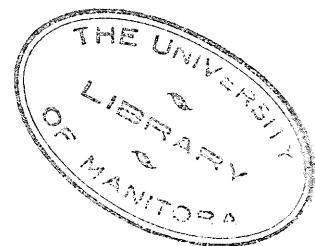


THE ADSORPTION
OF
NITROGEN BY MANGANESE

by
J. K. Royal

Being a thesis
submitted to the Committee
on Post-Graduate Studies of
the University of Manitoba in
candidacy for the Degree of
Master of Science.



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To Dr. A. N. Campbell

who directed and very generously
assisted in this work, the writer
wishes to acknowledge his great
indebtedness and to offer his
thanks.

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- THEORETICAL -

SORPTION OF GASES BY SOLIDS.

1. Historical Survey.

Sorption was first mentioned by C. W. Scheele in 1773, describing gases exposed to charcoal. In 1777, the Abbe F. Fontana described the experiment in which glowing charcoal is plunged under mercury and is allowed to rise into an inverted tube containing gas, which results in the disappearance of all or the greater part of the gas.

Sorption was also investigated by Priestly, de Morveau, Morozzo and Faraday. Faraday believed that it was a surface phenomenon due to the attractive forces exerted by the substances used, especially the solids. This conception of the superficial action of matter was replaced by the hypothesis of capillary condensation which explained adsorption in terms of liquid condensed in pores of the solid due to the lowering of the vapour pressure caused by surface tension effects. If this conception is true, then it would be impossible to obtain adsorption at plane surfaces such as are afforded by mica, nor would gases be adsorbed at temperatures higher than the critical temperatures. In spite of the many arguments against the hypothesis of porosity, it still persists in certain quarters.

De Saussure and Joulin believed that adsorption took place in thick, compressed layers due to long range attractive forces which extended from the surface of the solid with progressively falling potential. This hypothesis is known to-day as the Polanyi or compressed film hypothesis. De Saussure and Joulin

noticed, also, that they were dealing with true equilibria in the adsorption of gases by solids. Thermodynamic points of view could, therefore, be applied, since we have purely reversible changes of pressure in a two-phase system.

In 1915, Langmuir proposed the hypothesis of the unimolecular adsorption layer, which will be described in detail later. Both the compressed film hypothesis and the unimolecular layer hypothesis still have their adherents, although the kinetics provided by Langmuir and based on his hypothesis may be said to have gained universal acceptance.

2. The Classical Sorption Isotherm.

The Classical sorption isotherm is generally known, although erroneously so¹, as the Freundlich exponential isotherm. It was the first attempt to obtain a proportionality between the pressure of the gas or the concentration of the solution and the concentration of the solid. Thus if x grams of a substance are sorbed by m grams of a solid, the proportionality would be represented by $x/m = kp$ or kc , where p represents the pressure of the gas and c represents the concentration of the solution. If association had to be taken into account, p and c could be raised to some integral power.

It was found, however, that the experimental facts corresponded to a modified formula which may be written as follows,

$$x/m = kp^{1/n}$$

$$\text{or, } x/m = kc^{1/n}$$

where $1/n$, instead of being an integer, is an irrational fraction varying with circumstances from 1 to $1/10$.

This isotherm gives a good description of the approximate quantitative behaviour of sorption.

3. The Langmuir Formula.

The classical equation may be applied over a limited range of pressure for which a value of n may be found which adequately expresses the experimental observations. Over a large pressure range no such value of n can be obtained, and the equation derived by Langmuir for a uniform surface on the basis of his concept of unimolecular adsorption may be substituted. This equation is expressed as follows,

$$\frac{x}{m} = \frac{kbp}{1 + bp}$$

where k' and b are constants, and the other symbols have the significance given above. The Langmuir equation is a much more exact formulation of the sorption of gases by solids than the classical isotherm.

4. Reversible Equilibrium.

In every case of sorption investigated, the results observed represent true reversible equilibrium. This may be inferred from the fact that only a few seconds are required for the greater part of any gas to be taken up. The best way of proving this point, however, is to approach the equilibrium from both sides, that of supersaturation and of undersaturation. Joulin found that in both cases the same condition is attained.

5. Time.

Although an initial equilibrium is attained in the first

few seconds, it is found that further amounts of gas are taken up over long periods of time. McBain has carried out experiments with carbon and solutions of iodine which lasted for as long as eleven years, during which time the amount of sorption was doubled without any evidence of chemical reaction having taken place. This slow process is probably due to diffusion, absorption or solid solution. In certain cases, it may also be attributed to activated adsorption as will be shown later.

6. Temperature.

Temperature may change the type of adsorption observed. Dewar² found that oxygen adsorbed by charcoal at -185° , may be largely removed from the charcoal by evacuation. Calvert found that between 0° and 150° , the oxygen sorbed on charcoal is not readily recovered. At higher temperatures, very little oxygen is recovered as such on evacuation. The gas which is removed is found to be largely a mixture of carbon monoxide and carbon dioxide.

II. Types of Sorption and Related Phenomena.

1. Introduction.

McBain³ was the first to show that gases may be taken up by solids in many ways other than by causing them to adhere to the outer surface. In order to include all the processes by which a gas may be held by a solid, he introduced the general term "sorption". It is now generally conceded that there are three types of sorption, viz., physical adsorption, activated adsorption or chemisorption, and diffusion or solution.

2. Physical Adsorption.

Physical adsorption is usually attributed to the van der

Waals' forces. It takes place at low temperatures and is accompanied by small heats of adsorption. Benton found that hydrogen was physically adsorbed by iron, which was prepared by reduction of fused ferro-ferric oxide with hydrogen at 425-450°, at -195 and -183°; and the heat of adsorption was calculated to be about 1600 cal.⁴ Physical adsorption of carbon monoxide by iron prepared by the same method was found to take place at -183°⁵. For the permanent gases adsorbed on mica between -180 and -80°C., the heats of adsorption range between 500 and 2000 calories per mol. Benton and White⁶ showed that physical adsorption took place below -200°C. when hydrogen was adsorbed by nickel. Above this temperature physical and activated adsorption took place simultaneously.

The gases which are held by the van der Waals' forces are not strongly bound by the solid, and may usually be recovered by evacuation without heating.⁵ Dewar² recovered most of the oxygen adsorbed by charcoal at -185° by means of evacuation. Lowery and Hulett⁷ showed that only 50% of the oxygen adsorbed by charcoal at room temperature could be recovered as oxygen by evacuation. This seems to indicate that at least two types of sorption had taken place at that temperature.

In 1928, Lennard-Jones and Dent showed that the attraction of a crystal of potassium chloride on an argon atom outside it due to the van der Waals' forces was sufficient to give a heat of adsorption of the order of 2000 calories per gram atom. Experimental determinations of the heat of adsorption of an inert gas such as argon on a crystal of the potassium chloride

type can only be made with great difficulty, because of the small surface area presented by such a crystal per unit mass. Lennard-Jones⁸, therefore, calculated the heats of adsorption for systems which could be experimentally determined. The calculations for nitrogen on copper gave a result of about 2500 calories per gram mol, and that for hydrogen on copper a result of 1300 calories per gram mol. These calculated results agreed very closely with the experimental results obtained by Benton who found that the heat of adsorption of nitrogen on copper, prepared by the reduction of the oxide with hydrogen, mainly at 115° and finally at 140°, was in the neighbourhood of 4000-2000 calories, and that the heat of adsorption of hydrogen on copper prepared in the same manner was about 1000 calories at -195 to -183°.

The temperature range over which physical adsorption occurs alone varies for different systems of metal and gas. Benton⁶ showed that in the case of nitrogen on iron, physical adsorption is the only process involved from -191.5° to 0°C. In the case of carbon monoxide on iron, physical adsorption was found to take place from -183° to -78.5°C. At -78.5° a rapid adsorption took place followed by a slow process. Although the rapid process is undoubtedly physical adsorption, Benton does not explain the nature of the slow process that follows. The writer is of the opinion that the slow process is one of activated adsorption. This view is adopted after a survey of the following facts. The process of activated adsorption is relatively slow. Indeed, the slowness with which equilibrium

is reached has led Ward⁹ to believe that activated adsorption is non-existent and is being mistaken for diffusion. Moreover, certain types of activated adsorption are known to take place at relatively low temperatures, and are associated with comparatively low-binding energies. Maxted and Hassid¹⁰ have shown that in the case of adsorption of hydrogen by nickel, only primary adsorption takes place from -190 to -79°C . At -79° , 3.10 c.c. of hydrogen are adsorbed by 7 grams of nickel due to physical adsorption, and 0.24 c.c. is adsorbed by means of a secondary adsorption. The curve obtained by Maxted and Hassid is shown in Fig. 1. This amount is too great to be due to solution. Extrapolating the data of Sieverts for the solution of hydrogen in nickel, it is found that about 0.1 c.c. of hydrogen is dissolved in 100 grams of nickel at -79°C . and 760 mm. The amount of hydrogen adsorbed by 100 grams of nickel due to the secondary process observed by Maxted and Hassid is about 3.4 c.c.

Another case of overlapping of physical and activated adsorption at low temperatures was observed in the adsorption of hydrogen by iron. Benton⁵ found that physical adsorption and chemisorption took place simultaneously at -78.5°C .

3. Activated Adsorption.

Benton and White⁶ found that hydrogen was strongly adsorbed by nickel at very low temperatures of the order of -200°C . On raising the temperature, the adsorption diminished to a minimum at about -180°C ., then it rose to a maximum at -100°C .; and after that, it fell off steadily with further rise in temperature. The same results were obtained by Taylor

and Williamson¹¹ and Taylor and McKinney¹². The heats of adsorption at the higher temperatures were considerably greater than those observed at the extremely low temperatures.

The second type of adsorption, the exact nature of which is not yet known, was called activated adsorption by H. S. Taylor¹³ and chemisorption by Benton and White⁴. They suggest that the nickel surface at the higher temperatures is covered by activated hydrogen, which is probably in the atomic state, and is held by chemical forces.

The binding energies involved in activated adsorption are about ten times as large as those involved in physical adsorption. Beebe and Taylor¹⁴ found that the heat of adsorption of hydrogen on nickel at high temperatures was 20,000 calories. G. B. Taylor, Kistiakowsky and Perry¹⁵ found that the heat of sorption of hydrogen on platinum black was between 21,000 and 55,000 calories, depending on the type of platinum black used; and the heat of sorption of oxygen on platinum black was between 60,000 and 83,000 calories. The heat of adsorption of hydrogen on manganous oxide due to the van der Waal's forces was computed to be 1.9 Kg. Cals. by H. S. Taylor and A. Sherman¹⁶. From 0°C. upward, the energy of activation for the same system was found to be 19 Kg. Cals. They also found that the activation energy of hydrogen on alumina was 25,000 cals.

The amounts of gas adsorbed by means of activated adsorption are greater than those adsorbed in physical adsorption. Benton⁵ found that about 4.0 c.c. of carbon dioxide were adsorbed by copper at 200°K. and 300 mm. due to physical adsorption and that about 15 c.c. of the gas were adsorbed by copper at the same temperature and pressure due to activated

adsorption. He also found that in the case of hydrogen on copper, about 0.4 c.c. of hydrogen was adsorbed at 190°K. and 500 mm. due to physical adsorption, and about 8.7 c.c. were adsorbed by means of chemisorption at the same temperature and pressure. The maximum quantity of hydrogen adsorbed by copper due to physical adsorption was 5 c.c., and this amount was adsorbed at 60°K. and 500 mm. The maximum quantity of hydrogen adsorbed due to activated adsorption was 8.7 c.c. at about 190°K. and 500 mm.

4. Solution.

It has already been mentioned that Ward and others do not believe in the existence of activated adsorption, and they are convinced that it is being mistaken for solution of the gas into the solid. That a gas may be soluble in a metal was shown by Sieverts¹⁷, who also observed that the rate of solution increases with a rise in temperature. According to Ward¹⁸, therefore, it could be expected that diffusion of the gas into the solid would be a disturbing factor in adsorption experiments. At low temperatures, where the rate of diffusion is negligible, instantaneous adsorption only would be observed; and, with increase in temperature, slow solution would take place simultaneously with the adsorption, and equilibrium would be approached very slowly. At sufficiently high temperatures adsorption would have decreased and the rate of diffusion would become sufficiently fast to make solution the chief factor.

Steacie¹⁹ lends support to Ward's hypothesis. He shows that in most cases quoted by Taylor in support of the activated adsorption theory, the experimental data can be explained by the known solubilities of the gases and solids considered. That this is not the case in the adsorption of hydrogen by nickel has already been shown by the writer by means of a comparison of the data obtained by Maxted and Hassid with that of Sieverts.

A gas may diffuse into a solid in two ways,

- (a) through the lattice of the solid,
- (b) along grain boundaries.

In the first case, the atoms of the solid must be sufficiently far apart to allow the atoms or molecules of the gas to pass between. As the temperature is increased, the amplitude of the vibration of the atoms of the solid becomes greater. A point will be reached eventually when these atoms are displaced from each other to an extent great enough to permit the gas to pass through. This type of solution may be expected to become measurable at some critical temperature, and to increase in velocity on further heating.

The distance between the atoms is greater at the Smekal cracks, and planes of weakness. For this reason, spatial considerations alone are not so important in the case of diffusion along grain boundaries. Such diffusion should, therefore, become apparent at lower temperatures, and energy of activation will be necessary for the lateral diffusion along the surface.

In the cases where gas diffuses along the internal surface of fissures in the metal, the gas atoms or molecules are, strictly speaking, on the surface. A distinction between the two types of surfaces must be drawn. Firstly, there is the type of surface mentioned above; and secondly, the surface which is exposed to the bombardment of the gas phase. The term "adsorption" is limited to the second type of surface.

Ward¹⁸, in a quantitative study of solution, has shown that (1) for a given temperature and pressure, the amount of gas absorbed is proportional to the square root of the time, (2) for a given temperature, the amount absorbed divided by the square root of the time is proportional to the concentration on the outer surface, and (3) the process of adsorption depends on temperature according to an exponential factor $e^{-E/kT}$, where E is a constant, viz., an activation energy.

