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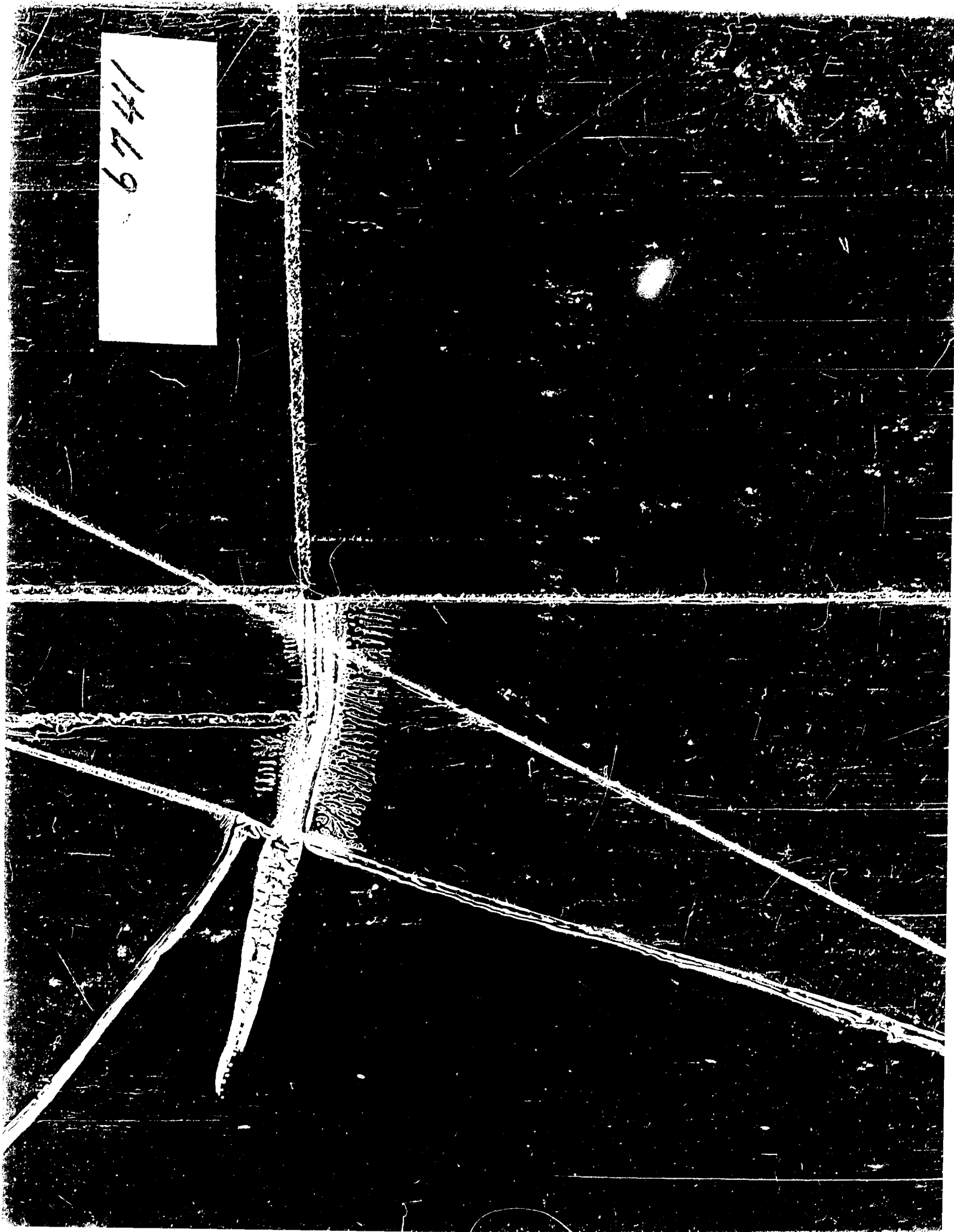
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NORTHWESTERN UNIVERSITY

Evanston, Illinois

The Technological Institute

September 30, 1952

Letter of Transmittal

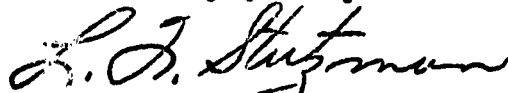
Chief of Naval Research
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Attention: Commander Thompson

Dear Sir:

Attached is the tri-monthly report for the period June 1-September 30, 1952 (inclusive) for Project NR 266-001 at Northwestern University. This report covers work done here principally in the past three months and which is at a satisfactory stage for reporting. Other phases which are not reported here but on which work is progressing are noted in the introductory summary.

Sincerely yours,



L. F. Stutzman, Director
Project 130
Chemical Engineering Department

IFS:ml

CHEMICAL ENGINEERING DEPARTMENT
NORTHWESTERN TECHNOLOGICAL INSTITUTE
Evanston, Illinois

TRI-MONTHLY REPORT
(July 1 - September 30, 1952)

NR 266-001
(N6-or1-158)

Respectfully submitted,
September 30, 1952

Director

Assistant Director

E. J. Stutenman
Wayne L. Dadd

TABLE OF CONTENTS

List of Figures	B
List of Tables	C
Distribution List	D
Introductory Summary and Future Work	E
Section I - CO_2 Absorption with Ag_2O	1
Section II - Low Temperature Absorption, CO_2 Solubility . .	47
Section III - Freezing out of CO_2 with Air Compression and Expansion	56

LIST OF FIGURES

<u>Figure Number</u>	<u>Title</u>	<u>Page</u>
1	Heat Capacity, Ag_2O , Ag_2CO_3 , CO_2	5
2	Equilibrium Constant, $\text{Ag}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{Ag}_2\text{CO}_3$	6
3	Equilibrium Pressure of CO_2 for $\text{Ag}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{Ag}_2\text{CO}_3$	7
4	Ag_2O Absorption of CO_2 , Process Details	10
5	Ag_2O , General Solution of Mechanism Equation	14
6	Ag_2O , Theoretical, y/y_0 vs $-M$	15
7	Ag_2O , Theoretical, $-M$ vs N	16
8	Ag_2O , Reactor Volume	19
9	Ag_2O , Switching Time vs. Initial Solid Concentration	20
10	Ag_2O , Equation Solution	27
11	Ag_2O , Reactor volume vs. Solid Feed Rate	29
12	Ag_2O , Experimental Equipment Flowsheet	31
13	Ag_2O Absorption Data, Run A-1	35
14	Ag_2O Absorption Data, Run A-2	36
15	Ag_2O Absorption Data, Run A-3	37
16	Ag_2O Absorption Data, Run A-4	38
17	Ag_2O Absorption Data, Run A-5	39
18	Ag_2O Absorption - Check of Mechanism Equation	44
19	Freeze-Out CO_2 Removal, Flowsheet	81
20	Freeze-Out CO_2 Removal, Reversing Exchanger	82
21	Freeze-Out CO_2 Removal, Air Stream Temperature after Compressors	83
22	Freeze-Out CO_2 Removal, Air Stream Temp. through H.E.	84
23	Freeze-Out CO_2 Removal, CO_2 -Air Equilibrium	85
24	Freeze-Out CO_2 Removal, Deriming Stream Temperature	86
25	Freeze-Out CO_2 Removal, Deriming Pressure and Temp.	87
26	Freeze-Out CO_2 Removal, Enthalpy of Air Stream	88
27	Enthalpy of Air	89
28	Enthalpy of CO_2	90
29	Freeze-Out CO_2 Removal, Air Stream Temp. (H_2O Discarded)	91
30	Compressor Efficiencies	92
31	Freeze-Out CO_2 Removal, HE-2	93
32	Freeze-Out CO_2 Removal, HE-1	94
33	Freeze-Out CO_2 Removal, HE-3	95
34	Freeze-Out CO_2 Removal, HE-4 Size	96
35	Freeze-Out CO_2 Removal, HE-5 Size	97

LIST OF TABLES

<u>Table Number</u>	<u>Title</u>	<u>Page</u>
I	Ag ₂ O, CO ₂ Thermodynamic Data	4
II	Ag ₂ O, CO ₂ Absorption Experimental Data	34
III	Ag ₂ O, Calculated Values of (y/y _o) _{avg}	41
IV	Ag ₂ O, Check of Mechanism Data	45
V	CO ₂ Solubility in Organic Solvents	52
VI	Temperature of the Oceans	75
VII	Freeze-Out, Compression Effect on Temperature and Enthalpy	76
VIII	Freeze-Out, Air Stream Temperature (H ₂ O Evaporized).	77
IX	CO ₂ Equilibrium Temperatures	78
X	Freeze-Out - Enthalpy of Air Stream	79
XI	Freeze-Out, Air Stream Temperature (H ₂ O Discarded)	80

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INTRODUCTORY SUMMARY

The present tri-monthly report covers three of the methods for removal of CO_2 from air which are under investigation by Project No. ori 158. These methods are: the removal of CO_2 by reaction with a regenerative type solid; the freeze out of CO_2 by lowering the air temperature, this temperature lowering being accomplished by compressing the air, cooling the air back to approximately room temperature and expanding back to one atmosphere pressure; and the absorption of CO_2 in regenerative solvents at below room temperature.

The information available on the regenerative type solid indicates that silver oxide is the best such material to be used. Theoretical mechanism equations have been derived for two modes of operation of the absorption step of a regenerative CO_2 -removal process using silver oxide as the absorbent. These equations have been solved for the case of CO_2 absorption at a rate of 7.5 lb/hr from air of 21% CO_2 content, by volume, and the results are presented in graphical form.

Experiments have been carried out on a small-scale fixed-bed absorption unit in order to evaluate the constants of the derived mechanism equations. Such experimental runs have indicated the repeatability of absorption - desorption cycle; i.e. - absorption at room temperature from air of 1% CO_2 content, and desorption by decomposition of the carbonate at 125°C . and 5 mm. Hg. Further work will support the conclusion of feasibility indicated by these preliminary experiments and will result finally in a complete process design for an operating unit.

The freeze out method feasibility study has been completed. This process does not lend itself readily to simple research techniques and construction of a unit, even in a small size was outside the present scope of the project. This process does have possibilities and investigation should continue further with the construction of a test unit to determine what difficulties, if any, might be encountered in making the process work.

The low temperature absorption method requires the determination and interpretation of data on the solubility of CO_2 in solvents at various temperatures. The latest data and interpretation are presented in this report. More such data and data on rate of absorption and heat exchange studies, also in progress, will be presented at a later date.

Other studies in progress are.

Absorption of CO_2 in sea water

Absorption of CO_2 on charcoal

Absorption of CO_2 on solid NaOH

Freezing out of CO_2 with outside mechanical refrigeration

Freezing out of CO_2 with liquid oxygen

These problems will be covered in later reports.

SECTION I

CO₂ ABSORPTION WITH Ag₂O

INTRODUCTION

One of the most promising regenerative chemical methods for removal of CO_2 from air is by reaction with silver oxide to form silver carbonate, which can later be regenerated to the original silver oxide. This method, along with many others, was listed in the complete survey of CO_2 -removal methods presented in a recent report of Project NR 266-001, dated March 31, 1952. The same general reaction will occur with many metal oxides, but silver oxide seems to offer the best possibility of easy reversibility, thus making possible a regenerative process for CO_2 removal.

During the past three months, considerable effort has been expended on a study of the possibilities of the silver oxide-silver carbonate system as a CO_2 -removal process. Theoretical mathematical expressions have been developed which represent the CO_2 addition step for two different modes of operation. In addition, several small-scale runs have been made to indicate the applicability of the theoretical expressions to the actual system and to determine the rate of CO_2 removal in such a system. This report will outline the results of the work to date and indicate the direction to be taken by future studies.

THERMODYNAMIC DATA

Addition of CO_2 to silver oxide, or to any other metal oxide, will occur only when the partial pressure of the CO_2 in contact with the solid is greater than the equilibrium value determined by:

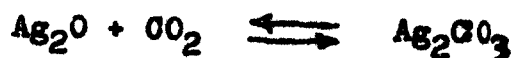
$$p_{\text{CO}_2} = \frac{1}{K_{\text{eq}}}$$

$$\text{where: } \ln K_{\text{eq}} = -\frac{\Delta G_T^\circ}{RT}$$

(In these expressions, K_{eq} is the equilibrium constant for the reaction, ΔG_T° is the standard free energy change of the reaction at temperature $T^\circ\text{K}$, and R is the gas constant.)

Similarly, decomposition of the metal carbonate will take place only when the partial pressure of the CO_2 in contact with solid is less than the above equilibrium value.

The reaction for the proposed silver oxide process is as follows:



Basic data for the various components are tabulated in Table I. In addition, heat capacity data are plotted on Figure 1; where necessary, extrapolations have been made.

Values for K_{eq} at various values of temperature have been calculated from the basic data presented, making use of the following relationships:

$$\Delta \bar{C}_p = \bar{C}_p (\text{Ag}_2\text{CO}_3) - \bar{C}_p (\text{Ag}_2\text{O}) - \bar{C}_p (\text{CO}_2)$$

$$\Delta (\Delta H_f^\circ) = \Delta \bar{C}_p \int_{291}^T dT$$

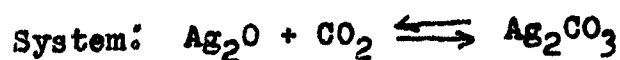
$$\Delta (\Delta S^\circ) = \Delta \bar{C}_p \int_{298}^T \frac{dT}{T}$$

$$\Delta G_T^\circ = \Delta H_{f,T}^\circ - T \Delta S_T^\circ$$

Results of these calculations are plotted on Figure 2, as $\log_{10} K_{eq}$ vs. $1/T(^{\circ}K)$. In addition, since eq. $p_{CO_2} = 1/K_{eq}$, values of the equilibrium p_{CO_2} have been calculated and are plotted on Figure 3 vs. $1/T(^{\circ}K)$. This latter plot will be of use in predicting the pressure-temperature combinations at which decomposition of the carbonate should take place.

TABLE I

BASIC THERMODYNAMIC DATA



Temperature		C_p (cal/gm mol - °K)		
(°K)	(°F)	CO_2 (1)	Ag_2O (2)	Ag_2CO_3 (2)
10	-442	---	1.08	0.49
25	-415	---	5.26	3.90
50	-370	---	8.44	10.22
100	-280	---	10.75	16.95
150	-190	---	12.47	20.79
200	-100	---	13.93	23.20
298.1	77	9.17	15.75	26.83
350	170	9.53	---	---
400	260	9.86	---	---
450	350	10.19	---	---
500	440	10.43	---	---

	CO_2	Ag_2O	Ag_2CO_3
$S^\circ_{298.1^\circ\text{K}}$ (cal/gm mol, °K)	51.1 (3)	29.1 (2)	40.0 (2)
$\Delta H^\circ_f, 298.1^\circ\text{K}$ (kcal/gm mol)	-94.03 (3)	-6.95 (3)	-120.5 (3)

- (1) Hougen and Watson - Chemical Process Principles, Vol. I, p. 214
 (2) K. K. Kelley - Bu. Mines Bull. 434 (1941)
 (3) Lange - Handbook of Chemistry

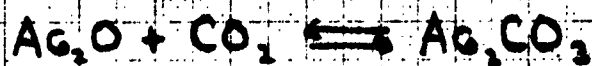
HEAT CAPACITY DATA



FIGURE 2

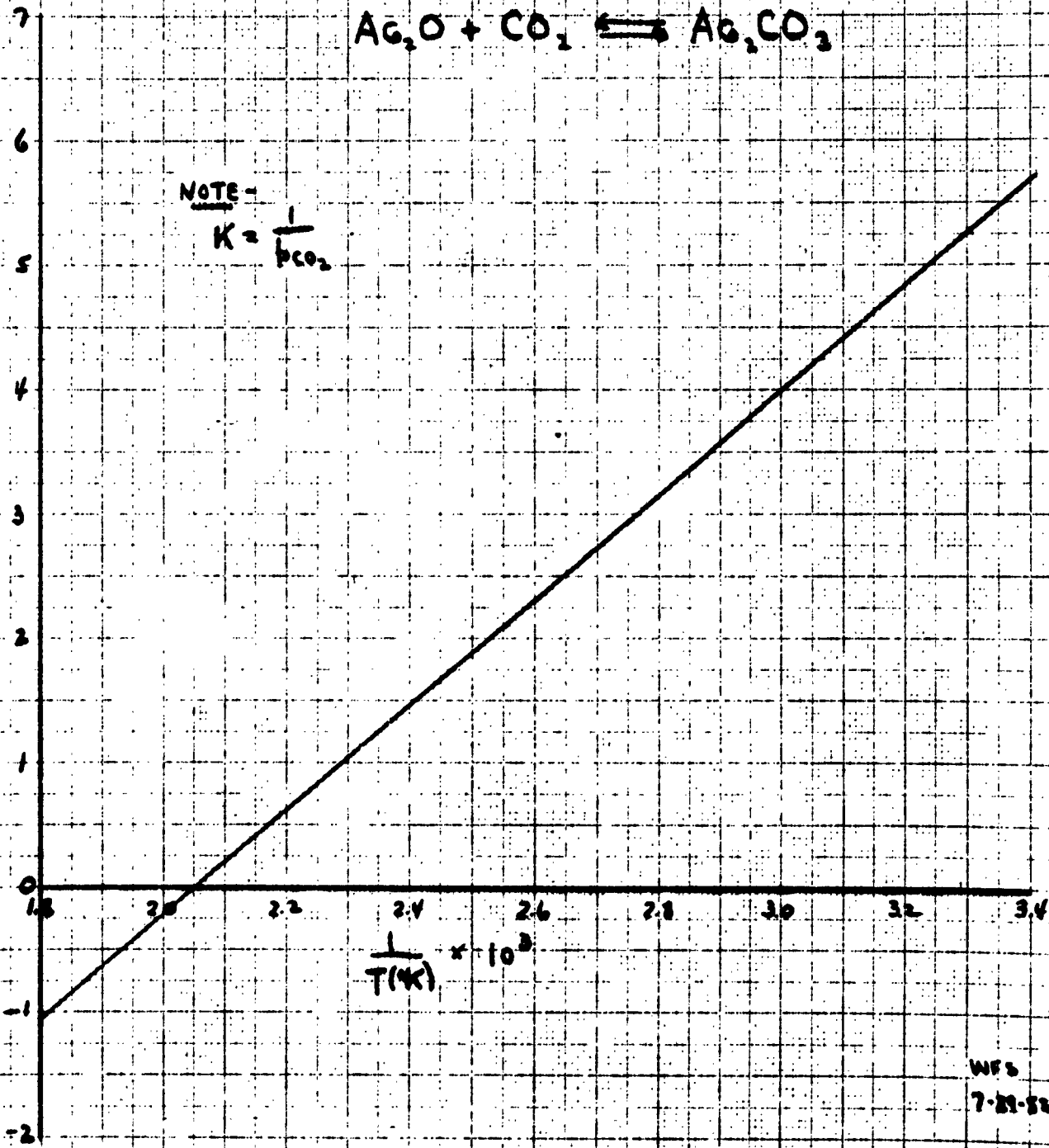
LOG₁₀ K vs. 1/T (°K)

FOR THE SYSTEM:



NOTE -
 $K = \frac{1}{p_{\text{CO}_2}}$

log₁₀ K



WFS
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FIGURE 3

EQUILIBRIUM PRESSURE
OF CO₂

FOR THE SYSTEM:



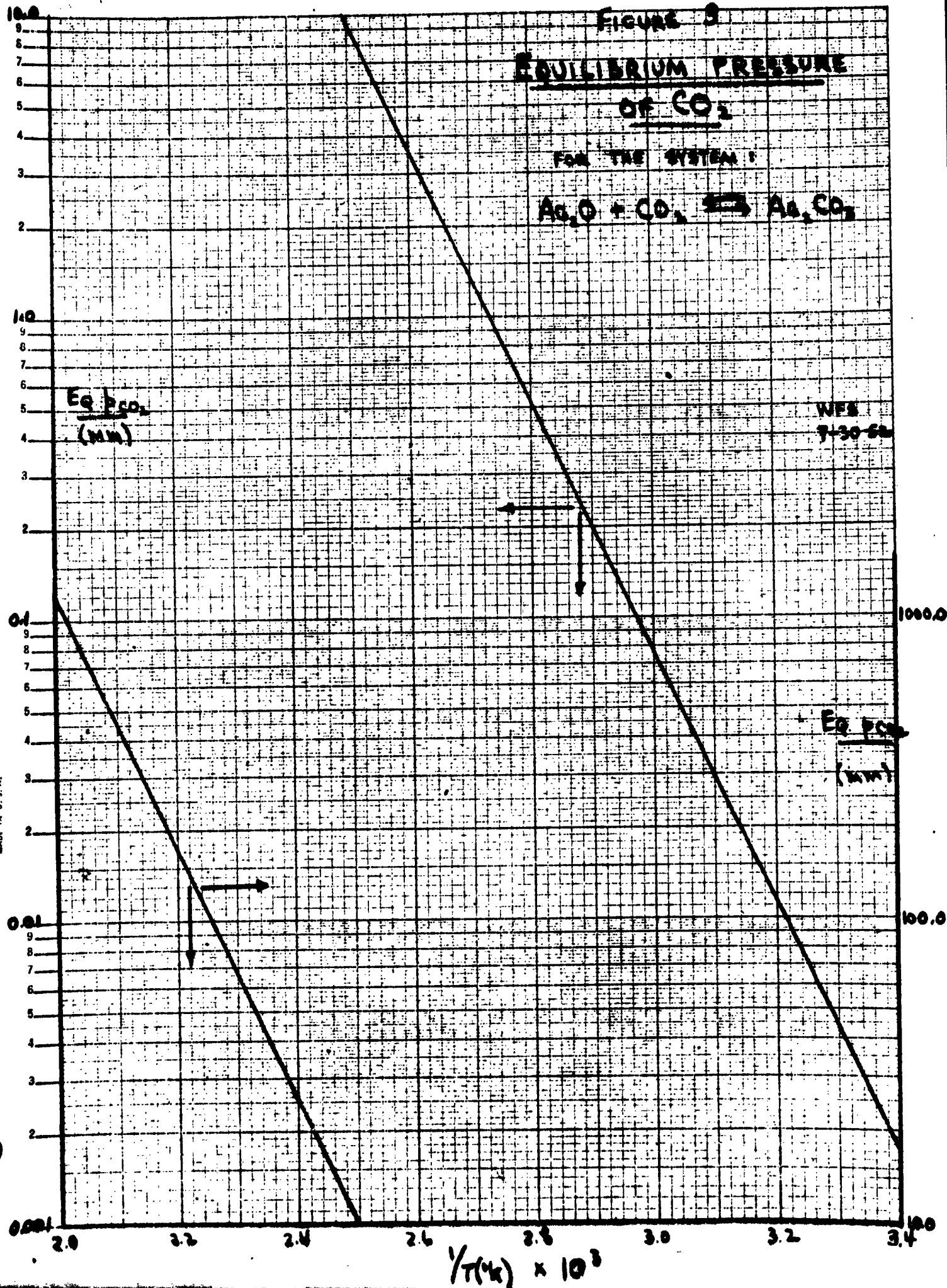
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Eg. p_{CO₂}
(mm)

Eg. p_{CO₂}
(mm)

KEUFFEL & ESSER CO., N. Y. NO. 305-41
Multi-Logarithmic, 6 Cycles X 10 to the inch.
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PROPOSED UNIT

Assuming that alternate absorption of CO_2 and decomposition of carbonate can take place over many cycles with little decrease in the activity of the silver oxide for further CO_2 absorption, there are several possible mechanical arrangements which might be employed for a full-scale unit. A final choice of the best method to use would be difficult to make at this time. Instead, three different processes will be proposed and their advantages and disadvantages pointed out. Then, at the completion of experimental work now in progress, a complete design will be presented, based on the most promising system of operation.

The investigation to date has shown the following modes of operation to be possible:

1) Employ two identical packed beds of silver oxide. Use one for CO_2 absorption while the other is being regenerated under heat and vacuum.

Advantages - Operation can be made completely automatic; no handling of solid required.

Disadvantages - Entire bed must be alternately heated and cooled to effect regeneration; complex automatic controls required; absorption and regeneration steps must remain in balance.

2) Use only one packed bed of silver oxide; and add fresh and remove spent solid continuously, countercurrent to the gas flow. Regenerate the spent solid at a separate location at any convenient time.

Advantages - No balance of absorption and regeneration steps required; less heat load.

Disadvantage - Complex solids handling procedure will be necessary.

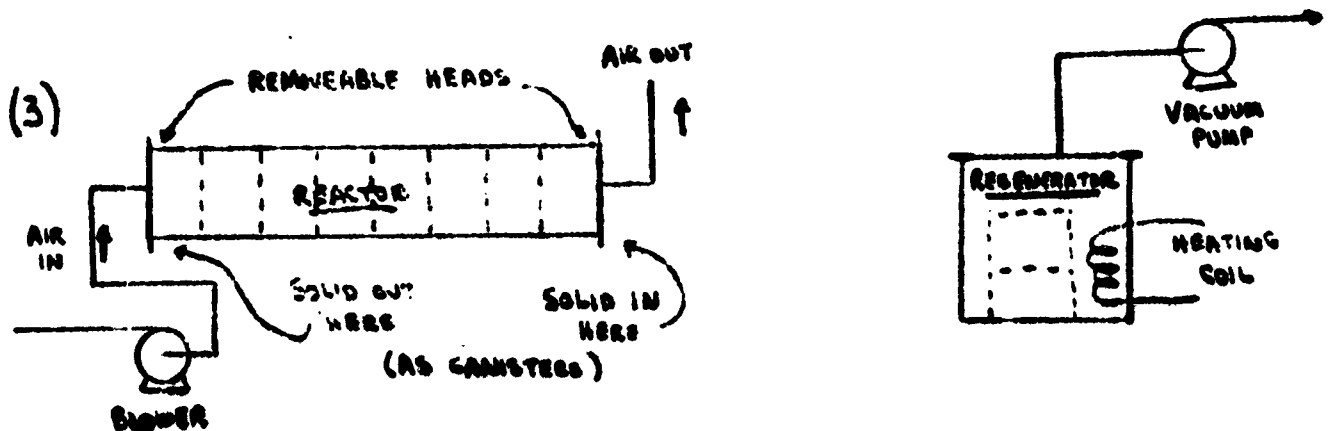
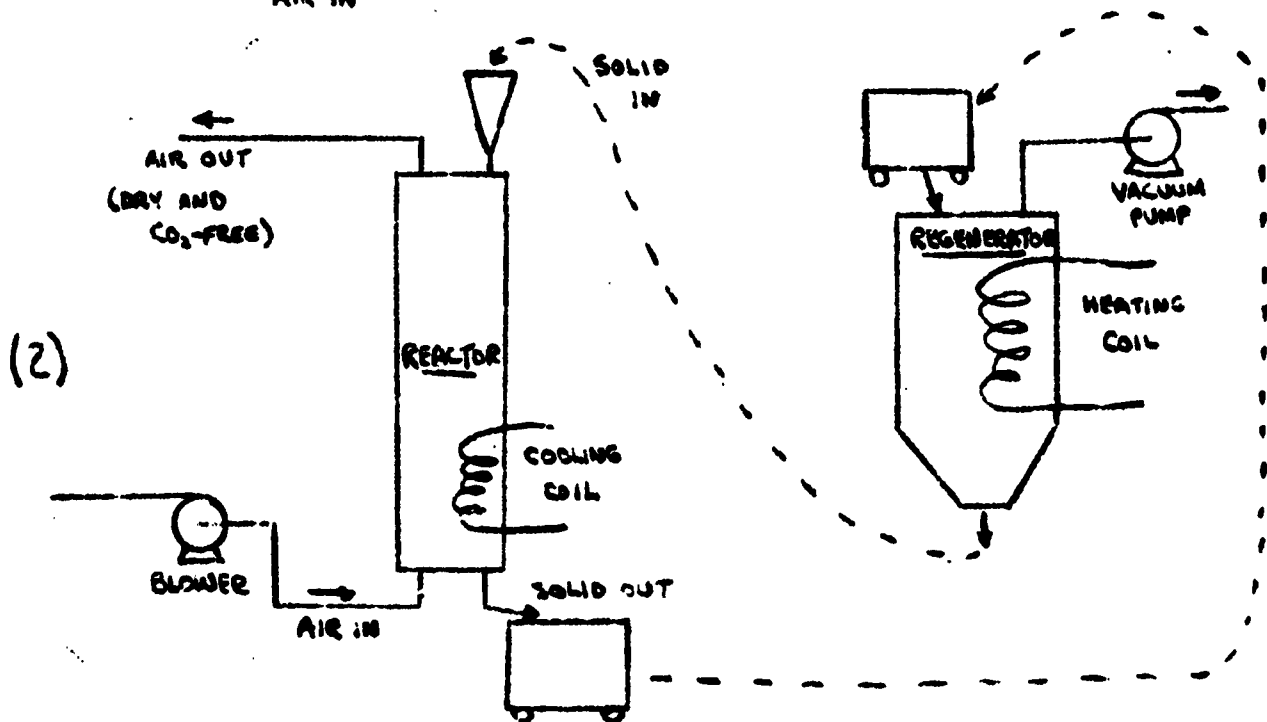
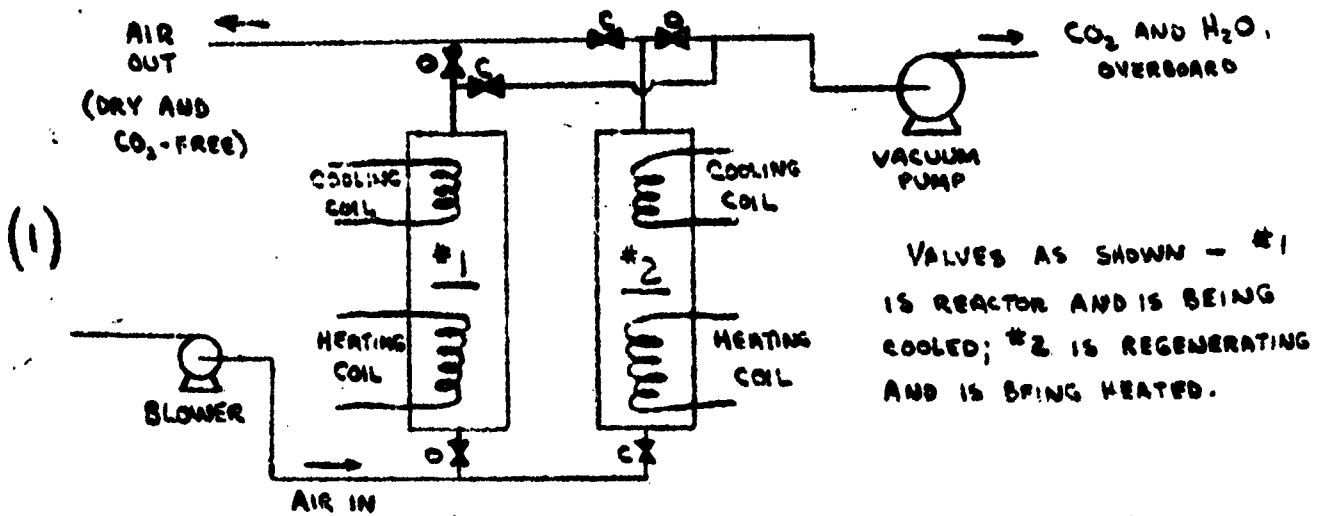
3) A combination of the first two; i.e., use only one packed bed; but add and remove solid at regular intervals, manually.

