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Surface chemistry*

Nobel Lecture, December 14, 1932

The phenomenon of adsorption has been known and has been studied for many years. For example, Sir James Dewar found that charcoal cooled in liquid air was capable of taking up large quantities of such gases as oxygen and nitrogen. This was known to be a surface action depending on the very fine state of division of the charcoal.

The effect of soap in lowering the surface tension of water depends upon the presence of a higher concentration of soap molecules in the surface layer than in the solution.

Willard Gibbs proved thermodynamically that there is a general relation between the surface adsorption, the lowering of the surface tension and the concentration of the solution. The equation that he deduced can readily be put in the form

$$\frac{dF}{d\,(\ln p)} = \sigma k T \tag{1}$$

where p is the partial pressure of the vapor of the adsorbed substance in equilibrium with the surface of the liquid, or it may be the partial osmotic pressure of a substance dissolved in the liquid, σ is the number of molecules adsorbed on the surface per unit area, T is the absolute temperature, and k is the Boltzmann constant 1.37×10^{-16} erg deg^{-1}, and F, which may be called the spreading force, is given by

$$F = \gamma_o - \gamma \tag{2}$$

where γ_o is the surface tension of the pure solvent (in dynes cm^{-1}) and γ is the surface tension of the solution.

The form of Gibbs' equation represented by Eq. (1) is thermodynamically valid if the film is in equilibrium with the two volume phases and if the law of ideal gases

* This lecture is designed to summarize the author's contributions and present views in this field, but does not adequately describe the work of others.

$$p = n\,k\,T \tag{3}$$

is applicable in the volume phases.

Prior to 1910 many different theories of adsorption had been proposed, but none of them had been very successful. In most of these theories the increased concentration of the adsorbed substance near the surface was thought to be analogous to the retention of the earth's atmosphere by the gravitational attraction of the earth. An adsorbed gas was thus regarded as a kind of miniature atmosphere extending out a short distance from a solid substance. In general such theories were called upon to account only for qualitative aspects of the adsorption of gases on solids. Most of the knowledge of adsorption was empirical. Even Gibbs' law had not been verified experimentally.

When I first began to work in 1909 in an industrial research laboratory[1,2], I found that the high-vacuum technique which had been developed in incandescent lamp factories, especially after the introduction of the tungsten filament lamp, was far more advanced than that which had been used in university laboratories. This new technique seemed to open up wonderful opportunities for the study of chemical reactions on surfaces and of the physical properties of surfaces under well-defined conditions. I resolved to try the effect of introducing very small quantities of various gases into a highly evacuated bulb containing a tungsten filament. Since by a McLeod gauge, pressures as low as 10^{-8} atmospheres could be measured, it was possible to observe the disappearance of an amount of gas of less than 0.1 cubic millimeter measured at atmospheric pressure. The use of a tungsten filament presented particular advantages, for this could be heated in high vacuum to temperatures of over 3,000°K, so that all impurities could readily be distilled out of the filament. The ease and accuracy with which any desired temperature could be produced and measured was also important.

When a hot body, such as a filament, is in contact with a gas at atmospheric pressure in a glass bulb, the convection currents and the uncertain temperature distribution in the gas, are factors which greatly complicate any interpretation of observed phenomena involving the interaction of the filament with the gas.

If the gas, however, is at a pressure as low as 100 baryes*, the mean free path of the molecules is many times greater than the diameter of the ordinary tungsten filament. Each molecule which strikes the filament has thus

* A barye or c.g.s. unit of pressure, 1 dyne cm^{-2}, is almost exactly 10^{-6} atmospheres.

made so many collisions with the bulb since its last collision with the fil-ament, that the effective temperature of the gas in contact with the filament may be taken to be the same as that of the bulb. The disturbing effects of convection currents are then entirely eliminated and the rate of arrival of gas molecules at the surface of the filament can be calculated according to the laws of the kinetic theory of gases. This theory leads to the equation

$$\mu = \frac{p}{(2 \pi m k T)^{\frac{1}{2}}} \tag{4}$$

where μ is the rate of arrival of the gas molecules expressed in molecules $cm^{-2} sec^{-1}$, and m is the mass of the molecule. By inserting numerical values this equation becomes

$$\mu = 2.65 \times 10^{19} p (MT)^{-\frac{1}{2}} \tag{5}$$

where M is the molecular weight of the gas (oxygen = 16) and p is ex-pressed in baryes. By using filaments of small size and bulbs of large size, it was possible to measure experimentally such high rates of disappearance of gas (clean-up) that every molecule that struck the filament disappeared. Un-der usual conditions, however, the rates of clean-up were far less than this theoretical maximum. The fraction (ε) of all the impinging molecules which reacted on striking the filament could thus be determined.

Working in this way, a systematic study was undertaken of the effects of such gases as oxygen, hydrogen, nitrogen, carbon monoxide, and their mixtures, etc., on filaments of tungsten, carbon, molybdenum, and plati-num. I shall refer only to those cases where the experiments have thrown light upon the phenomenon of adsorption.

Clean-up of hydrogen[3]

When a tungsten filament is heated to temperatures of 1,500°K in hydrogen at about 20 baryes pressure, the hydrogen slowly disappears, the pressure decreasing with time as indicated in Curve I of Fig. 1. The pressure falls to a very low value in 10 to 20 minutes. If more hydrogen is introduced, the rate of clean-up is somewhat slower, the pressure decreasing according to Curve II. Although analysis shows the residual gas to be pure hydrogen, the clean-up gradually comes to a standstill.

With a bulb containing two filaments, it is found that the lighting of the second filament does not cause a recovery in the rate of clean-up. This proves that the gas which disappears is not taken up by the filament itself. By keeping the bulb in liquid air, a greater total amount of clean-up is obtained. Such investigations show that the hydrogen which disappears becomes adsorbed on the surface of the bulb, but that the bulb is capable of adsorbing only a limited amount of hydrogen. This hydrogen adsorbed on the glass is capable of reacting with oxygen at room temperature after the filament has been allowed to cool. The adsorbed hydrogen is therefore in a chemically very active state. It was finally proved that the heated tungsten filament dissociates[4,5,6,7,8] a small fraction of the incident hydrogen molecules into atoms, and that these atoms, because of their unsaturated chemical nature, exhibit a strong tendency to be adsorbed on glass. These hydrogen atoms, however, are capable of reacting with one another and forming molecules. From this point of view, it should be impossible to hold on the glass more hydrogen than could form a layer one atom deep.

By cooling the bulb in liquid air the adsorption increased. The maximum amount of hydrogen adsorbed on the glass in these experiments was 0.03 mm^3 per cm^2, measured as molecular hydrogen at atmospheric pressure. This corresponds to $\sigma = 1.5 \times 10^{15}$ atoms of hydrogen per cm^2, which is equal to the number of spheres of diameter 2.8 Å which can be packed per cm^2 into a close-packed hexagonal lattice. The spacing of the adsorbed atoms is probably determined by the arrangement of the atoms in the underlying glass which provide "elementary spaces" in which atoms can be held. If the average diameter of the atoms of the glass can be assumed to be 2.8 Å, the observed maximum amount of adsorbed hydrogen thus agrees well with that to be expected in a monatomic film. If a glass surface saturated with atomic hydrogen at liquid-air temperature is allowed to warm up to room temperature, part of the hydrogen escapes as molecular hydrogen; the rest can be driven off at 300°C. Since adsorbed hydrogen atoms probably react on contact to form molecular hydrogen, then experiments indicate that the surface mobility of the adatoms* is very small at room temperature.

It was shown that the atomic hydrogen can diffuse long distances through glass tubing at room temperature (but not at liquid-air temperature) and can then reduce metallic oxides[9], such as WO_3 CuO, Fe_2O_3, ZnO, or PtO_2,

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* J. A. Becker, in *Trans. Am. Electrochem. Soc,* 55 (1929) 153, has suggested this term for adsorbed atoms.

and can dissolve in platinum sufficiently to raise its resistance[10]. It reacts at room temperature with phosphorus[3] to form PH_3.

Oxygen films on tungsten

When a tungsten filament is heated to 1,500°K or more in oxygen at very low pressures, such as 100 baryes or less, the oxygen reacts[11] with the tungsten to form the oxide WO_3 which evaporates from the filament at these temperatures as fast as it is produced, leaving the surface of the filament apparently clean. At temperatures below about 2,200°K the presence of extremely small amounts of oxygen (10^{-6} mm) decreases the electron emission from a tungsten filament to values that range from 10^{-2} to 10^{-5} of that from pure tungsten, depending on the temperature at which the emission is measured. This modification of the properties of the surface must depend upon the presence of a film which contains oxygen. When the filament temperature is high, such as 2,000° or more, the emission returns to a normal tungsten emission as soon as the oxygen is completely consumed or is removed by vaporizing into the bulb a "getter" such as magnesium. If, however, the filament temperature is as low as 1,500°, complete removal of oxygen from the gas phase, even by introducing caesium vapor as a getter, does not remove the oxygen film on the tungsten surface after it has once been formed. This means that the oxygen from such a film does not evaporate appreciably at 1,500°K. Measurements at higher temperatures show that about half of the adsorbed oxygen evaporates in 27 minutes' time at 1,860° and in about 20 seconds at 2,070°[12]. From the temperature coefficient at this rate of evaporation it can be concluded that it will take about three years at 1,500° to remove half the film by evaporation and that the heat of evaporation is of the order of 160 kcal per gram atom.

