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I hereby recommend that the thesis prepared under my supervision by Bernard L. Schulman

entitled "Theoretical Aspects of Gas Absorption in Packed Towers"

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

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Theoretical Aspects of Gas Absorption
in Packed Towers

A dissertation submitted to the Faculty
of the University of Cincinnati
in partial fulfillment of the requirements
for the degree of

Doctor of Philosophy

1950

by

Bernard Lamar Schulman

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Letter of Transmittal

To the Faculty of the Graduate School
University of Cincinnati
Cincinnati, Ohio

Gentlemen:

I herewith submit, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, a thesis entitled "Theoretical Aspects of Gas Absorption in Packed Towers".

The object of this investigation was to critically review the basic equations for the design of packed towers in view of the fact that much data obtained from such equations seem to be incorrect. Many conclusions based on such incorrect data are found to be in the literature and contradict the basic assumptions of the design equations.

The work presented here consists of the presentation of a more accurate concept of the liquid "film", a critical discussion of the basic assumptions underlying the design equations with examples of results which arise when the assumptions are invalid and an evaluation of the effect of "channeling" in packed towers. The quantitative evaluation of "channeling" failed but qualitative effects may be predicted by means of pressure drop data. Use of pressure drop data has not been attempted heretofore in the discussion of performance of a packed tower.

Respectfully submitted,



Bernard L. Schulman

Acknowledgement

The writer wishes to express his appreciation and respect for the advice of Professor R. S. Tour, under whose guidance this work was carried out. To him is due the credit for emphasizing the need for a careful evaluation of the absorption equations to ascertain sources of error. His suggestions and criticisms concerning this work are hereby gratefully acknowledged.

Abstract

The presentation of much absorption data in the literature which has been in direct contradiction to the general theories of gas absorption has suggested that there are still many weaknesses or errors in the theories. The deviation of much data is believed to be included in 3 categories:

- 1) Misconceptions about the nature of the liquid "film".
- 2) Deviation of experimental procedures from the requirements of the absorption equations.
- 3) Deviation of conditions in packed towers from those assumed in the absorption equations, viz. the presence of viscous gas which does not undergo absorption.

The lack of data for liquid "films" has led in the past to a "convenient" analogy of the liquid and gas films, the latter having been experimentally investigated rather well. As shown by the theories of fluid flow such an analogy is false. A discussion of the correct concept is given.

The effect of the deviation of experimental procedures from those required by the absorption equations is discussed and, where possible, illustrated with examples from the literature. Many misconceptions and erroneous data arise due to merely a faulty experimental technique. The elimination of such errors in technique is described.

The presence of viscous gas in packed towers is indicated by some absorption data and much pressure drop data. This "channeled" gas does not undergo absorption and the omission of this "channeling" from the absorption equations has caused much confusion in the interpretation and correlation of the experimental data.

The modification of the absorption equations has been made for this channeling of the gas. However, the reverse process of determining channeling from absorption data is indeterminate, due to the nature of the equations and their modification.

The use of pressure drop data to further study the effect of "channeling" on tower performance is indicated by numerical calculations of the various absorption functions for various distributions of tubes of different sizes in parallel with a fluid flowing through them. Comparison of the

calculated pressure drop curves with experimental curves indicates that only 20-75% (or less) of the total surface may be active in absorption and the amount of fluid channeled may range from 10-50% of the total flow rate. Simultaneously the variation of the "effective" area, or the absorption transfer coefficient, is found to vary as the 1.3 - 1.4 power of the flow rate. These findings, although not corresponding exactly to the experimental results, closely parallel them as is shown by examples.

Theoretical Aspects of Gas Absorption
in Packed Towers

Bernard Lamar Schulman

Table of Contents

	Page
Letter of Transmittal	i
Acknowledgement	ii
Abstract	iii
Table of Contents	1
List of Figures and Curves	2
Nomenclature	3
Part I Fundamental Theories of Gas Absorption	
1. Historical	6
2. The Effect of Flow Rates on Absorption Coefficients	23
3. Kinetics of Absorption	52
4. Absorption Equations	67
Part II The Effects of Channeling in Packed Towers	
5. The Presence of Channeling in Packed Towers	97
6. The Evaluation of Channeling from Absorption Data	114
7. The Evaluation of Channeling from Pressure Drop Data	122
Appendix	158
Bibliography	164

List of Figures and Curves

Figure	Title	Page
1.	Comparison of Two-Film Theory and Actual Fluid Flow	37
2.	Volume of CO ₂ absorbed vs Tower Height	58
3.	Rectification of Absorption Equation for Bubbles	59
4.	Effect of Diffusion in Bubbles	63
5.	Effect of Surface Temperatures on Absorption	75
6.	Channeling of Gas	108
7.	Evaluation of Channeling from Absorption Data	118
8.	Friction Factor vs Reynolds Number	131
9.	Velocity vs Diameter of Tubes	133
10.	Viscous, Turbulent, Total Flow Rates vs Pressure drop for Normal Distribution of Diameters ($m = 3.6428$)	143
	Pressure drop, effectual area and effective area vs total flow rate for:	
11.	Normal Distribution of Diameters ($m = 3.6428$)	144
12.	Normal Distribution of Diameters ($m = 2.6328$)	145
13.	Uniform Distribution of Diameters	146
14.	Normal Distribution of Squares of Diameters ($m' = 3.6428$)	147
15.	Normal Distribution of Cubes of Diameters ($m'' = 3.6428$)	148

Nomenclature

(These symbols do not correspond exactly to those used in Chapter 3, wherein they are redefined explicitly.)

- A - cross-sectional area of tower
- a - interfacial area per unit volume of tower
- C_A, C_B - concentration of component A, B in gas
- C_p - sp. ht.
- d - diameter of passage (or tube)
- d_c - "critical" diameter, i.e. boundary diameter between turbulent and viscous passages
- D - diffusivity of solute gas in carrier, variable of integration under example of channeling, Chapter 7. (diameter of passage)
- G - gas rate - mass per unit time
- h - height of tower
- Δh - loss in hydrostatic head (friction) in tubes
- h_H - heat transfer coefficient
- H - Henry's constant for solution in the equation $y^H = Hx$
- I - numerical values of integrals (in Chapter 7)
- J - interfacial area per unit volume of tower (same as "a")
- J_t - effectual (turbulent) interfacial area per unit volume of tower
- J_o - maximum amount of surface available for absorption in a tower
- j - fraction of total surface which is effectual for absorption, J_t/J_o
- $\oint_t$ - the effective interfacial area per unit volume of tower
- k_H - thermal conductivity

k_G, k_L - specific conductance of gas, liquid film,

$$\frac{\text{mass of solute transferred}/(\text{unit time})}{(\text{unit surface area})(\text{unit driving force})}$$

k_i - specific conductance of interface - (Miyamoto)

K_G, K_L - overall conductance of gas, liquid films

K_C - overall conductance of gas (or liquid) films

L - total length of tower

m - modulus for the normal distribution of tube diameters (Chapter 7); m' corresponds to the distribution of squares of diameters; m'' corresponds to the distribution of the cubes of diameters.

M - area under the "normal" distribution curve.

$$M = \frac{2m}{\sqrt{\pi}} \int_0^1 e^{-m^2(D - \frac{1}{2})^2} dD.$$

ΔL - thickness of length stagnant tower film

N - total number of passages in tube bundle (Chapter 7)

N_A - amount of solute gas diffusing through a stagnant film,
 $\frac{\text{mass/time}}{\text{unit area}}$

P - total pressure

Q - volumetric flow rate - volume of fluid per unit time
 (in numerical example of channeling)

t - temperature of a phase

u - lineal velocity of a phase, length/time

V - liquid rate in tower, mass per unit time

x - concentration of solute in liquid, mol fraction

y - concentration of solute in gas, mol fraction

X, Y, Z - general space coordinates

Greek

α_1, α_2 - proportionality constants

γ - fraction of gas in viscous flow in tower, the value of channeling

θ - time

Subscripts

A - component A

B - component B

G - bulk gas value

i - interface value

j - variable index for summation

L - bulk liquid value

lm - logarithmic mean

M - "mean" value

o - refers to specific values; see above

t - turbulent flow

T - total flow

v - viscous flow

x - variable value

1, 2 - values at the bottom, top of tower, respectively

Part I

The Fundamental Theories of Gas Absorption

CHAPTER 1.

HISTORICAL

The investigation and study of the absorption of gases with liquids has always been studied from two general standpoints: 1) the mechanism and kinetics of the transfer of the solute gas from the gas phase to the liquid phase, or vice versa, and 2) the effect of external conditions, i.e. the effect of changing the values of the operating variables, on the rate of absorption. The kinetics of the process indicates the effect of the concentrations of the various phases on the overall rate of absorption. At the same time, the influence of the flow rates of the phases, if a flow system is being considered, may be included inasmuch as their values affect the concentrations because of diluting effects, etc. The external conditions, or operating variables, add their effect to the overall process. Factors such as temperature, total pressure, degree of turbulence (agitation) of the system, may be varied independently of the concentrations in order to change the rate of absorption. These latter factors become of prime importance in the application of the theory of gas absorption to industrial processes.

Mechanism of Absorption

The process of absorption may be broken down into three component steps for study:

1. The transfer of the solute gas from the interior, or bulk, of the gas phase to the interface of the gas and liquid.

2. The transfer of the solute from the gas side of the interface to the liquid side. This is the step of the actual solution of the solute gas into the liquid.

3. The transfer of the dissolved gas from the liquid side of the interface into the bulk of the liquid.

Of the three steps outlined, only the first and third have been studied in great detail from a theoretical or experimental point of view. The actual mechanism of the process by which a gas molecule passes from the gas phase into the liquid phase is unknown as yet. The rate of transfer of a solute through an inert carrier, however, has received much theoretical work and experimental confirmation. The rate of transfer has been found to be dependent on the nature of the carrier phase, i.e. quiescent (or stagnant), viscous, or turbulent. In all these cases the transfer occurs by the general mechanism of diffusion.

Theory of Diffusion

The theory of diffusion of gases was first studied by Stefan and Maxwell (24) as part of the kinetic theory of gases. The fact that a difference of concentration of one gas in another caused a flow of the gases so as to bring about a uniform concentration of the two gases was well known. The

movement of the gaseous molecules from one point to another was known to be retarded by the collisions of the molecule with other molecules of the gas. These collisions tended to keep the molecules in a random state, acting as an overall inertia to a change in location of the molecules. Thus, in spite of the high velocities of individual molecules, the overall movement of molecules to equalize the molecular distribution was slow.

Maxwell assumed that the resistance to diffusion, expressed as change in concentration per unit length, was proportional to the concentration of each type of molecule present, the difference in the velocities of the diffusing molecule and the carrier molecule. For the case of equimolal diffusion where the diffusing gas is replaced by the other gas, the general differential equation was obtained:

$$\frac{\partial y}{\partial \theta} = D \left[\frac{\partial^2 y}{\partial x^2} + \frac{\partial^2 y}{\partial y^2} + \frac{\partial^2 y}{\partial z^2} \right] \quad (1)$$

and for steady flow in one direction:

$$N_A = - \frac{D}{P} \frac{dy}{dx} \quad (2)$$

where D is the "diffusion coefficient".

Several investigators (24) derived theoretical expressions for D in terms of the properties of the two types of molecules. Gilliland (10, 11) experimentally determined values of D for many vapors in air and though the numerical values were slightly lower than the theoretical, the overall form of the theoretical equations was found to be correct. Only the value

of a numerical constant had to be modified to make the experimental data check the theoretical equations. These investigations, together with the general acceptance of the kinetic theory on the basis of other results, justified the accuracy of Maxwell's views on diffusion. Insofar as the mathematical expression for diffusion is concerned, it is noted that for a steady state where N_A is constant, the drop in concentration is linear with distance, i.e. for a given length of diffusion path, the rate of diffusion is proportional to the difference of concentrations of the diffusing gas at the ends of the path. This simplicity of form has been the main reason for attempting to modify the theories of diffusion for each suitable case of absorption, if possible.

The treatment of diffusion in liquids has been more empirical than theoretical. The kinetic theory of liquids is much more complex than that for gases and so the assumption has always been that the equation of diffusion for liquids is of the same form as that for gases. In view of the fact that the arrangement of the molecules is closer and the molecular attraction and density are much greater for liquids, diffusion of a solute in a liquid is retarded appreciably. This is evidenced in the numerical values for the diffusivity in liquids which are of the order of 0.1% of those for gases (1).

The Two Film Theory

The application of the ideas and equations of diffusion

to commercial types of absorption processes and equipment is definitely limited. In most experimental and industrial work, both liquid and gas phases are agitated due to their motion, rather than being stagnant. Consequently there is internal mixing in each phase, increasing the rate of mass transfer above that where quiescent diffusion is the mechanism for transfer.

The first suggestion made as to this case was that of Donnan and Mason (8). In developing a new equation for the rate of solution of gases in liquids, they proposed that the overall process be considered still as being a first order process, as is diffusion, but with the proportionality constant of the equation being a function of the agitation of the phases. If the concentration of the solute in the gas is y and the concentration of the solute in the gas in equilibrium with the liquid is y^* , then their equation may be written as

$$N_A = K_G (y - y^*) \quad (3)$$

where K_G is the constant of proportionality and must be evaluated experimentally. As a result, any variations in the value of K_G must be attributed to and accounted for on the basis of the agitation and conditions of the system. It is seen by comparing equation (3) with equation (2) that K_G must contain the length of the path through which the solute diffuses.

The first interpretation of the factors which affect the value of K_G was made by Whitman (35) and has become known as

the "two-film theory". The work of several investigators (17) had previously shown that when a fluid moves past a surface, there is a small "film", formed next to the surface, which moves very slowly, in viscous form, irrespective of the nature of the flow in the bulk of the fluid stream. Whitman proposed that adjoining the interface of a liquid and gas there exists a gas film and a liquid film, each of these films being essentially stagnant (or moving in viscous flow). It is then these stagnant (or viscous) films which offer the resistance to the transfer of the solute gas. Hence any method that will decrease either film thickness would increase the rate of absorption due to the shorter path of transfer. This idea was confirmed experimentally by noting that the increased agitation of a phase, as shown by velocity distribution data in pipes, decreased the thickness of the viscous film and increased rate of absorption.

Assuming that the rate of absorption was proportional to a concentration difference, Whitman expressed his equations as

$$N_A = k_G(y - y_i) = k_L(x_i - x) = K_G(y - y^*) = K_L(x^* - x) \quad (4)$$

where y^* and x^* represent concentrations in the gas and liquid phase in equilibrium with the bulk of the opposite phase, and y_i and x_i represent the concentrations at the interface in the gas and liquid respectively. If the resistance of the interface is assumed to be zero, then y_i and x_i are in equilibrium; and if Henry's law applies in the form $y = Hx$, then the other relations between K_G , K_L , k_G and k_L are:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L} \quad (5)$$

$$\frac{1}{K_L} = \frac{1}{Hk_G} + \frac{1}{k_L} = \frac{1}{Hk_G}$$

The resolution of the overall mass transfer coefficient into its component parts served to indicate which phase might contain the main resistance to the absorption process. At the same time, the effect of changing flow rates or other operating variables on the value of K_L or K_G could be more easily ascertained, if it were known which of the resistances were the greatest and most important.

It was Whitman's recognition of the fact that for many gases, one of the fluid resistances was often much greater than the other which gave the "two-film" theory its importance. If $\frac{1}{k_g} = 0$, then the value of K_G becomes Hk_L and also $K_L = k_L$; or if $\frac{1}{k_L} = 0$, then $K_G = k_G$ and $K_L = k_G/H$. In the first case, the liquid film is said to control the rate of absorption and in the second, the gas film controls. Whitman showed that the first case arose when a relatively "insoluble" gas was being absorbed in a liquid and the second case was for a "soluble" gas. Hence, if an experimental study of the gas film was desired, a suitable system would be ammonia and water. Any values of K_G that would be obtained would represent the values of k_G and such values might be checked against any theoretical notions of diffusion through gaseous films. On the other hand,

the values of k_L could be obtained by calculating K_L for the absorption of such gases as CO_2 , O_2 , N_2 , etc. in water and the effect of operating variables on k_L could be ascertained. This idea of two films thus served to classify absorption systems and aid in the interpretation of absorption data.

The justification of using a difference of concentrations for the driving force may be shown by using the diffusion equations for the case of stagnant films, as presented by Sherwood (24). For the diffusion of one component A through a stagnant layer of B, the equation is

$$N_A = \frac{DP}{RT(\Delta L)} \ln \frac{y_{B2}}{y_{B1}}, \quad y_{B2} > y_{B1} \quad (6)$$

where y_{B1} and y_{B2} are the concentrations of the inert component B on either side of the film and ΔL the film thickness. Using the definition of the logmean value of y_B as

$$y_{BM} = (y_{B2} - y_{B1}) / \ln \frac{y_{B2}}{y_{B1}}$$

and noting that $y_A + y_B = 1$, equation (6) may be written as

$$N_A = k \times \frac{y_{A1} - y_{A2}}{y_{BM}} \quad (7)$$

This expression shows that the actual driving force is really a difference of the logarithms of the inert gas concentrations but that the use of the solute concentrations is approximately correct, if the mean inert concentration does not vary. This approximation is sufficiently accurate since in most cases the solute gas is present in low concentrations or else

the degree of absorption of the solute is small. The inclusion of the inert concentration in Whitman's equations has been made by Colburn (6) and are tabulated by Perry (21). However, the inclusion of the inert concentrations, which complicates the equations, has never been proven necessary by experimental work so that many investigators ignore it.

Miyamoto's Theory

The possible effect of the interface on the rate of solution of gases in liquids was given a semi-theoretical treatment by Miyamoto (19). He considered the problem of interfacial resistance to be more important than that of the films. He assumed that for a molecule of a solute gas to "enter" the liquid, it must have a velocity component perpendicular to the interface greater than some "threshold" value. Similarly, for the dissolved gas to "escape" from the liquid, the molecule in the liquid must also have a velocity component perpendicular to the interface greater than some other threshold value.

By assuming Maxwell's Distribution Law for the velocities of gases to hold in both the gas and liquid phases, Miyamoto showed that the rate of solution was proportional to the difference of the mol fraction of the solute in the gas phase and the concentration of the solute in the gas phase if the gas were in equilibrium with the prevailing liquid composition. Expressed algebraically

$$N_A = k_1(y_1 - Hx_1) \quad (8)$$

This derivation yields the same form of absorption equation as before but points out three important facts:

1. Another explanation or basis for the solution of a gas gives a first order reaction equation.
2. There is a possibility, in view of the same type of kinetic equation, that the interface resistance is not zero and may be of considerable magnitude, i.e. $y_1 \neq Hx_1$ necessarily.
3. Even if the interfacial resistance were appreciable, the driving force of absorption is still of the same form as given in the two-film theory. The two theories can be combined if we regard the values of y_1 and x_1 to be those existing between the interface and the film. Then $y_1 \neq Hx_1$ and the modified values of the overall coefficients may be expressed as

$$\frac{1}{K_G'} = \frac{1}{k_G} + \frac{H}{k_L} + \frac{1}{k_1}$$

$$\frac{1}{K_L'} = \frac{1}{Hk_G} + \frac{1}{k_L} + \frac{1}{Hk_1} = \frac{1}{HK_G'} \quad (9)$$

Using these modified values of the overall coefficients, the rate of solution may be expressed just as before using the average, or "bulk", values of y and x .

The insertion of a term for interfacial resistance seems erroneous, as defined by Miyamoto, since there is no reason not to assume that at the juncture of gas and liquid phase, i.e. the interface, the two phases are in equilibrium. However, the assumption that $y_1 = Hx_1$ does not infer that no mass transfer

can take place across the interface. For although $y_1 = Hx_1$, the driving force is the gradient of the concentration, i.e. $\frac{dy}{dx}$ or $\frac{dx}{dy}$, at any point and these terms are not necessarily zero.

Some absorption data when wetting agents were present in the liquid have been presented to show that the interface may show appreciable resistance to absorption. These data and their more probable explanation are discussed under "liquid films" at a later point. As a result, the assumption of equilibrium at the interface is still considered valid.

Design Equations

The use of rate equations for the purposes of design of packed towers was begun by Donnan and Mason in 1920. The equations developed by them have been succeeded by simpler and more useful forms. The purpose of such equations is to relate such dependent variables as volume of tower, outlet concentrations of various streams, etc. to the independent variables such as inlet concentrations, flow rates and pressure.

The simplest of the design equations is that of the log mean equation (24). If the inlet gas is dilute and the system follows Henry's law, then the rate equation is²

$$-G dy = K_G a(y - Hx) A dh \quad (10)$$

By a material balance

$$x = x_2 + \frac{G}{V} (y - y_2) \quad (11)$$

and

$$-G dy = K_G aA \left[y \left(1 - \frac{HG}{V} \right) - (Hx_2 - \frac{HG}{V} y_2) \right] dh$$

Integrating:

$$-\frac{K_G a A}{G} \int_0^L dh = \int_{y_1}^{y_2} \frac{dy}{y(1 - \frac{HG}{V}) - (Hx_2 - \frac{HG}{V} y_2)}$$

or

$$\begin{aligned} -\frac{K_G a A L}{G} &= \frac{1}{1 - \frac{HG}{V}} \ln \left\{ \frac{y_2(1 - \frac{HG}{V}) - Hx_2 + \frac{HG}{V} y_2}{y_1(1 - \frac{HG}{V}) - Hx_2 + \frac{HG}{V} y_2} \right\} \\ &= \frac{1}{1 - \frac{HG}{V}} \ln \frac{y_2 - Hx_2}{y_1 - Hx_1} \end{aligned} \quad (12)$$

Since a logarithmic term appears, it may be eliminated by using the definition of the log mean noting that:

$$\begin{aligned} (y_2 - Hx_2) - (y_1 - Hx_1) &= y_2 - Hx_2 - y_1 + Hx_1 = Hx_1 - y_1 + Hx_2 - y_2 + \frac{HG}{V} y_1 - \frac{HG}{V} y_2 \\ &= (y_2 - y_1)(1 - \frac{HG}{V}) \end{aligned}$$

Designating

$$y_2 - Hx_2 \equiv (\Delta y)_2$$

$$y_1 - Hx_1 \equiv (\Delta y)_1$$

equation (12) may be written as

$$\frac{K_G a A L}{G} = \frac{y_1 - y_2}{(\Delta y)_1 - (\Delta y)_2} \times \ln \frac{(\Delta y)_1}{(\Delta y)_2} = \frac{y_1 - y_2}{(\Delta y)_{lm}}$$

or

$$K_G a A L (\Delta y)_{lm} = G(y_1 - y_2) \quad (13)$$

*In all derivations for packed towers, the height is measured from the bottom to the top. Hence $\frac{dy}{dh}$ is negative and in order to make it positive the value $-\frac{dy}{dh}$ is used.

This corresponds to the familiar equation for heat transfer in form and its simplicity of form has earned it wide usage.

Tour and Garber (9) integrated the same rate equation for nondilute gases assuming isothermal operation and Henry's law applying. If the inlet liquor contains no solute, the differential rate equation becomes

$$-\frac{G_2(1-y_2)}{(1-y)^2} \frac{dy}{dh} = KCJA \left[y - \frac{HG_2}{V} \frac{y-y_2}{1-y} \right] \quad (14)$$

where G_2 and y are in molal units and KCJ has the same meaning as $K_G a$ in equation (13). The integrated form becomes:

$$\frac{2KCJAL}{V/H} = \ln \frac{(1-y_1)^2}{(1-y_2)^2} \cdot \frac{y_2(1-y_2)}{y_1(1-y_1) - \frac{HG_2}{V}(y_1-y_2)} \left[\frac{2y_1+i+\psi}{2y_2+i+\psi} \cdot \frac{2y_2+i-\psi}{2y_1+i-\psi} \right]^{\frac{i+2}{\psi}} \quad (15)$$

where

$$i = \frac{HG_2}{V} - 1$$

$$\psi = \sqrt{i^2 + 4 \frac{HG_2}{V} y_2}$$

Equation 15 may also be expressed in the simpler form (34) as:

$$\frac{2KCJAL}{V/H} = \left(i + \frac{i+2}{\psi} \right) \ln \left[\left(\frac{1-y_2}{1-y_1} \right) \left(\frac{y_2}{y_1 - Hx_1} \right) \right] + 2 \ln \left(\frac{1-y_1}{1-y_2} \right) \left(\frac{2y_1+i+\psi}{2y_2+i+\psi} \right)^{\frac{i+2}{\psi}} \quad (15a)$$

This form of equation 15 is much more suitable for calculations and shows the similarities between the log-mean form and the Tour-Garber equation.

While the use of the log mean equation and the more exact absorption equation have served as the basis of designing absorption equipment, the prediction and correlation of the values of KCJ have been improved by the concept of the height of transfer units, or HTU (5). The number of transfer units is

defined as the numerical value of $\int_{y_1}^{y_2} \frac{dy}{y - y^*}$ so that the value

of HTU is $G / \int_{y_1}^{y_2} \frac{dy}{y - y^*}$. The value of HTU then becomes $\frac{G/A}{KCJ}$.

The concept of HTU has many advantages in the estimation of the relative magnitudes of the film resistances. The greatest advantage from a practical point of view is that the numerical value of HTU does not vary a great deal with flow rates (as does KCJ) nor does it vary too much if a different absorption system is used on the same packing. This is quite useful in estimating the height of towers needed for a given amount of absorption. However, for the interpretation of absorption data, it is necessary to first evaluate KCJ and hence it is just as convenient to work with KCJ rather than KCJ/G or KCJ/L .

Nearly all the literature data for absorption has been expressed as $K_G a$ (or $K_L a$) while the work done at the University of Cincinnati has been reported as KCJ, based on the Tour-Garber equation. The variation of notation is not too important since the effect of operating variables is the same on both types of coefficients even though the numerical values may be slightly different (3). The development and integration of the differential equations in both cases make use of certain basic assumptions which are quite important to the validity of the final expressions. Garber tabulated these assumptions as follows:

1. The temperature and pressure throughout the tower are uniform and constant.
2. The flow rate per unit area and composition of the two fluids at any area on a given plane remain constant during the period of operation.

3. The area of interface for solute transfer per unit packed volume of tower is everywhere the same throughout the tower.

4. The conductivity of the transfer path, defined as the amount of solute transferred per unit time per unit area of solvent surface per concentration driving force, is constant throughout the tower.

5. The carrier gas is inert, i.e. its solubility in the solvent is zero.*

6. The system obeys Henry's law.

These six assumptions are the basis for the present-day absorption equations. In obtaining values of absorption coefficients from experimental data using these equations, care must be taken that such data were obtained under the above conditions for which the equations are valid. If any of the above conditions are not true, there may be large errors in the calculated values of K_{CJ} , K_{La} or K_{Ga} .

With the presentation of the two film theory and the concept of HTU's, the investigation of the nature of the various types of absorption coefficients, i.e. their variation with operating variables and their absolute values, was begun by many

*This also implies that no solvent is evaporated into the carrier gas. This may have an appreciable effect on the calculated results of experimental measurements of K_{CJ} , etc., as is discussed later.

workers and the results have been published frequently. As more and more data have been published for different systems and types of packings, a wide divergence of the interpretation of the data has occurred. While a great deal of the data seems to conform readily with the two-film idea, there is still much data which seemingly contradicts the theory.

These "contradictions" fall into two general categories and examples of these data may be best discussed under each. The categories may be designated as:

1. The values of KCJ do not vary with flow rates of the fluid phases as predicted by the two-film theory.
2. The experimental values of KCJ computed from the absorption equation are found to be functions of certain variables whereas the absorption equations are based upon the assumption of the invariability of KCJ over the tower. As an example, Spector and Dodge (26) specifically show data which indicate KCJ is a function of tower height. Inasmuch as the KCJ is assumed independent of height when integrating the absorption equations, the numerical value of KCJ will have no theoretical meaning and any conclusions based on such values will be of doubtful validity.

The presentation of such data in the literature suggests that the general form of the absorption equation may be in error and also that the basis of the two-film theory needs modification, especially with respect to the liquid resistance. The basis for the critical examination of the theory of gas absorption must then be the two above categories. Any failure of the

equation must be found by examining each assumption inherent in the present equations. The correction of this failure, either by modification of experimental procedure or the equation itself is suggested in this work.

