Physics. — *Adsorption of iodine on calciumfluoride.* By J. H. DE BOER. (Communicated by Prof. G. HOLST.)

(Communicated at the meeting of February 25, 1928.)

In case of a heteropolar crystal-lattice one has to expect that the ions at the surface of a crystal exert an electrical field still outside the crystal. This field is at distances comparable with the dimensions of the ions, so strong that dipoles are attracted noticeably. Neutral atoms or molecules, not in possession of a dipolmoment, will be polarised by this field, as a consequence of which also these atoms or molecules are attracted perceptibly. In the following it will be shown that in fact thin layers of salt are able to bind neutral atoms, to the effect that *adsorption* of these atoms on the layer of salt takes place.

This phenomenon also plays an important part in different industrial applications.

Indeed, in the manufacturing of electrical lamps the blackening of the wall of the bulb by evaporated tungsten in vacuum lamps is usually counteracted for instance by introducing some salt or other into the bulb [1]). Sometimes a chemical reaction is used, e.g. in case of $K_3Tl\,Cl_6$. This substance is able to split off chlorine, by which the tungsten, precipitated as a consequence of evaporation of the filament, is bound. In other cases, however, the salt exerts only a physical action, as has been shown by L. HAMBURGER, G. HOLST, D. LELY and E. OOSTERHUIS [2]). This is especially so in case of various heteropolar inorganic salts, which crystallise in coordination-lattices. Examples of auch salts are (L. HAMBURGER and others, loc. cit.) NaCl and CaF_2. Originally these salts are brougth on the filaments and after that evaporated to the wall of the bulb. So, for example, on glowing the filaments at about 2000° C. in vacuum, CaF_2 evaporates and is deposited on the wall of the bulb in the form of a thin, invisible layer of salt with a very large surface.

On closer investigation of the causes of this physical action, the question arose : of what order of magnitude is the electrical field which is brought about by the ions at the surface of such a thin layer of salt. We intended to find out whether a neutral atom, which is present above such a layer at a distance, comparable with the dimensions of the atoms, can be polarised by this field to a marked degree.

Before entering into the experiments, carried out in order to answer the

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[1]) See for example: G. HOLST, Elektrische Lichtbronnen V. U. B. 1920.

[2]) Proc. Roy. Acad. Amsterdam **21**, 1078 (1919).

above-mentioned question, we shall try first of all to show by calculation that the forces, exerted by the ions at the surface of the salt, are indeed strong enough to cause such an effect.

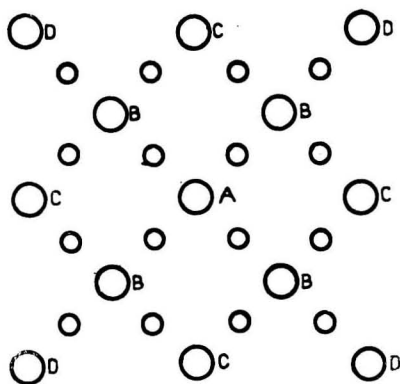On account of the fact that parallel to the cube-face of CaF_2 alternating layers of calcium- and fluorine-ions are present, one could expect that the surface of CaF_2 was built up out of either only positive, or only negative ions. The outermost ions, however, are drawn to the inside by the layers of ions lying under them, while, on the other hand, they themselves draw these layers a little into their own direction. Therefore, for the sake of simplicity, we shall in the following suppose that the surface of CaF_2 is built up out of both positive and negative ions, which ions form the twodimensional lattice represented in fig. 1; in this figure the larger circles represent the calcium-ions, the smaller ones the fluorine-ions.

Fig. 1.

Let us suppose that a polarisable atom is present above the calcium-ion A, at a distance $a \times r$; r is the distance of a calcium-ion from the nearest fluorine-ion. In this polarisable atom a dipole will be generated, as is indicated in fig. 2. The generated dipole, the moment of which is P, will
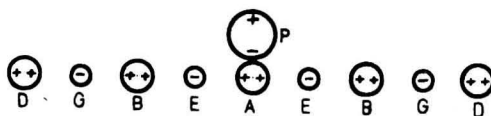

Fig. 2.

