Discussion

The deposits in Expts. 9 and 10 containing 0.58 mg. and 0.48 mg. of potassium were very small but could be detected by comparison with a blank.

The results indicated that zirconium sulfate will detect 0.48 mg. or more of potassium in 2 cc. of reaction mixture in the presence of large amounts of ammonium ions. This is a distinct advantage over other tests, in all of which ammonium interferes. Bray[6] found "With 1 mg. of NH_4 a precipitate formed in about 10 minutes (with sodium cobaltic nitrite); with 0.5 mg. on standing several hours." Ammonium salts also give precipitates with tartaric acid, perchloric acid and chloroplatinic acid. With perchloric acid or chloroplatinic acid the amount of potassium must be large or alcohol must be added. Zirconium sulfate will detect potassium when present to the extent mentioned in the presence or absence of ammonium ions and no alcohol is needed.

Summary

The sensitiveness of zirconium sulfate for potassium in the presence of ammonium ions was found to be 0.48 mg. or more of potassium per 2 cc. of reaction mixture. This is practically the same sensitiveness of zirconium sulfate for potassium when no other metal ions were present. This detection in the presence of ammonium is a distinct advantage over the other tests for potassium.

Columbus, Ohio

[6] Bray, This Journal, **31**, 633 (1909).

[Contribution from the Chemistry Laboratory of The Johns Hopkins University]

THE THICKNESS OF ADSORBED VAPOR FILMS. II[1,2]

By G. H. Latham

Received September 10, 1928 Published November 6, 1928

There are now three outstanding theories of adsorption, namely, the unimolecular theory of Langmuir, the multimolecular theory of Polanyi and the capillary theory of Zsigmondy. Experimental data in support of each of these theories have been submitted by different investigators. In this paper we are particularly interested in the work of McHaffie and Lenher[3] and in that of Frazer, Patrick and Smith.[4] Both of these investi-

---

[1] In memory of Ira Remsen.

[2] This paper has been taken from the dissertation submitted by the author to the Board of University Studies of The Johns Hopkins University as part of the requirement for the degree of Doctor of Philosophy.

[3] McHaffie and Lenher, *J. Chem. Soc.*, **127**, 1559 (1925); 1785 (1926).

[4] Frazer, Patrick and Smith, *J. Phys. Chem.*, **31**, 897 (1927).

gations are concerned with the adsorption of water vapor and of toluene on glass surfaces. This paper is a summary of some work recently done in continuation of that accomplished by these investigators.

McHaffie and Lenher studied the thickness of the water film adsorbed on the surface of a glass bulb which had been washed with strong acids and water. They also investigated the adsorption of water vapor upon platinum surfaces. In each case they found that the adsorbed film was multimolecular in thickness.

It was thought by Frazer, Patrick and Smith that the weak point in the work of McHaffie and Lenher was the assumption that the surface of the glass was plane from a molecular standpoint after treatment with acids and water. (McHaffie and Lenher had assumed that they were working with plane glass surfaces and that their results were obtained with such surfaces.) It appeared that such treatment would probably dissolve some of the alkali of the glass and form some amorphous silica on the surface, thus causing a general roughening of the surface. They believed, furthermore, that glass which has been thoroughly melted in a flame and allowed to cool without coming into contact with anything except dry air would present a plane surface for adsorption measurements.

In order to test the correctness of these considerations and to study the adsorption of vapor films upon such "fire-polished" surfaces, Frazer, Patrick and Smith undertook to repeat the work of McHaffie and Lenher using the same method of procedure and apparatus, toluene vapor and both fire-polished and acid-treated glass surfaces.

The results of their work indicated that the thickness of the adsorbed toluene film was never greater than unimolecular on fire-polished glass, while on acid-treated glass it was always multimolecular in thickness. These results confirmed the belief that fire-polished surfaces of glass were plane, while acid-treated ones were not.

There was, however, an objection to the general application of these ideas to adsorption on glass; that is, they did not necessarily hold good for other substances than toluene, especially in the case of polar substances. In other words, the results were true, possibly, of non-polar compounds only.

In order to ascertain whether this objection was valid or not and, if not, to eliminate it and complete the work of Frazer, Patrick and Smith by making the facts applicable to both polar and non-polar substances, the present investigation was undertaken.