This heat of evaporation is far greater than the heat of dissociation of oxygen into atoms; so we have very direct evidence that the forces that hold oxygen to a tungsten surface are comparable to the most powerful chemical forces known. This gives reason for believing that the oxygen film which so greatly decreases the electron emission from tungsten consists of a single layer of oxygen atoms which are chemically combined with the underlying tungsten atoms.

The electron emission from the tungsten filament in the presence of oxygen at temperatures below 1,800° is found to be independent of the pressure

of oxygen, provided that more than about 10^{-3} barye is present. This must mean that the surface is practically completely covered with oxygen and that an increase in oxygen pressure does not cause the thickness of the layer to increase beyond that of a single layer of atoms.
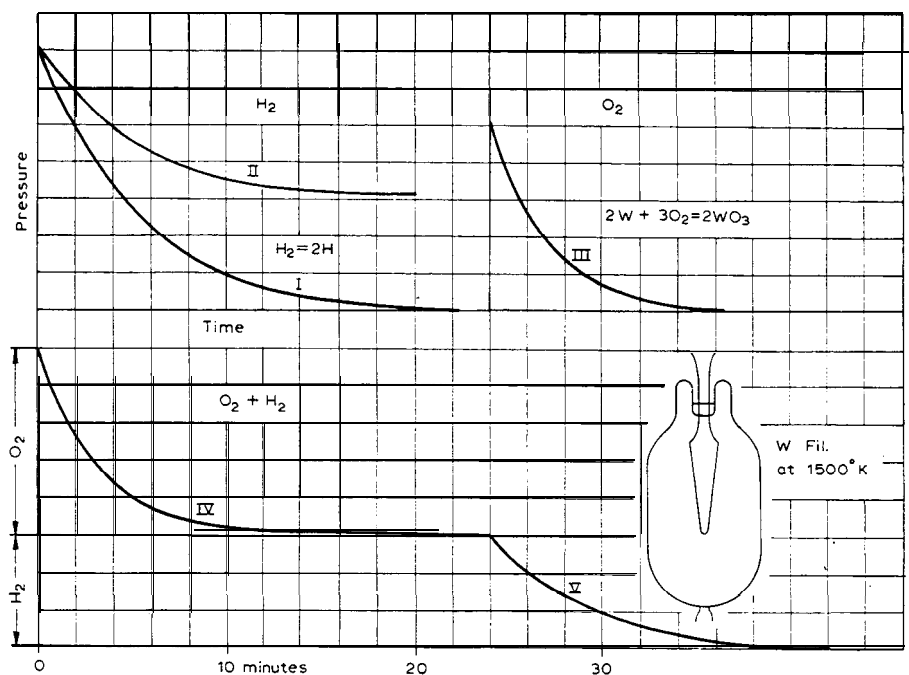

Fig. 1. Clean-up of hydrogen and oxygen in a tungsten filament lamp.

Curve III in Fig. 1 indicates the way in which the pressure of oxygen in the bulb decreases with time when the tungsten filament is maintained at 1,500°K. The rate of disappearance of the oxygen is proportional to the oxygen pressure and there is no fatigue effect, such as was observed during the clean-up of hydrogen.

Interaction of oxygen with hydrogen in contact with tungsten filament

Mixtures of oxygen and hydrogen at low pressures in a bulb containing a tungsten filament behave in an extraordinary manner[13-15]. Typical results obtained with a filament temperature of 1,500° are shown in Curves IV and V of Fig. 1. These curves were obtained with a mixture of 3 parts of hydrogen and 5 parts of oxygen. When the filament was lighted, the gas dis-

appeared at exactly the same rate as shown in Curve III when 5 parts of oxygen alone were present. After about 14 minutes practically all of the oxygen had disappeared. This was confirmed by analysis of the residual gas which was found to be pure hydrogen. This hydrogen, however, did not dissociate in the usual way into atoms and disappear by adsorption on the glass walls as shown in Curve I, but the pressure remained practically constant until after about 24 minutes, when the pressure suddenly began to decrease as indicated by Curve V. This Curve V, however, is identical with Curve I, which is characteristic of the clean-up of hydrogen in absence of oxygen. Repeated experiments with different amounts of oxygen and hydrogen prove that hydrogen does not interfere with the clean-up of oxygen, but that a minute trace of oxygen of about 10^{-3} barye completely prevents the dissociation of hydrogen into atoms by a tungsten filament at 1,500°K. The oxygen thus acts as a catalytic poison. Experiments of this kind can be used to make quite accurate chemical analyses of mixtures of oxygen and hydrogen.

The fact that a monatomic film of oxygen on tungsten does not react with hydrogen at 1,500° is a striking indication that the oxygen is in a condition far different from that of gaseous oxygen. The results, however, confirm our conclusion that the film consists of oxygen atoms which are chemically saturated by the tungsten atoms with which they are in contact.

In view of the fact that an oxygen film on tungsten at 1,500°K does not evaporate in less than a year, it is remarkable that in the presence of hydrogen the beginning of the hydrogen clean-up (Curve V) is so sharp. Since Curve V is exactly like the lower part of Curve I, it appears that once the hydrogen begins to dissociate, the oxygen is suddenly completely removed from the surface; in other words, hydrogen can remove monatomic oxygen films from the tungsten surface if the amount of oxygen on the surface is less than a definite amount. This probably means that the adsorbed oxygen molecules cannot react with hydrogen atoms directly but can react with hydrogen atoms adsorbed in adjacent spaces on the tungsten surface.

Thorium on tungsten[16]

When a tungsten filament which is made from tungstic oxide containing about I per cent of ThO_2 is heated to temperatures of 2,800° or more, a minute fraction of the thoria is reduced to metallic thorium. The thoria

exists in the filament in the form of minute spherical particles distributed throughout the tungsten crystals and not at the boundaries of crystals. If the filament is then heated for a period of a few minutes at 1,900 to 2,000°K, the metallic thorium which has been produced at the higher temperatures diffuses slowly through the crystal grains to the crystal boundaries, then diffuses rapidly along these boundaries to the surface of the filament and then spreads over the surface of the filament by surface migration and forms a monatomic film of adsorbed thorium atoms on the surface of the filament. At 2,000° the rate of evaporation of thorium from the filament is so small that sufficient thorium soon accumulates on the filament to form a nearly complete monatomic film. If the temperature is raised to 2,200 or 2,400°, the rate of evaporation of the thorium from the surface increases so much more rapidly than the rate of arrival from the interior by diffusion, that the actual surface concentration decreases greatly.

These changes in the thorium content of the adsorbed film can be studied by measurements of the electron emission from the filament at a standard low temperature, called the testing temperature, which is chosen so low that neither diffusion to the surface, nor evaporation from the surface, causes appreciable changes in the adsorbed film. A convenient testing temperature is 1,500°. At this temperature the presence of adsorbed thorium on the surface may increase the electron emission as much as 10^5-fold over that from a pure tungsten surface.

Such experiments make it possible to investigate the electrical properties of surface films having known amounts of thorium. On the assumption that each thorium atom on the surface acts as a dipole having a definite dipole moment, it is possible to show that the logarithm of the electron emission should increase linearly with the number of thorium atoms on the surface. The experiments showed that for low concentrations of thorium this relation holds approximately.

There are several indications that the adsorbed film of thorium that is formed by diffusion from the interior never exceeds one atom in thickness.

The interaction of carbon dioxide with carbon filaments

If a carbon filament is heated to a temperature above 1,700°K in the presence of carbon dioxide at low pressure, one molecule of carbon monoxide is liberated from every molecule of carbon dioxidez. If this carbon monoxide

is pumped out from the bulb and the filament is then heated to 2,300°K, a volume of carbon monoxide is slowly liberated equal to that originally formed from the dioxide. This proves that each carbon dioxide molecule which comes in contact with the filament and reacts, loses one oxygen atom to the filament and thus produces a carbon monoxide molecule. The oxygen atoms thus transferred to the filament form a monatomic film of oxygen atoms covering the surface, these atoms being chemically combined with the carbon atoms with which they are in contact, presumably by double bonds. This adsorbed film on the filament is very stable at 1,700°, but when heated to 2,300°, the film is destroyed, not by the evaporation of the oxygen atoms, but by the breaking of the bonds between the carbon atoms which are attached to the oxygen and the underlying carbon atoms with which they are in contact. Thus the oxygen escapes as carbon monoxide.

From this point of view we see that we can look upon the adsorbed film on the carbon filament either as consisting of adsorbed oxygen, or as an adsorbed film of oriented carbon monoxide molecules, or as carbonyl radicals which are chemically attached by their carbon atoms to the underlying carbon atoms in the filament. It is to be expected that the properties of the adsorbed film would be very different if it consisted of carbon monoxide molecules attached to the underlying surface through their oxygen atoms. These experiments thus led to the concept that the properties of adsorbed films should in general depend on the orientation of the molecules or radicals in the film. It seemed to the writer (in 1915) that evidence of such orientation could be found among the data on the surface tensions of pure liquids.

Surface energies of pure liquids[17,18]

If a prism of liquid having a cross section of 1 sq. cm is divided into two parts by an imaginary plane perpendicular to the axis of the prism, and the two portions of the liquids are then separated, there has been an increase in the surface of the liquid of 2 sq. cm. The total energy theoretically required per sq. cm of new surface to bring about this separation may be called the total surface energy y_o. This is related to the free surface energy y, which is equivalent to the surface tension of the liquid, by the relation

$$\gamma_0 = \gamma - T \frac{d\gamma}{dT}$$

By measurements of the surface tension, the surface energy y_o can thus be measured. This quantity represents the potential energy of the molecules which form the surface of the liquid (per sq. cm) in excess of that which the same molecules possess when they are in the interior of the liquid.