Advantages - Simple solids handling; less complex controls required.

Disadvantage - Requires services of an operator, at least part time.

A simplified sketch of each of these modes of operation can be found on the next page, Figure 4.

FIGURE 4



PROCESS DETAILS

WFS
9-9-52

MATHEMATICAL DEVELOPMENTS

The three possible modes of operation suggested in the previous section are in reality only two independent methods, since (3) is a combination of (1) and (2). A theoretical mathematical expression has been developed for the absorption step of each of the independent modes.

I - Fixed solid bed - steady flow of gas with constant inlet composition.

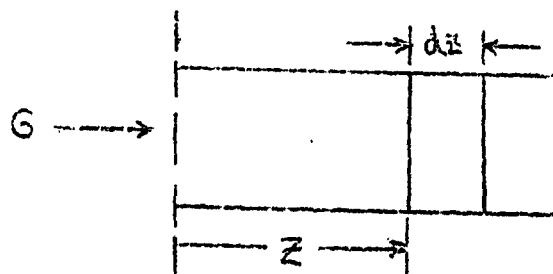
II - Moving solid bed of constant inlet composition - with countercurrent flow of constant inlet composition gas.

In the derivation of these expressions it has been necessary to make several simplifying assumptions. Such assumptions will be pointed out as they are encountered during the developments. None of these assumptions is a major one, and none affects the general applicability of the final solution.

Case I - Fixed Solid Bed - Steady Gas Flow

For the reaction: $\text{Ag}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{Ag}_2\text{CO}_3$

Consider a packed bed, as follows:



For a unit cross section (CO_2 balance):

$$G y \, dz = G (y + \frac{\partial y}{\partial z} dz) \, dz + (- \frac{\partial x}{\partial t}) \, dz \, dt \quad (1)$$

(input) (output) (accumulation
on solid)

where G = lb moles total air/ $\text{ft}^2 \cdot \text{hr}$

y = mole fraction CO_2 in total air

t = time, hours

z = distance down bed from inlet, feet

x = concentration of Ag_2O , lb moles/ ft^3 of reactor

(Neglect change of CO_2 content of the bed voids. This is OK for a flow process where bed volume is negligible compared with volume of fluid passed through.)

It will be assumed that:

$$\begin{aligned} r &= k_A p_{\text{CO}_2} C_{\text{Ag}_2\text{O}} - k_D C_{\text{Ag}_2\text{CO}_3} \\ &= k_A \pi y x - k_D (x_0 - x) \end{aligned} \quad (2)$$

where: $C_{\text{Ag}_2\text{O}}$ = concentration of Ag_2O , lb moles/ ft^3 of reactor

$C_{\text{Ag}_2\text{CO}_3}$ = concentration of Ag_2CO_3 , lb moles/ ft^3 of reactor

k_D = desorption rate constant, hr^{-1}

And, further, it will be assumed that absorption is taking place under conditions where the reverse reaction is negligible.

$$\text{Therefore: } r_A = k_A \pi y x = - \frac{dx}{dt} \quad (3)$$

where: k_A = absorption rate constant, $\text{atm}^{-1} \cdot \text{hr}^{-1}$

π = absorption pressure, atmospheres

r_A = absorption rate, lb moles $\text{CO}_2/\text{hr} \cdot \text{ft}^3$ reactor

From (1):

$$\frac{dx}{dt} = G \frac{dy}{dz}$$

So we have:

$$\frac{dy}{dz} = B x y$$

$$\frac{dx}{dt} = D x y$$

(4)

$$\text{where: } B = - \frac{k_A \pi}{G}$$

$$D = - k_A \pi$$

At this point, a change of variable is to be introduced:

$$\text{Define: } S_V = \frac{60 F}{V}$$

$$V = A Z; \quad 60 F = 359 GA$$

F = gas feed rate, std CFM

V = reactor volume, ft^3

A = cross section area of bed, ft^2

$$\text{Therefore: } \frac{60 F}{V} = \frac{359 G}{Z} \quad \text{or: } \frac{Z}{G} = 359 (1/S_V)$$

$$\text{So: } B Z = - \frac{k_A \pi Z}{g} = - 359 k_A \pi (1/S_V)' = B' (1/S_V)$$

and therefore:

$$\left. \begin{aligned} \frac{dy}{d(1/S_V)} &= B' x y \\ \frac{dx}{dt} &= D x y \end{aligned} \right\} \quad (4a)$$

$$\text{where: } B' = - 359 k_A \pi \quad y(0, t) = y_0$$

$$D = - k_A \pi \quad x(1/S_V, 0) = x_0$$

$$1/S_V = \frac{V}{60 F}$$

The solution for this pair of simultaneous partial differential equations is: (see pp.21 ff. for details)

$$\begin{aligned} \frac{x}{x_0} &= \frac{1}{1 + j(h-1)} \\ \frac{y}{y_0} &= \frac{j h}{1 + j(h-1)} \end{aligned} \quad (5)$$

where:

$$j = e^M$$

$$h = e^N$$

$$M = B' x_0 (1/S_V) = -359 k_A \pi x_0 (1/S_V)$$

$$N = - D y_0 t = k_A \pi y_0 t$$

Graphical presentations of this general solution are included on the following pages:

y/y_0 vs N at various values of M - Figure 5

y/y_0 vs $-M$ at various values of N - Figure 6

$-M$ vs N at various values of y/y_0 - Figure 7

It should be pointed out that there is an interesting relationship between $\frac{y}{y_0}$ and $\frac{x}{x_0}$. For a given value of M and N , there is a definite value for y/y_0 , as shown on Figure 5. For example, at $M = -2.0$ and $N = 3.0$, $y/y_0 = 0.76$. The value of x/x_0 at these same values of M and N can also be obtained from this same Figure 5, by determining the value of y/y_0 at $M = -N$ and $N = -M$ (i.e., at $M = -3.0$ and $N = 2.0$), which gives $x/x_0 = 0.278$. Therefore, the graphs supplied for y/y_0 values may also be used for

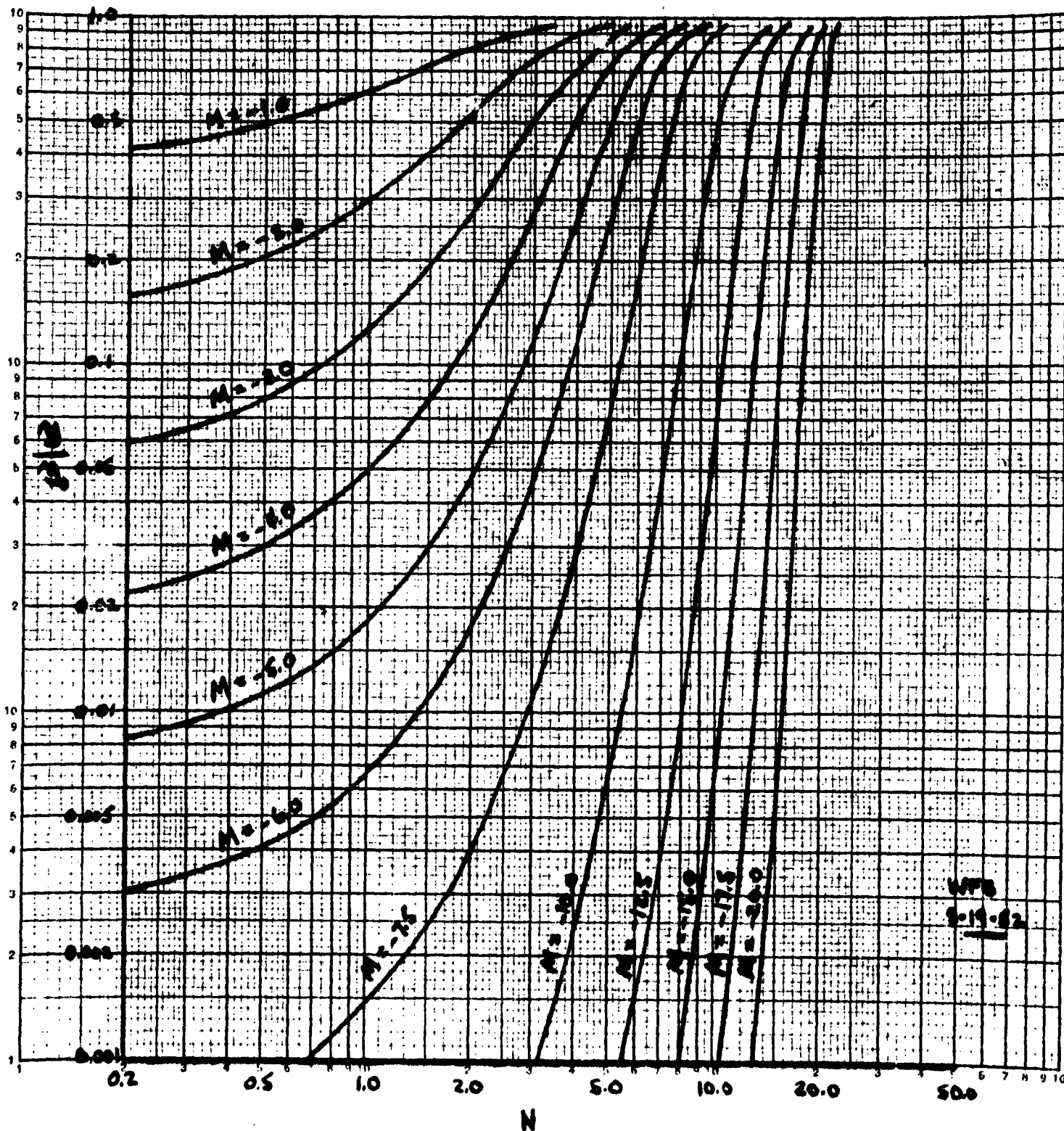
FIGURE 5

GENERAL SOLUTION OF :

$$\frac{y}{y_0} = \frac{jh}{1+j(h-1)}$$

where - $j = e^M$
 $h = e^N$

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For CO₂ ABSORPTION ON AG₂O :

$M = -359 k_A \pi x_0 (\%v)$ (DIMENSIONLESS DISTANCE VARIABLE)

$N = k_A \pi y_0 t$ (DIMENSIONLESS TIME VARIABLE)

FIGURE 6

GENERAL SOLUTION OF:

$$\frac{M}{h} = \frac{ah}{1+j(h-1)}$$

where - $j = e^M$
 $h = e^N$

(CROSS-PLOT FROM
 FIGURE 5)

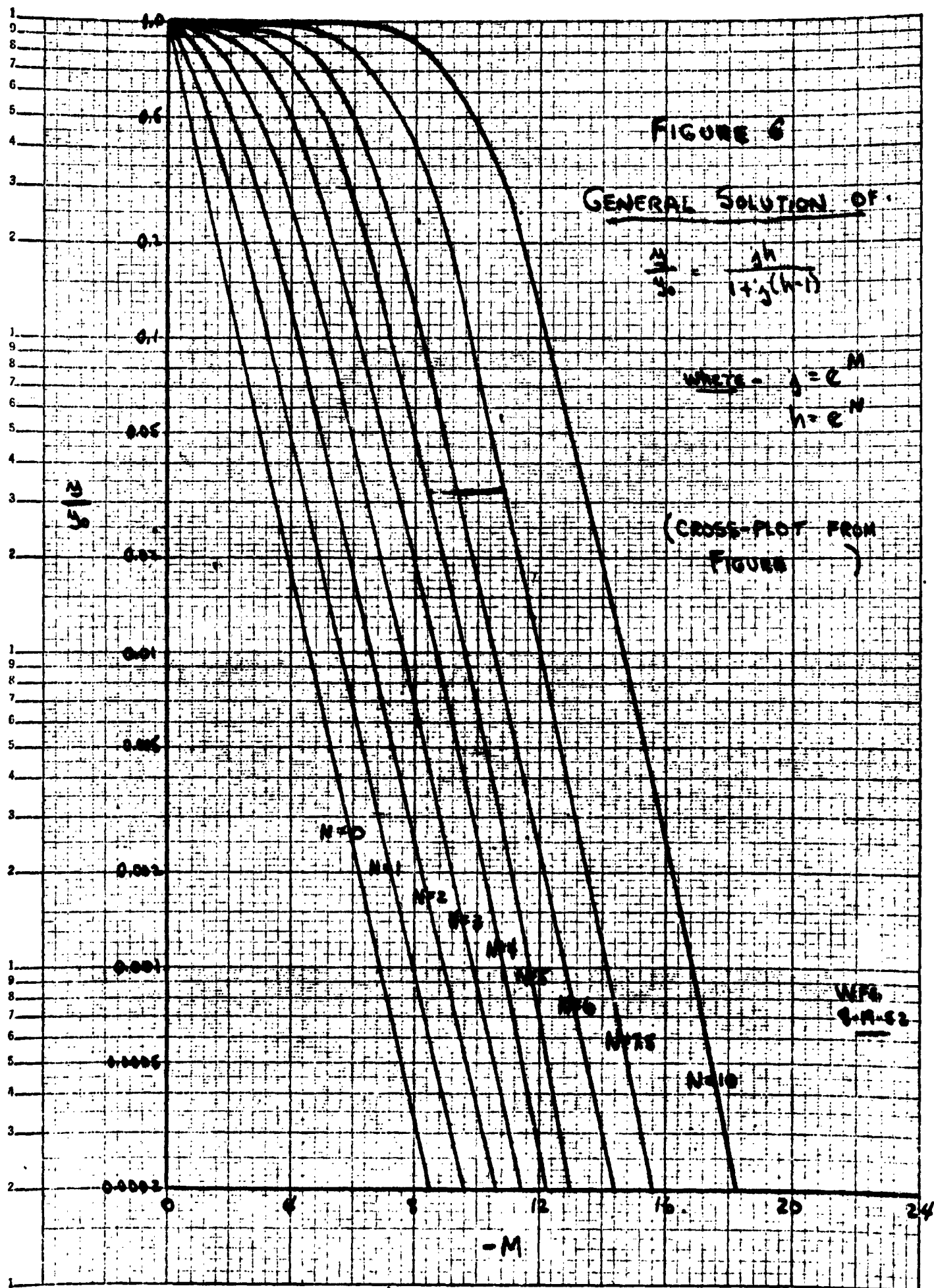
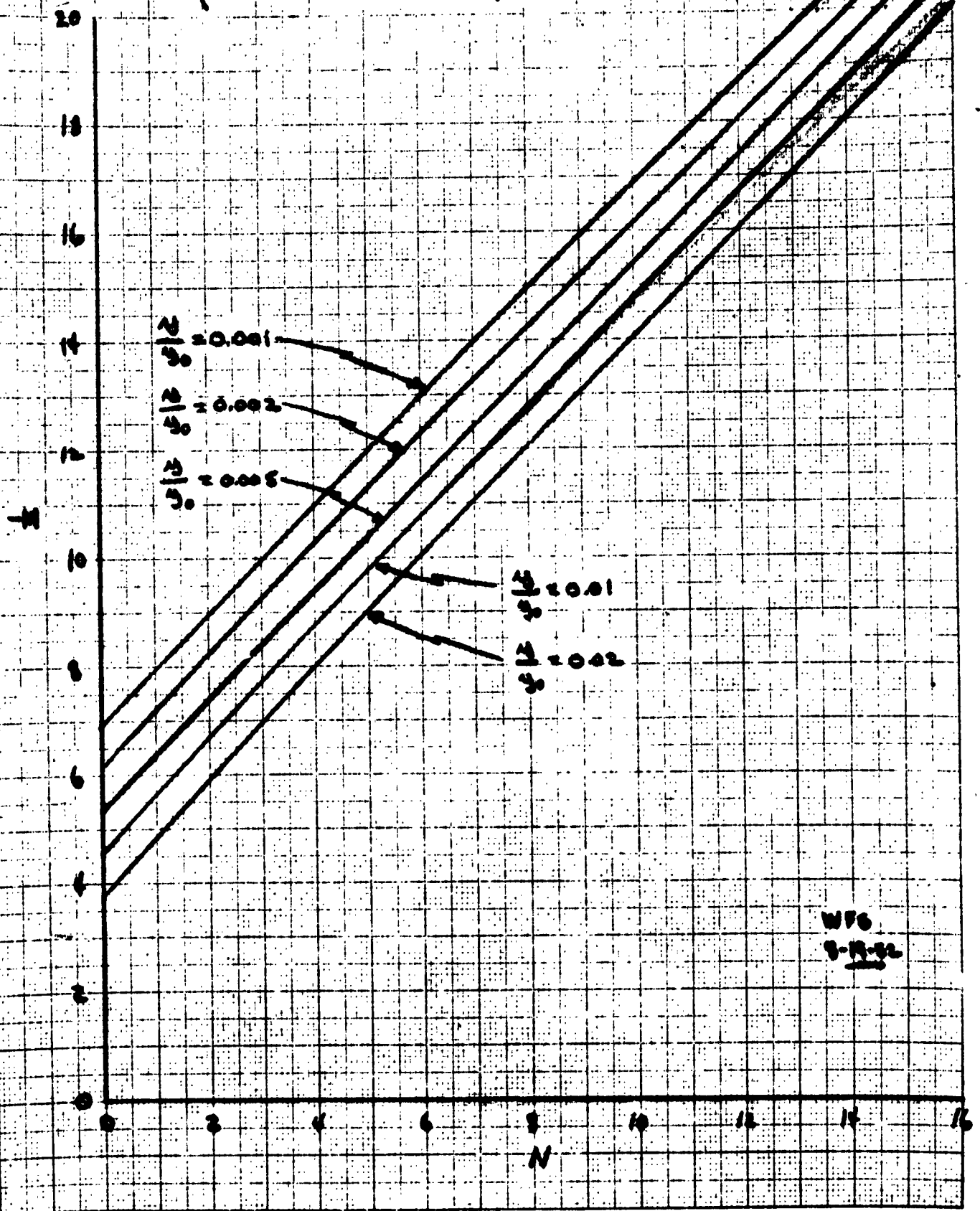


FIGURE 7

CROSS-PLOT OF:
 $-M$ vs. N
 (C CONSTANT $2/3$)



x/x_0 values, providing M and N are redefined properly. This can be proved as follows:

$$\frac{x}{x_0} = \frac{1}{1 + j(h-1)} = \frac{1}{1 + e^{\frac{M_x}{N_x}}(e^{\frac{N_x}{M_x}} - 1)} \quad \text{at } M_x, N_x$$

$$\frac{y}{y_0} = \frac{1}{1 + j(h-1)} = \frac{e^{\frac{M_y}{N_y}} e^{\frac{N_y}{M_y}}}{1 + e^{\frac{M_y}{N_y}}(e^{\frac{N_y}{M_y}} - 1)} \quad \text{at } M_y, N_y$$

Let: $M_y = -N_x$

$N_y = -M_x$

Therefore:
$$\frac{y}{y_0} = \frac{e^{-\frac{N_x}{M_x}} e^{-\frac{M_x}{N_x}}}{1 + e^{-\frac{N_x}{M_x}}(e^{-\frac{M_x}{N_x}} - 1)} = \frac{1}{1 + e^{-\frac{N_x}{M_x}} e^{-\frac{M_x}{N_x}} e^{-\frac{N_x}{M_x}} e^{\frac{N_x}{M_x}}} = \frac{1}{1 + e^{-\frac{N_x}{M_x}} e^{-\frac{M_x}{N_x}}}$$

at $-N_x, -M_x$

And:
$$\frac{y}{y_0} = \frac{1}{e^{\frac{N_x}{M_x}} e^{\frac{M_x}{N_x}} + 1 - e^{\frac{M_x}{N_x}}} = \frac{1}{1 + e^{\frac{M_x}{N_x}}(e^{\frac{N_x}{M_x}} - 1)} = \frac{x}{x_0} \quad \text{at } M_x, N_x$$

At this stage of the investigation, sufficient experimental work has been done to give a good idea of the rate of the absorption step of the process. This work and the results therefrom will be summarized in a later section. Here it is sufficient to state that the value of k_A in the previous relation has been determined to be of the order of $800 \text{ atm}^{-1}\text{-hr}^{-1}$. With this result, it is of considerable interest to solve the general relationship for the special case of CO_2 absorption from air at 1.0% CO_2 by volume. For this purpose, it will be assumed that the reaction will be carried out in such a manner that y/y_0 at the reactor outlet will be approximately zero during the absorption step. As soon as $y/y_0 = 0.01$, the reactors will be switched and freshly regenerated silver oxide will take over the CO_2 removal job. Air feed rate will be set at 110 std CFM, carrying 8.1 lb/hr of CO_2 through the unit. This will be essentially all removed during most of the cycle, so approximately four minutes out of every hour can be employed in switching and still operate with 7.5 lb/hr over-all CO_2 removal.

In general:

$$M = -359 k_A \pi x_0 (1/S_V)$$

$$N = k_A \pi y_0 t$$

$$1/S_V = V/60 F$$

For this particular case: $k_A = 800 \text{ atm}^{-1} \text{ hr}^{-1}$

$$\pi = 1.0 \text{ atm}$$

$$y_0 = 0.01 \text{ mole/mole}$$

$$F = 110 \text{ std CFM}$$

$$\text{outlet } y/y_0 = 0.01, \text{ at switch time}$$

Therefore:

$$M = (-359)(800)(1.0)(1/60)(1/110) x_0 V$$

$$N = (800)(1.0)(0.01) t$$

or:

$$M = -43.52 x_0 V$$

$$N = 8 t$$

$$\text{at } y/y_0 = 0.01$$

$$-M = 4.6 \text{ when } N=0 \quad (\text{From Figure 7})$$

Therefore:

$$-M = 4.6 + N$$

or:

$$43.52 x_0 V = 4.6 + 8 t$$

and, finally:

$$V = \frac{0.1057}{x_0} + \frac{0.1838}{x_0} t$$

and:

$$t = 5.44 x_0 V - 0.575$$

Curves representing these two equations have been plotted and are included as Figures 8 and 9. With these curves it is possible to read off the reactor volume required for operation at a definite switching interval, or the switching interval required when operating with a particular silver oxide initial concentration. It can be seen that the reactor volumes required and the switching interval indicated will be within reason, even at very low values of initial silver oxide concentration. Further experimental work will substantiate these preliminary conclusions and make possible the final design of an operating unit.

FIGURE 8

REACTOR VOLUME AS A
FUNCTION OF
SWITCHING INTERVAL

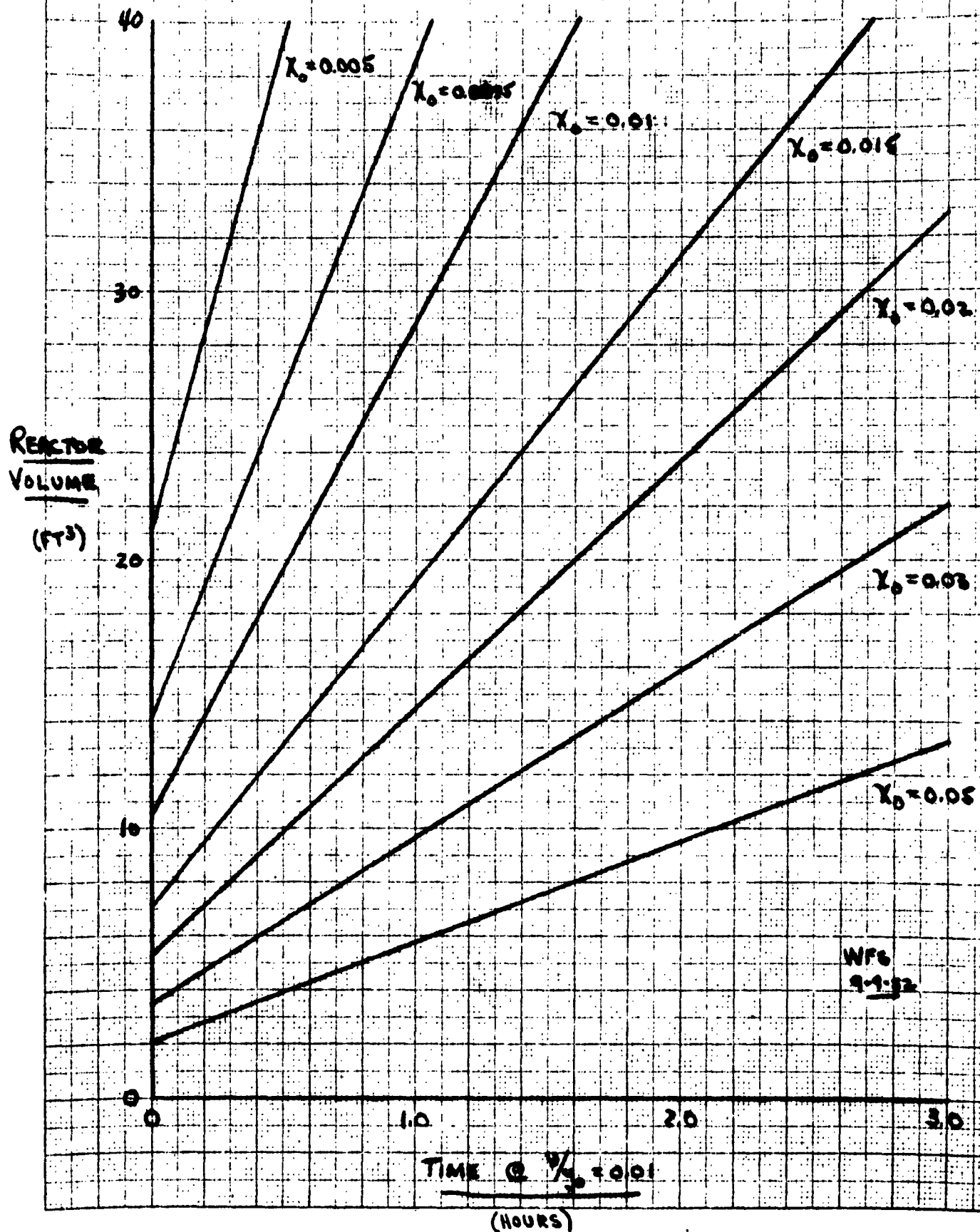
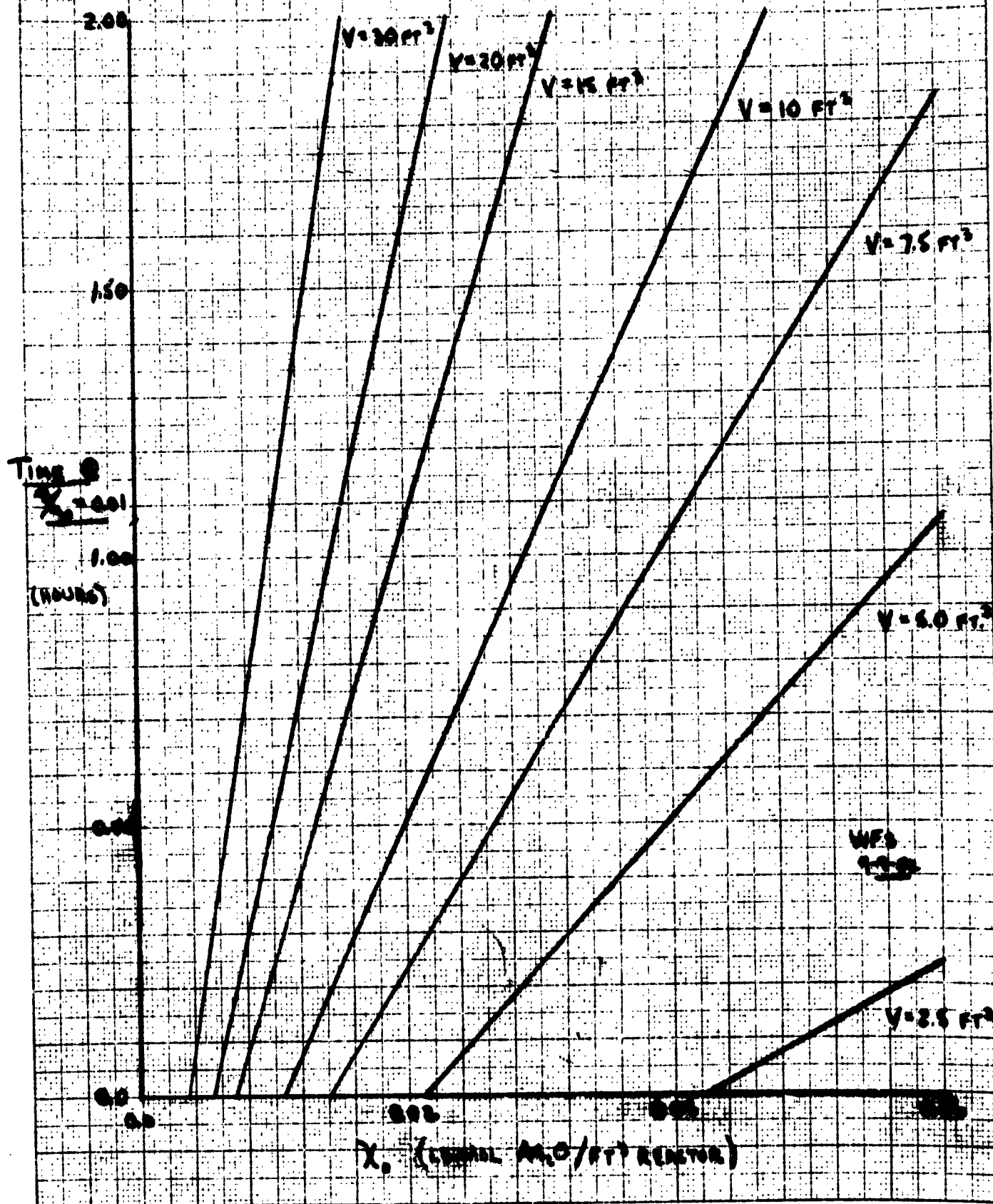


