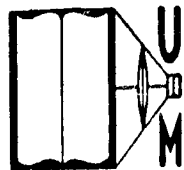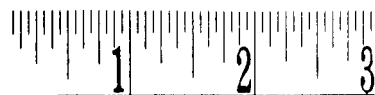TITLE _ADSORPTION OF ALIPHATIC AMINE VAPORS BY SILICA GEL_

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ADSORPTION OF ALIPHATIC AMINE VAPORS

BY SILICA GEL

by

Donald G. Dobay

A Dissertation Submitted in Partial Fulfillment
of the Requirements for the degree of
Doctor of Philosophy in the
University of Michigan

Committee in Charge:
Professor Floyd E. Bartell, Chairman
Professor Ernest F. Barker
Professor Joseph O. Halford
Professor Hobart H. Willard
Associate Professor Lee O. Case

Ann Arbor, Michigan
September, 1948

TO JANET

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INTRODUCTION

The adsorption of gases by solids has been studied for a long period of time, reports of such adsorption having been recorded over 170 years ago (1). During this period there have been a number of theoretical and experimental studies on the nature of adsorption. One of the latest of these adsorption theories has occasioned wide-spread interest and much activity in the adsorption field. In 1938, Brunauer, Emmett, and Teller (2) derived from kinetic considerations an equation which, with some later amplification by Brunauer, Deming, Deming, and Teller (3), could be used to express the manifold types of vapor and gas adsorption which had been observed experimentally.

Another theory which had historical precedence over this recent theory was the capillary condensation theory. Zsigmondy (4) studied the pore structure of silica gel by ultramicroscope methods and concluded that in the fine capillaries, the vapor pressure was much lower than that of the bulk liquid, and that hence condensation would occur in these capillaries at pressures lower than the vapor pressure of the bulk liquid. Zsigmondy's formulation was based upon the thermodynamic relationship between the radius of curvature of a liquid

surface, r, and the vapor pressure, p, which was de-
rived by Lord Kelvin,

$$ln \; P/p_0 \; = \; \frac{2 \gamma V}{r R T} \qquad (1)$$

where p_0 is the vapor pressure of a sample of the bulk
liquid (having a radius of curvature equal to infinity),
γ is the surface tension, V the molar volume, R the gas
constant, and T the temperature. A similar relationship
has been derived independently by Helmholtz.

Patrick and co-workers (5) investigated the
adsorption of several substances such as sulfur dioxide,
carbon tetrachloride, ethyl alcohol, water, carbon dioxide,
and nitrous oxide on silica gel and attempted at first
to explain the entire process of adsorption as capillary
condensation. Patrick later modified his views, allowing
for the existence of adsorption of a monolayer, but held
that all further apparent adsorption beyond the monolayer
was in fact a capillary condensation. Certain semi-
empirical equations were developed to describe such results,
but these have met with considerable objection on the
grounds both of the logic involved and the correlation
of experimental data obtained (6, 7).

Kubelka (8) has developed a theory of adsorption
based on the Kelvin equation, but modified by the use of
one empirical constant in place of the several physical

constants in equation (1). This method has been severely criticized by Lindau (9), on both theoretical and experimental grounds. Both Patrick's and Kubelka's followers attempted to extend the use of their equations to moderately low pressure regions, where the equations necessitated the assumption of adsorption in capillaries which were smaller than the adsorbate molecules.

Foster (10) has had considerable success in applying the Kelvin equation to various samples of porous oxide gels and has obtained good correlation for the capillary radii using different vapors. The vapor pressures of the bulk liquids of his adsorbate systems have all been of the same order of magnitude, however, and his arguments are weakened somewhat for want of additional evidence supporting the mechanism of capillary condensation.

The Brunauer-Emmett-Teller multimolecular theory (commonly abbreviated to BET theory) has been considered by some to be the answer to all adsorption phenomena. "Its most general equation includes all isotherm types as special cases and describes the shape of each isotherm type through the entire range of adsorption, from zero pressure to saturation pressure. This includes the region of unimolecular adsorption, multimolecular adsorption, and capillary condensation, in contrast to the separate treatments accorded to these three regions by the (other) theories." (11)

This universal theory is based upon the assumption that the same forces as those producing condensation are responsible for adsorption. The derivation of the isotherm equations is accomplished in a manner analogous to the derivation of the Langmuir equation for monolayer adsorption (12). At equilibrium the rate of condensation and of evaporation of molecules from each adsorbed layer is considered constant. Making some assumptions as to the forces of adsorption involved in each layer, the amount adsorbed is calculated by a summation procedure. For plane surfaces, the summation is carried out for an infinite number of layers. If there is spatial restriction to the number of layers, as is the case in capillaries, the summation may be carried only to the restricted number of layers that may be accommodated on the surface.

In some cases involving capillaries the BET equation did not predict sufficient adsorption to correspond to the experimental data. The BET equation was then extended by Brunauer, Deming, Deming, and Teller (3), by introducing an additional constant to account for the additional adsorption. The additional adsorption was considered due to additional energy liberated when the very last layer of molecules necessary to fill a given capillary was slipped into place; when this last layer was adsorbed not only was the normal heat of adsorption

liberated, but in addition surface energy was set free, since the surfaces of the walls of the capillary disappeared. The proponents of this theory considered it unnecessary to include the effect of curvature on the vapor pressure of the adsorbate, since the entire adsorption process was quantitatively describable without such inclusion.

In the present research the adsorption on silica gel of the lower members of the aliphatic amines has been investigated. The purposes and goals of this research may be outlined as follows:

A. To determine quantitatively the adsorption of aliphatic amines on silica gel as a function of their pressure.

B. To investigate any unusual features of the adsorption characteristics of the amine-silica systems.

C. To ascertain the applicability and limitations of the BET multimolecular theory in these systems.

D. To investigate the effect of the high degree of capillarity on the adsorption process and to determine whether it is necessary to consider capillary condensation effects in addition to multimolecular adsorption.

E. To determine the heats of adsorption of the amines on silica gel.

F. To evaluate the free surface energy changes involved in the process of adsorption.

It was believed that with the information to be obtained in the above proposed research it should be possible to acquire a better understanding of the processes involved in adsorption.

MATERIALS

Preparation of Silica Gel

Silica gel is ordinarily made by acidification of sodium silicate solutions (5). Gels with exceptionally high activity have been obtained by mixing solutions of iron or of other metals with the silicate solution (13, 14). Such gels are purified by prolonged washing with water, or with water and acid, to remove the soluble salts produced during the formation of the gel.

A gel which contained only volatile impurities has been prepared by the hydrolysis of silicon tetrachloride (15). The only substances present other than silica were water and hydrochloric acid, both quite volatile materials. The principle advantage of this gel is that it can be obtained in a condition of high purity.

A batch of gel sufficient for the entire research program was made by the following method: Silicon tetrachloride was redistilled. The middle fraction boiling between 56-58° was slowly distilled again, the end of the condensor adaptor dipping below the surface of a small beaker of mercury, placed in a large beaker of double distilled water. The mercury was needed as a trap to keep the adaptor from being clogged by silica. The distillation

was continued until the water showed a blue tinge. After
standing at room temperature the solution set to a gel.
This gel was broken up by stirring, was heated in an oven
at 70-80° C. and was stirred daily, for ten days, in order
to remove the bulk of the water and acid. The gel was
next heated at 300° C. with a stream of dried air passing
through it for five hours, and was then poured into a
large beaker of double distilled water. This rapid
cooling caused the large aggregates of gel to shatter
by action of the thermal strain set up in the particles.
The quenching in water also removed hydrogen chloride.
The high temperature heating and subsequent quenching in
pure water was repeated five more times. The gel particles
appeared quite uniform and were used without sieving. The
presence of chloride ion could not be detected after the
second cycle. The gel left no residue when treated with
hydrofluoric acid.

Purification of Liquids

The lower members of the aliphatic amine series were available as comparatively pure commercial products, the main impurity being water.

Diethylamine.

Commercial diethylamine was refluxed for twenty hours with excess sodium and distilled through a vacuum-jacketed packed column, the middle fraction boiling at $53.80 \pm .05°$ (733.9 mm.) being collected over sodium.

n-Butylamine.

Commercial normal mono-butylamine of 97.8% purity was refluxed for twenty-four hours with excess sodium and distilled through a vacuum-jacketed packed column, the middle fraction boiling at $75.70 \pm .05°$ (736.0 mm.) being collected over sodium. A portion of this material was redistilled at 130 mm. in an all glass apparatus and was shown to have refractive index and vapor pressures identical to those of the material distilled at atmospheric pressure.

Di-n-butylamine.

Commercial normal dibutylamine was refluxed with reagent potassium hydroxide for several hours and then distilled through a twenty stage vacuum-jacketed Brunn column and collected over reagent potassium hydroxide

pellets. The middle fraction with a boiling point of
158.1 ± .05° (732.2 mm.) was used. The refractive index
of this material was not altered by redistillation in
an all-glass apparatus at 4 mm. pressure.

Water.

Distilled water was redistilled from alkaline
permanganate solution in a Pyrex still and was stored in
a glass stoppered flask which had been used for double
distilled water for several years.

Mercury.

The mercury used in the manometers, gauges and
cutoffs was all of redistilled reagent quality. The
declared maximum amount of base metal present was 0.0001%
and of noble metal 0.003%.

Purification of Gases

Nitrogen.

The nitrogen used for adsorption determinations was obtained from a cylinder of water-pumped nitrogen and was of 99.8% purity. It was passed over a tube of anhydrous calcium chloride and then through fuller's earth impregnated with reduced, finely divided copper metal heated to 200° to remove any traces of oxygen. It was next passed successively through Drierite, activated silica gel, Dehydrite, and a liquid air trap.

The nitrogen used for other purposes was purified by being passed slowly through a tube of copper gauze heated to 500° (16). Analysis of the nitrogen had shown less than 0.0002% oxygen.

Helium.

The helium used for dead space determinations in the volumetric apparatus was obtained by passing medical grade helium through a trap which contained activated charcoal and which was immersed in liquid nitrogen. The helium used for filling and flushing the gravimetric apparatus was dried by passing it over Dehydrite and indicating Drierite.

Ammonia and hydrogen chloride.

The ammonia and the hydrogen chloride used for filling the vapor pressure thermometers were commercial anhydrous grades. Each gas was purified in its respective thermometer by freezing and continued evacuation of the frozen, solid phase.

APPARATUS

Gas Adsorption, Volumetric

The adsorption of nitrogen by silica gel was determined, volumetrically, by measuring the pressure of the gas before admission to the sample of adsorbent and again after equilibrium had been attained by the gas in contact with the sample of adsorbent. The volume of the system being known, the number of moles adsorbed could be calculated.

In general the apparatus and method approximated that described by Emmett (17) and also, in more detail, by Beamsderfer (18) and Dodd (19), and will not be described again here. Certain modifications were introduced to effect an improvement in reliability of the results while at the same time simplifying the experimental procedure and reducing the time necessary for the determinations. The most important of these modifications was the use of a vapor pressure thermometer to determine the pressures. This thermometer was constructed as shown in Figure (1). It was evacuated by a mercury diffusion pump with mercury in both arms. The system was flushed out ten times with highly purified nitrogen. While under evacuation, point A was sealed off and nitrogen was introduced into the

FIGURE 1

FIGURE 1

HIGH VACUUM

NITROGEN

A

D

B

C
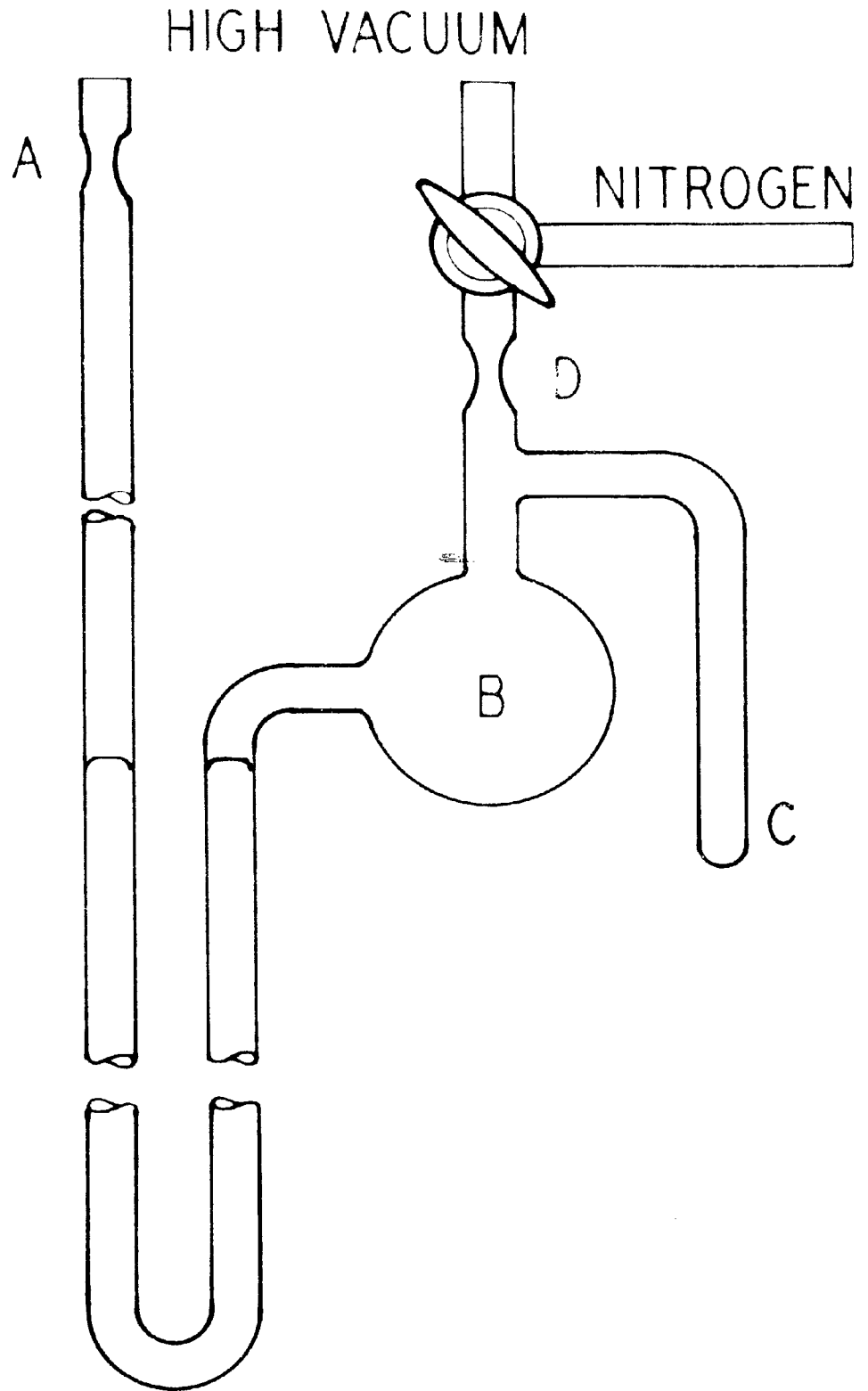
CONSTRUCTION OF NITROGEN
VAPOR PRESSURE THERMOMETER

reservoir B. A liquid nitrogen bath was placed around tube C and the space above the liquid nitrogen was evacuated slightly. This cooled the liquid nitrogen bath, thus reducing the pressure in the thermometer below atmospheric so that point D could be sealed off also.

In practice, tube C was introduced into the adsorbent bath. The nitrogen condensed and a two-phase, one component system was set up. Since there was only one degree of freedom under such conditions the pressure of the system was a single valued function of the temperature. However, this pressure was, by definition, the vapor pressure of liquid nitrogen at the temperature of the bath. For the adsorption measurements, this vapor pressure was employed and it was not necessary to ascertain the temperature of the bath. The advantages of measuring the pressure directly instead of measuring potential with a thermocouple (as was done by previous investigators), then calculating temperature, and finally calculating pressure, are immediately obvious. With the nitrogen vapor pressure thermometer the vapor pressure could be directly and continuously measured to within 1 mm. with an ordinary meter stick, whereas with the thermocouple an uncertainty in the calibration factor for the couple sometimes introduces errors amounting to 15-25 mm.

In the determination of pressures of nitrogen, before and after adsorption, it had been the practice to

eliminate the necessity for making a meniscus correction by adopting a special method of procedure. It was found that this correction could be easily determined, that it was constant over several millimeters length in the capillary and that much more reproducible results were obtained when it was used. Consequently, the meniscus correction method was used in this work.

Gas Adsorption Apparatus, Gravimetric

The volumetric method is not applicable when condensable vapors are present, since condensation would vitiate any pressure measurements. In such cases a gravimetric method is used. As early as 1926, McBain and Bakr (20) suggested a gravimetric method for adsorption measurements, utilizing the elongation of a quartz spiral. This method has been used, heretofore, only with systems in which equilibrium was reached in a comparatively short time. For this research the method was modified and the apparatus redesigned. Provision has been made for the complete exclusion of such contaminants as vacuum or stopcock greases from the adsorbent sample. It has also been made possible to investigate systems requiring a long period of time to reach equilibrium. The general arrangement of the apparatus is shown in Figures 2-4.

Adsorption chambers.

The quartz spring and the sample were housed in a Pyrex tube of 54 mm. O.D. (A, Figure 4, Figure 5). A standard taper 55/50 mercury seal joint was provided near the top so that the chamber could be opened, the spring calibrated and the sample introduced. No grease was ever used on these joints, but some lubrication was provided by carefully wiping the joints with a small amount of purified graphite. Glass handles were attached

FIGURES 2-5

Figure 2.   Close-up of Adsorption Apparatus
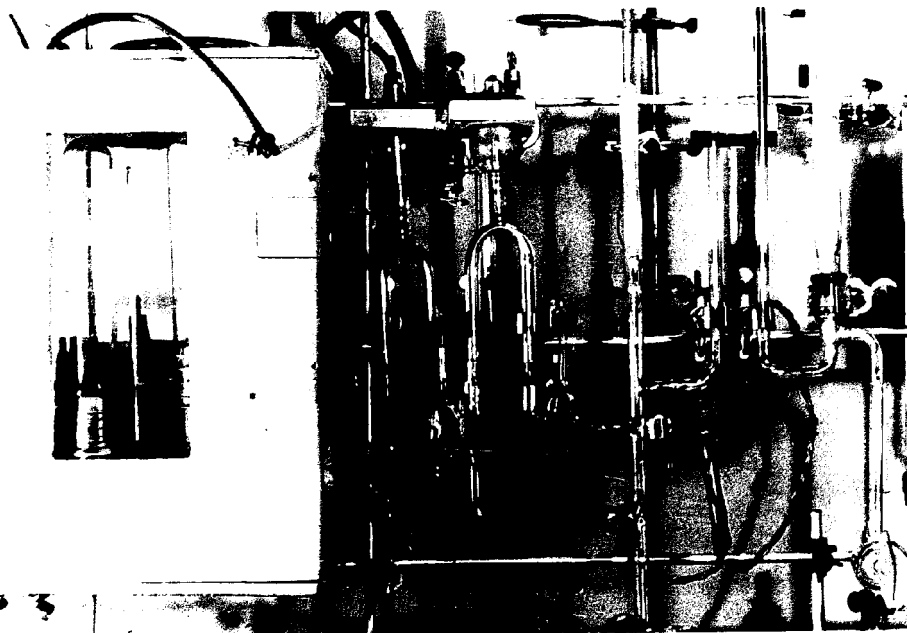
Figure 3.   Close-up of Double Adsorption
Apparatus with Thermostat in Place
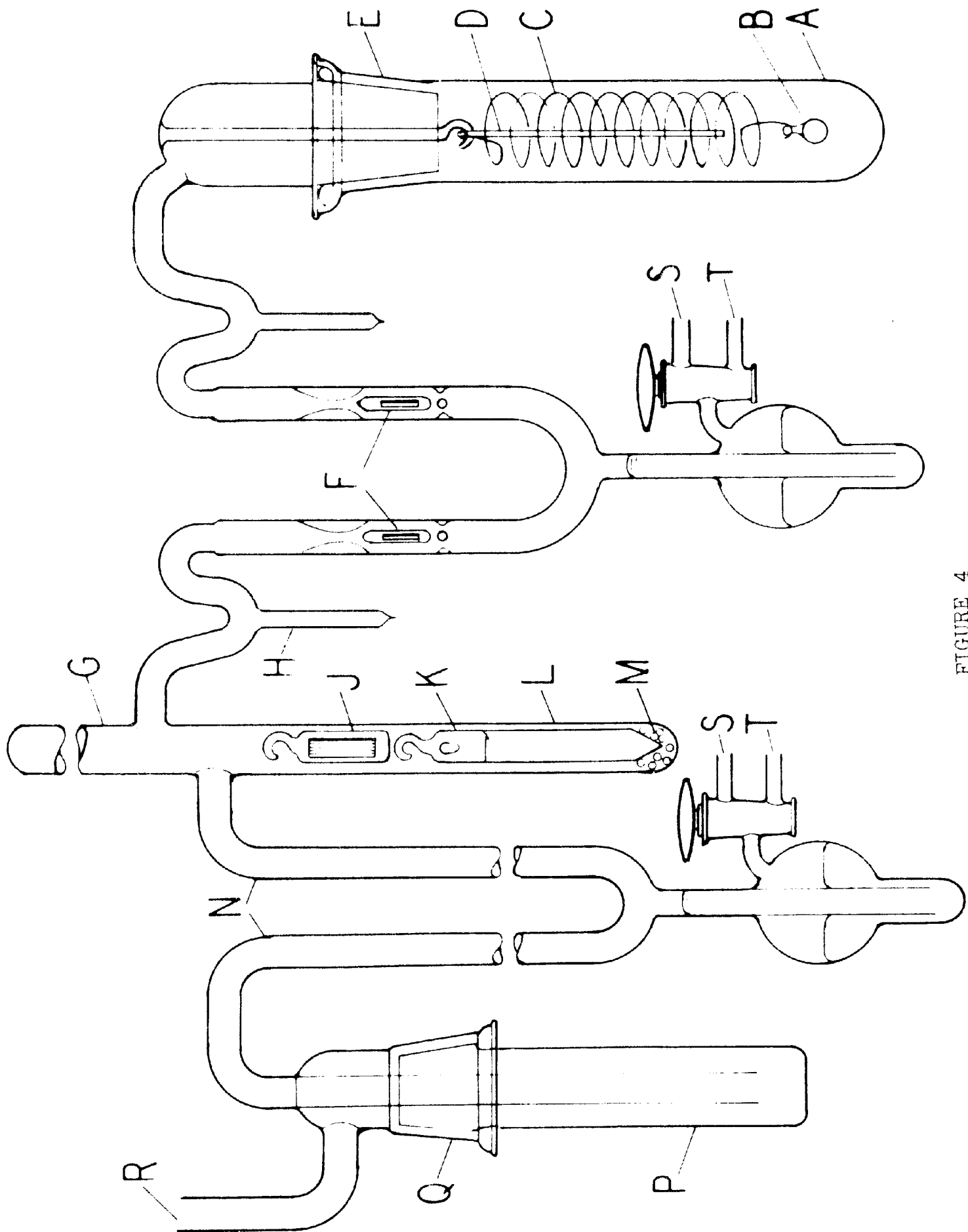
FIGURE 4
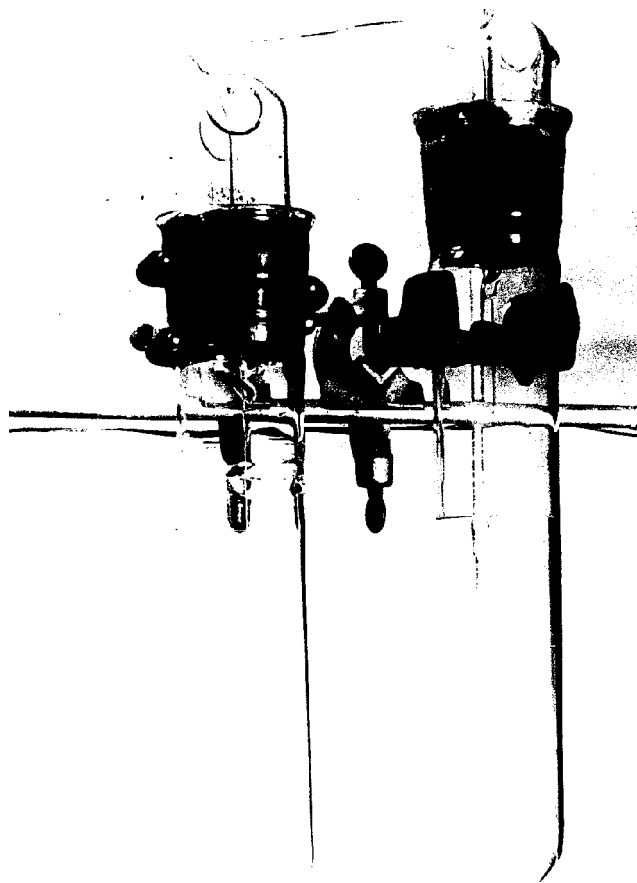
Figure 5. Double Adsorption Chambers

to facilitate opening of the chamber. The single chamber
arrangement used in the early part of this research is
shown in Figure 2. A second chamber was added (see Figure
5) so that check runs could be made on separate gel
samples. The second chamber was made to match the first
as closely as possible. A separate Stock cutoff (Figure 8)
was provided so that the individual isotherms could be
run at different pressure increments or different time
intervals if desired. The volumes of these chambers were
determined during construction of the apparatus by weighing
the water required to fill the chamber space.

