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Washington, D. C. 20546

Attention: Program Chief/Code SL
Planetary Atmospheres

Subject: Contract No. NASw-985

Gentlemen:

As contractually required, please find enclosed ten (10) copies of Quarterly Progress Report No. 3 covering the period 1 December 1964 through 28 February 1965.

Yours very truly,

Original Signed By
R. C. AUSTIN

Robert C. Austin
Senior Contract Administrator

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QUARTERLY PROGRESS REPORT NO. 3

UPPER ATMOSPHERE CHEMICAL RELEASE STUDY

(1 Dec - 28 Feb 1965)

NASw-985

Prepared by: Jerome Pressman

GCA CORPORATION
GCA TECHNOLOGY DIVISION
Bedford, Massachusetts

For

National Aeronautics and Space Administration
Washington, D.C.

I. INTRODUCTION

This report on the work accomplished in the last quarter summarizes briefly the advances in theory and experiment. Major emphasis was placed on the experimental phase. During this period the major build-up of equipment culminated and a considerable amount of data was taken.

II. THEORY

Work during this phase was primarily directed toward the evaluation of the release of atomic hydrogen to explore the OH airglow, and O_2 to explore the 6300Å mechanism.

A. 6300Å MECHANISM

A more elaborate mathematical analysis is under way to further elaborate the results of our first order study.

B. FORMATION OF ATOMIC HYDROGEN UNDER EQUILIBRIUM CONDITIONS

From equilibrium thermodynamic considerations one can calculate the percentage ionization on hydrogen gas as a function of temperature and pressure. Figure 1 shows the results of such calculations for hydrogen at pressures ranging between 10^{-3} atm to 10^{5} and temperatures ranging between $1000^{\circ}K$ to $6000^{\circ}K$.

Again using equilibrium considerations one can calculate the heat content of a given distribution of the various hydrogen species. Figure 2 displays the values for the heat content of two grams of hydrogen as a function of temperature and pressure. If we combine Figures 1 and 2, we