CHAPTER 2

THE EFFECT OF FLOW RATES ON ABSORPTION COEFFICIENTS

The use of design equations for absorption equipment is limited by the presence of the constant KCJ (or K_Ga). The prediction of the numerical value of the constant is impossible from theoretical methods alone and the determination of the values are still carried out on an empirical and experimental basis. However, the variation of these constants with operating conditions and the subsequent extrapolation of meager data may be attempted from fundamental considerations.

The overall coefficient may be conveniently divided into two parts for discussion, the value of KC (or K_G) and the interfacial area per unit volume of packing J (or a). The value of KC represents the conductance of the gas and liquid phases to the transfer of the solute from one phase to the other. As such, the KC portion of KCJ clearly depends on the degree of turbulence of each phase and consequently is a function of any variable that would affect the turbulence. Since many variables affect turbulence KC becomes a rather complicated function of physical properties as well as flow rates of the fluids. Moreover, some variables affect the resistances of both phases so that the separation of one resistance from another by changing such variables is made difficult.

The complexity of KCJ is further heightened by the nature of J, in addition to that of KC. The interfacial area between the gas and liquid in a packed tower is unmeasurable directly. In some cases, investigators assume the interfacial area to be the same as the surface area of the packing. However, this is known not to be the case because of the wetting effects of the liquid and the formation of small stagnant pockets of liquid or gas. If there are any portions of the packing which are not wet, or which are not in contact with gas, or which are filled with pockets of either phase which are stagnant, then that part of the packing will have a local value of $J = 0$. Consequently, the characteristics of the packing and the factors which affect the wetting must also be considered in the evaluation of the interfacial area.

By combining these two variables into a single function KCJ, the overall coefficient, a complicated and unknown function is obtained. It must be emphasized that the overall value is the only one which may be obtained as such from test data on packed towers. In order to disentangle the complicated function into the component parts, other methods must supplement the ordinary data obtained in the laboratory.

The most useful method for classifying and studying absorption data has been that of considering one resistance, or "film", to be controlling. If one of the three resistances, gas, surface (i.e. the interfacial) or the liquid, is much

greater than either of the other two, then the value of K_{CJ} will approximate the value of the greater resistance and the variation of K_{CJ} with any variable will be approximately the same as the variation of the individual resistance with that variable, PROVIDED THAT J REMAINS CONSTANT. This latter condition is quite important inasmuch as an unknown variation of J confuses the variation of the resistance. Hence, if a solute-solvent system may be found where one resistance controls, then the absorption data should represent the characteristics of the one film.

The categories under which we may classify all absorption data for discussion are three. They are:

1. Gas Film controlling.
2. Liquid film controlling.
3. General Case, neither film controlling.

Such a division is convenient for discussing the properties of the liquid and gas films. In discussing the films and the effect of flow rates, the emphasis is usually placed on K_C , or K_G , which is equivalent to assuming J is constant. Hence, the factors which influence J will be discussed under the topic of interfacial area, which is included in liquid film discussion since the distribution of the liquid has a great effect on the amount of wetted area available for absorption.

Case 1. Gas Film Controlling

The gas film is assumed to control when the solute is very soluble in the liquid, e.g. NH_3 or HCl in water. The

equilibrium constant for the solution of the solute from the gas to the liquid (i.e. $H = \frac{Y}{X}$) is very low, indicating that for a given rate of transfer, the drop in concentration through the liquid is far lower than the drop in concentration through the gas. The increased agitation of the gas phase would tend to keep the concentration through the gas more uniform, thus increasing the concentration near the interface resulting in an increased rate of absorption. At the same time, the length of path in the gas phase for the slow diffusion to occur would be decreased. When one such phase is the most important in the absorption process, that phase is said to "control" the rate.

The quantitative effects of changing the flow conditions on the gas phase depends greatly on whether the gas is in viscous or turbulent flow. Since the mechanism of mass transfer is different in each, the variation of the rate of transfer in each with the operating variables is different. Hence each will be discussed separately.

-Turbulent Gas Flow-

The description of turbulent flow is logically discussed first since turbulent flow is more often encountered in gaseous flow and the rate of mass transfer in turbulent gas streams is so much greater than in viscous streams. In the turbulent flow of a gas, there are relatively large displacements of gases in a lateral direction as well as in the longitudinal direction of flow. This lateral, or radial (if the gas is in a

pipe), flow keeps the concentration of the gas stream rather uniform over the radial distance so that the driving force for absorption is high. However, near the liquid surface there is a "film" of gas, which is not in turbulent, but rather viscous, flow and this film of gas resists the penetration of the solute molecules, causing the transfer of the solute molecules to the liquid surface to be retarded. Thus, in turbulent flow, the main resistance lies in the "film" and any variation on k_G or K_G (or K_C) may be accomplished by decreasing the size of the film.

The presence of such viscous films has actually been demonstrated for fluids flowing in pipes. It has been shown that these films also form the main resistance to heat transfer and also are the site of the development of most of the friction in fluid flow. From such velocity and friction measurements it has long been known that increased, flow rates (or more generally, increased Reynold's numbers) decrease the thickness of these films. Hence, with a great deal of heat transfer and friction data available, it is not surprising that the equations of gas absorption have been developed to correspond to those of heat transfer and fluid friction.

Attempts have been made to correlate both heat transfer and absorption coefficients directly to the friction factor (24, 15) but probably the best approach is still the empirical one used by Gilliland (10, 11). He vaporized liquids into gas streams in wetted wall columns so that the gas film was the only

resistance. (In using pure liquids there is no problem of liquid diffusion). He calculated the film thickness using equation (6) and correlated the values of ΔL by the equation

$$\frac{d}{\Delta L} = 0.023 \left(\frac{du\rho}{\mu} \right)^{0.83} \left(\frac{\mu}{\rho D} \right)^{0.44}$$

which is remarkably similar to that for heat transfer, as given by MacAdams (17)

$$\frac{h_H d}{k_H} = 0.023 \left(\frac{du\rho}{\mu} \right)^{0.8} \left(\frac{C_p \mu}{k_H} \right)^{0.4}$$

Other absorption data for wetted wall columns (7) tend to substantiate Gillilands results, especially with regard to the exponents on the Reynolds and Schmidt number. For convenience, the exponents of Gilliland are often changed to 0.8 and 0.4 to conform with the heat transfer equation.

The equations given above are definitely limited in their application to tower design since the interfacial area J cannot be directly obtained. Moreover, as will be discussed in more detail later, there are various sizes of gas passages in the tower which result in various Reynolds numbers so that the limitations of present knowledge as to the size and distribution of sizes of these passages make the quantitative use of the equations impossible. The equations do serve to show the relative effect of operating variables on KC however. Thus it would be logical to expect KCJ to vary as G , or u , to the 0.8 power, if J remained constant.

Some of the first experimental data indicated that the value of KCJ (or K_Ga) did vary as the 0.8 power of the gas rate. However, in other cases there have been exponents greater than 0.8 indicating that J must also be increasing with the gas rate (21, 36). This indication of increase in J has also been noted for liquid film data.

Excluding the variations in J this value of KCJ for gas films is altered primarily by changing the gas flow rate. The liquid rate should not affect the gas film at all. Also, changes in pressure and temperature will not affect KC for gases to too great an extent since μ , D and k_H change very little with temperature for gases. The same small effect of temperature has noted for heat transfer and friction where both of these values are influenced more by the mass velocity ($u\rho$) of the gas than any other physical variable.

-Viscous Gas Flow-

The absorption of gases from gas streams flowing in viscous motion has been studied mathematically by obtaining the solution to the general diffusion equation with the appropriate boundary conditions (24). The absorption data obtained in wetted wall columns for the viscous flow of the gas show a deviation from the analytical solution in that the experimental data fit best the solution which assumes a uniform radial distribution of velocity. Since the flow in viscous motion exhibits a parabolic distribution there is some sort of a discrepancy present.

The mechanism of solute transfer in viscous flow is much different from that for turbulent flow. In turbulent flow, the solute molecules are transferred from the bulk of the gas stream to the interface by the constant collision and movement with the molecules of the inert gas in a radial direction. The motion of the gas by these eddy currents causes the concentration of the solute in the main stream to be kept at a uniform value over the radial distance. If the gas is flowing in viscous form the transfer of solute occurs by molecular diffusion alone and so is much slower than in the case of turbulent flow.

The differences between the rates of diffusion in both cases may be seen also from the concepts of mean free paths of the molecules. In turbulent flow, the eddy currents cause masses of gas to flow over the entire radial distance of the passage in a very rapid manner. In viscous flow, the mean free path of a molecule tends to be its molecular mean free path which is exceedingly small. The 'diffusivity' of solutes in each flow pattern is a direct function of these types of lengths and hence the turbulent, or "eddy", diffusivity is much larger than the molecular diffusivity. At the same time, the "eddy" diffusivity is a function of the Reynolds number while the molecular diffusivity is not.

These concepts of mixing paths, or lengths, have long been evident from the analogy between mass transfer and friction. Inasmuch as friction is the loss in momentum of the fluid (which

is proportional to the amount of material being moved), the change in the amount of friction with the nature of flow which has long been known to be large, suggests the corresponding values of higher absorption in turbulent flow. While quantitative relationships between heat and mass transfer and friction have not reached a high degree of precision, the qualitative agreement has been found to be good.

The experimental verification of the differences between diffusion rates in viscous and turbulent flow was best shown by the classical experiments of Reynolds which were used to investigate the stability of liquid flow. The form of his experiments have been tabulated in many places but the essential facts noted by him confirm the relative rates of diffusion. When the color bands were introduced in viscous flow the color remained in the same position all the length of the tube with little or no spreading of the color in the radial direction. As the velocity of the stream was increased the flow passed into a region of instability and the flow pattern broke up the turbulent form. Under these conditions, the color band rapidly broke and mixed throughout the stream causing the stream to become colored. It was this "break" in the color band, i.e. the change in the rate of diffusion, which was used to denote the change in flow pattern.

It is evident that the goal of every packing for towers should be to furnish not only a large amount of contact surface but to give the gas in contact

with this surface a maximum degree of turbulence. It must be remembered that the degree of turbulence fixes the magnitude of KC which is an inherent part of the performance characteristic of the packing, KCJ . In many cases the value of KCJ is usually increased by making the passages of packing smaller, so as to increase J . However, if the passages are of a small size, the flow in these small parts may become viscous. In this case the decrease of KC may more than offset the increase in J so that KCJ may decrease. The larger amount of area then becomes less efficient for absorption purposes because of the increase in area. Such effects greatly reduce the efficiency of a tower and also render the use of towers for fundamental investigations of limited value. This will be discussed more under "channeling".

Case 2. Liquid Film Controls

A. Pure Liquids

The liquid resistance has been assumed to control in these cases where the solute gas is slightly soluble in the liquid, e.g. CO_2 , O_2 , N_2 in water. The rate of absorption is limited by the rate of diffusion of the dissolved gas away from the interface into the liquid for as soon as a little gas dissolves, the liquid near the interface tends to become saturated with the gas. As soon as the dissolved solute diffuses away from the interface more solute may be dissolved. The gas concentration, meantime, remains uniform since the slight unbalance in concentration keeps the solute supplied to the interface. If the rate of

diffusion of the solute in the liquid is small, the gas diffusion will be such that the gas film will offer little resistance in comparison to the liquid. Then the gas rate should have no effect on the value of $K_C J$ where the liquid resistance controls and only the liquid flow rates be of consequence.

No comprehensive work on liquid resistance in wetted wall towers has been presented, as in the case of the gas resistance. All the experimental work on liquid resistances has been carried out using packed towers. Inasmuch as towers give varying values of J much of the interpretation of liquid film data (which usually assumes J constant with changing flow rates) is believed to be in error.

One of the most comprehensive works on liquid resistances was that of Sherwood and Holloway (25) who studied the desorption of O_2 and CO_2 from water. They found that $K_L a$ increased as the 0.75 power of the liquid rate, was independent of the gas rate (unless "loading" of the column occurred), and also noted that the pressure drop over the column varied as the 1.8 power of the gas rate. This latter part was shown merely for completeness and yet, as will be shown later, tends to confirm the accuracy of their data. It was felt by these authors that the deviation of the value of 0.75 for the exponent on the liquid rate from 0.8 (for gas rate in the gas film) was small enough to conclude that the liquid film was quite analogous to the gas film and that 0.80 would be a better value for the exponent on the liquid rate.

Subsequent work has not confirmed this idea. The data of Greenberg (12) for CO_2 absorption in water indicates an exponent very close to unity. In addition he found that K_G varied approximately as the 0.20-0.25 power of the gas rate. The significance of this small effect of gas rate is thought to be larger than has been considered in the literature.

The existence of exponents on the liquid rate greater than 0.8 was also shown by Koch (16) who found that $K_L a$ for CO_2 absorption in water varied as the 0.96 power of the water rate. The data scattered too much to note any definite effect of gas rate.

Vivian and Whitney (32, 33) reported exponents on the liquid rate of 0.60 for the values of $K_L a$ for the absorption of SO_2 and Cl_2 in water. At the same time, the data indicates that $K_L a$ varies as the 0.17-0.20 power of the gas rate. In order to remove the 0.60 exponent and replace it with 0.80, Vivian and Whitney assumed that the driving force used originally was incorrect due to the incomplete hydrolysis of the SO_2 (or Cl_2) in the water. Making this correction and computing the amount of actual "molecular" SO_2 (or Cl_2), i.e. unreacted, for use as a new concentration unit, the new values of the "pseudo coefficient" $K_L a$, were found to vary more closely as the 0.8 power of the liquid rate. However, even these "pseudo-coefficients" were much lower in value than those predicted from the Sherwood-Holloway correlation.

These few data indicate the variation in ideas of the liquid resistance as well as the experimental results. The choice of the value of 0.80 for the exponent on the liquid rate on the basis of the analogy between the liquid film and gas film seems incorrect. This is due to the fact that there is no actual viscous film of liquid present at the gas-liquid interface as there is for the gas. If there were such a film present then such a choice would be permissible. But the theory of flow of liquid layers disproves the presence of such a viscous film of liquid.

If a liquid flows over a piece of packing, a viscous film of liquid does exist next to the material of the packing and extends out to form a definite layer. Provided the flow of the liquid is small, the entire thickness of the liquid layer will be in laminar flow. However, even in this case, the velocity distribution is such that the velocity next to the packing is zero while it reaches a maximum at the top of the layer. As a result of this distribution, only one half of the velocity parabola is present, whereas in pipes the maximum velocity is reached in the center and the complete parabola exists.

As the liquid velocity is increased, the viscous pattern of flow will change to turbulence. Once again there will be a thin viscous film next to the packing where there is a parabolic distribution of velocities. The maximum velocity will be reached again at the surface of the liquid which is in

turbulent flow. Consequently there is no actual liquid film present at the liquid-gas interface as conceived by Whitman. (Near the "loading point" of a column, the drag of the gas on the liquid may cause a viscous film to appear at the surface. For the usual absorption tests, the loading point is never reached.)

These conclusions have been borne out by various types of experimental work. One of the best illustrations is that of the tower hold-up of liquid as a function of liquid and gas velocities. By assuming that the resistance of flow of liquid layers was overcome by the force of gravity, Tour (29) showed that the thickness of the liquid layer in viscous flow is proportional to the $1/3$ power of the liquid rate, whereas for turbulent flow, the exponent was $7/12$. The liquid hold-up in the column was predicted to vary in a similar manner. The experimental results for a packed tower, as reported by Mirus (18), gave an exponent of 0.58, the value of $7/12$ being 0.583. At the same time, Mirus showed that the gas rate had no effect on liquid holdup until the liquid rate reached the loading point. For liquid rates above the loading point, the holdup becomes a function of the gas velocity due to the fact that, past the loading point, the friction between the gas and liquid increases rapidly up to the point where the drag of the gas on the liquid is appreciable. This drag increases the holdup in the tower and the velocity distribution in the liquid layer becomes slightly

distorted at the gas-liquid surface where the velocity is smaller than that at a short distance below the surface.

It is not to be implied that the absence of an actual viscous film at the interface upsets the general classification of absorption systems. For the case of CO_2 , etc., being absorbed in water, the liquid transfer is still the controlling step in the process. Because of the lower degree of turbulence of the water, as compared to the gas, and the greater inherent resistance to diffusion in the liquid, the mass transfer coefficient in the liquid is still much smaller than that for the gas. Thus the bulk of the liquid, rather than a viscous film, is the actual resistance. The comparison of the "film" theory and the above idea may be illustrated by a plot of the concentration of solute (in gas units) versus a transverse distance in the liquid and gas phases. The plot is shown in figure 1.

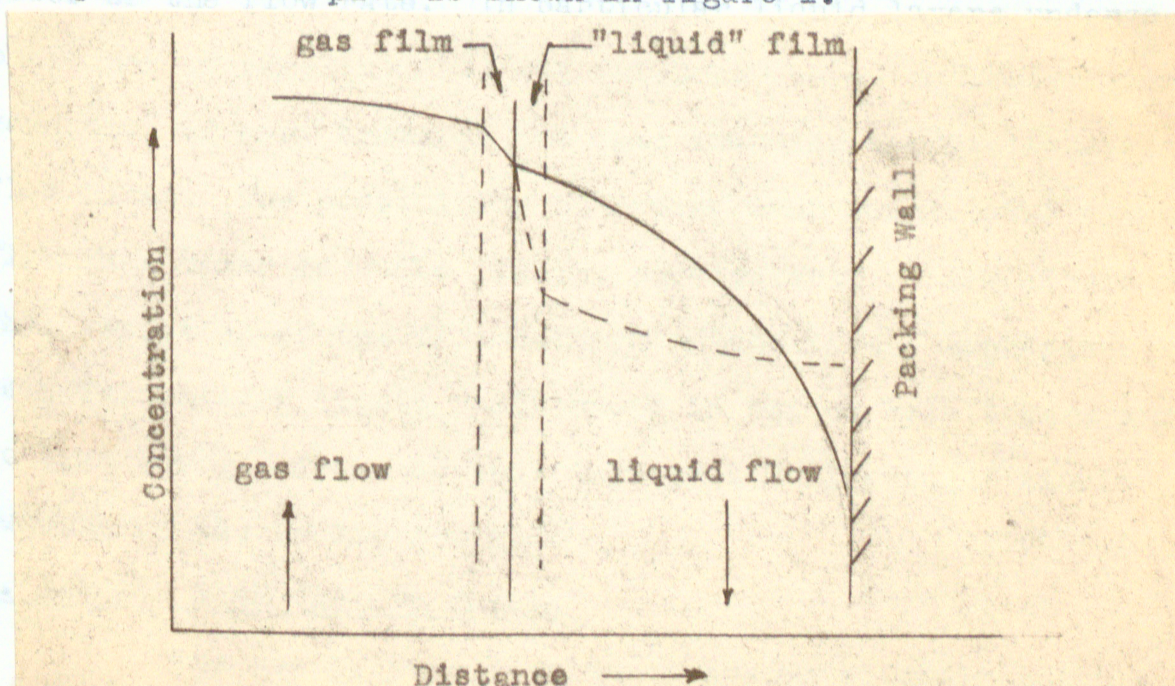


Fig. 1 Comparison of Two-film Theory and Actual Fluid Flow

— Actual

- - - Two-film Theory

The concentration gradient in the gas phase is small due to the small amount of gas resistance. The dotted lines represent the concentration gradient as offered by Whitman while the solid line represents the actual case as described above. In both cases the drop in concentration is the same but occurs in an entirely different manner. The replacement of the erroneous "viscous film" by a "turbulent film" suggests that the variation of KC for liquid resistances does not follow the same pattern as for the gas resistance and the assumption of the 0.8 exponent on liquid rates is not justified.

The presence of exponents on the liquid rate higher than 0.8 tends to parallel the heat transfer "transition region". In the intermediate range of Reynolds number of 2100-20000, the heat transfer coefficient increases much more rapidly than the 0.80 power of the flow rate. In particular liquid layers undergo the phenomena of rippling (13, 17) which causes an entirely different variation of heat transfer and mass transfer coefficients with flow rates. The possibility of having such complicated types of flow in a tower is quite likely, particularly at low liquid rates. This variation of the flow pattern of the liquid emphasizes the need for data on liquid resistances in wetted wall towers similar to that for gas films so that the exact influence of liquid turbulence may be ascertained.

B. Liquids with "Active Agents"

The use of pure liquids to absorb slightly soluble gases is of interest from a theoretical standpoint but commercial

use is limited. Both the rate of absorption and capacity of the liquid for the gas is often too low to be economical. Hence the addition of materials which affect the solubility and rate of solution of the gas in the liquid is usually made. Thus alkaline solutions are used to absorb acidic gases and acid solutions may be used for alkaline gases. The use of these solutions adds the mechanism of chemical reaction to that of diffusion to be considered in the absorption process. Besides the possibility of chemical reaction there is the additional effect on solubilities which may give seemingly confusing results. The discussion of the liquid resistance may be divided according to the properties of the "active agent" or solute in the liquid.

1. The liquid contains an inert material which is surface-active, i.e. a wetting agent. Usually the amount of material is quite small ($< 1\%$), so that its concentration does not affect the solubility of the gas in the bulk of the liquid.

2. The liquid contains an agent which increases the solubility of the gas in the liquid. This class may be further subdivided according to the product of the agent added and the gas absorbed.

- a) The agent and/or compound formed is surface-active. An important example is the use of the various ethanolamine solutions for the absorption of CO_2 and H_2S from gases.

- b) The agent and the compound formed are not surface-active. This is a more common case where the reaction products are inorganic salts, etc.

The case of the surface-active agents which do not affect the solubility is not of commercial interest but does serve to show certain points. Inasmuch as lowering surface tension improves the spreading of the liquid, the use of these agents increases the rate of absorption (the value of J increases). However, once the packing becomes thoroughly wetted due to the liquid velocity alone, a further increase in the amount of these agents actually causes a decrease in the rate of solution (16). This evidently indicates that the agent tends to concentrate at the surface of the gas and liquid causing a high local concentration of the agent, which decreases the solubility of the gas in the liquid at the surface. This decrease in surface solubility causes the rate of absorption to drop off and also limits the capacity of the liquid. If the liquid rate is increased, the turbulence of the liquid tends to redistribute the agent, throughout the bulk of the liquid lowering the concentration of the agent near the interface. This increases the driving force for absorption by increasing the gas solubility and the rate of absorption increases again.* It is interesting to note that in this case, a great part of the drop in concentration occurs at the liquid side of the interface so that a "film" of inert material, rather than the liquid itself, forms the main resistance to absorption.

*A similar effect on the driving force is possible if the gas temperature is higher than the liquid. See Chapter 4.

A similar occurrence is noted when the agents added react with the gas that is absorbed. At the liquid side of the interface, the gas reacts with the solute agent and the compound formed decreases the solubility of the gas in the liquid. If the compound is surface active, it will tend to accumulate at the surface. In any case, the solubility of the gas is decreased and the rate of absorption falls off. The agitation of the liquid serves to keep the concentration of reactant agent more uniform and so removes the compounds from the reaction zone into the interior of the liquid. If the rate constant of reaction of the solute is greater than the diffusion constant in either of the two phases, then the depletion of the reactant agent slows down the rate of absorption rapidly and the need for the agitation of the liquid becomes of primary importance.

These explanations are not different in the overall theory from those previously put forth by Hatta (24). However, there are two basic differences in the application to design of towers and the interpretation of absorption data for systems where there is a chemical reaction.

1. The transfer of the absorbent agent through the liquid layer is by the turbulence of the liquid and not by the diffusion through a stagnant film of liquid at the interface. This again implies that the variation of KC with the liquid rate must be in accord with a turbulent diffusion mechanism, rather than a viscous type, as previously discussed.

2. The driving force used in the accepted design equations is too high ordinarily since the assumed back pressure of the solute is too low, being usually computed on the bulk concentration of reactant. This is particularly true where the rate of reaction of the dissolved gas with the reactant agent is slow compared to the rate of absorption of the gas. The use of a high value of driving force makes the calculated value of K_{CJ} lower than the actual value based on the lower driving force. Also, as the gas reacts with the solute agent, the solubility of the gas changes over the distance from the gas to the liquid.* This changes the driving force to a different function of the liquid composition so that the integral

$$\int \frac{dy}{y - Hx} \text{ becomes } \int \frac{dy}{y - [\underline{H(x)}]x} \text{ and the simple integral}$$

where H is constant becomes incorrect for this case. As a result, the values of K_{CJ} based on the usual equation, become functions of tower height and agent concentrations in direct opposition to the assumption of the equation (7, 26, 28). The correction of the driving force for chemical reactions and its effect on solubility complicates the forms of the integral tremendously. Since only meager data exist for the rates of reaction, the correction of the driving force becomes uncertain and many investigators prefer to simply use the standard equation

*There is also a subsequent change of solubility with length of tower. This causes H to become a function of height as well as x. See Chapter 4.

in spite of the errors. Insofar as applications to commercial design are concerned the errors discussed may partially cancel when the design is based again on the erroneous equations but the values of K_{CJ} calculated from such data will have no theoretical meaning.

These effects of variation of the concentration of the active material have been illustrated in many practical cases. The data of Cryder and Maloney (7) for the absorption of CO_2 in aqueous diethanolamine solutions show the effects of the conversion of the amine to the carbonate (or bicarbonate) and the normality of the amine solution. For a constant value of the liquid and gas flow rates, they found that K_{Ga} decreased with increasing conversion of the amine. This indicates that the amount of reacted amine is increasing near the surface and the unreacted amine is being depleted so as to make the driving force smaller for absorption. Thus K_{Ga} , being based on the higher driving force, is decreased. The effect of varying the initial normality of the solution confirms this. Initially, as the normality of the solution is increased from zero, K_{Ga} increases, but finally goes through a maximum due to the change of the properties of the solution (i.e. increased viscosity, density, etc.) which retard diffusion through the liquid.

The error of their design equation may be easily noted. Since K_{Ga} is a function of the liquid concentration, the value of $(K_{Ga})_x$ varies and differs from a mean value $(K_{Ga})_m$ so that, in the integrated form,

$$\int \frac{dy}{(K_{Ga})_x (y - Hx)} \neq \frac{1}{(K_{Ga})_m} \int \frac{dy}{y - Hx} . \quad \text{The value desired is}$$

$(K_{Ga})_x$ but actually a fictitious sort of a mean value is obtained. The resolution of the type of function of $(K_{Ga})_x$ is difficult or impossible from packed tower data since the values of x and y are continually varying.

One particularly important example of the erroneous interpretations made from such data is given by van Krevelin and Hoftizer (31). Based on the fact_r that Cryder and Maloney found that $(K_{Ga})_m$ varies linearly with the conversion of the amine to the bicarbonate, van Krevelin proposed that the reaction between CO_2 and the amine be a third order reaction and then proceeded to include such a theory in their correlation work. However if such reasoning is to be rigorous, the kinetics of the reaction should be based on the variation of $(K_{Ga})_x$ with the conversion. By suitable differentiation of the equation in which $(K_{Ga})_m$ is linear in x , $(K_{Ga})_x$ turns out to be a parabolic function of x , rather than linear. Certainly such a variation is incompatible with any theory of a third order reaction. It is this sort of misconception about some ideas of absorption that make a review of the theory worthwhile.

The effect of conversion and concentration of the absorbing agent was found to be the same as above in the case of the absorption of CO_2 in aqueous NaOH solutions by Tepe and Dodge (28) and Spector and Dodge (26). In both cases, $(K_{Ga})_m$

decreased with increasing conversion and went through a maximum value with increasing normality of the Sodium. . Such variations of a "constant" emphasize the inadequacy of the absorption equations for application to chemical reaction.

C. The interfacial area J

The presence of the factor J in the overall coefficient is much more important in discussing liquid resistances since liquid rates may influence its value to a very great extent although the gas rate is important. At high liquid rates, the packing of a tower may be completely wetted so that J will be approximately constant. However, at low liquid rates the value of KCJ varies widely with a change in liquid rate (12, 18). There are two possibilities of explaining the variation of KCJ in this low liquid rate range. The first is that the liquid at these rates has not completely wetted the packing and that the increase in KCJ is due to the increase in the wetted area, caused by the increased spreading of the liquid. This would infer that the degree of turbulence of the liquid remains more or less constant until the whole packing is wet. Another explanation is that at the low flow rates, the actual flow of the liquid might be slow enough that a viscous pattern exists, as well as incomplete wetting of the packing occurring. As the liquid rate is increased, then both KC and J would increase due to the spread of the liquid and an increase of the turbulence of the liquid. No definite data or method has ever been presented to show which

explanation is correct although it may be inferred from surface tension effects that the first is more likely. It is more probable that the liquid would have to be in more or less turbulent flow to overcome the forces of surface tension which keep the water from spreading over the packing. If this is the case then KC would not change appreciably and the variation of KCJ would simply be due to the variation of the amount of wetted area.

