

**Chemistry.** — *The formation of two-dimensional nuclei by ionic molecules.*  
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(Communicated at the meeting of November 30, 1946.)

§ 1. The growth of ionic crystals from solutions has been a subject of many investigations, both from the experimental and from the theoretical angle<sup>1)</sup>. The importance of the differences of the potential energies of addition of ions to different positions on the various crystallographic planes has been very clearly pointed out by all authors. The addition of ions to edges or corners is favoured energetically, mainly because the electrostatic contributions to the total amount of the addition energies are, in these cases, far more important than the contributions by the VAN DER WAALS' forces. In practically all these cases more attention was given to the differences in rate of growth of crystallographic planes of already existing nuclei, or of small crystals which had already been formed beforehand, than to the formation of the nuclei themselves.

The present study deals with the formation of nuclei and of very small — sub-microscopical — crystals from the vapour phase. There are, therefore, some very important differences with respect to the investigations mentioned above. Firstly the formation of the nuclei and their growth do not occur from the ionic, but from the molecular state. Secondly neither the constituents nor the surfaces of the forming crystals are contaminated with molecules of a solvent. It simplifies the problem considerably, from an experimental as well as from a theoretical point of view, that solvation-energies need not be taken into account.

§ 2. When a salt like NaCl is evaporated in vacuo under such conditions that no collisions of salt molecules take place before the molecules reach the wall of the vessel, the question arises which structures will result from the agglomeration of these molecules on the wall and how the nuclei will develop when more molecules impinge upon them.

We will take NaCl as an example for our theoretical considerations, but it will be clear that, apart from the numerical values, the results which we obtain will hold good for similar compounds, as e.g. all alkali- and alkaline earth halides.

We may consider a molecule of NaCl as an ionic molecule<sup>2)</sup>. The

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<sup>1)</sup> For a survey of the work of ARTEMJEFF, VALETON, KOSSEL, STRANSKI, SCHNORR, NEUHAUS and others, see A. E. VAN ARKEL and J. H. DE BOER, *Chemische Binding*, 1930, or the reviewed French translation: "La Valence et l'Electrostatique", Paris, Félix Alcan, 1936, pages 284—297.

<sup>2)</sup> E. J. W. VERWEY and J. H. DE BOER, *Rec. Trav. Chim.*, **59**, 633 (1940).

distance between  $\text{Na}^+$  and  $\text{Cl}^-$  in the molecule is  $2.51 \times 10^{-8}$  cm at  $1200^\circ \text{K}$  <sup>3)</sup> and  $2.47 \times 10^{-8}$  cm at  $0^\circ \text{K}$  <sup>2)</sup>). In solid  $\text{NaCl}$  the distance between two neighbouring ions is greater, viz.  $2.814 \times 10^{-8}$  cm at room temperature ( $2.795 \times 10^{-8}$  cm at  $0^\circ \text{K}$ ). In the following considerations we are dealing with agglomerates of 2, 3 or 4 molecules; the interionic distances will, therefore, have values between those in the molecules and those in the crystal. For the sake of convenience we will insert in our calculations only one invariable value, viz:  $d = 2.5 \times 10^{-8}$  cm for the distance between two neighbouring ions in the single molecules as well as in the agglomerates.

In all calculations the electrostatic part of the energy has been calculated by straightforward summation of all attractive and repulsive parts. As it has been proved previously <sup>2)</sup> that the short range repulsion resulting from the interpenetration of the reciprocal electronic clouds may best be expressed by the term  $\frac{b}{d^n}$ , where  $n = 12$ , the electrostatic energy has been corrected for this repulsion just by subtracting  $1/12$  part from the value obtained by summation.

The contributions to the potential energy resulting from the VAN DER WAALS' attraction forces have been evaluated from the dipole-dipole parts of these forces only, thus using only the terms  $\frac{c}{d^6}$ . The other contributing terms have been neglected, because they are practically counter-balanced by the part resulting from the repulsive forces <sup>4)</sup>. Zero-vibration energy, polarisation energy and dipole interaction have also been neglected because, although they may have some influence on the numerical values, their contributions do not alter the importance of the qualitative results which are obtained from the following considerations; they would moreover only give contributions in such a way as to assist us to make the deductions. The following figures <sup>5)</sup> have been used in the evaluation of the VAN DER WAALS' forces:

$$\begin{aligned} C_{++} &= 1.68 \times 10^{-60} \text{ erg} \times \text{cm}^6 \text{ (action of } \text{Na}^+ \text{ on another } \text{Na}^+), \\ C_{+-} &= 11.2 \times 10^{-60} \text{ erg} \times \text{cm}^6 \text{ (action of a } \text{Na}^+ \text{ on a } \text{Cl}^-) \text{ and} \\ C_{--} &= 116 \times 10^{-60} \text{ erg} \times \text{cm}^6 \text{ (action of a } \text{Cl}^- \text{ on another } \text{Cl}^-). \end{aligned}$$

