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$$D = \frac{2,5}{z'-1} (d'-d) + d.$$

As the specific gravity of the solution must be determined for the viscosity measurements, it is easy to deduce the specific gravity of the particles. We find for molybdenum blue 1,83 to 1,93; for iron hydroxide 1,66 to 1,8. In this manner too, it becomes clear, that the particles suspended in the liquid cannot consist only of dissolved substance, the density of which is 3 or 4, but must also contain water. As has already been pointed out, the qualitative value of these conclusions is not attacked, if it should appear, that instead of  $2,5 \frac{v'}{v}$ , for instance,  $3 \frac{v'}{v}$  must be written. Neither would this be the case, when we introduce into EINSTEIN'S formula the second power of  $\frac{v'}{v}$ , as is necessary for the more concentrated solutions.

I hope to discuss later from the standpoint taken in this paper, the viscosity measurements previously published by other observers. A preliminary investigation already led to remarkable results, but a great part of what is known, cannot serve my purpose; I propose to fill up this lacuna by new determinations, and to discuss then at length the many questions, which arise in this field.

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**Physics.** — “*Some Remarks on the Capillarity Theory of the Crystalline Form*”. By Prof. P. EHRENFEST. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 29, 1915).

§ 1. As is known, W. GIBBS<sup>1)</sup> and P. CURIE<sup>2)</sup> have set forth the following view, and given further thermodynamic grounds for it. A crystal in a solution is in thermodynamic equilibrium only when it has that shape in which its surface energy has a smaller value than for any other shape with the same content. That this equilibrium

<sup>1)</sup> W. GIBBS: *Thermodyn. Studien* p. 320.

<sup>2)</sup> P. CURIE: *Bull. de la Soc. Min de France* 8 (1885) p. 145 of *Oeuvres* p. 153. Cf. for the relations between the theories of GIBBS and CURIE:

J. J. P. VALETON. *Kristalvorm en oplosbaarheid*. Proefschr. Amsterdam 1915. *Ber. d. Sächs. Ges. d. Wiss.* 67, (1915).

shape is not the sphere (i.e. the form with the smallest surface) but a polyhedron, is according to GIBBS and CURIE owing to the following circumstance. The surface energy of a surface element depends in a crystalline substance on the orientation of the surface element with respect to the crystalline substance, i.e. on the indices of the surface elements, and this in different ways for different substances.

If  $k_1, k_2, k_3, \dots$  are the capillarity constants of the differently orientated bounding planes;  $S_1, S_2, S_3, \dots$  the corresponding areas of the surfaces,  $V$  the volume of the crystal, then the equilibrium form is characterised by the condition:

$$\sum k_h S_h = \text{min. for } V = \text{const.} \dots \dots (1)$$

G. WULFF<sup>1)</sup> has derived a remarkably elegant geometrical property of the equilibrium diagrams from (1), which greatly facilitates the following expositions: In a figure characterised by the minimum condition (1) there always exists a point  $W$  (we will call this WULFF's point) lying so that the distances  $n_1, n_2, \dots$  of the different surfaces  $S_1, S_2, \dots$  from  $W$  are directly proportional to the constants  $k_1, k_2, \dots$

$$n_1 : n_2 : n_3 : \dots = k_1 : k_2 : k_3 : \dots \dots \dots (2)$$

This theorem of WULFF's immediately furnishes a construction of the equilibrium figure, if for every direction of the normal the corresponding value of  $k$  has been given. Draw from an arbitrary point  $W$  of the space in all directions lines whose lengths are proportional to the corresponding  $k$ 's and apply planes normal to them through their endpoints: then there remains a space in the neighbourhood of  $W$ , where none of these planes enters — this space is the required crystalline form. It is seen here at once that surfaces with a comparatively large value of  $k$  lie so far from  $W$ , that they cannot constitute a part of the boundaries of the crystal<sup>2)</sup>.

We derive the "law of the (small) rational indices" therefore in this theory in consequence of this that the surfaces with *small* index values in general must also possess particularly *small* capillarity constants  $k$ .

