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NATIONAL DEFENSE RESEARCH COMMITTEE

of

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

Progress Report on Investigation of Q Supply to November 1, 1941
E.R.G. Hilland

OSRD No. 291

Serial No. 135

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NATIONAL DEFENSE RESEARCH COMMITTEE

of

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

Progress Report on "Investigation of Oxygen Supply"

to
November 1, 1941

by
E. R. Gilliland
Professor of Chemical Engineering
Massachusetts Institute of Technology

OSRD-291
Serial No. 135
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Progress Report on "Investigation of Oxygen Supply" NL-B-42: AC-12

Endorsement (1) from E. R. Gilliland, Member Section B-7-B, to E. P. Stevenson, Chairman, Section B-7. Forwarding report.

(2) From E. P. Stevenson, Chairman, Section B-7 to Roger Adams, Chairman, Division B. Forwarding report and noting: "The use of a cobalt organic compound has been demonstrated as a practical material to use for the regenerative production of oxygen from the atmosphere. The principal features of the design of a self-contained unit to produce 4 cubic feet of oxygen per minute are reported."

(3) Twenty-one copies forwarded to Dr. Irvin Stewart, Secretary of the National Defense Research Committee, as Progress Report under Contract (B-69, CEMsr-4) with Massachusetts Institute of Technology.

Roger Adams, Chairman
by Harris M. Chadwell
Technical Aide

DIVISION B

NATIONAL DEFENSE RESEARCH COMMITTEE

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OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

Progress Report on "Investigation of Oxygen Supply"

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TABLE OF CONTENTS

I. SUMMARY

The problem under investigation is the study of various chemical compounds capable of absorbing oxygen from air and being regeneratable to give pure oxygen and the original compound.

The experimental work carried out in this program has so far been chiefly concerned with a study of the cobalt acetate-salicylaldehyde-ethylenediamine compound reported by Tsumaki and Calvin. A study of the physical-chemical properties of this material indicates that it forms a loosely bound compound with oxygen giving a divariant system, i.e., the amount of oxygen taken up by the compound is a function of the temperature and oxygen partial pressure. The properties of the compound are such that it works satisfactorily in the temperature region of 0 to 100° C.

A study of the absorption and desorption properties of Co-Sa-En in ½-inch i.d. steel tubes indicates that by using air pressures of 70 to 125 lbs./sq. in. ga. and absorption temperatures of 20° C. followed by regeneration with steam at 100° C., it will be possible to operate with complete cycles of from 6 to 10 minutes. The absorption rate decreases rapidly with increasing temperature but this can be partly offset by increasing absorption pressure. The regenerated oxygen can be obtained under a pressure of a few atmospheres if this is desired.

On the basis of the data obtained with the ½-inch tube, it has been estimated that an apparatus for producing oxygen at the rate of about 20 lbs./hr. could be constructed. Such a unit would weigh from 2,000 to 2,500 lbs. and would occupy a space 3½ ft. by 6 ft. by 4 ft. The unit would require from a gallon to a gallon and a half of gasoline per hour and about 25 gallons of cooling water per minute. With the exception of these requirements, the unit would be self-contained.

A literature search for inorganic compounds that might be used as oxygen absorbents indicates that most of these operate in a relatively high temperature region. However, it may be possible to use the alkali nitrate-nitrite system or the barium peroxide-metallic oxide systems in the temperature region of 300 to 600° C. No experimental work has been carried out on these inorganic compounds.

II. STATEMENT OF PROBLEM

The statement of the problem as given in the contract with NDRC is "To study and report on the availability of chemical substances which take up and give off oxygen reversibly and, if a promising chemical is found, to develop an experimental unit for the production of gaseous oxygen by such means. The investigation will not include a study of barium peroxide but will be directed toward the discovery of compounds which behave similarly but at lower pressures and temperatures."

The work carried out on this contract so far has been directed into two main fields:

1. a study of the cobalt-salicylaldehyde-ethylenediamine compound (Co-Sa-En) originally reported by Tsumaki, (1), and

2. a study of other compounds particularly those of inorganic nature.

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1. Bul. Chem. Soc. Japan 13, 252, (1938)

III. COBALT-SALICYLALDEHYDE-ETHYLENEDIAMINE COMPOUND

A. Preparation of Co-Sa-En

The major portion of the experimental effort has been expended on the study of this compound. The details of the preparations employed in making the Co-Sa-En compound are given in the Appendix, but the method employed was essentially that given by Tsumaki.[1] In this preparation, the cobalt acetate was dissolved in water and added to a solution of ethylenediamine in alcohol. The resulting mixture was carefully deoxygenated and then treated with the salicylaldehyde. The reaction is rapid and the mixture sets to a gel in a few minutes. This gel slowly changes over to a crystalline form, and as indicated by Dr. Calvin, (2) the type of crystals obtained can be varied by the temperature and time of crystallization. This product is recrystallized from pyridine, and these latter crystals then depyridinated to give the desired compound. The absorption capacity of the compound varies with the technique of preparation and the highest capacity so far obtained is that reported by Dr. Calvin which was 4.9 per cent oxygen by weight. This corresponds to an absorption of 1/2 mol of oxygen per cobalt atom.

B. Suspended Powder Experiments

The initial work in the study of the Co-Sa-En compound was directed to a study of its oxygen absorption and desorption properties under conditions of a fluid suspension of the powdered compound. This fluid suspension operation involves passing the gases through a bed of the finely divided material at a velocity sufficient to suspend the particles in the gas stream but low enough so as not to eject them from the system. This type of operation was employed since it gives excellent contact and mixing of the solid particles with

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1. Bul. Chem. Soc. Japan 13, 252, (1938)

2. Preliminary Report May, 1941

the gas stream.[1] The details of the apparatus used are indicated in Fig. 1. During the absorption cycle oxygen or an oxygen-nitrogen mixture was added to the system and this gas recirculated through the unit by means of the reciprocating compressor. Additional oxygen was added from the reservoir at a rate sufficient to maintain constant pressure within the circulating system, and this rate of oxygen addition measured the rate of absorption within the unit. During the regeneration cycle pure oxygen was recirculated through the unit and oxygen withdrawn from the system in order to maintain constant pressure. This unit was constructed of glass and was only suitable for atmospheric or lower pressure operation.

The preliminary data obtained on this unit are presented in Figs. 2, 3, and 4. Figs. 2 and 3 indicate the extent of absorption as a function of the absorption time, partial pressure of the oxygen, and the absorption temperature. In general, it will be noted that at temperatures around 20° the rate of absorption is very low for partial pressures of oxygen approximating those in the normal atmosphere. This rate of absorption increases relatively rapidly with the partial pressure of the oxygen or with a decrease in absorption temperature. These results also indicate that the ultimate amount of oxygen absorbed is a very definite function of the oxygen partial pressure. Before these data were obtained, it had been assumed that the action of the Co-Sa-En compound with oxygen was monovariant, i.e., there was a definite equilibrium pressure of oxygen at a given temperature independent of the degree of saturation of the material. However, the increasing values of the absorption asymptotes with increasing oxygen pressure indicated that the degree of saturation was a rather important variable and that instead of being monovariant, the reaction was probably divariant and was either of the adsorption type or the compound and the oxygenated-product formed "solid

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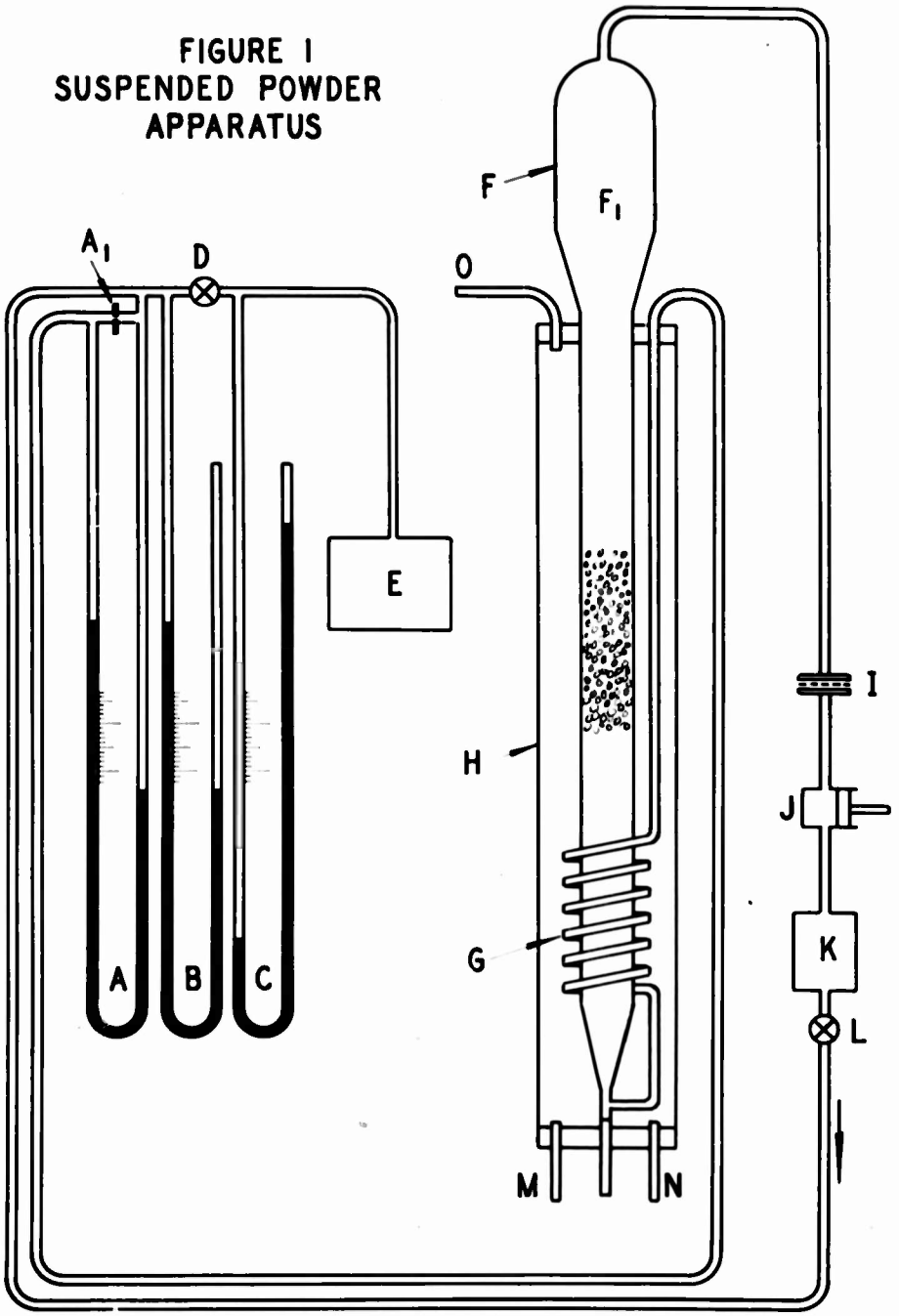
1. The suspended powder method in a commercial unit would operate continuously with the powder being introduced into the absorption unit with the air, then passing to a separator from which it would be introduced into the desorption unit. In the desorption unit heated oxygen would be circulated to give the suspension and the regenerated compound would be recycled to the absorption unit. In such an operation the heat transfer to the walls is good due to the fact that the whole gas-powder mixture behaves like a turbulent fluid.

