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CONTINUOUS MASS DIFFUSION IN A
NATURAL CONVECTION COLUMN

by

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	iii
LIST OF FIGURES	vi
LIST OF TABLES	viii
STATEMENT OF THE PROBLEM	ix
INTRODUCTION	1
MASS DIFFUSION	3
Fundamental Concepts	3
Theoretical Relationships	8
Single-Stage Separation Factor	12
Column Process	13
Transport Equation	13
Longitudinal Diffusion Term	15
Determination of $(y^{II}-y^I)$	17
Transport Equation Neglecting Thermal Diffusion .	20
Consideration of Thermal Diffusion	23
Thermal Diffusion in Column Operation	25
Column Effects	27
Varying Convective Streams	30
Back Diffusion into Vapor-Tube	31
THE HYDRODYNAMICAL PROBLEM	35
Velocity Profiles in Column Operation	42
Annular Velocity Profiles	44
Case I, Discussion	46
Case II, Discussion	46
Case III, Discussion	51
Density Gradient	52
EXPERIMENTAL APPARATUS AND EXPERIMENTAL PROCEDURES	55
Column I, Description	55
Column II, Description	61
Auxiliary Equipment	63
Feed and Product Gas Handling	63
Vapor Supply	65
Gas Analysis	67
Cooling System	69
Operational Procedure	70
Comments on Column Operation	74
Calibrations and Materials	76
EXPERIMENTAL RESULTS	79
Data	79
Calculations on Experimental Results,	
Helium-Methane System, Column I	93
Possible Manner of Column Operation, Discussion	97
Varying Convection Streams	102
Back Diffusion into Vapor-Tube	104

TABLE OF CONTENTS (CONT'D)

Air Separation	106
Helium-Oxygen Separation	107
Results of Column II	109
Over-all Transport Coefficient	113
SUMMARY AND CONCLUSIONS	117
FUTURE RESEARCH	121
APPENDIX	125
Table II	127
Table III	128
Table IV	129
Solutions for Enriching Section Transport Equation .	130
NOTATION	133
LITERATURE CITED	137

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Cross Section of Single-Stage Mass Diffusion Unit.	4
2	Cascade of Mass Diffusion Stages	5
3	Schematic Drawing of a Mass Diffusion Column	7
4	Total Composition Profile in a Single-Stage Mass Diffusion Unit	11
5	Vapor-Free Composition Profile in a Single-Stage Mass Diffusion Unit	11
6	Material Balance in a Differential Length of Column.	18
7	Convection Currents Between Hot and Cold Walls	38
8	Effect of the Constant x_0 on Convection Velocity Profile.	41
9	Effect of Material Balance Considerations on Convection Velocity Profile	43
10	Cylindrical Coordinate System.	45
11	Comparison of Velocity Profiles in Cylindrical and Cartesian Coordinates.	47
12	Effect of Transverse Flow on Velocity Profiles.	50
13	Schematic Flow Sheet of Experimental Equipment	56
14	Column I	58
15	Column II.	62
16	Thermal Conductivity Cell Calibration Curve.	78
17	Helium-Methane Separations - Column I.	81
18	Helium-Methane Separations - Column I.	82
19	Helium-Methane Separations - Column I.	83
20	Helium-Methane Separations - Column I.	84
21	Helium-Methane Separations - Column I.	85
22	Helium-Methane Separations - Column I.	86

LIST OF FIGURES (CONT'D.)

<u>Figure</u>		<u>Page</u>
23	Air Separation - Column I.	87
24	Helium-Oxygen Separations - Column I	88
25	Helium-Methane Separation - Column II.	89
26	Effect of Feed Rate on Separation in Column I.	91
27	Effect of Rate of Flow Through Column I on Its Separation	92
28	Vapor-Tube Pressure Drop	100
29	Comparison of Helium-Methane and Helium-Oxygen Separations.	108
30	Graphical Presentation of Equation (113) for the Helium-Methane System.	112
31	Over-All Transport Coefficient	115

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Key to Figures 17 Through 22, Helium-Methane Separations - Column I	80
II	Experimental Data and Calculations, Column I	127
III	Experimental Data, Column II	128
IV	Annulus Temperature of Column I.	129

STATEMENT OF THE PROBLEM

The separation of a gas mixture can be effected by the difference of the diffusivities of its components relative to an auxiliary, condensible vapor. This process, called mass diffusion, can be performed in various column-type apparatus, operating in different ways. This research was undertaken to investigate the separation that could be obtained from the continuous operation of a mass diffusion column that relied entirely upon thermal convection to produce the necessary countercurrent circulation within the column. Little data are available on the mass diffusion process, and none for a column operating by thermal convection alone.

Two columns were constructed and operated under controlled conditions to determine the effect that the operating variables had upon the resultant separation. These variables were: feed rate, products rate and ratio, vapor rate and temperature, and the cold wall temperature. Using steam as the condensible vapor, three gas systems were investigated: helium-methane, helium-oxygen, and nitrogen-oxygen.

INTRODUCTION

The three principal methods for separating gases by diffusion are thermal diffusion, gaseous diffusion,¹ and mass diffusion.² As Benedict³ points out, thermal diffusion has been used for small-scale separation of isotopes and for large-scale partial separation of uranium isotopes; its commercial utility being limited, however, by its comparatively low separation factor and poor thermal efficiency. Gaseous diffusion has been used to a marked success for large-scale separation of uranium isotopes; its commercial application to other separations having been limited by the requirements of a large number of high compression ratio gas compressors and large areas of special diffusion membranes. In brief, thermal diffusion is the process whereby a concentration gradient is set up in a gas mixture as a result of a temperature gradient in the gas. Gaseous diffusion is the process whereby a concentration difference is set up on opposite sides of a fine-pored membrane because of differences in the rates of the components in effusing through the membrane.

Mass diffusion, on the other hand, at the time this investigation was begun, had had few laboratory or commercial applications.⁴ Nevertheless, it has many advantages compared to thermal or gaseous diffusion which might cause it to be the preferred operation for certain separations. It has the highest separation factor of all diffusion

¹ Often termed "gaseous effusion".

² Often termed "atmolysis".

³ Literature cited will be found in the Appendix: Benedict (1).

⁴ After the experimental work for this paper had been well under way, a paper describing experimental work on mass diffusion by a "sweep diffusion" (liquid curtain) method was published: (3).

separation operations, and is more efficient than thermal diffusion, although not so efficient as gaseous diffusion. In addition, the equipment is of very simple construction, requiring no special pumps or membranes, and its operation is under more moderate conditions.

Mass diffusion is the process whereby a concentration gradient is established in a gas mixture due to the differences of the diffusivities of the component gases with regards to an auxiliary condensible vapor. After this preferential diffusion is established, the vapor effecting it is condensed and removed from the system.

In this research the mass diffusion process was investigated under conditions of continuous column operation, with the movement of the gases within the column being governed by natural convection. The binary gas systems of helium-methane, helium-oxygen, and oxygen-nitrogen were used, with steam as the separating vapor. The essential variables of operation were: gas feed rate, vapor rate and temperature, condenser temperature, and the ratio of top to bottom product withdrawal.

MASS DIFFUSION

Fundamental Concepts

Figure 1 shows the bare essentials of a single-stage mass diffusion unit. The condensible vapor enters the separating unit at right angles to the flow of the gas passing through.¹ The vapor diffuses across the unit through the gas mixture and condenses on the opposite wall. Two product streams are withdrawn from the unit; one near the vapor entry surface, and the other near the vapor condensing surface. The stream nearest the vapor entry surface is enriched with the gas component whose diffusivity through the vapor is greater than that of the other component:² The component enriching itself at the vapor entry surface is termed the "more diffusible" component of the two gases.

Although a readily condensible vapor is certainly the easiest handled separating agent, any material that can be removed from the gaseous system by processes such as adsorption, freezing, absorption, or chemical reaction could be used.

In general, the separation accomplished in a single-stage unit is very small and not too useful. However, the enrichment can be greatly increased, either by connecting many such units in cascade (Figure 2), or as was done in this research, by causing the two product streams to flow countercurrent to each other in a column-type process.

¹ Throughout this paper the term "vapor" will be used to denote the condensible vapor (steam in this research), and "gases" will denote the mixture or individual gases being separated.

² This research concerns itself with only binary gas mixtures, but a multicomponent mixture could be used with similar results.

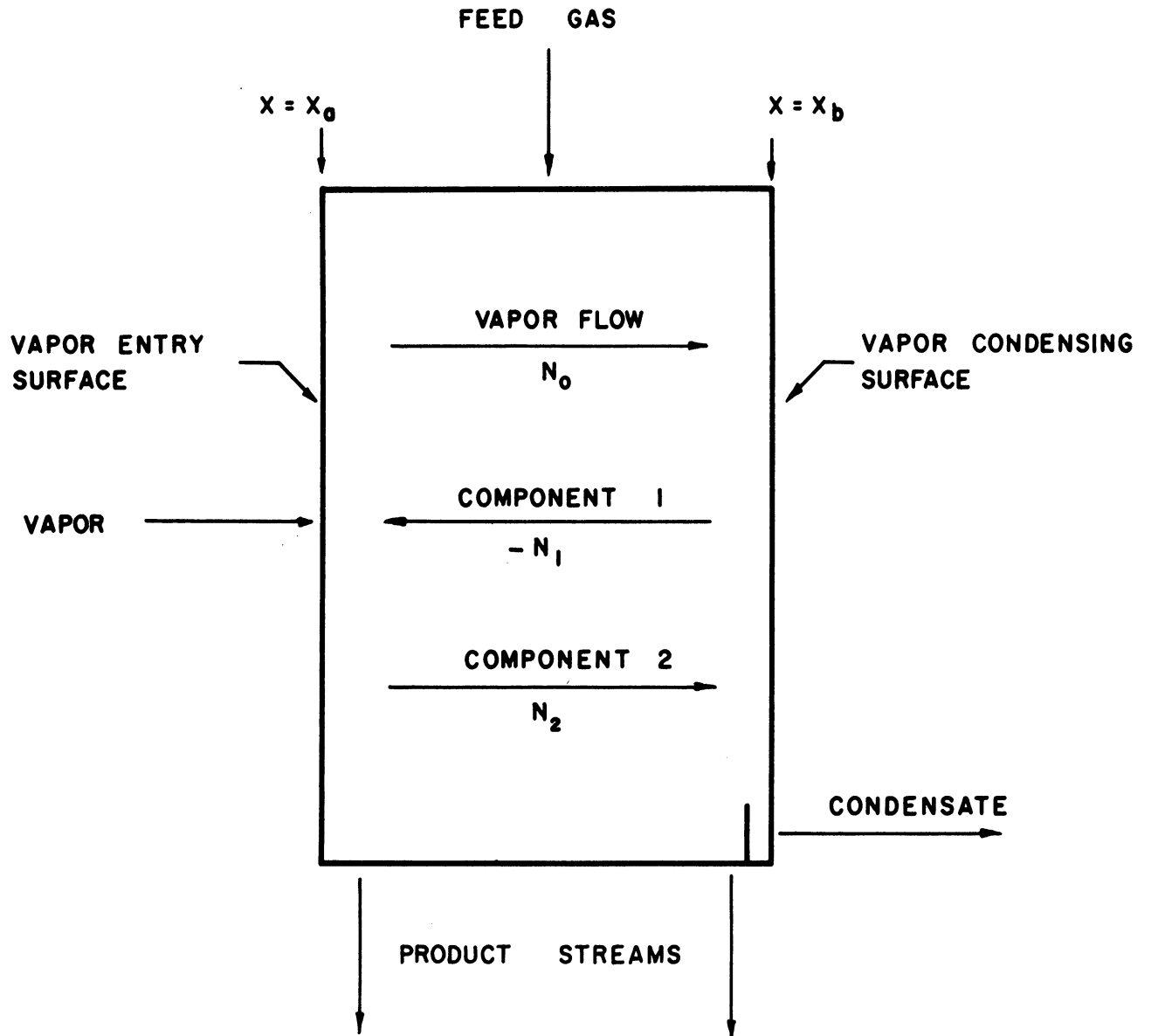


FIG 1 CROSS SECTION OF SINGLE-STAGE
MASS DIFFUSION UNIT

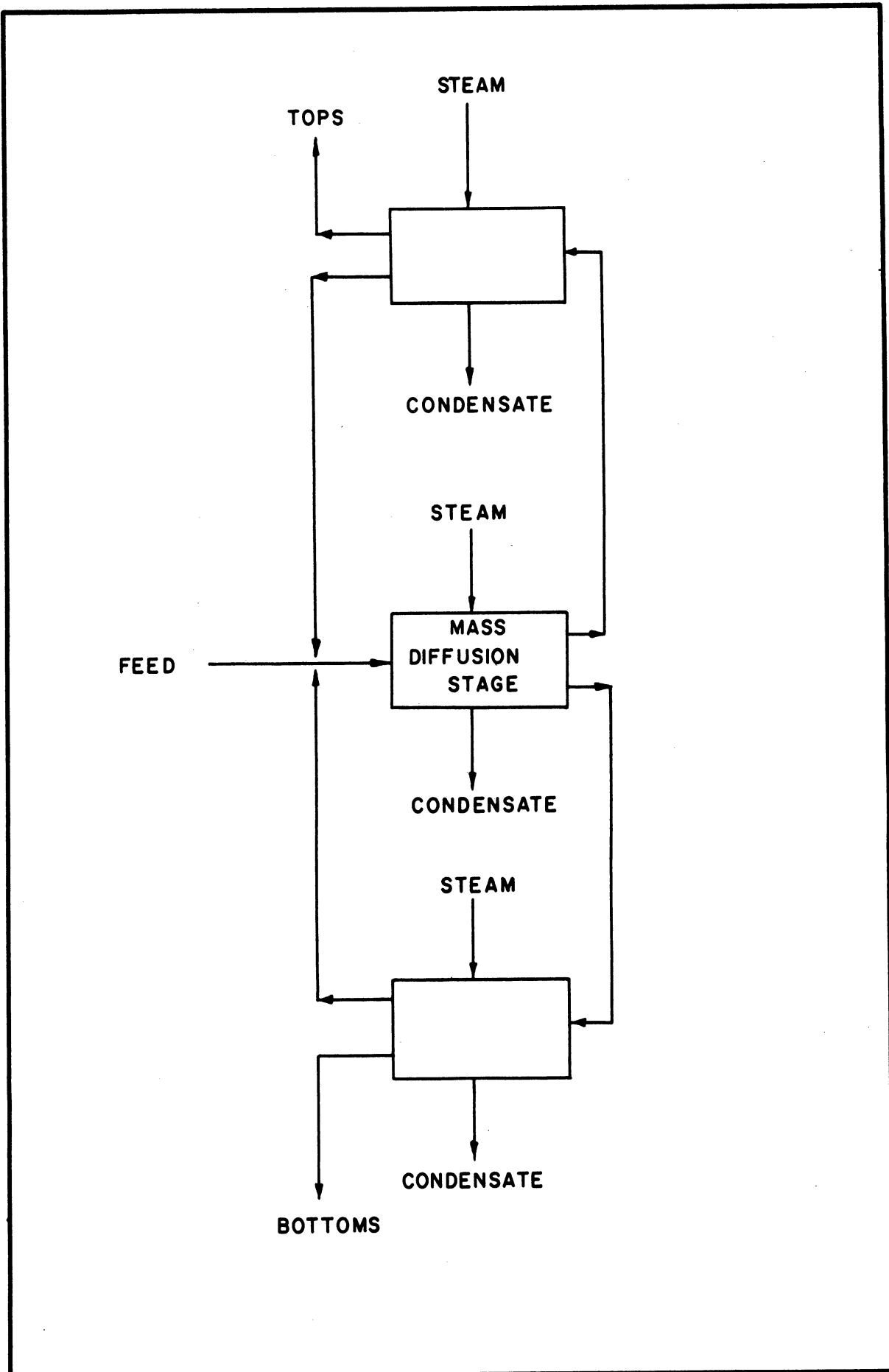


FIG 2 CASCADE OF MASS DIFFUSION STAGES

One of several devices may be employed to produce the desired countercurrent flow of the streams: a porous barrier between them and positive displacement, a mechanical escalator, a liquid stream flowing down the condensing surface and producing a drag effect, and natural convection as used here. Figure 3 is a schematic drawing of a mass diffusion column operating as a stripping column. There is no distinct reason for the column being circular in cross-section other than the ease of fabrication.

The column shown has a porous vapor-tube as its central member with a condenser concentrically surrounding it. The annular space between the condenser and the vapor-tube being the region where the gas separation is effected. The feed gas is introduced into the column by means of a circular distributor at the top of the column near the condensing surface. The top product, enriched in the more diffusible gas, is withdrawn through a circular intake at the top of the column near the vapor entry surface. The bottom product is withdrawn from the lower end of the column, as is the condensed vapor.

During the operation of the column, the following actions take place:

The condensible vapor enters the vapor-tube and diffuses radially outwards to condense on the condenser surface. This is assumed to happen without causing undue turbulence in the annular separating zone. The condensate forming on the vertical walls runs down to the bottom of the column and is withdrawn.

The hot surface of the vapor entry tube, and the relatively cooler surface of the condenser, being vertical and parallel to each other act to produce convection currents between them: a rising stream adjacent to the vapor-tube and a descending stream adjacent to the condenser wall. Because of the cross-flowing vapor, the gas stream flowing upward near the vapor-tube is continually being enriched with the more diffusible components as it passes up the column.

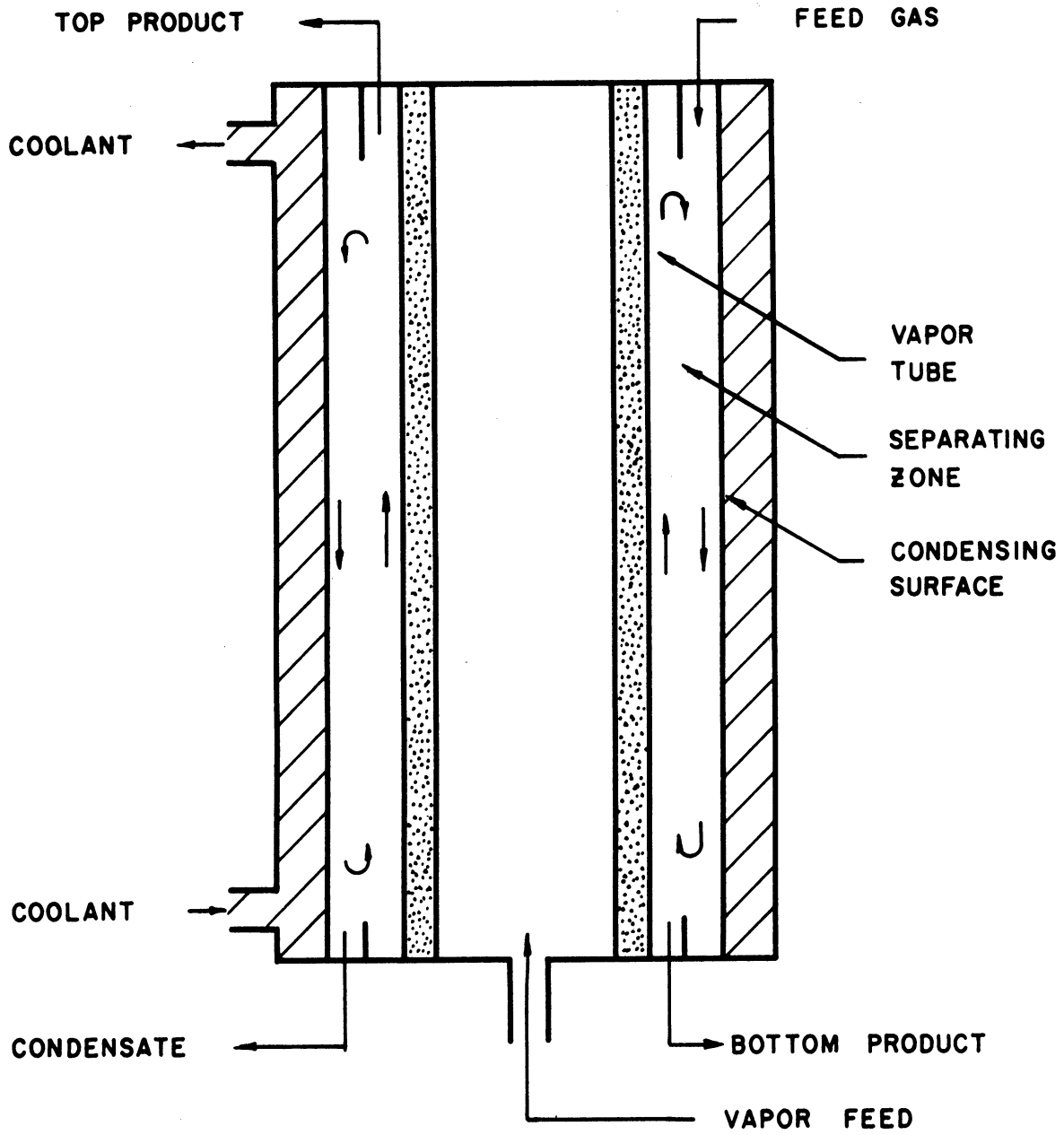


FIG. 3 SCHEMATIC DRAWING OF A
MASS DIFFUSION COLUMN

Similarly, the down-flowing gas stream near the condenser surface is being continually enriched with the less diffusible component as it flows down the column. These countercurrent streams tend to reverse themselves as they reach their respective ends of the column, thus producing a continual circulation in the annular space.

At the top of the column the top product is withdrawn from the ascending gas stream, while at the same time, the feed gas is being introduced into the descending stream. At the bottom of the column, the bottom product is removed, and the condensate drained off. As in distillation, increasing the length of the column would improve the difference in composition between the two product streams.

There is no reason why the feed gas could not enter the column at any elevation, producing an enriching section above, and a stripping section below this point.

Theoretical Relationships

The first equations to consider are those for the concentration profiles in a single stage mass diffusion stage.¹ The theory has been restricted to the separation of a binary mixture by means of a single condensible vapor, and it is assumed that the gases obey the perfect gas laws.

The Maxwellian equations for the interdiffusion of three gases are:

$$\frac{\partial p_1}{\partial x} = \frac{RT}{D_{12}P} [N_{2P_1} - N_{1P_2}] + \frac{RT}{D_{01}P} [N_{0P_1} - N_{1P_0}] \quad (1)$$

$$\frac{\partial p_2}{\partial x} = \frac{RT}{D_{12}P} [N_{1P_2} - N_{2P_1}] + \frac{RT}{D_{02}P} [N_{0P_2} - N_{2P_0}] \quad (2)$$

¹ The first derivations in this section follow Bowman's (3), with clarification of equations and additions or omissions as the processes differed.

$$\frac{\partial p_0}{\partial x} = \frac{RT}{D_{01}P} [N_1 p_0 - N_0 p_1] + \frac{RT}{D_{02}P} [N_2 p_0 - N_0 p_2] \quad (3)$$

Consider the single-stage unit of Figure 1. At steady-state there is no flow of gases in the x-direction, or normal to the vapor entry and condensing surfaces. Therefore, setting N_1 and N_2 equal to zero, Equation (1) becomes

$$\frac{\partial p_1}{\partial x} = \frac{p_1 N_0 RT}{D_{01}P} \quad (4)$$

Integration of Equation (4), holding T constant, yields

$$p_1 = p_{1b} e^{\frac{N_0 RT (x - x_b)}{D_{01}P}} \quad (5)$$

Similarly from Equation (2):

$$p_2 = p_{2b} e^{\frac{N_0 RT (x - x_b)}{D_{02}P}} \quad (6)$$

From the perfect gas laws:

$$p_1 = y(P - p_0) \quad (7)$$

$$p_2 = P - p_1 - p_0 \quad (8)$$

$$y_1 = \frac{p_1}{P}, \quad y_2 = \frac{p_2}{P}, \quad y_0 = \frac{p_0}{P} \quad (9)$$

Since all of the gases that enter one end of the stage leave at the other end, by material balance

$$\frac{\int_{x_a}^{x_b} y_1 dx}{\int_{x_a}^{x_b} y_2 dx} = \frac{y_F}{1 - y_F} \quad (10)$$

Substituting Equations (5) and (6) into Equation (9), and the result into Equation (10), yields upon integration and rearranging

$$\frac{P_b}{P_b} = \frac{y_F D_{02} \left(1 - \exp \left[\frac{-N_0 RT (x_b - x_a)}{D_{02} P} \right] \right)}{(1 - y_F) D_{01} \left(1 - \exp \left[\frac{-N_0 RT (x_b - x_a)}{D_{01} P} \right] \right)} \quad (11)$$

where the symbol $\exp(x)$ is the same as e^x .

From Equation (11) the ratio of p_{1_b}/p_{2_b} may be calculated knowing the values of p_{o_b} , P , T , N_0 , D_{01} , D_{02} , and y_F . The value of p_{o_b} is the vapor pressure of the condensate on the condensing surface. Combining this p_{1_b}/p_{2_b} ratio with Equation (8), in which p_{o_b} and P are known, the values of p_{1_b} and p_{2_b} may be determined. These values may then be substituted into Equations (5) and (6) to calculate p_1 and p_2 at any x value, and by the use of Equation (9), mole percent composition profiles may be drawn. Figures 4 and 5 show typical separation profiles on a gas-vapor, and vapor-free basis.

The curves in Figure 5, although apparently straight lines, do have slopes that are functions of x , with inflection points at

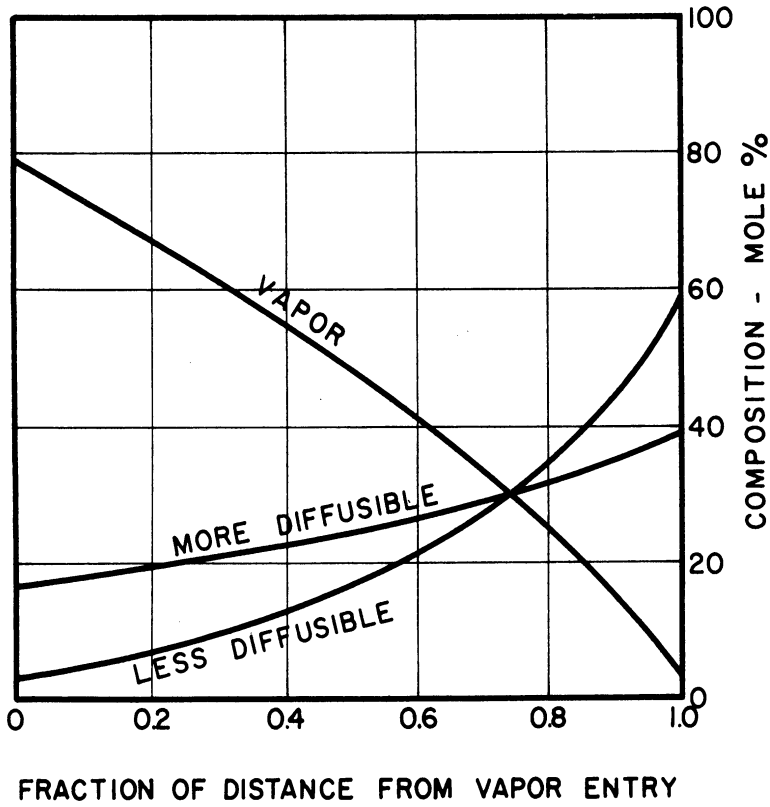


FIG. 4

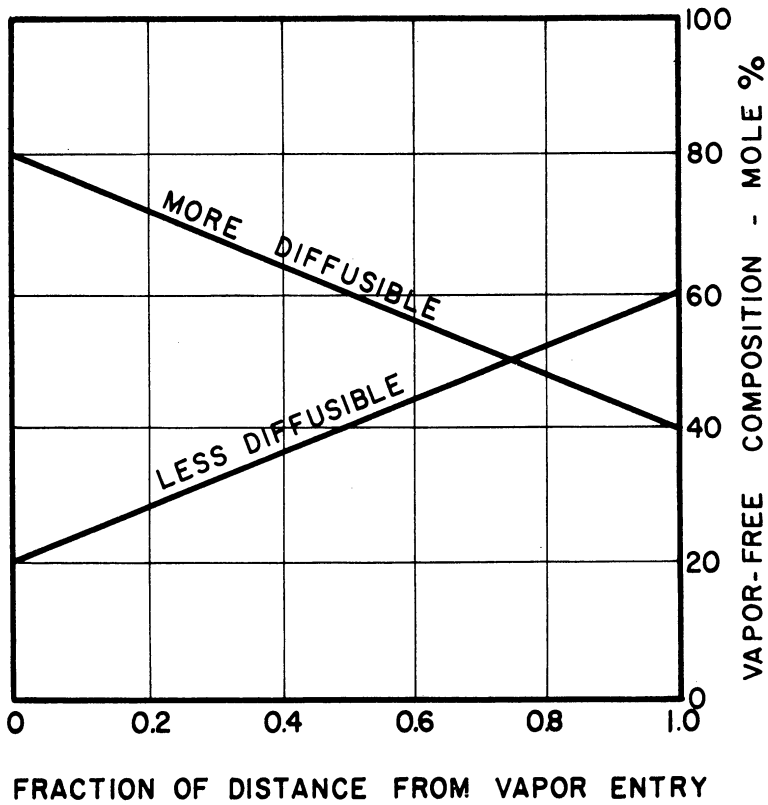


FIG. 5

COMPOSITION PROFILES-SINGLE-STAGE UNIT

their intersection. If the curves do not intersect each other, as would happen when the feed composition was predominantly one gas, they do not have any inflection points, and the curve above $y = 0.5$ is concave downwards, while the curve below $y = 0.5$ is concave upwards.

Single-Stage Separation Factor

The separation factor in gas separation processes is analogous to the relative volatility in distillation, but instead of the mixtures of different compositions being in different phases, as in distillation, they are in different locations. The separation factor in mass diffusion, as well as in thermal diffusion and gaseous diffusion, is the ratio of the more diffusible component of the gas mixture at one location to its mole ratio at another location at steady-state operation. In the single-stage unit, the locations chosen for the separation factor α° , by definition, are the vapor-entry surface and the vapor-condensing surface respectively:

$$\alpha^\circ = \frac{y_a^\circ [1 - y_b^\circ]}{y_b^\circ [1 - y_a^\circ]} \quad (12)$$

Combining Equations (7), (8) and (12) gives

$$\alpha^\circ = \frac{(P_{1a})(P_{2b})}{(P_{1b})(P_{2a})} \quad (13)$$

For steady-state conditions and no concentration gradients parallel to the vapor-entry and vapor-condensing surfaces, letting

$x = x_a$ in Equations (5) and (6) gives respectively the ratios p_{1a}/p_{1b} and p_{2a}/p_{2b} , and putting these results into Equation (13) gives

$$\alpha^o = \exp \left[\frac{(x_b - x_a) N_o RT}{P} \left(\frac{1}{D_{o2}} - \frac{1}{D_{o1}} \right) \right] \quad (14)$$

In as much as there is usually a temperature gradient in the x-direction, the values of diffusivity and temperature should be integrated or averaged for a more accurate evaluation of the separation factor. However, the correction due to the variation of diffusivities and temperature with x is normally so small as to be of negligible importance. The correction of the separation factor due to the superimposed effect of thermal diffusion is also small, and generally in a direction as to give a better separation than if it were not present. The thermal diffusion effect in column operation will be considered in the derivation of the transport equation.

In actual operation of a single-stage unit as shown in Figure 1, the effluent streams would not have compositions equal to y_a^o and y_b^o , but compositions equal to the values of y integrated over regions near the boundaries of the stage. If the stage were long enough, the separation would have been essentially completed before the streams reached their exits, and the condition of no concentration gradients parallel to the vapor and condensing surfaces would hold true.

Column Process

Transport Equation

In this section, equations will be derived to indicate what separations might be expected in a simplified mass diffusion column.

The thermal diffusion effect, neglected here, will be considered later. The development of the theory for the mass diffusion process is along the lines used by Jones and Furry (6) in their treatment of thermal diffusion.

In a mass diffusion column operating under steady-state, conditions, a material balance on the more diffusible component of the gas mixture, at any point below the feed point gives

$$B y_B = L y^{II} - V y^I + d_{1z} \quad (15)$$

where, on a vapor-free basis, per unit of time: $B y_B$ is the amount of the more diffusible component being withdrawn from the bottom of the column, $L y^{II}$ is the amount of the component being convected down the column, $V y^I$ is the amount of the component being convected up the column, and d_{1z} is the amount of the component diffusing down the column due to the concentration gradient in the longitudinal, or z-direction.