The experimental procedure and the apparatus were essentially the same as those used by Frazer, Patrick and Smith. Acetonitrile and nitromethane were the two polar substances selected as well suited for the work; toluene was used also as a check on the work of Frazer, Patrick and Smith and, later, water vapor was used in the work with platinum and silver amalgam surfaces. The use of several other polar substances was abandoned because they were not suitable for the purpose.

The method consisted essentially in measuring the pressure exerted within a small glass bulb by a known amount of vapor at constant volume, through a temperature range such that at the upper limit all of the substance would be in the gaseous condition while at the lower limit some would be present in the form of liquid. By plotting graphically the data thus secured, two curves would be obtained—one the curve for change of pressure with temperature of the substance in the form of vapor, and the other the vapor pressure curve of the liquid. Obviously these two curves on the graph would intersect at the dew point. From the type of curve obtained by plotting these *P-T* data, it was simple to ascertain whether adsorption had taken place at any time during the measurements and, if so, to what extent.

Measurements were made with a given vapor in bulbs of both fire-polished and acid-treated glass. These bulbs were made of soft glass, blown after thorough cleaning and melting in a flame. All glass-blowing was done through a phosphorus pentoxide bulb to prevent access of moisture. The bulb was cooled while attached to the phosphorus pentoxide bulb and sealed into the apparatus, using a phosphorus pentoxide bulb. It was evacuated with a mercury pump in series with an oil pump, all pressures being read on a McLeod gage. The vapor to be studied, previously freed from air, was admitted to the bulb while the temperature was at the upper limit of the range used. The bulb was closed by a mercury U-tube which served also as a manometer, and keeping the volume constant while gradually reducing the temperature, the corresponding pressures of the vapor were read. Each point obtained was approached both from above and below so that all data would represent equilibrium pressures and temperatures. All readings were checked at least twice and within 0.05 mm. As the saturation point was approached, the readings were made every 0.5 to 0.25 of a degree in order to locate the point accurately. The approximate position of this point on the curve could be foretold from the temperature of the liquid used to fill the bulb with vapor.

The temperature of the vapor in the bulb was controlled by a constant-temperature bath accurate to 0.02°. Pressure readings were made with a cathetometer which was accurate to 0.05 millimeter.

Having made the pressure–temperature measurements with a fire-polished bulb, it was removed from the apparatus and its area and volume were determined as accurately as possible. The area measured was that which had been exposed to the vapor. These data were used later in calculating the amount of vapor in the bulb during the measurements and the thickness of the film adsorbed, if any.

The bulb was then filled with chromic acid and kept at 40–50° for twenty-four hours. It was washed with distilled water, filled with concentrated nitric acid and kept at about the same temperature for twenty-four hours longer. The bulb was next thoroughly washed out with distilled water, evacuated at 180° for five hours and again sealed into the apparatus with the same precautions as before. Another sample of vapor was admitted to the bulb as before and the pressure–temperature measurements were repeated. The data secured from these measurements were plotted graphically and the type of curve obtained was determined.

Before going further into the experimental work and results, it will probably be desirable to describe briefly the method of determining the amount of adsorption taking place on these glass surfaces.

If a definite mass of vapor be kept at constant volume while the temperature is gradually lowered, its pressure at any time will be given by the equation

$$P = P_0(1 + \alpha t) \tag{1}$$

provided, of course, the vapor obeys the perfect gas laws. In the equation P is the observed pressure, P_0 is the pressure of the vapor at 0° (provided none of it condenses above or at this temperature), t is the temperature at the corresponding pressure P, and α is a constant, $^1/_{273}$. From the equation it is clear that under such conditions a series of pressure-temperature data secured from measurements on this vapor will give a straight line so long as no vapor condenses or is removed from the vapor phase in any other way. The slope of the curve will be $P_0\alpha$ and P_0 will be its intercept on the pressure axis. At the dew point, however, part of the vapor will condense and thereafter, as the temperature is lowered, the measurements will give the vapor pressure curve of the liquid. Consequently, at this dew point there will be a sharp break in the curve and the two parts of the curve will intersect at this point as two essentially straight lines. Such a curve is illustrated in Fig. 1, AOB. The curve is purely a theoretical one.