FIGURE 9

SWITCHING TIME AS A
FUNCTION OF
INITIAL SOLID CONCENTRATION



Case I. Fixed Solid Bed, Solution.

$$\left. \begin{aligned} \frac{\partial y}{\partial (1/S_V)} &= B' x y \\ \frac{\partial x}{\partial t} &= D x y \end{aligned} \right\} \quad (4a)$$

$$\left. \begin{aligned} x(1/S_V, 0) &= x_0 \\ y(0, t) &= y_0 \end{aligned} \right\} \quad (6)$$

Put: $U = y$ $X = 1/S_V$ $a = B'$
 $V = x$ $Y = t$ $b = D$

$$\left. \begin{aligned} \frac{\partial U}{\partial X} &= a U V \\ \frac{\partial V}{\partial Y} &= b U V \end{aligned} \right\} \quad (4b)$$

$$\left. \begin{aligned} V(X, 0) &= V_0 \\ U(0, Y) &= U_0 \end{aligned} \right\} \quad (6a)$$

Solve (4b) for U V and equate:

$$\frac{1}{a} \frac{\partial U}{\partial X} = \frac{1}{b} \frac{\partial V}{\partial Y}$$

or:
$$\frac{\partial(a V)}{\partial Y} = \frac{\partial(b U)}{\partial X} \quad (7)$$

$\therefore a V dX + b U dY$ is an exact differential
 and: $f(X, Y)$ exists such that:

$$U = \frac{1}{b} \frac{\partial f}{\partial Y} \quad V = \frac{1}{a} \frac{\partial f}{\partial X} \quad (8)$$

$$\frac{\partial U}{\partial X} = \frac{1}{b} \frac{\partial^2 f}{\partial X \partial Y} = a U V = a \frac{1}{b} \frac{\partial f}{\partial Y} \frac{1}{a} \frac{\partial f}{\partial X}$$

$$\therefore \frac{\partial^2 f}{\partial X \partial Y} = \frac{\partial f}{\partial Y} \frac{\partial f}{\partial X}$$

or:
$$\frac{\partial f}{\partial Y} = \frac{\partial^2 f}{\partial X \partial Y} \bigg/ \frac{\partial f}{\partial X} \quad (9)$$

Put: $h = \frac{\partial f}{\partial X} \quad \therefore \frac{\partial h}{\partial Y} = \frac{\partial^2 f}{\partial X \partial Y}$

and:
$$\frac{\partial f}{\partial Y} = \frac{1}{h} \frac{\partial h}{\partial Y} = \frac{\partial}{\partial Y} (\ln h) = \frac{\partial}{\partial Y} (\ln \frac{\partial f}{\partial X})$$

Integrate: $f = \ln \frac{\partial f}{\partial X} + \Phi(X)$

or: $\frac{\partial f}{\partial X} = e^{\sqrt{f} - \Phi(X)}$ (10)

From (6a) and (8):

$$\frac{\partial f}{\partial X} = a V \quad \frac{\partial f}{\partial X}(X, 0) = a V_0$$

$$f = a V X + \ln C \quad f(X, 0) = a V_0 X + \ln C$$

Therefore: $a V_0 = e^{\sqrt{a V_0 X + \ln C} - \Phi(X)}$

$$\ln a V_0 = a V_0 X + \ln C - \Phi(X)$$

Therefore: $\Phi(X) = \ln \frac{C}{a V_0} + a V_0 X$ (11)

so: $\frac{\partial f}{\partial X} = \frac{a V_0}{C} e^{\sqrt{f} - a V_0 X}$ (12)

Ordinary D.E. corresponding to (12) is:

$$\frac{dF}{dX} = \frac{a V_0}{C} e^{\sqrt{F} - a V_0 X} \quad (13)$$

Separate variables:

$$e^{-\sqrt{F}} dF = \frac{a V_0}{C} e^{-a V_0 X} dX = 0$$

$$-e^{-\sqrt{F}} + \frac{1}{C} e^{-a V_0 X} = \text{constant} \quad (14)$$

Or general solution of (12) is:

$$-e^{-\sqrt{f}} + \frac{1}{C} e^{-a V_0 X} = \psi(Y) \quad (15)$$

From (6a) and (3):

$$\frac{\partial f}{\partial Y} = b V \quad \frac{\partial f}{\partial Y}(0, Y) = b V_0$$

$$f = b U Y + K \quad f(0, Y) = b U_0 Y + K$$

$$\therefore -e^{-b U_0 Y - K} + \frac{1}{C} = \psi(Y) \quad (16)$$

From (8) and (12):

$$a V = \frac{a V_0}{C} e^{\sqrt{f} - a V_0 X}$$

$$C \frac{V}{V_0} = e^{\sqrt{f} - a V_0 X}$$

$$\ln C \frac{V}{V_0} = f - a V_0 X$$

$$\therefore f = \ln C \frac{V}{V_0} + a V_0 X \quad (17)$$

Put (17) and (16) into (15):

$$-\frac{1}{C} \frac{V_0}{V} e^{-a V_0 X} + \frac{1}{C} e^{-a V_0 X} = \frac{1}{C} - e^{-k} e^{-b U_0 Y}$$

and apply: $V(X, 0) = V_0$

$$-\frac{1}{C} e^{-a V_0 X} + \frac{1}{C} e^{-a V_0 X} = \frac{1}{C} - e^{-k}$$

$$\therefore e^{-k} = \frac{1}{C}$$

and:

$$e^{-a V_0 X} \left[1 - \frac{V_0}{V} \right] = 1 - e^{-b U_0 Y} \quad (18)$$

Differentiate (18) with respect to Y:

$$e^{-a V_0 X} \frac{V_0}{V^2} \frac{\partial V}{\partial Y} = b U_0 e^{-b U_0 Y}$$

Put in: $\frac{\partial V}{\partial Y} = b U V$

$$\frac{V_0}{V} e^{-a V_0 X} = \frac{U_0}{U} e^{-b U_0 Y}$$

Therefore:

$$\frac{U}{U_0} = \frac{V}{V_0} e^{a V_0 X} e^{-b U_0 Y} \quad (19)$$

$$\left[\frac{V_0}{V} - 1 \right] = e^{a V_0 X} \left[e^{-b U_0 Y} - 1 \right] \quad (20)$$

Put: $e^{a V_0 X} = j$
 $e^{-b U_0 Y} = h$

Then: $\frac{V_0}{V} = 1 + j(h - 1)$

or: $\frac{V}{V_0} = \frac{1}{1 + j(h - 1)}$

and: $\frac{U}{U_0} = \frac{j h}{1 + j(h - 1)}$

(21)

Replacing original variables:

$$\frac{x}{x_0} = \frac{1}{1 + j(h-1)} \quad (5)$$

$$\frac{y}{y_0} = \frac{j h}{1 + j(h-1)}$$

where:

$$j = e^M$$

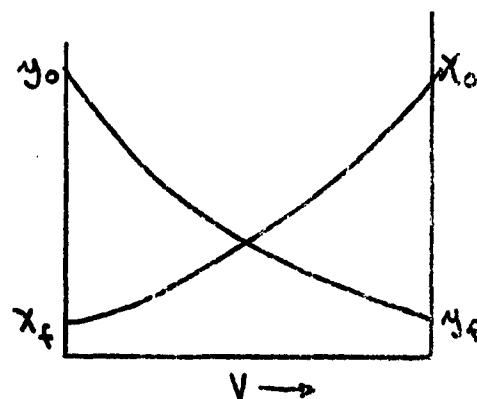
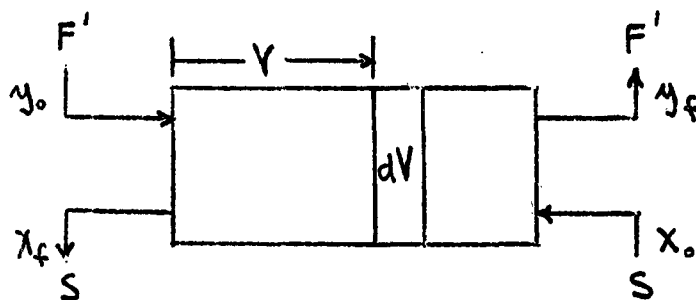
$$h = e^N$$

$$M = B' x_0 (1/S_V) = -359 k_A \pi_0 (1/S_V)$$

$$N = -D y_0 t = k_A \pi y_0 t$$

Case II - Countercurrent Gas and Solid Flow

For the reaction:



$$F' = \text{gas rate (over-all), lb moles/hr} = \frac{60 F}{359}$$

$$S = \text{solid rate (over-all), ft}^3/\text{hr}$$

$$y = \text{moles CO}_2/\text{mole total gas}$$

$$x = \text{moles of Ag}_2\text{O}/\text{ft}^3 \text{ of solid}$$

$$V = \text{volume of reactor, ft}^3$$

$$\text{At steady state: } F' (y_0 - y_f) = S (x_0 - x_f) = R$$

$$R = \text{removal rate (lb mol/hr)}$$

or: $-F' dy = S dx$ (in general)

By material balance on small section above (dV):

$$F' y = F' (y + \frac{d y}{d V} d V) = S (x + \frac{d x}{d V} d V) = S x$$

= moles CO_2 transferred/hr-ft³ of reactor

or: $-F' \frac{d y}{d V} = S \frac{d x}{d V}$

Also, it will be assumed that:

$$\text{moles } \text{CO}_2 \text{ transferred/hr-ft}^3 = r_A = k_A \pi y x$$

(as before)

Therefore: $-F' \frac{d y}{d V} = k_A \pi y x$

or: $\frac{d y}{y x} = - \frac{k_A \pi}{F'} d V$

Now, replace F' by $\frac{60 F}{359}$, its equivalent, and since $\frac{1}{S_V} = \frac{V}{60 F}$

$$\frac{d y}{F'} = \frac{359}{60 F} d V = 359 d (1/S_V)$$

Therefore: $\frac{d y}{y x} = -359 k_A \pi d (1/S_V)$

At any volume V : $F' (y_0 - y) = S (x - x_f)$

Therefore: $x = x_f + \frac{F'}{S} (y_0 - y)$

$$\frac{d y}{y \left[x_f + \frac{F'}{S} (y_0 - y) \right]} = -359 k_A \pi d (1/S_V)$$

or: $\frac{S}{F'} \int_{y_0}^y \frac{d y}{y \left[\frac{S}{F'} x_f + y_0 - y \right]} = -359 k_A \pi \int_0^{1/S_V} d(1/S_V)$

So consider: $\int_{y_0}^y \frac{d y}{y (A - y)} = \int_{y_0}^y \frac{d y}{A y - y^2}$

$$= \frac{1}{A} \ln \frac{-2 y + A - A}{-2 y + A + A} \Big|_{y_0}^y = \frac{1}{A} \ln \frac{y}{y - A} \Big|_{y_0}^y$$

$$= \frac{1}{A} \ln \frac{y (y_0 - A)}{y_0 (y - A)} = \frac{1}{S/F' x_f + y_0} \ln \frac{y (-S/F' x_f)}{y_0 (y - y_0 - S/F' x_f)}$$

where: $A = \frac{S}{F'} x_f + y_0$

and then: $\frac{S/F'}{S/F' x_f + y_0} \ln \frac{y (S/F' x_f)}{y_0 (S/F' x_f + y_0 - y)} = -359 k_A'' (1/S_V)$

From first material balance: $x_f = x_0 - \frac{R}{S}$

Therefore: $\frac{S/F'}{S/F' (x_0 - R/S) + y_0} \ln \frac{y S/F' (x_0 - R/S)}{y_0 [(x_0 - R/S) S/F' + y_0 - y]}$

$$= \frac{S/F'}{(S/F' x_0 + y_0) - R/F'} \ln \frac{y (S/F' x_0 - R/F')}{y_0 \{[(S/F' x_0 + y_0) - R/F'] - y\}}$$

or: $\frac{1}{S_V} = \frac{1}{359 k_A'' (q x_0 + y_0) - T} \ln \frac{y_0 \{[(q x_0 + y_0) - T] - y\}}{y (q x_0 - T)}$

$q = S/F'$ $T = \frac{R}{F'} = y_0 - y$

Rearranging:

$$-359 k_A'' x_0 (1/S_V) = \frac{q}{q + \frac{y_0 - T}{x_0}} \ln \frac{y (q - T/x_0)}{y_0 [(q + \frac{y_0 - T}{x_0}) - \frac{y}{x_0}]}$$

Substitute: $M = -359 k_A'' x_0 (1/S_V)$

$T = y_0 - y$

So: $M = \frac{q}{q + y/x_0} \ln \frac{y (q - \frac{y_0 - y}{x_0})}{\frac{y_0 q}{y_0 q}} = \frac{q}{q + y/x_0} \ln \frac{y [(q + y/x_0) - y_0/x_0]}{q y_0}$

$$= \frac{q \frac{x_0}{y_0}}{q \frac{x_0}{y_0} + y/y_0} \ln \frac{\frac{y}{y_0} [(q \frac{x_0}{y_0} + \frac{y}{y_0}) - 1]}{q \frac{x_0}{y_0}}$$

Let: $P = q \frac{x_0}{y_0}$

Then: $M = 2.303 \frac{P}{P + y/y_0} \log \frac{y/y_0 [(P - 1) + y/y_0]}{P}$ (Final solution)

where: $M = -359 k_A'' x_0 (1/S_V)$

$P = q x_0 / y_0$

$q = S/F'$

A graphical presentation of this solution can be found in Figure 10 next page.

FIGURE 10

GENERAL SOLUTION OF -

$$M = 2.303 \frac{P}{P + \psi_{30}} \log \frac{\psi_{30} [(P-1) + \psi_{30}]}{P}$$

$\frac{\psi}{\psi_{30}}$

NOTE - FOR VALUES OF $P < 1.00$, ψ_{30} CURVE IS ASYMPTOTIC TO SOME VALUE OF $\psi_{30} > 0.0$.

EX - FOR $P = 0.99$, ASYMPTOTE IS $\psi_{30} = 0.01$

(ALL CURVES ARE ASYMPTOTIC TO $\psi_{30} = 0.0$)

WFS
9-10-52

$P = 5.0$

$P = 3.0$

$P = 2.0$

$P = 1.5$

$P = 1.2$

$P = 1.00$

$-M$

where - $M = -2.303 \log \frac{\psi_{30} [(P-1) + \psi_{30}]}{P}$

$P = g \times \psi_{30}$

$g = S/P$

As in Case I, it will be of interest to solve the general relationship of Case II for the special situation of CO_2 absorption from air at 1% CO_2 by volume. As yet no experiments have been run using countercurrent gas and solid flow. However, the value of k_A ($800 \text{ atm}^{-1}\text{-hr}^{-1}$) determined from fixed-bed experiments will be assumed to hold in countercurrent operation as well. A gas flow of 110 std. CFM will be assumed, to allow comparison with Case I. For such a gas flow, a removal rate of 7.5 lb/hr will result if y/y_o at the reactor outlet is kept at 0.072.

In general: $M = -359 k_A \pi x_o (1/S_V)$

$P = q x_o/y_o$

$1/S_V = V/60 F$

$q = S/F'$

For this particular case:

$k_A = 800 \text{ atm}^{-1}\text{-hr}^{-1}$

$\pi = 1.0 \text{ atm}$

$y_o = 0.01 \text{ mole/mole}$

$F = 110 \text{ std CFM}$

outlet $y/y_o = 0.072$

Therefore: $M = (-359)(800)(1.0)(1/60)(1/110) x_o V$

$P = (359)(1/60)(1/110)(1/0.01) S x_o$

or: $M = -43.52 x_o V \quad P = 5.45 S x_o$

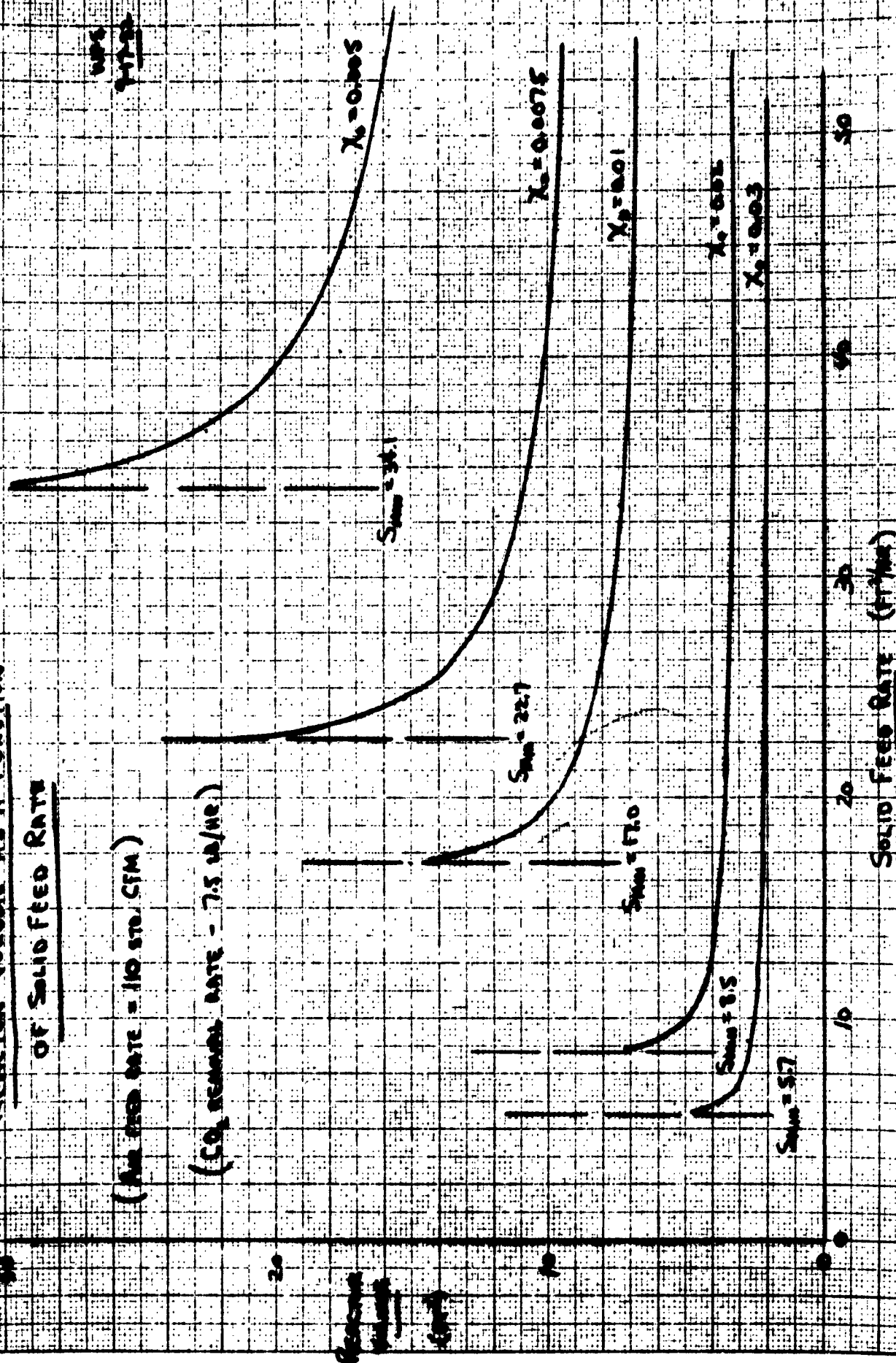
Values of x_o have been assumed and corresponding values of M and P determined from Figure 10 at $y/y_o = 0.072$. Then values for V and S are calculated. Results of these calculations are plotted on the next page, Figure 11. From this set of curves, it is possible to determine the reactor volume required for operation with a particular solid feed rate and initial solid concentration. It can be seen that the solid feed rate will need to be fairly high, especially if x_o , the inlet solid concentration is low. Further experimental work on this particular mode of operation will help to substantiate these preliminary conclusions.

FIGURE 11

REACTOR VOLUME AS A FUNCTION
OF SOLID FEED RATE

(AIR FEED RATE = 110 STD CFM)

(CO₂ REMOVAL RATE = 7.5 lb/hr)



EXPERIMENTAL

In order to determine the feasibility of using the silver oxide-carbon dioxide reaction as the basis of a regenerative CO_2 -removal process, it has been necessary to perform a series of small-scale experiments. These preliminary tests have been designed to provide answers to several important questions.

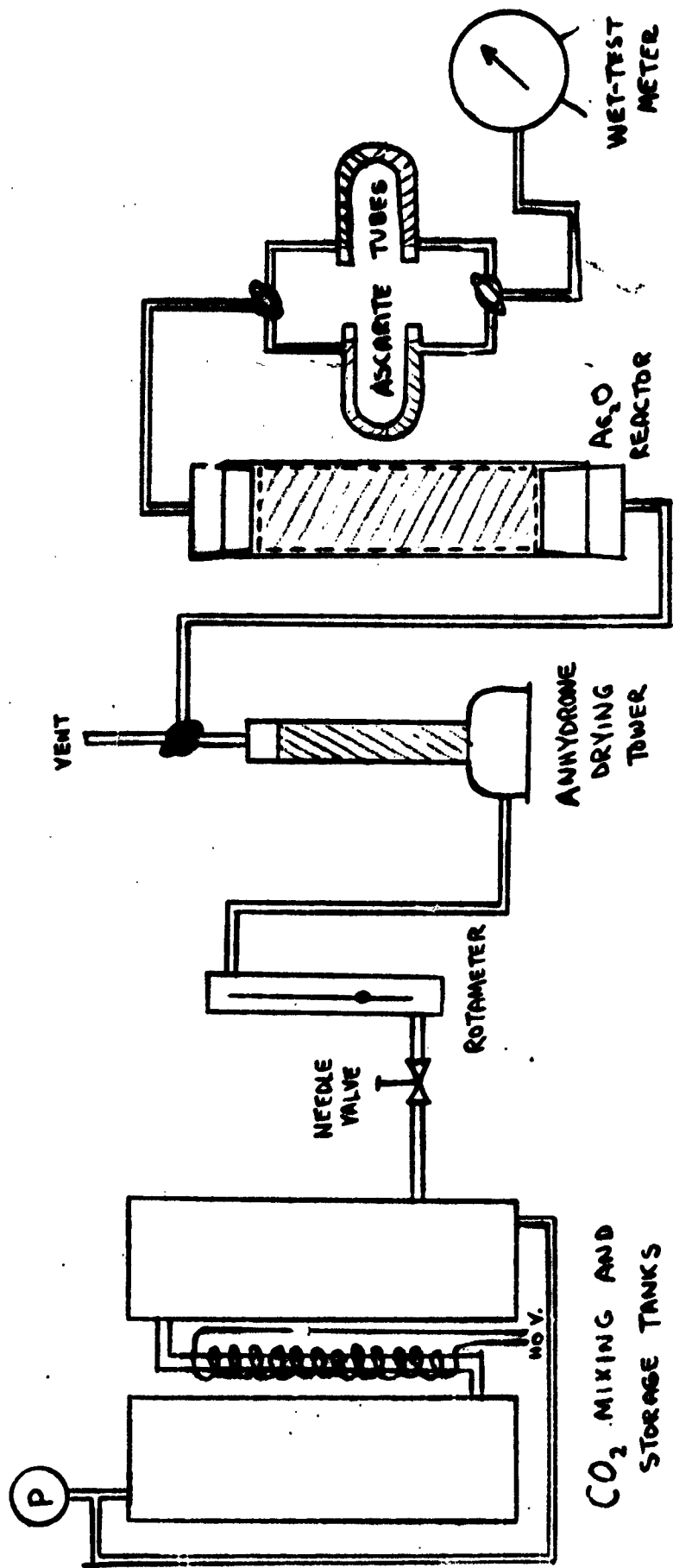
- (1) Is the reaction reversible, and can it be repeated several times using the same sample of silver oxide?
- (2) What are the variables affecting the rate of the absorption step?
- (3) What physical form of silver oxide is best for CO_2 removal .. pure, or deposited on an inert carrier?
- (4) What are the variables affecting the rate of the desorption step?

At the present writing, questions (1) and (2) have been fairly well answered, but further work will be necessary to determine answers for questions (3) and (4) satisfactorily. Experimental work is continuing and should result in satisfactory answers and a final process design in the near future.

Experiments with silver oxide have all been carried out in an apparatus similar to that sketched in Figure 12. This is a small-scale unit, one which provides considerable information in a relatively short time, and the data obtained should be applicable to the operation of a larger unit as well. The unit was operated with a fixed solid bed and an inlet gas of constant composition, which is identical with the operating conditions specified in Case I under Mathematical Development. Therefore, it is likely that the experimental results will fit the mechanism suggested in this development. Case II is more difficult to obtain in practice, and as yet no experiments have been run under this procedure.

An air- CO_2 mixture of known and constant composition is required for the inlet gas stream. Such a mixture is obtained by pumping CO_2 and air (in the desired pressure ratio) into the mix-

FIGURE 12



FLOW SHEET FOR Ag_2O EXPERIMENTS

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continued until the silver oxide is essentially saturated with CO_2 , as indicated by a constant CO_2 output rate. Then the basket containing the silver oxide is weighed and placed in the oven, where it is held overnight at 125°C and < 5 mm Hg, to decompose the carbonate and reform the active silver oxide.

Data from fourteen runs made to date, using three different samples of Ag_2O , are summarized in Table II. In addition, typical plots of the total CO_2 absorbed as a function of time are included in Figures 13 through 17, for all of the runs using Ag_2O sample A. (Similar plots have been made for the runs employing the other Ag_2O samples, but they are not included here.) It can easily be seen that the repeatability of the reaction is only fair. In general, it seems that the first run with any particular sample shows very good CO_2 removal. Subsequent runs show considerably less removal, but with much less of a trend toward lower values after the second run in any set. It is likely that this high capacity for the first run is due to adsorbed NaOH not completely washed off. Therefore, the true capacity is that exhibited by later runs, which seems to be falling off only slightly with use.

Reference to the experimentally determined CO_2 absorption data indicates that in all cases the run seems to have been made up of two distinct periods. In the early stages CO_2 is being absorbed at a relatively high and varying rate. Later in the run a considerably lower magnitude constant rate period is reached. Such a result would be expected if the absorption were taking place by two simultaneous processes: (1) Reaction of the CO_2 with surface layers of Ag_2O , according to the mechanism of Case I, and (2) Reaction of additional CO_2 with internal layers of Ag_2O , limited by diffusion. To determine the portion of the CO_2 absorption attributable to the mechanism of Case I, it seems a logical approximation merely to subtract the constant rate contribution, as determined graphically from the data. When this is done, the curves labelled "modified data" are obtained. It will be assumed that these curves represent fairly well the CO_2 absorption due to reaction with the available surface layers of Ag_2O , by the mechanism of Case I.

