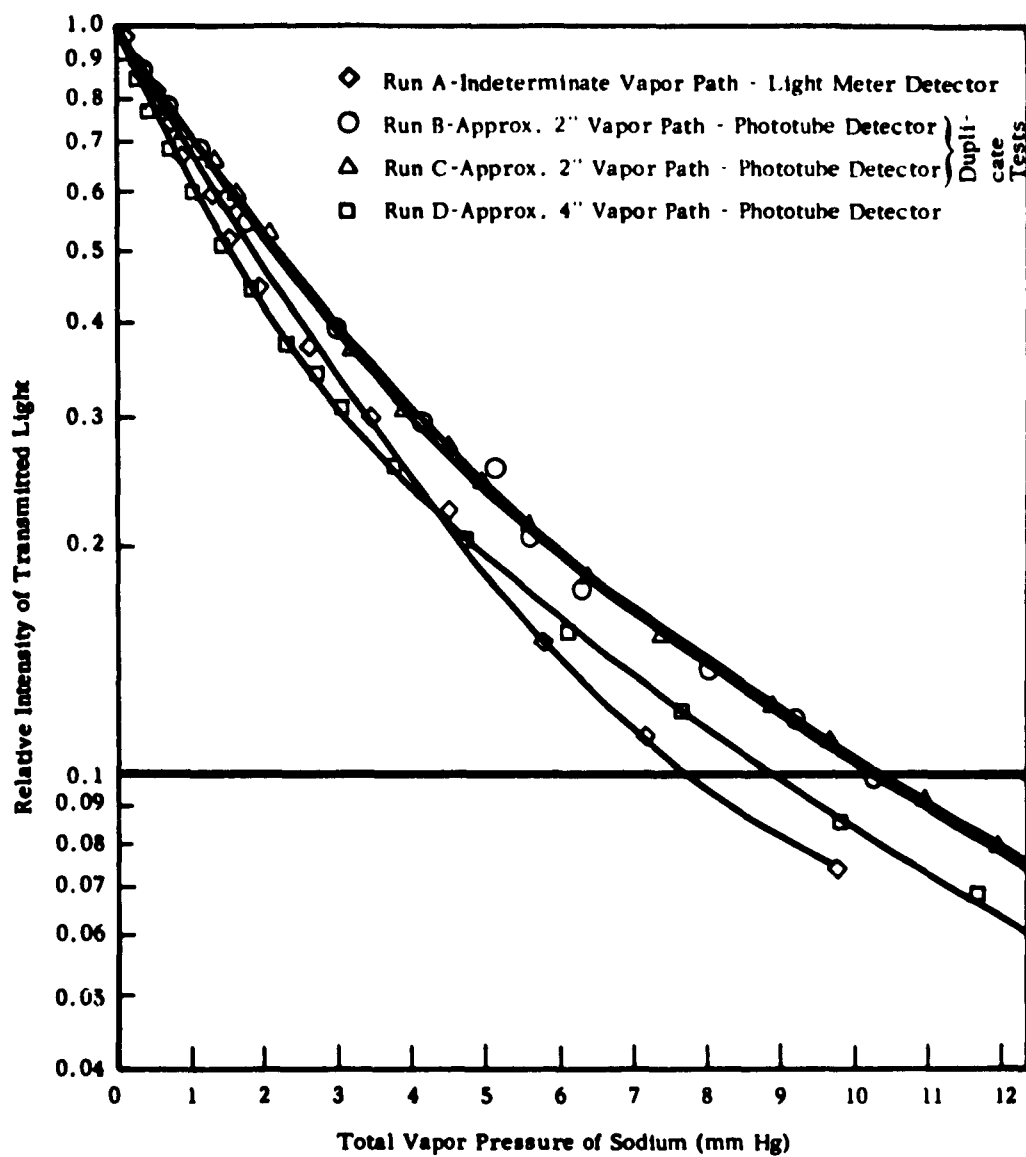


FIGURE 4
RESULTS OF PRELIMINARY TESTS



FIGURE 5



FIGURE 6



FIGURE 7

SPECTRA OF SODIUM VAPOR THROUGH BECK REVERSION SPECTRASCOPE

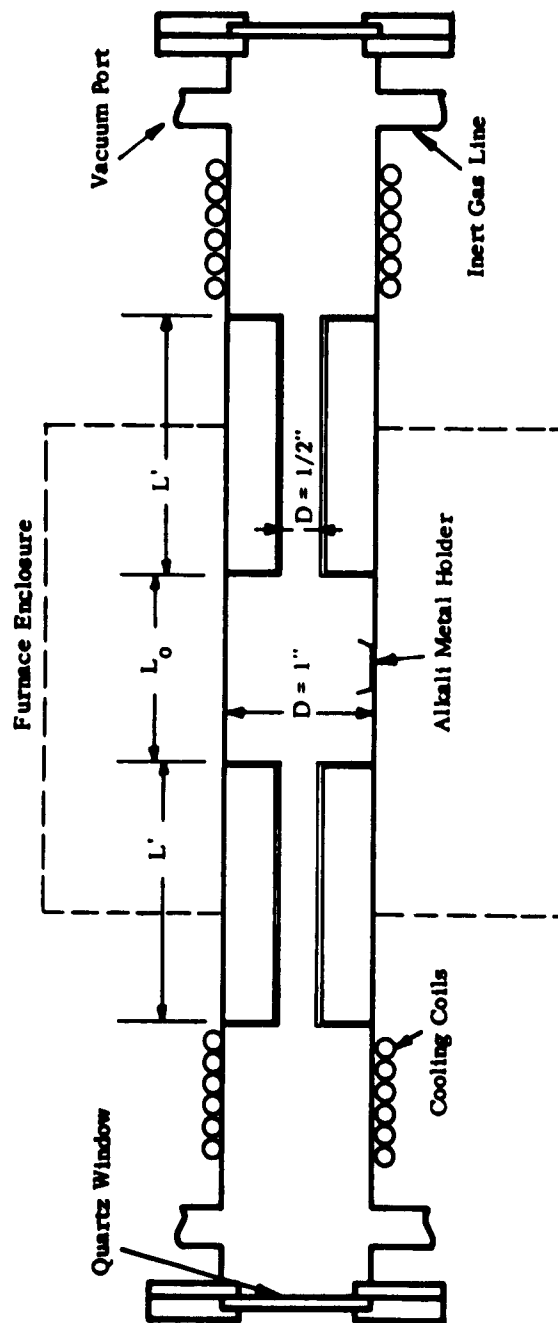


FIGURE 8
DIAGRAM OF PRELIMINARY ABSORPTION CELL

V. EXPERIMENTAL APPARATUS

A. ABSORPTION CELL

1. Absorption Tube and Heaters

Based upon the results of the preliminary experiments, we designed and constructed the absorption cell shown diagrammatically in Figure 9. The absorption tube consists of a 3/4-inch i.d., schedule 40 Inconel pipe, 40 inches long. The end pieces are two inches long, and each contains vacuum and inert gas connections, a thermocouple feed-through, and a one-inch diameter quartz window. "O" rings are used to seal the windows to the end sections and the end piece to the absorption tube. The end sections can be removed and reassembled rapidly. There are no constrictions in the absorption tube to hinder removal of the vapor barriers or to prohibit cleaning. Six-inch lengths of 1/4-inch copper coils are wrapped around the absorption tube near the ends of the tube. The absorption cell was heated in several sections. For experiments using both eight-inch and four-inch nominal vapor path lengths, three primary heaters and four auxiliary heaters were used. Temperatures of the cell were regulated by controlling the heater voltages with variable transformers and were measured at 16 points along the heated portion by chromel-alumel thermocouples. The thermocouple output was read on a 16-point recorder so that a continuous record of absorption cell temperatures could be obtained during the experiments. A discussion of the temperature profiles obtained in the cell is given later.

2. Vapor Barriers and Alkali Metal Boats

Several types of vapor barriers were used to obtain specified vapor path lengths. Figure 10 shows a photograph of the graphite vapor barrier used in sodium experiments with an eight-inch vapor path. The ridges on the outside of the barrier eliminate "light leakage" and provide for smooth insertion of the barrier into the absorption cell. As shown in the figure, stainless steel boats were attached to the inner face of the barrier. Directly above the boat in the center of the barrier is a small hole through which the light beam passes (and the vapor diffuses). The stainless steel is trimmed away from the hole in order not to obstruct the light path. The hole was 1/2 inch long and its diameter was varied from 0.060 to 0.125 inches. A 1/2-inch-diameter threaded hole was drilled through the remainder of the vapor barrier. The barrier could be accurately positioned within the cell by using a long rod threaded into the 1/2-inch hole. A stainless steel sheathed chromel-alumel thermocouple was passed through a hole near the periphery of the vapor barrier; the thermocouple junction was in direct contact with the stainless steel boat. The thermocouples used to measure the temperature of the boat and alkali metal were calibrated at the freezing and boiling points of water and at the freezing point of zinc (419.4°C). During the experiments the boat temperatures were read on a Leeds & Northrup potentiometer.

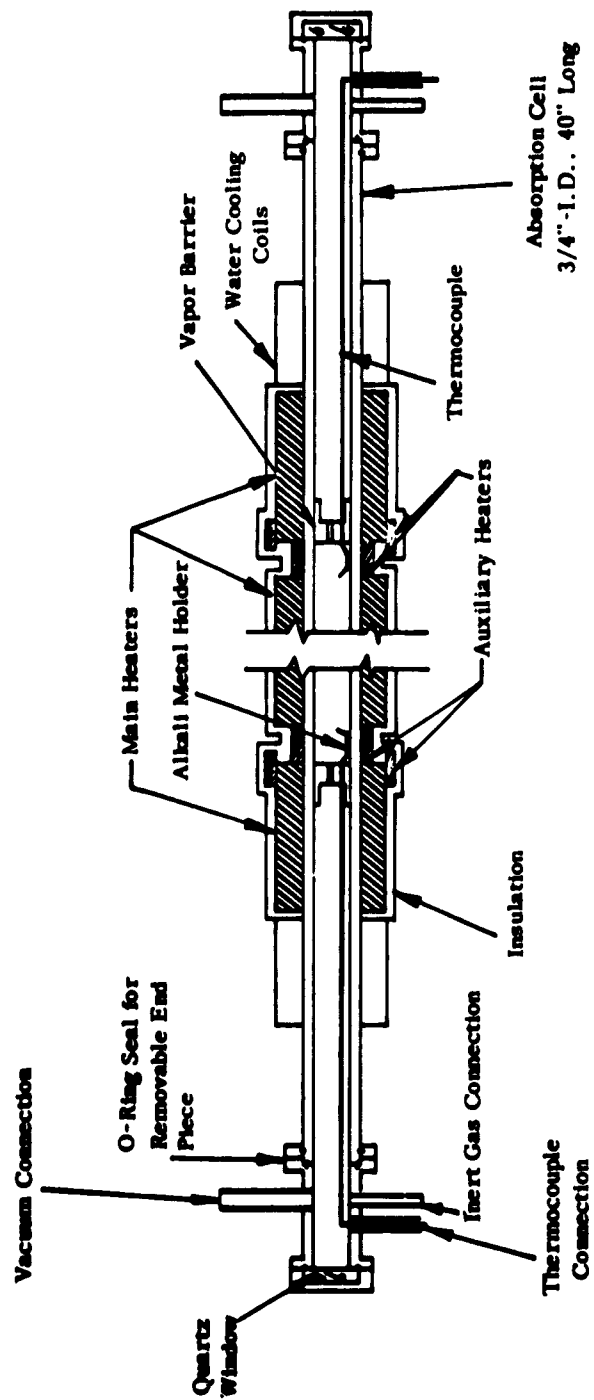


FIGURE 9
ABSORPTION CELL

The graphite vapor barriers performed satisfactorily during the sodium experiments. However, when potassium was used, the barriers were rapidly attacked by the vapor, and the light path became obscured. Figure 11 shows a photograph of a vapor barrier after reaction with potassium vapor. Stainless steel vapor barriers of similar design but slightly shorter over-all length were fabricated and used in all potassium vapor experiments and in experiments with a four inch sodium vapor path. These barriers showed no apparent reaction with the alkali metal and could be inserted into the absorption tube easily with little light leakage around the edges.

Two alkali metal boats were used in the experiments with an eight-inch vapor path; each was attached to a center-face of the vapor barrier. During any experiment, the temperatures of the boats were matched to within 2°C. A single stainless steel boat was used in the experiments with a four-inch vapor path. The boats were about 1/2-inch long, 1/4-inch high, and shaped like a segment of a cylinder with the center hollowed out to contain the alkali metal. A thermocouple was attached to the boat and was used to position the boat as well as to obtain the temperature of the alkali metal.

