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**Chemistry.** — *Intermolecular forces in soap crystals.* By V. VAND and J. H. DE BOER.

(Communicated at the meeting of October 25, 1947.)

§ 1. Soap molecules consist of long hydrocarbon chains terminating in polar carboxyl ions carrying single negative charges. The negative charges are neutralised by positive charges of metal ions. Soaps of univalent metals are therefore binary compounds of the type  $AB$ , like the alkali halides. The long hydrocarbon tails of the negative ions, however, make it impossible for them to form three-dimensional ionic lattices. A two-dimensional lattice of the metal- and carboxyl-ions results. There may even be a double ionic layer formed, but the presence of the long hydrocarbon chains attached to the negative ions make formation of more than a double ionic layer impossible. The chains stick out on both sides of the ionic lamella of one or two ions thick and they shield it on both sides from the addition of more ions. A bimolecular lamella is thus formed. In the real crystal more such lamellae may be on top of each other but it is easily seen that the forces between successive bimolecular lamellae must be of a far weaker nature than the forces prevailing in the lamellae.

The arrangement is similar to that in other so-called layer lattices (boric acid, talcum, cadmium iodide, graphite) where layers of molecular dimensions are found held together in two directions by strong forces — ionic or homopolar — whereas in the third direction perpendicular to the layers only relatively weak VAN DER WAALS' forces are operating. Such crystals split very easily along planes parallel to the layers, a property so prominent that the splitting takes place when the crystals are rubbed between the fingers, giving rise to a "fatty" touch. The same distribution of forces favours the two-dimensional growth of these crystal lattices to relatively large thin plates.

Turning to the orientation of the hydrocarbon chains which are on both sides of an ionic layer, it is easily seen that there is hardly room for them unless they stick out, forming parallel rods pointing away from the central ionic layer at right angles or anyhow forming steep angles with it.

The thickness of the lamellae in monoclinic soap crystals, as given by the "long spacing",  $d$ , is in accordance with this picture, the "long spacing" being:

$$d = c \sin \beta = (2N_1 l_1 + l_0) \sin \tau,$$

where  $c$  is the dimension of the edge of the lattice,  $\beta$  is the monoclinic angle,  $N_1$  is the number of  $-\text{CH}_2-\text{CH}_2-$  groups in the molecules,  $l_1$  the increase in length of the molecule per  $-\text{CH}_2-\text{CH}_2-$  group,  $l_0$  an additional length arising from the end groups on both sides of the molecules and  $\tau$

the angle of tilt of the axis of the molecules, measured from the ionic plane. It should be noted that  $\tau$  can be quite different from  $\beta$ .

§ 2. We will now direct attention to the so-called "short spacings" in the crystals, arising from X-ray reflections from planes determined by the side distances of the molecules within the lamellae. If the middle ionic layer were not present, the hydrocarbon chains would nevertheless, due to their mutual VAN DER WAALS' forces, be orientated, forming parallel rods. Experimentally such an arrangement is known to be present in the crystals of saturated hydrocarbons (paraffins). We may expect that owing to the increase of the total VAN DER WAALS' forces between neighbouring chains, the short spacings will decrease with increasing length of the chains<sup>1</sup>). This can easily be shown in the following way. Suppose we have only two single  $-\text{CH}_2$ -groups (of different molecules) and we study their mutual forces. The potential curve giving the mutual energy of such a pair as a function of the distance is given by the equation:

$$E = -\frac{C_1}{d^6} - \frac{C_2}{d^8} + \frac{B}{d^n}.$$

The first term stands for the dipole-dipole effect of the VAN DER WAALS' forces, the second for the dipole-quadrupole effect, whilst the third term stands for the repulsive action caused by the interpenetration of electronic clouds. We have neglected the quadrupole-quadrupole term; this term is small and does not affect our result in any way. It is a known empirical fact, that the first term  $\frac{C_1}{d^6}$ , when taken separately and when evaluated either with the approximation formula of London<sup>2</sup>) or that of SLATER and KIRKWOOD<sup>3</sup>) gives the right value of  $D$  (the dissociation energy) for all practical purposes<sup>4</sup>), which means that the second and third term balance each other almost completely at the point where  $d = d_m$  (the distance between the centres at equilibrium). The numerical value of  $D$  for a  $\text{CH}_2$  group in a chain is of the order 0.25 Kcal/mole (see footnote 7).