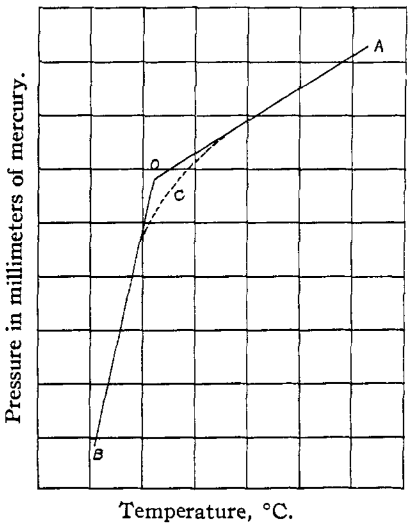

Fig. 1.

If, however, some of the vapor is adsorbed by the glass surface as the temperature is lowered, it is evident that the pressure will decrease more rapidly than is required by the gas laws, so that the curve will appear as shown in Fig. 1, ACB. The dotted line represents the portion of the curve where adsorption is taking place. From these considerations, it is clear that if adsorption occurs as the dew point is approached, there will be a gradual and more or less pronounced rounding off of one part of the curve into the other. The amount of this rounding off depends entirely upon the extent to which adsorption has occurred and from it the maximum pressure decrease due to such adsorption can readily be obtained by an inspection of the curve.

Now, if the decrease in pressure due to adsorption of a unimolecular film is known, it is only necessary to divide the total pressure decrease due to adsorption by this number in order to obtain the molecular thickness of the adsorbed film. As already stated, the volume and inside area of the adsorption bulb, together with the temperature and pressure at the point of maximum adsorption (that is, the dew point) are known, as are also the approximate molecular diameters of the substance worked with. By assuming that each molecule adsorbed is spherical and that it occupies an area on the glass surface included in a square whose side is the same length as the molecular diameter, it is a simple matter to calculate the pressure decrease caused by the adsorption of a unimolecular layer of such molecules. The thickness of the absorbed layer can then readily be calculated as already noted.

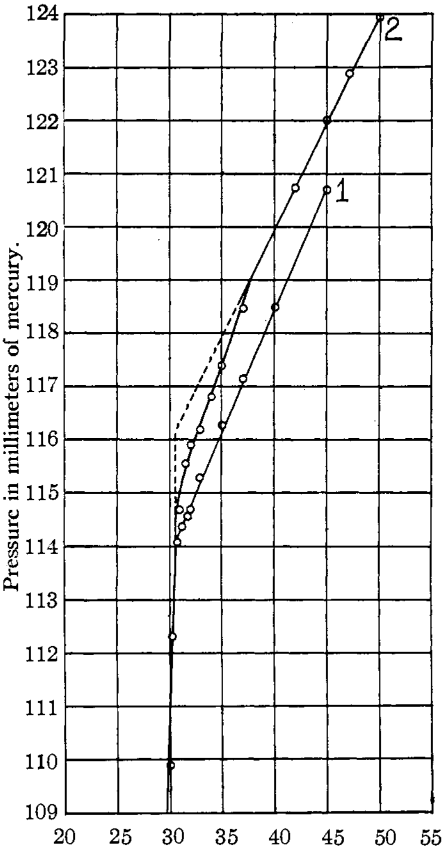

Fig. 2.

For the vapors and bulbs used during this work, the decrease in pressure caused by the adsorption of a unimolecular film varied from 0.01 to 0.04 mm., depending upon the size of the molecule.

Having thus pointed out the method by which the amount of adsorption was obtained, we can now turn to an examination of the experimental data.

The adsorption of acetonitrile vapor was first investigated. As already stated, both fire-polished and acid-treated bulbs were used. When the pressure-temperature data from measurements with a fire-polished bulb were plotted graphically, Curve 1, Fig. 2 was obtained. With the same vapor but after treating the bulb with acids and water, the measurements gave data which are shown graphically in Curve 2, Fig. 2.

Curve 1, Fig. 3, shows graphically the data obtained from measurements with nitromethane in a fire-polished bulb, while in the same figure Curve 2 is the corresponding one for an acid-treated bulb. The non-coincidence of the two vapor pressure curves is due to the fact that Curve 2 has been moved up vertically from its normal position in order to get both curves on the same graph.