be attracted by the ion A. As a consequence of this process, an amount of energy, equal to

$$\frac{2\,e\,p}{a^2 r^2},$$

is gained. The dipole is also attracted by an ion B (fig. 2); there are four of them (fig. 1). The energy, gained pro ion, is:

$$\frac{2\,e\,p}{(PB)^2} \cos BPA =$$

$$= \frac{2\,e\,p}{r^2} \cdot \frac{a}{(a^2 + 2^2)^{3/2}}$$

Taking into account all the calcium-ions, the energy becomes:

$$\varphi_1 = \frac{2a\,e\,p}{r^2} \Sigma \{a^2 + (2n)^2 + (2m)^2\}^{-3/2} = S_1 \frac{e\,p}{r^2}.$$

In this formula, n and m represent arbitrary integral numbers, both positive and negative, including zero. The fluorine-ions act in the opposite direction; for their action a similar sum can be written down. Thus the total energy of the dipole is obtained as the difference of two series of terms; this difference converges rather rapidly.

In figure 3 the numbers $S = S_1 - S_2$ (S is the factor by which $\frac{e\,p}{r^2}$ must be multiplied in order to obtain the total energy) are given as a function of the distance, between the polarisable atom and the layer of ions [1]).
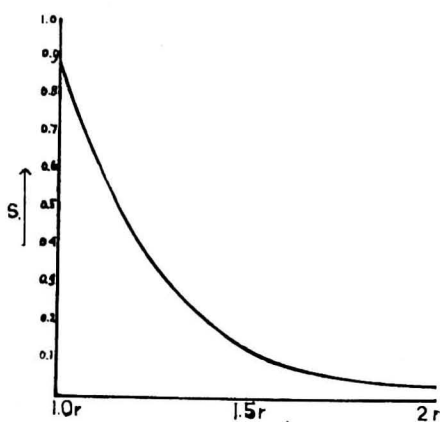

Fig. 3.

As can be seen in the figure, this sum S diminishes rapidly with increasing distance the atom.

Apart from this energy of attraction between the generated dipole and the field of the ions, we have to consider the energy, necessary for the generation of the dipole. This energy amounts to

$$\frac{p^2}{2\,a},$$

where a represents the polarisability of the atom. The total amount of energy (gained energy will be counted as negative) becomes therefore:

$$\varphi = - S\frac{e\,p}{r^2} + \frac{p^2}{2\,a} \quad \text{[2])}$$

A condition for the equilibrium, is:

$$\frac{\partial \varphi}{\partial p} = 0$$

therefore:

$$p = a\,\frac{Se}{r^2}$$

by which the expression for the energy changes to:

$$\varphi = - S^2 \cdot \frac{e^2\,a}{2\,.\,r^4}.$$

With iodine as the polarisable atom, and CaF_2 as the salt (compare the experiments, discussed below), we can determine the order of magnitude

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[1]) We intend to recur to this calculation, and also to the following considerations and calculations, more in detail elsewhere.

[2]) We do not take into consideration BORN's repulsion forces.

of φ. For the polarisability of the iodine-atom we assume the value to be 5.10^{-24} [1]) ; the distance r is in this case $1.93 . 10^{-8}$ cm. According to V. M. GOLDSCHMIDT [2]) the radius of the calcium-ion is equal to $1.06 . 10^{-8}$ cm, and that of the iodine-atom $1.35 . 10^{-8}$ cm. It follows from these figures that the distance from Ca++ to I equal to $1.25\ r$. As fig. 3 shows, in this case $S = 0.36$. Thus for the energy with which an iodine-atom is attracted, we obtain the value :

$$\varphi = - (0,36)^2 . \frac{(4,77)^2 \times 5}{2 \times (1,93)^4} . 10^{-12} \text{ erg.}$$

Per grammatom this becomes 7600 cal., a rather large energy. The dipole-moment, which, according to this view, would be generated in the iodine, amounts to

$$p = 2,3 . 10^{-18} \text{ e.s.e.,}$$

that is of the same order of magnitude as the dipole-moment of water [3]).

Thus, if vapour of iodine (or other gases or vapours which are polarisable) are present above a surface of such a salt, atoms (or molecules) of iodine will be bound at the surface ; this means, vapour of iodine will be *adsorbed* to the thin layer of salt [4]).