Making use of this, we write:

$$\begin{aligned} C_1 &= Dd_m^6, \\ B &= C_2d_m^{n-8}. \end{aligned}$$

Moreover we have the following condition for the equilibrium:

$$\left(\frac{dE}{dd}\right)_{d=d_m} = \frac{6C_1}{d_m^7} + \frac{8C_2}{d_m^9} - \frac{nB}{d_m^{n+1}} = 0.$$

<sup>1</sup>) A similar effect is observed with respect to the distance between the two-dimensional hexagonal layers in graphite. This distance, which is governed by VAN DER WAALS' forces increases from 3.345 Å in normal graphite to 3.6 Å for extremely small crystals (see J. H. DE BOER, Rec. Trav. Chim. 59, 826 (1940).

<sup>2</sup>) F. LONDON, Z. Physik, 63, 245 (1930); Z. physikal Chem. 11 B, 222 (1931).

<sup>3</sup>) J. C. SLATER and J. G. KIRKWOOD, Phys. Rev. 37, 682 (1931).

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

which leads to

$$C_2 = \frac{6}{n-8} C_1 d_m^2 = \frac{6}{n-8} D d_m^8.$$

In this way we can express all the constants  $C_1$ ,  $C_2$  and  $B$  in terms of  $d_m$  and  $D$ , and the resulting form of the potential curve is therefore:

$$E = -D \left[ \left(\frac{d_m}{d}\right)^6 + \frac{6}{n-8} \left(\frac{d_m}{d}\right)^8 - \frac{6}{n-8} \left(\frac{d_m}{d}\right)^n \right].$$

$E$  here is therefore a function of  $d_m/d$  and the whole form of the curve is only dependent on the choice of  $n$ . From a comparison of the equilibrium distances of molecules, bound by VAN DER WAALS' forces, and their collision diameters, we may derive that in many practical cases  $n$  may be taken as 20. In Figure 1 the curve for  $n = 20$  is given.

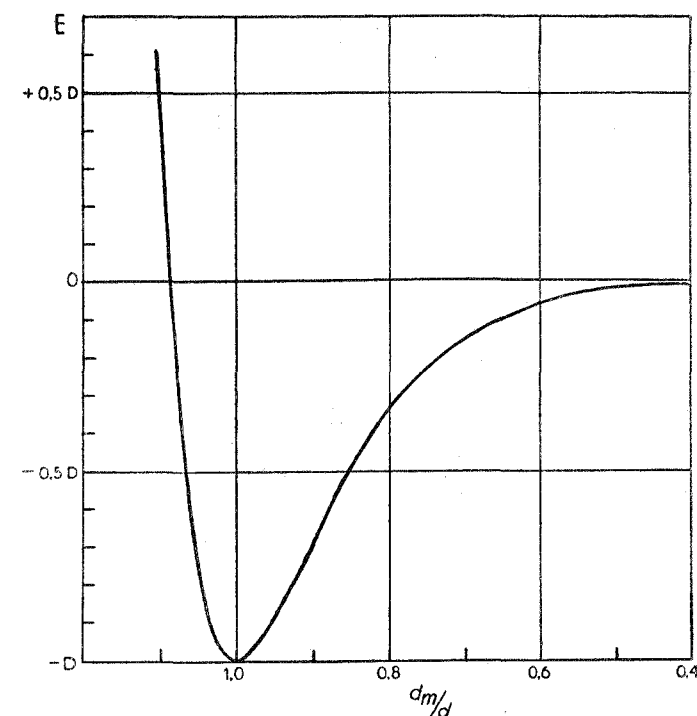


Fig. 1. Curve for mutual VAN DER WAALS' potential energy of a pair of  $\text{CH}_2$  groups.

We now take two bi-atomic molecules  $AB$  and  $CD$  in a position parallel to each other, and we assume that the distance between the atoms  $A$  and  $B$  in the molecule  $AB$  and between  $C$  and  $D$  in the molecule  $CD$  is a third of the distance  $d_m$  which we should find if the atoms  $A$  and  $C$  could attract each other separately. With the aid of the curve in Figure 1 it is now a relatively easy matter to assess the mutual energy of the two molecules as a function of their variable distance  $d$ . In such a way we may obtain a potential curve for this pair of bi-atomic molecules, and similarly

we can construct potential curves for straight molecular chains consisting of more than two atoms. In Figure 2 the curves for molecules consisting of 1, 2 and 3 atoms are given, and in Figure 3 those for 1, 2, 4, 6 and 8.

