

ASSOCIATION, ADSORPTION, AND DIELECTRIC CONSTANT

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ABSTRACT

Dielectric constant of water vapor at pressures 3 to 20 mm and at temperatures 23 to 165°C.—Using a heterodyne beat method previously described, a study has been made of the variation of the dielectric constant with pressure and temperature. At room temperature, the curve connecting $(\epsilon-1)$ with pressure consists of two straight parts connected by a transition curve. This change of slope is less marked at higher temperatures and disappears at about 47°C. The rectilinear portion below the transition pressure corresponds to the normal behavior of water vapor. The abnormal behavior above the transition pressure cannot be explained satisfactorily by the association theory suggested by Jona in connection with his results. It is suggested, rather, that the anomaly is due to the formation of an adsorbed layer of water on the condenser plates. As the number of adsorbed molecules increases, the vapor pressure increases, approaching the ordinary vapor pressure as a limit. The final thickness of the layer at saturation pressure is of the order of the radius of molecular attraction and comes out of the order of several microns, corresponding to about 200 molecular layers. The experimental results are in general agreement with this theory.

IN a recent series¹ of measurements of the dielectric constants of a number of dipole gases by the author, complete agreement with the Debye theory was obtained except for the possibility of very slight deviations in one or two cases. On the other hand experiments by Jona² showed marked anomalous increases of the dielectric constant near the liquefaction points of several vapors. SO₂ among others showed a considerable increase. More recent observations by the author did not show this effect. Jona attributed the effect to association of the molecules with an accompanying increase in the electric moment of the resulting molecule. On account of these apparent inconsistencies a more thorough investigation of this effect has been made both theoretically and experimentally.

ASSOCIATION AND THE DIELECTRIC CONSTANT

Debye's equation may be put in the form

$$(\epsilon-1) = N(a+b/T)$$

¹ C. T. Zahn, Phys. Rev. **4**, 400 (1924).

C. P. Smyth and C. T. Zahn, Journ. Amer. Chem. Soc. **47**, 2501 (1925).
And recent data on CO₂, NH₃, and SO₂ about to appear.

² M. Jona, Phys. Zeits. **20**, 14 (1919).

where ϵ is the dielectric constant, N the number of molecules per cubic centimeter, T the absolute temperature, a a constant representing the effect of molecular distortion, and b a constant proportional to the square of the molecular electric moment and representing the effect of molecular orientation. If the gas consists of a mixture of two kinds of molecules defined by N_1, a_1, b_1 and N_2, a_2, b_2 then

$$(\epsilon - 1) = N_1 a_1 + N_2 a_2 + (N_1 b_1 + N_2 b_2) / T$$

If these two types of molecules correspond to single and to double (associated) molecules and the law of additivity of refractivity be assumed; i.e., $a_2 = 2a_1$ then

$$\frac{\epsilon - 1}{N_1 + N_2} = (1 + c_2) a_1 + [1 + (r - 1) c_2] \frac{b_1}{T}$$

where $c_2 = N_2 / (N_1 + N_2)$, the concentration of double molecules and $r = b_2 / b_1 = \mu_2^2 / \mu_1^2$, the square of the ratio of the electric moments of the double and single molecules. As a first approximation it is assumed that the partial pressures of the two constituents can be determined from the ideal gas law which can be stated $p_1 = T N_1 / 273 N_0$ where N_0 is the number of gas molecules per cubic centimeter at 0°C and 760 mm Hg. Then

$$p = p_1 + p_2 = \frac{T}{273 N_0} (N_1 + N_2)$$

or

$$N_1 + N_2 = 273 N_0 p / T$$

and the modified Debye equation becomes

$$\frac{(\epsilon - 1) T}{273 N_0 p} = (1 + c_2) a_1 + [1 + (r - 1) c_2] \frac{b_1}{T}$$

or

$$\frac{(\epsilon - 1) T^2}{273 N_0 p} = (1 + c_2) a_1 T + [1 + (r - 1) c_2] b_1.$$

The concentration c_2 should be determinable from the thermodynamical consideration of equilibrium as Jona² has pointed out. According to Planck's³ expression for chemical equilibrium in gaseous systems

$$c_1^{v_1} c_2^{v_2} \dots = A e^{-B/T} T^C p^{-v}$$

or for the simple case of association

$$\frac{c_1^2}{c_2} = A e^{-B/T} T^C p.$$

³ Planck, Thermodynamik, 4 Aufl., 1913, § 241, p. 222.