A material balance on a total gas basis is

$$B = L - V \quad (16)$$

and combining Equation (16) and Equation (15) gives the transport equation

$$B(y_B - y^{II}) = V(y^{II} - y^I) + d_{1z} \quad (17)$$

This transport equation is of little practical value as it stands, and it remains for the succeeding development to transform Equation (17) into variables that can be readily evaluated experimentally, and then to solve the resultant equation, so that it will be

possible to predict the separation expected from a mass diffusion column as a function of its dimensions and operating variables.

Longitudinal Diffusion Term

Under ordinary operating conditions the longitudinal diffusion is negligible, and its approximation is sufficient.

Taking z positive up the column

$$d_{1z} = -N_{1z} \bar{E} (x_b - x_a) \quad (18)$$

N_{1z} may be evaluated from Equation (1) by replacing x by z, setting N_{0z} equal to zero, and letting $N_{1z} = -N_{2z}$:

$$N_{1z} = \frac{P}{RT \left[\frac{1}{D_{12}} + \frac{P_0}{(P-P_0)D_{01}} \right]} \frac{dp_1}{dz} \quad (19)$$

Taking p_0 at a constant average value \bar{p}_0 , substitution of Equation (19) into Equation (18) gives

$$d_{1z} = \frac{(x_b - x_a) \bar{E} P}{RT \left[\frac{1}{D_{12}} + \frac{\bar{P}_0}{(P-\bar{P}_0)D_{01}} \right]} \frac{dy}{dz} \quad (20)$$

where it is now necessary to evaluate \bar{p}_0 .

As the absolute magnitudes of the net horizontal flow of the component gases are much smaller than the horizontal flow of the vapor, Equation (3) with N_1 and N_2 set equal to zero may be used to evaluate the partial pressure of the vapor at any x:

$$\frac{dp_0}{dx} = \frac{-N_0 RT}{P} \left[\frac{p_1}{D_{01}} + \frac{p_2}{D_{02}} \right] = - \frac{N_0 RT (P-P_0)}{P} \left[\frac{y}{D_{01}} + \frac{1-y}{D_{02}} \right] \quad (21)$$

The average value of p_0 being

$$\bar{p}_0 = \frac{1}{x_b - x_a} \int_{x_a}^{x_b} p_0 dx \quad (22)$$

and yields upon integration

$$\bar{p}_0 = P - \frac{P - p_{0b}}{t(x_b - x_a)} \left[1 - e^{s(x_a - x_b)} \right] \quad (23)$$

where

$$t = \frac{N_0 RT}{P} \left[\frac{\bar{y}}{D_{01}} + \frac{1 - \bar{y}}{D_{02}} \right] \quad (24)$$

and \bar{y} is the average value of the composition of the products.

The final result is

$$d_{12} = K_d \frac{dy}{dz} \quad (25)$$

where

$$K_d = \frac{(x_b - x_a) \bar{E} P}{RT \left[\frac{1}{D_{12}} + \frac{P - p_{0b}}{t(x_b - x_a)} \frac{1 - \exp t(x_a - x_b)}{P - p_{0b}} \right]} \quad (26)$$

Determination of $(y^{II} - y^I)$

From Figure 5 it can be seen that the values of y and $(1-y)$ are essentially linear functions of x . Assuming that the convective flow in the column operation does not alter this linearity, there is the equation

$$y^{II} - y^I = 0.5(x_b - x_a) \frac{dy}{dx} \quad (27)$$

Here it is assumed that the average stream compositions may be taken at points $0.5(x_b - x_a)$ cm apart. The accuracy of this assumption depends upon the form and symmetry of the velocity profiles, and will be investigated in the section covering the hydrodynamical problems involved.

Now the problem is to evaluate dy/dx . Solving Equation (7) for y and differentiating with respect to x :

$$\frac{dy}{dx} = \frac{1}{P - P_0} \left[\frac{dP_1}{dx} + y \frac{dP_0}{dx} \right] \quad (28)$$

Substituting the values of $\frac{dP_1}{dx}$ and $\frac{dP_0}{dx}$ from Equations (1) and (3) into Equation (28) and rearranging:

$$\begin{aligned} \frac{dy}{dx} = \frac{RT}{P} & \left(N_0 \left[\frac{1}{D_{01}} - \frac{1}{D_{02}} \right] [1 - y] y \right. \\ & + N_1 \left[\frac{1}{D_{12}} + \frac{P_0}{(P - P_0) D_{01}} \right] [y - 1] \\ & \left. + N_2 \left[\frac{1}{D_{12}} + \frac{P_0}{(P - P_0) D_{02}} \right] y \right) \end{aligned} \quad (29)$$

Referring to Figure 6, a vapor-free material balance on a differential length of column at steady-state yields

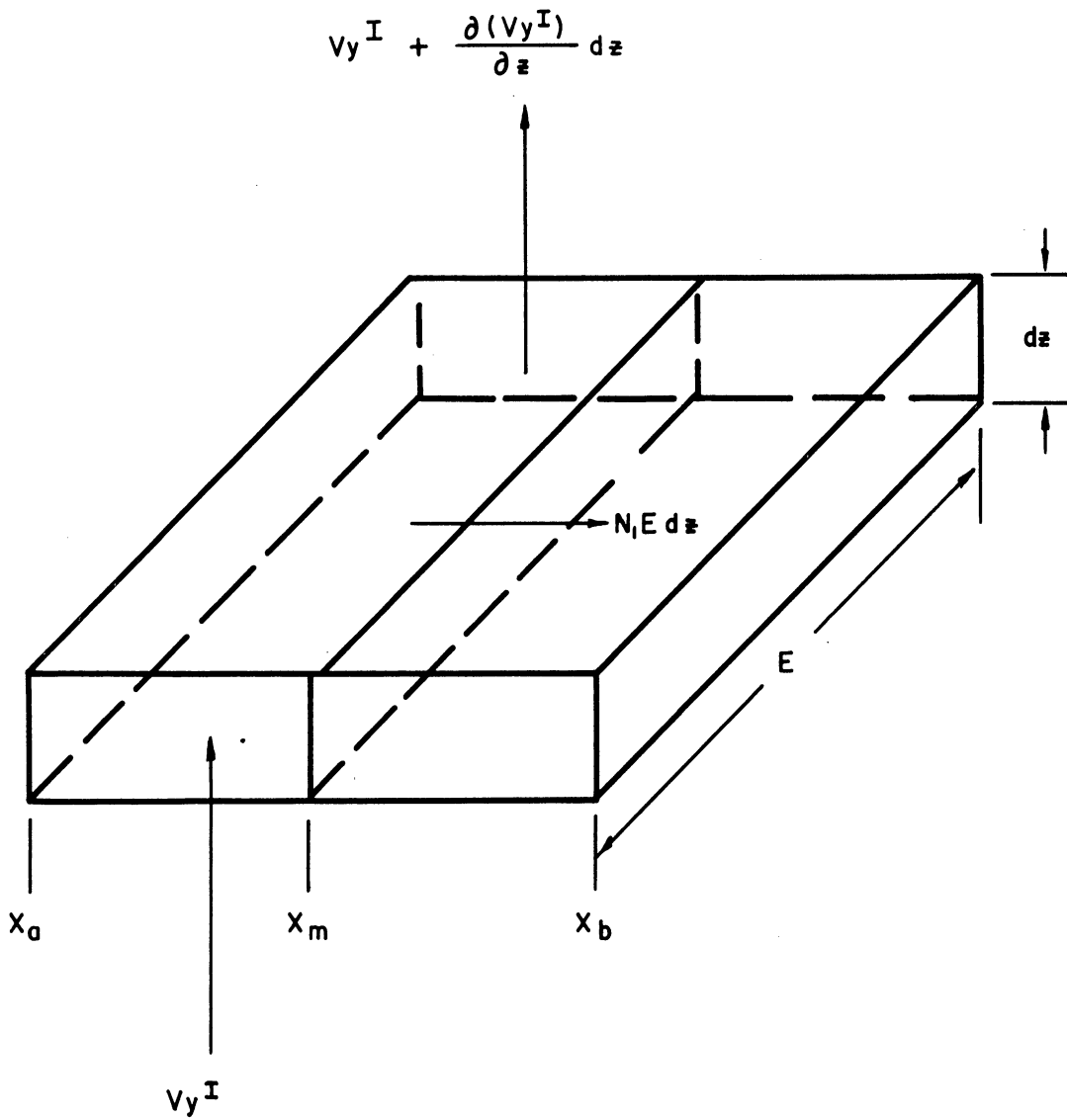


FIG 6 MATERIAL BALANCE IN A DIFFERENTIAL LENGTH OF COLUMN

$$N_1 = -\frac{1}{E} \left[y^I \frac{dV}{dz} + V \frac{dy^I}{dz} \right] \quad (30)$$

and

$$N_2 = \frac{1}{E} \left[(y^I - 1) \frac{dV}{dz} + V \frac{dy^I}{dz} \right] \quad (31)$$

Substituting the values of N_1 and N_2 from Equations (30) and (31) into Equation (29) and regrouping gives

$$\begin{aligned} \frac{\partial y}{\partial x} = \frac{RT}{EP} \left(N_0 \left[\frac{1}{D_{01}} - \frac{1}{D_{02}} \right] [1-y] y \right. \\ \left. + V \left[\frac{1}{D_{12}} + \frac{P_0}{P-P_0} \left(\frac{1-y^I}{D_{01}} + \frac{y^I}{D_{02}} \right) \right] \frac{dy^I}{dz} \right) \quad (32) \\ \left. + \left[\frac{y^I - y}{D_{12}} + \frac{P_0}{P-P_0} \left(\frac{y^I(y-1)}{D_{01}} + \frac{y(y^I-1)}{D_{02}} \right) \right] \frac{dV}{dz} \right) \end{aligned}$$

At any elevation in the column, the value of $\partial y/\partial x$ is relatively small, and y may be substituted for y^I in Equation (32), but the values of y^I will be used as the limits for the final integration in the z direction. In addition, if the streams in the column are constant, the value of $\partial V/\partial z$ is zero, and Equation (32) reduces to

$$\begin{aligned} \frac{\partial y}{\partial x} = \frac{RTN_0}{P} \left[\frac{1}{D_{01}} - \frac{1}{D_{02}} \right] [1-y] y \\ + \frac{RTV}{PE} \left[\frac{1}{D_{12}} + \frac{P_0}{P-P_0} \left[\frac{1-y}{D_{01}} + \frac{y}{D_{02}} \right] \right] \frac{dy}{dz} \quad (33) \end{aligned}$$

Substituting the value of $\partial y/\partial x$ from Equation (27) into Equation (33) gives

$$y^{\text{II}} - y^{\text{I}} = \frac{RTN_0(x_b - x_a)}{2P} \left[\frac{1}{D_{01}} - \frac{1}{D_{02}} \right] [1 - y]y$$

$$+ \frac{RTV(x_b - x_a)}{PE} \left[\frac{1}{D_{12}} + \frac{p_0}{P - p_0} \left[\frac{1-y}{D_{01}} + \frac{y}{D_{02}} \right] \right] \frac{dy}{dz} \quad (34)$$

Transport Equation Neglecting Thermal Diffusion

Equations (25) and (34) may now be substituted into Equation (17) to give

$$B(y_B - y^{\text{II}}) = -H_s(1-y)y + (K_d + K_c) \frac{dy}{dz} \quad (35)$$

where

$$H_s = \frac{RTN_0(x_b - x_a)}{2P} \left[\frac{1}{D_{02}} - \frac{1}{D_{01}} \right] \quad (36)$$

and

$$K_c = \frac{RTV^2(x_b - x_a)}{2PE} \left[\frac{1}{D_{12}} + \frac{p_0}{P - p_0} \left[\frac{1-y}{D_{01}} - \frac{y}{D_{02}} \right] \right] \quad (37)$$

Then Equation (35) may be written in the form

$$\frac{dy^{\text{II}}}{dz} = \frac{B(y_B - y^{\text{II}}) + H_s(1-y)y}{K} \quad (38)$$

where $K = K_c + K_d$.

The value of y incorporated in K is taken as the average value between the composition at the feed point and in the bottom product. The error introduced by this assumption is very small, as the changes of y produce relatively small changes in K , especially at low values of p_0 . Thus H_s and K may be treated as constants during the integration of Equation (38).

Equation (38) is a first-order, first-degree differential equation whose variables are separable, and can be integrated when written in the form of

$$\frac{dy}{ny_B + y(1-n) - y^2} = \frac{H_s}{K} dz \quad (39)$$

where $n = B/H_s$. (40)

Using the boundary conditions

$$\text{at } z = 0, \quad y = y_F \quad (41)$$

$$\text{at } z = -Z_s, \quad y = y_B$$

the exact solution is

$$\tanh \frac{b'H_s Z_s}{2K} = \frac{b'(y_F - y_B)}{y_B + y_F - n(y_F - y_B) - 2y_B y_F} \quad (42)$$

$$\begin{aligned} b' &= [(1-n)^2 + 4ny_B]^{1/2} \\ &= [(1+n)^2 - 4n(1-y_B)]^{1/2} \end{aligned} \quad (43)$$

The following approximate solutions may also be obtained:

For $0.3 < y < 0.7$

$$y_F - y_B = \frac{H_s}{4B} \left(1 - \exp \frac{-BZ_s}{K} \right) \quad (44)$$

For $y \ll 1$

$$y_B = \frac{y_F(n-1)}{n - \exp[Z_s(H_s+B)/K]} \quad (45)$$

For $(1-y) \ll 1$

$$y_B = 1 - \frac{(1-y_F)(1+\eta)}{\eta + \exp[-Z_s(H_s+B)/K]} \quad (46)$$

For total reflux, where B is zero, Equation (39) integrates to

$$\frac{y_B(1-y_F)}{y_F(1-y_B)} = \exp[-H_s Z_s / K] \quad (47)$$

Similar equations may be obtained for conditions above the feed point if the column is operated with a rectifying section. These equations are given in the Appendix.

The above equations show the separation that might be expected from a mass diffusion column as related to its dimensions and operating variables. In a properly designed column the feed is introduced into a stream of equal composition. When the column is operating as a stripper, the feed is introduced at the top of the column into the down-flowing stream; this stream having just reversed itself after some of it was removed as the top product. The value of y_D can be obtained from the material balance, $D y_D = F y_F - B y_B$. This is all true for $V = D$ at the top of the column, but for $V \neq D$, the situation is somewhat changed. If $V > D$, then the actual value of the feed composition, y_F^* , entering the column separating length is greater than that entering the column; $y_F^* = (V y_F^I - B y_B) / L$. When $V < D$, then the composition of the top product removed from the column, y_D , is lower than the top product being produced in the column, y_D^* ; $y_D^* = (L y_F - B y_B) / V$.

Consideration of Thermal Diffusion

The theory involved in the study of thermal diffusion is very complex, and only a few of the simplest cases have been solved. Even in these, approximations have to be made to be able to solve the differential equations.

The phenomenon of thermal diffusion consists of the fact that a temperature gradient in a mixture of two gases gives rise to a gradient of the relative concentrations of the constituent gases. Provided that the mixture as a whole is at rest, the equilibrium concentration gradient is such, that the effect of the thermal diffusion is just balanced by the re-mixing effect of ordinary diffusion.

The equation for ordinary steady-state diffusion is

$$c_1(\vec{v}_1 - \vec{v}) = -D_{12} \text{grad } c_1 \quad (48)$$

where v is the velocity of the gas as a whole.

The existence of thermal diffusion makes it necessary to add another term to Equation (48), so that it becomes

$$c_1(\vec{v}_1 - \vec{v}) = -D_{12} \text{grad } c_1 + (D_T/T) \text{grad } T \quad (49)$$

where D_T is the coefficient of thermal diffusion.

For present purposes it is sufficient to consider diffusion in the x-direction only, and Equation (49) may be rewritten

$$c_1(v_1 - v) = -D_{12} \frac{dc_1}{dx} + \frac{D_T}{T} \frac{dT}{dx} \quad (50)$$

Unlike the coefficient of ordinary diffusion D_{12} , which at first approximation is independent of the concentrations c_1 and c_2 , ($c_2 = 1 - c_1$), the coefficient of thermal diffusion is proportional to

the product $c_1 c_2$. Therefore another quantity, the thermal diffusion constant α_T is introduced, and is related to D_T by

$$D_T = D_{12} c_1 c_2 \alpha_T \quad (51)$$

The constant α_T is independent of pressure and may be positive or negative; when it is positive, as is almost always the case, the lighter gas is concentrated in the hotter zone. When α_T is negative the heavier gas concentrates in the hotter zone. Grew (4) gives a very good discussion of this inverse diffusion effect, as well as a good summary on thermal diffusion as a whole.

Another quantity found in the literature of thermal diffusion is the thermal diffusion ratio k_T ,

$$k_T = \frac{D_T}{D_{12}} \quad (52)$$

The separation that thermal diffusion can effect in the absence of convection currents, is analogous to the separation obtainable by mass diffusion in a single-stage unit. Writing Equation (50) in terms of α_T :

$$c_1(v_1 - v) = D_{12} \left[\alpha_T c_1 c_2 \frac{\partial \ln T}{\partial x} - \frac{\partial c_1}{\partial x} \right] \quad (53)$$

In the final equilibrium state, not only is $v = 0$ (no convection currents), but also $v_1 = 0$ (steady-state) and Equation (53) reduces to

$$\alpha_T c_1 c_2 \frac{\partial \ln T}{\partial x} = \frac{\partial c_1}{\partial x} \quad (54)$$

Remembering the $c_2 = (1 - c_1)$, and assuming that α_T is independent of temperature, Equation (54) can be integrated:

$$\ln \left[\frac{c_1}{c_2} \right] = \alpha_T \ln T + \text{constant} \quad (55)$$

As in mass diffusion, the relative concentration ratios at the two different locations, a and b, are used to define the separation factor α_T^0 , and the constant of integration drops out to give

$$\alpha_T^0 = \frac{[c_1/c_2]_a}{[c_1/c_2]_b} = \left[\frac{T_a}{T_b} \right]^{\alpha_T} \quad (56)$$

By means of Equation (56), knowing the value of α_T and the temperatures at the two different points in a gas mixture, the difference in compositions at these two points may be calculated. As with mass diffusion, this is the maximum separation obtainable unless cascading or countercurrent operations are employed.

Thermal Diffusion in Column Operation

The application of thermal diffusion, as regards isotope separation, is very well covered by Jones and Fury (6). The main adjustment that would have to be made in applying their derived equations to non-isotopic systems, would be the correction in densities due to concentration gradients.

To include the effect of thermal diffusion in a mass diffusion column, the partial pressure gradients that exist have to be corrected for the thermal diffusion effect. Rewriting Equation (54) in terms of mole fractions gives

$$\frac{\alpha_T y(1-y)(P-P_0)^2}{P} \frac{d \ln T}{dx} = \frac{d p_1}{dx} \quad (57)$$

Therefore, Equations (1) and (3) may be extended to give:

$$\begin{aligned} \frac{\partial p_1}{\partial x} = & \frac{RT}{D_{12}P} [N_2 P_1 - N_1 P_2] + \frac{RT}{D_{01}P} [N_0 P_1 - N_1 P_0] \\ & + \frac{\alpha_{T12} y(1-y)(P-p_0)^2}{P} \frac{\partial \ln T}{\partial x} \\ & + \frac{\alpha_{T10} y P_0 (P-p_0)}{P} \frac{\partial \ln T}{\partial x} \end{aligned} \quad (58)$$

and

$$\begin{aligned} \frac{\partial p_0}{\partial x} = & \frac{RT}{D_{01}P} [N_1 P_0 - N_0 P_1] + \frac{RT}{D_{02}P} [N_2 P_0 - N_0 P_2] \\ & + \frac{\alpha_{T01} y P_0 (P-p_0)}{P} \frac{\partial \ln T}{\partial x} \\ & + \frac{\alpha_{T02} P_0 (1-y)(P-p_0)}{P} \frac{\partial \ln T}{\partial x} \end{aligned} \quad (59)$$

The values of α_{T12} are positive if component 1 concentrates in the hotter zone, and it is understood that $\alpha_{T12} = -\alpha_{T21}$.

To isolate the effect of thermal diffusion in the mass diffusion column, Equations (58) and (59) are treated in the same manner as Equations (1) and (3) were in the previous derivations: substituted into Equation (28), letting $N_1 = -N_2$, combining the result with Equation (27) and the combined result substituted into Equation (17). The transport equation thus obtained, including the effect of thermal diffusion, is

$$\begin{aligned} B(y_B - y^A) = & -H_S (1-y)y + K \frac{dy}{dz} \\ - & \frac{(X_b - X_a) V y(1-y) [P_0 (\alpha_{T10} - \alpha_{T20}) + (P-p_0) \alpha_{T12}]}{2P} \frac{\partial \ln T}{\partial x} \end{aligned} \quad (60)$$

Making use of the approximation

$$\frac{d \ln T}{dx} = \frac{T_b - T_a}{(x_b - x_a) \bar{T}} \quad (61)$$

where \bar{T} is the arithmetic mean temperature, Equation (60) may be written

$$B(y_B - y^{\text{II}}) = -H(1-y)y + K \frac{dy}{dz} \quad (62)$$

where

$$H = H_S + H_T \quad (63)$$

and

$$H_T = \frac{V(T_b - T_a) [\bar{p}_0(\alpha_{T10} - \alpha_{T20}) + (P - \bar{p}_0)\alpha_{T12}]}{2P\bar{T}} \quad (64)$$

It can be seen that the effect of thermal diffusion is to augment the transport coefficient H_S by the factor H_T . H_T is generally positive and therefore aids in the separation of the gases. To correct the solutions of the transport equation, Equations (42) through (47), for thermal diffusion, the value of H is substituted for H_S . In general, $H_S \gg H_T$, and $H \approx H_S$.

Column Effects

The equations derived up to this point have been straightforward and describe the essence of separation by mass diffusion. However, in the light of the experimental results, two additional factors have to be taken into account to more fully describe mass diffusion in column operation. These factors are 1) "back diffusion" of the gas components into the vapor-tube, and 2) the "turning effect" of the gas streams at the column's ends.

Just as the vapor diffuses across the annulus, so do the gases tend to diffuse towards the vapor-entry surface; the difference in their rates of diffusion effecting their relative enrichments. However, whereas the vapor's diffusion stops when it condenses on the cold wall surface, the gases are confronted with the porous vapor-tube. Here, in comparison with the vapor rate in the annulus, the vapor rate is greatly increased by the factor of the reciprocal of the porosity of the vapor-tube wall. (The porosity being taken as the ratio of the open pore area to the area of the tube surface.) For all practical vapor rates in the annulus, and with porosity values of 0.10 or less, the vapor rate in the pores of the tube seriously limits the amount of gas that can diffuse back into the inside of the tube. But, as this back diffusion is selective according to the diffusivities of the gases, its effect as a part of the column's separation has to be investigated.

Moreover, and more important, is the fact that the steam enters at one end of the vapor-tube, and whatever gases diffuse into the vapor stream inside the tube are carried along to be emitted further along downstream. In the case of the steam entering at the bottom of the column, the gases entering the vapor-tube are richer in the more diffusible component than the gases in the annulus at that elevation, and they are carried up the column to be emitted along with the steam. This process tends to help move the more diffusible component up the column, thereby increasing the effectiveness of the column and aiding its separation. Conversely, if the steam entered at the top of the vapor-tube, back diffusion into the tube would tend to carry the more diffusible component down the column and reduce the effectiveness of the column's operation. If there was no longitudinal flow of the steam

at any place in the column, then the back diffusion of the gases would have no effect upon the separation produced in the column.

The "turning effect" is the result of a convective stream reversing its flow at the end of the column. This happens when $V > D$, or $L > B$. Considering the convective flow at the top of the column, when $V > D$, the difference of these streams, $(V - D)$, must reverse its flow and descend the column. This reversal of flow takes place in a finite length of column length, and in this length the L/V ratio is varying. Or, the value of $\partial V/\partial z$ is not zero as was previously assumed. By analogy to the McCabe-Thiele method for ordinary distillation, the L/V ratio increases as the top of the column is approached, and the operating line moves towards the equilibrium line reducing the separation for a given number of theoretical plates. This produces a curved operating line, concave towards the equilibrium line.

Another result of this variable convective flow is the effect that it has on the partial pressure of the vapor in the annulus. This effect is considered numerically in the section concerning the density gradients in the column, and will just be mentioned qualitatively here. If the value of $\partial V/\partial z$ is negative, there is a net flow of the gases towards the cold wall of the annulus. As this is in the same direction as the steam is diffusing, a smaller partial pressure gradient of the steam is required to transfer a given quantity of steam across the annulus. This results in lower partial pressures of steam in the annulus. In as much as the flow of the steam through the pores of the vapor-tube is considered as a mechanical process, governed by the pressure drop across the tube wall, this does not change the value of N_o , but just p_o .

Varying Convective Streams

With $\partial V/\partial z \neq 0$, Equation (33) must be written in the form of

$$\begin{aligned} \frac{\partial y}{\partial x} = & \frac{RTN_0}{P} \left[\frac{1}{D_{01}} - \frac{1}{D_{02}} \right] [1-y]y \\ & + \frac{RTV}{PE} \left[\frac{1}{D_{12}} + \frac{P_0}{P-P_0} \left[\frac{1-y}{D_{01}} + \frac{y}{D_{02}} \right] \right] \frac{\partial y}{\partial z} \\ & + \frac{RT}{PE} \left[\frac{y^I - y}{D_{12}} + \frac{P_0}{P-P_0} \left[\frac{y^I(1-y)}{D_{01}} + \frac{y^I(y^I-1)}{D_{02}} \right] \right] \frac{\partial V}{\partial z} \end{aligned} \quad (33a)$$

and the $\partial V/\partial z$ term is carried along so that Equation (38) becomes

$$\frac{\partial y^{II}}{\partial z} = \frac{B(y_B - y^{II}) + Hy(1-y) - Q \frac{\partial V}{\partial z}}{K} \quad (38a)$$

where

$$Q = \frac{(X_b - X_a)RTV}{2PE} \left[\frac{y^I - y}{D_{12}} + \frac{P_0}{P-P_0} \left[\frac{y^I(1-y)}{D_{01}} + \frac{y(y^I-1)}{D_{02}} \right] \right] \quad (65)$$

The value of Q is negative, so it can be seen that a negative $\partial V/\partial z$ reduces the value of $\partial y/\partial z$, giving poorer separation in the column. The solution of Equation (38a) depends upon the evaluation of this new

term $Q(\partial V/\partial z)$ as well as the other previously evaluated terms, and is therefore much more difficult to obtain. If $Q(\partial V/\partial z)$ could be assumed a constant, then for the case where $(1 - y)y \approx 0.25$, it could be grouped together with H to give a new transport coefficient. Otherwise, still considering it a constant, the $Q(\partial V/\partial z)$ term could be grouped with the $B y_B$ term. Either way, the difficulty in properly evaluating $Q(\partial V/\partial z)$ is not lessened.

Back Diffusion into Vapor-Tube

The case of back diffusion of the separating gases into the vapor-tube is, to a limited extent, similar to the case of mass diffusion taking place with a diffusion screen between the L and V streams. This case has been considered by Benedict (2) with the conclusion that explicit solution to the material balance is impossible, and recourse must be had to numerical methods. However, in the present situation, the difficulties are compounded by having three streams instead of the usual two; two upflowing, and one downflowing. It would seem that the best approach to approximating the magnitude of the effect of this back diffusion on the column separation, would be to simplify the case down to the one giving the maximum help (or hindrance) to the column separation. Then the actual column separation would lie some place between the column operating with, and without this effect. The equations neglecting this effect have already been derived, now it remains to estimate the maximum help that can be expected with the effect.

The maximum help that could be produced by back diffusion of the gases into the vapor-tube, when the steam enters at the bottom of the column, would be if just the more diffusible gas entered the tube

to be readmitted to the annulus further up the column. This wouldn't be too far from actuality if the ratio D_{O_1}/D_{O_2} was large. Thus, the vapor-tube would contain only vapor and the more diffusible gas. The flow of this gas, gas 1, into the tube would be indicated by the usual diffusion equation, Equation (1), with N_2 and p_2 set equal to zero.

$$\frac{\Delta P_1}{\Delta X_T} = \frac{RT}{D_{O_1} P} \left[N_{O_1} P_{1t} - N_{1t} P_{O_1t} \right] \quad (66)$$

As the net flow of gas and vapor is from the inside of the vapor-tube to the annulus, the values of p_1 and p_0 will be taken to be the same as the values inside the tube; p_{1t} and p_{O_1t} . The value of p_1 on the annulus side of the tube wall will be taken as $p_1 = y^I(1 - p_0)$, and Equation (66) may be written in the form

$$N_{1t} = P_{1t} \sum N_t + \frac{P_{1t} - y^I(1 - P_{O_1t}) D_{O_1} P}{\Delta X_t RT} \quad (67)$$

where

$$\sum N_t = N_{1t} + N_{O_1t} \quad (68)$$

Although some of the more diffusible gas may diffuse back up the vapor feed line, the boiler seals off that line and there is no net flow of gas out of the column by means of the vapor feed line. A material balance around the bottom of the column yields

$$W P_{1t} - B y_B = L y^{II} - V y^I \quad (69)$$

where W is the rate of gas and vapor flow up the vapor-tube at the same elevation that $L y^{II}$ and $V y^I$ are evaluated.

A material balance on a differential length of the annulus yields

$$N_i = \theta N_{lt} \frac{E_t}{E} \left[y^I \frac{dV}{dz} + V \frac{dy^I}{dz} \right] \quad (70)$$

where θ is the porosity of the tube. Equation (27) is written in the form of

$$\frac{dy}{dx} = \frac{y^{II} - y^I}{0.5(x_b - x_a)} = \frac{B(y_B - y^{II}) - (L - V - B)(1 - y^{II})}{0.5(x_b - x_a)} \quad (27a)$$

The substitution of N_{lt} from Equation (67) into Equation (70) and the result combined with Equations (27a) and (29) gives

$$B(y_B - y^{II}) + (L - V - B)(1 - y^{II}) + H(1 - y)y - Q \frac{dV}{dz} - K \frac{dy^I}{dz} = \frac{(x_b - x_a)VRT\theta}{2P} \left[\frac{1}{D_{12}} + \frac{P_0}{(P - P_0)D_{01}} \right] (y - 1) \left\{ \frac{Ly^{II} - Vy^I - By_B}{V} \left[\sum N_t + \frac{D_{01}P}{\Delta x_t RT} \right] - \frac{y^I(1 - P_0)D_{01}P}{\Delta x_t RT} \right\} \quad (71)$$

The quantity $(L - V - B)$, which is the rate of longitudinal flow of the more diffusible component in the vapor-tube, has a zero value at both ends of the column, but a varying positive value between the ends. At the lower end of the column, where N_{lt} is negative, the back diffusion of the more diffusible component reduces the separating effect of the column, but further up the column where N_{lt} becomes positive, the separation is enhanced. The value of $(L - V - B)$ is given by the equation

$$L - V - B = Ly^{II} - Vy^I - By_B = E_t \int_0^z N_{lt} dz \quad (72)$$

The value of N_{lt} is given by Equation (67), and it is evident that the integral in Equation (71) cannot be analytically

evaluated, but will have to be performed by some graphical method. In preparation for this, Equation (71) is rewritten in the form of

$$K' \frac{dy^I}{dz} = B y_B - (L - V)_{z_1} + H'(1-y)y + S(1-y) + y^I E_t \int_{z_1}^{z_2} N_{1t} dz - E_t \int_{z_s}^{z_1} N_{1t} dz - Q' \frac{\partial V}{\partial z} \quad (73)$$

where H', Q', and K' are the values of H, Q, and K with one V in their expressions changed to L, and S is defined by

$$S = \frac{(x_b - x_a) L N_{1t} R T \theta E_t}{2 P E} \left[\frac{1}{D_{12}} + \frac{p_0}{(P - p_0) D_{01}} \right] \quad (74)$$

The elevation of z_2 is higher up the column than that of z_1 , and the interval $(z_2 - z_1)$ may be taken as small as necessary or practical.

Without the back diffusion effect, the value of dy/dz approaches zero at the top of the column due to the balancing out of the $B(y_B - y^I)$ and $H(1 - y)y$ terms. Now with the back diffusion, these terms are still present, but new terms are added that tend to increase the value (positively) of dy/dz . All the material flowing up the vapor-tube must come out into the annulus by the time the upper end of the tube is reached. Therefore N_{1t} has to be positive in this region, and the integral from z_s to z_2 , which is detrimental to improving the separation, is approaching zero as nearly all gas that diffused into the tube has by now been returned to the annular space. The result is that additional separation is produced as a result of back diffusion into the vapor-tube.