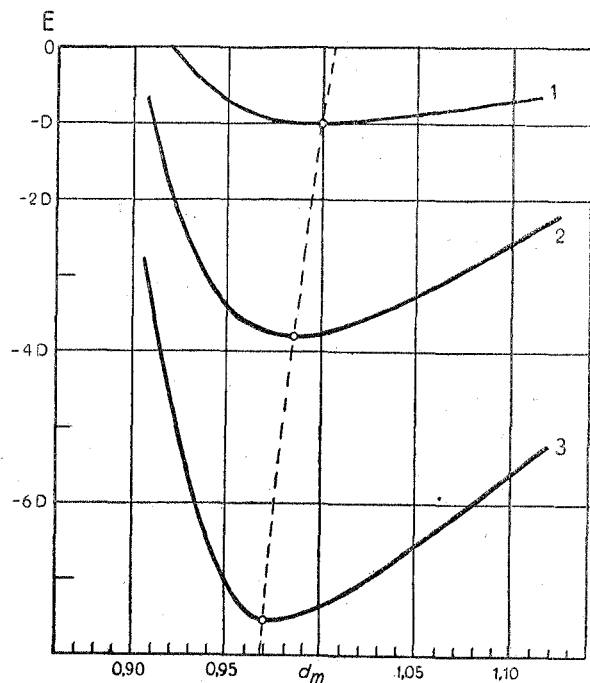


Fig. 2. Potential energy curves for pairs of molecules, each consisting of 1, 2 and 3 atoms or  $\text{CH}_2$  groups.

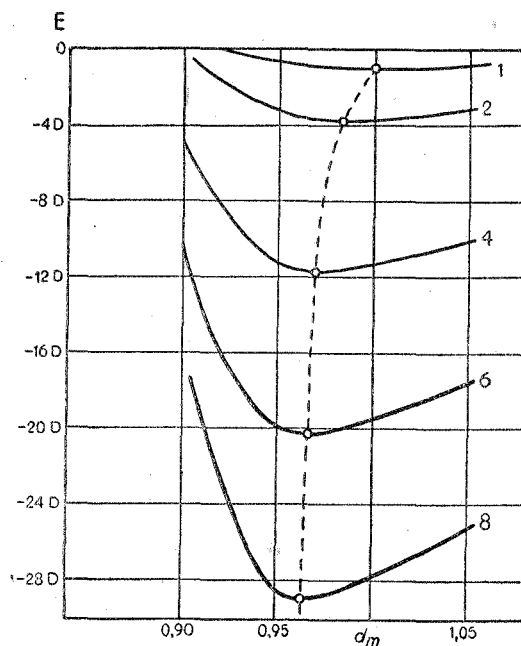


Fig. 3. Potential energy curves for pairs of molecules, each consisting of 1, 2, 4, 6 and 8 atoms or  $\text{CH}_2$  groups.

The distance is expressed in fractions of the distance  $d_m$ , which is the minimum for the two single atoms, and the energy is expressed in  $D$  as a unit. We see that as a result of the additivity of the VAN DER WAALS' forces the equilibrium distance of these curves decreases with increasing chain length. This is equally true for hydrocarbon chains, composed of  $\text{CH}_2$  groups, and the top curve in Figure 5 gives the decrease of the equilibrium distance as a function of  $1/N$ , where  $N$  is the number of  $\text{CH}_2$  groups in the molecule.

§ 3. Experimentally such a decrease with increasing chain length is indeed found. Even when one takes the earliest figures of MÜLLER and SAVILLE<sup>5)</sup> of 1925 for the dimensions of the unit cells of paraffin hydrocarbons this decrease is clearly demonstrated. We have taken available figures from the literature and calculated the cross-sections per molecule and their probable errors by the GAUSSIAN method of least squares assuming that the cross-section  $S$  may be expressed by the equation  $S = S_\infty + \frac{Q}{N}$ , where  $Q$  is a constant and  $S_\infty$  is the cross-section of an infinite chain. In doing this we treated the hydrocarbons with odd numbers of carbon atoms separately from those with even numbers, for it is possible that their crystal structures differ.

If the cell edges  $a$ ,  $b$ , of a monoclinic crystal are known, then we can calculate  $S$  from the following relation:

$$S = \frac{ab \sin \tau}{k}$$

where  $k$  is a multiplicity factor, which is equal to the number of molecules occupying one cell cross-section  $ab$ , and  $\tau$  is the angle of tilt of the molecules. Paraffins crystallise in two forms; one is orthorhombic, the other is monoclinic. Only the orthorhombic form is considered here, for which  $\tau = 90^\circ$ ,  $k = 2$ . The following results were obtained:

Odd series ( $N$  odd):

$$S_\infty = (18.12 \pm 0.10), \quad Q = 9.68 \pm 2.66, \quad \text{in } kX^2. \text{ } ^6)$$

Even series ( $N$  even):

$$S_\infty = (18.00 \pm 0.14), \quad Q = 10.00 \pm 4.00, \quad \text{in } kX^2.$$

The literature data and calculated values are given in Tables I and II.

