Adsorption of water vapour on solid surfaces

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An experimental study has been made of the adsorption of water vapour on solid surfaces. Two methods are used, the first a direct weighing of the adsorbed film on a microbalance and the second an examination of polarized light reflected from the surface. Both methods agree and show that, for the surfaces examined, the adsorption of water at vapour pressures near saturation corresponds only to about two molecular layers. The experiments suggest that the heavy adsorption, which has been previously observed and which has been quoted as evidence for long-range surface effects, is due to contamination.

The adsorption of water vapour on solid surfaces as recorded in the literature appears to be much heavier than we should expect. Adsorbed films of more than 100 Å in thickness have frequently been reported. For example, Stromberg (1930) using a microbalance to determine the adsorption of water on surfaces of quartz, platinum and gold found that the adsorption was heavy and for platinum varied from 60 molecular layers at a pressure of 0.8 of saturation pressure, to 100 layers at a relative pressure of 0.9. McHaffie & Lenher (1926) measured the adsorption of water on platinum by a gasometric method and found that the adsorption was not detectable by their apparatus at pressures below 0.8 of the saturation pressure, but increased sharply at relative pressures above 0.9 until it corresponded to a layer 30 molecules in thickness near to saturation. Barrett (1933) measured the increase in weight of a disk of gold exposed to water vapour and found it to be very large (equivalent to more than a hundred molecular layers) with correspondingly large heats of adsorption. He suggested that the results might be due to diffusion into the bulk of the metal rather than to true adsorption.

There is a great deal of work dealing with the adsorption of water on glass surfaces (from Faraday 1830 to Veith 1944) which indicates that the adsorbed film can be up to 1000 Å in thickness. It is well known, however, that the true surface area of glass can be greatly increased by the ordinary chemical cleaning techniques (Razouk & Salem 1948). The figures already quoted for adsorption on metals are also subject to some reduction when we make allowance for the differences between true and apparent surface areas, but the change in this case is less and not sufficient to reduce the results to conformity with the general picture of adsorption. It has been established by several independent methods (see, for example, Bowden & Rideal 1928, and Rhodin 1950) that the real area of a rolled metal surface, not subject to special preparation or attack, is between one and three times the apparent area. Even then, if all the values are reduced by two-thirds the results would still point to adsorption, the extent of which is to be reckoned in tens of molecules rather than single ones.
A review of the evidence in favour of 'long-range' surface effects has recently been given by Henniker (1949) and by McBain (1950). Some of the work quoted (for example, that of Eversole & Lhar 1941, and Deryagin 1933) is taken to suggest that water and other pure liquids in contact with solid surfaces possess a high viscosity or a 'rigidity' which is induced by the surfaces and which extends to a distance of many hundreds or even thousands of Ångstroms. These results and the heavy adsorption from the vapour are both explained by supposing that the effect of the surface is 'relayed' through successive molecular layers to a very great distance.

It is difficult, on general grounds, to account for these effects and much of the evidence is open to criticism. Measurements of the viscosity of thin films of water, of alcohol and of other liquids enclosed between flat surfaces of metal and of glass (Bastow & Bowden 1931, 1935) have shown that the liquid films obey Poiseuille's law, and their viscosity is normal down to a thickness which is limited only by the degree of polish of the surfaces. It is only when the liquids contain a small amount of dissolved impurity, such as ammonium oleate, that anomalous viscosities are observed. Courtney-Pratt (1950) working in this laboratory, has made a direct optical measurement of the thickness of the film left behind on a mica surface by the retraction of a drop of liquid stearic acid and has shown that it is unimolecular.

The two experimental methods which will be described in this paper agree with one another, and both suggest that the apparent heavy adsorption of water is spurious and is due to contamination. With clean surfaces the adsorption of water vapour is similar to that of organic vapours and shows no anomaly.

