ON THE BEHAVIOUR OF ADSORBED ATOMS.

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When a surface of a solid is exposed to the vapours of another substance, a rarified film of adsorbed molecules is formed at first. This film must have—and, as it was shown by the experiments of Volmer and Adhikari[1] on " creeping " of molecules of benzophenone, it apparently has—the properties of a two-dimensional gas. If the temperature of the surface is lower than the temperature of the vapours we shall obtain finally a deposit of condensed substance which will gradually grow.

It was pointed out by M. Knudsen[2] and R. W. Wood[3] that the formation of this deposit cannot take place if the temperature of the surface is not low enough. It was shown later by N. Semenoff and J. Chariton[4] that this " critical temperature of condensation " depends on the density of vapour acting on the surface, and from the figures obtained by them J. Frenkel[5] (who first gave the theory of the phenomenon), calculated the latent heat of evaporation of a cadmium " doublet "—two cadmium atoms

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[1] *Z. physik. Chem.*, **119**, 46, 1926.

[2] *Ann. Physik*, **50**, 472, 1916.

[3] *Phil. Mag.*, **30**, 300, 1915 ; **32**, 364, 1916.

[4] *Z. Physik*, **25**, 287, 1924.

[5] *Ibid.*, **26**, 117, 1924.

linked together. Later I. Estermann[6] and J. Cockroft[7] have done more accurate measurements for various substances. N. Semenoff[8] then proposed a very simple scheme of the phenomena, considering the equilibrium between three-dimensional vapour, two-dimensional vapour, and two-dimensional condensed phase. Semenoff's point of view is that the critical temperature for the given density of three-dimensional vapour corresponds to the point where the two dimensional "condensation" may take place. If the temperature of the surface is increased the density of two-dimensional gas must also be increased in order to be saturated, and this can be done by increasing the density of three-dimensional vapour. Thus at the critical temperature corresponding to a definite pressure of vapours (or at the critical pressure corresponding to a definite temperature)—shortly speaking, at the critical conditions—we have an equilibrium three-dimensional vapour—two-dimensional vapour—two-dimensional condensed phase.

The density of two-dimensional vapour is proportional (unless it is too large) to the pressure of three-dimensional vapour. Therefore from the critical temperature critical density curve (which shows at the same time how the pressure of two-dimensional vapour depends on temperature) it is possible to calculate the latent heat of two-dimensional evaporation. The slope of the curve mentioned must be smaller than the slope of the curve showing the normal three-dimensional pressure against temperature. Therefore, the two curves must intersect at some point corresponding to a certain temperature. At this temperature the surface need not be overcooled with respect to the substance in order that the deposit may appear. The theory of Semenoff predicts some discontinuities in the adsorbtion isothermal above the critical point. The remarkable results of experiments on adsorbtion of gases published by A. J. Allmand and L. C. Burrage[9] are, maybe, an example of such phenomena.

Some experiments have been done in order to find the above-mentioned point of intersection, *i.e.* to trace the curve in the region of higher temperatures than it, has been done before. In connection with these experiments it was necessary to use a method of registration of critical conditions which would give results certain enough. The method similar to that of I. Estermann was used, but more attention was paid to the factor of time. The deposit was formed on glass, or on a layer of naphthalene or sulphur previously condensed on glass from vapours. The temperature of the glass was kept constant by means of drops of liquid air, which was poured into the mercury filling the glass tube. The density of the stream of molecules falling on the glass (or any other substance) was determined by the temperature of the oven from which cadmium or mercury was evaporated. This temperature was measured by means of a thermocouple.

The results obtained[10] are very different from those published by Estermann. As a matter of fact it was possible to obtain a curve similar to that of Estermann, but only in cases when the time of the experiments was restricted to several minutes only, *i.e.* to the time necessary for an amount of substance sufficient to form a visible deposit to reach the surface. If, however, at a given density, we increase the tem-

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[6] *Z. physik. Chem.*, B. **7**, 471, 1930.

[7] *Z. Elektroch.*, **31**, 441, 1925.

[8] *Proc. Roy. Soc.*, **119**, 293, 1928.

[9] *Ibid.*, **130**, 610, 1931.

