

UNIVERSITY OF CINCINNATI

May 7, 1949

I hereby recommend that the thesis prepared under my supervision by Stanley H. Jury
entitled "Drying of Gases. The Adsorption Wave in Desiccant Beds"

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

Approved by:

William Licht Jr.
R. B. Jones
John F. Kahler

DRYING OF GASES. THE ADSORPTION WAVE
IN DESICCANT BEDS

A dissertation submitted to the
Graduate School of Arts and Sciences
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1949

by

Stanley H. Jury

Ch.E. University of Cincinnati 1942

M.Ch.E. University of Louisville 1947

UNIVERSITY OF CINCINNATI
LIBRARY
1949

UMI Number: DP15837

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI[®]

UMI Microform DP15837
Copyright 2009 by ProQuest LLC
All rights reserved. This microform edition is protected against
unauthorized copying under Title 17, United States Code.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

Table of Contents

	Page
List of Tables	i
List of Figures	iii
List of Symbols	v
Acknowledgements	ix
Abstract	x
Introduction	1
History	4
Structural Features of Soluble Anhydrite	6
The Diffusion Coefficient	22
Generalized Theory of the Adsorption Wave	27
Experimental:	
Static Tests:	
Procedure	42
Results	48
Discussion	58
Dynamic Tests:	
Outline of the Dynamic Experiments	68
The Frost Point Hygrometer	70
Procedure	102
Results	112
Discussion	123
Summary and Conclusions	137
Literature Cited	140
Appendix:	
Schumann-Furnas Chart	145

	Page
Reference Tables	149
Original Data	154
Commentary	179

List of Tables

Table No.		Page
I	Crystallographic Characteristics of The Calcium Sulphates	16
II	Free Space in the Unit Cell of Soluble Anhydrite	18
III	Ionic Radii	19
IV	Equilibrium Moisture Content of Drierite Samples	50
V	The Frost Point of Nitrogen Exhaust from Empty Test Assembly	121
VI	Calibration Chart for Copper-Constantan Thermocouple	149
VII	Relationship between Absolute Humidity and Frost Point of Air	150
VIII	Vapor Pressure of Ice	151
IX	Rotameter Calibration Chart	152
X	Vapor Pressure of Water	153
XI	Determination of the Adsorption Isotherm at Room Temperature	154
XII	Determination of the Moisture Adsorption of Annealed Samples	157
XIII	Adsorption Test of New Drierite Sample	158
XIV	Benzene Vapor Adsorption Test of Drierite	158
XV	Dynamic Tests: Run No. 1	159
XVI	Dynamic Tests: Run No. 2	162
XVII	Dynamic Tests: Run No. 3	164
XVIII	Dynamic Tests: Run No. 4	165

Table No.		Page
XIX	Dynamic Tests: Run No. 5	166
XX	Dynamic Tests: Run No. 6	167
XXI	Dynamic Tests: Run No. 7	168
XXII	Dynamic Tests: Run No. 8	169
XXIII	Dynamic Tests: Run No. 9	170
XXIV	Dynamic Tests: Run No. 10	171
XXV	Dynamic Tests: Run No. 11	172
XXVI	Dynamic Tests: Run No. 12	173
XXVII	Dynamic Tests: Run No. 13	174
XXVIII	Dynamic Tests: Run No. 14	175
XXIX	Dynamic Tests: Run No. 15	176
XXX	Dynamic Tests: Run No. 16	177
XXXI	Dynamic Tests: Run No. 17	178

List of Figures

Figure No.		Page
1	Activated Diffusion into Zeolite Lattice	11
2	Harmonic Motion	12
3	Proposed Structure of β Soluble Anhydrite Granules and Bed	15
4	Internal Diffusion through Zeolite Lattice	30
5	Internal Diffusion through Granule Pores	31
6	Adsorption Isotherms of <u>New</u> 2 - 2 $\frac{1}{2}$ mesh Drierite. Lower curve is "in" curve, upper is "out" curve.	51
7	Adsorption Isotherms of <u>New</u> 4 - 5 mesh Drierite. Lower curve is "in" curve, upper is "out" curve	52
8	Adsorption Isotherms of <u>Used</u> 10 - 12 mesh Drierite. Lower curve is "in" curve, upper is "out" curve.	53
9	Adsorption Isotherms of <u>Used</u> 20 - 24 mesh Drierite. Lower curve is "in" curve, upper is "out" curve.	54
10	Adsorption Isotherms of <u>New</u> 42 - 48 Mesh Drierite. Lower curve is "in" curve, upper is "out" curve.	55
11	A Comparison of Drierite Adsorption Isotherms Appearing in the Literature. A - 3 $\frac{1}{2}$ -6 Mesh by Wheat; B- 6-8 Mesh by Hammond and Withrow; C - .441" - .312" by Wheat; D - 10-20 Mesh by Wheat.	56
12	Frost Point Hygrometer and Test Assembly	77

Figure No.		Page
13	Cross Section of Frost Point Hygrometer	78
14	Cross Section of Optical Head	79
15	Optical Head	80
16	Circuit Diagram of Frost Point Hygrometer Electronic Unit	89
17	Flow Diagram of Dynamic Test Assembly	107
18	The Effect of Granule Size on the Adsorption Wave in 3 inch Beds (Volu- metric flow rate = $9.4 \text{ ft}^3/\text{hr}$)	114
19	The Effect of Bed Length on the Adsorption Wave in Beds Containing 20 - 24 Mesh Granules (Volumetric flow rate = $9.4 \text{ ft}^3/\text{hr}$.)	115
20	The Effect of Volumetric Flow Rate on the Adsorption Wave in 3 inch Beds (Granule Mesh = 20 - 24)	116
21	The Effect of Volumetric Flow Rate on the Adsorption Wave in 2 inch Beds (Granule Mesh = 20 - 24)	117
22	A comparison to Show the Reproducibility of the Adsorption Wave in 3 inch Beds Containing 20 - 24 mesh Granules	119
23	The Adsorption Wave for a 9 inch Bed Containing 20 - 24 Mesh Granules (Volumetric flow rate = $9.4 \text{ ft}^3/\text{hr}$)	120
24	The Effect of Granule Size on Break Time for 3 inch Beds (Volumetric flow rate = $9.4 \text{ ft}^3/\text{hr}$)	125
25	The Relationship Between Contact Time and Break Time for Beds Containing 20 - 24 Mesh Granules	126
26	Life-Thickness Curve for Beds Contain- ing 20 - 24 Mesh Granules	127

List of Symbols

A_T	= cross section area of tower	ft^2
a	= superficial surface of the granule (ignoring pore structure) per unit volume of bed	ft^2/ft^3
B	= slope of the straight line adsorption isotherm the formula of which is $W_e = B \cdot H_e$. (for low humidity $W_e =$ $B \frac{18.02}{100 \cdot 760 \cdot 28.97} R_{he}$)	dimensionless
D	= $\frac{B \rho_B}{\alpha V \rho_G}$	hr/ft.
D_I	= average internal diffusion coefficient for water molecules through porous granule	$\text{ft}^2/\text{hr.}$
d	= distance between equivalent water positions	cm or $\text{\AA}$
$E, \bar{n}, \bar{e}$	= activation energies	
G	= gas mass velocity through bed	$\#/\text{hr. ft}^2$
H	= absolute humidity of gas stream (based on bone dry air)	$\#/\#$
H_i	= absolute humidity of gas phase at some point in a pore of a porous granule	$\#/\#$
H_0	= absolute humidity at $Z = 0$	$\#/\#$
$I_n(Z)$	= Bessel function of order n	
K_g	= mass transfer coefficient for gas phase	$\#/\text{hr. ft}^2$
k^2	= Constant defined in text	1/hr.

M_1	= molecular weight of $\text{CaSO}_4 = 136.14$	
M_2	= molecular weight of $\text{H}_2\text{O} = 18.02$	
n_1	= number of molecules (atoms or ions) of solvent in the unit cell of the pure solvent	dimensionless
n_2	= average number of molecules (atoms or ions) of solute material in the unit structure, calculated from the concentration of the solid solution	dimensionless
p	= partial pressure of water vapor in air at temperature T and 760 mm Hg	mm Hg
p_0	= saturation partial pressure of water vapor in air at temperature T and 760 mm Hg = 20.1 at 72°F	mm Hg
q	= volumetric rate of total gas flow ($q = \propto V A_T$)	ft^3/hr
R	= average radius of granule assumed to be a sphere	ft
R_c	= gas constant = 1.987	cal/mole °K
R_h	= percent relative humidity of gas at T & 760 mm Hg total pressure ($R_h = 100 p/p_0$)	
r	= radial length of pores in porous granule or distance from center of granule	ft
S	= variable of integration	
T	= dimensionless group defined in text	

T_k	= temperature of experiment (abs)	$^{\circ}\text{K}$
t	= time	hr
V	= lineal gas velocity through the inter- stices between the granules in the bed	ft/hr
V_c	= volume of unit cell	$\text{A}^{\circ 3}$
v	= summation variable	
W	= moisture content of adsorbent (based on bone dry adsorbent)	#/#
W_e	= equilibrium moisture content of ad- sorbent (based on bone dry adsorbent)	#/#
W_i	= moisture concentration at some point in a granule	#/#
X	= dimensionless group defined in text	
$\bar{X}$	= a correction factor in kinetic theory	dimensionless
X_1	= dehydration fraction	
Z	= distance from entrance to bed	ft
α	= fraction external voids in bed	ft^3/ft^3
αV	= superficial gas velocity or actual velocity through empty tower	ft/hr
$\Gamma(Z)$	= Gamma function	
θ	= the angle involved in harmonic motion	radians
ρ	= density	g/cc
ρ_B	= bulk density of dry adsorbent bed (dry basis) (= 65.8)	#/ft ³
ρ_G	= density of air stream at temperature T abs. & 760 mm Hg (= .0747 at 72°F)	#/ft ³

ρ_p = apparent density of dry porous granule
(dry basis) #/ft³

ρ_s = true density of non porous dry
CaSO₄ = 185 #/ft³

Acknowledgement

This research was completed with the aid of a Laws Fellowship granted by the University. The author wishes to express his appreciation for this grant which made an extensive research program possible.

The author wishes to acknowledge the kind assistance and helpful guidance of Professor William Licht, Jr., who directed this research.

The author is also indebted to: Professor Herweh of the Electrical Engineering Department, Professor Kersten and Messrs. Stubbins and Blanchard of the Physics Department for their advice in the field of electronics; Professor Taylor of the Mathematics Department for his assistance in obtaining solutions to complex problems; and to Messrs. Carl Boch, Walter Scholl and Edward Graf of the Chemical Engineering Department for their excellent cooperation and generous assistance in the construction of equipment.

Abstract

The theory of the adsorption wave has in the past been developed for various cases depending upon the hypothetical mechanism for the kinetics of the adsorption process. The solution for the case of mass transfer controlling has appeared in the literature in the form of a standard chart which is convenient to use. In this paper the solutions for two other cases are presented. It is shown how in dimensionless form all three cases may be reduced to a single generalized theory. This treatment has many obvious advantages. This is especially so in problems of design and in studies of the kinetics of an adsorption process.

The second part of this thesis presents the results of a study to determine the kinetics of the reaction between humid air and the granular desiccant, calcium sulphate. Plots of the experimentally determined adsorption wave are presented for various gas velocities, granule sizes, and bed lengths. In view of the small internal diffusion coefficient for this system it would be expected that activated diffusion into the interior of the granule would control the adsorption process. That this is probably true is demonstrated by an analysis of the plots employing the generalized theory as well as other available means.

As a matter of implementing the above research it was necessary to determine the adsorption isotherms for the system calcium sulphate-water vapor. Plots of these are presented for five different granule sizes. Adsorption capacities shown in these plots refer to an absolute dry base weight of calcium sulphate determined by deactivation at 800°F, as contrasted with an unreliable base weight usually determined by regenerating the sample at 400°F.

The design and construction of an automatic electronic frost point hygrometer is also described. With it one may measure continuously frost points of humid gases ranging down to - 100°F with an accuracy apparently limited by the potentiometer employed in conjunction with the thermocouple which is an integral part of the hygrometer.

INTRODUCTION

The passage of a fluid stream through a stationary bed of granular solid may involve the transfer of material or heat to (or from) the solid from (or to) the fluid (1)(2). For example, the passage of hot gases through a checkerwork of cold brick involves heat transfer from the hot fluid to the cold solid. Likewise the passage of humid gas through a solid desiccant involves the transfer of material from the gas to the solid. In certain cases the transfer of material is due to adsorption. The transient conditions which prevail during adsorption in a desiccant bed give rise to an adsorption wave (3) (concentration gradient in the fluid stream) which originates at the entrance and gradually moves toward the opposite end of the bed. The concentration gradient arises from the fact that moist air becomes successively drier as it passes through a desiccant bed. Near the entrance face of the bed the concentration of moisture in the air stream is relatively high because the granules tend to become saturated and the rate of drying is low. The opposite is true for intermediate points in the bed. At more distant points in the bed the air becomes relatively dry and the rate of drying is again low. In general the humidity of the air stream drops very rapidly over a narrow section of the bed. This portion of the humidity gradient may be thought of as the wave front which moves deeper into the bed as the length of the saturated section increases. It is the theory of the movement of this wave and its applications that have attracted

much attention during recent years.

The theory (3)(4)(5)(6) has been developed for various special cases depending upon the hypothetical mechanism of the adsorption process. The solutions of the appropriate differential equations thus formulated vary in degree of complexity. The simpler ones have been applied to experimental results (1)(2)(3). Quite frequently they have failed and their failure has been attributed to numerous causes. As a result certain empirical procedures (3) have found favor in the analysis of data and design of large scale reactors or adsorption units.

One purpose of the present research is to reconsider the theoretical aspects of the adsorption wave and to formulate solutions to the other cases. The latter are an essential part of an effort to demonstrate a generalized theory in its simplest form.

The chief purpose of this thesis is to investigate the kinetics of the adsorption process involving soluble anhydrite (CaSO_4) as a desiccating agent to remove water vapor from air or other gases. Calcium sulphate was chosen for investigation because of interest aroused during the war in connection with its extensive use for drying oxygen and because little or no fundamental data were available concerning its behavior. The plan of the investigation is based on determining experimentally the adsorption wave for various bed lengths, air flow rates and desiccant granule sizes. The

analysis of the results to determine the kinetic mechanism depends primarily upon application of the generalized theory just mentioned. The empirical procedure is also employed for purpose of comparison. Such an analysis in general is not difficult provided the adsorption isotherms are known for the system. In the present case the isotherms must be measured. Determining the adsorption wave is a more difficult matter which required the design and construction of a frost point hygrometer (8) as an integral part of the investigation.

HISTORY

In reality the present investigation is a continuation and extension of the unpublished work begun by Wheat (9) and the latter will be discussed in a subsequent section in connection with results of the present work. Up to this time there had been no investigation reported on the kinetics of the reaction under consideration. There is however considerable literature concerning the physical-chemical properties of calcium sulphate in general. Some is devoted to the utility of this substance as a material of construction ("plaster of paris", etc) while others are specifically concerned with deciding the question of how water is held in the various hydrates and their relation to each other. It is obvious from this that calcium sulphate has several forms (32).

Gypsum is the dihydrate of calcium sulphate. Partial dehydration produces the half hydrate which may take on either the α - or β - form depending upon the conditions of dehydration. The difference between the two forms is due to a difference in crystal structure of the two substances. Further dehydration leads to the α - or β - water soluble anhydrite. Complete dehydration produces a more or less water insoluble anhydrite. Calcium sulphate for use as a desiccant is usually manufactured under those conditions which favor the formation of the β - soluble anhydrite (32).

Gaudefroy (10) was among the first to demonstrate the desiccating properties of soluble anhydrite. Hammond and Withrow (11), Werkinthen (12), Nacken and Fill (13) and

others (9)(14)(15) have contributed portions of the adsorption isotherm for soluble anhydrite and water vapor at room temperature. Unfortunately this work is incomplete in several respects. The low humidity portion of the curve has been neglected and yet because this is the range in which calcium sulphate excels as a desiccant it is the range which is of importance to the present work. Apparently none of the investigators mentioned have determined both the "in" and the "out" curves and thus questions as to adsorption hysteresis and attainment of equilibrium remain open. The fact that most of the data are based on a questionable dry basis and that some of the investigators have not considered the number of previous regenerations tend to cast some shadow of doubt which emphasizes the necessity for repeating and extending most of this work.

STRUCTURAL FEATURES OF
SOLUBLE ANHYDRITE

The structural features of soluble anhydrite are important to investigations of reactions in which this material is involved because the structure effects the course of the adsorption isotherm as well as that of the adsorption wave. In the case of crystal hydrates for example it is well known that the water of hydration is an integral part of the lattice structure. Removal of this water tends to cause a collapse of the lattice. The adsorption isotherm for a material of this type consists of square steps. On the other extreme one finds that water in cotton fibre for example does not materially affect the structure of the fibre. Its removal does not cause a collapse of the fibre structure. The adsorption isotherm is a continuous curve.

The two types of isotherms may be illustrated by considering only the coordinates of Figure 6 in a later section. One may sketch a connected series of steps starting at the origin. The riser of each step must be vertical and tread horizontal. Such an isotherm would illustrate that for a hydrated crystalline substance. If instead of the steps one sketched a diagonal line or curve starting at the origin the illustration would be that for a substance such as cotton.

The heat effects accompanying adsorption vary widely for different materials and this also is an indication of the structure of the adsorbent. The heat of adsorption of water on solid surface such as that of carbon granules is generally lower than that for materials which adsorb by chemical combination such as copper sulphate. It is logical to expect that these structural effects would influence the adsorption wave. As will be shown later the structural

features of the adsorbent actually determine the kinetic mechanism which is to be postulated in the development of the theory of the adsorption wave. It is important therefore at the outset to become acquainted with the structure of soluble anhydrite which is one of the so-called subhydrates of gypsum (16). The literature on this subject is confusing as will become evident in the remainder of this section. It is not impossible however to develop a hypothesis which appears to be satisfactory for the present investigation.

Perhaps the greatest contributions to the knowledge of structure are those concerned with the controversial subject of the nature of the subhydrates of gypsum. Weiser (16) (17) reviewed this subject in 1936 and stated that

"during the past few years several papers have appeared which reopen the question of the chemical individuality of the so-called calcium sulphate hemihydrate or plaster of Paris and the mechanism of its dehydration. Linck and Jung (18) deduced from dehydration data that plaster of Paris loses its water after the manner of zeolites. Balarew at different times has been on all sides of the question. At first (19) he claimed that the dehydration isobar would indicate that the water is present in the form of a true hydrate; later (20) he stated that the dehydration curves show the water to be held in a new way "half-hydrate and half zeolitic"; finally (21) he concluded that the water is lost in the manner of zeolites. Gibson and Holt (22) concluded from pressure-temperature curves that the water is lost continuously as in a zeolite. Parsons (23) claimed that all the water in gypsum may be lost by heating without the intermediate formation of a hemihydrate.

"Jung (24), Ramsdell and Partridge (25), and Caspari (26) reported that the X-ray diffraction pattern of calcium sulphate hemihydrate and its dehydration product are identical, in agreement with the view

that the hemihydrate is a zeolite. Onorato (27) and Gallitelli (28) found the hemihydrate and dehydrated hemihydrate to have the same type of structure but recognized minor differences in the powder X-radiograms. Feitknecht (29) likewise observed differences in the two patterns provided care was taken to prevent rehydration of the dehydrated hemihydrate. Feitknecht believed that Jung's dehydrated sample must have rehydrated before X-radiograms were made."

From the above survey it appears to be an open question whether "calcium sulphate hemihydrate" is a true chemical hydrate (properly represented by the chemical formula $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) which gives a definite X-radiogram and decomposes to "dehydrated hemihydrate" which gives a different X-radiogram or whether the system is zeolitic, yielding upon dehydration a product identical in crystal structure with the hydrated material.

Weiser et al from X-radiograms found that the hemihydrate and dehydrated hemihydrate do show small structural differences. In conjunction with this work they determined the isobaric dehydration curve and found that it showed sharp breaks both for the dihydrate and hemihydrate. The implications of the latter observation strengthened by the former lead to their conclusion that the hemihydrate is not zeolitic.

The above views are not shared by all writers. Emmeleus and Anderson (30) are of the opinion that the hemihydrate like the clay minerals, basic salts and hydroxides of the bivalent metals consists of a layer lattice structure from which the removal of water does not produce a new phase. If it did the system would be univariant. The water is packed

between the layers or in the interstices of the structures, frequently in an unordered manner, and its removal leaves the lattice completely unchanged or else alters only the spacing between successive sheets of a layer lattice. The system (hydrate + dehydration product + water vapor) is then bivariant, and the dissociation pressure at a fixed temperature is a continuous function of the composition. The stoichiometric formulae allotted to hydrates of this kind can represent only limiting compositions for the hydrated materials. This view is shared by Bunn (31) who reports that the composition of plaster is continuously variable between CaSO_4 and $\text{CaSO}_4 \cdot 2/3 \text{H}_2\text{O}$. To this range of hydrates he has given the name subhydrate. He contends that the subhydrate is the simplest substance behaving like zeolites. The entrance of water merely disturbs the balance of forces and slightly distorts the structure. In the setting of plaster the crystals first absorb water up to the $2/3 \text{H}_2\text{O}$ maximum and then the saturated crystals dissolve and are replaced by gypsum.

Kelley (32) et al have taken an intermediate stand in the controversy. They cite the fact that there is an α - and a β - form of the soluble anhydrite and hemihydrate. For α -hemihydrate they conclude that

"it loses water with the formation of an anhydrous soluble anhydrite in one step and is to be considered nonzeolitic."

The β -hemihydrate

"loses water with the formation of a soluble anhydrite containing several tenths per cent water. From 0.9 per cent down the water is removed with increasing difficulty hence this part may be considered as zeolitic if desired".

The views of Hey (33)(34)(35) on the entire subject appear to be most valuable in that they lead immediately to results which are of practical utility. In the development of his kinetic theory for the vapor pressure of zeolites he stated that the theory applied to

"any crystalline compound of a volatile and non-volatile component the crystal structure of which is such that the whole or a part of the volatile component can be removed without the structure collapsing. At present there is no comprehensive term for such compounds, and they are often referred to as "zeolite" compounds, after the best known examples of the class, but a more satisfactory term is desirable."

The theory of vapor pressure is based on a mechanism illustrated in figures 1 and 2. It is supposed that the dehydrated zeolite is a lattice structure which has definite vacant lattice positions which may be occupied by water. Due to the surface molecules of the lattice there exists a potential hump which surrounds the crystal. Between the potential hump and the surface of the crystal water molecules are attracted to the crystal. Beyond the potential hump water molecules are repelled. In figure 1 the mean velocity indicated at the water position is that which the water molecules must exceed in order to cross the potential hump and thus to evaporate from the lattice. Likewise the velocity

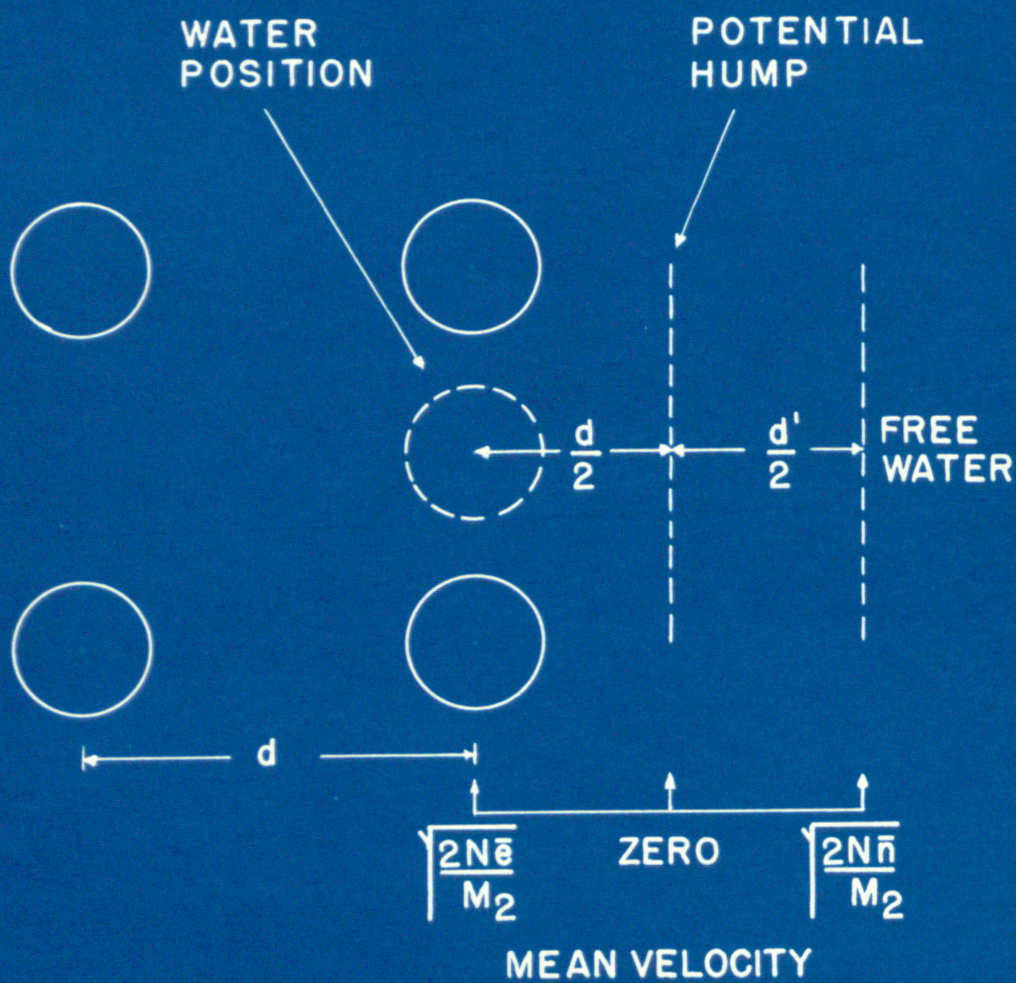


Figure 1
Activated Diffusion into Zeolite Lattice

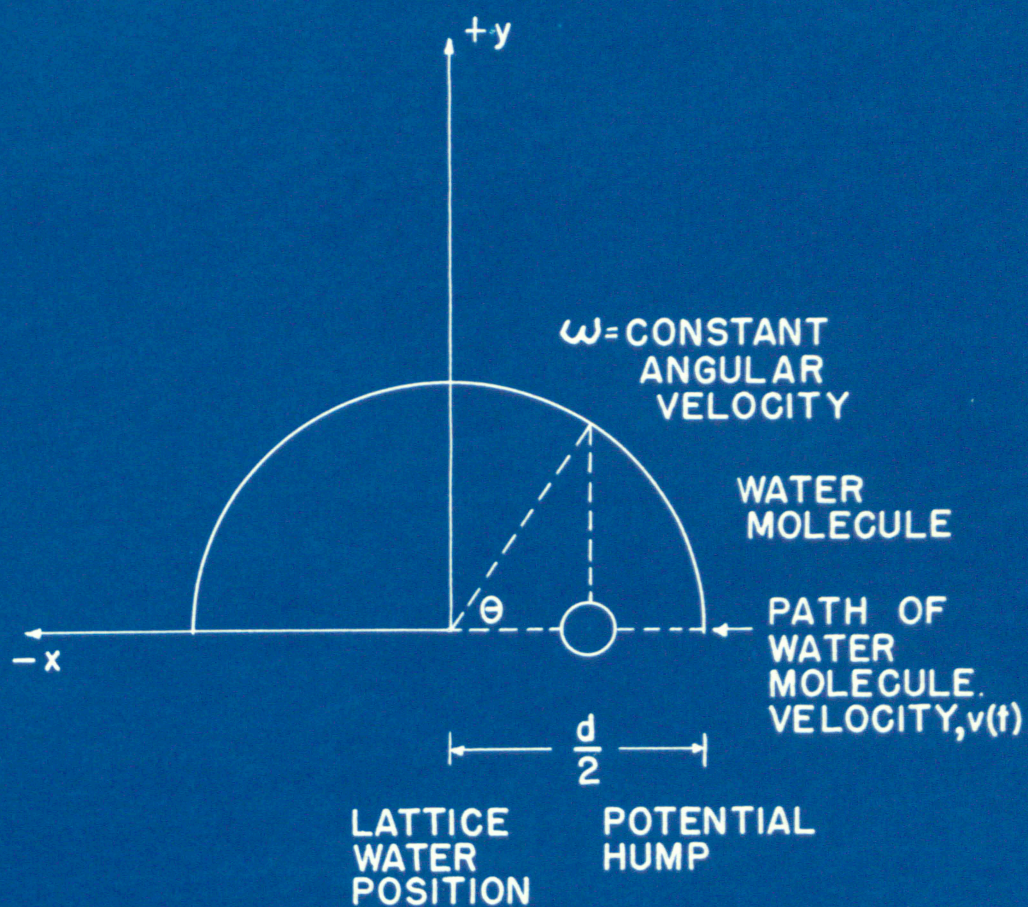


Figure 2
Harmonic Motion

indicated in the free water space is that which must be exceeded in order that the water molecules may condense in the water position. The law relating the terminal velocities to that at the potential hump is assumed by Hey to be that of harmonic motion illustrated in figure 2.

The importance of the vapor pressure theory to the present investigation is due to the type of crystal structure and mechanism with which the theory is concerned. The fact that Hey applied the theory to calcium sulphate is also important. Whether soluble anhydrite crystals are zeolitic or non-zeolitic in the usual sense is not important. What is important is that the crystal structure of the subhydrates does not collapse upon dehydration. Most investigators agree that subhydrate crystals satisfy the latter condition.

The above discussion has been limited to a crystal and it remains now to establish the relationship between crystal and granule. Since the dehydration of fine grained gypsum to the hemihydrate involves forming a new phase, nuclei should form and grow during the process. As a result the granule should consist of a mosaic of subhydrate crystals. Barrer (36) (37) as a result of static adsorption experiments with zeolites found that the rate of sorption was influenced by degree of subdivision of the powdered material. Although the pronounced effect was quantitatively in accord with diffusion theory the relation of the reciprocal of the particle

diameter to the velocity constant was not quantitatively obeyed as required by theory. The effect was attributed to the fact that the granule is not homogeneous but consists of a mosaic of crystallites each of which is homogeneous. It is the diameter of the latter which should obey the theory. It was also stated that "even if the particles (granules) could be obtained initially free of cracks, the outgassing may produce a mosaic from each fragment."

According to Hammond and Withrow (11), dehydration of pure gypsum involves no appreciable change in volume. It is clear that the dehydrated granule must be of a highly porous structure. In order to illustrate this and other remaining points regarding the structure of the granule figure 3 has been included. The numerical values shown in the figure are derived from data collected in table I. The remainder of this section is devoted to the procedures employed to arrive at the space fractions.

Application of the following formula (38) for interstitial solution shows that the density of the subhydrates can be predicted quite accurately:

$$\rho = \frac{n_1 M_1 + n_2 M_2}{V_c \cdot 10^{-24}} 1.649 \cdot 10^{-24} \quad (1)$$

where:

ρ = density, g/cc of crystal

n_1 = no. of molecules (atoms or ions) of solvent

in the unit cell of the pure solvent (see Table I)

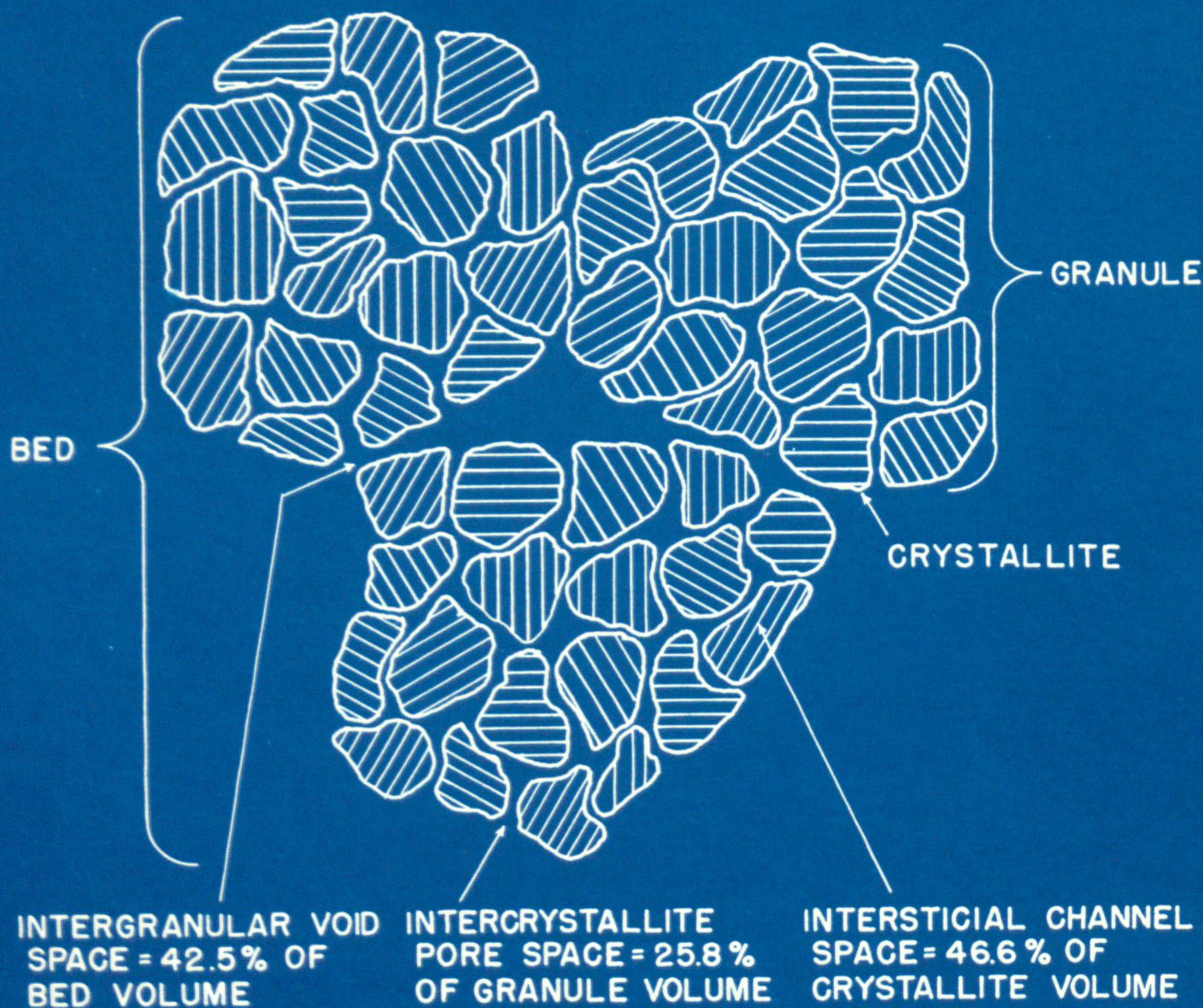


Figure 3
Proposed Structure of β Soluble
Anhydrite Granules and Bed

Table I
Crystallographic Characteristics of the Calcium Sulphates

Substance	Density g/cm ³	Crystal system	Space group	Cell dimensions	Mole- cules per unit cell	Mole- cular volume cc/ mole
Calcium sulphate dihydrate	2.31 (20.88% H ₂ O wet basis) (32)	Monoclinic prismatic	C _{2h} ⁶ (39)	a = 10.47A° b = 15.15A° c = 6.28A° β = 98.18° (39) (40)	4-8	74 (10)
Calcium sulphate α hemi- hydrate	2.757 (6.27% H ₂ O wet basis) (32)	Monoclinic	C ₂ ⁵	a = 11.94A° b = 6.83A° c = 12.70A° (28)	12	
Calcium sulphate β hemi- hydrate	2.637 (6.25% H ₂ O wet basis) (32) 2.63 (10)				12	55 (10)
α Soluble anhydrite		Monoclinic				
β Soluble anhydrite	2.84 (.25% H ₂ O wet basis) (32) 2.45 (10) 2.478 (dry basis) calculated					55 (10)
Anhydrite	2.96 (10)		V _h ¹⁷	a = 6.21A° b = 6.95A° c = 6.96A° (41) a = 6.24A° b = 6.98A° c = 6.98A° (42)	4	46 (10)

n_2 = average no. of molecules (atoms or ions) of solute material in the unit of structure, calculated from the concentration of the solid solution (= 6 for hemihydrate).