5. Mobility of Adsorbed Molecules.

Volmer and Estermann²⁰ allowed mercury at -10°C . to vaporize across an evacuated space to a glass surface which was kept at -63°C . They found that minute crystals of mercury formed on the glass surface. These crystals were flat and their thickness was not over $1/10,000$ part of their width. The flat portion of the crystal did not grow as fast as it received the mercury atoms. The sides, however, were found to grow a thousand times faster than the number of mercury atoms reaching them directly from the vapour would warrant.

Hence, Volmer and Estermann concluded that the mercury atoms which arrived at the flat surface travelled along that surface and fed the rapidly growing sides. Thus it may be seen

that atoms or molecules striking a crystal of the same material may move about on the surface until they evaporate again or are built into the space lattice.

In another experiment by Volmer and Adhikari²¹, it was shown that crystals of benzophenone arising in a drop of the liquid could grow through the surface to an extent of about 0.1 mm. The material for the growth of that part of crystal above the liquid is supplied by the movement of the adsorbed molecules of benzophenone along the surface of the crystal. Volmer²² suggests the following as an explanation of the mechanism of the spreading of adsorbed molecules over a solid surface. The adsorbed molecules, at low temperatures, are mostly rigidly fixed to atoms of the solid, and are not mobile. They oscillate only around their equilibrium positions. On raising the temperature, however, the amplitude of the oscillations is increased; and more and more often an adsorbed molecule, because of an occasional elongation will jump into the unoccupied field of an adjacent atom. The process requires a definite energy of activation, and its velocity will increase as the temperature rises in accordance with an exponential law.

The energy of activation for this process has been calculated by E. K. Rideal²³ for the oxidation of copper. The value obtained was 12,400 calories per gram mol.

6. Discontinuities in Adsorption Processes.

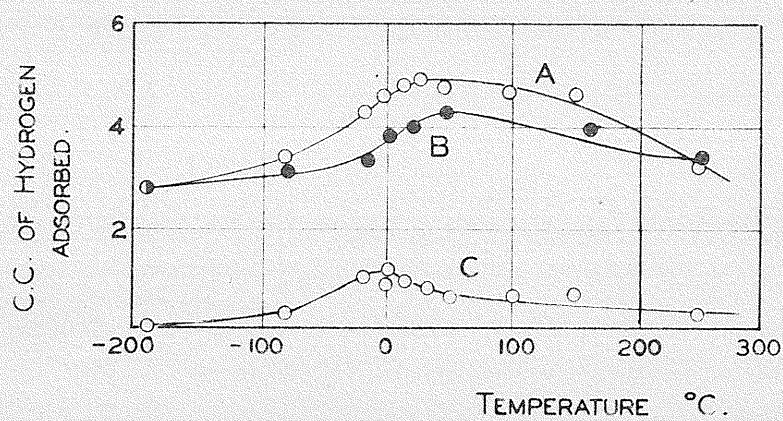
Allmand and Chaplin²⁴ first noticed discontinuities in the isosteres of all carbon tetrachloride - charcoal systems determined over temperature ranges between 0 and 90°C., whenever the carbon tetrachloride pressure exceeded 0.1 mm.,

the heat of adsorption, constant up to that pressure, underwent a sudden decrease. In 1931, Allmand and Burrage²⁵ obtained discontinuous isotherms for the adsorption of the vapours of carbon tetrachloride, benzene, water, carbon bisulphide, and carbon dioxide on various types of charcoal. In two cases, the broken isothermals for carbon tetrachloride were found to be reversible.

Benton and White⁴ observed that the adsorption of hydrogen by nickel at low temperatures increased with pressure in a discontinuous manner. They also obtained discontinuities for the adsorption of hydrogen by copper at -183 and $-195^{\circ}\text{C}.$, hydrogen by iron at these same temperatures, and nitrogen by iron at $-78.5^{\circ}\text{C}.$ Isotherms for Hydrogen on Iron are given in Fig. 2.

These discontinuities can only be ascribed to a large number of particles taking up a small quantity of gas abruptly and nearly simultaneously. The possibility that the steps represent the successive formation of complete layers over the surface of the sorbing material can be eliminated since Benton and White show that nearly a dozen steps occur without covering the sorbing surface with a unimolecular layer.

To explain the discontinuities, Benton⁴ proposed the hypothesis of concentric rows. He believes that the surface of metallic adsorbents are composed of plane crystal faces, and that all the faces of given indices are alike in properties, but may be different in size. For a given face, a step in the isotherm represents the nearly simultaneous completion on all such faces, of a row of adsorbed molecules parallel to the edge. The first row is believed to be at the edges themselves;



A - TOTAL ADSORPTION: B - PRIMARY ADSORPTION:
C - SECONDARY ADSORPTION.

FIG. 1. THE KINETICS OF THE ADSORPTION OF HYDROGEN ON NICKEL.

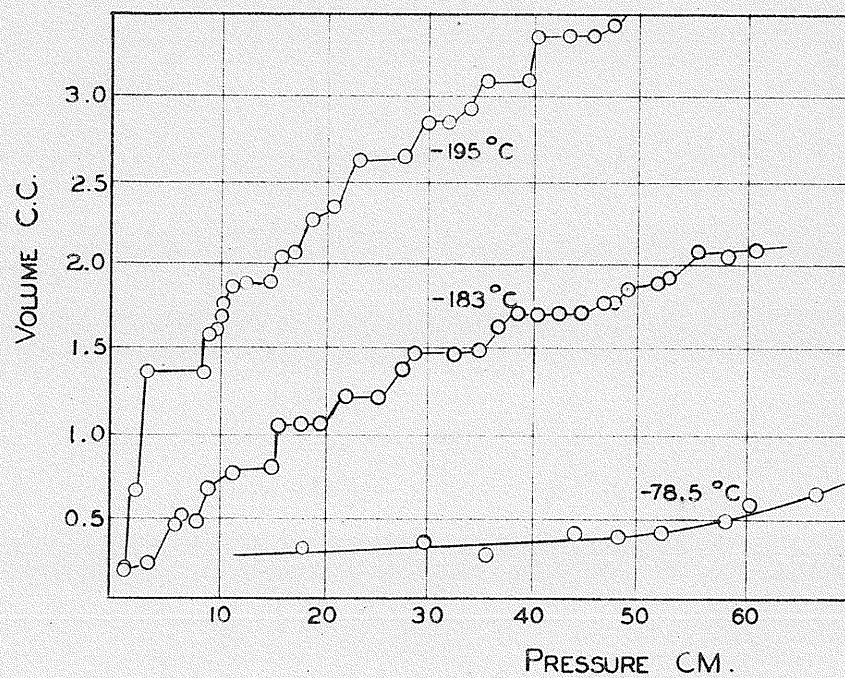


FIG. 2. ISOTHERMS FOR HYDROGEN ON IRON.

thereafter, additional rows form inside and adjacent to one another, until at last the rows reach the centre and the face becomes completely covered.

A similar hypothesis was formulated by Allmand, Burrage, and Chaplin.²⁶ They thought that the adsorption on charcoal started out from active centres, from which "islands" of sorbate spread out. An "island" consists of a series of concentric rings. The completion of a ring and the start of a new one is marked by a break in the curve. The spatial arrangement of the rings in relation to the active centres is variable. The rings are closer in at high temperatures and with low-boiling sorbates than at low temperatures or with high-boiling sorbates.

7. Heats of Sorption.

1. Comparison of Heats of Sorption with Latent Heats of Vaporization.

Some mention has already been made to heats of sorption in the discussion of physical and activated adsorption. It may be of interest to extend the data already given in order to include a comparison of the heats of sorption with heats of vaporization. McBain²⁷ gives table 1, the values recorded being obtained by Dewar for the heat of sorption by charcoal at -185°C .

Table 1.

Comparison of Heats of Sorption, q , of Gases by
Charcoal and their Latent Heats of Vaporization, p .

Gas	q (cals.)	p (cals.)
Helium	3,000	24

Gas.	q (cals.)	p (cals.)
Hydrogen	1,600	238
Nitrogen	3,684	1,372
Oxygen	3,744	1,664
Argon	3,636	1,500
Carbon monoxide.....	3,416	1,400
Electrolytic gas	2,414	-
Carbon monoxide and oxygen	3,960	-
Carbon dioxide at -78°	6,100	3,000

It is seen from the above that in each case the heat of sorption is considerably greater than the heat of vaporization. It is of interest to note, also, that the values for nitrogen, oxygen and argon bear no essential difference. This is of some significance when we consider that oxygen at low temperatures, nitrogen and argon are adsorbed by charcoal in approximately equal amounts.²⁸ It clearly shows a relationship between the heats of adsorption and the amounts adsorbed.

Lamb and Coolidge²⁹ obtained the results given in table 2. They used a steam activated coconut charcoal at 0°C . with the vapours of organic liquids. Q and p have the same significance given above.

Table 2.

Vapour	q (cals.)	p (cals.)
Ethyl chloride	12,000	6,220
Carbon bisulphide ...	12,500	6,830
Methyl alcohol	13,100	9,330
Ethyl bromide	13,900	6,850
Ethyl iodide	14,000	7,810

Vapour	q (cals.)	p (cals.)
Chloroform	14,500	8,000
Ethyl formate	14,500	8,380
Benzene	14,700	7,810
Ethyl alcohol	15,000	10,650
Carbon tetrachloride .	15,300	8,000
Ethyl ether	15,500	6,900

Lamb and Coolidge call the excess of heat of sorption over the latent heat of vaporization divided by the molecular volume of the corresponding free liquid at 0°C . the net heat of sorption per c.c. of liquid sorbed. They find that it is identical for the eleven liquids studied. They write, "This is a very illuminating fact. It indicates that the heat of adsorption is indeed due to attractive forces of the charcoal upon the liquid, and that for a given volume of liquid, that is, for a given volume of filled capillary space, the heat liberated is identical or nearly so for all the liquids studied."

ii. Experimental Methods of Studying Heats of Sorption.

Dewar²⁹ used a liquid air calorimeter at -185°C ., the heat evolved on the introduction of the gas to the charcoal being measured by the amount of liquid air evaporated from an insulated container surrounding the charcoal.

Lamb and Coolidge³⁰ used an ice calorimeter in their work on the adsorption of vapours of organic liquids by charcoal. Garner³¹ used a thermocouple which he placed in the middle of the charcoal and calculated the heats of sorption by the

rise in temperature of the sorbing material.

iii. Equations Used to Calculate the Heats of Sorption.

The formula used by Taylor and Williamson¹¹ is as follows:-

$$\log \frac{t_2}{t_1} = \frac{Q}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where t_1 and t_2 are the times taken for the same volume of gas to be adsorbed at temperatures T_1 and T_2 respectively.

Q is the heat of sorption, and R is the gas constant.

E. Hückel³² gives a formula which is as follows:-

$$q = RT^2 \left(\frac{\partial \log p}{\partial T} \right)_a - RT$$

q is the differential heat of adsorption measured at a constant volume, and $\left(\frac{\partial \log p}{\partial T} \right)_a$ is the temperature coefficient of the

logarithm of the equilibrium pressure under isosteric conditions.

In 1934, H. S. Taylor and G. Ogden³⁴ used the following formula:-

$$\log p_1 - \log p_2 = \frac{\lambda}{4.58} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

λ is the heat of adsorption. p_1 and p_2 are the equilibrium pressures for a given adsorption at T_1 and T_2 .

8. The Thickness of Adsorbed Films.

There are three points of view with regard to the thickness of the adsorbed layer. Chiefly through the influence of Langmuir, it is widely held that all sorbed molecules are in contact with the molecules or atoms of the solid. Langmuir himself maintains that under highly favourable conditions such as an environment of nearly saturated vapour, a second layer may be captured by the first and a third by the second

and so on with progressively weakening force. Such built-up polymolecular layers differ in principle from the third conception, that of the older physics, that all the molecules coming within a certain range of the solid are directly attracted, thus constituting a region of direct sorption whose thickness is very many times greater than a molecular diameter and which is not necessarily close packed with sorbed material.

Much experimental work has been done to distinguish between the third or classical hypothesis and the first or monomolecular conception. In this type of work it is necessary, first, to measure the actual amount of sorption, next to ascertain the real area of the surface involved, and finally to distinguish a thick, directly attracted film from a built-up structure of many layers.

Although it is found that sorption by glass usually corresponds at most to a monomolecular layer, Rinse³⁵ obtained a film about 667 molecules thick or $1,400 \text{ \AA}$ in his experiment on the sorption of mercuric iodide on high melting Jena combustion glass blown through a tube containing phosphorus pentoxide and heated in a stream of dry oxygen till the glass softened. Langmuir's experiments with mica³⁶ gave less than enough for one complete monomolecular layer, using gases at very low pressures and vapours at somewhat higher relative pressures. His experiments with platinum and his study of electronic emission from thoriated tungsten also indicate that the films are monomolecular or less.³⁷

It is evident that unless the area of the solid is accurately known, the thickness of the adsorbed film cannot be correctly determined. It is doubtful that microscopic methods are sufficiently exact since they do not take into account the network of cracks that crystals spontaneously develop owing to

19.
contraction due to unbalanced forces at the surface. These cracks, spaced about 100 atoms apart, will appreciably increase the area available for the sorption of small molecules.

Two methods for determining the true surface area of solids are described by McBain³⁸. In experiments with finely divided lead sulphate, thorium B was employed as a "radioactive indicator." During adsorption the isotope replaces some of the lead atoms on the surface of the lead sulphate, these lead atoms entering the solution until the ratio of the quantity on the surface to that in the solution is the same for the lead atoms and for its isotope. Reversible equilibrium establishes itself so quickly that it is safe to assume that the rearrangement is limited to the exposed atoms on the surface of the crystal, although it would include cracks and crevices. The distribution of the isotope is found by means of an electroscope, and the quantity of lead in solution is determined analytically. Hence the exposed surface of the lead sulphate becomes known. For lead sulphate it was found to be twice that estimated from microscopic observation.

The second method which may be employed in the determination of area is known as the method of electrolytic polarization.

A metal is made the cathode in a dilute acid and the quantity of electricity, ΔQ , which must pass across the interface to cause a given change in the electrode potential is measured. This quantity is found to be independent of the chemical nature of the metal employed; and, therefore, appears to measure the accessible area of the metal.