B. CALIBRATION TUBE

A water-cooled calibration tube was constructed to serve as a standard and eliminate the effects of: drift in photomultiplier sensitivity, instrument response, and small fluctuations in the intensity of the radiation source. The calibration tube consists of a copper pipe two inches in diameter and 46 inches long. Diaphragms containing small holes are fastened to each end of the tube. Hole size is adjusted to give approximately the same transmission as through the absorption cell (with no vapor present). The interior of the tube is painted with an optical black paint. Water cooling was incorporated to reduce temperature changes, since the calibration tube was located adjacent to the heated absorption cell. The calibration tube can be firmly fixed on the optical axis while the absorption cell is slightly displaced by rotation on hinged supports. After the transmission measurement is made, the calibration tube is removed, and the absorption cell is returned to the optical axis of the system.

C. OPTICAL COMPONENTS

Figure 12 shows a schematic diagram of the optical components and instrumentation used in the experiments. A tungsten strip lamp was used as a radiation source; its temperature was periodically measured by a calibrated Micro-Optical Pyrometer. A thick ground quartz slide (1-mm thick) was placed in front of the source to diffuse the radiation. Kodak neutral density Wratten Filters, mounted between quartz microscope slides, were used to attenuate the beam. A typical transmission curve for this filter is shown in Figure 13. Radiation transmitted by the Wratten filter passed through the quartz cell window, through the hole in the vapor barrier, and into the "vapor space." The radiation transmitted by the vapor was attenuated by the hole in the second vapor barrier and then passed through the second quartz cell window. Interference filters (Baird Atomic, Type B-5) were used to transmit radiation of specific wavelength bands. Four filters were used; their peak transmittance

occurred at 4545, 5505, 6515, and 7325 Å and the band width was approximately 15-20 per cent of the peak transmission wavelength. Figure 14 shows transmittance curves of the filters. Radiation transmitted by the interference filter passed through a ground quartz diffusion disc onto the photomultiplier tube. In the initial experiments, an RCA type 931-A tube was used. However, an RCA type 6217 gave more reproducible results over the wavelength region covered by the interference filters and was used for the majority of the tests. The 6217 tube has a type S-4 spectral response curve; it has a peak response between 3600 and 5800 Å, but gives a reasonable signal throughout the range investigated. An Eldorado Photomultiplier Photometer was used to supply the voltage for the tube to measure the intensity of the transmitted light. The instrument has provisions for suppressing the dark current and can read intensities over a 10^4 range. Calibration tests indicate the response of the instrument to be reasonably linear over the range of intensities used. A copper, light-tight, blackened housing encases the photomultiplier tube and the interference filter stray light is reduced in other portions of the system.