§ 3. When two molecules of  $\text{NaCl}$  (combination *A* in fig. 1) form an agglomerate the VAN DER WAALS' forces would tend to form a regular tetrahedron *B*. The energy of addition of the two molecules, however, would be small as in this configuration the electrostatic terms are just in balance. The VAN DER WAALS' forces lead to an energy of combination of

<sup>3)</sup> L. R. MAXWELL, S. B. HENDRICKS and V. M. MOSLEY, *Phys. Rev.*, **52**, 968 (1937).

<sup>4)</sup> J. H. DE BOER, *Trans. Far. Soc.*, **32**, 10 (1936).

<sup>5)</sup> J. E. MAYER, *J. Chem. Physics*, **1**, 270 (1933).

about  $-0.6 \times 10^{-12}$  erg per double-molecule. Configuration *C* is favoured by the electrostatic forces and the total contribution of these and of the VAN DER WAALS' forces leads to an energy of combination of  $-5.0 \times 10^{-12}$

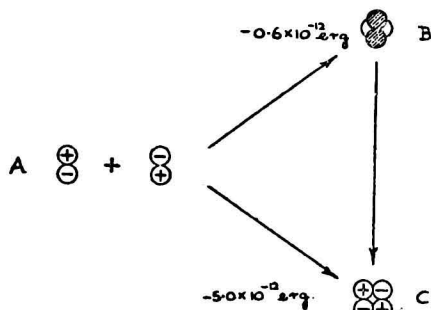


Fig. 1. Formation of a double-molecule from two single molecules.

erg per double molecule. *C* is by far the most stable combination, *B* is unstable and would always convert into *C*. It may be remarked that in a combination like *C* the individual character of the original molecules has already disappeared.

When a third molecule is added to this structure (fig. 2) a similar consideration leads to the conclusion that configuration *B* is unstable and is easily converted into *C*, which in turn is also unstable and passes into structure *D*, which is the only stable one. The resulting configuration, therefore, is a two-dimensional one in which all constituent ions are situated in the same plane.

§ 4. The addition of a fourth molecule to the stable configuration of *D* in fig. 2 represents a far more interesting case. In fig. 3 the relation between

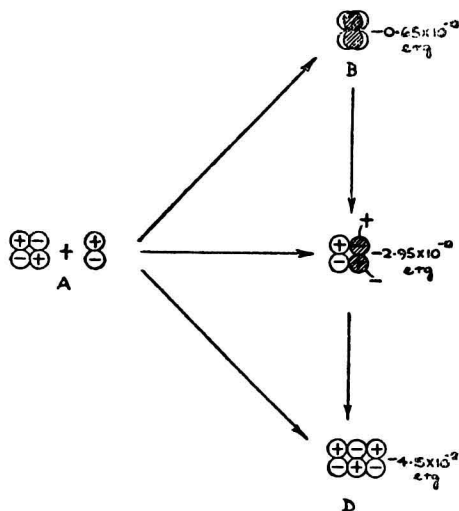


Fig. 2. Addition of a third molecule to the stable configuration of a double-molecule. (In all figures shaded circles mean ions situated on top of the first layer.)

all possible configurations which may form with a decrease of potential energy is given. The energy figures represent the energy of addition of the fourth molecule to the existing combination of three.