The work of Frazer, Patrick and Smith with toluene was next repeated as a check both on that piece of work and on the present one. The data thus secured are shown graphically in Fig. 4. The curve shown as a solid line represents the data from the run using a fire-polished bulb, while the curve obtained from measurements with an acid-treated bulb coincides with this almost throughout except at points near the saturation point, where it falls slightly below, as shown in the dotted line. This was to be expected from the work done by Frazer, Patrick and Smith and also from the theory of this method.

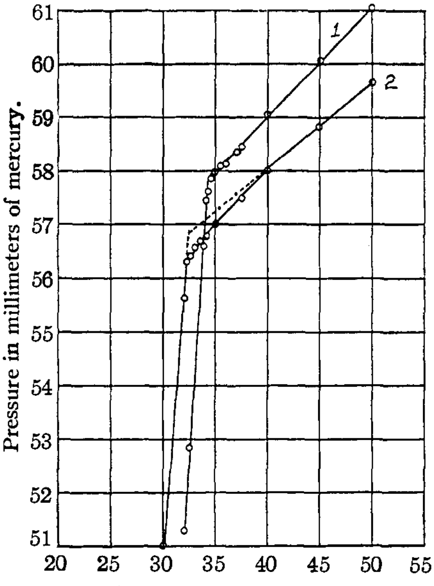

Fig. 3.

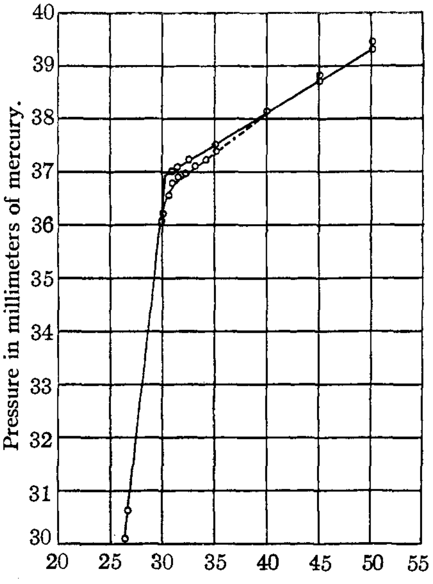

Fig. 4.

After an examination of the curves obtained (Figs. 2–4) it seemed that the amount of "rounding off" of the two parts of the several curves into each other was rather small—somewhat less than had been anticipated from the work of Frazer, Patrick and Smith. Accordingly, it was decided to make several experimental runs using different vapors in bulbs which also contained a small amount of activated silica gel. The bulbs themselves were of fire-polished glass. It was thought that since in this case we could be certain that adsorption was taking place strongly, the type of curve obtained would be interesting and instructive and might be of value in aiding one to interpret correctly the other curves. Two runs were made. One was made with 0.0003 g. of activated silica gel in a fire-polished bulb containing nitromethane as well in the vapor phase.

The other was run using the same amount of silica gel in a similar bulb with toluene vapor. The experimental results are shown graphically in Fig. 5 (for nitromethane) and in Fig. 6 (for toluene).

When we come to an examination of the experimental curves (Figs. 2–6), we see at once that in every case where a fire-polished bulb has been used, the pressure-temperature curve for the substance in the gaseous state is a straight line, and that where the two parts of the experimental curve intersect, there is a sharp break, with not the slightest trace of rounding off. On the other hand, wherever an acid-treated bulb has been used, the two parts of the curve do not intersect sharply but round off into each other more or less. Moreover, the curve for the substance in the form of vapor is not a straight line, but shows a pronounced tendency to round off near the saturation point. These facts can only be ascribed to adsorption on the acid-etched surfaces. Any other cause would show the same effect on each bulb.