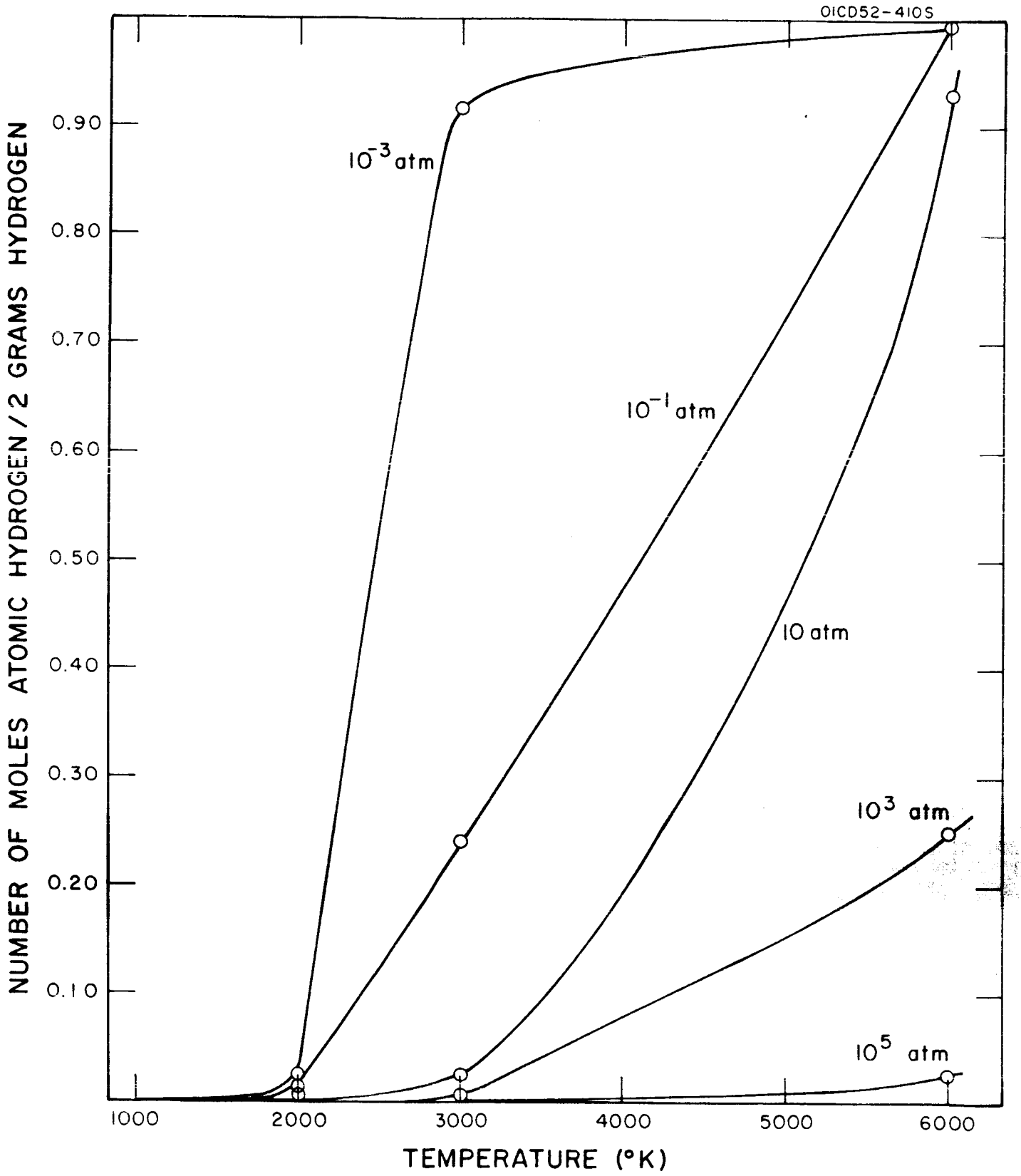


Figure 1. Fraction dissociated as function of temperature and pressure.

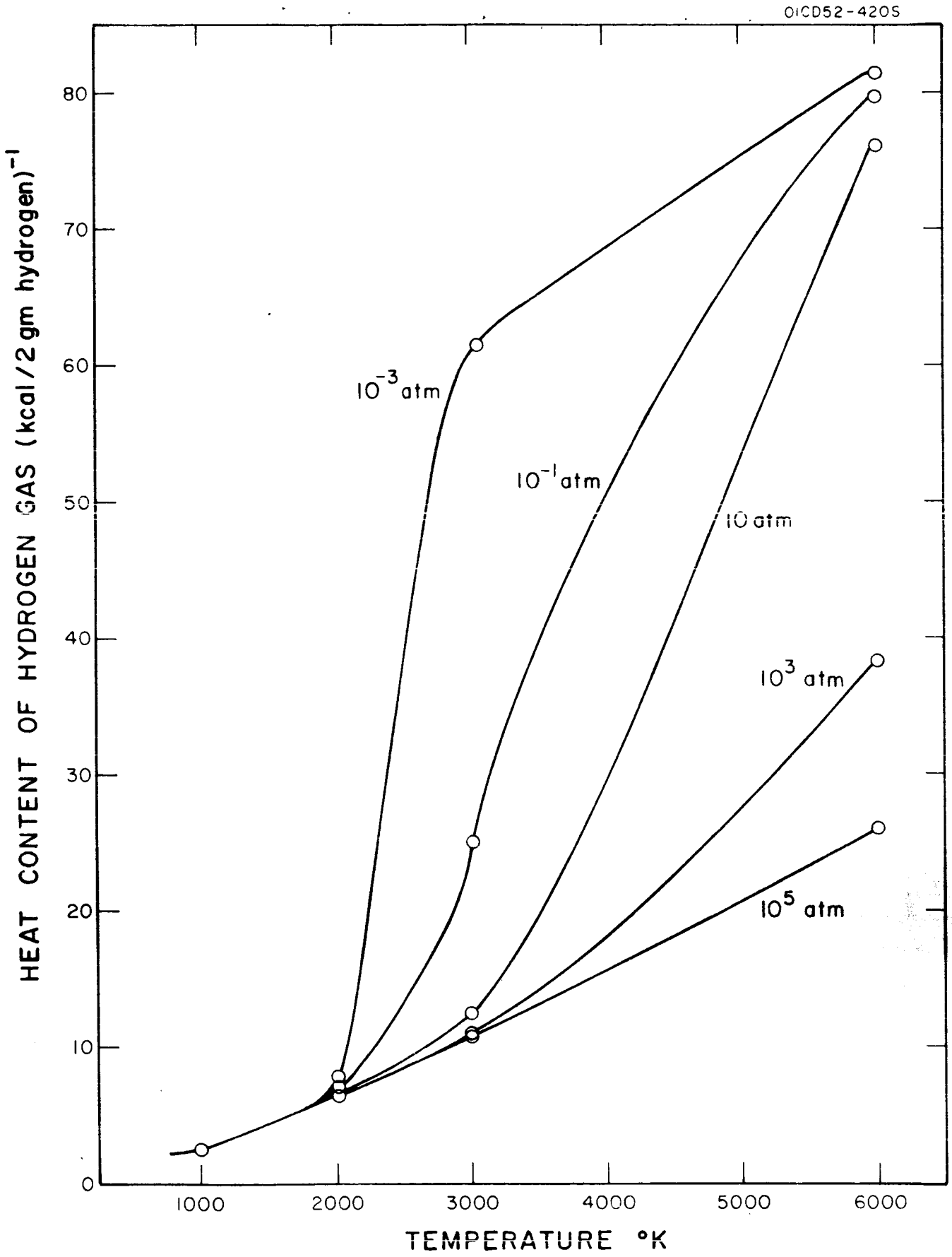


Figure 2. Heat content of 2 gm of hydrogen as a function of temperature and pressure.

can derive Figure 3 which gives the heat content of a container holding one mole of hydrogen atoms.

