December, 1967

A HYDROGEN - AIR DETECTOR SUITABLE FOR USE ABOARD SPACECRAFT

Final Report
Contract No. NAS8-20597

Prepared by

Robert J. Levine
Nassau Instruments, Inc.
26 - 206 Center
Princeton, N. J.

for

Geo. C. Marshall Space Flight Center
Huntsville, Alabama

TABLE OF CONTENTS

	Page
SUMMARY	
I. INTRODUCTION	1.0
II. OBJECTIVES	2.0
1. Background	2.0
2. H_2 Gas Properties	2.1
3. Commercial Instruments	2.1
4. Design Goals	2.3
III. TECHNICAL INFORMATION	3.0
1. H2/Air Flammability Limits	3.0
2. Catalytic Sensors	3.3
3. Sensor Poisoning	3.6
4. Depoisoning	3.8
5. Explosion Suppression	3.8
6. Theoretical Considerations for Sensor	3.9
7. Double Bridge Theory	3.11
IV. SYSTEM AND COMPONENTS DESCRIPTION	4.0
1. System	4.0
System Specifications	
2. Double Bridge Controller	4.1
3. Sensor	4.2
V. TEST RESULTS	5.0
1. General Comments	5.0
2. Controller Breadboard	5.0
3. Laboratory Sensors	5.1
4. Altitude Effect on Sensor	5.4
5. Temperature Tests	5.5
6. Flow Sensitivity	5.5
7. Calibration Gas Concentration vs.Indicated LEL	5.5
8. Voltage Supply Effects	5.6
9. Sensor Depoisoning	5.6
VI. RECOMMENDATIONS.	6.0
VII. REFERENCES	
ILLUSTRATIONS	

LIST OF ILLUSTRATIONS

Fig. 1 Minimum Ignition Energy vs. fuel/oxygen Ratios.

Fig. 2 SK-1067-27, Temperature vs. Indicated LEL - Commercial Instrument.

Fig. 3 SK-1067-11, Pressure vs. Indicated LEL, Commercial Instrument.

Fig. 4 Effect of Temperature on Flammability Limits of Hydrogen in Air

Fig. 5 Pressure vs. H_2/Air for ignition

Fig. 6 Ignition Energy vs. H_2/Air Mixture

Fig. 7 Ignition energy vs. pressure

Fig. 8 Pres. vs. Temperature for Explosion limits

Fig. 9 SK-1267-10 E_o vs. pressure Nassau Instruments, Inc. System.

Fig. 10 Not Used.

Fig. 11 SK-168-17 Block Diagram Double Bridge.

Fig. 12 SK-1067-3 Plot of √% LEL vs. E_o.

Fig. 13 SK-1266-1 Test Cht. No. 1 Wien Bridge.

Fig. 14 SK-367-7A Test Cht. No. 1.

Fig. 15 B-102-700-B System Diagram H_2/Air Sensing System.

Fig. 16 Photo of Sensor and Controller.

Fig. 17 C-102-104 Controller - Internal View & Test Points.

Fig. 18 Sensor-Internal View (Photo).

SUMMARY

An investigation was made of the conditions which could support ignition of Hydrogen-Air mixtures aboard a spacecraft. It was found that ignition of H_2/Air mixtures is a weak function of temperature and can be made to occur at altitudes as high as 120,000 ft. if sufficient ignition energy is supplied and if areas large enough to contain the ignited globule exist so as not to extinguish the ignition by wall quenching.

A catalytic type sensing system was developed which made use of the Nassau Instrument proprietary Double Bridge System. The instrument was shown to be capable of detecting 0.04% Hydrogen/Air (1% LEL), was temperature and flow insensitive, but did respond to altitude changes.

Recommendations for further improvements of the sensor to eliminate the altitude and contamination sensitivities are included.

I. INTRODUCTION

This report is submitted to fulfill the requirements for a final report on contract NAS8-20597. The project had as its objective the design and manufacture of two Hydrogen Gas Combustion Detectors for spacecraft application. The instruments supplied each consist of a sensor and an electronic package. The sensor has a range of from 0 to 150% of the lower explosion level of a hydrogen/air mixture with 100% being defined as 4.0% hydrogen in air by volume at normal temperature and pressure. The output signal is a dc voltage ranging from a minimum value to a maximum of 5 volts with the signal being proportional to the square root of the lower explosion level (LEL).

The design objectives stated in the next section included operation from a space vehicles' standard 28 V d.c. power supply, over a temperature range of from -55° to + 70° C. and an altitude range of from sea level to 50,000 feet which corresponds to a pressure range of 760 mm. to 87 mm. of Hg.

The basic principle employed was the use of catalytic and non-catalytic heat sensing devices both in feedback loops which made use of the Nassau Instruments proprietary Double Bridge system.*

By the use of the sensors in the Double Bridge system, a high speed of response has been obtained and a system designed which is essentially free of temperature changes.

The work consisted of 4 phases:

Phase 1: Definition of the Problem and Application Engineering.

Phase 2: Design and Test of Specific Equipment.

Phase 3: Manufacture, Delivery and Final Inspection of the two instruments.

Phase 4: Documentation and Report Preparation, of which this report is included.

* Patent pending.

II. OBJECTIVES

II-1. Background.

The explosive hazard associated with the presence of combustible gases has been the subject of major consideration for many years dating back to the hazards encountered in mines and enclosed areas where the exhaust gases of guns allowed a concentration of potentially explosive gas mixtures to accumulate. In space applications where the vehicle employs hydrogen as a fuel, the problem has been particularly severe because of the considerable quantity of the hydrogen gas present and because of the characteristics of hydrogen which is a colorless, tasteless gas and is combustible over a very wide range of its air/gas ratios. Because hydrogen in its ideal (stoichiometric) mixture requires less energy than any other gas to ignite, the problems associated with its use have become increasingly urgent.

There have been many studies describing the problems encountered with hydrogen [1,2, 3]. In these studies a number of different techniques have been described for the detection of combustible or potentially combustible hydrogen/air mixtures. The one which is almost exclusively used for commercial applications consists of a sensor in which catalytic and noncatalytic material is employed in a wheatstone bridge which is generally powered so as to be self-heating at some preselected operating temperature below the ignition point of hydrogen but high enough to provide good catalytic action on the sensitive element. As hydrogen/air burn catalytically on the active element, the bridge unbalances and this unbalance is taken as a measure of the hydrogen gas present. The devices are generally calibrated in terms of the per cent of the lower explosion level (LEL) of a hydrogen/air mixture which is generally taken as being 4.0% H_2 by volume. Thus an output reading of 50% would indicate 2% H_2/air present.

In addition to the catalytic sensors there have been other devices designed and tested which include the following:

(1) A chemical or electrical chemical detector which rely upon the electro-chemical consumption of hydrogen as opposed to the oxidation of hydrogen by combustion.

(2) The change in resistance of a thin film of palladium metal as a function of hydrogen concentration (not combustion).

(3) A measurement of the thermal-conductivity of the hydrogen/air mixture as compared to air having no hydrogen.

---

1. All references are collected at the end of this report by their numbers.

(4) A measurement of the change in the pressure in the volume of a sample when the hydrogen within the sample is oxidized.

Although each of these methods have been studied they all have severe inherent limitations which render them impractical for space application. Furthermore, none of them offer any advantages over the catalytic sensing method and they are all more complicated in execution. Perhaps the greatest objection, is that with the exception of the catalytic detector, none of the other methods use an intrinsic property which would monitor combustibility which was the factor of greatest concern. As an example, as instrument based upon thermal-conductivity might produce an output in the presence of some other gas having thermal conductivity properties similar to hydrogen but not necessarily explosive.

II-2. Hydrogen Gas Properties.

Hydrogen gas is colorless, oderless, and tasteless. Its atomic weight is 1.00797, its melting point is -437.46° F. Its boiling point is -422.5° F. and its specific gravity is approximately 7% in air. Although hydrogen has a higher ignition temperature than most hydrocarbons (1085° F. vs. a range of from 300 to 1300° F.)[2], the energy required to ignite a stoichiometric hydrogen/air mixture is only 0.02 millijoules as opposed to 0.3 millijoules for a stoichiometric air/pentane mixture. It is possible to build up a static charge on an insulated member with hydrogen or a combustible mixture of hydrogen and air flowing past such a member and there have been some experiences when the discharge of this static charge was sufficient to ignite the mixture. Combustion of a hydrogen/air mixture can take place over a very wide range. The hydrogen volume range is from 4.0 to 74% for air and from 4.0 to 94% for oxygen. Figure 1 shows a plot [4] of the minimum ignition energy vs. the fuel oxygen ratios for hydrogen in a variety of other hydrocarbons.

II-3. Commercial Instruments.

The detection of combustible gaseous mixtures, primarily of hydrocarbons, has resulted in the development of a now fairly well accepted group of instruments in which a fine filament of platinum wire or alternately, a catalytic sponge or film is placed in a wheatstone bridge circuit. Electrical currents pass through the bridge circuit causing the sensing elements to heat to a temperature at which the catalytic combustion occurs. This ranges from 200° to 700° C. Under these conditions the bridge is balanced and the sensing elements are then subjected to a sample of the potentially hazardous gas.

If the gas is present in a ratio below the LEL, it burns catalytically on the sensor surface causing one element of the bridge circuit to raise in temperature and thus in resistance so as to unbalance the bridge. The bridge unbalance is measured either directly or electronically and the degree of unbalance is calibrated in terms of percent of LEL. Devices using this principle are currently in use in industry and are generally satisfactory once their limitations are properly understood.

Virtually all of the present commercially available sensors are designed so that the sensing heads are of the diffusion type. This means that the elements are placed in a chamber so that the convection currents generated by the heat of the sensors set up a flow of air through the element. The claim is made that by such a design no external pumping is required.

It is important that the limitations of the commercial diffusion heads be properly understood. Diffusion sensors pump at a very slow rate. This rate is sufficient if there is H_2/air present because in the diffusion regime more H_2/air molecules are presented to the sensor than can be burned catalytically. Because the sensors pump by diffusion, however, it is apparent that the pumping process occurs at a very low rate and it means in effect that the hazardous gas must find the sensor.

During the burning process the heating rate of the sensing element with diffusion pumping is a function of the ambient temperature and pressure. Thus, while the standard commercial sensor is balanced for zero drift vs. temperature with no gas present its calibration becomes very much a function of both temperature and pressure once burning starts. This is illustrated in Figure 2 and 3 in which LEL output was observed with calibrated gases at various temperatures and pressures. Note that with 3% H_2/air (75% LEL) errors of +14, -10% were observed with temperature. At reduced pressures the errors increased with lowered pressure for a change of from 75 to 93% LEL with a 75% calibrated gas. This corresponds to a reading error of $\left(\frac{93-75}{.75} \times 100\right) = +24\%$.

Since it is to be expected that low pressure and low temperature would occur with increased altitude the error will add for a total of 14 x 24 = +38% error.

Some companies have made equipment which requires the use of pumps to sample the gas so as to get a much more positive and predictable sample of the air/gas mixture in an area being surveyed. The difficulty of pumping with standard sensing heads lies in the process of obtaining a predictable catalytic burning rate under anything other than diffusion pumping.

In the diffusion regime many more molecules of hydrogen and air are available for combinations than can be combined on the surface of the catalytic sensor. As a consequence, the heat developed on the surface of the sensor is a function only of the ratio of the hydrogen-air mixture rather than an additional factor of the rate at which the molecules are presented. If the gas is presented at a rate faster or slower than the predictable diffusion rate, the rate of heat developed and therefore bridge unbalance will no longer be so predictable and for this reason it is necessary, in a standard commercial unit, to pump at a well controlled and calibrated flow rate which means that not only is a pump required but a flow rate controller must also be employed and continuously observed to insure that the pumping rate does not change from the calibrated amount. Since safety monitoring is a 24 hour a day, seven day a week process it is easy to see why diffusion rather than mechanical pumping has become the accepted technique. The result of this is that unless a large number of diffusion sensors are used, it is possible for a substantial concentration to build up in one part of an area before it is observed by the diffusion sensor at a point, say, 5 or 10 feet away. Furthermore, the time required before the gas reaches the diffusion head may be such as to preclude the taking of the necessary precautionary counter measures.

II-4. Design Goals.

The goal of this effort was the development of a hydrogen/air combustible gas mixture detector to detect hydrogen accumulation in an area on board a Saturn vehicle. The contract called for the delivery of two complete instruments. The design goals were specified as follows:

1. Operational specification.

(a.) The system shall operate from 28 Volts D.C. $\pm$ 10% with 70 V. spikes. The output shall be a voltage ranging from 0 to +5 volts d.c. isolated from power ground which shall represent inputs from the minimum detectable concentration of hydrogen in air up to an upper range value on the order of 150% of the lower explosion limit (LEL). Output voltage shall be the square root of LEL.

(b.) The minimum detectable amount of hydrogen shall be at least 1% hydrogen in air.

(c.) The response of the system shall be less than 1 second.

(d.) The accuracy of the system shall be $\pm$ 1% of full scale.

2. Environmental specifications.

(a.) Vibration. 20 to 2,000 cps random noise. 0.6 g^2/cps for 12 minutes in each of 3 perpendicular planes.

(b.) Temperature -55 C. to + 70 C.

(c.) Pressure: the system shall be capable of operating with specifications at altitudes up to 50,000 ft.

(d.) The instrument must not cause an explosion in the presence of an explosive mixture.

(e.) The system shall meet RFI requirements.

(f.) Acceleration: 10 g maximum.

(g.) Accoustic noise: The system shall be required to operate within specifications and subject to accoustic noise of 160 db in a frequency range of from 100 to 10,000 cps with 0.0002 dynes/cm^2 reference.

(h.) Humidity: 95%, 48 hours, cycled between 25°C. and -70° C.

It was understood that while the equipment to be developed should be capable of meeting the above specified design goals if possible, it was not intended to actually operate on board a Saturn vehicle.

III. TECHNICAL INFORMATION

III.1 H_2/Air Flammability Limits.

There have been many investigations during the past 50 years to determine the combustion properties of hydrogen in air, in oxygen and in other mixtures including oxygen, nitrogen and third part gases. The most comprehensive information is contained in report No. 1383 "Survey of Hydrogen Combustion Properties" by Drell and Belles, published by the NACA in 1958[1]. In describing the flammability limits of hydrogen/air mixtures it is necessary to specify the operating temperature and pressure and to also understand that wall quenching may have an effect on the limits. It is also necessary to distinguish between coherent and noncoherent flames and upward and downward flame propagation.

The flammability limit for most fuels vary depending upon whether the measurements are made for an upward or downward propagating flame because of convection effects which assist the flame as it travels upward. This is particularly true for lean mixtures of hydrogen and air. The rich limit for hydrogen is the same for both upward and downward flame propagation, 75% by volume. The lean limit however, is affected for upward propagation by whether or not a coherent flame is observed. For upward or downward coherent flame propagation the limit is 9.0% by volume. This is the leanest limit of a hydrogen/air mixture that burns completely. Leaner mixtures down to the noncoherent limit of 4.0% hydrogen are flammable, but the flame is made up of separate "globules" which slowly ascend in the vessel in which the test is being conducted. Although these globules do not burn all the fuel they have to be reckoned with for safety and it is for this reason that the lower explosion limit for hydrogen air at normal pressures and temperature is taken at 4.0%.

Temperature effect: Heating a mixture of hydrogen/air widens the flammability range so that the lean limit occurs at lower concentrations and the rich limit at higher concentrations as the temperature is increased. This is shown in Figure 4.

Altitude effects: There has been much written and wide misunderstanding about the effects of pressures below one atmosphere on explosion limits. Extensive work was done by J. Drop5 which was summarized by Coward and Jones. Observations were made that the flammability range narrowed as the pressure was reduced, gradually at first then more rapidly to an absolute pressure of approximately 50 mm. of

mercury. At this point it was believed a minimum pressure was reached below which no mixture propagated a flame. Drell and Belles' have shown that the above observations of flammability limit against pressure is merely a curve showing the concentrations and pressures for which the quenching distance is equal to the diameter of the flame tube. From the most recent data it would appear that there is no measurable minimum pressure below which an explosion can occur and flame propagate if the flame tube is large enough.

At the outset of this project the assumption was made that the Drop and the Coward and Jones data was correct so that it was only necessary to be concerned with pressures down to about 80 mm. of mercury corresponding to 50,000 ft. of altitude. With the newly found data, however, it is now known that it is possible to obtain flammability at pressures as low as 4 mm. of mercury. A plot of hydrogen/air mixture vs. flame propagation at various tube diameters is shown in Figure 5 which is extracted from Ref. 1. This shows that as long as the flame diameter can be allowed to be big enough to support itself without being quenched by a nearby wall it is possible to get burning at pressures down to 4 mm. of mercury absolute corresponding to an altitude of 119,000 ft. To do so, however, requires a much greater ignition energy as discussed in the next section.

