

THE NATURE OF THE ADSORBED PHASE

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Surface phenomena are so complex that it is almost imperative to group them for discussion into sections. It has been found convenient to deal first with the kinetics of adsorption, then with the equation of state of a film, and finally with electrical properties of the adsorbed phase. The discussion will mainly be limited to the adsorption of a gas on a solid.

I. KINETICS

The condensation of molecular streams

The conditions controlling the condensations of molecular streams were first studied by Wood and Knudsen (1). They found that there was a critical surface temperature above which an atomic beam (composed for example of cadmium atoms) would not condense on glass, but would be reflected in a diffuse manner. Langmuir (2) pointed out that another interpretation could be given to these results by supposing that condensation occurred at all temperatures, followed by evaporation after a mean time which was a function of the temperature. This would account for the diffuse reflection at the higher temperatures. But later work has shown that the interaction between atomic beams and the surface is more subtle than was suspected. In some cases the beam acts as would a train of de Broglie waves of wave length $\frac{h}{mv}$ (h is Planck's constant, m the mass of the atom, v its velocity). Thus, Ellett, Olson and Zahl (3) showed that cadmium is reflected specularly from a sodium chloride crystal, with a velocity selection in the reflected beam. Here the reflection was that for a

space grating. Knauer and Stern (4) found that helium and hydrogen beams are diffracted by sodium chloride and potassium chloride as by a surface grating; Esterman and Stern (5) found a similar result for the reflection of the same gases from lithium fluoride; and Johnson (6) found that atomic hydrogen produces a reflection pattern from lithium fluoride satisfying cross-grating formulas. On the other hand, no specular reflection was found for sodium impinging on sodium chloride (7), or for lithium, potassium, and cesium on sodium chloride (8) and lithium fluoride. Similarly cadmium and arsenic are not reflected specularly from orthoclase or fluorite. It seems strange also that heavy atoms such as cadmium should penetrate through several layers, while lighter atoms are reflected by a surface grating. There is thus no general rule at present governing the reflection of atoms.

However, Langmuir's contention, requiring as it does the dependence of critical temperature on stream density, has been supported by the experiments of Chariton and Semenov (9), Esterman (10), and Cockroft (11), and forms the basis for the more elaborate analysis of Frenkel (12). Before passing on to the latter it will be well to discuss the adsorption time or mean life of a molecule on a surface.

The mean life of an adsorbed molecule

Suppose that νdt molecules fall on a surface S in time dt and that a fraction ρ is reflected. Then $(1 - \rho)\nu dt$ molecules are adsorbed in time dt : call this number b_0 . We wish to know the number b of these b_0 molecules which are left on the surface after time t .

If $w dt$ is the probability that a molecule leaves the wall in time dt , then

$$- db = b w \cdot dt \quad \text{and} \quad b = b_0 e^{-wt}$$

The mean life τ of the molecules which are adsorbed is therefore

$$\frac{1}{b_0} \int_{b_0}^0 - db \cdot t = \frac{1}{w}$$

The mean adsorption time of the molecules falling on the surface is

$$\tau_1 = (1 + \rho) \tau$$

On this basis, Clausius (13) derives Langmuir's familiar adsorption isotherm. Let us suppose that in the stationary state there are n molecules per area S : then $n = \nu \tau_1$. Let there be N' adsorption points on the surface, and let us suppose that a molecule hitting an adsorbed molecule is reflected, whereas one hitting a free spot is adsorbed with probability β . Then in the stationary state

$$\rho = \frac{n}{N'} + (1 - \beta) \left(1 - \frac{n}{N'}\right)$$

and hence,

$$\tau_1 = \left(1 - \frac{n}{N'}\right) \beta \tau$$

Since $n = \nu \tau_1$, this gives

$$n = \nu \left(1 - \frac{n}{N'}\right) \beta \tau, \quad n = \frac{\nu \beta \tau N'}{\nu \beta \tau + N'}$$

which is Langmuir's isotherm. Here $\beta \tau$ is the mean life of a molecule falling on the free surface. Langmuir took β to be unity.

Clausius calculates from Langmuir's data for the adsorption of gases on glass the following values for $\beta \tau$ at 90°K.: argon, 1.9×10^{-5} ; nitrogen, 2.27×10^{-5} and 5×10^{-5} ; oxygen, 1.4×10^{-5} ; carbon monoxide, 30.8×10^{-5} . Wertensein (14) found for mercury on glass at 21°C. that $\tau_1 = 1.08 \times 10^{-5}$.

Clausius has also measured the mean life of an adsorbed molecule directly. A vertical molecular stream was directed against a rotating horizontal plate. The molecules adsorbed on the plate were carried along by it, given off, and condensed on a cooled surface. The distance of the latter deposit from the point of

impact allowed the adsorption time to be measured. At 200°K. an upper limit of 10^{-6} was obtained for cadmium on various surfaces. Later, Clausing made more precise measurements by allowing a molecular stream at low pressure to pass through a glass capillary into an evacuated space. He thus found the time for a molecule to pass through the capillary. For argon on glass between 78° and 90°K. he found that τ_1 was given by $1.7 \times 10^{-4} e^{\frac{3800}{RT}}$ (at 78°K., $\tau_1 = 75 \times 10^{-5}$; at 90°K., $\tau_1 = 3.1 \times 10^{-5}$). These figures are sufficiently close to Langmuir's. Neon gave between 78° and 90°K. a value smaller than 2×10^{-7} .

The analysis of Frenkel

A variation with temperature of the adsorption time such as was found by Clausing is readily intelligible in terms of Frenkel's theory (12). As before, let us suppose that we have n atoms on an area S and that $n = \nu \tau_1$. If an adsorbed molecule executes an S.H.M. of period τ_0 perpendicular to the surface, the potential energy at a displacement z is given by

$$\Delta u = \frac{2 \pi^2}{\tau_0^2} \cdot m z^2$$

where m is the mass of the molecule, giving the total energy of a displaced molecule the value $-u_0 + \Delta u$, where u_0 is the energy in the equilibrium position. The thickness of the adsorption region, δ , may thus be defined by

$$\delta = \int_{-\infty}^{\infty} e^{\frac{-\Delta u}{kT}} dz = \tau_0 \sqrt{\frac{kT}{2 \pi m}}$$

Since

$$\nu = Sc \sqrt{\frac{kT}{2 \pi m}}$$

where c is the bulk concentration, and

$$\frac{n}{S} = c \cdot \delta \cdot e^{\frac{u_0}{kT}}$$

for small surface concentrations, i.e., neglecting the area occupied by the electron atmospheres of the molecules, we obtain

$$\tau_1 = \tau_0 e^{\frac{u_0}{kT}}$$

Frenkel then proceeds to consider the formation of agglomerates. Langmuir (15) demonstrated the presence of these by allowing a stream of cadmium atoms to impinge on a cooled glass surface for so short a time that no visible deposit was formed. On warming to room temperatures the agglomerates had not evaporated, as single atoms would have done, for they could act as condensation nuclei for cadmium vapor.