It should be noted here that there is apparently a misprint in Planck's fourth edition at the top of page 223. The statement is made that the conservation of molecular heats requires that $\Sigma \nu_1 C_{p_1} = 0$. The correct statement should be $\Sigma \nu_1 C_{v_1} = 0$ which is equivalent to $\Sigma \nu_1 C_{p_1} = \Sigma \nu_1$. Accordingly in Jona's article, page 19, Eq. (9) should be $C = 1$ instead of $C = 0$. This introduces a factor of T which he left out. Even so the principle of conservation of molecular heats seem untenable in view of the equipartition theory. A single molecule of water should have about 6 to 7 degrees of freedom judging from the ratio of the specific heats of steam. According to the quantum theory this would correspond to three degrees of translation and three degrees of rotation completely established and a small amount of vibrational energy for which the classical value is only partially established because of the low temperature. Hence the double molecule would be expected to have about the same molecular heat as the single molecule unless a large amount of vibrational motion is set up at low temperatures. One would then expect C to be considerably greater than unity. C must then be regarded as an indeterminate exponent probably greater than unity. This may be responsible for Jona's lack of agreement for the quantity a/R with Sackur's value.

The fact that C is an indeterminate exponent shows that Jona's extended Clausius-Mossotti equation is not correct as it stands and also that any predictions about association from the variation of the dielectric constant with temperature will be very questionable. However, the latter equilibrium equation suggests an experimental test by the measurement of the variation of the dielectric constant with pressure as follows:

Since $c_1 = 1 - c_2$ the equation for c_2 may be written

$$\frac{c_2}{(1 - c_2)^2} = \frac{p e^{B/T}}{ATC}$$

which shows that c_2 is proportional to p approximately for small pressures and that as the pressure is increased, c_2 becomes less than would correspond to true proportionality. This implies that the curve of $(\epsilon - 1)$ plotted against p should be linear or slightly convex from above, and suggests a simple test of the theory, independent of the indeterminate exponent C of T . From the latter equation it should be expected that the association concentration is markedly greater at low temperatures. For this reason a series of measurements were made of the dielectric constant of water vapor varying both the pressure and the temperature. The apparatus outside the experimental condenser was at room tem-

perature so that the maximum pressure that could be used was about 20 mm, the saturation pressure at room temperature. The dielectric constant for these small pressures could be measured fairly accurately because of the large value of the electric moment of water. However, the results are chiefly of qualitative interest and no claim is made to the degree of accuracy obtained in the measurements of the halogen hydrides mentioned above. The method used has been described fully in the above mentioned article on the electric moment of the halogen hydrides. It is a heterodyne beat method using two radio-frequency electron tube generators.

MEASUREMENTS OF WATER VAPOR

Variation of dielectric constant with pressure. The first measurements were made by allowing almost the full saturation pressure of water vapor to be established in the experimental condenser. Then measurements were made at various pressures pumping out a small amount of water vapor between readings until finally a reading was made for vacuum. The process was repeated in the reverse direction in order to be sure that the effects obtained are reversible and reproducible. In all cases the readings could be reproduced faithfully. Such measurements were made with the experimental condenser at various temperatures, ranging from room temperature up to 165°C. For room temperature, 23.3°C, the data are plotted separately for the sake of clearness; the data for all the temperatures are plotted in Fig. 2. The most striking of all the curves shown is that corresponding to room temperature, 23.3°C, in Fig. 1. A close examination shows that it consists of two nearly linear portions separated by a short transition interval and is similar in appearance to an ionization potential curve. (It immediately suggests itself that the anomalous effect here represented might be the electrical analogy to the effect found by Glaser of pressure variation on the magnetic susceptibility. However, such an effect depends upon the mean free time between collisions, and it would not shift so rapidly with the temperature as is indicated in Fig. 1).

