THE EQUILIBRIUM MOISTURE DISTRIBUTION BETWEEN AIR OR FREON-12 REFRIGERANT AND SELECTED COMMERCIAL DESICCANTS

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Submitted to the faculty of the Graduate School of the Oklahoma Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY May, 1954



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PREFACE

The present study of adsorption isotherms was made possible through grants from the Aluminum Company of America, the Davison Chemical Corporation, and the American Society of Refrigerating Engineers. The object of this investigation was partly to continue the work done at Louisiana State University by Gully and Tooke on the equilibrium moisture distribution between Freon-12 and desiccants and partly to determine other properties of these desiccants. The work is justified because the materials used are new and have never before been investigated.

The writer is indebted to Dr. Charles L. Nickolls and the late Dr. Luis H. Bartlett for their valuable guidance in this project. The author is particularly grateful to Mr. Eugene McCrosky for his skillful aid in constructing the equipment.

Stillwater, Oklahoma November 25, 1953

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INTRODUCTION

The presence of water is a serious hindrance in many industrial processes for reasons which are pertinent to the specific cases under consideration. It would be beyond the scope of this work to enumerate examples in which the presence of moisture is not desirable. However, when water must be eliminated, numerous methods of water removal are available to the engineer, methods which must be chosen specifically for each type application. In general, when there is little water present, the process used to decrease the moisture content is the process of adsorption which is defined as that process by which two gases, liquids, colloids or suspended materials are separated, the adsorbate or material to be separated concentrating on the surface of a solid or adsorbent. When the adsorbate is water, the adsorbent is called a desiceant.

The study of desiccants and their properties will allow the engineer to design comprehensive driers. The purpose of the present investigation is to present some data on certain desiccants, data which is not available in literature and which will help the engineer in his design.

The process of adsorption is well known. 14 The chemical and physical properties of the adsorbents can be easily found in literature together with the list of adsorbates for which they have an affinity.*

There is an abundance of literature on that subject.

The ultimate design of a drier depends on quantitative data on the drying capacity of the desiccants. This information is obtained by studying equilibrium relationships, i.e. the amount of adsorbate present at equilibrium per unit weight adsorbent or desiccant under certain conditions of temperature or pressure, equilibrium being defined as that point at which the adsorbent is saturated and cannot adsorb any more adsorbate. When the temperature is fixed, such equilibrium data is referred to as equilibrium adsorption isotherms. These isotherms must be determined with the utmost care because they represent equilibrium relationships. The data must indicate the nature of the mixture from which the adsorbate is to be removed.

The specific purpose of this investigation is the study of two new, not yet marketed desiccants, NB-14857 Silica Gel and XH-151 Activated Alumina. These materials, being similar to all other silica gels and activated aluminas, will have like properties. However, the design of a drier requires that specific data be given on their drying capacity.

Numerous mixtures could be analyzed for the drying capacity of these desiccants. The present study limits itself to the study of two mixtures: a water vapor-air mixture and a liquid water-liquid Freon-12 (dichloro-difluoro-methane) mixture. The water-air atmosphere was chosen because, among other reasons, experimental procedures are easier than with other systems and because air is cheap and in abundant supply; the other system was chosen because of the direct application which it has in refrigeration where minute quantities of water present in the liquid refrigerant cause freeze-ups, corrosion and copper plating.

This work is thus divided into two parts: a study of these desiccants in water-air atmospheres and a study in water-Freon-12 atmospheres. The air-water atmosphere study is generalized to include, as a comparison basis, already investigated desiccants, drierite, PA-100 silica gel and F-1 activated alumina. This study is time consuming and for that reason methods were investigated to determine whether or not quicker results of the same reliability could be obtained.

The F-12-water atmosphere investigation is generalized to include F-1 alumina. The other desiccants above mentioned are not investigated because reliable data is available in literature.

THEORY

EQUILIBRIUM

Equilibrium is defined as that point where no more transfer between materials can take place. In adsorption there is no further condensation of the gas on the surface of the adsorbent. It is possible to consider that the adsorbent is saturated under the specific point conditions of the experiment. Equilibrium is thus a measure of the drying capacity of a desiccant and thus a relative measure of its drying efficiency. The latter is defined as the ratio $(C_s-C)/C$ where C_s is the saturation concentration of the adsorbate on the surface of the adsorbent and C is the point concentration at equilibrium under the limited conditions of the experiment.

Equilibrium in adsorption is, however, slightly different from the above definition because, once equilibrium is reached, mass transfer occurs although all material which is adsorbed thereafter replaces in exact proportions the material which is lost simultaneously through the process of desorption. This phenomenon is a source of errors if static equilibrium is allowed to take place.

In the determination of adsorption equilibrium data the following conditions must be satisfied: 9

- (1) Equilibrium must be reached
- (2) Accurate measurements and determinations must be made to obtain the exact material balance at equilibrium
- (3) The moisture in the desiccant must be uniformly distributed
- (4) Temperature conditions must be constant

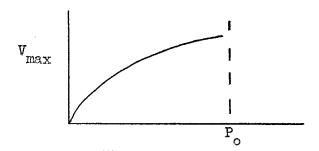
 These conditions are the basis for sound work and must be verified to prove the validity of any equilibrium data.

ADSORPTION ISOTHERMS

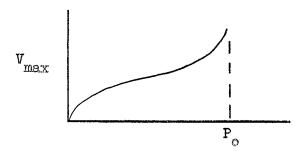
The adsorption isotherms of gases at temperatures not far removed from their dew points show definite curvatures toward the pressure axis. If the pressure is low, the isotherm is concave; if the pressure is high, the isotherm is convex. The high pressure convex portion has been attributed to condensation in the capillaries of the adsorbent or to the formation of multimolecular adsorbed layers.

There are five types of adsorption isotherms for the van der Waals type adsorption. The following are examples of each type where the maximum volume of gas adsorbed $V_{\rm max}$ is plotted versus the pressure of the gas, $P_{\rm o}$ being the saturation pressure. These examples are imaginary, and the isotherms are not real.

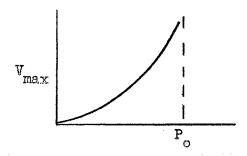
Type 1: Oxygen over charcoal at -183°



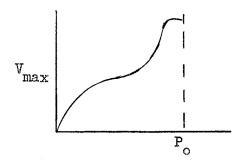
Type 2: Nitrogen over an iron catalyst at -1950



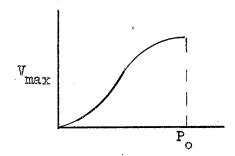
Type 3: Bromine over silica gel at 79°



Type 4: Benzene over ferric oxide gel at 50°



Type 5: Water vapor on charcoal at 100°



Langmuir interpreted the first type isotherm in his famous derivation of the isotherm equation for unimolecular layers. Brunaner, Emmet and Teller derived an isotherm equation for multimolecular layers that includes both the Langmuir isotherm and the S-shaped isotherm as special cases. Brunaner, Deming, Deming and Teller derived equations to cover cases III, IV and V. It is important to note that case III is also covered by the multimolecular isotherm equation when the forces between adsorbent and adsorbate are small.

As the present determination deals mostly with S-shaped curves it is necessary to study the equations for multimolecular layers of gases. The equations which are developed include:

(a)
$$\frac{P}{V(P_O - p)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \cdot \frac{P}{P_O}$$

(b)
$$V = \frac{V_m C x}{1-x} \cdot \frac{1-(n+1) x^n + n x^{n+1}}{1+(C-1) x-C x^{n+1}}$$

(e)
$$V = \frac{V_m C x}{1-x} \cdot \frac{D+(b-D)(2 x-x^2)}{1+(C-1)x+(b-1)C x}$$

where p is the pressure, p_0 is the saturation pressure of the gas, V is the total volume adsorbed, V_m is the volume of gas adsorbed when the entire adsorbent surface is completely covered with a complete unimolecular layer, C is a constant, x is equal to (p/g) $e^{E_1/RT}$, g is a constant, E₁ is the heat of liquefaction, R is the gas constant, T the absolute temperature, n is the number of molecules indicating the thickness of the adsorbed layer, D is equal to V_m/V_m , V_m is the total volume adsorbed in layers other than the first, b is equal to $d^{(E_1-E_1)RT}$ and E_b is the heat of adsorption of the second layer.

Equation (a) is convenient. A plot of $p/V(p_0-p)$ versus p/p_0 yields a straight line of intercept $1/V_mC$ and of slope $(C-1)/V_mC$. Thus V_m and C can be evaluated. C is approximately $e^{(E_a-E_1)/RT}$ where E_a is the heat of adsorption for the first layer.

If the thickness of the adsorbed layer cannot exceed n, equation (b) applies. When n = 1, the equation reduces to Langmuir's equation. When n is infinity, it reduces to equation (a).

At high pressures, the plot of (a) will be erroneous and equation (b) must be used. The value of n determined for this equation may vary for various values of p/p_0 . In that case, an average value is used. For S-shaped isotherms, the values of n range from 2 to 9 depending upon the nature of the substance used.

Since C is approximately equal to $e^{(E_a-E_1)/RT}$, and E_a-E_1 changes slightly with temperature, C may be calculated for any temperature if the value of E_a-E_1 at any other temperature is known. One may assume that V_m changes with temperature as the 2/3rd. power of the density d of the liquefied gas. The value of n varies as d.

Equation (c) describes the type I isotherm. Equations (a) and (b) describe a type II isotherm when the attractive forces between adsorbate and adsorbent are greater than the forces between the molecules of the gas in the liquefied state.

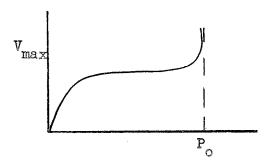
This multimolecular layer theory is considered superior to the capillary condensation theory because it includes unimolecular adsorption,
multimolecular adsorption on free surfaces and the adsorption taking place
in capillaries.

This adsorption theory is extended to the case in which the gases are under such pressure that they are in the liquid state.

CHEMISORPTION EQUILIBRIUM ISOTHERMS

Drierite (Anhydrous calcium sulfate) adsorbs water by the process of chemisorption. The anhydrous material adsorbs water until the hydrate is formed and the process is similar to a chemical reaction. The low adsorptive capacity of such a material is due to the fact that, once the hydrates have been formed, there is no longer any need for water

adsorption. In the hydrate-forming portion of the isotherm there is very little difference in the absolute moisture content of the mixture to be dried. The moisture content of the mixture changes appreciably only when there is a mixture of anhydrous and hemi-hydrate materials. Such isotherms have the following shape:



HYSTERESIS

Theoretically, adsorption-desorption isotherms should coincide although in practice they do not. Such a phenomenon is called hysteresis and has been explained through three proposed theories: the incomplete wetting theory, the ink bottle theory and the open-pore theory.

Anderson and van Bemmelen assumed that the vapor pressure of a liquid filling a capaillary tube is greater than that of the liquid being emptied since incomplete wetting tends to lessen the curvature of the meniscus of the liquid in the capillary and since the curvature of the meniscus is proportional to the vapor pressure of the liquid.

Kraemer¹² and McBain¹⁵ suggested that cavities with constricted necks are responsible for hysteresis. During adsorption the vapor pressure in these ink-bottle cavities is due to the condensation of the liquid in the large diameter portion of the cavity while during desorption, condensation occurs in the narrow neck of the cavity.

In the open-pore theory hystersis is attributed to a delay in the formation of the meniscus during adsorption. Cohan⁵ points out that gel structure consists predominantly of pores and clefts which widen toward their bases and behave as though open.

It is suggested by many authors that hysteresis could be modified or destroyed by a change in the manufacturing processes of the adsorbents.

PROPERTIES OF SOME ADSORBENTS

(a) Activated Alumina

Activated alumina is a highly porous adsorbent made by the thermal processing of certain forms of alumina hydrate (Al₂O₃ . XH₂O). The use of temperature, atmosphere, and various durations of heating on the surface areas of various forms of alpha alumina and beta alumina trihydrates, and alpha and beta alumina monohydrates will produce high adsorptive area alumina. The nature of the process used will determine the properties of the material, in particular the activation process.

There are numerous grades of activated alumina. Grade F-1, most widely used as a desiccant, has the following typical composition: Al_2O_3 , 92%; H_2O , 7%; Na_2O , less than 0.8%; SiO_2 and Fe_2O_3 , less than 0.1% each; and TiO_2 , less than 0.02%. Other properties are summarized by Mantell, Table 25, p. 91 of his text on adsorption. 14

XH-151 activated alumina is a new material. For this reason, no data can be furnished on it which would parallel the information on F-1 activated alumina.

(b) Silical Gel

Silica gel is an adsorbent prepared from the coagulation of a colloidal solution of silicic acid. The term gel merely indicates the

state of the material at one stage of its manufacture. The material may be represented symbolically as SiO2.

PA-100 silica gel is the grade of silica gel mostly used as a desiccant. Similar gels have properties summarized by Mantell in Table 46, p. 176 of his text on adsorption. 14 The composition of silica gel is generally indicated by a 99.5 + per cent SiO₂.

NB-14857 silica gel is a new material. No data can be given on this type gel.

It is interesting to report that the average diameter of the pores of silica gel is estimated as 4×10^{-7} cm., roughly ten times the diameter of the average molecule; these pores comprise approximately 50% of the total volume. The total interior area is about one acre per cubic inch. 11

PRECISION ESTIMATES

A high degree of precision is required in experiments which involve the determination of very small quantities. Precision can be improved by improving the precision of the measuring instruments, by refining the techniques and by replication of the experiments.

Statisticians have developed an equation which indicates the probable number of values occurring within definite limits for a certain number of observations. They have called such a measure of precision the STANDARD DEVIATION. 17

The standard deviation of the individual values from the average of values is defined by the equation

(c)
$$\sigma_{(x)} = \sqrt{\frac{\sum_{1 \text{ to } n} (x - \overline{x})^2}{n}}$$

where $\sigma(x)$ is the standard deviation of the average value from the average, x is the individual value, \overline{x} is the average value and n is the number of determinations. Such estimates of σ increase in precision with an increase in the number of determinations.

The probability theory states that 68.2 per cent of all observations will fall within plus or minus one σ of the average, 95.4 per cent within plus or minus two σ and 99.7 per cent within plus or minus three σ of the average.

The improvement of precision by replication is given by the formula:

$$(d) \qquad \mathcal{O}(\overline{x}) = \mathcal{O}(x)/\sqrt{n}$$

where $\mathcal{C}(\bar{x})$ is the standard error of the average of n observations from the correct value.

When experimental results are presented, a good estimate of the overall precision may be obtained by averaging a large number of separate estimates of standard deviations. Such an average is called VARIANCE by statisticians and is defined as

(e)
$$\sqrt{\frac{n_1 \sigma_1^2 + n_2 \sigma_2^2 + n_3 \sigma_3^2 + \dots }{n_1 + n_2 + n_3 + \dots }}$$

where σ_1^2 , σ_2^2 , etc. are estimates of variance based on a small group of variations and n_1 , n_2 , etc. are the degrees of freedom upon which σ_1^2 , σ_2^2 , etc. are based.

If two sources of error are present, the resultant error can be calculated by estimating the total variance as:

(f)
$$G_T^2 = G_{\overline{x}}^2 + G_{\overline{y}}^2 \frac{dx}{dy}$$

where $\binom{2}{T}$ is the variance resulting from both sources, \overline{x} is the standard error of one source, \overline{y} is the standard error of the other source, and dx/dy is taken from a plot of \overline{x} versus \overline{y} . By this method the data may be taken as being subject to errors only in x, y being known exactly.

If x and y are the only sources of error the 99.7 per cent confidence limit on the points of the determination are then

(g)
$$x \pm 3\sqrt{\sigma_T^2}$$

Whenever one set of data, y, has errors which can be neglected when compared to the magnitude of the errors of other sets of data, x, k, z, . . . to which y is related, a test of significance can be applied to correlate the x, k, and z sets to a common basis. If y has true values and known relations to the sets x, y, and z, then a T test of significance can be made

(h)
$$t = \frac{X - E}{6/\sqrt{n}}$$

where t is the significance of the data or of the way in which it is correlated. That value must be compared to the values given in statistical tables for predetermined probability limits. In (h), \bar{x} is the average value of the determinations, E the true value, and n the number of determinations.

However, when the y set of data does not have true values, an F test of significance is used and the significance is given by comparing

the result of the calculated F to the probable value of F given in statistical tables for predetermined probability limits. The calculation of F is made as follows:

Let $x_{1,2,3}$, $k_{1,2,3}$, and $z_{1,2,3}$ be three sets of determinations which correspond to the same conditions for one point of the y set of data. Calculate $3 \overline{x} = x_1 + x_2 + x_3$, and similarly $3 \overline{k}$ and $3 \overline{z}$. Then calculate a correction factor C. F. equal to $(3 \overline{x} + 3 \overline{k} = 3 \overline{z})$, and the quantity T equal to the sum of the squares of each individual determination x, k and z minus C. F. The next quantity to be calculated is B which is equal to $(1/3)(3 \overline{x} + 3 \overline{k} + 3 \overline{z})^2$. The quantity W is then evaluated by subtracting B from T.