M_1 = molecular weight of solvent (= 136.14 for CaSO_4)

M_2 = molecular weight of solute (= 18.02 for water)

V_c = volume of unit cell in $\text{\AA}^3$ (See Table I)

$1.649 \cdot 10^{-24}$ = the reciprocal of Avogadros number.

Application of the formula to data from table I shows that $\rho = 2.78$ for the α soluble hemihydrate as compared with 2.757 shown in table I. The above formula cannot be used to compute the density of β hemihydrate because V_c is not known. If it may be assumed that equation 1 applies to β hemihydrate then with the value of $\rho = 2.637$ given in table I it is possible to compute the cell volume of the β hemihydrate and this value is shown in table II. Using the data in table III the volume of 12 CaSO_4 molecules (as ions) in the unit cell have been computed on various bases as also indicated in table II. The first two bases do not represent fact because in the sulphate tetrahedron the oxygen atoms are too close to permit water to enter the interior spaces of the sulphate ion itself. Furthermore, repulsive forces due to contact would be expected to make this a prohibitive basis. To make the appropriate correction the third basis was assumed whereby the oxygen atoms were pictured as being so located that their centers coincided with the vertices of

Table II

Free Space in the Unit Cell of β Soluble Anhydrite

Basis for Calculation	Volume of 12 CaSO_4 molecules $\text{\AA}^3$	Approximate Volume of Unit Cell $\text{\AA}^3$	Pore Fraction $1 - \frac{\text{Vol. of molecules}}{\text{Vol. of Unit Cell}}$
Each atom considered as a sphere	516	1090	.527
Ca^{2+} ion as a sphere and SO_4^{2-} ion as a sphere of effective radius $1.5 + 1.32$	1181	1090	Basis for calculation cannot be realized
Ca^{2+} ion as a sphere and SO_4^{2-} ion as a tetrahedron solid of edge $2.45\text{\AA}$; the excess spherical volume of SO_4^{2-} not included in tetrahedron	582	1090	.466

Table III
Ionic Radii

Ion		Radius, A°
Ca ²⁺		1.02
SO ₄ ²⁻ Tetrahedron	S ⁶⁺	.29
	O ²⁻	1.32
	S to O	1.5 center to center
	O to O	2.45 " " "

the tetrahedron of edge equal to $2.45\text{\AA}$. First the volume of the tetrahedron was computed and to this was added the excess volume for the four oxygen atoms. The excess volume of course consisted of the volume of the four spherical oxygen atoms with an appropriate deduction for the spherical segments cut from the spheres by the tetrahedron and already included in the volume of the tetrahedron.

The fraction of space apparently available to water in β hemihydrate has been computed as shown in table II. On this basis the value, .466, seems most plausible. For general engineering purposes this figure is normally obtained from the ratio of the density of the soluble anhydrite (dry basis) divided by the density of anhydrite and subtracting from unity. If in table I the water is deducted from the figure, 2.637, a dry density of 2.478 is obtained. This figure with 2.96 for anhydrite gives a pore fraction of .163 which is low compared to the value .466 previously calculated. The low value is probably erroneous because in its derivation it is implied that anhydrite has no space available and this may not be true if it contains pores of smaller diameter than that of the water molecule.

The interstitial space (channel space) fraction in the crystallite has been calculated and now the inter-crystallite space fraction may be computed. Each cc of dihydrate granule contains $(2.32 - .2092 \cdot 2.32) = 1.835$ grams of β soluble anhydrite per cc of anhydrous granule. The

volume fraction of the β compound in the granule is $1.835/2.478 = .742$ and thus the intercrystallite space is 25.8% of the volume of the granule. In all probability this space would be available to something like benzene with a molecular diameter of $5.7 \text{ \AA}$ and could be checked by a benzene adsorption determination since the channel diameter in the crystallites is only $2.9 \text{ \AA}$ approximately (33). On the dry basis the granule should take up $(.879 \cdot .258/1.835) 100 = 12.3$ per cent provided the granule were in contact with liquid benzene. A point of interest is that the granule in contact with saturated benzene vapor may pick up less than 12.3% if the intercrystallite pores are greater than some $30\text{--}40 \text{ \AA}$. This is based on the fact that Harkins et al (43) observed that adsorbed films grow to something like $15 \text{ \AA}$ in thickness. This of course is very approximate.

The intergranular void space fraction shown in figure 3 is based on the author's observation that beds of dry granules average 65.8 pounds per cubic foot. This applies to beds of $2\text{--}2\frac{1}{2}$ mesh, 4-5, 10-12, and 20-24 mesh.

THE DIFFUSION COEFFICIENT

The structure of the granular bed illustrated in the previous section and the discussion accompanying it suggests that the drying process of air passed through the bed might consist of three steps. Water molecules must first experience free diffusion (mass transfer) to the surface of the granule and probably to the surface of the crystallites. At the potential barrier they must experience activation to enter the lattice. Last of all they must be further activated in the first lattice position so as to experience activated diffusion toward the inner portions of the crystallite. Prior to developing the theory for the adsorption wave one must make a decision as to "which of the three steps is probably the controlling one". Actually there is no rule for making such a decision and one must rely on past experience. Based on the work of Hey and Tiselius diffusion to the interior of the soluble anhydrite granule is suggested as the controlling step.

Tiselius (44) has measured the diffusion constants for many zeolite - gas systems. His results show that the rate of adsorption for different zeolites varies from fractions of a second to almost infinite time. They also vary with the different gases and temperatures. Experiments with single heulandite crystals in an evacuated system subsequently charged with water vapor of a controlled vapor pressure showed that diffusion in the drier crystals was much less

rapid than for crystals with higher concentrations of adsorbed water. This he attributed to the "hopping" process of diffusion. The first adsorbed water molecules are supposed to be more firmly bound and therefore less able to hop from one water lattice position to another. The activation energy for diffusion was only 40-65% that required to jump entirely out of the lattice. It is imagined that this is due to the adsorption spaces being so near to each other that their force fields overlap. Hey calculated that the distance between adjacent water positions is $3.6\text{\AA}$. The actual diffusion constants at 20°C range from $.04 \cdot 10^{-7}$ - $4.0 \cdot 10^{-7}$ cm^2/sec compared to $1.7 \cdot 10^{-3}$ - $7 \cdot 10^{-3}$ found by Wicke (45)(46) for CO_2 and carbon.

More recent work with analcite and ammonia has shown that the diffusion constant at 302°C is $1.0 \cdot 10^{-8}$ - $1.4 \cdot 10^{-8}$ cm^2/sec . The activation energy for diffusion is equal or greater than the heat of adsorption. One reason for this may be that the adsorption spaces in analcite are very widely separated as is known from its crystal structure and water content. Hey has given $5.93\text{\AA}$ as the distance between adjacent water sites. This value is almost twice that for heulandite. On this basis soluble anhydrite having the value $6.3\text{\AA}$ (according to Hey) would more nearly resemble analcite at least in this one respect. This is the first observation which suggests that the internal diffusion coefficient for soluble anhydrite is small and that internal

diffusion is slow. Actually one must consider the expression (47)

$$D_{oI} = \frac{d}{\pi \bar{X}} \sqrt{\frac{2 E_0}{M_2}} e^{-\frac{E_0}{R_c T_K}}$$

where

d = distance between water lattice position, $\text{\AA}^\circ$

M_2 = molecular weight of adsorbate

$\bar{X} \sim 1$ = a correction factor

D_{oI} = the maximum internal diffusion coefficient
(for water diffusion parallel to the channels)
assumed independent of x_1 , cm^2/sec . (x_1 =
adsorbate conc.)

R_c = gas constant

E_0 = the activation energy (assumed independent
of x_1) which water molecules must have in
order to migrate in a zeolite, calories per
gram mole of water

T_K = temperature, abs.

For the β hemihydrate it might be assumed that $d = 6.3\text{\AA}^\circ$,
and $E_0 = 15,424$ (based on the report by Kelley et al). Then
at 72°F , $D_{oI} = 2.95 \cdot 10^{-10} \text{ cm}^2/\text{sec}$. Actually d might be some
simple submultiple of 6.3. It is not known what law relates
 E_0 and d but if for some reason E_0 dropped to 50% of the
above value then $D_{oI} = 1 \cdot 10^{-4} \text{ cm}^2/\text{sec}$ is obtained which ap-
pears to be unreasonably high when compared with carbon.
The first value seems most likely especially considering

that the value for analcite would be much smaller at 72°F (22.2°C).

There are other reasons for considering D_{OI} as being small (E_o large). Barrer (36)(37) found that the zeolites, dehydrated chabazite and active analcite, had channels in the crystal which were about 5.58Å in diameter. Adsorbate molecules up to 4Å in diameter passed through the channels very rapidly and the process was recognized as free diffusion requiring no activation energy. Molecules 4.8Å in diameter diffused through the channels slowly and required an energy of activation which increases very rapidly as the diameter of the molecule approaches that of the channel through which it is diffusing. Molecules of 5.58Å diameter were excluded, i.e. they could not enter the channels. In the case of C_3H_8 the activation energy was about 50% of the heat of adsorption and the diameter of this molecule is about 88% that of the channel. Hey calculated that the channels in the β hemihydrate were 2.9002Å and that with water having a diameter of 2.9Å certainly indicates an activation energy of the same order of magnitude as that for adsorption. This is another reason for believing that internal diffusion might be the rate controlling step.

In all the work of Tiselius discussed above it is important to note that the experiments were static (no gas flow) and that for the large crystals (heulandite) used in the experimental work diffusion in the crystal was the rate

- controlling process. Tiselius stated that this was evident from the fact that the concentration at the surface remained constant throughout the experiment and was equal to the saturation value. The fact that the adsorption spaces are even farther apart in the case of soluble anhydrite suggests that the above conclusions should apply to this case as well.

GENERALIZED THEORY OF THE
ADSORPTION WAVE

The classical theory of the adsorption wave (3) is based on a material balance over a differential element of bed. The amount of water passed into the element is equal to that adsorbed by the element plus that which is exhausted from the element. Gas density and volume changes due to adsorption and pressure drop over bed are neglected. The process is assumed to be isothermal. Diffusion in the gas stream parallel to the axis of the bed is assumed to be negligible. Whenever the adsorption isotherm is involved it is assumed that it is a straight line. Both inlet humidity and gas flow rate are assumed to be constant. As a consequence of these assumptions the material balance applies to an ideal case. Such limited consideration is necessary in order to avoid insuperable mathematical difficulties which would arise later.

Klotz (3) has given a derivation of the material balance for the ideal case. It may be written as

$$\frac{1}{V} \frac{\partial H}{\partial t} + \frac{\partial H}{\partial Z} + \frac{1}{\alpha V} \frac{\rho_B}{\rho_G} \frac{\partial W}{\partial t} = 0 \quad (2)$$

where H = absolute humidity of gas stream (based on bone dry gas), lbs/lb. of gas.

t = time, hours

V = lineal gas velocity through the interstices between the granules in the bed, ft/hr.

W = moisture content of adsorbent (based on bone dry adsorbent), lbs/lb adsorbent

Z = distance from entrance to bed, ft.

α = fraction external voids in bed, ft^3/ft^3 of bed

ρ_B = bulk density of dry adsorbent bed, lbs/ft^3 .

ρ_G = density of gas stream at the prevailing temperature and atmospheric pressure, lbs/ft^3 of gas.

Wicke (45)(46) has discussed equation 2 and has pointed out that the first term of the left hand side is usually a comparatively small number which may be neglected. The reason is that the velocity through the interstices is normally so high that its reciprocal times the rate of change in humidity is comparatively small. Thus equation 2 reduces to

$$\frac{\partial H}{\partial Z} + \frac{1}{\alpha V} \frac{\rho_B}{\rho_G} \frac{\partial W}{\partial t} = 0 \quad (3)$$

In order to solve equation 3 one must replace W in terms of H , Z and t . This requires knowledge of or at least an assumption of the mechanism by which the adsorption kinetics operates.

It has been decided on the basis of the evidence of the preceding section to assume that in the case of soluble anhydrite diffusion within the granule is the rate controlling step. This implies of course that the surface of the granule is always in equilibrium with the surrounding air. Accordingly in order to relate W to the theory expounded it is necessary first to consider Ficks Law (47)

of Diffusion. Actually one might consider two cases of internal diffusion. The one in which diffusion takes place through a zeolitic lattice is illustrated in figure 4. That for diffusion through an activated carbon pore is illustrated in figure 5. Only figure 4 is of immediate interest.

The appropriate form of Ficks Law may be developed by considering the material balance over the elemental section, dr . The rate at which moisture permeates section 1 is equal to the rate at which moisture accumulates in the element plus the rate at which it permeates section 2. Barrer (47) has given the derivation for spherical zeolite granules and the appropriate form is

$$\frac{\partial W_i}{\partial t} = D_I \left[\frac{\partial^2 W_i}{\partial r^2} + \frac{2}{r} \frac{\partial W_i}{\partial r} \right] \quad (4)$$

where D_I = the internal diffusion coefficient, ft^2/hr .

W_i = the moisture concentration in the granules at a point r feet from its center and at time t , lbs/lb of elemental shell of the dry granule.

The partial differential equation, equation 4, has been solved for the same problem in heat transfer. The appropriate solution for the point concentration within the granule is (46)

$$W_i(r, t) = W_s + \frac{2R}{\pi} [W_i(o) - W_s] \sum_{v=1}^{\infty} \frac{1}{v} (-1)^{v+1} \frac{1}{r} e^{-v^2 k^2 t} \sin \frac{v\pi r}{R} \quad (5)$$

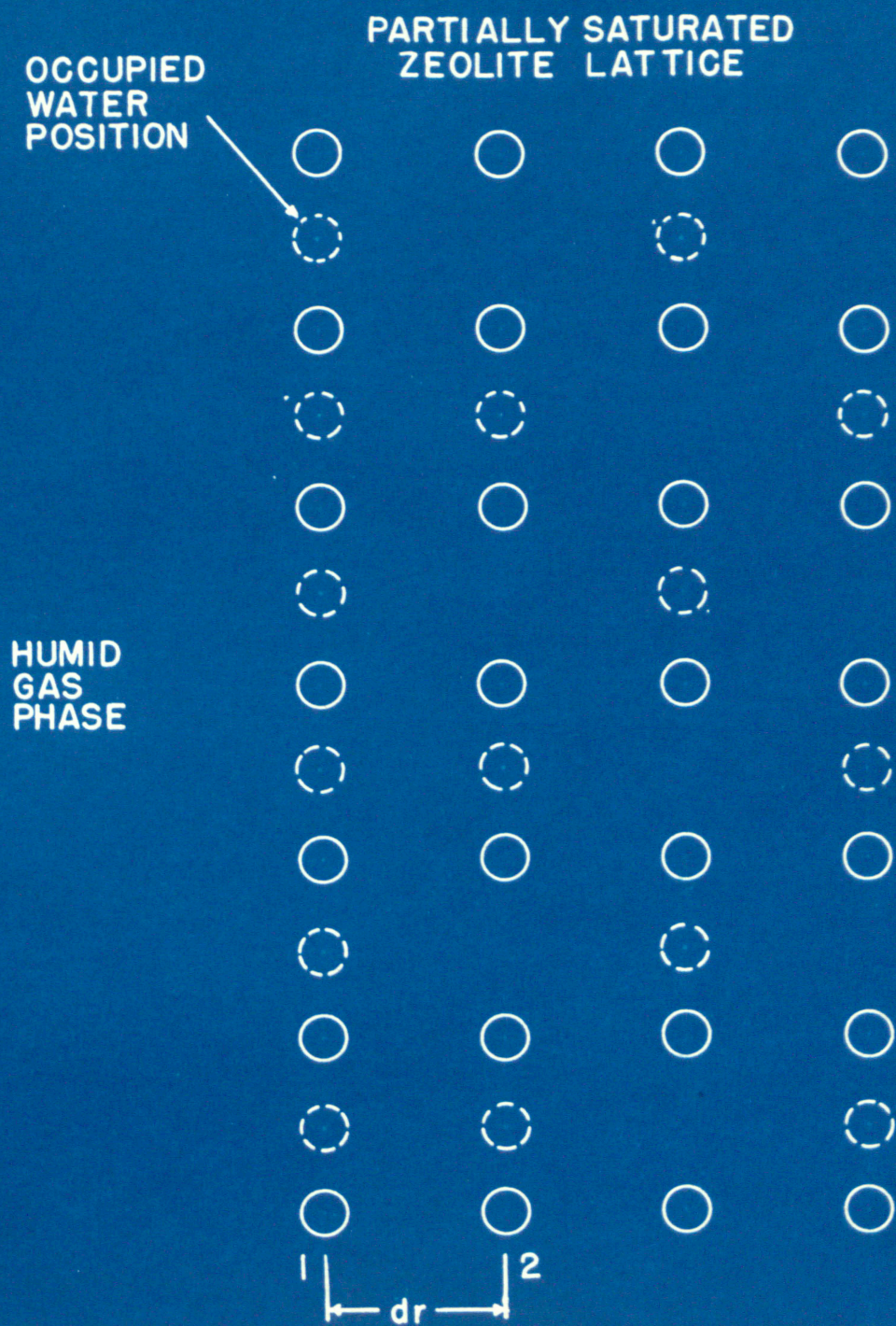


Figure 4
Internal Diffusion through Zeolite Lattice

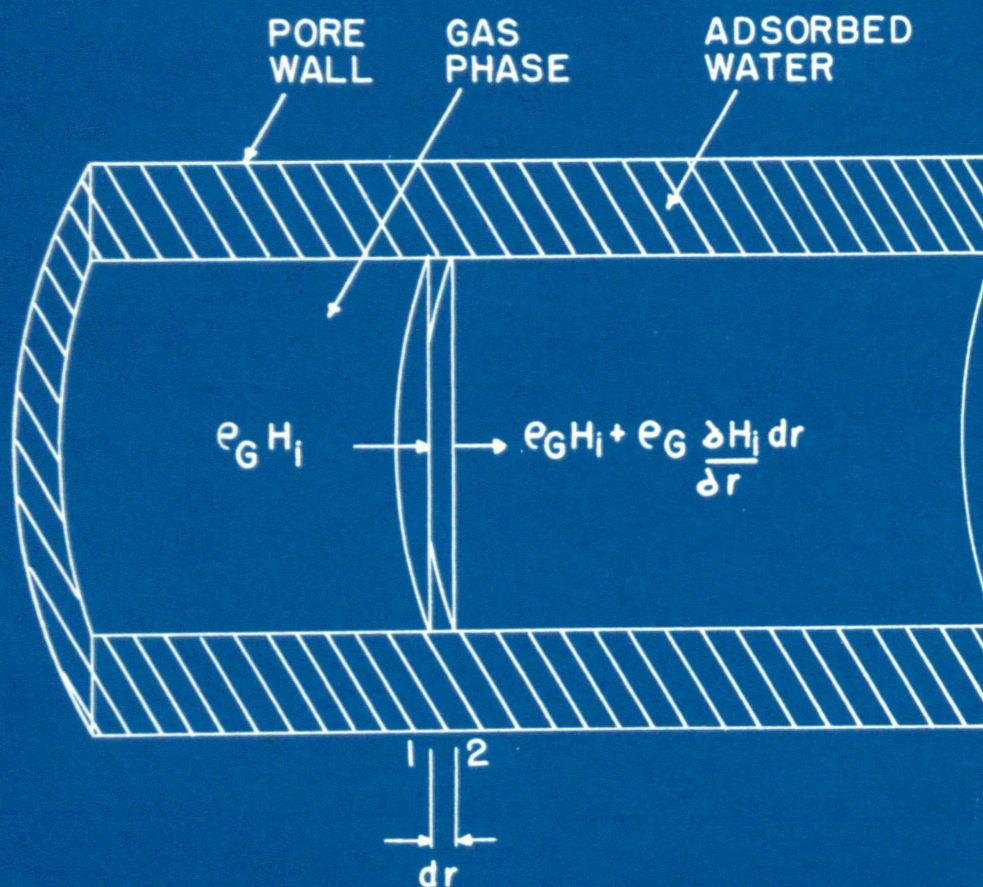


Figure 5
Internal Diffusion through Granule Pores

where subscript i indicates point concentration and

$W_i(o)$ = initial equilibrium concentration of
granule, lbs/lb of elemental shell

W_s = equilibrium granule surface concentration,
lbs/lb of shell

R = radius of granule considered to be a sphere

r = distance from center to point of concentra-
tion $W_i(r,t)$

$k^2 = (\frac{\pi}{R})^2 D_I$

v = index of summation

D_I = the proportionality constant in equation 4
or the internal diffusion coefficient for
the lattice structure.

Assuming that the adsorption isotherm is linear
and expressed by

$$W_s = BH \quad (6)$$

the W_s in the right side of equation 5 may be replaced by
 BH . The H in the resulting equation is a humidity which
at a given location in an adsorption tower is a function of
time. It is not a constant as assumed in the derivation of
equation 5.

In order to take H as a function of time into ac-
count Wicke applied equation 5 to a series of time inter-
vals during each of which $H(t)$ had successively different
values. By proceeding to the limit he has shown that

$$W_1(r, t) = BH(t) - \frac{2R}{\pi} \sum_{v=1}^{\infty} \frac{1}{v} (-1)^{v+1} \frac{1}{R} \sin \frac{v\pi r}{R} \left\{ [BH(0) - W_1(0)] e^{-v^2 k^2 t} + \int_0^t e^{-v^2 k^2 (t-s)} \frac{\partial H(s)}{\partial s} ds \right\} \quad (7)$$

where s is a variable of integration and $H(0)$ is the initial humidity of the air surrounding the granule. $W_1(r, t)$ is the weight of water contained in each pound of the elemental concentric shell of the spherical granule. The total weight of water of each elemental shell is $\rho_p W_1(r; t) 4\pi r^2 dr$ and the total for the entire granule is

$$\rho_p W(t) \frac{4}{3} \pi R^3 = \rho_p 4\pi \int_0^R r^2 W_1(r; t) dr \quad (8)$$

Substitution of 7 in 8, performing the indicated integration assuming the granule initially to be in equilibrium with the air surrounding it gives an expression for $W(t)$ which when differentiated with respect to t is

$$\frac{\partial W}{\partial t} = k^2 B \frac{6}{\pi^2} \sum_{v=1}^{\infty} \int_0^T \frac{\partial H}{\partial s} e^{-v^2 k^2 (t-s)} ds \quad (9)$$

In a bed $W(t)$ and $H(s)$ become $W(Z; t)$ and $H(Z; s)$.

The derivative, $\frac{\partial W}{\partial t}$, may be eliminated between equations 3 and 9 to obtain

$$\frac{\partial H}{\partial Z} + \frac{k^2 B \rho_B}{\alpha v \rho_G} \frac{6}{\pi^2} \sum_{v=1}^{\infty} \int_0^T \frac{\partial H}{\partial s} e^{-v^2 k^2 (t-s)} ds = 0 \quad (10)$$

In order that subsequent treatment of this equation be possible it is assumed that the first summation term ($v = 1$) represents the value of the series. This condition is better satisfied as the value of t increases (45)(46). If the resulting equation is multiplied by $e^{k^2 t}$, differentiated with respect to t and then multiplied by $e^{-k^2 t}$ the partial differential equation becomes

$$\frac{\partial^2 H}{\partial Z \partial t} + k^2 \frac{\partial H}{\partial Z} + k^2 D \frac{\partial H}{\partial t} = 0 \quad (11)$$

where for convenience

$$D = \frac{B \rho_B}{\alpha V \rho_G} \quad (12)$$

According to dimensional analysis

$$H \propto (k^2 t)(k^2 D Z) \quad (13)$$

At this point the treatment in general may be reduced to dimensionless form by letting

$$X = k^2 D Z; \quad T = k^2 t \quad (14)$$

Equation 11 reduces to

$$\frac{\partial^2 H}{\partial X \partial T} + \frac{\partial H}{\partial X} + \frac{\partial H}{\partial T} = 0 \quad (15)$$

This hyperbolic partial differential equation must be subjected to the boundary conditions

$$H = H_0 \quad \text{at } X = 0 \quad \text{for all } T$$

and to the initial condition

$$H = 0 \quad \text{at } X > 0 \quad \text{for } T = 0$$

It is these conditions which are of general interest. The solution to 15 under the specified conditions may be obtained by various standard procedures (48) (49) (50).

The method of Riemann (50) leads to

$$\frac{H}{H_0} = 1 + e^{-T-X} I_0(2\sqrt{XT}) - e^{-X} \int_T^{\infty} e^{-S} I_0(2\sqrt{SX}) \, ds \quad (16)$$

where I_0 denotes the Bessel function of imaginary argument. The integral appearing in this equation is one of historical interest. It is known to mathematicians as Webers first integral (51). It may be evaluated exactly in terms of a series involving products of Bessel functions and generalized hypergeometric functions all of which make computations very tedious. It may also be evaluated by a number of other methods one of which involves the form

$$I_0(Z) = \frac{1}{\Gamma(\frac{1}{2})\Gamma(\frac{1}{2})} \int_0^{\pi} e^{Z \cos \theta} \, d\theta \quad (17)$$

which may be expanded and integrated with respect to θ .

Substitution of the result in 16 and rearranging leads to

$$\frac{H}{H_0} = e^{-T-X} \left\{ I_0(2\sqrt{XT}) - \left[\frac{\pi}{4} + f_1(X,T) + f_2(X,T) + \dots \right] \right\} \quad (18)$$

The functions f_1 , f_2 , etc., in 18 are incomplete gamma

functions and again computations are long and involved.

The experience with numerical evaluation of any of the standard solutions to equation 16 is that they are in the wrong form from the start. The values of I_0 are tabulated (51) up to about I_0 (16). The values of interest here are nothing like sixteen. They may range up to 10 - 100 fold.

A solution to the difficulty is to use the asymptotic expansion

$$I_0(Z) = \frac{e^Z}{(2\pi Z)^{1/2}} \quad \text{as } Z \rightarrow \infty \quad (19)$$

and to proceed as demonstrated by Walter (52). Substitution of equation 19 in 16 shows

$$\frac{H}{H_0} = 1 + \frac{e^{-(T^{1/2}-X^{1/2})^2}}{2\sqrt{\pi}(XT)^{1/4}} - \frac{1}{2\sqrt{\pi}} \int_T^\infty \left(\frac{S}{X}\right)^{1/4} \frac{e^{-(S^{1/2}-X^{1/2})^2}}{S^{1/2}} ds \quad (20)$$

If it is assumed that $\left(\frac{S}{X}\right)^{1/4}$ is constant in the range of interest as it generally is, it may be removed from under the integral sign under the conditions described by Walter. The integral which remains is the familiar error integral and the solution becomes

$$\frac{H}{H_0} = 1 + \frac{\phi\left(\frac{T}{X}\right)}{4(XT)^{1/4}} - \frac{1}{2}\left(\frac{T}{X}\right)^{1/4} \left[1 - \phi\left(\frac{T}{X}\right) \right] \quad \text{for } T > X \quad (21)$$

and

$$\frac{H}{H_0} = 1 + \frac{\phi_1(X)}{4(XT)^{\frac{1}{4}}} - \frac{1}{2} \left[1 + \phi(X) \right] \quad \text{for } T < X \quad (22)$$

where both $\phi_1(X)$ and $\phi(X)$ are tabulated functions which are

$$\phi(X) = \frac{2}{\sqrt{\pi}} \int_0^X e^{-r^2} dr; \quad \phi_1(X) = \frac{2}{\sqrt{\pi}} e^{-r^2} \quad (23)$$

where

$$X = T^{\frac{1}{2}} - X^{\frac{1}{2}} \text{ for } T > X; \quad X = X^{\frac{1}{2}} - T^{\frac{1}{2}} \text{ for } X > T \quad (24)$$

For large values of X and T which are the usual case it has been found during the course of subsequent computations that the term involving $\phi_1(X)$ is negligible. The factor $\left(\frac{T}{X}\right)^{\frac{1}{4}}$ is always close to one and the solution reduces to

$$\frac{H}{H_0} = \frac{1}{2} \pm \frac{1}{2} \phi(X) \quad \begin{array}{l} + \text{ for } T > X \\ - \text{ for } T < X \end{array} \quad (25)$$

The assumptions on which equation 25 is based may be summarized as follows

- (a) Gas density and volume changes due to adsorption and pressure drop over bed are neglected.
- (b) The adsorption process takes place under isothermal conditions. Both inlet humidity and gas flow rate are constant.
- (c) Diffusion in the gas stream parallel to the axis of the bed is assumed to be negligible.
- (d) The adsorption isotherm is linear, $W = BH$

- (e) The term $\frac{1}{V} \frac{\partial H}{\partial t}$ in equation 2 is negligible compared to the remaining terms
- (f) Diffusion within the granule is the rate - controlling step.
- (g) The time is long enough so that in equation 10 the first term of the summation gives a good approximation to the complete summation.
- (h) $H = H_0$ at $X = 0$ for all T and
 $H = 0$ at $X > 0$ for $T = 0$
- (i) The product, XT , is large so that the asymptotic expansion for I_0 is a good approximation to I_0
- (j) The product, XT , is large so that the quantity $\frac{\phi_1(X)}{4(XT)^{\frac{1}{4}}}$ is negligible in equation 21 and 22.
- (k) The quantity $\left(\frac{T}{X}\right)^{\frac{1}{4}}$ approaches unity (eq. 20)

Typical curves for equation 25 are shown as dash curves in figure 19 of a subsequent section pertaining to results.

The chief purpose of the remainder of this section is to show that equation 25 applies to other cases and that it may therefore be considered as a generalized theory.

Consider the equation

$$\frac{H}{H_0} = 1 - e^{-T} \int_0^X e^{-S} I_0(2\sqrt{ST}) dS \quad (26)$$

which has been derived by (2) (53) (54) (55) (56) (57) assuming that mass transfer from the gas stream to the granule is

the controlling step. All symbols are the same as before. Upon removing the definite integral portion of equation 26, evaluating it, and rearranging the result one finds that after substituting the asymptotic expansion for I_0 (see equation 19)

$$\frac{H}{H_0} = \frac{1}{2\sqrt{\pi}} \int_X^{\infty} \left(\frac{S}{T}\right)^{\frac{1}{4}} \frac{e^{-(S^{\frac{1}{2}}-T^{\frac{1}{2}})^2}}{S^{\frac{1}{2}}} ds \quad (27)$$

The factor $(S/T)^{\frac{1}{4}}$ may be removed from under the integral sign under conditions similar to those considered above. This factor is the reciprocal of the one removed in the original treatment. Nevertheless one may easily verify that subject to the same considerations as before the solution is given by the generalized equation 25. The summary of assumptions is the same as before except that assumption (j) is not necessary. Assumption (f) must also be changed to mass transfer controlling.

The fact that the generalized solution applies to equation 26 naturally simplifies computations. In fact computation of the generalized equation is completely eliminated by the Schumann-Furnas chart (55)(56)(58) of the solution to equation 26. In this chart H/H_0 or its equivalent is plotted as ordinate and T as abscissa. Various curves are given for fixed values of X . When using the chart for internal lattice diffusion X and T are defined by equations 5, 12, and 14 whereas for mass transfer controlling one

must use

$$X = \frac{K_g a}{\alpha V \rho_G} Z; \quad T = \frac{K_g a B}{\alpha \rho_G} t \quad (28)$$

where K_g is the mass transfer coefficient and "a" is the superficial surface of the granule (ignoring pore structure) per unit volume of bed.

Internal diffusion through pores of a structure such as carbon may also be treated in accord with the generalized theory. In this case X and T are defined as follows:

$$X = \left(\frac{\pi}{R}\right)^2 D_I \frac{\rho_B}{\alpha V \rho_p} \left(1 - \frac{\rho_p}{\rho_s}\right) Z; \quad T = \left(\frac{\pi}{R}\right)^2 D_{IB} \frac{\rho_G}{\rho_p} \left(1 - \frac{\rho_p}{\rho_s}\right) t$$

where ρ_p is the density of the dry porous granule, ρ_s is that for insoluble anhydrite and all other symbols are the same as before. This is a third case to which the generalized theory applies. It may be deduced directly from the work of Wicke (46).

The fact that a so-called generalized theory exists is due in part to assumptions (j) and (k) in the summary of assumptions. It is not obvious to what extent other assumptions may have contributed toward making the generalized theory possible.

The implications of the generalized theory are many. Perhaps the most important one is that the theory may be extended to other cases which the author has not had time to investigate. The second order chemical reaction considered

by Thomas (59) and Walter (52) may well be reduced to generalized form. A controlling surface reaction considered as an activated diffusion process should certainly be reducible to this form (See Commentary).

EXPERIMENTAL STATIC TESTS

Procedure for Static Tests

The term "static" is used to imply that there is no gas flow as such during the course of testing. The desiccant under static test is exposed to moisture in a closed container. The humidity in the container may be such as to cause the desiccant to adsorb water in which case the test is referred to as the "in" test. The "out" test is distinguished by the fact that the humidity is such as to cause desorption of water from the desiccant.

Both the "in" and the "out" static adsorption isotherms were determined for the β soluble anhydrite which appears on the market under the trade name of "drierite". The method employed is similar in some respects to that used by Hammond and Withrow (11).

The work of Wheat (9) indicated that the equilibrium moisture content ("in" curve) of drierite might be a function of nominal granule size. In fact he investigated three different sizes; 0.441 - 0.312", $3\frac{1}{2}$ - 6 mesh and 10 - 20 mesh; and found that on the average the medium size picked up about 1 per cent more water than did the larger and smaller sizes. Hammond and Withrow (11) who determined the "in" curve for what corresponds to 6 - 8 mesh material gave data which suggests that the equilibrium charge lies between that of the two smaller samples investigated by Wheat. Consequently it was considered advisable to investigate a range of sizes which for this and other purposes seemed to be well covered by the selection; 2 - $2\frac{1}{2}$ mesh,

4 - 5 mesh, 10 - 12 mesh, 20 - 24 mesh and 42 - 48 mesh.
(Tyler Standard mesh).

