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Adsorption of alkyl halide gases on sodium chloride

Frank Clark Edwards
Iowa State College

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ADSORPTION OF ALKYL HALIDE
GASES ON SODIUM CHLORIDE

by

Frank Clark Edwards

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

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DEDICATION

This thesis is
dedicated to the memory
of my father,
Frank C. Edwards - - - -

Those who knew
him will understand - - - -

I. INTRODUCTION

The unsaturated forces which exist between all phase interfaces can be satisfied by an adsorbed material, called an adsorbate, by a process termed adsorption. If the binding forces involved are comparable with those leading to the formation of chemical compounds, of the order of 10^4 to 10^5 calories per mole, the process is called chemisorption. If the forces that operate are similar in magnitude to the weaker van der Waals forces between molecules, that is from a few hundred to a few thousand calories per mole, the term physical adsorption is used.

In practice the role of adsorption is a large one. A few examples include the separation of gases from gases by solids, the use of catalysts to alter reaction rates, the separation of solutes from solution, the use of detergents and wetting agents, the concentration of ores, chromatographic and ion exchange processes, solvent recovery, etc. These representative examples illustrate the scope of the science and point to the practical, as well as fundamental, interest in studies of the nature of the adsorption process. Recognizing the adsorption process is operative at all interfaces, we restrict further consideration to the physical adsorption phenomena of solid surface-gas systems.

The bulk of the published work on adsorption has dealt with adsorbent systems with a high ratio of surface area to

mass. This was a natural result, for in practice the role of adsorption is most obviously displayed in such systems.

Further, experimental measurements on systems with high surface area to mass ratios are easier to perform. As a consequence, a voluminous literature on physical adsorption of such systems exists - with the experimental data usually expressed in the form of adsorption isotherms. An adsorption isotherm represents the equilibrium amount adsorbed as a function of pressure at constant temperature.

On the theoretical side, various theories of adsorption have been advanced in the attempt to formulate analytically the results of experiment. These theories have met with varying degrees of success, but all fall short of the ultimate goal - that is, of providing a limited number of generalizations that would apply to any system of adsorbent, interface, and adsorbate.

Both experimental results and theoretical considerations have led to a picture of a distribution of activities among adsorption sites on adsorbent surfaces. These include interactions of adsorbate molecules with one another as well as with particular distributions of sites on the surface of the adsorbent.

The magnitudes and relative effects of all the contributing parameters of adsorbent and adsorbate must be defined precisely if these interactions are to be understood. Data

must be accumulated on series of systems varying specific parameters of adsorbent and adsorbate.

Without question, the large surface area to mass ratios of adsorbents, as used in practice and in most experiments, have made the gross determination of the correspondingly larger amount of adsorption easier to perform. On the other hand, any gain in the ease of the experimental measurement was often lost by the difficulty in interpreting the overall adsorption in terms of the many contributing factors. Such finely divided adsorbents (usually porous powders) presented entire distributions of sites resulting from the various interfaces, edges, pores, and pore shapes, etc., which were present. These combined to obscure, and thus discourage, any study focussing on a particular parameter. Again, the preparation and surface purification of such adsorbents was more of an art than a science. These undesirable features often made it difficult to reproduce or to compare results from one laboratory to another, and even, at times, for the same experimentalist from one run to another.

With the development of the science, an important fact became more evident, namely, that adsorption phenomena was shown to be the same per unit area of interface for a particular system - that is, it was not dependent on the state of subdivision of a particular massive material. It was precisely here that one trend of current and future work was

established - for the study of physical adsorption on materials with ordinary instead of large surface area to mass ratios would better permit both the variation of specific parameters and the control of all other contributing factors to overall adsorption. Ideally, the more satisfying experimental approach could be planned of varying specified adsorbent or adsorbate parameters in a more orderly manner rather than a reshuffling of the many. In practice, severe experimental limitations have prevented the exploitation of this approach. This fact is best demonstrated when it is recalled that Orr (1) first studied the adsorption of argon on specified surfaces of potassium and cesium iodides nineteen years ago and to date only a few similar studies have been reported.

An urgent need of the science is for experimental techniques which can measure precisely adsorption phenomena on adsorbent systems with ordinary surface area to mass ratios. Further, even the preliminary preparation of such adsorbent systems, their purification, and surface area determinations are imposing problems which demand new or more exacting methods. Such techniques, both for sample preparation and adsorption measurement, must come either from the refinement of the old or by the development of new methods.

Beginnings have been made in this direction as the work of Orr first indicated. The measurements of Armbruster and

Austin (2) and of Wooten and Brown (3) on adsorption at massive metal surfaces represented refinements in approach.

Rhodin (4) in a series of beautifully conceived and executed experiments, detected measureable differences for heats of adsorption of nitrogen on the (100), (110) and (111) faces of single crystals of copper. This work has shown the way for direct measurement by precision techniques.

In a later section a review of the experimental methods used in previous studies of adsorption on small surface areas will be given. However, at this time it should be said that the most precise work, including the work of Rhodin, has been done using delicate fused-silica fiber balances. The change in weight of the adsorbent material while suspended from one end of the balance beam was determined, furnishing thereby a direct measure of the amount of adsorption.

The present experiments were undertaken as part of the systematic investigation to obtain more precise information on adsorption equilibria. More specific objectives were:

1. To develop instrumentation suitable for precise measurement of adsorption of gases on small specific area adsorbents;
2. To investigate the characteristic behavior of a series of polar gas molecules on an ionic crystal with well characterized surface;
3. To determine the differences in the values of the

initial heat of adsorption with molecular species of polar adsorbates;

4. To investigate surface heterogeneity of the ionic crystal under these conditions.

The choice of the four alkyl halide gases (ethyl chloride, ethyl bromide, ethyl iodide, and methyl iodide) for use as the polar adsorbate gases depended in the main part on their favorable physical properties near room temperatures. Cubic form sodium chloride was chosen as a representative ionic surface because of its relative ease of preparation and because of previous investigations using this substance which will be discussed.

A special adsorption apparatus was designed, constructed, and used to make these measurements. Complete descriptions of the apparatus, suggestions for future improvements in design, and other potential research applications will be given. This apparatus employed two fused-silica fiber microbalances of unique design. One balance carried the adsorbent and therefore provided a direct determination of the amount of adsorption. The second balance was also located in the reaction chamber. This balance carried a buoyancy bulb and was used to determine gas densities which could be related directly to the equilibrium pressures of adsorption.

It is interesting to conjecture concerning the formulation that may be brought to the adsorption isotherm as a

result of future work. It is probable the generalizations will be ones of greater complexity and not of simplicity as the relations among surface, interface, and adsorbate parameters are understood. On the other hand, the very complexity of the problem has been the real reason why the theories of today describe adsorption phenomena as well as they do. For example, it has been said that the widespread applicability of the Freundlich adsorption isotherm and its origin in a distribution of adsorption energies are very significant when considered together.

It is hoped that the results of this study and also any future applications of this research apparatus and technique will contribute to the development of the ultimate theory.

II. LITERATURE REVIEW

A. Similar Adsorption Studies

The need for studies of the adsorption phenomena on well characterized uniform surfaces led naturally to the use of crystal faces as adsorbent surfaces. Because of the difficulties of the experimental measurement it was necessary to use samples furnishing an area of several hundred cm^2 provided one insisted precision correspond to the order of about one per cent of unimolecular adsorption. The adsorbent surface area in the work to be reported herein was about 800 cm^2 .

Rhodin's work (4) can be considered a classical effort in the study of adsorption on surfaces of low area; the adsorbent was a large single crystal of copper which he had machined painstakingly to expose the desired crystal face. No one could minimize the quality of that work, but it is true that even though he detected differences in heats of adsorption on different crystal faces, his precision was of the order of twenty per cent, and illustrates the sacrifice in precision attending the study of very low areas even by the most exacting technique.

We can hope for sufficient improvement so that precision studies can be made on a single crystal (or other surface) of an area of a few cm^2 - an area that can be prepared and

characterized conveniently - but the technique is not that far advanced at this time.

If a goal of \pm one per cent of monolayer coverage be established for precision, permitting resolution of molecular interaction effects as coverage of the surface increases, then sample selection appears at present to be limited to collections of small crystals, not too small to prohibit accurate microscopic characterization, but small enough to provide a specific surface area sufficiently large for the attainment of the specified precision in adsorption measurements. At present, this specific surface area must be of the order of several hundred cm^2 per gram. These are referred to as relatively low specific surface areas in comparison to 10^6 or 10^7 cm^2 per gram in common adsorbents such as carbon blacks, charcoals, and silica gels.

The alkali halide crystals have been well suited for this general purpose. These materials assume with ease certain habits in which only one type of face is exposed. Various methods of crystal preparation have been described including solvent displacement (5) and sublimation techniques (6).

As a result experiments have been made during the last twenty years using alkali halide crystals as adsorbent materials - including some unique studies where crystal habit was modified by the presence of certain organic dyes and inorganic salts. The studies have been few in number, in fact

to date only four non-polar molecules have been used as adsorbates and no studies at all have been made involving dipolar gas molecules on an ionic surface. Incidentally, all measurements were made by the volumetric method.

The work of Ross and co-workers (7), (8), (9), (10), was of special interest. Isotherms of the low temperature adsorption of ethane on cubic habit sodium chloride and potassium chloride exhibited unusual vertical discontinuities. These were interpreted as indicating a two-dimensional phase transition of the sort reported previously by Jura and others on such systems as n-heptane on graphite (11) and on ferric oxide (12). Prior to the work of Ross it had not been possible for others to reproduce the effect (13); this may be ascribed to the difficulties of reproducing the identical surface used by Jura. The existence of such discontinuities is of special interest because this feature in itself indicates that a large proportion of the sodium chloride surface was of a single type, and this was pointed out by Ross and Winkler (7). Such evidence made one even more confident that cubic habit sodium chloride presented a uniform surface.

Related studies included the adsorption of argon, oxygen, and nitrogen on cubic potassium chloride and cesium iodide as reported by Orr (1) and Tompkins and Young (14) respectively. The adsorption of argon on two samples of octahedral potassium chloride (lead and dye-modified) was also reported by Young

(15).

The experimental results of these studies led to the concept of adsorption in preferred positions above lattice centers (at least at low coverage), an orientation claimed to provide greater stability than the close-packed hexagonal array predicted when a structureless surface is assumed. In addition a number of authors, (16), (17), (18), (19), and notably Orr (1), have made theoretical calculations concerning the energy of interaction between a rare gas atom and an alkali halide crystal which have given this model a reasonable theoretical validity.

Therefore, as this research was commenced there was evidence that the surface of alkali halide crystals of a specified habit was largely uniform. More than this a model suggesting a regular lattice array of adsorption sites had developed.

The difficulty of adsorbate selection was reduced because the choice was so large, for only four non-polar gases (argon, nitrogen, oxygen, and ethane) had been studied and even these not at all exhaustively. For instance, though the variations of heats of adsorption with surface coverage were given, no explanation for the differences in the initial heats of adsorption with molecular species was suggested. There was also a practical concern. Eventual adaptation of the instrument for low temperature use was contemplated but it was deemed

prudent to perform the first experiments near room temperature.

With all this in mind it was decided to investigate the adsorption behavior of a series of molecules and the polar alkyl halide gases were selected for this series. These compounds had favorable physical properties for use near room temperature. In addition, studies of a series of molecules of a similar type, rather than an unrelated set, would be expected to be more informative as to the nature of the forces involved. For this purpose the ethyl halide series seemed particularly attractive for the dipole moments decrease from chloride to iodide in this series, while the molecular weight increases.

Adsorption behavior of the alkyl halides was not widely documented; however, Lamb and Coolidge (20) had reported data for the ethyl halide gases adsorbed on charcoal. They found that the heat of adsorption increased with increasing molecular weight. The implication was that dispersion forces were of greater importance than orientation forces in accounting for adsorption of these gases. Dispersion forces, by and large, do outweigh orientation forces; but whether this is also true of dipolar molecules in the large electric fields near the surface of an ionic crystal was unknown; and so experimental evidence was sought.

Recently, Hayakawa published a series of papers dealing

with adsorption on alkali halide surfaces (21), (22), (23), (24), (25), (26). One of his first comments was interesting. It was not that he had published a similar research, for actually he had chosen to study once again the low temperature adsorption of non-polar gases. It was, rather, one of his reasons for doing so:

. . . the choice of argon, oxygen, nitrogen, and carbon dioxide as nonpolar adsorbates mainly depended on avoiding complications which the presence of permanent dipoles would introduce . . .

(21, p. 125).

It turned out that Hayakawa's studies, and this was excellent work, confirmed previous experimental results; but more than this he was able to relate the differences in the values of the initial heat of adsorption with molecular species of adsorbates. The correlation was based on calculations of the potential energy of each isolated atom or non-polar molecule (argon, nitrogen, or carbon dioxide) adsorbed on the particular cubic alkali halide surface (sodium chloride, potassium chloride, and potassium bromide). In these calculations the quadrupole interactions of the adsorbed molecule and the crystal were considered and claimed to be predominant. Agreement was demonstrated between the theoretical and experimental values obtained for the initial heats of adsorption of these non-polar gases.

B. Measurement of Adsorption on Small Surface Areas

Current and possible future interest in experimental techniques which can measure adsorption on adsorbents with ordinary instead of high ratios of surface area to mass have been indicated. Several reviews of the experimental methods of the science of adsorption are available (27). No attempt will be made to recatalog the many general techniques that have been used. All the widely used methods were designed for use involving large adsorbent surface areas. However, those few refined procedures together with certain special methods which have been used for small surface area studies will be discussed.

1. Direct measure of pressure or volume change

The most widely used methods have been based on a measure of the volume or pressure change resulting from the adsorption process. Many different procedures, both static and dynamic, are grouped in this class. Such methods require the measure of a volume or a pressure difference, and are, therefore, restricted to the accuracy and precision of that volume or pressure difference measurement. To date, the greatest refinement has been made by Wooten and Brown (3) who were able to detect adsorption on surface areas as low as one hundred square centimeters. To accomplish this they worked under the restrictive conditions of very low temperatures

(liquid nitrogen temperatures), with gases having low pressures at these temperatures, and employed the most sensitive conventional pressure gauges. Even within such severe limitations, such refinement has not been sufficient to permit study of the surface chemistry of metal or crystal specimens of small enough area to be prepared conveniently.

For studies on adsorbents which can be prepared with the surface area required, the volume or pressure difference methods will continue to be of use. In a later section an improved technique of this sort that has been suggested by a phase of the present work will be described. However, at this time, it does not seem at all likely that adsorption measurements on small surface area systems will employ such methods to the degree they have been used to study large surface area adsorbents.

2. Direct measure of weight change

The second major class of methods uses a direct measure of the change in weight of the adsorbent to determine the amount of adsorption. The advantages of a direct measure of adsorption are self-evident. The limiting factor for this method is the "working sensitivity" of the balance. The term "working sensitivity" includes all those experimental factors which affect the reproducibility and precision of the weight measurement. One is concerned in practice with the smallest

weight change that can be observed, reproduced, or similarly defined at any desired time under predictable circumstances.

The work of Rhodin (4) using a balance as described by Gulbransen (28) and special experimental procedures demonstrated a "working sensitivity" of 10^{-7} grams which permitted the detection of the adsorption of as little as 10^{-4} cubic centimeters (S T P) of nitrogen gas - this amount of gas represents monolayer coverage of a surface area of about ten square centimeters. The present work will also employ fused-silica microbalances with that same order of "working sensitivity." Further, certain improvements in technique and equipment which make such studies both easier to perform and more versatile will be discussed.

3. Other indirect methods

Other techniques have been used to measure some property which could in turn be related to the adsorption process.

Brunauer (29) outlines the use of an optical method. It consists of shining light, plane polarized at 45° to the angle of incidence at the boundary layer between solid and gas, and analyzing the reflected beam. Functional relations exist between the ellipticity of the reflected light and the thickness of the adsorbed phase which may be used to calculate the thickness of the adsorbed layer.

Roberts (30) showed that the value of the so-called ac-

accommodation coefficient depends on the purity of the solid surface and could be used to indicate the degree of covering of the surface. This method was based on the observation that when a gas molecule strikes a hot surface it may be adsorbed, or may rebound, the collision resulting in an interchange of energy. The accommodation coefficient itself is defined as $a = (T_2 - T_1)/(T_2' - T_1)$, where the temperature of the gas is T_1 before and T_2 after collision with a surface of temperature T_2' .

The application of radioactive tracers is an approach which as yet has not been widely used to study the adsorption process. From the advantage of extending the lower limit of measurement, tracer use would seem to offer much promise. In practice, restrictions are imposed by the availability of radioisotopes of the desired element possessing convenient energies and half-lives. It is likely that advances can be expected in this area along with the greater availability of radioisotopes and more versatile detection instruments.

All of these indirect methods are important and interesting and will be used within their inherent limitations, which are many.

C. Fused-Silica Fiber Microbalances

Fused-silica fibers or, as they are often called, quartz fibers, serve an important function in a variety of precision

measuring instruments used in scientific research. This is because of the unique properties of single silica fibers as compared with other materials of research. These properties include great strength and elasticity along with electrical, thermal, and chemical resistance. One of the more extensive uses of silica fibers is in the microbalance field. Because certain significant improvements in both the design and techniques of construction of such microbalances will be reported here - as well as their essential and specific applications in the instrument developed for this research - the following brief review of the major developments in fiber microbalances will be given. For more complete information about theories, operation, and design, the reviews of silica fiber microbalance developments (31) (32), or the papers on specific balances should be consulted.