Further calculations have been made on the data of series A,

TABLE II

EXPERIMENTAL DATA - CO₂ ABSORPTION ON Ag₂O

Run No.	A-1	A-2	A-3	A-4	A-5	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-1	B-2	B-3	B-4
Date	6/12/52	6/20/52	6/24/52	7/1/52	7/3/52	6/17/52	6/20/52	6/25/52	6/26/52	7/8/52	7/10/52	7/16/52	7/18/52	7/22/52	7/24/52	8/1/52
Temperature (°F)	88.0	73.5	85.0	82.5	84.0	86.0	73.5	88.0	88.0	82.0	81.0	79.0	85.2	91.0	86.0	81.0
Pressure (mm)	746.3	747.2	740.2	745.0	748.7	743.8	746.3	743.2	743.2	750.0	746.5	748.0	748.0	747.3	755.0	751.6
% CO ₂	2.86	2.86	2.86	2.86	2.86	2.86	2.86	2.86	2.86	2.86	2.86	2.86	2.86	1.30	1.30	1.39
Rotameter	1.0	1.0	1.0	1.0	1.0	0.75	0.75	0.75	0.75	0.75	0.75	0.75	1.0	1.0	0.75	0.90
Wt. Before (gm)	70.025	70.425	70.752	70.584	70.579	73.100	73.491	73.461	73.461	73.398	73.399	73.378	75.463	76.024	76.234	76.996
Wt. After (gm)	70.829	70.696	71.034	70.823	70.784	73.885	73.718	73.672	73.672	73.584	73.642	73.584	76.110	76.326	76.516	76.803
H ₂ O Lost (gm)	0.804	0.271	0.282	0.239	0.205	0.785	0.227	0.211	0.211	0.186	0.243	0.206	0.629	0.020	0.005	0.807
Apparent CO ₂ (gm)	0.0041	0.0042	0.0034	0.0032	0.0055	0.0032	0.0032	0.0032	0.0032	0.0040	0.0029	0.0030	0.0029	0.0020	0.0027	0.0027
Constant Rate (gm CO ₂ /min)	0.0685	0.0700	0.0672	0.0682	0.0690	not calen- lated	0.0528	not calen- lated	not calen- lated	0.0529	0.0522	0.0527	not calculated	not calculated	not calculated	not calculated
Avg. Inlet Rate	0.0644	0.0658	0.0638	0.0650	0.0635	not calen- lated	0.0496	not calen- lated	not calen- lated	0.0489	0.0493	0.0497	not calculated	not calculated	not calculated	not calculated
Corr. Inlet Rate	0.0460	0.0460	0.0440	0.0445	0.0460	0.0440	0.0440	0.0440	0.0440	0.0420	0.0440	0.0460	0.0420	0.0420	0.0420	0.0420
Initial Absorption Rate	0.7350	0.2100	0.2600	0.1840	0.1600	0.1950	0.1950	0.1400	0.1400	0.1400	0.1250	0.1550	0.145	0.145	0.145	0.145
Asymptote (total gm CO ₂)	0.307	0.307	0.317	0.322	0.281	0.116	0.116	0.116	0.116	0.145	0.110	0.076	0.145	0.145	0.145	0.145
Initial Outlet y/y _o																

Sample A - 42.515 gm alumina
4.378 Ag₂O (apparent)

(series ended when solder on
basket melted)

Sample B - 43.822 gm alumina
4.754 gm Ag₂O (apparent)

(series ended when more Ag₂O was added
to alumina for B₃ series)

Sample B₃ - Sample B plus 1.976 gm Ag₂O (apparent)

(series ended when oil backed up into oven -
smoke poisoned Ag₂O-alumina)

FIGURE 13

ABSORPTION DATA - RUN A-1

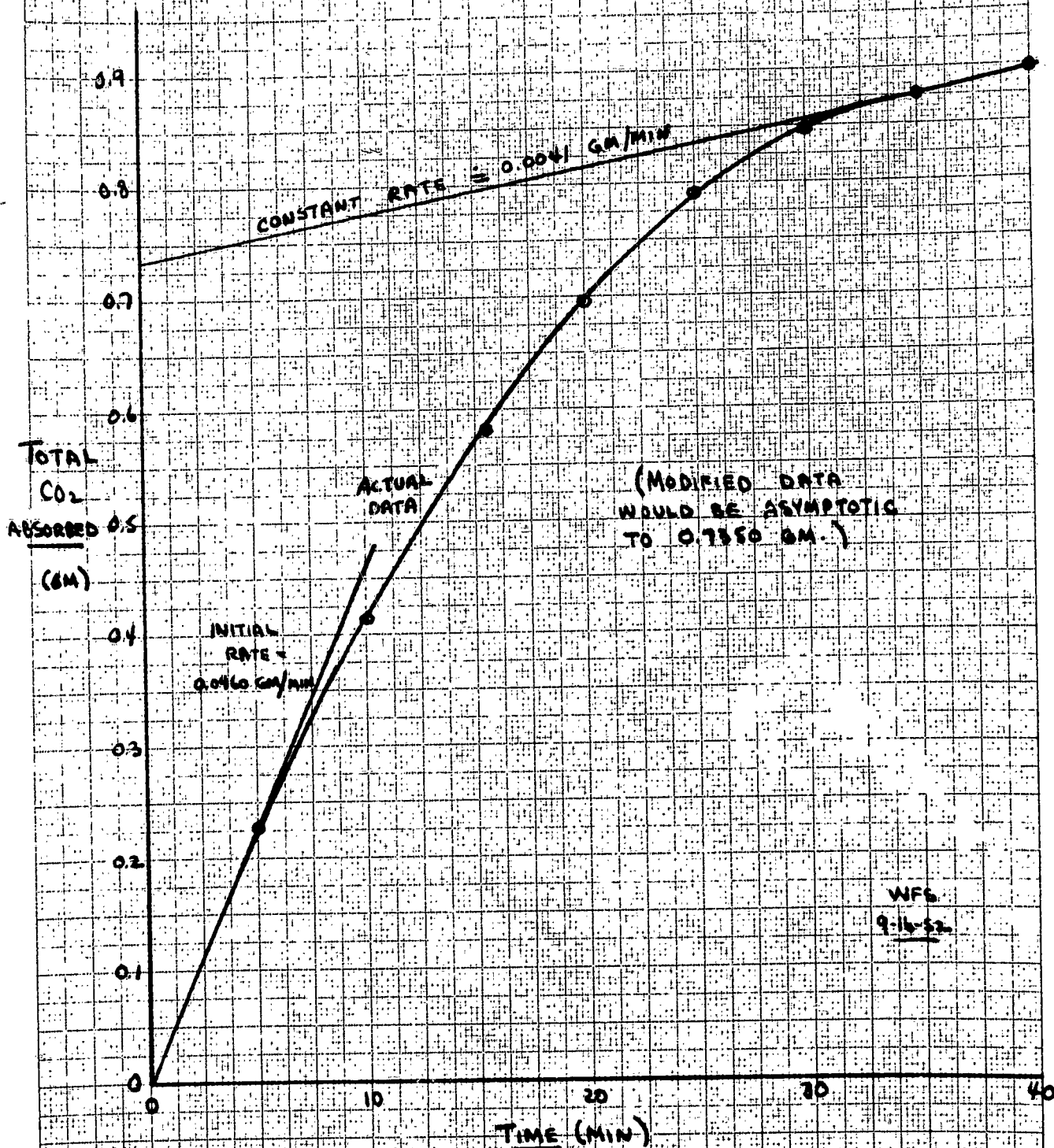
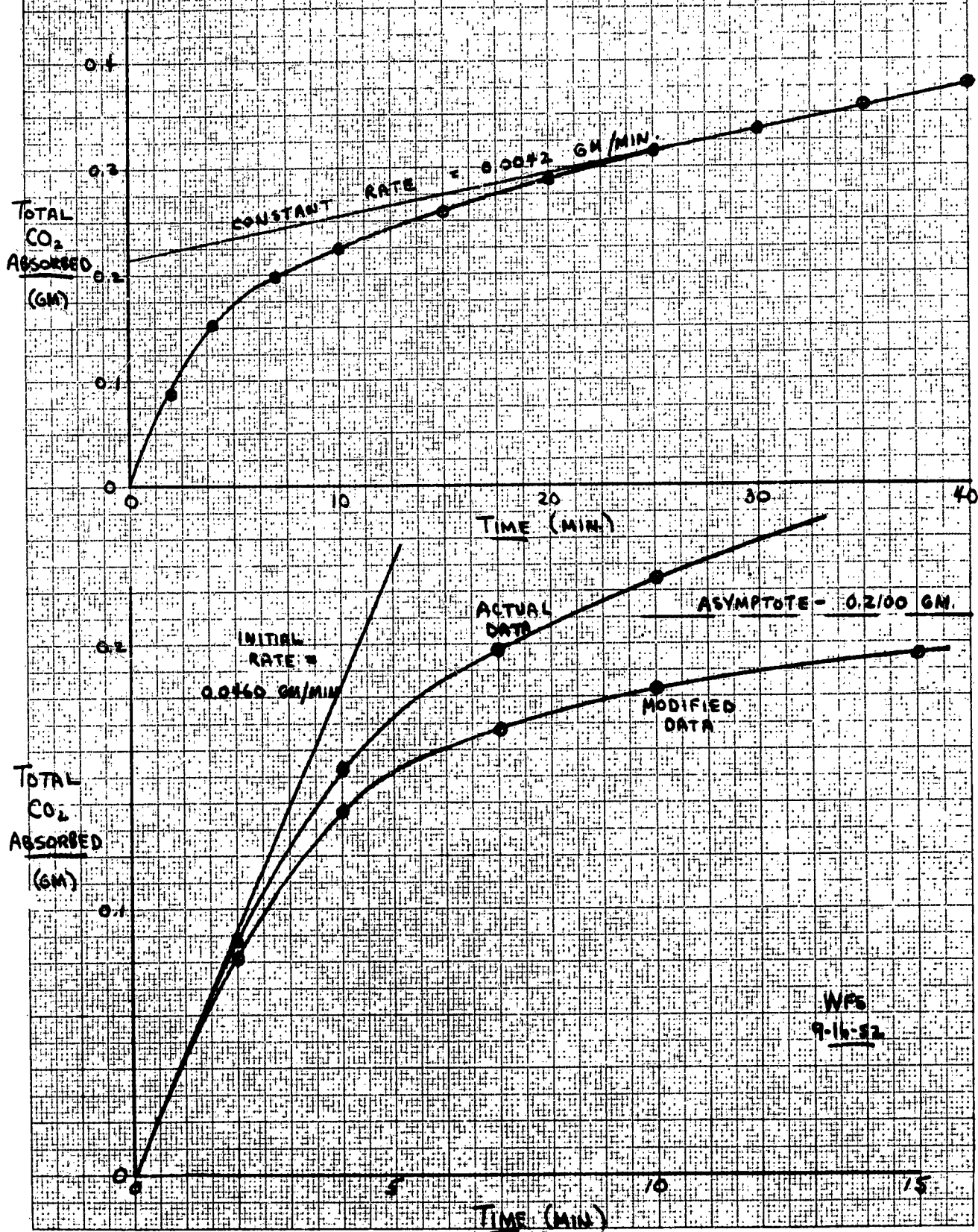


FIGURE 14
ABSORPTION DATA - RUN A-2



Not open to students who have received an, b, or c, heavy.

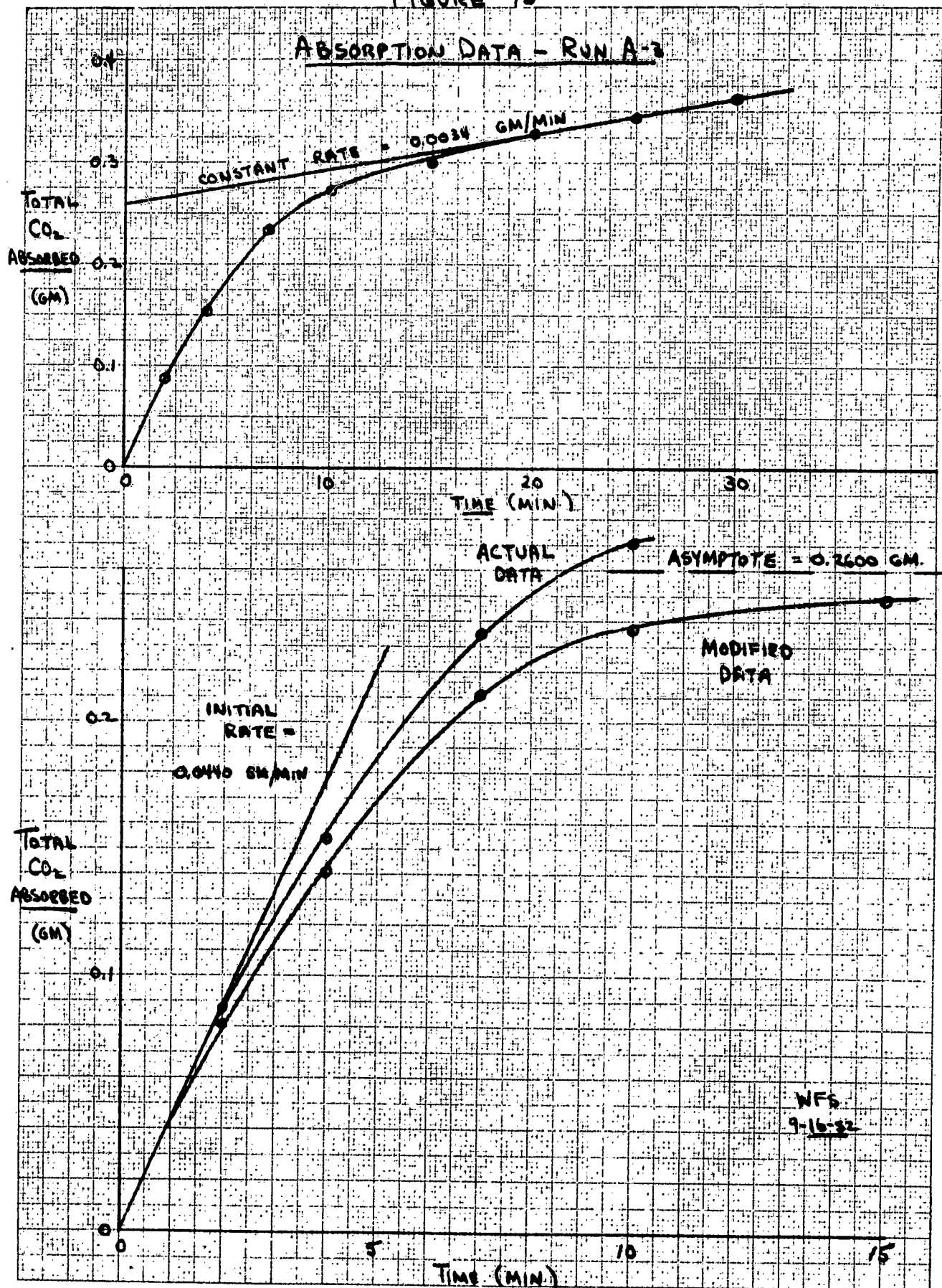


FIGURE 16
ABSORPTION DATA - RUN A-4

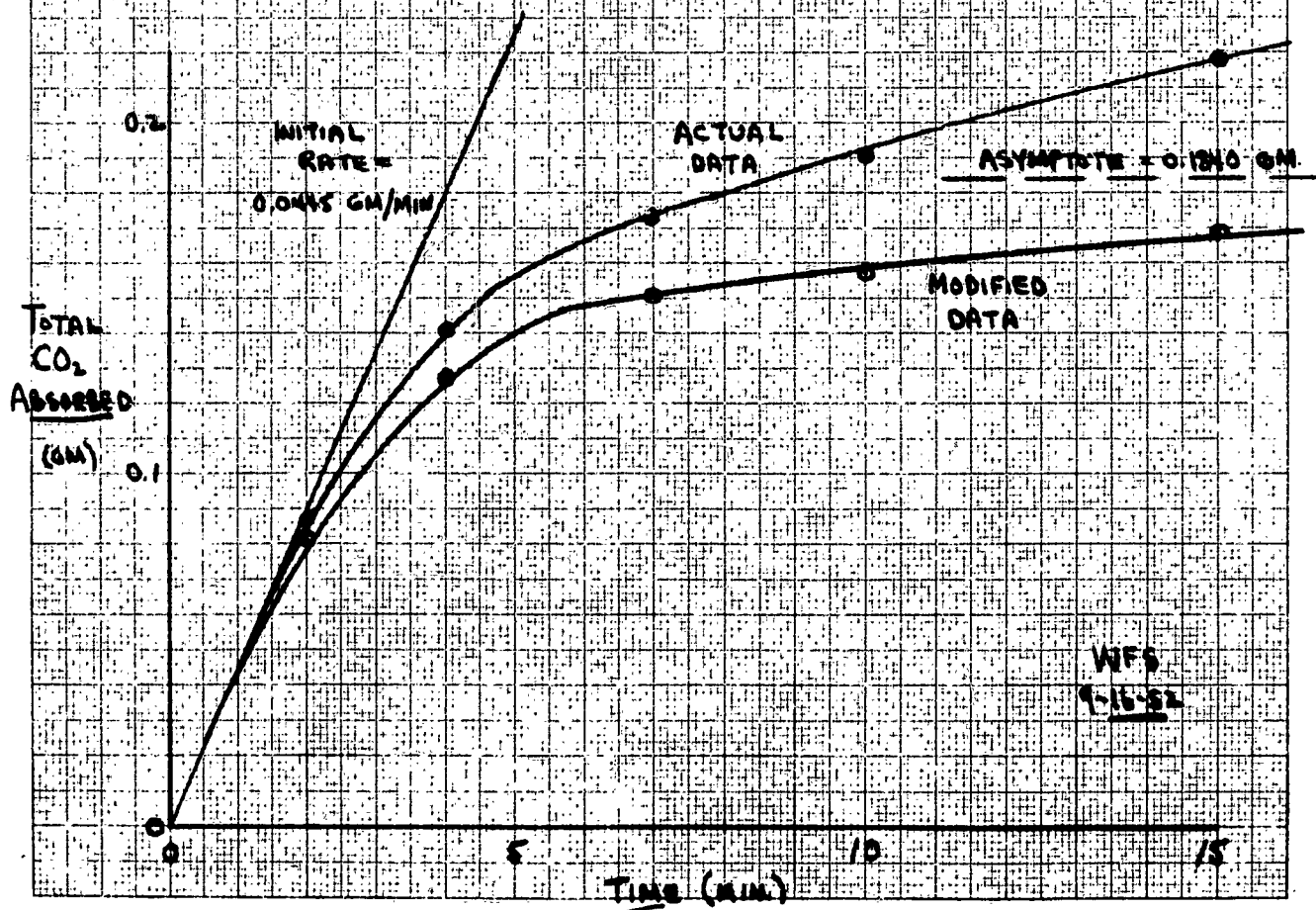
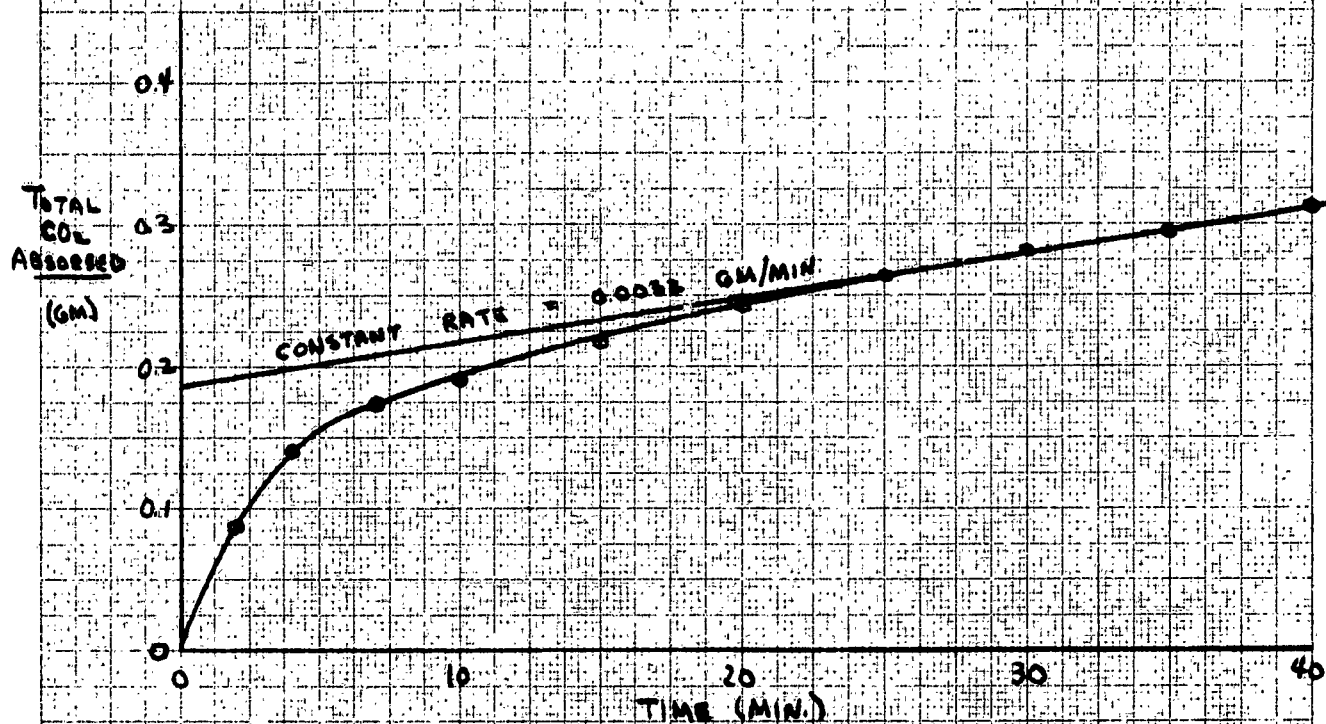
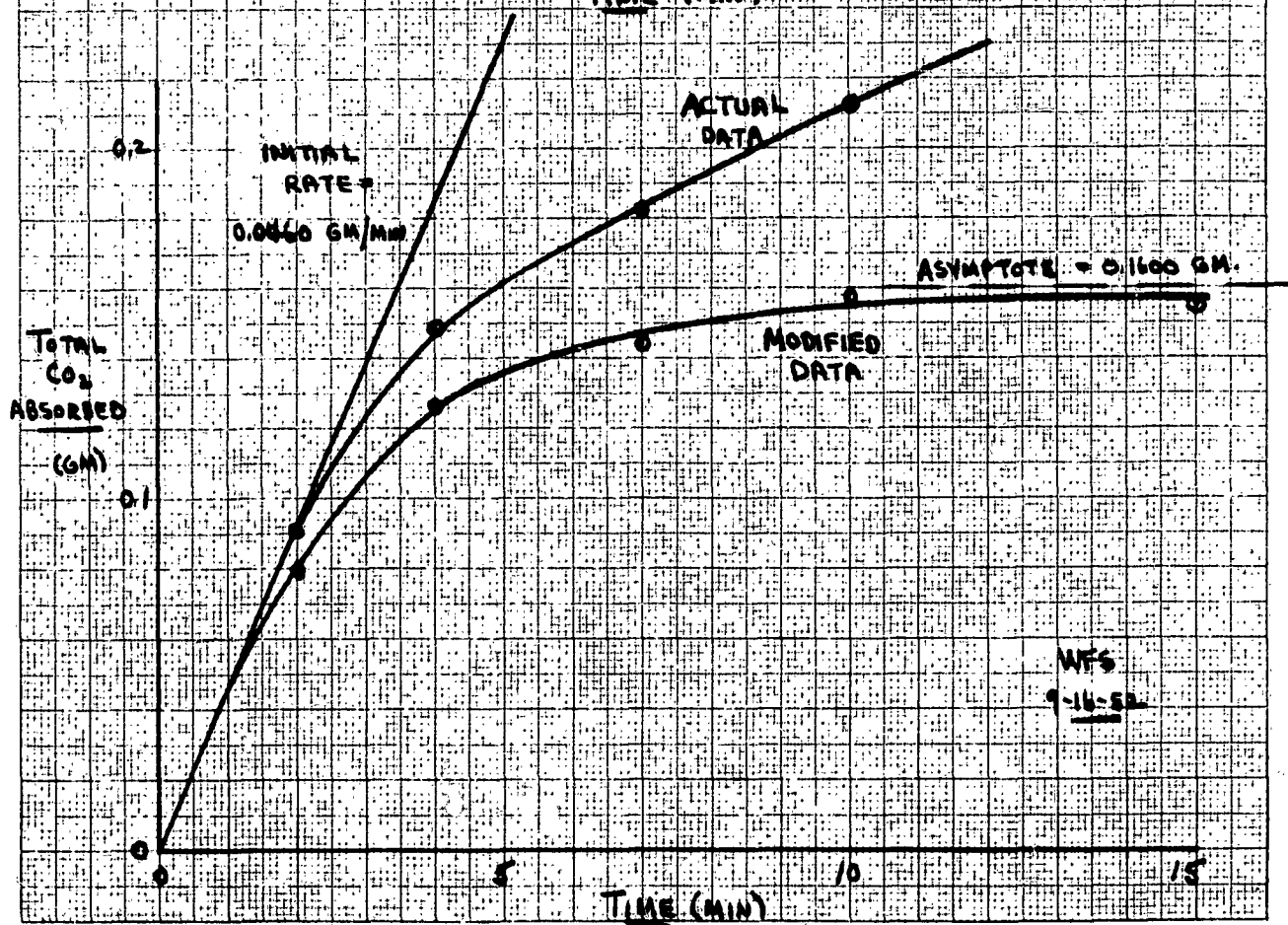
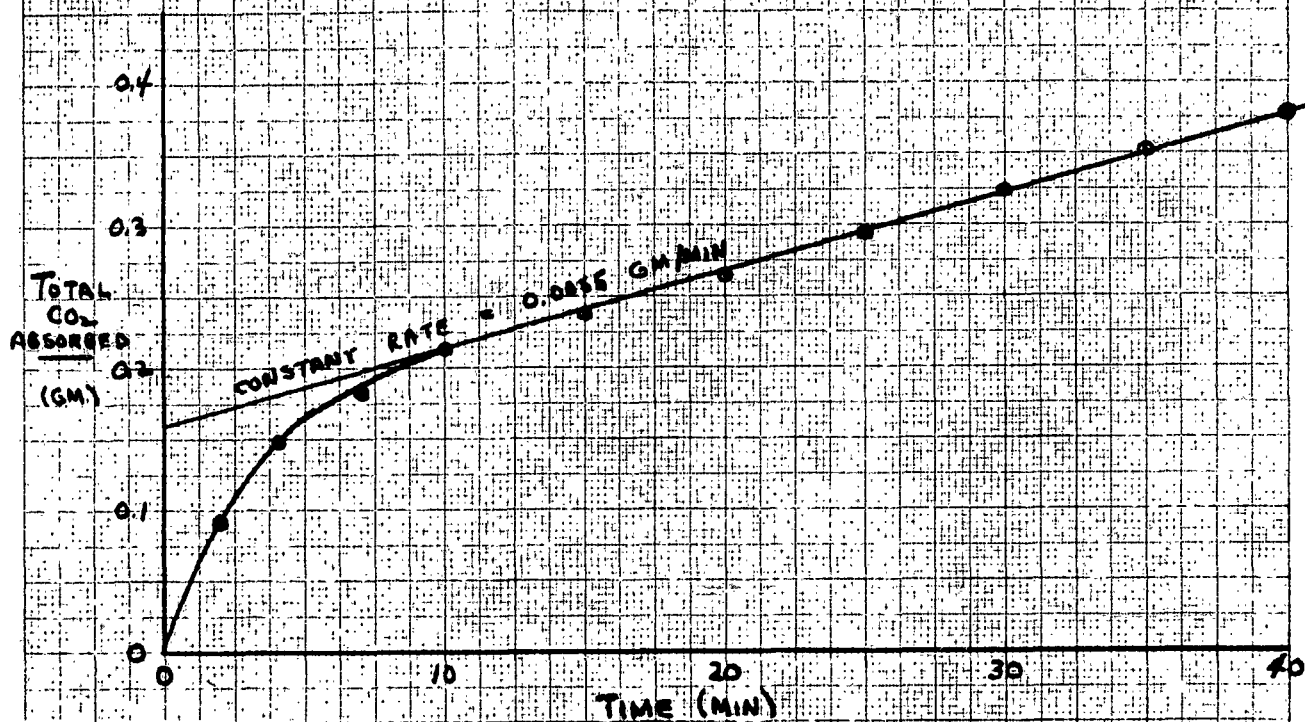


FIGURE 17
ABSORPTION DATA - RUN A-5



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using the modified data as explained above, to give effective values of CO_2 inlet rates. Knowing the CO_2 outlet rates, from weighings of the ascarite tubes, it is possible to calculate values of $(y/y_0)_{\text{avg.}}$ for each sample interval. This has been done for all of the runs, and the results are summarized in Table III. The relationship used is as follows:

$$\left(\frac{y}{y_0}\right)_{\text{avg.}} = \frac{1}{\frac{\text{gm CO}_2 \text{ in}}{\text{gm CO}_2 \text{ out}} (1 - y_0) + y_0}$$

TABLE III

CALCULATED VALUES OF $(y/y_o)_{avg}$

<u>Sample Interval</u>	<u>Outlet $(y/y_c)_{avg}$ Values</u>			
	<u>A-2</u>	<u>A-3</u>	<u>A-4</u>	<u>A-5</u>
t = 0	0.307	0.317	0.322	0.281
0-2	0.394	0.389	0.416	0.372
2-4	0.585	0.527	0.660	0.650
4-7	0.845	0.647	0.885	0.906
7-10	0.927	0.869	0.962	0.981
10-15	0.962	0.963	0.965	?
15-20	0.977	0.963	0.973	0.998
20-25	0.981	?	0.986	0.996
25-30	?	0.990	0.998	0.990
30-35	0.999	---	0.978	?
35-40	0.997	---	0.995	?