In Table 1, data are given for a few substances which serve to illustrate the interrelation [19,20] between the orientations of molecules and other properties of liquids. The latent heat of evaporation (λ) which, according to Trouton's rule, is approximately proportional to the absolute boiling point (T_B) serves as a measure of the energy needed to bring a molecule from the interior of the liquid out into the vapor phase. We have seen that the surface energy y_o is the energy per unit area needed to form a surface.

The molecular volume V given in this table is the volume of the liquid divided by the number of molecules. The molecular surface S is the surface of a sphere which has the volume V. The extremely low values of λ, the heat of evaporation, per molecule, for helium and hydrogen, indicate that the forces exerted by these molecules on their neighbours are unusually weak. This is in accord with the great stability of the electron pair which forms the K shell of atoms and the covalence bond. The diameters of the helium atom and hydrogen molecule given by the kinetic theory from viscosity measurements, viz. 1.9. and 2.4 Å, correspond to volumes V of only 3.6 and 7.2 Å^3, which are very small compared to the volumes occupied in the liquid. This very open structure of the liquid is again an indication of the weak attractive forces between these molecules.

The effect of replacing one of the hydrogen atoms in the hydrogen molecule by the hydroxyl radical, thus producing water, is to decrease the value

Table I. Surface properties of molecules

Substance	Volume V (Å^3)	Surface S (Å^2)	Boiling point T_B (°K)	Heat of evaporation λ (erg $\times$ 10^{-14})	λ/S (erg cm^{-2})	y_o (erg cm^{-2})
He	52	68	4.3	0.24	0.35	0.59
H–H	47	63	20.5	1.67	2.7	5.4
H–OH	30	48	373	67	140	118
Ar	47	63	88	11.3	18	35.3
CH$_4$	64	78	112	16.3	21	—
n-C$_8$H$_{18}$	266	200	398	56	28	50.7
n-C$_8$H$_{17}$OH	260	198	467	82	41.5	50.7

of V from 47 to 30, an indication of strong forces acting between the hydroxyl groups which compress the liquid. A better measure of these forces is given by the 40-fold increase in the value of λ from 1.67 to 67. The surface energy y_0 has been increased 24-fold.

The data for argon illustrate the properties of an atom having a complete electron shell or octet. The fact that in spite of the much larger electron configuration (with a kinetic theory diameter of 2.9) the volume per molecule in the liquid is the same as for hydrogen, shows that the field of force around the molecule is far greater than for hydrogen and helium. The heat of evaporation per unit area λ/S is a very convenient measure of the intensity of this field. With H_2 He and Ar it is about one-half of the surface energy y_0. The data for methane indicate that this molecule has a value of λ/S, about the same as that for argon. This molecule has a completed octet which shares pairs of electrons with hydrogen atoms. Evidently the presence of the hydrogen atoms does not appreciably alter the field of force; the main effect is to raise the molecular volume, thus raising λ and the boiling point T_B almost in proportion to S.

The values for λ/S for the saturated aliphatic hydrocarbons beyond propane are practically constant and equal to 28. The same constancy is shown in the surface energy y_0. The data for octane shown in the table are typical. The surfaces of the molecules of the higher-saturated hydrocarbons are thus very much like those of argon atoms, the effect of the chain formation manifesting itself principally in the increase in λ/S from 18 to 28.

The constancy of λ/S is also an indication that the molecules of the vapors of the higher hydrocarbons are approximately spherical in form. The known flexibility of the chain and the surface energy reduction resulting from the more compact form afford ample explanation of this spherical form.

The effect of substituting a hydrogen atom in octane by a hydroxyl radical is illustrated in the last line of the table by the data for n-octyl alcohol. There is a small decrease in V paralleling that observed in H_2O, except that now, since each OH group in the liquid cannot be close to many other OH groups, the decrease in volume is considerably less. The large field of force around the OH group is best illustrated by the increase of 26 units in the value of λ. The fact that this increase is less than half of that observed in the change from H_2 to H_2O shows that the OH group in the molecule of the vapor of octyl alcohol is able to bury itself, at least in part, in the approximately spherical molecule.

In spite of the large increase in λ and λ/S in octyl alcohol, the surface en-

ergy y_o is the same as for octane. This can be explained by the *orientation of the molecules* in the surface layer of octyl alcohol. The great attractive forces exerted by the hydroxyl groups cause them to be drawn down into the interior of the liquid. Thermal agitation tends to counteract this tendency. According to the Boltzmann equation the relative distribution of molecules between two regions of differing energy is measured by exp (W/kT), where W is the difference in the energy of the molecule in the two states. Now, judging from a comparison of the values of λ for octane and octyl alcohol, the energy necessary to bring an OH group from a hydrocarbon environment out into free space is at least 26×10^{-4} erg. The energy corresponding to kT room temperature is about 4×10^{-14} erg. Since W thus more than 6.5 times as great as this, we may conclude that nearly all of the molecules [all but about exp $(- 6.5) = 10^{-3}$] in the surface of octane will be oriented in such a way that the hydroxyl groups do not reach the surface.

We may now understand why the surface energy of octyl alcohol is the same as that of octane. We have previously seen that γ_o can be determined by the energy needed to separate a prism into two parts. We may conceive of this separation as taking place in two steps. The molecules on the opposite sides of an imaginary dividing plane may first be oriented so that the hydroxyl groups are turned away from this plane, leaving only the hydrocarbon parts of the molecule in contact with the plane surface. The two bodies of liquids are then separated from each other along this plane, which would require only the same energy as for pure octane. Because of the orientation of the molecules, y_o thus differs from that of octane only by the amount of energy needed to turn the molecules around in the interior of the liquid, which is probably negligible.

Referring again to Table I we see that a comparison of λ/S with y_o affords a measure of the effect of orientation. In general, for molecules with uniform fields of force, λ/S is from 0.5 to 0.55 of the value of γ_o.

When, however, a part of the molecular surface has a much weaker field of force than that of other parts, the surface of the liquid consists principally or wholly of the least active parts, so that γ_o is lower than normal. Thus for octyl alcohol λ/S is 0.82 of γ_o while for water it is 1.18, indicating that the water molecule is very unsymmetrical and is strongly oriented at the surface.

At present these illustrations will suffice. In a paper published in 1916 I showed that this theory was applicable to the surface tension of organic liquids in general, including cases of substituted benzene derivatives where the values of γ_o depend to a marked degree on the relative positions of the

substituted groups. Somewhat later W. D. Harkins and his co-workers investigated large numbers of organic substances in this way and completely demonstrated the importance of orientation of molecules in the surface layer of liquids consisting of unsymmetrical molecules.

Oil films on water[18,21]

When a pure saturated liquid hydrocarbon is placed upon the water, it remains on the surface as a drop or lens which has no effect on the surface tension of the surrounding water. If, however, an insoluble fatty or oily substance, such as the common vegetable and animal oils, is placed upon clean water, it spreads out almost instantly as a thin film over the surface. If the motions of the surface are made visible by dusting the surface with powdered talc, it may be seen that, with a limited amount of oil, the film only spreads out sufficiently to cover a definite area, or at least if the area exceeds a rather definite value, the oil has no effect on the surface tension of the water. A comparison of various insoluble organic substances has proved that the spreading tendency depends upon the presence of certain active groups or radicals in the organic molecule, these being the groups which tend to increase the solubility of organic substances in water. For example, pentane, C_5H_{12}, is practically insoluble in water but amyl alcohol, $C_5H_{11}OH$ is relatively soluble. Thus the OH groups in organic molecules exert strong attractive forces on the OH groups in the water molecules and these manifest themselves by an increase in solubility. Similarly the carboxyl group COOH tends to make the lower fatty acids much more soluble in water than the corresponding hydrocarbons.

Hydrocarbons with high molecular weight such as $C_{18}H_{38}$ are extremely insoluble in water. If the carboxyl group replaces the CH_3 group at the end of the chain $C_{18}H_{38}$, one end of the molecule only tends to dissolve in water, whereas the rest of the molecule still retains the insolubility of the hydrocarbons. By spreading over the surface of the water, molecules of this kind can bring their carboxyl group in contact with the water without separating from one another.

An oil film formed in this way must consist of a single layer of molecules packed closely on the surface layer of the water. If there is a surplus of the fatty acid, as compared with the limited area over which it can spread, the endeavor of the carboxyl groups to come in contact with water causes the

molecules to become so crowded at the surface that they stand nearly erect, side by side on the surface. The area occupied by each molecule is thus determined by the cross section of the hydrocarbon chain or by that of the head in contact with water, if this happens to be larger than the cross section of the chain. The thickness of the film is then determined by the length of the hydrocarbon chain.

By dissolving known weights of liquid or solid, oily or fatty substances in a volatile solvent such as hexane, and placing known amounts of these dilute solutions on the water surface, a definite number of molecules can be transferred to the water surface. The oil film can be confined to a given portion of the surface of water in a long tray by a floating strip of paper reaching across the tray. By measuring the forces exerted on the strip of paper, it is possible to measure directly the spreading force F in dynes per cm exerted by an oil film having a given number of molecules of oil per square cm of surface. This surface concentration we shall denote by the symbol σ. Such measurements as these, by which F can be expressed as a function of σ and T, give us then the two-dimensional equation of state of the oil film which corresponds exactly to the three-dimensional equation of state which characterizes ordinary gases and liquids. In fact, the movable paper strip in these experiments is the equivalent of a piston which compresses the gas in a cylinder.