Actually the drierite on hand was that left over from the work by Wheat. It consisted of some new 0.441" - 0.312" granular drierite and two lots, $3\frac{1}{2}$ - 6 mesh and 10 - 20 mesh, which were marked "used" indicating that they had undergone regeneration one or more times and were to be regenerated again. In subsequent sizing for the present experiments the new and used lots were never mixed. A preliminary screening of all three lots indicated that sizes marked on the cans meant no more than to indicate approximate maximum size to be expected. The size of the actual granules in each lot ranged from the maximum down to a dust with appreciable fractions belonging to the lower range.

The 2 - $2\frac{1}{2}$ mesh stock was screened from the new 0.441" - 0.312" lot in accordance with standard practice. The remainder was successively ground and sized to obtain stocks of 4 - 5 mesh and 42 - 48 mesh. Another stock of 4 - 5 mesh material was screened from the used $3\frac{1}{2}$ - 6 mesh lot. The balance along with the 10 - 20 mesh used lot was reduced to stocks of 10 - 12 mesh and 20 - 24 mesh. The history then of the stocks upon which the present work is based can be summarized in the following short notation:

2 - $2\frac{1}{2}$ ← 0.441" - 0.312" new

4 - 5 ← 0.441" - 0.312" new

4 - 5 $\leftarrow$ $3\frac{1}{2}$ - 6 mesh used

10 - 12 $\leftarrow$ 10 - 20 mesh used

10 - 12 $\leftarrow$ $3\frac{1}{2}$ - 6 mesh used

20-- 24 $\leftarrow$ 10 - 20 mesh used

20 - 24 $\leftarrow$ $3\frac{1}{2}$ - 6 mesh used

42 - 48 $\leftarrow$ 0.441 - 0.312 mesh new

where the arrow indicates the origin of the present stocks.

In accord with the recommendations of Kelley et al (32) and the Drierite Company all stocks were regenerated at 400°F for two hours. Higher temperatures and longer regeneration periods are permissible and tend to increase the drying efficiency. These conditions are not used normally because they tend to reduce the drying capacity of the desiccant. The material was spread in $\frac{1}{2}$ " - 1" layers in clean porcelain pans and these were placed in an electric furnace which was controlled to within $\pm 25^\circ\text{F}$ by a Leeds and Northrup Micromax controller. Each pan was supported in the furnace by $1\frac{1}{2}$ " angle iron skids to prevent direct contact between pan and furnace floor. The latter was an obvious precaution taken to avoid overheating of lower layers in the bed being regenerated. After regeneration the stocks were removed and bottled hot so as to effect a vacuum packaging.

Samples of about 5 - 10 grams of the drierite stocks were placed in tared ground glass covered weighing

dishes. These were weighed and then uncovered and placed in glass desiccators which had previously been charged with 1000 grams of sulphuric acid solutions to control the humidity when the glass cover was sealed to the desiccator with ordinary stop cock grease. The large quantity of sulphuric acid employed was sufficient so that changes in concentration during test were so small as to not change the humidity appreciably. All samples were started at low humidity and gradually transferred to higher humidity so as to determine the "in" curve. This procedure was followed by the successive return to the lower humidities to determine the "out" curve. The concentration of the acid solutions was based on the room temperature (72°F) data of Wilson (60) and the International Critical Tables (61)(62).

Reports in the literature (11) indicate that one week is sufficient time for equilibrium to be established at a given humidity. This point was checked by allowing the early samples to be run over a two week period with frequent weighing (1 - 2 day intervals). In some cases small amounts of moisture were still being taken up at the end of two weeks and consequently subsequent samples were run three weeks with less frequent weighings so as to minimize the disturbing influences on the process taking place in the desiccator. The rate of moisture adsorption at the end of three weeks was negligible for the most part. On

this basis the entire procedure consumed the better part of one year.

As a final step in all of the above work an absolute dry base weight was obtained by transferring the samples to tared covered porcelain crucibles which were dried overnight at 750 - 800°F in the same electric furnace previously mentioned. The samples were weighed hot followed by immediately emptying the crucibles, wiping clean, and reweighing to determine loss in weight by the crucible itself.

Other samples of drierite were run at isolated humidities to check certain points of interest. In each case the procedure was the same as that described above. In one case to determine the effect of annealing (32) (63) (64) (65) (66) (67) a new 4 - 5 mesh sample and a used 20 - 24 mesh sample from 10 - 20 mesh were annealed 12 days in the electric furnace at 212°F followed by the usual regeneration.

In another case a sample was tested in a desiccator charged with 200 cc of benzene containing 5 grams of paraffin. A dish of P_2O_5 had also been placed in the desiccator to remove traces of water. In this case the absolute drying step was eliminated because of the obvious hazard involved. In this test the paraffin served to reduce the benzene vapor concentration somewhat so as to avoid condensation difficulties due to small fluctuations in room temperature. Still other special runs were made but these

will be taken up in the section on results since they involve nothing new in procedure.

Results of Static Tests

The static experiments included all of those in which β soluble anhydrite was exposed for some period of time to a vapor laden atmosphere inclosed in a conventional ground glass grease sealed desiccator. The major part of this work had as its objective the determination of both the "in" and "out" adsorption isotherm for various sizes of stock. A summary of these results is given in table IV. The same data are plotted in figures 6 - 10. The lower curves are the "in" curves and the upper are the "out" curves. The original data are included in the appendix. Figure 11 is included for comparison only. The curves in the latter figure are "in" curves.

All static data were corrected to the absolute dry basis which means that it was computed based on the dry weight of sample as determined after heating at 750-800°F for a minimum of 24 hours. Thus it was possible to compute the water content of the samples after they were regenerated preparatory to running the adsorption isotherm experiments. These water contents on the absolute dry basis were found to be as follows: 2 - 2½ mesh new -0.282%; 4 - 5 mesh new -0.184%; 10 - 12 mesh used - 0.234%; 20 - 24 mesh used -0.237%; and 42 - 48 mesh new -0.512%.

Figures 6 - 10 demonstrate the fact that used material has a definitely lesser tendency to pick up water than new material. In an effort to prevent relating this effect to particle size a new sample of 10 - 20 mesh product

obtained from the Drierite Company was tested. A 10 - 12 mesh fraction was screened from this sample to make the results most convincing in the light of the adsorption isotherm already determined for used 10 - 12 mesh (see figure 8). Regeneration for this fraction was the same as that employed with all previous samples. The sample was run at 25% relative humidity to minimize the effect of variation in room temperature. The water adsorption on the absolute dry basis was found to be 6.04% by weight. This of course compares favorably with the new samples the data for which are plotted in figures 6, 7, and 10. It far exceeds corresponding values shown either in figure 8 or figure 9.

The question as to whether the used samples picked up less water because they were less pure or because they had been repeatedly regenerated was investigated further. Comparison alone of the present data with that of Wheat in figure 11 say at 25% RH for the 10 - 20 mesh range tends to support the regeneration hypothesis. For purposes of investigation a new 4 - 5 mesh sample and a used 20 - 24 mesh sample were selected as subjects. They were annealed 12 days at 212°F and then regenerated for the customary 2 hours. In equilibrium with 35% RH their absolute moisture contents were found to be 6.32% for the 4 - 5 mesh and 4.61% for the 20 - 24 mesh. In both cases the adsorption was decreased by about 0.2% compared with previous determinations on the same materials.

Table IV
Equilibrium Moisture Content of Drierite Samples
Temperature = 65 - 90°F

Per cent Relative Humidity $p/p_0 \cdot 100$	Water Adsorption (per cent by weight abs. dry basis)									
	2-2½ new		4-5 new		10-12 used		20-24 used		42-48 new	
	In	Out	In	Out	In	Out	In	Out	In	Out
.0313	.439		.426		.341		.324		.449	
.408	.735		.741		.615		.558		.802	
1.		6.12		5.97		3.97		4.27		5.81
2.		6.16		6.01		4.09		4.38		5.89
3.63	6.2		6.02		3.962		4.28		5.93	
5.		6.3		6.18		4.22		4.51		6.02
10.	6.42		6.25		4.21		4.51		6.13	
25.		6.53		6.4		4.52		4.79		6.28
35.	6.66		6.5		4.54		4.82		6.41	
40.		7.08		6.89		4.84		5.11		6.76
50.	7.57	7.74	7.31	7.42	5.04	5.21	5.37	5.53	7.05	7.42
65.	8.1		7.83		5.41		5.74		7.68	

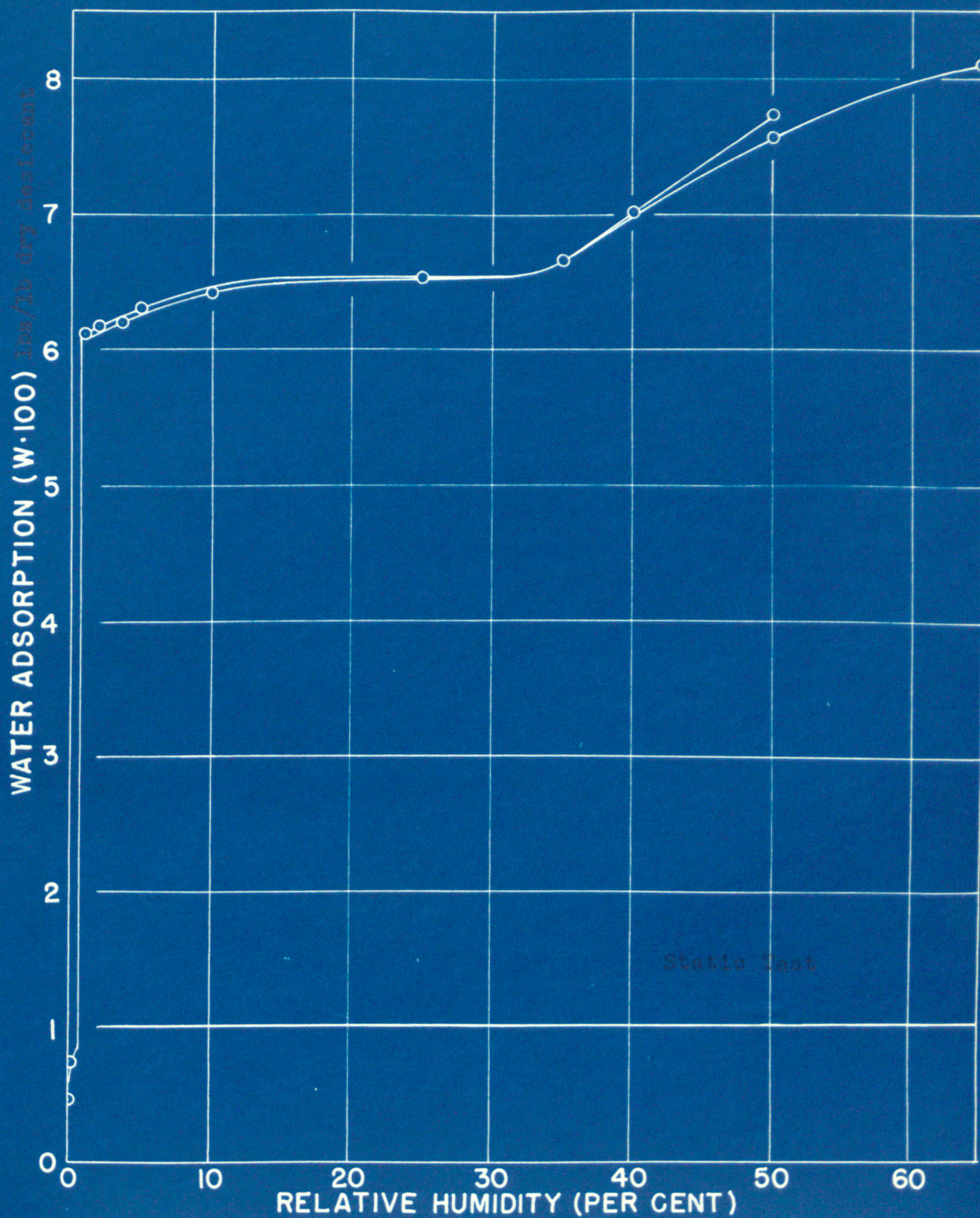


Figure 6
Adsorption Isotherms of New 2 - 2-1/2 mesh Drierite
Lower curve is "in" curve, upper is "out" curve.

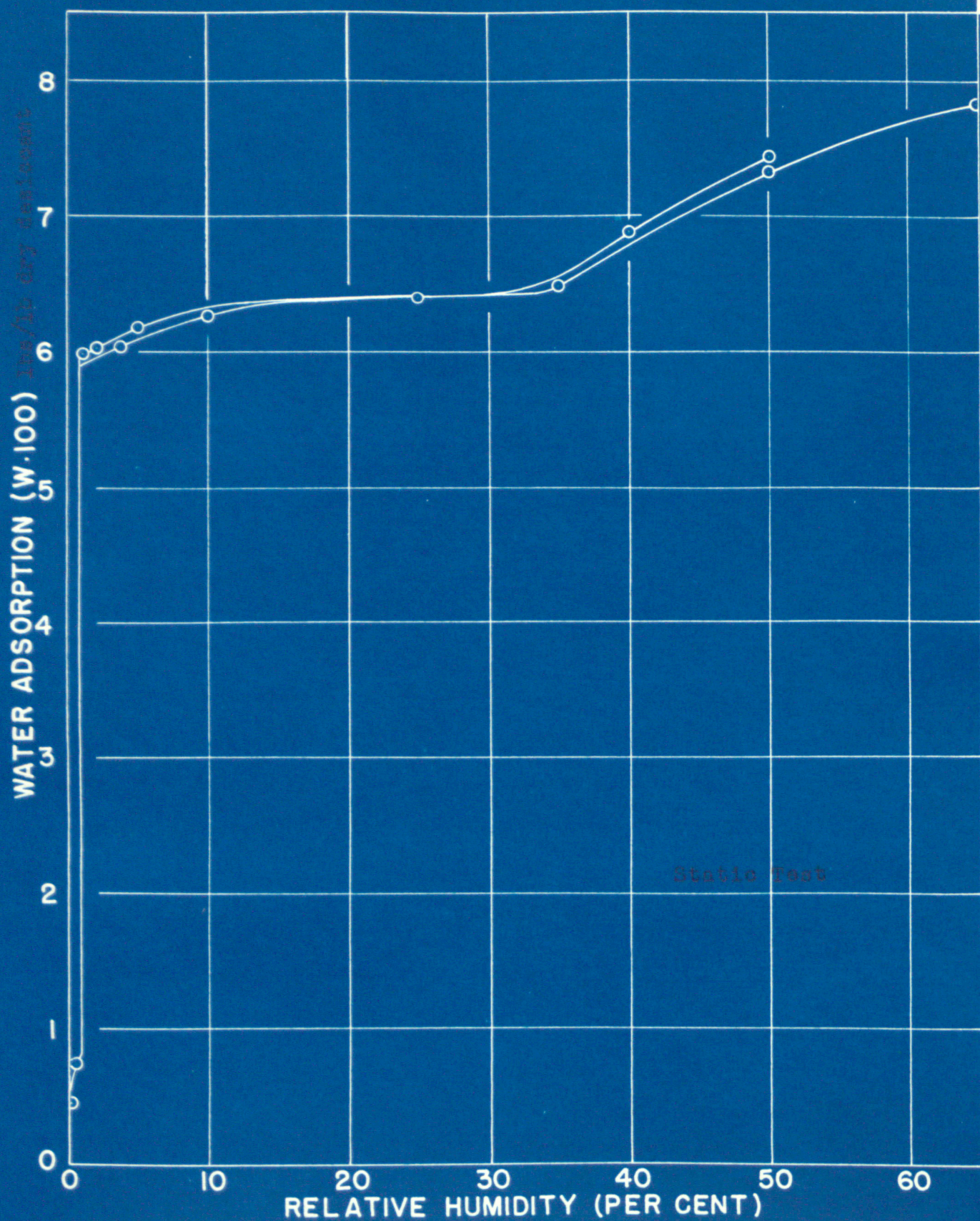


Figure 7
 Adsorption Isotherms of New 4 - 5 mesh Drierite.
 Lower curve is "in" curve, upper is "out" curve

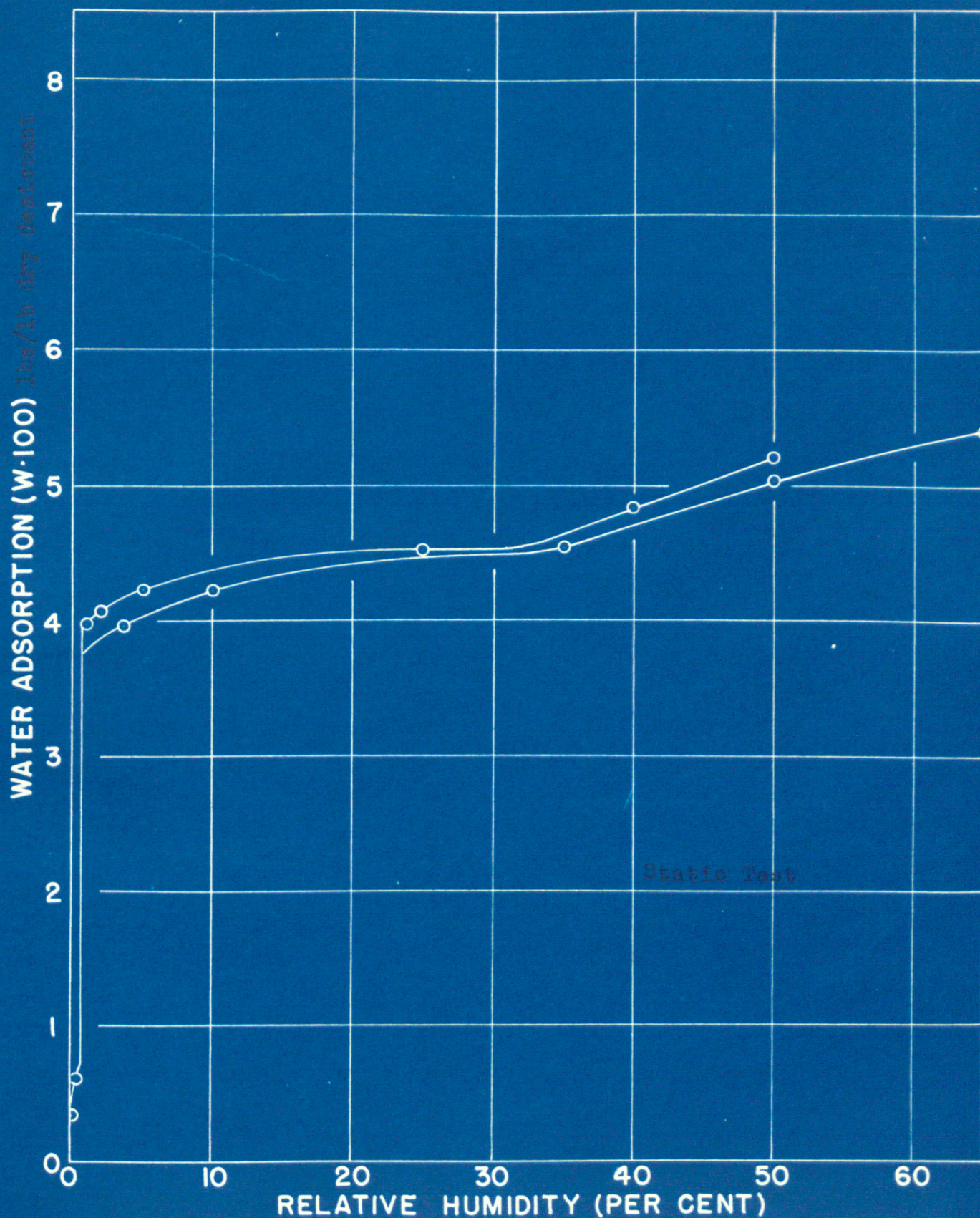


Figure 8
Adsorption Isotherms of Used 10 - 12 mesh Drierite.
Lower curve is "in" curve, upper is "out" curve

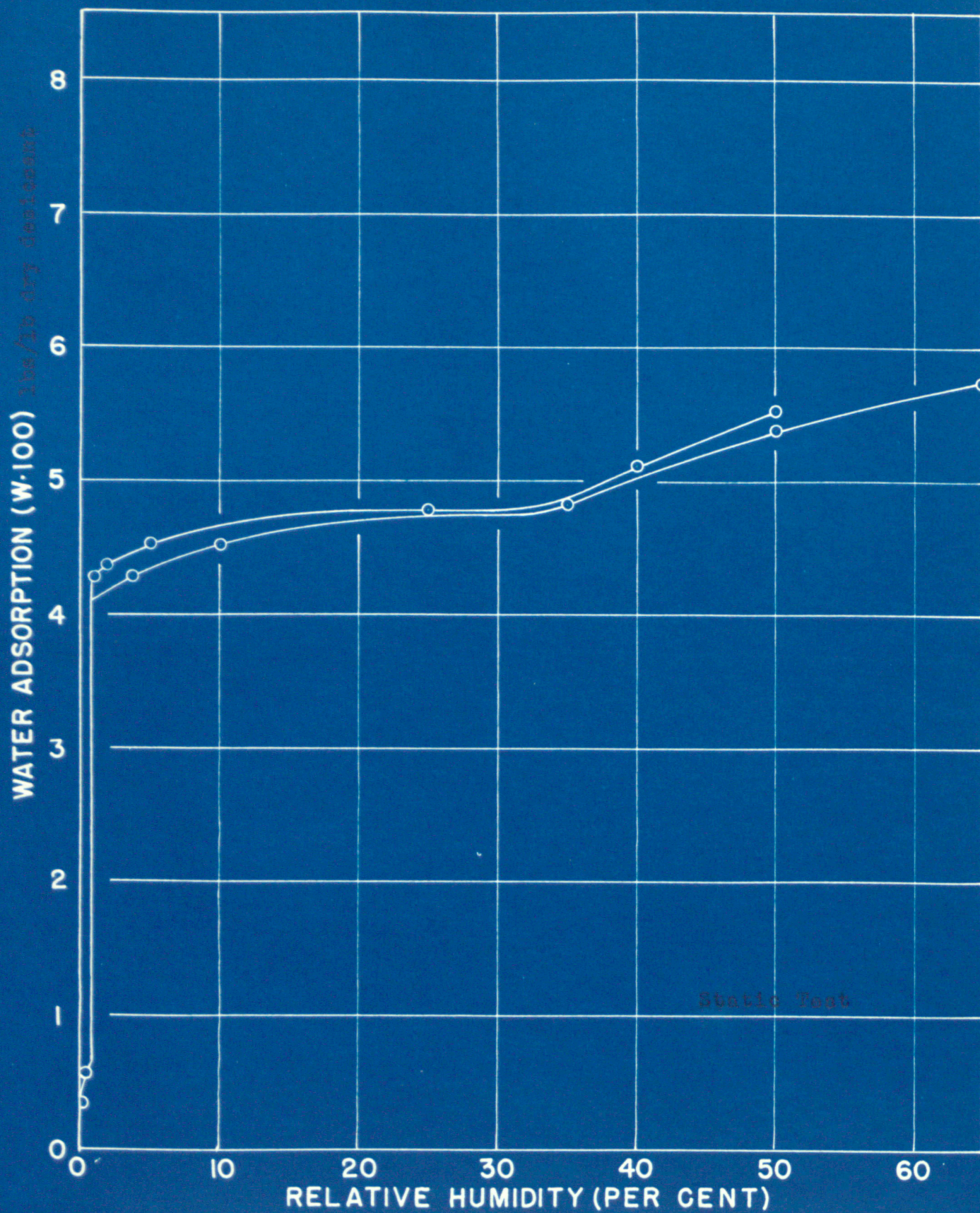


Figure 9
 Adsorption Isotherms of Used 20 - 24 mesh Drierite.
 Lower curve is "in" curve, upper is "out" curve.

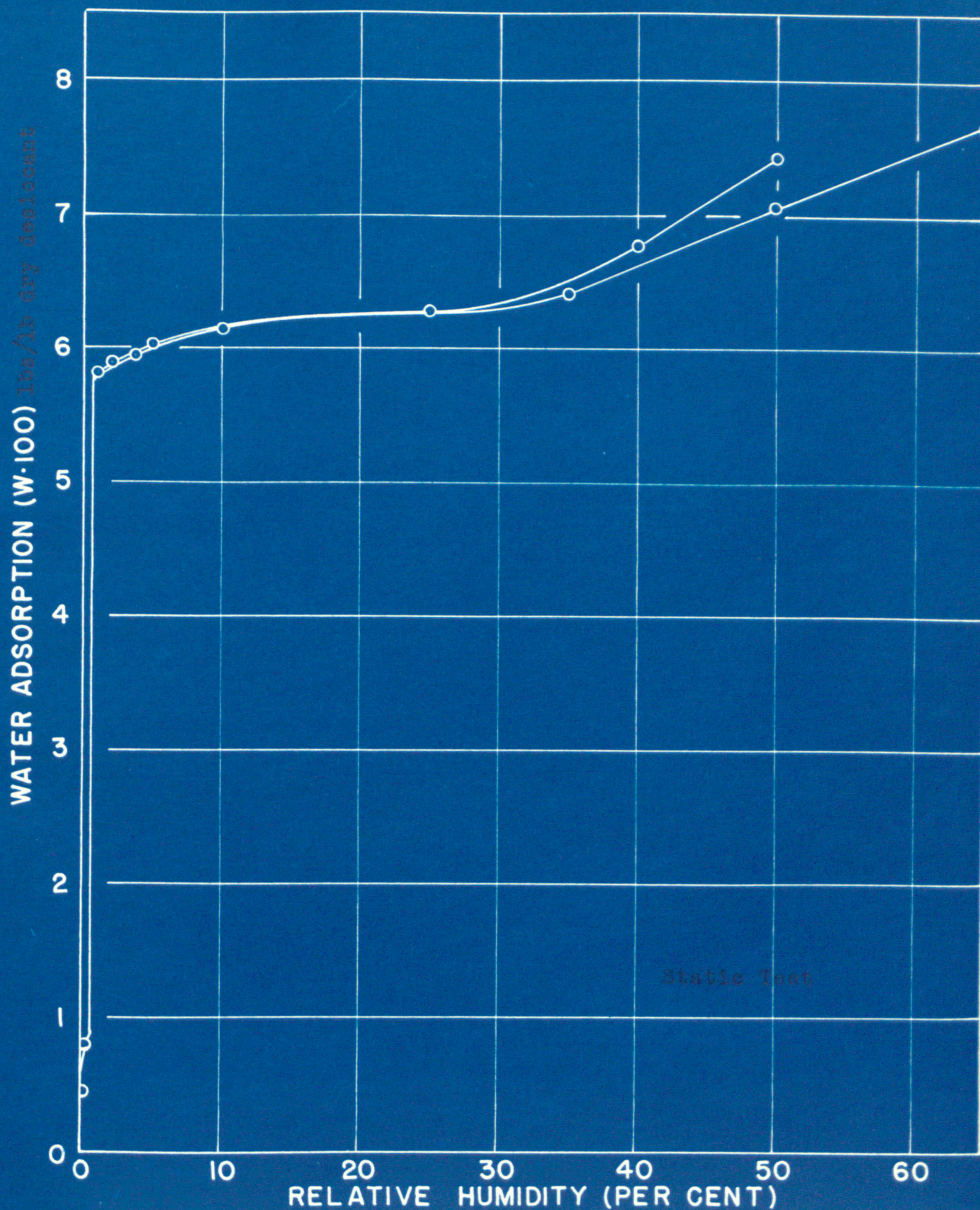


Figure 10
 Adsorption Isotherms of New 42 - 48 Mesh Drierite.
 Lower curve is "in" curve, upper is "out" curve

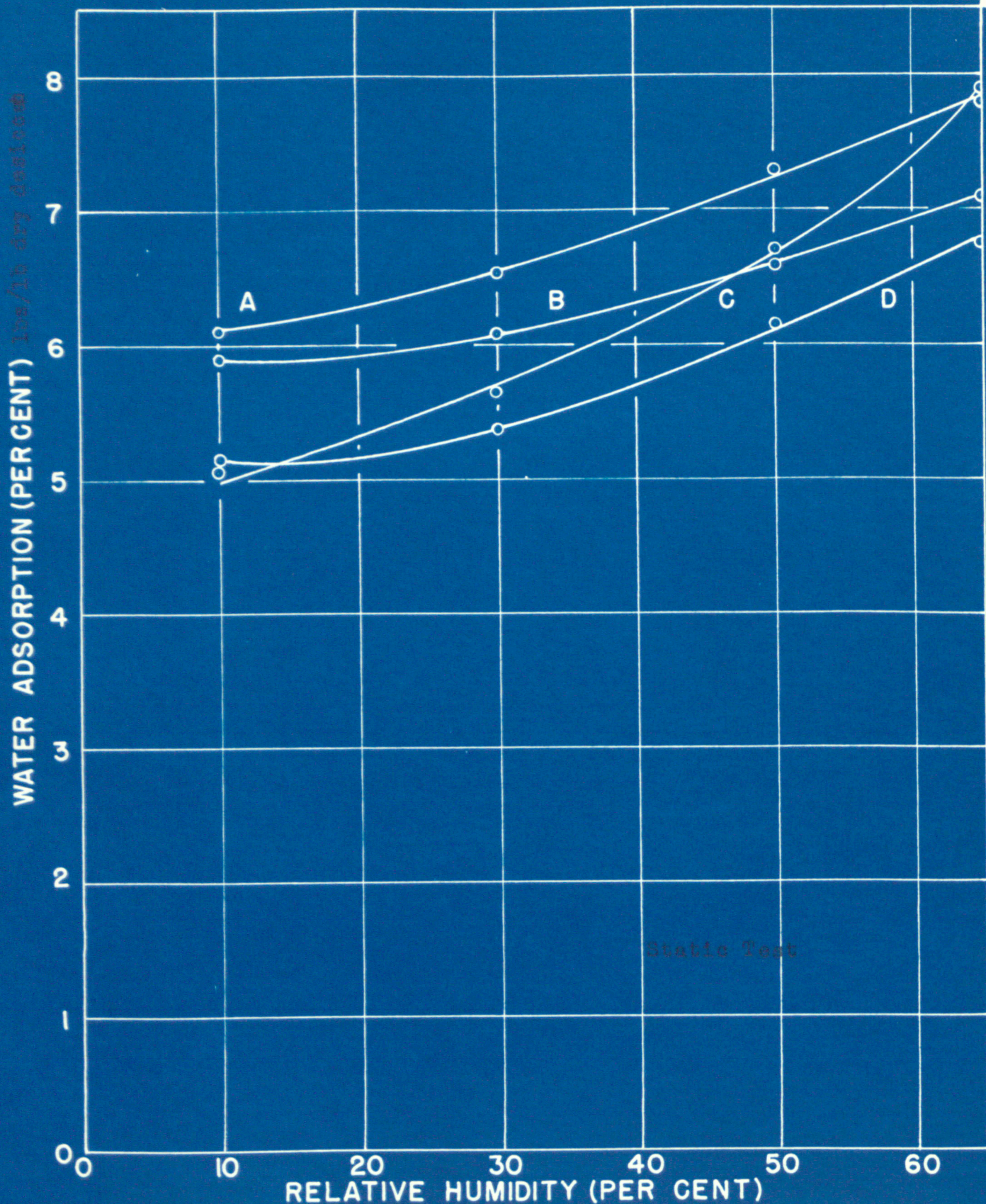


Figure 11

A Comparison of Drierite Adsorption Isotherms Appearing in the Literature. A - 3-1/2-6 Mesh by Wheat; B - 6-8 Mesh by Hammond & Withrow; C - .441"-.312" by Wheat; D - 10-20 mesh by Wheat.

The kinetics of adsorption in beds of desiccant may be related to the pore structure of the granule. For this reason benzene vapor was used to investigate pore size as previously discussed. For this purpose a new 4 - 5 mesh sample was exposed to dry air nearly saturated with benzene. Using the regenerated dry basis the sample was found to contain 7.34% by weight benzene. On an absolute dry basis this figure would be somewhat higher but not appreciably so.

Discussion of Static Tests

Qualitative examination of the adsorption isotherms leads one to agree that β soluble anhydrite is no ordinary crystal but that it is a crystal. Throughout the range of about 5% to 30% relative humidity the square shaped isotherm, except possibly for the knee, is exactly that expected for a typical crystal hydrate. Both above and below this range the crystal certainly resembles a zeolite. With regard to the lower range this conclusion is in accord with that of Kelly et al.

A comparison of adsorbed water concentrations along the flat portions of figures 6, 7, and 10 shows a gradual decrease with nominal particle size as follows: 2 - $2\frac{1}{2}$ mesh - 6.53%; 4 - 5 mesh - 6.4%; and 42 - 48 mesh - 6.25%. The effect is definite even though it is small. The actual reduction in capacity from the largest size to the smallest is 4.3%. Whether the reduction is due to heating during grinding (and consequently the formation of insoluble anhydrite), a sorting process during screening, or some other cannot be decided without further experiments. Certainly there is no reason to agree with Wheat that there is an optimum particle size at which adsorption is a maximum. There is also no relationship to repeated regeneration because the samples were all new.

Figures 8 and 9 and the tests of new and annealed samples show that heating during regeneration or for any other purpose causes degeneration of the material as a sub-

sequent desiccating agent. This effect is apparently independent of particle size and in this respect serves only to confuse the major issue. These findings are in accord with the opinion of Hougen and Dodge (1) and Kelley (32) et al but do not substantiate the conclusion of Hammond and Withrow (11). It appears that heating causes formation of insoluble anhydrite nuclei which probably grow with more extensive heating until eventually the entire granule would be consumed. The effect is the same as if non water adsorbing sand particles had been injected into the granule. The effect is even noticeable at temperatures as low as 212°F as compared with the regeneration temperature of 400°F .

A comparison of isotherms shown in figures 6, 7, 10, and 11 leaves little doubt that the absolute dry base weight and longer test periods have a definite effect on the appearance and general position of the "in" adsorption isotherm. In this one cannot agree with previous investigators that one week suffices to determine a datum point on these curves. On the contrary there may even be an underestimate of the situation as is perhaps indicated by the fact that the lower humidity portion of the "in" isotherms is slightly lower than that for the "out" (See knee portion of figures 6, 7, and 10). The knee is practically closed for the 42 - 48 mesh nominal particle size and this more strongly substantiates the viewpoint.

The above observations on the time required for equilibrium considered in the light of the benzene adsorption experiment seems to give the first clue as to what the mechanism of adsorption might be. It was previously shown that a Drierite granule should contain by volume 74.2% of β soluble anhydrite crystallites and the other 25.8% of the volume should be space between the crystallites of the granule. On this basis the benzene pickup should be 12.3% by weight (absolute dry basis) provided that this space was made up from pores of diameter greater than that of the benzene molecule, i.e., $5.7\text{\AA}$. Actually by experiment the benzene pickup was 7.34% by weight (regenerated basis). Now it is known that the latter figure is too low because of the regenerated basis for computation and because the experiment was run only one week and not at saturation pressures. Taking this into consideration a good share of the intercrystallite space probably has a dimension exceeding $5.7\text{\AA}$ and this is sufficient for free diffusion of water molecules which are about $2.9\text{\AA}$ in diameter. If some of the interstices between the crystallites had dimensions of the order of $40\text{\AA}$ or more then the pores could never be filled in the benzene experiment and this would also contribute to the lower experimental values. The latter would likewise be true for pores smaller than $5.7\text{\AA}$. Undoubtedly both factors play a part and only more elaborate experiments with a range of molecular sizes would distinguish between

them. The present work suffices to state however that in the first few days water molecules in the static experiments probably by a combination of free and activated diffusion saturate the crystallite surfaces and the latter area must be very great for a granule if its crystallites are small. The next two weeks and more is consumed in activated diffusion to saturate even the very centers of the very small crystallites. This further substantiates the idea that internal diffusion may be the rate-controlling process in the adsorption mechanism.