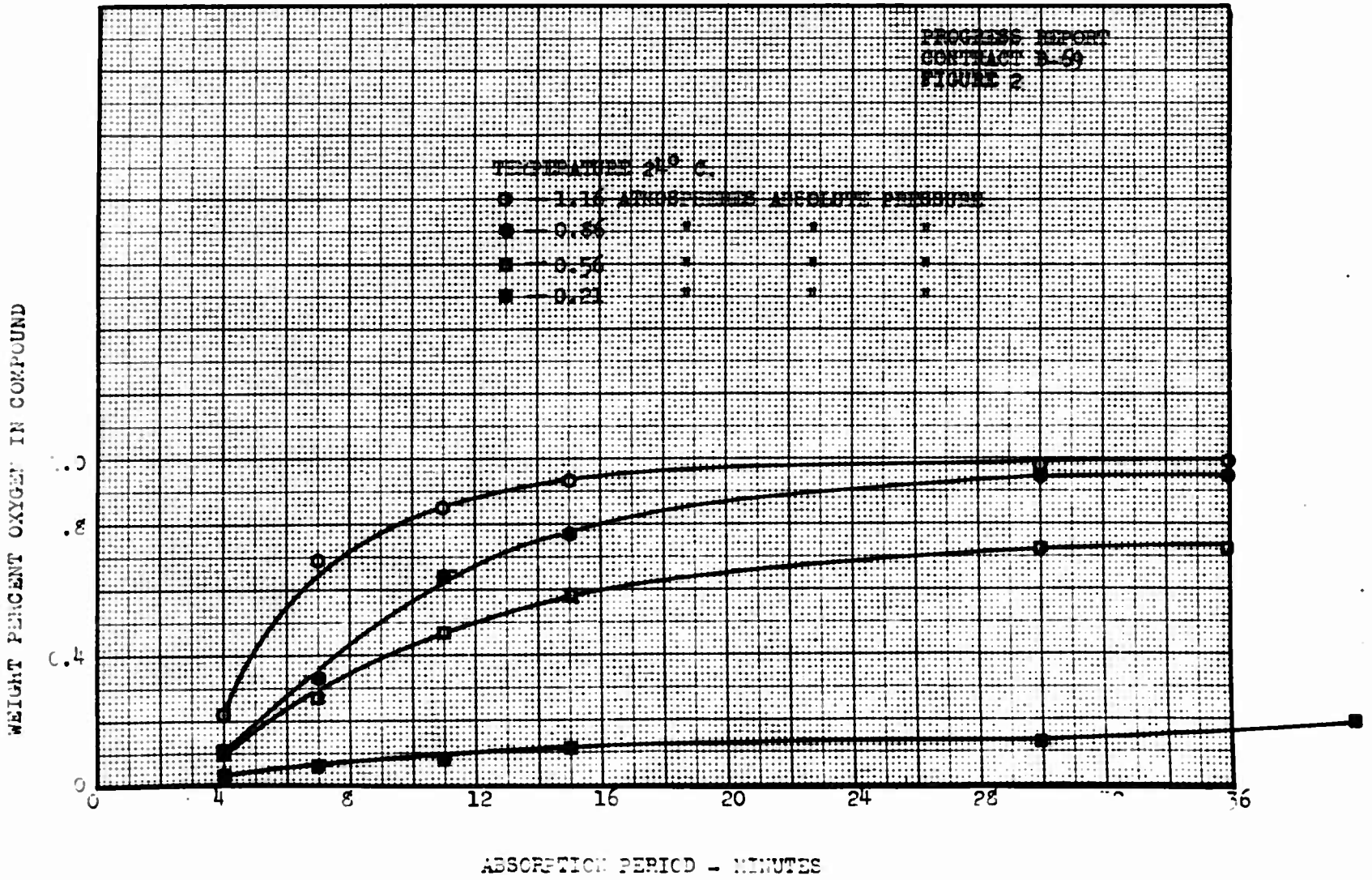
FIGURE 1
SUSPENDED POWDER
APPARATUS

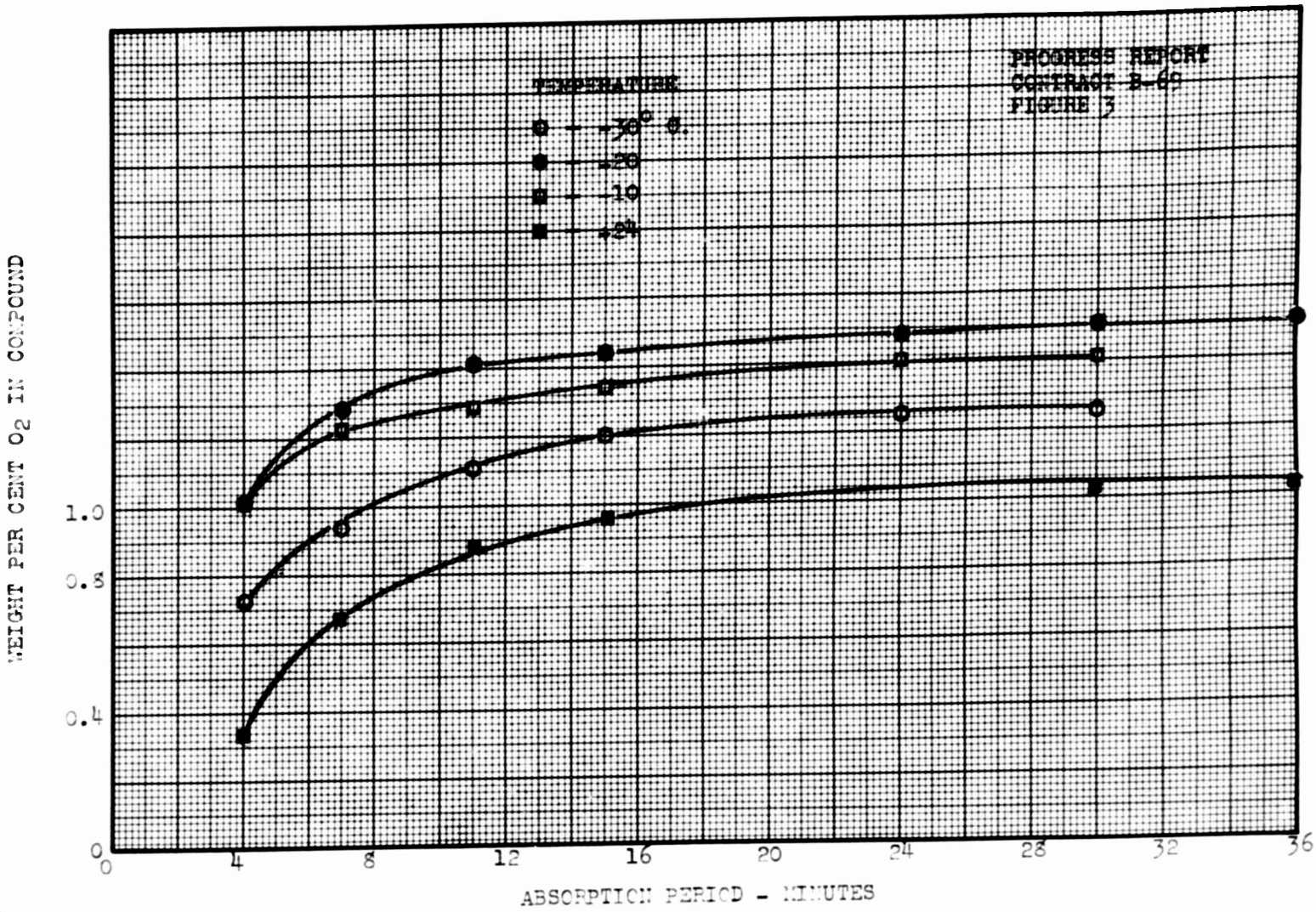


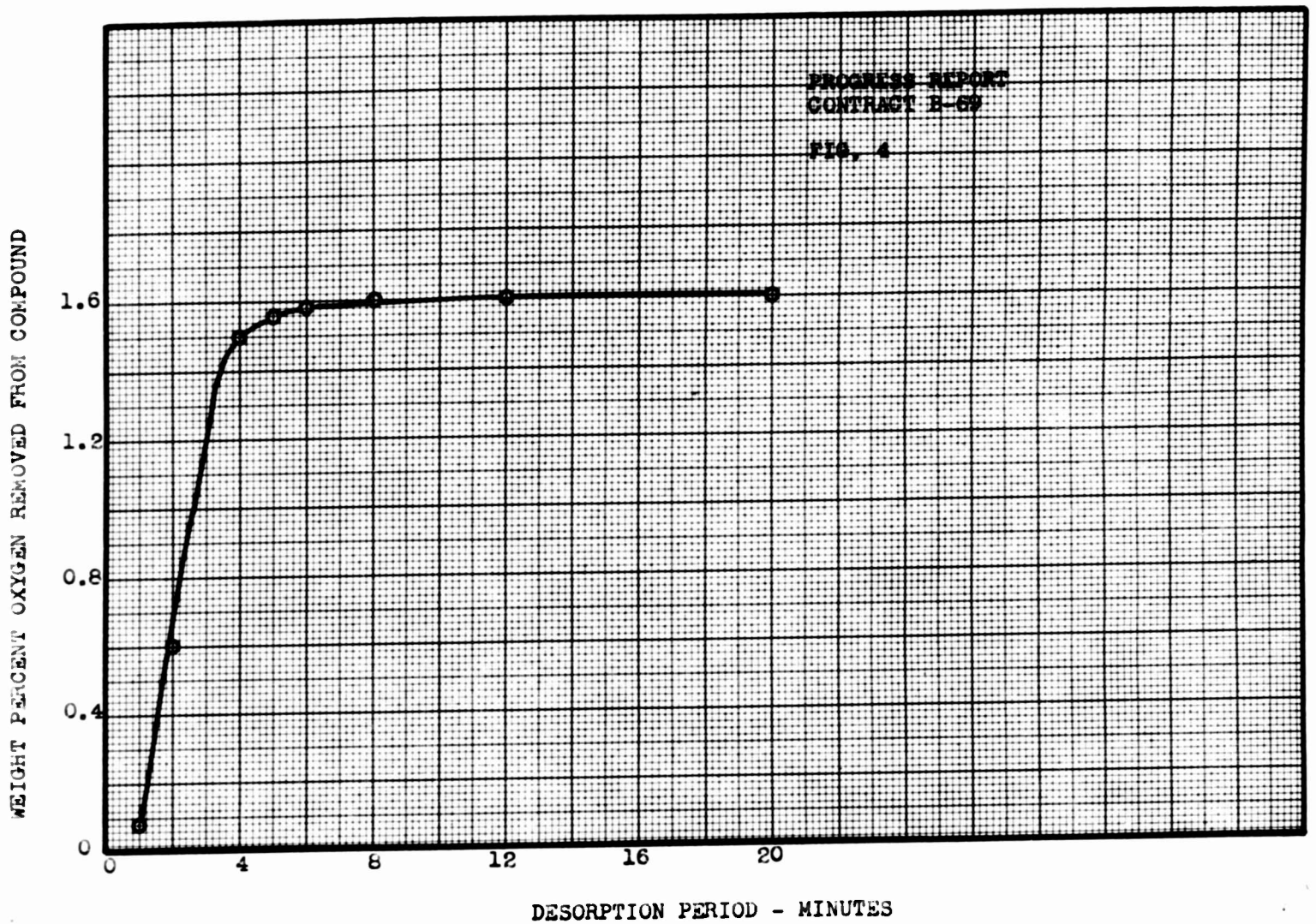
KEY FOR FIG. 1

SUSPENDED POWDER APPARATUS

A	FLOW METER MANOMETER
A_1	ORIFICE
B	MANOMETER FOR SYSTEM PRESSURE
C	MANOMETER FOR O_2 RESERVOIR
D	VALVE - REGULATED TO MAINTAIN CONSTANT PRESSURE IN SYSTEM
E	O_2 RESERVOIR
F	SUSPENDED POWDER TUBE
F_1	DUST SEPARATOR
F_2	SUSPENDED POWDER
G	AIR HEAT EXCHANGER
H	JACKET
I	DUST FILTER
J	COMPRESSOR
K	OIL FILTER
L	FLOW REGULATING VALVE
M	STEAM AND WATER IN
N	CONDENSATE OUT
O	STEAM AND WATER OUT







solutions" with each other.