<sup>1)</sup> G. WULFF: Zschr. f. Krystallogr. **34** (1901) p. 449. The proof, which WULFF had given in an imperfect form, has been improved by HILTON afterwards:

H HILTON Centralbl. f. Miner. 1901 p. 753 = Mathem. Crystallogi. (Oxford 1903) p. 106. Cf. H. LIEBMANN. z. f. Kryst. **53** (1914) p. 171.

<sup>2)</sup> Let in the regular system e.g. the  $k$ 's of cube planes be  $k_1$ , those of the octahedron planes  $k_2$ . It is required for the octahedron planes to occur by the side of those of the cube that:

$$\frac{1}{\sqrt{3}} < \frac{k_1}{k_2} < \sqrt{3}.$$

See: CURIE loc. cit. and WULFF loc. cit.

As is known, this theory of GIBBS and CURIE's plays a very important part in the crystallographical literature. Frequent crystallographical applications have been made of it<sup>1)</sup>; it has been now and then extended by the introduction of "side energies" and "angular point energies" by the side of "surface energies"  $k_1, k_2 \dots$ , and by making the former have a share in the determination of the equilibrium figure<sup>2)</sup>; of late years criticism has not been wanting either, which now and then even comes to a full rejection of GIBBS and CURIE's view.<sup>3)</sup>

On the other hand it seems that except SOHNKE's indications<sup>4)</sup>, which concur with BRAVAIS' views, no attempts have been made as yet to interpret the energetic theory of GIBBS and CURIE in a *molecular scheme*. Such an attempt would be the more desirable as there is in this region a whole series of dark or paradoxical points to be analysed.

In view of the great difficulties which are to be overcome here, I should like to confine myself to a single of these points, and demonstrate how this can entirely be elucidated by the aid of an extreme simplified molecular scheme. It is seen the more clearly on this occasion how much there remains to be done to elucidate other points.

§ 2. *Does the capillarity constant of a crystal plane depend continuously or discontinuously on its orientation? The problem of the vicinal planes.*

The polyhedral shape of the crystals and the law of the small rational indices easily gives rise to the supposition of a *discontinuous* dependence; accordingly it seems to have been made, at least implicitly by most crystallographers, as soon as they made use of GIBBS and CURIE's theory. Explicitly it is found expressed in two often

<sup>1)</sup> Chiefly to be able to draw some conclusions on the structure from the crystal form see: FEODOROW, Z. f. Kryst. Vol. 34—53, compare also the application to twin formations H. HILTON. The energy of twin crystals. Mineralog. Magazine 15 (1909) p. 245.

<sup>2)</sup> BRILLOUIN. Ann. Chim. Phys [7] 6 (1895) p. 540; VERNADSKY Bull. de la Soc. Imp. de Naturalistes de Moscou 1902 p. 495; P. PAWLOW. Zschr. f. Kryst. 40 (1905) 189; 42 (1906) 120; Zschr. f. phys. Ch. 72 (1910) p. 385.

<sup>3)</sup> A. BERTHOUD. Journ. de Chim. phys 10 (1912) p. 624; G. FRIEDEL. Journ. de chim. phys. 11 (1913) p. 478. — Cf. also J. J. P. VALETON. Thesis for the doctorate. loc. cit.

<sup>4)</sup> F. SOHNKE. Ueber Spaltungsflächen und natürliche Krystallfl. Z. f. Kryst. 13 (1888) p. 214.

cited papers by F. SÖHNKE and G. WULFF<sup>1)</sup>. Both these authors namely assume that the *capillarity constant* of a crystal plane (apart from a factor which continuously changes with the orientation) is in *inverse ratio to the net density of the plane in question*<sup>2)</sup>.

This net density, however, is, as is known, a very discontinuous function of the orientation: thus for irrationally orientated planes, which have been rotated however little with respect to the plane (1, 1, 1), the net density would still be infinitely small in proportion to that of the plane (1, 1, 1). Here the exceptional function of the planes with the smallest indices is at once seen.