At this point it seems logical to check the applicability of the mechanism proposed in the section on Mathematical Development. Calculations have resulted in values of $(y/y_0)_{avg}$ at the reactor outlet as a function of time, with all other variables held as constant as possible.

$$\begin{aligned} \text{That is: } M &= \text{constant} & \therefore j &= e^M = A \\ N &= \text{constant} \times t & \therefore h &= e^N = \left[e^{k_A \times y_0} \right]^t = B^t \end{aligned}$$

$$\text{Define: } y/y_0 = Y$$

$$\text{Therefore: } Y = \frac{A B^t}{1 + A(B^t - 1)}$$

$$Y(1 - A) = A B^t (1 - Y)$$

$$\frac{Y}{1 - Y} = \frac{A}{1 - A} B^t$$

$$\log \frac{Y}{1 - Y} = \log \frac{A}{1 - A} + t \log B$$

$$\text{Define: } Y' = \frac{Y}{1 - Y} \quad A' = \log \frac{A}{1 - A} \quad B' = \log B$$

$$\text{Therefore: } \log Y' = A' + B' t$$

When the function $\log \frac{y/y_0}{1 - y/y_0}$ is plotted versus t , a straight line will result if the experimental data follow the equations of the proposed mechanism. In addition, the slope and intercept of this line can be used to calculate the values of x_0 and k_A for the particular run. This function has been calculated and plotted for each of the runs using Ag_2O sample A. A typical plot, for Run A-2, is included here, as Figure 18. From this plot it can be seen that a straight line does result, for the data of the first ten minutes or so. After this time, the slope falls off considerably, probably because of errors in calculation when values of y/y_0 begin to approach 1.0. For a first approximation of the constants of the mechanism equation, the straight line portion of the early part of the run has been considered as representative and the best straight line fitted to the available five data points. This procedure has also been followed on the other runs of series A. Results are tabulated in Table IV, where average values of k_A and x_0 are also shown. Similar calculations

are in progress for the runs of series B and D_B. Results of these calculations and of additional experimental runs will be presented in the next report.

FIGURE 18

CHECK OF MECHANISM EQ.
(LOG Y' VS. TIME)

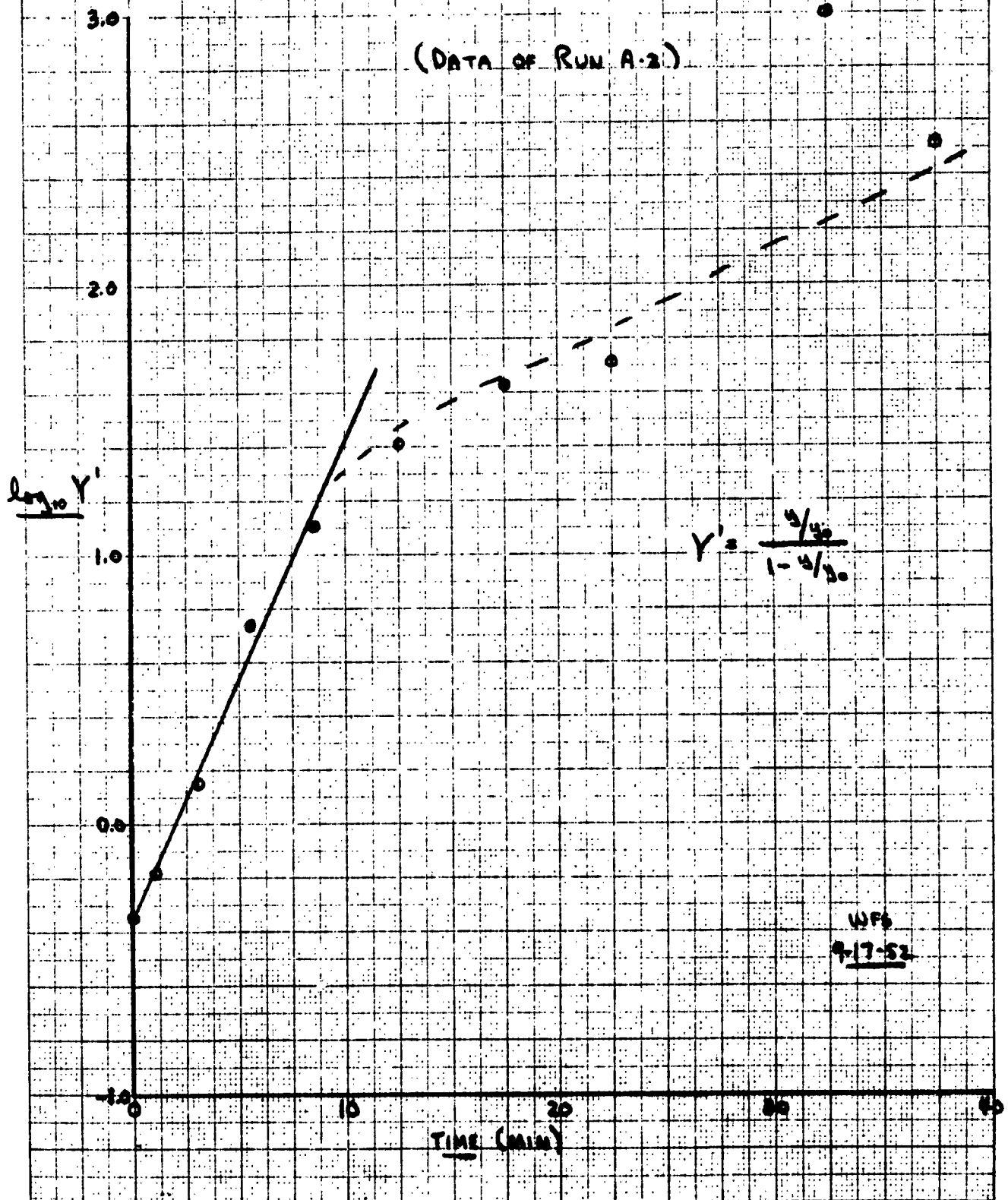


TABLE IV

CHECK OF MECHANISM - DATA

Time	A-2		A-3		A-4		A-5	
	y/y_0	$\log Y$	y/y_0	$\log Y$	y/y_0	$\log Y$	y/y_0	$\log Y$
0	0.307	-0.354	0.317	-0.333	0.322	-0.323	0.281	-0.414
1	0.394	-0.187	0.389	-0.196	0.416	-0.147	0.372	-0.227
3	0.585	0.149	0.527	0.047	0.660	0.288	0.650	0.269
5.5	0.845	0.737	0.647	0.263	0.885	0.886	0.906	0.979
8.5	0.927	1.104	0.869	0.822	0.962	1.403	0.981	1.713
slope = 10.66 (hr)		slope = 7.82 (hr)		slope = 12.65 (hr)		slope = 15.30 (hr)		
intercept = -0.35		intercept = -0.35		intercept = -0.33		intercept = -0.43		

avg. slope = 11.61 (hr)

avg. intercept = -0.365

$$Y = \frac{y/y_0}{1 - y/y_0}$$

avg. value of $k_A = 950 \text{ atm}^{-1} \text{ hr}^{-1}$
 avg. value of $x_0 = 0.00575 \text{ lb mol/ft}^3$

for series A

CONCLUSIONS

Sufficient experimentation has been carried out on the silver oxide process to allow several conclusions to be drawn. First, the process seems to be feasible for use as a regenerative system of CO_2 -removal, since several successive absorption-desorption cycles can be carried out on one sample with only a small decrease in capacity. A longer series of cycles will be necessary to support this conclusion definitely, however. Second, the most important variable in the absorption step seems to be the initial concentration of oxide available on the surface of the solid. If this quantity can be increased, the size of equipment required for the process can be materially decreased. It should be noted that it is the concentration of oxide available on the solid surface which is important. Therefore, there will probably be little to be gained by the use of pure silver oxide, since the quantity of oxide on the surface will not be materially different from that available on an alumina-supported sample of similar size. Future runs with pure Ag_2O will be necessary to prove this definitely, however.

The mechanism equations derived and presented in this report will be of considerable value in indicating the relative effects of the variables involved in the absorption step. In combination with similar equations for the desorption step, they will permit calculation of equipment sizes, feed rates, etc., so that the optimum process design will result. Such a complete design will form a major part of the write-up on the silver oxide process for the next report.

SECTION II

LOW TEMPERATURE ABSORPTION, CO₂ SOLUBILITY

INTRODUCTION

The search for suitable absorbents for use in the low temperature regenerative system of CO_2 removal is continuing. Previous data in this phase have been presented in earlier reports. Samples representing several classes of compounds are being evaluated as possible absorbents. At present, the most promising class of compounds is the esters. Consequently, more attention is being focused on compounds of this general classification. Also, this class of compounds will be evaluated to determine what trends may exist within the class.

Much additional work must be done before any one compound can be selected as the best absorbent for the low temperature process.

Experimental Procedure

The method for determining CO_2 solubility presently being used is the "open" method as described in the tri-monthly report of this project for the period January 1 to March 31, 1952. This method consists of bubbling the CO_2 through the solvent.

It has been necessary to modify the analytical procedure due to the fact that esters hydrolyze. The earlier procedure involved a volumetric analysis in which a known weight of sample was treated with a known excess of $\text{Ba}(\text{OH})_2$. The barium hydroxide then reacted with the carbon dioxide to form barium carbonate. The excess of barium hydroxide was then determined by titrating with standard acid. Thus the amount of carbon dioxide in the solution was determined. However, if this procedure is applied to the esters, the esters will hydrolyze and produce an acid, which will then react with the barium hydroxide and in the calculations will appear as carbon dioxide, thus producing erroneous values for CO_2 solubility.

The procedure now used is to treat the sample with an excess of $\text{Ba}(\text{OH})_2$. This reacts as before to produce barium carbonate, which precipitates. This precipitate is then filtered, washed, dried, and weighed to determine the amount of carbon dioxide which was present in the sample. The esters still hydrolyze to produce

an acid which also reacts with the barium hydroxide. However, as long as the barium salt produced is soluble, it does not appear in the weight of precipitate and hence causes no errors.

Data

The samples tested and the results obtained appear in Table V. This table lists the molecular weight of each solvent. The second and third columns list the temperature and pressure for each sample. The fourth column lists the mole fraction of CO_2 experimentally determined as present in the sample. The calculated value of γ is reported in the fifth column. This value of γ is calculated from the equation $\gamma = y p/x P$, where

γ = activity coefficient of CO_2 in solution

y = mole fraction of CO_2 in gas phase

x = mol fraction of CO_2 in liquid phase

p = total pressure of gas

P = vapor pressure of pure CO_2 at temperature of solution

The last column of the table reports the mole fraction of CO_2 which would exist in solution at a total gas pressure of 760 mm Hg and at the given temperature, assuming the calculated value of γ to apply.

This table extends the results previously reported in the tri-monthly report of this project (Jan. 1 - March 31, 1952). In the case of tributyl phosphate, these data correct the previous results for a better interpretation of the blank then being applied. Also it may be noticed that, in view of the present work, two values for toluene previously reported have been omitted as unreliable. The values for octyl acetate reported here differ widely from those previously reported. The earlier values were obtained by another experimental method which appears less reliable than the method now being used; and the present values are believed to be more accurate.

CONCLUSIONS

The survey of absorbents for use in the low temperature absorption system is not complete; but the class of compounds known as esters show the most promise. Consequently, more attention is being placed in compounds of this class.

The results show that γ increases as temperature decreases for all compounds tested to date. It was at first believed that γ would approach 1.00 as temperature decreased, due to composition effects. The effect of composition on γ is expressed by Margules' equation as follows:

$$\ln \gamma_1 = x_2^2 [A + 2 (B - A) x_1]$$

where: γ_1 = activity coefficient of CO_2 in solution

x_1 = mole fraction of CO_2 in solution

x_2 = mole fraction of absorbent in solution

A and B are constants dependent upon absorbent, temperature, and pressure.

This equation states that as x_1 increases and x_2 decreases, the value of γ should approach 1.00 as a limit. The present results, therefore, show that the temperature effect on A and B is quite large and overcomes the effect of composition change. The result is that the values of γ for saturated solutions always increase as the temperature decreases.

The values of γ are an indication of any deviation of the actual solutions from ideal solutions. A value of $\gamma = 1.00$ corresponds to an ideal solution; and the lower the value of γ is, the higher the absorption (mole fraction) of CO_2 will be. The molecular weight of the solvent is necessary to correct absorption values from mol fraction to weight per cent. Consequently, a compound possessing both a low molecular weight and a low value of γ is desired.

It would also be desirable to obtain a compound whose γ decreases with decreasing temperatures, since this will predict a larger change in CO_2 solubility with temperature. Unfortunately, this positive value of $d\gamma/dt$ does not appear to exist; and a

small negative value will probably have to be accepted. Hence, the important criteria of good solubility are a low value of χ and a low molecular weight; of secondary importance is the criterion of a positive or small negative value of $d\chi/dT$.

TABLE V

CO₂ SOLUBILITY IN ORGANIC SOLVENTS

Solvent	Temp- erature	Baro. Press. mm Hg	CO ₂ Mol. Fract. at Baro. Press.	$\gamma = \frac{V_R}{\pi P}$	CO ₂ Mol. Fract. at 760 mm Hg
Decalin m. w. = 138.24	82°F	745.8	0.00713	2.03	0.00727
	82°F	744.4	0.00682	2.12	0.00696
	82°F	744.4	0.00677	2.14	0.00691
Alkazo - 42 m.w. = 263.98	32°F	745.8	0.00695	2.09	0.00708
	82°F	744.4	0.00750	1.93	0.00766
			0.00779	2.13	0.00694
	-23°C	738.3	0.0145	3.78	0.0150
	-34°C	746.7	0.0133	4.37	0.0186
Dichloro-isopropyl-ether m.w. = 171.01	80.4°F	742.0	0.0160	0.920	0.0164
			0.0153	0.963	0.0157
	77.2°F	746.8	0.0152	1.02	0.0155
			0.0156	0.990	0.0159
	72.2°F	742.8	0.0165	0.992	0.0169
			0.0165	0.992	0.0169
	59.5°F	742.3	0.0187	1.03	0.0191
			0.0182	1.06	0.0186
	63.2°F	742.3	0.0185	0.995	0.0189
			0.0177	1.04	0.0181
	67.3°F	744.5	0.0171	1.02	0.0175
			0.0168	1.04	0.0171
	+1.4°C	752.6	0.0202	1.00	0.0204
			0.0200	1.01	0.0202
	+0.5°C	741.7	0.0256	1.10	0.0262
			0.0256	1.09	0.0262
	-1.0°C	749.5	0.0340	1.11	0.0345
			0.0344	1.10	0.0349
	-32.0°C	750.7	0.0579	1.30	0.0586
			0.0592	1.27	0.0599
	-34°C	746.7	0.0606	1.32	0.0617
	-36°C	752.9	0.0656	1.32	0.0663
	-47.0°C	745.5	0.0913	1.41	0.0931
			0.0488	1.45	0.0905
	-48°C	747.4	0.0762	1.77	0.0775
			0.0786	1.71	0.0799
Butyl-Collosolve m.w. = 118.11	80.4°F	742.2	0.0120	1.28	0.0123
			0.0123	1.20	0.0126
	77.2°F	746.8	0.0125	1.24	0.0127
			0.0115	1.34	0.0117
	72.2°F	742.8	0.0131	1.25	0.0134
			0.0129	1.27	0.0132
	59.5°F	742.3	0.0159	1.22	0.0163
			0.0145	1.35	0.0148

<u>Solvent</u>	<u>Temp- erature</u>	<u>Baro. Press. mm Hg</u>	<u>CO₂ Mol. Fract. at Baro. Press.</u>	<u>$\gamma = \frac{y \cdot v}{x \cdot P}$</u>	<u>CO₂ Mol. Fract. at 750 mm Hg</u>
Butyl-Cellosolve (continued)	63.2°F	742.3	0.0138	1.33	0.0141
			0.0138	1.33	0.0141
	67.3°F	744.5	0.0136	1.29	0.0139
			0.0131	1.34	0.0134
	+14°C	752.6	0.0160	1.26	0.0162
			0.0152	1.33	0.0153
	+0.5°C	741.7	0.0205	1.36	0.0210
			0.0203	1.38	0.0208
	-10°C	749.5	0.0283	1.34	0.0287
			0.0287	1.31	0.0291
	-32.0°C	750.7	0.0469	1.50	0.0475
			0.0487	1.54	0.0493
	-34°C	746.7	0.0495	1.61	0.0504
	-35°C	753.1	0.0544	1.54	0.0549
			0.0537	1.55	0.0542
	-47°C	745.5	0.0804	1.60	0.0820
			0.0799	1.61	0.0815
	-48°C	747.4	0.0828	1.62	0.0842
			0.0846	1.59	0.0861
Propylene glycol m. w. = 76.06	80.4°F	742.0	0.00328	4.49	0.00336
			0.00256	5.75	0.00262
	77.2°F	746.8	0.00353	4.37	0.00359
			0.00317	4.87	0.00323
	72.2°F	742.8	0.00338	4.84	0.00346
			0.00329	4.98	0.00337
	67.3°F	744.5	0.00347	5.04	0.00354
			0.00341	5.13	0.00348
	63.2°F	742.3	0.00369	4.99	0.00378
			0.00358	5.14	0.00367
Toluene m. w. = 92.06	72.4°F	744.7	0.00886	1.85	0.00904
			0.00965	1.70	0.00985
			0.00928	1.76	0.00947
	-37°C	749.1	0.0302	2.95	0.0306
	-38.5°C	749.1	0.0320	2.94	0.0320
			0.0426	3.14	0.0436
	-48°C	743.0	0.0395	3.39	0.0404
2-Ethylhexyl chloride m. w. = 148.67	78°F	751.3	0.0145	1.06	0.0147
			0.0136	1.13	0.0138
	26°C	751.3	0.0141	1.08	0.0143
			0.0138	1.10	0.0140
	74°F	748.2	0.0149	1.08	0.0151
			0.0154	1.05	0.0156
	69.5°F	744.9	0.0151	1.13	0.0154
			0.0148	1.15	0.0157

<u>Solvent</u>	<u>Temp- erature</u>	<u>Baro. Press. mm Hg</u>	<u>CO₂ Mol. Fract. at Baro. Press.</u>	<u>$\frac{y \cdot P}{x \cdot P}$</u>	<u>CO₂ Mol. Fract. at 760 mm Hg</u>
2-Ethylhexyl acid m.w. = 144.21	78°F	751.3	0.0180	0.855	0.0182
			0.0192	0.799	0.0195
	26°C	751.3	0.0229	0.666	0.0231
			0.0208	0.730	0.0211
	74°F	748.2	0.0231	0.697	0.0235
			0.0216	0.747	0.0219
2-Ethylhexanol m.w. = 130.23	69.5°F	744.9	0.0240	0.708	0.0245
			0.0231	0.737	0.0235
	78°F	751.3	0.00847	1.82	0.00857
			0.00960	1.60	0.00971
	26°C	751.3	0.00879	1.73	0.00889
			0.00863	1.76	0.00873
Ethyl Aceto Acetate m.w. = 130.14	74°F	748.2	0.00838	1.92	0.00851
			0.00817	1.97	0.00830
	69.5°F	744.9	0.00868	1.96	0.00886
			0.00889	1.91	0.00907
	+13°C	751.4	0.0255	0.813	0.0257
			0.0262	0.791	0.0265
	+0.5°C	741.7	0.0333	0.841	0.0341
			0.0325	0.862	0.0333
	-2°C	754.7	0.0356	0.856	0.0358
			0.0339	0.899	0.0341
	-7°C	748.0	0.0404	0.857	0.0410
	-10°C	749.5	0.0440	0.857	0.0446
			0.0430	0.878	0.0436
	-32°C	750.7	0.0833	0.900	0.0843
			0.0811	0.924	0.0821
	-38°C	748.4	0.0998	0.924	0.101
Octyl Acetate m.w. = 172.26			0.0975	0.946	0.0990
	-47.0°C	745.5	0.0964	1.34	0.0983
			0.111	1.16	0.113
	80.5°F	749.0	0.0250	0.574	0.0263
	79.5°F	748.9	0.0273	0.551	0.0277
	81°F	747.1	0.0232	0.645	0.0236
	+14°C	752.6	0.0303	0.667	0.0306
			0.0305	0.662	0.0308
	-10°C	749.5	0.0521	0.724	0.0528
			0.0538	0.701	0.0546
Tributyl Phosphate m.w. = 266.32	-32°C	751.8	0.0939	0.799	0.0949
			0.0944	0.795	0.0955
	-47°C	745.5	0.135	0.959	0.137
			0.117	1.10	0.119
	85°F	747.4	0.0346	0.405	0.0352
	77.5°F	746.5	0.0335	0.460	0.0341
	73.2°F	748.6	0.0340	0.479	0.0345
	72.4°F	749.7	0.0389	0.424	0.0394

<u>Solvent</u>	<u>Temp- erature</u>	<u>Baro. Press. mm Hg</u>	<u>CO₂ Mol. Fract. at Baro. Press.</u>	<u>= $\frac{V_L}{V_G}$ x P</u>	<u>CO₂ Mol. Fract. at 760 mm Hg</u>
Tributyl Phosphate (continued)	71.4°F	752.1	0.0342	0.490	0.0346
			0.0317	0.528	0.0320
	70.7°F	746.8	0.0336	0.500	0.0342
	69.7°F	749.1	0.0348	0.490	0.0353
			0.0340	0.502	0.0345
	-19°C	734.3	0.0846	0.570	0.0876
			0.0842	0.572	0.0872
	-23°C	738.3	0.0910	0.603	0.0937
	-34°C	746.7	0.125	0.642	0.127
		737.5	0.126	0.624	0.130
			0.127	0.621	0.131
		753.0	0.127	0.635	0.128
			0.120	0.673	0.121
	-36°C	747.0	0.143	0.602	0.145
	-38.5°C	749.1	0.139	0.653	0.141
	-48°C	743.0	0.199	0.671	0.204
			0.191	0.701	0.195
Triethyl Phosphate m.w. = 192.14	74.6°F	748.7	0.0256	0.627	0.0260
			0.0253	0.634	0.0257
	80°F	746.3	0.0248	0.600	0.0253
		746.2	0.0262	0.568	0.0267
			0.0255	0.584	0.0260
	73.6°F	742.8	0.0274	0.587	0.0280
			0.0258	0.623	0.0264
			0.0260	0.619	0.0266
			0.0258	0.623	0.0264
	71.8°F	747.1	0.0267	0.620	0.0272
			0.0276	0.600	0.0281
			0.0268	0.618	0.0273
	+13°C	751.4	0.0306	0.677	0.0309
			0.0308	0.671	0.0312
	-10°C	749.5	0.0589	0.640	0.0598
			0.0611	0.618	0.0619
	-14°C	750.7	0.0666	0.637	0.0675
			0.0651	0.652	0.0659
	-32°C	751.8	0.112	0.670	0.113
	-34°C	746.7	0.114	0.699	0.116
	-38°C	748.4	0.131	0.703	0.133
			0.130	0.712	0.132

SECTION III

FREEZING-OUT OF CARBON DIOXIDE

INTRODUCTION

In the last tri-monthly report (April 1 to June 30 1952) a preliminary treatment of the 'freeze-out' method of carbon dioxide removal was presented. During the past three months this method has been developed further to a point where the major problems are practically solved and the process appears entirely feasible.

The removal of carbon dioxide from air in closed atmospheres by a continuous process in which the carbon dioxide is frozen out of the air stream has several advantages over other processes. No storage space is required for chemicals or other supplies which are necessary in non-regenerative methods. No oxygen or nitrogen is removed along with the carbon dioxide as is the case when physical absorption is used. Power requirements are not excessive and space requirements are modest. The only significant materials and utilities required are sea water for cooling and electric power for compression. In addition to removing carbon dioxide from the atmosphere, this process reduces the humidity of the air to a low value.

DESCRIPTION OF PROCESS

A schematic flow diagram of this carbon dioxide 'freeze-out' process is shown in Figure 19. This shows the foul air containing 1% CO_2 and with a relative humidity of 65% entering the process at 80°F and 1 atma. This air stream enters the first compressor (Pa-1) at a rate of 500 lbs./hr. This inlet stream consists of 7.59 lbs/hr of CO_2 , 7.05 lbs/hr of H_2O , and 485.36 lbs/hr of dry, CO_2 -free air. After the first stage of compression the air is cooled with sea water. During this cooling some of the water vapor is liquefied and removed from the stream. Further compression and cooling removes more water.

The high pressure foul air leaving the second sea water cooler (HE-2) is passed through a gas-to-gas heat exchanger (HE-3) where it is cooled to about 35°F. In this exchanger additional water is condensed out and flashed to the low pressure side of the exchanger. The foul air with most of the water removed is next sent to a reversing heat exchanger (HE-4) where more of the water vapor is removed by freezing out on the exchanger surface.

The operation of this reversing exchanger is shown in more detail in Figure 20. During the first half of the cycle, the high pressure foul air is passed down one side of the exchanger depositing ice as it is cooled to about -150°F. (This temperature is just above the temperature at which CO_2 starts to freeze out.) While the high pressure air is depositing ice on one side of the exchanger, ice is being removed from the other side by passing low pressure purified air through it. After a suitable period of operation, during which ice builds up on the high pressure side and the low pressure side is derimed, the reversing valves are switched. This sends the high pressure air down the side which has just been derimed and the low pressure purified air back through the side which has fresh rime deposits. This reversing action is indicated in Figure 20. It should be noted at this time that all the water which is condensed in the sea water coolers is permanently separated from the air. On the other hand,

the water removed in these two heat exchangers (HE-3 and HE-4) is re-evaporated into the purified gas stream.

From the reversing heat exchanger (HE-4) the high pressure air next passes through side (3) of HE-6 (see Figure 19) where it is cooled slightly by raising the temperature of the exchanger to nearly -150°F . During this heating of HE-6 side (4) is being evacuated to remove CO_2 . After passing through side (3) the high pressure air is sent through side (2) of HE-5 where it is cooled to about -220°F by passing countercurrent to the low pressure air which has just left the expansion turbine. In cooling to about -220°F the high pressure air is purified by the removal of 99% of the CO_2 and most of the residual water. The CO_2 and H_2O are removed by being frozen out on the heat exchanger surface in the same manner that water is deposited in the reversing heat exchanger (HE-4). After a suitable interval of time during which side (2) is receiving rime deposits and side (4) is being derimed, the valves are switched to allow the high pressure stream leaving HE-4 to pass successively through sides (1) and (4). This change allows side (2) to be defrosted by heating and evacuation and side (4) to receive the rime deposits. After the same interval the valves are switched back. This reversing operation should prevent excessive plugging of the heat exchangers by removing all the rime that has been deposited in the previous cycle. However if by this procedure it is found that adequate deriming is not taking place, then a four step reversing procedure in which each of the four sides of HE-5 and HE-6 successively passes

- 1) high pressure air at about -150°F ,
- 2) high pressure air being cooled to about -220°F ,
- 3) CO_2 removal by evacuation,

and 4) low pressure air,

will definitely provide complete deriming in each cycle. In this case the high pressure air will pass through two sides in the following rotation:

- 1) side (3) and side (2)
- 2) side (1) and side (3)
- 3) side (4) and side (1)
- 4) side (2) and side (4).

The high pressure air at about -220°F (now containing only 0.01% CO_2 and a negligible amount of H_2O) next passes through an expansion turbine where some power and considerable cooling is achieved. (HE-7 shown on the flow sheet is not a separate heat exchanger for operation below 11 atmospheres when it merely indicates what heat leak exists.) The air leaves the turbine at about 1 atma and between -270 and -312°F depending upon the pressure on the inlet side (-270°F for about 3 atm inlet pressure and -310°F for about 11 atm).

The low pressure air leaving the turbine (now cold and purified) is passed back through side (1) of HE-5 (or one of the other sides of HE-5 or HE-6 depending upon which part of the cycle is in operation) where it picks up heat from the high pressure air which is being cooled to about -220°F . After leaving this heat exchanger the low pressure air stream may be split with part of it recycled back through the exchanger (HE-5). This recycling is not necessary if the two-step reversing procedure is used for the operation of HE-5 and HE-6. It may or may not be necessary for the four-step reversing procedure depending upon the effectiveness of the deriming by evacuation and heating.

The low pressure air next passes through the reversing heat exchanger (HE-4) where it picks up the ice deposits left by the high pressure air. Again some recycling may be necessary to insure complete deriming of this exchanger. From HE-4 the low pressure air passes through HE-3 where it picks up the water removed from the high pressure air and where it is heated up to 80°F and discharged to the atmosphere. This purified air contains only 0.01% CO_2 and has a relative humidity of about 3%.

POWER AND SPACE REQUIREMENTS

The results of detailed calculations indicate that the required power for processing 500 pounds per hour of foul air is between 12 and 20 kilowatts as is summarized below.

High Pressure Side atma	Required Power, kilowatts				
	<u>Compression</u>	<u>Evacuation</u>	<u>Pumping</u> <u>etc.</u>	<u>Turbine</u>	<u>Net</u>
5	14.0	0.2	0.8	2.0	15.0
11	22.4	0.2	0.8	2.7	20.1

These figures are based upon compressors and turbines designed to occupy small volumes. Efficiencies of 70% were assumed for both compression and for expansion.

A summary of the space requirements indicates that a total volume of between 40 and 80 cubic feet should be sufficient. A breakdown of this estimate is given below.

	<u>Volume, cubic feet</u>
Heat exchangers, bare	3 - 6
insulation	2 - 4
Compressors	5 - 10
Turbine	0.3 - 1
Piping, valves, controls	10 - 20
Free Space	20 - 39
Total	<u>40 - 80</u>

These figures are based upon equipment designed especially for conditions requiring small volumes. The heat exchangers, compressors, and turbine were carefully evaluated while the remaining items were roughly estimated.

OPERATING CONDITIONS

The operating temperatures, pressures and compositions of the various parts of the process shown in Figure 19 depend largely upon physical and thermal properties of the fluid-solid system air-CO₂-H₂O. They also depend upon the properties of available sea water, the desired atmospheric conditions of the region supplying the foul air, and the desired composition of the fresh air. In order to investigate the effect of the many process variables on the power and space requirements, it was necessary to consider as primary variables the operating pressure, P_2 , and the amount of CO₂ removed. In order to restrict the problem it was decided to consider removal of 99% of the entering CO₂. This choice was made since preliminary calculations indicated that the power and space requirements would be practically independent of amount of CO₂ removed, as long as about 95% or more CO₂ was removed. Since the optimum operating pressure was not known, it was decided to investigate pressures, for P_2 , up to 20 atmospheres. With these choices of primary variables the operating temperatures were fairly definitely established. Each of these temperatures and pressures is discussed in a following paragraph.