It can be seen that the value of  $Q$  is positive and significantly different from zero, and so the contraction seems to be real, and both  $S_\infty$  and  $Q$  are the same within experimental error for odd and even series. This allows us to combine the results, and we obtain for the paraffins finally:

$$S_\infty = (18.08 \pm 0.08), \quad Q = 9.78 \pm 2.40, \quad \text{in } kX^2.$$

<sup>5)</sup> A. MÜLLER and W. B. SAVILLE, J. Chem. Soc. 127, 599 (1925).

<sup>6)</sup> According to new values,  $1 \text{ \AA} = 1.00202 \text{ kX}$ . The older values of lattice constants were as a rule measured in  $\text{kX}$ , although denoted as  $\text{\AA}$ .

It should be noted that BUNN's (1939) value of  $S = 18.24$  for hydrocarbons having  $N$  between 130 and 1000, is a value which according to our relation would have  $S$  for  $N = 62$ , but it certainly lies within the experimental error of BUNN's measurements.

The effect can be expressed by the equation:

$$S = 18.08 \left(1 + \frac{0.54}{N}\right) \text{ in } kX^2,$$

and is even greater than would follow from our potential curves of Figures 2 and 3, or from the upper curve of Figure 5. Our calculation, however, was only for pairs of molecules; the effect will be increased in forming a lattice from a great number of molecules.

§ 4. In the soaps, however, we have in the first place the two-dimensional ionic sheet of the carboxyl and metal ions. If we take the sodium or silver soaps we might expect that the strong forces between such small cations and the anions in this ionic sheet would enforce a smaller cross-section on to the molecules, thus compressing them. The energy of combination for the ionic sheet would, moreover, be very much higher than that for the hydrocarbon chains. Consequently the potential curve of such an ionic pair would show a minimum at a far lower energy content and at a smaller distance. Let us assume the equilibrium distance to be 0.9 of that of our potential curve of VAN DER WAALS' attraction of two centres (Figure 1). The energy content of such

TABLE I. Paraffins N Odd.

$N$	$a$	$b$	$c$	$S = \frac{1}{2} ab$	$S_{\text{calc.}}$	Reference
19	7.55	5.01		18.91	18.63	MÜLLER (1932)
23	7.435	4.97		18.48	18.53	"
25	7.41	4.96		18.38	18.50	"
27	7.40	4.93		18.24	18.48	"
29	7.42	4.94	77.2	18.33	18.45	MÜLLER (1932)
29	7.45	4.97		18.51	18.45	MÜLLER (1928)
31	7.49	4.97	41.11	18.61	18.43	SCHOON (1938)
31	7.42	4.95		18.36	18.43	THIESSEN (1937)
31	7.45	4.94		18.40	18.43	RIGAMONTI (1936)
31	7.40	4.93		18.24	18.43	MÜLLER (1932)
35	7.43	4.97		18.46	18.39	HENGSTENBERG (1928)
> 130	7.40	4.93		18.24	18.12	BUNN (1939)

MÜLLER, A., Proc. Roy. Soc., A 138, 514 (1932).

MÜLLER, A., Proc. Roy. Soc., A 120, 437 (1928).

SCHOON, T., Z. phys., chem., B 39, 385 (1938).

THIESSEN, T. A. and T. SCHOON, Z. phys. chem., B 36, 216 (1937).

RIGAMONTI, R., Gazz. chim. ital., 66, 174 (1936).

HENGSTENBERG, J., Zeits. Krist., 67, 583 (1928).

BUNN, C. W., Trans. Far. Soc., 35, 482 (1939).

TABLE II.  
Paraffins N Even.

$N$	$a$	$b$	$S = \frac{1}{2} ab$	$S_{\text{calc.}}$	Reference
18	7.56	5.00	18.90	18.55	MÜLLER (1927)
24	7.41	4.94	18.30	18.42	MÜLLER (1932)
26	7.415	4.94	18.31	18.38	"
30	7.452	4.965	18.50	18.33	KOHLHAAS (1938)
30	7.51	4.955	18.23	18.33	SCHOON (1938)
30	7.33	4.92	18.03	18.33	MÜLLER (1932)
34	7.40	4.95	18.32	18.29	"
44	7.33	4.93	18.07	18.23	"
> 130	7.40	4.93	18.24	18.00	BUNN (1939)

MÜLLER, A., Proc. Roy. Soc., A 114, 542 (1927).