The factor J also decreases at the high liquid rates past the loading point. The "loading" or excessive buildup of liquid in the column plugs many of the passages for the gas. In spite of the fact that the packing is completely wet, the value of J decreases since the plugged holes represent a loss of active surface for absorption. ⁽¹⁸⁾ Mirus shows this effect quite well. In plotting KCJ for CO_2 in H_2O vs. liquid rate, he obtained a curve which shows KCJ to increase rapidly at low water rates, increase less rapidly as the water rates are increased and finally to show a maximum value.* This liquid rate for the maximum KCJ corresponds to the "loading" velocity as noted from pressure drop and tower hold-up data.

This complex variation of J in a packed tower emphasizes the need for data on liquid films obtained under constant conditions of surface area. Until such data are available the exact effect

*The same type of maximum value at loading is shown by the values of KCJ (for liquid films) given by Sherwood and Holloway.

of liquid rates on the liquid resistance will be unknown.

Case 3. General Case - No one resistance controls

The previous two classifications have been made in order to obtain more knowledge about the individual resistances from the total resistance. Since only the total resistance may be experimentally measured it is important to realize which of the two resistances may be of such magnitude so as to make the other negligible in comparison. The probable conditions have been mentioned whereby one resistance may control but, as has been also shown, both resistances may become important due to the range of operating conditions which may be used. This is especially true in experimental work where the range of flow rates may be greater than in commercial practice.

When both resistances are appreciable, then the variation of KCJ with flow rates becomes much different from that of either of the single resistances. The problem of recognizing this case and predicting the absorption coefficients may best be considered by considering the relation of the overall coefficient KCJ to the single resistances.

$$\frac{1}{KCJ} = \frac{1}{k_{GJ}} + \frac{1}{k_{LJ}} \quad (16)$$

the value of J now being inserted. In considering how KCJ should vary with flow rates, the forms of the expressions for the individual coefficients should be restated.

For k_G : $k_G = \alpha_1 G^{0.8}$, the value of 0.8 being taken from the wetted wall data as well as for heat transfer.

For k_L : $k_L = \alpha_2 V^n$, where n has been presumed to be 0.80 by some investigators because of the same exponent on G for k_G . However, as has been discussed, this assumption is false and since no conclusive data for liquid films exist, the value of n is uncertain. Also, if a chemical reaction occurs in the liquid n may be different from that for the pure liquid.

For J : $J = J(G, V)$ where J is an unknown function being especially complex for V as discussed. Some absorption data indicate that $J = \alpha_3 G^m f(V)$ where m ranges from 0-0.25 depending on the packing. For the present, the general functional notation will be retained.

Using these notations for the coefficients, the form of KCJ may be expressed as:

$$\frac{1}{KCJ} = \frac{1}{J(G, V)} \left[\frac{1}{\alpha_1 G^{0.8}} + \frac{1}{\alpha_2 V^n} \right]$$

or

$$KCJ = J \left[\frac{\alpha_1 \alpha_2 G^{0.8} V^n}{\alpha_1 G^{0.8} + \alpha_2 V^n} \right] \quad (17)$$

It is easily seen that if $\alpha_1 \rightarrow \infty$ the liquid resistance controls and if $\alpha_2 \rightarrow \infty$ the gas resistance controls and KCJ will vary as JV^n in the first case and $JG^{0.8}$ in the latter. However, if α_1 and α_2 are of the same order of magnitude, the variation of KCJ with V and G will be a complicated one. One special form

has tended to predominate in the literature because of its simplicity of form. It is:

$$KCJ = aG^aV^b \quad (18)$$

and infers that a plot of KCJ vs V or G on log-log paper is a straight line. This is, of course, inconsistent with the form of equation (17) but equation (18) may hold over a limited range of the variable flow rates encountered. However, if the equation (18) represents the data it must follow that $a < 0.8$ and $b < n$. In general, then, if equation (18) fits the data and the above conditions hold, both resistances will be appreciable. Since the value of n is not known definitely, this criterion is better applied to the effect of gas rate than the liquid rate.

Examples of these low exponents are frequent. Tepe and Dodge (28) found that $a = 0$ and $b = 0.28$ for their absorption data (CO_2 in NaOH solutions) showing the absence of a gas resistance and a low effect of liquid rate. This indicates the packing itself has a high influence on the degree of turbulence of each phase so that the main delay in absorption is the rate of chemical reaction.

Spector and Dodge (26) for the same system but different packing found $a = 0.35$ or 0.15 (depending on G) and $b = 0.20$. The value $a = 0.35$ was for the lower values of G, decreasing to 0.15 at higher values of G. As shown by their graphs, the data on log-log plots do not fall on two straight lines but rather

follow a smooth curve which may be approximated over the range by the two straight lines. This indicates the presence of the chemical reaction time being appreciable so that diffusion is not the limiting factor.

A more quantitative method for determining the relative magnitudes of each resistance is similar to that for heat transfer (24). Rather than deal with the overall conductance, the overall resistance, $(\frac{1}{KCJ})$, is used. From equation (17) it is seen that if J is constant, a plot of $\frac{1}{KCJ}$ vs $\frac{1}{G^{0.8}}$ or $\frac{1}{V^n}$ should be a straight line if one of the flow rates is held constant. Thus a plot of $\frac{1}{KCJ}$ vs $\frac{1}{G^{0.8}}$ would show an intercept equal to the liquid resistance and a slope equal to $\frac{1}{\alpha_1}$. The similar plot for the liquid rate is more complicated since no value of n is known. The method of choosing values of n to yield a straight line rectification of data is tedious and the usual absorption data are inaccurate enough so that a range of values of n would probably result. The method usually used for the liquid rate is to calculate the liquid resistance $(= \frac{1}{KCJ} - \frac{1}{\alpha_1 G^{0.8}})$ after the gas resistance has been evaluated and then determine α_2 and n from these values. However, again the presence of any inaccurate data makes suitable choices of α_2 and n difficult. Othmer and Schiebel (20) using this latter method for their data on the absorption of acetone in water found a value of n of 0.95.

Such empirical determination of exponents must be done cautiously. Most absorption data is simply not accurate enough to yield accurate resolution of individual resistances by this method. Hence any error in the value of α_1 , from the rectification of the data, will lead to large errors in n and α_2 , particularly since if J varies with liquid rate, the value of n may be of almost any magnitude.

CHAPTER 3

KINETICS OF ABSORPTIONBasic Forms of Driving Force

The previous discussions of overall coefficients have been based on the use of equations where the driving force was taken as a difference of appropriate concentrations. Insofar as diffusion through quiescent gases are concerned the driving force is a difference in concentration of the diffusing component. The driving force for the diffusion of one gas through a stagnant layer of another however was shown to be a difference of the logarithms of the concentration of the stagnant gas. For a dilute solute-gas mixture, the mean inert gas concentration is close to unity so that it does not vary appreciably while the solute is being absorbed. Under these conditions the driving force may be shown to closely approximate that of the difference of the concentration of the solute gas, at least in form if not numerically.

When the rate of mass transfer between phases in an agitated system is considered the same type of driving force is retained for simplicity and the theoretical acceptance is based on the idea of the presence of viscous films. However, the experimental determination of the kinetics of the absorption has received little attention. In most cases the assumption has been that the absorption is a first order process and the

kinetic data has only been used to evaluate the specific absorption coefficient. In some cases the data were obtained in such a way as to make only approximate agreement in the absorption coefficients.

In describing the rate of absorption of the gas in terms of concentrations there are two types of driving forces which may be used. The rate of absorption is given as the rate of solution of gas in the liquid minus the rate of dissolution. The first part is a function of the gas concentration y and the second is a function of the liquid concentration x . Algebraically stated:

$$N_A = f(y) - g(x) \quad (19)$$

where f and g represent the appropriate functions. If the liquid and gas are in equilibrium then $N_A = 0$ and $y = Hx$ assuming Henry's law to hold. Then equation (19) must be of such form that if we replace x by y/H , $N_A = 0$. This may be done by equating $g(x) = f(Hx)$ so that equation (19) may be rewritten as:

$$N_A = f(y) - f(Hx) \quad (20)$$

An alternate possible form is:

$$N_A = f(y - Hx) \quad \text{where} \quad f(0) = 0 \quad (21)$$

which is in accord with equilibrium conditions. An example of the driving force of equation (20) is the use of the logarithm of the inert concentrations for diffusion through stagnant films while equation (21) is the more usual form $f(x) = x$ or

$f(y - Hx) = y - Hx$. However, it would be possible to use $(y - Hx)^n$ or $y^n - (Hx)^n$ where $n > 1$. Any value of n other than one complicates the integration of the differential equation so that if the value of one may be used to represent the kinetic data accurately enough, it is quite convenient to accept that value in preference to any other.

Verification of Driving Force

The data of Guyer and Pfister (14) are of the correct form for kinetic analysis. They bubbled air with various CO_2 contents through columns of water and measured the CO_2 absorbed as a function of the height of the water. In attempting to rectify their data and justify a mechanism of absorption they treated the integration of the differential equation in an entirely erroneous manner. The error made was the assumption that the rate of solution of CO_2 into the water was independent of the concentration of the CO_2 in the bubble. Hence the equations developed here are different from those in the original article.

To consider the absorption of a solute from a bubble with an inert gas in it, we define the following variables, which are slightly different from the definitions used elsewhere:

G = total amount of gas in the bubble, CO_2 and inert; cm^3

y = mol fraction of CO_2 in the bubble;

K = specific rate of solution of CO_2 in water; $\frac{\text{cm}^3 \text{ CO}_2 / \text{sec}}{(\text{cm}^2) (\Delta y \text{ driving force})}$

S = velocity of the bubble; cm/sec

h = height of the liquid; cm.

If the bubbles are in contact with pure water and the bubbles are assumed to be spherical (so that the area of the bubble is $4\pi (\frac{3}{4\pi})^{2/3} G^{2/3}$); then the basic equation for the absorption may be written as:

$$-\frac{dG}{dh} = \frac{KC G^{2/3}}{S} y \quad (22)$$

where

$$C = 4\pi \left(\frac{3}{4\pi}\right)^{2/3} = (36\pi)^{1/3}.$$

Since the original data is expressed on a volumetric basis, it is more convenient to express y as a function of G and then integrate. If we denote the original gas volume and concentrations as G_0 and y_0 respectively, we have:

$$G = \frac{G_0(1 - y_0)}{1 - y} \quad \text{or} \quad y = \frac{G - G_0(1 - y_0)}{G} \quad (23)$$

Substituting in the above equation, and rearranging:

$$\int_{G_0}^G \frac{G^{1/3} dG}{G - G_0(1 - y_0)} = - \frac{KC}{S} \int_{h_0}^h dh$$

the lower limit of h_0 being inserted rather than zero since some absorption may occur at the tip of the nozzle while the bubble is forming. The value of h_0 represents the height of column necessary to absorb the same amount of gas as is absorbed at the tip of the nozzle.

In order to integrate the expression, the following substitutions are made:

$$z^3 = G, \quad z_0^3 = G_0, \quad a^3 = G_0(1 - y_0), \quad dG = 3z^2 dz$$

and the integrals become:

$$-\frac{KC}{S}(h - h_0) = \int_{z_0}^z \frac{3z^2 dz}{z^3 - a^3} = 3 \int_{z_0}^z \left[1 + \frac{a^3}{z^3 - a^3} \right] dz \quad (24)$$

The integration may be carried out by means of partial fractions or may be found in any table of integrals. The final result, after inserting the limits of integration, is:

$$\frac{KC}{S}(h - h_0) = f(z_0) - f(z) \quad (25)$$

where

$$f(z) = 3z + \frac{a}{2} \ln \frac{(z - a)^3}{z^3 - a^3} + \sqrt{3} a \tan^{-1} \frac{2z + a}{\sqrt{3}a}$$

Thus, if the amount of absorption is known as a function of height, a plot of $f(z_0) - f(z)$ vs height may be made and should be linear. If h_0 is zero, i.e. there is no absorption at the tip of the nozzle, then the lines should go through the origin of such a plot. Four sets of data were taken from the article of Güyer and Pfister. In all cases the original bubble size was 0.0266 cm³. The values tabulated below are:

1. y_0 , the original concentration of CO₂; mol fraction
2. h , height of column of water; cm
3. V , the Volume of CO₂ absorbed; cm³/bubble
4. $f(z_0) - f(z)$, as calculated from equation (25).
5. B , the amount of CO₂ in the bubble.

y_0	h	V	$f(z_0) - f(z)$	B
0.880	15.5	0.00875	0.1490	
	18.0	0.0095	.1629	
	23.0	.0115	.2082	
	28.0	.0133	.2522	
	35.5	.01525	.3102	
0.767	18.0	0.0073	0.1440	
	23.0	.0092	.1911	
	28.0	.0108	.2363	
	34.0	.0122	.2801	
0.513	10.5	0.0034	0.0940	0.0103
	15.5	.00425	.1199	.00945
	18.0	.0050	.1472	.0087
	23.5	.0059	.1808	.0078
	28.5	.0066	.2102	.0071
	36.5	.0075	.2501	.0062
0.423	9.5	0.0024	0.0789	0.0089
	15.5	.0033	.1123	.0080
	23.5	.0044	.1576	.0069
	28.3	.0049	.1942	.0064
	34.0	.00595	.2368	.0053

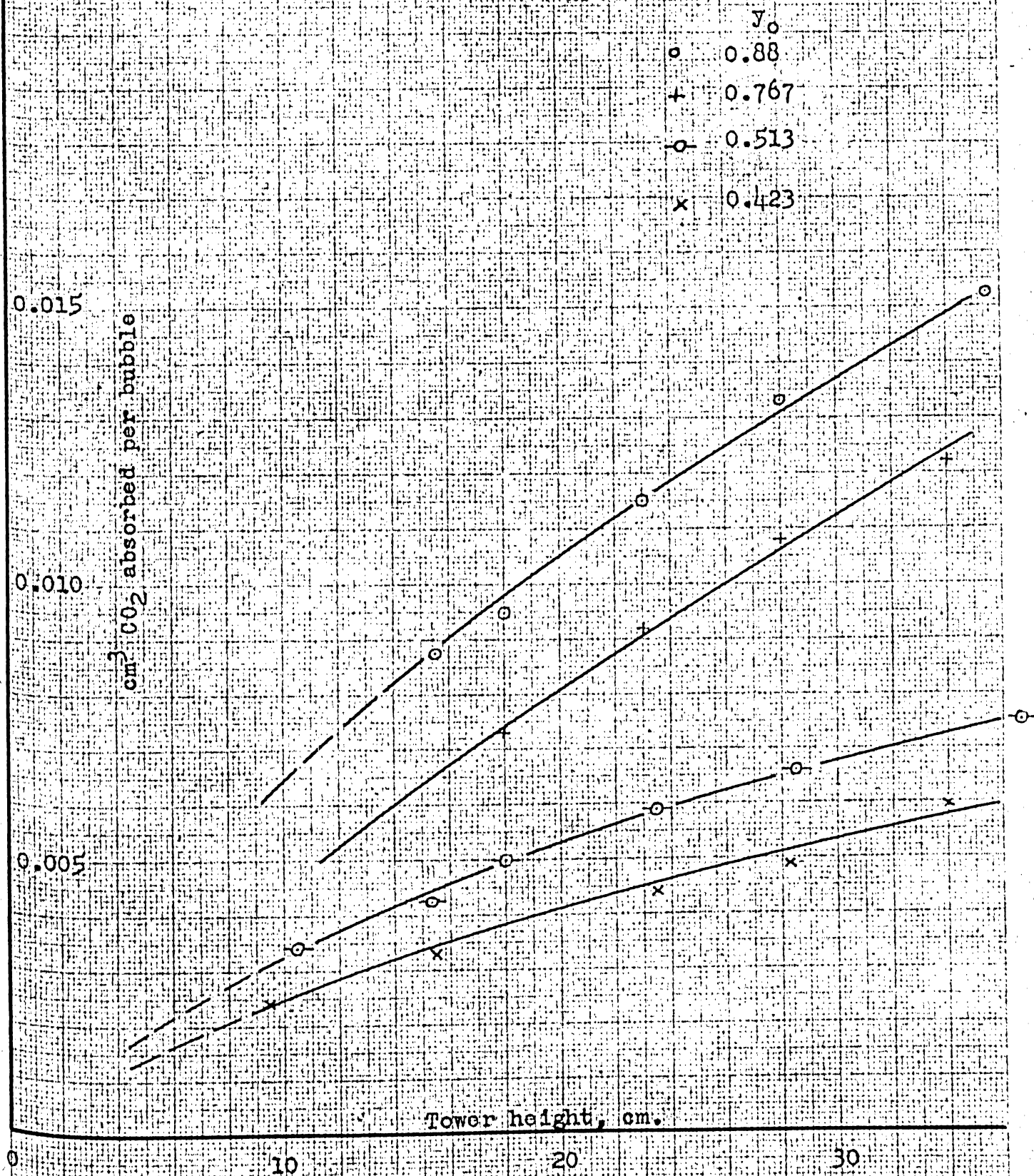
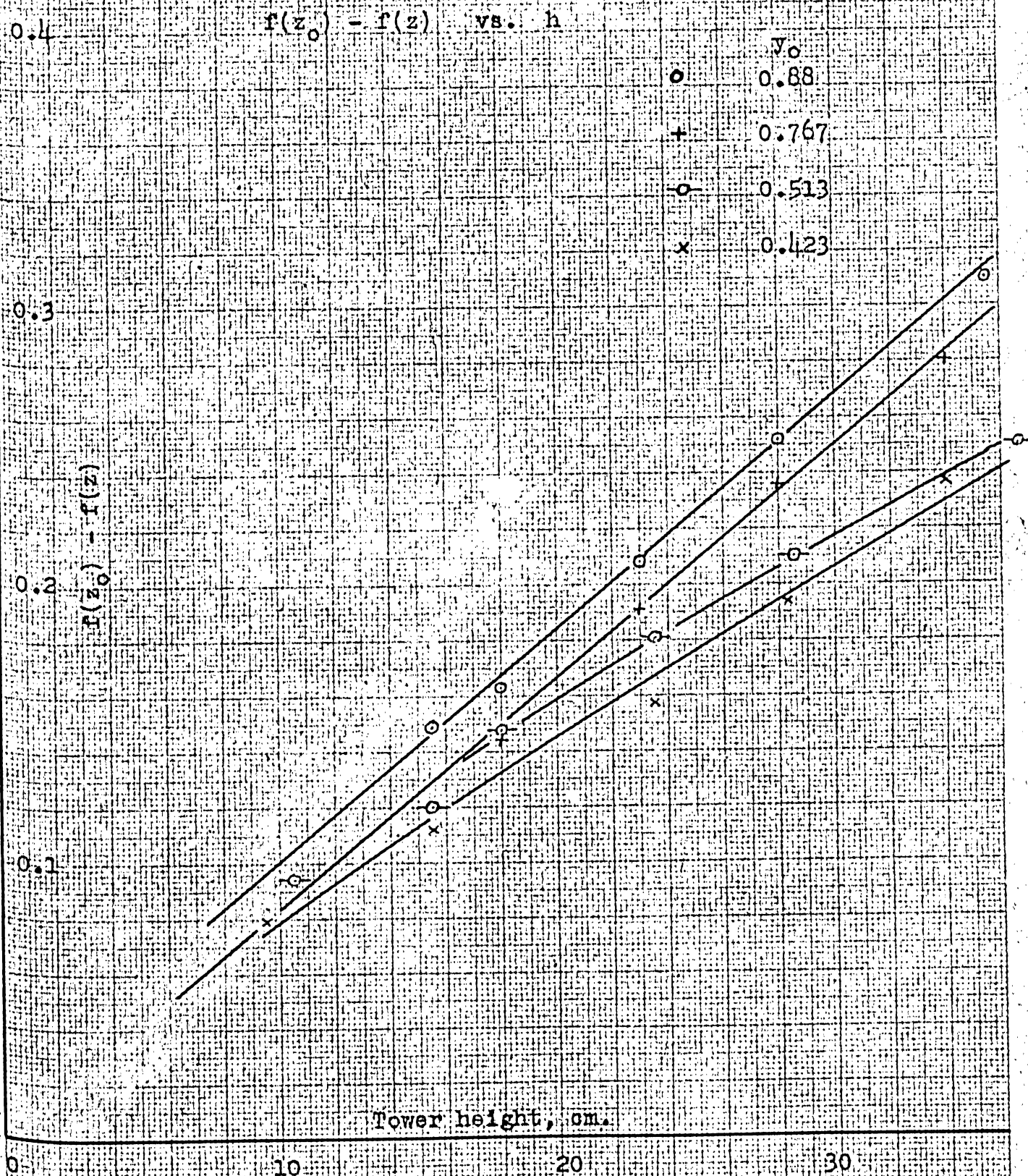
Fig. 2 Volume of CO_2 absorbed vs. Tower height

Fig. 3 Rectification of Absorption Equations
for Bubbles



The graph of V vs h is shown in figure 2. As such, its only value is to show which points may be in error. The rectified data is plotted in figure 3 and several conclusions may be drawn from it.

Equation (25) fits the data for the bubbles having high initial concentrations of CO_2 . In both cases the slopes of the lines are equal showing that KC/S is the same for each run. Thus the use of the average composition of the bubble for the driving force is correct for these high concentrations of solute.

The data for lower concentrations do not follow the simple kinetics of equation (25) since the rectified data shows a curve rather than a straight line. This deviation implies that the driving force used is incorrect. Moreover the deviation becomes larger as time continues and suggests that diffusion in the bubble is important. A more accurate picture of the absorption is that initially, the driving force is the concentration at the edge of the bubble, y_0 . As the CO_2 is absorbed the boundary concentration is decreased, the CO_2 slowly diffuses from the interior of the bubble to the edge. Thus the actual driving force is y at the edge rather than the "average" concentration in the bubble. Since a low value of y corresponds to a high value of $f(z_0) - f(z)$ the use of a lower

value for the driving force would tend to raise the curve to more nearly conform to a straight line. Another interesting point is that at the lower values of h , where diffusion has not taken much effect, the points tend to lie on the same straight line as for the higher concentrations. A more quantitative evaluation of the effects of diffusion may be made as follows.

Diffusion in Bubbles

In considering diffusion in bubbles, it is most convenient to solve the general differential equation for diffusion. In this case only one coordinate is needed for spherical notation and that is the value of r , a radial displacement from the center of the bubble, since the composition is uniform from the aspect of angular variations. The differential equation becomes: (19)

$$\frac{\partial y}{\partial \theta} = D \left(\frac{\partial^2 y}{\partial r^2} + \frac{2}{r} \frac{\partial y}{\partial r} \right) \quad (26)$$

with the following boundary conditions:

1. At $r = r_0$ $\frac{\partial y}{\partial r} = -Ky$, $K = \frac{(KC)}{D}$
2. At $\theta = 0$ $y = y_0$

Note that boundary condition (1) implies that the rate of solution of the solute at the boundary of the bubble follows a first order reaction. The solution to this equation is given by Barrer (19) and the analogous heat transfer solution is presented by Carslaw (20). The solution which expresses point concentrations y as a function of r and θ is:

$$\frac{y}{y_0} = \frac{2K}{r} \sum_{n=1}^{\infty} \frac{r_0^2 a_n^2 + (r_0 K - 1)^2}{r_0^2 a_n^2 + r_0 K(r_0 K - 1)} \frac{\sin a_n r_0 \sin a_n r \varepsilon^{-D a_n^2 \theta}}{a_n^2} \quad (27)$$

where a_n is the eigenvalue of the equation and is the solution to the following transcendental equation:

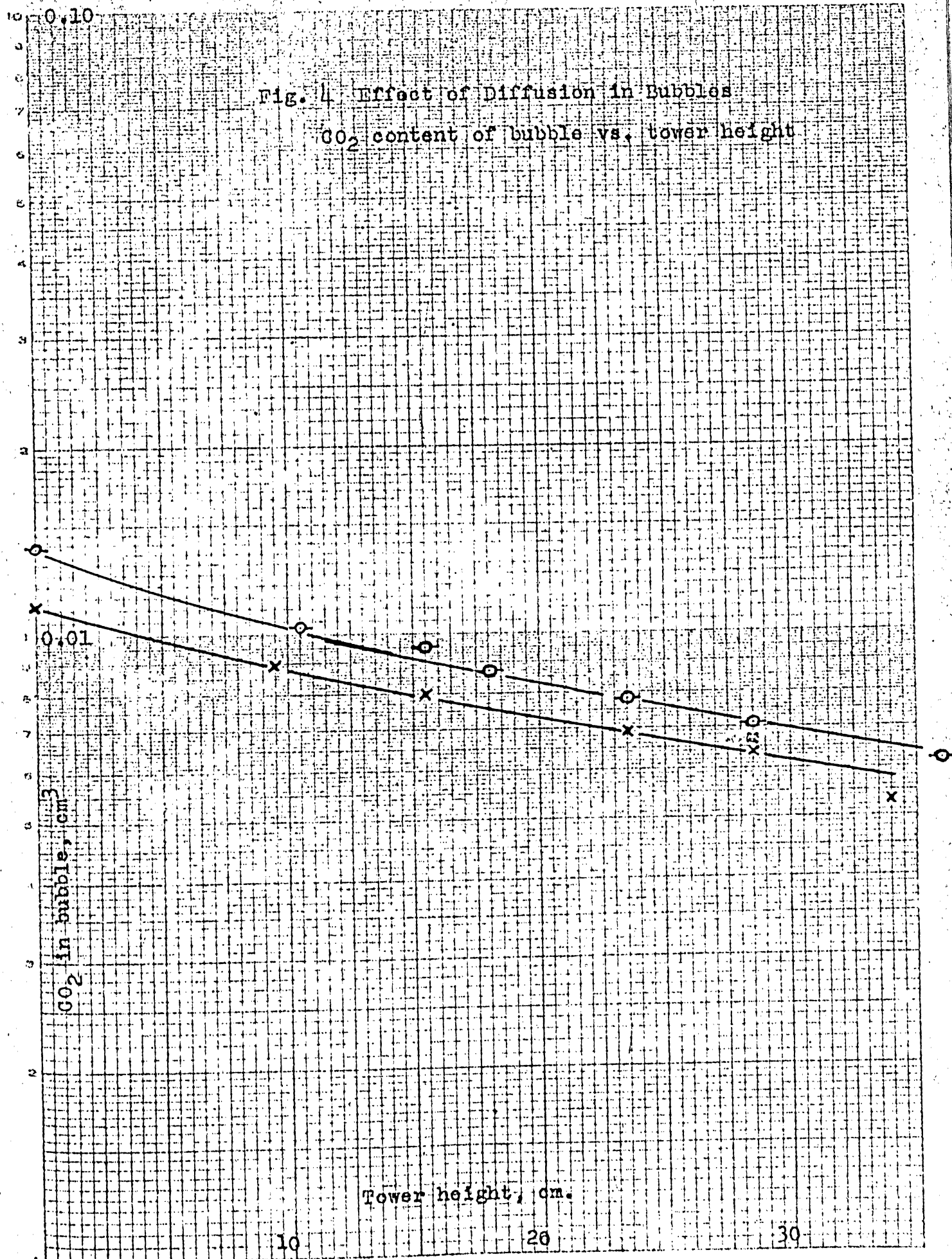
$$\frac{1}{a_n r_0} \tan a_n r_0 = - \frac{1}{r_0 K - 1} \quad (28)$$

The use of the above equation for testing data is impossible since no means are available to measure concentrations at a point. This difficulty may be overcome by using the total amount of CO_2 (or average concentration) in the bubble rather than point concentrations. Denoting the total solute present as B and the initial solute as B_0 , then:

$$\begin{aligned} B &= \int_V y dV = \int_0^r y (4\pi r^2) dr \\ &= \frac{6B_0 K^2}{r_0^2} \sum_{n=1}^{\infty} \frac{r_0^2 a_n^2 + (r_0 K - 1)^2}{r_0^2 a_n^2 + r_0 K(r_0 K - 1)} \frac{\sin^2 a_n r_0}{a_n^4} \varepsilon^{-D a_n^2 \theta} \quad (29) \end{aligned}$$

If a plot of $\log B$ vs θ (or h) is made, as θ becomes large, only the first term of the series becomes of consequence so that a straight line of slope $(-D a_1^2)$ should result. At low values of θ the plot should be a curve. Figure 4 shows the semi-log plot of B vs h for y_0 's of 0.513 and 0.423. It is easily seen for $h > 10$, both lines become straight and parallel which indicates the value of $\frac{D a_1^2}{S}$ is constant. This value should be constant since D is a function of the system only and a_1 and S

Fig. 4 Effect of Diffusion in Bubbles

CO₂ content of bubble vs. tower height

are determined by the bubble size alone.