The formation of a mono-molecular adsorbed layer can thus be explained with the add of the foregoing considerations. The question arises now whether only one layer can be bound by adsorption. Another iodine-atom, on the top of the first one, is not subjected to any noticeable attraction from the underlying field of the ions, on account of its large distance. This is clear from figure 3. The dipole of the first iodine-atom however, will generate a dipole also in this second iodine-atom, and this latter dipole in its turn will act upon the first one. Thereupon a third, a fourth, and so on, iodine-atom can be bound as a consequence of polarisation. The adsorption of more than one layer thickness will thus be represented by fig. 4 or fig. 5, which figures do not need a further explanation.

On account of the fact that both the iodine-atoms in the first layer and the atoms in the next layers exert influence on the binding of the first layer, the energy deduced higher-up is too large. If, in fig. 4, we take into

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[1]) The polarisability of the gaseous, non-deformed iodine-ion is equal to $7.5 . 10^{-24}$: see K. FAJANS and G. JOOS, Zts. f. Physik **23**, 1 (1924).

[2]) V. M. GOLDSCHMIDT, Ber. d. d. chem. Ges **60**, 1263 (1927).

[3]) The dipole-moment of water is equal to about $2 . 10^{-18}$ e. s. u.

[4]) In the meantime also O. BLÜH and N. STARK, Zts. f. Phys. **43**, 575 (1927) and also E. HÜCKEL, Adsorption und Kapillar-Kondensation, Leipzig, Ak. Verlagsges. 1928, have given similar explanations for the forces, which play a part in the adsorption. The first-mentioned authors arrive at the same conclusion as we do, viz. that the adsorption needs not to be limited to a mono-atomic layer. We have waited to publish our point of view till the experiments gave a sufficient confirmation.

account only the atoms of the first layer, then the energy per grammatom is already less, because all the dipoles of the first layer repel each other thus we a obtain an energy of 3450 cal. per grammatom. In case we include in the reckoning also the reaction of the following layers on the first one.
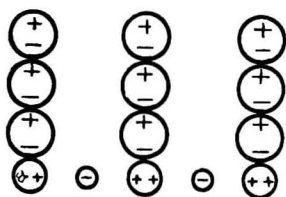

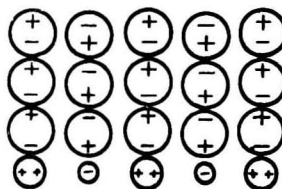Fig. 4.   Fig. 5.

we obtain something like 3750 cal. These calculations ought to be considered as approximations, giving only an idea of the order of magnitude, because, for example, we do not know what is the distance of the first layer of iodine-atoms to the second layer.

In the case of fig. 4 as well as in that of fig. 5, it can be calculated that the magnitude of the dipole in successive layers diminishes regularly, according to the following formula [1]):

$$p_n = K^{n-1} \cdot p_1$$

if p_n represents the dipole of an atom in the nth layer, p_1 that of an atom in the first layer; K is a constant, which depends on the distance of the iodine-atoms, their polarisability and contains constants of summation.

The energy of binding between successive layers also diminishes regularly :

$$\varphi_n = (K^2)^{n-1} \varphi_1.$$

In such an adsorbed system the energy of the attractions and repulsions between the dipoles will increase the heat of evaporation ; in fact, the nth layer, which is in equilibrium with the vapour above the adsorbed system, is bound by an energy, equal to :

$$\varphi_{\text{evap.}} + \varphi_n.$$

With regard to this layer, the relation must hold :

$$ln \, \pi = \frac{-(\varphi_{\text{evap}} + \varphi_n)}{RT} + B$$

if π represents the pressure of the iodine-vapour in equilibrium with the adsorbed system. In case π approaches the pressure of saturation π_0 at the temperature under consideration, n will increase ; if $\pi = \pi_0$, n will

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[1]) The following calculations will be published elsewhere more in detail, in collaboration with Dr. C. ZWIKKER.

become infinite. In this case φ_n is equal to zero, so that the ordinary equation for the vapour-pressure:

$$ln\,\pi_0 = \frac{-\varphi_{evap.}}{RT} + B$$

will hold. If the two equations are subtracted from each other, we obtain:

$$ln\,\frac{\pi}{\pi_0} = \frac{-\varphi_n}{RT}.$$

Substitution of the expression for φ_n gives:

$$ln\,\frac{\pi}{\pi_0} = \frac{-(K^2)^{n-1}\varphi_1}{RT} = C \cdot K_1^{n-1}$$

In this equation C and K_1 are two constants, if the temperature of the adsorbed system remains constant. Thus this equation represents an *adsorption-isotherm* for the adsorption in a layer of more than one molecule thickness.