In spite of this appeal to the relation with the net density the supposition that the capillarity constant depends *discontinuously* on the orientation, will yet be thought very uncommon, if not quite paradoxical! Besides it involves a great difficulty for the frequent occurrence of the so-called "vicinal planes".<sup>3)</sup>

For according to SOHNKE and WULFF these planes with particularly large indices (which are practically irrationally orientated) would possess extraordinarily large surface energy. Of course we are willing to admit deviations from the theoretical equilibrium figure, taking into consideration the small disturbances which are never entirely to be excluded (fluctuations of temperature, disturbances in the concentration etc.) But yet totally unexplained and even paradoxical it remains when these slight disturbances give rise exactly to those planes with extremely large surface energy, and particularly those which lie very near to the planes with particularly small surface-energy<sup>4)</sup>.

1) F. SOHNKE. Zeitschr. f. Krystallogr. 13 (1888) p. 221; G. WULFF. Zeitschr. f. Krystallogr. 4 (1901) p. 526. GIBBS and CURIE do not give any further indication on the continuous or discontinuous character of the dependence.

2) WULFF gives this formula and characterises the gist of SOHNKE's conception, partly in SOHNKE's own words in the following way: "Nach Sohnke muss ein Zusammenhang zwischen der Oberflächenenergie einer Kristallfläche und ihrer Flächendichtigkeit bestehen. Nämlich für eine Fläche von dichtester Besetzung können die Molekularkräfte keine Arbeit mehr leisten, weil die Theilchen einander nicht weiter genähert werden können: *die potentielle Energie einer solchen Fläche muss also ein Minimum sein.* In dem Masse, als die Flächendichtigkeiten der verschiedenen Kristallflächen geringere sind, müssen die Oberflächenenergien (Capillarconstanten) grösser sein . . . .

3) By "vicinal planes" we understand planes which differ exceedingly little in situation from the planes with small indices.

4) H. MIERS, Rep. of the Brit. Assoc. 1894 p. 654; Z. f. Kr. 9 (1904) p. 220 has demonstrated experimentally through accurate goniometric measurements during the growth of alum crystals, that the planes with small indices in this case (1, 1, 1), practically never occur, but nearly always vicinal planes. Cf. also C. VIOLA, Z. f. Kr. 35 p. 332.

§ 3. Geometrical-physical interpretation of the capillary-constant for a special molecular scheme; the surface energy appears then as continuous function of the orientation, and yet produces a polyhedron as equilibrium figure. The function of the "vicinal planes".

To throw this point into strong relief, the point which is our only purpose here, we make use of an exceedingly simplified molecular scheme:

1. a two-dimensional scheme instead of a three dimensional one;
2. we leave the thermal motion out of account and accordingly we simply seek the molecular groupings with the smallest potential energy;
3. the molecules may be squares, which tend to adjust their sides close against each other. (We might as well use circular molecules with four points of valency).

Let an enormously large number of such square molecules be given. We seek that grouping at which the maximum "saturation" of the molecules has set in. Complete saturation, at which all the molecule sides are occupied, is of course impossible — at least the

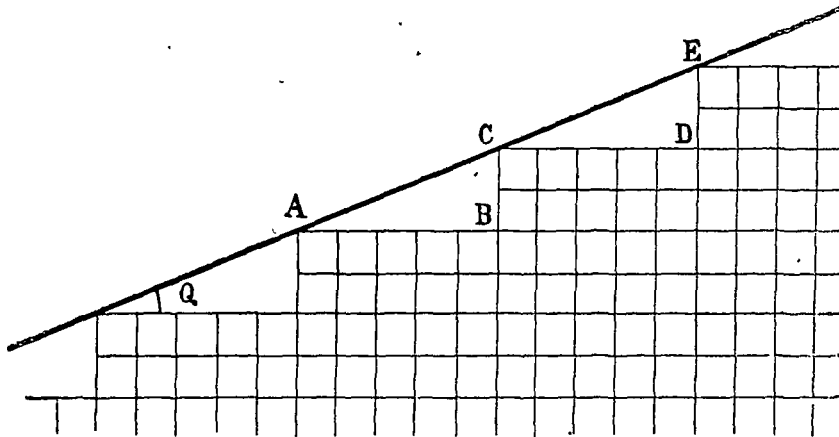


Fig. 1.