The volume of these various equilibrium distributions of hydrogen can be obtained with the aid of the ideal gas law. Figure 4 shows the volumes of containers that will be required in order to hold one mole of hydrogen atoms at various temperatures and pressures. This shows that in order to contain 0.1 of a mole of hydrogen atoms in a 10 liter container, we would have to heat it to 3300°K if it were pressurized at 10^5 atmospheres. Considering the very large values of the diffusion coefficient of hydrogen at high temperatures, these considerations lead to the conclusion that we will be faced with a rather severe materials problem if we were to attempt to produce the hydrogen by this method.

These calculations also point out that the major energy dissipation mechanism in this system is the dissociation of molecular hydrogen. In line with this it appears from these calculations that an appreciable amount of energy can not be stored in these systems by pre-heating them before launch.

Considering the various factors involved in producing an equilibrium mixture containing 0.1 mole of atomic hydrogen, (volume of system, weight of systems, weights of energy source, materials problems), it is felt that this is not the optimum method of producing the required atomic hydrogen.

However, it is evident from these graphs that, if the kinetics were favorable, the most efficient method of producing atomic hydrogen would be via some steady state process that can operate at a low pressure.

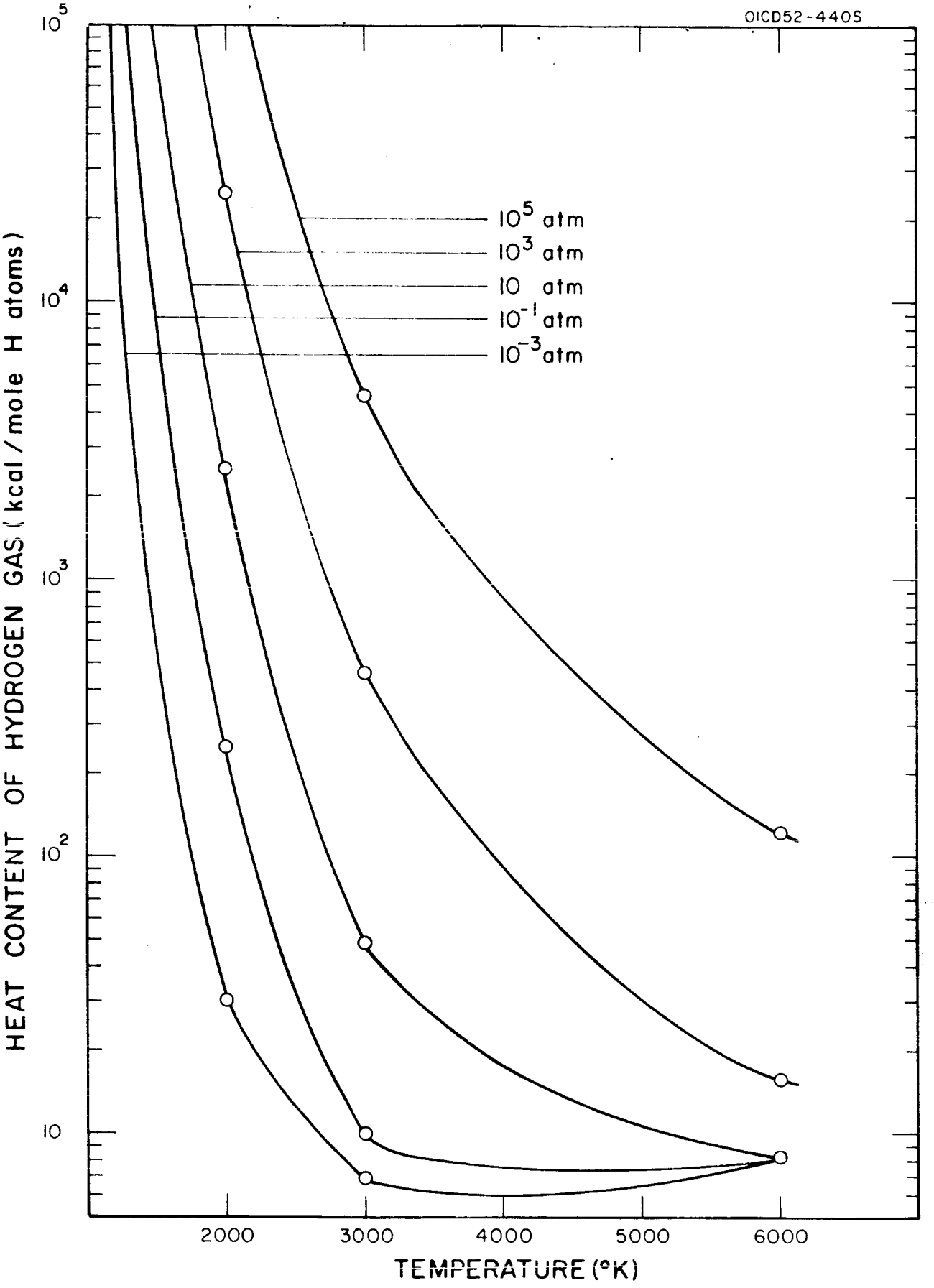


Figure 3. Heat content of hydrogen gas containing one mole of hydrogen atoms as a function of pressure and temperature.