Table 3 gives the ratio between the true surface and the apparent surface as found by the method of electrolytic polarization. The true surface is here defined as the surface

20.

available to hydrogen atoms. If a much larger or much smaller object than the hydrogen atom was used, the value for the area would change.

Table 3.

The Ratio between True Surface and the Apparent Surface as found by the Method of Electrolytic Polarization.

Surface	Ratio
Platinum, bright foil	2.2
Platinum, bright foil, cleaned in acid and heated in a flame	3.3
Platinum, platinized	1,830
Nickel, polished, new	75
Nickel, polished, old	9.7
Nickel, activated by alternate oxidation and reduction, new	46
Nickel, activated by alternate oxidation and reduction, old	29
Silver, freshly etched with dilute nitric acid..	51
Silver, etched with dilute nitric acid, after twenty hours	37
Silver, finely sandpapered	16

Elaborate apparatus was required to obtain the results listed in table 3, since the quantities of electricity and the time involved in measurement are both exceedingly small. It consisted essentially of an Einthoven string galvanometer with a moving film camera to photograph its indications. The total quantity of electricity required to change the hydrogen electrode potential on platinum to an oxygen potential is equal to that necessary to remove one hydrogen atom from each atom of platinum on the accessible surface and replace it by an

oxygen atom.

III. Sorption of Gases by Metals.

In order to have a basis of comparison, the writer believes it advisable to include a short survey of the work which has been done on the well-known sorbing agents, platinum and palladium; and, also, a review of the results obtained in the adsorption of nitrogen by metals.

1. Sorption of Gases by Platinum.

Langmuir³⁹ used platinum surfaces which were made catalytically active by contact with a mixture of oxygen and hydrogen at 300°C. and then evacuated at 350°C. He then admitted small amounts of oxygen, and found that the oxygen disappeared almost instantly until the quantity adsorbed corresponded to a monomolecular film. No further quantity of oxygen was then adsorbed, even when the pressure was greatly increased. The oxygen was very rigidly held as is evidenced by the fact that evacuating at 360°C. produced no trace of oxygen, and treatment with hydrogen or chlorine was needed to remove the sorbed gas.

Platinum black differs from platinum in having an exceedingly large surface. Mond, Ramsay and Shields⁴⁰ carried out experiments with this substance. They found that at room temperature approximately equal volumes of hydrogen, oxygen, carbon monoxide and sulphur dioxide were sorbed by the platinum black.

Benton⁴¹ found that platinum black sorbed equal volumes of hydrogen and carbon monoxide at 25°C. The amount of oxygen sorbed by the platinum black was more than half as great as

the amount of hydrogen sorbed. He could not remove the oxygen by evacuation and heating to 110°C . One volume of the platinum black was found to sorb 36.7 volumes of hydrogen and 37.8 volumes of carbon monoxide at 25°C . and 760 mm.

D. O. Shiels⁴² found that one volume of platinum black sorbed 84 volumes of sulphur dioxide at 25°C . Only 30 volumes of the gas was removed by heating for eight and a half hours at 250°C .

2. Sorption of Gases by Palladium.

Holt, Edgar and Firth⁴³ worked with a fresh piece of palladium foil. They found that the foil did not sorb any hydrogen until it was activated by heating in air followed by reduction or by heating in a vacuum or in an atmosphere of hydrogen when it took up 712 to 969 volumes of the gas.

In the form of black, palladium was found to take up 778 to 817 volumes of hydrogen.⁴⁴ Paal and Gerum⁴⁵ found that palladium in colloid solution took up 926 to 2,952 volumes of hydrogen.

The isotherms for the sorption of hydrogen by palladium at 0° , 30° , 80° , 160° , and 180°C . show three well-defined portions. The first portion shows a rapid increase in pressure with a relatively small volume of hydrogen sorbed. The second part shows a large volume of gas sorbed with no apparent change in pressure. The third portion has a slope very much similar to the first.⁴⁶

3. Sorption of Nitrogen by Metals.

Benton⁵ found that about 8 c.c. of nitrogen were adsorbed by 54.6 grams of iron at -183°C . and 200 mm. The sample of iron used was prepared by the reduction of fused ferro-ferrie oxide with hydrogen at 425 to 450°C . At -78.5°C . and 200 mm., about

0.8 c.c. of the gas was adsorbed. Benton also found that 51.51 grams of copper, prepared by the reduction of the oxide with hydrogen at 115 to 140°C., adsorbed about 28 c.c. at -183°C. and 200 mm. The isotherms obtained by him for the adsorption of nitrogen by copper and iron are reproduced in figures 3 and 4. Curve 1a in figure 4 is a plot on a reduced scale of the complete isotherm at -183°C., the first part of which is given by Curve 3. In these figures points designated by ordinary circles were obtained by proceeding from lower to higher pressures; black circles indicate the reverse order of procedure.

Sieverts⁴⁷ found that nitrogen is not sorbed by silver, cadmium, thallium, lead, bismuth, tin, antimony, gold, zinc, rhodium or nickel. Taylor and Russell⁴⁸ found that nitrogen was not measurably sorbed by nickel.

G. Valenski⁵⁴ studied the action of nitrogen on manganese and chromium. The metals were prepared by a variety of methods, and his results showed that the amount of absorption depends to a large extent on the origin of the metal. He used manganese and chromium samples prepared by the thermite process, the Moissan method, and pyrophoric manganese and chromium. Working at temperatures of about 300°C. to 1300°C., he found that the manganese samples started to absorb nitrogen at 460°C., while the thermite chromium started to absorb at 580°C. and the Moissan chromium at 710°C.

He obtained nitrides of the metals. The amount of nitrogen absorbed by the manganese agrees best with the formula Mn_3N_2 while for the chromium the formation of the compound CrN is the

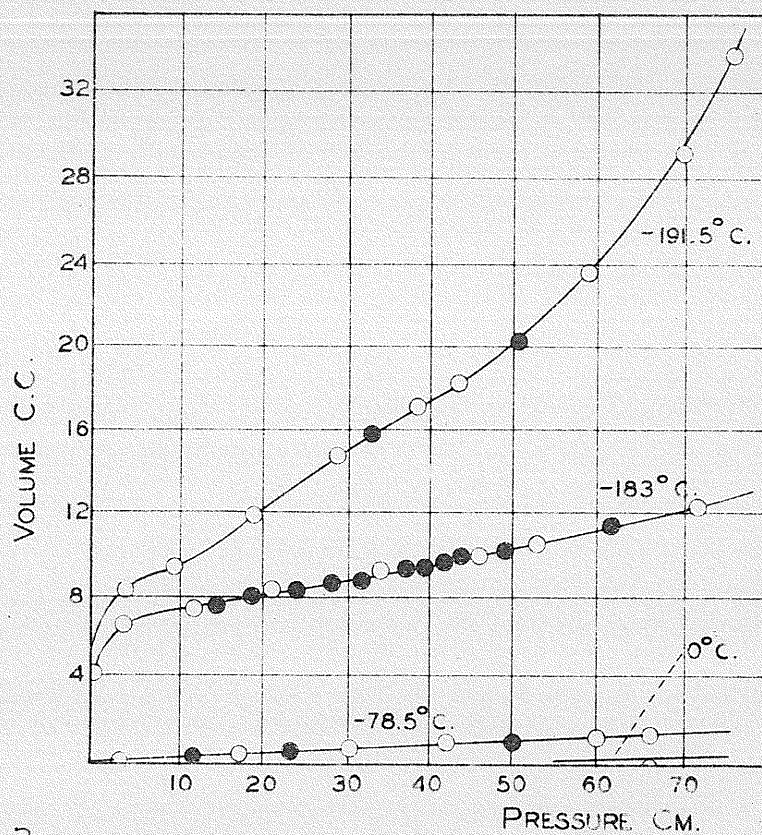


FIG. 3.
ISOTHERMS FOR NITROGEN ON IRON.

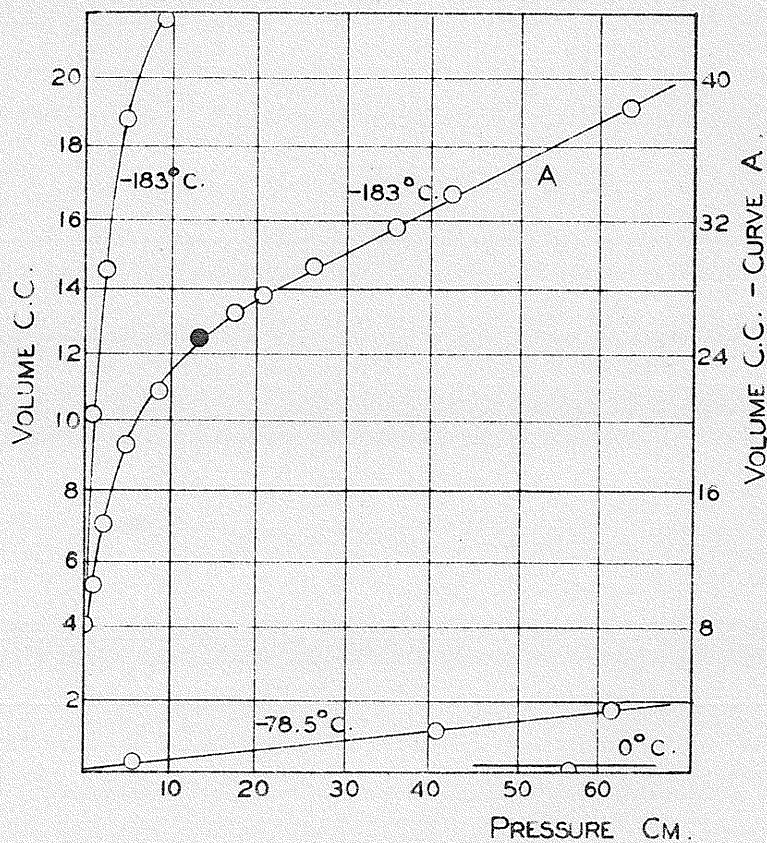


FIG. 4.
ISOTHERMS FOR NITROGEN ON COPPER.

most probable. Valenski found that at 390°C ., 15.4 grams of nitrogen attached itself to 100 grams of manganese. This amount decreases with rise in temperature; and, at 1050° only 6 grams of nitrogen are held by the same weight of the metal.

In the case of chromium, the quantity of nitrogen absorbed between 500° and 870°C . is fixed at 29% of the weight of the metal. Between 930 and 970° , it decreases slowly to 27% which exactly corresponds to the formula CrN . Between 1030 and 1200° , it decreases very rapidly to 12.6%.

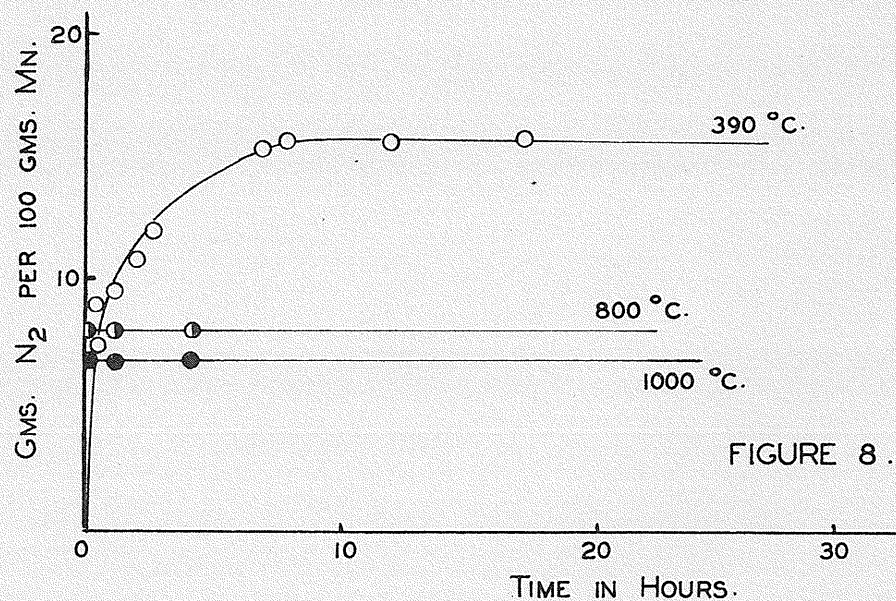
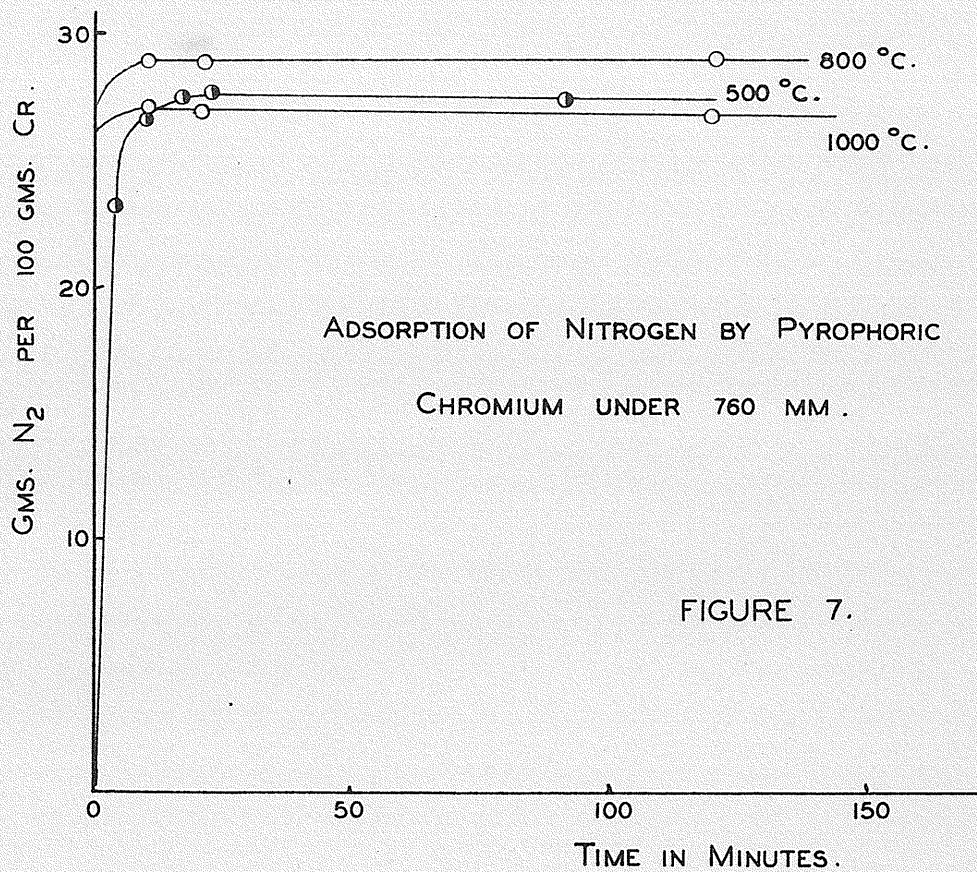
Valenski's results are given by the curves in figures 5, 6, 7, 8, 9 and 10.