Only paired atoms are considered. Let there be n_1 atoms singly, and n_2 atoms doubly linked on a surface S . Frenkel writes the probability that the distance of one molecule from another should not be greater than

$$\pi d_0^2 = \sigma_0,$$

where d_0 is the molecular diameter, as

$$(n-1) \frac{\sigma_0}{S}$$

Hence

$$n_1 = n \left[1 - (n-1) \frac{\sigma_0}{S} \right]$$

and

$$n_2 = n(n-1) \frac{\sigma_0}{S} = \frac{n^2 \sigma_0}{S}$$

Owing to the attractive forces between atoms this number n_2 must be multiplied by $e^{\frac{\Delta u}{kT}}$, where Δu is the dissociation energy of a doublet: we may write

$$\sigma = \sigma_0 e^{\frac{\Delta u}{kT}}$$

and

$$u_1 = u_0 + \Delta u$$

We may note that the law of mass action applied to the surface gives a similar expression. The surface concentrations are $\frac{n_1}{S}$ and $\frac{n_2}{S}$. Hence

$$n_2 = \frac{n_1^2}{S} \cdot K = \frac{n_1^2}{S} \cdot A e^{\frac{\Delta u}{kT}} = \frac{n_1^2}{S} \cdot A e^{\frac{\Delta u}{kT}}$$

for small n . A more accurate statistical mechanical treatment may also be applied. The free energy f_1 of a two-dimensional gas may be written

$$e^{\frac{-f_1}{kT}} = \frac{e^{-E/kT}}{n_1 h^2} \cdot 2 \pi m k T \cdot S$$

where m is the mass of a molecule. Allowing for rotation and interatomic vibration of the double molecule we can calculate the equilibrium constant as for a three-dimensional dissociation (16). This gives

$$n_2 = \frac{n_1^2}{S} \cdot \left(\frac{\pi k T}{m} \right)^{\frac{1}{2}} \cdot \frac{d_0}{\nu_0} \cdot e^{\frac{\Delta u}{kT}}$$

where ν_0 is the interatomic vibration frequency. In practice the inclusion of the power $T^{\frac{1}{2}}$ would have practically no effect. Hence the equilibrium equation becomes

$$\frac{dn}{dt} = \nu - w_1 n - w_2 n = 0$$

where the w 's are as above, giving

$$-n = \frac{(w_1^2 - 4 \beta' \nu)^{\frac{1}{2}} + w_1}{2 \beta'}$$

where

$$\beta' = (w_1 - w_2) \frac{\sigma}{S}$$

Since the discriminant must be positive

$$\nu > \frac{w_1^2}{4\beta'}$$

The critical stream density is therefore

$$\nu = \frac{w_1^2}{4(w_1 - w_2)} \cdot \frac{S}{\sigma}$$

Hence

$$e^{\frac{u_1}{kT}} \left(1 - \frac{\tau_0}{\tau_3} e^{-\frac{\Delta u}{kT}} \right) = \frac{S}{4\sigma_0\nu\tau_0}$$

where τ_3 is the period of the oscillation perpendicular to the surface of an atom bound in a pair. Hence (approximately)

$$e^{\frac{u_1}{kT}} = \frac{S}{4\sigma_0\nu\tau_0}$$

It is convenient to regard the agglomerate as a pair. This is in accordance with the low values found for u_1 as compared with the latent heat of evaporation of a cadmium crystal.

Frenkel's relation for the critical stream density was experimentally verified by Cockroft, for the condensation of cadmium on copper. Over the range -150°C . to -90°C ., the critical density varied with temperature according to

$$\nu = 4.7 \times 10^{22} e^{-\frac{2840}{T}}$$

Hence $u_1 = 5680$ calories per mole, whereas the latent heat of evaporation of cadmium crystal is 32,000 calories per mole. Cockroft found that the value of ν was the same for surfaces of copper, silver and glass, but that if a fresh silver surface were deposited immediately before condensation of the cadmium stream the density required to form a deposit decreased by a factor of ten. This shows that the specific surface forces do not normally come

into play, as the surface, without special precaution, is coated with a layer of adsorbed gas. In the same way the thermal accommodation coefficients $\left(\frac{T_1 - T_2}{T_1 - T_2'}\right)$, where T_1 is the temperature corresponding to the energy of a gas molecule approaching the surface, T_2 the temperature of one leaving the surface, and T_2' the surface temperature) are roughly independent of the nature of the surface.

The mobility of atoms in the surface phase

There is a good deal of experimental evidence to support the implication of Frenkel's theory that molecules can move about on the surface. Such a motion doubtless occurs in many cases on a cushion of adsorbed gas molecules.

Esterman (10) found that when V-shaped diaphragms were inserted in the path of the molecular stream no deposit occurred at the narrow part of the trace, when the surface temperature was just below the critical value for the stream density used. The critical density is therefore greater at the edge of a deposit than at a point inside, pointing to a lateral creep away from the edge.

Volmer and Adhirkari (17) were able to detect the motion of benzophenone over a glass surface. The benzophenone passed from a solid crystal over a strip of glass .01 cm. wide and was drawn off by mercury. The value 1.5×10^{13} dynes was calculated for the surface viscosity constant. Similarly, Volmer and Esterman, from the growth of mercury crystals in vapor at low pressure, came to the conclusion that free motion of adsorbed mercury molecules could occur over the surface.

Cockroft (11) placed a wire across his copper condensation surface at a very short distance from the surface, and allowed the beam from his oven to form the usual circular deposit. When the circle had reached a certain size the wire was moved to another position by an electromagnet. In this second position the region shadowed by the wire had been sensitized outside the circular deposit, and any molecules creeping in would be caught and held. It was found that when deposition was continued the shadow region outside the first circular deposit showed crystals of cadmium when examined under the microscope. These crystals had crept in from the sides.

The effect of a surface film of gas atoms on the reflection of electrons from a nickel surface was investigated by Germer (18). At room temperatures the results could be interpreted in terms of a regular two-dimensional lattice of gas atoms. On heating to 150°C. this lattice had melted to give an irregular arrangement.

There is no doubt that in such reactions as the reduction of cupric oxide by hydrogen (19), where the reaction region is the boundary between copper and cupric oxide, the rapidity of the reaction is due to the motion of adsorbed hydrogen over the surface to the reaction zone.