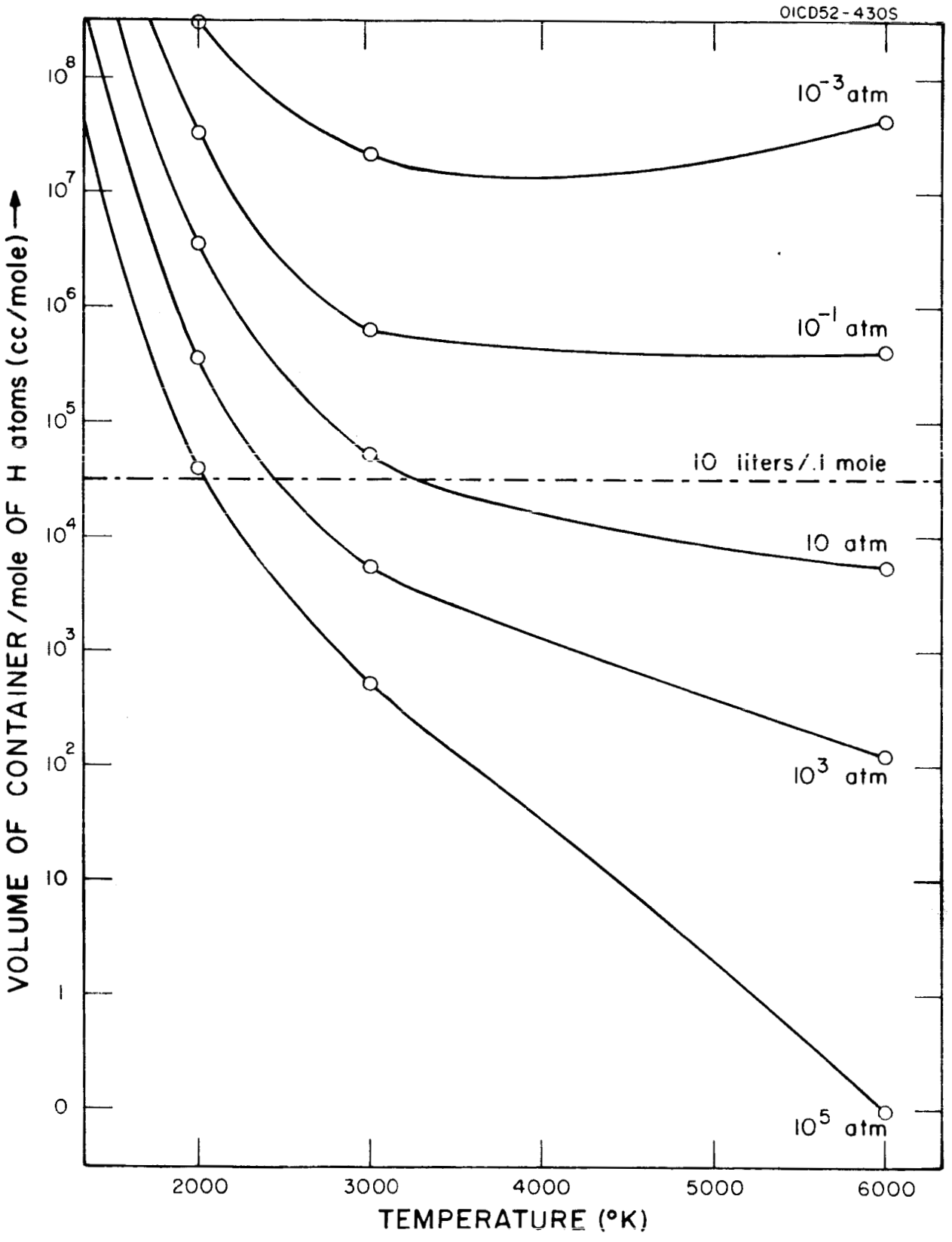


Figure 4. Container volume as a function of temperature and pressure.

A plasma gun, to be described later, is such a device. If the gases from such a plasma device could be made to exit at 3000°K at a pressure of 0.1 atm, it would require only about 16 kW to produce the 0.1 mole. These values are well within the present state of the art.

C. DESCRIPTION OF PLASMA GUN

This section outlines the hardware requirements which are needed to impart 40 kW of power for one second to 2 gms. of hydrogen. The design philosophy is based upon the assembling of existing components each of which has been tested and proven. These components consist of a plasma generator silver zinc battery package, supply of pressurized molecular hydrogen and a high frequency oscillator. The hydrogen, under a slight positive pressure, passes through the plasma generator arc, and is exposed to the enormous electric fields within the arc. The hydrogen emerges as a dissociated ionized gas at a high temperature. The arc can be started by means of a standard welding oscillator, that provides a high frequency discharge across the anode-cathode gap, which creates momentarily a low resistance current path. The arc, once started by the oscillator, is sustained by a bank of silver zinc batteries which are packaged to produce the current at the required arc operating voltage.