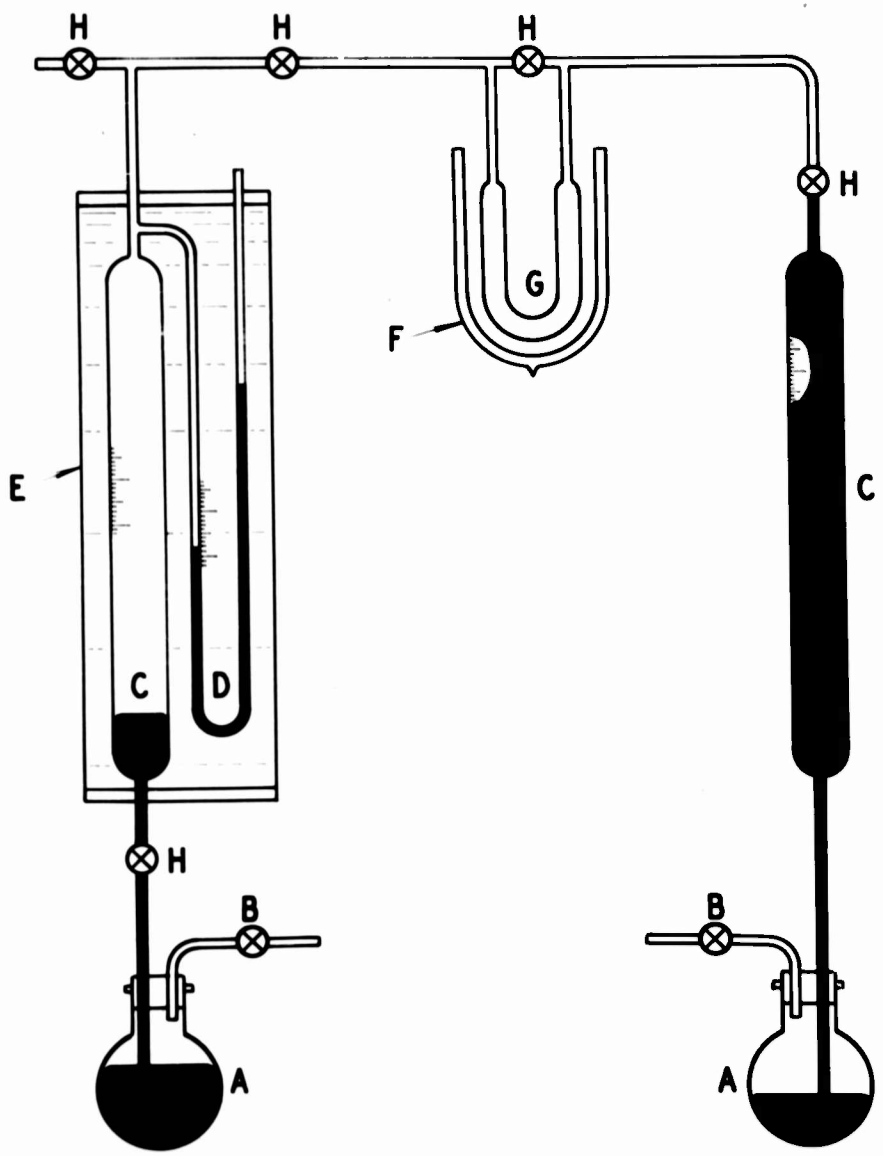
Fig. 4 presents results obtained on regeneration of the oxygenated compound at 100° C., and indicates that essentially complete regeneration can be obtained in 4 minutes including the heating time.

C. Study of Physical-Chemical Properties

These preliminary results indicated that the rate of absorption of the oxygen from air at atmospheric pressure was probably too slow to be of any importance and since the physical-chemical characteristics of the reaction were not monovariant, it was felt desirable to make a more detailed study of these characteristics in order to be able to choose more suitable operating conditions. For this reason a batch absorption apparatus (Fig. 5) was constructed for a study of the equilibrium properties of this compound. In this unit the oxygen-absorbing compound was charged into the U-tube, A, and the oxygen gas could be circulated over the solid back and forth between the burettes C and C_1. Constant pressure was maintained in the unit during the recirculation and periodically the volume changes were determined. Additional gas could be added or removed from the system if this were necessary. Temperature control was achieved by immersing the U tube in a Dewar of liquid maintained at the desired temperature.

The results obtained in this apparatus confirmed the tentative conclusions reached in the previous studies. For example, the unit was completely evacuated and the compound deoxygenated by heating and was then charged with oxygen under an absolute pressure of 5 mm. With the compound at room temperature the pressure slowly dropped over a period of several days to around 3 mm. indicating a very slow but definite absorption at these low pressures. A pressure of 5 mm. was much lower than had been expected for the monovariant system at this temperature. The compound was then treated with pure oxygen at 50 cm. pressure and a temperature of 23.2° C. for 22 hrs., and a relatively slow absorption of oxygen was obtained. The pressure was dropped a few cm. and a slow desorption of oxygen resulted. A number of successive decreases in pressure each gave additional amounts of desorption, thus the amount absorbed was a very definite function of the pressure indicating a divariant system. In these absorptions and desorptions the rates were low and there was a very definite indication of "auto-catalysis" i.e., the rate of absorption after a small amount of oxygen had been taken up by the compound was faster than the rate of absorption with a completely deoxygenated compound.

FIGURE 5
EQUILIBRIUM APPARATUS



KEY FOR FIG. 5

EQUILIBRIUM APPARATUS

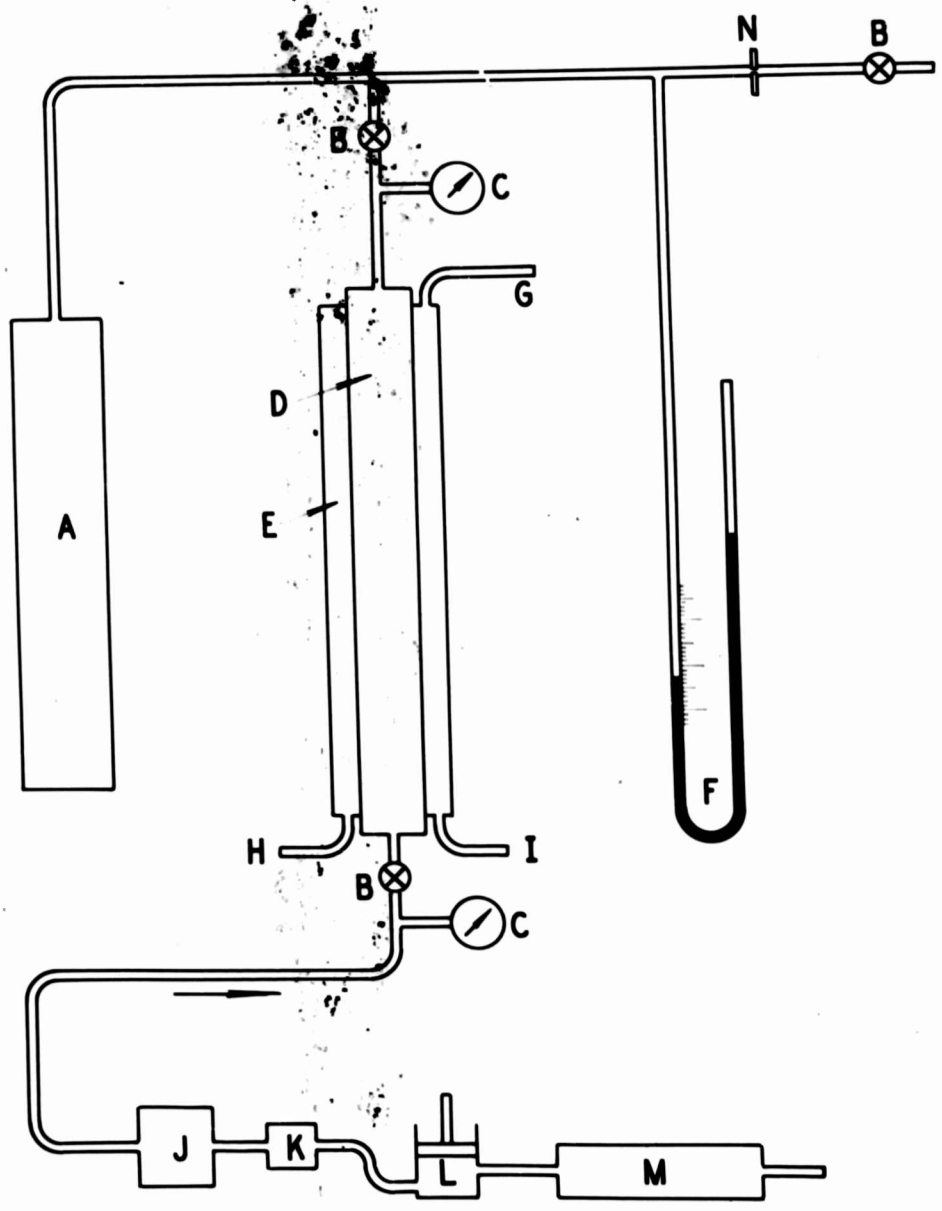
A	MERCURY RESERVOIRS
B	VALVES FOR ADJUSTING LEVEL IN BURETTES
C	BURETTE
D	MANOMETER
E	CONSTANT TEMPERATURE JACKET
F	DEWAR FLASK
G	U TUBE
H	STOPCOCKS

D. Absorption in Packed Tubes

At this stage of the investigation a conference was held with Dr. Furnas, and it was decided that the immediate experimental effort should be directed to the development of a small oxygen-producing unit. On the basis of available information it was concluded that the data necessary for designing such a unit could be most expeditiously obtained if the type of unit were limited to a fixed bed of the Co-Sa-En compound, particularly a unit containing a multiplicity of small tubes packed with the Co-Sa-En compound through which the air would be passed and around which cooling water would be circulated during the absorption cycle and steam during the desorption cycle. In order to obtain shorter absorption times, it was proposed to study higher air pressures.

In order to make these studies, an apparatus consisting of a single one-half inch i.d. tube packed with the Co-Sa-En compound was used. This tube was placed in a jacket so that it could be heated or cooled and a small reciprocating compressor was used for obtaining the air under pressure. This air was carefully filtered to remove any entrained oil before passing through the absorption unit. The unabsorbed portions of the air were expanded to substantially atmospheric pressure and then metered. During the absorption cycle constant pressure and constant rate of flow of the exit gas were obtained and cooling water of a constant temperature was circulated through the jacket. At the end of the absorption cycle the flow of air was discontinued and the pressure within the tube was allowed to drop to 1 atmosphere. The compound was then regenerated by flowing steam through the jacket around the tube and the amount of oxygen evolved was measured volumetrically by the displacement of water. This volume of oxygen was corrected for the expansion of the air in the voids due to the heating operation. When the evolution of oxygen had become extremely slow, the unit was evacuated while still being heated, and was then cooled while evacuated to prevent any oxygen absorption. After the unit was completely cooled, it was ready for the initiation of another absorption cycle. The absorption time reported in the following discussion of this work is the length of time from the period when air was readmitted to the unit, after cooling, up to the time that the flow of air was discontinued. The desorption time is measured from the time steam first enters the jacket up to the time desorption is discontinued and therefore this period includes the heating time. A diagram of this unit is given in Fig. 6.

FIGURE 6
APPARATUS FOR RATE STUDY
USING AIR UNDER PRESSURE



KEY FOR FIG. 6

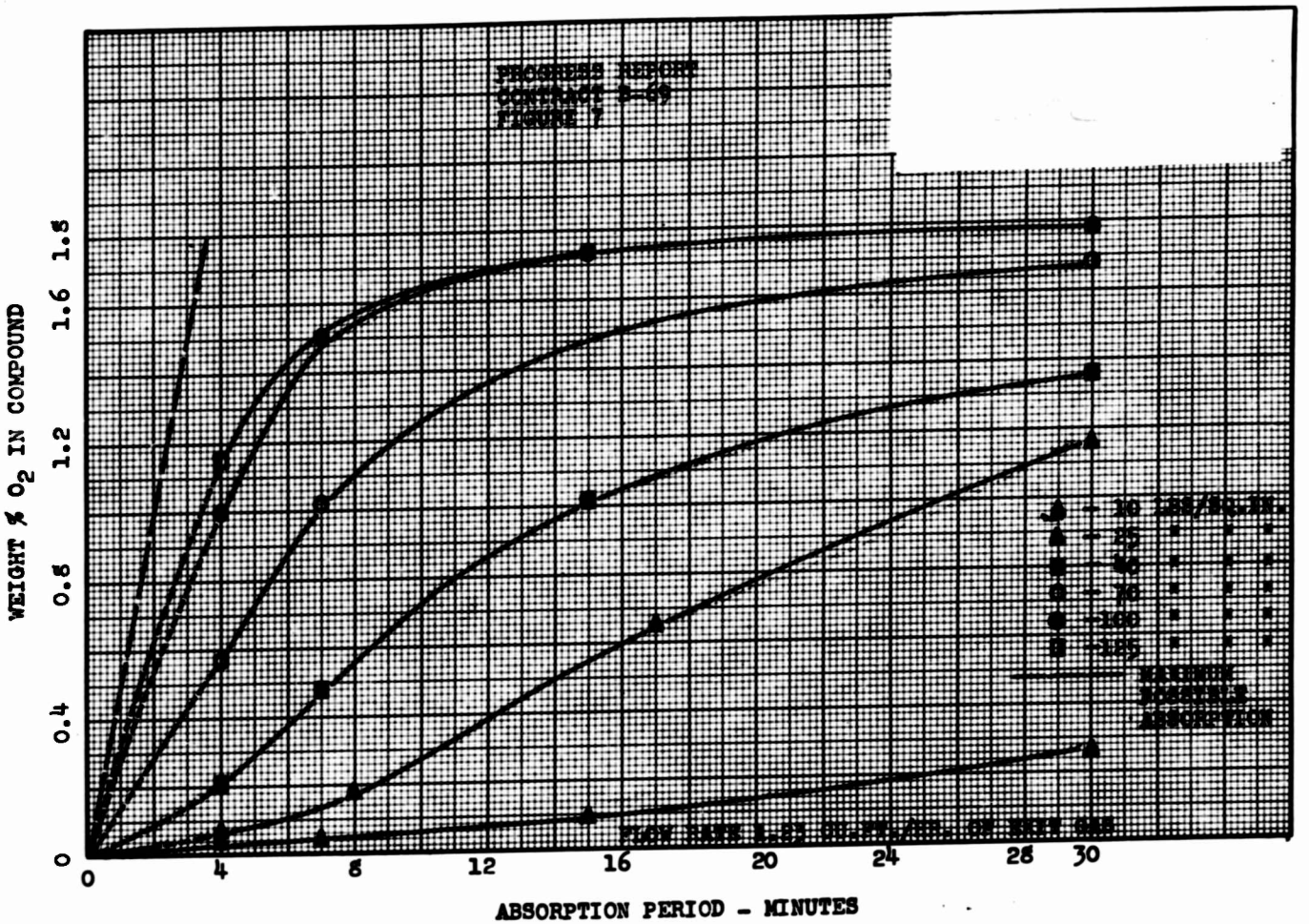
APPARATUS FOR RATE STUDY USING AIR UNDER PRESSURE