The fact that regenerated new desiccant contains 0.184% to 0.512% by weight (absolute dry basis) moisture agrees in general with the report by Kelley that this material contains 0.16% to 0.27% by weight (wet basis) and in some cases even more water. The fact that the vertical portion of the isotherm lies between 0.081 and 0.198 mm Hg does not agree with the estimated value, 0.0043, reported by Hammond and Withrow. The latter estimate is at least 20 times too low.

For large installations the interest of the chemical engineer in the adsorption isotherm for β soluble anhydrite is generally confined to the lower regions of humidity due to the comparative cost of Drierite and the fact that it is a good "finish drier" of low capacity as indicated by the isotherm already presented. In this regard the knee represents about 7.5% reduction in capacity and one

naturally is curious as to how this might come about. The theory of Damerell (63) seems to give a most plausible explanation.

The classical mechanism for decomposition of hydrates and related compounds has been one of sharp change from hydrate to lower hydrate or anhydrous substance and water, without the formation of intermediate phases. The new mechanism proposed by Damerell recognizes that a hydrate crystal at constant temperature may have adsorbed water on its surface at the start of dehydration and that if the vapor pressure of the surroundings is gradually lowered the adsorbed water is removed starting at some pressure greater than that for the hydrate. As the vapor pressure is decreased all the adsorbed water is removed and eventually water molecules will start leaving the surface lattice of the hydrate (condensation rate becomes less than evaporation rate) at a vapor pressure greater than the decomposition pressure. The portion of the original lattice left after this surface dehydration is called the skeleton lattice zone. It is in the behavior of this zone that the new mechanism differs most markedly from the classical one. Below the upper transition temperature the residual material is held as a stable film on the surface of the crystals, even in the presence of the other solid phase. The lattice symmetry of the film is not greatly different from that of the original hydrate.

Continuing dehydration causes two changes. The

increasing thickness of the skeleton lattice zone causes a decrease in the pressure exerted by the water molecules leaving the crystal and the stability of the outer part of the zone usually decreases as the valence forces exerted by the unchanged lattice act over greater distances. At the decomposition pressure the outer portions of the zone are so unstable that seeding or scratching will cause rearrangement to spread over the surface. If the crystal is untouched the transformation may be suspended until the process progresses to a degree of instability great enough to cause nuclei formation of the lower hydrate or anhydrous phase. At this point the vapor pressure will rise to the decomposition value.

As decomposition continues in the usual sense a zone of skeleton lattice of constant (on the average) thickness will always precede the lower hydrate or anhydrous substance into the crystal of the original hydrate, except in the neighborhood of the upper transition temperature. When the thickness of the zone is able to exceed a small number of molecules it may become infinite as is the case for zeolites. The latter condition is expected if the skeleton lattice zone becomes sufficiently stable to exist by itself without the help of stabilizing forces from the unchanged hydrate lattice. Since the latter forces probably become negligible at distances twice as great as the equilibrium distances between atom centers it is supposed that a

skeleton lattice zone is able to exist in thickness much greater than this should be able to exist in any thickness.

Assuming that surface dehydration takes place prior to decomposition in the usual sense it should become increasingly evident in pressure composition isotherms with decrease in crystallite size because of the increased surface and it is apparently this effect which is indicated by the knee.

It is interesting to note that the zeolites and other compounds which lose water continuously are classed under the new theory as capable of forming a stable skeleton lattice zone of any thickness. As the ratio of water molecules to molecules of anhydrous substance becomes smaller this phenomena should become more probable, particularly if the skeleton lattice structure is similar to that of the original hydrate. Experimentally this is usually the case with the higher hydrates giving up water in a stepwise manner and the lower hydrate products losing water continuously. Heptahydrate of sodium ammonium ferric oxalate is an exception because the first water is lost continuously while the remainder is a necessary part of the skeleton lattice.

A more general explanation of the complete isotherm is probably to be based on the combined theory of Hey (33) (34) (35), and Bunn (31) as distinguished from that of Harkins, Jura (43), Brunauer, Emmett and Teller (68) which

is primarily concerned with solid surfaces. Up to about 30% RH the 6 sites of $12 \text{ CaSO}_4 \cdot (6) \text{H}_2\text{O}$ are being filled and according to the basic theory of Hey these would be completely filled only at infinite pressure. At about 30% RH the much more volatile or "forbidden" 2 sites start to fill to give the $12 \text{ CaSO}_4 \cdot (6+2) \text{H}_2\text{O}$ proposed by Bunn. On this basis investigation at humidities exceeding 65% should show a maximum in the adsorption isotherm at about 8.8%.

This explanation would appear to be complete were it not for the apparent hysteresis which appears to be most pronounced for the 42 - 48 mesh sample. Moreover above 35% RH the "out" curves tend toward linearity for the two large sizes and the smallest whereas the "in" curves show marked curvature which decreases with particle size to linearity for the 42 - 48 mesh sample. The latter fact suggests that at the smaller particle size the gas pressure tends to behave according to the ideal gas law. Placing the 2 - $2\frac{1}{2}$ mesh curve over the 42 - 48 mesh curve shows that the "out" curves are parallel whereas the "in" curve of the 2 - $2\frac{1}{2}$ mesh tends to bend over to eventually intersect the 42 - 48 mesh curve. From a purely physical chemical point of view the isotherms should be investigated in detail beyond 35% relative humidity. To obtain small sizes and at the same time eliminate heat effects it may be necessary to ball mill the material mixed with dry ice for example. It may be that with more data the "in" isotherms may all be linear or

all curved. The exact nature and extent of the hysteresis loop should be determined. Then, too, the relationship of this entire portion of the plot to that for the dihydrate should be investigated. After all, according to the data of Kelley (32) one would expect dihydrate above about 22% relative humidity.

Without further data it is only possible to suggest that during grinding of large granules to small the larger intercrystallite spaces are destroyed first because they cause the granule to be weakest at these points. As grinding continues to produce smaller granules the next smaller size intercrystallite space is destroyed and so on until eventually at a sufficiently small size there remain for the most part a powder the particles of which are individual crystallites or groups of them with sufficiently small intercrystallite cracks as to be undetectable under the conditions of a particular experiment. On this basis one would expect a linear rise of pressure as water molecules filled more and more "forbidden" sites in the crystallites of small granules. The same process would be expected of a larger granule but the effect would be obscured by superimposition of another effect due to the tendency of intercrystallite pore walls to act something like solid surfaces. This explanation leaves the apparent hysteresis to be associated with the properties of the dihydrate. The latter

seems plausible in the light of a statement by Kelley that β hemihydrate "probably does not exist as such in the presence of H_2O (l) or in the presence of the implied equilibrium pressure of H_2O (g)." The implied pressure corresponds to about 22% RH at 25°C. This would not agree with the work of Bunn if it is accepted that the dihydrate forms only at an adsorption of 8.8% or greater.

EXPERIMENTAL DYNAMIC TESTS

Outline of the Dynamic Experiments

The preceding sections of this thesis have been devoted to developing various phases of a theory to explain what might be expected of soluble anhydrite under dynamic test conditions. The term "dynamic" is used here to imply that a bed of the desiccant is tested by passing through it a continuous humid gas stream. The object now is to present a scheme for testing and then to present test results in the light of the theory previously developed.

In order to carry out the proposed work and in particular to study the adsorption mechanism it is necessary to determine the adsorption wave under various conditions. Klotz (3) proposed an empirical procedure for determining the effective adsorption mechanism. For this purpose it is necessary to determine the effect (on the adsorption wave) of granule size in a bed of fixed length and for which the flow rate is also fixed. It is also necessary to select a given particle size for a series of beds in order to study the effect of gas velocity and bed length. It turns out that these data are more than sufficient for application of the generalized theory.

Actual determination of the adsorption wave for a given bed requires an instrument to continuously measure the moisture concentration of the effluent gas from the bed. In the case of soluble anhydrite it was recognized that such an instrument must measure water vapor concentrations

as low as 2 ppm (7). A brief survey showed that suitable instruments were not available. It was necessary therefore to design and construct for this purpose a frost point hygrometer which is the subject of the following section.

The Frost Point Hygrometer

The determination of small amounts of moisture in air is a familiar problem which has been discussed in several places (7)(8). Chemical methods, dew point hygrometers, infra red absorption instruments, conductivity instruments are available. Czepek (69) has reviewed dewpoint methods which consisted of (a) freezing out moisture and weighing, (b) closing of an electric circuit by the formation of a deposit (limited to range of -40 to 200°C), (c) change in radiation on a photocell at dew point, (d) passing air through a tube or over a rod having a temperature gradient along the length, (e) determining dew point from the break in cooling curve which appears after deposition, and (f) cooling a mirror to observe dew visually. At dewpoints down to -90°F and in the case of a rapid succession of measurements it becomes futile to consider chemical methods, infra red and methods a, b, e and f of Czepek. Conductivity instruments beside being expensive have still other limitations.

Preliminary Trials:

Halban and Siedentopf (70) have recommended a dew-point instrument the principle of operation of which is based on method (d) above. It is recommended for water vapor concentration below 1 g/metre^3 . Such an instrument was investigated during the course of the present work. A $3/4$ " brass rod about 18" long was enclosed in a 12" length of glass tube stoppered to fit at both ends. Glass tubes of

various diameters were tried. In each case an inlet and outlet for the air stream was provided at the ends of the glass jacket. The upper protruding end of the brass rod was terminated in an ordinary ice bath with the lower dipping into dry ice and alcohol or acetone. The test air stream was so directed over the enclosed rod as to flow into a successively lower temperature. Test air having a dewpoint ranging from 0 to -80°F was tried.

Results showed that it was difficult to conveniently insert into the instrument a traveling thermocouple to accurately read surface temperatures at the line of demarkation. Furthermore the line became much more obscure and indefinite at the lower frost points. At -80°F it was impossible to tell visually whether or not frost ever formed. Another disadvantage was that the instrument did not give absolute readings in the sense that it required calibration for each air flow rate.

In favor of an absolute instrument and the elimination of the traveling thermocouple an instrument was built consisting basically of two copper tubes. The one was 1" I.D. and 12" long with one end capped. In its midsection a $1/8$ " hole was drilled diametrically with a tilt of 45° to the tube axis. The $1/8$ " copper tube was inserted so that about 2" of the smaller tube extended out either side of the larger. The arrangement in general resembled that in figure 13. The joints between the two tubes were soft soldered. A copper constantan thermocouple was inserted into the $1/8$ "

tube and soft soldered flush with the opposite end and the end surface thus formed was polished since it was the test surface upon which the frost would be formed.

Between the polished surface and the large tube a nichrome heating element was wound on the insulated outer wall of the 1/8" tube. This element served to counterbalance the effect of the dry ice bath which was to be placed in the 1" tube which had in the meantime been insulated with 1" of magnesia covering. The polished surface was enclosed by a glass housing so that the test air stream could be admitted from the top being directed at the center of the surface. Exits for the exhaust air were provided at the periphery.

Operation of the instrument consisted of first mounting the instrument so that the polished surface was up and the 1/8" tube was vertical. The thermocouple leads projecting from the lower end were coupled with copper leads to a Leeds and Northrup Type 8662 portable precision potentiometer through an ordinary ice bath to form a hot end junction (32°F). In relation to the small tube the 1" tube angled at 45° with the capped end pointing downward. The charge of alcohol and dry ice was placed in the upper open end and test air was then admitted into the glass housing. Current was supplied to the heating coil so as to regulate the test surface temperature which could be read continuously on the potentiometer.

Early experiments showed that there existed a most

favorable relationship between the heating element and the length of small copper tubing on which it was wound. The shorter the tube the lower was the minimum temperature that could be attained. The minimum length however was limited by the fact that heaters had to be designed for the small remaining space.

Extended experiments showed that it was virtually impossible to detect frost visually on the polished surface and even the inclusion of a low power microscope failed because of unfavorable ventilation of lens elements which tended to coat over either with water or ice. In addition the instrument was sensitive to the air flow rate over the polished surface.

As a last resort the instrument was converted to use for detecting a flat in the cooling curve at the frost point. To do so a slop-jar resistor was included in the heater circuit. The plates of the resistor were so designed that when tap water which served as electrolyte was drained through a constant size opening the electrical "energy" was reduced at a uniform rate. Thus if practically dry air (frost point below -90°F) was run constantly through the instrument and the charged resistor permitted to drain a straight line time temperature curve would be obtained. Humid air (dewpoint 32°F to -80°F) gave a discontinuity which was not reproducible and extended experimentation only served to confirm this fact. The one favorable result

of all this work was that a properly proportioned instrument had been developed which was capable of controlling the frost point surface temperature down to about -90°F and was direct reading. The one defect in the instrument could apparently be remedied by utilizing a lighted surface under the continual observation of an electric eye and this of course emphasized the importance of method (c) mentioned by Czepek.

Up to this time the literature was more or less confused as to how a frost point surface should be lighted and as to the best arrangement of light and surface with respect to the photocell. The question of adequate ventilation of optical parts at low temperatures, the question of educating polished surfaces to form frost and not dew, and many others held promise of a very extensive research program to make practical the instrument previously discussed. Fortunately, at this time, Brewer, Cwilog and Dobson (8) published a paper entitled "Measurement of Absolute Humidity in Extremely Dry Air". This paper not only summarized the results of intensive research on the subject during World War II but also gave details of what the authors called a hand operated instrument which admittedly lacked perfection but which was extremely reliable down to dewpoints of -90°C (-130°F). This lower limit is established by the fact that below this temperature the frost deposit is in the form of an invisible glassy layer. Because the latter fact appears to have daunted the authors as indicated by the research

which followed, it seems at this point a matter of academic interest to suggest what appears to be a plausible explanation.

Glasstone (71) based on the work of Tammann and Bridgman has presented an integrated phase diagram down to -50°C for water-ice-vapor showing the pressure-temperature dependence of the phases. If one qualitatively extends the lines (which are actually curves) dividing Ice II - Ice I and Ice I - water vapor it is very easy to estimate that at atmospheric pressure Ice II, Ice I and water vapor should be in equilibrium at a temperature which certainly is below -80°C . Glasstone himself has stated that such an equilibrium is possible. Thus it appears that the frost point hygrometer is limited by the fact that Ice II is an invisible glass at least in thin layers.

The Electronic Instrument:

In view of the report by Brewer et al the frost point hygrometer which had been developed by the author was used as a model for the proportioning of a new instrument with increased capacity which was also sufficiently large so as to permit easy attachment of an optical head of the type recommended by Brewer (8). An electronic unit was also devised to replace that used by Brewer. The latter was necessary in order that the frost point hygrometer be automatic as well as an indicating instrument. It is this in-

strument which is described in the following pages.

The entire test assembly is shown in figure 12. Figures 13, 14, and 15 show the structural features of the Frost Point hygrometer proper.

The frost point hygrometer was built in two separate units. The one unit has been designated the frost point hygrometer proper which basically consisted of an insulated brass tank for cooling purposes, thermal element including a gold surface on which frost forms, heating element, and optical head. The latter contained the test air injection nozzle, exciter lamp, black absorber for reflected light, photoelectric cell to receive diffused light, shutter for controlling light intensity and the necessary lens elements for condensing and focusing light to and from the gold surface.

The second unit was an electronic device the sole purpose of which was not only to automatically supply the proper current to the heater of the first unit but also to notify an observer of the photoelectric effects and thus the status of frost deposited on the polished gold surface in the first unit. For description purposes, the electronic device may be thought of as being divided into three sections. The first section is connected to the photocell in the frost point hygrometer proper and generates a constant amplitude pulse the frequency of which varies in accordance with the

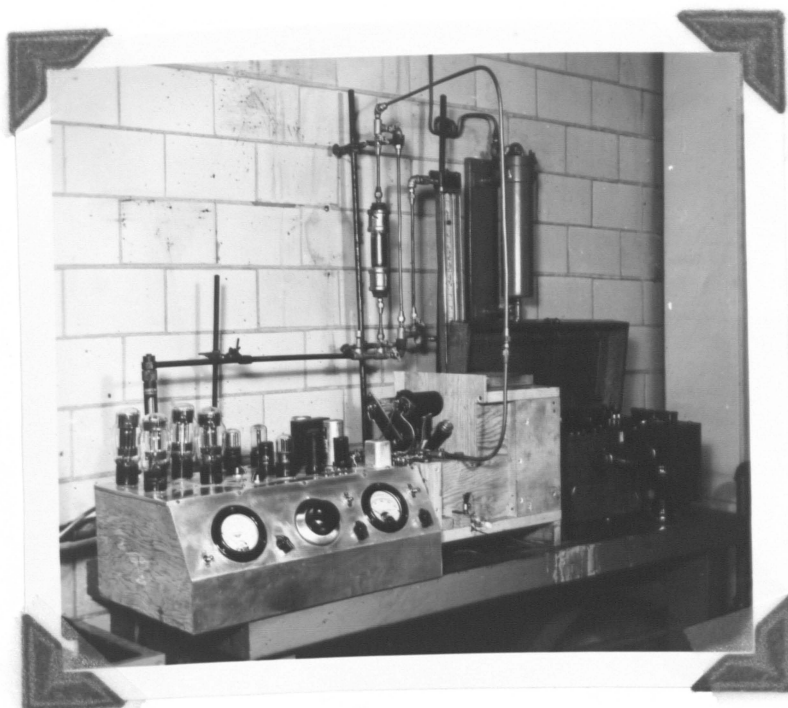


Figure 12

Frost Point Hygrometer and Test Assembly

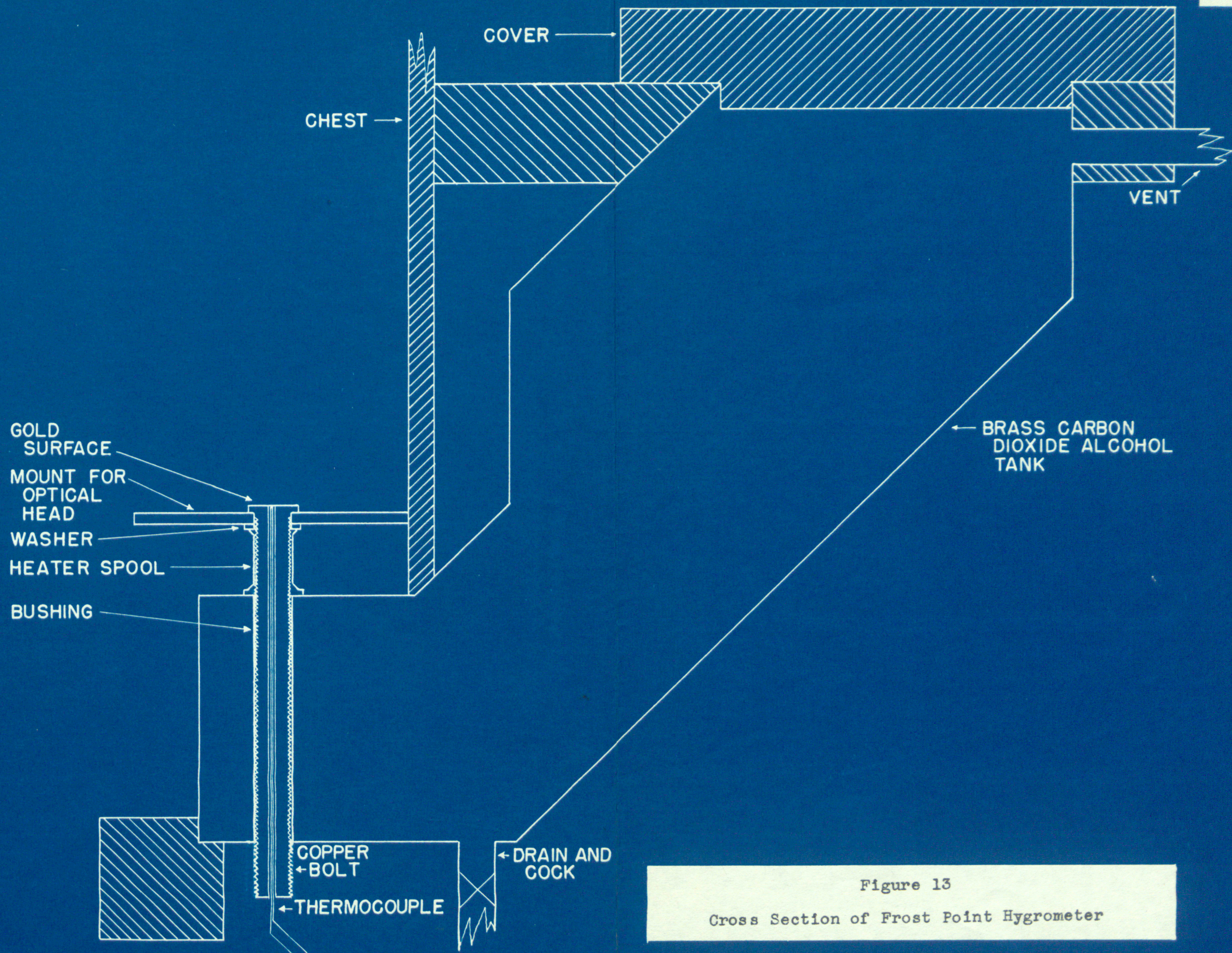


Figure 13
Cross Section of Frost Point Hygrometer

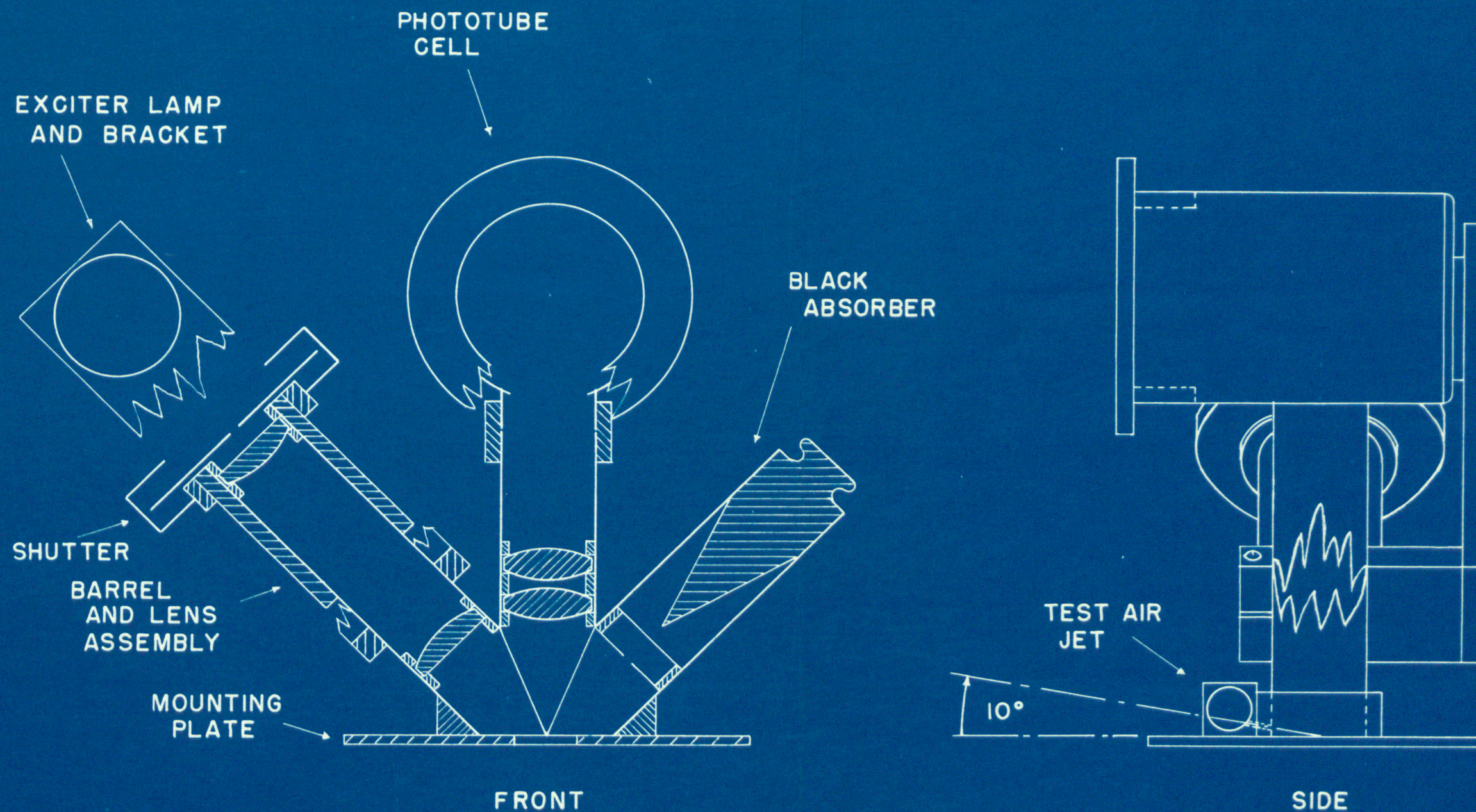


Figure 14
Cross Section of Optical Head

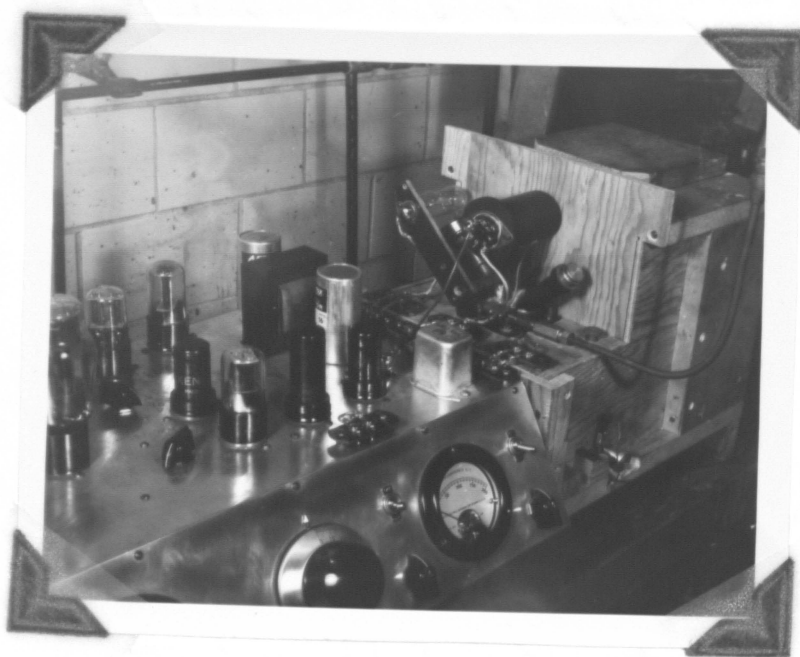


Figure 15
Optical Head

resistance of the phototube (which in turn depends upon the strength of diffuse light played upon it). This pulse is sent into a bridge circuit where it is detected (converted from ac to dc). The bridge includes a 0-200 microammeter. This meter although subjected to pulsating dc indicates a constant current for a given frequency because the mass of the meter parts prevent following the range of frequencies employed here. As the frequency increases the microamp indication increases and thus the observer is informed of an increase of light at the photocell and consequently an increase of frost deposited at the gold surface.

The second section receives a small fraction of the detected signal from the first and converts it into an electrical potential of such form and magnitude as to be capable of controlling the grid bias on the third section. The latter is nothing more than a bank of four power tubes which supply a 60 cycle half wave rectified current to the heater in the frost point hygrometer. The magnitude of the current supplied by the power tubes of course depends upon their grid bias voltage supplied by the second section. The latter in turn depends upon the frequency in the first section and thus the light and frost quantities in the frost point hygrometer proper. An increase of frost for example increases the frequency in the first section, decreases the bias put out by the second section, and increases the plate

current supplied by the third section. An increase of plate current raises the temperature of the gold surface in the frost point hygrometer and tends to evaporate the frost. Thus the reverse cycle would set in.

The two units were so constructed that when placed on the same level they could be pushed side by side in such manner as to align bus connectors to complete the electrical circuits between the two units. Completing the test assembly required connecting the air injection nozzle of the first unit to the test air supply. Also the leads from the thermocouple in the thermal element had to be connected to the potentiometer in order to determine the temperature of the gold surface upon which frost had formed.

Detailed Description of Frost Point Hygrometer Proper:

The carbon dioxide-alcohol tank was made from an 11-1/2" length of standard 4" brass tubing (1/16" wall). The ends were chamfered as shown in figure 13 and flat brass plates (1/16") soldered to the edge thus formed with the exception of the one opening at the top which was left so for charging purposes. The latter was provided with a wood cover. The tank was provided with the necessary vent and drain as shown. The lower end plate and adjoining top and bottom plates formed a square end box. Through the top and bottom of this box a hole .390" in diameter was drilled so as to permit inserting a copper bushing so that

its ends were just flush with top and bottom. The bushing was made so as to "push" fit and it was soldered in place. The internal wall of the bushing had been threaded with $3/8$ " SAE standard machine thread. It will be noted at this point that the bushing wall thickness was of the order of .010". It was found to be a necessary feature in order to minimize the length of heat transfer path so as to obtain minimum possible temperature at the gold surface to be discussed.

The thermal element consisted of a 4" length of $1/2$ " copper rod which was turned and threaded externally with $3/8$ " SAE standard machine thread so that it could be screwed into the bushing described above. In the turning operation a $1/16$ " head $1/2$ " in diameter was left. Actually the rod at this point took on the form of an ordinary bolt. A 0.128" hole was drilled along the axis of the bolt and completely through it so as to permit driving in 4" of a $1/8$ " copper tube which contained the desired $1/16$ " hole. A copper constantan thermocouple (Leeds and Northrup B & S 30 gage List No. 30 D 2) consisting of the two fine wires wound separately with fibreglass and then together with fibreglass was inserted into the $1/16$ " hole. The ends of the wires had been previously bared and twisted and then clipped back so close to the fibre glass jacket as to barely leave one twist sticking out of the end of the fibreglass.

This end was brought up flush with the head of the bolt and tacked in place with a minimum of solder. The head surface was polished to a glass finish and then a .005" gold disk 1/2" in diameter was sweated flat to the polished surface. The gold surface was then polished in one direction with a midget hand buff (the polish direction must be aligned with the direction of the light source as will be seen later).

A piece of 1/8" black cloth base Formica had a 3/8" hole drilled centrally into it so that it could be slipped over thermocouple leads and onto the copper bolt and snug against the bolt side of the head. Against this piece of Formica a copper spool was screwed on. Actually a thin rubber washer separated the two pieces. The spool was made from 1/2" copper rod a 1/2" section being turned to 0.395". The square shoulders of each end of this section were turned off to a 45° taper. One end of the spool was formed by cutting one end of the rod off at the end of one of the tapered portions. The other end was formed by cutting off 1/8" beyond the end of the other taper. A 1/16" x 5/8" square nut was slipped on to the 1/8" shoulder and soldered flush with this end of the spool. About fifty turns of 0.003" nichrome heating wire (64 ohms per foot) were wound on a mica sleeve which had been wound onto the spool. Spacing was obtained by winding another 0.003" wire along side of the first. The latter wire was removed.

The coil left on the spool was tapped at its midsection as well as both ends. The two half coils were connected in parallel. Leads were attached which could later be brought out to the two connecting tabs provided on the lower side of the 1/8" plate of Formica previously discussed. The heating element was coated with thermosetting silicone resin (Dow Corning Co. DC 996) and dried at 195°F and then cured for 6 hours at 300°F. The entire thermal assembly was then screwed down into the brass tank until the 1/16" nut on the heater spool just touched the end of the copper bushing in the tank. This portion of the frost point hygrometer proper was mounted in a box provided with a 1" minimum layer of spun glass insulation. The only exposed parts of the assembly were the charging hole at the top, the vent and drain, and the Formica plate containing the gold surface and heater tabs.

Detailed Description of Optical Head:

In order to attach the optical head to the above assembly a 1/16" brass plate was made the same size as the Formica plate and both were drilled and the Formica tapped so the two could be screwed flat together. An opening of course was provided in the brass plate so as to receive the gold surface head of the copper bolt. The hole was actually large enough to provide 0.008" to 0.010" clearance between the two so that thermal contact could not exist and

yet the Formica was practically completely covered. Alternate attaching screws were actually screwed in from the underside of the Formica so that they would serve as guides when the brass plate was placed over the Formica plate, (thus preventing damage to the gold surface). The remainder of the optical head was screwed to the brass plate so that the gold plate would be centrally illuminated. This part is shown in figures 14 and 15 and a comprehensive discussion is available elsewhere (8).

The base which was screwed to the 1/16" brass plate was a brass block 1-3/4" long, 3/8" high and 1" wide. It was hand tooled so as to receive the three brass tubes (3/4" x 20 gage, 1/32" wall). All tubes were soldered into the base. Lens elements in these tubes and the slotted diaphragm in the black absorber were all mounted by means of split brass rings which were provided with grooves to permit air passage and ventilation. The photocell compartment, attached to the central tube by means of a 3/4" I.D. Formica ring, was made from a 1-3/4" x 3" brass tube (1/16" wall) and was provided with a Formica cap and base. An octal tube socket and RCA 929 photocell were mounted on the latter so that the 929 could police the gold surface through a hole in the wall of the photocell compartment. This hole was 5/8" in diameter and therefore acted as a diaphragm to cut out wall reflections. The black absorber cone was turned from a brass rod so as to "push" fit. It was also provided

with small air passages about its periphery. The black surface on this and all the brass parts was produced by soaking in saturated cuprous carbonate ammonia solution, washing with water, oiling and then thoroughly drying.

A 4.2 amp 8.5 volt straight filament exciter lamp (Coleman Instrument Co. Division of Harshaw Co. part No. H 59530 - 7 or part No. H 59530 - 48, 14 - 500) provided the light source by being mounted on the appropriate brass tube by means of a simple Formica bracket. A 3/4" I.D. Formica tube was also mounted over this brass tube so as to provide a telescopic adjustment for the lens and Kodak diaphragm attached to it. The Kodak diaphragm was of the ordinary adjustable variety and would open from a pin hole to at least 1" diameter which was more than adequate for the purpose. Both condenser lenses had a 30 mm focal length and the two double convex lenses had a 38 mm focal length. All electrical connections for the exciter lamp and photo-cell as well as the heater tabs were brought onto a Formica terminal strip mounted on the insulated box.

Detailed Description of Electrical Circuit:

Since the Frost Point Hygrometer is considered a permanent instrument at the University those not familiar with this particular electronic unit may be called upon to service it from time to time and for that reason no effort is spared in the following pages to give a complete description of its proper operation. The necessity for employing

an oscilloscope and properly applying it in any service attempt cannot be overemphasized. With the oscilloscope servicing is reduced to comparing wave form and measured voltages with those to be described herein.