THE HYDRODYNAMICAL PROBLEM

The hydrodynamical behavior of the gases is of prime importance in a column depending upon natural convection to establish the countercurrent flow of the separating streams. This is not true where, 1) the streams may be moved individually by positive displacement due to a membrane between them, or 2) where the streams can be moved by the drag of moving walls. (3, 5).¹ The separation experiments reported in the literature, that have been operated by natural convection alone,² have not been analyzed as regards their convection velocities. Furry and Jones (7) made the first, and apparently, only derivation of an equation explicitly showing v as a function of the variables influencing it; rather than incorporating these variables directly into the H and K values of the column.

In all the separation equations derived up to this point, the convective flow has been assumed to be free from turbulence. Onsager and Watson (10) have shown experimentally, that spontaneous turbulence occurs in apparatus of the plane type, for Reynolds numbers greater than 25, when the Reynolds number is defined as

$$Re = \frac{(x_b - x_a)^3 g \rho^3 \Delta T}{48 \mu T} \quad (75)$$

Actual operation would require a Reynolds number less than 25, so that any disturbances caused by irregularities in the equipment would be quickly damped out. In mass diffusion columns, where the temperature

¹ In general, the rate of condensation of the separation vapor is too low to produce any appreciable drag due to the droplets running down the condenser walls.

² This is generally done by means of a "hot wire" column, where an electrically heated wire forms the central element of the column.

of the hot element does not approach that of a heated wire, Reynolds numbers below 10 are quite common.

The derivation of a hydrodynamical equation for steady, non-turbulent flow under the influence of gravity, begins with the Navier-Stokes equation:

$$\frac{\partial \vec{v}}{\partial \lambda} + \vec{v} \cdot \text{grad} \vec{v} = \vec{g} - \frac{1}{\rho} \text{grad} P + \frac{\mu}{\rho} \text{grad} \text{div} \vec{v} + \frac{\mu}{\rho} \Delta \vec{v} \quad (76)$$

The expanded form of Equation (76), in Cartesian coordinates, is:

$$\begin{aligned} & \frac{\partial v_x}{\partial \lambda} + \frac{\partial v_y}{\partial \lambda} + \frac{\partial v_z}{\partial \lambda} + i \left[v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \right] \\ & + j \left[v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} + v_z \frac{\partial v_y}{\partial z} \right] + k \left[v_x \frac{\partial v_z}{\partial x} + v_y \frac{\partial v_z}{\partial y} + v_z \frac{\partial v_z}{\partial z} \right] \\ = & i g_x + j g_y + k g_z - \frac{1}{\rho} \left[i \frac{\partial P}{\partial x} + j \frac{\partial P}{\partial y} + k \frac{\partial P}{\partial z} \right] \quad (77) \\ & + \frac{\mu}{\rho} \left[i \left[\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_y}{\partial x \partial y} + \frac{\partial^2 v_z}{\partial x \partial z} \right] + j \left[\frac{\partial^2 v_x}{\partial x \partial y} + \frac{\partial^2 v_y}{\partial y^2} + \frac{\partial^2 v_z}{\partial z \partial y} \right] \right. \\ & \left. + k \left[\frac{\partial^2 v_x}{\partial x \partial z} + \frac{\partial^2 v_y}{\partial y \partial z} + \frac{\partial^2 v_z}{\partial z^2} \right] \right] + \frac{\mu}{\rho} \left[\frac{\partial^2 \vec{v}}{\partial x^2} + \frac{\partial^2 \vec{v}}{\partial y^2} + \frac{\partial^2 \vec{v}}{\partial z^2} \right] \end{aligned}$$

Equation (77) can be of little help in its existing form, and radical simplification is needed. Considering first the approach used by Jones and Furry for the plane case, it is assumed that:

- 1) Steady-state conditions exist,
- 2) There is no flow in the x and y directions (refer to Figure 7),

- 3) There is no change at different elevations in the column, and no change in the y direction,
- 4) There are no centripetal forces.

By means of the above assumptions, Equation (77) reduces to

$$0 = \vec{k} g_z - \frac{\vec{i}}{\rho} \frac{\partial P}{\partial z} + \frac{\mu}{\rho} \frac{\partial^2 v_z}{\partial x^2} \quad (78)$$

or

$$\mu \frac{\partial^2 v_z}{\partial x^2} = \frac{\partial P}{\partial z} + \rho g \quad (79)$$

The quantity $\partial P / \partial z$ is equal to $-\rho g$, which, if substituted into Equation (79), and the resulting equation solved, gives a vanishing value of v_z . In order to obtain a non-vanishing value for v_z , Jones and Furry write the equation in the form of

$$\mu \frac{d^2 v_z}{dx^2} = g(\rho - \bar{\rho}) \quad (80)$$

where $\bar{\rho}$ is the average value of the density of the gases between the walls, and ρ is the point value of the density. Assuming that the temperature distribution is determined by conduction alone, and that the thermal conductivity of the gases is a constant, the density may be written as a linear function of the temperature:

$$\rho = \bar{\rho} [1 - (T - \bar{T}) / \bar{T}] \quad (81)$$

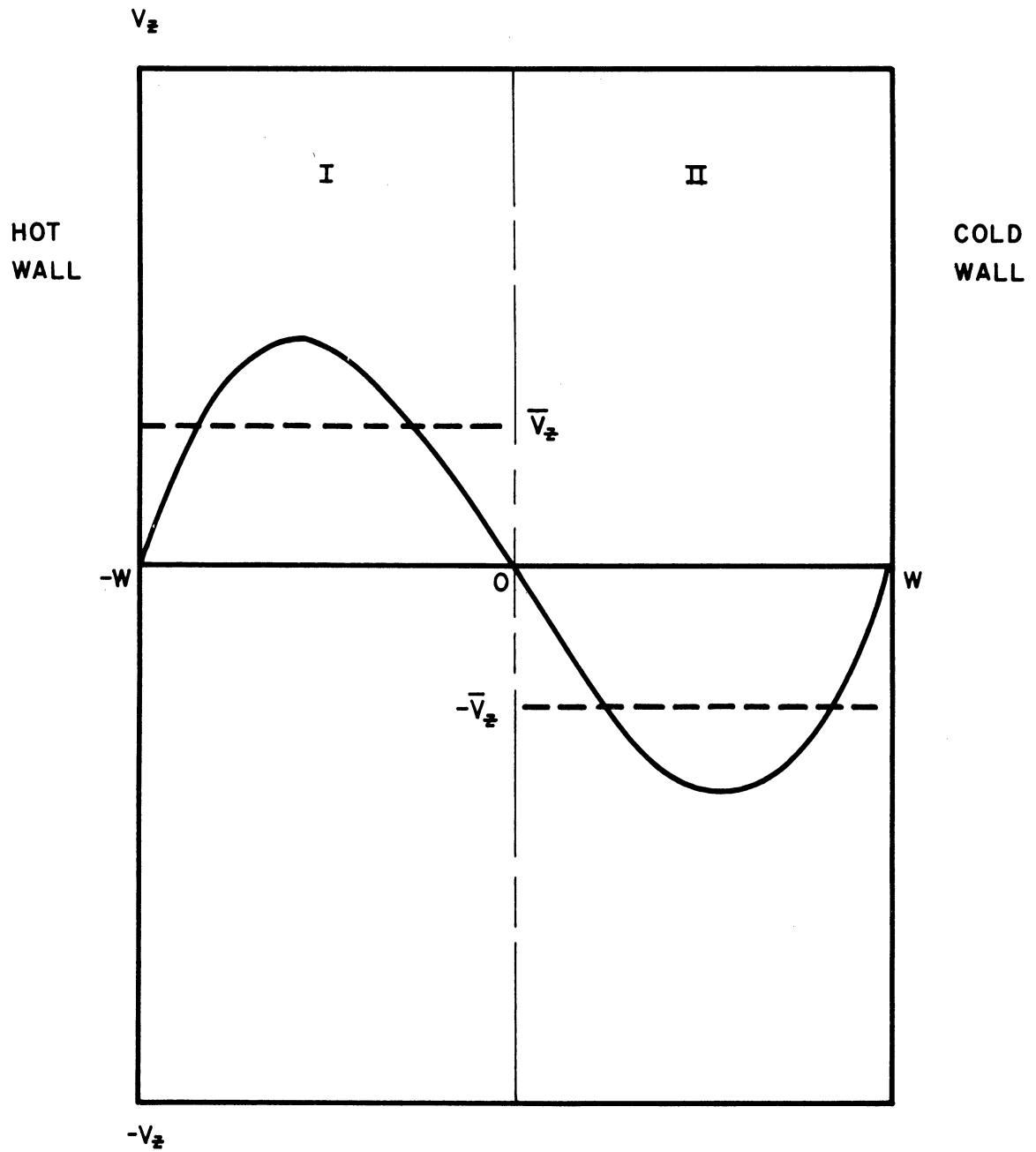


FIG 7 CONVECTION CURRENTS
BETWEEN HOT AND COLD WALLS

and the temperature as a linear function of x :

$$T = \bar{T} + x \Delta T / 2w \quad (82)$$

Where $2w$ is the distance between the walls, and ΔT is the temperature difference between the walls. Substituting Equation (82) into Equation (81), and the result into Equation (80) gives

$$\mu \frac{d^2 v_z}{dx^2} = -\bar{\rho} g \frac{x \Delta T}{2w \bar{T}} \quad (83)$$

Integrating Equation (83) and using the limits that $v_z = 0$ for $x = \pm w$ gives

$$v_z = \frac{\bar{\rho} g \Delta T}{12 \mu w \bar{T}} x(w^2 - x^2) \quad (84)$$

This equation is shown graphically in Figure 7. The average velocity of the upflowing and downflowing streams is

$$\bar{v}_z = \frac{1}{w} \int_0^w v_z dz = \frac{-1}{w} \int_{-w}^0 v_z dz = \frac{\bar{\rho} g w^2 \Delta T}{48 \mu \bar{T}} \quad (85)$$

Furry and Jones show how this solution can be corrected for the cylindrical case, but the resultant integral cannot be evaluated analytically, and approximate solutions are obtained for H and K values under certain conditions (ratio of the radii equal to 2.718, and the extreme cylindrical case).

The main objection to Equation (85) when applied to non-isotopic mixtures, is that it was derived ignoring the effect of composition of the density: a valid assumption for isotopic mixtures where the masses of the constituent gases are very nearly equal. To apply this derivation to a mixture of gases having very different molecular weights, and where a concentration gradient would cause a resultant density gradient, a better assumption would be to assume that the density was a linear function of x . Thus, Equation (83) would be written in the form of

$$\frac{d^2 v_z}{dx^2} = \frac{g}{\mu} (ax + b) \quad (86)$$

with the constants a and b being determined by the temperature and concentration gradients.

Avoiding the implied condition that the velocity is zero at the midpoint between the walls, Equation (86) is integrated between the limits $x = x_1$ and $x = x_2$, giving the boundary conditions

$$\begin{aligned} v_z(x_1) &= 0 \\ v_z(x_2) &= 0 \end{aligned} \quad (87)$$

and the resulting solution

$$v_z = \frac{ga}{\mu} \left[\frac{x^3 - x_1^3}{6} - \frac{x_0(x^2 - x_1^2)}{2} + \frac{x - x_1}{x_2 - x_1} \left[\frac{x_1^3 - x_2^3}{6} - \frac{x_0(x_1^2 - x_2^2)}{2} \right] \right] \quad (88)$$

where b was replaced by $-ax_0$; x_0 being a constant $x_1 < x_0 < x_2$.

Actually, x_0 is the x value at which $\partial^2 v_z / \partial x^2 = 0$, and $v_z(x_0) = 0$

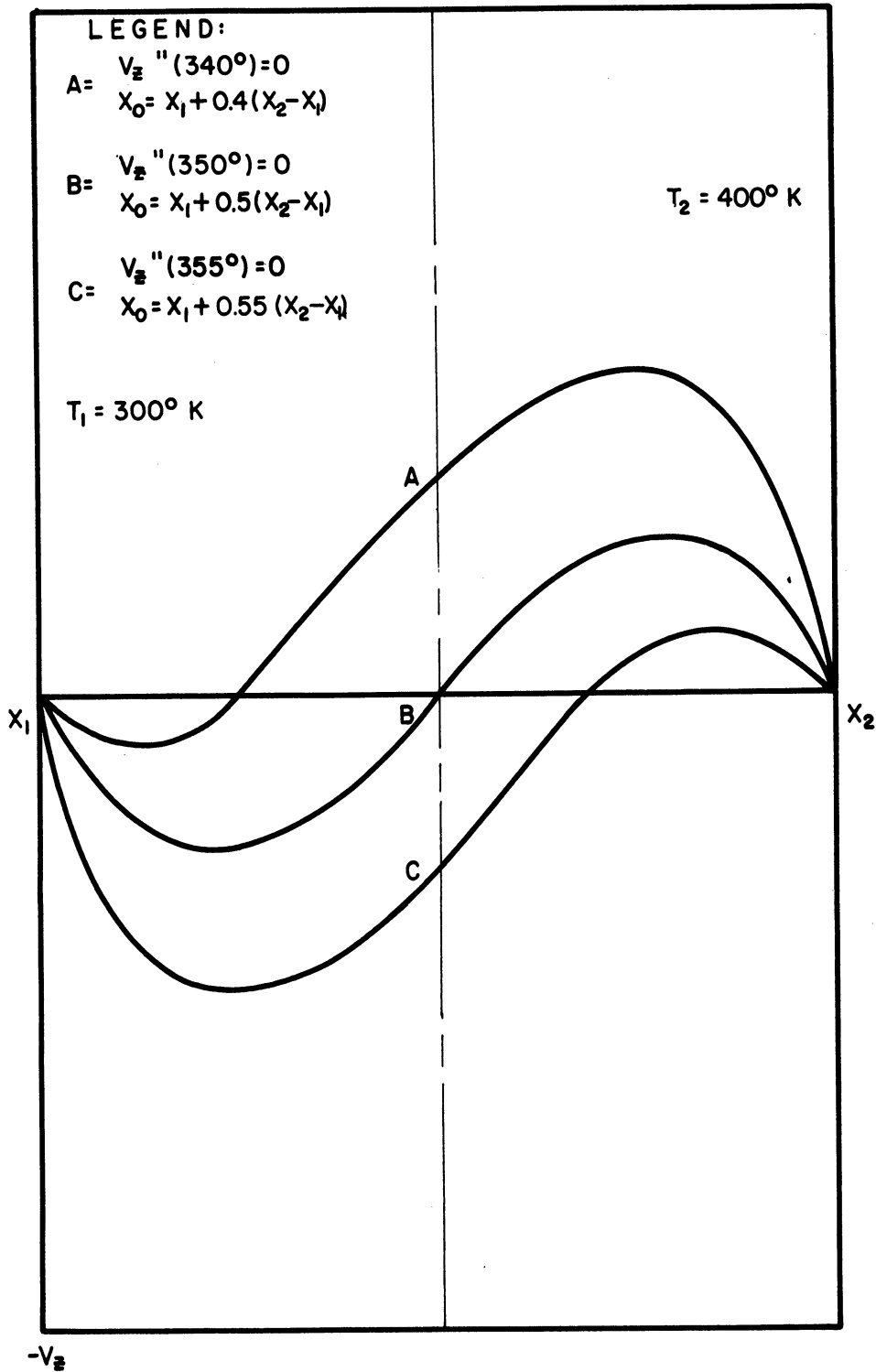


FIG 8 EFFECT OF THE CONSTANT X_0
ON CONVECTION VELOCITY PROFILE

only if $x_0 = (x_1 + x_2)/2$. This fact may be qualitatively seen in Figure 8. It is to be noted, that a relatively small change in the value of x_0 causes a much larger relative change in the velocity profile, the greatest effect being when $x_0 \approx (x_1 + x_2)/2$.

Velocity Profiles in Column Operation

Before considering the effect that the annular shape has on the velocity profile, it is necessary to investigate another effect: that the stream velocities may be insufficient to transport quantities of gas equal to, or greater than the amounts withdrawn at the ends of the column.

There have been no material balances considered in the derivations of the equations to predict the convective flows. Even in the plane wall, isotope case, with no products being withdrawn, there can be no symmetry of the velocity profile due to the unequal values of the mean densities of the countercurrent streams. Symmetry of the velocity profile would result in a net flow of material down the column.

A simple solution to this problem would be the superimposing of a material-balance velocity profile upon that predicted by the density gradient. Thus, if there was a net flow of material along the column, a symmetrical parabolic velocity profile, of the type used for laminar flow in the absence of density gradients, would be superimposed on the velocity profile produced by the density gradient. The result of combining these two effects is shown in Figure 9. The magnitude of the parabolic profile would be varied until the resultant mean velocities and cross-sections of the streams agreed with their material balance.

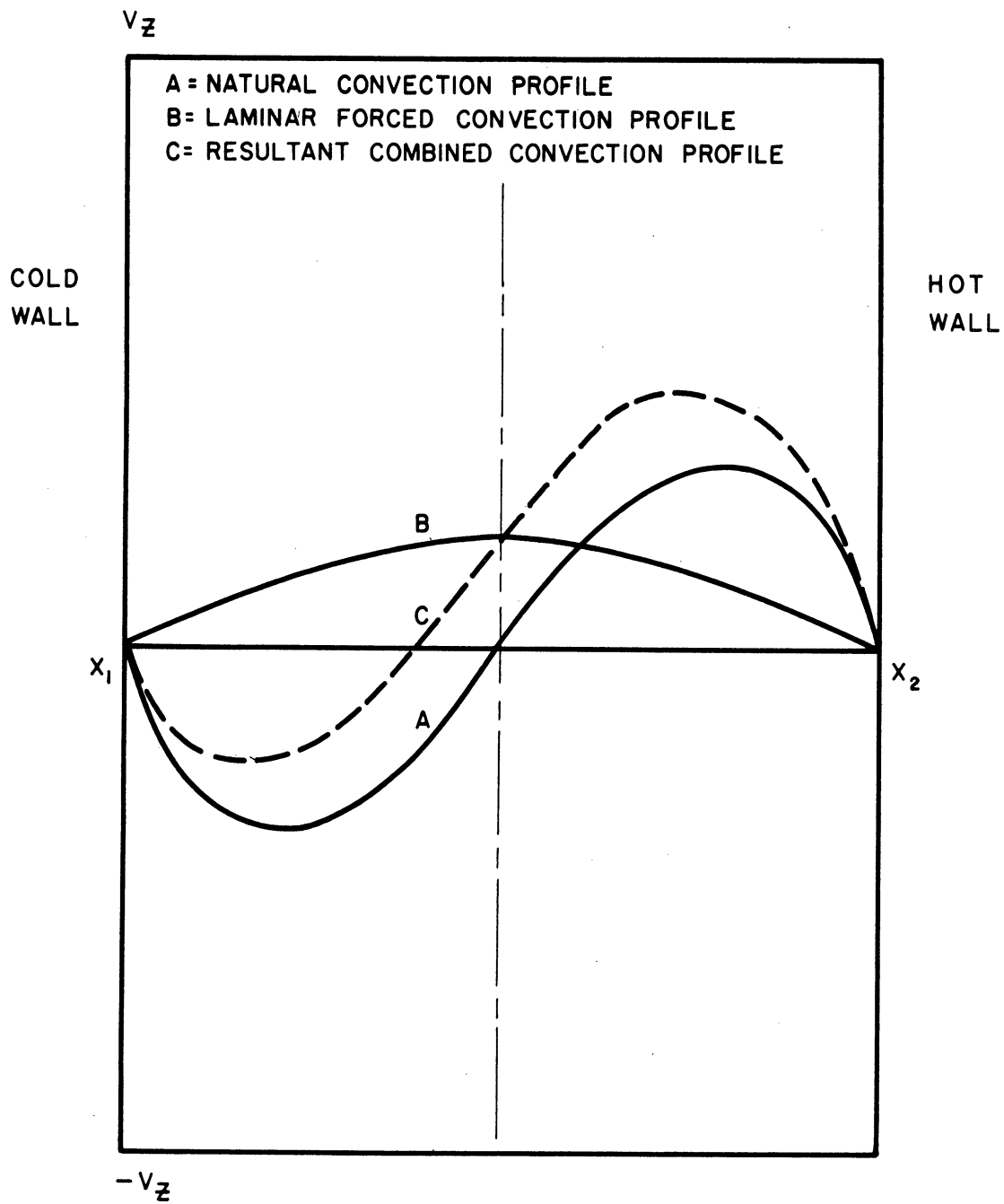


FIG 9 EFFECT OF MATERIAL BALANCE CONSIDERATIONS ON CONVECTION VELOCITY PROFILE

Annular Velocity Profiles

To observe the effect of the annular shape on the velocity profiles, the Navier-Stokes equation will be considered in terms of cylindrical coordinates. The coordinate system is shown in Figure 10. The geometrical relations between the Cartesian and cylindrical coordinates being

$$\begin{aligned} Z &= Z \\ X &= r \cos \phi \\ Y &= r \sin \phi \\ r &= \sqrt{X^2 + Y^2} \end{aligned} \tag{89}$$

It is assumed that:

- 1) Steady-state conditions exist.
- 2) All derivatives with respect to z are sufficiently small so that they can be neglected.
- 3) All velocities are symmetrical about the z-axis ($r = 0$).

Using these assumptions, Equation (77) may be rewritten in cylindrical coordinates for three different cases:

Case I; where $v_r = 0$

$$\mu \left[\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r} \frac{\partial v_z}{\partial r} \right] - \frac{\partial P}{\partial z} - \rho g = 0 \tag{90}$$

Case II; where $v_r = v_r$, $v_r = \text{constant}$

$$\mu \frac{\partial^2 v_z}{\partial r^2} + \left[\frac{\mu}{r} - \rho v_r \right] \frac{\partial v_z}{\partial r} - \frac{\mu v_r}{3r^2} - \frac{\partial P}{\partial z} - \rho g = 0 \tag{91}$$

Case III; where $v_r = v_r$, $\frac{\partial v_r}{\partial r} \neq 0$

$$\begin{aligned} \mu \frac{\partial^2 v_z}{\partial r^2} + 2\mu \frac{\partial^2 v_r}{\partial r^2} + \left[\frac{\mu}{r} - \rho v_r \right] \left[\frac{\partial v_z}{\partial r} + \frac{\partial v_r}{\partial r} \right] \\ + \frac{\mu}{3} \left[\frac{\partial^2 v_r}{\partial r^2} + \frac{1}{r} \frac{\partial v_r}{\partial r} - \frac{v_r}{r^2} \right] - \frac{\partial P}{\partial z} - \rho g = 0 \end{aligned} \tag{92}$$

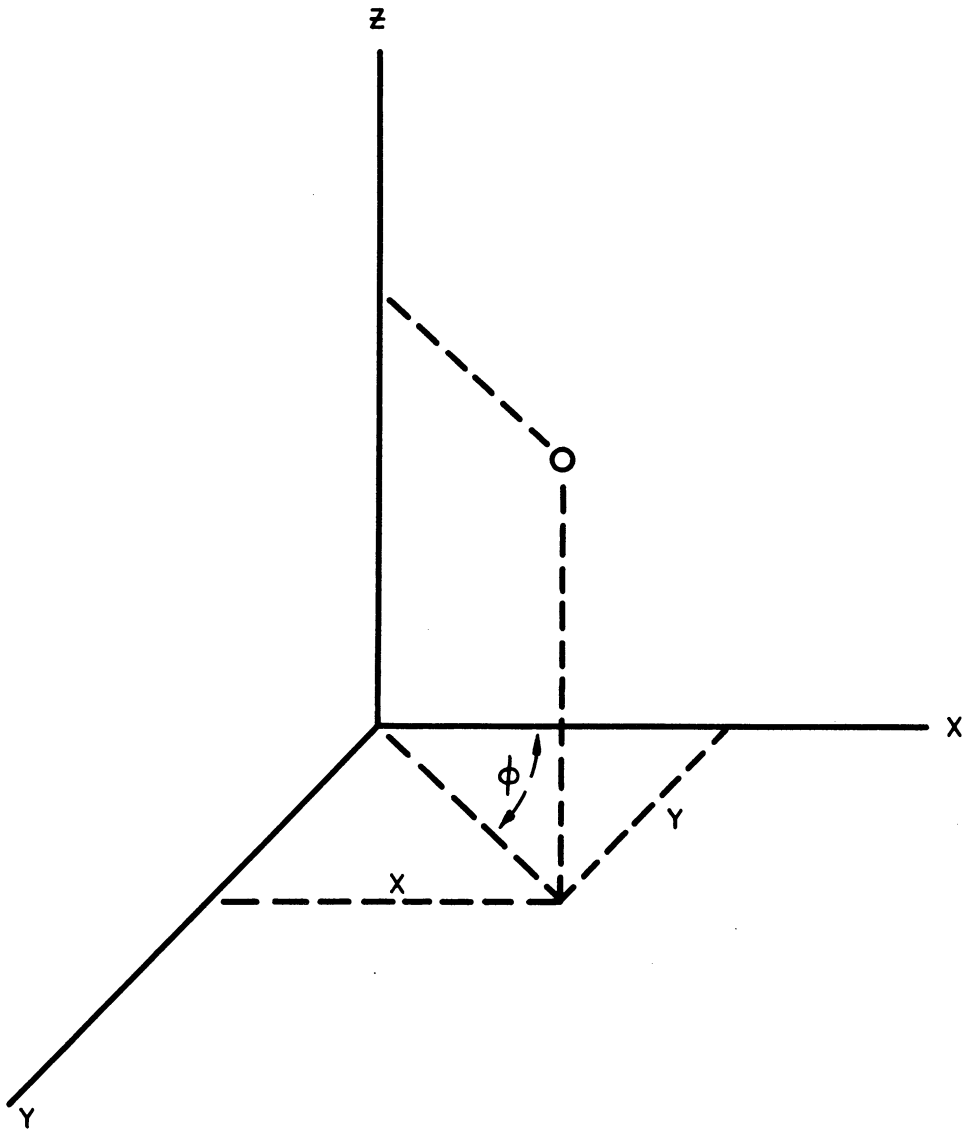


FIG 10 CYLINDRICAL COORDINATE SYSTEM

Case I, Discussion

This case is analogous to the plane-case with no flow in the x and y directions, and when written in the form

$$\frac{d^2 v_z}{dr^2} + \frac{1}{r} \frac{dv_z}{dr} = \frac{g}{\mu} (ar + b) \quad (93)$$

and integrated, using the limits

$$\begin{aligned} v_z(r_1) &= 0 \\ v_z(r_2) &= 0 \end{aligned} \quad (94)$$

gives the solution

$$\begin{aligned} v_z = \frac{ga}{\mu} & \left[\frac{r^3}{9} - \frac{r_0 r^2}{4} + \frac{(r_2^3 - r_1^3)/9 - r_0 (r_2^2 - r_1^2)/4}{\ln(r_1/r_2)} \ln r \right. \\ & \left. + \frac{\ln r_1 \left[(r_2^3 - r_1^3 \ln r_2/r_1)/9 - r_0 (r_2^2 - r_1^2 \ln r_2/r_1)/4 \right]}{\ln(r_2/r_1)} \right] \end{aligned} \quad (95)$$

where b has been replaced by $-ar_0$. A comparison of the results of Equation (88) and Equation (95) is given in Figure 11. The profiles are very similar except that they do not cross the axis $v_z = 0$ at the same point. As with the plane case, the point of crossing is dependent only upon b (for given r_1 and r_2 values).

Case II, Discussion

Before examining the mathematical results of this case, the physical reasons behind the assumption $v_r \neq 0$, will be considered; not only from the viewpoint of the column operation as expected from theory, but also in the light of the experimental results of this research.

When the convective stream reaches one end of the column and reverses its direction of flow, horizontal flow must exist. The fact that the whole stream cannot reverse itself at just the very end of the column, in an infinitely small region, means that horizontal flow

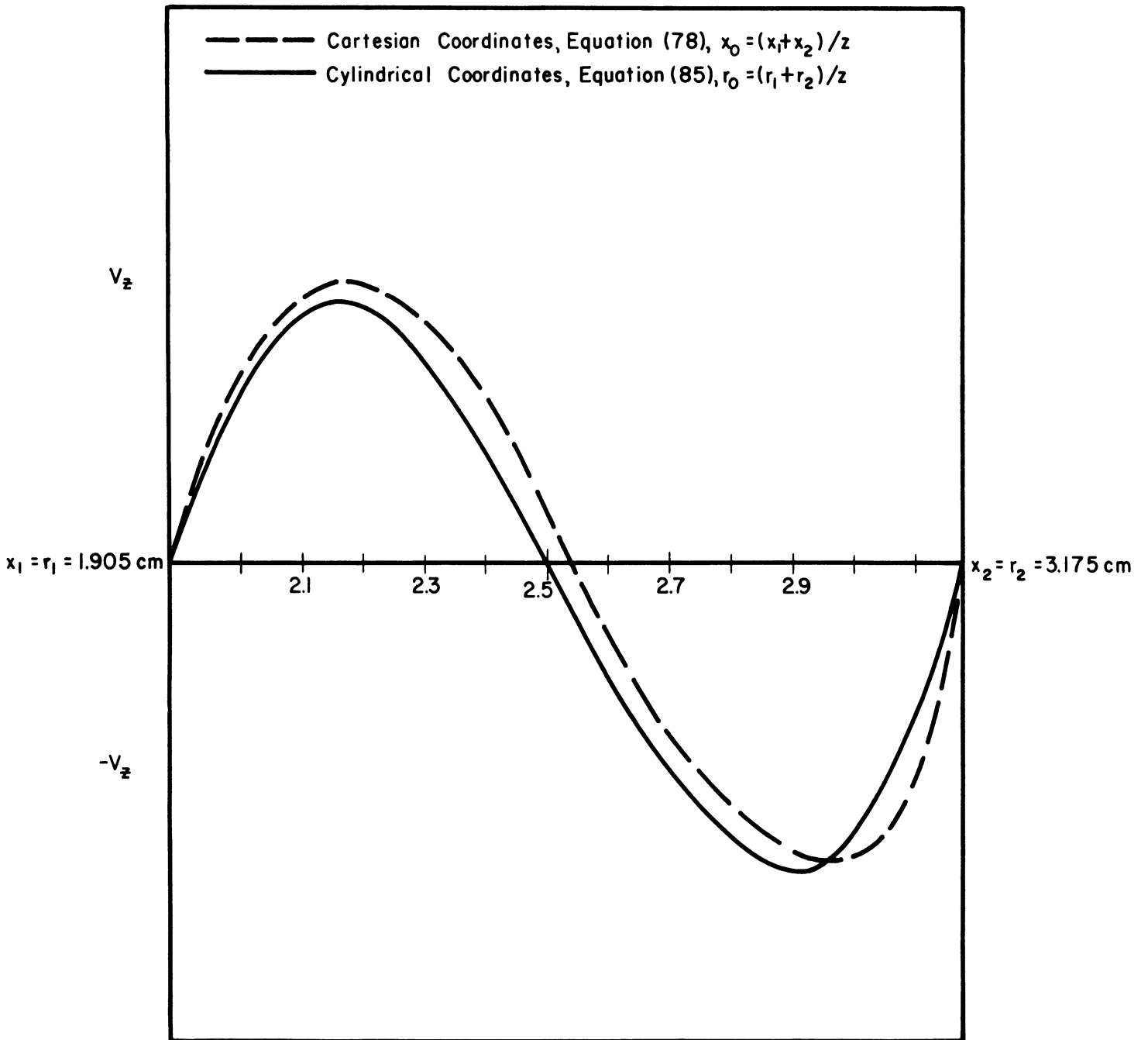


FIG II COMPARISON OF VELOCITY PROFILES
IN CYLINDRICAL AND CARTESIAN COORDINATES

exists at some length from the ends of the column. Conceivably, in a short column, there would be transverse flow along the whole length of the column due to this "turning effect" alone. Also, with a density gradient along the column, as well as across the column, the mean stream velocities would vary with z and produce a transverse flow.

Another factor in relation to the transverse gas flow in the column is the "back diffusion" of the gases into the vapor-tube. The existence of back diffusion is conclusively proven in the section concerned with the experimental results. This flow of the gases through the vapor-tube actually adds to, or subtracts from, the gases in the annular separating zone.

The flow of the vapor across the annulus, due to its condensing out on the opposite wall, does not affect the actual gas volume in the column as regards the gas material balance. Therefore, this transverse flow of vapor, or more precisely, transverse diffusion, does not affect the convection flow pattern, other than by its partial pressure properties.