The oil films observed on water may exist as two-dimensional solids, liquids or gases. The film on water obtained from stearic acid $C_{17}H_{35}COOH$ is solid. If it is compressed by a force of 10 dynes per cm exerted against the paper strip, this solidity is manifested if particles of talc are dusted on to the surface and the effects of air currents directed against the surface are watched. The talc particles do not move freely over the surface; if a strong wind displaces them, they return to their original positions when the wind stops, proving a surface rigidity and elasticity characteristic of solids. Other substances such as cetyl alcohol or oleic acid give films which are liquid, since talc particles circulate freely when small forces are exerted by the wind.

By slightly increasing the area available for these films of saturated fatty acids, it is found that the spreading force decreases very nearly to zero, which proves that these films do not act as two-dimensional gases but rather as two-dimensional liquids which have an unmeasurably small two-dimensional vapor pressure. With myristic acid[22], however, a definite two-dimensional vapor pressure of about 0.2 dyne cm^{-2} is observed. Still lower fatty acids give typical gaseous films, but they cannot be studied by this method because

the films are so easily soluble in water that the force exerted by a moving barrier causes them to go into solution.

Adsorbed films on solutions[18,21]

The foregoing method for studying the properties of oil films on water is inapplicable if the film is soluble or is volatile. In such cases measurements must be made in the presence of saturated vapor or saturated solution. Gibbs' equation, Eq. (1), gives us a means of determining the relation between the amount adsorbed on the solution and the spreading force F, in terms of the partial pressure p of the vapor of the adsorbed substance over the liquid or the partial osmotic pressure p of the dissolved substance in the underlying solution. Experimentally F can be measured as the decrease in the surface tension of the pure liquid produced by the presence of the dissolved substance. By the integration of this equation, using the experimentally determined values of F, one can obtain the equation of state of the two-dimensional film whether this is gaseous or liquid or solid.

For very high or very low surface concentrations, Gibbs' equation takes simple limiting forms. At very low concentrations the molecules in the adsorbed films are so far apart that they exert no appreciable forces on one another. Under such conditions σ, the surface concentration, will be proportional to the volume concentration which in turn is proportional to p. If we solve Eq. (1) on the assumption that σ is proportional to p, we find that it leads to the following equation of state

$$F = \sigma k T \tag{6}$$

which is the two-dimensional analogue of Eq. (3), the equation of state of an ideal gas, and it may therefore be called an equation of state of an ideal two-dimensional gas.

The effect of forces acting between the adsorbed molecules is to modify this equation. A two-dimensional analogue of Van der Waals' equation can be written in the form

$$F = \frac{\sigma k T}{\left(1 - \sigma/\sigma_I\right)} + a\sigma^2 \tag{7}$$

where a and σ_I are constants.

When the gas phase or the liquid phase contains a relatively high concentration, the concentration of the molecules in the adsorbed film tends to increase to a limiting value σ_I corresponding to a complete monomolecular adsorbed film such as those that we observed in the study of oil films on water. Although such films show surface elasticity, that is, they are compressible, the forces required to compress the liquid and solid films are so much greater than those required to compress the gaseous film, that the surface compressibility can be neglected as the first approximation, so that we can consider σ_I to be approximately constant, that is, independent of p and F. Making this substitution in Eq. (1) and integrating, we obtain the following equation which should be applicable for concentrated surface films

$$F = \sigma_I kT \ln (p/p_o) \tag{8}$$

These two limiting equations are completely in accord with the general relationships found by J. Traube[23]. In Eq. (8) p_o is an integration constant whose value cannot be found from Gibb's equation.

From the Boltzmann equation we can estimate the energy change λ involved in bringing a molecule from the vapor or liquid phase to the surface phase. We thus have

$$\sigma/p = \text{const} \exp (\lambda/kT) \tag{9}$$

Traube found that with molecules of aliphatic compounds having different lengths of hydrocarbon chains, the ratio F/p for dilute solutions (which should be proportional to σ/p) increases about threefold for each CH_2. When this is interpreted in accord with Gibb's and Boltzmann equations, we conclude that the energy λ involved in the adsorption of these molecules increases linearly with the length of the chain. This means that each CH_2 group in the molecule must be similarly situated in the surface film. In other words, in these dilute films where there is much free water surface available, the hydrocarbon molecules must lie flat on the surface. With the concentrated films in which σ is constant so that Eq. (8) applies, there is no available free surface of water and the molecules must stand nearly erect on the surface.

These two cases given by Eqs. (6) and (8) are only limiting cases and the complete equation of state for the whole range from dilute to concentrated films would be more complicated, since it must involve the intermediate

states between those in which the molecules lie flat on the surface and stand erect on the surface. The experimental difficulties of the accurate measurements of the surface tensions of solutions are such, that relatively little work has been done on the equation of state of these adsorbed films on solutions as compared with the large amount of work done by N. K. Adam[22] and others on the equations of state of films of insoluble substances on water.

The molecules in adsorbed films on liquids are of course free to move over the surface of the liquid except in so far as the film itself may possess the properties of a solid.

Adsorbed films on solids

Adsorbed films on solids may exist in three states corresponding to two-dimensional gases, liquids or solids. A new factor now appears, however, which was not present in the case of adsorbed films on liquids. The forces exerted by the underlying solid on adsorbed atoms or molecules tend to hold the molecules in definite positions fixed by the lattice of the solid. The solid surface is thus to be looked upon as a type of checker-board containing definite numbers and arrangements of elementary spaces[13,24], each of which is capable of holding an adsorbed molecule. To move a molecule from one elementary space to another thus presumably requires something analogous to an activation energy; only those molecules possessing a sufficient kinetic energy to pass over a potential barrier can succeed in hopping from one elementary space to another[25]. On this basis we should expect a surface mobility at high temperatures which would disappear at low temperatures. The logarithm of the rate of mobility, or the surface diffusion coefficient, should vary linearly with the reciprocal of the absolute temperature and the slope of this line should be proportional to the activation energy.

In general the surface diffusion coefficient increases with σ, for the ability of adatoms to cross the potential barrier is not determined solely by the thermal agitation of the molecules but depends on $dF/d\sigma$, since differences in the value of F over the surface contribute to the mobility.

We may thus consider that in general the adatoms on solids move over the surface by hopping between elementary spaces. If the adatoms move nearly independently of one another, so that they migrate freely on to all unoccupied portions of the surface, the adsorbed films can be regarded as a two-dimensional gas in spite of the fact that the atoms tend to occupy

definite positions. Such films constitute a two-dimensional crystalline gas, the crystalline character being imparted by the underlying lattice. If attractive forces exist between the adatoms which are sufficiently strong to cause them to form a definite two-dimensional condensed phase in equilibrium with a two-dimensional vapor phase, we clearly have to do also with a two-dimensional solid or liquid. If the mobility is high, this condensed film may have properties characteristic of liquids; with no mobility at lower temperatures, the conditions will be analogous to that of a two-dimensional glass. A two-dimensional solid analogous to ordinary three-dimensional solids would exist only if the forces exerted by the adatoms on each other can keep them from slipping past one another.

Condensation-evaporation theory of adsorption on solids

When molecules of a gas in contact with a solid impinge individually on the solid, they may either condense or may rebound from the solid as though elastically reflected. Those molecules that condense may subsequently evaporate. There is much theoretical and experimental evidence that a true reflection of molecules under these conditions is a rather abnormal occurrence, although the specular reflection of molecular rays from certain crystalline surfaces shows that it sometimes exists. In the great majority of cases, however, the observed phenomena indicate that the larger part of all incident molecules condense on the surface and reach thermal equilibrium with it before they evaporate[26,27]. With such gases as hydrogen and helium, accommodation coefficients materially less than unity have been found. In general these occur with gases striking solids at such temperatures that the rate of evaporation may be assumed to be so high that the life of the condensed molecule is of the order of 10^{-13} seconds, which is about the time required for a molecule to perform a single thermal oscillation on the surface. Under these conditions it is not surprising that thermal equilibrium is not reached.

When the rate at which molecules impinge on the surface is μ, as given by Eq. (4), and v is the rate at which they evaporate (molecules cm^{-2} sec^{-1}), then the rate at which they accumulate on the surface is given by

$$\frac{do}{dt} = \alpha\mu - v \tag{10}$$

where a, the condensation coefficient, in the majority of cases is equal to unity, but in any case can never exceed unity. The rate of evaporation v is in general dependent on the temperature and on σ, the surface concentration. Of course it also depends on the nature of the solid surface on which adsorption occurs. If the surface is strictly homogeneous, v may be a function of σ and T only for a given surface, but it may be possible that different portions of the surface are capable of exerting different forces on adatoms, so that v and σ may not be uniform over the surface.

In a stationary state when σ is not changing with time, the general condition that must be fulfilled is

$$\alpha\mu = v \tag{11}$$

If we divide the rate of evaporation v by σ, the number of atoms per square cm, we obtain the average probability per second for the evaporation of the individual atoms. The reciprocal of this (τ) is thus the average life of an adatom on the surface. Thus we have

$$\tau = \sigma/v \tag{12}$$

This time lag that exists between the condensation and the evaporation of adatoms may thus be looked upon as the fundamental cause of the adsorption of gases on solid surfaces.

In general, v should increase rapidly with temperature like the vapor pressure of substances. Thus the logarithm of v should increase approximately linearly when plotted against the reciprocal of the absolute temperature, and the slope of this line is proportional to the heat of evaporation and is a measure of the magnitude of the forces by which the adatoms are held on the surface. Thus v should be approximately given by an equation of the type

$$v = \text{const. } \exp\left(-\lambda/kT\right) \tag{13}$$

where λ is a measure of the energy required to remove an adatom from the surface. The reason for the large variations of v for different substances is due mainly to variations of λ rather than to difference[28] in the constant factor in Eq. (13). This is indicated by such approximate laws as Trouton's rule.