Ignition energy vs. altitude. A plot of minimum ignition energy vs. hydrogen/air mixture is shown in Figure 6. As is shown, while ignitions have been made to occur with as little as 0.02 millijoules of a stoichiometric mixture of hydrogen and air at one atmosphere, it took 0.6 millijoules at the lower explosion level. This became approximately 1.2 millijoules at an atmospheric pressure of 0.2 of sea level. Fig.7 is a logarithmic plot of the data shown on Fig. 6 from which a rough relationship between ignition energy and pressure can be determined. This is shown to be approximately:

$$I = KP^{-2}$$

I - Ignition Energy
P - Absolute Press
K - Constant

It therefore becomes apparent that while there is no definitive limit to the altitude at which it can be absolutely stated that an explosion will not occur, there are very definite practical limits above which it is reasonable to assume that ignition sources of a magnitude large enough to cause the explosion will not occur. The limiting factors are:

(a.) The magnitude of the available ignition energy.

(b.) The size of a flame which can be propagated before being quenched by a cool surface.

While (a) is difficult to estimate, (b) is entirely controlled by the local geometry. Using the data from Fig. 5 it is obvious that flames cannot propagate in areas having metal elements separated by 5 inches or less at pressures below 8 mm. Hg. abs. For distances of 20 inches the minimum pressure is 2 mm. Hg. abs.

These are extremely conservative estimates and only hold for mixtures well above a 9.0% H_2/air mixture. For non-coherent flames the limits appear to be at substantially higher pressures.

Altitude vs. Temperature Effect. The conditions under which hydrogen/air mixtures will ignite spontaneously as well as with external ignition is a function of the combination of pressure and temperature. Fig. 8 shows a collection of curves of the explosion limits as a function of temperature and pressure. The solid line is a curve of the stoichiometric hydrogen/oxygen mixture. The data was taken in a spherical vessel 7.4 cm. in diameter. From the previous data we will assume therefore that wall quenching would prevent ignition from occurring at pressures less than approximately 5 mm. of Hg. abs. Fig. 8 shows that at this pressure we do have the lowest temperature at which ignition can occur. This curve is used to describe the so called 1st, 2nd, and 3rd explosion limits of hydrogen air mixtures. Along a vertical line of constant temperature there is first no explosion. At some given pressure the first limit occurs and explosive conditions prevail until the vertical line intersects the curve at a higher pressure after which no explosion can occur. Finally, depending upon what the temperature is, a third limit occurs.

The explosion limits depend upon not only the quenching distance (the size of the vessel in which the tests are made) but also what is on the walls or surfaces. This is shown by the dashed curves in Fig. 8. The larger the vessel the lower the pressure of the third limit as it is shown in Fig. 5. The junction of the first and second limits is displaced to higher temperatures as the vessel is made smaller (i.e....the quenching distance is reduced).

Fig. 8 shows that under the best combination of temperature and pressure and with the stoichiometric mixture of hydrogen/oxygen, the lowest ignition temperature is just under 400° C. It was on the basis of these considerations that the maximum operating temperature of the sensor used for this equipment was chosen as 350° C. By maintaining this temperature under all conditions of either catalytic burning and/or outside ambient temperature there is no possibility that the sensor itself can ignite an explosion.

III-2. Catalytic Sensors.

The sensing principle used to detect the presence of small quantities of hydrogen/air mixtures is the use of two thermally sensitive elements placed in the air/gas stream, one being capable of producing catalytic burning on its surface and the other incapable of producing such burning. The system is designed to measure the effects of such burning which are proportional to the amount of hydrogen present.

The catalytic activity with heterogeneous catalysts is a surface process in which the gas is adsorbed, that is, it collects in layers so as to react with the surface. The surface reaction is a combination of chemical and electrical phenomena and is generally termed chemisorbtion. In the process, molecules of hydrogen and oxygen are made to react on the surface of the catalyst at temperatures and at mixtures at which they would not otherwise combine. In the process of combining to form water, heat is given off and it is this heat which is related to the amount of hydrogen present.

The chemistry, electronics and mechanics of catalysts are quite complex with much supporting literature 6,7,8,9. Although most of the theoretical considerations are beyond the scope of this report, certain conclusions are presented so as to understand the underlying reasons for the design of the sensors in the present form and also for an understanding of their limitations.

Catalytic adsorbtion is affected by the diffusion coefficient of the gases directly around the heated element, the temperature of the element and the catalytic activity coefficient of the elements' surface.

On a catalytic surface most of the available energy in the gas mixture will be converted to heat if all of the gas molecules are presented to the surface. From this one can conclude that there is a miximum gas velocity beyond which the effective catalytic activity will be reduced since not all of the available molecules will be presented to the surface. The velocity below which the catalytic activity is influenced is called the diffusion regime. In this range of gas velocities, fresh gas molecules are constantly presented to the catalytic surface for conversion and the amount of heat generated is only a function of the gas concentration and not the velocity of the gas. To eliminate any flow effects from a catalytic detector, it is therefore

necessary that it be designed to be operated in its diffusion regime. However, if it is so operated there are certain pressure effects which must be considered.

Rate of Combustible Gas Diffusion to the Hot Catalytic Surface.

The diffusion coefficient is a function of the rate of gas diffusion toward a hot surface. It is proportional to the square root of the hot surface temperature and inversely proportional to the gas density. The mass diffusion rate, in moles per second, is equal to the gas density multiplied by the diffusion coefficient and the concentration gradient. Thus, the mass diffusion rate is independent of the density and only dependent on the square root of the hot surface temperature.

Effect of the Combustion Process on the Hot Catalytic Element.

1. From these considerations there are two conditions of the combustion process on the hot catalytic element which must be considered. The first is the effect of pressure on the amount of combustion energy which is implanted in the heated catalytic element. The second is the effect of pressure on the amount of heat which is conducted away from the catalytic element.

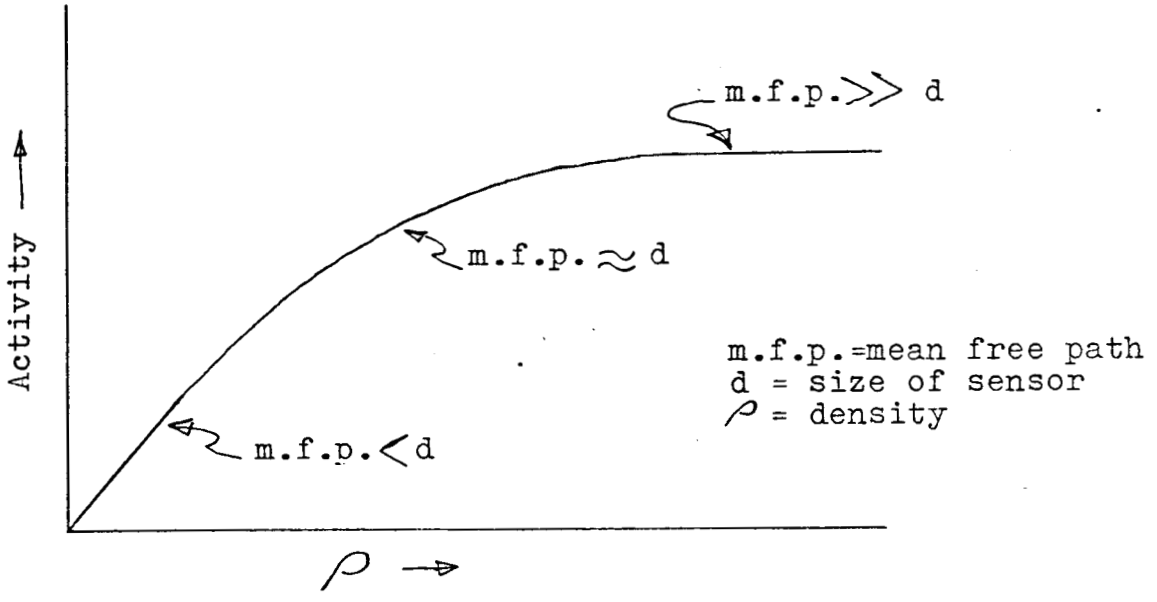
(a.) Pressure vs. Combustion Energy

The heat loss from the hot catalytic element due to gaseous conduction is proportional to the product of the thermal conductivity K, element surface area A, and the difference between the element temperature and the temperature of the chamber wall in which the sensor element is contained. The thermal conductivity is proportional to the square root of the gas temperature and is independent of the pressure. This independence of pressure assumes that the size of the sensing element, d (assumed here to be cylindrical) is much greater than the mean free path of the gas molecules. This means that the gas molecules collide with other molecules easily since the mean free path is so small. As a consequence, all the molecules striking the heated element are not at the wall temperature but are at a higher temperature having previously collided with other hot molecules. In this system we have a temperature gradient which extends from the heated element out to the cold wall.

(b.) Pressure vs. Heat Conducted Away.

If the mean free path is lengthened by reducing the pressure so that it is of the same order as the size of the sensing

element or less, many of the molecules which strike the element have not previously collided with hot molecules are therefore at the wall temperature. Thermal conductivity of the gas now becomes proportional to the density or pressure of the gas. The transition from one condition to the other is gradual as shown below.



Note that the flat part of the curve extends further to the left as the element size increases.

(c.) In a conventional catalytic detection system such as is used by most commercial manufacturers, the mean free path is much less than the sensor size.

$$E.P. + C.P. = KA\ (Twc - T_{\infty})$$

and

$$E.P. = KA\ (Twnc - T_{\infty})$$

E.P. is the electronic power
C.P. is the combustion power
Twc is wire temperature of the catalytic sensor
Twnc is the noncatalytic sensor temperature

Solving the above:

$$C.P. = KA\ (T_{wc} - Twnc)$$

or

$$T_{wc} - Twnc = C.P./KA$$

Since combustion power is independent of pressure the calibration is thus independent of pressure. However, when the mean free path is of the same order or less than the sensor size the above equation becomes:

$$C.P. = KA\rho (T_{wc} - T_{wnc})$$

or

$$T_{wc} - T_{wnc} = C.P./KAP$$

From this can be concluded that under these conditions the calibration is somewhat pressure dependent, increasing as the density is reduced.

(d) The Nassau Instruments sensor is designed to meet a number of the conditions for shock vibration, overall strength, electrical resistance, exact area matching and other factors resulting in it being very small with a dimension which approaches the mean free path at reduced pressures. Thus in the equation $T_{wc} = T_{wnc}$ and the two equations become:

$$A.C.P. + C.P. = KA\rho (T_w - T_\infty)$$

$$A.C.P. + D.C.P. = KA\rho (T_w - T_\infty)$$

where ACP is the a.c. power and DCP is the d.c. power in the Double Bridge System (See paragraph III-5). In this system the d.c. power (DCP) equals the combustion power (CP).

2. Effect of Pressure on Burning Power Deposited on Catalytic Element.

As the mean free path increases the oxidized molecule can move further away from the hot sensing element thus increasing the probability that some of the combustion power never reaches the wire. Thus at lower pressures, although the number of molecules diffusing on to the hot surface is independent of pressure, the fraction of the combustion power which is deposited there is reduced. As a consequence, the sensor developed under this contract is sensitive to reduced pressure operation as is shown in Figure 9.

In Section VI (Recommendations) methods of eliminating this pressure dependency are discussed.

III-3. Sensor Poisoning.

Heterogeneous catalysis is employed in the sensor being described herein. This type of catalysis is essentially a surface effect and is called adsorption or chemisorption. It requires that the gas molecule make physical contact with

the surface of the sensor before the reaction can occur. The surface mechanics of catalytic materials are not too well understood. What is known however is that the entire surface is not equally active but rather that there are zones or areas of catalytic activity and it is only in these zones that the reactions occur. These zones or areas make up only a small part of the total area of the catalytic material so that it is easily understood that very small amounts of material can desentize the catalytic areas.

To counteract the poisoning effect, commercial sensors employ catalytic materials having effective areas much larger than that which would be necessary simply to detect the presence of hazardous gas. By so doing they make it possible for a proportionately large part of the sensor to become poisoned without rendering it completely inactive. This increase in the area is done either by physically enlarging the catalytic surface materials such as by depositing a large area film of catalytic material or by the use of a coil of fine platinum wire much longer than would otherwise be needed. An alternate and very prominent practice is the use of a porous catalytic material deposited on the sensing element, generally in the form of a bead. The effective area of the porous material of the catalyst is many times larger than the observable surface area because of the thousands of fine pores in the surface. The use of this porous material not only increases the effective surface area so as to make the device much more sensitive than normal but also, to some extent, prevents the poisoning materials from entering the pores because these materials generally react with the catalytic material around the pores' entrance but do not go deep within the pore where the gases can penetrate.

The use of such material was considered for this project but was rejected because of some fundamental limitations. While the porous material reduces the poisoning problem there has been no way thus far found to use the material in a form that will meet the other requirements of the double bridge which are basic to the solution of the other problems such as temperature, flow and pressure-altitude. As an example, a commercial sensor employing the porous material had substantial temperature errors as is shown in Figure 10.

In a classical work on catalytic poisoning [6] Maxted states, "the poisoning of catalysts is essentially a preferential adsorption effect dependent on the formation of abnormally strong adsorptive bonds between a catalyst and certain types of adsorped species which are usually, but not always, foreign to the reacting system to be catalyzed. In most cases the strong adsorptive bond by means of which the poison

is held to the catalyst appears to be of a highly specific and chemical nature, the formation of such bonds being apparently dependent on definite types of electronic configuration both in the catalyst and in the poison. Although toxicity is of course a relative term, substances are in practice, only regarded as poisons if they exert an appreciable inhibitive effect on catalysis even when they are present in very small concentrations."

This preferential adsorption indicates that the poisoning process is highly selective so that depending upon the anticipated environment it may be possible to find catalytic material which will remain unpoisoned for long periods of time simply because the poisonous materials never appear. In this project a study was made to find such materials and while certain substances such as certain rare earth oxides were considered, other practical as well as time limitations precluded their use in the sensor developed. It is highly probable however that further work in this area would be productive and has been included in the recommendations in Section VI.

III-4. Depoisoning.

An alternate approach to the system design to eliminate poisoning effects would be to build in a mechanism which could automatically depoison at intervals frequent enough to insure that the system was always operational. There is much in the literature[6] on depoisoning but most processes require some chemical processing which would be impractical in an operational instrument. In the development work on this project means were found to depoison the various sensors built, primarily by raising their temperature to certain critical values in a combustible atmosphere. While this depoisoning was very effective in the limited work done, the sensors required recalibration after the depoisoning. The recalibration again was a relatively simple process but one which required additional work to be included in an automatic process which would happen at regular intervals.

III-5. Explosion Suppression.

One of the design goals on this contract was the design of a sensor which would be incapable of causing an explosion under operating conditions. In the work done two approaches were taken to this problem. In the first the data shown in Fig. 8 was used as a basis for the choice of the operating temperature of the sensors. As shown in Fig. 8 temperatures below approximately 400° C. were incapable of causing ignition

in any combination of pressures and/or mixtures since the data shown was for a stoichiometric mixture of hydrogen and oxygen. At any other mixture ratios the energy required for ignition would be greater and therefore the temperature higher. For this reason the operating temperature of the sensor was limited to approximately 350° C.

The body of the sensor element was designed to automatically provide quenching because of its physical size. This would limit any possible explosion therefore to only high concentrations of gas and air. Finally a flame trap was used as a diffuser. These flame traps [10] have been shown to stop flames in stoichiometric hydrogen/oxygen mixtures so that they are even more effective in lower concentration hydrogen/air flames. Both sintered bronze and sintered steel were found to be effective with the sintered bronze somewhat better. However because of the requirement to plate the sintered bronze it was decided for this project to use sintered stainless steel.

III-6. Theoretical Conditions for the Sensor.

The principle upon which the hydrogen/air detector operates is the use of two sensors one of which is catalytic and the other not catalytic operated in double bridge (described in Section III-7) so that both sensors are operated at the same temperature. This temperature is held constant under all conditions of ambient and input gas temperature. The sensors are held constant by being placed in a bridge circuit arranged so that the excitation voltage on the bridge causes current to flow through the sensor producing self heating. The circuit is arranged so that once the two sensors are at the exact same temperature, the feedback circuit acts to hold them at this temperature. A block diagram of the system in which they are used is shown in Fig. 11 and explained more in detail in Section III-7.

The first design consideration for the sensors is that for the two elements to remain at identical temperatures they must loose heat at the selected operating temperature at the same rate. Energy losses from any heat dissipating element fall into three categories: conduction, convection and radiation. The conduction losses consist of heat conducted away from the sensor by the mechanical members supporting it. The convection losses are those that are related to the aerodynamic properties of the sensor element and its gaseous environment, such as the gas density, velocity of the gas passing over the element, temperature gradient within the gas and to a minor extent, the absolute temperature of the gas. The radiation losses can be entirely accounted for

by the temperature differential and the emissivity of the sensor in the container body and are a fourth power of the temperature difference. In all of the above, the area of the sensor plays an identical role.