The first fused-silica fibers were made by Gaudin in 1839 but it was not until the gravimetric work of Boys (33) in 1887 that their use was exploited to make useful tools rather than mere articles of curiosity. Since that time individual fibers have been used in many different types of instruments. These include such applications as suspensions or as sensing elements in galvanometers (33), in gravimetric balances (34), in manometers (35), in magnetometers (36), and in various other devices.

Their extensive use in the construction of microbalances

is based on many features. With the entire device constructed of silica fibers it is possible to avoid errors due to different densities and coefficients of expansion of the various parts. Further, the high tensile and torsion strengths, the nearly perfect elasticity, the resistance to chemical attack, and the ease of cleaning, all combine to make silica fibers especially desirable as a construction material for balances.

The earliest microbalance using silica fibers was designed by Salvoni in 1901. This type balance determined the displacement of a cantilever fiber under changing load and is still used (37). It was Kernst and Riesenfeld (38) who introduced the design of a horizontal silica fiber attached to and supporting a fine glass rod and using a counterpoised pointer to indicate any deflection due to load. Following this, perhaps the work of Steele and Grant (39) was most significant to the development of the balance to be described in this work. They first constructed a complete balance entirely of fused silica. Their balance beam, however, was not fused to a torsion fiber but it was, rather, of the more conventional knife-edge type design, which meant their balance could be jarred out of alignment very easily. Several changes of design or of operation for applications to particular uses have been made. Of considerable significance was the work of Petterson (40) who improved the design and gave a detailed description of the theory of such instruments.

The idea of controlling a microbalance by using the interaction of an external electromagnetic field (Helmholtz coils) with the field of a permanent bar magnet mounted on the balance beam goes back to Angstrom in 1895 (41). Emich (42), Stock (43), and Wiesenberger (44) used Angstrom's idea of electromagnetic control in their investigations.

The author and his co-author Baldwin (45) described for the first time a fused-silica microbalance where the design and techniques of construction permitted a completed balance to be just one integral unit of fused silica fibers and seals - no sealing waxes or cements were used¹. Therefore, as long as a balance was not broken it was in alignment. The principal improvements to be presented here include the extension of load capacity from ten mg. to ten grams - a hundredfold increase, a correspondingly large extension of weighing range, along with complete retention of the same working sensitivity of at least 10^{-7} grams. Such electromagnetically compensated fused-silica balances are now more practical and versatile than ever because of the improved magnet materials and balance

¹It should be mentioned that the immediate precursors of these balances were those of Dr. I. B. Johns, now associated with Monsanto Chemical Company, but at that time of Iowa State College. Johns used waxes and selenium metal to effect his seals and consequently his balances could not be cleaned easily or used over a wide temperature range. Also, a lower load capacity resulted and the critical seals of the torsion fiber would even slip at times, thereby changing the operating characteristics of the balances.

designs. These balances are described properly as equal-arm lever balances in which the beam is rigidly fastened to a flexible supporting axis fiber. It is not a true torsion balance, for the force of gravity is only slightly compensated by the torsion of the support fiber. It is magnetic compensation that provides the major contribution to the total restoring force. This basic design was the first to combine the best features of a high sensitivity all fused-silica fiber microbalance and magnetic compensation, thereby allowing greater load capacity and range of weighing as well as external control. Later sections of this work will carry descriptions of the extensions and applications of these features which made it possible to develop the instrument used in this research.

Another line of microbalance development should be included in this review. This type relies entirely upon the torsion of the central support fiber to provide the necessary restoring force. The balance of Kirk, et al. (46) would be representative of this type, together with the modifications as described by Carmichael (47) and El-Badry and Wilson (48). These balances which are necessarily open to the atmosphere have been employed largely for conventional laboratory uses where vacuum operation and controlled atmospheres are not required.

Finally, the simplest and most widely used class of

silica fiber balances must be mentioned. These are frequently called McBain-Bakr balances (49) and they are the simple helical spring type. Discussions of their design (50), limitations, and specific applications can be found in the references cited. However, a general comment would be that high load capacity and high sensitivity with this type balance have not been realized simultaneously, though within their limitations the simplicity of their construction and use is appealing.

III. APPARATUS

A. Concept of Apparatus

A concept of the adsorption apparatus developed and used in this research may be gained from the block diagram in Figure 1. The reaction chamber houses two microbalances of the type described by Edwards and Baldwin (hereinafter called E-B balances) but with improved characteristics. One balance is used to make a direct measurement of adsorption. The second balance makes the pressure measurement on the gas density principle. The necessary valves leading to a dosing chamber, to the gas supply appendage, and to the vacuum system are of the all-metal Bayard-Alpert type so as to permit bakeout of the entire apparatus. The reaction chamber, adjacent dosing chamber, and valves, are of such a size as to permit immersion of the entire unit in a water bath.

B. Development of the High-Capacity Microbalances

Following the development of the E-B balance as first described (45), and before the modifications were made that are reported here, the author had carried out several changes in the balance design. These were all in the direction of providing a larger load capacity at the sacrifice of some sensitivity; and, indeed, several such balances, constructed and designed either wholly or in part by the author, were used

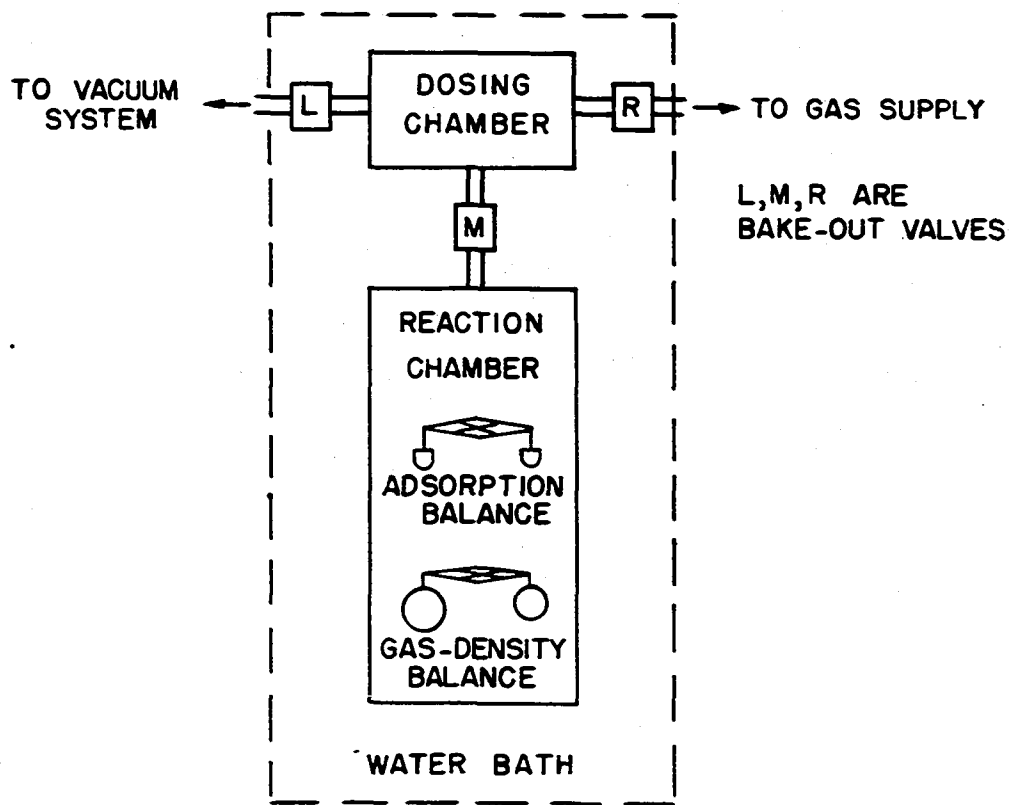


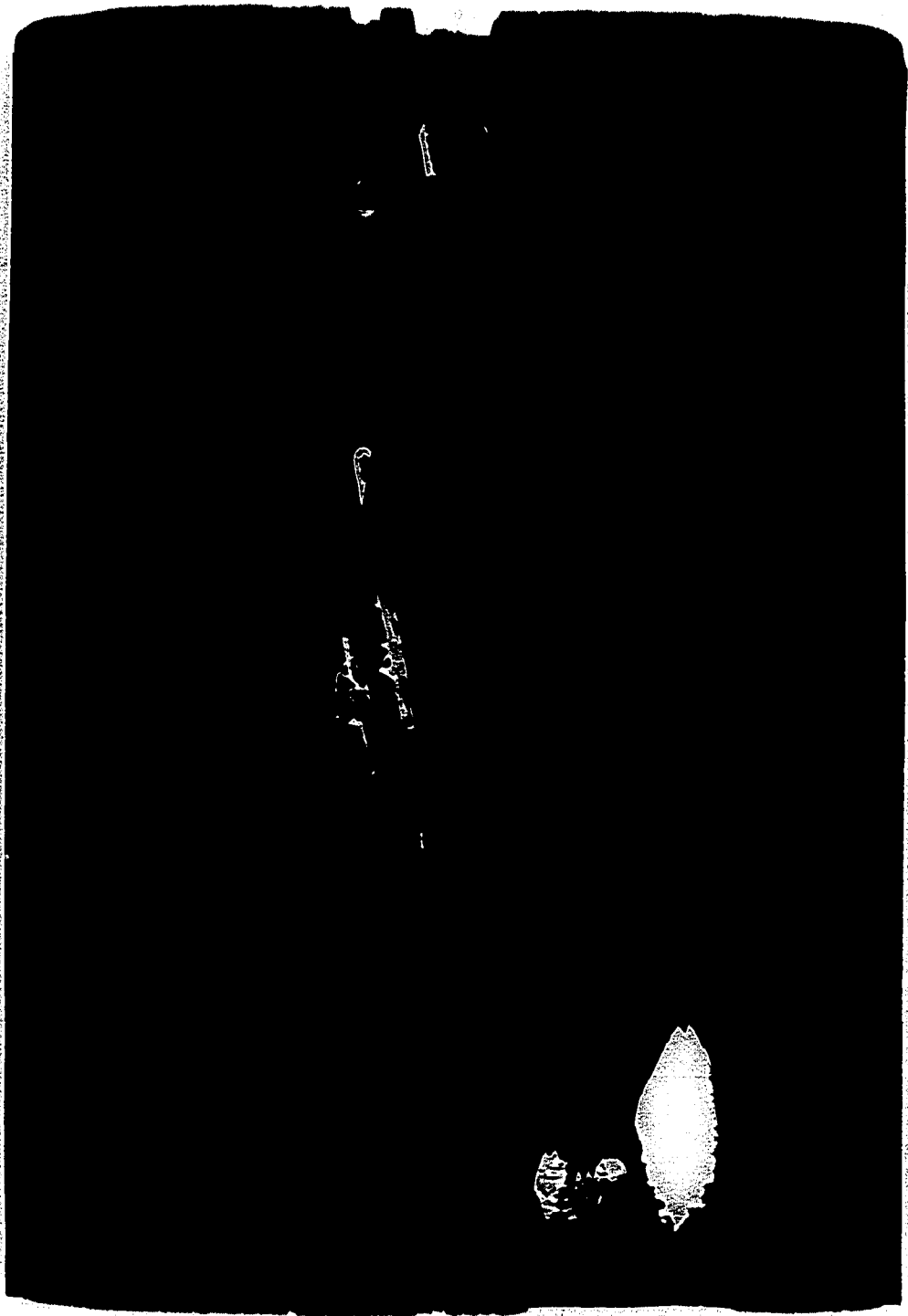
Figure 1. Adsorption apparatus - block diagram

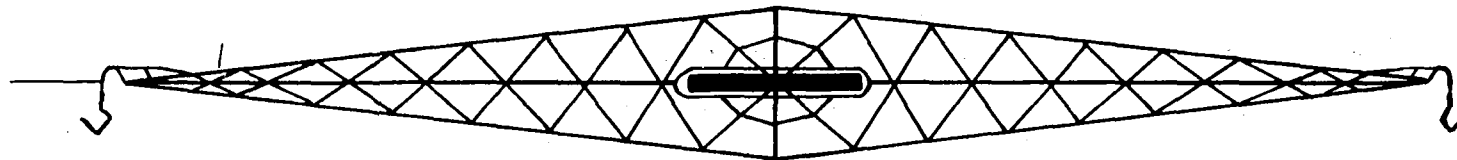
in these laboratories in several different researches where highest sensitivity was not demanded. These would include, for example, the effusion apparatus used by Daane for the determination of the vapor pressure of liquid metals (51), the film balance used by Christian for determining the surface tension of solutions (52), and the kinetic studies of Deal on the reaction of water vapor with calcium metal (53). Based on such experiences it was decided to undertake further modifications with the objective of extending load capacity while retaining high sensitivity.

The step by step procedure and unique technique described for the construction of the E-B balances were used again for this high capacity unit; therefore, in the interest of brevity, it is understood that the closest reference is to be made to that paper (45) - only essential changes in design and operating procedure will be described here. The photographs and drawings of Figures 2, 3, 4, and 5, should be helpful in this regard.

It will be noted that a three dimensional trussed beam design was adopted. This design provided a beam of sufficiently great strength to carry heavy loads (up to 10 grams) but of sufficiently low weight as to still permit high sensitivity (of the order of 10^{-7} grams). The drawing picturing the detail of the torsion fiber region, Figure 5, illustrates additional important features. Because the balances are used

Figure 2. Microbalance, containers, samples





SIDE VIEW



TOP VIEW

SCALE - ACTUAL SIZE

Figure 3. Microbalance - dimensions

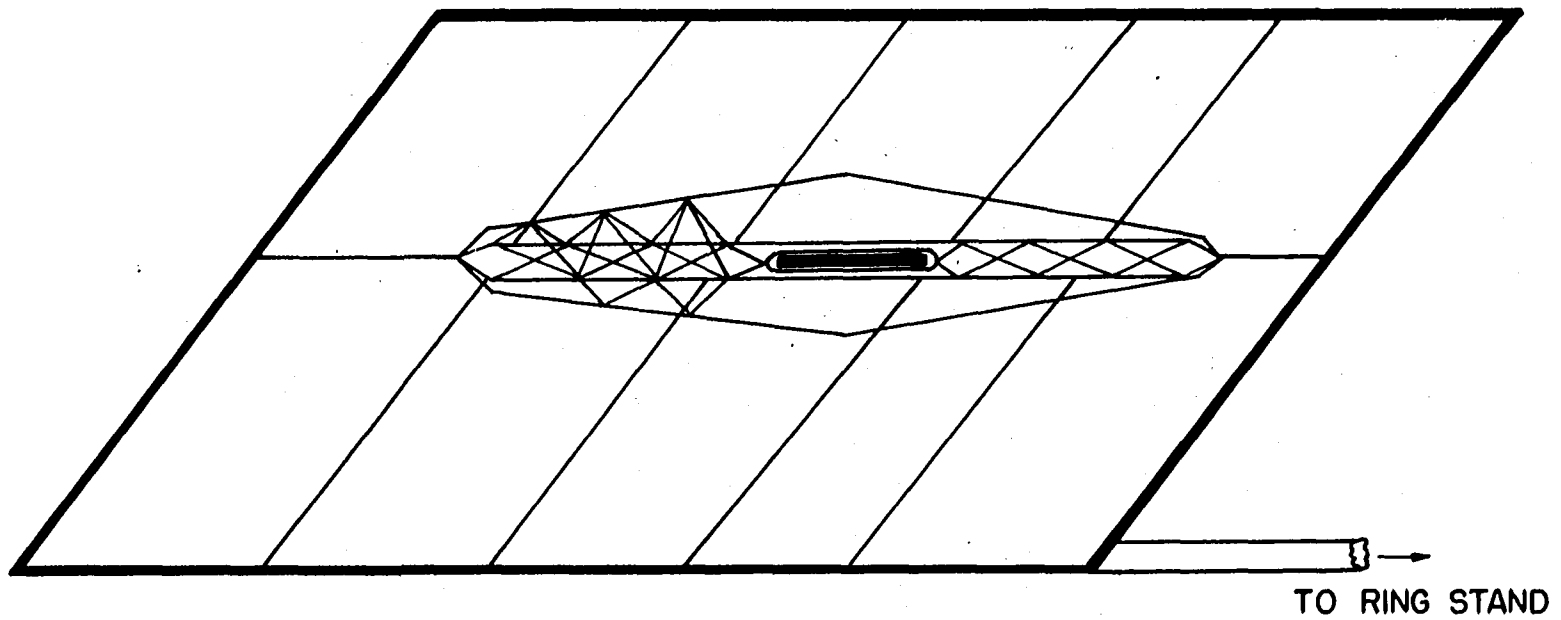
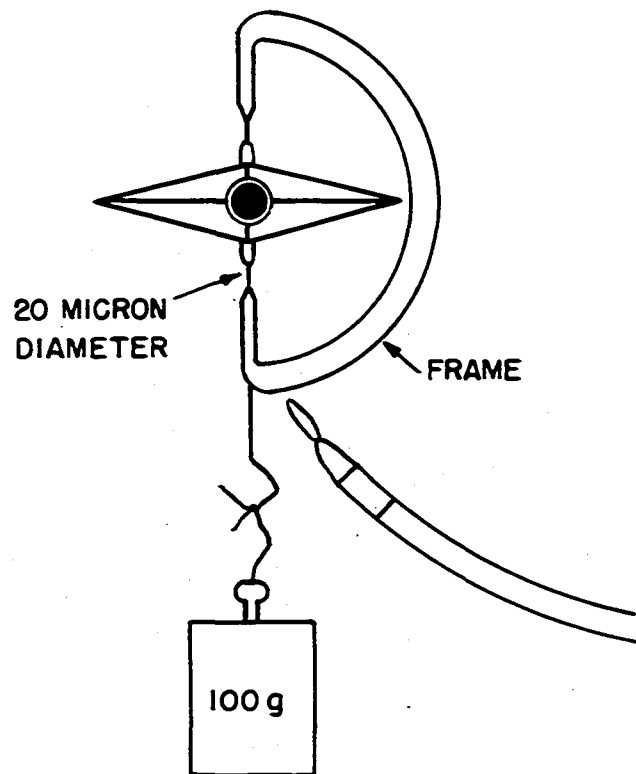


Figure 4. Microbalance - fused-silica jig used during free-hand bracing construction



SCALE: TWICE ACTUAL SIZE

Figure 5. Microbalance - detail of torsion fiber region during final tightening of fiber

as null instruments, movement of the beam may be restricted to a total deflection of a few minutes of arc. Consequently, the length of the fine section of the central axis fiber may be quite short. The diameter of the finest part of the axis fiber is of the order of twenty microns. These features coupled with a high tension mounting (of the order of one hundred grams) combine to give a high capacity, high sensitivity balance of the type used in this adsorption apparatus. The controllable weighing range was also extended by employing stronger Alnico V magnets.