IV. Hypotheses and Theory of Sorption.

1. Capillary Condensation⁴⁹.

Since porous bodies generally sorb great amounts of gases and vapours, an attempt was made to relate sorption to the behaviour in capillary tubes. This was done by Zsigmondy in 1911 for silicic acid jellies. He showed that such jellies consist of ultramicroscopic particles in loose contact with a great number of irregular spaces between. Zsigmondy considered that each particle was covered with an adsorbed layer of water molecules, but that under suitable conditions the water molecules could condense in the pores as liquid water. It is seen, therefore, that he differentiated between adsorbed and capillary condensed liquids. W.A.Patrick, on the other hand, believed that all the material sorbed by a porous body is in the form of a liquid.

The quantitative relation between capillarity and vapour



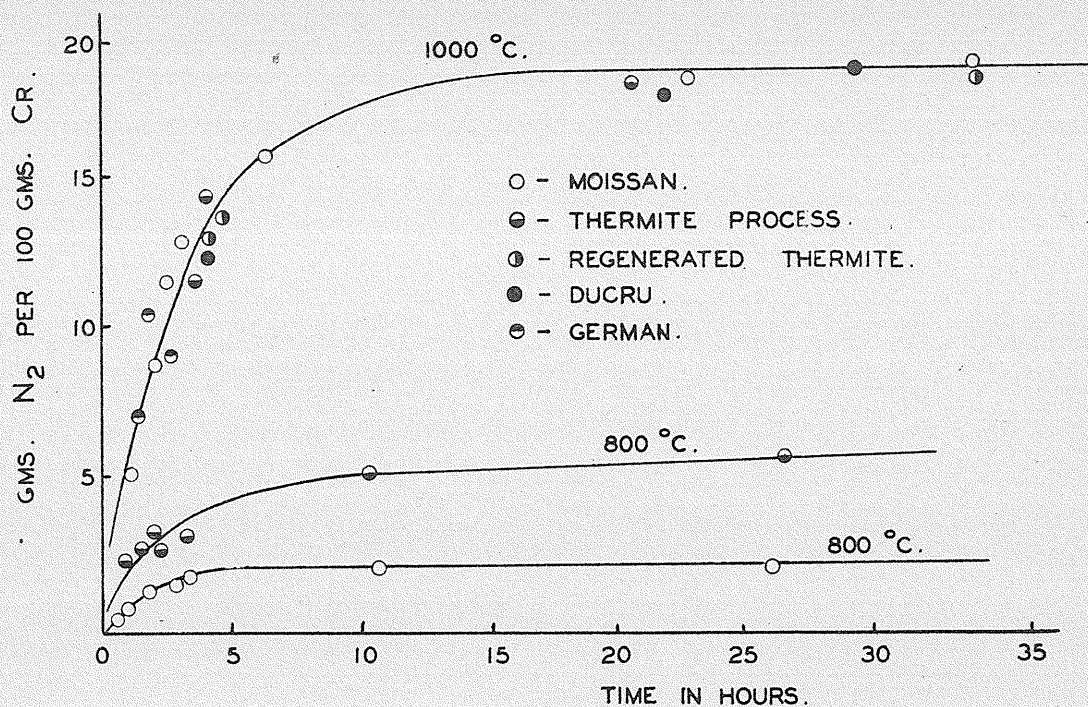


FIGURE 9 .

ADSORPTION OF NITROGEN ON CHROMIUM AT 760 MM. PRESSURE .

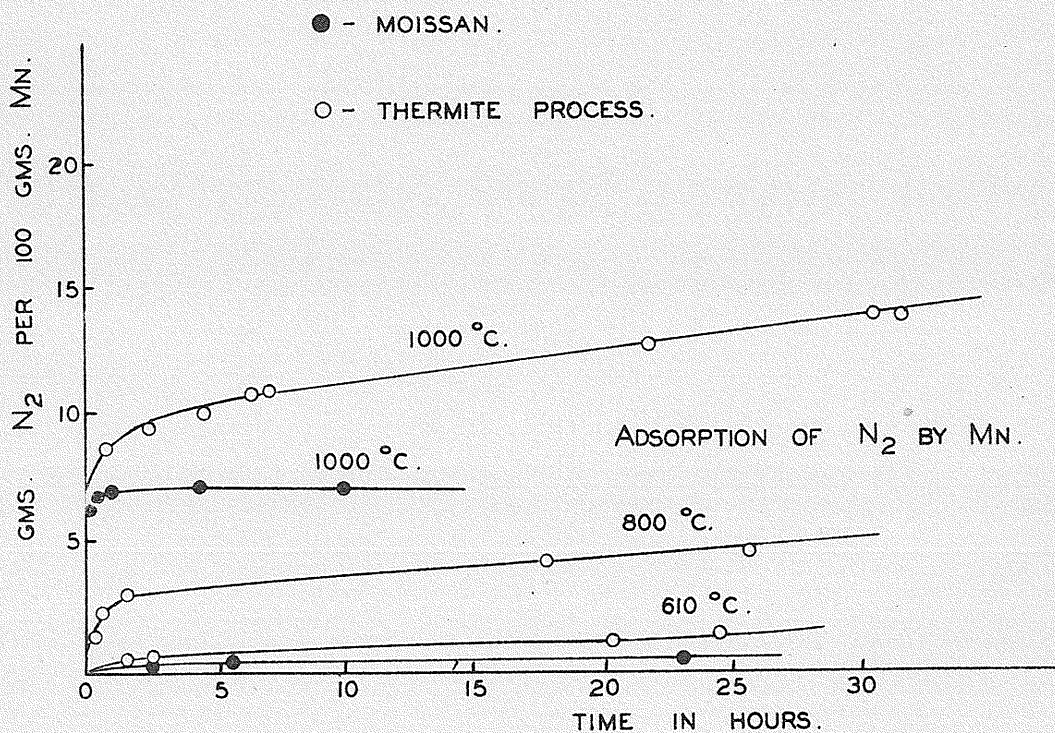


FIGURE 10 .

pressure was given by W. Thomson. Figure 11 shows a liquid which

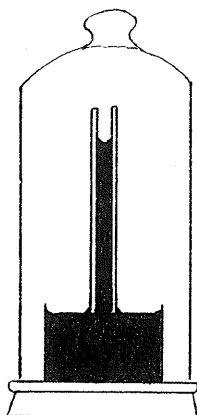


Fig. 11.

has risen in an open capillary tube. The concave meniscus at the top of the capillary tube is in equilibrium with the vapour of appreciably lower pressure than that in equilibrium with the plane surface of the liquid in bulk.

The relation between surface tension and the two vapour pressures is given by the formula:-

$$\ln \frac{p}{p_s} = \frac{-\sigma v}{rRT}$$

where p is the pressure at the concave surface, p_s is the pressure of the saturated vapour of the liquid in bulk at that temperature, σ is the surface energy of 1 gram mol of condensed liquid, r is the radius of the capillary, R the gas constant in ergs, T the absolute temperature, and \ln represents the natural logarithm to the base e . The radius, r , may be calculated from the formula

$$r = \frac{2\sigma}{p d_g} \cdot \ln \frac{p}{p_s}$$

where d_g represents the density of the vapour and d_l represents

the density of the liquid.

For liquids with the surface tension of water, if $p/p_s = 0.5$, the largest radius of the pores holding water is 15 \AA or $15 \times 10^{-8} \text{ cm}$. If $p/p_s = 0.1$, the radius of the largest pore in which water may condense would be about 4.6 \AA . This deduction is meaningless since this radius is down to molecular dimensions.

A corollary to the capillary condensation hypothesis is that the same specimens should sorb the same volume of various liquids independent of their chemical nature. This requirement was satisfied for the original silicic acid jellies used by Zsigmondy. McBain, Lucas and Chapman⁵⁰ found that this was not the case for toluene and acetic acid with charcoal.

Although the capillary condensation hypothesis breaks down in some instances, it cannot be entirely rejected. According to McBain, such condensation does take place when capillaries of suitable dimensions are exposed to nearly saturated vapours of liquids which wet them.

2. The Hypothesis of the Thick Compressed Film.⁴⁹

The hypothesis of the compressed film was proposed by de Saussure in 1814. It assumes long range attractive forces, and postulates the attraction between unlike molecules. By virtue of this attraction towards the solid surface, the gas or vapour is assumed to be under enormous pressure. Mitscherlich calculated this pressure to be at least 34.4 atmospheres. Chappius obtained a value of 6,150 atmospheres. Bunsen found the pressure to be 100 atmospheres. Polanyi found it to be 5,000 atmospheres. Harkins and Ewing deduced a value of 12,000 atmospheres. The pressure on the gas falls off with increasing

distance from the solid. Thus, there is a sorption region extending from the surface of the solid to an outer limit where the attraction between the solid and the vapour or gas is inappreciable.

Polanyi⁵¹ lists the assumptions in this theory of adsorption as follows:

1. The adsorption is independent of temperature.
2. The potential at every point is independent of whether or not the neighbouring space is empty or occupied by a molecule.
3. The molecules which are in the adsorbed state exert approximately the same force on one another as they do when they are free. In other words, the van der Waal's forces, or forces of cohesion, are unaffected by the sorption so that the ordinary equation of state will apply even within the sorbed layer.

McBain points out that the assumptions of Polanyi neglect the molecular constitution of matter, which necessitates localized forces on the surface, centering around the individual molecules of the surface which cannot be regarded as continuous.

3. The Monomolecular Adsorption Theory.

The monomolecular adsorption theory was developed by H. Kayser in 1881. He started from the fact that the solids hold together, proving thereby the existence of cohesive forces. A molecule in the interior of the solid is acted upon by these forces from all sides. Molecules on the surface, however, have one free side, and this side is capable of holding molecules of a liquid or gas, and thus form a monomolecular layer. This layer may hold another layer less firmly or completely, and so on. Sorption of this nature is favoured by pressure, but the

forces operative are opposed by thermal vibrations; and, therefore, the sorption will diminish with rising temperature⁴⁹.

Langmuir further developed this line of thought. He suggests that the time which elapses between the condensation of a molecule and its subsequent evaporation depends upon the intensity of the surface forces; and that adsorption is the direct result of this time lag. If the surface forces are relatively intense, the rate of evaporation of the molecules is negligible, and the surface will become completely covered with a layer of molecules. In the case of true adsorption, this layer will not be more than one molecule deep, because as soon as the surface is covered by a single layer, the surface forces are chemically saturated. On the other hand, where the forces are weak, the evaporation may occur so soon after condensation that only a small fraction of the surface becomes covered by a single layer of adsorbed molecules. In agreement with the chemical nature of these forces, their range has been found to be very small, of the order of 10^{-8} cm. That is, the effective range of the surface forces is usually much less than the diameter of the molecules. The molecules thus usually orient themselves in definite ways in the surface layer since they are held to the surface by forces acting between the surface and the particular atoms or groups of atoms in the adsorbed molecule.⁵²

Molecules striking a surface which is already covered may also condense, but they usually evaporate much more readily than from the first layer. Therefore, except when a vapour is nearly saturated, the amount of material adsorbed on a plane surface rarely exceeds that contained in a layer one atom or molecule thick.⁵³ Langmuir⁵² developed the quantitative formulation of the theory of monomolecular

adsorption which follows.

The rate at which molecules from a gas come into contact with an exposed surface is given by the equation for the rate of effusion of gases through small openings

$$m = p \sqrt{\frac{M}{2 \pi R T}}$$

where m is the number of grams striking the surface per sq. cm. per second, M is the molecular weight, T the absolute temperature, p the pressure in bars, and R the gas constant in ergs. If we let μ represent the number of gram molecules of gas striking each sq. cm. per second then $\mu = m/M$ whence

$$\begin{aligned} \mu &= \frac{p}{M} \sqrt{\frac{M}{2 \pi R T}} = \frac{p}{\sqrt{2 \pi M R T}} \\ &= 43.75 \times 10^{-6} \frac{p}{\sqrt{M T}} \end{aligned}$$

Nearly all these molecules will strike inelastically. The rate at which gas condenses on a bare surface will thus be $\alpha \mu$, where α is close to unity. If θ is the fraction of the surface which is bare, the rate of condensation becomes $\alpha \theta \mu$, because molecules striking an already occupied elementary space will be reflected elastically or will evaporate so quickly that the effect will be the same. Similarly, the rate of evaporation may be set equal to $\nu_1 \theta_1$ for a completely covered surface and $\nu_1 \theta_1$ for the fraction of the surface already covered. For the equilibrium, the rate of evaporation must equal the rate of condensation, $\alpha \theta \mu = \nu_1 \theta_1$

Furthermore, $\theta + \theta_1 = 1$

whence, $\theta_1 = \frac{\alpha \mu}{\nu_1 + \alpha \mu}$

If we set $\alpha/\nu_1 = \sigma_1$ this becomes

$$\theta_1 = \frac{\sigma_1 \mu}{1 + \sigma_1 \mu}$$

If η be the number of gram molecules of gas adsorbed per unit area of surface, then η is given by $N/N_0 \eta = \theta_1 = \frac{\sigma_1 \mu}{1 + \sigma_1 \mu}$ where N_0 is the number of elementary spaces per square centimetre of surface and N is the Avogadro number, 6.06×10^{23} molecules in a gram molecule. Since μ is proportional to the pressure p , the above equation is equivalent to the expression

$$\frac{x}{m} = \frac{k b p}{1 + b p}$$

where k and b are constants. K is proportional to N_0/N , the ratio of the number of molecules adsorbed per square centimetre when the surface is saturated to the Avogadro number. b is proportional to N/N_0 and to $\tau/\sqrt{2\pi M R T}$ where τ is the average life of all the molecules which strike the surface $\propto N_0/N$, or $N_0 \sigma_1/N$. This is distinguished from the quantity σ_1 which represents the average life of all the molecules which condense upon the surface N_0/N .