Inlet temperature, T_1 . The inlet temperature was arbitrarily chosen as 80°F to represent a reasonable basis.

Inlet pressure, P_0 . For the same reason the inlet pressure was chosen as 1 atmosphere.

Inlet composition. A relative humidity of 65% and a CO₂ concentration of 1.0% by volume were chosen as comfortable conditions which should be maintained.

Compressor discharge pressure, P_1 . Depending upon the operating pressure, P_2 , and the type of compressor selected, one, two, or possibly three stages of compression may be required. For one stage operation, $P_1 = P_2$. For two stage operation, $P_1 = \sqrt{P_2}$ where both pressures are expressed in atmospheres.

Compressor discharge temperature, T_2 . The discharge temperature is principally a function of the pressure P_1 , and of the efficiency of the compression. This function is plotted in the left hand

side of Figure 21 where three curves labeled $P_1 = P_2$ are plotted. These curves show how T_2 varies with P_1 and compression efficiency. T_2 is also presented in Table VII for values of P_1 between 2.24 atm and 6.81 atm.

Sea Water temperature, T_{14} . An analysis of reported sea water temperatures at various latitudes, longitudes, seasons, and depths indicated that 80°F was an acceptable figure to use for the purposes of this study. Table VI is a listing of surface temperatures throughout the world for two seasons of the year and temperatures at 200 and 400 meters below the surface, these submerged temperatures being almost independent of the season.

Sea water temperature, T_{16} . The temperature of the sea water leaving the heat exchanger, HE-1, was chosen as 90°F, which represents a 10°F rise in temperature.

Compressed air temperature, T_3 . It was assumed that the air could be cooled to within 10°F of the water temperature. This made T_3 equal to 90°F.

Compressor discharge temperature, T_4 . This discharge temperature depends upon the pressure, P_2 , and compressor efficiency as well as P_1 and T_3 . T_4 as a function of P_2 and compression efficiency is plotted in Figure 21 and listed in Table VII.

Sea water temperature, T_{15} . Same as T_{16} .

Compressed in temperature, T_5 . Same as T_3 . T_5 is shown as a function of P_2 in Table VIII and Figure 22.

Temperature of foul air leaving HE-3, T_6 and T_6' . This temperature was set as 35°F to be a few degrees above the freezing point of water, 32°F.

Temperature of foul air leaving HE-4, T_7 . In order to limit the deposition of solid CO_2 to HE-5 and HE-6, the temperature T_7 must be higher than the temperature at which a mixture of air and 1% CO_2 is in equilibrium with solid CO_2 . This temperature is tabulated in Table IX, plotted in Figure 23 as a function of pressure. It is also shown in Figure 22 and Table VIII.

Temperature of high-pressure clean air leaving HE-5, T_8 .

In order to remove 99% of the CO_2 from the foul air, the temperature of the air stream must be reduced until it is at the temperature at which a mixture of air and 0.01% CO_2 is in equilibrium with solid CO_2 . This temperature, T_8 , is plotted in Figures 22 and 23 and given in Table VIII as a function of pressure. This is also the temperature of the air inlet to the expansion engine for pressures below about 11 atm. In order to prevent liquid air from forming in the expansion engine, the temperature of the inlet stream must be that shown as T_8' or higher. For pressures above 11 atm., T_8' is higher than T_8 , and the stream must be heated (by HE-7 or other means). This indicates that compression to more than 11 atmospheres is of no advantage. These temperatures were obtained assuming 70% efficiency in the expansion engine.

Temperature of clean air leaving turbine, T_9 . Assuming expansion to 1 atm. at 70% efficiency in the expansion engine, the temperature leaving the turbine, T_9 , was calculated from T_8 . T_8' was obtained from T_9 for the higher pressures by using -312.8°F for T_9 .

Temperature of clean air leaving HE-3, T_{13} . The temperature of the clean air discharged from the process was assumed to be 80°F, which is 10°F cooler than T_5 . This represents conservative design conditions and in operation may be considerably different.

Temperature of clean air leaving HE-4, T_{12} . An energy balance around HE-3, assuming no heat leak and allowing for revaporization of condensate, fixes T_{12} as shown in Figure 22 and Table VIII. During actual operation, it may be as much as a few degrees lower due to heat leak.

Temperature of clean air entering HE-4, T_{11}' . The temperature of clean air entering HE-4 must be high enough to remove the ice deposits in the reversing exchanger. This temperature is related to T_7 as shown in Figure 24. For temperatures of T_{11}' lower than indicated on Figure 24, the low-pressure clean air will not derime the exchanger. In order to insure complete deriming, temperature T_{11}' has been chosen higher than shown in Figure 24. It is tabulated in Table VIII as calculated from 75% of the difference shown in Figure 24. In order to obtain this temperature, a recycle stream as shown in Figure 19 is necessary.

Temperature of clean air leaving HE-5, T_{11} . An energy balance around HE-4, assuming no heat leak in either HE-4 or HE-3, indicates the temperature for T_{11} which is shown in Figure 22 and Table VIII. In actual operation T_{11} will be lower, perhaps several degrees, due to heat leak.

Temperature of clean air entering HE-5, T_{10}' . If the two step deriming cycle satisfactorily prevents build up of solid CO_2 and solid H_2O in HE-5 and HE-6, then no recycle stream is required and $T_{10}' = T_{10}$. However, if the four step reversing procedure is necessary T_{10}' must be higher than T_{10} and related to T_8 as shown in Figure 24. In order to insure deriming of these exchangers, T_{10}' as plotted in Figure 22 and tabulated in Table VIII was calculated by using 75% of the permissible difference shown in Figure 24.

Temperature of clean air leaving turbine, T_{10} . An energy balance around HE-5 and HE-6, assuming no heat leak in any one of HE-3, HE-4, HE-5, HE-6, and neglecting the energy effects associated with the evacuation part of the cycle, indicates for T_{10} the temperatures plotted in Figure 22 and shown in Table VIII. At this time it can be noticed that T_9 and T_{10} represent the same stream and that the difference between T_9 and T_{10} is a quantitative measure of the permissible heat leak in the exchangers.

Temperature, T_{17} , and Pressure, P_3 , for evacuation. In order to remove CO_2 by evacuation the pressure must be reduced and/or the temperature raised by an amount at least as much as indicated by the equilibrium phase relationships of the air- CO_2 system. Figure 25 shows these relationships in terms of the process variables. The temperature rise, $T_{17}-T_8$, is plotted against the pressure factor P_2/P_3 . For removing 99% of the CO_2 , two lines are presented, one for $P_2 = 10$ atm and one for $P_2 = 5$ atm. One line ($P_2 = 10$ atm) is presented for removing 98% CO_2 .

In the preceding paragraphs are presented the underlying assumptions and reasons for establishing the various conditions of the process. It should be pointed out that, for this phase

of the problem, no consideration was given to pressure drop in the flow of air through the several exchangers and associated piping. This simplification has but little effect on the temperatures obtained and practically no effect on the conclusions of this study.

In making the energy balances to establish some of the process temperatures and to determine the heat exchanger duties, the enthalpies of the several streams were calculated. These enthalpies have been plotted in Figure 26 and tabulated in Table X. These values were based on individual enthalpies for air (Figure 27), for CO_2 (Figure 28) and for water (Keenan and Keyes, Steam Tables).

In the process described above the water condensed in HE-3 and the rime deposited in HE-4 were revaporized in the low pressure clean air. Calculations were also made assuming that these quantities were discarded. The resulting temperatures are given in Table XI and Figure 29.

SELECTION OF EQUIPMENT

Compressors. A survey of available industrial compressors indicated that practically all models occupy a relatively large volume (50 to 80 cubic feet total volume) and are therefore unsuited for the proposed process. The rotary lobe type (Elliott-Lysholm) as discussed in recent literature (Engineering 155 97-100, Jan. 29, 1943; SAE Journal 51 June 1943; Mechanical Engineering 68 514-8, June 1946; NDRG, Division 11, Summary Technical Report, Vol. 1, 1946) appears rather promising. It is estimated that a single stage compressor of this type capable of compressing 500 pounds per hour of air with a compression ratio of 2.5 or 3 can be designed to occupy a volume about 2.5 or 3 cubic feet (including drive). These compressors operate at about 70% efficiency (see Figure 30).

Turbine. Based on reports of Swearingen (Chemical Engineering Progress 43 85-90 Feb. 1947) and Rushton (NDRG, Division 11, Summary Technical Report, Vol. 1, 1946) it is estimated that for the proposed process a turbo-expander can be built which will occupy less than one cubic foot (about 0.3 cu. ft. for expansion from 5 atmospheres). This expander would operate with an efficiency of about 70-80%.

Heat Exchangers. In connection with the recent development of compact equipment for the production of oxygen, two types of heat exchangers have been used. The ribbon-packed annular exchanger (Trumpler and Dodge, Chem. Eng. Progress 43 75-84, February 1947) originated by Collins, and the sandwich type exchanger (Simpelaar and Aronson, Trans ASME 72 955-965, Oct. 1950) both have a considerably greater transfer surface to volume ratio than commercial heat exchangers. Either type could be used for the proposed process. Since the sandwich type exchanger has been more thoroughly tested and since it is of simpler construction, it was the basis for this work.

This heat exchanger consists essentially of thin copper

fins furnace bonded between brass plates. The exchanger is manifolded so that one fluid will flow in one direction through every alternate passage and the other fluid will flow in the opposite direction through the intermediate passages. This arrangement of surface provides over 300 sq. ft. of effective surface per cubic foot of heat exchanger volume and corresponds to over 3.5 sq. ft. per pound of metal.

For the specific design considered in this problem, the recommended equations and data of Simpelaar and Aronson were restricted and applied to a 3/32" strip fin throughout these calculations. The properties and necessary data associated with this particular fin were obtained from the above article. The distinct advantage of such type of heat exchange equipment over the conventional shell and tube types lies in the unusually high heat transfer coefficients attainable. In this connection, gas film coefficients as high as 60 Btu/(hr)(ft²)(°F) are ordinary against values of 3 to 5 commonly considered for the conventional shell-tube type exchangers. Conservative pressure drop considerations for both the warm and cold sides indicate that with the exclusion of end effects (entrance and exit plus piping), the total pressure drops through the finned-heat exchangers are as follows:

<u>Heat Exchanger</u>	<u>Pressure Drop, psi</u>	
	<u>Warm Side</u>	<u>Cold Side</u>
HE-1	0.393	- - -
HE-2	0.218	- - -
HE-3	0.248	1.17
HE-4	0.550	2.61
HE-5	0.135	0.63
HE-6	0.135	
	<u>1.679</u>	<u>4.41</u>

Warm Side: $\Delta p = 1.68$ psi.

Cold Side: $\Delta p = 4.41$ psi

These values were reached by considering heat exchangers

of one passage flow throughout and assuming a pressure of 73.5 psia for the unprocessed air through heat exchangers HE-3, HE-4 and HE-5. The cold side pressure drop most likely cannot be decreased unless more than one gas passage is selected for the exchangers.

Heat transfer coefficients for a 3/32" strip fin were evaluated from the j-factor relationship proposed by the above investigators. This relationship is presented below:

$$j_h = \frac{h}{G} \left[\frac{c_p \mu}{k} \right]^{2/3} = 0.245 / (Re)^{0.4}$$

where A = total heat-transfer area which is equal to the sum of the surface of the fins and that of the wall.

c_p = heat capacity of air, considered as 0.24 Btu/(lb)(°F)

D_o = equivalent passage diameter, $D_o = \frac{4}{\frac{A}{L} + 1}$, ft

G = core, air mass velocity, lb/(hr)(ft² of A_o)

h = surface heat transfer coefficient based on total heat transfer area, Btu/(hr)(ft²)(°F)

j_h = heat transfer factor (dimensionless)

L = length of flow passage

Re = Reynolds number $\frac{D_o G}{\mu}$

$\frac{c_p \mu}{k}$ = Prandtl group, assumed for air to be 0.74

μ = viscosity, lb/(hr)(ft)

The strip fins are 3/32" wide (direction of fluid flow), 0.485" long (distance between plates), 0.004" thick and are 3/32" apart in the direction of fluid flow and .082" apart perpendicular to fluid flow and the rows of fins are staggered.

The following physical characteristics were obtained from the specific heat exchanger employed by Simpelaar and Aronson

in their article (page 959).

Passage details: (Number = 18, height = 0.485", width = 12", length = 90" = 7.5 ft) Total Area (fins plus wall): $A = 1858$ sq ft
Free Cross Sectional Area: $A_o = 0.70$ sq ft

$$\frac{A}{A_o} = \frac{1858}{0.70} = 2655$$

$$\frac{A}{A_o} \cdot \frac{1}{L} = \frac{2655}{7.5} = 354$$

$$D_o = \frac{4}{\frac{A}{A_o} \cdot \frac{1}{L}} = \frac{4}{354} = 0.0113 \text{ ft.}$$

Heat transfer surface/passage per foot of length ($h = 0.485"$, $w = 12"$, $l = 12"$)

$$\frac{1858}{18 \times 7.5} = 13.7 \text{ sq ft of fin plus wall surface/passage}$$

per foot of length

HE-3 is selected to illustrate the calculation procedure. For this case unprocessed air at 73.5 psia containing carbon dioxide and water vapor is being cooled from 90 to 35°F counter-currently with processed air at substantially atmospheric pressure, the temperature of which rises from 25 to 80°F. The purpose of this exchanger is a twofold one: to cool the air stream to 35°F and simultaneously condense water vapor. This liquid condensate in turn is to be revaporized in the processed air stream. For this particular case the total exchanger duty is $117,977 - 108,706 = 9271$ Btu/hr. The temperature difference, for this case, calculates to be 10.0°F. Consequently $UA = 9271/10 = 927$ Btu/(hr)(ft²)(°F).

The length and total fluid volume necessary for this heat exchanger at the above given pressure of 73.5 psia are directly related to the number of passages. Arbitrarily cases dealing with 1, 2, 3 and 4 passages for each fluid stream were selected and the calculation procedure is presented below:

Heat Exchanger, HE-3:

High pressure side, $P_2 = 73.5$ psia

Air flow going from T_5 to T_6

Temperature = 90°F to 35°F ($T_{\text{avg}} = 62^\circ\text{F}$)

Viscosity = $\mu = 4.477 \times 10^{-2}$ lbs/ft x hr

Air Rate = $W = 485.36 + 7.59 + 0.42 + 2.54/2 = 494.64$ lbs/hr

Passage. $w = 12''$, $h = 0.485$, $L = ?$

Strip fin: Thickness = $0.004''$, $h = 0.458$, $L = 3/32''$

$a_c = A_c/h = 0.70/18 = 0.039$ ft² of cross-sectional free area/passage

$D_e = 0.113$

$$\frac{D_e \mu}{h}^{2/3} = (0.75)^{2/3} = 0.818$$

n , No. of Passages	A_c ft ²	$G = W/A_c$ (lb/(hr) (ft ²))	$\frac{D_e G}{\mu}$	$\left[\frac{D_e G}{\mu}\right]^{0.4}$	$j_h = \frac{0.245}{(Re)^{0.4}}$	$h_w = j_h \frac{c G}{(Pr)^{2/3}}$
1	0.0389	12,716	3210	25.3	0.00969	36.2
2	0.0778	6,358	1605	19.15	0.0128	23.9
3	0.1167	4,238	1070	16.25	0.01508	18.75
4	0.1556	3,179	802	14.5	0.0169	15.76

Low Pressure side, $P_o = 14.7$ psia

Air flow going from T_{12} to T_{13}

Air Rate = $W = 485.36 + 0.42 + (2.96 - 0.42) = 488.32$ lbs/hr

Temperature = 25°F to 80°F ($t_{\text{avg}} = 52^\circ\text{F}$)

$$\mu = 4.31 \times 10^{-2} \text{ lb/hr x ft}^2$$

n , No. of Passages	A_c ft ²	$G = W/A_c$ lb/(hr) (ft ²))	$\frac{D_e G}{\mu}$	$\left[\frac{D_e G}{\mu}\right]^{0.4}$	$j_h = \frac{0.245}{(Re)^{0.4}}$	$h_o = j_h \frac{c G}{(Pr)^{2/3}}$
1	0.0389	12,553	3291	25.5	0.00966	35.4
2	0.0778	6,276	1645	19.45	0.0126	23.2
3	0.1167	4,184	1097	16.45	0.01489	18.25
4	0.1556	3,138	823	14.7	0.01665	15.31

No. of Passages	$\frac{1}{h_w}$	$\frac{1}{h_o}$	$\frac{1}{U}$	U	A = 927/U	L = A/13.7h
1	0.02762	0.02825	0.05587	17.90	51.79 ft ²	3.78
2	0.04184	0.04310	0.08494	11.77	78.76	2.87
3	0.05333	0.05479	0.10812	9.25	100.2	2.44
4	0.06345	0.06532	0.12877	7.77	119.3	2.18

Volume, cu ft*

No. of Passages	Warm Side	Cold Side	Total
1	0.147	0.147	0.294
2	0.223	0.223	0.446
3	0.285	0.285	0.570
4	0.339	0.339	0.678

The variation of the heat exchanger length and fluid volume is dependent upon the absolute pressure of the unprocessed air (warm side). These variables are incorporated and related to the number of gas passages and appear in Figures 31-35 for heat exchangers HE-1, HE-2, HE-3, HE-4 and HE-5.

A compilation of conditions that might be selected for the operation of a cycle point to a total exchanger volume of from 3 to 6 cubic feet. In this connection, the maximum length necessary for a one passage arrangement is that of exchanger HE-4 which is 12 feet. This value reduces to 6.8 feet for a four-passage arrangement. If a one passage arrangement is to be chosen for this heat exchanger, it may be possible to consider two or three separate one-pass exchangers of shorter length, whose total effective length is 12 feet. The lengths of the other exchangers are not critical and vary from 0.72 to 4.8 feet.

*Note: The exchanger volumes calculated correspond to those occupied by the fluid alone and do not include the fin and wall partitions. In order to calculate the total volume (fluid plus fins) these values must be multiplied by the factor representing the total cross sectional area divided by the free cross sectional area or

$$\frac{0.485 \times 12}{144} / 0.0389 = 1.039.$$

CONCLUSIONS

The study has shown the feasibility of the process of freezing out the CO_2 since the size and power requirements are both reasonable. This concludes the phase of the work currently authorized.

Future work in the problem would involve the setting up of experimental equipment for confirming the results obtained and for observation of any factors which may have been minimized.

Problems that have to be investigated in this experimental phase would be:

1. Determination of heat leaks.
2. Determination of cycle times and coordination of the various parts of the cycle.
3. Time lag in initial start up.
4. Determination of problems involved in CO_2 formation in expansion engine.
5. Balance of refrigeration requirements in heat exchange reversing procedures.
6. Investigation of the actual CO_2 condensing and subliming conditions and confirming the heat transfer coefficients.
7. Checking of the process in general.
8. Mechanical operational problems, valving particularly, under the pressures and low temperatures involved.

SURFACE TEMPERATURE OF THE OCEANS

Latitude	Longitude										Depth (M)				
	0	20	40	60	80	100	120	140	160	180					
80	Less than -1 to 1														
60	7	-	-	-	-	-	-	-	-	-	1	2	3	8	Feb.
	13	-	-	-	-	-	-	-	9	6	13	-	8	12	Aug.
	9	-	-	-	-	-	-	-	-	3	6	-	5	8	200
	9	-	-	-	-	-	-	-	-	-	-	-	4	5	400
40	13	14	-	-	-	0	6	9	11	11	12	-	15	16	Feb.
	25	25	-	-	-	25	25	21	20	20	19	-	24	24	Aug.
	-	-	-	-	-	-	5	6	7	7	9	-	18	17	200
	-	-	-	-	-	-	1	5	7	6	6	-	10	16	400
20	-	-	26	23	-	24	25	25	24	22	21	-	26	23	Feb.
	-	-	30	24	-	28	28	28	27	24	25	-	29	26	Aug.
	-	-	-	16	-	15	22	21	18	16	10	-	20	19	200
	-	-	-	13	-	10	14	13	11	9	8	-	15	13	400
0	23	-	-	28	28	27	28	28	27	25	24	-	27	27	Feb.
	23	-	-	27	27	28	28	26	26	25	23	-	26	24	Aug.
	14	-	-	14	14	-	20	21	14	13	13	-	12	13	200
	8	-	-	10	10	-	9	9	9	10	10	-	8	9	400
20	23	-	24	27	26	25	29	27	26	26	26	-	21	25	Feb.
	18	-	24	23	22	22	23	23	24	24	22	-	23	21	Aug.
	13	-	16	20	19	18	17	-	20	21	21	-	16	16	200
	9	-	12	14	15	12	10	-	15	13	10	-	11	10	400
40	14	20	17	17	16	15	15	15	18	17	16	-	17	17	Feb.
	10	15	13	13	11	11	11	12	13	12	10	-	11	11	Aug.
	9	15	9	11	11	10	11	12	12	9	8	-	10	10	200
	8	11	8	10	11	10	9	9	9	7	7	-	5	7	400
60	0	-1	-1	-1	-1	1	1	3	4	3	2	-	3	0	Feb.
	-1	-1	-1	-1	-1	-1	-1	-1	-1	0	-1	-	-1	-1	Aug.
	1	1	1	1	1	1	1	1	2	2	2	-	0	0	200
	1	1	1	2	1	1	1	2	2	2	2	-	1	1	400
80	Less than -1 to 0														

TABLE VII

TEMPERATURE AND ENTHALPY CHANGE OF AIR STREAM FROM COMPRESSORS

Pressure Atm		Temperature °T						Enthalpy Change	
		T ₂			T ₄			Btu/lb	
		Efficiency			Efficiency			70% Efficiency	
		100%	85	70	100	85	70	Per Stage	Total
P ₁	P ₂								
2.24	5	220	245	281	231	256	292	48	96
2.45	6	242	266	309	253	277	320	55	110
2.65	7	260	284	331	271	295	342	61.5	123
2.83	8	272	300	349	283	306	351	66	132
3.00	9	283	315	365	294	316	376	70	140
3.16	10	293	329	382	304	328	392	73.5	147
3.32	11	302	341	396	313	339	407	76.4	152.8
3.57	15	337	380	439	348	391	450	86.8	173.6
4.47	20	373	418	484	384	429	496	98.5	197
5.00		395	448	524				107.8	107.8
6.81		470	537					135	135

TABLE VIII

AIR STREAM TEMPERATURE °F FOR 99% CO₂ REMOVAL WITH

CONDENSATE AND RIME REVAPOORIZED BY CLEAN AIR STREAM

	1	3	5	10	15	20
Foul air, operating pressure, atm						
Foul air, inlet to H.E. 1, T ₂	80.0	365.0	524.0			
Foul air, outlet from H.E. 1, T ₃	80.0	90.0	90.0	90.0	90.0	90.0
Foul air, inlet to H.E. 2, T ₄	80.0			393.0	450.0	496.0
Foul air, outlet from H.E. 2, inlet to H.E. 3, T ₅	80.0	90.0	90.0	90.0	90.0	90.0
Clean air, outlet from H.E. 3, T ₁₃	80.0	80.0	80.0	80.0	80.0	80.0
Foul air, outlet from H.E. 3, inlet to H.E. 4, T ₆	35.0	35.0	35.0	35.0	35.0	35.0
Clean air, inlet to H.E. 3, outlet from H.E. 4, T ₁₂	25.0	25.0	25.0	24.8	24.5	24.1
Foul air, outlet from H.E. 4, inlet to H.E. 5, T ₇	-187.5	-175.8	-169.0	-158.9	-153.2	-149.4
Clean air, 75% of minimum inlet to H.E. 4, T ₁₁	-189.4	-181.6	-177.8	-172.1	-168.8	-167.5
Clean air, inlet to H.E. 4, outlet from H.E. 5, T ₁₁	-199.5	-188.8	-182.9	-176.1	-174.0	-173.4
Clean air, inlet to expansion engine, T ₈	-236.0	-227.5	-223.7	-218.9	-216.8	-216.7
Clean air, minimum inlet to expansion engine T ₉						
Clean air, 75% of minimum inlet to H.E. 5, T ₁₀	-237.4	-231.3	-229.6	-227.4	-201.2	-186.0
Clean air, maximum required outlet from expansion engine, T ₁₀	-236.0	-258.9	-257.0	-259.5	-266.4	-275.5
Clean air, outlet from 70% efficient expansion engine, T ₉		-268.9	-287.9	-309.2	-312.83	-312.83

Note: At 11.08 atm T₉ coincides with T₈

TABLE IX
INLET AIR STREAM EQUILIBRIUM TEMPERATURES

Condition	Per Cent CO ₂ Removed	Temperature - °F	
		At 1 atm Pressure	At 13.6 atm Pressure
T ₇	0	-187.5	-154.3
T ₈	36	-193.0	-161.7
T ₈	68	-201.2	-172.7
T ₈	84	-209.3	-183.6
T ₈	92	-216.3	-192.7
T ₈	96	-223.7	-201.5
T ₈	98	-230.0	-209.1
T ₈	99	-236.0	-217.2
T ₈	99.5	-242.0	-223.8
T ₈	99.75	-247.2	-230.9
T ₈	99.875	-252.5	-237.0

Note: Curves are based upon the equilibrium temperatures of CO₂ under its own vapor pressure and corrected for total pressure.