[10] The experiments were carried out by O. Leypunsky, M. Lebedinsky and M. Gen. A detailed account will be published elsewhere.

perature of the surface above the "critical" value, the deposit will appear if we wait long enough. One might think that above the "critical" temperature the condensation (which must take place finally because the surface is over-cooled in respect to the vapour) proceeds by means of a mechanism substantially different, so that the critical temperature might remain, but an analysis of the results obtained leaves no room for this conception.

In Fig. 1 the time of formation of a visible deposit of cadmium is plotted against the temperature of the surface of the glass covered with naphthalene. The density of the molecular beam (calculated from the temperature of the substance and the dimensions of the apparatus) is equal to $2 \cdot 10^{14}$ molecules per cm.^{2} per second. It is obvious that the curve does not give anything like critical temperature, but just that the time of formation is gradually rising as the temperature increases.

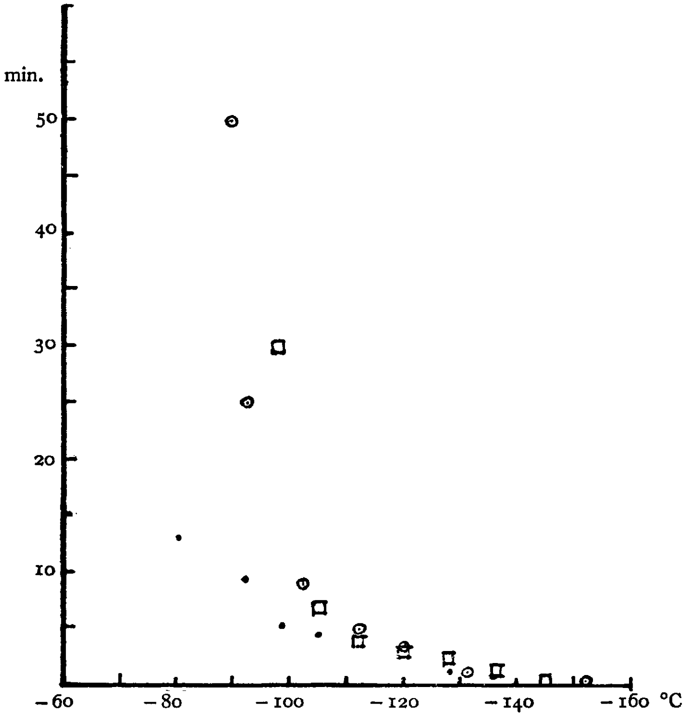

Fig. 1.

Quite similar results have been obtained with cadmium deposited on pure glass-surface or on glass covered with a layer of sulphur and with mercury deposited on copper. The experimental results for cadmium on glass and sulphur are also shown on Fig. 1 Fig. 2 shows the curves obtained with mercury.

This absence of critical temperature seems to contradict the theory of Semenoff. However, the discrepancy disappears if we take into account the inhomogeneity of the surface. Various points of the surface correspond to various heats of adsorbtion. At a certain temperature condensation may take place on the most active points, and then spread around these centres gradually covering the whole surface. At a lower temperature the condensation may begin on all points of the surface and the deposit becomes visible in a much shorter time. This supposition is supported by the fact that the deposit obtained at a higher temperature—corresponding to long time exposure—has not a smooth metallic appearance, but seems dark and very irregular in density, while a deposit obtained at a temperature 30° lower has a typical mirror-surface. The existence of points of various activity seems to be a fact well established by the work of Taylor, and it is quite reasonable to take into account these results when considering the mechanism of condensation. In this case the theory of critical temperature of condensation proposed by Semenoff explains the experimental results quite satisfactorily.