Insofar as the kinetics of the absorption process is concerned, it is seen that for $h > 10$, the presence of the straight line indicates that the rate of solution is proportional to the average concentration in the bubble. The driving force would be the average concentration if the line went straight back to $h = 0$ but in the neighborhood of $h = 0$ the diffusion of solute has not reached its maximum value and the concentration of solute near the interface is decreasing rapidly. As time progresses diffusion of the solute begins towards the interface so as to maintain a supply of solute.

The common form of the kinetic equation may easily be derived from the above equations in accord with the statements of the previous paragraph. The rate of solution of the solute is $-\frac{dB}{d\theta}$ since $\frac{dB}{d\theta}$ itself is negative. As time increases only the first term of the series is important so that:

$$-\frac{dB}{d\theta} = \left[\frac{6B_0K r_0^2 \alpha_1^2 + (r_0K - 1)^2}{r_0^2 r_0^2 \alpha_1^2 + r_0K(r_0K - 1)} \frac{\sin^2 \alpha_1 r_0}{\alpha_1^4} e^{-Da_1^2 \theta} \right] Da_1^2$$

$$= Da_1^2 B \quad (30)$$

Thus the diffusion equation reduces in form to the conventional type of overall first order reaction equations. The only difference is that equation (30) does not hold near $\theta = 0$ if diffusion is important.

Application to Packed Towers

From the preceding discussion it is seen that diffusion in gas streams will still lead approximately to a simple type of driving force for absorption equations provided that the range of contact time of the gas and liquid is fairly large. In applying these equations to packed towers several points may be made:

1. A knowledge of the specific rate of solution constant K must be known, as well as the size of the tube channel.
2. If the flow of gas in any channel is turbulent then the value of D , the actual diffusivity, must be replaced by another constant D' , the "eddy diffusivity" which is a function of the turbulence of the gas stream. Very little quantitative data are available for this term.
3. The overall contact time of the gas with the liquid must be known. This necessitates the knowledge of length of the gas passages.

Inasmuch as all three items are difficult or impossible to obtain for packed towers, several conditions may be noted that simplify the form of the driving force to that of a difference of the average concentration on the gas phase and the liquid phase. In the turbulent gas streams, the turbulent diffusion is so rapid compared to viscous diffusion that the concentration in the bulk of the gas stream is very close to being uniform. Hence the limiting diffusion is that across the

viscous film at the interface. Under these conditions, then, the only unknown to be determined (with the exception of the interfacial area) is the specific rate constant which may be a function of the liquid resistance and gas resistance. However, as far as the appropriate driving force is concerned, we may conclude that the simple difference of concentrations will suffice. The subsequent work will show that the appropriate value of a mean concentration is quite important but this is the only change made in the driving force, and is a change only in value, not in the form of the function.

CHAPTER 4

ABSORPTION EQUATIONS

The application of the equations for the rate of absorption of gases to the design of commercial equipment has been the main goal of most experimental work. The study of the performance of various types of packings continues to fill the literature and the effects of flow rates on tower performance is still being evaluated. The equations which have been used to describe the conditions in packed towers have already been given and their derivations shown. The factor used to characterize the packing and overall resistance to absorption KC_J (or its other forms) has been discussed as to its meaning, variation and component parts. However, in the discussion of KC_J , it has also been noted that the effect of flow rates on J is considerable and in some cases the explanation for variations in KC_J indicate that the assumptions made in order to integrate the differential equations have been violated or ignored. In order to better describe the conditions in a tower by a differential equation it is easiest to examine the differential equation and each assumption that arises in the solution of the equation. A clear statement of the method of solution of the problem and all assumptions made at any point will form a basis for further work and discussion.

Inasmuch as concentrations of the liquid and gas phases vary over the volume of the tower, any differential equation set up to express the rate of absorption must be applied to each portion of gas (or liquid) and then integrated over the entire volume of the tower. The most convenient manner is to locate an arbitrary horizontal plane in the tower and evaluate the total rate of reaction over that plane. Then the rate of reaction may be integrated over the length of the tower to include the total volume. For any one passage of gas, the rate of absorption at any point may be expressed as

$$-dG_j = [KCJA(y - Hx)]_j dh$$

where j refers to one particular gas stream. The first assumption made in deriving the absorption equations is that KCJ , y and x do not vary over a horizontal plane in a column. This assumption is equivalent to an integration over the entire horizontal plane. It implies, at the same time, that the gas passages are of the same size and that both the liquid and gas flow rates are uniformly distributed over the transverse area of the column.

In order to integrate the expression over the length of the tower it is important to realize just which terms are functions of concentrations, height of tower (explicitly) and those which are constant over the entire tower. Thus KC , y , x and H are functions of the concentrations of the two fluid phases while J would be a function of tower height. Insofar as x is

related to y by a material balance on the solute, the distribution of the liquid and gas phases becomes of importance with height. Again, the values of KCJ and H are assumed constant for simplicity of integration and the material balance over any one end of the tower gives x as a function of y .

Under these conditions the equation to be evaluated is:

$$\int_{y_1}^{y_2} \frac{dG}{y - Hx} = \int_0^L KCJA \, dh$$

The integration of the equation yields either the familiar log-mean design equation or the Tour-Garber form, previously described. The result obtained depends on the method of relating G and x to y , i.e. the units chosen. If y is expressed as mass of solute per unit mass of inert, then the log mean equation is obtained. Using y as mol or weight fraction, the Tour-Garber form is obtained.

The validity of either of the equations and the values of any term computed from such equations are determined by the soundness of the assumptions made in deriving the equations. In analyzing experimental absorption data the design equation is of no value if any of the assumptions are not valid for the experimental conditions. As a result, we may best discuss each of the assumptions made in the integration according to:

1. The conditions under which the assumptions fail to hold.

2. Specific examples (from the literature, if available) which show the effects of incorrect use of the absorption equations.

3. The correction of the failure of the assumption, i.e. making the assumption valid by modification of experimental technique or indication of the method of modifying the absorption equation.

Assumptions Made for Integration

The necessary (or simple) assumptions are those tabulated by Garber and have been already given. However, it is now in order to discuss each one in accord with the above outline. For convenience they will be discussed in the same order as listed before.

I. The temperature and pressure throughout the tower are uniform and constant.

The assumption of constant pressure is incorrect for packed towers since the friction between the gas and liquid phases causes a pressure drop. The main effect of pressure is on the solubility of the solute gas in the liquid. Thus, the value of H , as defined by $y^* = Hx$, is inversely proportional to P , the total pressure. Inasmuch as the pressure drop is of the order 0-5" H_2O , the relative variation in Hx is only $\frac{5 \times 100}{33.9 \times 12}$ or 1.2% at the most. In the cases where Hx is small compared to y , the error is of no consequence. Where $y - Hx$ is small, so that the related error of Hx to $y - Hx$ may be of

high consequence, the value of H should be corrected to the appropriate value. However, as will be seen later, the error in the assumption of constant pressure will be small as compared to others.

The subject of temperature is much more important in tower design. Temperature affects the rate of solution by changing the solubility of the solute gas in the liquid as well as influencing the properties of the gas and liquid phases. In general, the slight changes in gas temperature, say, of the order $5-15^{\circ}\text{F}$ do not change the turbulence of the gas enough to be noticeable. Liquids, on the other hand, are much more affected by changes in temperature, due primarily to the changes in viscosity. However, in tower operation the changes in water temperature are held to a minimum.

Changes in water temperature occur due to two factors: the heat of solution of the solute gas and the humidification of the gas phase (which tends to cool the water). The heats of solution are important commercially where the liquids are used to absorb large amounts of solute, e.g. making concentrated NH_4OH or HCl . In these cases, internal cooling is necessary for obtaining these high degrees of saturation. As far as experimental procedures are concerned, this heat effect is kept small by keeping the amount of solute low enough so that no heating effect is noticeable.

Humidification of the air often occurs, especially in experimental work where compressed air is used for the carrier. The compressed air is usually fairly dry and upon being contacted with water becomes humidified. This evaporation tends to cool the water but as may be shown, this temperature drop is usually quite low. (The humidification of the air also affects the material balances, see assumption V). The maximum temperature drop which occurs may be calculated using a high value of gas rate to water rate.

Consider the gas flow rate to be 800 cfm at 32.00⁽¹²⁾ "Hg and 80°F, as used approximately by Greenberg, and the water rate to be 35 ft.³/hr., both of these rates being the extreme values. In terms of mass flow rates:

$$G = \frac{800}{359} \times \frac{32.00}{29.92} \times \frac{492}{540} \times 29 = 63.0 \text{ lbs./hr.}$$

$$V = 35 \times 62.4 = 2180 \text{ lbs./hr.}$$

The air came from compressors operating at 60 psia so that the gas will be saturated at 60 psia and 80°F. This value of the humidity is $\frac{0.5067}{60 - .8067} \times \frac{18}{29} = 0.00528 \frac{\text{lbs. H}_2\text{O}}{\text{lb. dry air}}$. The saturation value at 32.00" Hg and 68°F (conditions at the top of the tower) is $\frac{0.3388}{15.70 - .3388} \times \frac{18}{29} = 0.01370 \frac{\text{lbs. H}_2\text{O}}{\text{lb. dry air}}$. Assuming* the outlet air to be at 68°F, the change of water temperature may be calculated by a heat balance.

*The exact value depends on the heat transfer coefficient and interfacial area of the column, as well as the relative gas and liquid rates. As may be seen, a small error in gas temperature does not affect the calculations to a great extent.

$$\begin{aligned}
 \Delta t &= \frac{63.0}{2180} [1054(.01370 - .00528) - 0.24(80 - 68)] \\
 &= \frac{63.0}{2180} (8.87 - 2.88) \\
 &= 0.17^{\circ}\text{F}
 \end{aligned}$$

Such calculations, based on adiabatic operation of the tower indicate that the change in water temperature is quite negligible. Nonetheless, as in the case of Koch (16), variations in the water temperature from a rise of one degree to a decrease of two degrees ($^{\circ}\text{F}$) are reported. Inasmuch as the outlet liquid was very nearly in equilibrium with the inlet gas, a small variation in temperature (affecting the choice of Henry's constant) can sharply change the value of the driving force used in the absorption equation. In some examples of his data, if the inlet temperature is used for the computation of the driving force at the bottom of the tower, such a driving force becomes negative, seemingly indicating that stripping of the liquid rather than absorption from the gas is occurring. Similar cases of these negative driving forces were obtained at the University of Cincinnati but were not published^{*}.

There remains a possibility of another type of temperature effect which has never been rigorously investigated in the literature. This is the problem of the temperature of the surface of the water, i.e. the layers of water adjacent to the water-gas

^{*}Professors R. S. Tour and H. J. Garber - personal communications.

interface. Whereas the above calculation showed that the bulk temperature of the water remained constant, no values for the surface temperature were given.

The temperature of the surface of the liquid may lie somewhere between that of the gas and liquid temperatures, or below both temperatures. The exact value of surface temperatures depends on the rate of humidification of the air and the relative heat resistances of the gas and liquid phases. If the surface temperature is appreciably different from the bulk temperature, then the solubility of the solute gas changes in the vicinity of the interface. This has the same effect as described under liquid resistance with "active" agents added.

Consider the absorption of a gas where the liquid resistance controls. The concentration of the solute in the gas is uniform at y_1 . The concentration of the solute in the liquid surface is $x_1 (= y_1/H)$. As the temperature of the surface increases above that of the bulk x_1 decreases so that $x_1 - x$ decreases, thus cutting down the rate of absorption (see equation 4). Under these conditions, the maximum concentration attainable in the liquid is that at the interface and not that in equilibrium with the gas at the bulk temperature. Hence, the overall capacity of the liquid is lowered.

On the other hand consider that the temperature of the gas is lower than that of the liquid. In this case the surface temperature of the liquid will be lower than the bulk temperature and the concentration of the solute at the surface will be greater than the saturation value of the liquid based on the bulk

temperature. This would infer that value of $(x_1 - x)$ increases due to the increase of x_1 . However, in this case the surface is supersaturated with respect to the bulk of the liquid so that as soon as the temperature near the surface reaches the bulk temperature the value of x at that point will be y_1/H , the value of H being taken at the bulk temperature. Hence, the maximum resistance of the path to absorption still lies in the bulk of the liquid rather than at the surface.

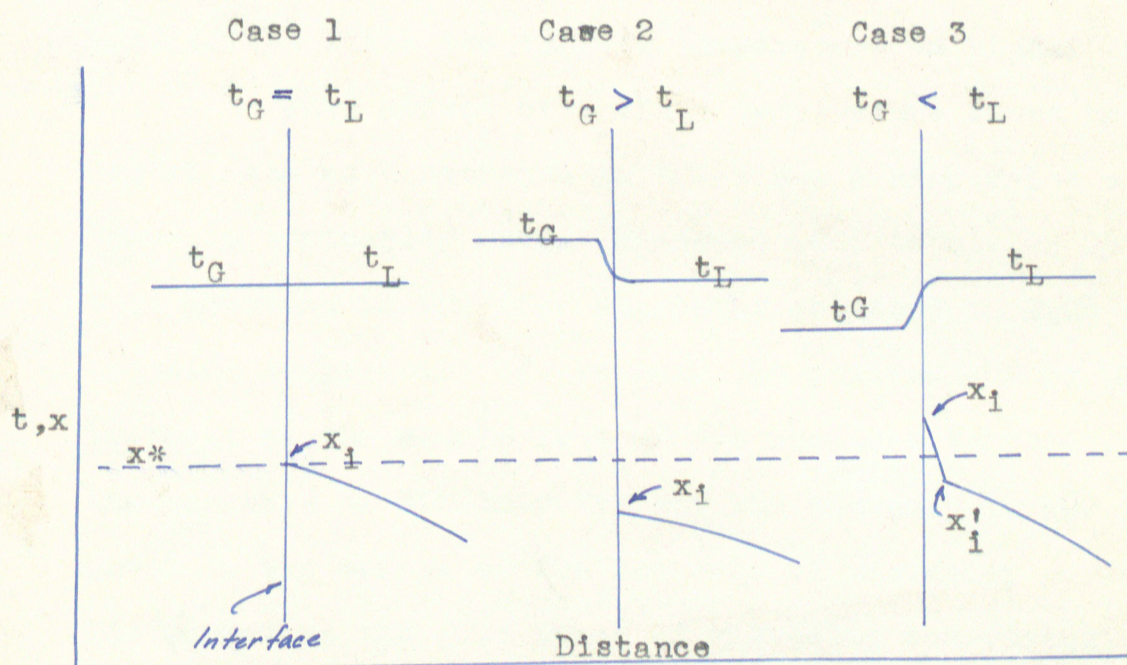


Fig. 5 Effect of Surface Temperatures on Absorption

Figure 5 shows graphically the variation of composition of the liquid with distance from the interface. Where $t_G = t_L$ (Case 1), the curve of x vs distance is of the form previously described. Where $t_G > t_L$, the value of x_1 is lower than in Case 1 and so the rate of absorption should be lower. When $t_G < t_L$, the value of x should correspond approximately to saturation at the given value of t_L . Hence, as soon as the temperature reaches the bulk value t_L , the composition of the liquid may be x_1' which is the same as x_1 for Case 1. Since the distance from the surface to the point where $t = t_L$, is very small, Case 3 tends to approximate Case 1. However, it is important to note that the slight change in temperature has the most effect where the surface temperature is higher than t_L .

This effect of surface temperature shows up in experimental data as a decrease in KCJ since a high value of driving force is ordinarily used. Sherwood (24) tabulates data showing this decrease in KCJ (for NH_3 being absorbed in H_2O) with increasing temperature of the gas. As pointed out by him, KCJ should increase as the square root of the absolute temperature (due to the increase of diffusivity) but the decrease in KCJ is attributed to the effect of the increase of viscosity of the gas. Since KCJ varies as the -0.4 power of viscosity and viscosity of a gas changes only slightly with moderate changes of temperature, such an explanation seems weak. Unfortunately such temperature effects were studied on soluble gas-liquid systems where the surface solubility

has a small effect. It would be expected that much larger variations would be noted for insoluble gases.

These temperature variations are undesirable because of their complex effects. Hence the simplest procedure is to precondition the inlet gas to the saturation humidity and temperature of the liquid. In this case all temperatures would remain constant.

II. The flow rates per unit area and composition of the two fluids at any area on a given plane are uniform and remain constant during the period of operation.

Outside of the obvious implication of steady state operation, this assumption is necessary in order to integrate the absorption equation over the horizontal plane, i.e. the use of the gas driving force as y and the liquid driving force as x , both y and x being the "average" or bulk concentrations of the gas and liquid respectively. However, unless special precautions are taken, this assumption fails to hold.

Lerman and Tour (30) showed that the liquid distribution in a packed tower followed a binomial expression which could be reduced to the form of a probability integral for special cases. In brief, the liquid tends to move towards the walls of the tower and stay there, following the walls to the bottom of the tower where it remixes with the water which stayed on the packing. This accumulation of liquid may affect the total wetted area J and also the value of x as used in the absorption

equation. The effect on J will be noted later under assumption III.

The value of x used in the absorption equation is always taken as the average value, i.e. the amount of solute absorbed divided by the total flow rate of the liquid. It is calculated by a material balance (see equation 11) which assumes the entire amount of liquid flow to be uniformly mixed and totally present on the packing. If there is an uneven distribution of liquid over a horizontal portion of the tower, the concentration of solute will vary also. Hence the use of an "average" x in the absorption equation may be meaningless. (This is similar to the channeling of the gas which will be described later).

A far more important effect of the liquid spreading is the variation of the amount of liquid on the packing with height. As the liquid goes down the tower, any liquid that happens to come in contact with the walls of the tower tends to remain there. This results in a depletion of water on the packing and makes the material balance as written (equation 11) incorrect. For a given change in gas concentration from the top of the tower to any point, the smaller the liquid flow rate at that point, the higher the concentration of solute in the liquid. This decreases the actual driving force appreciably if the gas is not very soluble and may actually result in saturation of the liquid on the packing while the liquid at the walls is relatively dilute with respect to solute.

This distribution of the liquid causes the calculated value of KCJ to be much lower than the actual value since the ordinary material balance equation for x yields low values of x and a subsequent high value of driving force. If the liquid distribution were known, the correct values of x might be calculated and used to obtain a correct value for KCJ. However, the incorporation of the liquid distribution into the absorption equations is objectionable because of the complex relationship of the liquid flow as a function of height. Moreover, such distribution of the liquid is inefficient from an economic standpoint and so it is desirable to correct this non-uniformity by correct design of equipment as far as commercial practice is concerned.

The effect of the "channeling" of the liquid was shown quite remarkably by some of the data of Mirus. (18). For the case of using Jack packing without redistributors, he found that KCJ, for a given liquid rate, increased with increasing gas rates and went through a maximum value decreasing from that point continuously. This indicates that a great part of the liquid was being kept at the walls of the tower so that as the gas rate increased the liquid became saturated higher in the tower. Thus less volume of the tower was being used. Since the value of KCJ was calculated using the total volume of the tower, rather than the rapidly decreasing "effective" volume, the value of KCJ decreases whereas the actual value, based on the "effective"

volume should be approximately constant or increase slightly.

In order to get the liquid away from the walls, redistributors were used. They were simply dams placed at the walls with spouts to place the water back towards the center of the column (12). The redistribution of the liquid caused the disappearance of the "maximum" value of KCJ and the new values of KCJ were found to increase slightly with gas rate, as well as being greater than in the previous case. The exact efficiency of redistribution is unknown but this increase in uniformity is noted also by the fact that the pressure drop and total liquid holdup was higher at identical flow rates with redistributors and also that with redistributions, "loading" of the column was reached at much lower water and gas rates whereas no such loading was noted without the redistribution.

The redistribution of the liquid serves to keep the liquid distribution more or less uniform over the width of the tower. However, even with this improved spreading of the liquid, the distribution of the gas passages, both as to size and number, are dependent on the openings between the pieces of packing and upon the liquid rate. Since the packing is ordinarily of a very non-uniform shape and is packed in a random manner, various sizes of gas passages are spread over the width of the tower. The variation in size of these passages causes a variation of the ratio of KCJ to G for each passage and hence a dependent variation of gas composition over the width of the column. Hence, the overall

gas driving force will not necessarily be the "average" composition as is ordinarily assumed. Inasmuch as this "channeling" is characteristic of the packing, and not experimental procedure, the absorption equations must be corrected. This method of correction will be discussed in a subsequent chapter.

III. The area of interface for solute transfer per unit packed volume is everywhere the same throughout the tower (and is independent of flow rates).

The interfacial area of the packing is of primary importance in the design of packing for towers since the overall coefficient includes the area directly. The validity of this assumption of constant and uniform distribution of the area depends almost entirely on the characteristics of the structure of the packing although the liquid flow rates are also important.

In order to have a uniform area, the packing must be so constructed that all parts are available to be wetted by the liquid and open to the gas flow. Thus, any packing that might break or crush easily, e.g. coke, some ceramic packings, might tend to clog passages at local points, thereby covering some of the area to be made inaccessible to the gas. Any packing that is made of small pieces, e.g. Raschig rings, Berl saddles, and dumped at random in the tower would hardly be expected to produce an exactly uniform area. However, over the entire volume of the tower such variations are assumed to be similar so that an average value of interfacial area may be used.

A greater effect of the structure of the packing is on the spreading of the liquid, as discussed under the previous paragraphs. As mentioned, the non-uniformity of the liquid distribution will cause parts of the packing to be wetted with saturated liquid, which renders that portion of the packing ineffective insofar as absorption is concerned.

If parts of the packing fit tightly together it may be possible for the liquid to fill these pockets so as to exclude the presence of gas. This absence of one phase also reduces the value of J . Such a reduction in J occurs near the walls more often since there may be large amounts of liquid on the packing with no gas. Also, the buildup of liquid on the packing due to an increase in friction between the gas and liquid may cause clogging of the gas passages. This is quite appreciable near the "loading" and "flooding" points in the tower.

Another factor which influences the wetting of the packing is of course, the surface tension of the liquid. The surface tension of the liquid tends to keep the area of exposed liquid to a minimum. Hence, the distribution of the water to all parts of the packing is retarded. In order to overcome this, larger liquid rates (and hence more kinetic energy) are needed, or else a better initial distribution of liquid may be used. This has the effect of making the initial surface of the liquid higher so as to minimize the work of forming new surface.

The net effect of surface tension is to cause a variation of J with h , since as less liquid becomes present on the packing, surface tension tries to draw the liquid up into smaller area and thus cause little or no liquid to be on some portions of the packing. In this case, the value of J varies with h and should be included in the absorption equations. However, inasmuch as this sort of irregularity is inefficient, it is again more feasible to try to keep the value of J uniform. Thus, packings made with larger free space between the solid materials (e.g. wire meshes) have found wide use in recent years. Also the use of the redistributors for the liquid increases J . Such redistributors however, have not been used industrially. Rather, the ratios of tower height to diameters have been held to within certain limits so as to hold the spreading of the liquid to moderate values.

The presence of ineffectual area in a tower is undesirable from an economic standpoint. From a theoretical standpoint, it is undesirable since, if the amount of effectual area changes with flow rates, the variation in KCJ due to J will be different from that of KC alone. Thus, in some cases of liquid film data, the gas rate has a small effect on KCJ . This suggests that some increase in J has occurred and indicates that some part of the total area is not actually being used for absorption. Methods of estimating the percentage of effectual area from

absorption and pressure drop data will be given in a later chapter.

IV. The conductivity of the transfer path, defined as the amount of solute transferred per unit time per unit area of solvent surface per concentration driving force, is constant throughout the tower.

This particular assumption ranks in importance to that of the assumption of constant temperature since the conductivity of the transfer path is a function of the mechanical turbulence of the fluids as well as the physical properties of each fluid. Thus, temperature, concentration of the solute and height of tower could easily cause variations in KC so as to make the appropriate integration of the absorption difficult or impossible. Hence, the assumption of a constant value for KC (and J) greatly simplifies the form of the integrated expression.

The assumption of constant conductivity probably is quite valid for the gas phase since the main variable for the gas is the rate of flow. Temperature and pressure changes are little consequence for the gas phase itself. Thus, if the gas film controls, the assumption is quite valid.

When the liquid resistance is appreciable or controlling, the idea of constant conductance must be carefully examined. The effect of a varying temperature has already been mentioned (under that category) although the principle discussion

at that time centered on the solubility of the solute gas. However, since viscosities of liquids may change rapidly with only a slight change in the temperature, the turbulence of the liquid may vary appreciably, thus changing KC. Since the relation between KC and the physical properties of liquids is undetermined as yet, and is undoubtedly of a complicated form for integration, it is important to keep the properties constant by maintaining constant liquid temperature.

A similar situation occurs with regard to the liquid distribution in the column. If there is a substantial depletion of the amount of liquid on the packing, the flow of the liquid on the packing tends to become less turbulent, causing a change in KC. If there is only a moderate amount of "channeling" of the liquid, then a variation of KCJ may be due to the incorrect driving force used, as discussed under the assumption (II) of uniform liquid distribution.

A much more important aspect of the exceptions to this assumption arises when the liquid contains materials which react to the solute gas. As discussed (under liquid resistance) the presence of the "active" material adds to the complexity of the absorption since a chemical reaction occurs in the liquid phase. The presence of a chemical reaction does not change the form of the absorption equation (24) if the driving force be taken as $(y - H'x)$ where H' is the new value of Henry's coefficient for the solution with the "active" agent present, and if the effect of the rate of

reaction is included in KCJ . (This form is given in Sherwood (24) and examples of correlation of data for absorption with chemical reaction is summarized by van Krevelin (31). The modification proposed by Sherwood is that the reaction be considered a first order reaction (this is true if the concentration of the active agent is constant) so that the same form of driving force will be used. However, KC then becomes a function of the concentration of the "active" material. Consequently as the active material is used up, KC changes and its variation should be included in the absorption equation. Notice that such a discussion refers to variation of KC over the length of the tower (since the concentration varies along the height also) whereas the previous discussion (under liquid films) dealt with concentrations varying through the liquid layers on a horizontal plane. It might be noted here that the discussion of concentration through the films enters into the equation as the form of the driving force and also into the numerical value of KCJ at a given horizontal plane in the tower where there is a definite concentration of the active substance.

The error in the integration then becomes obvious. If KCJ is a function of concentrations, it cannot be assumed constant so as to factor it out from under the integral sign. If liquid rates are high enough, or conditions such that only a slight change in concentration occurs, then the use of a mean

value of KCJ will be approximately correct. However, in much experimental work and probably most industrial applications (because of the cost of the active agent, etc.) the concentration (or conversion) of the active agent will vary widely over the length of the tower. Thus, if the height of the tower or liquid rates are to be changed, the "mean" value of KCJ may be completely unpredictable on any sound basis. Further, any attempt to correlate such data would immediately be difficult and the justification of the controlling reactions from such absorption data would be illogical and probably incorrect. Some specific examples have already been given under the discussion of liquid resistances.

There is no way this variation of KCJ may theoretically be neglected. A careful study of systems where the conversion of the active material is small will give an idea of the variation of the KCJ with concentration of the material. Then the integration could be carried out analytically or graphically.

In order to avoid this variation of KC over the length of the tower it is necessary to use pure liquids for absorbents. If this is done then the amount of gas dissolved in the liquid will not have as much effect as when the active material is present. Under these conditions KC may be assumed constant.

V. The carrier gas is inert, i.e. its solubility in the solvent is zero, and its volume remains constant over the length of the tower.

The use of an inert gas is necessary in the derivation of the absorption equations. The inert gas serves as the basis of all the calculations, especially the material balances. Thus the amount of absorption may be related directly to the composition of the gases which is highly desirable. In most industrial and experimental practice it is much more convenient (or essential) to know concentrations rather than the actual flow rates. Hence, in equation (10), the amount of the inert gas is assumed to be the total gas rate and the amount of absorption is $-Gdy$. The more exact form, used in the Tour-Garber equation, is $\frac{-G_1 dy}{(1 - y)^2}$, where G_1 is the inert gas rate.