II. THE EQUATION OF STATE OF THE ADSORBED PHASE

The equation of state

Various lines of evidence justify the treatment of a surface film as a separate phase, with properties analogous to those of the bulk material. In particular, the lateral mobility of adsorbed molecules, the ease with which such a concept allows the relations with the bulk gas to be derived, and the direct observation of films on liquids, support the view that a surface film exerts a surface pressure which is related to the area of the film and the temperature by an equation of state.

The equation of state of a dilute gaseous film may readily be derived in an approximate form. Consider a molecule of mass m and surface coördinates x, y , acted on by forces whose components are X, Y and by frictional resistances of the form $-k_1(\dot{x} \dot{y})$. Then

$$m \ddot{x} = X - k_1 \dot{x}$$

Multiplying this by $\frac{1}{2}x$ this equation is the same as

$$\frac{1}{2} \cdot \frac{d^2}{dt^2} (mx^2) + \frac{1}{2} \cdot \frac{d}{dt} (k_1 x^2) - \frac{1}{2} mx^2 = \frac{1}{2} Xx$$

On adding this to the similar equation in y , and putting

$$x^2 + y^2 = r^2$$

we obtain

$$\frac{1}{2} \cdot \frac{d^2}{dt^2} (mr^2) + \frac{1}{2} \cdot \frac{d}{dt} (k_1 r^2) = \frac{1}{2} mv^2 + \frac{1}{2} (Xx + Yy)$$

This is now summed over all the molecules on the surface S and integrated over a long time t giving

$$\frac{1}{t} \cdot \left[\frac{1}{2} \cdot \frac{d}{dt} \cdot \Sigma (mv^2) + \frac{1}{2} \Sigma (k_v r^2) \right]_0^t = \frac{1}{2} \overline{\Sigma mv^2} + \frac{1}{2} \overline{\Sigma Xx + Yy}$$

where $\overline{\Sigma mv^2}$ and $\overline{\Sigma Xx + Yy}$ are the average values over the time t . In the steady state the values of the expression in brackets are the same at times 0 and t . Hence we have the virial equation of Clausius

$$\frac{1}{2} \overline{\Sigma mv^2} = - \frac{1}{2} \overline{\Sigma Xx + Yy}$$

where $-\frac{1}{2} \overline{\Sigma Xx + Yy}$ is the virial.

Suppose that n molecules are enclosed in a surface S and exert a surface pressure F . The virial is made up of the intermolecular forces and the stresses across the boundary. If ds is an element of the latter, and l and m are the direction cosines of the outward normal to the boundary, the stress components are $-l \cdot F \cdot ds$, $-m \cdot F \cdot ds$, contributing to the virial

$$\begin{aligned} - \frac{1}{2} F \int (lx + my) ds &= \frac{1}{2} F \cdot \iint \left(\frac{\partial x}{\partial x} + \frac{\partial y}{\partial y} \right) \cdot dS \\ &= FS \end{aligned}$$

In order to obtain the contribution of the intermolecular forces to the virial, take two molecules whose centers are at x, y and x', y' . Let the force components be X, Y and X', Y' , and the intermolecular force $-\frac{\partial E}{\partial r}$. Then

$$X = - \frac{\partial E}{\partial r} \cdot \frac{(x - x')}{r}$$

$$X' = - \frac{\partial E}{\partial r} \cdot \frac{(x' - x)}{r}$$

and hence

$$xX + x'X' = - \frac{\partial E}{\partial r} \cdot \frac{(x - x')^2}{r}$$

The contribution of the intermolecular force to the virial is therefore $\frac{1}{2} r \cdot \frac{\partial E}{\partial r}$, and hence

$$\frac{1}{2} \overline{\Sigma mv^2} = F \cdot S + \frac{1}{2} \Sigma r \frac{\partial E}{\partial r}$$

The average number of pairs of two molecules whose centers are at a distance between r and $r + dr$ of one another is

$$\frac{1}{2} n^2 e^{-E/kT} \cdot \frac{2\pi}{S} \cdot r \cdot dr$$

for the number of pairs is $\frac{1}{2} n(n-1)$ and the factor $e^{-E/kT}$ allows for the intermolecular force. Hence, putting

$$\frac{1}{2} \Sigma mv^2 = nkt$$

$$FS = nkT - \frac{n^2 \pi}{2S} \cdot \int_0^\infty r^2 \cdot \frac{\partial E}{\partial r} \cdot e^{-E/kT} \cdot dr$$

On integrating this by parts we obtain the alternative form

$$FS = nkT - \frac{n^2 \pi kT}{S} \cdot \int_0^\infty r (e^{-E/kT} - 1) \cdot dr$$

provided that

$$\lim_{r \rightarrow \infty} r^2 (e^{-E/kT} - 1) = 0$$

or,

$$FS = nkT - \frac{nkTB}{S}$$

where B is the second virial coefficient. When S is replaced by its approximate equivalent $\frac{nkT}{F}$ in the right hand side of this equation, we get the inverted form

$$FS = nkT - BF$$

or

$$F(S - B) = nkT.$$

When E is known as a function of r , B may be formulated more explicitly. Putting

$$\frac{\partial E}{\partial r} = \frac{\lambda_q}{r^2} - \frac{\lambda_m}{r^m}$$

we can find B as Lennard-Jones (20) does for a three-dimensional gas. This gives

$$B = \frac{n \pi}{2 kT} \left(\frac{\lambda_q}{\lambda_m} \cdot \frac{m-1}{q-1} \right)^{\frac{2}{q-m}} \cdot F(y)$$

where

$$y = \left(\frac{q-1}{\lambda_q} \cdot kT \right)^{\frac{m-1}{q-1}} \cdot \frac{\lambda_m}{kT (m-1)}$$

$$F(y) = y^{\frac{2}{q-m}} \left[\Gamma \left(\frac{q-3}{q-1} \right) - \sum_{t=1}^{\infty} f(t) y^t \right]$$

and

$$f(t) = \frac{2}{t(q-1)} \cdot \Gamma \left[\frac{t(m-1)-2}{q-1} \right]$$

Unfortunately the temperature variation of the second virial coefficient is not sufficiently well known even for thin films on liquids to enable the force constants of molecules to be calculated on this basis.