Spring and adsorbent support.

Quartz springs have found wide favor for use
in adsorption systems, and have a number of advantages
which have made them particularly suitable for this re-
search. The springs follow Hooke's law closely over a
wide range and are capable of withstanding the high
temperatures which were used in the surface-treatment
process without distortion or hysteresis with respect to
elastic constants. Of special importance was the fact
that quartz can be used in studying adsorption on silica
gel without fear of its having any untoward effects upon
the vapor being adsorbed. Spring #1 consisted of 22
turns of fibre. The outside diameter of the helix was
2.54 cm. with a pitch of 0.16 cm. The fibre diameter was

0.025 cm. The elongation of this spring was 255 mm. per gram load. The largest total load used was about 400 mg.; the maximum load that the spring can carry was not determined. Spring #2 was ordered to the same specifications, but because of a slightly thicker fibre diameter the sensitivity of this spring was considerably less, the elongation per gram load being 153 mm. This was compensated for in practice by using larger samples of adsorbent with this spring, the largest total load used being 700 mg.

The springs were calibrated before and after the runs in order to insure that the heat treatments of the gel samples in situ did not alter the spring characteristics. The springs were found to have been unaltered. Calibration was accomplished by determining the change in elongation when known weights were added to the pan. The known weights were checked against a Bureau of Standards certified set of weights. It was demonstrated by experiment and calculation that, under the experimental conditions of pressure, temperature and volume of sample, the buoyancy correction need not be applied, this factor being below the limits of experimental error.

Several types of holders for the adsorbent (B, Figure 4) were tried. The most suitable was made from 8 mm. Pyrex tubing drawn down to about two mm. diameter and then worked in a micro flame. A bulb was blown in the end of this tube. Holes of controlled diameter were opened

up in the bulb by touching it with a sharp oxygen flame.
The stem through which the blowing had been done was then
thinned down over a very fine, pointed, high temperature
oxygen flame and was looped around to form a hook. Holders
of this type were successfully made weighing as little as
75-80 mg. and having a volume capable of containing over
320 mg. of silica gel. The springs and adsorption holders
may be seen in Figure 2.

Cathetometers.

Two cathetometers were used for this work. The
one used for the measurement of the elongation of the spring
could be read directly to 0.01 mm. and estimated to 0.001
mm. The other, used for the measurement of vapor pressure,
could be read directly to 0.05 mm. and estimated to 0.005
mm.

Reference rod.

In order to minimize any error due to a change
of relative position of the cathetometer with respect to
the spring, a reference rod was introduced. This was a
Pyrex rod about 2 mm. in diameter and about 100 mm. in
length, suspended from the same hook as the spring itself;
since this rod did not undergo any change in length at
constant temperature, it made possible the detection of
shift in the relative positions of the spring support and
the cathetometer.

Vacuum system.

In adsorption studies it is a prime requisite
that the surfaces be carefully purified and freed from
adsorbed impurities, even "inert" gases. This can best
be accomplished by heating the evacuated sample in situ.
The evacuation was accomplished by a two-stage mercury
diffusion pump, backed by a Hyvac oil pump. A McLeod
gauge calibrated to 10^{-5} mm. mercury was connected to the
vacuum manifold. The adsorption chambers could be isolated
from the rest of the apparatus by the mercury cutoffs F
and N in Figure 4. A trap (P, Figure 4), surrounded by
liquid nitrogen, protected the sample from back diffusion
of any traces of stopcock grease during the evacuation
process when the cutoffs were necessarily lowered. The
stopcocks along the main line of the high vacuum system
were of hollow plug, 10 mm. bore vacuum type. All stop-
cocks were lubricated with Apiezon grease of very low
vapor pressure (less than 5.10^{-7} mm. mercury at room tem-
perature (21)). The mercury diffusion pump was also pro-
vided with a liquid air trap and a dry ice-cellosolve trap.
It was consistently possible to achieve vacua of 10^{-5} mm.
mercury. When it was necessary to bring the system to
atmospheric pressure, connections were provided so that
this could be accomplished using dry helium gas. Helium
had the advantages of high diffusion upon subsequent
evacuation, negligible adsorption on the glass walls,

and freedom from condensation by the liquid nitrogen in the traps.

Heat treatment.

After being set in place in the adsorption chamber, the silica samples were heated prior to and during evacuation to 205-215° by means of a removable heater. The heater was constructed by winding nichrome ribbon over a thin sheet of moist asbestos which was on 54 mm. Pyrex tubing. The ribbon was then wrapped with several layers of thick moist asbestos sheeting and finally the outer layer was well saturated with sodium silicate solution. The moist assembly was slipped off the Pyrex form and dried electrically and in an oven. This heater was light in weight and could be slipped over the adsorption chambers to give a snug fit. The temperature of the heater was controlled by introducing a variable resistance in series.

The other portions of the adsorption system were treated by careful, intermittent flaming. The portions of the apparatus containing thick glass were baked more slowly by radiation from infrared heat lamps.

Temperature control.

Adsorption chambers. The necessity for elimination of all possible sources of vibration imposed serious restrictions in the design of the temperature control portions

of this apparatus. It was found early in the program that fluctuations in room temperature, though comparatively small in magnitude, could not be controlled by surrounding the chamber with vacuum flasks. Apparently the conduction of heat along the glass walls projecting into the room was sufficient so that this method merely reduced the room fluctuations.

Several designs of constant temperature boxes were made. The one found to be most satisfactory was constructed of Celotex and lined with asbestos. It was partitioned into two vertical chambers: one chamber housed the adsorption chambers (page 16), the other chamber housed the heating and cooling coils. Communication of the two chambers at the top and the bottom of the box allowed a continuous, cyclic circulation of the air in the box. The cooling was accomplished by a flow of water under steady hydrostatic head, through a copper finned tube. The heating was done electrically through a coil of Chromel-A wound on a section of quartz tubing, with variable resistors of several ranges, allowing fine adjustments, connected in series with the heating element. The circulation of air in the box was provided by a continuous stream of compressed air from the service lines. Copper baffles were placed above the heater and above the cooling fins so that thorough mixing of the air was achieved before it came into contact with the

adsorption chambers. Glass windows were arranged to permit illumination and observation of the adsorption chamber. The openings around the glass tubing leading to the vacuum system were stuffed with glass wool. The box was moderately light and could be disassembled conveniently to allow handling of the adsorption chambers.

Available thermoregulators to control the heater were not entirely satisfactory because of the comparatively small heat capacity of the air bath. At 40° it was possible to obtain fairly constant temperatures by adjusting the current so that the heater could be operated continuously. At 25° it was necessary to use intermittent heating controlled by a thermoregulator. The regulator adapted for use is shown in Figure 6. Regulation was based upon the change in vapor pressure of isopentane (A). The vapor pressure controls the motion of the mercury column (B), which opens and closes the heater circuit through an Aminco Supersensitive Mercury Relay. The stopcock in the horizontal arm permits storage of the regulator at ambient temperatures when it is removed from the thermostat, without requiring readjustment of the regulator when it is to be used again. A mercury droplet (C) seals off space D, maintaining a constant balancing pressure above the mercury column B. It was possible to control the thermostat temperature to 0.1° C. with this regulator.

Cryostat. The cryostat was mounted so as to surround the liquid adsorbate sample which was contained in tube L (Figure 4). For temperatures down to 0°, a one liter Dewar flask was used as the cryostat. However, with one of the systems investigated it was desirable to obtain temperatures at intervals down to -110°. In this range it was no longer possible to find convenient or safe eutectic salt mixtures or other simple means of providing fixed points which were spread at the desired intervals. For these temperatures a modification of the Bureau of Standards (22) cryostat was used (Figure 7). The adsorbate sample, suitable thermometers, and a glass stirrer provided with several blades were immersed in the cryostat fluid contained in the inner flask A. Flask A was a 500 ml. Dewar which had a 10 mm. tube sealed into it at the bottom. Flask B was a 4300 ml. Dewar flask. The space between flasks A and B was filled with liquid nitrogen, dry ice-cellosolve, or ice, whichever was appropriate to the temperature range desired. Tube C was connected to a mercury diffusion pump and Hyvac backing pump, and also had connections making it possible to admit dried helium gas. In operation, the refrigerant liquid D was allowed to cool the cryostat liquid E when helium was admitted into space F. By altering the degree of evacuation of space F, varying degrees of conduction across this space could be obtained, so that at the steady

FIGURES 6-7

FIGURE 6

C

D

A

MERCURY

B

TUNGSTEN
ROD
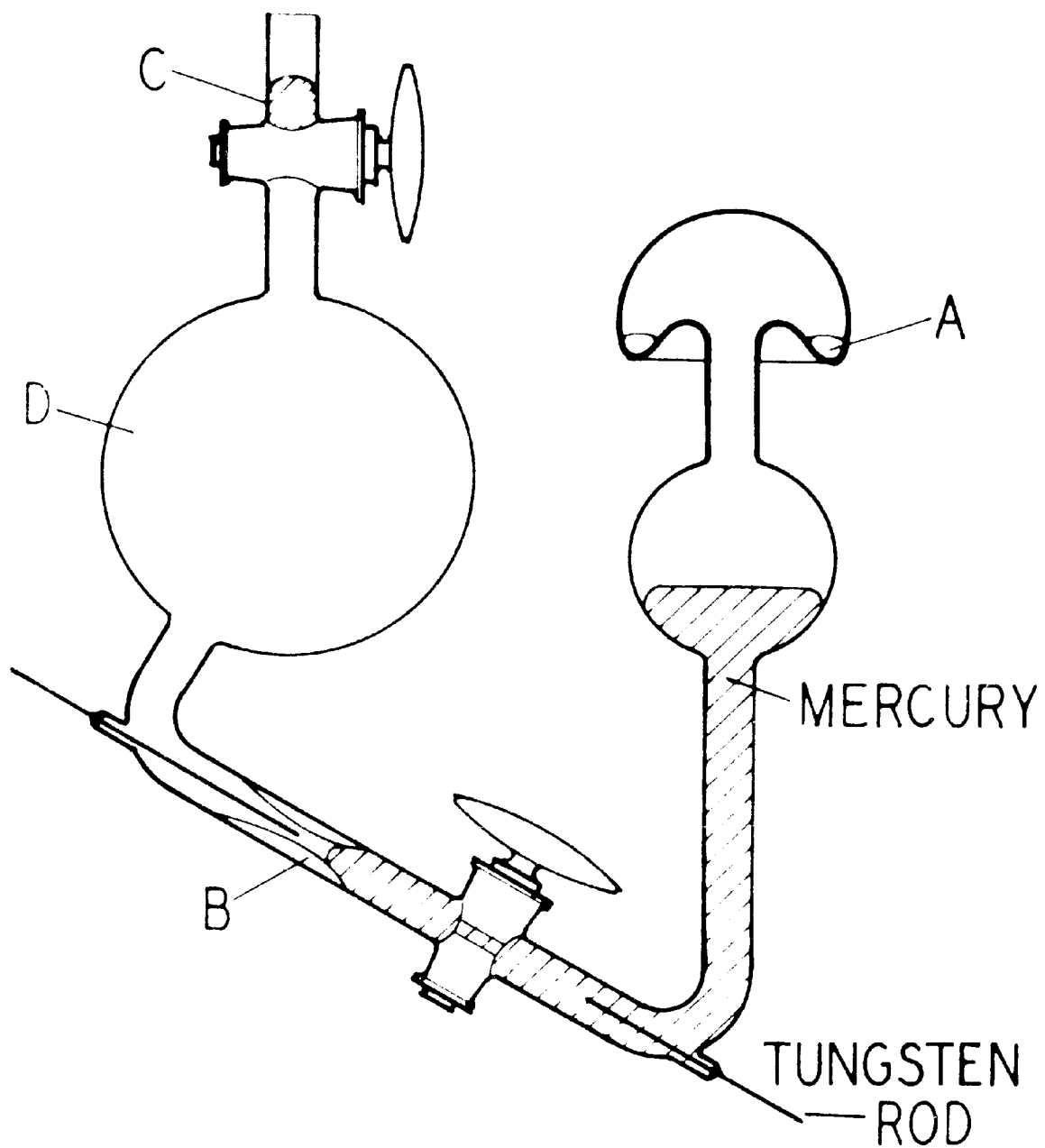
ISOPENTANE THERMOREGULATOR

FIGURE 7

HEATER

HIGH VAC. OR HELIUM

ADSORPTION SYSTEM

V. P. THERMOMETER

FLASK A

FLASK B

C

F

E

D
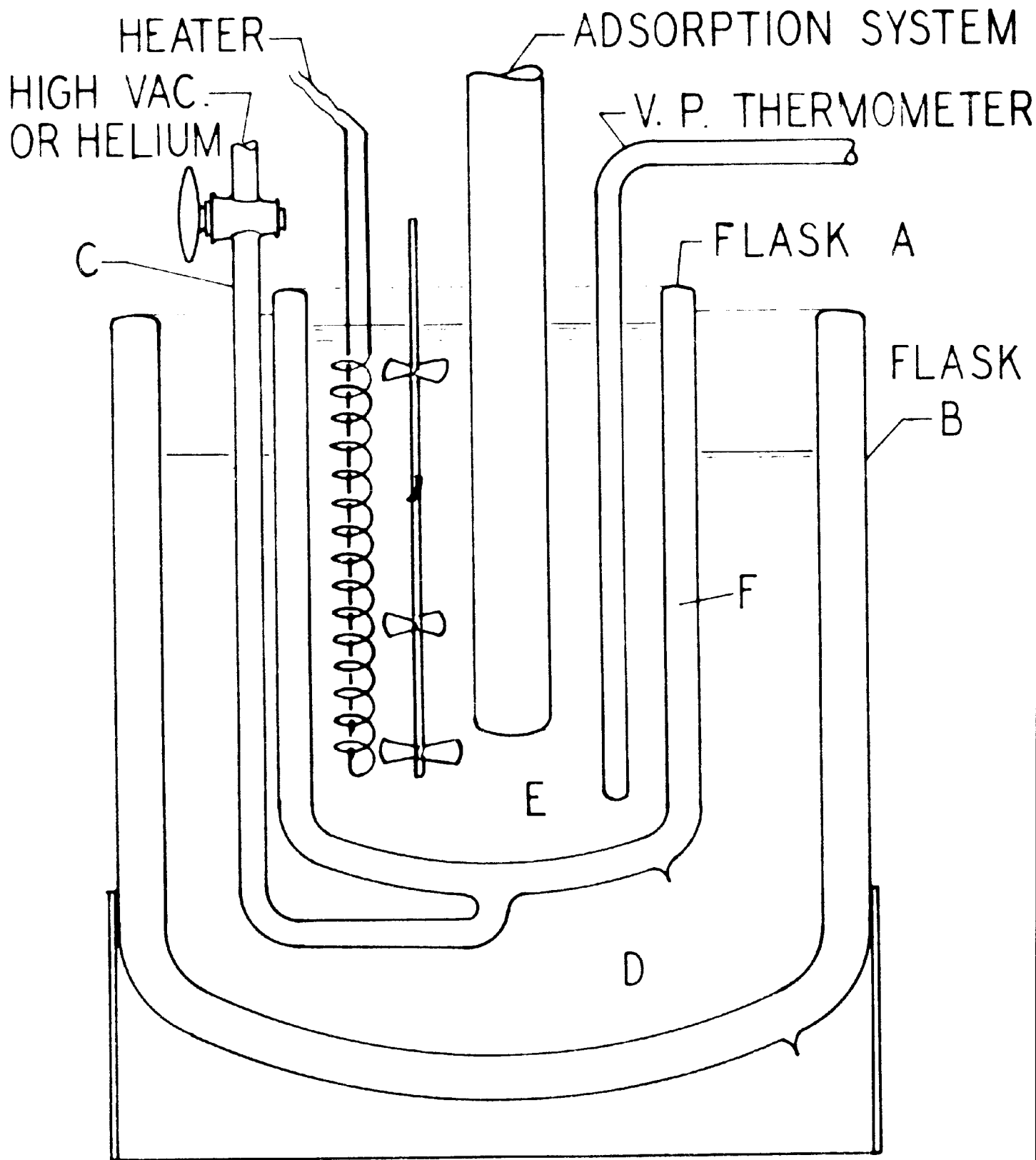
CRYOSTAT

state, the temperature of E was higher than that of D.
The temperature of the steady state could be raised at
will by altering the amount of heat input by means of
the heater. At the steady state it was possible to
maintain a constant temperature for considerable lengths
of time with little attention.

Temperature measurements.

All mercury thermometers used in this work were
calibrated against appropriate fixed points. For thermo-
meters used near room temperatures the fixed points were
the ice point and the transition point of sodium sulfate
decahydrate (23). The eutectic temperature of water-
sodium chloride was also used in calibrating the cryostat
thermometer.

For temperatures below $-36°$ it was no longer
possible to use a mercury thermometer. For these temper-
atures, vapor pressure thermometers were constructed using
a technique similar to that used in construction of the
nitrogen vapor pressure thermometer. The substances used
were ammonia for the range -27 to $-77°$ and hydrogen
chloride for the range -80 to $-110°$ C. The tables given
by Stock (24) were used.

Illumination.

The sharpest images were formed by illumination
with a lamp bulb placed to the side of the thermostat, its

light being reflected diffusely from the asbestos sheeting
in the box itself. The bulb was shifted around at the
side of the box until optimum intensity of diffuse illu-
mination was obtained and the image was very sharp.

The position of the spring was located most
satisfactorily by focusing on the hook either of the
bucket or of the spring itself. Attempts to provide the
spring fibers with distinct markings, such as very fine
scratches or fused pointers were not successful.

The positions of the mercury levels in the
manometer were best observed when the mercury was illu-
minated from above by a 6 volt bulb attached to the cath-
etometer and with a black and white meniscus reader behind
the mercury, the black portion being uppermost. In this
manner, the mercury appeared black against a white field
and the meniscus was quite distinct and reproducible.

Adaptation for slow processes.

In previous work reported in the literature,
the pressure in the system was determined by the temper-
ature of the cryostat; any fluctuation in this temperature
caused a corresponding fluctuation in pressure. For the
systems studied in this work it was sometimes necessary
to extend a single adsorption run over a period of several
weeks. It would be impractical, if not futile, to attempt
to maintain the necessary temperature control in the
cryostat for this length of time. The apparatus was,

therefore, designed so that the adsorption chambers
could be isolated from the liquid sample of adsorbate
which was in the cryostat. Since no stopcock grease
could be used and since the joints must be gas-tight,
Stock valves (25) of the type shown in Figure 8 and F,
Figure 4, were used for this purpose. When the mercury
levels were raised in these valves it was no longer
necessary to maintain temperature control in the cryostat.

With cutoffs of this type it was possible to
avoid the long, heavy columns necessary in the ordinary
mercury cutoffs, while retaining the advantage of a
pressure differential of up to one atmosphere or even
greater across the cutoff, since the mercury could not
creep across the ground glass surfaces in the glass
floats. The glass floats were provided at the lower
ends with iron plugs to give better seating of the float
as the mercury was raised, and also to enable the floats
to be dislodged by an Alnico magnet in case the floats
were to become frozen while seated under a high pressure.
The S-shaped bends at each side of the valve acted as
traps for mercury that might accidentally go beyond the
glass float. The trap could be emptied at the end of a
run by breaking off the tip of the attached tubing (H,
Figure 4).