In comparison to the E-B balances, it was possible to extend the counterbalanced load capacity of such systems to ten grams - a one hundredfold increase. The direct weighing range was increased to one gram - a one hundredfold increase. The sensitivity was maintained in the order of 0.1 microgram for six minutes of arc deflection of the balance beam. Depending on the requirements of a particular application, it is now possible to tailor-make a balance within these limits - and the end is not in sight.

C. Gas Density Balance

For the purpose of measuring the adsorption pressures a balance as described in the previous section was adapted for use as a gas density balance. This involved the mounting of a closed pyrex bulb on one end of a balance beam and an open

bulb on the other end. These bulbs were so designed that they were of about equal weight (eight grams) and total surface area (the inner surface of the smaller open bulb being counted), but they were greatly different as to the volume of gas displaced (a difference of the order of 50 cc.). Therefore, if the sensitivity of such a balance be 10^{-7} g., changes of gas density of the order of 2×10^{-9} g/cc. may be monitored. The gas density balance used in this research, Figure 6, was not pressed this hard, but such performance is possible.

D. Adsorption Apparatus

The actual adsorption apparatus developed according to the concept of Part A and employing balances as described in Parts B and C is pictured, its various parts are identified, and dimensions are listed in Figures 6, 7, 8, and 9.

1. Reaction and dosing chambers

Each balance was fused in position to its case by graded seals from the silica balance frame to the wall of the pyrex case. The two balance cases were mounted individually on the brass plate, Figure 9. They were connected by a glass tubing T which also connected to the middle valve M. This enclosed volume comprised the reaction chamber. Prior to this, the brass plate carrying the three valves had been rigidly secured

Figure 6. Microbalance - gas density balance and case

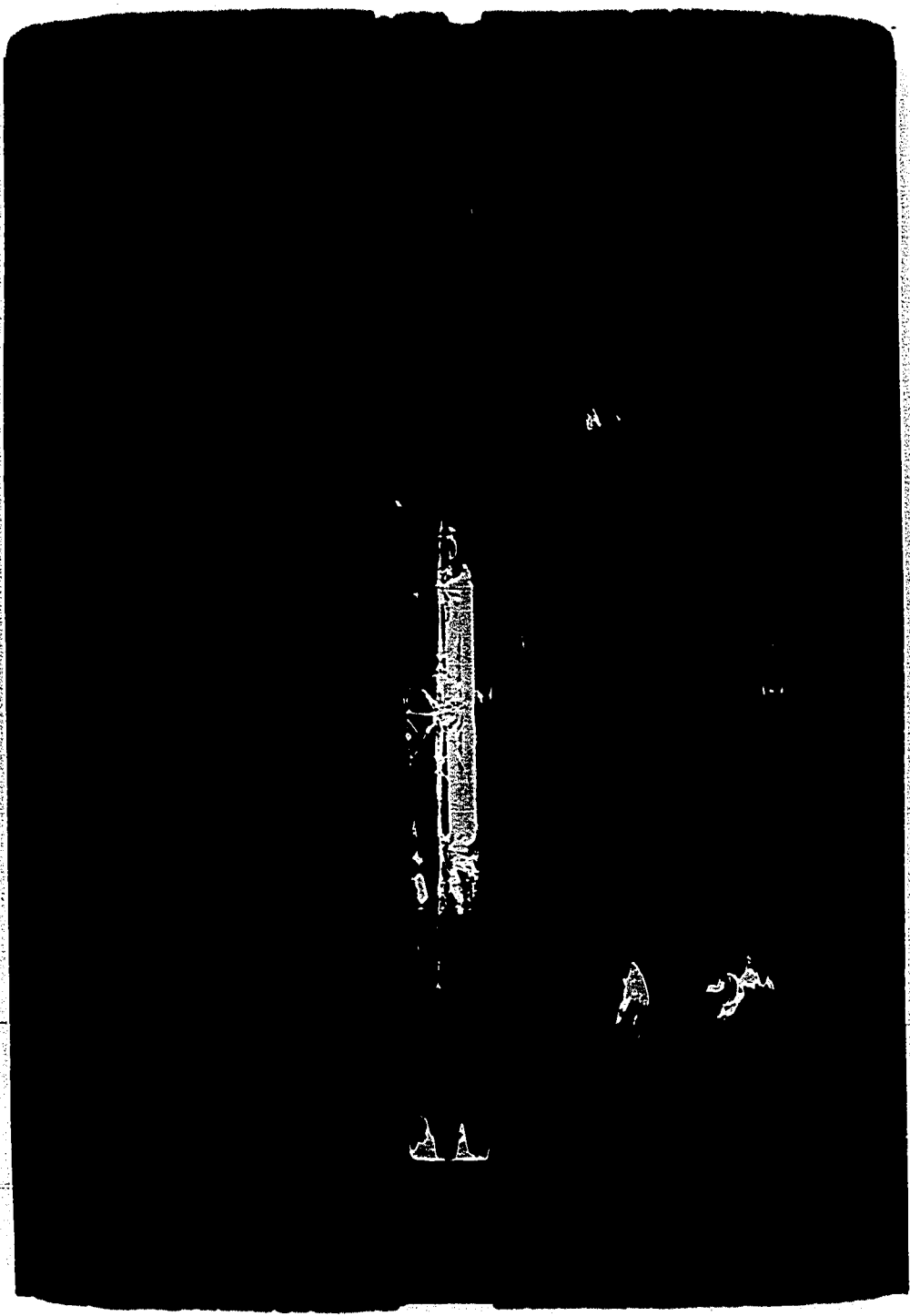


Figure 7. Microbalance - adsorption balance and case

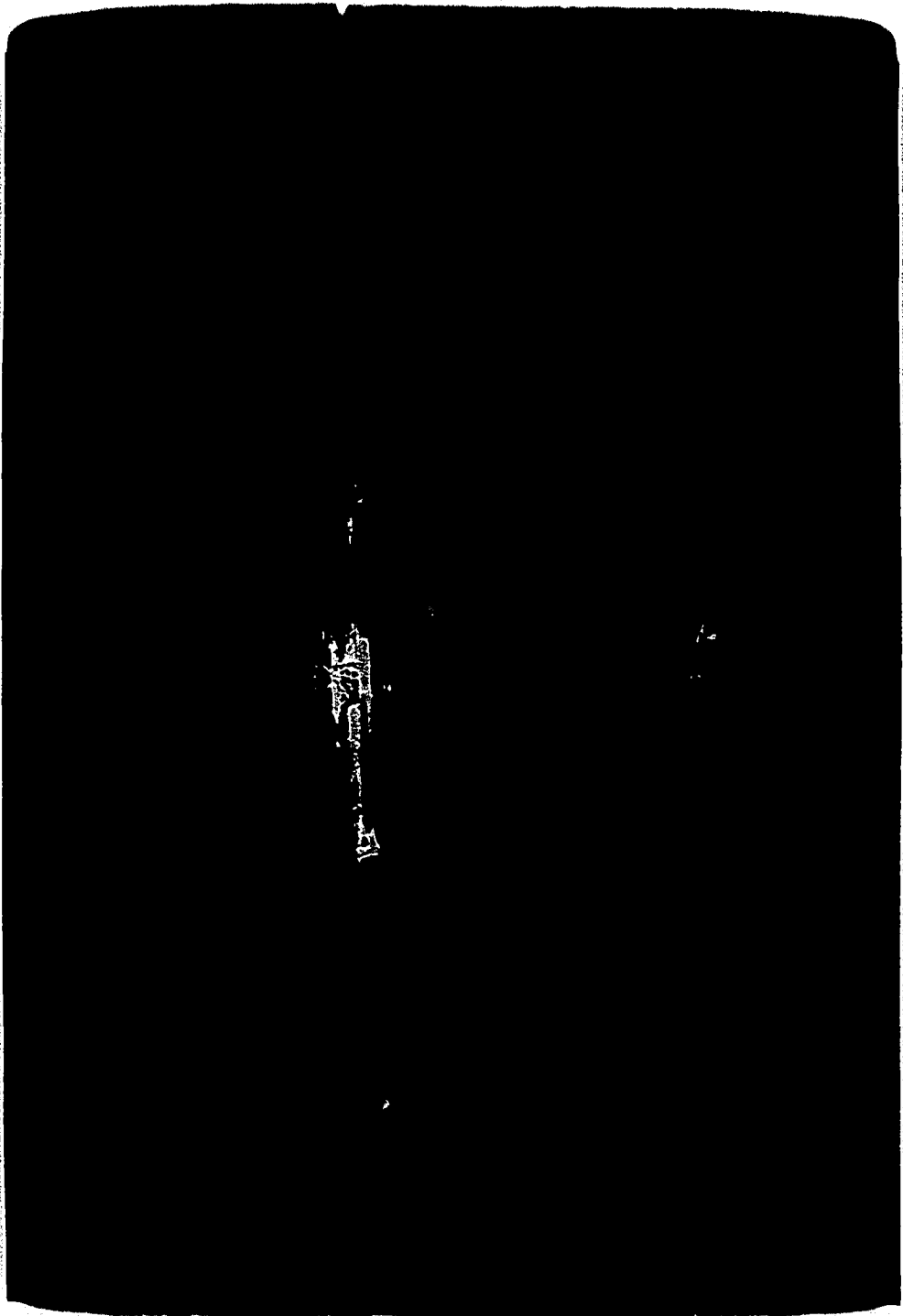


Figure 8. Adsorption apparatus - perspective view

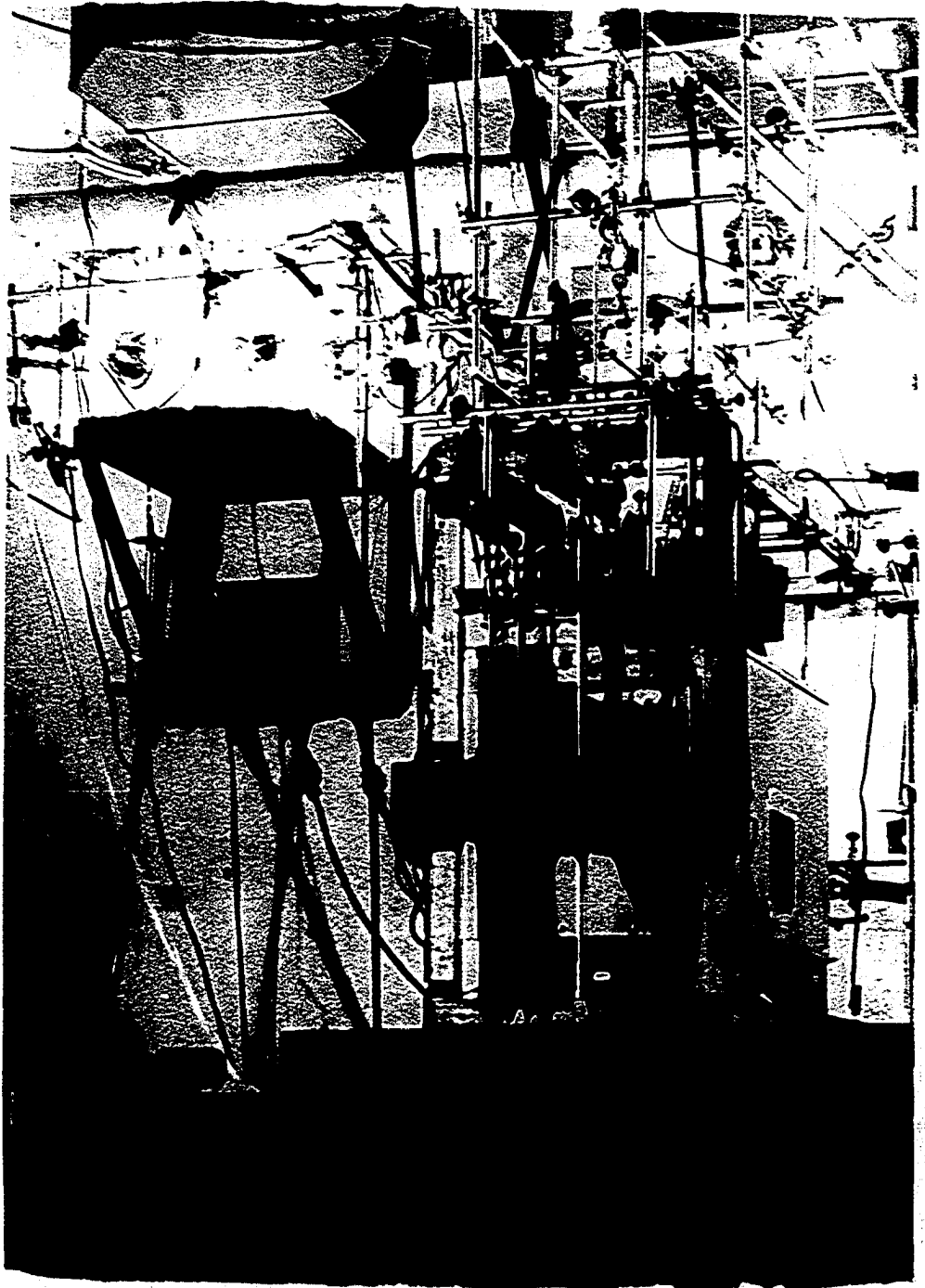
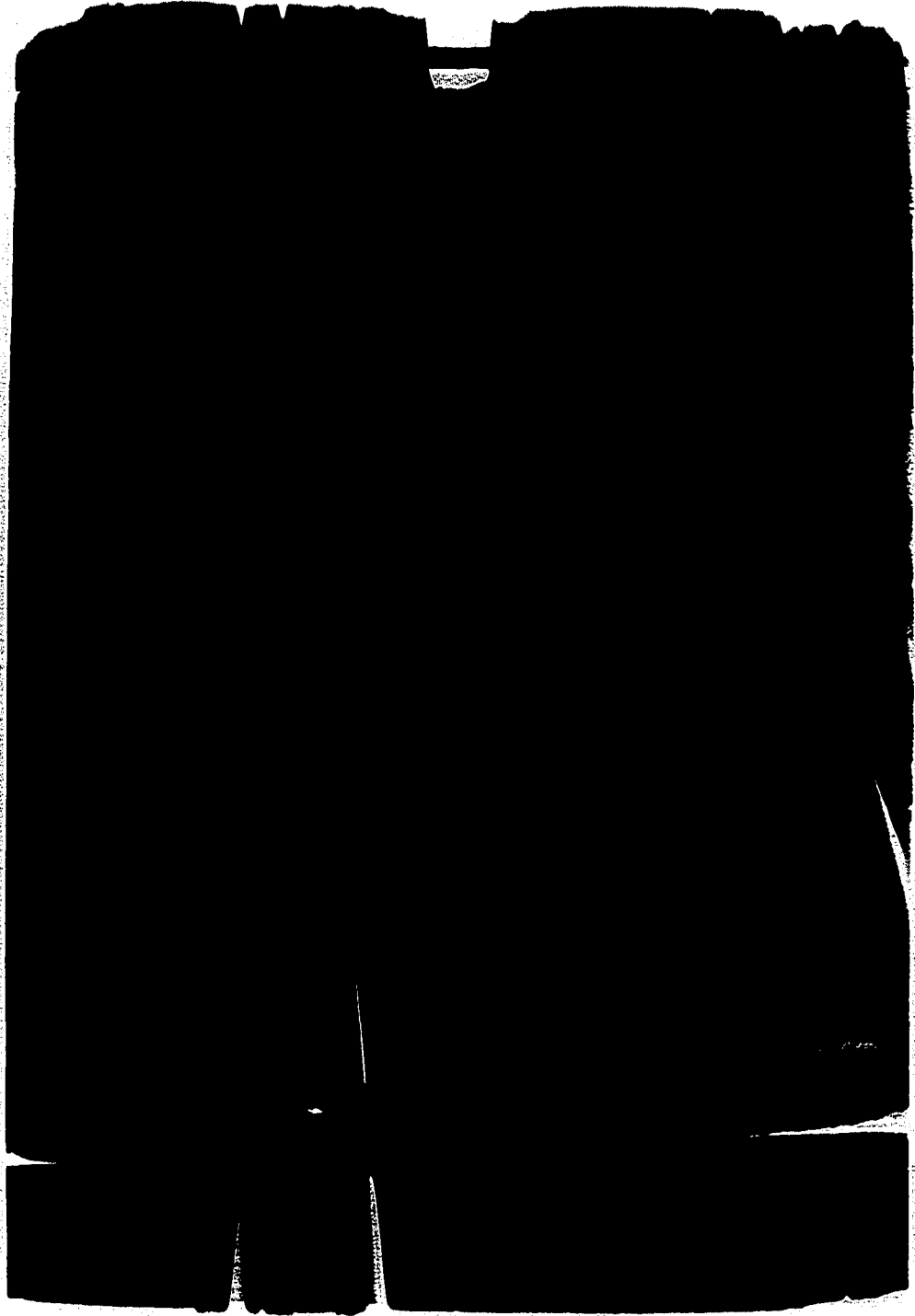


Figure 9. Brass mounting plate area



to the rack. Another glass tubing T connected the opposite side of the middle valve with the other two valves, L and R. This enclosed volume comprised the dosing chamber.