A simplified equation for heat loss in the sensor can be written as follows:

$$\frac{V^2}{R} + Q = K_1 A e \ (T_w^4 - T_\infty^4) \text{ (Radiation)}$$
$$+ K_2 A \ (pv)^{1/2} \ (T_w - T_\infty) \text{ (Convection)}$$
$$+ K_3 A \ (T_w - T_\infty) \text{ (Conduction)}$$

On the left hand or input side of the above equations is shown the temperature rise due to the electrical heating of the sensor resistance plus the heat of combustion (Q) caused by the catalytic burning of the gas. On the right hand side is a simplified formula for each of the three heat losses mentioned. Note that the area effect is identical for all three types. For radiation losses the effect of sensor temperature is a fourth power function. Emissivity (e) varies from a coefficient of 0 for a non radiating surface to a coefficient of 1.0 for a completely radiating surface. Since both of the sensor elements used in this equipment are bright, polished and silvery in appearance, the emissivity for both will approach 1.0. On the basis of the above equations it is apparent that the design requires that the radiating area and temperature be identical for both units. As a consequence both the catalytic and noncatalytic sensor were designed to have exactly the same physical shape and size and to the extent possible, the same color temperature. In practice it was found that the temperature could be held to within approximately 1° C. over the entire operating ambient and signal range. The areas of the two sensors elements were matched to within 1%.

At the outset of this contract the original sensor was conceived of as a multilayered platinum resistor with a catalytic coating covering the resistor but electrically isolated from it and with the entire unit being supported on a thin nonelectrically conducting substrate. The plan was to separate the catalytic heating from the resistive temperature sensing so as to allow flexibility in the choice of the catalytic material apart from that of the resistor. Subsequent events disclosed that this design was impractical. The requirements for a proper catalytic sensor to operate as a double bridge have been found to be as follows:

(a.) The <u>effective</u> heated areas of both the catalytic and noncatalytic sensors must be identical. This means that the

unit heat coming from each area of each sensor must be the same over the entire area of the sensor to insure predictable amounts of thermal radiation. Thus the integral of the temperature and the sensor area ($\int(TA)dt$) must be the same for both sensors.

(b.) The temperature of the catalytic surface must be at exactly the same temperature as the sensing resistor and furthermore must have the same property as the catalytic resistor, namely that its unit temperature over its entire area must be the same temperature so that the same degree of catalytic activity can be obtained from unit to unit.

To meet the above criteria it became apparent that no device which separated the heat radiation surface from the temperature radiation element could succeed. Furthermore tests on various substrate materials showed that the time constants on cooling associated with any practical size unit precluded the use of such substrates were far too great. As a consequence it became apparent that the catalytic metal had to be used as the sensing element.

III-7. Theory of the Double Bridge.

The hydrogen air sensing system described herein makes use of the Nassau Instruments, Inc. Double Bridge.* The Double Bridge allows the use of two sensors, one of which is a reference and the other the active sensor which needs to be matched at only one operating temperature since the bridge holds both sensors at a constant operating point under all conditions. The output signal is taken as a function of the voltage required to rebalance the reference sensor. The sensor for the hydrogen/air detector makes use of two platinum metal sensors which are differentially catalytic in a hydrogen/air mixture. One is much more so than the other. Both sensors are arranged so that they are exposed to the air/gas stream and are designed so that the gas is allowed to diffuse into the sensing chamber. The sensing elements are carefully matched for area and emissivity and placed in a bridge circuit so that they will always be maintained at a constant temperature. Figure 11 shows a block diagram of the sensors in a double bridge system. The sensor marked S_c is the active unit and the one marked S_{nc} is inactive. Potentiometer R3 is set initially so that the bridge will be balanced when S_c is at the required operating temperature. Because the circuit operates as a controller rather than as a true servomechanism, there is a slight unbalance from the bridge to provide the required excitation voltage E_f.

* Patent pending

In practice this unbalance is less than 1° C. The excitation voltage E_f is also supplied to the second bridge containing S_{nc} which is also made to balance at exactly the same temperature as S_c so that its output is zero under normal operating conditions. As the ambient temperature changes, S_c tends to heat or cool as the case may be, calling for more or less feedback voltage E_f to maintain it at a constant temperature. Since the heat dissipating characteristics of both sensors have been made identical at a given temperature the output of the second bridge remains zero over the entire ambient temperature range. When traces of hydrogen gas appear, catalytic burning occurs on the surface of sensor S_c tending to raise its temperature. Bridge No. 1 therefore calls for less rebalance voltage to maintain S_c at constant temperature. This unbalances Bridge No. 2 because S_{nc} is now too cool. Bridge No. 2 calls for more voltage which is obtained from E_o. To prevent the two rebalance voltages E_f and E_o intermixing, E_f is made to be AC and E_o DC. The circuit is arranged so that the rebalance voltage E_o is only applied across bridge No. 2. E_o then becomes the output function. Since E_o is balancing the heating required for S_{nc} which in turn is directly proportional to the mass and therefore % LEL of hydrogen gas, the percent LEL will be proportional to E_o^2/R where R is the effective resistance of bridge No. 2. E_o therefore is proportional to the square root of percent LEL in the circuit shown. To make the circuit linear will require a voltage squaring circuit at E_o. In the equipment being described the output function E_o was taken as shown and a calibration curve supplied as shown in Figure 12. It was felt that for the initial model it was preferable to have the increased sensitivity at the lower ranges of LEL. For later models it is a simple matter to provide a squaring amplifier to produce a linear voltage output vs. percent indicated LEL.

IV. SYSTEM AND COMPONENT DESCRIPTION

IV-1. System.

The Nassau Instruments H_2/air Combustible Gas Detector instrument is designed to sense the presence of small quantities of gaseous hydrogen in air over the range of 0 to 6 % hydrogen in air by volume corresponding to a range of 0 to 150% of the lower explosion limit (LEL), assuming that the most conservative figure of 4% is used for the LEL. As discussed in Section III-1 this is the limit for sea level temperature and pressure ambient, upward ignition and noncoherent burning.

The instrument consists of a sensor Model 102-119 and an electronic controller Model 102-100 shown in Fig. 16. It is a prototype designed for general use aboard a spacecraft. It differs from commercially available equipment in that it has been specifically designed to operate over the military temperature range (-55 to + 70° C.), makes use of military type electronic and mechanical components and operates from the spacecrafts standard 28 V. d.c. supply and is insensitive to flow. It has been demonstrated to operate at pressure altitude ranges equivalent to a range from sea level to 50,000 feet. The instrument is designed to be used with a vacuum source onboard the spacecraft. The vacuum, which can be supplied by a samll pump, is used to draw the gas/air sample through the sensor. Because the instrument has been designed to be relatively free of flow effects and because there is no impediment to the flow within the sensor, the pump need only be able to deliver a flow rate ranging from 3 to 10 liters per minute at a head of no more than 150 mm. of mercury.

The sensor shown in Fig. 16 is fitted with standard ¼ inch type pipe taps suitable for standard air tubing fittings. It can be mounted directly to the spacecraft without shock mounts.

The controller shown in Fig. 16 is housed in a drawn aluminum case and may also be directly mounted to the spacecraft. Connections between the controller and the sensor are by means of a multiconductor cable with connectors as shown on the outline drawings for both devices. The instrument was supplied with 6 foot long cables. However the system performance is not affected by the length of the cable between the sensor and controller. Table 1 lists the instrument specifications.

TABLE I

SPECIFICATIONS

Power Input:	28 V.D.C. ± 4 V. @ 0.6A. Negative ground
Operating Temperature Range:	-55 to + 70° C.
Gas Range:	0 to 150% LEL H_2/Air (0 to 6% H_2/Air)
Output Signal:	0.3 to 5 V.D.C. proportional to $\sqrt{H_2/Air}$
Min. Detectable Level:	1% LEL (0.04%) H_2/Air.
System Response:	1 sec. exclusive of time required to introduce gas to sensor
Pressure-Altitude Range:	Sea Level to 50,000 feet.
Altitude:	Sensor or Controller can be mounted in any direction and altitude variations will have negligible effects on the output.
Weight:	Sensor: 1.19 lb.
	Controller: 5.37 lb.
Range of Flow Rates thru Sensor:	3 to 9 l./min.

IV-2. Model 102-100 Double Bridge Controller.

A Photograph and an internal view of the controller is shown in Fig. 16 and Fig. 17 respectively. All electronic components in the controller are located on three printed circuit plug-in boards. Each board is identified and its connector has been made so that it can only mate with the proper connectors. The complete circuit block diagram is shown in Fig.15. Referring to Fig. 15, all of the components on the left side of the drawing are placed on the AC card and all of the components on the right side are on the DC card. The power supply board contains a 28 V. tube plus a 15 V. power supply, the 1 kc signal generator and the output operational amplifier shown in the upper right hand corner. All components within the dotted line on Fig. 15 are in the sensor.

The instrument was supplied with all calibrations having

been made at the factory. Under normal conditions no calibration need be done. However, provision is made within the controller housing for simple readjustment should it be required since all test points and controls are located at one end of the plug-in circuit board.

Standard printed circuit mechanical components as manufactured by Vero Inc. have been used in the controller. These units are simple to use, light weight and have withstood the military range of shock and vibration in certified tests.

IV-3. Sensor.

The sensor is housed in a welded aluminum case. Gas input and vacuum lines are connected through the ¼ inch pipe taps shown. The direction of gas flow is not important. Electrical connections to the controller are made through the connector.

All components within the sensor are mounted on the face containing the electrical connector as shown in Fig. 18. The sensor elements are contained within an aluminum metal block and are arranged so that the gas enters the sensing chamber through a diffuser bolted directly over the openings. This diffuser also acts as a flame trap as discussed in Section III-5.

The precision resistors used to complete the bridge as shown in Fig. 15 are all mounted on a circuit board below the block. Components have been chosen for their ability to withstand the environments to which they are subjected and specifically have very low thermal temperature coefficients.

All adjustments to balance the bridge circuits are made in the factory and must not be upset since these adjustments have been very carefully made to insure that both of the sensing elements are always at the exact same temperature. The only adjustment required in the sensor is that shown on Fig. 15 as P3. This adjustment is used to supply a small offset voltage to the DC section to produce a "live" zero calibration.

V. TEST RESULTS

V-1. General Comments.

The development effort on this contract was divided into two parts. The first was the design of a Double Bridge controller which would be suitable for the intended sensor. The second was the design of a sensor suitable for the intended environment.

Work was first directed towards the design of a breadboard electronic controller using a simulated sensor. Once this had been completed the final controller was packaged and tested.

Because of a series of difficulties in the development work on the sensors there were essentially three sub-programs carried out on the sensor development before the final sensor configuration evolved.

In the development process much valuable information was developed which, in the case of the controller, can have application far beyond the present hazardous gas detector. The sensor development has provided a much better understanding of the mechanics of hazardous gas detection using the catalytic type detector and points the way for further and perhaps dramatic improvement in the sensor development.

V-2. Controller Breadboard Development.

The first approach to the design of a feedback circuit was the use of a self oscillating circuit of the type shown in Figure 13 in which the resistive element was one leg of what is commonly considered to be a Wein bridge oscillator circuit. This circuit was tried as shown and while it maintained the voltage across the sensor, R_t it was very difficult to adjust for a selected value of R_t so that it was decided that a somewhat more elaborate circuit would have to be used Furthermore, analysis showed that with very fast responsive sensing elements, it was possible to get complex feedback modes unless the carrier frequency was made much higher than originally planned. Because of radio noise requirements in this equipment which, in accordance with MIL-I-6161, start at frequencies as low as 15 kc, it was decided to hold the carrier operating frequency to a maximum of 1 kc and to operate it in as pure a sinusoidel mode as possible to avoid harmonics. It was felt that to attempt to operate the system at, say 5 kc which would have put the third harmonic within

the radio noise spectrum, would be dangerous since if radio noise were ultimately found in the system it would be very difficult to lower the frequency of the carrier without extensive redesign. It would of course be impossible to test the system for radio noise until it was almost completely designed including final packaging.

For the above reasons it was decided to separate the feedback function in the bridge circuits from the excitation function and so the circuit shown in Figure 14 was designed.

Measurements on this circuit showed that it was capable of maintaining the temperature of the sensor within 0.16° C. with an overall amplifier gain of about 500. This constituted essentially the AC and DC feedback loops with provision for simply converting the AC to DC by rectification.

A complete frequency response of the system was not taken but observations of the circuit make it clear that the limits of the response time have to do with the time constants on the filter and the DC section and the LC series filter used to block the AC from the DC. All of these filters had time constants on the order of milliseconds. When the system was complete an observation was made where the sensor element was modulated with the voice frequencies by simply holding it close to the mouth and talking across it. Although the fidelity of the output left much to be desired, there was clear evidence of voice modulation indicating overall inherent frequency response of less than 100 milliseconds.

The 1 kc carrier frequency was generated in a simple parallel T oscillator circuit with a buffer amplifier to supply reference voltages to the discriminator circuits as well as input signals to both the AC and DC amplifier channels. This circuit was finally completed as a double bridge as shown in Fig. 15.

V-3. Laboratory sensors.

In the original concept it was planned to build the sensors on a nonconducting ceramic type substrate upon which would be placed first a platinum or nickel resistor, then a thin insulating film and finally a catalytic coating. Silk screen designs were made for the resistors in the form of a double S so that the resistance pattern covered most of the surface of the sensor. Calculations had shown that for purposes of heat dissipation an area on the order of 1 cm^2 was required. The initial sensors were printed on a variety of substrates

for evaluation including glass, polished aluminum, anodized aluminum and a smooth ceramic. It was found that even with the smoothest undercoat provided by the glass, the resistance from sample to sample varied so much so that a substantial amount of trimming would have to be done to obtain exact values of resistance. More important however was the fact that the overall area of resistors of the same value was not the same from unit to unit so that the radiating surface would be different.

It was impossible to fabricate the resistors using the thick film technique on anodized surfaces since the relatively rough surface provided discontinuities between the various areas of the resistor resulting either in open circuits or resistance values which varied over many orders of magnitude.

The glass base resistors were evaluated for their dissipation characteristics in air. It was at this point that it was discovered virtually impossible from a practical point of view, to make a unit whose effective heat dissipating area could be made uniform while at the same time controlling the exact resistance.

Reanalysis of the sensor requirements showed that it was mandatory that the resistance element be controlled very carefully. The second approach was the evaluation of a sensor which was essentially a very fine coil of resistance wire mounted between two very thin pure platinum metal layers and bonded to these layers with high heat transfer cement which transmitted the heat but insulated the outer shell from the resistance wire. Again dimensions on the order of 1 $cm.^2$ were maintained. Measurements were taken on the temperature of the inner heater element vs. the surface of the platinum which was to act as a catalyst. The theory followed was that the heat transfer rate would be reversible depending upon whether the coil was heated with the heat dissipating outward to the shell or alternately, the shell was heated with the heat being transferred inward to the coil. It was discovered that there was a large temperature difference between the coil temperature and the surface of the platinum. Furthermore, by scanning the surface of the platinum it was found that those parts of the surface directly over the center of the coil were considerably hotter than parts of the surface even as little as a 1/16 inch away. It was then realized that it would be virtually impossible to get a design in which the integral of the temperature and surface area would remain the same from unit to unit using this design approach.

At this point it became apparent that the catalytic material would have to be in such intimate contact with the heating element that for all practical purposes the only way it could be done was to make the catalytic material the heating element. The conditions for the sensor are detailed in Section III-6. Various forms were tried to determine whether one geometrical form had an advantage over another. There seemed to be no particular advantage to any form including the standard coil and so a very simple straight section was used.

The sensing elements were arranged in a holder such that they could be shielded from the outside environment by a porous diffusing material which would act both as a diffuser and also as an explosion suppressor as previously discussed. Considerable care was taken in the sensor to insure that the geometry of each unit was exactly the same both for the sensor shape itself and the surrounding environment. This eliminated possible differences in the rates of heat loss from each of the units.

The sensors were placed in an aluminum block with the diffuser secured across the top so that the gas could diffuse into each of the sensing chambers. On the bottom of the block all of the bridge resistors shown in Figure 15 were mounted so that the entire sensor could then be attached to the controller with a multi-conductor cable in which the resistance of the wires would not effect the sensor operation. As part of the calibration procedure both of the bridges were carefully balanced so that both sensors would be at the identical operating temperature. The assembly is shown in Fig. 18.

Before installing the sensor elements, exact data on temperature vs. resistance of the material was taken so that each bridge could be balanced to produce exactly the same operating temperature thereby guarantying that both sensors would operate at exactly the same temperature. Because of the results obtained with the double bridge circuit, it had been previously determined that once a temperature was established, the feedback control circuit held it within 1° C. over the entire operating range. This then insured that both sensors were within 2° C. of each other. Before finalizing this design various types of chambers, sizes of sensing material and variations in the mechanical arrangement of the sensor were tried. Although extensive testing was not done on each configuration, it appears that the simple design described above produced the same results as all of the other arrangements. Therefore the test data described below is that taken for the final sensor.

V-4. Altitude Effects on Sensor.

In Section III-1 it was shown that there was virtually no theoretical limit of altitude above which ignition cannot take place if enough ignition energy is supplied and if the gas air mixture is above certain minimums. It was shown that for ranges above 50,000 feet, however, the source of ignition energy required to cause an explosion increased substantially so that there is a practical limit above which it could be stated for purposes of safety, that no explosion hazard exists.

In Section III-2 the theoretical conditions for a catalytic type sensor were discussed and it was shown that a somewhat complex relationship existed between the heat generated on the surface of the catalytic material and pressures below sea level. For a constant temperature sensor with a limited area of the type used for this equipment it was shown that there was a direct pressure dependency on heat generated which effectively reduced the apparent output signal as shown in Figure 9.