The forces acting between atoms and molecules are normally of extremely

short range [27,29], so that the forces acting on an adatom, which determine the magnitude of λ, and therefore of v, depend mainly upon the atoms with which any given adatom is in contact. When the gas pressure is raised or the temperature is lowered so that σ increases to such a point that there is no longer room for any additional molecules in the first layer in contact with the solid, a still further increase in σ would require that a large number of adatoms must be contained in a second layer. Now these adatoms in the second layer cannot be in *contact* with the solid surface on which the primary adsorption occurs, and therefore for these atoms λ_2 should differ from the value of λ_1 that applies to the adatoms in the first layer. Since λ occurs in the exponent of Eq. (13), a relatively small change in λ is sufficient to cause a marked difference in the value of v.

Thus when the adsorbed substance is not nearly identical in its properties with the substance on which adsorption occurs, we should expect the value of v for atoms in the first and atoms in the second layer to be greatly different from one another. Naturally two cases may arise[28]: v_2 may be either greater or less than v_1.

Case 1: $v_2 < v_1$. If v_2 is less than v_1, the atoms in the second layer are held by stronger forces to those in the first layer than these latter are by the atoms of the underlying solid. There is therefore a tendency for the atoms in the first layer to form clusters and on these clusters the second and third, etc., layers begin to form long before the whole of the first layer is covered[27]. Such phenomena are of common occurrence. For example, when mercury, cadmium or iodine is vaporized in vacuum and is condensed on a glass surface, at a not too low temperature, discrete crystals of the condensed substances form on the glass. This is a direct indication that these atoms exert greater forces on one another than they do on the underlying glass.

If the glass surface is maintained at a temperature so high that these nuclei do not form, then the glass surface *appears* to reflect all the incident atoms, for they evaporate from the glass surface far more rapidly than they do from a cadmium surface at the same temperature. Such observations were made by R. W. Wood, who attempted to explain them by a large reflection coefficient. He believed that experiments indicated that molecules of mercury incident at low pressures on cold glass surfaces were completely reflected at temperatures above -90°C, but were completely condensed below that temperature.

From our present viewpoint such a critical temperature has nothing to do with a true reflection but is dependent on the fact that with a given stream

of mercury or cadmium atoms there is a definite temperature below which evaporation of the individual adatoms cannot take place fast enough to prevent accumulation sufficient to form a monatomic film, so that all further evaporation at these low temperatures ceases. Experiments show conclusively that at all temperatures the mercury atoms condense, but that, if the temperature conditions are favorable, single atoms re-evaporate from the glass at fairly low temperatures.

It is evident therefore that those cases in which v_2 is less than v_1 are characterized by the growth of crystals from nuclei and do not lead to the formation of monomolecular films but rather to discrete crystal particles.

Case 2: $v_2 > v_1$. In this case, as the pressure is gradually raised or the temperature is lowered, σ increases until a monomolecular film is formed, but it then takes a considerable decrease in temperature or increase in pressure before a second layer begins to form. These conditions therefore commonly lead to the formation of films which do not exceed a molecule in thickness over a wide range of experimental conditions. This case therefore is characterized by typical adsorbed films.

Adsorption isotherms

The fundamental equation governing the amount of adsorbed substances on a solid surface is given by Eq. (11). To put this into a definite form relating the pressure p of the external gas and σ, the surface concentration, we need only to be able to express a and v as functions of σ and T. The functional relation of v to σ depends not only on the forces exerted by the underlying solid, but on the forces acting between adatoms. Furthermore we must consider that the incident molecules corresponding to μ cannot all go directly into elementary spaces on the bare surface, but many of them will make their first contact at places already occupied by adatoms. An important aspect of the problem of the adsorption isotherm is the determination of the manner in which these incident atoms find places in the first layer. Many atoms may temporarily be forced to occupy places in the second layer from which they can either evaporate at a much higher rate than from the first layer, or may migrate until they drop into positions in the first layer.

It is natural. under these conditions to make assumptions which are as simple as possible and to see whether the resulting equations can find a field of application[24]. If the adatoms do not exert appreciable forces on one an-

other, we may thus assume that the life oft of each one is independent of
the presence of other atoms on the surface. Thus by Eq. (12), v is propor-
tional to σ.

Instead of dealing with the surface concentration of σ it is often con-
venient to use the covering fraction Θ defined by

$$\Theta = \sigma/\sigma_I \tag{14}$$

where σ_I is the surface concentration in a complete monomolecular film.
Thus we may put

$$v = v_I \Theta \tag{15}$$

where v_I represents the rate of evaporation from a completely covered sur-
face.

When molecules incident on the surface strike a part which is unoccupied
by other adatoms, we may assume that the fraction α_0 condenses. The frac-
tion of such surface which is bare may be represented by $I - \Theta$. Therefore
the number of incident atoms which go directly into the first layer may be
put equal to $\alpha_0 (I - 0) \mu$. The fate of the other incident atoms, viz. those
that first strike adsorbed atoms, will depend on many factors, some of which
we shall discuss later. A very simple, although not very probable, assump-
tion is that all these atoms re-evaporate so fast that they do not have oppor-
tunities to find positions in the first layer. On these assumptions we find

$$\alpha\mu = \alpha_0 \left(I - \Theta \right) \mu \tag{16}$$

Substituting this and Eq. (15) into Eq. (11) and solving for Θ, we obtain
the following simple adsorption isotherm,

$$\Theta = \frac{\alpha_0\mu}{v_I + \alpha_0\mu} \tag{17}$$

This equation has been found to apply with reasonable accuracy to a surpris-
ingly large number of cases of adsorption on plane surfaces. Considering the
nature of the simplifying assumptions made in its derivation, it should of
course not be looked upon as a general equation for the adsorption isotherm.
The cases where this equation is most likely to apply are those in which the

adsorption occurs only in elementary spaces which are so far separated from one another that the adatoms in the separate spaces do not exert appreciable forces on one another. This can justify the assumption of Eq. (15). Also in this case the condensation may reasonably occur according to Eq. (16), because if a given space is occupied, which has a probability proportional to Θ, the incident atom cannot merely slip into an adjacent elementary space but must fall on to an area on which it is held with so little force that it evaporates before it can move into any vacant elementary space. These assumptions will give us an equation like Eq. (17) except that the significance of Θ and of the coefficient α_0 is somewhat modified.

Recent experiments have shown that in the mechanism of condensation mobility plays an important part[30]. Thus in general an incident molecule striking a surface already covered may be assumed to move an appreciable distance before finally settling into a position in the first layer. Certainly if the surface is homogeneous so that all parts of it are available for adsorption, an incident molecule striking an isolated adsorbed molecule can hardly be regarded as being even temporarily in a second layer. Such an atom will slip into a position in the first layer before having any occasion to rebound or evaporate from the surface. An atom cannot be in a second layer even temporarily unless it is supported by at least three, or more often four, atoms in the underlying layer. Even if there is no mobility, the probability that an incident atom could occupy a place in the second layer would be proportional to Θ^n, where n is at least as great as 3 or 4. If the rate of evaporation is very high, we might expect these atoms to evaporate before finding places in the first layer. On this basis, therefore, instead of Eq. (16), the expression for the rate of arrival of atoms in the first layer should be

$$\alpha\mu = a, \left(1 - \Theta^n\right) \mu \qquad (18)$$

Some experiments were made to test the reasonableness of these conclusions. The bottom of a tray was covered with steel balls ($\frac{3}{8}$ inch diameter) closely packed into a square lattice and cemented into position. This surface thus possessed many of the features of a homogeneous crystal surface, the steel balls corresponding to the individual atoms. When other balls of the same size were thrown on to the surface, they occupied definite elementary spaces, each being in contact with four underlying balls. The number of such elementary spaces (except for an edge correction) was the same as the number of balls which were cemented into place (zero layer). A large number of

balls, sufficient to cover the fraction Θ of the available spaces, was placed in the tray (in first layer) and the tray was shaken to give a random distribution. A small number of additional balls were then dropped at random from a height of 5 cm to the surface, and the number of these which went into the second layer was counted. It was found that the probability P that a given incident ball would occupy a position in the second layer was quite accurately given by

$$P = \Theta^{4,5} \qquad (19)$$

The fraction of the incident balls finding positions in the first layer was thus $1 - \Theta^{4,5}$. A comparison of this with Eq. (18) gives a value of $n = 4.5$. The reason that n is greater than 4, the number of underlying atoms, is probably that the kinetic energy of the balls causes some of them to roll from their positions of first contact.

Applying these results to adsorption, we should expect that, until Θ is very close to unity, all atoms incident on the surface should reach positions in the first layer without any opportunity of evaporation or reflection, even if the evaporation rate in the second layer is very high.

Effect of forces acting between adatoms[28]

The fact that two adatoms cannot occupy the same elementary space at the same time must mean that they exert repulsive forces on one another. This will manifest itself in the equation of state of the adsorbed atoms by a factor such as the $1 - \Theta$ in the denominator of the first term of the second member of Eq. (7). This means that the spreading force tends to rise indefinitely as Θ approaches the value unity. Combining this equation of state with Gibbs' equation, and assuming $\alpha = 1$, we obtain for an adsorption isotherm the equation

$$\ln (v/O) = \ln [1/(1-0)] + 1/(1-0) + \text{const.} \qquad (20)$$

Thus we see that the rate of evaporation should increase indefinitely as Θ approaches unity. It is just this effect which limits the amount of material in typical adsorbed films on liquids or solids to that contained in a monomolecular layer.