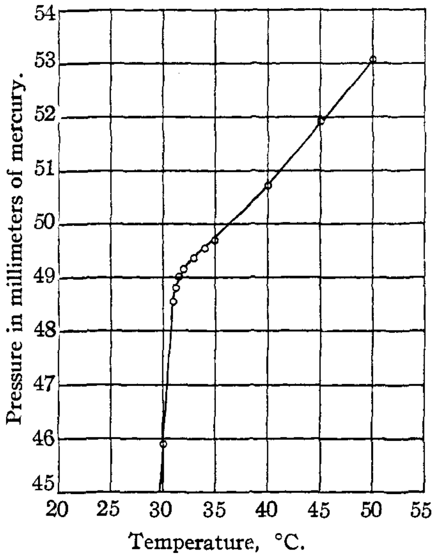

Fig. 5.

Since the pressure-temperature curves of the vapor are straight lines, it is permissible to calculate the number of moles of vapor present in the bulbs by means of the perfect gas laws. From this, together with the volume, area of the bulb, the temperature and pressure, the thickness of the adsorbed film of vapor can be calculated, as we have already indicated. These calculations have been made for each vapor. The results indicate that the adsorbed film is from 30 to 60 molecules thick at saturation pressures and temperatures on acid-treated glass, and not greater than unimolecular on fire-polished surfaces. The polar compounds appear to be somewhat more strongly adsorbed than toluene. This fact is indicated both in the character of the curves for these substances and in that for nitromethane and toluene in presence of activated silica gel.

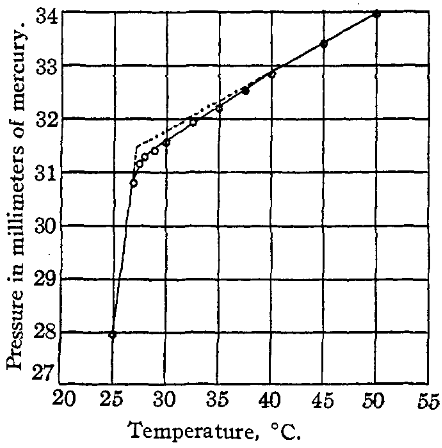

Fig. 6.

The calculation of the thickness of the adsorbed film was very simple. It was assumed that the film was of uniform thickness and that it covered the entire surface of the glass exposed to the vapor. The slopes of the curves obtained experimentally were in each case measured, and the theoretical slopes were calculated by means of Equation 1. The experimental and theoretical slopes agreed closely with the exception of those of the curves for nitromethane in presence of silica gel; this might have been expected. The dotted lines in the figures are prolongations of the straight portions of the curves and have the approximate theoretical slopes. These dotted portions represent the curves which would have been obtained had there been no adsorption at these points. Hence, the maximum distance, measured on the pressure axis, between the experimental and the dotted part of the curves is the maximum pressure decrease due to adsorption. This divided by the pressure decrease due to adsorption of a unimolecular layer gives directly the thickness of the adsorbed film.

In the case of the measurements with toluene and nitromethane in presence of silica gel, a calculation of film thickness is obviously out of the question, since the adsorption was presumably confined to the gel in the bulb, and the area of this is unknown. However, if we assume the adsorption to have taken place uniformly on the surface of the bulb as in the other experiments, the data for the run with toluene and 0.0003 g. of silica gel indicate a thickness of forty molecules for the adsorbed film, a result very closely agreeing with the other data. The curve (Fig. 6) bears a very marked resemblance to the curve for toluene vapor in an acid-treated bulb. These facts lead one to believe that it is not unreasonable to suspect that 0.0003 g. of silica may be formed on the glass by treatment with acids and water. In the case of the curve for nitromethane (Fig. 5) the similarity to that for the same vapor in an acid-treated bulb is not so clear; the adsorption of the vapor by the silica gel seems somewhat greater, especially at higher temperatures, than in an etched bulb, and also stronger than with toluene. It also seems from the curve that the silica gel was saturated with the nitromethane vapor just before condensation took place at the dew point.

It should be noted that this method does not and cannot show that there is no adsorbed film on fire-polished glass surfaces through the temperature range of 50 to 25°. It does, however, show that no additional adsorption occurs as the temperature is lowered—that is, none greater than a unimolecular layer. Calculation shows that adsorption of such a film causes a decrease in pressure within the bulb of from 0.01 to 0.04 mm., depending upon the vapor used. The pressure measurements made with the cathetometer were not accurate to more than 0.05 mm. Consequently, the method is not sufficiently sensitive to show the presence of a unimolecular layer but can detect anything essentially greater than that.