**Experimental**

(1) *The microbalance*

The method of weighing was chosen for measuring the adsorption since it is a direct one. Figure 1 illustrates the balance in its containing tube, with foil and counterweight in position. The weighing was done magnetically by varying the magnetic field on a piece of high permeability alloy (mumetal) sealed in the beam as suggested by Mitchell (private communication in 1948). A quite small field, of about 5 oersteds, was sufficient to magnetize the numetal to saturation, and it was then possible to obtain a linear relationship between the torque and the current producing the vertical component of the field. The mirror on the beam was used in conjunction with an auto-collimating telescope of 40 cm. focal length for following the deflexion of the beam. The actual weighing was performed by measuring the additional small current through the deflecting coils which was necessary to compensate for changes in the load. An advantage of the magnetic system of control is that the calibration depends only on the properties of the magnetic material sealed in the beam and not on the load on the balance. Thus, although a change of load did, in general, alter the sensitivity of the balance, the calibration in terms of current against weight increase was unaffected provided that the arms of the balance remained of the same length. The balance tube and the field coils were contained in an air thermostat which provided temperatures in the range...
20 to 45°C. The tube was connected to a pumping unit and was evacuated to a pressure of $10^{-5}$ mm. before adsorption measurements were begun. The vapour of the substance under examination was then admitted, its pressure being controlled by the temperature of a reservoir containing the liquid.

The metal foils used in these experiments (area 20 sq. cm.) were prepared from spectrographically standardized metals and rolled to a thickness of 0.0005 in. This operation was carried out between clean rollers without the use of a lubricant so as to avoid gross contamination. The specimens were cleaned by degreasing in a still with pure benzene.

In the first series of experiments the foil was baked out on the balance during the preliminary evacuation by means of a heating coil surrounding the tube, the field coils being removed. The balance and its load could be heated to 300°C in this way. It was later considered desirable to provide a more effectual means of cleaning the surface. An arrangement for heating the foil in situ by electronic bombardment was therefore installed. Its construction is shown in figure 1. It consists essentially of diode valve, the specimen forming the anode. In use the foil was made to rest on the anode frame, an additional magnetic field being applied to the balance for the purpose, and the filament and anode supplies (600 V a.c. for the latter) were switched on. A rectified current of some 20 mA. raised the foil to a red heat in a few seconds. While the apparatus was cooling before the adsorption measurements, any oxide film which normally exists on the metal surface would, no doubt, tend to re-form even at the very low pressure of oxygen in the apparatus, and the adsorption measurements, as before, would refer to the oxide-covered surface rather than to a perfectly clean one.

The organic substances used for adsorption were of A.R. quality and were dried before use.
Results

Measurements were made of the adsorption of water vapour and, for purposes of comparison, of a number of organic vapours. The results for ethyl alcohol and for furfural on gold foil are shown in figures 2 and 3. They are of the usual S-shaped form and indicate that the adsorption, even at pressures approaching saturation, does not correspond to more than a few complete molecular layers. It is generally accepted (Brunauer 1945) that on an isotherm of this type, adsorption equivalent to a completed monolayer occurs at the beginning of the almost linear portion of the curve (point $B$). Comparison of this with the calculated amount (point $A$)

![Figure 2. Ethyl alcohol on gold at 32·5° C. $\bigcirc$, first run; $\bullet$, second run; $\square$, desorption.](image1)

![Figure 3. Furfural on gold at 25° C.](image2)

indicates that the true surface area of the foil was about three times the geometrical surface. The calculations are based on the assumption that the adsorbate has approximately the same effective closeness of packing on the surface as in the bulk liquid. The vertical dotted line indicates the saturation pressure.

With water vapour, however, on foil which had not been baked at a temperature higher than 300° C, the results were very different. The isotherms, though still S-shaped, were much less reproducible and indicated adsorption nearly ten times as large (figure 4). Similar results were obtained for the adsorption of water vapour on platinum foil. Here also the organic vapours were adsorbed only to a modest extent by comparison.