To confirm these theoretical considerations a variety of tests were done. These tests were all performed in the laboratory in a Bell Jar used to simulate increasing altitude. The tests were performed both for the Nassau constant temperature device and for an uncontrolled temperature sensor as is generally found in commercial units. The results of these latter tests is shown in Figure 3. Other tests were run in still air/gas mixtures and with gases flowing through both the Nassau sensor and the commercial sensors. The results for the commercial sensors again shown in Figure 3. For the Double-Bridge sensor there was a slight effect with no flowing gas when the sensor was subject to changes in altitude. Referring to Figure 9, the curve shown fell off a little more rapidly. The curve shown was repeated in a number of different experiments with sensors of slightly different size but the same mechanical form. A variety of different diffusers was also tried ranging from a heavy porous paper to a thick section of porous stainless steel. As might have been expected from theoretical conditions the rate of diffusion through all of these materials was so fast that there was no observable effect. As is shown below there is no effect with varying flow rate with the Nassau Sensor once a minimum flow rate is established.

V-5. Temperature Tests.

Tests were run on each of the system components separately exposed to a temperature range of -55 to +70° C. Either the controller or the sensor was placed in the environmental chamber with the other component outside the chamber. Provision was made to flow the desired gas/air mixtures through the sensor at a constant flow rate of 3.8 liters/min. which had been determined to be a median flow rate within the flow range where the sensor would not be effected.

Power supply was constant at 28.0 volts and ambient termperature was 22° C.

V-5.1. Results.

(a.) Controller: There was no observable change in the output either at a zero % LEL gas or a 75% LEL gas as the temperature was varied over the entire range.

V-6. Flow Sensitivity.

The system was set up with provision for varying the flow rate of the H_2/gas from zero to 10 liters/min. Standard voltage and temperature was maintained. Data was taken for 75% LEL gas mixture. Flow was stabilized above 10 l./min. and then reduced.

V-6.1. Results.

Flow l./min.	E_o	Ind. % LEL
10	3.80	84
9.10	3.80	84
6.97	3.80	84
4.84	3.80	84
2.82	3.80	84
1.90	3.77	83
1.00	3.65	80

V-7. Calibration: Gas Concentration vs. Indicated LEL.

The system was set up at normal temperature, pressure and voltage. Provision was made to supply the sensor from various gas bottles having different H_2/air concentrations. Flow was regulated at a constant 3.8 liters/min. The gas was exhausted from the sensor into the atmosphere so that all pressures were at sea level. The instrument was initially calibrated so that a 75% LEL mixture yielded 3.52 volts

corresponding to 75% on drawing SK-1067-3. Readings of voltage were taken and LEL readings taken from SK-1067-3. The sensor was evacuated between each reading.

V-7.1. Results.

Gas Concentration % LEL	E_o V.DC	Indicated LEL % LEL
75	3.52	75.0
34.5	2.34	33.7
10	1.07	5.9
2	0.48	1.3
0	0.21	0.34

V-8. Voltage Supply Variations.

The system was set up at normal pressure and temperature with provision made to vary the supply voltage from 25 to 31 V. DC. Observations were made at 0% LEL and 75% LEL. There were no observable variations in the output indication under any of these conditions as a function of voltage variation.

V-9. Sensor depoisoning.

The catalytic detector elements employed in the H2/Air Combustible Gas Detector are subject to an effect called poisoning. The result of such poisoning is to change the response of the detector element so that it either has a smaller than known response or, in severe cases of poisoning, no response at all. As described in Sections III and IV, the poisoning of catalytic detectors is a surface effect which renders the detector inoperable unless the surface is decontaminated. A series of tests was conducted in an attempt to find a simple and possibly automatic, method to decontaminate sensors once they were poisoned. While the tests were not entirely successful in that an automatic method was not established, the results are reported here since it is possible that further work in this area can lead to such an automatic process.

The two primary poisoning agents to be considered are the products of various silicone materials the most important of which is silicone oil and grease and secondly, small amounts of Hydrogen Sulfide which are generally found as components of other materials. The tests were conducted with a standard

commercial grade of silicone oil which was applied to the sensor in a variety of ways none of which made any material difference. Ultimately the sensor was simply coated with the oil by using a small swab.

Tests were run on an operating sensor which was then poisoned by the above coating process, and retested to insure that it had lost its sensitivity. Various depoisoning techniques were employed to discover whether the sensor could be returned to its original level of sensitivity and secondly, to determine what effects if any such depoisoning activities had on the zero intercept of the % LEL curve.

The depoisoning techniques all centered around the heating of the catalytic element to a temperature of approximately 1500° F. in a combustible atmosphere for a short time. Although much data was taken, the variations in the data make it difficult to plot or tabulate. Essentially what happened was that assuming a reading of 100% for a 100% LEL gas mixture, directly after poisoning and depoisoning, the zero intercept which originally was very close to zero rose to a value equivalent to between 2 and 5% LEL and stabilized at this value. The sensor when initially exposed to gas after the depoisoning would produce an output as much as 50% higher than the original value. After approximately an hour, this value would gradually drop until readings close to the original were obtained. As the poisoning and depoisoning process was repeated the same effects were observed except that the time for stabilization was reduced. Although extensive tests were not run it was observed that there was apparently some relationship between the required stabilization period and the combustible air/gas ratio used during the depoisoning process. It is possible that an optimum value exists for a given sensor which would just return the sensor to its original value.

It is unfortunate that virtually all of the work in poisoning and depoisoning on this project had to be done empirically since there is no adequate theoretical basis for such work. An extensive search of the literature and of knowledgeable people in the field was made in the course of this project and it was generally concluded that although the generalities underlying the poisoning process are understood, it is impossible to quantify the available knowledge to produce a sensor which can be completely free of these defects. If a good theoretical understanding of this process were established catalysis could be a powerful tool for a large number of gas and vapor measuring instruments.

VI. RECOMMENDATIONS.

From the work reported herein it is clear that a very sensitive hydrogen/air gas detector can be made which, although it has certain limitations, will be suitable for spacecraft use. Further efforts should be directed in the following areas:

VI-1. Studies of nonplatinum materials which are catalysts for hydrogen/oxygen mixtures should be made with the objective of finding materials which:

(a.) are poison resistant to the commonly found materials around a spacecraft and

(b.) which can be fabricated to meet the requirements of the double-bridge i.e.....capable of having a resistance-area relationship which is readily controllable so that similar units can have identical heat dissipation characteristics at identical resistances.

VI-2. Catalytic sensors operating at constant temperature should be investigated for other sizes and shapes to reduce the effect of reduced pressures. One direction which theoretically appears fruitful is that of substantially increasing the area of the sensor to make the mean free path of the gas molecules much less than the effective area at reduced pressures. A second direction is the possible development of a porous coating which will allow hydrogen and oxygen molecules to pass through while discriminating against the larger molecules. Some of the work in this contract with the very fine diffusers indicated that such was possible.

Finally the sensor operating temperature can be lowered such that sufficient sensitivity is still obtained. An optimum temperature vs. pressure effect condition can be found.

Another direction which might prove fruitful although less elegant in principle, is to monitor pressure and increase the sensor temperature to compensate for the decreased activity. While theoretically possible this requires pressure ambient sensing and variations in system loop gain which could produce either stability problems or a long inherent response time.

VI-3. One of the important contributions to the art of hazardous gas sensing made on this contract was the use of

a sensor which was essentially non-flow sensitive. For this reason it is probable that a single sensor or a few sensors can be located and, with an appropriate vacuum pump and vacuum lines, can be set up to readily sense substantial volumes within the spacecraft. The sensing lines can either be set up all in parallel which is the simplest combination or, if it is desired to localize the source of the hydrogen/air, a pneumatic scanner which is presently available could be employed. A study of various operating modes of these sensors monitoring typical spacecraft areas should be made to arrive at an optimum or preferred techniques.

VI-4. Studies should be undertaken to obtain a clearer understanding of the mechanism of poisoning on platinum and platinum alloy materials for the purpose of developing methods which can be readily employed within an instrument to either prevent the poisoning, or since that is unlikely, to regularly allow a depoisoning cycle to be employed.

VI-5. The present controller measures 9 1/8 W x 7 1/4 H x 5 5/8 D and weighs 5.4 lbs. It was designed using readily available components and with the consideration of making all components readily available for initial evaluation. A second design employing either hybrid or preferably integrated circuits and tighter packaging could result in an instrument of approximately 1/4 the volume of the present unit and 50% less weight. It is also probable that the total power input could be reduced by approximately half.

REFERENCES

1. Report No. 1383, Survey of Hydrogen Combustion Properties, I. C. Drell and F. E. Belles, NACA, 1958.

2. Bulletin 503, Limits of Flammability of Gases and Vapors, Coward & Jones, Bureau of Mines, 1952.

3. Electronic Devices for Hydrogen Leaks and Fire Detection, Edw. H. Corcoran, Suppl. to IEEE Trans. on Aerospace. Electronic Systems, Vol. AES-2 #4, July, 1966

4. Electrical Ignition of Combustible Atmospheres, Alfred H. McKinney, Prec. ISA 1960 Symposium on Safety for Elec. Instr. in Hazardous Areas, May 1960.

5. J. Drop, Dissertation, Liedin 1936, Res. Trav. Chem. 54, 67 (1935) and 56,71,86 (1937).

6. Advances in Catalysis - III, Academic Press Inc., N. Y. 1951.

7. Catalysis and Catalysts, Marcel Prettre, Dover Pub. Inc., N. Y. 1963.

8. Diffusion and Chemical Surface Catalysis _ D.E. Rosner, J. Heat Transfer, Nov. 1962 pp. 386-394.

9. Catalytic Probes for the Determination of Atom Concentrations in High Speed Gas Streams, D. E. Rosner, ARS Jour. Vol. 32, No. 7 pp. 1065 - 1073, July 1962.

10. Egerton, A. C., Everett, A. J. Moore, N.P.W. Sintered Metals as Flame Traps 4th Symp. on Combustion, The Williams & Wilkins Co., Baltimore, 1953, pp. 689-695.