The system requirements are as follows:

Emerging gas:	Atomic hydrogen
Quantity (min.):	0.2 grams
Operating Time (min):	1.0 seconds
Input power (min):	40 kW
Flow rate (min):	0.2 gram/sec

A plasma generator which can satisfy the system requirements is commercially available. It's specifications are as follows:

Operating gases:	Argon, Nitrogen or hydrogen
Operating power:	40 kW (maximum operating power for sustained operation)
Operating voltage:	100 V dc (H_2)
Weight:	Less than 3 lbs.
Mass flow rate (max.):	0.5 gram/sec (H_2)
Volume:	Less than 0.1 $ft.^3$
Cost:	$1750
Availability:	Immediate
Cooling water required:	3 gallons per min.**
Efficiency:	50%-80% (with water cooling)
Operating Time:	2 seconds (max.)

**Cooling required to prevent cathode-anode erosion for sustained operation.

The plasma generator can operate at power levels exceeding 40 kW for only several seconds with subsequent erosion of the electrodes. Also, since water cooling decreases the plasma gun efficiency or actual energy imparted to the emerging gas, it is planned to operate the plasma gun without water cooling at 60 kW. Use of 60 kW would allow sufficient energy to be imparted to the atomic hydrogen in order to insure dissociation.

A battery package which can produce 600 amps dc at 100 volts dc for 2 seconds can be assembled from existing battery cells. The specifications of such a package are as follows:

Battery type:	Silver Zinc
Output voltage:	100 V dc nominal
Output current:	600 amps dc nominal
Operating time:	2 seconds
No. of cells:	100
Package volume:	1.2 $ft.^3$
Package weight:	170 lbs.
Availability:	3 months
Package cost:	$8,700
Temperature range:	60 - 100°F

A large savings in battery size, weight and cost can be effected if the operating temperature of the battery package were maintained from 90°F - 120°F. Self powered heaters emersed in the package and energized about one hour before the pulse is required can be used. The weight and volume reduction are 14% and 13%.

III. EXPERIMENTAL PHASE

A. INTRODUCTION

In this quarter, the experimental survey of several chemiluminescent reactions of various compounds with atomic oxygen, atomic nitrogen and ozone has been completed. The gaseous compounds and liquids of high vapor

pressure have been selected for the present study. The selection of substances for the present study is based on the information collected about their chemiluminescent reactions from allied fields e.g. chemical kinetics, atomic flames and combustion etc. The highlights of the results obtained in the present study are summarized in Table 1. We shall now discuss the results of the reactions of each atmospheric constituent separately.

B. REACTIONS WITH ATOMIC OXYGEN

The systematic study[1,2] of the reactions of atomic oxygen with some hydrocarbons has been undertaken in this laboratory. It has been concluded that triple bonded hydrocarbons produce more chemiluminescence than the double bonded hydrocarbons. The intensity of chemiluminescence produced by saturated hydrocarbon [2] is very feeble at ordinary temperature. The Table 2 shows the results of the present study of the chemiluminescent reactions of atomic oxygen with various substances. In this table column two indicates the difference in the heights of oil level in capillary flow meter which is a measure of the rate of flow of reactants into the system. Column three expresses the gain factor of the amplifier and indicates the intensity of the chemiluminescent radiation. Larger gain factor represents smaller intensity. Thus a spectral feature recorded at a gain factor of 20 is about (1.54)[10] lines less intense than that recorded with the same peak intensity at gain 10. It has been found the same type of compounds show similar characteristic spectrum of the chemiluminescence.

TABLE 1

CHEMILUMINESCENT REACTIONS OF SEVERAL SUBSTANCES WITH ATMOSPHERIC CONSTITUENTS

Titrant	Atmospheric Constituent		
	Atomic Oxygen	Atomic Nitrogen	Ozone
Nitric oxide	Continuum (4100Å - 6500Å) λ_{max} 5200Å		Continuum
Nitrocyl chloride	Continuum (4100Å - 6500Å) λ_{max} 5200Å		
Boron trichloride	BO_2 bands	BO bands	
Carbonyl chloride	Chemiluminescence doubtful	CN red and violet systems	
Carbon disulfide	Continuum (2700Å - 5200Å) λ_{max} 3450 ± 100Å	Faint glow NS bands	
Carbonyl sulfide	Continuum (2700Å - 5200Å) λ_{max} 3450 ± 100Å		
Hydrogen sulfide	Continuum (2700Å - 5200Å) λ_{max} 3450 ± 100Å		
Sulfur dioxide			
Hydrazene	NH_2, NH and OH bands		Faint Glow
Acetylene	C_2, CH, OH bands & Continuum	CN red and violet system	
Ethylene	C_2, CH, OH bands & Continuum	CN red and violet system	Faint Glow OH Band
Methyl acetylene	C_2, CH, OH bands & Continuum	CN red and violet system	
Allene	C_2, CH, Oh bands & Continuum	CN red and violet system	
Hexyne	C_2, CH, OH bands & Continuum	CN red and violet system	