It is then possible to determine F by constructing the following table where n is the number of degrees of freedom, originally 2 as we have three determinations per set:

Variation	n	S.S.		F.
В	2	В		(B/2)/(W/6)
M	6	M	W/6	
T	8	T		

EQUILIBRIUM ADSORPTION ISOTHERMS AT ROOM TEMPERATURE (AIR-WATER VAPOR SYSTEM)

EQUILIBRIUM ADSORPTION ISOTHERMS AT ROOM TEMPERATURE (AIR - WATER VAPOR SYSTEMS)

This phase of the investigation was concerned with the equilibrium moisture content of activated alumina, silica gel and drierite in air atmospheres of various humidities and at constant temperature.

The temperature investigated was 28.5°C, since it is an average room temperature and since it was the average between temperature variations during the experiment. It is necessary to point out at this time that temperature variations do not affect the final results as the variable is the relative humidity of the air atmosphere and the latter does not change appreciably when the temperature varies from 24 to 35°C. The maximum per cent error thus introduced would be 3% which is well within the allowable experimental error range.

The materials used were alumina, silica gel, and drierite. The drierite was obtained from the W. A. Hammond Drierite Company and was ordinary drierite, commercial grade. The silica gel studied was furnished by the Davison Chemical Corp. There were several grades of gels; PA-100 special sample No. 3537, PA-100 special sample No. 3751, PA-100 commercial grade and special sample NB-14857. The Aluminum Company of America provided the activated alumina and sent two types; F-1 alumina of commercial grade, and XH-151 alumina, a special sample.

In the work undertaken these materials were not reactivated. Their initial moisture content was therefore slightly higher than that of the freshly activated materials, and for that reason Table 1 is given which will supply the initial moisture content of the samples as received

from the shippers. This will explain the fact that desorption is observed for atmospheres of very low relative humidities. If the material had been freshly activated and desorption has occurred, then there would have been a discrepancy.

The actual experimental procedure was divided in two parts, a static investigation and a dynamic investigation. The reason behind such an action was to determine if there is a possibility to assemble data faster than by the conventional methods.

Static methods are accurate and slow; dynamic methods are quick but their accuracy has yet to be ascertained. It was thus decided to investigate the materials thoroughly by a static method and then devise dynamic methods in order to obtain the same results with less time consumption.

STATIC METHOD

A survey of literature shows that all static methods are based on the same principle, i.e., to put a sample of the material to be analyzed in a closed container where a definite humidity is maintained and weigh it periodically until constant weight is obtained.

The following procedure was thus adopted: constant humidity solutions were prepared by mixing sulfuric acid and water in the proportions given by the International Critical Tables. A check was made to verify that a 10°C range in temperature would not affect the overall relative humidities of these solutions so that the original assumption of constant temperature was verified. Sulfuric acid was chosen because it has a very small partial pressure of SO₃ over the solution and thus it can be assumed that the partial pressure in the constant humidity container is

entirely due to water vapor effects. The constant humidity containers were large desiccators provided with a stirring arrangement so that stratification of the acid solution was prevented by periodical stirring. The size of the desiccator is important only in the sense that the more samples in it the more water vapor is taken out of its atmosphere and the greater the change in relative humidity. If the desiccator is large enough, as was the actual case, such a problem is of minor importance and the ensuing error can be neglected. Once the sulfuric acid solutions were made by gravimetric mixing, they were checked for their exact water concentration by titration, and then they were placed in the prepared desiccators. The solutions were again titrated after the experiment to determine whether the water concentration of the solutions had varied during the determinations. The maximum deviation encountered between the initial and final concentrations in the desiccators was found to yield a difference of only 1/2% Relative Humidity, and this only in the case of very low humidities.

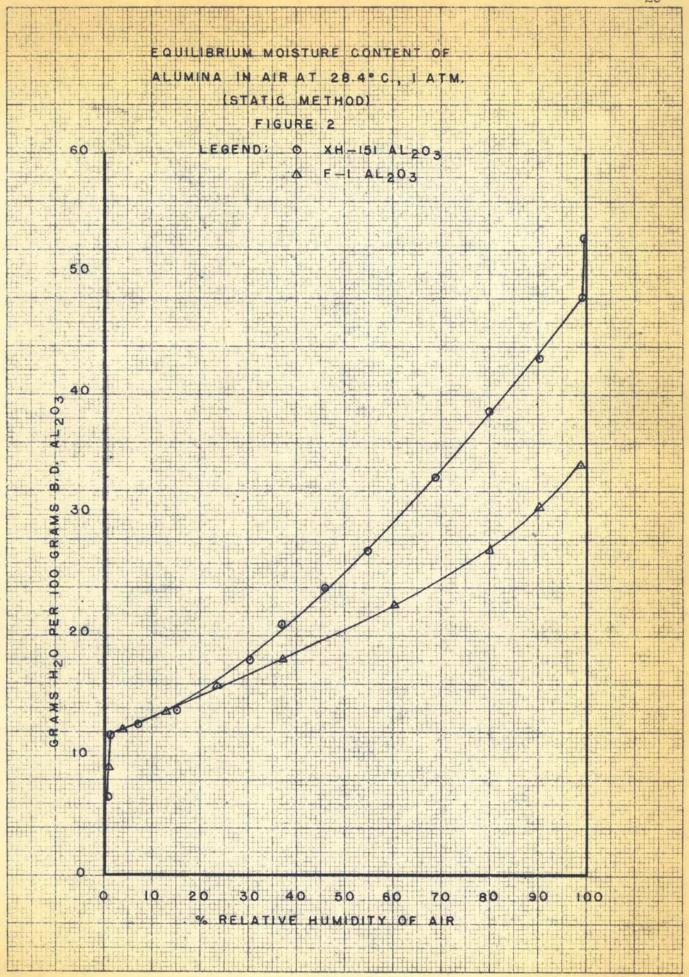
Four samples of the material to be investigated were prepared as follows: four glass stoppered weighing bottles were tared and approximately 10 grams of the material were put into each of them as quickly as possible; then the bottles were quickly stoppered. Four porcelain crucibles were tared after they had been dried in an oven at 450°C for 4 hours and allowed to cool in a vacuum desiccator. Each was filled with the material from a weighing bottle and the exact weight of the sample was determined by difference in the weights of the bottle before and after it was filled. This procedure eliminates serious errors due to the speed with which desiccants will adsorb water vapor from the room atmosphere.

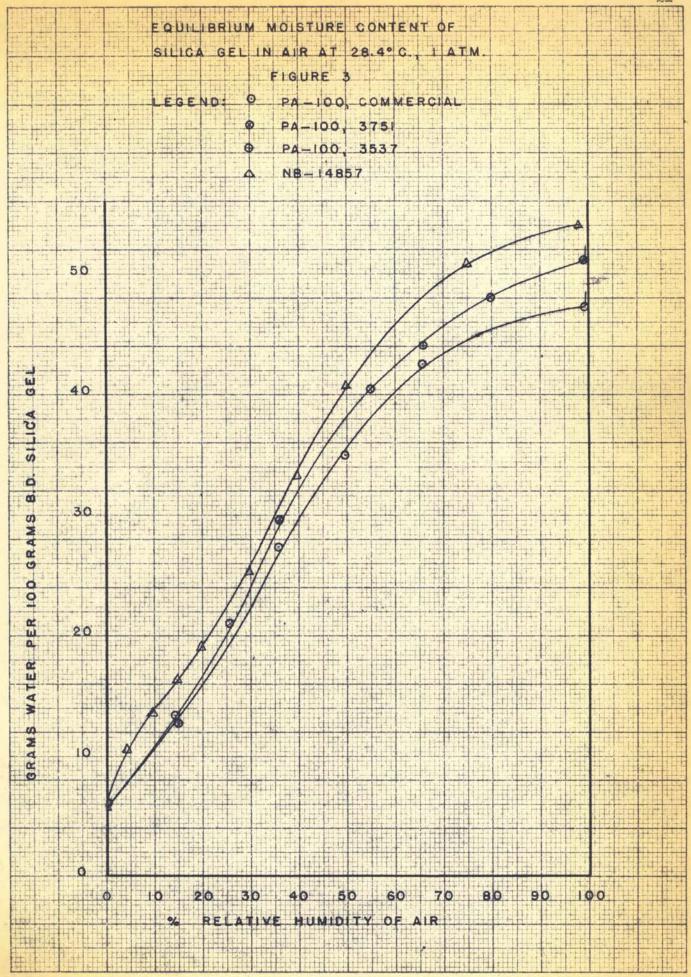
One of the crucibles was used as a humidity control. It was placed in an electric furnace operating at $1800^{\circ}F$ for one hour; at that time it was removed from the oven and placed in a vacuum desiccator where it was allowed to cool to room temperature and was then weighed. The difference between the weights before and after ignition indicated the amount of water originally in the sample. The heating conditions used drive all water off the sample; therefore, the sample is moisture-free after that operation. The term, bone dry (B.D.), is used to indicate that a sample is water-free. The data so obtained allowed the investigator to calculate the bone dry weight of the three other samples.

The three remaining samples were placed in the same desiccator and periodically removed and weighed until constant weight was attained.

The difference between bone dry and final weights allowed the computation of the exact water content of the sample after it had reached its equilibrium moisture content. Three samples were used so that a check could be obtained as to the accuracy of the results. If the three samples did not agree within 3%, the results were discarded and the determination rerun. The time required for the samples to reach equilibrium varied from five to seven weeks.

The results were calculated on a bone dry basis and reported as grams of water present at equilibrium per 100 grams of bone dry desiccant. Tables 2, 4, 6, and 7 give the calculated results for the materials investigated and Figures 1, 2 and 3 show plots of these results. Table 3, 5 and 8 show the standard error on the determinations and are used as a basis of discussion for the accuracy of the determinations.





REASONS FOR REPORTING THE RESULTS ON A BONE DRY BASIS

Some authors have objected to the drying of the desiccants at 1750° F for 1 hr. on the basis that such a procedure destroys the physical properties of the desiccant. This is true, but, on the other hand, no other method seems to yield reproducible results. Two methods were suggested and experiments were conducted to determine whether it would be advisable to use such a drying procedure.

The first method suggested drying the desiccant at 350°F, 1 atm., for 24 hrs. Four samples were thus prepared and each was split into two portions, one to be dried at 350°F, 1 atm., for 24 hrs., (Samples B). All data was converted to bone dry basis to have the same basis of comparison. The four samples were prepared as follows, all having been freshly activated prior to their specific treatment:

- (1) no treatment
- (2) 10 per cent water was added to the sample on the basis of its activated weight
- (3) 25 per cent water was added to the sample on the basis of its activated weight
- (4) 25 per cent water was added to the sample on the basis of its activated weight. The sample was then dried at 350°F for 24 hours and 25 per cent water was added again.

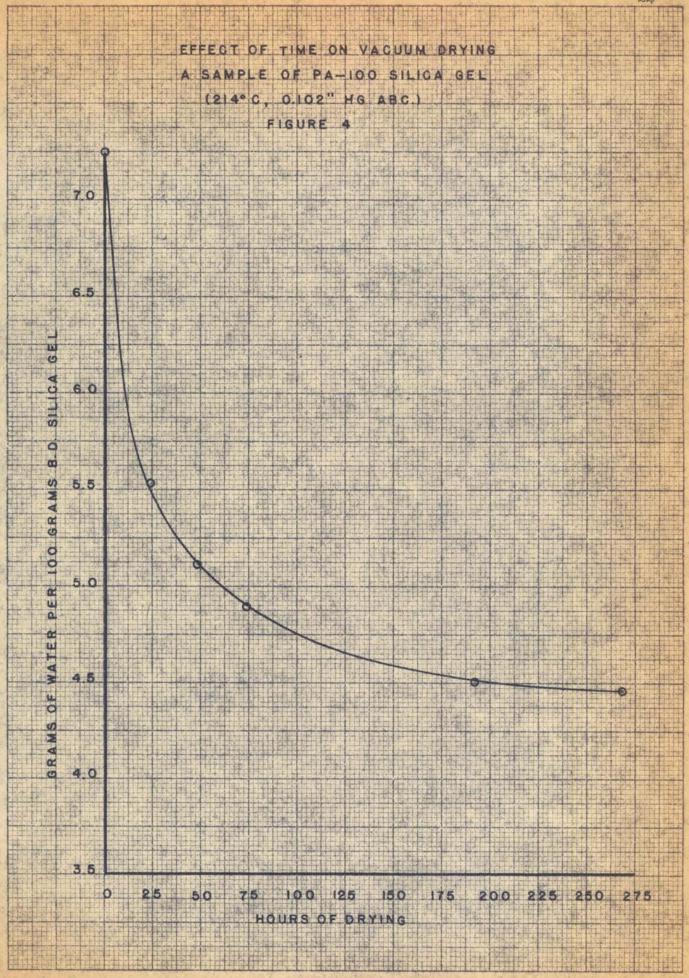
The respective samples (1) through (4) were dried by methods A and B. The results are given in Table 9. Only method B gives reproducible results.

The other suggestion was to dry the desiccant at 214°C under perfect vacuum. The following experiment was made to verify that method. A large sample of PA-100 commercial grade silica gel was put

into a copper cartridge. The initial moisture content of the sample was 7.25 grams of water per 100 grams of water-free silica gel. The cartridge was connected to a copper tube and placed in an oven. The copper tube was allowed to go through the wall of the furnace, and then it was connected to a vacuum pump. The furnace was then started and the thermostatic element adjusted for the desired temperature. At the same time the pump was started. The vacuum created was 0.102 inches of mercury, absolute. The system was allowed to operate for a definite period of time after which a sample was removed from the cartridge and analyzed for its water content. The cartridge was immediately reconnected and the operation was continued. The results are tabulated in Table 10 and are reported on a bone dry basis to facilitate comparison with previous analyses. It is readily seen that the method is time consuming and also that the sample will reach a constant weight asymptotically and thus reproducible results would be difficult to obtain by using this second suggested method.

The accuracy of the results on the previous analysis was checked by performing the same experiment with a sample of initial moisture content of 4.5 grams of water per 100 grams of bone dry silica gel. That sample required 72 hours to decrease its water content to 4.45 grams (bone dry basis). This indicates that the results of Table 10 are true as the latter point falls on the curve plotted from the given Table, (See Figure 4).

It is therefore possible to conclude that reproducible results are obtained if the desiccants are dried at 1750°F, 1 atm., for 1 hour. On the basis of that finding the results are reported on a bond dry basis because this method of drying drives all the water from the samples.



HYSTERESIS (Experimental)

Some investigators stated that silica gel was subjected to hysteresis in adsorption, i.e., that the equilibrium value obtained from the adsorption process was slightly different from the value obtained from the descrption process. Experiments were conducted to verify that statement using PA-100, special sample No. 3537, silica gel. The equilibrium values reached through adsorption were taken from Table 6 and are termed "equilibrium reached from below". The equilibrium values obtained from descrption are termed "equilibrium reached from above" and were obtained as follows: a sample of gel was wetted well above its equilibrium value by allowing it to adsorb water from a 100% relative humidity atmosphere and then it was analyzed as previously indicated in the static method. The results are given in Table 11. The results are the average of sets of three determinations per point and are plotted on Figure 5. The graph seems to indicate the presence of hysteresis.

DYNAMIC METHODS

The previous section of this chapter indicates the results and the method used for static determinations.

It is now possible to discuss some dynamic methods which were devised in order to eliminate the large time consumption of static methods. Two methods were investigated and the results were checked with the results given in Tables 4 and 7.

In method A, Figure 6, air was pulled through a train of washing bottles which gave it the desired humidifying conditions. The humid air was then passed through a tared Nesbitt bulb charged with the sample to be tested, PA-100 commercial grade silica gel and F-1 alumina, respec-

tively. Once the bulb had reached a constant weight, the experiment was stopped and the results calculated after the sample was ignited to obtain its bone dry weight.

A drying bottle was inserted at the beginning of the flow circuit to allow the air to be partially dried before entering the washing bottles. If higher humidities were required the drying bottle was charged with wetted adsorbent so that the air would approach the desired humidity before being stabilized by the washing bottles. The presence of this drying bottle increases the accuracy of the results.

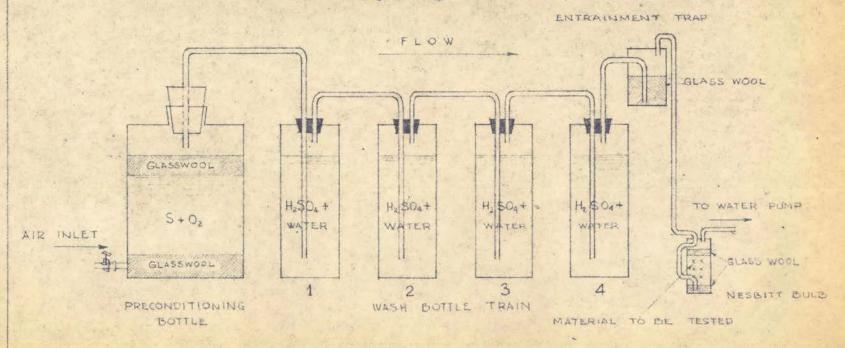
Four washing bottles were used in series and the sulfuric acid-water solutions in each washing bottle was the same. Determinations were made with 1, 2, 3 and 4 bottles, respectively, to see if the last bottle of the train would retain its specific gravity during the experiment. Four bottles were the minimum number which would allow constancy of the solution in the last bottle. The respective concentrations of the first and of the second bottle varied with the length of the run, but the extent of that variation was a direct function of the efficiency of the drying bottle. Bottle 3 gave the desired humidity condition and bottle 4 served as a stabilizer.

