JANUARY, 1929 *PHYSICAL REVIEW* *VOLUME 33*

AN OPTICAL STUDY OF ADSORBED FILMS

BY J. H. FRAZER

ABSTRACT

The optical method of Rayleigh and Drude for the study of surface "transition layers" (Uebergangsschichten) has been experimentally modified so as to give greater accuracy, and has been applied to the study of adsorption on glass. Various substances were investigated, and of these only two, water and methyl alcohol, showed definite adsorption. Curves for these, plotting thickness of adsorbed layer against partial pressure, are given. Up to 5 or 6 mm pressure there is no detectable adsorption of water vapor (apart from the probable presence of the first mono-molecular layer). From then on there is a cluster formation which results in a gradual covering of the surface until at 12.5 mm pressure there is another mono-molecular layer present. Above 13 mm there is strong condensation. The results for methyl alcohol were similar. Adsorption began at 30 percent saturation and continued linearly up to 90 percent saturation pressure, when strong condensation set in. It is pointed out that the method is applicable to the study of surface conditions at the interface between any two phases.

A METHOD for detecting adsorbed films was sought which should be free from the objections which obtain in the case of the previously used methods. These methods are:

(a) *Langmuir's method.* In this method a known quantity of the gas to be adsorbed is contained in a bulb of known volume, this bulb being connected by an initially closed stop-cock with a second bulb, also of known volume in which there is contained a large bundle of the surfaces on which the adsorption is to take place. When the stop-cock connecting the two bulbs is opened, the gas expands, filling both bulbs, and from a knowledge of the original pressure and the volume of each bulb, the pressure which should be finally established can be calculated by Boyle's Law. Any decrease in the observed pressure below the theoretical will then be accounted for by adsorption on the adsorbing surfaces and walls of the second bulb. To eliminate this second factor, an exactly similar run is made, but without the adsorbing surfaces. The difference between the adsorption observed in two cases is, then, that due to the adsorbing surfaces. This method can only be used at pressures far below saturation, since at the higher pressures the pressure change is so small, compared with the total pressure, as to be completely masked.

This constituted one objection for our purposes; a second being that we wished later to study adsorption on surfaces available only in rather restricted areas.

(b) The method of Frazer and Patrick, which takes the pressure-temperature curve of the adsorbed gas in a bulb of the adsorbing material around saturation pressures, the degree of rounding off of this curve on passing from the Charles Law curve to the vapor pressure curve determining the amount of adsorption. This method is limited in that it is restricted to a region close to saturation (it could not detect adsorption below one molecular layer) and as in Langmuir's method, by the large surface required and by the long time necessitated to make measurements.

Since it was desirable to make measurements right up to saturation pressures, and since sometimes only small areas of adsorbing material were available, a method was sought which should fulfill the following requirements: (a) It must be applicable at all pressures; (b) It would be highly desirable to have it applicable to small surfaces of adsorbing material; (c) It should be accurate to at least 1 A.U.; (d) It must be workable in a reasonably short time.

A method fulfilling these requirements was found in an optical method, the theoretical foundations of which were laid by Drude,[1] and which was first applied by Lord Rayleigh.[2] It has since been used by Raman and Ramdas,[3] recently by Ives and Johnsrud,[4] and very recently by Ellerbrock.[5]

The theory of the method is as follows: When light, polarized at 45° to the plane of incidence, falls on a perfectly abrupt boundary between two media at the polarizing angle, the reflected beam should be completely plane-polarized at right angles to the plane of incidence. Experimentally, when light, under these conditions, is reflected at the polarizing angle from any surface whatsoever, it is observed that these conditions are not quite strictly fulfilled. There is always a slight ellipticity to the reflected beam, the major axis of the ellipse lying perpendicular to the plane of incidence. Drude explained this theoretically by assuming that the transition from the refractive index n_1 of the first medium to the refractive index n_2 of the second medium is not abrupt as required by this elementary theory, but is gradual, passing over continuously from one medium to the other. This region in which the refractive index is gradually changing is called "a transition layer." The formula that he gives is as follows:

$$\rho = \frac{\pi}{\lambda}\left(\frac{\epsilon_1 + \epsilon_2{}^{1/2}}{\epsilon_1 - \epsilon_2}\right)\int\frac{(\epsilon - \epsilon_1)(\epsilon - \epsilon_2)}{\epsilon}dz$$

where ρ is the observed ellipticity, ϵ_1 and ϵ_2 the refractive index of the 1st and 2nd medium, ϵ that of the transition layer, λ is the wave-length of the light used, and Z the position in the transition layer, measured from the junction of the transition layer with medium number two. Experimentally, the effect is detected as follows:

The incident light, plane polarized at 45° to the plane of incidence, is reflected at the polarizing angle, and the analysing nicol set to the minimum, which is different from zero because of the ellipticity. A Babinet compensator

---

[1] Drude, Lehrbuch der Optik.

[2] Rayleigh, Phil. Mag. [6] **23**, 431 (1903); [5] **33**, 1 (1800); [6] **16**, 444 (1896).

[3] Raman and Ramdas, Proc. Royal Soc. **A108**, 561 (1925).

[4] Ives and Johnsrud, Journal of the Optical Soc. **15**, 374 (1927).

[5] Ellerbroek, Arch. Neerland, Sci. III **A10**, 42–90 (1927).

is introduced, the ellipticity of the reflected light compensated, and the ratio of the maximum to the minimum, the ρ of Drude's formula determined. Ellerbroek could determine an adsorbed layer of about 1 A.U., corresponding to a displacement of his compensator of about 0.001 mm, but he trusts his readings only to 0.01 mm displacement of the compensator.

In the present work, the following changes were introduced: (1) A Point-o-lite lamp was used, which was steadier and more convenient than the sunlight used by most previous investigators. (2) Instead of compensating the ellipticity of the reflected light, as has been done previously, we find the ellipticity by measuring the ratio of the two axes of the ellipse photometrically. This is done by using unpolarized incident light and analyzing the reflected light with a nicol prism which was set first in, and then perpendicular to, the plane of incidence (maximum and minimum of light intensity). The maxima and minima so transmitted by the nicol were measured photometrically, and their ratios were the ellipticity.

The advantages of our method were: (a) Greater sensitivity. Whereas Ellerbroek claims only 10 A.U., our probable error was less than 3 A.U. (b) Greater simplicity. By measuring the ellipticity photometrically, we have dispensed with the Babinet compensator and with the polarizing nicol. This simplifies the operation very much, since photometric readings are much easier to make than adjustments of a Babinet compensator. (c) Our set-up is considerably less expensive. The Babinet compensator is a highly specialized and very expensive piece of apparatus, whereas a very good photometer can be made easily.

An optical bench holding the Point-o-lite optical set-up, condensing lenses, and collimating lens was mounted on a divided circle over the axis of which the reflecting specimen was placed. The analyzing nicol and photometer were mounted on another table, far enough away from the rest of the apparatus to eliminate stray light. In operation, the procedure was to find the polarizing angle, set the analyzing nicol to the minimum, read the photometer, set to the maximum, read again, and the square root of the ratio of intensities so found was the ρ of Drude's formula.

The photometer deserves special mention. It was of the type in which the field is split by a 45° mirror, the mirror reflecting the light from a ground glass illuminated by the photometer light, the light to be measured passing by the edge of the mirror. The comparison was obtained by adjusting the distance of the photometer light from the ground glass. The photometer lamp itself was a small flashlight bulb, run at a constant current somewhat below its rated capacity to reduce the danger of burning it out. In some cases screens, transmitting a known percentage, had to be introduced in order sufficiently to reduce the intensity. These screens were calibrated on the instrument itself. The readings taken were the simple inverse of the photometer lamp distances, since it was the amplitudes which were desired. The absolute value of the readings were of no importance, since the ellipticity appears as the ratio of two readings. The following presented itself as a very serious experimental difficulty. Since the reflecting surface was rarely optically flat, the half of the field illuminated by the light to be measured differed so in texture from the comparison field, that no match was possible. A timely suggestion of Professor Pfund's eliminated this entirely. The light beam, after reflection and passage through the nicol, was brought to a focus on a piece of lightly ground glass by a good achromatic lens. A similar lens was placed at its principal focal distance from the illuminated spot, and the parallel beam of light so formed was extremely uniform and could be matched with ease.