The Adsorption of Water Vapor upon Amalgamated Platinum and Silver Surfaces

After the conclusion of the adsorption experiments with glass surfaces, an attempt was made to prepare a plane metallic surface upon which the adsorption of water vapor could be studied. A platinum bulb upon the inner surface of which a film of mercury was deposited electrolytically seemed to offer hope of such a surface. Accordingly, such a bulb was prepared, similar in shape and size to those of glass already described. This bulb was sealed into a piece of clean soft glass tubing and was then filled with a solution of mercurous nitrate containing a few drops of nitric acid. Using the bulb as the cathode, the solution was electrolyzed by a current from two dry cells in series. Preliminary experiments had shown that upon clean platinum surfaces a thin mercury film could be deposited electrolytically and that this film would stay on during washing of the surface with water, subsequent drying and other handling incidental to preparing the bulb for measurements. When such a film attained greater thickness, it showed a marked tendency to break and to form globules of mercury which would fall off of the surface.

After electrolysis of the solution the bulb was carefully cleaned by washing repeatedly and gently with conductivity water. It was then dried at room temperature while it was evacuated for five hours and examined Its inner surface appeared to be evenly covered with a film of mercury. (The inside surface of the bulb was not polished but was used just as it came from the makers, with a somewhat roughened appearance. It was cleaned with hot nitric acid before deposition of the mercury film.) The bulb was at once sealed into the same apparatus used for the glass bulbs, all glass-blowing being done through phosphorus pentoxide. During sealing, the bulb was not allowed to become heated (the glass tube attached to the bulb made this possible).

Water vapor was admitted to the bulb so prepared (having previously been carefully freed from all traces of air). The measurements of pressure as the temperature was gradually lowered were made in the same manner as for glass bulbs. Necessarily this procedure required that a small portion of glass surface of the glass tubing connected to the bulb be exposed to the water vapor in order that the cathetometer could be used in reading the height of the mercury. The method used by McHaffie and Lenher in their work on platinum (that is, using a sensitive voltmeter and dry-cells connected to bulb and to mercury in the reservoir to indicate contact of mercury with the bottom of the bulb) was tried in this work but was abandoned because of troublesome sticking of the mercury when it touched the bulb, so that no dependence could be placed on this method of obtaining a constant level of mercury in the bulb.

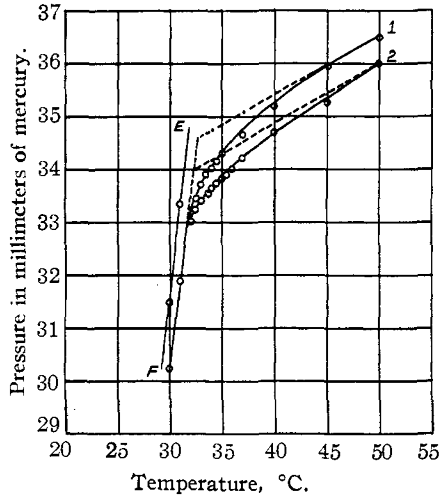

Fig. 7.

The data obtained during two runs using this apparatus and procedure are shown graphically in Fig. 7. Curve 1 was first obtained. The bulb was then evacuated, mercury was raised into it to fill it entirely for twenty-four hours, and after lowering the mercury out of the bulb again another sample of water vapor was introduced and a second run was made, with the results shown graphically in Curve 2 (Fig. 7).

It is evident from these curves that the mercury-platinum surfaces we are dealing with here adsorb water vapor strongly. The molecular thickness of the adsorbed film, calculated in the usual manner from Curve 1, is 28 molecules, and that from the second curve (2, Fig. 7) is 33 molecules. These two values may, on account of the approximate character of the calculations, be considered as a check.

It is interesting to point out here the fact that the parts of these curves which represent the vapor pressures of the condensed water do not coincide with the vapor pressure curve of water; the vapor pressure curve of water in this range is shown as EF, Fig. 7. This may be due to capillary effects in the surface or to the thin film of water, which would have a lower vapor pressure, as indicated in the experimental curves. These results obtained with amalgamated platinum are similar to those recently obtained by John William Smith, *J. Chem. Soc.*, 2045 (1928).