extreme edge of the "crystal" consists of unsaturated molecule sides. Let in fig. 1 the line  $ABCDE\dots$  be a portion of the "real" edge, the line  $ACE\dots$  a portion of the "apparent" edge. Let us put:

$$ABC = \Delta\sigma \text{ and } AC = \Delta s$$

then:

$$\Delta\sigma = (\cos \varphi + \sin \varphi) \Delta s.$$

The maximum saturation has evidently been reached for that grouping of the molecules, for which the length of the real edge, i.e.:

$$\Sigma \Delta\sigma = \Sigma k \Delta s \dots \dots \dots (2)$$

happens to be as small as possible. Hence the quantity:

$$k = \cos \varphi + \sin \varphi \dots \dots \dots (3)$$

plays the part of the capillarity factor in our scheme.

It is seen that

A. the capillarity factor  $k$  is here a *continuous function* of the orientation of the element of the apparent edge, which is the subject in view here. (To get a graphical representation,  $k$  should be considered as function of the direction of the normals to the edge element, and distances should be projected from a point  $W$  in all directions, which are proportional with the values of  $k$  for this direction of the normals. We obtain the curve dotted in figure (2), which is composed of 4 arcs of a circle.

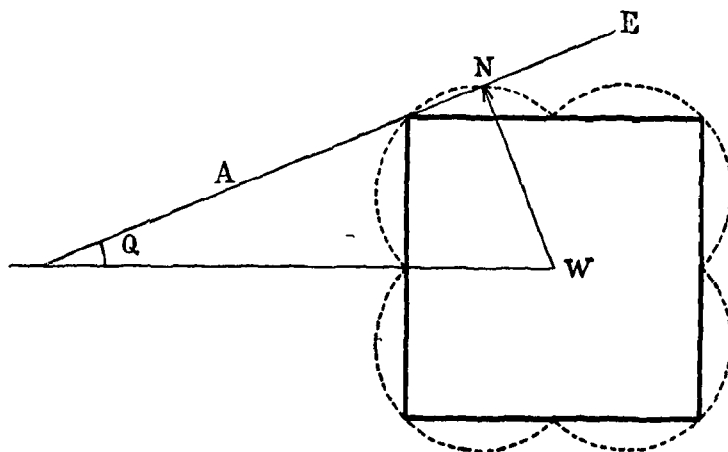


Fig. 2.

B. Yet the "equilibrium form" corresponding to it is a square. This is immediately to be seen by the aid of the construction mentioned in § 1. See fig. 2:  $W$  is WULFF's point:  $WN$  is proportional to  $k$  for this direction of the normal. If the straight line  $AE$  is constructed for all directions  $WN$ , they envelop conjointly the square drawn in fig. 2.<sup>1)</sup>

C. The occurrence of "vicinal planes" involves in our scheme no deviation worth mentioning from the minimum of energy. For our  $k$  depends continuously on the orientation, and the vicinal planes are only exceedingly little rotated with respect to the planes of the form of equilibrium. Here the contrast with SOHNKE and WULFF's supposition stands out very clearly.

D. Strictly speaking the form of equilibrium can do without vicinal

<sup>1)</sup> By slight changes in the definition of the scheme another dependence of  $k$  on the orientation can be obtained, hence other equilibrium polygons.

*planes only in particular cases.* Indeed: if the number of molecules happens to be the square of a whole number, then the form of equilibrium is exactly a square. When however successively more molecules are added, they must adjust themselves somewhere against the square to get maximum saturation, which leads to vicinal planes.

(In the formulae of § 1 this circumstance remains concealed, because there it is considered that the minimum must be determined with respect to infinitesimal changes of form. Here we realize, however, that it is a question of addition or displacement of a *whole number* of molecules).