The sources of experimental error in this method are as follows: (a) A possible error in the determination of the polarizing angle; (b) A possible error in the setting of the analyzing nicol prism; (c) Possible double refraction of the glass window through which the light had to pass after reflection in the case of the vacuum work; (d) The error in the photometric measurements.

If we take Drude's equations

$$\frac{R_p}{E_p}=\frac{\cos\phi(\epsilon_2)-\cos\chi(\epsilon_1)^{1/2}+i(2\pi/\lambda)\left[p\cos\phi\cos\chi-(l-q\epsilon_2\sin^2\chi)(\epsilon_1\epsilon_2)^{1/2}\right]}{\cos\phi(\epsilon_2)^{1/2}+\cos\chi(\epsilon_1)^{1/2}+i(2\pi/\lambda)\left[p\cos\phi\cos\chi+(l-q\epsilon_2\sin^2\chi)(\epsilon_1\epsilon_2)^{1/2}\right]}$$

$$\frac{R_s}{E_s}=\frac{\cos\phi(\epsilon_1)^{1/2}-\cos\chi(\epsilon_2)^{1/2}+i(2\pi/\lambda)\left[l\cos\phi\cos\chi(\epsilon_1\epsilon_2)^{1/2}-p+l\epsilon_2\sin^2\chi\right]}{\cos\phi(\epsilon_2)^{1/2}-\cos\chi(\epsilon_1)^{1/2}+i(2\pi/\lambda)\left[l\cos\phi\cos\chi(\epsilon_1\epsilon_2)^{1/2}+p-l\epsilon_2\sin^2\chi\right]}$$

and introduce a variation, α, in the setting of the nicol prism, and a variation, β, in the setting of the polarizing angle, we obtain the following formula expressing the dependence of the observed value of the ratio $(R_s/R_p)_{\text{obs}}$ on these two quantities

$$(R_s/R_p)_{\text{obs.}}=(R_s/R_p)(1+\beta+\alpha)$$

This formula is correct except for a function of the refractive index which would not change the expression markedly, and for higher powers of α and β. From this we see that an error of 0.01 percent, which means a variation in either of these two quantities of 0.3° means an error in R_s, and consequently in ρ, since the maximum is not appreciably affected, of about 10^{-4}, and this is about the limit of the accuracy with which the photometric measurements can be made.

Now a change of 10^{-4} in ρ means, in dealing with water layers on glass, a change in the adsorbed layer of 0.3 A.U. Accordingly this is the limit of accuracy obtainable in this case. It is interesting to note that in the case of the setting of the polarizing angle, and also in the setting of the nicol prism, it was observed experimentally that the calculated allowable deviations experimentally produced no change in the reflected intensity.

The lowest mean deviation in the photometer settings which could be obtained at these low intensities was from 1 to 2 percent. Accordingly groups of 6 to 12 settings were averaged together. These groups showed mean deviations less than 1 percent, and it is believed that they are accurate to 1 percent. It is the group of 6 to 12 settings which will hereafter be referred to as a reading.

In order to test for the possible double refraction of the glass window, a specimen was taken which showed a very good minimum, and its ellipticity was determined in the apparatus and in air. This was repeated several times and, in all cases, the results were smaller than the experimental error.