If the carrier gas is appreciably soluble in the solvent, these expressions are totally incorrect since the absorption of the "carrier" tends to keep the value of y higher than if the carrier were not absorbed. To be exact, the rate of solution of the carrier gas must be obtained. Thus, for each constituent being absorbed, a differential equation must be written, the result being that a system of simultaneous equations must be solved. This type of absorption occurs in the scrubbing of hydrocarbon gases to remove the heavier components. Usually, approximate methods are used to save the labor of solving the systems of equations.

Insofar as laboratory test data is concerned the above case is relatively unimportant. For most work, air or

some very insoluble gas is used and its solution in the liquid is negligible. However, in some cases, the most important ones being the study of liquid films, there may be evaporation of the solvent into the gas stream. Thus, while the solute gas is dissolving in the liquid, the liquid is being evaporated into the gas stream. This evaporation causes the gas to be diluted so that the exit mol fraction of the solute in the gas is lower than if the liquid had not evaporated.

Where the solute is quite soluble in the liquid and the change in gas composition is high, the dilution is unimportant. However, if the amount of absorption of the solute is small, as in the case of CO_2 in water, etc., the effect may be important. To show an approximate effect of this humidification we may consider the case of run 36b of Greenberg (12). If the carrier gas is taken as being air at 60 psia and 80°F , saturated with H_2O , the inlet concentration being 8.186 mol % CO_2 , the humidification of this gas without absorption of CO_2 may be readily computed. If we take as a basis 1 mol of dry air the final analysis of the gas (humid) may be determined as follows:

In the original gas:

$$\text{Air} = 1.000 \text{ mol}$$

$$\text{H}_2\text{O} = \frac{.5067}{60 - .5067} = .00852 \text{ mol}$$

$$\text{CO}_2 = \frac{8.186}{91.814} \times (1.000 + .00852) = 0.0899 \text{ mol}$$

For the saturated gas (at 32.00 "Hg and 68°F)

$$\text{Air} = 1.000 \text{ mol}$$

$$\text{CO}_2 = .0899 \text{ mol (no absorption)}$$

$$\text{H}_2\text{O} = \frac{.3388}{15.70 - .3388} \times (1 + .0899) = .02402 \text{ mols}$$

and the concentration of CO_2 becomes $\frac{.0899}{1 + .0899 + .02402}$ or 8.075% CO_2 . Thus, the humidification throws an error of approximately $\frac{8.186 - 8.075}{8.186 - 7.685}$ or 23% in the amount of CO_2 absorbed. This is the maximum error introduced due to humidification since the 8.075% CO_2 analysis assumes the inlet gas to be saturated immediately. A similar calculation may be made for correcting the outlet concentration rather than the inlet concentration.

If the outlet gas is saturated and the analysis is 7.685% CO_2 , the concentration of the CO_2 would be higher if no humidification occurred. To calculate the analysis based on a humidity of .00852 mol H_2O /mol air, the calculations are repeated as before:

For saturated gas, on a basis of 1 mol of saturated gas:

$$\text{CO}_2 = .07685 \text{ mol.}$$

$$\text{H}_2\text{O} = \frac{.02402}{1.02402} = .02349 \text{ mol.}$$

$$\text{Air} = 1.000 - .07685 - .02349 = .8997 \text{ mol.}$$

If the water is removed to make the humidity equivalent to the inlet gas, there will be $0.8997 \times .00852$ or .00767 mol H_2O .

The final concentration of CO_2 will be $\frac{.07685}{.8997 + .07685 + .00767}$ of 7.810% CO_2 . This indicates an error in the calculation of CO_2 absorbed of approximately $\frac{7.810 - 7.685}{8.186 - 7.685}$ or 25% based on the measured outlet concentration of CO_2 . The discrepancy of 2% between the two methods is due to the omission of the effect of the increased gas rate in the first calculation.

The driving force at the bottom of the column, $y_1 - Hx_1$, ignoring humidification effects may be calculated to be 1.66 mol % CO_2 . Using the corrected value of the outlet analysis for the material balance, the new driving force will be 2.924 mol % CO_2 since less CO_2 has been absorbed in the liquid than previously thought.

At higher gas rates, this error becomes more appreciable so that, combined with possible temperature changes of the water and experimental errors in the gas analysis, the calculated "ideal" value of $y_1 - Hx_1$ may actually become negative. This negative driving force may be shown to be the cause of all the negative terms which may occur in the Tour-Garber equation.

Outside of the term $y_1(1 - y_1) - \frac{HG_2}{V} (y_1 - y_2)$ in equation (15), which is $(1 - y_1)(y_1 - Hx_1)$, the only other term in that equation which can yield a negative number is the ratio $\frac{2y_2 + 1 - \psi}{2y_1 + 1 - \psi}$. Both the numerator and denominator are negative while the absolute value of the numerator is always greater than that of the denominator. To get the fraction to be negative, denominator must be positive while the numerator is still negative.

Then, the condition must be found for this inequality to hold:

$$2y_1 + \left(\frac{HG_2}{V} - 1\right) - \sqrt{\left(\frac{HG_2}{V} - 1\right)^2 + 4\frac{HG_2}{V}y_2} > 0$$

or

$$2y_1 + \frac{HG_2}{V} - 1 > \sqrt{\left(\frac{HG_2}{V} - 1\right)^2 + 4\frac{HG_2}{V}y_2}$$

Squaring both sides, the equation becomes:

$$4y_1^2 + 4y_1 \frac{HG_2}{V} - 4y_1 + \left(\frac{HG_2}{V} - 1\right)^2 > \left(\frac{HG_2}{V} - 1\right)^2 + 4\frac{HG_2}{V}y_2$$

and, upon simplification,

$$y_1(y_1 - 1) + \frac{HG_2}{V}(y_1 - y_2) > 0$$

or

$$y_1(1 - y_1) - \frac{HG_2}{V}(y_1 - y_2) < 0$$

Hence, the negative numbers can arise only in the event that the driving force at the bottom of the tower turns out to be negative. (This is also evident by direct inspection of equation (15a). This indicates that if such numbers do occur, there is a definite failure of experimental procedure at some point. The occurrence of such negative numbers cannot be attributed solely to the random errors made in analysis per se, but may be due also to the errors in water temperature and humidification effects which remain even after accurate analysis are obtained.

VI. The system obeys Henry's Law.

This assumption is made, of course, to simplify the

integration of equations such as (10) and (14). It is not essential to assume that $y^{\#} = Hx$ since theoretically any other function of x would suffice. However, in order to get a simple type of integrated equation the constancy of H is assumed. The assumption that H is constant does not hold in many cases. Ammonia, sulphur dioxide and others show marked variations of H with concentration, i.e. the solubility curve is not a straight line. As a result it might be thought that the non-linearity would make the integrated expressions incorrect. This is not always true.

If the gas is soluble enough in the liquid so that the back pressure $y^{\#}$ is small compared to y then a variation of H may be negligible in its effect. Thus if H varies by 200-300% so as to make $y^{\#}$ vary from 0.02-0.03 mol % where y is 2.00 % the variation in $(y - y^{\#})$ is only of the order of the experimental accuracy. The actual effect of a variation of H is in the term (see equation 11) $1 - \frac{HG}{V}$. If $\frac{HG}{V}$ is small, as it is in the case of very soluble gases being absorbed, $1 - \frac{HG}{V} \approx 1$ and a large/proportional variation of $\frac{HG}{V}$ will not affect the overall value of $1 - \frac{HG}{V}$ to any great extent.

On the other hand, when the gases are not soluble to a great extent in the liquid $\frac{HG}{V}$ becomes much greater than 1 so that the variation of H becomes of prime importance. In this case it is more feasible to evaluate the integral by some

approximate method rather than attempt to get an analytical solution. However, in experimental work, such procedures are too time consuming so that systems where Henry's law actually applies or where the back pressure is very small are usually used. In this manner, the relations between K_{Ga} , K_{La} , KCJ etc., become simpler and the integrated absorption equation is available for calculations. If a tower is to be designed for a gas which does not conform to either of these cases, then the simple methods are incorrect and the integrals must be evaluated by graphical methods, etc.

Summary on Assumptions

Whereas many details of the various integrations of the differential absorption equations have been presented many times, a thorough discussion of the assumptions has long been absent. As noted above, there are six main assumptions made, some of which are dependent on the same variables and some more important than the rest. It is believed that many of the "variations" of the data from the accepted theories in the literature are actually due to the failure of the experimental technique to fulfil the necessary assumptions listed.

In some cases the variations or errors in the data are such that they stand out as being incorrect. The examples of the maximum values of KCJ with gas rate (of Mirus), variation of K_{Ga} for CO_2 with conversion of $NaOH$, etc. show that at least

one of the important principles is being completely ignored. However, these particular violations are easily seen. In some data presented in the literature, where no detailed explanation of procedures or design of equipment is given, the occurrence of errors may not be evident.

One problem which is constantly encountered is that of the analysis of gases and liquids. In the case of the log mean equation, the compositions of both phases may be measured and used in the equation directly. This tends possibly to compensate the errors in each measurement. The more exact form of the absorption equation makes the errors in gas analysis cumulative. Thus, if the material being absorbed is computed by a balance over the gas, and the solute absorbed is in error, say greater than the actual amount, the driving force at the bottom of the column will be too low. This increases the error in KCJ. Hence, the need for accurate analysis for the insoluble gases cannot be over-emphasized.

All of the assumptions made in order to integrate the differential absorption equation are more or less subject to direct experimental procedures, the proper precautions in experimental technique making the assumptions valid. However, as pointed out, the uniformity of gas flow is known to be incorrect because of the properties of the packing and not because of any experimental technique. Hence the modification of the absorption

equation for this non-uniformity has a serious effect on the values of KCJ. As will be shown, this is the case and the subsequent work described here will be to determine just how much its importance is.

Part II

The Effects of
Channeling in Packed Towers

CHAPTER 5

THE PRESENCE OF CHANNELING IN PACKED TOWERSOccurrence of Channeling

The overall effects of channeling of streams has long been known. One of the main factors in the design of all diffusional or reaction types of equipment is always to secure good mixing and contact of the reacting phases. In this type of equipment any material that may pass through the reaction zones without contacting the suitable phase is said to be "channeled" or "short circuited". This channeling represents a waste of space as well as the cost of recovering the channeled material.

In packed towers channeling occurs in two cases:
1) the passage of the gas over dry portions of packing where $J = 0$ or portions covered with saturated liquid and 2) the passage of a slow stream of gas over wetted packing such that $KC = 0$. In both cases KCJ is zero or very close to that value, the net result being that there is no absorption occurring in that particular gas stream. From this concept, we may define here the term "channeling" to refer to any gas (or liquid) stream in a tower which is not undergoing the process of absorption. If the liquid rates are of correct magnitude and redistributors used (if necessary) the packing should be completely

wetted^{*} so that the channeling that may exist will be due to the low values of the local coefficient KC, the value of J being other than zero.

The variation of KC over the width of the tower is due to the non-uniformity of the size of the passages for the gas streams. The variation of size also effects the value of J but the low value of KCJ is due to KC, since J (per unit volume of passage) increases as the size of the passage decreases. Before the reasons for assuming a variation of KC and J are discussed, it is worthwhile to see what effect a variation of KCJ and gas rate G over the width (i.e. a horizontal plane) of the tower, will have on the absorption equations.

As mentioned in the previous chapter, the assumption of the uniform distribution of the gas and liquid is usually made so as to eliminate (or simplify) the integration of the absorption equation over the width of the tower. Thus, for the jth stream of gas at any level in the tower the absorption equation for that one stream is:

$$-dG_j = (KCJ)_j (y - Hx)_j A dh \quad (31)$$

If there are N streams of gas, the total amount of gas absorbed along the plane is the sum of the amount of absorption in each stream, i.e.

$$-dG = - \sum_{j=1}^N dG_j = \sum_{j=1}^N (KCJ)_j (y - Hx)_j dh \quad (32)$$

^{*}Certain packings, such as the Jack packing used at the University of Cincinnati (described by Mirus), may be designed such that certain portions, e.g. the bottom, will be dry or filled with stagnant liquid and this part of stagnant (or unef- fective) area cannot be removed so as to make it effective in the absorption process.

Notice that if $(KCJ)_j$ and $(y - Hx)_j$ are the same for each gas stream, then each is constant over the arbitrary plane and the form of equation (32) becomes the usual equation (14). However, if the sizes of the gas passages vary over the width of the tower $(KCJ)_j$ and G_j will change and the summation of these factors will involve a knowledge of the number of actual gas passages, their relative sizes as well as the relation of G_j and $(KCJ)_j$ to the size of the passage. Since the actual data needed for such a summation is unknown and would vary so greatly for various types of packing, a simpler approach is needed and a semi-theoretical method should be acceptable. (A simplified method of summation will be given later for a given choice of passage sizes.)

The method that has been proposed is based on assuming the gas streams to be divided into two categories: 1) those in turbulent flow where the amount of absorption is high and 2) those in viscous flow where there is no absorption. This is a logical separation inasmuch as the rates of absorption (or the value of KCJ) in turbulent streams is many times greater than in viscous streams.

The existence of both turbulent and viscous gas streams in packed towers is easily justified by a variation in the sizes of the passages. Since the pressure drop over the length of each passage is the same for all, the wider the passage

becomes the higher the gas rate (and hence the greater the turbulence) will be through that passage. Hence, the larger passages will be the sites of absorption whereas the smaller passages will be ineffectual for absorption. It is, then, these small, viscous-gas streams which constitute the "channeling" in the tower as well as gas which may be in contact with dry packing. Ordinarily the concept of channeling brings to mind the idea of large bulks of material, or slugging effects, going through a piece of apparatus. In this case of absorption, just the opposite is true.

A more quantitative way of verifying the idea of two types of gas flow is by pressure drop data. For turbulent flow the pressure drop is proportional to the 1.8 power of the gas rate approximately (29) and for viscous flow the exponent is 1.0. Thus, if the gas flow through the packing is totally turbulent then the pressure drop should vary as the 1.8 power of the gas rate. In most cases the empirical value is much less than this. William's data gives values of about 1.45-1.50 while Mirus's data were too inconsistent to get a definite value but did indicate values of about 1.4.

Other data (2, 23) on flooding velocities in packed towers show the same range of exponents. . . . Since most of the data presented is in the region of the loading and flooding points, the accurate values of slope for the lower

section of the curve is difficult to obtain. The data do indicate that the slope of Δp vs gas rate (on log-log paper) decreases with increasing liquid rate indicating an increased amount of viscous gas flow for a given pressure drop. This difference of the exponent from 1.8 is believed to be due to the presence of part of the gas in viscous flow. A more detailed use of this pressure drop data will be given later.

Effect of Channeling on Driving Forces and Absorption Area

It is important to realize the effect of this assumption of channeling on the absorption equation. The actual effect is such that the equation (32) becomes too involved for convenient use. The result of dividing the gas streams into two categories is an attempt to preserve the basic form of equation (31) to the whole plane of the width by suitably modifying the numerical values of KCJ and $(y - Hx)$. In doing this, the integrated expressions remain in the same form as developed previously.

Before the actual modification of the equation is carried out, several qualitative effects are easily discussed first. The effect of channeling as defined in this work is shown in both the value of J and y used in the absorption equation. In the standard equations for absorption the value of y used for the gas driving force is taken as the average composition of the gas stream. Using the concept of channeling it is seen

that the use of the average concentration of solute gives a high value of the driving force, since the turbulent gas streams have a value of y less than that of the combined viscous and turbulent streams. A simple example will indicate the differences in magnitude. Assume the inlet gas to an absorption column has a solute concentration of 1% and that 1% of the gas is channeled. At a point where the average concentration (i.e. total solute per unit volume or mass of gas) is 0.05%, the concentration of the solute in the unchanneled gas stream is $\frac{0.05 - 0.01 \times 1}{0.99}$ or 0.0404%. Hence, if there were no solute in the liquid at this point the overall driving force would actually be 0.0041 rather than 0.0050, or an error of 19% based on the "average" concentration. If the liquid contains enough solute to exert an appreciable back pressure, say equivalent to 0.01%, then the error in driving force is $\frac{.0009}{.0040} \times 100$ or 22.5% based on the use of the average concentration of the gas. As the amount of solute in the liquid increases the error increases. The extreme case may be noted readily. If the outlet gas of the tower is completely in equilibrium with inlet pure liquid then the concentration is zero and a calculated value of K_{CJ} would be infinite. If there is 1% channeling, the minimum outlet concentration is $0.01 \times 1 = 0.01\%$ of solute approximately. Thus if a value of K_{CJ} were based on a driving force of 0.01% a finite value would be obtained, whereas the

the actual value is enormous (or infinite) in order for the turbulent portion to be completely stripped of the solute gas. This numerical change of KCJ due to channeling is important, especially in comparing numerical values, say, between two types of packing.

The relation between the effective area J_t and the amount of gas channeled is important since the effectual area is a measure of the efficiency of the packing in the tower. The purpose of the packing is to supply a large area of contact between the gas and liquid. If the packing is arranged to have small passage sizes then the ratio of surface to volume is very high in these passages. However, if in addition to these many small passages there are a few large ones, most of the gas will go through these larger ones. If there are enough of these larger sized passages, the gas flow in the small tubes will drop off considerably and may become viscous in form. This renders the greater amount of the surface completely useless since the sharp decrease in KC more than offsets the increase in J . At the same time, in the small passages there is relatively little gas so that most of the gas is being contacted on (only a little of the total surface. An exact relation between J_t and the gas channeled is dependent on the exact sizes of passages and number of them, pressure drop, etc. A more complete analysis may be accomplished by choosing various

distribution of pipe sizes and actually calculating the flow characteristics through them.

From the standpoint of correlation of data, it is easily seen that channeling is of prime importance. In order to compare the efficiency of one packing with another, a knowledge of dry surface and size of packing is not sufficient. The mere fact that one type of packing may have a larger surface than another is inconclusive since, if it also has more channeling, the efficiency may be lower. At the same time, the variation of channeling with gas rates may cause the values of KCJ to change in an unusual manner with the flow rates.

Effect of Gas Rate on Channeling

The effect of the total gas rate on the amount of channeling and the effective transfer area may first be discussed from a qualitative point of view. As the gas rate is increased through the column the pressure drop is increased across each passage. The increase in pressure drop causes the flow through each passage to increase. Thus, the smaller tubes begin to approach conditions of turbulent flow. As the gas rates continue to increase, the upper limit of tube diameter which permits viscous flow decreases and more tubes are "converted" into turbulent flow. As soon as the flow in a tube becomes turbulent, that tube becomes effective in absorbing any soluble gas in the gas stream. Hence both the amount of gas channeled decreases and the effective area for absorption increases as

the gas rate rises. This is believed to be the reason for the increase of KCJ with gas rate where the liquid resistance controls, as previously mentioned.

At first it might be thought that the amount of gas channeled could be reduced to zero by raising the gas rate (or pressure drop) to such a value that the smallest passage in the column contained gas in turbulent flow. This could possibly be done except for the phenomenon of "loading" and "flooding". At low flow rates of the gas, the friction between the gas and liquid is small enough so that there is little effect of this drag on the liquid holdup. However, as the pressure drop is increased, the drag may become appreciable. At this point, the "loading" point, the liquid begins to build up more on the packing causing the smaller passages for gas flow to be constricted or else completely blocked. This results in the closure of passages and the area that was available for absorption has disappeared. The "flooding" point represents the state where enough passages have been closed that the increase in liquid holdup necessitates the use of high pressure drops.

Since these loading and flooding phenomena are sometimes reached at relatively low gas rates (depending on the packing and liquid rates), it is impossible to reach a point of zero channeling. However, it is evident that the loading point, or rather just below it, is the point of maximum

effective area and minimum amount of gas channeled. This is the underlying principle behind the rule-of-thumb of operating just under the loading point for maximum absorption.

These statements have been confirmed by the data of many observers although usually neglected. The data of Greenberg (12) for CO_2 absorption in water showed that the value of KCJ increased steadily with the gas rate, varying approximately as the 0.23-0.25 power of the gas rate. Others, previously mentioned, found similar variations. Since the liquid film offers the greatest resistance to absorption, thereby fixing the value of KC , the increase in KCJ is explained as being the increase in the conversion of the viscous passages to the turbulent form.

The idea that J , rather than KC varies with gas rate is not as arbitrary as might first be assumed by the preceding assumption of the liquid film controlling. Thus, it might be argued that even in the turbulent gas streams there is an appreciable gas film resistance and the increase in KCJ with gas rate is merely the result of the decrease in gas film resistance. If this were the case, then it would be expected that as the gas rate were increased, holding the liquid rate constant, the value of KCJ would "level off" and approach the value of the liquid resistance asymptotically. However, no such "leveling off" is noted usually and the values of KCJ increase steadily with gas rate, until

possibly flooding or loading of the column is reached.

Having defined the concept of channeling and discussed its importance, it becomes necessary to attempt an evaluation of its magnitude and its numerical effect on the effectual area in a packed tower. There exist two basic methods:

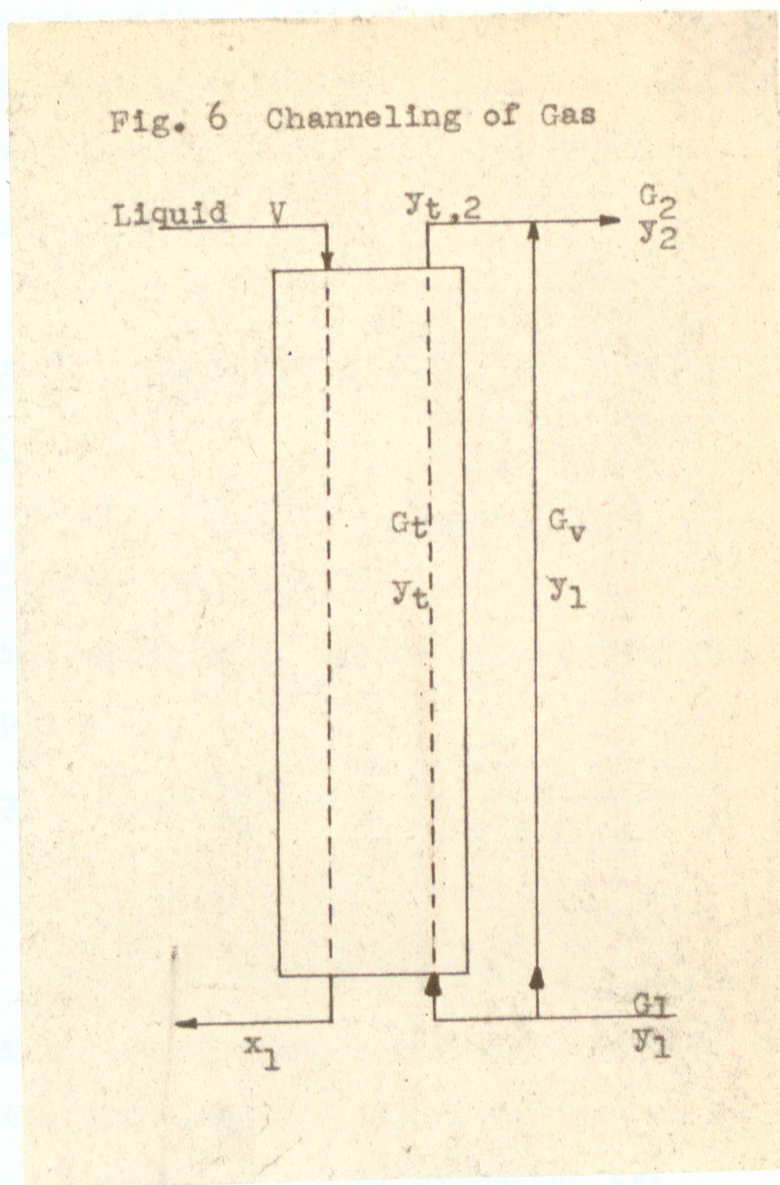
1. Evaluation from absorption data by suitable modification of the absorption equations to include the effects of channeling.

2. Evaluation from pressure drop data which shows the presence of channeling by the exponent n in the equation $\frac{\Delta p}{L} = \alpha G^n$.

Absorption Equations with Channeling

a. Tour-Garber. In order to develop an absorption equation to take channeling into account it is first necessary to define a numerical value of channeling and show its characteristics in the absorption equation. Referring to Figure 6, the idea of channeling may be taken into account more easily. The liquid in the tower is assumed to be uniformly distributed and all of the other assumptions are taken as being valid, except for the gas flow. The gas flow is pictured as being divided into two parts, the viscous and the turbulent streams. As the turbulent stream progresses up the tower, its composition continually changes but the viscous gas is assumed to be constant

in amount and concentration^{*}.



The amount of channeling, γ , defined by the ratio:

$$\gamma = \frac{G_V}{G_1} \quad (33)$$

and is assumed to be constant over the length of the tower.

^{*}This implies no mixing of the two types of streams. If complete mixing occurs on every horizontal plane the composition will be uniform and the original type of absorption equation will apply. This leaves the effect of channeling to occur only in J , which will be discussed under pressure drop data.

Since, in practice, only the average concentration, i.e. the concentration obtained upon mixing the two streams, may be experimentally measured, y_t must be related to y , y_1 and γ . Several material balances may be written.

Over the entire tower:

$$\text{Inert gas: } G_2(1 - y_2) = G_1(1 - y_1) = G(1 - y) \quad (34)$$

$$\text{Solute: } Vx = G - G_2 = G_2 \cdot \frac{(1 - y_2)}{1 - y} - G_2 = G_2 \frac{(y - y_2)}{1 - y} \quad (35)$$

At a plane h:

$$\text{Inert gas: } G_t(1 - y_t) + \gamma G_1(1 - y_1) = G_1(1 - y_1) = G_2(1 - y_2) \quad (36)$$

$$\text{Solute: } G_t y_t + \gamma G_1 y_1 = G y \quad (37)$$

The value of y_t may be solved from equation (38) and (39) to yield:

$$\begin{aligned} y_t &= \frac{G y - \gamma G_1 y_1}{G - \gamma G_1} = \frac{G_1 \frac{1 - y_1}{1 - y} y - \gamma G_1 y_1}{G_1 \frac{1 - y_1}{1 - y} - \gamma G_1} \\ &= \frac{y(1 - y_1) - \gamma y_1(1 - y)}{(1 - y_1) - \gamma(1 - y)} \end{aligned} \quad (38)$$

The amount of gas absorbed is $-dG$ and $dG = dG_t$. If we denote the effectual (or turbulent) area by J_t , the rate equation for absorption may be expressed as:

$$-dG_t = KCJ_t A(y_t - Hx)dh$$

which is the same equation as the Tour-Garber equation applied to the turbulent gas. We may express dG_t and y_t in terms of y to get:

$$-dG_t = -dG = -\frac{G_2(1-y_2)}{(1-y)^2} dy = KCJA \left[\frac{y(1-y_1) - \gamma y_1(1-y)}{1-y_1 - \gamma(1-y)} - \frac{HG_2}{V} \frac{y-y_2}{1-y} \right] dh \quad (39)$$

The integral form becomes: (40)

$$\frac{KCJAL}{G_2(1-y_2)} = - \int_{y_1}^{y_2} \frac{[(1-y_1) - \gamma(1-y)] dy}{(1-y) \left[y(1-y)(1-y_1) - \gamma y_1(1-y)^2 - \frac{HG_2}{V}(y-y_2) [(1-y_1) - \gamma(1-y)] \right]}$$

The integration of this expression is quite tedious. Since the Tour-Garber equation has already been evaluated, it may be shown that the integrated form may be modified by using the values of G_2 , y_2 for the turbulent gas rather than the average values of G_2 and y_2 .

Rewriting equation (14) as

$$\frac{KCJ_tAL}{G_{t_2}(1-y_{t_2})} = - \int_{y_1}^{y_{t_2}} \frac{dy_t}{(1-y_t) \left[y_t(1-y_t) - \frac{HG_{t_2}}{V}(y_t-y_{t_2}) \right]} \quad (41)$$

the procedure will be to replace all values of y_{t_2} in terms of y and show that equation (41) becomes the same as equation (40) with the exception of the upper limit. Using the following values:

$$y_t = \frac{y(1-y_1) - \gamma y_1(1-y)}{(1-y_1) - \gamma(1-y)}$$

$$dy_t = \frac{(1-\gamma)(1-y_1)^2}{[(1-y_1) - \gamma(1-y)]^2} dy$$

$$1 - y_t = \frac{(1-\gamma)(1-y)(1-y_1)}{(1-y_1) - \gamma(1-y)}$$

$$y_t(1 - y_t) = \frac{(1 - \gamma)(1 - y)(1 - y_1) [\bar{y}(1 - y_1) - \gamma(y_1(1 - y))]}{(1 - y_1) - \gamma(1 - y)}$$

$$y_t - y_{t_2} = \frac{(1 - \gamma)(1 - y_1)^2(y - y_2)}{[(1 - y_1) - \gamma(1 - y)]}$$

$$G_{t_2} = \frac{(1 - y_1) - \gamma(1 - y_2)}{(1 - y_1)} G_2$$

and substituting in equation (41), the absorption equation becomes:

$$\frac{-KCJAL}{G_2(1 - y_2)} = \int_{y_1}^{y_2} \frac{[(1 - y_1) - \gamma(1 - y)] dy}{(1 - y) y(1 - y_1) (-1 - y) - \gamma y_1(1 - y)^2 - \frac{HG_2}{V}(y - y_2) [(1 - y_1) - \gamma(1 - y)]}$$

which is the same as equation (40).