The forces holding adatoms on the surface in characteristic cases of adsorption are usually far greater than those acting between adatoms. If this were not the case, we would be dealing normally with the case in which v_2 is less than v_1, so that we would not have adsorbed films but crystal nuclei. The effect of these strong forces originating from the underlying surface is to polarize the adatoms. If these are all of one kind, they thus tend to become similarly oriented dipoles which repel one another with a force varying inversely as the fourth power of the distance between them. There may also be attractive forces of the Van der Waal's type, but these will vary with a much higher power of the distance. The dipole forces will have a range of action far greater than other forces involved. A knowledge of these factors which are probably important in most cases of adsorption can best be acquired by a detailed study of some one example in which quantitative determinations of all the factors are possible. The example that I have chosen for this purpose is that of adsorption of caesium vapor on tungsten, for in this case we can measure with great precision the surface concentration σ as well as the rates of evaporation v of atoms, of ions, and of electrons[30]. Thus we are able to express these values of v_a, v_p and v_e as functions of Θ and T. These measurements enable us not only to determine the forces acting between the adatoms but also to determine the electrical properties of the adsorbed films.

Caesium films on tungsten

The ionizing potential of caesium is *3.9* volts, which is lower than that of any other chemical element. The heat of evaporation of electrons from tungsten corresponds to *4.6* volts. Thus the energy necessary to detach an electron from a caesium atom is 0.7 volts less than that necessary to pull an electron out of metallic tungsten. It is therefore not surprising that experiments[31-32] show that every caesium atom which strikes a tungsten filament at high temperature loses its electron and escapes as a caesium ion. The electric current that thus flows from the tungsten is a quantitative measure of the number of atoms of caesium that strike the filament. Since currents of 10^{-17} A can be measured by an electrometer, it thus becomes possible to detect a pressure of caesium vapor so low that only 100 caesium atoms per second strike the surface of a filament.

The escape of the caesium ions from the tungsten surface is an evaporation

phenomenon. If the temperature is below about 1,100°K, the rate of evaporation of the ions may be so low that it does not keep pace with the rate at which the atoms arrive, so that there is an accumulation of adsorbed caesium on the surface. As a matter of fact, the rate of evaporation of the adsorbed caesium from the surface at a thousand degrees is about the same as that from a surface of metallic caesium at room temperature (300°K). Thus from Trouton's rule we should expect the heat of evaporation of caesium adatoms to be about three times as great as the heat of evaporation of caesium itself.

Such large forces between the adsorbed caesium atoms and the underlying tungsten surface are to be expected as a result of the fact that the caesium tends to lose its electron when close to the tungsten surface. Thus the positively charged caesium ion induces into the conducting tungsten surface a negative charge, which exerts a force of attraction on the ion (the "image force") equal to $e2/4x^2$, where x is the distance of the ion from the surface. This image force is of ample magnitude to account for the strong forces holding caesium on tungsten.

If a thoriated tungsten filament is used, and this is given the special heat treatment required to bring a complete monatomic film of thorium to the surface, the heat of evaporation of electrons falls to about three volts, which is 0.9 of a volt lower than the ionizing potential of caesium. In accord with this fact the experiments show that caesium atoms are not converted into ions by an activated thoriated filament, nor is there any observable tendency for the caesium to become adsorbed on the filament.

If, with a pure tungsten filament in presence of caesium vapor, the temperature is maintained low enough to permit an adsorbed film of caesium to be formed, the positively charged adatoms, which cause a positive contact potential against the pure tungsten surface, have the effect of lowering the heat of evaporation of the electrons. When such an amount of caesium is present on the surface that the heat of evaporation is materially below 3.9 volts, the tendency of the filament to rob incoming caesium atoms of their electrons and thus allow them to escape as ions is lost. This means that v_p, the rate of evaporation of ions, becomes very small as Θ, the fraction of the surface covered by caesium atoms, increases.

At temperatures of about 700°K, in presence of caesium vapor saturated at room temperature (pressure about 10^{-9} atmosphere), Θ increases to approximately 0.7 and the heat of evaporation has then been lowered to such a point that the electron emission is 10^{22} times greater than that of a clean tungsten filament at the same temperature.

Within the last three years, Dr. J. B. Taylor and I have made a detailed study[28,30] of the rates of evaporation of atoms, ions and electrons from these caesium films on tungsten as functions of Θ and T. In order to measure Θ, a method was devised for determining σ, the number of adsorbed atoms per square cm of tungsten surface. Two methods were found. When Θ is less than 0.08, a sudden heating or flashing of the filament at temperatures above 1,300° causes every caesium adatom to escape from the filament as an ion so that the ballistic kick measured with the galvanometer gives directly the value of σ. The second method, which is applicable at any values of σ (even those corresponding to polyatomic layers), involves the evaporation of the adatoms as atoms, in the presence of a retarding field which prevents the escape of ions. This burst of atoms falls on a parallel neighboring tungsten filament heated above 1,300° from which these atoms escape as ions. The ballistic kick of current from this second filament thus measures σ on the first filament. We call this the two-filament method of measuring σ.

The measurements of σ showed that as the caesium pressure is increased or the filament temperature lowered, σ increases to a definite limiting value of σ_I which is 4.8 x 10^{14} atoms per square cm of apparent filament surface. A study of the crystal habits of tungsten has shown that the surface lattice of surfaces etched by evaporation contains 1.425 x 10^{15} atoms per square cm. Since the diameter of the caesium atoms is almost exactly twice that of tungsten, and because of the tendency of the adatoms under the strong forces exerted by the tungsten, to occupy definite elementary spaces on the surface, we conclude that the maximum number of caesium adatoms is one quarter the number of tungsten atoms and therefore the true value of σ_I is 3.563 x 10^{14} atoms per square cm. Comparing this with the observed or apparent value of σ_I it appears that the true surface of the tungsten filament is 1.347 times the apparent surface, this difference being due to the slight etching of the filament surface by evaporation at high temperatures.

A study of transient states during which Θ increases or decreases with time has proved conclusively that the phenomenon of condensation or evaporation goes on independently of one another, the condensation being dependent on μ, while the evaporation v is strictly a function of Θ and T only, and does not depend upon the way the surface film has been formed.

The experiments show that within the accuracy of the experiments (about 0.5%) the condensation coefficient α is always equal to unity even when Θ is as great as 0.98. This proves that the incident atoms, which under these conditions must nearly all strike adatoms, can slide around in a second layer

until they find positions in the first layer. The experiments prove, however, that the number of atoms which exist at any time in the second layer is extremely minute, of the order of 10^7. The atoms in the second layer possess very high surface mobility.

The rate of evaporation of atoms v_a increases at any given temperature extremely rapidly as Θ increases. Thus at 1,000°K an increase of Θ from 0.1 to 0.9 causes a 10^{11}-fold increase in v_a. This indicates very strong repulsive forces between the adatoms in agreement with the fact that these adatoms tend to be positively charged as indicated by the effect of the film in increasing the electron emission. It has been possible to develop this relationship between v_a and v_e into a quantitative theory.

A single caesium adatom on a tungsten surface may be regarded as an ion held to the metal by its image force. The image and the ion thus constitute a dipole, having an electric moment M, oriented with its axis perpendicular to the surface. Because of the strong electric fields close to the ion when it is adsorbed on the surface, we should expect the conduction electrons in the metal to be drawn towards the ion so that the dipole moment should be considerably less than we would calculate for a caesium ion at a distance from an ideal metal surface equal to its radius. The experimental values of M have actually been found to be 16.2 x 10^{-18}, whereas we calculate 25 x 10^{-18} for a spherical caesium ion in contact with an ideal conducting plane.

The force f between two such adion dipoles is given by

$$f = (3/2) \; M^2/r^4 \tag{21}$$

where r is the distance between the adions.

We may now work out the equation of state of the adsorbed caesium films in terms of these forces by means of Clausius' virial equation which for surfaces takes the form

$$F = \sigma kT + (1/4)\,\sigma\,\Sigma\,(rf) \tag{22}$$

where the summation is to extend over all adatoms which act on any one adatom. The forces f are of two kinds: first, the long-range forces which correspond to the dipole repulsion given by Eq. (21), and second, the short-range forces acting between atoms in contact which prevent any two from occupying a single elementary space at the same time. These short-range

forces may be taken into account by dividing the second member of Eq. (6) by $(1-\Theta)$, as has already been done in Eq. (7). In this way by an integration process it has been possible to derive the general equation of state for adsorbed atoms which repel as dipoles. This equation is

$$F = \sigma kT/(1-\Theta) + 3.34\,\sigma^{5/2}M^2 \; + \; 1.53 \times 10^{-5}\sigma^2 T^{1/3}M^{4/3}I \qquad (23)$$

where I is an integral whose numerical value can never exceed 0.89 and which can be obtained from tables and curves from the value of M, σ and σ_1.

The spreading force F calculated in this way cannot be measured directly for a solid surface but it can be related to the rate of evaporation v_a by means of Gibbs' equation

$$\frac{\mathrm{d}F}{\mathrm{d}\ln v_2} = \sigma kT \qquad (24)$$

By substituting in this equation the values of F from Eq. (23), v_a can be calculated in terms of M. Actually we have reversed the process. From the experimentally determined values of v_u as functions of σ and T, *we* have calculated F by Eq. (24) and from these by Eq. (23) have obtained M. These values of M are found to be functions of σ but are not appreciably dependent on T, although a slight dependence is indicated by the form of Eq. (23).