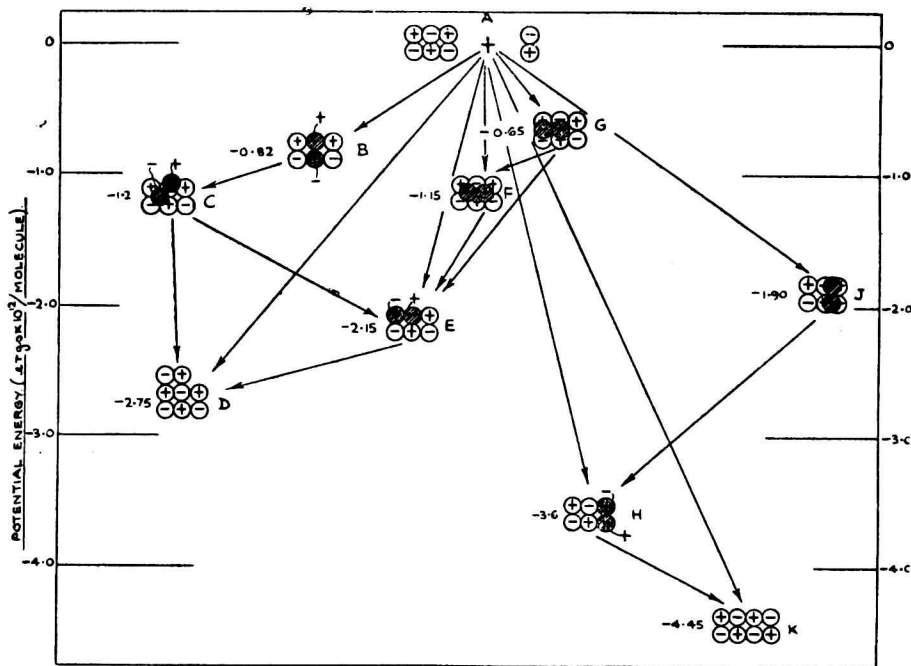


Fig. 3. Addition of a fourth molecule to the stable configuration of three.

Configuration *B* is quite stable with respect to sideward movements of the fourth molecule which is situated on top of the middle one of the three original ones. The orientation of this fourth molecule is such that its negative ion is on top of the positive ion of the underlying one and its positive ion on top of the negative ion of the lower molecule. This configuration, therefore, cannot be converted into *J*, where the orientation of the fourth molecule is just reversed.

Although configuration *B* is unstable with respect to configuration *D*, it would not be easy to convert *B* into *D* if there were no VAN DER WAALS' forces present. If only electrostatic forces were acting a considerable amount of activation energy would be necessary for this conversion. By the action of the VAN DER WAALS' forces, however, the negative ion of the fourth (top) molecule is easily shifted to a position on four direct neighbours, two of which are also negative ions. The electrostatic energy of this ion with respect to the whole underlying structure is zero; the VAN DER WAALS' energy, however, is large. The positive ion of the top molecule has to be pushed up a little, which results in a decrease of the electrostatic energy, which however is still negative.

A direct shift from *B* into *F* is not excluded, but both *C* and *F* are unstable and are ultimately converted into *D*.

The relation between  $J$ ,  $H$  and  $K$  is similar to the relation of the configurations of fig. 2.

From all the configurations mentioned in fig 3, therefore, all but two are unstable and converted into others. Only configurations  $D$  and  $K$  are not converted into others. Both  $D$  and  $K$  are characterised by the fact that all constituent ions are situated in one single plane. These nuclei are again two-dimensional nuclei.

§ 5.  $D$  and  $K$ , however, are not the most stable configurations. The stable configuration to be formed from four of these ionic molecules (eight ions) is the regular cube. Starting from configuration  $K$  a cube could be formed by moving the end-molecules of the row of four round until they meet on top of the middle two, as is indicated in fig. 4. This figure gives the change in the electrostatic part of the potential energy when both end-