The circuit diagram in figure 16 and the list of parts is the basis for the discussion. The RCA 929 photo-cell is actually in the Frost Point Hygrometer proper but is shown here since it is the starting point of the circuit. It constitutes a variable resistor in the grid circuit of the 6SJ7 pentode tube. Considering for the moment only the cathode and first and second grids of the pentode it is obvious from the diagram that the connecting parts form with this triode section what would normally be recognized as a series fed oscillator, the oscillator plate being the second grid. In any radio tube electrons normally flow from cathode to plate and the less so the more negative potential applied to the grid or vice versa. When the set is first turned on many electrical disturbances are present and the oscillator plate current might be rising toward some particular value. This current however flows through the primary of the coil which is so poled that under this circumstance the grid end of the secondary is becoming increasingly positive and therefore even more current is allowed to flow. Thus the vicious cycle has been initiated and a rise continues until the plate voltage reaches a minimum value and/or the grid becomes more negative for some reason.

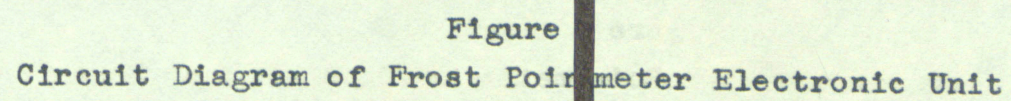


Figure 1
Circuit Diagram of Frost Pointmeter Electronic Unit

List of Parts Shown in Figure 16

Numerical Designation in Fig. 16	Name of Part	Rating
4.5 v	Battery	4.5 volts
90. v	Battery	90 volts
--	Coil, Blocking Oscillator	
15 H	Coil, Choke	15 Henry
16	Condenser, electrolytic	16 microfarads
10	Condenser, electrolytic	10 microfarads
33	Condenser, mica	33 micromicrofarads
100	Condenser, mica	100 micromicrofarads
.1	Condenser, paper	.1 microfarads
.01	Condenser, paper	.01 microfarads
.003	Condenser, paper	.003 microfarads
.25	Condenser, paper	.25 microfarads
.05	Condenser, paper	.05 microfarads
0-200 u a	Meter	0-200 micro amps, d.c.
0-1 amps	Meter	0-1 amps, a.c.
12K	Resistor, fixed	12,000 ohms
.47 M	Resistor, fixed	.47 meg ohm
22K	Resistor, fixed	22,000 ohms
.18 M	Resistor, fixed	.18 meg ohm
.5 M	Resistor, fixed	.5 meg ohm
.1 M	Resistor, fixed	.1 meg ohm
.12 M	Resistor, fixed	.12 meg ohm
1 K	Resistor, fixed	1,000 ohms
.22 M	Resistor, fixed	.22 meg ohm
40 K	Resistor, fixed	40,000 ohm
20 M	Resistor, fixed	20 meg ohm
5 M	Resistor, fixed	5 meg ohm
2.2 M	Resistor, fixed	2.2 meg ohm
5	Resistor, fixed	5 ohms
100	Resistor, fixed	100 ohms
50	Resistor, fixed	50 ohms
.35 M	Resistor, variable vol.control	.35 meg ohm
10 K	Resistor, variable vol.control	10,000 ohm
1 M	Resistor, variable vol.control	1 meg ohm
.25 M	Resistor, variable vol.control	.25 meg ohm
.1 M	Resistor, variable vol.control	.1 meg ohm

List of Parts Shown in Figure 16 (cont.)

Numerical Designation in Fig. 16	Name of Part	Rating
--	Switch, single pole single throw	
--	Switch, double pole single throw	
--	Switch, single pole double throw	
Fil. Tran.	Transformer, Filament	10 amps, 110-6.3 v
Fil. Tran.	Transformer, Filament	1.2 amp, 110-6.3v
Exciter Lamp Tran.	Transformer, Ex. Lamp	4.5 amp, 110-8 v
929	Tube, photocell	
6SJ7	Tube, radio	
6N7	Tube, radio	
6SL7	Tube, radio	
117Z6-GT	Tube, radio	
6SH7	Tube, radio	
6SN7	Tube, radio	
6AS7-G	Tube, radio	

When such changes take place the cycle reverses and continues down to some minimum current and then again reverses and repeats. In a normal oscillator on the upward swing the grid is run positive by the transformer and a positive grid means that it will attract electrons and therefore tend to become charged. Normally these electrons on this swing will tend to store up in the blocking condenser included in the triode grid circuit but on the downward swing they will flow through the grid resistor and thus drive the grid negative because the electron pressure is then greater than ground at that point. Normally the grid resistor is small (50,000 Ω) and the electrons leak off of the condenser quite rapidly. As a consequence the grid never swings below cutoff and actually the grid leak resistor establishes an operating bias on the triode grid, i.e., a reasonably negative potential about which the tube oscillates to generate something more or less approaching a sine wave on the oscilloscope.

The unique feature of the oscillator in the diagram is that the grid resistor varies from almost infinite resistance at no light down to several million ohms at operating light intensities (even resin from solder will short the circuit and wood alcohol washing is imperative). This means that the RC time constant in the grid circuit must be given generous consideration. Larger capacitors

of course store more electrons and larger resistors increase the time for them to leak back up to ground. Reconsideration of the oscillator circuit in this light now shows that with a large RC time constant the grid cannot establish a normal operating bias but instead it continues to (on the average) become more and more negative. This circumstance continues until on the last upward swing sufficient electrons are added to the storage that on the downward swing the grid actually swings more negative than cutoff and thus the tube is said to have blocked and for this reason the literature recognizes such an oscillator as a "blocking oscillator" (72)(73)(74). While the tube is blocked it is as non operational as if it were removed from the socket at least as far as output signal to subsequent tubes is concerned. The rapidity with which blocking may be made to occur can be increased by increasing the amplitude of the oscillation during the oscillatory part of the cycle. The increased amplitude in this case is brought about by the iron core RCA television horizontal blocking oscillator coil (208 T - 1, 21 turns ratio) especially designed for such a purpose in present day television sets. About 8 or 10 oscillations suffice for blocking as can be seen on the oscilloscope.

The 6SJ7 tube remains blocked until sufficient time has been allowed for enough electrons to leak off through the photocell so that the grid potential comes back

to the cutoff value. At this point natural oscillation sets in again at a frequency commonly called the natural frequency of the circuit as distinguished from the frequency of blocking or "blocking frequency".

So far as the true plate of the pentode is concerned it is said to be electron-coupled to the oscillator circuit. It sees only the combined effects of grids 1 and 2. The oscilloscope attached to this plate shows a saw tooth voltage wave form. The leading edge is vertical and thin compared to the heavier sloping trailing edge. The vertical edge corresponds to the spurt of pentode plate current just as the grid has risen back above cutoff and it is the pulse which is filtered out by the small grid condenser of the following 6N7 triode. The oscilloscope at this point shows a somewhat jagged base line with numerous vertical lines spaced at intervals corresponding to the blocking frequency. This frequency may be increased (i.e. lines brought closer together by decreasing C in the 6SJ7 grid or by increasing the light intensity on the photocell and vice versa). Actually C has been so chosen that at low light intensities C is small enough to give a frequency just large enough to prevent excessive oscillation of the microammeter needle. At the same time C is large enough so that at high light intensities the RC time constant is still sufficient to cause blocking. With the present set up when 8.5 volts is applied to the exciter lamp and the

Kodak shutter is fully closed (i.e. only a pin hole remains) a white paper slid slowly onto gold surface causes the microamps to exceed 600 above which point the RC constant is sufficiently small as to permit more and more natural oscillation and thus to decrease the microamp reading. Only 100 - 150 microamps are required for normal operation of the Frost Point Hygrometer.

The pulsing voltage on the grid of the first section of the duo triode 6N7 tube is in ac form because it passed the grid condenser. Because dc pulses are required for the microameter the grid is biased experimentally to some point just above cutoff so as to produce detection (rectification). The optimum setting of the variable resistor (on the chassis and not on panel) provided for this purpose is determined by turning the exciter lamp off zeroing the microameter and then turning the exciter lamp on and reading the microamps. Repeating for different bias settings of course permits selecting the optimum.

Excepting detection, the 6N7, its two plate resistors, and the microameter form a conventional bridge with the two triode sections being considered resistors. With no frost on the gold surface and 8.5 volts applied to the exciter lamp with the shutter closed and the resistance of the second section of the 6N7 is fixed by adjusting its variable bias rheostat so as to just balance the resistance (on the average) of the first section and therefore the

microammeter is brought to zero balance (zero reading). The variable resistor which by-passes the microammeter constitutes a sensitivity control. Its resistance is so great compared to that of the microammeter that when it is completely in the circuit only negligible amounts of current may by-pass the meter.

The automatic circuit includes all from the first section of the 6SL7 to and including the last section of the 6SN7. A small amount of signal voltage is taken from the bridge and placed on the grid of the first section of the 6SL7. The signal of course is in ac form with the pulse peaks pointing in the positive voltage direction. The grid is permanently biased beyond cutoff such that the pulse peaks can just drive the grid slightly positive. In other words the only time the triode section conducts is during application of a pulse voltage. At all other times it is non conducting and the condenser between the plate and -90v ground is being charged through the plate supply resistor. The rate of charging of course is governed by this resistor and the maximum charge on the condenser is again governed by the RC time constant. During a pulse the triode conducts and acts to short circuit the condenser thus discharging it. Consequently a saw tooth voltage wave is generated and applied to the grid of the 6SH7. It is obvious that the voltage amplitude of this saw tooth

wave depends upon the blocking frequency. The higher the frequency the shorter the time the condenser has to become charged and therefore the smaller the voltage amplitude at the 6SH7 grid.

The sole purpose of the 6SH7 tube is to amplify the saw tooth voltages impressed on its grid. The voltage gain for this stage is 116 with a maximum peak voltage output of 82 volts. The tube has conventional cathode bias.

The ac output of the 6SH7 is impressed upon the grid of the first section of the 6SN7 which serves as a voltage follower and rectifier. This triode has such a large cathode resistor that the triode is always near cutoff, i.e., the cathode is always about +12 volts above ground until an ac saw tooth voltage strikes the grid. On the positive grid swing of 82 volts the cathode swings up to about +94 volts. On the downward swing application of -82 volts to the grid can reduce the cathode only to zero volts thus the rectification. At the cathode then there is a rectified saw tooth voltage the amplitude of which depends upon the amplitude of the original ac saw tooth voltage applied to the follower grid.

The bank of condensers and resistors between the follower cathode and the grid of the second section of the 6SN7 constitutes a filter circuit. The second section of the 6SL7 in the filter bank serves only as a low resistance one way valve to permit the rapid escape of electrons from

the upper plate of the first condenser during the charging period, i.e., during the time the cathode swings up to some positive peak potential. Consequently the first large condenser can charge very rapidly whereas it can discharge only very slowly. The purpose of course is to have the potential of the filter follow the peak potential of the cathode rather than some average of the pulse potential were the 6SL7 absent. Subsequent resistors and condensers in the bank serve to smooth the voltage out to a steady dc potential for a saw tooth wave of given amplitude. The last variable resistor serves an additional purpose in that it permits placing a fixed bias potential on the grid of the last section of the 6SN7.

Suppose now that the pointer on the variable rheostat in the plate lead of the last section of the 6SN7 were turned down to the plate of the latter tube. Assume also that the gold surface in the frost point hygrometer has a little too much frost on it. For this amount of frost there will be a definite blocking frequency which will be high and thus a correspondingly low peak saw tooth voltage and thus a smaller positive voltage on the filter. If it is assumed that the permanent bias is now set sufficiently negative as to just place the last 6SN7 at cutoff then its plate resistor passes no current and consequently the pointer assumes a zero potential. If now for reasons to be

explained, the frost deposit begins to decrease the frequency will also decrease and the saw tooth peak voltage becomes more positive. The grid of the last 6SN7 becomes correspondingly more positive and because current then passes through the 6SN7 plate resistor the pointer becomes more and more negative. Shifting the pointer in the plate circuit only decreases the voltage range of the pointer during the above operations. When the pointer is placed at ground the range has been decreased to zero and there are no voltage effects at the pointer.

A glance at the bank of 6AS7 tubes shown in the circuit diagram reveals that they are acting as simple rectifier tubes which are hooked up in parallel. The resistors accompanying each of these tubes are for safety purposes, i.e., they prevent any one of the tubes from hogging the load and burning itself up. Because these tubes are all in series with the frost point hygrometer heater they permit current to flow through the heater in accord with the amount of bias on their grids which are connected directly to the plate pointer discussed above. At this point it should be quite obvious where the heat came from that caused the decrease in the frost deposit mentioned above.

Actually the 6AS7 tubes require about -60 volts to cut them off. If their grid pointer is set all the way down to the plate of the last 6SN7 then there will be some

delay action which of course is desirable in order to limit the control range. For example, it may be assumed that frost has just started to deposit on the gold surface and the last 6SN7 is full conducting and the pointer is at about -81 volts (allowing for voltage drop across the 6SN7 itself). As the frost increases the pointer voltage rises toward -60 volts. All this time the 6AS7 tubes have been cut off and thus supply no heat. If still more frost forms the pointer voltage will become still higher, i.e., less negative and then the 6AS7 will begin to supply heat. If the pointer were originally set at -60 volts then there would be no delay action from this source.

There is another source of delay action and that is due to overbiasing of the last 6SN7 grid. If this grid is overbiased then a certain amount of frost must evaporate before this grid can even get back up to cutoff. Of course lesser amounts of frost will then suffice to operate the control.

At times hand control might be preferred for some particular purpose. When such is the case the two rheostats on the last 6SN7 may be used with the plate rheostat being preferred for its fineness of control. It may be desirable to remove the 6SH7 and 6SL7 tubes from their sockets during hand control to prevent automatic control from trying to assist the operation. This maneuver also conserves the plate battery supply and for this reason

is recommended.

The 117Z6 tube and the two large condensers and choke which accompany it constitute the half wave rectified and filtered B + supply. This circuit is of conventional design. The filament transformers shown in the circuit of course supply the rated current to the filaments of the radio tubes previously discussed. The exciter lamp transformer supplies rated current to the exciter lamp. This transformer also has higher voltage taps and care must be taken that these are never used in order to prevent burning out the exciter lamp which is rated at 8.5 volts.

Procedure for Dynamic Tests

The dynamic experiments include all of those which involved use of the Frost Point Hygrometer and particularly those to measure the humidity of an air stream. The first series of these experiments was concerned with standardizing the hygrometer itself.

Before the hygrometer was assembled the gold surface was immersed first in carbon dioxide and wood alcohol and then an ordinary distilled water ice bath. The temperature for each as determined from the accompanying thermocouple agreed with the accepted values. The first temperature corresponded to that for sublimation of carbon dioxide (-109.3°F) and the other to $+32^{\circ}\text{F}$. The hygrometer was then assembled for test, care being taken of course to assure that the polish direction of the gold surface was aligned with the direction of the light source.

Early experiments with the light source and the shutter showed that a voltage regulator was necessary to give constant light for any one particular setting. It was also necessary to ground to earth the ac supply line, voltage regulator and the instrument itself since the supply lines were found to be free floating and from day to day may otherwise be at 0 - 50 volts with respect to ground. Without grounding, the instrument may become sensitive to touch.

After the above corrections had been made trial tests showed that it was best to operate the instrument

with an 8v exciter lamp voltage and with the shutter fully closed, i.e., only a 1 mm opening remained. Lower voltages caused the instrument to be less sensitive to a given increase in shutter opening. Larger shutter openings especially with the larger sizes tended to light more than the gold surface as could be verified by looking in through the black absorber while the cone was removed. In fact this test demonstrates the permissible range of shutter openings. With the smallest opening and 8 volts nearly all of the gold surface viewed through the absorber appeared to be a dazzling inferno of light. Actually the diaphragm could be opened somewhat without any real deleterious effect but subsequent tests with air streams showed this was not necessary.

Air streams of various humidities and velocities were tested to determine the effect on operating conditions. It was found that 2-10 ft³/hr of air at atmospheric pressure could be passed through the hygrometer without any ill effect. The stream velocity did not effect the frost point reading but it did effect the heating requirements to hold the gold surface at the frost point. Frost points ranging from -99°F to +32°F could be measured without difficulty. For this work certain conversion charts and rotameter calibrations were necessary. These are to be found in the appendix. All rotameter calibrations are based

on the wet test meter as standard.

Experiments with air streams over a range of frost points demonstrated that at high frost points (above -40°F) the hygrometer had more than adequate sensitivity over the range of zero microamps to several hundred microamps. For lower frost points and low air velocities the 100 microamp range seemed to be about the most sensitive. At 100 microamps the gold surface viewed through the black absorber appears slightly cloudy. It is only at something more than 200 microamps that the heavy white frost begins to appear. In all of the above work the microameter was zeroed for a freshly cleaned gold surface, 8 volts on the exciter lamp, and the shutter fully closed.

Efforts to standardize the hygrometer consisted of testing air of known humidity obtained from a special dehumidifier. The latter was made up of an ice trap followed by 40' of $1/4$ " copper tube wound on a 1" form and then stretched so that better than $1/4$ " spaces existed between each pair of coil twins. The entire coil was immersed in a carbon dioxide - wood alcohol bath and a copper constantan thermocouple was also immersed in the bath, at the last outlet turn of the coil. Laboratory air (20% RH approx.) was sent through the rotameter and thence to the bottom of the ice trap which was a $3/4$ " copper tube about 8" long. The air passed back to the top of the trap between the two concentric tubes (the air inlet tube and trap

wall) and out through the coil into the hygrometer. At first only 10 - 12' of 1/4" tubing was used and it was found that the hygrometer gave frost points around -90°F (about 20° too high). On this basis the heat transfer coefficient was computed and the coil consequently extended to the greater length to bring the outlet air and dehumidifier bath temperature within 1°F. The dehumidifier bath was lowered to -75°F and the hygrometer gave a perfect check. The bath was allowed to warm slowly and at -72°F both checked. At -64°F the two readings differed by 1°F. As time passed the readings differed more and more but it was obvious that the dehumidifier was at fault because nearly all the carbon dioxide had boiled out of the alcohol and the bath agitation was negligible. In all of this work the wood alcohol bath temperature was controlled by adding carbon dioxide chips. Considerable quantities of chips were used to maintain low temperatures. Higher temperatures were obtained by allowing the bath to warm up in which case comparatively few chips if any remained.

All tests with the above type of dehumidifier tended to confirm its accuracy and that in each case the efficiency and life of the dehumidifier was actually being determined by the frost point hygrometer. It was then realized that the frost point by definition is that temperature at which a given quantity of frost will remain in equilibrium

with saturated air of the same temperature. The real problem was concerned with the temperature gradient which could exist under these circumstances through a thin layer of frost on top of .005" of gold sheet. Accepting these facts the hygrometer was presumed to be an absolute reading instrument. During all of the above work the heating element electronic rheostat was manually controlled.

The next series of experiments were those actually concerned with determining the frost points of air effluents from beds of drierite. First it was necessary to make available a continuous supply of standard air which could be fed to the beds. For this purpose an air supply ranging from 35-60 or 100-104 lbs psig was reduced to 29 lbs psig and sent through the copper coil discussed above. The coil was immersed in a mixture of ice and water contained in a heavily insulated chest. The temperature remained at 32°F for several days before more ice was required. The coil spiraled downward through the bath and into the bottom of a water trap equipped with a blow down drain. The outlet air was drawn from the top of the trap. The outlet air was admitted to the beds through a small brass needle valve followed by the rotameter. The beds were equipped with a by-pass line for testing the inlet humidity. In addition a mercury manometer was also piped to the beds so that inlet and outlet pressures could be compared with atmospheric pressure. Copper tubing 1/4" in diameter and brass

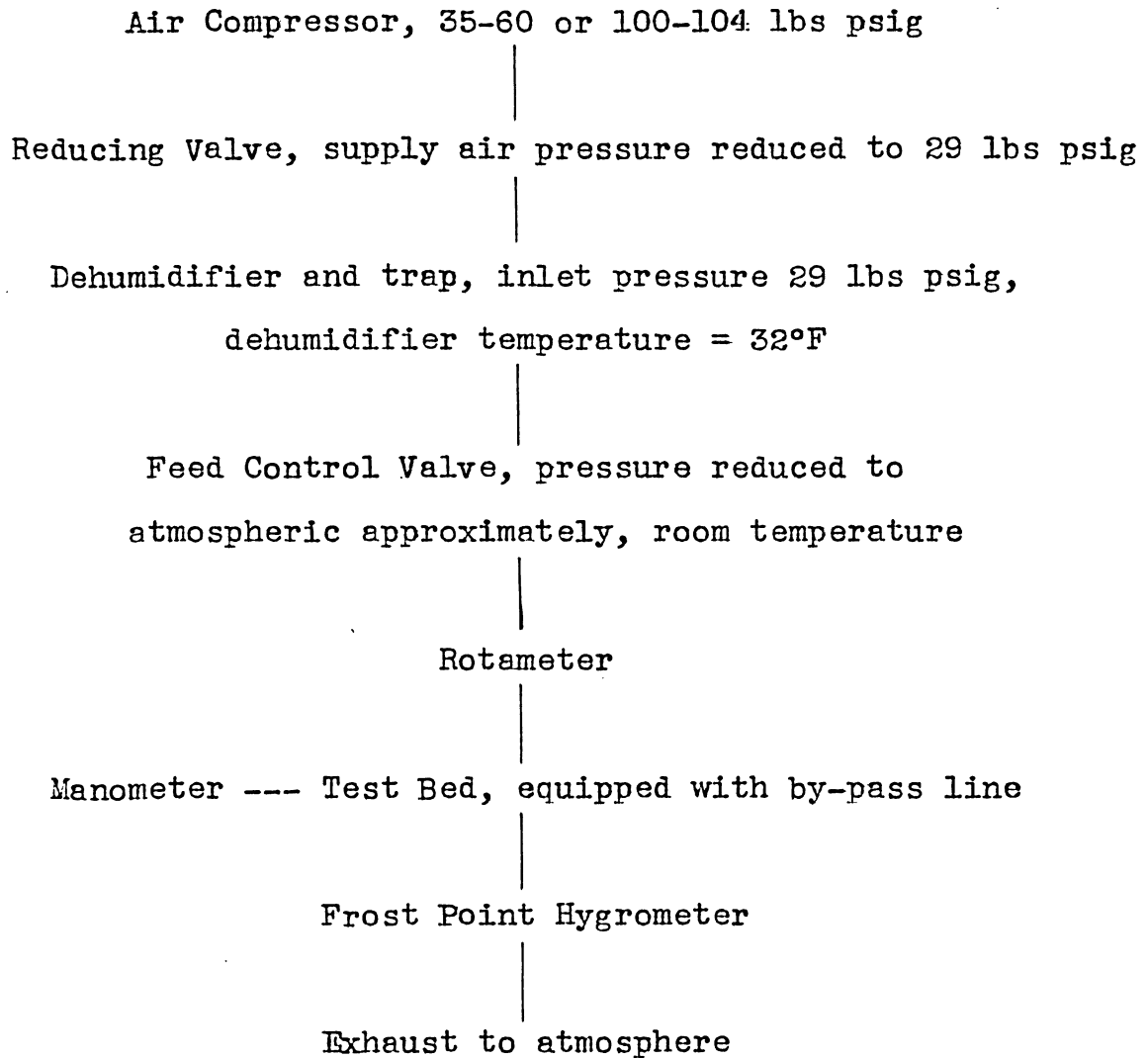


Figure 17 Flow Diagram of Dynamic Test Assembly

drain cocks were used throughout. The test assembly is illustrated in figures 12 and 17.

The conditions specified for temperature and pressure were convenient for obtaining a feed of about 8 per cent relative humidity. The latter choice was based on the desire to work in the linear region of the adsorption isotherm and at the same time employ a high enough feed concentration so as to cause the beds to expire in a reasonable time. The necessity for minimizing temperature effects due to adsorption made it desirable to use a low feed humidity.

Actual test of the standard air supply over extended periods of time confirmed that the frost point ranged from $+10$ to $+10.7$ if about 1 hour were allowed for dehumidifier equilibrium at the start. Saturated air at 4 atmospheres absolute pressure and 32°F should when expanded to atmosphere have a frost point of $+9.5^{\circ}\text{F}$. But the coil was designed assuming about 1°F driving force at the outlet. If one assumes the temperature of the air to be 33°F instead of 32°F in the previous computations the frost point should be $+10.3^{\circ}\text{F}$ approximately. It will be noted that the maximum deviation is $.4^{\circ}\text{F}$ when compared to $+10$ to $+10.7^{\circ}\text{F}$ as measured. During the first 17 minutes of a three and one-half hour standardizing run the measured frost point was $+5.5$ to $+7^{\circ}\text{F}$. During the next 69 minutes the frost point gradually built up and ranged from $+8$ to $+10^{\circ}\text{F}$. During the last two

hours the range was ± 10 to $\pm 10.7^{\circ}\text{F}$ with an average of 10.3°F for 16 readings taken during that period. The latter frost point agrees identically with the computed frost point. Part of the discrepancy in frost point at the start of the standardizing run may be due to the unsteady state of the dehumidifier itself and the variation in air pressure. Actually the pressure regulation appeared to be good so that the latter point would only account for small differences.

The drying towers or bed containers proper consisted of standard 1" brass nipples of 2", 3" and 4" lengths. A standard brass pipe coupling was screwed to each end and soldered in place. A 1" nipple with running pipe thread was cut to give threaded rings about $1/2$ " thick. A disk of brass screen (about 42 mesh) 1" in diameter was soldered to the end of a ring so as to form a stop for the bed when screwed into the coupling until it touched the end of the nipple. The screens of course pointed to the bed and screwed snug against it.

A 1" by $1/8$ " bushing equipped with a brass flare fitting was screwed snug into one end of each tower, bees wax being used to seal the threads. The screen was previously inserted into this end. As the towers were charged with newly regenerated desiccant the other screen and bushing was screwed in place. Bees wax was again used as

a seal. The brass flare fittings were capped until the beds could be tested. Just before the test they were uncapped and connected to the test assembly previously described. At the time of connecting the air supply was shut off. After connecting the inlet and outlet valves to and from the bed were left closed and the by-pass opened. The air was then set at the desired flow rate and the humidity determined until it reasonably approximated the previously determined value for the standard air. The latter procedure assured dryness of test equipment, gave a check on the standard air, and confirmed that all equipment was in working order. The same procedure was repeated at the end of each run. Manometric readings were taken during the runs.

Preliminary tests in a 1" diameter glass tube showed that 42 - 48 mesh desiccant was not practical because of fluidizing even at one to two cubic feet per hour gas flow rate. The upper limit was set by the 20- 24 mesh stock. These beds did not expand up to and including an air flow rate of $9.4 \text{ ft}^3/\text{hr}$. Exceeding this value by 10 - 15% caused the bed to show signs of agitation and at still higher values the bed began to expand and form eddies. The short lengths of bed were set by the above variables combined with the desire to complete any one run within 8 hours. If break values alone were to be determined for a bed then longer lengths would be permissible.

The desiccant for the beds was all prepared as before using standard screening procedure and a regeneration cycle of 400°F for 2 hours. New material was used throughout these experiments.

Results of Dynamic Tests

The adsorption wave runs reported herein were made with a two fold purpose in mind. The first was concerned with carrying out an empirical procedure recommended by Klotz (3) in order to determine the effective adsorption mechanism. For this purpose it was necessary to determine the effect of granule size in a bed of fixed length and for which the flow rate was also fixed. This data is shown by the solid lines in figure 18. The next step involved selection of a particular granule size and using it in subsequent runs to determine the effect of velocity and bed length. The solid lines on figures 19, 20, and 21 summarize the data obtained for the latter purpose. All original data is tabulated in the appendix. Each curve in the figures is labeled with a bracketed number which is the run number shown in the appendix.

The second purpose for which runs were made was for the test of the theoretical derivations and thus to also determine the effective adsorption mechanism in another way. The data obtained for the empirical analysis already mentioned are more than adequate for this purpose.

During the runs to be discussed bed containers and entrance and exhaust lines were checked for temperature changes by placing the hand at points of interest. There were no detectable temperature changes at least according to this test. The beds and lines seemed to remain at room temperature. The weight of the charge for several beds was

also checked and particularly so for duplicate runs. The weight of charge for a given container varied somewhat but did not exceed about 5 per cent variation by weight.

The 20 - 24 mesh granules in 3 inch beds were investigated in detail in order to determine the reproducibility of data. Runs 8, 13, and 14 are triplicates at a flow rate of $9.4 \text{ ft}^3/\text{hr}$. They are compared in figure 22. Likewise runs 10 and 15 are compared in figure 22 to show the reproducibility of data at a flow rate of $7 \text{ ft}^3/\text{hr}$. Run 15 easily could be plotted like run 10, i.e., with double knee.

A 9 inch bed was run to confirm certain theoretical predictions to be discussed later. The adsorption wave for this run is shown in figure 23.

In general all of the adsorption waves presented in figures 19 - 23 show a downward trend during the early stages of a given run. This of course is contrary to expectation. The cause may lie in the manner of preparation of the bed and/or in the fact that the steel wool filters in the system tend to hold up moisture which is removed during the initial portion of the run. A gradual decline in exit humidity followed by a sharp drop suggests that moisture is being desorbed from the exit end of the bed. The moisture in the end of the bed may be attributed to the fact that during loading of the bed container there is a tendency for the bed to cool and draw in higher humidity air from the surroundings. On the other hand a gradual

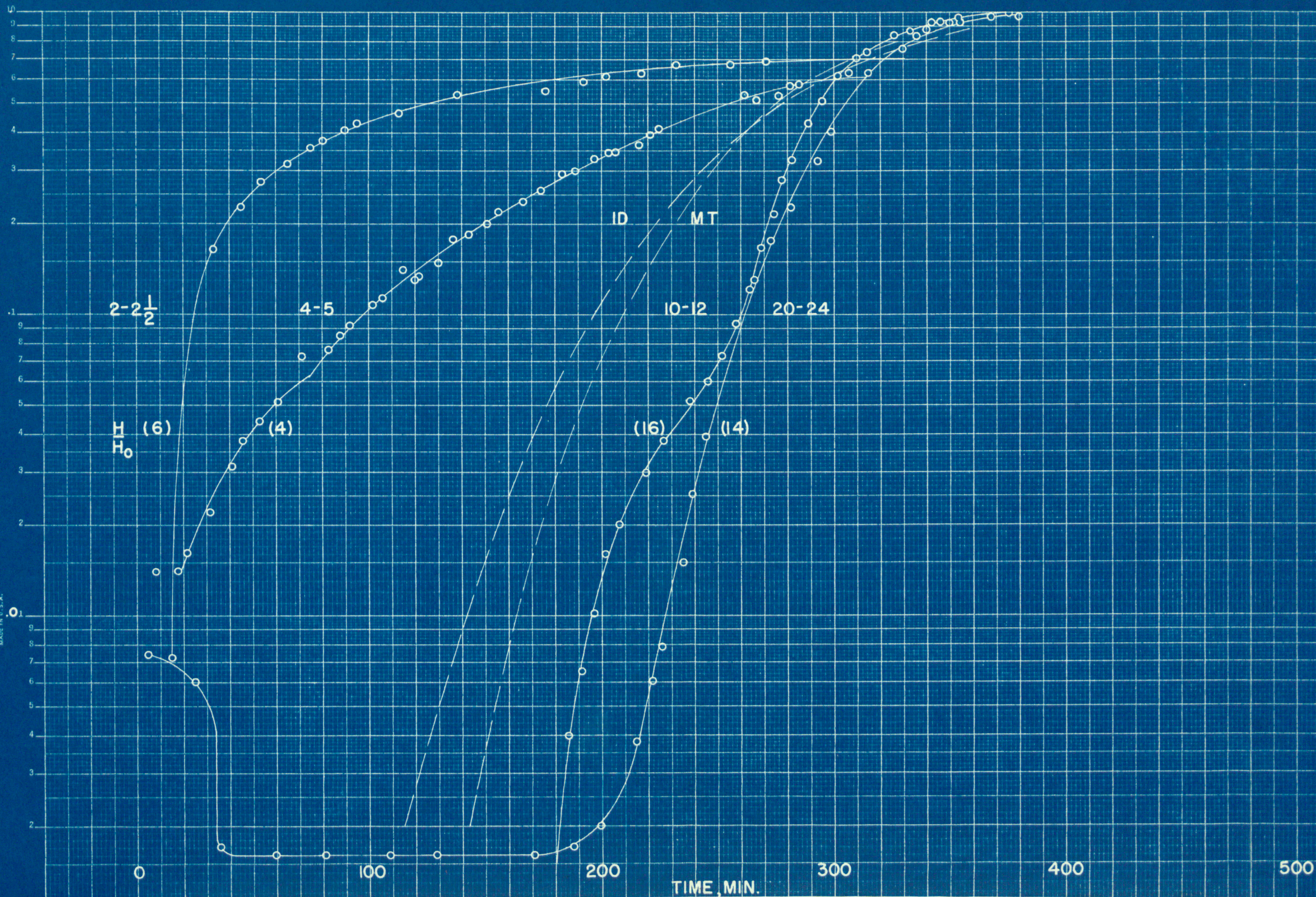


Figure 18
The Effect of Granule Size on the Adsorption Wave in 3 inch Beds
(Volumetric flow rate = 9.4 ft³/hr)

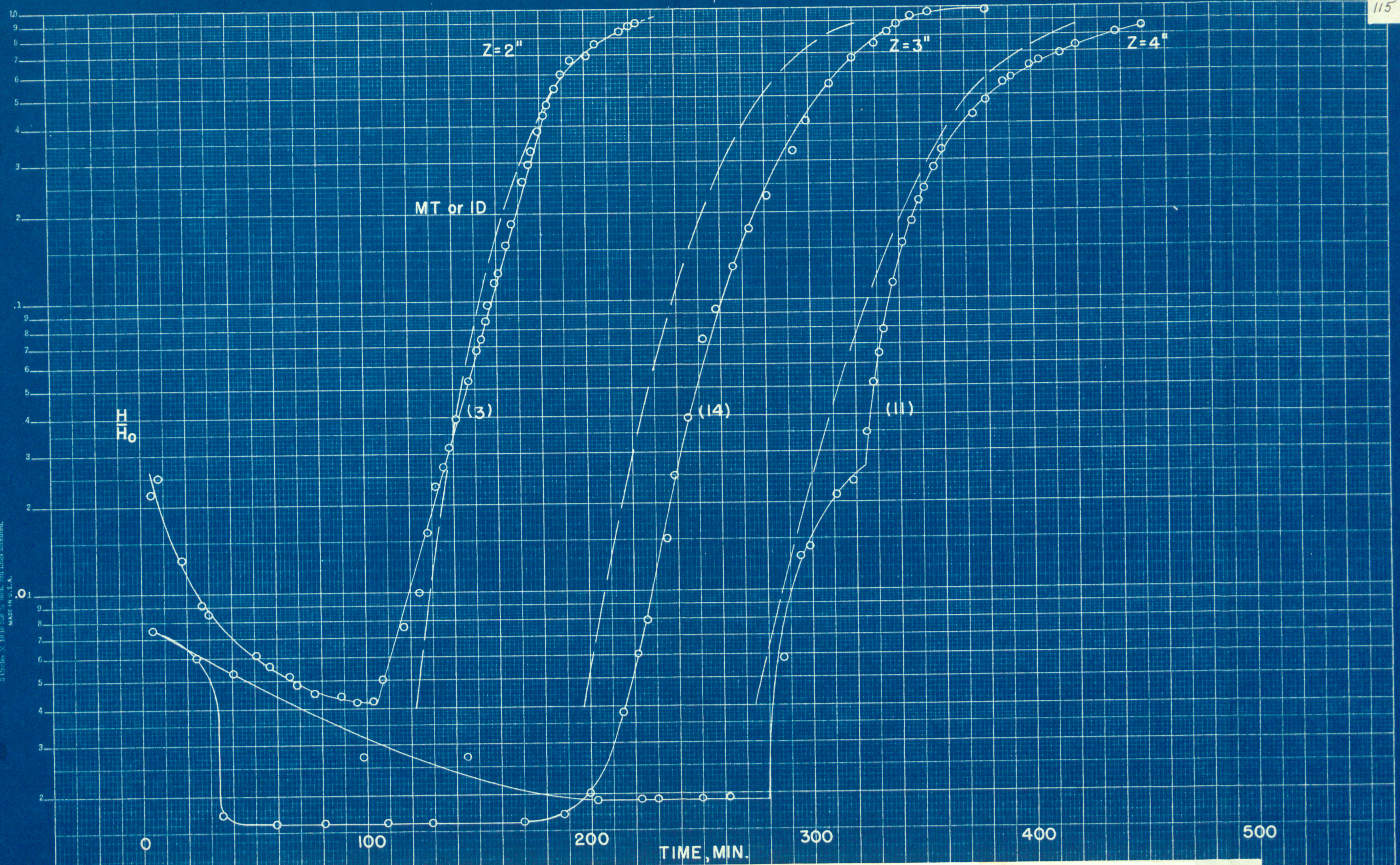


Figure 19
The Effect of Bed Length on the Adsorption Wave in Beds Containing 20 - 24 Mesh Granules
(Volumetric flow rate = 9.4 ft³/hr)

KEUFFEL & ESSER CO., N. Y. NO. 35-731
Semi-Logarithmic
5 Cycles X 10 to the 10th line covered.
MADE IN U.S.A.