The accurate solution to the effect of the transverse flow on the convection velocity profiles, or for that matter, the accurate prediction of the convection currents under any conditions, if at all possible, is beyond the scope of this research and is unwarranted by comparison to the other assumptions made. What will be sought is a practical solution, to show, if not quantitatively at least qualitatively, the velocity profiles that can be expected.

Equation (91) is a second-order equation with the dependent variable missing and could be solved directly if the indicated integrations could be analytically performed. This is not possible, but

a very good approximate solution is obtained by assuming

$$a'(r-r_0) \gg v_r/3r^2 \quad (96)$$

where

$$a' = g^a/\mu \quad (97)$$

The Inequality (96) is not valid at $r = r_0$ for $v_r \neq 0$, but is true elsewhere. (For $r_1 = 1.9$ and $r_2 = 2.1$, with $v_r = 1$, at the midpoint of the convective streams $a'(r - r_0)/(v_r/3r^2) \approx 3000$.) Therefore, Equation (91) is written in the form of

$$\frac{d^2 v_z}{dr^2} + \left[\frac{1}{r} + \beta \right] \frac{dv_z}{dr} = a'(r-r_0) \quad (98)$$

where

$$\beta = -\bar{\rho} v_r / \mu \quad (99)$$

Integrating Equation (98) using boundary conditions (94) gives

$$\frac{v_z}{a'} = f_1 r^2 + f_2 r + f_3 \ln r + f_4 \int_{r_1}^{r_2} \frac{e^{-\beta r}}{r} dr + f_5 \quad (100)$$

where

$$\begin{aligned} f_1 &= 1/2\beta \\ f_2 &= -(2/\beta^2 + r_0/\beta) \\ f_3 &= 2/\beta^3 + r_0/\beta^2 \\ f_4 &= \frac{f_1(r_2^2 - r_1^2) + f_2(r_2 - r_1) + f_3(\ln r_2/r_1)}{-\int_{r_1}^{r_2} \frac{e^{-\beta r}}{r} dr} \\ f_5 &= -(f_1 r_1^2 + f_2 r_1 + f_3 \ln r_1) \end{aligned} \quad (101)$$

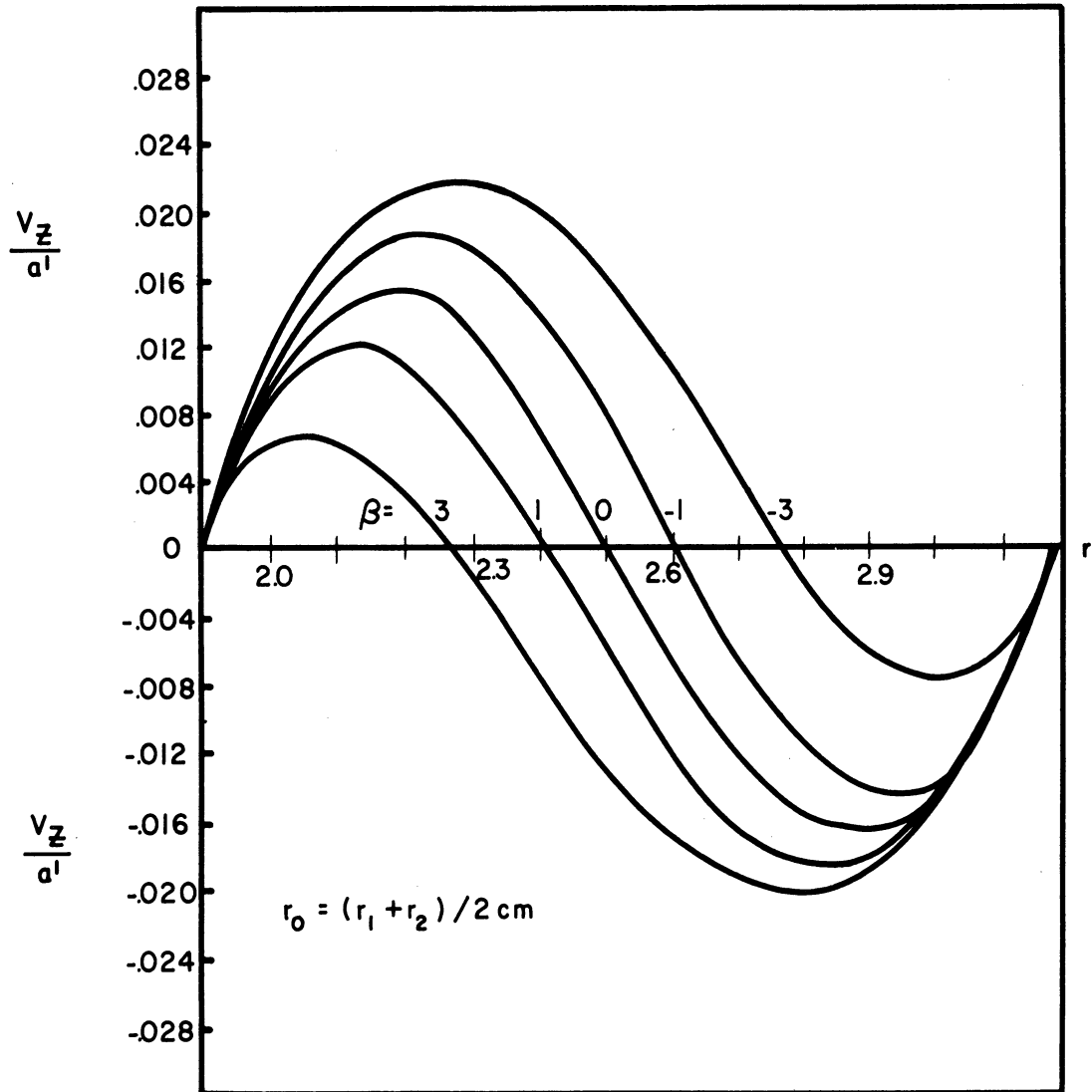


FIG 12 EFFECT OF TRANSVERSE FLOW ON VELOCITY PROFILES

Figure 12 shows Equation (96) plotted for various values of β . The value of r_0 was taken as $r_0 = (r_1 + r_2)/2$ and the curve for $\beta = 0$ was determined from Equation (95) for Case I. The values used for r_1 and r_2 correspond to the actual dimensions of the experimental columns used in this research. Here r_1 is the hot wall and r_2 is the cold wall.

Figure 12 graphically shows the relationship between the transverse and longitudinal flow. When the streams differ from the "normal" flow pattern of no transverse flow ($\beta = 0$), a transverse flow is produced in such a direction as to tend to cause the streams to return to their normal flow. This is not unexpected, as it is a form of damping and the means for returning the system to equilibrium. Thus, should the hot, rising stream (on the left in Figure 12) be increased in some manner, gas flows to the right to increase the counter-flowing cold stream, tending to equalize the two streams. On this basis it will be assumed that should the hot stream either increase or decrease its volume due to the diffusion of the gas through the vapor-tube wall, then the column streams will tend to equalize themselves. Or, from the experimental viewpoint, aside from the material balance considerations, transverse flow through the vapor-tube will not be considered in evaluating the mean velocities of the convective streams.

Case III; Discussion

The differential equation given in Equation (92) was not solved, and could not be without making further simplifying assumptions. It is given here for the sake of completeness. The solution to Case II can be manipulated adequately for the needs of this research.

It should be noted, that the simplified form of the Navier-Stokes equation used here is very similar to its form for the case of a homogeneous, incompressible fluid. For in that case, the static pressure and gravity force can be neglected, since the action of the gravity on the individual elements of the fluid is eliminated by their buoyancy. For that case, the equation at steady-state may be written

$$\vec{v} \cdot \text{grad} \vec{v} = -\frac{1}{\rho} \text{grad} P + \frac{\mu}{\rho} \Delta \vec{v} \quad (102)$$

And with no transverse flow in the plane case it becomes

$$0 = \frac{\partial P}{\partial z} + \mu \frac{\partial^2 v_z}{\partial x^2} \quad (103)$$

which may be compared with Equation (79).

Density Gradient

All the solutions for the velocity profiles show that the velocity is directly proportional to a (or a'), where a was assumed a function of the density gradient:

$$\begin{aligned} a &= \frac{\partial \rho}{\partial r} = (\rho_b - \rho_a) / (r_b - r_a) \\ \text{or} \\ a &= \frac{\partial \rho}{\partial x} = (\rho_b - \rho_a) / (x_b - x_a) \end{aligned} \quad (104)$$

It is necessary to determine this gradient in order to evaluate the convective velocities in the column.

The density of the gases (assumed ideal), at any point in the column, is a function of the composition, temperature, and pressure at that point. Due to the very small changes in pressure throughout the column, the pressure will be assumed constant. Thus, to

determine the density gradient between two points of known temperature, there only remains the determination of the composition at these points.

For the mass diffusion column, the composition is made up of the gases and their separating vapor. The relative compositions for a single-stage unit are shown in Figure 4. The composition profiles for column operation will be similar, but the assumption of no net transverse gas flow cannot be made.

Beginning with Equation (3), and using Equations (7), (8), and (9), and the relationship $y = mx + n'$, for a total pressure of one atmosphere ($P = 1$), Equation (3) may be written in the form

$$-\frac{\partial p_0}{\partial x} = (k_1 x + k_2) p_0 - k_1 x + k_3 \quad (105)$$

where

$$\begin{aligned} k_1 &= m R \bar{T} N_0 \left[\frac{1}{D_{02}} - \frac{1}{D_{01}} \right] \\ k_2 &= -R \bar{T} \left[\frac{N_0}{D_{02}} + \left(\frac{1}{D_{02}} - \frac{1}{D_{01}} \right) N_0 n' \right. \\ &\quad \left. + \left(\frac{N_2}{D_{02}} - \frac{N_1}{D_{01}} \right) \right] \\ k_3 &= R \bar{T} \left[\frac{N_0}{D_{02}} + \left(\frac{1}{D_{02}} - \frac{1}{D_{01}} \right) N_0 n' \right] \end{aligned} \quad (106)$$

Equation (105) is linear in p_0 , and using the boundary condition

$$p_0(x_b) = p_{0b} \quad (107)$$

and treating k_1 , k_2 , and k_3 as constants, it may be solved in the form

$$P_0 = 1 + \frac{k_2 + k_3}{|V - k_1|} \exp\left\{\frac{-k_1}{2}\left(x + \frac{k_2}{k_1}\right)^2\right\} \int_{\frac{|V - k_1|(x + k_2/k_1)}{|V - k_1|(x + k_2/k_1)}}^{|V - k_1|(x_b + k_2/k_1)} e^{-r^2/2} dr$$

$$- (1 - P_{0b}) \exp\left\{\frac{-k_1}{2}\left[x^2 - x_b^2 + \frac{2k_2}{k_1}(x - x_b)\right]\right\} \quad (108)$$

For the case where $|k_2/k_1| \gg x_b$, Equation (108) reduces to

$$P_{0a} = -\frac{k_3}{k_2} - (1 - P_{0b}) \exp\left\{\frac{-k_1}{2}\left[x_a^2 - x_b^2 + \frac{2k_2}{k_1}(x_a - x_b)\right]\right\} \quad (109)$$

Generally, Equation (109) is satisfactory for calculating the partial pressure of the vapor at $x = x_a$ (vapor entry surface). In the cases where Equation (108) has to be used, the integrals may be evaluated from error function (probability integral) tables.

Unless the ratio D_{01}/D_{02} is large, the values of m and n' do not have much affect upon the calculated values of p_0 . But the values of N_1 and N_2 , magnitude and sign, do affect p_0 appreciably. Using the above equations the density profile can be calculated for known mean values of N_0 , N_1 , N_2 , m , n' , D_{01} , D_{02} , and T .

EXPERIMENTAL APPARATUS AND EXPERIMENTAL PROCEDURES

The mass diffusion separation process was investigated experimentally by means of two laboratory columns and their auxiliary equipment shown in Figure 13. These columns and their operation will be described first in general design and operation, and then as regards their specific behavior.

Each column consisted of an annular separating zone between the inner, porous vapor-tube and the surrounding condenser. The elements were circular in cross-section and concentric in spacing, with their longitudinal axis being vertical.

The feed gas was introduced into the annular working space at the top of the column by means of a circular, distributing cap. This distributor not only served to inject the feed gas along the inner circumference of the condenser, but also as the means for withdrawing the top product form along the periphery of the vapor-tube. The bottom stream was withdrawn from the dead gas space above the condensate level at the bottom of the column.

The condensible vapor was continuously generated in a boiler, and fed into the central, porous vapor-tube to diffuse radially outwards and condense on the inner wall of the condenser. The condensate collected at the bottom of the column and was withdrawn continuously. The condenser temperature was maintained by recirculation of the thermostatically controlled coolant.

Column I: Description

This column (Figure 14), which furnished the preponderance of the experimental data, had a vapor-tube nine feet in length, with its vapor entry at the bottom. The vapor-tube was made from Oilite

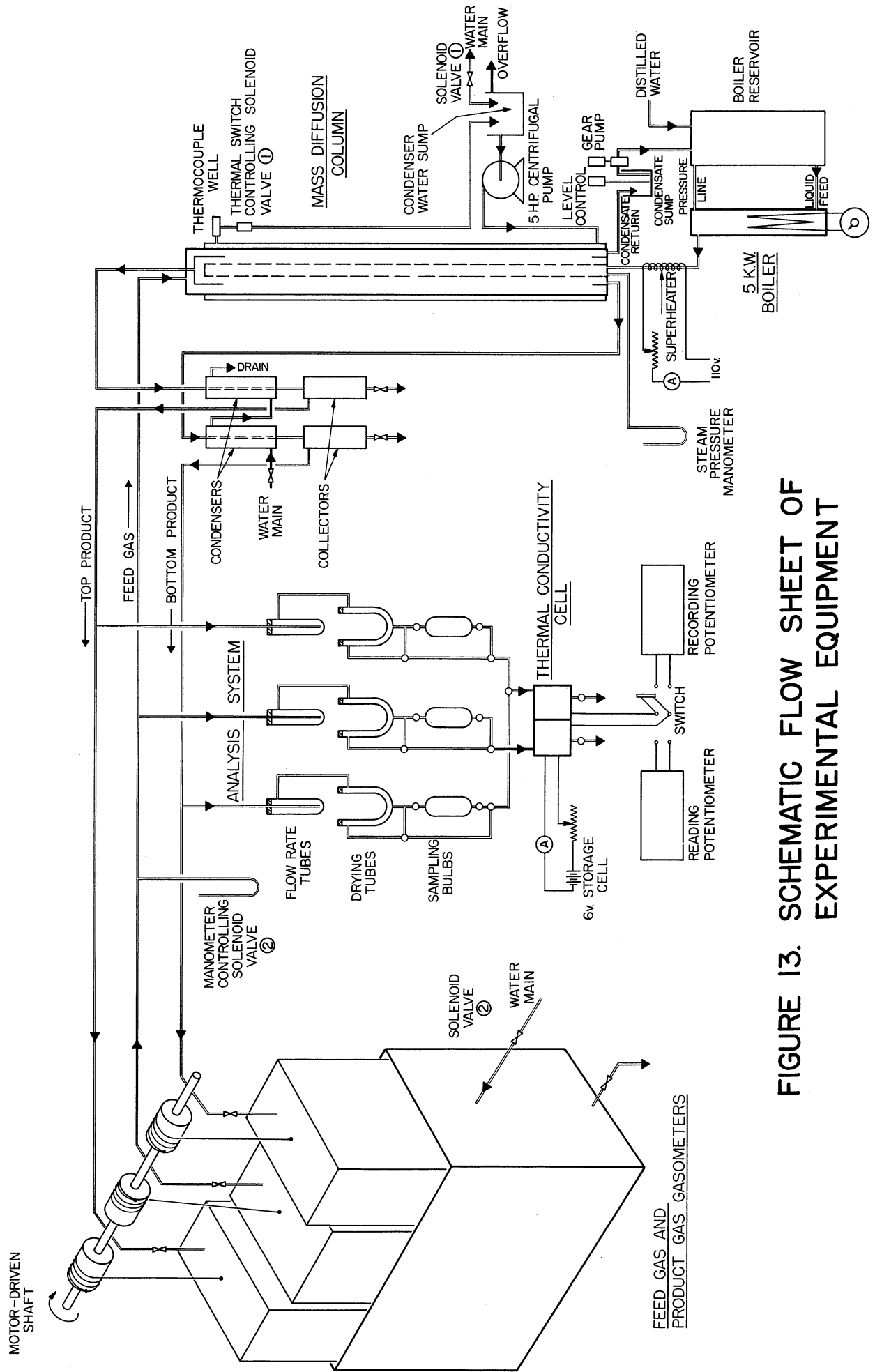


FIGURE 13. SCHEMATIC FLOW SHEET OF EXPERIMENTAL EQUIPMENT

Strip Stock; a porous bronze sheet, $1/64$ inch thick, rolled in the form of a tube with an outside diameter of $1-1/2$ inches. The holes in the tube were estimated by the manufacturer¹ to have diameters of the magnitude of ten microns; with the term "diameter" being used rather loosely as the holes were formed by the removal of flake-like particles from the sintered sheet.

This tube had a small, longitudinal soldered seam due to its method of being formed, and this soldered area was closed to any vapor flow. The vapor-tube was kept concentric to the surrounding condenser by means of the top and bottom headers and three spacers, placed at 120° to each other, half way up the column's length. These spacers were $1/2$ inch lengths of $1/8$ inch copper wire soldered to the vapor-tube.

The vapor-tube was closed at the top of the column by means of a metal disc soldered across the inside diameter at a point $1/4$ inch from the end. This formed a shallow depression that fitted over the central member of the top header, thereby spacing the tube accurately with regards top product exit and condenser walls.

At its lower end, the tube was soldered to, and supported by, a 5 inch length of $1-1/2$ inch copper tubing that rested on the bottom header. This lower end was open and provided the entry for the condensable vapor.

The condenser consisted of two concentric pieces of copper tubing with $2-1/2$ inch and $3-1/2$ inch inside diameters. Both pieces were 10 feet 4 inches in length, and were of type M tubing. The ends were closed by soldering brass rings into the annular spaces between the tubing. To allow for the passage of the coolant, nipples of

¹ Chrysler Manufacturing Company, Detroit, Michigan.

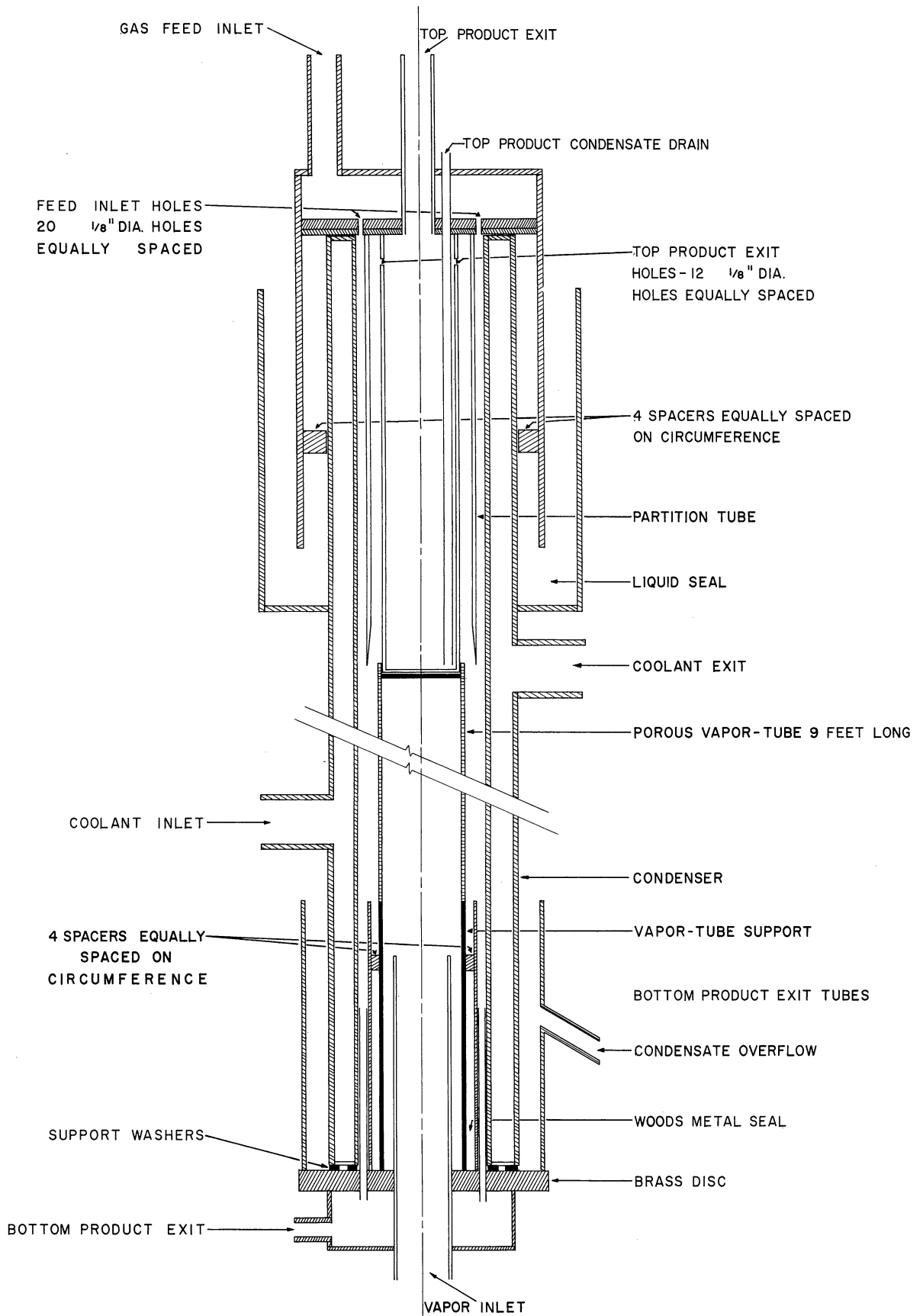


FIGURE 14
COLUMN I

1 inch copper tubing were soldered to the holes in the outside tube at points 7 inches from each end. A 6 inch length of 6 inch i.d. tubing was sealed at its lower end to the outside condenser tube at a point 7 inches down from the top of the condenser. The annular space between this short length of tubing and the condenser was to provide for a water seal.

The bottom header, besides acting as the support for the rest of the column, provided the openings for removing the bottom product and the condensate streams, and the admitting of the vapor. It consisted of a horizontal brass disc, $1/2$ inch in thickness and $5-1/2$ inches in diameter, drilled and fitted in such a manner that there were, on concentric diameters: 1) a 6 inch length of 1 inch tubing extending 4 inches above its hole in the disc, 2) a 5 inch length of $1-1/2$ inch tubing fastened to the top of the disc, 3) ten tubes, $3/16$ inch tubing and 4 inches long, equally spaced on a $2-1/4$ inch diameter circle, and extending $1/8$ inch below the bottom surface of the disc, 4) the manifold chamber consisting of a 1 inch length of $3-1/2$ inch tubing soldered at its top to the bottom of the disc, and sealed at its lower end by means of an annular ring between it and the vapor entry tube mentioned in 1) above, and 5) a 5 inch length of $4-1/2$ inch tubing soldered to the top of the disc. All joints were made with commercial grade 50-50 solder. This bottom header as well as the top header (cap of the column) are shown in Figure 14.

The top header, besides sealing off the top of the column, provides the means for introducing the feed gas and removing the top product. Like the bottom header, the top header consisted of a brass disc with short lengths of tubing jointed to it. This disc was $1/4$ inch

thick and 4-1/2 inches in diameter, with 1) a 3 inch length of 3/4 inch tubing soldered to a central hole and extending upwards from the disc, 2) an 8 inch length of 1-1/4 inch tubing fastened to the bottom of the disc, with its lower end sealed by means of a solid disc, and twelve 1/8 inch holes drilled at equal spacings in its circumference 1 inch down from the top, 3) an 8 inch length of 2 inch tubing soldered to the bottom of the main disc, and with its lower end tapered down from the inside diameter to the outside diameter on the last inch of length, 4) twenty 1/8 inch holes drilled in the main disc at equal spacings on a 2-1/4 inch diameter circle, and 5) a 7 inch length of 4-1/2 inch tubing soldered to the periphery of the main disc with 1 inch of its length extending above the disc, and the top of this 4-1/2 inch tubing closed off with an annular disc to which a 3/4 inch nipple was fastened.

The top header was also equipped with a length of 1/8 inch tubing, penetrating and soldered to both 4-1/2 inch discs, and extending down to near the bottom of the central 1-1/4 inch tubing. This allowed the removal of any liquid that collected in the 1-1/4 inch tube.

The column was assembled by first mounting the bottom header on an angle iron support that was fastened to the floor and wall at their juncture, so that the bottom of the column was approximately 1 foot off the floor and 1 foot out from the wall. The condenser, with the vapor-tube inside of it, was raised into the vertical position above the base and the vapor-tube was allowed to slide into place over the 1-1/4 inch tube of the bottom header. With the condenser still raised off the base, molten Woods Metal was poured into the annulus between the 1-1/2 inch and 2 inch tubes to the depth of about 4 inches. This was to act as a seal for the steam in the vapor-tube.

The Woods Metal would be liquid at operating temperatures and would provide a liquid of high density, without the corrosion problems with the copper tubing that mercury would present.

A ring of 1/2 inch flat washers was made in the annulus surrounded by the 4-1/2 inch tube, and the condenser was lowered to rest on it. These washers, lying horizontally, served to support the condenser, and at the same time allowed the condensed vapor to flow under the bottom edge of the condenser and out of the column.

The condenser was fastened to the wall with brackets and checked by means of levels and plumb lines to make certain that its longitudinal axis was vertical.

The column was closed in by slipping the top header over the top of the condenser, making certain that the bottom of the 1-1/4 inch tubing in the header slid into the recessed top of the vapor-tube.

Column II: Description

In comparison with Column I, Column II was shorter, the vapor entered from the top, and the condenser was made of Pyrex glass. Column II is shown in Figure 15.

The vapor-tube was a length cut from the same piece of Oilite material that was used to make the vapor-tube of Column I. Thus, it had the same physical properties, and the same outside diameter dimension of 1-1/2 inches, only it was 3 feet (later reduced to 2 feet) in length. It was closed off at the bottom, and its top was soldered to the column header. (This column had only one header, the one at the top.)

The construction of the column header was similar in construction to the top header of Column I, except that in Column II the

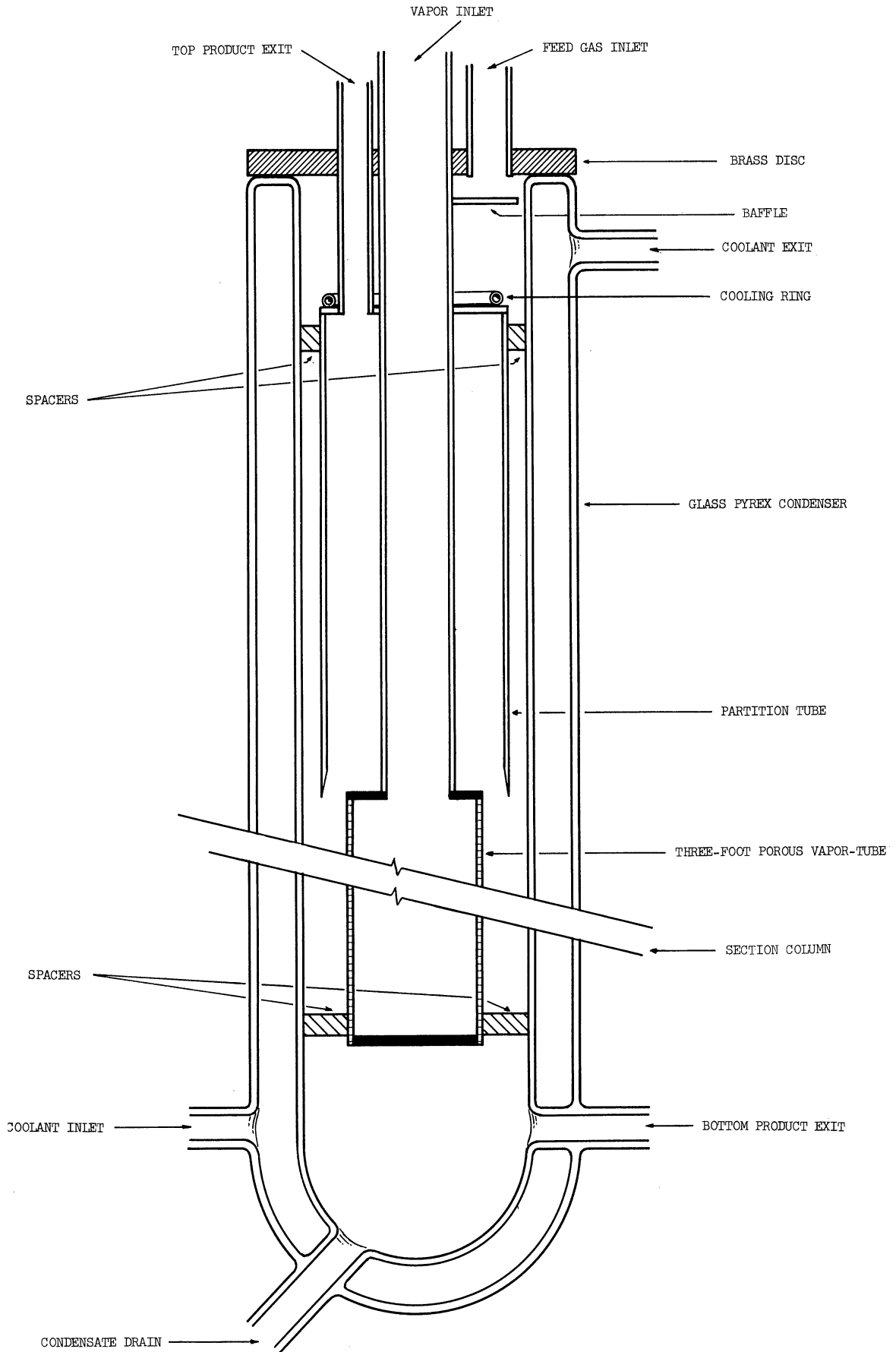


FIGURE 15
COLUMN II

central tube is the vapor inlet rather than the top product outlet. The top product outlet was a 3/4 inch tube penetrating the header disc and going down into the annular space around the vapor-tube. The feed gas was introduced through another 3/4 inch nipple in the brass disc with a baffle opposite its opening so as to produce an even flow of gas down along the inside circumference of the condenser.

As shown in Figure 15, there is a small cooling ring at the top of the 2 inch partition tube used to separate the feed and top product streams. This was a circle of 1/4 inch tubing soldered to the top of the 2 inch tubing support, and had its ends brought out of the top of the column through the brass disc. Cooling water could be put through this tubing to cool the separating partition tube.

Besides the usual coolant openings into the annular space between the condenser's glass wall, there were two additional openings into the inside of the condenser. These were at the lower end of the condenser, and were 1/4 inch nipples, one above the other. The lower one was used to remove the condensate, and the upper one to remove the bottom product. The condenser's inside diameter was 2-1/2 inches and the walls were 3 mm thick.

The column header was cemented to the top of the condenser and the vapor-tube was centered in the condenser by means of spacers at its top and bottom. The column was mounted vertically and supported by means of a bracket under the bottom of the condenser and a stabilizing clamp near its top.

Auxiliary Equipment

Feed and Product Gas Handling

By far the largest pieces of apparatus used in this research were the gasometers (or gas-holders) used to 1) effect the movement of

the gas streams through the column, and 2) to conserve the gases used by acting as their collectors.

These gasometers, of which there were three, were tanks in the form of rectangular parallelepipeds without bottoms. They were made of #18 gage galvanized sheet iron and braced on their closed tops so that they could be hung from this brace. All the tanks were five feet high and 27 inches in width, but varied in depth such that their horizontal cross-sectional areas were 4.05, 5.02 and 2.51 square feet.

These tanks were suspended over a water filled tank by means of a wire cable to the top of each tank. The cables were each fastened to a separate spindle, with all three spindles being mounted on the same shaft that ran the length of the water tank and was six feet above it. Thus, turning the shaft caused the gasometers to ascend or descend in their guides as the cables wound or unwound on their spindles.

As the spindles turned on the same shaft, winding the cables in different directions, clockwise or counterclockwise, would cause the tanks to move in opposite directions. The shaft was driven by a 1/3 h.p. reversible motor through a set of reduction gears and V-belt pulleys.

The water level in the bottom tank could be controlled by solenoid valves in the water inlet and drain lines. These valves were actuated by either a manual switch, or by electrical contacts in a mercury manometer that indicated the pressure within the tanks.