FIGURE 10
GRAPHITE VAPOR BARRIER USED IN SODIUM EXPERIMENTS

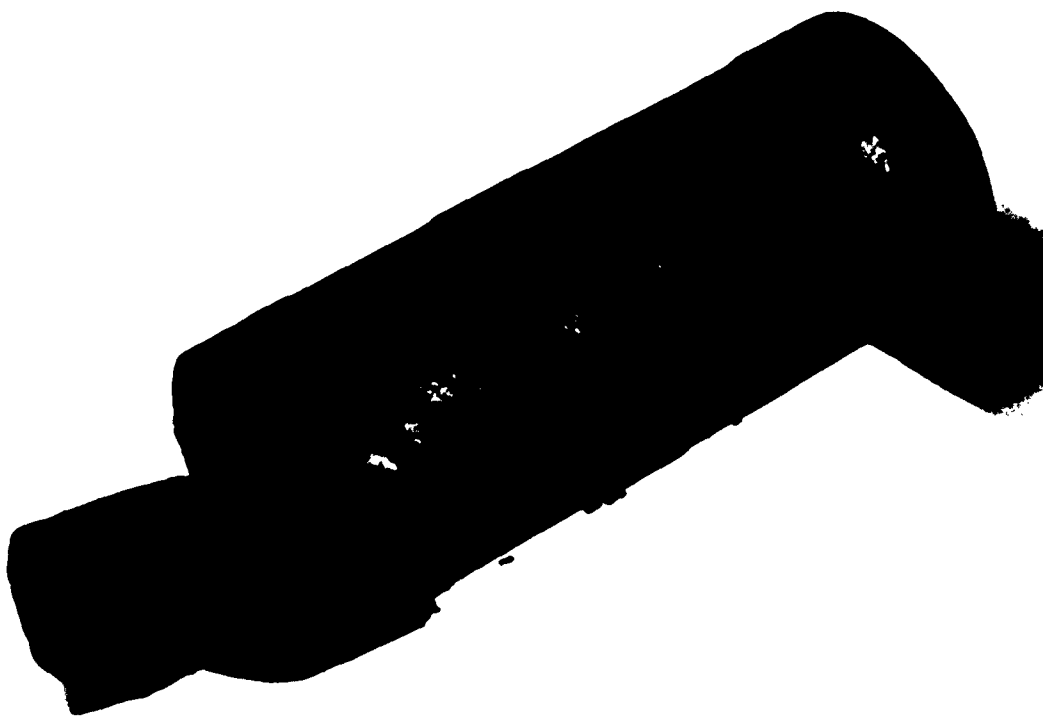


FIGURE 11
GRAPHITE VAPOR BARRIER AFTER ATTACK BY POTASSIUM VAPOR

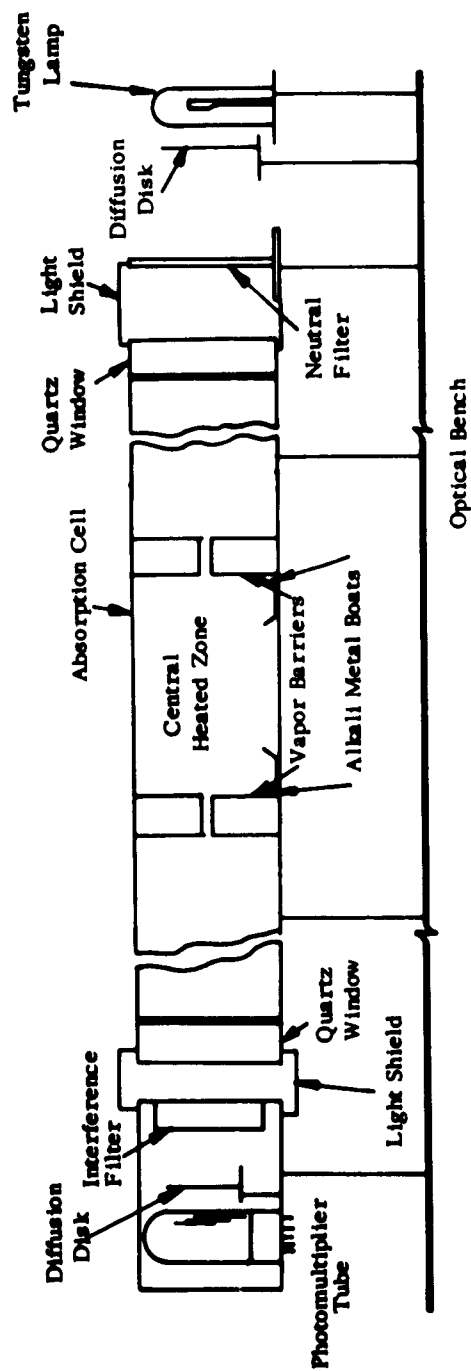


FIGURE 12
SCHEMATIC DIAGRAM OF OPTICAL COMPONENTS

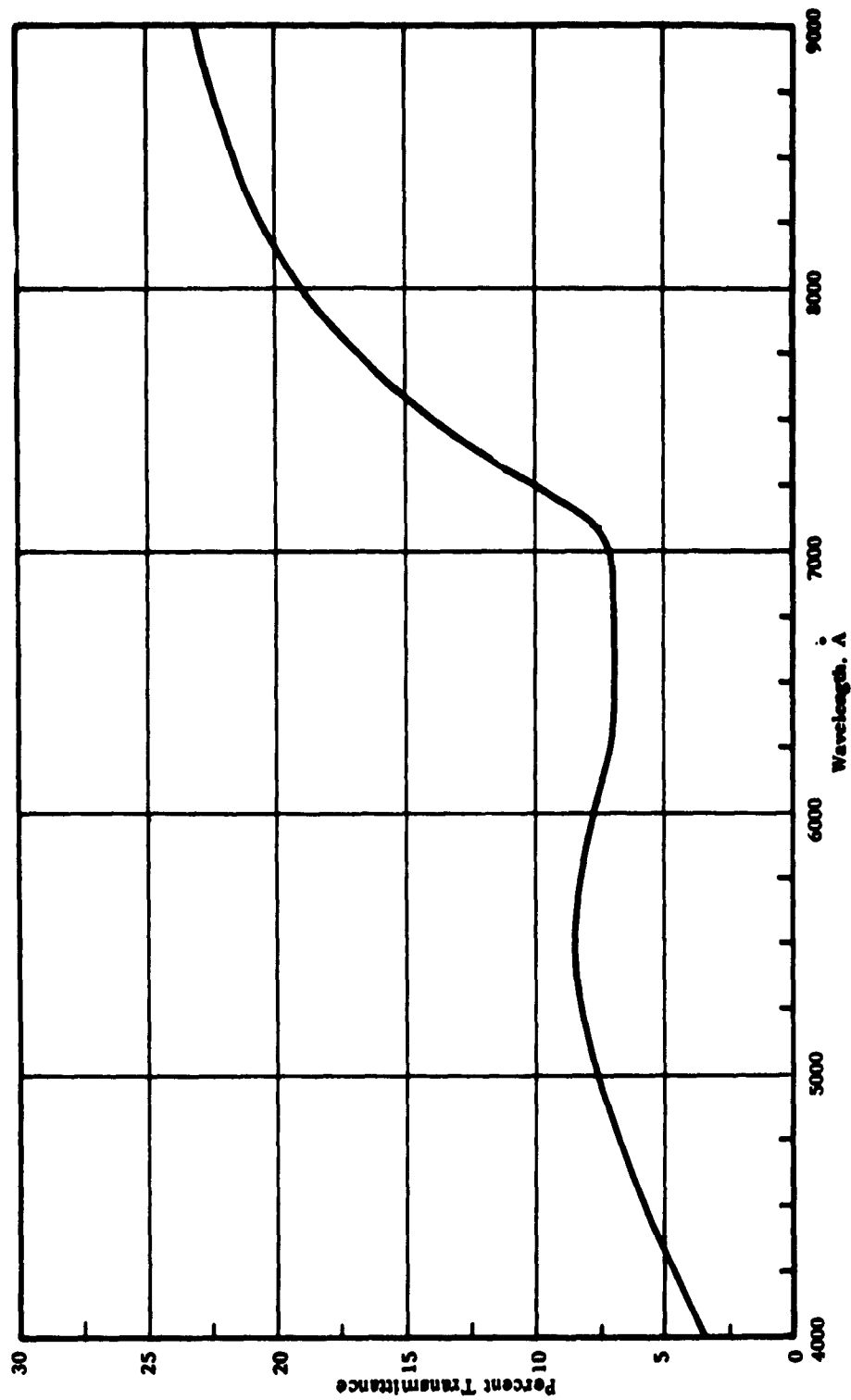


FIGURE 13

TRANSMITTANCE OF WRATTEN FILTER NO. 1 PLACED BETWEEN TWO QUARTZ PLATES

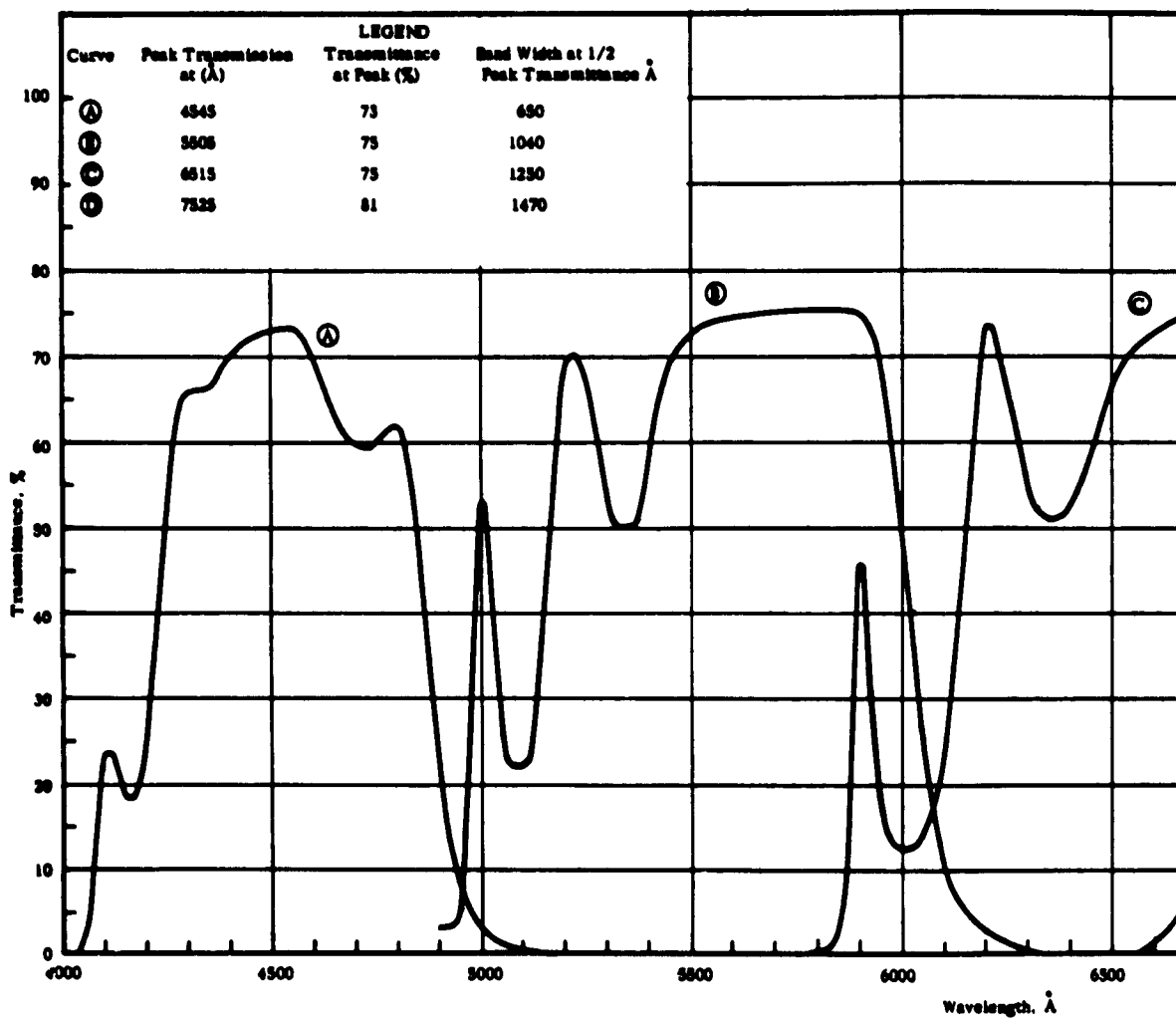


FIGURE 14

TRANSMITTANCE OF INTERFERENCE



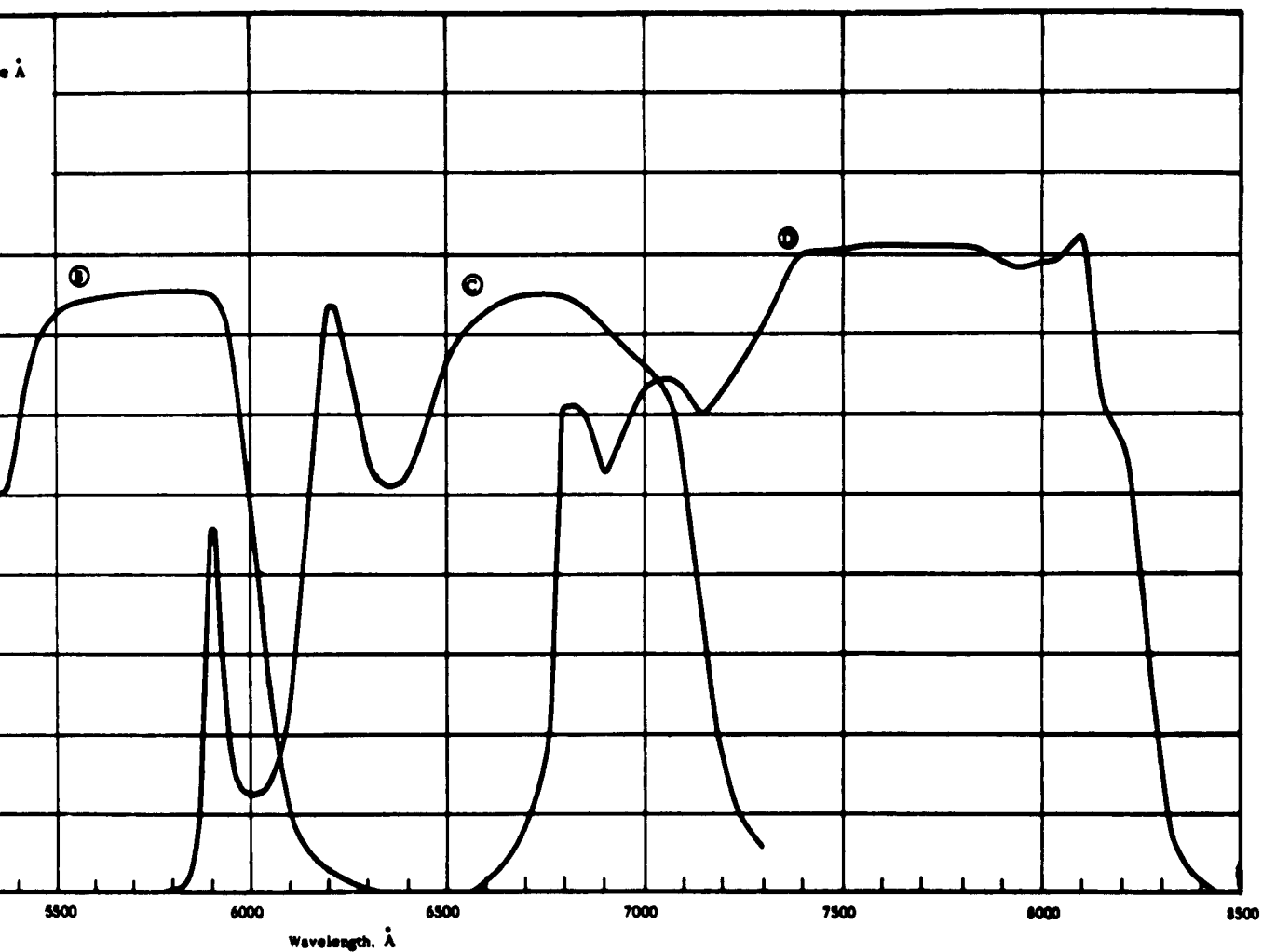


FIGURE 14

TRANSMITTANCE OF INTERFERENCE FILTERS

VI. PROCEDURE AND DATA REDUCTION

A. EXPERIMENTAL PROCEDURE

The following procedure, with occasional slight variations, was followed in all experimental tests.

1. The absorption tube was aligned on the optical bench, and the lamp, filter, holder, and phototube were fixed in place.

2. The ends of the absorption cell were removed, and the alkali metal, stainless steel boats, and graphite or stainless steel vapor barriers were positioned within the cell. Thermocouples were positioned, and the ends of the absorption cell were returned to their original location. During this time the alkali metal and absorption tube were kept under a blanket of dry argon.

3. The tungsten lamp was set at a desired temperature (1675°C), the photometer compensated for dark current, one of the interference filters was inserted in the optical path, and a measurement of light transmitted through the absorption tube was made. (During this experiment the absorption cell was at room temperature with water flowing through the cooling coils.) The absorption cell was rotated from the optical axis, and the calibration tube placed in the optical axis. The transmission of light through the calibration tube was measured. Different interference filters were placed in the optical path, and the photometer readings of radiation transmitted through the cell and calibration tube were recorded. The temperature of the strip lamp was recorded and checked periodically. When measurements had been made for four interference filters, the strip lamp was adjusted to a new temperature (1920°C), and the procedure was repeated. Measurements were repeated with a lamp temperature of 2170°C. This procedure constituted a "cold run." Ratios of the intensity of radiation transmitted through the absorption cell to that transmitted through the calibration tube ($I_{\text{cell}}/I_{\text{cal}}$) were calculated for different source temperatures and bulb temperatures. In general, there was little variation among the ratios. However, differences in bulb filament position, utilization of different locations on the photomultiplier tube, slight misalignment of the absorption cell and calibration tube on the optical axis, etc., resulted in variations of some ± 8 percent in the values of these ratios for different lamp temperatures, and less than ± 5 percent for different interference filters at the same lamp setting. Particular values of the ratios could be reproduced at any time during the "cold run," so that the variation was not a random type.

4. The cell temperature was raised gradually until the boat or boats containing the alkali metal were at the desired temperature. Boat temperatures corresponding approximately to total vapor pressures of 0.1, 1, 2, 4, 8 and 16 mm Hg were chosen. The temperature profiles in the absorption cell were adjusted so that the temperature of the alkali metal boat was lower than the remainder of the central heated portion. The remainder of the vapor space (including the vapor barriers) was kept 15 to 25°C above the boat temperature to prevent condensation on the tube wall. Thus, the vapor in the central portion of the tube was

slightly superheated above the saturation temperature. Typical temperature profiles are shown in Figures 15 and 16, for runs in which one and two alkali boats were used. We carried out several experiments in which we attempted to superheat the vapor 100 to 150°C above the saturation temperature; these will be discussed later.

After the desired temperature profile was achieved, the system was allowed to stabilize for 1/2 to 1-1/2 hours. When all temperatures were steady, transmission measurements were made. The same technique was used, i.e., alternate measurements of the intensity of radiation passing through the cell containing the vapor, and through the empty calibration tube. Measurements were repeated with various combinations of lamp temperatures and interference filters. Temperatures of the alkali metal boats were measured periodically. Ratios of $I_{\text{cell}}/I_{\text{cal}}$ were calculated.

5. The procedure of Step 4 was repeated at a higher absorption cell temperature and higher partial pressures of the alkali metal. During each test, we observed the vapor by eye and through a hand spectrometer. The observations were noted and recorded periodically.

6. After five to eight series of measurements at various alkali metal partial pressures, the absorption cell was cooled. When the cell had returned to room temperature, another "cold run" (Step 3) was conducted.

7. The cell was disassembled, the internal components were inspected, and the parts were cleaned with water and acetone. The apparatus was prepared for the next test.

In six to eight of the calibration tests and experiments, we felt that data obtained were not valid (e.g., runs in which the vapor barriers were attacked, or in which there were problems in obtaining desired temperature profiles). Three tests using both sodium and potassium vapors were carried out with an eight-inch nominal vapor path (i.e., eight inches between the inner face of the vapor barriers). Two tests using both sodium and potassium vapors were conducted with a four-inch nominal vapor path. Several tests in which the vapor in the tube was superheated over 100°C above the saturation temperature were conducted. Each test consisted of measurements in four wavelength bands, three lamp temperatures, and from five to eight average vapor partial pressures. Test duration was from 12 to 20 hours. The total pressure in the absorption cell was maintained at an approximately constant value of one or two psig. Argon was used as the inert gas in all tests.

B. CALCULATIONS AND DATA REDUCTION

When a beam of monochromatic radiation passes through a vapor of constant composition and part of the radiation is absorbed and reradiated, the transmitted radiation can be expressed in terms of the incident radiation, an absorption coefficient, and the vapor characteristics, according to a Beer's law type of formulation given below:

$$I_{\lambda} = I_{0\lambda} \exp (- \sigma_{\lambda} N'L) \quad (8)$$

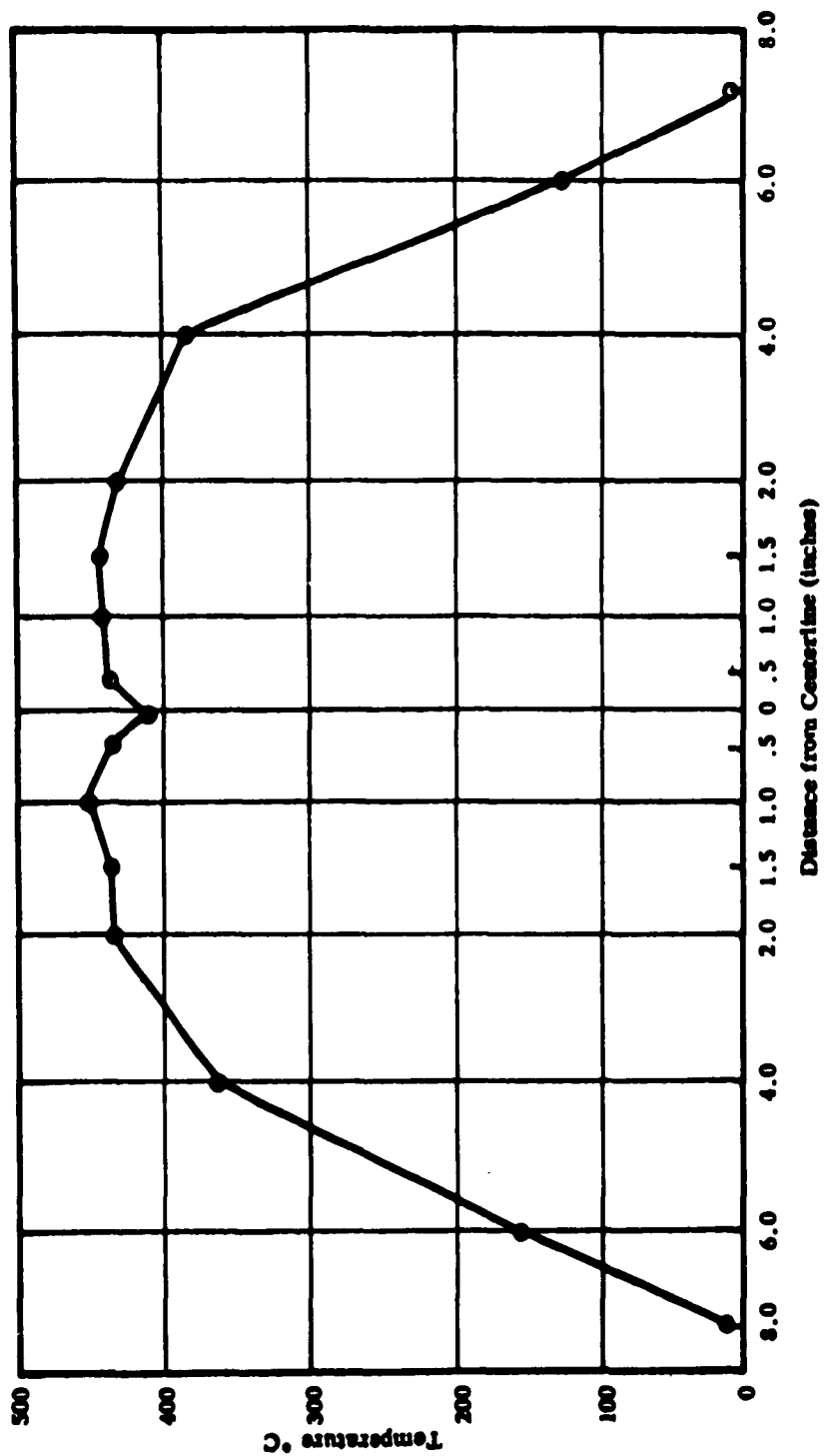
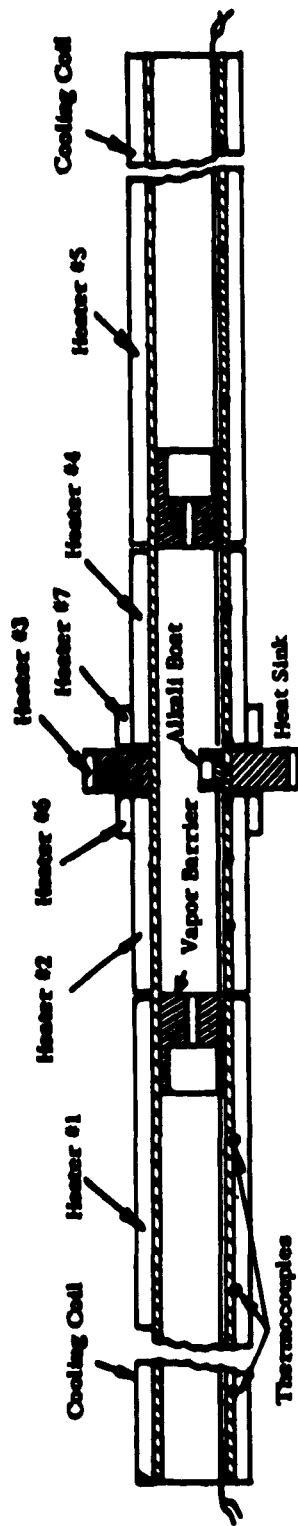


FIGURE 15
TEMPERATURE PROFILE IN ABSORPTION CELL - 4 1/2" VAPOR PATH

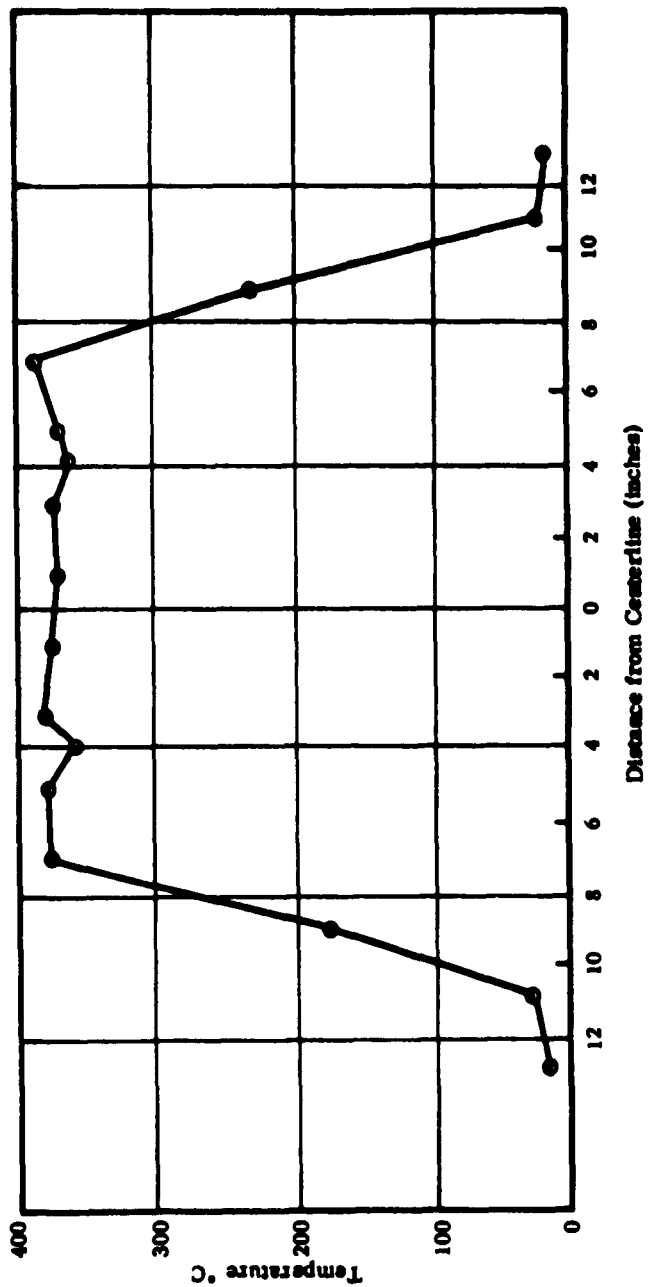
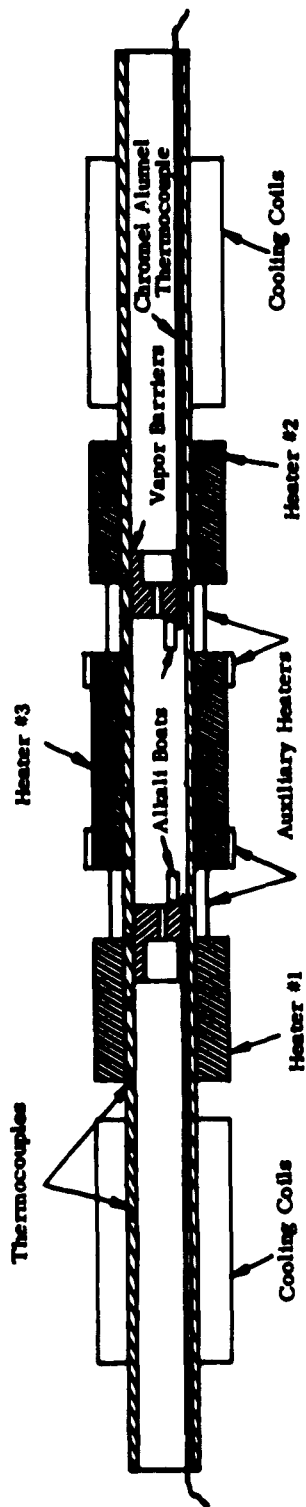


FIGURE 16
TEMPERATURE PROFILE IN ABSORPTION CELL - 8 1/2" VAPOR PATH

where I_λ and $I_{0\lambda}$ are the transmitted and incident radiations, σ_λ is the absorption coefficient at wavelength λ (cross section), N is the number of atoms per unit volume of the absorbing vapor, and L is the path length. This equation indicates that the atoms are absorbing the energy, and is sometimes alternately written in terms of the partial pressure of the vapor as:

$$I_\lambda = I_{0\lambda} \exp \left(-\sigma_\lambda N \frac{273}{T} \frac{P}{760} L \right) \quad (9)$$

where N is the number of atoms/cm³ at standard temperature and pressure, P is the partial pressure of the vapor, and T is its absolute temperature. A plot of $\ln(I/I_0)$ versus $\frac{PL}{T}$ should give a straight line, and the absorption coefficient can be determined from the slope of the curve.

In the experiments, however, monochromatic radiation was not used; instead the transmission over bands of 800 to 1300 Å was measured. If the absorption coefficient is constant over the wave band and the attenuation of radiant energy is due to atomic absorption, a plot of $\ln(I/I_0)_{\text{band}}$ should also be linear with $\frac{PL}{T}$. (There are several other factors, such as response of phototube, source spectrum, etc., which can cause nonlinearity; these will be discussed later.) The data were arranged as plots of $\ln I/I_0$ versus $\frac{Px273}{T}$ and $\frac{PLx273}{T}$. Since absorption is expected to be molecular in nature, it is desirable to interpret the results in terms of number of molecules of vapor. For sodium, molecular vapor pressures are available and can be used; for potassium, it would be best to plot the intensity ratio versus $\frac{K^2P^2L}{T}$, since the molecular pressure should be proportional to the square of the equilibrium constant times the square of the pressure (K , however, varies with temperature).

In reducing and analyzing the data, one needs the intensity ratios, partial pressures, path lengths, and temperatures. The intensity ratios are obtained from the following equation:

$$\left(\frac{I_{\text{cell}}}{I_{\text{cal}}} \right)_{\text{temp}} \times \left(\frac{I_{\text{cal}}}{I_{\text{cell}}} \right)_{\text{cold}} = I/I_0 \quad (10)$$

The first term represents the ratio of light passing through the absorption cell containing vapor to that passing through the calibration tube; the second term represents the ratio of light passing through the calibration tube to that passing through the absorption cell when no vapor is present. By referring the measurements of radiation passing through the cell to measurements of the radiation passing through the calibration tube, we eliminate small variations in source lamp temperature, and photomultiplier amplification or drift.

The average temperature of the vapor in the cell can be determined from the temperature of the alkali boat and the temperature profile in the system. In most cases, the average vapor temperature was 20°C above the alkali boat temperature. In several experiments with a four-inch nominal vapor path, we attempted to superheat the vapor to 100 to 150°C above the saturation temperature. Under these conditions we noticed vapor condensation on the surfaces of the boat and on the absorption cell directly over the alkali boat. The pressure-path length product could not be determined accurately, and the data are not reliable. An alternate method of superheating the vapor has been designed, and is included in our recommendations for future work.

The following discussion summarizes the method of determining the vapor pressure-path length product. Consider a vapor space in a long absorption cell having the geometrical arrangement and final temperature profile indicated in Figure 17. Alkali metal is placed in boats at positions indicated in the diagram. Let us assume that the system is initially filled with an inert gas, so that the total pressure is P_T (which equals P_I , the inert gas pressure when the cell is cold). If the cool portions of the cell are large compared to the heated portion, or if the cell is attached to a gas reservoir of large volume, the pressure within the system P_T will remain essentially constant during the heating of the central portion. As the cell containing the alkali is heated and the alkali vaporizes, the alkali metal vapor displaces some of the inert gas as it diffuses through the central heated zone. The vapor then diffuses through the narrow passage in the vapor barrier into the space outside the barrier, where it condenses on the cooled portions of the cell. The sum of the partial pressures of alkali and inert gas remain constant at P_T . After the equilibrium condition is reached, there is no net motion of the inert gas, but alkali metal vapors gradually diffuse from the center of the cell to the cool ends. Both the presence of the inert gas and the small apertures in the vapor barrier reduce the diffusion of the alkali to the tube ends. The alkali condenses only outside the heated vapor space, since the central portion of the cell is maintained at a higher temperature than the alkali in the boat.