§ 4. *Observations.* A. If a certain number of molecules is originally grouped in the form of two squares of different sizes, potential energy may be still diminished by the removal of a row of molecules from the small square, which are then laid against the large square. Decrease of energy also takes place when a rectangular grouping is changed into a square one. Until we take the temperature motion into consideration and consider the process of solution and sublimation, we can of course not ascertain whether in our molecular scheme these transitions will take place spontaneously. A somewhat trustworthy treatment of this question seems difficult to me, because for this the unevennesses of the edge are to be considered, i.e. those molecules which at a given moment are only bound singly or doubly, and not threefold.

B. It has been experimentally proved that for crystal powder e.g. of gypsum with a radius of about one micron the saturation concentration of the solution around it still appreciably depends on the radius. But for a radius of some microns this dependence already loses its significance with respect to disturbances of various nature. In virtue of this doubts will rise as to whether the changes discussed under A will appear spontaneously, and whether the actually occurring crystalline forms really agree with a minimum of surface energy<sup>1)</sup>. Shortly ago VALETON<sup>2)</sup> defined this view in the following way:

“For *microscopic* and *submicroscopic* crystals the surface energy has a measurable influence on the solubility. Such crystals can be in equilibrium with a solution only when their form corresponds with the minimum of surface energy. For *macroscopic* crystals this

<sup>1)</sup> A. BERTHOUD, Journ. de Chim. Phys. 10 (1912) p. 624. — G. FRIEDEL, Journ. de Chim. Phys. 11 (1913) p. 478.

<sup>2)</sup> l.c. p. 42. Compare there the fuller report of HULETT's experiments. Z. f. phys. Chem. 37 (1901) 385 with crystal powder of gypsum and barium sulphate.



influence is practically not existing. With regard to the crystalline form the equilibrium of these crystals is *indifferent*.

C. For our special model the whole still unused store of energy may be comprised in the one expression

$$\Sigma k \Delta s$$

with which the *surface* energy of the crystal corresponds in the three dimensional case; by the side of this there is left nothing that could answer to an energy of angular points or sides in the three-dimensional case, with which BRILLOUIN, VERNADSKY and PAWLOW<sup>1)</sup> work. Now however the model can be made more general by making e. g. moreover those isotropic attractive forces act between the molecules, with which LAPLACE, GAUSS, and VAN DER WAALS work with action spheres, which still contain many molecules<sup>2)</sup>. It remains noteworthy that then actually special side and angular point energies appear, whose numerical value remains undetermined for the present<sup>3)</sup>.

D. We have for the present not entered any further into the molecular interpretation of the cleavage directions. More recent views on this head are found in a study of P. P. EWALD<sup>4)</sup> on the structure of diamond. It would be interesting to ascertain whether one has also as a rule to do with vicinal planes of the ideal cleavage planes in the cleavage process. For the rest it would not be sufficient for a complete analysis of the cleavage process to ascertain what cleavage planes break a minimum of bindings; also the elastic deformation preceding the cleaving is in principle a factor to determine the orientation of the cleavage planes.

<sup>1)</sup> See the citations § 1.

<sup>2)</sup> In this connection it may be mentioned that EINSTEIN Ann. d. Phys. 34 (1911) p. 165, comes to the conclusion from the law of EÖTVÖS that also in liquids an attraction may be assumed only between those neighbouring molecules that are in immediate contact.

<sup>3)</sup> In the current derivation of the fundamental equations of the capillarity the terms in question vanish, because in a certain point of the derivation the assumption is made use of that the curvature rays of the surface remain everywhere above a definite finite value. Cf. among others H. MINKOWSKI, Art. Kapillarität, Math. Encykl. V. 9, § 14, transition between equation (24) and (26). First of all this supposition does not hold for crystal sides and angles, but moreover also e. g. at the side in which three liquids are in contact with each other. BRILLOUIN, Ann Chim. et Phys. [7] 6 (1895) p. 540 has demonstrated that the structure of the groove which is formed when glass and other substances are scratched is chiefly determined by the side and angular point energy.

<sup>4)</sup> Ann. d. Phys. 44 (1914) p. 281.