FIGURE 1

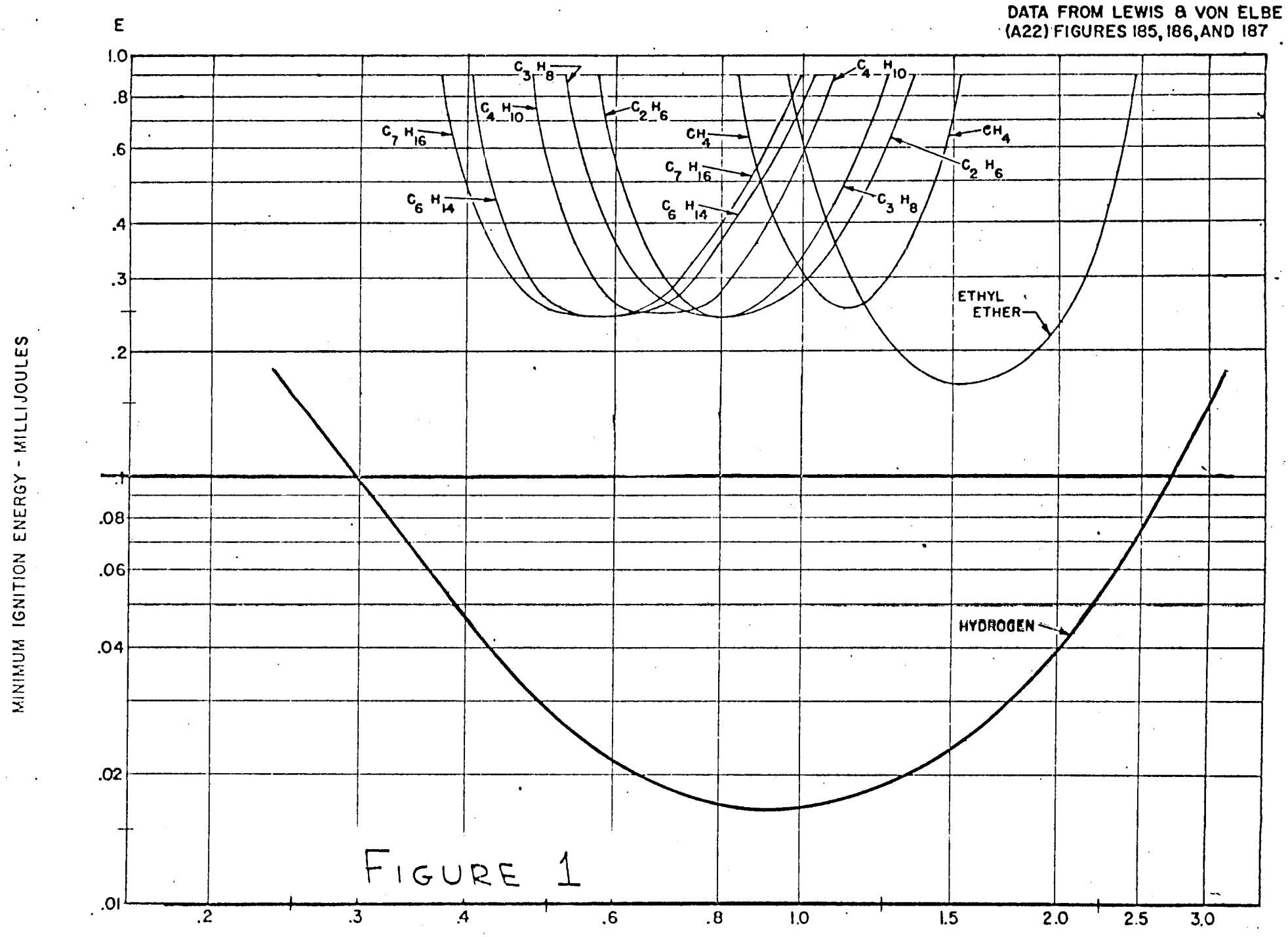


FIGURE 1

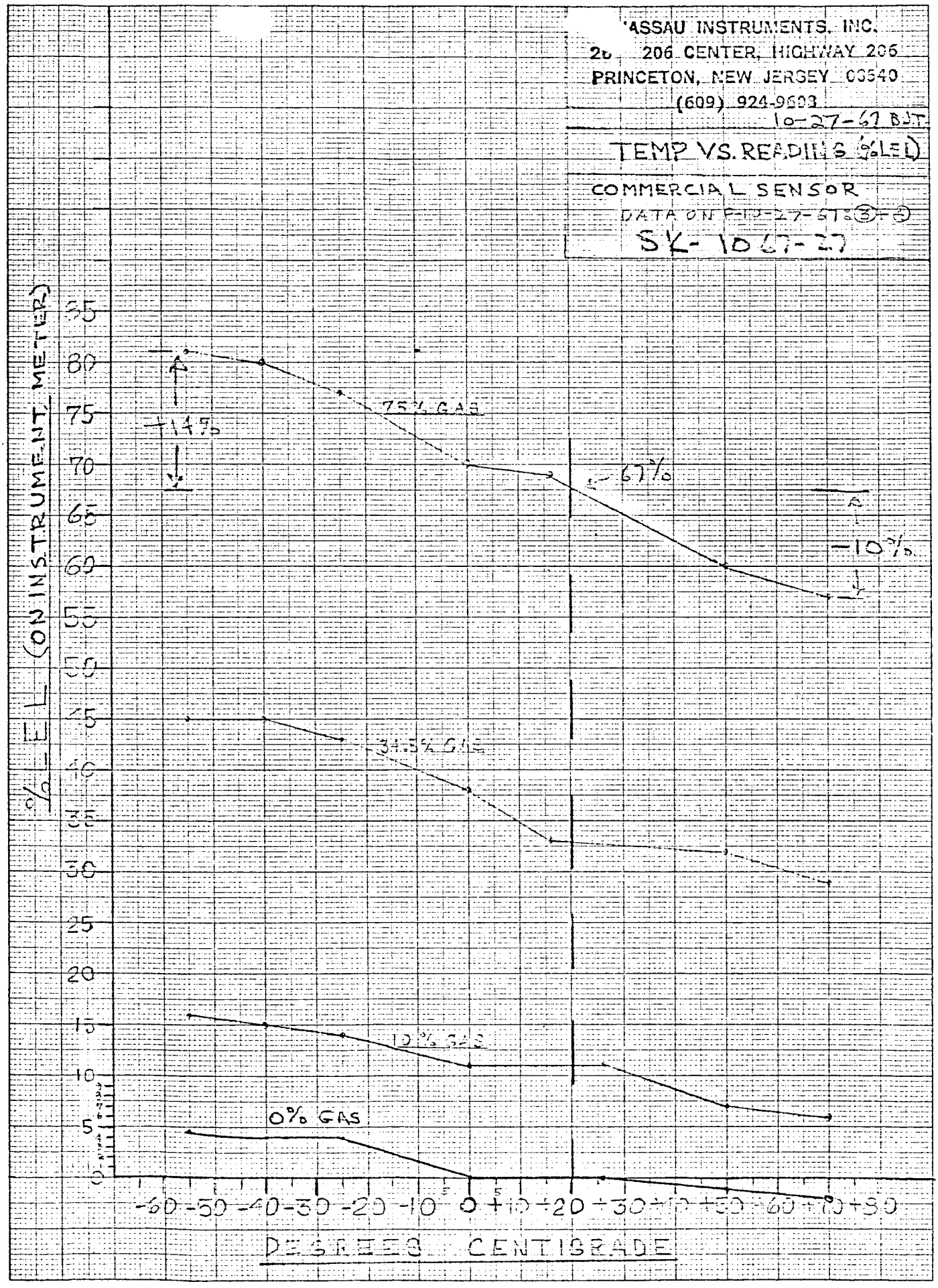
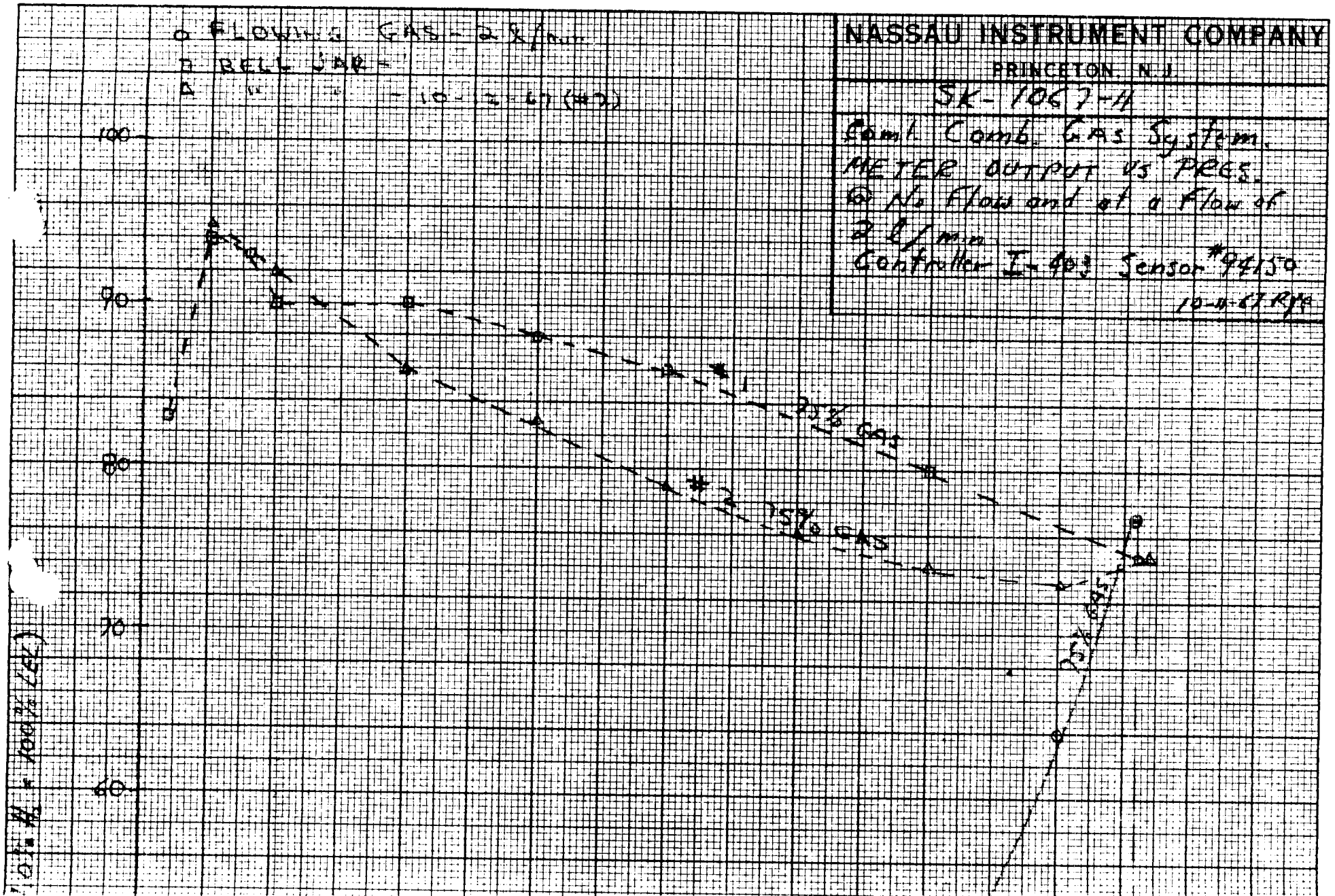

ASSAU INSTRUMENTS, INC.
206 CENTER, HIGHWAY 206
PRINCETON, NEW JERSEY 08540
(609) 924-9603
10-27-67 BJT
TEMP VS. READINGS (SCALED)
COMMERCIAL SENSOR
DATA ON P-10-27-67 ③-④
SK-1067-27
% FULL (ON INSTRUMENT METER)
75% GAS
67%
+14%
-10%
34.5% GAS
10% GAS
0% GAS
-60 -50 -40 -30 -20 -10 0 +10 +20 +30 +40 +50 +60 +70 +80
DEGREES CENTIGRADE

FIG. 2

K&E 10 X 10 TO THE ½ INCH 359T-11LG
KEUFFEL & ESSER CO.
ALBANENE



79 3-1

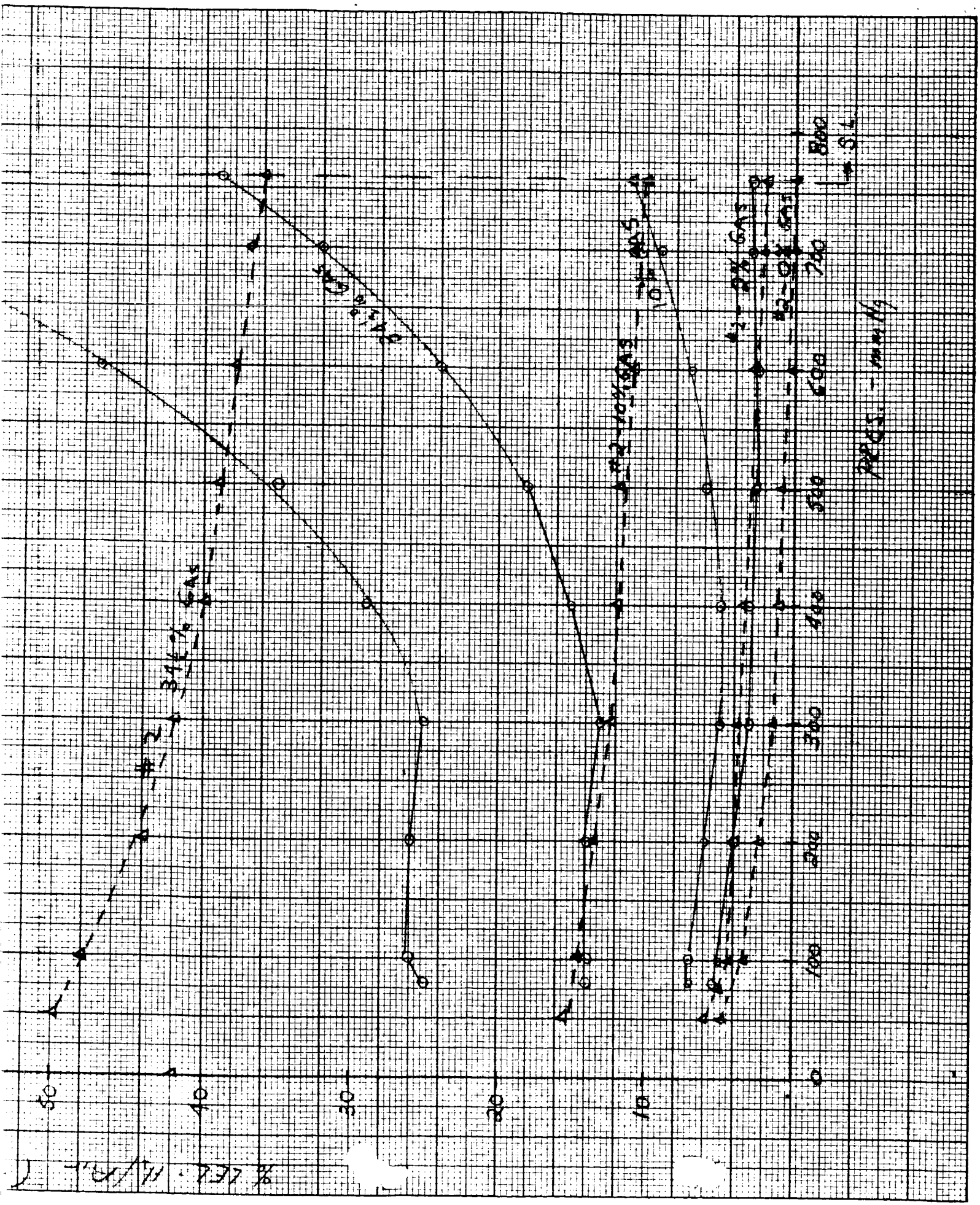


FIG. 3-2

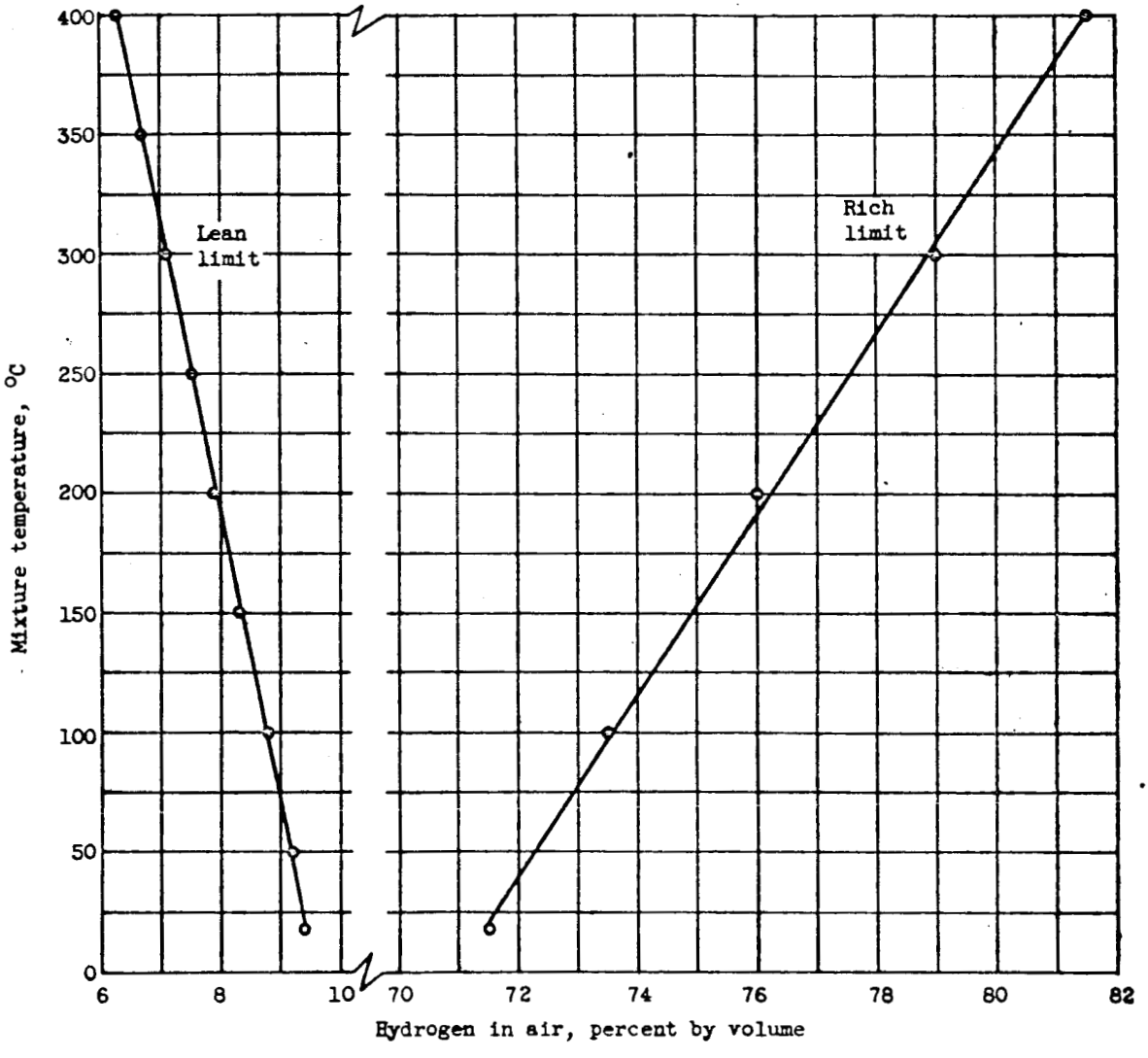
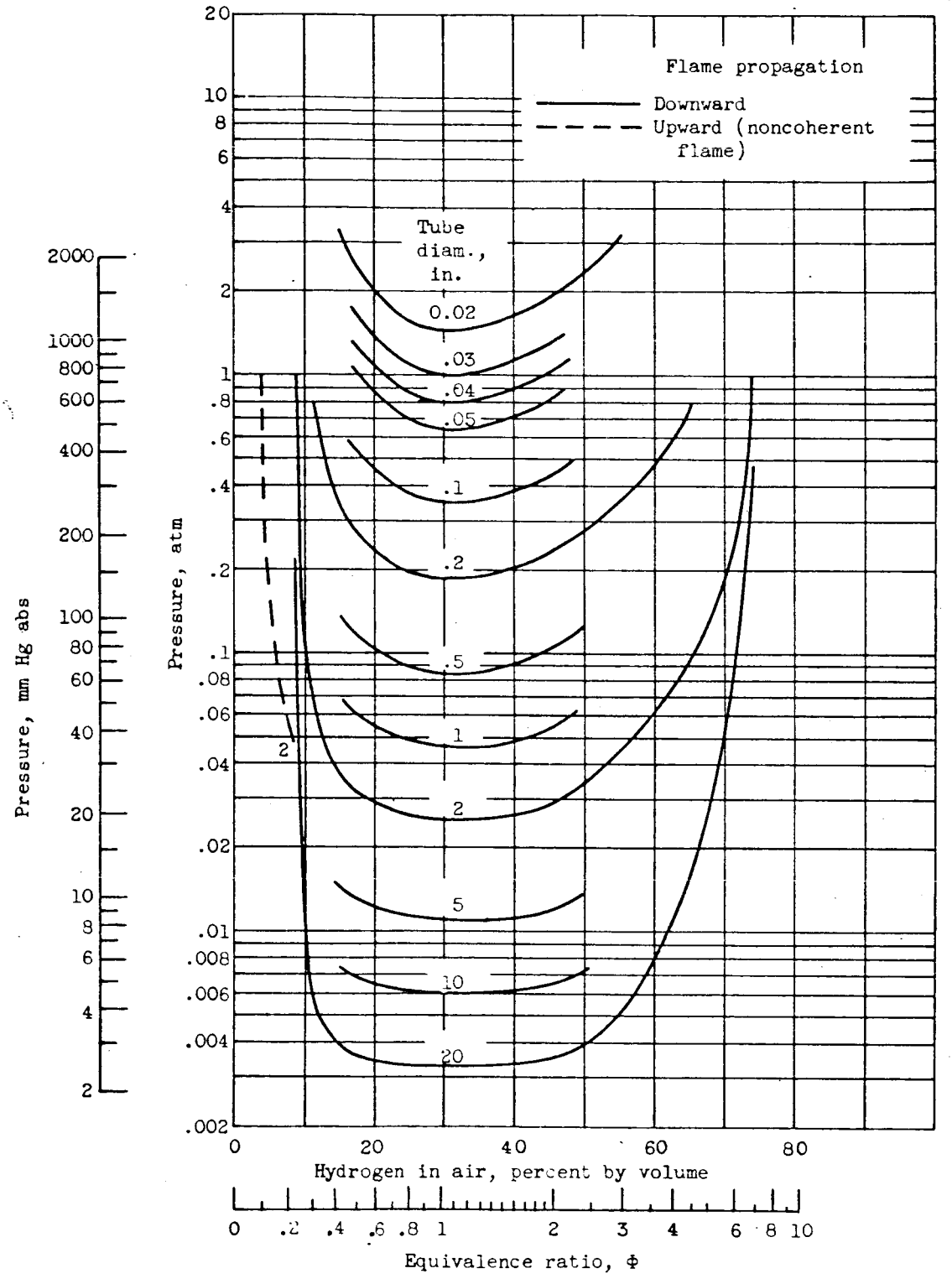


Figure 14. - Effect of temperature on flammability limits of hydrogen in air for downward propagation (ref. 44).

FIGURE 4



F1G. 5

Figure 16. - Estimated pressure limits of flame propagation for hydrogen-air mixtures with various tube diameters. Based on extrapolations of quenching data of reference 37.