FIGURE 8
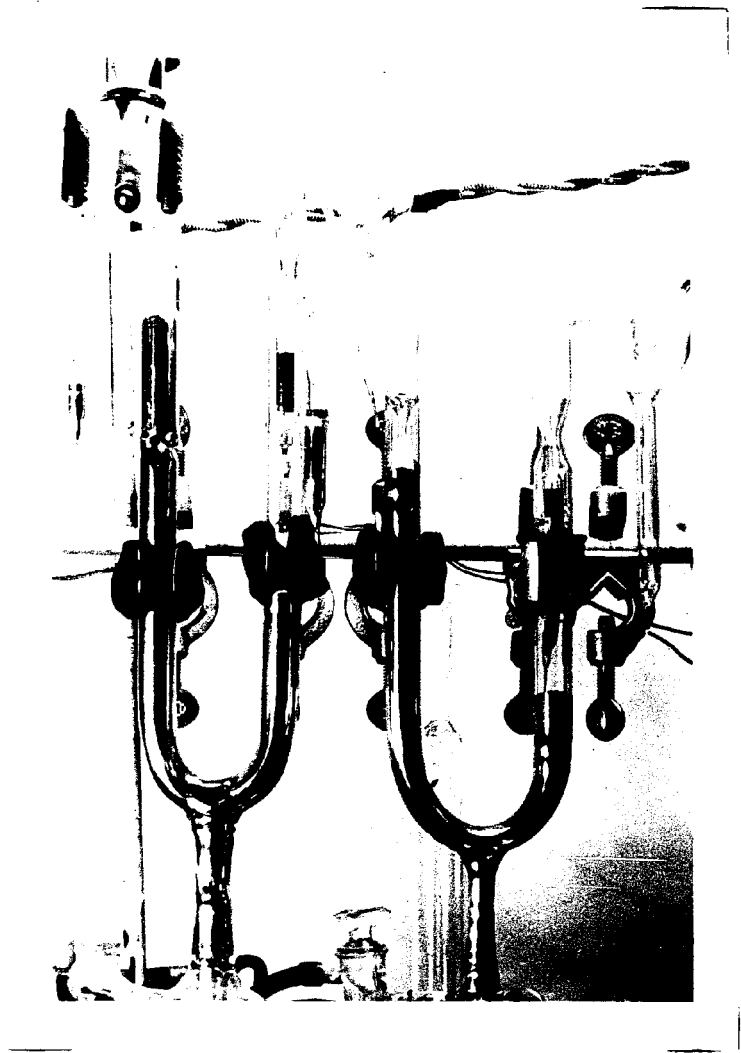
Figure 8. Stock Valves

Manometer.

The mercury cutoff N shown in Figure 4 had the functions of confining the adsorbate to the proper portions of the system, of preventing the diffusion of vacuum greases to the adsorbate or adsorbent and of serving as a manometer for the determinations of adsorption pressures and of vapor pressures. This section was made of 14 mm. tubing which permitted rapid evacuation of the adsorption chambers and also reduced the importance of the corrections due to the depression of the mercury meniscus. The meniscus correction was always determined, but in most cases it was found to be not more than 0.01 mm.

TECHNIQUES AND EXPERIMENTAL RESULTS

In this research, in addition to the measure-
ment of amine adsorption by silica gel, the specific sur-
face area of the adsorbent was determined by interpretation
of data obtained on nitrogen adsorption by the silica
gel. The total internal volume of the adsorbent was
determined by a method independent of adsorption processes.
The physical properties of the adsorbates, i.e., surface
tensions, densities and vapor pressures, were measured.

Adsorption of Nitrogen by Silica Gel

The adsorption of nitrogen by silica gel was
measured in the volumetric apparatus. The gel samples
were readied for the determinations by heating to 215° C.
at pressures of 10^{-5} for 3 hours or more. The volume of
the system was determined by observing the change in the
pressure of a fixed amount of helium upon expansion into
the system containing the sample. In this determination
it was assumed that the amount of helium adsorbed by the
sample was negligible compared with the amount of nitrogen
which was subsequently to be adsorbed. In view of the
great difference in the boiling points of the two elements
(4.3° K. for helium, 77.4° K. for nitrogen), this

assumption appeared quite reasonable. Experimental
verification has been obtained by Howard and Hulett (26).

The volumes were calculated for standard temper-
ature and pressure conditions. The adsorption runs were
made at the temperature of liquid nitrogen, and the volumes
of nitrogen were corrected for deviations from the ideal
gas laws by the factor 5.0% suggested by Emmett (17) for
this temperature. The vapor pressure of the nitrogen was
read directly from the vapor pressure thermometer which
was in contact with the adsorption sample bulb.

Summarized data for runs on six different samples
are given in Table 1. These data are represented graph-
ically in Figure 9. Two sets of runs of three samples
each were made several months apart. The mean values of
the two sets agree quite well. This excellent agreement
contraindicates alteration of the surface area of this gel
with time.

TABLE 1

ADSORPTION OF NITROGEN BY SILICA GEL

Wgt. of Sample (g.)	Pressure Initial (mm.)	Final (mm.)	Rela- tive	Volume Ads'd. (ml. STP)	$\dfrac{P}{V(P_o-P)}$ (ml.)$^{-1}$	$\dfrac{P}{(V/G)(P_o-P)}$ (ml./g.)$^{-1}$
0.5527	340.0	87.1	.092	42.36	.00287	.00157
	152.6	128.1	.167	46.10	.00409	.00226
	202.0	172.7	.222	49.54	.00551	.00305
0.7600	365.8	61.9	.067	51.00	.00141	.00107
	141.7	99.3	.124	57.68	.00244	.00185
	184.0	141.7	.176	63.20	.00338	.00257
	201.8	176.2	.219	67.08	.00418	.00318
	242.5	216.5	.270	70.93	.00523	.00397
0.6266	139.6	8.9	.011	22.32	.00049	.00031
	148.1	42.4	.053	39.75	.00140	.00088
	164.5	106.0	.132	48.78	.00312	.00195
	201.6	162.8	.202	54.54	.00468	.00293
	235.5	208.6	.260	58.42	.00600	.00376
0.5860	192.1	17.5	.022	29.62	.00073	.00043
	143.3	71.5	.087	41.30	.00229	.00134
	166.9	129.1	.156	47.15	.00392	.00230
0.7632	225.1	7.8	.009	37.10	.00024	.00019
	224.6	85.5	.104	59.72	.00195	.00149
	236.0	169.5	.205	69.94	.00370	.00282
	263.2	223.6	.271	75.95	.00490	.00374
0.9317	223.8	2.2	.003	37.80	.00008	.00007
	214.5	49.8	.060	64.20	.00100	.00093
	226.2	131.8	.159	78.96	.00239	.00223
	268.4	205.2	.247	88.54	.00370	.00345
	324.6	268.4	.322	97.09	.00491	.00457

FIGURE 9
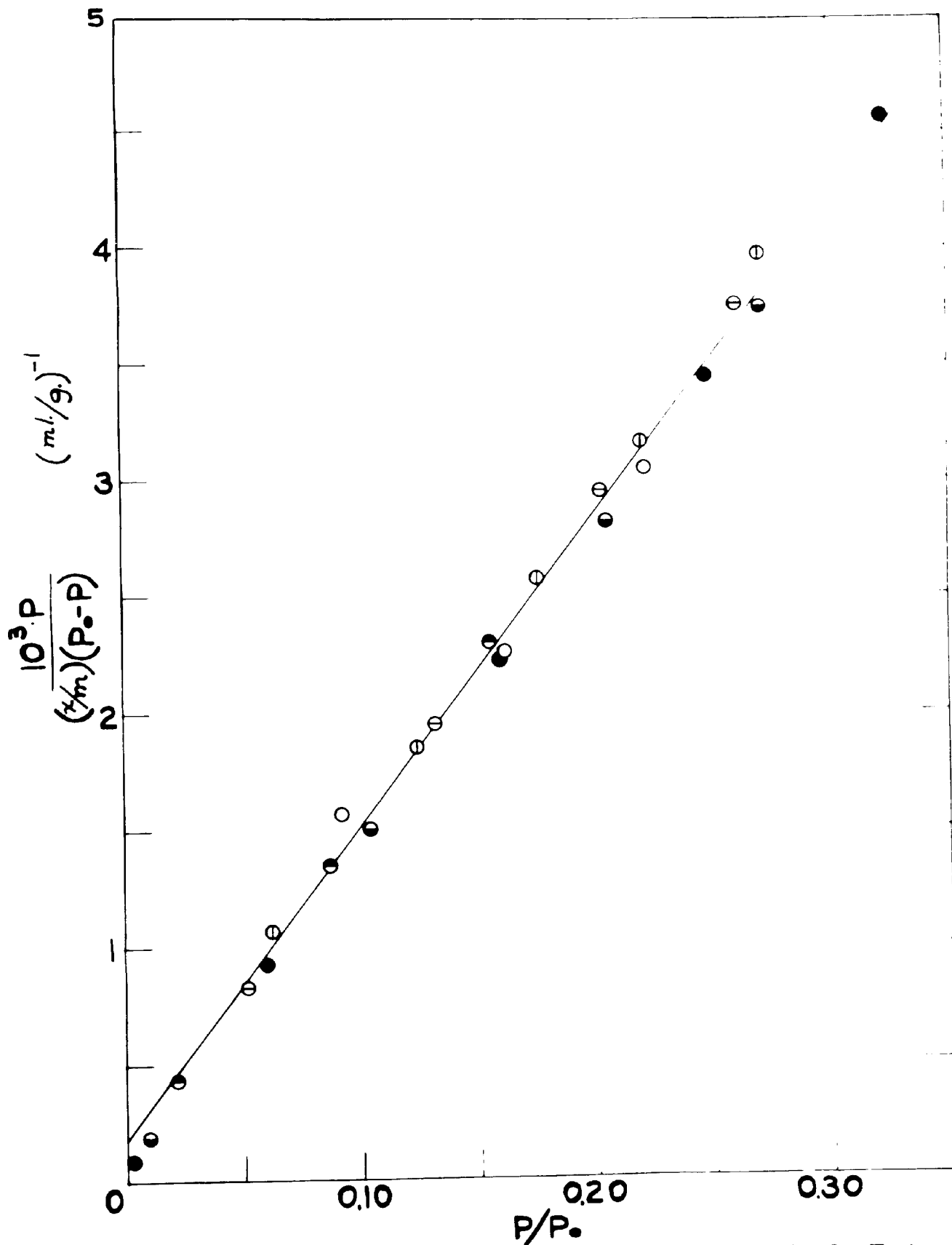
B.E.T. PLOT FOR ADSORPTION OF NITROGEN
BY SILICA GEL 78°K.

Surface Tensions of the Amines

The surface tensions of the amines were determined by the capillary rise method. The capillary was one arm of an all-glass U. The other arm was wide tubing (40 mm.) which contained the bulk of the liquid sample. Both arms were provided with standard taper caps, which were interconnected with fine tubing.

The height of the capillary rise was determined directly, using a Gaertner comparator provided with a dial reading to 0.01 mm. Measurements were made in a water bath controlled to $\pm 0.01^{\circ}$ C. The experimental results are presented in Table 2.

TABLE 2

SURFACE TENSIONS OF THE AMINES AT 25.00° C.

Diethylamine .... **19**.08 dynes/cm.

n-Butylamine 22.96

Di-n-butylamine 23.60

Densities of the Amines

The densities of the amines were determined by a direct weighing of measured volumes of the liquid samples. The pyconometers used were about 25 ml. capacity. An exact volume of sample was obtained by inserting tightly a ground glass stopper into the filled pycnometer flask, the stopper being provided with a capillary exit tube which allowed the excess liquid to escape. The determinations were made at room temperature with samples that had been at room temperature for several hours; the exact temperature of each sample was determined at the conclusion of each run by immersion of a thermometer into the sample. The values have been calculated to 25.0° C., using the literature values of the expansion coefficients for the small temperature range involved (less than 2°). The results are given in Table 3, below.

TABLE 3

DENSITIES OF THE AMINES AT 25.0° C.

Diethylamine 0.6961

n-Butylamine 0.7339

Di-n-butylamine 0.7556

Determinations were made using two different pyconometers with each liquid. In the cases of diethyl- and dibutylamine, agreement of the results was obtained even in the

fifth decimal place. This is felt to have been purely
fortuitous, however, since limit of experimental accuracy
is probably ± 0.00003.

Vapor Pressure Measurements

The pressure in the adsorption system was controlled by the temperature of the bath surrounding the liquid sample. Consequently it was necessary to know the pressure-temperature relationships for the liquids used as adsorbates. A search of the literature revealed that there were no adequate data available for the amines used; hence investigation was made of the vapor pressures of these liquids.

For temperatures below room temperature the direct static method was used with diethylamine and n-butylamine. The determinations were conducted in the gravimetric adsorption apparatus by raising the mercury in the Stock cutoffs (page 27) in order to isolate the liquid sample from the adsorbent gel sample. The pressure was observed through the Gaertner cathetometer with an accuracy of 0.02 with pressures up to 20 mm. and of 0.04 mm. with pressures above this. The pressure above the vacuum arm of the manometer was checked with the McLeod gauge and was always held at less than 0.001 mm. The mercury meniscus corrections were taken from the Smithsonian tables (27). The length of the mercury column was corrected to standard conditions. The readings recorded were obtained after both the thermometer in the cryostat and the pressure had reached and maintained a steady state for at least thirty minutes. It was found

that the equilibrium conditions were approximated within a few minutes.

With di-n-butylamine, the vapor pressure was too low to allow accurate measurement of the pressure directly at the available temperature range of the cryostat. The gas transpiration method (28) was used for this liquid. Highly purified nitrogen (page 11) was used as the carrier gas. The saturator was all-glass and was packed with pellets of reagent potassium hydroxide to insure absence of water while also serving to break up the bubbles of nitrogen for better saturation conditions. The sample of amine volatilized was collected by bubbling the gas stream through concentrated sulfuric acid contained in a Wesson bulb packed with glass wool.

Vapor pressures of all the amines at temperatures between that of the room and the boiling point were obtained by the use of the isotensiscope method (29). The purified samples were dried in situ by potassium hydroxide. The isotensiscope was mounted in a boiling vapor thermostat, using various organic liquids to obtain different temperatures. "Precision Anscheutz" thermometers were suspended in the thermostat adjacent to the isotensiscope. A dibutyl phthalate manometer was read with a Gaertner cathetometer. The vacuum on the manometer was maintained by continuous operation of a Hyvac pump connected directly to one arm of the manometer.

All thermometers used in this work were cali-
brated at suitable standard temperatures (sodium chloride-
water eutectic, ice point, sodium sulfate hydrate transi-
tion point, and steam point).

Vapor Pressure Results

Probably the most familiar formula relating
vapor pressure and temperature is the simple equation:

$$\log p = A + \frac{B}{T} \tag{2}$$

where p is the pressure, T the absolute temperature, and
A and B are constants. This equation is derived from
the integrated Clausius-Clapeyron Equation by including
the following assumptions: (a) the vapor is a perfect
gas; (b) the volume of the liquid is negligible with
respect to the volume of the vapor, and (c) the heat of
vaporization is constant over the temperature range in-
volved. For approximate results, this relationship may
be satisfactory, particularly over short temperature
ranges. However, careful studies have shown that the
deviation of values calculated from this equation exceed
the experimental errors of more highly accurate work, and
that the deviations show a systematic trend. Some more
complicated formulae undoubtedly represent the data more
adequately, but their empirical constants are difficult
to determine and the resulting equation may not be in a
form which can be readily used for calculations.

A much simpler equation was used by Antoine (30)
who substituted (t + C) for T in the Clausius-Clapeyron

form, obtaining

$$log\ p\ =\ A\ +\ \frac{B}{t+C} \tag{3}$$

where A, B, and C are constants and t is the temperature
in degrees Centigrade. Quite extensive studies have been
made of the applicability of the Antoine equation and it
has been found better than the 1/T form for all cases,
excepting low-boiling compounds and monatomic elements
where the value of C is close to 273. Examples have been
found where the Antoine equation represents the data
better than much more complicated equations and over
wider pressure ranges (31).

The value of C can be derived from the experi-
mental data in several ways (32). If three widely spaced
and reliable experimental points are available, three
simultaneous equations can be set up and solved for the
three constants, A, B, and C. The resultant vapor pressure
equation is then applied to the rest of the data and is
satisfactory if no systematic deviation is found. If
systematic deviations do occur, other points can be chosen
for the evaluation of the constants.

The constants can be evaluated graphically by
the following method, if one point is known to a higher
degree of precision than the others. This point is

designated by t_o, p_o. Then it follows that

$$\log p_o = A + \frac{B}{t_o + C} \qquad (4)$$

From this equation and the general Antoine equation it can be shown by algebraic operation that

$$\frac{\log p/p_o}{t - t_o} = \frac{A}{t_o + c} - \frac{\log p}{t_o + C} \qquad (5)$$

A plot of log (p/p_o) $\cdot$ $1/(t-t_o)$ against log p is linear, and the slope has the value $-1(t_o + C)$. The value of C can be obtained directly from this. The constants A and B can then be obtained graphically from a plot of log p against reciprocal ($t + C$) in the customary manner, or analytically from two selected points.

The derived equations for the vapor pressure of the amines have been found to be:
(for diethylamine over the temperature range -60 to 55° C.)

$$\log p \ (mm.) = 7.1332 - \frac{1148.4}{t + 227.0} \qquad (6)$$

(for n-butylamine over the temperature range -35 to 80° C.)

$$\log p (mm.) = 7.0478 - \frac{1235.0}{t + 216.2} \qquad (7)$$

(and for di-n-butylamine over the temperature range 0 to 160° C.)

$$log\ p(mm.) = 6.5677 - \frac{1233.5}{t + 175.0} \qquad (8)$$

The experimental data are compared with calculated values in Tables 4-6. The average deviation between calculated and experimental pressures is 0.3 mm. for diethylamine, 0.1 mm. for n-butylamine, and 0.1 mm. for di-n-butylamine. The average deviation in temperatures is 0.08°, 0.05°, and 0.11°, respectively.

The boiling points at the standard pressure of 760 mm. are calculated as 54.8° C., 76.7° C., and 159.6° C. for the amines in the above order. A correlation may be noted between the boiling point and the value of C used in the Antoine equation:

$$C = 254.0 - 0.493\ t_b \qquad (9)$$

where t_b is the standard boiling point in degrees Centigrade (Figure 10). The value of C as calculated in this manner is within 0.3° of the experimental value for the three amines investigated. In view of the known

FIGURE 10

FIGURE 18
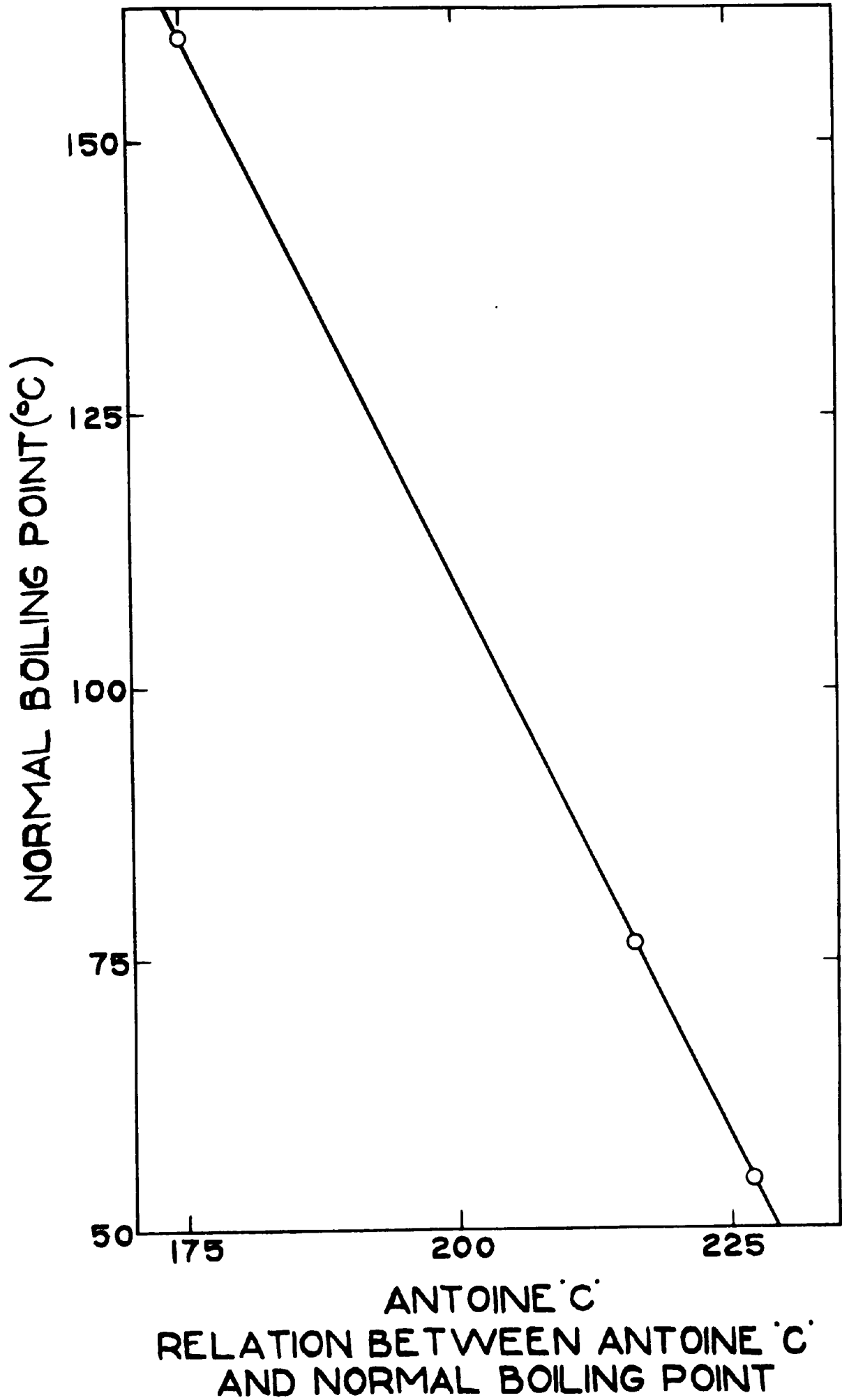
RELATION BETWEEN ANTOINE ′C′
AND NORMAL BOILING POINT

relationships among vapor pressures of homologous series of organic compounds, the above equation may be useful in determining the value of C for other aliphatic amines.