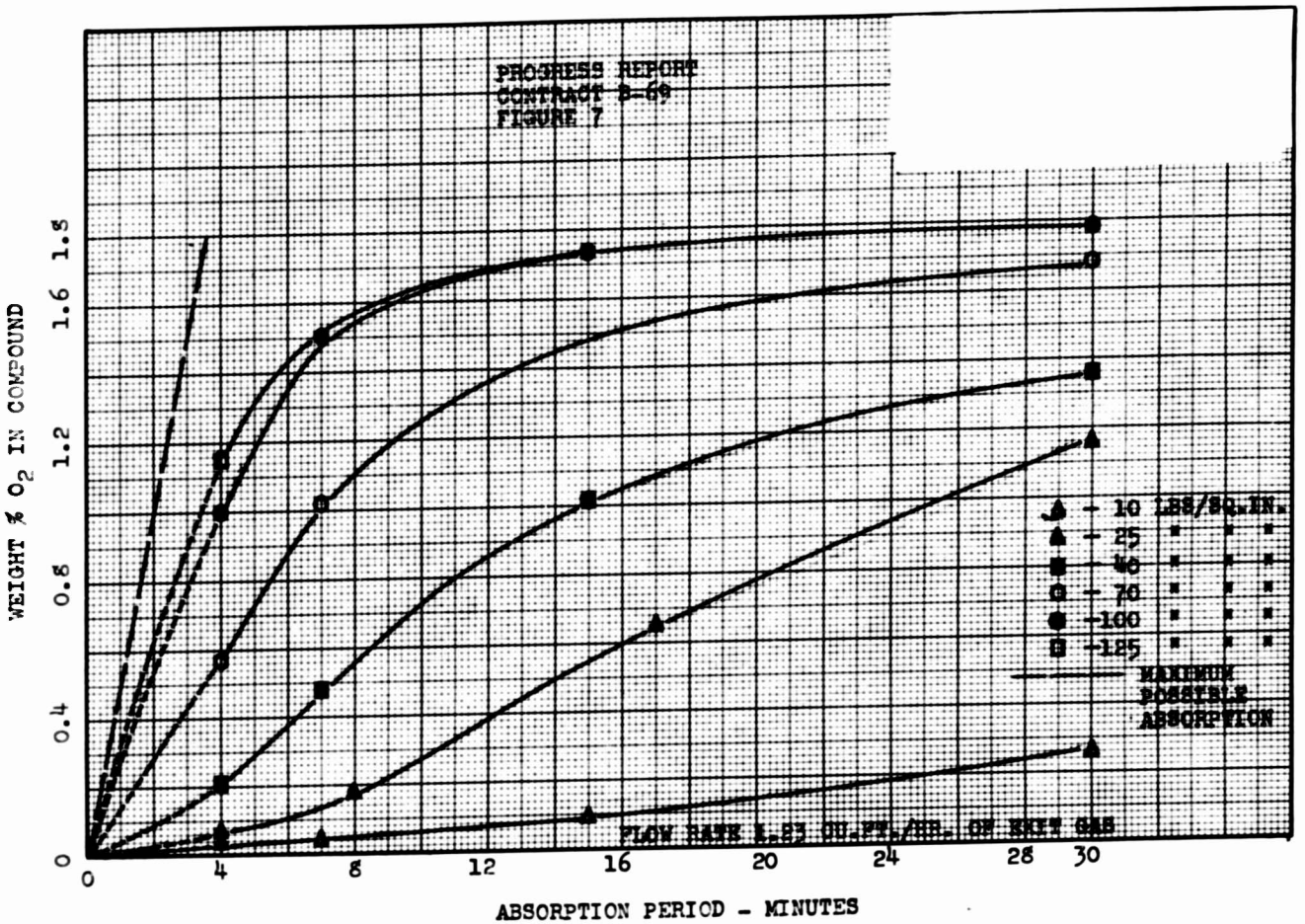
A	OXYGEN RECEIVER
B	VALVE
C	GAUGE
D	1/2" TUBE
E	JACKET
F	MANOMETER
G	STEAM AND WATER OUT
H	STEAM IN
I	CONDENSATE OUT
J	OIL FILTER
K	PRESSURE REGULATOR
L	COMPRESSOR
M	DRIER
N	ORIFICE

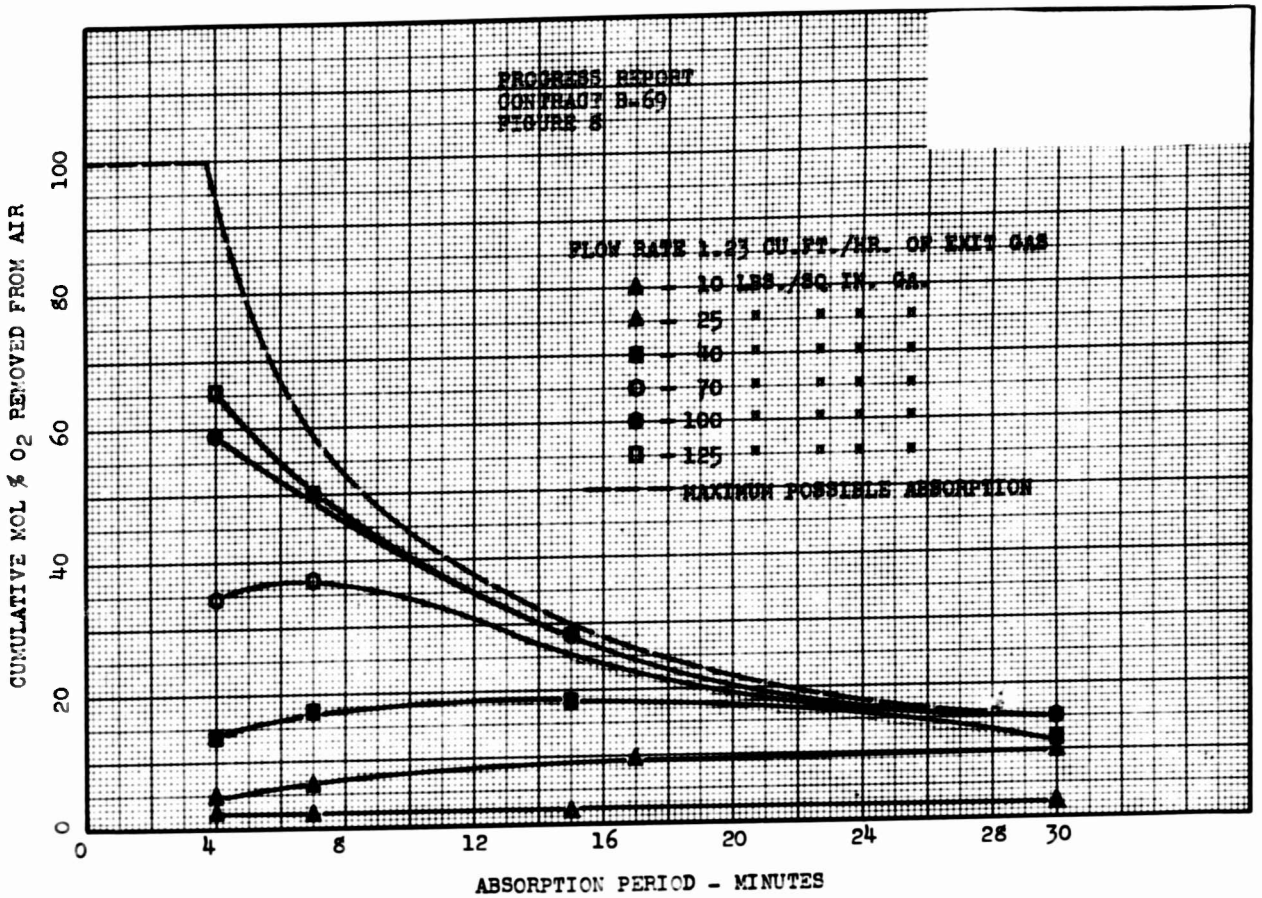
In the first runs that were made with this apparatus, it was found that moisture was condensing in the unit during the absorption cycle. The air being used had been compressed and then cooled to approximately 20° C. and was undoubtedly saturated with water vapor under the high pressure at this temperature. During the oxygen absorption a proportion of this moisture condensed due to the decreasing number of mols of gas. On regeneration this moisture revaporized and due to a portion of it remaining in the voids at the end of this period, the actual amount of gas evolved was somewhat uncertain. The presence of this moisture on the compound at 100° C. did not appear to decrease the absorption activity. This effect of moisture on the absorption activity is not conclusive due to the fact that only 15 desorption runs of about 5 minutes each were made in the presence of moisture. In order to increase the accuracy of the results and to avoid any possibility of lowering the absorption activity due to the presence of moisture, the equipment was modified to predry the air before compression.

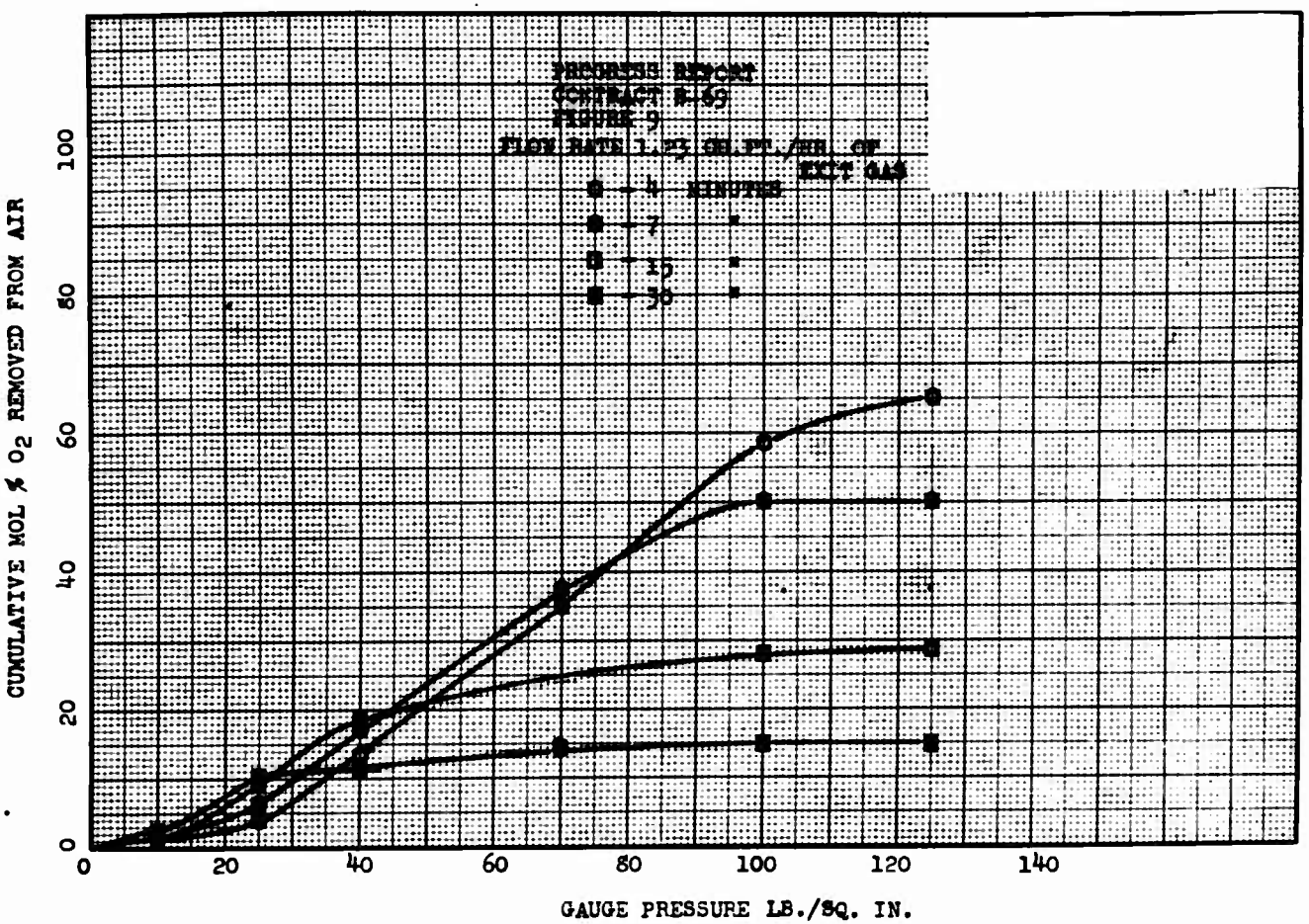
The ½-inch tube was charged with 40.7 grams of the Co-Sa-En compound, 4-8 mesh, which filled it to a depth of about 32 inches, indicating an apparent bulk density of 0.4 g./cc. A series of runs were made on this tube at pressures from 10 to 125 lbs./sq. in. ga. with varying rates of air flow and with absorption temperatures from 3.5° C. to 35° C. In all cases the desorption runs were carried out at 100° C., although the desorption pressure was varied from atmospheric to as high as 115 lbs./sq. in. The results of this series of runs are plotted in Figs. 7 to 15 and summarized in Table I. Two different charges of Co-Sa-En were studied, one having an absorption capacity of about 1.8 weight per cent oxygen, and the other having an absorption capacity of 4.5[illegible] weight per cent oxygen.