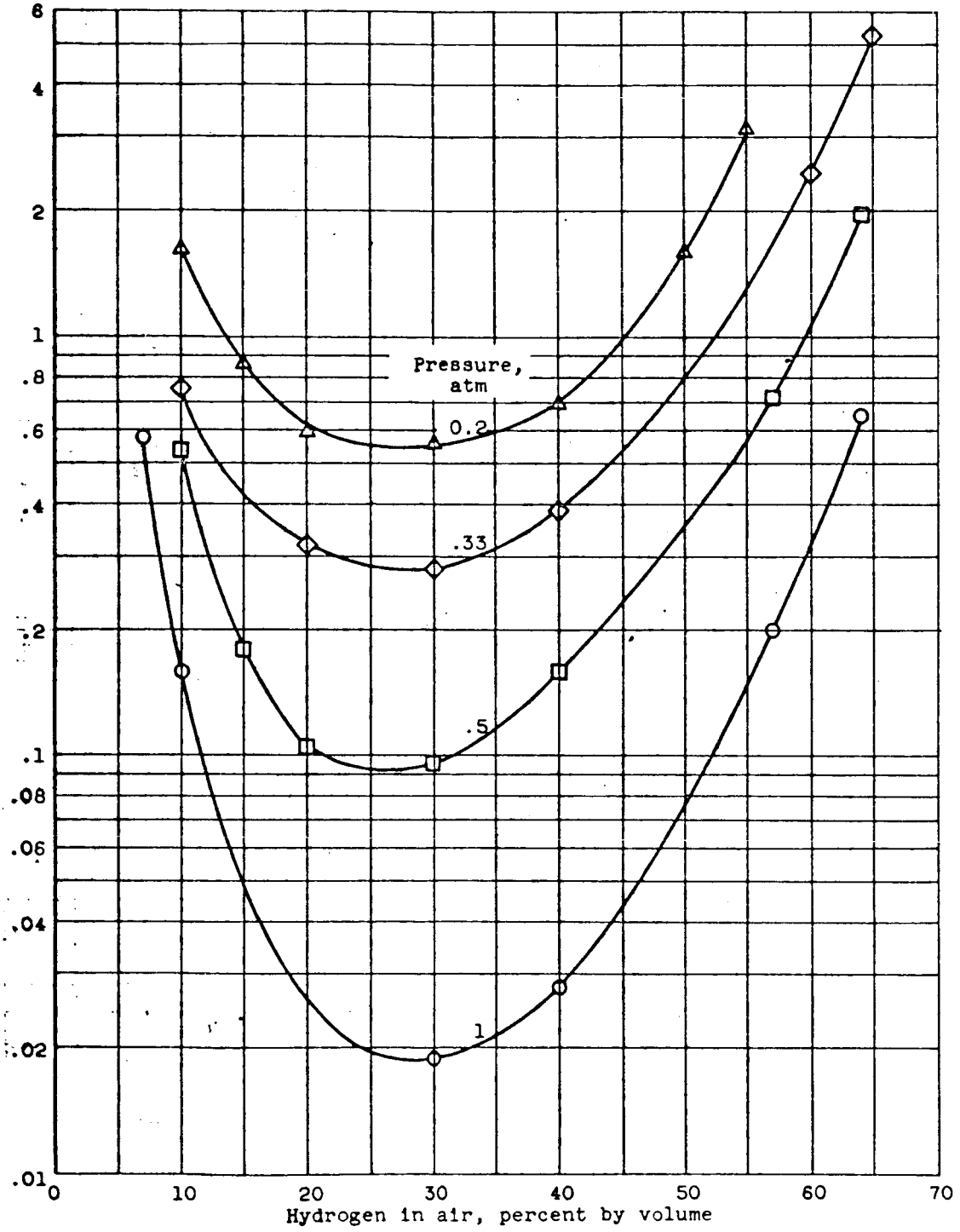


Figure 17. - Spark ignition energies for hydrogen-air mixtures at various pressures (ref. 36).

FIG. 6

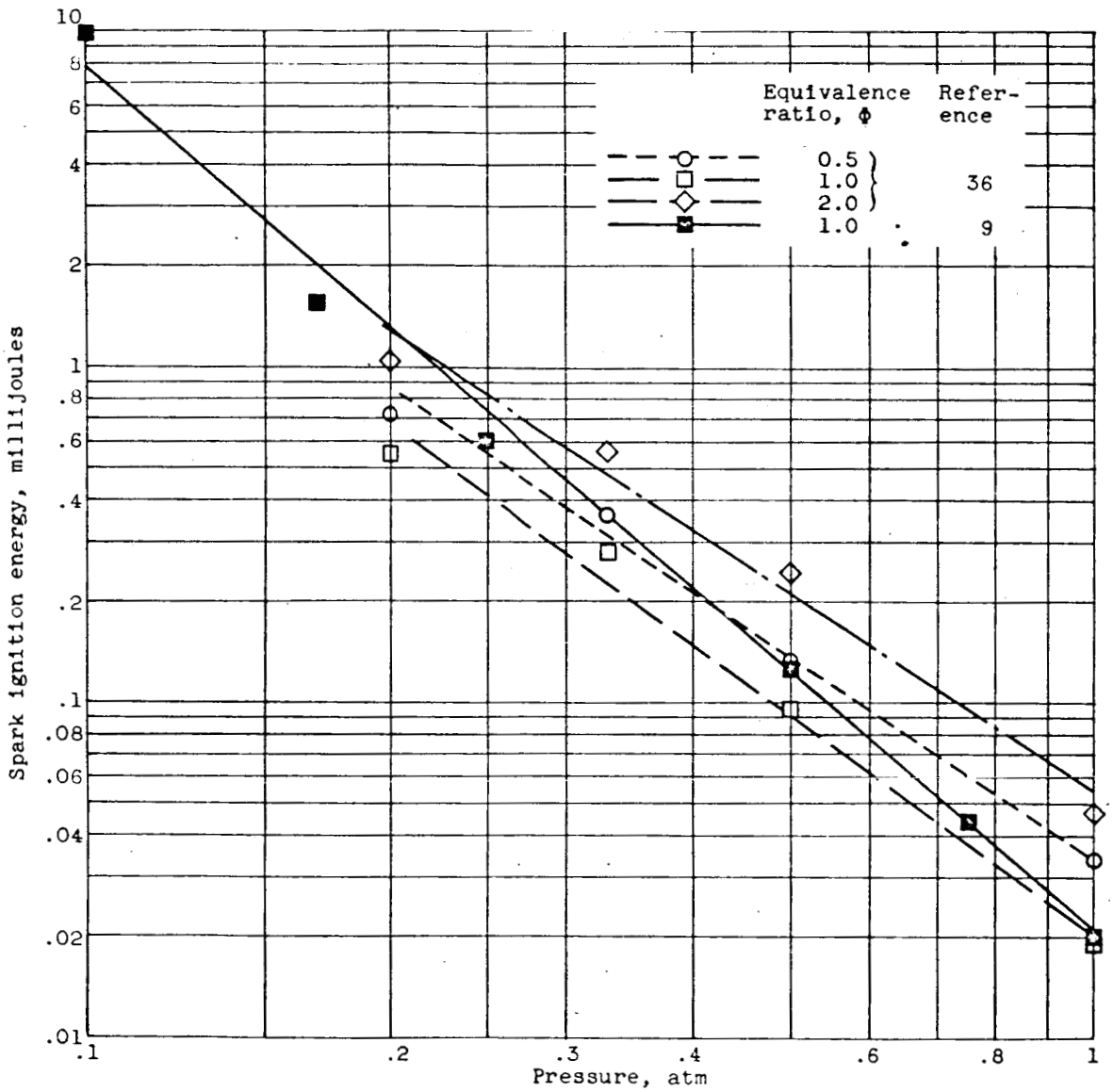


Figure 18. - Effect of pressure on spark ignition energy.

FIG. 7

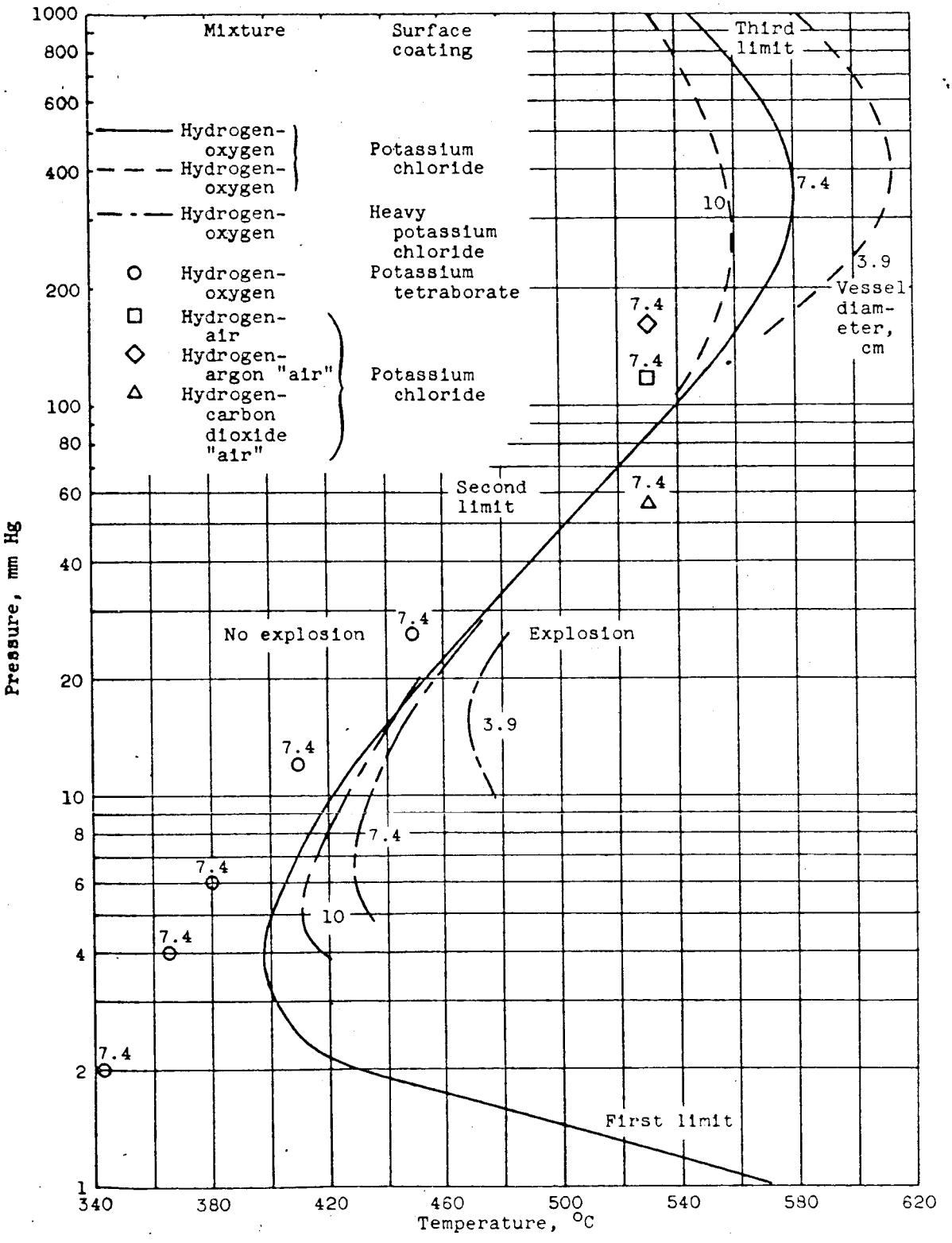
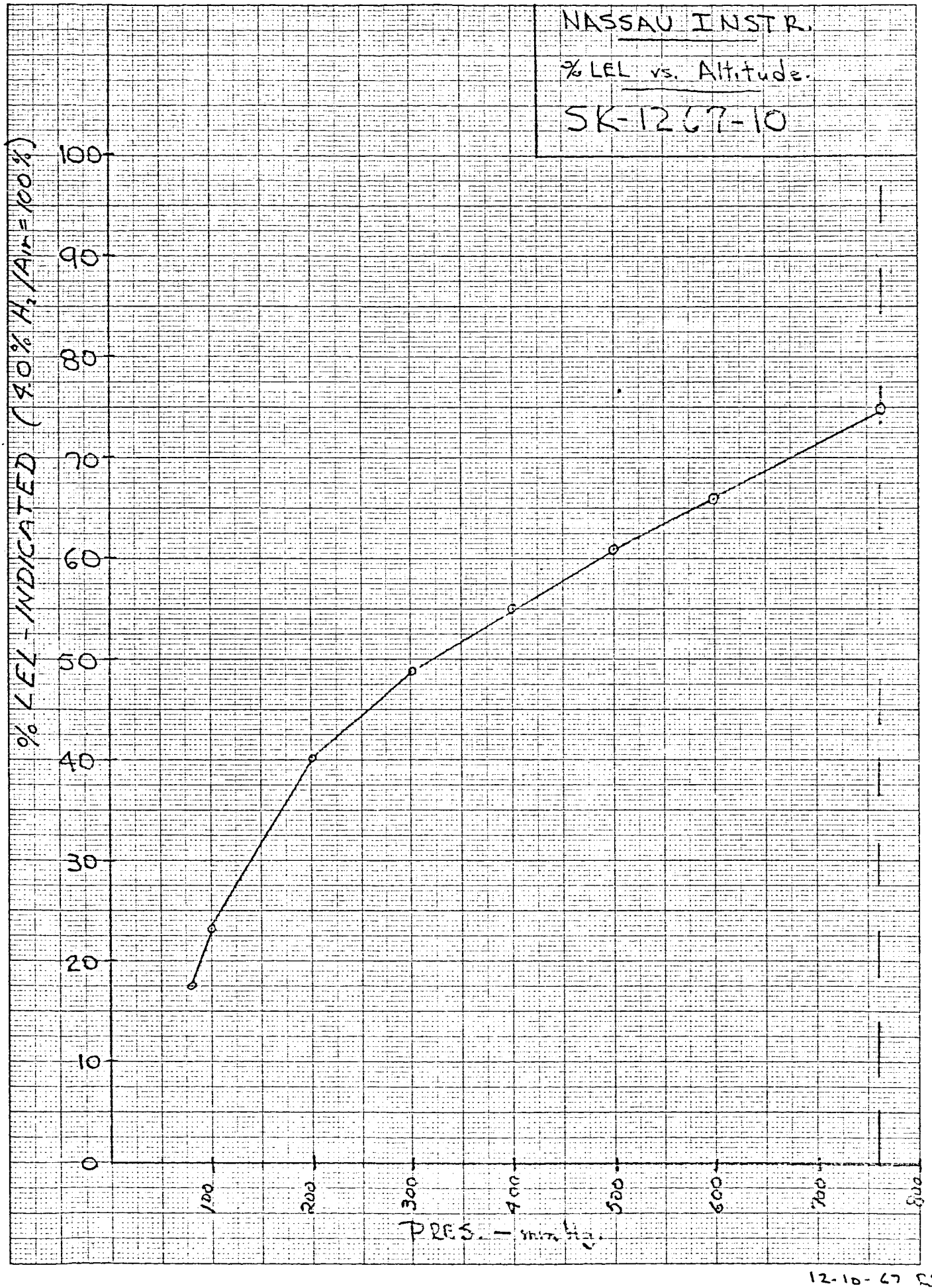


Figure 25. - Explosion limits of stoichiometric hydrogen mixtures (ref. 36).