We get,

$$\eta = \frac{\tau \mu}{1 + \sigma_1 \mu}$$

At sufficiently low pressures, where the denominator approaches unity, $\eta = \tau \mu$ or $x/m = kbp$. At high pressures, where $\sigma_1 \mu$ becomes large in comparison to unity, the amount adsorbed η approaches a saturation value

$$\eta_{\infty} = \frac{\tau}{\sigma_1} = \frac{N_0}{N}$$

where every elementary space is occupied by one adsorbed molecule.

Langmuir's view that the collision of a gaseous molecule with a surface is inelastic, and that adsorption arises from the time lag between condensation and evaporation presupposes that activation is not necessary for this primary adsorption. This, however, does not oppose the viewpoint adopted by H. S.

Taylor, since the adsorbed molecule or atom may act in a variety of ways. It may evaporate, or it may diffuse into the solid, or combine with adjacent adsorbed atoms, or it may combine with other molecules or atoms striking the surface. Some of these processes will have a high temperature coefficient and may, therefore, be interpreted as requiring activation.

- EXPERIMENTAL -

APPARATUS AND MATERIALS.

The apparatus used in this experiment consisted of three flasks, a gold-leaf mercury vapour trap, a McLeod Gauge, an open and closed manometer, a mercury vapour diffusion pump backed by a "Highvac" pump, a purifying train and an electric bell.

The flasks were made of soft glass, as was the rest of the system proper. The diffusion pump was of hard glass. Flask A (figure 12) had a volume of 54.45 c.c. This volume was determined by weighing the flask, first empty and then filled with water, and making suitable corrections for the temperature of the water. Flask B had a volume of 63.17 c.c. This volume was found by the same method used above. Flask C had a volume of 129.77 c.c. The writer, will hereafter refer to these flasks as the manganese flask (flask A), the blank (flask B), and the reservoir (flask C).

The blank and the manganese flasks constituted what may be termed the inner system. These flasks were separated from the rest of the system, or outer system, by means of stop-cocks. The volume of the tubes leading from the stop-cocks to the blank and manganese flasks was found by filling the glass tubing with mercury and then weighing the mercury and making the appropriate corrections. The volume of all narrow glass tubing employed in this apparatus was determined by this method. The volume of the manganese flask to the stop-cock was found to be 57.10 c.c. The volume of the blank to the stop-cock was determined to be 65.36 c.c.

The volume of the outer system, the McLeod Gauge, E,

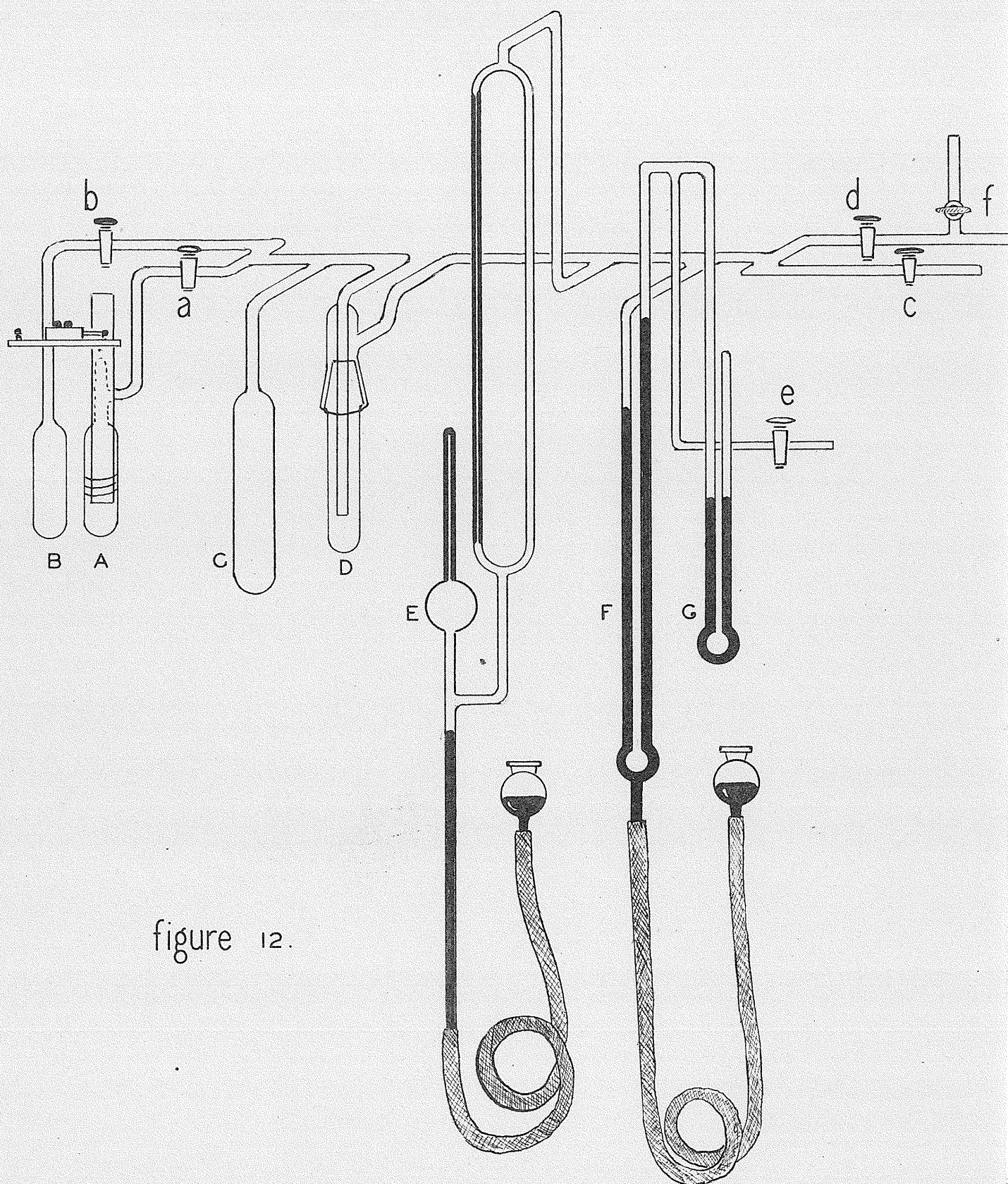


figure 12.

excluded, was found to be 197.8 c.c. The volume of the McLeod Gauge to the cut-off was found to be 121.5 c.c. Therefore, the volume of the outer system with the mercury in the McLeod Gauge at the cut-off was 319.3 c.c.

Gold-Leaf Trap.

The gold-leaf trap, D, was employed to protect the manganese from the mercury vapour present in the system. The trap was constructed in two parts, in order that the volume might first be determined and the gold leaf then introduced. Moreover, building the trap in two parts made the gold leaf easily accessible should it become necessary to replace the old, contaminated leaf by new. The two parts of the trap were joined together by means of a ground glass joint. On the ground surfaces picien cement was spread, and the two portions of the trap were sealed in this manner. This joint was then covered with friction tape, and a layer of picien was applied over the tape. The gold leaves, three in number, were wrapped around the tube extending into the outer jacket.

The McLeod Gauge.

The McLeod Gauge, E, was of the usual moveable reservoir type. It was capable of measuring to 10^{-5} mm. The volume of the McLeod to the cut-off has already been mentioned.

The Manometers.

Two manometers were employed in this experiment. One of these was an open manometer of the type commonly known as the constant-level manometer, F. The other was an ordinary closed manometer, G.

The constant-level manometer consisted of a U-tube, the arms of which were longer than 760 mm.; and a T-tube coming out of the bend of the U-tube. A reservoir was connected to the T-tube by means of pressure tubing. By raising or lowering the mercury reservoir, it was possible to maintain the level of the mercury column at a fixed point in the manometer tube leading into the system. The volume of the manometer was determined from this point. Changes in the volume of the system due to the changes in the height of the mercury column were avoided by this means.

The other arm of the constant-level manometer was joined to the closed manometer. A side arm, bearing the stop-cock, e, was attached between the two manometers. By pumping out the closed manometer system, i.e., the closed manometer, the outer limb of the constant-level manometer and the connecting tubing, the constant-level manometer could be converted into a closed manometer. This arrangement was adopted in order to gain greater accuracy over the relatively wide range of pressures employed in this experiment. When high pressures were measured, the constant-level manometer was used as an open manometer by opening the stop-cock, e, to the atmosphere. In order to measure pressures of the order of 1-20 mm., the constant-level manometer was used as a closed manometer. By this means, the difference in the heights of the two mercury columns was kept small while

measuring relatively small pressures; and, moreover, the pressure measurements were now independent of the atmospheric pressure.

The closed manometer was employed to indicate the degree of vacuum in the closed manometer system. If the two mercury columns in the closed manometer were at the same height, it would indicate that the manometer system was pumped down beyond the range of the cathetometer, and the difference in the heights of the mercury columns in the constant-level manometer would directly give the pressure in the system. On the other hand, if the columns in the closed manometer were not at the same level, the difference in their heights would have to be added to the difference in the heights of the two columns in the constant-level manometer in order to determine the pressure in the system.

Cathetometers.

Two cathetometers were used to measure the differences in the heights of the mercury columns. One of these had a range of 1000 mm. The other had a range of 30 mm. and was equipped with a micrometer screw. The cathetometer having the larger range did not have a micrometer screw.

Stop-Cocks.

Six stop-cocks were employed in the apparatus at first. Later, a seventh stop-cock was incorporated. Fig. 12 shows the first system of stop-cocks employed. The stop-cocks a, b, c and d, may be said to be in the system proper; and,

therefore, it was necessary that they should be highly efficient. A leak in any one of these would entirely vitiate the results. The tap, e, was employed to control the pressure in the manometer system. The stop-cock, f, was used as an outlet for nitrogen while flushing out the purifying train.

The first set of stop-cocks employed were of the ordinary, horizontal bore variety. They were carefully reground, using a mixture of very fine carborundum and water. They were greased with a special vacuum grease obtained from the Central Scientific Co. They were found capable of holding a vacuum for varying periods of time, after which they developed leaks. This necessitated re-grinding and frequent applications of grease. A three-way stop-cock was then incorporated into the apparatus, and the stop-cocks, c and d, were used to back the three-way tap.

The changes in the volume of the outer system due to the alteration of the stop-cock system will be indicated in the data. The volume of the outer system already stated was the volume obtained when the system contained the first set of stop-cocks.

Connecting Tubing.

Since the connecting tubes, that is, the tubes leading from the flasks to the various instruments, were exposed to the atmosphere throughout the experiment, it was necessary

to use narrow glass tubing. The tubing employed had an internal diameter of 4 mm.

Purifying Train.

The purpose of the purifying train was to remove any moisture and oxygen which might be present in the nitrogen. The nitrogen was passed through two traps containing concentrated sulphuric acid. The oxygen was removed by passing the gas over a hot copper gauze, contained in a combustion tube. The copper was heated by means of an electric furnace which consisted of two layers of nichrome wire wrapped around the combustion tube. The wire was insulated by means of asbestos paper. The nitrogen was then passed through a U-tube containing calcium chloride, and, finally, through a tube containing phosphorous pentoxide.

Vacuum Pumps.

The pumps employed in this experiment were a Toepler, a diffusion pump, and a "Highvac" pump. The Toepler was a hand-operated pump, and pumping by means of it was found to be slow. It was replaced by a mercury vapour diffusion pump, backed by the "Highvac" pump. This combination of pumps was capable of pumping down to at least 1×10^{-5} mm. The "Highvac" alone was capable of pumping down to about 20×10^{-3} mm.

Method of Agitation.

An electric bell was used to agitate the manganese. A

brass strip was wired to the manganese flask, and the hammer of the bell was so placed as to strike the brass. The flask was rapidly shaken by this means and the manganese agitated.

The Manganese Sample.

The manganese employed in this experiment was purchased from the Johnson Matthey Co. It was in the form of a fine powder. Analysis of the sample showed it to contain 96.84% manganese, 1.74% iron, 0.61% silicon, and 0.12% carbon. This analysis was checked by determining the total metallic content of the sample. The two determinations gave the following results: (1) 98.67% and (2) 98.79%.

The surface area of the manganese was determined microscopically. The dimensions of the largest manganese particle obtainable were measured. The length was found to be 0.0018 mm. and the width 0.00112 mm. Half these dimensions may be considered to be those of an average particle. Therefore, the dimensions of the average particle, which is taken to be cylindrical, are as follows:-

$$\text{length} = \frac{.0018}{2} = 0.0009 \text{ mm.}$$

$$\text{diameter} = \frac{.00112}{2} = 0.0006 \text{ mm.}$$

The volume of the particle $= \pi r^2 l = 3.14 \times (0.0003)^2 \times 0.0009$
 $= 254 \times 10^{-12} \text{ c. mm.}$ Since 1 gram of manganese occupies
 $\frac{1000}{7.42} = 134.8 \text{ c. mm.}$, the number of mean particles per
 gram of manganese $= \frac{135}{254} \times 10^{12} = 5.32 \times 10^{11}$.

The area of the mean particles = area of the curved surface + the area of the two ends.

Area of the curved surface $2\pi r l = 3.14 \times .0003 \times .0009 = 1.696 \times 10^{-10}$ sq. mm.

Area of the two ends $= 2\pi r^2 = 2 \times 3.14 \times (.0003)^2 = 5.65 \times 10^{-9}$ sq. mm.

Therefore, area of mean particle $= 16.96 \times 10^{-9} + 5.65 \times 10^{-9} = 2.26 \times 10^{-10}$ sq. mm.

The area per gram of manganese $= 2.26 \times 10^{-10} \times 5.32 \times 10^{11} = 121.9$ sq. mm.

Nitrogen.