TABLE 4

VAPOR PRESSURE OF DIETHYLAMINE

p(mm.) exptl	log p exptl	t(°C.) exptl	t+227.0	$\frac{1198.4}{(t+227.0)}$	log p calcd	p(mm.) calcd
0.60	-.222	-64.5	162.5	7.3748	-.2416	0.573
2.09	0.3202	-50.8	176.2	6.8013	.3319	2.147
8.90	0.9494	-33.2	193.8	6.1837	0.9495	8.90
20.26	1.3066	-21.4	205.6	5.8289	1.3043	20.15
20.82	1.3185	-21.0	206.0	5.8175	1.3157	20.69
71.28	1.8530	- 0.1	226.9	5.2816	1.8516	71.06
71.43	1.8539	0.0	227.0	5.2792	1.8539	71.43
100.05	2.0002	6.6	233.6	5.1301	2.0031	100.7
105.15	2.0216	7.5	234.5	5.1104	2.0228	105.4
109.19	2.0381	8.2	235.2	5.0952	2.0380	109.15
122.90	2.0896	10.6	237.6	5.0438	2.0894	122.9
131.45	2.1188	11.8	238.8	5.0184	2.1148	130.3
142.75	2.1547	13.8	240.8	4.9767	2.1565	143.4
172.30	2.2363	17.6	244.6	4.8994	2.2339	171.4
181.95	2.2601	19.0	246.0	4.8715	2.2617	182.7
183.56	2.2638	19.1	246.1	4.8695	2.2637	183.53
193.94	2.2877	20.3	247.3	4.8459	2.2873	193.8
197.80	2.2962	20.8	247.8	4.8361	2.2971	198.20
198.16	2.2970	20.9	247.9	4.8342	2.2990	199.1
211.33	2.3249	22.2	249.2	4.8090	2.3242	211.0
216.82	2.3361	22.8	249.8	4.7974	2.3358	216.7
218.60	2.3396	23.0	250.0	4.7936	2.3396	218.60
240.76	2.3816	25.4	252.4	4.7480	2.3852	242.8
244.16	2.3877	25.6	252.6	4.7443	2.3889	244.8
485.6	2.6863	42.5	269.5	4.4467	2.6865	485.8
733.9	2.8656	53.8	280.8	4.2678	2.8654	733.5

TABLE 5

VAPOR PRESSURE OF n-BUTYLAMINE

p(mm.) exptl	log p exptl	t(°C.) exptl	t+216.2	$\dfrac{1235.0}{(t+216.2)}$	log p calcd	p(mm.) calcd
2.16	0.3345	-33.6	182.6	6.7634	0.3344	2.16
9.37	0.9717	-14.6	201.6	6.1260	0.9718	9.37
11.29	1.0528	-12.0	204.2	6.0480	1.0498	11.22
14.60	1.1644	- 8.2	208.0	5.9375	1.1603	14.47
24.20	1.3838	0.0	216.2	5.7123	1.3855	24.30
28.73	1.4584	2.7	218.9	5.6418	1.4560	28.58
36.01	1.5564	6.6	222.8	5.5431	1.5547	35.87
36.95	1.5676	7.1	223.3	5.5307	1.5671	36.91
43.05	1.6340	9.8	226.0	5.4646	1.6332	42.97
54.95	1.7400	14.4	230.6	5.3556	1.7422	55.23
66.52	1.8230	18.0	234.2	5.2733	1.8245	66.76
67.36	1.8284	18.2	234.4	5.2688	1.8290	67.45
70.89	1.8506	19.2	235.4	5.2464	1.8504	70.86
77.55	1.8896	21.0	237.2	5.2066	1.8912	77.84
80.21	1.9042	21.6	237.8	5.1934	1.9044	80.24
82.06	1.9141	22.0	238.2	5.1847	1.9131	81.87
85.55	1.9322	22.9	239.1	5.1652	1.9326	85.62
91.71	1.9624	24.3	240.5	5.1351	1.9627	91.77
736.0	2.8669	75.7	291.9	4.2309	2.8668	735.9

TABLE 6

VAPOR PRESSURE OF DI-n-BUTYLAMINE

p(mm.) exptl	log p exptl	t(°C.) exptl	t+175.0	$\dfrac{1233.5}{(t+175.0)}$	log p calcd	p(mm.) calcd
2.62	0.4183	25.0	200.0	6.1675	.4002	2.51
21.02	1.3226	60.2	235.2	5.2445	1.3232	21.05
44.66	1.6499	75.8	250.8	4.9183	1.6494	44.61
99.0	1.9956	94.8	269.8	4.5719	1.9958	99.04
119.0	2.0756	99.6	274.6	4.4920	2.0757	119.0
732.2	2.8646	158.1	333.1	3.7031	2.8646	732.2

Internal Volume of Silica Gel

The apparent density of silica gel was determined by measuring the volume of mercury displaced by weighed amounts of the solid. The form of the pycnometer and filling siphon devised for this determination is shown in Figure 11. The pycnometer was made of 8 mm. tubing. The mercury was filled each time to a scratch made in the constriction A in the neck of the pycnometer. The capacity of the bulb was approximately 5 ml. The pycnometer was attached to the siphon by a short length of rubber tubing and then evacuated by a Hyvac pump through C with stopcock D closed. The volume of the bulb was easily determined with accuracy of better than 0.1% by weighing the amount of mercury required to fill the bulb.

Silica gel was shaken through the constriction A and lodged in bulb B by tapping the pycnometer in an inverted position. After evacuation of the bulb and sample, mercury could be admitted with care so as to trap all the gel particles in bulb B.

The density of the solid is then determined by the formula:

$$D = \frac{(c-a)\,M}{(b-d) + (c-a)} \qquad (10)$$

FIGURE 11

FIGURE 11
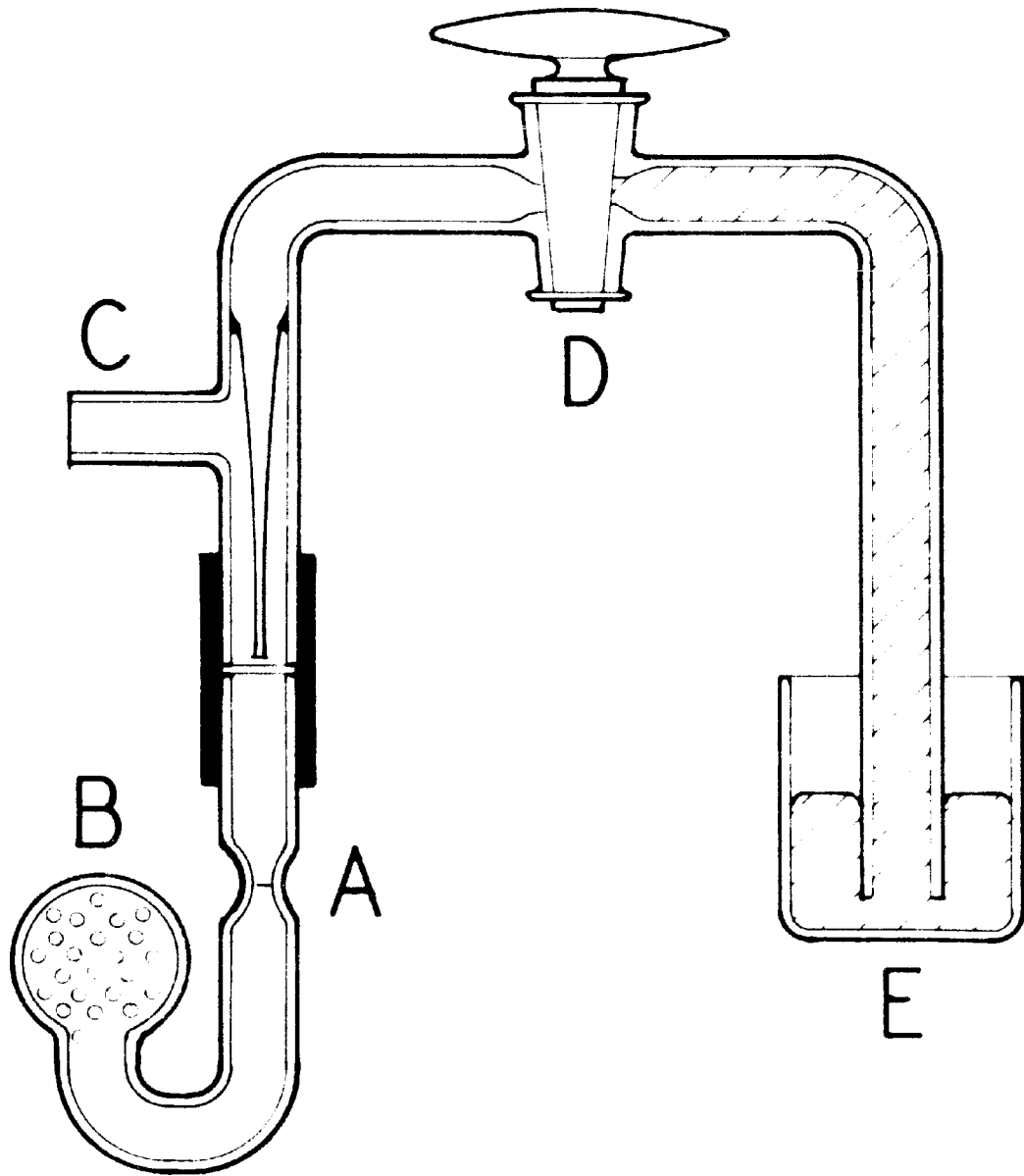
MERCURY PYCNOMETER

Where D = density of the silica gel
     M = density of mercury
     a = weight of the empty pycnometer
     b = weight of pycnometer plus mercury
     c = weight of pycnometer plus silica gel
and d = weight of pycnometer plus silica gel
        filled with mercury.

Important conclusions concerning the structure of adsorbents can be drawn from density measurements. The value of the apparent density of a solid as determined by liquid displacement is affected by the degree of penetration of the liquid into the solid. With compact crystals, there is no internal space into which any liquid can penetrate, so this effect does not manifest itself; however, with porous solids, the degree of penetration is dependent upon the diameter of the pores, the number of the pores, the size of the liquid molecules, and the contact angle of wetting of the solid by the liquid.

Mercury forms a contact angle with siliceous surfaces of greater than 90° and will not spontaneously rise in capillaries of glass or silica. This is commonly seen by the depression of mercury in manometers or fine tubes. This same property can be utilized in a study of the structure of silica gel: if the density of silica gel is determined by mercury, the volume of mercury displaced will include the volume of the pores in the gel sample also, for mercury will not penetrate into these pores. The density of the silica gel was determined by this method

as 0.6536 ± .0005. The volume per gram gel is consequently 1.530 ± .0001 ml.

The volume of these pores in silica gel may then be deduced by subtracting the volume of the solid compact silica matter itself from the volume of the silica plus pores as determined by mercury. In order to determine the maximum volume of pore spaces in the silica gel it is necessary to consider the most compact possible arrangement of the silicon and oxygen atoms of the gel. The densest, most compact form of silicon dioxide recorded is quartz, having a density of 2.649 ± 0.002 (33). The next most dense form is cristabolite, having a maximum density of 2.325 (33). It has been shown by X-ray diffraction analysis that dried silica gel has almost the same pattern as vitreous silica, the difference being additional small angle scattering which may be attributed to the gaps and voids in the gel samples. One may conclude from this that the interatomic arrangement of silica gel is similar to that of vitreous silica. The density of vitreous silica is approximately 2.20 (33). In view of these relationships, it may be conservatively assumed that silica gel will never exceed the density of packing that occurs in quartz. On this basis, it may be claimed that the minimum space occupied per gram of gel by the solid silica framework is 0.377 ml. The maximum pore volume per gram gel is hence determined as 1.153 ml.

Gravimetric Adsorption Apparatus Techniques

Storage of liquid adsorbate samples.

After the purification processes, the adsorbate
samples were degassed and sealed into sample tubes for
storage. The sample tubes were made from Pyrex which had
been thoroughly cleaned with chromic acid, washed, and
dried. After fabrication and before filling, the tubes
were flamed carefully while under evacuation. The tubes
had a thin curved tip and were indented near the tip so
that the tube could be handled with fine wire hook. A
thickened constriction was drawn in the other end of the
tube. The liquid sample was introduced by distillation
in the case of the more volatile substances or through a
fine funnel with less volatile substances. The sample
was frozen with either dry ice mixtures or with liquid
nitrogen and then evacuated. The pump was stopped and
the liquid was allowed to warm up slowly, its own vapor
filling the space above. It was noted that if the
freezing was done slowly and carefully, bubbles formed
at the solid-liquid interface and then escaped from
the liquid. This was attributed to the much lower
solubility of gases in the solid than in the original
liquid solution. When the evacuated solid was sub-
sequently thawed, occluded gas bubbles were seen to rise
through the liquid, the thawing being conducted rapidly

so that the gas did not have time to reach equilibrium solubility conditions. The freezing, evacuating, thawing process was repeated until no bubbles were observed on two consecutive cycles. This required from four to eight cycles depending on the sample. The liquid was finally frozen, evacuated, and sealed by careful and slow heating of the constriction in the sample tube.

Introduction of adsorbate to adsorption system.

The upper end of tube G in Figure 4 was heated and blown open. Several pellets of reagent potassium hydroxide (M, Figure 4) were added, and the sample tube of adsorbate (K, Figure 4) and a glass-enclosed iron hammer (J, Figure 4) were lowered into the tube by means of long hooked wire. The end of tube G was drawn off and sealed. (Additional lengths were sealed onto tube G as this became necessary from repeated glass working.) The entire system was evacuated, flamed and heated. When the gel samples were thoroughly prepared, the mercury levels F were raised and the manometer level N was raised. The adsorbate sample tube was surrounded by liquid nitrogen and the iron hammer raised by a powerful Alnico magnet. On removing the magnet, the hammer fell and, usually, broke the tip of the sample tube. The walls of the apparatus (except, of course, the adsorption chambers proper, which were isolated from the liquid sample by the

Stock valves) were flushed with the new sample by distilling the liquid from the sample tube to the mercury levels and then back to the sample chamber. The sample was frozen again, the manometer level lowered and the sample chamber evacuated. This entire process was repeated three or four times and is believed to completely remove the possibility of any dissolved inert gases vitiating the subsequent pressure and adsorption measurements. It has been found that different samples of the same compounds introduced in this manner gave perfectly concordant vapor pressure measurements.

Treatment of gel.

The gel sample was weighed in air into the sample pan, transferred to a silica spring and the elongation of the spring determined. The heaters were slipped around the adsorption chambers and heating and evacuating started. The sample was brought to 200-215° C. and evacuation of 10^{-5} mm. or better maintained for 16-20 hours, using liquid nitrogen in the traps to protect the system from back-diffusion of traces of any contaminants. The mercury cutoff levels were raised while the samples were still hot. After cooling, the heaters were removed and the elongation of the spring again determined. The gel as weighed contained some superficial water, not as part of the gel structure, but adsorbed on the surfaces. The

evacuation removed the water and brought the various gel samples to a uniform reproducible condition. It had been shown in previous work by Bartell and Almy (34) that in driving the water from silica gel at 220°, the major portion of the water is removed in the first few minutes.

From the change in elongation of the spring before and after heat-evacuation treatment, the amount of this "surplus" water driven off was calculated and subtracted from the mass of the gel as determined in the room atmosphere.

Adsorption equilibrium determinations.

The pressure in the adsorption system was brought to a suitable constant value by control of the temperature of the cryostat, before opening the Stock valves to the samples of silica gel. As vapor was adsorbed by the gel, the sample became heavier and the spring more elongated. The change in position of the spring as a function of time was followed until no further elongation was noted for at least one-half hour. The mercury levels in the Stock valves were then raised and the position of the spring observed further. In initial runs with new adsorbates, these periods were perhaps extended much longer than might have been necessary to ascertain that no secondary, slow process (of the magnitude of days) occurred. With the provision of

the Stock valves, no inconveniences were occasioned other than the time delays involved. Reading of the reference rod (page 19) was always taken at the same time as the final spring reading.

The procedure above was repeated with progressively higher pressures obtained by higher cryostat temperatures.

Desorption equilibrium determinations.

The procedure involved in determining the desorption rates and equilibrium values was in all respects similar to the adsorption process except that the pressure was decreased by maintaining the cryostat at progressively lower temperatures.

Adsorption of Amines by Silica Gel

The determinations of the adsorption of amines by silica gel were done using the gravimetric apparatus and techniques previously described. Both adsorption and desorption equilibria were determined. It was found that the heating and evacuation treatment used in preparing the gel for the original adsorption run was sufficiently rigorous to remove adsorbed amine molecules also, so that subsequent adsorption runs could be conducted on the same sample of gel by heating and evacuating the gel sample at the conclusion of a run. After construction of the second adsorption chamber (page 17), it was possible to obtain confirmatory data with two different gel samples simultaneously. Hence the data presented offer double confirmation: the same vapor adsorbed on two different samples of gel, and different vapors adsorbed on the same sample.

The data for the adsorption of diethylamine, n-butylamine, and di-n-butylamine, each at 25° and at 40° C., are given in Tables 7-12. These data are shown graphically as isotherms (the amount adsorbed per gram gel as a function of the relative pressure at specified temperatures) in Figures 12-16. In the tables, the time intervals allowed for assurance of equilibria were given as Δ time.

The relative pressures listed refer to the actual pressure in the adsorption system divided by the saturation vapor pressure of adsorbate at the temperature of the gel sample; relative pressure is seen to be a generalized "relative humidity." The recorded change in elongation of the spring (Δ Elongation) has been corrected for any possible motion of the cathetometer with respect to the spring (page 19). The amount adsorbed was calculated from the change in elongation by the calibrations of the springs using accurately determined standard masses.

TABLE 7

ADSORPTION OF DIETHYLAMINE
BY SILICA GEL, 25° C.

Run	Weight of Sample (g)	P/P_0	Δ Time (hours)	Δ Elongation (mm.)	Δ Weight (mg.)	Amount Adsorbed (mg./g.)
1	0.1540	0.0001	9	0.155	0.574	3.75
		.0016	23	3.234	11.97	78.2
		.0518	50	3.913	14.50	94.7
		.0871	72	4.003	14.84	96.9
		.407	550	5.190	19.02	124.2
		.228	15	4.482	16.61	108.5
		.0462	5	3.953	14.64	95.6
		.0213	19	3.858	14.28	93.3
		.0128	49	3.727	13.82	90.3
		.0045	24	3.617	13.41	87.6
		.0018	7	3.401	12.60	82.3
2	0.1531	.0025	12	3.459	12.81	83.7
		.0263	4	3.856	14.30	93.4
		.100	8	4.114	15.22	99.4
		.170	24	4.292	15.91	103.9
		.452	24	5.454	20.19	131.9
		.601	34	6.996	25.92	169.3
		.663	18	9.079	33.61	219.5
		.774	54	15.355	56.88	371.5
		.854	141	31.447	116.82	763.0
		.576	25	6.810	25.23	164.8
		.372	10	5.050	18.71	122.2
		.0567	14	4.026	14.91	97.4
3	0.1453	.0474	47	3.631	14.16	92.5
		.220	10	4.114	16.03	104.7
		.441	24	5.091	19.86	129.7
		.515	24	5.758	22.44	146.6

(TABLE 7 CONTINUED)

Run	Weight of Sample (g)	P/P_O	Δ Time (hours)	Δ Elongation (mm.)	ΔWeight (mg.)	Amount Adsorbed (mg./g.)
4	0.1540	0.304	14	4.689	18.51	120.2
		.535	30	6.166	24.34	158.1
		.672	21	9.567	37.77	245.2
		.757	8	13.624	53.78	349.2
		.846	36	26.717	105.47	684.8
		.908	20	32.013	126.38	820.6
		.924	5	32.104	126.74	823.0
		.948	7	32.217	127.19	825.9
		.964	11	32.319	127.59	828.5
		.896	6	32.146	126.90	824.0
		.790	5	29.187	115.22	748.2
		.778	5	26.307	103.85	674.4
		.761	10	21.042	83.07	539.4
		.736	24	19.643	77.55	503.5
		.710	42	13.936	55.02	357.2
		.672	30	10.599	41.84	271.7
		.612	2	8.122	32.06	208.2
		.466	4	5.890	23.25	151.0
5	0.3145	.304	14	5.697	37.23	118.4
		.535	30	7.524	49.18	156.4
		.672	21	10.340	67.58	214.9
		.757	8	15.079	98.56	313.4
		.846	36	31.660	206.93	658.0
		.908	20	39.759	259.86	826.3
		.924	5	39.817	260.24	827.5
		.948	7	39.920	260.92	829.6
		.964	11	40.050	261.77	832.3
		.896	6	39.872	260.60	828.6
		.790	5	38.062	248.77	791.0
		.778	5	34.382	224.72	714.5
		.761	10	25.084	163.95	521.3
		.736	24	22.492	147.01	467.4
		.710	42	16.111	105.30	334.8
		.672	30	12.346	80.69	256.6
		.612	2	9.677	63.25	201.1
		.466	4	7.117	46.52	147.9

TABLE 8

ADSORPTION OF DIETHYLAMINE
BY SILICA GEL, 40° C.

Run	Weight of Sample (g)	P/P_o	Δ Time (hours)	Δ Elon- gation (mm.)	Δ Weight (mg.)	Amount Adsorbed (mg./g.)
6	0.1540	0.170	19	3.724	14.70	95.5
		.235	1	3.932	15.52	100.8
		.302	18	4.220	16.66	108.2
		.359	4	4.460	17.61	114.3
		.398	2	4.630	18.28	118.7
		.518	17	5.612	22.15	143.9
		.541	4	5.829	23.01	149.4
		.590	8	6.456	25.49	165.5
		.048	28	3.379	13.34	86.6
		.020	8	3.185	12.57	81.6
7	0.3098	.170	19	4.525	29.57	95.5
		.235	1	4.774	31.20	100.7
		.302	18	5.138	33.58	108.2
		.359	4	5.404	35.32	114.0
		.398	2	5.604	36.63	118.2
		.518	17	6.673	43.61	140.8
		.541	4	6.962	45.50	146.9
		.590	8	7.637	49.91	161.1
		.048	28	4.092	26.74	86.3
		.020	8	3.877	25.34	81.8

TABLE 9

ADSORPTION OF n-BUTYLAMINE
BY SILICA GEL, 25° C.