A gas equation of the form deduced above, i.e.,

$$F(S-B) = nkT,$$

was postulated by Volmer (21). It has the merit of giving a simple derivation of Langmuir's isotherm. Adopting the treatment of the author (22), the free energy, f , per molecule is

$$\int \frac{S}{n} \cdot dF = kT \log \frac{nkT}{S-B} + \frac{BkT}{S-B} + \text{constant}$$

Since the corresponding value for the bulk gas is $kT \log p + \text{constant}$, at equilibrium

$$kT \log \frac{nkT}{S - B} + \frac{B kT}{S - B} = kT \log p + K_1$$

where K_1 is a constant, approximately independent of temperature. Hence

$$\log \frac{p(S - B)}{n} = \frac{B}{S - B} + K_2$$

and if $\frac{B}{S - B}$ is small compared with K_2 ,

$$\frac{n}{S} = p (K_2 + B p/n)^{-1}$$

which is Langmuir's isotherm (B is proportional to n). We note that at saturation $\frac{1}{S} = \frac{1}{B}$ and that

$$K_2 = kT e^{\phi/kT}$$

where ϕ is a constant. From this point of view the isotherm is an expression of the distribution law, if the effective concentration is taken to be $\frac{n}{S - B}$ for the surface phase.

The gas equation of surface films on liquids may be directly studied in certain cases, and it is interesting to compare the results with theory. The surface concentration of a capillary active solute may be deduced by Gibb's equation, and a relation found between this and the surface pressure

$$F = \sigma'_0 - \sigma'$$

where σ'_0 and σ' are the surface tensions of the pure solvent and the solution. Traube (23), for example, found that for small values of F ,

$$FS = nkT$$

and the analogy between this and the equation of a perfect gas led him to regard the lowering of the surface tension of the solvent as the effect of the two-dimensional pressure. However, for larger F 's this approximation no longer holds. Clearly

$$\frac{F}{kT} \frac{S}{n} = \frac{F}{kT} \cdot \frac{d f_2}{d \sigma'} = \frac{d (\log a)}{d (\log F)}$$

where f_2 is the partial molar free energy, and a the activity, of the solute. Assuming that activity and concentration were equal Rideal and Schofield (24) calculated $\frac{FS}{nkT}$ for water solutions of the lower fatty acids from Szyszkowski's data, and found that

$$F(S - B) = x'nkT$$

which is similar to the equation of simple theory, except for the factor x' . This equation is in fact the analogue of Amagat's equation for a gas at high pressure. Jones and Bury (25) have pointed out that in these solutions concentration and activity diverge widely, and find that for high concentrations of solute the Gibb's surface excess remains a constant with increasing concentration, instead of decreasing, the result obtained when activity is replaced by concentration. This, however, scarcely affects the form of the gas equation deduced from measurements at low concentrations.

Similar results are obtained with insoluble films on water: Adam and Jessop (26) found that the equation of state of gaseous films was the analogue of Amagat's equation. It would be interesting in this connection to examine binary mixtures for departures from additivity. We have

$$\frac{F}{kT} = \frac{n_1 + n_2}{S} - \frac{1}{S^2} \left[\frac{1}{2} \rho_{11} n_1^2 + \rho_{12} n_1 n_2 + \frac{1}{2} \rho_{22} n_2^2 \right]$$

where

$$\rho_{\alpha\beta} = 2 \pi \int_0^\infty (e^{-E_{\alpha\beta}/kT} - 1) r \cdot dr$$

Putting $n_1 = x n$, and $n_2 = (1 - x)n$, we get

$$\frac{F}{kT} = \frac{n}{S} - \frac{1}{2} \frac{n^2}{S^2} [\rho_{11} x^2 + 2 \rho_{12} x(1 - x) + \rho_{22} (1 - x)^2]$$

so that a linear dependence on x , the mole fraction, would be exceptional (27).

The adsorption isotherm

We should expect that the actual equation of state of a surface layer would be the analogue of Onnes' equation for a bulk gas

$$pV = A + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} \dots$$

where the coefficients A , B , etc. vary with temperature. The equation of Beattie and Bridgman (28) has the merit of giving a virial development in terms of only five constants. The equation runs

$$\begin{aligned} P &= \frac{RT}{V} + \frac{RT}{V^2} \left(B_0 - \frac{C}{T^3} - \frac{A_0}{RT} \right) + \frac{RT}{V^3} \left(\frac{c B_0}{T^3} - b B_0 + \frac{a A_0}{RT} \right) - B_0 \frac{c b RT}{V^4 T^3} \\ &= \frac{RT}{V} + \frac{RT}{V^2} \beta + \frac{RT}{V^3} \gamma + \frac{RT}{V^4} \delta \end{aligned}$$

where A , B , a , b , c are constants, V the gram-molecular volume, and β , γ , and δ vary with temperature as shown. The free energy takes the form

$$\int V dp = RT \left[-\log V + \frac{2\beta}{V} + \frac{3\gamma}{2V^2} + \frac{4\delta}{3V^3} \right] + \text{constant},$$

and, analogously, for a surface phase

$$\int A dF = RT \left[-\log A + \frac{2\beta}{A} + \frac{3\gamma}{2A^2} + \frac{4\delta}{3A^3} \right] + F_0$$

where A is the area per gram-molecule.

Bradley (29) has used this equation to study Langmuir's isotherm. If z is the number of gram-molecules adsorbed per unit area, $z = \frac{1}{A}$,

$$\log p + \frac{F_0'}{RT} = \log z + 2\beta z + \frac{3}{2}\gamma z^2 + \frac{4}{3}\delta z^3 + \frac{F_0}{RT}$$

This is the adsorption isotherm, and it remains to link it with Langmuir's. The latter may be written

$$z = \frac{c_1 c_2 p}{1 + c_2 p} \quad \text{or} \quad p = \frac{z}{c_1 c_2 - c_2 z}$$

Hence

$$\begin{aligned} \log p &= \log z - \log (c_1 c_2 - c_2 z) \\ &= \log z - \log c_1 c_2 + \frac{z}{c_1} + \frac{z^2}{2c_1^2} + \dots \end{aligned}$$

since z is always less than c_1 . This is indeed the theoretical form, provided

$$\frac{1}{c_1} = 2\beta = 2 \left(B_0 - \frac{C}{T^3} - \frac{A_0}{RT} \right), \text{ and } \frac{\Delta F_0}{RT} = -\log c_1 c_2$$

These two equations are in fact approximately obeyed. The work of Zeise (30) has shown that the adsorption of gases on charcoal can be represented better in terms of Langmuir's theory than by means of Polanyi's adsorption potential. He finds that the parameters c_1 and c_2 vary with temperature according to

$$c_1 = a_1 - b_1 T \quad c_2 = \frac{10^{a_2}}{T^{b_2}}$$

The results deduced above are equivalent to these two equations, for, taking the case of carbon dioxide, for which there are most points, c_1 can be expressed by

$$\frac{1}{c_1} = -.509 + \frac{15.9}{T} + \frac{3 \times 10^5}{T^3}$$

while the plot of $\log c_1 - c_2$ against $\frac{1}{T}$ is a straight line except at low temperatures: ΔF_0 is regarded as approximately invariant with temperature. We may note that Zeise's equation for c_1 is theoretically inadequate in that it predicts a negative adsorption at high temperatures.