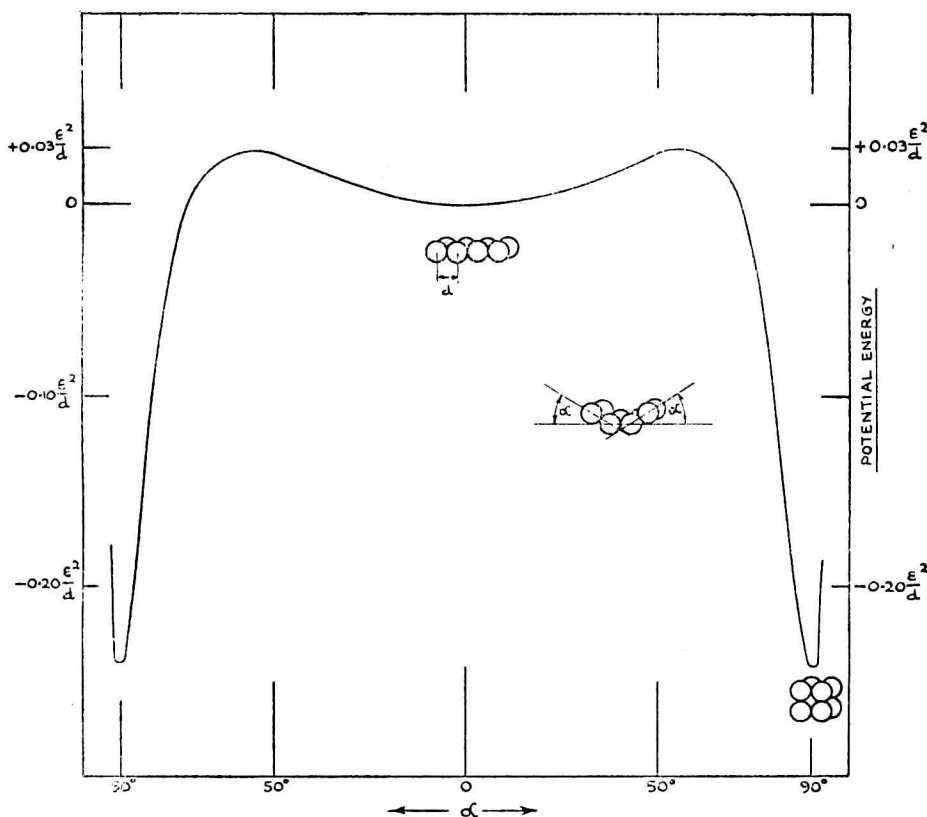


Fig. 4. Energetical relation between the flat configuration of 4 molecules and the cubical one; potential energy as a function of the angle  $\alpha$ .

molecules are turned simultaneously over an angle  $\alpha$  as is indicated in the figure. Obviously configuration  $K$  is not an unstable one, but only meta stable with respect to the cubical configuration ( $\alpha = 90^\circ$ ). An activation

energy of  $0.03 \frac{\epsilon^2}{d}$  is required to transform configuration  $K$  into the cubical one. In our example of NaCl, with  $d = 2.5 \times 10^{-8}$  cm this means  $0.275 \times 10^{-12}$  erg, a value nearly seven times the value of  $kT$  at room temperature, viz.  $1.38 \times 10^{-16} \times 290 = 0.04 \times 10^{-12}$  erg. It will be easily seen that if the two end-molecules are not turned simultaneously the activation energy will be higher still. It will also be obvious that the VAN DER WAALS' contribution to the potential energy will not alter the result appreciably. Consequently the result of these considerations is that configuration  $K$ , though not the most stable form of this agglomerate of four molecules, does not easily transform into the stable cubical configuration. It may be remarked that the reciprocal relation of these two configurations has some resemblance to steric isomers in organic chemistry.

The transformation of  $D$  into  $K$  or into the cubical form is also not possible without passing an energy maximum of activation energy. The ultimate result of all these considerations is, therefore, that the addition of a fourth molecule to the combination of three also leads to a configuration with all molecules in the same plane. In other words the two-dimensional nucleus grows only two-dimensionally.

§ 6. Similar results will be obtained with the continuation of this process, hence in the further addition of molecules there is a strong tendency of the nucleus to grow in two dimensions only. Molecules which impinge upon the two-dimensional plane will migrate over this plane until they reach the edge, whereupon they will turn over the edge and contribute to the growth of the two-dimensional structure. It may, however, be expected that at higher temperatures these two-dimensional structures will transform into more stable three-dimensional cubical sub-microscopic crystals.

§ 7. In all our considerations so far we have dealt with ionic molecules and it is largely due to the electrostatic repulsion forces that the formation of two-dimensional structures will be favoured. When the vapour molecules do not consist of ions but of atoms bound together by homopolar forces we will get another picture. Even in the case of metallic oxides, which in the solid state may give ionic crystals but the molecules of which in the gaseous state are to be considered as atomic molecules (with a small dipole), we may expect a different behaviour. In these cases, the VAN DER WAALS' forces will largely govern the formation of the nuclei and consequently compact structures will result.