Run	Weight of Sample (g)	P/P$_0$	Δ Time (hours)	Δ Elongation (mm.)	ΔWeight (mg.)	Amount Adsorbed (mg./g.)
8	0.1359	0.024	24	4.134	16.19	119.3
		.116	24	4.554	17.84	131.4
		.264	14	4.920	19.28	142.0
		.391	21	5.164	20.25	149.0
		.562	20	5.868	23.04	169.3
		.814	78	19.995	78.41	577.0
		.851	30	28.266	110.80	815.6
		.815	16	27.581	108.23	795.9
		.743	28	17.501	68.65	505.0
		.693	18	11.157	43.75	321.9
		.646	2	7.757	30.44	223.8
		.552	1	6.049	23.74	174.5
		.448	3	5.474	21.45	158.0
		.249	1	4.936	19.38	142.4
		.152	14	4.721	18.53	136.2
		.061	3	4.460	17.50	128.7
		.028	45	4.276	16.77	123.4
9	0.1359	.102	3	4.604	18.04	132.8
		.195	2	4.856	19.07	140.1
		.284	5	5.044	19.75	145.5
		.397	12	5.303	20.80	153.0
		.556	12	6.047	23.70	174.5
		.608	17	6.630	25.98	191.3
		.672	66	9.390	36.80	271.0
		.774	26	16.338	64.03	471.4
		.847	32	23.408	91.74	675.5
		.906	13	29.517	115.68	851.7
		.000	170	-0.026	-0.10	-0.6
10	0.1344	.199	16	4.582	17.95	133.7
		.331	2	5.010	19.63	146.2
		.418	5	5.272	20.66	153.8
		.632	10	7.363	28.85	214.8
		.702	42	10.800	42.32	315.1
		.912	24	29.247	114.62	853.4
		.846	18	29.040	113.82	847.3
		.683	66	13.006	50.97	379.5
		.584	26	6.522	25.55	190.3
		.494	18	5.675	22.26	165.6

(TABLE 9 CONTINUED)

Run	Weight of Sample (g.)	P/P_0	Δ Time (hours)	Δ Elongation (mm.)	Δ Weight (mg.)	Amount Adsorbed (mg./g.)
11	0.1344	0.637	11	6.961	27.30	203.1
		.720	21	9.180	35.98	267.9
		.745	64	12.797	50.16	373.4
		.790	72	19.408	76.07	566.3
12	0.1508	.254	4	5.355	21.00	139.3
		.762	48	13.021	51.06	338.6
		.830	62	21.586	84.65	561.4
		.936	44	32.957	129.24	857.1
		.852	3	32.640	128.00	848.8
		.818	5	32.040	125.65	833.2
		.751	84	19.876	77.95	516.9
		.687	6	9.385	36.80	244.1
		.642	19	7.795	30.56	202.7
		.594	4	7.103	27.85	184.7
		.0002	19	2.032	7.97	52.8
13	0.3199	.254	4	6.874	44.92	140.4
		.598	18	8.754	57.21	178.8
		.766	72	17.371	113.53	354.9
		.854	2	40.981	267.85	837.3
		.818	6	40.720	266.14	831.9
		.789	72	38.313	250.41	769.5
		.759	18	30.026	196.25	613.5
		.710	7	16.906	110.50	345.4
		.645	19	10.139	66.27	207.2
		.584	55	8.839	57.77	180.6
		.0002	19	3.326	21.74	68.0

TABLE 10

ADSORPTION OF n-BUTYLAMINE
BY SILICA GEL, 40° C.

Run	Weight of Sample (g)	P/P_o	Δ Time (hours)	Δ Elongation (mm.)	Δ Weight (mg.)	Amount Adsorbed (mg./g.)
14	0.1508	0.126	6	4.873	19.11	126.7
		.264	19	5.234	20.53	136.1
		.500	72	6.046	23.71	157.2
		.635	3	7.003	27.46	182.1
		.127	12	5.018	19.68	130.5
		.030	12	4.583	17.97	119.2
		.0$_4$7	21	1.424	5.58	37.0
15	0.3199	.126	6	6.310	41.24	128.9
		.264	14	6.800	44.44	138.9
		.511	82	7.840	51.24	160.2
		.638	16	8.964	58.59	183.1
		.127	14	6.438	42.08	131.5
		.031	24	5.803	37.93	118.6
		.0$_4$7	28	2.176	14.22	44.5

TABLE 11

ADSORPTION OF DI-n-BUTYLAMINE
BY SILICA GEL, 25° C.

Run	Weight of Sample (g)	P/P_0	Δ Time (hours)	Δ Elongation (mm.)	ΔWeight (mg.)	Amount Adsorbed (mg./g.)
16	0.3145	0.129	22	6.861	44.84	142.6
		.341	19	8.565	55.98	178.0
		.496	23	10.929	71.43	227.1
		.603	24	16.947	110.76	352.2
		.756	33	42.453	277.47	882.3
17	0.3145	.795	44	43.000	281.04	893.6
		.759	52	42.871	280.20	890.9
		.609	92	40.845	266.96	848.8
		.518	92	18.241	119.22	379.1
		.402	24	10.033	65.58	208.5
18	0.3145	.788	30	42.451	277.46	882.2
		.753	4	42.334	276.69	879.8
		.596	140	31.700	207.19	658.8
		.544	72	21.609	141.23	449.1
		.487	44	13.948	91.16	289.8
		.263	20	7.753	50.67	161.1
19	0.3145	.263	20	7.778	50.84	161.5
		.636	10	19.474	127.28	404.7
		.732	48	34.430	225.36	716.6
		.824	72	42.882	280.27	891.2
		.925	11	43.161	282.10	897.0
		.941	2	43.164	282.12	897.0
20	0.1540	.014	6	5.007	19.77	128.4
		.129	22	5.631	22.23	144.3
		.346	19	7.068	27.90	181.2
		.500	23	9.184	36.26	235.4
		.611	24	14.760	58.27	378.4
		.767	33	34.472	136.09	883.7
21	0.1540	.838	44	34.744	137.17	890.7
		.772	52	34.611	136.64	887.3
		.643	92	31.771	125.43	814.5
		.518	92	14.891	58.79	381.7
		.402	24	8.318	32.84	213.2

(TABLE 11 CONTINUED)

Run	Weight of Sample (g)	P/P_O	Δ Time (hours)	Δ Elongation (mm.)	Δ Weight (mg.)	Amount Adsorbed (mg./g.)
22	0.1540	0.788	30	34.250	135.22	878.0
		.753	4	34.197	135.01	876.7
		.592	140	25.714	101.52	659.2
		.548	72	17.620	69.56	451.7
		.487	44	11.890	46.94	304.8
		.263	20	6.405	25.29	164.2
23	0.1540	.263	20	6.407	25.29	164.2
		.636	10	16.691	65.89	427.9
		.732	48	28.869	113.97	740.1
		.824	72	34.613	136.65	887.3
		.925	11	34.912	137.83	895.0
		.941	1	34.918	137.85	895.1

TABLE 12

ADSORPTION OF DI-n-BUTYLAMINE
BY SILICA GEL, 40° C.

Run	Weight of Sample (g)	P/P_o	Δ Time (hours)	Δ Elongation (mm.)	ΔWeight (mg.)	Amount Adsorbed (mg./g.)
24	0.1540	0.005	24	4.656	18.38	119.4
		.048	2	5.084	20.07	130.3
		.127	3	5.406	21.34	138.6
		.302	22	6.311	24.92	161.8
		.710	24	25.146	99.27	644.6
		.608	20	22.269	87.92	570.9
		.471	22	9.941	39.25	254.9
		.286	54	6.364	25.12	163.1
25	0.3145	.005	24	5.565	36.37	115.6
		.048	2	6.154	40.22	127.9
		.124	3	6.511	42.55	135.3
		.295	22	7.460	48.76	155.0
		.294	54	7.593	49.63	157.8

FIGURES 12-16

FIGURE 12

ADSORPTION OF DIETHYLAMINE BY
SILICA GEL, 25°C
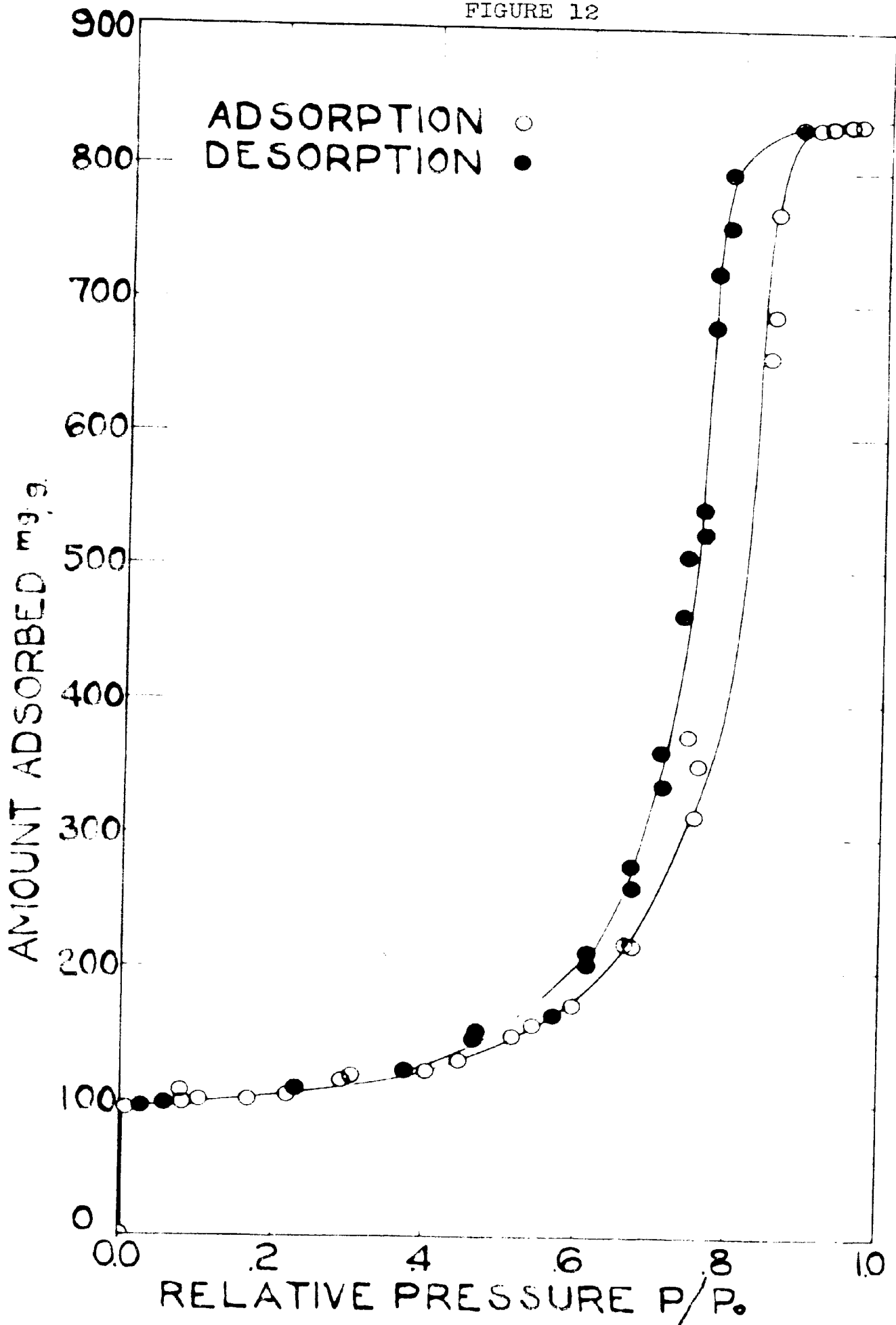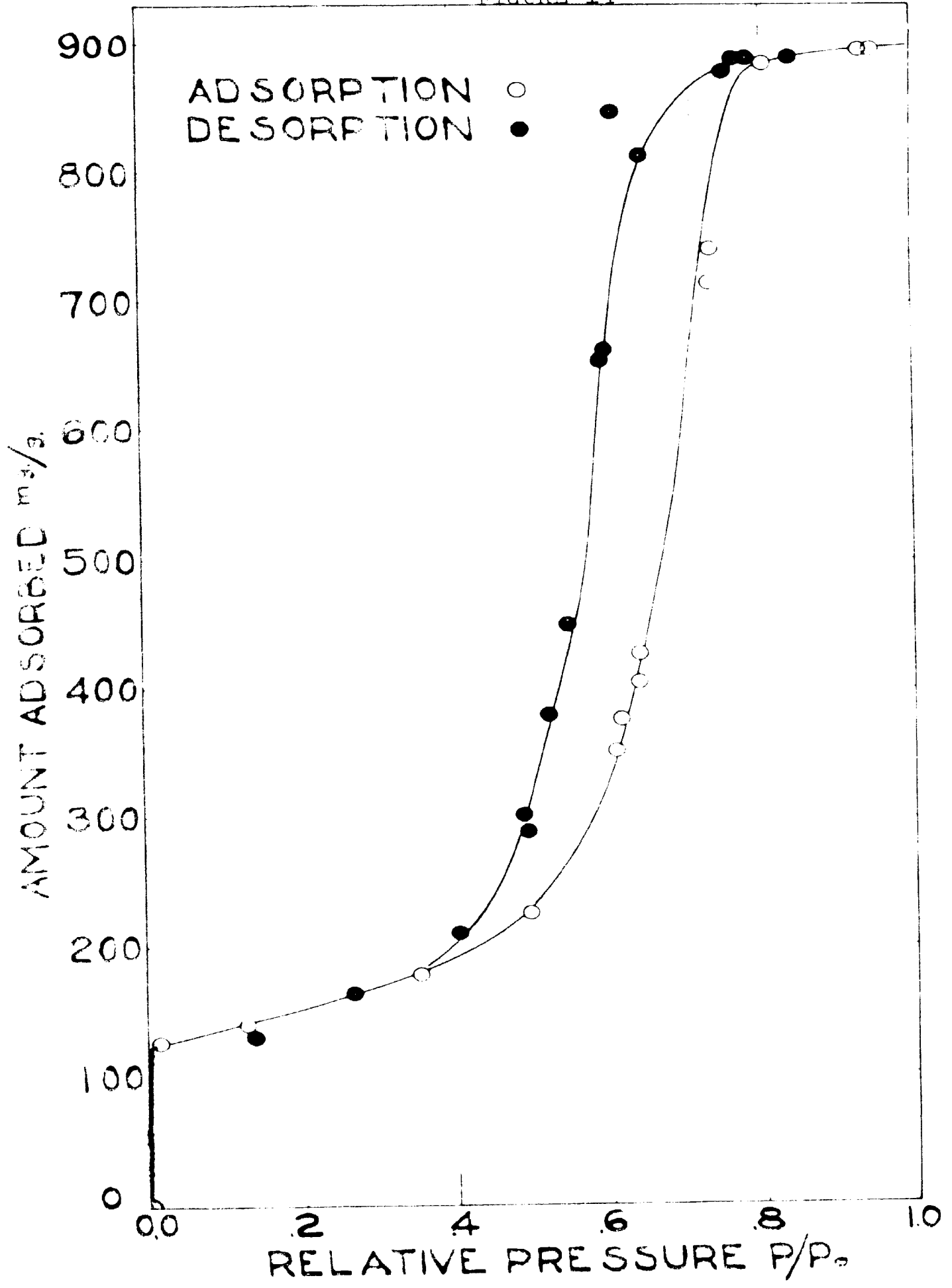
FIGURE 13

ADSORPTION OF n-BUTYLAMINE
BY SILICA GEL. 25°C.
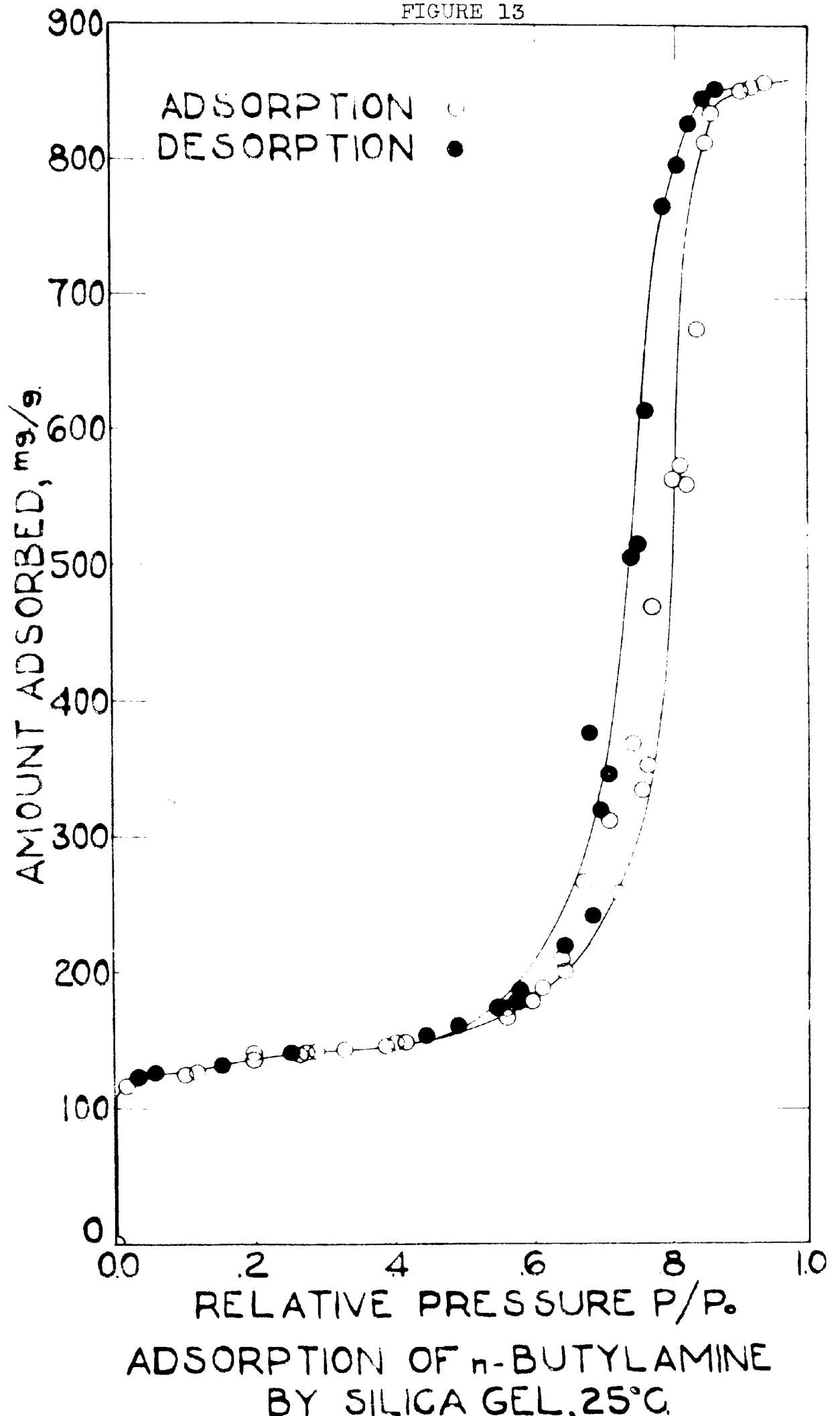
FIGURE 14