PREPARATION OF ADSORBING SURFACES

Various methods of obtaining good glass surfaces were tried. Polishing seemed too tedious a process, and the contact with the abrasive would have left the glass in a doubtful condition. Thin blown pieces of glass showed a fair surface condition, but difficulty was experienced in eliminating the reflection from the back surfaces. Glass exposed to a flame showed a very bad surface condition. Finally, on a suggestion of Professor Pfund's,the glass was cracked in the following way. A piece of plate glass was scratched at its edge for about an inch, and a crack started. Then a steady pull at the cracked edge would produce a break which would be sometimes, over areas as great as 1/2 cm^2, almost as good as plate glass. Numerous pieces of glass cracked in this way showed consistent small ellipticities of about 0.01. Expressed as a transition layer, this would mean a layer about 30 A.U. thick. To calculate this value, we considered the region or layer occupied by the hills and depressions of the glass surface as a region with a statistical refractive index approximately the average of the refractive index of the glass and air. This is legitimate since the irregularities here considered are small in comparison with the wave-length of light. The ellipticity of the light reflected from a piece of glass broken in air in this way showed no change with time, and also showed no change on being placed in a fairly good vacuum (10^{-6} mm) on a McLeod gauge. A piece of glass could be allowed to stand exposed to the atmosphere for as much as two days without showing appreciable change, and could probably have remained longer, although this was not tried. One experiment was tried in which it was attempted to crack the glass in a vacuum, and the value of the ellipticity so obtained was not changed on admitting air to within the experimental error, which in this case, however, was rather large, due to the bad surface produced because of a lack of technique for cracking the glass in vacuum. In any case, the hot wire used to crack the glass probably evolved enough gases to vitiate the experiment. The reason for mentioning this is that Dr. Langmuir, with whom we had the opportunity of discussing the subject, believes that in all the following work there is already present a mono-molecular layer of water held very tightly by the secondary valence bonds of the various constituents of the glass, and that whatever adsorption we observe would be a second or subsequent layers.

ADSORPTION

Previous theories. Langmuir had suggested in contradiction to previous theories, especially of Polanyi, that only mono-molecular layers of gases were adsorbed below the saturation point. His experiments on the adsorption of nitrogen, oxygen, methane and carbon monoxide on glass and mica confirmed this view.

The same result follows from the experiment of Frazer and Patrick, who took the pressure-temperature curve of a volume of water vapor enclosed in a freshly blown glass bulb.

They showed that there was no rounding off of the curve such as would have been caused by adsorption of considerable amounts of water, but, that in passing from the Charles law to the vapor pressure curve, they pass not to the vapor pressure curve of pure water, but to a somewhat lower vapor pressure. They attributed this to a solution in the water of the alkali from the glass, and actually succeeded in titrating the amount of this alkali present, and determining the concentration of alkali necessary to produce the vapor pressure lowering below that of pure water which they observed. This work was all done with freshly blown glass surfaces, always protected from exposure to water vapor. However, the situation was quite different when these surfaces were allowed to stand in contact with water vapor for any length of time. Under these circumstances, the curve showed considerable rounding off on passage from the Charles Law to the vapor pressure curve, and consequently considerable adsorption. But correlative with this activation of the glass, it was shown that sufficient alkali had been dissolved from the glass to turn phenolpthalein pink, and these results seemed to indicate that the activation consisted in dissolving the alkali from the complex silicate of the glass, leaving there something analogous to silica gel, which readily adsorbs great quantities on account of its large surface.

Investigations with the new method. The first results obtained were those on water vapor. If water vapor be admitted to a specimen of glass standing in vacuum, there is no observable change in the ellipticity until pressures of around 6 mm are reached. From then on the ellipticity increases almost linearly with the pressure, until at about 12.5 mm pressure there is a sharp discontinuity, the curve from then on again increasing almost linearly with the pressure, but much more sharply than before. The calculated film-thickness at which this break occurs is about 3.0 A.U. At any stage in this process, the system can be re-evacuated, and the adsorbed film, as measured by the ellipticity of the reflected light, can be completely removed; the ellipticity can be returned to its original value. More than this, the thickness of film is a function only of the pressure, and not of the past history of the specimen. The time taken to establish equilibrium at any value of the pressure, either ascending or descending, is certainly less than the time required to read the instrument, and this was, on an average, about 3 min.