2. Mounting the apparatus

Obviously the greatest care and consideration must be given to the problems of mounting all the apparatus in a secure manner to prevent the pickup of mechanical vibrations insofar as possible. The rigid steel table and the angle iron framework mounted on the three inch thick soapstone were quite adequate, Figure 10. Three thickness of $1/4$ inch slab rubber were placed under each table leg and between the stone and the wooden table top. In addition, all auxiliary apparatus was attached in such a way as to minimize vibration. In this connection much use was made of a framework attached to the ceiling and hanging down over the main apparatus.

3. Valves

The Valves were the all-metal bakeout valves as developed by Bayard and Alpert and furnished by the Granville-Phillips Company. These performed satisfactorily, though it would be most desirable if similar valves were available that could be opened and closed with less effort. For example, these valves were opened and closed with a torque wrench to the range of 15 to 30 foot-pounds in most cases. This was quite severe

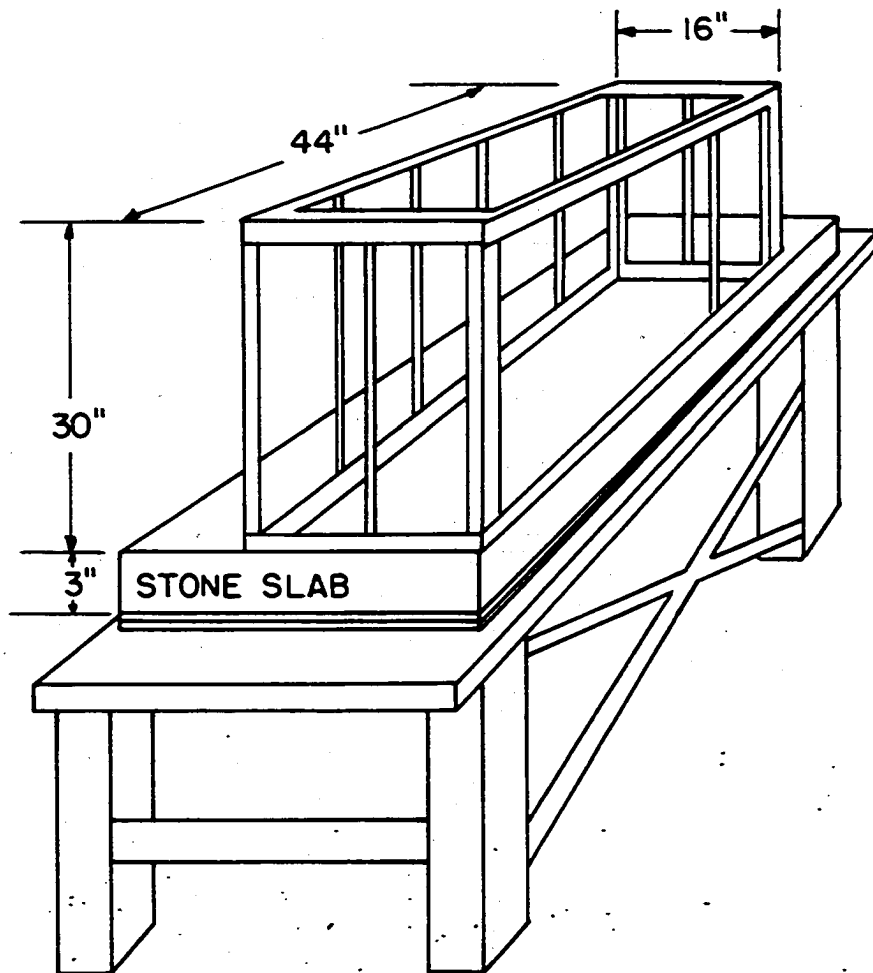


Figure 10. Table and rack

treatment but the mounting was rigid enough to withstand it though the precision of the adsorption balance was markedly affected as discussed in V C. Estimates of Precision.

4. Vacuum system

The vacuum system consisted of a two-stage Martin mercury vapor pump backed by a Welch duo-seal mechanical pump and connected through the valve L to the dosing chamber. A trap encased by a Dewar of liquid nitrogen protected the system from the vapors of the mercury pump.

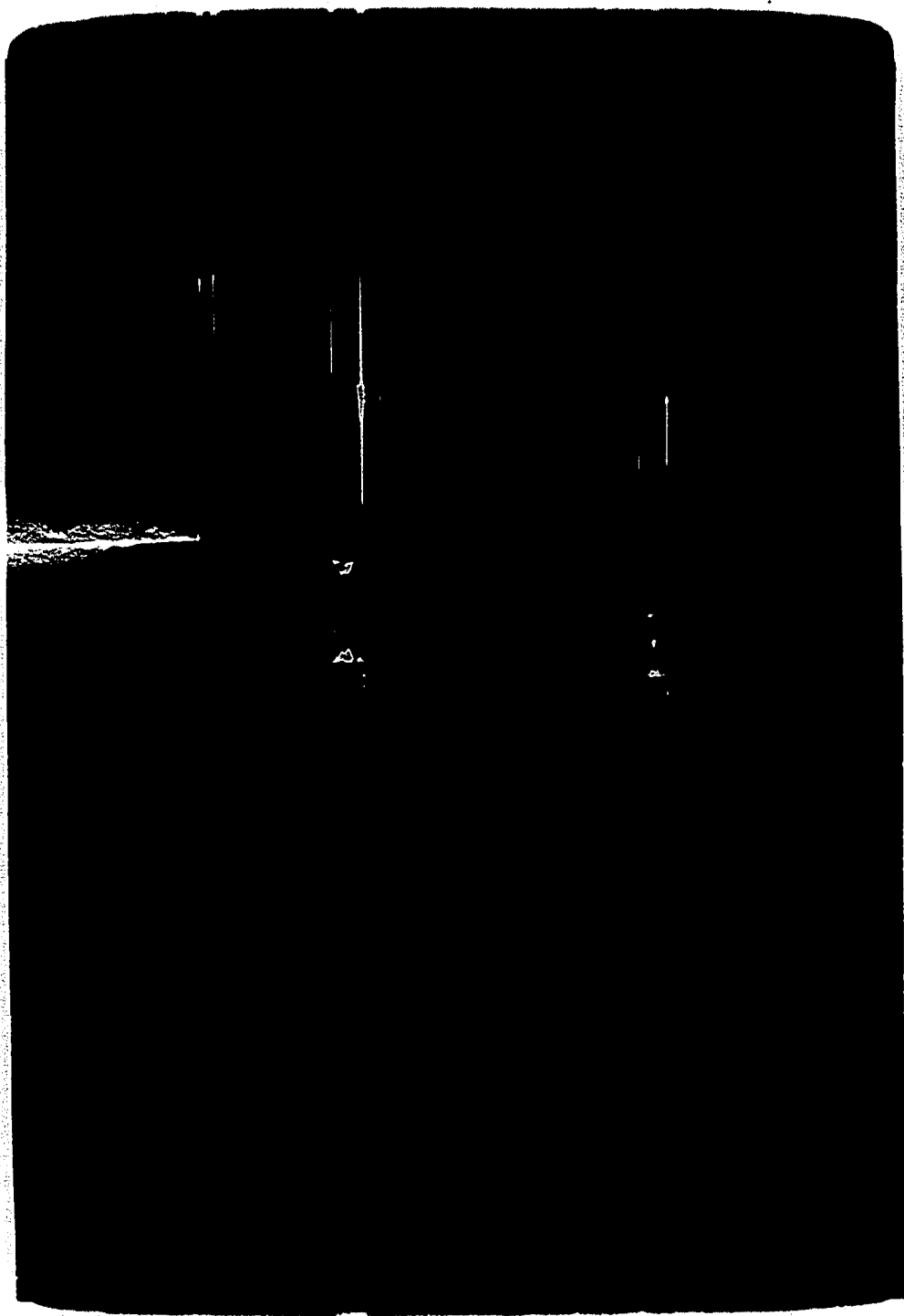
5. Gas supply

The gas supply appendage was attached by the connecting glass tubing to the dosing chamber through valve R. This consisted of the seal-off tube holding its gas supply and, of course, the essential bubble-breaking iron slug. This is pictured in Figure 11.

6. Electro²-magnetic-regulating system

Substantially the same sort of electrical system was used to regulate and monitor the balances as was described for the E-B balances. Storage batteries, supplying from two to twenty-four volts as needed, provided a source of steady current. This current was regulated in coarse adjustment by a 1000 ohm variable resistance wired as a potentiometer, and in fine

Figure 11. Gas supply tubes



adjustment by three, series wired, variable resistances of 1000, 20, and 1 ohm values. The brass forms and Helmholtz coils are clearly shown in Figure 12. This type coil was used so that the coils could be removed as needed during bake-out procedures. The current was monitored as before by measuring the voltage drop across a fixed standard resistance which was in series with the Helmholtz coils. A type K-2 potentiometer and a Rubicon shadow-box galvanometer were used to make this voltage value measurement. Reversing switches were used to connect the desired set of Helmholtz coils (adsorption of gas density balance) and to reverse the direction of coil-current flow as necessary.

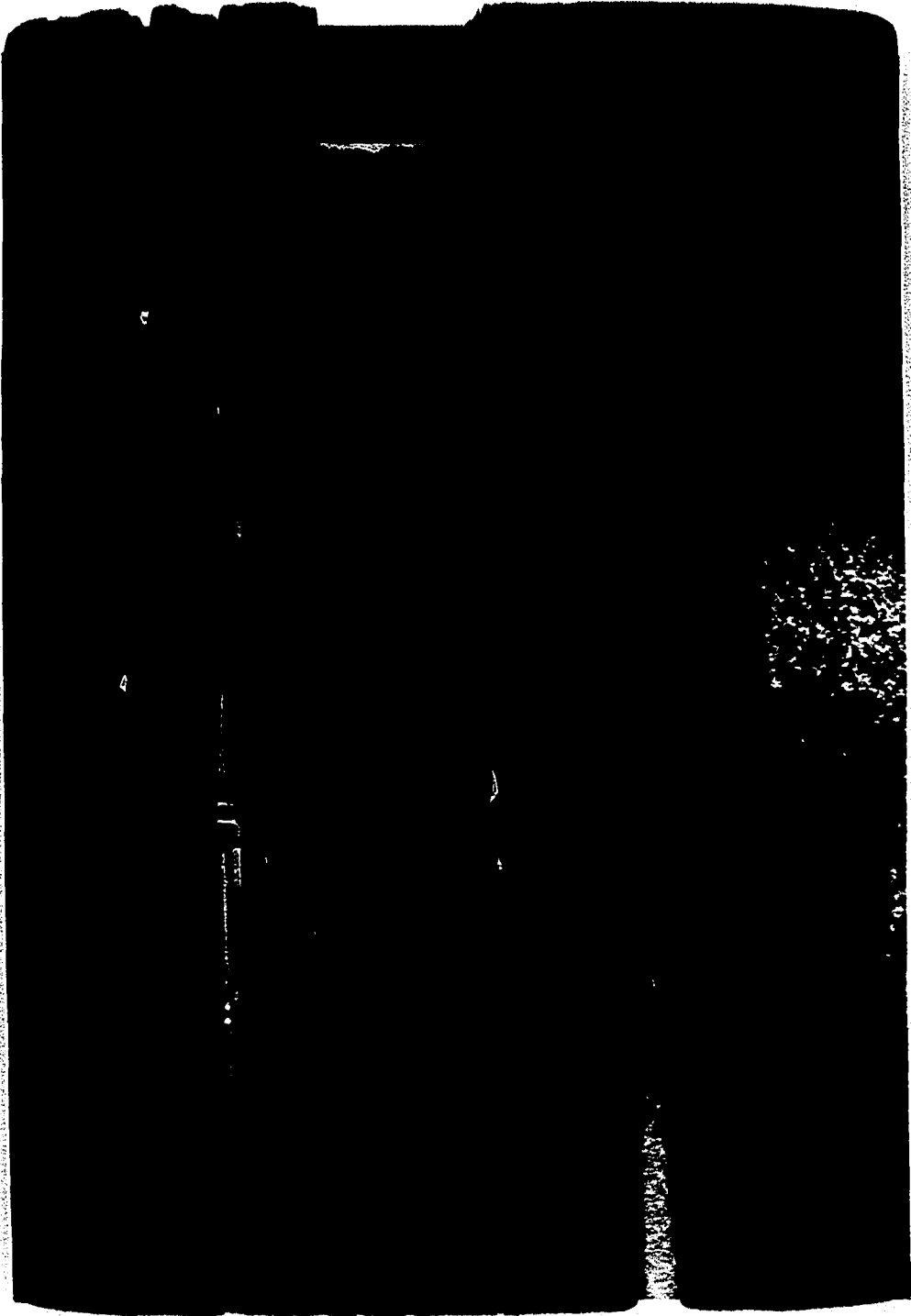
7. Optical system

Observations of the motion of the pointer fiber were made with Gaertner microscopes of four cm. focal length. The eyepiece of each scope was fitted with a scale and cross-hair. The extreme positions of the pointer fiber were on scale and so could be used as a check for possible accidental movement of the apparatus. The scopes themselves were mounted rigidly to the same brass plate that held the balance cases.

8. Method of thermostating

The general method of establishing fixed temperatures for the experiments was based on the immersion of the entire

Figure 12. Helmholtz coils - in position and empty coil holder



reaction chamber in a water bath. Preliminary experiments established that vibrations and stray fields from the stirring motor (and even uneven lighting from the flashing I. R. bulbs) adversely affected the balances if stirring and temperature regulation were done in the water bath tank proper. Therefore, the temperature of the water was regulated in a second tank and the water was siphoned from that tank to the water bath tank. Overflow from the water bath tank was caught in a third overflow tank from which the water was finally returned by a circulating pump to the regulated tank.

a. Temperature regulated tank The tank where the water was regulated to temperature was located on a shelf some three feet above the water bath tank. The merc-to-merc thermoregulators were connected to an electronic relay (Model E-3 as supplied by the Emil Greiner Co.). The relay actuated a series of I. R. bulbs (one to five as needed) providing the on-off heat source. Constant cooling was provided by tap water circulating through one of three assorted lengths of copper tubing immersed in the tank. Stirring to the point of turbulence was provided by a combination of an electric stirrer and the flow of water by the actions of the siphons and circulating pump. Auxiliary knife-blade heaters were used only to help adjust the water to temperature - once there the I. R. bulbs provided all the heat. Water was siphoned from this tank down and into the water bath tank through two tygon

tubes of five-eighths inch internal diameter. The volume of water used in the temperature regulated tank was about the same in amount as in the water bath tank (about two cubic feet).

b. Water bath tank The water bath tank was raised to surround and immerse the apparatus mounted on the brass plate. This included the reaction and dosing chambers, and the valves (L, M, and R). In the raised position the tank was supported by a stack of wood blocking placed between the stone slab and the bottom of the tank. The dimensions of the tank were, width twelve inches, length eighteen inches, depth fifteen inches. Temperature regulated water was siphoned into this tank through the two tygon tubes. The central part of the back edge of this tank was formed to make an overflow spout. The water flowed out this spout into a third tank which was suspended from the ceiling rack so as to keep overflow vibrations from the main apparatus. The flow of water from the siphons into the water bath tank did not jar the system.

c. Circulating pump The water was returned from the overflow tank to the upper temperature regulated tank by using a 1/5 h.p. circulating pump. The pumping speed of this pump was regulated by means of a variac and could be adjusted to match the flow rate of the siphon tubes.

d. Refrigerated tank The method of thermostating as described above was used for all the experiments made at 19.70° C. and 28.63° C. The experiments made at 2.40° C. were made by using a refrigerated tank. The thermo-regulator and heat sources were then used in connection with this tank. Because this tank was lower than the water bath tank the circulating method was reversed. The regulated cold water was pumped up into the water bath tank and siphoned back from the overflow tank into the refrigerated tank.

e. Room temperature The stability of the entire thermostatted system was affected by heat exchange to the surroundings. As a result it was found necessary to install a room air conditioner to insure steady operation of the system (and incidental comfort of the operator).