The distribution of alkali partial pressure in the cell can be obtained from consideration of the equations for diffusion of one gas through a stagnant layer of another gas. In any constant area portion of the absorption cell, the rate at which molecules of the vapor move through the inert gas in the x direction is given by the equation:

$$N_v = \frac{-D P_T dP_v}{RTP_I dx} \quad (11)$$

where N_v is moles of vapor diffusing per unit time per unit area of tube, and P_v and P_I represent the partial pressures of the vapor and inert gas, D is the diffusion coefficient, and T is the absolute temperature. Neglecting the variation of diffusion coefficient with partial pressure, and assuming a constant temperature over each constant area zone, we can obtain the following equations for the pressure of the vapor in each zone:

$$P_v = P_T - P_I(o)e^{ax} \quad (12)$$

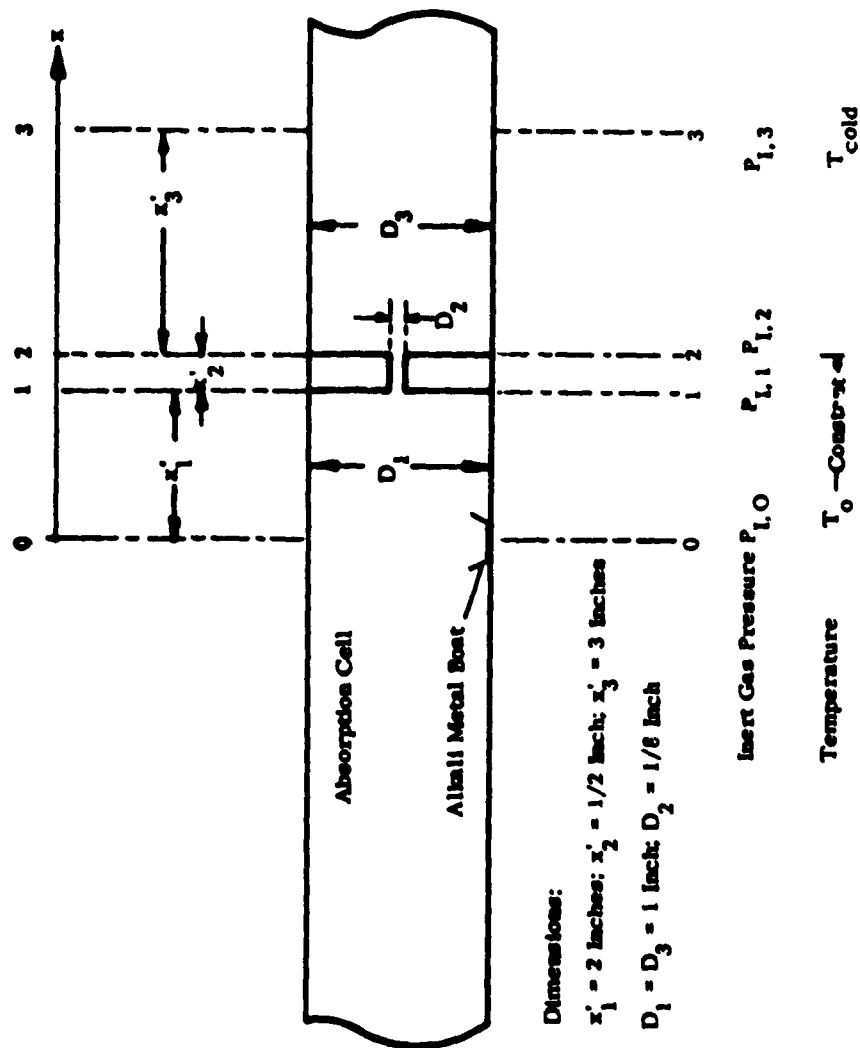


FIGURE 17

DIAGRAM OF ABSORPTION CELL SHOWING GEOMETRY FOR VAPOR PATH ANALYSIS

where P_v is the partial pressure of the alkali at distance x from the beginning of a constant cross section zone, $P_{I(0)}$ is the partial pressure of the inert gas at the beginning of the zone, and α is given by the relation:

$$\alpha = \frac{RTN_v}{DP_T} \quad (13)$$

Representing the pressure of inert gas at planes 0,0; 1,1; 2,2; and 3,3 in Figure 17 by $P_{I,0}$, $P_{I,1}$, $P_{I,2}$ and $P_{I,3}$, we obtain the relationship:

$$\text{for } x > 0 < x_1 \quad P_v = P_T - P_{I,0} e^{\alpha_{0-1} x} \quad (14)$$

$$x > x_1 < x_2 \quad P_v = P_T - P_{I,1} e^{\alpha_{1-2}(x-x_1)} \quad (15)$$

$$x > x_2 < x_3 \quad P_v = P_T - P_{I,2} e^{\alpha_{2-3}(x-x_2)} \quad (16)$$

It should be noted that $\alpha_{0-1} \neq \alpha_{1-2} \neq \alpha_{2-3}$ since the diffusion rate per unit area is not the same in each section of the cell. However, the total diffusion rate must be the same in each section; this gives the relationship:

$$\alpha_{0-1} A_{0-1} = \alpha_{1-2} A_{1-2} = \alpha_{2-3} A_{2-3} \quad (17)$$

Thus the partial pressure of the vapor in each constant area section decreases in accordance with an equation similar to Equation (12); however, the α terms are inversely proportional to the cross section area of the cell. The pressure of the alkali vapor, therefore, decreases slowly with length in the section with large area, and rapidly in the section with small area. As a numerical example, consider the following dimensions, which are typical of those actually used in the experiments:

$$x_1 = 2", \quad x_2 - x_1 = 1/2", \quad x_3 - x_2 = 3"$$

$$A_{0-1} = A_{2-3} = 3.14 \text{ in}^2, \quad A_{1-2} = 0.049 \text{ in}^2 \text{ (radius ratio of } 1/8)$$

For conditions where $P_{v,0} = 10$ mm Hg, $P = 760$ mm Hg, and $P_{v,3}$ is assumed to be 10^{-4} mm Hg (in equilibrium with cooling water), $P_{v,1}$ and $P_{v,2}$ are found to be approximately 9.44 mm Hg and 0.56 mm Hg, respectively. Thus, the major drop in the partial pressure of the alkali occurs in the narrow portion of the tube. In experiments we performed, the ratio of cell cross-sectional area to vapor barrier area was even larger than the 64/1 ratio used in the example, therefore, the partial pressure is even more constant in the wide

portion of the cell, and decreases more rapidly in the narrow vapor barrier. The above estimates of the partial pressure profile have neglected the effects of discontinuities between small and large cross sections, temperature variation, variation of diffusion coefficients, and convection currents. These effects have been analyzed by Ditchburn⁽¹²⁾ and found to be small in absorption tubes similar to the ones used in this investigation. The combination of vapor barrier and inert gas adequately contains the alkali vapor within the heated portion of the cell, so that the concentration profile is very close to a "square wave" type.

An analysis similar to that above was conducted using the dimensions of the experimental apparatus. The results showed that the path length-pressure product in all experiments could be approximated to within five to 10 percent by assuming a constant partial pressure of vapor within the space between the vapor barriers, a linear decrease to zero in partial pressure in the narrow portion of the vapor barrier, and a zero alkali metal partial pressure in the remainder of the absorption tube.

VII. EXPERIMENTAL RESULTS AND DISCUSSION OF RESULTS

Typical data and results showing the decrease in intensity of radiation passing through alkali metal vapors are given in Figures 18 through 23. The results can be examined and interpreted in view of several factors: 1) reproducibility of data, 2) effect of source temperature, 3) effect of wavelength, 4) effect of alkali metal pressure, and 5) effect of vapor path length.

A. DATA REPRODUCIBILITY

Figure 18 shows the fractional transmission of radiant energy through potassium vapor plotted versus $P \times \frac{273}{T}$. The vapor path length was 8-1/2 inches (8-inch nominal length) for these tests and the lamp source temperature was 1920°C. The results of three tests are shown; the curves are drawn through the data points by inspection. Although there is considerable scatter of the data, the trends can be readily observed and the data can be applied to a practical system. Scatter in the data can be attributed to several factors, the principal factor being optical alignment of the system. As the absorption tube is heated and expands the vapor barrier may shift in position slightly. The shifting has the same effect as changing the value of $(I_{\text{cell}}/I_{\text{cal}})$ cold, and may result in an error of ± 10 percent, in the calculated transmission. Several experiments were performed in which the absorption cell was heated with no alkali metal present and the variation of $(I_{\text{cell}}/I_{\text{cal}})$ with average cell temperature was noted. In some cases the variations amounted to 10 per cent and were not reproducible. Although initial experiments showed the photometer to be relatively linear, some error in the values of I_{cell} and I_{cal} can be attributed to errors in photometer readings and drift of the phototube. In some experiments the vapor condensed outside the vapor barriers in small particles which could scatter the radiation incident on them. Experiments in which we noted particle formation are not used in the analysis. Errors in temperature measurement introduce uncertainty in the alkali metal pressure and also introduce some scatter. The over-all accuracy of the data is estimated to be better than ± 20 per cent in the range of transmission from 1 per cent to 80 per cent.

Tests with sodium vapor and with four inch nominal path lengths showed the same type of reproducibility indicated in Figure 18.

B. EFFECT OF SOURCE TEMPERATURE

The temperature of the tungsten strip lamp source was varied from 1000°C to 2170°C. Experiments with lamp temperatures below 1600°C were not reproducible due to fluctuations in lamp temperature and movement of the filament on heating. Above 1600°C, filament expansion and movement did not seem to influence the intensity of the radiation reaching the phototube. The intensity of radiation reaching the phototube was also low at low lamp temperatures. When the cell was heated, the background radiation emanating from the absorption tube and vapor barriers became significant compared to the radiation passing through the vapor

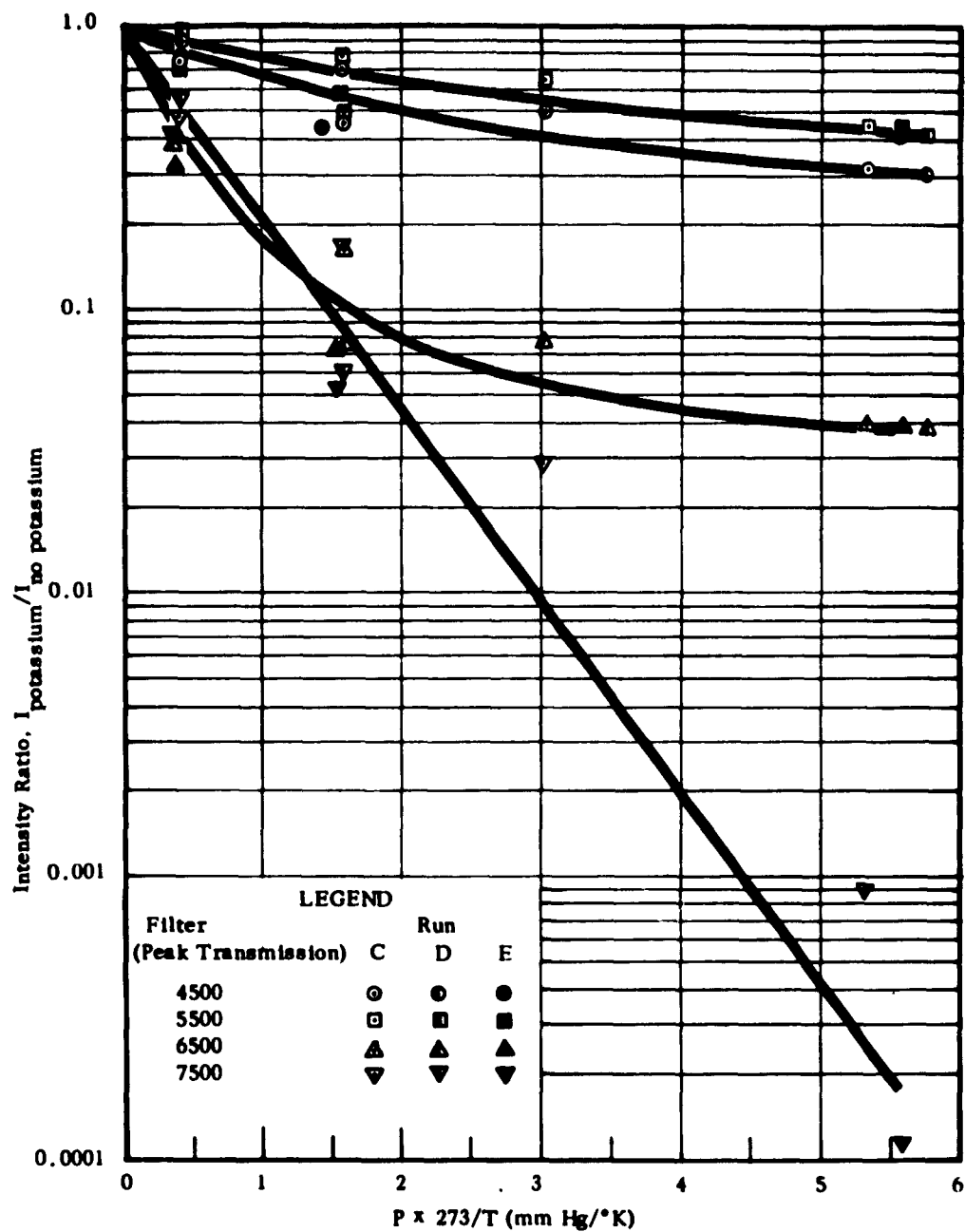


FIGURE 18

TRANSMISSION OF RADIANT ENERGY THROUGH POTASSIUM VAPOR SHOWING
REPRODUCIBILITY OF DATA

from the lamp source. This made transmission results at low source temperatures and high vapor pressures unreliable. A ground quartz diffusion plate was placed between the lamp and the absorption cell or calibration tube to reduce the effect of movement of the lamp filament. The apparent brightness temperatures of the ground quartz (which acted as a secondary source) were 1400, 1575, and 1750°C when the lamp brightness temperatures were 1675, 1920 and 2170°C, respectively. The lamp was not operated at higher temperatures in order to insure the lamp life over a complete test. Figure 19 shows the fractional transmittance of radiation through sodium vapor (path length 8 1/2 inches) for various source temperatures. Little effect of source temperature can be noted. The same results were obtained for other experimental conditions using both sodium and potassium vapor. If the absorption of the vapors is essentially constant over the wavelength bands measured, than the effect of source temperature should be small. The small range of source temperatures used also results in only a small effect. The similarity between the results for different lamp temperatures gives confidence to the data since apparent dips and changes in the shape of the absorption curves were the same independent of source temperature.