A test of this theory can be made since the values of M obtained from v_a may be compared with values of M obtained from the contact potential which may in turn be obtained from measurements of v_e. The contact potential V of a surface covered with an adsorbed film as compared with that of a pure metal surface is given by

$$V = 2\pi\sigma M \qquad (25)$$

Furthermore the electron emission v_e is related to the contact potential V by the Boltzmann equation

$$v_e/v_w = \exp\,(Ve/kT) \qquad (26)$$

where v_w is the electron emission from pure tungsten at the same temperature. The full line curve in Fig. 2 gives values of V calculated by Eq.

(25) from M as determined from v_a. The points shown by small circles represent values of V obtained from v_a by Eq. (26).

The values of V obtained by these two independent methods agree nearly perfectly when Θ <0.5. The deviations at higher values of Θ seem to indicate that for high values of Θ the short-range forces are somewhat greater than those given by the factor $1-\Theta$, the denominator of the first term of the second member of Eq. (23). Calculation shows that for a value of $\Theta = 0.75$, that part of the spreading force which is due to the short-range forces is actually 45 percent greater than is given by the first term in the second member of Eq. (23).

It is also possible to calculate the contact potential from data on v_p, the rate of evaporation of ions from the surface. The values of v_a, v_e and v_p must be so related to one another that they give concentrations of atoms, electrons and ions in the vapor space near the filament which agree with the thermodynamical requirement for equilibrium among these particles. We may thus put

$$n_e n_p / n_a = K \tag{27}$$

where K is the equilibrium constant that can be determined from the ionizing potential in accordance with the Saha equation. When this is done, and we combine with the Boltzmann equation and the Dushman equation for the electron emission from tungsten, we obtain

$$\ln\left(2 v_p\right) = \ln\, v_a + \left(e/kT\right)\left(V_w - V_i - V\right) \tag{28}$$

where V_i is the ionizing potential of caesium, and V_w is the heat of evaporation of electrons from tungsten. The values of the contact potential V calculated from v_p in this way are indicated in Fig. 2 by crosses. These points lie on the curve obtained from v_a.

This agreement of the values of V obtained by these three methods shows that our theory gives a complete account of the electrical and chemical properties of moderately dilute adsorbed films of caesium on tungsten. It proves also that the surface of these tungsten filaments was essentially homogeneous, so that the probability of evaporation of any adatom or adion was independent of the position of the atoms on the surface and was determined wholly from the value of σ at that point.

The experiments showed, however, that this conclusion, although true for over 99 per cent of the surface, did not hold exactly. Deviations at very
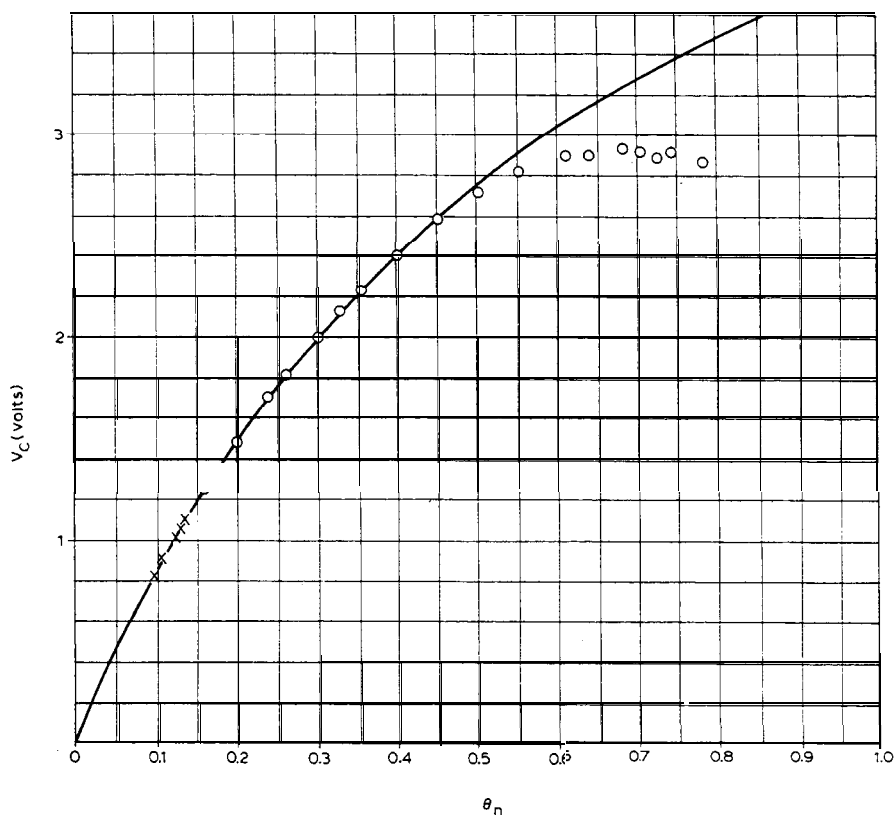
Fig.2. Contact potentia lof caesium films on tungsten against clean tungsten.

low values of Θ indicated that about 0.5 per cent of the surface consisted of what we may call active spots which adsorbed caesium far more strongly than the rest of the surface, so that the heat of evaporation of these areas was about 37 per cent greater than that for atoms on the normal part of the surface. Experiments also showed that adsorption on this part of the surface was of the type indicated by Eq. (17) : the simple type of adsorption iso-therm. This means that the atoms adsorbed in the active areas did not exert appreciable forces on one another. Evidently the active spots consist of separated elementary spaces distributed over the surface, probably near grain boundaries or at steps in the crystal faces.

A variation of the dipole moment M with σ results from the depolarizing effect of neighbouring dipoles. The electric fields due to these dipoles can be calculated by an integration process similar to that used in calculation of F, and are of the order of 5×10^7 volts cm^{-1}.

When a tungsten filament is heated to about 1,100° in caesium vapor and there is an accelerating field drawing ions from its surface, two coexistent surface phases may occur. For one of these Θ is about 0.15, while in the other it is very close to zero. The atoms that strike the less concentrated phase evaporate as ions, while those that strike the concentrated phase evaporate as atoms. The phase boundary is perfectly stable and stationary at a definite temperature in the presence of a given pressure of caesium. If the temperature is raised slightly, the phase boundary moves towards the concentrated phase, so that the whole filament gradually becomes bare; a lowering of the temperature causes the whole surface to become covered with the concentrated phase. A detailed analysis of the mechanism at the boundary between the phases which involves diffusion from one phase to the other, makes it possible to measure the surface diffusion coefficient D. Results have shown that

$$\log\ D\ =\ -\ 0.70\ -\ 3060/T$$

From the temperature coefficient of D it can be calculated that the surface diffusion activation energy is about 0.6 volts. This means that between each of the elementary spaces there is a potential barrier of the height of 0.6 volts over which the adatoms must hop in order to migrate over the surface.

The experimental methods involved in these studies of caesium films on tungsten are capable of very great accuracy and sensitiveness, so that they seem to offer a rich field for the detailed study of adsorption phenomena. Dr. Taylor and I are continuing work in this field. We are planning to make accurate comparisons between the properties of films of adsorbed caesium, rubidium and potassium. We have developed a method of introducing definite small amounts of oxygen by diffusion through a heated silver tube. In this way known numbers of oxygen atoms may be placed on the surface of a tungsten filament thus forming negative dipoles. These attract the positive caesium dipoles which tend to form clusters around them, forming a kind of two-dimensional colloidal distribution of caesium. We hope by the detailed study of such systems to learn the effects not only of repulsive but also of attractive forces between adatoms. Experiments are also in progress to study the adsorption of caesium on tungsten surfaces containing known numbers of adsorbed thorium atoms.

In such ways as these, together with the methods involving the spreading of oil films on water, it becomes possible to determine the equations of states

of two-dimensional gases, with nearly the same degree of accuracy as in the case of three-dimensionals, but with the further advantage that the conditions are especially favorable for the determination of the mechanism of all of the processes involved.

Types of adsorption

The classical kinetic theory of gases, as for example in the treatment of viscosity by Sutherland and of the continuity of the transition from gas to liquid by Van der Waals, led to the recognition of attractive forces between molecules at large distances and of strong repulsive forces at short distances. The chemist has long known that exceptionally large attractive and repulsive forces are associated with the chemical union between adjacent atoms, which he represents by the valence bond (primary valence) and that weaker forces, which he has called secondary valence forces, usually correspond to other types of chemical combinations. The physicist has studied the forces between charged particles, such as ions and dipoles, and more recently has discovered the interchange forces, which are best explained in terms of quantum mechanics.

In the structure of matter there can be no fundamental distinction between chemical and physical forces: it has been customary to call a force *chemical,* when it is more familiar to chemists, and to call the same force *physical,* when the physicist discovers an explanation of it. There are also usually no sharp dividing lines between attractive and repulsive forces or between the various kinds of attractive or repulsive forces. Nevertheless a recognition of various types of forces responsible for the stability of matter proves useful in classifying natural phenomena. Thus in a qualitative way we may consider the following types of force[29].

(1) Coulomb forces between ions or ions and electrons varying with $1/r^2$ where r is the distance between ions. The best examples of these forces are in salt-like substances.

(2) Forces between dipoles which vary with $1/r^4$ and depend on the orientation of the dipole.

(3) Valence forces, associated with the sharing of electrons between atoms.

(4) Van der Waals' attractive forces, which depend on the mutual polarizability of molecules. These forces are usually considered to vary with $1/r^7$.