Variation of dielectric constant with temperature. If experimental points on the low pressure rectilinear portions of the various curves are used, it is found that within the limits of experimental error the values of $(\epsilon-1)T^2/273$ plotted against T give a Debye straight line which leads to a value of the electric moment of water vapor consistent with that found by Jona for steam consisting of single molecules. These values are plotted in Fig. 3. The dotted points correspond to values at 17.3 mm Hg, and the crossed points to values at the low pressures. The

two lower points on the Debye line are somewhat high, but this deviation might well be due to experimental error since, for the low pressures

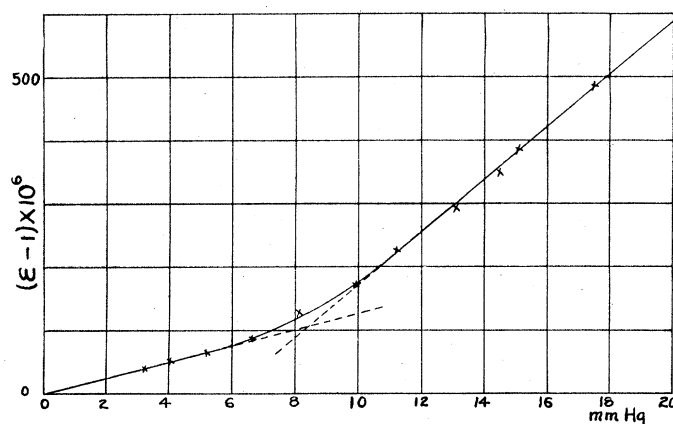


Fig. 1. Variation of $(\epsilon - 1)$ with pressure at 23.3°C.

to which these points correspond, the measured capacity change is very small.

It is therefore concluded that whatever the anomalous increase in ϵ is due to, it is practically absent on the lower portion of the pressure

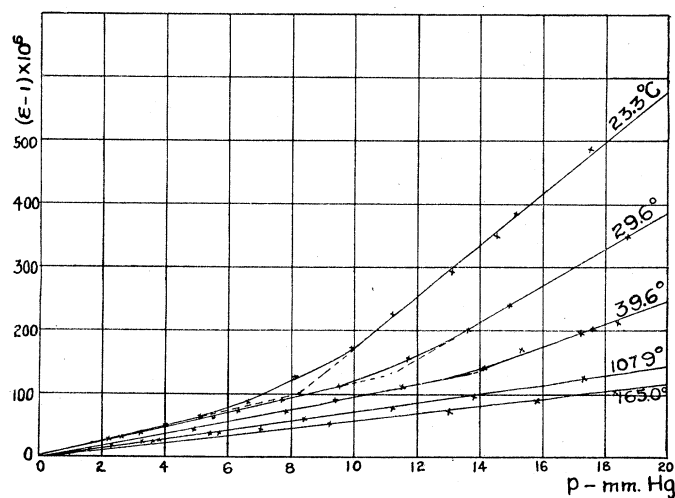


Fig. 2. Variation of $(\epsilon - 1)$ with pressure and temperature.

curves. The theory of association outlined above requires that the curve in $(\epsilon - 1)$ and p be rectilinear or slightly convex from above, whereas the experiment curve is decidedly concave. Hence Jona's explanation

by association into double molecules seems inadequate to explain these observations. One might explain the observed slope of the curve of Fig. 1 on the assumption of association into triple molecules in which case the equilibrium equation is

$$\frac{c_3}{(1-c_3)^3} = \frac{p^2 e^{B/T}}{ATC}$$

This would give a curve in $(\epsilon-1)$ and p concave from above, and the approximation to a straight line might be explained as due to a compensation of the increase in $(\epsilon-1)$ due to the term p^2 and the effect produced by the increasing importance of the expression $(1-c_3)^3$ as c_3 becomes large. Now vapor density measurements on water vapor preclude the possibility of association to any degree greater than a few percent at

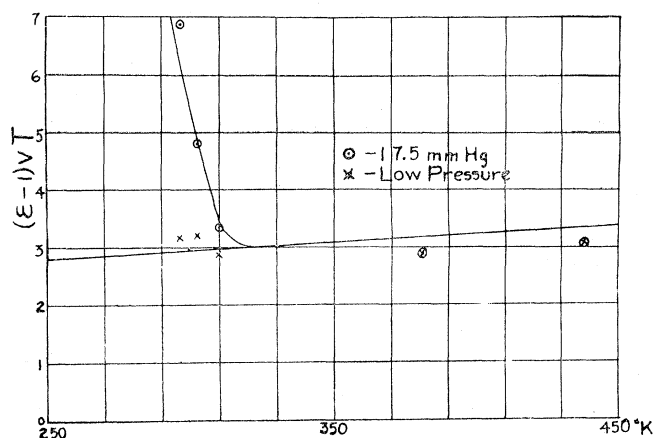


Fig. 3. Variation of $(\epsilon-1)T^2/273$ with temperature.

most, whereas if one assumes any reasonable value for the moment of the double or triple molecule (Jóna assumed that the moment doubled on association) it requires large percentages of association to account for the observed dielectric constants. For example, if one supposes the associated molecule to have four times the moment of the single molecule, it requires about 10 percent association. This fact makes the interpretation on the basis of association seem very doubtful.

