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VAPOR PRESSURES, EVAPORATION, CONDENSATION AND ADSORPTION

BY IRVING LANGMUIR

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The adsorption of gases or vapors on solids is due to the time lag between the condensation and the evaporation of the molecules from the surface. The relation between the pressure and the amount of gas adsorbed thus depends primarily upon the laws of condensation and of evaporation. In an earlier paper¹ several different relationships for condensation and evaporation were chosen to illustrate some simple typical examples of adsorption phenomena.

In Case I, which was there considered as "simple adsorption," it was postulated that the forces acting between adjacent adsorbed atoms or molecules² are negligible, so that the average life of each adsorbed atom (adatom) is independent of the presence of others on the surface. If Θ represents the fraction of the surface covered by adatoms, the rate of evaporation ν is thus equal to $\nu_1\Theta$, where ν_1 is the rate of evaporation from a completely covered surface. It was also assumed, for the sake of simplicity, that atoms condense only on that part of the surface which is bare, so that the rate of condensation was taken to be $\alpha_0\mu(1 - \Theta)$, where μ , the rate at which incident atoms strike the surface per unit area is given by

$$\mu = (2\pi mkT)^{-1/2} p = 2.653 \times 10^{19} p(MT)^{-1/2} \quad (1)$$

p being the pressure in baryes, k the Boltzmann constant, 1.371×10^{-18} erg. deg.⁻¹, m the mass of an atom in the gas and M the atomic or molecular weight of the gas on the basis of O = 16.

The factor $\alpha_0(1 - \Theta)$ is the fraction of the incident atoms which condense, α_0 being a numerical factor not exceeding unity, which measures the efficiency of the condensation on a *bare surface*.

For a steady state the rates of condensation and evaporation are equal. Equating them and solving for Θ we have

$$\Theta = \frac{\alpha_0\mu}{\nu_1 + \alpha_0\mu} \quad (2)$$

The average life of τ of an adsorbed atom on the surface is

$$\tau = \sigma_1/\nu_1 \quad (3)$$

where σ_1 is the number of adsorbed atoms per unit area for a saturated surface, $\Theta = 1$. Thus equation (2) may also be written

¹ I. Langmuir, THIS JOURNAL, 40, 1361 to 1403 (1918).

² The word molecule properly includes the atom. However, in the applications of the theories developed in this paper, we shall deal principally with adsorption of atoms such as cesium and therefore for brevity shall use the word atom. In most cases the statements will be valid if atom is replaced by molecule.

$$\theta = \frac{\alpha_0 \sigma \mu}{\sigma_1 + \alpha_0 \sigma \mu} \quad (4)$$

This equation has been found to apply, with reasonable accuracy, to a surprisingly large number of cases of adsorption on plane surfaces. Considering the nature of the simplifying assumption made in its derivation, it should, of course, not be looked upon as a general equation of the "adsorption isotherm."

Several recent quantitative studies of adsorption phenomena in this Laboratory have given, as expected, data on evaporation and condensation which are very different from those indicated by Eqs. (2) or (4). It therefore seems desirable to present a more up-to-date analysis of the factors determining the rates of evaporation and condensation and to derive equations giving the amount of adsorbed gas, taking into account the effect of the forces acting between adjacent adsorbed atoms.

The evaporation of adsorbed atoms or adatoms from a surface must be governed by laws very similar to those that apply to homogeneous solids and liquids.

Vapor Pressures of Liquids.—The vapor pressures of solids and liquids or their rates of evaporation in vacuum depend principally upon the heats of evaporation since at least approximate values of the latent heats can be calculated from the boiling points by such rules as Trouton's rule. In general the vapor pressure is given with considerable accuracy over a wide range of temperature by an equation of the type

$$p = AT^\gamma e^{-b/T} \quad (5)$$

which is analogous to the Richardson equation for electron emission.

The curve obtained by plotting $\ln p$ against $1/T$ is a straight line if $\gamma = 0$. If γ differs from zero the line must be curved, but because of the very rapid increase of p with T , the range of temperature over which p can be observed is usually so limited that the curvature is extremely small, if not wholly imperceptible. For example, by measurements of electron emission it has not been possible to decide whether $\gamma = 0.5$ or 2.

Thus within a limited range extending symmetrically above and below a mean temperature T_M , we can always replace Eq. (5) by

$$p = A_0 e^{-b_0/T} \quad (6)$$

by so choosing A_0 and b_0 that the two equations give at $T = T_M$ not only the same value of p but the same slope dp/dT . Under these conditions we have

$$A_0 = AT_M^\gamma e^\gamma \text{ and } b_0 = b + \gamma T_M \quad (7)$$

The slope of the $(\ln p)$ vs. $(1/T)$ curve from Eq. (6) is constant, $S_0 = -b_0$, while that obtained from Eq. (5) is variable and at any point has the value

$$S = S_0 + \gamma(T - T_M) \quad (8)$$

A series expansion of the equation obtained by dividing Eq. (5) by Eq. (6) shows that

$$\ln \frac{p}{p_0} = (\gamma/2) \left(\frac{T - T_M}{T_M} \right)^2 \quad (9)$$

where p and p_0 are the values of p given by Eqs. (5) and (6), respectively, after choosing the constants in accord with Eq. (7).

The temperature change $\Delta T = T - T_M$ needed to cause a 5% change in p is

$$\Delta T = 0.05 T^2/b_0$$

With $T = 800$ and $b_0 = 32,000$, which are typical experimental data such as we shall have occasion to use in studies of cesium films on tungsten, it is thus necessary to know the filament temperatures within 1° in order to get p within 5%.

By Eq. (9) we see that Eqs. (5) and (6) give values of p agreeing within 5% as long as $(T - T_M)/T_M$ is numerically less than $0.32 \gamma^{-1/2}$. With $\gamma = 2$ and $T_M = 800$ there is thus a range of temperature extending about 180° on each side of T_M in which Eqs. (5) and (6) are experimentally indistinguishable if temperatures can only be measured within 1° . Over this total range of 360° , p increases more than 10^8 -fold.

According to the Clapeyron equation and the laws of ideal gases, λ , the latent heat of evaporation per atom, at constant pressure is

$$\lambda = -k \frac{d \ln p}{d(1/T)} = kb_0 = k(b + \gamma T) \quad (10)$$

The exponent γ is thus a measure of the temperature coefficient of λ and the constant A may be regarded as the integration constant of the Clapeyron equation.

Le Chatelier pointed out long ago³ that the integration constants of the Clapeyron equation for reactions of the same type have approximately the same numerical value.

Trouton's rule states that L , the latent heat in calories per gram molecule, is proportional to the boiling point T_B . The value of the ratio L/T_B from data on ordinary liquids is usually given as 20.7. Examination of Eq. (6) shows that Trouton's rule follows from this equation at once if A_0 is a universal constant. Placing $p = 10^6$ baryes (1 atmosphere) and $b_0/T = 20.7/R = 10.4$, we obtain $A_0 = 3.4 \times 10^{10}$ baryes.

When Trouton's rule is applied to substances having very low or very high boiling points, it is soon seen that L/T_B varies considerably and in general is higher for substances having higher boiling points.

Hildebrand⁴ has reasoned that different substances should be compared, not at their boiling points, T_B , but at temperatures T_0 at which the liquids have the same vapor concentration.

³ See H. S. Taylor, "Treatise on Physical Chemistry," Van Nostrand Co., N. Y., 1924, Vol. II, p. 1135.

⁴ J. H. Hildebrand, THIS JOURNAL, 37, 970 (1915); 40, 45 (1918).

Replacing p by its value nkT , in terms of the atomic concentration n , and putting $\lambda = kb_0$, Eq. (6) becomes

$$n = (A_0/kT)e^{-\lambda/kT} \quad (11)$$

Hildebrand's rule states that if, for each of a series of substances, we chose a temperature T_0 which gives the vapor of that substance an arbitrary concentration n_0 (the same for all), then the ratio λ/T_0 is the same for all the substances. By Eq. (11) this must mean that A_0/kT_0 is also the same for all the substances. Thus instead of A_0 being constant, as it should be by Trouton's rule, Hildebrand's rule requires that A_0 shall be proportional to T_0 , so that in Eq. (6) we can replace A_0 by CT_0 where C is a universal constant. We may now get rid of T_0 , a troublesome arbitrary factor, by transforming the equation by means of Eq. (7), obtaining ($\gamma = 1$)

$$p = A_1 T e^{-b_1/T} \quad (12)$$

where A_1 is a universal constant having the value C/ϵ and

$$b_1 = b_0 - T_0 \quad (13)$$

This conclusion from Hildebrand's rule is not strictly in accord with the Clapeyron equation since by Eq. (10) b_1 must have the value

$$b_1 = b_0 - T = (\lambda/k) - T \quad (14)$$

The errors made by replacing T by T_0 are, however, far less than those due to other causes of variability of the "universal constant" A_1 . The experimental evidence in support of Hildebrand's rule is thus equally good evidence that the constant A_1 in Eq. (12) is approximately the same for all substances. This formulation of Hildebrand's rule has the advantage that it does not involve any arbitrarily selected standard concentration such as that needed to define T_0 .

When a liquid or solid is in equilibrium with its vapor, evaporation and condensation go on simultaneously. In general every incident atom condenses, so that $\alpha = 1$ and the rate of condensation μ is given by Eq. (1); this must also equal the rate of evaporation ν_1 . The average life τ of the atoms on the surface, as given by Eq. (3), can thus be expressed by

$$\tau = (2\pi mkT)^{1/2} \sigma_1/p \quad (15)$$

The velocity constant K of a monomolecular reaction varies with temperature according to the equation

$$K = K_0 e^{-b/T} \quad (16)$$

Dushman⁵ calls attention to the fact that K_0 has the dimensions of a frequency. The constant b may also be related to a frequency ν_b by the Einstein equation $b = h\nu_b/k$. Dushman makes the hypothesis that these two frequencies are the same, $K_0 = \nu_b$. Let us generalize this hypothesis by assuming that

$$K_0 = \beta \nu_b \quad (17)$$

where β is a numerical factor which Dushman takes equal to unity.

⁵ S. Dushman, THIS JOURNAL, 43, 397 (1921).

The average life τ of a reacting molecule is $\tau = 1/K$. We may thus apply Eq. (16) to evaporation by identifying this average life with that of an atom on the surface of an evaporating substance. From Eqs. (16) and (17) we obtain

$$\tau = (h/\beta b k) e^{b/T}$$

or

$$\tau = 4.8 \times 10^{-11} (1/\beta b) e^{b/T} \text{ seconds} \quad (18)$$

Elimination of τ from Eqs. (15) and (18) gives⁶

$$p = (\beta b \sigma_1 k/h)(2\pi m k T)^{1/2} e^{-b/T} \quad (19)$$

The value of σ_1 depends primarily on the atomic volume but also on the arrangement of the atoms of the solid or liquid. For a crystal having a body-centered cubic lattice, such as tungsten, the crystal faces having closest packing of the atoms are the dodecahedral faces (110) and for these

$$\sigma_1 = 0.897 (\rho/m)^{2/3} = 6.43 \times 10^{15} (\rho/M)^{2/3} \quad (20)$$

where ρ is the density of the solid. The shortest distance δ_0 between atoms is

$$\delta_0 = 1.091 (m/\rho)^{1/3} = 1.289 \times 10^{-8} (M/\rho)^{1/3} \quad (20a)$$

With a close-packed lattice (face-centered) the octahedral faces contain most atoms per unit area and σ_1 is given by an equation like (20) having a coefficient 0.916 instead of 0.897. The coefficient for the expression for δ_0 is 1.122 instead of 1.091. Even for liquids we may use Eq. (20) with sufficient accuracy.