It follows, therefore, that up to 5 or 6 mm there is no detectable adsorption (apart from the probable presence of the first mono-molecular layer). From then on there is a cluster formation which results in a gradual covering of the surface until at 12.5 mm pressure there is another mono-molecular layer present. Above 13 mm there is strong condensation. That this occurs below saturation pressure of 18 mm is accounted for on the basis of Frazer and Patrick's work as a hydration of the glass by the first layer of water, and a consequent lowering of the vapor pressure of the water by the dissolved alkali. However, one objection at once comes to mind in that, if the system is again exhausted, the water can be removed from the glass completely, restoring the ellipticity to its original value. This would indicate that the alkali recombined with the glass. An attempt to test the existence of a possible decomposition of the glass was made in the following way:

Water vapor was admitted which contained a small percentage (about 1 percent) of hydrochloric acid gas. When it was attempted to pump off this layer, it was found that there remained a residual ellipticity, indicating about 9 A.U., which could not be removed by any amount of pumping. It is thought that the hydrochloric acid combined with the alkali of the glass leaving a film even when all the water was pumped off. It is realized quite well that this is open to the objection that possibly the hydrochloric acid produced the decomposition instead of rendering permanent an already produced decomposition. However, it is an indication.

The second substance tried was methyl-alcohol, which showed in general the same type of curve showed by water, namely a linear increase in ellipticity starting in roughly at about 30 pecent saturation pressure, and continuing up to within about 90 percent of saturation. Then there was an abrupt break in the curve, the ellipticity from this point on increasing very rapidly. It is not quite understood what the significance of these results is. The break occurred at about 9 A.U., a value considerably larger than the normally accepted value for the size of a methyl-alcohol molecule. However, it must be remembered that if there is any asymmetry of the molecules they will, under these conditions of adsorption, orient themselves with a long axis perpendicular to the glass surface. A second fact which is hard to understand is the presence of the steep part of the curve indicating either a large amount of adsorption, very near saturation, or a double decomposition of the glass of the same type as that occurring with water and glass. Subsequently, this will have to be tested for. The curves and data for these two substances are presented in Figs. 1 and 2.

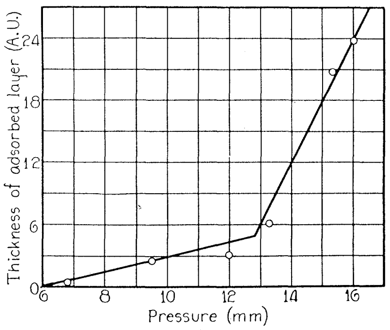

Fig. 1. Adsorption of water vapor on glass.

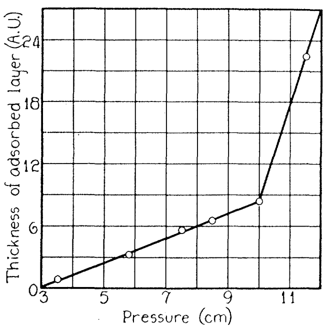

Fig. 2. Adsorption of methyl alcohol vapor on glass.

Other things were tried, and in all cases except one they were selected because of a high value of their dielectric constants, but in all cases the results were negative. In fact, it was even impossible to force these substances to condense on the glass at saturation pressures. The substances falling in this class were nitromethane, acetone, toluene, and formaldehyde.

This method enjoys a distinct advantage over other methods in that it is possible to detect, by its use, adsorption at the boundary of any two phases, and is not necessarily restricted to the solid-gas interface. One experiment was tried to detect adsorption at a solid-liquid interface. The light was reflected from a piece of heavy lead glass immersed in a light gasoline previously purified by the department of organic chemistry. The ellipticity was measured and then a small quantity (about 2 percent) of oleic acid was added. The polarizing angle was then redetermined, since the oleic acid added changed the refractive index of the gasoline. The observed change inellipticity was about 0.0005, which means a layer of about 4.5 A.U.

The author wishes gratefully to acknowledge the timely assistance of Professor A. H. Pfund in the optical set-up; and wishes also to express his indebtedness to Professor K. F. Herzfeld, who suggested the problem, and supervised its growth and completion.

THE JOHNS HOPKINS UNIVERSITY,
June, 1928.