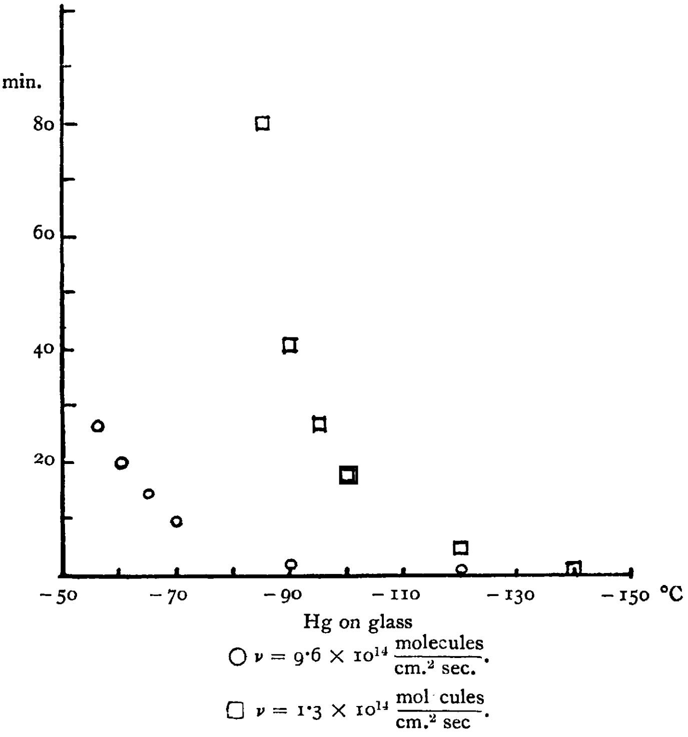

FIG. 2.

In this theory, as well as in many other cases, the conception of a two-dimensional gas is used. It must be noticed that in the case considered this conception is not absolutely necessary. It is possible to consider the equilibrium between singlets and doublets or larger complexes from a purely energetical point of view, taking into account only the exchanges produced by condensation from the volume and evaporation from the surface into the volume. It will be shown[11]

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[11] See page 176.

that the equilibrium is obtained more quickly through the "two-dimensional" collisions. Regard must also be had to the fact that the existence of the atoms bombarding the surface makes it possible to produce the centres of condensation in a quite peculiar way. For example several atoms can group themselves together into two layers and the evaporation of such a complex will be much more difficult than the evaporation of a complex consisting of the same number of atoms, but lying in one layer.

We shall reproduce now the results of some very simple calculations by one of us (J. Chariton) concerning the behaviour of rarified adsorbed layer.

There is a great difference in the character of the motion of molecules of an ordinary three-dimensional gas and those of a two-dimensional gas formed on the surface of a solid. For the molecules of ordinary gas the mean free path is determined only by the density of the gas. It is quite obvious that this does not hold for "two-dimensional" molecules. The fact of formation of deposits geometrically limited by the slits forming molecular beams shows that the molecules stay near enough to the place where they fall. If the molecules could move freely along the surface colliding only one with another a molecular beam of density, say 10^{13} molecules per cm.^{2} per second could not give any image at all.

From experiments of Clausing [12] we know that the time of the life of an atom on the surface of the adsorbent is less than 10^{-6} second. Let it be even 10^{-6} second, then the number of molecules per cm^2 of the surface n shall be

$$n = \nu\tau = 10^{13} \times 10^{-6} = 10^{7}$$

The mean free path corresponding to this n may be calculated from the formula.[13]

$$R = \frac{1}{2dn} \cong \frac{1}{2 \,.\, 2 \,.\, 10^{-8} \,.\, 10^{7}} = 2{\cdot}5 \text{ cm.},$$

where d is the diameter of the adsorbed atoms. Thus the atoms of the beam striking the surface might distribute over a large surface and we could not get anything like a sharp-defined image of the slit.

On the other hand the movement of the molecules along the surface of a solid certainly exists. This has been shown extraordinarily clearly by the experiments of Volmer and Adhikari.[1] Other indirect experiments also give evidence of the creeping of the molecules.[14]

Let us consider the character of the movement of an atom remaining on the surface. It is quite clear that even on an ideal surface of a crystal different points must possess different properties. For example an atom adsorbed just "above" one of the ions of the lattice must certainly have a somewhat different potential energy from that of an atom placed "between" two ions. The surface is, in an energetic sense, "wavy." Therefore an atom possessing a certain amount of vibrational energy cannot leave a point of minimum potential energy unless the energy of its vibration is sufficient to reach the heights of surrounding maximums. If the maximum is reached the adsorbed atom may pass to the next minimum, where it will stay for some time, etc.

[12] *Over den Verblyftyed van Moleculen en de strooming van zeer verdunde Gassen*, 51, Amsterdam, 1928.

[13] Referring only to the order of magnitude.