Air was pulled through the system by means of a water type vacuum pump. The pull was controlled by inserting a small capillary tube in the line between the Nesbitt bulb and the pump. The length of the capillary gave the exact pull conditions. The rate was stabilized at 4 liters per hour. It was found that higher rates would require a larger washing bottle train which is considered impractical.

The time required for equilibrium was from 4 to 6 days for each sample. Experiments were run on PA-100 silica gel and F-1 alumina and

DYNAMIC METHOD A FOR EQUILIBRIUM DETERMINATIONS

FIGURE NO 6



the results obtained are tabulated in Table 12 for an average of 5 days per determination.

These results check with the results of Tables 4 and 7 and the method A was thus deemed to be satisfactory. The time consumption was judged to be too large, and, for this reason, method B was investigated.

In method B, Figure 7, the time consumption was greatly decreased. The samples reached equilibrium in periods ranging from 12 to 50 hours, at least the samples which would represent practical humidity conditions for industrial application.

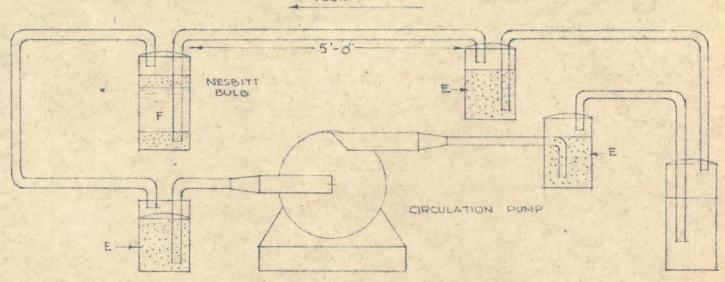
The main difference between methods B and A, is that the flow of air is a closed system instead of an open system. A vacuum-pressure type pump was used as a circulation medium of rate 3.48 liters per minute at standard conditions. The only matter requiring attention was the effect of the vapor pressure of the oil. However, as the oil used was a Hyvac low pressure type oil, its vapor pressure could be neglected for accuracies well within the range of experimental errors. In order to eliminate temperature variations due to the heating of the pump after it had run for several hours, copper tubing was coiled and placed in water baths, and the exit air from the pump was passed through that coil before it was admitted in the system at bulb E of Figure 7. This controlled the temperature within plus or minus 1°F.

Once the Nesbitt bulb had reached equilibrium its weight was constant and results were calculated.

In both methods, readings were taken every hour after the first 5 hours. In method B the same samples were tested as in method A and the results are tabulated in Table 12. These results averaged 32 hours of running time. All given results have been corrected for oil vapor

DYNAMIC METHOD B FOR EQUILIBRIUM DETERMINATION

FIGURE NO 7



E. ENTRAINMENT TRAP FILLED WITH GLASS WOOL

F. SAMPLE TO BE ANALYZED

HUMIDEFYING BOTTLE.

pressure, but in any case, the non-corrected results were within plus or minus 2.5% of the corrected ones.

Once again the results check favorably with Tables 4 and 7 and the method was deemed satisfactory. Method B is thus recommended for this type investigation. It has the advantage that quick checks can be made in case of errors, and that it can be used in the investigation of equilibrium moisture content of desiccants in various atmospheres provided the proper pump lubricant is used.

The equilibrium moisture content of NB-14857 silica gel was evaluated by this method although the results are give in Table 7. Table 13 is a specific table of results for that determination because it shows the time study on this type experiment. The determination was made by using the same sample all the way through so that no time would be lost. The points marked with stars indicate samples for which the results were checked by the static method. The time function is indicated on Figure 8. The relation indicated on that graph is that the time required to reach equilibrium is practically a linear function of the percent relative humidity of the atmosphere in which the sample is placed.

It is thus possible to conclude that method B has very definite advantages over method A and over static methods. Such a method is strongly recommended for practical investigations as the maximum time consumption for average humidity samples would be about 40 hours, compared to 4 days by method A, and 5 to 7 weeks by the static method. The accuracy is excellent and the maximum deviation from the results obtained by the static method is of the order of 2.27% which is well within the accepted range for experimental errors.

PROOF THAT EQUILIBRIUM IS REACHED

The methods used, both static and dynamic, are based on the fact that, at equilibrium, the weight of the sample stabilizes itself and thus remains constant. Because of several sources of error which are inherent in such type determinations, great care was taken to ascertain that the readings indicated a constant weight. First, the stability of the equilibrium reached was studied, second, corrections due to atmospheric variations were considered, third, errors due to weighing were analyzed, and fourth, variations in weight while weighing were checked.

The stability of equilibrium is considered because of the possible state of pseudo-equilibrium in which an unstable balance is present. This phenomenon occurs very little in adsorption, but in order to prevent it from occurring, the samples were stirred several times after evidences of constant weight were available. This procedure always breaks any unstable equilibrium. If the weight was still the same, then it was assumed that equilibrium was reached.

Atmospheric variations will cause the containers to have a slightly different weight. This difference is not significant provided the sample is large in size. This consideration required the author to discard any data obtained from samples which were smaller than 5 grams, and to define an average weight of sample as 10 grams. Small samples have an error of 1 to 3 per cent due to atmospheric variations. In the study of constant weight attained at equilibrium, atmospheric variations cause some error because the weight of the same sample will slightly differ from day to day. It was thus considered that equilibrium is reached if the variation in weight within several weighings averaged to plus or minus 0.05 per cent. This consideration is of great importance for static deter-

minations because of the length of the runs. In static determinations, such a study can be neglected because it is rare that atmospheric variations are great within a few hours; however, if the time required for equilibrium was larger than 12 hours, it would be erroneous to neglect the above mentioned phenomenon.

Errors due to weighing and errors due to the change of weight of the sample while it is weighed are the largest ones. The latter can be prevented by using tared stoppered crucibles so that no change in weight occurs while weighing. This error is more common in the case of static determinations than for dynamic determinations. For the latter, errors are due to the fact that during the transfer of the Nesbitt bulb to the scale or during the determination the blub will collect dust. It is thus necessary to provide means to keep the bottles in moisture free containers and to transfer them to the scale with greater care. Gloves should be used for that last operation because body moisture could be deposited on the walls of the bulb which would cause erroneous weighings. The last type of error is due to the analytical balance itself. It can be eliminated by weighing each sample twice with one balance and then once with another balance. The results of the three weighings are then averaged and if all weights thus obtained are constant, it is reasonable to believe that equilibrium is reached.

ACCURACY OF THE MEASUREMENTS

Preliminary estimates of the accuracy for desiccant moisture determinations was made by Gully and Tooke. They found a standard deviation of 0.05 per cent moisture and determined that determinations were to be replicated to improve accuracy. To that effect it was decided that

all determinations of this type should be triplicated; thus eliminating the possibility of errors due to inhomogeneity of some desiccants.

Table XIV indicates the study on deviations from the average for a single determination. It also indicates that the accuracy decreases with the moisture content of the desiccant. However, the average deviation for all desiccants for a single determination was calculated as 0.0887 grams of water per 100 grams of bone dry desiccant. In view of the fact that the minimum moisture encountered was 4.45, it follows that 0.089 is negligible when compared to the moisture content of the desiccant. No further study of the errors involved is thus required. It is however necessary to state that a 99.7 per cent probability that all points will have the determined moisture contents given in the results requires that the results be within plus or minus 0.089 grams per 100 grams bone dry desiccant of the experimental data.

Tables III, V, and VIII show the calculated error on the average. This data was averaged for all the desiccants together, and each average given in the results was found to be within plus or minus 0.04 grams of water per 100 grams of bone dry desiccant. The average will thus be $\overline{x} \pm 3(0.04)$ or within plus or minus 0.12 grams of water per 100 grams of bone dry desiccant from the true value for a 99.7 per cent confidence limit.

The accuracy of reporting the results on a bone dry basis was calculated from the given data. The average determination has a standard deviation of 0.02 grams water per 100 grams bone dry desiccant and 0.08 for a 99.7 per cent confidence limit.

This allows the author to conclude that the data is accurate. However, there is another phase to the discussion of the accuracy of the data and that is the accuracy of the sulfuric acid solutions. Very little work was done to determine the exact degree of the error involved because of the way in which the data is reported.

The data is reported as per cent relative humidity of the atmosphere. This ratio varies very little with small errors in making the solution of with errors resulting from the fact that some moisture was removed from the solution by the desiccant. Such errors were calculated roughly as 0.5 per cent of the given value. In view of the shape of the isotherms, errors of such magnitude are negligible. The error in making the solution was eliminated by making a solution and titrating it twice. The average calculated per cent was taken as the data from which the relative humidity was calculated. Calculating errors were eliminated by making all calculation by logarithms.

Further calculations of accuracy on that phase of the experimental data are not justified by the equipment, time, and allowable error conditions for such determinations.

MOISTURE DISTRIBUTION IN THE DESICCANT AND TEMPERATURE CONDITIONS

It is necessary to determine whether the equilibrium which is obtained is thorough, i.e., that samples of the desiccant at any layer would have the same moisture content. This was verified by placing large samples (300 grams) in large containers and allowing equilibrium to be reached. Once equilibrium was reached, samples were withdrawn from the top, middle and bottom of the container and analyzed for moisture.

Three such experiments were made on NB-14857 silica gel and XH-151 activated alumina, each experiment at a different per cent relative humidity. The results are not given because they were identical for all

three layers within plus or minus 0.12 grams of water per 100 grams of bone dry desiccant from the average.

It is not necessary to repeat that experiment on all the samples analyzed and for every humidifying condition because of the relatively small size of the samples analyzed.

Temperature conditions have already been discussed for this phase of the investigation. An average of 28.4°C is given for the data with the understanding that atmospheric variations and room temperature changes were calculated to amount to that temperature for the range of 25°C. The variation of temperature would have a double effect if it were not corrected to a definite temperature: first, it would change the relative humidity of the humidifying containers, and second, it would change the absolute equilibrium of each sample. However, it was pointed out earlier that such changes have little effect on the relative humidity of the solution (provided the temperature range is well restricted).

HYSTERESIS AND DRYING METHODS

Hysteresis is very apparent in Figure 5. It is, however, thought that hysteresis is only due to the fact that it is practically impossible to obtain true equilibrium from above and below. The time conditions on any experiment are limited. In order to introduce a reasonable doubt probability on the existence of such a phenomenon, the following additional experiment was conducted: two samples of PA-100 (No. 3537) silicated which were used in the determination of Table XI were left in presence of their humidifying atmosphere. These were checked one year later and the following results were obtained:

% relative humidity:	15	55
Sample from below: (Moisture content)	13.05%	13.02%
Sample from above: (Moisture content)	41.12%	41.075%

It is therefore possible to doubt the existence of hysteresis and attribute its existence to the fact that equilibrium is reached so slowly that hysteresis seems to exist. In all practical determinations hysteresis will be present because of the time limits imposed on determinations. The above discussed factor applies mostly to static determinations. In the case of dynamic determinations it was found that Method B would not yield any hysteresis if the experiments were run for 15 to 20 days.

The same results are obtained by dynamic methods or by static methods provided enough care is exercised. Method B has been discussed previously and it seems possible to recommend it for such type determinations over any other method presented in this paper.

COMPARISON OF DESICCANTS AND SUMMARIZED CONCLUSIONS

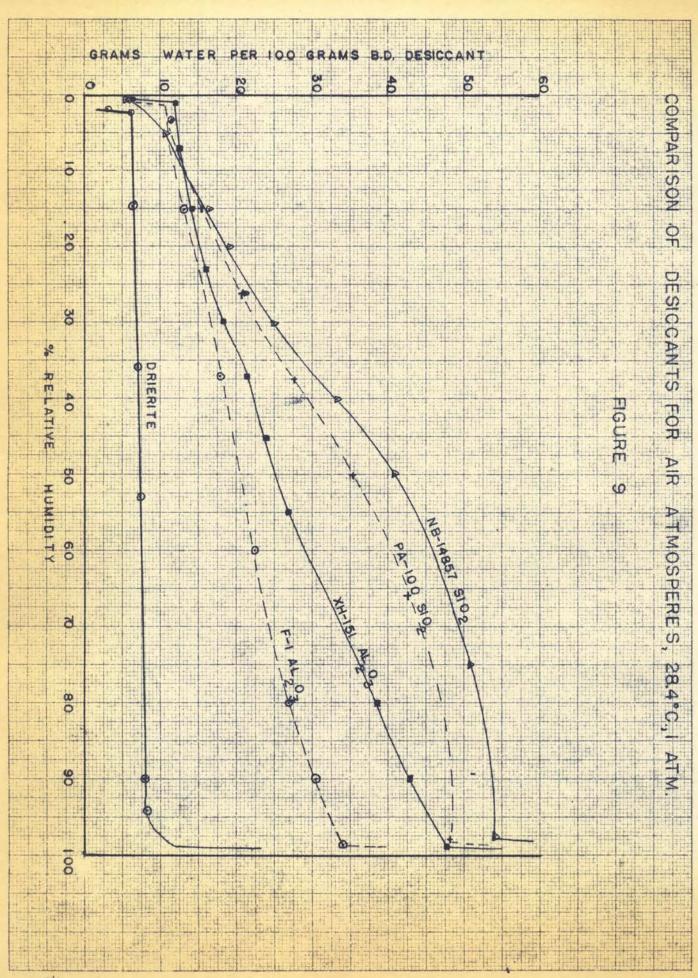
The equilibrium isotherms at room temperature give the designer the data which he requires to determine the quantity of desiccant to be used in his drier. Figure 9 was prepared to give some qualitative information. The best desiccant is the one with the highest capacity for moisture adsorption. On that basis, Figure 9 shows that the best desiccant is NB-14857 silica gel, and then, in order of their respective capacity, PA-100 silica gel, XH-151 activated alumina, F-1 activated alumina and drierite. This is true for atmospheres of relative humidities higher than 8 per cent. At lower humidities it seems that activated alumina, independent of the form or grade studied, is better than silica gel,

again independent of the grade studied.

It is therefore possible to summarize the findings of this investigation as follows:

- (1) The data is accurate and a high degree of precision is available in the results
- (2) At high relative humidities NB-14857 silica gel is recommended.

 At relative humidities below 8 per cent, any type activated alumina is recommended.
- (3) Method B of determining equilibrium isotherms is recommended because of its time saving characteristic and because of its degree of accuracy which is comparable to the degree of accuracy of static methods
- (4) Hysteresis is only a matter of time allowed for the samples to reach equilibrium
- (5) A bone dry basis should be used in reporting the results.



EQUILIBRIUM ISOTHERMS AT 0, 25 AND 50°C (WATER-FREON-12 SYSTEMS)

EQUILIBRIUM ISOTHERMS AT 0, 25 AND 50°C (WATER-FREON-12 SYSTEMS)

Three of the same materials which were used in the previous discussion were used for this part of the investigation. They are XH-151 activated alumina, F-1 activated alumina and NB-14857 silica gel. The specific purpose of this series of experiments is to determine the equilibrium isotherms for water-Freon-12 systems at 0, 25 and 50°C.

The same type investigation was made at Louisiana State University by Gully and Tooke. In their work, two methods were developed depending on the temperature conditions of the experiment; a dynamic method for temperatures below room temperature or at about that temperature, and a static method for higher temperatures. In the present work only one method was used so that the same method could be discussed throughout the entire range of temperatures to be investigated. This method is somewhat similar to the static method of Gully and Tooke.

The apparatus consists of a cast steel cylinder fitted with a discharge tube which extends to the bottom of the cylinder as shown in Figure 10. A porous bronze filter was soldered to the end of the tube to prevent entrainment of solid particles. A needle valve was provided to regulate the flow of refrigerant from the system and another needle valve was provided in the discharge line to adjust the flow rate with greater accuracy. The cylinder was filled with pre-wetted desiccant and then vacuum was applied. When all the air had been ejected, the valve was closed and the cylinder was connected to the Freon-12 supply bottle. (See Figure 11). Freon was flushed into the line, and the pet cock was

MODIFIED REFRIGERATION BOTTLE FIGURE NO 10

NEEDLE VALVES

TO NESBITT BULB TRAIN OR TO CHARGING LINE

COPPER TUBING

FLAR NUT

CAST IRON SHELL

_COPPER TUBING

F-12 VAPOR

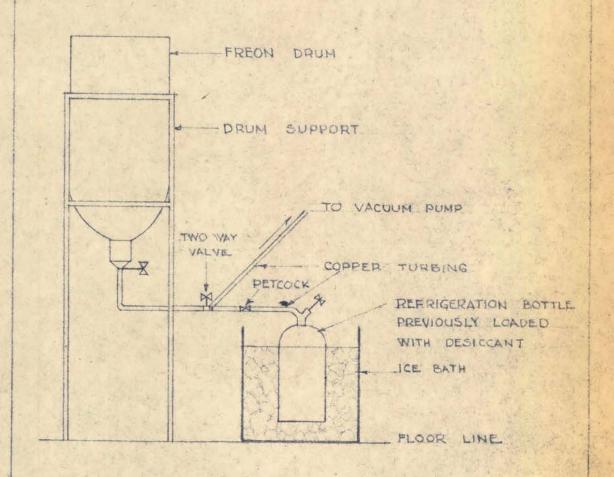
_VAPOR-LIQUID INTERFACE

_F-12 LIQUID

_DESICCANT

BRONZE FILTER

CHARGING THE BOTTLE WITH LIQUID FREON 12 FIGURE NO 11



opened until all the air was chased from the charging lines. The cylinder valve was then opened and the bottle was charged with Freon-12. Care was taken that enough Freon-12 was admitted so that the vapor-liquid interface would be several inches above the top of the desiccant bed. The valve was then closed, the bottle was weighed and transferred to the constant temperature chamber.