By substituting this value of σ_1 in Eq. (19) and by introducing numerical values of the constants, we obtain as a general equation for vapor pressure

$$p = 5.1 \times 10^9 \beta b \rho^{2/3} M^{-1/3} T^{1/2} e^{-b/T} \quad (21)$$

where

$$b = b_0 - (1/2T) \quad (22)$$

We now have three equations, (6), (12) and (21), which should give p in terms of b . Let us test them by the data on vapor pressures in "International Critical Tables" (I. C. T.), Volume III. In most cases the tables contain the constants B and A_c in the equation

$$\log_{10} p_{\text{mm.}} = 0.05223 A_c/T + B \quad (23)$$

together with the range in temperature over which this relation is known to hold. Comparing this equation with Eqs. (6), (12), (21) and (7) we find that

$$\log A_0 = B + 3.125 \quad (24)$$

$$\log A_1 = B - \log T_M + 2.690 \quad (25)$$

$$\log \beta = B - \log (b \rho^{2/3} M^{-1/3}) - (1/2) \log T_M - 3.80 \quad (26)$$

$$b_0 = -0.1203 A_c \quad (27)$$

⁶ This equation, with $\beta = 1$, has already been tested by Dushman and Langmuir. See Dushman's chapter in H. S. Taylor's "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1924 ed., Vol. II, pp. 1041-1042.

In the case of substances for which B is not given in I. C. T., we may calculate B from two fairly widely separated values of vapor pressure (in mm.) by the equation

$$B = (T_1 \log p_1 - T_2 \log p_2)/(T_1 - T_2) \quad (28)$$

Table I contains values of B and b_0 for eighteen chemical elements, selecting those for which the vapor pressure data are probably of greatest accuracy. The second column gives T_M , the mid-point of the temperature range covered by the data which were used in calculating the values of B and b_0 in the third and fourth columns. All these data were obtained from I. C. T. except in the case of rubidium and cesium. The positive ion method⁷ developed in this Laboratory is believed by the writer to be far more accurate than other published data for these two elements.

If Trouton's rule is valid, the values of A_0 , and therefore by Eq. (24) the values of B , should be the same for all substances. At the bottom of the table the average value of B is given and also the "standard deviation" (S. D.) of the individual values from the mean, *viz.*, the root-mean-square deviation. The average value of $\log A_0$ is therefore 10.65 with a S. D. of 1.19.

The fifth column gives the $\log A_1$ calculated from B by Eq. (25). These data serve as a test of Hildebrand's rule. The S. D. from the average value is only 0.52, which is less than half of that observed with Trouton's rule.

TABLE I
VAPOR PRESSURE DATA OF COMMON ELEMENTS

1	2	3	4	5	6	7
	T_M	B	b_0	$\log A_1$	$\log \beta$	$\log A_{1.4}$
He	4.0	4.65	17.3	6.74	+0.03	6.22
H ₂	19.3	5.48	122	6.88	-.20	6.02
N ₂	75	6.86	709	7.68	-.41	6.52
O ₂	79	7.09	872	7.88	-.38	6.72
A	88	6.96	821	7.71	-.54	6.52
Kr	114	6.92	1,130	7.55	-.84	6.31
Cl ₂	221	7.59	2,580	7.94	-.57	6.55
Br ₂	293	7.88	3,810	8.10	-.68	6.65
I ₂	423	7.98	5,370	8.04	-.90	6.51
P ₄	373	7.80	6,260	7.92	-.89	6.42
Hg	470	7.90	7,260	7.92	-1.45	6.36
Cd	700	8.16	12,500	8.00	-1.43	6.36
Zn	790	8.18	14,300	7.97	-1.48	6.31
Na	600	7.55	12,400	7.46	-1.48	5.83
Rb	340	7.43	9,500	7.59	-1.40	6.11
Cs	320	7.53	9,200	7.71	-1.31	6.25
C	4400	9.60	65,000	8.65	-0.87	6.61
W	2800	9.92	108,000	9.16	-1.11	(7.22)
Average		7.53		7.83	-0.88	6.37
S. D.		±1.19		±0.52	±0.46	±0.22

⁷ Langmuir and Kingdon, *Proc. Roy. Soc. (London)*, [A] **107**, 61 (1925); Killian, *Phys. Rev.*, **27**, 578 (1926).

The data of the sixth column, which serve as a test for the validity of Eq. (21), show that the average value of $\log \beta$ is -0.88 and the individual values have an S. D. of 0.46 . Thus if we place $\beta = 0.13$ in Eq. (21) we have an expression for vapor pressure which is more accurate than Eq. (12). By Dushman's hypothesis β should be unity; the observed value is of about the same order of magnitude although distinctly less than unity.

In some preliminary tests of Eq. (21), $\log \beta$ was calculated from Eq. (26), by using approximate values of b from Trouton's rule placing $b = 11.5 T_B$. This gives a term $(3/2) \log T_M$ instead of $(1/2) \log T_M$. The resulting equation was found to agree with the experimental data much better than does Eq. (21). Furthermore, it was observed that the factor $\rho^{2/3} M^{-1/6}$ did not contribute materially to this accuracy. It was therefore decided to test also the empirical equation

$$p = A_{1.5} T^{3/2} e^{-b/T} \quad (29)$$

where

$$b = b_0 - (3/2)T = (\lambda/k) - (3/2)T \quad (30)$$

to see if $A_{1.5}$ is not more nearly constant than A_1 or β . The data in the seventh column⁸ were thus calculated, in accord with Eqs. (7) and (23), from

$$\log A_{1.5} = B - (3/2) \log T_M + 2.473 \quad (31)$$

It is seen in fact that the S. D. of $\log A_{1.5}$ is now only 0.22 , which is only about one-third as great as the S. D. for $\log A_1$ and less than one-half that of $\log \beta$. The average value corresponds to

$$A_{1.5} = 2.5 \times 10^6 \text{ baryes deg.}^{-3/2} \quad (32)$$

The data on the vapor pressures of liquid chemical compounds in I. C. T., Vol. 3, pp. 213-214, are in agreement with these conclusions. Certain "associated" substances, such as H_2O and NH_3 give values A_1 and $A_{1.5}$ about ten times above normal. The following ten liquids, for which accurate data are available, give $\log A_{1.5} = 6.50 \pm 0.16$: HCl , HBr , HI , CCl_4 , CS_2 , $SiCl_4$, $SnCl_4$, C_2H_6 , C_4H_{10} , C_6H_6 (benzene). The data for fused salts are similar, although naturally less reliable. Thus the seven salts: $PbCl_2$, $HgCl_2$, $LiCl$, $NaCl$, KCl , KI , LiF , give $\log A_{1.5} = 6.43 \pm 0.47$, the mean value of T_M being $1340^\circ K$.

We may thus conclude that Eq. (29) with the value of $A_{1.5}$ given by Eq. (32) is the most accurate of the expressions we have tested, giving the vapor pressures of liquids usually within about 40%, if the value of b_0 is known.⁹

⁸ In forming the average, the value for W was discarded as this metal was in the solid state. The data for C are said in I. C. T. to apply to liquid carbon.

⁹ These deviations from Eq. (29) are of course not to be regarded as errors. Any rigorous calculation of vapor pressures must involve either knowledge of specific heats and chemical constants or a detailed knowledge of the constitution of the liquid and gas phase such as we may hope to obtain from spectroscopic data, etc. This knowledge is so seldom available that it is a matter of considerable practical importance to have an empirical equation like Eq. (29) which is so generally applicable.

Vapor Pressures of Solids.—If the latent heat of fusion L_F is known, the vapor pressure of a solid below the melting point T_F may be calculated from that of the liquid above this temperature. Thus we have

$$P_S = A_S T^\gamma \exp. (-L_S/RT) \text{ and } p_L = A_L T^\gamma \exp. (-L_L/RT)$$

Equating $p_S = p_L$ at T_F and noting that $L_S - L_L = L_F$ we have

$$A_S = A_L \exp. (L_F/RT_F) \quad (33)$$

The heats of fusion of twenty-one metallic elements are given in I. C. T., Vol. II, p. 458. The ratio L_F/T_F , which we shall call f , is approximately constant, the average value for all these elements (except Sb, which gives 5.3) being 2.34 calories per g. atom per degree, while the S. D. of the individual values is ± 0.72 . For the non-metallic elements (I. C. T., Vol. V, p. 131), taking L_F as the heat of fusion per gram molecule, we find that the ratio $f = L_F/T_F$ is about 2.3 for A, O₂, H₂, N₂ and P₄, but rises to about 9.7 for Cl₂ and Br₂.

Among compounds such as HCl, CCl₄, C₆H₆, NaCl, which have rather compact molecules, f has values ranging from 3 to 8, but for organic substances consisting of large molecules such as stearic acid and tristearine, f rises to large values (40 and 124, respectively), increasing roughly in proportion to the number of atoms in the molecule.¹⁰

Equation (33), after putting $R = 2$ calories, thus becomes

$$\log A_S = \log A_L + 0.218 f \quad (34)$$

We may thus apply Eq. (29) to the vapor pressures of solids if we increase the value of $A_{1.5}$ in accord with Eq. (34). For solid elementary substances or those having relatively rigid molecules, we may put $f = 2.3$ and thus the value of $A_{1.5}$ instead of being given by Eq. (32) should be

$$\text{(for solids)} A_{1.5} = 8 \times 10^6 \text{ baryes deg.}^{-2/3} \quad (35)$$

Chlorine and bromine having less rigid molecules give values of $f = 9.7$ so that by Eq. (34) the value of $A_{1.5}$ for these substances in solid form is about 150 times as great as for ordinary liquids. This agrees well with the

¹⁰ These large values of f are understandable when we consider that a large part of the heat of fusion of such substances must represent an *internal* heat of fusion of the molecules themselves which would increase roughly in proportion to the size of the molecule. Thus in solid tristearine the three hydrocarbon chains are undoubtedly rigidly arranged within the solid lattice so that the molecule itself is solid. But when the substance melts, the molecule also melts.

With such large molecules it is probable that the *molecules of the vapor* may also exist in two states in which they are internally solid or liquid; however, the transition will probably occur in a temperature range far below the melting point of the solid phase. In this range the specific heat of the vapor would have abnormally high values.

From this point of view the large increase in A observed with some solids is due to the fact that the molecules "melt" during the evaporation process so that the vapor molecules have an internal mobility not possessed by those in the solid. If the molecules evaporated as solid molecules, f would have a normal value but the heat of sublimation L_S would no longer be equal to the sum $L_L + L_F$.

data of I. C. T. on the vapor pressures of these solids. For example, for solid chlorine B is given as 9.95, while for liquid chlorine (see Table I) it is 7.59. For organic substances such as tristearine ($f = 124$) according to Eq. (34) $A_{1.5}$ must rise to the enormous value of 10^{33} .

We may thus conclude that $A_{1.5}$ in Eq. (29) may be regarded approximately as a universal constant as applied to liquids and as another constant when applied to solids having rigid molecules; but for other solids the values of $A_{1.5}$ may increase to very much larger values.

Evaporation of Adsorbed Atoms.—The average life τ of an atom on the surface of an evaporating liquid or solid was given by Eq. (15) in terms of σ_1 and p . Disregarding for the present solids with non-rigid molecules, we may consider that p can be expressed in accord with Eq. (29) as a function of T and b . In this way a general expression for τ can be derived

$$\tau = (2\pi mk)^{1/2} (A_{1.5} T)^{-1} \sigma_1 e^{b/T} \quad (36)$$

or if we put $A_{1.5} = 8 \times 10^6$ by Eq. (35)

$$\tau = 4.7 \times 10^{-27} M^{1/2} \sigma_1 T^{-1} e^{b/T} \quad (37)$$

The atoms of solids and liquids as well as gases have kinetic energies corresponding approximately to $(3/2)kT$, so that their average velocity v may be taken to be $1.45 \times 10^4 (T/M)^{1/2}$. It is of interest to know δ , the average total distance measured along its path, which the surface atom travels in the time τ , so that we may estimate the number of oscillations that occur during its life τ . Putting $\delta = v\tau$ and combining with Eqs. (37), (20) and (20a), we thus obtain

$$\delta/\delta_0 = 34(\rho/M) T^{-1/2} e^{b/T} \quad (38)$$

where b is given by Eq. (30).