We are going to describe now some experiments, which are in accordance with the above-given considerations. In the apparatus, represented in fig. 6, calciumfluoride is present on the wall of the glassbulb opposite to the filament. This CaF_2 has been obtained by evaporation from the filament. There is solid iodine at B. We choose iodine, in the first place because it can easily be obtained in state of vapour, and further because it would be easily polarisable (higher-up we assumed for the polarisability the value 5.10^{-24}). Besides it is coloured, and it can be determined quantitatively without difficulty. If now the iodine at B is cooled by means of liquid air, there is practically no vapour of iodine in the apparatus and no perceptible adsorption (the layer of calciumfluoride is invisible). If then the temperature at B is raised to for example $0°$, the pressure of the vapour of iodine corresponds to that of $0°$, that is 0.027 mm. As a consequence of this iodine is deposited at A and there it appears as a brown, transparent layer. Keeping A at room-temperature and raising the temperature of B will make grow the layer thicker, until, if B too is brought to room-temperature,

Fig. 6.

distillation of iodine takes place (this process is influenced by small fluctuations in the temperature). In this case small *crystals* of iodine are formed on the wall of the glass-bulb, also on spots where there is no calciumfluoride.
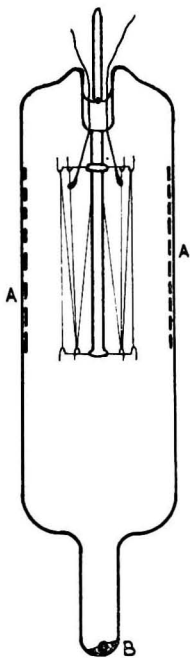
Thus we can regulate the pressure of the vapour of iodine π by keeping

B at different temperatures. If now the quantity of iodine on the CaF_2 is determined analytically, we are able to study the relation between this quantity and the pressure π [1]).

In this way we have determined several adsorption-isotherms, corresponding to different quantities of CaF_2 on the wall of the glass-bulb. The surface of the CaF_2-layer is often much larger than the area of the glass, covered by it. Therefore it is impossible to determine the thickness of the layer from the quantity of iodine ; but in every case the following relation between the quantity of iodine *m* and the pressure π must hold :

$$ln\,\frac{\pi}{\pi_0} = C\,.\,K_2^m,$$

K_2 still depends on the surface (quantity of CaF_2) ; for one and the same surface, however, it is a constant. Fig. 7 shows an example of such an adsorption-isotherm ; it relates to the adsorption on a glass-surface of
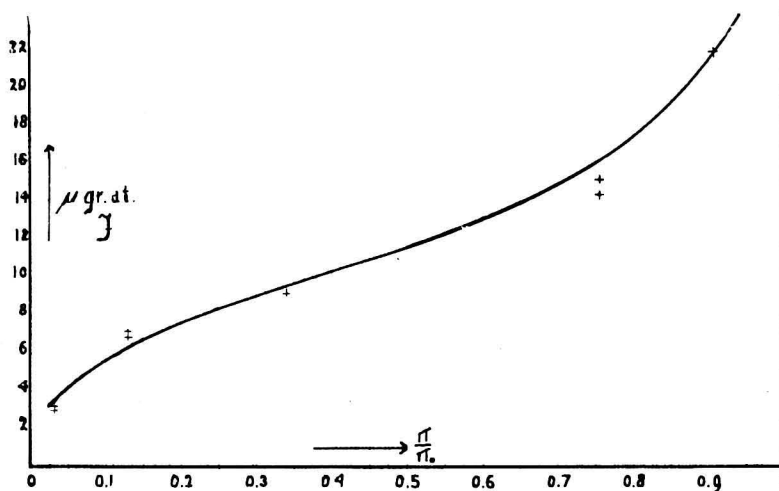

Fig. 7.

about 75 cm². , which was covered with about 7.5 mgr. of CaF_2 [2]).

In fig. 8 the quantity of iodine *m* is shown as a function of $log\left(-log\,\dfrac{\pi}{\pi_0}\right)$. The corresponding points must lie on a straight line. The line, drawn in the figure, has been determined by means of the theory of least squares ; before, in view of possible sources of error, different weights had been given to the various points. The line can be represented by :

$$log\left(-log\,\frac{\pi}{\pi_0}\right) = -0,086\,m + 0,495.$$

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[1]) To the measurements and the other results deduced from them we will recur elsewhere.