When the arrangement for bringing the foil to a red heat was brought into use a most pronounced difference resulted. The adsorption of water vapour became
no greater than the adsorption of organic vapours (figure 5). Under these circumstances the adsorption on the counterweight, which could not be heated, would presumably become comparable with that on the foil instead of about 1% of it as hitherto. For this reason the recorded values may be too low. It is clear, however,

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**Figure 4.** Water on gold not strongly heated. O, first run; ●, second run; △, third run.

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**Figure 5.** Water on platinum. a, not strongly heated; b, made red-hot before adsorption.

... that when the foil has been made red-hot during the preliminary outgassing process and is then allowed to cool, it will no longer take up water equivalent to tens of molecular layers. The adsorption of organic vapours, on the other hand, was not markedly affected by this treatment. Figure 6 shows the adsorption of ethyl alcohol on platinum which had been heated *in vacuo*. Some samples of gold foil, cut from a different roll, were found to adsorb water to quite a small extent even without special treatment.
When plane-polarized light falls on a transparent isotropic substance with a perfectly clean, sharply defined surface, the reflected light is plane-polarized also, and its azimuth is related to that of the incident light in a manner which can be calculated from the Fresnel coefficients. If the boundary between the two media is not sharply defined, however, or if the surface material differs from the substrate, the reflected light is elliptically polarized and cannot be completely extinguished by an analyzing prism. Opaque reflectors yield elliptically polarized light even when clean, and the effect of a surface layer in this case is a change in the ellipticity. The relationship between the optical constants of the surface layer and the nature of the reflected light was deduced by Drude (1889, 1902), who showed that measurements of the ellipticity could be used to provide an estimate of the thickness of the layer.

The method has been frequently used for the study of films produced by superficial oxidation and tarnishing. It has not been used much for physically adsorbed layers because these are usually so thin that the apparatus has to be worked near the limit of its sensitivity. Frazer & Herzfeld (1929), in measuring adsorption on rock-salt, overcame this difficulty by employing a photometric method in place of the usual compensator to measure the ellipticity. This arrangement considerably improved the sensitivity, but is only applicable to transparent reflectors. For the work described here, using metallic reflectors, the necessary degree of sensitivity was obtained by subjecting the incident light to eight reflexions (figure 8) multiplying the effects eightfold. Figure 7 shows the system set up for a single reflexion. For the eight reflexions the collimator was displaced sideways and set to parallelism with the viewing system by the aid of a glass rhomb.

The compensator consisted of a mica plate of known retardation which could be rotated in a divided circle. It was followed by an analyzing prism with half-shade devices sensitive to ellipticity and to inclination of the polarized light. In use, the plate was rotated until plane-polarized light was restored and the azimuth of the latter was measured with the analyzer. The ellipticity angle \( \epsilon \) (\( \tan \epsilon \) being the axial ratio) and the inclination of the major axis were then obtainable from the settings of analyzer and compensator by applying standard formulae.

With the two metallic reflectors it was convenient to make the geometry of the system such that each angle of incidence was the principal one (i.e. the one at which...
the parallel and perpendicular components of the reflected light differ in phase by 90°). An even number of reflexions then yields plane-polarized light which develops a small ellipticity as adsorption occurs on the surfaces. This makes it possible to fix the angle of principal incidence within narrow limits and thus to determine the optical constants of the reflectors without relying on the accuracy of a compensator, as was first pointed out by O'Bryan (1936). It was necessary to perform a determination of this sort since some of the reflecting surfaces consisted of evaporated metal films the optical properties of which depend on the mode of preparation and often differ appreciably from the published values for the bulk metal.
The windows were fixed obliquely on the ends of the containing tube so as to be normal to the incident light. Under these conditions the ellipticity caused by adsorption on them is negligible. After the windows had been sealed in position the tube was evacuated to a pressure of $10^{-4}$ mm. The substance to be adsorbed was stored in a side-arm frozen in liquid air. The tap was then closed, the tube mounted on the optical system and the reservoir was raised to the required temperature.