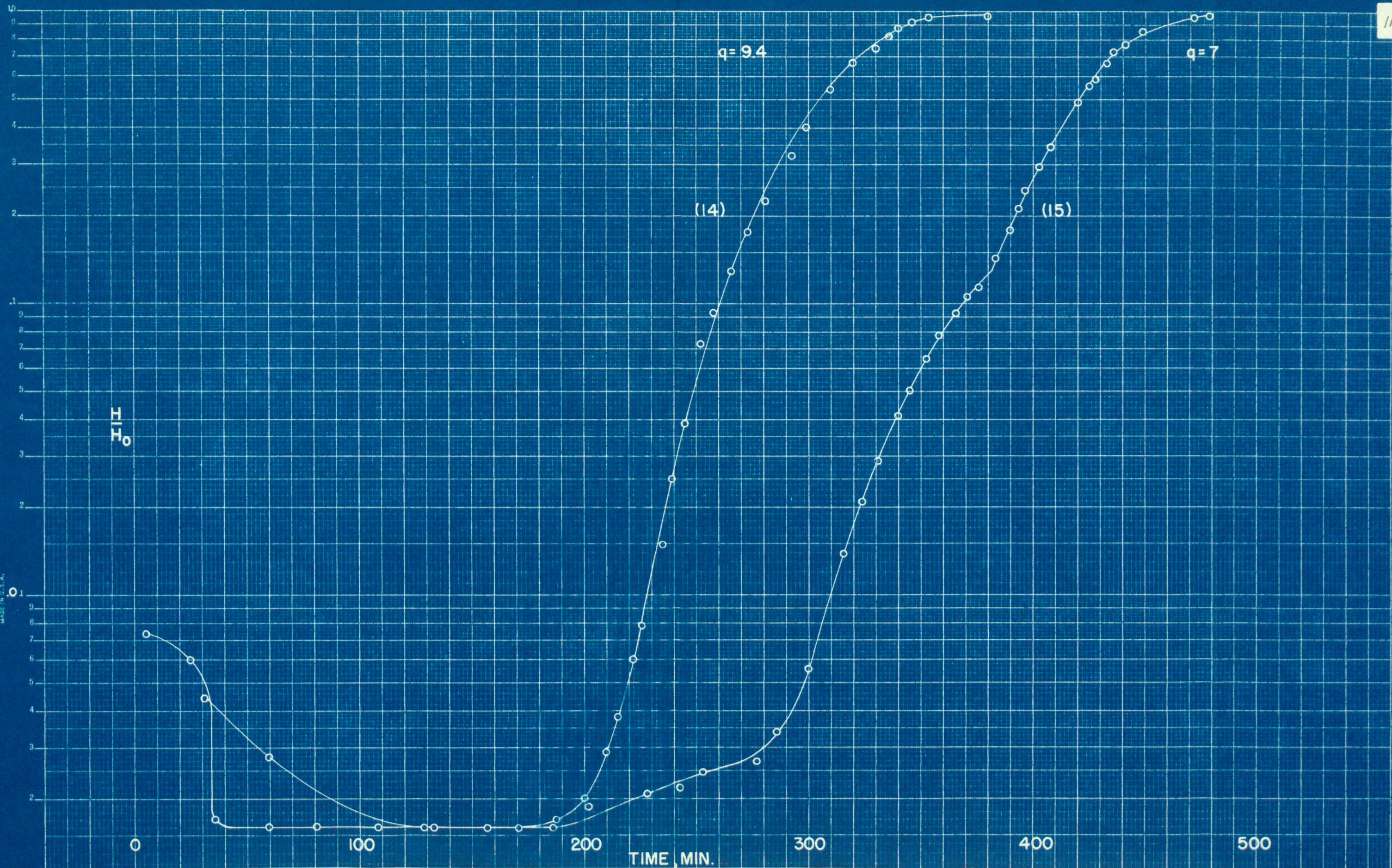


Figure 20
The Effect of Volumetric Flow Rate on the Adsorption Wave in 3 inch Beds
(Granule Mesh = 20 - 24)

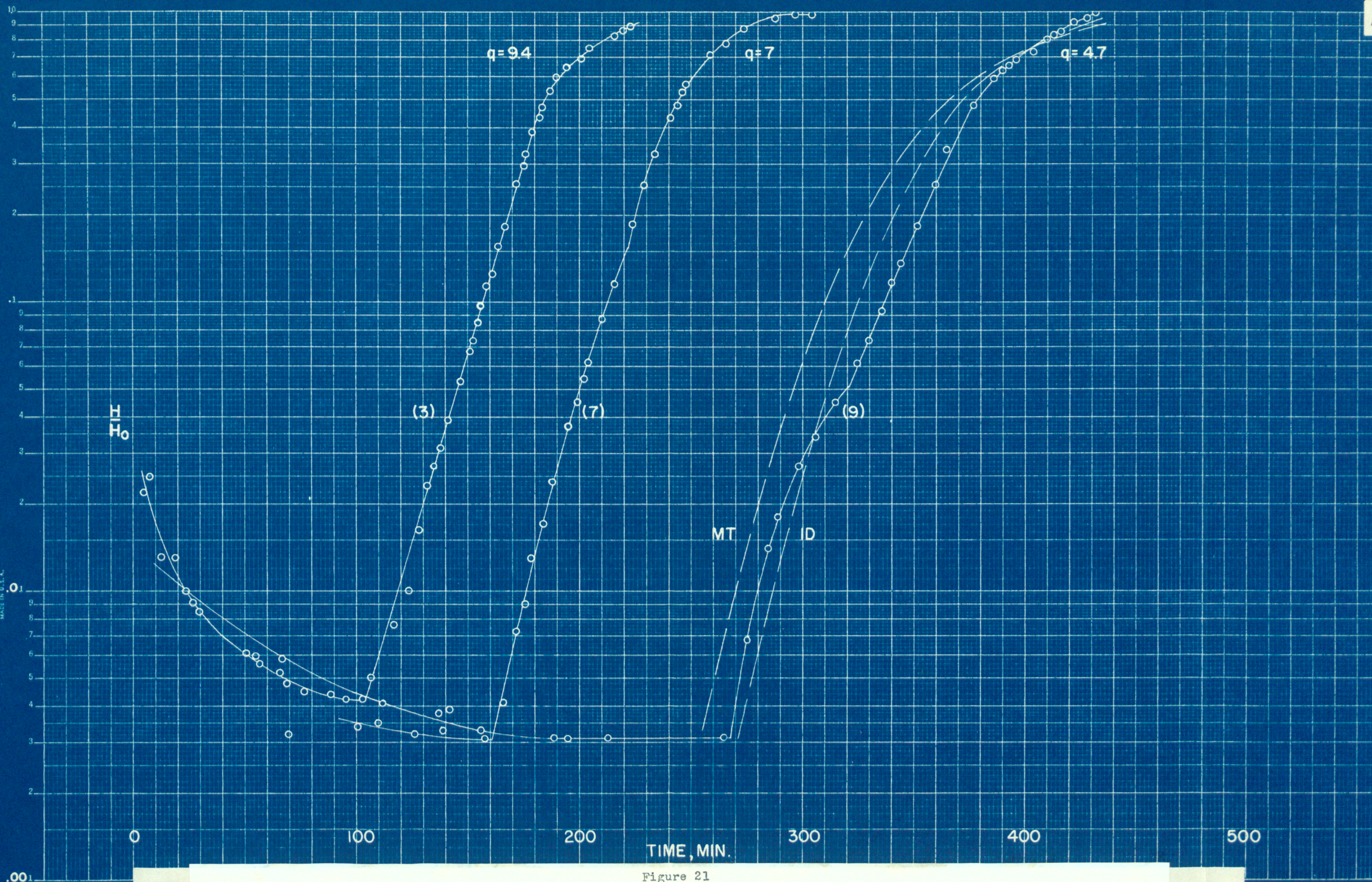


Figure 21
The Effect of Volumetric Flow Rate on the Adsorption Wave in 2 inch Beds
(Granule Mesh = 20 - 24)

decline throughout the early stages suggests that the filters are at fault.

In order to determine the effect of the filters the 9 inch bed container was placed in the test assembly without a desiccant charge. Instead of the dehumidifier a new tank of nitrogen was connected to the system and the gas flow rate to the test assembly was adjusted to $9.4 \text{ ft}^3/\text{hr.}$ The frost point of the gas exhausted from the assembly was determined in the usual manner. The results are tabulated in table V. This experiment confirms the fact that the apparatus holds up a certain amount of moisture.

In the figures discussed above it will be noted that runs 1, 2, 5, and 12 have been omitted although the original data for these runs are given in the appendix. The reason is that these runs were obviously defective. At the time of the frost run a makeshift dehumidifier was employed. It was the first run which demonstrated the necessity for constructing the heavily insulated ice chest previously described as a part of the dehumidifier.

During run number 2 the test was interrupted in order to check the inlet humidity. It was found that the inlet humidity was approximately the same as at the start. Because the bed had been idle for about ten minutes in the middle of the run the adsorption wave for this particular bed could not be considered representative.

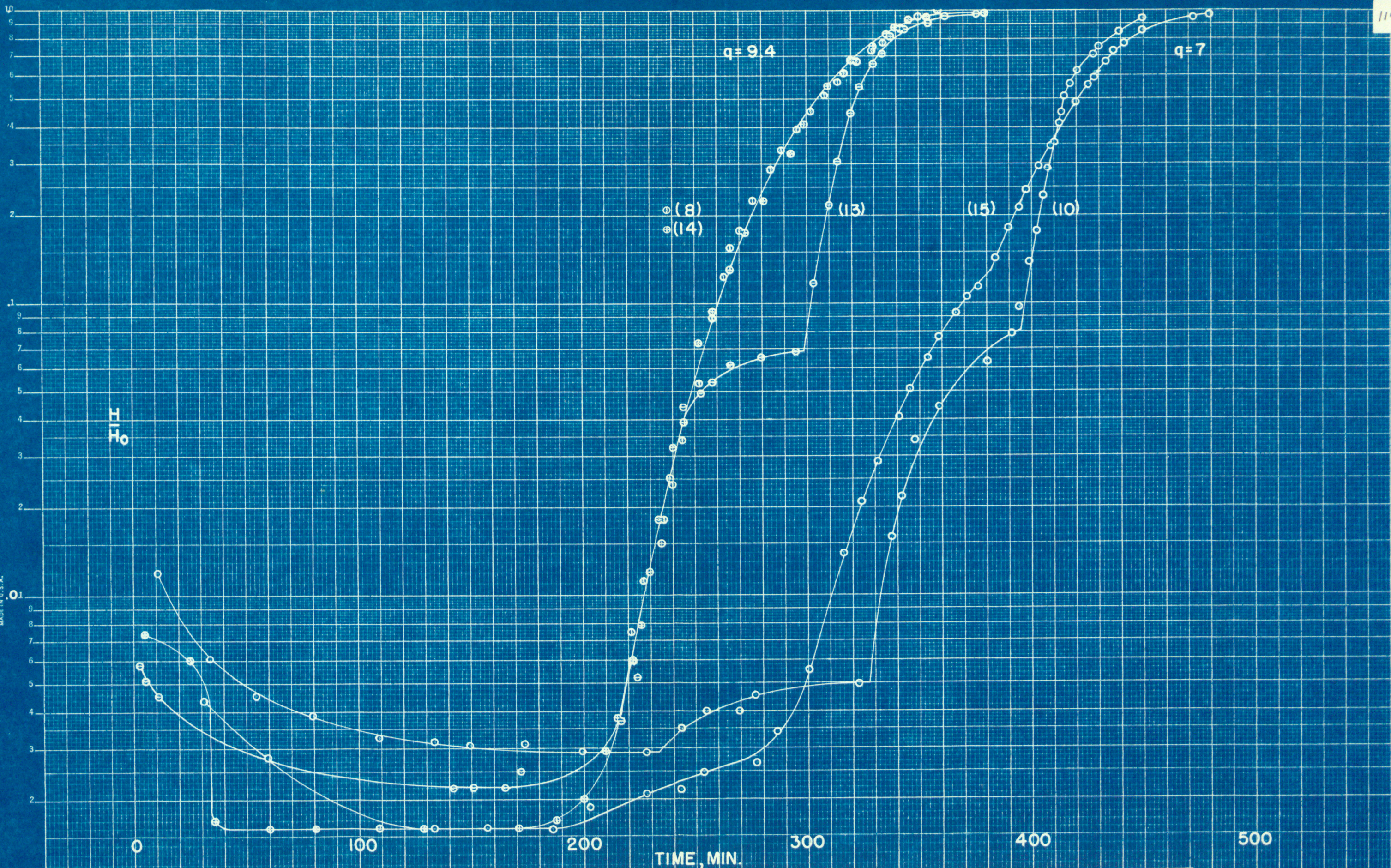


Figure 22
A Comparison to Show the Reproducibility of the Adsorption Wave in 3 inch Beds Containing 20 - 24 mesh Granules.

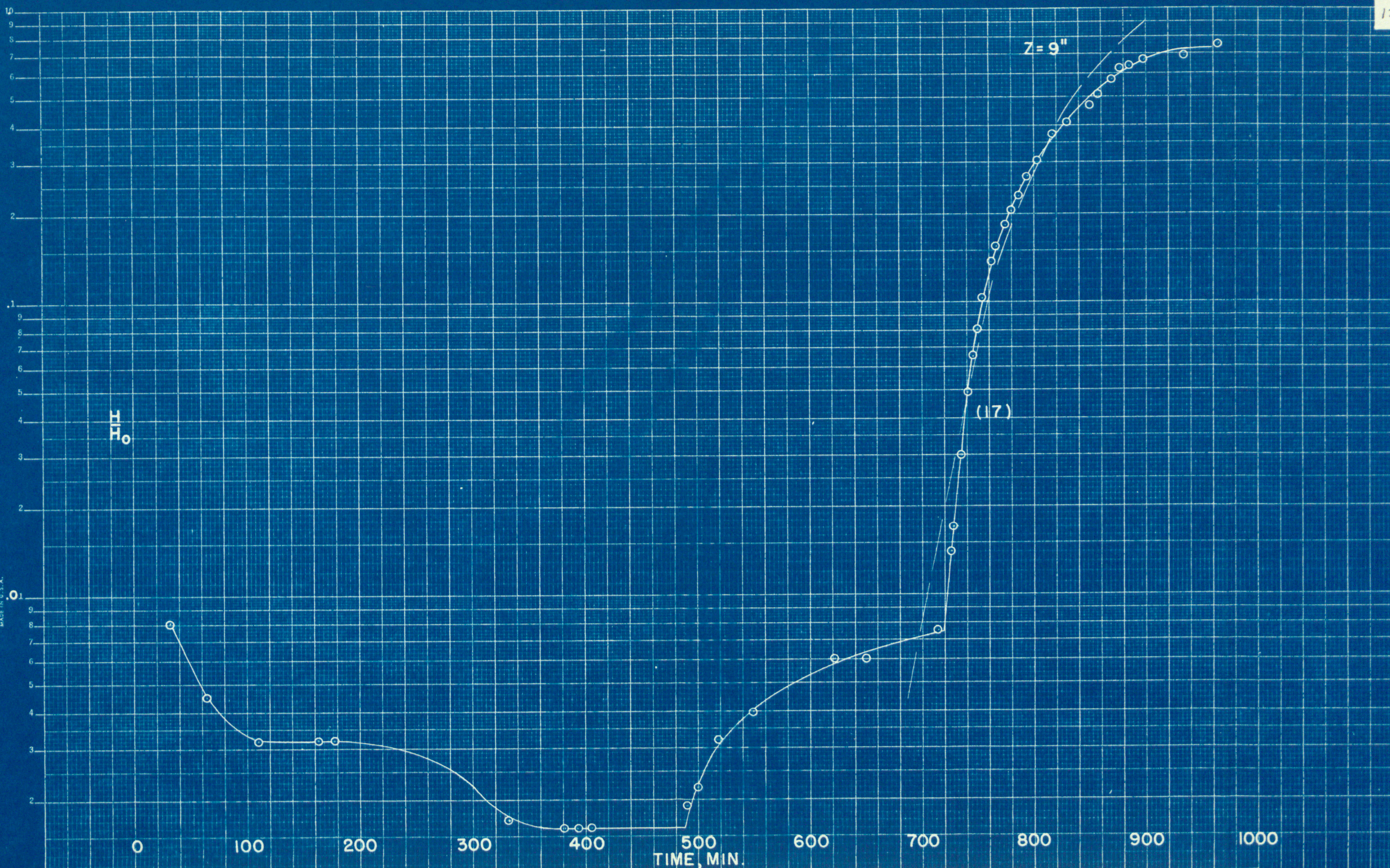


Figure 23
The Adsorption Wave for a 9 inch Bed Containing 20 - 24 Mesh Granules
(Volumetric flow rate = 9.4 ft³/hr)

KEUFFEL & ESSER CO., N. Y. NO. 359-731
Semi-Logarithmic
3 Cycles X 10 to the 10th. 5th lines uncorrected.
MADE IN U. S. A.

Table V
The Frost Point of Nitrogen Exhaust
from Empty Test Assembly

Time, min.	Frost Point, °F	Pressure in Nitrogen Bottle
0		1750 psig
21	-32.5	
36	-33.5	1550
42	-34	1540
72	-50	1390
98	-50	1260
121	-51.5	1150
Nitrogen by-passed around bed container and filters		
150	-51.5	1050

The fifth run was defective because the pressure drop over the bed was abnormally low indicating that the bed was probably loosely packed.

The twelfth run behaved in a very unusual manner. Investigation revealed that the regenerating furnace had gone out of control because of dead batteries in the Micro-max controller. The contents of this bed were probably heated to a high enough temperature to cause degeneration rather than regeneration.

Discussion of Dynamic Tests

In accord with the empirical method of analysis an arbitrary break concentration may be selected and designated, $H_b/H_o = .01$. The break time, t_b , corresponding to the break concentration may then be read from figure 18 for the four granule sizes and plotted as in figure 24. In this and other plots to follow each datum point is identified by a bracketed number which is the run number. Now, in accord with the postulates of the analysis, the curve should rise to longer break times as the particle size decreases provided mass transfer is a contributing factor. This is attributed to the fact that mass transfer becomes less important as rate-controlling step for the small granule sizes. Were it not for the fact that this type behavior appears to be contradictory to figure 25 one would conclude that mass transfer does play a part.

Figure 25 has been constructed for the arbitrary break concentration based on figures 20 and 21. Consequently a particular flow rate is associated with each datum point. The criterion is that if those points associated with one flow rate fall on a line distinctly different from those for other flow rates then mass transfer is a contributing factor. This is based on the observation by Klotz (3) that the solution to the partial differential equation for mass transfer controlling shows that t_b is a function of V as well as Z/V . For other cases which he examined he observed that t_b was a function of Z/V but not of V . Figure 25

suggests that mass transfer is not controlling in the present case. The contradiction between figures 24 and 25 lies in the fact that in figure 24 the 20 - 24 mesh granules lie on the steep portion of the curve. Had this curve been determined at $4.7 \text{ ft}^3/\text{hr}$ rather than $9.4 \text{ ft}^3/\text{hr}$ flow rate the curve should certainly be expected to shift considerably to the left. Consequently the 20 - 24 mesh material would be located on the portion of the curve where mass transfer supposedly plays a major role. The contradiction is not real. In equation 14 of the theory it will be noted that since k^2 is proportional to the reciprocal of R^2 , X and T are likewise. At $H_b/H_o = .01$ on the Schumann Furnas chart $T_b = 70$ if $X = 100$. If R is reduced to half its value then $X = 400$ and $T_b = 340$. If $k^2 = 1$ originally then when R is decreased to half $k^2 = 4$. Consequently t_b has increased from 70 to 85. The numerical values employed here are for illustration purposes only. They do serve, however, to account for figure 24. In this regard it must be remembered that channeling for large granules in a 1" tube may also tend to decrease t_b . Thus it appears that of the two factors considered, mass transfer is not the one which is important.

The life thickness curve plotted in figure 26 has been constructed based on data taken from figure 19. Its only purpose is to show its probable linearity and illustrate the fact that the critical bed depth for soluble

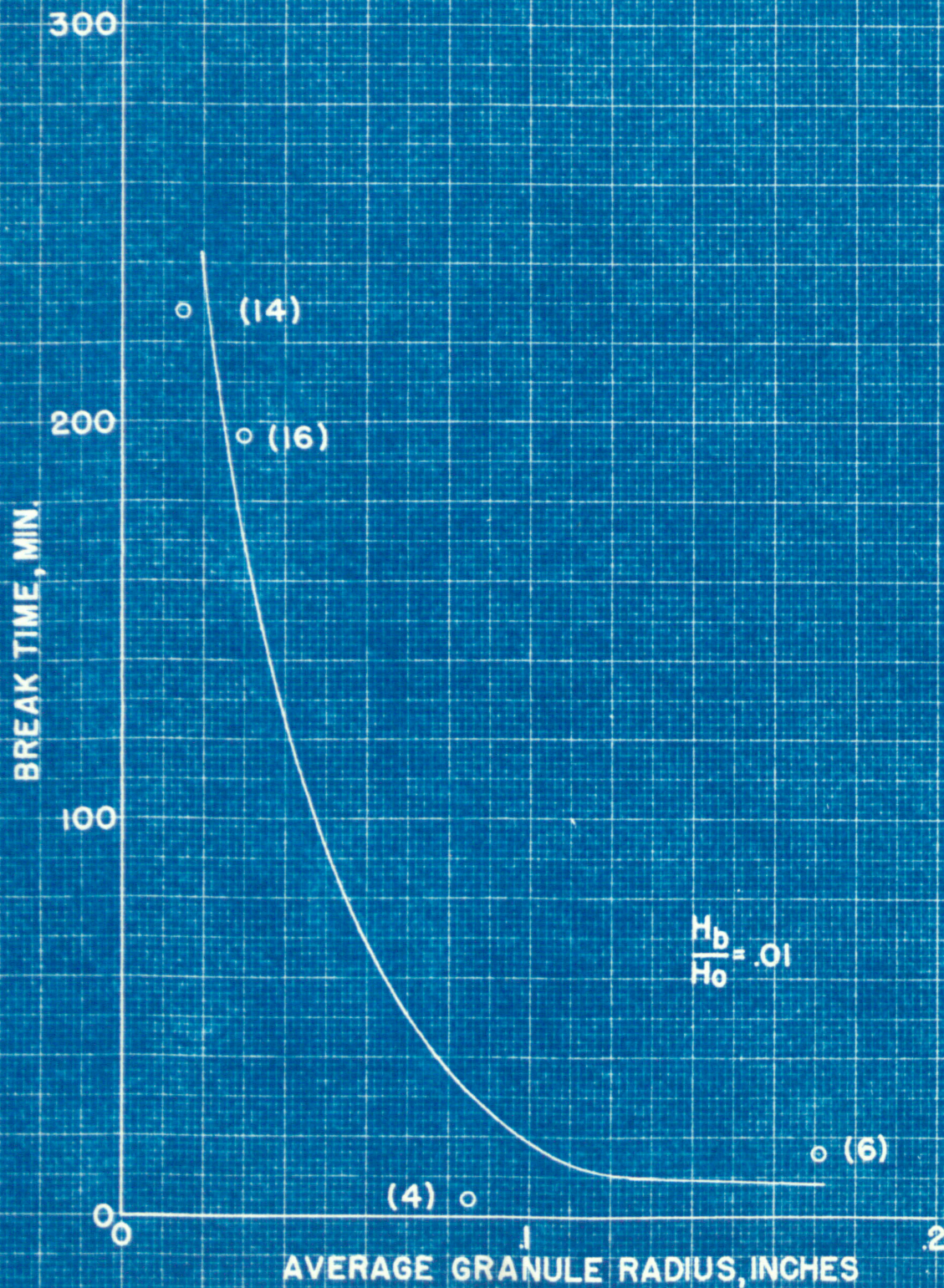


Figure 24

The Effect of Granule Size on Break Time for 3 inch Beds (Volumetric Flow Rate = 9.4 ft³/hr.)

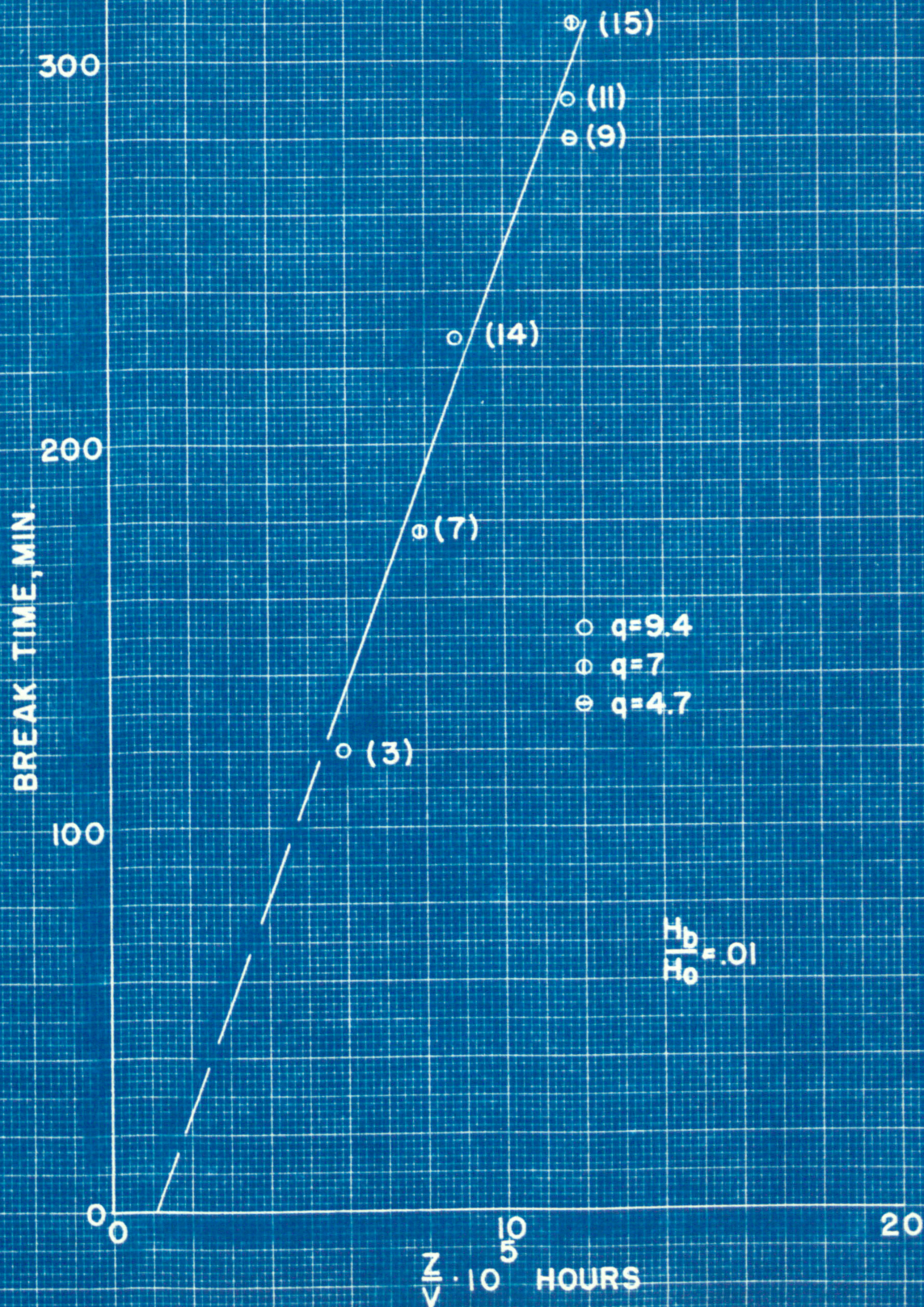


Figure 25
The Relationship Between Contact Time and Break Time for Beds Containing 20-24 Mesh Granules.

NO. 2 TOND SEMI-CROSS SECTION PAPER
TO 3.10 PER HALF INCH
GUARANTEED ALL RAG PAPER

SPAULDING MOSS COMPANY
BOSTON MASS
PRINTED IN U. S. A.

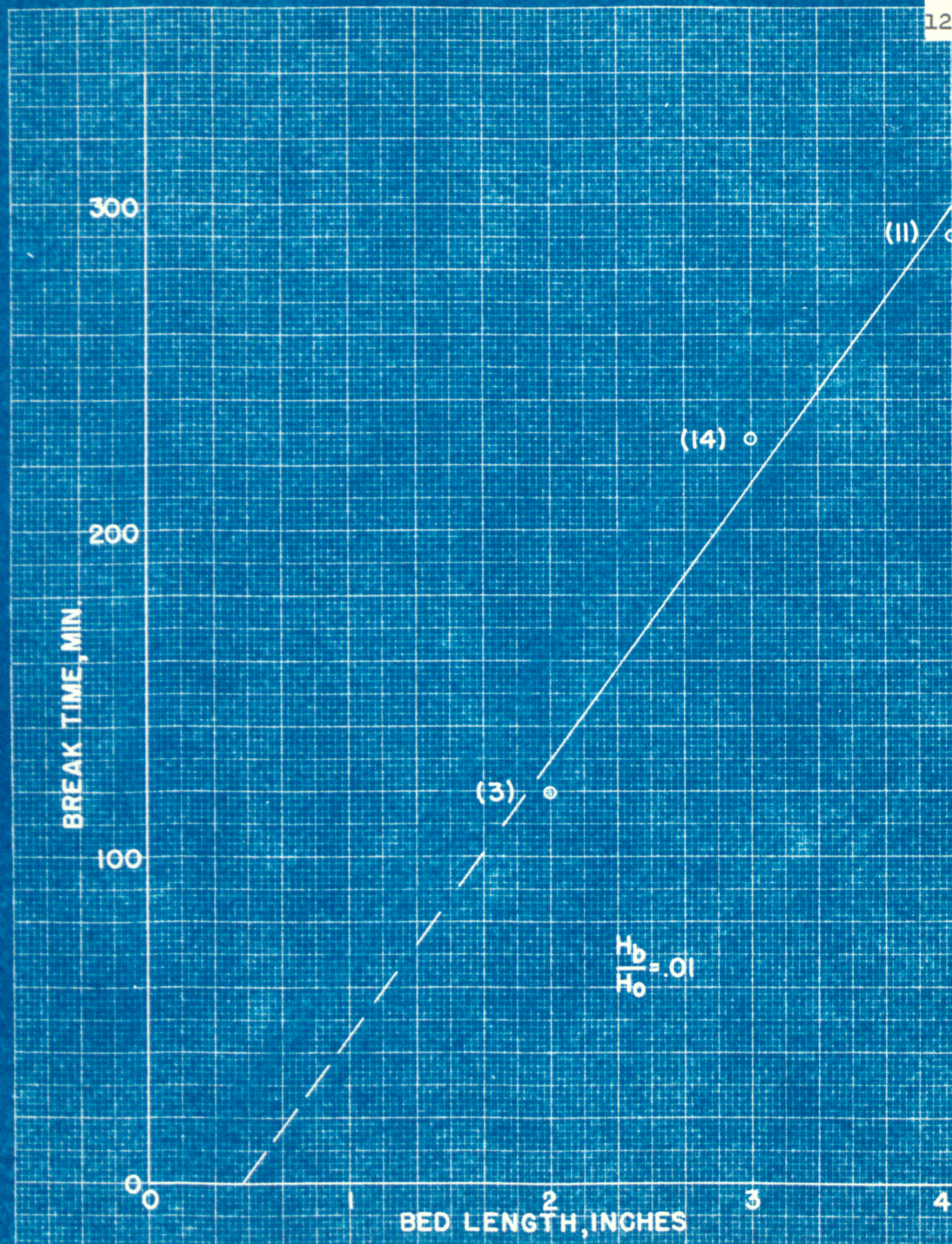


Figure 26
Life-Thickness Curve for Beds Containing
20 - 24 Mesh Granules

anhydrite under these test conditions is very small. For adsorbents used in small portable units such as activated carbon in gas masks the critical bed depth becomes an important factor. The critical length is the shortest bed that will produce an effluent concentration less than or equal to the break value. This bed has no life because although the bed starts with an effluent at or below the break value an instant after operation the effluent concentration rises above this value.

The empirical analysis leaves much to be desired. The entire procedure depends upon the selection of an arbitrary break point which should be representative. In the present case this selection is complicated by the fact that the adsorption wave exhibits discontinuities. The latter fact also has some bearing on attempts to fit the generalized theory to the data. The generalized theory may, however, be fit to a particular adsorption wave in which the discontinuities are not apparent. It can then be extended to all other wave forms as a medium of comparison and at the same time serve to detect the nature of the adsorption kinetics. It is this analysis which follows.