Having failed to obtain a plane surface with mercury-covered platinum, it was next decided to make a series of measurements with water vapor and a silver bulb upon the inner surface of which a film of mercury had been deposited as before. It was hoped that such a bulb would present a plane surface for the study of adsorption of water vapor. A silver bulb was prepared having a platinum band attached to its narrow neck so that it could be sealed into glass tubing and thus into the apparatus. The bulb, after careful cleaning by heating in a flame and repeated washing with conductivity water, was filled with a solution of mercurous nitrate as in the case of the platinum bulb and was used as the cathode while the solution was electrolyzed. The solution was renewed twice during electrolysis. The bulb was then carefully cleaned with conductivity water, dried at room temperature and evacuated for five hours. Upon examination the inner surface appeared to be evenly amalgamated. The bulb was sealed into the apparatus without becoming heated, and a run was made with it, using water vapor as the substance to be studied. The resulting curve is shown in Fig. 8.

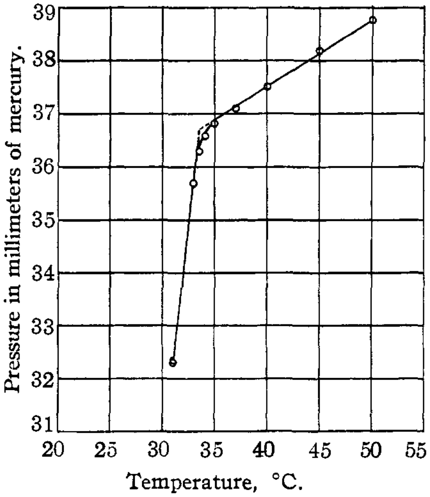

Fig. 8.

The upper part of this curve (that is, the curve for the pressure change with temperature for the water in the gaseous state) has the same slope as the theoretical value calculated for this amount of vapor from the gas laws and, as can be seen from the figure, is a straight line except for a very slight rounding off into the vapor pressure curve of the condensed vapor. This rounding off is, however, confined to the immediate temperatures at the dew point, and is very slight compared to the same phenomenon in the previous curves. Moreover, the slight adsorption may be explained by the fact that, as already stated, during the measurements a small amount of glass surface was exposed to the vapor as well as the silver amalgam surface. This was a necessary consequence of the way in which measurements were made. Moreover, this glass surface had been in contact with liquids and was undoubtedly not plane, so that it probably adsorbed vapor to the same extent that etched surfaces did in the previous work by McHaffie and Lenher, Frazer, Patrick and Smith and the author. If, then, the adsorption indicated in the curve (Fig. 8) is considered as upon the glass surface exposed only, calculation shows that the thickness of the adsorbed film upon the silver-mercury surface cannot be greater than unimolecular. If we are to consider that adsorption occurs only on surfaces that are not plane, then we are justified in considering the silver-mercury surfaces as plane, while those of platinum-mercury are not plane.

In conclusion, the author of this paper wishes to express his appreciation to Dr. J. C. W. Frazer and to Dr. W. A. Patrick who suggested this study and under whose direction it was performed.

Summary

1. The work of McHaffie and Lenher and of Frazer, Patrick and Smith has been continued, using various vapors and both glass and metallic surfaces.

2. Soft glass which has been thoroughly melted and cooled without coming in contact with anything except dry air may be considered as offering a plane surface for adsorption measurements, but acid-treated surfaces of such glass cannot be considered as plane from the standpoint of adsorption measurements.

3. The thickness of the adsorbed vapor film on fire-polished glass surfaces is not essentially greater than unimolecular for either polar or non-polar substances.

4. With acid-treated glass surfaces, the thickness of the adsorbed film appears to be about fifty molecules for both polar and non-polar substances investigated.

5. Platinum surfaces upon which mercury has been deposited electrolytically adsorb water vapor quite strongly. The thickness of the adsorbed layer appears to be approximately thirty molecules.

6. Silver surfaces amalgamated electrolytically may be considered as plane. The thickness of the film of water vapor adsorbed upon such a surface is never greater than unimolecular.

BALTIMORE, MARYLAND