SURFACE LAYERS AND THE DIELECTRIC CONSTANT

An alternative to the assumption of association is to suppose the effect to be due to adsorption of a layer of water on the surface of the condenser plates. It is a well known fact that the surface tension of films of water decreases when the film thickness becomes less than a cer-

tain minimum. This is explained by supposing that this minimum thickness is equal to the radius of the sphere of molecular attraction. When the thickness of the film becomes less than this radius the surface tension is less than the normal value because there are fewer molecules in the sphere of attraction. Accompanying this lower surface tension there is, therefore, a greater vapor pressure. If, however, the film is adsorbed on the surface of a substance such as a metal, which it wets (i.e. a substance having great attraction for the molecules) the reverse state of affairs should be expected. The sphere of molecular attraction for a molecule in the free surface of the film contains some of the metal molecules and consequently the attraction is greater than if it contained all water molecules. The surface tension should be abnormally high and the vapor pressure should be low since the increased attraction reduces the number of molecules escaping per second.

Condensation of this sort might be regarded as a limiting case of capillary adsorption where the curvature of the adsorbing surface vanishes. Capillary adsorption below the saturation pressure must be due to the fact that for great curvature of a surface the attraction for a molecule must be increased. There is fundamentally no difference in the two kinds of adsorption. The chief difference is that for a curved surface the adsorption forces are greater.

An upper limit to the thickness of such layers is the radius of the sphere of molecular attraction of the metal molecules for a water molecule, and should be of the order of magnitude found by Rucker for soapy water. Furthermore, the thickness of the film at saturation pressure should be equal to this limiting value. This thickness can be calculated approximately from the data of Fig. 1. Let t be the distance between the condenser plates and d the thickness of the adsorbed water layer (both plates). The experimental value of t was .05 cm. Hence d will be small compared with t . The apparent change in the condenser plate separation on the insertion of a slab of thickness d and dielectric constant K is $d(1 - 1/K)$ if the original dielectric constant is only negligibly different from unity. If K is large the apparent change is approximately equal to the actual thickness of the slab.⁴ Hence d/t is the apparent fractional change in plate separation. This must equal the apparent fractional change in ϵ over what it would be if the lower part of the curve of Fig. 1 were extended to the saturation pressure.

⁴ Possibly the dielectric constant of such a layer of water is different from the ordinary dielectric constant, but one would expect only a small difference. At any rate the importance of K is small. For $K=80$ as for ordinary water an error of only a little more than one percent is made in neglecting $1/K$.

In this manner d is found to be 1.65×10^{-5} cm. Since this includes the films on both plates the actual film thickness is 8.25×10^{-5} cm. This agrees very well with the minimum thickness of soap films of from 4.5 to 9.5×10^{-5} cm found by Rucker and Reinhold.⁵

The fact that the apparent radius of the sphere of molecular attraction is about 100 to 200 molecules long is not necessarily in contradiction with the fact that the force due to an individual molecule is not appreciable at distances farther than a few molecular diameters at most. In a substance like water, whose dielectric constant is very large, the field of force due to a single molecule should induce orientations in the surrounding molecules and this orientation in turn would set up an additional field for molecules farther out and so on. In this manner the force on a single molecule might depend upon induction effects which it produces many molecules away from itself. The distance at which this induction effect is inappreciable is to be regarded as the apparent radius of molecular attraction.