[14] I. Estermann, *Z. Physik*, **33**, 320, 1925. *Z. physik. Chem.*, **106**, 403, 1923. M. Volmer und I. Estermann, *Z. Physik*, **7**, 1, 13, 1921.

The distance from one minimum to another must be of the order of inter-atomic distances in a solid, *i.e.* several units multiplied by 10^{-8} cm. The movement of the adsorbed atoms should consist of jumps of, say $3 \cdot 10^{-8}$ cm. distributed chaotically in all directions. Thus we can apply to our case the well-known formulæ of brownian movement and write

$$\frac{\delta}{t} = \frac{\Delta^2}{\tau_0} = 2D \quad . \quad . \quad . \quad (1)$$

where δ is an average displacement in a certain direction of an adsorbed atom during the time t, Δ is the elementary displacement, *i.e.* the distance between two minimums of potential energy, τ_0 the time corresponding to each replacement, and D the diffusion coefficient of two-dimensional gas. Let ω be the frequency of vibrations of adsorbed atoms, then the probable value of a displacement occurring during one second will be

$$\omega e^{-\frac{h}{RT}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where h is the "height" of the maximum in relation to the minimum. Then

$$\tau_0 = \frac{1}{\omega e^{-\frac{h}{RT}}} = \frac{1}{\omega} e^{\frac{h}{RT}} \quad . \quad . \quad . \quad . \quad (3)$$

from 1 and 3 we obtain :

$$h = RT \log \omega\tau_0 = RT \log \frac{\omega\Delta^2}{2D} \quad . \quad . \quad . \quad (4)$$

As the order of magnitude of ω and Δ is known we need only the diffusion coefficient in order to get a rough estimate of h.

We can obtain the value of D if we utilise some results of other authors. For example D can be calculated from Volmer and Adhikari's[1] experiments on the creeping of benzophenone, on a glass surface. We can write

$$G = Ds \frac{dn}{dt} t,$$

where G is the amount of transported benzophenone, s—the length of the line over which the molecules are creeping, $\frac{dn}{dt}$—the gradient of density of molecules on the surface, and t—the time of experiment. One of Volmer's experiments gives :

$$G = 22 \times 10^{-7} \text{ gr.},$$

$$s = 0{\cdot}05 \text{ cm.},$$

$$\frac{dn}{dt} = 5 \times 10^{-6} \frac{gr}{\text{cm.}^3},$$

$$t = 2{\cdot}5 \text{ hours.},$$

whence we get

$$D \cong 5 \times 10^{-4},$$

and

$$h = RT \log \frac{\omega\Delta^2}{2D} \cong RT$$

and

$$\tau_0 \cong \frac{1}{\omega}.$$

This is certainly too small a value,[15] because it gives for real velocity v of the molecule $\frac{\Delta}{\tau_0}$ a value bigger than the corresponding value obtained from the formula,

$$v = \sqrt{\frac{3RT}{\mu}}$$

which cannot take place. This strange result may depend on the fact that our calculations may not be applicable to such a large complex as a benzophenone-molecule, which probably covers at once many minima and maxima points of the surface, and might therefore have Δ corresponding to several inter-atomic distances.

Another estimate might be done on the basis of the experiment of Cilliers described in Stern's article on molecular rays in *Ergebnisse der exacten Naturwissenschaften, Vol. III.*[16] A deposit of antimony was obtained by means of a diaphragm having its width unequal along its length. The deposit was formed much more readily under wide parts of the diaphragm than under the narrow central part. It is stated that the intensity of the beam was constant over all the image. The difficulty of formation of the image in the narrow parts ($< 10^{-2}$ cm.) is explained on the assumption that in these parts the equilibrium is shifted because the adsorbed atoms may creep away from the exposed surface, while in the wide parts only the atoms on the very edge of the image will not be replaced by newcoming ones. As the equilibrium between three-dimensional and two-dimensional gas is reached in the time of the order τ, we must allow for the atoms of antimony to creep over 10^{-2} cm. during the time τ (if they should creep more slowly the equilibrium would not be appreciably shifted. Thus

$$\frac{10^{-4}}{\tau} = \frac{\Delta^2}{\tau_0}.$$

or

$$\tau_0 = \frac{\Delta^2}{10^{-4}}\tau \simeq \frac{10^{-15}}{10^{-4}}\tau = 10^{-11}\tau.$$

The absence of data for τ makes it impossible to get a numerical value for τ_0.