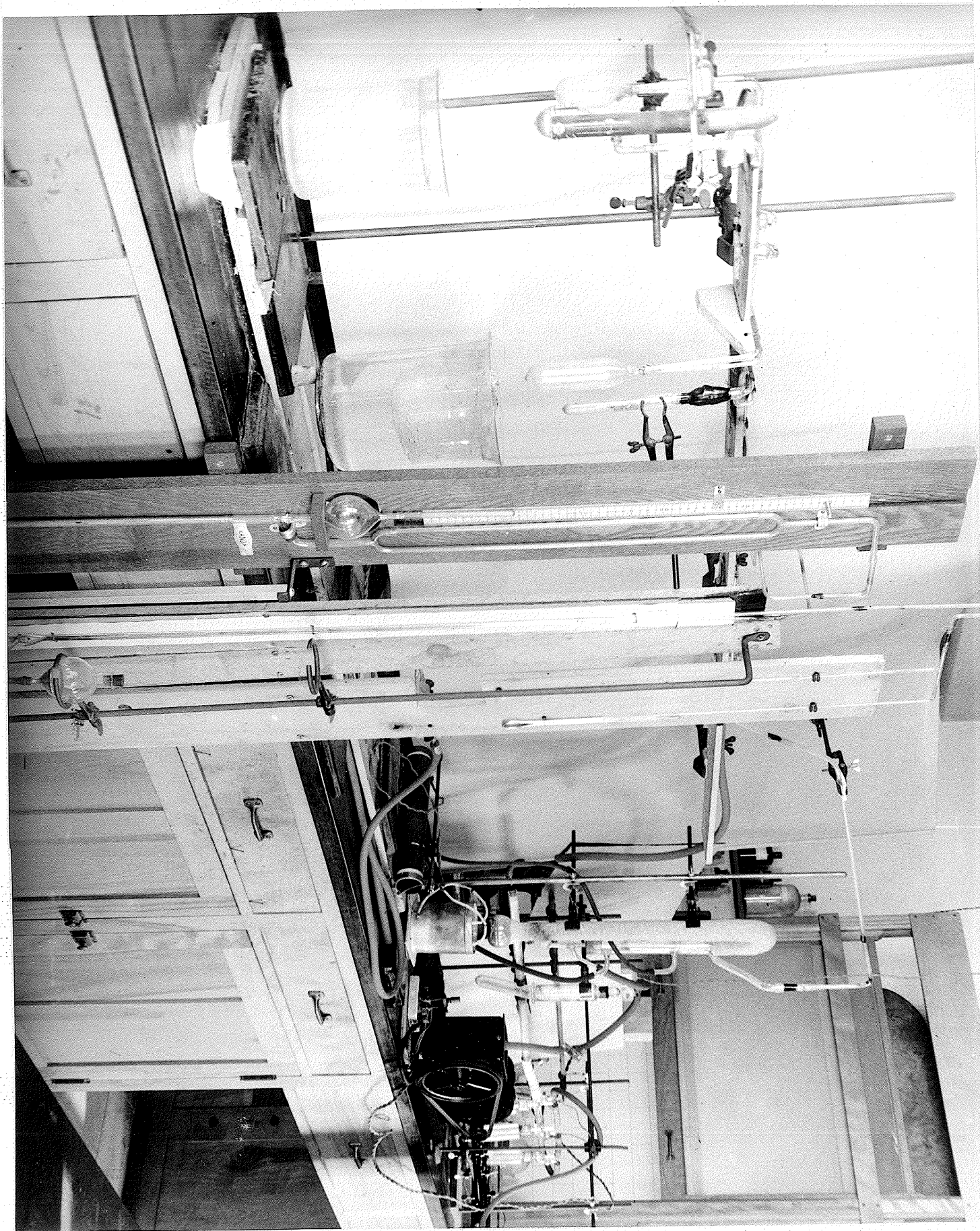
The nitrogen employed in this experiment was ordinary "tank" nitrogen obtained from the Canadian Liquid Air Co. The method of purifying it has already been mentioned.

The area of the cross section of a nitrogen molecule was calculated as follows:-

Diameter of a nitrogen molecule $= 3.15 \times 10^{-8}$ cm.

Area of the cross section $= \pi r^2 = 7.72 \times 10^{-16}$ sq. cm.

or 772×10^{-16} sq. mm.



METHOD AND RESULTS.

Preliminary Treatment of the Manganese.

Into the manganese flask, 54.8776 grams of manganese were introduced through the neck of the flask. The opening was then sealed.

Before the adsorption measurements could be made, it was necessary to rid the manganese surface of the gases which it already held. Two methods of outgassing were tried. In the first method, the system was pumped down; and hydrogen, obtained by the electrolysis of a concentrated sodium hydroxide solution, was introduced into the system to atmospheric pressure. The system was then pumped down to 0.306 mm. Hydrogen was again admitted, and the system pumped down to 0.376 mm. The hydrogen was then allowed to stream through the system for 26 hours. Samples of the hydrogen leaving the apparatus were collected over water, and were found to burn quietly. The manganese flask was placed in an electric furnace, and heated at 320 - 350°C. for 75 hours. At the end of this time, the system was pumped down to 21×10^{-3} mm., and the heating was continued for 20 hours. The pressure was found to have risen to 15.1 mm. during this time. The system was then pumped down to 93×10^{-3} mm. and left to stand for 20 hours. At this time, the pressure was found to be 1.0 mm.

The process of pumping out the system and letting it stand for 20 hours was repeated four more times. The initial

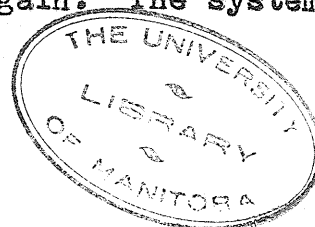
pressures and the final pressures after 20 hours of standing are given in table 4.

Table 4.

Initial Pressure (mm.)	Pressure after 20 Hours. (mm.)
21×10^{-3}	15.1
93×10^{-3}	1.0
21.5×10^{-3}	155×10^{-3}
26×10^{-3}	26×10^{-3}
11×10^{-4}	13×10^{-4}
10×10^{-4}	16×10^{-4}

Since the increase in pressure on standing is due to the desorption of the gas from the metal, it is seen from the preceding table that a large amount of hydrogen is sorbed by the manganese at the temperature of the outgassing, viz., 320 - 350°C.

An unfortunate accident, in which it was believed that mercury entered the manganese flask, occurred at this point. It was necessary to take down the apparatus, clean the connecting tubes of mercury, introduce a new sample of manganese, and again assemble the apparatus. At this point, the gold-leaf trap was added to the system. The fresh sample of manganese, weighing 44.4007 grams, was outgassed, the hydrogen treatment being employed again. The system



was pumped down to 10×10^{-3} mm., and hydrogen was allowed to stream through the apparatus for six hours at room temperature. At this time, the hydrogen was sufficiently free of oxygen to allow the heating of the flasks. The three flasks were heated at 300°C . The streaming of the hydrogen was continued for 10 hours. The hydrogen generator was then stopped, and the system was left to stand for 55 hours. At the end of this time, the system was pumped to 146×10^{-3} mm. After 20 hours, the pressure was found to be 2.0 mm. The pumping was resumed, while the heating was discontinued. When the manganese cooled to room temperature, nitrogen was admitted into the system, and was left to stand for about 15 hours at atmospheric pressure. A rapid stream of nitrogen was then passed through the system for an hour. The system was pumped down to 17×10^{-4} mm., and left to stand for about 20 hours at 200°C . The pressure rose to 232×10^{-3} mm. The pressure was brought down to 14×10^{-3} mm., and the system was left for four days. The pressure rose to 241×10^{-3} mm. in this time. The system was pumped down to 38×10^{-5} mm. The manganese flask was shut off, and the pumping was discontinued for 15 hours. During this time, the pressure in the outer system and in the blank rose to 6×10^{-4} mm. This increase in pressure was probably due to moisture on the walls of the flasks and the connecting tubes. On opening the manganese flask, there was a further increase in pressure, the reading for the total system being 23×10^{-3} mm.

The heating was discontinued, and the system was pumped to 3×10^{-4} mm. After 15 hours, this pressure was found to be unchanged.

Adsorption of Nitrogen by Manganese at 0°C.

The manganese was now considered sufficiently outgassed to permit the accurate measurement of the adsorption of nitrogen by the metal. The manganese flask, the reservoir, the blank and the gold-leaf trap were placed in an ice and water mixture. The system was pumped down to 1×10^{-5} mm., and the manganese flask was shut off. Nitrogen was then introduced into the outer system and into the blank. The pressure in this part of the system was 41×10^{-4} mm. The manganese flask was opened, and the time noted. Pressure readings for the total system were now taken, and the time of each reading was observed.

The volume of nitrogen adsorbed was calculated by a method which will be described later. The results obtained appear in table 5.

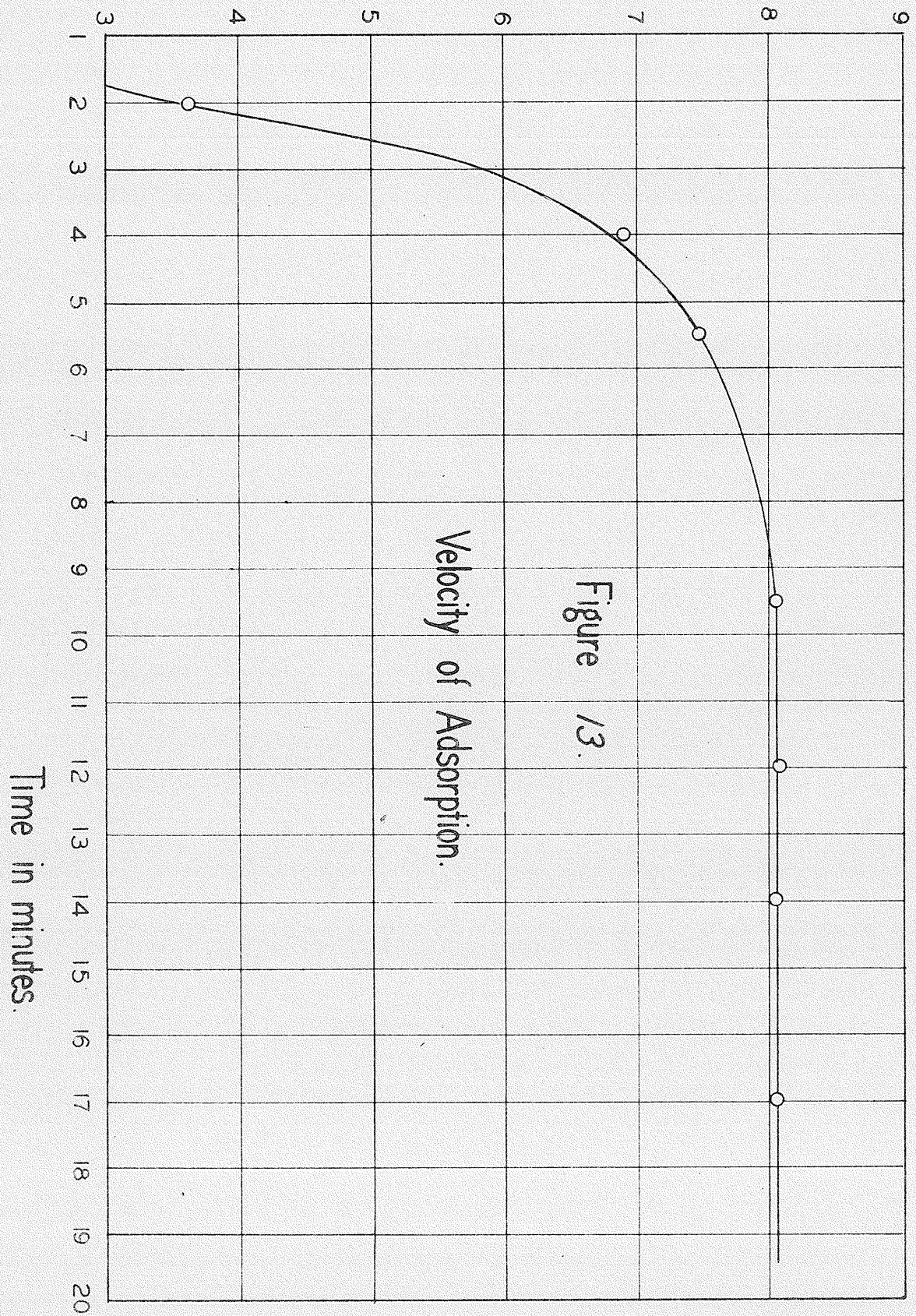
Table 5.

Time (minutes)	Pressure of Total System. (mm.)	Volume of Nitrogen Adsorbed by 44.4 Grams of Manganese. (c.c. at S.T.P.)
2	33×10^{-4}	3.61×10^{-4}
4	28×10^{-4}	6.92×10^{-4}
5.5	26×10^{-4}	7.46×10^{-4}
9.5	25×10^{-4}	8.06×10^{-4}
12	25×10^{-4}	8.06×10^{-4}
14	25×10^{-4}	8.06×10^{-4}
17	25×10^{-4}	8.06×10^{-4}
24	25×10^{-4}	8.06×10^{-4}
30	25×10^{-4}	8.06×10^{-4}
35	25×10^{-4}	8.06×10^{-4}
60	25×10^{-4}	8.06×10^{-4}

Fig. 13 shows the curve obtained by plotting the volume of nitrogen adsorbed against the time. It is a smooth curve which becomes asymptotic to the time axis at about 9.5 minutes. After this time, the equilibrium pressure is attained, and no further adsorption takes place.

It was intended to increase the pressure in the outer system progressively to atmospheric pressure while retaining the equilibrium pressures in the manganese flask. At each pressure interval, the volume of nitrogen adsorbed by the metal was to be determined. By adding the volumes adsorbed

Volume - C.C. x 10^{-4}



from 1×10^{-5} mm. to atmospheric pressure, the total amount of gas adsorbed by the manganese could be calculated. Unfortunately, a leak developed in the apparatus, thereby invalidating any further measurements.