C. EFFECT OF WAVELENGTH

Figures 20 and 21 indicate the variation of transmission through alkali metal vapors with wavelength. The average absorption coefficients for sodium vapor increase for wavelength regions having their peak transmission in the order of 4500, 7500, 5500, 6500 Å at relatively high total vapor pressures (4-20 mm Hg). At lower vapor pressures the order appears to be changed to 7500, 5500, 4500 and 6500. At high partial pressures very little radiation passes through sodium vapor in the yellow and red regions of the spectrum. From visual observation this is due to the strong band structure extending from near the D lines to the red ($1\Sigma_g^+ \leftrightarrow 1\Sigma_u^+$). There is also considerable absorption in the blue and green corresponding to the band 4900 Å ($1\Sigma_g^+ \leftrightarrow 1\Pi_u$). The sodium vapor appears violet at high temperatures since there is little absorption in this portion of the spectrum.

Potassium vapor appears to absorb less strongly in the region covered by this investigation. As seen in Figure 21, there is little absorption in the wave bands with peaks at 4500 and 5500 Å. Greater absorption observed in the 6500 and 7500 Å region. Absorption in the latter region is due to the strong band centered near 6500 Å ($1\Sigma_g^+ \leftrightarrow 1\Pi_u$), whereas the former corresponds to the weaker band system centered near 4500 Å. The potassium molecules also should show a very strong band structure near 8500 Å (beyond the range covered in this investigation) due to $1\Sigma_g^+ \leftrightarrow 1\Sigma_u^+$ transitions. This band corresponds to the band observed near the D lines for sodium and should have approximately the same absorption strength. Thus the band structure observed in potassium vapor in the red corresponds to the weaker system observed in the blue for sodium vapor. We conclude that although the absorption by potassium was apparently less than for sodium for the partial pressures and wavelength regions investigated, potassium vapor should show strong absorption in the 8500 to 9500 Å region.