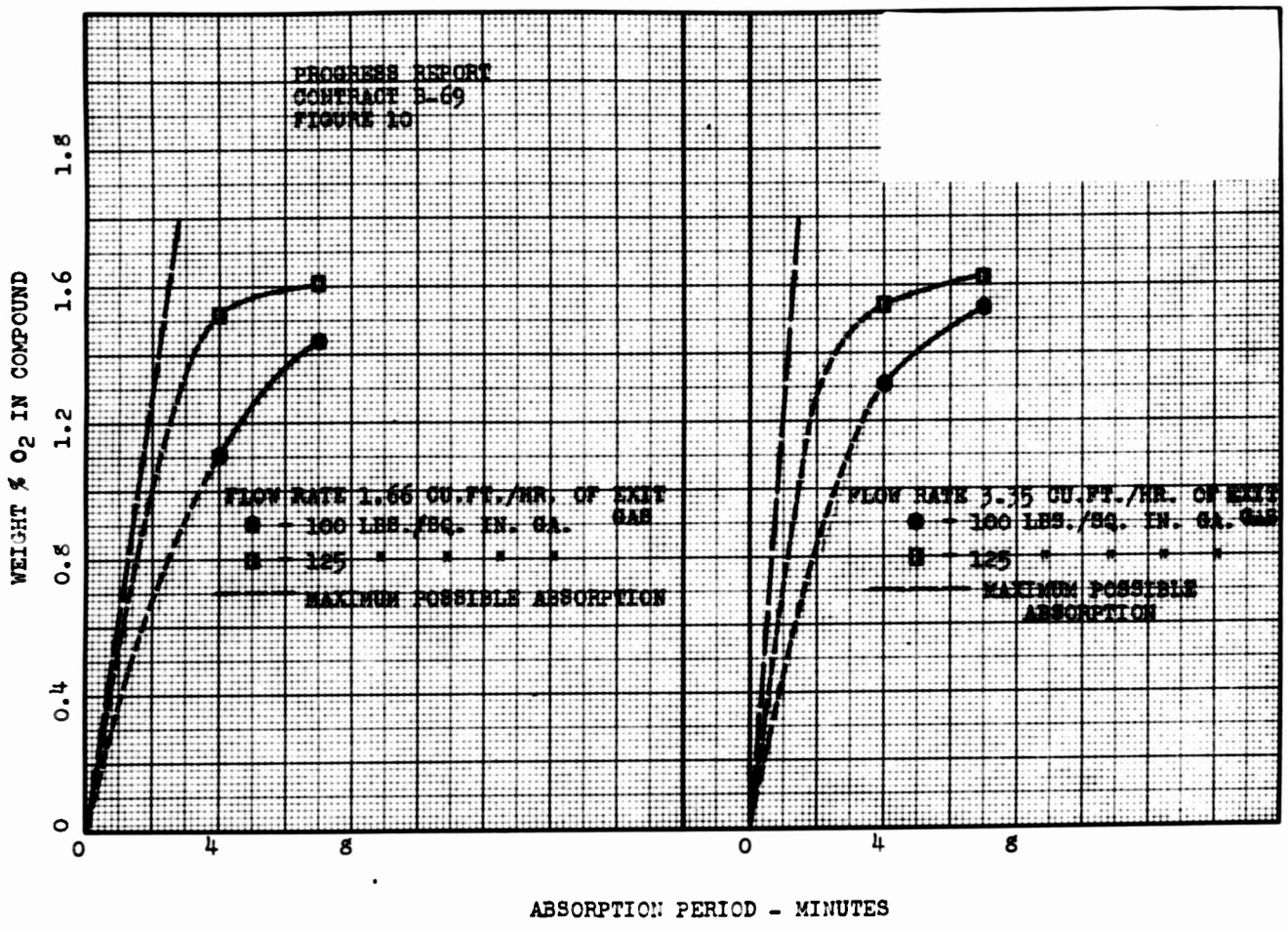
The results for the compound having the 1.8 per cent oxygen absorption capacity are given in Figs. 7 to 13. Fig. 7 indicates the weight per cent oxygen in the compound as a function of the absorption time for a constant rate of flow of exit gas as a function of the absorption pressures at an absorption temperature of 20° C. At low pressures i.e. 10 to 25 lbs./sq. in. ga. the rate of absorption is very slow, but increases rapidly with pressure. These curves also illustrate the "auto-catalytic" effect at the lower pressures in that the slope of the curves at 25 and 40 lbs./sq. in. increase with the per cent saturation up to about 0.[illegible] per cent by weight of oxygen in compound. The effect of pressure is very