Treatment of results

As is well known, Fresnel showed that problems involving the reflexion of polarized light are best treated by resolving the light vector into components parallel and perpendicular to the plane of incidence. The ratio of the amplitudes before and after reflexion are given by the ‘Fresnel coefficients’ which are simple functions of the angles of incidence and refraction. Drude used these in an accurate formula he derived for the effect of a uniform isotropic film. The formula is

$$r' = \frac{r_{12} + r_{23} e^{-2i\delta}}{r_{12}r_{23} e^{-2i\delta} + 1},$$

where the $r$’s denote Fresnel coefficients ($r_{13}$ air-film, $r_{23}$ film-substrate) and $\delta$ is the phase lag introduced by one reflexion in the film. By computing $r'$ for both components the effect of a given surface layer can be obtained. With a metallic reflector, where $r_{23}$ is complex, the computation is very tedious even when graphical methods (Winterbottom 1946) are used, and various approximations have been devised. Drude himself produced a formula giving a direct evaluation of $\Delta - \Delta'$, the change which the film brings about in the phase lag of one component with respect to the other. A second formula takes account of amplitude changes. These are very much more convenient to apply, and it has been shown experimentally (Rothen & Hanson 1949) that they are reasonably accurate over a wide range of film thickness. They have been used here in the somewhat improved form given by Tronstad (1935).

Results

In order to obtain a clear idea of the validity of Drude’s approximate formula, some experimental results for layers of known thickness were compared with the results predicted from this formula and also with the predictions from his accurate formula. Figure 9 shows the ellipticities caused by successive layers of calcium stearate on sphalerite (zinc sulphide), plotted according to the stereographic projection. The mineral sphalerite was chosen because of its high refractive index, transparency and isotropy. The first point indicates a slight ellipticity even in the reflected light from the bare specimen, and the second corresponds to the deposition of one soap layer by the first dipping in the Langmuir-Blodgett technique. The remaining points correspond to double layers put on by successive dippings. The limitations of the approximate formula are apparent from this, but it is clear that it is very adequate for films which do not exceed 100 Å in thickness. The actual increments in ellipticity for each double layer are, however, greater than the calculated values by nearly 8%. This discrepancy is outside the limits of experi-
mental error, and its cause is not known with certainty. A change in the refractive index of the film (regarded as isotropic) from 1.45 to 1.55 alters the calculated thickness by only 3%, so uncertainty in this respect is not responsible. The formulae are more sensitive to anisotropy, however, and it seems probable that the discrepancy would be removed if the anisotropic nature of the layers were completely taken into account.

An attempt was made to measure the adsorption of water vapour on the same piece of sphalerite after cleaning. The sensitivity of the apparatus was insufficient for precise measurements, but a small effect was observed when the pressure was increased from zero to 95% of saturation. This effect, though only just significant, was reversible. The change in ellipticity was equivalent to a water layer 4 Å in thickness (probable error of mean of four readings 1 Å). It was not possible, in this instance, to improve the sensitivity reflexions because of the prohibitively large loss in intensity with each reflexion.

With metallic reflectors arranged as in figure 8 the sensitivity was good enough to permit the determination of an adsorption isotherm. The results for n-heptane on evaporated silver films are shown in figure 10. The ellipticity changes were quite reproducible and were completely reversible, without hysteresis, when the pressure was reduced. The isotherm is of the familiar sigmoid shape and resembles that obtained by Harkins & Loeser (1950) for the adsorption of heptane on silver powder. The calculated thicknesses for the adsorbate layer are in conformity with the now well-established picture of multimolecular adsorption. Taking the point B as corresponding approximately to the completion of a monolayer on the surface we see that the layers are about 4 Å thick (i.e. the heptane molecules are not erect but are almost horizontal).
The estimations of film thickness depend on its refractive index. It is, in principle, possible to calculate the latter from the optical measurements, but for silver, which has an abnormally low refractive index (0.20), the formulae become such as to require a very accurate knowledge of the change in the amplitude ratio and the change in ellipticity angle.