MÜLLER, A., Proc. Roy. Soc., A 138, 514 (1932).

KOHLHAAS, R., and K. SOREMBÄ, Z. Krist., A 100, 47 (1938); Z. anorg. Chem., 51, 483 (1938).

SCHOON, T., Z. phys. Chem., B 39, 385 (1938).

BUNN, C. W., Trans. Far. Soc., 35, 482 (1939).

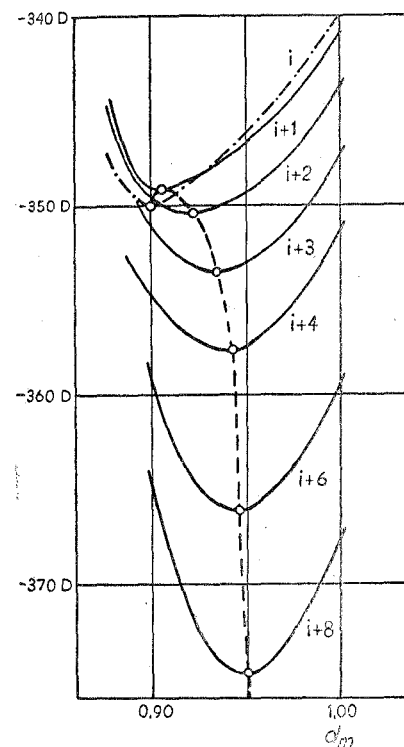


Fig. 4. Potential energy curve for an ionic pair ( $i$ ) and for an ionic pair in which each ion is combined with a chain containing 1, 2, 3, 4, 6 and 8 atoms or  $\text{CH}_2$  groups.

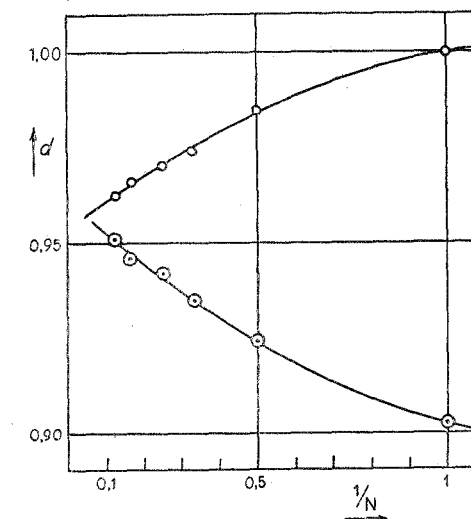


Fig. 5. Calculated effect of the chain length on the equilibrium distance of between the chains. Top curve: VAN DER WAALS' forces alone. Bottom curve: Ionic forces combined with VAN DER WAALS' forces.

an ionic pair will be about 350 times <sup>7)</sup> the value of that of  $D$  in Figure 1. With these two figures for the fixation of the minimum of the potential curve of the ionic pair, namely distance is  $0.9 d_m$ , and energy is  $350 D$ , the potential curve for the ionic pair can be easily constructed; it is the curve indicated with the letter  $i$  in Figure 4.

In order to see what happens in soap crystals, we have now to combine this curve with the set of curves of Figures 2 and 3. The result is shown in Figure 4. We obtain curves indicated with  $i = 1$  for 1 atom in the chain to  $i = 8$  for 8 atoms in the chain. Although the VAN DER WAALS' forces are smaller than the ionic forces and are even of another order of magnitude, the influence of the VAN DER WAALS' curves on the equilibrium distance is paramount. Consequently we must expect here a dilation of the lattices when we proceed towards longer length of the hydrocarbon chains, as is indicated in the lower curve of Figure 5 where the distance of these minima are plotted against  $1/N$ .

§ 5. The experimental figures for the cross-sections of silver soaps and  $\gamma$ -sodium soaps were calculated as follows:

The volume  $V_1$  occupied by one molecule is obtained from the density  $\rho$  by means of the following relation:

$$V_1 = \frac{1.6502 M}{\rho},$$

where  $M$  is the molecular weight and  $V_1$  is measured in cubic  $kX$  units. There are 2 molecules along the  $c$ -cell edge in these soaps.