The scope of Langmuir's isotherm thus appears to be considerably wider than was supposed, and the temperature variation of the coefficients can be accounted for in general terms. More recently Langmuir's simple kinetic treatment has been replaced by statistical derivations. Frenkel introduced his result

$$\tau = \tau_0 e^{\frac{u_0}{kT}}$$

into the isotherm in the form given in Section I, viz.,

$$n = \frac{\nu \beta \tau N'}{\nu \beta \tau + N'}$$

when $\beta = 1$. Writing

$$\nu = \frac{Sp}{\sqrt{2\pi mkT}}$$

we get

$$\frac{N'}{n} = 1 + \frac{N'}{S} \frac{\sqrt{2\pi mkT}}{p \tau_0} \cdot e^{u_0/kT}$$

which is Frenkel's isotherm if $\frac{S}{N'}$ is replaced by σ_0 . We note that $c_1 c_2$ is proportional to

$$\frac{\tau_0}{T^{\frac{3}{2}}} \cdot e^{-u_0/kT}$$

The same result may be derived by writing the distribution law between the phases of three and two dimensions in the form

$$\frac{n}{S - n \sigma_0} = \frac{p \tau_0}{\sqrt{2\pi mkT}} \cdot e^{u_0/kT}$$

Kar (31) has deduced the equation

$$F(S - B) = nkT$$

statistically. He finds that Langmuir's equation holds with

$$\frac{1}{c_1 c_2} = \frac{kT}{\rho} \cdot \sqrt{2 \pi mkT} \cdot e^{-u_0/kT}$$

where ρ is a multiple of Planck's constant h . This result is equivalent to Frenkel's if the oscillation of the adsorbed molecule is quantized, for then (32)

$$\tau_0 = \frac{1}{\nu} = \frac{m_1 h}{kT}$$

Hückel (33) writes

$$c_2 = v e^{u_0/kT}$$

where u_0 is the adsorption potential, and v the active volume of an adsorbed molecule. Since v , according to Herzfeld (34), is equal to

$$\frac{1}{(2 \pi mkT)^{\frac{3}{2}}} \left(\frac{kT}{\nu} \right)^3$$

we obtain the result

$$c_2 \propto \frac{1}{T^{\frac{3}{2}}} \cdot e^{u_0/kT}$$

if the oscillation is quantized.

Analogies between phases of two and three dimensions

Reference has frequently been made in this article to the striking analogy between a surface phase and a bulk material. Rideal and Lyons (35) have pointed out that for films on liquids the various types of film—solid condensed, liquid condensed, liquid expanded, and vaporous—are analogous to the bulk phases—

solid, liquid crystal, liquid, and vapor. The pressure-temperature curves delimit phase regions for films exactly as for the bulk phases, so that the films show a triple point. Various thermal constants may be calculated, such as the two-dimensional latent heat of evaporation. There is thus the possibility of the coexistence of two or more surface phases, separated by the boundary regions, in this case lines. There will be adsorption at these lines according to an equation analogous to that of Gibbs, and these lines may themselves be treated as separate regions, with an equation of state (Schwab and Pietsch (36)). We may refer to linear just as to surface energy, and indeed the former has been calculated for the edges of certain salts. These lines, which are regions of greater activity than the rest of the surface, are clearly of importance to heterogeneous catalysis, especially when it is remembered that actual crystals are composed of small units separated by cracks.

Many of these analogies have not been exploited. It would be interesting, for example, to study the homogenous reaction between two components of a surface phase.

III. ELECTRICAL PROPERTIES OF THE ADSORBED LAYER

General remarks on polarization

From the viewpoint of dielectric theory (37) molecules fall into two types. In the one the molecular polarization is a constant; in the other it splits up into two parts, one of which is a constant, while the other varies inversely as the absolute temperature. The second type is explained by assigning to the molecule a permanent electric doublet, μ . This is found by classical statistics to contribute $\frac{4\pi N\mu^2}{9kT}$ to the molecular polarization, which is therefore given by

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4}{3} \cdot \pi N \left(\alpha + \frac{\mu^2}{3kT} \right)$$

Here ϵ is the dielectric constant, M the molecular weight, d the density, N Avogadro's number, k Boltzmann's constant, T the absolute temperature, α the polarizability. This result was dis-

puted by the old quantum theory, but has been confirmed by the new wave mechanics.

A molecule is dipolar if the moments of its charges about the coördinate axes, $\Sigma e_i x_i$, $\Sigma e_i y_i$, $\Sigma e_i z_i$, do not all vanish. If the moments vanish, but what might be called the inertial moments, $\Sigma e_i x_i^2$ etc. do not, the molecule has a quadrupole: the effect of this may, however, be neglected when there is an appreciable dipole.

The potential of a dipole whose center is at O is, at a point P , $\frac{\mu \cos \theta}{r^2}$, where $r = OP$, and θ is the angle between OP and the dipole axis. The mutual potential energy of two dipoles, μ , μ' is

$$\frac{\mu \mu'}{r^3} (\sin \theta \cdot \sin \theta' - 2 \cos \theta \cos \theta')$$

where the line joining their centers O , O' makes angles θ and θ' with the axes of the dipoles, and $r = OO'$.

The dipole theory of adsorption

There have been various attempts to interpret adsorption in terms of polarization. In general, the conditions are so complex that only a partial treatment has been adopted, applicable to special cases.

At first sight the adsorption of a polar molecule such as water seems readily explained by the presence in the water of an electric doublet. The molecules would stick to the surface just as would small magnetic doublets to the surface of cast iron. The attraction is caused by the charges induced on the surface, and these can be replaced, as Kelvin showed, by the mirror image of the inducing charges. While all metals would exert the same attraction, dielectrics would differ, as in this case the induced dipole is $\mu \left(\frac{\epsilon - 1}{\epsilon + 1} \right)^{\frac{1}{2}}$, where ϵ is the dielectric constant of the adsorbent.

However, this treatment uses the theory of images in the atomic realm without justification, and it leaves out of account altogether the effect of the surface field of the adsorbent. Thus mirror image forces play only a partial rôle in adsorption.