It should be noted that the coefficient of $e^{b/T}$ is of the order of magnitude of unity. Thus at very high temperatures or for very small values of b (b/T small), δ becomes approximately equal to δ_0 , so that the atoms evaporate in the time necessary to perform one oscillation. Under such conditions we may hardly consider that an impinging molecule condenses and reevaporates.

We need to examine a little more closely the meaning of τ and σ_1 . The life τ may be called the *evaporation life*; a diffusion of a surface atom into the interior of a liquid should not be regarded as a termination of its life. More rigorously τ may be defined by stating that dt/τ is the probability that a given surface atom will evaporate in the time dt .

We have seen that Eq. (29), with the appropriate values of $A_{1.5}$, is applicable with reasonable accuracy to the evaporation of atoms or molecules from surfaces of such widely different types as those of liquid helium, phosphorus, mercury or carbon.

The life of any atom on the surface thus depends essentially on the value of b , in accord with Eqs. (36) and (37). In general, with homogeneous

bodies, the heat of evaporation ($\lambda = kb_0$) is the same for all the atoms. If there are on the surface atoms of more than one kind which differ in composition or in their geometrical relation to one another, the values of b for different atoms may vary. This should not affect the validity of Eq. (36); it would merely give a separate value of τ for each atom dependent upon the b for that atom. Since it is very unlikely that the validity of this equation requires that the evaporating atoms shall be similar to those in contact with them on the surface, we are justified in applying Eqs. (36) and (37) to adsorbed films.

Adjacent adsorbed atoms may exert strong forces on one another, but this will produce its effect on τ , in accord with Eq. (36), by the change in the value of b . However, if the surface is homogeneous, we may take the same value of b for all the adsorbed atoms, although b will vary with the surface concentration σ because of the forces between adatoms. In the following discussions we postulate homogeneous surfaces, but in a later section shall treat the case of heterogeneous surfaces where b varies from atom to atom, not because of the interactions of adatoms, but because of non-uniform forces exerted by the underlying surface.

Consider now a homogeneous surface on which there is an adsorbed film containing σ atoms per unit area, the value of τ being the same for all atoms. The rate of evaporation (atoms $\text{cm.}^{-2} \text{sec.}^{-1}$) is proportional to the probability per sec. ($1/\tau$) for the evaporation of each atom, so that

$$\nu = \sigma/\tau = \sigma_1\Theta/\tau \quad (39)$$

Taking the value of τ from Eq. (36) we have

$$\nu/\Theta = A_{1.6}(2\pi mk)^{-1/2}T\epsilon^{-b/T} \quad (40)$$

or, after inserting numerical values including $A_{1.6} = 8 \times 10^6$ from Eq. (35) and transforming by Eq. (7), we have

$$\nu/\Theta = 5.7 \times 10^{26} M^{-1/2} T_M \epsilon^{-b/T} \quad (41)$$

where

$$b = b_0 - (1/2)T \quad (42)$$

In deriving these equations for the evaporation of adatoms we have not needed to assume that Θ is small or that the interactions between the adatoms are negligible. These relations should thus be applicable to concentrated as well as to dilute adsorbed films. Since, however, b is in general a function of Θ , it does not follow from Eq. (40) that ν is proportional to Θ , except at such low values of Θ that b is close to the limiting value that it must approach as Θ becomes zero.

It is frequently of interest to know the relation between Θ and the gas pressure p in equilibrium with an adsorbed film. Since the rates of condensation and evaporation are then equal we may put

$$\nu = \alpha\mu \quad (43)$$

By combining Eqs. (40), (43) and (1) we obtain the useful result

$$p = (\Theta/\alpha)A_{1.6}T^{3/2}\epsilon^{-b/T} \quad (44)$$

which becomes identical with Eq. (29) if $\Theta = 1$ and $\alpha = 1$. After inserting numerical values according to Eq. (35) and transforming by Eq. (7), this becomes

$$\Theta = 2.8 \times 10^{-3} \alpha p T_M^{-3/2} e^{b/T} \quad (45)$$

Comparison with Experimental Data

In studies of the electron emission of thoriated tungsten filaments,¹¹ the rate of evaporation of adsorbed thorium atoms over the temperature range from 2055 to 2450°K. and at an average value $\Theta = 0.5$ was found to be given by

$$\log \nu = 31.43 - 44,500/T$$

By Eq. (41), putting $M = 232$, $T_M = 2250$ and $\Theta = 0.5$, we obtain

$$\log \nu = 28.62 - b/2.3T$$

The difference of 2.8 between 31.43 and 28.62 is far greater than the S. D. of 0.2 in $\log A_{1.5}$ which we found in Table I. This does not necessarily indicate, however, that the accuracy of Eq. (41) as applied to evaporation of adsorbed substances is not comparable with that of Eq. (29) for vapor pressures. If we put

$$\log \nu = 29 - 39,000/T$$

we find that these values of $\log \nu$ agree, with a S. D. of 0.12, with those experimentally determined. This S. D. is certainly within the possible experimental error.

Measurements¹² of the rates of evaporation of adsorbed oxygen atoms from a tungsten surface have given the data in Table II.

TABLE II

THE RATES OF EVAPORATION OF OXYGEN ATOMS FROM A TUNGSTEN SURFACE

T	$t_{1/2}$, min.	$\log (\nu/\Theta)_{\text{obs.}}$	$\log (\nu/\Theta)_{\text{calcd.}}$	Diff.
1856	27.5	11.77	11.82	-0.05
1978	2.00	12.91	(12.91)	(0.0)
2070	0.292	13.75	13.64	+0.11

The time in minutes required to evaporate half of the adsorbed oxygen is shown in the second column. The *ratios* of these values are far more accurate than the absolute values. Converting these times to seconds and dividing by $\ln 2$ we get τ , and then we may calculate $\nu/\Theta = \sigma_1/\tau$ according to Eq. (39). Since oxygen atoms or ions are smaller than tungsten atoms and are held by extremely strong forces, we may take σ_1 to be the same as for the tungsten atoms on the surface, $\sigma_1 = 1.42 \times 10^{15}$. This gives the values under $(\nu/\Theta)_{\text{obs.}}$ in the table. In these experiments Θ varied in a range between 0.3 and 0.1.

Putting $M = 16$ and $T_M = 2000$ in Eq. (41) and choosing b so that the value of ν/Θ at 1978° agrees with that observed, we obtain

$$\log (\nu/\Theta) = 29.45 - 32,720/T \quad (46)$$

¹¹ Langmuir, *Phys. Rev.*, **22**, 357 (1923). See Table VI and Eq. (41) on p. 391.

¹² Langmuir and Villars. *THIS JOURNAL*, **53**, 495 (1931).

and from this equation the values of $\log(\nu/\Theta)_{\text{calcd.}}$ were calculated. Table II shows that the agreement is within the probable experimental error, as the S. D. corresponding to the differences is only 0.07. The value of b_0 by Eqs. (42) and (46) is 76,400, and the heat of evaporation per gram atom b_0R is 152 kg. cal., which is to be compared with 162 obtained¹² from the temperature coefficient of $t_{1/2}$.

The adsorption of oxygen on tungsten calls into play powerful chemical forces which are often regarded as very different in type from those involved in the evaporation of such substances as are listed in Table I. It is therefore of particular interest to find that Eq. (40) applies so well to a case of this kind.

Forces Acting on Adatoms.—There are two types of forces to be considered: those exerted by the underlying atoms, and those acting between the adatoms.

The underlying atoms always exert attractive forces but these may have an enormous range of intensities. If the surface is covered with adatoms having a heat of evaporation $\lambda = kb_0$, the energy per unit area which must be expended to remove them is $\sigma_1 kb_0$. If the effective range of the forces is 10^{-8} cm., the force per unit area which must be exerted to pull them off is thus $10^8 \sigma_1 kb_0$. With an oxygen film on tungsten $b_0 = 76,000$ and $\sigma_1 = 1.4 \times 10^{15}$, so that this force corresponds to 10^{12} baryes or 10^6 atmospheres.

The smallest forces that are likely to occur are those involved when helium atoms or hydrogen molecules strike a chemically saturated surface such as that of tungsten covered by adsorbed oxygen. In such cases¹³ there is no appreciable adsorption and the incident atoms remain on the surface for a time so short that they do not even reach thermal equilibrium, so that the accommodation coefficient is much less than unity (0.1 to 0.2).

The stability of an adsorbed film depends primarily on the magnitude of b_0 and on the pressure in the gas phase. The condition under which an approximately complete monatomic film is in equilibrium at the pressure p can be found by putting $\Theta = 1$ in Eq. (45)

$$\alpha p e^{b_0/T} > 3.6 \times 10^7 T_M^{3/2} \quad (47)$$

We shall see later in most cases that $\alpha = 1$ except when Θ approaches closely to unity. Thus under high vacuum conditions when $p = 1$ barye, the surface will be completely covered only when b_0/T exceeds 25.9 or 28.6 at values of T_M of 300 or 2000°, respectively. At atmospheric pressure ($p = 10^6$), the corresponding values of b_0/T are 12.1 and 15.2. From these data we find, for example, that an oxygen film in presence of 1 barye of oxygen should cover a tungsten surface ($b_0 = 76,000$) up to about 2600°K.; this conclusion is in accord with experiments.¹⁴ A filament at room

¹³ Blodgett and Langmuir, *Phys. Rev.*, **40**, 78 (1932).

¹⁴ Langmuir, *THIS JOURNAL*, **38**, 2271 (1916).

temperature in presence of gas at 1 barye would be covered if b_0 exceeds 7000.

When b_0/T is so large that the first layer of adatoms is nearly complete, it is possible that a second layer may form; let Θ_2 be the fraction of the surface covered by this second layer.

The conditions under which Θ_2 becomes comparable with unity are given, as before, by Eq. (47) if we replace b_0 by b' which measures the heat of evaporation of atoms from the second layer. There are now two important cases to consider according as b' is less than or is greater than b_0 .

Case I, $b' < b_0$.—There will be a range of temperature in which the film will be a complete monatomic film. For example, with a gas pressure of 1 barye and a temperature range in the neighborhood of $T_M = 600^\circ$, Eq. (47) shows that a complete film forms if b/T exceeds about 27. The temperature T_1 at which the first layer becomes complete is thus $T_1 = b_0/27$, whereas the second layer becomes complete at $T_2 = b'/27$. If $b_0 = 20,000$ and $b' = 15,000$, we have $T_1 = 740$ and $T_2 = 555^\circ$. By Eq. (45) we calculate that at 740° where the first layer is complete, $\Theta_2 = 0.0012$. The temperature coefficients are so great that above 740° the value of Θ in the first layer decreases to 0.14 at 800 and 0.01 at 900° ; in the second layer Θ_2 increases to 0.019 at 650° , 0.13 at 600° and 1.0 at 555° .

Thus even when b' is as great as $0.75 b_0$, the monatomic character of the adsorbed film is very striking, and there is a range of about 100° in which the film is complete.

Let us consider some typical cases in which $b' < b_0$.

The forces between tungsten atoms in solid tungsten (roughly measured by $b_0 = 108,000$ as given in Table I) are comparable in magnitude with those holding the atoms in the most stable of chemical compounds. These forces at a clean tungsten surface are very much unsaturated, each atom having only 6, instead of 8, neighbors. Although in other solids the forces are less intense than in tungsten, comparison with Table I shows that b_0 for typical solids will be at least as great as 10,000.