In the curve fitting procedure the 2" bed solid curve shown in figure 19 was used as starting point. The Schumann Furnas curve for $X = 100$ gave the best average fit as shown by the dashed curve in the same figure. Thus for the 2" bed, $q = 9.4 \text{ ft}^3/\text{hr}$, and 20 - 24 mesh material

($R_{av} = .0151"$) it was possible to compute $k^2 = 32.42$ and $D = 18.5$ from which it was found that $D_I = 5.21 \cdot 10^{-6}$ ft²/hr and $B = 34.2$. The computed value of D_I compares favorably with the theoretical value $D_I = 1.1 \cdot 10^{-9}$ ft²/hr. The value of D_I based on experiment could be made to coincide with the theoretical by employing a value of R supposedly corresponding to the crystallite radius rather than R_{av} for the granules. If this is not the case then the experimental diffusion coefficient represents an average for diffusion through small cracks as well as the lattice or the activation energy for lattice diffusion is only 60 to 70 per cent of the value employed in the theoretical computation. This all presumes of course that the curve fitting attempt is acceptable. The value of B seems reasonable compared to $B = 46.4$ computed for a fictitious isotherm. The latter is a straight line through the ($W \cdot 100$, R_h) coordinates (0,0) and (6.2, 8.1). The first coordinate is based on the fact that practically dry desiccant was employed in the experiments. The relative humidity of the inlet air to the beds was 8.1 per cent. Based on the 2 - 2½ and 42 - 48 mesh isotherms $W \cdot 100 = 6.2$ per cent for 8.1 percent relative humidity (See figures 6 and 10).

Equation 14 defines X and T so that the fit of the 2" bed above could be used in conjunction with the Schumann Furnas chart to determine the fit for any other bed. These dashed curves are shown in the figures for

representative cases of changes in bed length, velocity and granule size. Neglecting $(T/X)^{\frac{1}{4}}$ in the range of interest introduces appreciable error only for the 10 - 12 mesh granules but even then the error is within 15 per cent at the upper and lower ends of the rising portion of the adsorption wave. As T approaches X this error disappears.

As a basis for comparison it was assumed that mass transfer was controlling even though the empirical procedure suggests that it is not. The starting point was the same theoretical curve for the 2" bed discussed above. In order to use the definitions of X and T according to equation 28 it was assumed that $a = \text{constant} \cdot R^{-1}$ and $K_g = \text{constant} \cdot V^{.5} \cdot R^{-.5}$. Thus $X = \text{constant} \cdot V^{-.5} R^{-1.5} Z$ and $T = \text{constant} \cdot V^{.5} \cdot R^{-1.5} t$. In figure 19 the 2" bed curve is marked MT or ID because it is assumed the same for mass transfer controlling or internal diffusion controlling. By means of the definitions the 2" bed curve was converted to that for other cases shown in figures 18 and 21 and labeled MT to distinguish them from ID for the same case. In figure 18 the dash curves are for 10 - 12 mesh granules.

At first it appears to be difficult to decide whether mass transfer or internal diffusion is controlling. Figure 21 suggests that the internal diffusion theory gives the best fit of data. Figure 18 suggests the contrary. Apparently the decision rests upon consideration of the effect of particle size alone. In accord with the

postulates of the theory of mass transfer the internal structure of the granules is disregarded. It is supposed that a stagnant gas film surrounds the granule as a whole. The extent of this film depends therefore on nominal granule size as considered above. Thus in figure 18 there appears to be no chance of improving the fit of the mass transfer theory to the adsorption wave for 10 - 12 mesh granules. This is not true of the internal diffusion theory. The radius, R , in the internal diffusion theory might refer not to the granule but to a smaller unit of the granule such as the crystallite discussed earlier. This of course would promote a better fit of experimental data at least in the case of 10 - 12 mesh granules.

It will be noted in figure 18 that there is little difference between the general position of the 10 - 12 mesh curve and that for the 20 - 24 mesh material. This phenomena strongly suggests that nominal granule size is not of basic importance. This fact may be accounted for by figure 3 wherein it is suggested that the crystallite size rather than granule size is a fundamental quantity. That crystallite size is important has also been previously suggested by the computation of the experimental value of D_I . Thus the internal diffusion theory may be made to fit the experimental data in figure 18 for 10 - 12 mesh material by assuming a value for R which supposedly is related to crystallite size as contrasted with nominal granule size.

Actually the 20 - 24 mesh 3 inch bed theoretical curve shown in figure 19 gives an excellent fit of the 10 -12 mesh data in figure 18. The fact that the adsorption wave for 2 - $2\frac{1}{2}$ and 4 - 5 mesh material deviates from that for the smaller sizes indicates either that the crystallite size is some function of nominal granule size, or that for the larger granules the wall effect and diffusion through the larger pores is of some importance.

Beside determining the adsorption kinetics the generalized theory is of value in problems of design. The theoretical adsorption wave for the 9 inch bed is an illustration of this application. All previous runs were concerned with short beds which could be saturated within an 8 hour day. The internal diffusion theory thus developed was used to predict the adsorption wave for a bed which could be saturated or nearly so in 15 - 16 hours (6 AM - 10 PM), i.e. a 9 inch bed. Figure 23 confirms the success of this application. In fact it works so well that one is lead to wonder why the theory did not do a better job of predicting the 3" bed in figure 19.

Because of its utility it seems advisable to outline the method for predicting the dash curve mentioned in the previous paragraph. The method is based on the Schumann-Furnas chart. The coordinates of the chart are H/H_0 and T . The chart contains adsorption waves corresponding to various values of X . Values of H/H_0 greater than .9 are not shown.

Thus the problem is to determine which wave contains the point corresponding to $H/H_0 = .9$ and $t = 15$ hours. The value, $T = 32.42 \cdot 15 = 486$, must be used in conjunction with the chart. The wave containing the point, $(.9, 486)$, is the one labeled "450". Thus $X = k^2 DZ = 450 = 32.42 \cdot 18.5 \cdot Z$ and $Z = .75$ ft. (9").

A detailed examination of the various adsorption waves presented herein reveals several facts of qualitative interest which are not represented by the theory in its present form. The first and most obvious is that some curves exhibit double or triple breaks, i.e., the rising portion of the curve shows two or three humps. These become more prominent at lower flow rates and for longer beds. The cause of this phenomena may be attributed to the discontinuities of the adsorption isotherm. For each break in the adsorption isotherm one would expect a corresponding break in the adsorption wave. In effect a single bed actually consists of several beds in series the length of each being a function of time. Each bed of the series has its own adsorption wave and it is a composite of these which is illustrated in the figures presented above. The vertical break in the adsorption isotherm at about .75 per cent relative humidity corresponds to $H/H_0 = .155$ approximately. The discontinuity for 10 - 12 mesh material of figure 18, for the curve of $q = 7 \text{ ft}^3/\text{hr}$ in figure 20, and for the $7 \text{ ft}^3/\text{hr}$ curve of figure 21 occurs approximately

at this value. The low level of the lower hump in figure 23 indicates either a greater departure from the theoretical value due to the particular conditions or the appearance of a new hump which corresponds to a very low humidity break in the adsorption isotherm. The latter break in the isotherm could have escaped detection in the present work and is a reason for investigating this matter in further detail. The break if present should appear at a relative humidity corresponding to H/H_0 ranging from .005 to .05 approximately.

Runs 8, 13 and 14 in figure 22 suggest that certain other factors also aggravate the discontinuous behavior of the adsorption wave. The only apparent difference in these three runs is that run number 13 was started a little before the dehumidifier had a chance to come to equilibrium. The inlet humidity probably increased by 5 to 10 per cent during the course of the run.

Other points of interest are those regarding reproducibility of data and the minimum humidity of the exhaust gas. Figure 22 shows that the data can be reproduced quite well without any special precautions. The difference between runs 10 and 15 may be related to a difference between the amounts of desiccant in the two beds. The pressure drop over the bed of run 10 was noticeably greater than that for run 15. This suggests more desiccant and better packing in the bed of run 10. Exact duplication apparently

depends upon exact duplication of the regeneration cycle, the loading and above all maintaining a constant inlet humidity.

The minimum frost point attainable is a direct consequence of the regeneration cycle, and other factors. In run 16, figure 18, it was necessary because of the schedule of experiments to leave the charge in the regeneration furnace a half hour longer than the 2 hours normally employed. The minimum frost point in this case was less than -91°F which was the lowest ever obtained during all the experiments. Those concerned with the manufacture of Drierite suggest that -100°F can be obtained with a 4 hour - 450°F regeneration cycle. Amero (7) has calculated the minimum frost point as -87°F . This no doubt is based on the normal regeneration cycle of 2 hours at 400°F .

A final point is that with regard to the time interval during which a bed produces the minimum humidity. The total time of this product is always small compared to the complete drying cycle. This is even true for the effluent for the 9 inch bed the adsorption wave of which is shown in figure 23. The latter figure shows that contrary to expectation the minimum humidity interval is reduced by a correspondingly longer time for the initial decline in exit humidity. The lower (first) break of the bed is also magnified and consequently detracts from the time interval

during which the minimum humidity product is produced. The longer time for the initial decline in humidity might be related to the method of charging the bed containers. Earlier it was stated that the bed containers were charged with desiccant taken directly from the regenerating furnace. During the assembling of container, screens, etc. the desiccant tends to cool and draw in moist air. The amount drawn in may be greater for a longer bed. Thus more moisture would have to be removed from the exhaust end of the bed during the initial stages of the run.

There appears to be no real good reason why the lower break for the 9 inch bed should be magnified. There is the possibility that the phenomenon is related to the method of charging. In any event this matter should be investigated. This could be done by charging as usual then running the bed first with dry air and then with the wet air feed previously employed. The dry air (frost point = -100°F or less) might be obtained as exhaust from a magnesium perchlorate bed which would have to be investigated first. The dry air would be fed to the drierite bed until its exhaust humidity dropped to that of its inlet. One could be certain then that the drierite bed was completely regenerated and was ready to run to determine the adsorption wave.

SUMMARY AND CONCLUSIONS

The theory of the adsorption wave has been reviewed with emphasis on the utility of the Schumann Furnas chart which has been published for the case of mass transfer controlling the adsorption process. The solutions for two other cases (diffusion through pores and activated lattice diffusion) are presented. It is shown how in dimensionless form all three cases may be reduced to a single generalized theory. This treatment has many obvious advantages. This is especially so in problems of design and in studies of the kinetics of an adsorption process.

There has been presented the results of a study to determine the kinetics of the reaction between humid air and the granular desiccant, calcium sulphate. Plots of the experimentally determined adsorption waves are given for various gas velocities, granule sizes, and bed lengths. In view of the small internal diffusion coefficient for this system it would be expected that activated diffusion into the interior of the granule would control the adsorption process. That this is probably true is demonstrated by an analysis of the plots employing the generalized theory as well as empirical methods.

As a matter of implementing the above research it was necessary to determine the adsorption isotherms for the system. Plots of these are presented for five different granule sizes. Adsorption capacities in these plots refer

to an absolute dry base weight as contrasted with an unreliable regenerated base weight usually employed. The plots show that the adsorption capacities of new material decrease slightly with decreasing particle size. There is no indication of an optimum particle size as had been found by Wheat. A comparison of the plots for new material with those appearing in the literature demonstrate that previous investigators had not allowed sufficient time in order to attain equilibrium. Repeatedly regenerated drierite (used material) show a decrease in adsorption capacity.

According to the adsorption isotherms calcium sulphate acts very much like a zeolite. Its adsorption capacity is noticeably reduced even at low temperatures. Numerous other peculiarities have also been discussed. The fact that the desiccant probably shows no adsorption hysteresis below 30 percent relative humidity is worthy of note.

The porous structure of soluble anhydrite beds and granules has also been considered. It has been shown by calculations, benzene adsorption experiments, and measurement of bed density, that: (a) the granule probably consists of a mosaic of crystallites each of which contains 46.6 per cent by volume interstitial channel space; (b) that the granule contains intercrystallite pore space to the extent of about 25.8 per cent of its volume; and that (c) the bed (consisting of 2 - $2\frac{1}{2}$, 4 - 5, 10 - 12, or 20 - 24

mesh granules) contains 42.5 per cent by volume of intergranular void space. Presumably the pores in the crystallite are of about the same cross sectional diameter as that of the water molecule whereas the intercrystallite pore diameter is certainly larger than the diameter of the benzene molecule and may range up to $40\text{\AA}$ or more.

The design, construction, operation, and maintenance of an automatic electronic frost point hygrometer is also described in detail. It has been shown that with this instrument one may measure continuously frost points ranging down to -100°F with an accuracy apparently limited by the potentiometer employed in conjunction with the thermocouple which is an integral part of the hygrometer. Frost point hygrometers utilizing liquid air have been discussed and it has been observed that the lower limit of their useful range (-130°F) is probably dictated by the appearance of Ice II which probably is a transparent glass. To the latter the frost point hygrometer either reacts very poorly or not at all.

LITERATURE CITED

- (1) Hougen, O.A. and Dodge, F.W., "The Drying of Gases", Ann Arbor, Michigan, Edwards Brothers, Inc., 1947 (Originally issued in an edition of 30 copies for office of Tech. Services, U. S. Dept. of Commerce).
- (2) Thiele, E.W., "Material or Heat Transfer between a Granular Solid and Flowing Fluid", Ind. Eng. Chem., 38, 646 (1946).
- (3) Klotz, I.M., "The Adsorption Wave", Chem. Rev., 39, 241-268 (1946).
- (4) Wilson, I.N., "A Theory of Chromatography", J. Am. Chem. Soc. 62, 1583- (1940).
- (5) DeVault, D., "The Theory of Chromatography", J. Am. Chem. Soc. 65, 532- (1943).
- (6) Weiss, J., "On the Theory of Chromatography", J. Chem. Soc. 1943, 297.
- (7) Amero, R.C., Moore, J.W., and Capell, R.G., "Design and Use of Adsorptive Drying Units", Chem. Eng. Progress, 43, 349-370 (1947).
- (8) Brewer, A.W., Cwilong, B., and Dobson, G.M.B., "Measurements of Absolute Humidity in Extremely Dry Air", Proc. Phys. Soc. 60, 52-70 (1948).
- (9) Wheat, T.C., "Mass Transfer in Beds of Chemical Desiccants", U.C. Thesis (M.S.) 1948.
- (10) Gaudefroy, G., "The Dehydration of Gypsum", Compt. rend., 158, 2006-7, (1915).
- (11) Hammond, W.A. and Withrow, J.R., "Soluble Anhydrite as a Desiccating Agent I. Preparation and General Characteristics", Ind. Eng. Chem., 25, 653-9 (1933).
- (12) Werkinthin, T.A., Monograph U.S. Bureau of Ships (1940).
- (13) Nacken, R. and Fill, K., "The Transformation of Gypsum Hemihydrate into Anhydrite in Moist Air at Atmospheric Pressure", Tonid. Ztg, 55, 1194-6 (1931).
- (14) Krauss, F., "The Chemistry of Gypsum", Tonind, Ztg., 55, 1222-4 (1931).
- (15) Tone, Kawatake, "A Study on Gypsum", Repts, Imp. Ind., Research Inst. Osaka, 15, #6, 1-56 (1934).

- (16) Weiser, H.B., Milligan, W.O. and Ekholm, W.C., "The Mechanism of the Dehydration of a $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ", J. Am. Chem. Soc. 58, 1261-1265 (1936).
- (17) Weiser, H.B. and Milligan, W.O., "The Mechanism of the Dehydration of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ II. Observations with Large Crystals", J. Am. Chem. Soc., 59, 1456-1457 (1937).
- (18) Linck and Jung, Z. Anorg. Allgem. Chem., 137, 407 (1924).
- (19) Balarew, Z. Anorg. Allgem. Chem., 156, 258 (1926).
- (20) Balarew, Kolloid.-Z., 48, 63 (1929).
- (21) Balarew and Koluschewa, Kolloid.-Z., 70, 288 (1935).
- (22) Gibson and Holt, J. Chem. Soc., 638 (1933).
- (23) Parsons, Univ. Toronto Studies, Geol. Ser., No. 24, p. 24 (1927).
- (24) Jung, Z. Anorg. Allgem. Chem., 142, 73 (1925).
- (25) Ramsdell and Partridge, Am. Mineral., 14, 59 (1929).
- (26) Caspari, Nature, 133, 648 (1934).
- (27) Onorato, Periodico Min., 3, 138 (1932).
- (28) Gallitelli, Periodico Min., 4, 1, 132 (1933).
- (29) Feitknecht, Helv. Chim. Acta, 14, 85 (1931).
- (30) Emeleus, H. J. and Anderson, J.S., "Modern Aspects of Inorganic Chemistry", N.Y. D. Van Nostrand Co., Inc., 1939.
- (31) Bunn, C. W., "Chemical Crystallography", Cambridge, England, Oxford University Press, 1946.
- (32) Kelley, K.K., Southard, J.C. and Anderson, C.T., "Thermodynamic Properties of Gypsum and its Dehydration Products", U. S. Bureau of Mines Tech. Paper. #625 (1941).
- (33) Hey, M.H., "Studies on the Zeolites. Part III. A Theory of the Vapor Pressure of the Zeolites, and of the Diffusion of Water or Gases in a Zeolite Crystal" Mineralogical Magazine, 24, 99-130 (1935).

- (34) Hey, M.H., "Studies on the Zeolites. Part IX. Scolecite and Metascolecite" Mineralogical Magazine, 24, 227-253 (1936).
- (35) Hey, M.H., "Diffusion in Zeolitic Solids", Philosophical Magazine, 22, 492-497 (1936).
- (36) Barrer, R.M. and Ibbitson, D.A., "Occlusion of Hydrocarbons by Chabazite and Analcite", Trans. Faraday Soc., 40, 195-206 (1944).
- (37) Barrer, R.M. and Ibbitson, D.A., "Kinetics of Formation of Zeolitic Solid Solutions", Trans. Faraday Soc., 40, 206-216 (1944).
- (38) Davey, W.P., "Study of Crystal Structure and its Applications" first edition, pg. 526, N.Y., McGraw-Hill Book Co., Inc., 1934.
- (39) Palacios, J. and Cabrera, J. (See C.A. 29:6812).
- (40) Onorato, E., "The Fine Structure of Gypsum", Z Krist., 71, 277-325, (1929).
- (41) Rinne, F., Hentschel, H., and Schiebold, E., "The Structure of Anhydrite and Barite", Z. Krist., 61, 164-76 (1925).
- (42) Wasastjerna, J.A., "Structure of Anhydrite Structure of Sulphate Group", Soc. Sci. Fennica Commentationes Phys. - Math, #2, 19-30, 46 (pp) (1927).
- (43) Harkins, W.D. and Jura, G., "The Surfaces of Solids and Liquids and the Films that Form upon Them. Part II. Solids and Adsorption at the Surface of Solids or Liquids", Alexander, J. "Colloid Chemistry", Vol VI pgs. 1-76, N.Y., Reinhold Publishing Corporation, 1946.
- (44) Tiselus, A., "Adsorption and Diffusion in Zeolite Crystals", Weiser, H.B., "Colloid Symposium - 1935", pgs 101-110 Baltimore, Md., The Williams and Wilkins Company, 1936.
- (45) Wicke, E., "Empirische und Theoretische Untersuchungen der Sorptionsgeschwindigkeit von Gasen an Porösen Stoffen", Kolloid. Z., 86, 167-186, 296-313 (1939).
- (46) Wicke, E., "Untersuchungen über Ad- und Desorptionsvorgänge in Kornigen, durchstromten Adsorbenschichten", *ibid* 93, 129-157 (1940).

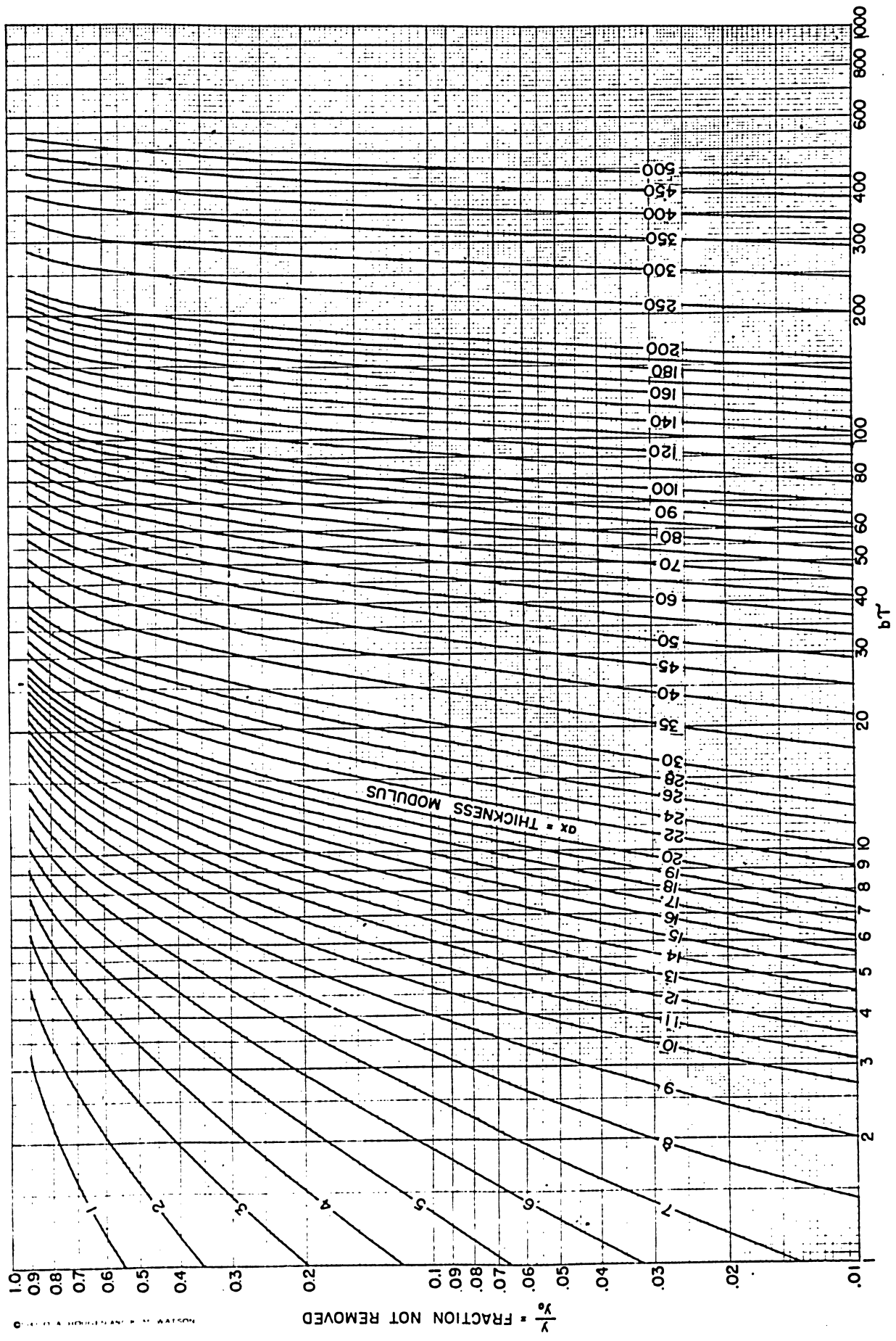
- (47) Barrer, R.M., "Diffusion in and Through Solids", N.Y., The MacMillan Company, 1941.
- (48) Bateman, H., "Partial Differential Equations of Mathematical Physics", 1st American edition, pp. 123-135, N.Y., Dover Publications (1944).
- (49) Churchill, R.V., "Modern Operational Mathematics in Engineering", N.Y., McGraw-Hill Book Company, Inc. 1944.
- (50) Courant and Hilbert, "Methoden der mathematischen Physik," Vol. II, pp. 311-317.
- (51) Watson, G.N., "A Treatise on the Theory of Bessel Functions", 2nd ed., pg. 393, N.Y., The MacMillan Company, (1944).
- (52) Walter, J.E., "Rate-Dependent Chromatographic Adsorption", J. Chem. Phys., 13, 332 (1945).
- (53) Anzelius, A., Z. angew. Math. Mech., 6, 291-4 (1926).
- (54) Nusselt, W., Z. Ver. deut. Ing., 71, 85 (1927).
- (55) Schumann, T.E.W., J. Franklin Inst., 208, 405 (1929).
- (56) Furnas, C.C., Bur. Mines, Bull. 361 (1932).
- (57) Hougen, O. and Marshall, W.R., Jr., "Adsorption from a Fluid Stream Flowing through a Stationary Granular Bed", Chem. Eng. Progress, 43, 197-208 (1947).
- (58) Hougen, O. and Watson, K., "Chemical Process Principles Charts", 1st ed., pg. 216, N.Y., John Wiley and Sons, Inc., (1946).
- (59) Thomas, H., "Heterogeneous Ion Exchange in a Flowing System", J. Am. Chem. Soc., 66, 1664-1666 (1944).
- (60) Wilson, R.E., "Humidity Control by Means of Sulphuric Acid Solutions with Critical Compilation of Vapor Pressure Data", Ind. Eng. Chem. 13, 326-331 (1921).
- (61) International Critical Tables, Vol. III, pp. 302-3, N.Y., McGraw-Hill Book Company, Inc. (1929).
- (62) Greenewalt, Ind. Eng. Chem., 17, 522 (1925).
- (63) Damerell, V.R. and Tower, D.F., "A Hydrate Decomposition Mechanism", Weiser, H.B., "Colloid Symposium -

1935" pgs. 143-52, Baltimore, Md., The Williams and Wilkins Company, 1936.

- (64) Rae, J. Chem. Soc., 109, 1230 (1916).
- (65) Garner and Tanner, J. Chem. Soc., 47 (1930).
- (66) Crowther and Coutts, Proc. Roy. Soc. London, 106, 215 (1924).
- (67) Kohlschutter and Nitschmann, Z. physik, Chem., Bodenstein Festband, 494 (1931).
- (68) Brunauer, S., "The Adsorption of Gases and Vapors," 1st ed., Princeton, New Jersey, Princeton University press (1943).
- (69) Czepek, R., "Moisture Determination in Air and other Gases by the Dew Point Method", Arch. tech. Messen, Lfg. 110, T85-6, 4 pp (1940); Chem. Zentr., 1940 II 2511.
- (70) Halban, H. and Siedentopf, K., "The Measurement of Small Vapor and Partial Pressures", Z. angew. Chem., 40, 661-6 (1927).
- (71) Glasstone, S., "Textbook of Physical Chemistry" 2nd edition pg. 473, N.Y. D. Van Nostrand Co., Inc. 1946.
- (72) Muller, R. H., Garmand, R. L., and Droz., M.E., "Experimental Electronics", New York, Prentice-Hall, Inc., 1942.
- (73) Blanchard, F.A., "Photocell-Fluorescent Screen Measurement of X-Ray Intensities", U.C.Thesis (M.S.) 1948.
- (74) Anderson, E.P., "Phototube Circuit for Measuring Low Values of Light", "Audel's Electronic Devices and their Application", Theo, Audel and Co., Publishers, N.Y. (1938).
- (75) Lange, N.A., "Handbook of Chemistry", 6th Ed., p. 826, Sandusky, Ohio, Handbook Publishers, Inc., 1946.
- (76) Brunt, D., "Physical and Dynamical Meteorology", pp. 101-104, Cambridge England, The University Press, 1941.

APPENDIX

Schumann-Furnas Chart



TIME MODULUS

Figure 27

Schumann-Furnas Chart (58). Originally Devised as the Solution to Equation 26 in Text where $H/H_0 = y/y_0$, $bT = T$ and $ax = X$.

Reference Tables

Table VI

Calibration Chart for Copper-Constantan Thermocouple

Taken from Expanded Plot of Data in Lange Handbook (Values Shown
are Millivolts) (75)

°F	0	1	2	3	4	5	6	7	8	9
+30	.04	.02	0							
+20	.25	.23	.21	.19	.17	.15	.13	.10	.08	.06
+10	.46	.44	.42	.40	.38	.36	.34	.31	.29	.27
+ 0	.67	.65	.63	.60	.58	.56	.54	.52	.50	.48
- 0	.67	.69	.71	.73	.75	.77	.79	.81	.83	.85
-10	.87	.89	.91	.93	.95	.97	.99	1.01	1.03	1.05
-20	1.07	1.09	1.11	1.13	1.15	1.17	1.19	1.21	1.23	1.25
-30	1.27	1.29	1.31	1.33	1.35	1.37	1.39	1.41	1.43	1.45
-40	1.47	1.48	1.50	1.52	1.54	1.56	1.58	1.60	1.62	1.64
-50	1.65	1.67	1.69	1.71	1.73	1.75	1.77	1.79	1.80	1.82
-60	1.84	1.86	1.88	1.90	1.92	1.93	1.95	1.97	1.99	2.01
-70	2.02	2.04	2.06	2.08	2.10	2.12	2.14	2.15	2.17	2.19
-80	2.21	2.23	2.25	2.26	2.28	2.30	2.32	2.34	2.35	2.37
-90	2.39	2.41	2.42	2.44	2.46	2.48	2.49	2.51	2.53	2.55
-100	2.56	2.58	2.60	2.62	2.63	2.65	2.67	2.68	2.70	2.72
-110	2.73	2.75	2.77	2.78	2.80					

Table VIII
Vapor Pressure of Ice
Calculated from the equation

$$\log \frac{p}{p_{32_{ice}}} = 9.95 \frac{t - 32}{460 + t} - .445 \log \frac{t + 460}{492}$$

where $p_{32_{ice}} = 4.59 \text{ mm Hg}$ (76)

[illegible]

Table IX

Rotameter Calibration Chart

Fischer Porter Rotameter - 10" tube
 Atmospheric Pressure and 72°F Saturated Air

Reading	Air Flow Rate ft ³ /hr	Reading	Air Flow Rate ft ³ /hr
2.0	.38	9.0	4.24
2.5	.48	9.5	4.62
3.0	.62	10.0	5.03
3.5	.80	10.5	5.45
4.0	1.00	11.0	5.88
4.5	1.23	11.5	6.30
5.0	1.50	12.0	6.72
5.5	1.77	12.5	7.14
6.0	2.08	13.0	7.60
6.5	2.40	13.5	8.00
7.0	2.75	14.0	8.48
7.5	3.10	14.5	8.90
8.0	3.48	15.0	9.40
8.5	3.85		

Table X
Vapor Pressure of Water

t°C	mm Hg	t°C	mm Hg	t°C	mm Hg	t°C	mm Hg
0	4.579	10	9.209	20	17.535	30	31.824
1	4.926	11	9.844	21	18.650	31	33.695
2	5.294	12	10.518	22	19.827	32	35.663
3	5.685	13	11.231	23	21.068	33	37.729
4	6.101	14	11.987	24	22.377	34	39.898
5	6.543	15	12.788	25	23.756	35	42.175
6	7.013	16	13.634	26	25.209	36	44.563
7	7.513	17	14.530	27	26.739	37	47.067
8	8.045	18	15.477	28	28.349	38	49.692
9	8.609	19	16.477	29	30.043		

Original Data

Table XI

Determination of the Adsorption Isotherms at Room Temperature

Date	Time	Sample Weight (g)				
		2 - 2½ mesh	4 - 5 mesh	10-12 mesh	20-24 mesh	42-48 mesh
Humidity =		<u>0.0313% RH</u>				
24 Jan 48	12:00 N	9.2453	7.1576			
26 Jan 48	10:30 AM	9.2485	7.1618			
27 Jan 48	11:30AM	9.2503	7.1644			
29 Jan 48	10:45 AM	9.2554	7.1726			
2 Feb 48	10:15 AM	9.2563	7.1718			
3 Feb 48	10:30 AM	9.2579	7.1728			
5 Feb 48	10:30 AM	9.2585	7.1737			
7 Feb 48	10:30 AM	9.2598	7.1749			
Humidity =		<u>0.408% RH</u>		<u>0.0313% RH</u>		
7 Feb 48	10:30 AM	9.2598	7.1749	8.0241	10.2382	
12 Feb 48	10:30 AM	9.2703	7.1833	8.0280	10.2427	
16 Feb 48	2:00 PM	9.2818	7.1929	8.0312	10.2462	
20 Feb 48	10:00 AM	9.2847	7.1953	8.0329	10.2585	
23 Feb 48	3:45 PM	9.2871	7.1974	8.0327	10.2471	
Humidity =		<u>3.63% RH</u>		<u>0.408% RH</u>		<u>0.0313% RH</u>
23 Feb 48	3:45 AM	9.2871	7.1974	8.0327	10.2471	9.3781
1 Mar 48	2:00 P.M.	9.5944	7.5181	8.0479	10.2642	9.3773
6 Mar 48	10:30 AM	9.7672	7.5708	8.0518	10.2685	9.3739
13 Mar 48	11:45 AM	9.7911	7.5741	8.0546	10.2710	9.3722
Humidity =		<u>10% RH</u>		<u>3.63% RH</u>		<u>0.408% RH</u>
13 Mar 48	11:45 AM	9.7911	7.5741	8.0546	10.2710	9.3722
20 Mar 48	11:45 AM	9.8132	7.5923	8.3187	10.6410	9.3893
27 Mar 48	11:00 AM	9.8130	7.5922	8.3244	10.6527	9.4006
3 Apr 48	11:00 AM	9.8109	7.5902	8.3230	10.6517	9.4051
Humidity =		<u>35% RH</u>		<u>10% RH</u>		<u>3.63% RH</u>
3 Apr 48	11:00 AM	9.8109	7.5902	8.3230	10.6517	9.4051
12 Apr 48	11:00 AM	9.8356	7.6101	8.3432	10.6751	9.8796
24 Apr 48	12:00 N	9.8337	7.6087	8.3424	10.6757	9.8830

Table XI (cont)

Date	Time	Sample Weight (g)				
		2 - 2½ mesh	4 - 5 mesh	10-12 mesh	20-24 mesh	42-48 mesh
Humidity =		<u>50% RH</u>		<u>35% RH</u>		<u>10% RH</u>
24 Apr 48	12:00 N	9.8337	7.6087	8.3424	10.6757	9.8830
8 May 48	10:00 AM	9.9147	7.6647	8.3678	10.7066	9.9004
15 May 48	9:30 AM	9.9170	7.6659	8.3691	10.7081	9.9016
Humidity =		<u>65% RH</u>		<u>50% RH</u>		<u>35% RH</u>
15 May 48	9:30 AM	9.9170	7.6659	8.3691	10.7081	9.9016
1 June 48	12:00 N	10.0607	7.6984	8.4044	10.7573	9.9243
5 June 48	11:30 AM	9.9657	7.7036	8.4093	10.7640	9.9276
Humidity =		<u>50% RH</u>		<u>65% RH</u>		<u>50% RH</u>
5 June 48	11:30 AM	9.9657	7.7036	8.4093	10.7640	9.9276
19 June 48	10:30 AM	9.9399	7.6814	8.4419	10.8057	9.9925
26 June 48	9:30 AM	9.9325	7.6744	8.4381	10.8019	9.9883
Humidity =		<u>40% RH</u>		<u>50% RH</u>		<u>65% RH</u>
26 June 48	9:30 AM	9.9325	7.6744	8.4381	10.8019	9.9883
10 July 48	11:30 AM	9.8693	7.6356	8.4210	10.7772	10.0437
17 July 48	11:00 AM	9.8708	7.6356	8.4223	10.7791	10.0464
Humidity =		<u>25% RH</u>		<u>40% RH</u>		<u>50% RH</u>
17 July 48	11:00 AM	9.8708	7.6356	8.4223	10.7391	10.0464
31 July 48	11:30 AM	9.8265	7.6071	8.3954	10.7395	10.0197
7 Aug 48	11:00 AM	9.8213	7.6013	8.3917	10.7369	10.0214
Humidity =		<u>5% RH</u>		<u>25% RH</u>		<u>40% RH</u>
7 Aug 48	11:00 AM	9.8213	7.6013	8.3917	10.7369	10.0214
21 Aug 48	10:00 AM	9.7993	7.5839	8.3660	10.7032	9.9671
28 Aug 48	12:00 N	9.8000	7.5849	8.3670	10.7040	9.9604
Humidity =		<u>2% RH</u>		<u>5% RH</u>		<u>25% RH</u>
28 Aug 48	12:00 N	9.8000	7.5849	8.3670	10.7040	9.9604
18 Sep 48	11:30 AM	9.7878	7.5740	8.3427	10.6743	9.9158
Humidity:		<u>1% RH</u>		<u>2% RH</u>		<u>5% RH</u>
18 Sep 48	11:30 AM	---	---	8.3427	10.6743	9.9158
2 Oct 48	10:00 AM	9.7878	7.5740	8.3313	10.6601	9.8899