$$\text{The expression } S' = \frac{2 V_1}{d},$$

where  $d$  is the value of the long spacing, which can be directly measured, gives the surface areas per molecule measured in a plane parallel to (001). The surface area  $S$  of a molecule measured in a plane perpendicular to its axis is thus:

$$S = \frac{2 V_1 \sin \tau}{d},$$

<sup>7)</sup> The VAN DER WAALS' interaction energy of two  $-\text{CH}_2-$  groups at an equilibrium distance of  $4.0 \text{ \AA}$  is  $0.25 \text{ Kcal/mol}$ , as calculated with the formula of SLATER and KIRKWOOD, (loc. cit 3)

$$E = \frac{163 \times 10^{-12} n^3 \alpha^3}{a^6} \text{ Kcal/mol.}$$

where  $n$  is the number of outer electrons and  $\alpha$  is the polarizability; we took  $n = 6$  and  $\alpha = 1.9 \times 10^{-24} \text{ cm}^3$ . An ionic pair at a distance  $3.6 \text{ \AA}$  has an interaction energy of  $84 \text{ Kcal/mol}$ , as calculated with

$$E = \frac{e^2}{d} \left(1 - \frac{1}{n}\right),$$

where  $n = 12$ , the exponent of the repulsion term.

where  $\tau$  is the angle of tilt of the chains measured from the (001) plane.

The angle of tilt  $\tau$  can be calculated from the increment of the long spacing on increasing the chain length, assuming tetrahedral angle and carbon to carbon bond length. It should be noted that the calculation assumes (a) constancy of the parameters of the unit cell not directly affected by the chain increase, including constancy of the angle of tilt, (b) constancy of the tetrahedral angle and carbon to carbon distance in various compounds. For the carbon to carbon distance, a value of  $1.54 kX$  is usually assumed, whilst for the angle between the C—C bonds the tetrahedron valency angle of  $109^\circ 28'$  is taken. This angle, however, may be strained to various degrees, so that the angle of tilt cannot be calculated with any degree of accuracy. However, this does not affect our results much.

Table III contains the data for  $\gamma$ -sodium soaps and Table IV for silver

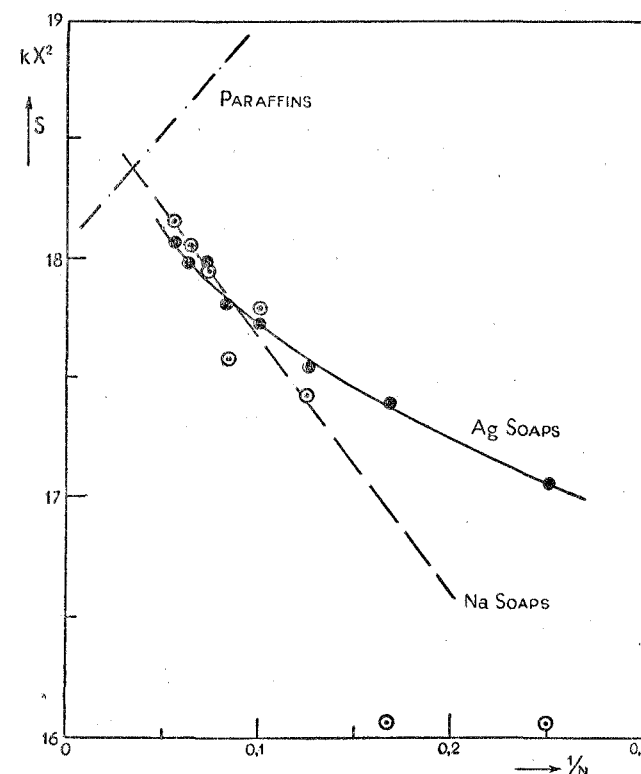


Fig. 6. Cross-section  $S$  of the chains in paraffins, in silver soaps and in sodium soaps as a function of the chain length.

soaps. The values for  $S$  for both these soaps are plotted in Figure 6. We see, indeed, that the cross-section increases with increasing chain length as predicted from the co-operation of ionic and VAN DER WAALS' forces.

§ 6. Let us direct our attention for a few moments to the mutual orientation of the molecules in the layers. There are several possibilities of



TABLE III.  
Sodium soaps.  
Form  $\gamma$

$$\sin \tau = 0.8461, \quad \tau = 57^\circ 48'$$

Soap	$N$	$M$	$\rho$	$V_1$	$d$	$S$
Sodium butyrate	4	110.10	1.340	135.6	14.30	16.04
„ caproate	6	138.16	1.290	176.7	18.65	16.03
„ caprylate	8	166.21	1.170	234.4	23.15	17.42
„ caprate	10	194.24	1.135	282.4	27.30	17.80
„ laurate	12	222.31	1.110	330.5	31.80	17.58
„ myristate	14	250.36	1.090	379.0	35.70	17.96
„ palmitate	16	278.42	1.075	427.4	40.00	18.08
„ stearate	18	306.47	1.060	477.1	44.40	18.18

TABLE IV.  
Silver soaps.