TABLE 1 (Continued)

CHEMILUMINESCENT REACTIONS OF SEVERAL SUBSTANCES WITH ATMOSPHERIC CONSTITUENTS

Titrant	Atmospheric Constituent		
	Atomic Oxygen	Atomic Nitrogen	Ozone
Hexene	CH, OH bands & Continuum	CN red and violet system	Faint glow
Carbon tetrachloride		CN red and violet system	
Trichloro ethylene		CN red and violet system	
Ethyl alcohol	OH and CH bands	CN red and violet system	
Benzene	OH and CH bands		
Nitromethane	OH and NO_2 Continuum		

TABLE 2

REACTIONS WITH ATOMIC OXYGEN

Reactant	Flow Meter Reading	Gain Factor	Spectral Feature & Intensity* (2 bands) 4700-5000	CH band 3143, 3900 4300	CH band 3064	Other Bands	Continua
Nitric Oxide		4					6100Å - 6500Å λ_{max} 5150
Nitrocyl chloride	30 cm	20					6100Å - 6500Å λ_{max} 5150(6)
Boron trichloride	14 cm	15				BO_2(8)	Probably continuum
Carbonyl chloride							Continuum (to be checked)
Carbon disulfide	7 cm	10					2700Å - 5200Å λ_{max} 3200Å(5)
Carbonyl sulfide	20 cm	19					2700Å - 5200Å λ_{max} 3200Å(8)
Hydrogen sulfide	19 cm	12					2700Å - 5200Å λ_{max} 3200Å(5)
Hydrazene	9 cm	17			(4.5)	NH (0.5) NH_2(7)	6200Å - 6500Å λ_{max} 5600(6)
Acetylene	18	10	(7.5)	(>>10)	(0.4)		3800Å - 6000Å λ_{max} 5000Å(3)
Ethylene	8 cm	20	(1.0)	(7,6)	(11)		Possibly continuum
Methyl acetylene	3 cm	20	(3)	(>>10)	(6)		3800Å - 6000Å λ_{max} 5000Å(2)
Allene	4 cm	19	(1.5)	(>>10)	(9)		Possibly continuum

TABLE 2 (Continued)

REACTIONS WITH ATOMIC OXYGEN

Reactant	Flow Meter Reading	Gain Factor	Spectral Feature & Intensity* (2 bands) 4700-5000	CH band 3143, 3900 4300	OH band 3064	Other Bands	Continuum
exyne	3 cm	15	7	(>10)	(>>10)		Continuum possible
Hexene	3 cm	20		(4.5)	(>>10)		Continuum as above possible (3) (3800 - 6000)
Ethyl alcohol	12 cm	20		(1.5)	(3.6)		
Benzene	16 cm	20		(>10)	(4.5)		
Nitromethane	7 cm	17			(8.7)		NO_2 Continuum 6100 - 6500Å λ_{max} 6500(3.8)
Trichloroethylene	8 cm	20	4.5	11	8.7		3800 - 6000Å λ_{max} 5000Å(4)

*The figure in the bracket indicates the peak relative intensity of the strongest observed spectral feature indicated by the recorder.

1. Hydrocarbons

It has been previously mentioned that the chemiluminescence of the reaction between saturated hydrocarbon and atomic oxygen is very weak as compared with unsaturated ore. Therefore, mainly unsaturated hydrocarbons were studied together with some other hydrocarbons. The spectrum of the chemiluminescence consists mainly of CH, OH and C_2 bands and a continuum. Table 3 shows the relative intensity of various spectral features in different reactions. From Table 3, it can be concluded that acetylene and hexyne are more efficient in producing chemiluminescence during the reaction with atomic oxygen. Moreover, the other organic compounds like halogen substituted hydrocarbon, ethyl alcohol, benzene, nitromethane do not show marked chemiluminous efficiency.