**Figure 10.** n-Heptane (17.8° C) on evaporated silver films.

**Figure 11.** Water (17.8° C).

data were not precise enough. The refractive index at all levels was, therefore, taken to be the same as that of the liquid in bulk, giving a direct proportionality between the changes in $\Delta$ (and, with close approximation, the changes in the ellipticity angle) and the calculated thickness. It is believed that this assumption is not far from the truth for layers exceeding one or two molecules in thickness, but it is clearly inaccurate for a partially filled monolayer, whose 'thickness'...
cannot be less than the relevant dimension of the molecules. Up to about 4 Å, then, the estimated heights merely give an indication of the extent to which the first layer is complete, but above this they should give, with fair accuracy, the mean thickness of the adsorbed layer.

The corresponding isotherm for water vapour (figure 11) is significant for the low degree of adsorption which it reveals even at high relative pressures. The same reservations about estimated heights apply here, but it is plain that even at 95 % of saturation the layer is less than two molecules thick.

**Discussion**

The weighing experiments on foils which had been cleaned by heating show that the adsorption of water vapour is no greater than that of organic vapours. It can correspond to about one molecular layer when the relative vapour pressure is ca. 0·6, and even at 90 % saturation does not appear to be greater than two. The heavy adsorption, which has been reported elsewhere in the literature and which we observed on some specimens, is probably attributable to uncertainty about the area of the surface or to the presence of a trace of impurity. A quite small quantity of contaminant distributed on the surface, if ionic or hygroscopic in nature, could account for all the heavy adsorption as well as explaining why it was so much greater for water than for other substances. The contaminant would tend to take up water until the resulting solution had a vapour tension equal to the pressure of vapour in the system. With potassium hydroxide, for instance, a relative pressure of 0·5 is provided by a solution containing about 40 % by weight of hydroxide. That is to say, a contamination with potassium hydroxide to the extent of $10^{-7}$ g./sq.cm. would, under these conditions, give rise to an ‘adsorption’ of $1 \times 10^7$ g./sq.cm. of water—the equivalent of five molecular layers. At a relative pressure of 0·9, the figure would be 25 molecular layers. It is, perhaps, significant in this connexion to refer to the early work (e.g. Richardson 1916) on thermionic emission. Richardson found that samples of platinum when heated at first emitted a copious supply of positive ions which were identified as those of potassium. In our experiments it was found that the contamination induced by washing a metal specimen with tap water before suspending it from the balance was always sufficient to bring about heavy ‘adsorption’ in a previously clean foil. In a typical case a relative pressure of water vapour of 0·8 gave the equivalent of 48 molecular layers.

The observations on polarized light reflected from the adsorbing surface are of interest, since they provide a completely independent check, and show that at pressures below 95 % saturation thick layers of water are not formed under any conditions. The film formed on a reflecting surface which had been purposely contaminated with tap water was not significantly thicker than the film on a virgin surface. The inference is that when contamination brings about an apparent heavy adsorption the adsorbate does not spread uniformly over the surface but collects for the most part round the regions of contamination. The optical method, of course, measures the thickness of the film only, and if condensation occurred on isolated regions of a hygroscopic impurity it would make itself felt, not by simulating...
thicker layers, but by increasing the amount of scattered light and thus making the readings less precise.

When several reflexions are employed the method is a sensitive one and an adsorption isotherm can be drawn. The isotherm for heptane may be compared with the results obtained with calcium stearate in the tests of the theory of the method. The polar molecules of calcium stearate are, of course, standing erect on the surface, but the heptane isotherm indicates that here the monolayer is only about 4 Å thick. Apparently a saturated hydrocarbon molecule like heptane lies almost flat on the surface. The same conclusion was reached by Kemball (1946) from consideration of the entropy of adsorption for n-heptane on liquid mercury.

The conclusion that, on all the surfaces we have examined (gold, platinum, silver, aluminium and zinc blende), water films formed from the unsaturated vapour do not attain a thickness of much more than two molecular layers is of some interest, since reports of much heavier adsorption are often quoted in support of the theories of long-range surface effects.

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