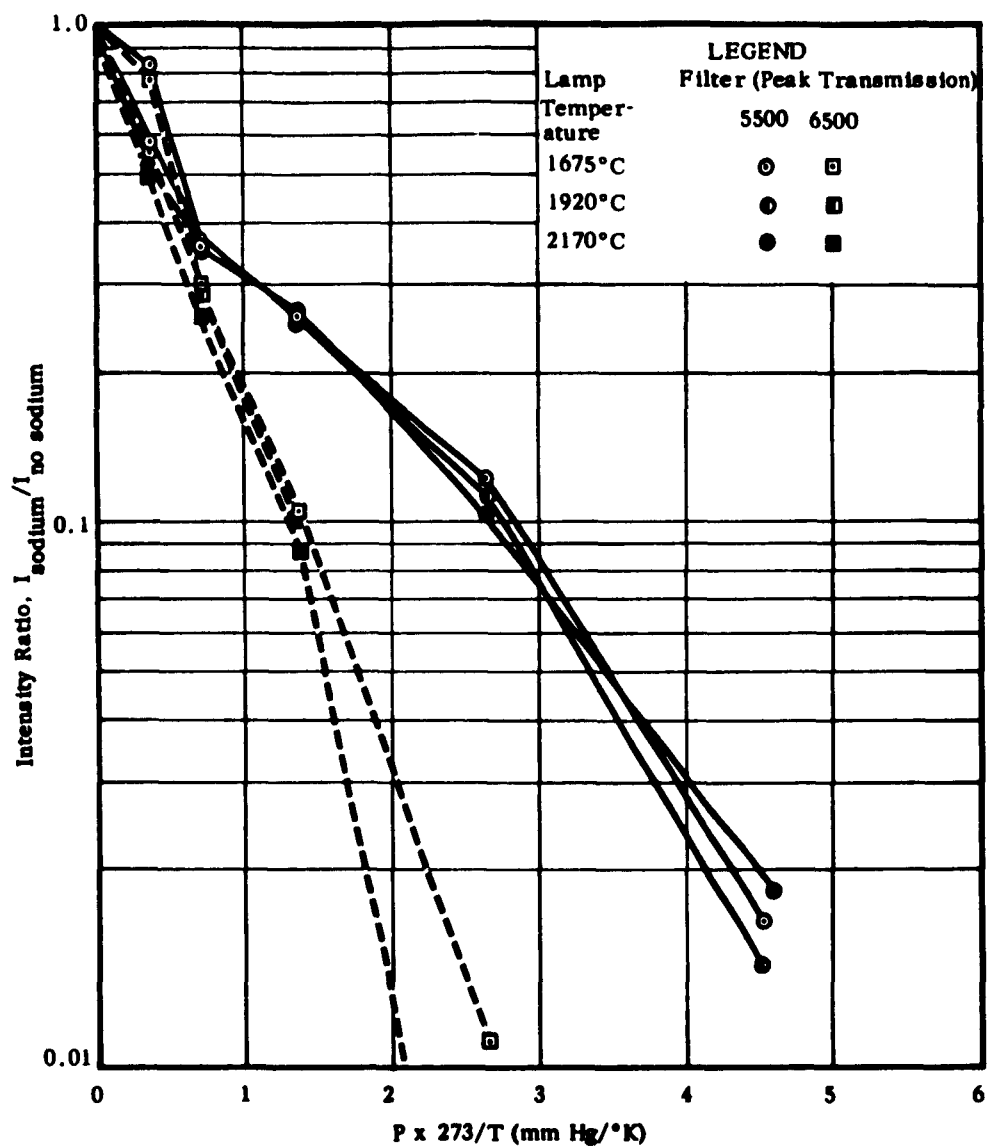


FIGURE 19
EFFECT OF SOURCE TEMPERATURE ON TRANSMISSION OF SODIUM VAPOR

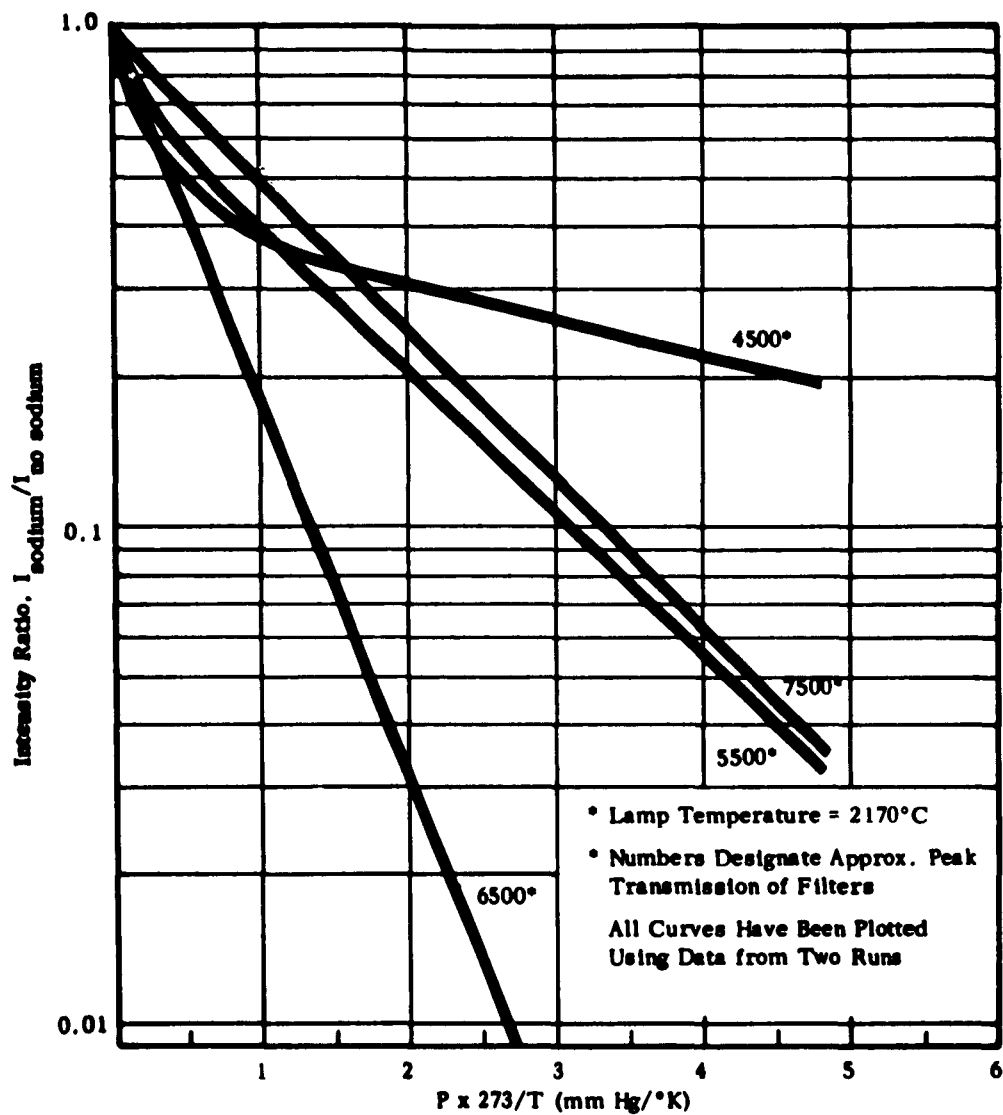


FIGURE 20
TRANSMISSION OF SODIUM VAPOR IN VARIOUS WAVELENGTH BANDS

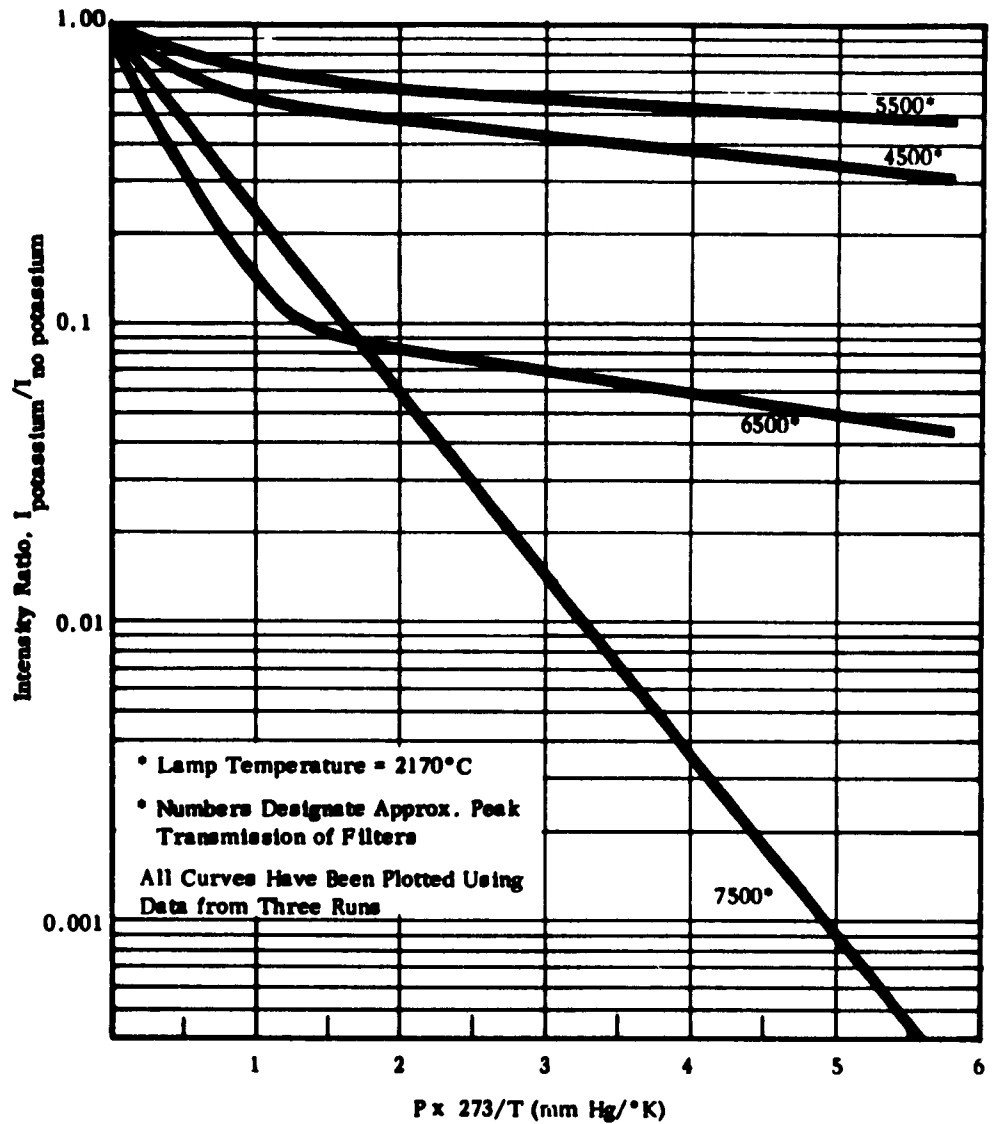


FIGURE 21
TRANSMISSION OF POTASSIUM VAPOR IN VARIOUS WAVELENGTH BANDS

D. EFFECT OF PRESSURE OF ALKALI METAL

The data shown thus far have been presented in terms of intensity ratio versus $\frac{P \times 273}{T}$, a term proportional to the number of atoms of vapor per unit length. Although in some cases a straight line relationship can be drawn (for example sodium vapor, 6500 Å and 7500 Å band centers; potassium 4500 Å and 5500 Å band centers) this may be misleading, since molecular absorption is the important mechanism of radiant attenuation. If the data are replotted as logarithm of intensity ratio versus partial pressure of alkali molecules, more curvature is observed in the lines connecting the data points, i.e., an increase in partial pressure does not produce as great a decrease in the logarithm of the transmission as a direct proportionality would indicate. (For sodium vapor in the band 6000 to 7000 Å, a direct proportionality with molecular pressure still exists.) The curvature should not, however, be interpreted to discount the evidence of molecular absorption. The relationship between the logarithm of transmission and molecular pressure is not expected to be linear since the absorption is not constant over the wavelength bands measured but consists of absorption lines at specific wavelengths. Other factors such as nonlinearity of photomultiplier response with wavelength and variation of transmission coefficient with wavelength of the filters used in the apparatus also contribute to the relationship between intensity ratio and pressure.

For purposes of extrapolation of the data near the range of the experimental investigation it is not important whether the partial pressure of atoms or molecules is used provided the proper "absorption coefficients" are used, and the mechanism of the absorption is realized. Table II gives absorption coefficients for various spectral regions for alkali metal vapors. Values in the visible range were calculated from the results of this investigation, values in the ultraviolet range were obtained from the literature.⁽¹²⁾ The coefficients can be used in the equation:

$$\frac{I}{I_0} = \exp \left(-N \sigma \frac{P}{760} \frac{273}{T} L \right) \quad (18)$$

where P is the alkali metal pressure in mm Hg (monatomic or diatomic) and σ is the corresponding absorption coefficient (cm^2), N is the number of atoms (or molecules) per cm^3 at S.T.P., T is the temperature ($^{\circ}\text{K}$) and L is the path length (cm).

E. EFFECT OF VAPOR PATH LENGTH

In experiments with a four-inch nominal path length much less absorption was noted than in experiments with eight-inch path lengths at corresponding vapor pressures. Figures 22 and 23 show typical data for experiments with two vapor path lengths. The data fall reasonably well on the same curve. Variations can be explained on the fact that the absorption is not constant over the entire wavelength band. If a spectral line (or group of lines) is completely absorbed in a short path length, further increases in path length may not decrease the absorption over a band containing these lines. In some cases, with the four-inch nominal vapor path, there was difficulty in preventing condensation in the region near the alkali metal boat. Thus, the data for these runs are not as reliable as data for the eight-inch vapor path. The data presented above indicate that relatively strong molecular absorption occurs in vapor columns of alkali metals. Information on spectral absorption coefficients would be useful in extrapolating data to systems different from those considered in this investigation.

TABLE II

EFFECTIVE ABSORPTION CROSS SECTIONS
FOR ALKALI METAL VAPORS

	ATOMIC BASIS ⁽¹⁾	ABSORPTION CROSS SECTION (cm ²)			
		Wave Length Region			
		4000-5000 Å	5000-6000 Å	6000-7000 Å	7000-8300 Å
	Sodium Vapor	0.5 - 2.1 x 10 ⁻¹⁸	1.0 - 2.0 x 10 ⁻¹⁸	2.0 - 3.0 x 10 ⁻¹⁸	1.0 - 1.6 x 10 ⁻¹⁸
	Potassium Vapor	1.0 - 3.5 x 10 ⁻¹⁹	0.3 - 2.0 x 10 ⁻¹⁹	0.7 - 1.8 x 10 ⁻¹⁸	1.2 - 1.9 x 10 ⁻¹⁸
	MOLECULAR BASIS ⁽¹⁾				
	Sodium Vapor	0.7 - 2.5 x 10 ⁻¹⁹	1.2 - 3.0 x 10 ⁻¹⁹	2.5 - 3.7 x 10 ⁻¹⁹	1.1 - 2.5 x 10 ⁻¹⁹
45	ATOMIC BASIS ⁽²⁾	1600 - 2000 Å	2000-2400 Å	2400-2800 Å	2800-3200 Å
	Sodium Vapor	1 - 4 x 10 ⁻²⁰	2 - 11 x 10 ⁻²⁰	-	-
	Potassium Vapor	-	2 - 6 x 10 ⁻²⁰	1 - 2 x 10 ⁻²⁰	-
	Cesium Vapor	-	-	9 - 16 x 10 ⁻²⁰	9 - 20 x 10 ⁻²⁰
	Rubidium Vapor	-	-	1 - 3 x 10 ⁻²⁰	3 - 10 x 10 ⁻²⁰
	Lithium Vapor	1 - 2. x 10 ⁻¹⁸	2 - 2.5 x 10 ⁻¹⁸	-	-

(1) Experimental Results

(2) Reported by Ditchburn⁽¹²⁾

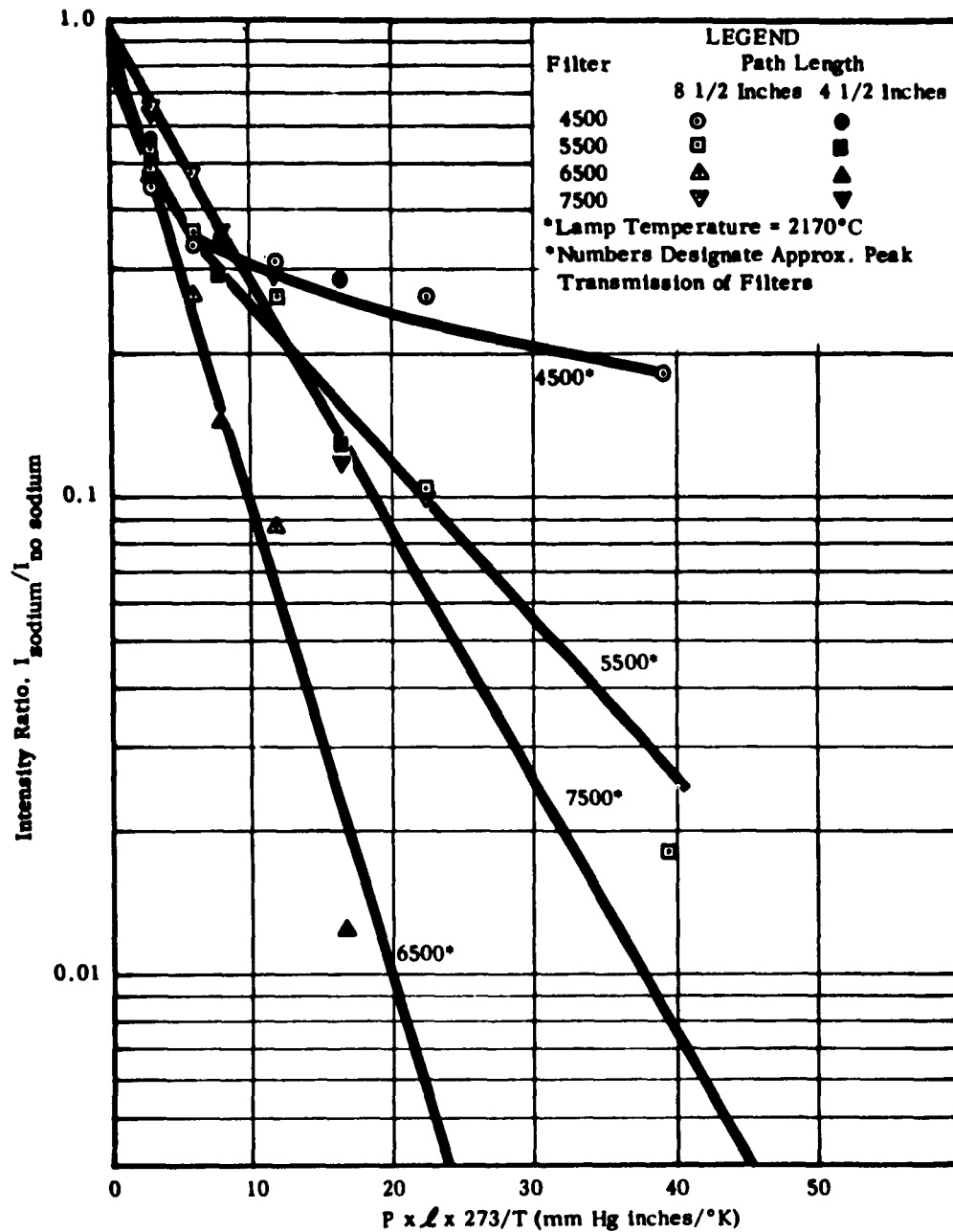


FIGURE 22
EFFECT OF PATH LENGTH ON TRANSMISSION THROUGH SODIUM VAPOR

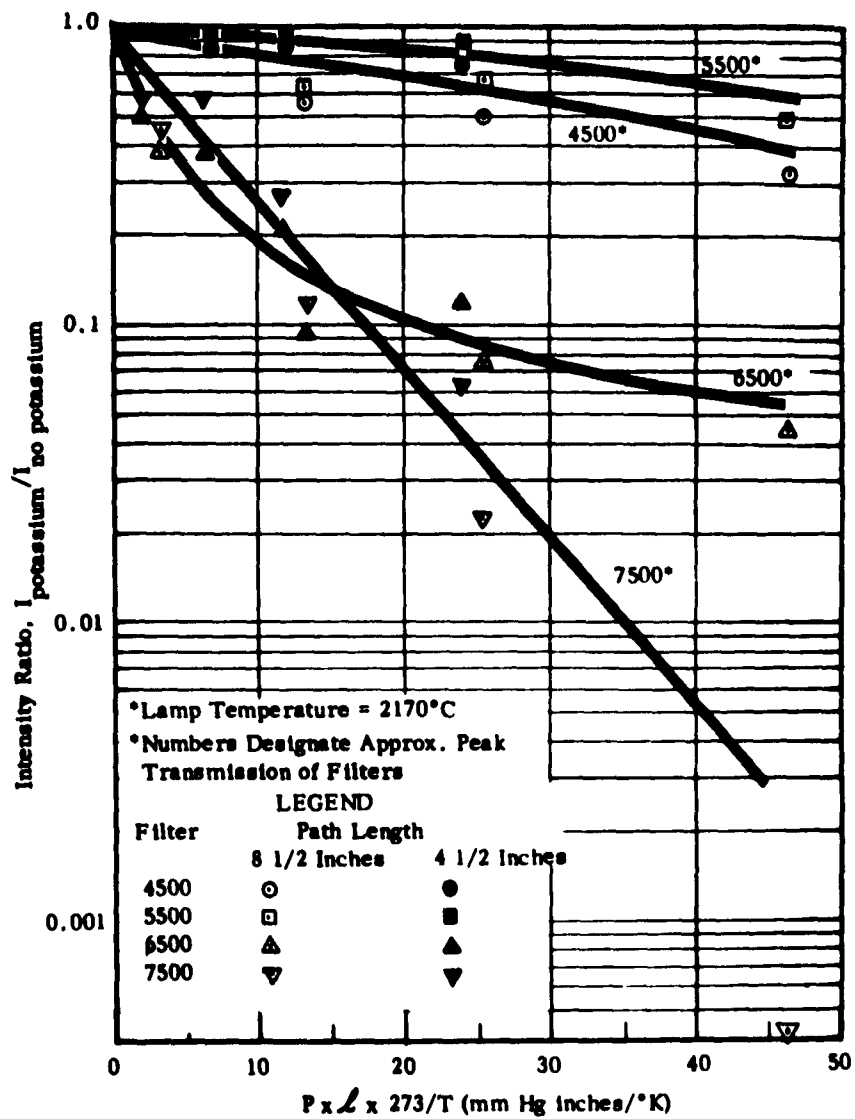


FIGURE 23
 EFFECT OF PATH LENGTH ON TRANSMISSION THROUGH
 POTASSIUM VAPOR

VIII. APPLICATION OF RESULTS TO SYSTEMS WITH RADIANT HEAT TRANSFER

From the results presented above and from calculations based on literature data of absorption due to the photoionization effect, we can make some estimates of the effect of alkali metal vapors on radiant heat transfer.