In operation the largest gasometer (the one with the 25 cubic foot capacity) was used to hold the feed gas mixture, and the shaft was rotated in such a direction as to cause this tank to descend into the water-filled tank. This action forced the feed gas out of a valve

in the top of the descending tank and through 3/4 inch rubber hose and 3/4 inch piping into the column. The remaining two tanks were used to collect the top and bottom products of the column. Their cables were wound opposite to that of the feed tank cable, thereby inhaling through their top valves as they were raised out of the water tank.

The spindle diameters were machined to dimensions such that the volume being displaced by the descending feed tank was equal to the sum of the increased volumes of the rising product tanks. By changing the rate of shaft rotation by means of the V-belt pulley ratios, the feed rate to the column could be varied while keeping the D/B ratio constant. To change the D/B ratio, the diameters of the spindles of the collecting tanks were changed, such that although the total of their increasing volumes remained constant, each tank received a different fraction of this volume.

Vapor Supply

Superheated steam was used as the condensible vapor in all runs. This steam was continuously generated by boiling distilled water in a small electric boiler and causing the vapor to flow to the column through a electrically heated vapor feed line.

The boiler was a vertical, heavy gage copper pipe, 3 inches in inside diameter, and 3 feet long. The bottom end had a female thread into which was screwed a 5 K.W. Calrod electric heater. This heater consisted of two copper-jacketed elements; both 20 inches long, and each with a 2.5 K.W. capacity.

The power input to the boiler was controlled by using the heating elements either singly, or in series or parallel connection in

conjunction with a variable transformer fed by a 220 volt line. Although a wattmeter was connected to the heating elements, it was used merely as an approximate measurement of the amount of vapor being produced; the actual vapor rate being determined by measuring, over a known length of time, the quantity of condensate withdrawn from the column. The boiler was thoroughly insulated with a one inch thickness of asbestos in the form of the usual steam pipe covering. The vapor passed out of the boiler through a $3/4$ inch vapor feed line that entered the boiler one inch below its top, and normal to the boiler wall.

Distilled water was fed to the boiler through a $1/2$ inch siphon line from the five gallon carboy used as the distilled water supply tank. There was a pressure-equalizing line from the top of the boiler to the top of the carboy. Thus, the visible liquid level in the carboy, mounted at the same elevation as the boiler, was indicative of the quiescent liquid level in the boiler.

Experimental results proved the negligible solubility of the separating gases in the condensate, and the condensate was continually returned to the carboy. The condensate was returned by means of a small electric pump that was actuated by the level of the condensate collected in a 250 c.c. sump.

The vapor feed line, between the boiler and the column, was a 6 foot length of $3/4$ inch copper tubing incorporating three right-angle elbows in its length. The entire length was heated by nichrome resistance wire wound over a thin layer of asbestos sheeting on the tubing. There was an additional one inch layer of asbestos insulation on the outside of the nichrome windings. The power to the windings was manually controlled with a variable resistor off of the 110 volt

line. The temperature of the vapor fed to the column was measured by means of a thermocouple at the entrance of the vapor-tube. This thermocouple was at the end of a length of $1/8$ inch copper tubing that was inserted into the vapor-tube by passing it through the elbow fitting that joined the vapor feed line to the bottom header of the column. This same elbow was also equipped with a line for measuring the static pressure within the vapor-tube at its bottom. The opening of this pressure line in the vapor-tube was at a right angle to the axis of the column.

Gas Analysis

The primary means for analyzing the feed and product gas streams during the helium-methane runs, was a Gow-Mac thermal conductivity cell. For analyzing the helium-oxygen and nitrogen-oxygen runs, an Orsat apparatus was used. In some of the runs, a mass spectrometer was used to check results, but generally, the results of the mass spectrometer, as indicated by material balances, were the least reliable, and the thermal conductivity and Orsat analyses were used in computations and plotting.

The analysis systems for the feed, top and bottom products streams were all identical: a 10 foot length of $1/8$ inch tubing bled the gases from the midpoint of their $3/4$ inch main lines into the analysis train. This train consisted of, in sequence: a bubble-tube to indicate flow rate, a drying U-tube, a gas sampling bulb, and finally the thermal conductivity cell. Because the column was operated under the slight positive pressure of 2 inches of water, the gas flow through the analyzing equipment was controlled by a small stopcock on

the down-stream side of the conductivity cells. After passing through the cells the gases were released to the atmosphere.

The bubble-tube was where the analyzing end of the 1/8 inch tubing was placed 1/2 inch under the surface of the water in a side vented test tube. The bubbling of the gases up through the water giving a visual indication of the rate of sampling. This rate was not at all critical as regards the analysis results, and by counting the bubbles formed, the rates could be calibrated and duplicated.

Drying the gases, the removal of the water vapor present, was accomplished by passing the gases through a 6 inch U-tube filled with "Drierite". This material changes from blue to pink as it absorbs moisture, and thus, its condition was always readily observable. When the "pinkness" was present in half of the tube length, the entire contents of the tube were replaced with fresh "Drierite".

The sampling bulb was of the 150 c.c. size with a stopcock at both ends. The analysis gases were continually flowing through the bulb, but it could be by-passed and removed at any time in order to have its contents analyzed.

The thermal conductivity cell at the end of the analysis train was equipped with a current source and potentiometers. The current source was a six volt storage battery, and was controlled by means of a variable resistor and milliammeter in series connections with the cell. There were two potentiometers; one was a Brown recording type, and the other was a Leeds-Northrup reading type potentiometer. The recording type was used to follow fluctuations in the gas stream analyses, and the reading type was used to make accurate readings.

The thermal conductivity cell was of the bridge-type, actually consisting of two compartments with different gas streams connected to each compartment. The measured e.m.f. on the potentiometer compared the heat losses in the two compartments to each other. In operation, the feed gas to the column was continuously bled through one compartment, and one of the product streams was bled through the other. The measured e.m.f., when compared to the cell calibration curve, indicated the difference in their compositions. To determine the absolute compositions of the gas streams, methane gas from the supply cylinder was passed through the chamber used by the product streams, and the composition of the feed could be read directly off of the calibration curve. The difference e.m.f. then gave the absolute value of the product stream. The thermal conductivity cell analyses were estimated to be able to be read to ± 0.02 mole percent.

The Orsat analyzer consisted of a measuring burette equipped with leveling fluid and alkaline pyrogallol solution for absorbing the oxygen. As only binary gas mixtures were used, it was assumed, that after the oxygen was removed, the remaining volume of gas was entirely of the other component (nitrogen or helium). The accuracy of these analyses were estimated at ± 0.2 mole percent.

In operation, each analysis stream was allowed to flow at the rate of 10 c.c. per minute, so that a change in the composition of the streams being sampled could be noted in about fifteen seconds, the time required for the gas to flow through the analysis train.

Cooling System

A five h.p. centrifugal pump was used to circulate water through the column condenser. The water was recycled from a five

gallon sump, through the condenser, and back to the sump at a rate of five to six gallons per minute.

A Fenwall thermal switch, installed in the exit stream from the condenser, controlled a solenoid valve admitting tap water to the sump. This switch opened the water valve when the temperature of the water leaving the condenser rose to a preset value, and closed the valve when the temperature dropped below this value. The sensitivity of the thermal switch was better than $\pm 0.5^{\circ}\text{F}$, and could be adjusted to any desired temperature within the range of operation. The sump had an overflow to drain off all water above the four gallon level.

Operational Procedure

The feed tank was charged at least several hours before a run was made. This was done by submerging the empty tank in the water tank, and by means of suitable connecting hoses, blowing in the feed components from their high pressure supply cylinders. These gases raised the feed tank up, out of the water. No attempt was made to obtain a feed of an exact composition, but by raising the tank half way with each gas, an approximate 50-50 mixture was obtained. To facilitate the mixing in the tank, one side wall was heated, from the outside, with an infra-red heat lamp to produce convection currents inside the tank.

The steam generating boiler and the superheating nichrome windings were turned on. The top of the column was vented to the atmosphere and the column was flushed by the steam passing through it. After five minutes of flushing by steam alone (the condenser was allowed to heat up during this time so that condensate formation was at a minimum), several cubic feet of feed gas was passed through the column

and out of the product lines at the points where they fastened to their collecting tanks. The water seal at the top of the column was checked and the condenser pump was turned on. The product lines were connected to their respective tanks and the gasometer drive shaft was set in motion.

Then there followed a period of about ten minutes for adjusting the column variables to their desired values for that run; the pressure inside the column was set at two inches of water (above atmospheric) by raising or lowering the water level in the gasometer basin, the temperature of the vapor was set by means of the thermocouple and variable resistor, the condenser temperature was checked, and the current to the thermal conductivity cell was turned on and set at its recommended value.

The condenser temperature always stabilized itself very quickly (within minutes), while the superheat temperature was always the last variable to reach equilibrium, often taking half an hour. Once this steam temperature became constant, the analysis stopcocks were opened and the bubbling rates adjusted. The feed gas was passed through one compartment of the conductivity cell, and methane from the supply cylinder was passed through the other. The reading potentiometer was used to take the cell reading to determine the feed gas composition, and then the methane compartment was switched back to one of the product streams and the cell connected to the recording potentiometer.

Generally, by this time the column had reached steady-state operation, and the recording potentiometer, depending upon the particular conditions of the run (rates and temperatures), showed either a steady recording or small fluctuations back and forth across what

was deemed to be the average analysis value. When this average value was being recorded on the graph, the cell output was quickly switched to the reading potentiometer and an accurate reading made.

After this measurement, the cell was connected to the remaining product stream and switched back to the recording potentiometer. When the graph once again settled down so as to indicate a steady value, the cell reading was taken for this stream, and the cell again switched back to the first product stream. In this manner, the top and bottom product streams were compared to the feed gas several times during a run.

During the run the condensate rates from the column and from the product streams were measured. This was done by averaging the timings of several fillings of a 200 c.c. calibrated flask. These timings were consistently within five percent of each other.

Several times during the run, the condenser temperature, column pressure, steam pressure and steam temperature were checked. When repeated readings of the top and bottom stream analyses showed little or no variation, the feed analysis was taken again and the run concluded.

However, if there was still an appreciable volume of gas remaining in the feed tank, another run could be made immediately by changing one or more variables such as steam rate, steam temperature, or condenser temperature. These three changes required no mechanical alteration of the equipment and could be made easily and quickly. Often three runs could be made with one filling of the feed tank. When the column was shut down, everything was simply turned off. The only care that had to be exercised was to see that a negative pressure was

not produced due to the condensation of the last steam in the column. The raising of the water level in the gasometer basin would prevent this.

As all three gasometer tanks were connected together by means of, and through the column, and as the steam boiler effectively closed off the vapor-tube, the gases could be returned to the feed tank by simply reversing the motor driving the spindle shaft. This was a slow process, but by connecting the motor to a timing clock, the gases could be "reshuffled" during the night. So that any atmospheric pressure change would not cause a negative pressure within the system and draw in air, the water inlet to the gasometer basin was controlled by a solenoid valve activated by a mercury manometer switch. This manometer indicated the pressure within the tanks, and if it dropped to atmospheric, the water level was raised to compress the gases.

In the nitrogen-oxygen and helium-oxygen runs, systems for which the thermal conductivity cell was not calibrated, the cell was still used as described above, but only to the extent of indicating when the column had reached steady-state conditions. When the recording potentiometer indicated this, the gas sample bulbs were closed and removed, to be analyzed later.

Fresh gases were charged to the system to make up for losses due to analysis bleeding, and the entire contents were renewed when the analyses indicated the presence of impurities from the outside air.

Additional "one purpose" runs were made: 1) placing a thermocouple in the separating zone annulus at the top of the Column I and taking its readings as a function of steam rate and condenser

temperature, and 2) observable condensing length in Column II as a function of steam rate and temperature.

Comments on Column Operation

In general, the equipment operated well, the exception being the difficulty encountered in obtaining the initial passage of steam through the walls of the vapor-tube in Column I.

When starting up the steam boiler, the vapor-tube in the column was cold and its pores were either full of water (condensed steam) from the previous run, or rapidly became filled by the condensation of the first vapor entering the column. It required about 75°C of superheat and a steam pressure of several feet of water to effect a "break-through" of the vapor through the pores. Once the vapor started flowing through the tube, as indicated by condensate flow from the bottom of the column, the boiler pressure began a steady drop to its normal operating value.

It generally took ten minutes to obtain steam flowing through the pores in the tube; and it took much longer if the condenser pump was not kept turned off and the condenser walls were allowed to become warm from the trickle of vapor that did find its way through the larger pores.

Due to this pronounced effect, it became apparent that the temperature of the condenser walls had a very marked influence on the porosity of the vapor-tube.

This starting difficulty was not encountered in the operation of Column II; presumably because of the low thermal conductivity of the glass walls. With these walls having a thermal conductivity of only 1/500 of the copper condenser walls, the small quantity of vapor that

made its way through the few larger pores at the beginning of the run quickly caused local hot spots. These small areas grew as their heat was not removed through the condenser by either conduction or radiation. As more pores were blown open, the porosity of the tube grew progressively, until steady-state conditions were reached.

As Column II had glass walls, the formation of condensate droplets on its inside surface could be readily seen. These droplets formed very densely and quickly at the top of the column, but their rate of formation decreased down the column in a tapered effect, stopping completely at a point about two-thirds of the way down the three foot tube. This elevation, at which the condensation was observed to cease, varied according to the steam flow rate; being further down the column with higher steam rates (see Table I).

With this high steam flow across the annulus at the top of the column, and the poor conductivity of the glass condenser walls, the partial pressure of the vapor in the top product was high, and much condensate was removed from the top stream. Also, with little steam flowing across the separating zone at the lower end of the column, very little condensate was observed in the bottom product stream. This situation was the complete reversal of the results in the operation of Column I, where the bottom product had the high partial pressure of the vapor. However, as discussed in the sections concerned with the theory of the column operation and performance, this lack of condensate in the top stream of Column I did not indicate low porosity in that region.

It was also noted that the steam pressure within the vapor-tube was greater in the case of Column I than in Column II. This, in

spite of the fact, that the active length of Column I was over three times as great as that of Column II. This fact could only be explained in terms of varying porosities and non-uniformity of the pores.

Calibrations and Materials

The calibration of the equipment used was simply and easily done. Although great accuracy was not required due to the nature of the experiments, nevertheless, the precision of the calibrations was judged to be greater than the measurable experimental data.

The gas feed and withdrawal rates were measured by means of a wet gas meter that could be read to 0.001 of a cubic foot. The gases were passed through the meter under a positive pressure of two inches of water (the same as used during the experimental runs), by having the gasometer drive shaft lower the tanks in identical fashion to the operational procedure during the experimental runs. The volume passing through the meter in one hour was noted, corrected for water saturation at 20°C, and used as the values for gas flow in all succeeding calculations. The tanks were sufficiently true in their cross-sectional areas so as to produce displacement rates constant to within two percent during the entire length of travel. Causing the feed tank volume to flow directly into the two receiving tanks did not alter the pressure within the gas system by more than 1/2 inch of water.

All thermocouples were of the copper-constantan type. After fusing their junctions, their outputs were compared to the values in the standard calibration tables. Using a calibrated thermometer in a water bath, the hot junction was checked at temperatures up to that of

boiling water. The deviation from the standard tables was less than 0.5°C at all temperatures, and these tables were used throughout.

The thermal conductivity cell was calibrated by passing gas mixtures of known composition through the cell and recording its output. These mixtures were made up by passing the constituent gases from their high pressure cylinders into a five gallon carboy. The gases, entering under a slight known pressure, displaced the water with which the carboy was initially completely filled. The displaced water was measured, and assuming that the gases mixed with no change in individual volumes, the mole percentage was calculated from the volume percentage.

The gas mixture in the carboy was agitated by sloshing around the gallon or so of water allowed to remain. This mixture was forced through the analysis train by allowing water to re-enter the carboy under a slight pressure, and with methane from its supply cylinder flowing through the second compartment of the thermal conductivity cell, potentiometer readings were taken. These readings became steady in less than two minutes. The calibration curve is given in Figure 16.

The gases used, with the exception of atmospheric air for the nitrogen-oxygen runs, were those commercially supplied by Mathewson. The helium was better than 99.6 percent pure, and the methane was better than 96.3 percent pure. These gases were treated as 100 percent pure gases in analysis and calculations. The contents of new cylinders were checked against the contents of the exhausted cylinders by means of the thermal conductivity cell, and differences of less than 0.1 percent were found.

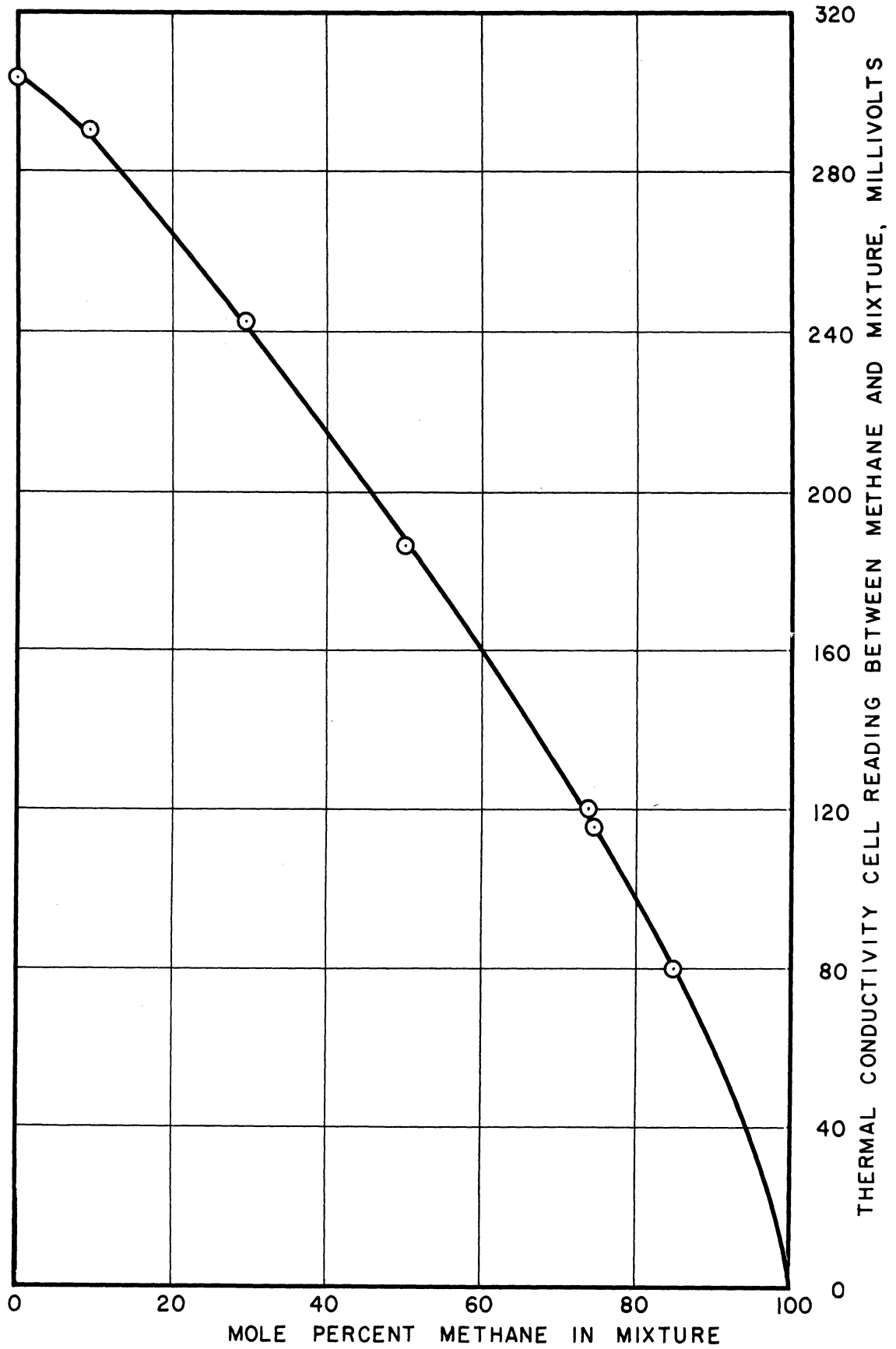


FIG 16 THERMAL CONDUCTIVITY CELL CALIBRATION

EXPERIMENTAL RESULTS

Data

The results of the experimental gas separations are shown graphically in Figures 17 through 25. The mole percent of the more diffusible component in the product streams is plotted against the column vapor rate. The numerical values from which these figures were made, are given in Table II, page 125.

A "run" is defined as the determination of the top and bottom product compositions for the column operating under one set of conditions. A "series" is a number of runs, all performed under the same set of conditions with the exception of the vapor rate. Thus a series show the effect of the vapor rate on the separation. The effect of the feed rate is observed by comparing the ordinate values at the same value of vapor rate. The feed rates are expressed as cubic feet per/hour, saturated with water vapor at 20°C.

A key to the graphs showing the helium-methane separations obtained in Column I is given in Table I. Here, the fractions in the boxes indicate the series number over the number of the Figure in which that series is shown.

The separations of helium-oxygen and nitrogen-oxygen in Column I are shown graphically in Figures 23 and 24. The separation of helium-methane in Column II is shown in Figure 25.

The numerical values used in these graphs are tabulated in the appendix, along with pressure drop, and column length measurements.

TABLE I. KEY TO FIGURES 17 THROUGH 22, HELIUM-METHANE SEPARATION IN COLUMN I

Condenser Temp. °C	Vapor Temp. °C	Products Ratio, D/B = 1		Products Ratio, D/B = 2.1	
		Feed Rate, c.f.h.	14.60	Feed Rate, c.f.h.	14.60
25	125	13/17 ²	14/17	1/18	2/19
25	150	6/21	3 ¹² /21	3 ¹⁰ /21	7/21
50	125	17/19	18/19	5/20	8/20
50	150		20/19	3 ¹¹ /22	9/22
75	125			4/21	