The leak was traced to a stop-cock. By regrinding and regreasing it, the system was again found to hold pressures of the order 1×10^{-5} mm. Since some air had entered the apparatus, it was decided to repeat the hydrogen treatment of the manganese. Hydrogen was streamed through the apparatus for seven hours. After this time, the streaming was discontinued, and the manganese flask was heated at 300°C . for 75 hours. The system was then pumped down to 22×10^{-3} mm., and left for 20 hours. The pressure rose to about 1 mm. during this time. The system was evacuated to 74×10^{-4} mm., and was again left to stand for 20 hours. The pressure increased to 172×10^{-3} mm. While the evacuation of the system was being repeated, the "Highvac" pump broke down. Oxygen entered the system; and, since at this time the manganese was being heated at 300°C ., the manganese was oxidized forming manganese dioxide. The oxidized manganese was replaced by a fresh sample of manganese of the same weight, viz., 44.4007 grams.

In the preliminary outgassing of the new sample, it was decided to eliminate the hydrogen treatment, because of the lengthy time required to remove the hydrogen sorbed by the manganese. The displacement of the gases held on the surface of the metal was effected by treating the manganese with

nitrogen instead of hydrogen.

The system was pumped down to 15×10^{-4} mm. and left to stand for 48 hours. During this time, the pressure rose to 88×10^{-3} mm. The system was again evacuated, the final pressure being 3×10^{-5} mm. The pumping was discontinued, and the system was left for 15 hours. The pressure increased to 20×10^{-4} mm. during this time. The evacuation was resumed till the pressure fell to 32×10^{-5} mm. This pressure was but slightly changed after 30 minutes. The relative constancy of the pressure indicated that the gases sorbed by the manganese had been removed to a large extent by the evacuation. A steady stream of nitrogen was now passed through the apparatus for 15 hours. The system was pumped down to 30×10^{-3} mm., and nitrogen was again introduced to atmospheric pressure. The pressure was then lowered to 26×10^{-3} mm., and nitrogen was again admitted into the system.

The manganese was not heated during this process of outgassing; since, from the data of T. H. Martin, working in this laboratory, it was learned that the formation of a nitride of manganese started at about 125°C .

Desorption of Nitrogen from Manganese at 0°C .

The problem of finding the amounts of nitrogen adsorbed by the manganese was now studied from the point of view of supersaturation, i.e., the amounts of nitrogen desorbed from the manganese were measured. This procedure was adopted in order to save time. The completion of the desorption

isothermal necessarily leaves the manganese sample in the proper condition for the start of a new adsorption isothermal.

The method consisted of keeping the pressure in the manganese flask at a certain value, and pumping the outer system to about half this value. By opening the stop-cock, a, (Fig. 12) an expansion takes place from the manganese flask to the outer system. A new pressure is established in the total system which is necessarily higher than the initial pressure of the outer system. The difference between the pressure of the total system and the pressure of the outer system is due to the expansion of the nitrogen and to the desorption of the nitrogen from the manganese. By suitable calculations, the amount of nitrogen adsorbed by the manganese may be determined.

The temperature of the system was maintained at 0°C. throughout this run. This was done by placing the manganese flask, the blank, the reservoir and the gold-leaf trap in an ice and water mixture. Unfortunately, a certain portion of the system could not be placed in a thermostat. This part of the apparatus included the McLeod Gauge, the connecting tubes, and a small portion of the open manometer. It was necessary, therefore, to make a correction for this part of the apparatus. It was primarily for this reason that the blank was included in the system. By making expansions from the blank to the outer system, and from the outer system to the blank, the effective volumes of the outer system and of the manganese flask could be determined. This method, however, was not

employed. It was believed that a higher degree of accuracy would be attained by determining the volume of the unthermostated portion by weighing, and correcting this volume to the working temperature.

The mean room temperature was 20°C . The volume of the outer system exposed to the atmosphere was 147.8 c.c. At 0°C . this volume = $147.8 \times \frac{273}{293} = 137.3 \text{ c.c.}$

The difference between the true volume and the effective volume at 0°C . = $147.8 - 137.3 = 10.5 \text{ c.c.}$

The effective volume of the outer system at 0°C .

$$= 319.3 - 10.5 = 308.8 \text{ c.c.}$$

Although every possible precaution was taken in the construction of the purifying train to make it air tight, it was thought advisable to flush out the train thoroughly before admitting nitrogen into the system. This was done by passing a rapid stream of nitrogen through the train for an hour or more while allowing the gas to escape into the atmosphere through the open stop-cock, f, (Fig. 12). The rate of streaming was then decreased; the stop-cock, f, shut; stop-cock, d, opened slightly; and the gas slowly admitted into the evacuated system until a pressure of 752 mm. was attained. The manganese flask and the blank were then shut off, and the outer system was pumped down to 369 mm. Thereupon the manganese flask was opened, and an expansion from the manganese flask to the outer system took place. The

pressure readings of the total system were taken at suitable intervals of time, till equilibrium was established. After equilibrium was attained, the gas was allowed to remain in contact with the manganese for periods varying from 6 to 15 hours. This procedure was found necessary since there was a likelihood of a second, slower desorption taking place. The equilibrium pressure was found to be 421.1 mm. The manganese flask was then shut off, and the outer system was pumped down to 210.7 mm. The expansion was repeated, and the equilibrium pressure was again noted. In this manner, the pressures were progressively lowered until pressures of 0.0099 mm. in the manganese flask and 0.0028 mm. in the outer system were attained.

The method of calculating the amount of nitrogen adsorbed by the manganese can best be shown by a determination using actual experimental data. In one instance, the pressure in the manganese flask was 420.5 mm. (second expansion, table 6). The volume of this flask, after a correction had been made for the space occupied by 44.4 grams of manganese, was found to be 50.94 c.c. The volume of nitrogen in this flask at 0°C. and 760 mm.

$$= \frac{420.5}{760} \times 50.94 = 28.17 \text{ c.c.}$$

The effective volume of the outer system at 0°C = 308.8 c.c.

The volume of nitrogen in the outer system at 0°C. and

$$760 \text{ mm.} = \frac{210.7}{760} \times 308.8 = 85.61 \text{ c.c.}$$

The total volume of nitrogen in the system before the expansion

$$= 28.17 + 85.61 = 113.78 \text{ c.c. at S. T. P.}$$

After the expansion, the pressure in the total system was found to be 242.9 mm. The volume of the total system, the blank excluded, = the volume of the manganese flask, + the volume of the outer system

$$= 50.94 + 308.8 = 359.74 \text{ c.c.}$$

The volume of nitrogen in the total system after the expansion

$$= \frac{242.9}{760} \times 359.74 = 114.9 \text{ c.c. at N.T.P.}$$

The increase in the volume of nitrogen in the system after the expansion is due to the gas being given off by the manganese. Therefore, the volume of nitrogen desorbed

$$= 114.9 - 113.78 = 1.12 \text{ c.c. at S.T.P.}$$

The same method of calculation was employed in the first determination of adsorption. In the case of adsorption, however, the volume of gas in the total system will be less after the expansion takes place than before. The difference between the two volumes is a measure of the gas adsorbed.

The number of layers of nitrogen leaving the manganese may be determined in the following manner. Using the same data employed in the preceding calculation, it is found that the weight of nitrogen desorbed from 1.0 gram of manganese

$$= \frac{1.12 \times 28}{22,400 \times 44.4} = 3.15 \times 10^{-5} \text{ grams.}$$

The number of molecules of nitrogen in 3.36×10^{-5} grams of the gas

$$= \frac{3.15 \times 6.06 \times 10^{18}}{28} = 6.81 \times 10^{17}.$$

By methods already described, the area of the cross section of a nitrogen molecule was calculated to be 772×10^{-6} sq. mm., and the surface area per gram of manganese was determined to be 121.9 sq. mm. Therefore, the area of the cross section of 6.81×10^{17} molecules of nitrogen

$$= 6.81 \times 10^{17} \times 772 \times 10^{-6} = 52,500 \text{ sq. mm.}$$

The number of layers of nitrogen leaving the manganese

$$= \frac{52,500}{121.9} = 431.6$$

The total number of layers of nitrogen leaving the manganese was calculated to be 652, and the total volume of nitrogen desorbed was found to be 1.6973 c.c. The results for the desorption are given in table 6. Figure 14 shows the curve obtained by the logarithms of the equilibrium pressures +3 against the logarithms of the volumes of nitrogen desorbed (c.c. at S.T.P.) +4. Figure 15 shows the isothermal at 0°C . obtained at the low pressures.

Adsorption of Nitrogen by Manganese at 0°C .

The desorption experiment left the manganese in a suitable condition for the study of adsorption from the point of view of undersaturation. Before the amounts adsorbed were measured, however, certain changes in the apparatus were made.

TABLE — 6.
DESORPTION OF NITROGEN FROM MANGANESE.

INITIAL PRESSURE IN MANGANESE FLASK. MM.	INITIAL PRESSURE IN OUTER SYSTEM. MM.	EQUILIBRIUM PRESSURE. MM.	VOLUME OF N ₂ DESORBED FROM 44.4 GRAMS OF MANGANESE. CC. AT S.T.P	WEIGHT OF N ₂ DESORBED FROM 44.4 GRAMS OF MANGANESE. GRAMS.	WEIGHT OF N ₂ DESORBED FROM 1.0 GRAM OF MANGANESE. GRAMS.	NUMBER OF N ₂ MOLECULES DESORBED FROM 1.0 GRAM OF MANGANESE.	SURFACE COVERED BY N ₂ MOLECULES. SQ. MM.	NO. OF LAYERS OF N ₂ DESORBED FROM MANGANESE.	SUM OF VOLUMES OF N ₂ DESORBED. CC. AT S.T.P	SUM OF LAYERS OF N ₂ DESORBED.
752	369.5	421.1								
420.5	210.7	242.9	1.12	14.0 X 10 ⁻⁴	3.15 X 10 ⁻⁵	6.81 X 10 ¹⁷	52500	431.6	1697.3 X 10 ⁻³	652
241.7	113.8	131.7								
130.6	37.3	51.4	0.44	5.49 X 10 ⁻⁴	1.24 X 10 ⁻⁵	2.68 X 10 ¹⁷	10700	169	577.3 X 10 ⁻³	220
49.4	16.9	21.4								
20.98	4.81	7.35	0.119	1.48 X 10 ⁻⁴	3.20 X 10 ⁻⁶	6.94 X 10 ¹⁶	5350	43.9	137.3 X 10 ⁻³	50.9
6.5	0.241	1.132	7.3 X 10 ⁻³	9.09 X 10 ⁻⁶	20.5 X 10 ⁻⁸	4.43 X 10 ¹⁵	342	2.81	18.29 X 10 ⁻³	7.04
1.132	0.116	0.271	5.4 X 10 ⁻³	6.74 X 10 ⁻⁶	15.2 X 10 ⁻⁸	3.28 X 10 ¹⁵	254	2.08	10.987 X 10 ⁻³	4.23
0.263	0.058	0.091	1.88 X 10 ⁻³	2.34 X 10 ⁻⁶	5.28 X 10 ⁻⁸	1.14 X 10 ¹⁵	88.2	0.724	5.587 X 10 ³	2.15
0.091	0.012	0.029	2.75 X 10 ⁻³	3.43 X 10 ⁻⁶	7.73 X 10 ⁻⁸	1.67 X 10 ¹⁵	129	1.06	3.707 X 10 ³	1.43
0.029	0.006	0.0099	3.0 X 10 ⁻⁴	3.75 X 10 ⁻⁷	8.45 X 10 ⁻⁹	1.82 X 10 ¹⁴	14.1	0.115	9.57 X 10 ⁴	0.367
0.0099	0.0028	0.0052	6.57 X 10 ⁻⁴	6.21 X 10 ⁻⁷	18.5 X 10 ⁻⁹	3.98 X 10 ¹⁴	30.7	0.252	6.57 X 10 ⁴	0.252

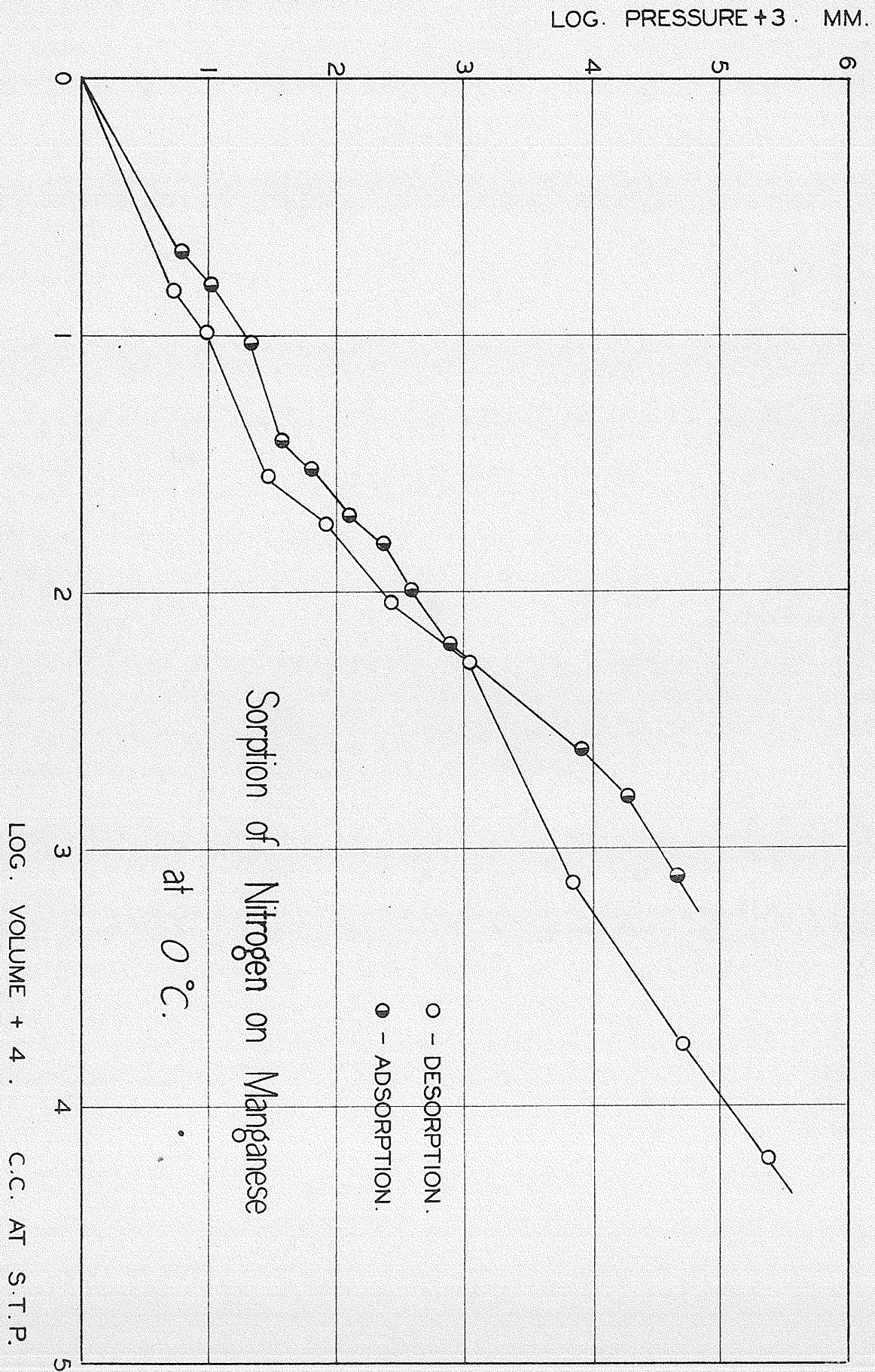


Figure 14.