FIG. 8



12-10-67 DL

FIG. 9

10 X 10 TO THE CENTIMETER 46 1510
10 X 25 CM. MADE IN U.S.A.
KEUFFEL & ESSER CO.

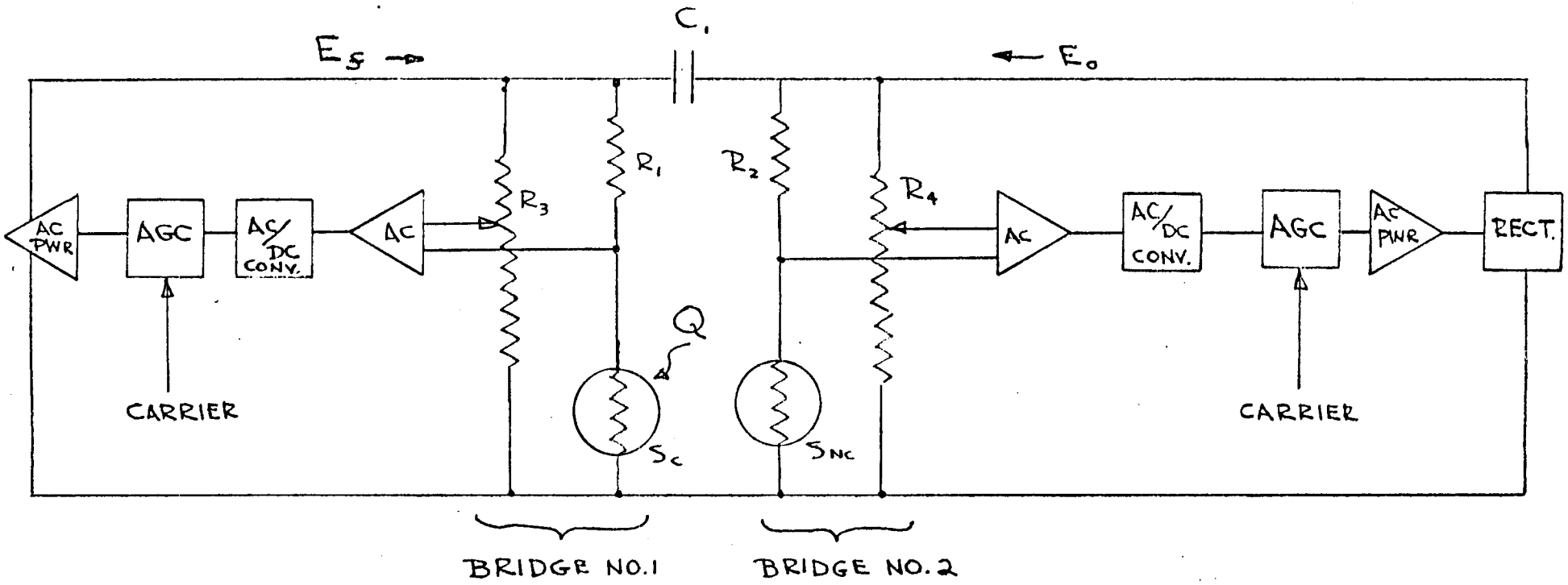


FIGURE 11

NASSAU INSTRUMENT COMPANY
PRINCETON, NEW JERSEY

SCALE:	APPROVED BY:	DRAWN BY KHS
DATE: 12-20-67		REVISED

BLOCK DIAGRAM-DOUBLE BRIDGE SYSTE

DRAWING NUMBER
SK-168-17

K+E SEMI-LOGARITHMIC 359-71
KEUFFEL & ESSER CO. MADE IN U.S.A.
3 CYCLES X 70 DIVISIONS

NASSAU INSTRUMENTS, INC.
206 CENTER, HIGHWAY 206
PRINCETON, NEW JERSEY 08540
(609) 924-9608

$E_o \approx K\sqrt{\%\,LEL}$

150% LEL = 5.0 VDC

SK1067 3

5.0

4.0

40

36

34

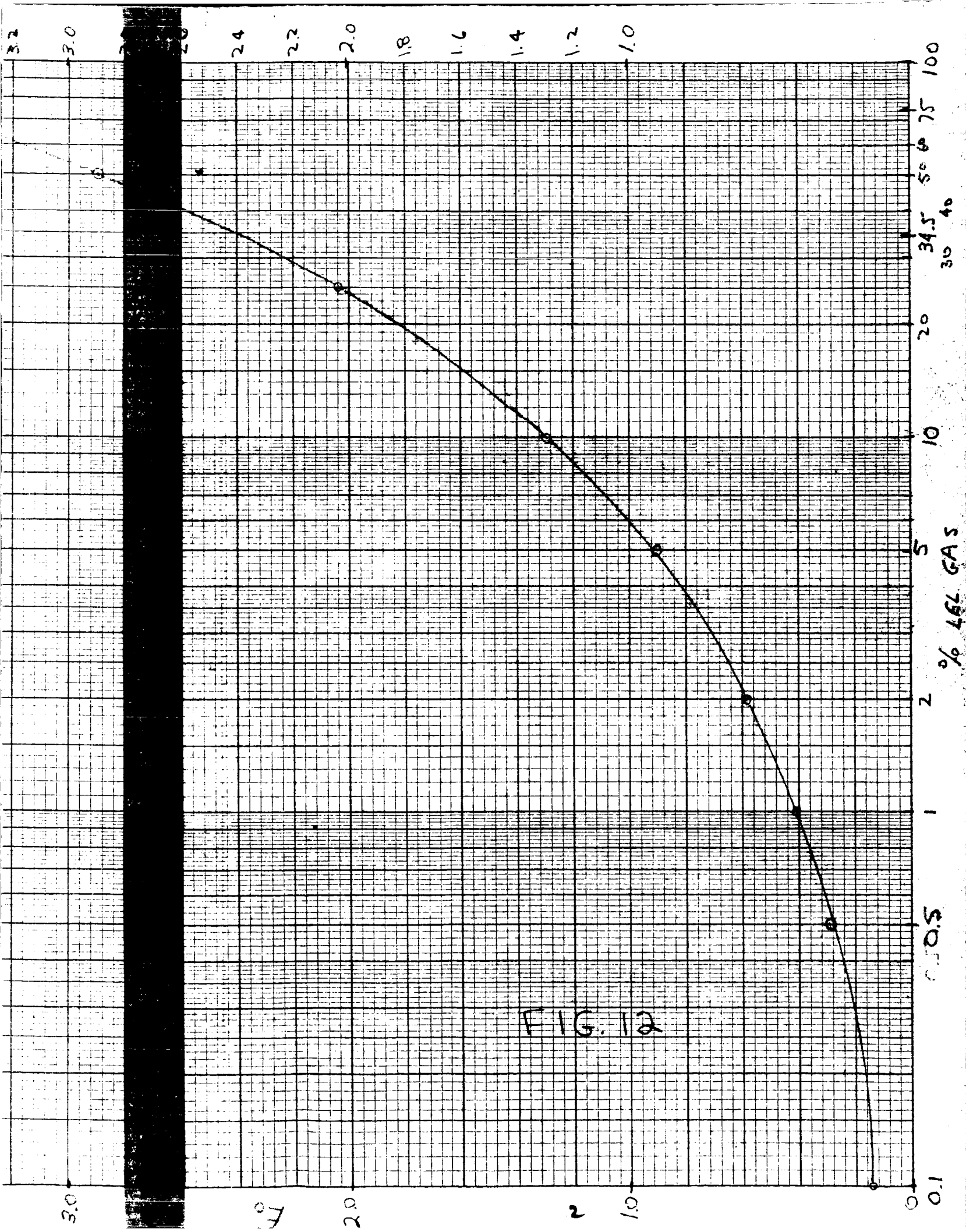
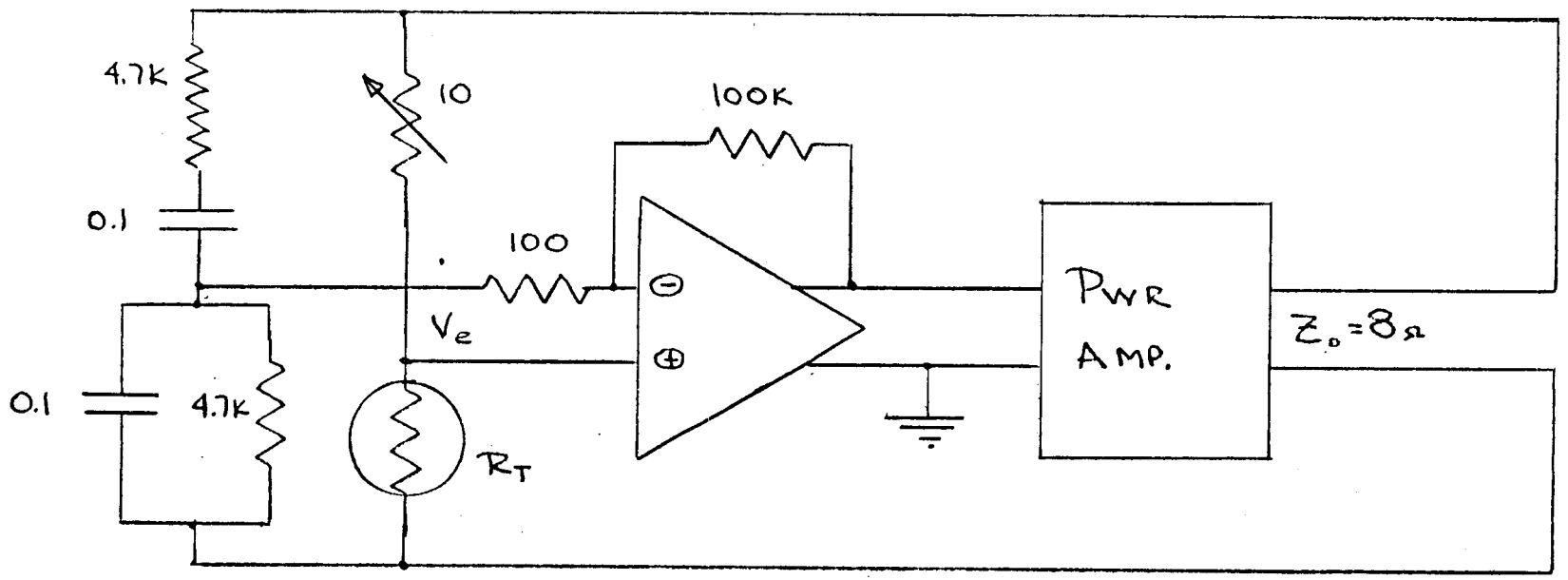


FIG. 12



NASSAU INSTRUMENT COMPANY
PRINCETON, NEW JERSEY

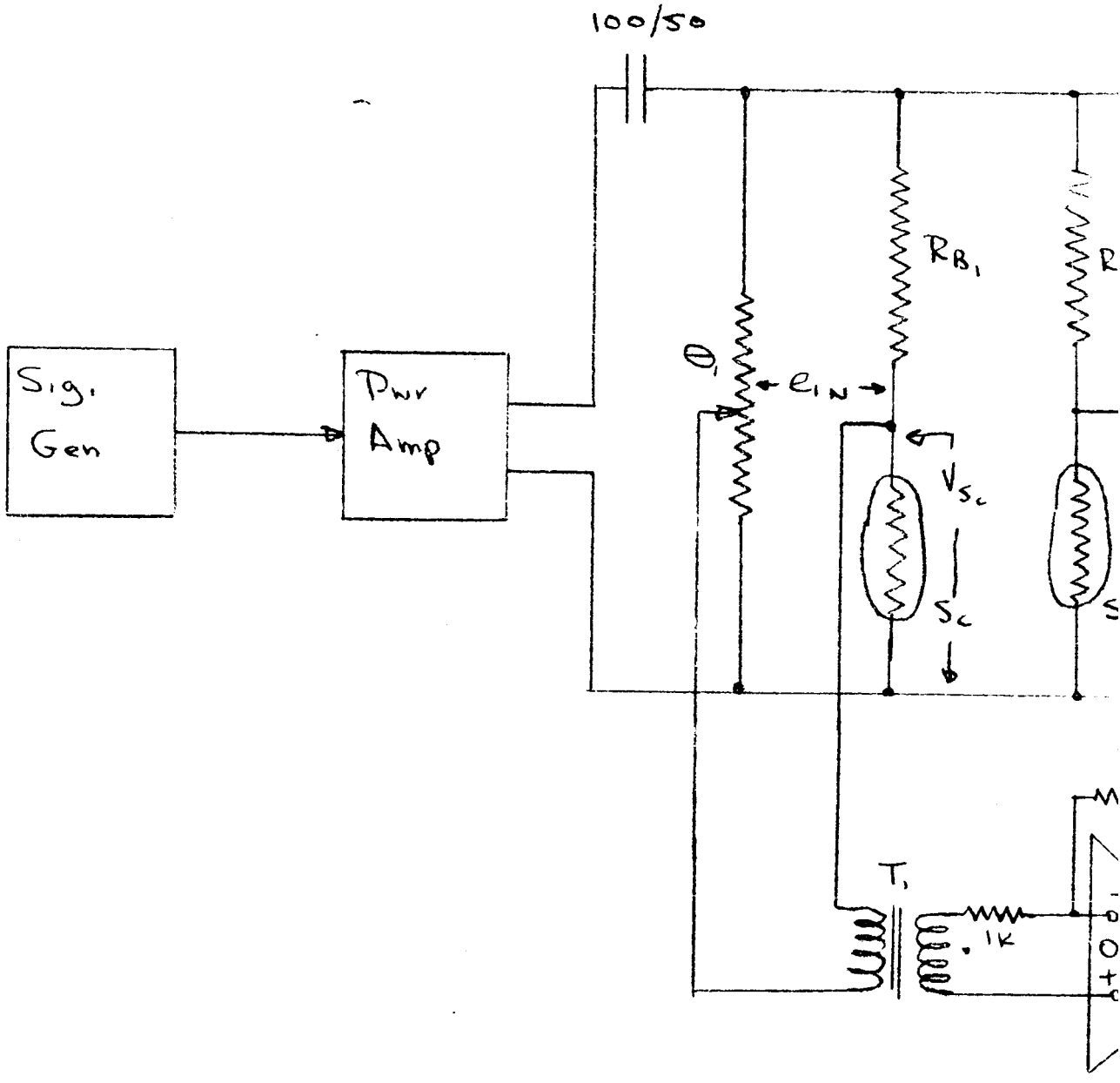
SCALE:	APPROVED BY:	DRAWN BY KIIS
DATE: 12-3-66		REVISED

TEST CIRCUIT - WIEN BRIDGE SENSOR

FIG. 13

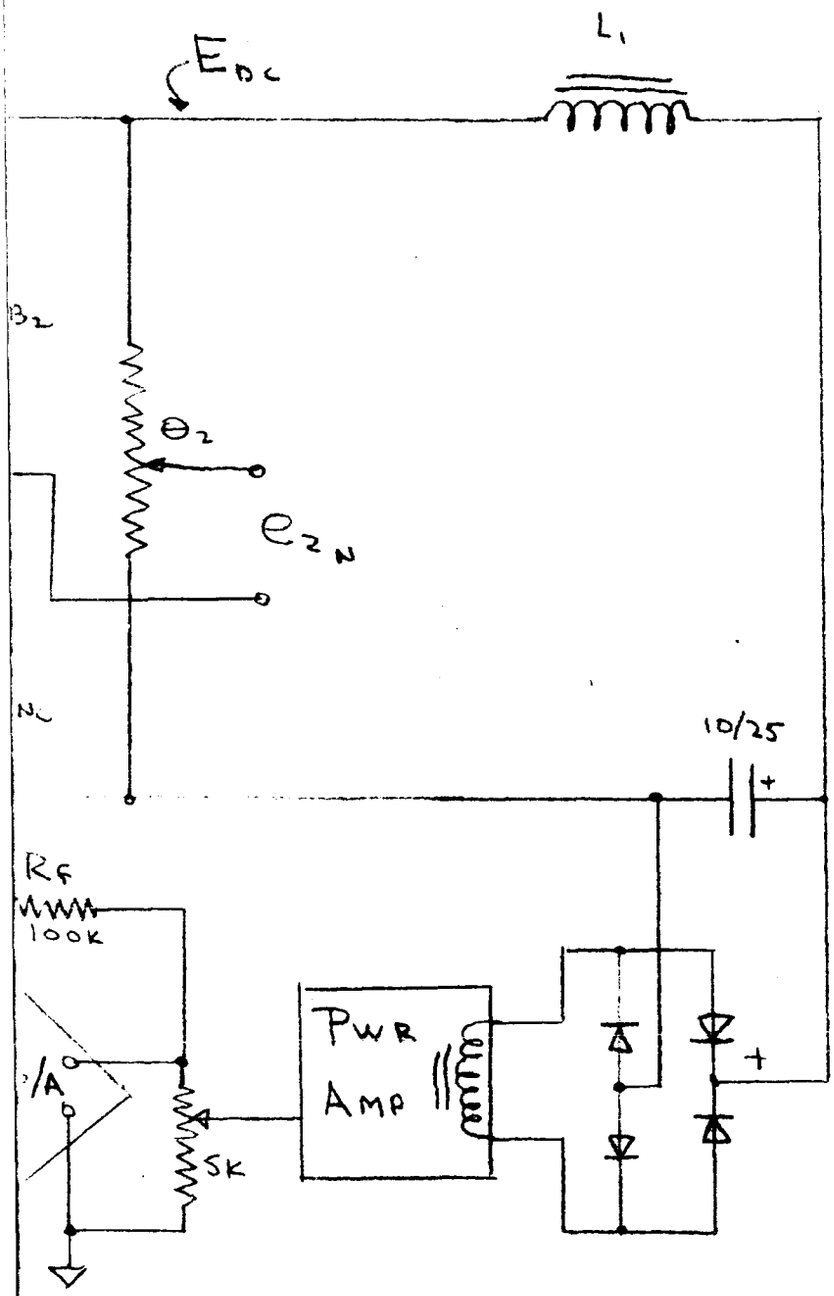
DRAWING NUMBER SK-1266-1

B. K. ELLIOTT CO. #118 ELLCO VEL T/P



PRINTED ON B. K. ELLIOTT CO., 115 ELLCO VEL T/P

Fig 14-1



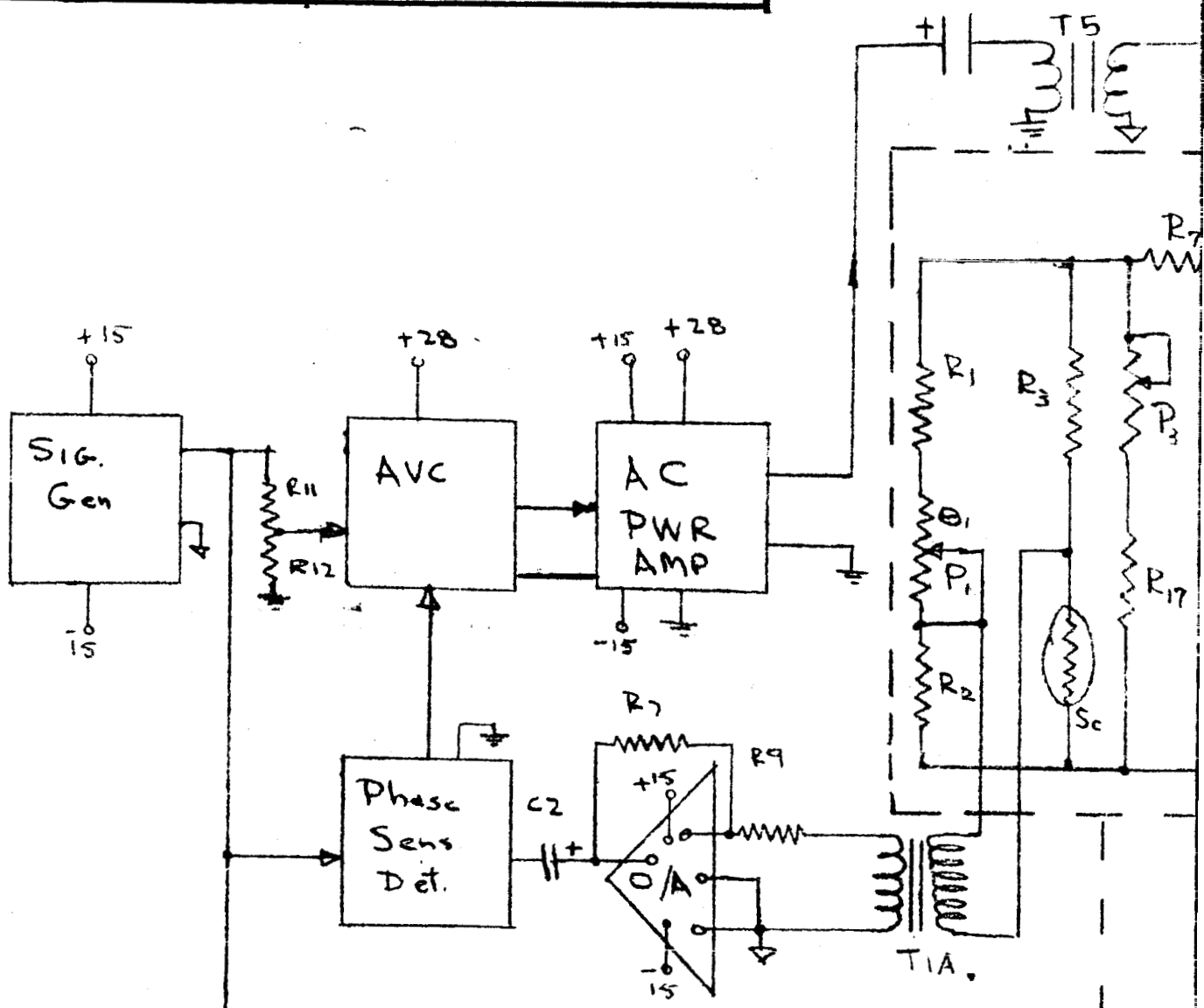
NASSAU INSTRUMENT Co
PRINCETON, N.J.