1 Saturated with water vapor at 20°C

2 Fractions represent: series number/figure number

3 One run only

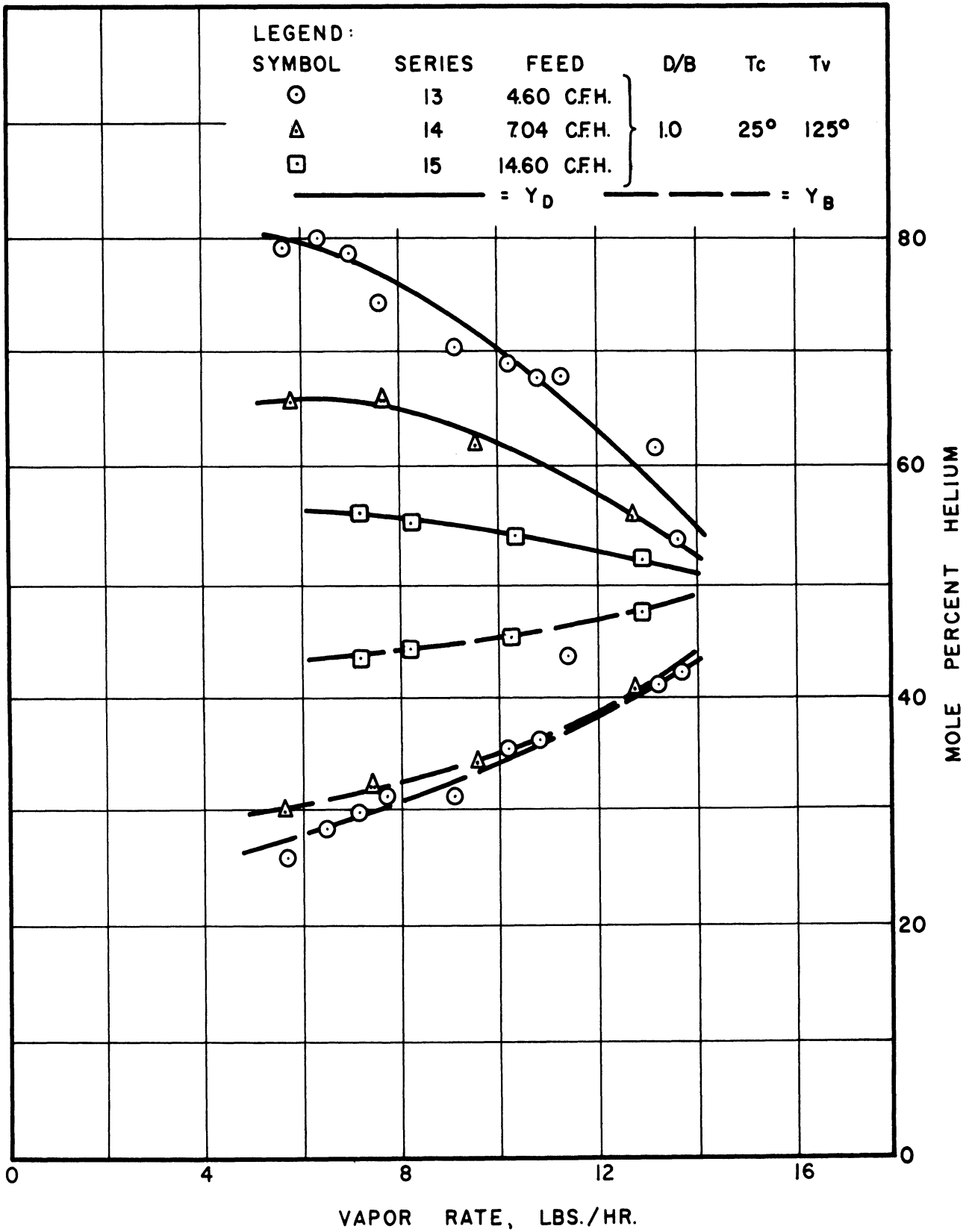


FIG 17 HELIUM - METHANE SEPARATION
COLUMN 1

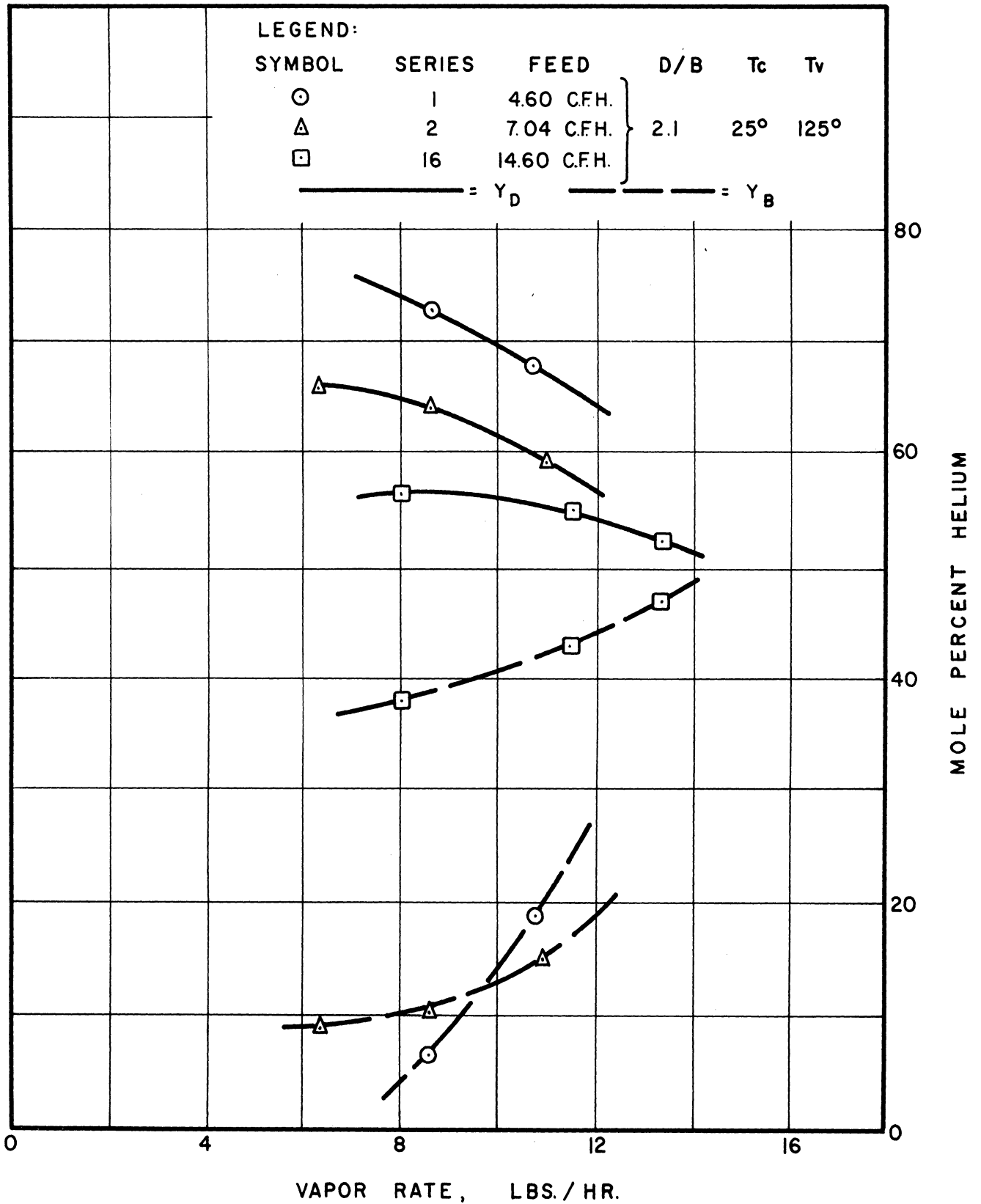


FIG 18 HELIUM-METHANE SEPARATION
COLUMN 1

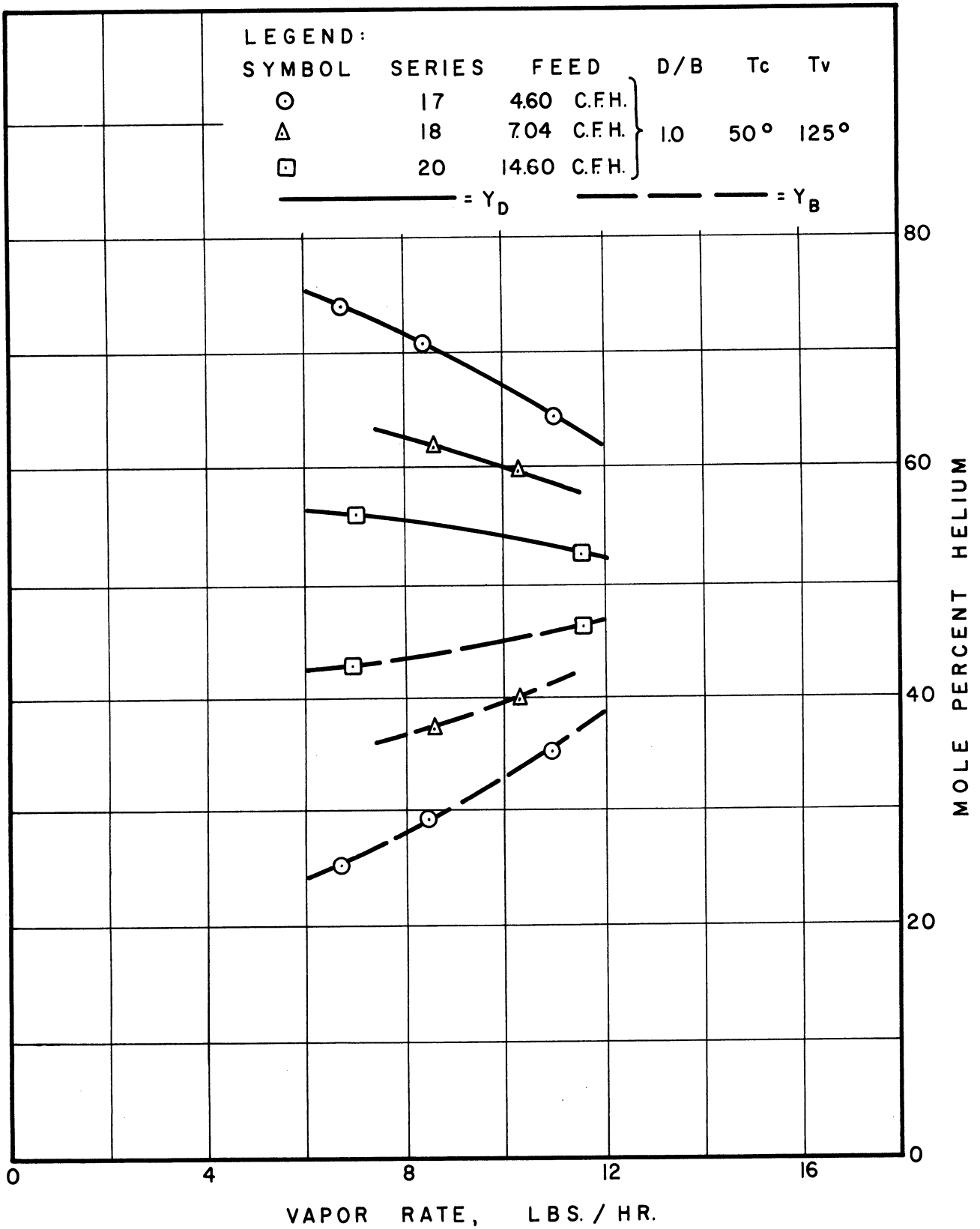


FIG 19 HELIUM - METHANE SEPARATION
COLUMN 1

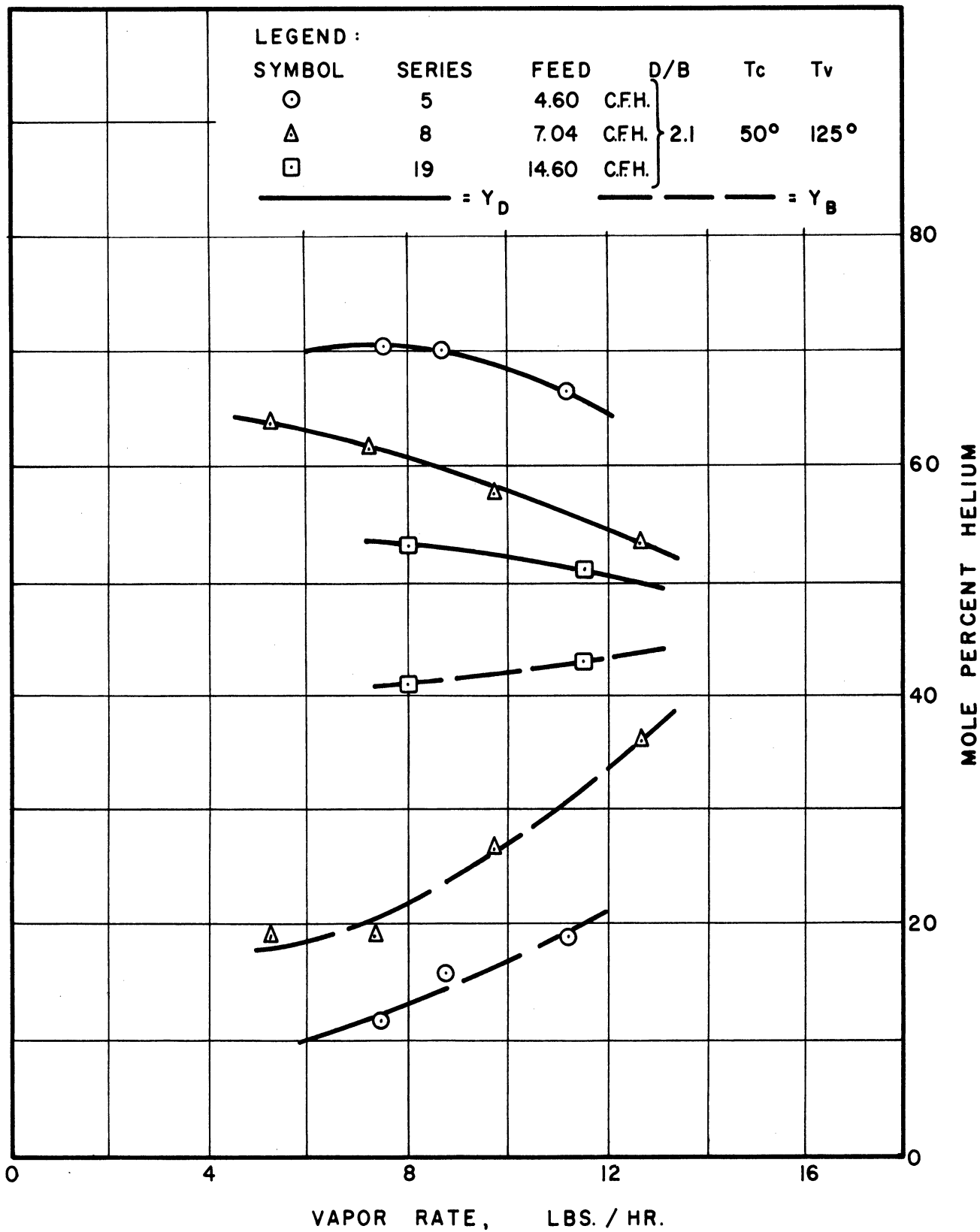


FIG 20 HELIUM-METHANE SEPARATION
COLUMN I

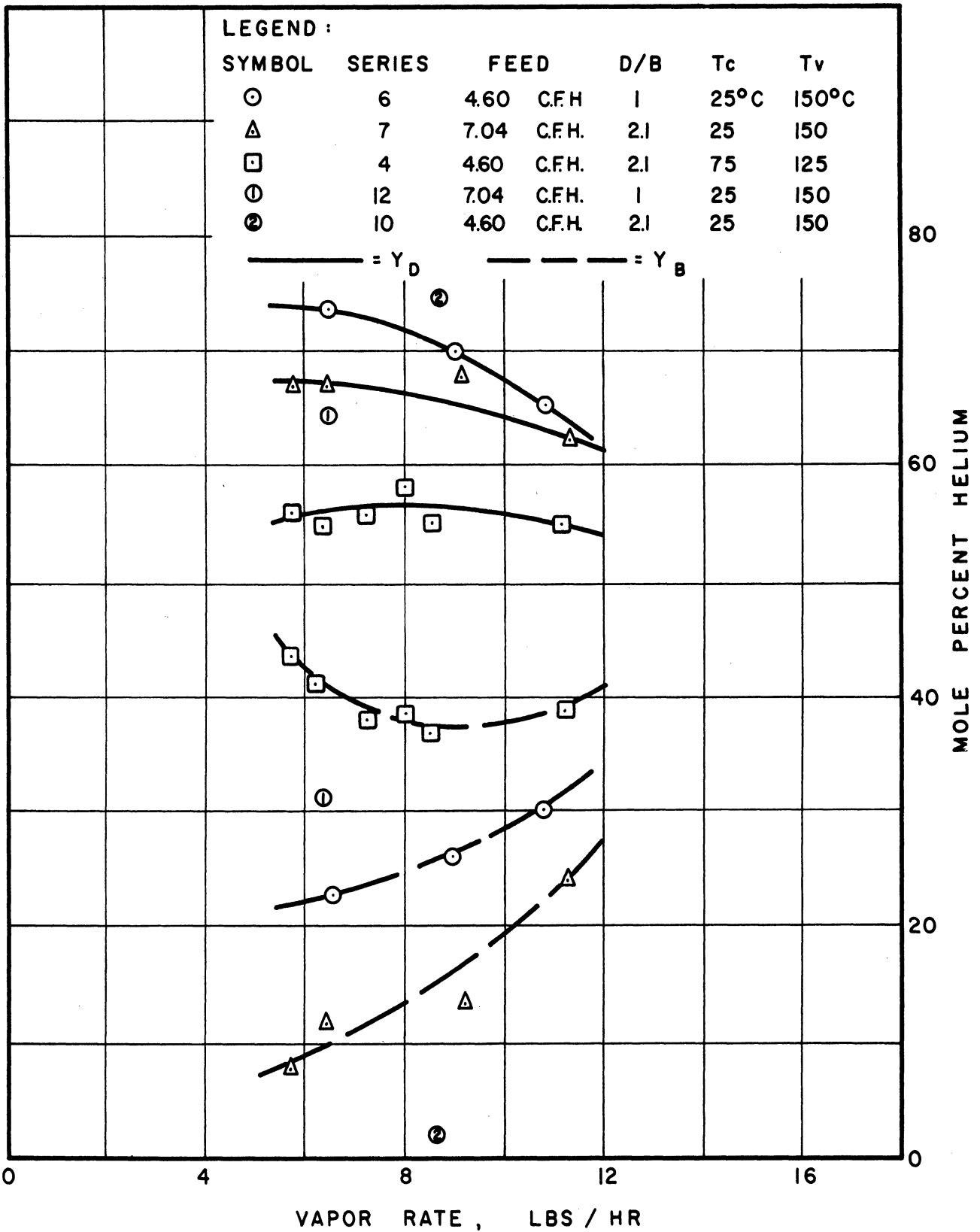


FIG 21 HELIUM-METHANE SEPARATION
COLUMN I

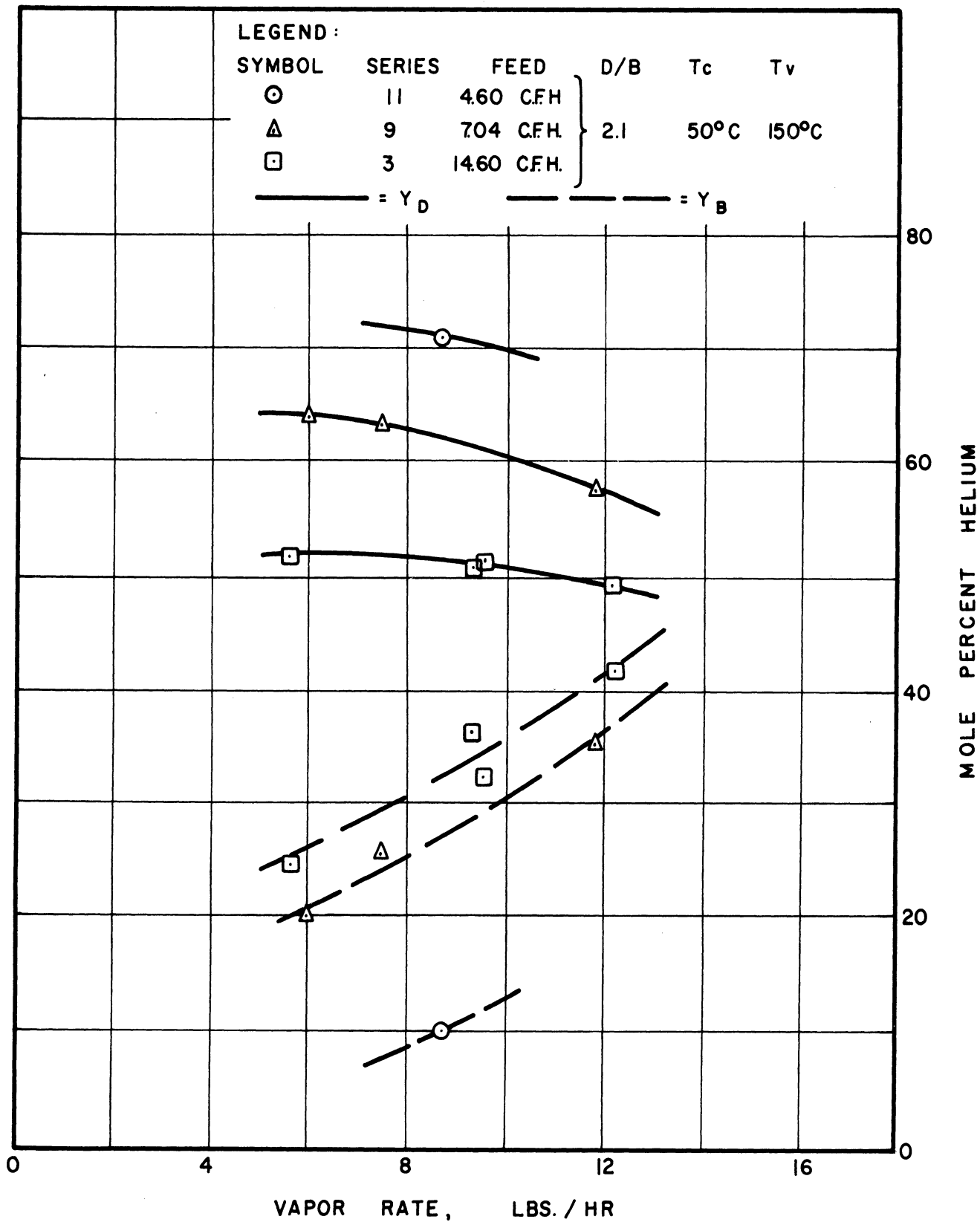


FIG 22 HELIUM - METHANE SEPARATION

COLUMN I

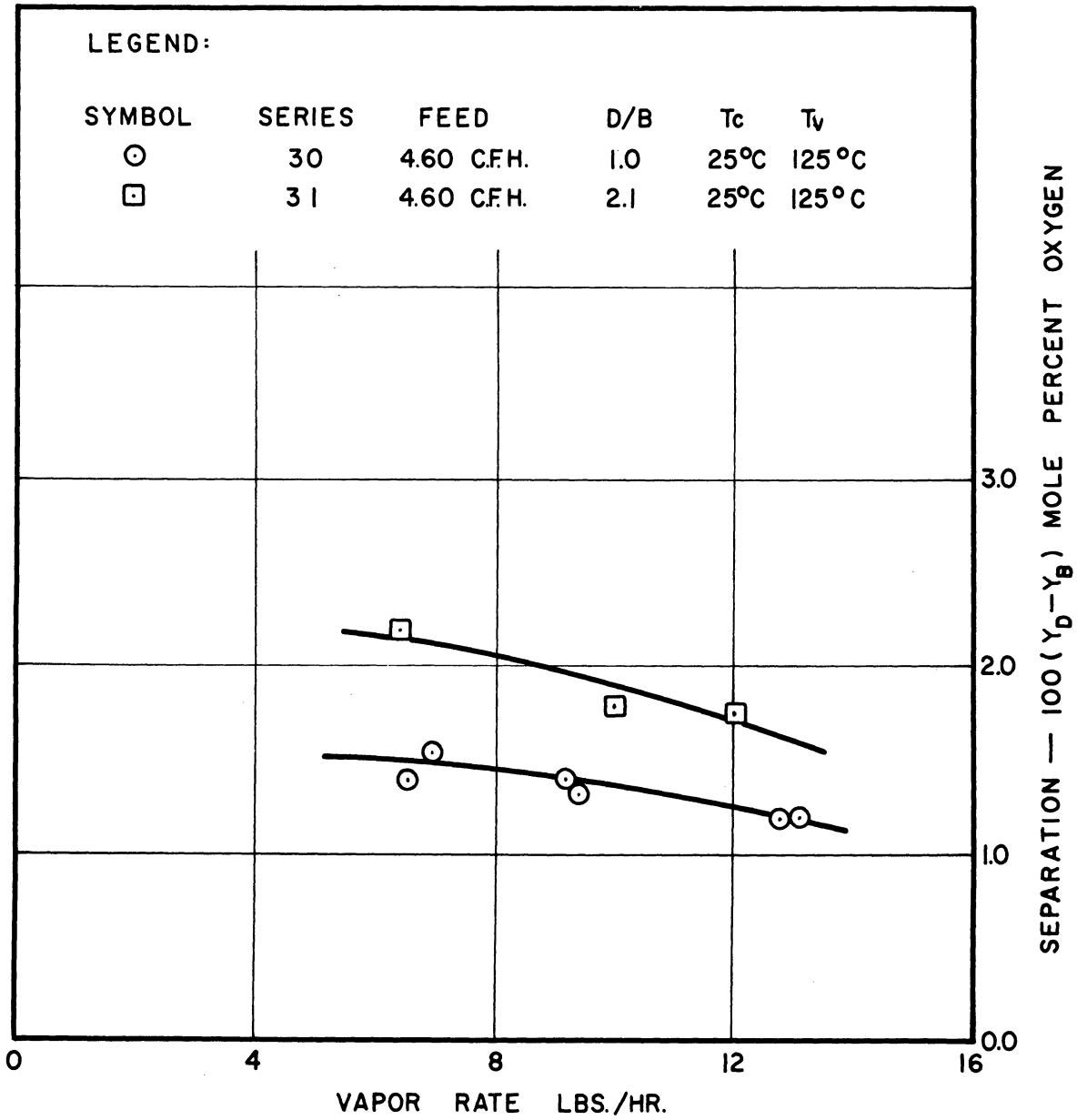


FIG 23 AIR SEPARATION
COLUMN I

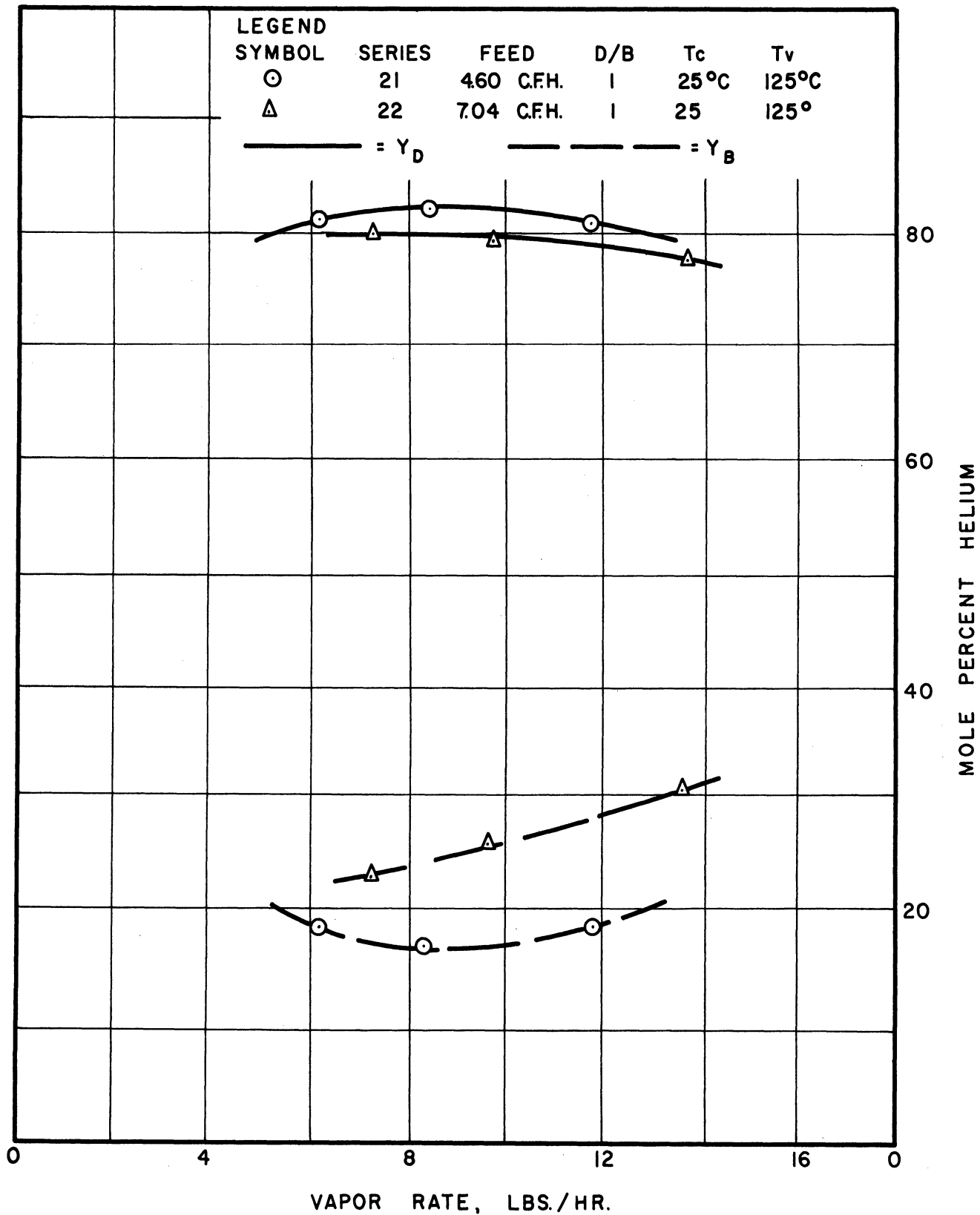


FIG 24 HELIUM - OXYGEN SEPARATION
COLUMN I

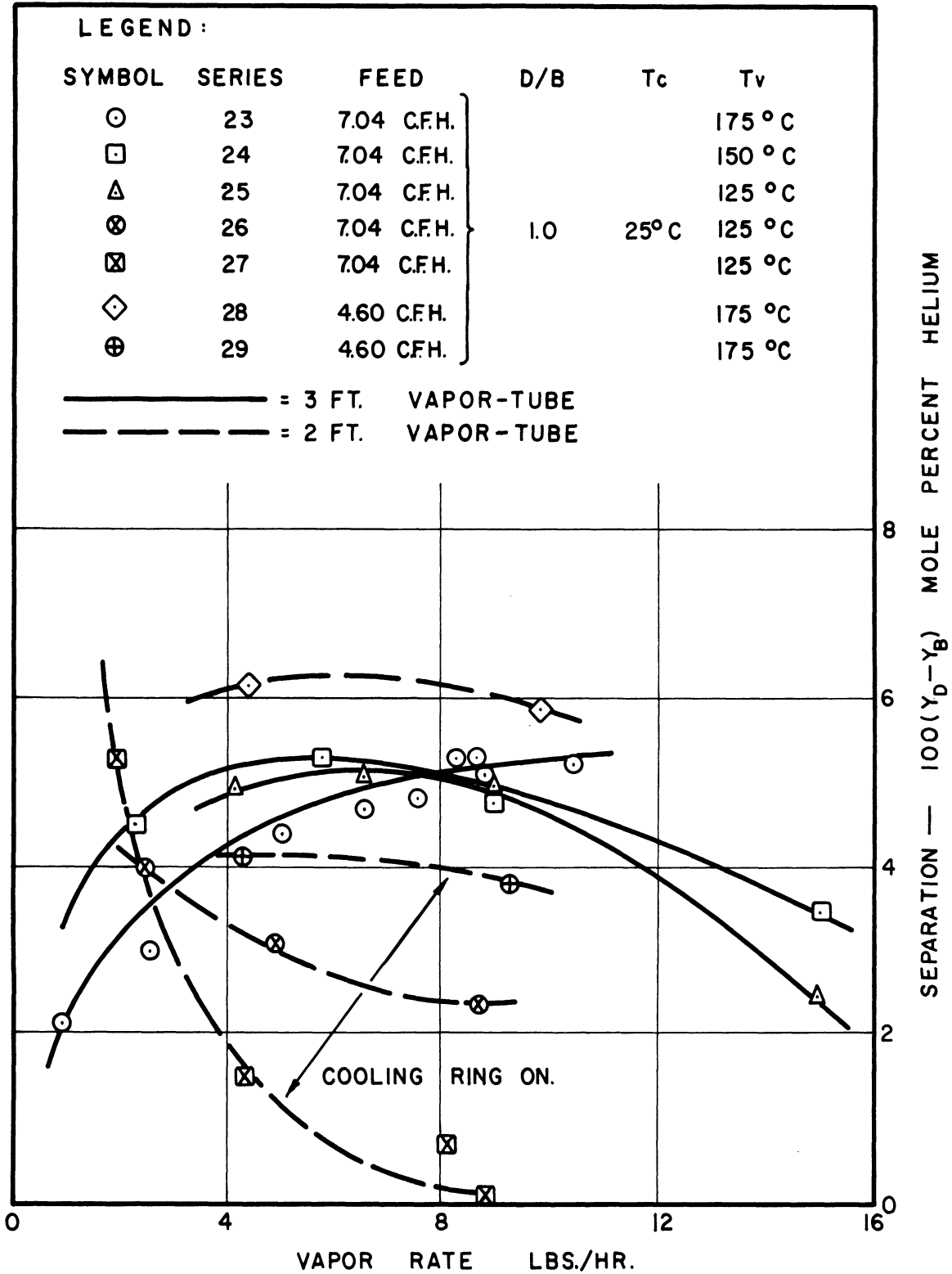


FIG 25 HELIUM-METHANE SEPARATION
COLUMN II

Although the thermal conductivity cell was capable of detecting a difference of ± 0.02 mole percent in the gas compositions, the analyses were never recorded to better than ± 0.1 mole percent because: 1) the calibration curve of the thermal conductivity cell was believed to be accurate to only ± 0.1 mole percent, and 2) the continual, small fluctuations of the product streams, as indicated by the thermal conductivity cell readings, made more exact recordings impractical. At times the cell readings would indicate analysis compositions varying within a 0.5 mole percent range. When this happened, the recorded value corresponded to the mean value as indicated by the swing of the galvanometer on the reading potentiometer.

The range of vapor flow values was determined by the equipment. The lower limit of 5-6 lbs./hr. was the lowest steam rate that would keep the vapor-tube in steady-state operation. Dropping below this value would allow the pores to begin to fill with condensate and cause the pressure drop through the tube to fluctuate in erratic fashion. The upper limit of 15-16 lbs./hr. was the maximum output of the 5 K.W. boiler.

Cursory examination of Figures 17 through 24 shows; 1) that Column I effected good separation of the gases (the separation being the difference in the compositions of the top and bottom product streams), and 2), that the runs of each series plot well with regard to each other. Further examination shows that trends expected from theory are present; a) decreased separation with increased feed rate, as shown in Figure 26, and b) increased separation with decreased flow through the column, as shown in Figure 27. There is also decreased

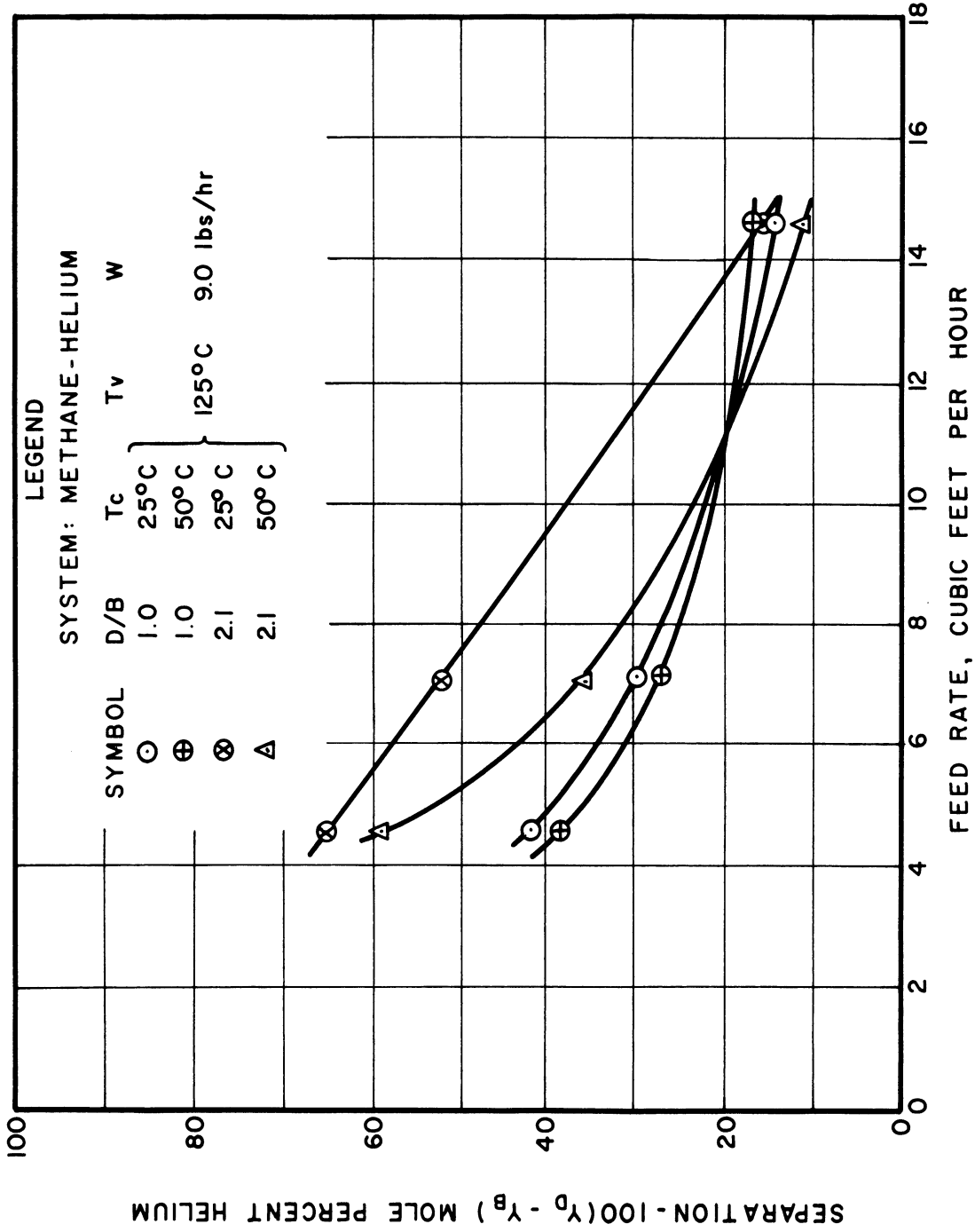


FIG 26 EFFECT OF FEED RATE ON SEPARATION IN COLUMN I

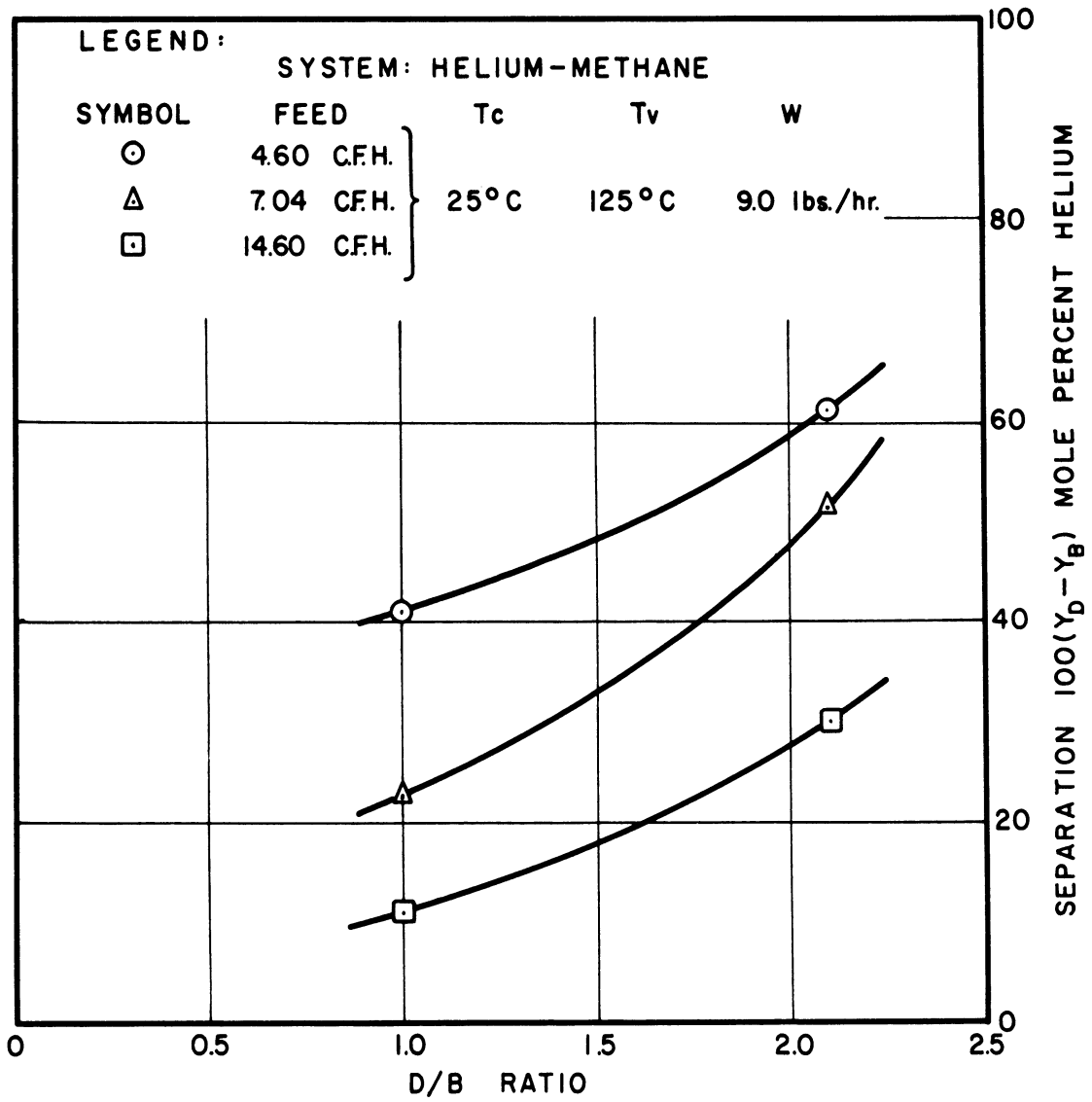


FIG 27 EFFECT OF RATE OF FLOW THROUGH COLUMN I ON ITS SEPARATION

separation with lower temperature differences across the annulus, but this is not obviously predictable in that the separation can theoretically pass through a maximum with increasing V.