Consider, for example, an arc or plasma device which radiates in certain regions as a black body at temperatures of 8000, 10,000, and 20,000°K. If radiation from this source passes through a layer of alkali metal vapor before reaching the walls of the system enclosure, energy can be absorbed and reradiated to other parts of the system. Table III shows the radiant energy that can be absorbed (and reradiated in all directions) by a vapor column of indicated path length pressure product over specific spectral ranges. Heat transfer rates to boundaries of the system may undergo similar changes. The spectral ranges chosen are those where data on absorption coefficients are available. For purposes of calculation, the vapor assumed was to be at a temperature of 1000°K. Examination of the table shows that columns of sodium, potassium or cesium vapor require large path length-pressure products to absorb most of the energy in the ranges below the series limits. The fraction of the total energy in these ranges varies from five to 34 per cent. Similar calculations show that lithium vapors will absorb almost completely the radiation in the range of 1600 to 2300 Å for the path length products which are an order of magnitude less. Rubidium vapors will have approximately the same absorption characteristics as cesium vapors.

Similar calculations can be made using the experimental results obtained for sodium and potassium vapors. The graphs and absorption coefficients presented earlier show that absorption in the visible region will be greater than absorption due to the photoionization effect. Table IV shows some results using the experimental data. The values reported are typical for transmission through alkali metal vapors in the temperature range of 650 to 800°K for sodium and for potassium for path lengths of 10 to 25 cm and vapor pressures from one to 16 mm Hg. It was assumed that vapor systems will have similar ratios of molecules to atoms as existed in our experimental work.

In the region where little data is available, i.e., between the series limits and the visible region, sodium and potassium vapors are expected to absorb slightly due to molecular band absorption and spectral line absorption. Potassium vapor will also show strong absorption in the near infrared, a factor which may be important in lower temperature systems. Cesium vapor is also expected to absorb in the infrared as well as the visible regions.

In the above analysis, black body radiation sources were assumed. In most plasma and arc systems, except perhaps high pressure systems, the majority of the radiation will occur at specific wavelengths rather than in a continuous spectrum. It is possible that a source will radiate strongly in or near a strong absorption band of the alkali metal, or in a region where the photoionization effect is strong. Under these conditions heat transfer by radiation could be attenuated to a much greater degree than is estimated above. Absorption data as a function of wavelength will be useful in making estimates of radiation attenuation from specific types of plasma or arc devices.

TABLE III

**ABSORPTION BY METAL VAPORS DUE
TO PHOTOIONIZATION EFFECT (Literature Data)**

	Spectral Range λ	Black-Body Radiation Temperature					
		8000°K		10000°K		20000°K	
		% Absorption	Rate of Energy Absorption	% Absorption	Rate of Energy Absorption	% Absorption	Rate of Energy Absorption
<u>SODIUM</u>							
% of Total Radiation in Range	1500-2412	5.4	1255 w/cm ²	12.9	7310 w/cm ²	33.8	307,000 w/cm ²
Energy Absorbed in PL=224 cm mm Hg		10	125.5	8	585	7	21,500
Energy Absorbed in PL=2240 cm mm Hg		56	702	49	3580	46	141,000
<u>POTASSIUM</u>							
% of Total Radiation in Range	2200-2861	8.3	1925 w/cm ²	14.2	8050 w/cm ²	16.5	149,700 w/cm ²
Energy Absorbed in PL=224 cm mm Hg		4	77	5	403	6	8,980
Energy Absorbed in PL=2240 cm mm Hg		32	616	34	2740	39	58,400
<u>CESIUM</u>							
% of Total Radiation in Range	2400-3150	11	2550 w/cm ²	16.7	9470 w/cm ²	15.5	140,500 w/cm ²
Energy Absorbed in PL=224 cm mm Hg		22	560	22	2080	22	30,900
Energy Absorbed in PL=2240 cm mm Hg		91	2320	91	8620	90	126,500

TABLE IV
 ABSORPTION IN VISIBLE REGION BY
 ALKALI METAL VAPORS (Experimental Data)

	Spectral Range Å	Black-Body Radiation Temperature					
		5000°K		10000°K		20000°K	
		% Absorption	Rate of Energy Absorption	% Absorption	Rate of Energy Absorption	% Absorption	Rate of Energy Absorption
<u>SODIUM</u>							
% of Total Radiation in Spectral Range	4000-8300	44.1	1380 w/cm ²	38.6	21,900 w/cm ²	12.0	109,000 w/cm ²
Energy Absorbed in PL=10 cm mm Hg		12	166	13	2,845	12	13,100
Energy Absorbed in PL=100 cm mm Hg		76	1050	74	16,200	73	79,500
<u>POTASSIUM</u>							
Energy Absorbed in PL=10 cm mm Hg	4000-8300	18	248	14	3,940	13	14,200
Energy Absorbed in PL=100 cm mm Hg		61	842	50	10,950	47	51,200

IX. CONCLUSIONS AND RECOMMENDATIONS

From the analyses and experiments in this investigation we conclude the following:

1. Attenuation of radiation by alkali metal vapors and the resultant modification in heat transfer to boundary surfaces can be important phenomena in the spectral range from 1600 to 9000 Å due to molecular band absorption and photoionization effects.
2. For sodium, potassium, cesium, and rubidium vapor in a gas at 1000°K, vapor layers with path length-pressure products greater than 1000 cm mm Hg are required to give significant absorption by photoionization. This could indicate that in large systems operating at moderate pressures sufficient quantities of alkali metal could be present to give appreciable changes in heat transfer in the region from 1600 to 3500 Å. For lithium vapor, path length-pressure products in the order of 100 cm mm Hg are required for significant absorption.
3. Absorption can also occur for sodium and potassium vapor in the visible region due to molecular band absorption. Path length-pressure products from 10 to 100 cm mm Hg are sufficient for significant absorption to occur, when black body radiation from high temperature sources is considered. Potassium vapor should also absorb strongly in the near infrared. Lithium, cesium, and rubidium are expected to absorb radiation in the same manner with approximately the same pressures and path lengths required.
4. Since the absorption by alkali vapors is primarily molecular in nature and occurs in specific spectral regions, conditions can exist in an arc or plasma system where the energy radiated from the source lies near or in absorption bands of the alkali. Strong radiant energy absorption and modification of local heat transfer rates can then occur.
5. In this preliminary investigation, it was shown that the absorption of radiant energy in certain spectral regions can significantly affect heat transfer conditions in plasma and arc systems. These results, therefore, justify the use of more elaborate spectrographic techniques in order to apply absorption data to actual arc or plasma systems without measurements under many specific conditions. More information is also needed on the dimerization reaction of the alkali metals and the partial pressure of molecules in alkali metal systems.

X. FUTURE WORK

Based on our experience in this investigation, we have proposed a design of an absorption apparatus which will eliminate some of the problems arising in the present work. In the design shown in Figure 24, the alkali metal holder is heated and cooled independently of the remainder of the absorption tube. The absorption cell will be of a dual type, one portion containing alkali metal vapor and inert gas, the other containing only an inert gas. Instead of shifting the absorption cell and calibration tube in and out of the optical axis, we anticipate the use of a mirror and lens system to record the transmission of radiant energy through the vapor filled and empty tubes alternately. The spectral range of any future investigations should be extended to include that between the ultraviolet and visible and the near infrared.

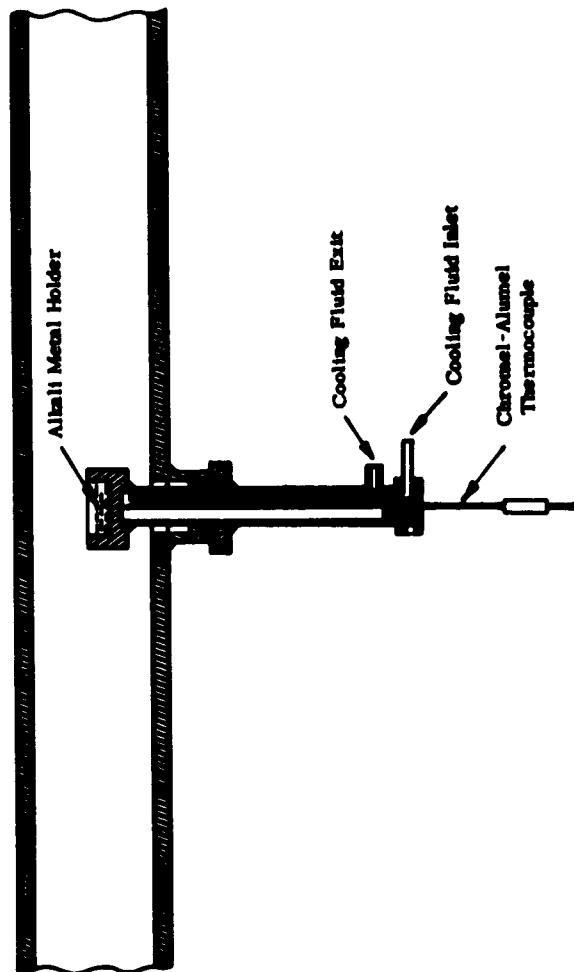
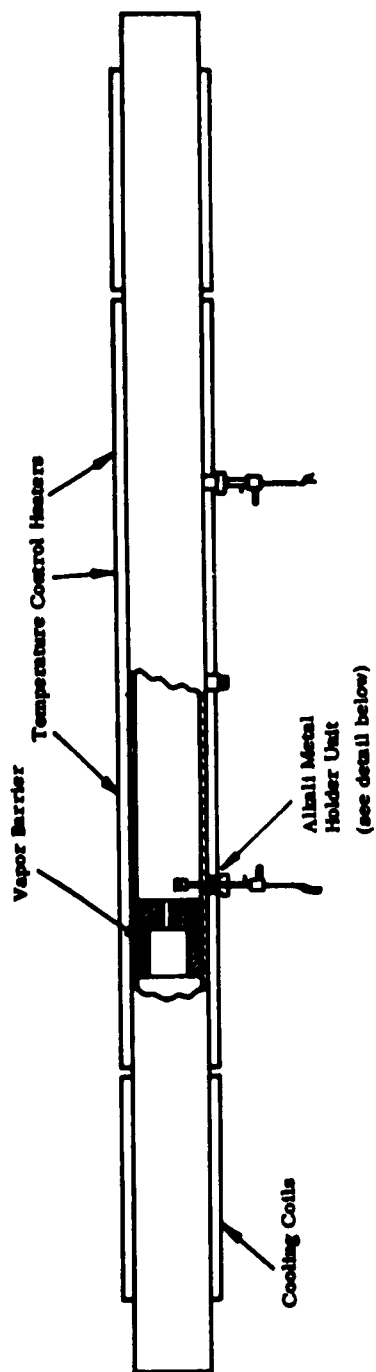


FIGURE 24
DIAGRAM OF PROPOSED ABSORPTION CELL

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Unclassified Report

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(over)

The results are reported in terms of the decrease in intensity of light passing through alkali metal vapors as functions of vapor pressure, temperature and path length. Calculated absorption cross sections are in the order of 10⁻¹⁸ to 10⁻¹⁹ cm² for sodium and potassium vapor over the wavelength region studied.

The absorption of radiation by alkali metal vapors has been shown to have an observable effect on the heat transfer in arc and plasma systems and warrants a more detailed study over a larger spectral range.

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