When gas molecules such as H_2 , N_2 or O_2 , or even inert gas atoms He or A, are brought into contact with the clean surface of solid bodies, attractive forces must usually come into play which are much larger than those holding these gas molecules on surfaces of their own liquid phases. Such attraction would result merely from the polarization of the molecules produced by their deformation in a strong field of force,¹⁵ but these "molecular" forces will never rise to very high values.

At sufficiently low temperatures in presence of gas the surfaces of solids must become completely covered with adsorbed films. Additional gas

¹⁵ A discussion of the nature and magnitude of such forces was given in a paper "Forces Near the Surfaces of Molecules," I. Langmuir, *Chem. Rev.*, **6**, 451 (1929); see particularly pp. 457-462.

molecules striking such surfaces are acted on only by the weak forces exerted by the adsorbed molecules and not the strong forces characteristic of the solid and therefore in all such cases $b' < b_0$.

An estimate of the magnitude of b_0 involved in typical molecular adsorption on non-metallic surfaces may be made from measurements¹⁶ of the adsorption of gases on plane surfaces of glass and mica at the temperature of liquid air.

The amount of gas adsorbed by a given surface was found to vary with the pressure p in accord with the equation

$$q = abp/(1 + ap) \quad (48)$$

where a and b are constants at any given temperature. The parameter a has the dimensions of the reciprocal of a pressure and its value does not depend upon the amount of surface exposed nor upon the units used in measuring q and b . Comparison of Eq. (48) with Eq. (4) shows that they are of the same form and that

$$ap = \alpha_0 r \mu / \sigma_1$$

Combining with Eqs. (43), (39) and (44)

$$1/a = p/\Theta = (1/\alpha)A_{1,0}T^{3/2}e^{-b/T} \quad (49)$$

where b is given by Eq. (30).

For argon, oxygen and nitrogen at 90°K. in contact with dry glass the values of a were found to be 0.051, 0.079 and 0.088 (baryes)⁻¹. The adsorption of these gases on mica gave 0.065, 0.080 and 0.156. From Eqs. (49), (35) and (30), putting $\alpha = 1$, we obtain values of b_0 that average 1950 with a S. D. of only ± 27 .

Table I shows that the average b_0 for the evaporation of these gases is 800. Thus the heat of evaporation of these adsorbed molecules from glass or mica surfaces is about 2.4 times as great as from the corresponding liquid phases.

In the experiments referred to, pressures from 1 to 100 baryes were used. At somewhat higher pressures or lower temperatures the adsorbed films approached saturation ($\Theta = 1$). The forces tending to hold molecules in a second layer are probably not appreciably greater than those that would act in the liquid phases of these gases. It is true that the adsorbed molecules in the first layer are not wholly in the condition of normal molecules in the liquid phase; they are polarized by deformation in a strong field of force. But surely the forces they exert on molecules in the second layer are much closer to the forces characteristic of gas molecules than they are to the forces exerted by the underlying solid upon the molecules in the first layer.

Transmission of Polarization through Molecular Layers.—The forces acting between successive layers of molecules may be characterized

¹⁶ Langmuir, *THIS JOURNAL*, 40, 1361 (1918). See particularly Eq. (31) and the Tables on pp. 1390–1391.

by a series of values of b such as b_0, b', b'' . These must rapidly approach a limiting value b_∞ which would be the same as for a condensed phase of the adsorbed material. Almost the whole of the transition from b_0 to b_∞ must occur between b_0 and b' .

The experiments of de Boer¹⁷ on the adsorption of iodine vapor on solid films of calcium fluoride enable us to estimate the magnitude of these transmitted effects. His experimental results, in terms of our nomenclature, may be summarized by the equation

$$\log [-\log(p/1.1 p_0)] = -4.3 \times 10^{-16} \sigma_1 n + 0.43 \quad (50)$$

where n is the number of layers of molecules of I_2 , each layer containing σ_1 molecules per sq. cm.; p is the pressure of iodine vapor in equilibrium with the film at a given temperature (*ca.* 20°), while p_0 is the vapor pressure of solid iodine at the same temperature. In the experiments p/p_0 was varied only between 0.1 and 0.95.

De Boer and Zwikker¹⁸ have calculated that in a series of layers of polarizable molecules the polarization in the $(n + 1)^{\text{st}}$ layer is K_1 times that in the n th, where K_1 is a constant numerical factor less than unity, but which is proportional to the polarizability α of the molecules. From this they obtain an expression for the vapor pressure, which we may put in the form

$$p = K_2 p_0 \exp. (K_1 K_1^n) \quad (51)$$

Although de Boer does not give the numerical value of K_1 , comparison of Eqs. (50) and (51) shows that

$$\log K_1 = -4.3 \times 10^{-16} \sigma_1; K_2 = -6.2; K_3 = 1.1 \quad (52)$$

Assuming that the arrangement of atoms in the CaF_2 film (produced by evaporation) is like that of octahedral faces of a fluorite crystal, de Boer calculates that the number of fluorine ions per sq. cm. is 7.75×10^{14} . He considers that this number of iodine atoms per unit area are adsorbed. Applying Eq. (20) to molecular iodine we obtain $\sigma_1 = 4.56 \times 10^{14}$ molecules cm.^{-2} .

Harris, Mack and Blake¹⁹ have shown that iodine crystals belong to the orthorhombic system and that the atoms are grouped in pairs as molecules. The distances between the centers of the two atoms in a molecule is 2.79 \AA. , while the shortest distance between the centers of atoms which are not in the same molecule is 3.51 \AA. The unit cell of dimensions $a = 4.795 \text{ \AA.}$, $b = 7.255 \text{ \AA.}$ and $c = 9.780 \text{ \AA.}$, contains four molecules whose centers are at the corners and at the centers of the faces.

From these data we find that in crystal faces parallel to two axes the values of σ_1 are: for ab 5.75, for bc 2.82 and for ca 4.26 (unit = 10^{14} mole-

¹⁷ J. H. de Boer, *Z. physik. Chem.*, [B] **13**, 134 (1931); *Proc. Acad. Amsterdam*, **31**, 906 (1928); see particularly the equation at top of p. 152.

¹⁸ J. H. de Boer and C. Zwikker, *Z. physik. Chem.*, [B] **3**, 407 (1929).

¹⁹ P. M. Harris, E. Mack and F. C. Blake, *THIS JOURNAL*, **50**, 1583 (1928).

cules cm.⁻²). The 111 faces contain $\sigma_1 = 4.35 \times 10^{14}$ molecules. It is evident that if one molecule is located above each fluorine ion ($\sigma_1 = 7.75 \times 10^{14}$) the molecules are very much crowded so that repulsive forces (neglected by de Boer) must be of very great importance. These facts invalidate the particular structure assumed by de Boer, in which *atoms* are considered to be arranged in vertical columns over the fluorine ions. Although the molecules in the first layer are probably attached to the fluorine ions, those in the next few layers are thus probably arranged as irregularly as those of liquids, with a tendency to assume a more stable crystalline form at greater distances from the disturbing CaF₂ surface. In any case, however, the exponential decrease in polarization as the number of layers increases should be approximately true, except in the case of the first and second layers.

If we take $\sigma_1 = 5.75 \times 10^{14}$ as the most probable value (after the first layer), we find from the expression for K_1 in Eq. (52)

$$K_1 = 0.57$$

If $\sigma_1 = 4.56 \times 10^{14}$ as given by Eq. (20), the value of K_1 would be 0.64.

In calculating the coefficient 4.3×10^{-16} in Eq. (50) de Boer assumed that the surface of the CaF₂ film was the same as that of the glass on which it was deposited. If the actual surface was 50% larger, this would decrease K_1 from 0.57 to 0.43.

Roughly speaking, therefore, the polarization of any layer of molecules is about one-half of that in the next lower layer. Langmuir,²⁰ by a study of the dissociation constants of the chlorine-substituted fatty acids, found that the polarizing forces along an aliphatic hydrocarbon chain deformed near one end decrease in the ratio 2.1:1 (or $K_1 = 0.37$) for each successive carbon atom.

Comparing Eqs. (51) and (6) and using the values $K_1 = 0.5$, $K_2 = -6.2$, $K_3 = 1.1$, and $T = 293$ we see that

$$b_n = b_s - 29 + 1800(0.5)^n \quad (53)$$

where b_s is the value of b_0 for solid I₂, which is 7570 according to the data of I. C. T. The term -29 is the contribution of the factor K_3 . The disturbance in the regular arrangement of molecules which results from the underlying CaF₂ film raises the limiting vapor pressure for thick layers by 10% ($K_3 = 1.1$), but this is equivalent to a change of b of only 29 out of 7570 or only 0.4%. When we consider that the difference between the liquid and solid state alters b_0 from 5370 to 7570 (see Table I), we realize how insignificant these disturbances are, and how little we should be justified in assuming a value for σ_1 which is appreciably different from that characteristic of solid iodine.

The term $1800(0.5)^n$ in Eq. (53) results from the polarization transmitted from layer to layer. Thus the polarization of the second layer

²⁰ See reference (15), particularly p. 467.

increases the value by 450 which is only 6% of the value of b_0 for solid iodine.

The exponential factor $(0.5)^n$ is certainly not applicable to the first layer of molecules for these are exposed directly to the powerful polarizing forces of the ions with which they are in contact. We have already seen that glass surfaces (far less effective than CaF_2) raise the value of b_0 for the first layer of nitrogen molecules 2.4-fold, although the polarizability α of N_2 is small compared to that of I_2 . If a similar factor can be applied to iodine, the value of b_0 for the first layer on CaF_2 would be about 13,000; compared to this, the effect of the polarization in the second layer is almost wholly negligible.

When, however, the vapor in contact with an adsorbed film is nearly saturated, even these weak polarizing forces naturally produce marked effects. Substituting the values of K_1 , K_2 and K_3 in Eq. (51), we calculate that the values of p/p_0 for the successive layers are (for $n > 2$).

n	p/p_0	n	p/p_0
1.01	0.0005	2.0	0.235
1.1	.006	3	.504
1.2	.014	4	.744
1.4	.038	5	.906
1.6	.082	6	1.00

For values of n less than 2, where the exponential relation cannot hold, we have assumed a linear relation between b and n . In the exponent of Eq. (51), $-6.2(0.5)^n$ has been replaced by $1.55(3 - n)$, which gives the same value (1.55) for $n = 2$ and gives a value twice as great as this for the evaporation of isolated molecules from the second layer.²¹ The values of p/p_0 obtained by Eq. (51), in the range below $n = 2$, were then multiplied by $\Theta_2 = n - 1$ in accordance with the occurrence of the factor Θ in Eq. (44).

Over the range of pressures p/p_0 from 0.1 to 0.95 covered by de Boer's experiments, n varied only from 1.6 to 5.5. At pressures less than 0.01 p_0 the second layer of molecules rapidly disappears, and the film becomes monomolecular. If b_0 has any such value as 13,000, this monomolecular film would be stable in presence of an iodine pressure as low as $10^{-8} p_0$; the average life τ of the molecules in the first layer would be 2000 sec., while that of isolated molecules in the second layer ($b' = 8440$) would be only 4×10^{-4} seconds.

These conclusions, while only approximate, help us to form a clear conception of the relative magnitudes of the factors determining the character of typical adsorbed films. The reasons for the nearly universal

²¹ A similar assumption has been found to be approximately true for cesium films on tungsten and is in accord with de Boer's calculation that the mutual repulsion of the dipoles in a complete layer decreases the heat of evaporation (due to dipoles) to one-half of that for single dipoles; see *Proc. Amsterdam Acad.*, **31**, 909 (1928).

monomolecular character of adsorbed films become apparent, but at the same time we are led to understand that under rather special conditions multimolecular layers may form.

Case II, $b' > b_0$.—Liquid mercury (or cadmium) does not wet a glass surface. We may infer that the forces between mercury atoms in liquid mercury are greater than those between a glass surface and mercury atoms in contact with it. Thus the heat of evaporation (kb_0) of adsorbed mercury atoms on glass is less than the heat of evaporation (kb') of atoms from a second or third layer of mercury atoms on glass.