Landé and Lorenz (38) write the energy of a permanent dipole μ in the field of its mirror image in the form

$$\frac{-\mu^2}{8\delta^3} \cdot (1 + \cos^2 \beta)$$

where the dipole is distant δ from the surface, and makes an angle β with the surface normal. The number of molecules whose angles with the surface normal are between β and $\beta + d\beta$ is therefore

$$x_\infty e^{-\frac{\mu^2 (1 + \cos^2 \beta)}{8\delta^3 kT}} \cdot 2\pi \sin \beta d\beta$$

Averaging over all angles, the number of molecules adsorbed per sq. cm. is found to be

$$x_\infty \frac{\delta_0}{6} \cdot \frac{e^2 y_0}{y_0^2}$$

where x_∞ is the concentration of the bulk gas, δ_0 is the radius of a molecule, and

$$y_0 = \frac{\mu^2}{8\delta_0^3 kT}$$

However, when x_∞ corresponds to an atmospheric pressure at 0°C. and $\mu = 10^{-18}$, only a small fraction of the surface can be covered on this basis.

When the effect of a surface field E on the permanent dipoles (without electron polarization) is included, so that the energy of a dipole is

$$\frac{\mu^2}{8\delta^3} (1 + \cos^2 \beta) + \mu E \cos \beta$$

Blüh and Stark (39) find that the adsorption without E must be multiplied by a factor $e^{\frac{\mu E}{kT}}$. When μ is 10^{-18} this factor is given for various values of E (E.S.U.)

E	10^4	10^5	2×10^5	2.5×10^5	3×10^5	5×10^5	8×10^5	3×10^6
$e^{\frac{\mu E}{kT}}$01	.3	1	2	3	9	23	525

They find that for an ionic lattice with a lattice constant 2 A. U. the field at a distance 1 A. U. from the surface is 4.3×10^6 E.S.U., sufficient to account for adsorption. A similar calculation has been made by Lennard-Jones (40) for the 100 plane of NaCl: the van der Waals, as well as the ionic, field was studied.

Zahn (41) measured the dielectric constant ϵ of water at various temperatures and pressures. He found that $\epsilon - 1$ plotted against the pressure gave two intersecting straight lines. This is inconsistent with Jona's (42) interpretation of the anomalous behavior of water vapor as due to association. Zahn assumes that the dipoles condense on the electrodes, and finds that on the basis of mirror image forces

$$c = c_{\infty} \left(1 + \frac{y_0}{3} + \frac{y_0^2}{10} + \frac{y_0^3}{4^3} + \frac{y_0^4}{4^{15}} \right)$$

where c is the concentration at a distance δ_0 from the electrode surface, and y_0 is as above. At the pressure at which deviations from normality first occur

$$\begin{aligned} \frac{c}{c_{\infty}} &= \frac{\text{saturated pressure}}{\text{equilibrium pressure of film}} \\ &= \frac{20}{6.2} \text{ at } 23.3^{\circ}\text{C.} \end{aligned}$$

This gives y_0 the value 2.5 and thence δ_0 is found to be 2.2 A. U., which agrees well with the radius of a water molecule.

The above theory of the action of mirror image forces is inadequate in two respects. The electron polarization of the adsorbed molecules is neglected, as is the interaction between the various adsorbed molecules and their mirror images. Bradley (43) assumes the first dipole, the one next to the surface, to be strongly held and completely oriented by the surface forces, and studies the effect of building up successive layers. The surface forces are supposed not to extend beyond the first dipole, whose energy is not considered. For simplicity this three-dimensional problem is replaced by one-dimensional study of an adsorption chain perpendicular to the surface, which is strictly the case already considered. Consider n dipoles of diameter a to form

the chain; let the force on the p^{th} dipole be F_p ; let μ_s be the moment, perpendicular to the surface, of the s^{th} dipole. Then

$$F_p = \sum_{s=1}^{s=p-1} \left[\frac{2 \mu_s}{(p-s)^3 a^3} + \frac{2 \mu_s}{(p+s-1)^3 a^3} \right] + \sum_{s=p+1}^{s=n} \left[\frac{2 \mu_s}{(s-p)^3 a^3} + \frac{2 \mu_s}{(p+s-1)^3 a^3} \right] + \frac{2 \mu_p}{(2p-1)^3 a^3}$$

This equation merely gives the force on the p^{th} dipole due to dipoles on either side, and due to the mirror images of the sequence of dipoles. Also

$$\mu_s = \mu L \left(\frac{\mu F_s}{kT} \right) + \alpha F_s$$

where

$$L(x) = \coth x - \frac{1}{x} = 1 - \frac{1}{x} \text{ for } x \gg 1$$

Since $\frac{\mu E}{kT} > 1$ for a molecule such as water at room temperature, all the μ 's in the equation for F_p can be replaced by F 's. To a first approximation these n equations are linear in F 's, writing

$$1 - \frac{kT}{\mu F} = 1$$

and the various F 's can be found in the form of determinants. The second approximation is then obtained by inserting the values of F so found in the terms $1 - \frac{kT}{\mu F}$ and resolving for F . In this way F is calculated, and the energy of the p^{th} dipole is

$$- \mu F_p L \left(\frac{\mu F_p}{kT} \right) - \frac{1}{2} \alpha F_p^2 + \frac{2 \lambda}{(n-1) a^{n-1}}$$

the last term representing the repulsive energy. The evaluation of the latter is uncertain. It may be computed on the assump-

tion of a neon-like sheath for the pseudo-atom water, and is relatively small. The calculation is laborious, and was performed only for layers of two and three molecules. The difference between the total energies of chains of three and two molecules gives the energy required to remove a molecule from a chain of three molecules, and this is the latent heat of evaporation, per molecule, of the film. In the case of water at 25°C. we find for a layer of three molecules $F_3 = 1.61 \times 10^5$, $F_2 = 2.85 \times 10^5$, $F_1 = 3.13 \times 10^5$. And for a layer of two molecules $F_2 = 1.62 \times 10^5$, $F_1 = 2.69 \times 10^5$. This gives 8600 calories for the latent heat of evaporation per gram-molecule of a film of three molecules, agreeing well with Lehner's (44) figures for

$$-R d_n \frac{(\log p_n)}{d \left(\frac{1}{T} \right)} = L_n$$

n as above, viz., at 25°C. $n = 5$, $L = 9100$; $n = 10$, $L = 10530$.

By a calculation in some respects similar to the above, in that adsorption is viewed as the building up of successive layers, rather than the establishment of a concentration gradient up to the surface, Boer and Zwikker (45) have explained the peculiar adsorption isotherm of a polarizable molecule (without permanent dipole) on an ionic lattice. The amount adsorbed at first increases quickly with p , the pressure, then more slowly, and finally near saturation, there is again a rapid rise; in no case does n remain constant as p increases.