Consider now the phenomena which might take place as the pressure of the water vapor is increased from vacuum. Two types of adsorption might take place: first, the type where the molecules are held rigidly (similar to solid molecules); and second, the type where the molecules are free to move about and be oriented easily by an electric field (liquid molecules). So far as can be told from these measurements there may be no adsorption of the first type at all, and if there is any it seems probable from experiments⁶ on monomolecular oriented films that there is only one such layer. As regards the subsequent formation of liquid layers over this solid layer the solid layer would behave essentially as the metal, so that it will not be considered in what follows. Edser⁷ has shown that about 94 percent of the surface energy of a liquid resides in the first layer. Consequently after the formation of the first liquid layer on a metal surface the surface energy should be of the same order of magnitude as the normal liquid surface energy. Likewise the vapor pressure above this layer should be of the ordinary order of magnitude but somewhat less because of the increased attraction by the metal molecules. After this the change in pressure with thickness depends on the fact that as the film gets thicker the distance of the surface water molecules from the more strongly attracting metal molecules becomes greater. Conversely, as the vapor pressure increases from vacuum, a single liquid layer will be established only after the pressure has reached

⁵ Rucker and Reinhold, *Phil. Trans.* **177**, 2, 627 (1886).

⁶ See Taylor's *Physical Chemistry*, vol. I, p. 136.

⁷ E. Edser, 4th British Assoc. Report on Colloid Chemistry, p. 94.

a definite value somewhat less than the ordinary vapor pressure of water, but of the same order of magnitude. As the pressure is increased still further, the layers will form rapidly. As regards the electrical effect produced in the present measurements, the water would virtually start to condense at this definite pressure since the first layer would have a negligible effect on the apparent dielectric constant. Thus an explanation is given for the apparent critical pressure observed in Fig. 1. The general behavior of the curve is, then, qualitatively according to what would be expected.

SURFACE CONDENSATION AND KINETIC THEORY

So far the question of surface condensation has been regarded from the point of view of the properties of liquids. It was seen that the existence of a condensed surface layer in the liquid state is palusible from the properties of liquids. Such a condensed layer can also be predicted from the kinetic theory of gases in an interesting manner.

From Jona's work and the present data, water is known to have a large electric moment, 1.8×10^{-18} e.s.u. As such a molecule approaches a metal surface it will be attracted by electric induction which can be represented by the mirror image of the doublet in the surface of the metal.⁸ As a result of this attraction there will be an increased concentration of the molecules near the metal surface. The potential energy of a doublet inclined at an angle θ to the normal and at a distance x from the surface is by simple electrostatics

$$W = -\mu^2 \cos^2 \theta / 8x^3$$

Applying Boltzmann's theorem for the distribution of molecules:—

$$\begin{aligned} dn &= A e^{\mu^2 \cos^2 \theta / 8x^3 kT} \sin \theta d\theta \\ &= A e^{a \cos^2 \theta} \sin \theta d\theta \quad \text{where } a = \mu^2 / 8x^3 kT \end{aligned}$$

The total number of molecules per cc at a distance x

$$N_x = A \int_0^\pi e^{a \cos^2 \theta} \sin \theta d\theta = -2A \int_0^1 e^{ay^2} dy$$

For $x = \infty$, $a = 0$ and

$$N_\infty = -2A$$

$$\therefore N_x = N_\infty \int_0^1 e^{ay^2} dy$$

⁸ Richardson, Schottky, Langmuir, and Dushman have used this idea in relation to the work function for an electron leaving a metal surface.

or

$$p_x/p_\infty = N_x/N_\infty = \int_0^1 e^{ay^2} dy$$

where p is the pressure. This probability integral can be evaluated in series

$$N_x/N_\infty = \left[1 + \frac{a}{3} + \frac{a^2}{10} + \frac{a^3}{46} + \frac{a^4}{216} + \frac{a^5}{1200} + \dots \right].$$

The concentration N_x thus increases as the surface is approached. As the doublet approaches the metal surface to within distances of molecular magnitude, the above integral will not hold but will have to be replaced by some unknown function which includes the repulsive effects of the electronic orbits at collision. Then, assuming that a negligible amount of molecules penetrate into the metal lattices, N_x/N_∞ follows the above integral until the repulsive effects are appreciable after which it goes through a maximum and falls to zero at the point of nearest approach of the water molecules.