It has been proved experimentally²² that isolated cadmium atoms evaporate from a glass surface at room temperature enormously more rapidly than do atoms in contact with other cadmium atoms. When cadmium vapor at low pressure strikes a glass surface at -40° , nearly all the atoms reëvaporate before they come in contact with other cadmium atoms. If, however, small groups of atoms are formed by raising the pressure of the vapor or by further lowering of the temperature, then these serve as nuclei for the formation of crystals from which there is no appreciable evaporation at room temperature.

Under such conditions the only uniform adsorbed films that can occur are those that cover an extremely small fraction of the surface ($\theta \ll 1$); with higher surface concentrations nuclei are formed and the condensed film is discontinuous. Strong lateral attractive forces between adatoms may also cause these colloidal or granular condensed films to form.

The cases where $b' > b_0$ are to be found particularly where the adsorbate is a substance having a large heat of evaporation (low vapor pressure) and is the type of substance that would be difficultly soluble or miscible with the substance of the adsorbent. Thus since molten metals are not generally miscible with non-metallic liquids, we understand the behavior of mercury and cadmium toward glass.

Such effects may be greatly enhanced by covering the surface of the adsorbent with a monomolecular oil film such as that of a fatty acid. For example, glass surfaces in contact with saturated cesium vapor show marked electrical conductivity because of adsorbed cesium; but a monomolecular oil film on the glass tends to cause the cesium to condense in separated particles and eliminates the conductivity. The hydrocarbon surface is covered with chemically saturated hydrogen atoms from which cesium atoms evaporate far more readily than from cesium metal. A similar phenomenon is responsible for the injurious effect of traces of oily substances on the operation of mercury condensation pumps.

In our present study of evaporation and condensation of adsorbed films, we shall confine ourselves to cases where $b' < b_0$.

Forces Acting between Adatoms.—From measurements of the rate of

²² Langmuir, *Proc. Nat. Acad. Sci.*, **3**, 141–147 (1917).

evaporation of cesium adatoms on oxygen-covered tungsten, Becker²³ has concluded that the heat of evaporation decreases as θ increases, and from kinetic theory considerations deduces an equation similar to Eq. (40) in which b is a linear function of θ .

Dr. John Bradshaw Taylor has recently²⁴ completed an extensive series of accurate measurements of the rates of evaporation of atoms (ν_a), of ions (ν_p) and electrons (ν_e) as functions of T from surfaces of pure tungsten on which are adsorbed known numbers (σ) of cesium atoms per unit area. These data afford an opportunity of studying in detail the electrical properties of adsorbed films and the forces acting between adatoms.

The values of ν/θ at 800°K. were found to increase about 10¹⁰-fold as θ increases from 0 to 1, indicating very strong repulsive forces between adatoms. The following analysis enables us to determine these forces quantitatively.

Equation of State of Adsorbed Films.—The Gibbs equation for the adsorption isotherm is readily expressed²⁵ in the form

$$\frac{dF}{d \ln \mu_a} = \sigma kT \quad (54)$$

where μ_a is given by Eq. (1) and F is the spreading force of the adsorbed film (dynes cm.⁻¹). This equation is thermodynamically rigorous if the ideal gas laws apply in the gaseous phase, the surface is homogeneous and is in equilibrium with the vapor. Variations in surface mobility of the adatoms cannot affect the value of F if equilibrium prevails, but they may determine the time of relaxation, *i. e.*, the time required for restoration of equilibrium after a disturbance.

If ν_a can be expressed as a function of θ , then by Eqs. (43) and (54) the spreading force is

$$F = kT \int \sigma d \ln (\nu_a/\alpha) \quad (55)$$

The effect of forces acting between molecules on the equation of state of gases can be calculated by the virial equation²⁶

$$pV = RT + \frac{1}{3} \Sigma (rf)$$

where f is the repulsive force that acts between two molecules when their distance apart is r ; the summation is to be extended over all pairs of molecules in a gram molecule of gas. In the van der Waals equation

²³ J. A. Becker, *Trans. Am. Electrochem. Soc.*, 55, 153-173 (1929).

²⁴ A brief preliminary description of the method used in obtaining these data and of the conclusions drawn from them has been published: Langmuir, *THIS JOURNAL*, 54, 1252 (1932). The derivation of the equations there given is contained in the present paper.

²⁵ See Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 250; Langmuir and Kingdon, *Proc. Roy. Soc. (London)*, [A] 107, 72 (1925).

²⁶ See Jeans, "Dynamical Theory of Gases," University Press, Cambridge, England.

$$(p + a/V^2)(V - b) = RT$$

the presence of the factor $V - b$ can be deduced by considering the virial of short range repulsive forces which act when molecules come into contact. The term a/V^2 corresponds to the attractive forces of relatively long range.

In an entirely analogous manner the virial may be used to calculate an equation of state for adatoms. In this case

$$FA = RT + \frac{1}{2} \Sigma (rf) \quad (56)$$

where A is the area which contains a gram atom and the summation extends over all the pairs of adatoms in area A .

The two-dimensional van der Waals equation, considering that the long range forces are now repulsive instead of attractive, takes the form

$$(F - a/A^2)(A - A_1) = RT \quad (57)$$

The ordinary derivation of this equation considers only first-order effects as the surface concentration increases; the value of A_1 is then found to be *one-half* the area actually covered by a gram atom of adatoms. Langmuir²⁷ has tested this equation with experimental data of N. K. Adam on oil films at high surface concentrations and finds that A_1 corresponds to a close packed film in which the molecules unquestionably completely cover the surface. Dr. Lewi Tonks has made a theoretical analysis for the case of adatoms at high concentrations and finds in fact that the value of A_1 should then correspond to the actual area covered instead of one-half that area.

In carrying out the summation in Eq. (56), we may select arbitrarily any atom P as typical and form the sum $\Sigma_1(rf)$ for all the pairs which include the atom P . Since f must decrease very rapidly as r increases, this sum $\Sigma_1(rf)$ is independent of the area over which the summation extends as long as it greatly exceeds molecular dimensions. To form the summation indicated in Eq. (56) we must thus select each atom in turn as a P -atom, finding

$$\Sigma (rf) = (1/2)\sigma A \Sigma_1(rf)$$

where the factor $1/2$ has been introduced in order that we shall not count each pair twice. Substituting this value in Eq. (56) and noting that $A\sigma = R/k$ we obtain

$$F = \sigma kT + (1/4)\sigma \Sigma_1(rf) \quad (58)$$

In order to bring out the relationship between Eqs. (58) and (57) we may rewrite the latter in the form

$$F = \sigma kT / (1 - \sigma/\sigma_1) + a'\sigma^2 \quad (59)$$

and this may be further modified to

$$F = \sigma kT + \sigma^2 kT / (\sigma_1 - \sigma) + a'\sigma^2 \quad (60)$$

By considering the origins of the terms in Eq. (60) and comparing these with the corresponding terms in Eq. (58), we see that the virial term in the

²⁷ Langmuir, "Third Colloid Symposium Monograph," 1925, p. 72.

latter can be split into two parts: one, $\sigma^2 kT/(\sigma_1 - \sigma)$, corresponds to the short-range forces acting when atoms are in contact, and the other, $a'\sigma^2$, to the long-range repulsive forces. The actual form of the $a'\sigma^2$ term has, however, been based on approximations which will not be sufficiently good for our needs and therefore we may write in place of Eq. (59)

$$F = \sigma_1 kT\theta/(1 - \theta) + F' \quad (61)$$

where

$$F' = 0.25 \sigma \Sigma_1(rf_2) \quad (62)$$

f_2 being the *long range* repulsive force at distance r .

Ordinarily in gas theory the force function $f(r)$ is not definitely known and it falls off with such a high power of the distance that structural properties of the molecules cannot be neglected. Therefore the virial method has not been particularly successful in gas theory. In the theory of electrolytics, however, where the forces decrease less rapidly, the virial proves very useful.²⁸

The attractive forces holding adsorbed molecules on surfaces are ordinarily far stronger than those acting among the adsorbed molecules and thus the adsorbed molecules will usually be highly polarized so that they become dipoles having parallel orientations. In general, therefore, we should expect repulsive forces rather than attractive forces to be active between the adsorbed molecules.

In the case of cesium films we have very direct proof that the adatoms act as dipoles. Adsorption of alkali metal atoms occurs strongly only when the electron affinity of the adsorbent metal exceeds the ionizing potential of the alkali, so the act of adsorption probably involves a transfer of the valence electron to the underlying metal. The force holding the atom may thus be regarded as the attraction of the cesium ion and the negative charge induced in the metallic surface (image force). The positive charge on the adatoms manifests itself by changing the contact potential (by as much as 3.0 volts²⁹ and by a corresponding increase in the electron emission.

The measurements of Langmuir and Kingdon³⁰ have shown that for a given temperature the electron emission has a maximum at a particular value of θ . With the surface in this condition the emission is given by $I = AT^2 e^{-b/T}$ with $A = 3.26$ amp. cm.⁻² deg.⁻² and $b = 15,820$, whereas for a pure tungsten surface the constants are $A = 120$, $b = 53,650$. A comparison of these data gives for the contact potential of the optimum cesium surface against pure tungsten $3.26 - 0.31 (T/1000)$ volts or 3.01 volts at 800°K.

²⁸ See Milner, *Phil. Mag.*, **25**, 742 (1913), and A. A. Noyes, *THIS JOURNAL*, **46**, 1080 (1924).

²⁹ Langmuir and Kingdon, *Phys. Rev.*, **34**, 129 (1929).

³⁰ Langmuir and Kingdon, *Proc. Roy. Soc.*, (London), **A107**, 61 (1925).

Taylor's experiments have shown that at low temperatures and high cesium pressures, the surface concentration approaches a definite limiting value of 4.8×10^{14} atoms per cm.² of apparent surface (πld) corresponding to $\Theta = 1$. In the preliminary treatment of the filament it was heated for a considerable time to 2800°K. so that appreciable etching by evaporation occurred. Under these conditions the dodecahedral forces (110) are developed.³¹ The true surface on which adsorption takes place must therefore exceed the apparent surface. Tonks³² has shown, on the assumption that the crystal grains have random orientation, that the lowest possible value for the surface excess for dodecahedral faces is 0.225. The number of tungsten atoms per sq. cm. in a dodecahedral face is 1.425×10^{15} .

Simon and Vohsen³³ have found that cesium crystallizes in a body-centered cubic lattice with a lattice constant 6.05 Å. at liquid air temperature (about 6.17 Å. at room temperature). Tungsten has the same type of lattice but the constant is 3.15 Å. Thus if cesium atoms arrange themselves on the face of a dodecahedral tungsten crystal so that there is one cesium atom for every four tungsten atoms, the surface lattice is identical in type and in spacing (within 2%) with that occurring in a similar face of a cesium crystal. Since the strongest forces exerted on the adatoms are those originating from the underlying tungsten atoms, we may therefore, with considerable confidence, take for $\Theta = 1$

$$\sigma_1 = 3.563 \times 10^{14} \text{ atoms cm.}^{-2} \quad (63)$$

for the true surface density of a complete monatomic cesium film on tungsten. Comparing this with the apparent surface density 4.8×10^{14} we conclude that the ratio of the true to the apparent surface is 1.347 as compared to 1.225 for the *minimum value* of this ratio calculated by Tonks.

Taylor's data show that the optimum electron emission occurs at $\Theta = 0.67$ corresponding to $\sigma = 2.4 \times 10^{14}$.

Simon and Vohsen's data give 5.34 Å. as the shortest distance between the atoms in metallic cesium. A sphere of this diameter, having unit positive charge, in contact with an ideal plane conducting surface, produces an external electric field equivalent to that of a dipole (without neighboring conductor) having a moment $M = 25.4 \times 10^{-18}$.