Let p be the moment induced in a molecule in the n th layer from the surface, b the distance between adjacent molecules in a layer, c the distance between adjacent layers. The energy ϕ_1 of the first layer is

$$- A p_1 + \frac{B p_1^2}{b^3} - \frac{C}{c^3} p_1 p_2 - \frac{D}{c^3} p_1 p_3 \dots \dots$$

where A , B , C etc. are summation constants for the action of the ionic lattice, the neighboring dipoles in the first layer, those in the second layer, and so on. Similarly

$$\phi_k = \frac{p^2 k}{2 \alpha} + B \frac{p^2 k}{b^3} - C \left[\frac{p_{k-1} \cdot p_k}{c^3} + \frac{p_k p_{k+1}}{c^3} \right] - D \left[\frac{p_{k-2} p_k}{c^3} + \frac{p_k p_{k+2}}{c^3} \right] + \dots$$

Here no account is taken of mirror images. The total energy per sq. cm. is

$$\frac{\phi}{N} = -A p_1 + \left(\frac{B}{b^3} + \frac{1}{2\alpha}\right) \Sigma p_k^2 - \frac{C}{c^3} \Sigma p_k p_{k+1} - \frac{D}{c^3} \Sigma p_k p_{k+2} \dots$$

Since the variables are $p_1 \dots p_n$ for equilibrium $\frac{d\phi}{dp_k} = 0$. These differentiations give the series of equations

$$\begin{aligned} \beta p_1 + \gamma p_2 + \delta p_3 + \dots &= A \\ \gamma p_1 + \beta p_2 + \gamma p_3 + \delta p_4 + \dots &= 0 \\ \dots & \\ \gamma p_{n-1} + \beta p_n &= 0 \end{aligned}$$

where β, γ, δ , are constants. Solution of these gives ϕ_n in the approximate form

$$\frac{-A^2}{2\beta} \cdot \left(\frac{K}{1-K^2}\right)^{2n-2}$$

where K is a constant. Knowing ϕ_n, π , the pressure of gas in equilibrium with the adsorbed film, can be found in terms of unknown constants (as an approximation) giving the isotherm

$$\log \frac{\pi}{K_3 \pi_0} = K_2 K_1^n$$

where π_0 is the vapor pressure of the liquid, and K_1, K_2, K_3 , are constants. This gives a curve exactly of the form found experimentally by Boer (46) for the adsorption of iodine on calcium fluoride.

A similar calculation has been made by Herzfeld (47), who considers the interaction between pairs of adjacent molecules in the layer next to the surface, with a view to explaining the change in the heat of adsorption with the amount adsorbed. According as the two adjacent polarizable molecules are adsorbed on ions of the same, or of opposite sign, the heat of adsorption is lowered

or raised as the number of pairs increases. Calculation shows that repulsion between adjacent molecules of an agglomerate could not change the heat of adsorption for a salt, and might lower it by about 10 per cent for a metal: attraction could increase the heat by about 10 per cent for salts, and by about 40 per cent for metals.

In view of the complexity of the polarization phenomena of adsorbed films one would not expect the simple relation between dielectric constant and amount adsorbed found by Illin (48). His work has been criticized by Hückel (49), and by Cassel (50).

The effect of adsorption on electric surface properties

No extensive study has been made of the effect on adsorption of varying the surface field, as high enough fields are not under our control. Loeb (51) found that water would condense first on a negative electrode, in a vessel containing both electrodes, which is in line with the condensation of water vapor on the negative ions first in the Wilson expansion chamber. Evidently water has an asymmetric dipole. However, the effect of the surface film on various electric properties has been studied, notably the effect on the polarization of reflected light, photo-electric and thermionic emission, and the diffraction of electrons.

When light incident at the polarizing angle is reflected from a plane surface, the reflected beam is not plane, but elliptically, polarized. Drude explained this by assuming a gradually changing transition region between the two media. If ρ is the ellipticity, ϵ_1 , ϵ_2 , ϵ the dielectric constants of the first, the second and the transition media, then

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

where z is the position in the transition region. This sets a lower limit to the thickness of the adsorbed layer, not very different from the actual value, equal to

$$\frac{\lambda \rho}{\pi (1 + n_1^2)^{\frac{1}{2}}} \cdot \frac{n_1 + 1}{n_1 - 1}$$

where n_1 is the refractive index of medium 2 with respect to medium 1. Frazer (52) and Silverman (53) have used this method to study the formation of films, Frazer using water and methyl alcohol on glass, Silverman methyl alcohol on rock salt. The thickness of the layer could be determined to .5 A. U. Silverman found that between 1×10^{-5} and 1×10^{-4} cm. the first layer was built up and that there was no further adsorption until the pressure reached 2 to 3 cm. From this pressure until about 10 cm. the second layer was attached. The first layer was about 4.9 A. U. thick, the second 4.3 A. U. These pressures are what we should expect if the first molecule is held by the surface force of the rock salt, and the second by cohesive forces between methyl alcohol molecules.

Surface films affect thermionic and photo-electric emission by providing at the surface an additional potential step, which may be positive or negative. If x is the number of atoms per sq. cm., ΔV , the potential increment, is equal to $4 \pi \times \mu$. If the fraction covered is θ the thermionic current is therefore of the form

$$i_{\theta} = i A T^2 e^{\frac{\phi + \alpha_1 \theta}{kT}}$$

where α_1 is positive or negative. Thus the effect of the surface film is very great, a monatomic layer of thorium or tungsten at 1500°C . increasing the emission by a factor of 10^6 . A wave mechanics study of the effect of the modification of the surface potential hump has been made by Georgeson (54), following Nordheim (55). He finds that the A of Richardson's formula is of the form

$$B l^{\frac{1}{2}} (\delta\chi)^{\frac{1}{2}} e^{-.71 (\delta\chi)^{\frac{1}{2}}}$$

where B is a constant, l is the thickness of the layer, $\delta\chi$ is the potential drop in the layer. In this way he deduces a value 5.3 A. U. for the thickness of a layer of thorium on tungsten, a reasonable result.

The study of the interference beams formed by reflection of electrons offers an interesting method of investigating surfaces. This method is especially useful if slow electrons are employed,

for these penetrate only a short distance into the interior. As an example, Rupp (56) found that with hydrogen on a nickel surface new interference maxima appear, in addition to those for clean nickel. On standing for two days only the latter change, becoming smaller. This is ascribed to the penetration of the gas into the nickel lattice, where it is irregularly arranged, in contrast to the gas on the surface. On heating, the new hydrogen maxima disappear, leaving those for nickel lower than for the clean surface.