TABLE X

TOTAL ENTHALPY OF HIGH PRESSURE AIR STREAM IN BTU/HR

Pressure - atm	1	3	5	10	15	20
Inlet to H.E. 3 at T ₂	122799	120344	117977	116104	115331	114844
Outlet from H.E. 3 at T ₆ assuming H ₂ O present as a vapor at T ₃	116324	113875	111503	109615	108805	108271
Outlet from H.E. 3 at T ₆ (including condensate)	110863	109173	108706	108227	107880	107572
Inlet to H.E. 4 at T ₆	110848	109160	108698	108223	107878	107570
Outlet from H.E. 4 at T ₇ assuming H ₂ O present as a vapor at T ₂	84441	84011	84240	84591	84538	84336
Outlet from H.E. 4 at T ₇ (including H ₂ O)	81837	83151	83724	84333	84366	84207
Inlet to H.E. 5 at T ₇	82159	83257	83788	84365	84387	84223
Outlet from H.E. 5 at T ₈ (including solid CO ₂ , 92% CO ₂ removed)	76924	77751	78009	77853	77396	76573
Inlet to expansion engine at T ₈ (92% CO ₂ removed)	76925	77732	77981	77811	77346	76521
Outlet from H.E. 5 at T ₈ (including solid CO ₂ , 99% CO ₂ removed)	74418	75013	75070	74556	73517	72216
Inlet to expansion engine at T ₈ (99% CO ₂ removed)	74459	75036	75085	74562	73518	72217

Basis: Air (oxygen and nitrogen): Saturated liquid 1 atm pressure (141.7 °R) enthalpy = 46.33 Btu/#
 entropy 0.0 Btu/# °R

Water: Saturated liquid at 32 °F; enthalpy = 0.0 Btu/#, entropy = 0.0 Btu/# °R

CO₂: Saturated liquid at 32 °F; enthalpy = 180.0 Btu/#, entropy = 1.0 Btu/# °R

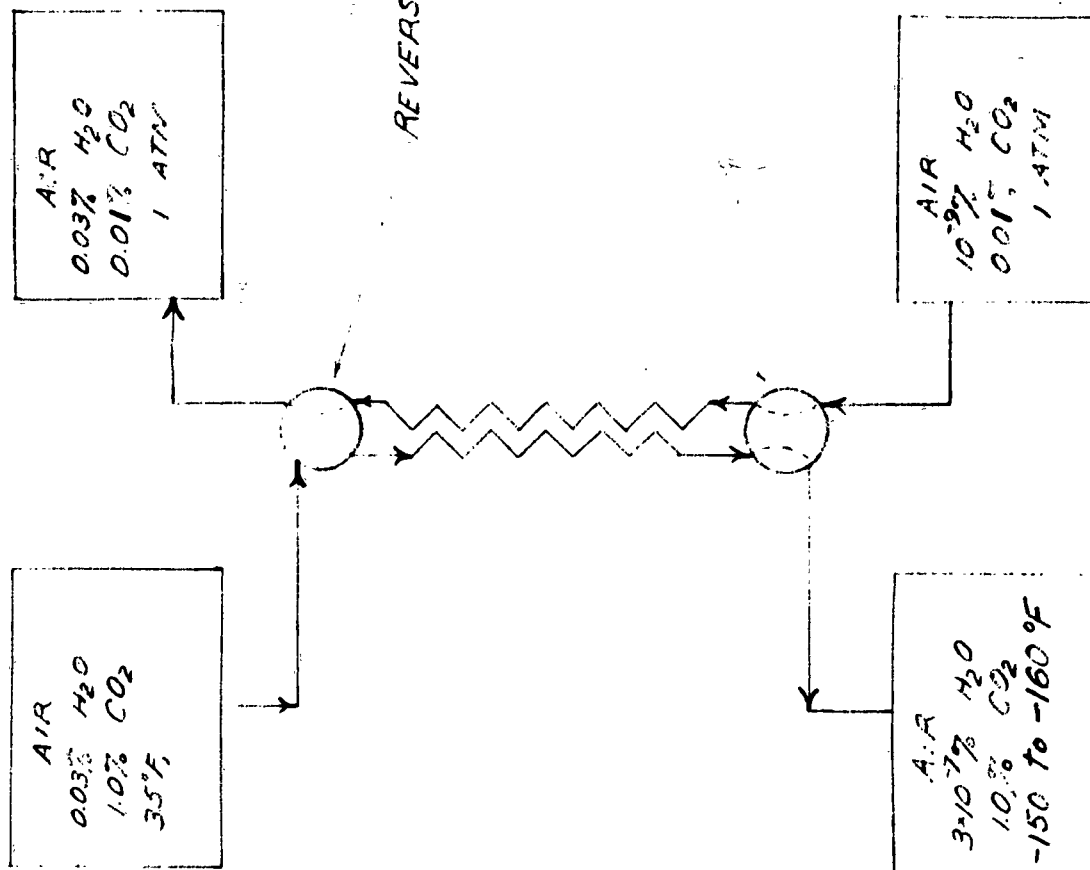
TABLE XI

AIR STREAM TEMPERATURES °F FOR 99% CO₂ REMOVAL

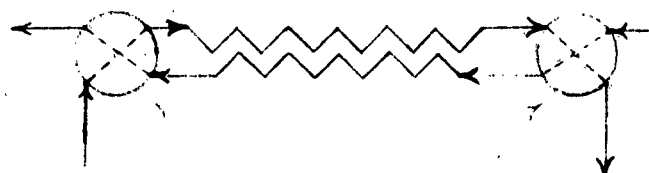
WITH CONDENSATE AND RIME DISCARDED

	1	3	5	10	15	20
Foul air, operating pressure, atm						
Foul air, inlet to H.E. 1, T ₂	80.0	365.0	524.0			
Foul air, outlet from H.E. 1, T ₃	80.0	90.0	90.0	90.0	90.0	90.0
Foul air, inlet to H.E. 2, T ₄	80.0			393.0	450.0	496.0
Foul air, outlet from H.E. 2 inlet to H.E. 3, T ₅						
Clean air, outlet from H.E. 3, T ₁₃	80.0	90.0	90.0	90.0	90.0	90.0
Foul air, outlet from H.E. 3, inlet to H.E. 4, T ₆	90.0	80.0	80.0	80.0	80.0	80.0
Clean air, inlet to H.E. 3, outlet from H.E. 4, T ₁₂	35.0	35.0	35.0	35.0	35.0	35.0
Foul air, outlet from H.E. 4, inlet to H.E. 5, T ₇	-22.5	-15.1	1.1	13.0	16.6	18.1
Clean air, 75% of minimum inlet to H.E. 4, T ₁₁	-187.5	-175.8	-169.0	-158.9	-153.2	-149.4
Clean air, inlet to H.E. 4, outlet from H.E. 5, T ₁₁	-189.4	-181.6	-177.8	-172.1	-168.8	-167.5
Clean air, inlet to expansion engine, T ₈	-266.4	-235.3	-210.7	-189.8	-183.2	-180.4
Clean air, minimum inlet to expansion engine, T ₈	-236.0	-227.5	-223.7	-218.9	-216.8	-216.7
Clean air, 75% of minimum inlet to H.E. 5, T ₁₀						
Clean air, maximum, T ₉ , outlet from expansion eng., T ₁₀	-237.4	-231.3	-229.6	-227.4	-227.0	-227.8
Clean air, outlet from 10% efficient expansion engine, T ₉	-331.8	-305.2	-284.7	-273.2	-275.6	-282.5
	-236.0	-268.9	-287.9	-309.2	-312.83	-312.83

Note: At 11.08 atm T₈ coincides with T₉



(a) DURING FIRST HALF OF CYCLE



(b) DURING SECOND HALF OF CYCLE

FIG: 20

CHEMICAL ENGINEERING DEPARTMENT NORTHWESTERN TECHNOLOGICAL INSTITUTE EVANSTON, ILLINOIS	
TITLE: <i>Reversing Exchanger</i>	
DR. BY: <i>MTK</i>	DATE: <i>June 16, 1952</i>
CH'KD BY:	SCALE: <i>None</i>
APPD. BY:	ASS'BY NO:
DRAWING NO. <i>602-1</i>	
PROJECT: <i>130</i>	
A	

FIG. 21

CO₂ FREEZE-OUT METHOD

Temperatures of air stream from compressors

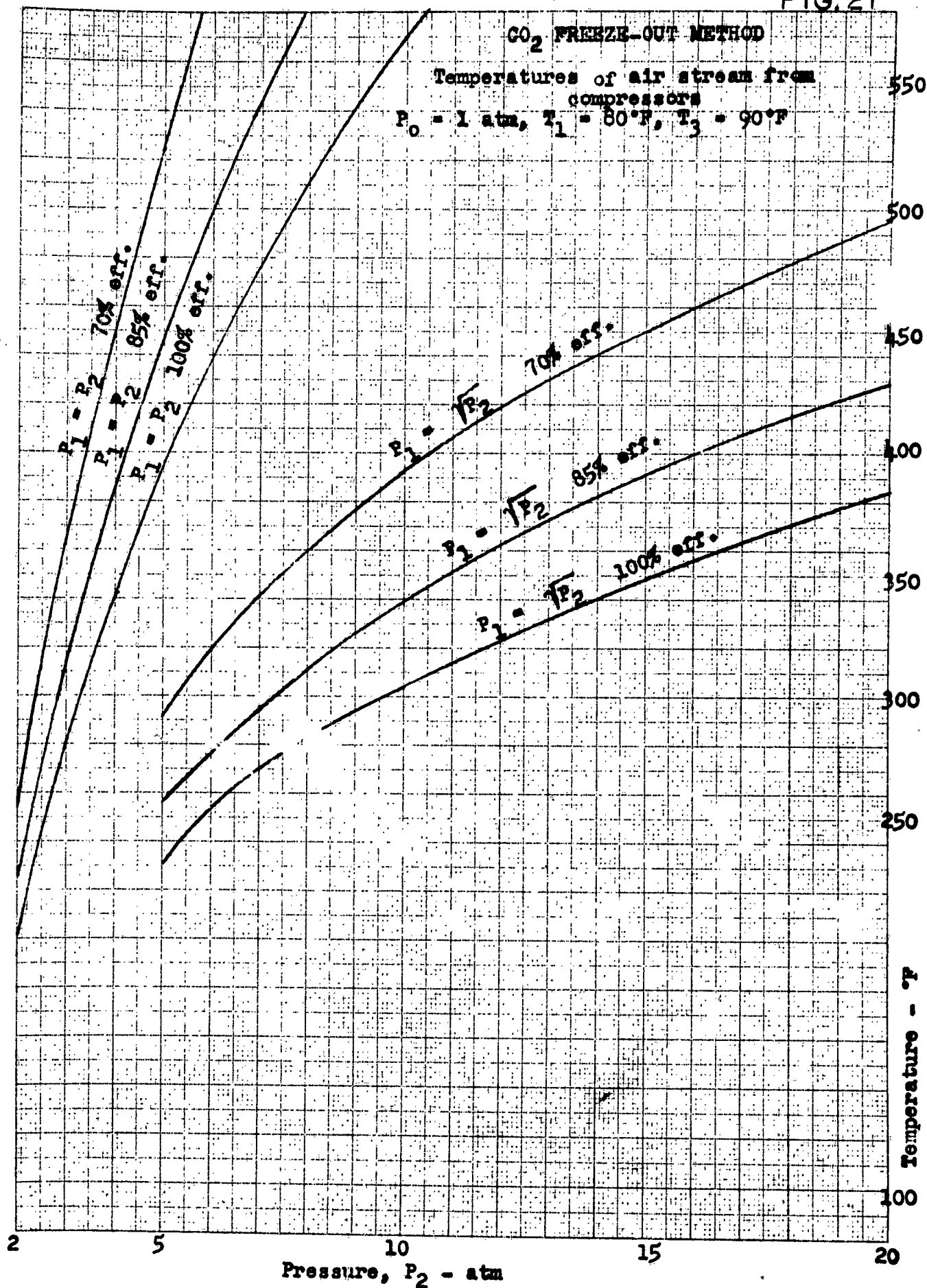
 $P_0 = 1 \text{ atm}, T_1 = 80^\circ\text{F}, T_3 = 90^\circ\text{F}$ 

FIG. 22 150

CO₂-FREEZE-OUT METHOD

Air Stream Temperatures

Condensate and Rime Revaporized by Clean Air Stream
99% CO₂ Removal

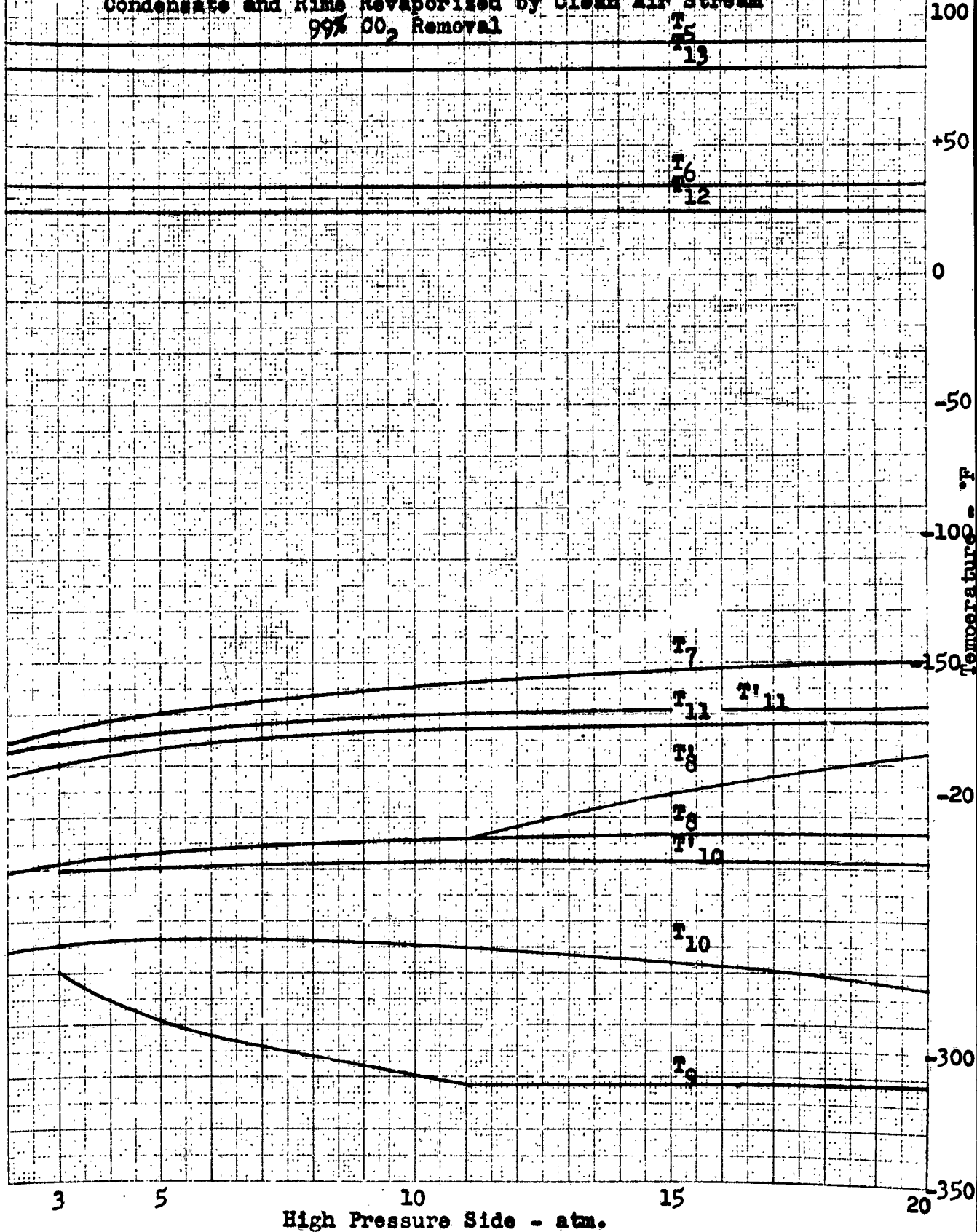


FIG. 23

COPIES & REPRODUCTIONS
Semi-Logarithmic, 2 Cycles, 20 to the Inch.
MADE IN U. S. A.

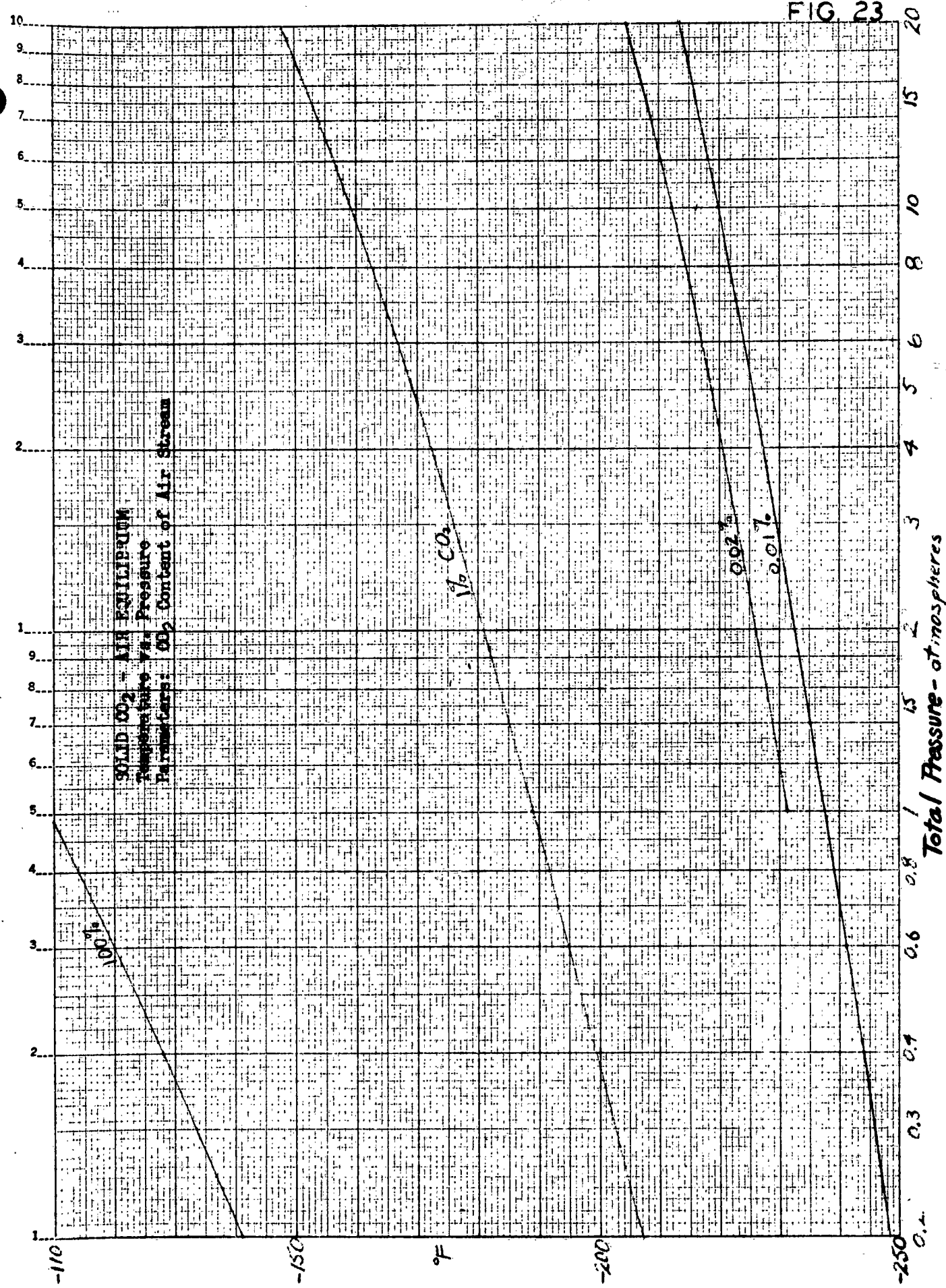
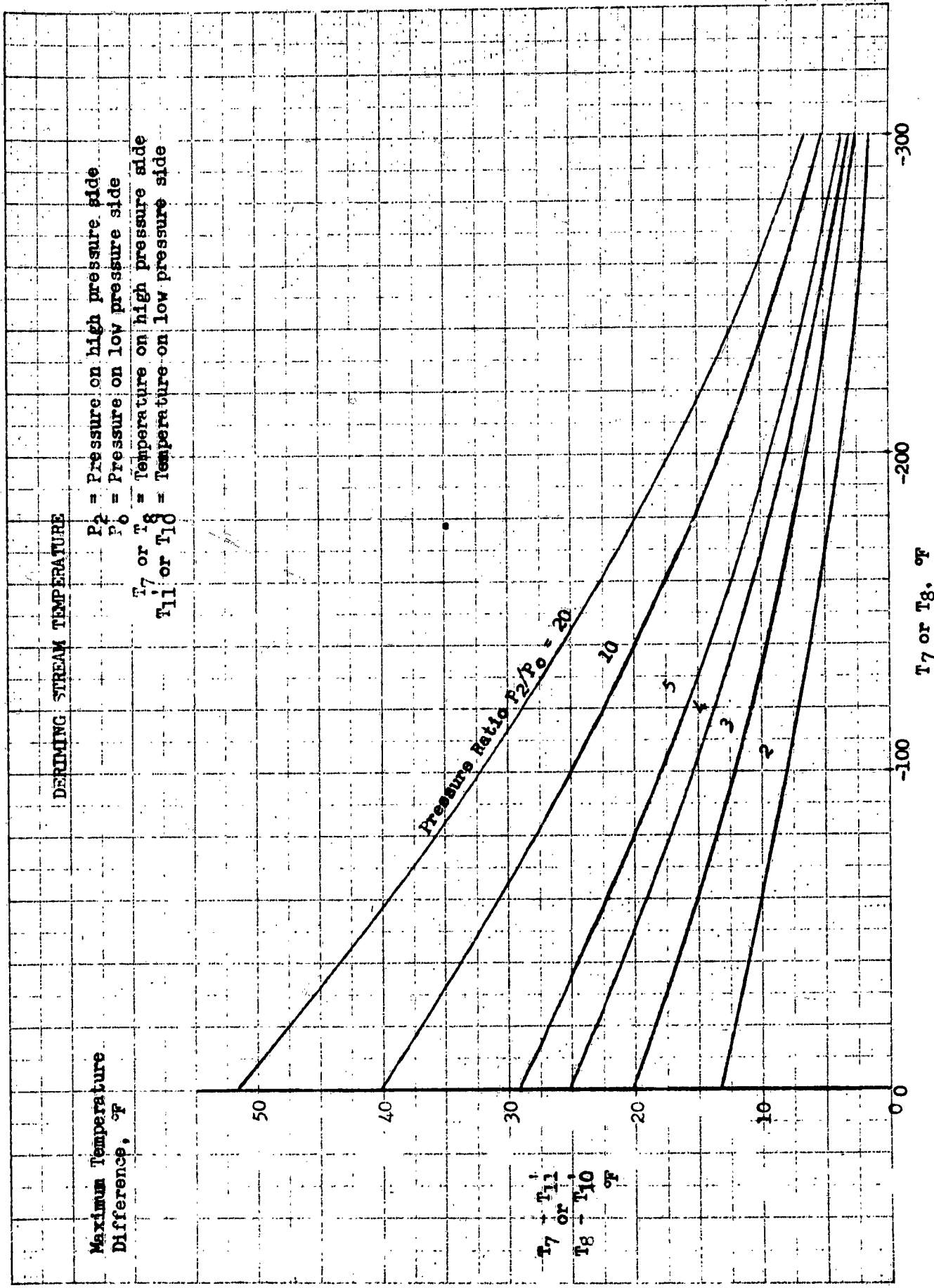


FIG. 24



359-11
 KEUFFEL & ESSER CO.
 10 N. 1st to the E. 12th. 5th floor
 MADE IN U.S.A.

FIG. 25

HEAT EXCHANGER DERIVING

Basis: Initial CO_2 Content of Air is 1%
100% CO_2 in Deriving System

P_1 : High pressure in operating part of cycle

P_2 : Low pressure in deriving part of cycle

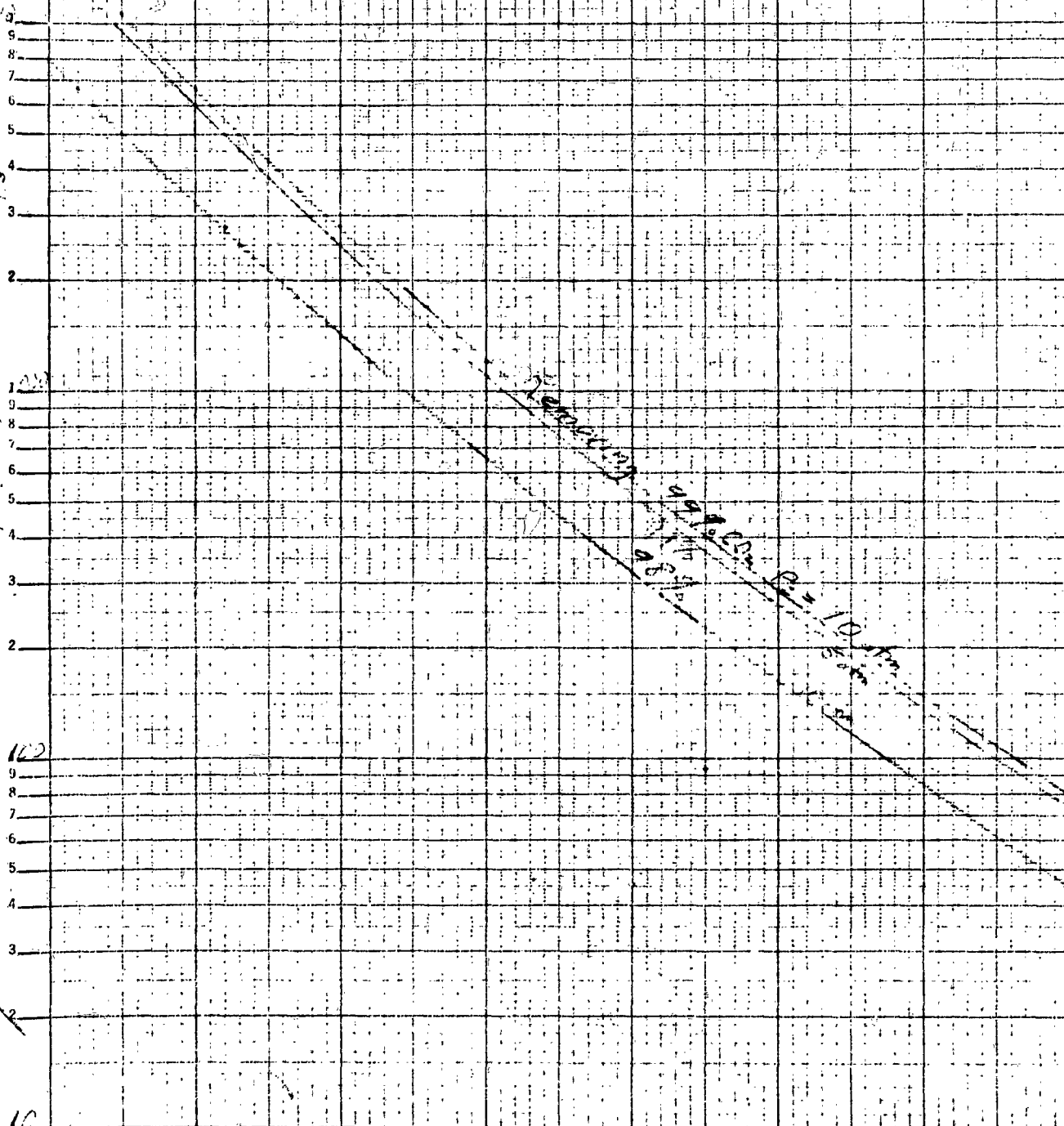
T_8 : Coldest end of CO_2 exchanger operating section

T_7 : Minimum temp. for deriving part of cycle

Parameters: Pressure P_2

: % CO_2 removal

Small Inverted, 4 Cycles X 10 to the inch.
MADE IN U.S.A.



Temp. Rise $T_8 - T_7$

CO₂ FREEZE-OUT METHOD

Total Enthalpy of Air Stream

Basis: Initial Air Stream

500#/hr (7.06 # H₂O, 7.59 # CO₂)H of air stream entering H.E. 3 at $T_5 = 90^\circ\text{F}$ H of air stream leaving H.E. 3 at $T_6 = 35^\circ\text{F}$ (assuming H₂O is present as vapor at $T_{13} = 80^\circ\text{F}$)H of air stream leaving H.E. 3 and entering H. E. 4 at $T_6 = 35^\circ\text{F}$ H of air stream leaving H.E. 4 at T_7 (assuming rime is present as a vapor at T_{12})H of air stream leaving H. E. 4 and entering H.E. 5 at T_7 H of air stream leaving H.E. 5 and entering expansion engine (92% CO₂ removed)H of air stream leaving H.E. 5 and entering expansion engine (99% CO₂ removed)Enthalpy, H, - Btu/hr $\times 10^{-3}$

Pressure - atm.

MADE IN U.S.A.