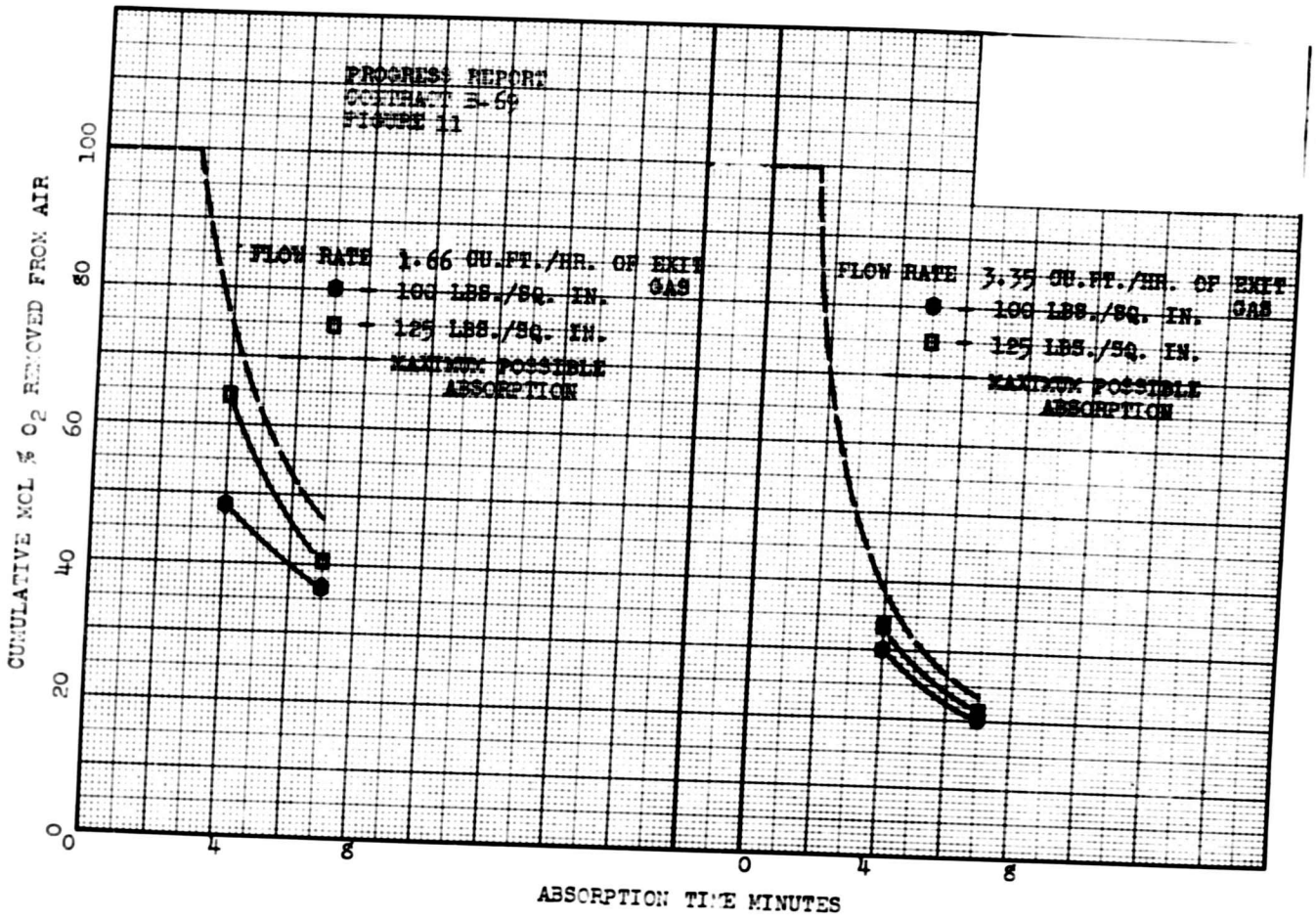


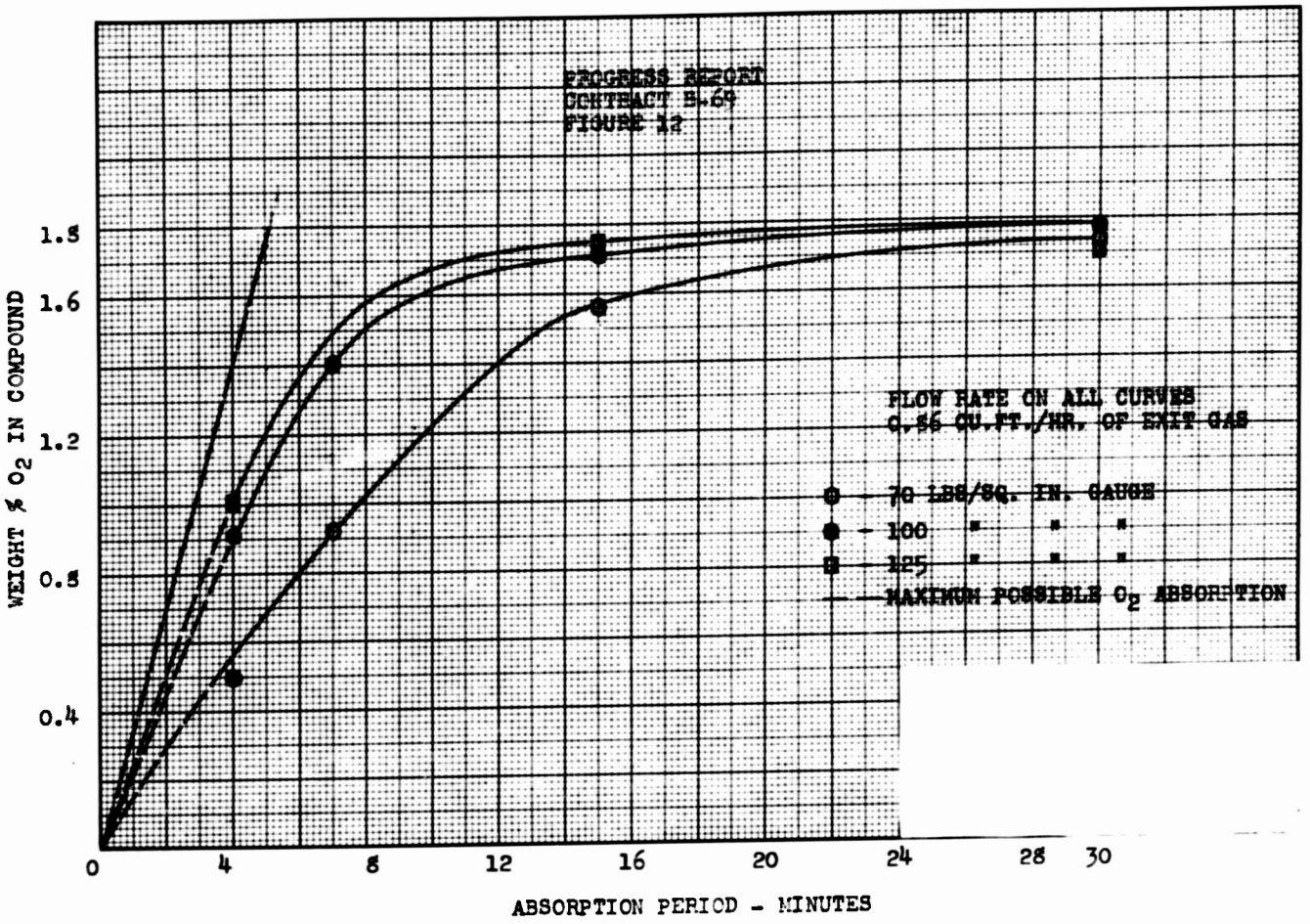


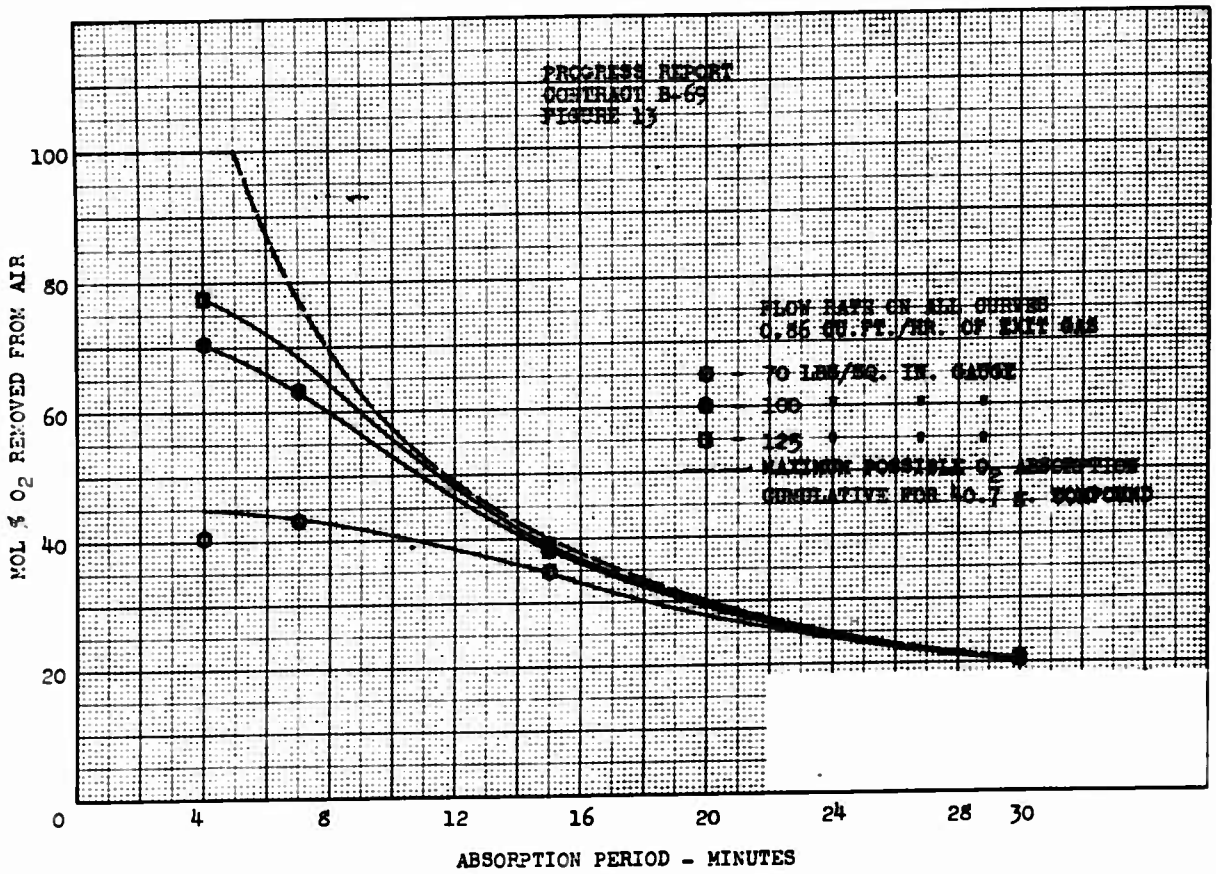








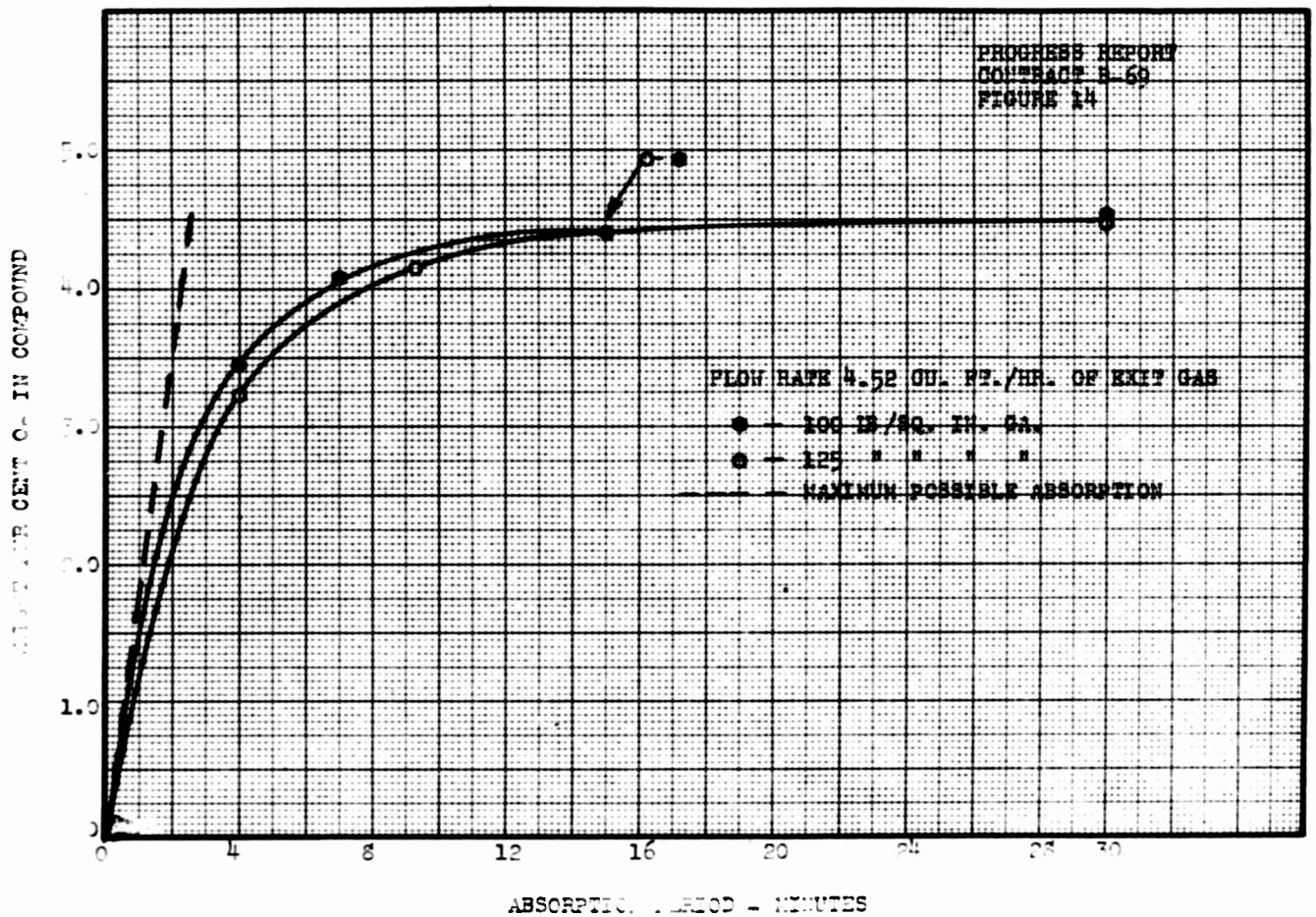


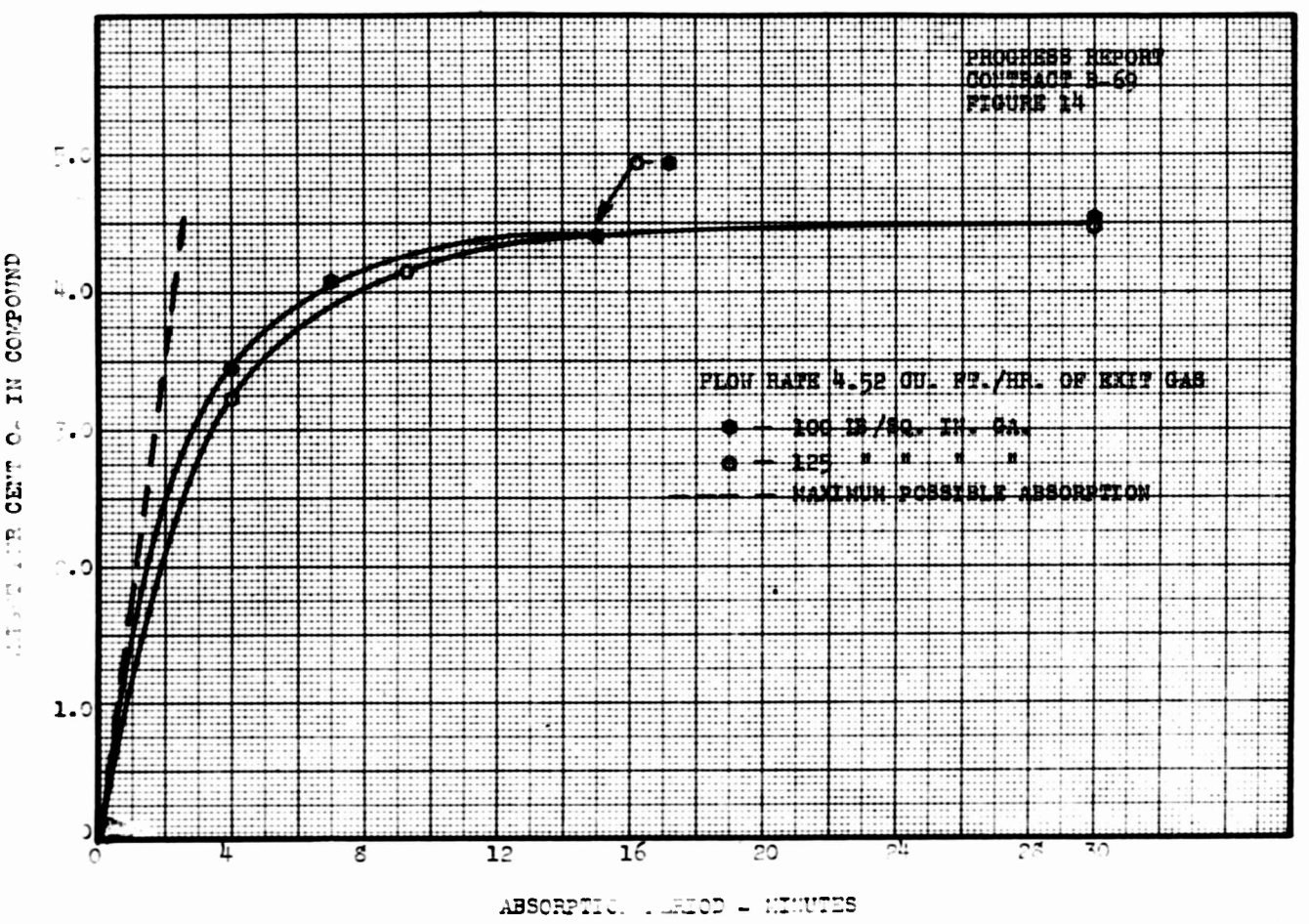


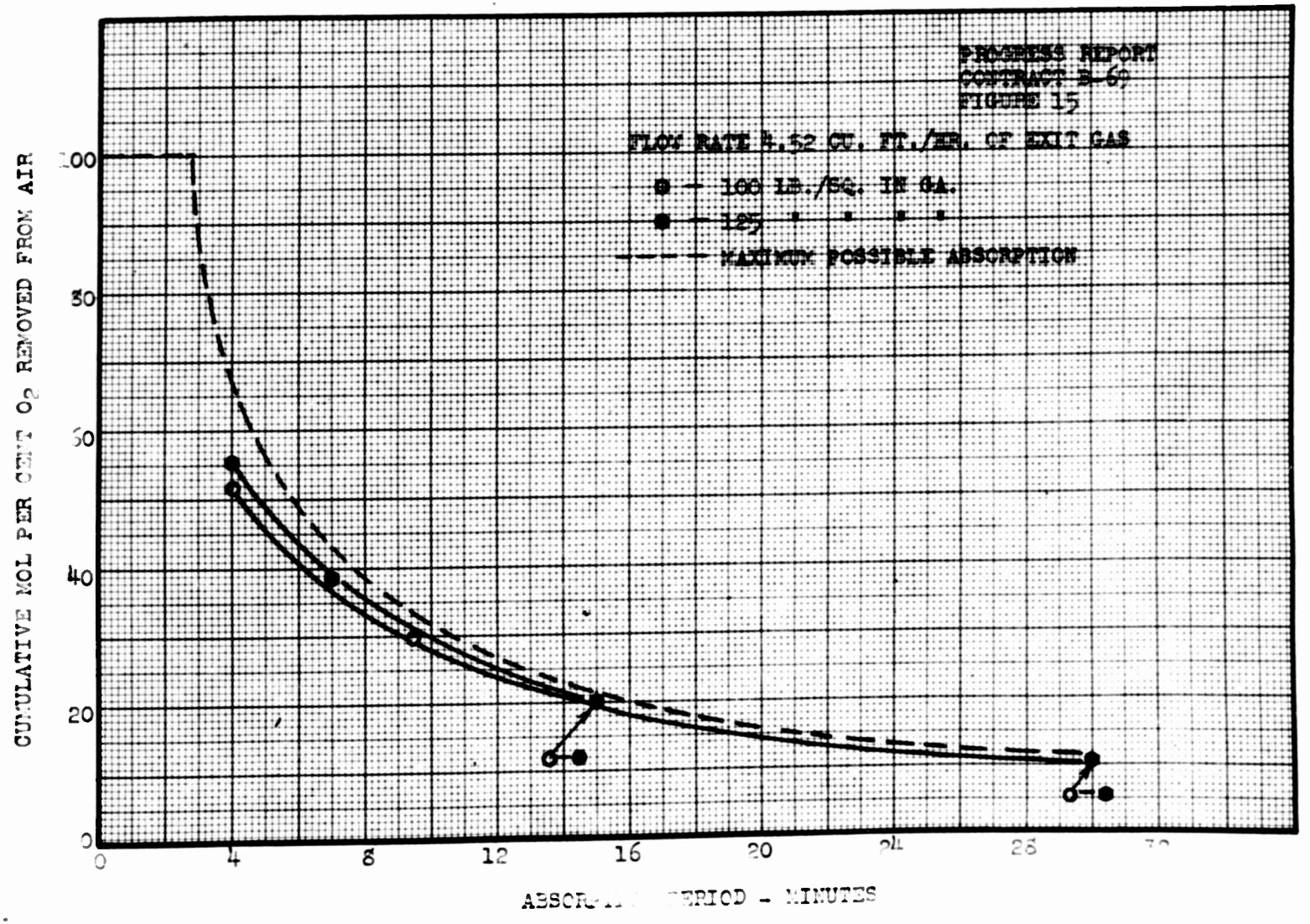
beneficial up to the order of 100 lbs./sq. in. gs. but appears to be less advantageous for further increases in the pressure, but at the higher pressures the rate of absorptions given by this figure are partially limited by the stoichiometry of the operation. Thus, the maximum possible absorption, if 100 per cent of the oxygen were removed from the air, is indicated by the straight dashed line to the left of the diagram. The curves obtained at the higher pressures are approaching this asymptote indicating that a high percentage of the oxygen has been removed from the air and the oxygen supply limits the absorption at short periods of time. At longer absorption times, the compound is very near saturation and therefore shows little effect of pressure. The per cent removal of oxygen from the air as a function of the absorption time is given in Fig. 8 for the same runs. Fig. 8 illustrates the high percentage oxygen removal that can be obtained by using high absorption pressures. The "auto-catalytic" effect is clearly illustrated by the curves at 25, 40, and 70 lbs./ sq. in. In order to determine the effect of the per cent removal of oxygen from the air on the rate of absorption in the initial stages of the cycle, similar runs were carried out at the higher pressures for air rates of 0.86, 1.66 and 3.35 cu. ft./hr., and the results of these runs are given in Figs. 10 to 13. As would be expected the higher rates of air flow increase the rates of absorption and improve the results obtained at 125 lbs./sq. in. relative to the results for the lower pressures. This improvement at the higher flow rates is undoubtedly largely due to the higher residual oxygen pressures in the exit gas. On the basis of these data it would be expected that still higher rates of absorption could be obtained at higher pressures and rates of air flow.

Figs. 14 and 15 present similar data for the more active compound. These runs were obtained at air rates of 4.52 cu. ft./hr. exit gas. This corresponds to the 1.66 cu. ft./hr. for the 1.8 compound, i.e., 1.66 is to 1.8 roughly as 4.52 is to 4.54. The curves are very similar to those obtained with the lower absorbent capacity compound and indicate approximately the same percentage saturation of the compound as a function of the time.

A few runs were made in order to determine the effect of absorption temperature and these are summarized in Table II. It will be noted that increasing the temperature to 35° causes a very marked decrease in the rate of absorption. Thus, at this temperature no significant absorption was obtained when the total pressure







of the air was 70 lbs./sq. in.; and the rate of absorption at 125 lbs./sq. in. and 35° C. was less than 1/5th as rapid as obtained at 20° C. although the partial pressure of oxygen in the air was higher. Data obtained at absorption temperature of 3.5° C. are also given in Table II and the absorption rates are higher than were obtained at 20° C., although the per cent oxygen in the residual air has been reduced. These results indicate that when using the Co-Sa-En compound, it will be desirable to employ low absorption temperatures. If temperatures of the order of 35° must be employed, then still higher pressures, probably of the order of 200 to 300 lbs./sq. in., should be employed during the absorption cycle.

In all of these runs a period of 4 minutes was sufficient to complete the desorption; this time includes the time of heating.

E. Preliminary design calculations on a heat exchanger type of unit employing Co-Sa-En.

On the basis of the data presented in Tables I and II, it appears that a very practical unit for the production of oxygen could be made using the Co-Sa-En compound as the absorbent. Thus, if the unit employed ½-inch i.d. tubes packed with this material, it should be possible to operate at 20° C. with an absorption period of about 4 minutes, although periods as short as two minutes might be used. With these times of absorption it should be possible to obtain saturations of the compound of the order of 80 per cent employing pressures somewhere in the region of 70 to 150 lbs./sq. in. Similar results could probably be obtained at higher absorption temperatures by the use of higher pressures. At the end of the absorption period, it would be desirable to have a short and rapid evacuation of the unit in order to remove the air from the voids around the Co-Sa-En and thus avoid contamination of the regenerated oxygen with the residual air. The arrangement of the bed and the method of heating should be such that the initial oxygen evolved would tend to sweep any residual gases out of the unit. The desorption phase could then be carried out at 100° C. by the use of steam with a heating plus desorption time of 2 to 4 minutes. The desorption would then be followed by a cooling period, and a complete cycle would require about 6 to 10 minutes. The calculations are on the basis of 4.9% O_2 in the saturated compound.

In order to obtain a preliminary orientation as to what a small oxygen-producing unit might involve, a basis of 4 cu. ft. of oxygen per minute was taken. Such a unit