(3) Repulsive forces due to the mutual impenetrability of completed elec-

tronic shells. It is primarily these which determine the collision areas of mole-
cules in the kinetic theory. Born and Mayer[33] find that the potential energy
of these repulsive forces between two completed shells is given by

$$A \exp \left[(r_1 + r_2 - r)/r_0 \right]$$

where r_1 and r_2 are the effective radii of the two shells and r_0 is a universal
constant equal to 0.435 A, while A is another universal constant. This means
that this type of repulsive force between two atoms can be expressed as a
function of the distances between the *surfaces of the atoms,* this function being
the same for nearly all atoms (or molecules) which have completed shells,
regardless of their electric charge. From a consideration of several of the
other properties of solids and liquids I had previously drawn a similar con-
clusion[20], that the repulsive forces should be regarded "as surface forces
which should be expressed as functions of the distances between the surfaces
of the atoms (fixed by the electron orbits), rather than in terms of the dis-
tances between the centers of the atoms". A consideration of Van der Waals'
forces showed that for these also the "intensities of the fields around dif-
ferent non-polar molecules are practically identical when regarded as surface
forces".

The fact that these repulsive forces, according to Born and Mayer, de-
crease to $1/e^{th}$ value for each increment of 0.435 A° in the distance between
the atoms, indicates that they have a very small range of action.

(6) *Electron pressures* - The force that counterbalances the Coulomb attrac-
tion of the electrons and ions in the alkali metals - and probably in other
metals - is that due to the pressure of the Fermi electron gas.

Since all of these forces can be effective at the surface as well as in the
interiors of solids and liquids, they must take part in adsorption phenomena.
There should thus be various types of adsorption corresponding to the sev-
eral types of forces which hold the atoms or molecules on the surface. Let us
consider some examples:

Caesium on tungsten - The caesium ions are held by Coulomb attractive
forces (here a modified image force) to the underlying metal. The corres-
ponding repulsive forces which hold the ion a definite distance from the sur-
face (and thus determine the dipole moment M) result from the pressure
gradient in the Fermi electron gas which extends beyond the lattice of tung-
sten atoms. The forces between the caesium adatoms are typical dipole repul-
sions.

Oxygen on tungsten or carbon - The attractive forces are probably typical

valence forces. That they are not ordinary Coulomb forces, such as those effective in caesium adsorption, is suggested by a consideration of the relation of the contact potential to the heat of evaporation of the adatoms. A film of caesium which has the maximum effect on the electron emission (Θ = 0.67) has a contact potential of + 3.0 volts against tungsten, while the heat of evaporation of the adatoms corresponds to 1.9 electron volts. With an oxygen film produced when a tungsten filament at 1,600° is in contact with oxygen at low pressure, the contact potential against tungsten at 1,600° is ‑ 1.6 volts, but the heat of evaporation is about 7 volts.

The adsorption of oxygen, hydrogen and carbon monoxide on platinum[36] affords other examples of adsorption dependent on primary valence forces.

Oil films on water - In these cases the attractive forces that cause the active heads to spread over the surface are principally dipole forces between the heads and the water molecules with some contribution from Van der Waals' forces. Above the heads there is a hydrocarbon phase in which Van der Waals' forces and the repulsive forces between completed shells predominate.

Non-polar gases on glass - The adsorption of such gases as nitrogen, argon, etc. on glass or mica at low temperatures is determined by typical Van der Waals' forces[24].

Activated adsorptions

Because of the various types of adsorption that exist, a single gas may be adsorbed by a given surface in several different ways. At sufficiently low temperatures Van der Waals' forces alone would be sufficient to cause adsorption (Van der Waals' adsorption). At higher temperatures molecules on the surface may undergo chemical change and thus be held by valence forces. The heat of adsorption is then far greater than corresponds to the Van der Waals adsorption. The only reason that such adsorption does not occur at low temperatures is that the reaction velocity of the chemical change may be too low. Since there is an activation energy associated with each such reaction, H. S. Taylor[34] has proposed the term *activated adsorption* for the adsorption which involves such chemical changes.

In some cases, such as the adsorption of caesium atoms on tungsten, the adsorption involves only the transfer of one electron and can thus occur at very low temperatures so that activation is not required, and only one type of adsorption is observed.

The distinction between Van der Waals' adsorption and activated adsorption was pointed out by the writer[24] in 1918 and illustrated by the adsorption of carbon monoxide and of oxygen on platinum. At the temperature of liquid air and with a clean platinum surface in contact with carbon monoxide at a pressure of 16 baryes, the surface concentration σ of the adsorbed carbon monoxide was 3.9×10^{14} molecules cm^{-2}, but, as the temperature of the platinum gradually rose to 20°C, σ *decreased* to 1.4×10^{14} and then *increased* again to 3.9×10^{14} and remained nearly constant until 200°C had been reached. When oxygen was brought into contact with platinum at liquid air temperature, 1.5×10^{14} molecules cm^{-2} were adsorbed immediately. On raising the temperature to 20°C, σ increased very slowly (in 18 hours) to 3.0×10^{14}. At 360°C σ rose to 4.8×10^{14}. It was concluded "that at liquid-air temperature platinum adsorbs carbon monoxide in much the same way that glass does, that is, by secondary valence forces. With a moderate rise in temperature this gas is released, but in the neighborhood of room temperature the reaction velocity becomes sufficient for the platinum to react (primary valence) with the carbon monoxide to form a much more stable adsorbed film."

In a discussion of the mechanism of the dissociation of hydrogen on tungsten filaments in 1916 the writer considered[7] the possibility that the adsorbed hydrogen exists on the surface in two forms and that the velocity of interaction between these forms may determine the rate of production of atomic hydrogen. The mathematical formulation which was given is applicable to many cases of activated adsorption.

Within recent years H. S. Taylor[34] and his co-workers have discovered many cases of activated adsorption and have demonstrated their importance in an understanding of contact catalysis. The velocity of the activation reaction, which is often low even at a temperature of several hundred degrees, has been measured and the activation energy calculated. Other investigators have sought to explain these slow surface reactions by assuming solution of the adsorbed gas in the underlying substance or slow penetration into cracks or capillary spaces.

That this cannot be a general explanation is proved by some experiments[35] that Dr. Blodgett and I have made on the thermal accommodation coefficient of hydrogen in contact with tungsten. At temperatures from 200°K to 600°K a stable adsorbed film of hydrogen on tungsten is formed which gives an accommodation coefficient α of about 0.22. As the temperature is raised, this film goes over slowly into a much more stable film which is charac-

terized by a value of $\alpha = 0.14$. The reaction velocity is such that the forma-
tion of the stable film requires several minutes at 600°K and a small fraction
of a second at 900°, indicating an activation energy of the order of at least
20 kg calories per molecule. Since the accommodation coefficient is a purely
surface property, these experiments prove that these two forms of hydrogen
film are both monatomic films which probably represent two kinds of
chemical binding by valence forces. At temperatures below liquid-air tem-
perature a clean tungsten surface would undoubtedly show also Van der
Waals' adsorption of hydrogen. This would thus be a third kind of adsorbed
film of hydrogen on tungsten.

Catalytic action of surfaces

A monatomic film of oxygen on tungsten at 1,500° acts as a catalytic poison
for nearly all the reactions which would otherwise occur in contact with the
tungsten surface[15]. Thus the dissociation of hydrogen into atoms at 1,500°K
is stopped by a trace of oxygen, as is also the decomposition of ammonia,
methane, or cyanogen. The effect of the oxygen is to cover the surface so
that the other gas cannot make contact with the tungsten surface.

Similarly hydrogen and carbon monoxide act as catalytic poisons on plati-
num surfaces[36]. The rate at which carbon monoxide and oxygen combine
in contact with platinum is proportional to the pressure of oxygen and in-
versely proportional to the pressure of the monoxide. The reaction velocity
depends on that fraction of the platinum surface which is *not covered* by ad-
sorbed molecules of carbon monoxide. The oxygen molecules that can be-
come adsorbed in these vacant spots and so be adsorbed on the platinum
surface can thus react with adjacent adsorbed molecules of carbon monoxide.

In numerous cases investigated, the action of a surface in catalyzing a gas
reaction involves just such interaction between molecules adsorbed in ad-
jacent elementary spaces on the surface. On this basis it is possible to de-
velop[7,13,36] a "law of mass action" for the velocity of surface reactions by
which the observed reaction velocities can be explained quantitatively. It has
been pointed out[15] that reactions of this sort are extremely sensitive to the
actual distances between the atoms in the surface of the catalyst. Thus with
many surfaces 'there is only a relatively small fraction of the surface on which
the reaction can occur with extreme rapidity, while over the larger part of
the surface it takes place at a negligible rate. A quantum theory explanation

of the importance of the spacing of the atoms in the catalyst has recently been given by Sherman and Eyring[37].

The presence of a second layer of adsorbed atoms or molecules, although this second layer may cover only a minute fraction of the surface, is often of great importance in the mechanism of gas reactions brought about by a surface catalyst.

Thus in the oxidation of heated tungsten filaments in oxygen at low pressures by which WO_3 is formed, the oxygen molecules incident on a surface already nearly completely covered by a monatomic film of oxygen atoms, condense and momentarily exist in a second adsorbed layer[29]. Although the rate of evaporation from this second layer is so high that the surface concentration is very low, the adsorbed atoms or molecules in this layer move freely over the surface and thus fill up the holes in the first layer, formed when WO_3 molecules evaporate, far faster than would otherwise be possible. These atoms in the second layer can also interact with those in the first layer and with the underlying tungsten to form the molecules of WO_3 which escape from the surface.

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