IV. MATERIALS

A. Alkyl Halide Gases

1. Purification

The ethyl iodide, ethyl bromide, and methyl iodide were fractionally distilled using a Wheeler fractionating column (reflux time 29 seconds, take-off time 0.25 seconds). Starting materials were reagent grade ethyl bromide and ethyl iodide as supplied by Matheson, Coleman, and Bell. The methyl iodide starting material was Eastman Kodak white label grade. In each case the distillate was collected in a series of six seal-off tubes by means of a special adapter which could be moved to bring one seal-off tube at a time under the delivery tip. In each case only the central fifty per cent portion of the distillate was collected for use. Following this, as a preliminary to the seal-off operation, the samples were mounted on a vacuum line and reduced in volume by evaporation to about eighty per cent of the total amount. The liquids were gradually frozen by use of a Dewar of liquid nitrogen, and the side delivery arm of the tube was then sealed off using a glass blowing torch while the pumping operation continued.

Because of the low boiling point of ethyl chloride (12.3°C) it was not put through the fractionating column. Instead, a flask of the Eastman Kodak white label starting

material was mounted on a simple vacuum line which also held the adapter and its six seal-off tubes. Distillation was carried out by use of appropriately placed Dewars of liquid nitrogen. The central portion was again collected in the seal-off tubes and these were sealed off as described above. Samples of five to six milliliters resulted in all cases.

2. Criteria of purity

In addition to the constancy of the boiling points as observed for all the gases (except the ethyl chloride), the vapor pressure of a random sample of each of the four gases was determined at the ice point temperature on the vacuum line setup established for this purpose by Dr. Riley Schaeffer's research group. The pressure value was approached from both the low temperature and high temperature side in each case. Finally, all samples were wrapped in foil and stored in brown bottles until used. There was no evidence of discoloration of any of these samples at any time. Table I summarizes the physical constants observed as these materials were purified and tested.

B. Cubic Sodium Chloride

1. Preparation

The adsorbent sample of cubic habit sodium chloride was prepared according to the procedure of Marshall (5). This

Table 1. Gas sample physical constants

Gas sample	Boiling range (not corrected)	Vapor pressure mm. Hg ^a (rising)	Vapor pressure mm. Hg ^b (falling)	Literature value ^c
C ₂ H ₅ Br	37.0°C	165.5	165.5	165.8
C ₂ H ₅ I	71.0°C	41.4	41.6	41.5
CH ₃ I	41.2°C	144.0	144.0	144.2
C ₂ H ₅ Cl	-	469 (at 0.1°C)	469 (at 0.1°C)	468

^{a, b}Values determined at 0.0°C except as shown.

^cValues from Ref. (54)

article also presents a discussion of the several factors relating to crystal production. The general method was one of solvent displacement. This involved the mixing of two solutions; one, a nearly saturated solution of sodium chloride; and, two, a solution of nearly pure ethyl alcohol.

The recipe followed for the preparation of the sample used in this research will be given, but it is understood that following the same recipe will not guarantee that uniform crystals of exactly this same dimension will result. In our case over one hundred different batches were made under various conditions - there is still a good bit of chance in this procedure and microscopic examination must be used to establish size and uniformity of the crystals.

Starting materials were Baker and Adamson reagent grade sodium chloride, conductivity water, and absolute alcohol as collected from a thirty plate Oldershaw distilling column. A saturated solution was decanted and diluted with ten per cent water by volume - this was solution A. Solution B was a solution of ten volumes of water to ninety volumes of absolute alcohol. Equal volumes of A and B were poured together and shaken vigorously for five minutes. The resulting slurry was filtered rapidly under suction and the crystals collected on a coarse fritted-glass filter crucible which was then placed in a desiccator for final drying prior to the microscopic examination.

2. Microscopic determination of surface area

Preliminary examination of a batch of small crystals was made using a binocular microscope. Samples that appeared uniform in size and cubic in form were then examined more closely by means of a regular microscope equipped with a calibrated eyepiece scale and a travelling cross hair. A stage micrometer was used to calibrate the scale.

In order to estimate the surface area an average length of cube edge was determined. The value used was an average value based on a measurement of 50 cubes. A random sample was used - the cubes were not selected; as the stage of the microscope was moved each cube that came on scale was measured.

Surface area was calculated as

$$A = 6V / \bar{l} = 810 \text{ cm}^2$$

where $\bar{l} = \Sigma l / 50$ and V was the volume of the sample (calculated from sample weight, 1.4650 grams, and density, 2.165 g/cm³).

Uncertainty in an area value was estimated as about 4 per cent using the relation

$$A = \bar{l}^2 \pm 2\sigma \bar{l}$$

where

$$\sigma = \sqrt{\frac{\Sigma d^2}{50(50-1)}}$$

d being the deviation of a length from the mean, and 50 the number of observations.

A second method of averaging was also used (and is preferred in this case) and gave a corresponding area value

$$A = 6V \times \overline{1/l} = 832 \text{ cm}^2$$

This estimate of surface area by microscopic examination was also checked by a water vapor isotherm. Agreement was good and the results are presented in chapter VI.

V. METHOD OF PROCEDURE

A. Preliminary Operations

1. Cleaning apparatus

All the glass tubing used to construct the apparatus was thoroughly cleaned just prior to final assembly. In fact, the balances and balance cases were cleaned even after the balances were fused in place. The principal cleaning solution used was a strong oxidizing mixture made of 33 ml. 85 per cent H_3PO_4 , 67 ml. 30 per cent fuming H_2SO_4 , 6 g. CrO_3 , and 1 g. KIO_3 . This solution was heated to $140^\circ C.$ and used hot. The balance cases containing the balances, as well as all tubing, were filled with this solution, then rinsed thoroughly with distilled water and oven dried. After final assembly, and before any adsorption run, bake-out of the system, particularly in the region of the sample, was carried out. This was done using cylindrical resistance furnaces as sleeves around the balance case near the adsorbent and counterbalance crystals, by the use of resistance heating tape, and by flaming for the other parts of the system.

2. Adsorbent and counterbalance crystals

a. Size and weight Sample weight and crystal size were determined by the sensitivity and load capacity of the adsorption balance in relation to the precision of measurement

desired. A precision of one per cent of monolayer coverage was first selected as a goal. It was then decided to be conservative in regard to the performance expected of the adsorption balance as to sensitivity and load capacity because experiments extending over several months time were anticipated. This was probably a fortunate decision for the system survived severe accidental jarring without mishap. Therefore, an estimated working sensitivity of only 5×10^{-7} grams was used to calculate the surface area required; and a total load capacity of just four grams was used to calculate the dimensions of the small cubes. A sample of about two grams was actually used, because two grams of the total capacity was allotted to container weight. This sample consisted of a collection of small crystals and each small cube was about fifty microns on an edge. The preparation and microscopic characterization of these crystals was reported in the preceding chapter. The weight of sample used was 1.4650 grams. The container for the sample was fabricated from platinum foil and wire, and its weight was 2.4110 grams.

The counterbalance was a large single crystal of halite and a similar container, of total weight approximately equivalent of that of the sample and its container. The area of this large counterbalance crystal was low compared to the total area of the small crystals (about 5 cm² to 800 cm²). Because of this, the adsorption on the counterbalance crystal

was of the order of the precision, and therefore, no correction for such adsorption was necessary.

b. Weight and volume taring Gravimetric procedures on the macro-scale are not often concerned with buoyancy effects; however, in the microgram range buoyancy effects become important. To illustrate, consider a balance of 10^{-7} grams sensitivity operating in a gas of representative molecular weight 112 and at standard conditions of temperature and pressure. The density of such a gas is equivalent to 5000 micrograms per milliliter. Consequently the volume displaced by the sample and counterbalance would need to be identical to 2×10^{-5} ml., if the buoyancy is to be no larger than the sensitivity.

There are additional complicating factors. It may be that the densities of the sample and counterbalance materials are not identical, so that an exact weight taring may not accomplish volume taring. Also the balance may not be symmetrical; the length of the two lever arms and the volumes of the two sides of the beam may not be exactly the same. In addition, a pointer fiber mounted on one end of the beam contributes to asymmetry. All these factors combine in an observed buoyancy effect.

If the buoyancy effect is not eliminated - by a painstaking volume taring operation - a correction for it must be made. In general this could be calculated if the difference

in the "effective volumes" of the two sides and the pressures are known with sufficient accuracy; this knowledge is usually difficult to obtain.

For the apparatus described herein, corrections are calculated quite readily. The general principle will be described here, and an actual sample calculation is given in D.

Treatment of Data. A calibration run is made to determine the buoyancy effect alone as related to gas density. This is done by admitting a gas to the reaction chamber that will not adsorb; in this case the total apparent weight change observed will be caused by buoyancy. The calibration is made at several pressure values to demonstrate that the buoyancy is proportional to gas density and to obtain the constant of proportionality. Once this factor is established, the raw adsorption balance data reflecting combined adsorption and buoyancy may be corrected for buoyancy. The correction for the contribution due to buoyancy is calculated from the gas density observation, see D. Treatment of Data. The precision is sufficiently high that even though large correction values may be needed (as in our case), the absolute precision of the result - representing adsorption alone - is still the "working sensitivity" of the balance, and relative precision is still adequate and the same as if no buoyancy correction had been necessary.

Realizing this, a time consuming precision volume taring

operation was not made in this research. There was a volume difference. A large buoyancy correction was necessary, and this correction was made with no loss of precision; in fact, this may well demonstrate the best way to determine such corrections.

c. Mounting samples on balances After the sample and counterbalance buckets were hung in place the open hang-down tubes were sealed off and the entire system baked-out under vacuum.

3. Mounting the gas samples

The containers holding the gas samples were sealed to the tubing leading from valve R, valve R being closed. Before this seal was made a soft iron slug, encased by pyrex tubing, was inserted in the tubing line for the purpose of breaking the glass bubble when desired. The entire apparatus was now baked-out down to the break-off bubble.

B. Operating Procedure

1. Adsorption runs

The procedure used to operate the apparatus will be described as carried out for all the adsorption runs and for the water vapor isotherm which was determined to help establish surface area. Modifications for calibration runs will be

treated separately.

a. Thermostat system Just prior to a run the thermostat system was brought to temperature. This involved filling the water bath tank (previously drained to permit bake-out), starting the circulation cycle, and bringing the entire system to temperature. The usual procedure was to fill the water bath tank by means of a rubber tubing leading from the water tap. After this tank was filled the siphon tubes were started. Usually these siphon tubes were clamped off while full of water and the upper regulated tank was full during the bake-out time, so that siphon flow resulted as the screw clamps were opened. If for some reason the siphon flow was broken the water supply tube from the tap was inserted in the bottom end of the siphon to fill it and start the siphon action. As soon as overflow from the water bath commenced, the circulating pump was started to return the water from the overflow tank to the regulated tank. In most cases this just involved turning on the switch to the pump as the pump would be standing by in a primed condition. If this were not so the siphon flow was stopped by clamping until the pump was reprimed. The easiest way to prime the pump was to use the rubber tube from the tap to fill the pump and its tubes with water, filling at the outlet end (at the point of delivery into the upper regulated tank). Siphon flow and pump operation were established with the pump return flow rate adjusted

by means of the variac control to balance the siphon flow. The overflow tank was a six inch diameter, two feet long, glass cylinder so that the rise or fall of the water level in this tank could be seen easily and could indicate any change in the relative flow of siphons and pump. To minimize the threat of flooding, the pumping rate was pitched a bit faster than the overflow rate so that the pump would be sucking some air along with the overflow water. This was not only a safety device to prevent flooding but the volume of water in the overflow tank at any time was constant and no more than half a liter in amount which assisted steady operation of the thermostat. As the entire system came to temperature final adjustments of the water flow rate in the cold source tubing and adjustments of the number and locations of the I. R. bulbs were made. Usually, about two I. R. bulbs were on constantly with three others actuated by the relay. Adjustments were made until the on-off heat cycle time was regular and in the range of five to fifteen seconds.

In most cases the bath temperature became steady within an hour after starting. For the first run at a new temperature the same adjustments were made but usually required more time. A different thermoregulator was used for each of the three temperatures to make it easier to re-establish a temperature for repeat runs, though usually all gases were run before changing temperature because it was easier to change

gases than to adjust the baths to a different temperature. A Beckman thermometer was used to monitor possible changes of water bath temperatures in the vicinity of the balances.

b. Gas supply When the system was ready for gas the following procedure was followed.— Valves M and R were closed to prevent fine particles of glass from reaching the valve seats. The alkyl halide was frozen with liquid nitrogen and the glass bubble broken by means of the iron slug and a permanent magnet. The alkyl halide was then adjusted to temperature by appropriate baths. Before any gas was admitted to the reaction chamber the dosing chamber was flushed several times with gas by using valve L and R and the vacuum system.

The principal method of adding increments of gas to the reaction chamber was to first load the dosing chamber, valve L and M closed (during an adsorption run M would remain closed), valve R open. Then valve R was closed and valve M opened admitting gas to the reaction chamber. Valve M was then closed and balance readings taken. The dosing chamber would be dosed again, etc. The volume of the reaction chamber was about seventy times as large as the dosing chamber (1340 cc. to 20 cc.), so the pressure increment added each time was about $1/70$ of the pressure established in the dosing chamber. That pressure was determined, of course, by the vapor pressure of the liquid gas sample and so this was established at any desired value by a temperature bath (a small Dewar was used)

around the liquid gas sample.

Sometimes it was more convenient to add larger gas amounts; this was done by opening both M and R admitting gas directly and not using the dosing chamber. At one time it was thought that the principal dosing method would be based on that idea so as to decrease the number of valve openings required (and this was the basis of the calibration run relating $P_{C_2H_5Br}$ and $\Delta E_{g.d.}$); however, because of the small valve openings, it took about thirty minutes for the reaction chamber to come to pressure equilibrium after the temperature of the liquid sample was changed. Using the dosing chamber method, equilibrium was instantaneous and readings could be taken as fast as the balances could be adjusted (one set of readings could be made every five minutes).

Description usually was carried out more rapidly; only a few points were taken in most cases. If one used only the central chamber method, about 1/70 of the gas in the reaction chamber would be removed each time. The gas removed was either pumped out of the system, or more frequently condensed out, either in the original liquid supply tube or in a new seal-off tube if its future use was contemplated.

Gas samples were changed with valve R closed isolating the gas supply appendage. Any remaining alkyl halide was frozen and sealed off, and the next sample mounted as previously described.

Bake-out of the line down to the glass bubble was then made (L and R open, M closed), and finally bake-out of the entire system was made (M, L, and R open).

c. Operation of the balances The principles and procedure as described for the operation of the E-B balances (45) by the method of magnetic compensation also apply to this apparatus. Therefore, they are not repeated here. The characteristics of these balances will be presented in C. Estimates of Precision.

2. Calibration procedure

a. Adsorption balance weight-voltage calibration The adsorption balance was calibrated to determine the factor relating weight change to regulating voltage prior to sealing off the system before starting the adsorption runs. Previous tests with other balances (and with these) had always demonstrated a linear relation between the regulating voltage and weight change. Therefore, the calibration was made by determining the change in voltage required to restore the balance to the null position after a ten milligram standard weight was added to the bucket holding the sample. Both weighings were made with the reaction chamber evacuated. This was checked again at the conclusion of the experiments. The factor was the same in each case, namely, 0.0980 milligram per millivolt.

b. Gas density balance calibration The gas density balance was calibrated by determining the regulating voltages required to null the balance at several different pressures of ethyl bromide gas at 28.63° C. The pressure values were established by placing constant temperature slush baths around the liquid ethyl bromide (valves M and R open, L closed). The bath temperatures were determined by a thermocouple method and the vapor pressures calculated for these temperatures from vapor pressure - temperature relations available in the literature (54). It took about one-half hour for the reaction chamber to reach pressure equilibrium after changing a slush bath temperature. This was probably related to the small openings in the valves M and R.

A linear relation resulted, based on seven experimental points over the pressure range 0 to 300 mm. The factor established was 792.3 ± 0.1 mm. pressure ethyl bromide gas per volt.

c. Buoyancy effect calibration The buoyancy effect calibration was carried out by admitting dry air (it was presumed that dry air would not absorb) to the reaction chamber. Readings of both balances were then made. Several such sets of readings were taken over a one atmosphere pressure range.

If there were no buoyancy effect (reflecting good volume taring) the adsorption balance readings would not change as the dry air pressure increased. This was not our case and it was necessary to correct each adsorption datum for this effect

in the manner fully explained in the section of this chapter titled, D. Treatment of Data.

Room air was slowly admitted to the reaction chamber through valve R after passing it through a drying train consisting of a tube packed with MgClO_4 and a trap surrounded by liquid nitrogen. The relation was linear, resulting in the factor: $\Delta E_{\text{ads. corr.}} / \Delta E_{\text{g. d.}} = .00969$.

C. Estimates of Precision

This research was concerned with an amount of adsorption, at various pressures, under isothermal conditions. In this section, estimates of the precision of the measurements which established these three quantities will be given.