2. Sulfur Compounds

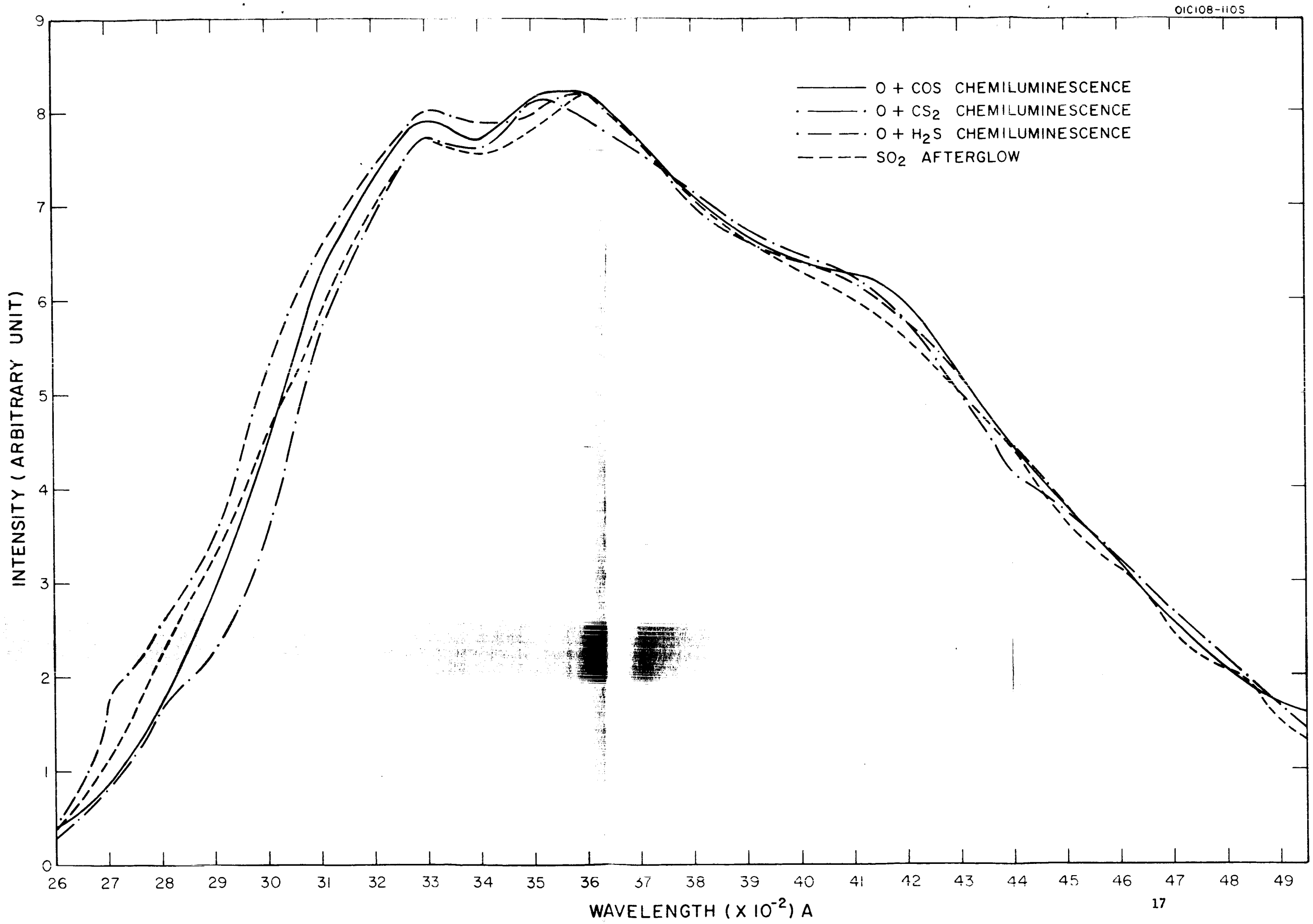
The chemiluminescent reactions of carbon disulfide, carbonyl sulfide and hydrogen sulfide were studied. It was found that all the above three substances show similar continuous spectrum (Figure 5). It was further observed that the spectrum is similar to that of sulfur dioxide afterglow. Recently, Herman et al.[5] and Halstead et al.[6] have concluded that the SO_2 afterglow is due to the recombination of SO with atomic oxygen. This is analogous to the recombination of NO and CO with O which have already been studied[3,4] in this laboratory.

It can be concluded from Table 2 that carbon disulfide is the most efficient, among the above three sulfur compounds, in producing chemiluminescence with atomic oxygen. Moreover, it is also evident from the table that the intensity of the chemiluminescence produced by the reaction of carbon

TABLE 3

CHEMILUMINESCENCE OF HYDROCARBONS WITH ATOMIC OXYGEN

Reactant	Gain	Δh	Spectral Feature 8.0,3150 OH-3064 CH-3143	9.3,3480 OH,3430 72	10.9,3870 CH-3900	12.4,4270 CH,4300	14,4690 C_2Swan $\Delta\theta$=+1	15.5,5050 C_2Swan $\Delta\theta$=0	17.2,5510 C_2Swan $\Delta\theta$=-1	19.2,6030 C_2Swan $\Delta\theta$=-2	20.9,0460 C_2Swan $\Delta\theta$=-3	Continuum
Acetylene	10	18 cm	0.4		1.6	>>10	7	7.6	2.8	1.0		(λ4200-600 (3)
Ethylene	20	8 cm	11		0.5	7.5	0.7	0.8	0.5	0.5		
Methyl Acetylene	20	3 cm	5.9		1.6	>>10	2.4	2.9	1.5	1.7		λ4200-6000(2)
Allene	19	4 cm	8.8		1.0	>>10	1.0	1.3	0.8	0.8		λ4200-6000(1)
Hexyne	15	3 cm	>10	1.1	4.0	>>10	3.0	3.7	1.9	2.0	1.0	λ4200-6000 (2.5)
Hexene	20	3 cm	>10			4.4						λ3000 5000(3.5)
Carbon tetrachloride												
Trichloro ethylene	20	8 cm	8.7		1	11	3.8	4.5	2.7	1.8	0.7	λ4200-6000(4)
Ethyl alcohol	20	12 cm	3.6			1.6						
Benzene	20	16 cm	4.4		1	>>10						
Nitro methane	20	Large										6000-6500 (3.7)