While the statistical equation cannot be applied for points very near the metal surface, it ought, nevertheless, to be possible to determine the order of the magnitude of the concentration produced by the adsorption forces. A limit will be set on x by the distance of nearest approach of the water molecule. If the metal molecule were fixed in space during a collision of the water molecule, this lower limit would be approximately equal to the molecular radius, but since the metal molecule must be moved in the direction of impact, this limiting value of x may be somewhat less than the molecular radius. Although the repulsive forces at collision change the shape of the actual curve for N_x/N_∞ the maximum value of N_x/N_∞ should be of the same order of magnitude as the value of N_x/N_∞ calculated from the probability integral for x equal to the distance of nearest approach.⁹ If it be supposed that condensation in more than a single layer cannot exist until the actual maximum value of N_x exceeds the ordinary saturation concentration, the order of magnitude of the distance of nearest approach can be calculated from the above integral. Setting p_x equal to the pressure plotted in Fig. 1, at the point where deviations become appreciable $N_x/N_\infty = p_x/p_\infty = p_x/p = 20.0/6.2 = 3.2$ approximately. The value of a corresponding to this value of N_x/N_∞ can be found by approximation to be about 2.5. Then x can be found from:

$$x^3 = \mu^2/8KTa$$

⁹ Cf. Langmuir's discussion of the work function for thermionic emission, Trans. Amer. Electrochem. Soc. **29**, 161 (1916).

taking $\mu = 1.8 \times 10^{-18}$, $K = 1.346 \times 10^{-16}$, and $T = 300^\circ\text{K}$. In this manner x is found to be approximately 2.2×10^{-8} cm, which is a little greater than the molecular radius of water.¹⁰ Hence the result is in good accord with the above considerations.

According to this view for any given value of pressure p_∞ the maximum value of N_x should be limited by the distance of nearest approach, or by the size of the molecule. In the above rough consideration the doublet was considered as concentrated at the center of the molecule. Now if the doublet is concentrated on one side of a molecule; i.e., if the molecular field is strongest on one side, the maximum value of N_x should be greater than if the doublet were concentrated at the center of the molecule. For example, such might be expected to be the case where there is an OH group in the molecule. In general the values of the critical pressure, shown in Fig. 1, for various substances might give qualitatively some knowledge of the distribution of the electric moment within molecules.

In a similar manner condensation should take place on dielectric surfaces. (The induced image is $-\mu(K-1)/(K+1)$ in this case.) There is in fact experimental evidence for this. Professor Menzies¹¹ gives a value of about a micron for the thickness of such layers on glass. In the case of glass, complications are introduced by solution in the alkali constituents of the glass. This process should be slow. Menzies' results show a change in absorption with time, which is in accord with the supposition that there are both an "instantaneous" effect like that for a metal surface and a volume absorption which takes a long time to reach equilibrium.

CONCLUSIONS

The results of the experiments here described are of interest from the points of view of both the dielectric constant and adsorption. The apparent anomaly in the behavior of the dielectric constant of water vapor is probably not due to association as supposed by Jona, but to surface condensation produced by molecular attraction. Probably all of the anomalous values of dielectric constant measured by Jona are due to this surface condensation. If the deductions of the foregoing discussion on surface layers are correct, these anomalies could be avoided by measuring dielectric constants only at pressures below the critical condensation pressure, which could be found experimentally. (This will probably depend considerably on the particular metal used

¹⁰ Kaye and Laby, *Physical and Chemical Constants*, p. 35.

¹¹ A. W. C. Menzies, *Jour. Amer. Chem. Soc.* **42**, 10, 1952 (1920).

for the condenser plates.) The difference between the author's measurements on SO_2 , etc., and those of Jona may be due to different surface conditions of the condenser plates.

The properties of the adsorbed liquid layer of water postulated above may be summarized as follows. As the number of adsorbed liquid molecules approaches the number corresponding to a mono-molecular layer, the vapor pressure rises rapidly until it reaches a value somewhat less than the ordinary vapor pressure of water. After this, as the number of molecules increases, or as the thickness of the film increases (since now there are many layers), the rate of change of pressure with thickness drops rapidly to a final constant value (Fig. 1).

If n be the number of adsorbed molecules and p the vapor pressure, then as p increases to the ordinary saturation pressure n will first increase to the negligibly small number in a monomolecular layer while p increases to a virtual critical value less than the ordinary vapor pressure. Then as p increases further n increases rapidly reaching a uniform rate of increase just above the critical pressure. Correspondingly dn/dp is practically zero until the critical pressure is reached, after which it rises rapidly to a constant value which it retains up to the final saturation point. The final thickness of the layer is of the order of several microns, which corresponds to about two hundred molecular layers.

In conclusion the author wishes to express his indebtedness to Prof. K. T. Compton for his valuable advice and criticism in this investigation.

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