1. Temperature control

The temperature of the water bath was determined with a mercury thermometer calibrated to 0.01°C . In addition, a Beckman thermometer was used to help detect any change in bath temperature. No change larger than $\pm 0.01^\circ \text{C}$. was observed; this value was used as the estimate of temperature control, though it may have been somewhat better than this.

2. Precision of adsorption measurement

The precision of the adsorption measurements was not determined primarily by the sensitivity of the adsorption bal-

ance. The precision was determined principally by the effect on the balances caused by opening and closing the valves. This was evident after tests were made of the stability of the system under operating conditions.

We have mentioned the calibration of the adsorption balance in terms of regulating voltage but sensitivity should also be expressed in terms of the deflection of the balance beam and the optical system. These interrelated quantities for the adsorption balance are summarized for comparison as follows: 1 microvolt regulating voltage \cong 0.1 microgram \cong 1/3 eyepiece division \cong 6 minutes of arc pointer deflection.

Operating conditions affected the situation as follows:

a. Precision if valves were not used The following experiment was carried out: The system was brought to temperature equilibrium (28.63° C.) after bake-out under vacuum, and the reaction and dosing chambers were isolated by closing valves L, M, and R. A series of twenty readings were then taken; between each reading, the coil current was turned off and the rheostats and potentiometer settings were also changed. The twenty null values were identical to a microvolt - suggesting precision at least as good as the sensitivity.

b. Precision if valves were used The same sort of stability test was carried out, but this time the valve M was

opened and closed to twenty foot-pounds torque. To further simulate operating conditions these readings were taken over a thirty-six hour period with four separate bake-outs made during this time. Thirty-one readings were taken - this time the null values were not identical; there was an average deviation of three microvolts from the average, and a maximum deviation of eight microvolts.

As a consequence of this the precision of the adsorption measurements was estimated as ± 0.3 to 0.5 microgram.

3. Precision of pressure measurement

The precision of the pressure measurement was affected by the reproducibility of the gas density balance readings and by the temperature control.

a. Temperature effect The temperature control was estimated as about ± 0.01 C. This would reflect an uncertainty in a pressure measurement of about one part in thirty thousand; at pressures of 300 mm. of Hg, an uncertainty of about 0.01 mm. would result.

b. Reproducibility of gas density balance readings
The presence of gas in the reaction chamber improves the precision of the gas density balance readings by a helpful damping effect. For instance, a series of readings taken at about 12 mm. pressure of ethyl bromide resulted in an average

deviation from the average of 0.00004 volts, or about ± 0.03 mm. uncertainty. However, at 118 mm. pressure, the uncertainty decreased to ± 0.01 .

Consequently, the precision of the pressure readings was estimated to be in the range ± 0.01 to 0.03 mm. of Hg.

D. Treatment of Data

1. Raw data

The raw data used to establish a point on an isotherm consisted of the voltage values necessary to null the adsorption and gas density balances. In this section the treatment of these data to transform them to the corresponding amounts of adsorption and reduced pressures will be described. In addition, the transform equations will be applied to a representative set of data for illustrative purposes.

a. Adsorption balance voltage ($E_{ads.}$) to billimoles

The adsorption balance voltage value ($E_{ads.}$) was first subtracted from the starting voltage value (sample in out-gassed condition) to give a so-called $\Delta E_{ads.}$ value. This value was then corrected for the buoyancy effect, transformed to the unit called billimoles (one billimole = 10^{-9} moles), and used in this form as the ordinate value.

$$\text{billimoles of gas RX} = \Delta E_{\text{ads.}} - (\Delta E_{\text{g.d.}} \times 0.00969) \text{ volts} \times \dots$$

$$\dots 0.098 \frac{\text{grams}}{\text{volt}} \times \frac{1}{\text{g. mol. wt. RX}} \frac{\text{mole}}{\text{grams}} \times \dots$$

$$\dots 10^9 \frac{\text{billimoles}}{\text{mole}} \quad \text{V, Eq. 1}$$

We apply this equation to the data for a point on the isotherm of ethyl bromide at 2.40° C., Figure 13. Starting data:

$\Delta E_{\text{ads.}} = 0.001881$, $\Delta E_{\text{g.d.}} = 0.14073$; resulting in the isotherm point 467 billimoles at $P/P_0 = 0.556$.

$$\text{billimoles of } C_2H_5Br = 0.001881 - (0.14073 \times 0.00969) \text{ volts} \times \dots$$

$$\dots 0.0980 \frac{\text{grams}}{\text{volt}} \times \frac{1}{108.98} \frac{\text{mole}}{\text{gram}} \times \dots$$

$$\dots 10^{-9} \frac{\text{billimoles}}{\text{mole}} = 467 \text{ billimoles}$$

b. Gas density balance voltage ($E_{\text{g.d.}}$) to P/P_0 A

$\Delta E_{\text{g.d.}}$ value was first obtained by subtracting the $E_{\text{g.d.}}$ value from the starting value. This $\Delta E_{\text{g.d.}}$ value was then transformed to the corresponding $P_{C_2H_5Br}$ by means of the factor determined in the calibration relating these two quantities ($P_{C_2H_5Br}/\Delta E_{\text{g.d.}} = 792.3 \text{ mm./volt}$). For gases other than ethyl bromide and temperatures other than that of the calibration run (28.63° C.) gas law corrections were made, that is,

the pressure varies directly as the temperature, inversely as the molecular weight of the gas. The reduced pressure P/P_0 was then obtained by dividing the pressure, P , by the saturated vapor pressure of the gas at the isothermal temperature, P_0 . The P_0 values were obtained from the literature. The equation used was:

$$P/P_0 = \Delta E_{\text{g.d. of gas RK}} \text{ volts} \times 792.3 \frac{\text{mm.}}{\text{volt}} \times \dots$$

$$\dots \text{ mol. wt. } C_2H_5Br \times \frac{T_{\text{run}}}{T(301.79^{\circ}A)} \times \dots$$

$$\dots \frac{1}{P_0(\text{RK})} \frac{1}{\text{mm.}} \quad \text{V, Eq.2}$$

Using this for the sample calculation:

$$P/P_0 \text{ of } C_2H_5Br = 0.14073 \text{ volts} \times 792.3 \frac{\text{mm.}}{\text{volt}} \times \frac{275.6}{301.8} \times \frac{1}{183} \frac{1}{\text{mm.}} = .556$$

Except for ethyl chloride, corrections of the gas pressures for non-ideality were not necessary (Berthelot equation corrections) and for our purposes all calculations were made to slide-rule accuracy.

VI. RESULTS

The experimental results for the adsorption of the alkyl halide gases on sodium chloride over the entire pressure ranges and at several temperatures are presented in the form of isotherms expressing the amount of adsorption in millimoles (ordinate values) as a function of reduced pressure, P/P_0 , (abscissa values); ethyl bromide, Figure 13; ethyl iodide, Figure 14; methyl iodide, Figure 15; ethyl chloride, Figure 16.

Experimental values are represented by individual points. The theoretical isotherms, calculated according to the theory as developed in chapter VII, are presented on the same graphs as continuous lines.

Data for the adsorption of water vapor on sodium chloride are presented on Figure 17. The pronounced break in the curve appears at a millimole value which checks the estimate of surface area based on the microscopic examination.

Adsorption is seen to be reversible in each case and check runs were made for each system at each temperature.

The data for ethyl bromide, ethyl iodide, and methyl iodide were used in subsequent calculations. No adsorption of ethyl chloride was observed at the 28.63°C temperature and the data at 19.70°C were not sufficient to use though the general form of the isotherm is evident.