[2]) On account of the fact that each point has been determined with the aid of another glass-bulb (the bulbs were as much as possible alike) and also as a consequence of other sources of error, there is always a possibility for deviations in the situation of the points.

On account of the fact that

$$0,495 = log \frac{\varphi_1}{4.57\,T}$$

and because $T = 293°$, it follows from this that

$$\varphi_1 = 4150 \text{ cal.}$$

This figure is of the same order of magnitude as that which was calculated with aid of the considerations given above.
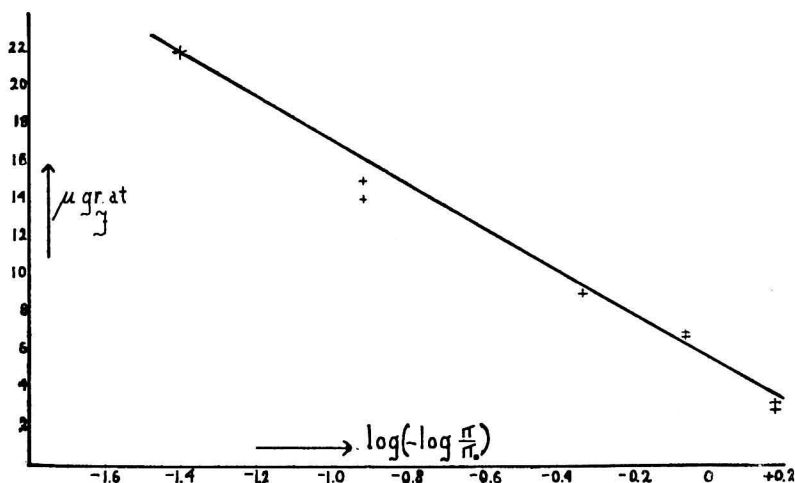

Fig. 8.

In case other quantities of CaF_2 are used, the magnitude of the constant K_2 is different; it appears, however, that the constant C always keeps the same value, exactly as one would expect according to our view.

Our measurements cannot be represented by an adsorption-isotherm of the usual form. A characteristic feature is the rise of the curve, if $\frac{\pi}{\pi_0}$ approaches the value 1. Such a rise in the vicinity of the pressure of saturation has already been observed many times; in such cases, however, this has been ascribed to other phenomena [1]).

As already mentioned above, the colour of the adsorbed layer of iodine is brown. In case iodine become polarised to a high degree, we must expect that the absorption-band of the iodine will be shifted in the direction of shorter wave-lengths, as a consequence of which the colour of the iodine changes to brown. We have measured the absorption-spectrum of the brown layer [2]), and we have found that the absorption starts at about

[1]) E. HÜCKEL, in his already mentioned book, ascribes a similar rise to condensation in capillar spaces, We hope to prove later that this explanation cannot be applied to the present case.

[2]) We like to express also in this place our sincere thanks to Drs. A. VAN WIJK for his help with the measuring of the absorptionspectrum.

6000 ÅU. It increases at shorter wave-lengths, shows a maximum at about 2950 ÅU and then decreases rather rapidly. According to the measurements of L. S. ORNSTEIN and H. C. BURGER [1]) the maxima of the absorption for violet solutions of iodine (in carbonsulfide and in chloroform) lie at about 5100 ÅU; in alcoholic solutions the maximum lies at about 4300 ÅU. The maximum of absorption in solutions of iodine in potassium-iodide, according to CH. WINTHER [2]), at about 3500 AU. From these measurements we see that with increasing polarisation of iodine, the absorption-band seems to shift to shorter wavelengths. On account of this we can assume that the polarisation of iodine in the adsorbed layer is larger than in solutions of KI_3. Indeed, also in KI_3 one can imagine the binding of the iodine as a consequence of polarisation [3]).

I have pleasure in thanking Mr. J. BROOS for his valuable help with the experiments.

Eindhoven, 22 February 1928.

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[1]) Verslag Kon. Akad. Wet. Amsterdam, **29**, (1920) 573.

[2]) Z. Phys. Chem. **108** (1924) 236.

[3]) See Dr. A. E. v. ARKEL. and J. H. DE BOER, Rec. d. trav. chim. d. Pays Bas, **47** (1928) 593.