The one, apparent incongruous behavior, is that the separations decrease with increased vapor rates. In some cases the separation passes through a maximum, but generally, within the range of column operation, it falls off steadily with increasing vapor rate. Simple mass diffusion theory would predict increasing separation with increasing vapor rates.

Calculations on Experimental Results, Helium-Methane System, Column I

The numerical investigation of the data consists of comparing the observed results with the results expected from theory, and attempting to explain any differences. These differences might be explained by means of efficiency factors, or by explaining how the actual operation of the column differs from its assumed operation.

In as much as the column separation process is an actual physical process, no discontinuities in its operation would be expected, and its performance should be a continuous function of its operating variables. This was found to be true in the graphing and tabulating of the experimental data, and any one of the runs could have been chosen for a sample calculation. A run from the series with the most runs was deemed the best choice. This run was:

Column; Column I	Top Product Composition;
System; Helium-Methane	68.0% Helium
Series; 13	Bottom Product Composition;
Condenser Temperature; 25°C	35.5% Helium
Steam Temperature; 125°C	Condensate from Bottom Product Stream
Vapor Rate; 10.80 lbs./hr	0.24 lbs./hr.
Feed Rate; 4.60 c.f.h.	Condensate from Top Product Stream;
Products Ratio; D/B = 1.0	0.00 lbs./hr.
Feed Compositions; 51.9% Helium	Pressure Drop Through Tube Wall;
	40.2CM of water

Values of H, K, and B will be calculated and the predicted separation calculated by means of Equation (44)

$$y_F - y_B = \frac{H}{4B} \left[1 - \exp \left[\frac{-BZ_s}{K} \right] \right] \quad (44)$$

Evaluation of H_s

The values of D_{01} , D_{02} and D_{12} were taken from the literature (10,11) as $D_{01} = 1.00$, $D_{02} = 0.33$, and $D_{12} = 0.61$ cm.²/sec. at 75°C., and from Equation (36) $H_s = 0.585V$.

Evaluation of \bar{p}_o

The value of \bar{p}_o cannot be accurately solved for without knowing the value of dy/dz . However, its value can be well approximated by assuming a reasonable value of dy/dz and latter correcting it if the value of dy/dz is far different from the assumed value.

Letting $N_1 = -N_2$, $V = 0.001$, $dy/dz = 0.005$, $m = 0$, $n' = 0.50$, $N_o = 1.70 \times 10^{-5}$ (based upon $\bar{E} = 16$ cm. and $Z_s = -275$ cm.), the following values may be calculated; $k_1 = 0$, $k_2 = -0.94$, $k_3 = 0.92$ and for $p_{o_b} = 0.05$, Equation 109 gives $p_{o_a} = 0.68$. The value of $\bar{p}_o = 0.39$.

Evaluation of H_T

The mean value of α_T can be calculated from the equation

$$\alpha_T = \frac{105}{108} \left(\frac{M_2 - M_1}{M_2 + M_1} \right) R_T \quad (110)$$

or from more exact equations in the literature (5). The constant R_T is the ratio of the actual value of the thermal diffusion constant to the value it would have for hard sphere molecules, and can be found in the literature (6). As will be seen by the relative magnitudes of H_T and H_S , an approximation of α_T is very adequate. The values used were $\alpha_{T10} = 0.34$, $\alpha_{T12} = 0.24$, and $\alpha_{T20} = 0.03$, whereby the value of H_T from Equation (64) is $H_T = 0.04V$.

Evaluation of K_d

K_d is evaluated from Equation (26), with the substitution of \bar{p}_O as just calculated above instead of using \bar{p}_O as derived from Equation (23); and $K_d = 0.000,36$.

Evaluation of K_c

K_c is evaluated from Equation (37); and $K_c = 2,730 V^2$

Evaluation of B

The feed rate was 4.60 c.f.h. at 20°C and saturated with water vapor. At 20°C the vapor pressure of water is 0.05 atmospheres.

$$B = \frac{(4.60)(28,320)(0.95)(273)}{(22,400)(293)(3600)(2)} = 0.000,71 \text{ gm.moles./sec.}$$

Predicted Separation

Substituting the above values into Equation (44) gives

$$(y_F - y_B) = \frac{0.625V}{0.002,84} \left\{ 1 - \exp \left[\frac{(0.000,71)(-275)}{(0.000,36 + 27,300V^2)} \right] \right\}$$

Due to the length of the column and the low K value, the exponential part of the above equation is very small and may be dropped, leaving

$$(y_F - y_B) = \frac{0.625V}{0.002.84}$$

Using the experimentally determined values of y_F and y_B , $V = 0.000,74$. Considering this flow to take place over half of the annulus' cross-sectional area at 330°K , the mean linear velocity would have to be

$$\frac{(0.000,746)(22,400)(330)}{(273)(10 \text{ cm.}^2)} = 2.02 \text{ cm./sec.}$$

This is a very practical velocity, but can it be expected under the conditions that the column is operating?. Taking the conditions at the top of the column; $y^I = 0.680$ and $y^{II} = 0.519$, and by assuming symmetry and linearity of compositions, $y_a = 0.76$ and $y_b = 0.44$. Using $p_{O_a} = 0.68$ and $p_{O_b} = 0.05$, the average molecular weights at each side of the annulus are; at x_a m.w. = 14.47 and at x_b m.w. = 11.14 . Correcting for the temperature of 125°C at x_a and 25°C at x_b ;

$$\rho_a = 0.000,443 \text{ gm./cm.}^3$$

$$\rho_b = 0.000,456 \text{ gm./cm.}^3$$

And the value of a is

$$\frac{0.000,456 - 0.000,443}{1.27 \text{ cm.}} = 0.000,010 \text{ gm./cm.}^4$$

The viscosity of the mixture can be calculated from equations derived for such purposes (11), but comparison of these results to the viscosity of the mixture as calculated by proportioning the viscosities according to their mole fractions showed negligible difference. The viscosity of the mixture as calculated by mole fractions at 75°C was 0.015 centipoises, and

$$a' = \frac{(980)(0.000,010)}{(.000,150)} = 65 \text{ cm.}^{-2} \text{ sec.}^{-1}$$

Referring to Figure 12 for $\beta = 0$, the integrated average value of v/a' for the ascending stream is 0.011 and therefore the predicted

mean velocity is equal to $(0.011)(65)$ or 0.71 cm./sec.

This value of 0.71 cm./sec., is for vapor and gases, so correcting for the partial pressure of the vapor in the V stream (about 0.54), the predicted V is only 0.000,12 as compared to the required value of 0.000,74, and the expected separation by simple mass diffusional means would be only 16% of that actually realized. Clearly, the column was not operating as initially believed.

Possible Manner of Column Operation, Discussion

The experimental data are indisputable evidence that Column I very effectively separates the gases passed through it. The exact method by which this separation is accomplished is yet to be determined, in as much as the predicted separations are much less than those actually obtained. Had the observed separations been less than those predicted by theoretical equations, this fact could no doubt have been explained in terms of efficiency factors due to turbulence, improper construction, faulty operation, non-steady-state conditions and the like. But, separation far in excess of that expected, could only mean that the column is operating other than as a pure mass diffusion column, as the theoretical development is not conservative. The following discussion, although numerically associated with the foregoing sample calculation, is entirely general to all the series of runs made in Column I.

Pressure Drop Considerations

When steam was passed through a 6" length of the porous vapor-tube and allowed to escape into the atmosphere (the short length being free of any surrounding condenser surfaces), a pressure drop of 3.0 p.s.i. was recorded for a vapor flow of 0.79 lbs./hr. This corresponds to 40.7

lbs./hr./ft.² Unfortunately, no other vapor rates and their corresponding pressure drops were recorded. But based upon this value, and the assumptions that the porosity of the vapor-tube in the column was the same and that the flow through the pores was laminar, then proportioning calculations show that only 41% of the vapor-tube's length was operative.

The amount of condensate removed from the bottom product stream corresponds to a partial pressure of water vapor of 0.55. This would certainly indicate that the bottom section of the vapor-tube, that part near the bottom product exit, was operative. And, as no vapor condensed out of the top product stream, this would seem to indicate that the top part of the vapor-tube was inoperative, or closed to the passage of any vapor. These two facts tend to substantiate the result of the pressure drop calculation that only part of the vapor tube was effectively porous, and that this part was the lower section.

However, if that were the case, how would the less diffusible component of the gas mixture be preferentially, transported down the column? The thermal convection streams certainly are functioning along this "dead" section of the tube, but a difference in their compositions would be required to transport more of one component than the other down the column. Could thermal diffusion produce this difference?

The maximum difference in the composition of the two counter-current flowing streams, that could be expected from the thermal diffusion effect, can be calculated from Equation (56). Using the values; $\alpha_{T12} = 0.24$, $T_a = 398^\circ\text{K}$, $T_b = 298^\circ\text{K}$, and assuming that $(c_1/c_2)_a = 1.0$, then $c_{1b} = 0.482$. Thus, the difference in the compositions of the two

streams, measured across the entire width of the annulus, is only 1.8%. The mean values of the streams would give a lesser difference of compositions, not only because of their locations relative to the hot and cold walls, but the conditions in the column are those of steady-state, and not equilibrium. Even if the V and L streams differed by 1.8 mole percent in their compositions, it would require a V of 0.005 gm.mols./sec. to effect the bottom composition of 35.5 mole percent helium. The maximum predicted V due to the difference in temperature of the walls would be only 0.0022. Therefore, it is impossible for thermal diffusion alone to bridge any gap between the bottom active section and the top of the column.

The only other possibility that would allow the column to operate with a top section closed to vapor flow would be the situation where the gases that back-diffused into the vapor tube lower down in the column, diffused back out into the annulus by diffusing through the condensate slugs in the pores of the tube. However, the diffusion coefficients of the gases through water are so low, and the area so limited, that this is not possible to the extent required to give the observed separations.

The conclusions to be drawn up to this point are : 1) the vapor-tube must be operative near the top of the column, and 2) the pressure drop data can only indicate that the porosity of the vapor-tube is quite variable, and 3) that thermal diffusion cannot be itself effect the obtained separations.

The further unreliability of the pressure drop data can be seen in Figure 23. Here the pressure drop through the tube is plotted

against the column vapor rate. Although the points are generally well scattered, there appears to be an inverse trend; a lower pressure drop with higher vapor rate. This would indicate increasing porosity with the higher vapor rates; brought about by opening more of the pores.

The pores are not uniform in size, and the capillary action of the fluid they contain makes the smaller ones more difficult to clear than the larger ones. They are cleared by both the steam pressure and the heat supplied from the superheated vapor.

The vapor-tube loses heat to its surroundings by conduction, convection and radiation. The end furthest away from the incoming vapor is the coldest part of the tube as heat is lost all along the length of the tube. Therefore, although the pressure drop through the tube wall is as great here as at the hotter end (assuming negligible longitudinal pressure drop along the tube), the temperature is lower. This lower temperature means not only greater surface tension of the fluid in the capillaries, but less heat available to boil the fluid out of the larger capillaries. Thus the porosity of the tube decreases toward the colder end. That the upper end of the vapor-tube became warmer as the vapor rate was increased, is shown by Table IV in the Appendix. Here a thermocouple was placed in the annular gas-separating zone, and the higher the vapor rate, the higher the temperature it registered

This effect was visible in Column II with its glass condenser walls. There was a high rate of condensation at the end of the tube where the vapor entered, and then a sharp drop in condensation rate at points further along the tube's length. This tapering off of the

condensation rate seemed more exponential than linear. The poor conductivity of the glass walls reduced the rate of heat loss from the vapor-tube to the extent that a high porosity was obtained along a sufficient length of tubing to result in low pressure drops across the tube. The length of the observed condensing section of the condenser was between 20 to 29 inches, and because of the greater porosity in Column II, it had a smaller pressure drop for a shorter length of tube, than in the case of Column I. The values of pressure drop for Column II are given in Table III.

Varying Convective Streams

The next experimentally observed phenomenon to be investigated was that of the lack of vapor in the top product. The top product stream of Column I was passed through a four foot long condenser, cooled by tap water. This should have reduced the vapor content of the product stream to that of saturation at about 20°C, or some 5%. The difference between the original vapor content and this 5% appearing as condensate from the product stream.

Conceding that the top section of the vapor-tube is porous to gaseous flow to some extent, the lack of vapor in the top product stream withdrawn at this point might possibly be explained in several ways: 1) By the condensation of this vapor on the walls of the column header before the vapor and gas are drawn into the small holes in the central member of the header. 2) By having dV/dz sufficiently negative at this point so as to reduce the partial pressure of the vapor. 3) By having sufficient back-diffusion take place along the lower section of the vapor-tube, so that, by the time the top of the column is reached

the contents of the vapor-tube are essentially gas. 4) Having such a low porosity in this region that the vapor rate across the annulus is very low. 5) By having a small (1-2 cm.) length of inactive tube at the very top where the vapor-tube is in contact with the top header. 6) By having some of the entering feed gas spill over into the top product withdrawal duct, diluting the vapor content of the top stream.

Any one, or any combination of the above situations would cause a lowering of the vapor content of the top product stream, but only the possibility of a large amount of back diffusion accompanied by a negative value of dV/dz would seem to be able to reduce the vapor content to that of saturation at the condenser temperature.

The extent to which dV/dz can effect the partial pressure of the vapor can be seen by assuming some dV/dz value and calculating the resultant partial pressure. Assuming a value of $dV/dz = -0.001$, and using the same other conditions that were assumed in the calculation of \bar{p}_O , the value of $p_{O_a} = 0.21$. This is to be compared with $p_{O_a} = 0.69$ for $dV/dz = 0$, and represents a drop of 0.48 in the partial pressure of the vapor at the vapor entry surface. The effect of dy/dz is small in this case, as increasing its value from 0.005 to 0.10 reduces the partial pressure of the vapor by only 0.01 mol fraction, to 0.20.

The above values were for a N_O of 1.7×10^{-5} , which was the vapor rate based upon uniform porosity for the whole length of the vapor-tube. Having shown that the porosity decreases towards the upper end of the tube, the value of N_O will be correspondingly lower. Just halving this vapor rate reduces the value of p_{O_a} to 0.084 for $dV/dz = -0.001$, whereas for $dV/dz = 0$, the value of p_{O_a} is dropped to only 0.54. Or, on a percentage basis, halving N_O , decreases p_{O_a} by 60% for the case of $dV/dz = -0.001$,

but decreases it only 22 % for the case where $dV/dz = 0$. This points out the fact that the lower the vapor rate across the annulus, the more marked is the effect of varying stream flow.'

Both the negative dV/dz term and the reduced vapor flow rate at the top of the column have the effect of reducing dy/dz . In fact, there is the possibility that their effect would cause a negative dy/dz value, meaning that the separation in the column had passed through a maximum before the streams reached the end of the column. A negative dy/dz , although reducing the separation, has the effect of increasing the value of dy/dx . This can be seen from the relationships of Equation (32). It was this inability to maintain a great enough value of $(y^I - y^{II})$ that made thermal diffusion inadequate to account for the column's performance. This increased difference in the compositions of the streams is necessary if their quantities become smaller at the top of the column. The equality $(y^I - y^{II}) = (y_D - y_F)$ is true only if $V = D$, otherwise $(y^I - y^{II}) < (y_D - y_F)$, depending upon whether $V < D$, or $V > D$.

Therefore, due to the reversal of flow of the ascending stream at the top of the column, and the low porosity of the vapor-tube at that point, it is quite possible to have a low partial pressure of the vapor, while at the same time maintaining a sufficiently large difference in the stream compositions. The relationships of this variables are all interdependent, but there are no incompatibilities.

Back Diffusion

The effect that the back diffusion of the gases into the vapor tube has on the separation effected in the mass diffusion column could

be readily determined experimentally: it would require comparing the results obtained from operating the column with the vapor entering at the bottom of the column, to the results obtained from the same column operating with the vapor entering at the top of the column. Most unfortunately, the experimental columns used in this research were dismantled before the possibility of such an effect was realized.

The theoretical calculation of the effect of back diffusion depends upon the ability to evaluate N_{1t} ; the rate of flow of the more diffusible component through the pore area of the vapor-tube. As seen from Equation (67), the evaluation of N_{1t} is dependent upon, among other quantities, the value of $\sum N_t$; the rate of flow of gas and vapor through the pores of the tube. It is the impossibility of determining $\sum N_t$ that stops any quantitative calculations as to the effect of back diffusion.

Since all the gases that diffuse into the vapor-tube eventually return to the annulus, the net flow through the tube is that of the vapor from the boiler. This quantity is known from the measured condensate of the column, and if the porosity of the tube were known, then $\sum N_t$ could be easily computed. But the porosity of the tube is not known. It is not only unknown from the standpoint of its mechanical formation, but also indeterminate because of the two-phase flow in the pores. The porosity varies with the vapor rate and condenser temperature both as regards the tube's average porosity, and its point values.

As the determination of the effect of this back diffusion would have to be accomplished by graphical, or numerical means, in a stepwise procedure, each succeeding step depends upon those preceding ,

and all errors are cumulative. The final results depend upon the paths by which they are reached. There is no manner in which assumptions of the tube's porosity can be made so that the errors incurred by wrong assumptions will cancel out.

Therefore, although it can be shown theoretically that back diffusion of the gases into the vapor-tube both improves the separation of the column and reduces the amount of vapor present in the tube at the end away from the vapor entry, lack of definite knowledge of the tube's porosity prohibits any numerical evaluation of this effect.

As to the other possibilities mentioned above, they probably all take place to some extent, their exact degree of influence being unknown. But it is believed that they play a much lesser role than the combined effects of back diffusion, varying stream rates, and decreasing porosity.

Air Separation

The separations obtained when air was fed into Column I are shown in Figure 23. Although they are small in magnitude, they are in correct proportion to the values of D_{O_1} and D_{O_2} for the system, and are significant in that the top product is enriched with oxygen, the heavier component.

This enrichment of the top product with oxygen is predicted by the theory of a mass diffusion column, as oxygen has a greater diffusivity with regards to steam than does nitrogen. At 56°C the value of D_{O_1} (steam oxygen) is 0.318 cm.²/sec., whereas D_{O_2} (nitrogen-steam) is 0.303 cm.²/sec. (10). However, the relative value of these coefficients

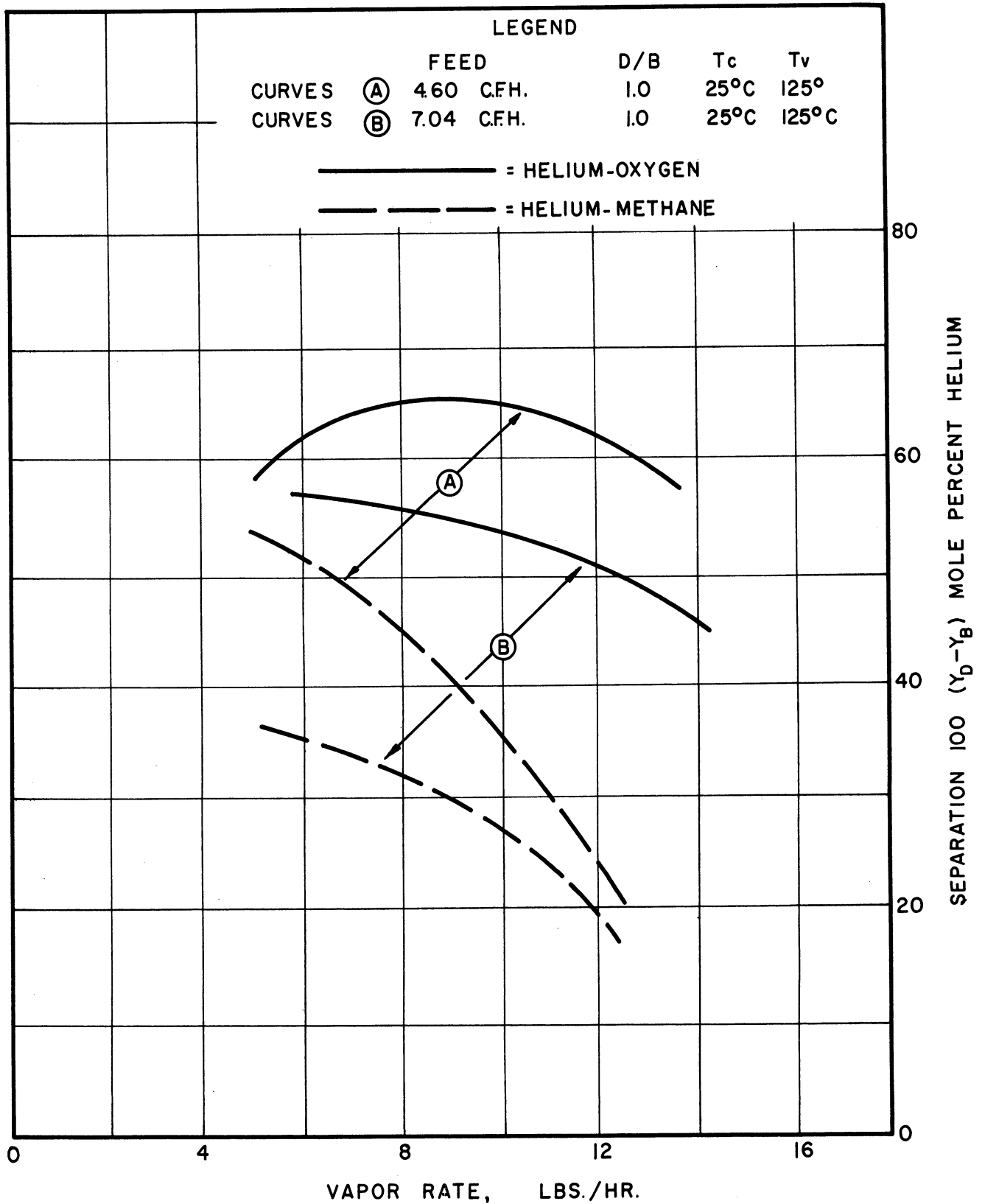
is very temperature sensitive, for at 79°C their ratio is only 0.359/0.352. Thus, if these reported values are accurate, a rise of 23°C reduces the value of H_S by 69%, and any numerical prediction of the H_S value is questionable.

The essential flatness of the separation curve is probably due to the fact that, in this system, the vapor is of lighter molecular weight than the gases being separated. So although its partial pressure reduces the V rate due to its occupying some of the volume of the ascending stream, it has a compensating beneficial effect in that it has a lower density than the gases. As the hot V stream is always richer in vapor content than is the colder L stream, the less dense the separating vapor the better, from a convective viewpoint.

Helium-Oxygen Separation

The helium-oxygen separations obtained from Column I are shown graphically in Figure 24. They are similar to the results of the helium-methane system, but with better separations due to the greater density of the less diffusible component.

The values of the coefficients D_{01} and D_{02} are essentially the same for the two systems, helium-methane and helium-oxygen (10). Therefore, the differences in their separations can be attributed to the difference in densities of the two systems. The less diffusible component of the gas mixture tends to concentrate near the cold wall, so the heavier this component is, the greater is the density gradient for any given dy/dx . The transfer coefficient H is directly proportional to V, so the greater the V, the better the separation. It is true that V also appears to the square power in the K_c term, but this term is



**FIG 29 COMPARISON OF HELIUM-METHANE
AND HELIUM - OXYGEN SEPARATIONS
COLUMN I**

always grouped together with Z_s , and in a sufficiently long column the value of K_c does not affect the amount of separation.

The greater separations obtained in the helium-oxygen system, when compared to the helium-methane system, are shown graphically in Figure 29. This increase in separation is due to the greater density of the less-diffusible component, as the values of D_{O1} and D_{O2} for both systems are essentially identical.

The fact that a favorable V value can be calculated for this system does not mean that the column's operation can be explained in terms of pure mass diffusion alone. There still remain the difficulties of unknown porosities, back diffusion and varying stream velocities. These quantities, as they are related to increasing the column's separation, are themselves increased by larger V values. So regardless of the combination in which they function to produce the final result, a good countercurrent circulation is desirable.

Results of Column II

By comparison to Column I, Column II effected very little separation. The results of its separation are presented graphically in Figure 25.

Due to the poor conductivity of the glass condenser walls and the short length of the column, the partial pressure of the vapor was quite high in the annulus; being in the range of 0.35 to 0.95 for most of the runs. The combination of high vapor content and low temperature difference across the annulus makes it impossible to calculate any positive V value. If there is a positive V , then it can only be caused by the inhaling action at the top product outlet, and it is

doubtful if this effect extends down into the separating zone for any appreciable distance.

Under ordinary conditions of column operation, the absence of a positive V value would mean no separation. However, in this case, there was the unusual condition of variable porosity and its resultant effect of varying vapor content in the separating zone. This produced a partial pressure gradient in the z direction; positive in value, or the partial pressure of the vapor increasing up the column, toward the vapor inlet. With this gradient, the vapor would tend to diffuse down the column, and the gases would diffuse up the column. This would produce a separating effect upon the gas mixture, as the more diffusible gas component would move up the column at a greater rate than the less diffusible component. The extent to this effect is shown in the following equations.

Solving Equation (7) for y and differentiating with respect to z gives

$$\frac{\partial y}{\partial z} = \frac{1}{P-p_0} \left[\frac{\partial p_1}{\partial z} + y \frac{\partial p_0}{\partial z} \right] \quad (111)$$

The value of $\frac{\partial p_1}{\partial z}$ can be determined from Equation (1) by changing x to z and using the substitutions:

$$\begin{aligned} N_1 &= -By_B/\bar{E}(x_b-x_a) \\ N_2 &= -B(1-y_B)/\bar{E}(x_b-x_a) \\ N_0 &= -B(p_0/1-p_0)/\bar{E}(x_b-x_a) \\ p_2 &= 1-p_1-p_0 \end{aligned} \quad (112)$$

where the equations have been written for a total pressure of one atmosphere ($P = 1$). The substitution of Equations (112) into Equation (1) and the result into Equation (111) gives

$$\frac{\partial y}{\partial z} = \frac{1}{1-p_0} \frac{BRT}{PE(y_B - x_a)} \left[[y_B - y] \left[\frac{p_0}{D_{01}} + \frac{1-p_0}{D_{12}} \right] + y \frac{dp_0}{dz} \right] \quad (113)$$

Even with assuming $\frac{dp_0}{dz}$ a constant, Equation (113) cannot be solved analytically, but an approximate idea of its capabilities can be realized from Figure 30.

In Figure 30 lines of constant p_0 are graphed against the coordinates of $\frac{\partial y}{\partial z}$ and $\frac{dp_0}{dz}$. It can be seen, that as the value of p_0 increases, the value of $\frac{\partial y}{\partial z}$ increases at a very great rate. Naturally, there are limiting effects present, so that the greater the separation becomes, the more difficult it is to obtain additional separation.

If the visual observation of varying rates of condensate formation can be relied upon to indicate a positive gradient of vapor, then the equations would seem to be the best way to explain the separation mechanism of Column II. No doubt this effect was also present in Column I, and with an adverse effect upon the separation. But, with a much longer length of column and colder condenser walls, the partial pressure gradient of the vapor would be very small. The ordinary longitudinal diffusion, without any gradient of the vapor's partial pressure, is expressed by the K_d term.

Even though with the 36" tube, the condensation on the condenser wall was rarely observed at an elevation more than 24" down from the top,

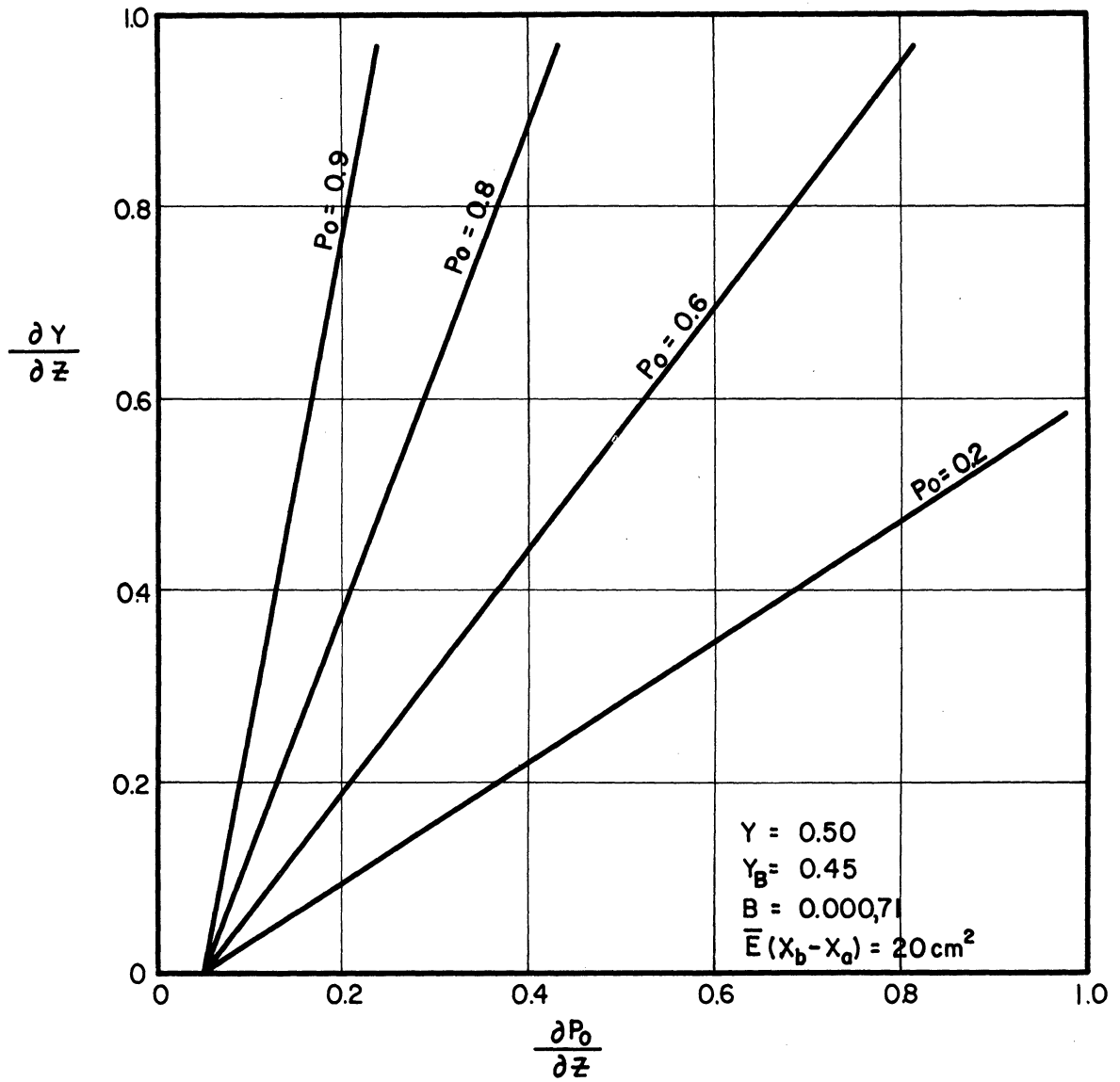


FIG 30 GRAPHICAL PRESENTATION OF EQUATION (113) FOR THE HELIUM-METHANE SYSTEM

reducing the length of the whole tube to 24" reduced the separation effected by the column. This would seem to indicate that the additional foot of tube produced some separation by means of thermal diffusion. Using Equation (44) with only H_T in place of H , a separation of 1% for the one foot of column can be calculated.

The action of the small cooling ring on the F and V stream partition in the column header is a matter of conjecture. The experimental evidence shows that it reduced the column's separation. At first thought it would seem that by keeping the incoming feed stream cool, it would help to promote desirable convection currents. But then, with these currents being rather impossible due to the high flux of vapor in the top region, a cooler partition might disturb the vapor gradient that was effecting the separation. Or, a cooler partition would condense out some of the vapor in the top product stream as it was leaving the column, and the dripping of condensate back into the annulus (an effect that was not visually observed), would tend to set up turbulence of an undesirable nature.

Over-all Transport Coefficient

Due to the smooth continuity and essentially proper relationship of the experimental data, it would seem that the factors that were effecting the separation in the column could be grouped into one factor that would be a function of the operating variables. The ability to reproduce the data after periods of months indicates that the separation process was a stable one, and not some chance operation.