$$\sin \tau = 0.9537, \quad \tau = 72^\circ 30'$$

Soap	$N$	$M$	$\rho$	$V_1$	$d$	$S$
Silver butyrate	4	195.0	2.403	133.9	14.95	17.08
„ caproate	6	223.0	2.043	180.1	19.74	17.40
„ caprylate	8	251.1	1.838	225.4	24.48	17.56
„ caprate	10	279.1	1.686	273.2	29.36	17.74
„ laurate	12	307.2	1.588	319.2	34.18	17.81
„ myristate	14	335.2	1.506	367.3	38.93	17.99
„ palmitate	16	363.3	1.452	412.9	43.82	17.97
„ stearate	18	391.3	1.403	460.2	48.56	18.07

orientation, in all of which the axes of the molecules are parallel. In a parallel row, for instance, the planes through the zig-zag configurations of the hydrocarbon chains may be parallel (see case *a* on Figure 7) or in alignment (*b*), or they may alternate (*c*). They may also be in general positions (*d*), or finally, they may even rotate (*e*) at higher temperatures. If they are in alignment it may easily be seen that such a mutual orientation of the hydrocarbon chains is not unfavourable even from the point of view of the anisotropy of the polarisability. There are hardly any cases of parallel axes of greatest polarisability then. When, however, the planes of the zig-zags are parallel, the attraction due to the VAN DER WAALS' forces at the same distance will be smaller because of the unfavourable position with regard to the anisotropy of polarisability. We see that there are distinct possibilities that even in the bimolecular lamellae the forces are much stronger in one direction than in another. In such cases the plates can easily be split to needles or fibres. Many soap lattices grow easily as needles or fibres. In all such cases we find that the molecules are perpendicular or nearly perpendicular to the needle or fibre axis, an orientation quite different therefore from that found in fibres of high polymers where the molecules are stretched in the direction of the

fibre axis. An orientation of the molecules perpendicular or nearly perpendicular to the needle or fibre axis may always be expected from such

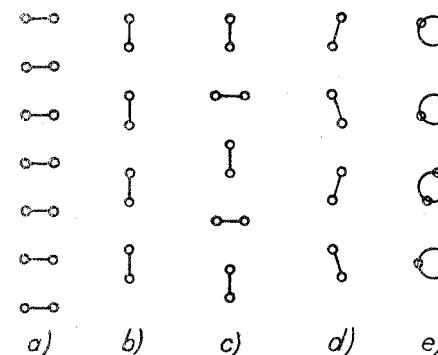


Fig. 7. Possible arrangements of the hydrocarbon chains in a parallel row. Cross-sections perpendicular to the axes of the chains are shown for chains (*a*) parallel, (*b*) in alignment, (*c*) alternating, (*d*) in general positions, (*e*) rotating.

lattices which, because of the forces operating in them, might not only be called layer lattices but even rod lattices. Many long shaped molecules of dyestuffs crystallise in this way.

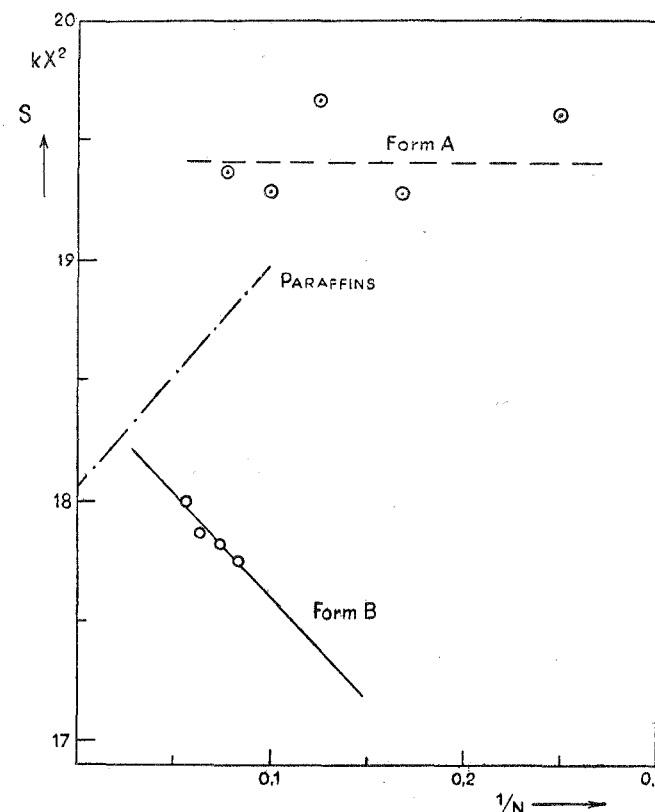


Fig. 8. Cross-section  $S$  of the chains in paraffins and in two forms A and B of potassium soaps as a function of the chain length.