Hence the absorption equation for channeling is of the same form as the original Tour-Garber equation except that the values of G_2 , y_2 must be replaced by the values of the same term for the turbulent stream, i.e.

$$y_{t_2} = \frac{y_2(1 - y_1) - \gamma y_1(1 - y_2)}{(1 - y_1) - \gamma(1 - y_2)}$$

$$G_{t_2} = G_2 \left[\frac{(1 - y_1) - \gamma(1 - y_2)}{1 - y_1} \right] \quad (42)$$

Thus, knowing the flow rates and exit concentrations of the fluids values of y_{t_2} and G_{t_2} may be calculated for any value of γ that holds under the conditions of operation and KCJ calculated by inserting these values into equation (15) or (15a). The introduction of the additional variable γ complicates the

absorption equation due to the fact that instead of having one factor to characterize the tower performance (KCJ) there are now two, KCJ_t and γ . These two terms are not independent variables, however. The value of KC is dependent on the turbulence of the fluid phases whereas J_t is a function of the total surface available to the gas, J_o , and the amount of gas channeled, γ .

b. Log-mean. The use of the channeling in absorption equations for dilute gases suggests the modification of the simpler type of equation, the log mean. The same procedure may be applied to the derivation of the log mean formula as was done for the Tour-Garber. The overall result is the same. Equation (13) is found to apply if y_2 is replaced by y_{t2} in the driving force. The expression $G(y_1 - y_2)$ is the amount of solute absorbed so that $G(y_1 - y_2) = G_t(y_1 - y_{t2})$.

For dilute gases we may approximate y_{t2} by:

$$y_{t2} = \frac{(y_2(1 - \gamma_1) - \gamma y_1(1 - y_2))}{y(1 - y_1) - \gamma(1 - y_2)} = \frac{y_2 - \gamma y_1}{1 - \gamma}$$

which assumes that $(1 - \gamma_1) = (1 - \gamma_2)$. The use of this value of y_{t2} has been illustrated earlier in this chapter and it is convenient to use equation (12) with this value of y_{t2} . The modified equation is then:

$$K_G a \, AL = \frac{(1 - \gamma)G}{1 - \frac{(1 - \gamma)HG}{V}} \ln \frac{y_1 - Hx_1}{\frac{y_2 - \gamma y_1}{1 - \gamma} - Hx_2} \quad (43)$$

This equation will be used later in determining the effect of channeling on K_{ga} for the case where gas films control the rate of absorption. Its simplicity of form, as compared to the more accurate equations, justifies the use.

CHAPTER 6

EVALUATION OF CHANNELING FROM ABSORPTION DATA

The introduction of the concept of channeling to the design equation indicates that another variable has been used to describe the conditions of tower operation. Previously the value of KCJ was assumed to be sufficient as a characterization factor. The effect of channeling has been shown to be present in both the value of J and the driving force. As a result, with channeling present the overall value of KCJ_t is changed and the value of KCJ_o , i.e. based on the total interfacial area, is much higher than KCJ_t . For a given tower, once the packing is completely wetted, J_o remains fairly constant. However, the nature of the size and distribution of sizes of the gas passages determine J_t and γ since the viscous gas is assumed to be unabsorbed. There is a relation between J_t , J_o and γ but since this involves the sizes of the passages, coefficients of friction etc., a theoretical relationship is unattainable as such, hence the need to determine KCJ_t and γ empirically or experimentally.

The experimental evaluation of these two factors is made difficult by the nature of γ and its relation to J_t . Both gas and liquid rates affect γ and J_t , and possibly J_o , so that a first requirement must be to maintain constant flow rates for a possible experimental determination of γ and KCJ_t . This leaves

only two independent variables left; height of tower and concentration of solute. The use of both of these factors will be considered.

The starting point in each case is the fact that KCJ_t and γ , as discussed, are to be functions of flow rates only and should be independent of the height of tower and concentration of solute. Hence, if for given flow rates and inlet concentration of solute, the length of the tower may be varied the value of KCJ , based on no channeling, should vary also. This is due to the fact that the outlet concentrations should vary differently with height if channeling is present. Thus, if absorption data were available for various heights of columns for given flow rates, the values of γ could be assumed so that the computed values of KCJ_t would be the same. The method would be to make plots of KCJ_t vs values of γ and find the point of intersection where KCJ_t and γ would be the same for each height. This method, and its limitation, will be illustrated later under the effect of concentration.

Very little data have been published in the literature on the effect of height on the value of KCJ . The little that has been given (26, 36) shows no definite trend and the possibility of abnormal liquid distribution with length of tower as discussed previously, would probably change the value of channeling over the length of the tower. Hence the use of the literature values has not been made.

The Variation of Concentration

The use of concentrations as the independent variable inherently suggests itself since the definition of channeling, i.e. γ , is made on the basis of the concentration driving force. Since the presence of channeling causes a lower effective driving force than if it were absent, the variation of overall driving force with inlet concentration should be noticeable, particularly if the driving force at the top of the tower is small. If no channeling is assumed and a value of KCJ is computed on this basis, then it might be expected to find that KCJ varies with inlet concentration since an incorrect form of driving force was used.

The procedure of using the inlet concentration as the parameter consists of obtaining absorption data for identical gas and liquid flow rates but with different inlet concentrations. For each set of data values of KCJ_t should be calculated assuming arbitrary values of γ . In this manner, curves of KCJ_t vs γ are obtained for each inlet concentration. A plot of these two curves should intersect at the value of KCJ_t and γ which are determined by the conditions in the column. This method is subject to certain restrictions as pointed out by this example.

Consider the data of runs 38 and 53 of Greenberg.(12)
The experimental data tabulated by him are as follows:

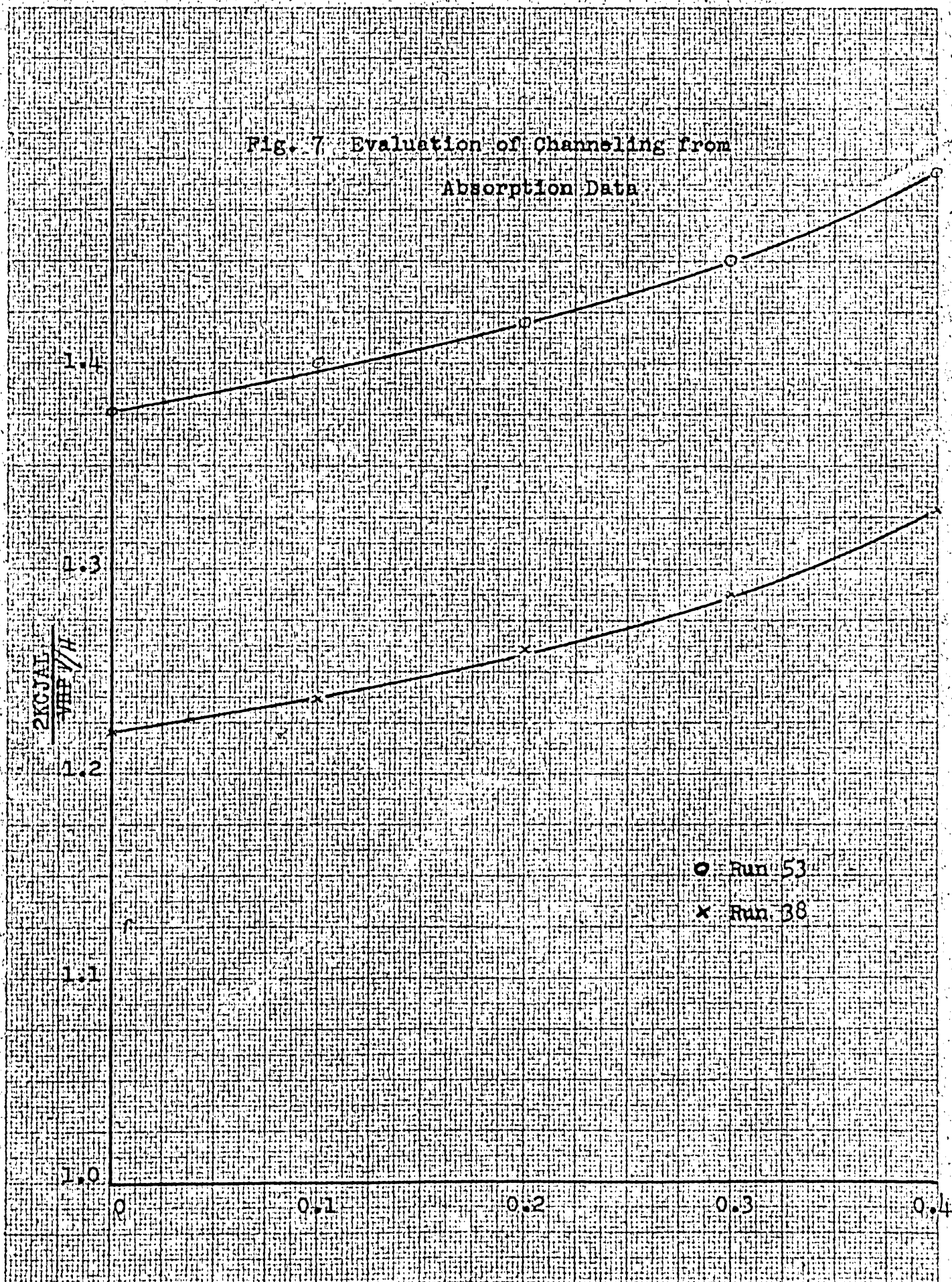
Run	$G_1(\text{ft.}^3/\text{hr.})$	$V(\text{ft.}^3/\text{hr.})$	y_1	y_2	$\frac{HG_1}{V}$
38	203.75	49.71	.09438	.07966	4.418
53	206.41	52.73	.10110	.08492	4.219

By assuming values of γ , y_{t_2} and G_{t_2} are computed by equation (42) and $\frac{2KCJ_tAL}{V/H}$ are computed from equation (15), replacing y_2 by y_{t_2} and G_2 by G_{t_2} . In order to get a measure of KCJ_t on the same basis, the value of V was taken as 49.71, i.e. the value of $\frac{2KCJ_tAL}{V/H}$ for Run 53 was multiplied by $\frac{52.73}{49.71}$ to obtain the values tabulated below. Also tabulated are the values of y_{t_2} .

Run	γ	y_{t_2}	$\frac{2KCJ_tAL}{V/H} = A'$
38	0.00	0.07966	1.221
	.10	.07800	1.237
	.20	.07800	1.261
	.30	.07320	1.288
	.40	.06958	1.329
53	0.00	0.08492	1.378
	.10	0.08309	1.400
	.20	0.08078	1.420
	.30	0.07780	1.451
	.40	0.07380	1.494

The graphs of these two curves are shown in figure 7. It is easily seen from the plot that the curves do not intersect, or even tend to intersect, as the values of γ are taken out of even the most reasonable limits. This lack of intersection is typical of such duplicate data and is due to the fact that the slopes of the curves must be the same at identical values of γ

Fig. 7 Evaluation of Channeling from
Absorption Data



as will be shortly proved (next page). The two values of A' at $\gamma = 0$ may be adjusted to the same value by multiplying the values of A' for Run 53 by $\frac{1.221}{1.578}$. When this correction is made, the two curves become superimposed upon one another.

The reason for the failure of such a method of determination of γ and KCJ_t may be shown by use of the simplified log mean equations. The suggested method of calculating a value of γ is based on a variation of a predicted outlet concentration with inlet concentration. Thus, if at a given set of operating conditions for a tower, the inlet concentration is y_1 and the outlet concentration is y_2 and the inlet concentration is changed to Y_1 a value of the new outlet concentrations, Y_2 , may be computed from the log mean equation assuming no channeling. It would be expected, then, that the calculated value of Y_2 , assuming no channeling, would then differ from the observed value if channeling were present.

For the case of no channeling, knowing the experimental values of y_1 , y_2 and Y_1 , the value of Y_2 may be calculated by equating values of KCJ (or $K_G a$) in equation (12). If this is done the following equation results:

$$\ln \frac{y_2}{y_1 - \frac{HG}{V} (y_1 - y_2)} = \ln \frac{Y_2}{Y_1 - \frac{HG}{V} (Y_1 - Y_2)}$$

and

$$\frac{y_2}{y_1 - \frac{HG}{V} (y_1 - y_2)} = \frac{Y_2}{Y_1 - \frac{HG}{V} (Y_1 - Y_2)}$$

which is satisfied if $\frac{y_2}{y_1} = \frac{Y_2}{Y_1}$ (44)

If there is any channeling, then the equations must be modified as suggested previously to yield:

$$\frac{(y_2 - \gamma y_1)/(1 - \gamma)}{y_1 - \frac{HG(1 - \gamma)}{V} (y_1 - \frac{y_2 - \gamma y_1}{1 - \gamma})} = \frac{(Y_2 - \gamma Y_1)/(1 - \gamma)}{Y_1 - \frac{(1 - \gamma)HG}{V} \left[Y_1 - \frac{Y_2 - \gamma Y_1}{1 - \gamma} \right]}$$

which is also satisfied by $\frac{y_2}{y_1} = \frac{Y_2}{Y_1}$ (45)

The agreement between equations (44) and (45) indicates that the value of channeling is indeterminate by this method since its explicit value cancels out^{*}. At the same time it shows that if design data have been obtained assuming no channeling, then these same data may be used to predict the effects of height on concentration, etc., for the same tower without taking into account the factor of channeling at all.

However, this does not mean that the effects of channeling are absent. The value of KCJ computed from test data still will be incorrect numerically, since the incorrect numerical values of driving force were used, i.e. if there were no channeling, y_2 would be lower. As it happens, when the same incorrect value of KCJ is revised in design the errors in KCJ cancel yielding a correct final result.

In cases where the absolute value of KCJ is desired, e.g. correlations between mass and heat transfer, the presence of channeling would make the attempted correlation incorrect. Similarly, comparing values of KCJ for different types of packing may lead to erroneous correlations if no term is included to represent the amount of ineffectual surface present. In particular, if packings which have various amounts of channeling are compared as to values of KCJ, the variation of the absorption coefficient with flow rates may be different for each one.

^{*}If the inlet solvent contains a solute concentration of x_2 equations (44) and (45) become, with the same effect on channeling:

$$\frac{y_2 - Hx_2}{y_1 - Hx_2} = \frac{Y_2 - Hx_2}{Y_1 - Hx_2}$$

Such variations of exponents on the liquid rate in the case of liquid resistances controlling, are believed to be due to the channeling of the liquid as described.

CHAPTER 7

THE EVALUATION OF CHANNELING FROM PRESSURE DROP DATA

The failure of the use of the absorption equation to determine experimentally the value of the channeling coefficient indicates the complexity of a complete solution to the problem of modifying the absorption equations. Nevertheless, the general assumption that various size gas passages exist in the column is so very reasonable that the presence of simultaneous viscous and turbulent gas flow seems logical. It would then seem that evidences of channeling, other than absorption data, should be present.

The best example is that of pressure drop data for packed towers. As the gas passes through the various passages, undergoing the stripping of the soluble gases from it, there are various amounts of friction in the general turbulence and mixing of streams as well as enlargement and contraction losses. These frictional losses are overcome by the pressure of the gases, the drop in pressure being directly proportional to the friction. The values of such pressure drop are of importance in tower design since they represent pumping costs and also limit the capacity of the tower due to loading and flooding.

The presence of channeling, or rather the coexistence

of the two types of flow, can be shown in a plot of pressure drop versus total gas rate. This is the most common type of plot shown in the literature. If the gas flow were entirely viscous, the slope of Δp , the pressure drop, versus G , the gas flow rate, would be 1.0 on log-log paper. If the flow were entirely turbulent, the slope would be 1.8, approximately. This latter value depends on the fact that the coefficient of friction decreases as the 0.20 power of the gas rate. The gas rates used on the tower are sufficiently high to prevent the entire flow from being viscous. However, most of the experimental data yield slopes which lie between 1.0 and 1.8. This may be explained by the fact that if there exist the two types of flow, the equation for the pressure drop curve will be of the form

$$G = G_V + G_t = a(\Delta p) + b(\Delta p)^{1/1.8} \quad (46)$$

and thus a plot of Δp vs $(G_t + G_V)$ will not have a slope of either 1.0 or 1.8 but some value in between the two. As may be seen from the form of the equation, a log-log plot should not be an exact straight line and, true enough, most pressure drop data do show distinct curvatures but are usually called straight lines for simplicity. The curvature of such a line, or its slope, is dependent, obviously, on the specific numerical values of a and b . Briefly we may say that a and b are functions of the sizes of the passages, the number of tubes of each specific size and the physical properties of the gas, i.e. viscosity and density.

If "a" and "b" were constants for any one tower and gas, then equation (46) would be suitable for a more accurate estimation of channeling or the effective turbulent area. However, both are functions of the pressure drop (or the gas rate) and the form of equation (46), complicated as it is, becomes more unwieldy. The variance of "a" and "b" is due to the increased number of smaller passages which transfer from viscous to turbulent flow as the pressure drop increases. Specific examples of this variance will be shown later under an example.

In order to more thoroughly investigate the relation between pressure drop and channeling, an indirect approach must be made. Rather than deal with any type of packed tower, it was believed to be comparable (and much simpler) to use a set of tubes of various diameters with a known "frequency" (or distribution) with respect to size. Using the approximate solutions developed by Tour⁽²⁹⁾ for turbulent flow and the Hagen-Poiseuille equation for viscous flow, the analysis of pressure drop, turbulent area, channeling could be made in a more quantitative way. (In order to obtain smooth curves it was necessary to assume a continuous variation of tube sizes so as to be able to carry out integrations rather than the more tedious summations). Once the calculations have been made, they may be compared to the absorption cases and see what similarities exist and what conclusions drawn.

Numerical Examples of Channeling

In order to make a numerical evaluation of channeling for a given set of tubes, it is necessary to:

1. Choose a distribution and magnitude of tube sizes.
2. Choose properties of the fluid to be used.
3. Have relationships for the frictional flow of fluids.
4. Have a mathematical criterion to decide whether a fluid is flowing in viscous or turbulent flow.

The choice of a distribution of tube sizes is somewhat arbitrary since no definite pattern has ever been suggested from experimental work. The distribution will be some probability function which will hereafter be taken in the form of the "binomial" or "normal" distribution. This symmetrical distribution may be taken with respect to:

- A. the diameter of the tube
- B. the cross-sectional area, i.e. the square of the diameter, of the tube
- C. the volume, i.e. the cube of the diameter, of the tube.

The size of the tubes may be taken as extending from 0 to 1" in diameter. Such a range is quite general since any other range of sizes, e.g. 0 to 1 millimeter, could be changed to this range by a simple change of variable. Since all the results of calculations will be plotted on log-log paper, this

change of variable, which is merely a multiplication factor, will not change the shapes of the curves. Wherever slopes of such curves are taken (on log-log paper), the multiplication factor will not appear and the slope of any curve will be independent of units of variables, etc.

A. "Normal" Distribution of Diameters

Choosing this distribution of tube diameters, the fraction of tubes $\frac{dn}{N}$ having a diameter between D and $D + dD$ will be given by:

$$\frac{dn}{N} = \frac{m}{M} \times \frac{1}{\sqrt{\pi}} e^{-m^2(D - D_0)^2} dD$$

where N = total number of tubes

m = distribution modulus

M = area under the curve $y = \frac{m}{\sqrt{\pi}} e^{-m^2(x - \frac{1}{2})^2}$ between the limits of diameter chosen. (This makes the area under the distribution curve equal to unity, an obvious necessity).

D_0 = midpoint, or arithmetic mean, of diameters.

The velocity of the fluid through a pipe of diameter D depends on the type of flow. Using consistent units, the equations are:

Viscous Flow: $u = \frac{g}{32} \frac{\rho}{\mu} \left(\frac{\Delta p/L}{\rho} \right) D^2$

Turbulent Flow: $u = \left[(8g)^5 \frac{\rho}{\mu} \right]^{1/9} \left[\left(\frac{\Delta p/L}{\rho} \right)^5 D^6 \right]^{1/9}$

If we designate $\Delta h = \frac{4p}{L\rho}$, where Δh is the drop in head of fluid per unit length, the notation may be abbreviated to

$$u_V = C_V \Delta h D^2, \quad C_V = \frac{g}{32 \mu}$$

$$u_t = C_t (\Delta h^5 D^6)^{1/9}, \quad C_t = \left[(8g)^5 \frac{\rho}{\mu} \right]^{1/9}$$

Designating the diameter which separates the viscous from the turbulent flow as the "critical" diameter, d_c , the viscous and turbulent flow rates may be expressed as:

$$\begin{aligned} Q_V &= \int_0^{ds} \frac{\pi}{4} u D^2 \times \frac{1}{\sqrt{\pi}} \frac{m}{M} e^{-m^2(D - D_0)^2} dD \\ &= \frac{\pi}{4} \times (\Delta h) \frac{m}{M} C_V \int_0^{dc} \frac{1}{\sqrt{\pi}} D^4 e^{-m^2(D - D_0)^2} dD \end{aligned} \quad (47)$$

$$Q_t = \frac{\pi}{4} \frac{m}{M} C_t (\Delta h)^{5/9} \int_{dc}^1 \frac{1}{\sqrt{\pi}} D^{8/3} e^{-m^2(D - D_0)^2} dD \quad (48)$$

the limits being chosen as such since the larger tubes will be turbulent and the smaller viscous. Hence the values of Q_t , etc., represent "average" flow rates per tube. The total flow rate will be $Q_T (= Q_t + Q_V)$.

Turbulent Areas

There are two types of turbulent areas to be considered. The first is the actual, or "effectual", surface area which is

exposed to fluid in turbulent motion, i.e. the circumferential area of the tube. For a given diameter D , this value of J_t is πD per unit length. For a series of tubes, the value becomes

$$J_t = \pi \frac{1}{\sqrt{\pi}} \frac{m}{M} \int_{d_G}^1 D e^{-m^2(D - D_0)^2} dD \quad (49)$$

The second type of area may be termed the "effective turbulent" area, $\mathcal{J}_t$. This term takes into account the fact that a given area is more effective if the turbulence of the gas exposed to it is higher. Thus, 1 sq. ft. of area in contact with a gas with a Reynolds number of 200,000 has a higher KC than 1 sq. ft. where the Reynold number is, say, 100,000.

As mentioned earlier the value of KC for flow inside tubes is proportional to the 0.8 power of the Reynolds number. For turbulent flow the value of the Reynolds number is given by

$$\begin{aligned} Re_t &\equiv \frac{Du\rho}{\mu} = D \left[(8g)^5 \left(\frac{\rho}{\mu} \right) \right]^{1/9} \left[(\Delta h)^5 D^6 \right]^{1/9} \frac{\rho}{\mu} \\ &= \left[(8g)^5 \left(\frac{\rho}{\mu} \right)^{10} \right]^{1/9} (\Delta h D^3)^{5/9} \end{aligned}$$

The value of the "effective turbulent area" may then be expressed as

$$\begin{aligned} \mathcal{J}_t &= \pi \frac{1}{\sqrt{\pi}} \frac{m}{M} \int_{d_G}^1 Re^{0.8} D e^{-m^2(D - D_0)^2} dD \\ &= \left[(8g)^4 \left(\frac{\rho}{\mu} \right)^8 \right]^{1/10} \pi \frac{m}{M} (\Delta h)^{4/9} \int_{d_G}^1 \frac{1}{\sqrt{\pi}} D^{7/3} e^{-m^2(D - D_0)^2} dD \quad (50) \end{aligned}$$

In the graphs shown later, the ratios J_t/J_0 will be plotted, rather than J_t where J_0 is the total value of J_t , i.e. with $d_c = 0$. For J_t , no similar term may be defined because for $d_c = 0$, $\Delta h = \infty$ and $J_{t,0} = \infty$. In the plots, the factor $\left[(8g)^{0.4} \left(\frac{\rho}{\mu}\right)^{0.8}\right] \frac{m\pi}{M}$ will be omitted, since only the slope of this curve will be of importance.

Value of d_c .

The expressions defined above are directly dependent on the values of the "critical" diameter inasmuch as it enters into the integral explicitly as a limit of integration and implicitly into the value of Δh . Exclusive of the values of m , etc. which must be stated for a given problem, the relation of the "critical" diameter, d_c , to the pressure drop, Δh , is independent of such considerations and depends only on the nature of fluid flow, in general, and the properties of the transition of viscous to turbulent flow. The question to be answered is: Under what conditions of pressure drop and diameter, for a given fluid, will flow be turbulent or viscous. Various experiments have led to these conditions, which are in themselves, not mathematically specific:

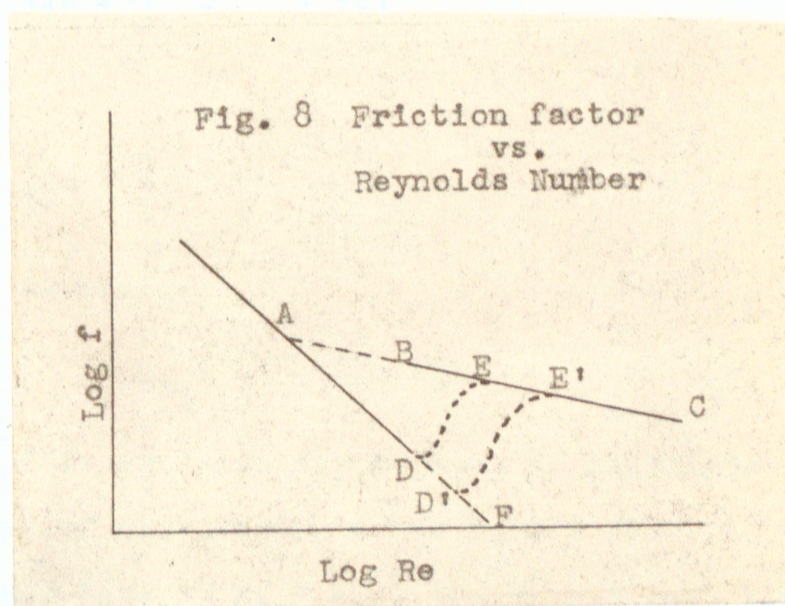
a) Viscous flow has no definite upper limit of Reynolds number, i.e. the change from viscous flow to turbulent depends not only on the Reynolds number but also on factors such as initial "quiescence" of the liquid, vibrations of the pipe, etc.

b) Turbulent flow tends to have a definite lower limit. It has been found that as this pressure drop in a pipe is lowered, the turbulent flow ceases to exist over a narrow range of Reynolds number approaches this range, the turbulence of the fluid decreases markedly and viscous movement occurs.

Since no definite mathematical criterion may be stated for a "critical" Reynolds number, a modification of the actual case must be made. In order to make a continuous function out of this discontinuous "break" in flow, a more convenient, but somewhat erroneous, criterion may be taken. The criterion may be stated as: Any flow that exists at a Reynolds number less than 1024 will be considered viscous, and any flow at a Reynolds number greater than 1024 will be considered turbulent.

The choice of the number 1024 is due to a simplification in the calculations to be made. Its implications have been noted fully by Tour⁽²⁹⁾ but a brief description of its properties will justify its choice. Figure 8 shows the familiar sketch of the friction factor, f , versus the Reynolds number. The line ADF represents the curve for viscous flow and line BC for turbulent flow (the approximate solution). If the curve BC is extended to intersect the viscous line the point of intersection will be at A. This point has been found to be 1024. Whereas turbulent flow does not actually exist along the line AB, it will here be assumed to do so. At point A, it will be seen that the

friction factor for both types of flow is the same. This equality of f implies that at this point the change of character of flow from viscous to turbulent is "smooth", i.e. the velocity remains the same.