would require from 125 to 175 lbs. of Co-Sa-En depending on the saturation used and the length of the complete cycle. If this material were packed in ½-inch i.d. tubes 3 ft. long, about 1,000 to 1,500 such tubes would be required. If these tubes were made of steel with a wall thickness of 1/32 inch, the weight of tubes would be from 400 to 600 lbs, The headers would add an additional 300 lbs. and the shells would weigh around 100 lbs. Thus, the total weight of steel involved would be about 1,000 lbs. These tubes should be arranged in two or more units to make the oxygen supply continuous. If two units are employed, the desorption time should be slightly longer than the cooling plus absorption time in order to insure the continuity of oxygen flow. If three units are employed, the desorption time should be a little longer than half the cooling plus absorption time.

The power required for the air compression would vary with the pressure employed and the per cent oxygen removed from the air, but would be from 5 to 10 h.p. The small air compressor and gas motor necessary for this compression would weigh about 500 lbs. and would probably consume from 3 to 6 pounds of gasoline per hour. In addition, heat and cooling would be needed to the extent of 100,000 B.t.u. an hour for the unit itself plus whatever cooling was necessary for the engine and compressor. The major portion of this heat is required to raise the temperature of the steel from 20 to 100° C. in each cycle The heat available in the exhaust gas of the engine is insufficient for this operation and external heat will have to be obtained. The extra heat could be easily supplied from a small gasoline burner and would require about 4 lbs. of gasoline per hour. This heat consumption could be materially reduced if a type of absorption unit could be developed which employed lower ratios of metal to active compound. Larger diameter tubes would reduce this weight factor but would probably decrease the absorption rate and therefore might require more Co-Sa-En so that the total weight of steel might not be any less. Other types of absorption units such as large beds with internal finned cooling coils might be employed or the material might be placed in a series of thin layers with a provision for cooling or heating between the layers. Such constructions might decrease the weight ratio of the metal to the absorption compound, but at present data are not available to evaluate such designs.

Thus, on the basis of present data, a unit for producing 4 cu. ft. of oxygen per minute would probably weigh

between 2,000 and 2,500 lbs. and could be contained in a space 3½ ft. high by 6 ft. long by 4 ft. wide. Such a unit would require from a gallon to a gallon and a half of gasoline per hour and about 25 gallons of cooling water per minute. Except for these requirements the unit would be self-contained.

Future Program

The immediate program of work is outlined to furnish additional information to serve as a basis for the design of a small unit. In this program it is planned to study:

(a) The absorption cycle at pressures up to 300 lbs./sq. in.
(b) The effect of tube diameter, with a 1-inch diameter being next on the program.
(c) The length of the packed bed.
(d) The effect of sorption temperature in more detail.
(e) Other types of fixed beds.
(f) Suspended powder operation under high pressure.

IV. INORGANIC COMPOUNDS FOR OXYGEN ABSORPTION

Although the major experimental effort has been expended on the Co-Se-En compound, a literature study and a small amount of preliminary work have been carried out on inorganic compounds capable of reversibly absorbing and desorbing oxygen.

Compounds of this kind have long been known and the Brin process, involving the barium oxide-barium peroxide reaction, was the basis of a commercial operation which was made obsolete by air fractionation. While there are large numbers of inorganic compounds that can be used as reversible oxygen absorbents, essentially all of them require rather high temperatures to give equilibrium pressures of oxygen near one atmosphere. In fact, this is the main drawback to their use. For example, the barium peroxide reaction is very rapid at temperatures in the region of 800°to 900° C. and the solid can absorb about 10 per cent oxygen by weight as against the 4.9 per cent for the Co-Se-En compound, but the heating and cooling and equipment would all be at the elevated temperatures. If an inorganic compound could be found that would rapidly and reversibly absorb oxygen in the temperature range of 300 to 500° C., it could furnish the basis of a practical oxygen-producing unit.

The literature reveals a large number of inorganic compounds which will absorb and evolve oxygen and a few of the more promising are discussed below.

(1) Barium peroxide-Barium oxide
Barium peroxide furnished the basis of the Brin process which operated commercially in the latter part of the last century. The process was based on the fact that in the temperature region of 700° to 900° C. the barium peroxide-barium oxide system will reversibly absorb or give off oxygen depending on the partial pressure. Thus, it is possible to absorb at 1 temperature and regenerate at a higher temperature, or it is possible to operate at constant temperature by a variation in pressure.

(2) Alkali nitrate-nitrite
The alkali nitrates, for example the sodium nitrate, begin the evolution of oxygen at atmospheric pressure around 400° C., the nitrate changing to the nitrite. This decomposition is not complete due to the solution formed, but it appears possible that decompositions as high as 25 per cent might be

obtained at temperatures below 600° C. This partial decomposition would not be a serious drawback due to the fact that the per cent oxygen by weight evolved in going from the nitrate to the nitrite is rather high. Thus, a 25 per cent decomposition of lithium nitrate would correspond to about 7 per cent oxygen by weight. These nitrate-nitrite systems would be liquid in the range of operating temperatures, which might be quite advantageous from a mechanical viewpoint.