Another experiment of similar kind has been published by I. Estermann,[17] who worked with cadmium. In this case we might use the value of τ estimated by Clausing, *i.e.* $\tau \cong 10^{-6}$ sec. But here we come again to an absurd result, since τ_0 becomes 10^{-17} sec. (the dimensions of the deposit were of the same order as in the experiment of Cilliers, so that we can use the same formula). This again leads us to the assumption that the elementary displacement is not of the order of interatomic distances. Let the elementary displacement be λ, then the time corresponding to it will be $\frac{\lambda}{v}$, where v is the velocity of the adsorbed atom.

Then

$$\frac{10^{-4}}{\tau} = \frac{\lambda}{\left(\frac{\lambda}{v}\right)^2} = \lambda v,$$

or

$$\lambda = \frac{10^{-4}}{\tau \cdot v} \cong \frac{10^{-4}}{10^{-6}\sqrt{\frac{3RT}{\mu}}} \cong \frac{10^{-4}}{10^{-6}\sqrt{\frac{3 \times 8{\cdot}31 \times 10^7 \times 180}{112}}} \cong 5 \times 10^{-3}\,\text{cm}.$$

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[15] ω is of the order $\sim 10^{12} \sim 10^{13}$, let it be 3×10^{12}. Δ is of the order $3{\cdot}10^{-8}$.

[16] The original dissertation could not be obtained.

[17] *Z. Physik*, **33**, 320, 1925.

In this case (as well as in the case of benzophenone) λ should probably be treated in the light of Frenkel's[18] conception. Anyway, this high mobility is rather surprising; it might be due to the fact that in the experiments cited one never deals with a really clean surface. The impurities might make the surface energetically smooth. However this explanation does not seem to be entirely satisfactory.

The results of some experiments, as yet unpublished, suitable for calculation of τ_0 and h were kindly given to me from the laboratory of Electro-Vacuum Works "Swetlana" in Leningrad. The experiments dealt with creeping of thorium along the surface of tungsten. The velocity of creeping at temperatures about 2000° K. was estimated to be about 1 micron per minute. This corresponds to the value of h about 100,000 cal./mol. if the elementary displacements is put equal to 3×10^{-8} cm. The value of the same order was obtained for h from the measurements of the thermal coefficient of diffusion of thorium to the surface of a tungsten wire, and it has been shown previously that this diffusion takes place along the surfaces of the micro-crystals forming the wire. It is interesting to notice that in this case where the surface is probably really clean we obtain reasonable results with Δ equal to interatomic distance.

The experiments cited, which were carried out for quite a different purpose, cannot indeed be taken as the confirmation of the expressed point of view on the movement of adsorbed molecules. A special experimental investigation is indeed absolutely necessary. It seems to us, however, quite unquestionable that the periodic structure of the surface must produce effects of the type described.

Let us consider now the problem, what kind of collision plays the more important part in the building-up of equilibrium in a two-dimensional layer formed by adsorption. There are collisions between adsorbed molecules and molecules of three-dimensional gas and purely two-dimensional collisions. The number of molecules per cm.^{2} is $n = \nu\tau$. During one second the number of collisions of the first type will be $N_1 = \nu n\sigma = \nu^2\tau\sigma$, where σ is the area of the molecule. The number of two-dimensional collisions per second will be $N_2 = \frac{n^2\Delta d}{2\tau_0}$ (d being the diameter of the molecule) and the ratio

$$\frac{N_1}{N_2} = \frac{2\nu^2\tau\sigma\tau_0}{n^2\Delta d},$$

as however $d\Delta$ is (in the case of clean surface) of the order of σ and $n = v\tau$,

$$\frac{N_1}{N_2} \simeq \frac{\tau_0}{\tau}.$$

Thus in equilibrium the number of "two-dimensional" collisions is as many times greater than the number of "mixed" collisions as τ_0 is greater than τ. As τ is in most cases less than 1 second and the equilibrium is reached practically in the same time it is obvious that, unless the density of two-dimensional gas is very large (and therefore not proportional to ν), mixed collisions should not play any important rôle in the considered processes on the surface.

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[18] *Z. Physik*, **59**, 640, 1930.