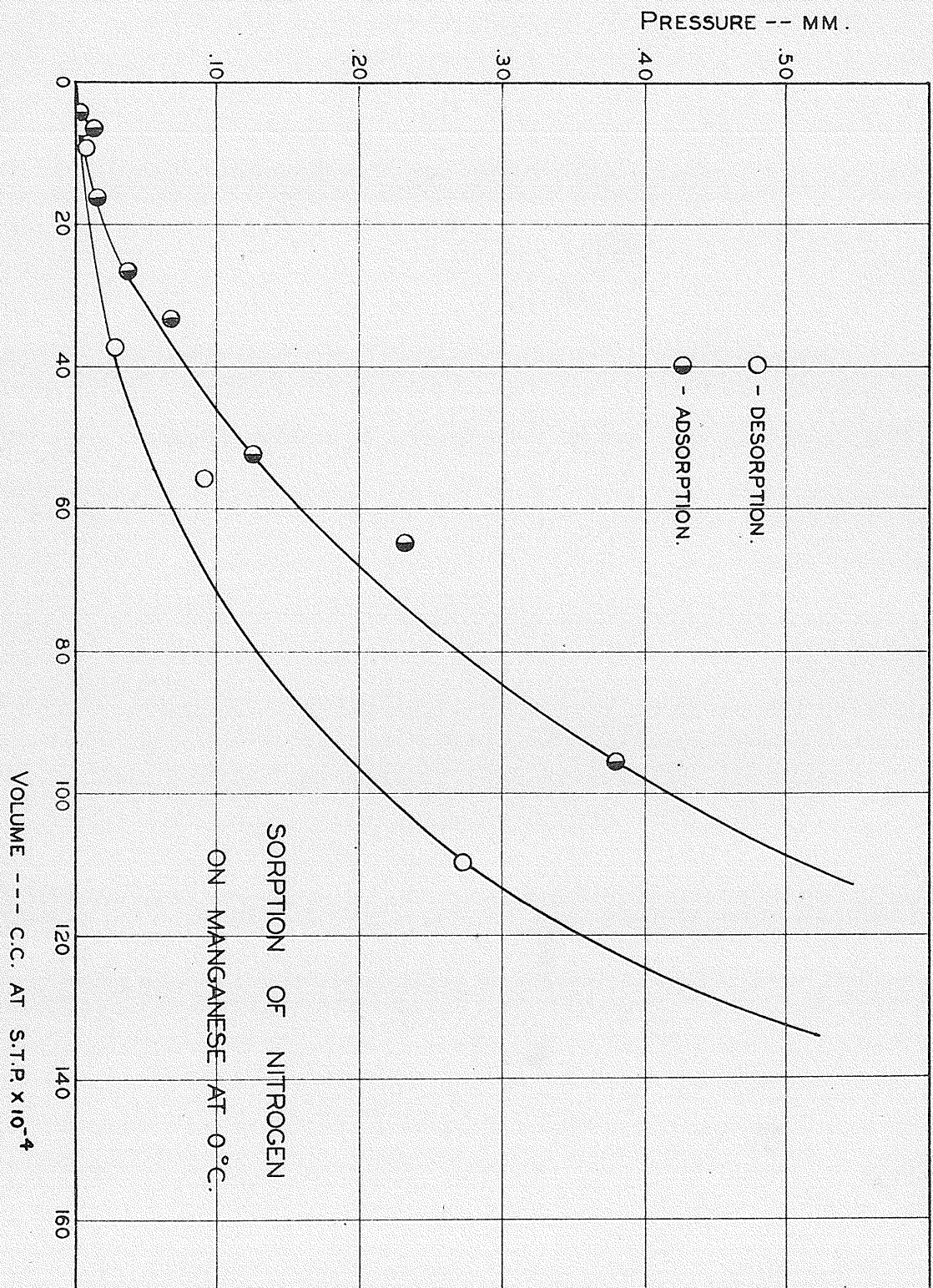


FIGURE 15.

A three-way stop-cock which was specially ground for high vacuum work was inserted in the position occupied by stop-cocks, c and d, (Fig. 12). These stop-cocks were then joined to two of the arms of the three-way cock. The stop-cock, f, which was used in flushing out the purifying train was also retained.

Since the three-way cock was made of hard glass, glass to glass joints could not be made, the remainder of the apparatus being of soft glass. Two arms of the three-way stop-cock were connected to the stop-cocks, c and d, by means of pressure tubing over which picien cement was spread. The third arm of the three-way tap was connected to the system by a method frequently employed in vacuum work.

A piece of soft glass tubing of the same external diameter as the arm of the three-way stop-cock was coated with a thin layer of picien cement, and was slipped half way into a snugly fitting brass tube. The arm of the three-way stop-cock was then similarly coated with picien, and pushed into the brass tube from the opposite end until it touched the soft glass tube. After the cement had hardened, the joint was covered with friction tape and a layer of picien was spread over the tape. The soft glass tube attached to the three-way stop-cock was then joined to the system by fusion.

The volume of the outer system was slightly altered by the addition of the new stop-cock. The volume of the outer system was now found to be 318.5 c.c., or 0.8 c.c. less than

the former volume. The volume of the unthermostated portion, therefore, became 147 c.c.

Since the volume of nitrogen adsorbed by the manganese was found to be much smaller than was first anticipated, it was necessary to refine the corrections made for the unthermostated portion of the outer system. This was done by wrapping the exposed tubing with cotton wool, and the bulb of the McLeod Gauge with cotton wool and felt. By this means, rapid changes in the temperature of the unthermostated portion were eliminated. A thermometer, having a range of 50° and graduated in 0.1° , was placed against the bulb of the McLeod, since this bulb constituted about 70% of the exposed part of the system containing gas. At the time of each reading of the initial pressure in the outer system and the equilibrium pressure, the temperature was noted and the effective volume of the outer system was calculated.

The method employed to measure the volume of nitrogen adsorbed by the manganese was the reverse of the process used to measure the desorption. In this instance, the pressure in the manganese flask was lower, before the expansion, than the pressure in the outer system. On opening the stop-cock, a, an expansion took place from the outer system to the manganese flask; and a new pressure for the total system was set up. This pressure was less than the initial pressure in the outer system. The decrease was due to the expansion and to the adsorption of nitrogen by the metal.

By observing the initial pressures in the manganese flask and in the outer system, and, finally, the equilibrium pressure, the volume of gas adsorbed may be calculated by the method already described.

The results for the adsorption of nitrogen by manganese are given in table 7. The isothermals obtained are shown in figures 14 and 15.

TABLE — 7.

ADSORPTION OF NITROGEN BY MANGANESE.

INITIAL PRESSURE IN MANGANESE FLASK. MM.	INITIAL PRESSURE IN OUTER SYSTEM. MM.	EQUILIBRIUM PRESSURE. MM.	VOLUME OF N ₂ ADSORBED BY 44.4 GRAMS OF MANGANESE. C.C. AT S.T.P.	WEIGHT OF N ₂ ADSORBED BY 44.4 GRAMS OF MANGANESE. GRAMS.	WEIGHT OF N ₂ ADSORBED BY 1.0 GRAM OF MANGANESE. GRAMS.	NUMBER OF N ₂ MOLECULES ADSORBED BY 1.0 GRAM OF MANGANESE.	SURFACE COVERED BY N ₂ MOLECULES. SQ. MM.	NO. OF LAYERS OF N ₂ ADSORBED BY MANGANESE.	SUM OF VOLUMES OF N ₂ ADSORBED. C.C. AT S.T.P.	SUM OF LAYERS OF N ₂ ADSORBED.
36.5×10^{-4}	65×10^{-4}	59.5×10^{-4}	4.6×10^{-4}	5.74×10^{-7}	12.92×10^{-9}	2.78×10^{14}	21.5	0.176	4.6×10^{-4}	0.176
60.0×10^{-4}	123×10^{-4}	110.5×10^{-4}	1.7×10^{-4}	2.12×10^{-7}	4.78×10^{-9}	1.03×10^{14}	7.95	0.065	6.3×10^{-4}	0.241
112.0×10^{-4}	231×10^{-4}	207.0×10^{-4}	4.21×10^{-4}	5.27×10^{-7}	11.85×10^{-9}	2.56×10^{14}	19.7	0.161	10.51×10^{-4}	0.402
20.06×10^{-3}	43×10^{-3}	36.0×10^{-3}	1.58×10^{-3}	1.97×10^{-6}	4.45×10^{-8}	0.958×10^{15}	74.1	0.608	26.31×10^{-4}	1.01
36.5×10^{-3}	73×10^{-3}	66.5×10^{-3}	0.65×10^{-3}	0.81×10^{-6}	1.83×10^{-8}	0.388×10^{15}	30.5	0.25	32.81×10^{-4}	1.26
68.5×10^{-3}	139×10^{-3}	125×10^{-3}	198×10^{-3}	2.46×10^{-6}	5.48×10^{-8}	1.2×10^{15}	93.0	0.562	52.61×10^{-4}	1.82
125.0×10^{-3}	252×10^{-3}	231.5×10^{-3}	1.24×10^{-3}	1.54×10^{-6}	3.48×10^{-8}	0.753×10^{15}	58.2	0.477	65.01×10^{-4}	2.30
233×10^{-3}	410×10^{-3}	378×10^{-3}	3.11×10^{-3}	3.88×10^{-6}	8.75×10^{-8}	1.89×10^{15}	146.0	1.2	96.11×10^{-4}	3.50
0.377	0.943	0.848	0.0067	8.35×10^{-6}	18.85×10^{-8}	4.07×10^{15}	315	2.58	163.11×10^{-4}	6.08
0.755	9.71	8.39	0.025	3.12×10^{-5}	7.04×10^{-7}	1.53×10^{16}	1180	9.7	413.11×10^{-4}	15.8
8.39	20.1	18.4	0.019	2.42×10^{-5}	5.45×10^{-7}	1.18×10^{16}	915	7.52	603.11×10^{-4}	23.3
18.4	44.1	40.3	0.067	8.35×10^{-5}	18.85×10^{-7}	4.07×10^{16}	3150	25.8	1273×10^{-4}	49.1

DISCUSSION OF RESULTS.

DISCUSSION OF RESULTS.

The volume of nitrogen adsorbed by the 44.4 grams of manganese at 0°C . was found to be 1.6973 c.c. at S.T.P. by the desorption experiment. This amount is necessarily too small since at the final pressure of the desorption, 52×10^{-4} mm., there will still be some residual nitrogen held by the manganese surface. The volume of the residual gas, however, will be very small; and, therefore, it will not change the total volume to any appreciable extent. This will also be true of the volume of nitrogen measured by direct adsorption.

From Figures 14 and 15, it is seen that the curves for the adsorption and desorption do not coincide. This is probably due to experimental error. It has already been mentioned that no special precaution was taken in correcting for the unthermostated portion of the system containing gas during the desorption run. This may account for the deviation of the two curves.

Manganese, chromium and iron have many similar properties. It would be of interest, therefore, to compare the amounts of nitrogen adsorbed by these metals. Benton⁵ found that about 0.4 c.c. of nitrogen was adsorbed by 54.6 grams of iron at 0°C . (Fig. 3). Thus, 44.4 grams of iron would adsorb 0.32 c.c. of nitrogen. This volume is of the same order as that obtained with manganese. No data are available on adsorption of nitrogen by chromium at 0°C .

The total number of layers of nitrogen adsorbed by the manganese was found to be 652. This number is too large if the

monomolecular adsorption theory of Langmuir is accepted. The result, however, can be explained by accepting Polanyi's theory of thick compressed films, or, by assuming that the area of the manganese surface as determined by the microscopic method is too small. The latter is the most probable explanation, since the microscopic method does not take into account the network of cracks which develop in the metal. These cracks will greatly increase the surface available to the gas molecules.

The acceptability of either the Langmuir theory or the Polanyi theory cannot be discussed at this time. The adsorption of nitrogen by manganese will have to be determined at other temperatures first. If it is found that the adsorption is independent of temperature, then it will appear that Polanyi's theory is the more acceptable one. Langmuir's theory indicates that adsorption is dependent on the temperature. If by further work this is found to be the case, it may be supposed that only a monomolecular layer is formed. In this case the value obtained for the surface area of the manganese will appear to be about 650 times too small.

In the meantime, the work is being continued. The adsorption of nitrogen by manganese will be investigated at other temperatures, and the heat of adsorption calculated. This additional data will lead to a clearer understanding of the various types of adsorption which may take place in the system, nitrogen on manganese.

SUMMARY.

SUMMARY.

1. Two methods of outgassing of the manganese were employed.
2. The velocity of adsorption at a relatively low pressure was determined.
3. The desorption of nitrogen from manganese was studied at 0°C.
4. The adsorption of nitrogen by manganese was studied at 0°C.
5. The number of layers of nitrogen adsorbed by the manganese was determined.

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