(3) Barium peroxide-metallic oxide
The literature indicates that the decomposition pressure of barium peroxide can be greatly increased by the addition of other metal oxides, or the decomposition temperature can be lowered at a given pressure. Such oxides as, copper oxide, calcium oxide, magnesium oxide, cesium oxide, and a number of other oxides with barium peroxide will give oxygen decomposition pressures of 1 atmosphere in the temperature range 300° to 400° C. However, the literature does not give any indication as to whether these mixtures will reabsorb oxygen in this temperature region.

There are a number of other compounds such as calcium plumbate, a mixture of sodium plumbate and sodium manganate, cuprous chloride, manganese dioxide, and others, but they do not appear as promising as the alkali nitrates, barium peroxide, or barium peroxide-metallic oxide systems.

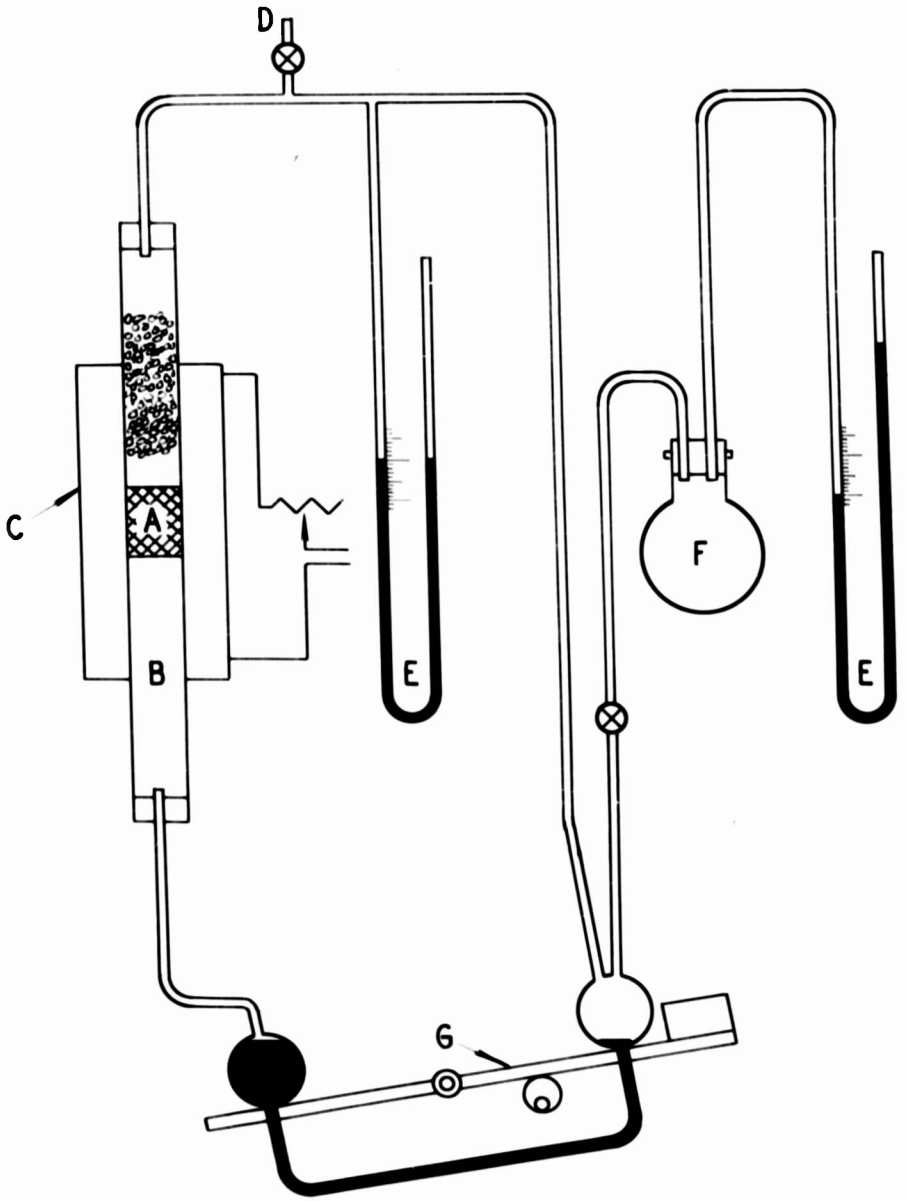
Experimental

Only a few experimental runs have been carried out on barium peroxide in order to obtain an orientation in this field. An apparatus for the study of this absorption has been constructed in which oxygen or oxygen-nitrogen mixtures can be passed over the compound being studied at the desired temperature and pressure, and in which the rate of oxygen absorption or evolution can be measured. This apparatus is shown schematically in Fig. 16.

Future Program

Work on the inorganic systems has been discontinued for the immediate future in order to concentrate all effort on the development of a small unit using the Co-Sa-En compound. The future program on inorganic compounds is contingent upon the rapidity with which the results are obtained and the work is completed on the Co-Sa-En compound.

FIGURE 16
APPARATUS FOR STUDYING INORGANIC COMPOUNDS



KEY FOR FIG. 16

APPARATUS FOR STUDYING INORGANIC COMPOUNDS

A COMPOUND INVESTIGATED

B BROKEN SILICA BRICK PACKING

C ELECTRIC FURNACE

D GAS INLET AND OUTLET

E MERCURY MANOMETERS

F OXYGEN STORAGE FLASK

G TILTING MERCURY GAS PUMPS

V. APPENDIX

A. Preparation of the Compound

Add 3.11 liters of C_2H_5OH and 89 grams 60 per cent ethylenediamine to a 5 liter flask in a water bath at 40° C. The oxygen is removed by evacuation and shaking of the solutions for 15 minutes. Add 1.39 liters of distilled water to a 2-liter flask and deoxygenate as above.

Fill the 2 liter flask with nitrogen to one atmosphere pressure and add 276 grams of cobalt acetate, $CoAc_2.4H_2O$. Re-evacuate the flask and shake well until the solid is dissolved. In order to prevent any hydrolysis the solution should be completed within a period of 5 minutes after adding the cobalt acetate to the water. Immediately run the cobalt solution into the alcohol solution inthe absence of oxygen. The 2 and 5 liter flasks are interconnected with rubber tubing. Shake well and add 276 grams of salicylaldehyde to the solution through a dropping funnel with thorough shaking. All of the aldehyde must be added rapidly and the solution shaken immediately as the mixture soon sets to a thick gel.

It is believed that it is desirable to avoid contact of the solutions with oxygen. The maximum oxygen that could be dissolved in the reactants when saturated with air at one atmosphere amounts to approximately .01 mols per 1 mol of the compound or a maximum irreversible oxidation of 2%. The important factor is probably oxidation by the air in contact with the solution. The rate of irreversible oxidation during the reaction has not been determined but it is not advisable to give it an opportunity to take place and it is easier to avoid oxidation than to determine its extent.

One of the variables is the time-temperature interval of standing after mixing the reactants. If filtered immediately the compound is red and not crystalline at 970 magnifications. If the gel from the initial mixture is allowed to stand 24 hours at 50° C. it forms red crystals. The size of the crystals increases with longer standing. Batch No. 9 was allowed to stand 11 days at room temperature at which time the crystals were of a black, purple color and they stained the hands red on rubbing the crystals between the fingers.

After standing in the reaction liquid in a vacuum, the crystals are filtered while exposed to air and washed with 3-200 cc. portions of alcohol and 2-300 cc. portions of distilled water. They are then allowed to stand over night on filter paper to dry and then weighed. These crystals do not absorb oxygen. The compound is activated by recrystallization from pyridine, a saturated solution being prepared at the boiling point and filtered at -100 C. The pyridine is removed by evacuation at 160° C.

TABLE I

ABSORPTION RATES I ONE-HALF INCH TUBES

A. OXYGEN ABSORBING CAPACITY - 1.8 WEIGHT PER CENT

PRESSURE LB/SQ.IN.GA.	EXIT GAS RATE CU.FT./HR.*	ABSORPTION TIME MINUTES	WEIGHT % O_2 IN COMPOUND	CUMULATIVE MOL % O_2 REMOVED FROM AIR
Temperature During Absorption Runs - 20° C.				
125	0.86	4	1.01	77.5
"	"	15	1.75	38.8
"	"	30	1.73	20.1
"	1.23	4	1.15	65.2
"	"	7	1.49	50.2
"	1.66	4	1.52	64.1
"	"	7	1.60	40.6
"	3.35	4	1.54	33.5
100	0.86	4	1.62	21.3
"	"	7	0.91	70.5
"	"	15	1.4	63.5
"	"	30	1.71	38.1
"	1.23	4	1.78	20.7
"	"	7	1.03	58.5
"	"	15	1.50	50.2
"	"	30	1.73	28.4
"	1.66	4	1.78	15.1
"	"	7	1.10	48.2
"	3.35	4	1.50	38.5
70	0.86	4	1.31	29.8
"	"	7	1.53	20.2
"	"	15	0.495	40.6
"	"	30	0.914	43.1
"	1.23	4	1.56	35.0
"	"	7	1.74	20.2
"	"	30	0.57	34.7
40	"	4	1.07	37.2
"	"	7	1.68	14.3
"	"	15	0.21	13.3
"	"	30	0.48	17.2
25	"	4	1.08	18.3
"	"	7	1.35	11.5
"	"	17	0.06	4.1
			0.17	6.2
			0.65	9.9

*Measured at 25° C. and 1 atmosphere.

TABLE I CONTINUED

PRESSURE LB/SQ.IN.GA.	EXIT GAS RATE CU.FT./HR	ABSORPTION TIME MINUTES	WEIGHT % O_2 IN COMPOUND	CUMULATIVE MOL % O_2 REMOVED FROM AIR
25	1.23	30	1.16	1.0
10	"	4	0.03	2.2
"	"	7	0.04	1.5
"	"	15	0.08	1.4
"	"	30	0.25	2.2
Temperature During Absorption Runs - 35° C.				
70	0.86	4	0	0
"	"	7	0	0
125	"	4	0.14	13.1
"	"	7	0.3	16.5

B. OXYGEN ABSORBING CAPACITY - 4.54 WEIGHT PER CENT

Temperature During Absorption Runs - 20° C.				
125	4.52	4	3.47	55.0
"	"	7	4.09	38.5
"	"	15	4.38	20.0
"	"	30	4.51	10.5
100	"	4	3.24	51.6
"	"	9.5	4.13	29.2
"	"	15	4.39	20.0
"	"	30	4.50	10.5

TABLE II

Effect of Temperature

PRESSURE LB/SQ.IN.GA.	EXIT GAS RATE CU.FT./HR.*	ABSORPTION TIME MINUTES	WEIGHT % O_2 IN COMPOUND	CUMULATIVE MOL % O_2 REMOVED FROM AIR
Temperature During Absorption Runs - 35° C.				
70	0.86	4	0	0
"	"	7	0	0
125	"	4	0.14	13.1
"	"	7	0.3	16.5
Temperature During Absorption Runs - 3.5° C.				
70	0.86	4	0.92	53.7
"	"	7	1.35	45.5
"	"	15	1.60	26.5
"	"	30	1.65	13.9
125	"	4	1.14	67.5
"	"	7	1.49	68.8
"	"	15	1.70	39
"	"	30	1.73	20.7
"	1.23	4	1.41	77.5
"	"	7	1.57	52.5
"	"	15	1.73	28.5
"	"	30	1.72	14.6

OXYGEN ABSORBING CAPACITY - 1.8 WEIGHT PER CENT

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*Measured at 25° C. and 1 atmosphere.

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ABSTRACT:

Various chemical compounds capable of absorbing oxygen from air and being regenerable to give pure oxygen and the original compound were investigated. A study of the absorption and desorption properties of Co-Salen in 1/2-in. ID steel tubes indicates that, by using air pressures of 70 to 125 lb/sq in. ga. and absorption temperatures of 20°C followed by regeneration with steam at 100°C, it will be possible to operate with complete cycles of from 6 to 10 min. The absorption rate decreases rapidly with increasing temperature, but this can be partly off set by increasing absorption pressure. The regenerated oxygen can be obtained under a pressure of a few atmospheres, if this is desired. On the basis of the data obtained with the 1/2-in. tube, it was estimated that an apparatus for producing oxygen at the rate of 20 lb/hr could be constructed.

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