Because the quantity of desiccant employed was large, 450 - 550 grams, changes in its moisture content with changes in the Freon-12 moisture content were negligible. Approximately 2,500 grams of refrigerant were charged. Accounting for extreme variations in moisture such as 200 ppm in the refrigerant upon coming to equilibrium, the desiccant would change its moisture content by 0.1 per cent. This variation is negligible when compared to the quantity of desiccant employed, but the cylinder could not be refilled with refrigerant indefinitely without a significant change in the moisture content of the refrigerant.

Another factor of importance in using this apparatus is the vaporliquid equilibrium in refrigerant-water systems. Gully and Tooke extrapolated the relationship given by Ellsey and Flowers and found that the
ratio of vapor moisture content to liquid moisture content in a Freon-12water system is approximately 4.1 at 50°C. The importance of this statement is that the withdrawal of liquid Freon-12 from the cylinder results
in a decrease in the moisture content of the liquid remaining in the
cylinder. An error of 15 per cent could thus be introduced. However,
with the withdrawal of refrigerant from the system, water is continuously
transferred from the desiccant to the refrigerant to offset the change.
A practical equilibrium can be reached if the refrigerant is withdrawn
very slowly. A study of rates of refrigerant withdrawal was made with

XH-151 activated alumina, and it was found that withdrawing the refrigerant at any rate below 18 grams per hour would yield a practical equilibrium.

In order to prepare the desiccants for the runs, the dynamic method B described in the previous discussion was used. At first, the samples were spread in thin layers in order that they could adsorb water from the air atmosphere to which they were exposed. When they had picked up the desired amount of moisture by weight, they were put in a copper cylinder and the latter was inserted in place of the Nesbitt bulb of Figure 7. Air was circulated for 4 to 6 hours to insure perfect moisture distribution in the desiccant. Samples of the desiccant were then analyzed as described in the static method for air determinations, and the exact water content of the desiccant was thus determined. Calculations were made on a bone dry basis to eliminate errors in reporting the results, errors which would occur in reporting the results on an "as activated" basis as the latter depends on the method of activation and also on the water of constitution of the desiccant.

DETERMINATION OF MOISTURE IN REFRIGERANTS

Gully and Tooke made an intensive survey of moisture determination methods, and they came to the conclusion that phosphorous pentoxide absorption methods are best suited in the case of refrigerants. They adopted Pennington's method for the determination of moisture in Freon-12 which gives an accuracy of plus or minus 1 ppm up to concentrations of 35 ppm water in the refrigerant. They remark that extreme care must be exercised in order to obtain reproducible results. In this investigation, the same method was followed in its greater part.

Essentially, wet refrigerant was passed through a train of Nesbitt bulbs packed with a phosphorus pentoxide—asbestos mix, the refrigerant vapors were then flushed with dry air.

Shredded asbestos was mixed with phosphorus pentoxide to provide large surfaces for water absorption and to reduce large pressure drop through the bulbs. Equal volumes of dry shredded asbestos and phosphorus pentoxide were mixed together in large necked bottles which were shaken until complete mixing was attained. This operation was made as quickly as possible to prevent water absorption during mixing, (the drier the mixture, the higher its drying efficiency).

Dried Nesbitt bulbs were then prepared by placing a pad of glass wool at the bottom, and the P2O5 asbestos mix was transferred into them as quickly as possible. Great care was taken to prevent the mix from contacting the outside of the ground surface of the bulbs. If contact was made, the bulbs were discarded and new ones were prepared. Before putting the bulbs into service, they were placed in an adsorption drying train which allowed dry air to pass through the bulbs for four hours. If the bulbs changed in weight during the operation, they were discarded because it indicated that some phosphorus pentoxide contaminated the ground glass or the outside of the bulbs. If no appreciable gain or loss in weight resulted, the bulbs were ready for service.

The adsorption drying train is sketched in Figure 12. It is important to make sure that absolutely dry air be used for the drying of the bulbs before servicing. An air supply was fitted with a pressure regulator to insure constant air flow. A small water trap was also inserted in the line to catch most of the moisture in the air line before entering the adsorption train. The emerging air was passed through a large silication.

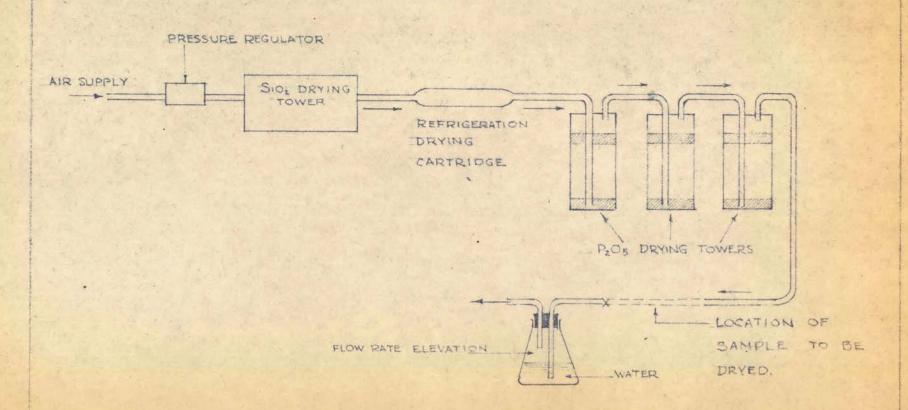
gel (PA-100) tower which contained about five pounds of that desiccant. It was then passed through a refrigeration drying cartridge to insure further drying. The cartridge was inserted to provide a means by which more efficient drying could be quickly obtained and easily ascertained. It also was easy to reactivate after each operation. Following this silica gel drying, the air passed through three consecutive phosphorus pentoxide—asbestos mix drying towers, and it was assumed that it was completely dry at that stage. At the end of the system, a water bubbling device was inserted in order to control the flow through the apparatus. Sixty bubbles per minute was the rate which was used.

Once the Nesbitt bulbs were ready for service, a Nesbitt bulb train was prepared. Three bulbs were connected in series and placed in containers which prevented them from breaking or getting dirty. The purpose of the first bulb was to adsorb all the moisture of the material entering the train. The second was used as a protective standard which would give changes in the tare weight or was used to balance deviations. The third bulb was used as a tare to compensate for changes in atmospheric conditions which affect all three bulbs similarly. As mentioned by Gully and Tooke, the practice is of questionable value, but, since a better accuracy or precision resulted, the corrections were applied. Here again a water bubbler was used to regulate flow rates through the equipment, and the rates were adjusted at 60 to 80 bubbles per minute.

CONSTANT TEMPERATURE CHAMBER

In the previous investigations, water baths were used to secure constant temperature for the cylinders. The present investigation was made by using a forced circulation air bath instead of a water bath because

APSORPTION DRYING TRAIN FIGURE NO 12



it seemed to eliminate errors due to water since only a few parts per million would yield results which would induce 100 per cent error.

A constant temperature chamber was then built. The chamber was made of transite sheets fastened together by sheet metal angles. The thickness of the transite sheets was 1/4 inch. An outside box of transite was built so that the chamber could be inserted in it. A space of 1/2 inch was provided in which cork insulation was packed to insure better isothermal conditions. The insulated box was placed on a steel table provided with rollers to give it mobility.

The inner chamber was partitioned lengthwise so that the heating elements and cooling elements could be separated from the space where constant temperature determinations were to be made. Figure 13 is a photograph of the back of the box and shows the working elements.

Heating was provided by six 600 watts socket type cone shaped heating elements wired in two systems so that one could be manually controlled and the other thermostatically controlled. The manual control gave units respectively of 600 and 1200 watts, the thermostatic control, 300 and 600 watts. The thermostatic element was an immersion type Fenwall thermoswitch of 0.1°F sensitivity.

Cooling was provided by 80 feet of 1/2 inch copper tubing, coiled as indicated in the figure, and connected to a one third horsepower Freon-12 charged compressor. A manually operating expansion valve controlled the amount of refrigeration. As manual control is not the best possible type of control, a liquid trap was inserted in the line between the bottom of the refrigeration coil and the compressor head. A drying cartridge was inserted in the liquid line to reduce the moisture in the Freon-12 to its minimum.



Figure 13

The compressor was installed on the lower part of the steel table so that it would be conveniently located if the table was to be rolled to another location. The compressor was connected to another type Fenwall thermoswitch of 0.1°F sensitivity so that the temperature of the chamber could be controlled through either the cold or the hot elements.

The refrigeration coil was placed on a drip pan provided with a drain so that the chamber would not be flooded when the tubes were allowed to defrost.

The transite partition was slit as can be seen on Figure 13. The hole at the left of the partition is for the incoming forced circulation air, and the slit at the right is for the exit of the air. The air is drawn through the heating and cooling elements by means of a 50 ft. min. blower, is discharged through the above mentioned hole in the constant temperature part of the chamber, and is then forced back to the conditioning units through the vertical slit.

The thermoswitches were placed at the air inlet point as can be seen on Figure 14. The exact temperature of the chamber could be read on a mercury type thermometer located at the mid-point of the chamber, as can be seen on Figure 15.

The constant temperature chamber was provided with a removable back, also cork insulated. The front of the chamber was provided with two doors as can be seen from Figure 15. The capacity of the constant temperature chamber was $18^n \times 36^n \times 24^n$.

Figure 15 shows the control panel of the chamber. At the extreme left the motor of the blower can be seen. It is equipped with a cooling fan. To the right of the motor, the knobs of the two thermoswitches are

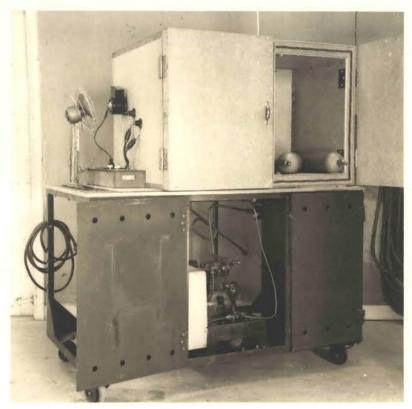


Figure 15

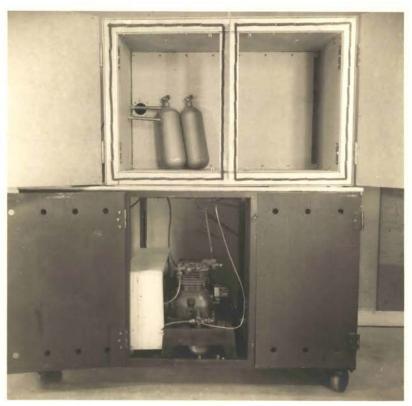


Figure 14

indicated and can be seen to be connected to a switch box provided with point switches for changing the wattage of the heating elements.

The temperature of the chamber could be maintained within plus or minus 1°F.

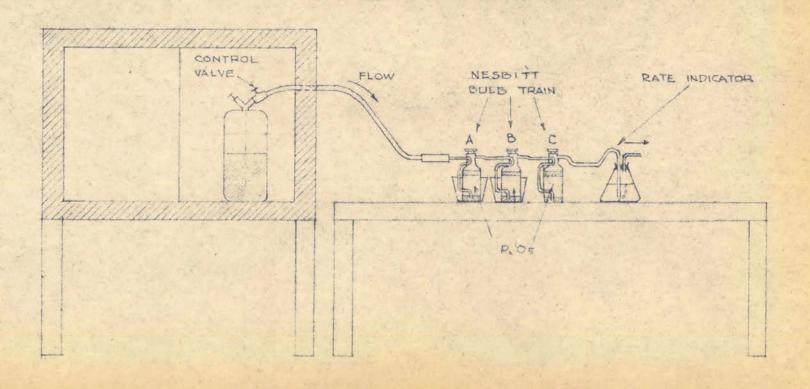
OPERATING PROCEDURE

The prepared bottle was placed in the constant temperature chamber and was shaken periodically to prevent static equilibrium. After equilibrium was reached, the cylinder was connected to a copper tube which was allowed to pass through the walls of the constant temperature chamber, and which was equipped with a needle valve to regulate the exact flow rate which was desired. The copper tube was flushed with about 50 grams of the Freon from the cylinder and connected to the Nesbitt bulb train. The refrigerant was allowed to expand through that system at a rate of 15 grams per hour, and after about 300 to 500 grams of the refrigerant had passed through the system, the flow was stopped. (See flow diagram, Figure 16).

The Nesbitt bulb train was then placed in the adsorption drying train and dry air was passed through it for one hour in order to flush out all traces of Freon which could be present.

The Nesbitt bulbs were then weighed and the equilibrium moisture content of the refrigerant was calculated by subtracting the change in weight of the second Nesbitt bulb from that of the first one, dividing by the change in weight of the cylinder during the expansion through the Nesbitt bulb train, and multiplying by 10⁶ to obtain the results in parts per million of water in the refrigerant.

FLOW DIAGRAM OF F-12 MOISTURE DETERMINATION FIGURE NO 16



PROOF OF THE VALIDITY OF THE METHOD

(1) Equilibrium moisture concentration in the liquid and in the solid were determined accurately because of the extreme care exercised in the determinations and because of the careful selection of the methods used. The absolute proof of this point was ascertained by running samples in triplicate. All samples were in perfect agreement.

A special investigation was carried on to prove that point. A sample of PA-100 silica gel was prepared, weighed exactly and analyzed for its water content. It was then placed in a cylinder, the latter evacuated and filled with a known quantity of Freon-12 whose moisture content was known. The bottle was placed in the constant temperature chamber for a week at 25°C, and during that time, it was periodically shaken to prevent the formation of static equilibrium. After that, the refrigerant was analyzed for its moisture content. The desiccant was placed in a copper cylinder, and dry air was passed through it to flush any adhering refrigerant; an analysis was then made on the water content of the desiccant. A material balance was calculated on the results which are shown on Table XV. It is seen in that Table that the water lost by the desiccant compares closely to the water gained by the refrigerant. There is a 2.9 per cent difference which is within the per cent error allowed for such type determinations.

(2) Moisture was uniformly distributed throughout the mass of the solid. After the pre-wetted desiccant was prepared, a check was made to that effect by taking five samples, two from the top, one from the middle, and two from the bottom of the dessicant bed. These were analyzed and the results are shown on Table XVI. The results indicated in the Table show that there was a perfect moisture distribution in the desiccant

layers after air had been circulated through them for four hours.

(3) Lewis and Randall¹³ state that "every system which has not reached a state of equilibrium is changing continuously toward that state with greater or lower speed". Thus, if enough time is allowed, every system will reach a state of equilibrium. Experiments were conducted to prove that fact, and the results are tabulated on Table XVII. The same methods were used for various temperatures, and, as the effect of temperature is to speed up equilibrium, as can be seen on Table XVII, the only discussion of importance is that of the investigation made at the lowest temperature, i.e., 0°C, on a sample of HX-151 activated alumina.

The desiccant was pre-wetted at 38.9 per cent moisture on a bone dry basis, and a set of determinations was run when the initial moisture content of the refrigerant was less than its equilibrium value. It was found that 72 hours was the minimum time required for the sample to reach equilibrium. The same desiccant was then placed in contact with wetted refrigerant and equilibrium was also reached after 72 hours as indicated by the results; note that there is no indication of hysteresis. Therefore, it is seen that the same values were obtained in both cases so that equilibrium was reached in 72 hours. If the temperature increases, equilibrium is reached faster.

The experiment was run on XH-151 alumina because that material requires more time to reach equilibrium than any of the silica gel samples.

RESULTS AND RELIABILITY OF THE EXPERIMENTAL DATA

The experimental data and results are presented in Tables XX, through XXVIII. Graphical representation is made in Figures 17, 18 and 19.