§ 7. Usually it is accepted, though without sufficient proof, that long chain molecules such as soap molecules are all parallel to each other in the crystalline state. This, however, need not be so. Recently VAND, LOMER and LANG<sup>8)</sup> have found that in the so-called *A* form of potassium caprate rows of molecules with parallel axes alternate with other rows of molecules, the directions of the axes of which, however, are such that they cross the directions of the axes in the first set of rows. A row of hydrocarbon chains which stick out from the ionic layer with an angle of tilt of  $58^\circ$  is bordered on both sides by another row of hydrocarbon chains sticking out from the ionic layer with an angle of tilt of  $122^\circ$ . The two directions of chains, therefore, cross each other with an angle of  $66^\circ$ .

It is remarkable that this *A*-form, found in potassium soaps of up to 12 C-atoms does not show the increase of cross-section with increasing chain length. The so-called *B*-form, found with potassium soaps of 12 C-atoms and higher, however, shows the same effect as the sodium- and silver-soaps, as is shown in Figure 8.

#### Acknowledgments.

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#### Summary.

It is shown from theory and by experiment that in a series of homologous long chain compounds, such as paraffins or soaps, cross-sections of the hydrocarbon chains vary with the chain length, so that the side spacings and the shorter edges of the unit cells do not remain strictly constant.

These effects are due to the interplay of the VAN DER WAALS' forces between the chains and ionic forces within the ionic parts of the structures.

With paraffins, when only VAN DER WAALS' forces are operating, the cross-sections per molecule decrease with increasing chain-length. In the case of sodium- and silver-soaps, however, a smaller cross-section is caused by the ionic forces, which is increased with increasing chain-length.

<sup>8)</sup> V. VAND, T. R. LOMER and A. LANG, *Nature* 159, 507 (1947).

### Chemistry. — On the Graphical Representation of Chemical processes. By L. G. M. BAAS BECKING D. Sc., Ph. D., Buitenzorg.

(Communicated at the meeting of September 27, 1947.)

1. G. G. STOKES, in 1891, proposed a graphical representation of the properties of three components by means of an equilateral triangle that has been in general use ever since.

The method is based upon a property of the equilateral triangle; that the sum of the distances of any point within this triangle to the sides is constant. In this paper the method will be used to represent by points on an equilateral triangle compounds of C—H—O, N—H—O, S—H—O, respectively.

2. In order to take into account the valencies of the atoms, the corners of the triangles represent C—4H—2O (figure 1), 2N—6H—5O (figure 2),

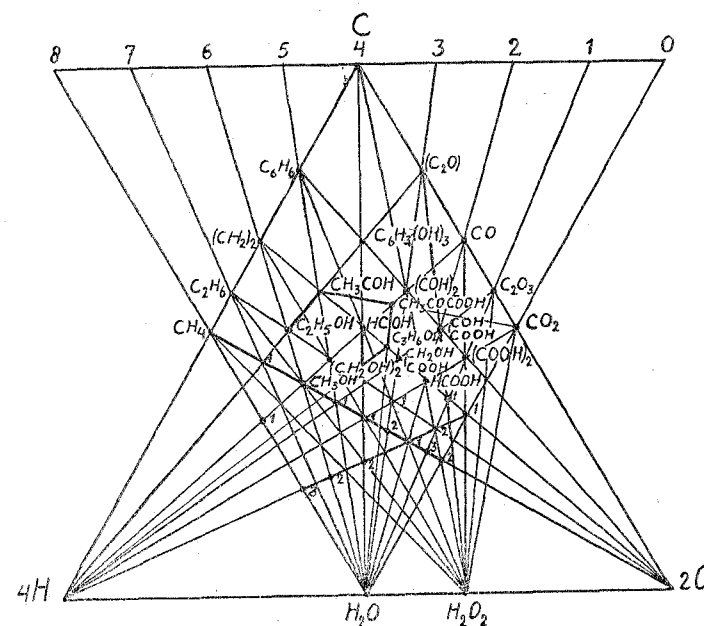


Fig. 1.

S—2H—3O (figure 3) respectively. To construct the point H<sub>2</sub>O a line parallel and equal to the base is run through the apex (C, N or S) of the triangle. This line is divided into eight equal parts, in recognition of the fact that there are 8 H-atoms required to reduce the highest oxidation-stage (CO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>) of the element to the highest stage of reduction (CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>S).