01C108-110S
O + COS CHEMILUMINESCENCE
O + CS2 CHEMILUMINESCENCE
O + H2S CHEMILUMINESCENCE
SO2 AFTERGLOW
INTENSITY (ARBITRARY UNIT)
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2
3
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Figure 5

disulfide with atomic oxygen is of the same order of magnitude as that of acetylene with atomic oxygen.

3. Nitrogen Compound

The spectra of chemiluminescence produced by the reaction of nitrosyl chloride and nitromethane with atomic oxygen were found to be the same as that produced during the reaction of nitric oxide with atomic oxygen. In agreement with the findings of Moore et al.,[7] we observe the bands of NH_2, NH and OH in the spectrum of the chemiluminescence produced in the reaction of hydrazene with atomic oxygen. From the short length of the luminous region in the reaction tube, it may be concluded that the rate of chemical reaction between hydrazene and atomic O is large, but the chemiluminous efficiency is not very high.

C. REACTIONS WITH ATOMIC NITROGEN

An extensive study of the chemiluminous reactions of several hydrocarbons with atomic nitrogen has been reported by Kiess et al.[8] A summary of our observations of the chemiluminous reactions of the above substances with atomic nitrogen is given in Table 4. It may be concluded from the Table 4 that the intensity of the chemiluminescence produced during the reaction of trichloro ethylene is, hexene and hexyne with atomic nitrogen is more than other hydrocarbons.

Weak luminescence is observed during the reaction of carbon disulfide and hydrogen sulfide with atomic nitrogen. Although Pannetier[9] et al. have reported the presence of NS bands in the spectrum of the chemiluminescence produced by the reaction of hydrogen sulfide and atomic nitrogen, but we were

TABLE 4

CHEMILUMINOUS REACTIONS OF ATOMIC NITROGEN

Reactant	Flow-Meter Reading	Gain	Spectral Feature and Intensity		
			CN Violet Band	CN Red Bands	Other Bands
Acetylene	~	15	(10)	(1.5)	
Ethylene	17	16	(11)	(1.5)	
Methyl Acetylene	17	15	(11)	(1)	
Allene	17	15	(12)	(1)	
Hexyne	7	13	(7)	(1)	
Hexene	3	14	(9)	(1.5)	
Ethyl Alcohol	19	20	(9)	(1.5)	
Benzene		20			
Nitromethane	>30	20			
Carbon Tetrachloride	23	20	(4)	(2)	
Trichloro ethylene	22	9	(6.5)	(1.8)	
Carbonyl chloride	24	20	(11)	(4)	

not able to detect it. This may be due to the fact that we are working at a lower pressure.

D. REACTION WITH OZONE

Bernanose and Rénè[10] have listed many compounds which have been reported to show chemiluminescence with ozone. Many of the compounds selected for the present study were from the above list. It was found that at a pressure less than 1 mm Hg and at room temperature, many of the compounds mentioned by Bernanose and Rénè do not show visible chemiluminescence with ozone. Among the compounds listed in Table 1, only nitric oxide, ethylene, hexene and hydrazene show faint chemiluminescence. Myne et al.[11] have given the details of chemiluminescent reaction of NO with ozone. After increasing the ozone concentration to the safe upper limit in the reaction of ozone with ethylene we have found an indication of the presence of OH band at 3070Å in the spectrum of its chemiluminescence. The reactions of some organometallic compounds like trimethyl aluminum are under present investigation.

E. EQUIPMENT

The ozone handling system has been modified. A reservoir for storing gaseous ozone has been added there by increasing the relative concentration of ozone in the reaction chamber.

In order to obtain correct relative intensity in the spectra of the chemiluminescence the spectral response of the detecting system has been determined.

F. CONCLUSIONS

On the basis of our present studies we can conclude that nitric oxide, acetylene and carbon disulfide may be relatively more suitable substance for the chemiluminous titration of atomic oxygen in the atmosphere. From the viewpoint of chemiluminous efficiency, it appears that trichloro ethylene, hexene and hexyne are suitable for the chemiluminous titration of atomic nitrogen.

The investigations of some organometallic compounds with atomic oxygen nitrogen and ozone molecule are being carried out.

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