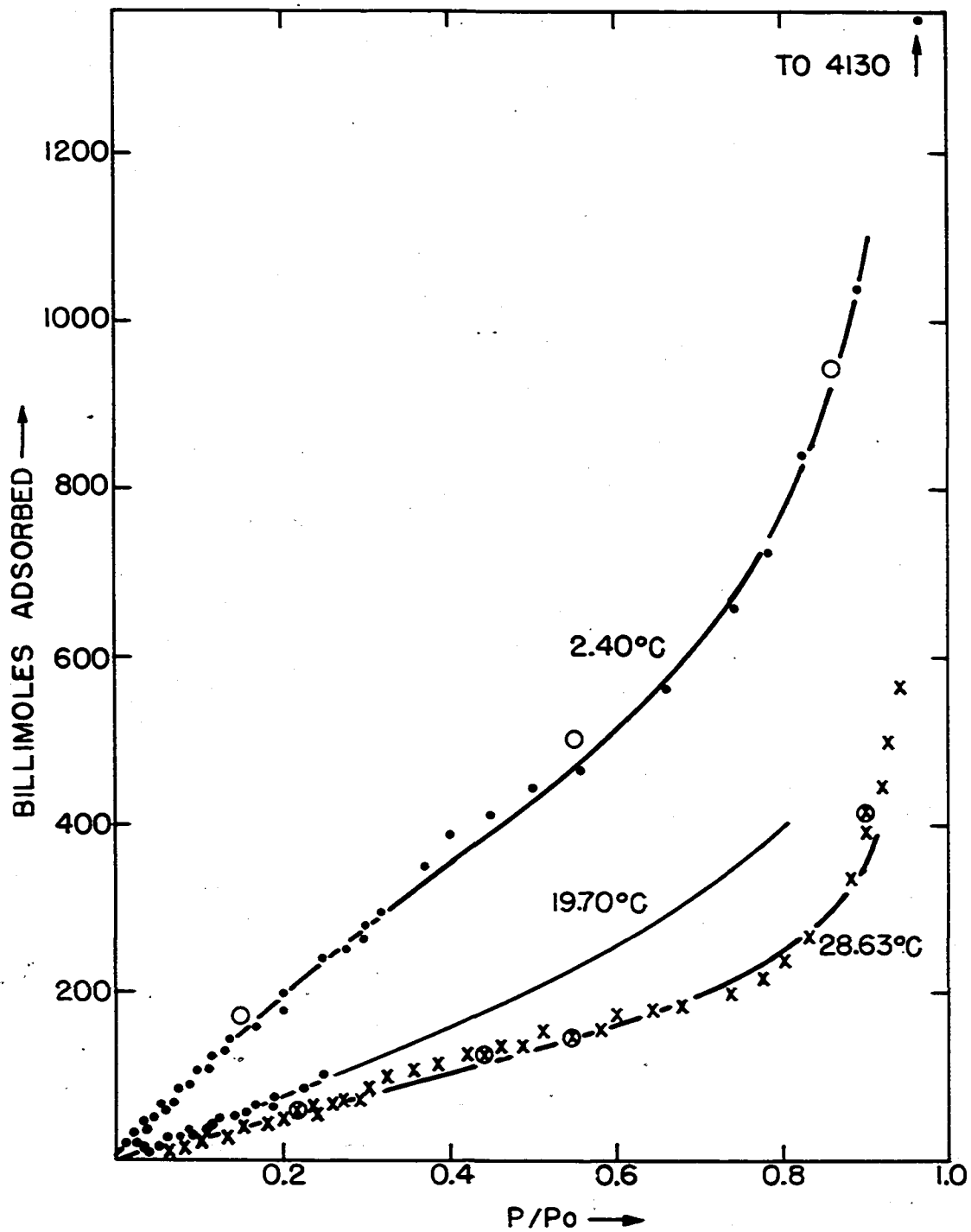


Figure 13. Ethyl bromide on sodium chloride
 ·, x, adsorption; ○, ⊗ desorption

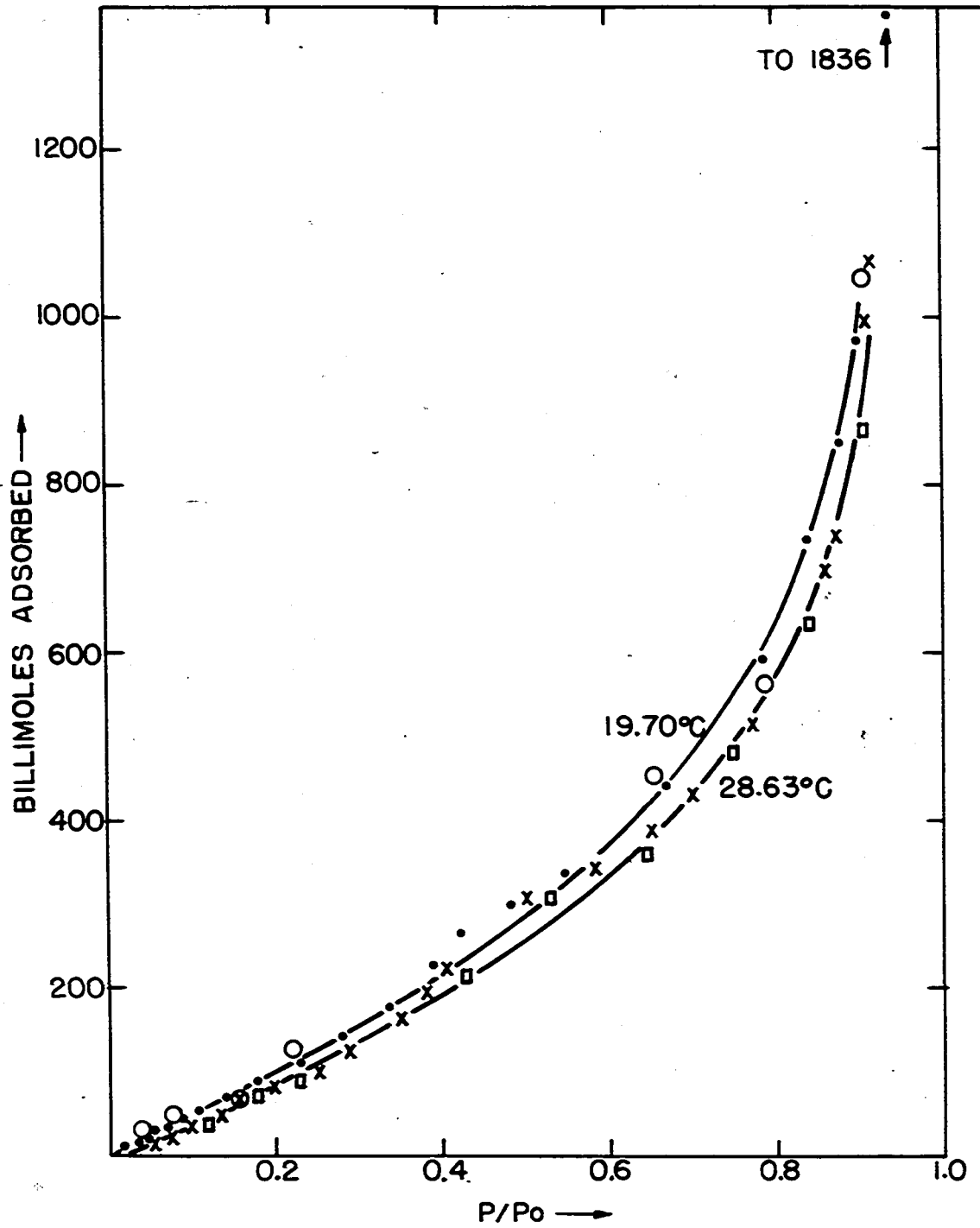


Figure 14. Ethyl iodide on sodium chloride
 ·, x adsorption, ○, □ desorption

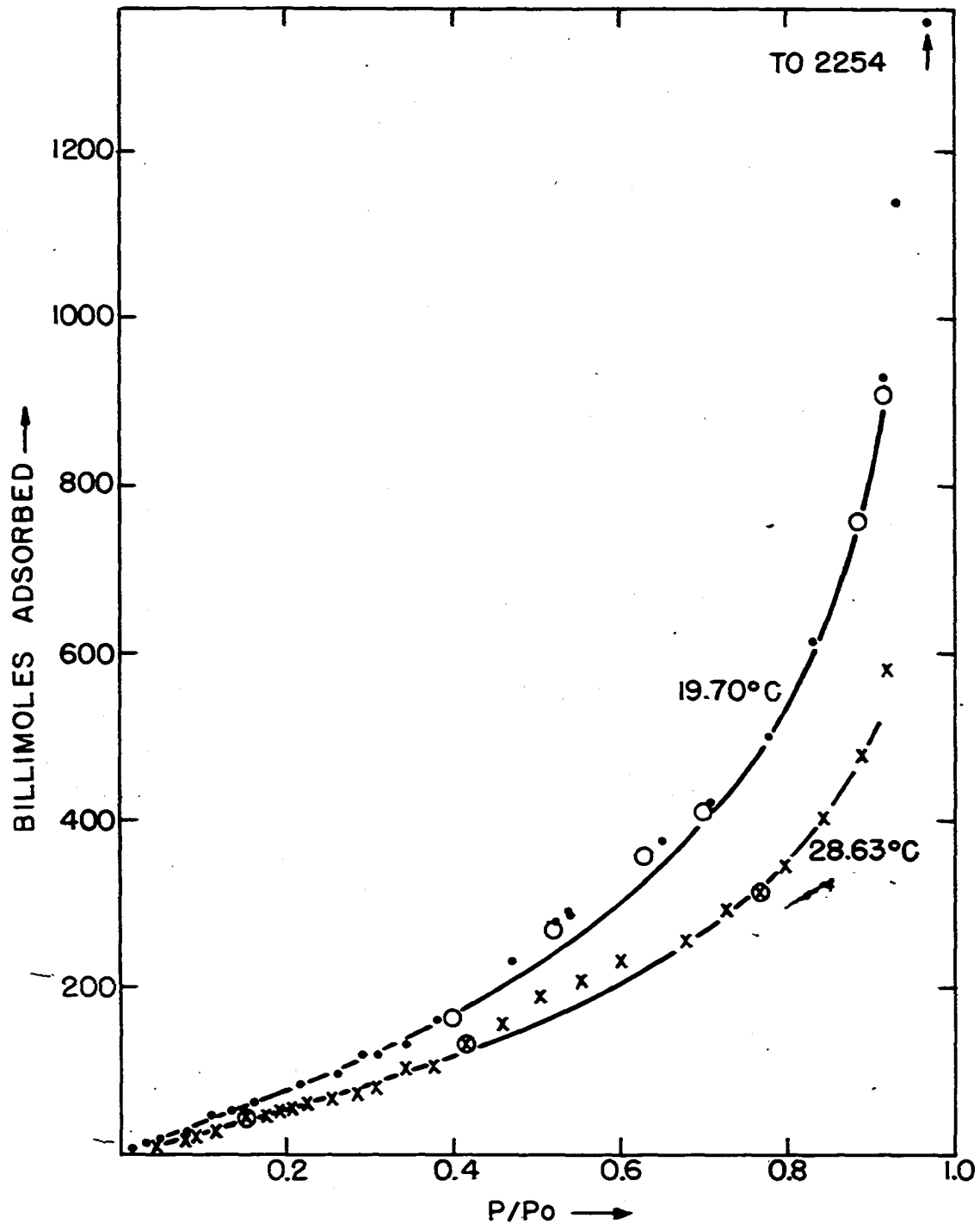


Figure 15. Methyl iodide on sodium chloride
•, x adsorption; ○, ⊗ desorption

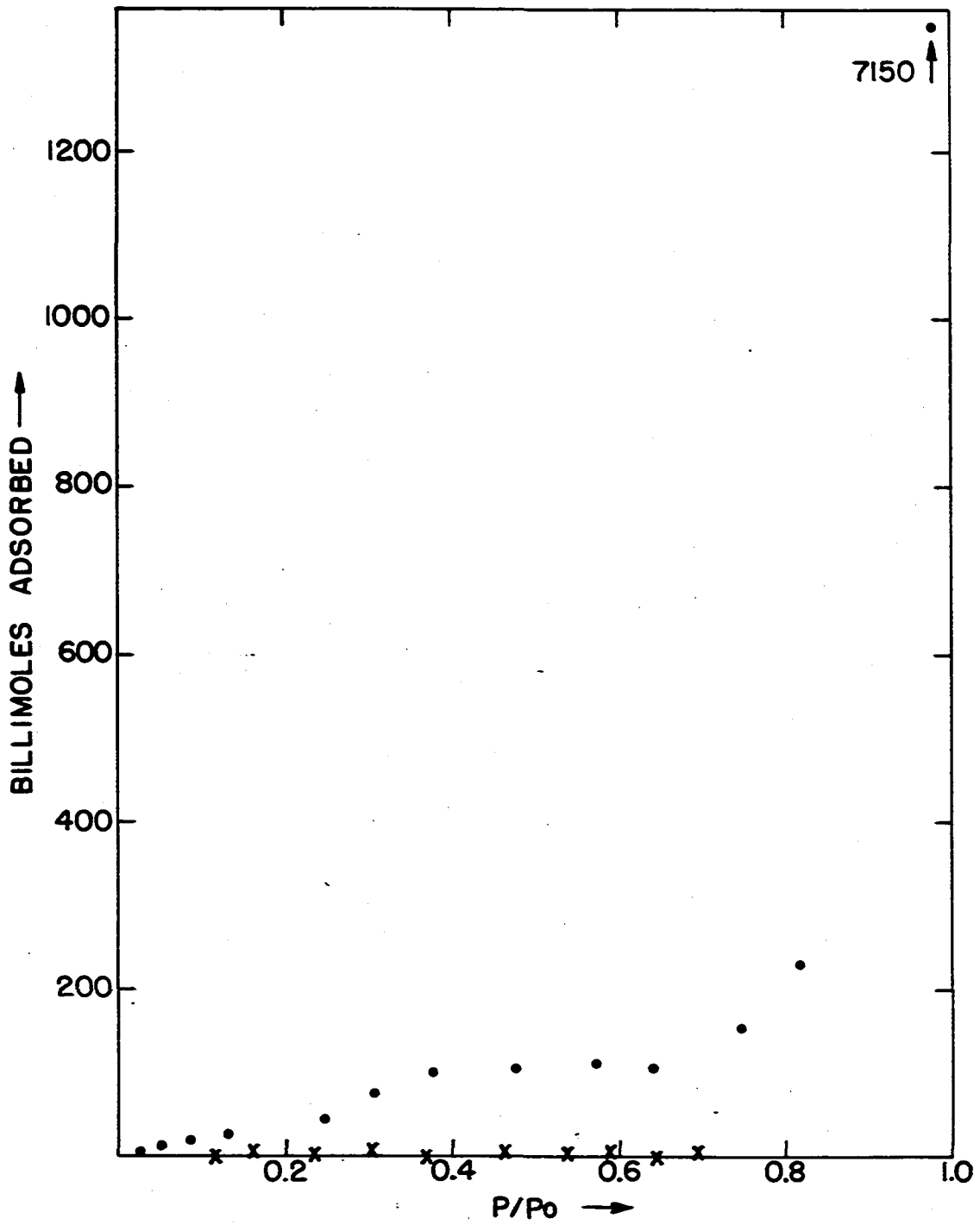


Figure 16. Ethyl chloride on sodium chloride
• 19.70° C adsorption; x 28.63° C adsorption

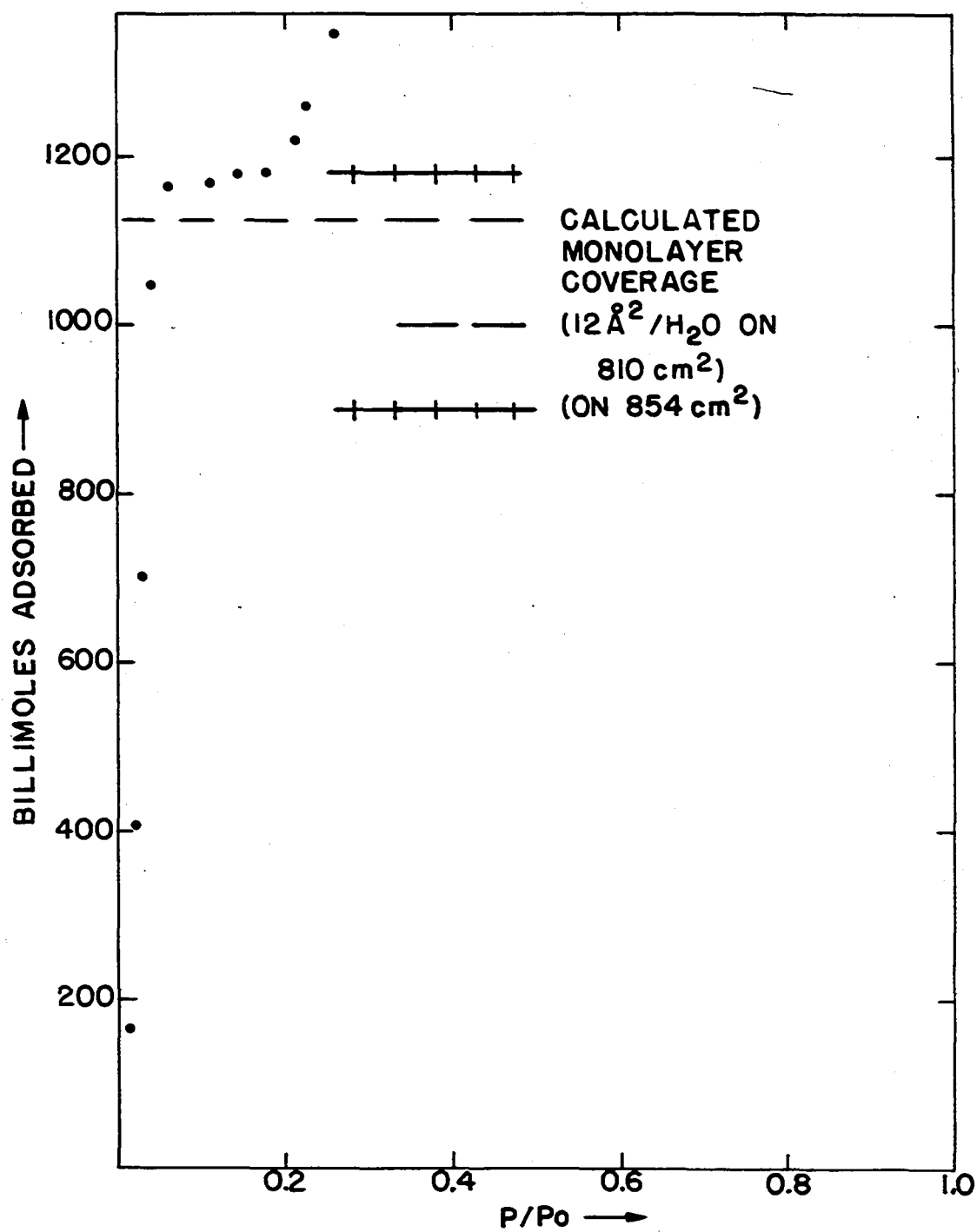


Figure 17. Water vapor on sodium chloride - isotherm temperature 26.63°C .

VII. DISCUSSION

A. Development of Theory

This discussion of results is based on a theoretical formulation for multi-layer adsorption as invented recently by Dr. R. S. Hansen and represents, as a matter of fact, the first independent test of his theory.¹ The character of the experimental adsorption isotherms is such as to provide an interesting test - as well as a successful application - of the theory.

The expression used to calculate the theoretical isotherms (these are presented by the solid lines on Figures 13, 14, 15, and 16) may be written as follows:

$$n/N_0 = \theta + \theta^m \left[\frac{K}{\ln^P \frac{P_0}{P}} - 1 \right]. \quad \text{VII, Eq. 1}$$

By the use of this expression the amount of adsorption, n , may be calculated from the adsorption equilibrium pressures P . P_0 is the saturated vapor pressure at the temperature of the isotherm. The relationship between θ , the fraction of the surface covered, and P/P_0 is given, in this case, by

$$P/P_0 = \frac{\theta 10^{-\gamma\theta}}{\alpha(1 - \theta)}. \quad \text{VII, Eq. 2}$$

¹The theory in the form it was first developed by Hansen, and applied by him to Arnold's data (55) on the adsorption of oxygen and nitrogen on anatase, proved to be not completely satisfactory for these data. Therefore, modifications were made in collaboration with Hansen, which resulted in the form used in this work. It is understood that Hansen will be publishing on all this in the near future.

This is a Langmuir type expression modified for gas molecule interactions. Consequently the terms N_0 , m , β , α , γ , and K are the parameters that are selected in the curve-fitting process. However, at high coverages both θ and θ^m become unity, and, therefore, the principal adjustable parameters are N_0 , K , and m . The significance of these parameters will be discussed individually and in detail, but it should be mentioned at this time that not one of these parameters is free. For example, N_0 refers to the moles of adsorbate gas that would just cover the surface (monolayer coverage) and is determined primarily by the adsorbent surface area, crystal structure, and the cross sectional area of an adsorbate molecule. The parameter m is related to the number of first layer gas molecules a second layer molecule must contact before condensing, and so, is limited to small numbers. Reasonable values for α and γ are also demanded for the free energies of adsorption involve α values, while the quantity γ must reflect reasonable gas molecule lateral interaction energies. Further, the parameter β is restricted by the form of the van der Waals interaction potential.

Critical reviews of the theories of physical adsorption are readily available, for example in Brunauer's book (29) and more recently by Halsey (56). Because of the importance of the Langmuir equation, its relationship to the treatment of Hansen, and in particular to provide identification for

certain of the parameters we will use, a derivation of the Langmuir equation will be outlined. In addition, the models of the Brunauer, Emmet and Teller theory (B.E.T. theory) and of Halsey's treatment will be discussed briefly to provide sufficient background. At the present time no theory is completely satisfactory either theoretically or in ability to represent all experimental data.

The Langmuir equation,

$$\frac{\theta}{1 - \theta} = bP, \quad \text{VII, Eq.3}$$

was advanced in 1915 (57), and has been perhaps the most important single equation in the field of adsorption. It was based on assumptions of non-interacting gas molecules and unimolecular adsorption. At present there are isotherm equations that fit experimental data not obeying the Langmuir equation and others that fit the data over a wider range; however, in most cases, the starting point in their development is the Langmuir equation. Langmuir's original derivation was based on a kinetic approach, but since that time its derivation has been made from both thermodynamic and statistical considerations; these are reviewed in (29).

Equations which express the chemical potential of adsorbed molecules in terms of surface coverage have been derived statistically for several models. Complete derivations are given, for example in Fowler and Guggenheim (56). The model

used for our purpose is the regular localized monolayer. This model is based on site-wise adsorption, in principle to completely localized adsorbed molecules, but it is also applicable in good approximation to mobile adsorbed molecules. The chemical potential derived statistically is (Fowler and Guggenheim, ref. 58, p. 431, Eq. 1007,8)

$$\mu_{a.g.} = kT \ln \frac{\theta}{1-\theta} - \ln a_0(T) + \frac{2\theta W}{kT} \quad \text{VII, Eq.4}$$

where θ is the fractional coverage of the surface, a_0 is the partition function for internal degrees of freedom of a molecule adsorbed in such a way that the surrounding sites are vacant, and $2w/z$ (where z is the surface coordination number) is the enthalpy change when two separate adsorbed molecules come to occupy adjacent sites.

This expression for the chemical potential, may be rearranged arbitrarily (and conveniently) for the purpose of calculating a standard free energy of adsorption. The rearrangement results in a constant term (identified with the chemical potential of a reference state), a term identified as a product of temperature and the idealized relative partial molar entropy of adsorbed molecules, and a term which could be called a surface activity coefficient. This means that, in analogy to gas phase chemical potentials, the rearrangement gives an expression of the form:

$$\mu = \mu^0 + TS + kT \ln \gamma' \quad \text{VII, Eq.5}$$

Consequently, the identification is made

$$\mu^{\circ} = -kT \ln a_o(T) \quad \text{VII, Eq.6}$$

$$TS = kT \ln \frac{\theta}{1-\theta} \quad \text{VII, Eq.7}$$

$$kT \ln \gamma' = 2\theta W \quad \text{VII, Eq.8}$$

The adsorption isotherm results when the chemical potentials in the gas and adsorbed states are equated; that is $\mu_{a.g.} = \mu_g$. This leads to the relation

$$\frac{\theta}{1-\theta} e^{-\frac{2\theta W}{kT}} = \frac{P}{P_o} e^{-\frac{\mu_{a.g.}^{\circ} - \mu_g^{\circ}}{RT}} = \frac{P}{P_o} e^{-\frac{\Delta F_{a.g.}}{RT}} \quad \text{VII, Eq.9}$$

In this form, the standard states are pure liquid for the gas phase, and the hypothetical idealized standard state of half filled surface for the adsorbed phase (that is $\gamma'_{a.g.} = 1$, $\theta/1 - \theta = 1$). In the discussions of the individual parameters we will use this expression VII, Eq. 9.

A theory of Brunauer, Emmett, and Teller (B.E.T. Theory) (59) has received wide application. The model for this theory suggests that higher layers build before the first layer is completed. It assumes that the binding energy everywhere above the first layer is the same as in the liquid phase. This picture, involving the vertical stacking of columns of molecules, is not physically satisfactory for where a molecule in such a stack lacks a full complement of nearest

neighbors its binding energy must be less than it would have in the liquid state.

Halsey's model (60) was based on a consideration of the van der Waal's energy of interaction between gas and solid. This led to the picture that the free energy changes involved could be expressed in terms of an inverse r^3 law as follows:

$$RT \ln P_0/P = K'/r^3 \quad \text{VII, Eq. 10}$$

and as a consequence of this, the isotherm resulting was

$$n = \frac{K'}{(\ln P_0/P)^{1/3}} \quad \text{VII, Eq. 11}$$

This equation provides the sigmoid character of isotherms observed at high relative pressures, characteristic of multi-layer adsorption. At the same time, this form predicts that the isotherm will come into the origin with an infinite slope and this is not a physically satisfactory picture. This is a consequence of allowing the interaction distance, r , between surface and gas molecule to become arbitrarily small - an unrealistic picture as the dimension of a molecule cannot become vanishingly small. In this connection, but from another point of view, the Halsey model implies a continuous distribution of adsorbate molecular centers as one moves away from the solid. Hansen's succinct comment on all this was, "a surface half-covered with whole molecules is not at all the same as a whole surface covered with half-molecules."

In the Hansen model, first layer and higher layer adsorption are treated separately and then uniquely combined in the expression VII, Eq. 1. A Langmuir type model is used for the first layer adsorption. Along with this, condensation is considered to proceed for the higher layers according to an inverse r^3 law (Halsey approach), or, more generally, according to an inverse r^{β} law - providing the first layer sufficiently resembles bulk liquid.