Let an over-all transport coefficient, H_u , be defined by the equation

$$\frac{dy^I}{dz} = \frac{(1-y^I)H_u + B(y_B - y^I)}{K} \quad (114)$$

This is a hybrid equation in that it does not contain the usual $y(1-y)$ term, and is written in terms of y^I and y_B rather than y^{II} and y_B . However, it was arrived at after trying various equations by means of which the data could be reasonably well plotted, and since the counter-current streams are varying in an undefined manner, the relationship between dy^I/dz and dy^{II}/dz is unknown.

Equation (114) can be integrated, and using the boundary condition that $y = y_B$ when $z = -Z_s$ gives

$$y^I = \frac{By_B - H_u}{B - H_u} + \left[y_B - \frac{By_B - H_u}{B - H_u} \right] \exp \left[\frac{(B-H)(z - z_s)}{K} \right] \quad (115)$$

Assuming that Equation (115) can be used over the whole length of the column, the exponential term becomes negligible and

$$H_u = B \left[\frac{y^I - y_B}{y^I - 1} \right] \quad (116)$$

If, in all series of the data the value of y^I is taken as y_D at $z = 0$ (top of the column), then a plot of H_u against the vapor rate results in a wide scattering of the points, but if y^I is corrected for conditions such that $V < D$ in some of the series, then the values of H_u plot well as shown in Figure 31. The corrected value of y^I at the top of the column is given by the equation.

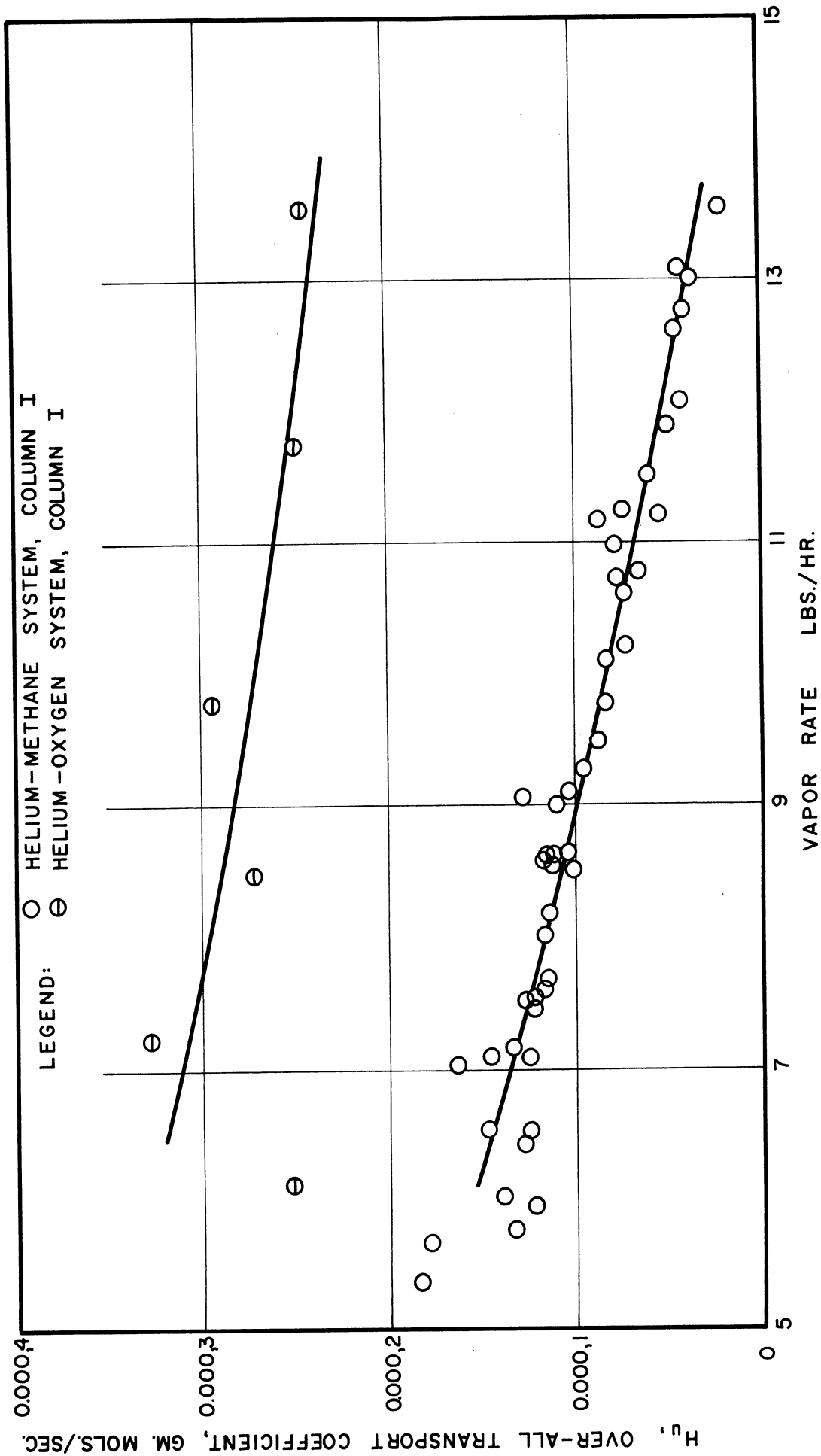


FIG 31 OVERALL TRANSPORT COEFFICIENT

$$y_{z=0}^I = \frac{y_D D - y_F (D - V_{z=0})}{V_{z=0}} \quad (117)$$

When $V > D$, then $y_{z=0}^I = y_D$, but if $V < D$, then $y_{z=0}^I > y_D$. The relationship between V and D was assumed until a consistency between V and the conditions of the series developed. This consistency became apparent when the maximum allowable V values for the helium-methane system were taken as:

T_c	T_v	Maximum $V_{z=0}$
25°C	125°C	0.001,4 gm.mols./sec.
50	125	0.000,8
75	125	0.000,2

The values of H_u thus calculated and plotted in Figure 31 are given in Table II along with the experimental data.

Figure 31 also shows how the denser system of helium-oxygen gives a greater over-all transport coefficient than does the system of helium-methane. This is a direct result of a more favorable density gradient which causes larger V values.

SUMMARY AND CONCLUSIONS

The present investigation has resulted in showing that gas mixtures can be very effectively separated by means of a mass diffusion column wherein the countercurrent streams are moved by thermal convection alone.

The primary variables of operation were the gas system (helium-methane, helium-oxygen, and nitrogen-oxygen), the rate of feed gas to the column (4.60 to 14.60 c.f.h.), the ratio of the top to bottom product streams (1.0 and 2.1), steam vapor rate and temperature, and condenser wall temperature. The separations were obtained by means of two columns; a nine foot column with a copper condenser, and a three foot column with a glass condenser. The preponderance of the data was from the nine foot column which gave the better separation, while the three foot column gave valuable insight of the column behavior.

The major conclusions resulting from this research can be summarized as follows:

1. The separations under varying conditions of operation were good, and generally along the lines predicted by the developed theory, but careful examination of the data showed that processes other than plain mass diffusion were present in the column. These additional processes included back-diffusion of the gases into the vapor-tube, the effect of the gases reversing their flow at the ends of the column, thermal diffusion, and a longitudinal partial pressure gradient of the vapor. The combined result of these processes was to augment the separation as predicted by mass diffusion alone. The experimental results that could be predicted from theory were increased

separation with: lower feed rates, higher D/B ratio, and lower condenser temperature.

2. With all other operational variables fixed, increasing the vapor rate to the column tended to decrease the separation produced. Calculations could be made to show that this was due to the vapor taking up a larger fraction of the volume of the convecting streams, and, in the case of the helium-methane system, adversely affecting the density gradient across the separating annulus. Therefore, in a column operating by thermal convection, the proper choice of the separating vapor depends not only upon its relative diffusivities with the gas component, but also upon its density relative to these gases. The lighter the separating vapor, consistent with good diffusion properties, the better.

3. The separation obtained, as well as the successful prediction of other separations, depends to a large extent, upon the ability to control the porosity of the vapor-tube. The porosity must be known all along the length of the tube in order to be able to correlate the data with the variable of operation, and its control is necessary to assure optimum operating conditions. The heat loss from the tube, and the consequent blocking of the pores by condensate, cannot be controlled by the amount, within reason, of the superheat of the vapor alone; this lack of control results in varying, unknown porosity along the vapor-tube. Pressure-drop measurements across the vapor-tube's wall cannot alone be used to determine the tube's porosity.

4. The separating vapor should be introduced into the vapor-tube at its lower end; thus any gases that back-diffuse into the vapor-tube will be carried up the column. As these gases will be enriched

in the more diffusible component, this mechanism helps to preferentially move the more diffusible component up the column, increasing the column's performance. This back-diffusion effect may be increased with increasing vapor rates, for although this higher vapor rate through the pores of the tube reduces the amount of gases diffusing countercurrent to the vapor flow, the gases that do diffuse into the tube will be all the richer in the more diffusible component.

5. The difficulty encountered in obtaining satisfactory density gradients across the separating space under all conditions would recommend that additional means be employed to produce the necessary countercurrent motion of the streams. This could best be done by using a liquid curtain on the condensate wall (3). The liquid would be the same material as the vapor, and would flow from a distributor at the top of the column, producing a drag effect at the cold wall surface. This would provide for more latitude in the operation of the column, increase the separation, and put more emphasis on the diffusional properties of the vapor (where it should be) than on its density.

Finally, the mass diffusion column is a simple, effective way of separating gases. It would be an excellent piece of general laboratory equipment in that it is simple and economical to build, easy to operate, requires little maintenance and is quite flexible in operation. Although its capacity would not be too large, small quantities of relatively pure gases could be obtained by recycling the products.

Where large quantities of waste steam are available, this process, in single-stage or column operation, could be used

industrially, and would be especially useful for separating close boiling components that exhibit different diffusivities with respect to steam.

FUTURE RESEARCH

The results of this investigation are certainly indicative that future research on mass diffusion column operation is merited. Especial emphasis should be placed on the properties of the vapor-tube, the manner of introducing the vapor to the column, and the liquid curtain on the condenser wall. Some data are available on the effect of the liquid curtain on column operation, but not in conjunction with satisfactory introduction of the vapor (3).

Additional heat must be supplied to the porous tube to offset its losses to the surroundings. This heat could be easily supplied by electrical heating elements inside the vapor-tube. Some degree of control of the porosity of the tube could be achieved by varying the heat input along the length of the tube, but more accurate experimental conditions would be maintained by keeping the entire vapor-tube hot enough to prohibit the condensation of any of the vapor in the tube pores. Tubes of various mechanical porosities should be used, and combinations of these different tubes could be used to make up the entire length of the vapor-tube.

Using tubes of different porosities will show the degree of the back-diffusion of the gases into the vapor-tube; for with a given vapor input to the column, the vapor flux across the annulus will be the same, but the vapor rate in the pores of the tube will vary inversely with the porosity. The vapor rate in the tube's pores should be the controlling factor for back-diffusion.

And, as mentioned previously, introducing the vapor at different ends of the vapor-tube changes the effect of this back-diffusion

from increasing the separation to decreasing it, or vice-versa. This could be accomplished by putting a solid tube all the way along the inside of the porous tube, and a simple valve arrangement would switch the vapor entry point from one end to the other. The experimental results of this "switching" should be quite dramatic and conclusive.

No doubt, that if the column is operated with just a stripping or rectifying section, where two counterflowing streams exist at one end of the column, then the design of the equipment at this point has some effect on the degree of mixing of these streams. The equipment designed and used in this investigation performed very well, but that is no assurance that it could not have been designed better. The length that the dividing partition extends into the separating annulus, and the fraction of the annular area that is allotted to each stream are two variables that might be investigated.

A liquid curtain on the condenser surface would increase the circulation within the column, and could be easily controlled by varying the amount of liquid flowing down the walls. This liquid need not be the same at the vapor, although heat transfer considerations might make this desirable. A more important factor could be the desirability of making certain that the entire surface of the wall is wetted by this curtain and producing a uniform drag around the periphery of the annulus. (Making the central element of the column the condensing surface might facilitate this.) In that case, immiscibility of the vapor and curtain fluid would provide for their easy separation.

With a liquid curtain, its fluid might be such that the less diffusible component of the gas mixture would be preferentially dissolved in it. This would help the separation by its scrubbing action: an effect that might be present with the condensing of some vapors alone.

The use of vapors other than steam would have to be carefully considered. There are few substances that can be vaporized and condensed under such moderate conditions of temperature and pressure that have the low molecular weight of water. This low weight is important, for even with a liquid curtain, unless the separating gases have high molecular weights themselves, there will be difficulty encountered in obtaining satisfactory countercurrent circulation in the column.

The construction of the experimental column should also allow for extensive sampling. This would mean sampling of the contents of the vapor-tube along its length as well as the means for determining composition profiles in the separating annulus.

APPENDIX

TABLE II. EXPERIMENTAL DATA AND CALCULATIONS, COLUMN I

Series Number	Gas System	Gas Feed Rate c.f.h.	D/B Ratio	Condenser Temperature T _c =°C	Inlet Vapor Temp. T _v =°C	Vapor Rate lbs/hr	Column Condensate lbs/hr	Bottom Product Condensate lbs/hr	Top Product Condensate lbs/hr	Feed Gas Composition Mole % of Helium	Top Product Composition Mole % of Helium	Bottom Product Composition Mole % of Helium	Material Balance Feed Composition Mole % of Helium	Vapor-Tube Pressure cm. Water	Calculated R _i	
1	Helium-Methane	4.60	2.1	25	125	8.70	8.60	0.10	0.0	52.0	73.0	7.0	51.7	38.0	1.18	
						10.8	10.64	0.16	0.0	52.0	68.0	19.0	52.1		0.75	
2	Helium-Methane	7.04	2.1	25	125	6.40	6.34	0.06	0.0	48.1	64.0	9.1	46.2	38.4	1.13	
						8.70	8.55	0.15	0.0	48.1	64.1	10.4	46.3		1.11	
						11.00	10.60	0.40	0.0	48.0	59.3	15.3	45.1		0.80	
3	Helium-Methane	14.60	2.1	25	150	5.70	5.22	0.48	0.0	46.1	53.5	29.2	45.6	33.6	1.78	
						9.30	8.46	0.84	0.0	47.0	52.0	37.0	47.1		0.95	
						9.50	8.65	0.85	0.0	46.8	52.5	32.1	45.9		0.85	
						12.10	10.90	1.20	0.0	47.0	49.5	33.0	44.1		0.75	
4	Helium-Methane	4.60	2.1	75	125	5.80	5.40	0.50	0.0	52.1	56.0	43.0	51.8	16.0	1.80	
						6.30	5.88	0.42	0.0	50.3	54.7	41.0	50.2		1.60	
						7.10	6.67	0.43	0.0	50.3	56.3	38.1	50.4		1.24	
						8.00	7.55	0.45	0.0	52.0	58.4	38.4	51.9		1.45	
						8.50	8.00	0.49	0.01	50.1	55.4	38.1	49.4		1.00	
						11.10	10.51	0.50	0.09	50.1	55.2	39.0	49.9		0.94	
5	Helium-Methane	4.60	2.1	50	125	7.60	7.37	0.23	0.0	51.5	70.5	12.0	51.6	24	1.22	
						8.70	8.44	0.26	0.0	52.0	70.0	16.0	52.5		1.14	
						11.20	10.83	0.37	0.0	51.5	67.0	19.0	51.5		0.87	
6	Helium-Methane	4.60	1.0	25	150	6.50	6.43	0.07	0.0	48.0	74.0	23.0	48.5	34	1.47	
						9.00	8.83	0.17	0.0	48.0	70.0	25.5	47.7		1.10	
						10.70	10.49	0.21	0.0	49.0	65.0	30.0	47.5		0.25	
7	Helium-Methane	7.04	2.1	25	150	5.80	5.75	0.05	0.0	51.0	67.0	8.0	47.9	37.0	1.32	
						6.50	6.40	0.06	0.0	51.0	67.1	12.1	49.4		1.24	
						9.20	9.04	0.16	0.0	51.0	68.2	12.8	50.2		1.27	
						11.20	10.94	0.26	0.0	51.0	61.9	24.3	49.7		0.74	
8	Helium-Methane	7.04	2.1	50	125	5.30	5.08	0.22	0.0	50.1	64.0	18.9	49.5	37.4	1.86	
						7.30	7.00	0.30	0.0	48.0	61.8	19.2	48.1		1.66	
						9.80	9.35	0.45	0.0	48.0	58.0	26.9	48.0		0.83	
						12.60	12.01	0.59	0.0	48.0	53.9	36.1	48.1		0.44	
9	Helium-Methane	7.04	2.1	50	150	6.00	5.76	0.24	0.0	50.0	63.9	20.1	49.8	32.6	1.38	
						7.50	7.16	0.34	0.0	50.0	63.0	25.9	51.0		1.21	
						11.80	11.20	0.60	0.0	50.0	56.8	35.4	49.9		0.49	
10	Helium-Methane	4.60	2.1	25	150	8.60	8.55	0.15	0.0	52.1	75.1	3.1	51.7	30	1.15	
11	Helium-Methane	4.60	2.1	50	150	8.60	8.57	0.13	0.0	52.1	71.0	10.0	51.3	34	1.02	
12	Helium-Methane	7.04	1.0	25	150	6.40	6.29	0.11	0.0	48.1	65.1	30.9	48.0		1.11	
13	Helium-Methane	4.60	1.0	25	125	5.62	5.60	0.02	0.0	52.1	79.0	26.5	52.7	42	1.88	
						6.28	6.24	0.04	0.0	54.0	80.0	28.1	54.0		1.94	
						7.00	6.91	0.09	0.0	54.1	78.7	29.5	54.1		1.63	
						7.60	7.51	0.09	0.0	53.0	74.3	31.0	52.6		1.26	
						9.10	8.93	0.17	0.0	51.5	70.7	31.0	50.8		1.02	
						10.10	9.90	0.20	0.0	53.1	69.1	35.0	52.0		0.83	
						10.80	10.56	0.24	0.0	51.9	68.0	35.3	51.7		0.76	
						11.20	10.95	0.25	0.0	55.9	68.0	43.8	55.9		0.54	
						13.10	12.73	0.37	0.0	52.0	62.1	41.0	51.6		0.42	
						13.60	13.20	0.40	0.0	47.1	54.0	42.0	48.0		0.20	
14	Helium-Methane	7.04	1.0	25	125	5.90	5.81	0.09	0.0	48.1	66.0	30.0	48.0	36	1.22	
						6.52	6.40	0.12	0.0	48.1	65.0	31.0	48.0		1.12	
						7.60	7.40	0.20	0.0	48.1	66.0	32.0	48.0		1.15	
						7.70	7.50	0.20	0.0	48.1	66.1	32.1	49.1		1.15	
						9.50	9.21	0.29	0.0	48.1	62.3	33.9	48.1		0.87	
						12.80	12.24	0.56	0.0	48.1	56.1	40.5	48.3		0.40	
15	Helium-Methane	14.60	1.0	25	125	7.20	6.88	0.32	0.0	50.1	57.0	43.0	50.0		1.33	
						8.20	7.80	0.40	0.0	50.3	56.0	44.0	50.0		1.14	
						10.30	9.63	0.67	0.0	50.2	54.5	44.5	49.5		0.72	
						13.00	11.72	1.28	0.0	50.2	52.5	47.5	50.0		0.36	
16	Helium-Methane	14.60	2.1	25	125	8.00	7.76	0.24	0.0	51.0	57.2	38.0	51.0		1.12	
						11.50	11.00	0.50	0.0	51.0	54.8	43.2	51.0		0.60	
						13.40	12.60	0.80	0.0	51.0	53.0	46.6	50.9		0.32	
17	Helium-Methane	4.60	1.0	50	125	6.80	6.54	0.26	0.0	50.1	74.0	26.2	50.1		1.40	
						10.30	9.94	0.36	0.0	50.1	70.8	29.1	49.9		1.07	
						11.00	10.49	0.51	0.0	50.1	64.9	35.0	49.9		0.64	
18	Helium-Methane	7.04	1.0	50	125	8.40	7.80	0.60	0.0	49.8	62.5	37.5	50.0		1.06	
						10.20	9.49	0.71	0.0	49.8	59.8	40.0	49.9		0.75	
19	Helium-Methane	14.60	2.1	50	125	8.00	7.30	0.70	0.0	49.1	53.0	41.0	49.0		1.15	
						11.50	10.40	1.10	0.0	49.1	51.6	43.5	52.5		0.6	
20	Helium-Methane	14.60	1.0	50	125	7.00	6.10	0.90	0.0	49.6	56.0	43.3	49.0		1.35	
						11.50	9.85	1.65	0.0	49.6	52.5	46.6	49.5		0.60	
21	Helium-Oxygen	4.60	1.0	25	125	6.10	6.04	0.06	0.0	49.7	81.3	18.0	49.6	52	2.50	
						8.50	8.35	0.15	0.0	49.7	82.2	17.3	49.7		2.70	
						11.80	11.50	0.30	0.0	49.7	81.0	18.6	49.8		2.47	
22	Helium-Oxygen	7.04	1.0	25	125	7.20	6.97	0.23	0.0	53.4	80.2	22.8	51.5	66	3.28	
						9.70	9.41	0.29	0.0	53.4	79.3	26.2	52.7		2.95	
						13.50	12.89	0.61	0.0	53.4	77.8	30.6	54.2		2.44	
30	Nitrogen-Oxygen	4.60	1.0	25	125	6.6				20.9	21.6	20.2	20.90	16		
						7.0				20.9	21.7	20.1	20.90			
						9.1				20.9	21.6	20.3	20.95		15	
						9.4				20.9	21.5	20.2	20.85			
						12.6				20.9	21.5	20.2	20.85			
						12.8				20.9	21.5	20.3	20.90			14.4
31	Nitrogen-Oxygen	4.60	2.1	25	125	6.4				20.9	22.0	19.7	20.85			
						10.0				20.9	21.8	20.2	21.00			
						12.0				20.9	21.8	20.0	20.90			

TABLE III. EXPERIMENTAL DATA, COLUMN II

Series Number	Gas System	Vapor-Tube Length inches	Gas Feed Rate c.f.h.	D/B Ratio	Condenser Temp. °C	Inlet Vapor Temp. °C	Vapor Rate lbs/hr	Column Condensate lbs/hr	Bottom Product Condensate lbs/hr	Top Product Condensate lbs/hr	Feed Gas Comp. Mole % Helium	Separation: 100(Y _D -Y _B) Mole % Helium	Vapor-Tube Pressure cm. water	Visual Condensation Length inches	Cooling Ring	
																Condenser Temp. °C
23	Helium-Methane	36	7.04	1.0	25	175	1.00	0.80	T	0.20	56.2	2.1	11.0	22.1	Off	
							2.60	1.10	R	1.50	56.2	3.4	16.5			21.5
							3.40				56.2	4.4				
							5.10		A	4.30	56.2	4.5				
							6.60	2.30		4.7	56.2	5.3				
							7.50	2.00	C	5.2	56.2	5.3				
24	Helium-Methane	36	7.04	1.0	25	150	2.50	1.30	T	1.20	55.8	4.5	0.0	22.0	Off	
							5.80	3.50	R	2.3	55.8	5.3				
							6.60		A	4.4	55.8	4.7				
							9.00	4.60	C	9.00	55.8	3.5				
							12.10	6.00	E		55.8	4.8				
							15.00				55.8	5.0				
25	Helium-Methane	36	7.04	1.0	25	125	3.4	3.40	T	0.70	56.0	4.8	0.0	25.0	Off	
							4.10	4.50	R	2.00	56.0	5.0				
							6.5	5.20	A	3.80	56.0	4.6				
							9.0		C	7.60	56.0	2.40				
							12.1	7.40	E		56.0	4.0				
							15.0				56.0	3.0				
26	Helium-Methane	24	7.04	1.0	25	125	2.5				54.0	4.0	0.0	25.0	Off	
							4.8	TRACE			54.0	3.0				
							8.8				54.0	2.6				
27	Helium-Methane	24	7.04	1.0	25	125	2.0				54.0	5.3	5.0	25.0	On	
							4.3				54.0	1.4				
							8.1	TRACE			54.0	0.65				
							8.9				53.0	0.0				
28	Helium-Methane	24	7.04	1.0	25	175	4.50	TRACE			53.0	6.2	22.5	26.1	Off	
							9.80				53.0	5.8				
29	Helium-Methane	24	7.04	1.0	25	175	4.6	TRACE			53.0	4.2	22.5	26.1	On	
							9.3				53.0	5.8				

TABLE IV. ANNULUS TEMPERATURE OF COLUMN I

Temperature at middle of annulus, eight
inches below top end of vapor-tube
System: helium-methane
Feed Rate: 460 c.f.h.
D/B: 1.0

Vapor Rate lbs/hr	Inlet Vapor Temp. °C	Condenser Temp. °C	Annulus Temp. °C
9.0	150	50	70
14.0	150	50	85
9.0	125	25	44
14.0	125	25	59

SOLUTIONS FOR ENRICHING SECTION TRANSPORT EQUATION

The differential equation is

$$\frac{dy}{-ny_D + y(1+n) - y^2} = \frac{H}{K} dz \quad (39e)$$

where

$$n = D/H \quad (40e)$$

Using the boundary conditions

$$\begin{aligned} \text{at } z=0 \quad y &= y_F \\ z=z_e \quad y &= y_D \end{aligned} \quad (41e)$$

the exact solution is

$$\tanh \frac{b'H/z_e}{2K} = \frac{b'(y_D - y_F)}{y_D + y_F - n(y_D - y_F) - 2y_D y_F} \quad (42e)$$

$$\begin{aligned} b' &= \{(1+n)^2 - 4ny_D\}^{1/2} \\ &= \{(1-n)^2 + 4n(1-y_D)\}^{1/2} \end{aligned} \quad (43e)$$

For $0.3 < y < 0.7$

$$y_D - y_F = \frac{H\{1 - \exp(-Dz_e/K)\}}{4D} \quad (44e)$$

For $y \ll 1$

$$y_D = \frac{y_F(1+n)}{\exp\{-z_e(H+D)/K\} + n} \quad (45e)$$

For $(1-y) \ll 1$

$$y_D = 1 - \frac{(1-y_F)(1-\tau_2)}{\exp\{Z_e(H-D)/K\} - \tau_2} \quad (46e)$$

For total reflux

$$\frac{y_D(1-y_F)}{y_F(1-y_D)} = \exp(HZ_e/K) \quad (47e)$$

NOTATION

- a = a constant, density gradient, defined by Equation (104).
 a' = a constant, defined by Equation (97).
 b = a constant, density, equal to $-ax_0$ or $-ar_0$.
 b' = defined by Equation (43).
 B = bottom product withdrawal rate, gm. moles./sec.
 c = mole fraction in binary system
 D_{12} ,
 D_{10} ,
 D_{01} = coefficient of ordinary diffusion, cm^2/sec .
 D_T = coefficient of thermal diffusion, $(\text{gm. moles})^2/(\text{cm}^4)(\text{sec.})$
 E = width of column perpendicular to x direction, cm.
 g = gravitational constant, 980 cm./sec.^2
 H = $H_T + H_S$
 H_S = transport coefficient for mass diffusion, defined by Equation (36), gm. moles./sec.
 H_T = transport coefficient for thermal diffusion, defined by Equation (64), gm. moles./sec.
 H_U = generalized transport coefficient, given in Equation (114), gm. moles./sec.
 k_1 ,
 k_2 ,
 k_3 = constants defined in Equation (106).
 k_T = thermal diffusion ratio, D_T/D_{12} .
 K = $K_c + K_d$
 K_c = coefficient for convection term in column operation, given in Equation (37), $(\text{cm.}) (\text{gm. moles.})/(\text{sec.})$.
 K_d = coefficient for longitudinal diffusion in column operation, given in Equation (26), $(\text{cm.}) (\text{gm. moles.})/(\text{sec.})$.

NOTATION (CONT'D.)

- L = downflow rate of vapor-free gas, gm. moles./sec.
- m = vapor-free composition gradient, $\partial y/\partial x$ or $\partial y/\partial r$, mole fraction/cm.
- M = molecular weight.
- n = B/H.
- n' = defined by relationship $y = mx + n'$.
- N = mass transfer rate, gm. moles./(cm^2)(sec.).
- P_1
 P_2
 P_0 = partial pressure of one component of gas-vapor mixture, atm.
- P = total pressure, atm.
- Q = varying stream coefficient, defined by Equation (65), (mole. fract. l)(cm.).
- r = radial distance, cm.
- r_0 = radial value where $\partial^2 v_z/\partial r^2 = 0$, cm.
- R = gas constant, 82.06 (cm^3)(atm.)/(gm. mole.)(°K).
- R_T = ratio of actual value of thermal diffusion constant to value it would have for hard molecules.
- Re = Reynolds number, defined by Equation (75).
- S = defined by Equation (74), gm. moles./sec.
- t = constant, defined by Equation (24).
- T = absolute temperature, °K.
- v = velocity, cm./sec.
- V = upflow rate of vapor-free gas, gm. moles./sec.
- w = one-half of the distance between the hot and cold walls, $w = 1/2 (x_2 - x_1) = 1/2 (r_2 - r_1)$, cm.
- W = rate of vapor feed to column, lbs./hr.
- x = distance perpendicular to vapor-entry and vapor-condensing walls, cm.
- x_0 = x value where $\partial^2 v_z/\partial x^2 = 0$, cm.

NOTATION (CONT'D.)

- y_0, y_1, y_2 = mole fraction of components 0, 1, and 2 respectively on a total gas-plus-vapor basis
- y
- y_a, y_b = mole fraction of the more diffusible gas component of gas mixture on a vapor-free basis.
- y^I, y^{II}
- y_B, y_D, y_F
- z = vertical distance, cm.
- Z = length of column between feed point and product withdrawal point, cm.

Greek Letters:

- α = separation factor
- β = transverse flow factor, defined by Equation (99)
- Δ = a finite increment, or difference value
- θ = vapor-tube porosity
- λ = time, sec.
- μ = viscosity, (gm.)(cm.)/sec.
- ρ = density, gms./cm³.
- Σ = summation sign
- ϕ = angle of cylindrical coordinate system, shown in Figure 10, defined by Equation (89)

Superscripts:

- o = condition of no net gas diffusion in the x or z direction.
- I = average conditions in the upflowing stream.
- II = average conditions in the downflowing stream.
- = a bar above a value indicates a mean value.
- * = a starred value is one that is calculated by material balance considerations.
- = an arrow above a symbol indicates a vector quantity.
- ' = a prime on the H, K, and Q values indicates that one V term in their definitions has been replaced by an L term.

NOTATION (CONT'D.)

Subscript refers to:

For Dimension System

- 1 = vapor entry or hot surface
- 2 = vapor condensing or cold surface

For Gas-Vapor System

- o = vapor
- 1 = more diffusible gas component
- 2 = less diffusible gas component
- a = vapor entry surface
- b = vapor condensing surface
- B = bottom product
- c = convection, or condensing
- d = diffusion
- D = top product or top product location
- e = enriching section
- F = feed gas or feed location
- s = stripping section
- S = mass diffusion
- T = thermal diffusion
- U = over-all
- v = vapor
- x = x direction
- y = y direction
- z = z direction

LITERATURE CITED

1. Benedict, M., Chem. Eng. Progress, 43, No. 2, T41, (1947).
2. Benedict, M. and Boas, A., Chem. Eng. Progress, 47, No. 2, 51, (1951).
3. Bowman, J. R., et al., Chem. Eng. Progress, 47, No. 2, 63, (1951).
4. Grew, K. W., Thermal Diffusion in Gases, Cambridge Univ. Press, (1952).
5. Hirschfelder, J. O. and Spatz, E. L., Chem. Rev., 44, 205, (1949); also J. Chem. Phys., 16, 968, (1948).
6. Jones, R. C. and Furry, W. H., Rev. of Mod. Phys., 18, No. 2, 151, (1946); also Phys. Rev., 56, 818, (1946).
7. Korshing, Z., Naturforsch, 6a, 213, April, (1951).
8. Maier, C. G., J. Chem. Phys., 7, 854, (1939); also U. S. Bur. Mines Bull., No. 431, (1940).
9. Onsager, L. and Watson, W. W., Phys. Rev., 56, 474, (1939).
10. Schwartz and Brow, J. Chem. Phys., 19, 640, May, (1951).
11. Wilke, C. R., J. Chem. Phys., 18, 517, (1950); also Trans. Am. Soc. Mech. Engrs., 71, 921, (1949).

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