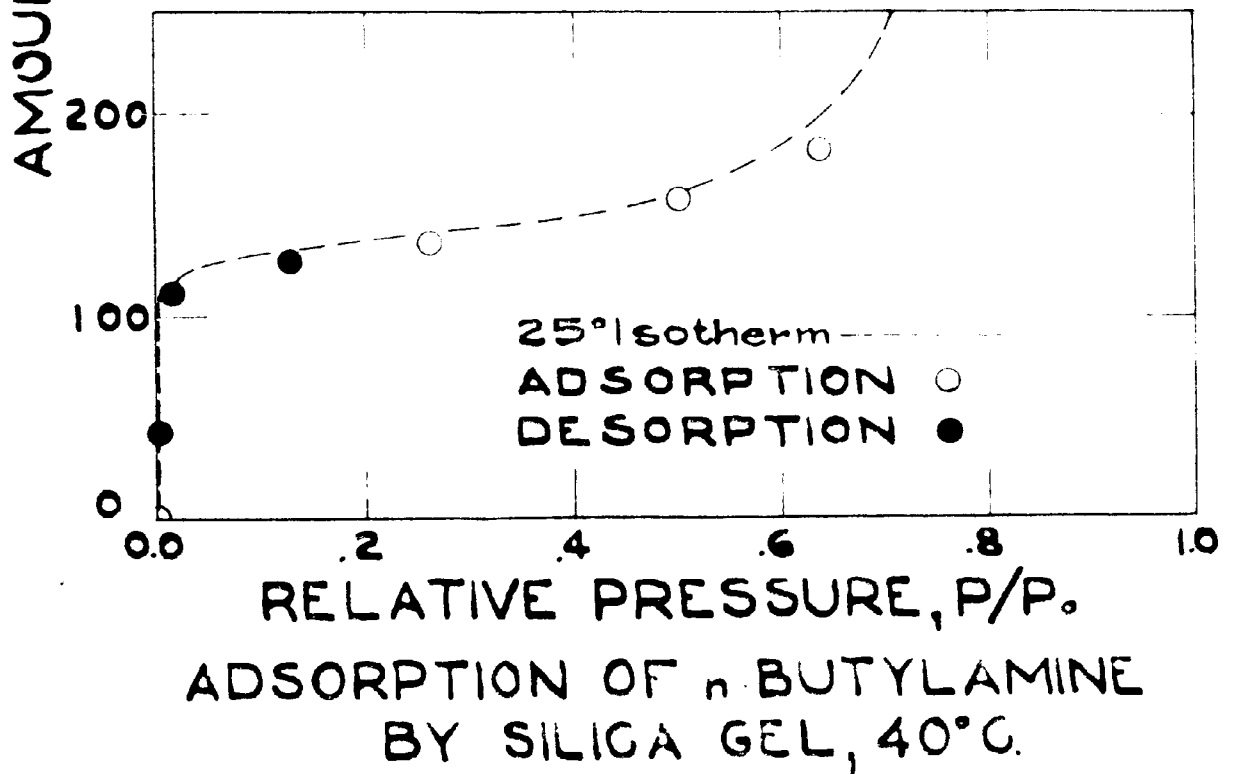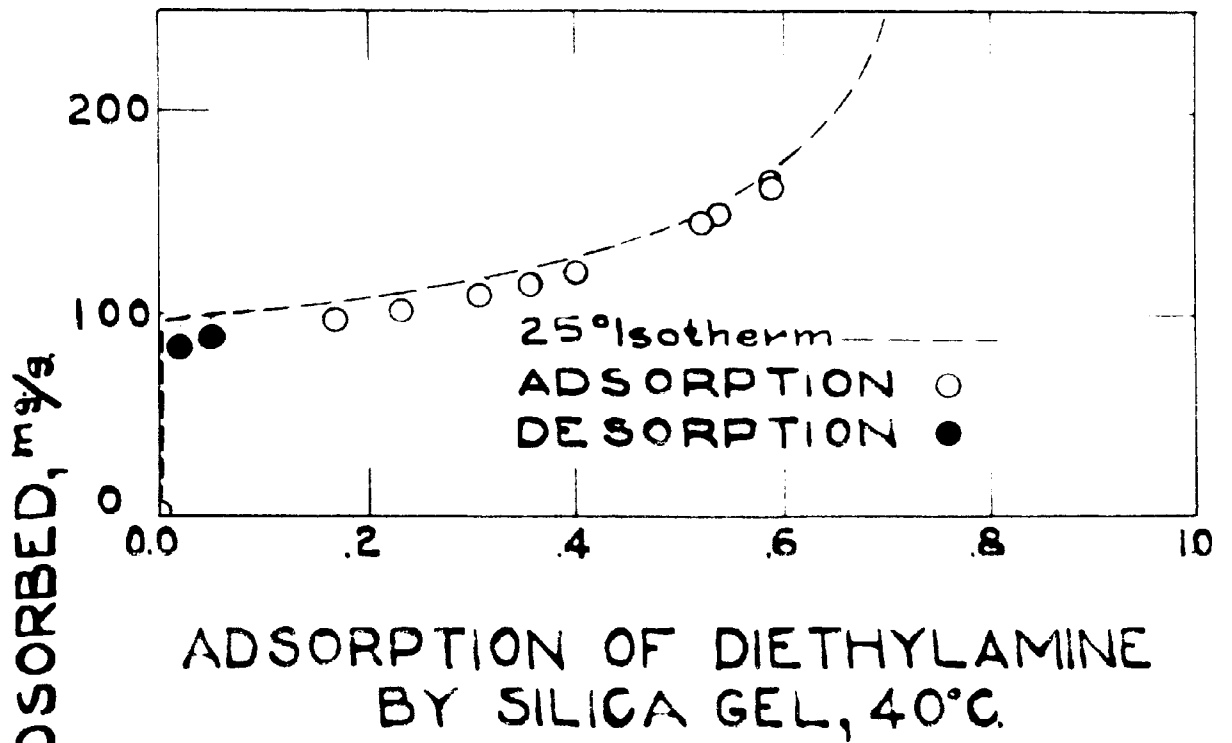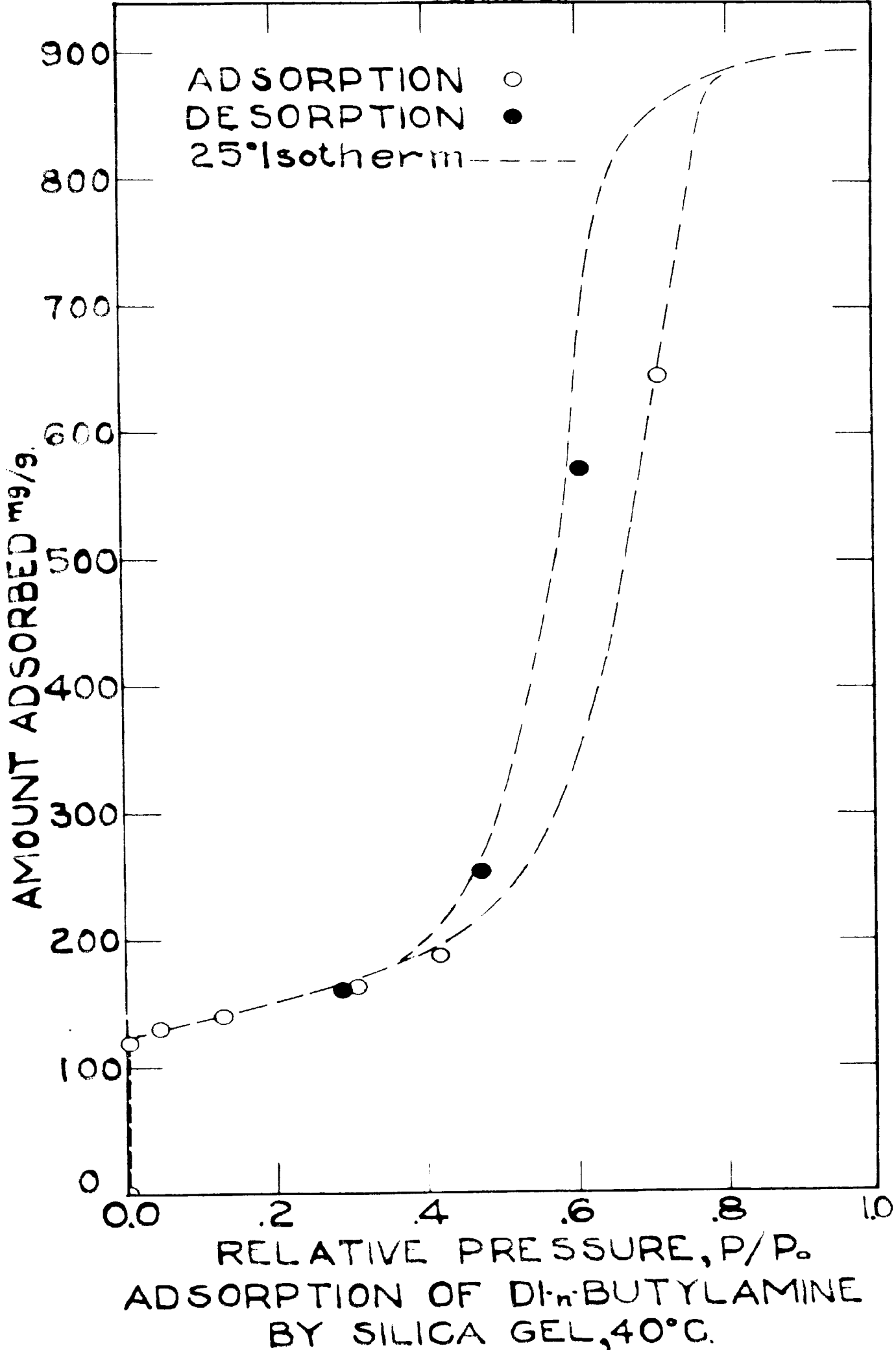ADSORPTION OF DI-n-BUTYLAMINE
BY SILICA GEL, 25°C

FIGURE 15

ADSORPTION OF DIETHYLAMINE
BY SILICA GEL, 40°C.

ADSORPTION OF n BUTYLAMINE
BY SILICA GEL, 40°C.

FIGURE 16

ADSORPTION OF DI-n-BUTYLAMINE
BY SILICA GEL, 40°C.

DISCUSSION AND THEORY

Specific Surface Area

A knowledge of the specific surface area, i.e., the area per unit weight of the adsorbent, is highly desirable in the study of adsorption. Even though many methods for the determination of area have been proposed in the past, it was only after the advent of the multi-molecular theory of Brunauer, Emmett, and Teller (2) that a generally accepted method became available. The BET theory postulates van der Waal's forces as being the cause of the adsorption. Adsorption by this theory may be expressed by the following equation:

$$\frac{x}{m} = \frac{(x/m)_m \, c \, p}{(p_0 - p)[1 + (c-1)(p/p_0)]} \qquad (11)$$

where x/m is the amount adsorbed at pressure p by unit weight of the adsorbent, p_0 is the saturation pressure, i.e., the vapor pressure of the adsorbate in the liquid state at the temperature of the solid adsorbent, c is a constant related to the heat of adsorption, and $(x/m)_m$ is the amount of adsorbate required to form a complete monolayer on the solid surface. By rearrangement,

equation (11) can be written as

$$B \equiv \frac{P}{(x/m)(P_0-P)} = \frac{1}{(x/m)_m c} + \frac{c-1}{(x/m)_m \cdot c}\left(\frac{P}{P_0}\right) \qquad (12)$$

A linear relation exists between B and p/p_0. By plotting the function B against p/p_0, $(x/m)_m$ may easily be evaluated from the slope and the intercept of the straight line. The specific area of the adsorbent can be calculated from $(x/m)_m$ if the area per molecule, A, of the adsorbate is known. The value of A will depend, of course, upon the adsorbate molecule and the nature of its packing upon the surface of the solid.

For surface area evaluations, nitrogen has been used commonly since it is comparatively inert and the adsorption of nitrogen has been found to follow the BET equation up to a moderately high pressure on most solids. The area occupied by each molecule on the surface has been estimated from the packing arrangement of the molecules in the solidified gas (face-centered cubic). For the plane of closest packing, the average area per molecule is given by

$$A = 1.092 \left(\frac{M}{N \cdot d}\right)^{2/3} \qquad (13)$$

where M is the molecular weight, N is Avogadro's number, and d is the density of the solidified gas. If the

packing on the surface approximates that of the molecules
in the liquified gas, the area per molecule is obtained
using the above equation with the value of the density
being that of the liquid. In general the choice of the
latter value gives better agreement with independent
data (17). This has been done in the present research,
the area occupied by each molecule of nitrogen at -196° C.
being taken as 16.2 $\overset{o2}{A}$ (17).

The adsorption data on six different sized
samples were all expressed in terms of unit weight and
plotted on one figure (Figure 9). Using equation (12)
the average value of $(x/m)_m$ was determined as 139.5 ml.
(STP) per gram and the area of the silica gel as 320
square meters per gram. The actual values obtained for
each of the different samples were 317, 317, 321, 313,
328, 315; these values show good agreement.

Silica gels used by other investigators have
been found to have areas of 584 and 614 square meters
per gram (35) for commercial gel (prepared from sodium
silicate) and 657, 248 and 478 square meters per gram
(36) for samples of unspecified origin.

Adsorption of Aliphatic Amines

General discussion of isotherms.

The isotherms for the amines are shown in Figures 12-16, representing the amount adsorbed as a function of the relative pressure. Certain salient features characteristic of the amine systems investigated may be noted.

Following the adsorption isotherms from zero pressure, it is seen that initially the curves rise steeply. The curves are linear and even on greatly enlarged diagrams appear to be asymptotic to the vertical axis. Briefly, the interpretation of this feature is that when the amine vapors are first introduced to the silica surface, the amine molecules are highly attracted and held firmly by the surface, leaving only a small number of molecules in vapor phase. The residual pressure in the vapor phase is exceptionally low until a considerable fraction of the surface is covered by adsorbed molecules. In this respect, the adsorption of amines differs significantly from the adsorption of other substances such as benzene and ethyl alcohol, etc., by silica (37).

After the initial demands of the surface have been satisfied at about $(p/p_o) = 0.01$, the isotherms exhibit a sharp change in slope; it is seen that in all three systems the pressure must be increased more than fifty fold (to 0.50 or higher) in order to double the

initial amount adsorbed at p/p_o = 0.01. This portion of the isotherm in which relative pressures p/p_o are between 0.01 and 0.50 is approximately linear, although a slight curvature is detectable. The interpretation is that a very low attractive force exists between the covered surface and the vapor phase; molecules now striking the surface are held but feebly and it is fairly easy for these molecules to evaporate again. A large increase in the number of molecules in the vapor phase is necessary in order to increase the amount adsorbed.

At a relative pressure of about 0.5 the curves turn upward sharply. The extent of the upward rise is far greater than the initial rise at the lower pressures. In distinction to the results noted in the immediately preceding region, a very small increase in pressure causes a large increase in the amount of amine retained by the sample. While the slope of the curves is not as steep as that over the relative pressure range 0.00 to 0.01, these curves extend over a wider relative pressure range (i.e., from 0.5 to 0.9). The major fraction of the amine held by the gel is taken up in this range. It is to be noted also that in this region the adsorption and desorption curves do not coincide. This phenomenon is known as hysteresis.

As relative pressures are increased above a value of about 0.9, the hysteresis loop closes, and the

slope of the isotherm drops to practically zero. This indicates that the forces responsible for the hysteresis no longer exist, and that only a small residual force remains which causes slight additional amounts of adsorption.

The implications of these features will be discussed in some detail.

Multimolecular adsorption.

The multimolecular theory of adsorption (the BET theory) has been the one most successful to date in correlating the wide variety of adsorption data. It may be helpful to consider some of the applications of this theory and then discuss some of its limitations.

Low pressure region.- a. Evaluation of $(x/m)_m$. At relative pressures below 0.2, the multimolecular adsorption theory in the form of equation (12) may be successfully applied. The values of $(x/m)_m$ may be obtained from the slope and the intercept of the straight lines, as was done in the adsorption of nitrogen (page 66). By this method it was found that $(x/m)_m$, the amount of amine required to form a monolayer on the gel, was 90.0 mg./g. for diethylamine, 119.4 mg./g. for n-butylamine, and 123.8 mg./g. for di-n-butylamine. It may be noted from the adsorption isotherms that the formation of a monolayer is complete at very low pressures in each case.

From a large scale plot of the data at the low pressures, it has been estimated that the relative pressures for the formation of the monolayers are 0.008, 0.011, and under 0.010 for the three amines respectively. These relative pressures are exceptionally low. For comparison with other gases adsorbed on silica the following values for the adsorption of gases on silica are cited (38): 0.10 for nitrogen (-196° C.), 0.12 for nitrogen (-183°), 0.15 for argon (-183° C.), 0.17 for oxygen (-183°), 0.33 for carbon dioxide (-78°), and 0.30 for butane (0°). The following values were obtained at 25° C. (39): 0.1 for acetone, 0.2 for toluene, 0.2 for acetic acid, and 0.3 for hexane. At 79° C. it has been found that a relative pressure of 0.5 is necessary before a monolayer of bromine is formed on silica gel (40).

The terms "chemisorption" and "physical adsorption" have often been used in the literature to distinguish adsorption processes involving strong interaction between the solid and the adsorbed vapor (of energy comparable to chemical reactions) from those adsorption processes involving weak interaction (of energy comparable to liquid condensation processes). This distinction may be done for convenience, realizing that there exist cases in which the energies involved are intermediate in magnitude and that in such cases it would be futile to attempt to label the adsorption process as

either chemisorption or physical adsorption. In the cases of the amines on silica gel, however, the completion of the monolayers at such very low relative pressures suggests that the initial adsorption may appropriately be termed chemisorption.

b. Evaluation of BET n. After the formation of the monolayer additional adsorption in the second and succeeding layers was found to occur to a slight extent as the pressure was increased. At relative pressures slightly above $p/p_0 = 0.2$, a modification of the above BET equation is necessary. In the derivation of the general equation (11) the summations were carried out to include an infinite number of layers of adsorbed molecules, such as may occur on a plane surface. With a porous solid such as silica gel, owing to the presence of many capillaries and crevices, there are physical hindrances to the adsorption of an infinite number of layers and the summation must be restricted to n layers. It was shown by the original authors (2) that in the case of restricted adsorption equation (11) cannot be applied but that the following equation should be used:

$$\frac{x}{m} = \frac{(x/m)_m \cdot c \cdot (P/P_0) \left[1 - (n+1)(P/P_0)^n + n(P/P_0)^{n+1} \right]}{(1 - P/P_0) \left[1 + (c-1)(P/P_0) - c(P/P_0)^{n+1} \right]} \tag{14}$$

The symbols have the same meaning as before. Joyner, Weinburger, and Montgomery (41) have suggested a

separation of the variables (p/p_o) and n from equation (14), resulting in equation:

$$\frac{x}{m} = \frac{(x/m)_m \; \phi(n, \pi)}{\frac{1}{c} + \Theta(n, \pi)} \qquad (15)$$

where

$$\pi = P/P_o \qquad (16)$$

$$\phi(n, \pi) = \frac{\pi[(1-\pi^n) - n\pi^n(1-\pi)]}{(1-\pi)^2} = \sum_{i=1}^{n} i\pi^i \qquad (17)$$

and

$$\Theta(n, \pi) = \frac{\pi(1-\pi^n)}{(1-\pi)} = \sum_{i=1}^{n} \pi^i \qquad (18)$$

Both ϕ and Θ are independent of the nature of the adsorbent and adsorbate and of the nature and magnitude of the adsorptive forces. Furthermore $\phi/(x/m)$ is linear with respect to Θ so that with the proper value of n the plotting of $\phi/(x/m)$ yields a straight line.

At low relative pressures, π to the nth power will be much smaller than one, and the equation (14) reduces to equation (11). It is this relation of the equations which enables one to use the simpler form of the BET equation for evaluation of $(x/m)_m$ at low relative pressures. At relative pressures as great as 0.2, however, the deviation between the two equations becomes

becomes apparent and one can then evaluate n by the
Joyner, Weinburger and Montgomery method. For diethyl-
amine n was found to approximately 2.3, for n-butylamine
slightly below 2, and for di-n-butylamine, approximately
2.3.

The physical significance of n was originally
thought to be the maximum number of layers of adsorbed
molecules that could be accommodated by a surface.
Subsequently evidence was found that indicated that
this interpretation of n should be viewed with reserve
(42). The latter view has been borne out in the present
research. A given capillary may accommodate fewer layers
of large, long molecules than short, small molecules, and
hence according to the original concept, the value of
n should be smallest for the largest molecule. Dibutyl-
amine molecules are undoubtedly larger than diethyl- or
butylamine molecules, yet the value of n found applicable
for dibutylamine was the same as for diethylamine and
even a little larger--instead of smaller--than the value
of n for monobutylamine.

Comparisons with other estimates of the size
of the capillaries will also show that the values of n
are smaller than the maximum number of layers expected
(see page 86). The conclusion to be reached from these
facts is that the physical significance of n is obscure

and that it should be considered merely as a third parameter of the adsorption processes.
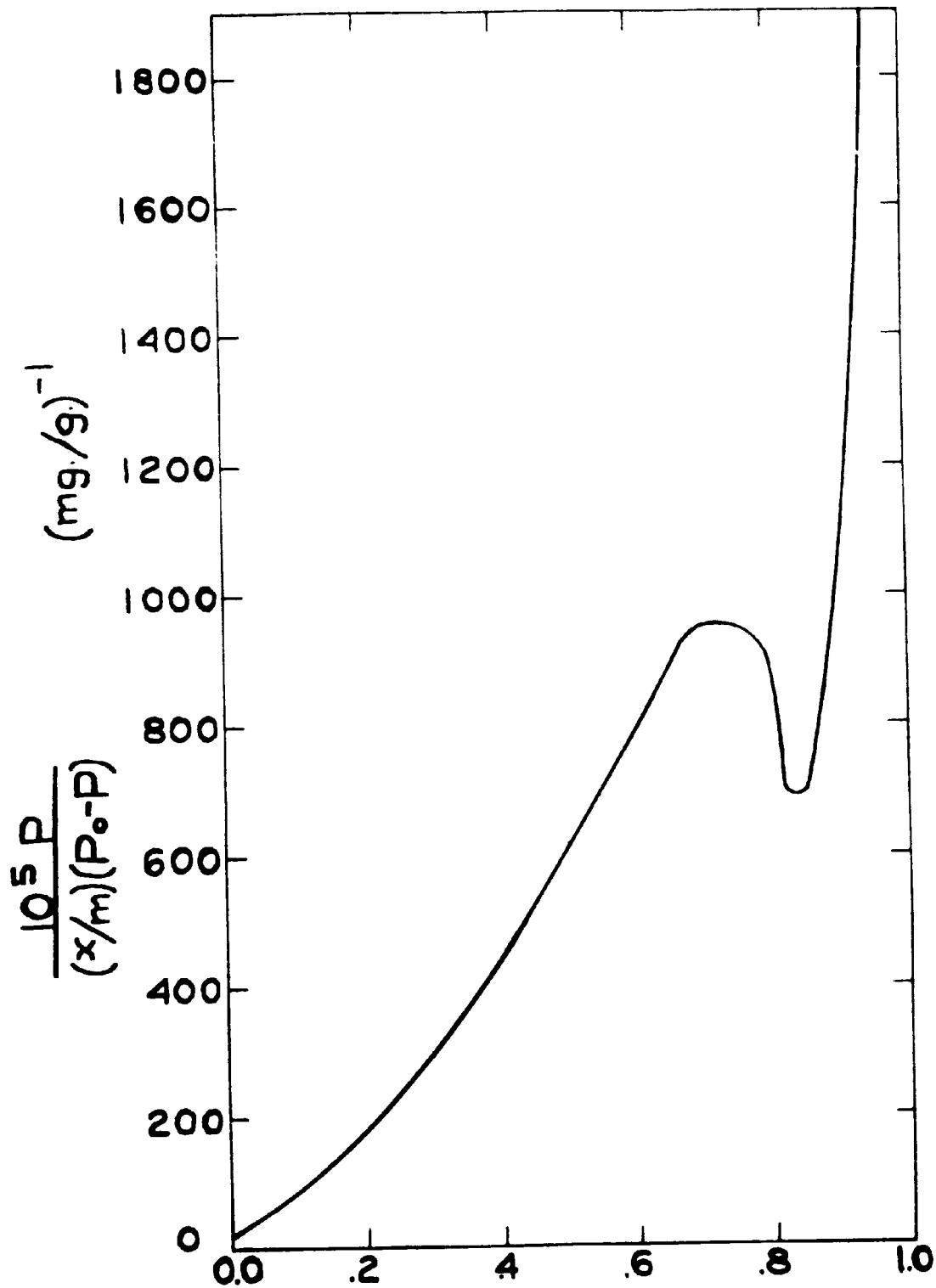
Intermediate and high pressure regions.- a. Deviations from theory. At relative pressures up to approximately 0.4, the BET equation (14) represented the adsorption data fairly well.

At relative pressures above 0.4, however, greater adsorption was observed than predicted by values calculated from equation (14) using the constants determined at the lower relative pressures. At still higher relative pressures, however, the calculated amount adsorbed was less than the observed amount adsorbed, even though the constant n was changed to infinity. A diagram of the BET function $\dfrac{P}{(x/m)(P_0-P)}$ $vs.$ P/P_0 for one of the runs, using n = infinity, is given in Figure (17). If the BET equations were to hold over the entire pressure range the curve should approximate a straight line.

Greater adsorption than would be called for by the theory would be indicated by a downward deviation from the straight line, since the amount adsorbed is represented in the denominator of the BET function. In Figure (17) more than a minor deviation in the slope is involved, for a maximum is reached and the slope becomes negative, indicating that the adsorption has been greatly

FIGURE 17

B.E.T. PLOT OF ADSORPTION
OF n-BUTYLAMINE BY SILICA GEL

The y-axis is labeled $\dfrac{10^5 \; P}{(x/m)(P_o - P)}$ $(mg./g.)^{-1}$ with values 0, 200, 400, 600, 800, 1000, 1200, 1400, 1600, 1800.

The x-axis is labeled RELATIVE PRESSURE, P/P_o with values 0.0, .2, .4, .6, .8, 1.0.

enhanced in this portion of the isotherm. Either the
process predominantly operative over the first portion
of the isotherm has been supplanted by another process,
or a second attractive force in addition to the original
one has become operative. The latter possibility appears
to be more reasonable.

The portion of the curve having a negative slope
is limited in range. At even higher relative pressures,
the curve exhibits a minimum beyond which the slope again
becomes positive. This last feature of the curve may be
easily appreciated by examination of the nature of the
BET function, $p/(x/m)(p_o-p)$. As p approaches p_o, (p_o-p)
approaches zero and hence the entire function approaches
infinity.