Germer's work (18) has already been referred to (Section I). G. P. Thompson has used fast electrons to investigate surfaces.

Gas films do not influence the diffraction. Reflection measurements may be made photographically, and there is in general a diffuse diffraction, on which may be superimposed a system of spots, due to a single surface crystal, or concentric rings, due to a polycrystalline surface. Polished copper gives the diffuse background, but on standing in air faint rings appear, whose intensity and clearness are greatly increased by heating the copper. The rings correspond to a cuprous oxide lattice. Similarly, passive iron, whose original polish had been only slightly dimmed, gave good rings corresponding to ferric oxide. The passivity had, however, probably been lost during the test, and when special care was taken no change could be observed from polished iron.

REFERENCES

- (1) WOOD: *Phil. Mag.* [6] **30**, 300 (1915); [6] **32**, 364 (1916).
KNUDSEN: *Ann. Physik.* [4] **50**, 472 (1916).
- (2) LANGMUIR: *Phys. Rev.* **8**, 149 (1916).
- (3) ELLETT, OLSON, AND ZAHL: *Phys. Rev.* **34**, 493 (1929).
- (4) KNAUR AND STERN: *Z. Physik.* **53**, 779 (1929).
- (5) ESTERMAN AND STERN: *Z. Physik.* **61**, 95 (1930).
- (6) JOHNSON: *Phys. Rev.* **35**, 1432 (1930).
- (7) ELLETT AND OLSON: *Phys. Rev.* **31**, 643 (1928).
- (8) TAYLOR: *Phys. Rev.* **35**, 375 (1930).
- (9) CHARITON AND SEMENOW: *Z. Physik.* **25**, 287 (1924).
- (10) ESTERMAN: *Z. Physik.* **33**, 320 (1925).
- (11) COCKROFT: *Proc. Roy. Soc. (London)* **119A**, 293 (1928).
- (12) FRENKEL: *Z. Physik.* **26**, 117 (1924).
- (13) CLAUSING: *Ann. Physik.* [5] **5**, 489, 522 (1930).
- (14) WERTENSEIN: *J. phys. radium* [6] **4**, 281 (1923).
- (15) LANGMUIR: *Proc. Nat. Acad. Sci.* **3**, 141 (1917).
- (16) HERZFELD: *Kinetische Theorie der Wärme*, p. 190. Vieweg, Braunschweig (1925).

- (17) VOLMER AND ADHIRKARI: *Z. physik. Chem.* **119**, 46 (1926).
VOLMER AND ESTERMAN: *Z. Physik.* **7**, 13 (1921).
VOLMER: *Z. Physik.* **9**, 193 (1922).
- (18) GERMER: *Z. Physik.* **54**, 408 (1929).
- (19) TAYLOR: *J. Am. Chem. Soc.* **43**, 2179 (1921).
LARSON: *J. Am. Chem. Soc.* **47**, 346 (1925).
- (20) LENNARD-JONES: *Proc. Roy. Soc. (London)* **106A**, 463 (1924).
- (21) VOLMER: *Z. physik. Chem.* **115**, 253 (1925).
- (22) BRADLEY: *Phil. Mag.* [7] **8**, 202 (1929).
- (23) TRAUBE: *Ann.* **256**, 27 (1891).
- (24) RIDEAL AND SCHOFIELD: *Proc. Roy. Soc. (London)* **109A**, 56 (1925).
- (25) JONES AND BURY: *Phil. Mag.* [7] **4**, 843 (1927).
- (26) ADAM AND JESSOP: *Proc. Roy. Soc. (London)* **112A**, 376 (1926).
- (27) FOWLER: *Statistical Mechanics*, p. 206. Cambridge University Press, London (1929).
- (28) BEATTIE AND BRIDGMAN: *J. Am. Chem. Soc.* **49**, 1665 (1927); **50**, 3133 (1928).
- (29) BRADLEY: *Phil. Mag.* [7] **11**, 690 (1931).
- (30) ZEISE: *Z. physik. Chem.* **136**, 407 (1928).
- (31) KAR: *Physik. Z.* **26**, 615 (1925).
- (32) GANGULI: *Z. Physik.* **66**, 704 (1930).
- (33) HÜCKEL: *Adsorption und Kapillarkondensation*, p. 172. Akad. Verlag, Leipzig (1928).
- (34) HERZFELD: *Physik. Z.* **22**, 186 (1921).
- (35) RIDEAL AND LYONS: *Proc. Cambridge Phil. Soc.* **26**, 419 (1930).
- (36) SCHWAB AND PIETSCH: *Z. physik. Chem.* **1B**, 385 (1928); **2B**, 262 (1929).
- (37) DEBYE: *Polar Molecules*. Chemical Catalog Co., New York (1929). Also *Handbuch der Radiologie*, Band 6.
- (38) LANDÉ AND LORENZ: *Z. anorg. allgem. Chem.* **125**, 47 (1922).
- (39) BLÜH AND STARK: *Z. Physik.* **43**, 575 (1927).
- (40) LENNARD-JONES AND DENT: *Trans. Faraday Soc.* **24**, 92 (1928).
- (41) ZAHN: *Phys. Rev.* **27**, 329 (1926).
- (42) JONA: *Physik. Z.* **20**, 14 (1919).
- (43) BRADLEY: *Phil. Mag.* [7] **10**, 323 (1930).
- (44) LEHNER: *J. Chem. Soc.* **1927**, 272.
- (45) BOER AND ZWIKKER: *Z. physik. Chem.* **3B**, 407 (1929).
- (46) BOER: *Proc. Acad. Sci. Amsterdam* **31**, 906 (1928).
- (47) HERZFELD: *J. Am. Chem. Soc.* **51**, 2608 (1929).
- (48) ILLIN: *Phil. Mag.* [6] **48**, 193 (1924); [6] **50**, 1144 (1925).
- (49) HÜCKEL: *Adsorption und Kapillarkondensation*, p. 193. Akad. Verlag, Leipzig (1928).
- (50) CASSEL: *Physik. Z.* **26**, 862 (1925).
- (51) LOEB: Short notice in reference 39.
- (52) FRAZER: *Phys. Rev.* **33**, 99 (1929).
- (53) SILVERMAN: *Phys. Rev.* **36**, 311 (1930).
- (54) GEORGESON: *Proc. Cambridge Phil. Soc.* **25**, 175 (1929).
- (55) NORDHEIM: *Proc. Roy. Soc. (London)* **122A**, 36 (1929).
- (56) RUPP: *Ann. Physik.* [5] **5**, 453 (1930).
- (57) THOMPSON, G. P.: *Proc. Roy. Soc. (London)* **128A**, 649 (1930).