SCALE: None	APPROVED BY:	DRAWN BY RJC
DATE: 3-1-67		REVISED

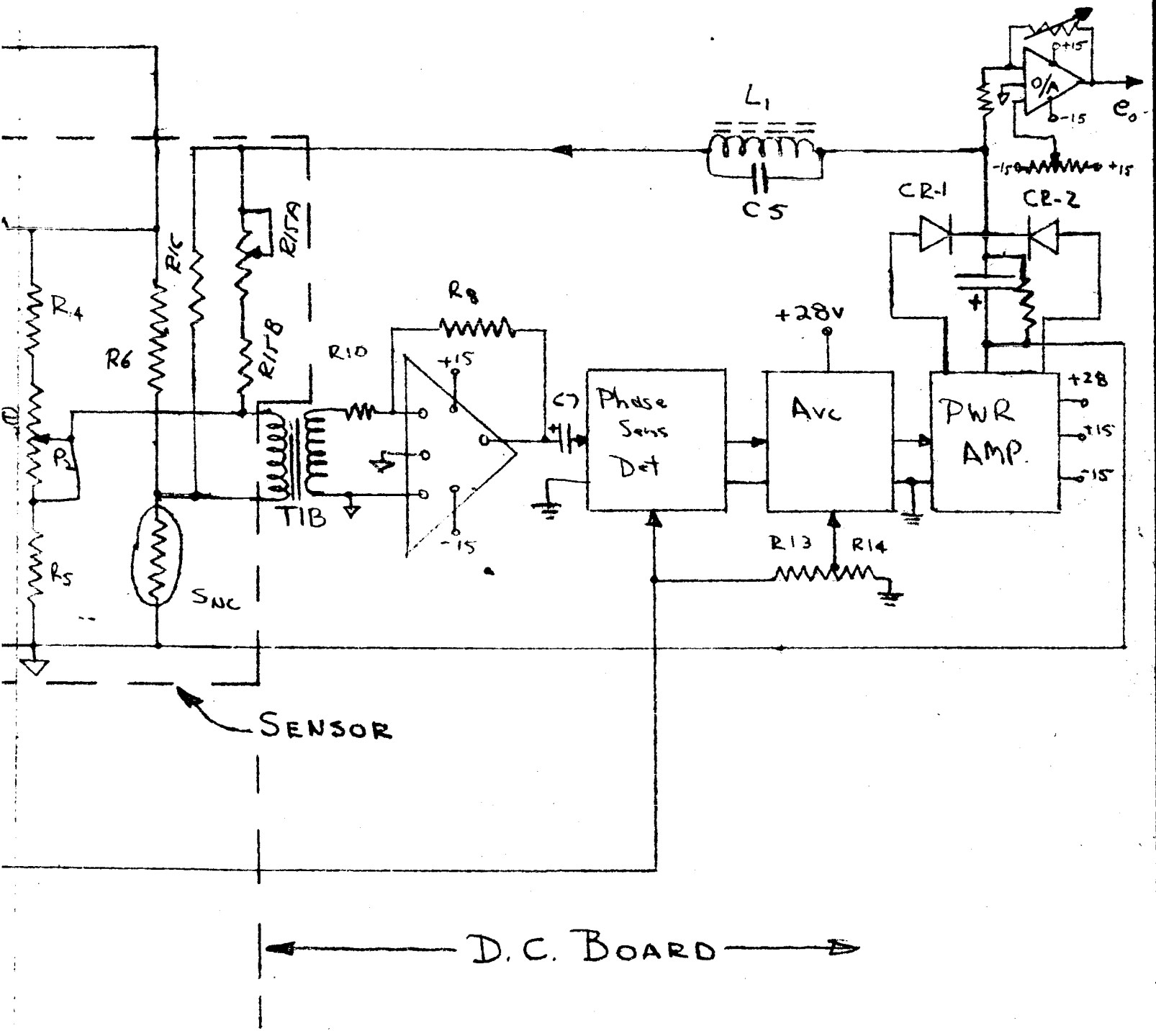
TEST CKT NO. 1 - DOUBLE BRIDGE FOR H_2/Air Comb. DETECTOR

NASA NSG-2054	FIG. 14-1	DRAWING NUMBER SK-367-7A

THESE DRAWINGS AND SPECIFICATIONS ARE THE PROPERTY OF NASSAU INSTRU. COMPANY, AND SHALL NOT BE REPRODUCED OR COPIED, OR USED AS THE BASIS FOR THE MANUFACTURE OR SALE OF APPARATUS OR DEVICES WITHOUT PERMISSION.



PRINTED ON B. K. ELLIOTT CO., 115 ELLCO VEL T/P



REVISED BJE	12-12-67
WAS SK 367-13D	11-30-67
DESCRIPTION	DATE

NASSAU INSTRUMENT COMPANY
PRINCETON, N.J.

SCALE: NONE	APPROVED BY:	DRAWN BY RJL
DATE: 3-5-67		REVISED 11-30-67

SYSTEM DIAGRAM
H_2/AIR SENSING SYSTEM

FIG. 15-2

DRAWING NUMBER B-102-700 B

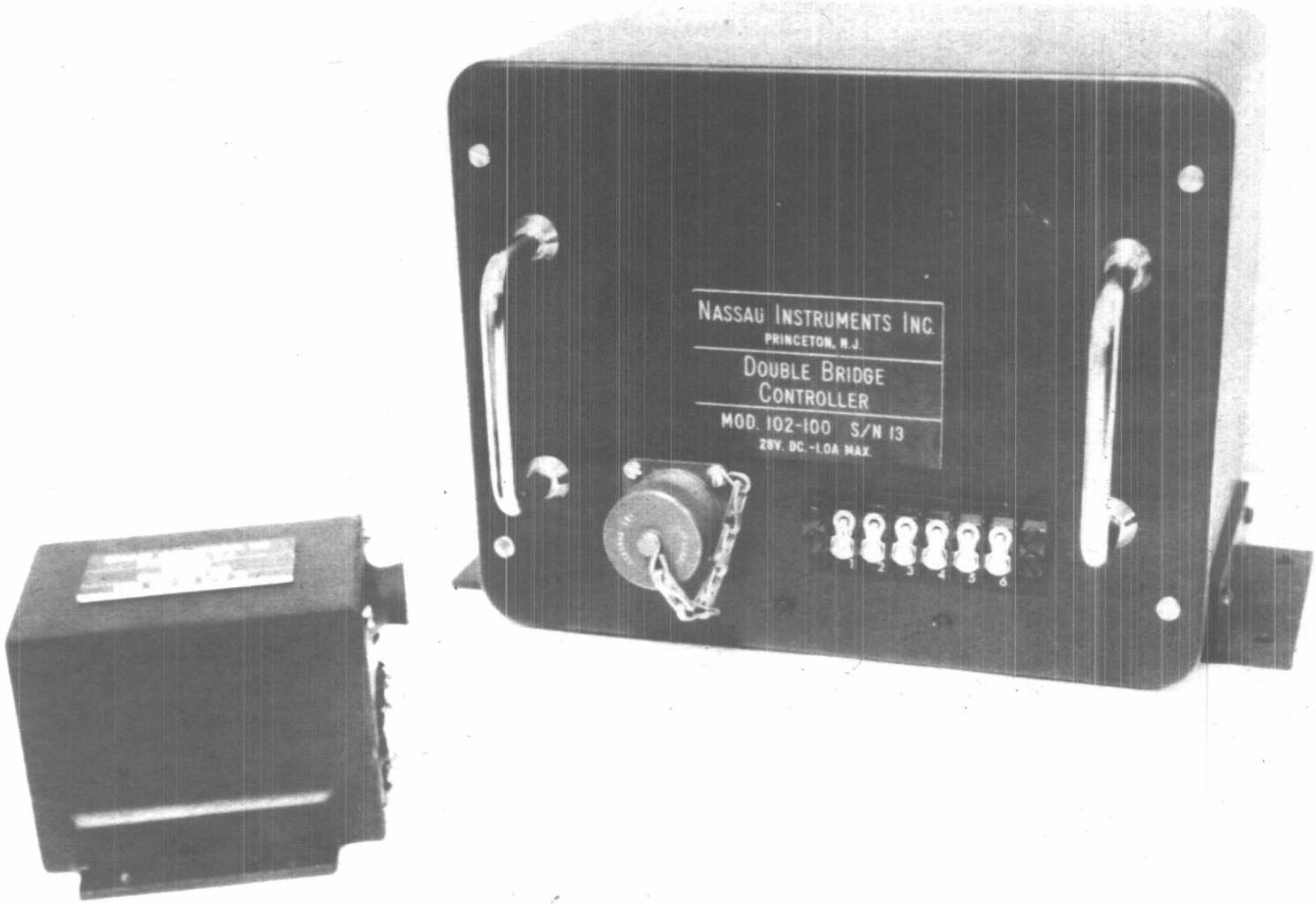

NASSAU INSTRUMENTS INC.
PRINCETON, N.J.
DOUBLE BRIDGE
CONTROLLER
MOD. 102-100 S/N 13
28V. DC. -1.0A MAX.
1
2
3
4
5
6

FIG. 16

THESE DRAWINGS AND SPECIFICATIONS ARE THE PROPERTY OF NASSAU INSTRU. COMPANY AND SHALL NOT BE REPRODUCED OR COPIED. OR USED AS THE BASIS FOR THE MANUFACTURE OR SALE OF APPARATUS OR DEVICES WITHOUT PERMISSION

REVISIONS				
SYM	ZONE	DESCRIPTION	DATE	APPROVED

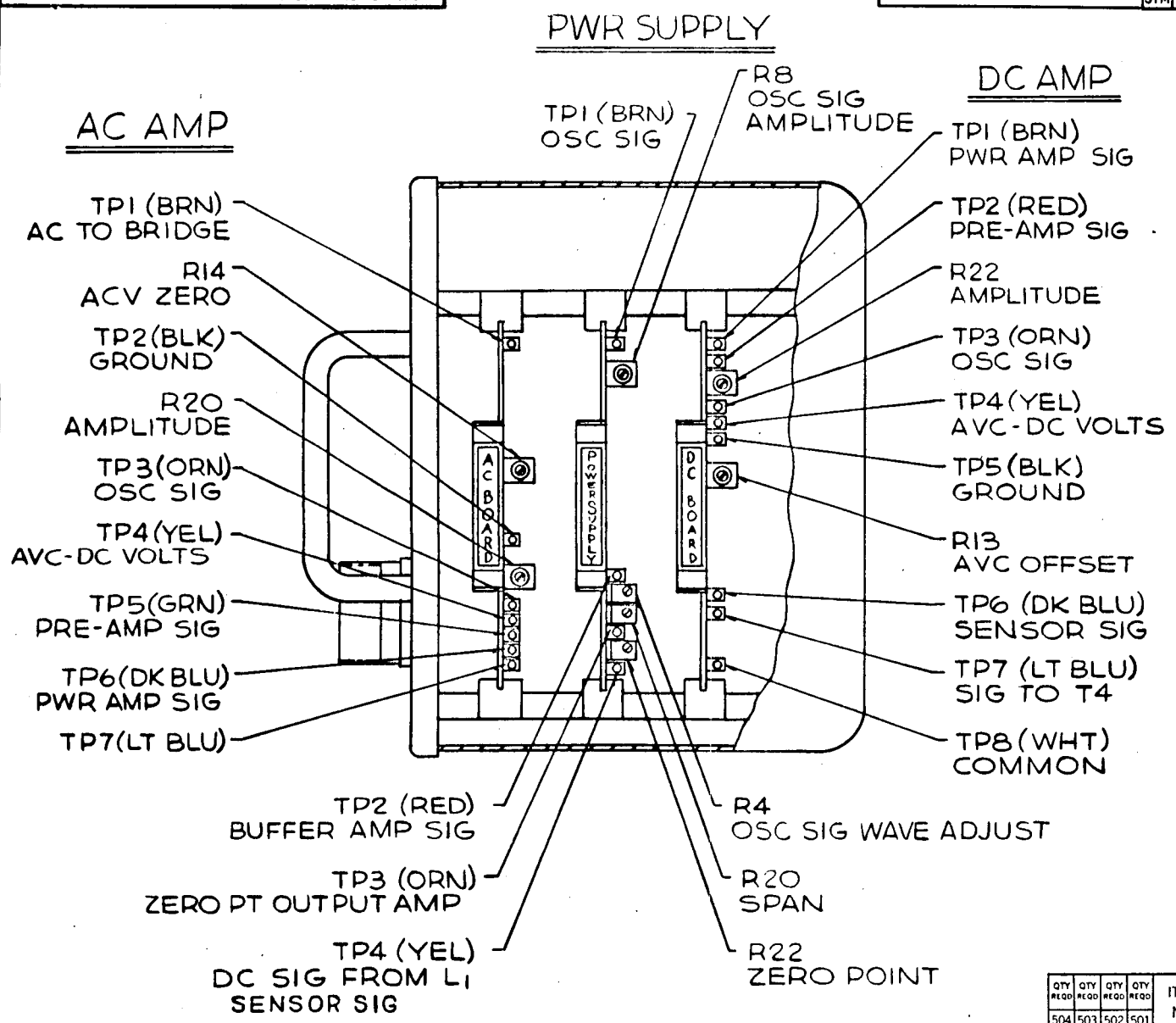


FIG. 17

102-100

QTY REQD	QTY REQD	QTY REQD	QTY REQD	ITEM NO.	CODE IDENT	PART OR IDENTIFYING NO.	NOMENCLATURE OR DESCRIPTION
504	503	502	501			LIST OF MATERIALS	

CONTRACT NO. NAS 8-20597	NASSAU INSTRUMENT COMPANY PRINCETON, N.J.
DRAWN Nov 25 1967 DATE GEO RAUSCHER	CONTROLLER 102-100 CONTROLS & TEST POINTS
CHECKED DATE	
DESIGN ACTIVITY APPD. DATE	SIZE C 102-104
	SCALE 1/1 WEIGHT SHEET 1 OF 1

DIMENSIONS ARE IN INCHES AND INCLUDE THICKNESS OF PLATING.
TOLERANCES ON FINISHED DIMENSIONS UNLESS OTHERWISE SPECIFIED

BASIC DIMENSIONS	2 PLACE DECIMALS	3 PLACE DECIMALS
UP TO 6	±.02	±.005
ABOVE 6 TO 24	± 03	±.010
ABOVE 24	± 06	±.015

ANGULAR DIMENSIONS ±½°

FIRST MADE FOR	
NEXT ASS'Y	USED ON

ALL EXTERNAL THREADS TO BE CLASS 2A BEFORE PLATING, AND CLASS 2 AFTER PLATING. ALL INTERNAL THREADS TO BE CLASS 2B, UNLESS OTHERWISE SPECIFIED.

FIG. 18