The criterion for resemblance of first layer to bulk liquid is taken as meaning the existence of sets of contiguous molecules on the surface. The fraction of the surface area covered by adsorbed molecules in sets of at least m contiguous molecules is proportional to θ^m . Considerations of packing for spherical and elongated molecules would seem to restrict probable values of m to the range two to six, and most likely to three for molecules of interest in the present work (i.e. cylindrical rather than spherical molecules). This feature of the model is particularly attractive, especially as one recalls the reservations in accepting the "poker chip stacking" suggested by the B.E.T. approach, and the ever-diminishing r implication of Halsey's theory.

Before the discussion of the individual parameters (which will present the application of the theory to the experimental results), consider once again the equation, VII, Eq. 1:

$$n/n_0 = \theta + \theta^m \left[\frac{K}{\ln P_0/P} - 1 \right]$$

n represents the amount adsorbed.

N_0 represents the sites on the surface.

θN_0 represents the number of molecules in the first layer.

θ^m is proportional to the fraction of first layer area that can accommodate a higher layer.

The entire bracket expression represents the thickness of the liquid layer in molecular units. The "minus one" is present in the bracket term to "subtract away" the first layer, to avoid counting it twice.

The parameter values used to construct the theoretical isotherms, presented as solid lines on Figures 13, 14, and 15, are summarized in Table 2.

Table 2. Tabulation of parameter values

Adsorbate gas	See figure	Isotherm temperature	N_0	m	β	γ	α	\bar{x}
C_2H_5Br	13	2.40°C	450	3	0.435	0.511	2.390	0.90
"	13	19.70°C	"	"	"	0.479	0.900	0.90
"	13	28.63°C	"	"	"	0.466	0.580	0.90
C_2H_5I	14	19.70°C	"	"	"	0.520	1.090	1.30
"	14	28.63°C	"	"	"	0.505	1.000	1.30
CH_3I	15	19.70°C	"	"	"	0.476	0.843	1.75
"	15	28.63°C	"	"	"	0.462	0.615	1.75

B. Application of Theory

Application of the theory will be made by a discussion of each parameter.

1. N_0

The parameter N_0 which represents the sites on the surface (the number of molecules to give monolayer coverage) has the same value of 450 billimoles for all the systems. This value is consistent with the independent estimates of surface area as determined from the experimental water vapor isotherms and the microscopic examination.

In many cases N_0 values vary inversely as the cross sectional area of the adsorbate molecules. Because no such effect is observed for these systems it appears likely that the number of sites may be determined primarily by the lattice dimensions of the surface rather than by the area of the adsorbate molecules. That is to say, that there are preferred sites on the ionic crystal surface, and these are far enough apart so that each type adsorbate molecule may fit into place without crowding. That this might be the case is supported by a later discussion of the $\bar{\gamma}$ parameter values. These values are uniformly low as compared with bulk liquid values - thereby implying somewhat greater inter-molecular distances which such a model based on lattice spacing could provide. A model

representing such a limiting arrangement for the alkyl halide molecules adsorbed on the surface (100) planes of a sodium chloride crystal is shown in Figure 18. Ethyl iodide was selected as representative and because it was the largest of the ethyl halides.

Another possibility must be considered, namely, that the molecules are erected along their long dimension. In this case, the cross sectional areas presented to the surface would be similar. On the other hand, this sort of ordering would result in a mutual alignment of the permanent dipoles, an unattractive model in this case, for it is possible to account for the adsorption without involving the permanent dipoles in the argument. This feature is also covered, in a sense, in the sections dealing with the parameters α and K .

2. \underline{m}

The parameter m has the value of three in all cases. This suggests that the number of contiguous sites that are occupied by first layer molecules before a second layer molecule will condense is three, which appears reasonable from a consideration of Figure 18.

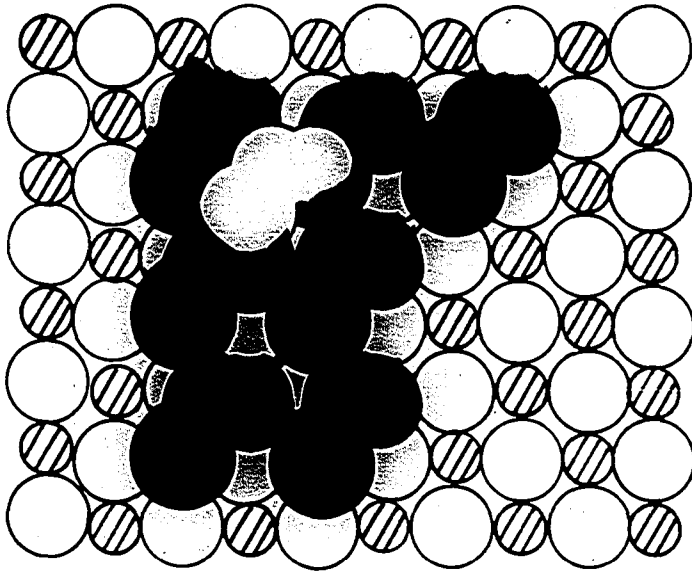
3. $\underline{\beta}$

The parameter β is related to the form of the power law expressing the fall off of the van der Waals energy with

Figure 18. Limiting arrangement of ethyl iodide molecules on sodium chloride surface

Chart of dimensions for Figure 18
(Angstrom units)

Na ⁺ radius	0.98
Cl ⁻ radius	1.83
I van der Waal radius	2.15
CH ₃ van der Waal radius	2.00
C-C distance	1.54
C-I distance	2.12

 Cl^-  Na^+  $\text{C}_2\text{H}_5\text{I}$ (layer 1) $\text{C}_2\text{H}_5\text{I}$ (layer 2)

distance from the surface. Hill (61) has pointed out that based on assumptions of a homogeneous (no preferred sites on the surface) planar surface and simple London forces the power law is $E = 1/x^n$ where n is 3. β is identified as $1/n$; therefore, an n value of 2.3 is indicated as the experimental values of β were uniformly 0.435.

Considering that the surface is not homogeneous and planar (and these irregularities are of the same order of magnitude as the dimensions of the adsorbed molecule) a value of 2.3 as compared to 3 is perhaps reasonable.

4. γ

The parameter γ has to do with interaction between gas molecules. Identification of a so-called surface activity coefficient was given in VII, Eq. 9 as

$$e^{\frac{-2\theta w}{kT}}$$

For our purpose, we rearrange this expression:

$$e^{\frac{-2\theta w}{kT}} = 10^{\frac{-2w\theta}{2.303 kT}} = 10^{-\gamma\theta}$$

We identify γ in this form

$$\gamma = \frac{2w}{2.303 kT} \quad \text{VII, Eq. 10}$$

We will use VII, Eq. 10 to estimate the magnitude of γ and we also note the temperature dependence implied; γ should vary inversely with temperature.

a. Magnitude of γ We may estimate the order of magnitude of γ by relating it to the energy of vaporization $\Delta E_{\text{vap.}} = N_0 z' w$, where N_0 is Avogadro's number, z' is the bulk coordination number and w is the interaction energy per molecule. Therefore, $w = \Delta E_{\text{vap.}} / N_0 z'$ and using this in VII, Eq. 10,

$$\gamma = \frac{2w}{2.3 kT} = \frac{\Delta E_{\text{vap.}}}{2.3RT}$$

assuming the ratio of surface to bulk coordination number is $1/2$ ($z/z' = 6/12$). For the compounds of interest here, the energies of vaporization are approximately 6500-7000 cal./mole. Hence, one would expect γ to be approximately $1/2$. It is seen in Table 2 that observed γ values are lower and of the order of $1/2$. A reasonable explanation for the lowering is based on an increase in the intermolecular distances between adsorbed molecules as compared with bulk liquid values which the N_0 parameter values also suggested (see also Figure 18.)

b. Relation of γ to $\Delta H_{\text{vap.}}$ An explicit relation between γ and $\Delta H_{\text{vap.}}$ was sought, and they were found to be proportional as the preceding treatment might have suggested, see Table 3.

c. Temperature dependence of γ It was noted in VII, Eq. 10, that the value of γ for a particular gas should vary inversely with the absolute temperature. Using the

Table 3. Ratio of γ to ΔH_{vap} .

Alkyl halide	γ^a	ΔH_{vap}^b	$(\gamma/\Delta H_{\text{vap}}) \times 10^4$
$\text{C}_2\text{H}_5\text{I}$.520	7115	.730
$\text{C}_2\text{H}_5\text{Br}$.479	6586	.728
CH_3I	.476	6515	.730

^aValues from Table 2 for runs at 19.70° C.

^bValues from Ref. (62)

19.70° C. experimentally determined γ values as reference this temperature dependence was tested by calculating γ values for the other temperatures and comparing these calculated values with the experimental values (that is, the values that resulted from the curve fitting process). The results are shown in Table 4 and the calculated and experimental values are seen to be identical.

Table 4. Inverse temperature dependence of γ

Alkyl halide	Temperature	calc. γ	exper. γ
$\text{C}_2\text{H}_5\text{Br}$	19.70°C	(.479) ^a	
	2.40°C	.511	.511
	28.63°C	.466	.466
$\text{C}_2\text{H}_5\text{I}$	19.70°C	(.520) ^b	
	28.63°C	.505	.505
CH_3I	19.70°C	(.476) ^c	
	28.63°C	.462	.462

^{a, b, c}value of γ used to calculate values at other temperatures

5. α

The parameter α is identified as the coefficient of P/P_0 in VII, Eq. 9. Therefore the parameter α is interpretable in terms of a standard free energy of adsorption, thus

$$-\Delta F_1^\circ = RT \ln \alpha \quad \text{VII, Eq. 11}$$

The standard states in ΔF_1° are bulk liquid adsorbate and a hypothetical state of the adsorbed molecules in which the monolayer is half completed and the surface activity coefficient is unity. A second standard free energy of adsorption can be defined in terms of an initial state of gaseous adsorbate at 1 atm. and the same final state as in the case of ΔF_1° , namely

$$\Delta F_2^\circ = \Delta F_1^\circ + \Delta F_l^\circ \quad \text{VII, Eq. 12}$$

where ΔF_l° is the standard free energy of liquefaction.

Using the same subscript notation we have also

$$\Delta H_1^\circ = RT^2 \frac{d \ln \alpha}{dT} \quad \text{VII, Eq. 13}$$

$$\Delta H_2^\circ = \Delta H_1^\circ + \Delta H_l^\circ \quad \text{VII, Eq. 14}$$

$$\Delta S_1^\circ = \frac{\Delta H_1^\circ - \Delta F_1^\circ}{T} \quad \text{VII, Eq. 15}$$

$$\Delta S_2^\circ = \frac{\Delta H_2^\circ - \Delta F_2^\circ}{T} \quad \text{VII, Eq. 16}$$

Values of ΔH_1° , ΔH_2° , ΔS_1° , and ΔS_2° thus calculated are tabulated in Table 5.

The dependence of the standard enthalpy of adsorption on adsorbate dipole moment and polarizability was investigated. It was assumed that, if the principle force holding the

Table 5. Summary of ΔH and ΔS values

Compound	ΔH_1°	ΔH_2°	ΔS_1°	ΔS_2°
C_2H_5Br	-8.87	-15.5	-32.4	-51.2
C_2H_5I	-1.69	-8.8	-5.7	-29.8
CH_3I	-6.22	-12.7	-23.4	-41.3

adsorbate to the surface in the first adsorbed layer were ion-dipole the enthalpy of adsorption ΔH_2° should be proportional to the adsorbate dipole moment; if the principle force were of the London dispersion type the ΔH_2° should be proportional to the molar polarizability, and if both forces were important ΔH_2° should be of the form

$$\Delta H_2^\circ = a_1\mu + a_2P \quad \text{VII, Eq.17}$$

It was not found possible to represent the data in Table 5 by an equation of this form. The enthalpies of adsorption of ethyl bromide and methyl iodide were closely proportional to their respective polarizabilities, but the enthalpy of

adsorption of ethyl iodide was much too low to satisfy this proportionality. It is possible that this result is due to experimental uncertainty, since the temperature dependence of adsorption of ethyl iodide was least thoroughly investigated in the group of adsorbates studied.

6. K

If the interaction energy between adsorbent and gas is of the van der Waals type then a molecule at a distance x from the surface would be subjected to an interaction energy of the form

$$E(x) = c/x^3 \quad \text{VII, Eq.16}$$

and if this is greater than the free energy of liquefaction a liquid film should extend at least to a distance x from the surface. Hence a film of thickness x_0 should form such that

$$c/x_0^3 = RT \ln P_0/P \quad \text{VII, Eq.17}$$

where P is the pressure of the bulk gas, and P_0 the saturated vapor pressure of the corresponding liquid. Hence

$$x_0 = \left(\frac{c}{2.303RT} \right)^{1/3} \log^{-1/3} P_0/P \quad \text{VII, Eq.20}$$

and the number of moles per unit area accommodated by this film will be

$$\frac{x_0}{\bar{v}} = \frac{1}{\bar{v}} \left(\frac{C}{2.303RT} \right)^{1/3} \log^{-1/3} P_0/P \quad \text{VII, Eq.21}$$

or, for the complete adsorbent sample

$$\frac{n}{N_0} = \frac{A}{\bar{v} N_0} \left(\frac{C}{2.303RT} \right)^{1/3} \log^{-1/3} P_0/P \quad \text{VII, Eq.22}$$

where \bar{v} , n , N_0 , and A are respectively, molar volume, moles adsorbed by the sample at a given P , moles required to complete a monolayer on the sample, and sample area. Evidently the parameter K of VII, Eq. 1 is related to the coefficient of $\log^{-1/3} P_0/P$ in this expression; the exponent $1/3$ has been replaced by the adjustable parameter β which is of the order of magnitude $1/3$ (actually 0.435), so we identify K as follows

$$K = \frac{A}{\bar{v} N_0} \left(\frac{C}{2.303RT} \right)^{\beta} \quad \text{VII, Eq.23}$$

The coefficient C depends on the character of the intermolecular interaction energies between adsorbent and adsorbate; for rare gas atoms interacting with adsorbents such as carbon Steele and Halsey (63) use

$$E(x) = \frac{\bar{E}}{3} \frac{a_1 a_2}{\frac{a_1}{\chi_1} + \frac{a_2}{\chi_2}} \quad \text{VII, Eq.24}$$

$$\text{implying } C = \frac{\bar{E} a_1 a_2}{\frac{a_1}{\chi_1} + \frac{a_2}{\chi_2}}$$

where B is proportional to x^3 , x is distance of closest approach, a 's are polarizabilities, and χ 's are diamagnetic susceptibilities, but the present gases are polar gases, the adsorbent an ionic solid, and the interaction energies are correspondingly more complex. Considering the relation of K to C its dependence on polarizability, diamagnetic susceptibility, dipole moment, and molar volume was investigated. In the case of ethyl iodide and methyl iodide K appeared to be inversely proportional to the molar volume, but the K for ethyl bromide was much less than expected from this relation, nor could any other relation be found which represented the parameter K for all three substances.

C. Suggestions for Future Work

The uncertainty in the correlation of the α and K values might be overcome with additional studies, preferably at lower temperatures so as to increase the relative precision and magnify the temperature dependence and also to be able to include ethyl chloride in the series.

The ethyl iodide molecules are almost filling the space determined by the structure of the surface. It would be interesting to observe the effect of increasing the chain length by one or two CH_2 groups. This might encourage an orientation effect for such dipolar molecules.

Extensions of technique are possible. An immediate improvement would result from remounting the valves separate from the reaction chamber mounting so as to minimize the valve closure effects. Replacement of the valves with improved types would be desirable.

Several advantages would result if it were not necessary to observe the deflection of the beam optically. The system could be adapted more easily for low temperature work in addition to eliminating spurious lighting effects. Automatic operation and recording would be a possibility.

For some purposes a balance mounted in a small volume would be desirable. For example a gas density type balance could be used for a volumetric method of adsorption study. If the volume of the buoyancy bulb were significantly larger than the free volume the lower level of detection would be improved (for balances of equal sensitivity) by a factor established by the ratio of the buoyancy bulb volume to the free volume.

VIII. SUMMARY

1. The Edwards-Baldwin magnetically compensated fused-silica fiber microbalance was adapted for gas adsorption studies. Based on this balance, a gas adsorption apparatus was devised with the following properties:

- a. Weight measurements can be made in absolutely controlled atmospheres without disturbing the system.
- b. Weight sensitivity is 0.1 microgram with two grams load.
- c. Pressure measurement is by a second magnetically compensated microbalance on the gas density principle, with sensitivity to 0.03 mm. for representative gases.
- d. The whole assembly can be conveniently immersed in a water bath of moderate size.
- e. All valves are of the Bayard-Alpert type, permitting bake-out of the entire apparatus.

2. The apparatus proved practical for gas adsorption measurements with low area adsorbents - sufficiently low to be well characterized in crystal habit.

3. Isotherms for the adsorption of ethyl chloride, ethyl bromide, ethyl iodide, and methyl iodide on cubic habit sodium chloride were determined over the entire pressure ranges and at several temperatures in each case.

4. These isotherms were found to be reasonably well represented by a new treatment of gas adsorption developed in this laboratory. The parameters necessary for these

representations were determined (including temperature dependence) and found to be physically reasonable. It is concluded that the adsorption of alkyl halides by sodium chloride can be well characterized by a regular localized monolayer for the first adsorption layer, with a liquid film building on top of that fraction of the first layer sufficiently densely populated to accommodate it.

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