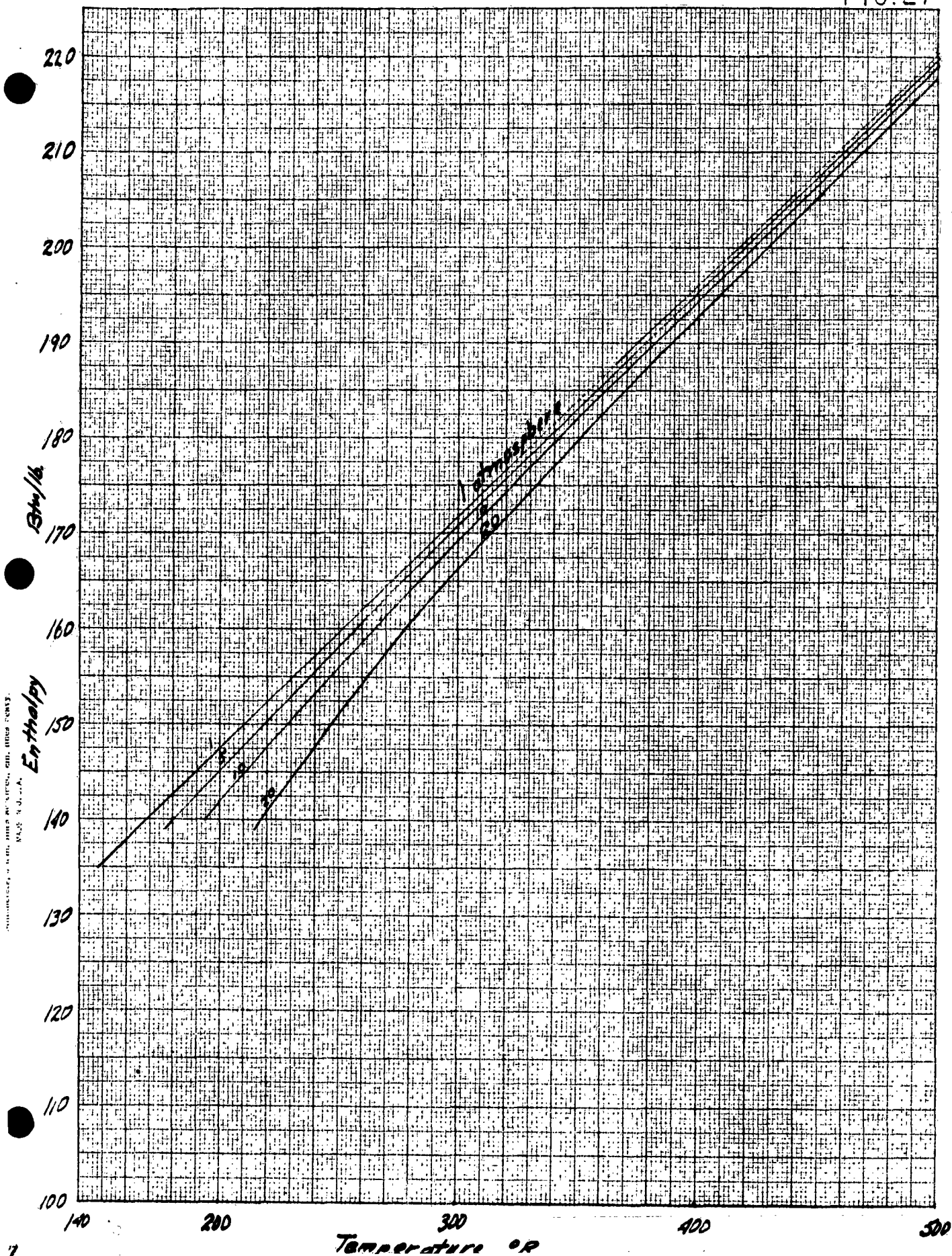


FIG. 28

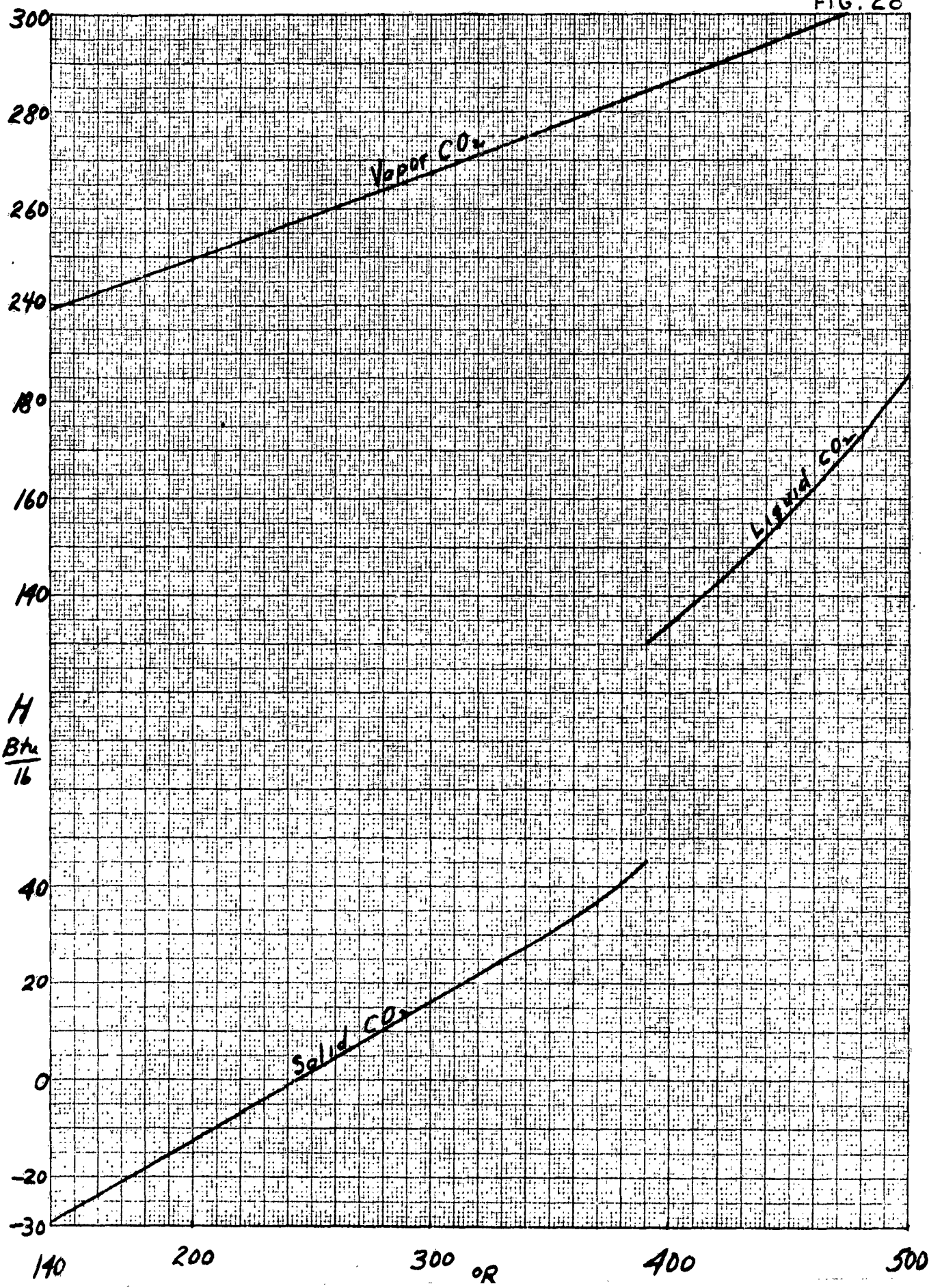
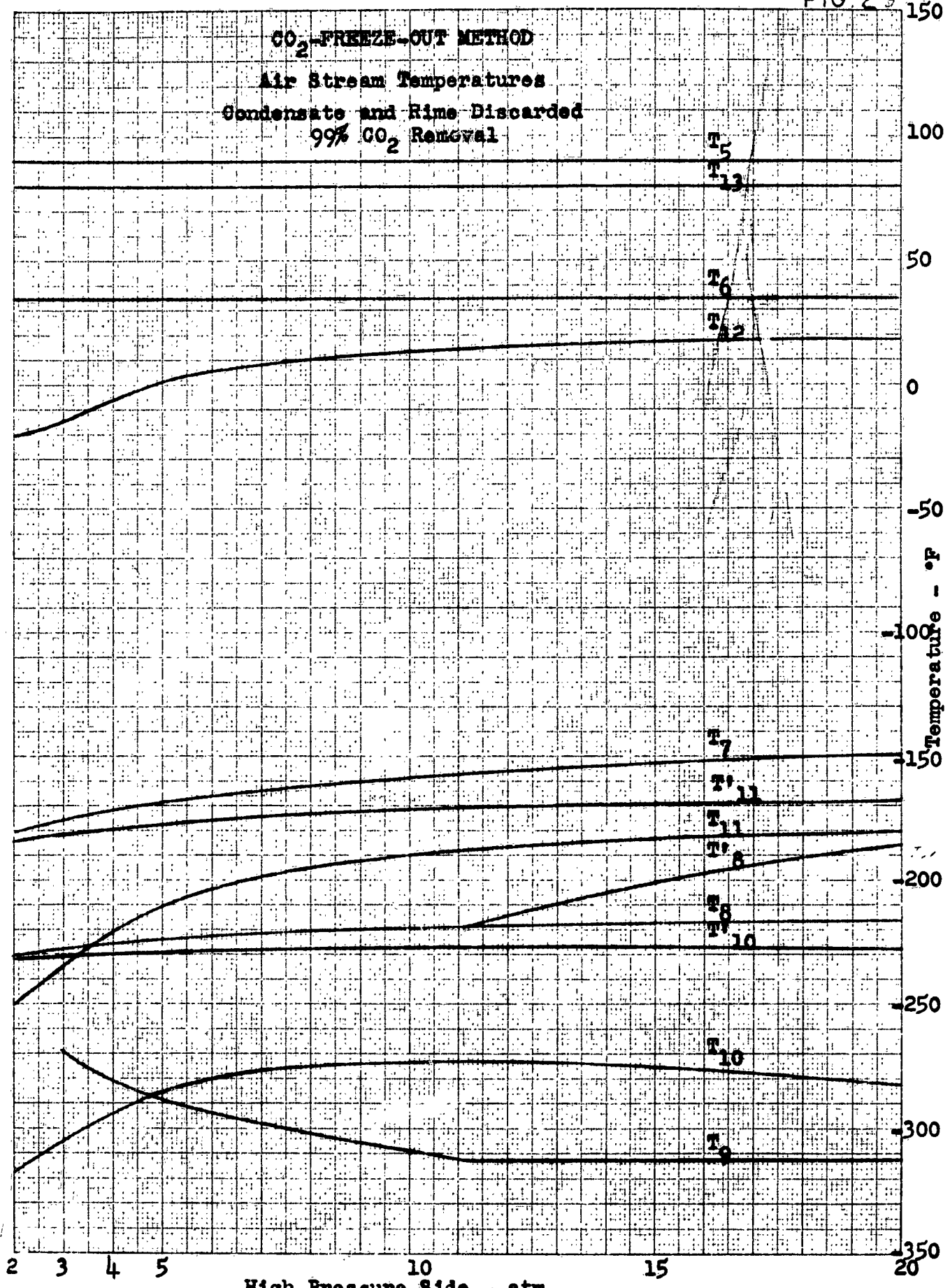


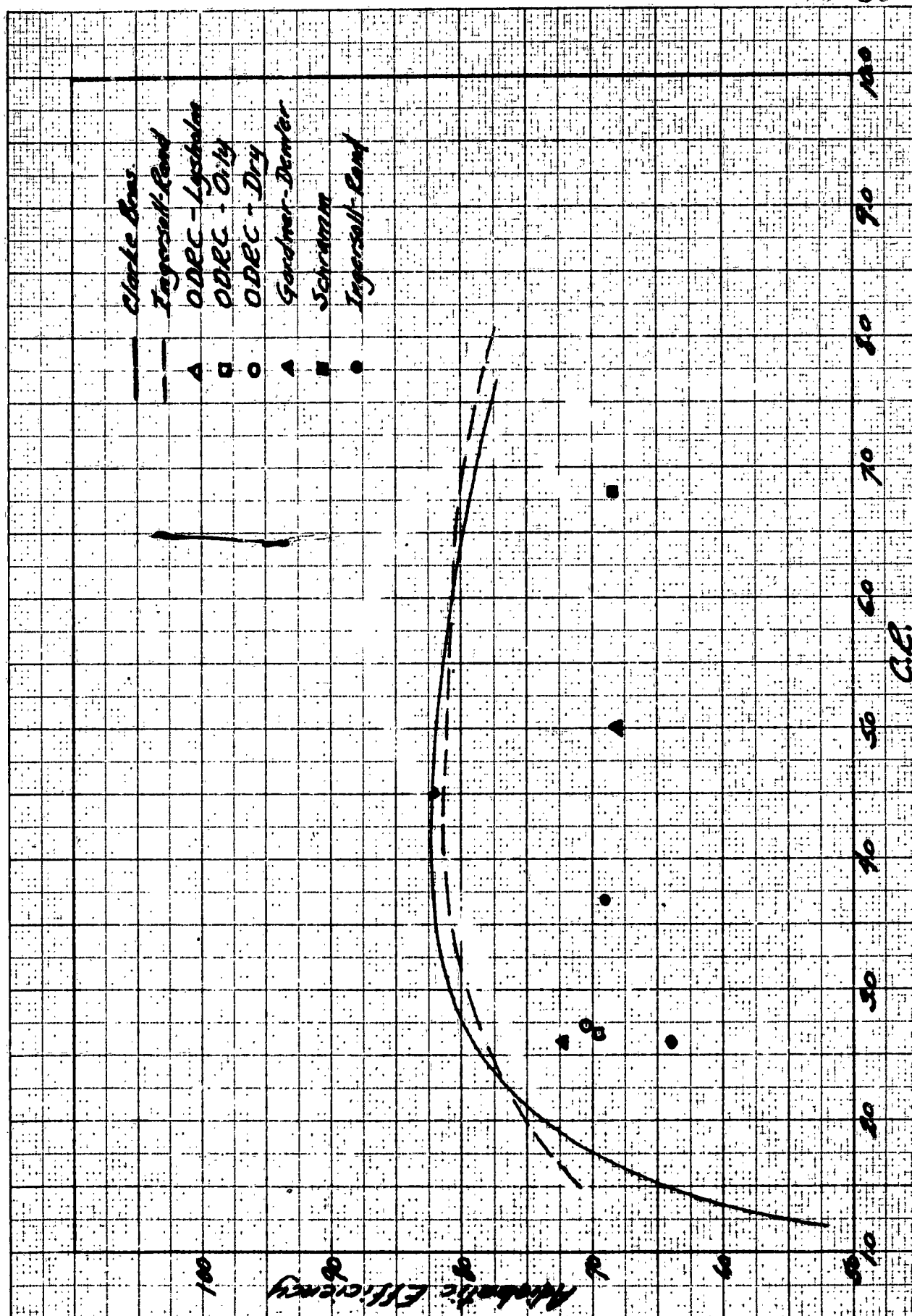
FIG. 29

CO₂-FREEZE-OUT METHOD
Air Stream Temperatures
Condensate and Rime Discarded
99% CO₂ Removal



Millimeters - mm. in. - centimeters - cm. in. - inches - in.

FIG. 30



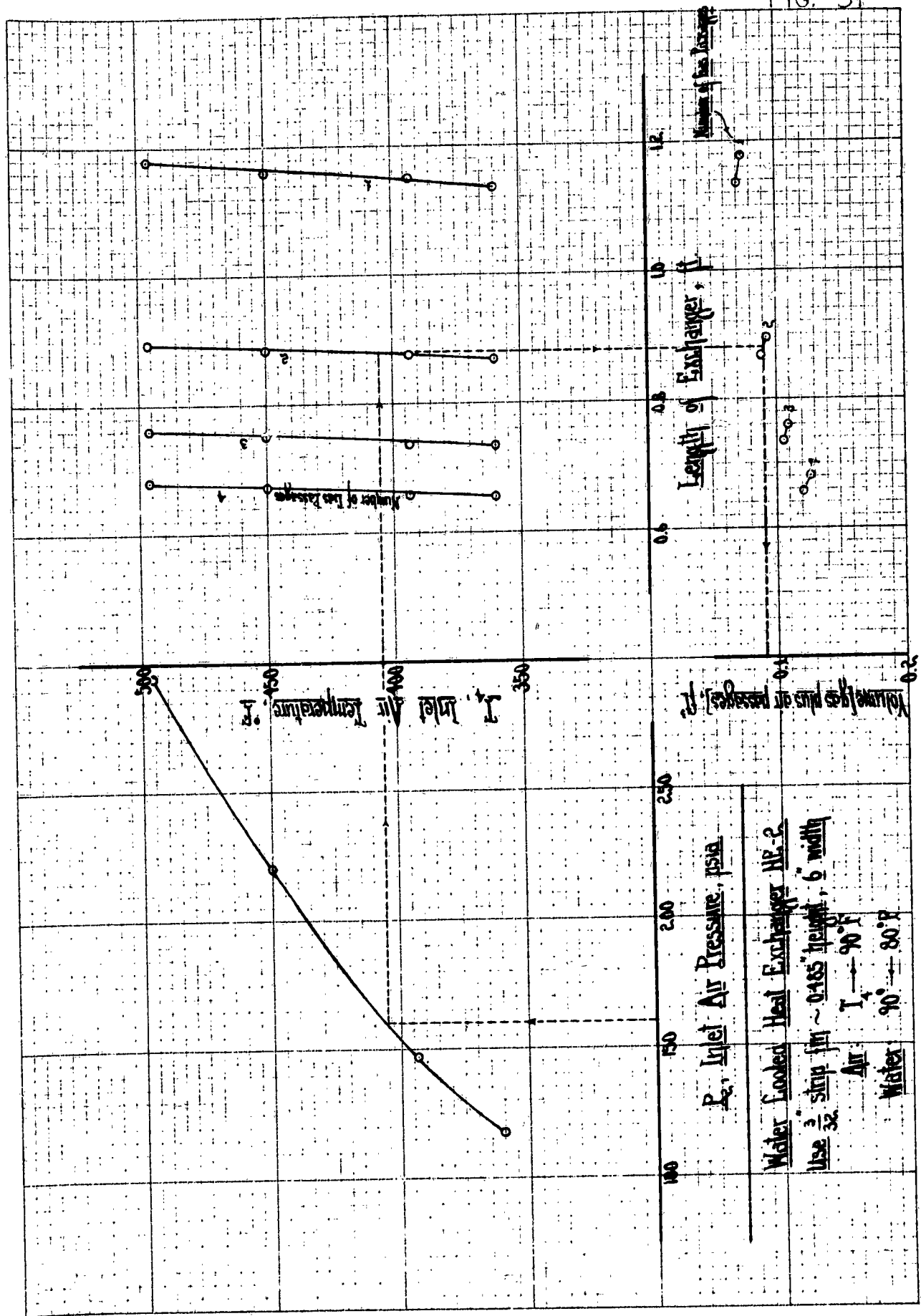


FIG. 31

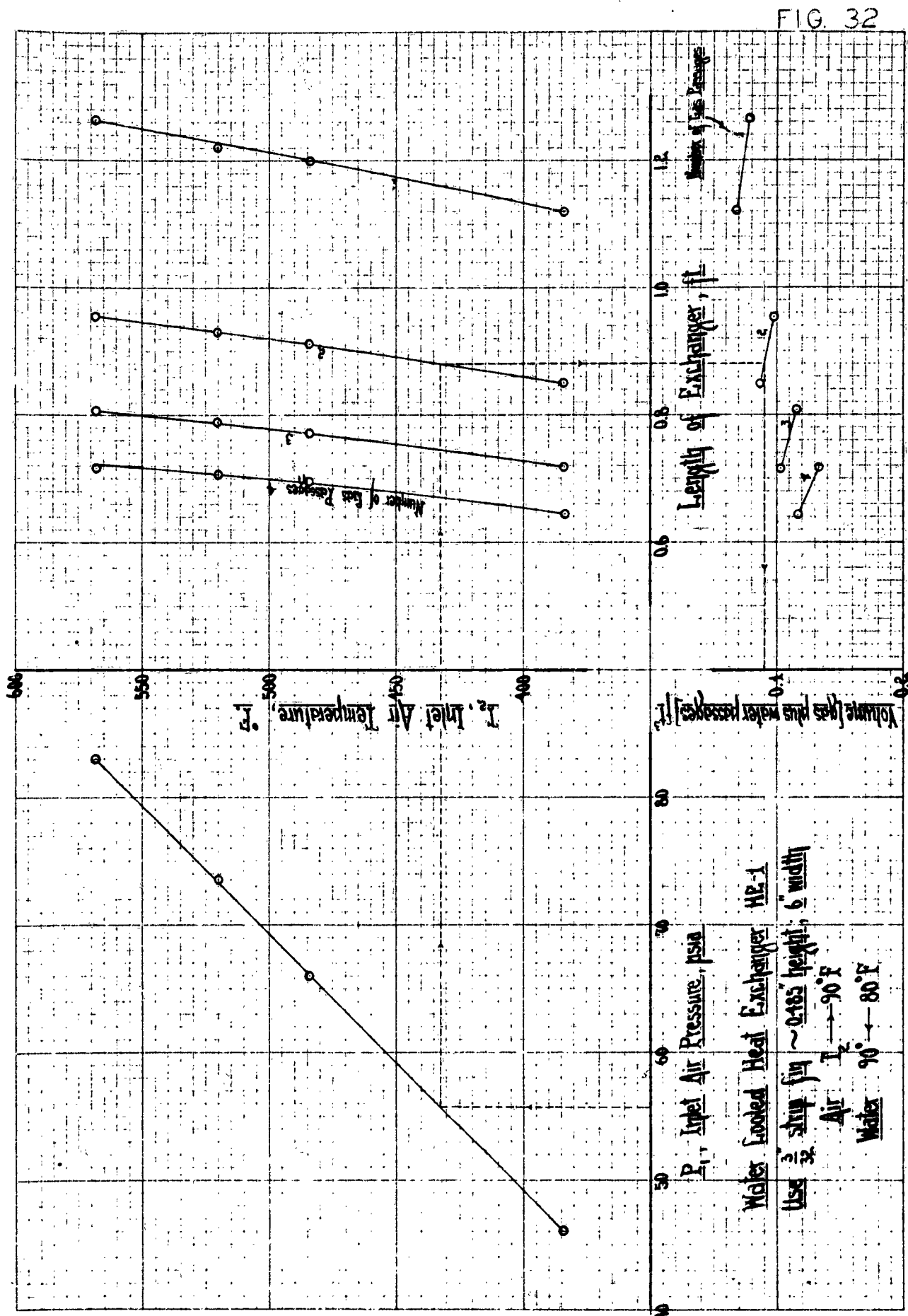
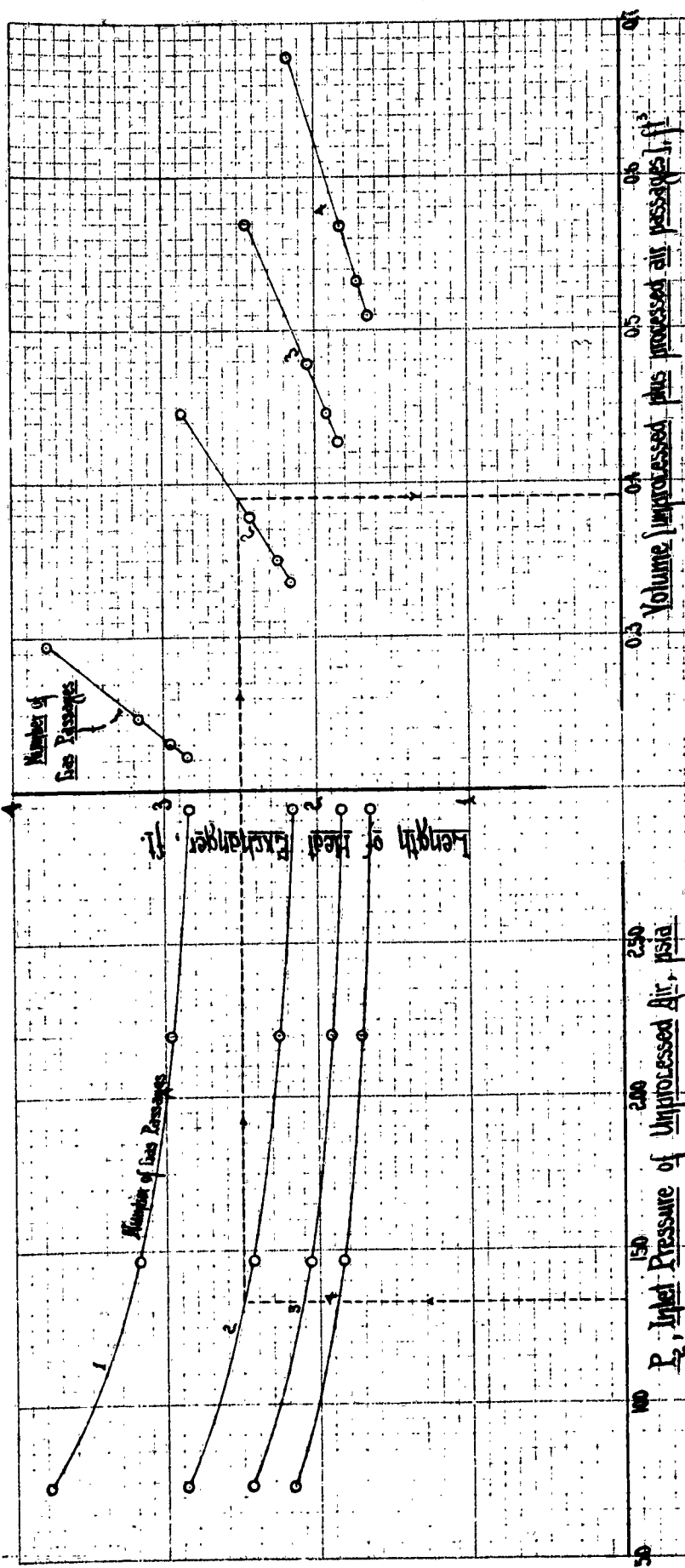


FIG. 32



Air to Air Heat Exchanger HE-3

$\frac{3}{32}$ strip fin, height 0.185, width 12"

Warm Side (unprocessed air)

Cold Side (processed air)

$T_1 = 90^\circ\text{F}$ --- $T_2 = 35^\circ\text{F}$

$T_3 = 80^\circ\text{F}$ --- $241 \leq T_4 \leq 250^\circ\text{F}$

Volume (unprocessed plus processed air) passages, ft³

FIG 33

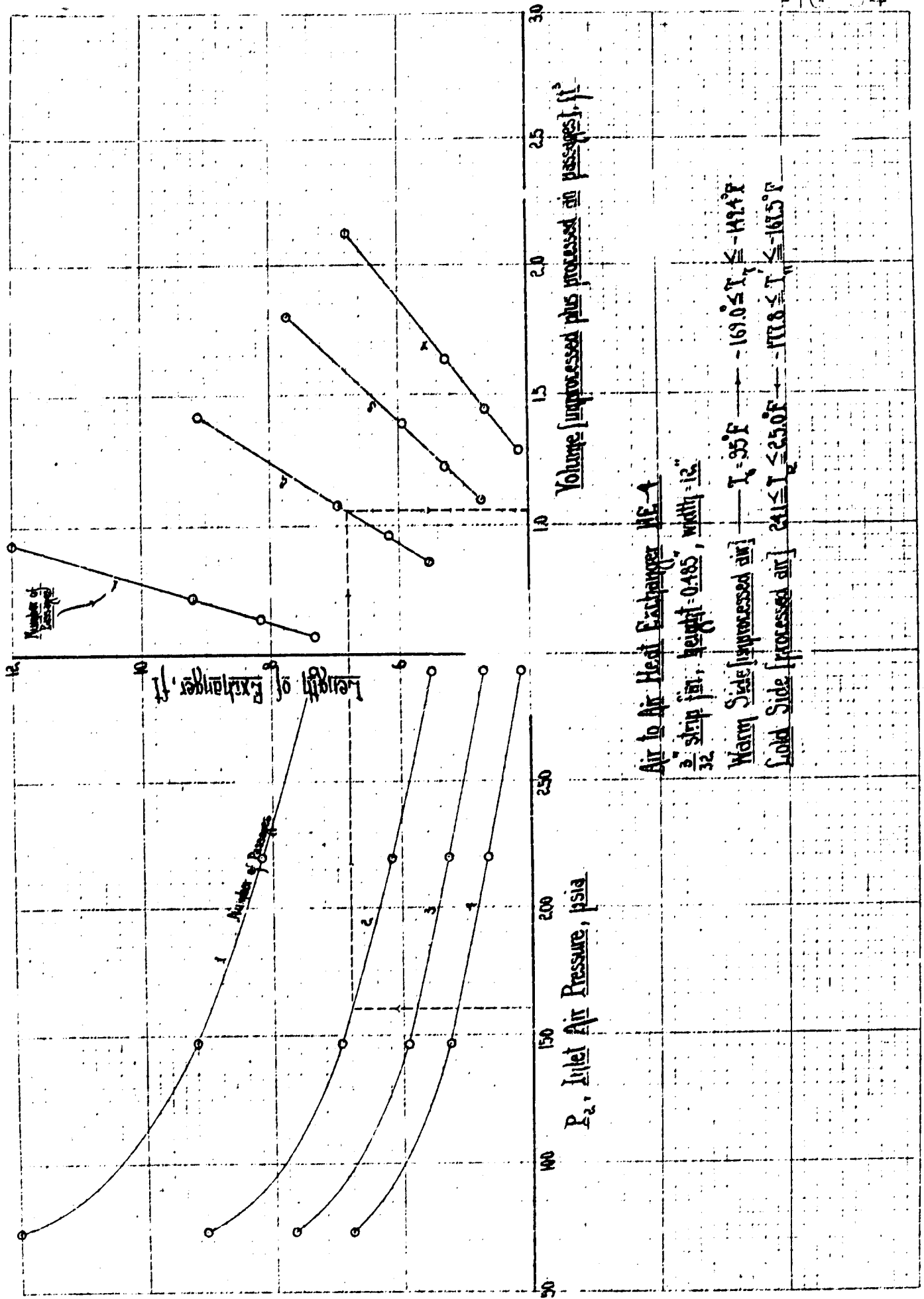


FIG. 34

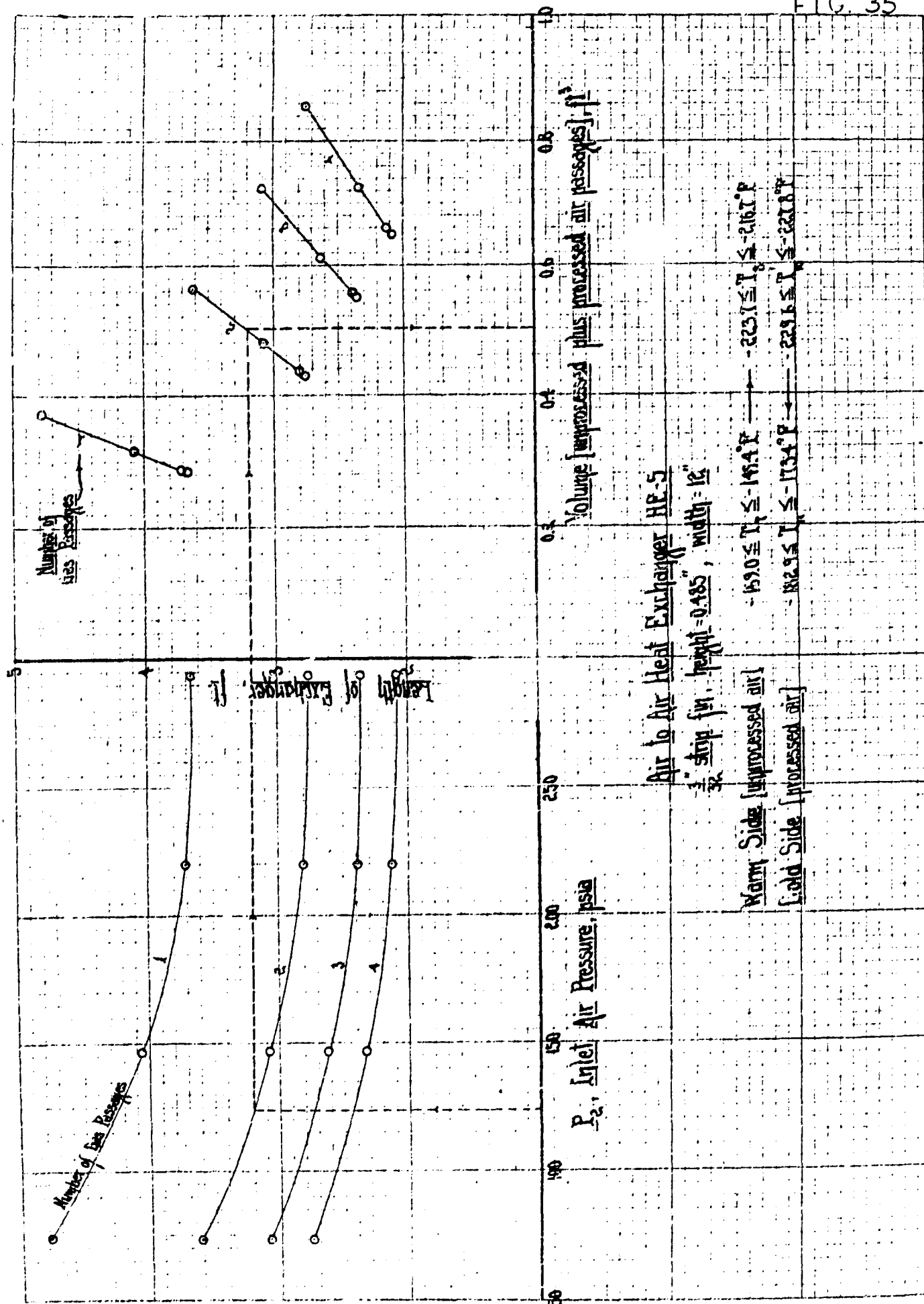


FIG. 35