If a conducting surface is covered with σ such ions per unit area, each having a dipole moment M , the contact potential V_c against a bare surface of the same material would be

$$V_c = 2\pi M\sigma \text{ (c. g. s. u.)} = 1885 M\sigma \text{ volts} \quad (64)$$

Placing $\sigma = 2.4 \times 10^{14}$ and $M = 25.4 \times 10^{-18}$ we obtain $V_c = 11.6$ volts, which is 3.84 times the 3.01 volts observed for the surface of optimum emission.

³¹ Langmuir, *Phys. Rev.*, **22**, 374 (1923).

³² Tonks, *ibid.*, **38**, 1030 (1931).

³³ Simon and Vohsen, *Z. physik. Chem.*, **133**, 165-187 (1928).

It is evident that the strong field (10^8 volts per cm.) in the double layer draws electrons from the tungsten to a plane which lies only 0.69 \AA . below that of the centers of the adatoms. The actual dipole moment per atom in a film of optimum emission is thus only $M = 6.1 \times 10^{-18}$.

Assuming that M is independent of surface concentration Langmuir has calculated³⁴ that the logarithm of the electron emission of a metal partly covered by adatoms of an electropositive metal should be a linear function of θ . Becker²³ has determined the electron emission from monatomic barium films on tungsten at 1100°K . The curve of $\log_{10} (i/i_w)$ against θ gives a maximum at $\theta = 1$ of 11.3 while the initial slope is 25. We may interpret this as indicating that for low values of θ , M is 2.2 times as great as for a film giving the optimum emission. Becker implies that the curve for cesium on tungsten is closely similar. If we may thus use the factor 2.2, we conclude that for very dilute cesium films $M = 14.6 \times 10^{-18}$, which is 0.57 of that which we estimated for cesium ions on an idealized plane conductor. The decrease in M as θ increases is to be attributed to the depolarizing effect of the field produced by the adatoms.

Let us now calculate by the virial method the equation of state of adsorbed cesium atoms. Although the electric field produced by an ion on a conducting surface is the same as that of a dipole (without the presence of the conductor), the force acting between adions is not equal to that between the two dipoles, for we must consider only the force on the real ion and not that on its image. The force acting between two adions separated by the distance r , being half that between dipoles is thus

$$f = (3/2) M^2/r^4 \quad (65)$$

and the potential energy in electron volts is

$$Ve = (1/2)M^2/r^3 \text{ or } V = 3.14 \times 10^{11} M^2/r^3 \text{ volts} \quad (66)$$

The effect of the repulsive forces between adatoms is to decrease the concentration of other atoms in the neighborhood of a given atom in accord with the Boltzmann equation

$$\sigma = \sigma' e^{-Ve/kT} \quad (67)$$

where e/k has the value 11,600 degrees per volt. To form an estimate of the magnitude of this effect, let us imagine for simplicity that the elementary spaces which can hold adatoms are arranged in an hexagonal lattice (honeycomb structure). With $\sigma_1 = 3.563 \times 10^{14}$ this gives $r_1 = 5.69 \text{ \AA}$. for the shortest distance between atoms. At this distance for $M = 14.6 \times 10^{-18}$ we find by Eq. (66) that $V = 0.365$ volt and thus by Eq. (67) at $T = 800$ the probability that one of the six available spaces adjacent to a given atom will be occupied is only 0.005 as great as that for the distant spaces. The next ring contains 12 spaces, half of which are at a distance 9.9 \AA . and

³⁴ Langmuir, *Phys. Rev.*, **22**, 364 (1923). A fuller discussion is given by W. Schottky and H. Rothe, "Handbuch Exptl. Physik," XIII, [2] 1928, pp. 160-167.

the other half at 11.8 Å. from the central atom. For these $V = 0.069$ and 0.041 volt and the corresponding probabilities are 0.37 and 0.55.

Since these nearest 18 spaces tend to be far less densely populated than an average space, the distribution of the atoms will be much more uniform than if there were no forces acting and will approximate to a regular lattice arrangement. Let us therefore at first calculate the virial term $\Sigma_1(rf)$ in Eq. (62) on the assumption that the atoms are in an hexagonal lattice,³⁵ the shortest distance r_1 between them being given by

$$r_1 = (4/3)^{1/2} \sigma^{-1/2} = 5.69 \times 10^{-8} \theta^{1/2} \text{ cm.} \quad (68)$$

Using the value of f from Eq. (65) we see that

$$\Sigma_1(rf) = (3/2) M^2 \Sigma_1(1/r^2) \quad (69)$$

By adding the values of $1/r^3$ for the separate atoms in an hexagonal surface lattice, using an accurate empirical integration process for the more distant atoms, it was found that

$$\Sigma_1(1/r^2) = 11.044/r_1^3 \quad (70)$$

Combining Eqs. (61), (62), (69), (70) and (68)

$$F = \sigma_1 k T \theta / (1 - \theta) + 3.338 \sigma^{3/2} M^2 \quad (71)$$

This gives the equation of state on the assumption that the adatoms are arranged in a plane hexagonal lattice. This should be a fairly good approximation at higher values of θ . The last term must quite accurately represent the virial contribution of all the adatoms which are at distances as great as r_1 . The atoms nearer than this must, however, often contribute materially to the virial. We may take these into account as follows.

At distances much less than r_1 the concentration is determined largely by the potential energy of the adatoms in accord with Eq. (67).

The contribution to $\Sigma_1(1/r^3)$ furnished by the atoms that lie within a circular ring is thus

$$\Sigma_1(1/r^3) = \int_{r_0}^{r_2} 2\pi r \, dr (1/r^3) \sigma_2 \exp. (-Ve/kT) \quad (72)$$

where r_2 and r_0 are the outer and inner radii of the ring, σ_2 is the surface concentration of atoms at $r = r_2$ and Ve is the change in potential energy when an atom is moved from r_2 to r .

At distances greater than about r_1 , given by Eq. (68), V remains constant because the forces from the separate atoms must on the average balance one another. If we choose a suitable value for r_2 , somewhat less than r_1 , we may thus put in accord with Eq. (66).

$$Ve/kT = (M^2/2kT)(r^{-3} - r_2^{-3}) \quad (73)$$

For values of r greater than r_2 we may take $V = 0$ and may replace the actual discontinuous distribution of adatoms by an equivalent continuous

³⁵ It should be noted that this hypothetical lattice is not related to that of the underlying tungsten atoms, but varies continuously in lattice constant as θ changes. It expresses merely the fact that the repulsive forces are effective in establishing a far more uniform distribution than if the adatoms were in random positions.

distribution. Thus the contribution to $\Sigma_1(1/r^3)$ resulting from adatoms beyond r_2 is

$$\Sigma_1(1/r^3) = \int_{r_2}^{\infty} 2\pi r \, dr(1/r^3)\sigma_2 = 2\pi\sigma_2/r_2 \quad (74)$$

Since we have already found that the contribution of the more distant atoms is given by Eq. (70), we may compare these two expressions to determine the appropriate value of r_2 . Since σ_2 may be identified with σ , we thus find from Eqs. (70), (74) and (68)

$$r_2 = 2\pi\sigma r_1^3/11.044 = (2\pi/11.044)(4/3)^{3/4}\sigma^{-1/2} = 0.7059\sigma^{-1/2} \quad (75)$$

With this value of r_2 , we can now derive an improved expression for F by merely adding to Eq. (71) a term

$$F'' = (3/8)\sigma M^2 \Sigma_1(1/r^3) \quad (76)$$

in accord with Eqs. (62) and (69), the sum $\Sigma_1(1/r^3)$ being given by Eq. (72). To integrate Eq. (72) we may substitute

$$u^3 = M^2/2kTr^3 \quad (77)$$

and obtain

$$\left. \begin{aligned} F'' &= (3\pi/4)(2kT)^{1/3} M^{4/3} \sigma^2 I \\ F'' &= 1.531 \times 10^{-3} \sigma^2 T^{1/3} M^{4/3} I \end{aligned} \right\} \quad (78)$$

or

where the integral I is

$$I = \exp. (u_2^3) \int_{u_2}^{u_0} dx \exp. (-x^3) \quad (79)$$

The values of u_2 and u_0 are found by Eq. (77) from the corresponding values of r_2 and r_0 . The former is given by Eq. (75), while r_0 may be obtained from this same equation by replacing σ by σ_1 . Thus, after introducing the numerical value of k , we have

$$\left. \begin{aligned} u_0 &= 2.181 \times 10^5 M^{2/3} T^{-1/3} (\sigma_1)^{1/2} \\ u_2 &= 2.181 \times 10^5 M^{2/3} T^{-1/3} (\sigma_1)^{1/2} \theta^{1/2} \end{aligned} \right\} \quad (80)$$

The spreading force F' due to the long range forces between adatoms, as defined by Eq. (62), can be obtained by adding F'' from Eq. (78) to the last term of Eq. (71) giving

$$F' = 3.338 \sigma^{3/2} M^2 + 1.531 \times 10^{-5} \sigma^2 T^{1/3} M^{4/3} I \quad (81)$$

The complete equation of state of the adsorbed film is then given by Eq. (61) after inserting this expression for F' .

Calculation of F' from Experimental Data on ν_a .—Differentiation of Eq. (61) gives

$$dF = \sigma_1 k T d\theta / (1 - \theta)^2 + dF' \quad (82)$$

Taylor's experiments have shown that for cesium films $\alpha = 1$ and therefore by Eq. (43) we may identify ν_a with μ_a . Thus integration of Eq. (54) gives

$$\ln \nu_a = \frac{11}{\sigma_1 k T} \int \frac{dF}{\theta} \quad (83)$$

Introducing the value of dF from Eq. (82) and integrating

$$\ln \nu_a = \ln [\theta/(1 - \theta)] + 1/(1 - \theta) + (1/\sigma_1 k T) \int dF'/\theta \quad (84)$$

Taylor's experimental data on ν_a can be expressed in the form

$$\ln [\nu_a(1 - \theta)/\theta] - 1/(1 - \theta) = A - B/T \quad (85)$$

where A and B are functions of θ only. The data give

$$A = 61.0 + 4.8\theta - 2.4\theta^2 \quad (86)$$

For values of θ up to 0.6 the values of B can be represented within the experimental error (about 0.3%) by the empirical equation

$$B = 32,380/(1 + 0.714\theta) \quad (87)$$

Beyond $\theta = 0.6$ the experimental values of B gradually become somewhat larger than those given by Eq. (87), but this deviation is only 2% at $\theta = 0.8$ and 4% at $\theta = 0.9$.

By eliminating ν_a from Eqs. (84) and (85) we obtain

$$\int (1/\theta)dF' = \sigma_1 k T(A - B/T) \quad (88)$$

Differentiation with respect to θ and multiplication by θ gives

$$\frac{dF'}{d\theta} = \sigma_1 k \theta \left(T \frac{dA}{d\theta} - \frac{dB}{d\theta} \right) \quad (89)$$

By integration we obtain an expression for F'

$$F' = \sigma_1 k \left[T \int \theta(dA/d\theta)d\theta - \int \theta(dB/d\theta)d\theta \right] \quad (90)$$

Inserting the values of A and B from Eqs. (86) and (87) and placing $\sigma_1 k = 0.04884$ in accord with Eq. (63), we get from Taylor's data

$$F' = (0.1172\theta^2 - 0.078\theta^3) T + 2215 [\ln(1 + \beta\theta) - \beta\theta/(1 + \beta\theta)] \quad (91)$$

where $\beta = 0.714$, the coefficient in the denominator in Eq. (87). The integration constant was so chosen as to make $F' = 0$ at $\theta = 0$. This expression gives that part of the spreading force (in dynes cm.⁻¹) which is due to the dipole repulsion of the cesium atoms.

Values of F' calculated by Eq. (91) for $T = 800$ are given in the third column of Table III. The second column gives the total spreading force F obtained from F by Eq. (61).