These results are not exact. Experimental errors are present in

spite of the great care which was taken to eliminate uncontrolled variables in the investigation. For this reason estimates of standard deviations were made per group of three determinations. These estimates are relatively poor because they do not include enough determinations. If the deviations were independent of moisture concentration, the estimates would be good. However, it was found that, in general, the precision decreased with an increase in the moisture concentration. Tables XXIX, XXX and XXXI indicate the values of these estimates. In order to obtain enough information on the standard deviation for this type of determination, the data were grouped in ranges of moisture concentration. Table XXXII indicates the grouping, and the information is plotted in Figure 20. From that plot, it is seen that there is a definite relation which can be expressed by the following empirical equation:

$$y_{average} = 0.236 x^{0.233}$$

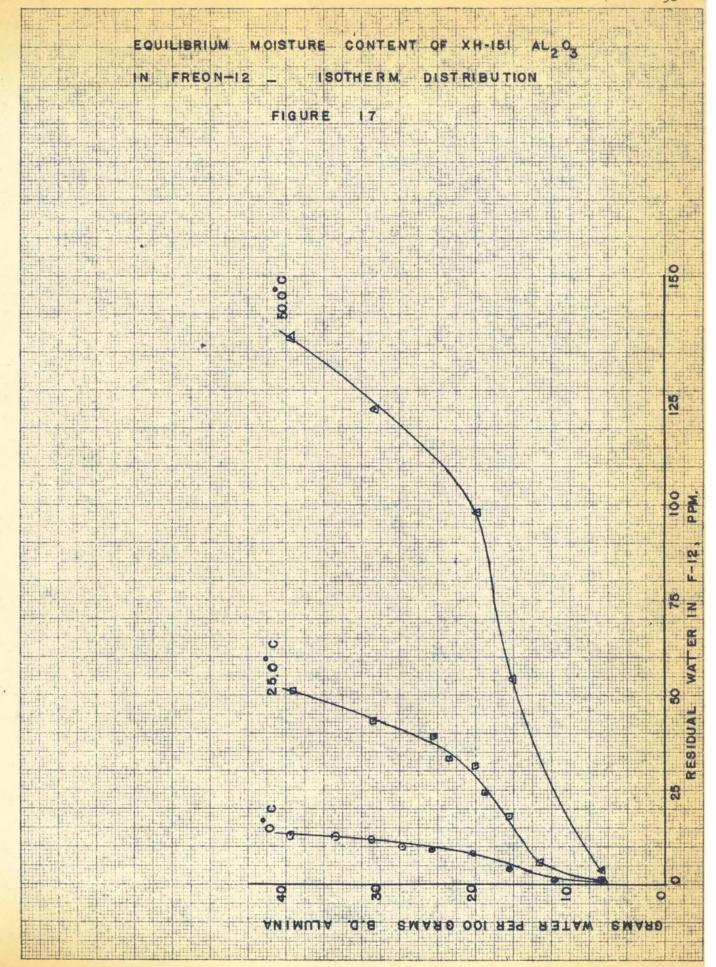
where y is the average standard deviation and where x is the residual moisture content of Freon-12, both quantities expressed in parts per million. Theory gives a 99 per cent probability of the existence of such a relationship. It follows that the error on the average standard deviation is

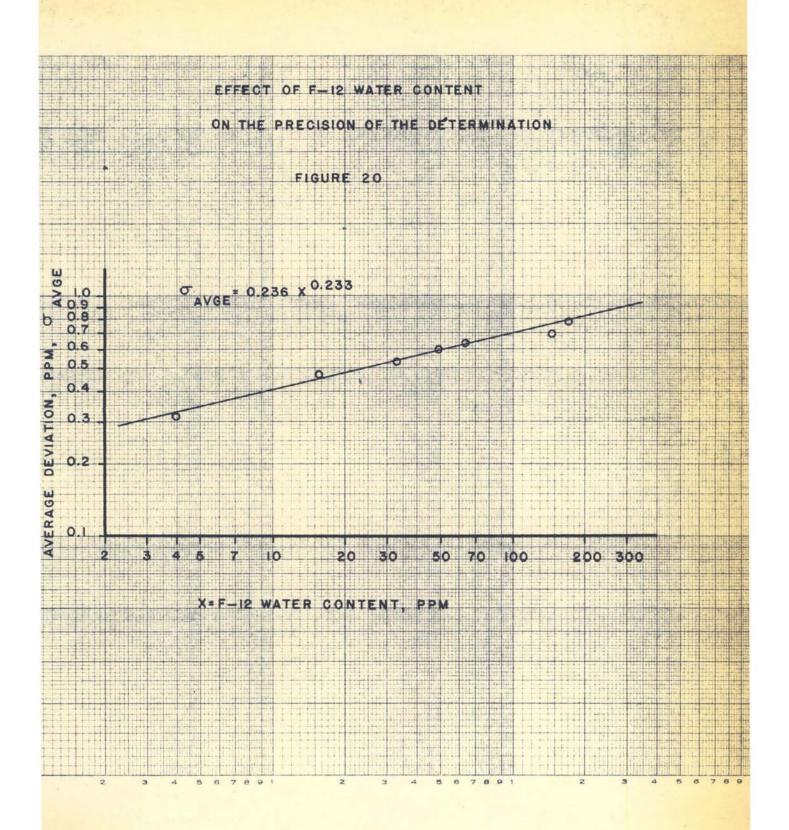
$$6\overline{x} = \frac{0.236 \text{ x}^{0.233}}{3} = 0.136 \text{ x}^{0.233}$$

because the results were a combination of triplicate determinations.

A 99.7 per cent probability limit that the results would fall within a certain given error estimate can thus be calculated as

True value =
$$\bar{x} \pm 3(0.136) x^{0.233} = \bar{x} \pm 0.408 x^{0.233}$$





where \overline{x} is the average of three determinations in ppm and x is the F-12 moisture concentration in ppm.

The preceding discussion dealt with variations in the results arising from the uncertainty of the refrigerant moisture determinations. The desiccant moisture determinations were also subject to variations as was discussed in the latter chapter of this work.

Three moisture determinations were made for each of the desiccant samples. Only the averages are given in the tables of results. The average standard deviation for desiccants was found to be 0.12 grams of water per 100 grams of bone dry desiccant, NB-14857 silica gel, F-1 and XH-151 activated alumina. This accuracy was discussed in the preceding chapter and indicates the 99.7 per cent confidence limit on the results. It is thus possible to say that there are present the two following sets of average deviations (99.7% confidence limit)

$$X = \overline{x} \stackrel{+}{=} 0.136 \text{ m}^{0.233} \text{ ppm water in F-12}$$

Y = \overline{y} $\overset{\star}{=}$ 0.12 grams water/100 grams b.d. desiccant To correlate the resultant variation between the two sources of error, the total variance was estimated on the basis of equation (f) of the theory section. The average magnitude of the error was then triplicated to account for a 99.7 per cent confidence limit. As the reliability of the data was not uniform, it was necessary to calculate confidence limits for each individual point. Gully and Tooke employed the same procedure and indicated the magnitude of the error as bars crossing their points on their graphical representation of the data. This procedure was rejected in this particular investigation because it was found that if the point-deviations were calculated and then grouped as a

function of certain given intervals of moisture concentration in the refrigerant, they would present a linear relation which is

$$X = \overline{x} + 3(0.0528 x + 0.0678)$$

where X is the total possible deviation, \overline{x} is the average calculated from the data and x is the point-determination, all three expressed in parts per million.

THE FREON-12 EQUILIBRIUM ISOTHERMS

When the experimental data were plotted (Figures 17, 18, and 19) it was possible to define fairly accurate equilibrium isotherms relating desiccant moisture content to the residual refrigerant moisture content. With a few exception, all points were found to fall on the average curve. Statistical curve fitting methods failed to apply to the data, and, consequently, the curves were drawn visually. This was also the case for the data reported by Gully and Tooke.

The isotherms of all desiccants are S-shaped, except at 0° C where a linear relation could be approximated. However, as only a small portion of the curve was investigated, it is not possible to ascertain linearity upon extrapolation of the 0° C curve. Gully and Tooke reached the same conclusion.

The data was found to be similar to the data obtained by Gully and Tooke. As in their case, at low concentration ranges, the data follows Langmuir type adsorption isotherms with wide deviations resulting at high concentration ranges. There is evidence that adsorption at low concentrations is due to the formation of monomolecular layers of adsorbate on the adsorbents but that further adsorption is still possible after that layer has become saturated. At high concentrations, capillary or multi-

molecular adsorption would occur. Hansen attributed sigmoid curves to multimolecular adsorption for binary liquid solutions.

THE EFFECT OF TEMPERATURE ON EQUILIBRIUM RELATIONSHIPS

Figures 17, 18 and 19 seem to indicate that temperature has a great effect on the moisture content of Freon-12 in equilibrium with a prewetted desiccant. It is also apparent that the increase in moisture content with temperature is not linear.

R. K. Taylor 18 reported that, at room temperature, the water adsorption by silica gel at a given relative humidity is independent of temperature. Pennington 16 suggested that this could be extended to Freon-12, and Gully and Tooke proved that fact experimentally. They obtained the values of the saturation concentrations of water in Freon-12 by making a Cox type plot, extrapolating the solubility data supplied by Williams. 19 The following saturation concentrations were obtained:

The same figures were used in calculating relative saturations tabulated in Tables XX through XXVIII. Figures 21, 22 and 23 represent the relative saturation of Freon-12 in presence of pre-wetted desiccants.

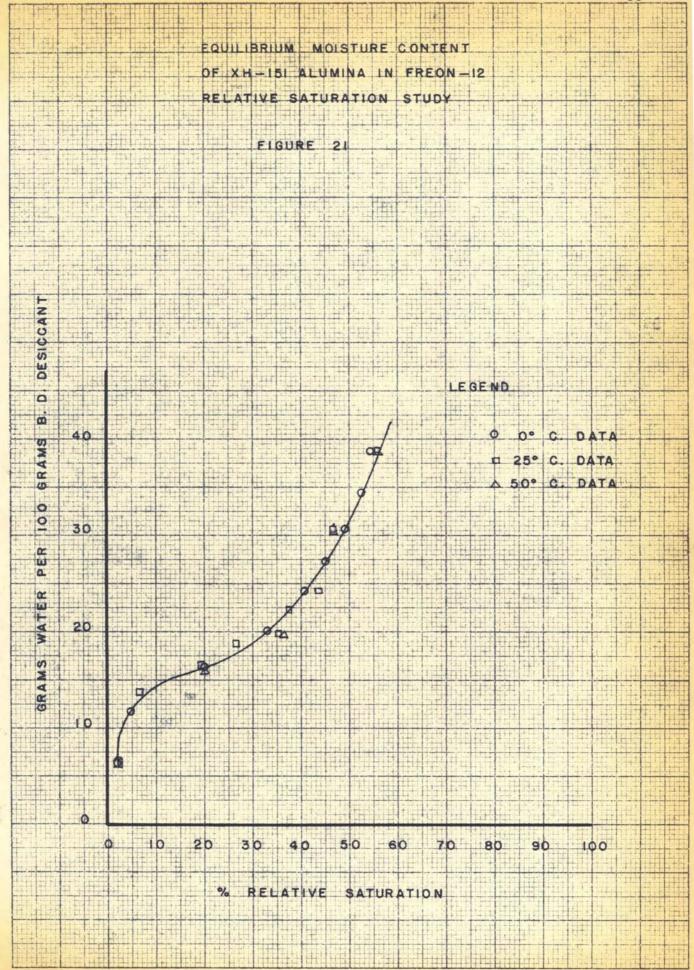
It was found that a single curve could represent all three temperatures. However, and in this, the data differs from the data of Gully and Tooke, the points at 0°C were in no larger percentage error than points at any other temperature.

Gully and Tooke assumed that the average curve represented the data for all three temperature conditions and applied a significance test to prove that the 0° C data did differ from the average curve. That curve

was, however, not postulated. They used that curve as a basis for a "true" test of significance. The same "T" test was applied as a comparative measure in this investigation. It showed that the probability of there being no real difference between the 0°, 25°, and 50°C data was less than 0.001. (See Tables XXXIII, XXXIV and XXXV). The test seems to indicate the data which is the closest to the visual average curve is the 50°C, followed respectively by the 25°C, then the 0°C. Thus the higher the temperature, the closer the average curve will be to the data.

An "F" test of significance was, however, applied to justify the assumption that the average curve represented the data. To that effect, the same pre-wetted desiccant was used for all three temperatures, and the variation in the relative saturation with temperature was studied. Fixing the moisture in the desiccant was chosen because the error in that determination is generally 100 times less than the error in the refrigerant moisture determination. Tables XXXVI and XXXVII show the results. A study of the probability chart shows that there is 99 per cent probability that the curve will represent the average value for all three temperatures, and this for each desiccant in particular. Gully and Tooke's assumption is thus verified and the applied "T" test has more true significance although its results cannot be accepted with 100 per cent certainty.

Drying efficiency curves are given (Figures 24, 25 and 26). No statistical study was made on this data as it varies as a function of the relative saturation and has the same conclusions, mainly that the drying efficiency is not a function of temperature.



EFFECT OF EXPANSION RATES ON THE EQUILIBRIUM DATA

In the description of the method used in this investigation, it was emphasized that special attention should be given to the rates of expansion. Preliminary investigations showed that this factor had its greater effects on alumina while silica gel was little affected. A study was made on XH-151 activated alumina in presence of pre-wetted desiccant (30.5% water) at 25°C. The data is included in Table XXI, and its graphical interpretation is given on Figure 27. It seems that the error due to the expansion rate is a linear function. That error can be approximated from the graph, and such a procedure is recommended in order to save time.

Relations could be determined for each desiccant, and then the equilibrium could be studied without having too much time consumed due to very slow expansion rates. The absolute error or standard deviation introduced by this procedure was calculated as 0.0872 ppm for XH-151 activated alumina.

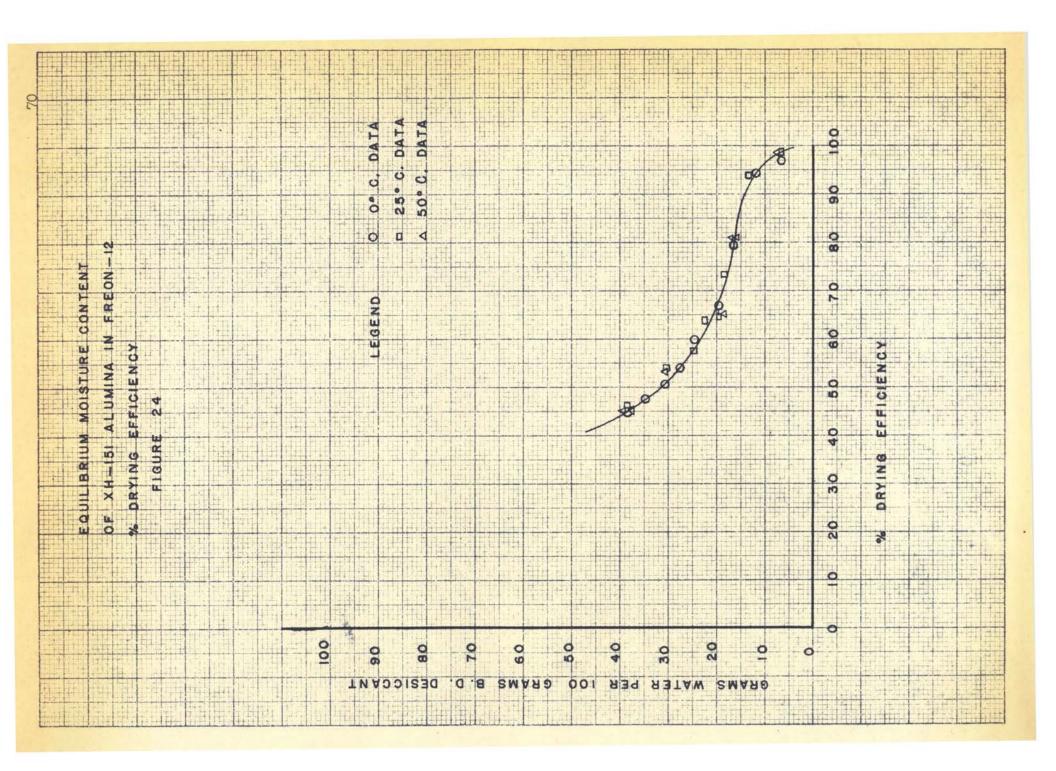
Figure 27 allows the derivation of the following relationship indicating the studied effect within a 99.7 per cent confidence limit:

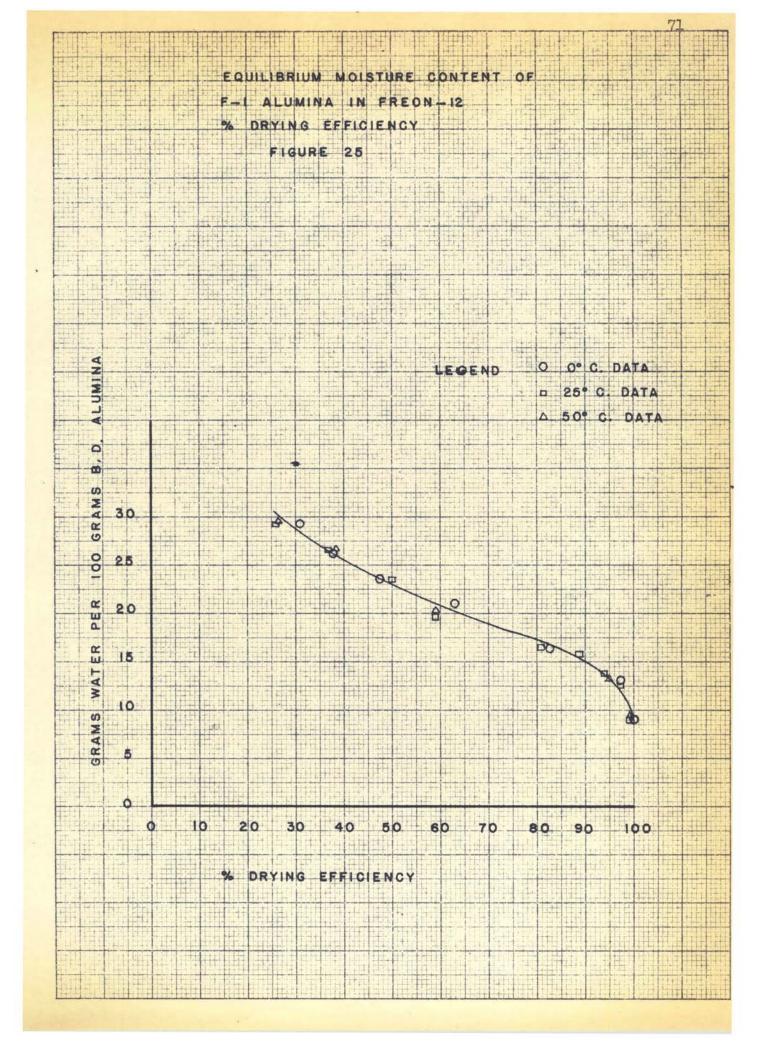
$$X = \overline{x} - 0.343 y + 6.174 \pm 3(0.0872)$$

where X is the corrected amount of water present in the desiccant (ppm) and \overline{x} is the average value (ppm) at the rate y (grams per hour). This relationship applies for rates ranging from 18 to 60 grams per hour.