While this is not the actual case, it has been found that the curves shown later more closely resemble those for the tower performance than if another type of point were chosen. One other choice that was made may be briefly described, to illustrate the point. This choice was the assumption that the transformation of flow may take place at a constant pressure drop, i.e. when the transformation occurs, it will do so without

a necessary increase in pressure drop. Under these conditions the Δh and d_c must be the same for the transition. This implies, of course, that the velocity will decrease due to the increased coefficient of friction. In terms of Reynolds numbers:

$$[\Delta h d^5]_t = \frac{[Re_t]^{9/5}}{(8g)(\frac{f}{\mu})^2}$$

$$[\Delta h d^5]_v = \frac{32}{g} \frac{Re_v}{(\frac{f}{\mu})^2}$$

Equating:

$$(Re_t)^{9/5} = 256 Re_v \quad (51)$$

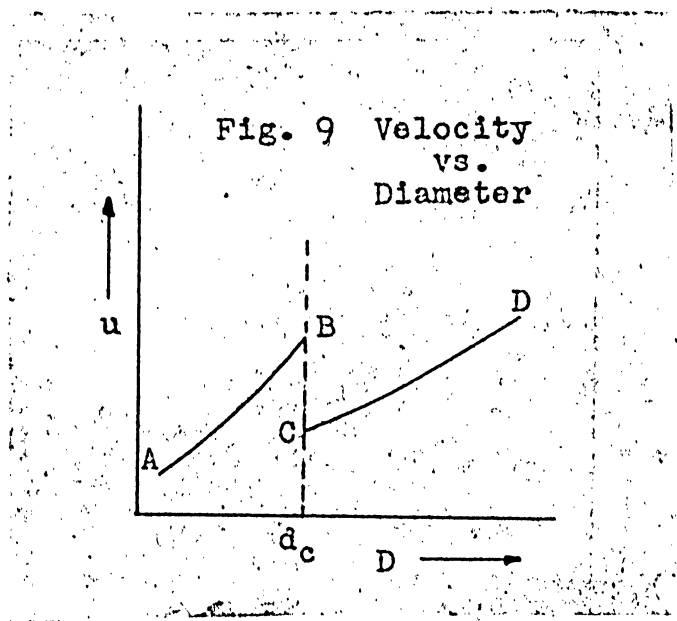
This equation may be used to calculate the Reynolds number of one type of flow after it has formed from the other. Thus, if turbulent flow at $Re = 2100$ transforms into viscous, the viscous flow will have a value of

$$Re_v = \frac{(2100)^{9/5}}{256} = 3730$$

This indicates an increase of velocity of 77.5% based on the turbulent values. A plot of velocity versus pipe diameter would be similar to Figure 9. AB represents viscous flow and CD represents turbulent flow. The break of C to B causes a distortion of any calculations made. It was found that a plot of

constant mechanical energy and vibration, the packing and liquid flow. Hence, any viscous air flow would not have much chance of going into the unstable viscous region.

pressure drop versus flow rate showed a point of inflection (on log-log paper) with slopes of approximately 4. This seemed so inconsistent with experimental data that this latter choice was rejected.



At the "critical" Reynolds number of 1024, the values of Δh for a given diameter may be obtained by equating Re_t or Re_v to 1024 in either of the formulae. The result is:

$$\Delta h d_c^3 = \frac{32}{g} \times \frac{1024}{\left(\frac{\rho}{\mu}\right)^2} \quad (52)$$

This is the equation which determines which tubes are in "turbulent" or "viscous" flow, according to the above definitions. It is felt that the use of the value 1024 is not too inaccurate since in a packed column the air flow is subjected to constant mechanical shocks and vibrations by the packing and liquid flow. Hence, any viscous air flow would not have much chance of going into the unstable viscous region.

Numerical Values of The Functions

The evaluation of the previous expressions numerically was made by choosing a standard range of tube sizes and distribution (as well as a typical fluid). The following choice was made for the example given:

Tube size: 0 to 1".

Distribution: For normal law distribution M was taken as 0.9900 with $D_0 = \frac{1}{2}$ ".

Fluid properties: = 0.0750 lbs./ft.³
 = 180×10^{-4} centipoise =
 $1.209 \times 10^{-5} \frac{\text{lbs.}}{(\text{ft.})(\text{sec.})}$

The previous functions were developed for the use of consistent units. For a specific case, the choice of units for Q's will be ft.³ fluid/hr. per tube while Δh will be in inches of H₂O/ft. of tube length. Any other expressions will be dimensionless or in arbitrary units.

The value of m is obtained by the probability expression:

$$\frac{m}{\sqrt{\pi}} \int_0^1 e^{-m^2(D - \frac{1}{2})^2} dD = 0.99000.$$

This may be expressed as:

$$\frac{2}{\sqrt{\pi}} \int_0^{m/2} e^{-u^2} du = 0.9900$$

and from tables (27),

$$\frac{m}{2} = 1.8214, \quad m = 3.6428$$

*This distribution is equivalent of specifying 99% of the area to be between 0 and 1" about a center of $\frac{1}{2}$ " under the normal curve of distribution. This serves as a convenient method to determine m.

Flow rates

$$Q_V = \frac{\pi}{4} \times \frac{3.6428}{2} \times \frac{\Delta h}{12} \times \frac{32.2}{32} \times \frac{0.0750}{(1.209 \times 10^{-5}) \times (144)^2} \int_0^{d_C} \frac{2}{\sqrt{\pi}} D^4 e^{-m^2(D-D_0)^2} dD$$

$$= 129.1 \Delta h I_V \text{ (ft.}^3\text{/hr./tube)} \quad (47a)$$

$$Q_t = \frac{\pi}{4} \times \frac{3.6428}{2} \times \left[\frac{(8 \times 32.2)^5 - 0.0750}{1.209 \times 10^{-5}} \right]^{1/9} \left(\frac{\Delta h}{12} \right)^{5/9} \int_{d_C}^1 \frac{2}{\sqrt{\pi}} D^{8/3} e^{-m^2(D-D_0)^2} dD$$

$$= 99.4 (\Delta h)^{5/9} I_t \text{ (ft.}^3\text{/hr./tube)} \quad (48a)$$

where

$$I_V = \int_0^{d_C} \frac{2}{\sqrt{\pi}} D^4 e^{-m^2(D-D_0)^2} dD$$

$$I_t = \int_{d_C}^1 \frac{2}{\sqrt{\pi}} D^{8/3} e^{-m^2(D-D_0)^2} dD$$

Turbulent Areas

$$J_t = \frac{\pi m}{12} \int_{d_C}^1 \frac{1}{\sqrt{\pi}} D e^{-m^2(D-D_0)^2} dD$$

Letting $u = m(D - D_0)$

$$J_t = \frac{\pi}{24m} \int_{m(d_C-D_0)}^{m(1-D_0)} \frac{2}{\sqrt{\pi}} (u + D_0 m) e^{-u^2} du$$

$$= \frac{\pi}{24m} \int_{u_C}^{u_1} \frac{2}{\sqrt{\pi}} u e^{-u^2} du + \frac{D_0 \pi}{24} \int_{u_C}^{u_1} \frac{2}{\sqrt{\pi}} e^{-u^2} du$$

$$= \frac{\pi}{48m} \left[\frac{2}{\sqrt{\pi}} e^{-u_C^2} - \frac{2}{\sqrt{\pi}} e^{-u_1^2} \right] + \frac{D_0 \pi}{24} [P(u_1) - P(u_C)] \quad (49a)$$

where

$$P(u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-x^2} dx$$

and, by the method of integration used here,

$$P(-u) = -P(+u)$$

For the transition point:

$$\begin{aligned} \Delta h d_C^3 &= \frac{32}{32.2} \frac{1024x(1.209 \times 10^{-5})}{(0.075)} \times 1728 \times 12 \\ &= 0.550 \end{aligned} \quad (52a)$$

The total surface, J_0 , is given by taking u_C for

$D = d_C$. Then $u_C = m(0 - D_0) = -\frac{m}{2}$, and

$$\begin{aligned} J_0 &= \frac{\pi}{48m} \left[\frac{2}{\sqrt{\pi}} e^{-\frac{m^2}{4}} - \frac{2}{\sqrt{\pi}} e^{-\frac{m^2}{4}} \right] + \frac{\pi}{48} \left[P\left(\frac{m}{2}\right) - P\left(-\frac{m}{2}\right) \right] \\ &= \frac{\pi}{48} \times 2P\left(\frac{m}{2}\right) = \frac{\pi}{48} \times 2 \times 0.99000 \end{aligned}$$

Using this value of J_0 , we may use the fraction of surface

which is turbulent as $J_t/J_0 (= j_t)$

$$j_t = \frac{J_t}{J_0} = \frac{1}{1.9800} \left\{ \frac{1}{3.6428} \left(\frac{2}{\sqrt{\pi}} e^{-u_C^2} - \frac{2}{\sqrt{\pi}} e^{-u_1^2} \right) + P(u_1) - P(u_C) \right\} \quad (53)$$

The "effective turbulent" area, $\mathcal{J}_t$, may be expressed as; omitting the physical property function,

$$\mathcal{J}_t = (\Delta h)^{4/9} \int_{d_C}^1 \frac{2}{\sqrt{\pi}} D^{7/3} e^{-m^2(D - D_0)^2} dD$$

or, again omitting the constant relating Δh to d_C ,

$$J_t = \frac{1}{d_c^{4/3}} \int_{d_c}^1 \frac{2}{\sqrt{\pi}} D^{7/3} e^{-m^2(D - D_0)^2} dD \quad (54)$$

This will be the function actually plotted later, since the slope, rather than the absolute values will be of interest. The value of the integral must be determined by numerical methods, as for I_v and I_t .

Evaluation of the integrals

Except for the value of J_t/J_0 , the integrals are too difficult to evaluate by means of simple functions. Hence all were evaluated by numerical methods. The specific type chosen was the Gauss three-point method (22). The interval of 0 - 1" was divided into ten subdivisions and the values of the integrals for each subdivision computed by the Gauss method. The total value of the integrals was then computed by adding together the correct number of subdivisional integrals. The values of the integrals for this case are given in table II in the appendix.

Pressure drop - Flow Rate Relations

Having the values of the necessary integrals, the values of viscous, turbulent and total flow rates may be computed from equation (47a) and (48a). The results in terms of each of the flow rates and the amount of channeling γ are included in table II. The plot of Q_v , Q_t and Q_T versus the pressure drop, Δh , is shown in figure 10. Also plotted is a curve of γ versus Q_T . The significance of these curves will be discussed at a later point.

Other Distributions of Diameters

In order to ascertain any effect of changing the shape of the probability curve, other values of "m" were chosen. The first value was $m = 2.6328$ which corresponds to 90% of the area under the "normal" curve between 0 and 1 inch. The calculated quantities for this choice are given on Table III and plotted in figure 12. For convenience, in the tables, only Q_T and γ are listed for the flow rates. However, the numerical equations of Q_V and Q_t are given below in the tables.

For the extreme case, a uniform distribution of diameters was chosen, i.e. the same number of each size tubes. In this case $\frac{dn}{N} = 1 \times dD$ and the previous expressions for Q_V , etc. may be integrated directly to give:*

$$\begin{aligned}
 Q_V &= \frac{\pi}{4} \times 3.61 \times \frac{3600}{144} \Delta h \int_0^{d_C} D^4 dD \\
 &= \frac{\pi}{4} \times 3.61 \times \frac{3600}{144} \times \frac{0.550}{d_C^5} \times \frac{d_C^5}{5} \\
 &= 7.79 d_C^2
 \end{aligned} \tag{55}$$

Similarly:

$$\begin{aligned}
 Q &= \frac{\pi}{4} \times 2.77 \times \frac{3600}{144} \times \left(\frac{0.550}{d_C^5} \right)^{5/9} \int_{d_C}^1 D^{8/3} dD \\
 &= 10.66 \left(\frac{1}{d_C^{5/3}} - d^2 \right)
 \end{aligned} \tag{56}$$

*The numbers 3.61 and 2.77 are the values of C_V and C_t in equation (47) and (48) respectively for Δh expressed in inches of H_2O per ft. length of tube and D expressed in inches.

$$J_t = \frac{\pi}{12} \int_{d_c}^1 D \, dD = \frac{\pi}{12} (1 - d_c^2)$$

and

$$\frac{J_t}{J_o} = 1 - d_c^2 \quad (57)$$

$$J_t = \frac{1}{d_c^{4/3}} \int_{d_c}^1 D^{7/3} \, dD = \frac{3}{10} \left(\frac{1}{d_c^{4/3}} - d_c^2 \right) \quad (58)$$

The numerical values corresponding to these functions are given in Table III and plotted in figure 13.

B. "Normal" Distribution of Squares of Diameters.

Since the exact type of distribution of diameters in a packed column is unknown, other types of distributions should be tested to see if they more closely conform to the experimental data. Rather than relying on a "normal" distribution of diameters, a skewed distribution was tested. To do this, a "normal" distribution of the squares of the diameters (which corresponds to a normal distribution of cross-section areas) was used. The distribution equation then became:

$$\begin{aligned} \frac{dn}{N} &= \frac{m'}{\sqrt{\pi}} e^{-m_1^2 (D^2 - D_o^2)^2} d(D^2) \\ &= 2 \frac{m'}{\sqrt{\pi}} D e^{-m_1^2 (D^2 - D_o^2)^2} dD \end{aligned} \quad (59)$$

If the same range of diameters is chosen, i.e. 0 - 1", then $D_o^2 = \frac{1}{2}$ and $D_o = 0.7071$, so that the distribution curve

has been skewed with respect to D and moved to a new midpoint. Using, for comparison, a value of $m = 3.6428$ (for 99% of the values of D^2 to be between 0 and 1), the new values of the integrals become:

$$Q_V = \frac{\pi}{4} m' \times 3.61 \times \frac{3600}{144} \times \Delta h \int_0^{d_C} \frac{2}{\sqrt{\pi}} D^5 e^{-m'^2(D^2 - D_0^2)^2} dD \quad (60)$$

$$= 2 \times 129.1 \Delta h I_V$$

$$Q_t = \frac{\pi}{4} m' \times 2.77 \times \frac{3600}{144} \times (\Delta h)^{5/9} \int_{d_C}^1 \frac{2}{\sqrt{\pi}} D^{11/3} e^{-M'^2(D^2 - D_0^2)^2} dD \quad (61)$$

$$= 2 \times 199.4 (\Delta h)^{5/9} I_t$$

$$J_t = \frac{\pi}{12} \times m' \int_{d_C}^1 \frac{2}{\sqrt{\pi}} D^2 e^{-m'^2(D^2 - D_0^2)^2} dD \quad (62)$$

$$J_t = \frac{1}{d_C^{4/3}} \int_{d_C}^1 \frac{2}{\sqrt{\pi}} D^{10/3} e^{-m^2(D^2 - D_0^2)^2} dD \quad (63)$$

All of these integrals were evaluated numerically.

The results are tabulated in Table V and are plotted in figure 14.

C. "Normal" Distribution of Cubes of Diameters

In analogy to the "normal" distribution of cross-sectional areas, the "normal" distribution of the cubes of diameters was considered to be representative of a tower where the distribution of volumes followed the "normal" law of probability.

The introduction of the idea of the third dimension of height into the probability function complicates the exact

formulation of the flow equations. Since the flow through spherical shapes, etc., is complicated by enlargement and contraction losses, the distribution of volumes was modified to the concept of flow through tubes. This furnishes a better method of comparing the results with the previous distributions.

The probability function chosen is now:

$$\begin{aligned}\frac{dn}{N} &= \frac{m''}{\sqrt{\pi}} e^{-(m'')^2 (D^3 - D_0^3)^2} d(D^3) \\ &= 3 \frac{m''}{\sqrt{\pi}} D^2 e^{-(m'')^2 (D^3 - D_0^3)^2} dD\end{aligned}\quad (64)$$

Again choosing the range of D to be 0 - 1 inch with $D_0^3 = \frac{1}{8}$, and $m'' = 3.6428$, the equations for the various functions become:

$$\begin{aligned}Q_V &= 3 \times 129.1 \times \Delta h \int_0^{d_C} \frac{2}{\sqrt{\pi}} D^6 e^{-(m'')^2 (D^3 - D_0^3)^2} dD \\ &= 387.3 \Delta h I_V\end{aligned}\quad (65)$$

$$\begin{aligned}Q_t &= 3 \times 99.4 \times (\Delta h)^{5/9} \int_{d_C}^1 \frac{2}{\sqrt{\pi}} D^{14/3} e^{-(m'')^2 (D^3 - D_0^3)^2} dD \\ &= 298.2 (\Delta h)^{5/9} I_t\end{aligned}\quad (66)$$

$$J_t = \frac{\pi}{12} m'' \int_{d_C}^1 \frac{2}{\sqrt{\pi}} D^3 e^{-(m'')^2 (D^3 - D_0^3)^2} dD \quad (67)$$

$$f_t = \frac{1}{d_C^{4/3}} \int_{d_C}^1 \frac{2}{\sqrt{\pi}} D^{13/3} e^{-(m'')^2 (D^3 - D_0^3)^2} dD \quad (68)$$

The values of these functions were computed after suitable numerical integration and are tabulated in Table VI and are plotted in figure 15.

- (1) Viscous Gas Flow Rate, Q_v
 (2) Turbulent Gas Flow Rate vs Pressure gradient, Δh
 (3) Total Gas Flow Rate, Q_T

Fig. 10

Fraction of Gas Channeled, γ , vs Total Flow Rate, Q_T

for Normal Distribution of Diameters with $m = 3.6428$

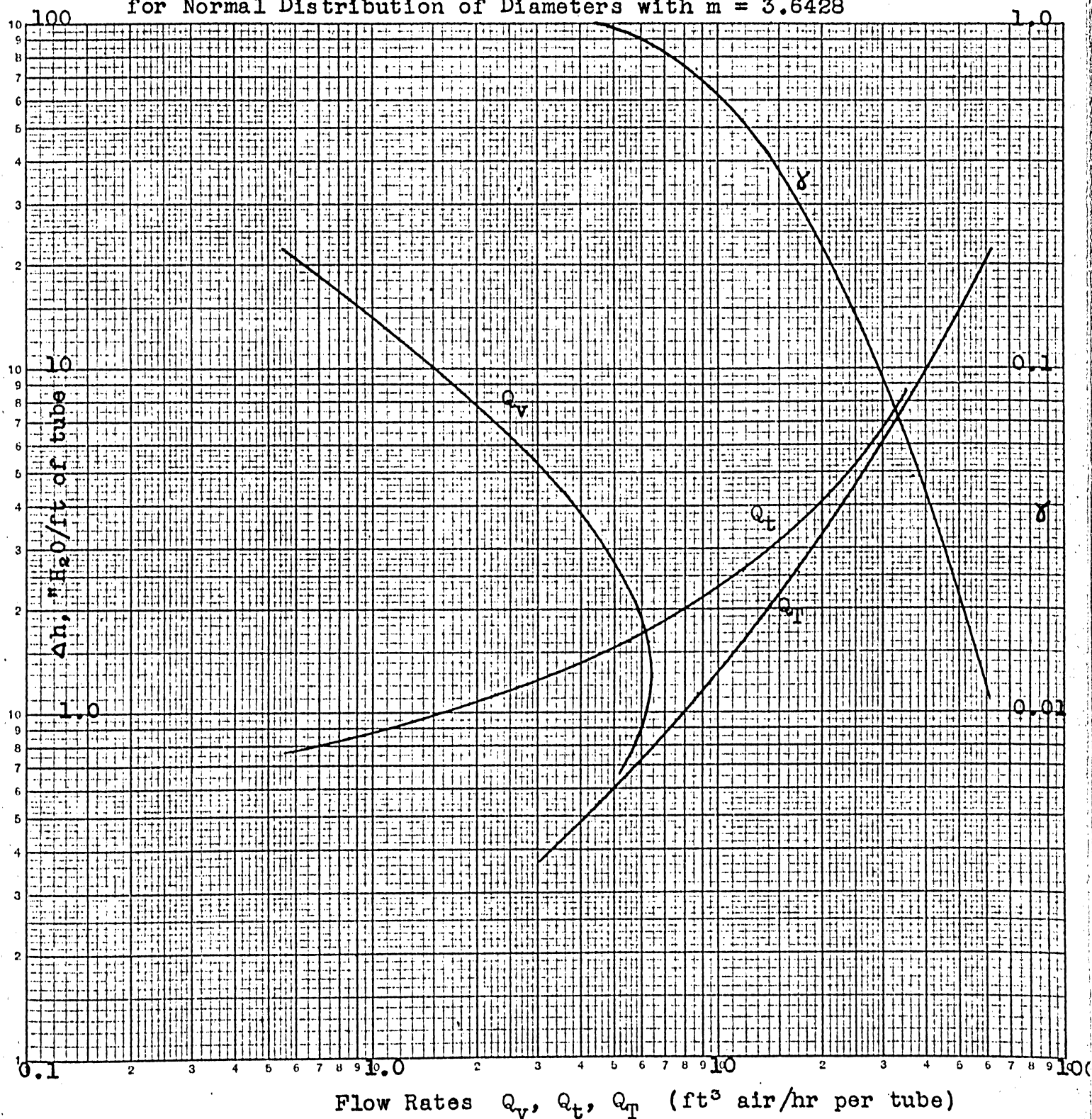
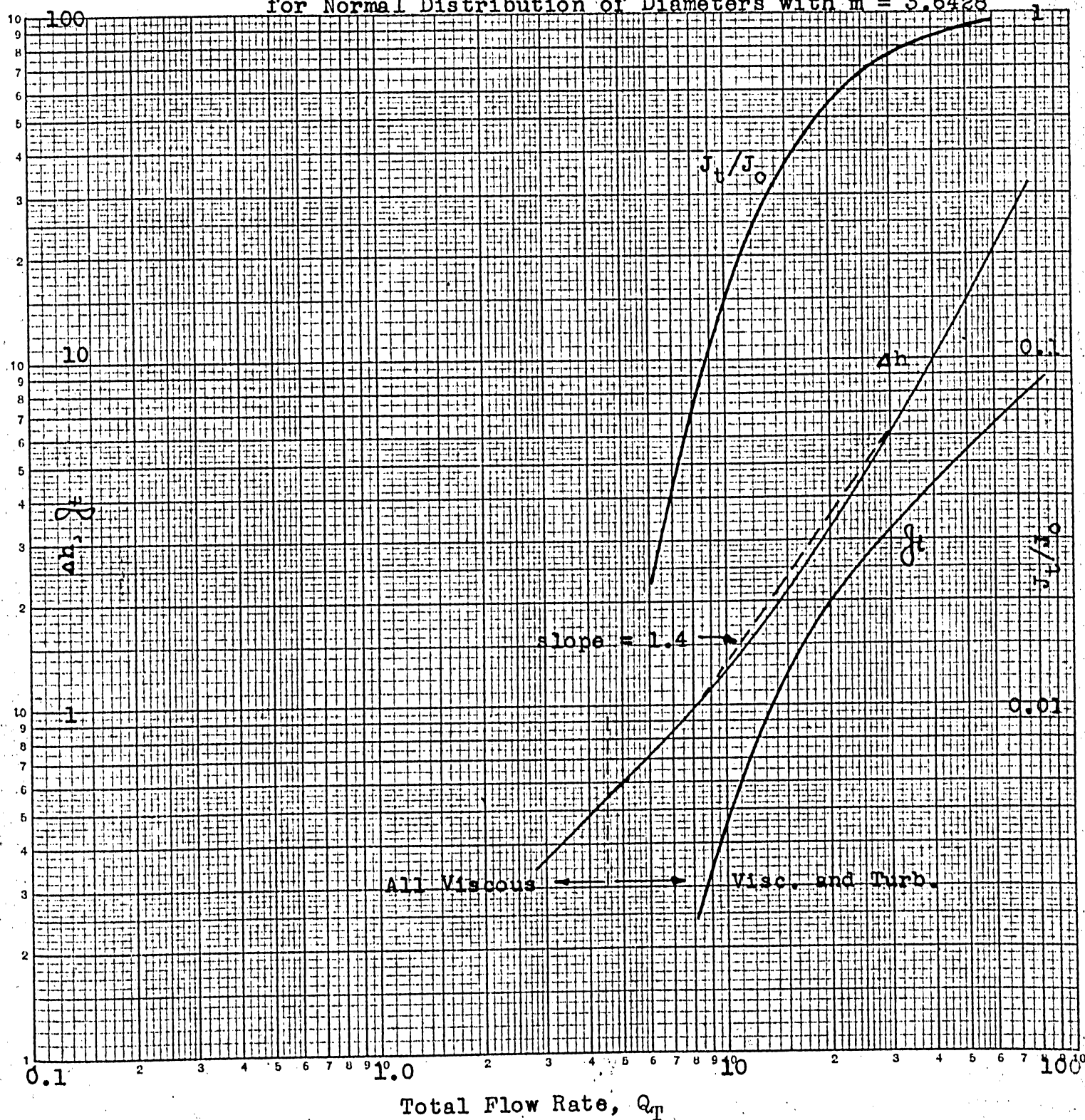


Fig. 11 (1) Pressure gradient, Δh
 (2) Fraction of effectual area, J_t/J_o
 (3) Effective area, J_t
 vs.
 Total Flow Rate, Q_T

for Normal Distribution of Diameters with $m = 3.6428$



Total Flow Rate, Q_T

- (1) Pressure Gradient, Δh
 (2) Fraction of effectual area, J_t/J_o

Fig. 12

vs

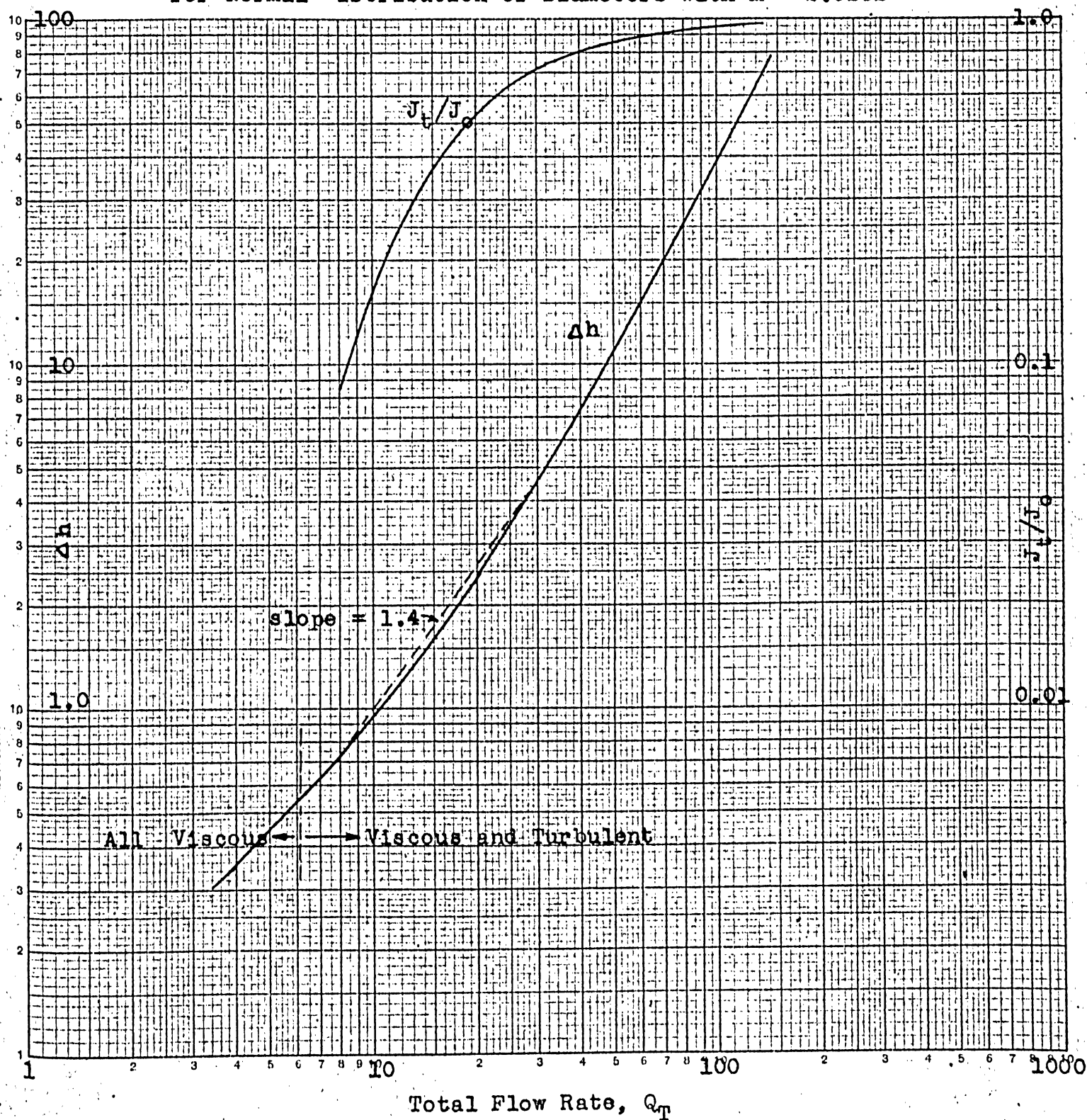
Total Flow Rate, Q_T for Normal Distribution of Diameters with $m = 2.3262$ 