§ 8. The results obtained above give an excellent explanation of the experimental facts. Extensive studies of adsorption phenomena of different substances on salt films, obtained by sublimation in a high vacuum, revealed that these salt layers have a lamellar structure and consequently a highly

developed surface <sup>6)</sup>. The crystalline lamellae have an average thickness of only a few molecules. These results were completely confirmed by electron diffraction measurements on films of  $\text{CaF}_2$  obtained by sublimation in a high vacuum. The molecules form flat plates perpendicular to the vapour beam and parallel to the under layer <sup>7)</sup>.

This behaviour is shown by all alkali-halides and alkaline earth halides, as well as by several other fluorides, such as lead fluoride, or by complex fluorides such as potassium zirconium fluoride ( $\text{K}_2\text{ZrF}_6$ ). In all these cases lamellar structures are obtained when the salts are deposited on a cool wall (room temperature) by sublimation in a high vacuum.

When, however, substances such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  or several other oxides, or salts like the silver halides are sublimated in a similar way, only compact layers are obtained which show no signs of formation of two-dimensional lamellae and show no capacity to adsorb substances by VAN DER WAALS' forces <sup>8)</sup>. It is known that these latter substances, though they may form ionic crystals in the solid state ( $\text{AgCl}$ ) are nevertheless to be considered as atomic-molecules in the gaseous state.

Obviously the experimental results are in harmony with the theoretical considerations, as described above, and it may be assumed that by sublimation in a high vacuum those substances which have ionic molecules in the gaseous state form two-dimensional deposits with a highly developed lamellar surface structure, showing a well-developed capacity for adsorption by VAN DER WAALS' forces. Substances with atomic molecules in the gaseous state, however, under similar conditions form compact layers, on which only electrostatic adsorption on active spots will be possible.

§ 9. One of the experimental conditions for the formation of these films is a high vacuum, such that no collisions take place before the molecules reach the wall. If the sublimation takes place in a diluted inert atmosphere, agglomeration takes place in the gas phase and a loosely built layer is formed <sup>8)</sup>.

When the lamellar structure is heated a sintering takes place. In this sintering process the lamellae are only bound together by VAN DER WAALS' forces. Adsorption by suitable substances, such as caesium, gives a separation of these layers again, restoring the original surface structure. This process is comparable with the swelling of other lamellar structures such as the swelling of graphite <sup>9)</sup>. It is only at still higher temperatures (depending on

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<sup>6)</sup> J. H. DE BOER, *Z. physikal. Chem.*, B **13**, 134 (1931); B **14**, 149 (1931); J. H. DE BOER and C. J. DIPPEL, *Z. physikal. Chem.*, B **21**, 198 (1933); C. J. DIPPEL and J. H. DE BOER, *Rec. Trav. Chim.*, **57**, 277 (1938); See also J. H. DE BOER, "Electron Emission and Adsorption Phenomena", Cambridge 1935, p. 184 et seq.

<sup>7)</sup> W. G. BURGERS and C. J. DIPPEL, *Phys'ca*, **1**, 549 (1934).

<sup>8)</sup> J. H. DE BOER and J. F. H. CUSTERS, *Physica*, **4**, 1017 (1937).

<sup>9)</sup> C. J. DIPPEL and J. H. DE BOER, *Rec. Trav. Chim.*, **57**, 277 (1938).

the salt) and when favoured by the presence of water vapour that a real recrystallisation to minute cubical crystals sets in. In this latter process the films lose their transparency and become opaque.

§ 10. It may be remarked that several metals also tend to form films of a character similar to that described above as being characteristic of substances with ionic molecules <sup>10)</sup>. The well-known experiment of VOLMER and ESTERMANN <sup>11)</sup> with mercury may be mentioned here. These authors found that mercury atoms migrated over the surface of the hexagonal basic plane and contributed to the two-dimensional development of these planes, giving rise to the formation of a lamellar structure.

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13th November 1946.

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<sup>10)</sup> Cf. e.g. V. VAND, Proc. Phys. Soc., **55**, 222 (1943); O. E. BEECK, A. E. SMITH and A. WHEELER, Proc. Roy. Soc., **A 177**, 62 (1940); D. D. ELEY, Nature, **158**, 449 (1946).

<sup>11)</sup> M. VOLMER and I. ESTERMANN, Z. Physik., **7**, 13 (1921).