COMPARISON OF THE DESICCANTS

In order to make a comparison of desiccants which would include the same type desiccants as in the water-air study, equilibrium data for PA-100 silica gel and drierite were taken from the work of Gully





and Tooke. These are tabulated in Table XIX. All the data was then correlated on Figure 28.

Throughout the whole range of relative saturation, drierite is the least efficient desiccant. The following table has been prepared to indicate the effectiveness of the desiccants for limited ranges of relative saturation, the desiccants being given in the order of their capacity:

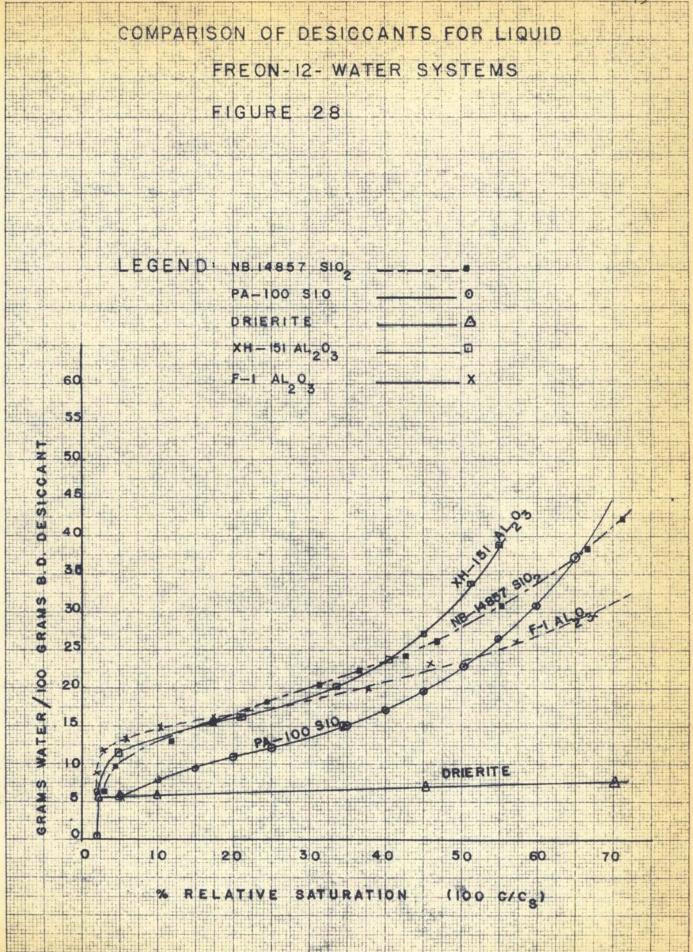
TABLE XXXVIII

Comparison of Desiccants (F-12 system)

Range of relative saturation	·
0 - 15	F-l alumina, XH-151 alumina, NB-14857 silica gel and PA-100 silica gel
15 - 22	F-1 alumina, NB-14857 silica gel, XH-151 alumina and PA-100 silica gel
22 - 27	NB-14857 silica gel, F-l alumina, XH-151 alumina and PA-100 silica gel
27 - 39	NB-14857 alumina, XH-151 alumina, F-1 alumina and PA-100 silica gel
39 - 52	XH-151 alumina, NB-14857 silica gel, F-1 alumina and PA-100 silica gel
52 - 65	XH-151 alumina, NB-14857 silica gel, PA-100 silica gel and F-1 alumina
over 65	XH-151 alumina, PA-100 silica gel, NB-14857 silica gel and F-1 alumina

COMPARISON OF THE WORK IN AIR AND FREON ATMOSPHERES

Comparing the desiceants for their performance in air or in Freon-12 shows that at low humidities the same results are obtained regardless of the atmosphere. When the relative humidity is higher than eight, no



direct comparison can be made. However, Figures 29 through 33 were prepared to show a comparison of the individual desiccants.

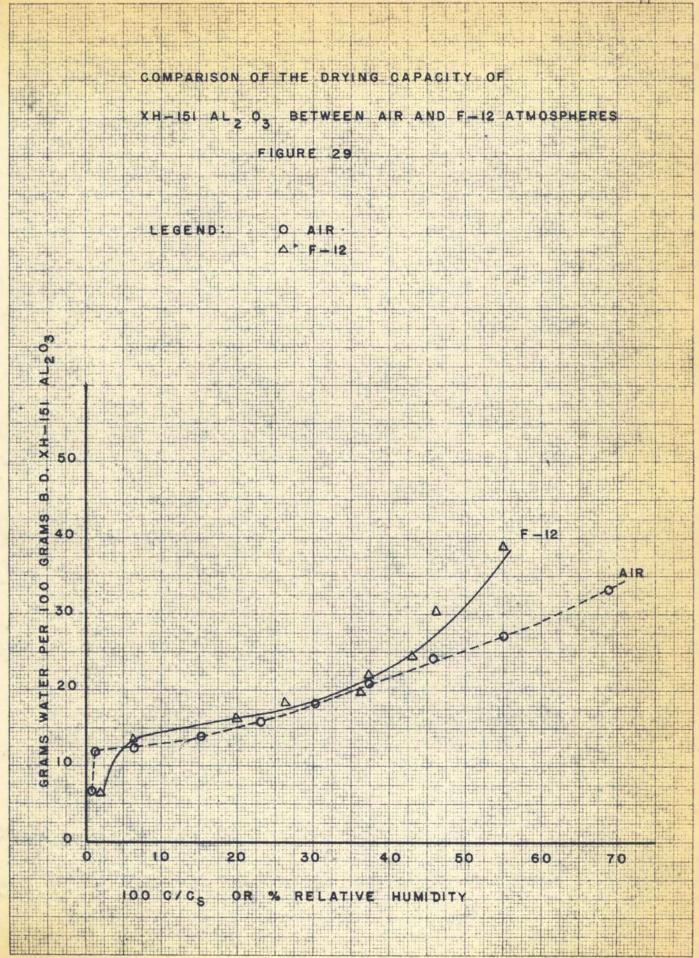
An analysis of these graphs shows that drierite (Figure 33) has a drying capacity which is independent of the atmosphere it has to dry. It seems reasonable to advance the theory that for chemisorption processes this would occur, the chemical affinity between water and the desiccant being greater than the influence of the atmosphere.

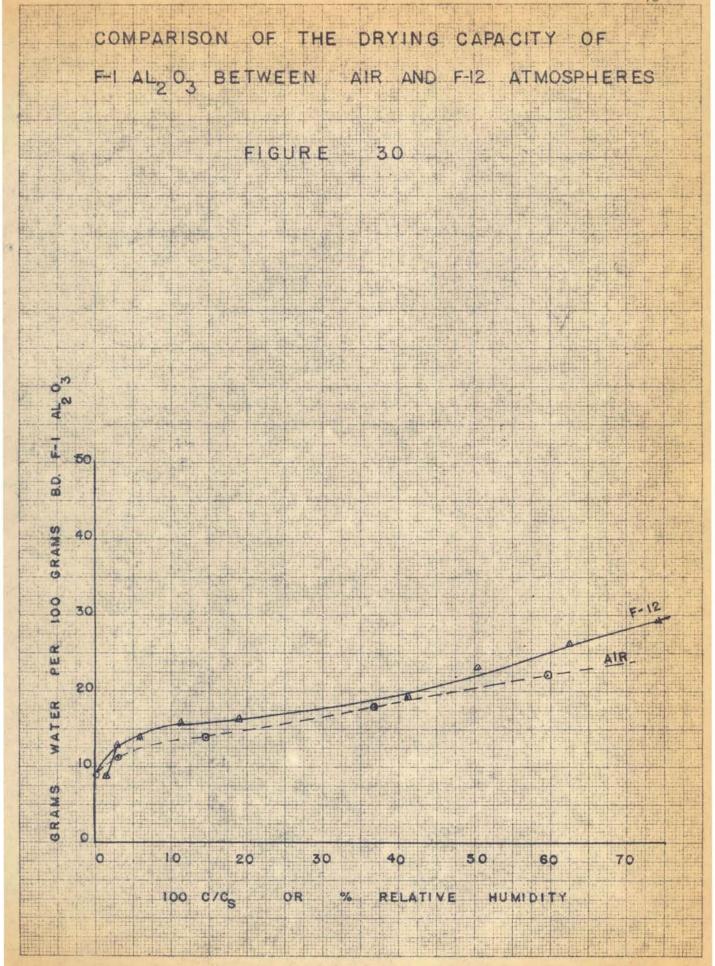
Figures 29 and 30 show that the drying capacity of activated alumina is larger in Freon-12 than in air; Figures 31 and 32 show that, for silica gel, the contrary is true. The amount of the difference in the respective capacity of the desiceants in air or in Freon-12 cannot be calculated. It is a function of the manufacturing processes of the various materials and thus cannot be estimated because these processes are not known.

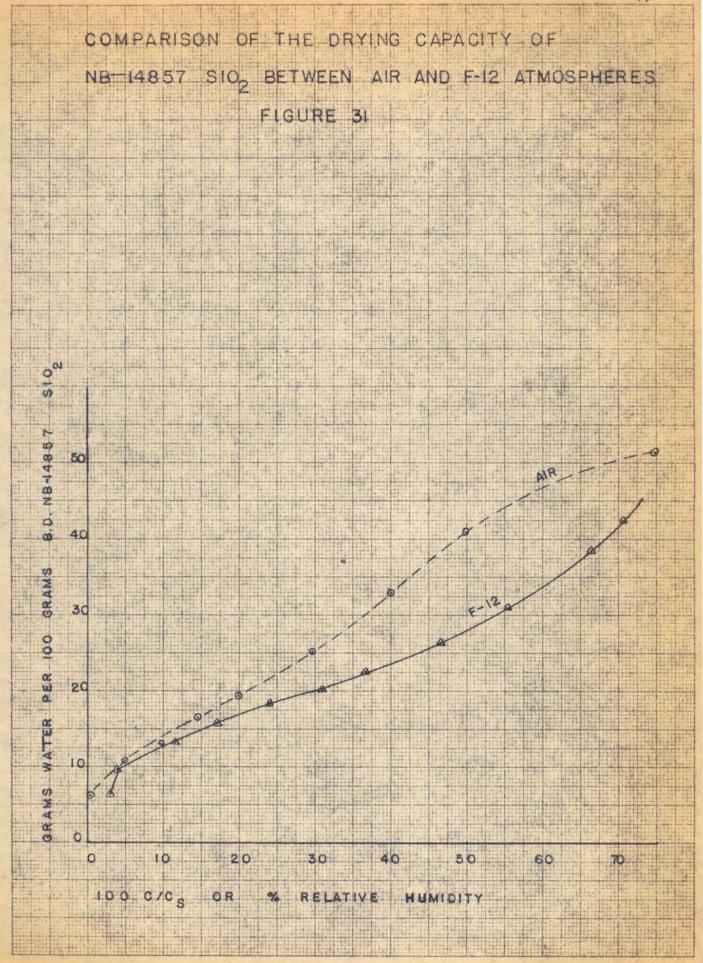
It is suggested that the influence of the atmosphere to which the desiccants are submitted be studied in a special investigation where one typical desiccant, known in all its physical aspects, would be subjected to different atmospheres, air, benzene, ammonia, methyl chloride, other types of Freon, etc. . .

SUMMARIZED CONCLUSIONS

- (1) A comparison of the desiccants shows that each grade has its special advantages within limited ranges of relative saturations, as shown in Table XXXVIII.
- (2) The method used is accurate and shows relatively good precision.
- (3) Time could be saved by computing correction curves similar to Figure 27.

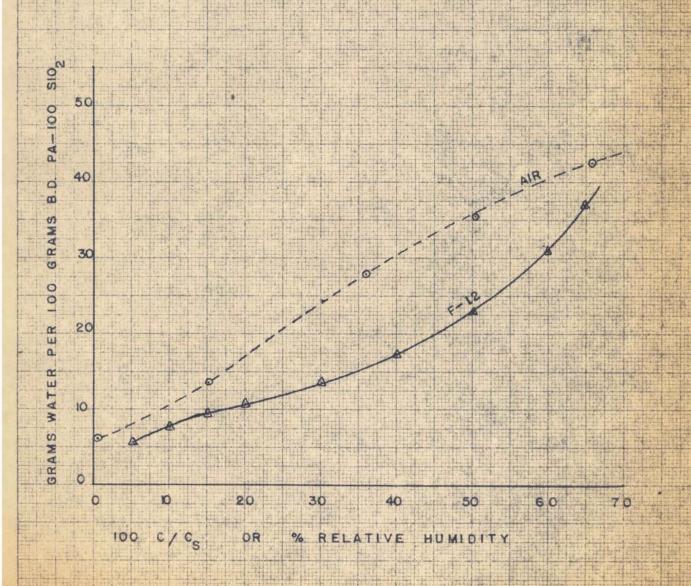


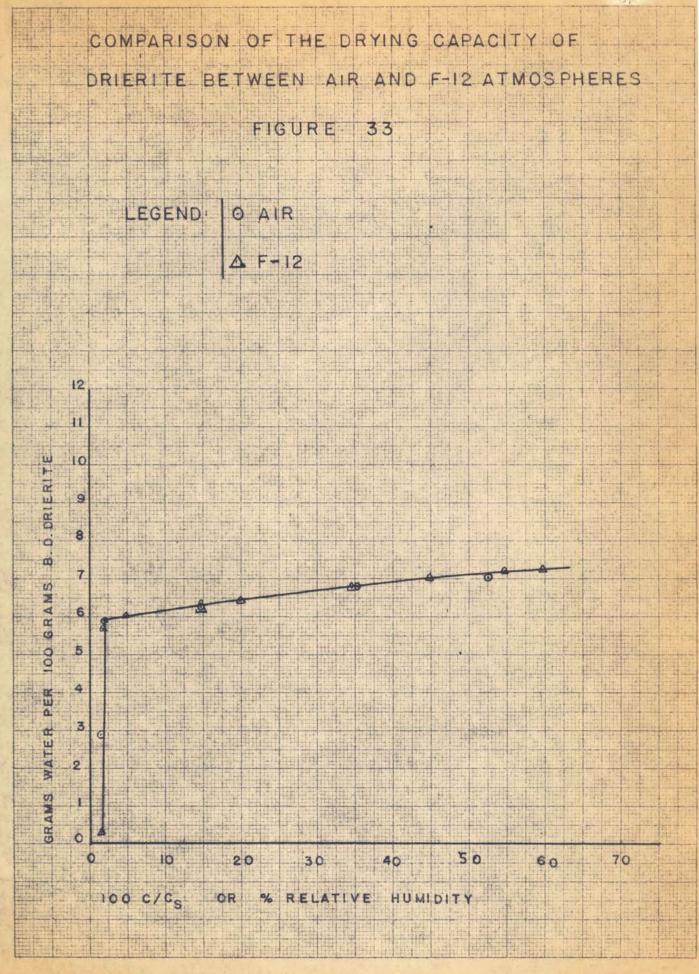




COMPARISON OF THE DRYING CAPACITY
OF PA-100 SIO BETWEEN AIR AND F-12
ATMOSPHERES

FIGURE 32





- (4) The results are accurate and are felt to be a true source of information for the designing engineer.
- (5) The effect of temperature on the capacity of the desiccant is nil.
- (6) The chemisorption equilibrium data shows the same results regardless of the atmosphere to which drierite was submitted.
- (7) No relationship was found on the influence of the atmosphere to which a van der Waals adsorption type desiccant is submitted, and it is suggested that such a relationship be the subject of some further research.

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APPENDIX

Tables

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TABLE I

INITIAL WATER CONTENT OF THE DESICCANTS AS RECEIVED

(These desiccants were not reactivated for the determinations. Their activation moisture content is therefore less than the values indicated in this table).