Table XI (cont)

Date	Time	Sample Weight (g)				
		2 - 2½ mesh	4 - 5 mesh	10-12 mesh	20-24 mesh	42-48 mesh
Humidity (cont)=		<u>1% RH</u>		<u>2% RH</u>		<u>5% RH</u>
9 Oct 48	8:30 AM	9.7845	7.5709	8.3326	9.6616	9.8910
23 Oct 48	10:00 AM	9.7842	7.5704	--	--	--
Humidity =				<u>1% RH</u>		<u>2% RH</u>
9 Oct 48	8:30 AM			8.3326	9.6616	9.8910
23 Oct 48	10:00 AM			8.3255	10.6531	9.8811
30 Oct 48	9:30 AM			8.3233	10.6503	9.8799
Humidity =						<u>1% RH</u>
30 Oct 48	9:30 AM					9.8799
13 Nov 48	10:30 AM					9.8740
1 Dec 48	9:15 AM					9.8716
Anhydrous CaSO ₄ in sample:		9.2193	7.1445	8.0054	10.2140	9.3304
Water in original sample:		.0260	.0131	.0187	.0242	.0477

Table XII

Determination of the Moisture Adsorption of Annealed Samples

Date	Time	Sample Weight (g)	
		4-5 mesh new	20-24 mesh used
Humidity =		35% RH	
15 Mar 48	4:00 P.M.	7.6780	5.1624
20 Mar 48	12:00 N.	8.1471	5.3856
27 Mar 48	11:00 A.M.	8.1477	5.3959
3 Apr 48	11:00 A.M.	8.1459	5.3938
Humidity =		Room Humidity	
3 Apr 48	11:00 A.M.	8.1459	5.3938
23 Oct 48	12:00 N.	8.1559	5.4037
Anhydrous CaSO_4 in sample (g) =		7.6612	5.1563
Water in original sample (g) =		.0168	.0061

Table XIII

Adsorption Test of New Drierite Sample

		<u>Sample Weight (g)</u>
Date	Time	10-12 mesh
Humidity =		<u>25% RH</u>
1 Nov 48	2:00 PM	13.4975
13 Nov 48	10:30 AM	14.2757
1 Dec 48	9:15 AM	14.2733
Anhydrous CaSO_4 in sample (g) =		13.4615
Water in original sample (g) =		.0260

Table XIV

Benzene Vapor Adsorption Test of Drierite

Date	Time	<u>Sample Weight (g)</u>
		4 - 5 mesh
2 Feb 48	11:30 AM	4.9103
5 Feb 48	10:30 AM	5.2678
7 Feb 48	10:30 AM	5.2708
9 Feb 48	2:00 PM	5.2244

Table XV Run No. 1

Description of Run: Bed Diameter = 1.03"
 Bed Length = 3.00"
 Granule Mesh = 20-24 new
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 44 psig
 $H_0 = 1060 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H_0	Dehumidifier Temp, °F	Time min.	Frost Point °F	H/H_0	Dehumidifier Temp, °F
<u>Feed</u>				64	-66.5	.013	
				67	-69	.011	
0				69	-67.5	.012	
11				72	-67	.012	
25				75	-68	.012	
38			44	78	-68	.012	
46	+12.5			80	-68	.011	
49	12.0			83	-69	.011	40
52	11.0			88	-69	.011	
54			43	92	-69.5	.010	
58	11.0			98	-69	.011	
61	11.0			104	-69.5	.010	
64	11.0		43	107	-71.5	.009	
<u>Bed</u>				110	-72.0	.009	
				114	-72.7	.008	
				117	-72.7	.008	
0				120	-72.7	.008	
4	-52.5	.034		127	-72.7	.008	
8	-53.	.032		132	-72.7	.008	
10	-55	.028		136	-74.5	.007	
13	-53.7	.030		142	-75.5	.006	
17	-55	.029		147	-75.	.007	
21	-56	.026	42	152	-75.	.007	
24	-58.5	.022		157	-75.	.007	38
28	-57.	.025		162	-76.	.006	
32	-59.	.022		171	-77.	.006	
36	-60.5	.019		176	-77.	.006	
38	-60.5	.019		184	-77.5	.006	
40	-60.5	.019	40	188	-78.	.005	
45	-62	.018		195	-78.5	.005	
51	-63	.016		199	-79.0	.005	37.5
57	-64	.015		204	-79.0	.005	
61	-64	.015		219	-79.0	.005	

Table XV (cont.)

Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F	Time Min	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F
223	-79.0	.005		312	-24	.193	
224	-77	.006		314	-22.5	.216	
225	-75	.007		316	-21.7	.226	
227	-74.5	.007		317	-20	.248	
229	-74.2	.007		319	-19	.263	
231	-71.5	.009		320	-19	.263	
232	-70.	.010		322	-17.5	.286	
234	-70	.010		325	-16.5	.302	
237	-69	.011	37	327	-15.5	.316	
238	-66.5	.013		328	-15.5	.316	
239	-66	.013		330	-14.0	.348	
241	-63.5	.016		331	-13.7	.356	
245	-62	.018		335	-12	.387	
246	-61	.019		337			37
247	-59.5	.021		339	-10	.434	
249	-58.2	.023		343	- 9.7	.442	
251	-56.5	.026		352	- 9	.465	
253	-55.5	.028		355	- 7	.512	
256	-54.5	.029		357	- 7	.512	
259	-54.2	.030		359	- 6.5	.526	
261	-52.5	.034		361	- 6.5	.526	
265	-52.2	.034		364	- 5.0	.565	
267	-51.5	.036		366	- 4.5	.590	
269	-50.5	.038		372	- 3.5	.615	
272	-50	.040	37.5	374	- 3.0	.635	
275	-48.	.045		377	- 3.0	.635	
279	-46	.051		380	- 2.5	.650	
283	-43.7	.059		383	- 1.5	.681	36
286	-42.2	.064		385	- 1.2	.691	
288	-40.0	.074		389	- 1.0	.696	
290	-39	.078		390	± 0.0	.735	
292	-37.5	.087		395	± 1.0	.775	
297	-34.5	.105		401	± 1.5	.795	
299	-32.7	.118		406	± 1.5	.795	
301	-32	.124		410	± 2.5	.832	
302	-30.5	.136		416	± 3.0	.852	
304	-29.5	.143		424	± 3.5	.875	
306	-27.7	.156		428	± 3.5	.875	
308	-26	.171		432	± 4.0	.900	
311	-24.5	.190		436	± 4.0	.900	

Table XV. (cont.)

Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp. °F
439	+ 5.5	.966	
447	+ 5.0	.938	
452	+ 4.5	.918	39.5
456	+ 6.0	1.00	
<u>Feed</u>			
0	+ 6.5		
6	+ 6.5		
9	+ 5.5		
11	+ 6		
22	+ 6		
25	+ 5.2		
30	+ 5.5		
31	+ 6		

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
72	29.21	.8	.2
		.8	.1

Table XVI Run No. 2

Description of Run: Bed diameter = 1.03"
 Length of bed = 3"
 Granule Mesh = 10-12 new
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1332 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H_0	Dehumidi- fier Temp °F	Time min.	Frost Point °F	H/H_0	Dehumidi- fier Temp °F
<u>Feed</u>				<u>Bed</u>			
0				100			
31	+ 9.5		32	109	-73	.0062	
34	+11.			112	-73.7	.0059	
35	+10.7			124	-74	.0058	
				130	-74.2	.0057	
	<u>Bed</u>			139	-74	.0058	
				148	-74.5	.0055	
0	-77.5			153	-61.5	.015	
7	-60.5	.015		157	-60	.016	
10	-62.5	.014		164	-59	.017	32
13	-68	.0092	32	174	-59	.017	
18	-70.5	.0078		180	-54.5	.023	
24	-70.5	.0078		184	-50	.031	
31	-70	.0080		188	-50	.031	
38	-71.7	.0070		194	-45.7	.041	
44	-73.5	.0060		201	-41.5	.054	
51	-75	.0053		208	-38.5	.065	
57	-75.2	.0052		212	-38.5	.065	
63	-76	.0049		215	-37	.071	
74	-76	.0049	32	223	-34	.086	
87	-76.5	.0048	32	228	-33	.092	
96	-77	.0046		231	-32	.098	
100				234	-30	.111	
				240	-28	.123	
	<u>Feed</u>			244	-25.5	.142	
				250	-22.5	.172	
0				254	-20	.197	
4	+ 9			259	-17	.234	32
7	+ 9.5			263	-16	.246	
9	+10			266	-13	.295	
10				271	-10.5	.340	

Table XVI (cont.)

Time min.	Frost Point °F	H/H _o	Dehumidi- fier Temp. °F
274	- 9	.370	
277	- 6.5	.418	
282	- 3.5	.490	
283	- 2.5	.516	
285	- 1.5	.541	
290	+ 1	.616	
292	+ 1.5	.631	
294	+ 2.3	.656	
298	+ 4	.715	
300	+ 4.5	.730	
302	+ 5.5	.770	
305	+ 6	.795	
308	+ 7	.832	
310	+ 7.5	.852	
315	+ 8.2	.880	
317	+ 8.5	.894	
322	+ 9.2	.926	
327	+ 9.7	.951	
336	+10.2	.979	
344	+10.5	.990	
<u>Feed</u>			
0			
22	+10.7		
24	+10.7		32
28	+10.7		
35	+10.7		
40	+10.7		

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
77	29.54	.45	.1

Table XVII Run No. 3

Description of Run: Bed diameter: 1.03"
 Bed length: 2"
 Granule mesh = 20-24
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1350 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H_0	Dehumidi- fier Temp. °F	Time min.	Frost Point °F	H/H_0	Dehumidi- fier Temp. °F
<u>Feed</u>				138	-50	.031	
				141	-46.5	.039	
0				147	-41.5	.053	
67	+ 9			151	-38	.067	
71	+ 9			153	-36	.073	
75	+ 8.5		32	155	-34	.085	
79	+ 9			156	-32	.097	
82	+ 8.2			159	-29	.115	
				161	-27.5	.124	
<u>Bed</u>				164	-23.7	.155	
				167	-21	.182	
0				172	-15	.256	
5	-55	.022		175	-13	.292	
8	-53	.025		176	-11	.329	
19	-62.5	.013		179	- 8	.384	
27	-68	.0091		182	- 5.5	.435	
30	-69	.0085		183	- 4	.468	
51	-73	.0061		187	- 1.5	.535	
57	-74.2	.0056		190	+ .5	.593	
66	-75	.0052		194	+ 2.5	.653	
69	-76	.0048	32	201	+ 3.5	.687	
77	-77	.0045		205	+ 5.5	.760	
89	-77.5	.0044		216	+ 7.2	.830	
96	-78	.0042		220	+ 8.2	.870	
103	-78	.0042		223	+ 8.5	.881	
107	-75.5	.0050					
124	-66	.010		<u>Feed</u>			
128	-60	.016		0			
132	-54.7	.023		1	+10.5		
135	-52	.027		6	+11		
				7	+11		

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
70	29.73	.6	.1

Table XVIII Run No. 4

Description of Run: Bed diameter = 1.03"
 Bed length = 3"
 Granule Mesh = 4 - 5
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1350 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp. °F	Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp. °F
	<u>Feed</u>			151	-19.5	.200	
				156	-18	.219	
0	#11			167	-16.5	.236	
				174	-15	.256	
	<u>Bed</u>			183	-13	.292	
				189	-12.5	.298	
0	-			197	-11	.328	
9	-61.5	.014		203	-10	.340	
18	-62	.014		206	-10	.340	
22	-60	.016		216	-9	.364	
32	-55	.022	32	221	-7.5	.396	
41	-50	.031		225	-6.5	.414	
46	-47	.038		262	-1.5	.535	
53	-44.5	.044		267	-2.5	.510	
61	-42	.051		276	-1.7	.530	
71	-37.7	.072		281	-.5	.561	
83	-35.5	.076		285	0	.576	
88	-34	.085		307	+1.5	.624	
92	-33	.091		315	+1.5	.624	
102	-30.5	.107			<u>Feed</u>		
106	-29.5	.112					
115	-25.5	.140		0			
120	-26.5	.130		4	+11.9		
122	-26	.134		5	+11		
130	-24.5	.149	32	6	+11		
137	-21.5	.179		9	+10.7		
143	-21	.182					

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
75	29.73	.4	.1

Table XIX Run No. 5

Description of Run: Bed diameter = 1.03"
 Bed length = 4"
 Granule mesh = 20 $\bar{3}$ 24
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1320 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F	Time Min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F
<u>Feed</u>				322	-16.5	.242	
				334	-13.5	.290	
0				344	-11.5	.324	
10				352	- 9	.373	
				361	- 7	.410	32
<u>Bed</u>				370	- 5	.455	
				399	- 3	.510	
0				407	- 1.5	.547	
16				424	- .5	.575	
124			32	441	+ 1.5	.638	
150	-83.5	.0028		446	+ 2.3	.663	
172	-86	.0023		456	+ 3.5	.703	
188	-86	.0023		464	+ 4.5	.736	
238	-81	.0034		472	+ 5.5	.778	
249	-74	.0059		483	+ 7.2	.849	
256	-66	.010		500	+ 8.5	.904	
260	-59	.017		505	+ 9.2	.935	
267	-48.5	.035		519	+10	.976	
271	-43.5	.048		526	+10	.976	
278	-37.5	.070					
283	-34	.087			<u>Feed</u>		
289	-30	.112					
294	-27	.130		0			
300	-24	.155		-9	+10		
304	-22.5	.174		14	+10.2		
309	-21	.186		17	+10.5		
314	-19	.212		18	+10.5		

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
72	29.40	.8	.1

Table XX Run No. 6

Description of Run: Bed diameter = 1.03"
 Bed length = 3"
 Granule mesh = 2 - 2½
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1302 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F	Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F
<u>Bed</u>							
0				138	- 2.5	.529	
15	-71.5	.0072		176	- 1.5	.555	
33	-23.5	.163		193	- .5	.582	
40	-20	.202		202	+ .5	.615	
45	-18	.227		217	+ 1	.630	32
50	-16	.252		232	+ 2	.661	
54	-14.5	.274		256	+ 2.3	.670	
65	-12	.315		271	+ 2.8	.686	
75	-10	.352		310	+ 3.2	.700	
81	- 9	.378					
90	- 7.5	.406			<u>Feed</u>		
95	- 6.5	.428					
113	- 5	.460		0			
				1	+10.2		
				9	+10.2		

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
76	29.54	.4	.1

Table XXI Run No. 7

Description of Run: Bed diameter = 1.03"
 Bed length: 2"
 Granule mesh = 20 - 24
 Flow Rate = 7 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1320 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F	Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F
<u>Feed</u>				210	-34	.087	
0 60				216	-29.2	.116	
				224	-21	.186	
				229	-15.7	.252	
				234	-11.5	.324	
				241	- 6	.435	
<u>Bed</u>				244	- 4	.479	
0				246	- 2.5	.522	
70	-82	.0032	32	248	- 1	.560	
101	-81	.0034		259	+ 3.5	.703	
110	-80.5	.0035		266	+ 5.5	.779	
127	-82	.0032		271	+ 7.5	.860	
139	-81.5	.0033		274	+ 8	.877	32
158	-82	.0032		288	+ 9.5	.950	
166	-78.5	.0041		297	+10.2	.989	
172	-71.5	.0072		305	+10.2	.989	
176	-68.5	.0090					
179	-63	.013		<u>Feed</u>			
184	-59	.017					
188	-54	.024	32	0			
195	-47.2	.037		7	+10.5		
199	-44.5	.045		11	+10.5		
202	-41.5	.054		17	+10.5		
204	-39	.062					

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
73	29.42	.45	.1-

Table XXII Run No. 8

Description of Run: Bed diameter = 1.03"
 Bed length = 3"
 Granule mesh = 20 - 24
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1332 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F	Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F
<u>Feed</u>				240	-54	.024	
				245	-49	.034	
0				252	-41.5	.053	
119	+10		32	258	-33.5	.089	
120	+10			263	-28	.123	
				266	-24	.154	
<u>Bed</u>				270	-22	.178	
				276	-18	.222	
0				284	-13.5	.286	
11	-65.5	.011		289	-11	.333	
18	-64	.012		296	- 8.5	.397	
23	-62.5	.014		302	- 5	.450	
42	-63.5	.013		308	- 2.5	.516	
55	-70.5	.0077		314	- .5	.570	
64	-74.5	.0055	32	317	+ 1	.616	
87	-88	.0020		323	+ 2.7	.669	
97	-85	.0025		329	+ 4.5	.730	
109	-83	.0029		334	+ 5.5	.770	
126	-83	.0029		342	+ 8	.867	
148	-81	.0034		350	+ 9.7	.950	
153	-74.5	.0055		359	+10.5	1.00	
160	-71	.0074		<u>Feed</u>			
170	-71	.0074	32				
180	-70	.0080					
191	-74.5	.0055		0			
200	-75.5	.0051		4	+10.5		
222	-71	.0074		7	+10.7		
227	-65.5	.011		9	+10.7		
236	-58.5	.018					

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
74	29.62	.75	.1

Table XXIII Run No. 9

Description of Run: Bed diameter = 1.03"
 Bed length = 2"
 Granule mesh = 20 - 24
 Flow rate = 4.7 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1320 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H_0	Dehumidifier Temp °F	Time Min.	Frost Point °F	H/H_0	Dehumidi- fier Temp °F
<u>Feed</u>				325	-39.5	.061	
				331	-36	.074	
0				336	-33	.093	
115	+10.5			340	-29	.118	
120	+10			344	-26.2	.136	
				352	-21.5	.183	
<u>Bed</u>				360	-15.5	.254	32
				365	-11	.336	
0				371	- 7.5	.401	
13	-63	.013		377	- 4	.479	
24	-67	.010		386	0	.590	
55	-73.5	.0060	32	390	+ 1.5	.637	
67	-74	.0058		393	+ 2.1	.656	
98	-77.5	.0045		396	+ 2.9	.681	
112	-78.5	.0041		404	+ 4.5	.737	
142	-79.2	.0039		410	+ 6	.804	
156	-81.5	.0033		413	+ 7	.840	
189	-82	.0032		416	+ 7.5	.860	
195	-82	.0032		422	+ 9	.925	
213	-82	.0032		428	+ 9.5	.951	
265	-82	.0032		432	+10.5	1.00	
276	-72	.0068					
285	-62.5	.014			<u>Feed</u>		
289	-58.5	.018					
299	-52.5	.027		0			
306	-49	.034		7	+11		
315	-44.5	.045		10	+10.5		

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
74	29.55	.15	0

Table XXIV Run No. 10

Description of Run: Bed diameter = 1.03"
 Bed length = 3"
 Granule mesh = 20 -24
 Flow Rate = 7 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1350 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H_0	Dehumidi- fier Temp °F	Time min.	Frost Point °F	H/H_0	Dehumidi- fier Temp °F
	<u>Feed</u>			347	-48.5	.034	
				359	-44.5	.044	
0				380	-38.5	.064	
25	+10.2			391	-35	.079	
29	+10.7			394	-32	.097	
				399	-25.5	.140	
	<u>Bed</u>			402	-21.5	.179	
				405	-16.5	.236	
0				407	-13	.292	
11	-64	.012		410	- 9.5	.354	
34	-73	.0061		412	- 6.5	.414	
54	-77	.0046		413	- 4.5	.456	
80	-79	.0039		415	- 2.5	.511	
109	-81	.0033		417	- .5	.562	
133	-81.5	.0032		420	+ 1.5	.624	
149	-82	.0031	32	427	+ 4	.706	
174	-82	.0031		430	+ 5.5	.760	
199	-83	.0029		439	+ 8	.856	
210	-83	.0029		449	+10	.955	
228	-83	.0029					
244	-80.5	.0035			<u>Feed</u>		
255	-78.5	.0040					
270	-78.5	.0040		0			
276	-77	.0046		5	+11		
322	-75.5	.0050		7	+11		
337	-59.5	.016		9	+11		32
342	-55	.022					

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
72	29.66	.55	.025

Table XXV Run No. 11

Description of Run: Bed diameter = 1.03"
 Bed length = 4"
 Granule mesh = 20 - 24
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1320 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H_0	Dehumidi- fier Temp °F	Time min.	Frost Point °F	H/H_0	Dehumidi- fier Temp °F
	<u>Beed</u>			325	-47	.039	
				328	-42.5	.051	
0				331	-38.5	.065	
25	+10.5			333	-35.5	.078	
				337	-30	.112	
	<u>Bed</u>			342	-24	.155	
				346	-21.5	.183	
0				349	-18.5	.218	
24	-73.5	.0060		352	-17	.236	
41	-75	.0053		356	-14	.280	
99	-84	.0027		360	-11.5	.324	
145	-84	.0027		374	- 6.5	.423	
203	-88	.0019		380	- 4	.479	
223	-88	.0019		387	- 1.5	.546	
230	-88	.0019	32	391	- .5	.575	
250	-88.5	.0019		399	+ 1	.623	
262	-89	.0019		403	+ 2	.653	
287	-74	.0058		413	+ 3	.684	
295	-63.5	.013		420	+ 4.5	.736	
299	-62.5	.014		438	+ 6	.805	
311	-56	.021		450	+ 7	.842	
319	-52.5	.027					

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
77	29.43	1.4	.1

Table XXVI Run No. 12

Description of Run: Bed length = 4"
 Bed diameter = 1.03"
 Granule mesh = 20 - 24
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 29 psig
 H₂O = undetermined

Time min.	Frost Point °F	H/H ₂ O	Dehumidi- fier Temp °F
<u>Feed</u>			
0			
13	+10.5		
17	+10.5		
18	+10		
<u>Bed</u>			
0			
6	-47		
13	-52.5		
22	-57		
29	-59		
45	-61.5		
57	-62		
73	-62.5		
86	-61.5		
94	-60		
101	-58		
108	-52		
118	-47		32
140	-33		
152	-32.5		
172	-33.5		
197	-33.5		
235	-33		
250	-31		
256	-25		
267	-25.5		
275	-25		

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
78	28.94	1.05	.05

Table XXVII Run No. 13

Description of Run: Bed diameter = 1.03"
 Bed length = 3"
 Granule mesh = 20 - 24
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1320 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F	Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F
	<u>Feed</u>			258	-41.5	.054	
				266	-39.5	.061	
0	+8			280	-38.5	.065	
				295	-38	.068	
	<u>Bed</u>			303	-29	.118	
				310	-18.5	.217	
0				314	-12.5	.304	
3	-74	.0058		320	- 5.5	.445	
5	-75.5	.0051		324	- 1.5	.547	
11	-77.5	.0045		330	+ 2	.653	
142	-86.5	.0022		334	+ 3.5	.703	
151	-86.5	.0022		338	+ 6	.804	
165	-86.5	.0022		344	+ 7.5	.860	
172	-85	.0025		354	+ 8.5	.900	
217	-80	.0037		262	+ 9.5	.955	
224	-75.5	.0052		376	+10.0	.977	
230	-64	.012					
234	-58.5	.018			<u>Feed</u>		
240	-50	.032					
245	-45.5	.042		0	+10.2		
253	-43	.049		2	+10.5		
				3	+10.5		

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
72	29.5	.7	.05

Table XXVIII Run No. 14

Description of Run: Bed diameter = 1.03"
 Bed length = 3"
 Granule mesh = 20 - 24
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1320 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F	Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F
	<u>Feed</u>			239	-53.5	.025	
				245	-47	.039	
0	+10.5			252	-36.5	.073	
2	+10.5			258	-33	.093	
				266	-27	.130	
	<u>Bed</u>			273	-22.5	.174	
				281	-18	.224	
0				293	-11.5	.324	
5	-71	.0074		299	- 7.5	.401	
25	-73.5	.0060		310	- 1.5	.547	
36	-90	.0017		320	+ 2.7	.676	
60	-90.5	.0016		330	+ 5	.754	
81	-90.7	.0016		336	+ 6.5	.822	
109	-91	.0016		340	+ 8	.876	
129	-91	.0016	32	346	+ 9	.926	
171	-90.5	.0016		354	+ 9.5	.955	
188	-90	.0017		380	+10	.977	
200	-88	.0020					
215	-79.5	.0038			<u>Feed</u>		
222	-73.5	.0060					
226	-70.5	.0078		0	+10		
235	-60.5	.015		5	+10.5		

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
66	29.22	.65	.05

Table XXIX Run No. 15

Description of Run: Bed diameter = 1.03"
 Bed length = 3"
 Granule mesh = 20 - 24
 Flow Rate = 7 ft³/hr
 Air pressure in dehumidifier = 29 psig.
 $H_0 = 1320 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H ₀	Dehumidifier Temp. °F	Time min.	Frost Point °F	H/H ₀	Dehumidifier Temp. °F
	<u>Feed</u>			358	-35.5	.078	32
				366	-33	.093	
0	+10.5			371	-31	.106	
				376	-29.5	.115	
	<u>Bed</u>			384	-25.5	.143	
				390	-22	.180	
0				394	-19	.212	
32	-77.5	.0044		397	-16.5	.242	
60	-83.5	.0028		403	-13	.298	
133	-90.5	.0016		408	-10	.348	
157	-90.5	.0016		420	- 3.5	.494	
186	-90.5	.0016		425	- 1	.560	
202	-88.5	.0019		428	0	.591	
228	-87	.0021		433	+ 2.8	.679	
243	-86.5	.0022		436	+ 4	.723	
253	-85	.0025		441	+ 5.5	.777	
277	-84	.0027		449	+ 7.5	.860	
286	-81	.0034		472	+ 9.5	.950	
300	-74.5	.0056		479	+10.00	.976	
316	-62.5	.014					
324	-56.5	.021			<u>Feed</u>		
331	-51.5	.029					
340	-46	.041		0	+10		
345	-42.5	.051		2	+10.5		
353	-38.5	.065					

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
70	29.12	.4	.05

Table XXX Run No. 16

Description of Run: Bed diameter = 1.03"
 Bed length = 3"
 Granule mesh = 10 - 12
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1320 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F	Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F
	<u>Feed</u>			258	-32.5	.096	
				264	-28.5	.121	
0	+10.2			269	-23	.168	
				274	-19	.212	
	<u>Bed</u>			278	-14	.280	
				282	-11.5	.324	
0				289	- 6.5	.423	
60	-30.5	.0016		295	- 3	.510	
71	-90.5	.0016		303	+ 1	.623	
95	<-91			314	+ 4.5	.738	
105	<-91			326	+ 6.5	.822	
141	<-91			333	+ 7.5	.860	
170	<-91			342	+ 8.5	.901	
186	-79	.0040		350	+ 8.7	.911	
192	-72.5	.0065		355	+ 9	.927	
197	-67	.010		368	+10	.976	
202	-61.5	.016		376	+10.5	1.000	
208	-57	.020					
219	-51	.030			<u>Feed</u>		
227	-47	.038					
238	-42.5	.051		0	+10.5		
246	-40	.060	32				

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
72	29.16	.4	.05

Table XXXI Run No. 17

Description of Run: Bed diameter = 1.03"
 Bed length = 9"
 Granule mesh = 20 - 24
 Flow Rate = 9.4 ft³/hr
 Air pressure in dehumidifier = 29 psig
 $H_0 = 1320 \cdot 10^{-6}$ lbs/lb (basis for H/H_0)

Time min.	Frost Point °F	H/H ₀	Dehumidifi- er Temp., °F	Time min.	Frost Point °F	H/H ₀	Dehumidi- fier Temp °F
	<u>Bed</u>			750	-35	.081	
				754	-31.5	.102	
0				763	-26	.137	
32	-70	.0081		767	-24	.155	
64	-77.5	.0045		775	-21.5	.183	
110	-82	.0032		780	-19.5	.205	32
163	-82	.0032		787	-17.5	.230	
177	-82	.0032		795	-14.5	.270	
332	-90	.0017		803	-12.5	.306	
381	-90.5	.0016		817	- 9	.374	
393	-90.5	.0016	32	830	- 7	.411	
405	-91	.0016		851	- 4.5	.466	
490	-89	.0019		859	- 3	.511	
500	-86.5	.0022		870	- .5	.575	
518	-82	.0032		877	+ 1	.623	
549	-79	.0040		885	+ 1.5	.638	
622	-73.5	.0060		899	+ 2.3	.664	
649	-73.5	.0060		935	+ 3	.684	
715	-71	.0075		965	+ 5	.754	
726	-62	.014					
728	-59	.017			<u>Feed</u>		
735	-51	.030					
741	-43	.049		0	+10.5		
745	-38.5	.065					

Pressure Drop Data:

Room Temp °F	Barometer Pressure Hg"	Inlet Pressure Hg"	Outlet Pressure Hg"
72	29.20	1.85	.05

Commentary

During the course of research reported herein a variety of problems were recognized as being worthy of additional investigation. The purpose here is simply to make note of them.

The adsorption isotherm both for increasing and decreasing humidity should be determined between 0 - 1 per cent R_h and 30 - 100% R_h . The first would show whether isotherm is continuous or not. It would also reveal other hydrates if they exist as the dynamic experiments tend to indicate. The second would add light to the nature of water adsorbed in Drierite. Other ideas have already been discussed in the thesis proper.

The adsorption wave for beds differing in length by 1/4 to 1/2" between 2" - 4" would permit plotting H vs Z to confirm the series bed concept. Beds of $Mg(ClO_4)_2$ and $Mg(ClO_4)_2 \cdot 3H_2O$ could also be run in series to study the series bed idea (See article by Amero). The concept is also susceptible to mathematical treatment based on the fact that the length of the beds are a function of time.

Beds of different diameters and large particle size would determine what the wall effect might be during the adsorption wave runs.

Running a very long bed of drierite would show whether the minimum output humidity is constant for any length of time or whether it gradually rises to the break

point.

The frost point hygrometer could be used in the procedure discussed by Wicke to actually measure the diffusion coefficient for various thicknesses of drierite. The drierite granule could be molded into lucite and ground flat on both sides.

Drierite granules could be placed over H_2SO_4 solution to saturate them just up to foot of vertical rise in isotherm. These could then be subjected to dynamic experiments to see whether one hump in the adsorption wave remains.

Further additions to the generalized theory could also be made.

During the early stages of an adsorption wave run there could be a time lag in the humidity of the air passed through the hygrometer compared to the humidity of the air just as it leaves the bed. The effect would be due to the steel wool filter and the tubing between the exhaust end of bed and inlet to hygrometer. The effect might be minimized by employing a Cottrell type precipitator or a miniature cyclone separator to protect hygrometer from dust instead of the steel wool filter. The Cottrell precipitator could be easily constructed by stringing a wire in one of the copper tube leads to hygrometer. A high voltage power pack such as that employed in television sets could be used to apply 2000 volts to

the wire. The precipitator would be made demountable so as to permit removal and flushing after each run. Plexiglass wool is notorious for low moisture absorption and might be tried instead of steel wool. The entire attempt discussed here must be considered in the light of the method of charging the beds which was discussed in the thesis proper.

Investigations of beds containing mixed particle sizes would be of interest. Likewise it would be interesting to determine the effect of different regeneration cycles mentioned in the thesis proper.

Attempts to extend the generalized theory to two other cases have been successful. The thesis was being typed at the time and the results are added here in the form of a comment. The procedure used is given in Marshall, W.R. and Pigford, R.L., "The Application of Differential Equations to Chemical Engineering Problems", 1st ed. pp. 163-170, Newark, Delaware, University of Delaware, 1947. The particular case treated in this reference is the one for mass transfer controlling.

The first new case developed by the author is the one for diffusion through the outer shell of the granule itself considered as the rate controlling process. The solid shell coefficient is K_s lbs per lb per hr. ft^2 per unit of driving potential. The surface of the granule

has the equilibrium concentration W^* and all symbols are the same as before. Internal diffusion is very rapid.

Thus

$$\frac{\partial W}{\partial t} = K_s a(W^* - W)$$

and from the bed equation (text)

$$\frac{\partial H}{\partial Z} = - \frac{1}{\alpha V} \frac{\rho_B}{\rho_G} K_s a(W^* - W)$$

If these two equations are rearranged and one sets

$$T = K_s a t$$

$$X = \frac{1}{\alpha V} \frac{\rho_B}{\rho_G} K_s a B Z$$

then the two equations may be written

$$\frac{\partial W}{\partial T} = - (W - BH)$$

$$B \frac{\partial H}{\partial X} = (W - BH)$$

If $1/B$ is m , W is x , T is τ , H is y and X is n , these two equations reduce to those solved by Marshall and Pigford and the notation is the same as that employed by the latter authors. In this form the solution to the present problem is the same as that for that of mass transfer in the gas stream. The generalized theory applies if T and X have the definitions given above in terms of t and Z and the accompanying constants.

The next new case is that discussed by Walter

and mentioned in the text. A second order chemical reaction is assumed to be controlling and the rate constants, k_b and k_f are assumed to be equal. Therefore the subscripts, b and f, may be dropped. From the work of Walter it has been deduced that

$$\frac{1}{k \rho_{GH_0}} \frac{\partial W}{\partial t} = \frac{W_0}{H_0} H - W$$

where W_0 is the capacity per unit length of the tube and all other symbols mean the same as before. From the bed equation one has that

$$\frac{\frac{W_0}{H_0}}{\frac{1}{\alpha V} \rho_B k W_0} \frac{\partial H}{\partial Z} = - \left(\frac{W_0}{H_0} H - W \right)$$

If the two equations are rearranged and one sets

$$T = k \rho_{GH_0} t$$

$$X = \frac{1}{\alpha V} \rho_B k W_0 Z$$

then

$$\frac{\partial W}{\partial T} = \frac{W_0}{H_0} H - W$$

$$\frac{W_0}{H_0} \frac{\partial H}{\partial X} = - \left(\frac{W_0}{H_0} H - W \right)$$

If H_0/W_0 is m , W is x , T is γ , H is y and X is n , then the remaining treatment is the same as for the previous case and the generalized theory again applies. The quantities T and X have the new definitions given above in terms of k , t and Z , and the other constants.