Calculation of Dipole Moment M .—By equating the theoretical and the experimental expressions for F' , given by Eqs. (81) and (91), an equation is obtained which may be solved for M . By inserting the value of σ_1 from Eq. (63), Eq. (81) may be written

$$F' = 8.00 x^3 \theta^{3/2} + 1.943 x^2 T^{1/2} \theta^2 I \quad (92)$$

where

$$x = 10^{12} M^{2/3} \quad (93)$$

The values of F' for any particular values of θ and T are first calculated from Eq. (91) and these are inserted in Eq. (92). These cubic equations in x may be readily solved by Horner's method. A difficulty arises from the fact that the integral I , according to Eqs. (79) and (80), is itself a function

of α . However, by a series of rapidly converging approximations, it is found possible without much labor to evaluate the integral with sufficient accuracy to get α to 3 or 4 significant figures. This procedure is facilitated by the fact that the term in Eq. (81) which contains I is small compared to the other term. (Ratio is 0.4 at $\Theta = 0.1$, 0.18 at $\Theta = 0.3$, 0.09 at $\Theta = 0.7$.)

TABLE III
CESIUM FILMS ON TUNGSTEN³⁶

Spreading force F , dipole moment M , contact potential V and depolarizing field E , all calculated from ν_e at $T = 800^\circ\text{K}$.

1 θ	2 F , dynes cm. ⁻¹	3 F' ,	4 I	5 $10^{18} M$ c. g. s. (e. s.)	6 V , volts	7 $10^{-4} E$ volt cm. ⁻¹
0.0	0	0	0.893	16.16	0	0
.1	10.35	6.01	.315	13.01	0.874	10.4
.2	31.9	22.1	.237	11.17	1.500	22.2
.3	62.6	45.9	.200	9.94	2.003	34.6
.4	101.4	75.4	.180	9.01	2.420	47.0
.5	148.2	109.1	.163	8.28	2.780	59.2
.6	204.3	145.7	.148	7.67	3.089	71.1
.7	271.9	180.7	.130	7.10	3.328	81.6
.8	366.9	210.6	.102	6.54	3.515	90.4
.9	586.9	235.2	.048	6.06	3.663	96.8

The values of I and M obtained in this way are given in the fourth and fifth columns of Table III. The contact potential V of the cesium covered surface against a pure tungsten surface, as calculated from M by Eq. (64), is given in the sixth column.

Depolarizing Field.—Every adatom on the surface is acted on by the electric field produced by all the neighboring adatoms. A dipole of moment M on a surface, with its axis normal to the surface, produces a field of intensity M/r^3 at a point on the surface whose distance from the dipole is r . To obtain the total field E acting on a given adatom we must sum the contributions of all neighboring adatoms

$$E = M\Sigma_1(r^{-3})$$

By eliminating f between Eqs. (62) and (65) we find that

$$F' = (3/8)\sigma M^2\Sigma_1(r^{-3})$$

and therefore

$$E = (8/3\sigma_1)F'/\theta M = 2.245 \times 10^{-12} F'/\theta M \text{ volts cm.}^{-1} \quad (94)$$

The last column in Table III contains values of E (in millions of volts cm.⁻¹) calculated by this equation. The magnitude of these fields seems adequate to cause the marked decrease in M that occurs as Θ increases.

Electron Emission ν_e .—Consider a plane tungsten surface part of which is bare while the rest is covered by an adsorbed film of cesium con-

³⁶ The values of Θ in the 1st column refer to the cesium on the homogeneous part of the surface (see later section). These were obtained from the observed values Θ_{obs} by the equation $\Theta = \Theta_{\text{obs}} - 0.005$.

taining σ atoms cm.^{-2} . Under equilibrium conditions at temperature T the concentration of electrons over the surface is governed by the Boltzmann equation and therefore if there is no appreciable reflection of low velocity electrons from the surface we have

$$\nu_e/\nu_w = \exp. (Ve/kT) \quad (95)$$

where ν_e and ν_w are, respectively, the rates of evaporation of electrons from the cesium covered and from the bare tungsten surfaces, V being the contact difference of potential between these surfaces.

The electron emission from pure tungsten according to Dushman is given by

$$I = 60.2 T^2 e^{-b/T} \text{ amp. cm.}^{-2}$$

where $b = 52,400$ was obtained by experiments in the range of temperatures from 1400 to 2400°K . The coefficient 60.2 was calculated by the Sackur-Tetrode relation. At the time of Dushman's derivation the electron-spin was not known to exist. If this is taken into account³⁷ the coefficient should be 120.4 . This change of coefficient requires a change of b from $52,400$ to $53,650$ if the values of I and of dI/dT are to keep their same values at $T = 1800^\circ\text{K}$. At 1400 and at 2400° the values of I obtained by the new equation differ by less than 20% from those given by the original equation, although over this range of temperature the emission increases 2×10^7 -fold. These differences are probably within the experimental error. Since our present interest lies in the range of temperature down to 600° , where the difference between the two equations amounts to a factor of about 4 , it seems better to adopt the equation which is in accord with modern theory.

The revised equation can be expressed

$$\nu_w = 4\pi m (kT)^2 h^{-3} \exp. (-V_w e/kT) \quad (96)$$

where $V_w e/k = 53,650$ and V_w , the electron affinity of pure tungsten, has the value

$$V_w = 4.622 \text{ volts} \quad (97)$$

Within the range from 600 to 1000° the values of ν_w from Eq. (96) are very closely given by

$$\ln \nu_w = 63.44 - 55,250/T \quad (98)$$

Combining this with Eq. (95) we get

$$\ln \nu_e = 63.44 - e/kT(4.760 - V) \quad (99)$$

By inserting the values of V from Table III for any particular value of θ (and T), the electron emission ν_e can be calculated from data on ν_a . Since these values are derived on the assumption of equilibrium, they correspond to the electron emission at zero accelerating field.

Positive Ion Emission ν_p .—In an enclosure containing cesium vapor,

³⁷ See Fowler's "Statistical Mechanics," University Press, Cambridge, England.

under conditions of equilibrium, the law of mass action requires that the concentrations n_e , n_p and n_a of electrons, ions and atoms fulfil the condition

$$K_n = n_e n_p / n_a \quad (100)$$

Using the third law of thermodynamics, the equilibrium constant K_n is found⁸⁸ to be

$$K_n = \frac{\omega_e \omega_p}{\omega_a} \frac{(2\pi m_e kT)^{3/2}}{h^3} \exp. (-V_i e / kT) \quad (101)$$

where V_i , the ionizing potential, is

$$V_i = 3.874 \text{ volts}$$

for cesium. The statistical weights ω have the values $\omega_e = \omega_a = 2$ and $\omega_p = 1$. The concentrations n are related to the corresponding ν according to the kinetic theory by

$$\nu = n(kT/2\pi m)^{1/2} \quad (102)$$

We may thus place

$$K_\nu = \nu_e \nu_p / \nu_a = 2\pi m (kT)^2 h^{-3} \exp. (-V_i e / kT) \quad (103)$$

Combining this equation with Eqs. (96) and (95) we get

$$\ln (2\nu_p) = \ln \nu_a + (e/kT)(V_w - V_i - V) \quad (104)$$

Using the values of V in Table III we see that the rate of ion evaporation ν_p (for zero accelerating field) can be calculated wholly from atom evaporation data.

Comparison with Experiment.—The values of M and V in Table III have been calculated from the data on ν_a given by Eq. (85) taking $T = 800^\circ$. The values obtained by similar calculations using $T = 600$ or $T = 1000$ are practically identical with those at 800° (within about 0.02 volt for V). This shows that the temperature coefficient of F' is adequately represented by the last term in Eq. (92) which originates from the changing distribution of the adatoms in accord with the Boltzmann equation. At low temperatures the distribution is governed mainly by the repulsive forces which tend to bring about a regular lattice arrangement, but at high temperatures thermal movements cause some of the atoms to approach closer to one another than corresponds to this lattice. We see by Eq. (90) that the temperature coefficient of F' is associated with a dependence of A on Θ .

The value of A from the experiments, as given by Eq. (86), is of the same order of magnitude as that given by Eq. (41) which we obtained from our general vapor pressure equations. Thus inserting $T = 800$ and $M = 133$ in Eq. (41) and comparing with Eq. (85) (neglecting the terms containing $1 - \Theta$) we find $A = 65.8$ in place of the values given by Eq. (86). This equation gives $A = 65.8$ at $\Theta = 0.66$.

In our derivation of Eqs. (40) and (41) b was assumed to be independent

⁸⁸ Fowler, "Statistical Mechanics," 1929, p. 281.

of temperature. The variation of the adatom distribution with temperature, due to the Boltzmann effect, must cause slight changes in the heat of evaporation, at constant Θ , and corresponding changes in b . This is indistinguishable in its effect from a dependence of A upon Θ and therefore in the present case with strong forces between the adatoms we should not expect A to be strictly constant.

In his experiments Taylor has determined ν_e and ν_p as functions of T , Θ and the accelerating field. At high fields, such as are obtained with 40 to 200 volts on the cylinder (field of 3000 to 15,000 volts cm.⁻¹ at filament), the variation is approximately in accord with Schottky's theory, but at lower fields the variation is far greater than given by this theory.³⁹ By plotting the logarithms of ν_e or ν_p against the cylinder potential, a rapid change of slope (kink) occurs as the field changes from retarding to accelerating. The values of ν_e at this kink are about one-half to one-seventh of those obtained with accelerating fields of 3000 volts cm.⁻¹. These are presumably the values that correspond to the thermodynamic equilibrium implied in Eqs. (99) and (104). As a matter of fact, the experimentally determined values of ν_e and ν_p at the kink agree very satisfactorily with those calculated by these equations (from data on ν_a) up to values of $\Theta = 0.5$. The observed values of ν_e for $\Theta > 0.5$ fall below those calculated. A full report of Taylor's experiments, soon to be published, will contain a more detailed comparison of the experimental and theoretical results.

The agreement obtained seems sufficient to justify the belief that the foregoing analysis of the effects of dipole forces between adatoms on plane surfaces is substantially correct, except for very concentrated films.

General Characteristics of Atom Evaporation from Cesium Films.—The observed variation of ν with Θ as expressed in Eqs. (85), (86) and (87) is very different from that of the adsorption isotherm of Eq. (2). The occurrence of Θ in the denominator of the B term in Eq. (85) causes an increase of ν with Θ of the exponential type.

This characteristic of the evaporation is illustrated in another way in Fig. 1 which shows the rate of decrease in Θ by evaporation when a filament is maintained at constant temperature in a space free from cesium vapor (bulb in liquid air). Within any narrow range in values of Θ the rate of evaporation ν_a is approximately proportional to an exponential function of Θ so that we can put

$$\nu_a = Ke^{H\Theta}$$

where H varies only slowly with Θ . To construct a given curve, for example that for 700°, having a time scale covering one-half hour, we are interested only in values of ν_a from 10¹⁰ to 10¹² which occur for values of Θ between 0.23 and 0.40. In this range H varies only from 34 to 30.

³⁹ K. T. Compton and I. Langmuir, *Rev. Modern Phys.*, **2**, 123-242 (1930); see especially pp. 146-157.

Since $\sigma_1(d\theta/dt) = \nu_a$, we can calculate the time interval required to pass from θ_2 to θ_1 by integration, treating H as constant in this range; thus

$$t = \frac{\sigma_1}{H} \left(\frac{1}{\nu_1} - \frac{1}{\nu_2} \right) \quad (105)$$

where ν_1 and ν_2 are the values of ν_a corresponding to θ_1 and θ_2 . The four full-line curves in Fig. 1 have been prepared in this way.