It is difficult to determine the nature of the
additional force which caused the enhanced adsorption
on the basis of the multimolecular theory alone.
Brunauer, Deming, Deming, and Teller (3) have elaborated
upon the original BET theory and have proposed that the
entire adsorption process occurs by one mechanism through-
out the entire pressure range and that if additional
adsorption was found to occur in higher pressure regions,
this was due to additional energy of binding in the last
layer that was adsorbed in any given capillary. The
last layer of adsorbed molecules was considered to be
attracted by "both sides" of the capillary, and hence a

greater amount of energy was expended when these molecules were adsorbed. A fourth constant was added to the three already used in equation (14) and the resultant equation became lengthy and unwieldy. The derivation was further complicated by the necessity of using alternative equations depending upon whether the width of the capillaries was an even or an odd integral multiple of the width of each adsorbed layer. (This was due to the modification necessary in carrying out the summation in the derivation.) Another form of the equation was necessary in case the last adsorbed layer did not form exactly in the middle of the capillary. It is difficult to decide whether conformity or non-conformity of the data to the equations was of significance, since in the derivation of this group of equations it was assumed that the capillaries were all of the same shape and diameter. However, most porous adsorbents do not meet these requirements but have capillaries of differing sizes. Furthermore it is difficult to explain the existence of hysteresis phenomena by this multimolecular adsorption theory. This additional adsorption which was responsible for the negative slope in the BET curve will later be considered from the viewpoint of the capillary condensation theory (page 80).

b. Extrapolation of the BET equation. It may be of interest to estimate approximately the additional

amount of amine taken up by the adsorbent due to the second force which appeared in the higher relative pressures. This may be done by extrapolating to the saturation pressure, (i.e., to $p/p_o = 1$) the BET function which had been found to apply satisfactorily over the lower pressures. The difference between the amount actually adsorbed at the saturation pressure and the amount calculated by extrapolation is this additional amount taken up by the gel due to the additional forces just mentioned in the previous paragraph.

For this extrapolation equation (14) must be used, inasmuch as the simple equation (11) was found to no longer be applicable even at relative pressures as low as 0.2. The method of performing the extrapolation was by means of the functions ϕ and Θ (equations 17 and 18). Although at p/p_o, (or π), equal to 1, the functions are indeterminate, the limit of the functions as the relative pressure approaches 1 may be determined by application of Lhopital's Theorem. The value of $\phi/(x/m)$ at the value of Θ which corresponds to the saturation pressure may be determined by extrapolation of the straight line function $\phi/(x/m)$ vs. Θ. This was done for the values of nearest integral values of n which had been found applicable for each amine system (page 74). The value of x/m at saturation, $(x/m)_s$, may be then calculated, since the limit of ϕ at saturation is known. The values

of $(x/m)_s$ as calculated in this manner represent the
amounts that would have been adsorbed at saturation had
the BET equation (14) been operative throughout the
entire relative pressure range to $p/p_o = 1$. These values
are tabulated in Table 13 in the column "$(x/m)_s$ calc."
The column "$(x/m)_s$ obs." lists the limiting values of
the amounts adsorbed which were actually observed from
the adsorption isotherms. The values in the column
"$\Delta (x/m)_s$" are the differences between corresponding
data in the above mentioned columns and represent the
total additional amounts of amine taken up due to the
forces operative in addition to the BET forces.

TABLE 13

SATURATION ADSORPTION VALUES
OBSERVED AND CALCULATED FROM THE BET EQUATION

	n	$(x/m)_s$ calc.	$(x/m)_s$ obs.	$\Delta(x/m)_s$
Diethylamine	2.0	138 mg./g.	831 mg./g.	693 mg./g.
	3.0	181	831	650
n-Butylamine	2.0	178	860	682
Di-n-butylamine	2.0	208	898	690
	3.0	274	898	624

It is to be noted that this additional amount
of amine taken up is relatively great--being approximately
three times the calculated amount which would have been
adsorbed by the multimolecular adsorption process alone.

Capillary condensation.

The adsorption isotherms showed greatly en-
hanced adsorption in the intermediate pressure range.
It was postulated that this phenomenon was due to some
additional force acting over this range (see page 75).
It was also shown that the multimolecular adsorption
theory did not account simply for the additional force.

A reconsideration of the method of formation
of the silica gel may give insight into this problem.
Hydrolysis of silicon tetrachloride vapor yielded a two
phase gel system of interlacing siliceous solid fibers
in a continuous aqueous phase. The water and acid were
removed by heating and eventually by evacuation, leaving
a solid framework of silica. Such a system may easily
be imagined to be interspersed with fine channels,
capillaries, and with crevices formed by intersections
of silica fibers. X-ray studies have shown quite
conclusively that irregularities and discontinuities
exist in the gel structure (43).

Kelvin and Cohan equations. A film of liquid
covering the fine siliceous fibers would have a highly
convex surface, whereas a thin film of liquid wetting
the intersection of two such fibers and the surface of
the liquid within the fine capillaries and pores would
have a highly concave surface. The effect of curvature

upon the properties of liquids was firmly established on
a theoretical basis by the thermodynamic equations of
Lord Kelvin, who developed the relation between the vapor
pressure and the radius of curvature of surfaces

$$ln\ p/p_0 = \frac{2\gamma M}{rRTd} \qquad (19)$$

where p is vapor pressure of the sample of liquid drop
having radius r, p_0 is the normal vapor pressure, γ is
the surface tension, M is the molecular weight of the
liquid, and d its density at the temperature T.

The consequence of the Kelvin relation is
that on convex surfaces (where the radius of curvature,
r, is positive) the liquid has a higher vapor pressure
than does the bulk sample; whereas on concave surfaces
(where the radius of curvature is negative) the liquid
has a lower vapor pressure than does the bulk sample.
Applied to the present problem, this would mean that in
fine capillaries the vapor would be condensed to liquid
although the pressure in the vapor phase might be far
less than the normal condensation pressure for that
temperature.

The above Kelvin equation applies to curved
surfaces having spheroidal shapes. Cohan (44) has de-
rived the equation relating the properties of curved
surfaces of cylindrical form

$$\ln P/P_0 = \frac{\gamma M}{2 R T d} \qquad (20)$$

where the symbols have the same meaning as before. The difference is a factor 2. Whereas the Kelvin equation would deal with condensation in capillaries formed by wedges or pits, the Cohan equation applies to pores which are open at both ends--tubular capillaries. Actually it is expected that both types of capillaries might be present in a sample of silica gel. The pressure at which a capillary of a given size is filled will be dependent not only on radius of the capillary, but also on its shape. In emptying, however, the situation is different: the meniscii in both types of capillaries are spheroidal and the desorption process would thus be governed solely by the Kelvin equation. This gives rise to hysteresis in the open type capillaries.

In closed capillaries, hysteresis may be accounted for if a constriction occurs along the capillary; in filling, the condensation pressure will be governed by the wider portion of the capillary, but in desorption the wide portion of the capillary is blocked off by the liquid held at the constriction with a smaller radius. The entire capillary will not be emptied until the pressure is reduced sufficiently to remove the liquid

from the constriction. This will be at a lower pressure than that at which the wide portions of the capillary are filled, thus accounting for hysteresis.

The Kelvin equation is applicable to both open and constricted capillaries in the desorption process. The radius of the capillary which is emptied at a given value of p/p_0 may be calculated by means of equation (19). The inflection point in the isotherm figure will cause an inflection point also in the figure representing the amount adsorbed as a function of the capillary radius. The radius at the inflection point is actually the most probable radius. (For convenience this radius has been called the "mean" radius in the literature. It is recognized that this is not the true mean radius but deviates from it slightly.) Calculating the radius by this method from the isotherms of the three amines at 25° C., the results are 56 Angstroms for diethylamine, 58 for n-butylamine, and 58 for di-n-butylamine (Table 14). These results are in excellent accord when it is considered that a difference of 0.01 relative pressure unit will alter the calculated radius by 2 Angstroms. The agreement is all the more impressive when one considers the difference in the absolute pressures involved. The absolute pressures, p, corresponding to the above radii are 187, 69.3 and 1.41 mm. respectively.

TABLE 14

RADII CALCULATED FROM CAPILLARY
CONDENSATION THEORIES AT 25° C.

	Amine		
	Diethyl-	n-Butyl-	Di-n-butyl-
Surface tension (dynes/cm.)	19.08	22.96	23.60
Molecular weight (g.)	73.1	73.1	129.2
Density (g./ml.)	.6972	.7335	.7556
Vapor pressure (mm.)	238.4	94.98	2.51
p/p_0 at adsorption inflection point	0.82	0.80	0.67
p/p_0 at desorption inflection point	0.75	0.73	0.57
Cohan radius (A.)	41	41	42
Kelvin radius (A.)	56	58	58

A further implication may be found in the agree-
ment of radii obtained. The Kelvin equation involves the
surface tension and density of the liquid sample. In the
above calculations values of these properties in the bulk
phases were used, no experimental data on these properties
in capillaries as small as 60 Angstroms being available.
It has long been a matter of speculation as to the effect
of capillary radius on these properties. From the agree-
ment in radii values obtained it appears reasonable to
conclude that the ratio of surface tension to density is
still approximately the same in capillaries of 60 Angstroms
as in bulk.

Radii calculated by application of the Cohan
equation to the inflection point of the adsorption branch
of the hysteresis loop were found to be 41, 41 and 42

Angstroms. The difference between the two sets of radii values can be accounted for as follows: assume that the value 60 Angstroms, as determined by the desorption branch, is correct. Comparison of the two equations, (19) and (20), shows that the Cohan radius is one-half the Kelvin radius at a given value of p/p_o. If the capillaries were all of the constricted type, application of the Cohan equation to the adsorption data would give one-half the radius of the bodies (not the necks) of the capillaries. Since the bodies must have radii at least slightly larger than 60 Angstroms, the radius as calculated by the Cohan method will be some value over 30 Angstroms, the exact value depending upon the size of body. However if the capillaries were exclusively of the open type, the calculated value of the radius would be 60 Angstroms.

Single capillary method. There is another method for arriving at an estimate of the mean pore radius which has been often used, and may be of interest for comparison. The entire capillary space is assumed to be cylindrical and of uniform width. The radius is calculated from the relationship between the surface and volume of cylinders, $r = 2 V/A$. The surface area of this gel has been determined as 320 m.^{2}/g. (page 67) and on page 48 the maximum volume of the pores was calculated as 1.15 ml./g. The pore radius as determined by this

method is 72 Angstroms. It is very unlikely that the pore volume is actually as high as 1.15 m., since this figure involved the use of the density of quartz. Using 2.25 g./ml. as a more likely density for the solid substance in silica gel, the pore volume of the silica gel sample then would be 1.08 ml./g. and the radius calculated by the above method would be 67 Angstroms. When one considers the assumptions involved, both of these radii values are in surprisingly good agreement with the values obtained by the use of the Kelvin equation.

Discussion of BET n. A further examination of the concept of the BET parameter n is now in order. It was shown that the value of n obtained for n-butylamine was 2. The maximum length of the n-butylamine molecule is estimated as 7.0 Angstroms. In this computation the end hydrogens were considered as being parallel to the length of the molecule (45). The maximum radius of the capillary as calculated from the n value would then be 14 Angstroms. Similarly with diethylamine, the maximum length of the molecule would be about 4.5 Angstroms, and considering n = 3 in this case, the calculated maximum capillary radius would be about 13 Angstroms. With di-n-butylamine, the value of n was also under 3. Assuming the dibutylamine molecule was attached to the

silica surface by one end of the butyl radicals (although presumably the attachment is through the nitrogen), and that the entire molecule was stretched to its full length of 12 Angstroms, and that each of the two succeeding layers was also stretched to 12 Angstroms, the maximum capillary radius would be 36 Angstroms.

Even the most liberal allowances for the length of the adsorbed molecules do not appear to give a radius compatible with those calculated by the other two methods. This further substantiates the belief that the concept of n as the maximum number of layers must be viewed with reserve.

Comparison of theories. In view of the experimental evidence obtained in this research, the objections to the capillary condensation theory of Brunauer, Deming, Deming, and Teller (abbreviated for convenience to BDDT) may be discussed in more detail. They have ascribed the entire phenomena of adsorption to the operation of van der Waal's forces, and disregarded the possibility of the Kelvin effect.

One of their objections to the capillary condensation theory was that the adsorption isotherms that had been observed were of the form shown in Figure (A) (the BDDT equation may be made to fit this curve), rather than of that shown in Figure (B), which according to them would represent capillary condensation.
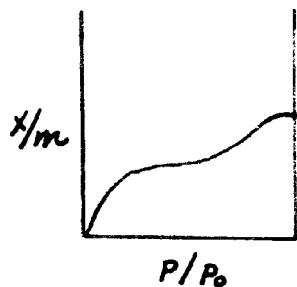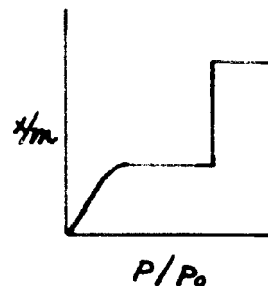
Fig. (A)

Fig. (B)

Two comments may be made on this argument. In the first place, direct evidence on the impossibility of the capillary condensation type of isotherm was not presented. Secondly, both isotherm diagrams were derived on the basis of the existence of one uniform capillary size in the entire sample. This accounts for the infinite vertical slope in the capillary condensation diagram; all the capillaries were to be filled at exactly the same pressure. A distribution of capillary radii is to be expected, however, in the adsorbent, and the capillary theory diagram should therefore be drawn with a steep, yet finite, slope. The experimental curves obtained in the present research (Figures 12-16) are believed to resemble closely the form representing capillary condensation.

Two advantages of the BDDT theory over the capillary condensation theory have been claimed by its authors. The BDDT scheme was said to present a unified theory which included unimolecular adsorption, multimolecular adsorption and the "enhanced adsorption that

occurs in capillaries," whereas the capillary condensation
theory was said to include but one of these processes.
It has been seen in this research, however, that all cases
of "enhanced adsorption" are not represented by the multi-
molecular adsorption theory. (A further amplification
of this will be found in the consideration of the ener-
getics of these systems presented later.)

The second advantage claimed for the multi-
molecular adsorption theory was that it had developed an
equation which described the form of the isotherms which
have been obtained experimentally, whereas the capillary
condensation concept may not be expressed in the form of
an isotherm equation. While admitting the desirability
of an isotherm equation, it does not seem that such an
equation is a necessity, nor does it seem that lack of
such an equation is sufficient grounds for dismissal of
a theory which is able to aid in the interpretation of
known facts.

Energetics of the Adsorption Process

The data discussed on the basis of the form of the isotherms in the previous section are considered in this section on the basis of the heats of adsorption and free surface energy changes involved. These considerations will be shown to substantiate the arguments presented previously.

Isosteric heats of adsorption.

Kruyt and Modderman (46) have shown that the heat of adsorption can be calculated from isotherms at two different temperatures by application of the following equation:

$$\frac{dQ}{d(x/m)} = \frac{R T_1 T_2}{T_1 - T_2} \ln \frac{p_1}{p_2} \qquad (21)$$

where $dQ/d(x/m)$ is the differential heat of adsorption (the heat evolved per mole of the gas adsorbed), R is the gas constant, and p_1 and p_2 are the equilibrium pressures necessary for the adsorption of the same amount of gas, x/m, at temperatures T_1 and T_2. Values obtained in this way have been termed "isosteric" heats of adsorption. This equation is analogous to the Clausius-Clapeyron equation, the differential heat of adsorption taking the place of the heat of condensation. The application of

the equation is subject to the usual restrictions of a moderate range of pressure and temperature.

In this research, isotherms over the entire pressure range were obtained at 25° C., and over a partial range of pressure at 40° C. The 40° runs were carried somewhat beyond the beginning of the hysteresis loop for all three amines. The method used to calculate the heats of adsorption was as follows: the value of p_1/p_0 at 40° for a given value of x/m was determined from Tables 8, 10 and 12. The value of p_2/p_0 at 25° for the same value of x/m was determined from the 25° isotherms (Figures 12-14). In this manner, only one graphical interpolation is necessary for each calculation. Since all the data have been presented as functions of relative rather than of absolute pressure, it is convenient to change equation (21) to the form:

$$\frac{dQ}{d(x/m)} = \frac{R\,T_1\,T_2}{T_1 - T_2}\left[\ln\frac{(p_1/p_{01})}{(p_2/p_{02})} + \ln\frac{p_{01}}{p_{02}}\right] \qquad (22)$$

where p_{01} and p_{02} are the vapor pressures at T_1 and T_2, respectively. The results are presented in Table 15. In Figure 18, the differential heats of adsorption are shown as a function of the amount adsorbed. Also shown in this figure, by broken lines, is the mean value for the heat of condensation in the temperature range involved.

TABLE 15

ISOSTERIC HEATS OF ADSORPTION

	x/m (mg./g.)	P_1/P_{01}	P_2/P_{02}	$\dfrac{P_1/P_{01}}{P_2/P_{02}}$	$\dfrac{d\ Q}{d(x/m)}$ (kcal./mole)
Diethylamine	81.7	.020	.0020	10.0	36.1
	86.4	.048	.0044	10.9	37.2
	95.5	.170	.052	3.27	22.4
	100.8	.235	.125	1.88	15.4
	108.2	.302	.230	1.31	10.9
	114.2	.359	.29	1.24	10.3
	118.4	.398	.32	1.24	10.3
	142.4	.518	.49	1.05	8.2
	148.2	.541	.52	1.04	8.1
	163.3	.590	.57	1.03	7.7
n-Butylamine	118.9	.031	.014	2.21	18.4
	127.8	.126	.055	2.29	18.8
	137.5	.264	.18	1.47	13.3
	157.2	.500	.47	1.06	9.3
	160.2	.511	.49	1.04	9.0
	182.5	.636	.60	1.06	9.3
Di-n-butylamine	117.5	.005	-	-	-
	129.1	.048	.016	3.0	25.8
	137.0	.125	.11	1.14	13.9
	160.4	.298	.25	1.19	14.4
	161.8	.294	.27	1.09	13.3
	163.1	.286	.27	1.06	13.0
	254.9	.471	.45	1.04	12.8
	570.9	.608	.59	1.03	12.6
	644.6	.710	.71	1.00	12.3

FIGURE 18
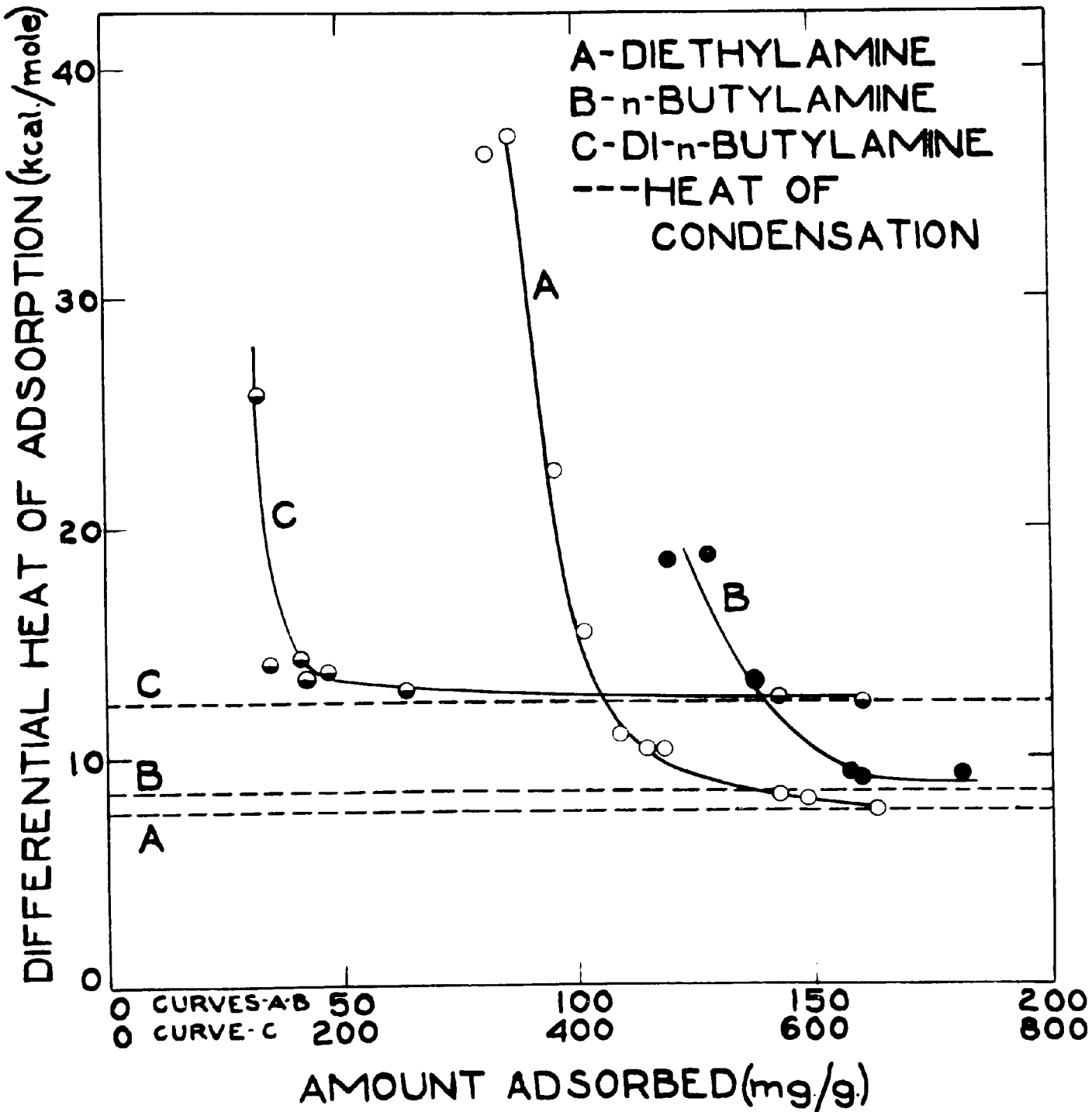
HEATS OF ADSORPTION
ON SILICA GEL

The curves all have the general features of showing high heats of adsorption for the low pressure range of the isotherm, with the heat approaching the heat of liquefaction as the pressure is increased. This is in general conformity with the majority of cases in a review of heat of adsorption curves (46). It is easy to understand why this should be the case. The first molecules being adsorbed on a surface will seek those surface sites where the adsorptive forces are the highest. After the surface is covered by a monolayer of adsorbed molecules, the forces holding the second and subsequent layers are much weaker, and after several layers are adsorbed on the surface, the properties of the adsorbed phase may not be much different from those of the bulk liquid, and hence the heat of adsorption would approach the heat of condensation.

Comparison of theories. Further comparison of the BDDT and the capillary condensation theories may be made at this point. It will be recalled that BDDT theory accounted for "enhanced adsorption" in capillaries as being due to the relatively higher energy available when the last layer of a capillary was filled. Inasmuch as this enhanced adsorption, $\Delta (x/m)_s$ (Table 13), amounted to more than three times the total amount which would have been adsorbed, $(x/m)_s$ calc., without this additional energy, it is to be expected that the additional energy

should be large in amount. By Brunauer's method (47),
the order of magnitude of this additional energy, Q_1,
is given by the equation

$$Q_1 = 2 \gamma \frac{3^{1/2}}{2^{2/3}} N^{1/3} V^{2/3} \qquad (23)$$

where γ is the surface tension, N is Avogadro's number,
and V is the molar volume. For the amines studied the
value of Q_1 is approximately 2.8 kilocalories. It is
further to be expected that since the enhanced adsorp-
tion is due to this additional energy, said available
energy should become liberated when the additional
adsorption occurs, namely at the start of and along the
hysteresis loop. The experimental results (Figure 18),
however, do not show evidence of the presence of any such
additional energy either at the inception of hysteresis
or anywhere further along the isotherm.