	Grams	Water per	100 Gr	ams Bone	Dry Des	iccant
Run No.	1	2	3	4	5	Average
Silica Gels			and the second s	, , , , , , , , , , , , , , , , , , ,		
PA-100 (3537)	7.160	7.220	7.220	7.200	7.210	7.205
PA-100 (3751)	6.609	6.615	6.611	6.612	6.608	6.611
PA-100 (com- mercial grade)	4.490	4.505	4.520	4.500	4.510	4.525
NB-14857	6.020	6.040	6.050	6.030	6.040	6.030
Alumina	erene eta duri ellera	<u>and a second second and a second sec</u>		- ANT Green was a Province of the Child Ch		
F-1	7.600	7.610	7.620	7.615	7.610	7.611
NH-151	5.930	6.240	6.130	6.030	6.090	6.084
<u>Drierite</u>	2.715	2.620	2.690	2.680	2.700	2.681

TABLE II

EQUILIBRIUM MOISTURE CONTENT OF DRIERITE IN AIR

(Temperature Range: 25 - 35°C) (Static Method)

% Relative	Grams of Water per 100 Gram	s of Bone Dry Drierite
Humidity of Air	Individual	Average
1.9	2.850	2.850
	2.820	
	2.870	
2.2	5 . 830	5.840
	5.850	
	6.840	
15	6,120	6.210
	6.290	
	6.210	
36	6.725	6.741
	6.760	
	6.740	
53	7.000	7.001
	6,980	
	7.030	
90	7.580	7.510
	7.420	
	7.530	
99•5	25.800	25.900
	26,000	
	25.900	

TABLE III

STANDARD DEVIATION ON THE RESULTS OF TABLE II

(Drierite in Air)

% Relative	Grams of Water per 1	00 Grams of Bone Dry Drierite
Humidity	Standard deviation $\sigma(x) \propto 10^2$	Standard deviation on average 6 $(\overline{\mathbf{x}})$ x 10^2
1.9	2.82	1.63
2.2	1.40	0.82
15	6.94	4.00
36	4.54	2.62
53	2.00	1.15
90	6.63	3.82
99•5	7.75	4.47

TABLE IV EQUILIBRIUM MOISTURE CONTENT OF ALUMINA IN AIR

(Temperature Range: 25 - 35°C) (Static Method)

<pre>% Relative Humidity</pre>	Grams of Water XH-151 A		rams of Bone Dr F-1 Alur	
of Air	Individual	Average	Individual	Average
0.10	6.61 6.59 6.60	6.600	8.940 8.900 8.920	8.920
1.10	11.70 11.80 11.75	11.750	gende in de mengant de glaceter villen der effensilen der fellen in der	ont (unggived) w skillman, i pik einegeneg) z (gö
3.50			11.200 11.250 11.220	11.230
7.00	12.25 12.20 12.21	12.220	aka amandak a mananan aka amanda angar di Panda a manin kangar	
15.00	13.78 13.84 13.91	13.840	13.620 13.610 13.615	13.615
23	15.81 15.74 15.77	15.770		
30	18.10 18.00 17.95	18.020		
37	20.65 20.90 20.84	20.860	17.850 18.050 17.900	17.930
46	24.15 24.08 24.09	24.108		
55	27.15 27.20 27.25	27.200	A STATE OF S	AND THE PROPERTY OF THE PROPER

% Relative	Grams of Water	per 100 G:	rams of Bene 1	Dry Alumina	
Humidity of Air	XH-151 A	lumina	F-1 Al1	F-1 Alumina	
	Individual	Average	Individual	Average	
60			22.61 22.48 22.55	22.53	
69	32.97 33.01 33.00	32.99			
80	38.40 38.60 38.50	38 . 50	27.05 26.98 27.01	27.01	
90	43.05 42.90 43.00	42.95	30.50 30.45 30.40	30.45	
99	47.95 48.00 48.05	48.00	34.00 33.95 34.15	34.03	
99:85	53.10	53.10			

TABLE V

STANDARD DEVIATION ON THE RESULTS OF TABLE: IV

(Alumina in Air)

% Relative Humidity		er per 100 Gra		
numar ty	$G(x) = \frac{XH-151}{x \cdot 10^{+2}}$	Alumina $G(\overline{x}) \times 10^{+2}$	$G(x) \times 10^{12}$	
0.1	0.815	0.470	2.830	1.630
1.1	4.060	2.340		
3.5			3.740	2.160
7.	2.160	1.250		
15	5.310	3.060	0.706	0.407
23	2.890	1.720		
30	6.240	3.600		
37	15.100	8.660	14.200	8.200
46	2.160	1.250		
55	4.060	2.340		
60			9.640	5.550
69	1.730	1.000		
80	8,150	4.710	5.000	2.890
90	7.050	4.060	7.060	4.070
99	4.060	2.340	14.700	8.500
99.85	0	0		

TABLE VI

EQUILIBRIUM MOISTURE CONTENT OF SILICA GEL IN AIR

(Temperature Range: 25 - 35°C)

(Static Method)

% Relative	Grams of Wate	er per 100 Gra	ms of Bone Dry	Silica Gel
Humidity of Air		Special Sample, Code 0-8 PA-100 No. 3751		
	Individual	Average :	Individual	Average
0.1	5.95 5.91 5.96	5.94	6.21 5.80 5.90	5.97
15	12.71 12.65 13.01	12.79	12.90 12.80 12.85	12.85
26	20.89 21.12 21.02	21.01		
36	29.50 29.41 29.59	29.50	29.10 29.75 29.70	29.51
55	40.62 40.55 40.49	40.55		
66			44.62 44.49 44.45	44.52
80	48.10 48.05 47.95	48.10		
99.6	51.20 50.97 50.80	50.99	51 . 00 50.30 50.80	50. 50

TABLE VII

EQUILIBRIUM MOISTURE CONTENT OF SILICA GEL IN AIR

(Temperature Range: 25 - 35°C)
(Static Method)

% Relative	Grams of Water p	er 100 Grams o	of Bone Dry Silica Gel
Humidity of Air	PA-100 Comme	rcial Grade	NB. 14857 Sample
	Individual	Average	(Average) (Dynamic Method B)
0.1	6.18 5.96 5.98	6.01	5 . 78
5			10.48
10			13.51
15	12.89 12.82 12.92	12.87	16.22
20		riche Talle All der verstehen bezoek der Dientze ist zu ein zu zu web zur einem der dem zu zu zu der der zu zu	19.10
30		and Carrier and Pro-Christian and Alexander	25.00
36	27.32 27.38 27.83	27.51	
40		Ochemick (In the profession of	33.10
50	34.79 35.23 35.37	35.13	40.75
66	42.62 42.49 42.45	42.52	
75			50 .82
98 .			54.00
99.6	46.89 47.25 47.25	47.12	

TABLE VIII

STANDARD DEVIATION ON TABLES VI AND VII

(Silica Gel in Air)

% Relative	Grams of	Water per 10	O Grams o	f Bone Dr	y Silica	Gel
Humidity	PA-100 #	3751	PA-100 #	¹ 35 3 7	PA-100,0	ommercial
	6 (x) x 10 ²	6 (₹) x 10 ²	6 (x)10 ²	((₹)10 ²	5 (x)10 ²	(x)10 ²
0.1	2.16	1.25	17.40	10,10	10.30	5.95
15	15.70	9.05	5 . 15	2.97	4.24	2.44
26	10.70	6.17				
36	7.35	4.25	29.50	17.05	22.70	13.10
50					24.70	14.20
55	4.69	2.71				
66			13.60	7.85	7.20	4.15
80	9.14	5.26				
99•6	15.95	9.20	21.00	12.10	16.90	9.75

REASONS FOR USING A BONE DRY BASIS IN REPORTING THE RESULTS

TABLE IX

Sample	Grams of Water per 100 Grafor one hour at 1750°F	ms of Bone Dry Desiccant, dried
	PA-100 Silica Gel (Commercial Grade)	F-1 Alumina
l-a	4.07	7.08
2 - a	4.57	7.20
3 - a	4.84	7.55
4 - a	5.04	7.75
1-b	4.49	7.60
2 - b	4.52	7.61
3 - b	4.50	7.62
4 - b	4.51	7.61

Table X

Hours of Heating at 214°C Under Vacuum	Grams of Water per 100 grams of Bone Dry PA-100 Silica Gel (special sample)
0	7.25
24	5.53
48	5.11
74	4.88
192	4.50
264	4.45

TABLE XI

DETERMINATION OF HYSTERESIS IN THE EQUILIBRIUM DATA OF THE WATER CONTENT OF PA-100 (No. 3537) IN AIR

(Static Method)

% Relative Humidity	Grams of Water per 100 Grams of Bone Dry Silica Gel	
	Equilibrium Reached from above	Equilibrium Reached from below
0.1	7.07	5.96
15	13.94	12.77
36	31.21	29.50
55	41.68	40.55
80	49.45	48.10

TABLE XII

EQUILIBRIUM MOISTURE CONTENT OF DESICCANTS IN AIR BY DYNAMIC METHODS

% Relative	Grams of Water per 100 Grams of Bone Dry Desiccant	
Humidity	PA-100 Silica Gel	F-1 Alumina
Method A		
0.1	6.05	8.91
15	12.78	13.63
36	27.62	17.78
55	39.71	20.62
Method B		egykejőkőjáklandján sambánnásagómánag emántő hagyíttő ünvezet (amana antáma csaegástánegs), g til (3300)
0.1	6.02	8.95
15	12.76	13.61
36	27.69	17.59
55	39.63	20.72

TABLE XIII

EQUILIBRIUM MOISTURE CONTENT OF NB-14857 SILICA GEL IN AIR, (DYNAMIC METHOD B)

% Relative Humidity	Grams of Water per 100 grams of Bone Dry Silica Gel	Time for Equilibrium, hours between each successive stage
0.1	5.78	6
5	10.48*	7
10	13.51	4
15	16.22	7
20	19.10*	7
30	25.00	9
40	33.10	13
50	40.75*	11
75	50.82	20
98	54.00	20

Determinations checked by the Static Method.

TABLE XIV

PRECISION ESTIMATE ON AIR DETERMINATIONS
(Combined Data for all Type Refrigerants)

Moisture Concentration Interval of Desiccant (g/100 g.B.D.Desiccant)		Desiccant	Average Moisture Concentration (g/100 g.B.D.Desiccant)	
0	-	- 10	6.34	0.0525
10	-	20	13.89	0.0594
20	5	30	25.52	0.1061
30	•••	40	34.25	0.1128
40	-	52	46.84	0.0960
			Ave	rage 0.0887

TABLE XV

MATERIAL BALANCE OF A RUN ON THE MOISTURE CONTENT OF A FREON-12-WATER-PA-100 ${\rm Slo}_2$ SYSTEM

Before Equilibrium

Weight of F-12 + H ₂ 0 Water Content B.D. Refrigerant	2,127 g. 0.0074 g. 2,126.9926 g.	(3.48 ppm)
Weight of PA-100 S10 ₂ + Water Water Present B. D. S10 ₂	492.1 g. 46.72 g. 445.38 g.	(10.5%)

After Equilibrium

<u>Data</u>	F-12 Moisture con	tent	19 ppm
	PA-100 S10, + Wat		492.07 g.
	B.D. Moisture Con	tent of S10	10.48 %

WATER BALANCE

Water in Desiccant

Before Equilibrium	46.72 g	0
After Equilibrium	46.69 g	•
Transfer	0.03 g	ð

Water in Refrigerant

After Equilibrium	0.0383 g.
Before Equilibrium	<u>0.0074</u> g.
Transfer	0.0309 g.

<u>Result</u> 0.03 ≅ 0.0309

TABLE XVI
UNIFORM DISTRIBUTION OF MOISTURE THROUGHOUT THE DESICCANT BED

Time of Air	Sample Mois	ture Content,	Per Cent	on a Bone	Dry Basis
Circulation (hours)	Bottom #1	Bottom #2	Middle	Top #1	Top #2
1	10.20	10.33	10.78	11.20	11,27
2	10.25	10.38	10.72	10.90	10.98
3	10.38	10.44	10.62	10.81	10.84
3.5	10.56	10.58	10.62	10.64	10.69
4	10.62	10.61	10.61	10.62	10.61

TABLE XVII

PROOF THAT EQUILIBRIUM WAS REACHED
(Sample: NB-14857 at 25°C)

Grams Water per 100 Grams Desiccant	ppm Water in F-12, Initially	ppm Wate in F-12 Finally		Time for Equilibrium, Hours
9.81	3.42	3.98 4.07 3.89 4.15 4.09	, 00	18 24 36 48 60
		Average	4.03	
9.81	17.00	4.52 3.92 4.03 3.99 4.05		18 24 36 48 60
		Average	4.10	

(Sample: XH-151 at 0°C)

38.9	3.42	24.00 18.00 11.56 12.05 11.34	36 48 72 92 110
38.9	(Minimum Tim 17.21	50.00 50.00 36.00 12.31 11.82 12.12 11.95	nours) 24 36 72 94 110 132

TABLE XVIII

MOISTURE CONTENT OF THE FREON-12 BOTTLES (ppm)

	Bottle 1, (ppm)	Bottle 2, (ppm)
Determinations	4.08	4.04
	3.05	3.62
	3.12	3.92
	3.61	3.54
	3.23	
Average:	3.42 ppm	3.78 ppm
Standard Deviation:	0.526 ppm	0.197 ppm
Standard Deviation on the Average:	0.304 ppm	0.099 ppm

TABLE XIX

EQUILIBRIUM MOISTURE CONTENT OF PA-100 SILICA GEL AND DRIERITE, IN F-12
DATA FROM THE WORK OF GULLY AND TOOKE

c/c _s	Grams of Water per 100 Grams	of Bone Dry Desiccant
	PA - 100 Silica Gel	Drierite
1.8		0.25
2		5.75
5	5.5	6.00
10	7.9	6.20
15	9.3	6.25
20	10.8	6,35
25	12.0	6.50
30	13.5	
35	15.0	6.75
40	17.0	
45	19,6	7.00
50	22.6	eneration of the School and Every and Association of the School and Association (School and Association Control
55	26.1	7.20
60	30.9	7.30
64.6	37.0	
70		7.55
75		7.69

TABLE XX

EQUILIBRIUM MOISTURE CONTENT OF XH-151 ALUMINA IN FREON-12

Temperature: 0°C Initial Water Content of Freon: 3.78 ppm Rate of Expansion: 14 - 18 g/h

% H ₂ O of XH-151 (B.D.Basis)	Final H ₂ 0 Content of F-12, (ppm)	Average Concentration (ppm)	Relative Saturation (100 C/C _s)
30.50	12.00 11.48 12.89	12.12	49.00
6,55	0.51 0.48 0.52	0.50	2.04
16.21	5.12 4.63 5.34	5.03	20.25
11.73	1.27 0.98 1.42	1.22	4.92
19.95	7.99 8.32 8.57	8.29	33.40
24.05	10.00 10.25 9.78	10.00	40.40
27.32	11.21 10.67 11.57	11.13	44.90
34.31	12.92 13.61 12.25	12.92	52.10
38.90	13.59 14.32 12.39	13.43	54.40

TABLE XXI

EQUILIBRIUM MOISTURE CONTENT OF XH-151 ALUMINA IN FREON-12

Temperature: 25°C
Initial Water Content of Freon: 3.42 ppm

			er (en Carpa) laka melali gaj kija aktikki in tera arbitako er kila in tila in kila in kila in kila in kila i			THE PARTY OF THE P
% Water in XH-151 (B.D.Basis)	Final H ₂ O in F-12, ppm	Expansion Rate g/hr	Correction ppm	Corrected Concentra- tion ppm	Average ppm	Relative Satura- tion (100C/C _s)
6.55	1.94 0.92 2.32	14.4 12.7 16.1	nade all one were appears have garden account to the control of th	1.94 0.92 2.32	1.72	1.89
13.69	5.56 9.12 19.25	15.2 26.2 52.0	4.0 13.4	5.56 5.12 5.86	5.51	6.06
16.21	35.21 18.08 17.56	60.5 14.7 16.2	16.8	18.41 18.08 17.56	18.01	19.80
19.85	36.60 33.50 31.82	26.2 14.2 13.1	3.8	32.80 33.50 31.82	32.71	35.90
24.25	39.17 40.12 53.50	14.4 15.3 55.6	15,0	39.17 40.12 38.50	39.26	43.10
30.50	51.80 41.50 49.40 42.30 42.50 46.20 55.50 61.80	43.5 14.8 34.5 9.1 20.5 25.0 50.1 70.1	10.2 6.9 1.4 3.2 12.8 19.1	41.60 41.50 42.50 42.30 41.10 43.00 42.70	42.17	46.40
38.90	49.90 51.50 59.10	14.2 12.1 40.0	9.00	49.90 51.50 50.10	50.50	55.05
18.51	24.21 23.71 24.12	12.3 14.7 16.2		24.21 23.71 24.12	24.01	26.40
22.48	34.25 33.71 34.02	10.2 17.1 15.3		34.25 33.71 34.02	33.99	37.25

TABLE XXII

EQUILIBRIUM MOISTURE CONTENT OF XH-151 ALUMINA IN FREON-12

Temperature: 50°C Initial Water Content of Freon-12: 378 ppm Rate of Expansion: 14 - 18 g/hr

% H ₂ O of XH-151 (B.D.Basis)	Fural Water Content of F-12, ppm	Average Concentration ppm	Relative Saturation (100 C/C _s)
38.9	149.82	149.75	55.50
	150.63		
	148.72		
30.5	125.78	125.27	46.45
	125.21		
	124.82		
19.95	97.07	97.73	36.20
	97.81 98.32		
16.21	53.87	53.45	19.75
	53.45		
	53.04		
6.55	4.80	4.94	1.83
	5.05		
	4.97		

TABLE XXIII

EQUILIBRIUM MOISTURE CONTENT OF F-1 ALUMINA IN FREON-12

Temperature: O°C

Initial Moisture Content of F-12: 3.42 ppm

Average Expansion Rate: 14 - 18 g/hr.