Fig. 13

- (1) Pressure gradient, Δh
 (2) Fraction of effectual area, J_t/J_o
 (3) Effective area, J_t
 vs
 Total Flow Rate, Q_T

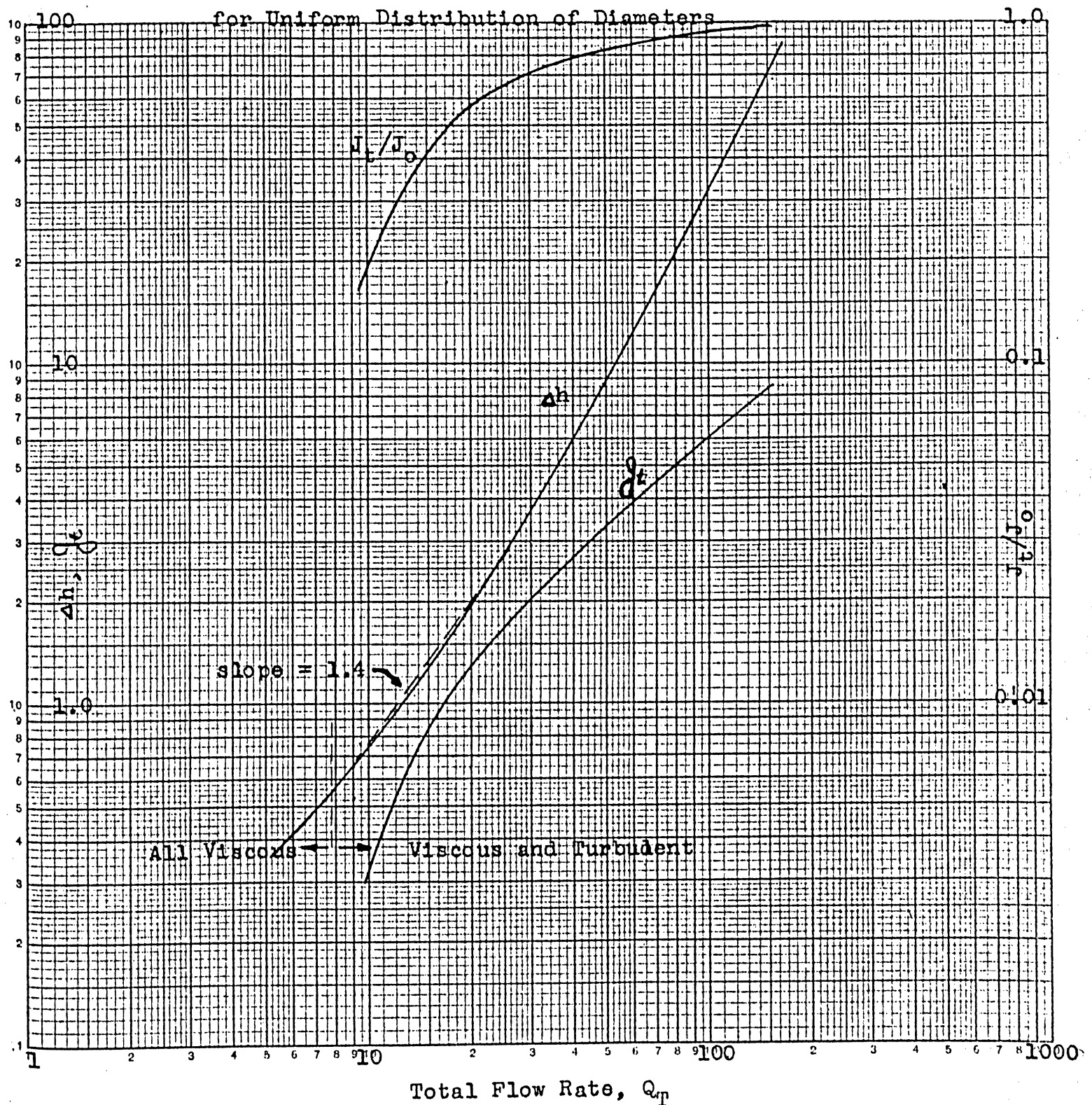


Fig. 14

- (1) Pressure gradient, Δh
 (2) Fraction of effectual area, J_t/J_0
 (3) Effective area, J_t
 vs

Total Flow Rate, Q_T

for Normal Distribution of Squares of Diameters with $m' = 3.6428$

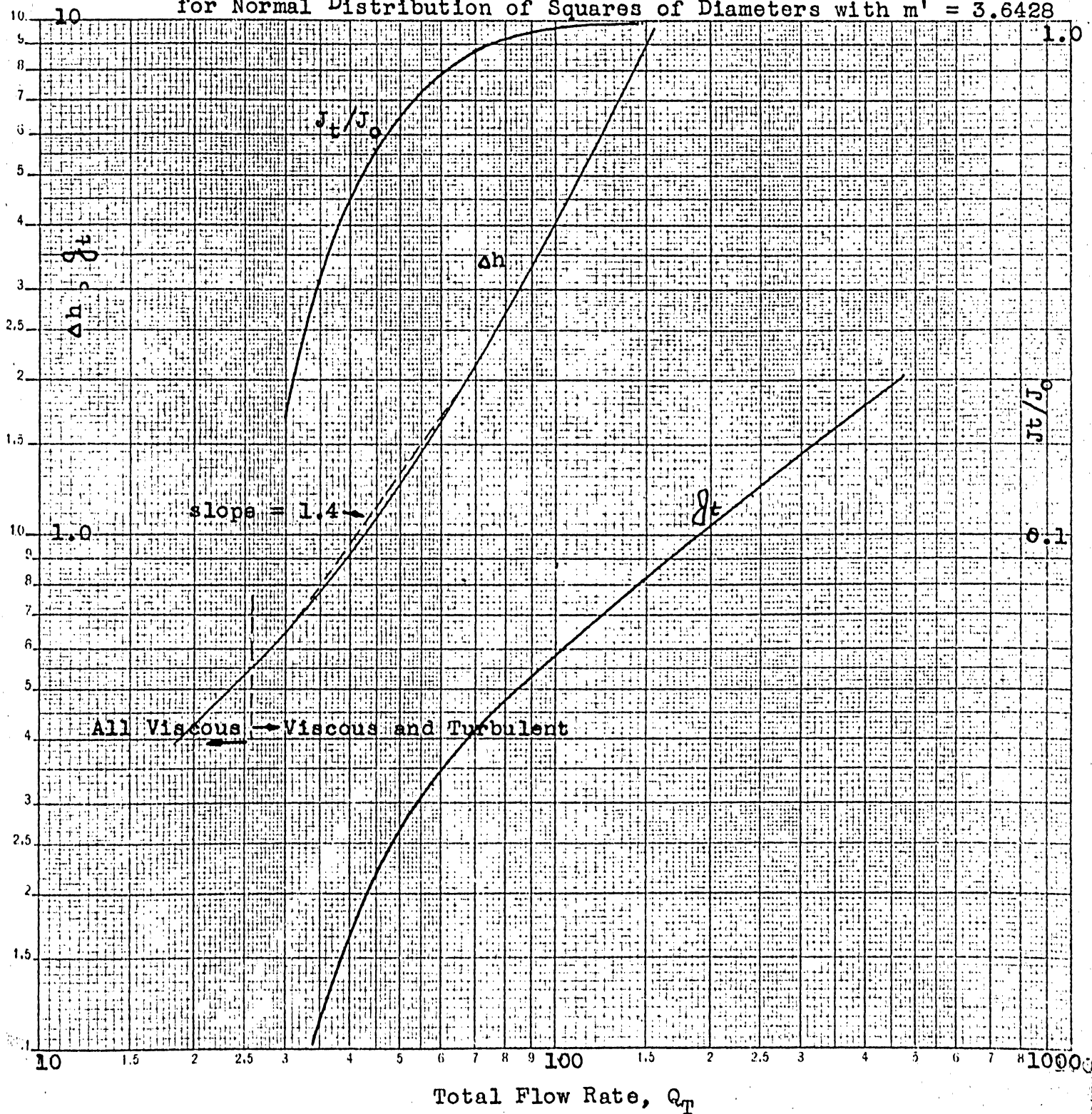
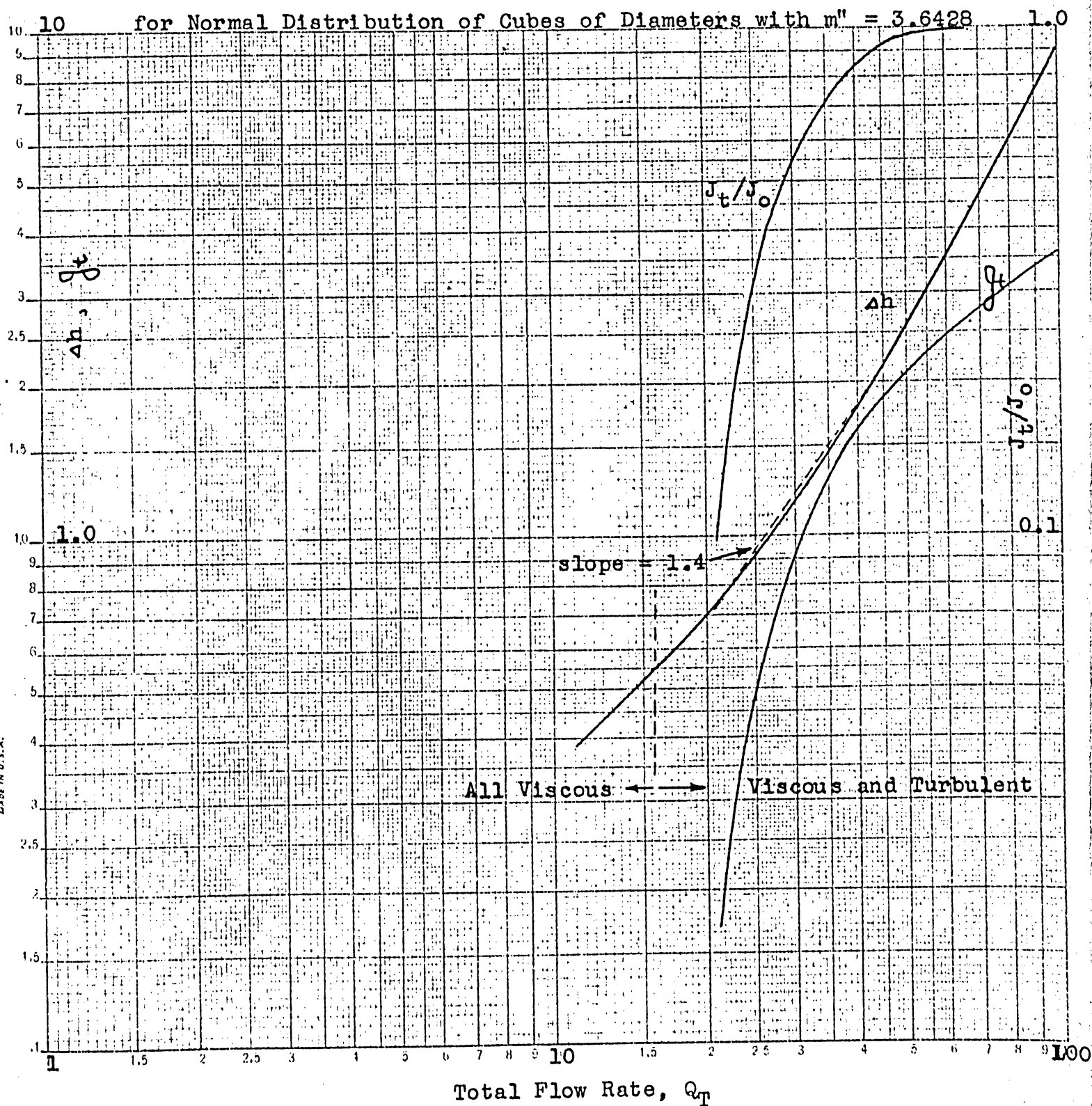


Fig. 15 (1) Pressure gradient, Δh
 (2) Fraction of effectual area, J_t/J_o
 (3) Effective area, J_t
 vs
 Total Flow Rate, Q_T



Interpretation of Graphs

The curves of Figure 10 for a "normal" distribution of diameters show the typical variations of the individual and total flow rates as a function of the pressure drop. The presence of a maximum value of Q_V arises due to the fact that for such a distribution chosen, the value of I_V remains fairly constant at low values of Δh (or high d_G) and then, as Δh increases, it drops off sharply, causing the value of $\Delta h \times I_V$ to decrease.

Of more interest is the plot of Δh vs Q_T since this curve should be similar to the familiar pressure drop curves for packed towers. Referring to figure 11, where the curve is repeated, it may be seen that at the lower values of Q_T , below the vertical dashed line, the total flow is viscous and the slope of the line is unity. As Q_T (or Δh) increases, the slope of the pressure drop curve increases evenly to 1.8 as a limit.

As mentioned previously, quite often slopes of about 1.4 occur. Under the pressure drop curve (on each of the subsequent figures) is drawn a line of slope 1.4 extending over the Q_T range for which the pressure drop curve also has a reasonably constant slope of 1.4. These lines will serve to locate the appropriate values of flow rates to discuss the effect of channeling. It is to be noted the range of pressure drops for these lines to represent the curves are about 5 to 1 or 3 to 1 (in the later graphs). This range is fairly representative of experimental curves before the "loading" or "flooding" points are reached.

The fraction of effectual surface area, J_t/J_o , as shown in figure 11, varies widely over the range of flow rates included by the line of 1.4 slope. At the lower values of Q_T , there is only about 7% of the actual area being used for absorption. As the flow rate increases, the fraction rises to about 60%, indicating that still a great portion of the area is not being used. By referring back to figure 10, the range of the amount of fluid channeled decreases from 75% to 20% of the total flow rate. The low amounts of active surface and turbulent fluid emphasizes the decrease in efficiency caused by the presence of different sizes of tubes.

The variation of the "effective" area, i.e. a measure of $KC \times J_t$, is found to be greater than that noted where both pressure drop and absorption data are available. Over the particular range noted here, the slope of the line J_t is about 1.4 or 1.5. In the case of William's data for the absorption of NH_3 in water a slope of 1.0 was obtained for $K_G a$ vs gas rate. The higher values of exponents are illustrated by some of the data of Simmons (shown in Sherwood or Perry) at the very low gas rates. At the higher gas rates $K_G a$ is proportional to the 0.8 power of the gas rate but at the lower gas rates (and liquid rates) the slope increases to a value of 1.3 although in the actual graph a line of 0.8 slope is shown.

The curves of figures 12-15 show substantially the same shapes of each curve. Depending on how accurately the line of slope of 1.4 is placed, the values of J_t/J_0 will increase from about 20% to 70-80% as the upper limit. In all cases, the amount of channeling decreases from 50% to about 10%, as estimated by interpolation in the tables in the appendix.

The close agreement of the values of channeling, etc. from these curves indicates that the exact distribution of the tube sizes is not critical so long as the variation of quantities are considered. This is undoubtedly due to the fact that the independent variable in all the calculations is Δh (or d_c). Once, for any distribution of tube sizes, either Δh or d_c is specified, then all other quantities may be computed. Hence, Q_T is a dependent variable and the graphs of J_t/J_0 , f_t , etc. vs Q_T represent a plot of one dependent variable against another. Such plots must then cancel out the essential differences between conditions which change for each graph, viz. the change of distribution of tube sizes.

The application of the graphs to the effect of gas rate of KCJ where the liquid resistance is appreciable or controlling is incorrect since the functions used for the evaluation of f_t must be modified. Whereas the value of KC for the gas film controlling was taken as proportional to the 0.8 power of the gas velocity, the variation of KC, where the liquid resistance is appreciable, with the gas velocity will be of the form of

equation (17). If KC is independent of the gas velocity, once the gas flow has become turbulent, then the curve for f_t for this case should correspond closely to the curves of J_t/J_0 . At the slope of the pressure drop curve of 1.4 or 1.5, the slope of the J_t/J_0 curve is approximately unity. But as noted previously, the experimental exponent on the gas rate for its effect on KCJ is about 0.20.

The low value of 0.20 for this exponent indicates that the extent of turbulence in the gas stream has but little effect for this case and emphasizes the importance of the condition of the liquid flow, i.e. the effect of channeling of the liquid must also be considered in such plots. Thus for the case of the liquid resistance controlling, if turbulent gas comes into contact with viscous liquid, or dry packing, there will be little or no absorption and the "effectiveness" of the area exposed to the turbulent gas will be small or zero.

The use of the example of a tube bundle in determining the effect of liquid rate on the liquid resistance is not applicable since the space between the packing does not run full, and since the pressure drop on the liquid is always constant: the force of gravity.

However, a simpler qualitative effect of spreading of the liquid over a surface may be made by again considering the equations of flow of films (29). The flow rate of the fluid is proportional to the breadth of the liquid film and to a function

of the thickness of the liquid film. As more liquid is forced to flow over the surface, the liquid will tend to spread further over the surface until the entire surface is wetted. If the film thickness remains constant, the amount of wetted area available for absorption will vary as the first power of the liquid flow rate. Once the surface is completely wetted, a further increase in liquid flow rate will cause an increase in the film thickness, which results in a change in the liquid turbulence. Then the area for absorption is constant and the value of KC will increase at a rate less than the first power of the liquid rate.

Thus, the presence of exponents of 1.0 on the liquid rate (for the variation of KCJ) indicates only a change in J , not KC . The lower exponents of 0.7 or 0.8 indicate a simultaneous increase in the wetted surface and turbulence of the liquid. Since the exact effect of turbulence of the liquid on KC is unknown, there is no way to determine from the above exponents just how much increase in wetted area is included in the values of 0.7 and 0.8.

It is felt that such examples as worked out for the channeling of the gas, indicate that a large portion of the packing may be ineffective for absorption and the presence of channeling, as well as a relative idea of its magnitude may be detected from pressure drop data. The lack of simultaneous absorption data and pressure drop data in the literature indicates the complete disregard for a possible correlation between the two. It is believed that the validity of absorption data (for a constant value of J) could be easily confirmed by noting how closely the slope of pressure drop curves approximated 1.8. Much of the pressure drop data published (2, 18, 23) show exponents lower than 1.8, which serves to show that J does vary widely with liquid and gas rates. However, a strictly theoretical evaluation of J_t/J_0 , etc. from examples as these merely confirm the idea of using such pressure drop data. The actual numerical evaluation of J_t/J_0 awaits a suitable experimental technique.

Recent Methods of Evaluating Wetted Area

One of the most logical methods proposed to actually measure the "effectual" area in a packed tower has been proposed by Weisman and Bonilla (37) based on the work of Hougen, Gamson and Thodos (15). The latter workers evaluated numerical values of K_C for the evaporation of water into air by porous packings filled with water. The value of $K_C J$ (or $K_G a$) was computed and since J was the total surface, the value of K_C (or K_G) could be evaluated.

Weisman and Bonilla used the same shape packings as Hougen, et. al, but made the packing non-porous and used a flow of water over the packing. By measuring $K_C J$ under these conditions and computing the value of K_C from the data of Hougen, the value of J_t or J_t/J_o was obtained. By obtaining simultaneous heat transfer data, the value of J_t/J_o for heat transfer could also be obtained.

Their results indicated that J_t/J_o for humidification varied as the 0.3 power of the gas rate and the 0.5 power of the liquid rate. While their experimental procedures and method of rectifying the data are open to criticism, it is interesting to note that they obtained values of J_t/J_o of 4-25%, indicating the very low efficiency of the packing. Such methods were applied to larger sized towers based on the data of other investigators. The same low values of J_t/J_o were obtained but the erratic forms

of equations obtained cast doubts upon the validity of the results.

The general method of evaluating J_t/J_o seems more reliable and direct than any others proposed. As yet no data has been presented on the absorption of gases but rather the data have all been concerned with the evaporation of liquids or sublimation of solids into gas streams. The extension of this method to absorption of soluble gases to porous packings and the evaluation of "effectual" area in packed towers seems highly desirable.

Summary

The presence of "channeling" has been indicated by both absorption and pressure drop data. The evaluation of the amount of gas channeled in a packed tower by means of absorption data has been found to be indeterminate due to the cancellation of the explicit value of channeling from the comparison of absorption equations for duplicate absorption data. This indicates that the values of absorption coefficients, which are based on the assumption of no channeling, may be used to correctly design towers if the same design equation is used. The errors simply cancel to yield a correct final answer. However, due to the fact that the amount of channeling varies with gas and liquid flow rates as well as with types of packing, the numerical value of absorption coefficients will be of no use for purposes of correlation.

The relative magnitudes and effects of channeling may be approximated from pressure drop data. By choosing various distributions of tubes of different sizes (in parallel), it is possible to compute the pressure drop-flow rate characteristics, effectual (or turbulent) surface area and the effectiveness of the turbulent surface area for the set. By comparing the computed pressure drop curves with the experimental curves, it is estimated that only 20-75% of the total available surface for absorption may be in actual use.

This range of values of "effectual" area are even higher than those reported by Weisman and Bonilla (37) for the wetting of glass spheres. The amount of gas which may be in viscous flow, thus being ineffective for absorption, ranges from 10-50% of the total flow. The variation of the "effective" area, i.e. KCJ , with flow rate, for the examples worked out, is found to be approximately as the 1.3 or 1.4 power of the flow rate. This variation is slightly higher than that usually noted although a few data do show such a variation. In particular, some data for liquid resistances tend to closely parallel the numerical example.

It is believed that the use of pressure drop data for detecting the presence of channeling in packed towers has long been overlooked. The deviation of the exponent on the gas rate from 1.8 is a good indication of just how serious the overall effect may be.

The experimental determination of effectual areas for absorption has just begun to be undertaken. The work of Hougen, Gamson and Thodos⁽¹⁵⁾ has laid a good foundation for the determination of values of KC , so that, knowing values of KCJ , the estimation of J may be made. Such work would supplement the use of pressure drop data for the verification of channeling quite well.

Appendix

Table II - Normal Distribution of Diameters
(Area under normal error curve = 99%)

A. Values of Integrals and Related Quantities.

d_G	Δh	$(\Delta h)^{5/9}$	I_V	I_t	J_t/J_0	f_t
1.0	0.5500	0.7269	0.06415	0	0	0
0.9	0.7540	0.8664	0.05782	0.00685	0.0279	0.0805
0.8	1.073	1.054	0.04628	0.02129	0.0984	0.3058
0.7	1.600	1.317	0.03090	0.04396	0.2342	0.7604
0.6	2.545	1.703	0.01614	0.07014	0.4325	1.531
0.5	4.396	2.308	0.006175	0.09209	0.6508	2.641
0.4	8.588	3.345	0.001593	0.10516	0.8301	4.114
0.3	20.36	5.407	2.436×10^{-4}	0.11043	0.9384	6.407
0.2	68.71	10.63	1.686×10^{-5}	0.11178	0.9850	11.18
0.1	550.0	33.73	2.724×10^{-7}	0.11195	0.9982	28.24
0.0	∞	∞	0	0.11196	1	∞

B. Values of Flow Rates

d_G	Q_V	Q_t	Q_T	γ
1.0	4.550	0	4.550	1
0.9	5.630	0.588	6.218	0.852
0.8	6.42	2.235	8.66	0.744
0.7	6.37	5.540	11.91	0.526
0.6	5.31	11.83	17.14	0.310
0.5	3.505	21.06	24.57	0.143
0.4	1.765	34.90	36.66	0.0481
0.3	0.639	59.05	59.69	0.0107
0.2	0.1496	117.9	118.0	0.00127
0.1	0.0162	3740	3740	0.00004
0.0	0	∞	∞	0

Table III - Normal Distribution of Diameters
(Area under normal error curve = 90°/o)

d_c	I_v	I_t	Q_T	γ	J_t/J_o
1.0	0.1205	0	6.06	1	0
0.9	0.08992	0.03277	8.21	0.757	0.0927
0.8	0.05976	0.07025	11.07	0.530	0.2202
0.7	0.03475	0.1074	15.03	0.338	0.3755
0.6	0.01692	0.1389	20.58	0.192	0.5424
0.5	0.00664	0.1615	28.94	0.092	0.6998
0.4	0.00197	0.1749	42.7	0.036	0.8288
0.3	3.90×10^{-4}	0.1811	69.8	0.010	0.9133
0.2	3.96×10^{-5}	0.1832	137.1		0.9717
0.1	8.83×10^{-7}	0.1836			0.9947
0	0	0.1836	∞	0	1

$$Q_v = 916.2 \Delta h I_v$$

$$Q_t = 70.43 (\Delta h)^{5/9} I_t$$

Table IV - Uniform Distribution of Diameters

d_C	Q_T	γ	J_t/J_o	f_t
1.0	7.79	1	0	0
0.9	9.42	0.669	0.1900	0.5408
0.8	13.62	0.366	0.3600	0.7065
0.7	17.90	0.213	0.5100	1.109
0.6	23.95	0.117	0.6400	1.616
0.5	33.08	0.058	0.7500	2.270
0.4	48.6	0.026	0.8400	3.23
0.3	78.9	0.009	0.9100	4.89
0.2	155.4		0.9600	8.51
0.1	495		0.9900	21.53
0	∞	0	1	∞

$$Q_V = 7.79 d_C^2$$

$$Q_t = 10.66 \left(\frac{1}{d_C^{5/3}} - d_C^2 \right)$$

$$\frac{J_t}{J_o} = 1 - d_C^2$$

$$f_t = \frac{1}{d_C^{4/3}} - d_C^2$$

Table V - Normal Distribution of Squares of Diameters
(Area under normal error curve = 99%)

dG	I _V	I _t	Q _T	γ	J _t /J _o	f _t
1.0	180,380x10 ⁻⁶	0	25.65	1	0	0
0.9	94,250	0.0918	34.20	0.538	0.3122	0.1076
0.8	43,980	0.1545	44.50	0.274	0.5622	0.2140
0.7	16,840	0.1941	58.2	0.1198	0.7651	0.3256
0.6	4,484	0.2157	75.7	0.0390	0.9022	0.4492
0.5	843	0.2236	103.5	0.00913	0.9675	0.5969
0.4	117	0.2240	149.2	0.00174	0.9907	0.8126
0.3	11.6	0.2241	240.7	0.00025	0.9977	1.195
0.2	0.64	0.2241	473	2.41x10 ⁻⁵	0.9995	2.054
0.1	0.0075	0.2241	1500	7.08x10 ⁻⁷	0.9999	5.175
0.0	0	0.2241	∞	0	1	∞

$$Q_V = 258.2 \Delta h I_V$$

$$Q_t = 198.8 (\Delta h)^{5/9} I_t$$

Table VI - Normal Distribution of Cubes of Diameters
(Area under normal error curve = 99.7%)

d_C	I_V	I_t	Q_T	γ	J_t/J_o	f_t
1.0	$74,220 \times 10^{-6}$	0	15.81	1	0	0
0.9	58,340	0.01737	21.48	0.792	0.1336	0.0205
0.8	24,640	0.05928	28.82	0.355	0.5126	0.0836
0.7	5,744	0.08663	37.43	0.0950	0.8116	0.1481
0.6	955.7	0.09493	49.00	0.0192	0.9572	0.2008
0.5	136.2	0.09669	66.6	0.0035	0.9888	0.2614
0.4	17.09	0.09703	96.6	5.87×10^{-4}	0.9971	0.3534
0.3	1.638	0.09709	155.8	8.2×10^{-5}	0.9993	0.5190
0.2	805×10^{-10}	0.09710	306.8	7.0×10^{-6}	0.9999	0.8913
0.1	5.88"	0.09710	973	1.3×10^{-7}	1.0000	2.246
0.0	0	0.09710	∞	0	1	∞

$$Q_V = 387.3 \Delta h \times I_V$$

$$Q_t = 298.2 (\Delta h)^{5/9} I_t$$

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