According to the capillary condensation theory,
the retention of the additional amount of amine is caused
by condensation of the vapor to liquid within the capil-
laries; the heat evolved in such a process may be expected
to be approximately that of the heat of condensation.
According to this theory, the heat evolved in the portion
of the isotherm representing the hysteresis loop should
approach the normal heat of condensation of the adsorbate
molecules. This was observed to be the case. This

confirms other evidences in this thesis that the capillary condensation theory explains much more satisfactorily than the multimolecular adsorption theory the various phenomena observed in the hysteresis portion of the isotherms (page 87).

Free surface energy changes.

The change in free surface energy which occurs when a vapor is adsorbed on the surface of a solid may be derived from the classical adsorption equation of Gibbs. The fundamental Gibbs equation may be expressed in the form

$$d\gamma = -S^s dT - \sum_{i=1}^{n} \Gamma_i d\nu_i + vd\rho \qquad (24)$$

where γ is the interfacial tension, or free surface energy per unit area, S^s the entropy of the surface per unit area, T the temperature, the "surface excess" and the chemical potential of the i th component. The exact definition of the concept of surface excess depends on the exact position assigned to the mathematical surface and is a matter of considerable discussion in cases involving boundary transitions of greater than one molecular thickness. For a discussion of such cases, one is referred to the papers by Guggenheim and Adam (48) and Guggenheim (49). In the present case involving a solid and a single component vapor, the hypothetical

mathematical surface may be identified with the physical boundary of the solid phase. The surface excess of the solid (component 1) is zero in this case and may be considered as x/mA, the amount adsorbed per unit area. At constant temperature and pressure the Gibbs' equation may be reduced to

$$d\gamma = -\frac{x}{mA} d\nu_2 \qquad (25)$$

If within the pressure ranges the gas may be considered to obey the ideal gas laws with sufficient exactness, equation (25) may be written

$$d\gamma = -\frac{x}{mA} RT \, d\ln p = -\frac{x}{mA} RT \, d\ln(P/P_0)$$

$$= -\frac{x}{mA} RT \frac{d(P/P_0)}{(P/P_0)} \qquad (26)$$

since d ln p = d ln p/p$_0$.

This method for the calculation of $\Delta\gamma$ was first proposed by Bangham (50) and has been investigated by Boyd and Livingston (51) but has never been applied to isotherms exhibiting hysteresis.

In common with all other studies on the adsorption of gases, it was found that at very low pressures the adsorption of diethylamine varies linearly with the pressure. (In the other cases, it was not possible to achieve sufficiently low pressures experimentally to observe this phenomenon.) In this pressure range, the

change in free surface energy is simply

$$\Delta \gamma = - \frac{x}{m} \frac{RT}{A} \qquad (27)$$

At higher pressures, $\Delta \gamma$ can be evaluated by graphical integration.

It would be most desirable to know the magnitude of the free surface energy change when adsorption takes place on a clean surface. However, even a partially covered surface may be used as reference surface, i.e., the integration may be performed over the limits $(p/p_o)_2$ to $(p/p_o)_1$ as well as from $(p/p_o)_2$ to $p/p_o = 0$. It may be necessary to use a partially covered surface as the reference condition if it is not possible to extrapolate the data to $p/p_o = 0$ with sufficient certainty. The effect of using a partially covered, instead of a clean, surface as reference is merely that of shifting the curve along the $\Delta \gamma$-axis without altering its general features.
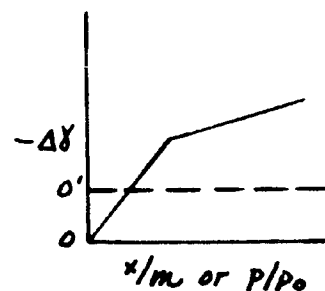
The integration of equation (26) was carried out by plotting $(x/mA)/(p/p_o)$ against p/p_o and determining the area with a planimeter. The integral was converted to ergs per square centimeter by using the proper constant factors. Data at convenient intervals are summarized in Table 16. The data for the saturation

pressure were obtained by extrapolation of the adsorption isotherms.

Free surface energy as a function of relative pressure. In Figure 13, the free surface energy change is plotted against relative pressure. For diethylamine the original surface of silica gel was taken as the reference state, whereas for the butylamines the reference state was taken as that of the gel in equilibrium with the respective vapors at 0.01 relative pressure.

It is seen that at low pressures, the free surface energy drops rapidly in all three cases. This is quite similar to the change of the free surface energy (or the numerical equivalent, surface tension) observed in liquids due to the presence of surface active agents.
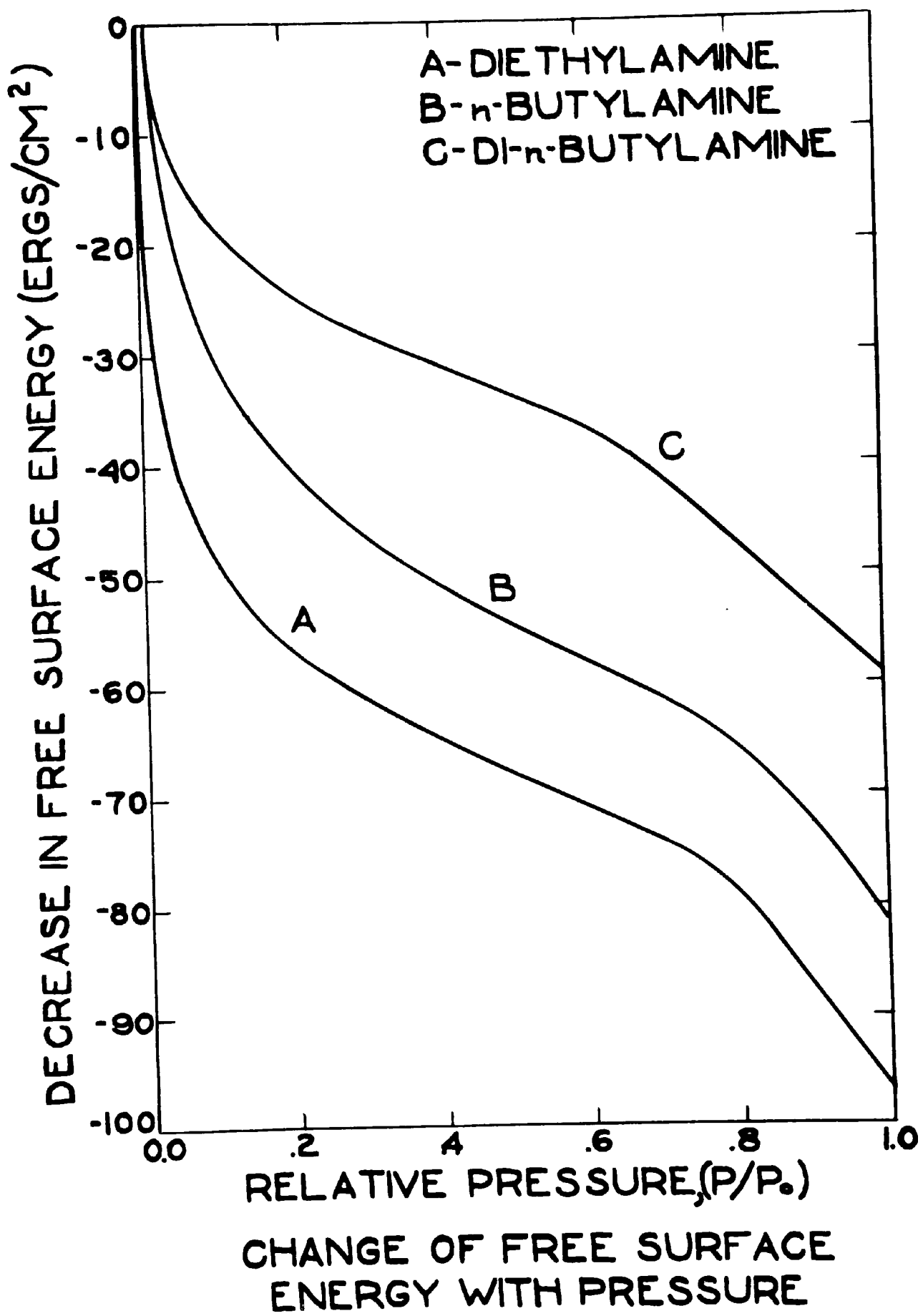
However a feature different from liquid systems appears in that an inflection point occurs in the curve, beyond which the curve bends down toward the relative pressure axis. The inflection points were found to occur at values of the relative pressures corresponding quite closely (within 0.02 relative pressure units) to the point in the adsorption isotherms at which the lower loop of the hysteresis begins. If this feature is found to be of general validity, it will be of value in locating the inception of hysteresis from adsorption data alone, without necessitating a large number of desorption points.
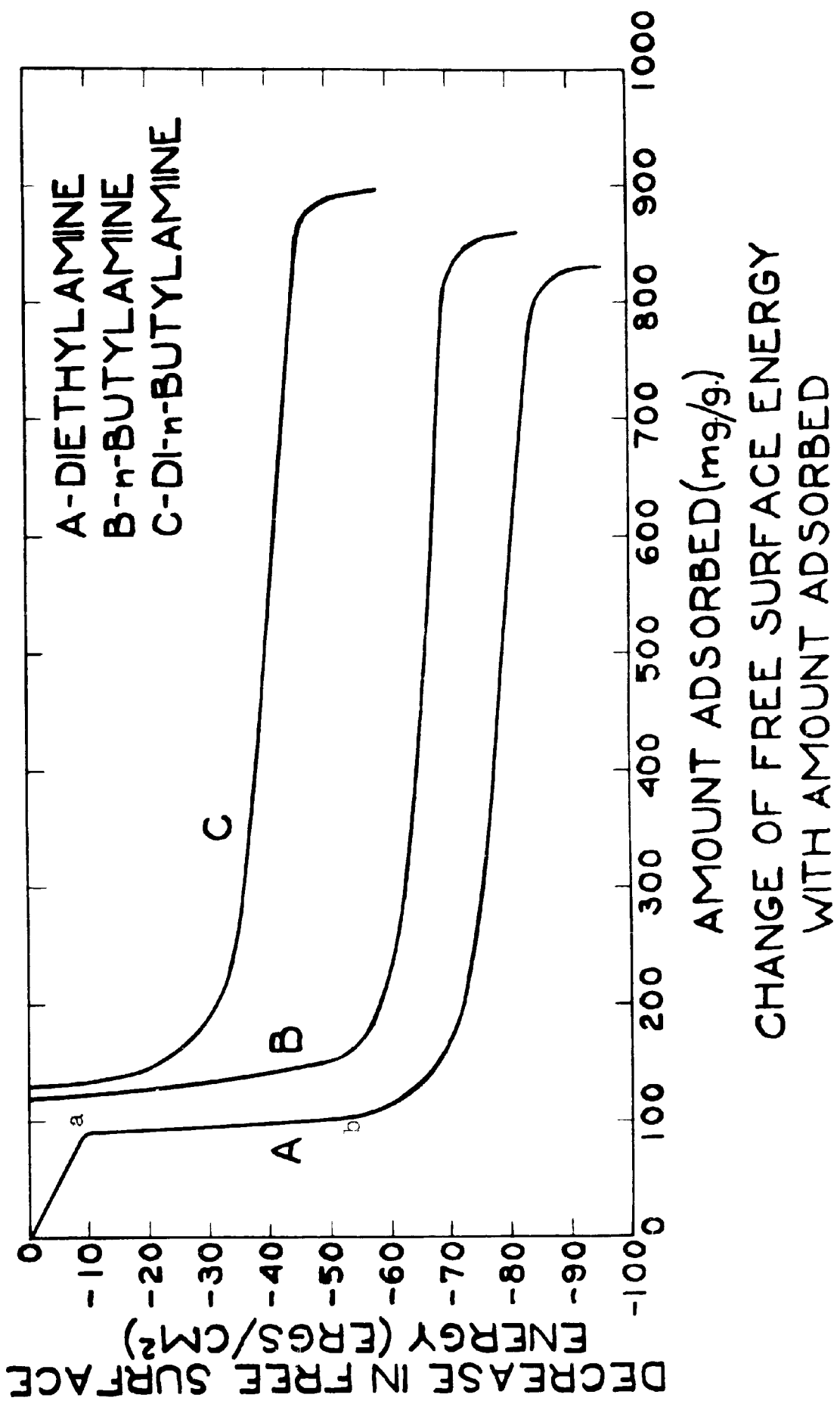
TABLE 16

CHANGE IN FREE SURFACE ENERGY

	Diethylamine		n-Butylamine		Di-n-butylamine	
P/P_O	x/m (mg./g.)	$-\Delta\gamma$ (ergs/cm.^{2})	x/m (mg./g.)	$-\Delta\gamma$ (ergs/cm.^{2})	x/m (mg./g.)	$-\Delta\gamma$ (ergs/cm.^{2})
0.005	88	18.4	-	-		
.01	91	25.4	118	0.0	128	0.0
.02	93	32.5	121	8.8	129	5.4
.03	94	36.4	123	14.0	131	8.5
.04	95	39.4	124	17.8	132	10.8
.05	96	41.4	126	20.8	133	12.5
.10	100	48.9	132	30.4	140	18.2
.15	104	53.2	135	36.1	147	21.7
.20	106	56.4	138	40.2	154	24.3
.25	110	58.5	141	43.5	160	26.4
.30	115	61.1	145	46.3	170	28.2
.35	119	62.9	148	48.6	180	29.4
.40	126	64.7	151	50.8	192	30.9
.45	134	66.4	155	52.7	210	32.3
.50	144	67.9	162	54.5	232	33.7
.55	157	69.4	171	56.1	275	35.1
.60	173	70.9	189	57.8	340	36.7
.65	200	72.5	210	59.5	450	38.6
.70	245	74.2	243	61.2	600	40.8
.75	310	76.3	315	63.1	800	43.7
.80	490	78.8	475	65.8	885	47.1
.85	725	82.9	800	69.1	892	50.3
.90	823	87.6	850	72.9	896	53.4
.95	830	92.5	858	77.1	897	56.3
1.00	831	96.8	860	81.6	898	59.0

FIGURES 19-20

CHANGE OF FREE SURFACE
ENERGY WITH PRESSURE

A-DIETHYLAMINE
B-n-BUTYLAMINE
C-DI-n-BUTYLAMINE

AMOUNT ADSORBED(mg./g.)

CHANGE OF FREE SURFACE ENERGY
WITH AMOUNT ADSORBED

DECREASE IN FREE SURFACE ENERGY (ERGS/CM²)

Free surface energy as a function of the amount
adsorbed. The change of free surface energy as a function
of the amount adsorbed is shown for the amines in Figure
20. Again the reference states are the original silica
gel for diethylamine, and the partially covered surfaces
for butyl- and dibutylamine. The first part of the curve
in Figure 20 for diethylamine corresponds to the initial
portion of the isotherm (Figure 12) having the steep
slope asymptotic to the vertical axis. The horizontal
portion of the adsorption isotherm showing a very gradual
increase in amount adsorbed with increasing relative
pressure corresponds, on the energy diagram, to the
steep, almost linear portion of the curve (a to b). In
this portion, only a small amount of additional adsorp-
tion is sufficient to cause a relatively great decrease
in the free surface energy of the system. It is also in
this region that the reference states (referred to on
page 97) for the butylamines are located.

Continuing along the curve beyond b, a marked
change in slope is noted; the nearly vertical portion
changes abruptly into nearly horizontal portion, which
again approximates a straight line. In this horizontal
region, the free surface energy does not appear to be
altered significantly by further adsorption. Finally,
at large values of x/m, the horizontal curve breaks

quite sharply downward again and terminates at the
saturation value of x/m.

The features of this curve may be interpreted
quite satisfactorily from a thermodynamic basis. The
differential heat of adsorption was observed to be high
when the total amount adsorbed was low (Figure 18).
For diethylamine the slope of the free energy curve,
which corresponds to the differential free energy change,
is seen to increase sharply only when the amount adsorbed
reaches about 90 mg./g. (The value of 90 mg./g. is
significant for it may be recalled that by application
of the BET theory to the low pressure region of the
adsorption isotherm, 90.0 mg./g. constituted a monolayer.)
The relation between Δ F, the change in free surface
energy, and Δ H, the change in total energy at constant
temperature is

$$\Delta F = \Delta H - T\Delta S \qquad (28)$$

Since the adsorbed molecules are held in position on the
surface by strong forces, and, moreover, are probably
oriented, it is to be expected that there would be a
decrease in entropy of the amine molecules in going from
a random vapor state to the oriented adsorbed state which
is in addition to the decrease in entropy caused by the
increase in concentration in the adsorbed phase. The Δ H

term is negative, heat being evolved, and the $-T\Delta S$

term is positive because ΔS is negative, so that ΔF

is less negative and has a lower absolute value than it

would have if the entropy decrease were not so large.

The entropy of the second and the succeeding adsorbed

layers is greater than that of the first, since the

adsorptive forces are much weaker than in the first layer

and consequently the degree of orientation in the second

layer is much less than in the first, resulting in a

lesser decrease in entropy. The value of ΔF has there-

fore a higher absolute value, approaching more closely

the value of ΔH, since the $T\Delta S$ term is now much less.

This explains the change in slope of the free energy

curve noted at point a in the diethylamine curve, Figure

20.

At values of x/m somewhat above 100, another

change in the slope of the curve is noted, and it is

seen that the addition of several hundred milligrams

of the amine to the system reduces the free surface

energy but slightly as compared with the relatively

great change in the immediately preceding portion of

the curve. This may be readily interpreted from the

capillary condensation viewpoint, but is difficult to

interpret from the multimolecular adsorption viewpoint.

The multimolecular adsorption theory indicated that the

shape of the entire isotherm could be accounted for by

one continuous mechanism, the increase in adsorption
represented in the latter part of the isotherm being
due to the extra decrease in free energy when the final
channels in the capillaries were filled. The capillary
condensation theory, on the other hand, interpreted the
additional apparent adsorption in capillaries as a
condensation of vapor caused by the lower vapor pressure
of the concave liquid surface within the capillary. The
condensation of vapor to liquid at constant temperature
and pressure involves no change in free energy, i.e.,
in ΔF. The constancy in ΔF values observed over the
nearly horizontal portion of the curve indicates that a
large number of molecules are being condensed and that
these condensed molecules have not lowered the free
energy of the system appreciably.

Closer inspection of the free energy curve
reveals the fact that although the slope in this region
is quite low, it is not zero, but is finite. A reasonable
interpretation would be that the smaller capillaries may
be completely filled by condensation, while the larger
capillaries are not completely filled, and the adsorption
process could continue in these large capillaries in
accordance with the multimolecular adsorption theory.
The amine molecules so adsorbed by the gel would thus
contribute their normal share to the decrease in the free
surface energy and thus would account for the finite slope
of the curve.

The hysteresis loops in the adsorption isotherms close when the amounts adsorbed were about 830, 850 and 890 mg./g. for diethyl-, n-butyl- and di-n-butylamines respectively. It is noted on the free energy curves that at these values of the amounts adsorbed the curves resume approximately the slope shown by the curves before the inception of capillary condensation. This substantiates the view that multimolecular adsorption continues throughout the pressure range but it is supplemented in a restricted portion of the pressure range by capillary condensation.

Postulated Mechanism of the "Adsorption" Process

The facts observed in this study of the adsorption of the lower aliphatic amines by silica gel seem to suggest the following mechanisms: when the fresh silica surface is first exposed to amine vapor, the amine molecules are strongly adsorbed as a monolayer by the silica. Only a very low relative pressure is required for this adsorption. In the formation of the succeeding layers (multimolecular adsorption) a considerable increase in pressure is required. At the intermediate relative pressures, additional amounts of amine vapors are condensed in the capillaries of the gel. The amount of amine thus held is several fold the amount held by adsorption alone. After the capillaries have become filled and the pressure of the system approaches the saturation pressure of the amine, a slight additional amount of multimolecular adsorption occurs on the external surface of the gel. In the process of desorption the capillaries are emptied only at lower pressures than the pressures at which the capillaries were filled. This hysteresis is attributed to constrictions in the capillaries.

CONCLUSIONS

1. The adsorption isotherms for diethylamine, n-butylamine, and di-n-butylamine on silica gel have been determined. At 25° C., the entire pressure range from zero to the saturation pressure of the respective amines was investigated; at 40° C., only a part of this pressure range was investigated. The isotherms of the amines on silica gel were found to be unusual in form. The previous non-existence of this form of isotherm had been used as an argument against the possibility of capillary condensation in the process of adsorption on porous solids.

2. Evidence has been found in these systems of high forces existing between the amine molecules and the original silica surface. With each amine it has been found that the silica surface becomes covered with a monolayer at the low relative pressure of about 0.01. This indicates that this adsorption process is one which may appropriately be termed chemisorption.

3. The BET three-constant equation has been applied to this data and has been found to represent the experimental results down to very low pressures--a relative pressure of 0.002 in the case of diethylamine.

The upper limit to the applicability of the equation was found to be near 0.3. The value of the constant n in the BET equation was determined as being less than 3 in all cases. It appears doubtful that n actually represents the maximum number of adsorbed layers.

4. A high degree of concordance was obtained in the values of the mean capillary radius of the gel as calculated by application of the Kelvin equation to the isotherm data. It is significant that this concordance was obtained despite the greater than hundred-fold difference involved in the absolute pressures of the three amine systems. This indicates that the Kelvin equation is applicable and hence that capillary condensation cannot be neglected but must be considered in addition to multimolecular adsorption.

5. Differential isosteric heats of adsorption were determined from the isotherms. At the lower pressures, the heat of adsorption was found to be as much as four times as great as the heat of condensation. At somewhat higher pressures, the differential heat of adsorption approached the heat of condensation. This was in complete accord with the other conclusions reached here: namely that at low relative pressures high attractive forces exist resulting in chemisorption; at the intermediate relative pressures capillary condensation (as determined by the curvature of the adsorbed liquid surfaces) occurs.

6.   Free surface energy changes have been calculated for these adsorption systems. When the change in free surface energy was considered as a function of the relative pressure, an inflection point was noted at the relative pressure corresponding to the inception of the hysteresis. This may enable location of the region of adsorption-desorption hysteresis from adsorption data alone. When the change in free surface energy was considered as a function of the amount adsorbed, several changes in the slope of the curve were noted. These have been interpreted thermodynamically and have indicated the existence of two disparate phenomena in the adsorption of amines by silica gel.

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