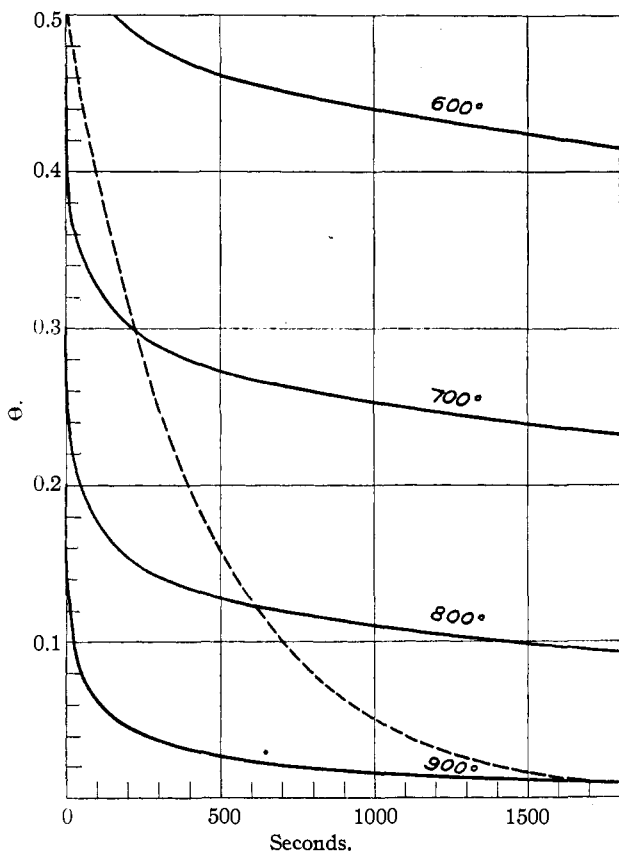


Fig. 1.—Evaporation of cerium films from tungsten at various temperatures. The dotted line is an exponential curve.

The dotted line curve gives for comparison an ordinary exponential curve $y = be^{-ax}$, which corresponds to evaporation on the assumption that the rate is proportional to θ , *i. e.*, that there are no repulsive forces between adatoms. A striking feature of the evaporation from cesium films on tungsten is the fact that θ decreases almost instantly from $\theta = 1$ down to a certain value and then tends to approach a limiting value. Thus at 700°, θ falls to 0.4 in 10 sec., to 0.25 in 1080 sec., but would take 10.5 hours to fall

to 0.15 and 80 hours to reach 0.1. Similar effects are observable with oxygen films on tungsten and point to the presence of strong repulsive forces between adatoms.

Homogeneity of the Tungsten Surface.—In this paper we have so far tacitly assumed that the tungsten surface is homogeneous in the sense that the life τ of any adatom is independent of its position on the surface. The variation of τ with Θ has been taken to be evidence of forces between adatoms.

In the author's 1918 paper on adsorption⁴⁰ the second and third typical cases that were considered were based on the assumed presence of more than one kind of elementary space. The surface may be considered as divided into infinitesimal fractions $d\beta$, each element having its own characteristic evaporation rate ν_1 if saturated with adatoms. Thus ν_1 expressed as a function of β gives a "law of distribution" of the evaporation rate ν_1 over the surface. If there are no forces acting between adatoms, Eq. (2) can be applied to each element $d\beta$ and thus by integration it was found for the whole surface that

$$\sigma = \sigma_1\Theta = \int_0^1 (\nu_1 + \alpha_0\mu)^{-1} \alpha_0\mu d\beta \quad (106)$$

The practical importance of *active areas* in determining the catalytic properties of surfaces (even plane surfaces) was pointed out in a later paper.⁴¹ Within recent years many experimental and theoretical studies have been made of active spots, especially by H. S. Taylor and his collaborators.

It is evident from Eq. (106) that by assuming a heterogeneous tungsten surface, that is, by properly choosing the function $\nu_1(\beta)$, any observed law of variation of ν_a with Θ , such as that expressed by Eqs. (85), (86) and (87), can be accounted for without the necessity of postulating forces between adatoms. However, in this case M would be zero and thus the electron emission ν_e would not vary with Θ . The fact that the observed values of ν_e and ν_p agree with those calculated by Eqs. (99) and (104) from the values of M in Eq. (81) proves conclusively that the tungsten surface is essentially homogeneous.

Active Spots on Tungsten Surface.—The foregoing conclusion is justified by Taylor's experimental data on ν_a for values of Θ greater than about 0.05. In our first detailed analysis of the data obtained with still more dilute cesium films, it was found that the observed values of ν_a were considerably less than those calculated by Eqs. (85), (86) and (87). Since the equation of state of the two-dimensional gas film should approach more nearly to the ideal gas law $F = \sigma kT$ at low concentrations, it appeared to

⁴⁰ Langmuir, *THIS JOURNAL*, **40**, 1361 (1918), see particularly p. 1371.

⁴¹ Langmuir, *Trans. Faraday Soc.*, **17**, 607 (1921), see especially pp. 617 and 618. This paper was reprinted in *Gen. Elec. Rev.*, **25**, 445 (1922).

be impossible to account for these deviations on assumption that the tungsten surface was wholly homogeneous.

It was found that this difficulty disappeared entirely if it was assumed that about 0.50% of the tungsten surface holds cesium so much more firmly than the rest, that this *active surface* becomes saturated before more than 0.5% of the remaining surface is occupied. The total surface concentration may thus be divided into two parts

$$\sigma = \sigma_a + \sigma_n = \sigma_1(\Theta_a + \Theta_n) \quad (107)$$

where the subscripts refer to the *active* and to the *normal* parts of the surface. Evidently when the active surface becomes saturated, so that $\Theta_a = 0.005$, we may put

$$\Theta_n = \Theta_{\text{obs.}} - 0.005 \quad (108)$$

If ν_a is calculated by Eqs. (85), (86) and (87), using Θ_n instead of $\Theta_{\text{obs.}}$, the values are found to agree with those found by Taylor's experiments down to values of $\Theta_{\text{obs.}}$ as low as 0.01. The reason for the discrepancies that remain at still lower values of Θ are then explainable as due to a lack of complete saturation on the active surface. In this way, by Eq. (107), subtracting the calculated values of Θ_n from $\Theta_{\text{obs.}}$, we can obtain Θ_a from experiments carried out with known values of T and μ . In an analysis of Taylor's data (to be published) it will be shown that

$$\ln [\mu(0.005 - \Theta_a)/\Theta_a] = 65.8 - 44,440/T \quad (109)$$

expresses quite accurately the variation of Θ_a with T and μ .

The degree of saturation of the active surface, $\theta' = \Theta_a/0.005$, thus approaches unity as μ increases or T decreases. Comparison of Eq. (109) with Eqs. (85), (86) and (87) shows that B is independent of θ' . The experiments show strikingly that the evaporation from the active surface resembles that illustrated by the dotted curve in Fig. 1 instead of the full line curves. A moderate increase of temperature causes practically all of the adatoms to evaporate from the active surface.

This constancy of B proves that repulsive forces do not act between the adatoms on the active surface. This must mean that the active areas consist of isolated elementary spaces, each capable of holding one adatom. It is probable that these active spots are located at points where the spacing of the tungsten atoms is abnormal and is particularly favorable for holding cesium atoms. Such positions may occur close to grain boundaries where the tungsten lattice must be disturbed. The filaments in Taylor's experiments had a very fine-grained crystalline structure which had been considerably etched by heating to 2800°K.

It is probable that the extent of the active area can be made to vary by heat treatment of the filament, but that the properties of the normal part of the surface are uninfluenced by such treatment.

If we solve Eq. (2) for ν_1 we find

$$\nu_1 = \mu(1 - \theta)/\theta \quad (110)$$

Since the rate of evaporation ν_1 for a saturated surface varies with temperature in such a way that $\ln \nu_1$ is a linear function of $1/T$, we thus see that Eq. (109) is of a form that is directly derivable from Eq. (2).

It seems probable that the cases in which Eq. (2) is applicable to adsorption on plane surfaces are those in which the elementary spaces available for adsorption are isolated from one another. Only in such cases does it seem reasonable that the average life of adatoms shall be independent of θ and that the rate of condensation shall be proportional to $\theta_s - \theta$, where θ_s corresponds to saturation of these spaces. In general, therefore, when Eq. (2) applies we should expect θ_s to be considerably less than unity. This was observed in the case of adsorption of gases on glass and mica.¹

Effect of Oxygen.—The foregoing theories of the nature of cesium films on tungsten aid in understanding the effects observed when the tungsten is partly covered by adsorbed oxygen before bringing into contact with cesium vapor. The oxygen decreases the rate of evaporation of cesium atoms so greatly that the filament can be heated about 250° higher before losing its cesium film. This is now explainable as the result of attractive forces between the negative dipoles of the oxygen adatoms and the positive cesium dipoles. The cesium atoms thus form clusters about every oxygen adatom and will also cover the oxygen atoms. The effect of the oxygen will also be to increase the dipole moment of the cesium adatoms. The presence of minute amounts of oxygen should manifest itself by producing active spots which can be investigated by the methods outlined above.

It is our plan to investigate experimentally these effects of traces of oxygen.

Summary

The vapor pressures of liquids can be expressed (in baryes) by

$$p = AT^\gamma \exp. (-b/T)$$

where A , γ and b are constants. Trouton's rule is equivalent to postulating that $\gamma = 0$ and $A =$ a universal constant. Vapor pressure data of "International Critical Tables" give $\log A = 10.65$ with a standard deviation (S. D.) of 1.19. Hildebrand's rule is equivalent to taking $\gamma = 1$ and A is then a universal constant for which $\log A = 7.83$ with S. D. = 0.52. A rule which agrees still better with the data is obtained by putting $\gamma = 1.5$ and then it is found that $\log A_{1.5} = 6.37$ with a S. D. = 0.22, which is less than half as great as that for Hildebrand's rule.

The vapor pressures of solids whose vapors have rigid molecules are also given by this equation with $\gamma = 1.5$ and $\log A = 6.9$. Much larger values of A are obtained for solids if the molecules possess internal degrees of freedom. The concept is advanced that such molecules in the vapor phase at higher temperatures may possess high internal mobility (as though

liquid) while at lower temperatures they may become rigid (as though solid). Such effects probably do not exist with molecules of vapors of liquids.

These vapor pressure equations may be applied to adsorption phenomena. The rate of evaporation of atoms or molecules from monatomic films on surfaces is thus given by

$$\nu = A_{1.6}(2\pi mk)^{-1/2} \Theta T \exp. (-b/T)$$

This is found to agree reasonably well with experimental data on thorium, oxygen and cesium films on tungsten.

The conditions are discussed which lead to the formation of monatomic and of polyatomic adsorbed films. It is emphasized that the latter can occur on plane surfaces only under rather unusual conditions.

In general adsorbed molecules on plane homogeneous surfaces are acted upon by strong forces originating from the underlying solid. The resulting polarization causes the adsorbed molecules to repel one another as dipoles, with forces varying in proportion to M^2r^{-4} where M is the dipole moment and r the distance. Attractive forces predominate only if two kinds of adsorbed molecules are present which become polarized in opposite senses, as for example cesium and oxygen on tungsten (or salt-like substances on metals, such as mercurous sulfate on mercury).

The equation of state of the two-dimensional gas constituting the adsorbed film is worked out for molecules which repel as dipoles by means of the Clausius virial. By use of Gibbs' equation for the adsorption isotherm the rate of evaporation ν can be worked out in terms of Θ , T and M . The equations are found to be of the form required by experimental data on cesium films on tungsten. Thus the experimental data furnish values of M as a function of Θ .

The Boltzmann equation and the Saha equation then permit the calculation of the rates of evaporation of electrons (ν_e) and of ions (ν_p) from $M(\Theta)$ and T , yielding results in agreement with experiment. The results indicate that the tungsten surface is essentially homogeneous except for about 0.5% of the surface which holds cesium atoms much more firmly than the rest.

SCHENECTADY, N. Y.