% Water of F-1 Alumina (B.D.Basis)	Residual Water of F-12, ppm	Average ppm	Relative Saturation (100 C/C _S)
29.45	16.220 17.820 17.770	17.270	69.600
23.55	12.610 13.520 13.270	13.130	53.100
16.35	4.860 4.750 4.230	4.480	18.000
8.92	.487 .412 .522	.473	1.905
12.87	.812 .787 .832	.810	3.260
20.72	9.400 8.920 10.140	9.380	37.800
26.25	16.080 14.930 15.620	15.540	62.600

TABLE XXIV

EQUILIBRIUM MOISTURE CONTENT OF F-1 ALUMINA IN FREON-12

Temperature: 25°C Initial Moisture Content of F-12: 3.42 ppm Average Expansion Rate: 14 - 18 g/hr.

% Water of F-1 Alumina (B.D.Basis)	Residual Water of F-12, ppm	Average ppm	Relative Saturation (100 C/C _S)
8.89	1.93 0.92 2.15	1.66	1.82
13.85	5.36 5.57 6.02	5.65	6.20
19.55	38.30 36.90 37.10	37.42	41.10
23.45	46.40 45.50 46.05	45.98	50.40
16.55	17.21 16.95 17.52	17.22	18.91
29.45	67.60 66.90 68.10	67.53	74.40
26.25	57 .41 56 . 82 57 . 95	57.39	62.95
12.71	2.85 2.55 2.93	2.77	3.04
15.5	9.82 10.57 10.12	10.17	11.17

TABLE XXV EQUILIBRIUM MOISTURE CONTENT OF F-1 ALUMINA IN FREON-12

Temperature: 50°C Initial Moisture Content of F-12: 3.78 ppm Average Expansion Rate: 14 - 18 g/hr.

% Water of F-1 Alumina (B.D.Basis)	Residual Water in F-12,ppm	Average ppm	Relative Saturation (100 C/C _s)
8.92	4.72 4.85 4.68	4.75	1.76
13.78	16.92 16.14 16.07	16.37	6.05
20.02	111.21 112.05 112.97	112.07	41.60
26.17	168.98 169.27 169.92	169.39	62.80
29.45	198.74 200.82 201.31	200.32	74.4

TABLE XXVI

EQUILIBRIUM MOISTURE CONTENT OF NB-14857 SILICA GEL IN FREON-12

Temperature: O°C

Initial Moisture Content of F-12: 3.42 ppm

Average Expansion Rate: 14 - 18 g/hr.

% Water of NB_14857 Silica Gel (B.D.Basis)	Residual Water of F-12, ppm	Average ppm	Relative Saturation (100 C/C _s)
42.5	17.38 16.82 16.21	16.8	67.90
6.18	1.35 .98 .99	1.11	4.48
15.52	4.25 3.83 3.72	3.93	15.83
31.	13.92 14.42 13.61	14.01	56.50
37.22	15.21 16.11 16.98	16.10	64.90
26.87	12.05 11.72 11.23	11.66	47.00
11.92	2.11 1.95 2.25	2.1	8.49
21.17	8.27 8.71 8.93	8 . 63	34.80

TABLE XXVII

EQUILIBRIUM MOISTURE CONTENT OF NB-14857 SILICA GEL IN FREON-12

Temperature; 25°C

Initial Moisture Content of F-12: 3.42 ppm.

Average Expansion Rate: 14 - 18 g/hr.

% Water of NB-14857 Silica Gel (B. D. Basis)	Residual Water of F-12, ppm	Average ppm	Relative Saturation (100 C/C _S)
6.165	2.81 3.22 1.51	2.51	2.76
20	28.70 27.50 29.10	28.43	31.27
9.81	4.25 4.01 3.56	3.94	4.33
22.40	33.30 34.20 33.10	33.53	36.80
12.71	10.80 10.15 11.23	10.72	11.80
31	50.45 49.27 51.12	50.28	55.20
15.50	14.95 15.91 15.68	15.51	17.10
38.30	60.50 61.80 59.70	60.66	66.60
42.45	65.40 63.92 64.62	64.64	71.10
18.12	21.81 22.45 22.05	22.10	24.25
26.13	41.89 43.45 43.21	42.85	47.00

TABLE XXVIII

EQUILIBRIUM MOISTURE CONTENT OF NB-14857 SILICA GEL IN FREON-12

Temperature: 50°C Initial Moisture Content of F-12: 3.78 ppm Average Expansion Rate: 14 - 18 g/hr.

% Water of NB-14857 Silica Gel (B. D. Basis)	Residual Water of F-12, pp,	Average ppm	Relative Saturation (100 C/C _S)
6.18	7.52 7.08 6.88	7.16	2.65
18.31	63.73 64.21 64.87	64.27	23.77
26.23	122.98 123.87 122.74	123.19	45.58
31.50	143.71 144.73 145.21	144.58	53.50
41.92	182.90 184.73 183.18	183.60	68,00

TABLE XXIX

EQUILIBRIUM MOISTURE CONTENT OF XH-151 ALUMINA IN FREON-12

Standard Deviation, $\mathcal{G}(x)$, ppm Standard Deviation on Average, $\mathcal{G}(\overline{x})$, ppm Drying Efficiency, η

% H ₂ O of XH-151 (B.D.Basis)	Average Water Concentration of F-12,ppm	Temperature °C	ppm (x)	$\mathcal{O}(\bar{x})$	ŋ
6.55 11.73 16.21 19.95 24.05 27.32 30.50 34.31 38.90	•505 1.220 5.030 8.290 10.000 11.130 12.120 12.920 13.430	0 0 0 0 0 0 0	.015 .182 .278 .198 .192 .350 .581 .555	.009 .105 .161 .114 .111 .202 .336 .321	96.5 93.9 79.6 66.6 59.6 54.0 51.1 47.9 44.5
6.55 13.69 16.21 19.88 24.25 30.50 38.90 18.51 22.48	1.72 5.51 18.01 32.71 39.26 42.17 50.50 24.10 33.99	25 25 25 25 25 25 25 25 25 25	•599 •304 •350 •731 •665 •631 •710 •218 •221	.346 .175 .202 .428 .384 .223 .410 .126 .128	98.1 93.9 80.4 64.1 57.0 53.6 45.5 72.5 62.6
6.55 16.21 19.95 30.50 38.9	4.94 53.45 97.73 125.27 149.75	50 50 50 50 50	.097 .417 .522 .394 .780	.057 .241 .302 .228 .450	98.1 80.4 63.9 53.5 44.5

TABLE XXX

EQUILIBRIUM MOISTURE CONTENT OF F-1 ALUMINA IN FREON-12

Standard Deviation, $\sigma(x)$, ppm Standard Deviation on Average, $\sigma(\overline{x})$, ppm Drying Efficiency, $\sigma(x)$

% H ₂ O of F-1 ² Alumina (B.D.Basis)	Average Water Concentration of F-12, ppm	Temperature °C	ppm (x)	Ç(₹) ppm	% ๆ
29.45 23.55 16.35 8.92 12.87 20.72 26.25	17.27 13.13 4.48 .47 .81 9.38 15.54	0 0 0 0 0	.735 .384 .305 .460 .173 .512	.425 .222 .176 .266 .100 .296 .267	30.17 47.05 82.00 98.10 96.60 62.30 37.35
8.89 13.85 19.55 23.45 16.35 29.45 26.25 12.71 15.50	1.66 5.65 37.43 45.98 17.22 67.53 57.39 2.77	25 25 25 25 25 25 25 25 25 25	.526 .275 .619 .416 .223 .491 .461 .164	.304 .159 .356 .240 .129 .273 .266 .095	99.00 93.60 58.90 49.40 81.00 25.75 36.95 96.90 88.60
8.92 13.78 20.02 86.17 29.45	4.75 16.37 112.07 169.39 200.32	50 50 50 50 50	.072 .122 .718 .352 1.120	.041 .071 .415 .203 .646	98.25 94.00 58.50 37.30 25.85

TABLE XXXI

EQUILIBRIUM MOISTURE CONTENT OF NB-14857 SILICA GEL IN FREON-12

Standard Deviation, $\sigma(x)$, ppm Standard Deviation on Average, $\sigma(x)$, ppm Drying Efficiency, $\sigma(x)$

% H ₂ O of NB-14857 Silica Gel (B. D. Basis)	Average Water Concentration of F-12, ppm	Temperature °C	G(x)	σ(x) ppm	% ŋ
6.18 11.92 15.52 21.17 26.87 31 37.22 42.5	1.11 2.10 3.93 8.63 11.66 14.01 16.10	0 0 0 0 0 0	.171 .122 .226 .219 .244 .421 .684	.099 .071 .131 .121 .199 .244 .394	95.6 91.5 84.2 65.1 53.0 43.5 35.1 32.2
6.165 9.81 12.71 15.5 18.12 20. 22.4 26.13 31 38.3 42.42	2.51 3.94 10.72 15.51 22.10 28.43 33.53 42.85 50.28 60.66 64.64	25 25 25 25 25 25 25 25 25 25	.730 .304 .465 .409 .264 .680 .479 .685 .759 .865	.421 .175 .268 .236 .152 .428 .276 .395 .437 .499	98.3 95.7 88.4 83.0 75.6 70.0 63.1 53.0 44.9 33.4 28.9
6.18 18.31 26.23 31.50 41.92	7.16 64.27 123.19 144.58 183.60	50 50 50 50 50	.250 .467 .485 .625 .805	.144 .269 .280 .361 .465	97.5 76.1 54.4 46.5 32.0

TABLE XXXII

EFFECT OF MOISTURE CONCENTRATION OF REFRIGERANT ON PRECISION OF DETERMINATION

(Combined Results for all Desiccants at 0, 25 and 50°C)

Moisture Concentration Interval, ppm	Average Moisture Concentration,ppm	Average Standard Deviation, ppm
0 - 10	3.94	.315
10 - 20	14.49	.476
20 - 40	31.40	.526
40 - 60	48 . 94	.603
60 - 95	62.85	.626
95 - 200	145.10	.688
(140 - 200)	(169.52)	(1776)

TABLE XXXIII $\mbox{DEVIATION OF THE O^C DATA FORM C/C}_{\mbox{\scriptsize S}} \mbox{ AVERAGE CURVE}$

Material	C/C _s	Deviation from Average Curve,ppm	$\widehat{n}_{\mathrm{L}}(\mathbf{x})$
NB-14857 \$10 ₂	0.6790 0.0448 0.1585 0.5650 0.6490 0.4700 0.0849 0.3480	- 0.0190 0.0090 - 0.0180 0.0215 - 0.0072 0.0005 - 0.0001 0.0061	0.01060 0.00561 0.00754 0.01012 0.01048 0.00974 0.00650 0.00906
XH-151 Al ₂ 0 ₃	0.4900 0.0200 0.2020 0.0490 0.3340 0.4040 0.4490 0.5210	0.0000 0.0002 - 0.0005 0.0001 - 0.0010 - 0.0050 0.0000 - 0.0008 - 0.0250	0.00979 0.00470 0.00799 0.00572 0.00895 0.00936 0.00961 0.00994
F-1 Al ₂ 0 ₃	0.6960 0.5310 0.1800 0.0191 0.0326 0.3780 0.6260	- 0.0250 0.0010 0.0000 0.0000 - 0.0100 - 0.0300 0.0000	0.01062 0.01001 0.00775 0.00460 0.00521 0.00924 0.01041
Average		- 0.0043	0.00848

 $t = \frac{0.0043}{0.00848}$ 24 = 2.48

t_{Table} = 3.767 (Maximum for 99 % probability)

TABLE XXXIV DEVIATION OF THE 25° C DATA FROM THE C/C AVERAGE CURVE

MATERIAL	C/C _s	Deviation from Average Curve,ppm	♂ (x) ppm
NB-14857 SlO ₂	0.0276 0.3127 0.0433 0.3680 0.1180 0.5520 0.1710 0.6660 0.7110 0.2430 0.4700	- 0.005 0.010 0.000 - 0.005 0.022 0.000 0.015 0.015 - 0.021 0.015 0.000	0.00185 0.00326 0.00206 0.00354 0.00260 0.00374 0.00284 0.00390 0.00396 0.00308
XH-151 Al ₂ 0 ₃	0.0189 0.6000 0.1980 0.5590 0.4310 0.4640 0.5500 0.2640 0.3730	0.000 - 0.015 - 0.010 0.022 - 0.026 0.000 - 0.009 - 0.016 - 0.010	0.00169 0.00222 0.00293 0.00336 0.00351 0.00357 0.00372 0.00314
F-1 A1 ₂ 0 ₃	0.0182 0.0620 0.4110 0.5040 0.1891 0.7440 0.6300 0.0300 0.1120	0.000 0.000 0.042 0.017 0.000 0.015 0.000 - 0.010 - 0.015	0.00168 0.00223 0.00348 0.00366 0.00290 0.00398 0.00383 0.00189 0.00255
Average		0.00107	0.00304

 $t = \frac{0.00107}{0.00304}$ 29 = 1.895

 $t_{Table} = 3.674$ (Maximum for 99 % probability)

TABLE XXXV DEVIATIONS OF THE 50°C DATA FROM THE C/C AVERAGE CURVE

Material	C/C _s	Deviation from Average Curve,ppm	$\mathcal{O}(x)$
NB-14857	Account of the second s		and the second s
SIO	0.0265	- 0.005	0.000721
2	0.2377	- 0.027	0.000960
	0.4558	0,005	0.001506
	0.6805	- 0.015	0.001660
		0.000	0.001729
XH-151			
Al ₂ 0 ₃	0.5550	- 0.005	0.001591
72.3	0.4650	- 0.021	0.001510
	0.3620	0.028	0.001468
	0.1980	0.000	0.001338
	0.0183	0.000	0.000728
F-1 Al ₂ 0 ₃	0.0176	0,000	0.000738
2-3	0.0605	0.000	0.001325
	0.4160	0.024	0.001542
	0.6280	0.001	0.001602
	0.7440	0,010	0.001691
Average		0.00034	0.001274

$$t = \frac{0.00034}{0.001274} \qquad 15 = 1.031$$

t_{Table} = 4.140 (Maximum for 99% probability)

TABLE XXXVI

"F" TEST OF SIGNIFICANCE FOR XH-151 ALUMINA - PROBABILITY THAT ALL THREE TEMPERATURES' DATA LIE ON THE SAME CURVE

Percent Moisture Content of the	Relative Saturation Values			18 E.18
Desiccant (B.D.Basis)	o°c	25 ⁰ C	50° C	Value
6.55	0.0207 0.0196 0.0210	0.0213 0.0101 0.0255	0.0178 0.0187 0.0184	0.167
16.21	0.2065 0.1956 0.2101	0.2027 0.1986 0.1930	0.1990 0.1973 0.1965	1.414
19.95	0.3220 0.3356 0.3457	0.3600 0.3685 0.3500	0.3595 0.3615 0.3640	0.887
30 . 5	0.4845 0.4617 0.4989	0.4555 0.4649 0.4515	0.4650 0.4640 0.4617	3.594
38.9	0.5457 0.5780 0.5185	0.5490 0.5655 0.5510	0.5545 0.5560 0.5500	1.538

[&]quot;F" Value From the Table: 10.92 (Maximum Value for 99% Probability)

TABLE XXXVII $\mbox{"F" TEST OF SIGNIFICANCE FOR NB-14857 Slo}_2 \mbox{ AND F-1} \mbox{ Al}_2\mbox{O}_3$

% Moisture of Desiccant	Relative Saturation Values			nFn Value
(B.D. Basis)	0°C	25 ⁰ 0	50°G	
NB-14857 S10 ₂ 6.18	0.05500 0.03978 0.04015	0.03085 0.03540 0.01660	0.02785 0.02620 0.02545	5.581
26.23	0.47600 0.47300 0.47450	0.46000 0.47600 0.47500	0.45900 0.47800 0.45500	1.213
F-1 Al ₂ 0 ₃ 8.92	0.01963 0.01662 0.02107	0.02120 0.01010 0.02465	0.01750 0.01796 0.01732	1
26.17	0.64550 0.60300 0.63050	0.63000 0.62450 0.63550	0.62500 0.62600 0.62870	1
29.45	0.65500 0.71950 0.71610	0.74400 0.73500 0.74900	0.73500 0.74400 0.74550	4 .3 83

[&]quot;F" Value From the Table: 10.92 (Maximum Value for 99% Probability)

VITA

Marc Francis René Fontaine candidate for the degree of Doctor of Philosophy

Thesis: THE EQUILIBRIUM MOISTURE DISTRIBUTION BETWEEN AIR OR FREON-12

AND SELECTED COMMERCIAL DESICCANTS

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Minor: Mathematics

Biographical:

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THESIS TITLE: THE EQUILIBRIUM MOISTURE DISTRIBUTION BETWEEN

AIR OR FREON-12 REFRIGERANT AND SELECTED

COMMERCIAL DESICCANTS

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